

Supporting Information for:

Functionalized linear low-density polyethylene by ring-opening metathesis polymerization

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1. Supplemental Data Noted in Main Article

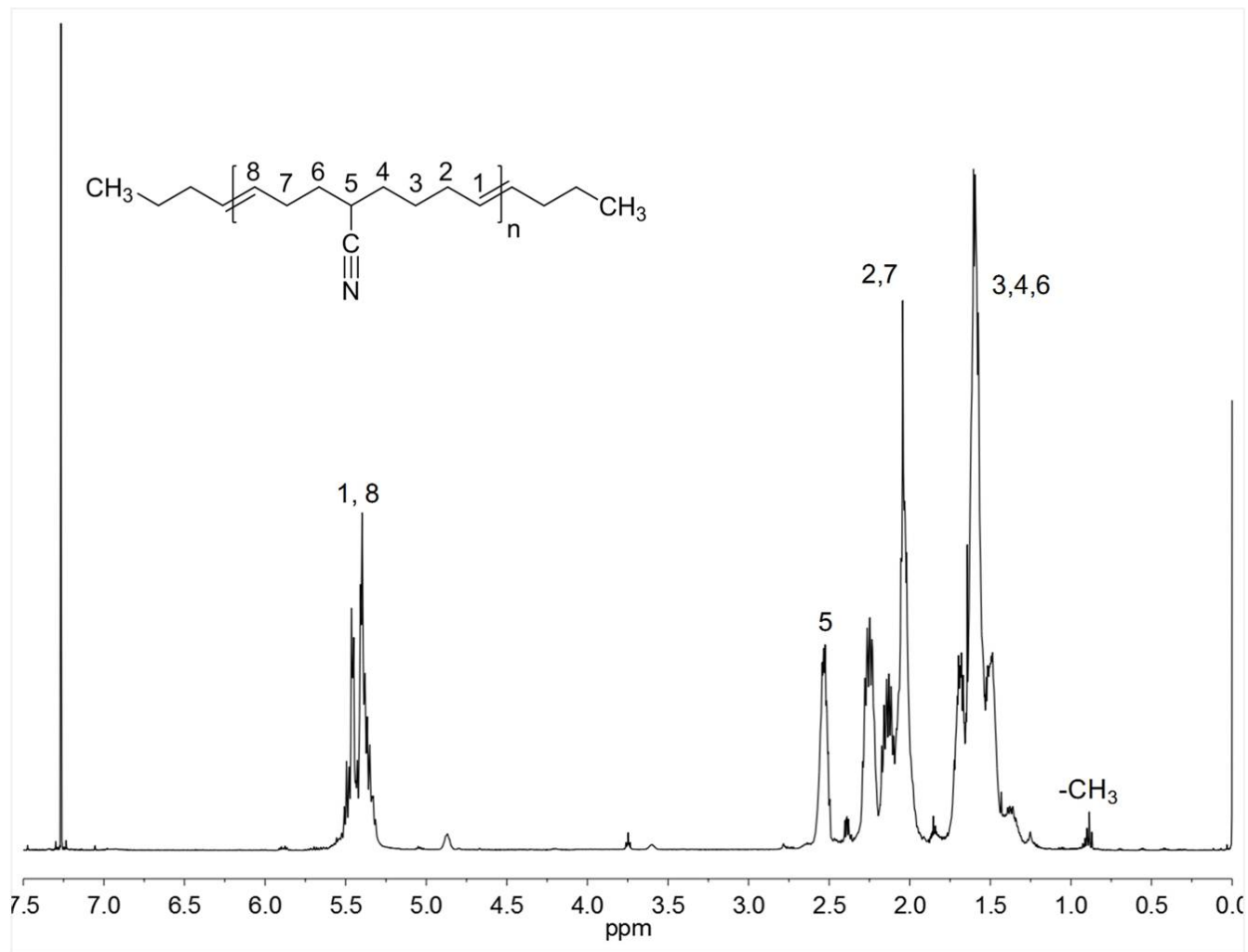


Figure S1. ¹H NMR spectrum of poly(5-cyano-1-cyclooctene) [poly(CNCOE)], in CDCl₃, 500 MHz.

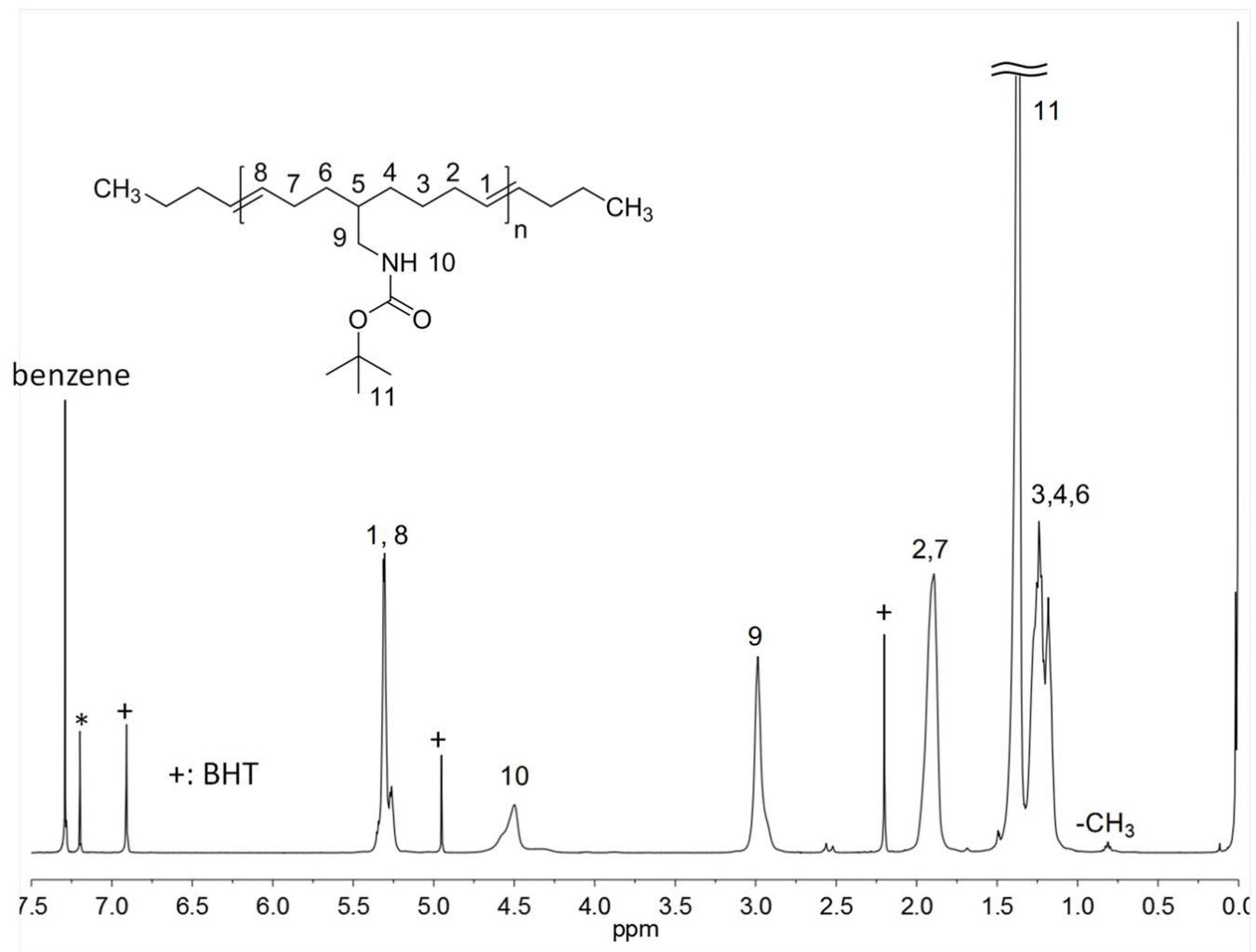


Figure S2. ¹H NMR spectrum of poly[5-(*N*-tert-butoxycarbonyl)aminomethyl-1-cyclooctene] [poly(^tBOCNHCOE)], in CDCl₃, 500 MHz]. (* and + represents what?)

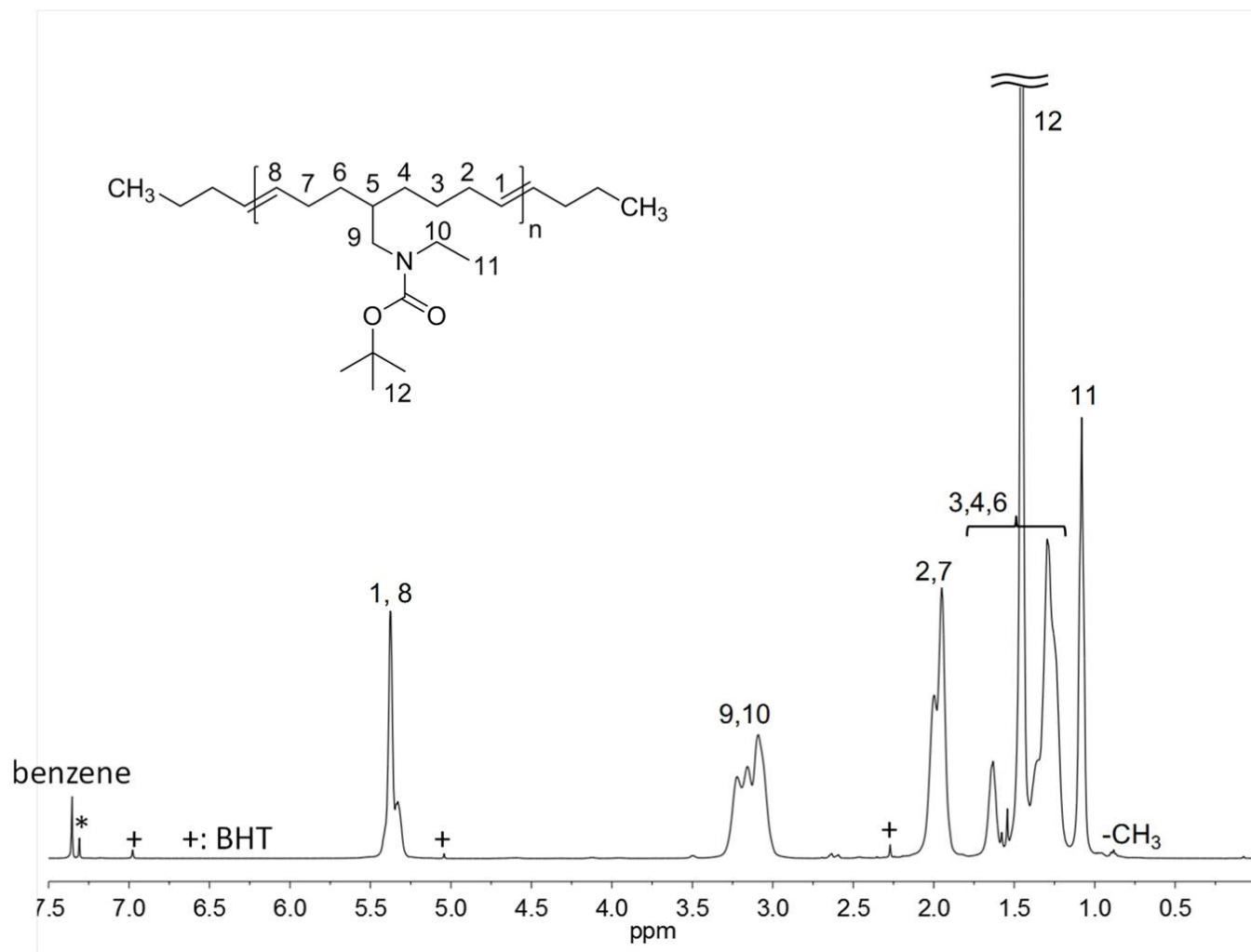


Figure S3. ¹H NMR spectrum of poly[5-(*N*-*tert*-butoxycarbonyl-*N*-ethyl)aminomethyl-1-cyclooctene] [poly('BOCNEtCOE), in CDCl₃, 500 MHz].

2. Materials

1,5-Cyclooctadiene was purchased from Aldrich (purified by redistillation, $\geq 99\%$) and *cis*-cyclooctene (95%) purchased from Acros Organics was purified by passing through a basic Al_2O_3 column and vacuum distillation over CaH_2 . Grubbs second generation catalyst was used as received; samples were either purchased from Aldrich or donated by Materia, Inc. The chain transfer agent *cis*-4-octene (97%) was purchased from GFS chemicals and purified by vacuum distillation over CaH_2 . 5-Hexyl-1-cyclooctene (HexCOE) was synthesized as we previously reported.³¹ 5-Cyano-1-cyclooctene (CNCOE) was synthesized as described in reference.³² Dry tetrahydrofuran (THF) for monomer synthesis and dry cyclohexane for catalytic hydrogenation were purified with a M. Braun solvent purification system. Other dry solvents were purified by distillation over CaH_2 . Other commercially available reagents were used without further purification.

3. Molecular Characterizations

^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 or Varian INOVA-500 spectrometer with CDCl_3 at room temperature benzene- d_6 at 75 °C. Proton chemical shifts are referenced to TMS (0.00 ppm, in CDCl_3), benzene- d_6 (7.16 ppm), or tetrachloroethane- d_2 (6.00 ppm). Carbon chemical shifts are referenced to CDCl_3 (77.1 ppm), benzene- d_6 (128.5 ppm), or tetrachloroethane- d_2 (74.2 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 or CI conditions. Molar mass and \bar{M}_w of the polymers were determined on a Hewlett–Packard 1100 series liquid chromatograph fitted with a Hewlett–Packard 1047A refractive index detector and three PLgel columns (Jordi Gel columns of 500, 10^3 , and 10^4 Å pore sizes) at a flow rate of 1 mL min^{-1} at 35 °C. All the columns were calibrated with polystyrene standards (Polymer Laboratories). The molar mass showing at here is the absolute molecular weight measured before the hydrogenation of polymer backbone because the amino functionalized polymers could not be measured on high temp SEC due to the adsorption onto SEC column.

4. Preparation of Monomers and Analytical Data

Preparation of 5-aminomethyl-1-cyclooctene (NH₂COE, Figure S4, S5)

Lithium aluminum hydride (LAH, 7.5 g, 203 mmol) was dispersed in dry THF (200 mL). A solution of 5-cyano-1-cyclooctene (13.5 g, 100 mmol) in dry THF (30 mL) was added dropwise over 30 min at 0 °C under argon flow. The reaction mixture was stirred overnight at room temperature then quenched by the sequential addition of water (7.5 mL), aqueous sodium hydroxide (7.5 mL, 15% NaOH), and water (22 mL). The quenched reaction mixture was stirred until the color of precipitated salt turn white. The salt was filtered and washed with 400 mL of THF, and the combined THF solution was concentrated on a rotary evaporator. The resulting oil was dissolved in 2N HCl and washed with CH₂Cl₂. The aqueous layer was basified by NaOH and was extracted with CH₂Cl₂. The organic layer was dried over anhydrous K₂CO₃. After removal of the solvent under vacuum, the crude product was purified by fractional distillation over CaH₂ and afforded 5-aminomethyl-1-cyclooctene (NH₂COE, 11.9 g, 85.5 mmol, 86%, bp = 43-45 °C / 0.45 mmHg) as a colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.72 – 5.55 (m, 2H), 2.50 (ddd, *J* = 41.2, 12.4, 6.5 Hz, –CH₂–NH₂, 2H), 2.40 – 1.99 (m, 4H), 1.77 – 1.58 (m, 2H), 1.56 – 1.43 (m, 1H), 1.43 – 1.24 (m, 3H), 1.24 – 0.96 (m, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 130.29, 130.04, 50.00 (–CH₂–NH₂), 41.38, 33.03, 30.95, 28.32, 26.00, 24.89 ppm.

IR (neat): 3370, 3495, 3059, 3013, 2914, 2852, 2749, 1649, 1597, 1465, 1450, 1384, 1330, 1267, 1245, 1207, 1069, 1034, 990, 964, 884, 819, 752, 723 cm⁻¹.

HRMS(EI): *m/z* calcd for C₉H₁₇N: 139.1361, found: 139.1351.

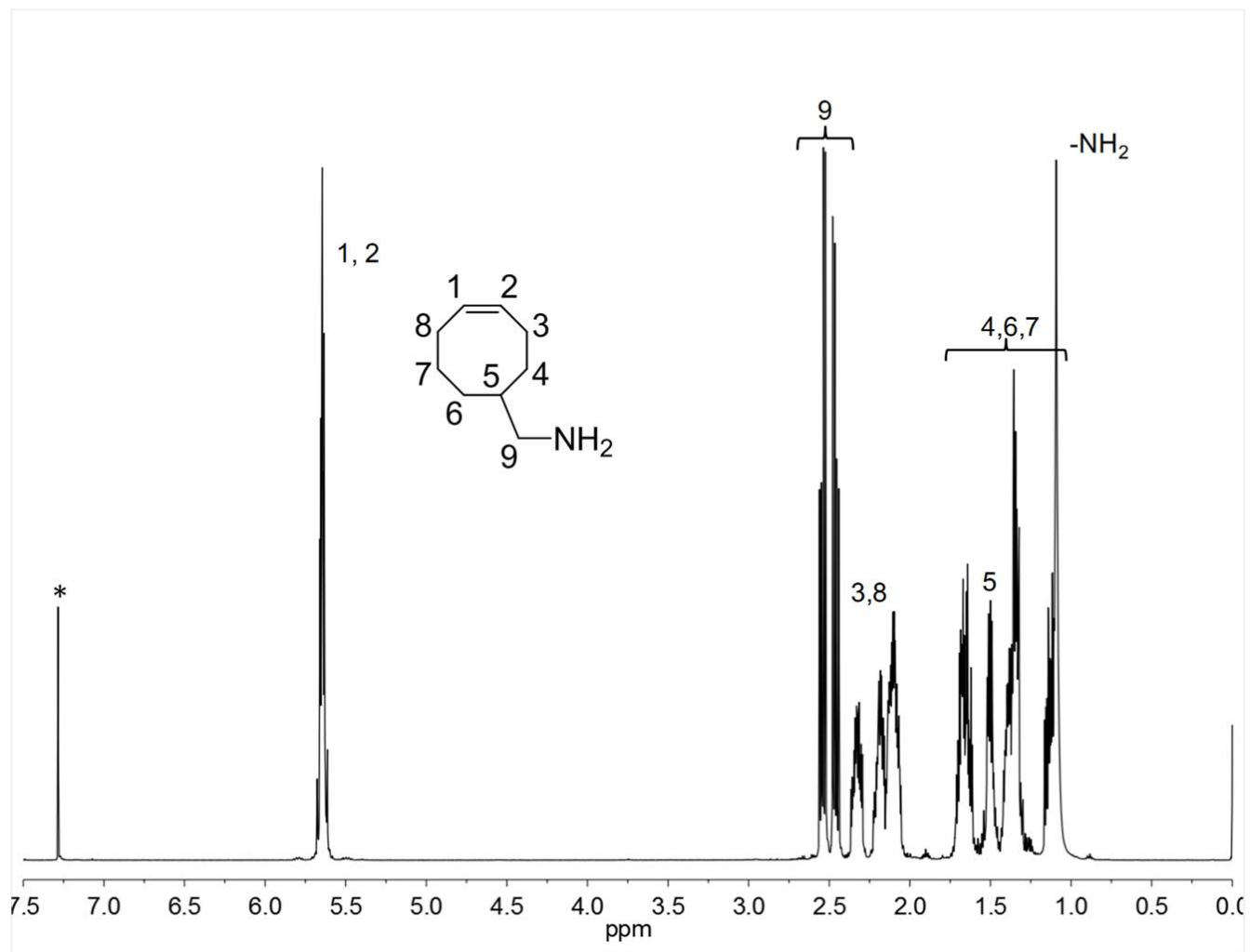


Figure S4. ^1H NMR spectrum of 5-aminomethyl-1-cyclooctene (NH_2COE , in CDCl_3 , 500 MHz)

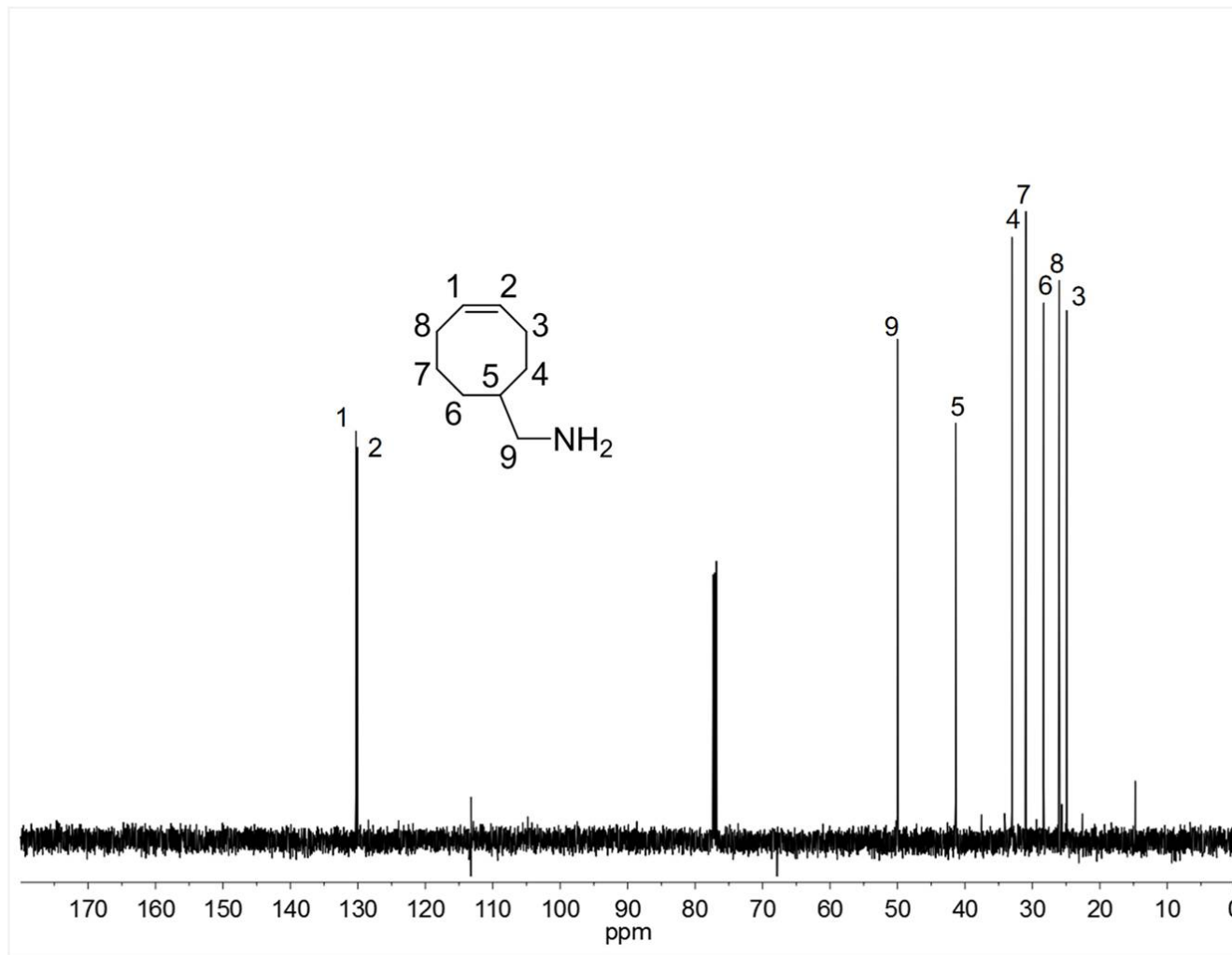


Figure S5. ^{13}C NMR spectrum of 5-aminomethyl-1-cyclooctene (NH_2COE , in CDCl_3 , 125 MHz)

Preparation of 5-(*N,N*-diethyl)aminomethyl-1-cyclooctene (NEt₂COE, Figure S6, S7)

A solution of bromoethane (18.5 g, 170 mmol) in DMF (30 mL) was added dropwise to a solution of NH₂COE (11.6 g, 83.5 mmol) and K₂CO₃ (20.0 g,) in dry DMF (60 mL) and stirred for overnight at room temperature. The reaction mixture was poured into water and extracted by CH₂Cl₂. The organic layer was dried over anhydrous K₂CO₃. After removal of the solvent under reduced pressure, the crude product was purified by fractional distillation over CaH₂ and afforded 5-(*N,N*-diethyl)aminomethyl-1-cyclooctene (NEt₂COE, 9.96 g, 51.0 mmol, 61%, bp = 36-39 °C / 0.37-0.40 mmHg) as a viscous colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.73 – 5.55 (m, 2H), 2.60 – 2.38 (m, 4H), 2.38 – 2.26 (m, 1H), 2.25 – 2.15 (m, 1H), 2.15 – 2.01 (m, 4H), 1.67 (m, 3H), 1.59 – 1.45 (m, 1H), 1.38 – 1.17 (m, 2H), 1.07 – 0.91 (m, 7H). ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 130.56, 130.03, 67.90, 61.31, 47.39, 35.83, 34.05, 31.07, 28.47, 26.11, 25.15, 14.78, 11.76. ppm.

IR (neat): 3014, 2968, 2929, 2871, 2850, 2796, 1465, 1383, 1370, 1344, 1292, 1249, 1201, 1166, 1120, 1068, 991, 885, 755, 720 cm⁻¹.

HRMS(EI): m/z calcd for C₁₃H₂₅N: 195.1987, found: 195.2003.

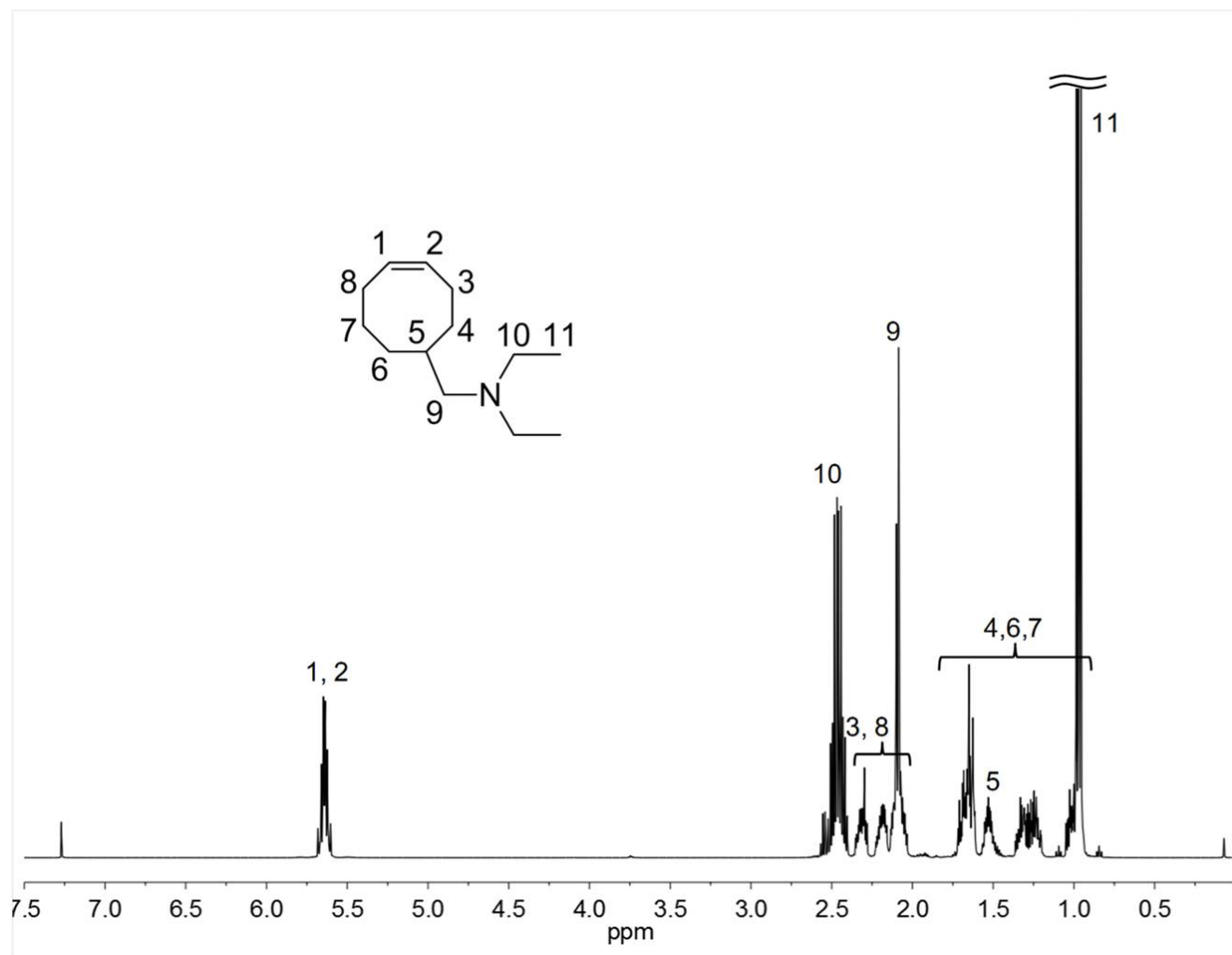


Figure S6. ¹H NMR spectrum of 5-(*N,N*-diethylaminomethyl)-1-cyclooctene (NEt₂COE, in CDCl₃, 500 MHz)

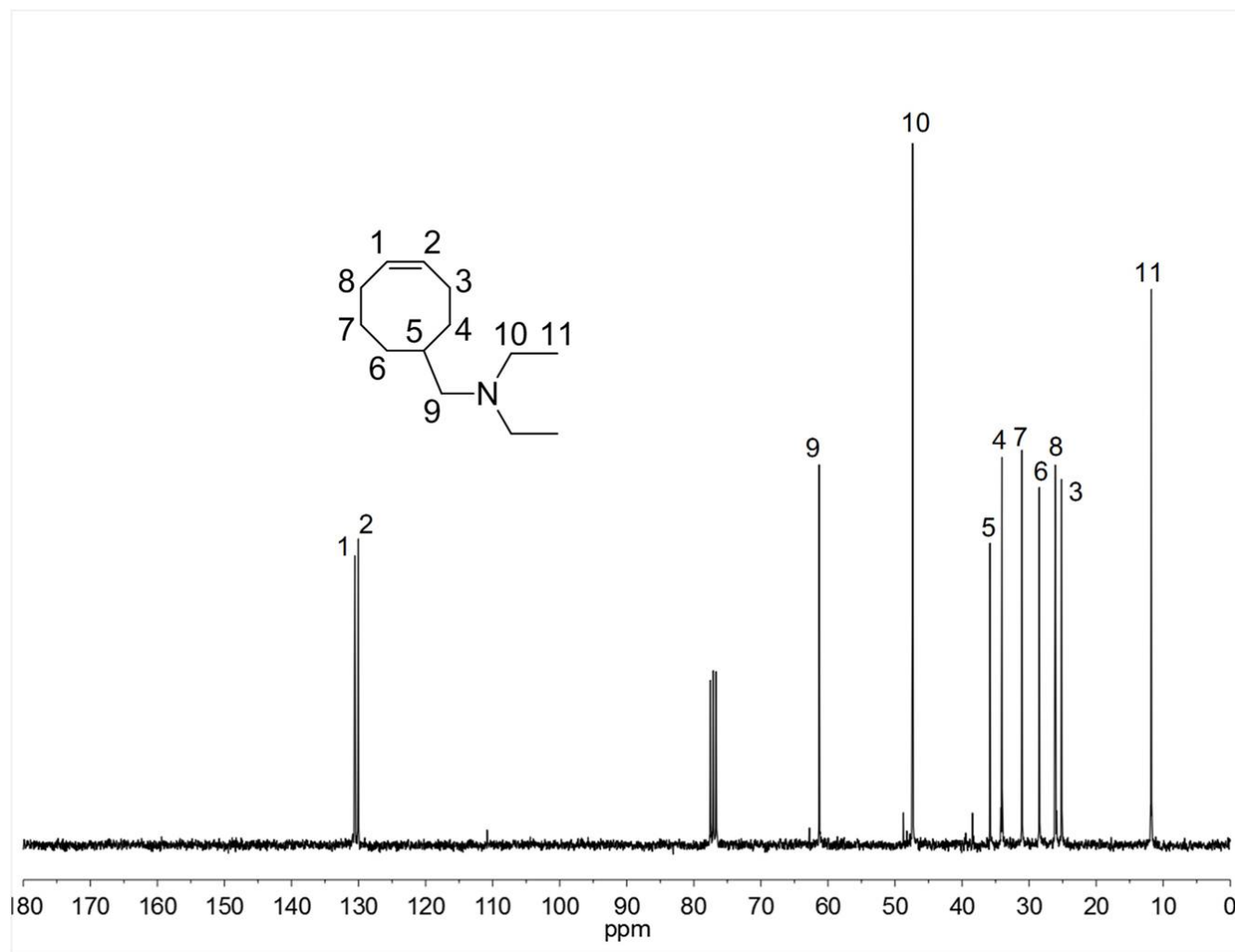


Figure S7. ¹³C NMR spectrum of 5-(*N,N*-diethyl)aminomethyl-1-cyclooctene (NEt₂COE, in CDCl₃, 125 MHz)

Preparation of 5-(*N-tert*-butoxycarbonyl)aminomethyl-1-cyclooctene (^tBOCNHCOE, Figure S8, S9)

A solution of di-*tert*-butyl dicarbonate (14.2 g, 65.0 mmol) in CH₂Cl₂ (30 mL) was added dropwise to a solution of NH₂COE (8.7 g, 62.5 mmol) in CH₂Cl₂ (30 mL) at 0 °C. The reaction mixture was allowed to stir for 3 h at room temperature then washed with 2N HCl, saturated NaHCO₃ aq., and water. The organic layer was dried over anhydrous K₂CO₃. After removal of the solvent under reduced pressure, the crude product was purified by fractional distillation over CaH₂ and afforded 5-(*N-tert*-butoxycarbonyl)aminomethyl-1-cyclooctene (^tBOCNHCOE, 10.9 g, 45.5 mmol, 73%, bp = 77-84 °C / 0.27 mmHg) as a highly viscous colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.74 – 5.47 (m, 2H), 4.56 (brs, –NH^tBOC, 1H), 3.11 – 2.78 (m, 2H), 2.41 – 1.99 (m, 4H), 1.74 – 1.22 (m, 17H), 1.14 (m, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 156.23, 130.14, 130.12, 79.01, 47.89, 38.17, 32.96, 30.57, 28.49, 28.05, 27.48, 25.89, 24.75 ppm.

IR (neat): 3352, 3013, 2977, 2927, 2856, 1812, 1697, 1521, 1466, 1432, 1391, 1366, 1342, 1271, 1250, 1173, 1121, 1075, 1040, 992, 886, 869, 780, 723 cm⁻¹.

HRMS(CI): m/z calcd for C₁₄H₂₆NO₂ [M+H]⁺: 240.1964, found: 240.1961.

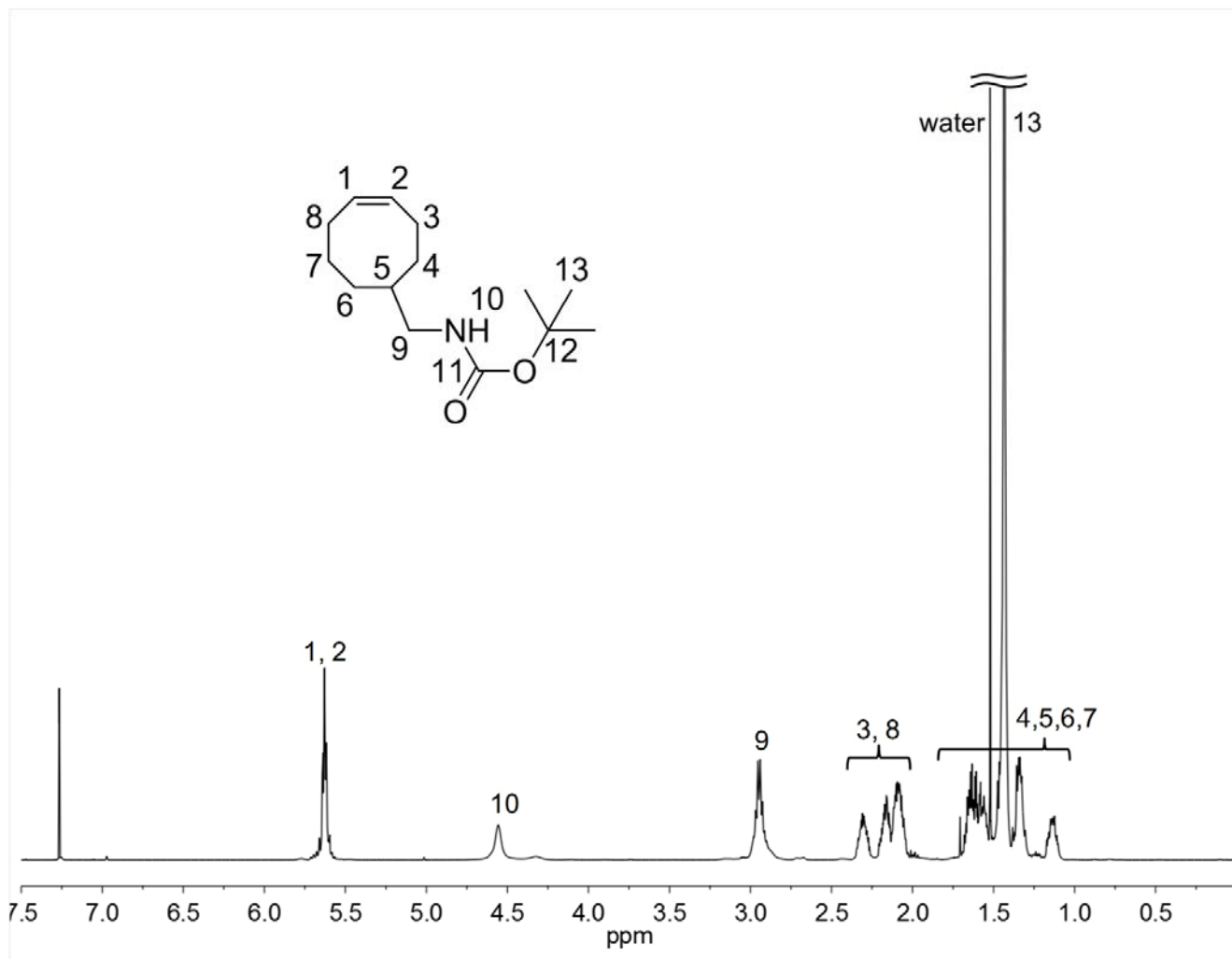


Figure S8. ¹H NMR spectrum of 5-(*N*-*tert*-butoxycarbonyl)aminomethyl-1-cyclooctene (*t*-BOCNHCOE, in CDCl₃, 500 MHz)

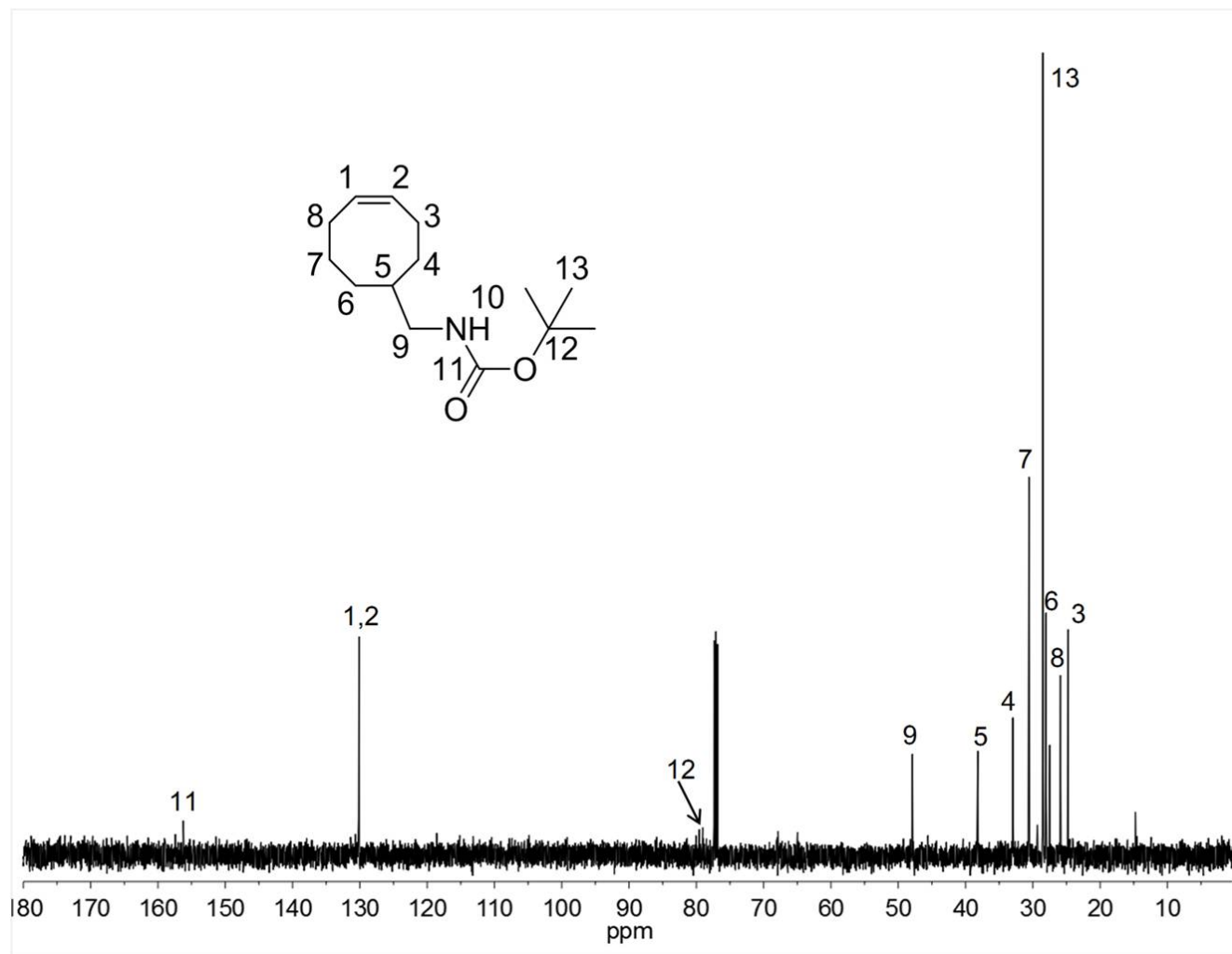


Figure S9. ¹³C NMR spectrum of 5-(*N*-*tert*-butoxycarbonyl)aminomethyl-1-cyclooctene (*t*-BOCNHCOE, in CDCl₃, 125 MHz)

Preparation of 5-(*N-tert*-butoxycarbonyl-*N*-ethyl)aminomethyl-1-cyclooctene
(^tBOCNEtCOE, Figure S10, S11)

Sodium hydride (1.4 g, 60 mmol) was dispersed in dry *N,N*-dimethylformamide (DMF, 40 mL). A solution of ^tBOCNHCOE (9.90 g, 41.4 mmol) in dry DMF (20 mL) was added dropwise and stirred for 2 h at room temperature. A solution of bromoethane (6.5 g, 60 mmol) in dry DMF (10 mL) was added dropwise over 30 min at room temperature and the mixture was stirred overnight. The reaction was quenched by pouring it into water and the mixture was extracted by CH₂Cl₂. The organic layer was dried over anhydrous K₂CO₃. After removal of the solvent under reduced pressure, the crude product was purified by fractional distillation over CaH₂ and afforded 5-(*N-tert*-butoxycarbonyl-*N*-ethyl)aminomethyl-1-cyclooctene (^tBOCNEtCOE, 6.62 g, 24.8 mmol, 60%, bp = 64-68 °C / 0.37 mmHg) as a viscous colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.82 – 5.37 (m, 2H), 3.08 (m, –CH₂–N–, 4H), 2.43 – 2.00 (m, 4H), 1.86 – 1.25 (m, 15H), 1.14 – 1.04 (m, 4H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 156.75, 130.86, 130.68, 79.64, 53.84, 53.60, 42.48, 37.10, 33.24, 30.67, 30.58, 29.17, 28.66, 26.57, 25.51, 14.26, 13.79 ppm.

IR (neat): 3013, 2974, 2857, 1694, 1469, 1417, 1390, 1365, 1305, 1272, 1253, 1172, 1146, 1106, 1071, 909, 986, 869, 791, 773, 722 cm⁻¹.

HRMS(CI): m/z calcd for C₁₆H₃₀NO₂ [M+H]⁺: 268.2277, found: 268.2256.

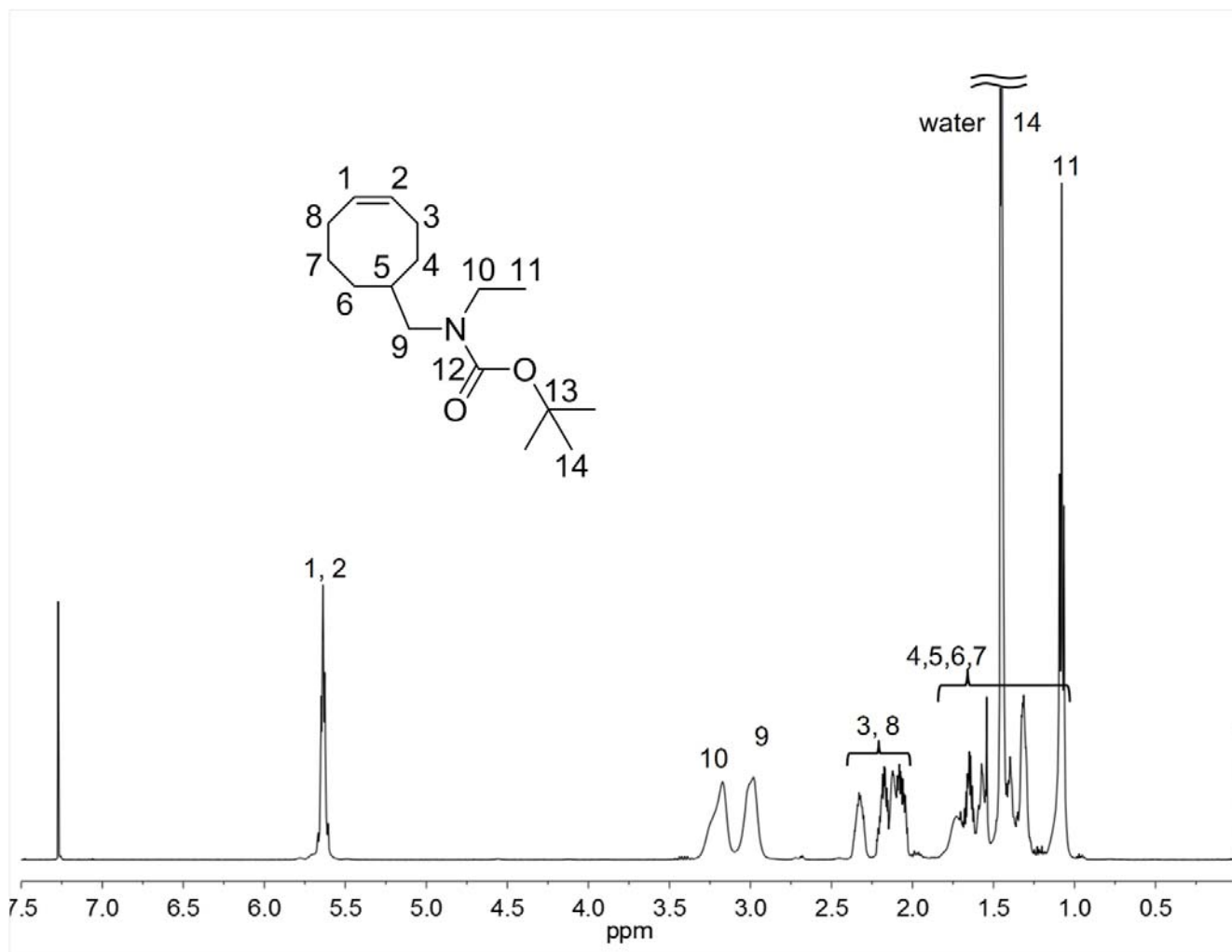


Figure S10. ¹H NMR spectrum of 5-(*N*-*tert*-butoxycarbonyl-*N*-ethyl)aminomethyl-1-cyclooctene (BOCNEtCOE, in CDCl₃, 500 MHz)

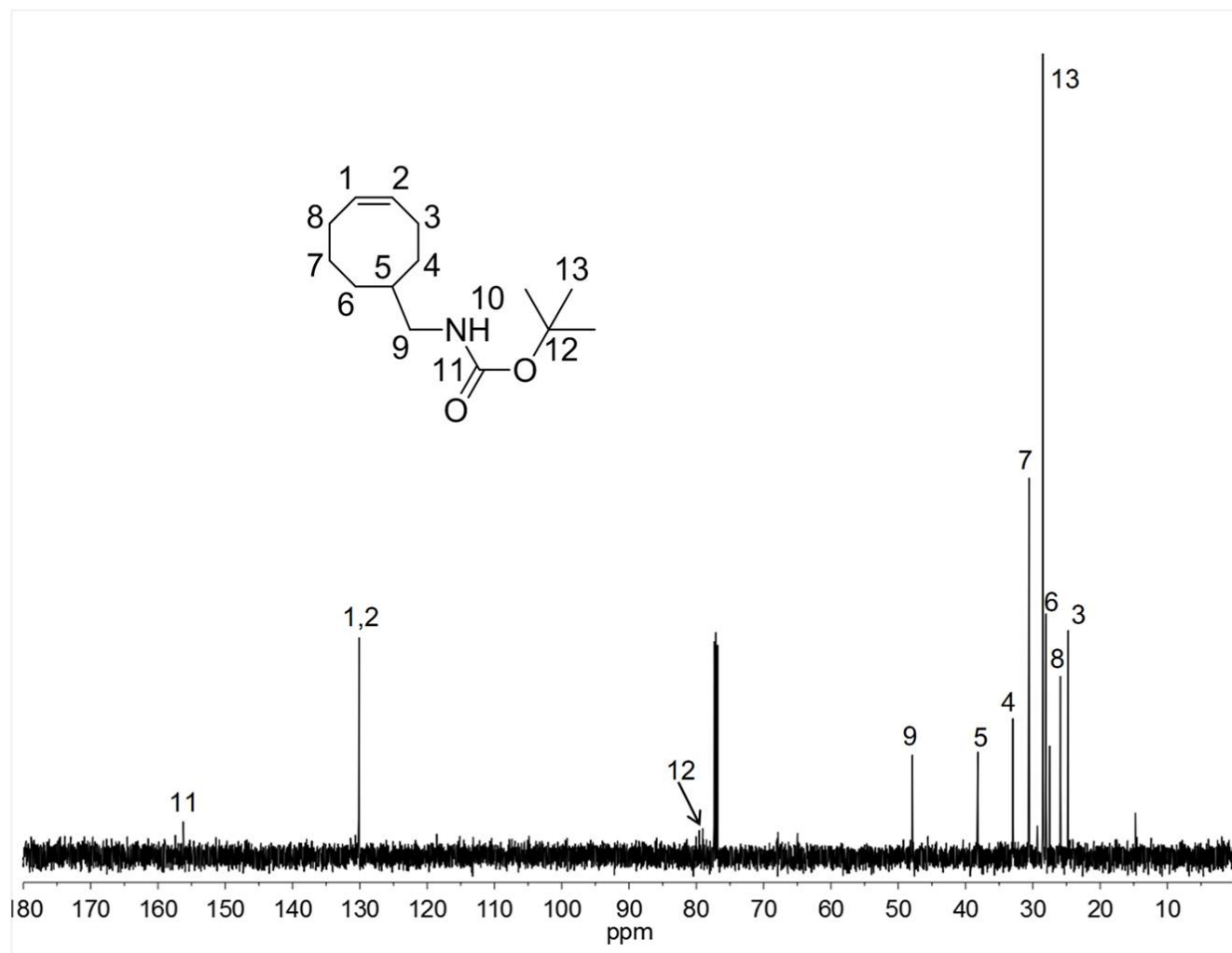


Figure S11. ¹³C NMR spectrum of 5-(*N*-*tert*-butoxycarbonyl-*N*-ethyl)aminomethyl-1-cyclooctene (*BOCNEtCOE*, in CDCl₃, 125 MHz)

Preparation of 5-(*N*-ethyl)aminomethyl-1-cyclooctene (NHEtCOE, Figure S12, S13)

Trifluoroacetic acid (15 mL) was added to a solution of ¹BOCNEtCOE (5.40 g, 20.2 mmol) in CH₂Cl₂ and stirred for 3 h at room temperature. Water was added to the mixture and was basified by NaOH. The mixture was extracted with CH₂Cl₂ and the organic layer was dried over anhydrous K₂CO₃. After removal of the solvent under vacuum, the crude product was purified by fractional distillation over CaH₂ and afforded 5-(*N*-ethyl)aminomethyl-1-cyclooctene (NHEtCOE, 2.61 g, 15.6 mmol, 78%, bp = 37-39 °C / 0.47-0.50 mmHg) as a colorless liquid.

¹H NMR (500 MHz, CDCl₃): δ = 5.73 – 5.54 (m, 2H), 2.70 – 2.52 (m, 2H), 2.52 – 2.36 (m, 2H), 2.32 (m, 1H), 2.22 – 2.02 (m, 3H), 1.73 – 1.45 (m, 4H), 1.41 – 1.29 (m, 2H), 1.19 – 1.04 (m, 4H), 0.83 (br.s, 1H).

¹³C NMR (125 MHz, CDCl₃): δ = 130.30, 130.04, 57.83, 44.27, 37.87, 33.64, 31.59, 28.29, 26.07, 24.94, 15.45. ppm.

IR (neat): 3286, 3014, 2963, 2920, 2850, 2810, 1683, 1649, 1465, 1371, 1333, 1267, 1133, 1030, 989, 962, 884, 755, 722 cm⁻¹.

HRMS(EI): m/z calcd for C₁₁H₂₁N: 167.1674, found: 167.1675.

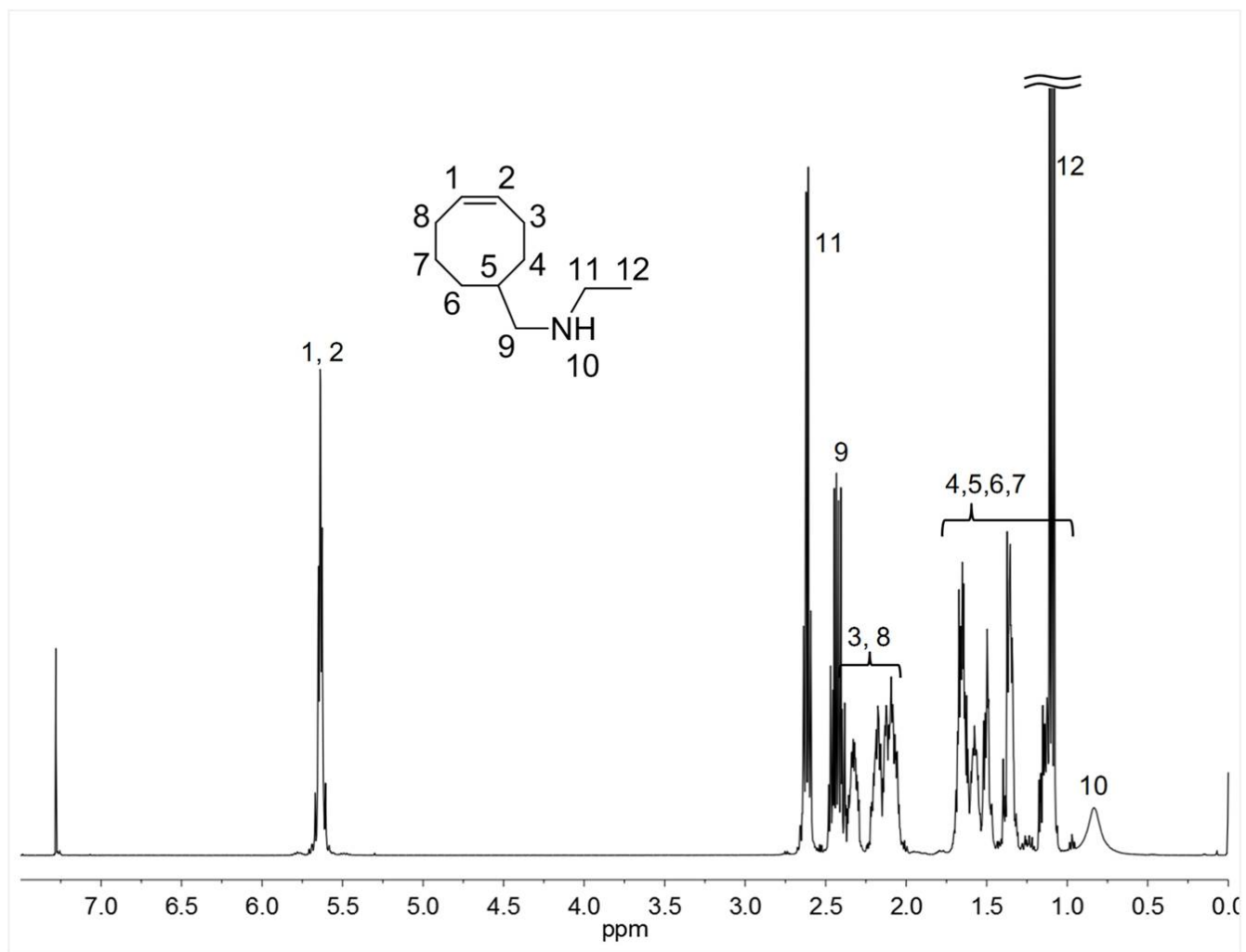


Figure S12. ¹H NMR spectrum of 5-(*N*-ethyl)aminomethyl-1-cyclooctene (NHEtCOE, in CDCl₃, 500 MHz)

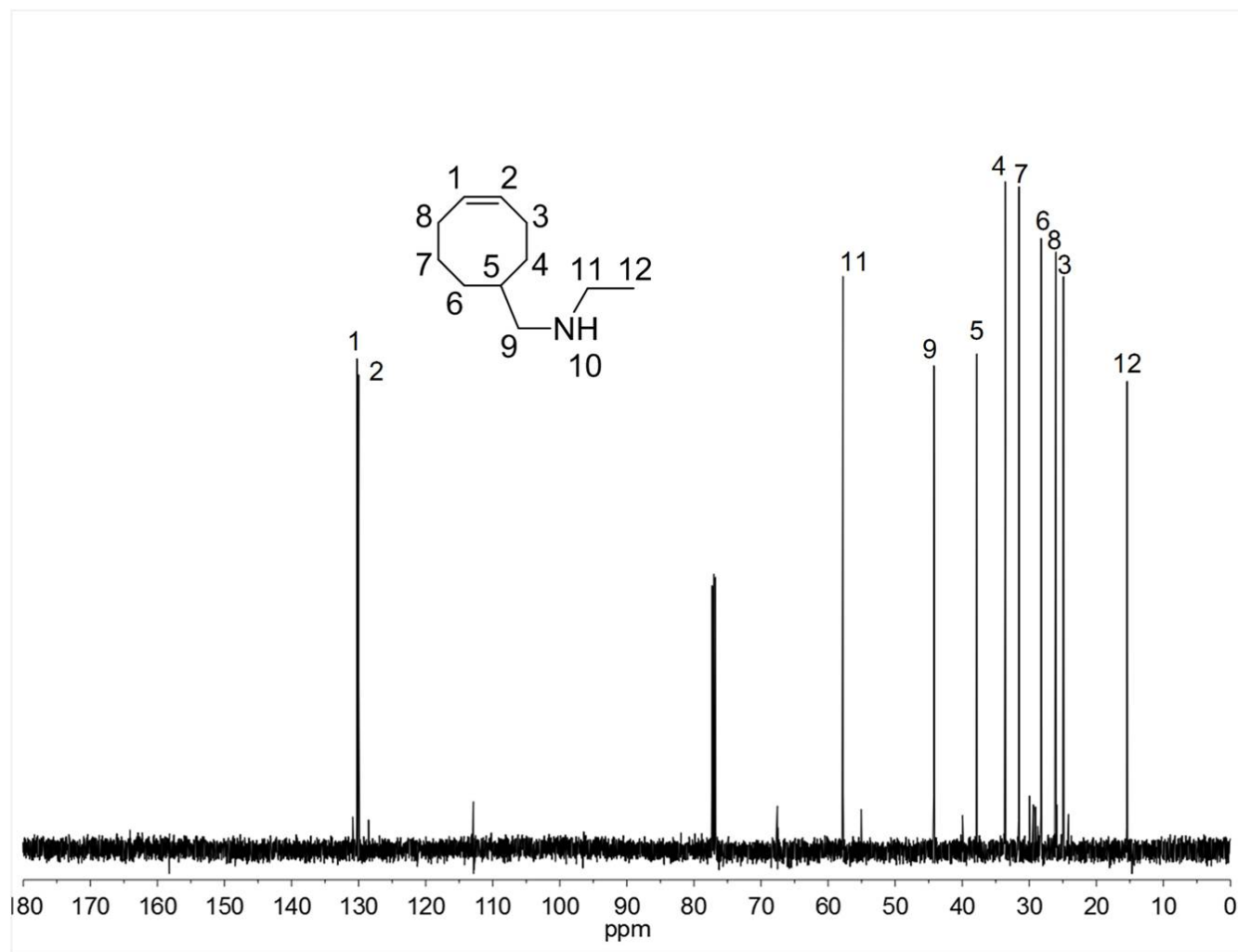


Figure S13. ¹H NMR spectrum of 5-(*N*-ethyl)aminomethyl-1-cyclooctene (NHEtCOE, in CDCl₃, 500 MHz)

5. General Polymerization Procedure

An example of the polymerization procedure is described for LLDPE-NH₂. A mixed monomer solution of ^tBOCNHCOE (0.289 g, 1.21 mmol), HexCOE (6.81 g, 35.1 mmol), COE (9.21 g, 83.8 mmol), and *cis*-4-octene (24.4 mg, 218 μmol) in dry CHCl₃ (2.0 M, 60 mL total volume) was prepared under an argon atmosphere and was thoroughly purged by bubbling argon with stirring for 30 min. A septum-sealed 250 mL flask that contained a magnetic stirrer bar was thoroughly purged with dry argon gas using evacuation–refilling cycles. An argon filled balloon was fitted to the flask. Grubbs second generation catalyst (8.9 mg, 11 μmol) was added as a 1.0 mL solution of dry CHCl₃ using a gas-tight syringe. The reactor was heated to 60 °C and the 2.0 M mixed monomer solution was added continuously to the flask over 1 h using a glass syringe and syringe pump. After additional stirring for 20 h at 60 °C, the reaction mixture was cooled to room temperature and quenched by adding 0.5 mL of ethyl vinyl ether. After additional stirring for 30 min, the reaction mixture was poured into a large excess of slightly acidified methanol chilled with liquid N₂ to precipitate the resulting polymer. The precipitated polymer was filtered off at low temperature and purified by repeated reprecipitations using a THF/methanol system until the methanol appeared free of color. The polymer was isolated and freeze-dried overnight from a benzene solution to afford polymer (15.1 g, 92%) as a sticky solid. Polymers thus obtained were characterized by ¹H NMR, ¹³C NMR and IR. Polymer backbones showed exactly the same spectrum as we reported in a previous paper. (ref.17) Followings are the characteristic signals for each functional group in the ternary copolymer:

¹H NMR (500 MHz, CDCl₃): δ = 4.47 (br, ^tBOCNHCH₂-), 3.07 (br, ^tBOCNHCH₂-); 3.28 – 3.00 (m, ^tBOCN(CH₂CH₃)CH₂-); 2.52 (br, -CHR-CN).

IR (neat): 3464, 1725 (^tBOCNHCH₂-); 1698 (^tBOCN(CH₂CH₃)CH₂-); 2239 (-CN) cm⁻¹.

Followings are the complete list for homo-polymers:

poly(CNCOE)

¹H NMR (500 MHz, CDCl₃): δ = 5.55 – 5.25 (m, 2H), 2.59 – 2.48 (m, 1H), 2.27 – 1.95 (m, 4H), 1.75 – 1.42 (m, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ = 131.18, 130.79, 130.14, 129.95, 129.60, 129.35, 128.89, 128.37, 128.22, 122.17, 122.12, 32.20, 32.14, 32.00, 31.81, 31.71, 31.09, 30.98, 30.13, 27.20, 27.00, 26.93, 26.79, 26.72, 25.01, 24.95 ppm.

IR (neat): 3006, 2930, 2860, 2235, 2181, 2128, 1732, 1647, 1457, 1406, 1365, 1313, 1245, 1119, 1022, 970, 862, 811 cm^{-1} .

poly($^t\text{BOCNHCOE}$)

^1H NMR (500 MHz, CDCl_3): δ = 5.37 – 5.23 (m, 2H), 4.64 – 4.27 (br, 1H), 3.06 – 2.88 (m, 2H, $^t\text{BOCNHCH}_2-$), 2.05 – 1.77 (m, 4H), 1.48 – 1.10 (m, 16H).

^{13}C NMR (125 MHz, CDCl_3): δ = 156.18, 156.16, 130.37, 129.90, 128.39, 125.57, 78.99, 72.87, 43.68, 37.78, 32.96, 31.71, 31.19, 30.38, 29.79, 28.52, 26.60 ppm.

IR (neat): 3460, 3354, 3140, 2976, 2928, 2857, 1698, 1520, 1455, 1391, 1366, 1250, 1174, 1099, 968, 862, 780 cm^{-1} .

poly($^t\text{BOCNEtCOE}$)

^1H NMR (500 MHz, CDCl_3): δ = 5.44 – 5.27 (m, 2H), 3.32 – 2.97 (m, 4H, $^t\text{BOCN}(\text{CH}_2\text{CH}_3)\text{CH}_2-$), 2.07 – 1.87 (m, 4H), 1.63 (brs, 1H), 1.53 – 1.16 (m, 15H), 1.08 (br, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ = 155.83, 155.57, 130.27, 129.76, 78.99, 50.20, 41.94, 36.47, 36.13, 33.09, 31.48, 31.32, 30.95, 29.60, 28.49, 28.03, 27.67, 26.46, 24.35, 13.53, 12.95 ppm.

IR (neat): 3366, 2973, 2928, 2855, 1693, 1477, 1457, 1418, 1365, 1277, 1168, 1067, 967, 865, 793, 772 cm^{-1} .

6. General Catalytic Hydrogenation Procedure

An example of the hydrogenation procedure is described for LLDPE-NH₂. Hydrogenation was performed in a 300 mL high-pressure stainless steel reactor equipped with baffles and a gas dispersion impeller. The hydrogenation catalyst, 5% platinum-rhenium on silica (Pt-Re/SiO₂, 1.3 g, 10 wt-% based on the polymer), was added to the reactor then sealed. The reactor was purged with argon by using an evacuation–refilling cycle. A solution of 13.0 g of polymer dissolved in 200 mL of cyclohexane was purged with argon. The polymer solution was transferred to the reactor and the reactor was pressurized to 3.4 MPa with H₂. The hydrogenation was then allowed to proceed in the sealed reactor with stirring at 90 °C for 18 h. During the reaction, the pressure was maintained at 3.4 MPa of H₂. The reactor was cooled to room temperature and the excess hydrogen was vented. After the collection of the slurry reaction mixture, the reaction solvent cyclohexane was removed on a rotary evaporator and toluene was added to dissolve the hydrogenated polymer at high temperature. The hydrogenated polymer solution was separated from the catalyst by high temperature filtration using a Millipore high-pressure filter with a 0.22 μm porous Teflon filter membrane. The hydrogenated polymer was precipitated by pouring the filtrate directly into methanol and was isolated by filtration. The isolated polymer was dried in a vacuum oven at 50 °C for 2 days to afford LLDPE-NH^tBOC (11.9 g, 92 wt%) as a white solid. Polymers thus obtained were characterized by ¹H NMR, ¹³C NMR and IR. Polymer backbones showed exactly the same spectrum as we reported in a previous paper. (ref.17) Following are the characteristic signals and absorptions for each functional group:

¹H NMR (300 MHz, C₆D₆, 80 °C): δ = 4.09 (br, ^tBOCNHCH₂–), 3.07 (t, ^tBOCNHCH₂–); 3.23 – 3.08 (m, ^tBOCN(CH₂CH₃)CH₂–); 1.87 (br, –CHR–CN, in C₂D₂Cl₄ at 100 °C).

IR (film): 3463, 1727 (NH₂CH₂–); 1699 (NH(CH₂CH₃)CH₂–); 2240 (–CN) cm⁻¹.

7. General Deprotection Procedure

An example of the deprotection reaction procedure is described for LLDPE-NH₂. LLDPE-NH^tBOC (9.67 g, containing 0.79 mmol of amino group) and butylated hydroxytoluene (BHT, ca 3 mg) was dissolved in benzene (200 mL) at 80 °C. The mixture was cooled to 70 °C and trifluoroacetic acid (10 mL) was added. The mixture was stirred for 2 h at 70 °C and poured into excess amount of methanol to precipitate the polymer. The precipitated polymer was washed in methanol twice, stirred in aqueous solution of sodium bicarbonate for overnight with stirring, in water for overnight with stirring, and in methanol. After filtration to collect the polymer, it was dried in vacuo to yield LLDPE-NH₂ (9.57 g, 99 wt%) as a white solid. Polymers thus obtained were characterized by ¹H NMR. Following are the characteristic signals for each functional group:

¹H NMR (300 MHz, C₆D₆, 80 °C): δ = 2.54 (br, NH₂CH₂-); 2.60 – 2.48 (m, NH(CH₂CH₃)CH₂-).

IR (film): 3448, 3370 (NH₂CH₂-); 3369 (NH(CH₂CH₃)CH₂-) cm⁻¹.