

Supporting Information for:

Model linear low density polyethylenes from 5-hexyl-1-cyclooctene

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Molecular Characterization methods

¹H and ¹³C NMR spectra were recorded on a Varian INOVA-300 or a Varian INOVA-500 spectrometer at room temperature. CDCl₃ was used as solvents. Proton chemical shifts are referenced to CDCl₃ (7.26 ppm). Carbon chemical shifts are referenced to CDCl₃ (77.1 ppm). DSC measurements were performed using a TA Instruments Q1000 at the rate of 10 °C/min with N₂ as the purge gas.

Supporting Information for Synthesis of 1

We firstly tried to synthesize **1** by the most common alkane–alkane coupling reaction using Grignard reagent with/without lithium tetrachlorocuprate (II) in diethyl ether and in THF. However, the coupling reaction of 5-bromo-1-cyclooctene with *n*-hexylmagnesium bromide never afforded the target compound **1** in good yield. Also, we tried a solvent exchanging to CH₂Cl₂ but was fail in attempt to obtain **1** with one-step reaction. We attempted to obtain a Grignard reagent from 5-bromo-1-cyclooctene also, however, only a complicated mixture of alkanes was obtained due to the rearrangement of cyclooctene-ring which was considered to be occurred by the radical-producing initial step. We thus chose a multi-step synthetic pathway as shown in Scheme 1.

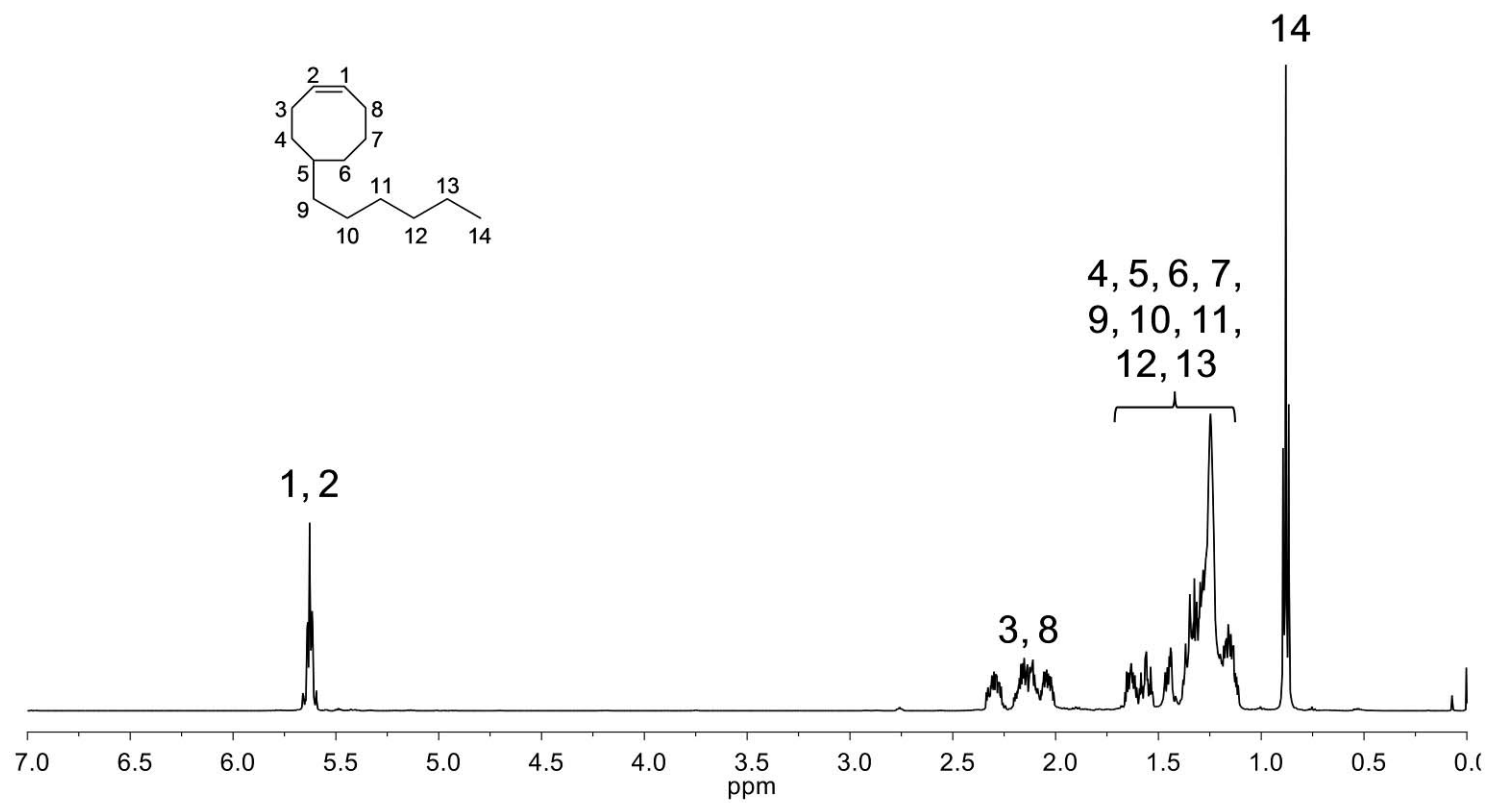


Figure S1. ^1H NMR spectrum of **1** (in CDCl_3 , 500 MHz).

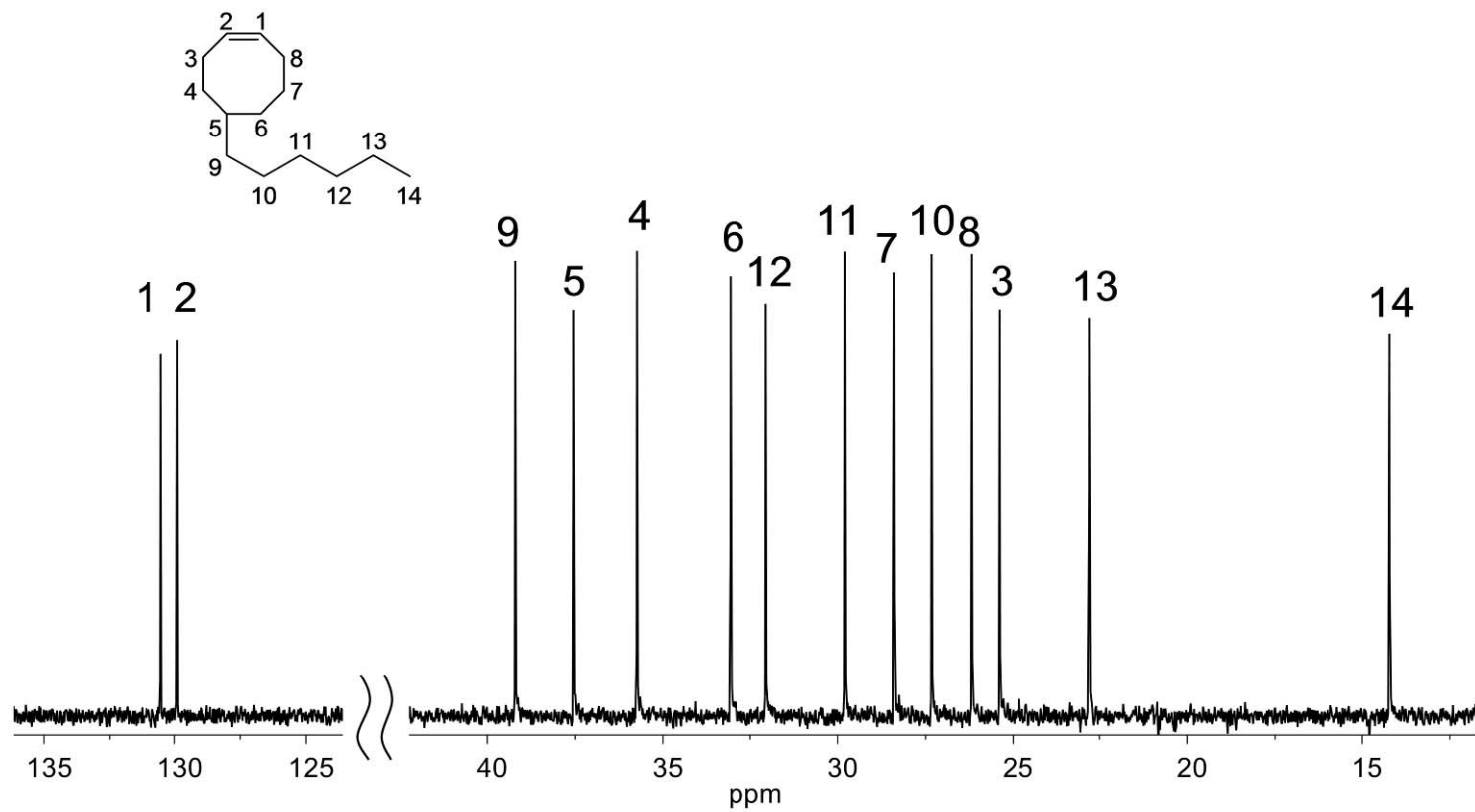


Figure S2. ^{13}C NMR spectrum of **1** (in CDCl_3 , 125 MHz).

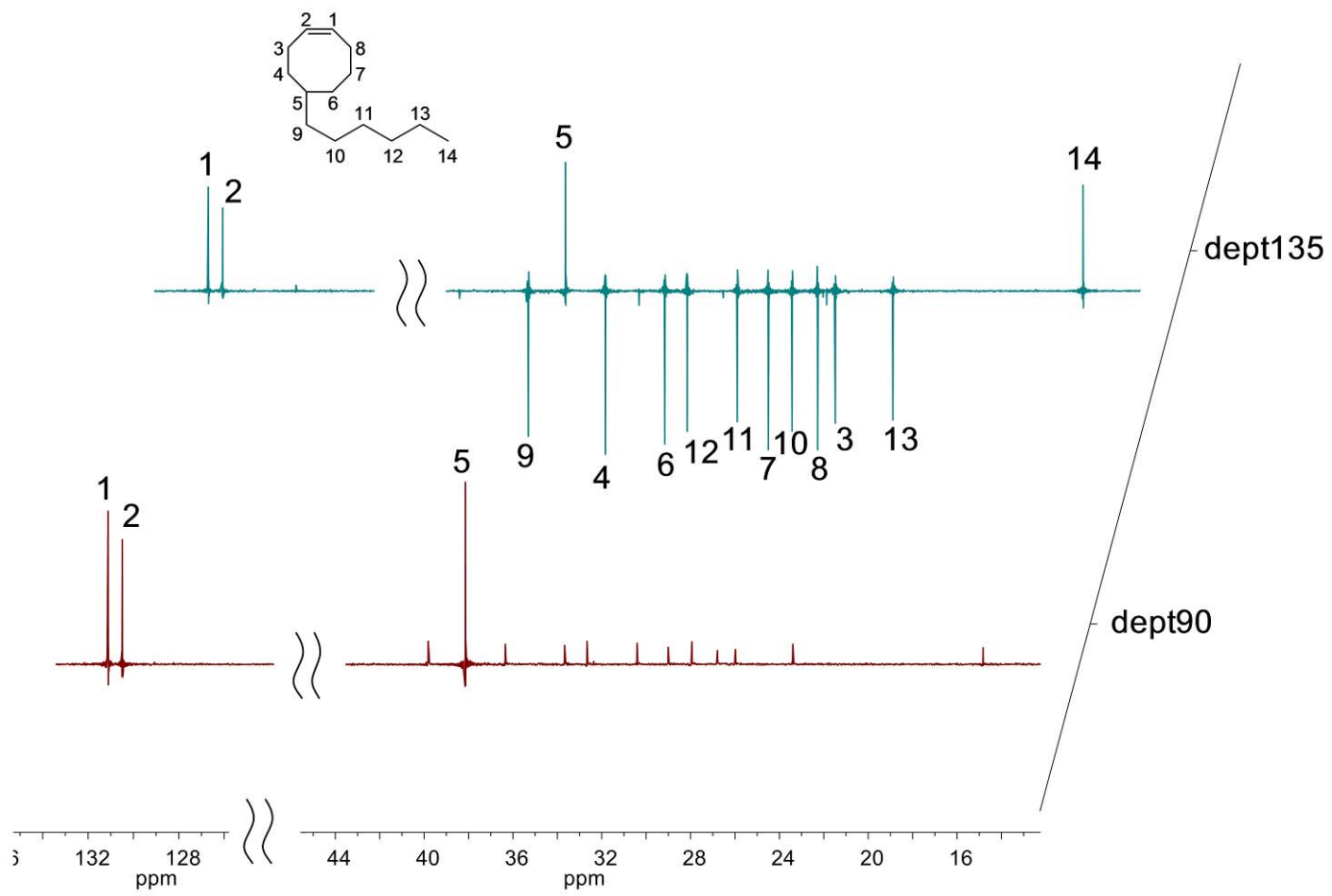


Figure S3. DEPT spectrum of **1** (in CDCl₃, 75 MHz).

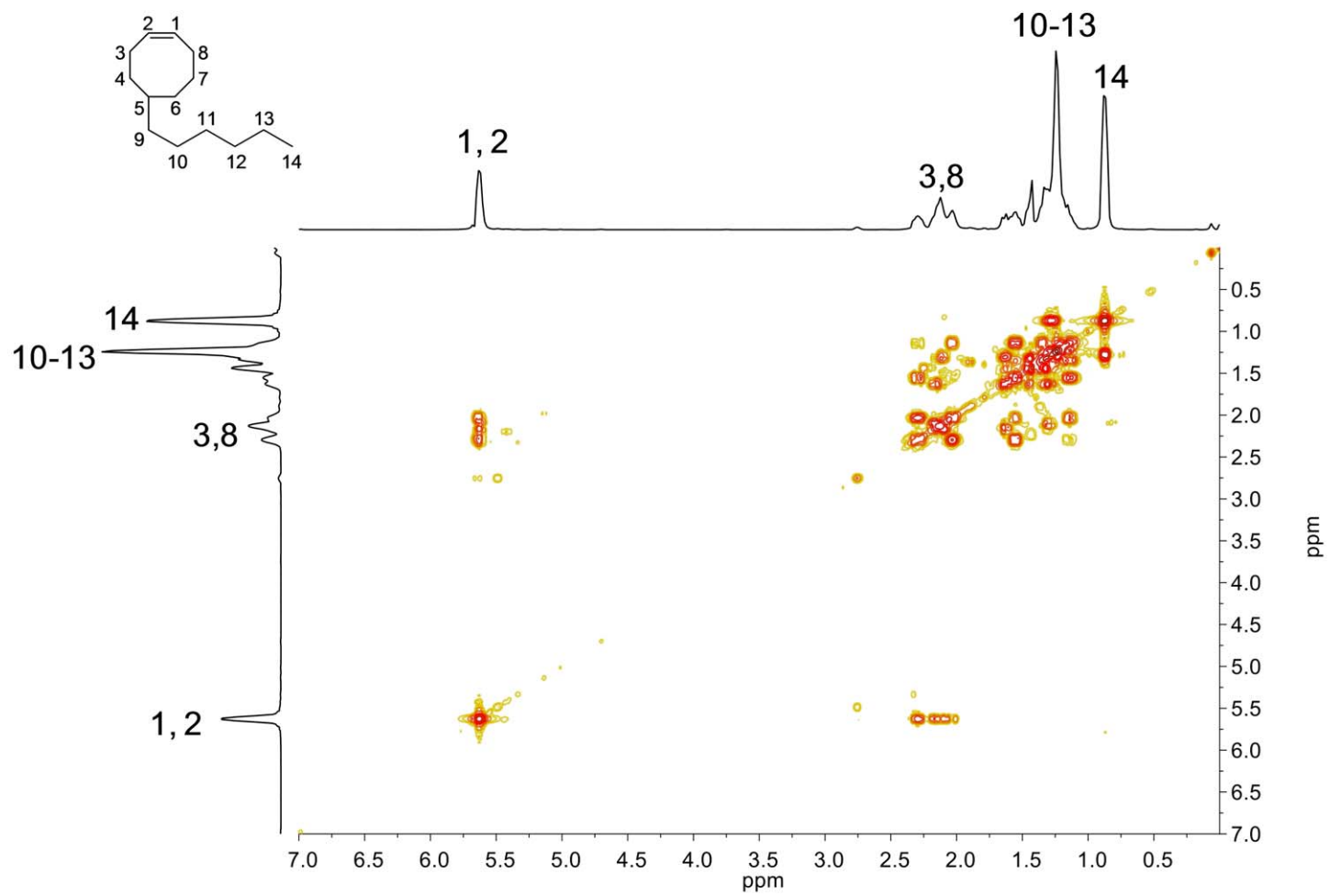


Figure S4. ^1H - ^1H COSY spectrum of **1** (in CDCl_3 , 500 MHz).

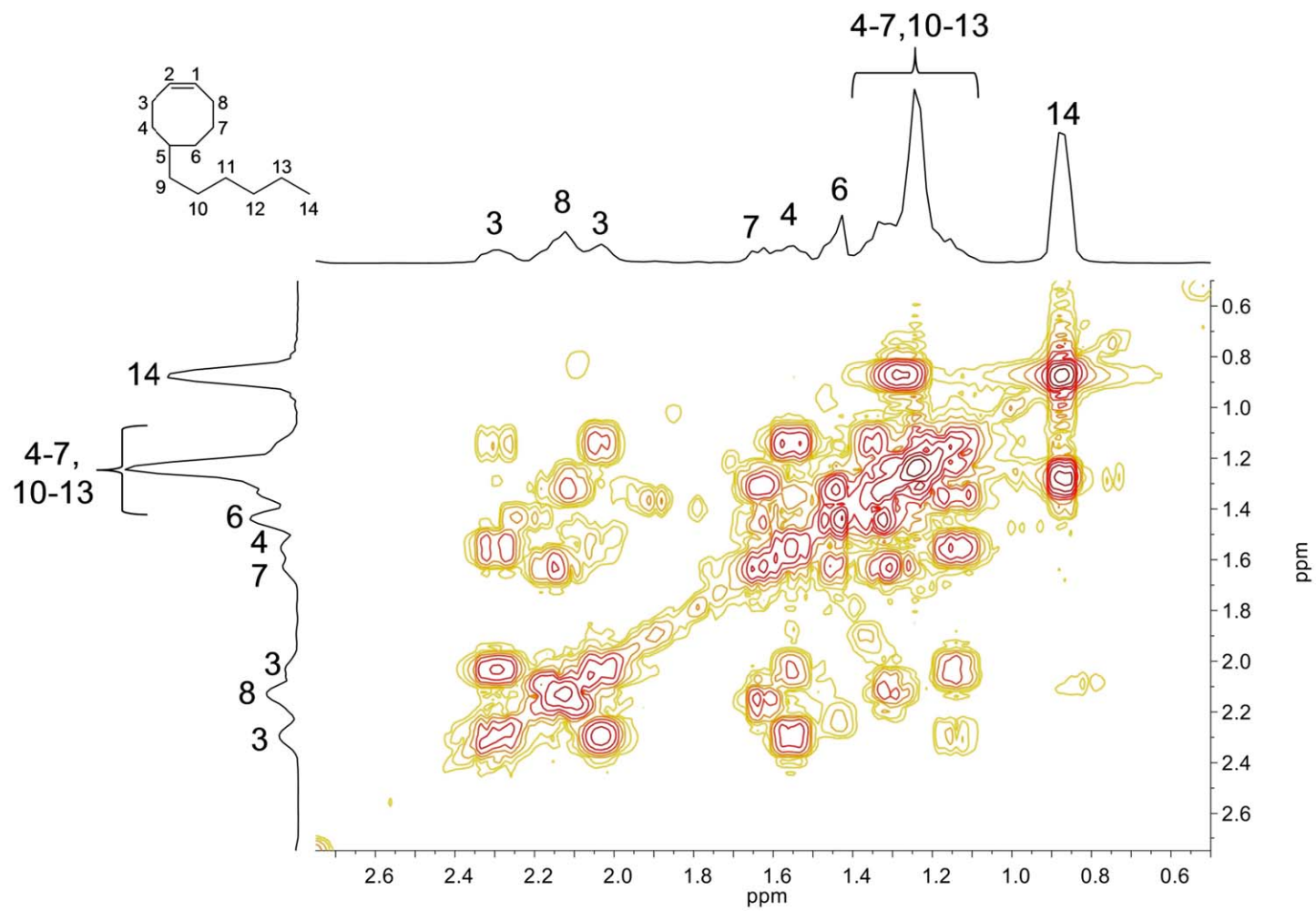


Figure S5. ^1H - ^1H COSY spectrum of **1** (in CDCl_3 , 500 MHz, expanded).

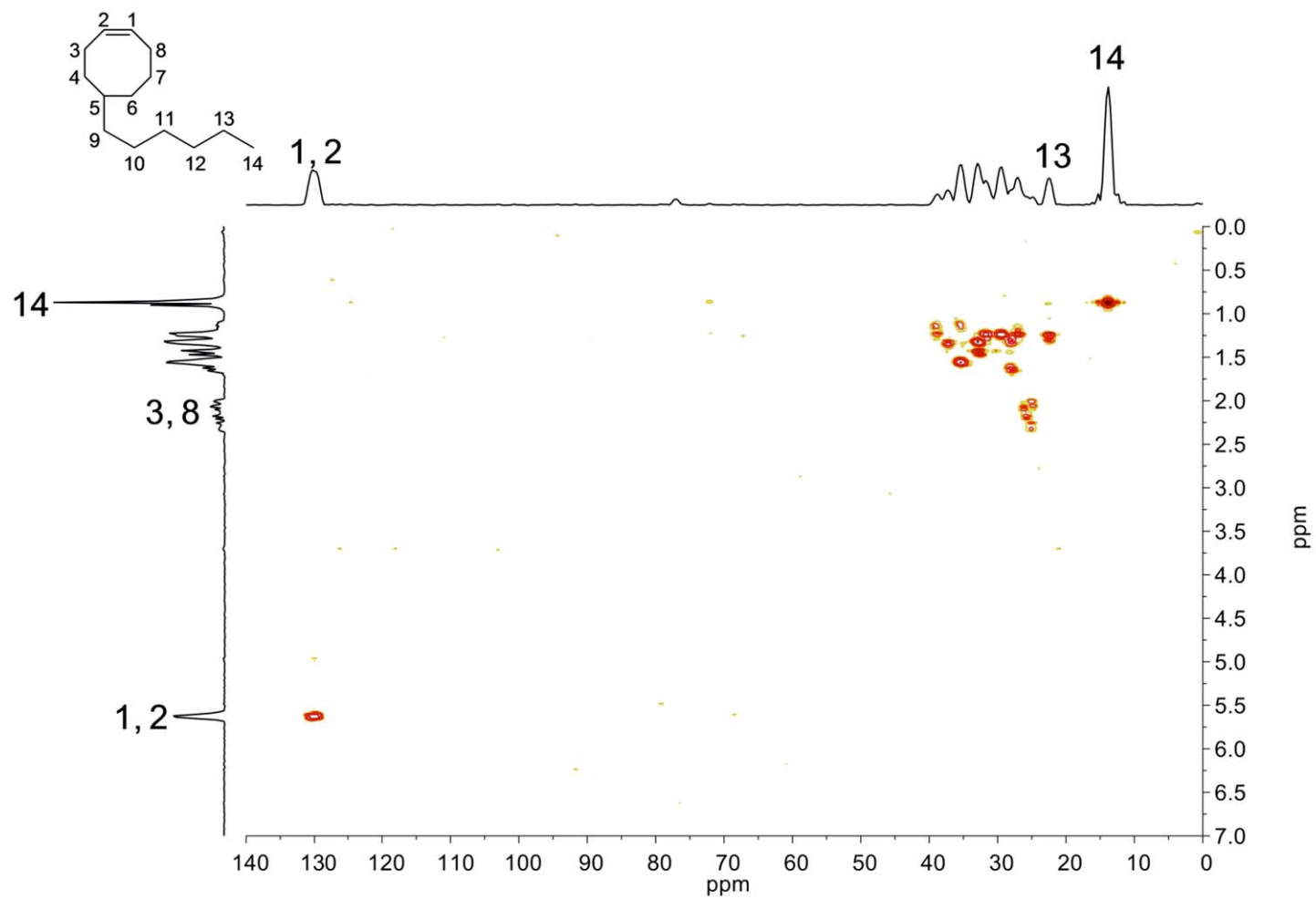


Figure S6. HMQC spectrum of **1** (in CDCl₃, 500 MHz).

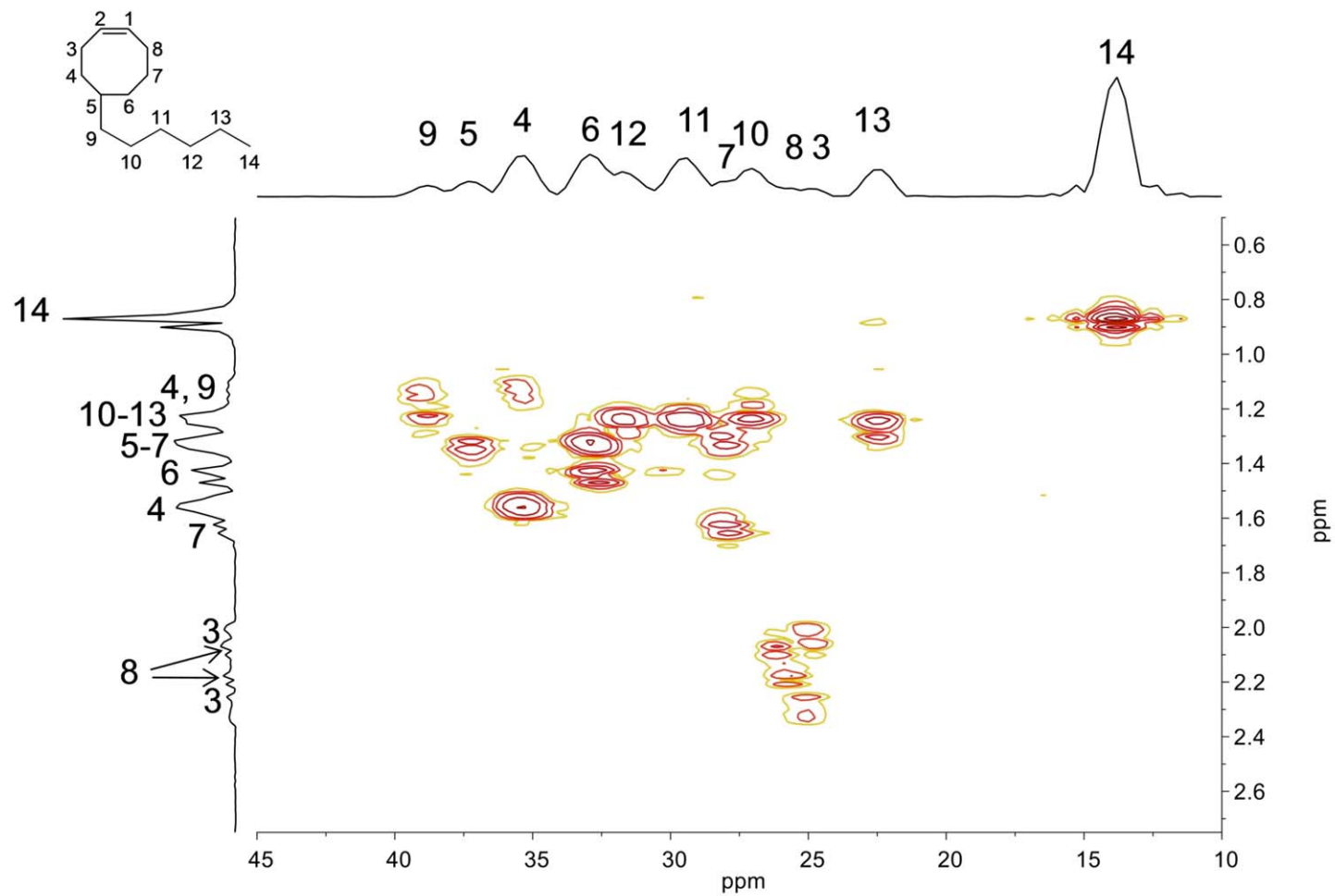


Figure S7. HMQC spectrum of **1** (in CDCl₃, 500 MHz, expanded).

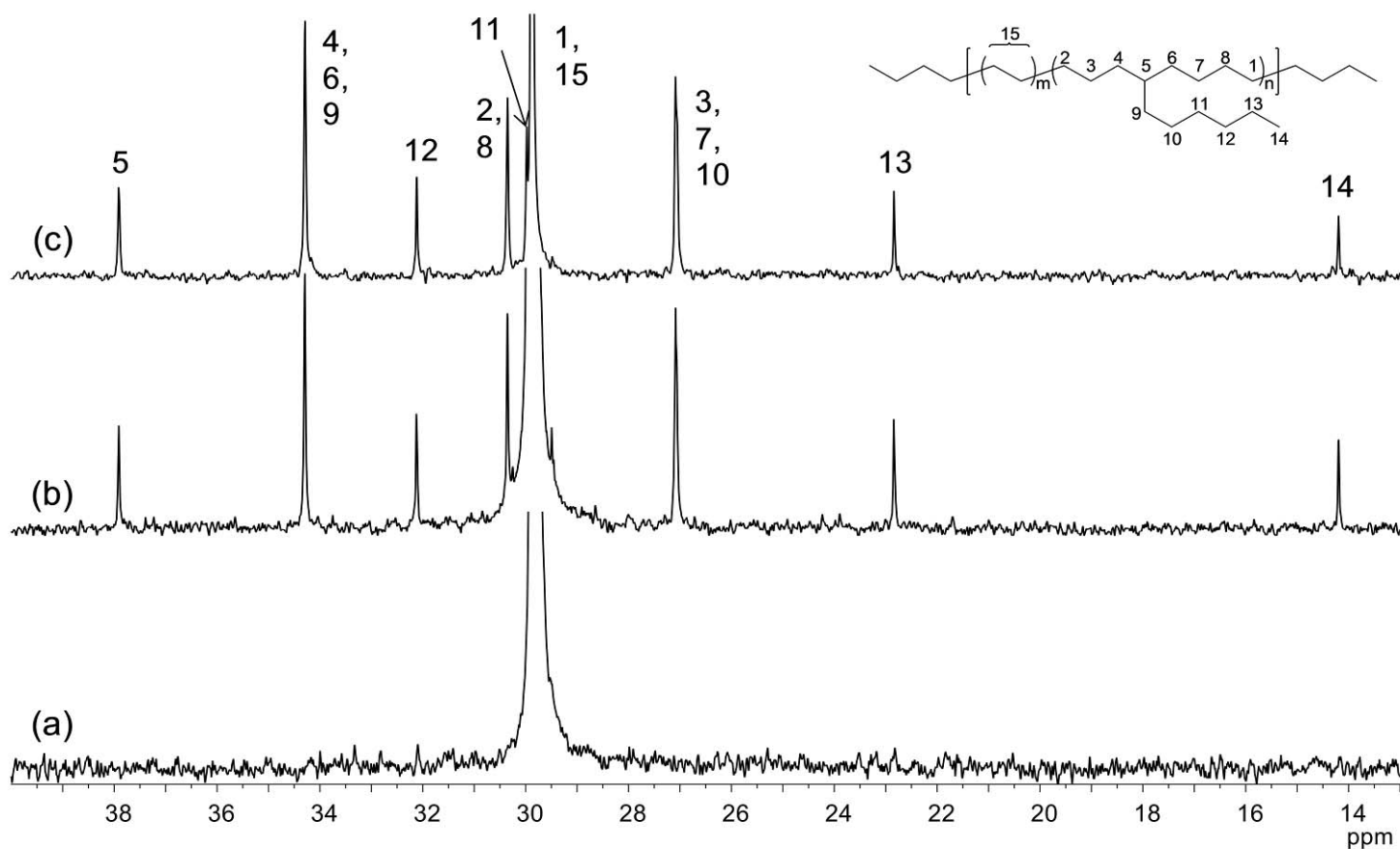


Figure S8. ^{13}C NMR spectra of hydrogenated polymers C8-LLDPE measured in 1,1,2,2-tetrachloroethane- d_2 at 100 °C; (a) 0 branch/1000 backbone carbons, entry 8h; (b) 10 branches/1000 backbone carbons, entry 4h, and (c) 40 branches/1000 backbone carbons, entry 2h.

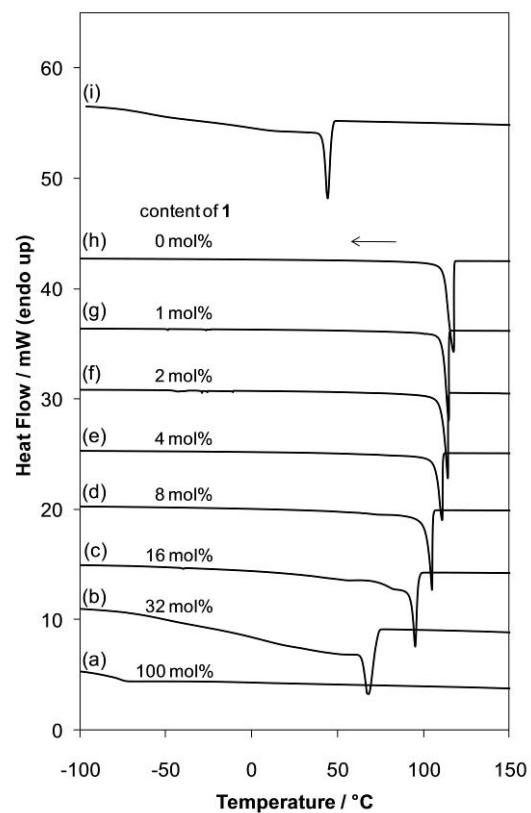


Figure S9. DSC thermograms of hydrogenated polymers at the cooling rate of 10 °C/min (cooling cycle); entry 1h (a), 125 branches/1000 backbone carbons; entry 2h (b), 40.0 branches/1000 backbone carbons; entry 3h (c), 20.0 branches/1000 backbone carbons; entry 4h (d), 10.0 branches/1000 backbone carbons; entry 5h (e), 5.0 branches/1000 backbone carbons; entry 6h (f), 2.5 branches/1000 backbone carbons; entry 7h (g), 1.3 branches/1000 backbone carbons; entry 8h (h), 0 branch /1000 backbone carbons; commercial C8-LLDPE (i), 73 branches /1000 backbone carbons, ENGAGE EG8200 (DOW chemical).

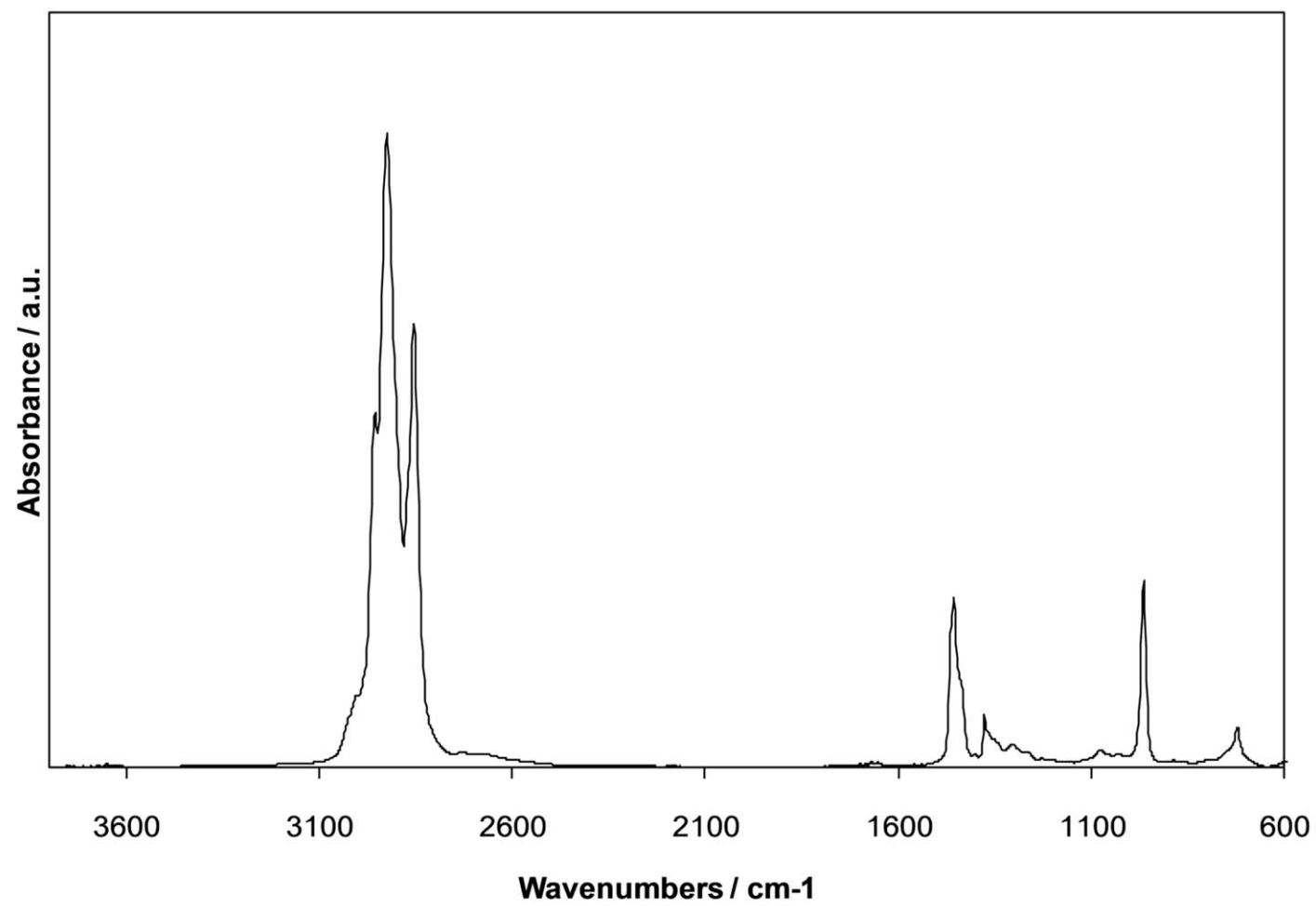


Figure S10. IR spectrum of poly(**1**) (entry 1, on NaCl plate).

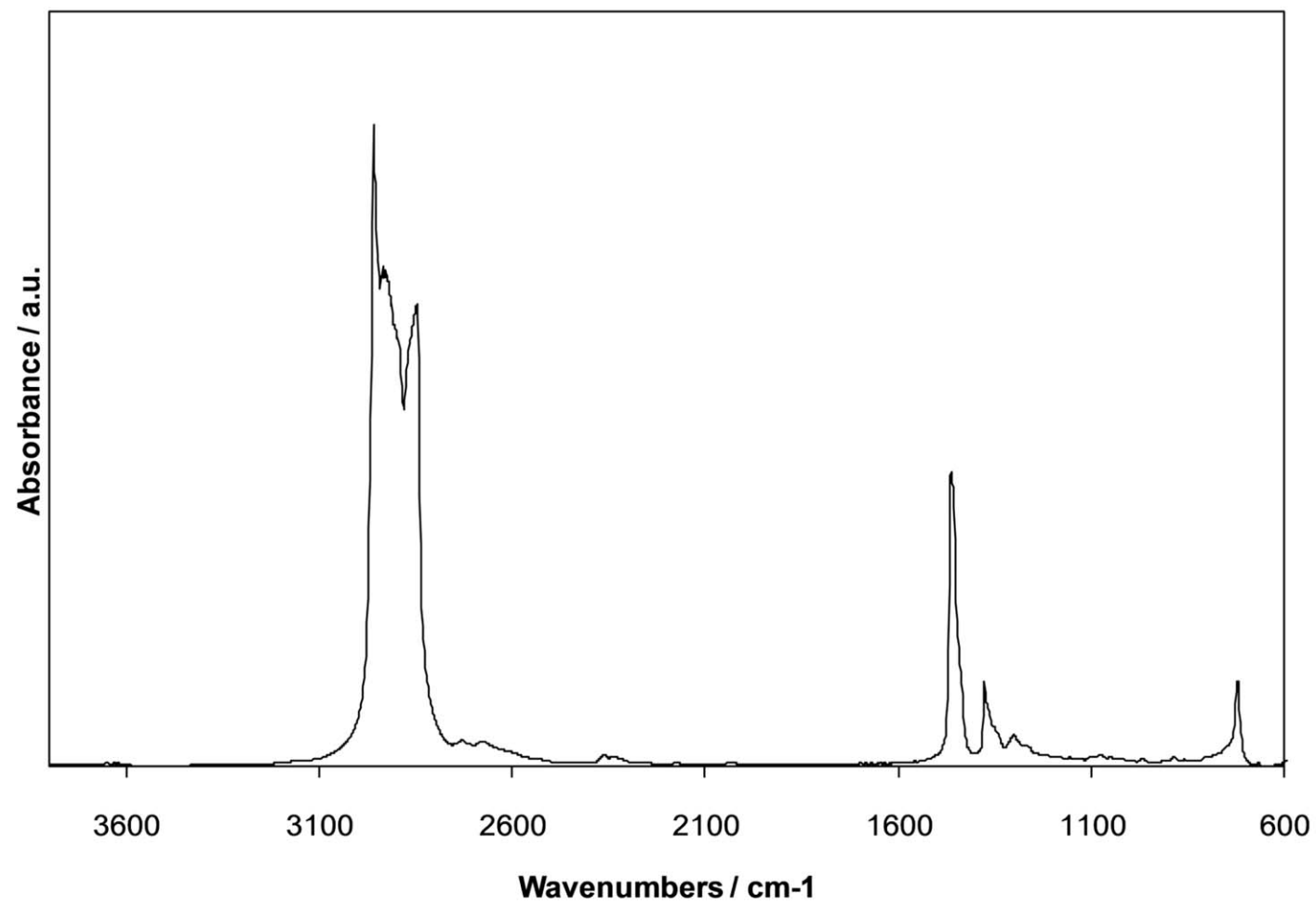


Figure S11. IR spectrum of C8-LLDPE (entry 1h, on NaCl plate).