Supporting Information

Biobased Polymers via Radical Homopolymerization and Copolymerization of a Series of Terpenoid-Derived Conjugated Dienes with *exo*-Methylene and 6-Membered Ring

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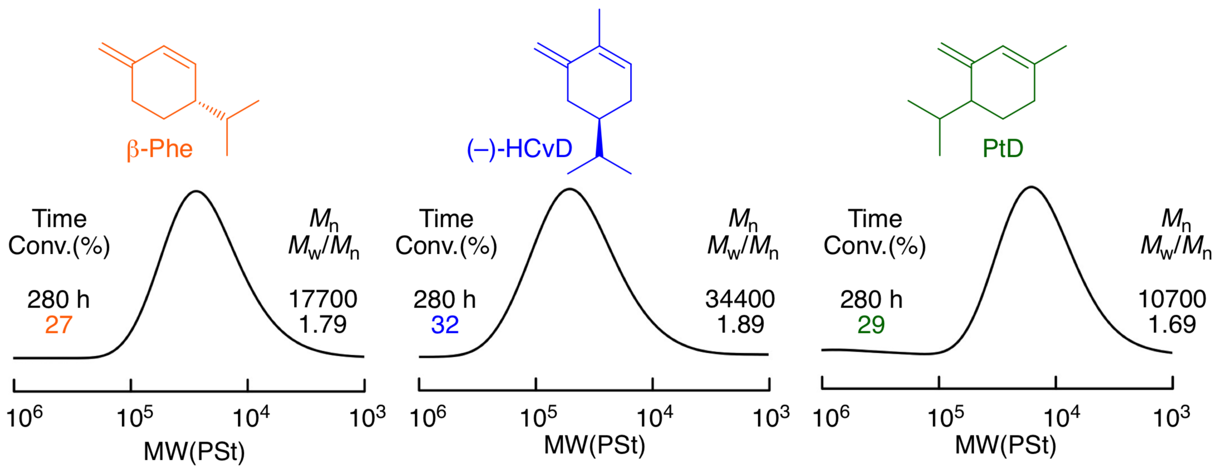


Figure S1. SEC curves of the homopolymers obtained in the radical polymerization of β-Phe, (–)-HCvD, and PtD: $[M]_0/[VAm\text{-}110]_0$ = 5000/30 mM in toluene at 100 °C.

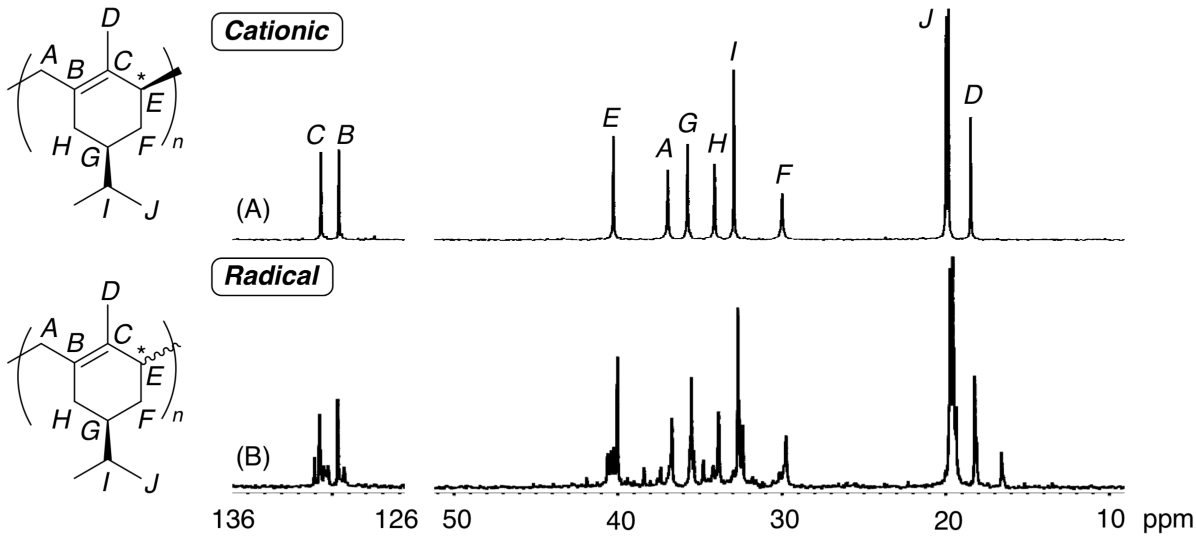


Figure S2. ^{13}C NMR spectra (in $C_2D_2Cl_4$ at 100 °C) of poly((–)-HCvD) obtained in the cationic (A) and radical (B) polymerization: $[(–)\text{-HCvD}]_0/[\text{CEVE-HCl}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C (M_n(Calcd) = 15200) (A) or $[(–)\text{-HCvD}]_0/[VAm\text{-}110]_0$ = 5000/30 mM in toluene at 100 °C (B).

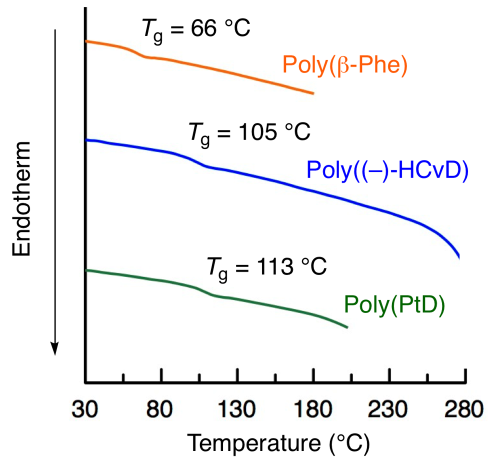


Figure S3. Differential scanning calorimetry (DSC) curves of poly(β-Phe), poly((–)-HCvD), and poly(PtD) obtained in the radical polymerization: $[M]_0/[VAm\text{-}110]_0$ = 5000/30 mM in toluene at 100 °C.

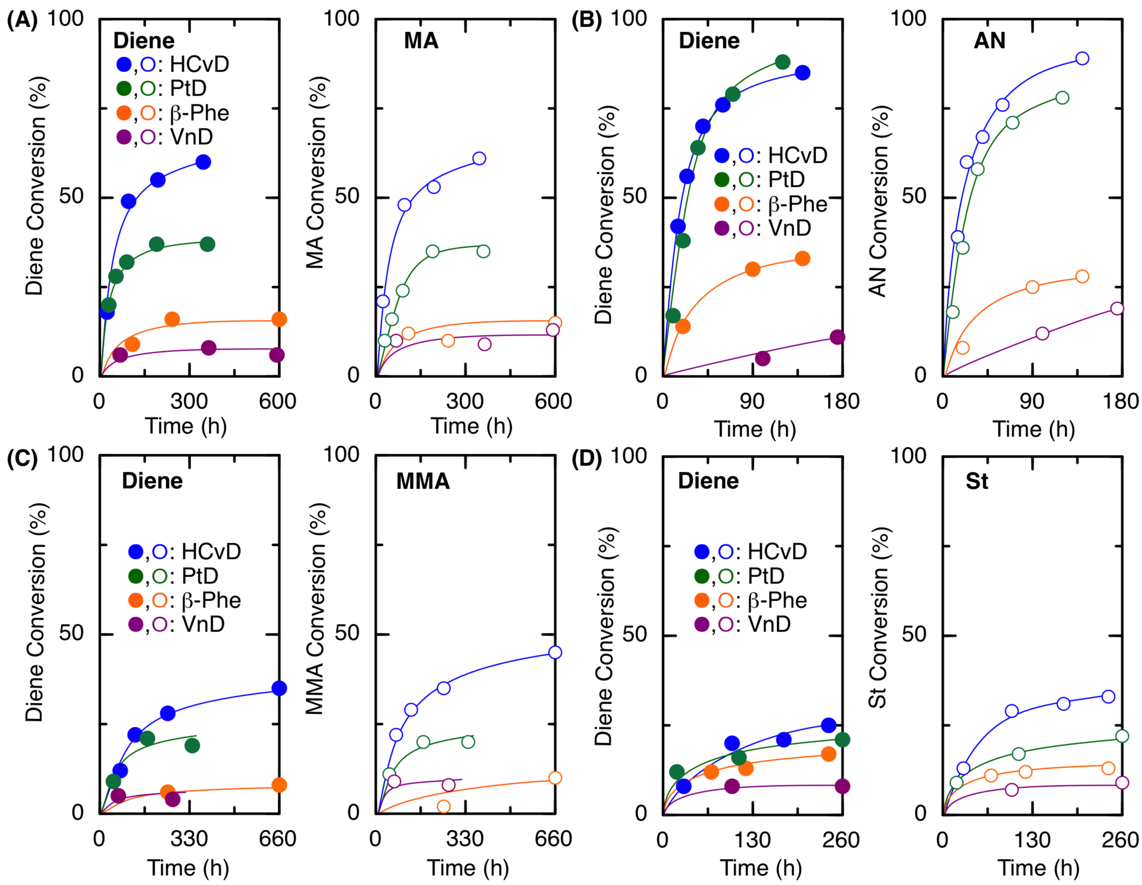


Figure S4. Time-conversion curves for the radical copolymerization of terpenoid-derived *exo*-methylene 6-membered ring conjugated dienes with MA (A), AN (B), MMA (C), and St (D) as a comonomer: $[\text{diene}]_0/[\text{comonomer}]_0/[AIBN]_0$ = 1500/1500/30 mM in toluene at 60 °C.

Table S1. Radical copolymerization of terpenoid-derived *exo*-methylene 6-membered ring conjugated dienes (M_1) and various common vinyl monomers (M_2) in toluene at 60 °C[a].

Entry	M_1	M_2	Time (h)	Conv. (%)[b] M_1/M_2	M_n(SEC)[c]	M_w/M_n[c]
1	β-Phe	MA	242	17/11	1600	2.80
2	HCvD	MA	96	49/48	11700	1.62
3	PtD	MA	90	32/25	6300	1.68
4	VnD	MA	364	8/9	480	1.87
5	β-Phe	AN	90	30/25	4700	1.96
6	HCvD	AN	24	56/60	19400	1.68
7	PtD	AN	35	64/58	14700	1.61
8	VnD	AN	175	11/19	1100	1.65
9	β-Phe	MMA	130	6/2	1700	2.60
10	HCvD	MMA	340	22/29	7900	1.91
11	PtD	MMA	250	19/20	4500	2.49
12	VnD	MMA	268	4/8	350	1.80
13	β-Phe	St	240	17/13	1400	2.51
14	HCvD	St	175	21/27	6600	2.20
15	PtD	St	110	16/17	2400	1.87
16	VnD	St	260	8/9	460	1.36

[a]Polymerization condition: $[M_1]_0/[M_2]_0/[AIBN]_0$ = 1500/1500/30 mM in toluene at 60 °C. [b]Determined by ^{1}H NMR of reaction mixture. [c]Determined by SEC.

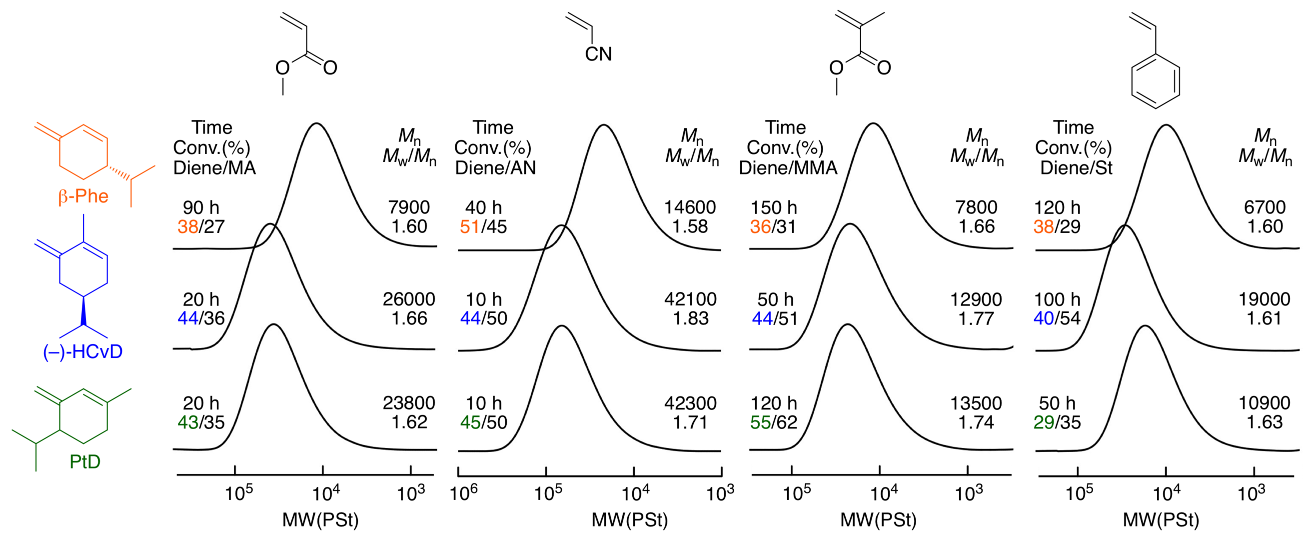


Figure S5. SEC curves of the copolymers obtained in the radical copolymerization of terpenoid-derived *exo*-methylene 6-membered-ring conjugated dienes (M_1) with various common vinyl monomers (M_2): $[M_1]_0/[M_2]_0/[VAm\text{-}110]_0$ = 1500/1500/30 mM in toluene at 100 °C.

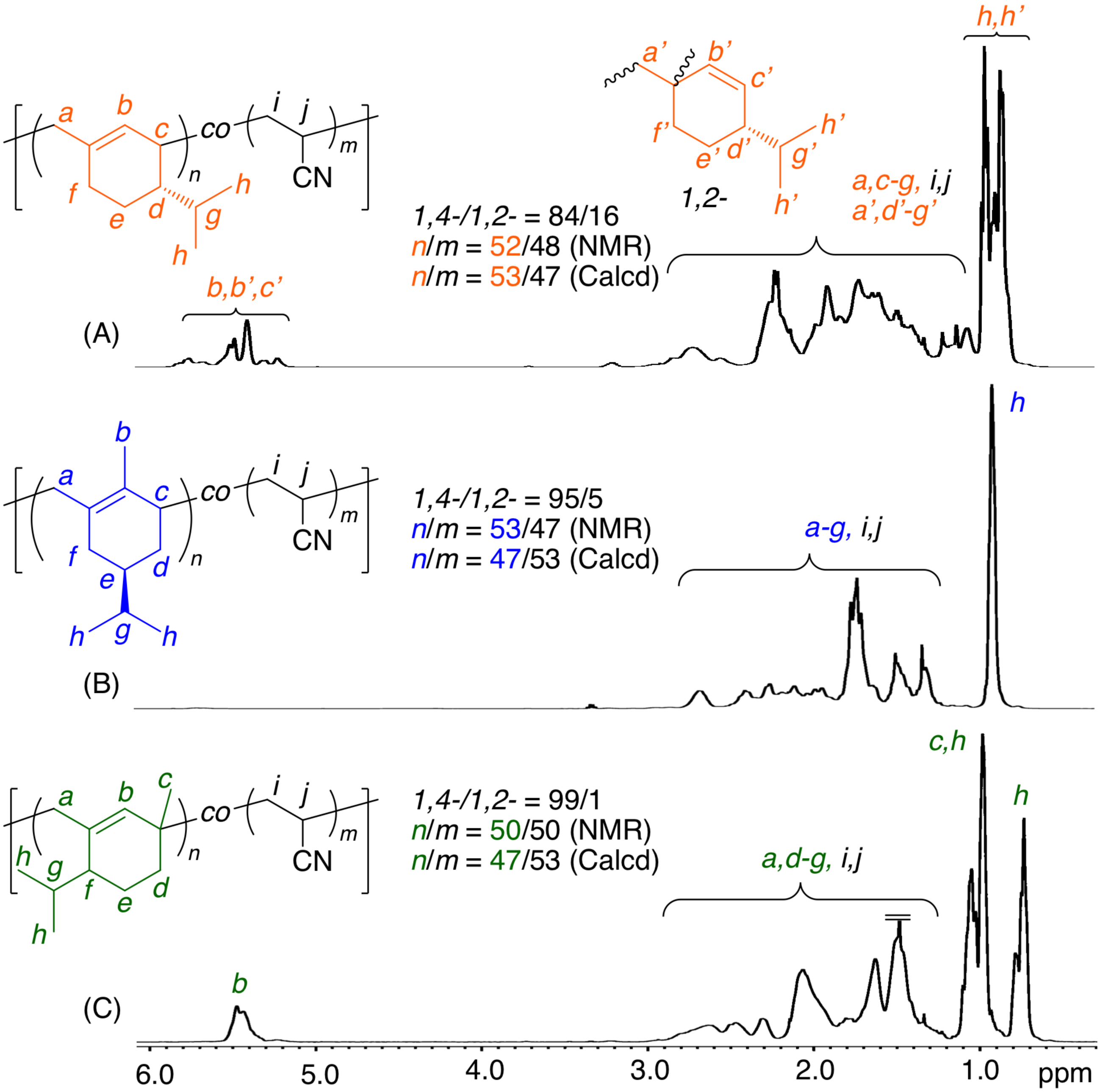


Figure S6. [1]H NMR spectra (in $CDCl_3$ at 55 °C) of copolymers obtained in the radical copolymerization of β-Phe (A), (–)-HCvD (B), or PtD (C) with AN: $[\text{diene}]_0/[\text{AN}]_0/[\text{VAm-110}]_0$ = 1500/1500/30 mM in toluene at 100 °C.

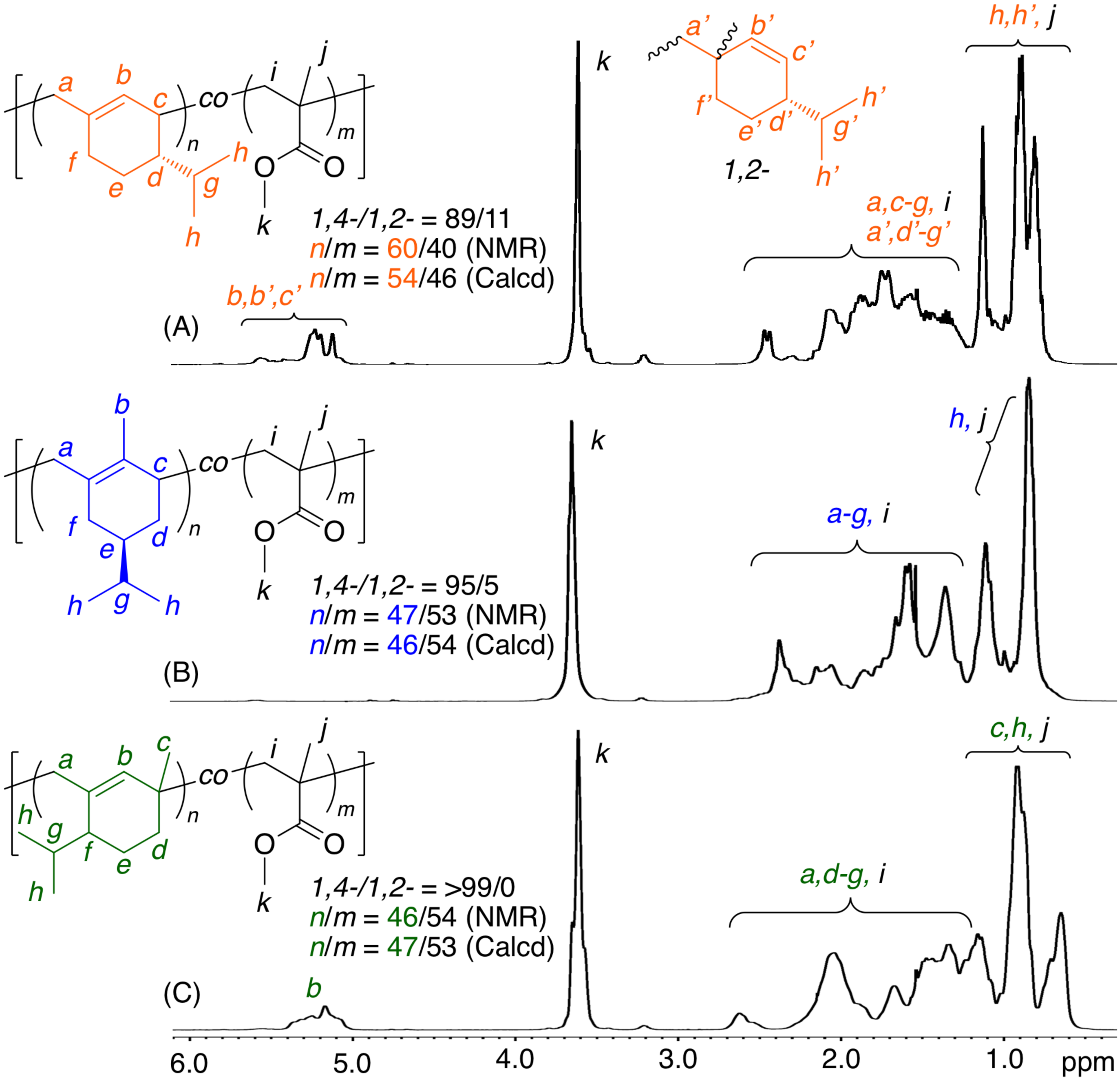


Figure S7. [1]H NMR spectra (in $CDCl_3$ at 55 °C) of copolymers obtained in the radical copolymerization of β-Phe (A), (–)-HCvD (B), or PtD (C) with MMA: $[\text{diene}]_0/[\text{MMA}]_0/[\text{VAm-110}]_0$ = 1500/1500/30 mM in toluene at 100 °C.

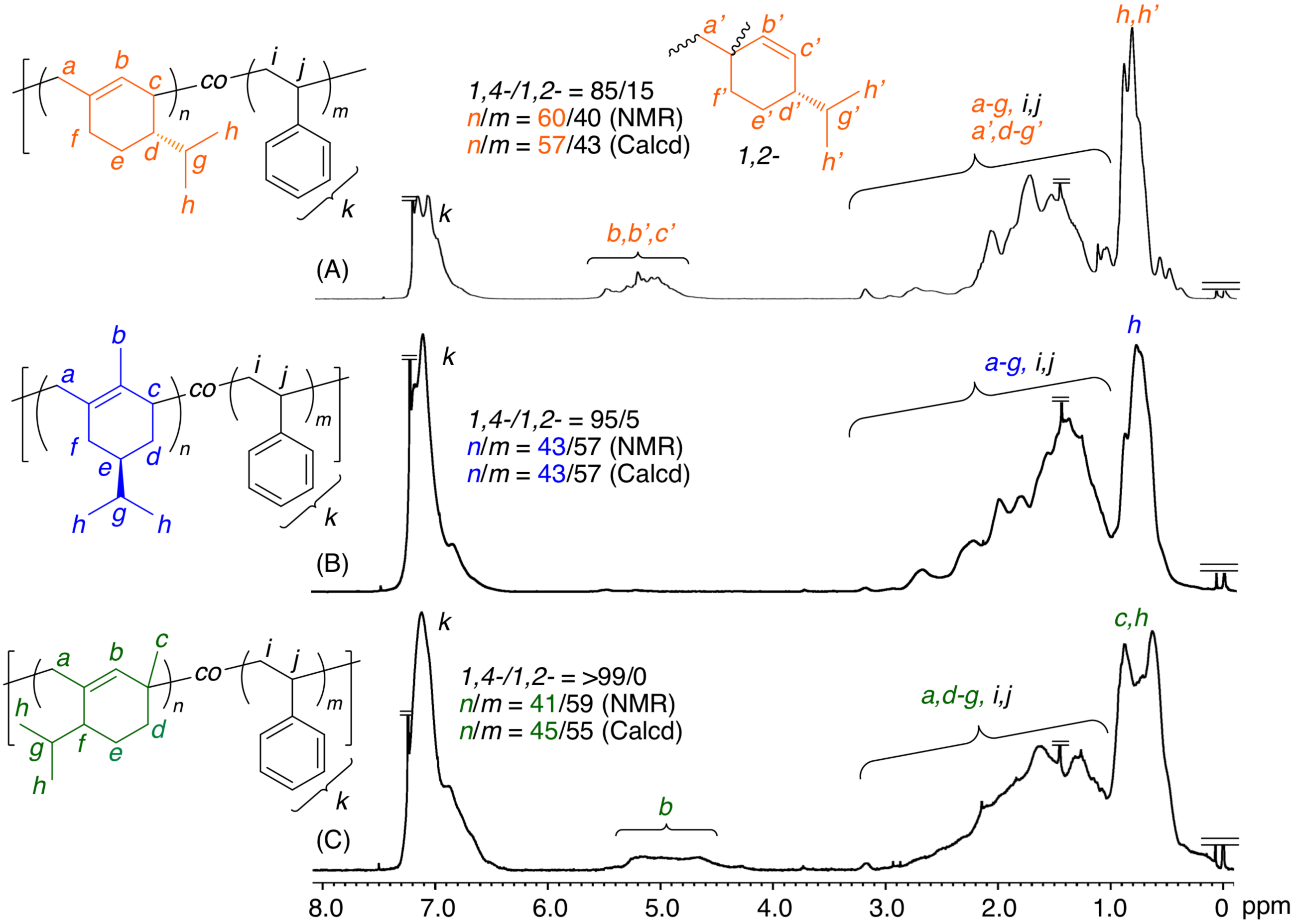


Figure S8. [1]H NMR spectra (in $CDCl_3$ at 55 °C) of copolymers obtained in the radical copolymerization of β-Phe (A), (–)-HCvD (B), or PtD (C) with St: $[\text{diene}]_0/[\text{St}]_0/[\text{VAm-110}]_0$ = 1500/1500/30 mM in toluene at 100 °C.

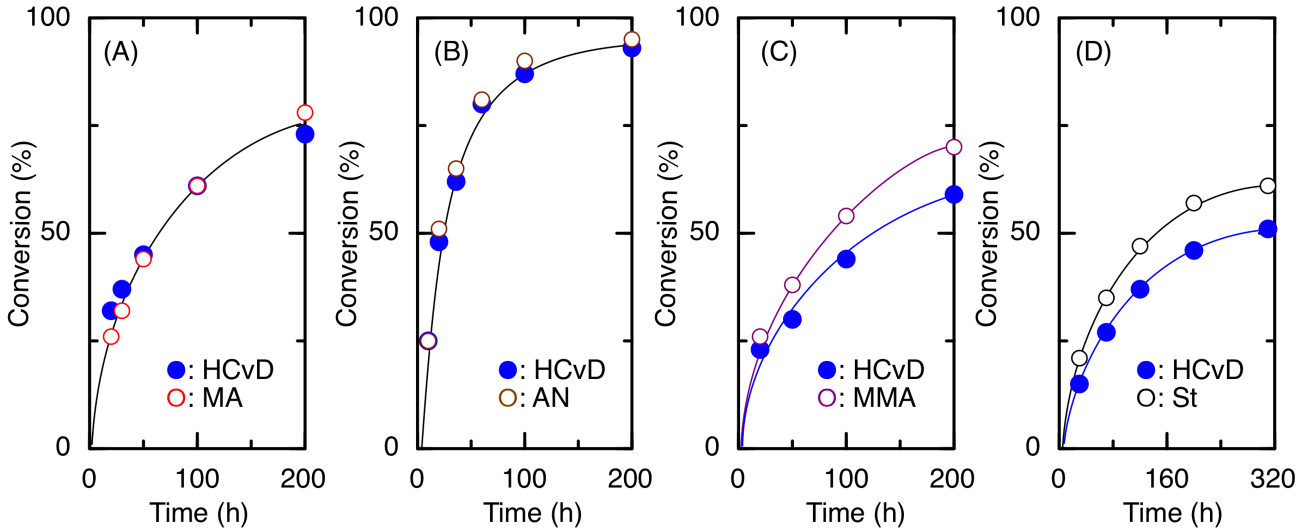


Figure S9. Time-conversion curves for the RAFT copolymerization of (–)-HCvD with MA (A), AN (B), MMA (C), and St (D) as a comonomer: $[(–)\text{-HCvD}]_0/[\text{comonomer}]_0/[\text{CBTC}]_0/[\text{VAm-110}]_0$ = 1500/1500/30/10 mM in toluene at 100 °C.

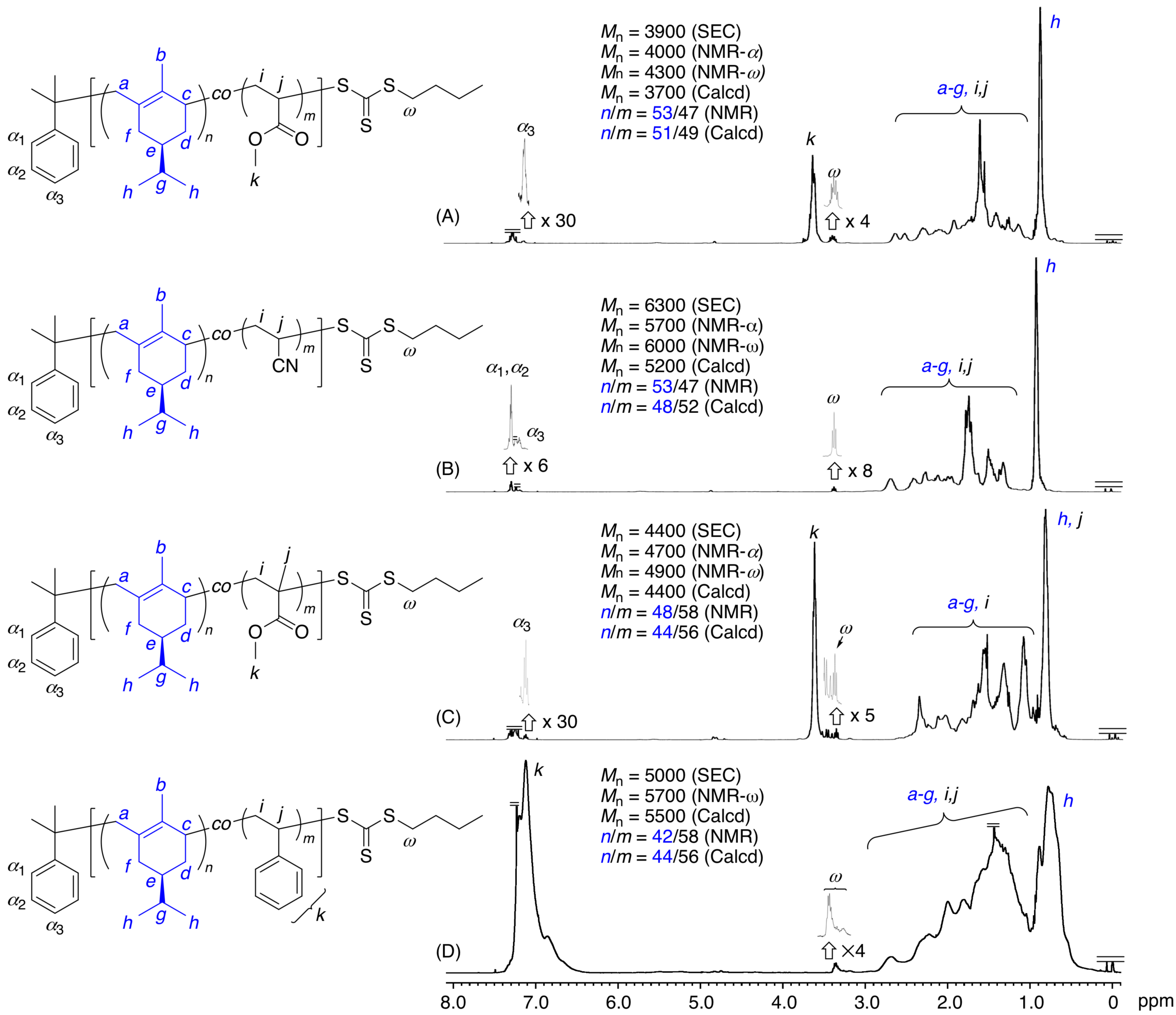


Figure S10. [1]H NMR spectra (in $CDCl_3$ at 55 °C) of copolymers obtained in the RAFT copolymerization of (–)-HCvD with MA (A), AN (B), MMA (C), or St (D) as a comonomer: $[(–)\text{-HCvD}]_0/[\text{comonomer}]_0/[\text{CBTC}]_0/[\text{VAm-110}]_0$ = 1500/1500/30/10 mM in toluene at 100 °C.

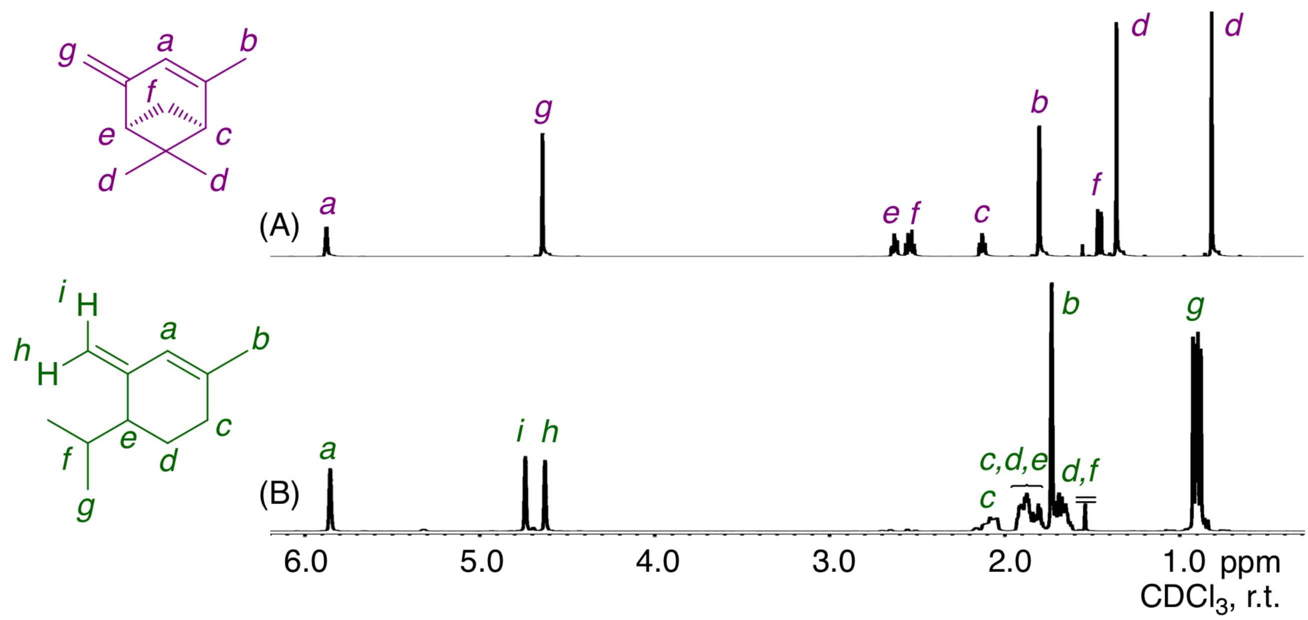


Figure S11. ^{1}H NMR spectra of (–)-VnD (A) and PtD (B) in $CDCl_3$ at 25 °C

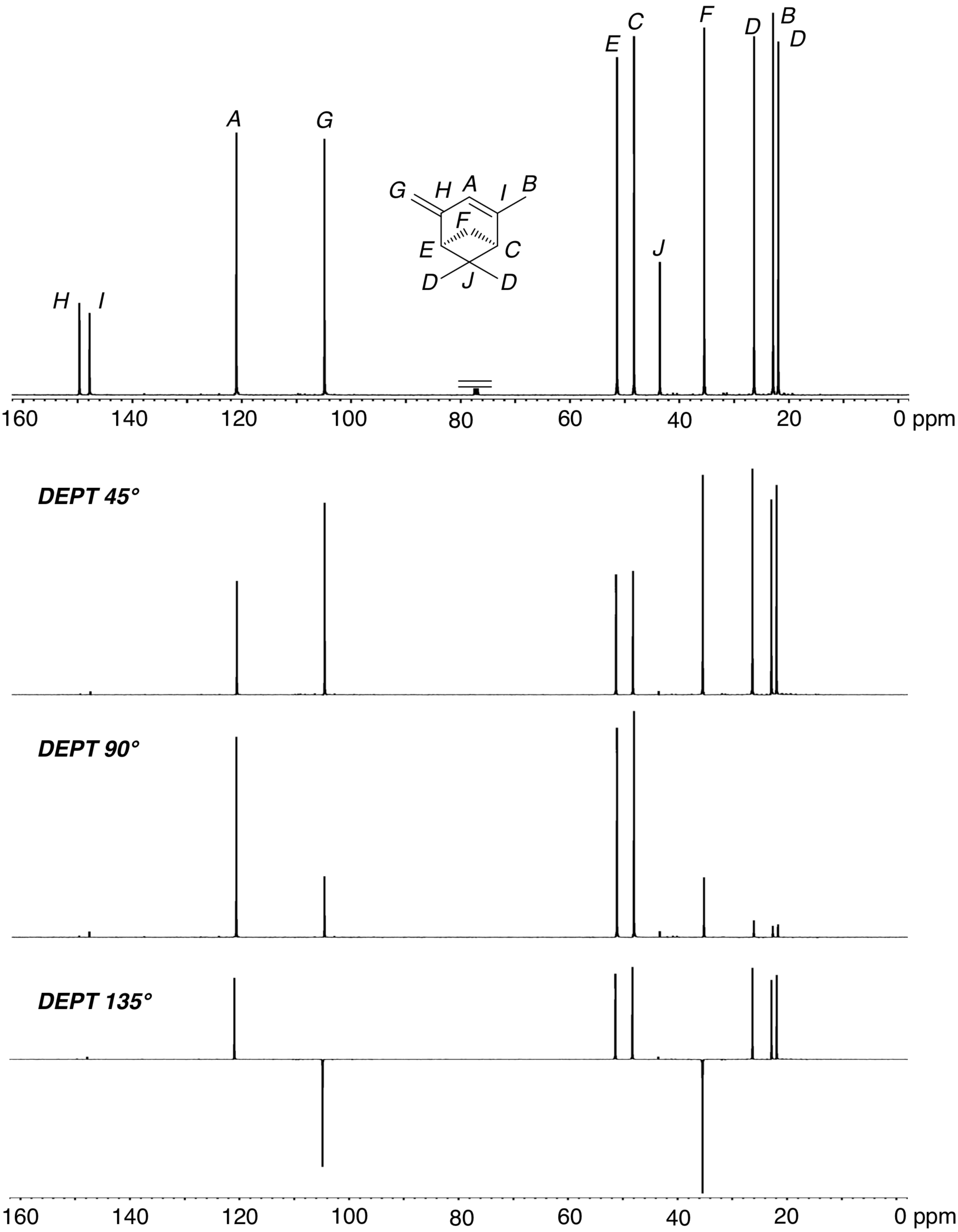


Figure S12. ^{13}C NMR and DEPT spectra of (–)-VnD in $CDCl_3$ at 25 °C.

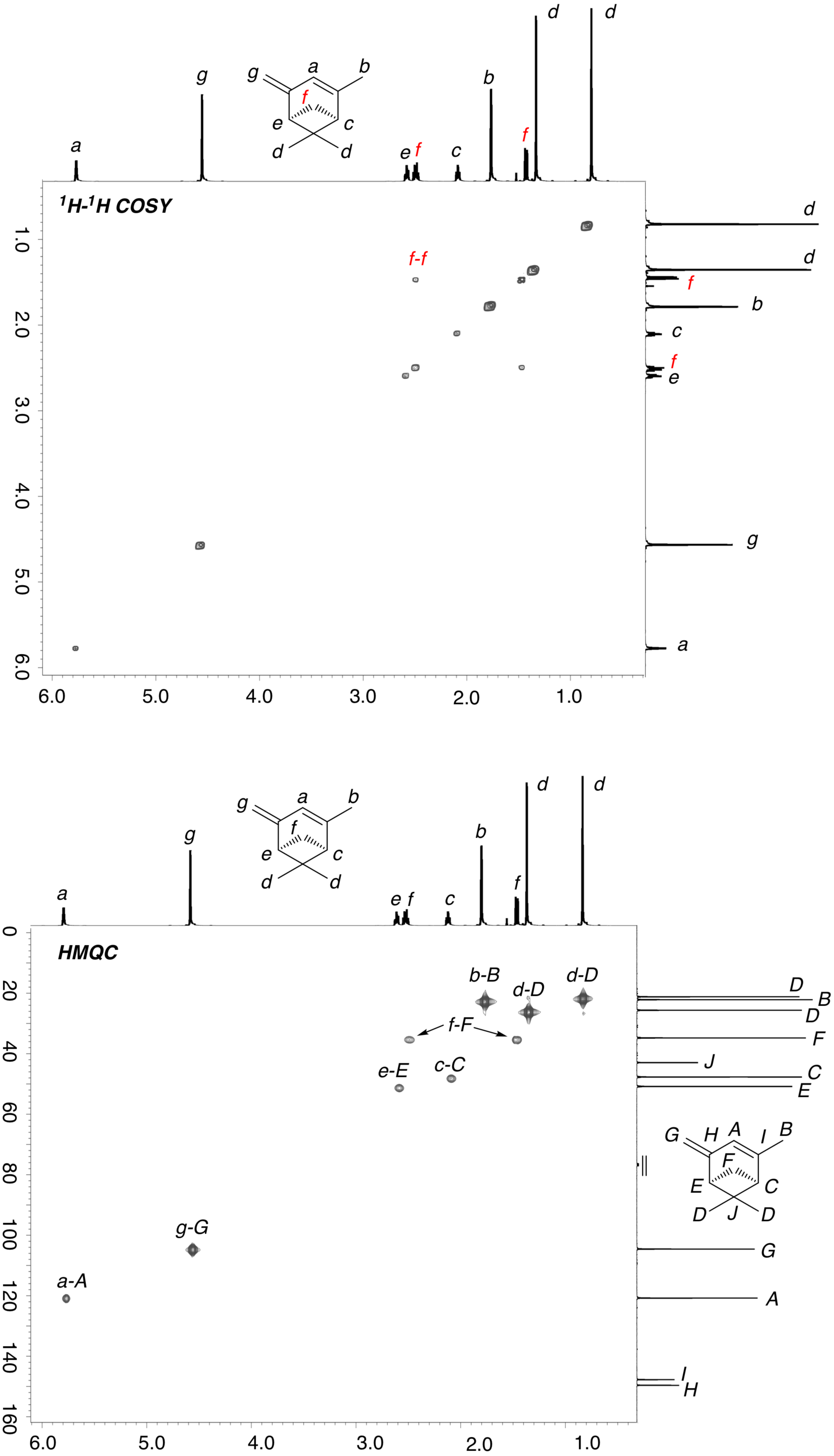


Figure S13. ^{1}H-^{1}H COSY and HMQC spectra of (–)-VnD in $CDCl_3$ at 25 °C.

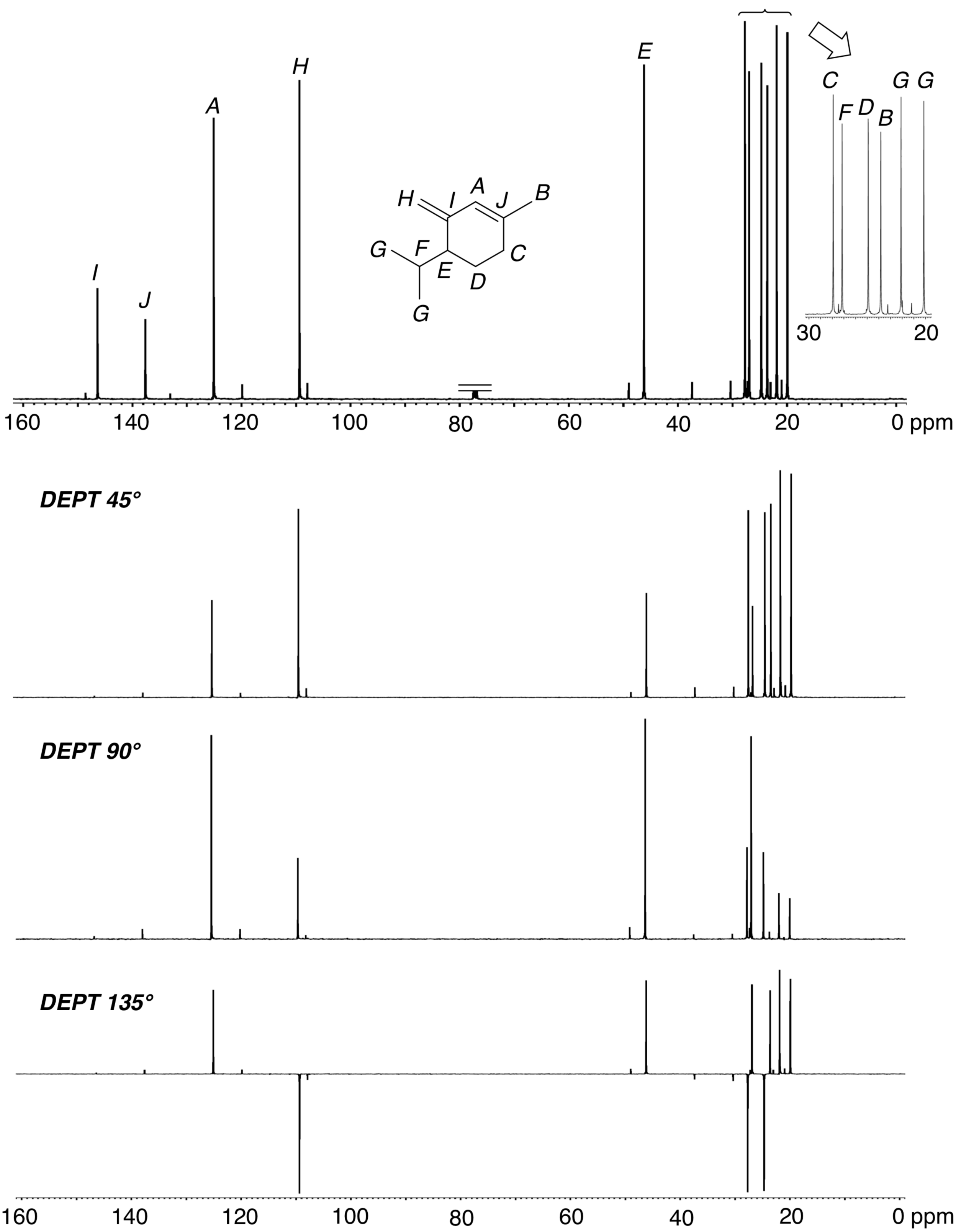
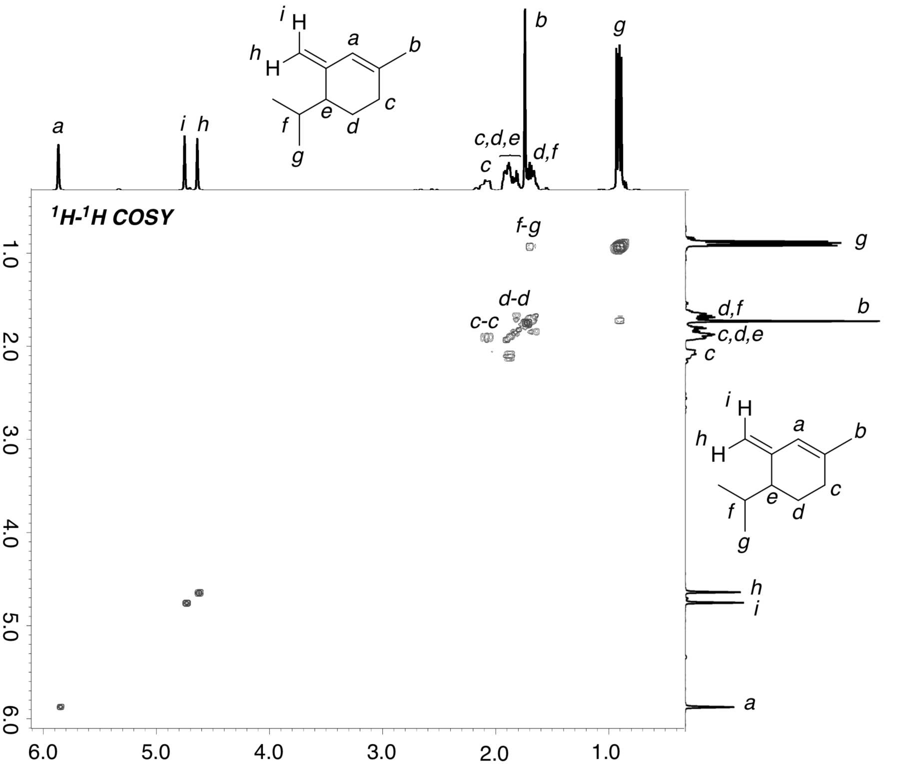


Figure S14. ^{13}C NMR and DEPT spectra of PtD in $CDCl_3$ at 25 °C.



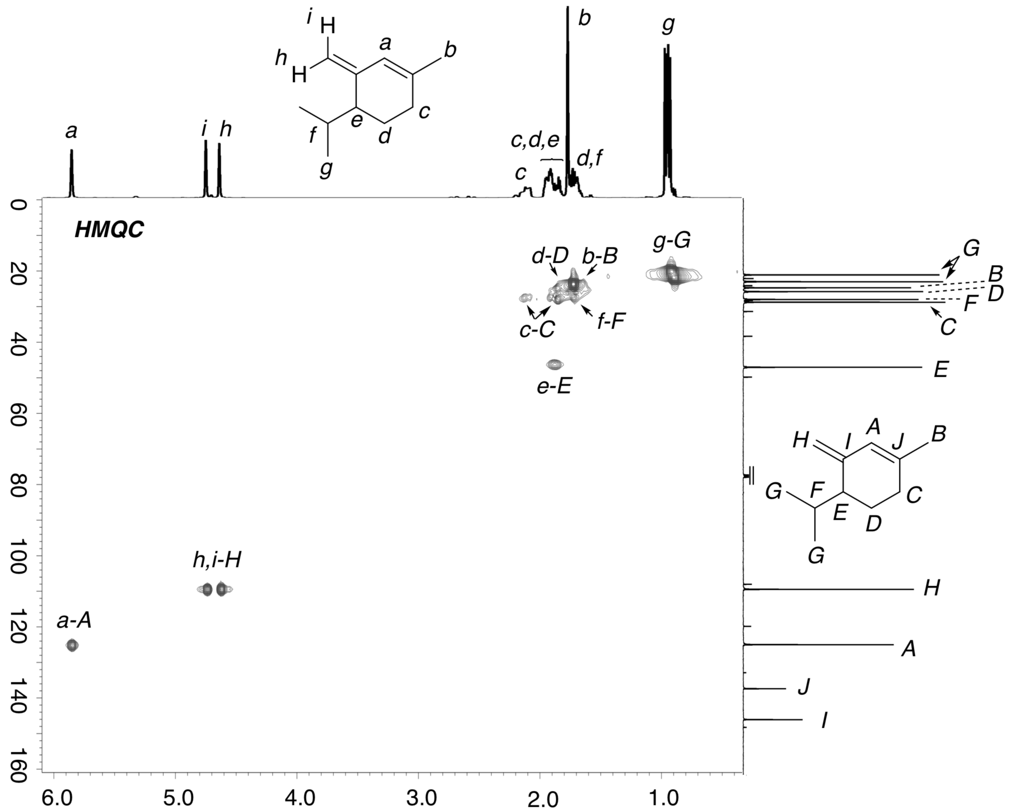


Figure S15. ^{1}H-^{1}H COSY and HMQC spectra of PtD in $CDCl_3$ at 25 °C.