

Supporting Information for:

Regio- and stereoselective ROMP of 3-substituted cyclooctenes

Shingo Kobayashi, Louis M. Pitet, and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, U.S.A.

<u>Table of Contents</u>	Page
1. Supplemental Data Noted in Main Article	
Polymerization Results	
Table S1: ROMP of 3 R COEs with G1	S3
Table S2: ROMP of 3 R COEs with G2	S4
Table S3: ROMP of 3 R COEs with G3	S5
Expanded ¹ H NMR spectra of olefinic protons of poly(3 R COE)s	
Figure S1: Poly(3 R COE)s obtained on ROMP with G2	S6
Figure S2: Poly(3 Me COE) obtained on ROMP with G1 , G2 and G3	S7
Figure S3: Reaction products obtained on stoichiometric experiment using G2	S8
DSC thermograms of poly(3 R COE)s	
Figure S4: Poly(3 R COE)s and their hydrogenated versions	S9
Figure S5: Comparison of precision LLDPEs from ROMP and ADMET	S10
2. Molecular Characterization Methods	S11
3. Materials	S11
4. Preparation of Monomers and Analytical Data	
3-Bromo-1-cyclooctene (Figure S6-Figure S11)	S12
3-Methyl-1-cyclooctene (3 Me COE, Figure S12-Figure S17)	S19
3-Ethyl-1-cyclooctene (3 Et COE, Figure S18-Figure S23)	S26
3-Hexyl-1-cyclooctene (3 Hex COE, Figure S24-Figure S29)	S33
3-Phenyl-1-cyclooctene (3 Ph COE, Figure S30-Figure S35)	S40
5. General Polymerization Procedure and Analytical Data	S47
Poly(3 Me COE) (Figure S36-Figure S41)	S47
Poly(3 Et COE) (Figure S42-Figure S47)	S55
Poly(3 Hex COE) (Figure S48-Figure S53)	S62
Poly(3 Ph COE) (Figure S54-Figure S59)	S69
6. General Chemical Hydrogenation Procedure and Analytical Data	S76

Hydrogenated poly(3 Me COE) (Figure S60-Figure S65)	S76
Hydrogenated poly(3 Et COE) (Figure S66-Figure S71)	S83
Hydrogenated poly(3 Hex COE) (Figure S72-Figure S77)	S90
Hydrogenated poly(3 Ph COE) (Figure S78-Figure S83)	S97

1. Supplemental Data Noted in Main Article

Table S1. Ring-opening metathesis polymerization of monomers using Grubbs first generation catalysts (**G1**)^a

entry	R ^b	M/ G1	Conversion ^c %	yield %	M_n (kg mol ⁻¹)		M_w/M_n^f	<i>trans</i> - ^c %	HT ^c %	<i>trans</i> -HT ^c %
					calcd ^d	LSSEC ^e				
S1	Me	428	6	4	4.2	2.8	3.51	86.3	70.2	66.4
S2	Et	412	<1	trace						
S3	Hex	412	<1	trace						
S4	Ph	412	<1	0						

^a Polymerization performed in bulk condition at 60 °C for 20 h. ^b Substituted alkyl groups. **Me**=methyl, **Et**=ethyl, **Hex**=hexyl, and **Ph**=phenyl. ^c Determined by ¹H NMR spectroscopy. ^d M_n calcd = (MW of monomer) × [monomer]/[catalyst] × conversion. ^e Determined by SEC including MALLS detector using THF as an eluent at 30 °C. ^f Determined by SEC using CHCl₃ as an eluent at 35 °C.

Table S2. Ring-opening metathesis polymerization of monomers using Grubbs second generation catalysts (**G2**)^a

entry	R ^b	M/ G2	M/CTA	Conversion ^c	yield	M_n (kg mol ⁻¹)			M_w/M_n^f	<i>trans</i> - ^c	HT ^c	<i>trans</i> -HT ^c
				%	%	calcd ^d	LSSEC ^e	SEC ^f		%	%	%
S5	Me	1061	5	>99	63	0.73	1.42	1.33	1.39	96.5	95.5	92.6
S6	Me	4278	99	>99	94	19.4	12.4	17.9	1.54	96.4	95.9	92.6
S7	Me	4251	-	93	81	491	341	335	1.29	96.8	93.5	91.4
S8	Et	1062	5	88	92	0.72	1.22	1.20	1.26	98.7	97.1	96.3
S9	Et	4261	99	>99	92	19.3	10.9	24.0	1.64	98.2	95.8	94.6
S10	Et	4250	-	56	48	329	220	258	1.39	98.5	96.8	95.9
S11	Hex	1063	5	64	38	0.48	1.24	1.21	1.23	98.6	97.8	96.8
S12	Hex	4341	98	>99	97	19.3	13.9	17.9	1.54	98.6	97.6	96.4
S13	Hex	4245	-	38	34	313	162	168	1.57	98.8	98.0	97.2
S14	Ph	1061	5	89	48	0.94	2.03	2.40	1.40	98.3	98.7	97.3
S15	Ph	4245	100	26	26	4.90	10.8	12.8	1.65	99.7	99.9	99.6
S16	Ph	4245	-	84	77	664	468	416	1.14	98.4	99.9	98.4

^a Polymerization performed in CHCl₃ at 60 °C for 20 h. *cis*-4-Octene was used as CTA. ^b Substituted alkyl groups. **Me**=methyl, **Et**=ethyl, **Hex**=hexyl, and **Ph**=phenyl. ^c Determined by ¹H NMR spectroscopy. ^d $M_{n,calcd} = (\text{MW of monomer}) \times [\text{monomer}] / ([\text{CTA}] + [\text{catalyst}]) \times \text{conversion} + (\text{MW of CTA})$. ^e Determined by SEC including MALLS detector using THF as an eluent at 30 °C. ^f Determined by SEC using CHCl₃ as an eluent at 35 °C.

Table S3. Ring-opening metathesis polymerization of monomers using Grubbs third generation catalysts (**G3**)^a

entry	R ^b	M/ G3	M/CTA	Conversion ^c	yield	M_n (kg mol ⁻¹)			M_w/M_n^f	<i>trans</i> - ^c	HT ^c	<i>trans</i> -HT ^c
				%	%	calcd ^d	LSSEC	SEC ^f		%	%	%
S17	Me	1108	5	99	69	0.73	1.30	1.04	1.75	97.2	91.7	89.6
S18	Me	4434	100	96	69	12.0	12.4	17.7	2.30	97.6	94.2	92.1
S19	Me	4429	-	>99	76	550	477	312	1.38	98.0	94.7	93.0
S20	Et	1108	5	85	59	0.70	0.96	0.77	1.48	99.0	98.9	98.0
S21	Et	4432	100	50	35	7.00	8.45	10.8	1.79	98.5	94.7	93.7
S22	Et	4432	-	>99	81	613	314	276	1.42	98.6	96.9	96.0
S23	Hex	1106	5	75	28	1.08	1.05	0.92	1.34	98.9	98.2	97.3
S24	Hex	4429	100	33	28	6.40	8.00	9.69	1.70	99.0	98.1	97.3
S25	Hex	4424	-	96	92	825	434	348	1.54	99.0	98.3	97.4
S26	Ph	1061	5	25	7	0.35	1.31	1.64	1.17	99.2	98.1	97.5
S27	Ph	4428	100	47	39	8.80	12.0	14.9	1.53	98.8	98.1	97.1
S28	Ph	4428	-	76	73	627	426	368	1.23	99.1	99.6	98.7

^a Polymerization performed in CHCl₃ at 60 °C for 20 h. *cis*-4-Octene was used as CTA. ^b Substituted alkyl groups. **Me**=methyl, **Et**=ethyl, **Hex**=hexyl, and **Ph**=phenyl. ^c Determined by ¹H NMR spectroscopy. ^d $M_{n,calcd} = (\text{MW of monomer}) \times [\text{monomer}]/([\text{CTA}]+[\text{catalyst}]) \times \text{conversion} + (\text{MW of CTA})$. ^e Determined by SEC including MALLS detector using THF as an eluent at 30 °C. ^f Determined by SEC using CHCl₃ as an eluent at 35 °C.

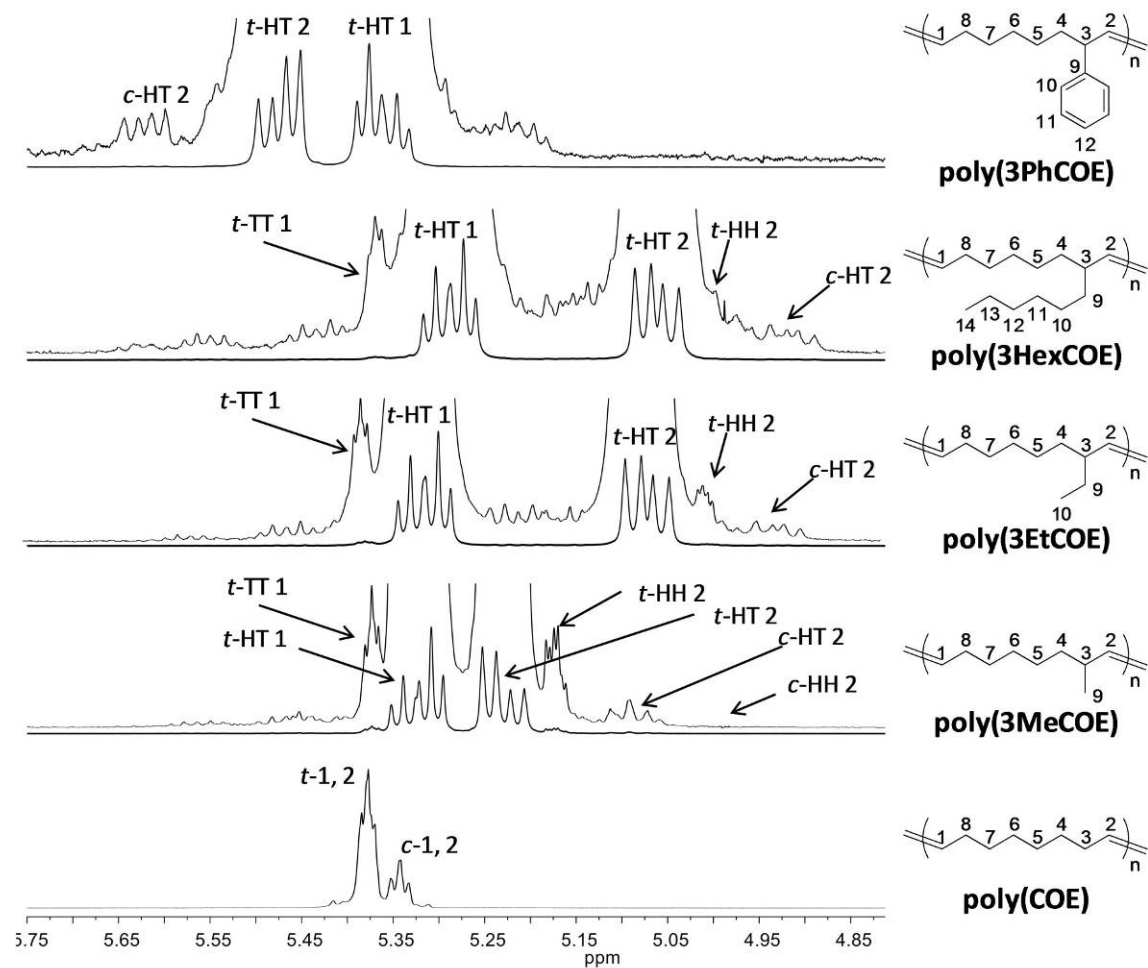


Figure S1. ^1H NMR spectra of olefinic protons of poly(3RCOE)s obtained with **G2**. (in CDCl_3 , 500 MHz) Each spectrum shows the signals at low scaling to accentuate the doublet of triplet and doublet of doublet multiplicity and at high scaling to magnify the baseline to identify signals from the low concentration of irregular sequences.

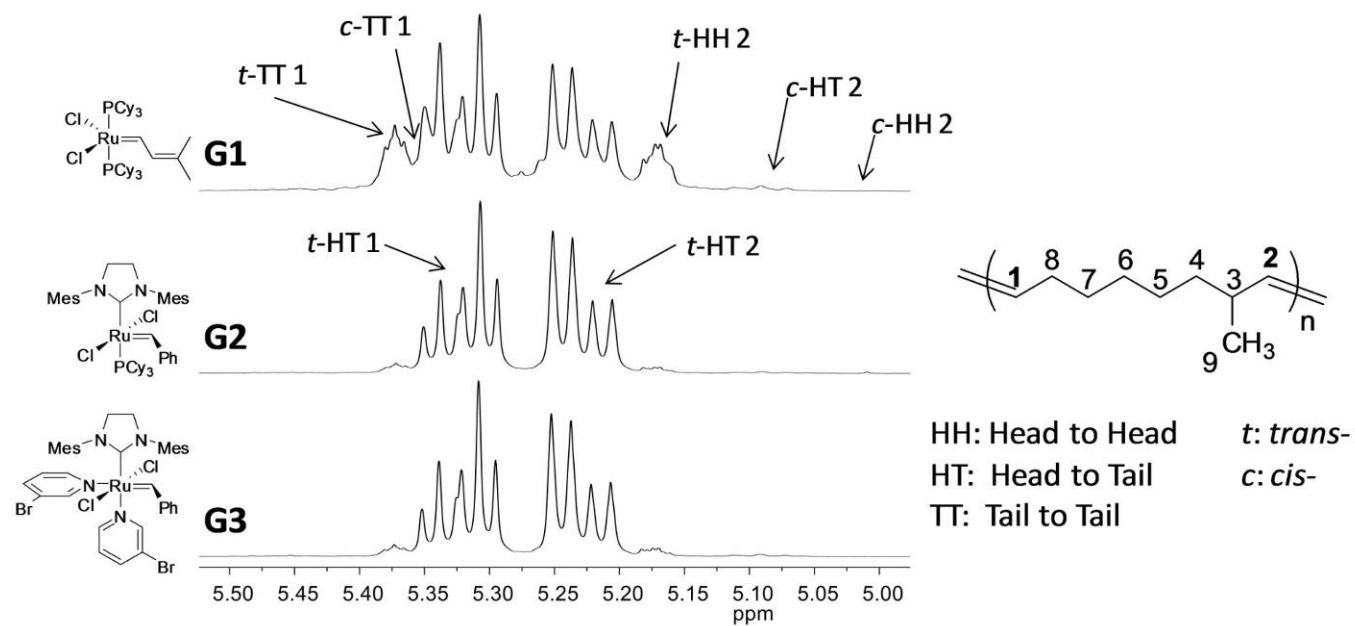


Figure S2. ^1H NMR spectra of olefinic protons of poly(3MeCOE)s obtained with Grubbs catalysts; **G1** (top, entry S1 in Table S1); **G2** (middle, entry S7 in Table S2); and **G3** (bottom, entry S19 in Table S3). (in CDCl_3 , 500 MHz)

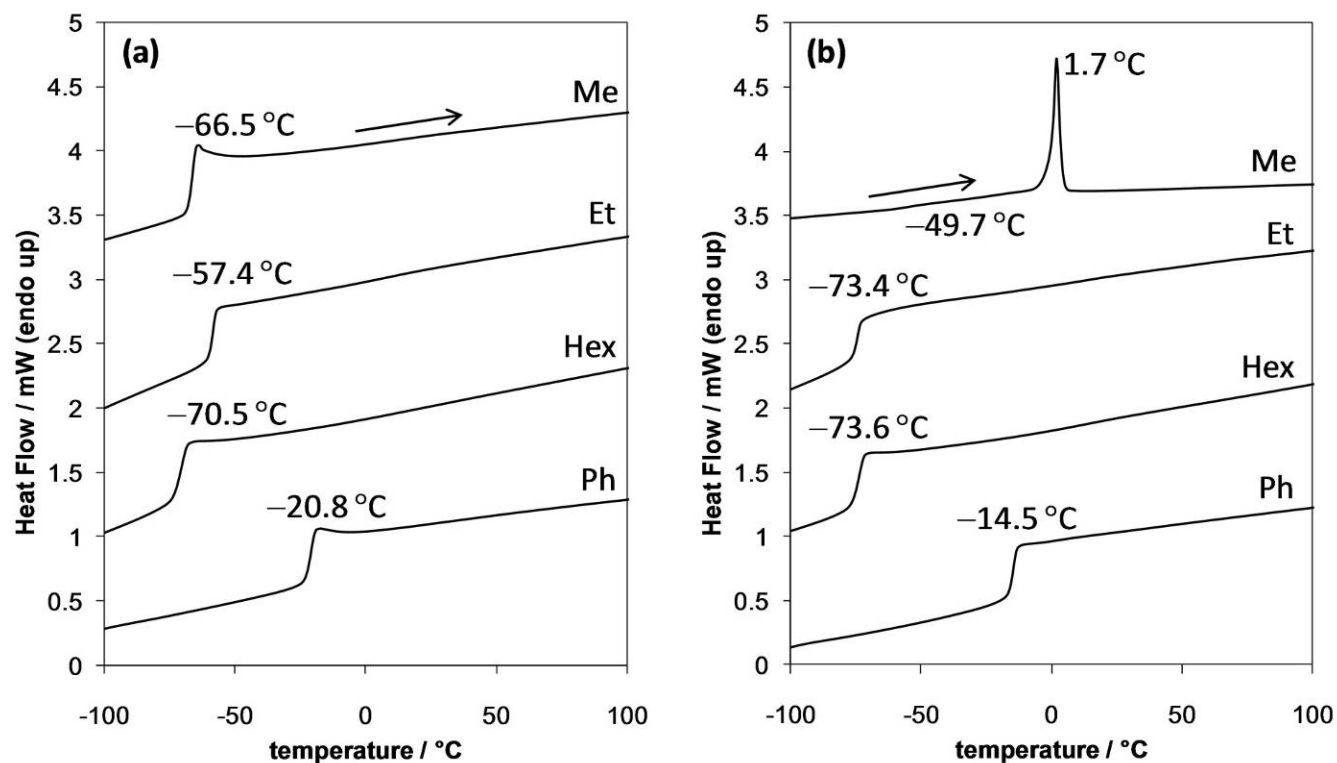


Figure S4. DSC thermograms of poly(3RCOE)s at the heating rate of 10 °C/min (heating cycle) (refer to Table S2 for entries); (a) original poly(3RCOE)s; **Me**, entry S6; **Et**, entry S9; **Hex**, entry S12; **Ph**, entry S15. (b) hydrogenated poly(3RCOE)s synthesized from; **Me**, entry S6; **Et**, entry S9; **Hex**, entry S12; **Ph**, entry S15.

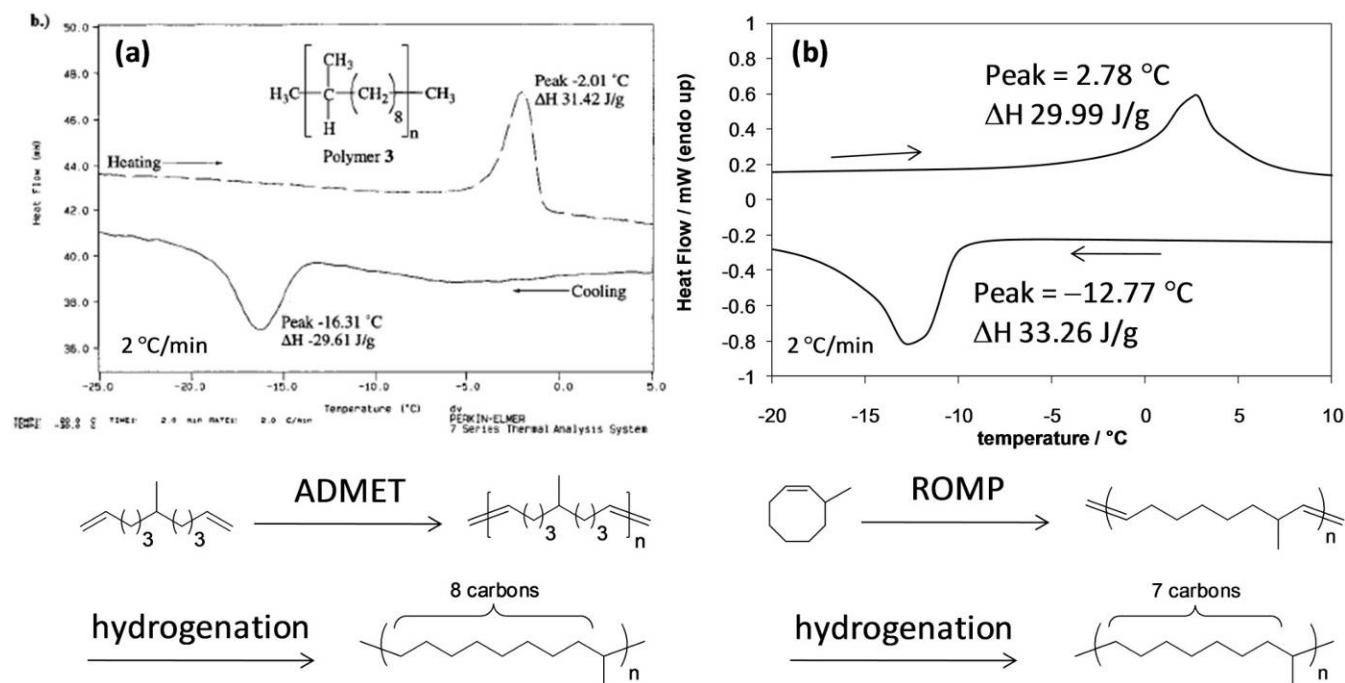


Figure S5. DSC thermograms of precision LLDPEs having precisely placed methyl branches at the heating rate of 2 °C/min; (a) ADMET precision LLDPE possessing methyl branches on every 9th backbone carbon. (taken from Wagener et al. *Macromolecules*, **1997**, 30, 6688–6690.) (b) ROMP precision LLDPE possessing methyl branches on every 8th backbone carbon synthesized from regio- and stereoregular poly(3MeCOE) (entry S6 in Table S2).

2. Molecular Characterization Methods

^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 or Varian INOVA-500 spectrometer at room temperature. CDCl_3 was used as solvents. Proton chemical shifts are referenced to TMS (0.00 ppm). Carbon chemical shifts are referenced to CDCl_3 (77.1 ppm). IR spectra were recorded on a Nicolet Magna-IR FTIR 550 spectrophotometer. High-resolution mass spectral data (HRMS) was collected on a Finnigan MAT 95 instrument using EI conditions with the sample introduced by a Hewlett-Packard Series II model 5890 gas chromatograph. Molecular weight and PDI of the polymers were determined by SECs and all the columns were calibrated with polystyrene standards (Polymer Laboratories). M_n SEC was determined on a Hewlett-Packard 1100 series liquid chromatograph fitted with a Hewlett-Packard 1047A refractive index detector and three PLgel columns (Polymer Laboratories columns with 500, 10^3 , and 10^4 Å pore sizes) with chloroform as the eluent at a flow rate of 1 mL/min at 35 °C. M_n LSSEC was determined on a system includes a Wyatt OPTILAB RI detector, a Wyatt multiangle light scattering detector (MALS), and three Phenogel columns (Phenomenex of 10^3 , 10^4 , and 10^5 Å pore sizes). The columns were at ambient temperature, and the RI detector was set at 40 °C. THF was used as the eluent at a flow rate of 1 mL/min. DSC measurements were performed using a TA Instruments Q1000 with N_2 as the purge gas at the rate of 10 °C/min and 2 °C/min.

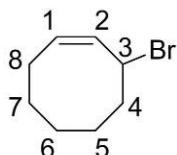
3. Materials

cis-Cyclooctene (95%) purchased from Acros Organics for monomer synthesis was purified by passing through a basic Al_2O_3 plugged column. Grubbs first generation [**G1**: Dichloro(3-methyl-2-butenylidene)bis(tricyclohexylphosphine)ruthenium(II)] and second generation {**G2**: [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium(II)} catalyst were used as received; samples were either purchased from Aldrich or donated by Materia, Inc. Grubbs third generation {**G3**: [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(benzylidene)bis(3-bromopyridine)ruthenium(II)} catalyst was synthesized as described in Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035–4037. The chain transfer agent *cis*-4-octene (97%) was purchased from GFS chemicals and purified by vacuum distillation over CaH_2 . CHCl_3 for polymerization was purified by passing thorough a basic Al_2O_3 plugged column and distillation over CaH_2 prior

to polymerization. Other commercially available reagents were used without further purification.

4. Preparation of Monomers

Preparation of 3-Bromo-1-cyclooctene. (Figure S6-Figure S11)



A mixture of *cis*-cyclooctene (40 mL, ca. 305 mmol), *N*-bromosuccinimide (40 g, 225 mmol), and AIBN (30 mg, 0.183 mmol) in carbon tetrachloride (150 mL) was thoroughly purged with dry Ar gas and then stirred at reflux temperature for 2 h. The reaction was quenched by cooling the system to 0 °C and white precipitate was removed by filtration. After concentration of the solution, the resulting crude product was purified by fractional vacuum distillation afforded 3-bromo-1-cyclooctene (31.4 g, 166 mmol, 74% yield, bp = 46–48 °C at 150–160 mTorr) as a colorless liquid.

^1H NMR (500 MHz, CDCl_3): δ = 5.83–5.75 (m, 1H, =C(2)*H*–), 5.65–5.55 (m, 1H, =C(1)*H*–), 4.99–4.92 (m, 1H, –C(3)*HBr*–), 2.29–2.16 (m, 2H, –C(4)*HH*–, –C(8)*HH*–), 2.11 (m, 1H, –C(8)*HH*–), 2.05–1.94 (m, 1H, –C(4)*HH*–), 1.75–1.64 (m, 2H, –C(7)*HH*–, –C(6)*HH*–), 1.62–1.47 (m, 2H, –C(5)*H*₂–), 1.45–1.23 (m, 2H, –C(6)*HH*–, –C(7)*HH*–).

^{13}C NMR (125 MHz, CDCl_3): δ = 133.30 (C2), 129.91 (C1), 49.07 (C3), 40.94 (C4), 29.08 (C7), 26.62 (C5), 26.21 (C8), 25.75 (C6).

IR (neat): 3026, 2927, 2855, 2683, 1653, 1643, 1559, 1457, 1447, 1395, 1327, 1385, 1254, 1240, 1217, 1179, 1130, 1079, 999, 956, 891, 845, 784, 763, 722, 707 cm^{-1} .

HRMS(EI): m/z calcd for $\text{C}_8\text{H}_{13}\text{Br}$ [M^+]: 188.0201, found: 188.0187.

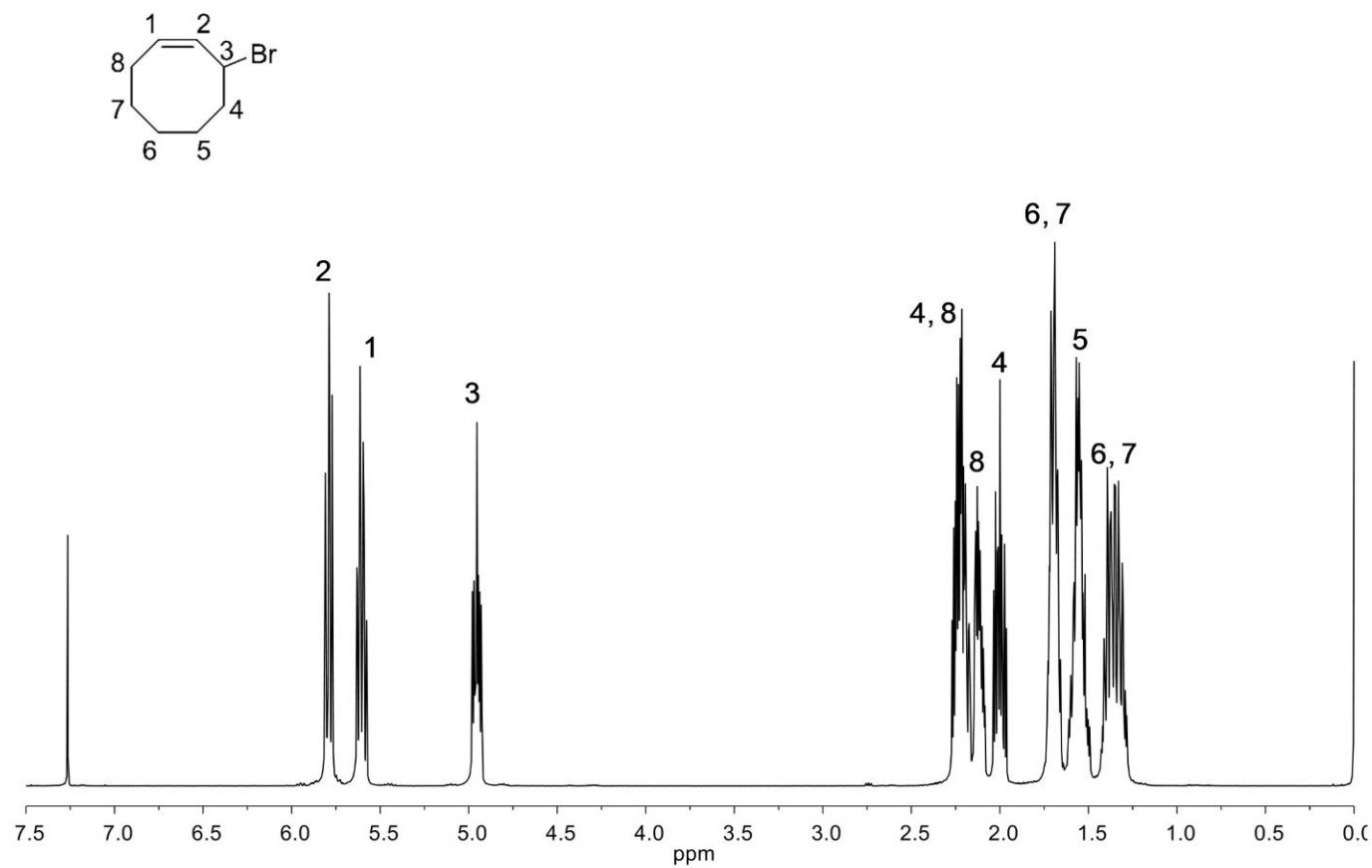


Figure S6. ^1H NMR spectrum of 3-bromo-1-cyclooctene (in CDCl_3 , 500 MHz).

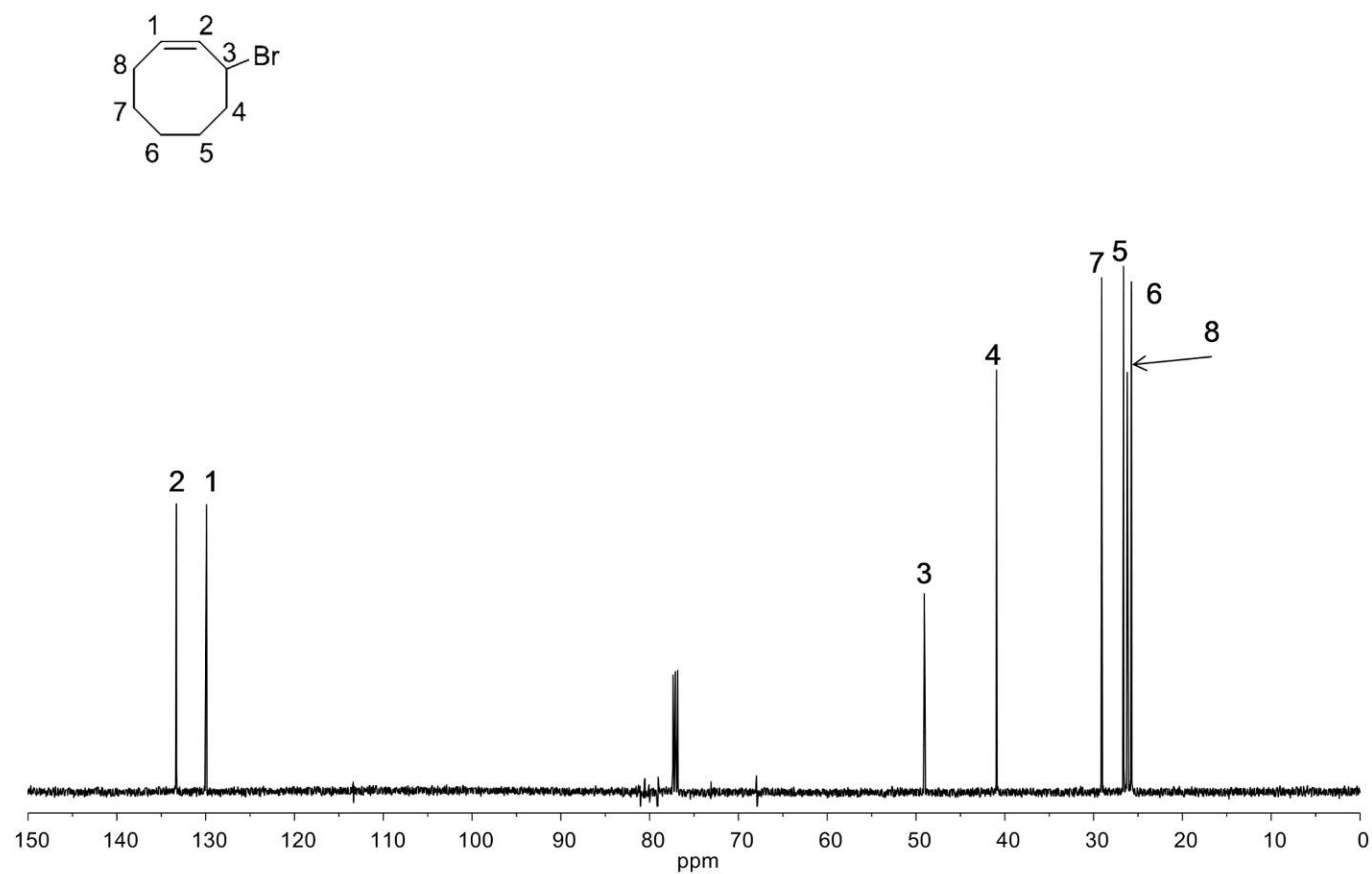


Figure S7. ^{13}C NMR spectrum of 3-bromo-1-cyclooctene (in CDCl_3 , 125 MHz).

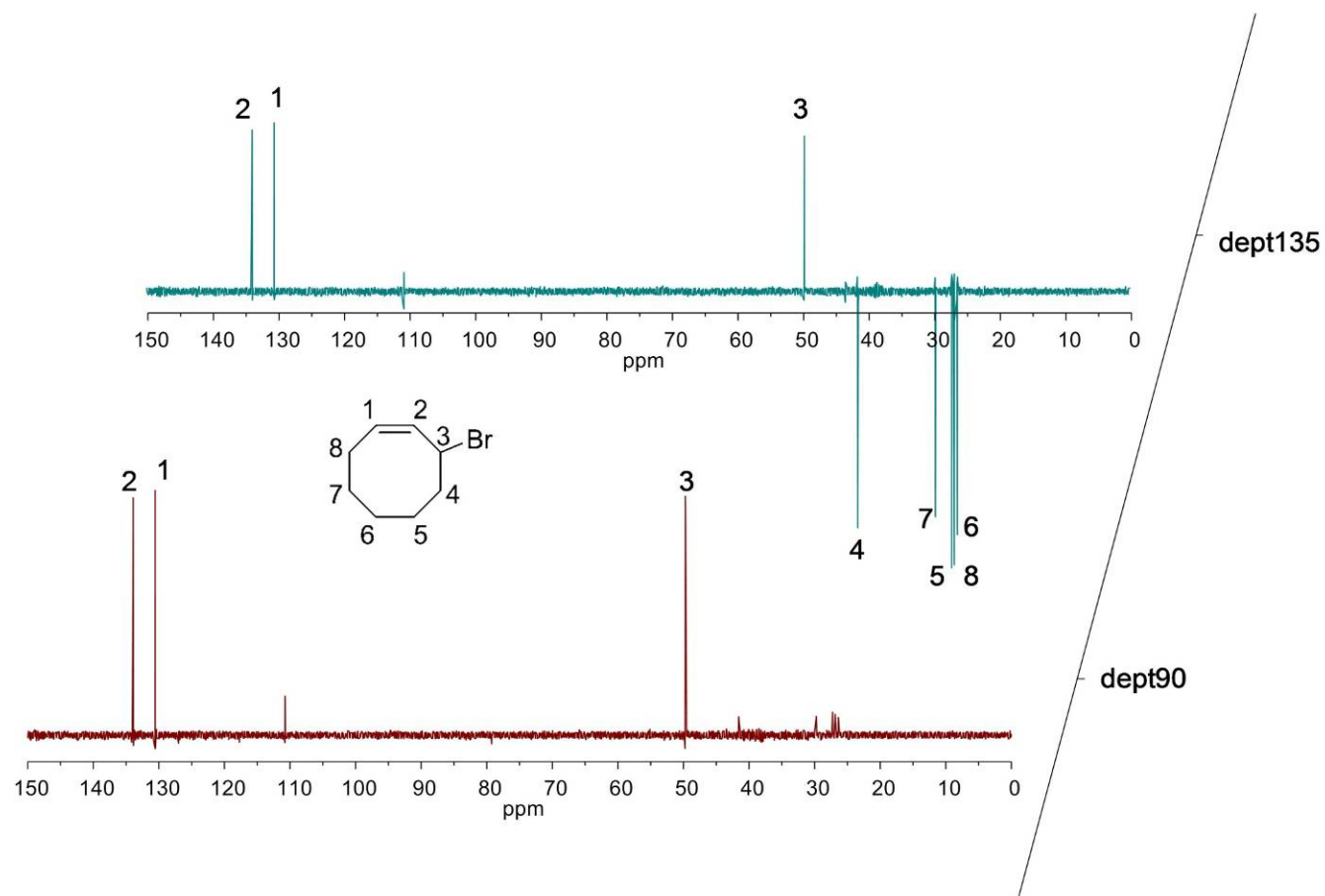


Figure S8. DEPT spectrum of 3-bromo-1-cyclooctene (in CDCl_3 , 75 MHz).

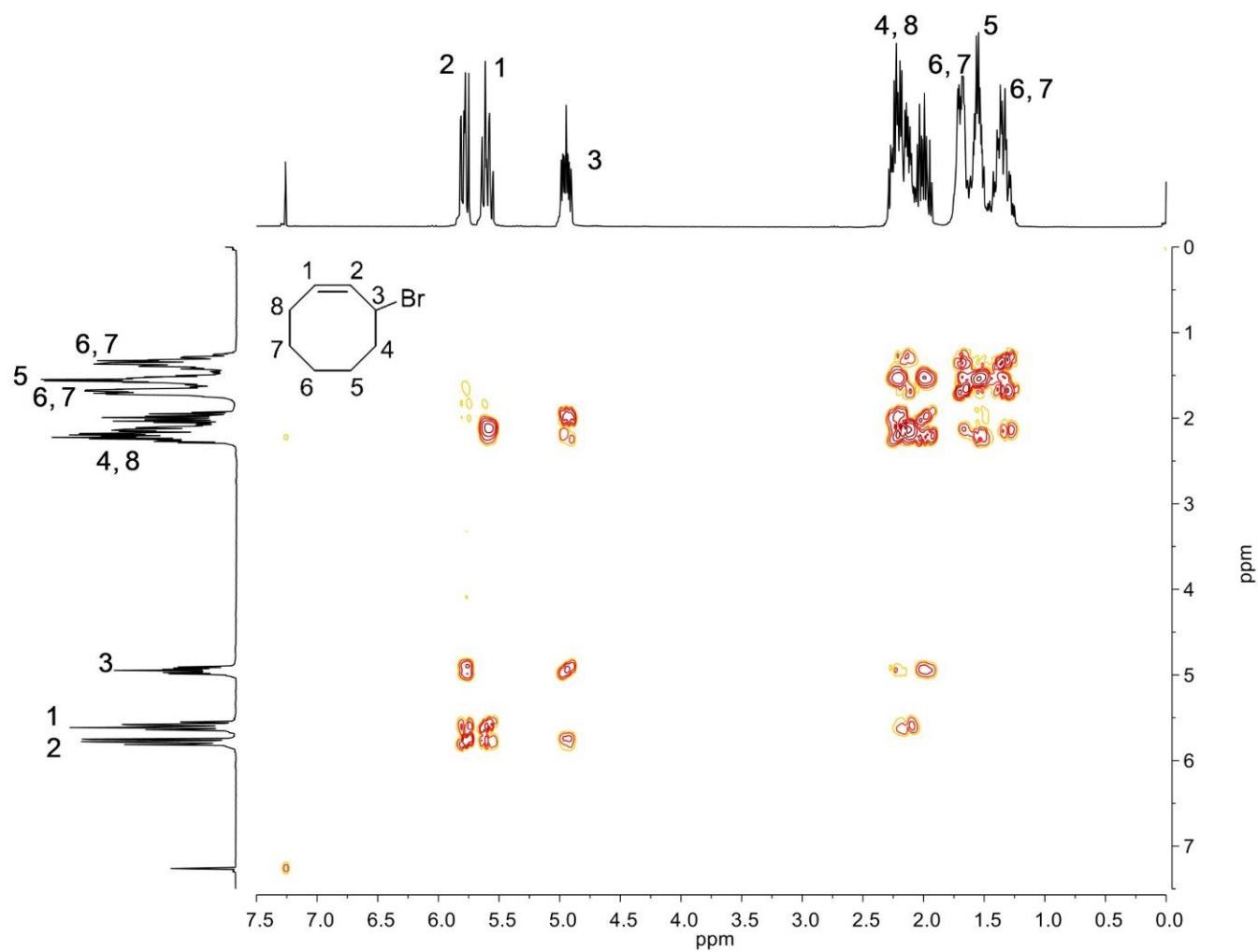


Figure S9. ^1H - ^1H COSY spectrum of 3-bromo-1-cyclooctene (in CDCl_3 , 300 MHz).

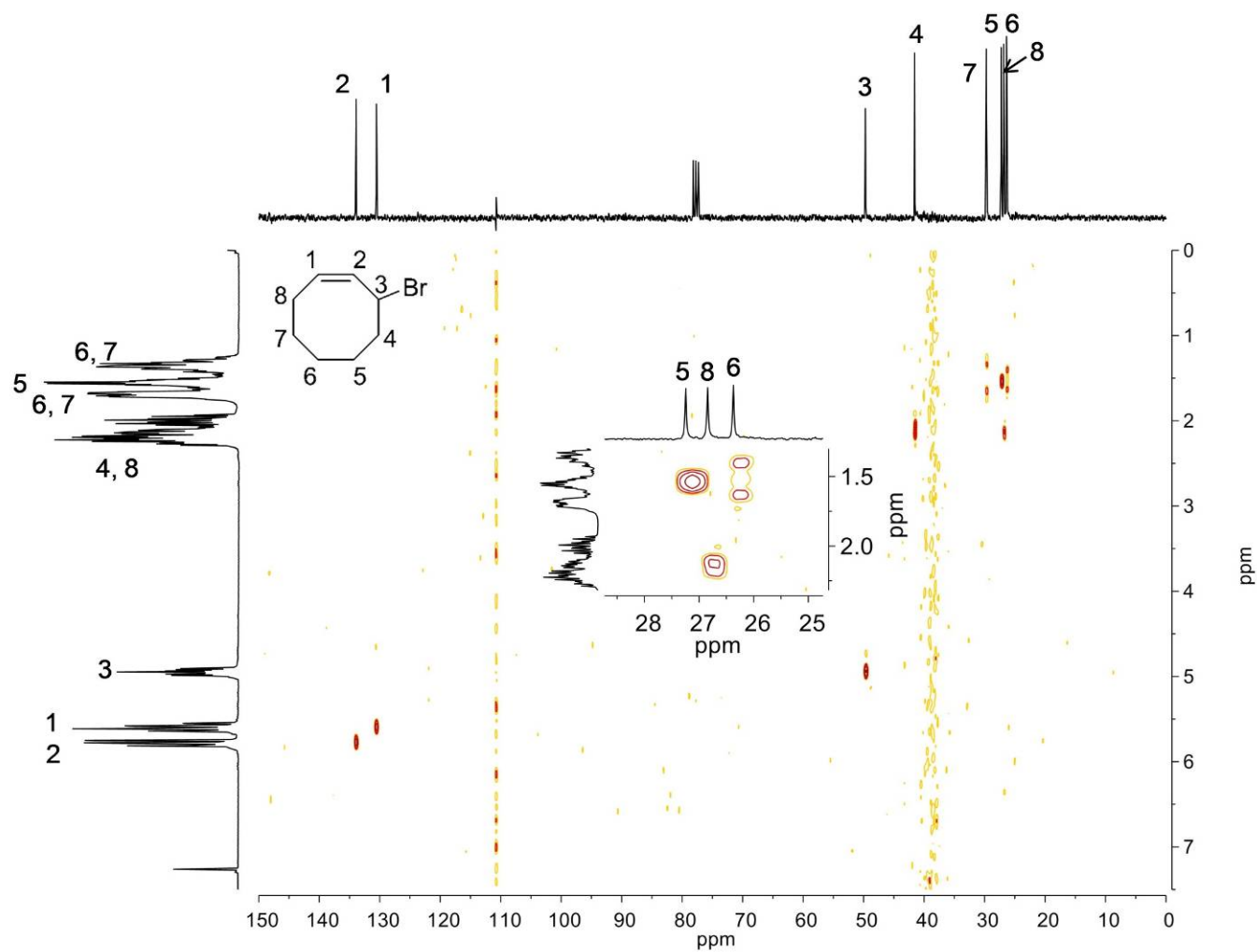


Figure S10. HETCOSY spectrum of 3-bromo-1-cyclooctene (in CDCl_3 , 75 MHz).

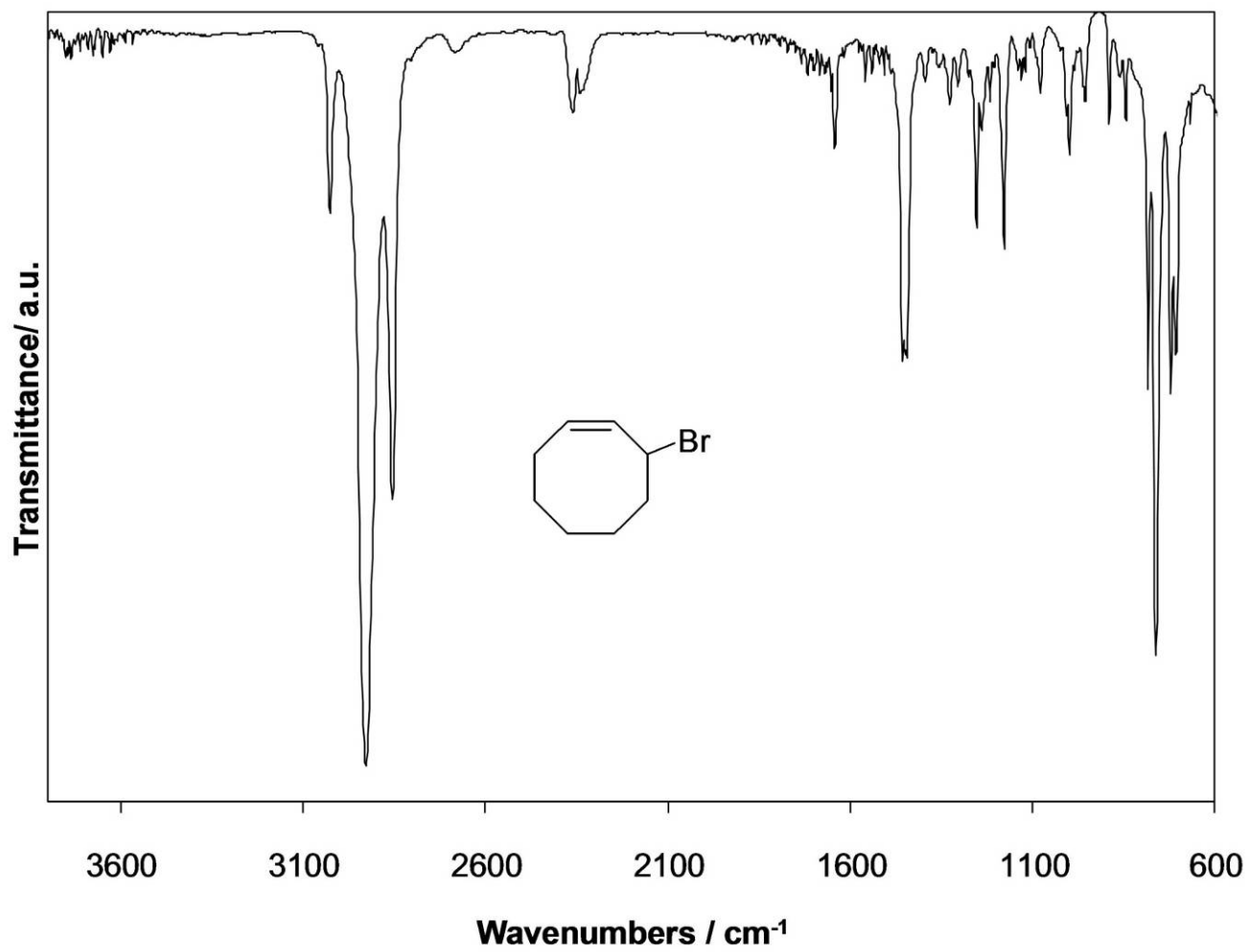
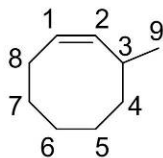


Figure S11. IR spectrum of 3-bromo-1-cyclooctene (neat).

Preparation of 3-Methyl-1-cyclooctene. (3MeCOE) (Figure S12-Figure S17)



Methylmagnesium iodide was prepared by the reaction of methyl iodide (14.2 g, 100 mmol) and magnesium (3.6 g, ca. 150 mmol) in dry diethyl ether (80 mL). To the solution of 3-bromo-1-cyclooctene (9.5 g, 50 mmol) and CuI (100 mg, 0.53 mmol) in dry THF (100 mL), the prepared methylmagnesium iodide in ether solution was added dropwise at 0 °C over 15 minute under argon flow. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was carefully quenched by pouring to ice water and then neutralized with 2N HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was dried over anhydrous MgSO₄. After concentration of the solution, the resulting crude product was purified by fractional vacuum distillation from CaH₂ afforded 3-methyl-1-cyclooctene (3.9 g, 31 mmol, 62% yield, bp = 66–68 °C at 40–50 Torr) as a colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.56 (dddd, J = 10.5, 8.7, 7.2, 1.4 Hz, 1H, =C(1)H–), 5.24 (ddd, J = 10.5, 8.4, 1.5 Hz, 1H, =C(2)H–), 2.56 (m, 1H, =CH–C(3)HMe–), 2.42–2.11 (m, 1H, –C(8)HH–), 2.01 (m, 1H, –C(8)HH–), 1.70–1.53 (m, 3H, 7H, –C(4)HH–, –C(5)HH–, –C(7)HH–), 1.53–1.45 (m, 2H, –C(6)H₂–), 1.44–1.25 (m, 2H, –C(5)HH–, –C(7)HH–) 1.15 – 1.05 (m, 1H, –C(4)HH–), 1.08 – 0.92 (d, J = 6.6 Hz, 3H, –C(9)H₃).

¹³C NMR (125 MHz, CDCl₃): δ = 136.87 (C2), 128.38 (C1), 38.68 (C4), 30.63 (C3), 29.69 (C7), 26.77 (C5), 26.60 (C8), 26.19 (C6), 22.25 (C9).

IR (neat): 3008, 2926, 2851, 2684, 1708, 1670 1649, 1456, 1373, 1337, 1265, 1191, 1154, 1072, 1047, 988, 973, 938, 920, 877, 832, 748, 710, 595 cm^{–1}.

HRMS(EI): m/z calcd for C₉H₁₆ [M⁺]: 124.1252, found: 124.1259.

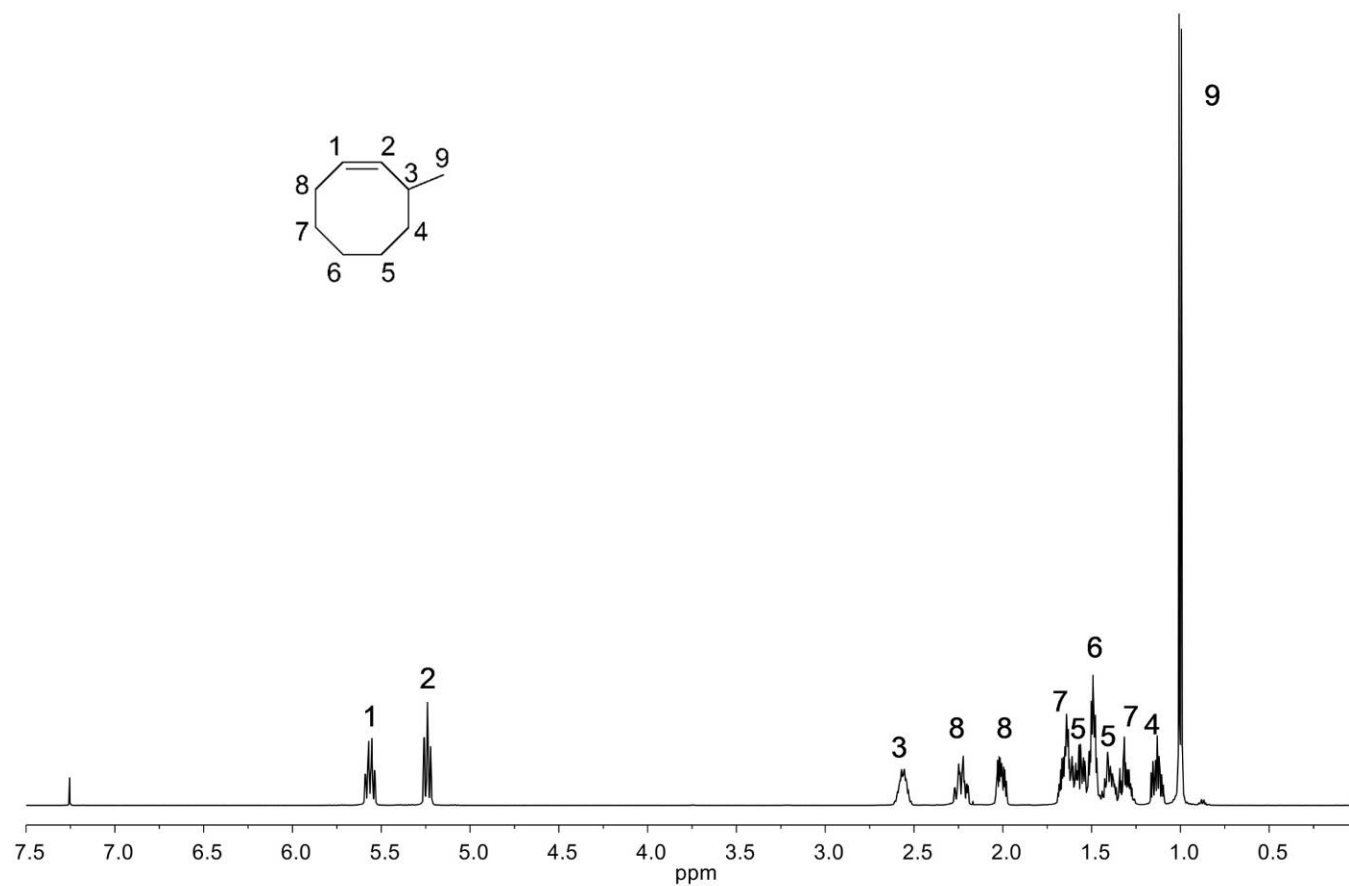


Figure S12. ^1H NMR spectrum of 3-methyl-1-cyclooctene (in CDCl_3 , 500 MHz).

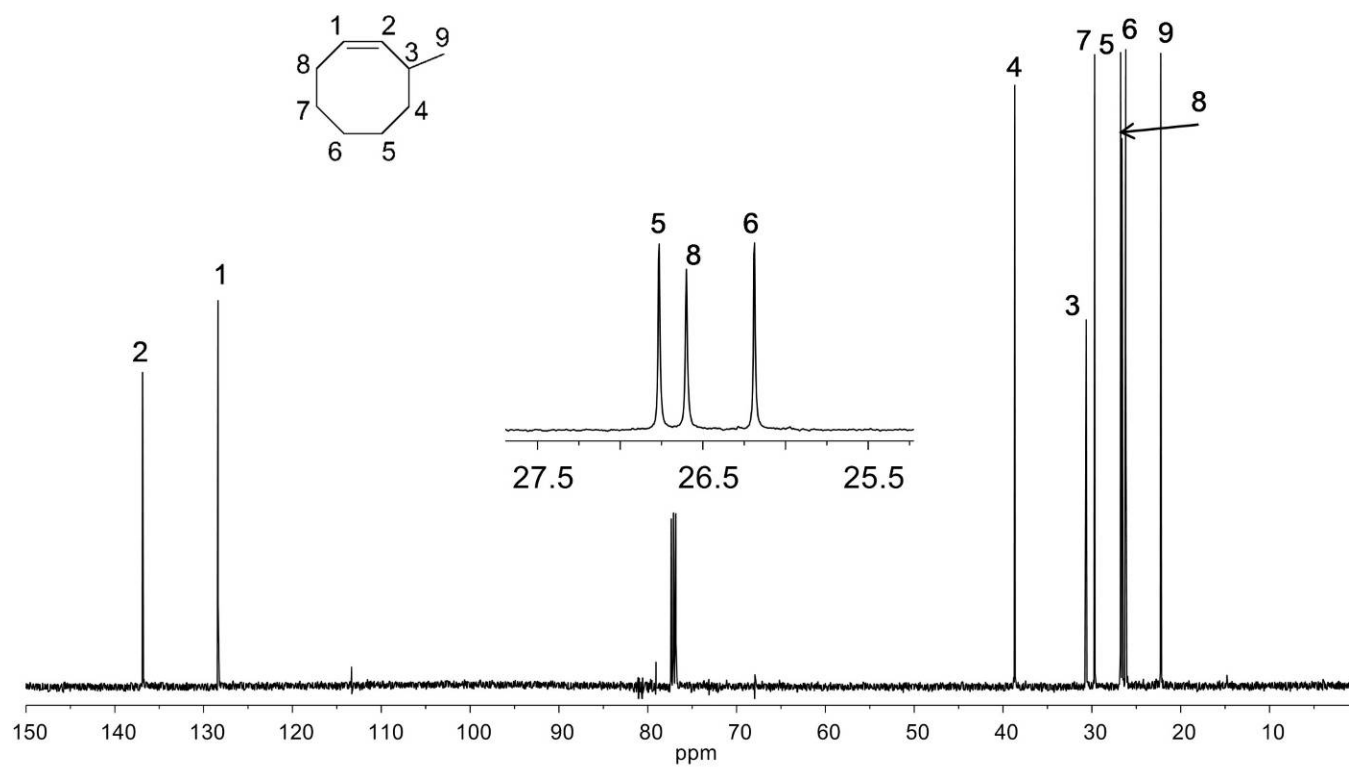


Figure S13. ^{13}C NMR spectrum of 3-methyl-1-cyclooctene (in CDCl_3 , 125 MHz).

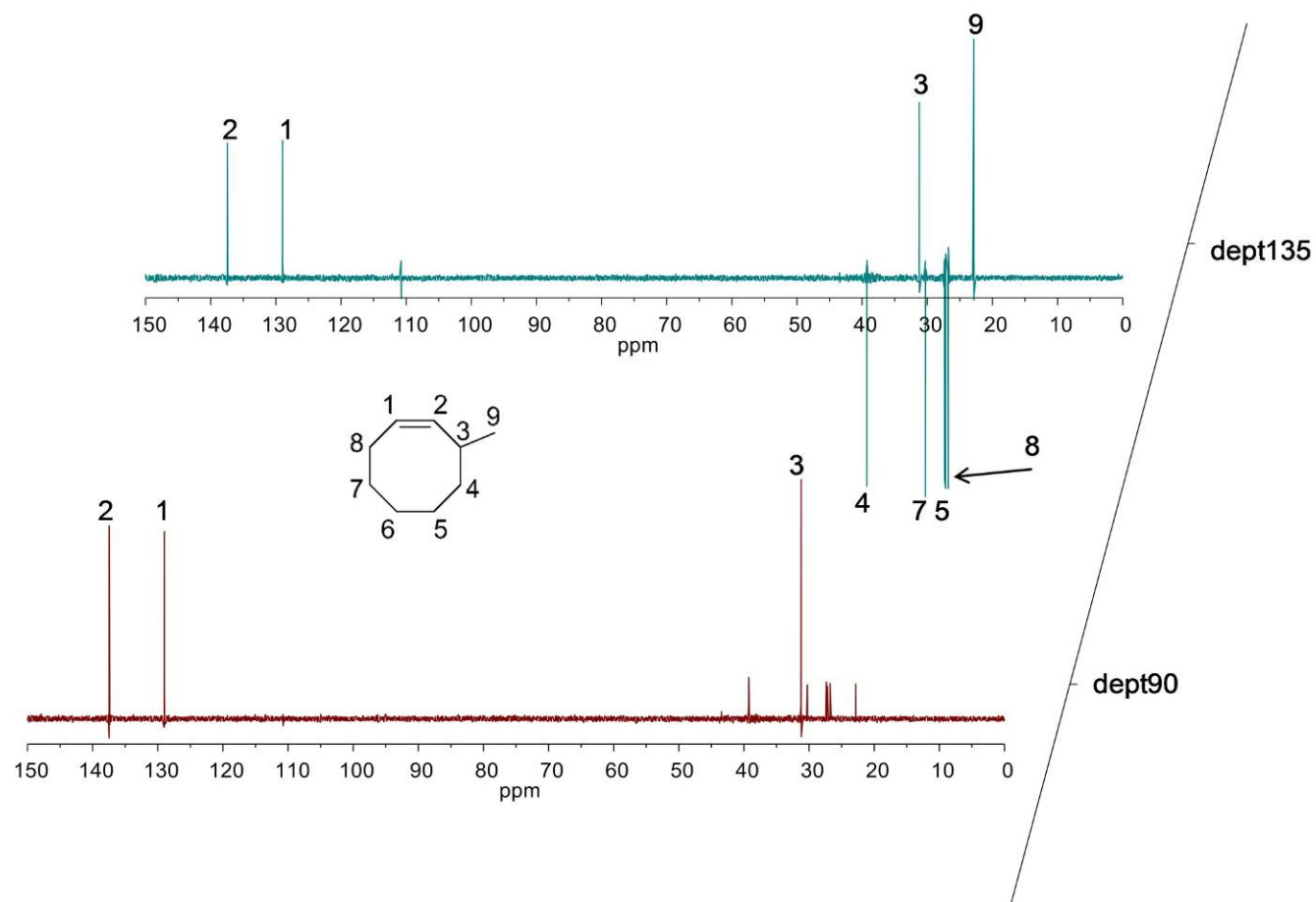


Figure S14. DEPT spectrum of 3-methyl-1-cyclooctene (in CDCl₃, 75 MHz).

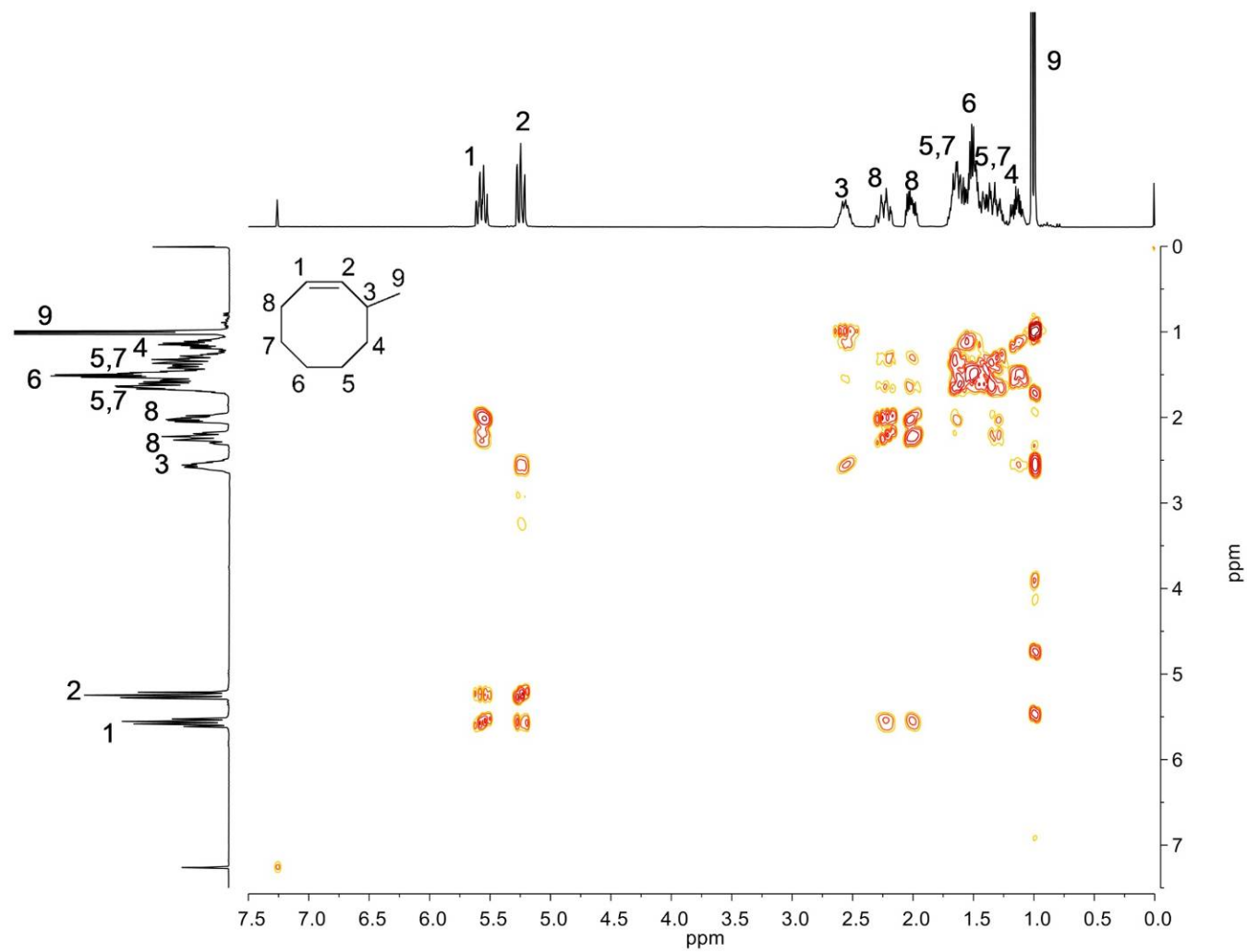


Figure S15. ^1H - ^1H COSY spectrum of 3-methyl-1-cyclooctene (in CDCl_3 , 300 MHz).

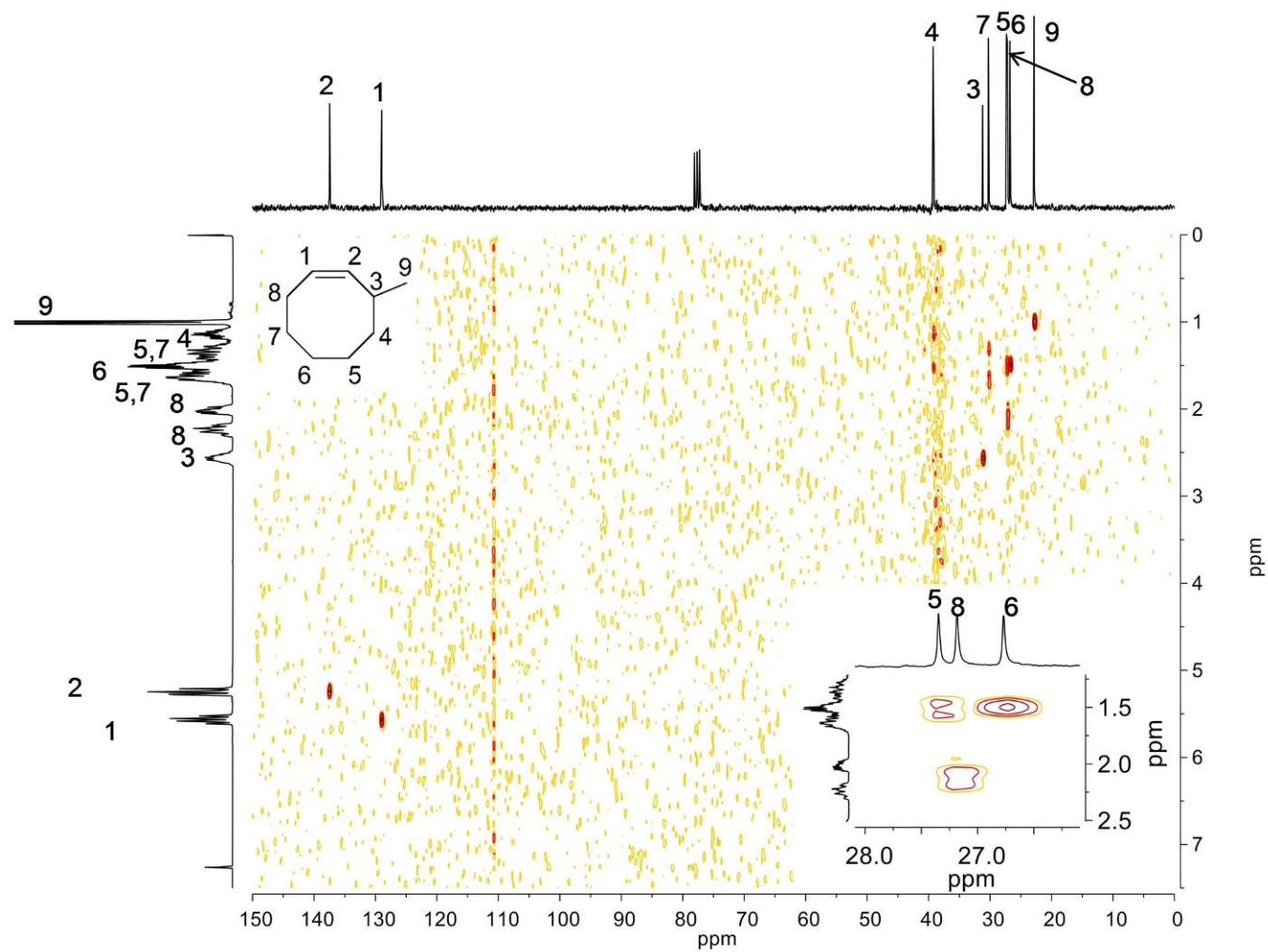


Figure S16. HETCOSY spectrum of 3-methyl-1-cyclooctene (in CDCl_3 , 75 MHz).

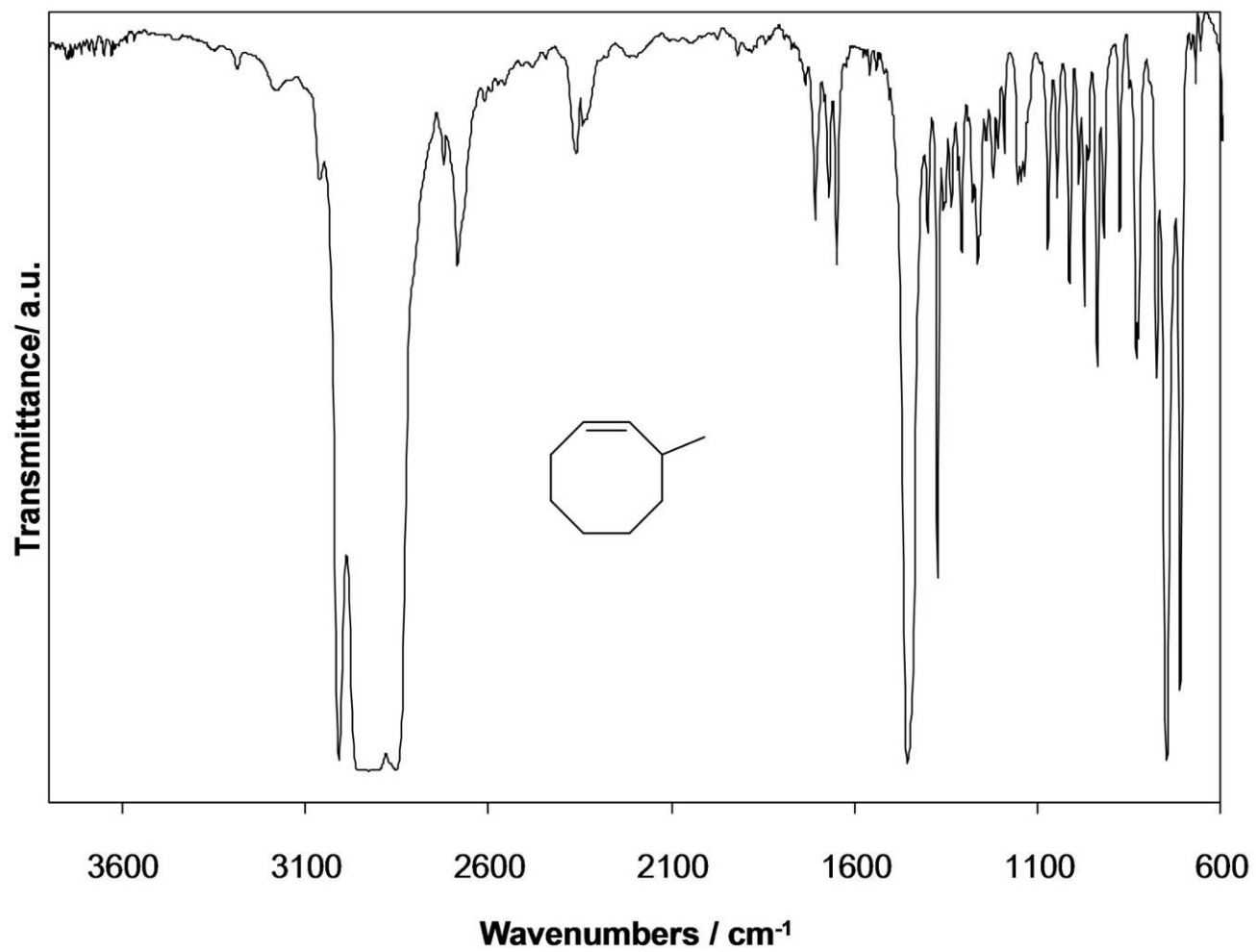
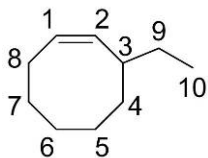


Figure S17. IR spectrum of 3-methyl-1-cyclooctene (neat).

Preparation of 3-Ethyl-1-cyclooctene. (3EtCOE) (Figure S18-Figure S23)



Synthesized as above. Ethyl iodide (15.7 g, 100 mmol) was used to prepare Ethylmagnesium iodide. After purification, 3-ethyl-1-cyclooctene (4.5 g, 34 mmol, 67% yield, bp = 53–54 °C at 6–8 Torr) was obtained as a colorless liquid.

^1H NMR (500 MHz, CDCl_3): δ = 5.64 (dddd, J = 10.4, 8.7, 7.2, 1.4 Hz, 1H, =C(1) H –), 5.21 (ddd, J = 10.4, 8.6, 1.6 Hz, 1H, =C(2) H –), 2.33 (m, 1H, =CH–C(3) HEt –), 2.28–2.17 (m, 1H, =CH–C(8) HH –), 2.11–1.92 (m, 1H, =CH–C(8) HH –), 1.73 – 1.56 (m, 3H, –C(4) HH –, –C(5) HH –, –C(7) HH –), 1.56 – 1.45 (m, 2H, –C(6) H_2 –), 1.45 – 1.22 (m, 4H, –C(5) HH –, –C(7) HH –, –C(9) HH –), 1.15 – 1.03 (m, 1H, –C(4) HH –), 0.88 (t, J = 7.4 Hz, 3H, –C(10) H_3).

^{13}C NMR (125 MHz, CDCl_3): δ = 135.74 (C2), 129.40 (C1), 37.90 (C3), 36.43 (C4), 29.71 (C7), 29.63 (C9), 27.01 (C5), 26.79 (C8), 26.02 (C6), 12.41 (C10).

IR (neat): 3006, 2959, 2924, 2853, 2680, 1650, 1455, 1378, 1358, 1261, 1133, 997, 954, 916, 861, 841, 777, 754, 712 cm^{-1} .

HRMS(EI): m/z calcd for $\text{C}_{10}\text{H}_{18}$ [M^+]: 138.1409, found: 138.1410.

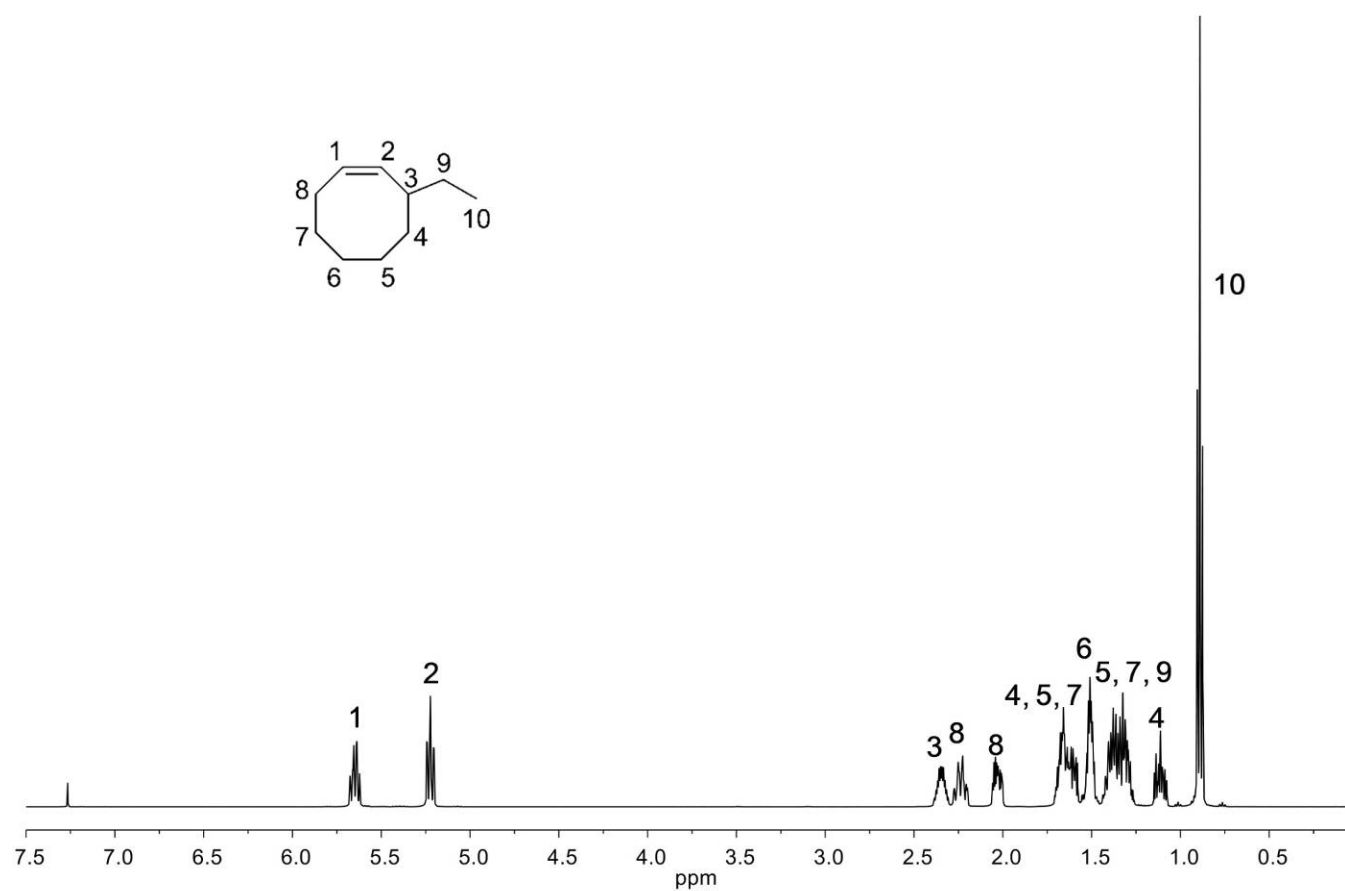


Figure S18. ^1H NMR spectrum of 3-ethyl-1-cyclooctene (in CDCl_3 , 500 MHz).

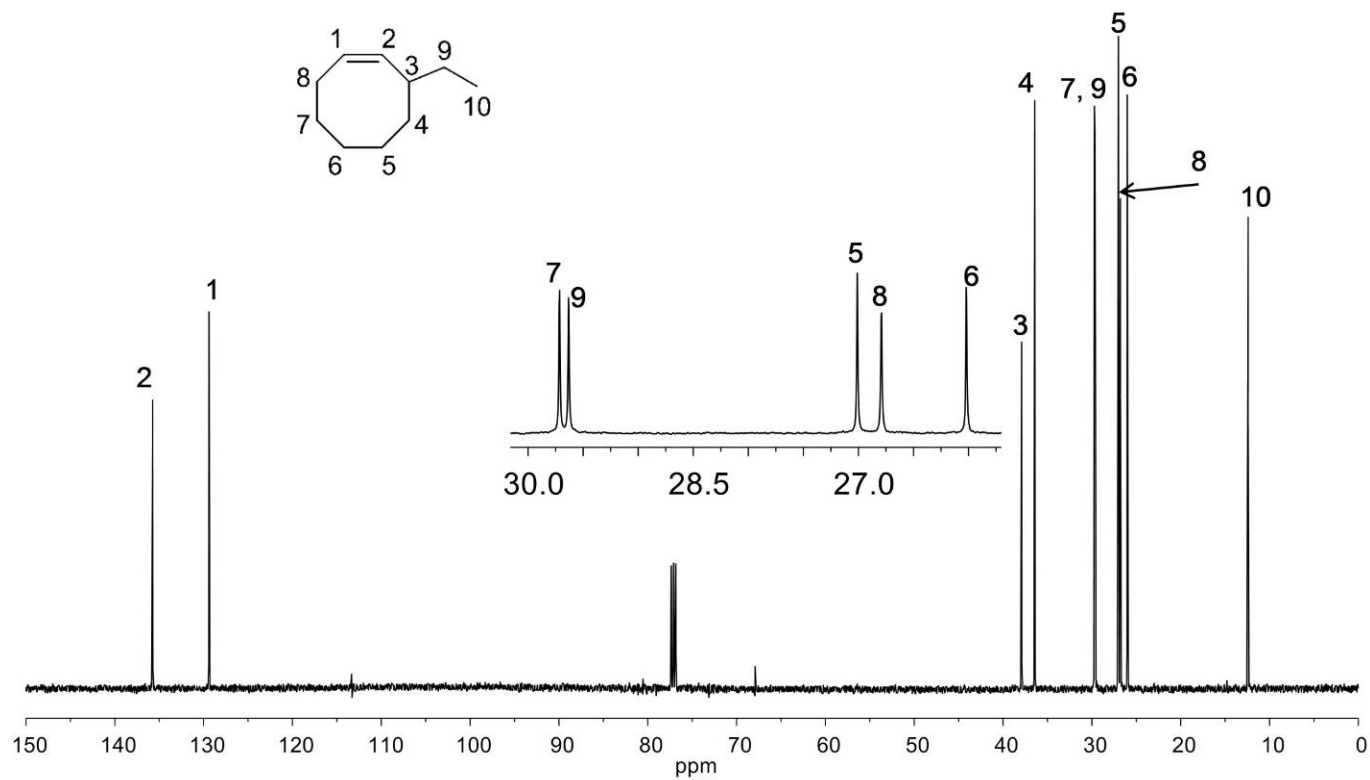


Figure S19. ^{13}C NMR spectrum of 3-ethyl-1-cyclooctene (in CDCl_3 , 125 MHz).

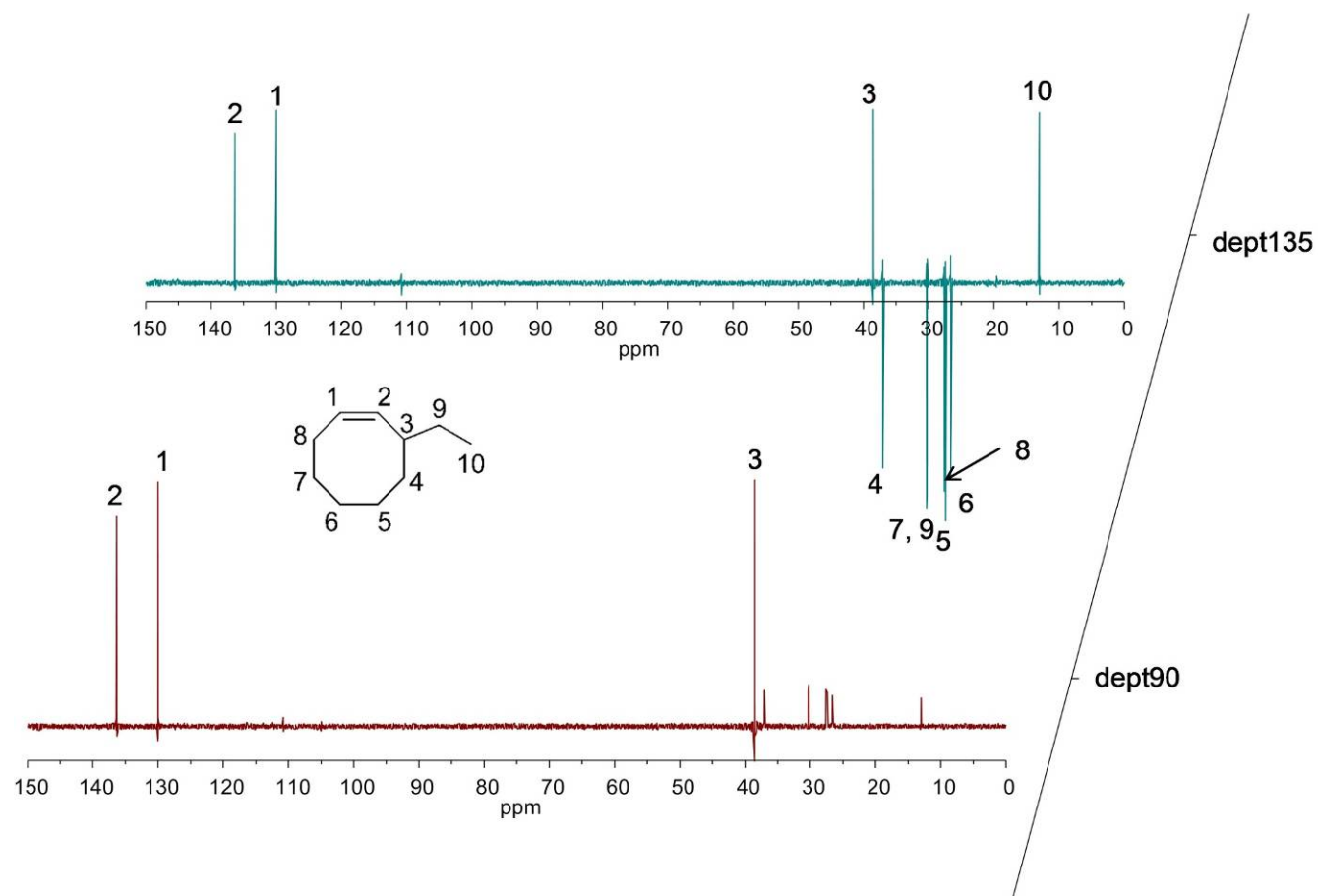


Figure S20. DEPT spectrum of 3-ethyl-1-cyclooctene (in CDCl₃, 75 MHz).

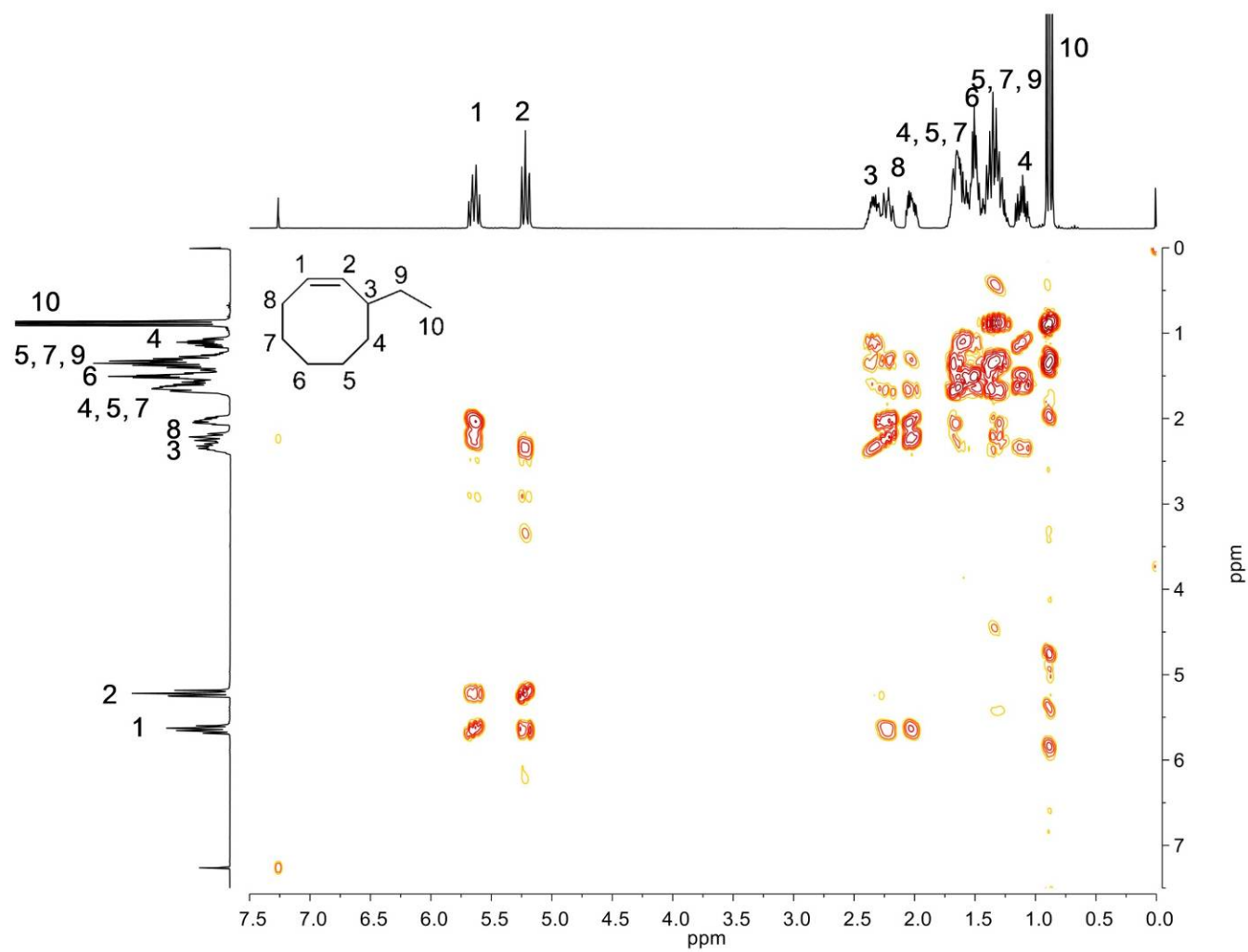


Figure S21. ^1H - ^1H COSY spectrum of 3-ethyl-1-cyclooctene (in CDCl_3 , 300 MHz).

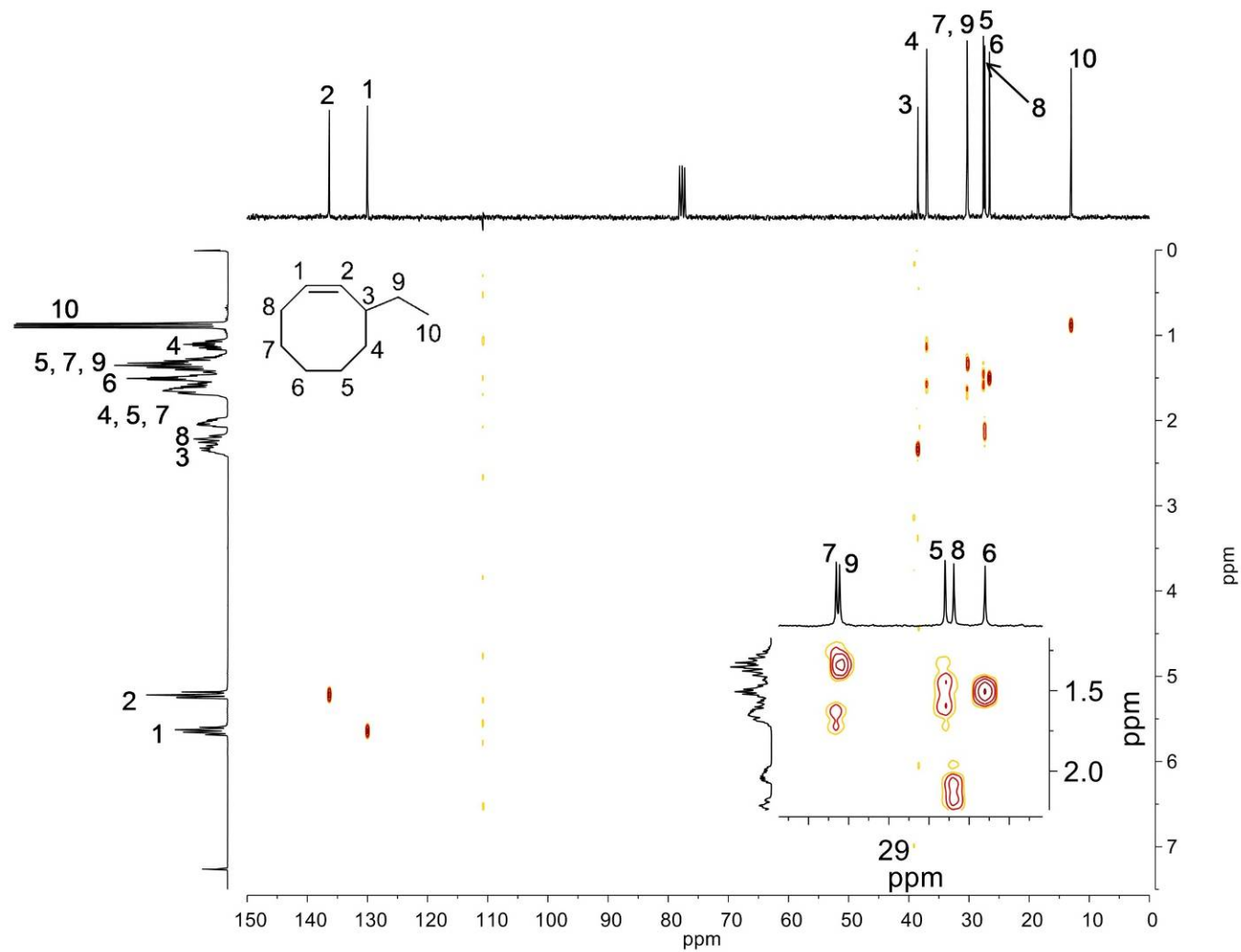


Figure S22. HETCOSY spectrum of 3-ethyl-1-cyclooctene (in CDCl_3 , 75 MHz).

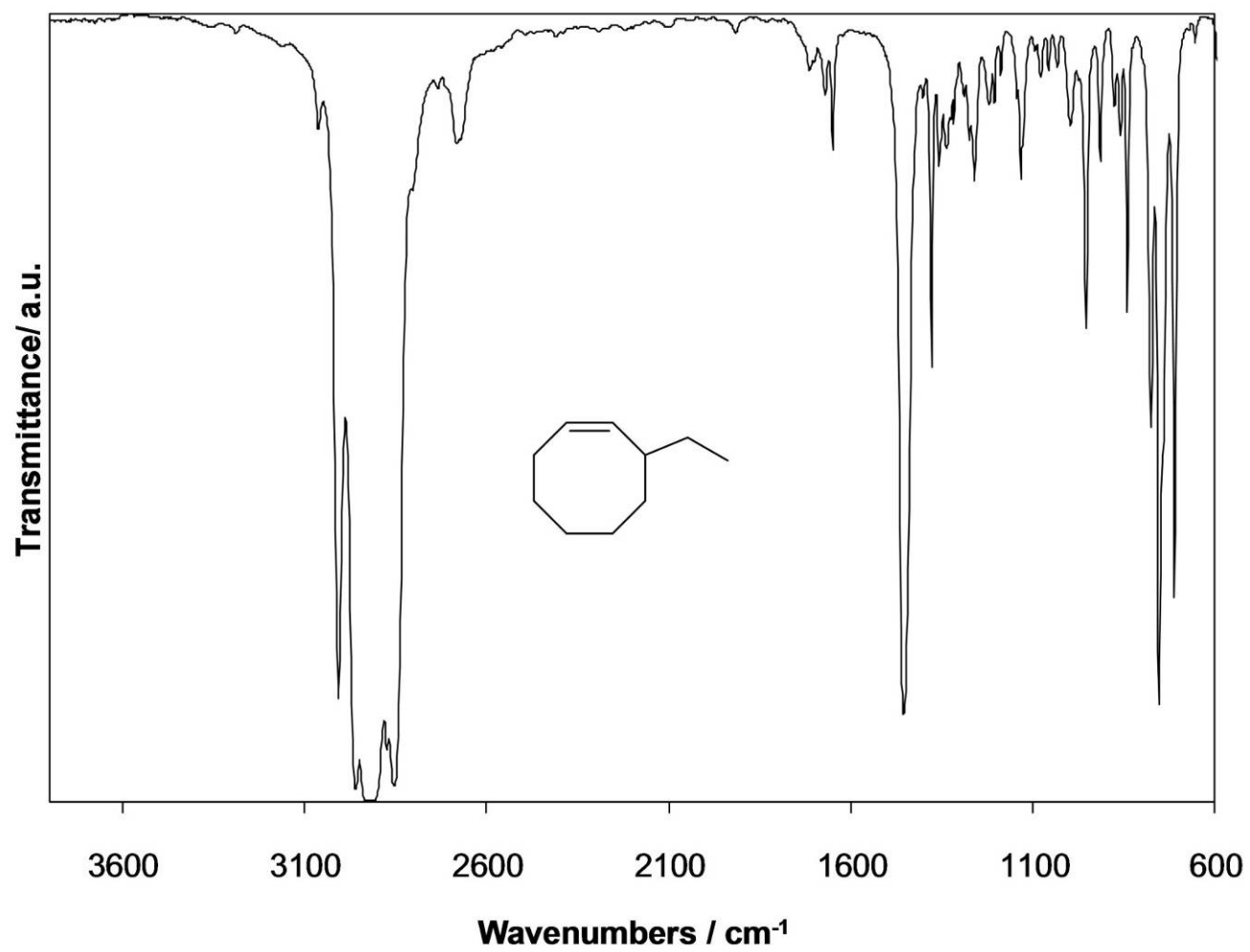
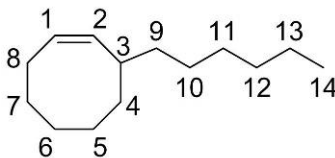


Figure S23. IR spectrum of 3-ethyl-1-cyclooctene (neat).

Preparation of 3-Hexyl-1-cyclooctene. (3HexCOE) (Figure S24-Figure S29)



Synthesized as above. 1-Bromohexane (16.4 g, 100 mmol) was used to prepare *n*-Hexylmagnesium bromide. After purification, 3-hexyl-1-cyclooctene (6.3 g, 33 mmol, 66% yield, bp = 53–57 °C at 53–55 mTorr) was obtained as a colorless liquid.

^1H NMR (500 MHz, CDCl_3): δ = 5.62 (dddd, J = 10.5, 8.7, 7.2, 1.5 Hz, 1H, =C(1)*H*–), 5.20 (ddd, J = 10.5, 8.7, 1.6 Hz, 1H, =C(2)*H*–), 2.42 (m, 1H, =CH–C(3)*HH*Hex–), 2.21 (m, 1H, =CH–C(8)*HH*–), 2.02 (m, 1H, =CH–C(8)*HH*–), 1.73 – 1.54 (m, 3H, –C(4)*HH*–, –C(5)*HH*–, –C(7)*HH*–), 1.54 – 1.43 (m, 2H, –C(6)*H*₂–), 1.45 – 1.18 (m, 12H, –C(5)*HH*–, –C(7)*HH*–, –CH₂–), 1.10 (m, 1H, –C(4)*HH*–), 0.88 (t, J = 6.8 Hz, 3H, –C(14)*H*₃).

^{13}C NMR (125 MHz, CDCl_3): δ = 135.97 (C2), 129.21 (C1), 36.94 (C9), 36.74 (C4), 35.98 (C3), 32.01 (C12), 29.77 (C7), 29.63 (C11), 27.95 (C10), 27.06 (C5), 26.85 (C8), 26.00 (C6), 22.77 (C13), 14.21 (C14).

IR (neat): 3006, 2956, 2924, 2853, 2681, 1650, 1455, 1378, 1358, 1261, 1134, 960, 836, 776, 756, 712 cm^{-1} .

HRMS(EI): m/z calcd for $\text{C}_{14}\text{H}_{26}$ [M^+]: 194.2035, found [$\text{M}+\text{H}$] $^+$: 194.2050.

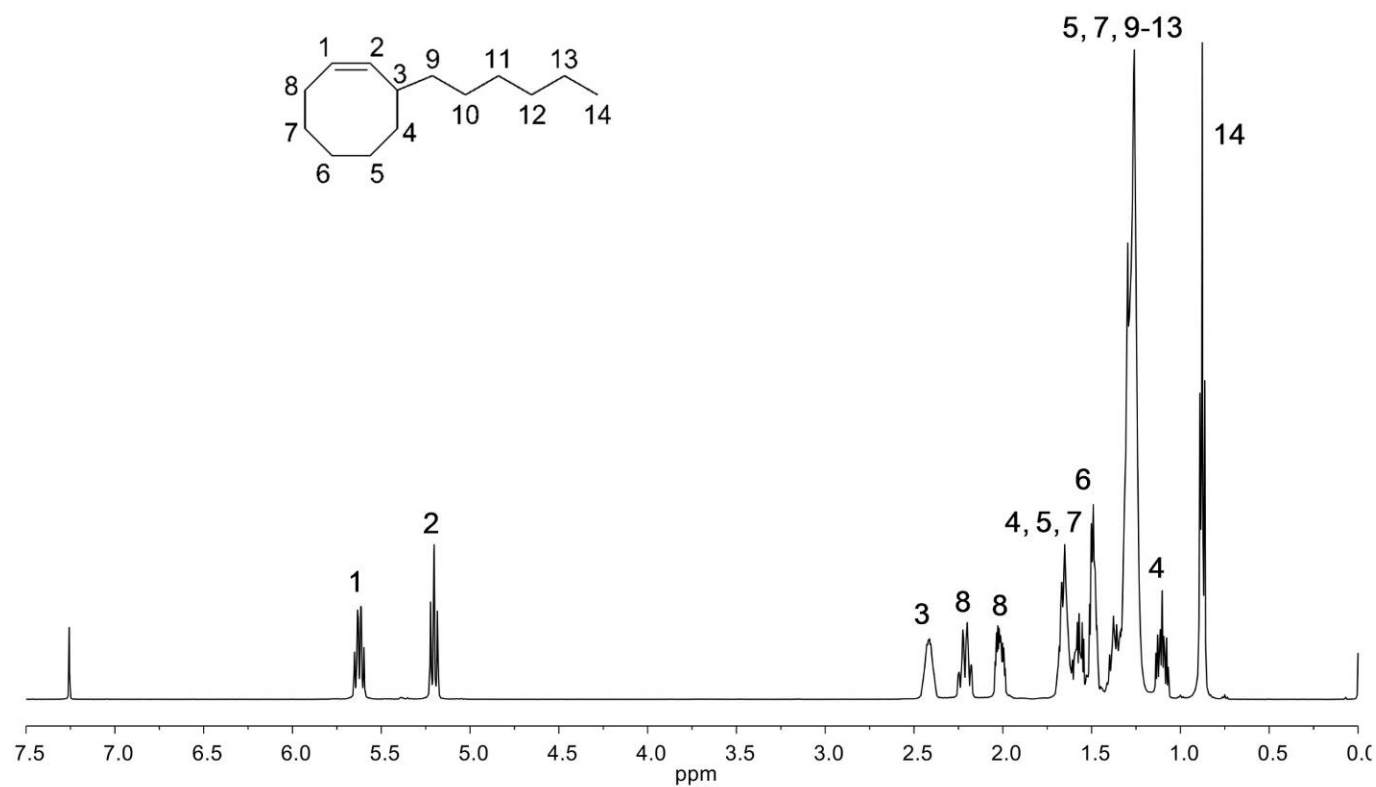


Figure S24. ^1H NMR spectrum of 3-hexyl-1-cyclooctene (in CDCl_3 , 500 MHz).

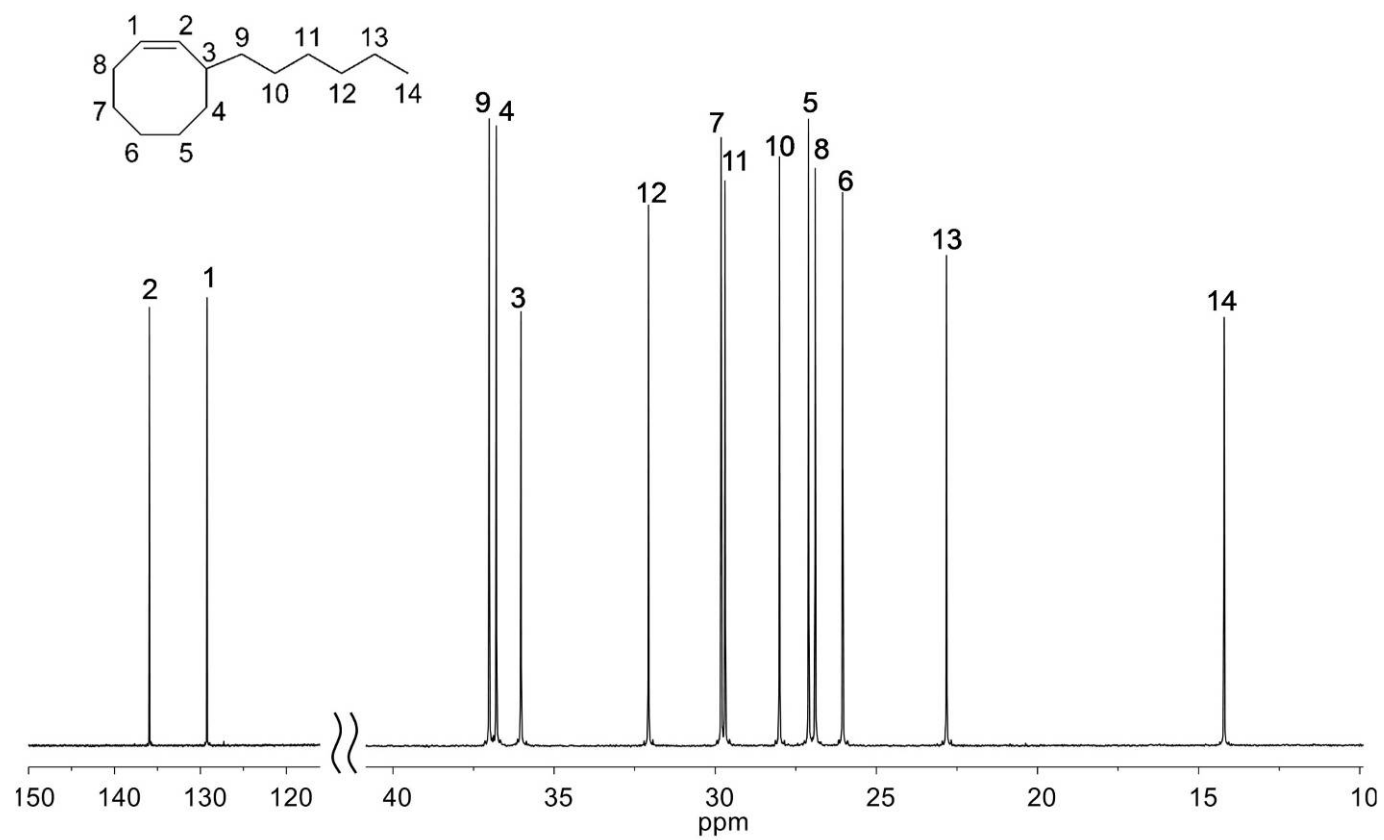


Figure S25. ^{13}C NMR spectrum of 3-hexyl-1-cyclooctene (expanded spectrum, in CDCl_3 , 125 MHz).

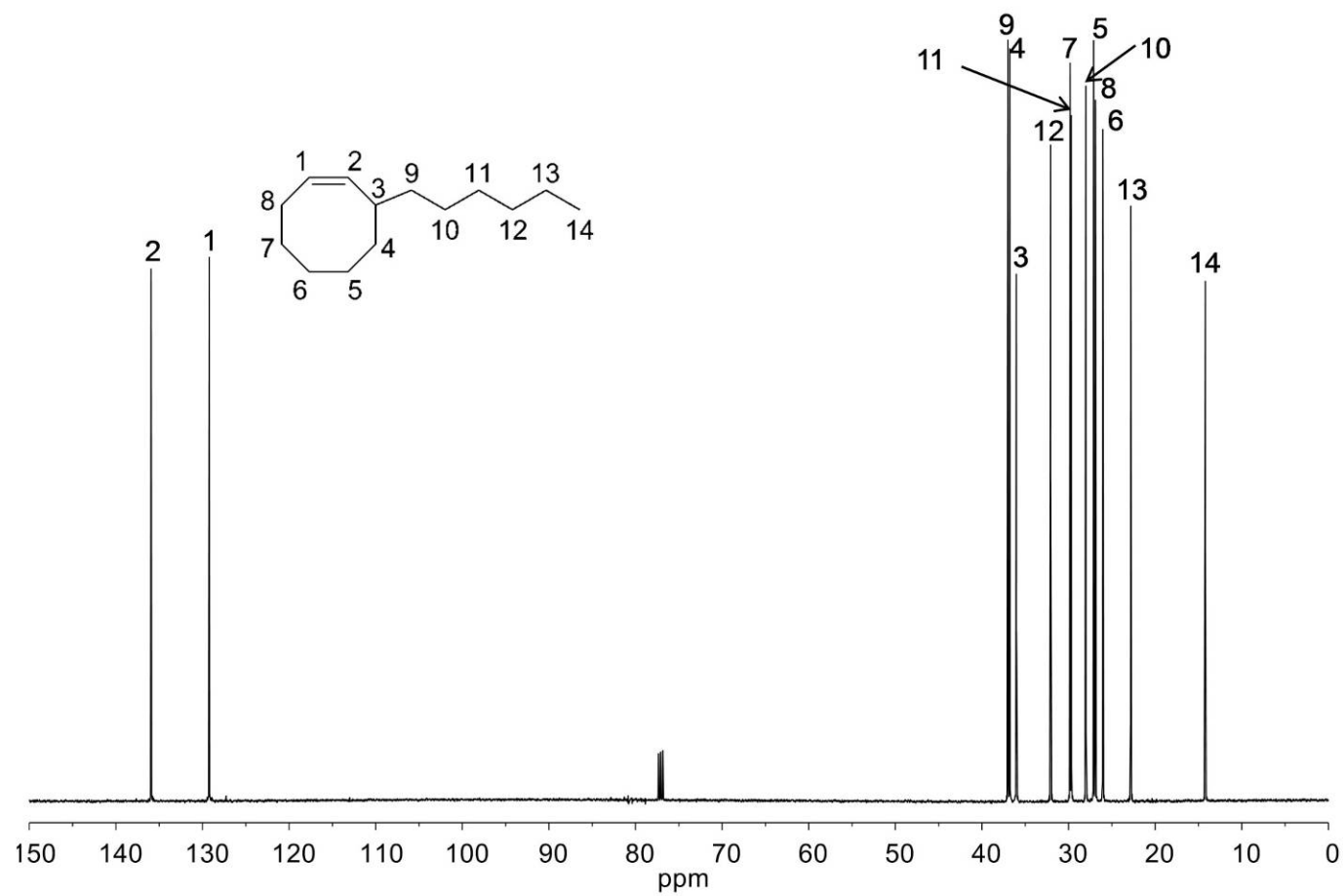


Figure S25a. ^{13}C NMR spectrum of 3-hexyl-1-cyclooctene (full spectrum, in CDCl_3 , 125 MHz).

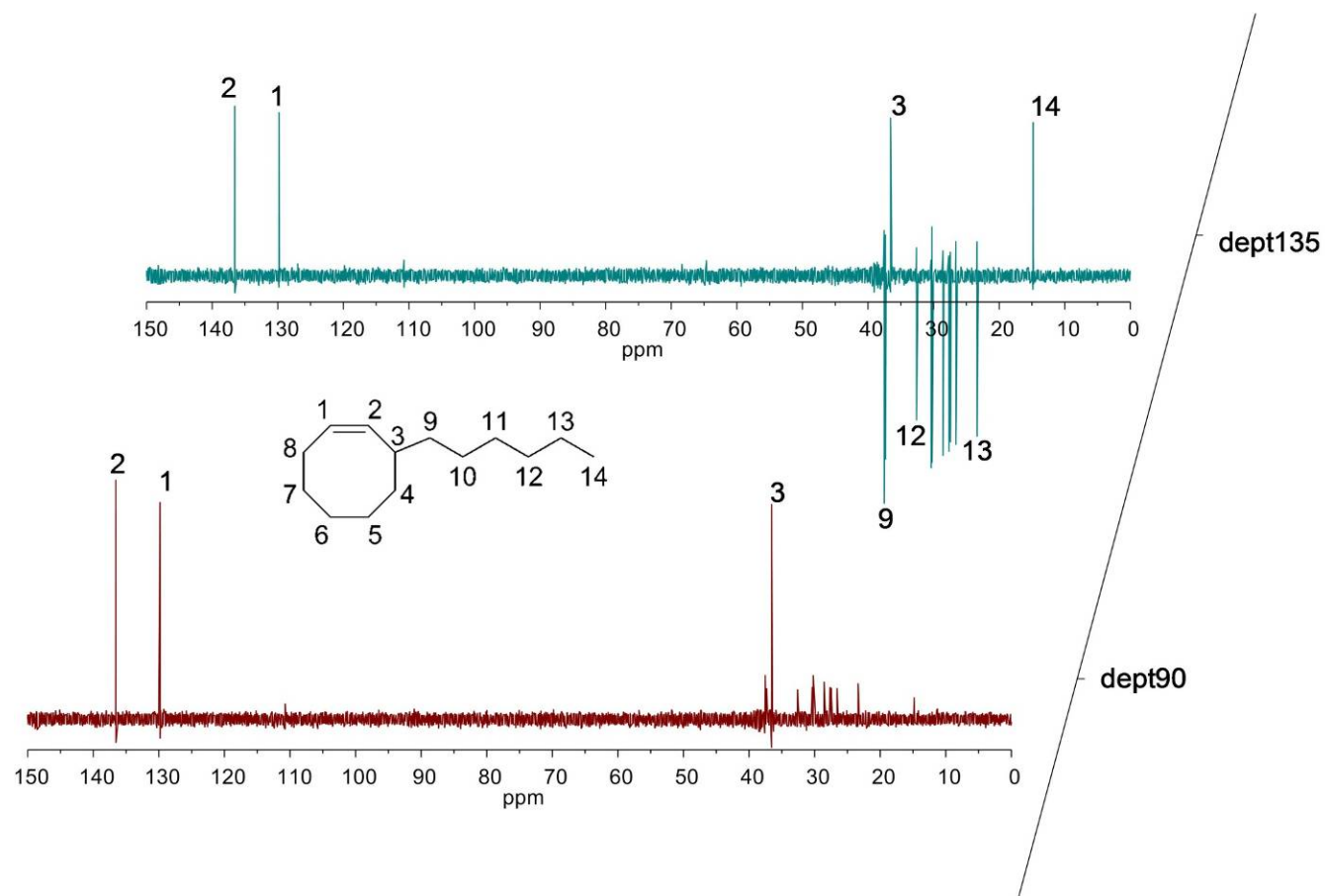


Figure S26. DEPT spectrum of 3-hexyl-1-cyclooctene (in CDCl₃, 75 MHz).

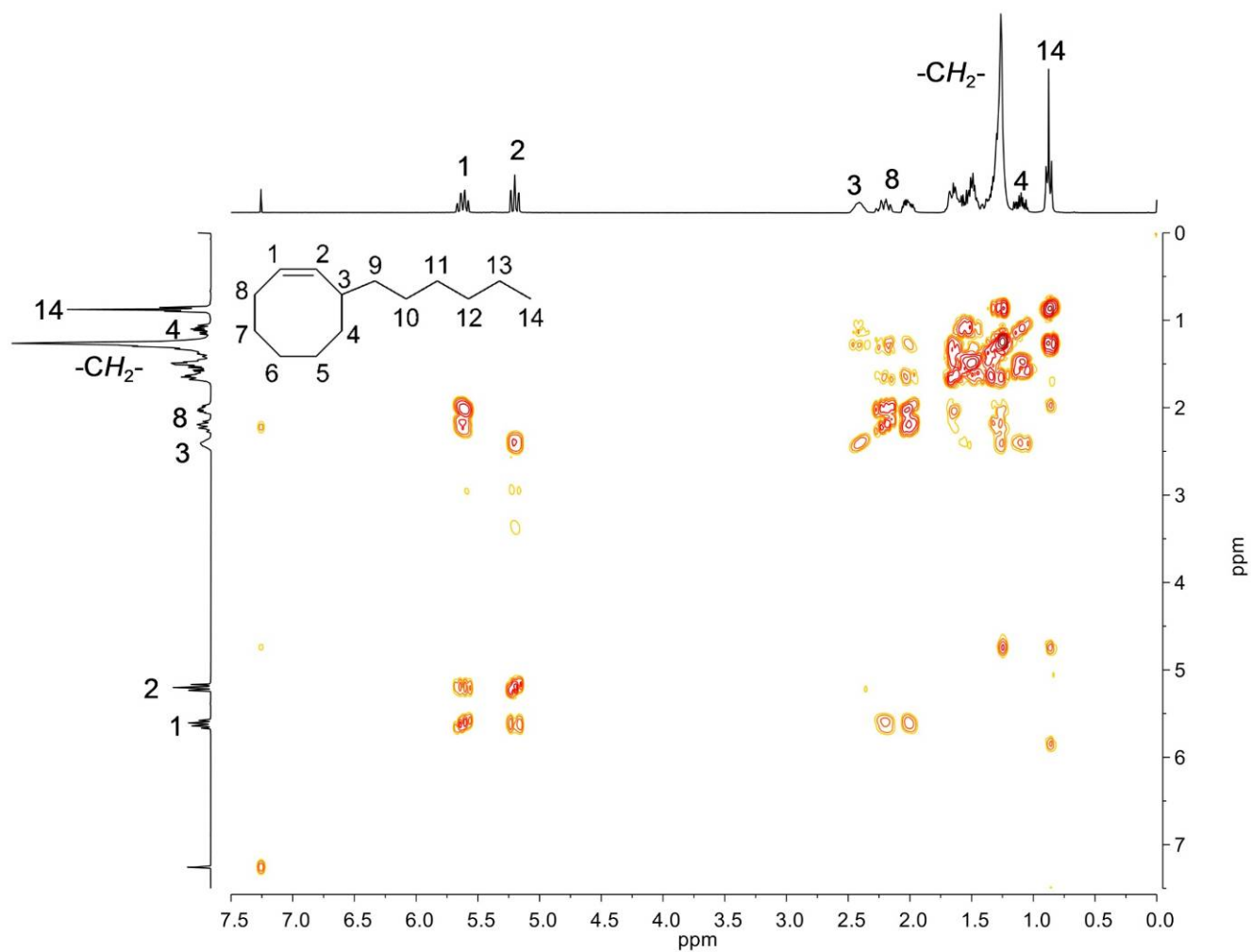


Figure S27. ^1H - ^1H COSY spectrum of 3-hexyl-1-cyclooctene (in CDCl_3 , 300 MHz).

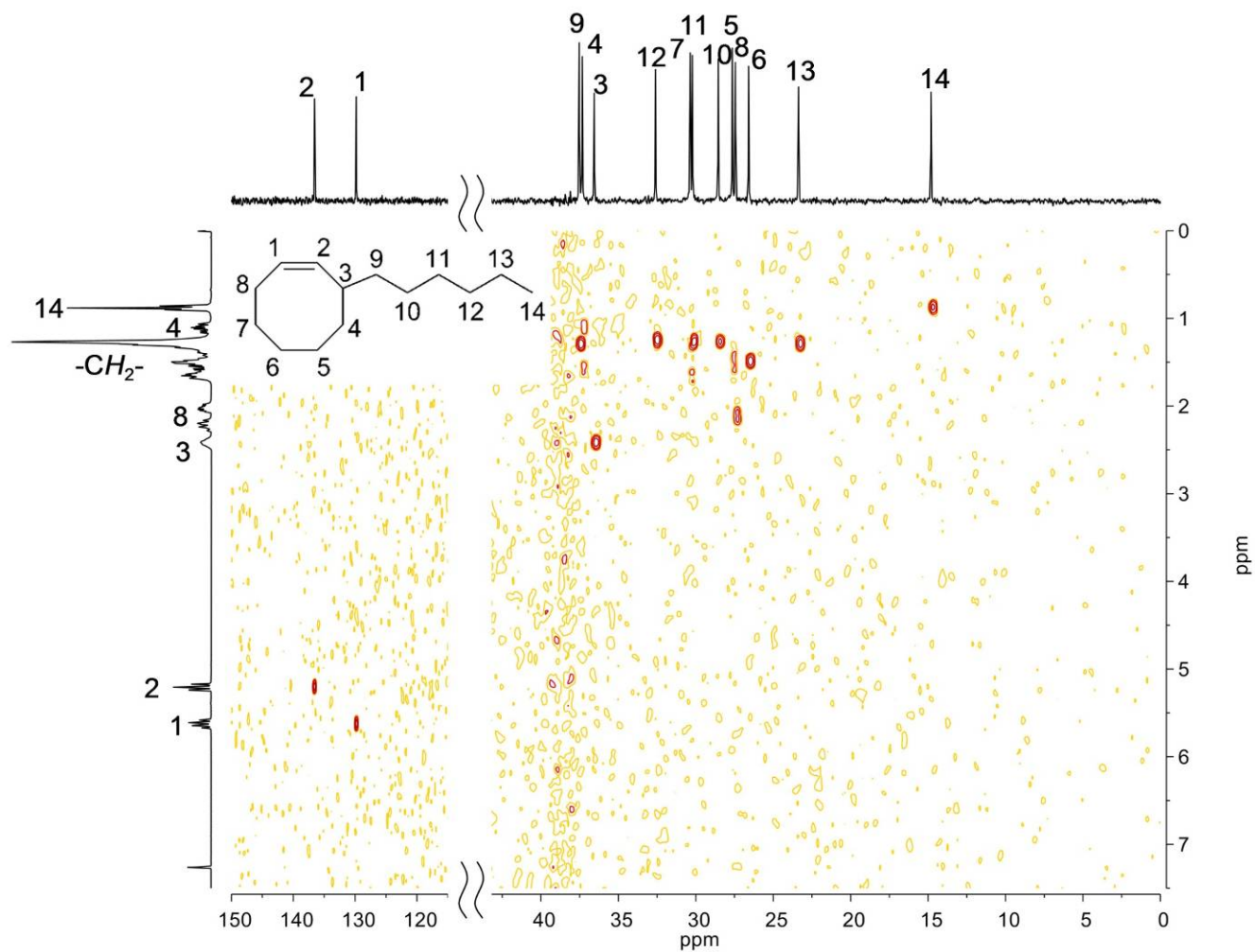


Figure S28. HETCOSY spectrum of 3-hexyl-1-cyclooctene (in CDCl₃, 75 MHz).

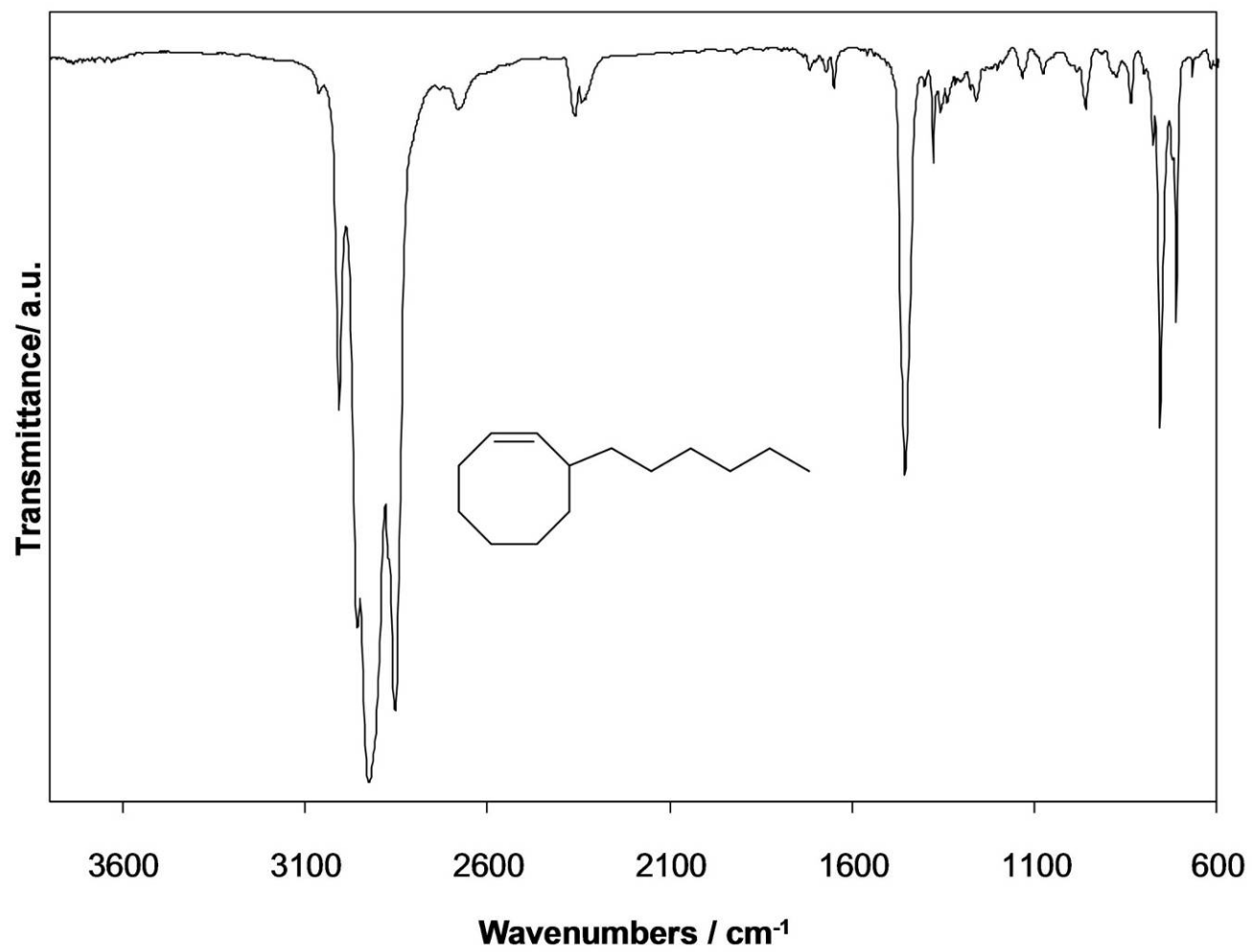
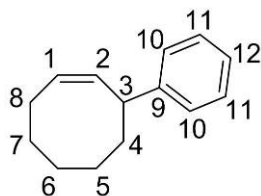


Figure S29. IR spectrum of 3-hexyl-1-cyclooctene (neat).

Preparation of 3-Phenyl-1-cyclooctene. (3PhCOE) (Figure S30-Figure S35)



Synthesized as above. Bromobenzene (15.7 g, 100 mmol) was used to prepare Phenylmagnesium bromide. After purification, 3-phenyl-1-cyclooctene (5.8 g, 32 mmol, 64% yield, bp = 69–72 °C at 65–70 mTorr) was obtained as a colorless liquid.

^1H NMR (500 MHz, CDCl_3): δ = 7.33–7.25 (m, 4H, aromatic C(10)*H*, C(11)*H*), 7.22–7.15 (m, 1H, aromatic C(12)*H*), 5.70 (dddd, J = 10.5, 8.7, 7.2, 1.3 Hz, 1H, =C(1)*H*–), 5.60 (ddd, J = 10.5, 8.8, 1.4 Hz, 1H, =C(2)*H*–), 3.83–3.64 (m, 1H, =CH–C(3)*HPh*–), 2.44–2.31 (m, 1H, =CH–C(8)*HH*–), 2.13–2.09 (m, 1H, =CH–C(8)*HH*–), 1.89–1.81 (m, 1H, –C(4)*HH*–), 1.81–1.57 (m, 5H, –C(4)*HH*–, –C(5)*H*₂–, –C(6)*H*₂–, –C(7)*HH*–), 1.56–1.45 (m, 1H, –C(5)*HH*–), 1.45–1.31 (m, 1H, –C(7)*HH*–).

^{13}C NMR (125 MHz, CDCl_3): δ = 146.62 (C9), 134.24 (C2), 129.08 (C1), 128.47 (C11), 127.35 (C10), 125.94 (C12), 42.38 (C3), 37.60 (C4), 29.73 (C7), 26.80 (C5), 26.59 (C8), 26.16 (C6).

IR (neat): 3060, 3025, 2926, 2851, 2678, 1940, 1868, 1798, 1647, 1601, 1583, 1491, 1450, 1359, 1339, 1302, 1275, 1207, 1156, 1113, 1067, 1031, 1005, 987, 962, 906, 858, 841, 775, 743, 711, 698, 640, 530 cm^{-1} .

HRMS(EI): m/z calcd for $\text{C}_{14}\text{H}_{18}$ [M^+]: 186.1409, found [$\text{M}+\text{H}$] $^+$: 186.1416.

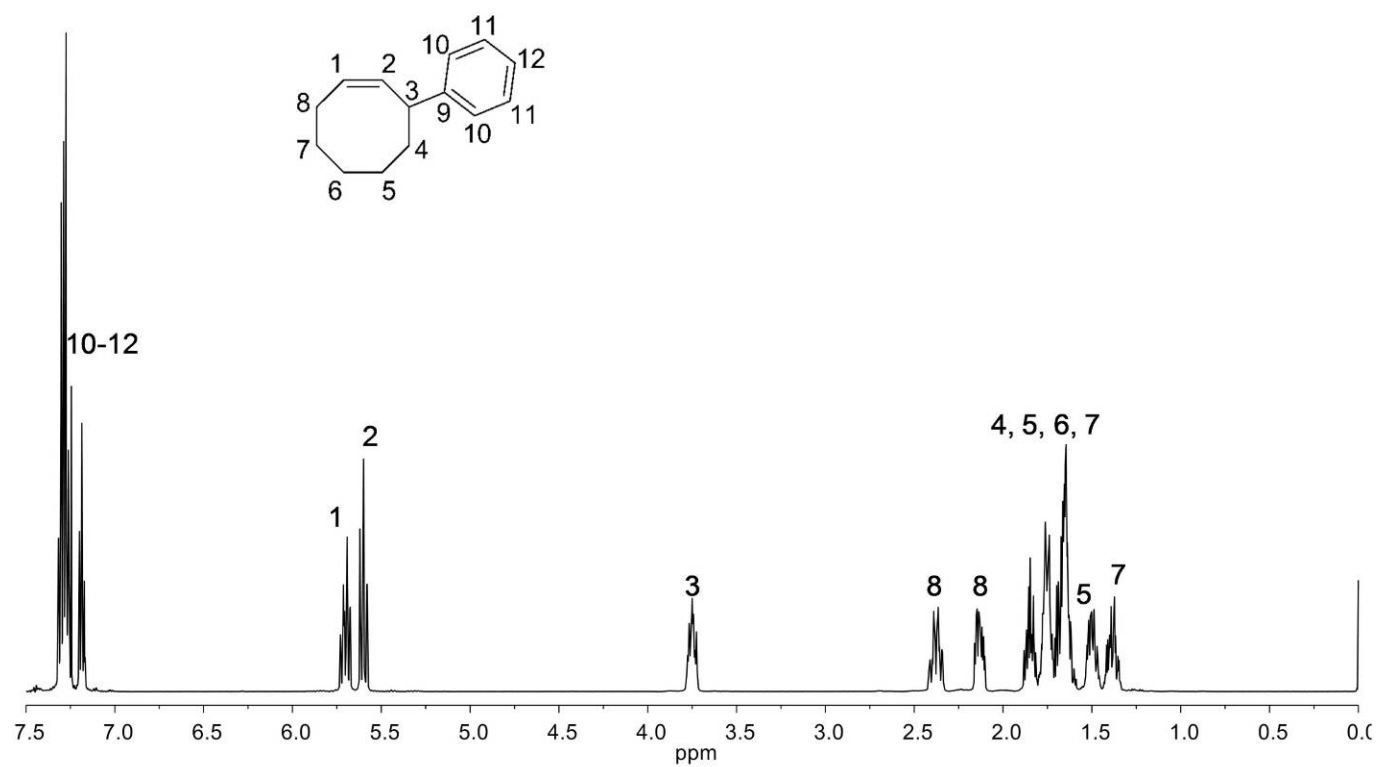


Figure S30. ^1H NMR spectrum of 3-phenyl-1-cyclooctene (in CDCl_3 , 500 MHz).

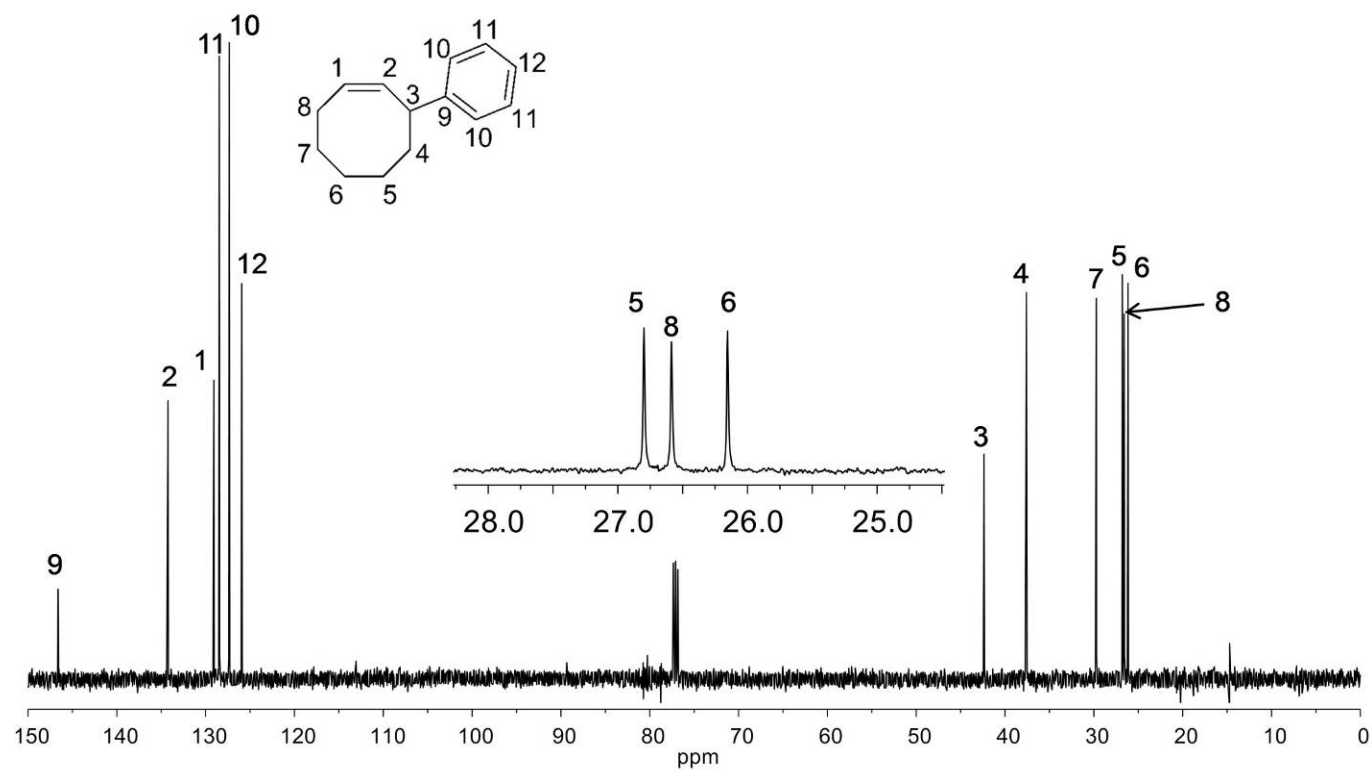


Figure S31. ^{13}C NMR spectrum of 3-phenyl-1-cyclooctene (in CDCl_3 , 125 MHz).

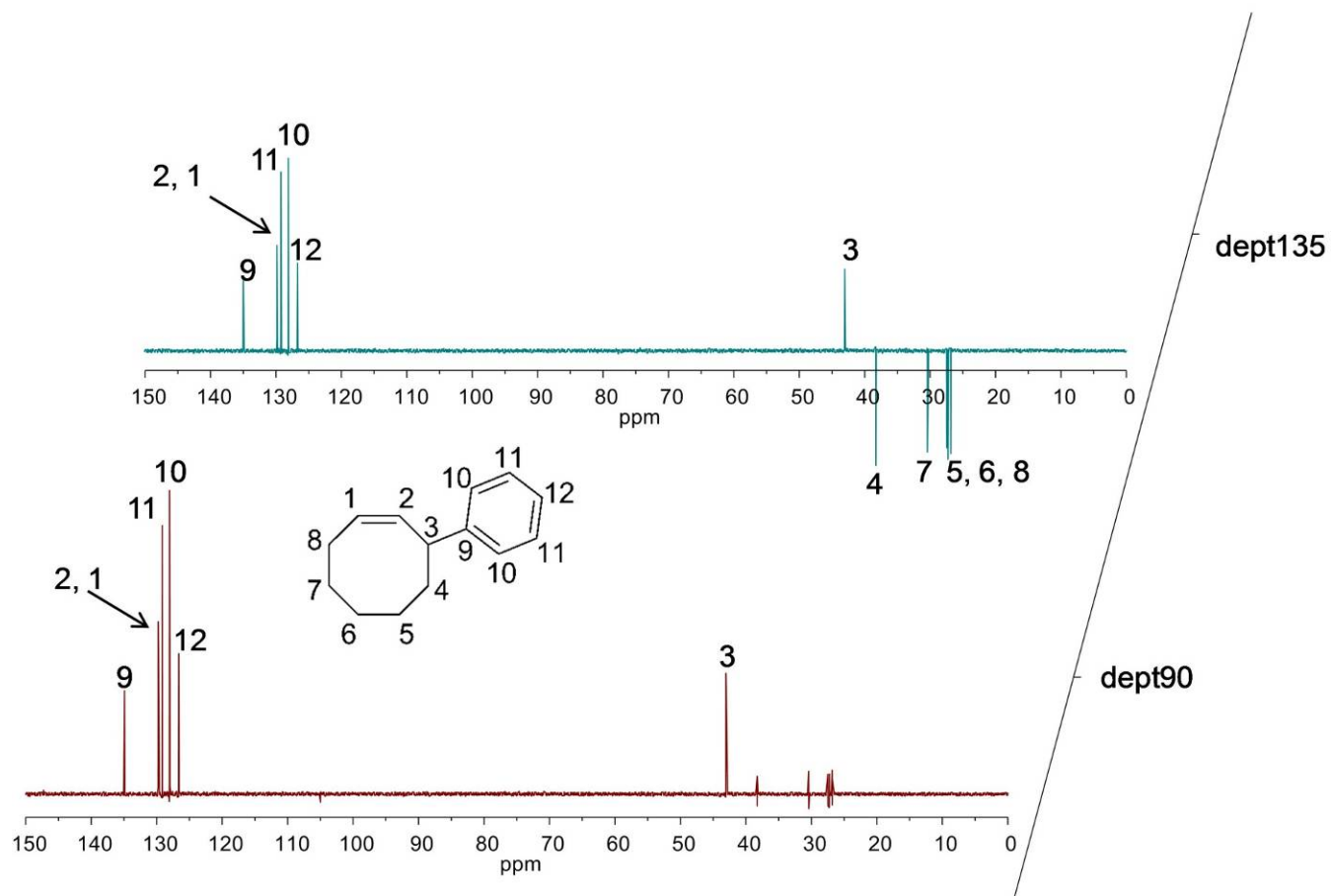


Figure S32. DEPT spectrum of 3-phenyl-1-cyclooctene (in CDCl₃, 75 MHz).

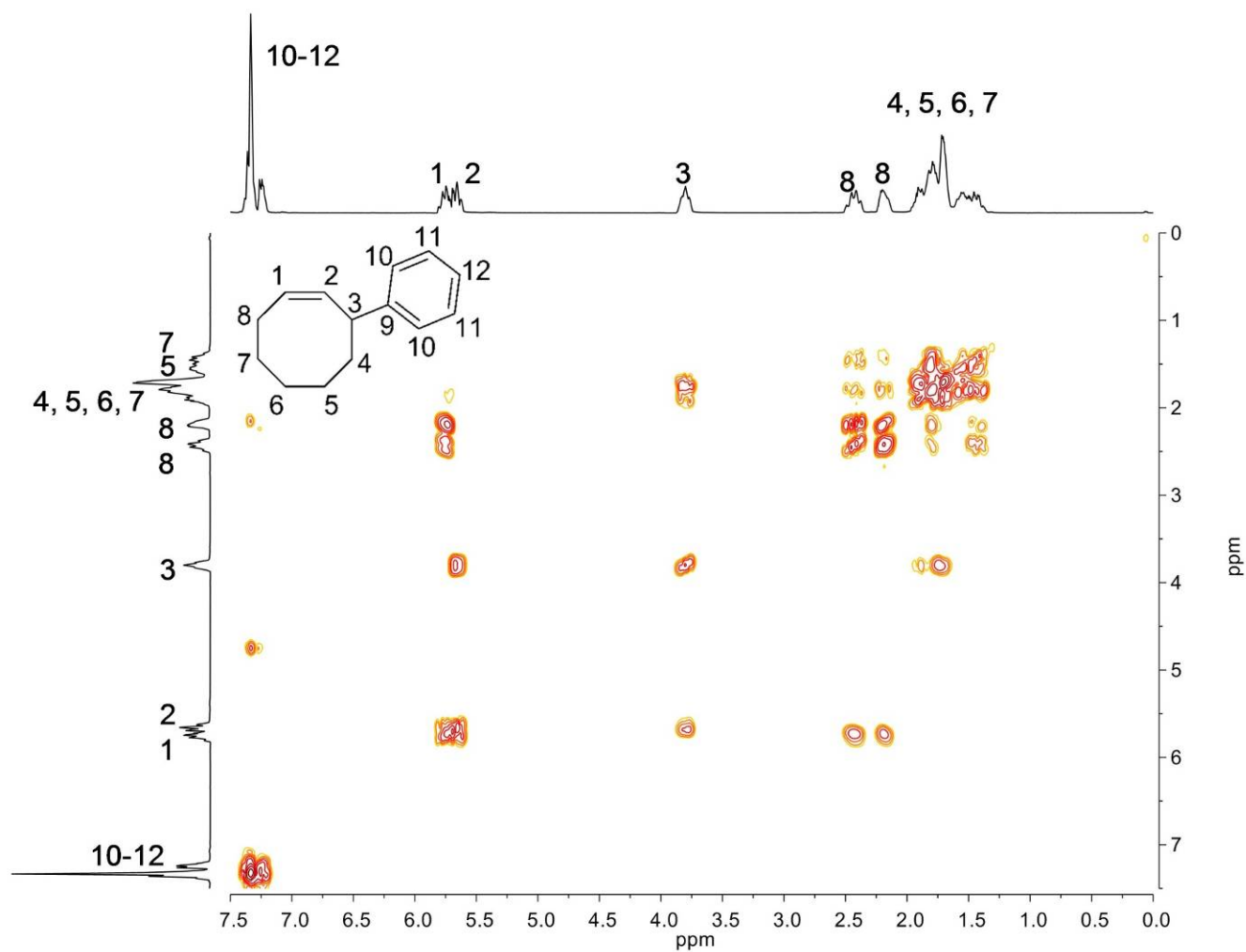


Figure S33. ^1H - ^1H COSY spectrum of 3-phenyl-1-cyclooctene (in CDCl_3 , 300 MHz).

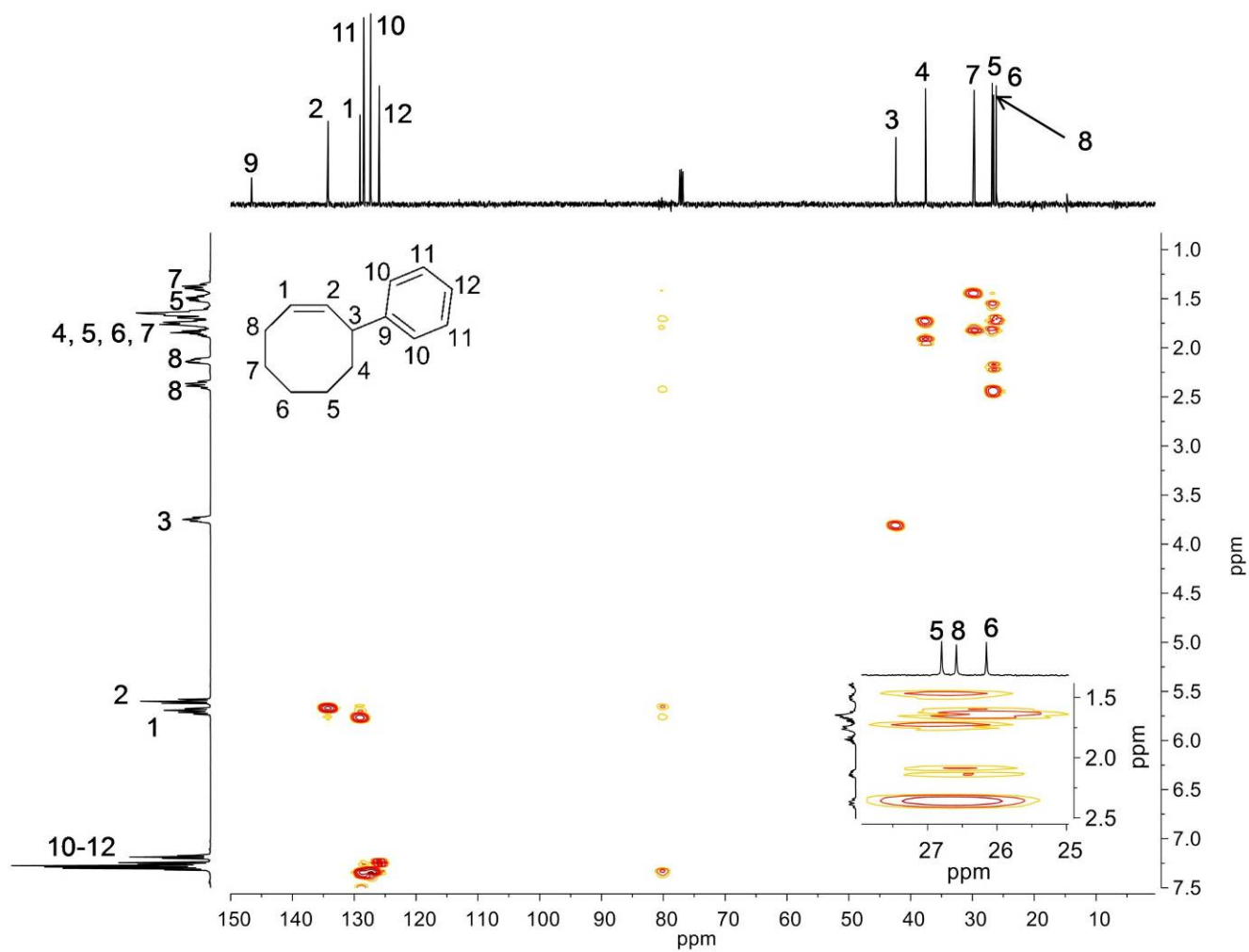


Figure S34. HMQC spectrum of 3-phenyl-1-cyclooctene (in CDCl_3 , 125 MHz).

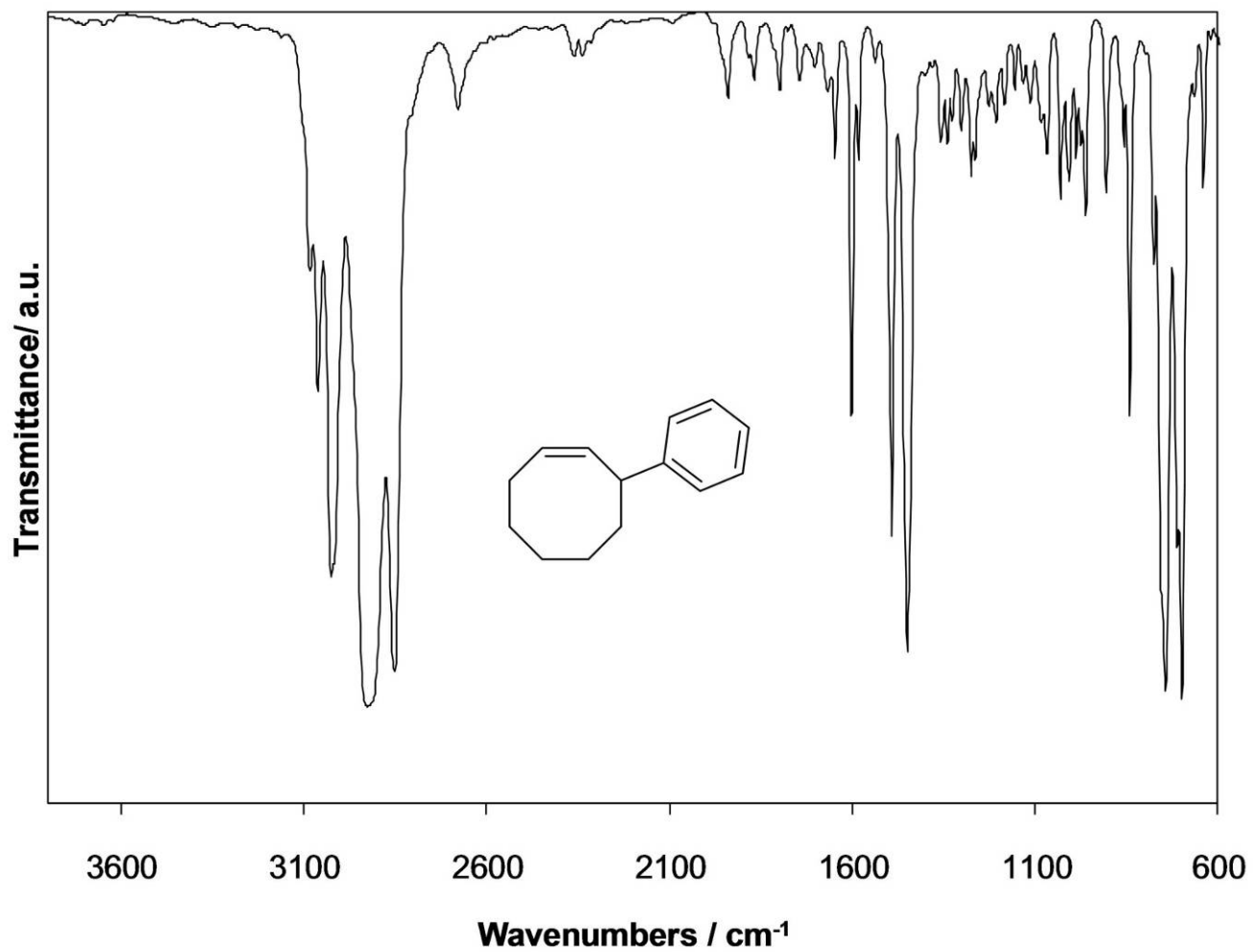
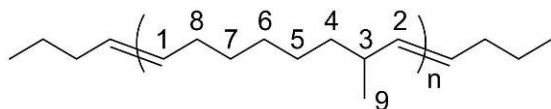


Figure S35. IR spectrum of 3-phenyl-1-cyclooctene (neat).

5. General Polymerization Procedure.

An example of the polymerization procedure is described for the entry 1 in Table 1. A monomer solution of 3MeCOE (1.25 g, 10.1 mmol) in dry CHCl₃ (2.0 M, 5.0 mL total volume) was prepared and was thoroughly purged with dry Ar gas. An Ar filled balloon was fitted to the flask. A 0.1 M solution of *cis*-4-octene (CTA, 0.011 mg, 0.10 mmol) in dry CHCl₃ (1.0 mL total volume) was added to the flask using a syringe. Grubbs second generation catalyst (2.0 mg, 2.4 μmol) was added as a 0.5 mL solution of dry CHCl₃ using a syringe. Then the mixture was heated to 60 °C and stirred for 20 h. The reaction was quenched by adding ethyl vinyl ether (100 μL, 1.0 mmol) using syringe and stirred for 30 min at room temperature. The reaction mixture was diluted with CHCl₃ and the catalyst residue was removed by passing through a basic Al₂O₃ column. The solution was concentrated and the crude product was dissolved in THF. The polymer was precipitated by pouring the solution into a large excess amount of liq. N₂ chilled methanol. The solution was allowed to warm up to room temperature and precipitated polymer was isolated by decantation. The polymer was freeze dried overnight from it benzene solution to afford poly(3MeCOE) (1.18 g, 94% yield) as a viscous liquid. The following is the complete list.

poly(3MeCOE) (Figure S36-Figure S41)



¹H NMR (500 MHz, CDCl₃): δ = 5.32 (dt, *J* = 15.3, 6.6 Hz, 1H, =C(1)*H*-), 5.23 (dd, *J* = 15.3, 7.6 Hz, 1H, =C(2)*H*-), 2.02 (m, 1H, =CH-C(3)*H*Me-), 1.95 (m, 2H, =CH-C(8)*H*₂-), 1.23 (m, 8H, -CH₂-), 0.94 (d, *J* = 6.7 Hz, 3H, -C(9)*H*₃).

¹³C NMR (125 MHz, CDCl₃): δ = 136.52 (C2), 128.51 (C1), 37.33 (C4), 36.80 (C3), 32.71 (C8), 29.83 (C6), 29.38 (C5), 27.31 (C7), 21.05 (C9).

IR (neat): 3649, 3020, 2958, 2923, 2853, 2717, 2681, 1766, 1667, 1456, 1372, 1304, 1142, 1092, 967, 860, 800, 725 cm⁻¹.

The assignments above are for the *trans*- HT regio- and stereoregular sequence. The minor signals (see Figure S1) were assignable to irregular sequences based on comparison with literature assignments of small molecules. For the assignment, see: (a) Carballeira, N. M.; Sostre, A.; Restituyo, J. A. *Chem. Phys. Lipids* **1999**, 97, 87-91. (b) Jung, M. E.; Liu, C. Y. *J. Org. Chem.* **1986**, 51, 5446-5447. (c) Backvall, J. E.; Sellen, M.; Grant, B. *J. Am.*

Chem. Soc. **1990**, *112*, 6615-6621. (d) Sonnet, P. E. *Journal of Chromatography* **1984**, 292, 295-304. (e) Didiuk, M. T.; Morken, J. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 7273-7274.

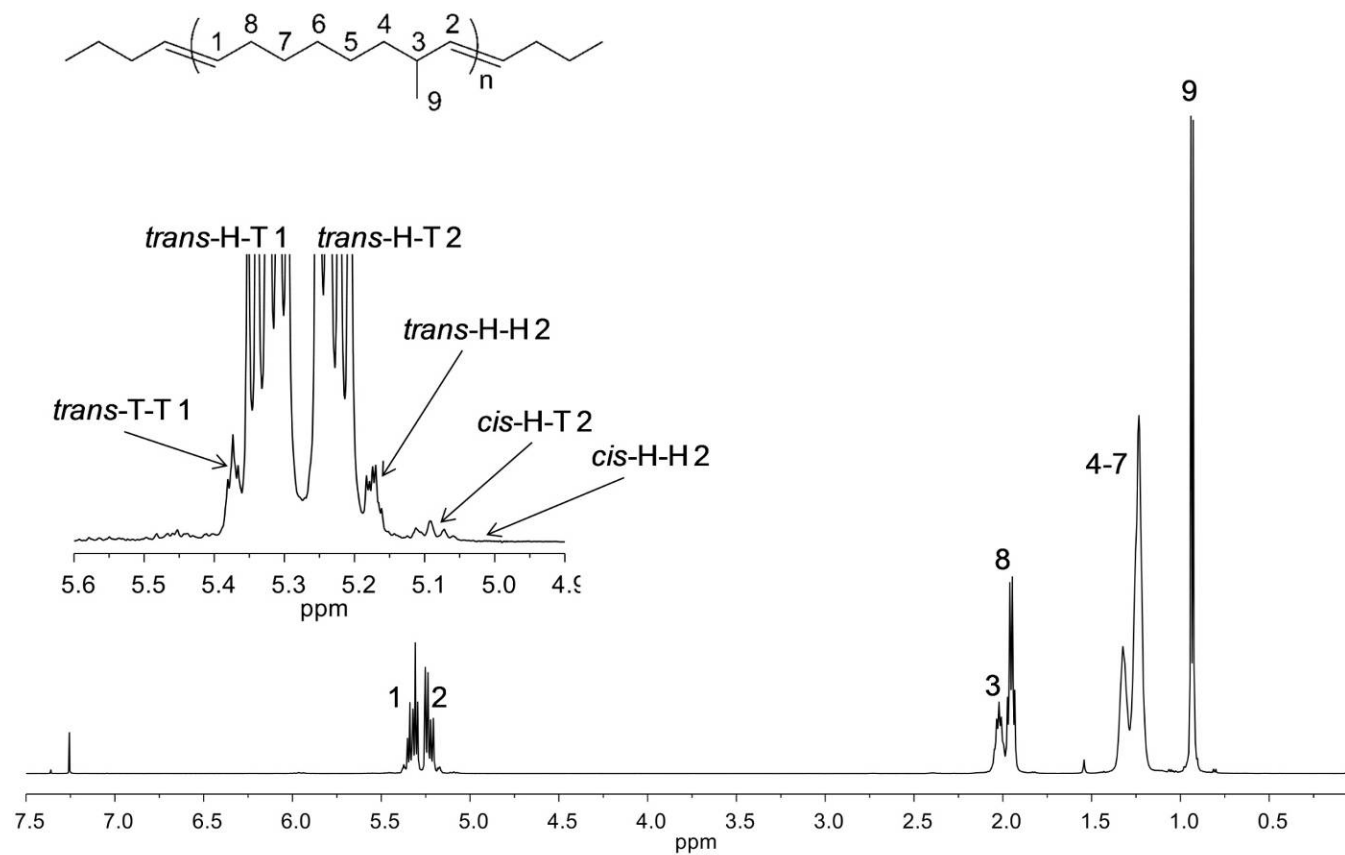


Figure S36. ^1H NMR spectrum of poly(3-methyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

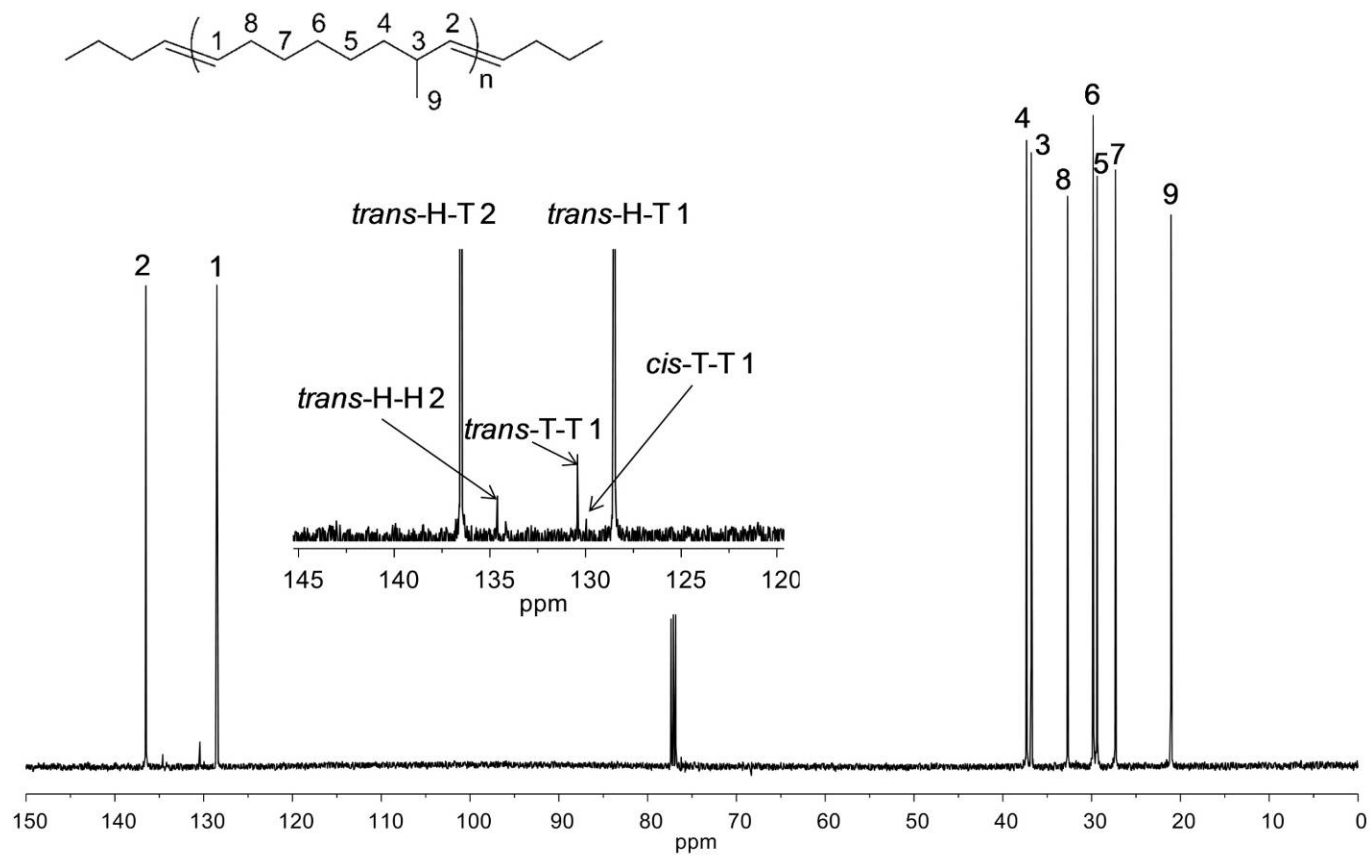


Figure S37. ^{13}C NMR spectrum of poly(3-methyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

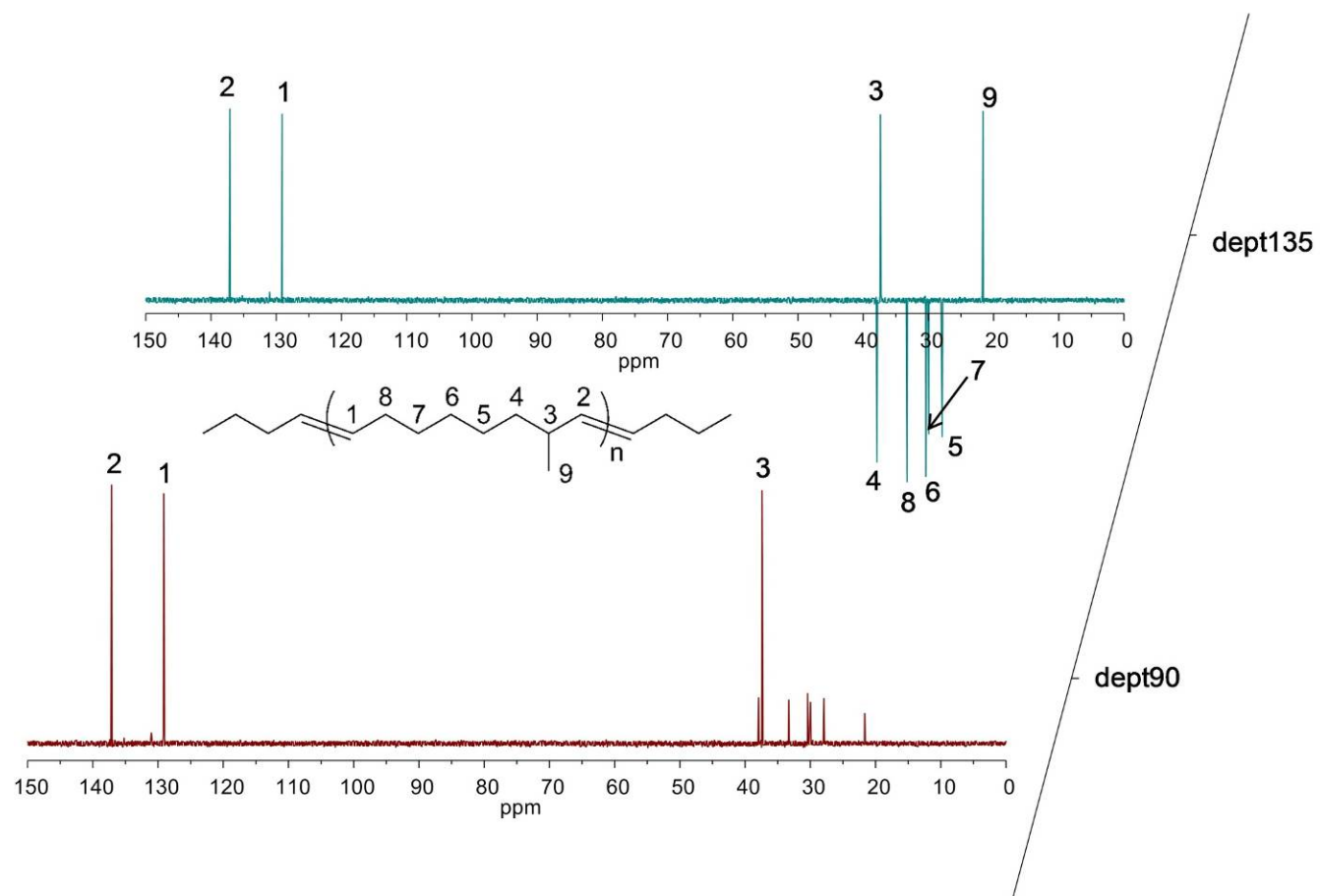


Figure S38. DEPT spectrum of poly(3-methyl-1-cyclooctene) (in CDCl₃, 75 MHz).

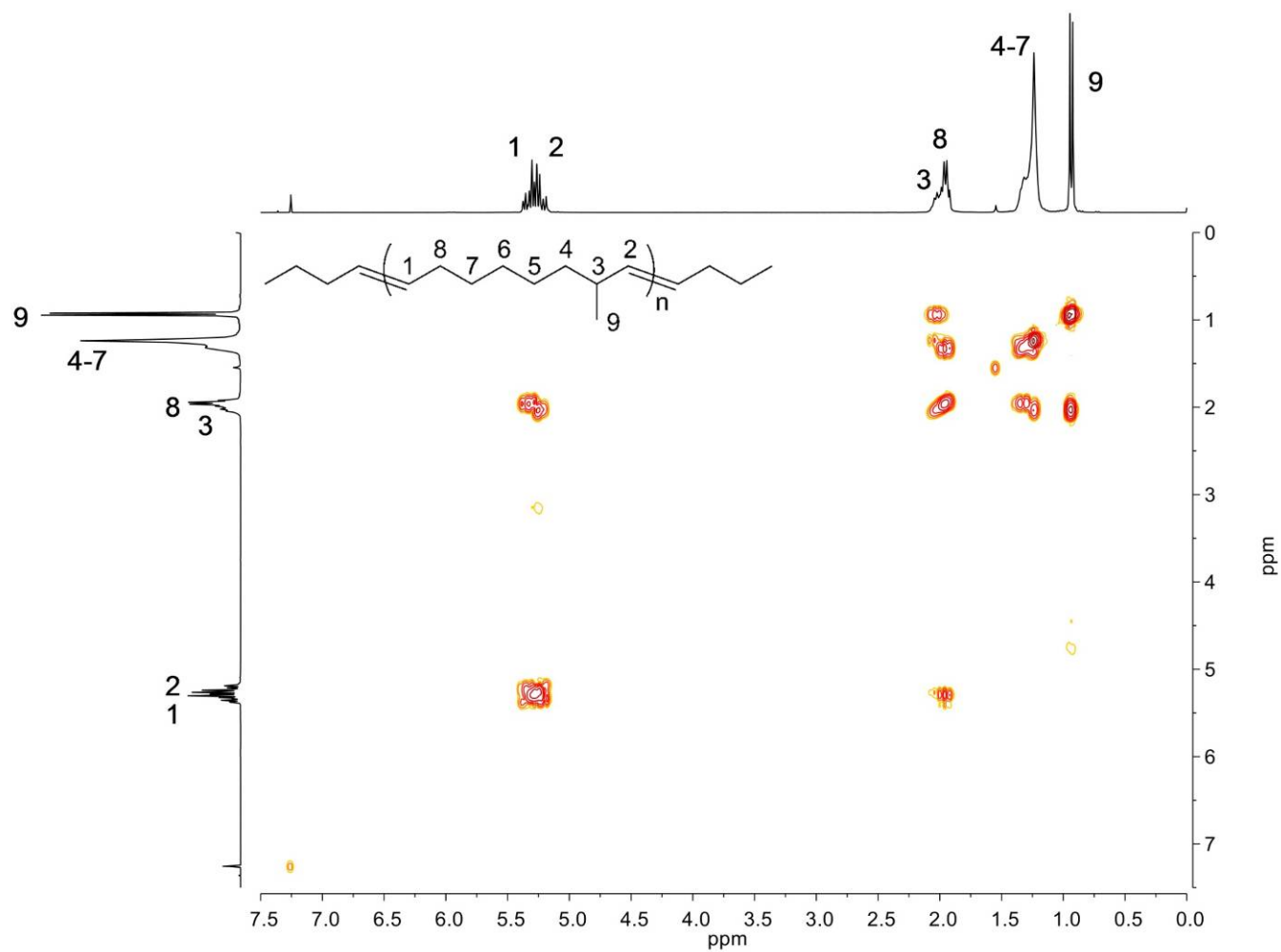


Figure S39. ^1H - ^1H COSY spectrum of poly(3-methyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

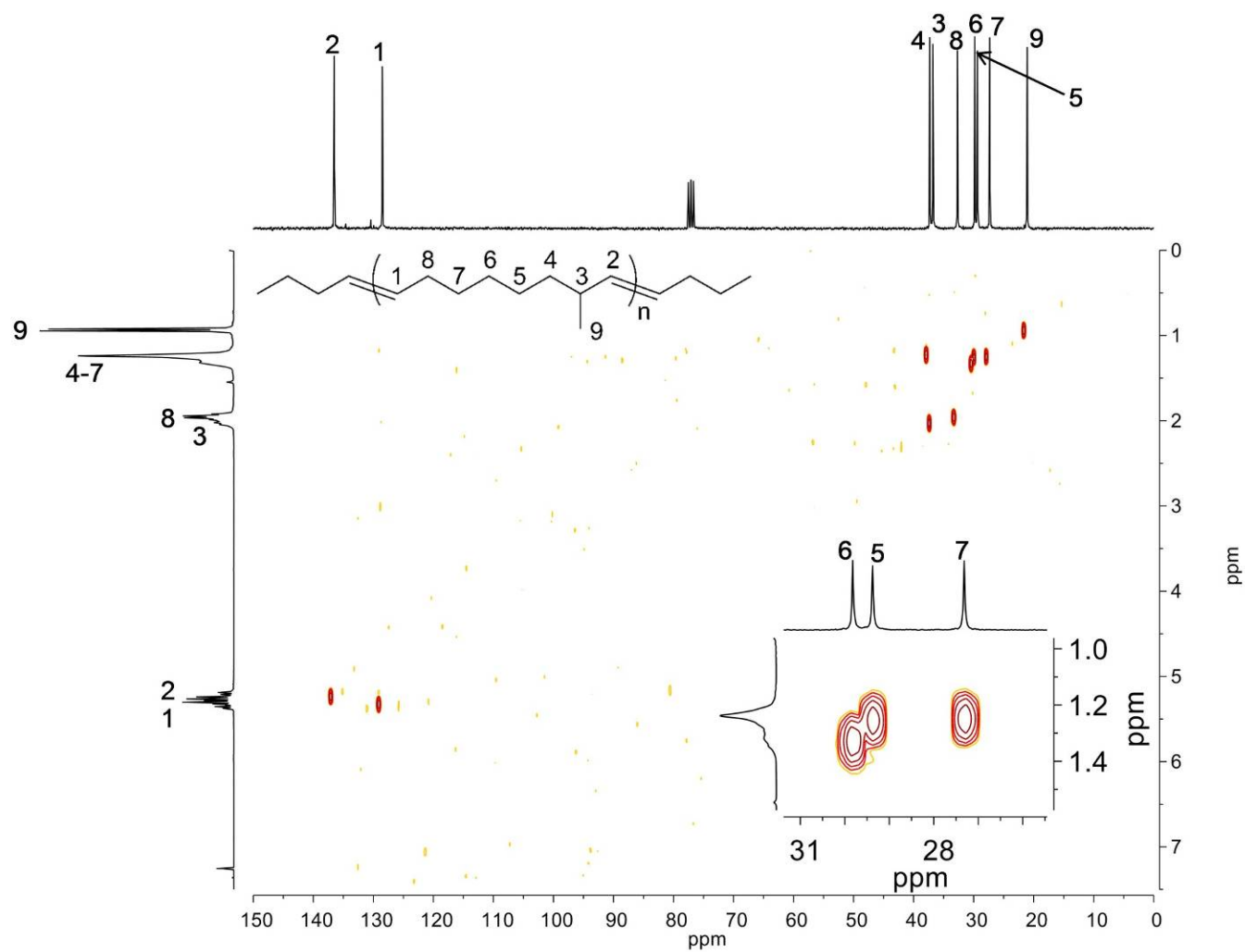


Figure S40. HETCOSY spectrum of poly(3-methyl-1-cyclooctene) (in CDCl₃, 75 MHz).

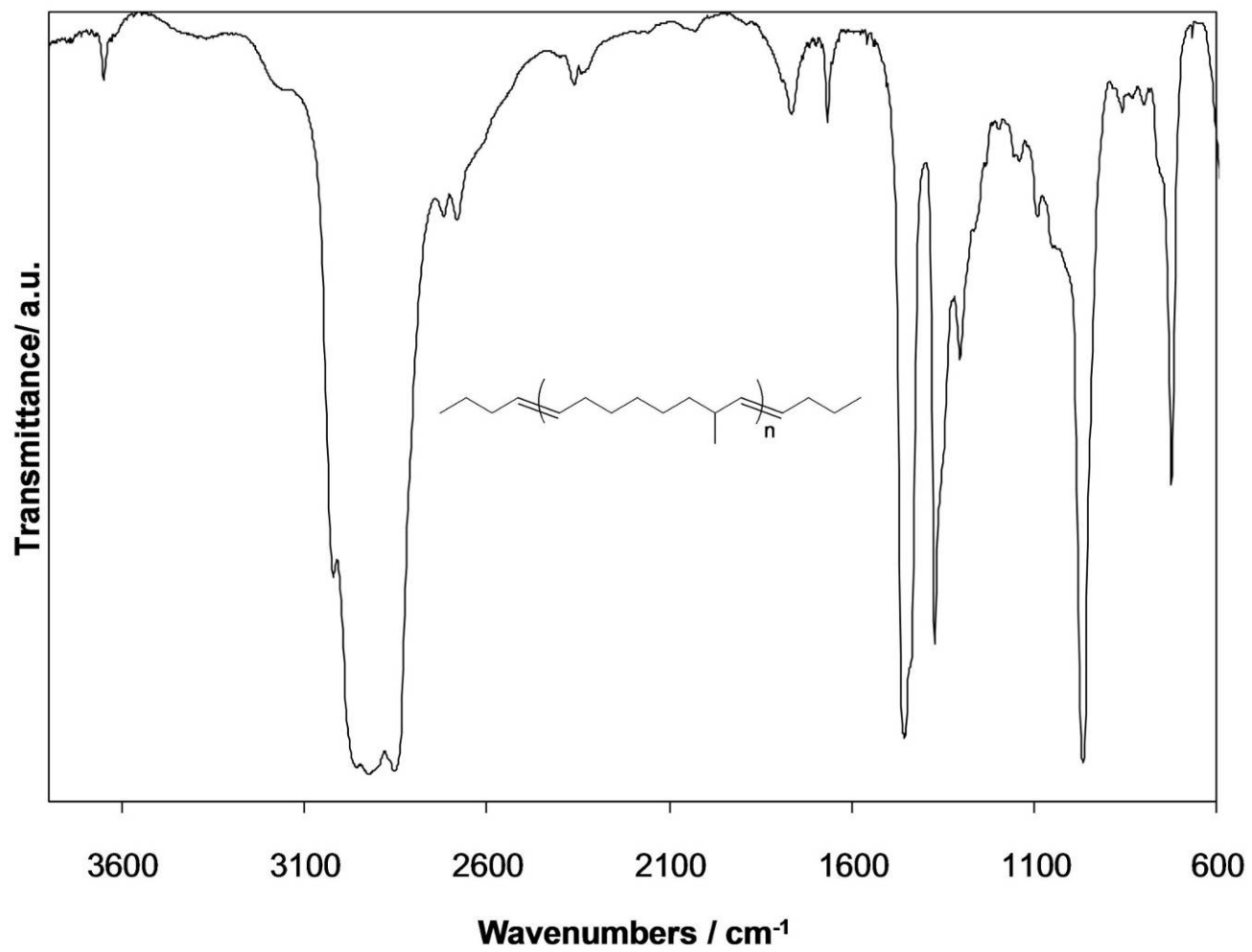
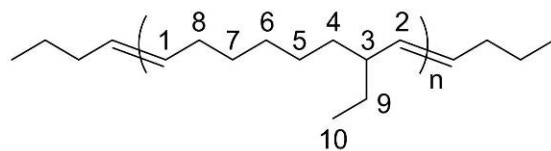


Figure S41. IR spectrum of poly(3-methyl-1-cyclooctene) (neat).

poly(3EtCOE) (Figure S42-Figure S47)



^1H NMR (500 MHz, CDCl_3): δ = 5.32 (dt, J = 15.3, 6.8 Hz, 1H, $=\text{C}(1)\text{H}-$), 5.07 (dd, J = 15.3, 8.8 Hz, 1H, $=\text{C}(2)\text{H}-$), 1.98 (m, 2H, $=\text{CH}-\text{C}(8)\text{H}_2-$), 1.76 (m, 1H, $=\text{CH}-\text{C}(3)\text{HEt}-$), 1.47 – 1.07 (m, 10H, $-\text{CH}_2-$), 0.83 (t, J = 7.4 Hz, 3H, $-\text{C}(10)\text{H}_3$).

^{13}C NMR (125 MHz, CDCl_3): δ = 134.78 (C2), 130.39 (C1), 44.67 (C3), 35.33 (C4), 32.77 (C8), 29.90 (C6), 29.40 (C5), 28.31 (C9), 27.26 (C7), 11.89 (C10).

IR (neat): 3649, 2959, 2871, 2853, 2728, 2682, 1772, 1667, 1461, 1378, 1364, 1304, 1131, 1046, 968, 776, 724 cm^{-1} .

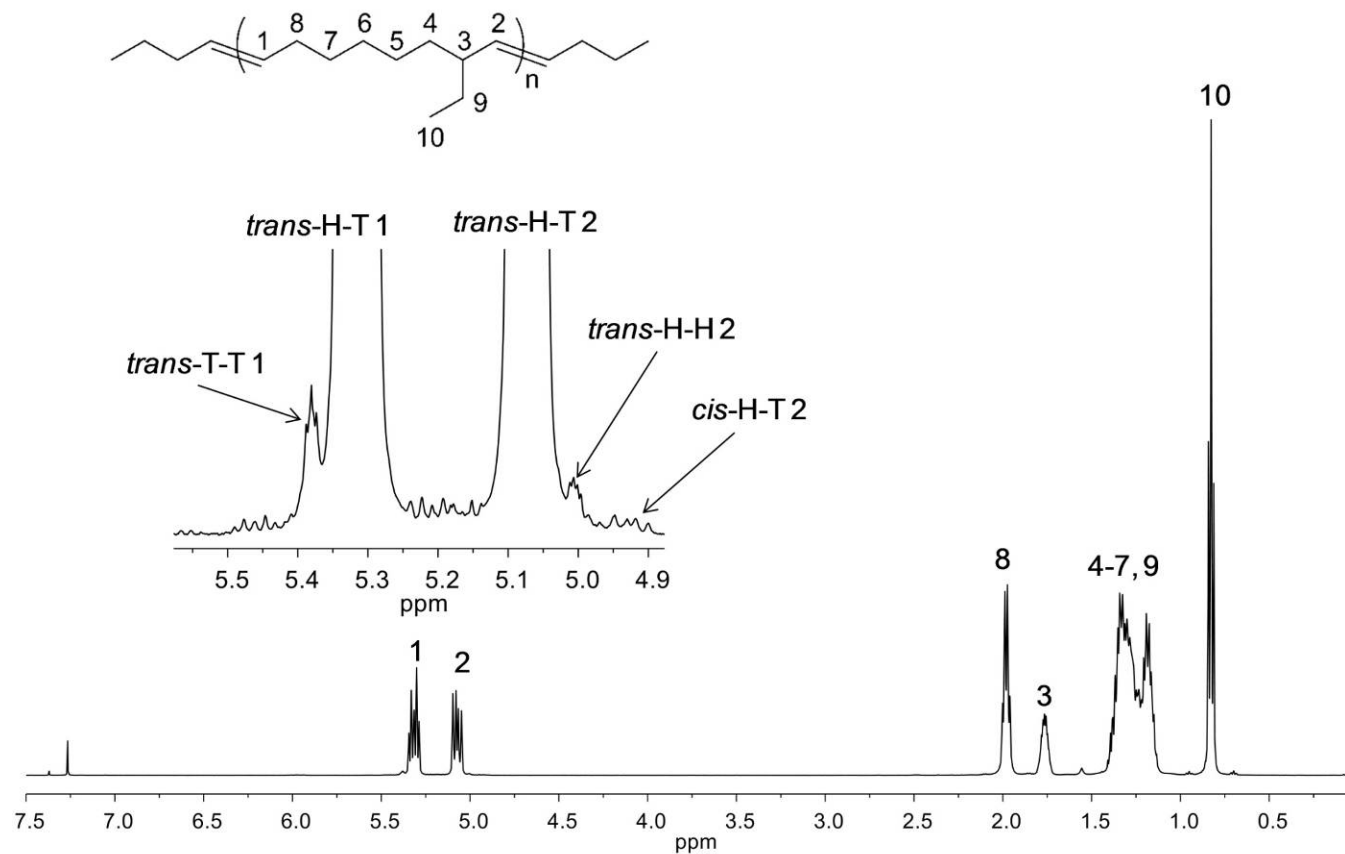


Figure S42. ^1H NMR spectrum of poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

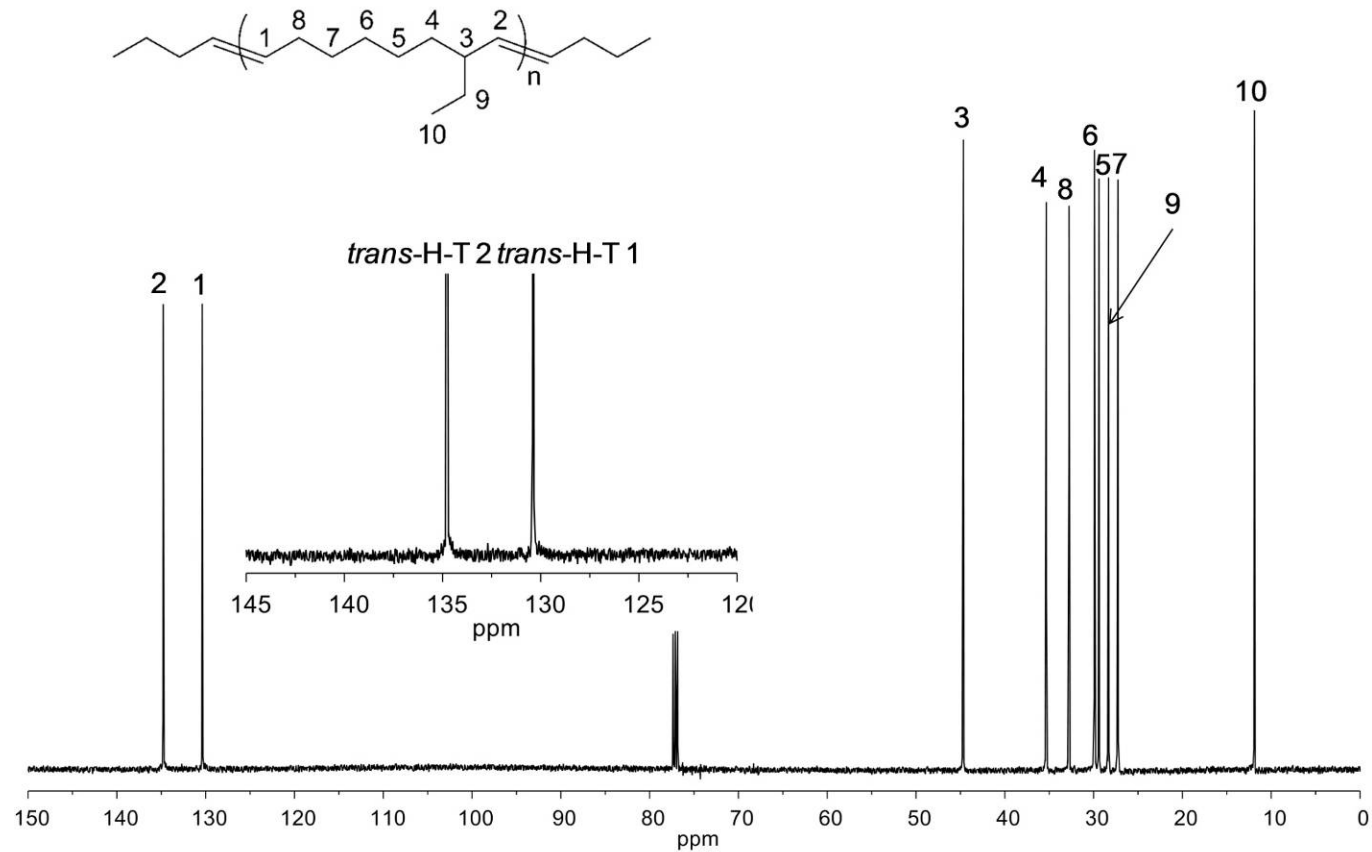


Figure S43. ^{13}C NMR spectrum of poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

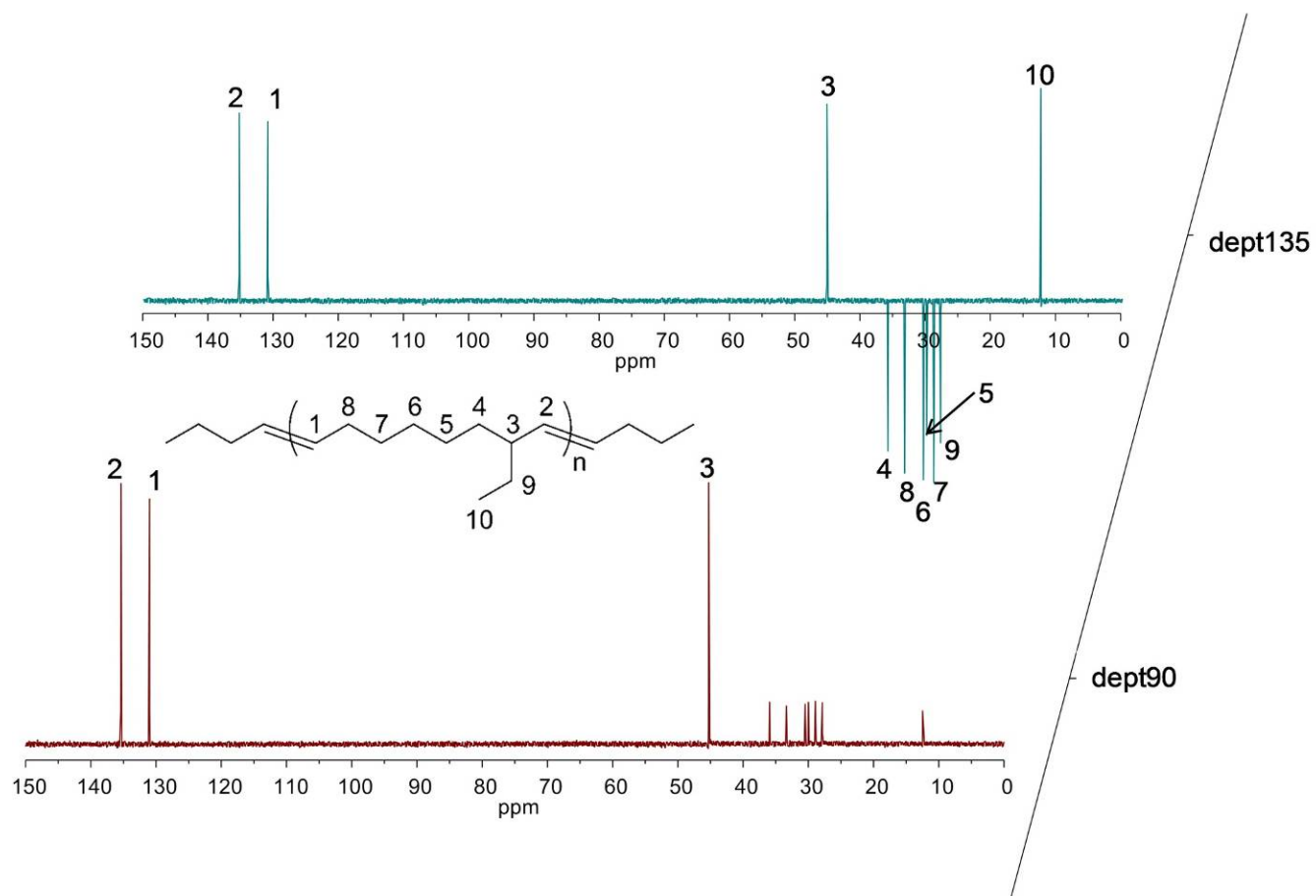


Figure S44. DEPT spectrum of poly(3-ethyl-1-cyclooctene) (in CDCl₃, 75 MHz).

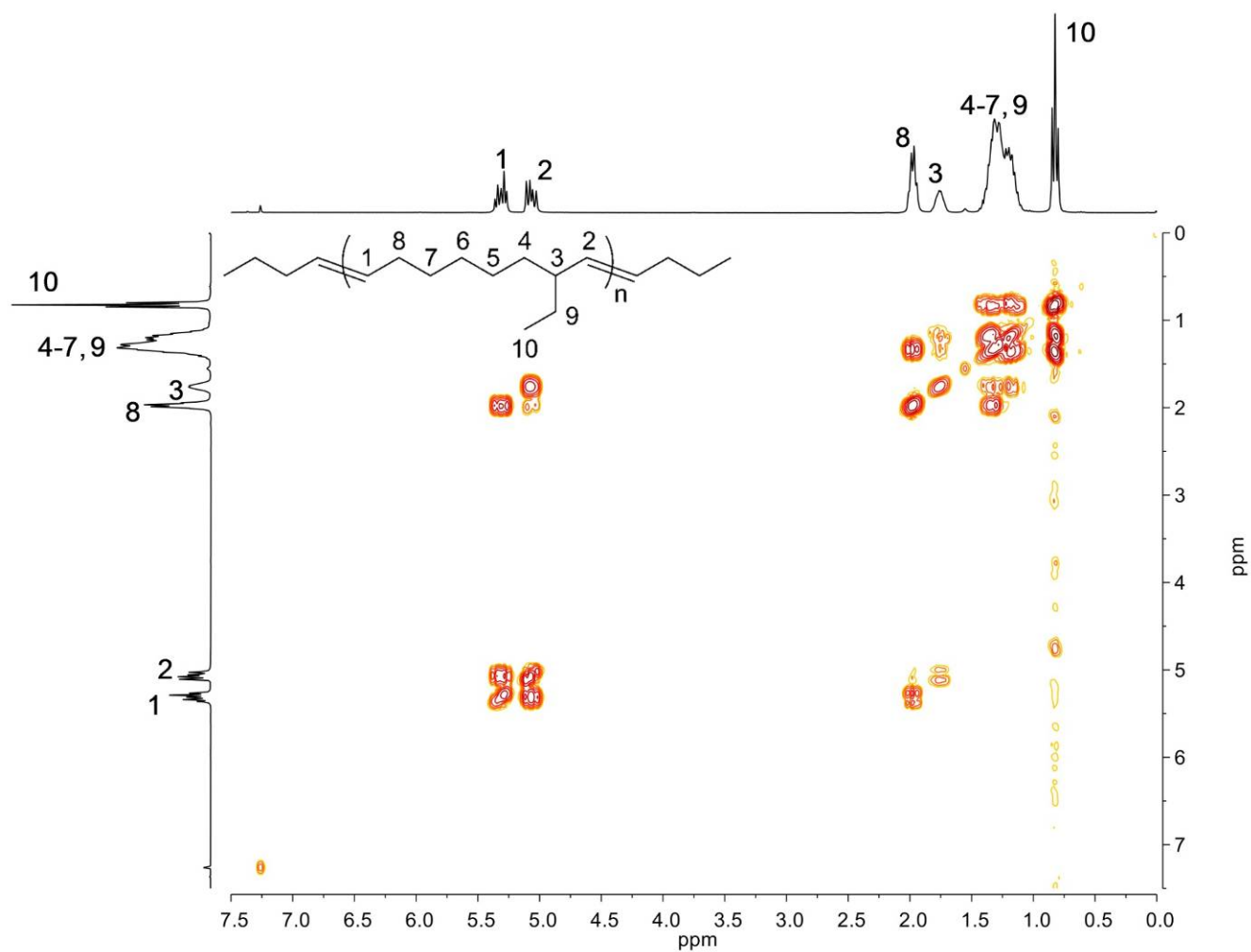


Figure S45. ^1H - ^1H COSY spectrum of poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

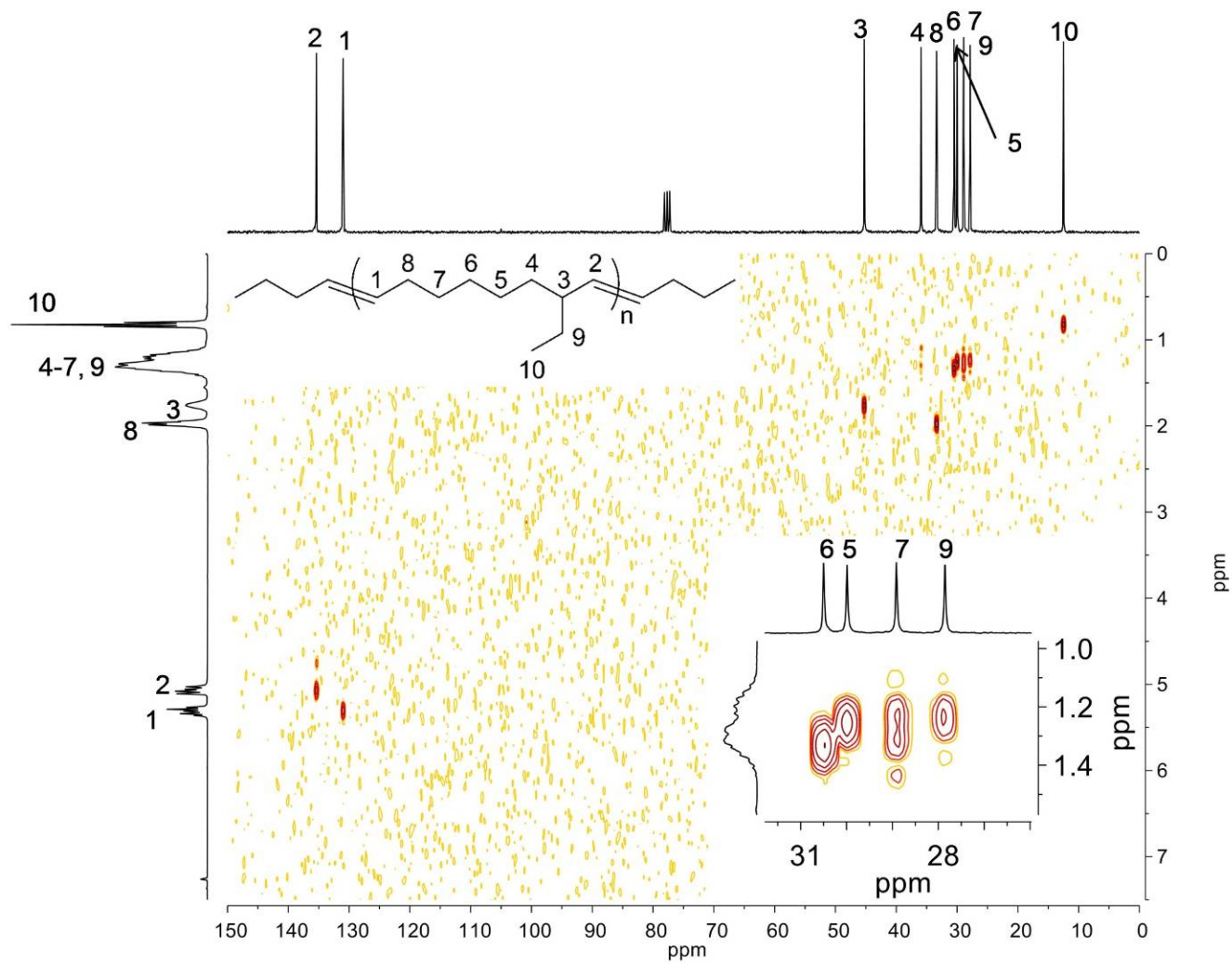


Figure S46. HETCOSY spectrum of poly(3-ethyl-1-cyclooctene) (in CDCl₃, 75 MHz).

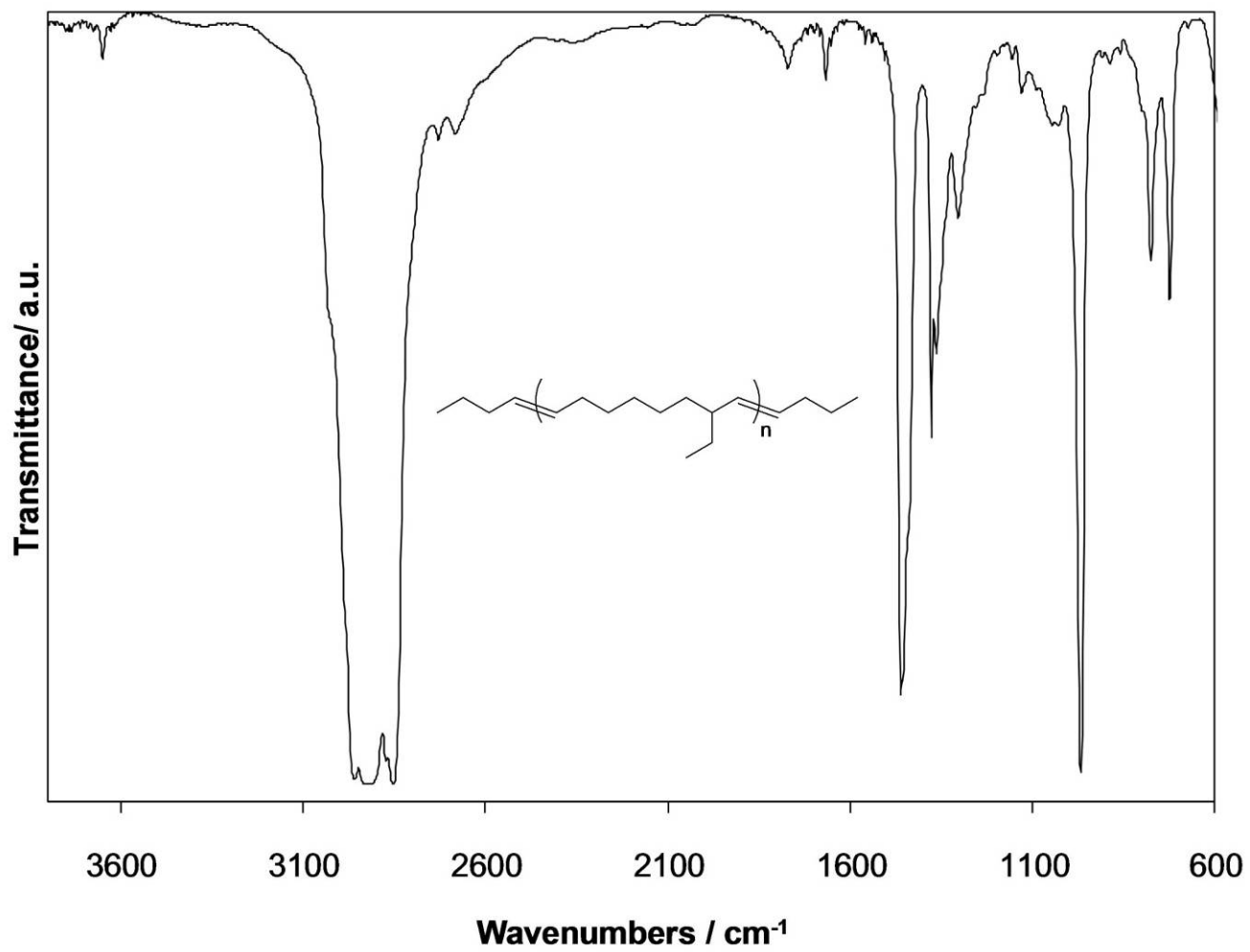
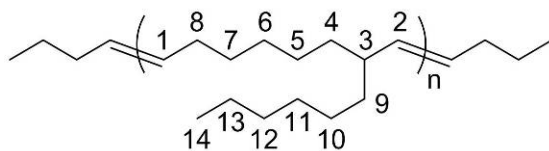


Figure S47. IR spectrum of poly(3-ethyl-1-cyclooctene) (neat).

poly(3HexCOE) (Figure S48-Figure S53)



^1H NMR (500 MHz, CDCl_3): δ = 5.29 (dt, J = 15.3, 6.7 Hz, 1H, =C(1) H -), 5.06 (dd, J = 15.3, 8.8 Hz, 1H, =C(2) H -), 1.96 (m, 2H, =CH-C(8) H_2 -), 1.84 (m, 1H, =CH-C(3) HH_{Hex} -), 1.43 – 1.04 (m, 18H, $-CH_2-$), 0.87 (t, J = 6.9 Hz, 3H, -C(14) H_3).

^{13}C NMR (125 MHz, CDCl_3): δ = 135.15 (C2), 130.11 (C1), 42.95 (C3), 35.75 (C4), 35.72 (C9), 32.75 (C8), 32.07 (C12), 29.88 (C6), 29.62 (C11), 29.41 (C5), 27.38 (C10), 27.26 (C7), 22.82 (C13), 14.24 (C14).

IR (neat): 2955, 2923, 2853, 2730, 2678, 1776, 1667, 1463, 1377, 1367, 1304, 968, 889, 785, 724 cm^{-1} .

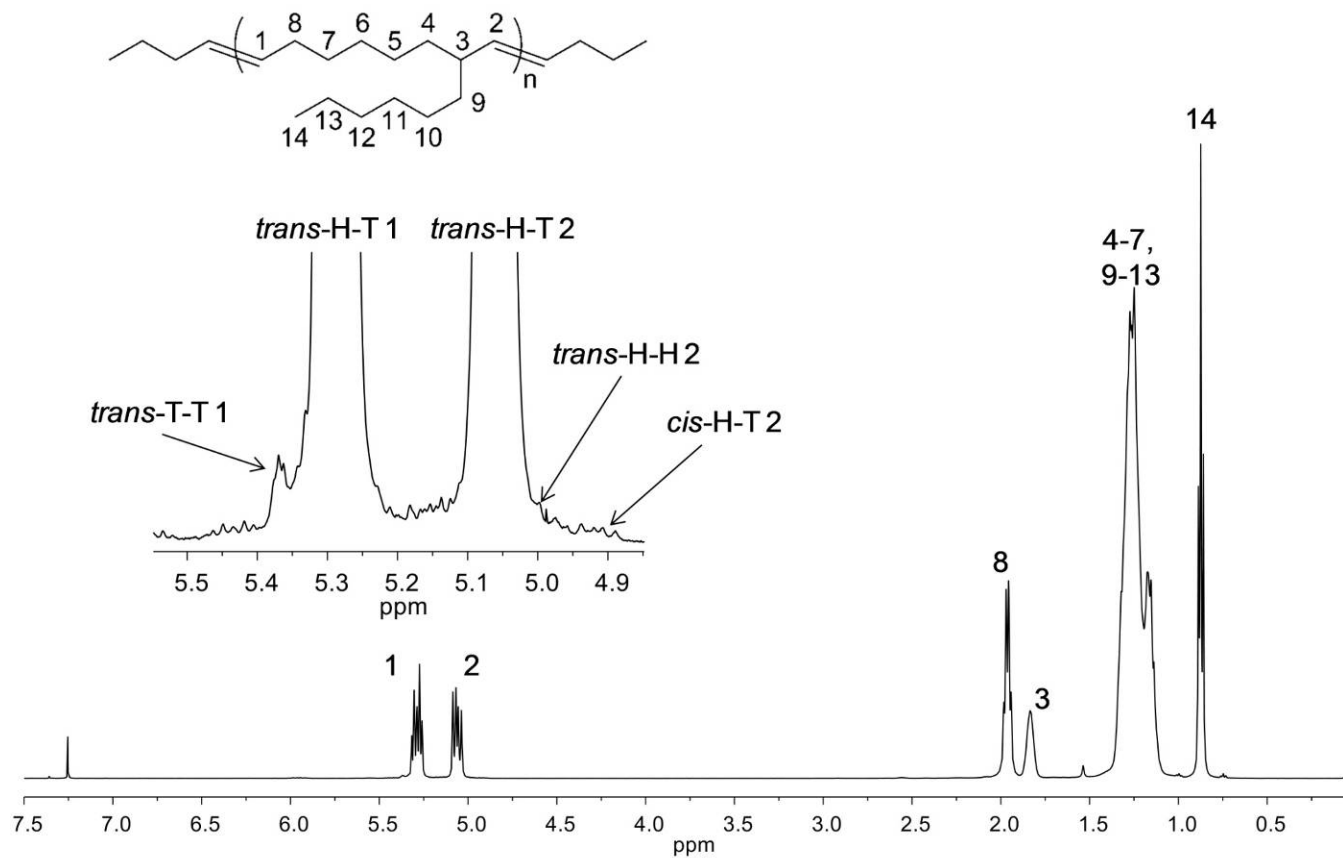


Figure S48. ^1H NMR spectrum of poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

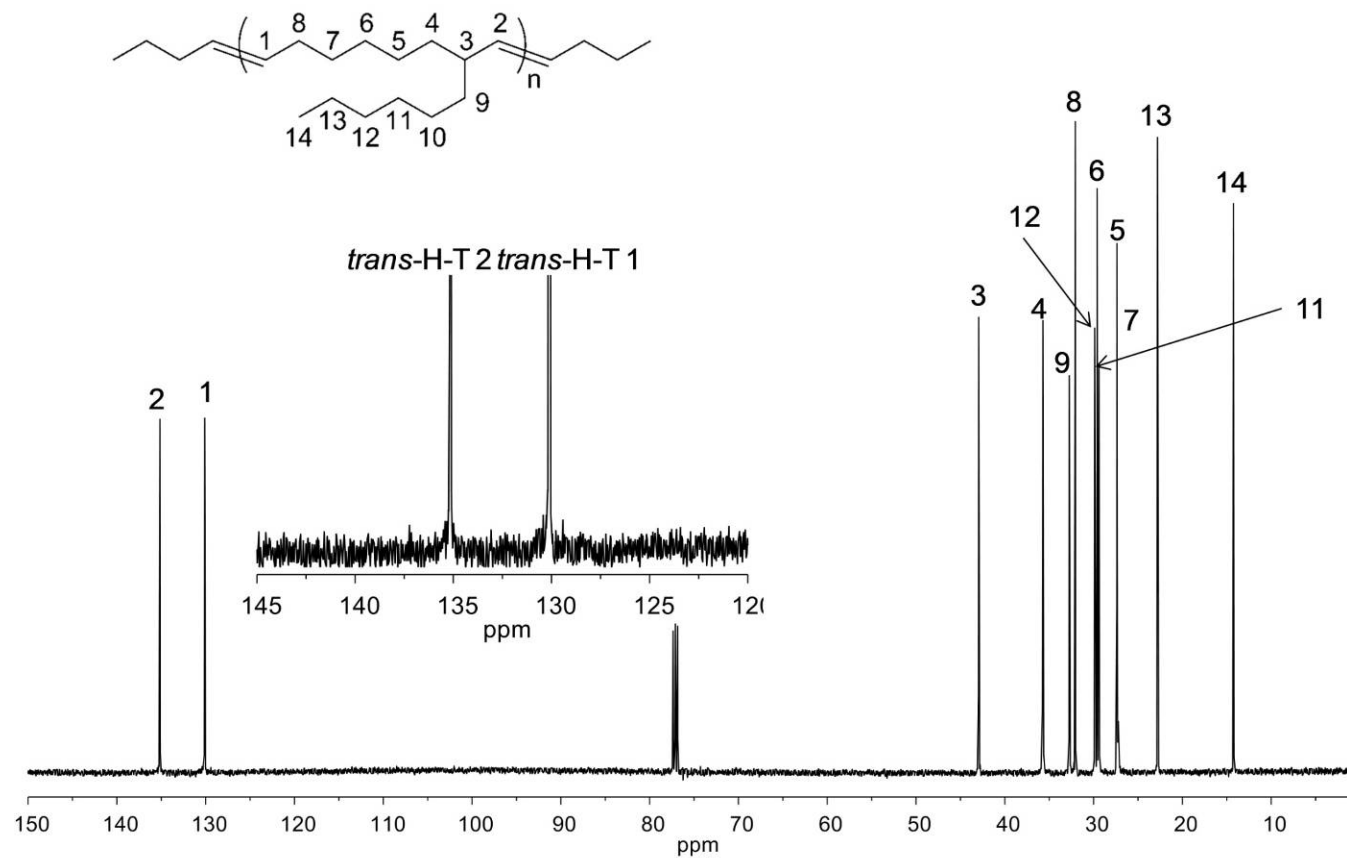


Figure S49. ^{13}C NMR spectrum of poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

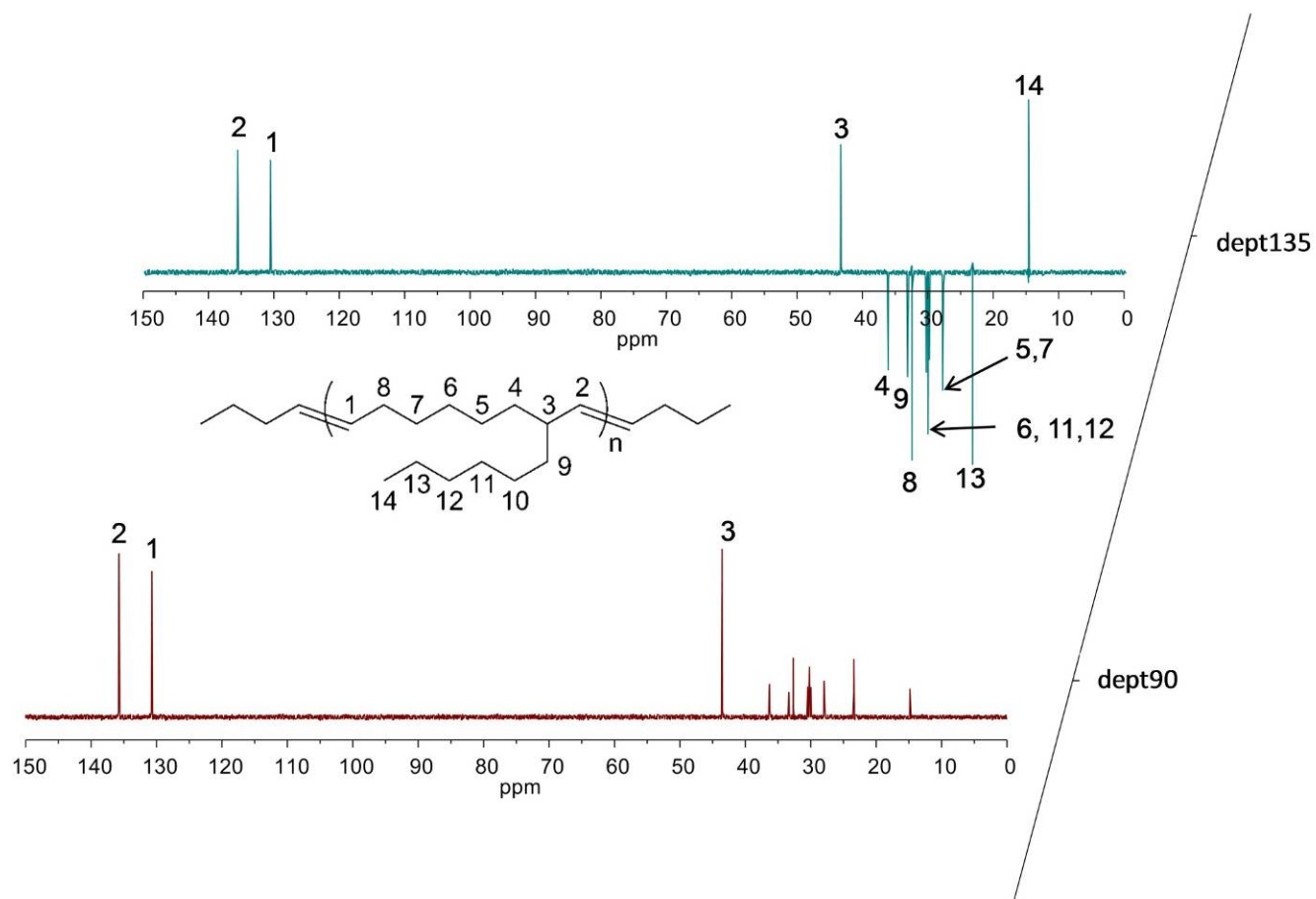


Figure S50. DEPT spectrum of poly(3-hexyl-1-cyclooctene) (in CDCl₃, 75 MHz).

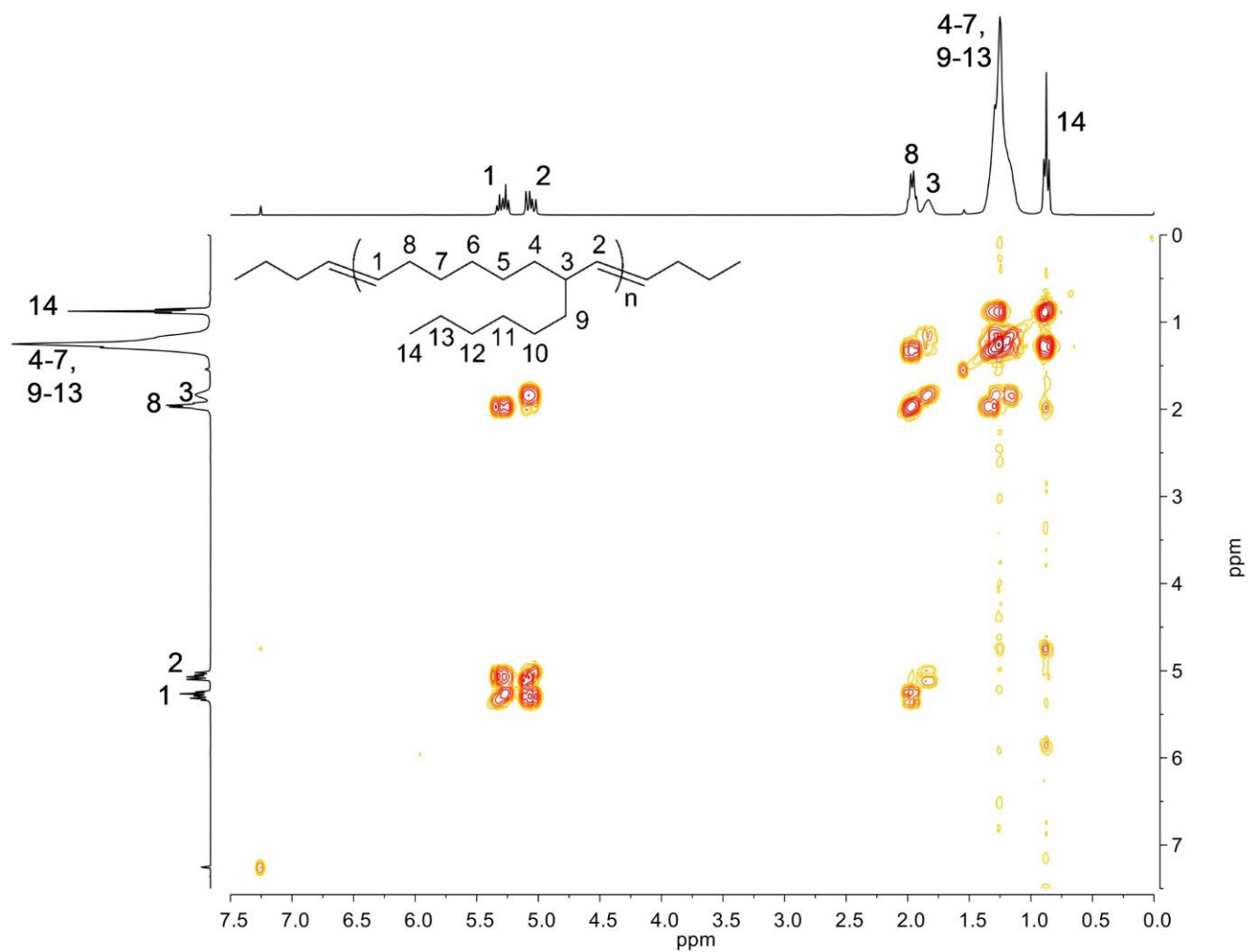


Figure S51. ^1H - ^1H COSY spectrum of poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

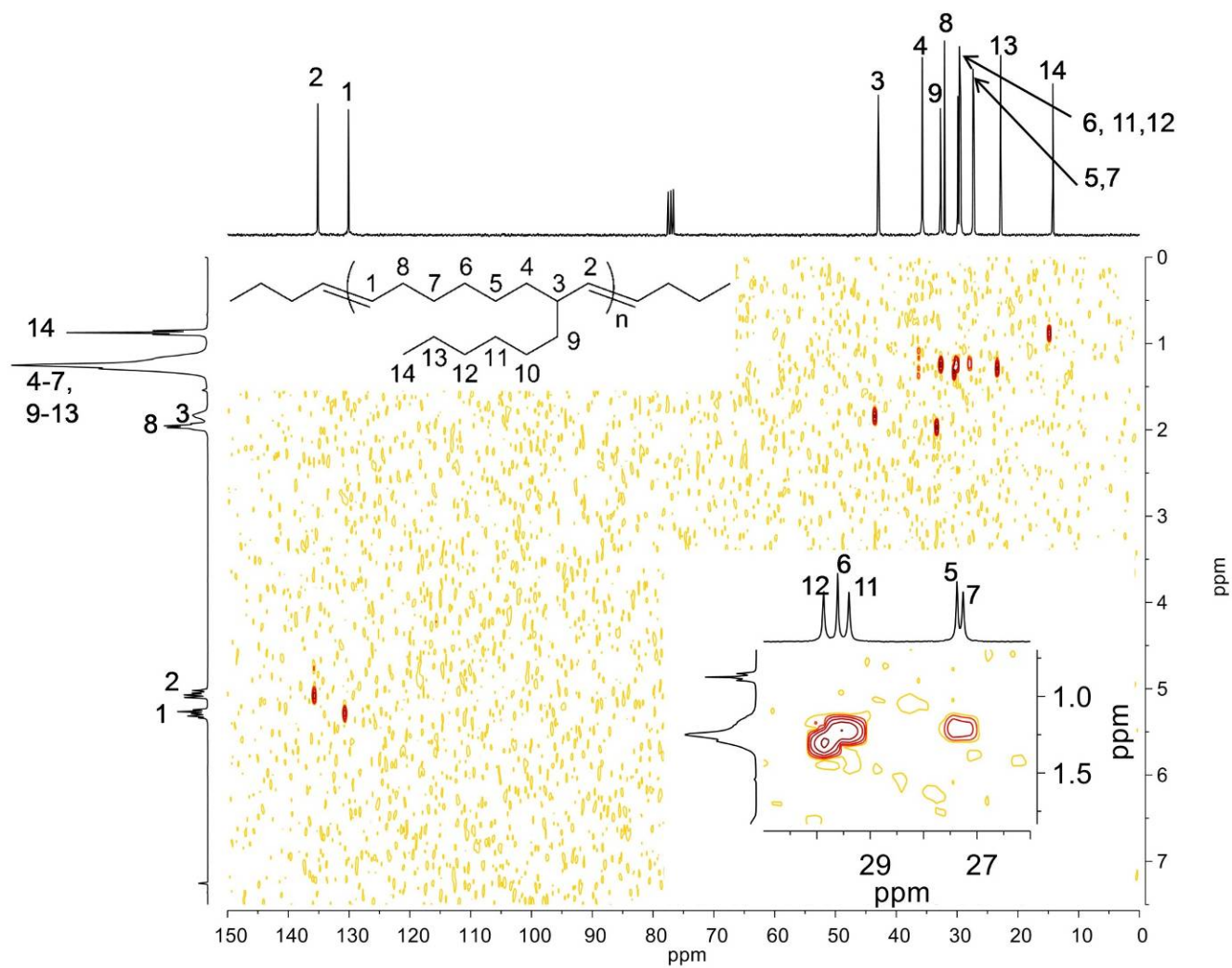


Figure S52. HETCOSY spectrum of poly(3-hexyl-1-cyclooctene) (in CDCl₃, 75 MHz).

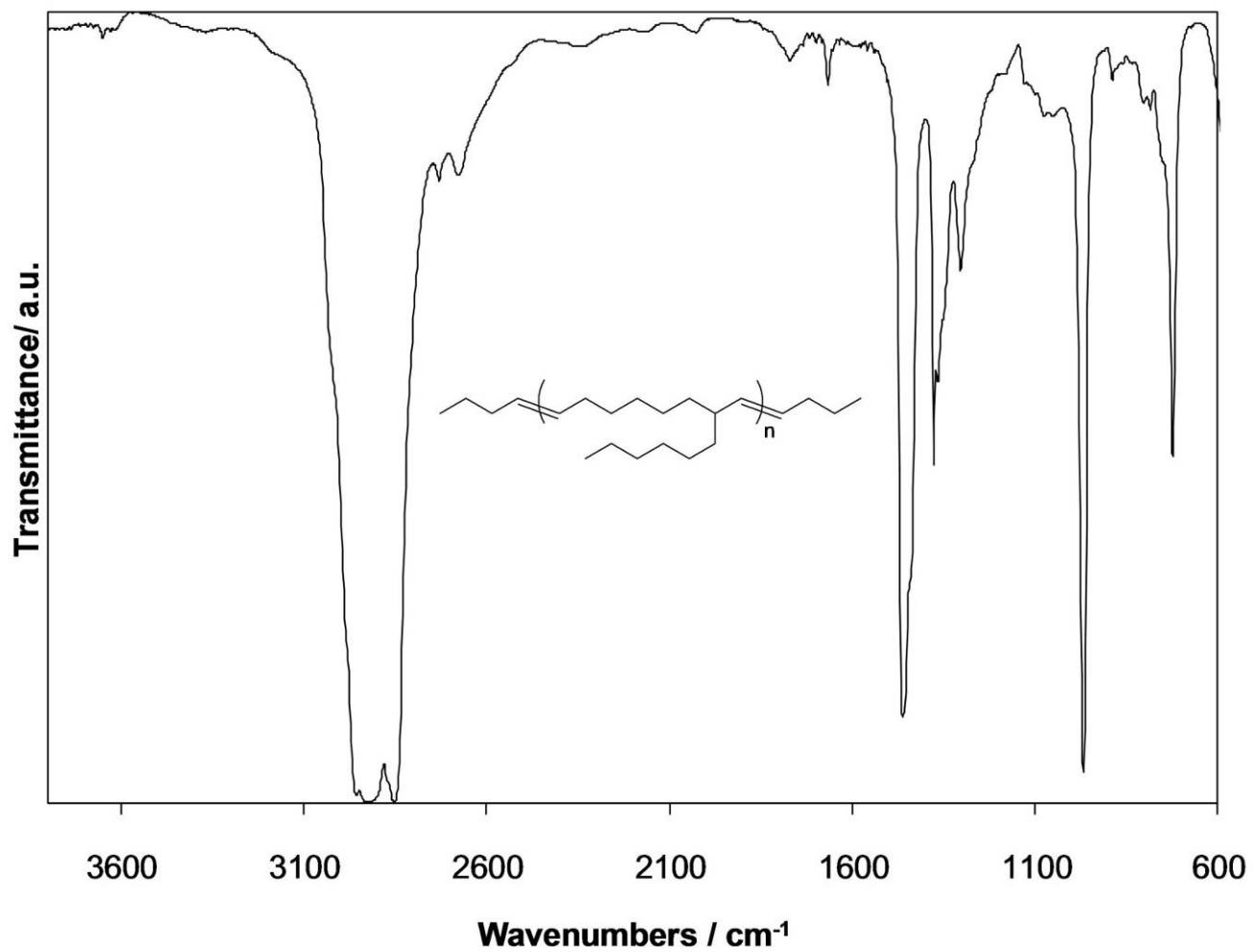
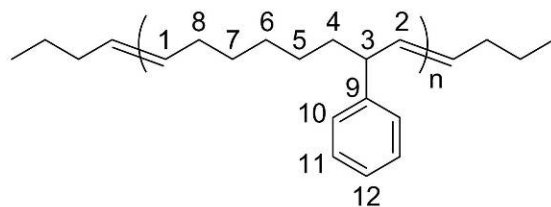


Figure S53. IR spectrum of poly(3-hexyl-1-cyclooctene) (neat).

poly(3PhCOE) (Figure S54-Figure S59)



^1H NMR (500 MHz, CDCl_3): δ = 7.27–7.21 (m, 5H, aromatic), 5.47 (dd, J = 15.3, 7.7 Hz, 1H, =C(2) H –), 5.42 – 5.26 (dt, J = 15.3, 6.6 Hz, 1H, =C(1) H –), 3.12 (m, 1H, =CH–C(3) H Ph–), 1.93 (m, 2H, =CH–C(8) H_2 –), 1.61 (m, 2H, =CH–C(4) H_2 –), 1.42 – 0.95 (m, 6H, – CH_2 –).

^{13}C NMR (125 MHz, CDCl_3): δ = 145.69 (C9), 134.11 (C2), 130.06 (C1), 128.36 (C11), 127.55 (C10), 125.89 (C12), 48.90 (C3), 36.15 (C4), 32.61 (C8), 29.46 (C7), 29.19 (C6), 27.48 (C5).

IR (neat): 3082, 3060, 3025, 3001, 2923, 2853, 2680, 1941, 1868, 1800, 1745, 1694, 1664, 1601, 1583, 1539, 1493, 1480, 1452, 1363, 1307, 1181, 1155, 1074, 1030, 967, 906, 840, 757, 726, 698, 677, 619 cm^{-1} .

The assignment shown above is for the *trans*- head-to-tail regio-/stereo- regular sequence. The minor signals (see Figure S1) were assignable to irregular sequences based on comparison with literature assignments of small molecules. For the assignment, see: (a) Didiuk, M. T.; Morken, J. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 7273-7274. (b) Rieke, R. D.; Daruwala, K. P.; Forkner, M. W. *Organometallics* **1991**, *10*, 2946-2955. (c) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109-3118.

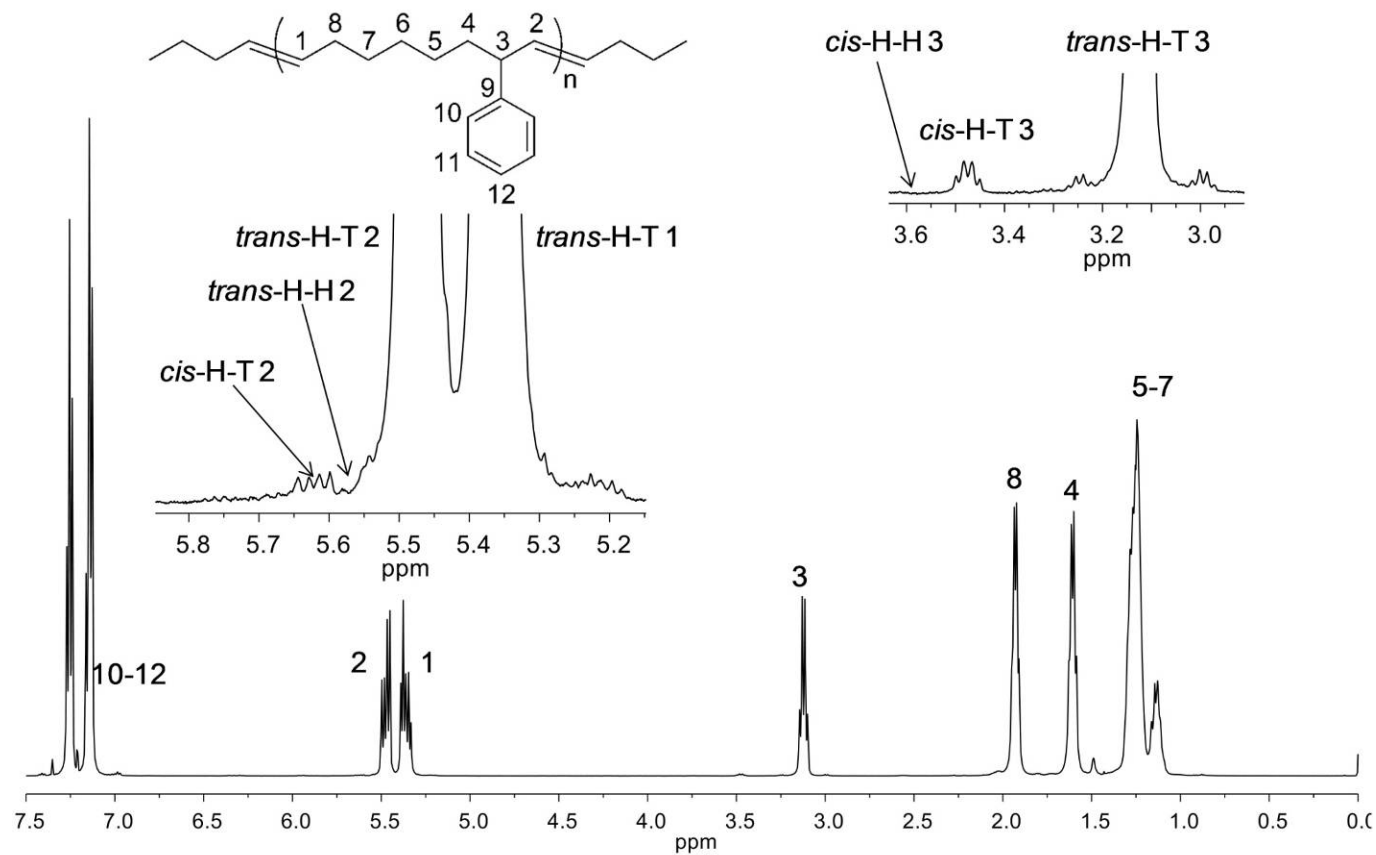


Figure S54. ^1H NMR spectrum of poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

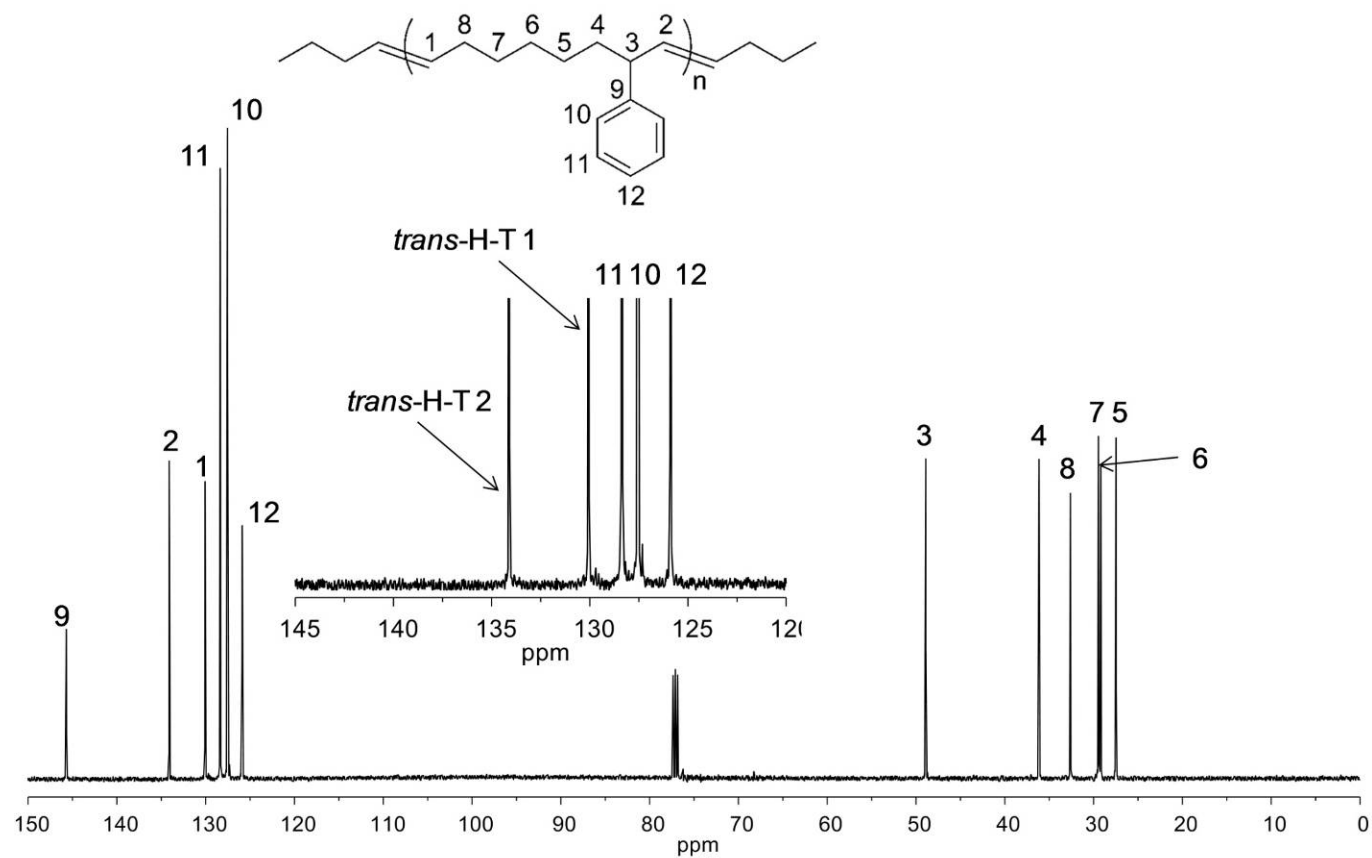


Figure S55. ^{13}C NMR spectrum of poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

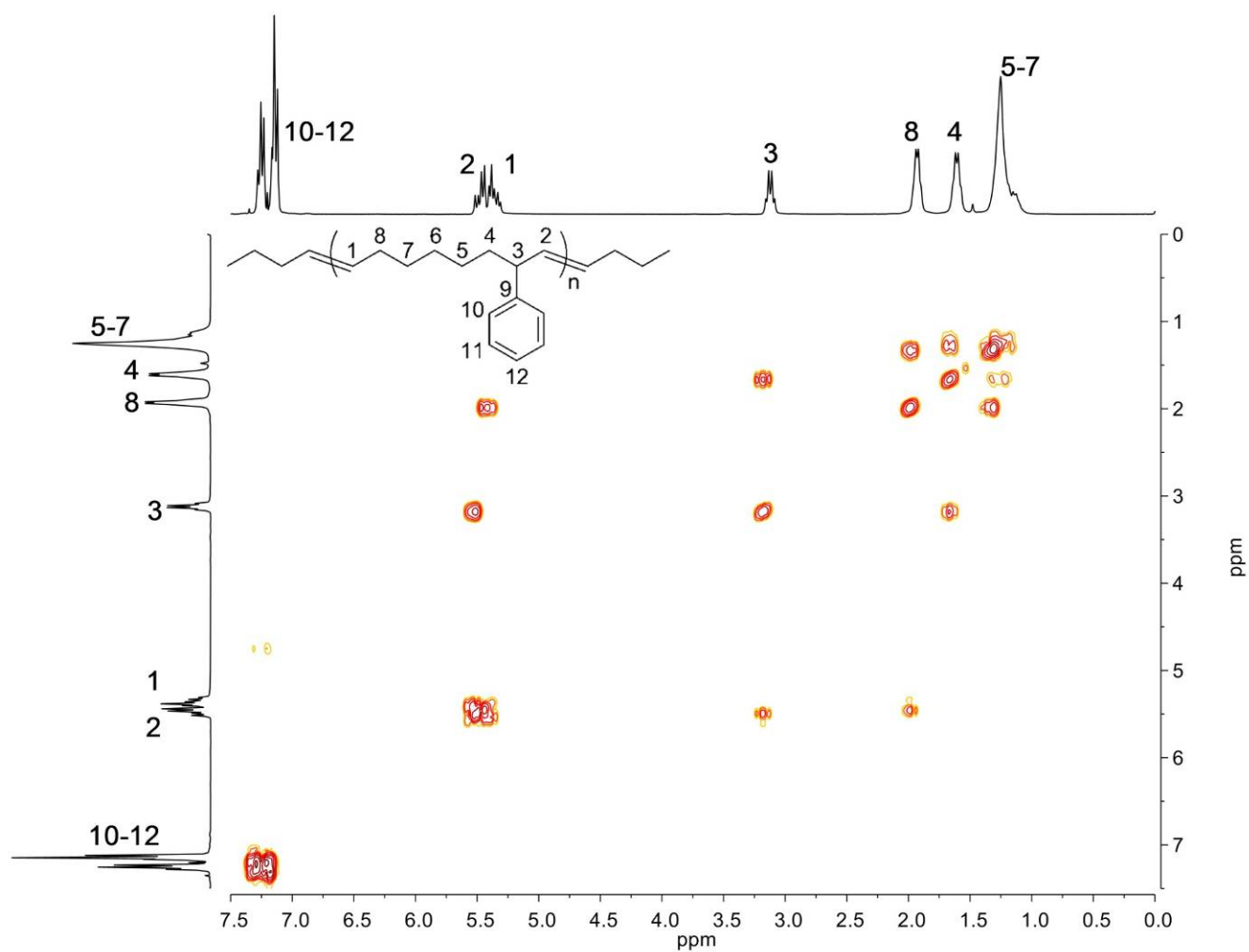


Figure S57. ^1H - ^1H COSY spectrum of poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

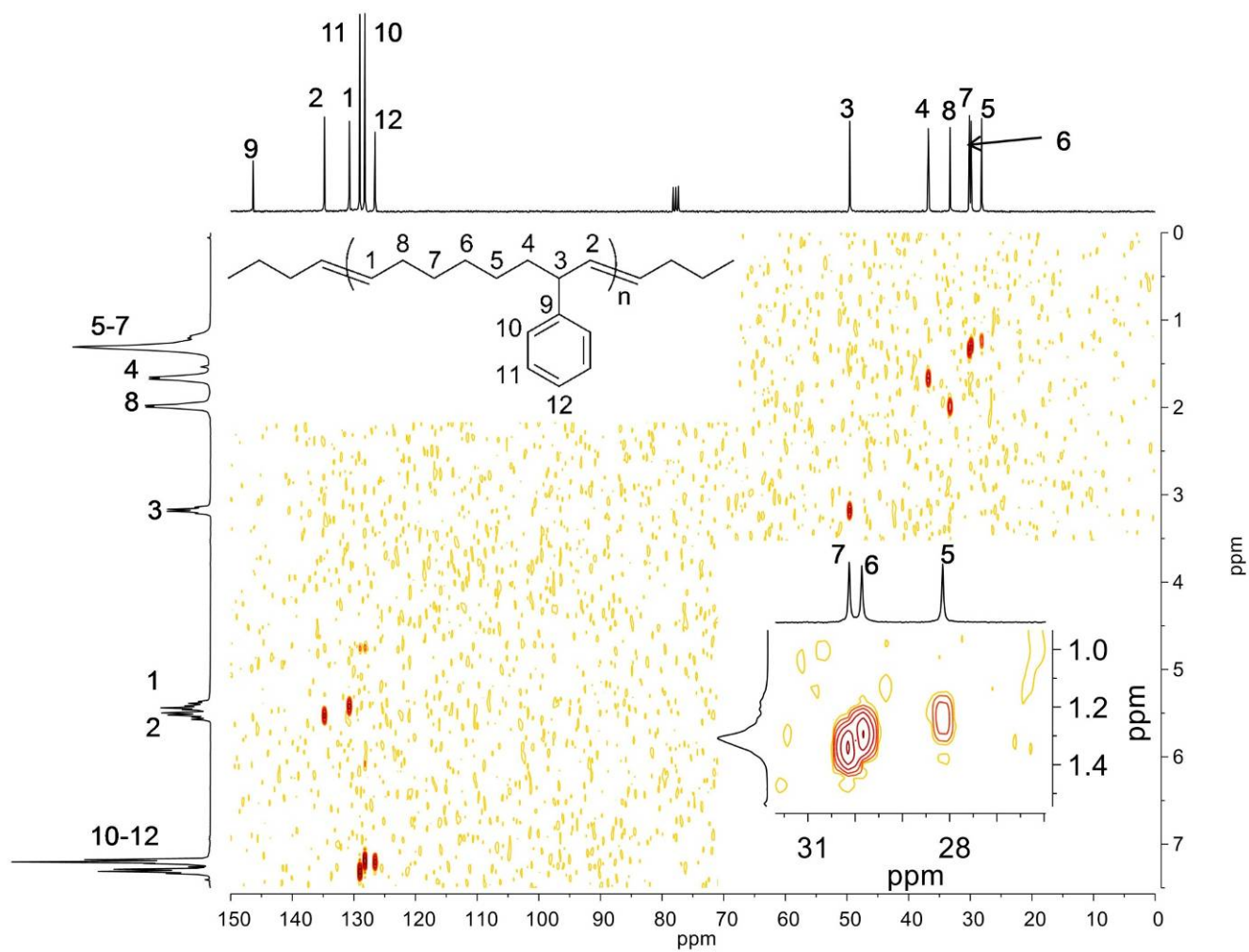


Figure S58. HETCOSY spectrum of poly(3-phenyl-1-cyclooctene) (in CDCl₃, 75 MHz).

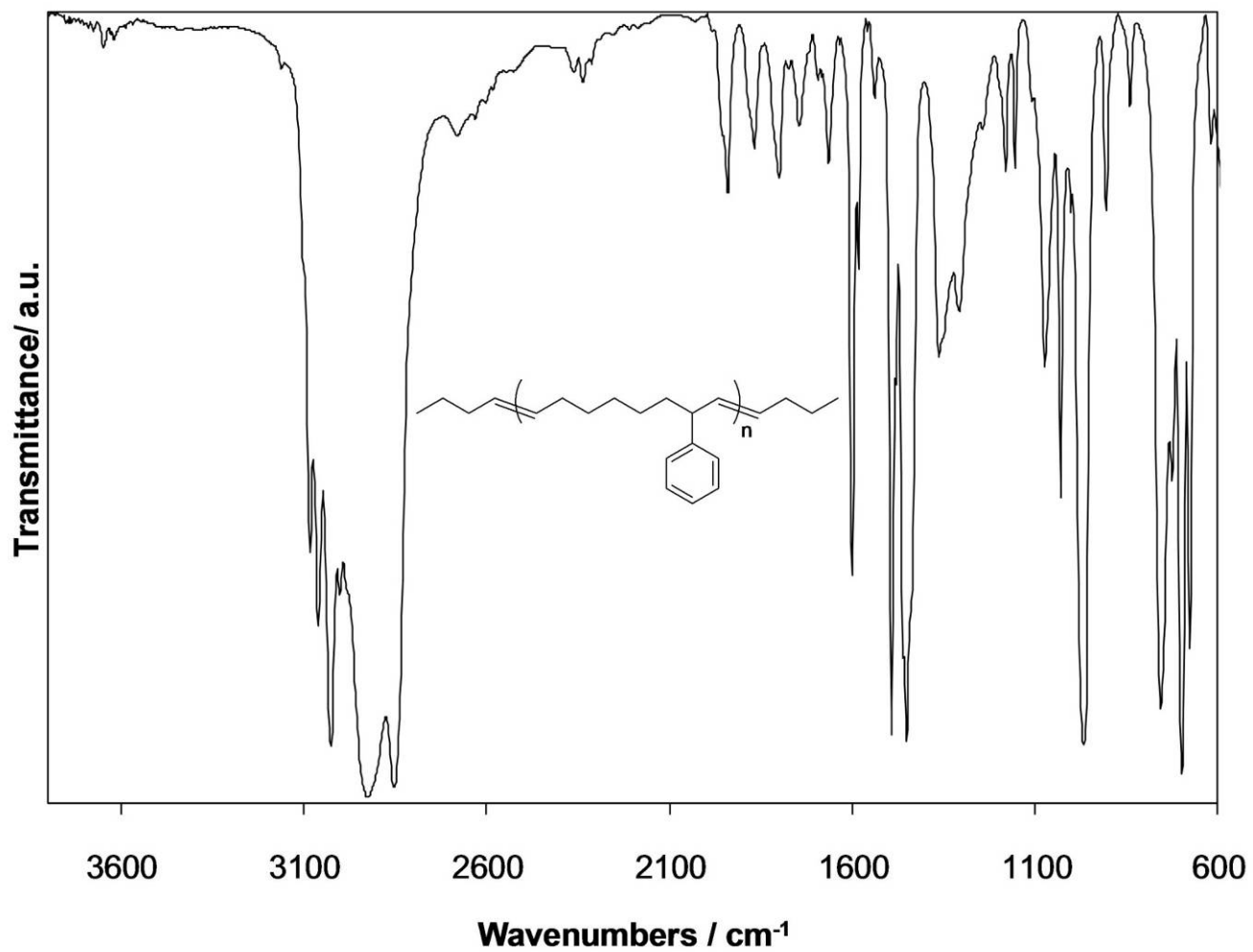
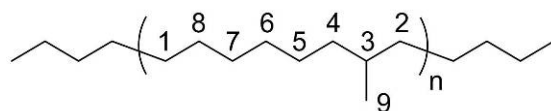


Figure S59. IR spectrum of poly(3-phenyl-1-cyclooctene) (neat).

6. General Chemical Hydrogenation Procedure.

An example of the chemical hydrogenation procedure is described for the hydrogenation of poly(3HexCOE) (entry 5 in Table 1). A mixture of poly(3HexCOE) (1.10 g, 5.66 mmol of olefin), *p*-toluenesulfonhydrazide (5.0 g, 25 mmol), tributylamine (5.2 g, 28 mmol), small amount of BHT (ca. 5 mg), and *o*-xylene (50 mL) was refluxed for 8 h, and then allowed to cool to room temperature. The reaction mixture was poured into methanol and the polymer precipitated. The precipitated polymer was isolated by decantation and purified by repeating reprecipitation using benzene/methanol system. The polymer was freeze dried overnight from its benzene solution to afford hydrogenated poly(3HexCOE) (1.03 g, 94wt%) as a viscous liquid. The following is the complete list.

hydrogenated poly(3MeCOE) (Figure S60-Figure S65)



^1H NMR (500 MHz, CDCl_3): δ = 1.41–1.16 (m, 13H, $-\text{CH}_2-$, $-\text{C}(3)\text{HMe}-$), 1.15–1.02 (m, 2H, $-\text{C}(2)\text{HH}-$, $-\text{C}(4)\text{HH}-$), 0.84 (d, J = 6.5 Hz, 3H, $-\text{C}(9)\text{H}_3$).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.23 (C2, C4), 32.87 (C3), 30.18 (C6, C8), 29.91 (C7), 27.22 (C1, C5), 19.84 (C9).

IR (neat): 2953, 2920, 2851, 2722, 2686, 1742, 1558, 1464, 1376, 1303, 1262, 1155, 1088, 1024, 940, 805, 722 cm^{-1} .

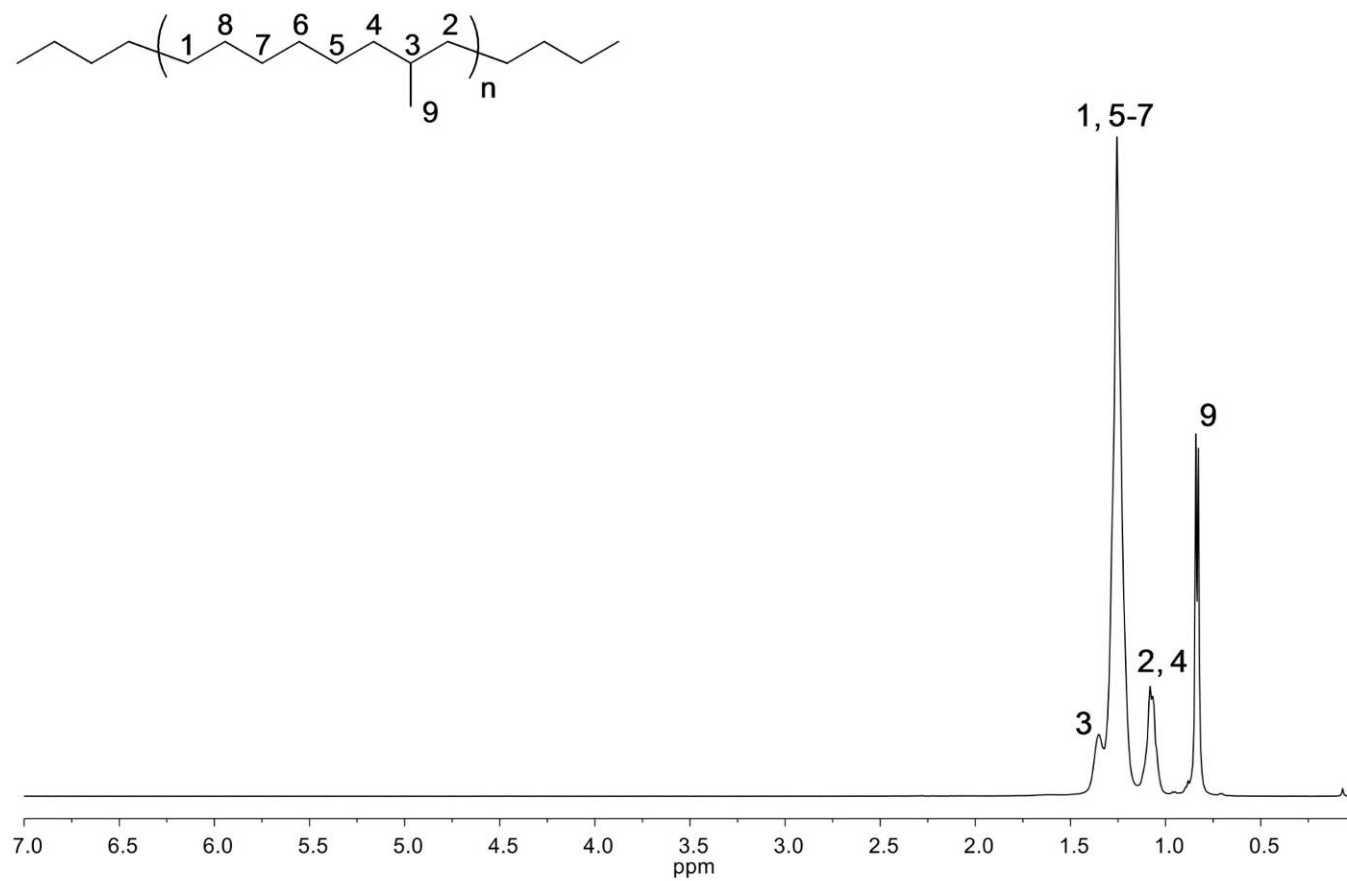


Figure S60. ^1H NMR spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

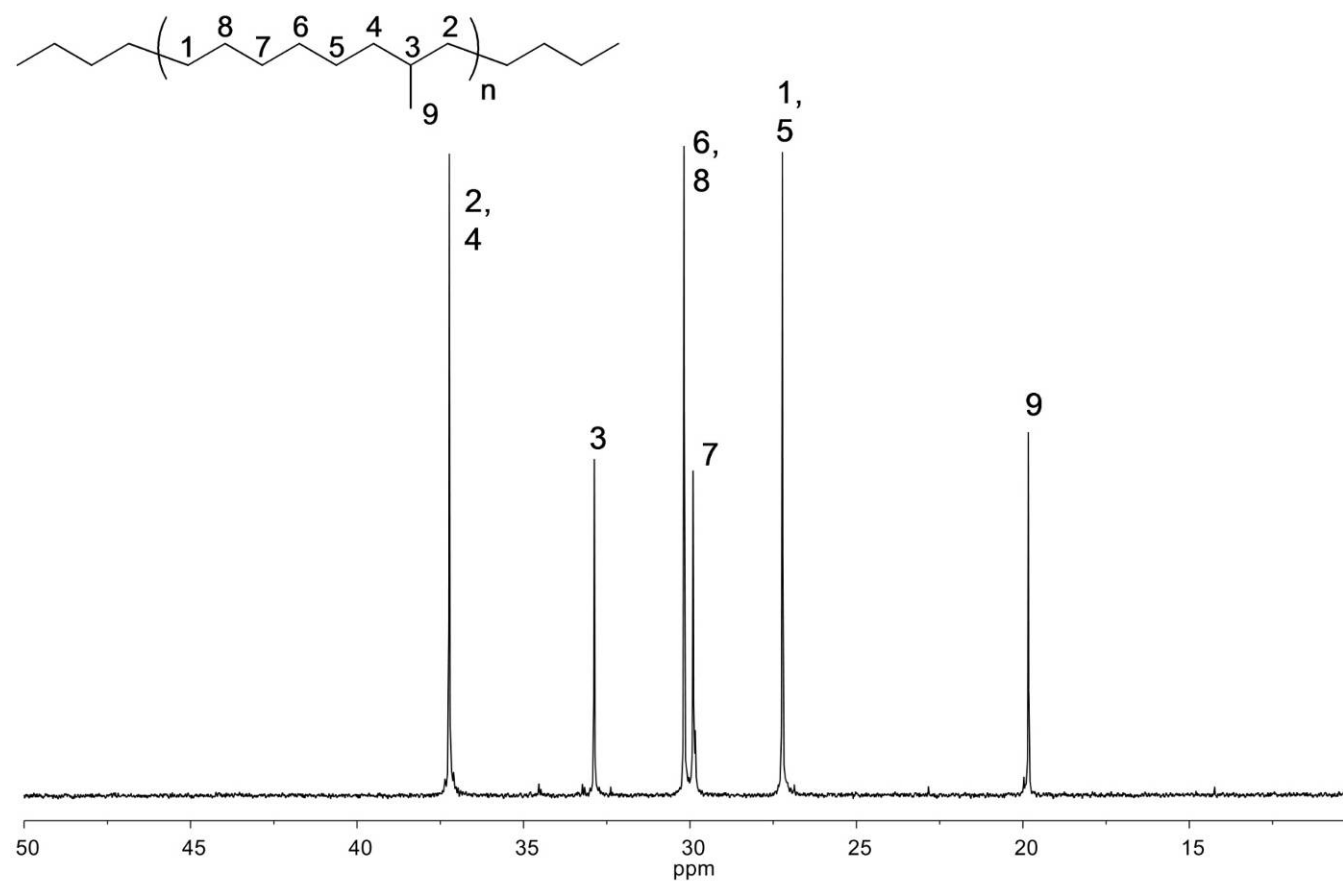


Figure S61. ^{13}C NMR spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

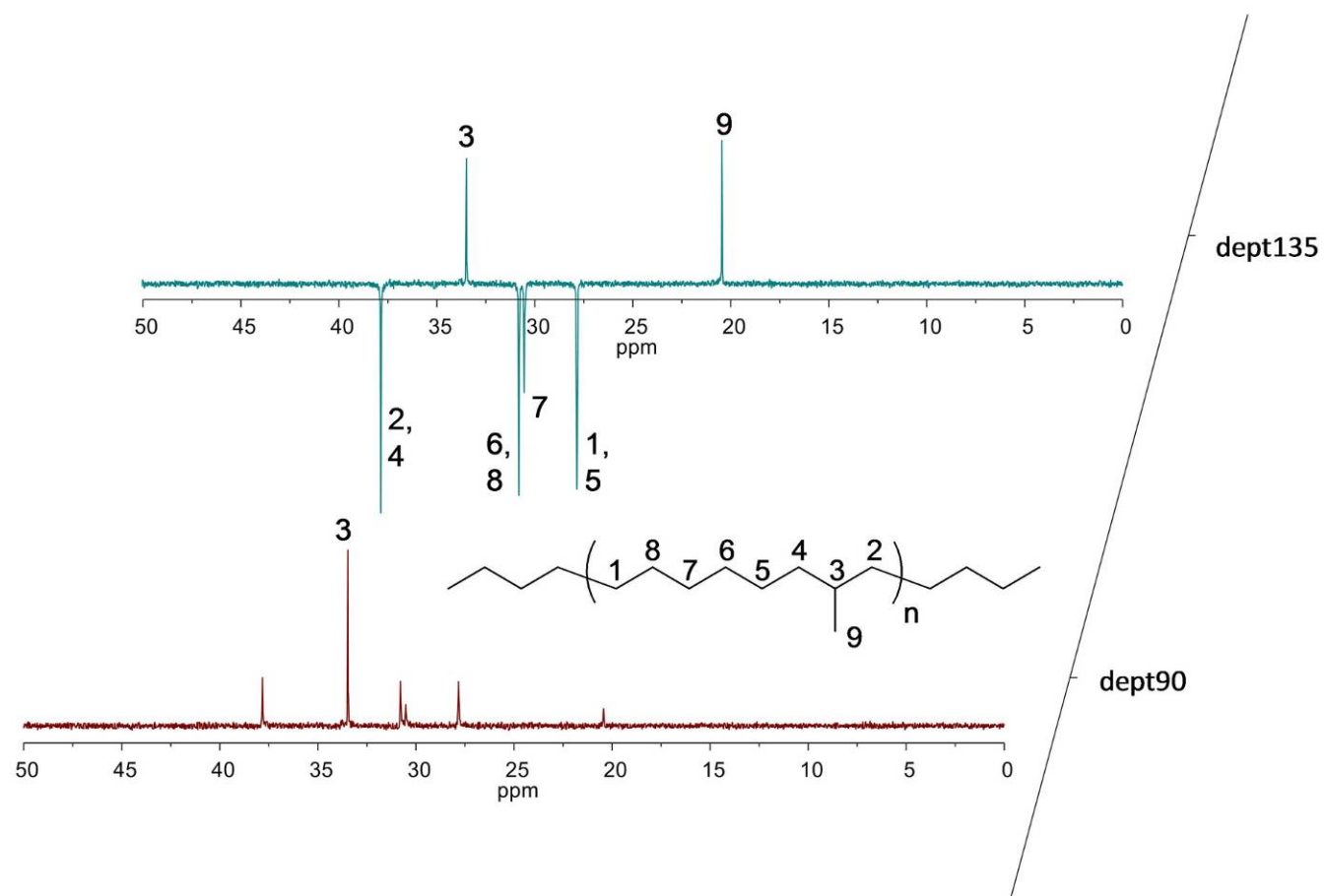


Figure S62. DEPT spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (in CDCl₃, 75 MHz).

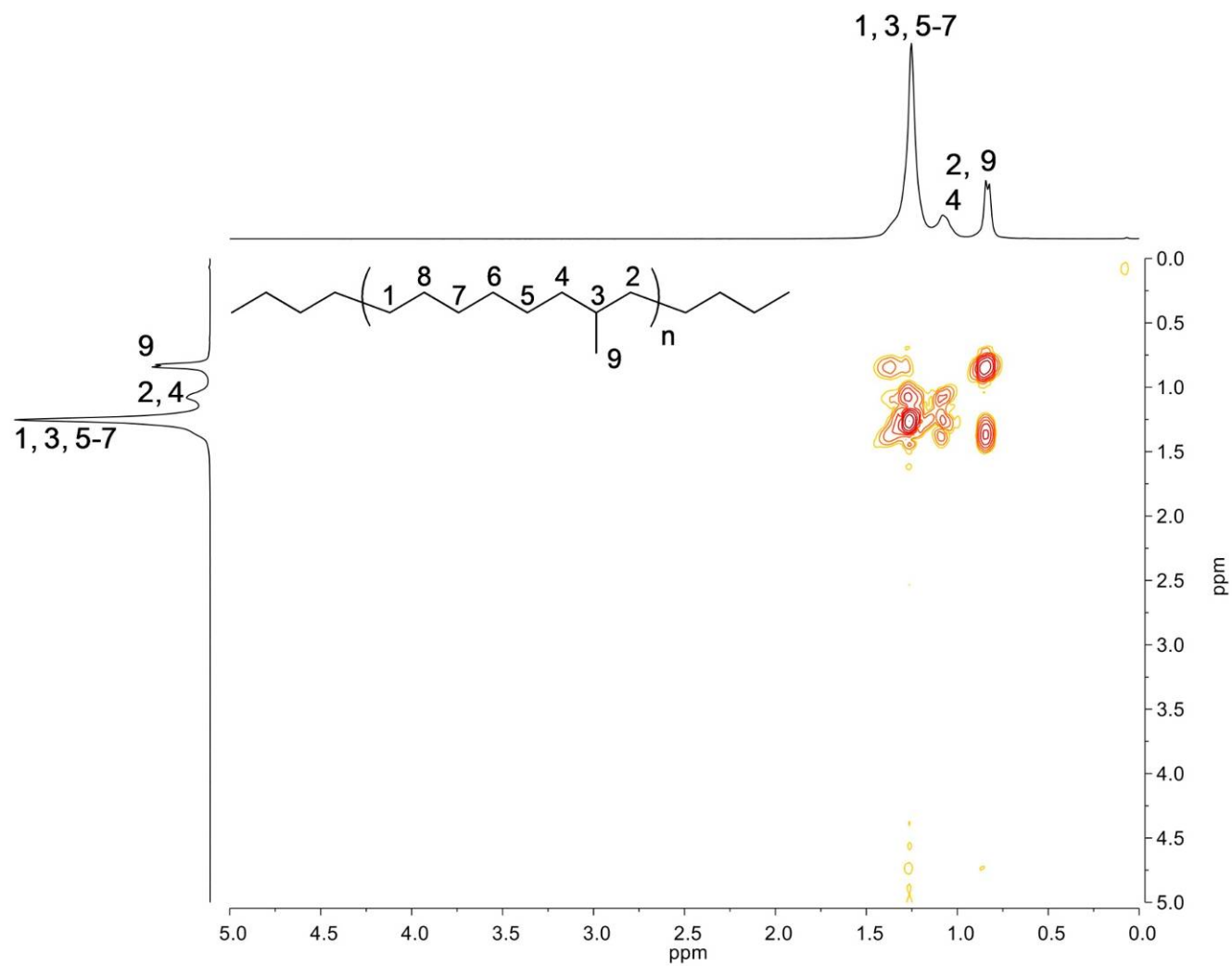


Figure S63. ^1H - ^1H COSY spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

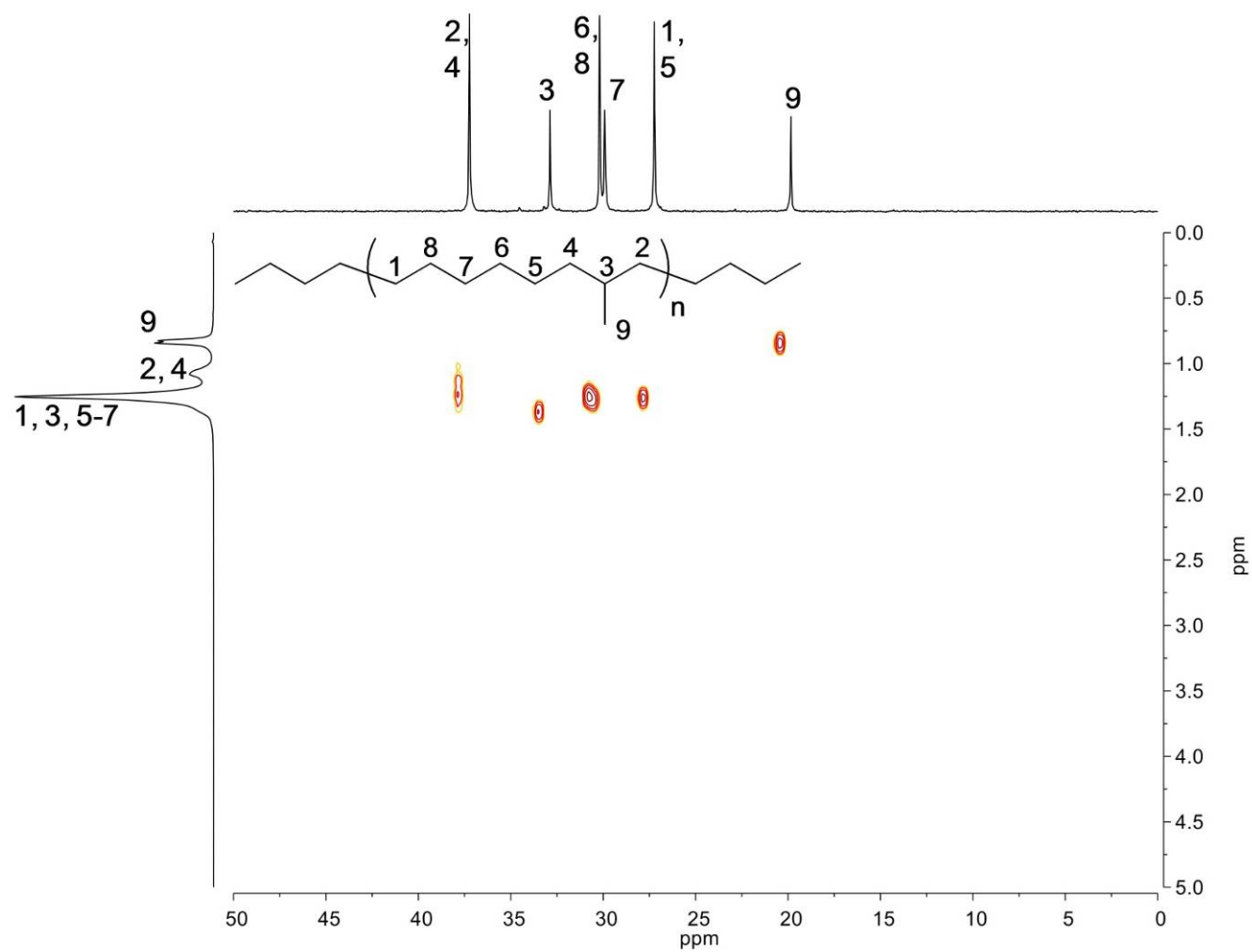


Figure S64. HETCOSY spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (in CDCl_3 , 75 MHz).

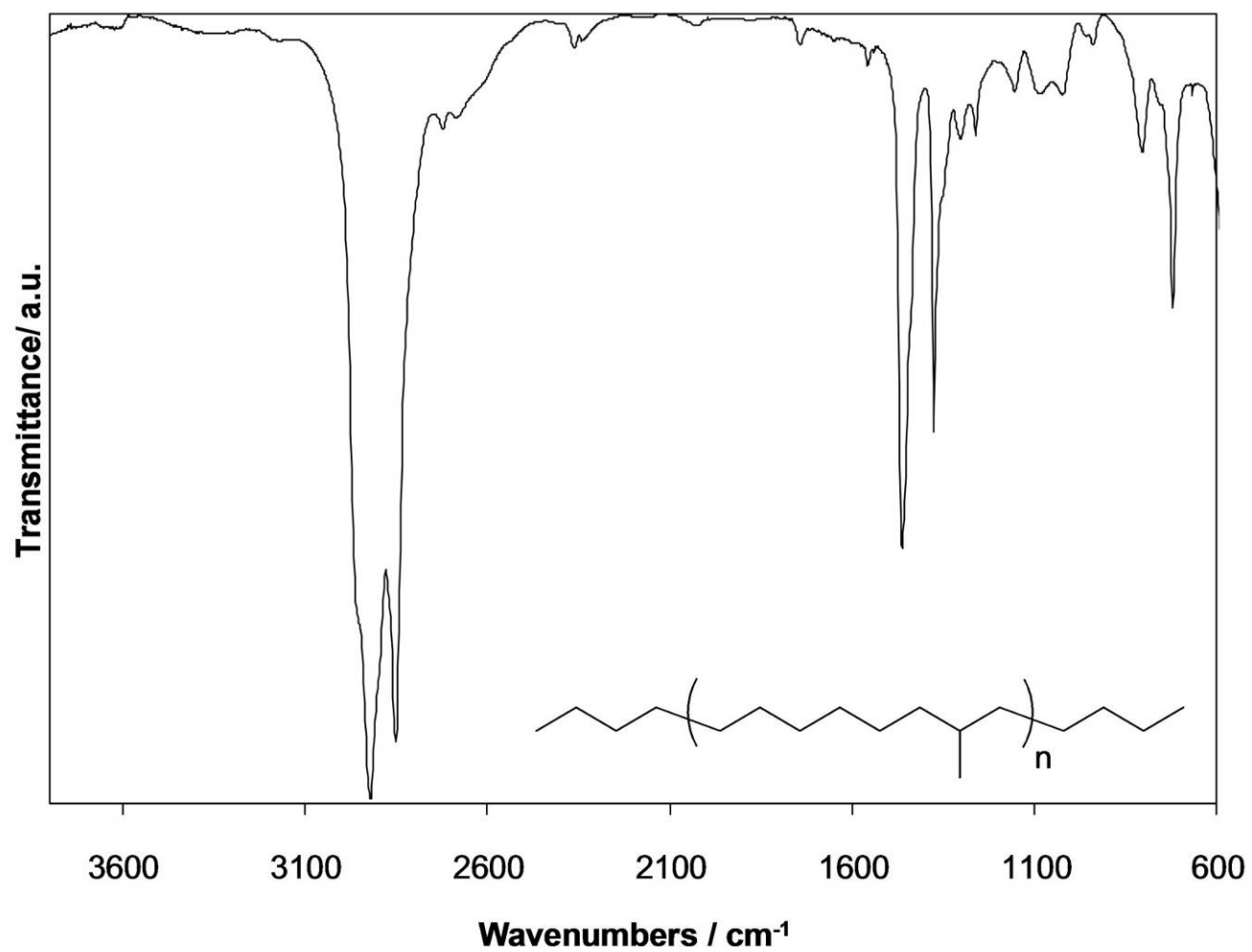
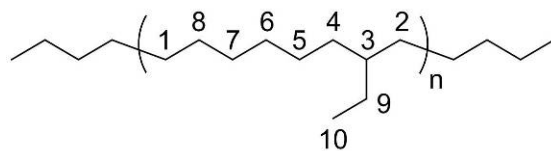


Figure S65. IR spectrum of hydrogenated poly(3-methyl-1-cyclooctene) (neat).

hydrogenated poly(3EtCOE) (Figure S66-Figure S71)



^1H NMR (500 MHz, CDCl_3): δ = δ 1.45–1.07 (br, 17H, $-\text{CH}_2-$, $-\text{C}(3)\text{HEt}-$), 1.01–0.75 (t, J = 3H, 7.3 Hz, $-\text{C}(10)\text{H}_3$).

^{13}C NMR (125 MHz, CDCl_3): δ = 38.98 (C3), 33.34 (C2, C4), 30.32 (C6, C8), 29.91 (C7), 26.88 (C1, C5), 26.00 (C9), 10.99 (C10).

IR (neat): 2959, 2923, 2854, 2728, 2681, 1462, 1379, 1302, 1262, 1088, 1032, 803, 773, 721 cm^{-1} .

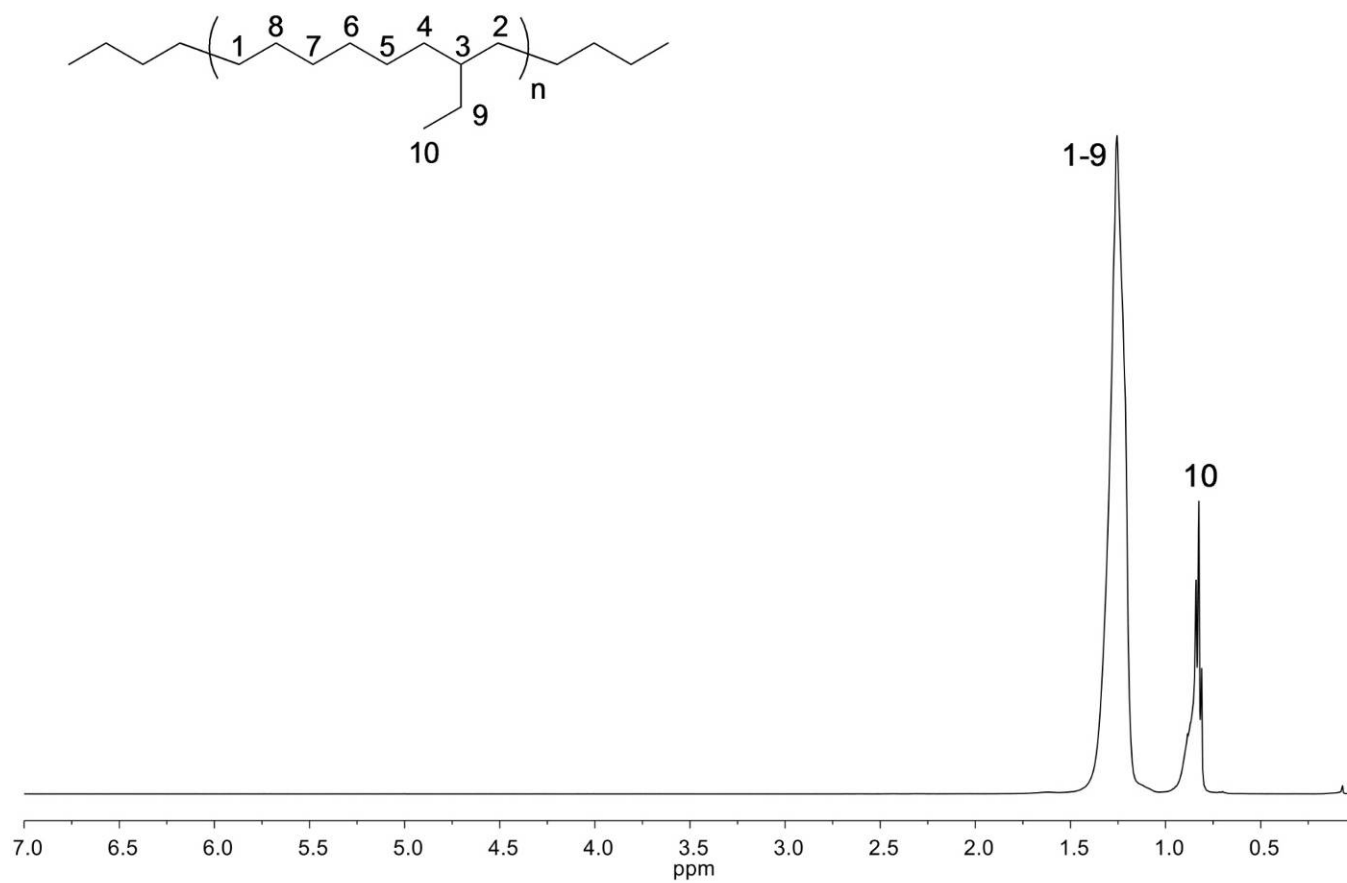


Figure S66. ^1H NMR spectrum of hydrogenated poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

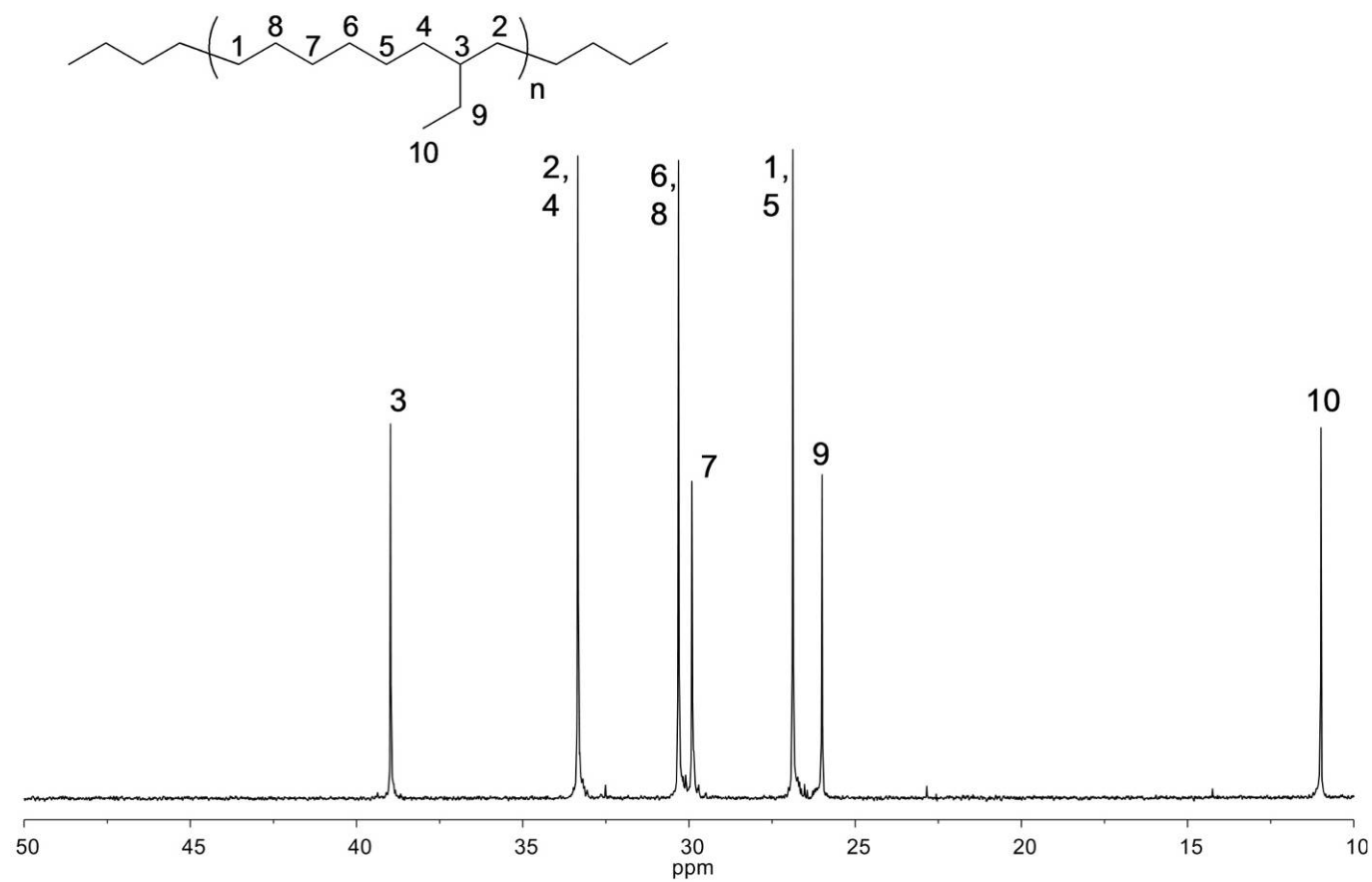


Figure S67. ^{13}C NMR spectrum of hydrogenated poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

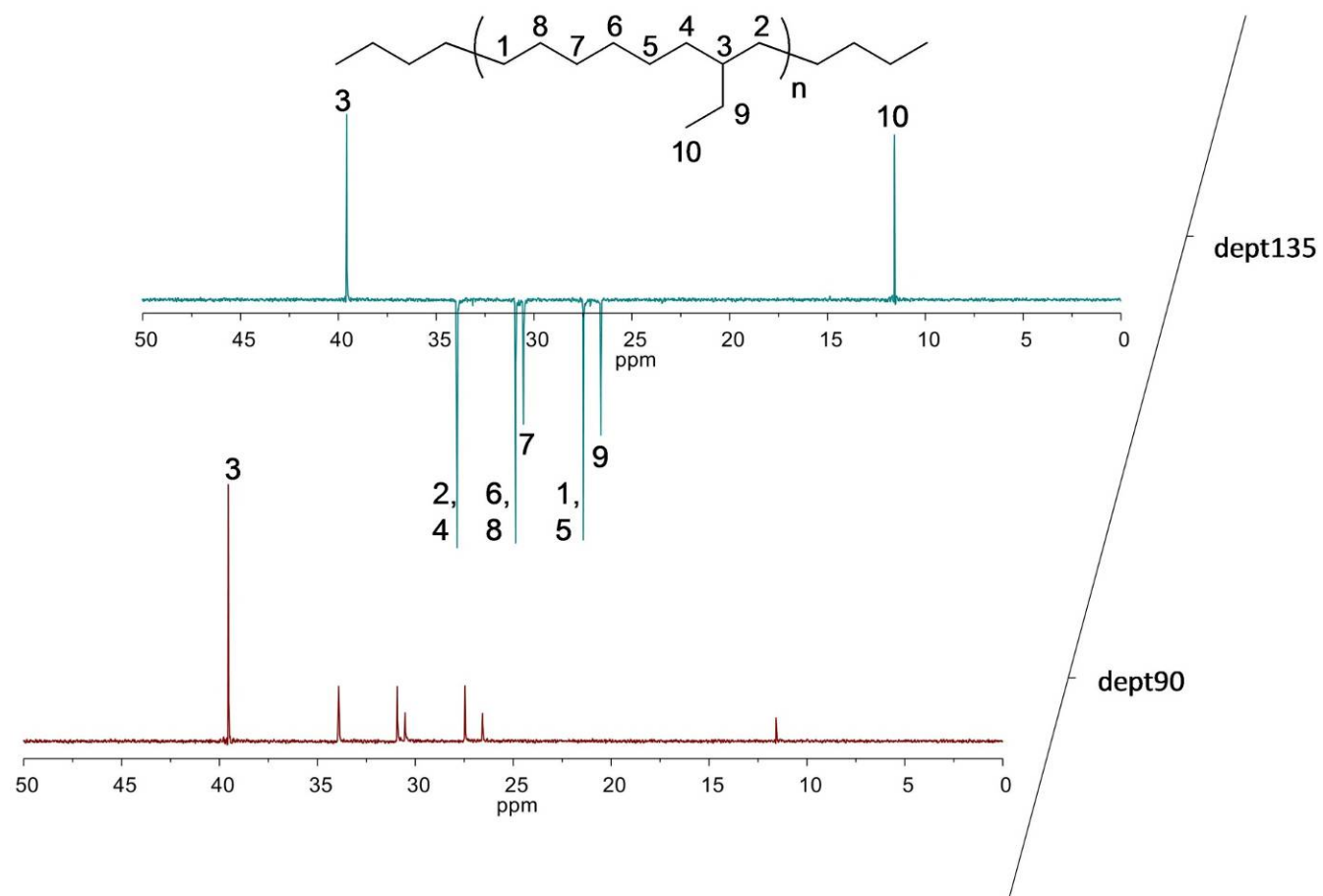


Figure S68. DEPT spectrum of hydrogenated poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 75 MHz).

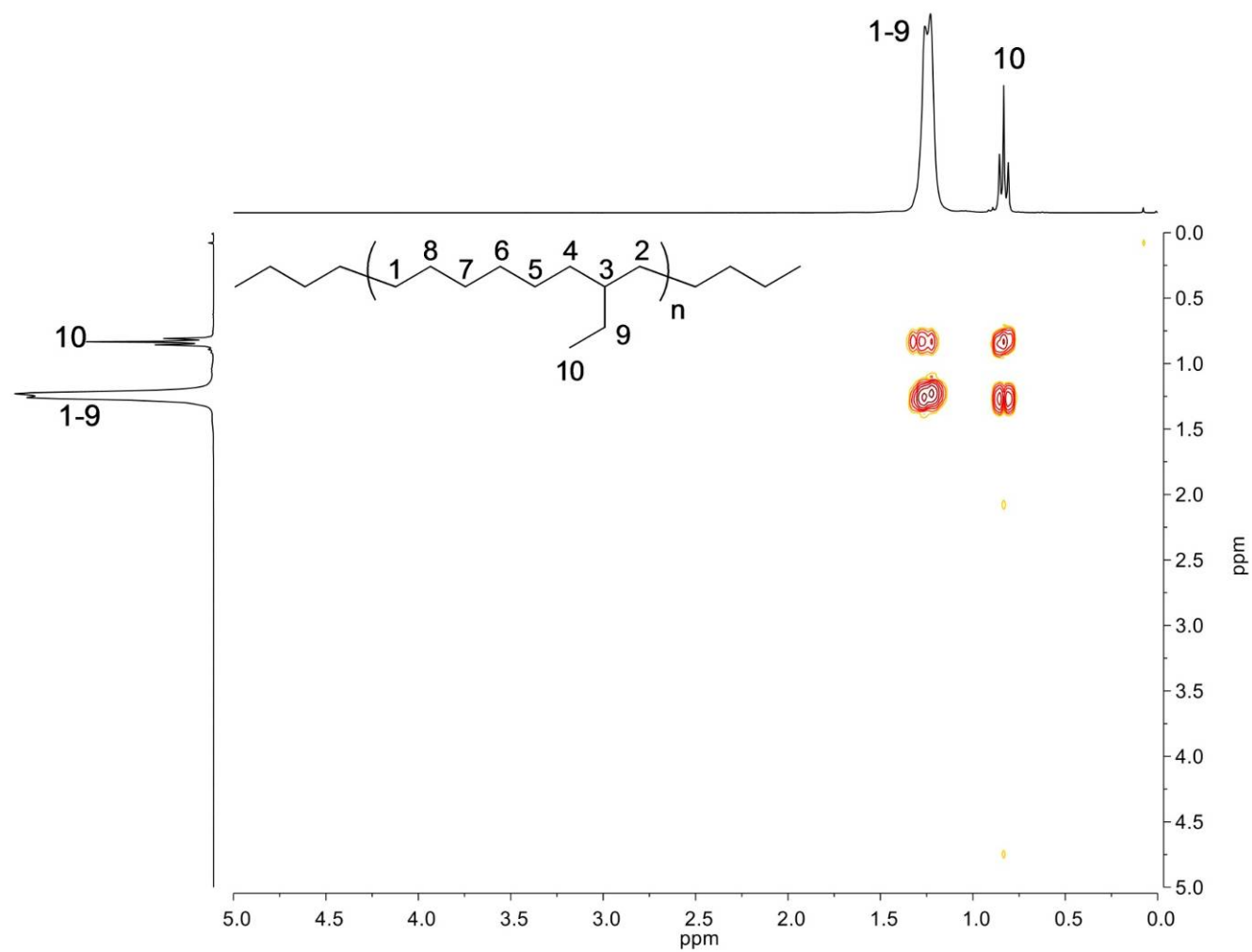


Figure S69. ^1H - ^1H COSY spectrum of hydrogenated poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

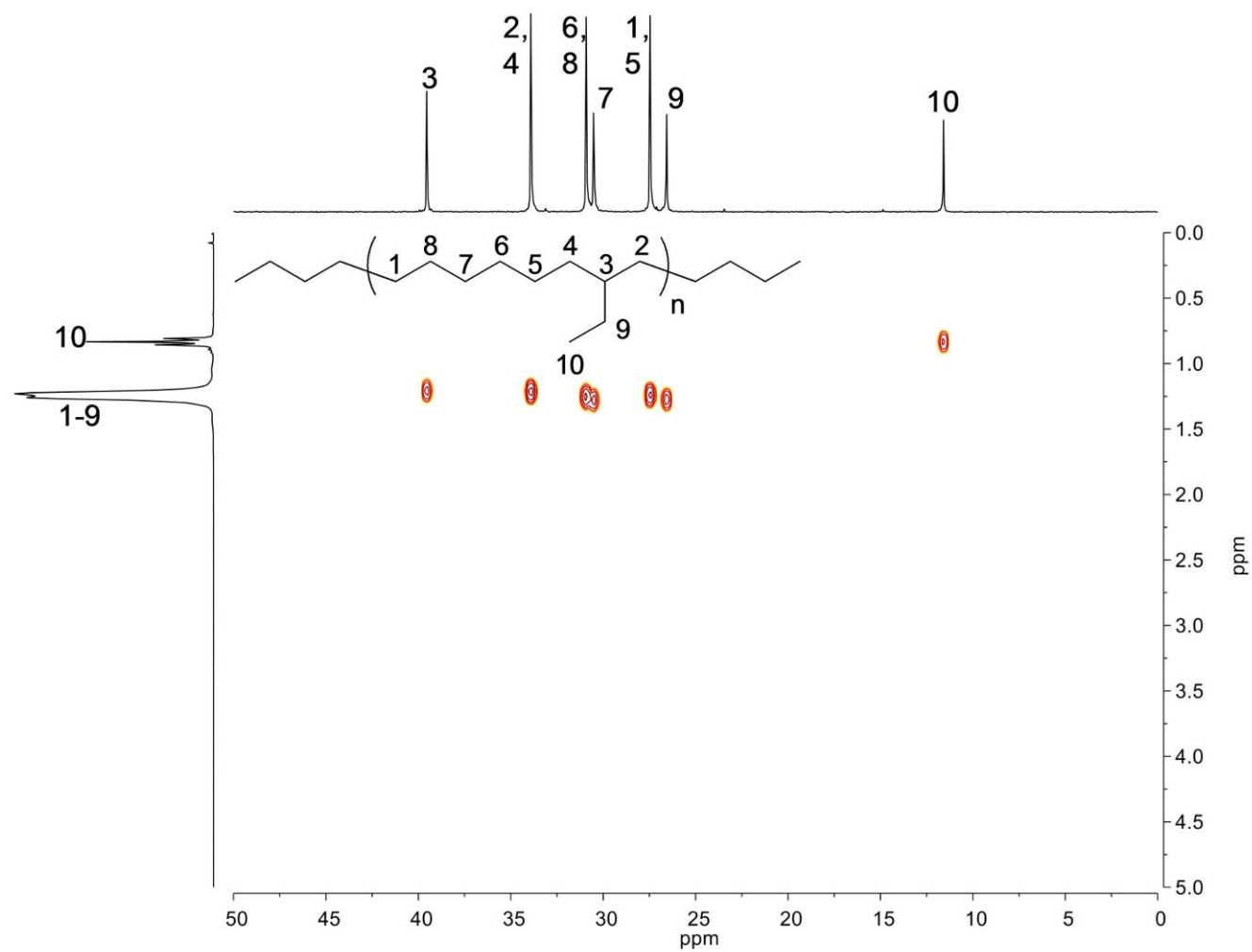
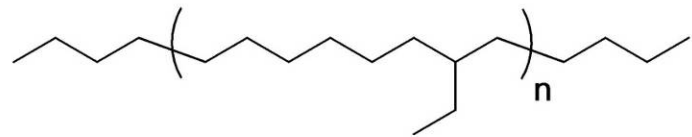
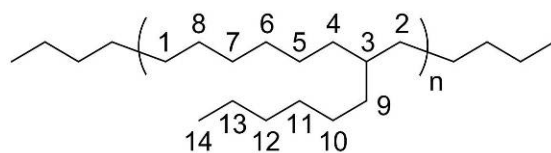


Figure S70. HETCOSY spectrum of hydrogenated poly(3-ethyl-1-cyclooctene) (in CDCl_3 , 75 MHz).



S90

hydrogenated poly(3HexCOE) (Figure S72-Figure S77)



^1H NMR (500 MHz, CDCl_3): δ = 1.35–1.11 (m, 25H, $-\text{CH}_2-$, $-\text{C}(3)\text{HHex}-$), 0.88 (t, J = 6.9 Hz, 3H, $-\text{C}(14)\text{H}_3$).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.55 (C3), 33.85 (C2, C4), 33.81 (C9), 32.10 (C12), 30.34 (C6, C8), 29.98 (C11), 29.92 (C7), 26.86 (C1, C5), 26.80 (C10), 22.85 (C13), 14.25 (C14).

IR (neat): 2953, 2923, 2854, 2729, 2677, 1465, 1377, 1302, 1077, 1017, 802, 722 cm^{-1} .

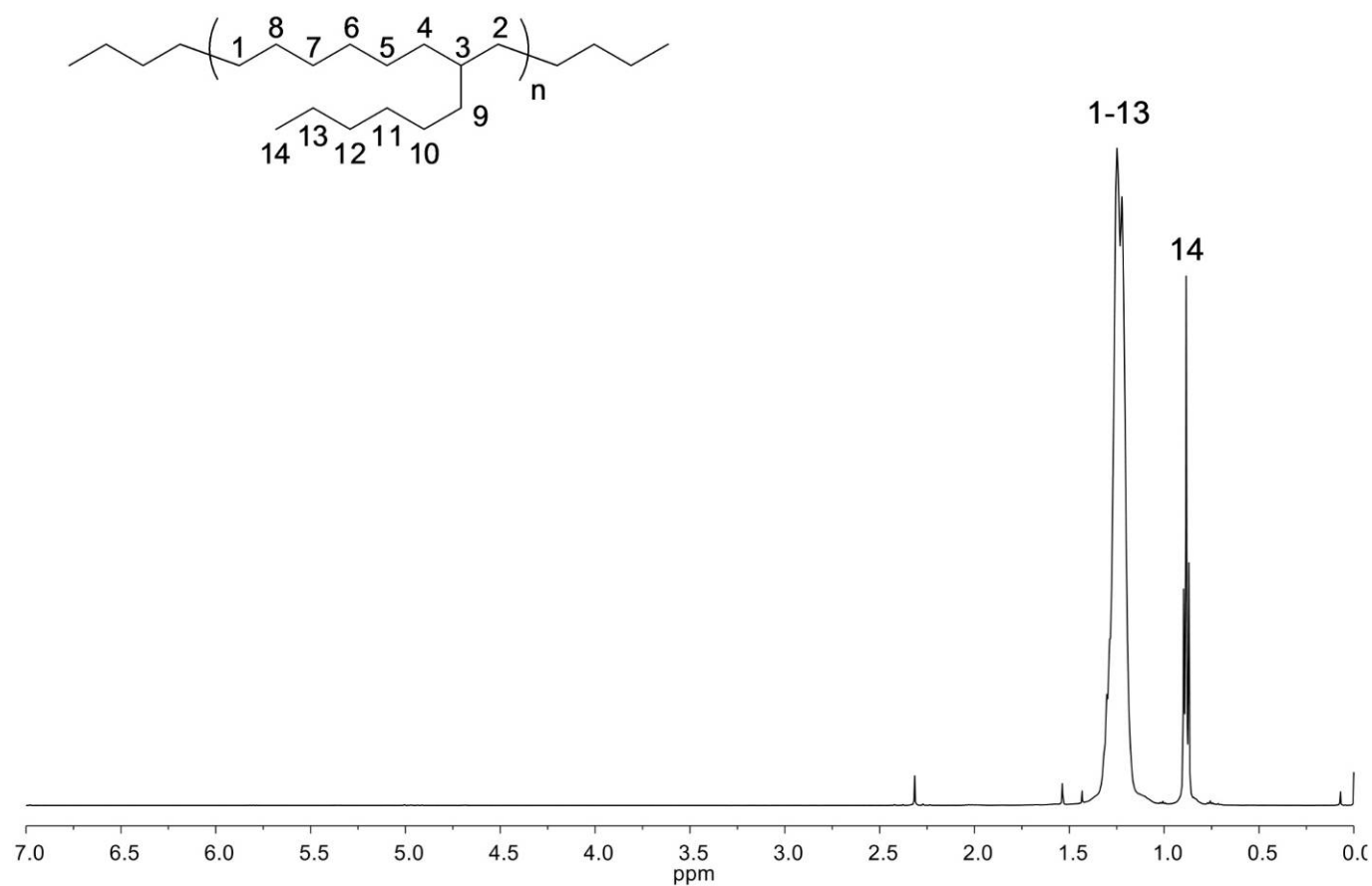


Figure S72. ^1H NMR spectrum of hydrogenated poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

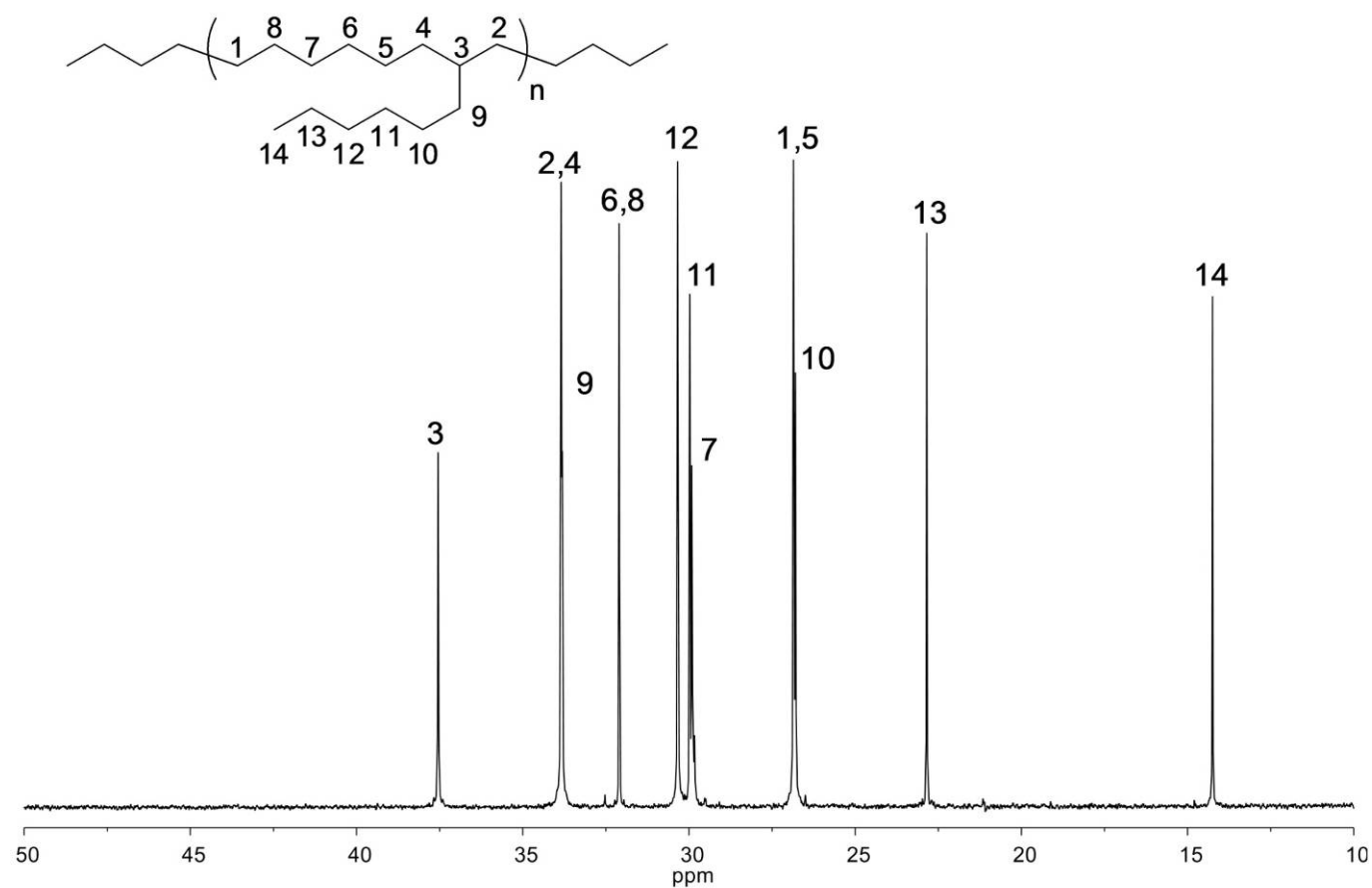


Figure S73. ^{13}C NMR spectrum of hydrogenated poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

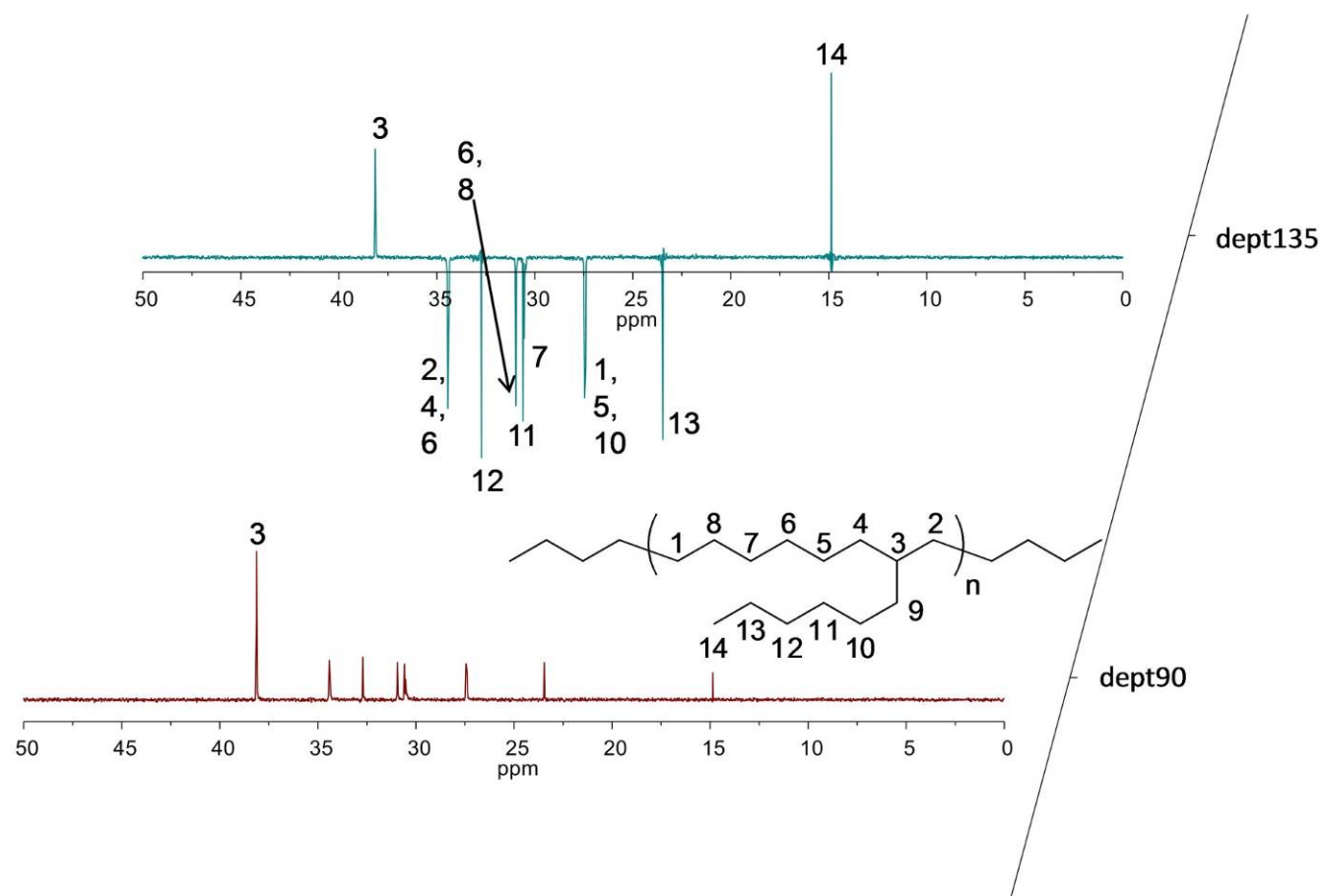


Figure S74. DEPT spectrum of hydrogenated poly(3-hexyl-1-cyclooctene) (in CDCl₃, 75 MHz).

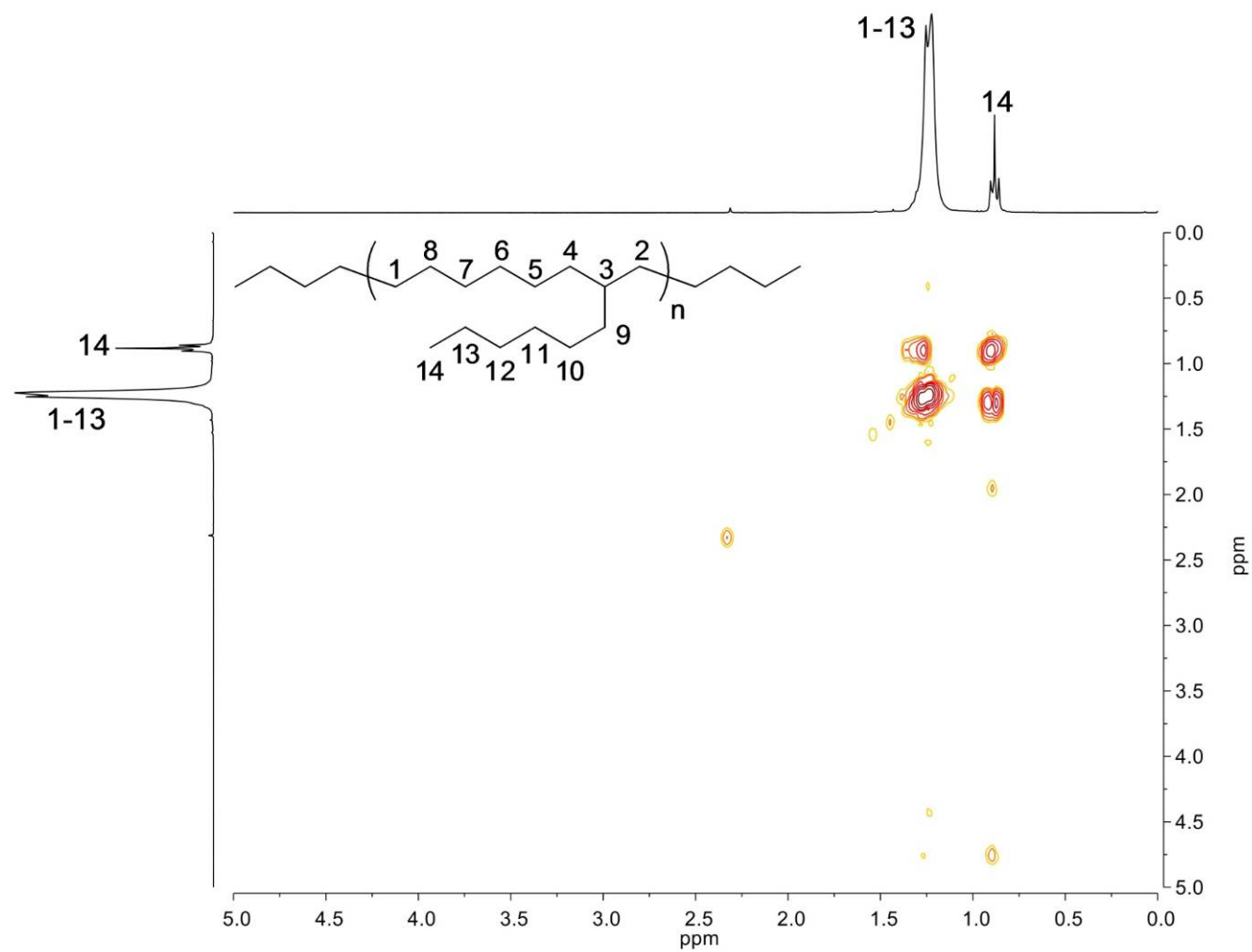


Figure S75. ^1H - ^1H COSY spectrum of hydrogenated poly(3-hexyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

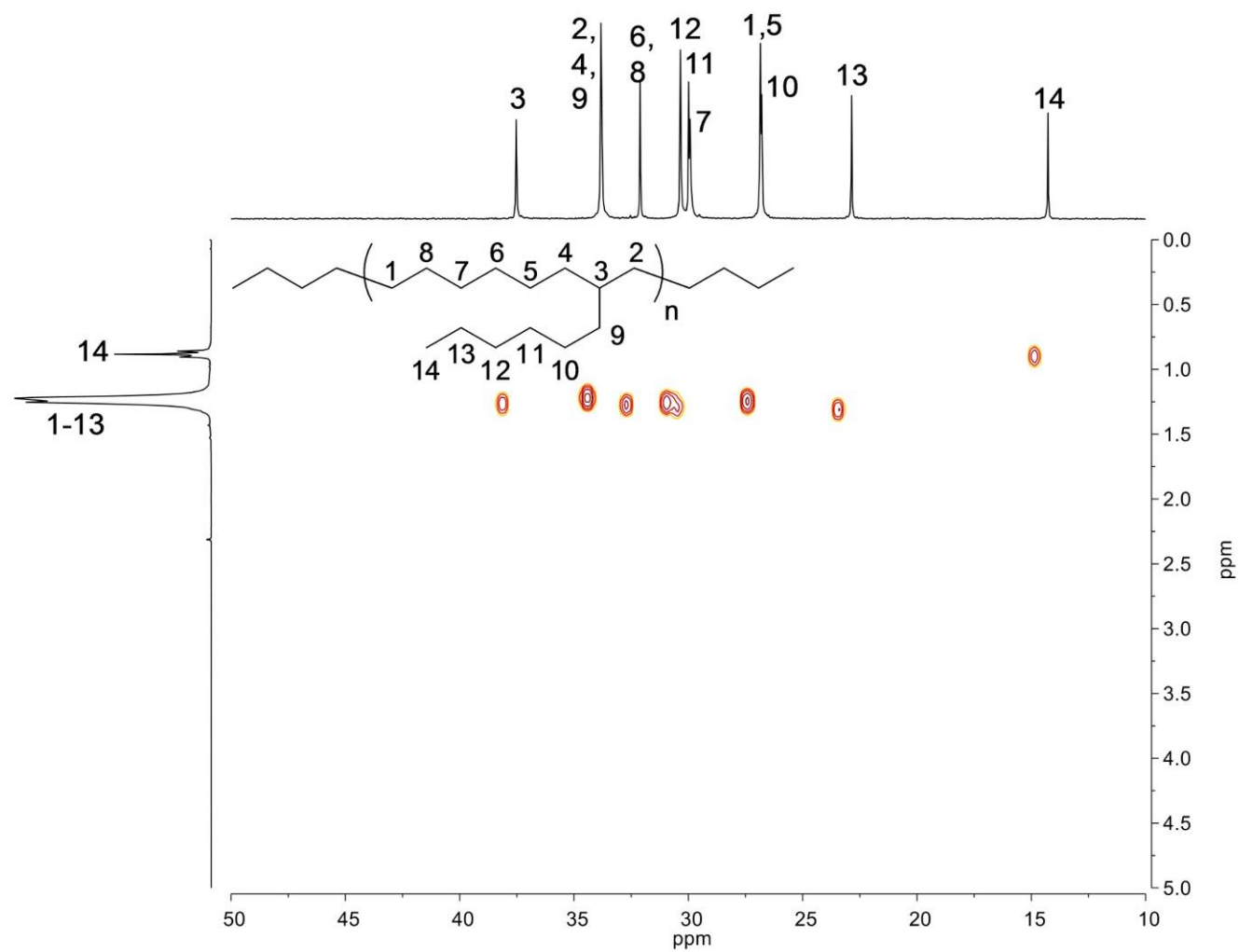
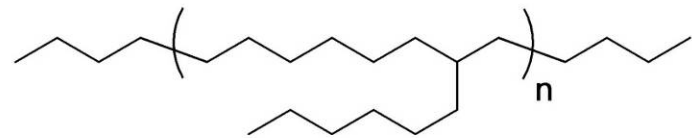
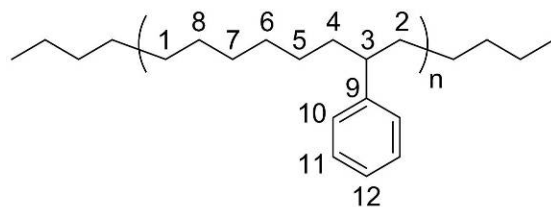


Figure S76. HETCOSY spectrum of hydrogenated poly(3-hexyl-1-cyclooctene) (in CDCl₃, 75 MHz).



S97

hydrogenated poly(**3PhCOE**) (Figure S78-Figure S83)



^1H NMR (500 MHz, CDCl_3): δ = 7.22–6.98 (m, 5H, aromatic), 2.32 (m, 1H, $-\text{C}(3)\text{HPh}-$), 1.53–1.33 (m, 4H, $-\text{C}(2)\text{H}_2-$, $-\text{C}(4)\text{H}_2-$), 1.18–0.88 (m, 10H $-\text{CH}_2$).

^{13}C NMR (125 MHz, CDCl_3): δ = 146.47 (C9), 128.18 (C11), 127.71 (C10), 125.71 (C12), 46.13 (C3), 37.04 (C2, C4), 29.82 (C6, C8), 29.52 (C7), 27.68 (C1, C5).

IR (neat): 3082, 3061, 3025, 2924, 2852, 1939, 1602, 1494, 1452, 1368, 1181, 1068, 1030, 905, 760, 722, 699 cm^{-1} .

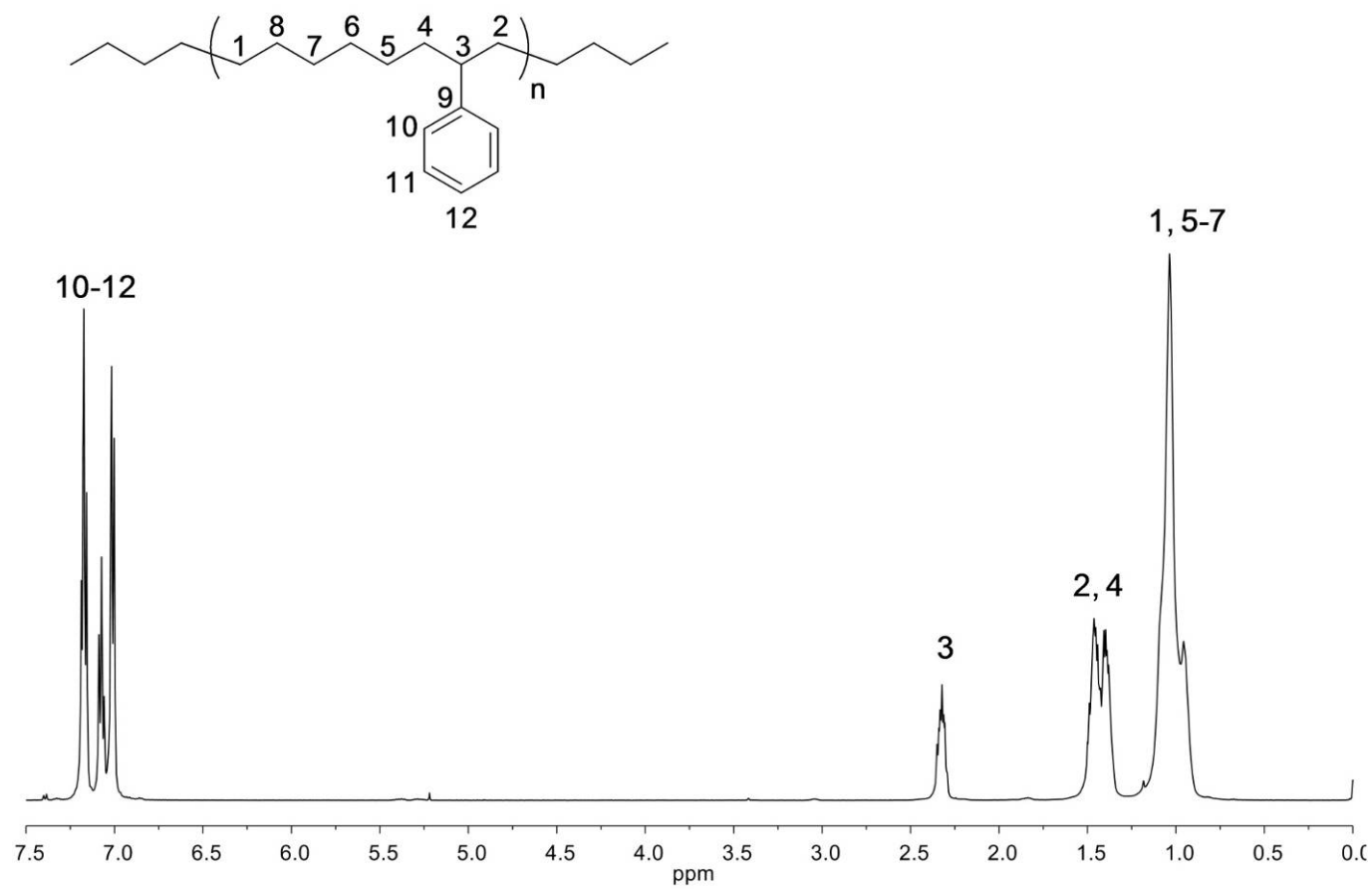


Figure S78. ^1H NMR spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 500 MHz).

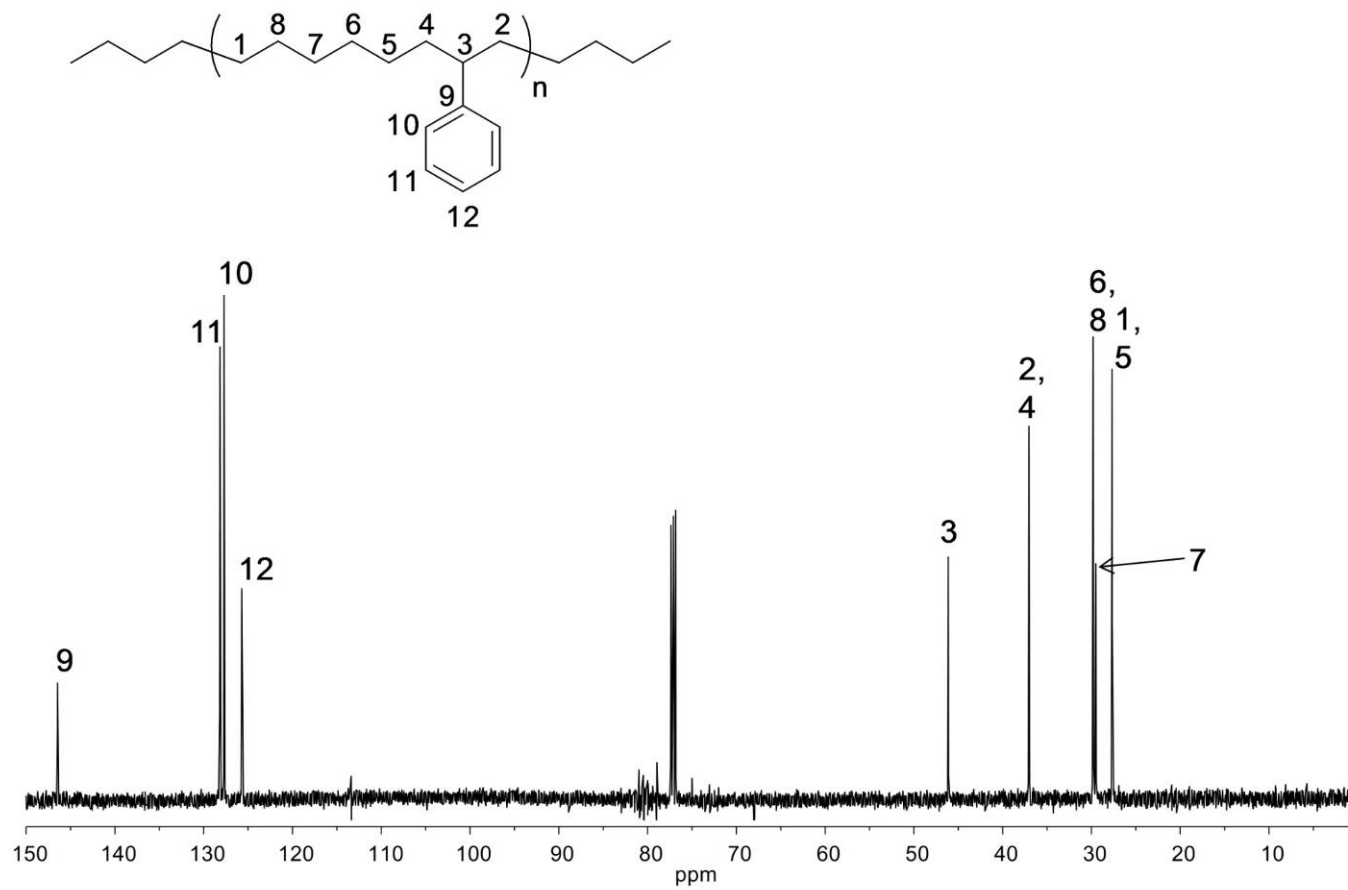


Figure S79. ^{13}C NMR spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 125 MHz).

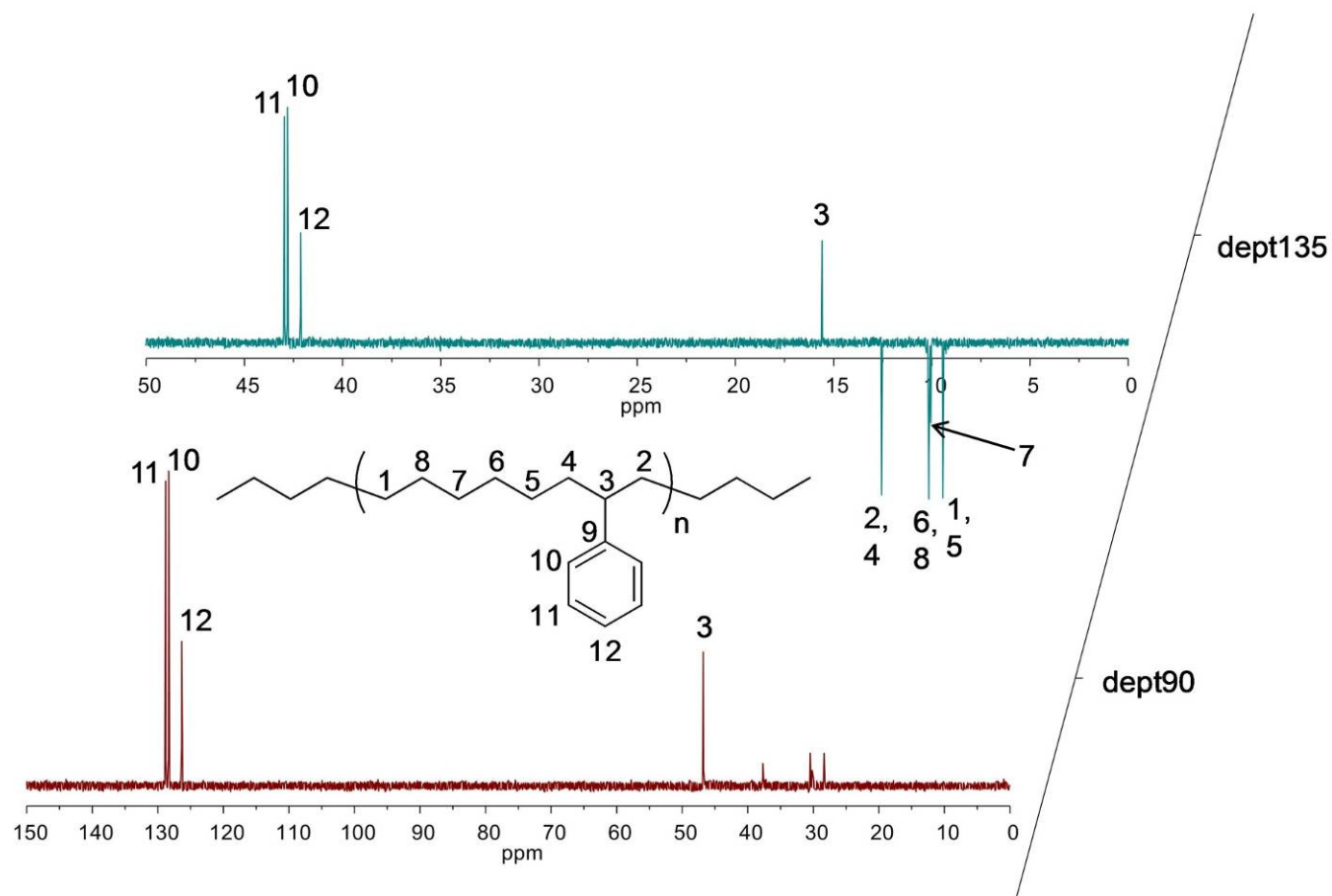


Figure S80. DEPT spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 75 MHz).

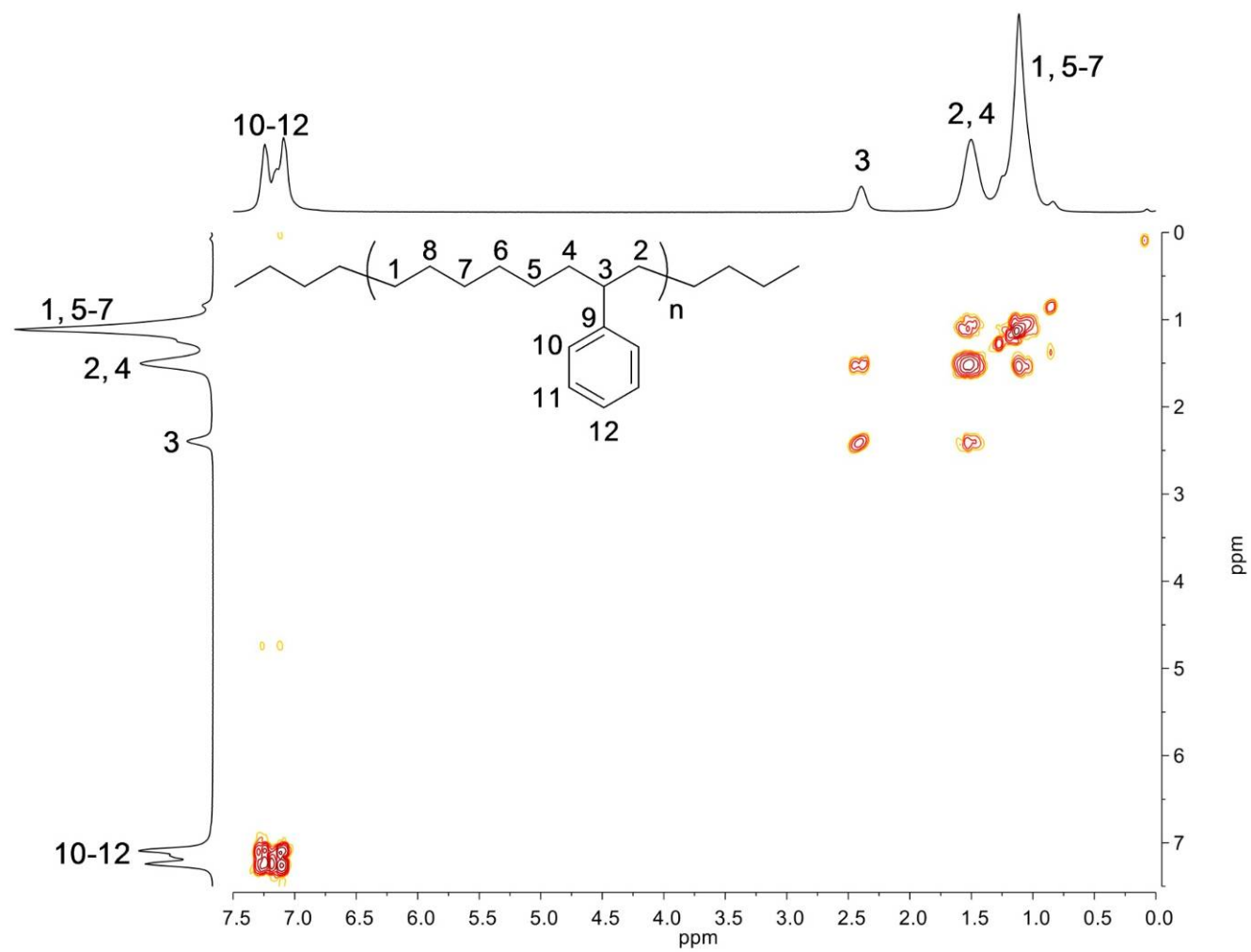


Figure S81. ^1H - ^1H COSY spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (in CDCl_3 , 300 MHz).

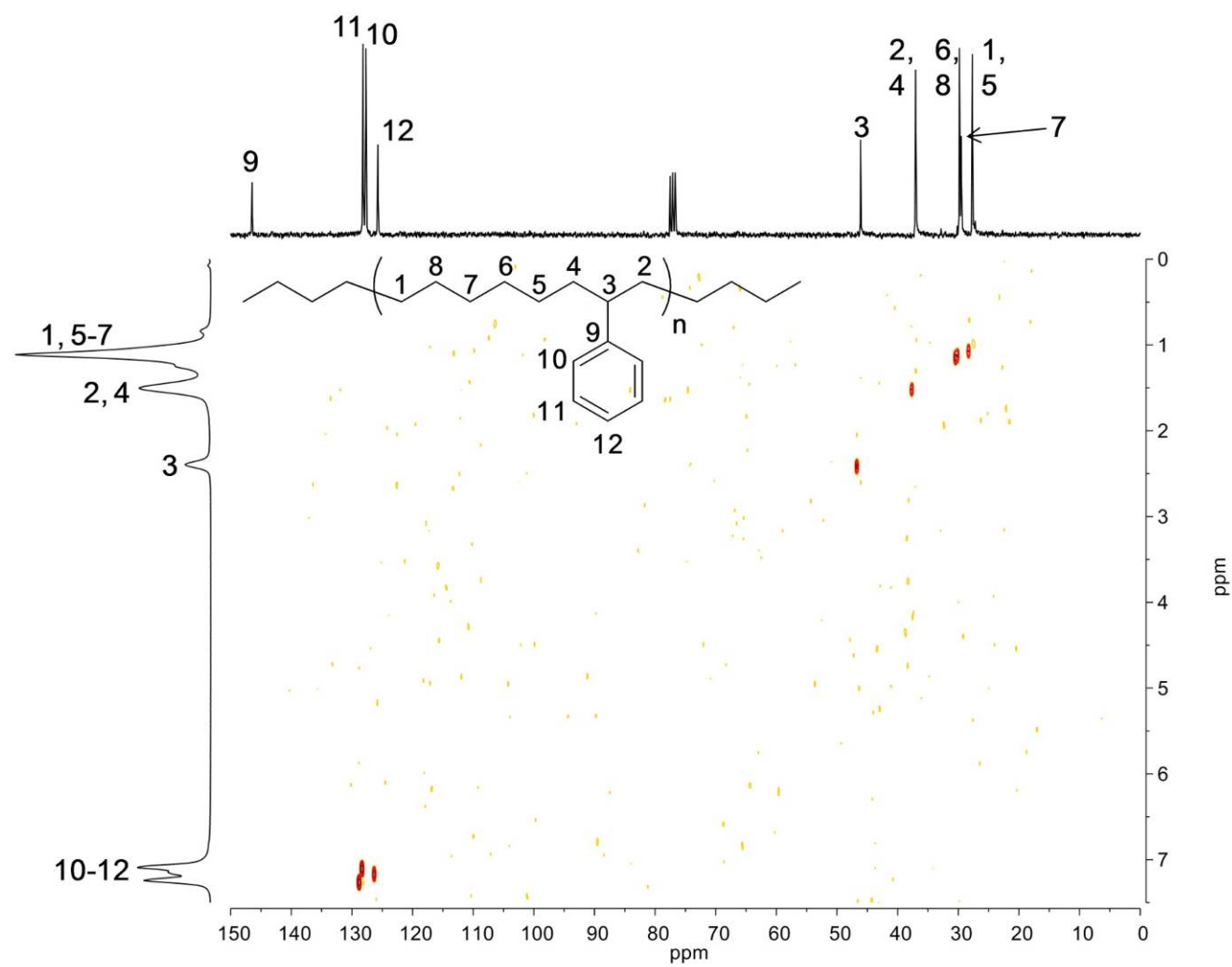


Figure S82. HETCOSY spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (in CDCl₃, 75 MHz).

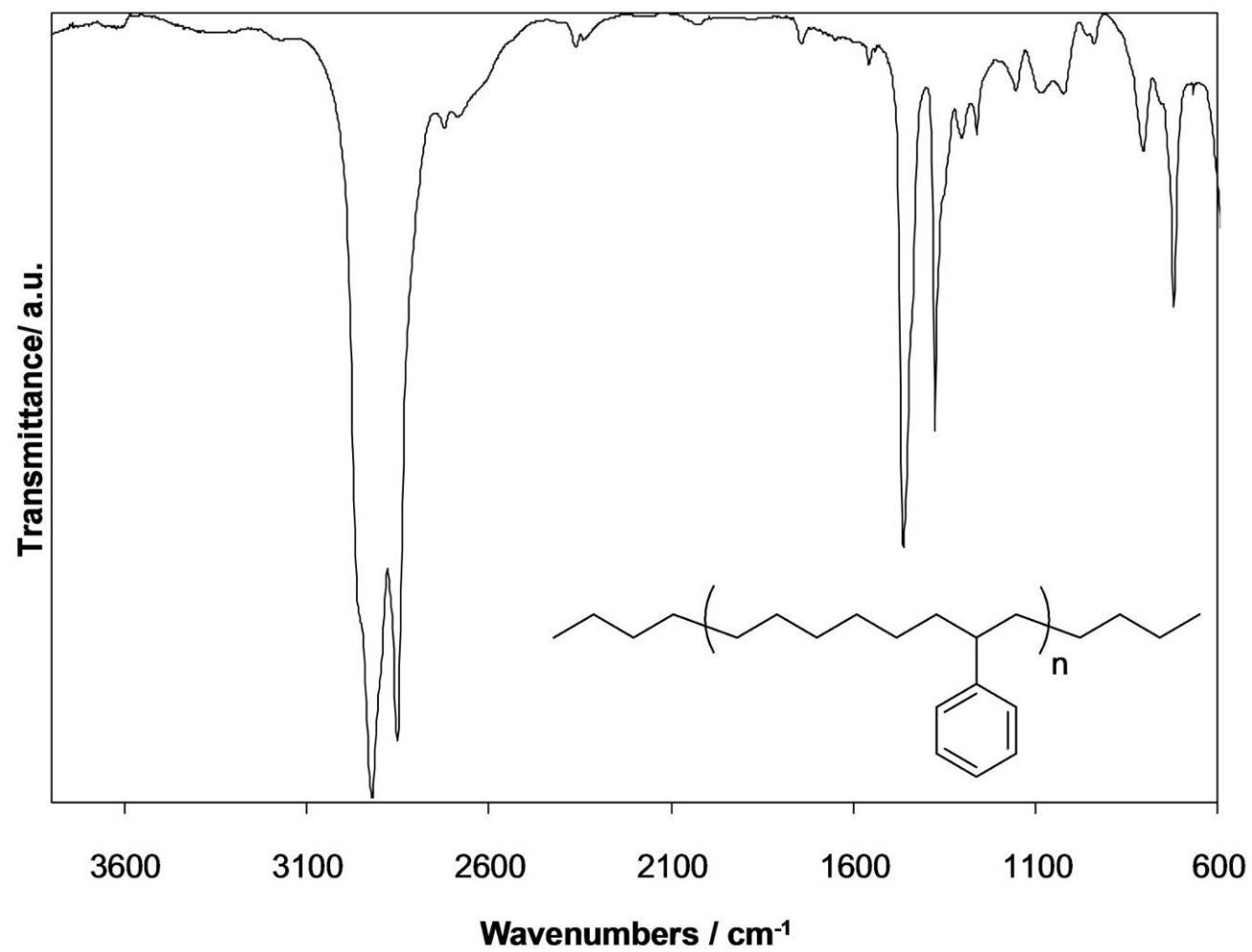


Figure S83. IR spectrum of hydrogenated poly(3-phenyl-1-cyclooctene) (neat).