

Increase in Activity and Selectivity in Catalysis via Surface Modification with Self-Assembled Monolayers

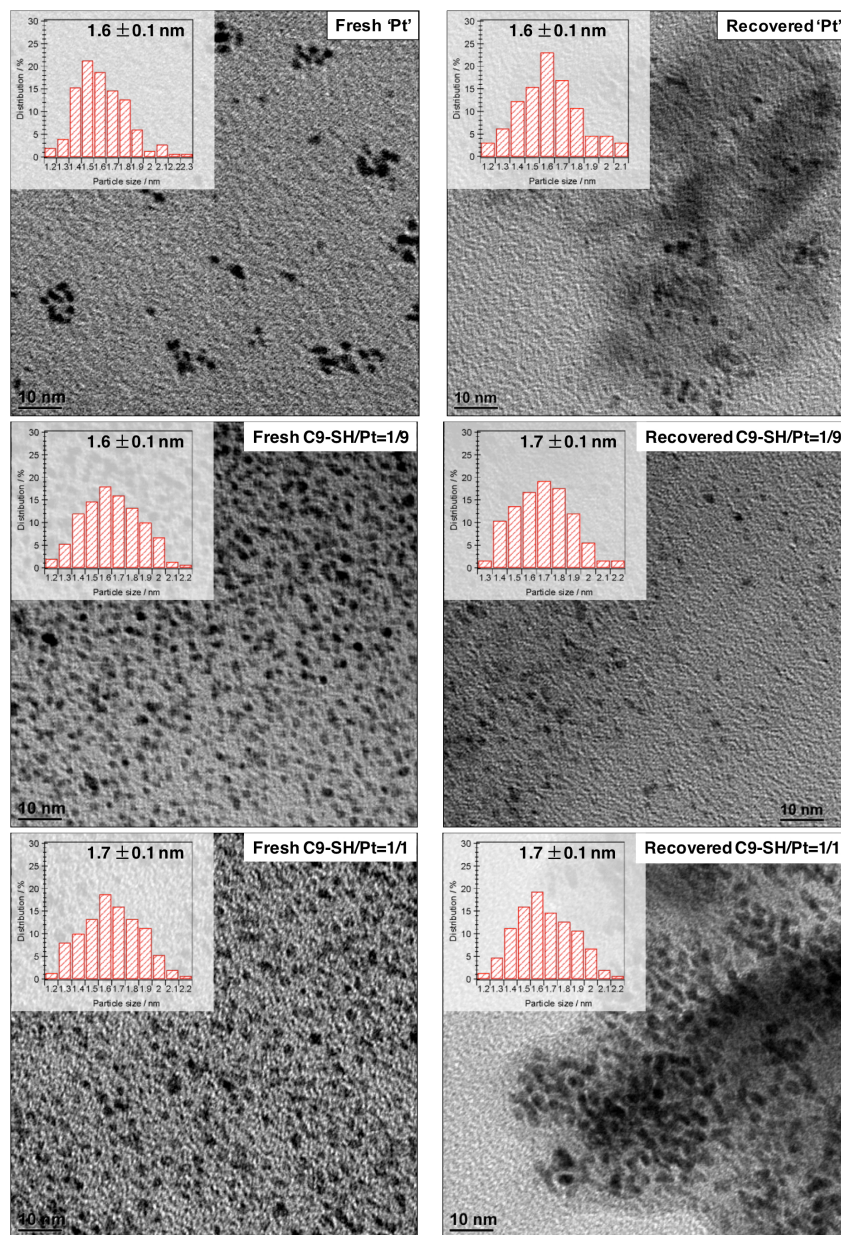
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Supporting Data

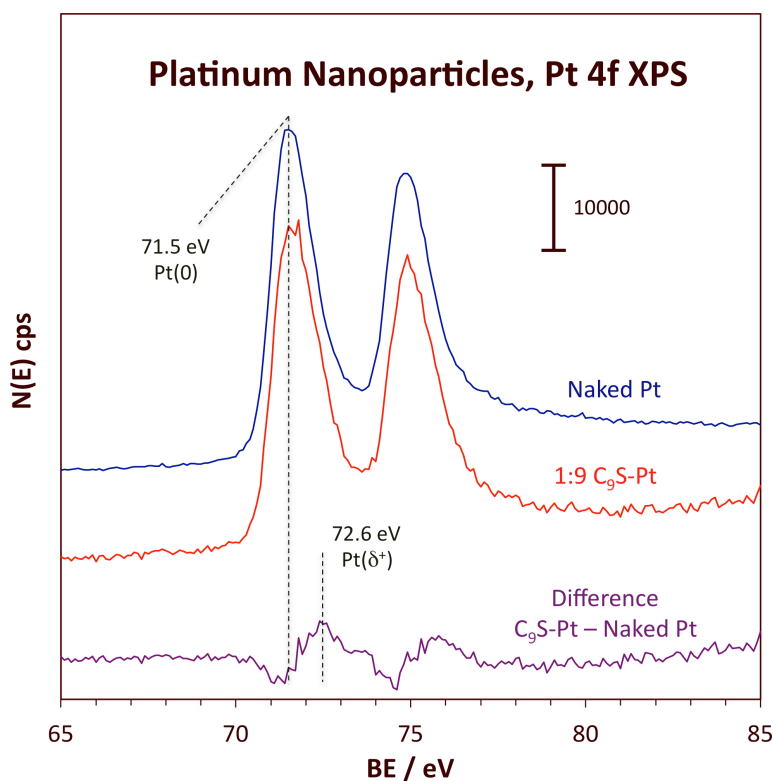
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Figure S1. Transmission Electron Microscopy (TEM) Images of Pt Nanoparticles



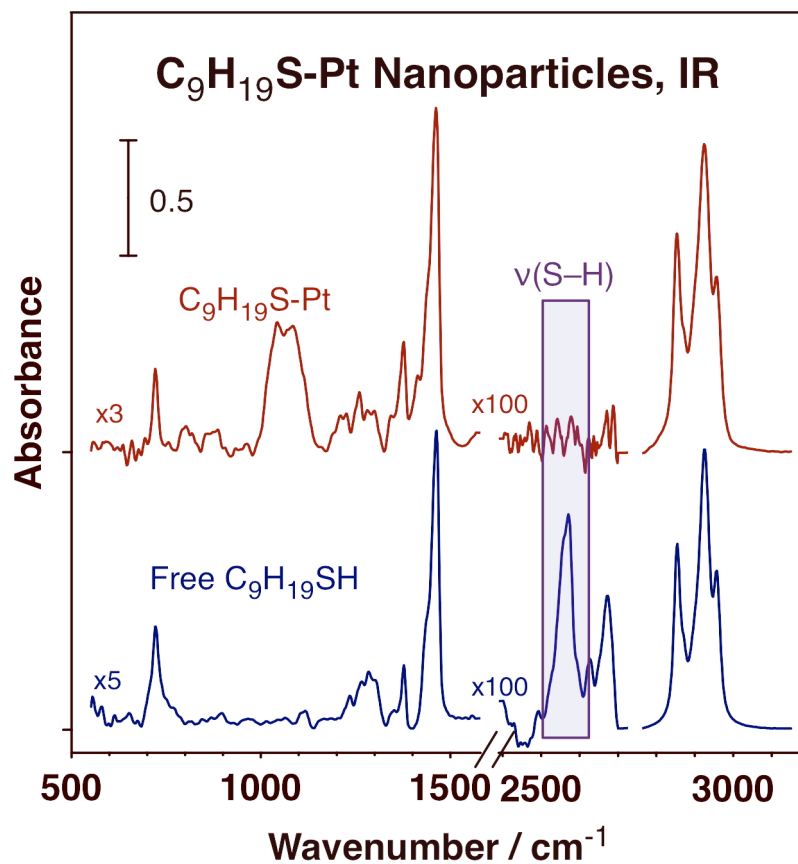
TEM images of Pt nanoparticles before (left) and after (right) being used for catalysis. Three sets of images are shown, for the "naked" nanoparticles (top), and for nanoparticles capped with 1-nonanethiol ($\text{C}_9\text{H}_{19}\text{SH}$). Images for two thiol:Pt ratios are provided, 1:9 (center) and 1:1 (bottom). Each image is accompanied with a size distribution histogram. All particles display narrow size distributions around 1.6 - 1.7 nm.

Figure S2. X-ray Photoelectron Spectra (XPS) of C₉H₁₉S-Pt Nanoparticles



Pt 4f XPS for "naked" (blue) and thiol-treated (C₉H₁₉SH, red) platinum nanoparticles. A difference trace is also provided at the bottom (purple) to highlight the changes. The main Pt 4f_{7/2} peak corresponds to metallic platinum, Pt(0), whereas the shoulder that develops at 72.6 eV upon thiol adsorption corresponds to partially-positively-charged platinum atoms, Pt(δ⁺) generated by bonding to the sulfur atoms. This is corroborated by the binding energy value measured for the S 2p peak at 162.5 eV, more than 1 eV lower than that of pure alkyl thiols and consistent with adsorption on the Pt surface.[Li, Z., Chang, S.-C., Williams, R. S., *Langmuir* 19 (2003) 6744-6749][Tu, W., Takai, K., Fukui, K-i., Miyazaki, A., Enoki, T., *J. Phys. Chem. B* 107 (2003) 10134-10140]

Figure S3. Infrared (IR) Absorption Spectra in the S–H Stretching Region for Thiol Adsorption on Pt Nanoparticles



Infrared (IR) absorption spectra of $\text{C}_9\text{H}_{19}\text{SH}$ free (blue) and adsorbed on Pt nanoparticles (red). The disappearance of the peak at 2573 cm^{-1} , the one corresponding to the S–H bond stretching mode, corroborates the adsorption and the formation of thiol self-assembled layers on the Pt nanoparticles.

Table S1. Initial TOFs from the Samples in Figure 1a.

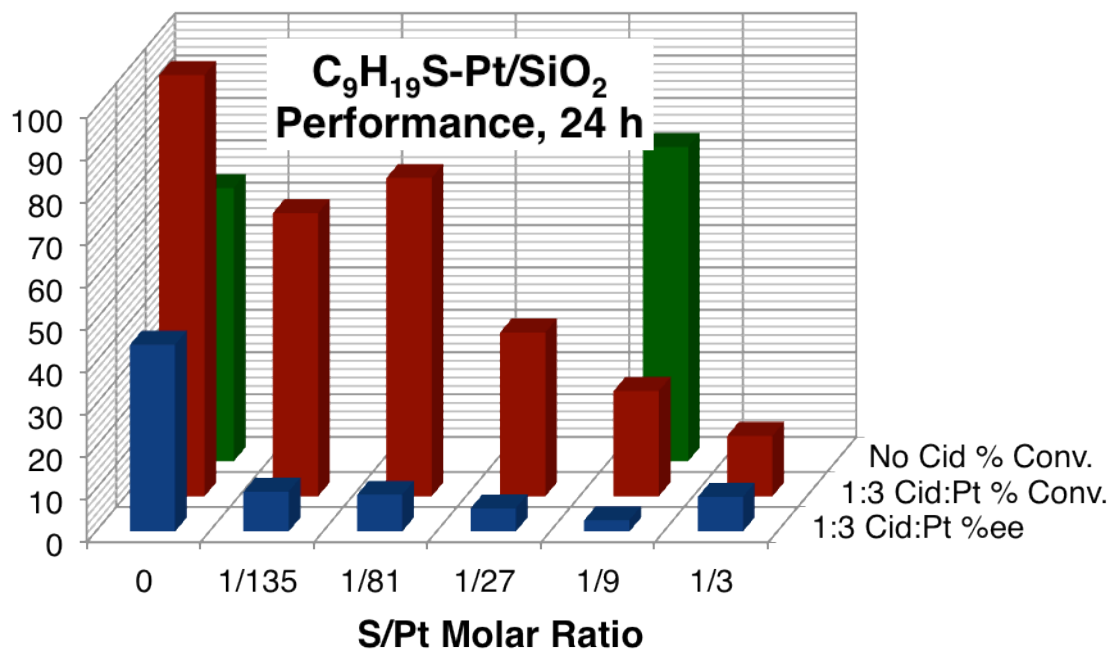
Sample	TOF / molec Pt-atom ⁻¹ s ⁻¹
Pt	0.0044
Na ₂ S-Pt	0.0024
C ₃ H ₇ S-Pt	0.0067
C ₉ H ₁₉ S-Pt	0.0218
C ₁₆ H ₃₃ S-Pt	0.0315

Table S2. Summary of Data from Analysis of the IR Absorption Spectra in Figure 2

Figure 2a		Free C ₉ H ₁₉ SH	6:1 C ₉ H ₁₉ S-Pt	1:1 C ₉ H ₁₉ S-Pt	1:3 C ₉ H ₁₉ S-Pt	1:6 C ₉ H ₁₉ S-Pt	1:9 C ₉ H ₁₉ S-Pt	1:27 C ₉ H ₁₉ S-Pt
Peak 1	Frequency / cm ⁻¹	2853.5	2853.5	2853.5	2853.5	2853.5	2853.5	2853
	Width / cm ⁻¹	15	15	17	23	22	22	18
	Intensity /abs cm ⁻¹	1.53	1.28	1.28	1.88	1.59	1.63	1.66
Peak 2	Frequency / cm ⁻¹	2870.9	2870.9	2872	2875	2875	2876	2874
	Width / cm ⁻¹	13	11	15	15	15	15	14
	Intensity /abs cm ⁻¹	0.48	0.30	0.40	0.39	0.27	0.38	0.44
Peak 3	Frequency / cm ⁻¹	2895	2895.8	2897	2897	2897	2898.5	2899
	Width / cm ⁻¹	25	26	26	26	26	26	26
	Intensity /abs cm ⁻¹	1.20	1.15	1.20	1.62	1.29	1.52	1.65
Peak 4	Frequency / cm ⁻¹	2925	2925	2925	2924.5	2924.5	2924.5	2924.5
	Width / cm ⁻¹	24	22	22	23	23	22.5	21
	Intensity /abs cm ⁻¹	3.61	3.35	3.17	3.11	3.25	3.17	3.37
Peak 5	Frequency / cm ⁻¹	2957.4	2957	2957	2956	2956	2955.8	2956
	Width / cm ⁻¹	19	18	22	25	21	28	21
	Intensity /abs cm ⁻¹	1.56	1.13	1.56	1.94	1.42	1.78	1.34

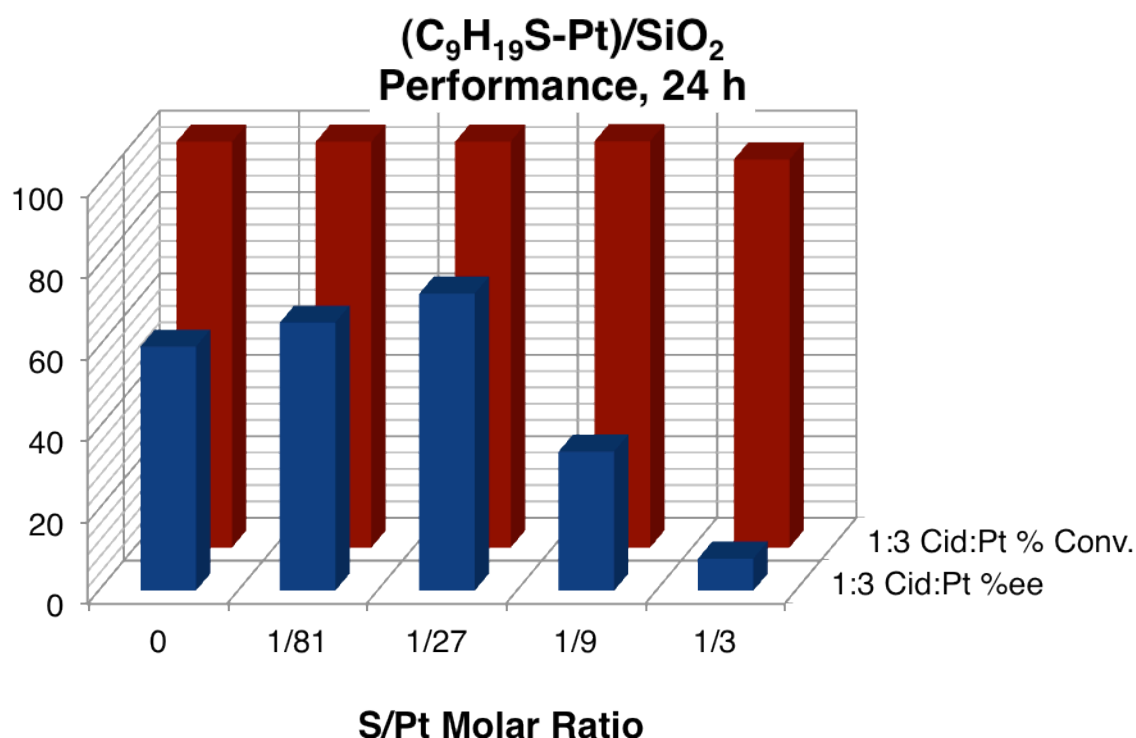
Figure 2b		1:9 C ₁₆ H ₃₃ S-Pt	1:9 C ₉ H ₁₉ S-Pt	1:9 C ₃ H ₇ S-Pt	C ₁₆ H ₃₃ SH	C ₉ H ₁₉ SH
Peak 1	Frequency / cm ⁻¹	2852.9	2853.5	2853.5	2852.9	2853.5
	Width / cm ⁻¹	17	22	27	17	15
	Intensity /abs cm ⁻¹	1.55	1.47	2.13	1.93	1.52
Peak 2	Frequency / cm ⁻¹	2873.2	2876	2875	2874.2	2870.9
	Width / cm ⁻¹	15	15	16	12	13
	Intensity /abs cm ⁻¹	0.33	0.34	0.40	0.35	0.47
Peak 3	Frequency / cm ⁻¹	2895.9	2898.5	2896.5	2896.4	2895
	Width / cm ⁻¹	26	26	23	21	25
	Intensity /abs cm ⁻¹	1.27	1.36	1.31	1.16	1.19
Peak 4	Frequency / cm ⁻¹	2923.9	2924.5	2925	2923.9	2925
	Width / cm ⁻¹	22.5	22.5	25	22.5	24
	Intensity /abs cm ⁻¹	3.34	2.85	3.37	3.50	3.57
Peak 5	Frequency / cm ⁻¹	2955.4	2955.8	2959	2956.9	2957.4
	Width / cm ⁻¹	21	28	21.5	25	19
	Intensity /abs cm ⁻¹	0.93	1.61	1.37	1.36	1.55

Figure S4. $C_9H_{19}S$ -Pt/SiO₂ Catalyst Performance



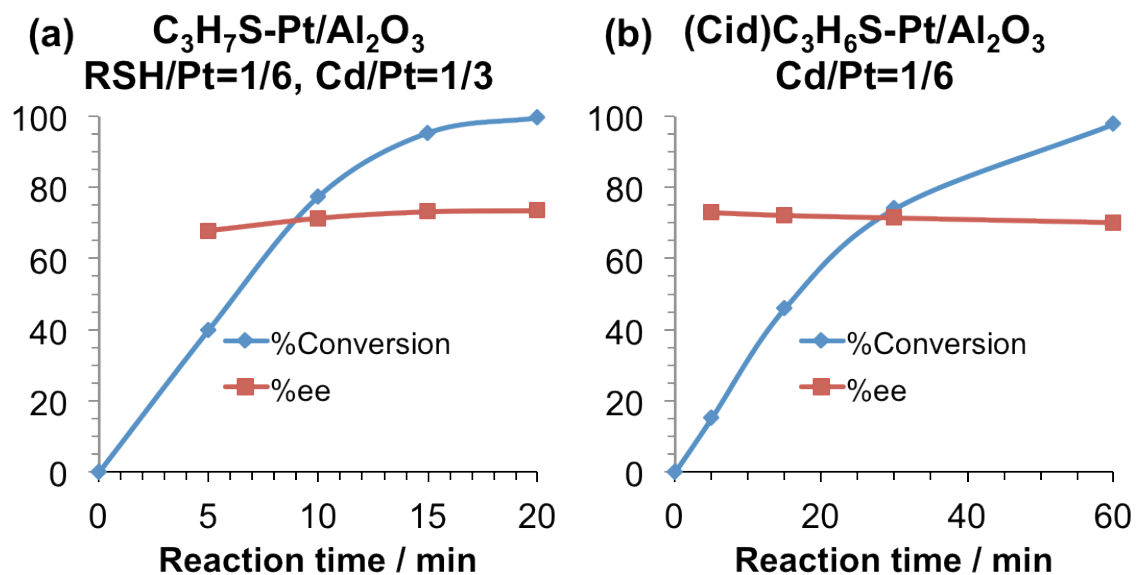
Activity (in %conversion after 24 h of reaction, red) and enantioselectivity (%ee, blue) of a thiol-pretreated commercial 1 wt% Pt/SiO₂ catalyst (Sigma-Aldrich) for the hydrogenation of ethyl pyruvate in the presence of cinchonidine (Cid) as a chiral modifier. The data are reported as a function of the concentration of C₉H₁₉SH used for pretreatment (expressed as a S:Pt molar ratio). Reaction conditions: 1.25 mmol ethyl pyruvate, 20 bar H₂, 5 μmol Pt, 1.5 μmol cinchonidine, 10 ml toluene (solvent), 300 K. Both activity, and enantioselectivity in particular, decrease rapidly upon the addition of the thiols to the catalyst. Reference activity data are also provided for a couple of cases where no cinchonidine was added to the solution (green). In that case the thiols may enhance reactivity, but the reaction lacks enantioselectivity.

Figure S5. (C₉H₁₉S-Pt)/SiO₂ Catalyst Performance



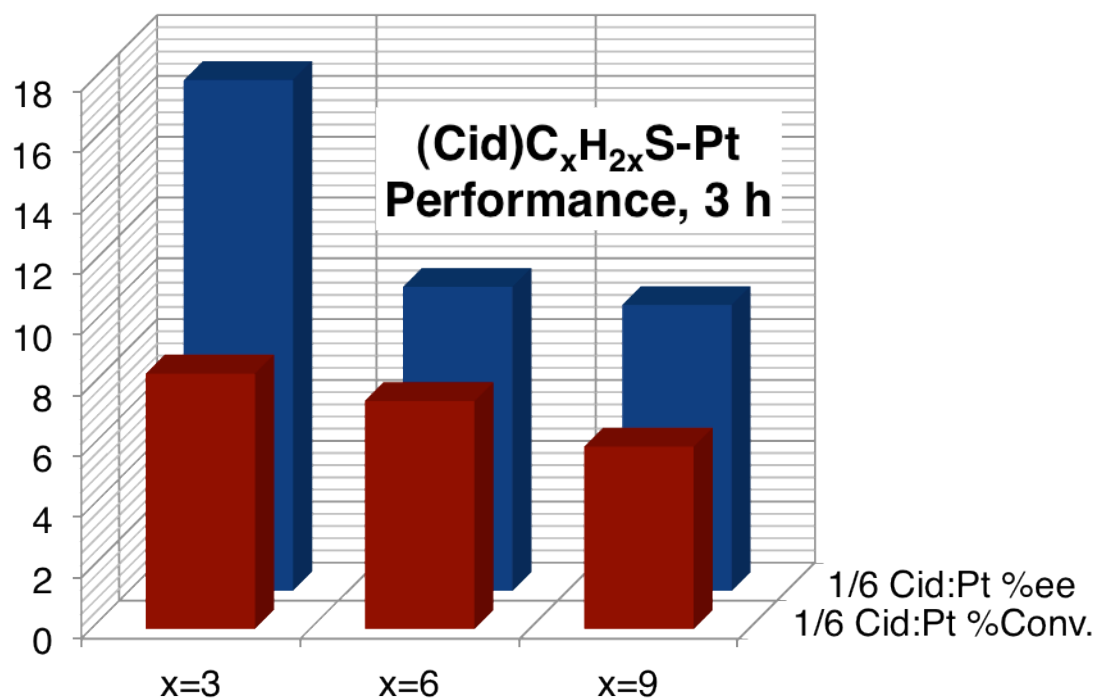
Catalytic activity (in %conversion after 24 h of reaction, red) and enantioselectivity (%ee, blue) for the hydrogenation of ethyl pyruvate in the presence of cinchonidine (Cid) as a chiral modifier. The experiments were carried out using catalysts prepared by dispersing the thiol-treated C₉H₁₉S-Pt nanoparticles on a commercial silica support (Aerosil 200, Degussa, surface area = 200 m²/g). The data are reported as a function of the concentration of C₉H₁₉SH used for pretreatment (expressed as a S:Pt molar ratio). Reaction conditions: 1.25 mmol ethyl pyruvate, 20 bar H₂, 5 μmol Pt, 1.5 μmol cinchonidine, 10 ml toluene (solvent), 300 K. The performance in this case is optimum for a S:Pt ratio of approximately 1:27.

Figure S6. Kinetic Data for EtPy Conversion on $\text{C}_3\text{H}_7\text{S-Pt/Al}_2\text{O}_3$ (a) and $(\text{Cid})\text{C}_3\text{H}_6\text{S-Pt/Al}_2\text{O}_3$ (b) Catalysts.



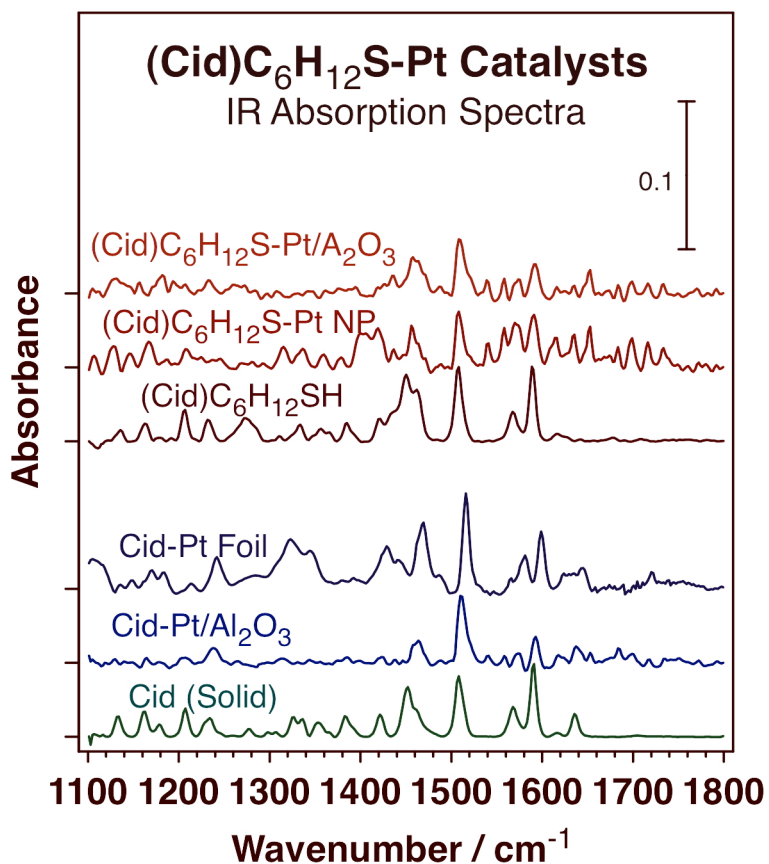
Catalytic conversion (% , blue) and enantioselectivity (%ee, red) kinetic data as a function of reaction time for the hydrogenation of ethyl pyruvate with two types of catalysts: $\text{C}_3\text{H}_7\text{S-Pt/Al}_2\text{O}_3$ (a), and $(\text{Cid})\text{C}_3\text{H}_6\text{S-Pt/Al}_2\text{O}_3$ (b).

Figure S7. (Cid) $C_xH_{2x}S$ -Pt Catalyst Performance



Catalytic activity (in %conversion after 3 h of reaction, red) and enantioselectivity (%ee, blue) for the hydrogenation of ethyl pyruvate with catalysts prepared by depositing Cid-derivatized thiol SAMs on Pt nanoparticles. The data are reported as a function of the length of the alkyl chain in the thiol SAMs. Reaction conditions: 1.25 mmol ethyl pyruvate, 20 bar H_2 , 5 μ mol Pt, 1.5 μ mol cinchonidine, 10 ml toluene (solvent), 300 K. These samples all show poor catalytic performance.

Figure S8. IR Absorption Spectra in the Hydrocarbon Deformation Region for Catalysts Prepared by Using Cinchonidine-Derivatized (Cid)C₆H₁₂SH Thiols.



IR traces for, from bottom to top: solid cinchonidine (green), cinchonidine adsorbed on Pt/Al₂O₃ (blue), cinchonidine adsorbed on a Pt foil (dark blue), free (Cid)C₆H₁₂SH (dark red), (Cid)C₆H₁₂SH adsorbed on Pt nanoparticles (red), and (Cid)C₆H₁₂SH adsorbed on Pt/Al₂O₃ (brick color). These results correspond to experiments carried out with a Pt/Al₂O₃ (instead of Pt/SiO₂) catalysts and a shorter thiol than in Figure 6, but the results and general conclusions are similar.