

Supporting Information

Phosphonium Intermediate for Cationic RAFT Polymerization

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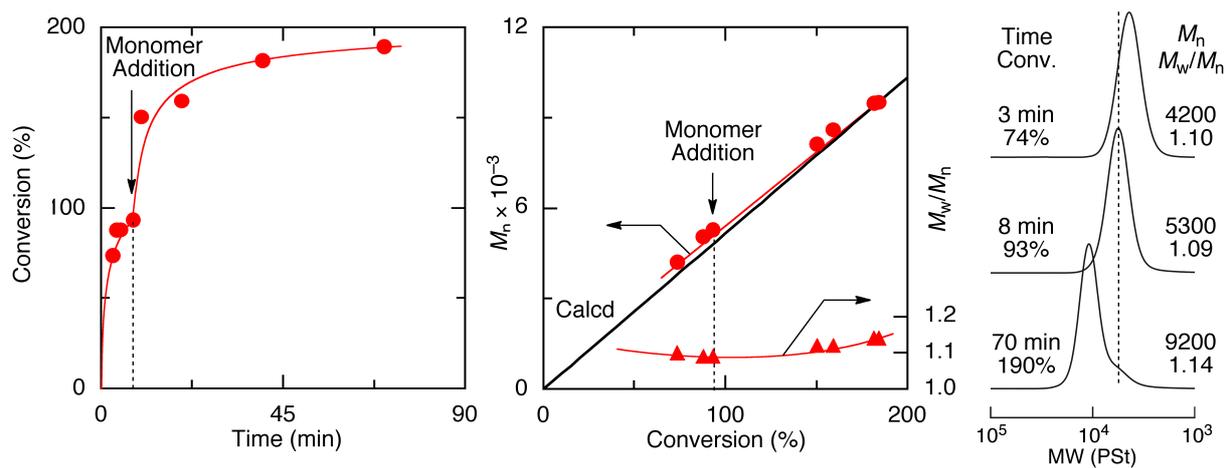


Fig. S1. Time-conversion curve, M_n , M_w/M_n , and SEC curves for monomer-addition experiment in cationic polymerization of IBVE in the presence of **1b** in *n*-hexane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10 vol%) at $-40\text{ }^\circ\text{C}$: $[\text{M}]_0/[\text{M}]_{\text{add}}/[\mathbf{1b}]_0/[\text{TfOH}]_0 = 500/500/10/0.05\text{ mM}$.

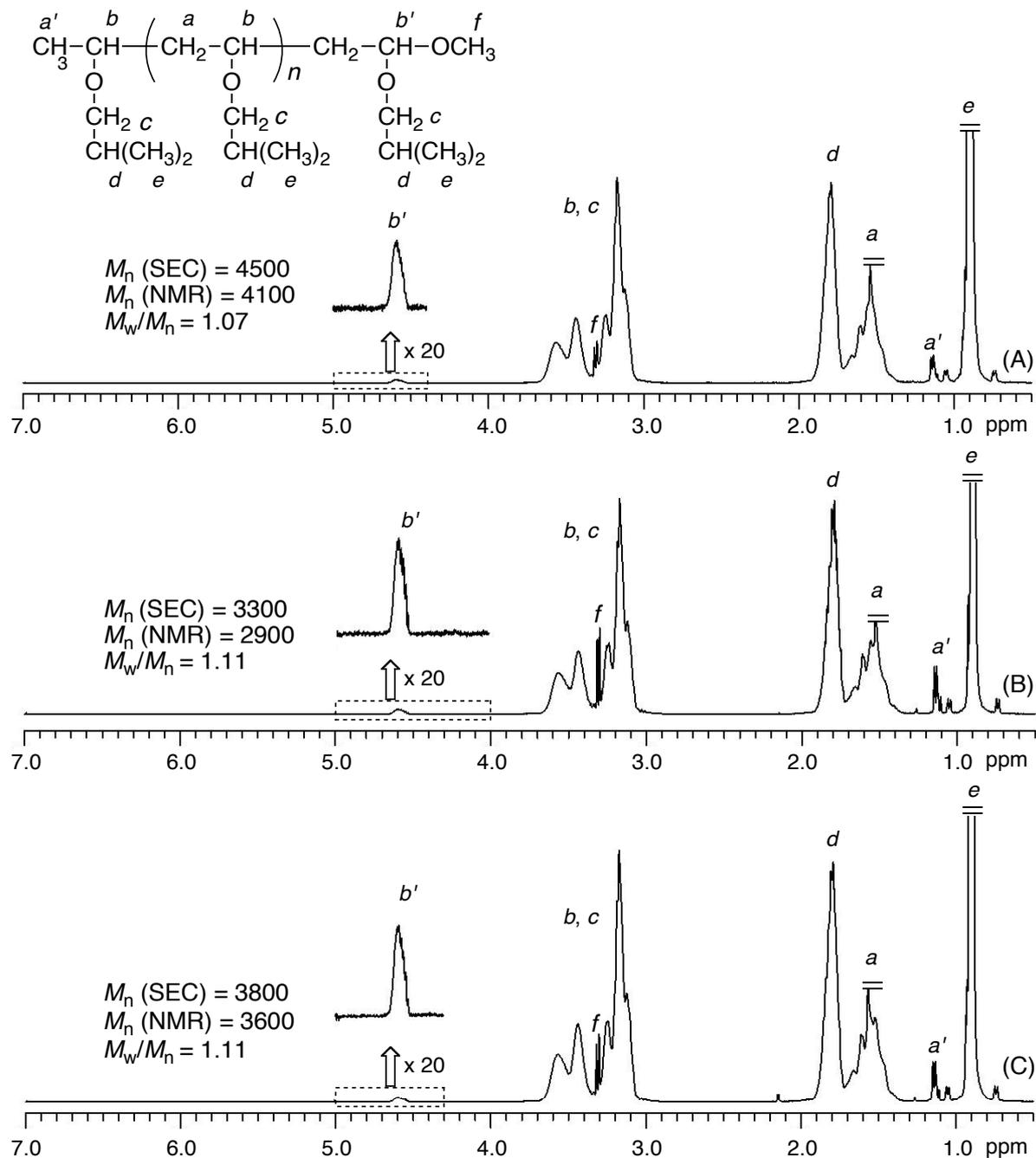


Fig. S2. ^1H NMR spectra (in CDCl_3 at $55\text{ }^\circ\text{C}$) of poly(IBVE) obtained with **1b** (A), **2b** (B), and **3b** (C) under the same conditions for Fig. 3 upon quenching with MeOH.

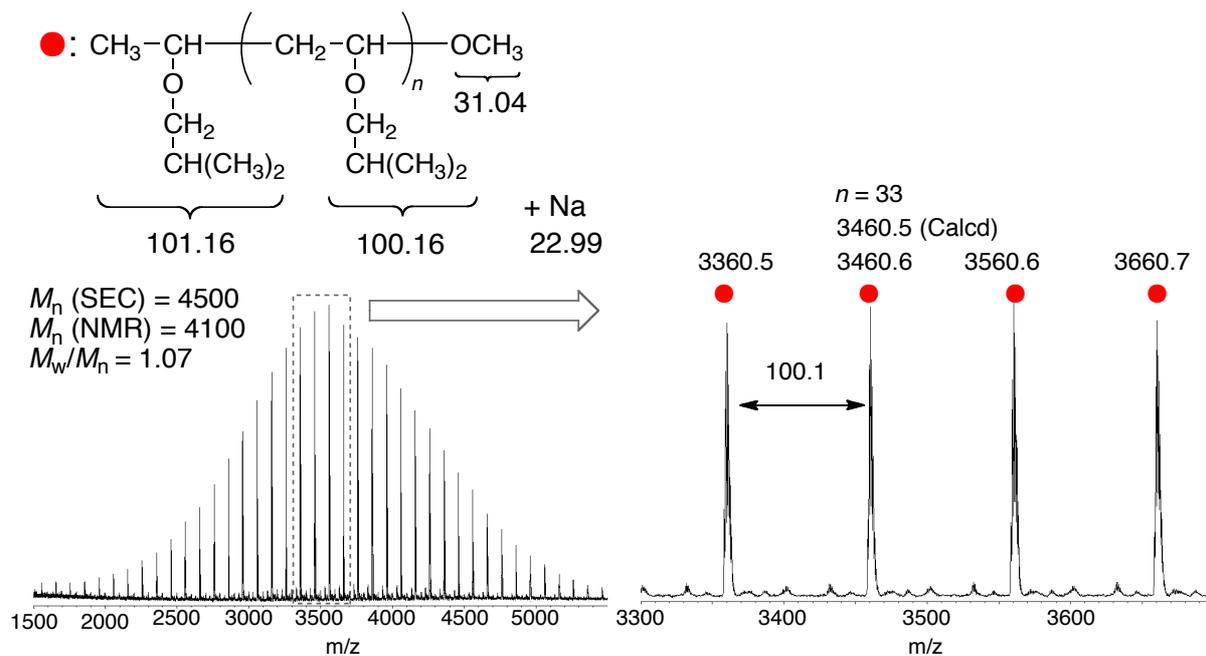


Fig. S3. MALDI-TOF-MS spectrum of poly(IBVE) obtained with **1b** under the same conditions for Fig. 3 upon quenching with MeOH.

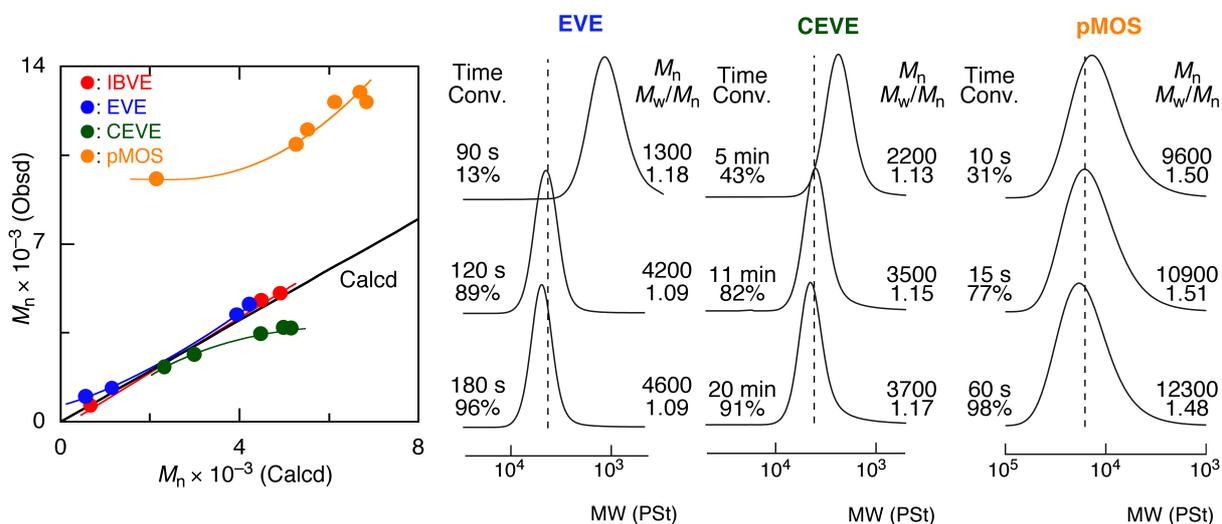


Fig. S4. M_n , M_w/M_n , and SEC curves in cationic RAFT polymerization of various monomers: $[M]_0/[1b]_0/[TfOH]_0 = 500/10/0.05$ mM in *n*-hexane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10 vol%) at -40 °C (IBVE) or -40 °C (EVE), in toluene/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10 vol%) at -40 °C (CEVE), in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (90/10 vol%) at 0 °C (pMOS).

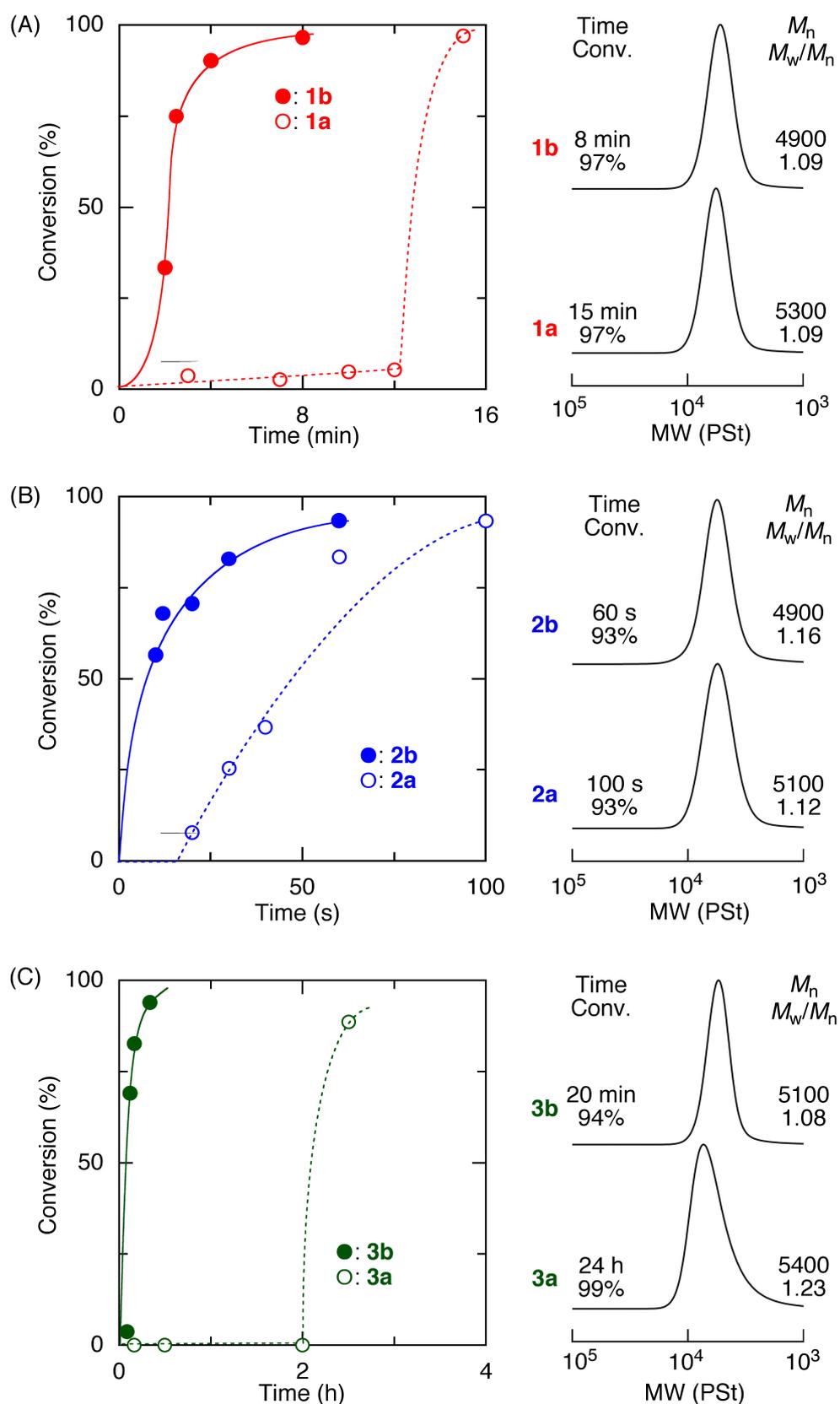


Fig. S5. Time-conversion curves and SEC curves for cationic polymerization of IBVE using **1a** and **1b** (A), **2a** and **2b** (B), and **3a** and **3b** (C) in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10 vol%) at -40 °C: $[M]_0/[chain-transfer\ agent]_0/[TfOH]_0 = 500/10/0.05$ mM.

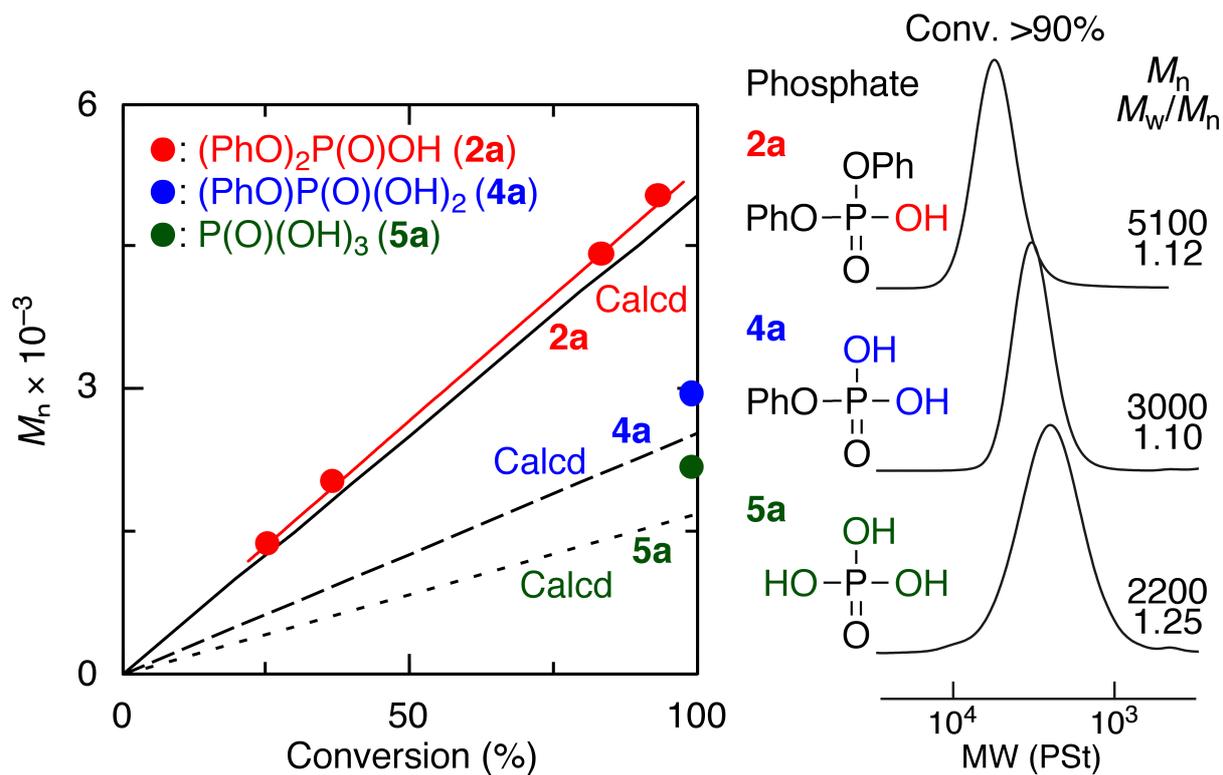


Fig. S6. M_n and SEC curves of the obtained polymers in cationic RAFT polymerization of IBVE using phosphoric mono-, di-, tri-acids in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10 vol%) at -40 °C: $[M]_0/[phosphoric\ acid]_0/[TfOH]_0 = 500/10/0.05$ mM.

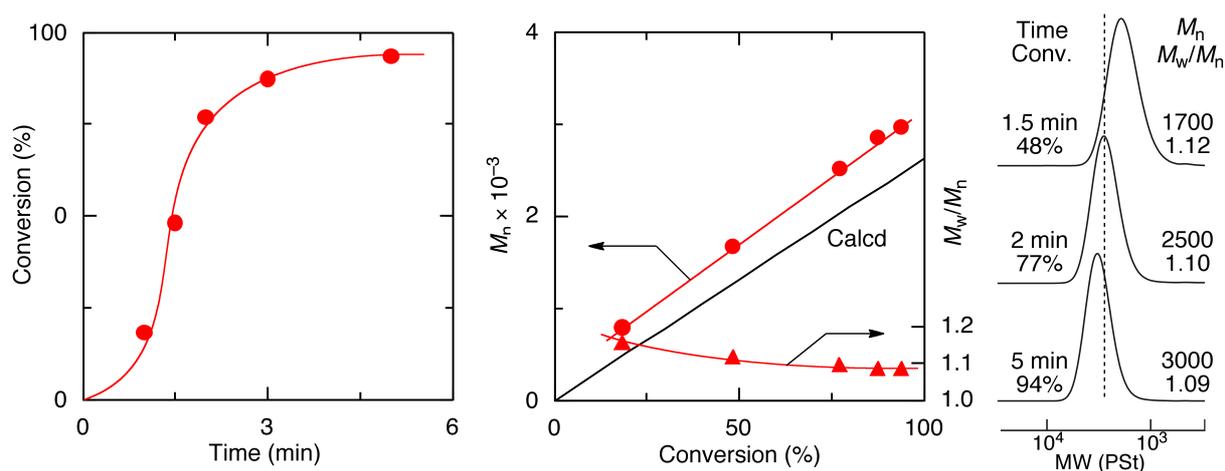


Fig. S7. Time-conversion curve, M_n , M_w/M_n , and SEC curves for cationic polymerization of IBVE with the mixture of **1b** and **6** as chain transfer agents in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10 vol%) at -40 °C: $[IBVE]_0/[1b]_0/[6]_0/[TfOH]_0 = 500/10/10/0.05$ mM.

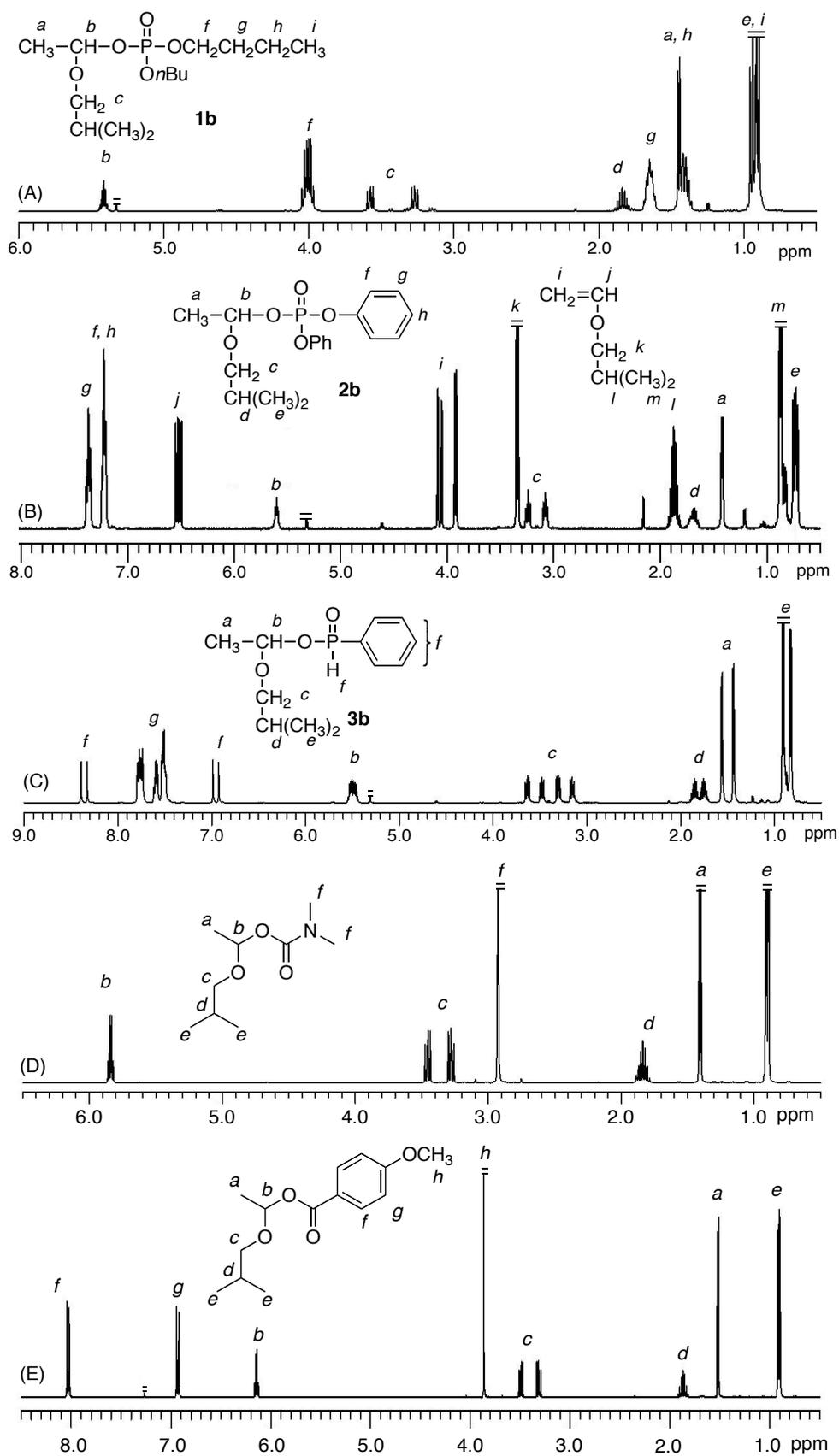


Fig. S8. ^1H NMR spectra of **1b** (A), **2b** (B), **3b** (C), IBVE-OC(O)NMe₂ (D), and IBVE-OC(O)C₆H₄OCH₃ (E) (in CDCl₂ at 0 °C for **1b**, **2b**, and **3b** or CDCl₃ at r.t. for IBVE-OC(O)NMe₂ and IBVE-OC(O)C₆H₄OCH₃).

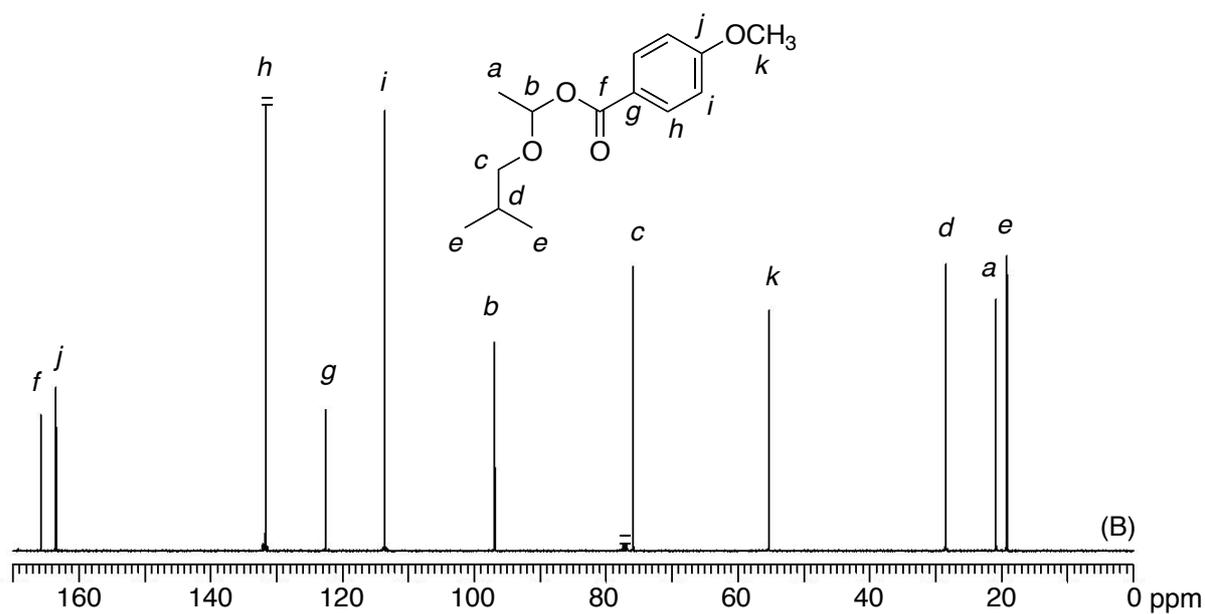
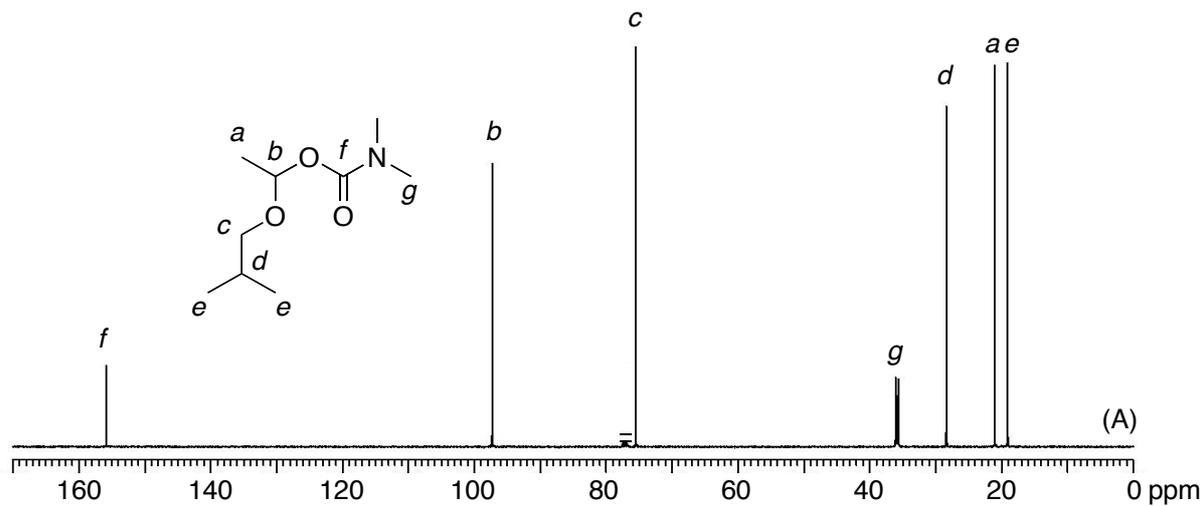


Fig. S9. ^{13}C NMR spectra of IBVE-OC(O)NMe₂ (A), and IBVE-OC(O)C₆H₄OCH₃ (B) in CDCl₃ at r.t..