

SUPPORTING INFORMATION

Hydrogen-Free Homogeneous Catalytic Reduction of Olefins in Aqueous Solutions

*Carina Gaviglio and Fabio Doctorovich**

Departamento de Química Inorgánica, Analítica y Química Física/INQUIMAE-CONICET,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria,
Pabellón II, Piso 3, (C1428EHA) Buenos Aires, Argentina

Table of Contents

1. General Considerations.....	S2
2. Reactions Conditions for Table 3.....	S3
3. Selected NMR Spectra.....	S4
4. Selected Mass Spectrum.....	S10
5. Kinetic Studies of the Catalytic Reduction of Cinnamic Acid.....	S11
6. Kinetic Isotope Effect on the Catalytic Reduction.....	S13

1. General Considerations

Unless otherwise noted, all manipulations were carried out with exclusion of oxygen using standard Schlenk techniques or septa; N₂ or Ar were used as inert gasses. All solvents were reagent grade or better. All non-deuterated solvents were distilled under a nitrogen atmosphere. Deuterated solvents were used as received. Water used in all reactions was MilliQ obtained from deionized water. Commercially available reagents were used as received. ¹H NMR spectra were recorded at 200 or 500 MHz spectrometers. ¹H NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ¹H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.26 ppm, CHCl₃; 1.94 ppm, CH₃CN; 3.53 ppm, Dioxane).

Compound **1** described in the literature was characterized by comparing its UV-Vis spectra to the previously reported data. Reported yields in the publication are indicated whether they are isolated, spectroscopically or chromatographically determined. They represent an average of at least two independent runs. For known compounds prepared using the new method described, a copy of the ¹H NMR spectrum of representative examples is included.

2. Reaction Conditions for Table 3

TABLE S1. Reaction Conditions for Table 3

Entry	Substrate (mmol)	2 (mmol)	NH ₂ OH (mmol)	T (°C)	Yield ^a (%)	Medium
1	3 ; 0.25	0.02	2.5	100	95	aqueous borax buffer
1	3 ; 0.25	0.02	5	100	96 ^b	aqueous borax buffer
2	5 ; 0.25	0.025	2.5	60	42	aqueous borax buffer:ethanol=1:1
3	6 ; 0.25	0.025	2.5	90	44	aqueous borax buffer:ethanol=1:1
3	6 ; 0.25	0.02	12.5	90	93 ^b	aqueous borax buffer:ethanol=1:1
4	8 ; 0.25	0.025	2.5	100	94	aqueous borax buffer
5	10 ; 0.25	0.025	2.5	100	11 (19); 12 (36)	aqueous borax buffer
6	13 ; 0.25	0.02	2.5	100	36	aqueous borax buffer
7	15 ; 0.25	0.02	2.5	100	7	aqueous borax buffer
8	17 ; 0.25	0.025	2.5	70	38 ^c	aqueous borax buffer:ethanol=1:1
9	19 ; 0.25	0.025	2.5	100	20 (29); 21 (3); 22 (40)	aqueous borax buffer:ethanol=1:1
10	23 ; 0.25	0.02	2.5	80	86	phosphate buffer in D ₂ O: <i>p</i> -dioxane-d ₈ =1:1
11	25 ; 0.25	0.02	2.5	80	55	phosphate buffer in D ₂ O: <i>p</i> -dioxane-d ₈ =1:1
12	27 ; 0.25	0.02	2.5	80	21	phosphate buffer in D ₂ O: <i>p</i> -dioxane-d ₈ =1:1

13 **29**; 0.25 0.025 2.5 60 8 phosphate buffer in D₂O:*p*-
dioxane-d₈=1:1

^a Relative yields determined by ¹H NMR analysis of crude reaction mixtures (except where noted). ^b Isolated yield. ^c Yield determined by gas chromatography with an internal standard.

3. Selected NMR Spectra

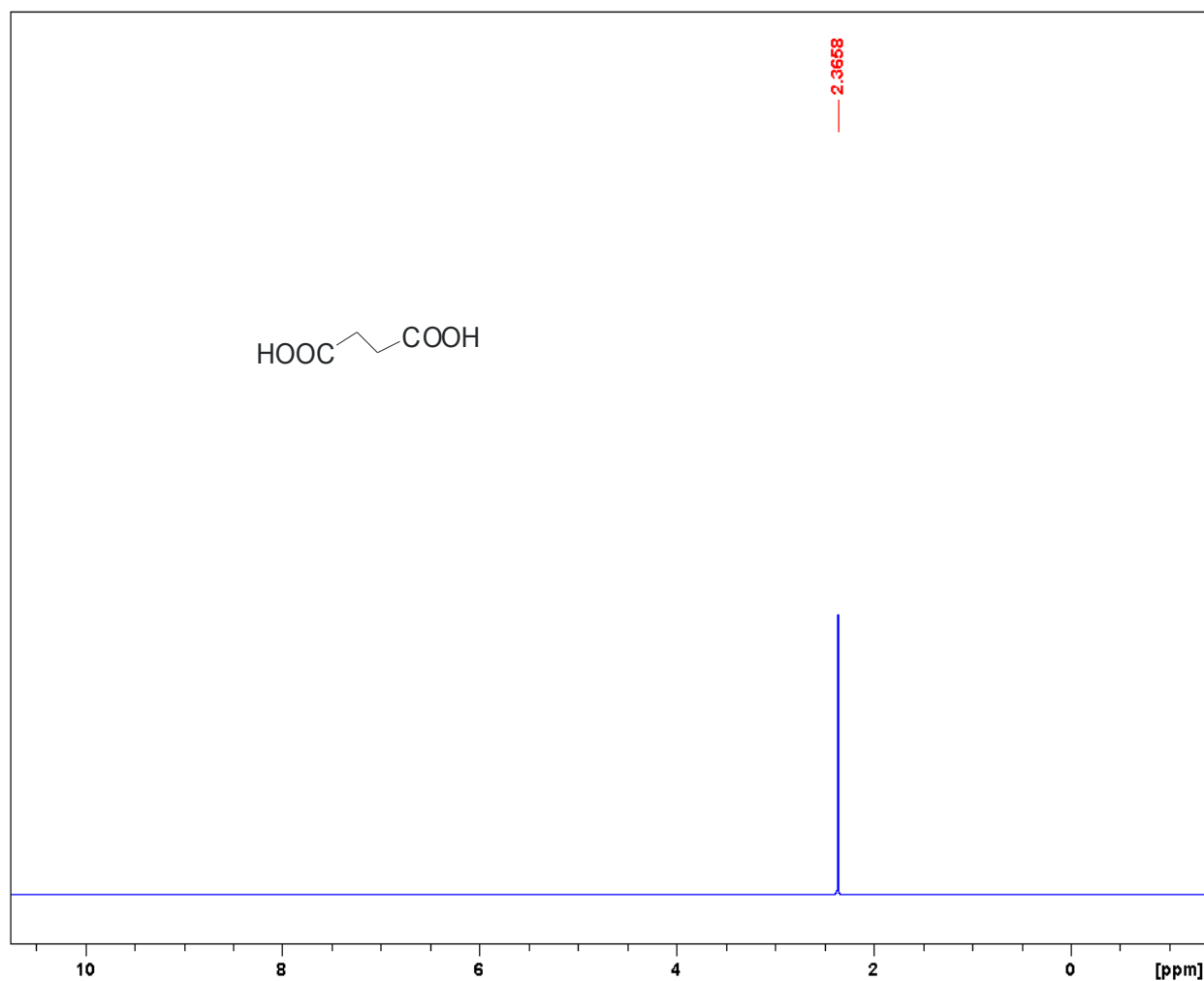


FIGURE S1. ¹H NMR (500 MHz) spectrum of **4**.

Characterization of 4: ¹H NMR (D₂O): 2.37 (s, 4H, 2 CH₂).

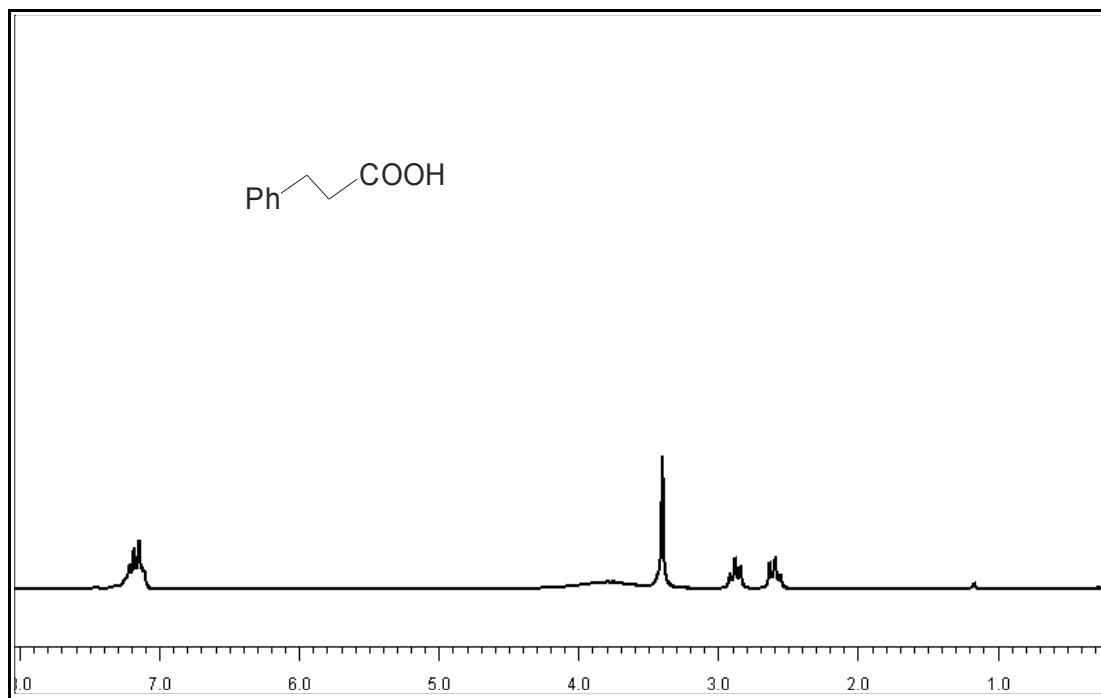


FIGURE S2. ^1H NMR (200 MHz) spectrum of **7**.

Characterization of 7: ^1H NMR (CDCl_3): 7.23-7.06 (m, 5H, Ar), 2.87 (t, $J = 7.6$ Hz, 2H, CH_2), 2.58 (t, $J = 7.6$ Hz, 2H, CH_2). Internal standard: CH_3OH , 3.40 (s, 3H, CH_3).

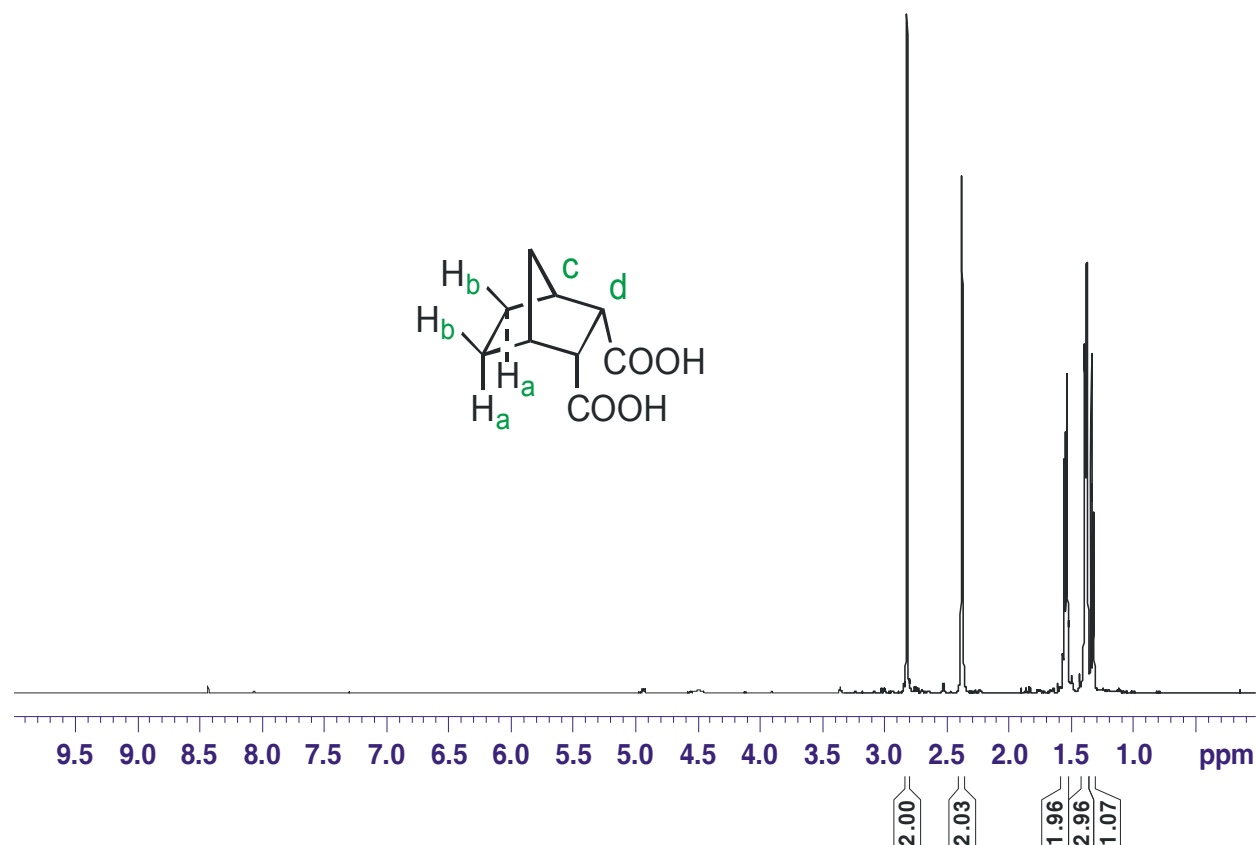


FIGURE S3. ^1H NMR (500 MHz) spectrum of **9** (crude reaction mixture).

Characterization of 9: ^1H NMR (D_2O): 2.82 (s, 2H, H_d), 2.39 (s, 2H, H_c), 1.55 (dd, $J = 7.7$ Hz, $J = 2.0$ Hz, 2H, H_a), 1.39 (br d, $J = 8.1$ Hz, 3H, 2 H_b and 1 H from CH_2), 1.36 (dt, $J = 9.5$ Hz, $J = 1.7$ Hz, 1H, CH_2).

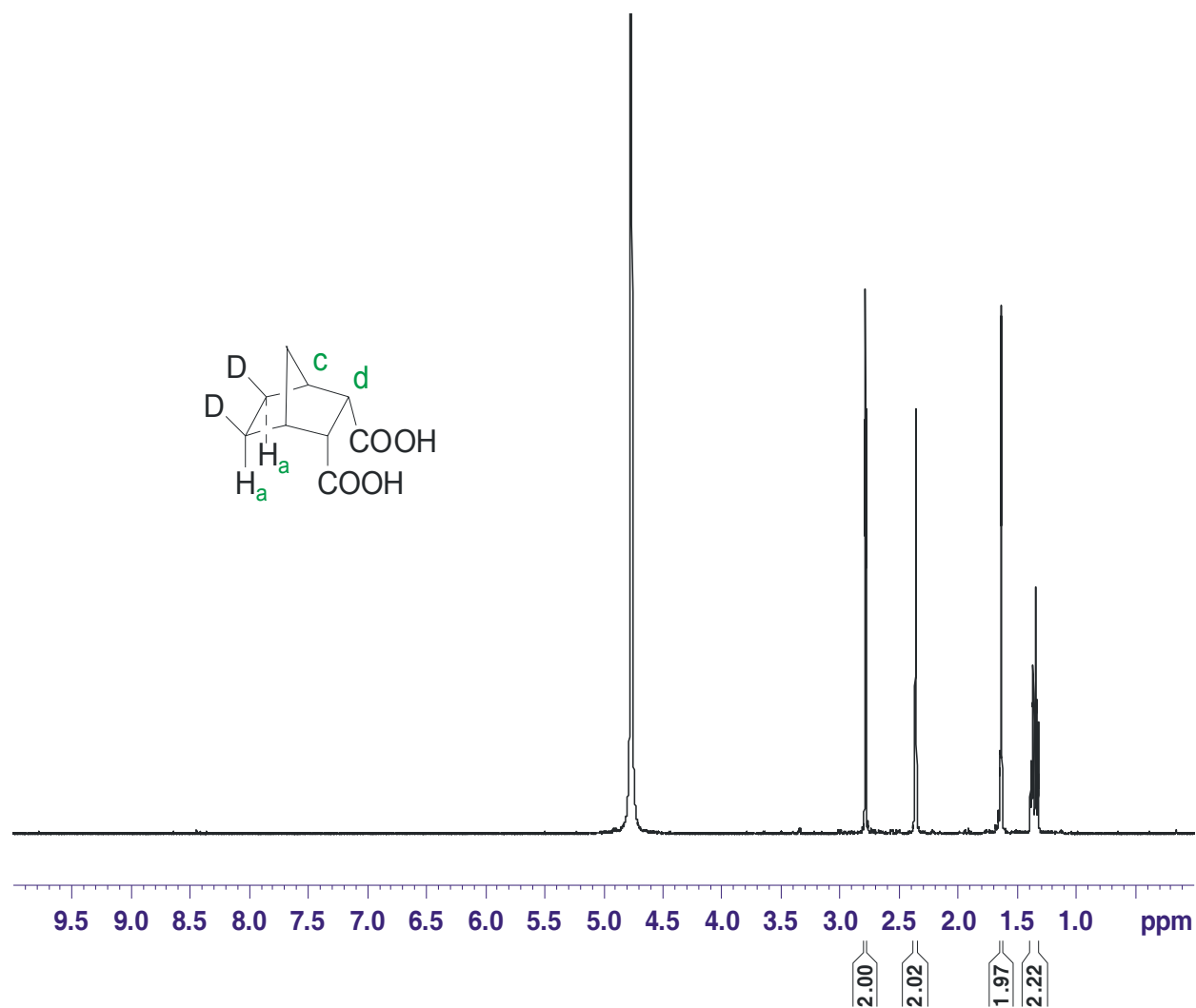


FIGURE S4. ^1H NMR (500 MHz) spectrum for the reduction of the norbornene derivative **8** carried out in D_2O (crude reaction mixture).

Characterization: ^1H NMR (D_2O): 2.79 (t, $J = 2.3$ Hz, 2H, \mathbf{H}_d), 2.36 (m, 2H, \mathbf{H}_c), 1.64 (d, $J = 2.2$, 2H, \mathbf{H}_a), 1.35 (ddt, $J = 13.4$, $J = 9.2$, $J = 1.6$, 2H, \mathbf{CH}_2).

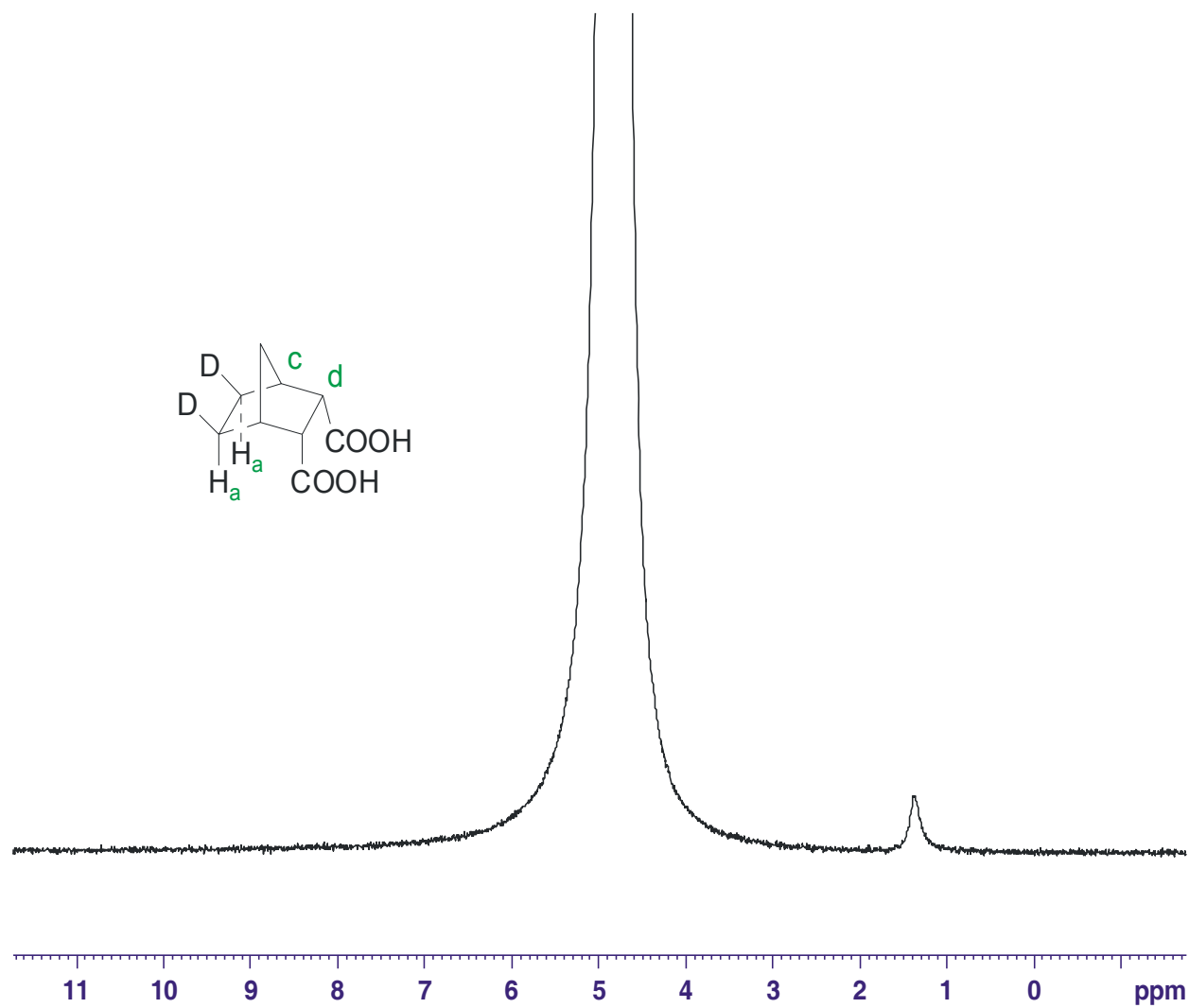


FIGURE S5. ^2D NMR (500 MHz) spectrum for the reduction of the norbornene derivative **8** carried out in D_2O (crude reaction mixture).

Characterization: ^2D NMR (D_2O): 1.37 (br s, 2D)

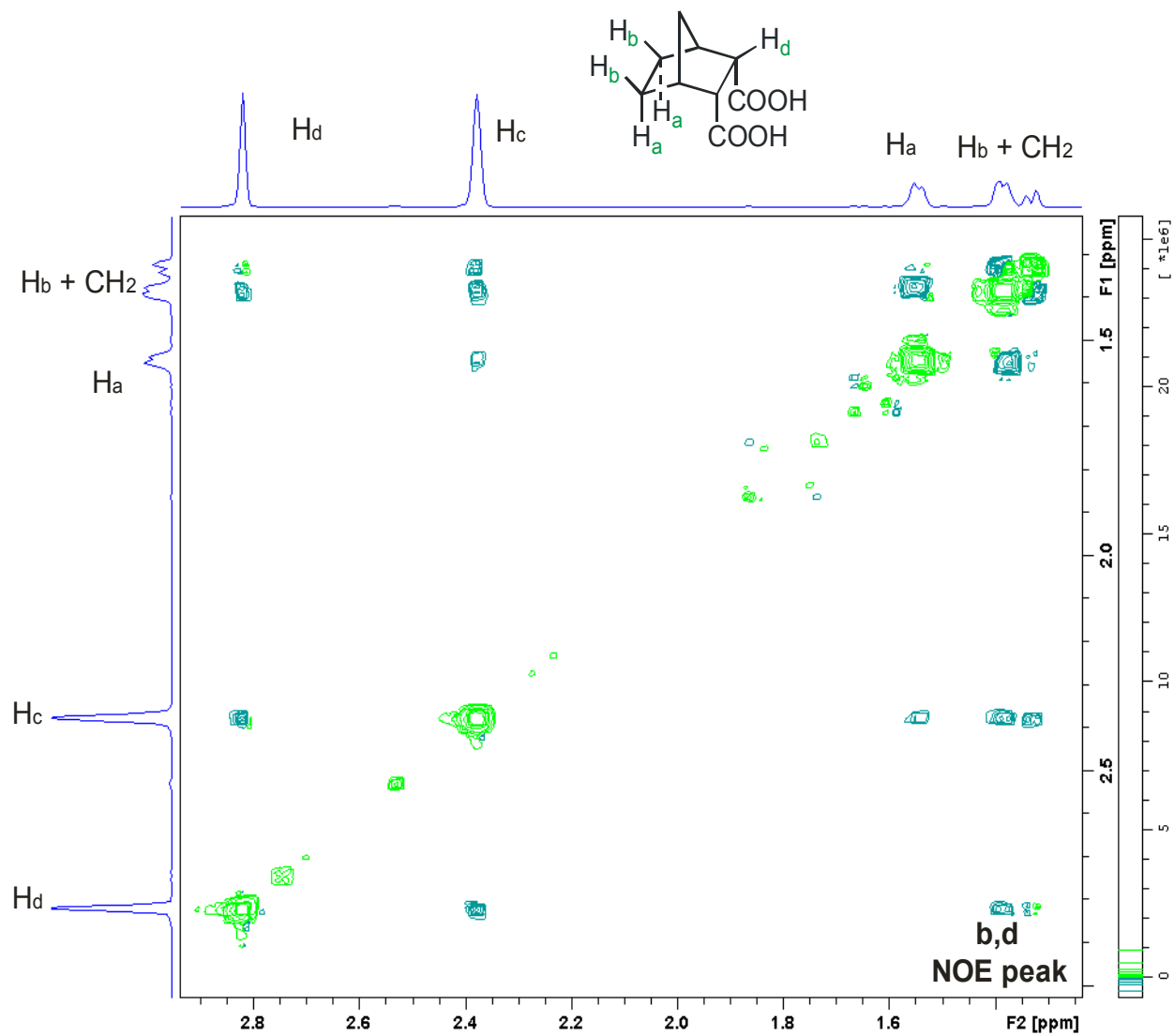


FIGURE S6. 2D Noesy (500 MHz) spectrum of **9** (crude reaction mixture).

4. Selected Mass Spectrum

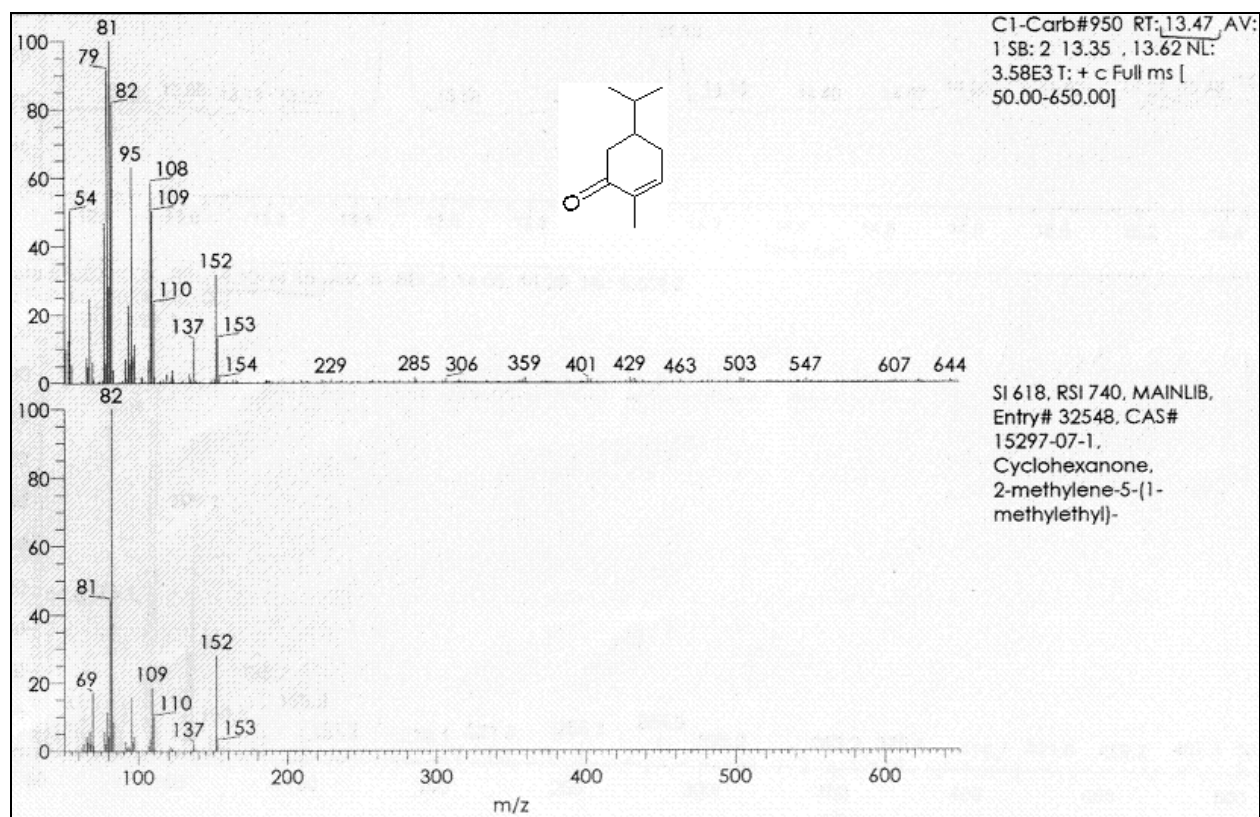


FIGURE S7. Mass spectrum of **16**.

5. Kinetic Studies of the Catalytic Reduction of Cinnamic Acid

Reduction of Cinnamic Acid by $Na_3[Fe(CN)_5N_2H_2]$:

[CA]: cinnamic acid concentration

$[Fe^{II}(CN)_5N_2H_2]^{3-}$: coordinated diazene concentration

Working at high $[Fe^{II}(CN)_5N_2H_2]^{3-}$ with respect to [CA] we can assume that during the reaction $[Fe^{II}(CN)_5N_2H_2]^{3-}$ remains constant. This last observation was confirmed by following the 440 nm band due to $[Fe^{II}(CN)_5N_2H_2]^{3-}$ throughout the experiments.

$$\nu_{obs} = k_{obs} [CA]^n \quad (n = 1)$$

Where the sub index *obs* refers to the observed kinetics parameters.

Rate measurements involving cinnamic acid were done in spectrophotometric cells at 30°C, measuring the disappearance of the absorption at 268 nm ($\epsilon_{268nm} = 18579 \pm 699 \text{ M}^{-1} \text{ cm}^{-1}$). The observed rate constants (k_{obs}) for the spontaneous decay process due to the reduction of cinnamic acid by $[Fe^{II}(CN)_5N_2H_2]^{3-}$ were determined by initial rates showing that all kinetics were pseudo-first-order with respect to cinnamic acid concentration with an observed rate constant $k_{obs} = 2.4 \cdot 10^{-5} \pm 1.7 \cdot 10^{-6} \text{ s}^{-1}$ at 30°C. These reactions were carried out in borax aqueous buffered solutions.

The data were collected directly from the spectrophotometer to a PC and commercial software was used to obtain values of the first order rate constants. Values of k were reproducible.

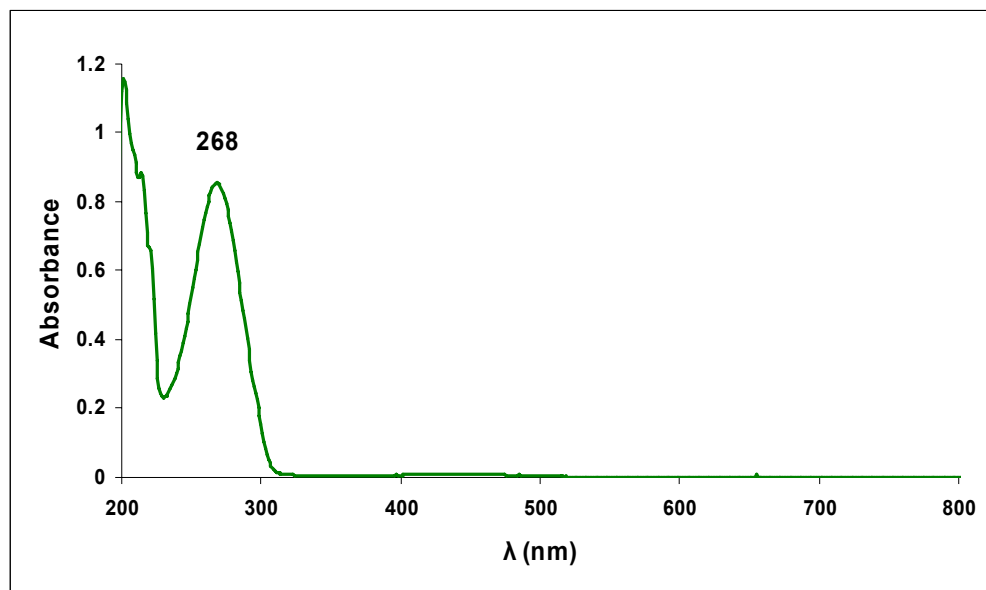


FIGURE S8. UV – visible spectrum of **6** ($\lambda_{\text{max}} = 268 \text{ nm}$) in borax aqueous buffer.

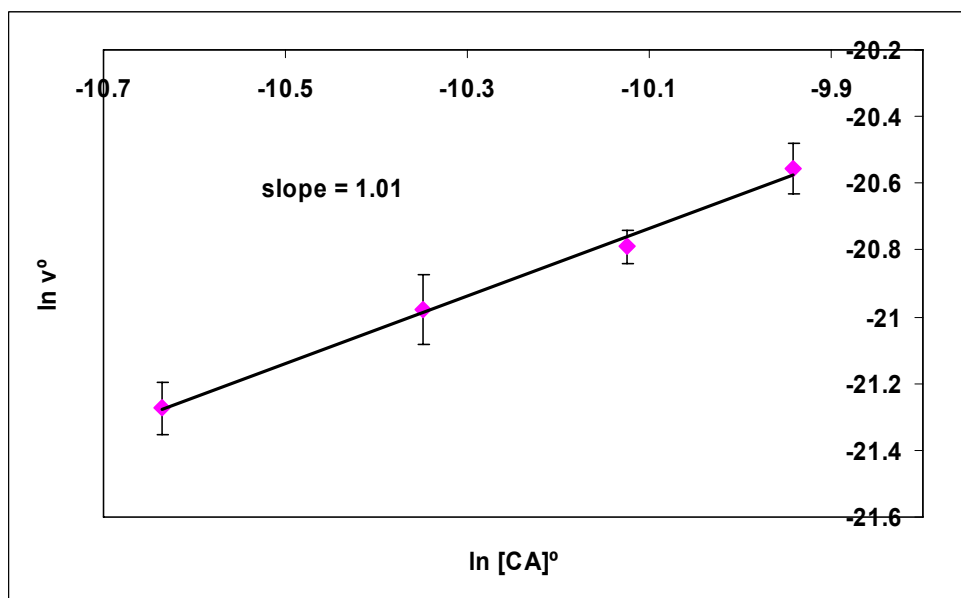
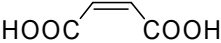
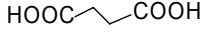


FIGURE S9. Dependence of $\ln \nu^\circ$ vs $\ln [\text{AC}]^\circ$ for different cinnamic acid concentrations.

6. Kinetic Isotope Effect on the Catalytic Reduction

TABLE S2. Kinetic Isotope Effect on the Catalytic Reduction of Maleic Acid^a

Entry		2	NH ₂ OH	Solven	T	
	3 (mmol)	(mmol)	(mmol)	t	(°C)	4 (yield [%]) ^b
1	0.25	0.02	2.5	H ₂ O	25	67
2	0.25	0.02	2.5	D ₂ O	25	65

^a All reactions were run in aqueous borax buffer (3 ml). ^b Relative yield determined by ¹H NMR analysis of crude reaction mixtures.