Supporting Information

Diverse approaches to star polymers via cationic and radical RAFT cross-linking reactions using mechanistic transformation

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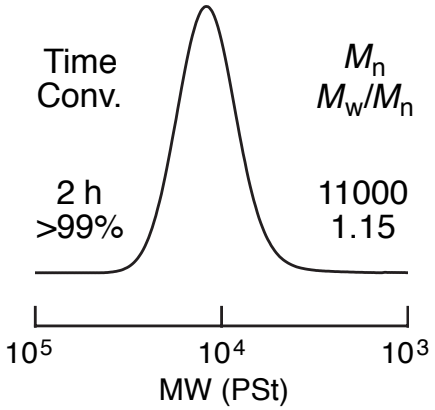

Fig. S1. SEC curve of the polymer obtained via cationic RAFT polymerization of IBVE in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10) at –78 °C: $[IBVE]_0/[CTA]_0/[TfOH]_0 = 400/4.0/0.02$ mM.

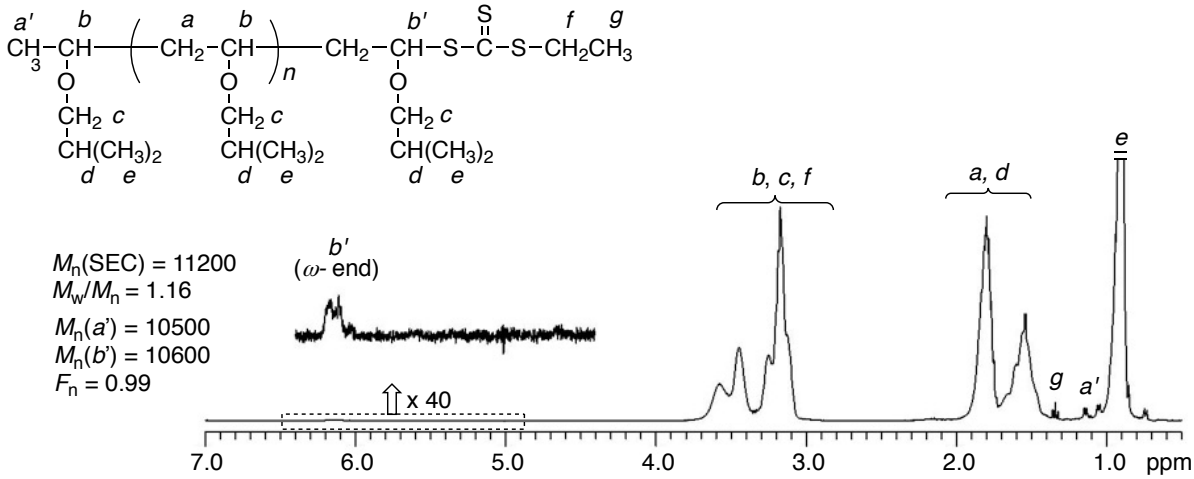

Fig. S2. ^1H NMR spectrum (in $CDCl_3$ at 55 °C) of poly(IBVE) obtained in the same experiments as for Fig. S1.

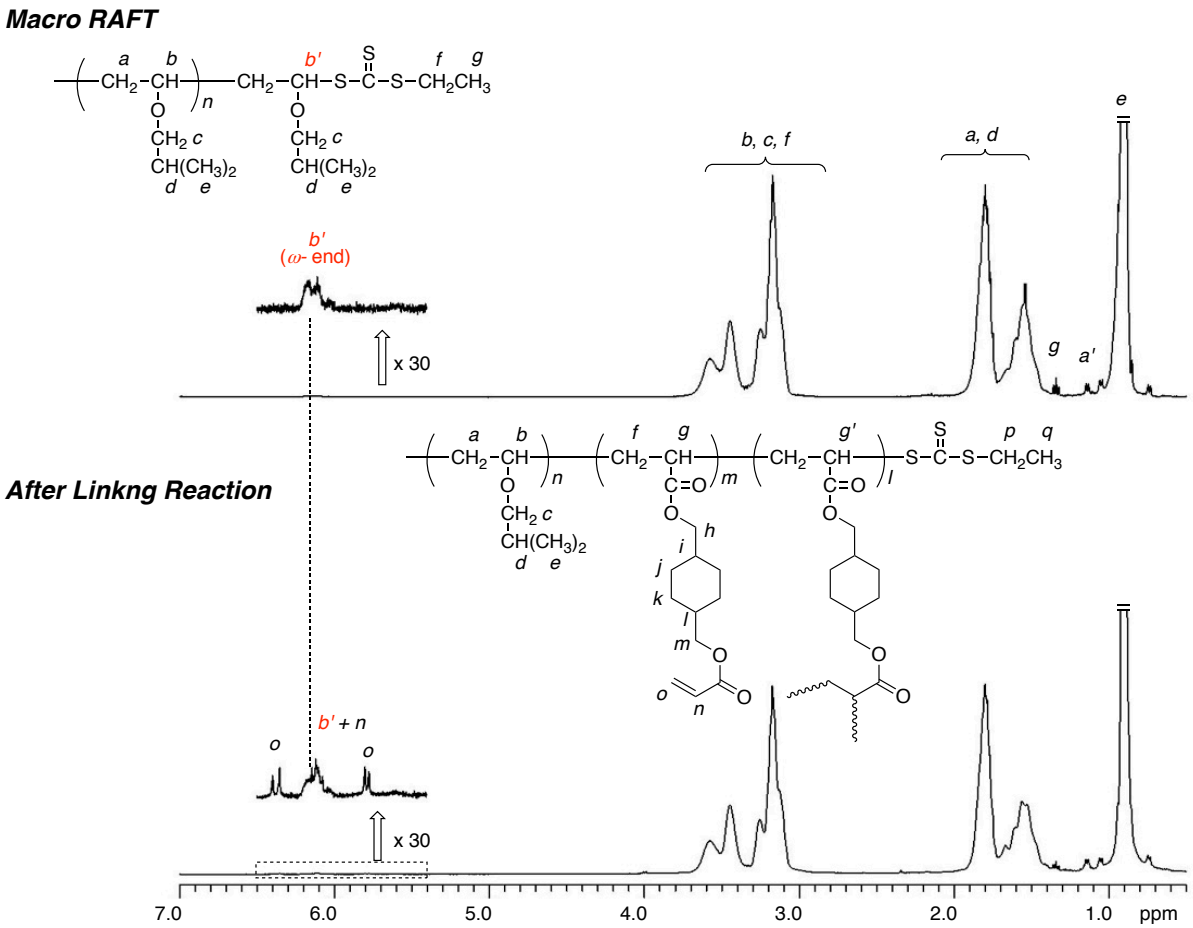

Fig. S3. ^{1}H NMR spectra (in $CDCl_3$ at 55 °C) of macro RAFT and the polymers obtained after radical cross-linking reaction of macro RAFT using **4** as divinyl compound.

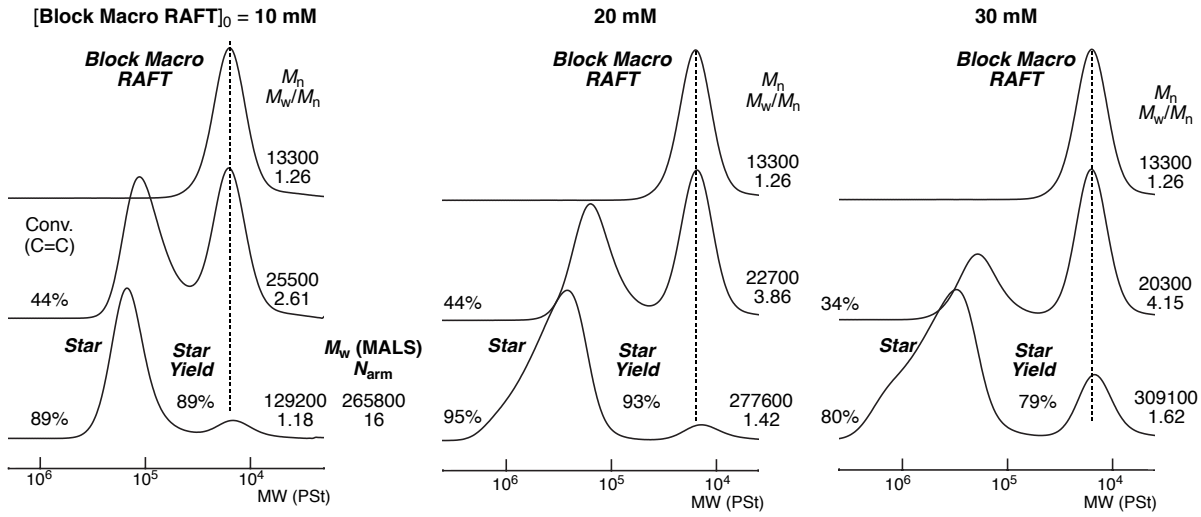

Fig. S4. SEC curves of the polymers obtained via cationic RAFT block polymerization and radical RAFT cross-linking reaction of block macro RAFT: $[\text{block macro RAFT}]_0/[\text{V-70}]_0 =$ 10–30/6.0 mM at 20 °C.

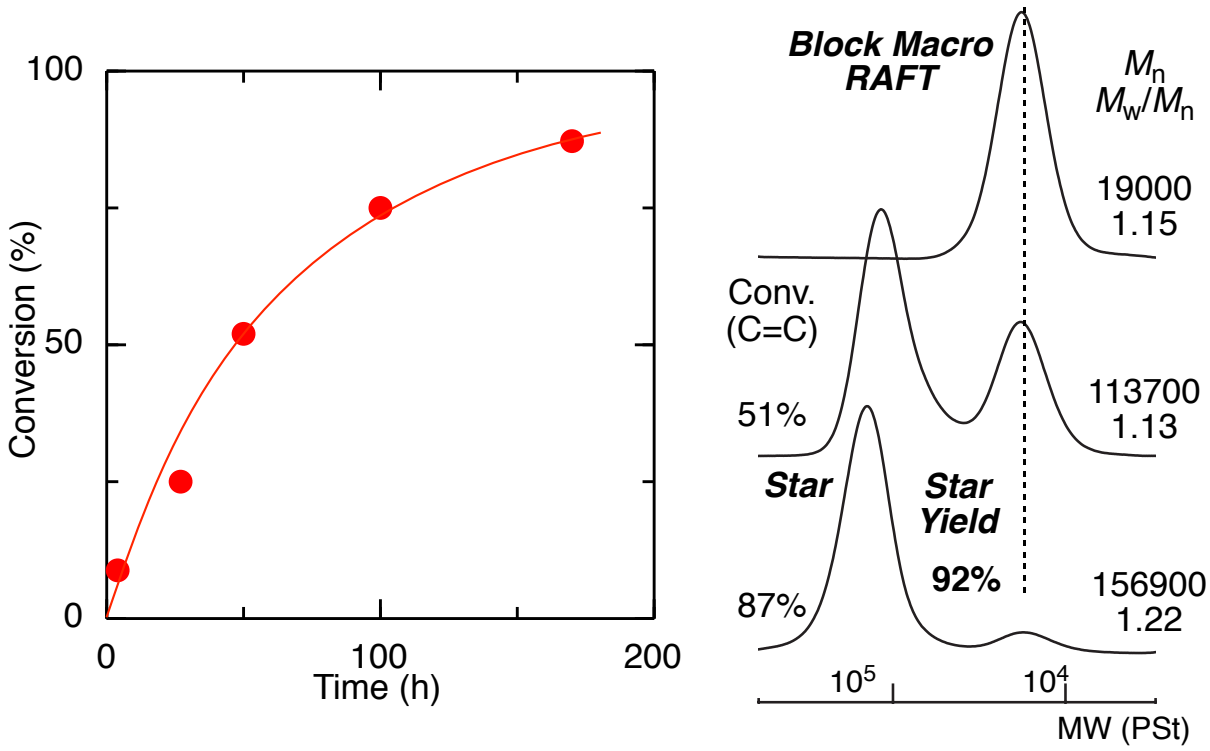

Fig. S5. Time-conversion curve and SEC curves of the polymers obtained via cationic RAFT block polymerization and radical RAFT cross-linking reaction of block macro RAFT under UV irradiation: $[\text{block macro RAFT}]_0$ = 10 mM in toluene at 20 °C under UV irradiation (λ = 366 nm).

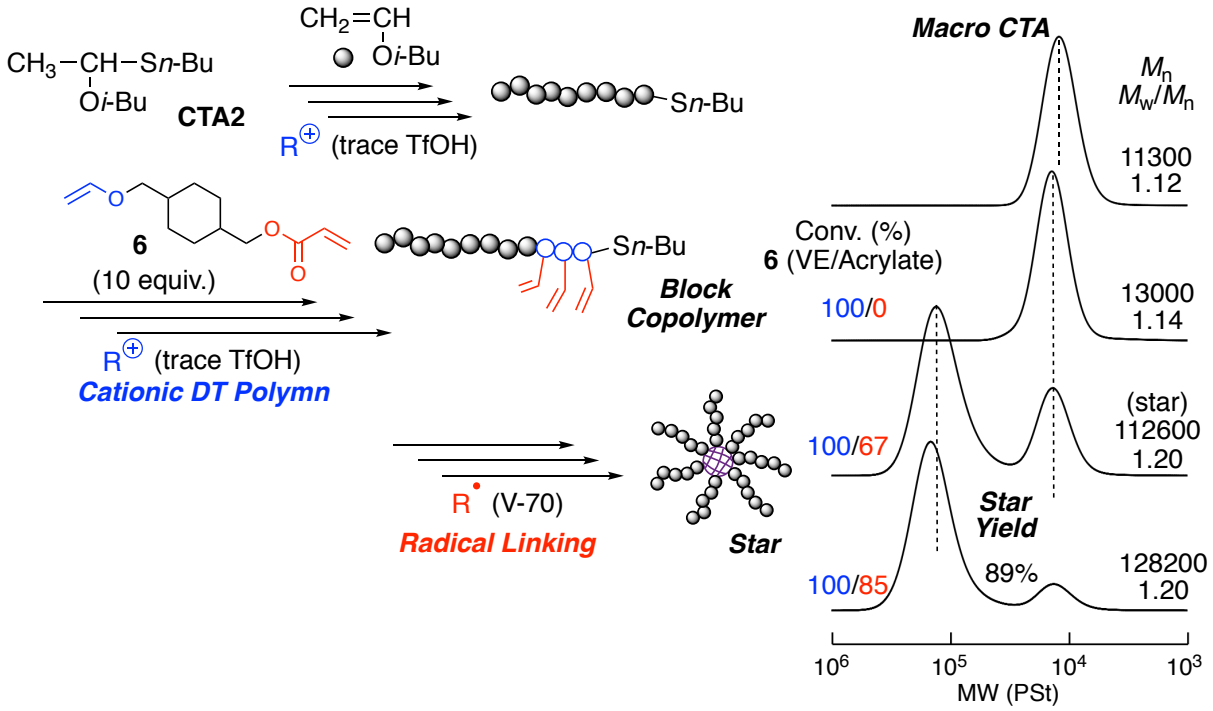

Fig. S6. SEC curves of the polymers obtained via combination of cationic block DT polymerization and radical cross-linking reaction: $[IBVE]_0/[CTA2]_0/[TfOH]_0/[\mathbf{6}]_{add}$ = 400/4.0/0.02/40 mM in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10) at –78 °C; [block copolymer]$_0$/[V-70]$_0$ =10/6.0 mM in toluene at 20 °C.

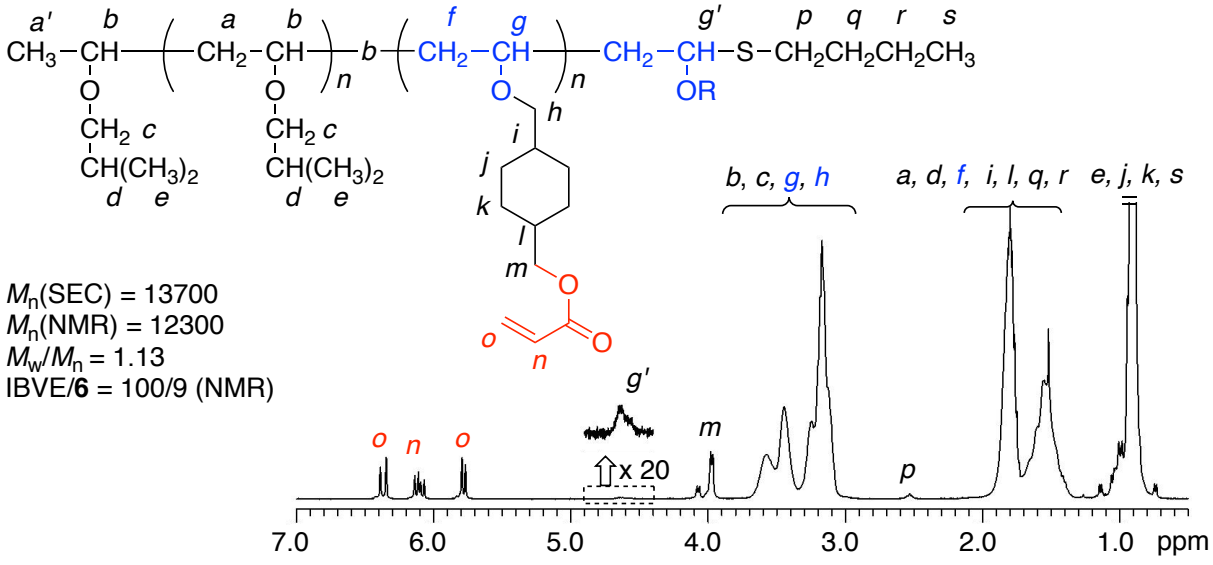

Fig. S7. ^{1}H NMR spectrum (in $CDCl_3$ at 55 °C) of poly(IBVE-*b*-**6**) obtained via cationic block DT polymerization of IBVE and **6** with CTA2 in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10) at –78 °C, M_n = 13700, M_w/M_n = 1.13: $[IBVE]_0/[CTA2]_0/[TfOH]_0/[\mathbf{6}]_{add}$ = 400/4/0.02/40 mM.

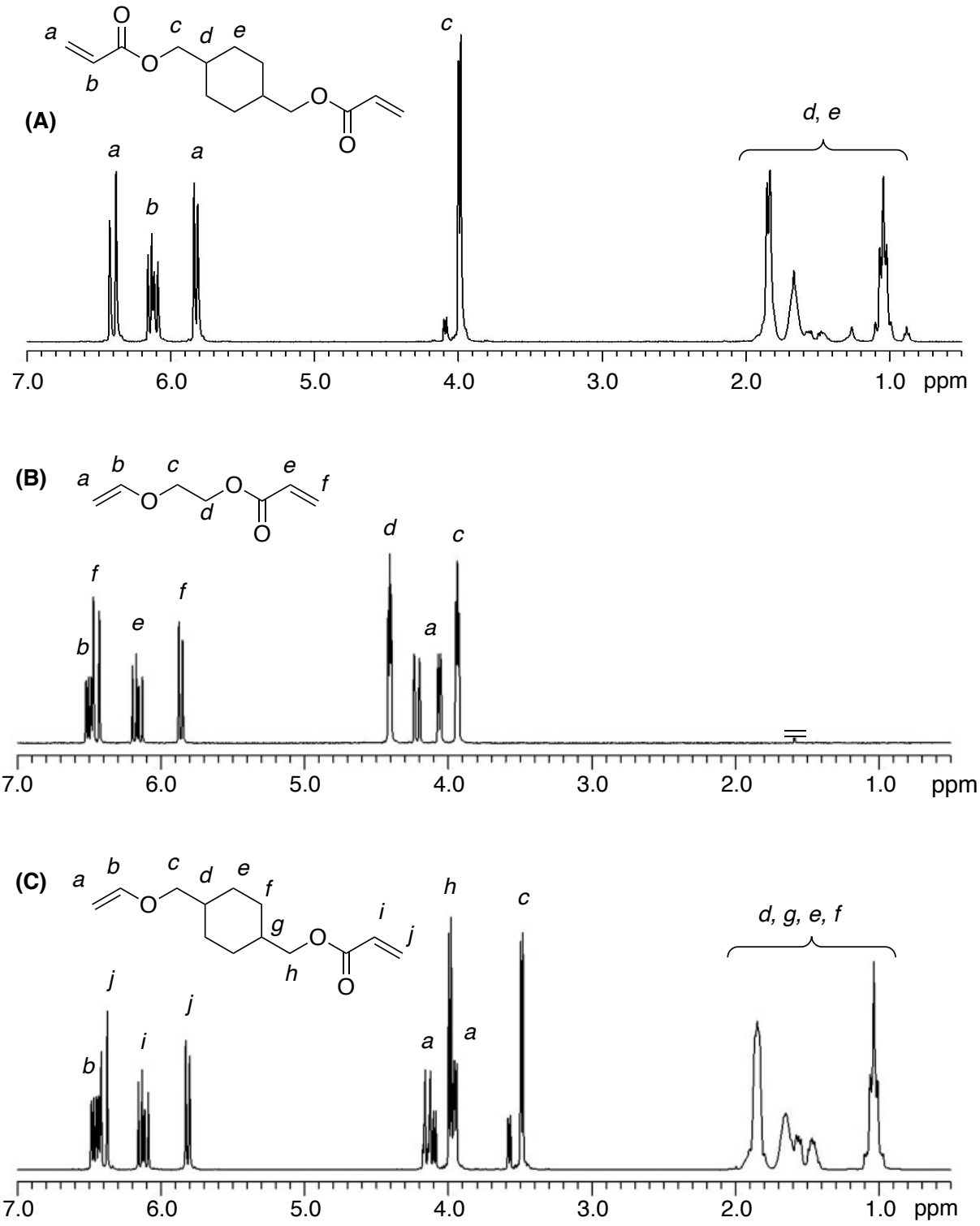

Fig. S8. ^{1}H NMR spectra (in $CDCl_3$ at r.t.) of divinyl compounds **4** (A), **5** (B), **6** (C).

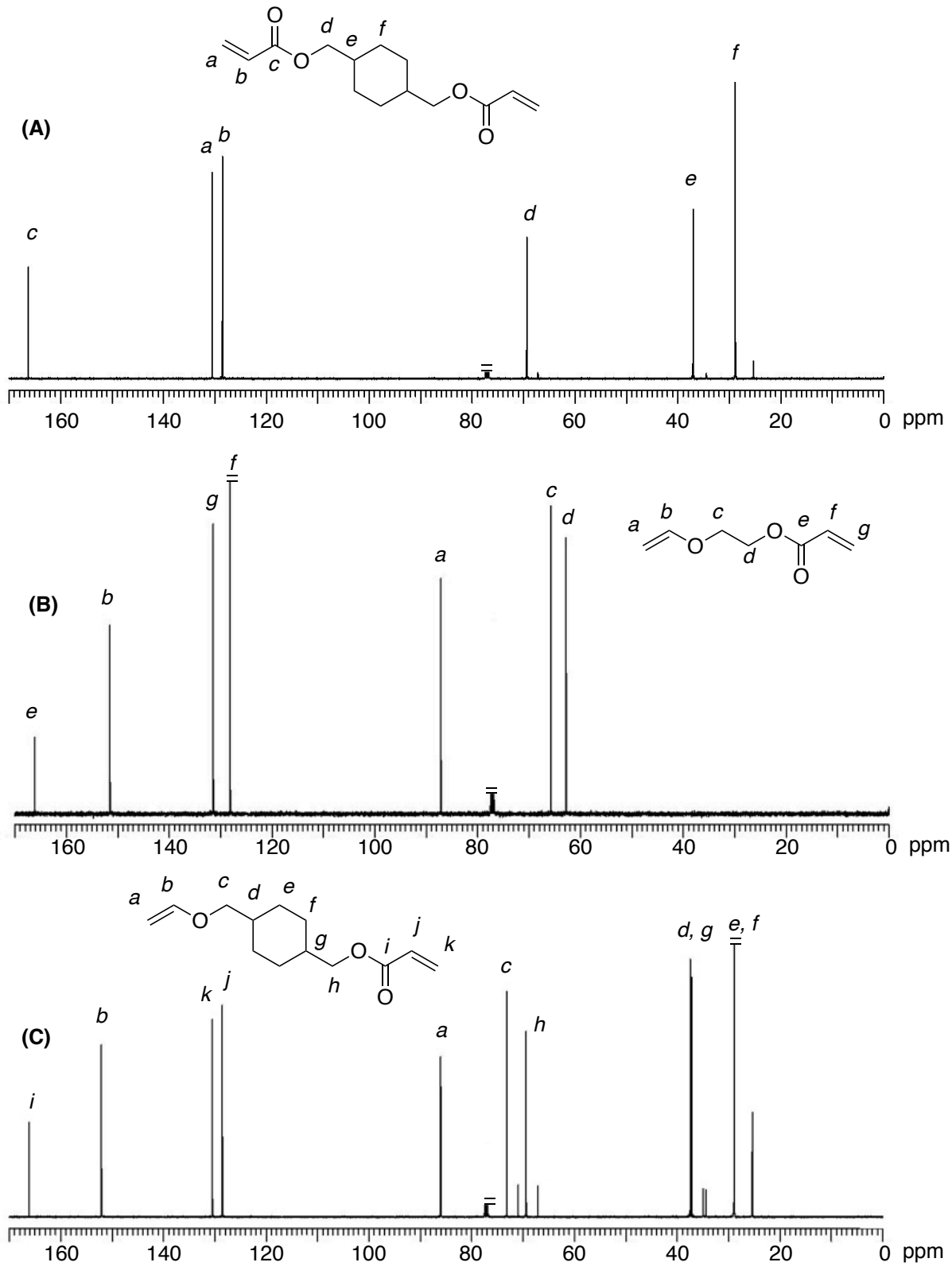

Fig. S9. ^{13}C NMR spectra (in $CDCl_3$ at r.t.) of divinyl compounds **4** (A), **5** (B), **6** (C).