

## Reaction chemistry and ligand exchange at cadmium selenide nanocrystal surfaces

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### Experimental

**Figure S1.**  $^1\text{H}$  NMR of purified, 4 nm CdSe nanocrystals in  $d_8$ -toluene.

**Figure S2.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of purified, 4 nm CdSe nanocrystals in  $d_8$ -toluene.

**Figure S3.**  $^1\text{H}$  NMR of the reaction between CdSe nanocrystals and **4** in  $d_8$ -toluene.

**Figure S4.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between 4 nm CdSe nanocrystals, and  $\text{Me}_3\text{SiCl}$  in  $d_8$ -toluene.

**Figure S5.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of *n*-hexylphosphonic acid anhydride in  $d_8$ -toluene.

**Figure S6.**  $^1\text{H}$  NMR of O-O'-bis(trimethylsilyl)-*n*-hexylphosphonic acid anhydride  $d_8$ -toluene.

**Figure S7.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of O-O'-bis(trimethylsilyl)-*n*-hexylphosphonic acid anhydride in  $d_8$ -toluene.

**Figure S8.**  $^1\text{H}$  NMR of 4 nm CdSe nanocrystals in  $d_8$ -toluene after ligand exchange with **7**.

**Figure S9.**  $^1\text{H}$  NMR of the reaction between 4 nm CdSe nanocrystals and **9**.

**Figure S10.** Integrated  $^1\text{H}$  NMR of purified CdSe nanocrystals with adsorbed **9**.

**Figure S11.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between 4 nm CdSe nanocrystals and **9**.

**Figure S12.**  $^1\text{H}$  NMR of the reaction between CdSe nanocrystals and **9**.

**Figure S13.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between 4 nm CdSe nanocrystals, **9**, and  $\text{Et}_3\text{N}$ .

**Figure S14.** XPS spectra of as-prepared CdSe nanocrystals and Cl-terminated CdSe nanocrystals.

**Figure S15.** Orbit Trap mass spectrum of hexane soluble byproducts from reaction of nanocrystals with chlorotrimethylsilane and **8**.

## Experimental

**General Methods.** All air- and/or moisture-sensitive compounds were manipulated using standard Schlenk techniques or in a glovebox under an argon atmosphere. 99.99% Selenium shot and anhydrous toluene, hexane, and chloroform were purchased from Aldrich and stored in a glovebox. Acetone was purchased from Aldrich, and stored over sieves in the glovebox. *n*-Octadecylphosphonic acid was purchased from Polycarbon and 99% Reagent Grade Plus tri-*n*-octylphosphine oxide from Aldrich and recrystallized as described below. *n*-Tridecyltrimethylammonium chloride (99%) was purchased from Aldrich and dried under vacuum at 125 °C for 16 hours prior to storing it in the glovebox. Triethylamine (99%) and chlorotrimethylsilane (99%) were purchased from Aldrich, dried over calcium hydride, distilled, and stored under argon prior to use. *d*<sub>8</sub>-Toluene was dried with sodium and benzophenone prior to distillation and storage under argon. Tri-*n*-octylphosphine was purchased from Strem Chemicals and stored in the glovebox. Bis(trimethylsilyl)selenide was purchased from Strem Chemicals and stored in the glovebox freezer. Dimethylcadmium was purchased from Strem Chemicals and vacuum transferred in the absence of light and stored in an amber jar in the glovebox freezer. *CAUTION! Bis(trimethylsilyl)selenide, bis(trimethylsilyl)sulfide and dimethylcadmium are extremely toxic and have high vapor pressures at room temperature. Care must be taken to quench these chemicals thoroughly prior to handling contaminated glassware outside of the glovebox or fumehood.* Samples of 2,5,8,11-tetraoxatridecane-13-thiol, 2-methoxyethanethiol, and *n*-hexylphosphonic acid anhydride were prepared as described previously.<sup>1,2</sup> Trimethylsilyl protection of 2,5,8,11-tetraoxatridecane-13-thiol was performed according to Glass.<sup>3</sup> *O,O'*-Bis(trimethylsilyl)-*n*-tetradecylphosphonic acid ester was prepared according to Morita.<sup>4</sup> NMR spectra were recorded on Bruker AVQ-400 and DRX-500 spectrometers.

***O,O'*-bis(trimethylsilyl)-*n*-tetradecylphosphonic acid ester.**<sup>3</sup> <sup>1</sup>H NMR (400 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 0.278 (br, 9H), 0.91 (t,  $J_{\text{H-H}}$  = 7.0 Hz, 12H), 1.1 – 1.4 (br, 22H), 1.5 – 1.8 (br, 4H); {<sup>1</sup>H}<sup>31</sup>P NMR (162.0 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 13.26.

**Reaction of 3 with 4 and bis(trimethylsilyl)sulfide (5).** *n*-Octadecylphosphonic acid (50.0 mg, 0.150 mmol) and *d*<sub>8</sub>-toluene (0.6 mL) were mixed in a J. Young NMR tube. **4** (25.0  $\mu$ L, 0.1185 mmol, or 31.6  $\mu$ L, 0.150 mmol) was then added with a microliter syringe and the cap sealed tightly and the mixture shaken. Outside of the glovebox, the sample was heated gently with a heat gun until the solids had dissolved. Both <sup>1</sup>H and {<sup>1</sup>H}<sup>31</sup>P NMR spectra were recorded showing signals for **5** as well as hydrogen selenide ((400 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = -1.56 ppm). The volatiles were then removed under vacuum and *d*<sub>8</sub>-toluene (0.6 mL) was used to dissolve the residue, and the clear and colorless solution transferred to a J. Young NMR tube in the glovebox. <sup>1</sup>H NMR (400 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 0.28 (br), 0.923 (t, *J*<sub>H-H</sub> = 6.9 Hz, 3H), 1.17 - 1.49 (br, 32H), 1.56 - 1.73 (br, 2H); Less than one equivalent of bis(trimethylsilyl)selenide produces a mixture of the mono and the bis(trimethylsilyl) protected octadecylphosphonic acid, while one equivalent produces exclusively the doubly protected product. {<sup>1</sup>H}<sup>31</sup>P NMR (162.0 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 13.1 (bis), 25.3 (mono).

***O*-*O'*-bis(trimethylsilyl)-*n*-hexylphosphonic acid anhydride (6).** Prepared analogously to **5** as described above, using *n*-hexylphosphonic acid anhydride and an equimolar amount of **4**. <sup>1</sup>H NMR (400 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 0.33 (s, 9H), 0.87 (t, *J*<sub>H-H</sub> = 7.5 Hz, 3H), 1.08 – 1.28 (br, 6H), 1.55 – 1.75 (br, 2H), 1.77 – 2.00 (br, 2H); {<sup>1</sup>H}<sup>31</sup>P NMR (162.0 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 14.2, 14.8. {<sup>1</sup>H}<sup>31</sup>P NMR (162.0 MHz, *d*<sub>8</sub>-toluene)  $\delta$  = 14.18, 14.84.

**Recrystallization of *n*-octadecylphosphonic acid (3).** 100 grams of **3** were dissolved in 150 mL ethanol with stirring and heat. Once dissolved the clear, colorless solution was slowly diluted with hexane to a total volume of 1 liter. The solution was left standing overnight on the benchtop during which time crystals formed. The solution was then placed in the refrigerator for 6 hours and subsequently filtered. The solids were transferred to a round bottom flask with a stir bar and heated to 100 °C under vacuum with stirring to remove ethanol that would otherwise remain trapped within the solid. 300 mL of toluene was slowly added, with stirring, and the flask removed from the heat producing a white suspension. The mixture was allowed to cool to room temperature and the solid

isolated by filtration and dried under dynamic vacuum for 24 hours (yield: ~75 g).  $\{^1\text{H}\}^{31}\text{P}$  NMR (162.0 MHz,  $d_4$ -methanol)  $\delta = 29.1$ .

**Recrystallization of tri-*n*-octylphosphine oxide.** 400 grams of 99% Reagent Plus Grade tri-*n*-octylphosphine oxide (Aldrich) were dissolved with stirring and heat in acetonitrile (3 L total volume). After complete dissolution the clear, colorless solution was allowed to cool to room temperature overnight causing colorless plates to form. The solid was isolated by filtration and dried under dynamic vacuum over 24 hours. (yield: 90 - 95%).  $\{^1\text{H}\}^{31}\text{P}$  NMR (162.0 MHz,  $d_8$ -toluene)  $\delta = 40.1$  ppm.

**Injection Solutions.** Dimethylcadmium (1.612 g, 11.31 mmol) was weighed into a vial in the glove box and diluted with two equivalents of tri-*n*-octylphosphine (8.388 g, 22.63 mmol) to a total mass of 10 g. The clear, colorless solution was tightly sealed, mixed thoroughly and stored in the glove box freezer. Selenium shot (0.893 g, 11.31 mmol) was weighed into a vial to which was added tri-*n*-octylphosphine (9.107 g, 24.57 mmol) to a total mass of 10 g. A small stir bar was added, the vial tightly sealed, and the suspension left stirring overnight until all the solids had dissolved. This solution was stored at room temperature in the glovebox until needed. Diethylzinc (0.608 g, 0.492 mmol) was weighed into a vial in the glove box and diluted with tri-*n*-octylphosphine (9.392 g, 25.3 mmol) and stored in the glovebox freezer. Bis(trimethylsilyl)sulfide (0.439 g, 0.246 mmol) was weighed into a vial in the glovebox and diluted with tri-*n*-octylphosphine (9.561 g, 25.8 mmol) and stored in the glovebox freezer. Dimethylcadmium solutions in tri-*n*-octylphosphine are light, heat and moisture sensitive and should be protected from light with aluminum foil.

**Synthetic protocol for CdSe Nanocrystals.** This preparation is routinely run at 5 $\times$  the scale reported without affecting the kinetics of nanocrystal size evolution. Recrystallized **1** (15.00 g, 38.80 mmol) and recrystallized **3** (0.6426, 1.921 mmol, 1.8 equiv.) were weighed into a 50 mL, three-neck flask. The flask was equipped with a one inch magnetic stirbar, a glass thermocouple adapter, a

reflux condenser and a rubber septum. The flask was heated to 100 °C under vacuum and stirred vigorously for at least 30 minutes to degas the reaction mixture. After this time argon was admitted to the flask and the temperature raised to 275 °C. Trioctylphosphine solutions (1.065 g each) of dimethylcadmium and tri-*n*-octylphosphine selenide were brought out of the glovebox in septum sealed vials with the cadmium solution wrapped in aluminum foil to protect it from light. 0.95 grams of the dimethylcadmium solution was slowly added dropwise to the reaction mixture, which caused gas to evolve and foaming of the reaction mixture. (Care must be taken to allow efficient mixing of the dimethylcadmium solution with the surfactant mixture to avoid thermal decomposition of the dimethylcadmium to a yellow or grey color.) The temperature was then equilibrated at 330 °C and the selenium solution rapidly injected into the reaction mixture with vigorous stirring. After the injection, the temperature was lowered to 315 °C and the reaction allowed to proceed for seven to ten minutes. At ~2 minutes after the injection, a yellow color appeared that transitioned through orange, red and brown. After the desired reaction time had passed the reaction was submerged in a stirred, room temperature silicon oil bath to facilitate cooling. Once the reaction mixture cooled below 100 °C, the cleaning was immediately started. (After 7 min. of reaction time at 315 °C the isolated nanocrystals have a diameter = ~ 4 nm,  $PL_{\max} = 580 \text{ nm}$ ,  $PL_{fwhm} \leq 30 \text{ nm}$ )

**Synthetic protocol for CdSe/ZnS nanocrystals.** In a typical synthesis, recrystallized **1** (10.000 g, 25.86 mmol) and **3** (0.197 g, 0.590 mmol, 1.2 equiv./Zn) were loaded into a 50 ml three neck flask equipped with a magnetic stirbar, a glass thermocouple adaptor, a reflux condenser, and a rubber septum. The reaction mixture was heated to 100 °C under vacuum with vigorous stirring for at least 30 min. Argon was admitted to the flask and the temperature raised to 275 °C. The diethylzinc stock solution (1.0 g, 0.492 mmol Zn) was brought out of the glovebox and added dropwise *via* syringe and the temperature subsequently lowered to 250 °C. Dry CdSe nanocrystals, prepared as described above, were dissolved in tri-*n*-octylphosphine (1.000 g, 2.70 mmole) and injected into the reaction mixture under argon. Immediately after adding the nanocrystals, the

temperature controller was set to 235 °C and addition of the bis(trimethylsilyl)sulfide stock solution (1.0 g, 0.246 mmole S) was initiated with a syringe pump (0.015 ml/min). After the addition of bis(trimethylsilyl)sulfide is complete, the reaction mixture was slowly cooled to 50°C, at which point the cleaning was immediately started as described below. CdSe/ZnS nanocrystals prepared in this way showed variable fluorescence quantum efficiency (24 - 55%).

**Cleaning Procedure.** This cleaning procedure was applied to the CdSe and CdSe/ZnS core-shell nanocrystals described above. After the reaction temperature dropped below 100 °C, dry degassed acetone was added via syringe to dilute the solution to 50 mL of total volume and the mixture transferred to the glovebox under argon. The milky precipitate that formed was separated from the supernatant by centrifugation and redissolved in anhydrous chloroform (15 mL), giving a dark solution that readily formed a layer of foam upon agitation. 5 mL of octylamine was added to this solution, resulting in a obvious decrease in surface tension, and the sample diluted to 50 mL with acetone, causing the formation of a milky precipitate. The solids were immediately removed by centrifugation giving a thin layer of nanocrystals and a clear or cloudy, slightly colored supernatant. The film of nanocrystals was then dissolved in hexane (15 mL), resulting in a clear or cloudy solution, and acetone was slowly added until solids began to precipitate. Shaking or sonicating the sample caused redissolution of the solids that could be reprecipitated by the dropwise addition of small amounts of acetone until the sample could no longer be made clear by shaking. The solids formed in this way were separated from the supernatant by centrifugation and discarded. Additional acetone was added to the deeply colored supernatant to precipitate the nanocrystals, which were isolated by centrifugation. This step was repeated a second time producing a sample of nanocrystals that are freely soluble in hexane, toluene, chloroform and other relatively nonpolar solvents. Samples prepared in this way were dried under vacuum to remove volatile impurities prior to dissolving in  $d_8$ -toluene for NMR spectroscopy. Clean samples showed no  $^1\text{H}$  or  $^{31}\text{P}$  NMR resonances characteristic of free molecules (Figures S1 and S2).

**Ligand exchange with chlorotrimethylsilane and *n*-tridecyltrimethyl ammonium chloride.** A similar procedure, as described below for CdSe/ZnS core-shell nanocrystals, was applied to the CdSe nanocrystals. CdSe/ZnS nanocrystals (8.9 mg) with 24.7% quantum efficiency were dissolved in the *d*<sub>8</sub>-toluene (0.543 g) and transferred into a J. Young NMR tube. A ferrocene standard (0.167 g, 0.0817 mmol Fe), prepared by dissolving ferrocene (0.103 g, 0.554 mmol) in the *d*<sub>8</sub>-toluene (1.030 g), was added to the nanocrystal solution. The concentration of surface ligands in the sample was determined by integrating the alkyl chains *versus* the ferrocene standard (0.489 mmol/g).

A sample of this stock solution (0.053 g, 1.431  $\mu$ mol *n*-octadecyl chains) was saturated with *n*-tridecyltrimethylammonium chloride, to which, a toluene stock solution of chlorotrimethylsilane (0.029 g, 0.0978 mmol / g, 2 equiv. Si / C<sub>18</sub>H<sub>37</sub>) was added. After an hour, undissolved *n*-tridecyltrimethylammonium chloride was discarded by filtering the mixture through a Teflon syringe filter (0.2  $\mu$ m pore diameter) and the photoluminescence QE measured (20.1%).

**Mass Spectrometry.** Molecular reaction products from the ligand cleavage reactions described above were analyzed with electrospray ionization mass spectrometry. Spectra were acquired on LTQ-Orbitrap XL (Thermo Fisher Scientific, Waltham, MA) and Q-ToF Premier (Waters, Milford, MA) instruments. The reaction mixture in toluene or chloroform solution was diluted with methanol to a final concentration of  $\sim$ 10-100  $\mu$ moles/L, centrifuged, and filtered through a Teflon syringe filter (0.2  $\mu$ m pore diameter) prior to analysis. Typical spectra showed both trimethylsilyl esters of octadecylphosphonic acid and its anhydride, as well as the free acid, which presumably form by alcoholysis of the trimethylsilyl-phosphonate linkage. A typical spectrum is shown below in Figure S15.

**Photoluminescence quantum efficiency (QE) measurements.** Nanocrystal photoluminescence QE was measured by comparing the integrated emission spectra for CdSe/ZnS (PL<sub>Nanocrystals</sub>) and R6G (PL<sub>R6G</sub>) according to Equation S1, where  $\Phi_{R6G}$  is the quantum yield of R6G<sup>5</sup>, and  $\eta_{Toluene}$  and  $\eta_{Ethanol}$  are

the refractive indices of the toluene and ethanol. Solutions for QE measurements were prepared in toluene with an optical density less than 0.1. A UV-Vis absorption spectrum was obtained to determine wavelength where the CdSe/ZnS solution and R6G have the same absorption intensity. This wavelength was then used as the excitation wavelength for CdSe/ZnS and R6G solutions in the fluorescence measurement.

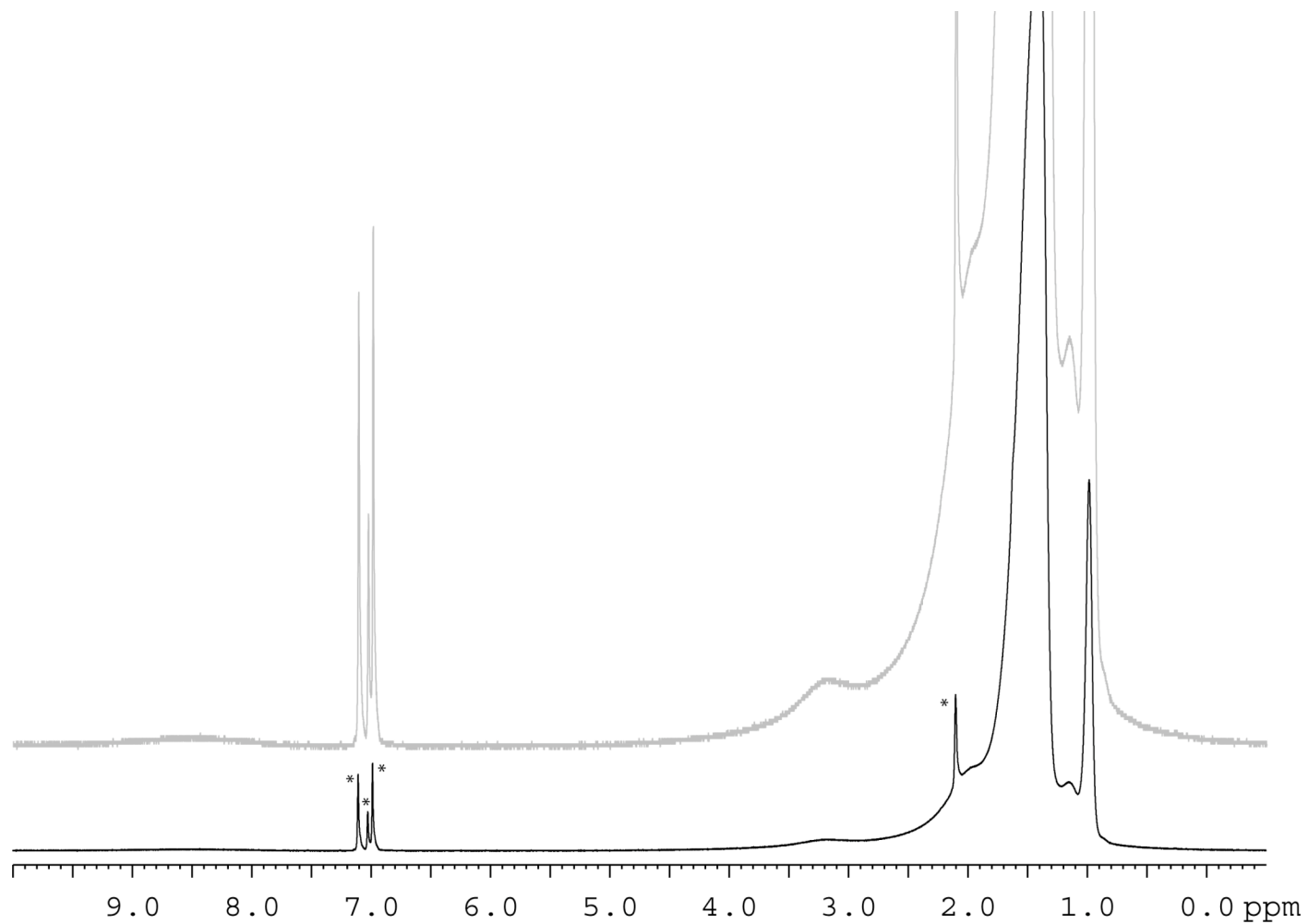
$$QE = \Phi_{R6G} \times \left( \frac{\eta_{Toluene}}{\eta_{Ethanol}} \right)^2 \times \left( \frac{PL_{Nanocrystals}}{PL_{R6G}} \right) \quad (S1)$$

**X-ray Photoelectron Spectroscopy.** XPS samples were prepared on silicon wafers coated with 50 nm of gold. Toluene solutions of as-prepared CdSe nanoparticles, and Cl-terminated nanoparticles prepared in the presence of anhydrous *n*-tridecyltrimethylammonium chloride, were dropcast onto this wafer. Cadmium chloride and *n*-tridecyltrimethylammonium chloride were run as control experiments, and embedded in silver paint spread on the wafer. Measurements were performed at  $\sim 1 \times 10^{-8}$  Torr and all spectra referenced to the position of the Au 4*f* peaks. Scans were collected over a range of 20 eV around the peak of interest with a pass energy of 23.5 eV.

	Cd 3 <i>d</i> <sub>3/2</sub> (eV)	Cd 3 <i>d</i> <sub>5/2</sub> (eV)	Se 3 <i>d</i> <sub>3/2</sub> (eV)	Se 3 <i>d</i> <sub>5/2</sub> (eV)	Cl 2 <i>p</i> <sub>1/2</sub> (eV)	Cl 2 <i>p</i> <sub>3/2</sub> (eV)
CdSe:as synthesized	412.4	405.6	57.5	54.8		
CdSe:Cl terminated	412.4	405.7		54.8	200.3	199

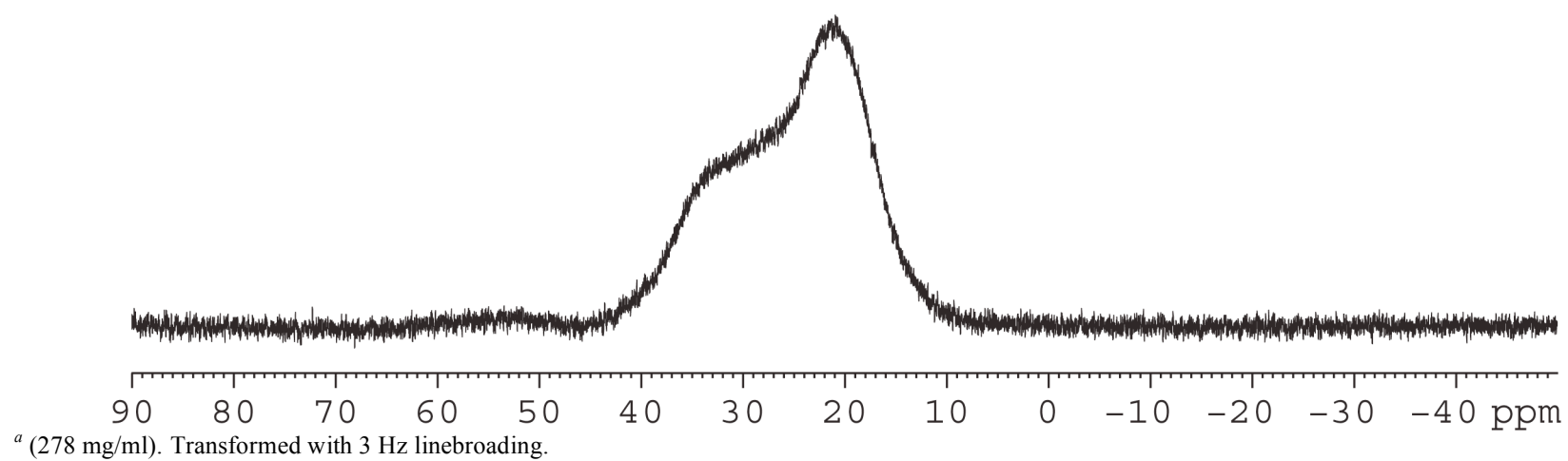


**Figure S1.**  $^1\text{H}$  NMR of purified, 4 nm, CdSe nanocrystals in  $d_8$ -toluene.<sup>a</sup>

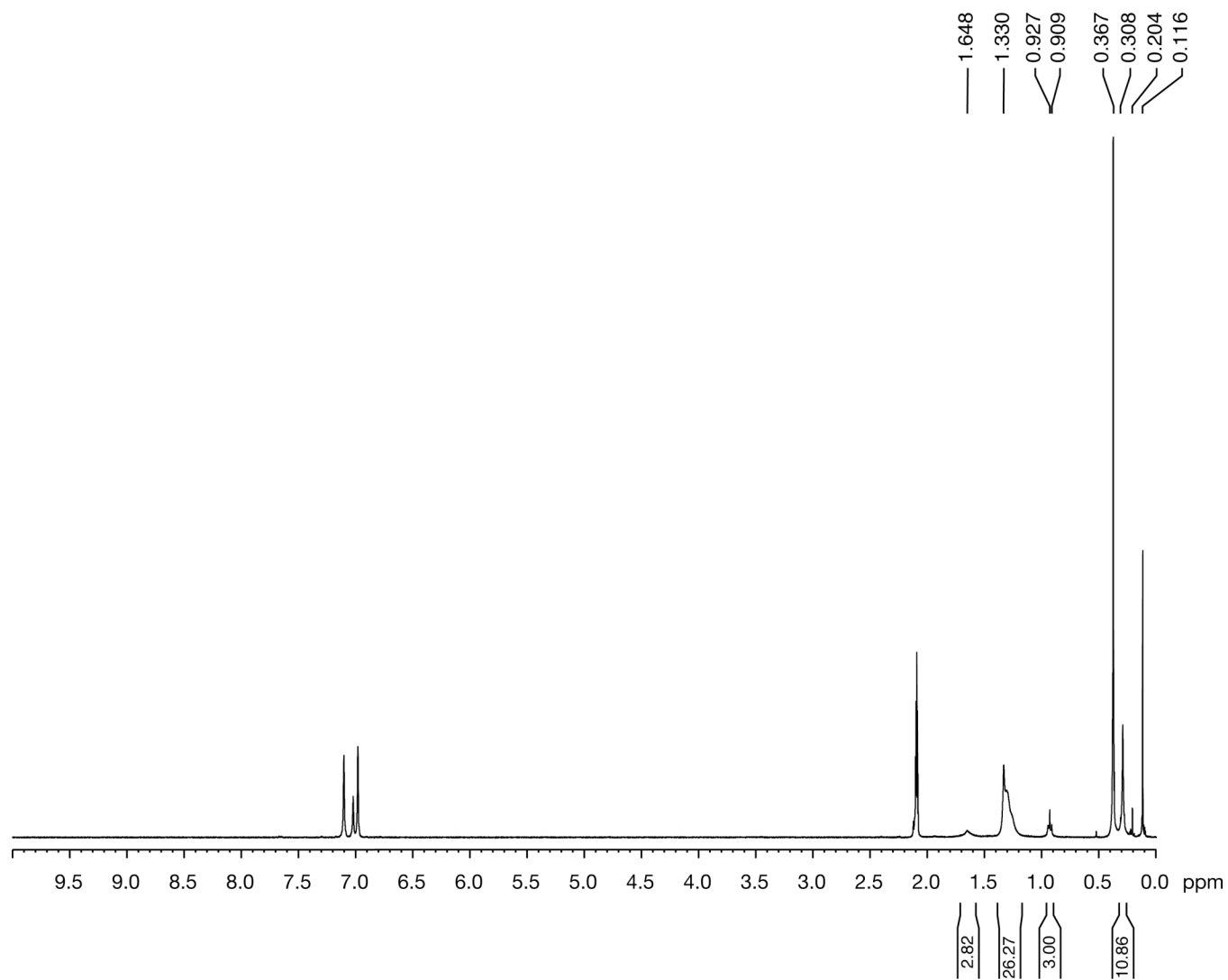


<sup>a</sup> 278 mg/ml. Resonances labeled with (\*) denote the proton impurity in the  $d_8$ -toluene solvent. A magnified spectrum is included in gray to make the low intensity resonances visible in the region ( $\delta = 7.8 - 9.2$  ppm).

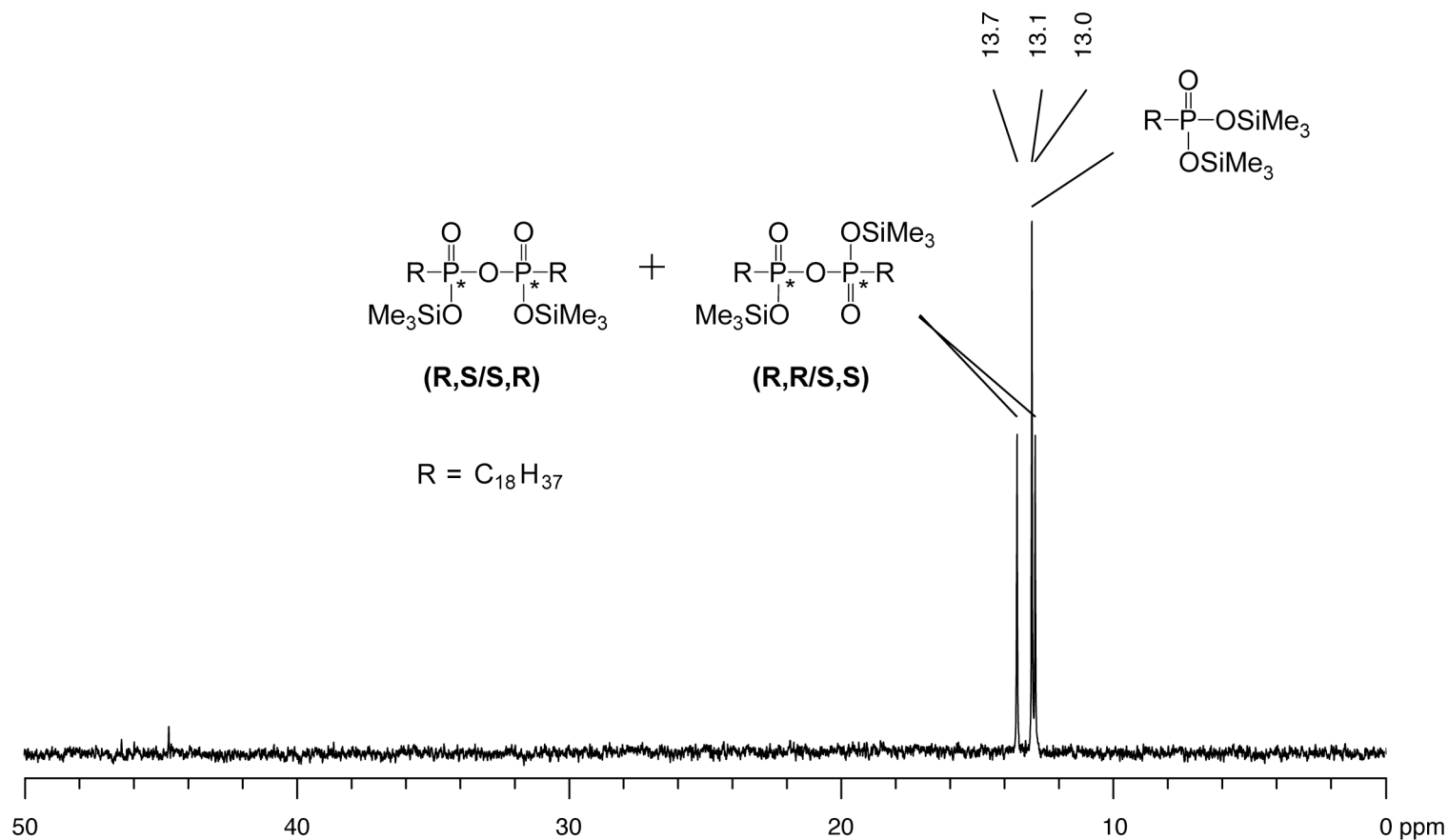
**Figure S2.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of purified, 4 nm CdSe nanocrystals in  $d_8$ -toluene.<sup>a</sup>



**Figure S3.**  $^1\text{H}$  NMR of the reaction between 4 nm CdSe nanocrystals and **4** in  $d_8$ -toluene.

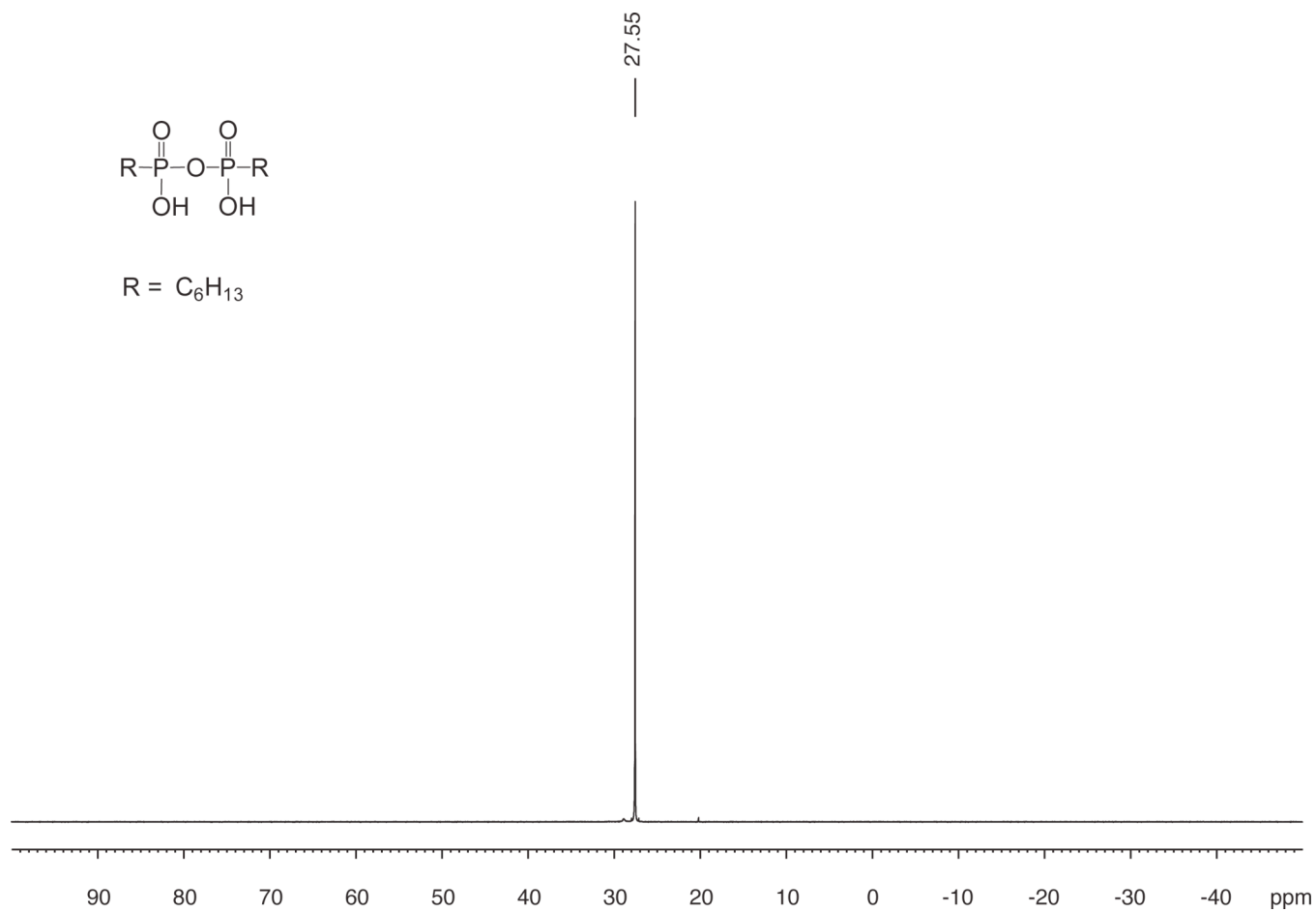


**Figure S4.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between CdSe nanocrystals and  $\text{Me}_3\text{SiCl}$  in  $d_8$ -toluene.<sup>a</sup>



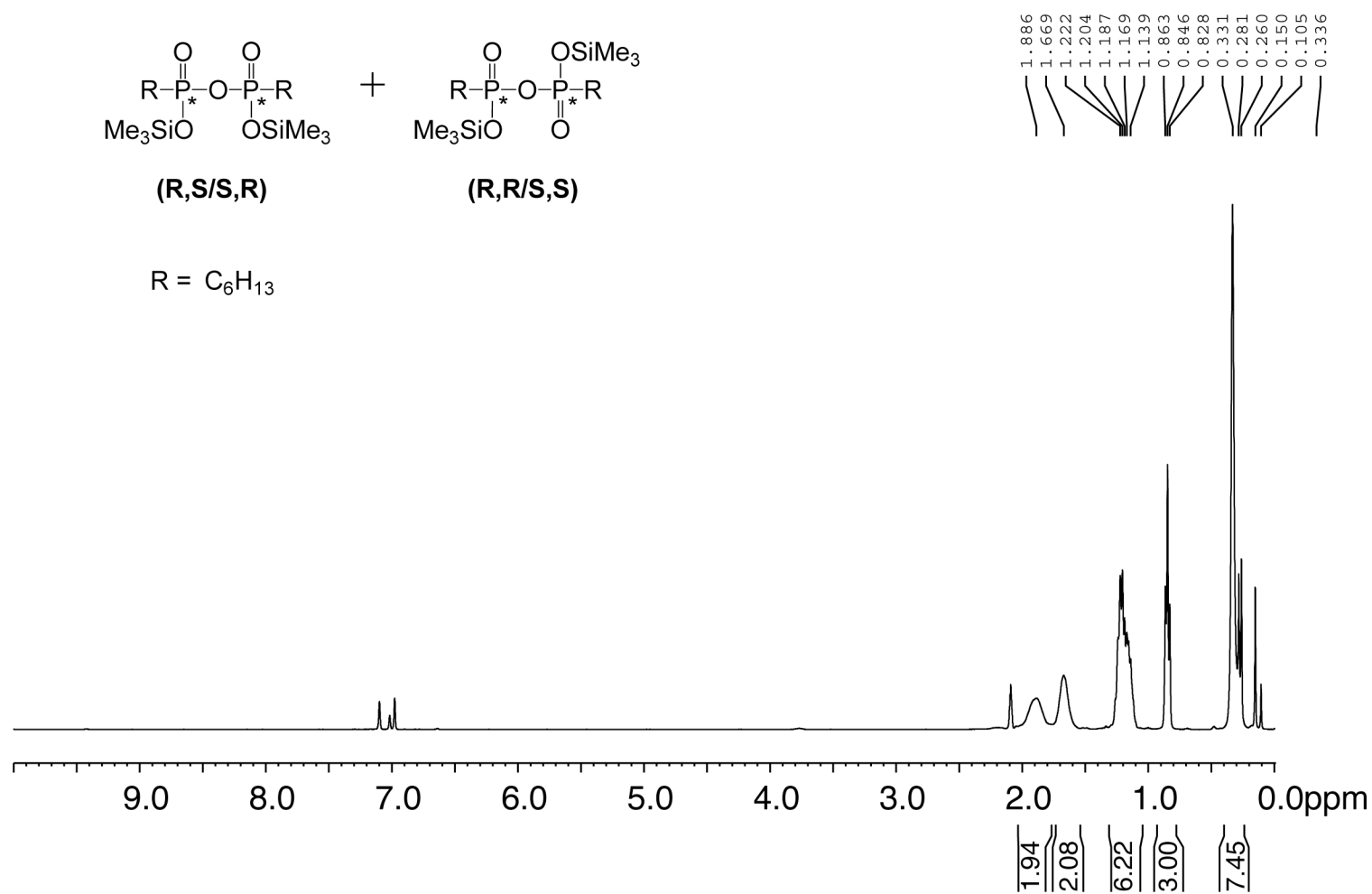
<sup>a</sup> Similar  $\{^1\text{H}\}^{31}\text{P}$  NMR spectra were obtained for the reaction between CdSe or CdSe/ZnS nanocrystals, and **4** or **7**.

**Figure S5.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of *n*-hexylphosphonic acid anhydride in  $d_8$ -toluene.<sup>a</sup>

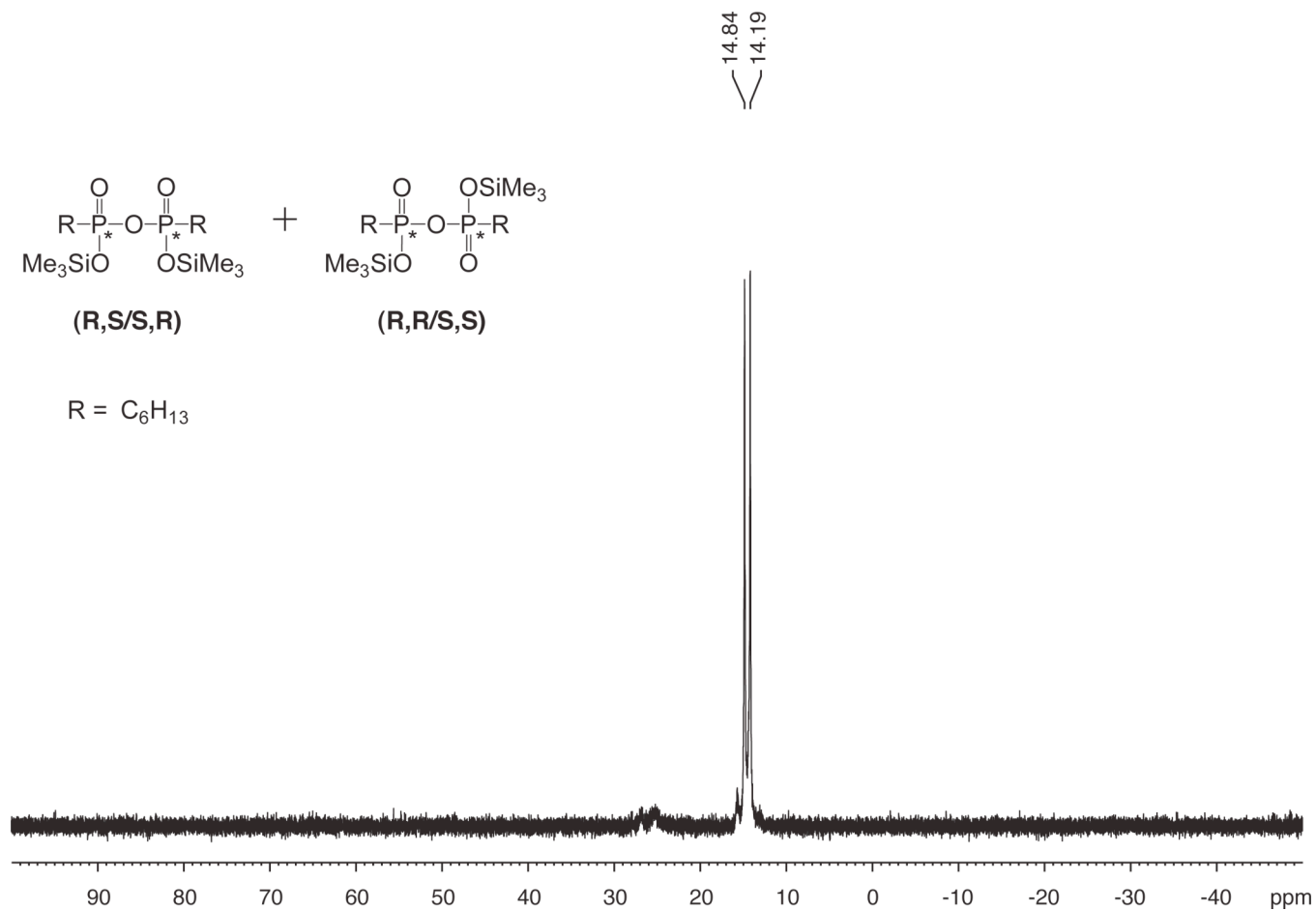


<sup>a</sup> A single resonance is obtained because of rapid proton exchange that interconverts the racemic and meso forms on the timescale of the NMR experiment.

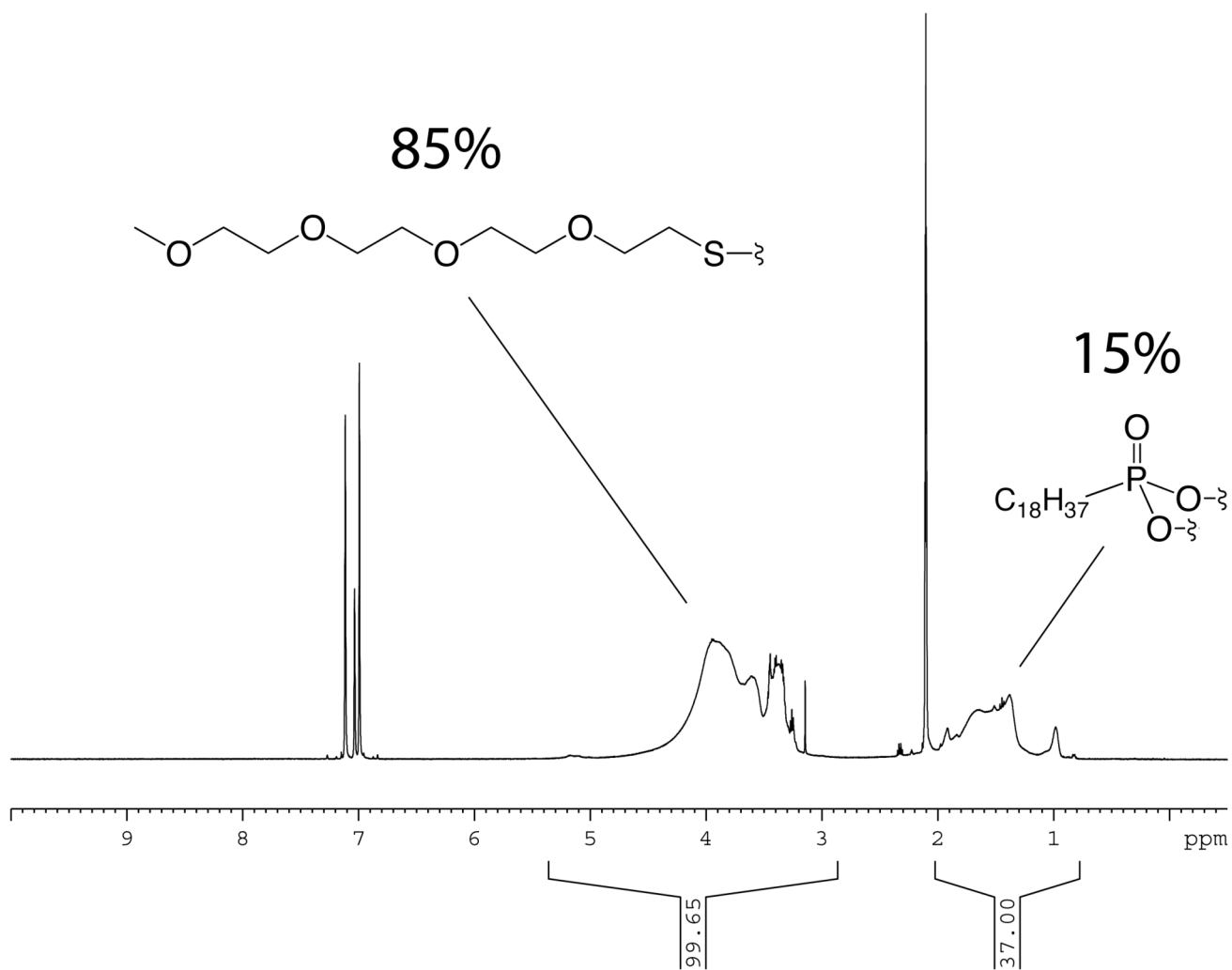
**Figure S6.**  $^1\text{H}$  NMR of O-O'-bis(trimethylsilyl)-*n*-hexylphosphonic acid anhydride  $d_8$ -toluene.



**Figure S7.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of *O*-*O'*-bis(trimethylsilyl)-*n*-hexylphosphonic acid anhydride in  $d_8$ -toluene.

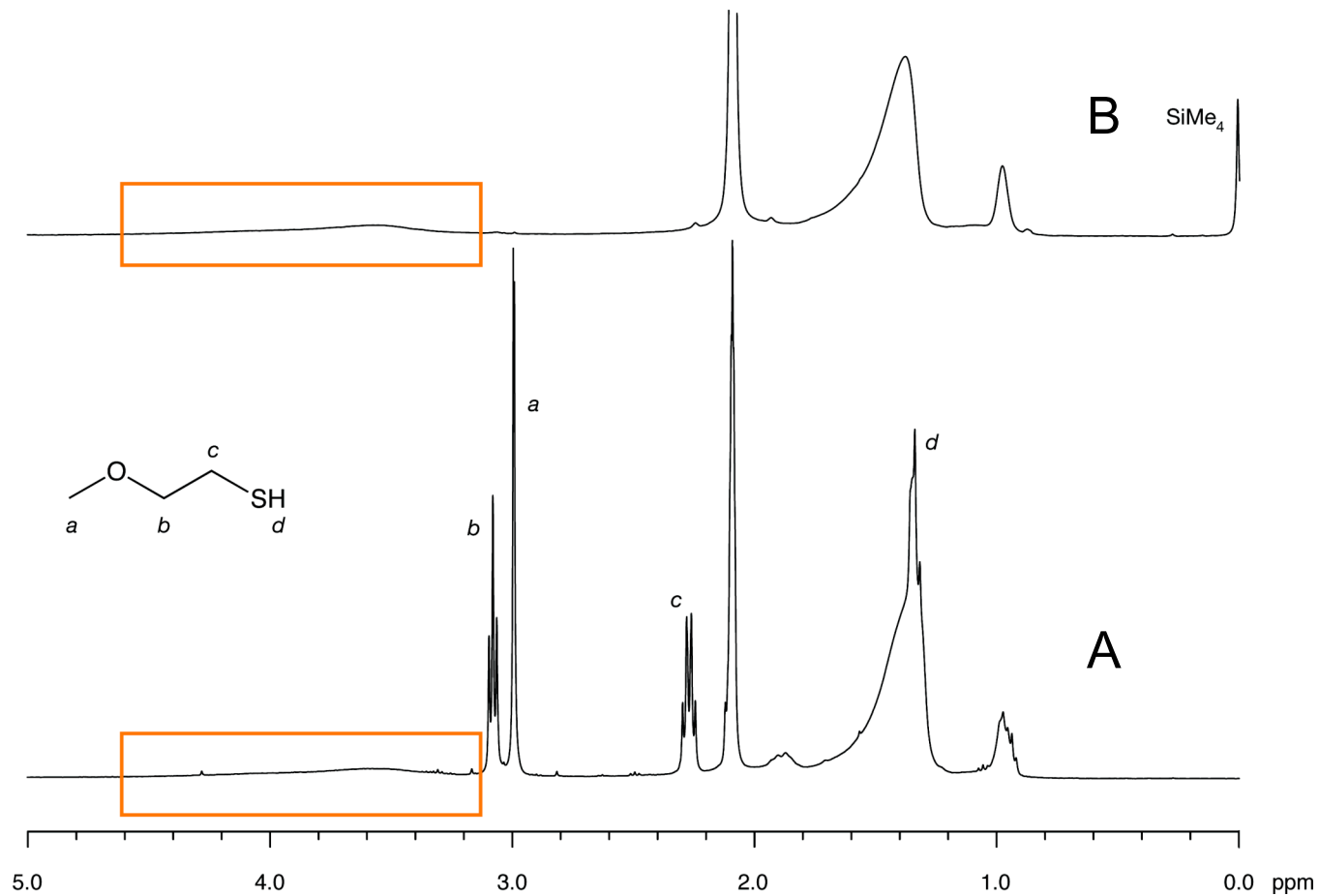


**Figure S8.**  $^1\text{H}$  NMR of 4 nm CdSe nanocrystals in  $d_8$ -toluene after ligand exchange with **7**.



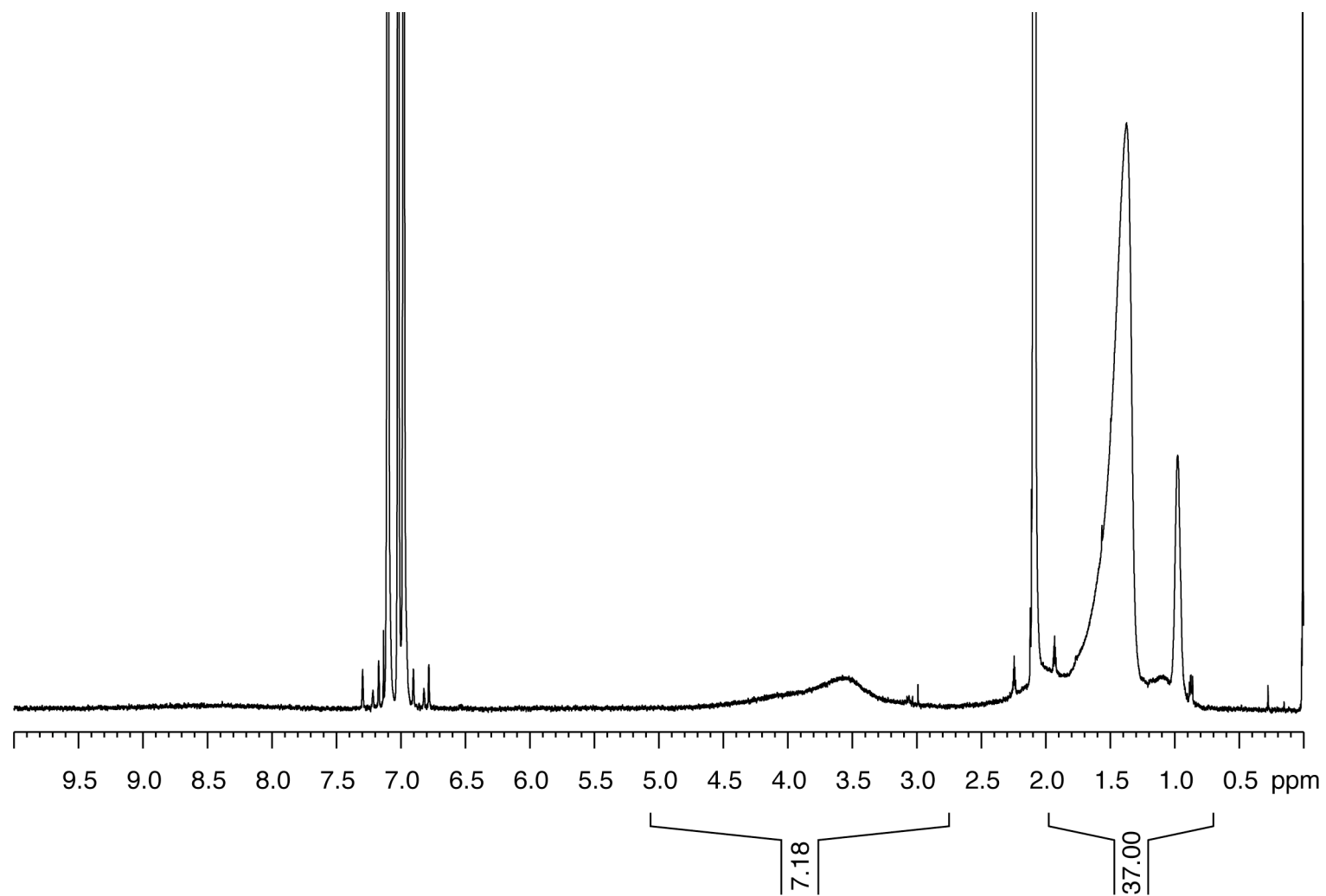


**Figure S9.**  $^1\text{H}$  NMR of the reaction between CdSe nanocrystals and **9**.<sup>a</sup>

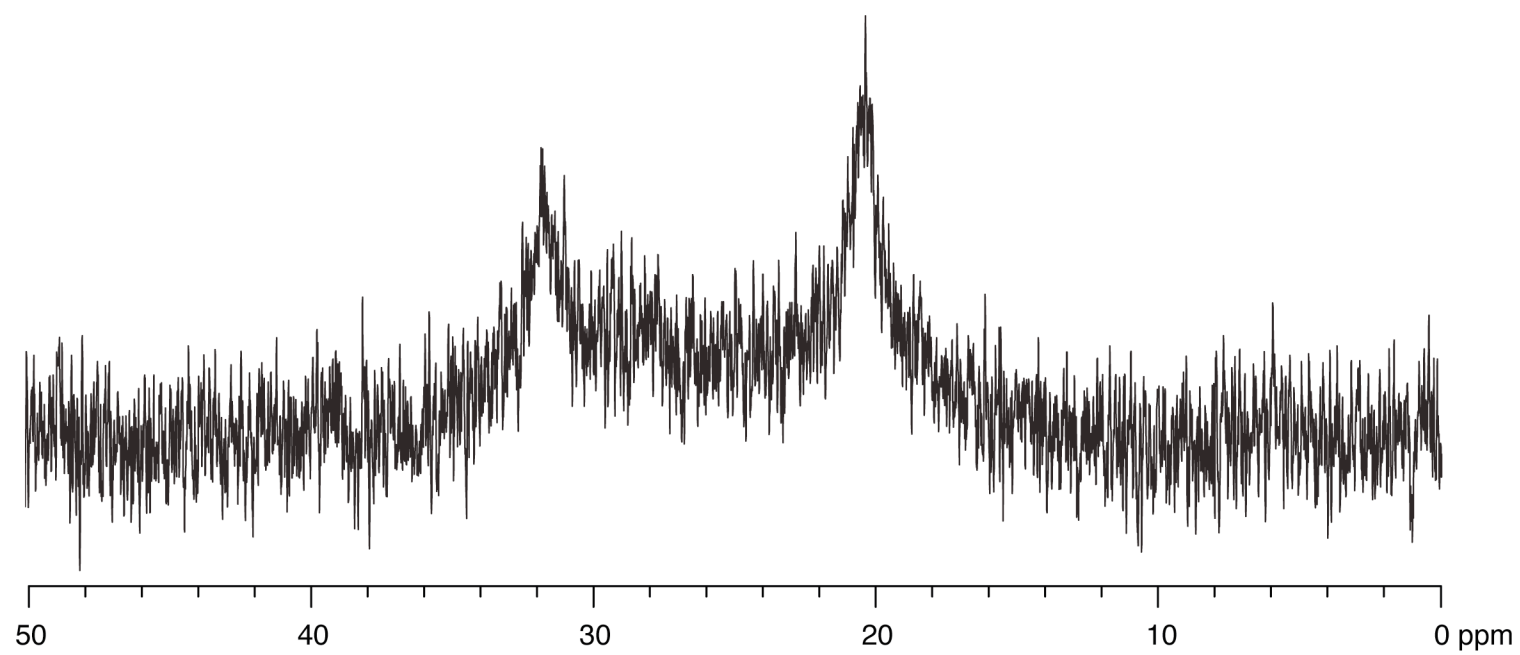


<sup>a</sup> (A) Before and (B) after isolation and washing of the nanoparticles. The broad resonance ( $\delta = 3.2 - 4.5$  ppm) highlighted by an orange boarder is assigned to the bound thiol ligand.

**Figure S10.** Integrated  $^1\text{H}$  NMR of purified CdSe nanocrystals with adsorbed **9**.



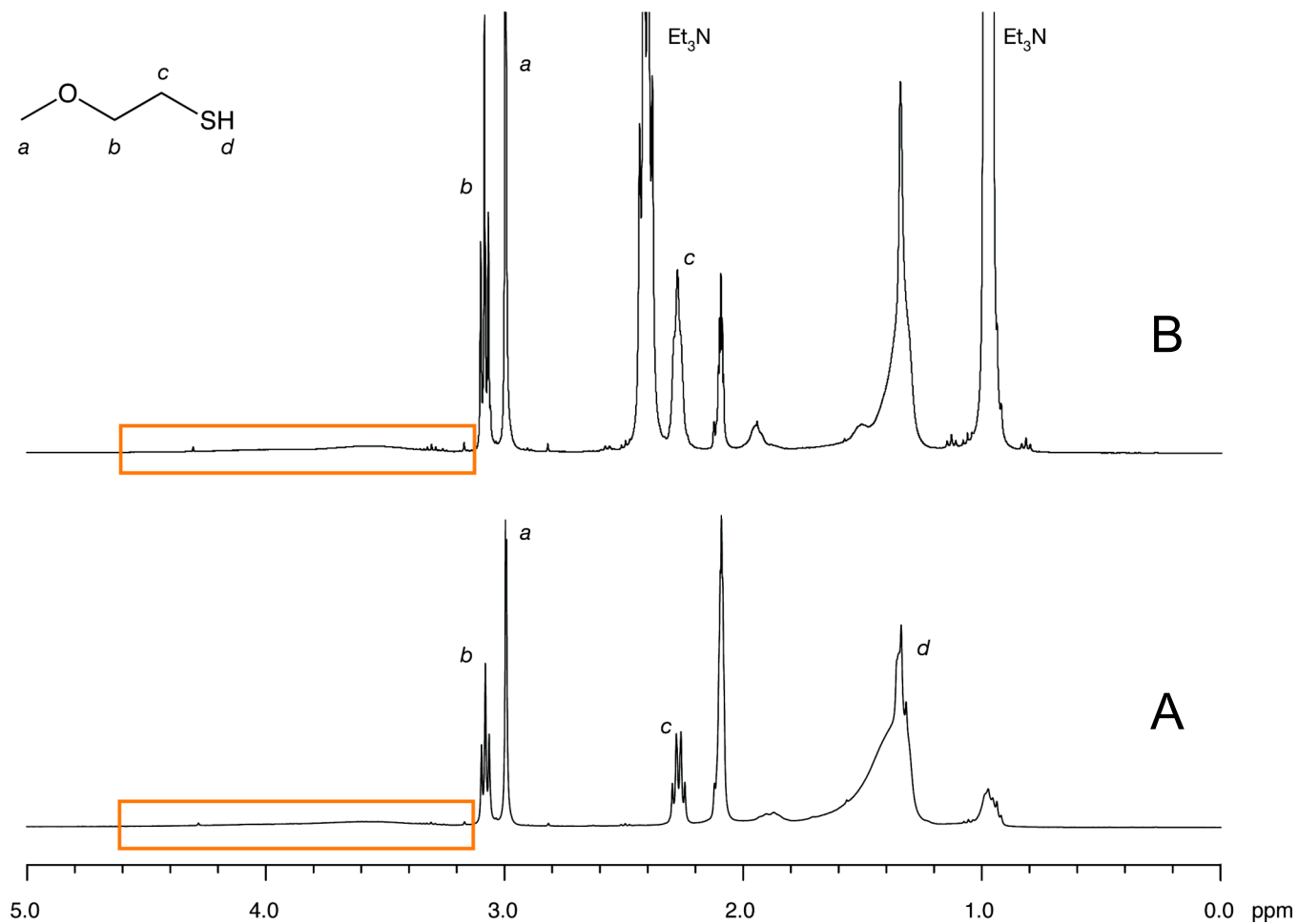
**Figure S11.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between 4 nm CdSe and **9**.<sup>a</sup>



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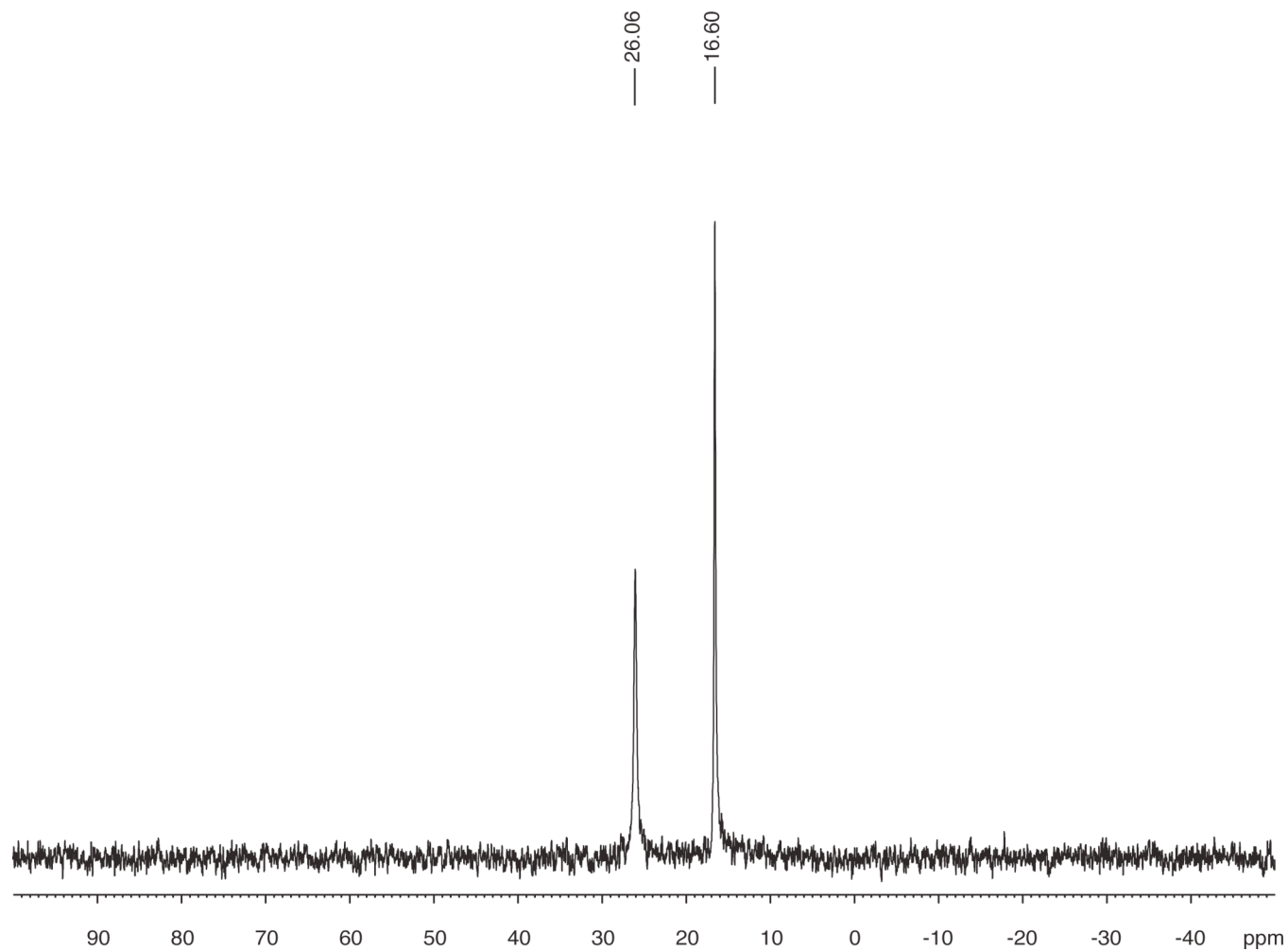
<sup>a</sup> Transformed with 3 Hz line broadening.

**Figure S12.**  $^1\text{H}$  NMR of the reaction between CdSe nanocrystals and **9**.<sup>a</sup>



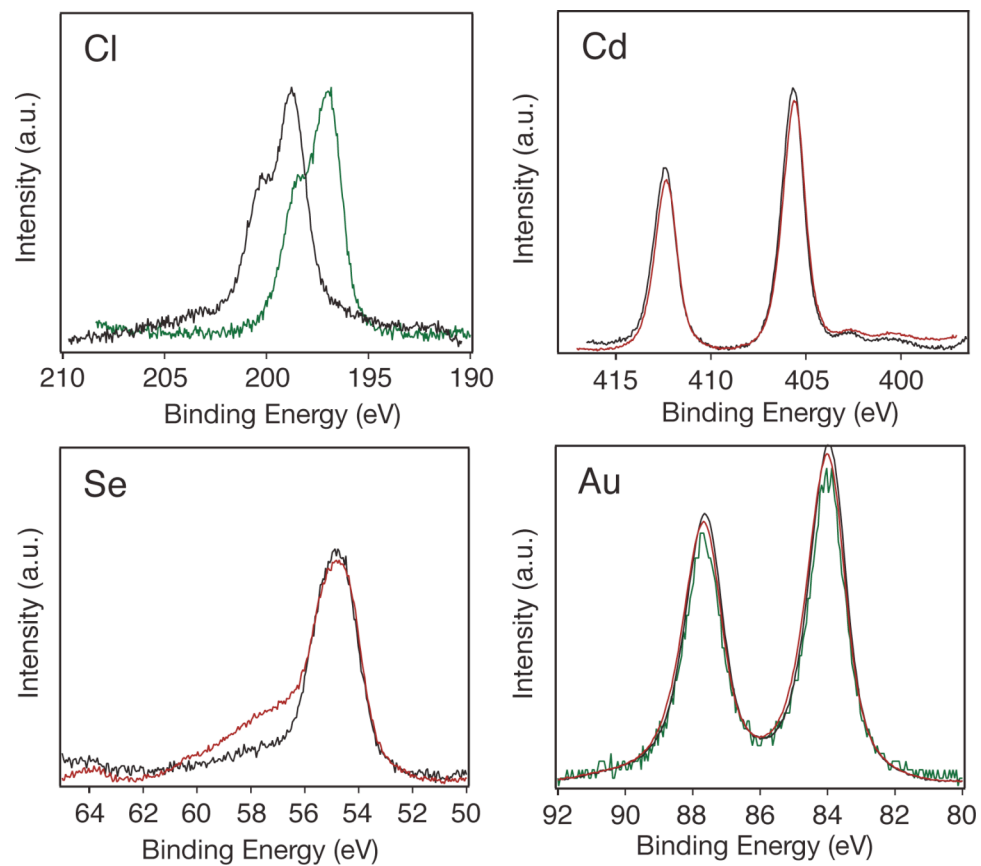
<sup>a</sup> (A) Before and (B) after the addition of  $\text{Et}_3\text{N}$  in  $d_8$ -toluene. The broad resonance ( $\delta = 3.2 - 4.5$  ppm) highlighted by an orange boarder is assigned to the bound thiol ligand.

**Figure S13.**  $\{^1\text{H}\}^{31}\text{P}$  NMR of the reaction between 4 nm CdSe, **9**, and  $\text{Et}_3\text{N}$ .<sup>a</sup>



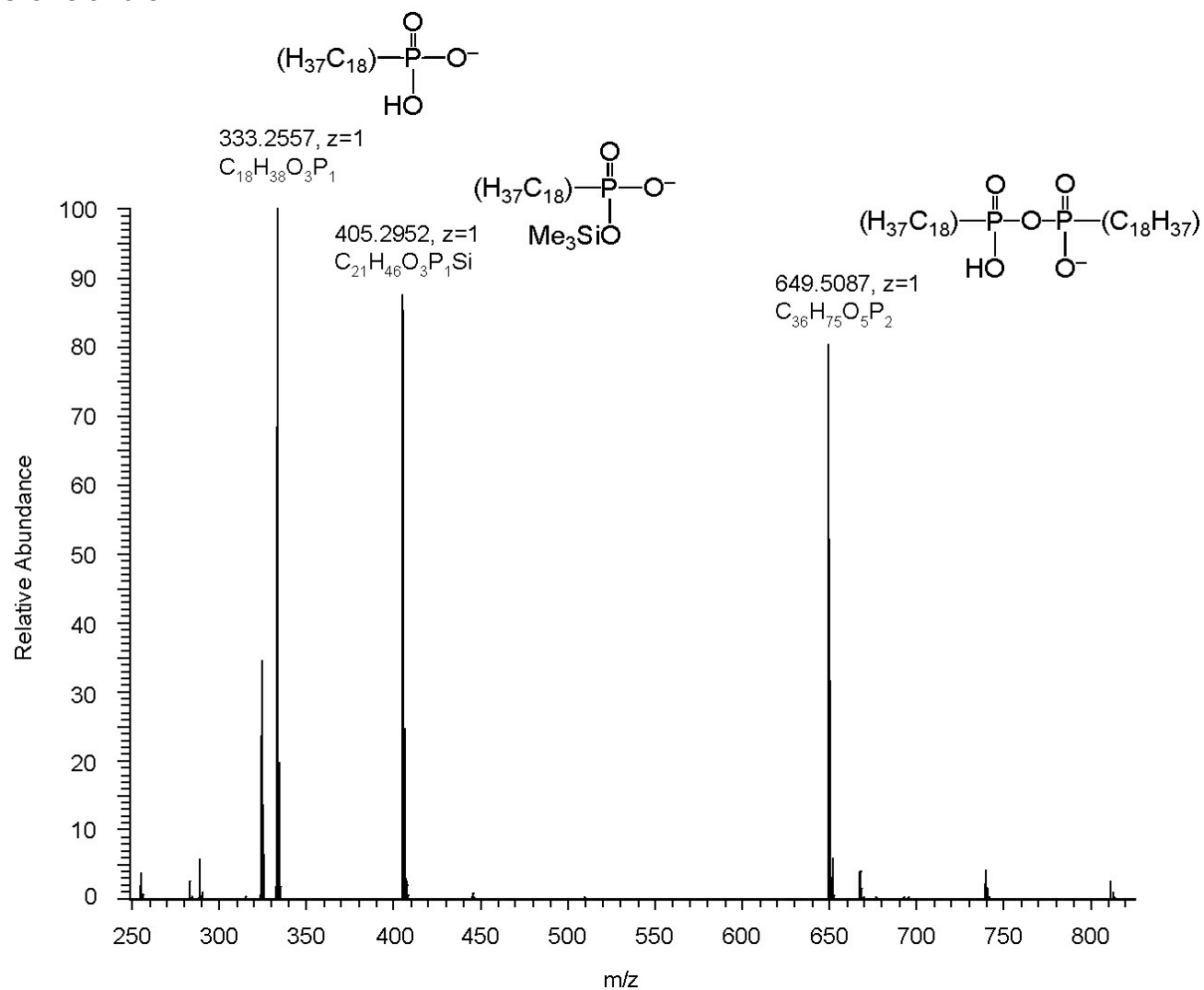
<sup>a</sup> Transformed with 8 Hz line broadening.

**Figure S14.** XPS spectra of as prepared nanocrystals and Cl-terminated nanocrystals.<sup>a</sup>



<sup>a</sup> XPS of chloride-terminated CdSe nanocrystals (–) (See Scheme 3), **8** (–), and underivatized nanocrystals (–). Au 4f binding energies of the substrate were used as an internal reference.

**Figure S15.** Orbit Trap mass spectrum of hexane soluble byproducts from reaction of nanocrystals with chlorotrimethylsilane and **8**.



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<sup>2</sup> Bruger, A.; Anderson, J. J. *J. Am. Chem. Soc.*, **1957**, 79, 3575 - 3579.

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<sup>5</sup> Qu, Laihua; Peng Xiaogang, *J. Am. Chem. Soc.* **2002**, 124, 2049.