

Supporting Information

Surfactant-tail Control of CsPbBr₃ Nanocrystal Morphology

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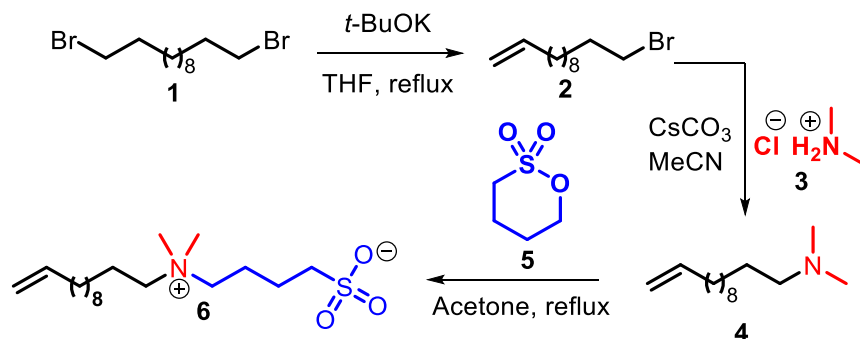
General remarks	S2
Synthesis of ASDC12 and S-ASDC12	S3-S4
NMR spectra of ASDC12 and S-ASDC12	S5-S10
General procedure for CsPbBr ₃ NCs synthesis	S10-S11
TEM micrographs and their respective histograms	S12-S18
Ligand density studies	S19-S23
DFT Calculations	S24-S29

General remarks

All reagents and solvents were obtained from Sigma-Aldrich. Toluene and methyl acetate were dried before use and stored over 4 Å molecular sieves. All progress of the organic reactions were monitored by TLC using silica gel 60 (ALUGRAM SIL G/UV); the spots were visualized under UV light (254 nm) or with vanillin, and KMnO₄. All reactions were performed under a dry N₂ atmosphere unless otherwise specified. **¹H and ¹³C NMR spectra** were recorded on Bruker AV 400 MHz model spectrometer using CDCl₃, D₂O and DMSO-*d*₆ as solvents. Chemical shifts (δ) are reported in parts per million relative to Si(CH₃)₄. Coupling constants (*J*) are reported in hertz (Hz), and peak multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, and bs: broad signal for proton spectra. **IR spectra** were obtained with a Agilent ALPHA II-Platinum FT-IR spectrometer with Platinum Diamond-ATR. **High-resolution mass spectra** were recorded with an AccuTOFLC equipped with an IonSense DART controller ionization source. **PXRD patterns** were collected in Bragg–Brentano geometry at room temperature with CuKα radiation ($\lambda = 1.54183$ Å) in an Ultima IV diffractometer (from Rigaku) equipped with a D/tex Ultra detector. The patterns were recorded from 5 to 60° (2θ) in 0.02° steps and 10°/min scan speed. **Morphological analysis** of CsPbBr₃ NCs were studied by transmission electron microscopy (TEM) using a JEOL ARM-200F Cs-corrected microscope, located at Laboratorio Universitario de Microscopía Electrónica (LUME-UNAM). Images were acquired in conventional high-resolution TEM and high-angle annular dark-field (HAADF) scanning-mode. **UV-vis measurements** were carried out in a DS5 Dual Beam UV-vis spectrophotometer from Edinburgh Instruments. **Ligand density studies** were conducted by combining particle size analysis obtained from TEM measurements with quantitative Nuclear Magnetic Resonance (qNMR). To ensure the utmost accuracy in quantification, a certified internal standard (TCNB = 1,2,4,5-Tetrachloro-3-nitrobenzene, TraceCERT, Sigma Aldrich) served as the internal reference for NMR. The weights of both nanocrystals (NCs) and TCNB were determined using a METTLER TOLEDO XS105 Analytical Balance with a readability of 0.01mg, which is certified and calibrated with PR-001 (SARTORIUS), Class E2 weights. It's noteworthy that the signal from the standard does not overlap with the signals from our materials, facilitating seamless integration during analysis. **PL and PLQY measurements** were obtained in an Edinburgh Instruments FS5 fluorometer with a 150W CW Ozone-free xenon arc lamp, and Czerny–Turner monochromators, using an SC-05 (standard cuvette) and SC-30 (Integrating Sphere) modules, respectively.

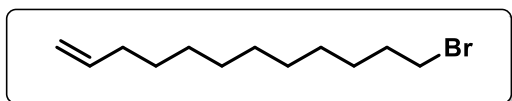
Synthetic approach to ASDC12.

Organic synthesis. In a typical synthesis, we carried out an E_2 type elimination of 1,12-dibromododecane to afford the desired bromo alkene **2** in 49% yield. With **2** in hands, we promoted an S_N2 type substitution reaction by using dimethyl amine hydrochloride and CsCO_3 to provide the tertiary alkene-amine **4**. Finally, we promoted the aperture of the butyl sultone **5** to give the desired zwitterionic sulfobetaine ligand ASDC12 **6** in a quantitative yield.



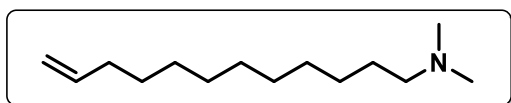
Scheme S1. Synthetic route toward ASDC12 (**6**)

12-bromododec-1-ene (**2**).



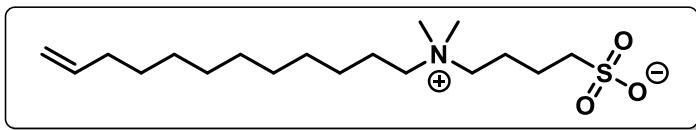
In a round-bottom flask, 1,12-dibromododecane (1 equiv., 4.00 g, 12.26 mmol) was added to 121 mL of anhydrous THF under inert atmosphere. After, $t\text{-BuOK}$ (1.15 equiv., 1.57g, 14 mmol) was added in a portionwise order over 30 min. Then, the mixture was stirred under reflux for 16 h. Finally, the reaction was cooled and subsequently quenched with water and extracted several times with Et_2O . The crude reaction was purified by flash chromatography with hexanes to afford the title compound as colorless oil in 49% yield (1.47 g). The RMN spectroscopy data of the isolated product agree with the reported literature values. ^1H NMR (301 MHz, CHLOROFORM-D) δ : 5.93-5.72 (m, 1 H), 5.04-4.91 (m, 2 H), 3.42 (d, 2 H, $J = 6.8$ Hz), 2.05 (q, 2 H, $J = 6.8$ Hz), 1.86 (p, 2 H, $J = 6.9$ Hz), 1.50-1.20 (br m, 14 H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ : 139.4, 114.3, 34.2, 34.0, 33.0, 29.6, 29.6, 29.3, 29.1, 28.9.

N,N-dimethyldodec-11-en-1-amine (**4**).



In a round bottom flask equipped with a magnetic stirring bar, 12-bromododec-1-ene (1 equiv., 1.3 g, 5.28 mmol), Cs_2CO_3 (1.5 equiv., 2.58 g, 7.92 mmol) and dimethylamine hydrochloride (1.5 equiv., 0.65 g, 7.92 mmol) were added to 12 mL of dry MeCN. Then, the reaction mixture was refluxed for 12 h. Finally, the crude product was extracted with DCM and water and purified by short length silica gel flash chromatography using AcOEt as eluent to yield the desired amine as a clear oil in quantitative yield. ^1H NMR (301 MHz, CHLOROFORM-D) δ : 5.87 – 5.74 (m, 1H), 5.02 – 4.91 (m, 2H), 2.35 – 2.23 (m, 4H), 2.21 (s, 6H), 2.03 (d, $J = 4.6$ Hz, 2H), 1.47 – 1.36 (m, 4H), 1.28 (s, 10H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ : 139.3, 114.2, 60.1, 45.6, 33.9, 29.7, 29.7, 29.6, 29.3, 29.1, 27.9, 27.6. IR $\text{g}(\text{cm}^{-1})$: 3045, 2923, 2852, 2813, 2761, 1640, 1462, 1041, 992, 908, 721, 634. HRMS (DART+) m/z calcd for $^{12}\text{C}_{14}^{1}\text{H}_{30}^{14}\text{N}_1$ $[\text{M}+\text{H}]^+$ 212.23782, found 212.23760.

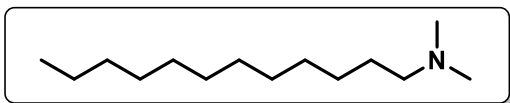
4-(dodec-11-en-1-yl)dimethylammonio)butane-1-sulfonate (6).



In a typical procedure, *N,N*-dimethyldodec-11-en-1-amine (1 equiv., 1.0 g, 4.74 mmol) was dissolved in 5 mL of acetone. Subsequently, a solution of 1,4-butane sultone (5 equiv., 23.70 mmol, 3.226 g) in 5 mL of acetone was added dropwise. The mixture was kept under reflux for 12 hours. Finally, the desired zwitterionic sulfobetaine compound was isolated as a white solid after carrying out vacuum filtration with acetone in 97% yield. **¹H NMR (400 MHz, D₂O) δ:** 5.73 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 4.97 – 4.81 (m, 2H), 3.27 – 3.16 (m, 4H), 2.99 (s, 6H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.96 (q, *J* = 6.8 Hz, 2H), 1.82 (t, *J* = 8.4 Hz, 2H), 1.72 (q, *J* = 7.5 Hz, 2H), 1.64 (s, 2H), 1.32 – 1.21 (m, 14H). **¹³C NMR (101 MHz, D₂O) δ:** 137.8, 114.2, 63.7, 63.0, 50.9, 49.7, 33.7, 29.4, 29.1, 28.9, 28.8, 26.0, 22.1, 21.3, 21.0. **IR g (cm⁻¹):** 3447, 3034, 2918, 2851, 2343, 2113, 1637, 1483, 1464. **HRMS (DART+) *m/z*** calcd for ¹²C₁₈¹H₃₈¹⁴N₁¹⁶O₃³²S₁ [M+H]⁺ 348.25724, found 348.25868.

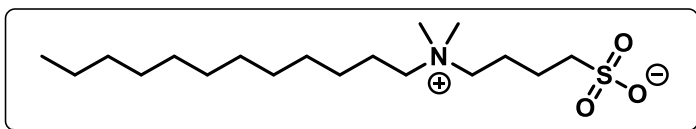
Synthetic approach to S-ASDC12.

N,N-dimethyldodecan-1-amine (7).



In a round-bottom flask equipped with a magnetic stirring bar, dimethylamine hydrochloride (3 equiv., 3.74 g, 45.9 mmol) was dissolved in 50 mL of an ethanol-water solution (v/v=95:5). Then, NaOH (2.20 g, 55 mmol) was added to the solution. After that, 1-bromododecane (1 equiv., 3.38 g, 15.3 mmol) was added, and the resulted mixture was stirred under reflux at 100 °C for 24 h. Finally, the volatiles were removed and 40 mL of a 10% NaOH solution was added. The mixture was extracted three times with 20 mL of DCM to afford the desired compound as a colorless oil in 85% yield (2.77 g). The RMN spectroscopy data of the isolated product agrees with the reported literature values. **¹H NMR (301 MHz, CHLOROFORM-*D*) δ:** 2.27 – 2.23 (m, 2H), 2.21 (d, *J* = 2.9 Hz, 6H), 1.49 – 1.41 (m, 2H), 1.27 (d, *J* = 9.4 Hz, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). **¹³C NMR (76 MHz, CHLOROFORM-*D*) δ:** 59.9, 45.4, 31.9, 29.6, 29.6, 29.3, 27.7, 27.5, 22.7, 14.0.

4-(dodecyldimethylammonio)butane-1-sulfonate (8).



In a typical procedure, *N,N*-dimethyldodecan-1-amine (1 equiv., 2.77 g, 13 mmol) was dissolved in 13 mL of acetone. Subsequently, a solution of 1,4-butane sultone (5 equiv., 65 mmol, 7 mL) in 13 mL of acetone was added dropwise. The mixture was kept under reflux for 12 hours. Finally, the desired zwitterionic sulfobetaine compound was isolated as a white solid after carrying out vacuum filtration with acetone in 97% yield (4.4 g). **¹H NMR (400 MHz, D₂O) δ:** 3.30 – 3.16 (m, 4H), 3.01 (s, 6H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.76 – 1.59 (m, 4H), 1.28 (s, 4H), 1.21 (s, 14H), 0.85 – 0.78 (m, 3H). **¹³C NMR (100 MHz, D₂O) δ:** 63.6, 62.9, 50.9, 50.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.0, 26.1, 22.6, 22.2, 21.4, 21.0, 13.9. **IR g (cm⁻¹):** 3495, 3034, 2917, 2850, 1468, 1182, 1035, 939, 909, 793, 722, 606, 522. **HRMS (FAB+) *m/z*** calcd for ¹²C₁₈¹H₄₀¹⁴N₁¹⁶O₃³²S₁ [M+H]⁺ 350.2729, found 350.2734.

12-bromododec-1-ene (2).

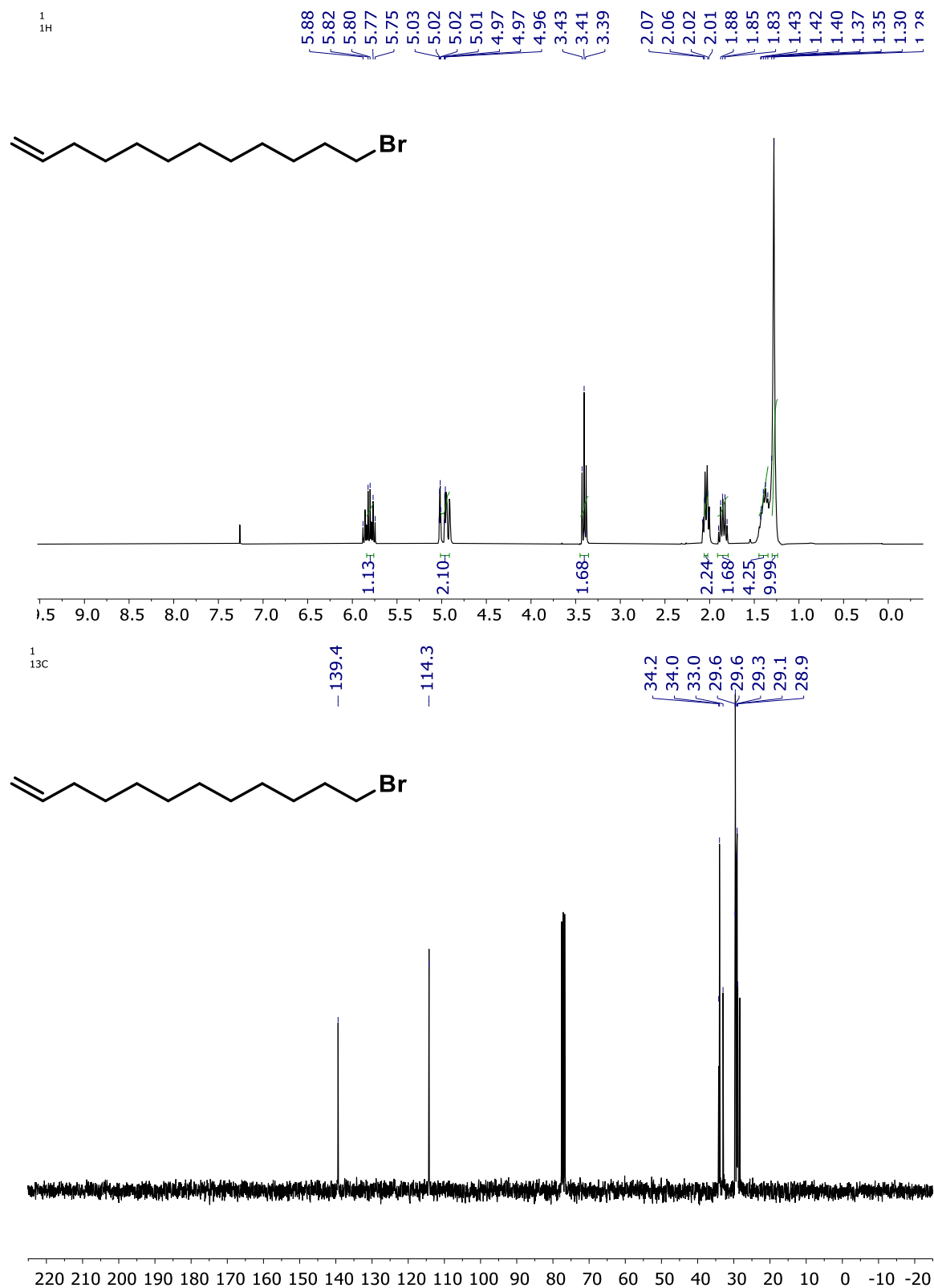
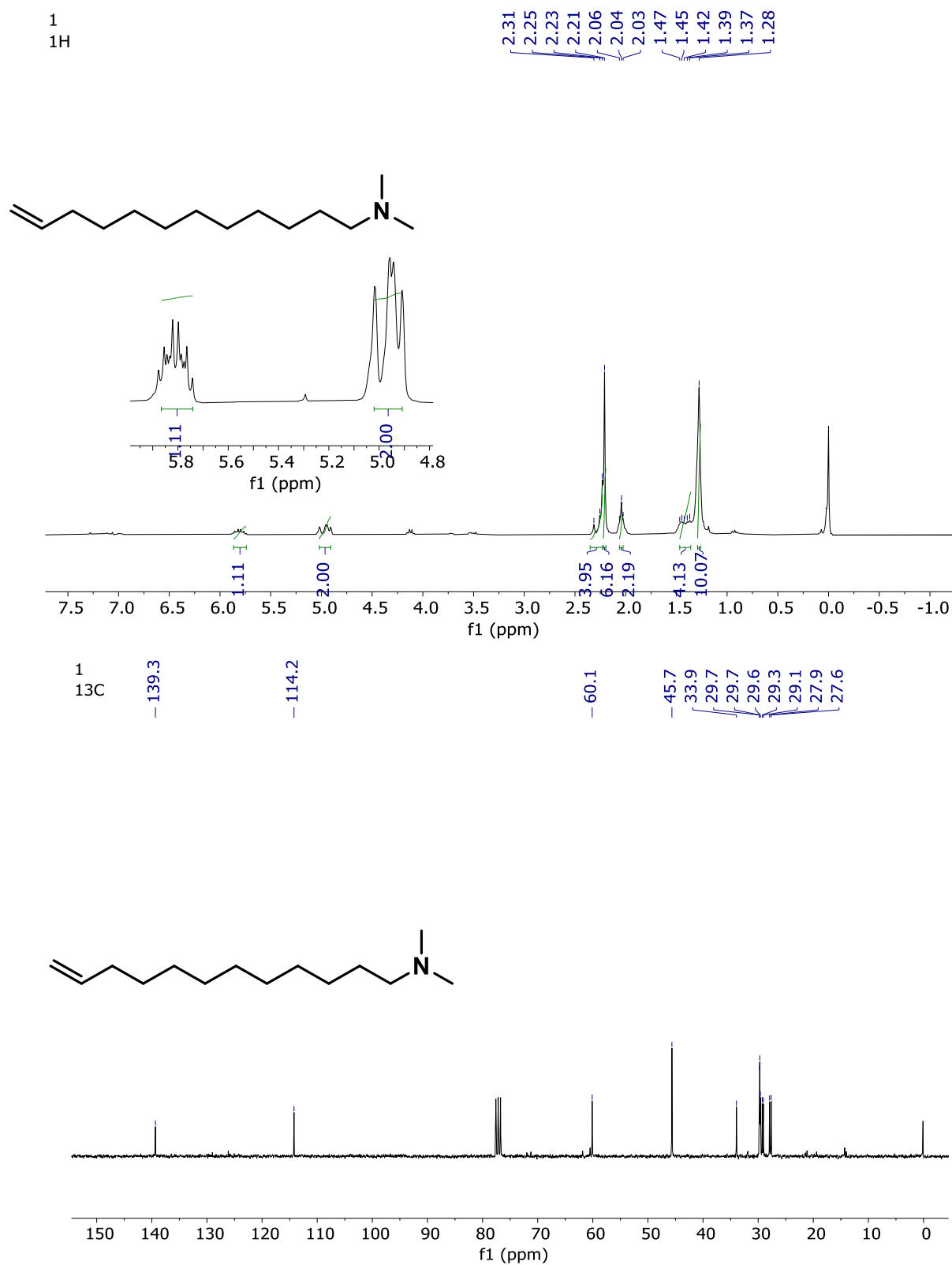


Figure S1. ¹H NMR and ¹³C NMR of compound 2 in CDCl₃ at 300 MHz.

N,N-dimethyldodec-11-en-1-amine (**4**).



4-(dodec-11-en-1-yl)dimethylammonio)butane-1-sulfonate (ASDC12) (**6**)

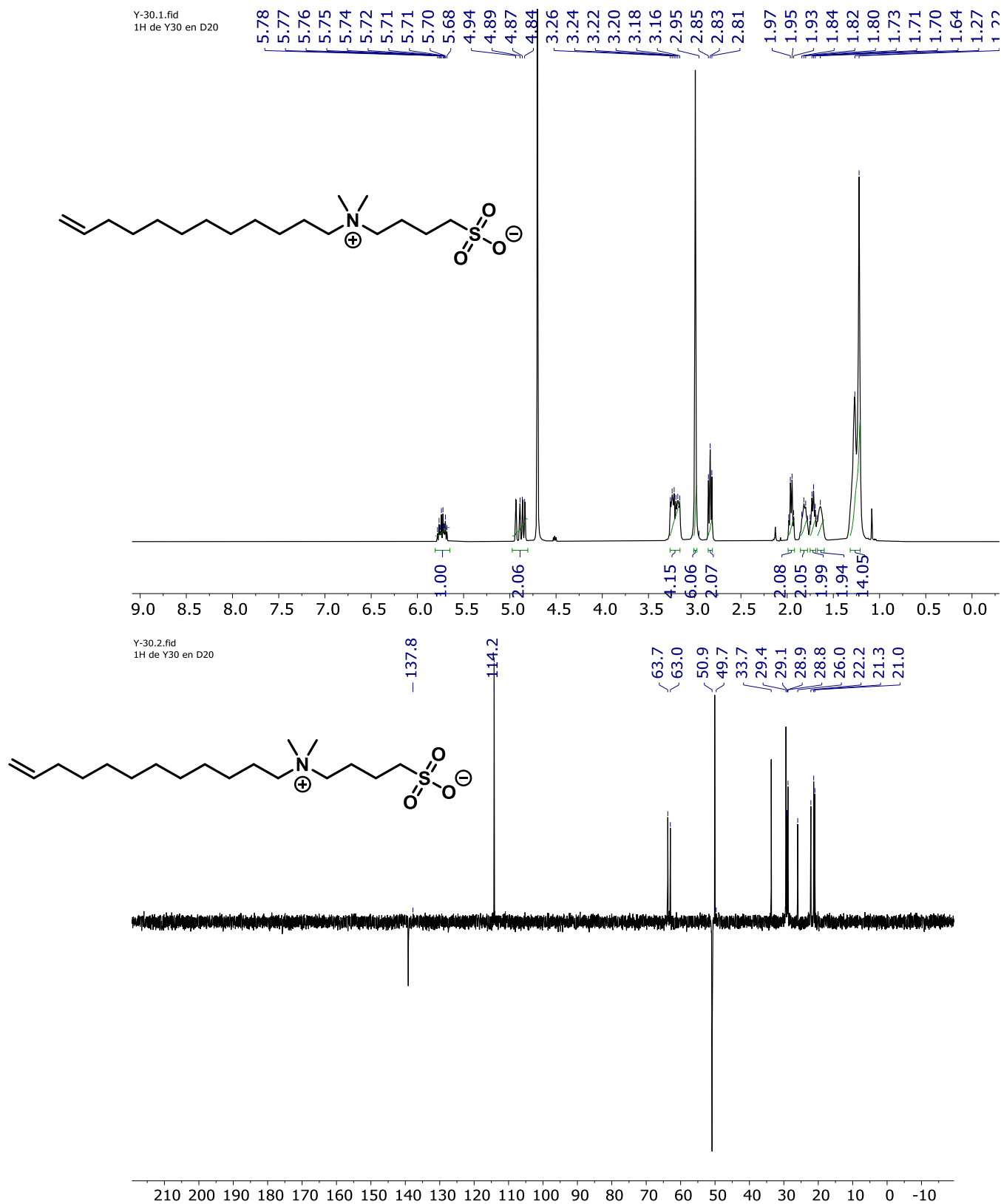


Figure S3. ¹H NMR and ¹³C APT NMR of compound **6** in D₂O at 400 MHz.

N,N-dimethyldodecan-1-amine (7).

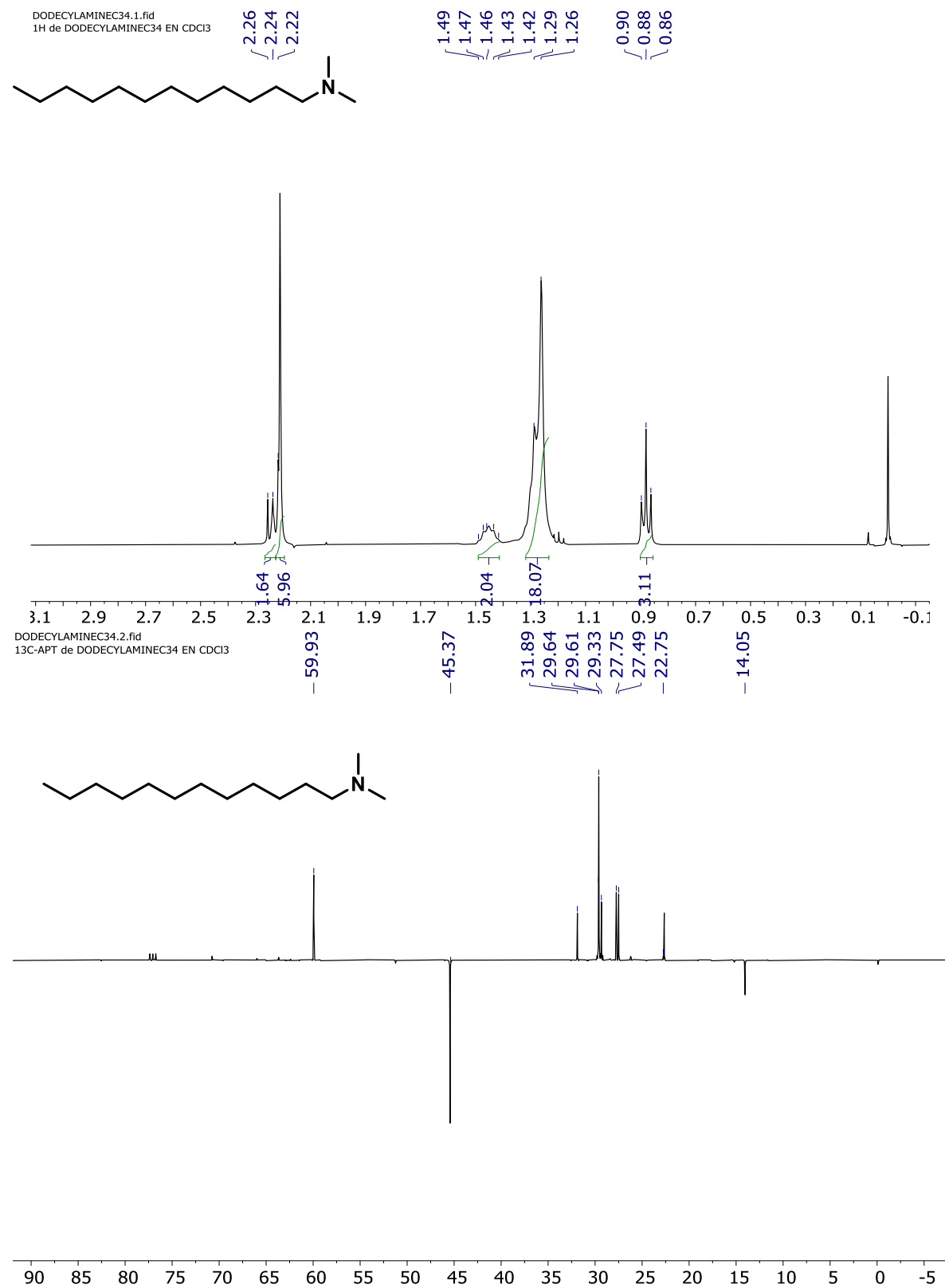
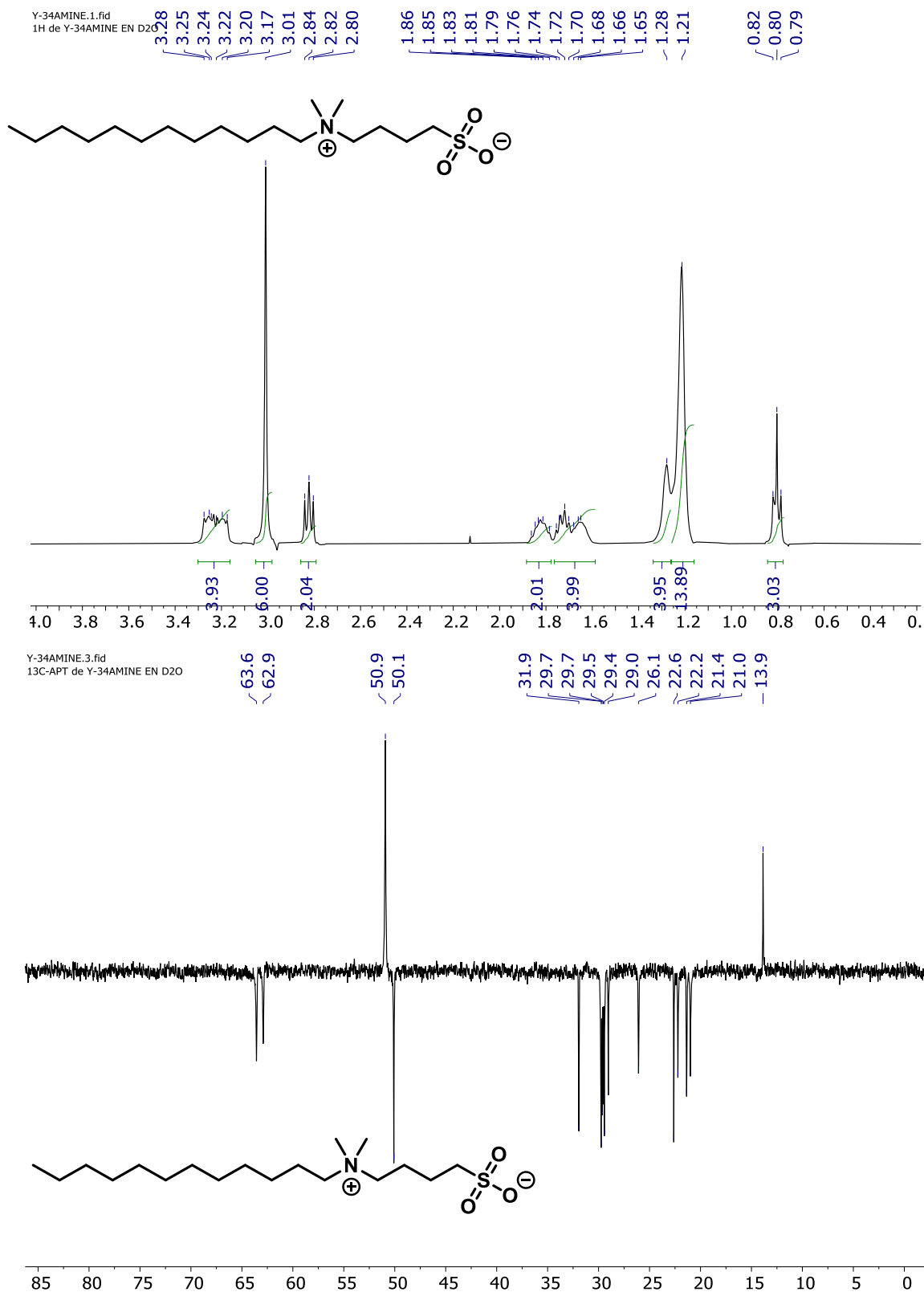


Figure S4. ¹H NMR and ¹³C APT NMR of compound 7 in CDCl₃ at 400 MHz.

4-(dodecyldimethylammonio)butane-1-sulfonate (**8**).



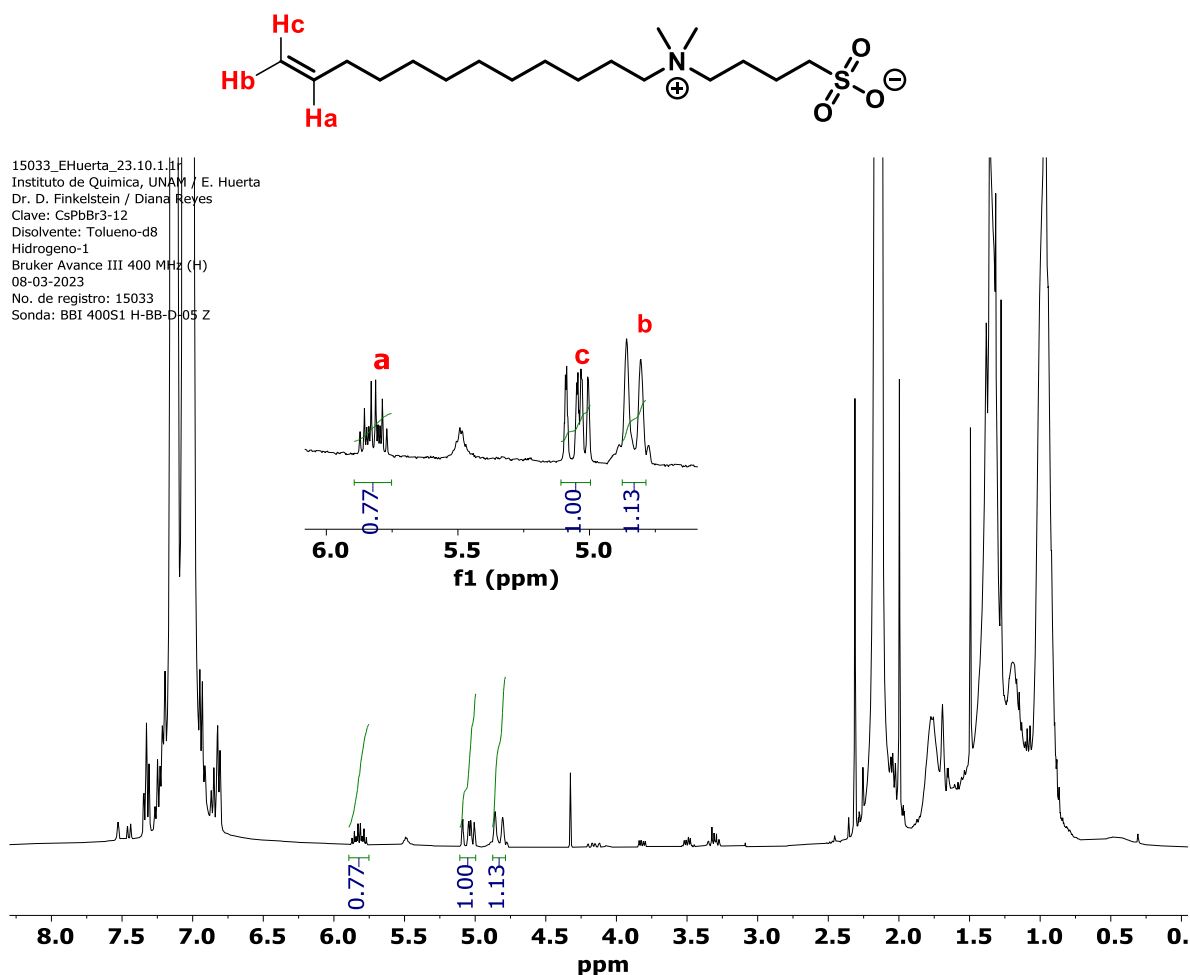


Figure S6. ¹H NMR of isolated SRO CsPbBr₃ NCs in toluene d₈ at 400 MHz.

Synthesis of CsPbBr₃ perovskite nanocrystals.

Synthesis of cesium oleate (Cs-oleate) in octadecene 0.4 M.

In a round-bottom flask equipped with a magnetic stirring bar, 1.628 g (5 mmol) of Cs₂CO₃ and 5 mL (16 mmol) of oleic acid (OA) were dissolved in 20 mL of octadecene (ODE). Immediately, the reaction mixture was heated at 120 °C under vacuum for 60 min. The Cs-oleate was placed in a glove box which was kept inside until use.

Synthesis of lead oleate (Pb-oleate) in octadecene 0.5 M.

In a two-necked round-bottom flask equipped with a magnetic stirring bar, 4.607 g (12 mmol) of lead (II) acetate trihydrate and 7.6 mL (24 mmol) of oleic acid (OA) were dissolved in 16.4 mL of octadecene. Immediately, the reaction mixture was heated at 120 °C under vacuum for 60 min to completely remove any remnant of water and acetic acid. The desired oleate was placed in a glove box which was kept inside until use.

Synthesis of trioctylphosphine-Br₂ (TOP-Br₂) adduct in toluene 0.5 M.

In a Schlenk-type flask filled with N₂, trioctylphosphine (TOP) (6 mL, 13 mmol) were dissolved in 18.7 mL of dry toluene. Subsequently, the reaction mixture was cooled in an ice bath, and 0.6 mL (11.5 mmol) of Br₂ was injected. The formation of the adduct is observed by the jellification of the reaction mixture inside the Schlenk flask. The Schlenk-type flask was heated to 70 °C in order to promote the formation of a clear liquid, which can be handled more efficiently. Finally, the desired TOP-Br₂ was placed in a glove box which was kept inside until use.

CsPbBr₃ NCs Synthesis. In an initial experiment, we carried out the colloidal CsPbBr₃ NCs synthesis using ASDC12 as ligand through a slightly modified procedure reported by Krieg *et al.*¹ Briefly, a three-necked round bottom flask containing a mixture of 5 mL (0.5 M, 2.5 mol) of lead (II) oleate, 4 mL (0.4 M, 1.6 mmol) of cesium oleate, 0.5 mmol of ASDC-12 (or, S-ASDC12) and 10 mL of octadecene, was fully evacuated under vacuum and heated to 120 °C for 1 h. At this point, the reaction atmosphere was switched to N₂ and the reaction mixture heated up to 200 °C. To initiate the NCs nucleation, 5 mL (0.5 M, 2.5 mmol) of trioctylphosphine-Br₂ adduct (TOP-Br₂) was added to the mixture, and then immediately cooled down in a water-ice bath. For the purification process, an aliquot of 1 mL of the reaction crude was centrifuged at 8500 rpm for 15 min and the supernatant discarded. The precipitate was then diluted with 1 mL of dry toluene, centrifuged at 8500 rpm for another 15 minutes, and washed with 1 mL of dry methyl acetate. These purification steps were repeated a second time. Additionally, the synthesis of CsPbBr₃ NCs capped with the typical OAm/OA ligands was carried out following the same procedure described above using the same precursor concentrations (OAm, 0.5 mmol and OA, 0.5 mmol).

Truncation degree index τ calculation. The index was calculated using the following expression as described by S. Disch *et al.*²

$$\tau_i = \frac{2t_i}{l_i}$$

Where t_i is the average truncation length, and l_i the length of cubes edges.

CsPbBr₃ NCs capped with OA/OAm ligands.

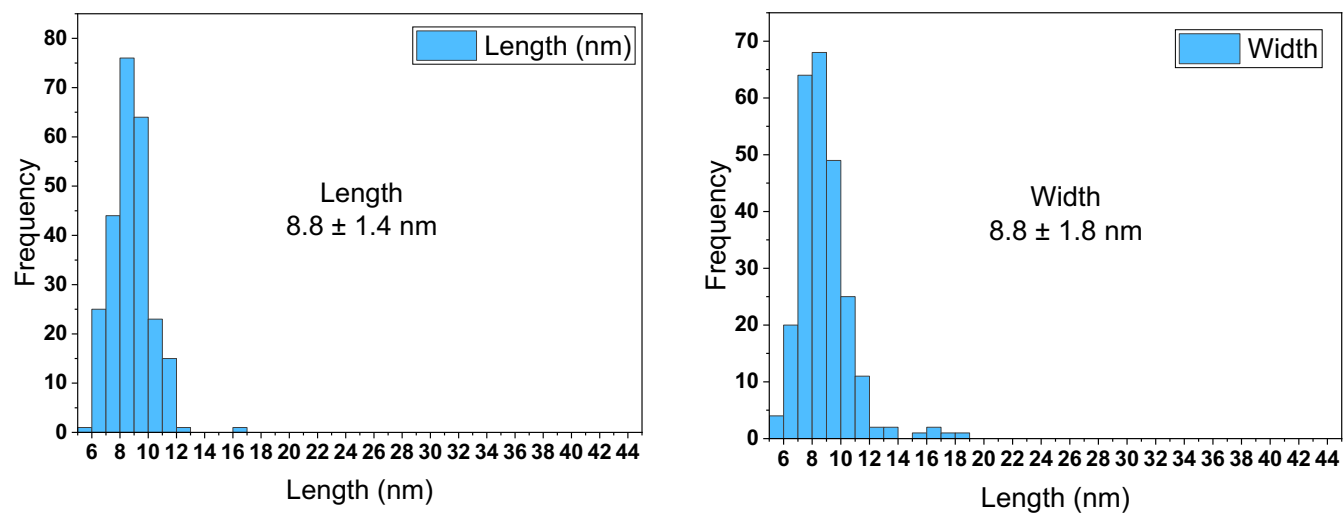
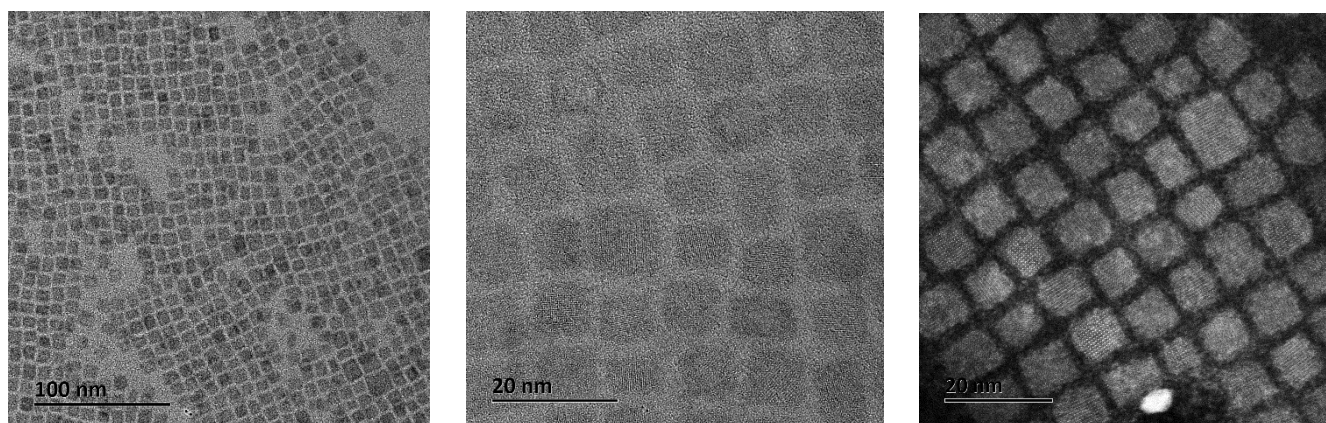


Figure S7. TEM micrographs and histograms
CsPbBr₃ NCs capped with OA/OAm at a ligand concentration of 0.5 mmol.

CsPbBr₃ NCs capped with S-ASDC12.

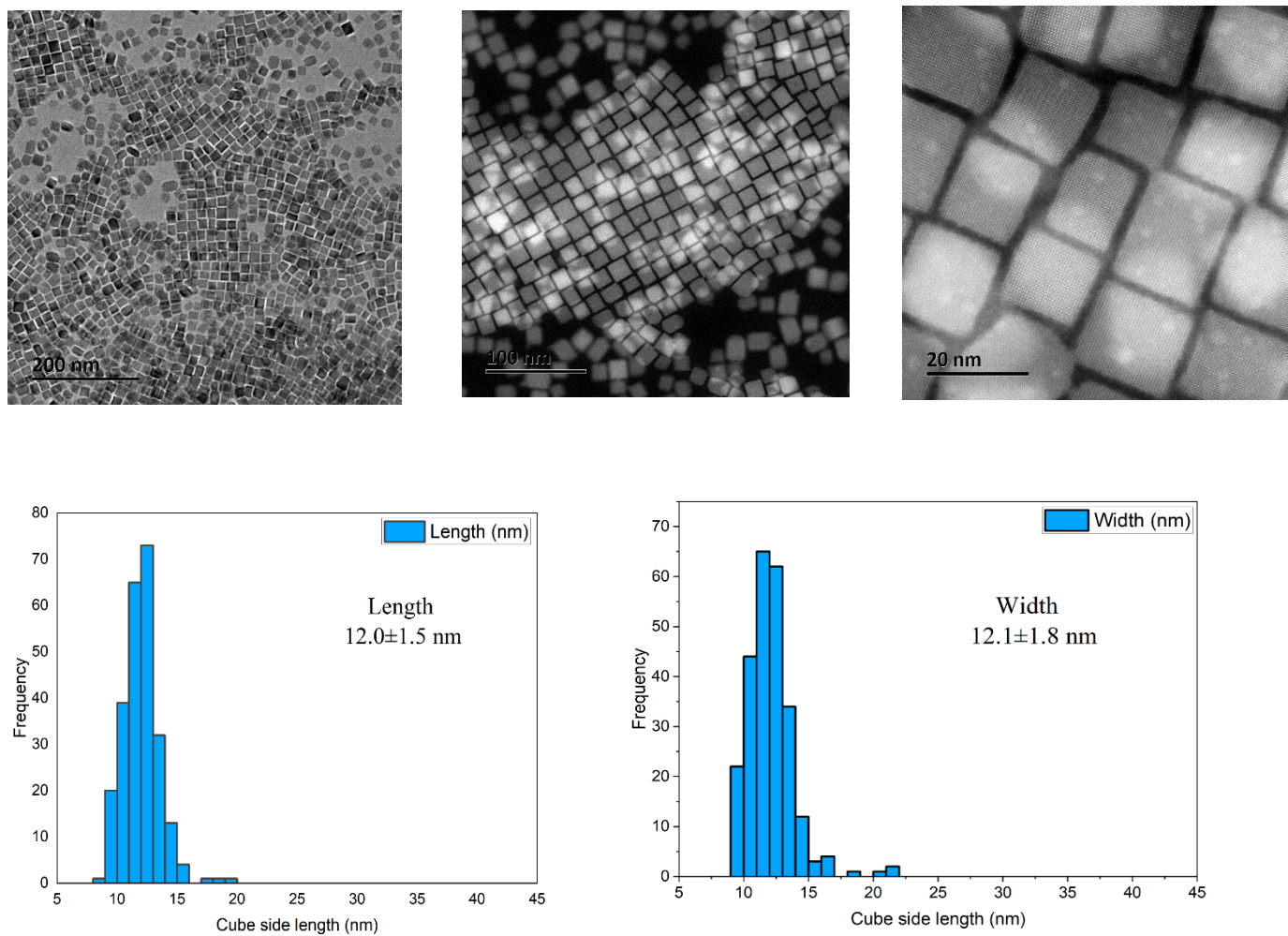


Figure S8. TEM micrographs and histograms CsPbBr₃ NCs capped with S-ASDC12 at a ligand concentration of 0.5 mmol.

CsPbBr₃ NCs capped with ASDC12.

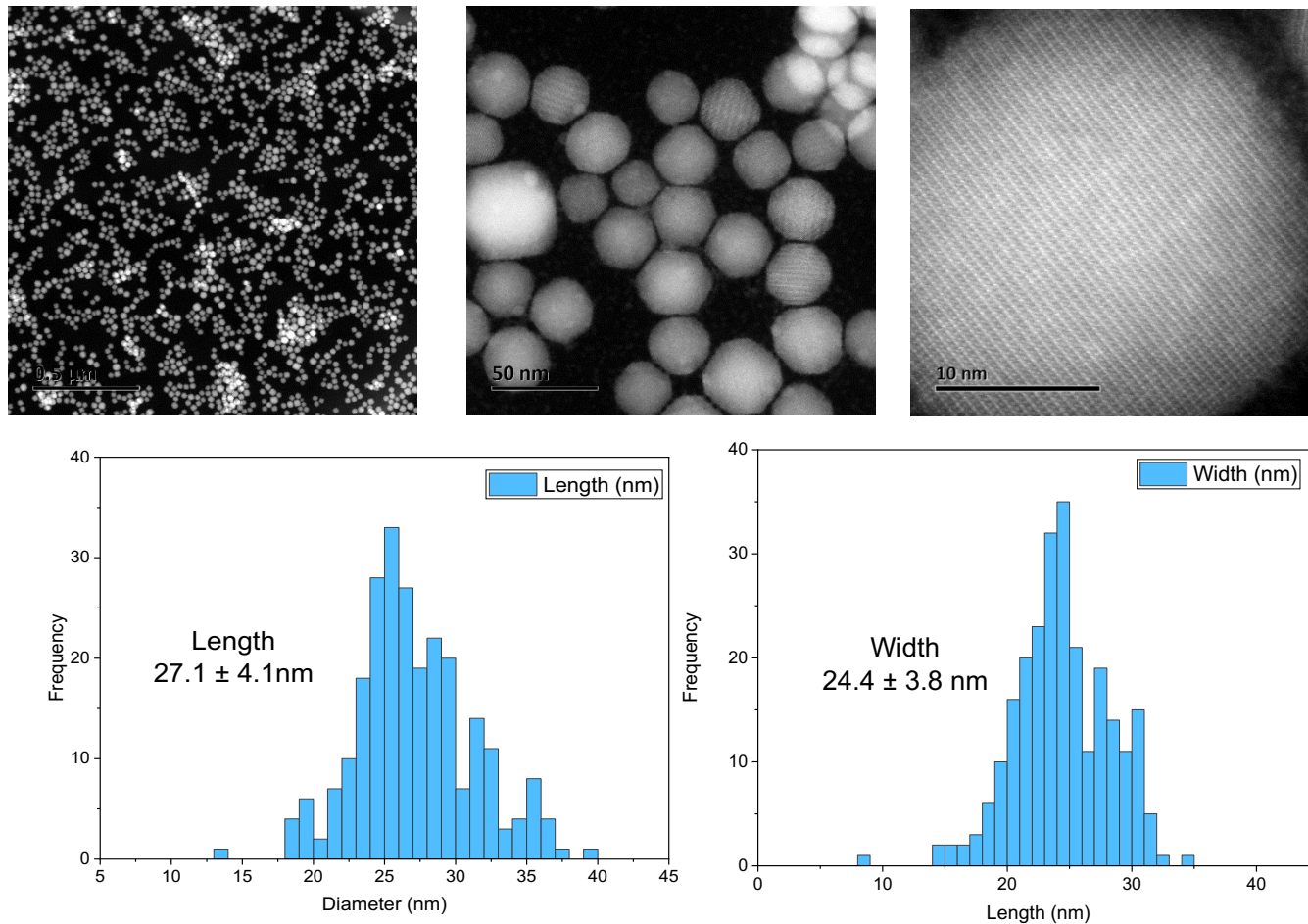


Figure S9. TEM micrographs and histograms CsPbBr₃ NCs capped with ASDC12 at a ligand concentration of 0.5 mmol.

CsPbBr₃ NCs capped with ASDC12 after 6 months.

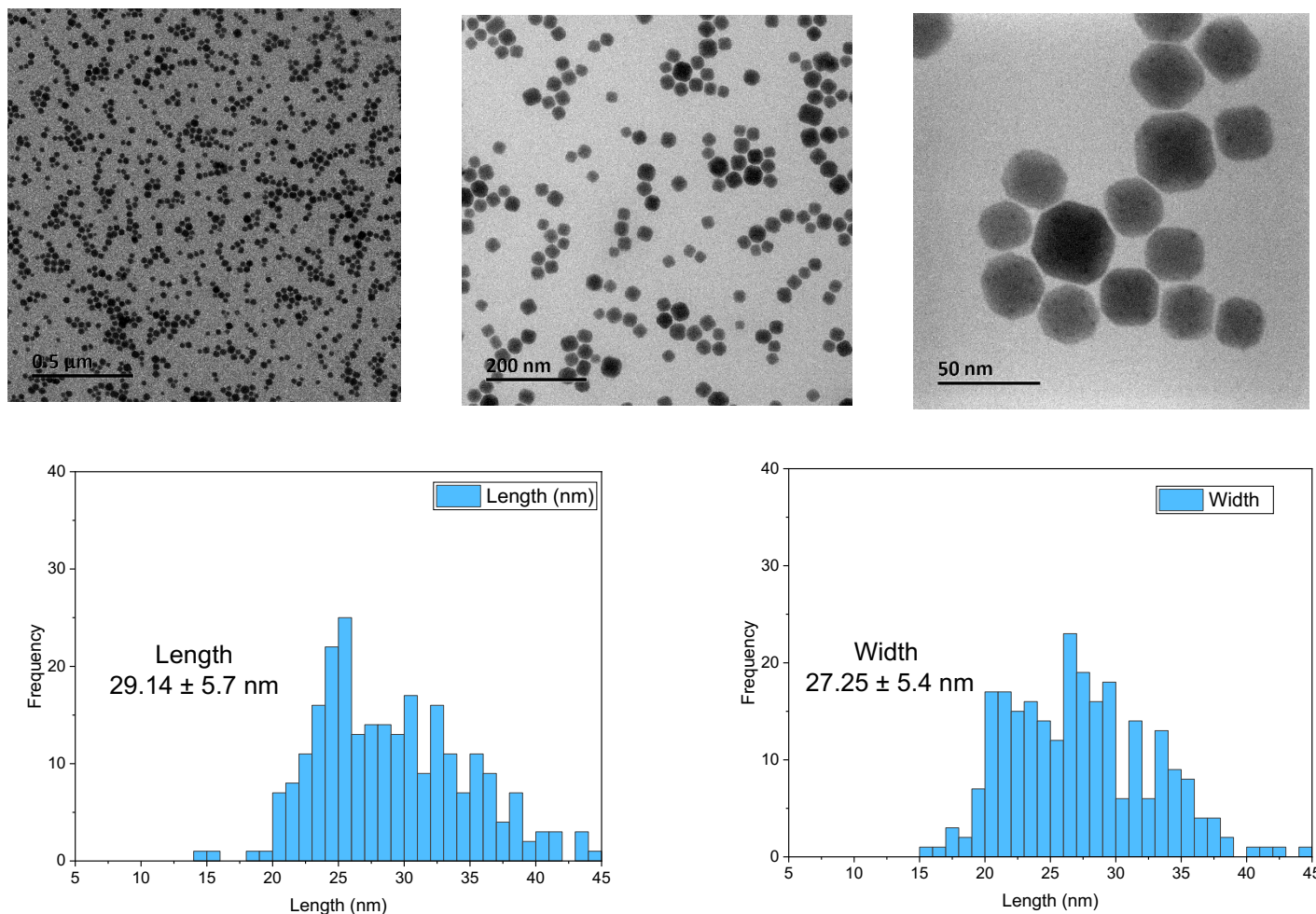


Figure S10. TEM micrographs and histograms CsPbBr₃ NCs capped with ASDC12, at a ligand concentration of 0.5 mmol, after 6 months. The reaction crude of the HI injection protocol that contains the SRO-shaped CsPbBr₃ nanocrystals was preserved at room temperature in a MBRAUN glove box under inert atmosphere (N₂). For TEM measurements, an aliquot of 1 mL of the reaction crude was centrifuged at 8500 rpm for 15 min and the supernatant discarded. The precipitate was then diluted with 1 mL of dry toluene, centrifuged at 8500 rpm for another 15 minutes, and washed with 1 mL of dry methyl acetate. These purification steps were repeated a second time.

CsPbBr₃ NCs capped with OA/OAm after 6 months.

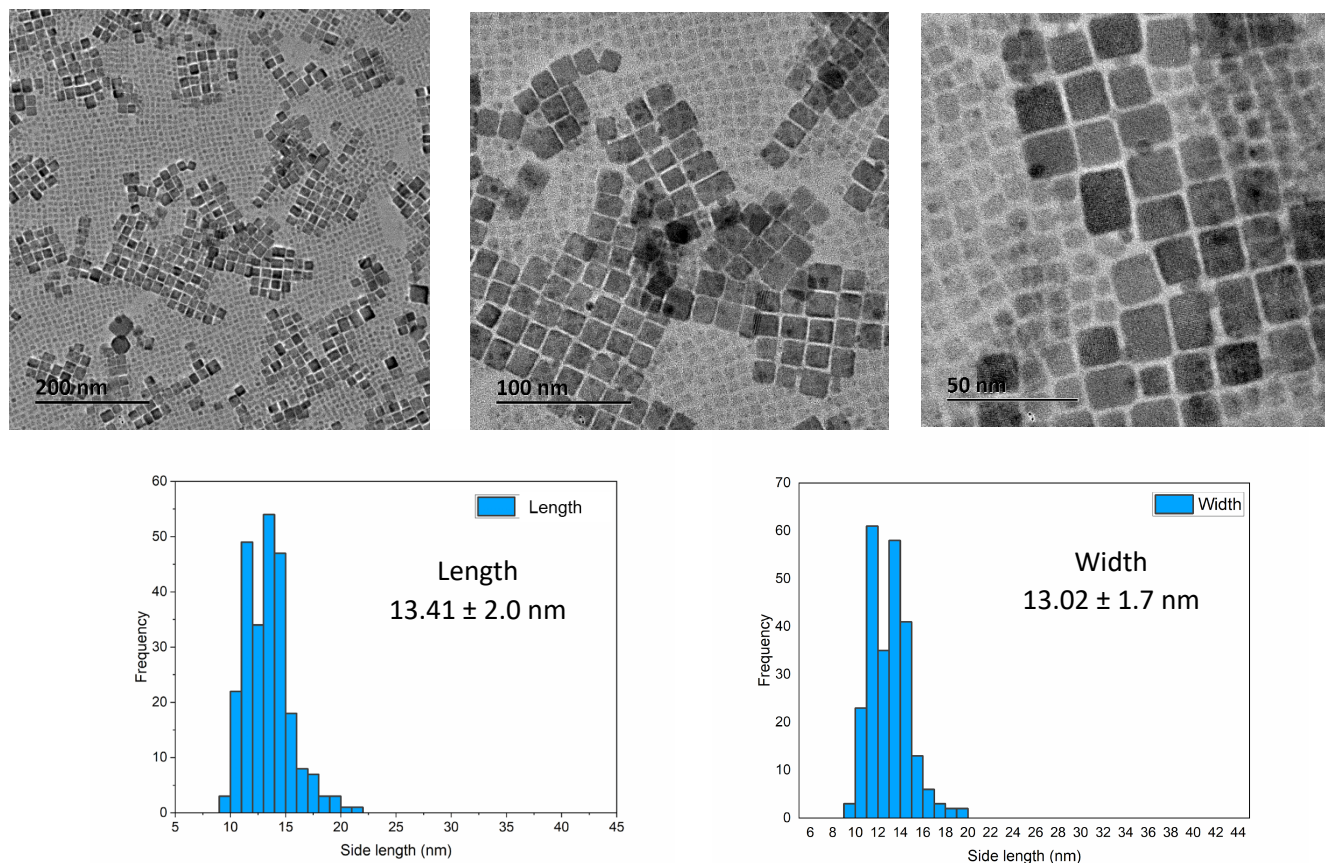


Figure S11. TEM micrographs and histograms CsPbBr₃ NCs capped with OA/OAm, at a ligand concentration of 0.5 mmol, after 6 months. The reaction crude of the HI injection protocol that contains the cubical-shaped CsPbBr₃ nanocrystals were preserved at room temperature in a MBRAUN glove box under inert atmosphere (N₂). For TEM measurements, an aliquot of 1 mL of the reaction crude was centrifuged at 8500 rpm for 15 min and the supernatant discarded. The precipitate was then diluted with 1 mL of dry toluene, centrifuged at 8500 rpm for another 15 minutes, and washed with 1 mL of dry methyl acetate. These purification steps were repeated a second time.

ASDC12 concentration effect

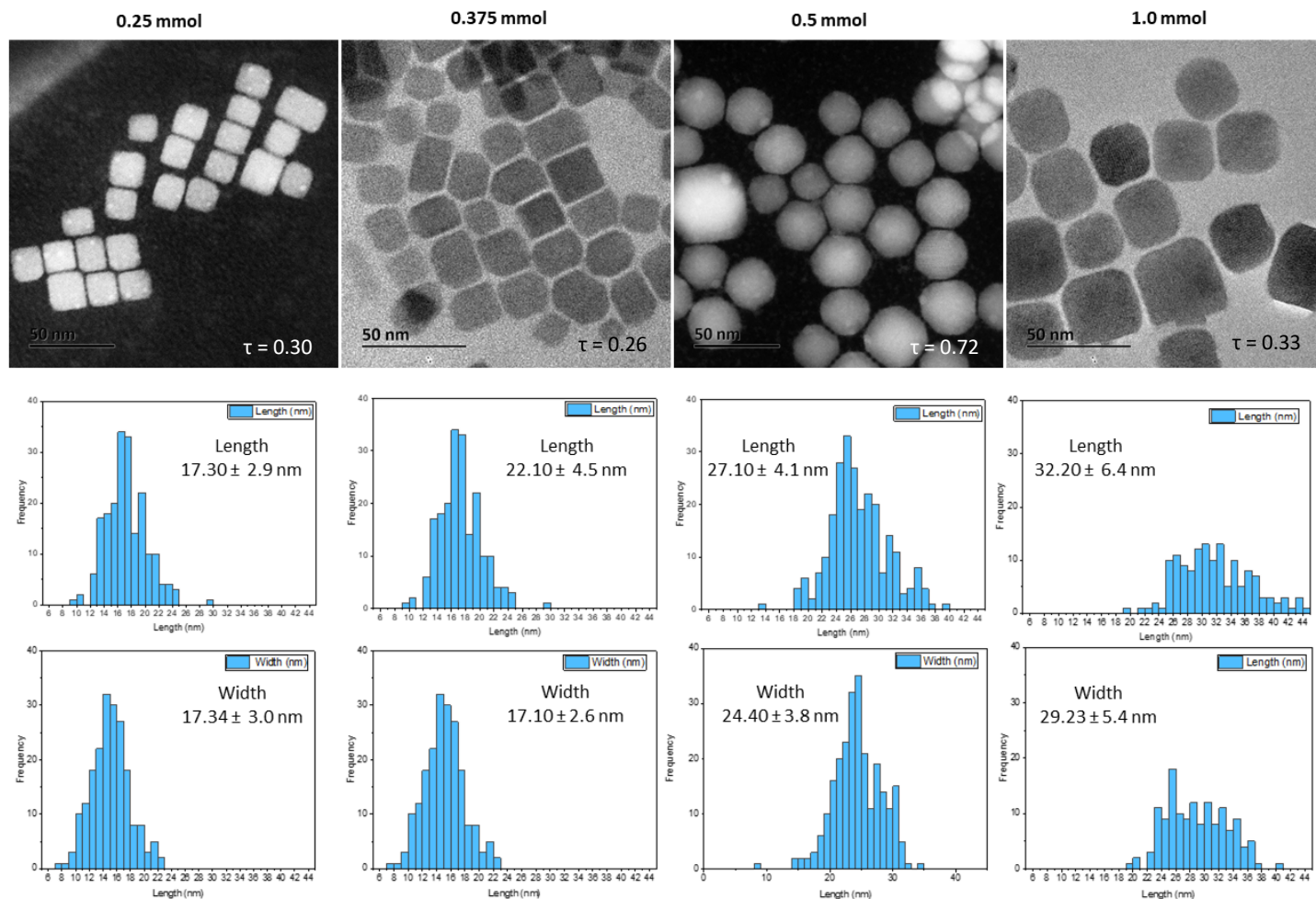
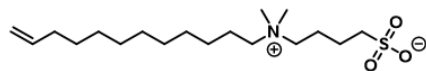


Figure S12. TEM micrographs and histograms of CsPbBr₃ NCs capped with ASDC12 in different concentrations.

S-ASDC12 concentration effect

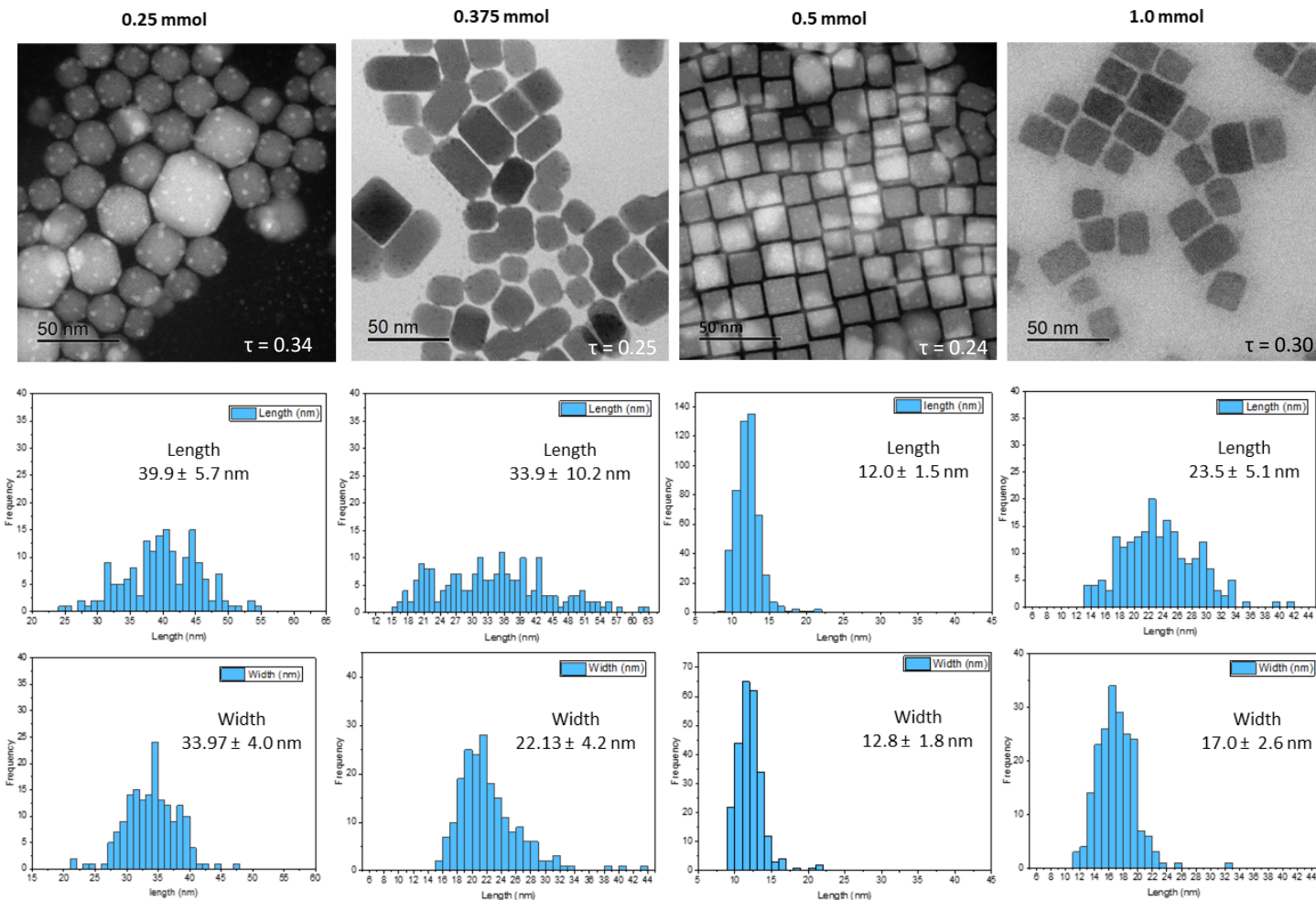
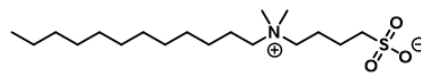


Figure S13. TEM micrographs and histograms of CsPbBr₃ NCs capped with S-ASDC12 in different concentrations.

Ligand density studies.

Ligand density studies were conducted using a modified procedures reported in the literature.³ Briefly, 0.5 mL of the reaction crude was centrifuged at 8500 rpm for 15 minutes, and the supernatant was discarded. The resulting precipitate was then diluted with 0.5 mL of dry toluene, followed by another centrifugation at 8500 rpm for 15 minutes and a wash with 0.5 mL of dry methyl acetate. These purification steps were repeated once more. Subsequently, volatiles were removed under reduced pressure for 5 hours, yielding 80.2 mg of CsPbBr₃ rhombicuboctahedron NCs (capped with ASDC12) and 30.4 mg of cubic NCs (capped with S-ASDC12).

For the determination of ligand concentrations, qNMR (quantitative Nuclear Magnetic Resonance) experiments were conducted. To ensure the utmost accuracy in quantification, a certified internal standard (TCNB = 1,2,4,5-Tetrachloro-3-nitrobenzene, TraceCERT, Sigma Aldrich) served as the internal reference for NMR. Importantly, the signal from the standard did not overlap with the signals from our materials, facilitating seamless integration during analysis. The ¹H RMN experiments of the isolated NCs capped with ASDC12 and S-ASDC12 were recorded on a Bruker Avance RMN spectrometers operating at a 500 MHz and 400 MHz frequency, respectively.

To determine the optimal standard concentration (TCNB), considerations were given to the total amount of the isolated nanomaterial, its nanocrystals area, and its respective volume, resulting in 1.2 mg of TCNB for NCs capped with ASDC12 and 2.52 mg for NCs capped with S-ASDC12. Initially, the standard and the isolated material were dissolved in 0.6 mL of DMSO-*d*₆ for the subsequent NMR experiment. The ¹H qNMR spectrum was recorded with a relaxation delay of 30 s to ensure full relaxation of the NMR actives nuclei and accurate quantification. Ligand density was then calculated by combining particle size data (obtained by counting 250 nanocrystals from TEM) and the concentration of ASDC12 and S-ASDC12 (obtained from NMR spectra) (Figures S14 and S15).

Ligand density in SRO-shaped CsPbBr₃ NCs

Initially, the overall moles of ASDC12 were calculated by considering the total material mass obtained after the purification processes. To achieve this, a qNMR experiment was conducted using the total mass of SRO-shaped CsPbBr₃ nanocrystals (80.2 mg) and the calculated mass of the internal standard (1.2 mg of TCNB, TraceCERT, Sigma Aldrich). With the spectrum in hand, the peaks at 5.78 ppm, corresponding to the H3 proton, and the peak at 8.14 ppm, corresponding to the H14 protons (Figure S14) were integrated against the peak at 8.43 ppm of the standard. Through this analysis, it was determined that $1.3522242238 \times 10^{-5}$ moles and $1.379839019 \times 10^{-5}$ moles of ASDC12 ligand were bound, respectively. Subsequently, the total number of ligands was determined by converting the resulted moles of ASDC12 to the number of molecules using Avogadro's number:

$$\text{Number of ligand molecules} = \text{number of ligand moles} \times \text{Avogadro's number}$$

$$\text{Number of ligand molecules in H3} = 1.269451897 \times 10^{-5} \text{ mol} \times 6.022 \times 10^{23} = 8.143094276 \times 10^{18} \text{ ligands}$$

$$\text{Number of ligand molecules in H14} = 1.379839019 \times 10^{-5} \text{ mol} \times 6.022 \times 10^{23} = 8.309390571 \times 10^{18} \text{ ligands}$$

To calculate the ligand density, it is crucial to determine the total surface area ($A = (18 + 2\sqrt{3}) a^2$) and volume $V = ((12 + 10\sqrt{2})/3) a^3$ of the SRO-shaped CsPbBr₃ nanocrystals within the 80.2 mg of material. Initially, the total volume of nanocrystals was determined, considering the density of CsPbBr₃:

$$\text{Total NC volume} = \frac{\text{mass of isolated CsPbBr}_3 \text{ NCs}}{\text{CsPbBr}_3 \text{ density}} = \frac{0.0802 \text{ g}}{4.55 \text{ g/cm}^3} = 0.01763 \text{ cm}^3$$

To determine the total number of SRO-shaped CsPbBr₃ nanocrystals in 80.2 mg of isolated material, it is necessary to find the volume of a single nanocrystal. This calculation utilizes average particle size data obtained by measuring the length and width of 250 nanocrystals from TEM analysis.

$$\text{Volume of a single NC} = \frac{12 + 10\sqrt{2}}{3} \times a^3 = \frac{12 + 10\sqrt{2}}{3} \times 25.75 \text{ nm}^3 = 148782.3825 \text{ nm}^3 = 1.487823825 \times 10^{-16} \text{ cm}^3$$

Therefore, to establish the total number of nanocrystals found in 80.2 mg, the division of the total volume by the volume of a single nanocrystal was performed:

$$\text{Number of NCs} = \frac{\text{total NC volume}}{\text{volume of a single NC}} = \frac{0.01763 \text{ cm}^3}{1.487823825 \times 10^{-16} \text{ cm}^3} = 1.184708386 \times 10^{14}$$

To determine the total nanocrystal area, it is necessary to ascertain the area of a single SRO-shaped CsPbBr₃ nanocrystal:

$$\text{Area of a single NC} = (18 + 2\sqrt{3}) \times a^2 = (18 + 2\sqrt{3}) \times (25.75 \text{ nm})^2 = 14232.041 \text{ nm}^2$$

The total nanocrystal area found in 80.2 mg of material was calculated by multiplying the area of a single nanocrystal by the total number of SRO-shaped nanocrystals:

$$\text{Total NC area} = \text{total number of SRO NCs} \times \text{area of a single SRO NC}$$

$$\text{Total NC area} = 1.184708386 \times 10^{14} \times 14232.041 \text{ nm}^2 = 1.6860981832 \times 10^{18} \text{ nm}^2$$

Finally, the ligand density was obtained by dividing the number of ligands determined in the qNMR analysis by the total nanocrystal area (Figure S14):

$$\text{Ligand density (H3)} = \frac{\text{total number of ligands}}{\text{total NC area}} = \frac{8.143094276 \times 10^{18}}{1.6860981832 \times 10^{18} \text{ nm}^2} = 4.83 \text{ ligands/nm}^2$$

$$\text{Ligand density (H14)} = \frac{\text{total number of ligands}}{\text{total NC area}} = \frac{8.309390571 \times 10^{18}}{1.6860981832 \times 10^{18} \text{ nm}^2} = 4.92 \text{ ligands/nm}^2$$

$$\text{Ligand density average} = 4.87 \text{ ligands/nm}^2$$

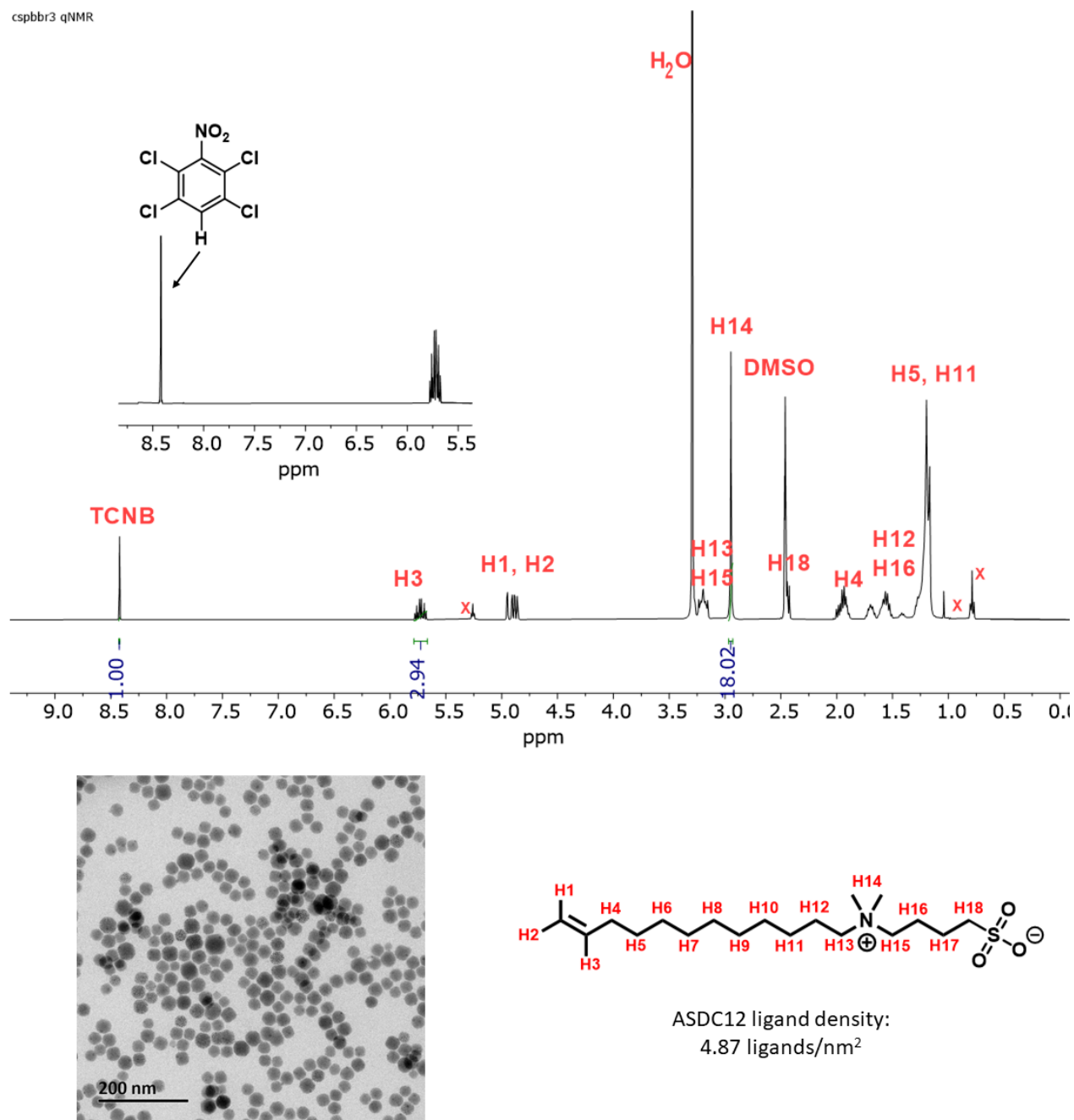


Figure S14. Quantitative Nuclear Magnetic Resonance (qNMR) spectrum of CsPbBr₃ NCs capped with 0.5 mmol of ASDC12 with relaxation delay of 30s., acquired using 80.2 mg of NCs obtained from a 0.5 mL colloidal suspension and 1.2 mg of 1,2,4,5-Tetrachloro-3-nitrobenzene (TCNB) as the internal standard.

Ligand density in cubic CsPbBr₃ NCs capped with S-ASDC12

In a similar procedure to determine the ligand density in ASDC12, the overall moles of S-ASDC12 were calculated by considering the total material mass obtained after the purification processes. To achieve this, a qNMR experiment was conducted using the total mass of cubic CsPbBr₃ nanocrystals (30.4 mg) and the calculated mass of the internal standard (2.52 mg of TCNB, TraceCERT, Sigma Aldrich). With the spectrum in hand, the peaks at 0.84 ppm, corresponding to H1 protons, and the peak in 2.98 ppm corresponding to H13 protons were integrated against the peak at 8.43 ppm of the standard (Figure S15). Through this analysis, it was determined that $1.439172097 \times 10^{-5}$ and $1.323265619 \times 10^{-5}$ moles of S-ASDC12 ligand were bound, respectively. Subsequently, the total number of ligands was determined by converting the resulted moles of S-ASDC12 to the number of molecules using Avogadro's number:

$$\text{Number of ligand molecules} = \text{number of ligand moles} \times \text{Avogadro's number}$$

$$\text{Number of ligand molecules in H1} = 1.439172097 \times 10^{-5} \text{ mol} \times 6.022 \times 10^{23} = 8.666694366 \times 10^{18} \text{ molecules}$$

$$\text{Number of ligand molecules in H13} = 1.323265619 \times 10^{-5} \text{ mol} \times 6.022 \times 10^{23} = 7.968705558 \times 10^{18} \text{ molecules}$$

To calculate the ligand density, it is crucial to determine the total surface area ($A = 6a^2$) and volume ($V = a^3$) of the cubic-shaped CsPbBr₃ nanocrystals within the 30.4 mg of material. Initially, the total volume of nanocrystals was determined, considering the density of CsPbBr₃:

$$\text{Total NC volume} = \frac{\text{mass of isolated CsPbBr}_3 \text{ NCs}}{\text{CsPbBr}_3 \text{ density}} = \frac{0.0304 \text{ g}}{4.55 \text{ g/cm}^3} = 6.681318681 \times 10^{-3} \text{ cm}^3$$

To determine the total number of cubic CsPbBr₃ nanocrystals in 30.4 mg of isolated material, it is necessary to find the volume of a single nanocrystal. This calculation utilizes average particle size data obtained by measuring the length and width of 250 nanocrystals from TEM analysis.

$$\text{Volume of cubic NC} = a^3 = (12.4 \text{ nm})^3 = 1906.624 \text{ nm}^3 = 1.906624 \times 10^{-18} \text{ cm}^3$$

Therefore, to establish the total number of nanocrystals found in 80.2 mg, the division of the total volume by the volume of a single nanocrystal was performed:

$$\text{Number of NCs} = \frac{\text{total NC volume}}{\text{volume of a single NC}} = \frac{6.681318681 \times 10^{-3} \text{ cm}^3}{1.906624 \times 10^{-18} \text{ cm}^3} = 3.504266537 \times 10^{15}$$

To determine the total nanocrystal area, it is necessary to ascertain the area of a single cubic CsPbBr₃ nanocrystal:

$$\text{Area of cubic NC} = 6a^2 = 6(12.4 \text{ nm})^2 = 922.56 \text{ nm}^2$$

The total nanocrystal area found in 30.4 mg of material was calculated by multiplying the area of a single cubic nanocrystal by the total number of cubic nanocrystals:

$$\text{Total NC area} = \text{total number of NCs} \times \text{area of a single cubic NC}$$

$$\text{Total NC area} = 3.504266537 \times 10^{15} \times 922.56 \text{ nm}^2 = 3.232896136 \times 10^{18} \text{ nm}^2$$

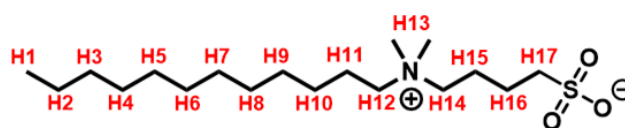
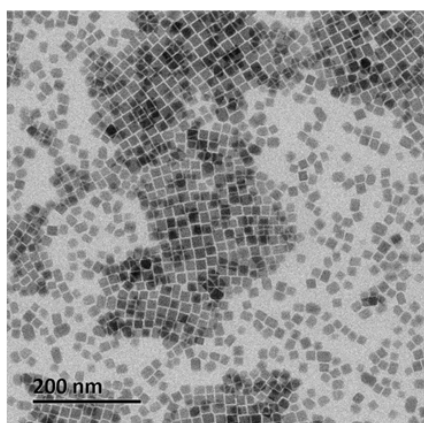
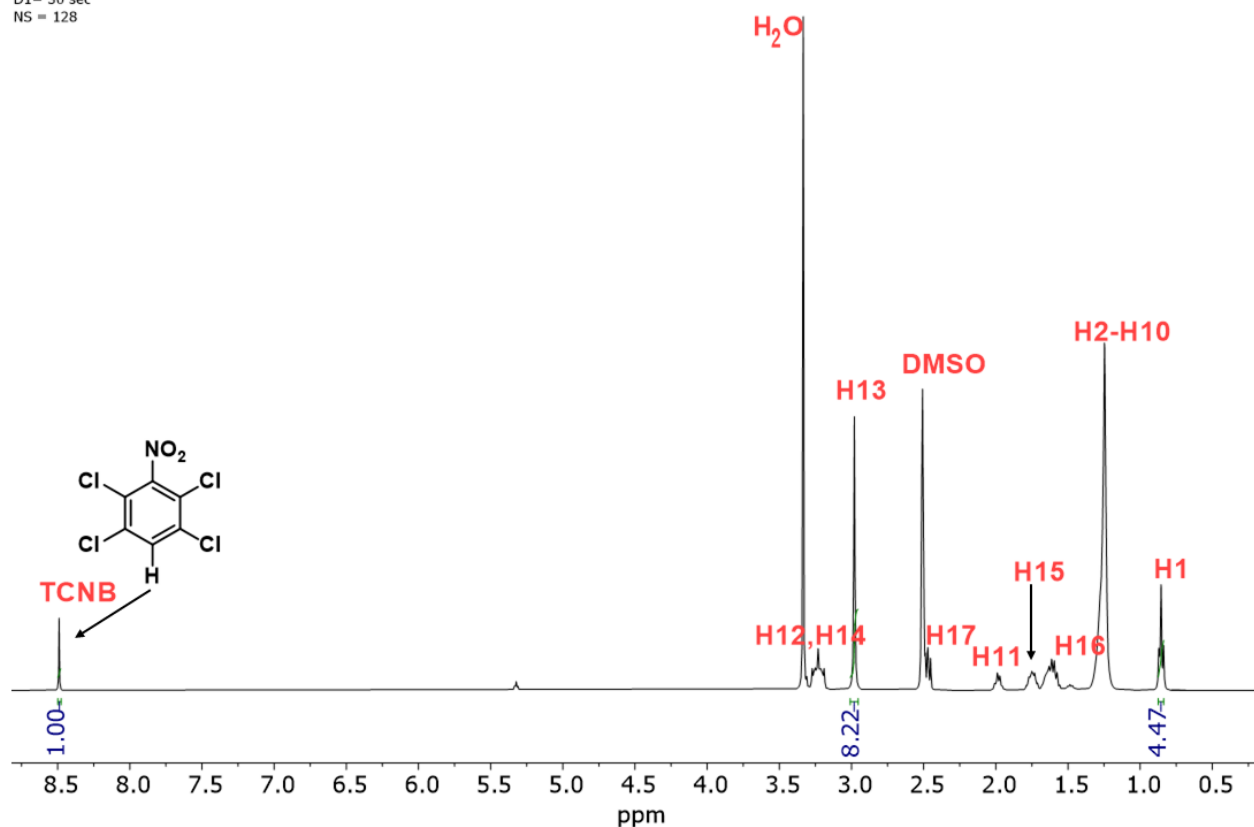
Finally, the ligand density was obtained by dividing the number of ligands determined in the qNMR analysis by the total nanocrystal area (Figure S15):

$$\text{Ligand density (H1)} = \frac{\text{total number of ligands}}{\text{Total NC area}} = \frac{8.666694366 \times 10^{18}}{3.232896136 \times 10^{18} \text{ nm}^2} = 2.68 \text{ ligands/nm}^2$$

$$\text{Ligand density (H13)} = \frac{\text{total number of ligands}}{\text{total NC area}} = \frac{7.968705558 \times 10^{18}}{3.232896136 \times 10^{18} \text{ nm}^2} = 2.46 \text{ ligands/nm}^2$$

$$\text{Ligand density average} = 2.57 \text{ ligands/nm}^2$$

yaas-qnmrsasdc12.2.fid
 1H de qnmrsasdc12 en DMSO-d6
 D1= 30 sec
 NS = 128



S-ASDC12 ligand density:
 2.57 nm^{-2}

Figure S15. Quantitative Nuclear Magnetic Resonance (qNMR) spectrum of CsPbBr₃ NCs capped with 0.5 mmol of S-ASDC12 with relaxation delay of 30s., acquired using 30.4 mg of NCs obtained from a 0.5 mL colloidal suspension and 2.52 mg of 1,2,4,5-Tetrachloro-3-nitrobenzene (TCNB) as the internal standard.

DFT Calculations

To study the effect of the double bond in the hydrocarbon chain of ASDC12 and S-ASDC12 in the surface of the NCs we chose dodecane (saturated chain), 1-dodecene and 6-dodecene (unsaturated chains) as model compounds. An array of nine hydrocarbon chains was used to study the interactions (or lack thereof) and packing of the chains. The quantum chemical calculations for the 3x3 array of 9 hydrocarbon chains were carried out using Density Functional Theory (DFT)^{4,5}. Optimized geometries were obtained at the GGA PBE/6-31G*^{6,7} level of theory, with auxiliary 6-31G* basis set for all atoms.⁸ Grimme's DFT-D3 dispersion corrections,⁹ with Becke and Johnson (BJ)-damping,¹⁰ were included. All optimizations were done with the Turbomole code.¹¹ The occupied convergence tolerances for all calculations were 1×10^{-6} Ha, 1×10^{-6} Ha, 1×10^{-3} Ha/Bohr, and 1×10^{-3} for self-consistent field (SCF) cycles, energy, gradient, and displacement, respectively. For the study, a chain of 12 carbon atoms was selected, in the 3x3 array each chain is placed at 4.128 Å from its first neighbors, which is the minimum separation between two bromide positions in the idealized CsPbBr₃ structure. This distance served as the initial point for geometry optimization, without imposing any restrictions on the symmetry. Figure S16 displays the optimized structure (PBE/6-31G*) for a 3x3 array of 9 chains of Dodecane (a) and 1-Dodecene (b). The figure highlights the average C—C distances observed in the structures.

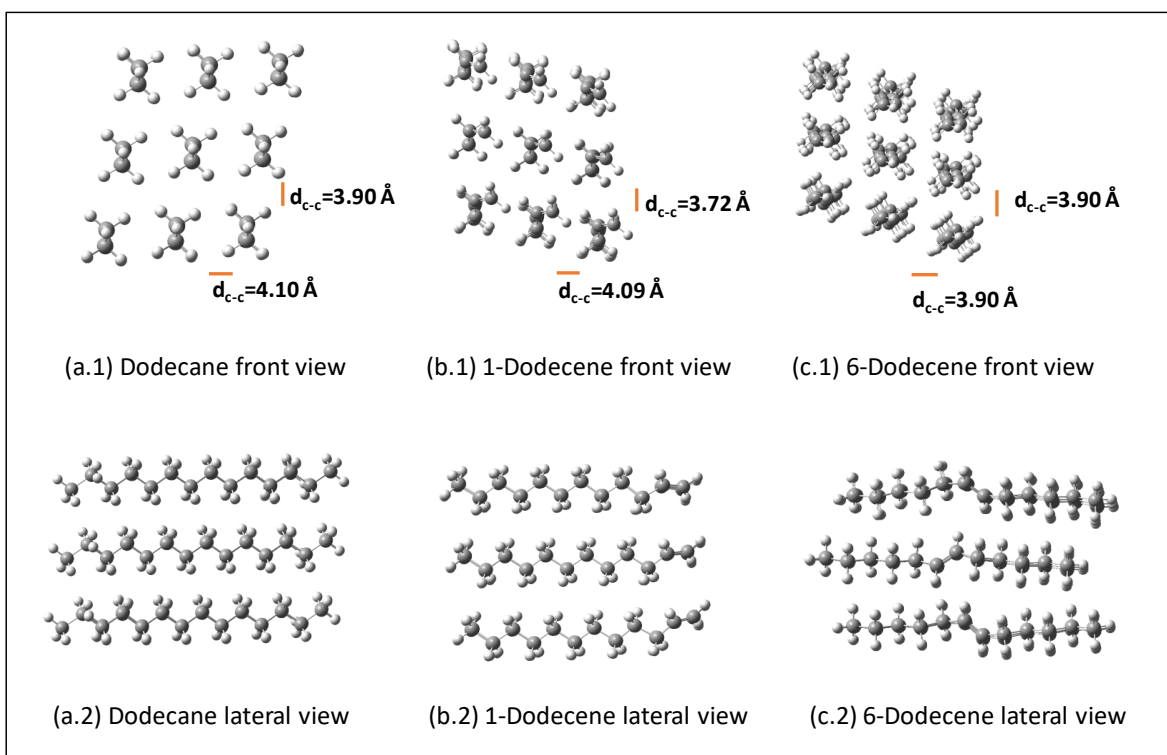


Figure S16. Optimized structures (PBE/6-31G*), front and lateral views (up and down, respectively) for (a) Dodecane, (b) 1-Dodecene and (c) 6-Dodecene. Average C—C distances in the structures are displayed.

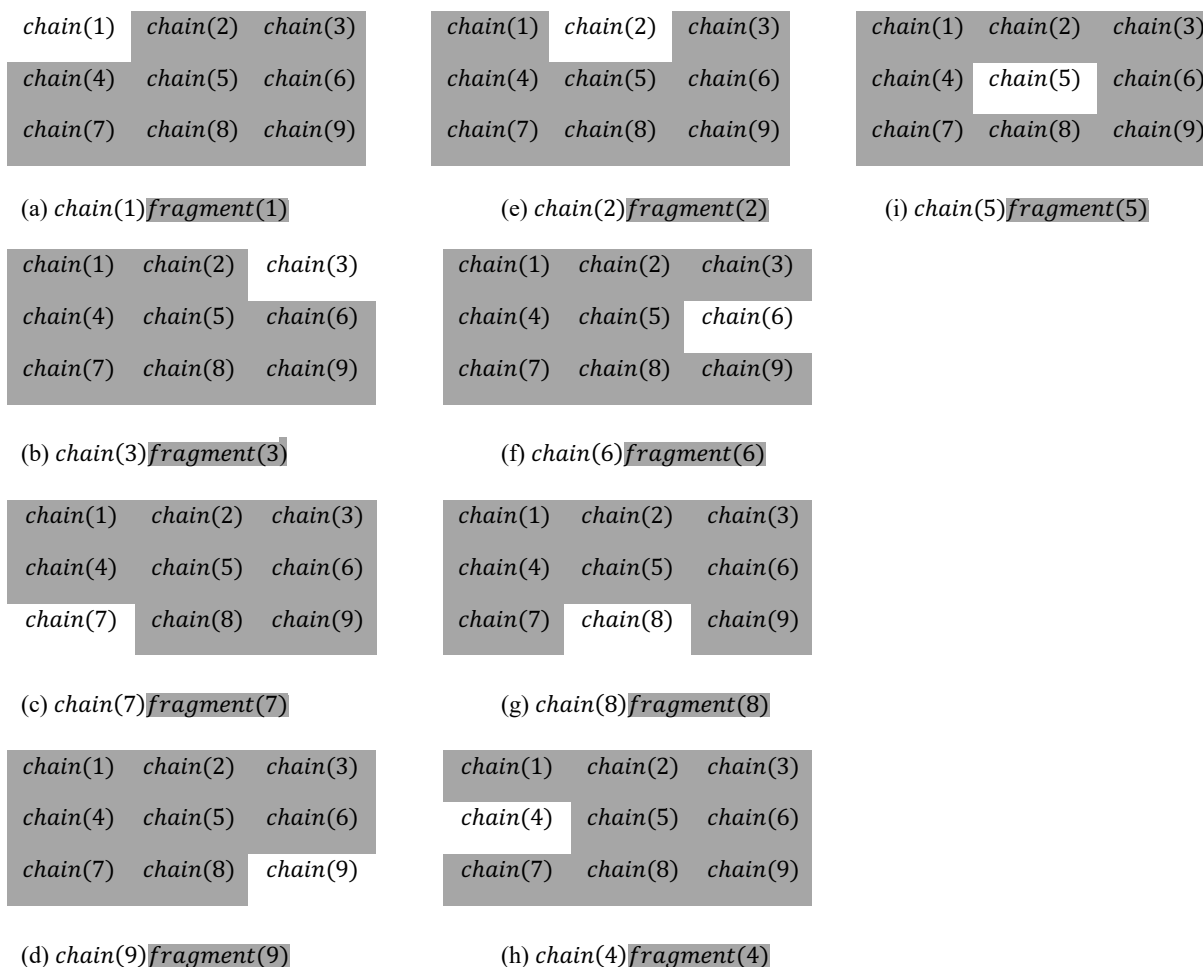
The arrangement is schematized as follows:

chain(1) *chain*(2) *chain*(3)

chain(4) *chain*(5) *chain*(6)

chain(7) *chain*(8) *chain*(9)

Where the *chain*(*i*) represents the position of the chain (*i*) in the arrangement, such that the *chain*1, *chain*2, and *chain*5 are nonequivalent positions in the arrangement. Scheme S2 shows the structure of the fragments considered in this study. The fragments considered as equivalents have the same type and number of interactions with the surroundings.



Scheme S2. Fragments considered for CP corrections used to calculate the interaction energy. Grey region corresponds to *fragment*(*i*). Fragments (a), (b), (c) and (d) are treated as equivalent, while fragments (e), (f), (g) and (h) are regarded as equivalent. Fragment (i) represents a unique configuration.

The equation used to calculate the interaction energy for these three chains (*chain*(1), *chain* (2) and *chain*(5)) considering the counterpoise correction (CP) is as follows:

$$E_{int}^{CP} (chain(i)/fragment(i)) = E_{fragment(i) \cdots chain(i)} - (E_{fragment(i)} + E_{chain(i)}) \quad \text{Eq. 1}$$

Where $E_{int}^{CP} (chain(i)/fragment(i))$ is the interaction energy for the chain (*i*) with the fragment building with all other chains, namely *fragment*(*i*).

$E_{fragment(i) \cdots chain(i)}$ is the energy of the *fragment*(*i*) interacting with *chain*(*i*).

$E_{fragment(i)}$ is the energy of the *fragment*(*i*) taking into account *chain*(*i*), but with ghost basis sets without electrons or nuclear charges for *chain*(*i*).

$E_{chain(i)}$ is the energy of *chain*(*i*) , taking into account *fragment*(*i*), but with ghost basis sets without electrons or nuclear charges for *fragment*(*i*)

The average interaction energy (\underline{E}_{int}) of the 3x3 arrange of hydrocarbon chains was obtained by the contributions for *chain*(1) (considering that the interactions of *chain*(1) are equivalents to those for *chain*(3), *chain*(7) and *chain*(9)), *chain*(2) (considering that the interactions of *chain*(2) are equivalents to those for *chain*(4), *chain*(6) and *chain*(8)) and, finally, the contribution of *chain*(5). The average interaction energy was calculated as shown in equation 2

$$\underline{E}_{int}^{CP} = \frac{1}{9} [4E_{int}^{CP} (chain(1)/fragment(1)) + 4E_{int}^{CP} (chain(2)/fragment(2)) + E_{int}^{CP} (chain(5)/fragment(5))] \quad \text{Eq. 2}$$

Table S1 shows the energies with CP corrections of fragments for 9 chains of dodecane, 1-dodecene and 6-dodecene in a 3x3 square planar arrangement. Table 2 displays the CP corrected energy and average interaction energies for the dodecane, 1-dodecene and 6-dodecene in a 3x3 square planar arrangement.

Table S1. PBE/6-31G* energies (Hartrees) with dispersion corrections for Dodecane, 1-Dodecene, and 6-Dodecene, chains in the 3x3 array. Counterpoise corrected energies (E^{CP}) and interaction energy \underline{E}_{int}^{CP} (kcal/mol)

3x3 array of 9 hydrocarbon chains (Fragment contribution)	Dodecane		1-Dodecene		6-Dodecene	
	E^{CP}	\underline{E}_{int}^{CP}	E^{CP}	\underline{E}_{int}^{CP}	E^{CP}	\underline{E}_{int}^{CP}
$E_{chain(1)/fragment(1)}^{CP}$	-4250.663	-16.73	-4239.616	-18.60	-4239.771	-14.61
$E_{chain(1) \cdots fragment(1)}^{CP}$	-3778.368		-3768.546	--	-3768.686	--
$E_{chain(1)}^{CP}$	-472.269		-471.041	--	-471.061	--
$E_{chain(2)/fragment(2)}^{CP}$	-4250.657	-26.45	-4239.610	-27.97	-4239.757	-20.44
$E_{chain(2) \cdots fragment(2)}^{CP}$	-3778.346		-3768.524	--	-3768.663	--

$E_{chain(2)}^{CP}$	-472.269		-471.041	--	-471.061	--
$E_{(chain(5)/fragment(5))}^{CP}$	-4250.652	-39.06	-4239.604	-39.891	-4239.780	-46.05
$E_{(chain(5)\cdots fragment(5))}^{CP}$	-3778.321		-3768.500	--	-3768.65	--
$E_{chain(5)}^{CP}$	-472.269		-471.041	--	-471.061	--

Table S2. PBE/6-31G* Counterpoise corrected average interaction energies ΔE (kcal/mol) for the dodecane, 1-dodecene and 6-dodecene in a 3x3 arrays.

3x3 array of 9 hydrocarbon chains	E_{int}^{CP}	ΔE_{int}^{CP} *
Dodecane	-23.53	1.6
1-Dodecene	-25.13	--
6-Dodecene	-20.69	4.4

*
Relative to 1-dodecene

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