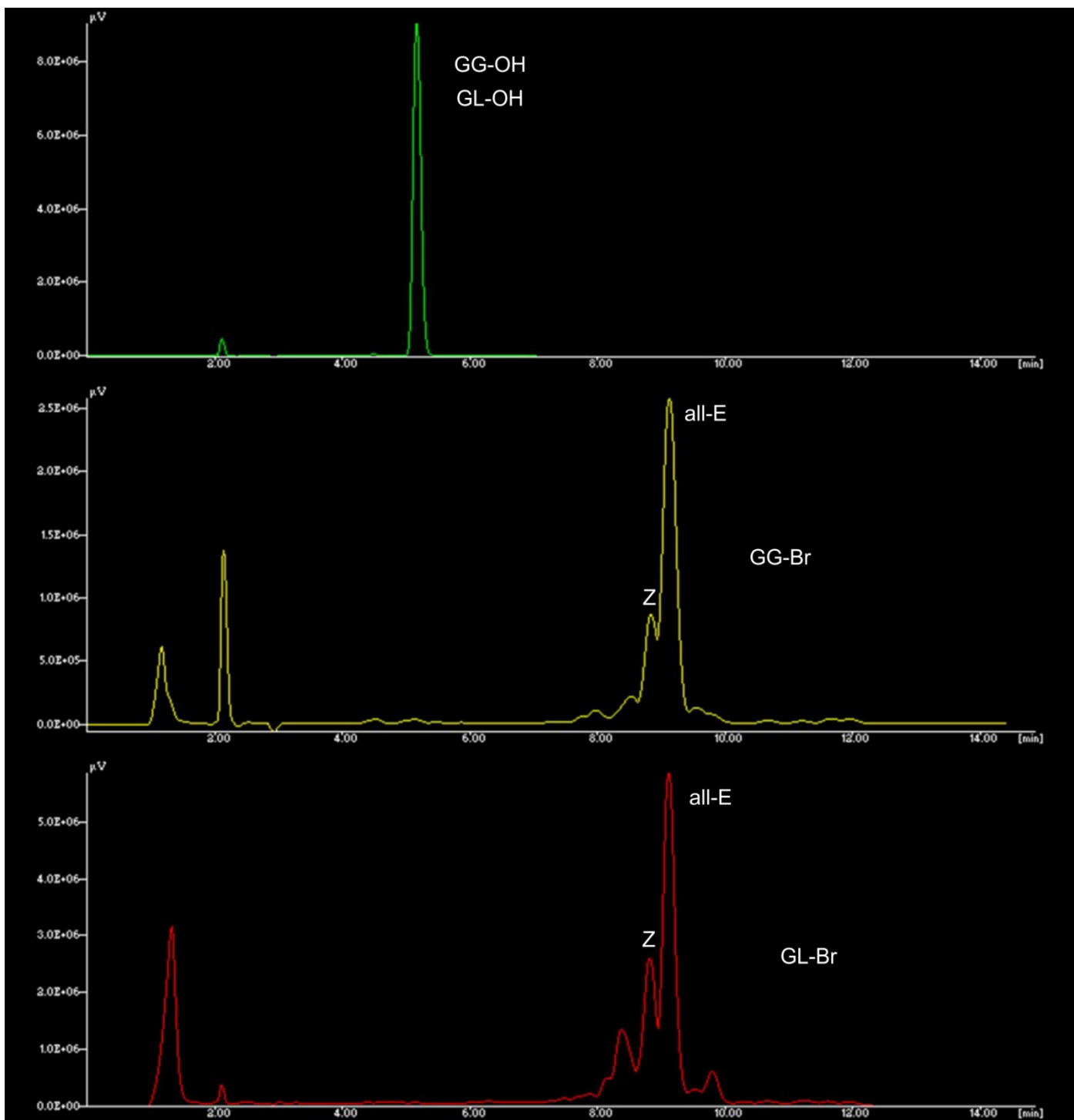
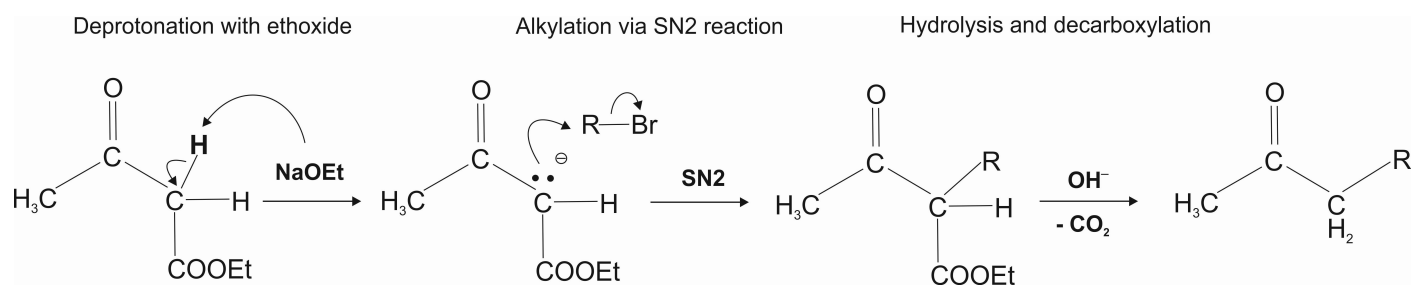


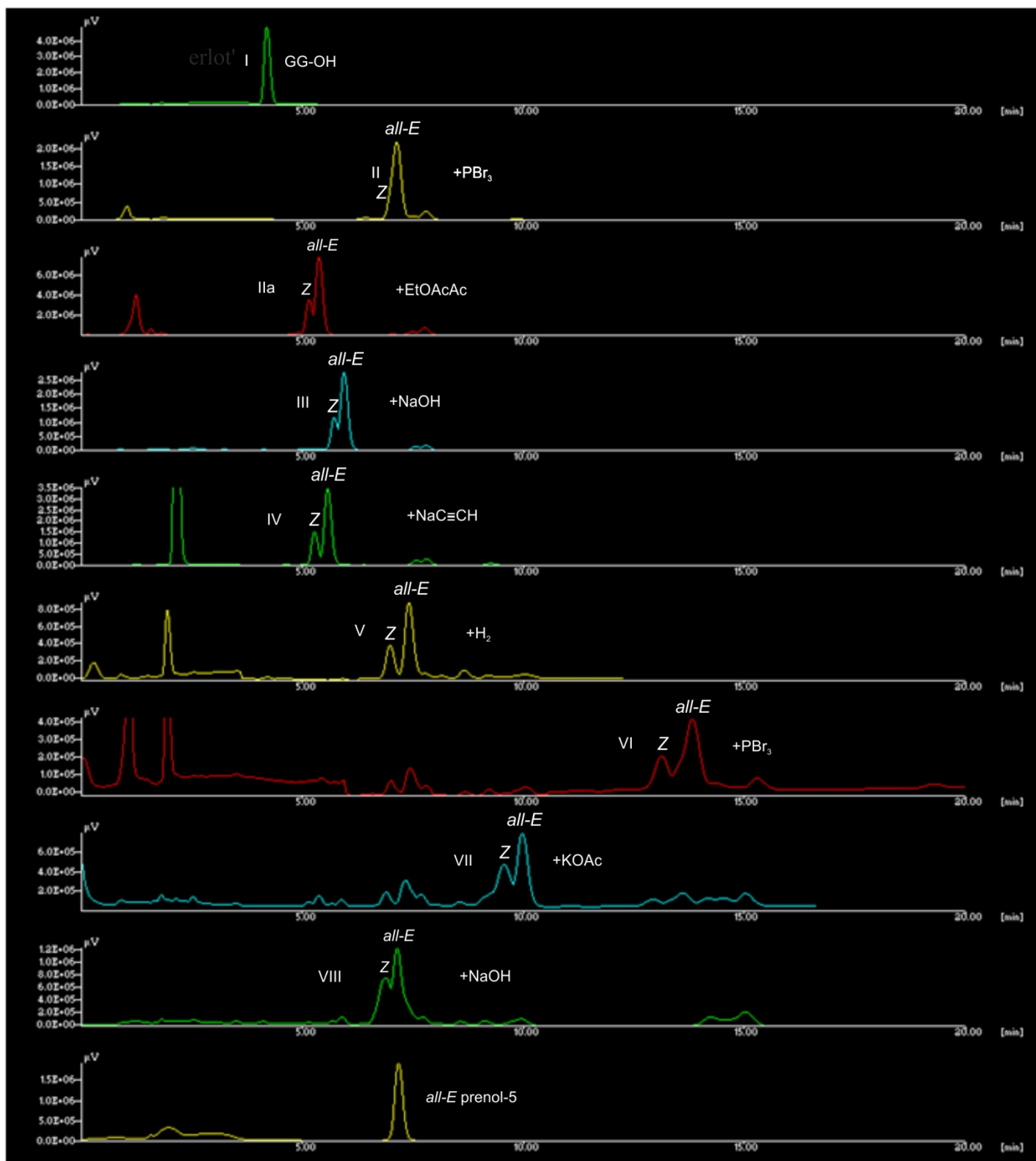
**Figure S1.** Chemical synthesis of polyprenols according to [9].



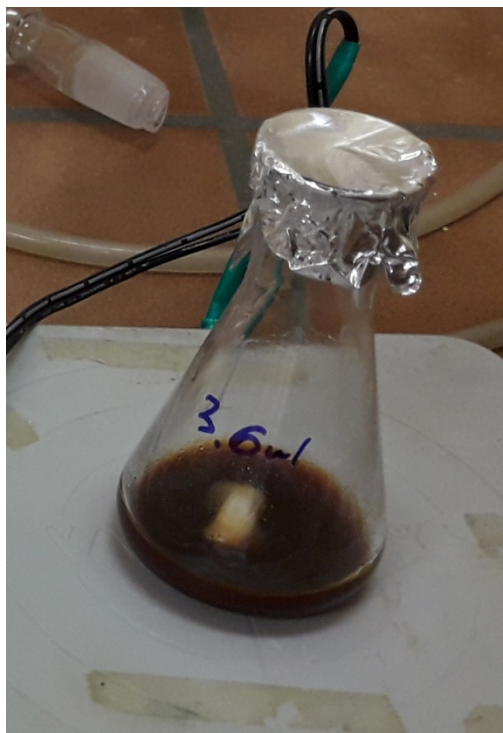
**Figure S2.** HPLC chromatograms of geranylgeraniol (GG-OH), geranylgeraniol hydroperoxide (GL-OH) and their bromination products after  $PBr_3$  treatment (Acclaim C30 column, ACN/MeOH/H<sub>2</sub>O 72/8/5, v/v). Absorption detection was at 210 nm.



**Figure S3.** Acetoacetic ester synthesis.



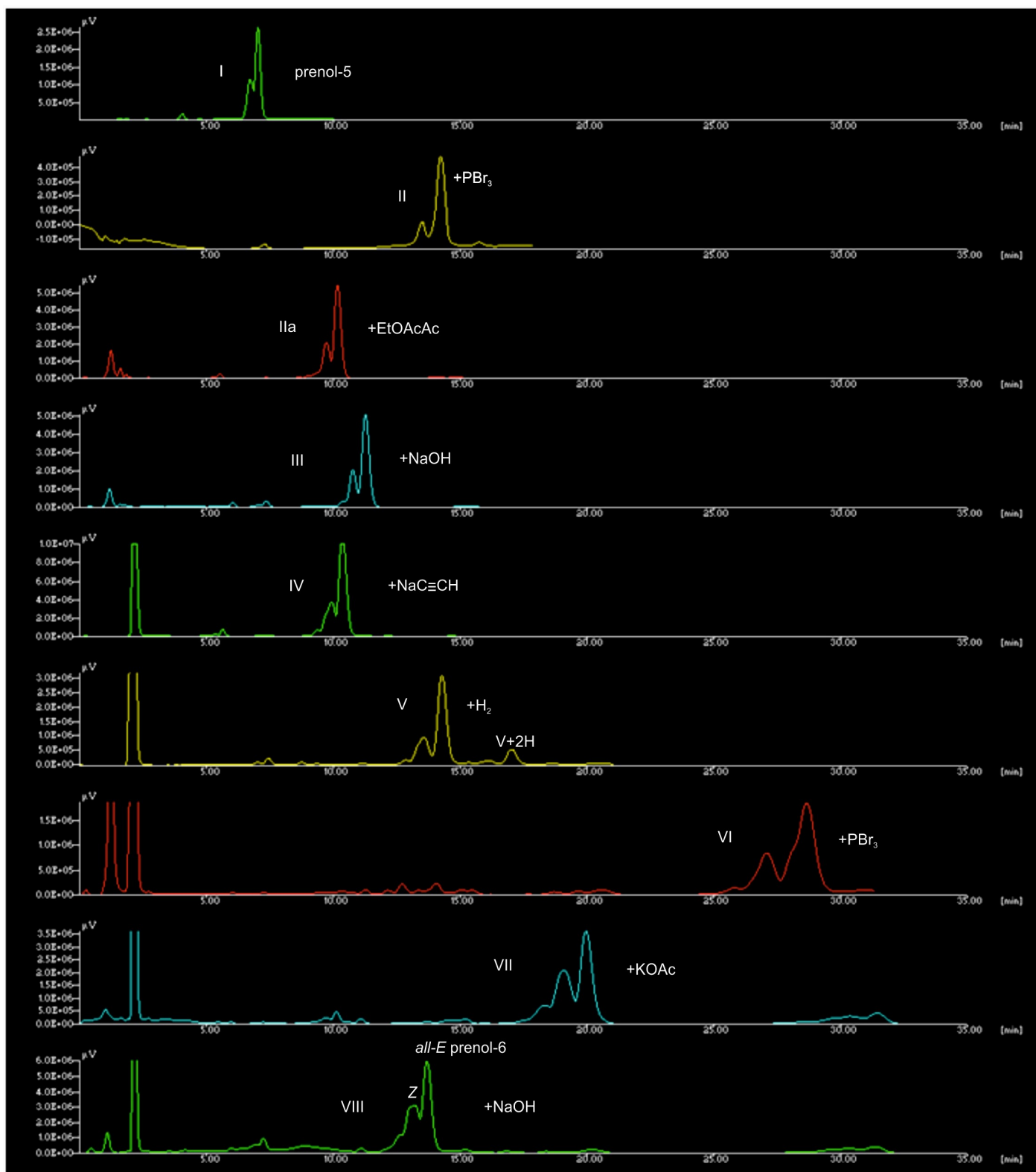
**Figure S4.** HPLC chromatograms of reaction products during chemical synthesis of pentaprenol (Nucleosil 100 C18 column, ACN/MeOH/H<sub>2</sub>O, 72/8/1, v/v). Absorption detection was at 210 nm.



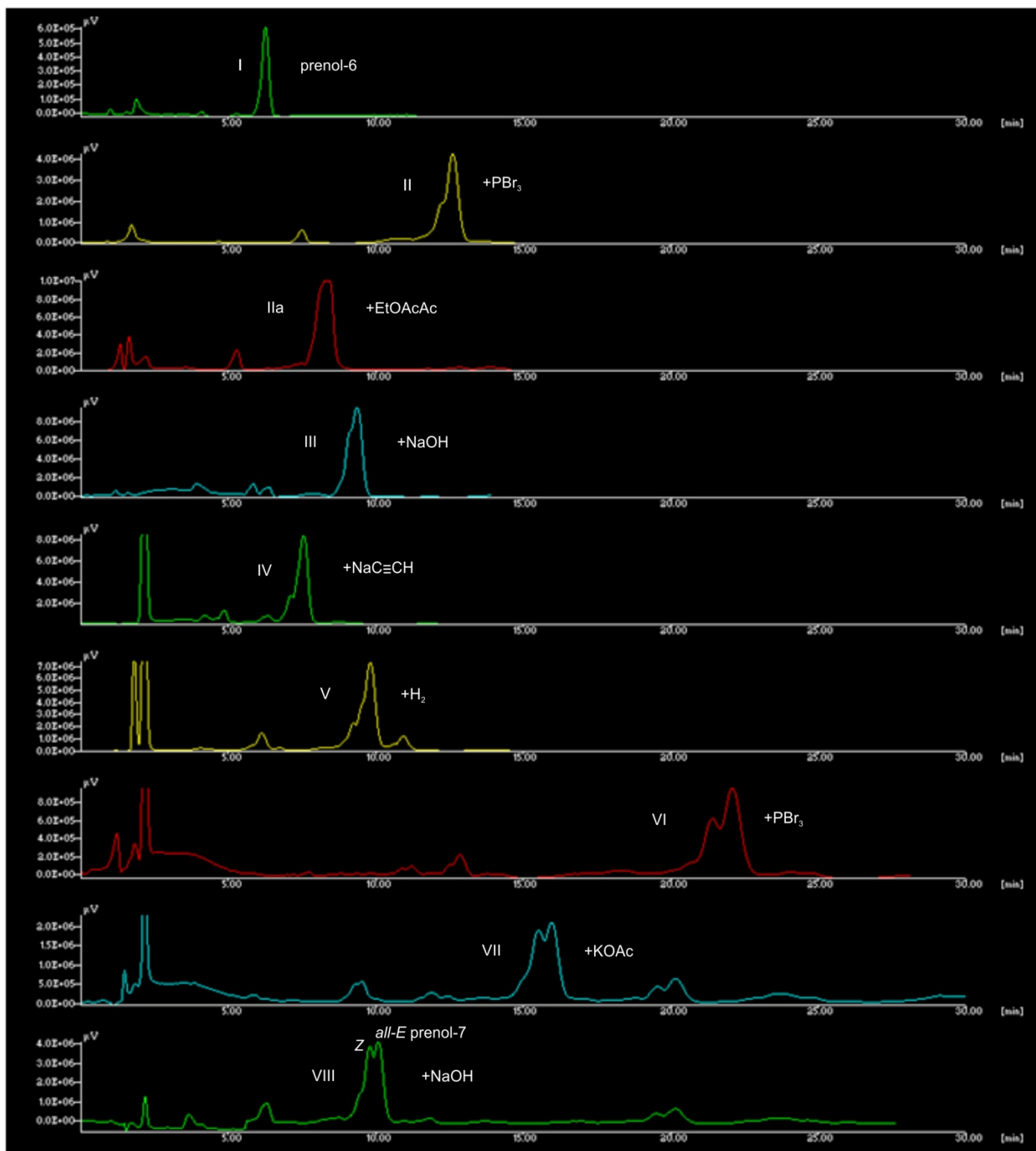
**Figure S5.** Reaction of ketone III with Na-acetylene in DME.



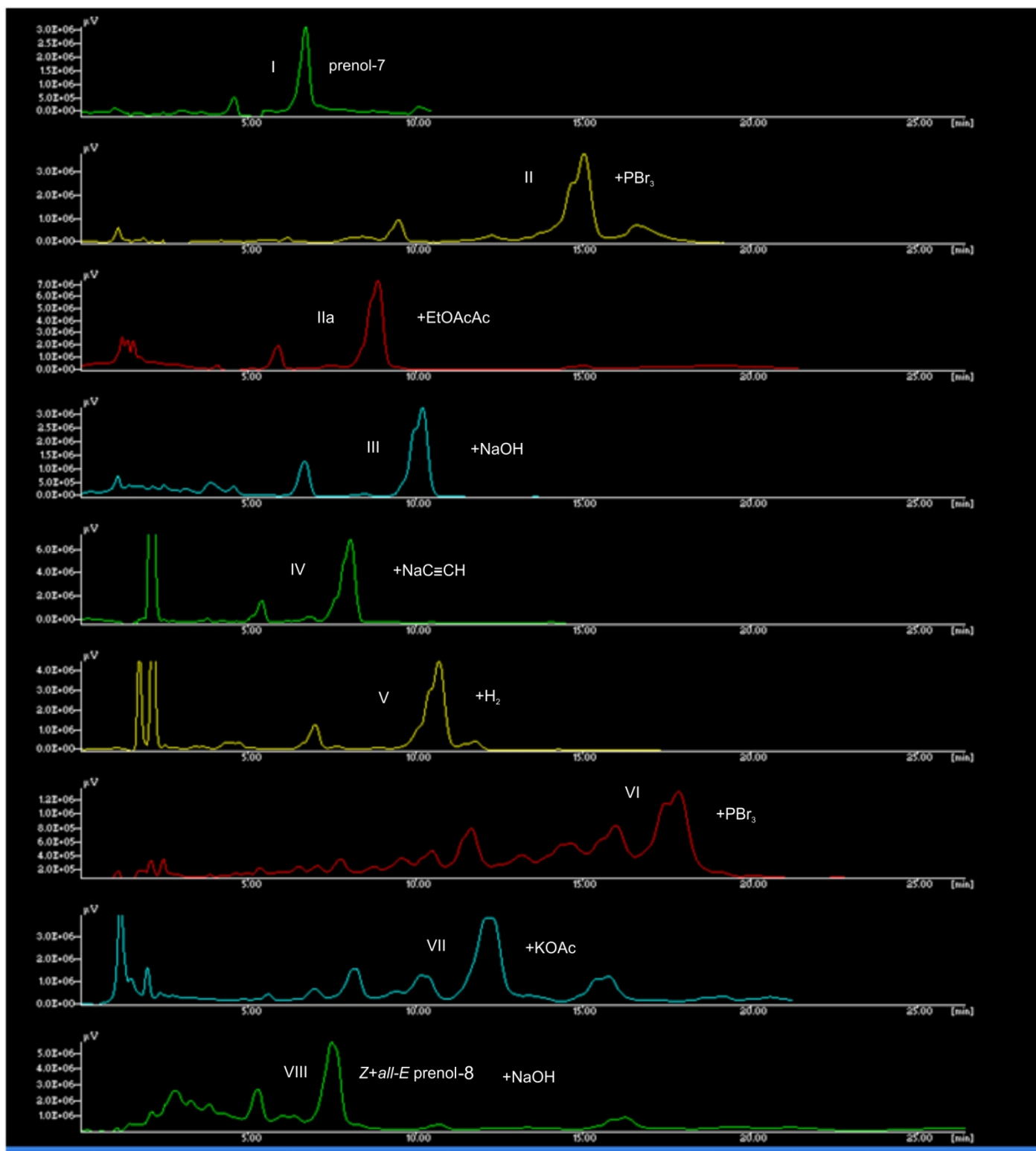
**Figure S6.** Experimental setup for hydrogenation of IV. The stainless-steel filter is taken out of the solution for visualization.



**Figure S7.** HPLC chromatograms of reaction products during chemical synthesis of hexaprenol (Nucleosil 100 C18 column, ACN/MeOH/H<sub>2</sub>O, 72/8/1, v/v). Absorption detection was at 210 nm.

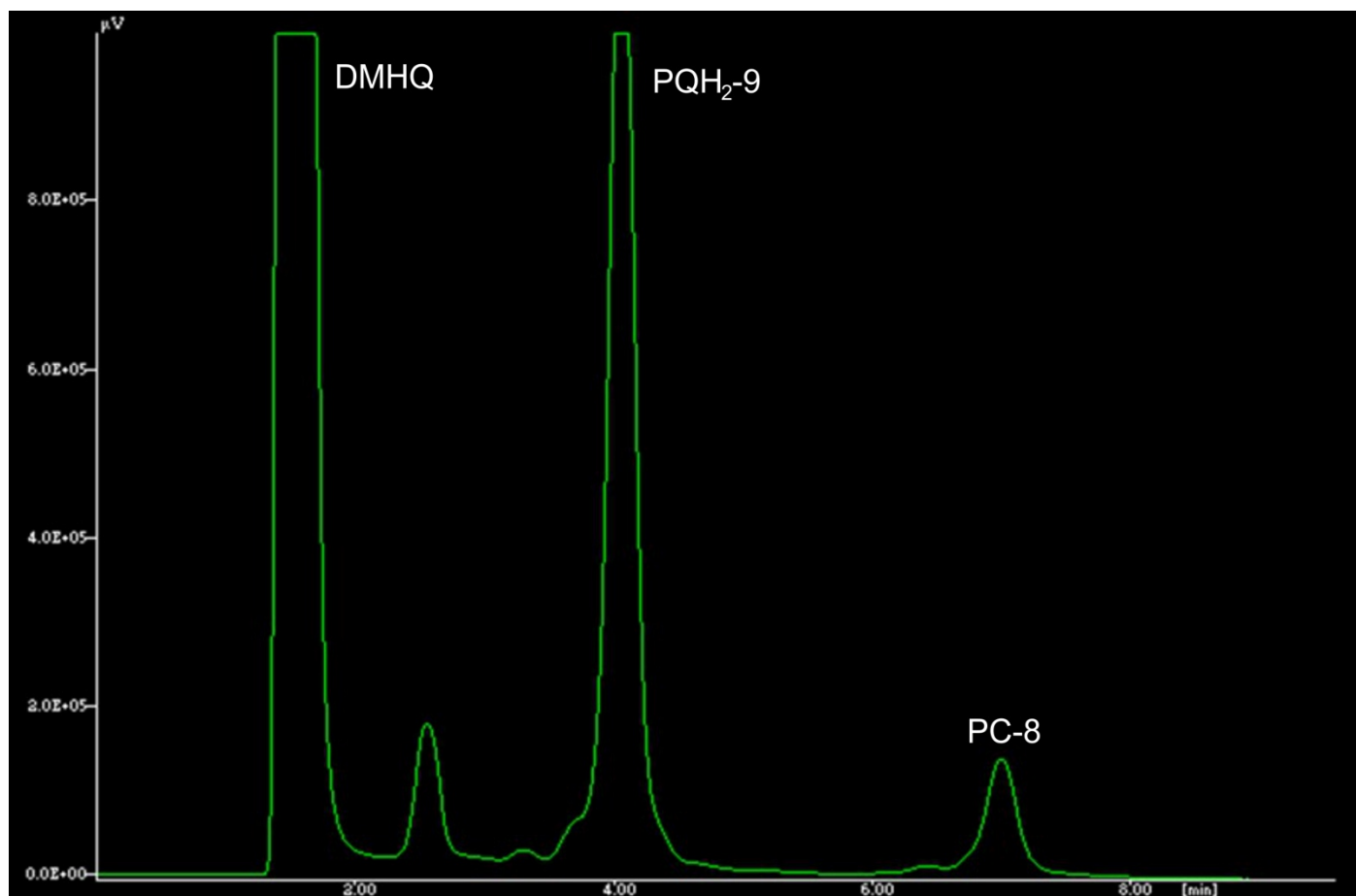


**Figure S8.** HPLC chromatograms of reaction products during chemical synthesis of heptaprenol (Nucleosil 100 C18 column in MeOH). Absorption detection was at 210 nm.

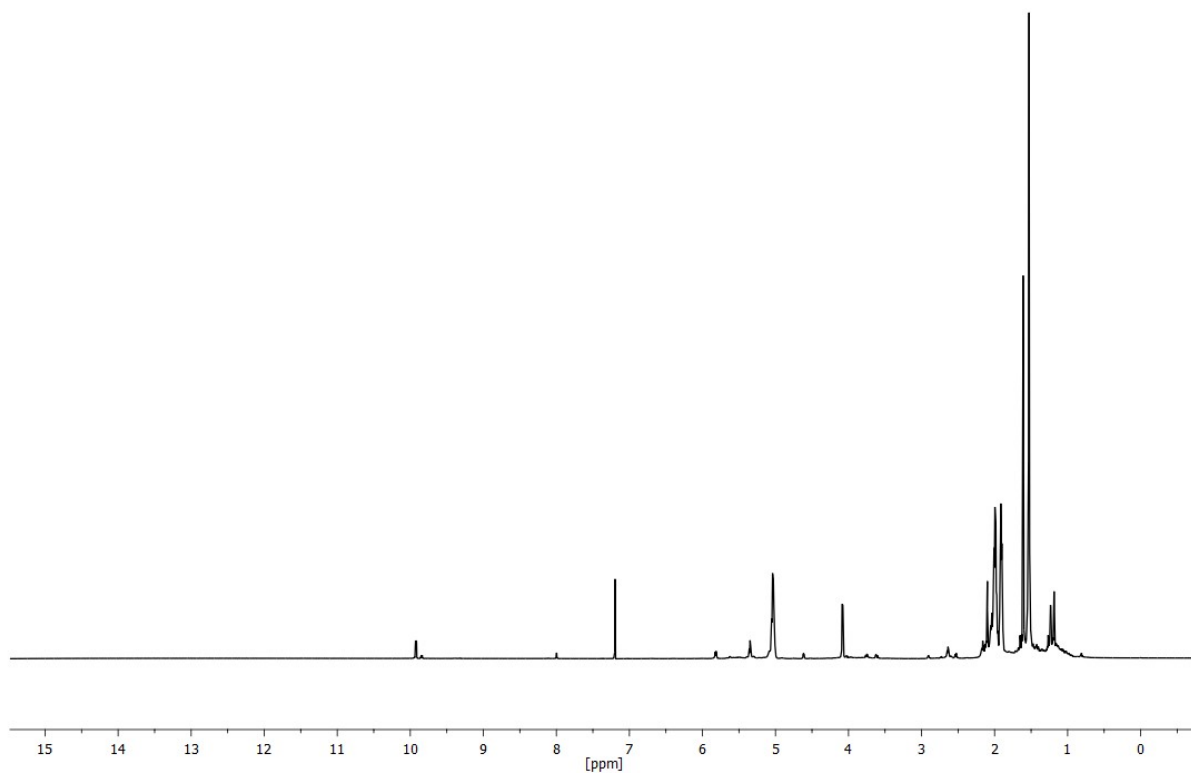


**Figure S9.** HPLC chromatograms of reaction products during chemical synthesis of octaprenol (Nucleosil 100 C18 column, methanol/hexane, 340/20, v/v). Absorption detection was at 210 nm.

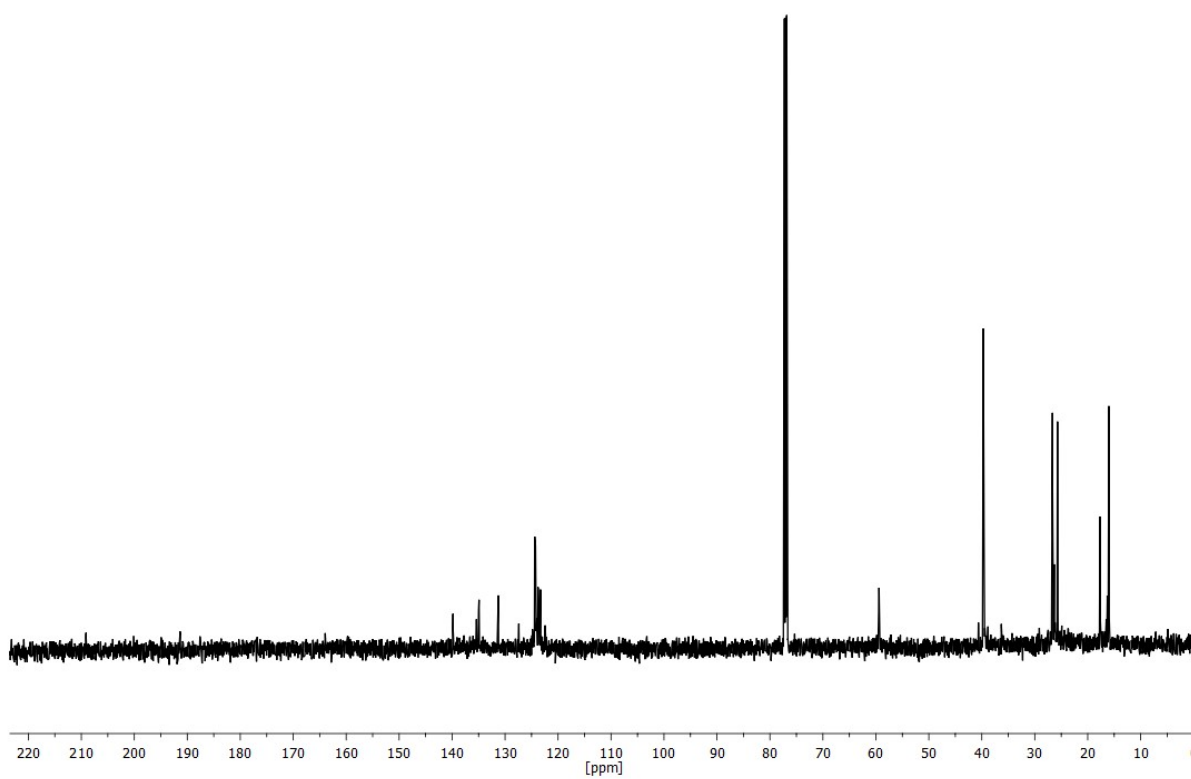




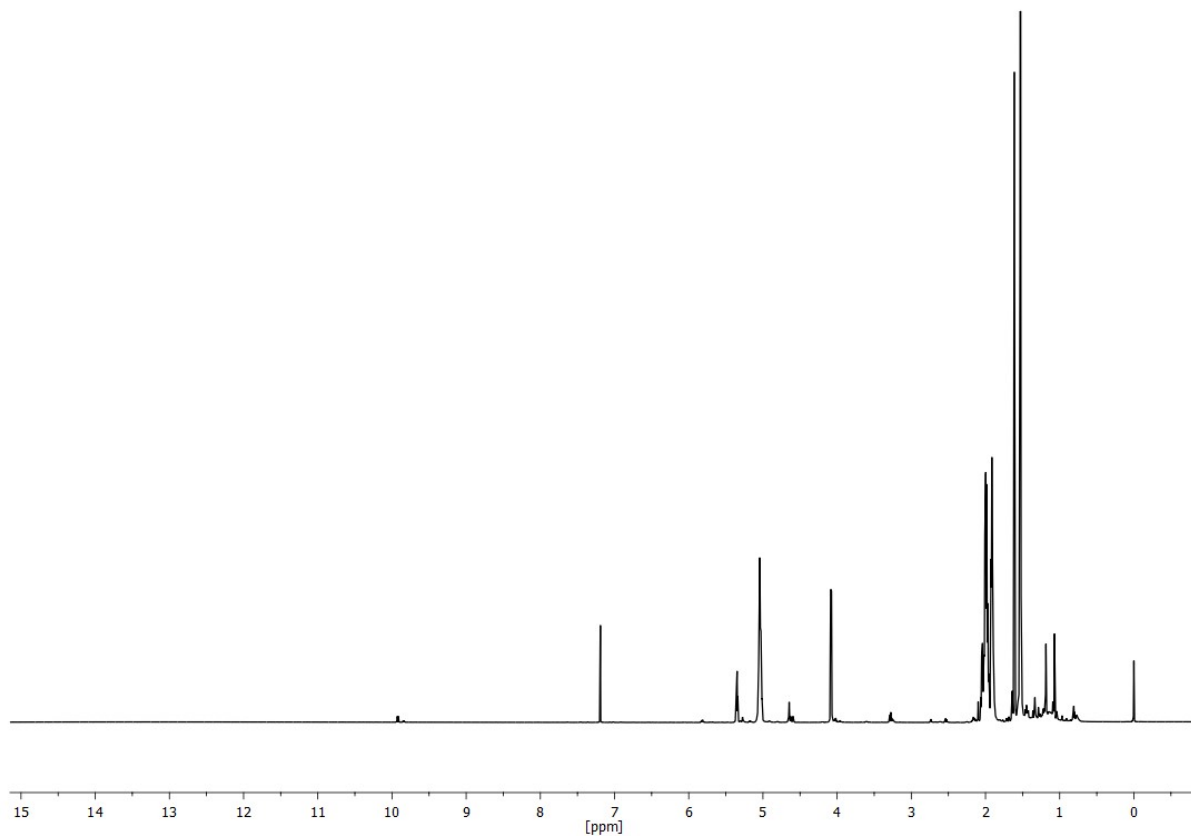
**Figure S10.** HPLC chromatogram of the reaction mixture during synthesis of plastoquinone-8 (PC-8) (Nucleosil 100 C18 column, methanol/hexane, 340/85, v/v), using fluorescence detection at 290/330 nm (ex./em).



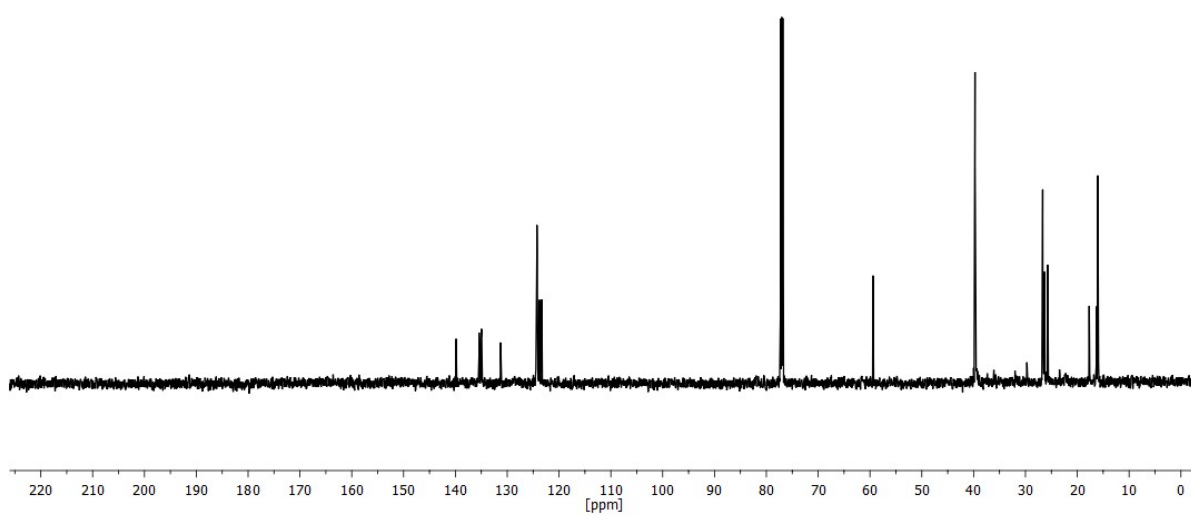
**Figure S11.**  $^1\text{H}$  NMR spectrum of pentaprenol.



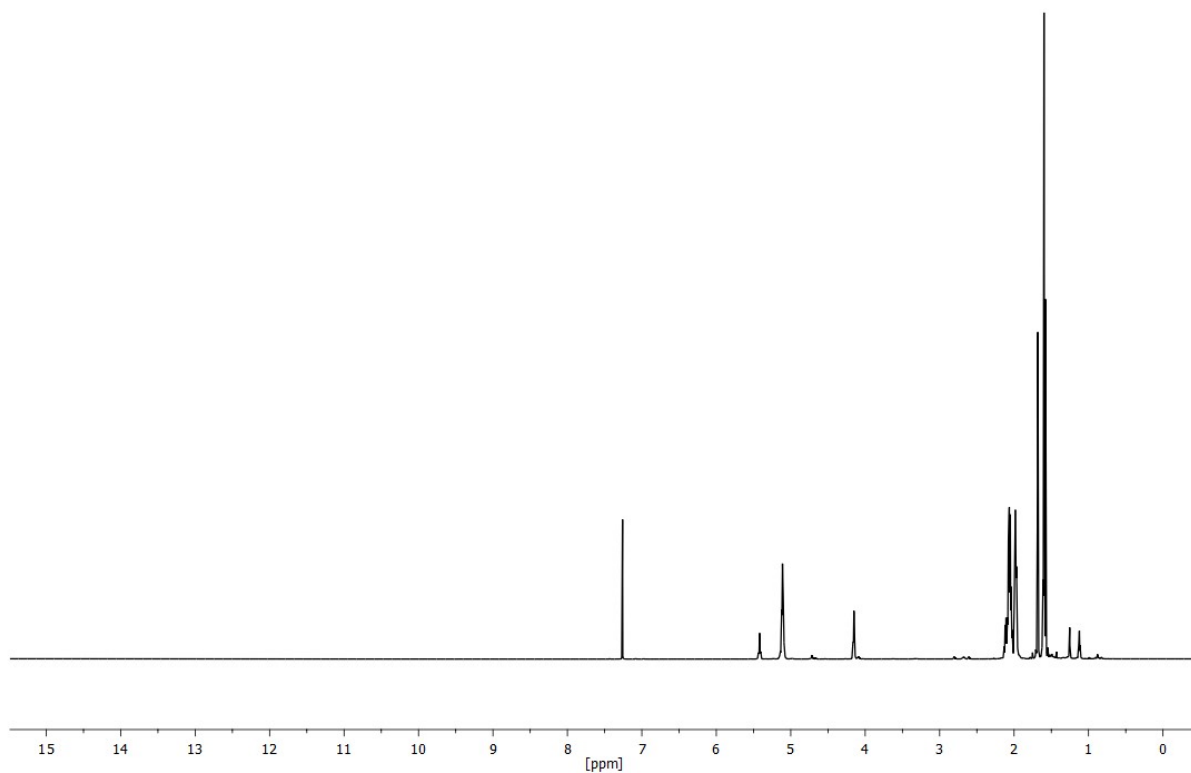
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of pentaprenol.



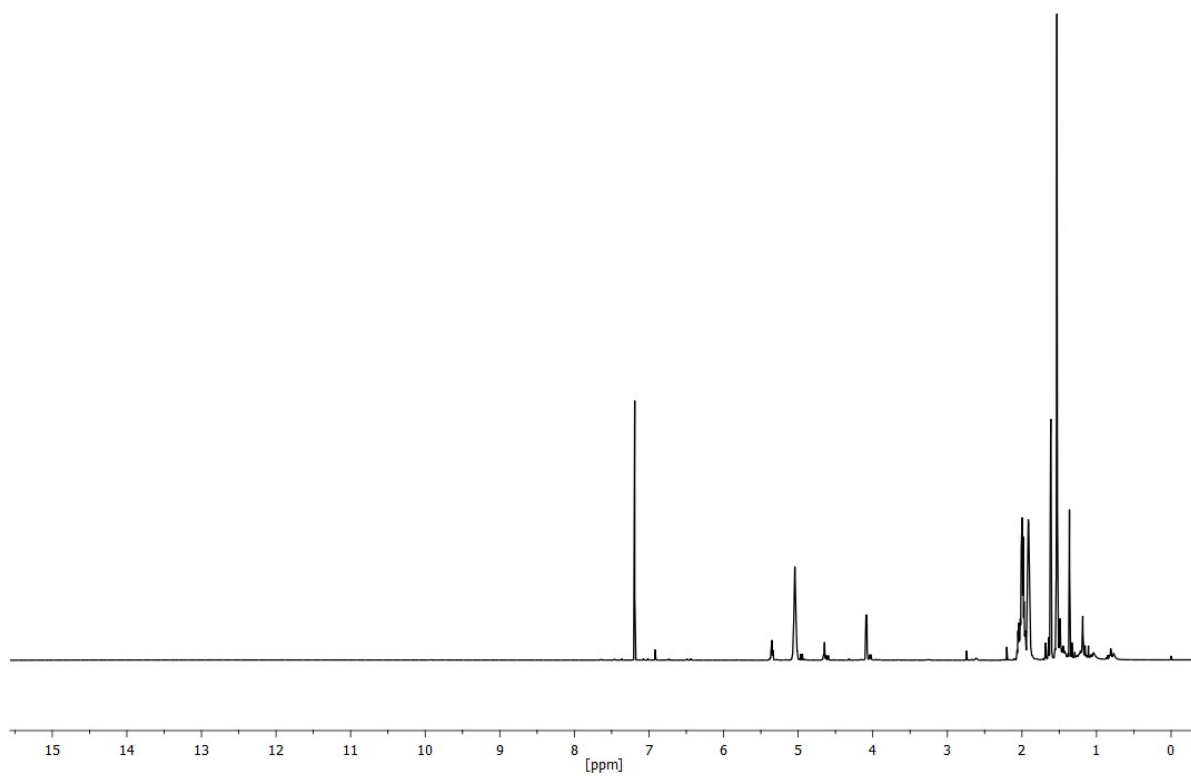
**Figure S13.**  $^1\text{H}$  NMR spectrum of hexaprenol.



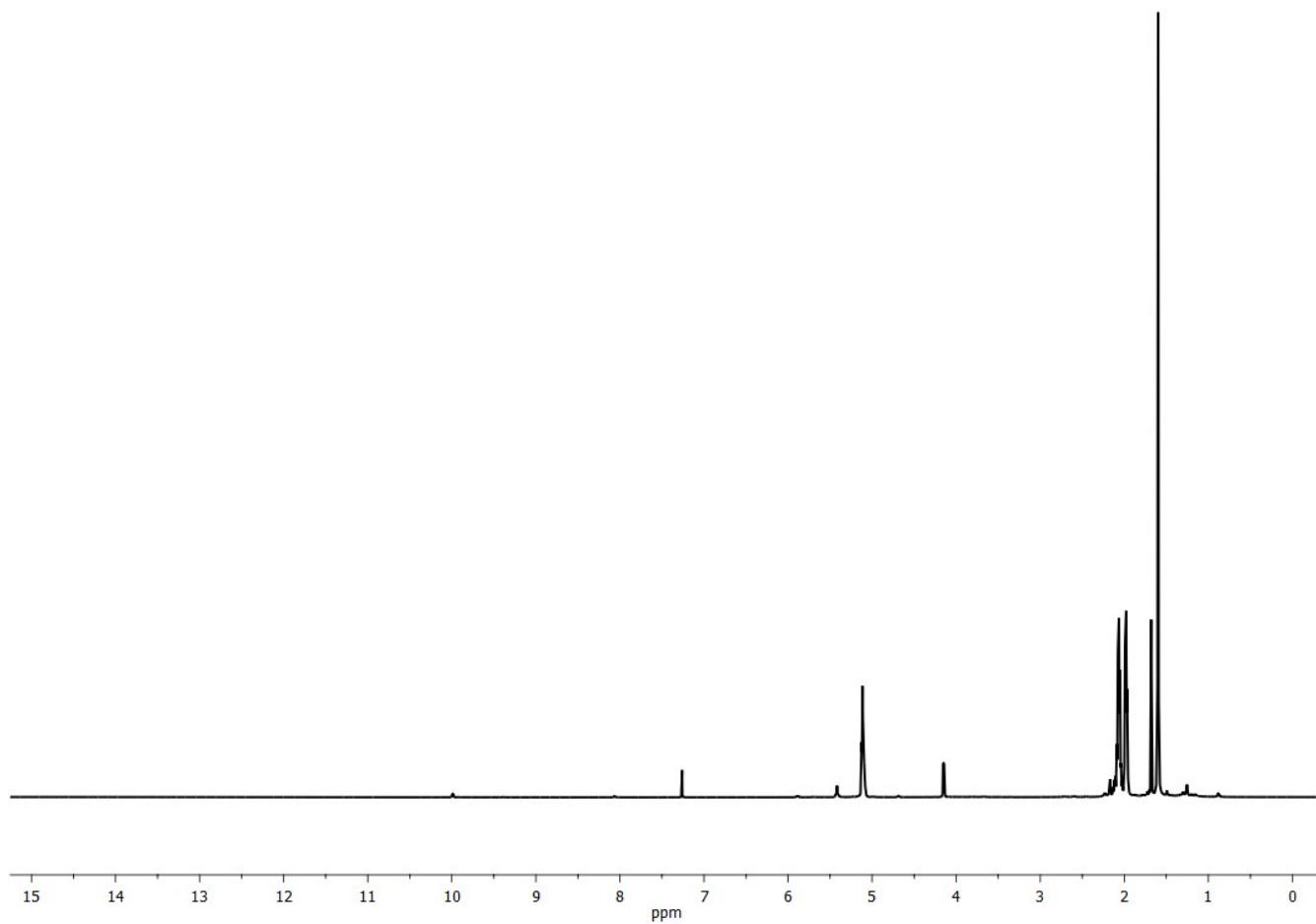
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of hexaprenol.



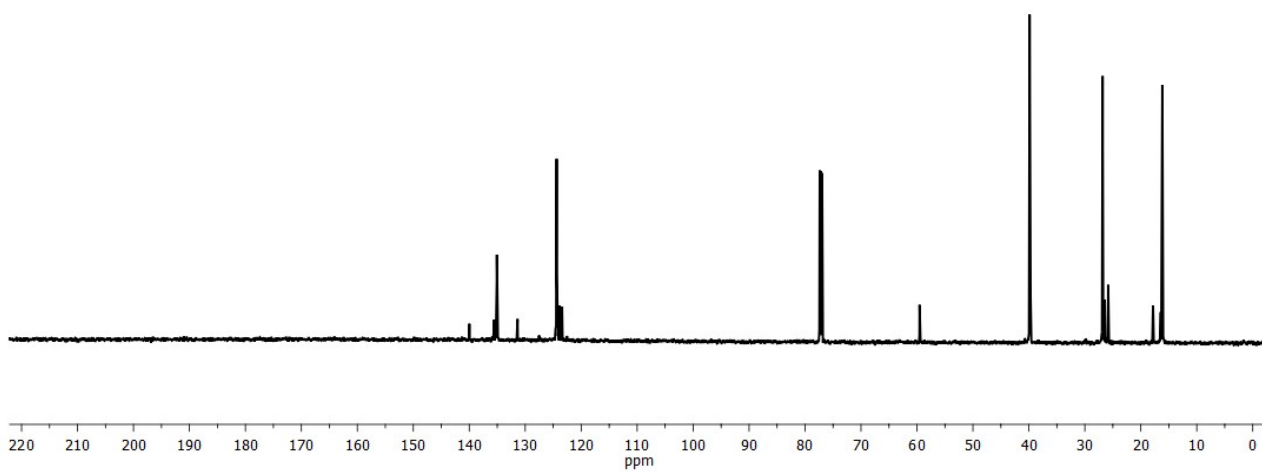
**Figure S15.**  $^1\text{H}$  NMR spectrum of heptaprenol.



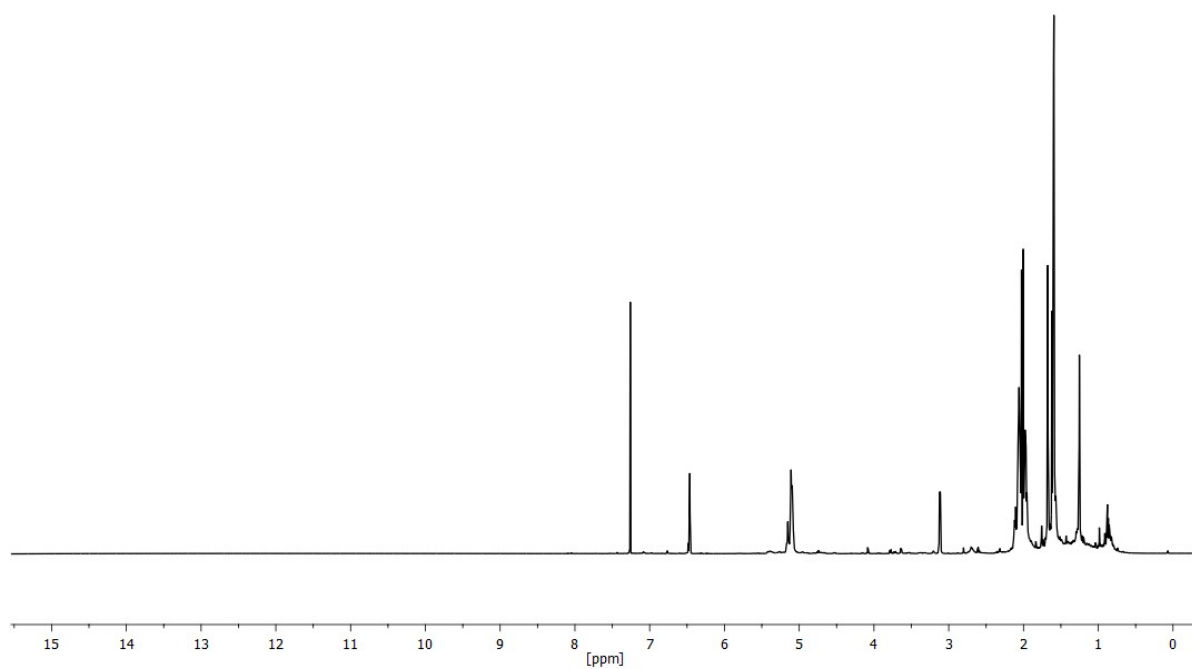
**Figure S16.**  $^1\text{H}$  NMR spectrum of octaprenol.



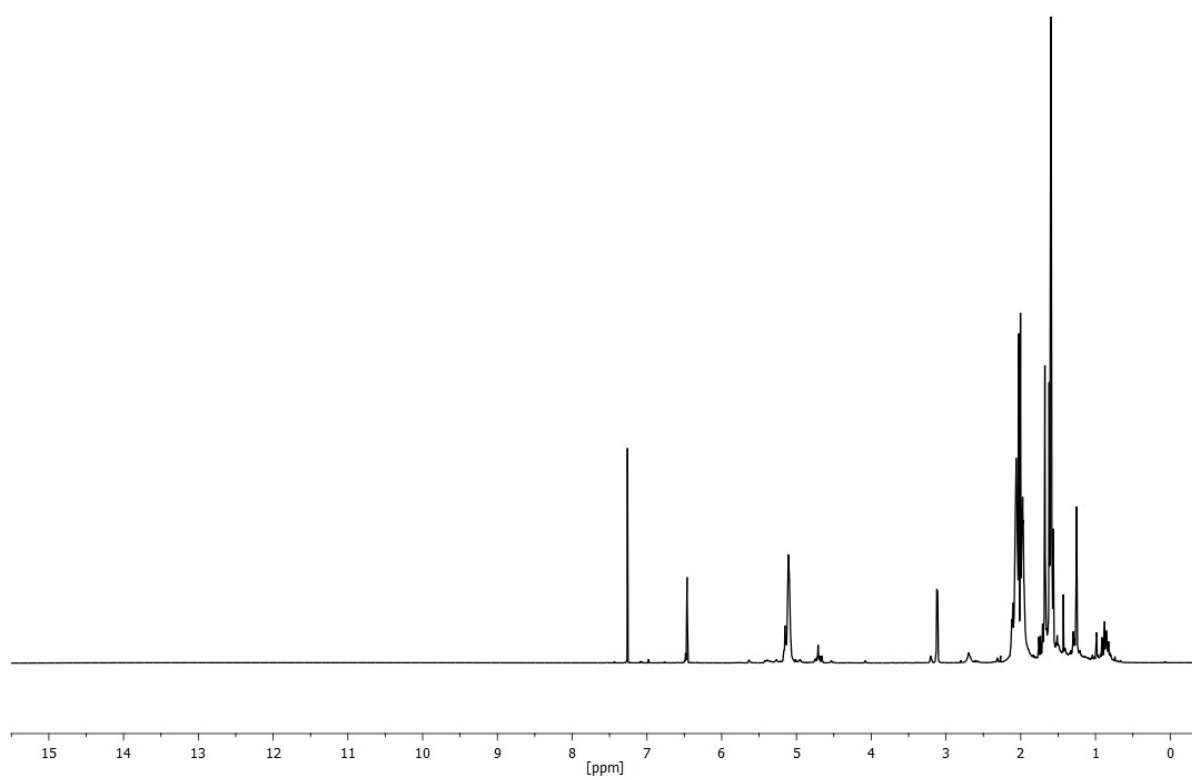
**Figure S17.**  $^1\text{H}$  NMR spectrum of decaprenol.



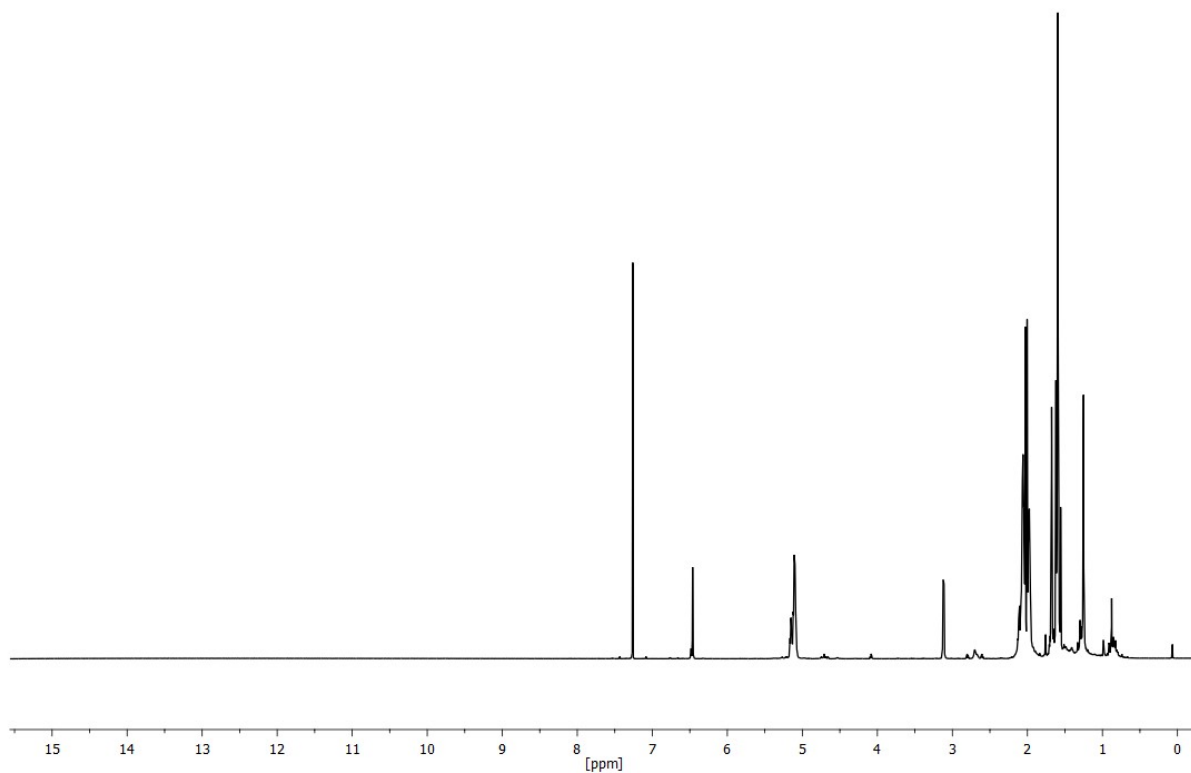
**Figure S18.**  $^{13}\text{C}$  NMR spectrum of decaprenol.



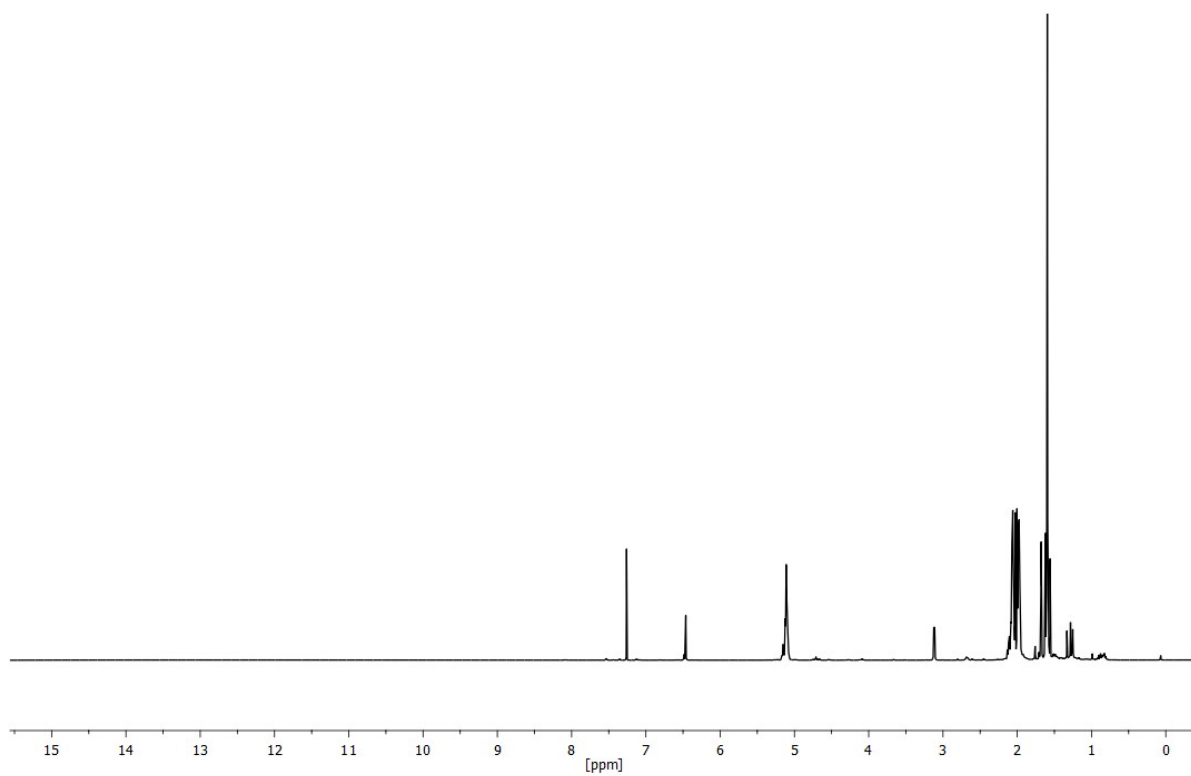
**Figure S19.**  $^1\text{H}$  NMR spectrum of PQ-5.



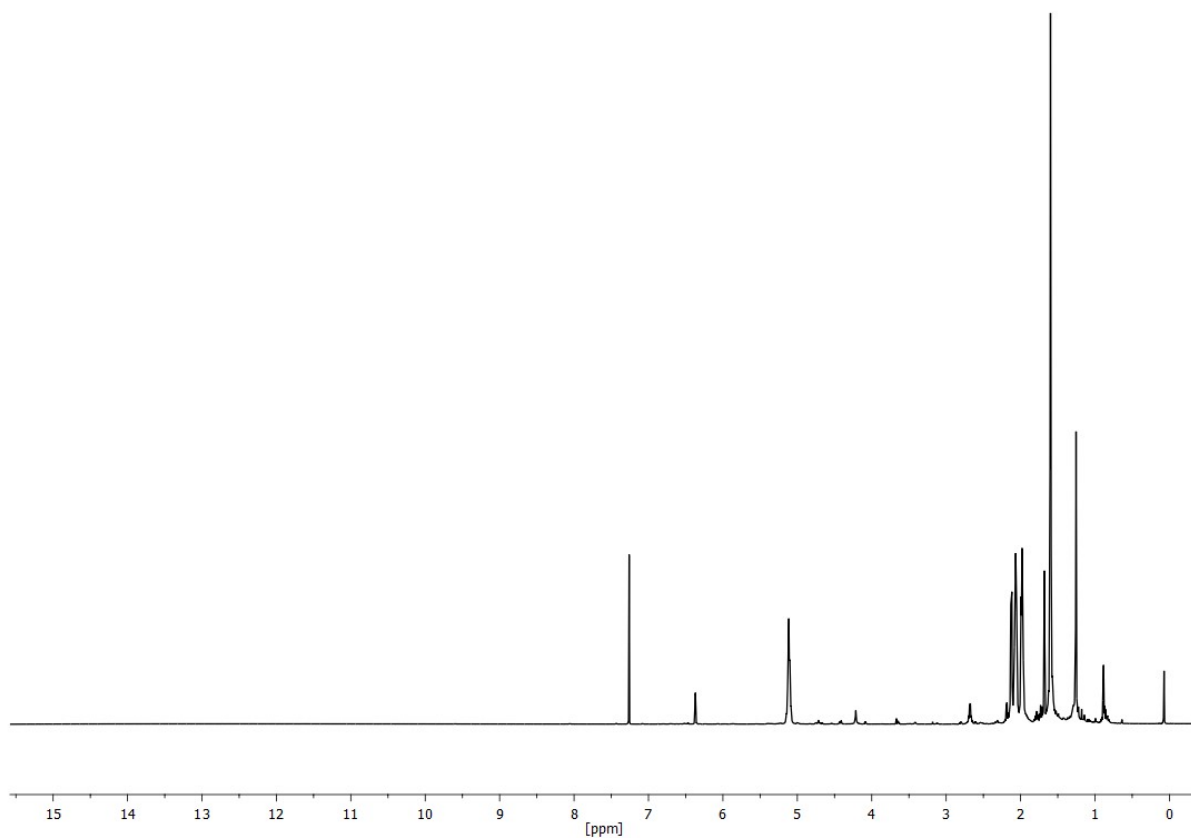
**Figure S20.**  $^1\text{H}$  NMR spectrum of PQ-6.



**Figure S21.**  $^1\text{H}$  NMR spectrum of PQ-7.



**Figure S22.**  $^1\text{H}$  NMR spectrum of PQ-8.



**Figure S23.**  $^1\text{H}$  NMR spectrum of PC-8.