Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information
for

Copolymerization of 1-Alkenes with Bulky Oxygen-containing Olefins for Dual-Stage Functionalization of Polyolefin

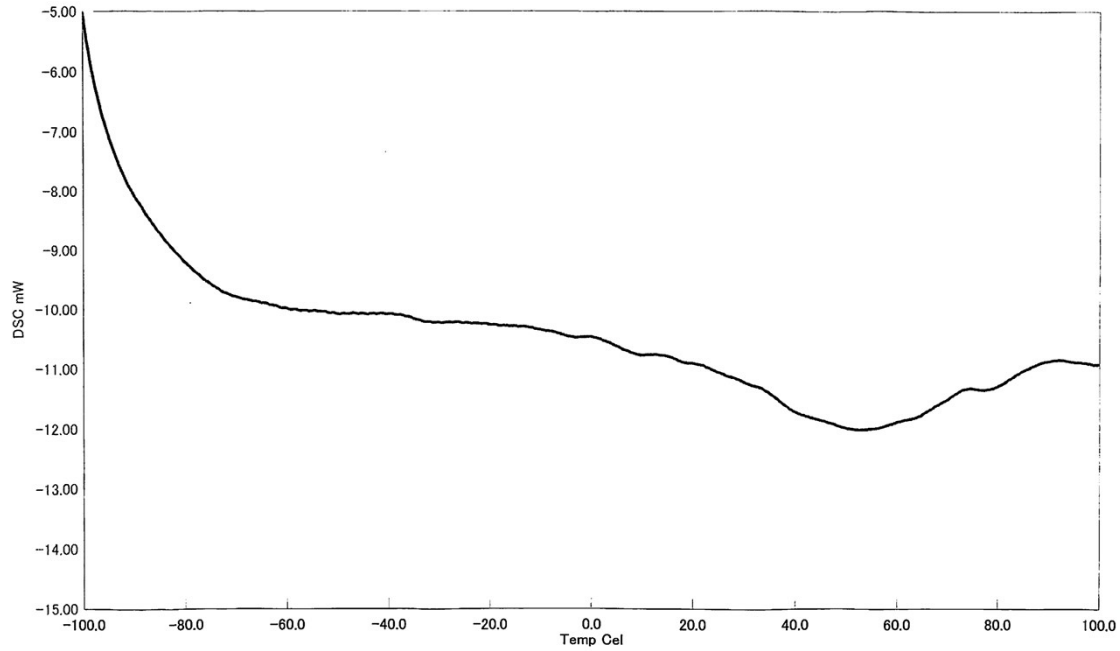

Figure S-1. DSC chart of polydecene obtained by Pd catalyst **II** (Table 1, run 6) (heating : 10°C/min, cooling : 20°C/min 2nd scan**)**

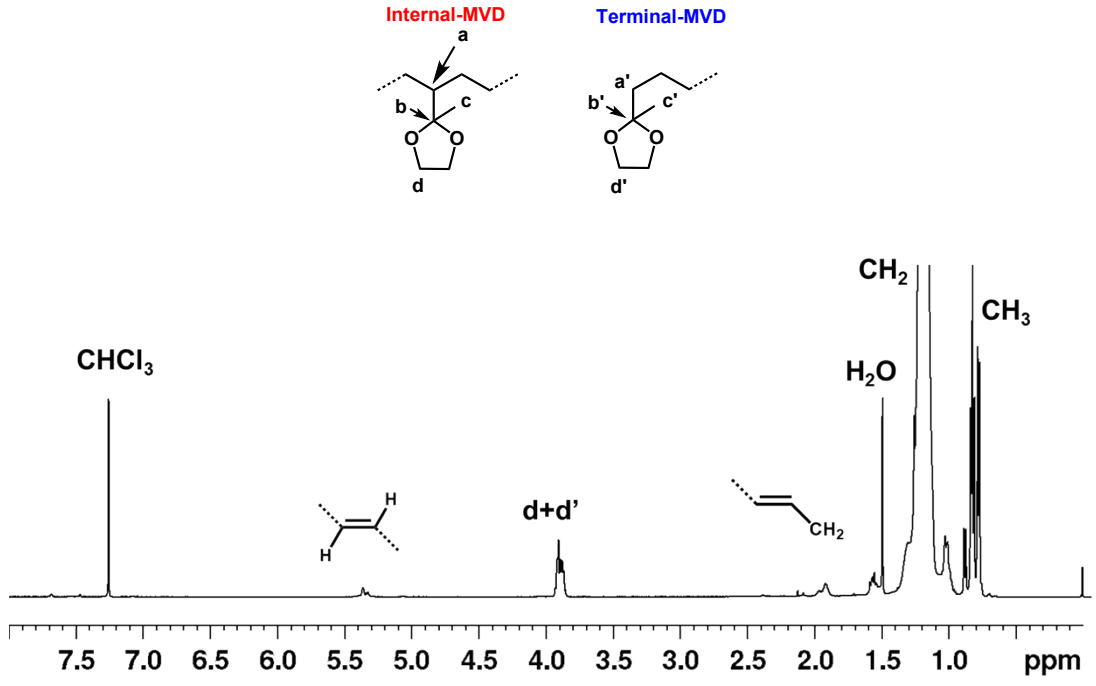

Figure S-2. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of poly-**2a** obtained by Pd catalysts **I** (Table 1, run 7)

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.38 (vinylene), δ 3.94-3.90 (m, OCH_2CH_2O), δ 1.26(-CH_2-), δ 0.94-0.83 (-CH_3).

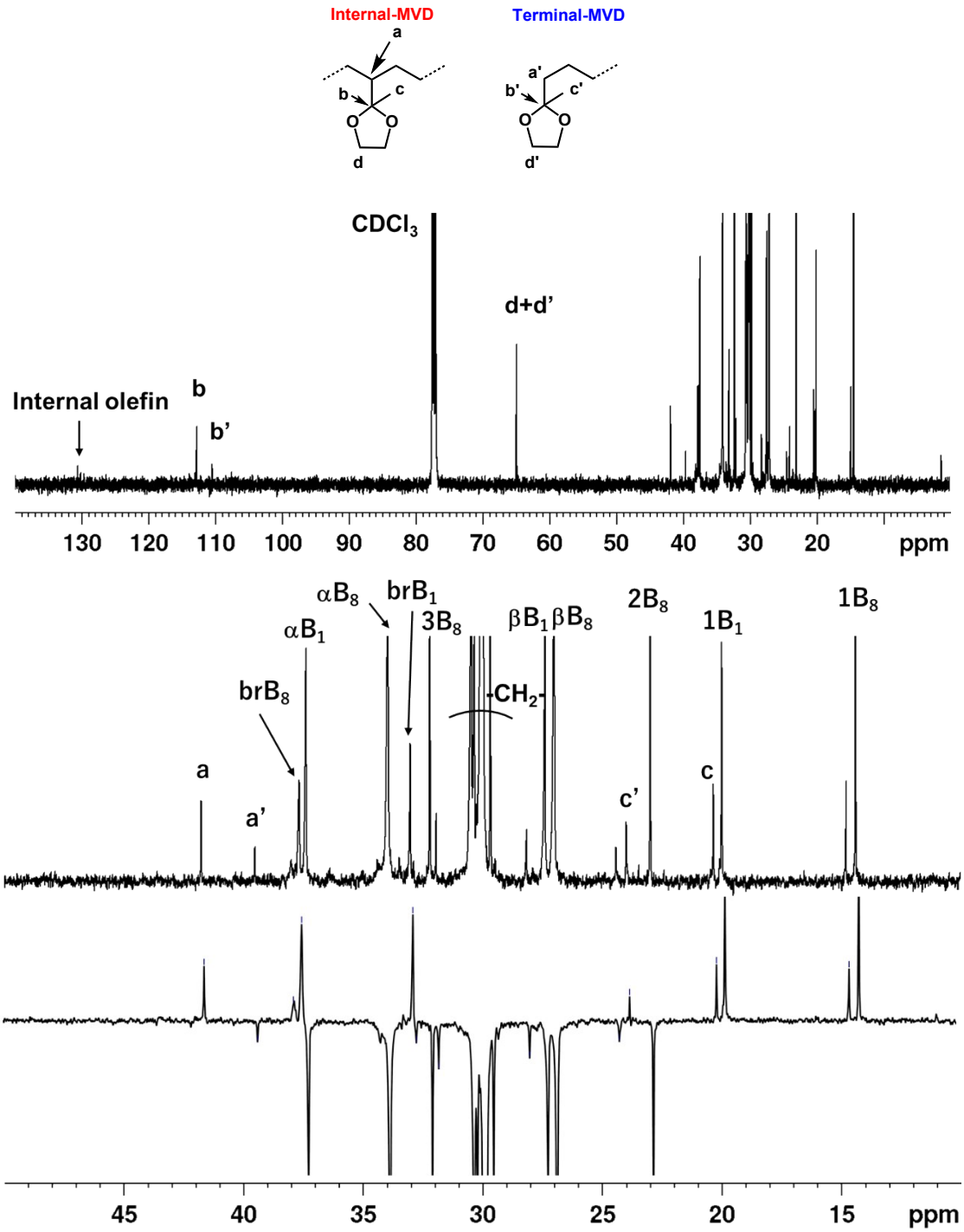

Figure S-3. $^{13}C\{^{1}H\}$ NMR and DEPT spectra ($CDCl_3$, at r.t.) of poly-**2a** obtained by Pd catalysts **I** (Table 1, run 7)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 112.8(b), δ 110.6 (b'), δ 64.8 (-OCH_2CH_2O-), δ 41.8 (a), δ 39.5 (a'), δ 23.8 (c'), δ 20.2 (c).

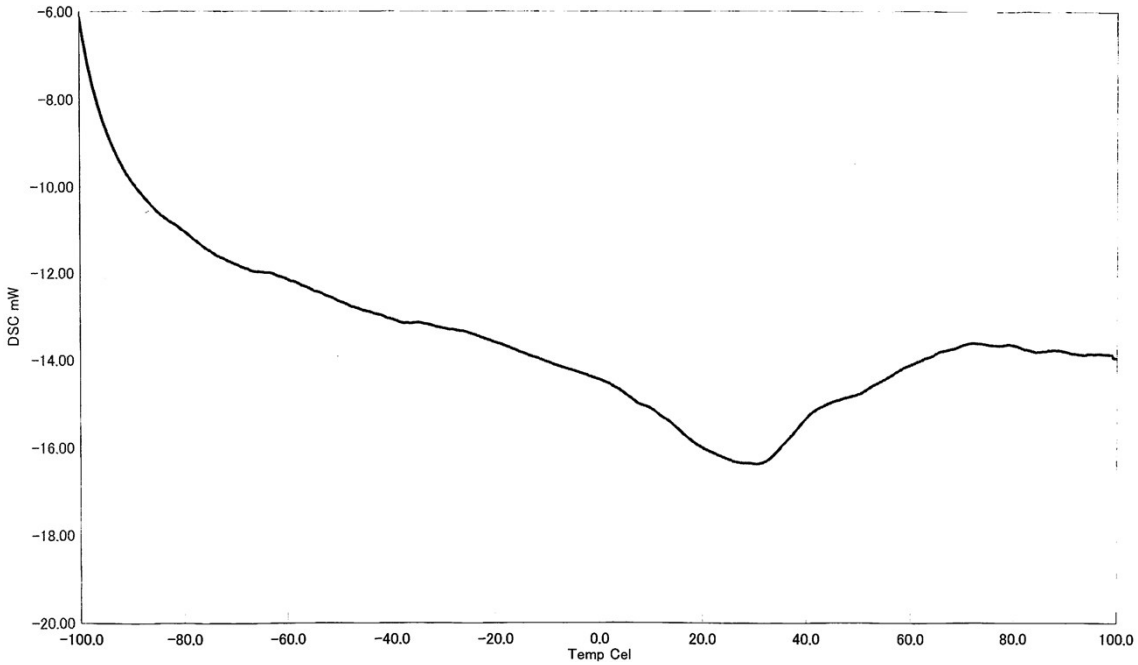

Figure S-4. DSC chart of poly-**2a** obtained by Pd catalysts **I** (Table 1, run 8)
(heating : 10^{o}C/min, cooling : 20^{o}C/min 2nd scan**)**

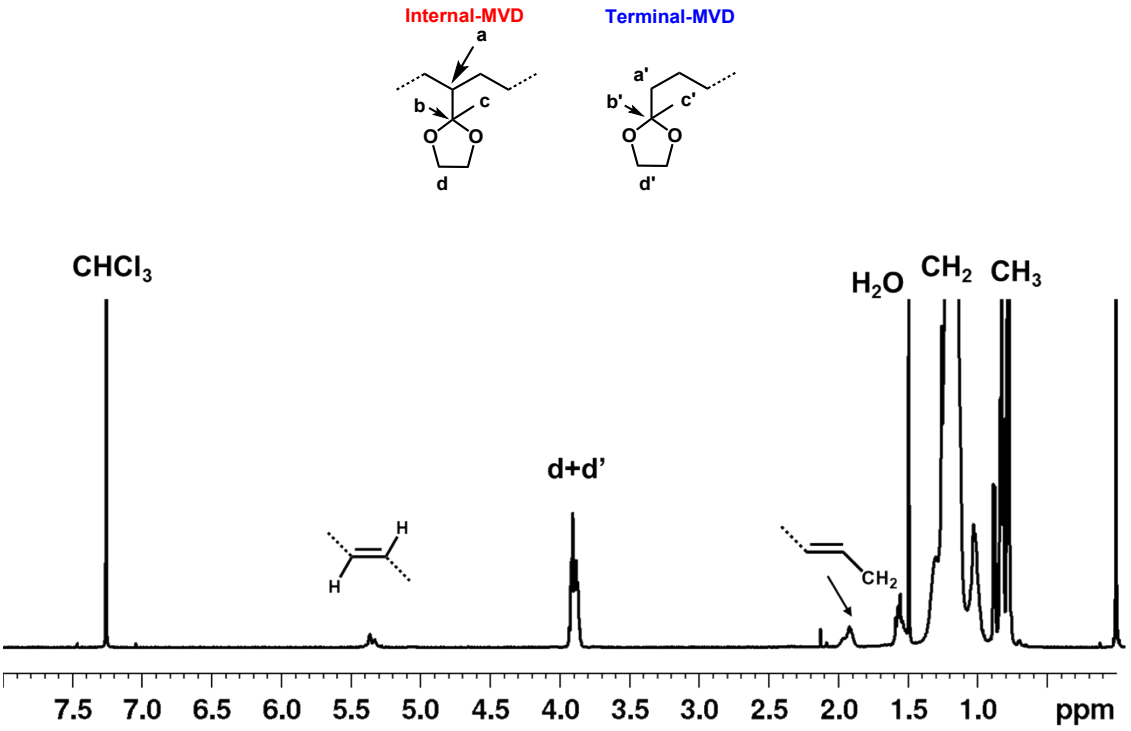

Figure S-5. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of poly-**2b** obtained by Pd catalysts **I** (Table 1, run 13)

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.38 (vinylene), δ 3.94-3.90 (m, OCH_2CH_2O), δ 1.23(-CH_2-), δ 0.94-0.83 (-CH_3).

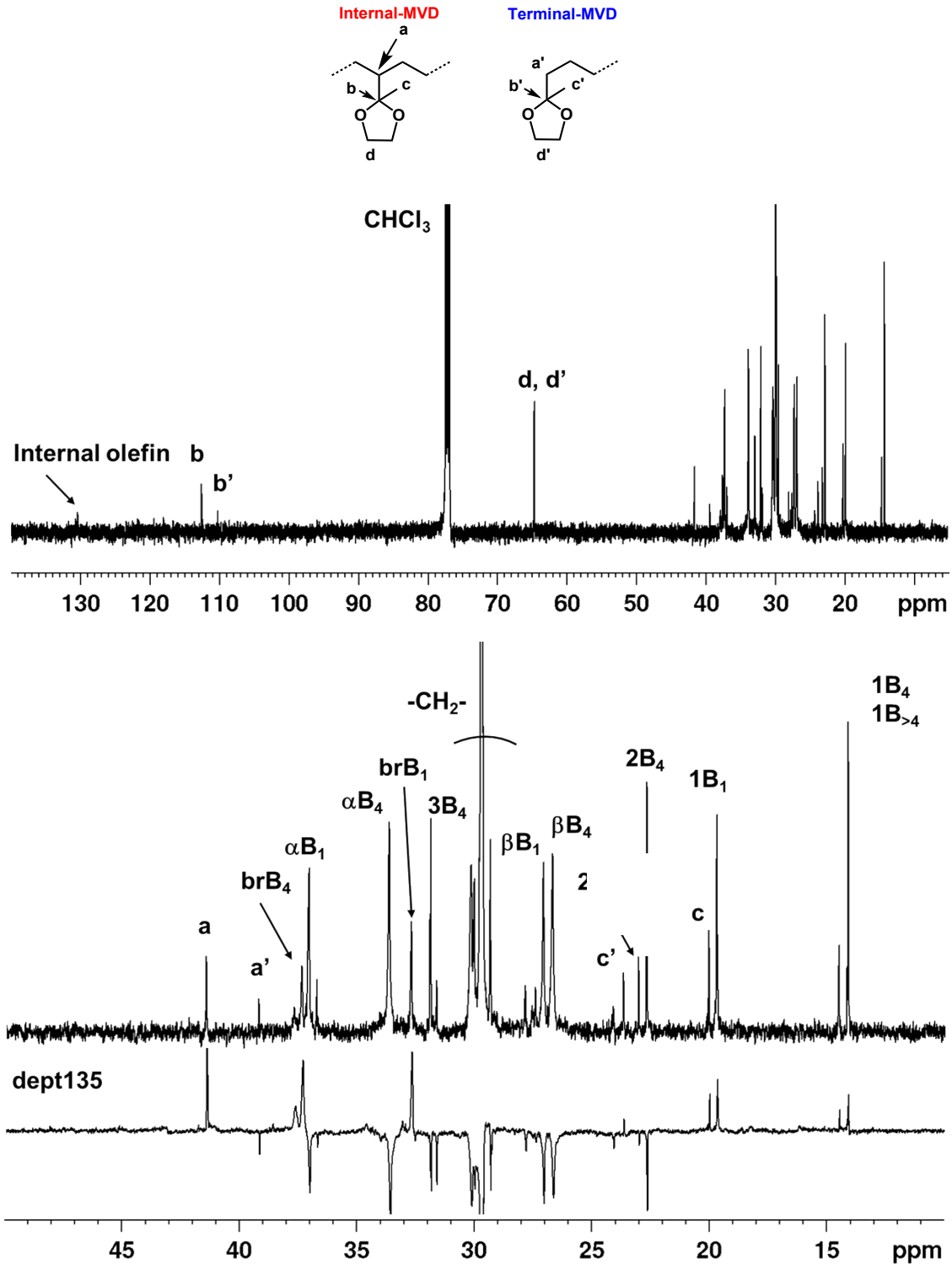

Figure S-6. $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, at r.t.) of poly-**2b** obtained by Pd catalysts **I** (Table 1, run 13)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 112.5 (b), δ 110.2 (b'), δ 64.6, 64.5 (-O*C*H$_2$*C*H$_2$O-), δ 41.4 (a), δ 39.3 (a'), δ 23.7 (c'), δ 20.1 (c).

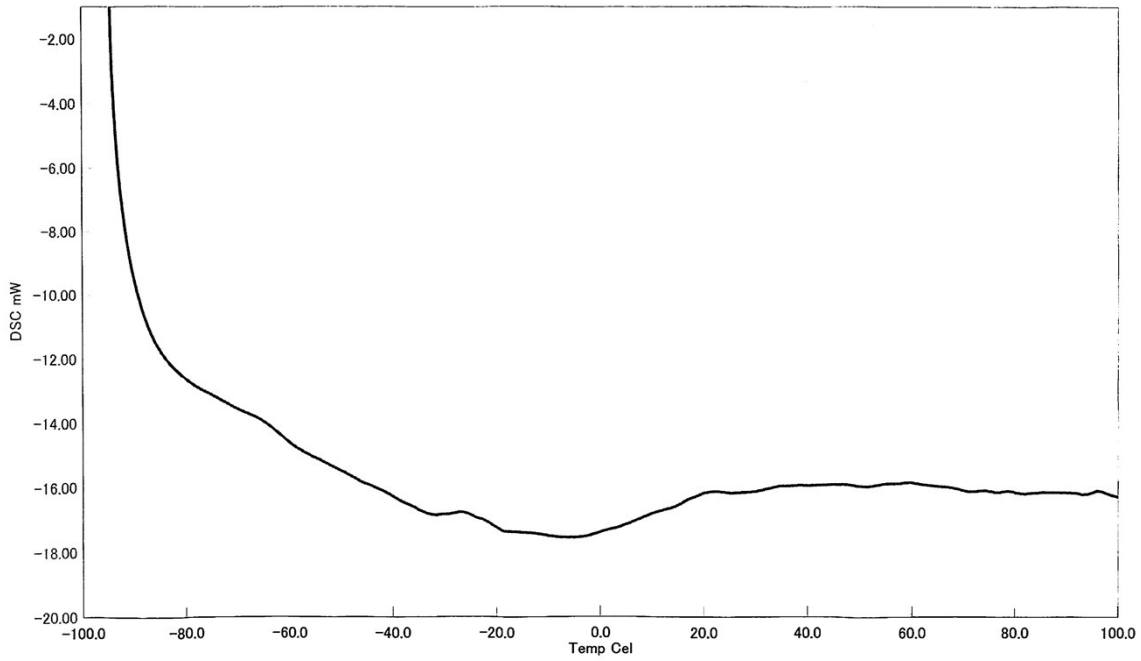

Figure S-7. DSC chart of poly-**2b** obtained by Pd catalysts **I** (Table 1, entry 14) (heating : 10°C/min, cooling : 20°C/min 2nd scan)

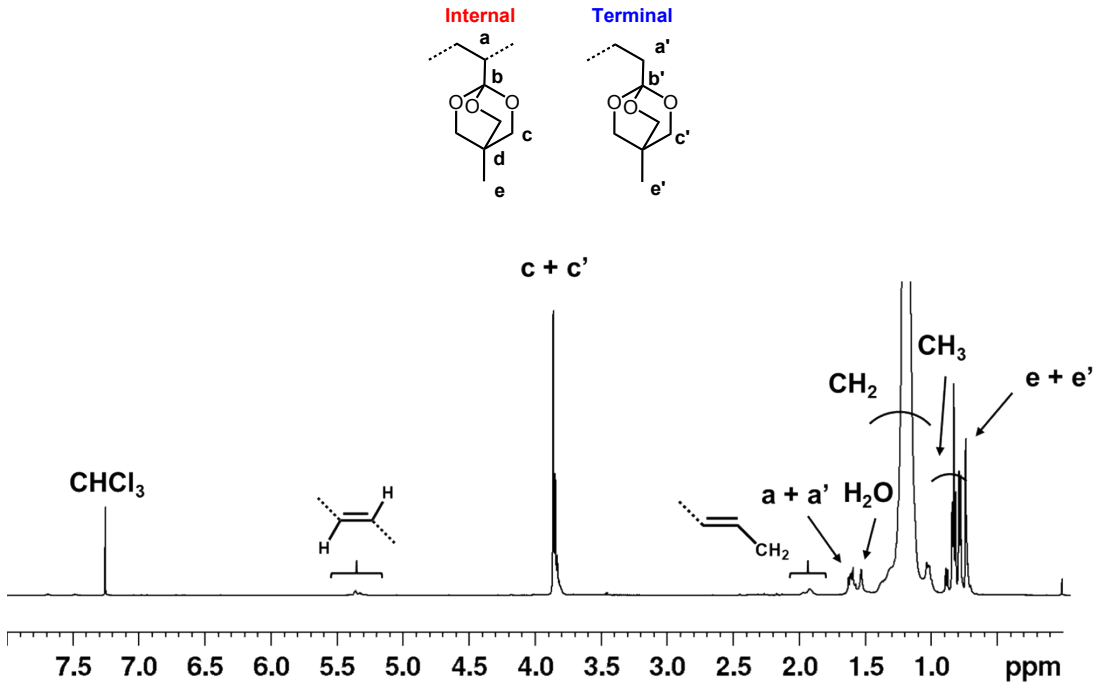

Figure S-8. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of poly-**1a** obtained by Pd catalysts **I** (Table 1, run 4)

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.38 (vinylene), δ 3.89,3.86 (s, d+d'), δ 1.67, 1.62 (m, a+a'), δ 0.79,0.78 (s, e+e') δ 1.25 (-CH_2-), δ 0.94-0.83 (-CH_3).

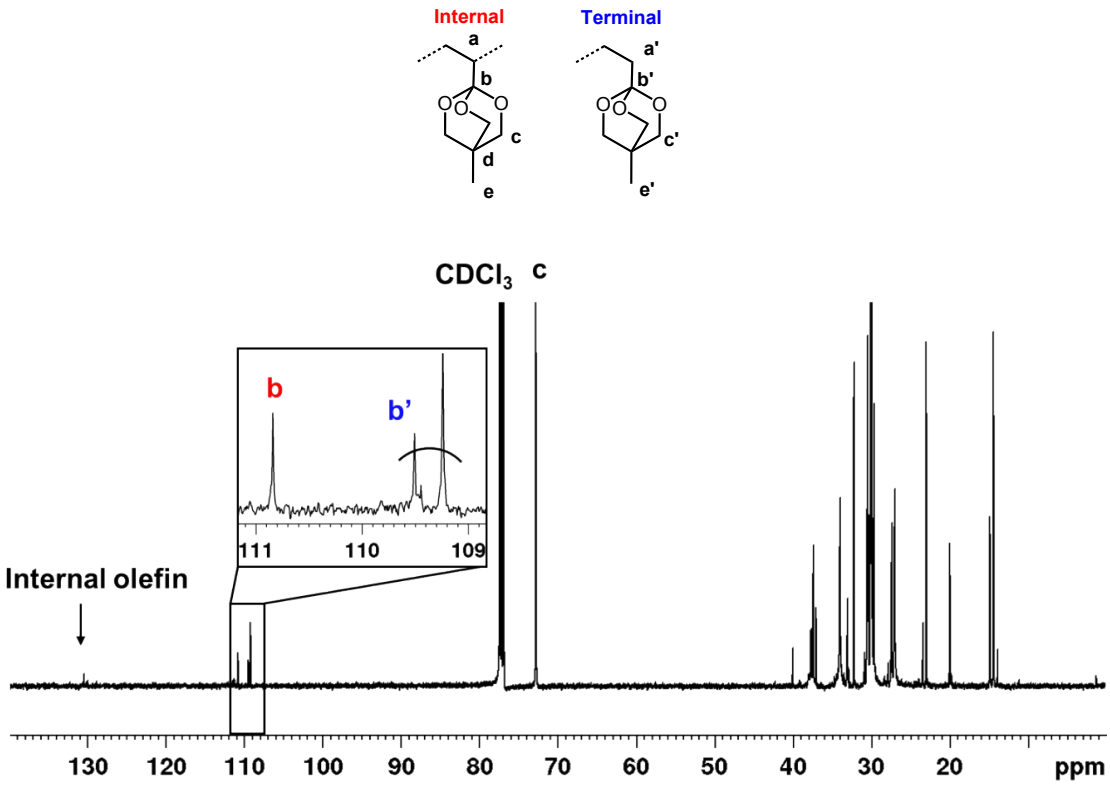

Figure S-9. $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, at r.t.) of poly-**1a** obtained by Pd catalysts **I** (Table 1, run 4)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 110.9(b), δ 109.5, 109.2 (b'), δ 72.7 (c+c'), δ 39.9 (a), δ 36.9 (a'), δ 13.7 (e+e').

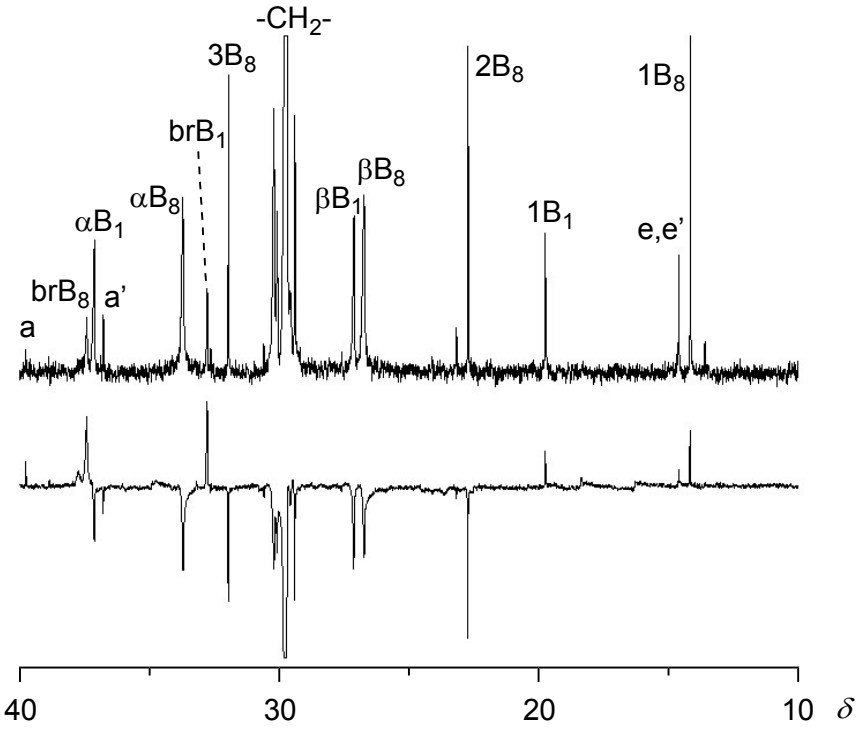

Figure S-10. ^{1}H decoupled and DEPT (135°) ^{13}C NMR spectra ($CDCl_3$, at r.t.) of poly-**1a** obtained by Pd catalysts **I** (Table 1, run 4)

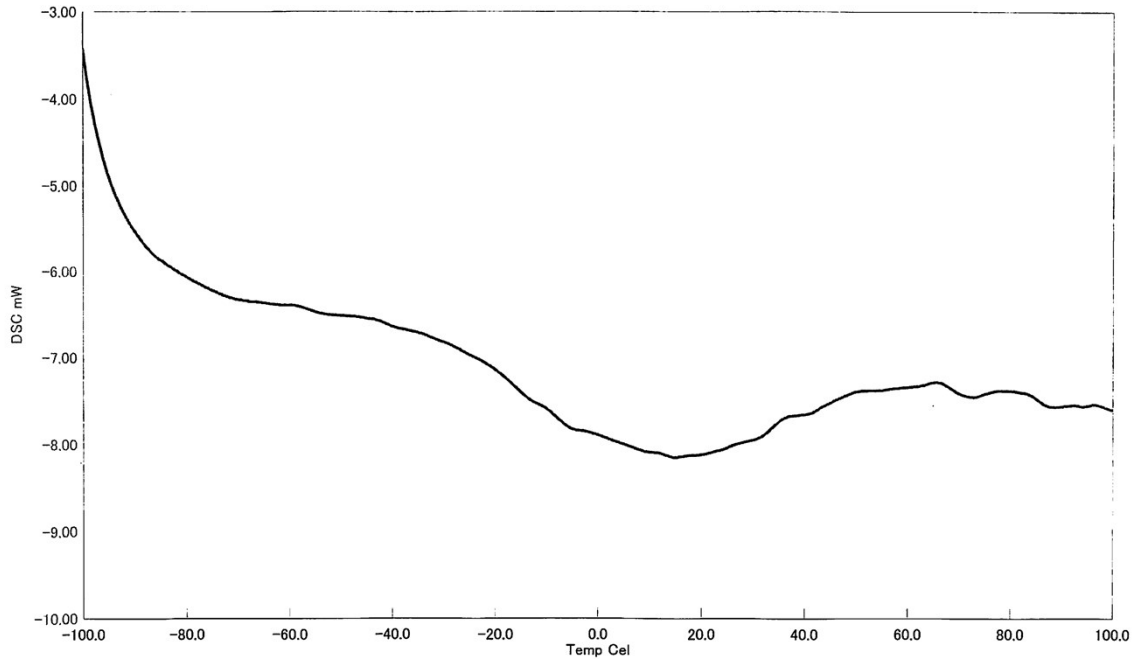

Figure S-11. DSC chart of poly-**1a** obtained by Pd catalysts **I** (Table 1, run 4) (heating : 10 ^{o}C min^{-1}, cooling : 20 ^{o}C min^{-1}, 2^{nd} scan**)**

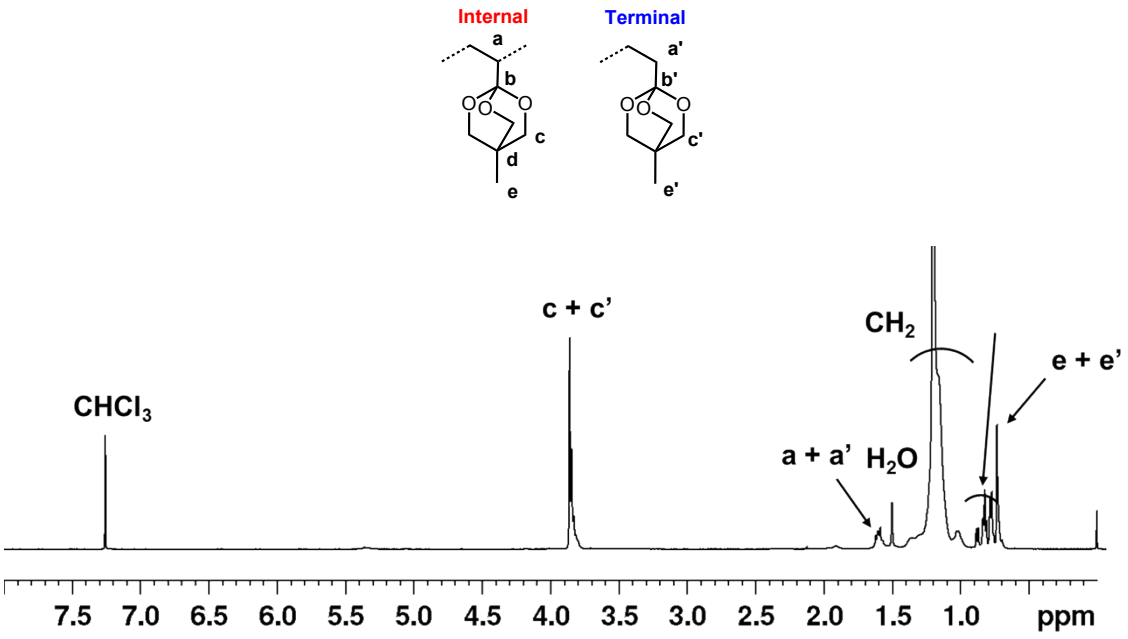

Figure S-12. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of poly-**1b** obtained by Pd catalysts **I** (Table 1, run 11)

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.38 (vinylene), δ 3.89,3.87 (s, d+d'), δ 1.67, 1.62 (m, a+a'), δ 0.79,0.78 (s, e+e') δ 1.25 (-CH_2-), δ 0.94-0.83 (-CH_3).

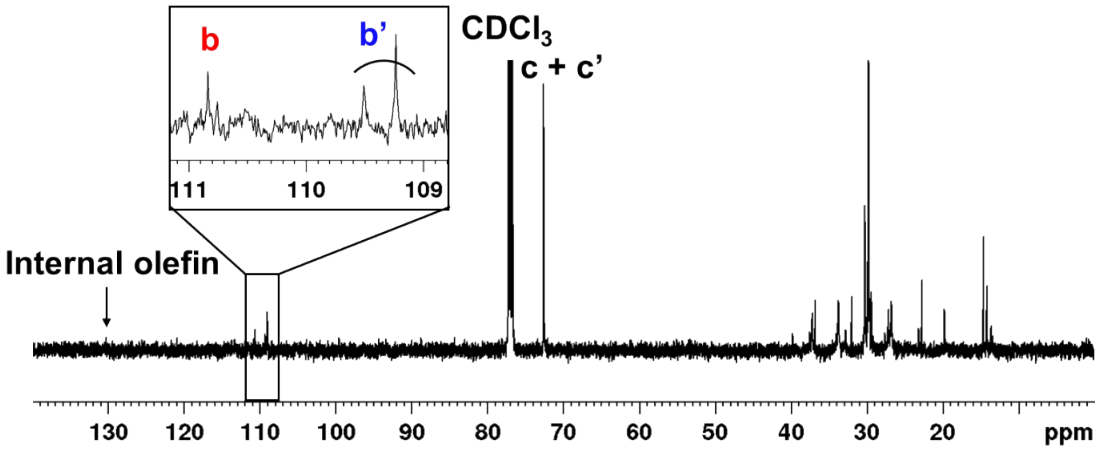

Figure S-13. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, at r.t.) of poly-**1b** obtained by Pd catalysts **I** (Table 1, run 11)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 110.8(b), δ 109.5, 109.2 (b'), δ 72.7 (c+c'), δ 39.9 (a), δ 36.9 (a'), δ 13.7 (e+e').

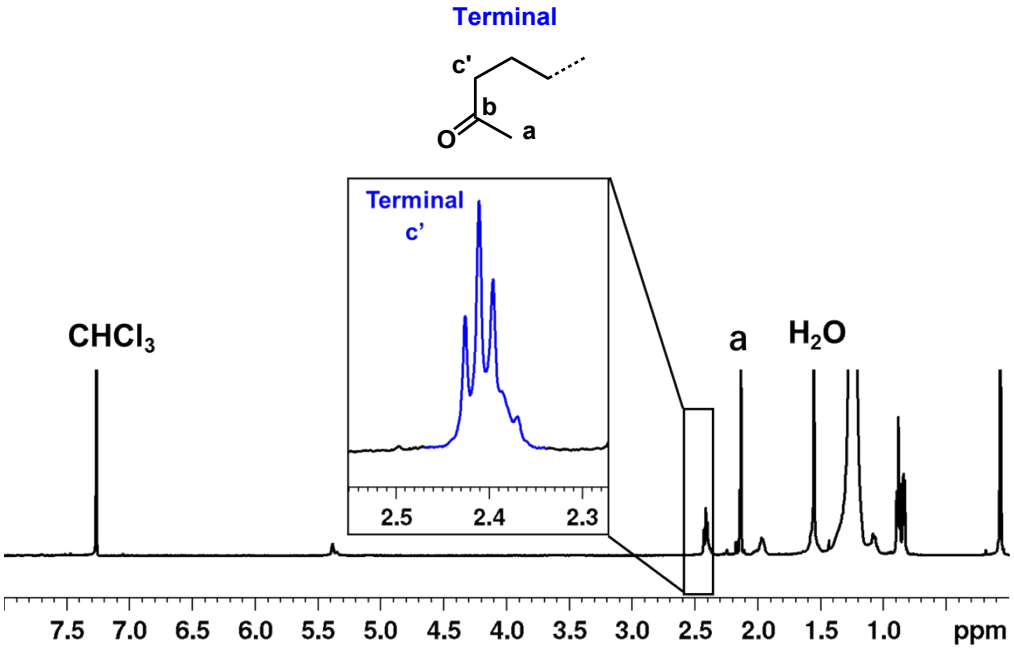

Figure S-14. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of the copolymer of 1-decene with MVK obtained by Pd catalyst **I** (Table 1, run 15)

^{1}H NMR(500 MHz, $CDCl_3$, r.t.) δ 5.38(vinylene), δ 2.41(t, c'), δ 2.13(s, CO*Me*), δ 1.25 (-CH_2-), δ 0.89-0.83 (-CH_3).

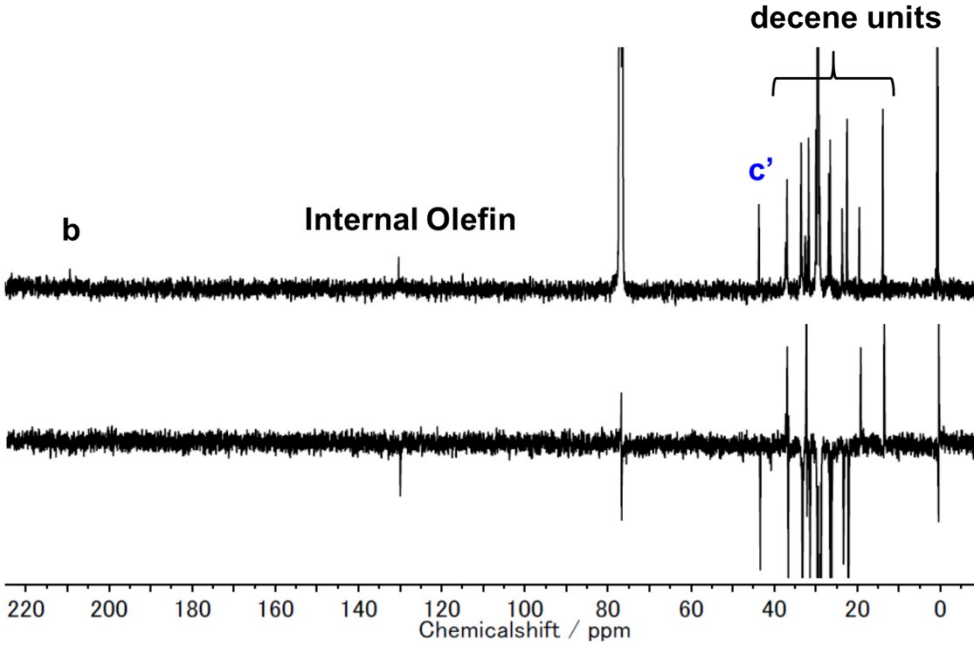

Figure S-15. ^{13}C{^{1}H} NMR and DEPT spectra ($CDCl_3$, at r.t.) of the copolymer of 1-decene with MVK (Table 1, run 15)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.) δ 209.5 (b), δ 130.47(vinylene), δ 43.9 (c').

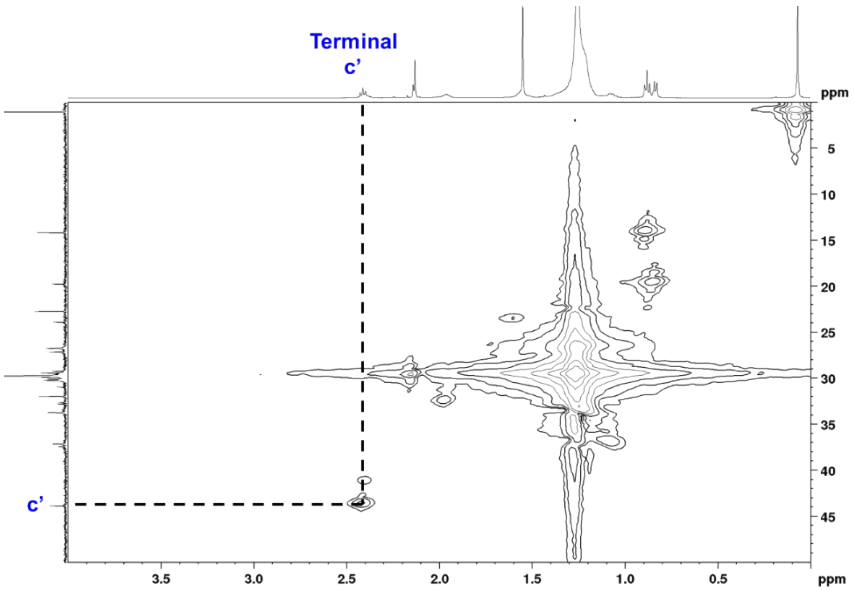

Figure S-16. HMQC spectrum ($CDCl_3$, at r.t.) of the copolymer of 1-decene with MVK (Table 1, run 15)

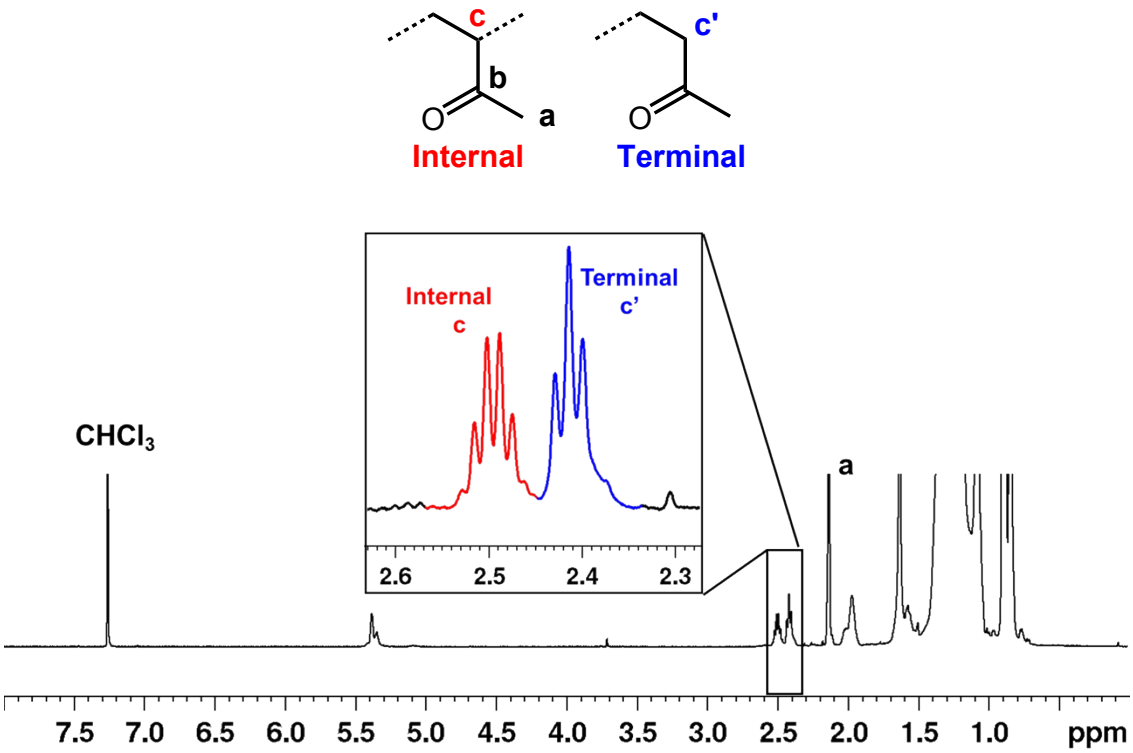

Figure S-17. ^1H NMR spectrum ($CDCl_3$, at r.t.) of poly-**4** obtained by polymer reaction
^1H NMR(500 MHz, $CDCl_3$, r.t.) δ 5.38(vinylene), δ 2.51-2.47 (m, c), δ 2.42 (t, c'), δ 2.13(s, CO*Me*), δ 1.25 (-CH_2-), δ 0.89-0.83 (-CH_3).

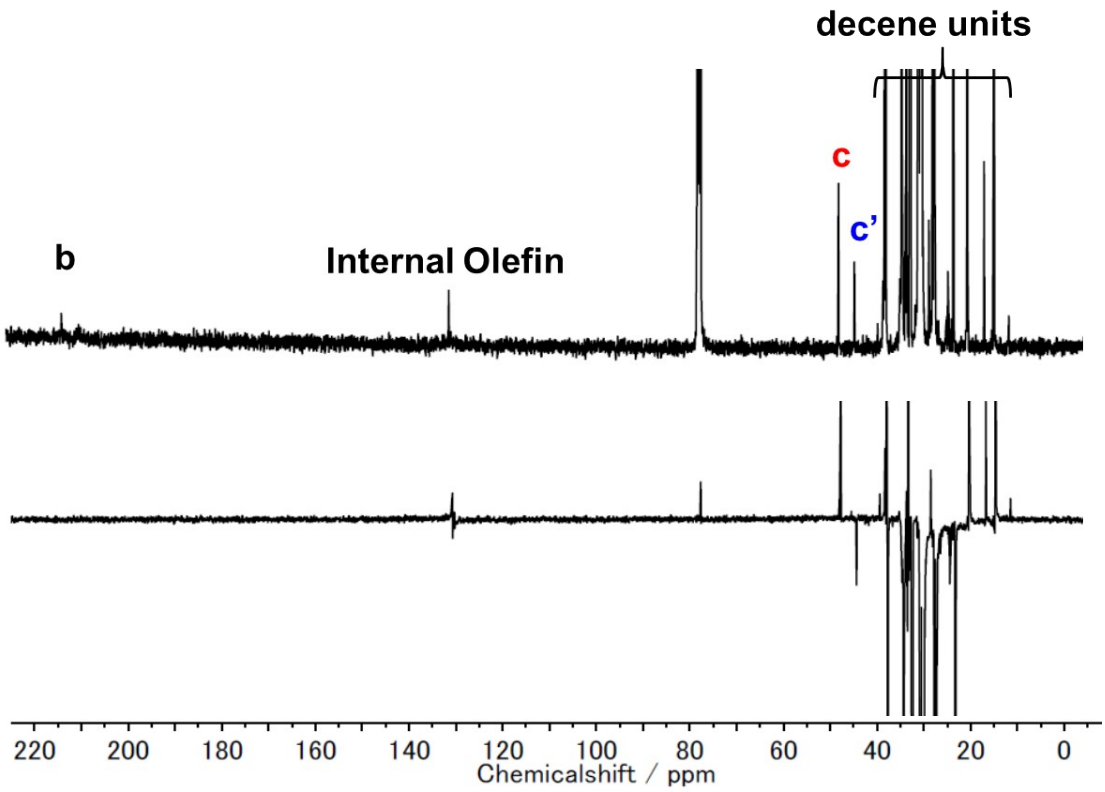

Figure S-18. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, at r.t.) of poly-**4** obtained by polymer reaction.

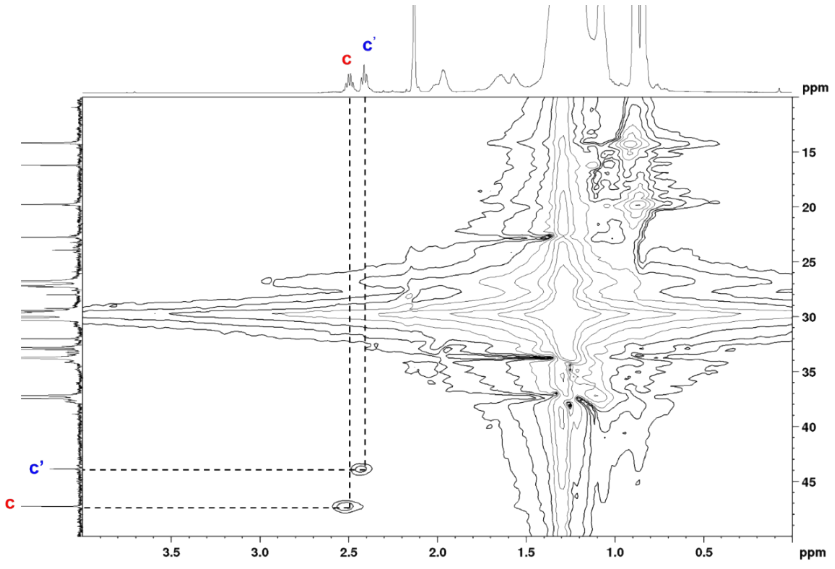

Figure S-19. HMQC spectrum ($CDCl_3$, at r.t.) of poly-**4** obtained by polymer reaction.

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, r.t.) δ 213.2 (b), δ 47.4 (c), δ 44.0 (c').

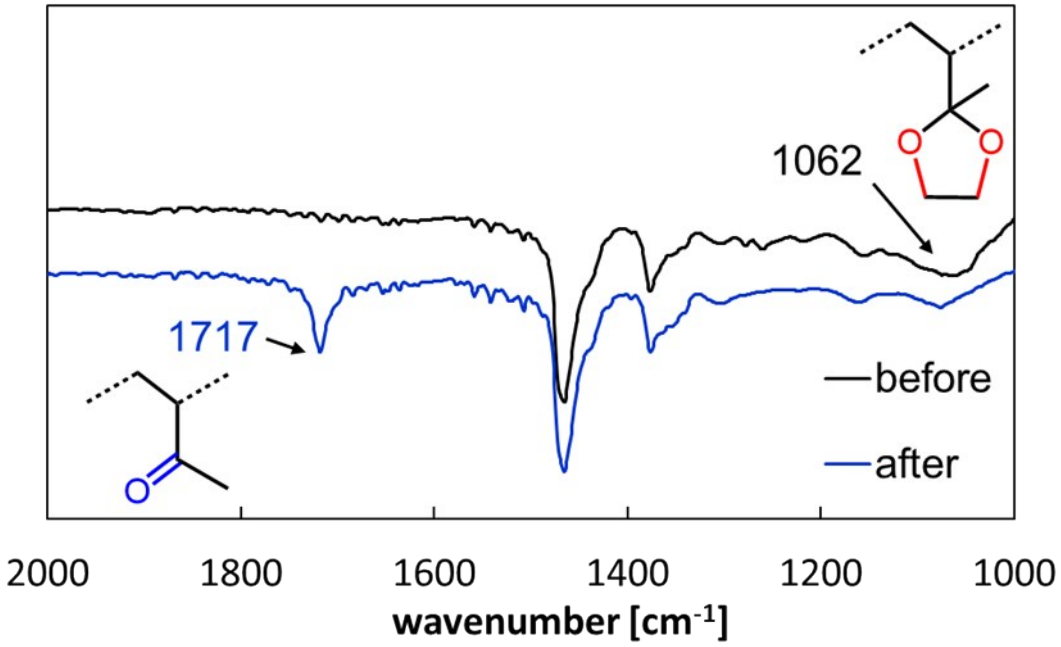

Figure S-20. IR spectra of poly-**2a** and poly-**4**.

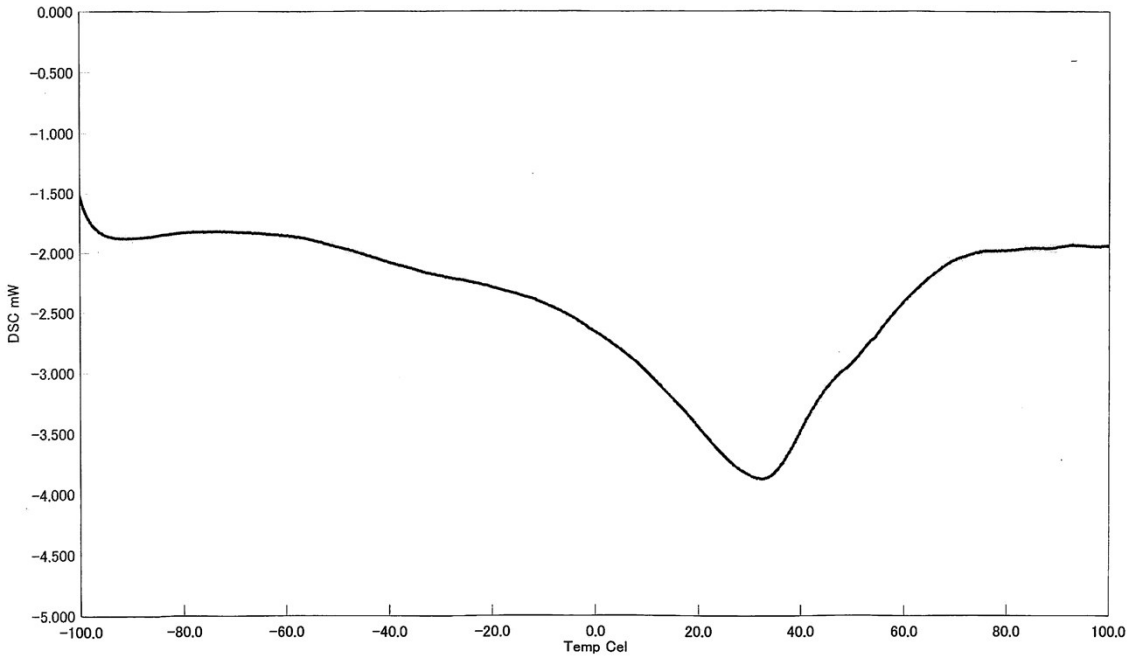

Figure S-21. DSC charts of poly-**4**
(heating : 10 ^{o}C min^{-1}, cooling : 20 ^{o}C min^{-1}, 2nd scan)

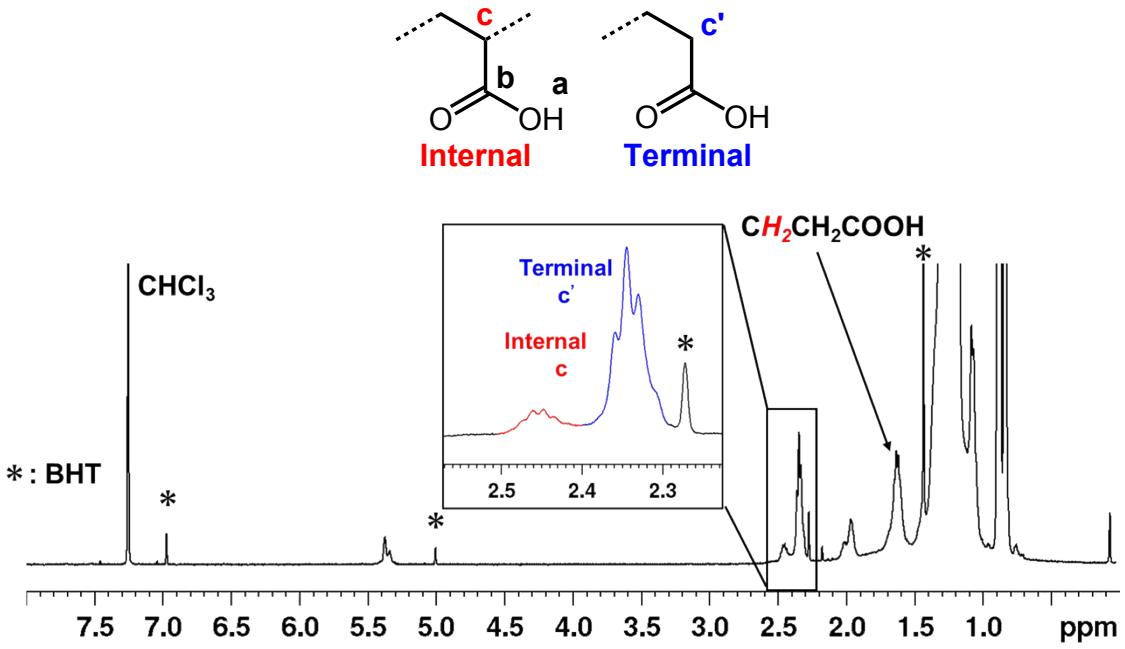

Figure S-22. ^{1}H NMR spectrum ($CDCl_3$, at r.t.) of poly-**3** obtained by polymer reaction

^{1}H NMR (500 MHz, $CDCl_3$, r.t.) δ 5.38(vinylene), δ 2.47-2.43 (m, c), δ 2.34 (t, c'), δ 1.63-1.61 (m, C*H*$_2$CH$_2$COOH), δ 1.25 (-CH_2-), δ 0.89-0.83 (-CH_3).

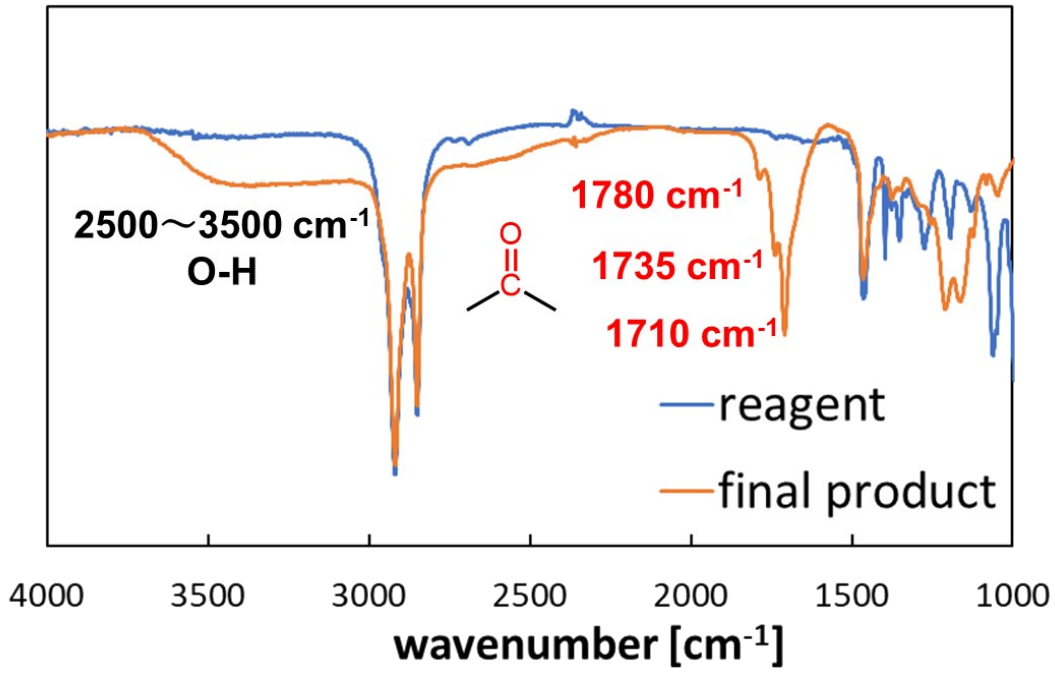

Figure S-23. IR spectra of poly-**1a** (25% of the VTO unit in the copolymer) and its hydrolyzed polymer.

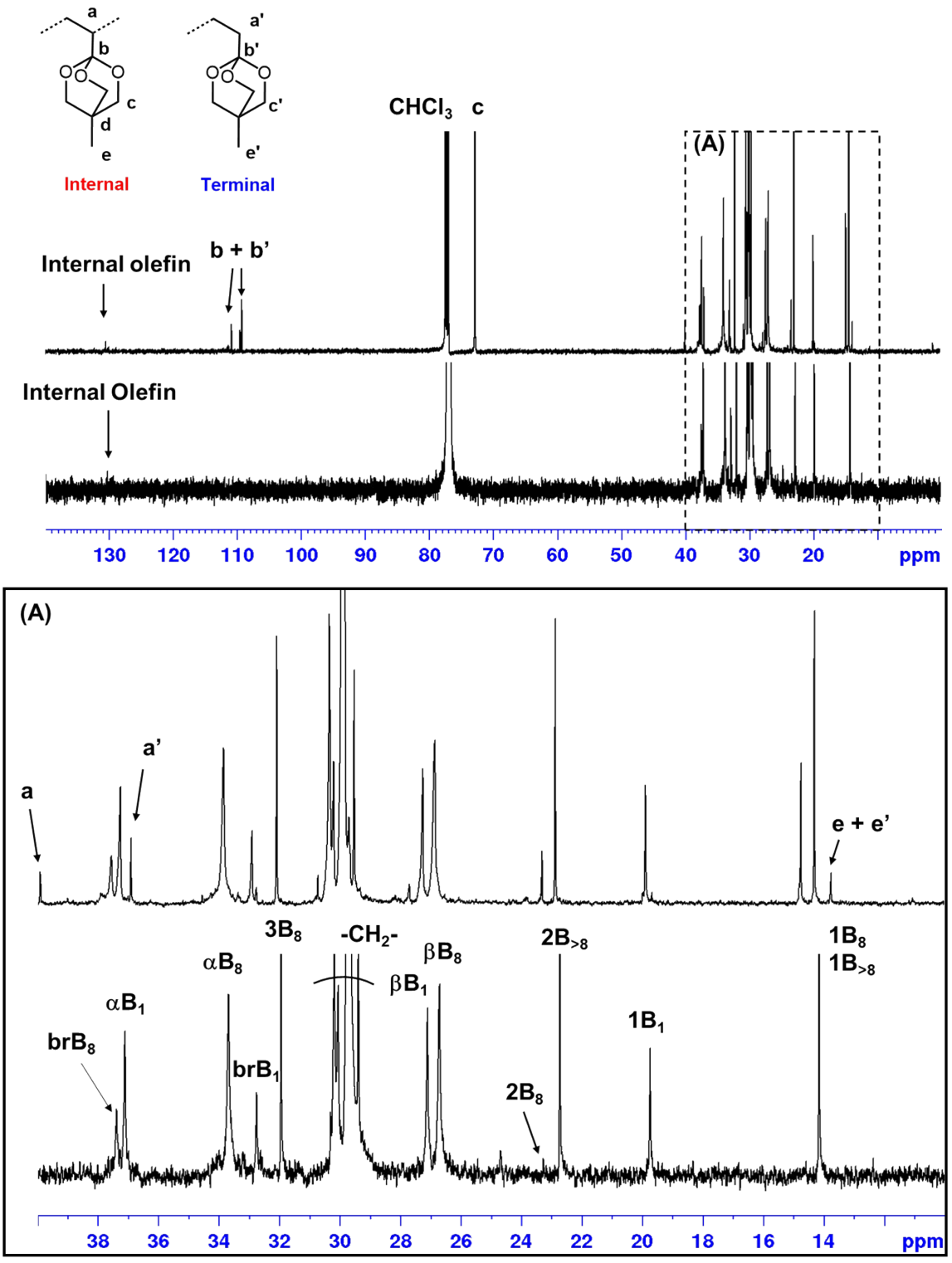

Figure S-24. $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, at r.t.) of poly-**1a** (upper) and poly-**3** (lower) obtained by polymer reaction.

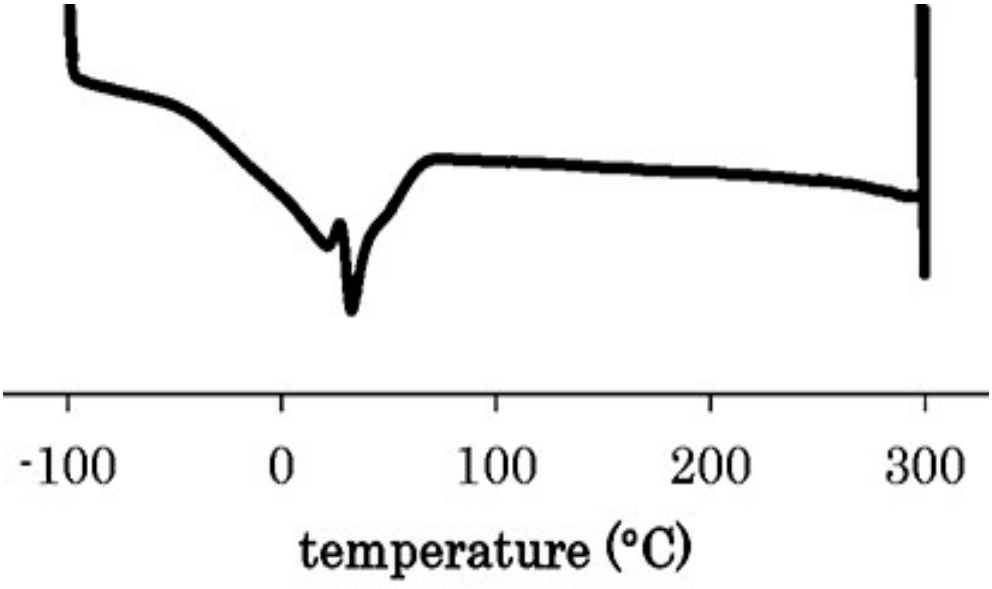

Figure S-25. DSC charts of poly-**3**
(heating : 10 ^{o}C min^{-1}, cooling : 20 ^{o}C min^{-1}, 2nd scan**)**