

Reversal of Enantioselectivity in the Hydroformylation of Styrene with [2S,4S-BDPP]Pt(SnCl<sub>3</sub>)Cl at High Temperature Arises from a Change in the Enantioselective Determining Step

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**Supporting Information**

**General Methods.** All air sensitive materials were handled under nitrogen in an inert atmosphere glovebox or using high vacuum techniques.  $^1\text{H}$  NMR spectra were obtained using a Bruker AC300, AC250, or a Varian Unity500 spectrometer.  $^{13}\text{C}$  (126 MHz) and  $^{31}\text{P}$  (202 MHz) NMR spectra were obtained on a Varian Unity500 spectrometer.  $^{31}\text{P}$  NMR spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$ . Mass spectra were determined on a Kratos MS-25 spectrometer attached to a Carlo Erba gas chromatograph equipped with a 60 m Restek Rtx-5 (5% diphenyl / 95% dimethyl polysiloxane) column. Gas chromatography was performed using a Supelco  $\square$ -Dex ( $\square$ -cyclodextrin) 250 chiral capillary column on a Hewlett-Packard 5890A gas chromatograph connected to an HP3390A integrator.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$ . Benzene, hexane, and ether were distilled from purple solutions of sodium and benzophenone. Toluene was distilled from sodium. Styrene was either distilled prior to use or purified through a disposable inhibitor remover column, purchased from Aldrich. Phenylacetylene and 4-methylstyrene were purchased from Aldrich and distilled prior to use. (2*S*,4*S*)-Bis(diphenylphosphino)pentane was purchased from Strem Chemicals. Anhydrous  $\text{SnCl}_2$ , ethylbenzene, octane, 2-phenylpropanal, 3-phenylpropanal, tributylamine, methyl (S)-(+)-mandelate [(S)- $\text{PhCH}(\text{OH})\text{CO}_2\text{Me}$ ], 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and  $(\text{COD})_2\text{PtCl}_2$  were purchased from Aldrich and used as received. ((2*S*,4*S*)-BDPP) $\text{PtCl}_2$ , and ((2*S*,4*S*)-BDPP) $\text{Pt}(\text{SnCl}_3)\text{Cl}$  (**1**) were prepared according to literature procedures.<sup>1</sup> CO and  $^{13}\text{CO}$  were purchased from AGA and Cambridge Isotopes respectively. An analyzed 1:1 mixture of  $\text{H}_2$ :CO was obtained from Gas Tech.

**(2*S*,4*S*)-BDPP) $\text{PtCl}_2$**  was prepared as described by Kollár.<sup>1</sup> A solution of (2*S*,4*S*)-BDPP (1.72 g, 3.90 mmol) and  $(\text{COD})_2\text{PtCl}_2$  (1.42 g, 3.80 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was stirred for 24 h under  $\text{N}_2$ . Solvent was evaporated under vacuum and the residue was washed with ether to

give ((2*S*,4*S*)-BDPP)PtCl<sub>2</sub> (2.03 g, 76%) as a white solid. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 7.86 (ddd, 4 H, J<sub>PH</sub> = 9.2 Hz, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, *ortho* Ph), 7.83 (ddd, 4 H, J<sub>PH</sub> = 9.2 Hz, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, *ortho* Ph), 7.41-7.60 (m, 12 H, *meta* and *para* Ph), 2.79 (d of sextets, 2 H, J<sub>PH</sub> = 9.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe), 2.05 (tt, 2 H, J<sub>PH</sub> = 19.5 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>2</sub>), 1.05 (dd, 6 H, J<sub>PH</sub> = 14.5 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 135.3 (d, J<sub>PC</sub> = 5.1 Hz), 135.2 (d, J<sub>PC</sub> = 5.1 Hz), 133.9 (d, J<sub>PC</sub> = 3.8 Hz), 133.8 (d, J<sub>PC</sub> = 3.8 Hz), 131.9 (s), 131.4 (s), 128.8 (d, J<sub>PC</sub> = 7.5 Hz), 128.5 (d, J<sub>PC</sub> = 7.5 Hz), 36.1 (s, CH<sub>2</sub>), 17.8 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 7.21 (s, J<sub>PP</sub> = 3415 Hz, satellites). HRMS (ESI) m/z calculated for C<sub>29</sub>H<sub>30</sub><sup>35</sup>ClP<sub>2</sub><sup>195</sup>Pt (M-Cl<sup>+</sup>) = 670.1159, found 670.1143.

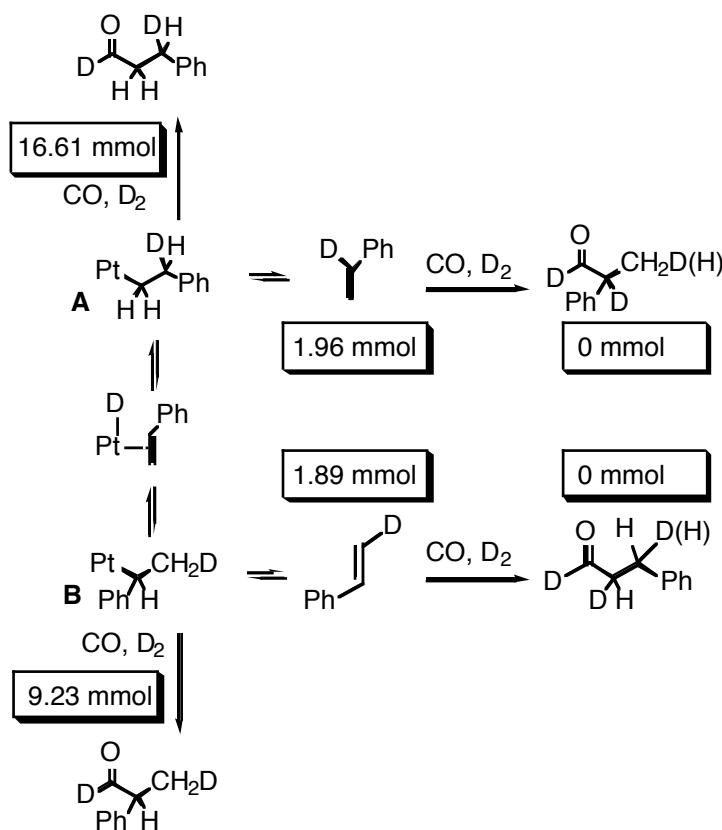
**((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (1)** was prepared as described by Kollár.<sup>1</sup> A solution of ((2*S*,4*S*)-BDPP)PtCl<sub>2</sub> (1.30 g, 1.84 mmol) and SnCl<sub>2</sub> (0.36 g, 1.90 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was stirred for 23 h under N<sub>2</sub>. The solution was concentrated under vacuum and cooled to -30 °C to give ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (1) (1.41 g, 86%) as white needles. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 7.43-7.87 (m, 20 H, Ph), 2.92 (m, 1 H, CHMe), 2.80 (m, 1 H, CHMe), 2.11 (m, 2 H, CH<sub>2</sub>), 1.14 (dd, 3 H, J<sub>PH</sub> = 16.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHCH<sub>3</sub>), 1.09 (dd, 3 H, J<sub>PH</sub> = 16.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 135.3 (d, J<sub>PC</sub> = 10.2 Hz), 134.3 (d, J<sub>PC</sub> = 10.7 Hz), 134.0 (d, J<sub>PC</sub> = 9.8 Hz), 133.6 (d, J<sub>PC</sub> = 9.1 Hz), 133.2 (s), 132.9 (s), 132.7 (s), 132.0 (s), 130.0 (d, J<sub>PC</sub> = 11.5 Hz), 129.7 (d, J<sub>PC</sub> = 11.5 Hz), 129.4 (d, J<sub>PC</sub> = 11.0 Hz), 129.1 (d, J<sub>PC</sub> = 11.3 Hz), 36.4 (s, CH<sub>2</sub>), 29.0 (s, CH), 26.5 (s, CH), 18.1 (s, CH<sub>3</sub>), 17.5 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>) □ 13.8 (d, J<sub>PP</sub> = 24.3 Hz, J<sub>PtP</sub> = 2759 Hz, satellites, P *trans* to Sn), 7.5 (d, J<sub>PP</sub> = 24.3 Hz, J<sub>PtP</sub> = 3342 Hz, satellites, P *cis* to Sn). LRMS (ESI) m/z calculated for C<sub>29</sub>H<sub>30</sub><sup>35</sup>ClP<sub>2</sub><sup>195</sup>Pt (M-SnCl<sub>3</sub><sup>+</sup>) = 670.1, found 670.9. LRMS (ESI) negative ion mode calculated for <sup>119</sup>SnCl<sub>3</sub><sup>-</sup> 224.8, found 224.7.

**Hydroformylation of Styrene at 40 °C.** Toluene (9.0 mL), styrene (2.0 mL, 17 mmol), ((2S,4S)-BDPP)Pt(SnCl<sub>3</sub>)Cl (**1**) (13 mg, 0.015 mmol), and benzene (0.5 mL, 5.9 mmol, internal standard) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub> and pressurized to 1000 psi with a 1:1 mixture of CO:H<sub>2</sub> and heated to 40 °C. After stirring for 138 h, the reactor was cooled and vented, and the products were immediately analyzed by GC. The oven temperature was started at 100 °C and after 35 min ramped 10 °C/min to a final temperature of 200 °C. The N<sub>2</sub> flow was kept at 70 mL/min. Typical retention times (min) were: 6.5 (benzene), 7.7 (toluene), 9.9 (ethylbenzene), 11.5 (styrene), 38.9 ((R)-2-phenylpropanal), 39.3 ((S)-2-phenylpropanal), and 45.1 (3-phenylpropanal). Conversion of styrene to aldehydes was 5%, *n:i* = 2.2; and 60% ee (S)-2-phenylpropanal. Peak assignments were confirmed with samples of the commercial compounds. The assignments for (R)- and (S)-2-phenylpropanal were confirmed by <sup>1</sup>H NMR spectroscopy of (R,S) and (S,S) methyl mandelate ester derivatives, (R,S)-**4** and (S,S)-**4**. The GC response factor for 3-phenylpropanal and 2-phenylpropanal (calibrated relative to benzene using standards made from commercial samples) were also compared to the *n:i* ratio obtained by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy for the aldehyde products of hydroformylation and deuterioformylation at high and low temperatures. The estimated error for *n:i* ratios and % ee's calculated from GC integrations is ± 5%.

**Deuterioformylation of Styrene at 39 °C.** Toluene (35.0 mL), styrene (11.0 mL, 95.7 mmol), and ((2S,4S)-BDPP)Pt(SnCl<sub>3</sub>)Cl (**1**) (48 mg, 0.054 mmol) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub>. The reactor was pressurized to 600 psi with D<sub>2</sub> followed by 600 psi of CO. The reactor was heated to 39 ± 2 °C (p = 1220 psi) and stirring was begun. After 118.5 h the reactor was cooled to room temperature, vented, and benzene (0.50 mL, 5.9 mmol, internal standard) was added. The products were analyzed by chiral GC (same

parameters as stated above) and by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and  $^2\text{H}$  NMR (toluene- $d_8$ ) spectroscopy using a 1:1  $\text{CD}_2\text{Cl}_2:\text{CH}_2\text{Cl}_2$  internal standard. Percent composition of the product mixture at 27% conversion of styrene to aldehydes was: ethylbenzene, (1.0%); 2-phenylpropanal, (9.5%); 3-phenylpropanal, (17.7%);  $n:i = 1.8$ ; 71% ee (S)-2-phenylpropanal.

**Scheme 1.** Deuteroformylation of styrene at 39 °C



**(E)- $\square$ -Deuteriostyrene.<sup>2</sup>** DIBAL-H (200 mL, 1M in hexanes) was added to a solution of phenylacetylene (24.2 g, 0.24 mol) in hexane (200 mL) under  $\text{N}_2$ . The solution was stirred at 60 °C for 5 h. Solvent was evaporated under high vacuum and the residual red oil was dissolved in  $\text{Et}_2\text{O}$  and cooled to -78 °C. MeOD (18 mL) was added dropwise and the solution was slowly warmed to room temperature. An additional 200 mL  $\text{Et}_2\text{O}$  and 500 mL 2M sodium potassium

tartrate were added to dissolve the aluminum salts. The layers were separated and the aqueous layer was extracted with 200 mL Et<sub>2</sub>O. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), Et<sub>2</sub>O was removed by distillation through a Vigreux column, and the remaining yellow liquid was bulb-to-bulb transferred under high vacuum to give 15.0 g of clear liquid. <sup>1</sup>H NMR spectroscopy revealed a 67:33 mixture of (*E*)-□-deuteriostyrene (10.1 g, 48%, 93 ± 5% D<sub>trans</sub>) : recovered phenylacetylene (4.9 g, 20%). Partial removal of phenylacetylene was achieved by adding this mixture to a suspension of AgNO<sub>3</sub> (10.2 g, 0.06 mol) and tributylamine (17.2 mL, 0.07 mol) in tetraglyme (20 mL). A white precipitate formed. The mixture was stirred for 30 min and the volatile components were vacuum transferred to give 10.9 g of an 85:15 mixture of (*E*)-□-deuteriostyrene : phenylacetylene.

Attempted deuterioformylation of the 85:15 (*E*)-□-deuteriostyrene : phenylacetylene mixture catalyzed by ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (48 mg, 0.054 mmol) in toluene (30 mL) under 1200 psi 1:1 D<sub>2</sub> : CO at 39 °C for one week failed. GC and <sup>1</sup>H NMR spectroscopy showed styrene and phenylacetylene but no aldehydes. Removal of solvent by distillation led to the recovery of 1.4 g of 85:15 (*E*)-□-deuteriostyrene:phenylacetylene. This mixture was added to a suspension of AgNO<sub>3</sub> (6.4 g, 0.04 mol) and tributylamine (7 mL, 0.03 mol) in tetraglyme (40 mL). A white precipitate formed immediately. The mixture was stirred for 15 min and the volatile components were vacuum transferred from the solution, diluted with 4 mL toluene, washed with 4 mL 2 M HCl, 4 mL H<sub>2</sub>O, and dried (MgSO<sub>4</sub>). The volatile components were vacuum transferred to give 4.4 g of a toluene solution of (*E*)-□-deuteriostyrene (0.96 g, 89% recovery, 93 ± 5% D<sub>trans</sub> by integration). <sup>1</sup>H NMR of (*E*)-□-deuteriostyrene (300 MHz, CDCl<sub>3</sub>) □ 7.37-7.42 (m, 2 H, Ph), 7.19-7.34 (m, 3 H, Ar), 6.70 (dt, 1 H, J<sub>trans</sub> = 17.5 Hz, J<sub>HD</sub> = 1.5 Hz,

$=\text{CHPh}$ ), 5.72 (d, 1 H,  $J_{\text{trans}} = 17.5$  Hz,  $=\text{CH}_{\text{trans}}\text{D}$ ), 5.23 (dd, 0.07 H,  $J_{\text{cis}} = 11.0$  Hz,  $J_{\text{gem}} = 1.0$  Hz,  $=\text{CH}_{\text{cis}}\text{D}$ ). No phenylacetylene was visible by  $^1\text{H}$  NMR (5% detection limit).

### **Hydroformylation of (*E*)- $\square$ -Deuteriostyrene and Derivitization of the Aldehyde Products.**

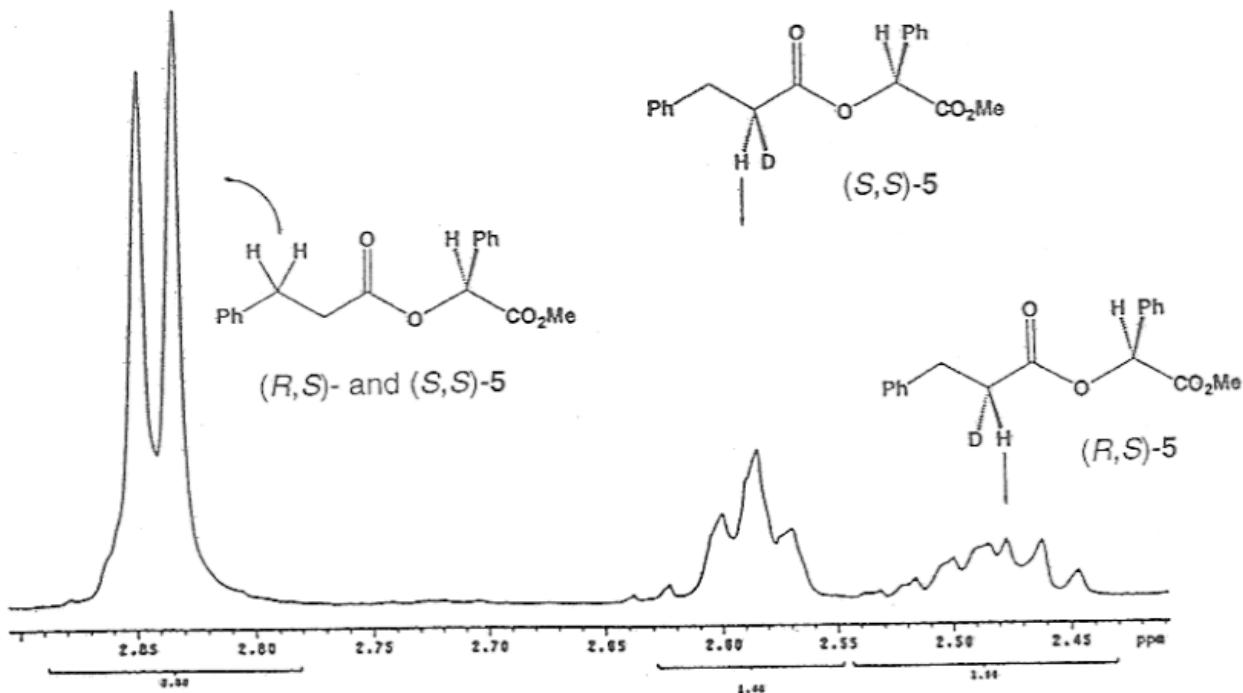
**(A) Hydroformylation.** (*E*)- $\square$ -deuteriostyrene (0.96 g, 9.1 mmol) in toluene (4.0 mL) and ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (**1**) (24 mg, 0.027 mmol) were added to a 250 mL stainless steel Parr reactor. The reactor was sealed under 1 atm of N<sub>2</sub> and pressurized to 1200 psi with a 1:1 mixture of CO:H<sub>2</sub>. After stirring for 196 h at 39 ± 2 °C, the reactor was cooled and vented. Immediate analysis by GC showed 6.0% ethylbenzene, 60.6% 3-phenylpropanal, and 33.3% 2-phenylpropanal (15.9% of which was (*R*)-2-phenylpropanal, and 84.1% (*S*)-2-phenylpropanal). Conversion to aldehydes = 93%; *n:i* = 1.8; 68% ee (*S*)-2-phenylpropanal.<sup>3</sup>

**(B) Oxidation of 2- and 3-Phenylpropanal to 2- and 3-Phenylpropanoic Acids.**<sup>4</sup> The 1.8:1 mixture of deuterium labeled 2- and 3-phenylpropanal (1.15 g, 8.55 mmol) from the above hydroformylation of (*E*)- $\square$ -deuteriostyrene was added to a solution of 1M KMnO<sub>4</sub> (28 mL), 1.3M KH<sub>2</sub>PO<sub>4</sub> (15 mL), *t*-BuOH (10 mL), and stirred for 1 h. The residual MnO<sub>2</sub> was dissolved with saturated Na<sub>2</sub>SO<sub>3</sub> and the reaction mixture was extracted with Et<sub>2</sub>O (5 x 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent was evaporated under reduced pressure to give a 1.8:1 mixture of 3-[<sup>2</sup>H]-2-phenylpropanoic acid and 2-[<sup>2</sup>H]-3-phenylpropanoic acid [1.08 g, 84%, ratio determined by average  $^1\text{H}$  NMR integrations (0.5615H / 0.316H = 1.78)].  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.14-7.33 (m, 5.00 H, Ph), 4.15 (br s,  $\Delta_{1/2} = 50$  Hz, CO<sub>2</sub>H); 2-[<sup>2</sup>H]-3-phenylpropanoic acid: 2.94 (br d, 1.28 H,  $J = 7.8$  Hz, CH<sub>2</sub>Ph), 2.65 (m, 0.483 H, CHDCO<sub>2</sub>H); 3-

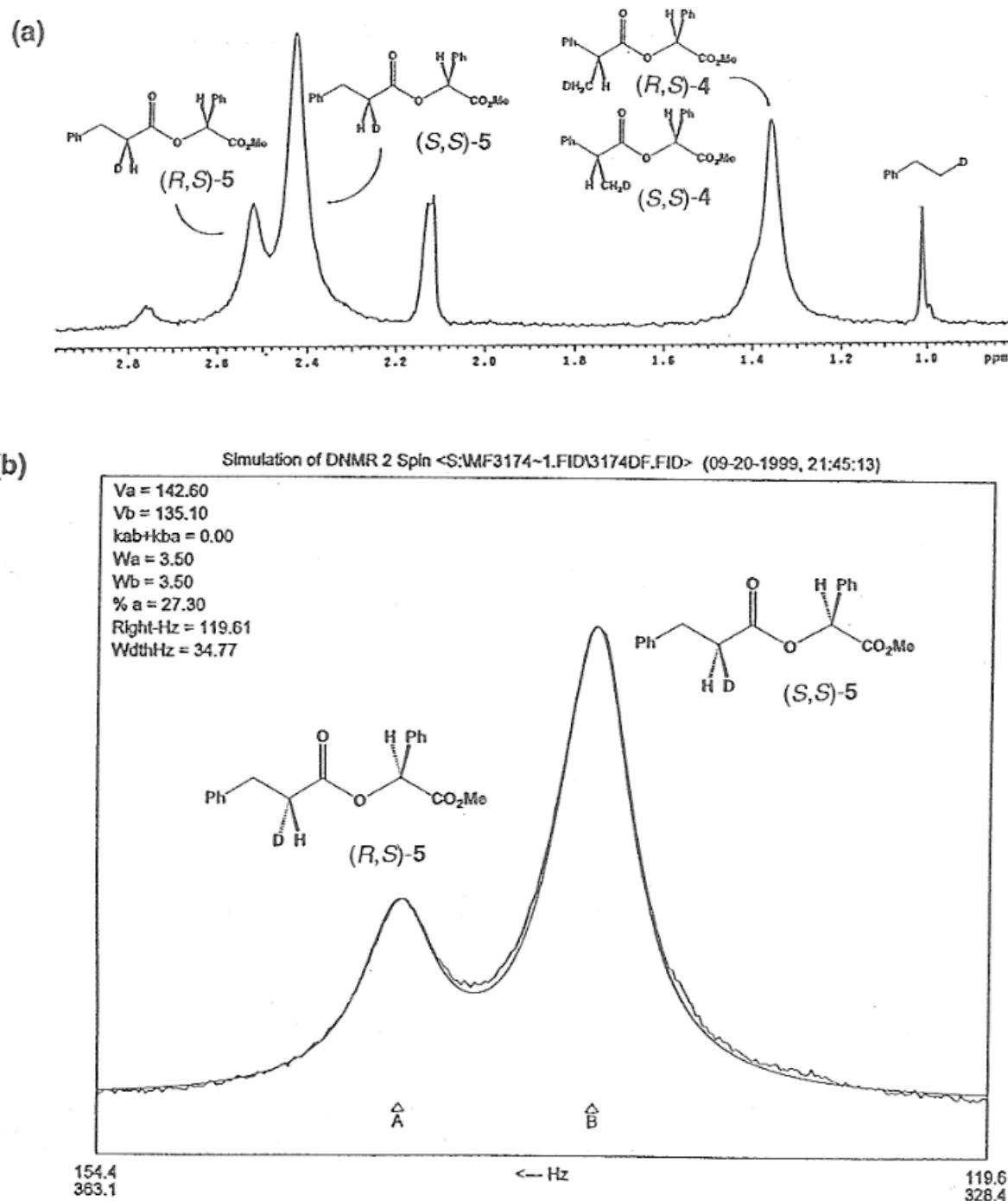
[<sup>2</sup>H]-2-phenylpropanoic acid: 3.72 (br t, 0.277 H,  $J = 7.5$  Hz,  $\text{CHCH}_2\text{D}$ ), 1.49 (dt, 0.710 H,  $J_{\text{HH}} = 7.5$  Hz,  $J_{\text{HD}} = 1.8$  Hz,  $\text{CH}_2\text{D}$ ).

**(C) Methyl (S)-(+ Mandelate Esters (*R,S*)-4, (*S,S*)-4, (*R,S*)-5, and (*S,S*)-5.** The above 1.8:1 mixture of 3-[<sup>2</sup>H]-2- and 2-[<sup>2</sup>H]-3-phenylpropanoic acids (1.08 g, 7.2 mmol), methyl (S)-(+ mandelate (1.22 g, 7.3 mmol), 1,3-dicyclohexylcarbodiimide (DCC, 1.43 g, 7.0 mmol), and 4-(dimethylamino)pyridine (DMAP, 58 mg, 0.47 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) and stirred under  $\text{N}_2$  at -10 °C for 3 h. The reaction mixture was filtered to remove 1,3-dicyclohexylurea (DCU), a reaction by-product, concentrated to 2 mL, and stored at -20 °C. After a second filtration to remove DCU, solvent was evaporated under reduced pressure to give a mixture of **4-d** and **5-d** (1.31 g, 61%). <sup>1</sup>H NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) □ 6.97-7.45 (m, 10 H, Ph, all compounds), 6.04 (s, 0.80 H,  $\text{CHCO}_2\text{Me}$ , (*S,S*)-4, (*S,S*)-5, and (*R,S*)-5), 6.01 (s, 0.20 H,  $\text{CHCO}_2\text{Me}$ , (*R,S*)-4), 3.78 (t, 0.06 H,  $J = 6.9$  Hz, CH, (*R,S*)-4), 3.69 (t, 0.31 H,  $J = 6.9$  Hz, CH, (*S,S*)-4), 3.18 (s, 5 H,  $\text{CO}_2\text{CH}_3$ , (*R,S*)- and (*S,S*)-5), 3.10 (s, 0.13 H,  $\text{CO}_2\text{CH}_3$ , (*R,S*)-4), 3.07 (s, 0.26 H,  $\text{CO}_2\text{CH}_3$ , (*S,S*)-4), 2.84 (br d, 1.4 H,  $J = 7.4$  Hz,  $\text{CH}_2\text{Ph}$ , (*R,S*)- and (*S,S*)-5), 2.57 (tt, 0.67 H,  $^3J_{\text{HH}} = 7.4$  Hz,  $^1J_{\text{HD}} = 1.8$  Hz,  $\text{CHDCO}_2\text{R}$ , (*S,S*)-5), 2.47 (m, 0.32 H,  $\text{CHDCO}_2\text{R}$ , (*R,S*)-5), 1.48 (m,  $\text{CH}_2\text{D}$ , (*R,S*)-4, partially obscured by cyclohexyl CH<sub>2</sub> of DCU), 1.43 (m,  $\text{CH}_2\text{D}$ , (*S,S*)-4, partially obscured by cyclohexyl CH<sub>2</sub> of DCU). <sup>2</sup>H{<sup>1</sup>H} NMR (77 MHz,  $\text{C}_6\text{H}_6$ ) □ 2.52 (0.54 D,  $\text{CHDCO}_2\text{R}$  of (*R,S*)-5), 2.42 (1.45 D,  $\text{CHDCO}_2\text{R}$  (*S,S*)-5), 1.40 and 1.36 (0.96 D,  $\text{CH}_2\text{D}$  of (*R,S*)-4 and (*S,S*)-4), 1.01 (0.11 D,  $\text{CH}_2\text{D}$  of 2-[<sup>2</sup>H]-ethylbenzene). The combined integral for (*R,S*)-5 and (*S,S*)-5  $\text{CHDCO}_2\text{R}$  is 1.99 D; the two peaks were not separated at the baseline and were simulated with the winDNMR<sup>5</sup> program to give  $27.3 \pm 2\%$  (*R,S*)-5 and  $72.7 \pm 2\%$  (*S,S*)-5 (45.4% ee).

**Figure 1.** Methylene resonances in the  $^1\text{H}$  NMR spectrum of  $(R,S)$ -**5** and  $(S,S)$ -**5** from the hydroformylation of  $(E)$ - $\square$ -Deuteriostyrene



**Figure 2.** (a)  $^2\text{H}$  NMR spectrum of  $(R,S)$ -**4**,  $(S,S)$ -**4**,  $(R,S)$ -**5**, and  $(S,S)$ -**5** in benzene from the hydroformylation of  $(E)$ - $\square$ -deuteriostyrene. (b) Expansion of the  $\square$ -CHD resonances; simulated  $(R,S)$ -**5** and  $(S,S)$ -**5** peaks are overlayed.



## Hydroformylation of (*Z*)- $\square$ -Deuteriostyrene<sup>6</sup> and Derivitization of the Aldehyde

### Products.

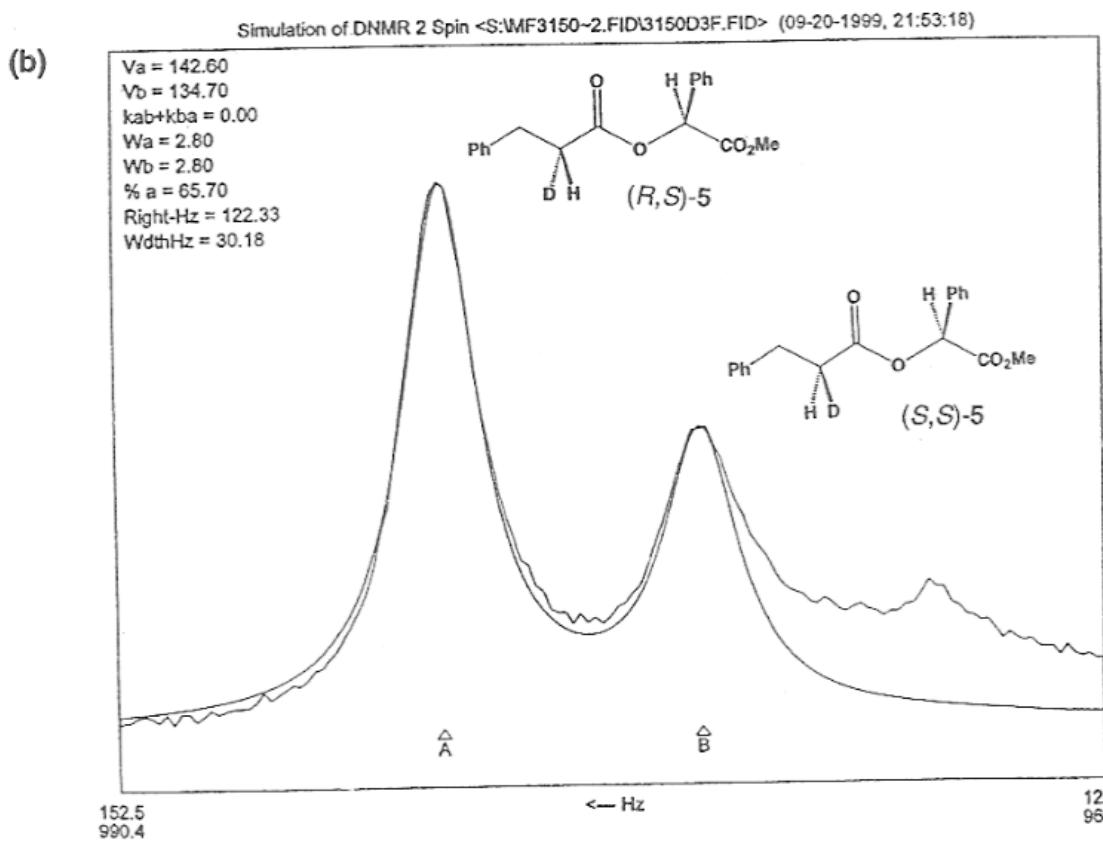
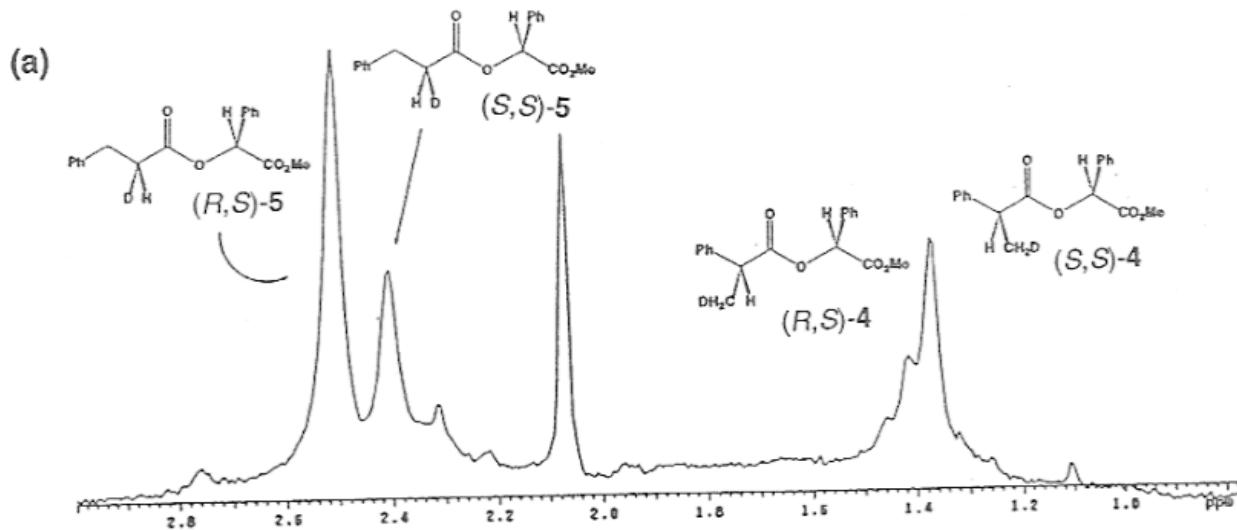
**(A) Hydroformylation.** A mixture of (*Z*)- $\square$ -deuteriostyrene (2.2 g, 21 mmol, 93 ± 5% D), phenylacetylene-*d*<sub>1</sub> (0.7 g, 7 mmol, 45 ± 5% D), styrene (2.7 g, 26 mmol); ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (30 mg, 0.033 mmol); and toluene (15 mL) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub> and pressurized to 1200 psi with a 1:1 mixture of CO:H<sub>2</sub>. After heating to 39 ± 2 °C, the reaction was stirred for 192 h. The reactor was then cooled, vented, and the products were immediately analyzed by GC.<sup>3</sup> Ethylbenzene, (4.0%); 3-phenylpropanal, (57.4%); (*R*)-2-phenylpropanal, (5.7%); (*S*)-2-phenylpropanal, (25.5%); unidentified compound, (7.3%). Conversion to aldehydes: 89%; *n:i* = 1.8; 63% ee (*S*)-2-phenylpropanal.

**(B) Oxidation of 2- and 3-phenylpropanal to 2 and 3-phenylpropanoic acids.** The previously described oxidation procedure was applied to the above 1.8:1 mixture of deuterium labeled 2- and 3-phenylpropanal (6.4 g, 48 mmol) from the hydroformylation of (*Z*)- $\square$ -deuteriostyrene using 1M KMnO<sub>4</sub> (28 mL), 1.3M KH<sub>2</sub>PO<sub>4</sub> (15 mL), and *t*-BuOH (10 mL). Yield: 1.78 g (25%) of a 2:1 mixture of 3-[<sup>2</sup>H]-2-phenylpropanoic acid and 2-[<sup>2</sup>H]-3-phenylpropanoic acid [ratio determined by average <sup>1</sup>H NMR integrations (0.315 H / 0.16 H = 1.97 ≈ 2)].  $\square$  <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\square$  7.14 - 7.33 (m, 5.0 H, Ph), 4.15 (br s,  $\square_{1/2}$  = 50 Hz, CO<sub>2</sub>H); 2-[<sup>2</sup>H]-3-phenylpropanoic acid:  $\square$  2.90 (t, 0.63 H, *J* = 7.8 Hz, CH<sub>2</sub>Ph), 2.59 (t, 0.63 H, CHDCO<sub>2</sub>H); 3-[<sup>2</sup>H]-2-phenylpropanoic acid:  $\square$  3.72 (br q, 0.16 H, *J* = 7.5 Hz, CHCH<sub>2</sub>D), 1.49 (dt, *J<sub>HH</sub>* = 7.5 Hz, CH<sub>2</sub>D).

**Preparation of Methyl (S)-(+)-Mandelate Esters (*R,S*)-**4**, (*S,S*)-**4**, (*R,S*)-**5**, and (*S,S*)-**5**.**

Compounds (*R,S*)- (*S,S*)-**4** and (*R,S*)- (*S,S*)-**5** (0.48 g, 24%) were prepared with the above 2:1 mixture of 3-[<sup>2</sup>H]-2- and 2-[<sup>2</sup>H]-3-phenylpropanoic acids (1.78 g, 6.7 mmol), methyl (S)-(+)-mandelate (1.09 g, 6.6 mmol), DCC (1.64 g, 7.9 mmol), and DMAP (54 mg, 0.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at -10 °C in the manner previously described. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): □ 6.97 - 7.45 (m, 10 H, Ph, all compounds), 6.04 (s, 0.80 H, CHCO<sub>2</sub>Me, (*S,S*)-**4**, (*S,S*)-**5**, and (*R,S*)-**5**), 6.01 (s, 0.11 H, CHCO<sub>2</sub>Me, (*R,S*)-**4**), 3.76 (q, 0.03 H, *J* = 6.9 Hz, CH, (*R,S*)-**4**), 3.67 (q, 0.06 H, *J* = 6.9 Hz, CH, (*S,S*)-**4**), 3.18 (s, 1.7 H, CO<sub>2</sub>CH<sub>3</sub>, (*R,S*)- and (*S,S*)-**5**), 3.09 (s, 0.50 H, CO<sub>2</sub>CH<sub>3</sub>, (*R,S*)-**4**), 3.07 (s, 0.24 H, CO<sub>2</sub>CH<sub>3</sub>, (*S,S*)-**4**), 2.84 (t, 1.0 H, *J* = 7.8 Hz, CH<sub>2</sub>Ph, (*R,S*)-**5** and (*S,S*)-**5**), 2.57 (m, 0.23 H, CHDCO<sub>2</sub>R, (*R,S*)-**5**), 2.44 (m, 0.32 H, CHDCO<sub>2</sub>R, (*S,S*)-**5**), 1.49 (d, 0.11 H, *J* = 6.9 Hz, CH<sub>2</sub>D, (*R,S*)-**4**), 1.44 (d, 0.35 H, *J* = 6.9 Hz, CH<sub>2</sub>D, (*S,S*)-**4**). <sup>2</sup>H{<sup>1</sup>H} NMR (77 MHz, C<sub>6</sub>H<sub>6</sub>): □ 2.52 (1.86 D, CHDCO<sub>2</sub>R, (*R,S*)-**5**), 2.42 (1.00 D, CHDCO<sub>2</sub>R (*S,S*)-**5**), 1.42 and 1.38 (1.30 D, CH<sub>2</sub>D, (*R,S*)-**4** and (*S,S*)-**4**), 1.01 (0.1 D, CH<sub>2</sub>D of ethylbenzene). The peaks for CHDCO<sub>2</sub>R of **5-d** were simulated with the winDNMR<sup>5</sup> program to give 65.7 ± 2% (*R,S*)-**5** and 34.3 ± 2% (*S,S*)-**5** (31.4% ee).

**Figure 3.** (a)  $^2\text{H}$  NMR spectrum of  $(R,S)$ -**4**,  $(S,S)$ -**4**,  $(R,S)$ -**5**, and  $(S,S)$ -**5** in benzene from the hydroformylation of  $(Z)$ - $\square$ -deuteriostyrene. (b) Expansion of the  $\square$ -CHD resonances; simulated  $(R,S)$ -**5** and  $(S,S)$ -**5** peaks are overlayed.



**Preparation of the Methyl (S)-(+)-Mandelate Ester of Nonracemic 2-**

**Phenylpropanoic Acid.<sup>7</sup>** (S)-2-Phenylpropanoic acid (25 mg, 0.17 mmol), racemic 2-phenylpropanoic acid (75 mg, 0.50 mmol), methyl (S)-(+)-mandelate (111 mg, 0.67 mmol), DCC (137 mg, 0.666 mmol), and DMAP (6 mg, 0.05 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred under N<sub>2</sub> at -10 °C for 4 h. The reaction mixture was filtered to remove dicyclohexylurea (DCU), a reaction by-product, concentrated to 2 mL, and stored at -20 °C. After a second filtration to remove DCU, the solvent was evaporated under reduced pressure and the resulting oil was distilled at 120 °C, 10<sup>-5</sup> Torr to give (R,S)- and (S,S)-4 (90 mg, 45%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.97 - 7.37 (m, 10 H, Ph), 6.03 (s, 0.63 H, CHCO<sub>2</sub>Me, (S,S)-4), 6.00 (s, 0.34 H, CHCO<sub>2</sub>Me, (R,S)-4), 3.74 (q, 0.41 H, J = 6.9 Hz, CH, (R,S)-4), 3.67 (q, 0.75 H, J = 6.9 Hz, CH, (S,S)-4), 3.09 (s, 1.0 H, CO<sub>2</sub>CH<sub>3</sub>, (R,S)-4), 3.07 (s, 2.1 H, CO<sub>2</sub>CH<sub>3</sub>, (S,S)-4), 1.49 (d, 0.94 H, J = 6.9 Hz, CH<sub>3</sub>, (R,S)-4), 1.44 (d, 1.8 H, J = 6.9 Hz, CH<sub>3</sub>, (S,S)-4).

**Preparation of the Methyl (S)-(+)-Mandelate Ester of 3-Phenylpropanoic Acid.** 3-

Phenylpropanoic acid (180 mg, 1.20 mmol), methyl (S)-(+)-mandelate (199 mg, 1.20 mmol), DCC (248 mg, 1.20 mmol), and DMAP (9 mg, 0.07 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred under N<sub>2</sub> at -10 °C for 3.5 h. The reaction mixture was filtered to remove DCU, a reaction by-product, concentrated to 3 mL, and stored at -20 °C. After a second filtration to remove DCU, the solvent was evaporated under reduced pressure to give a yellow oil that was distilled at 120 °C, 10<sup>-5</sup> Torr to give the product (337 mg, 94 %). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.43 - 7.39 (m, 8 H, Ph), 7.11 - 6.93 (m, 2 H, Ph), 6.06 (s, 1 H, CHCO<sub>2</sub>Me), 3.18 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 2.84 (t, 2 H, J = 7.8 Hz, CH<sub>2</sub>Ph), 2.57 (m, 1 H, *pro-R* CHHCO<sub>2</sub>R), 2.44 (m, 1 H, *pro-S* CHHCO<sub>2</sub>R).

**Hydroformylation of Styrene at 100 °C.** Toluene (9.0 mL), styrene (2.0 mL, 17 mmol), ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (13 mg, 0.015 mmol), and benzene (0.5 mL, 5.9 mmol, internal standard) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub> and pressurized to 1000 psi with a 1:1 mixture of CO:H<sub>2</sub>. Once the reactor temperature stabilized at 100 °C, stirring was begun and continued for 4.5 h. After cooling and venting the reactor, the products were immediately analyzed by GC.<sup>3</sup> Conversion to aldehydes: 89%; 3-phenylpropanal (63.4%), 2-phenylpropanal (25.9%), ethylbenzene (10.6%), *n:i* = 2.4; 10% ee (*R*)-2-phenylpropanal.

**Deuteroformylation of Styrene at 96 °C.** Toluene (35.0 mL), styrene (11.0 mL, 95.7 mmol), ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (48 mg, 0.054 mmol), and benzene (0.5 mL, 5.9 mmol, internal standard) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub>. The reactor was pressurized to 600 psi with D<sub>2</sub> followed by 600 psi of CO. The reactor was then heated for 10 min before the temperature stabilized at 96 ± 2 °C and stirring was begun. An aliquot (~0.4 mL) was collected every 30 min for 4.5 h and immediately analyzed by GC. Each aliquot was analyzed by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy in 1:1 CH<sub>2</sub>Cl<sub>2</sub>:CD<sub>2</sub>Cl<sub>2</sub>. Percent composition of the product mixture after 4.5 h was: ethylbenzene (6.8%), styrene (6.2%), 2-phenylpropanal (24.3%), 3-phenylpropanal (62.7%).<sup>3</sup> <sup>1</sup>H NMR chemical shifts of product mixtures (300 MHz, 1:1 CH<sub>2</sub>Cl<sub>2</sub>:CD<sub>2</sub>Cl<sub>2</sub>): □ 7.2 - 7.8 (m, Ph, all compounds); 3-phenylpropanal: □ 9.88 (t, *J* = 3.3 Hz, CHO), 3.06 (m, CH<sub>2</sub>Ph), 2.80 (m, CH<sub>2</sub>CHO); 2-phenylpropanal: □ 9.82 (d, *J* = 3.3 Hz, CHO), 3.72 (br t, *J* = 6 Hz, CH), 1.60 (d, *J* = 6.9 Hz, CH<sub>3</sub>), 1.58 (dt, *J*<sub>HH</sub> = 6.9 Hz, *J*<sub>HD</sub> = 2.2 Hz, CH<sub>2</sub>D); ethylbenzene: □ 2.79 (m, CH<sub>2</sub>, overlaps with CH<sub>2</sub>CHO of 3-phenylpropanal), 1.15 (m, CH<sub>3</sub>); styrene: □ 6.93 (dd, *J*<sub>trans</sub> = 17.5 Hz, *J*<sub>cis</sub> = 11.0 Hz, internal vinyl CH), 5.96 (dd, *J*<sub>trans</sub> = 17.5 Hz, *J*<sub>gem</sub> = 1.2 Hz, terminal vinyl CHH), 5.45 (dd, *J*<sub>cis</sub> = 11.0 Hz, *J*<sub>gem</sub> = 1.2 Hz,

terminal vinyl CHH).  $^2\text{H}\{\text{H}\}$  NMR (77 MHz, 1:1  $\text{CH}_2\text{Cl}_2:\text{CD}_2\text{Cl}_2$ ): 3-phenylpropanal: δ 9.93 (CDO), 3.09 ( $\text{CD}_2\text{Ph}$ ), 2.83 ( $\text{CD}_2\text{CDO}$ ); 2-phenylpropanal: δ 9.86 (CDO), 3.72 (CD), 1.61 ( $\text{CD}_3$ ); ethylbenzene: δ 2.8 ( $\text{CD}_2$ , overlaps  $\text{CD}_2\text{CHO}$  of 3-phenylpropanal), 1.46 ( $\text{CD}_3$ ); styrene: δ 6.98 (internal vinyl CD), 6.01 (terminal vinyl CDD), 5.49 (terminal vinyl CDD).

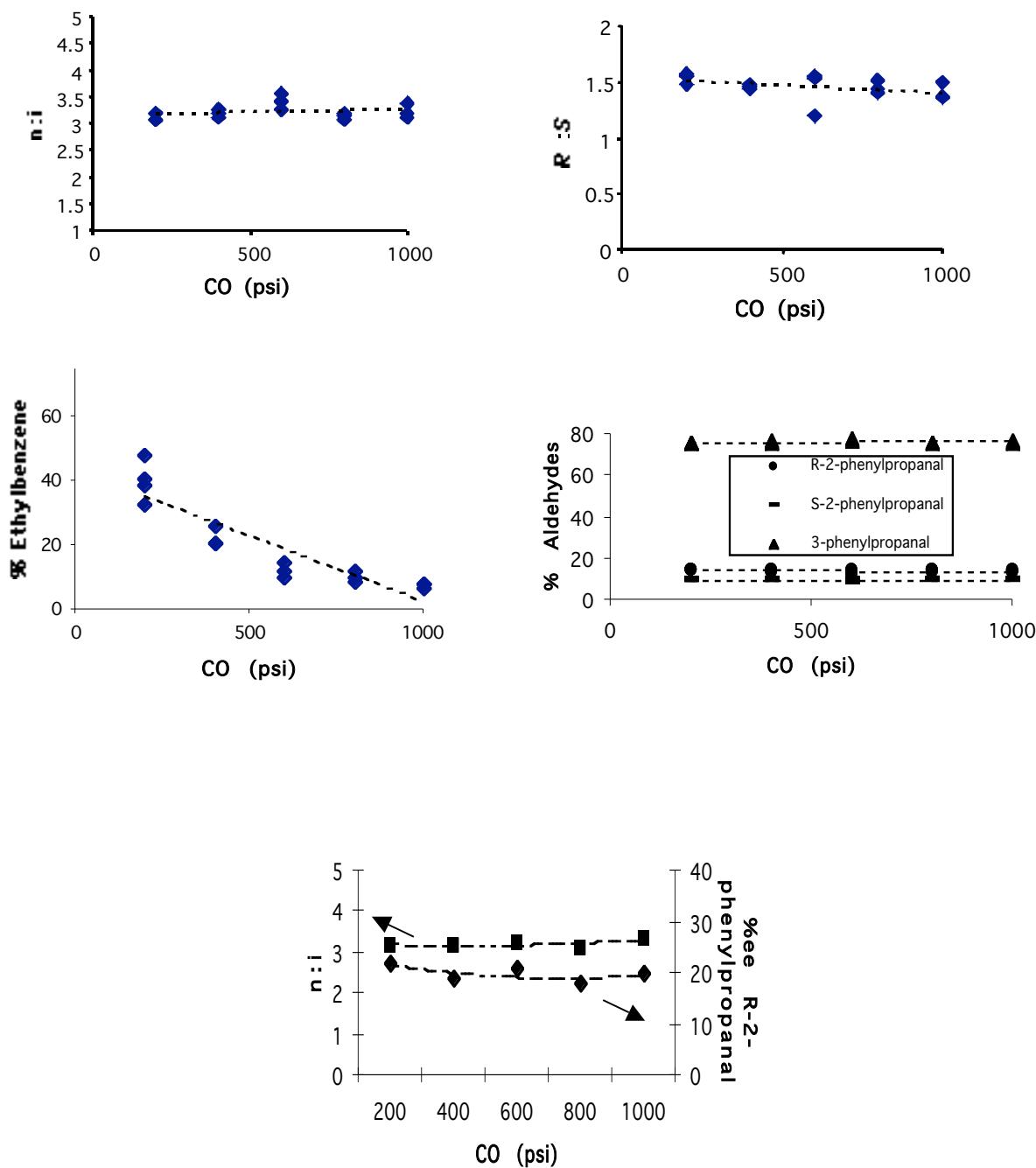
Two other deuterioformylations of styrene were performed on the same scale with 600 psi  $\text{D}_2$  and 600 psi CO at ~96 °C. One experiment was stopped at 90% conversion and the other at 31% conversion of styrene to aldehydes. Percent composition of the product mixture at 91% conversion was:<sup>3</sup> ethylbenzene (7.4%), styrene (2.2%), 3-phenylpropanal (64.3%), 2-phenylpropanal (26.2%), *n:i* = 2.5. Percent composition of the product mixture at 30% conversion was:<sup>3</sup> ethylbenzene (2.3%), 3-phenylpropanal (21.2%), 2-phenylpropanal (9.0%), *n:i* = 2.3. Accurate determination of enantiomeric excess was difficult because the separation of deuterium labeled (*R*)- and (*S*)-2-phenylpropanal in the GC traces was poor. The products of these two deuterioformylations were also analyzed by  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy. Samples of 2.0 mL of reaction solution and 60 μL of 1:1  $\text{CH}_2\text{Cl}_2:\text{CD}_2\text{Cl}_2$  were made for NMR analysis in  $\text{CDCl}_3$  or toluene-*d*<sub>8</sub>.  $^1\text{H}$  NMR chemical shifts of the product mixtures (300 MHz,  $\text{CDCl}_3$ , 1:1  $\text{CH}_2\text{Cl}_2:\text{CD}_2\text{Cl}_2$  internal standard): δ 6.8 - 7.5 (m, Ph); 3-phenylpropanal: δ 9.49 (t, *J* = 3.3 Hz, CHO), 2.72 (m,  $\text{CH}_2\text{Ph}$ ), 2.41 (m,  $\text{CH}_2\text{CHO}$ ); 2-phenylpropanal: δ 9.46 (d, *J* = 3.3 Hz, CHO), 3.32 (m, CH), 1.27 (dt,  $J_{\text{HH}} = 6.9$  Hz,  $J_{\text{HD}} = 2.2$  Hz,  $\text{CH}_2\text{D}$ ); ethylbenzene: δ 2.53 (br q, *J* = 6.5 Hz,  $\text{CH}_2$ ), 1.14 (m,  $\text{CH}_3$ ); styrene: δ 6.63 (dd,  $J_{\text{trans}} = 17.5$  Hz,  $J_{\text{cis}} = 11.0$  Hz, internal vinyl CH), 5.66 (dd,  $J_{\text{trans}} = 17.5$  Hz,  $J_{\text{gem}} = 1.0$  Hz, terminal vinyl CHH), 5.15 (dd,  $J_{\text{cis}} = 11.0$  Hz,  $J_{\text{gem}} = 1.0$  Hz, terminal vinyl CHH).  $^2\text{H}\{\text{H}\}$  NMR (77 MHz, toluene-*d*<sub>8</sub>, 1:1  $\text{CH}_2\text{Cl}_2:\text{CD}_2\text{Cl}_2$  internal standard): 3-phenylpropanal: δ 9.30 (CDO), 2.53 ( $\text{CD}_2\text{Ph}$ ), 2.10 ( $\text{CD}_2\text{CDO}$ ); 2-phenylpropanal:

9.32 (CDO), 3.04 (CD), 1.11 (CD<sub>3</sub>); ethylbenzene: 2.37 (CD<sub>2</sub>), 1.01 (CD<sub>3</sub>); styrene: 6.53 (internal vinyl CD), 5.56 (terminal vinyl CDD), 5.04 (terminal vinyl CDD).

**Table 1.** CO pressure dependence on the hydroformylation of styrene at 100 °C. (See text for experimental procedure).

CO (psi)	H <sub>2</sub> (psi)	n:i	ee	Ethylbenzene	R-aldehyde	S-aldehyde	n-aldehyde	R:S	R:n	S:n	TOF (h <sup>-1</sup> )
200	400	3.18	22% R	41%	14.5%	9.4%	76.1%	1.55	0.19	0.12	25
200	400	3.08	21% R	39%	14.9%	9.6%	75.5%	1.55	0.20	0.13	60
200	400	3.07	19% R	48%	14.7%	9.9%	75.4%	1.48	0.19	0.13	29
200	400	3.20	22% R	33%	14.5%	9.3%	76.2%	1.57	0.19	0.12	61
400	400	3.20	19% R	21%	14.1%	9.7%	76.2%	1.46	0.19	0.13	142
400	400	3.13	18% R	21%	14.3%	9.9%	75.8%	1.44	0.19	0.13	113
400	400	3.25	19% R	26%	14.0%	9.5%	76.5%	1.47	0.18	0.12	117
600	400	3.26	21% R	12%	14.2%	9.3%	76.5%	1.53	0.19	0.12	94
600	400	3.42	21% R	15%	12.3%	10.3%	77.4%	1.19	0.16	0.13	113
600	400	3.56	21% R	10%	13.3%	8.6%	78.1%	1.55	0.17	0.11	78
800	400	3.13	18% R	10%	14.2%	10.0%	75.8%	1.43	0.19	0.13	107
800	400	3.07	20% R	12%	14.8%	9.8%	75.4%	1.51	0.20	0.13	106
800	400	3.20	17% R	9%	13.9%	9.9%	76.2%	1.41	0.18	0.13	163
1000	400	3.35	20% R	7%	13.8%	9.2%	77.0%	1.50	0.18	0.12	68
1000	400	3.18	15% R	8%	13.8%	10.1%	76.1%	1.37	0.18	0.13	86
1000	400	3.10	16% R	8%	14.1%	10.3%	75.6%	1.37	0.19	0.14	57

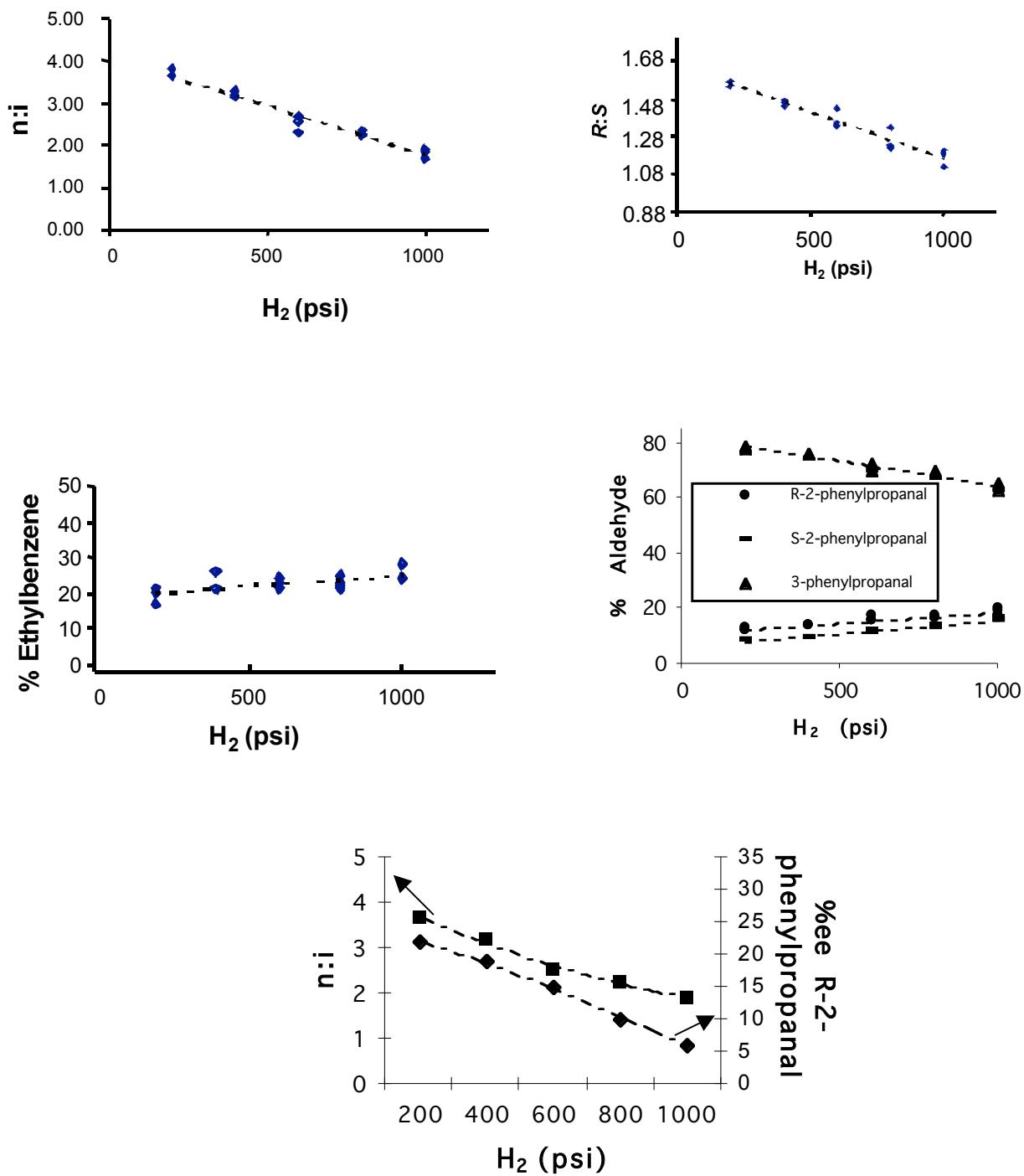
**Figure 4.** Graphs related to CO pressure dependence on the hydroformylation of styrene at 100 °C. (See text for experimental procedure).



**Table 2.** H<sub>2</sub> pressure dependence on the hydroformylation of styrene at 100 °C. (See text for experimental procedure).

H <sub>2</sub> (psi)	CO (psi)	n:i	ee	Ethylbenzene	R-aldehyde	S-aldehyde	n-aldehyde	R:S	R:n	S:n	TOF (h <sup>-1</sup> )
200	400	3.69	22% R	20%	12.8%	8.5%	78.7%	1.51	0.16	0.11	44
200	400	3.61	21% R	21%	13.1%	8.6%	78.3%	1.52	0.17	0.11	37
200	400	3.81	21% R	17%	12.2%	8.6%	79.2%	1.42	0.15	0.11	38
400	400	3.20	19% R	21%	14.2%	9.6%	76.2%	1.48	0.19	0.13	142
400	400	3.17	18% R	21%	14.2%	9.8%	76.0%	1.44	0.19	0.13	113
400	400	3.25	19% R	26%	14.0%	9.5%	76.5%	1.47	0.18	0.12	117
600	400	2.54	15% R	21%	16.2%	12.0%	71.8%	1.35	0.23	0.17	163
600	400	2.30	18% R	24%	17.8%	12.5%	69.8%	1.42	0.25	0.18	71
600	400	2.70	15% R	23%	15.5%	11.5%	73.0%	1.35	0.21	0.16	163
800	400	2.25	10% R	21%	16.9%	13.9%	69.2%	1.22	0.24	0.20	201
800	400	2.24	10% R	22%	17.0%	13.9%	69.1%	1.22	0.25	0.20	237
800	400	2.26	14% R	25%	17.5%	13.2%	69.3%	1.33	0.25	0.19	189
800	400	2.34	10% R	23%	16.4%	13.5%	70.1%	1.21	0.23	0.19	422
1000	400	1.92	6% R	24%	18.1%	16.2%	65.7%	1.12	0.28	0.25	443
1000	400	1.69	9% R	28%	20.3%	16.9%	62.8%	1.20	0.32	0.27	389
1000	400	1.82	9% R	24%	19.3%	16.2%	64.5%	1.19	0.30	0.25	755

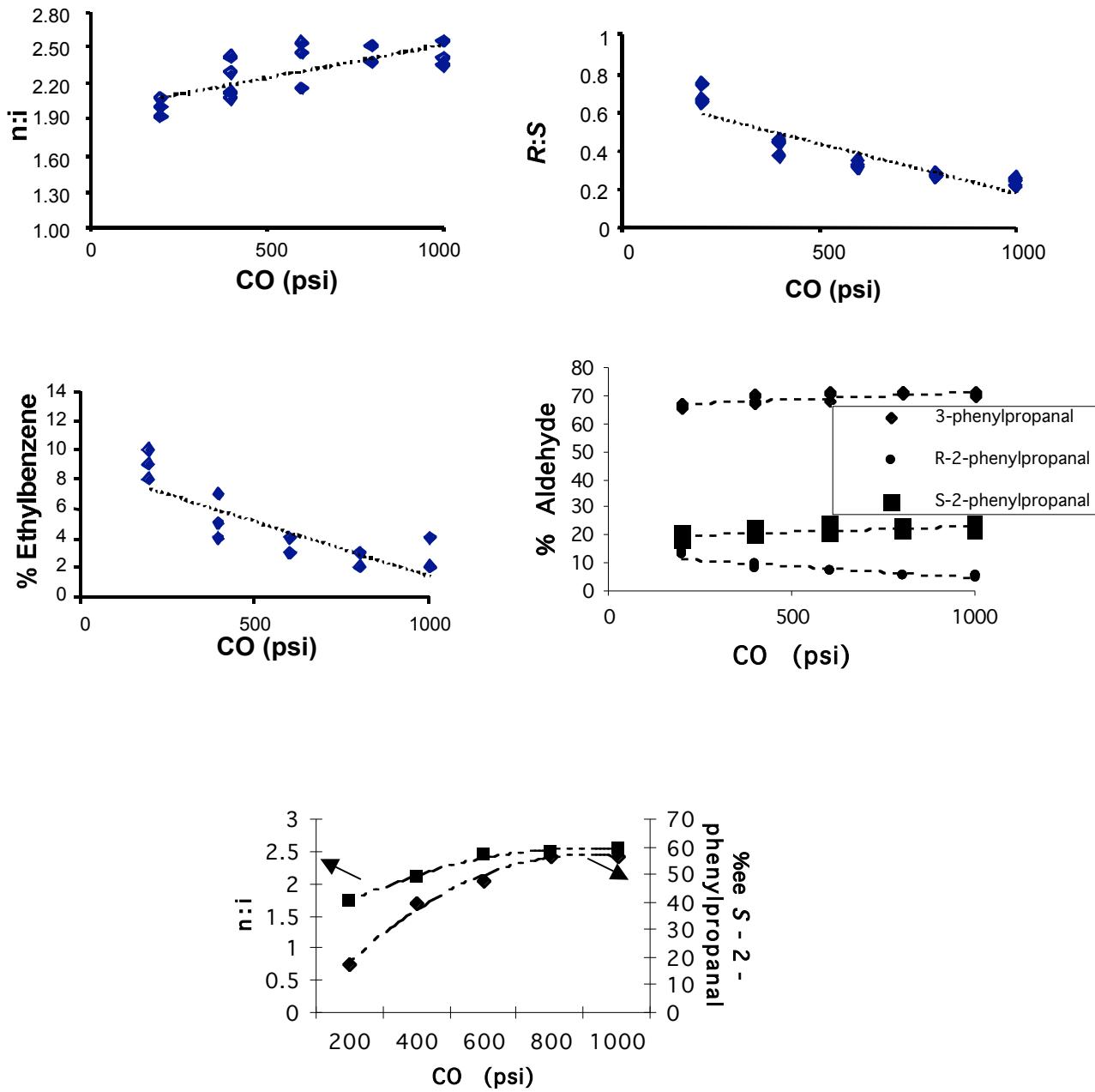
**Figure 5.** Graphs related to H<sub>2</sub> pressure dependence on the hydroformylation of styrene at 100 °C. (See text for experimental procedure).



**Table 3.** CO pressure dependence on the hydroformylation of styrene at 50 °C. (See text for experimental procedure).

CO (psi)	H <sub>2</sub> (psi)	n:i	ee	Ethylbenzene	R-aldehyde	S-aldehyde	n-aldehyde	R:S	R:n	S:n	TOF (h <sup>-1</sup> )	
200	400	2.07	14% S		8%	14.0%	18.6%	67.4%	0.75	0.21	0.28	-
200	400	2.00	20% S		9%	13.3%	20.0%	66.7%	0.67	0.20	0.30	11
200	400	1.92	22% S		10%	13.4%	20.8%	65.8%	0.64	0.20	0.32	3
400	400	2.29	46% S		4%	8.2%	22.2%	69.6%	0.37	0.12	0.32	4
400	400	2.12	40% S		7%	9.6%	22.5%	67.9%	0.43	0.14	0.33	5
400	400	2.07	37% S		5%	10.3%	22.3%	67.4%	0.46	0.15	0.33	4
400	400	2.42	38% S		4%	9.1%	20.1%	70.8%	0.45	0.13	0.28	-
600	400	2.15	52% S		4%	7.6%	24.2%	68.2%	0.31	0.11	0.36	6
600	400	2.46	48% S		3%	7.5%	21.4%	71.1%	0.35	0.11	0.30	8
600	400	2.53	51% S		3%	6.8%	21.5%	71.8%	0.32	0.09	0.30	13
800	400	2.38	57% S		3%	6.3%	23.3%	70.4%	0.27	0.09	0.33	13
800	400	2.51	56% S		2%	6.3%	22.2%	71.5%	0.28	0.09	0.31	5
800	400	2.51	57% S		2%	6.2%	22.3%	71.5%	0.28	0.09	0.31	7
1000	400	2.32	66% S		4%	5.3%	24.8%	69.9%	0.21	0.08	0.35	-
1000	400	2.55	57% S		2%	6.1%	22.1%	71.8%	0.28	0.08	0.31	7
1000	400	2.41	60% S		2%	5.9%	23.4%	70.7%	0.25	0.08	0.33	7

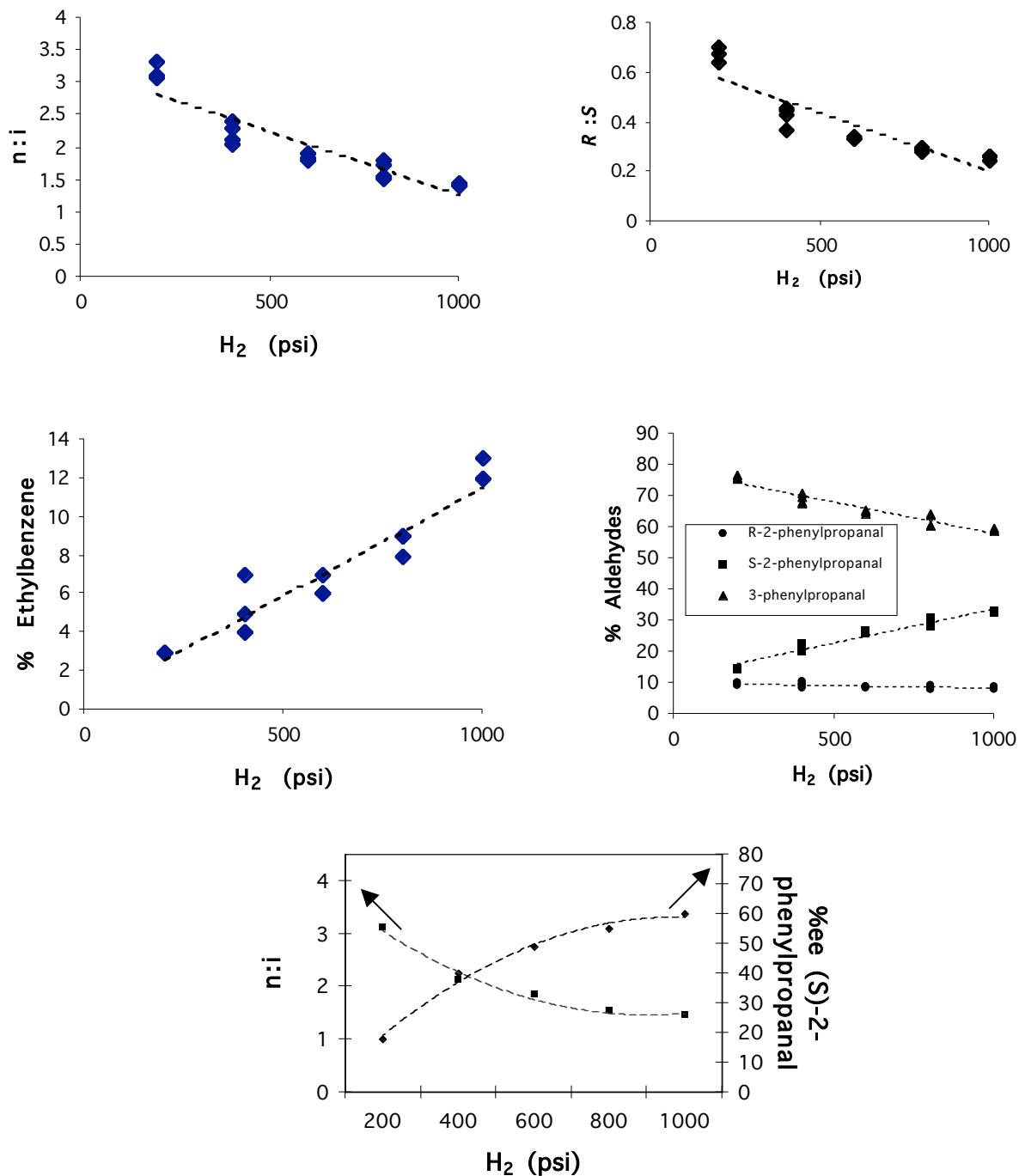
**Figure 6.** Graphs related to CO pressure dependence on the hydroformylation of styrene at 50 °C. (See text for experimental procedure).



**Table 4.** Graphs related to H<sub>2</sub> pressure dependence on the hydroformylation of styrene at 50 °C.  
(See text for experimental procedure).

H <sub>2</sub> (psi)	CO (psi)	n:i	ee	Ethylbenzene	R-aldehyde	S-aldehyde	n-aldehyde	R:S	R:n	S:n	TOF (h <sup>-1</sup> )
200	400	3.08	19% S	3%	9.9%	14.6%	75.5%	0.68	0.13	0.19	2
200	400	3.11	18% S	3%	10.0%	14.3%	75.7%	0.70	0.13	0.19	3
200	400	3.31	22% S	3%	9.1%	14.1%	76.8%	0.64	0.12	0.18	5
400	400	2.07	37% S	5%	10.3%	22.3%	67.4%	0.46	0.15	0.33	4
400	400	2.12	40% S	7%	9.6%	22.4%	68.0%	0.43	0.14	0.33	5
400	400	2.29	46% S	4%	8.2%	22.2%	69.6%	0.37	0.12	0.32	4
400	400	2.42	38% S	4%	9.1%	20.1%	70.8%	0.45	0.13	0.28	-
600	400	1.80	50% S	6%	8.9%	26.8%	64.3%	0.33	0.14	0.42	23
600	400	1.84	49% S	7%	8.9%	26.3%	64.8%	0.34	0.14	0.41	10
600	400	1.91	51% S	6%	8.5%	25.9%	65.6%	0.33	0.13	0.39	4
800	400	1.53	56% S	9%	8.7%	30.8%	60.5%	0.28	0.14	0.51	11
800	400	1.54	55% S	9%	9.0%	30.4%	60.6%	0.30	0.15	0.50	10
800	400	1.75	55% S	8%	8.1%	28.3%	63.6%	0.29	0.13	0.44	23
800	400	1.79	56% S	9%	8.0%	27.9%	64.1%	0.29	0.12	0.44	1
1000	400	1.42	58% S	13%	8.6%	32.8%	58.6%	0.26	0.15	0.56	8
1000	400	1.42	59% S	12%	8.5%	32.8%	58.7%	0.26	0.15	0.56	-
1000	400	1.46	60% S	12%	8.1%	32.5%	59.4%	0.25	0.14	0.55	10

**Figure 7.** Graphs related to H<sub>2</sub> pressure dependence on the hydroformylation of styrene at 50 °C. (See text for experimental procedure). Variable H<sub>2</sub> pressures at 50 °C.



**Deuteroformylation of 4-Methylstyrene in a Toluene Solution of 2-phenylpropanal**

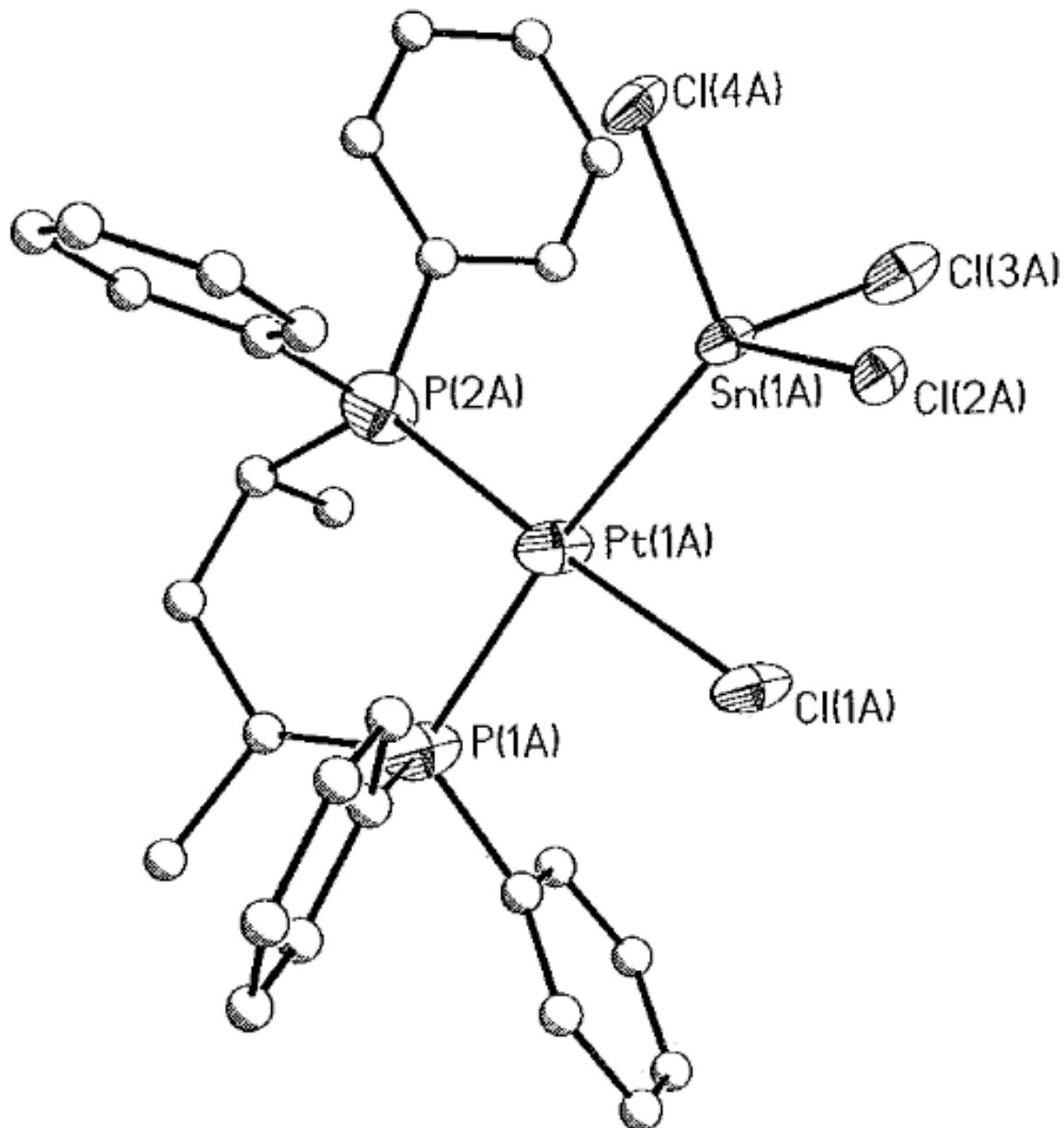
**and 3-phenylpropanal.** Toluene (35.0 mL), 4-methylstyrene (7.0 mL, 53 mmol), 3-phenylpropanal (14 mmol), 2-phenylpropanal (16 mmol), and ((2*S*,4*S*)-BDPP)Pt(SnCl<sub>3</sub>)Cl (48 mg, 0.054 mmol) were added to a 250 mL stainless steel Parr reactor sealed under 1 atm of N<sub>2</sub>. The reactor was pressurized to 600 psi with D<sub>2</sub> followed by 600 psi of CO. After the temperature stabilized at 96 ± 2 °C, (p = 1350 psi), stirring was begun. Two runs were conducted and stopped after 4 h (100% conv.) and 1 h (78% conv.).<sup>8</sup> The products of each experiment were analyzed by GC, low resolution GC/MS, and <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy in 1:1 CH<sub>2</sub>Cl<sub>2</sub>:CD<sub>2</sub>Cl<sub>2</sub>. Average retention times (min) for 4 runs at 150 °C on the chiral  $\alpha$ -cyclodextrin column were: (100 % conv.) 0.90 (*p*-ethyltoluene), 3.2 (2-phenylpropanal), 5.9 (3-phenylpropanal), 6.9 (2-(*p*-tolyl)propanal), and 7.9 (3-(*p*-tolyl)propanal). GC(/MS) retention times (min) for the Restek Rtx-5 (5% diphenyl / 95% dimethyl polysiloxane) column were: 6.72 (2-phenylpropanal), 7.82 (3-phenylpropanal), 8.64 (2-(*p*-tolyl)propanal), and 9.79 (3-(*p*-tolyl)propanal). At 100% conversion, low resolution GC/MS (EI) found for 2-phenylpropanal (C<sub>9</sub>H<sub>10</sub>O) [m/e (intensity)] [M + 2]<sup>+</sup> 136 (0.13), [M + 1]<sup>+</sup> 135 (1.64), [M]<sup>+</sup> 134 (11.70), [M - 29]<sup>+</sup> 105 (100). Found for 3-phenylpropanal (C<sub>9</sub>H<sub>10</sub>O) [M + 2]<sup>+</sup> 136 (0.63), [M + 1]<sup>+</sup> 135 (6.10), [M]<sup>+</sup> 134 (44.78), [M - 1]<sup>+</sup> 133 (7.31), [M - 43]<sup>+</sup> 105 (100). Calculated for (C<sub>9</sub>H<sub>10</sub>O): 136 (0.6), 135 (9.9) 134 (100). Found for 2-(*p*-tolyl)propanal (C<sub>10</sub>H<sub>12</sub>O) [M + 4]<sup>+</sup> 153 (6.59), [M + 3]<sup>+</sup> 152 (10.20), [M + 2]<sup>+</sup> 151 (10.27), [M + 1]<sup>+</sup> 150 (9.07), [M]<sup>+</sup> 149 (4.09), [M - 1]<sup>+</sup> 148 (0.90). Found for 3-(*p*-tolyl)propanal (C<sub>10</sub>H<sub>12</sub>O) [M + 5]<sup>+</sup> 154 (1.94), [M + 4]<sup>+</sup> 153 (17.69), [M + 3]<sup>+</sup> 152 (29.96), [M + 3]<sup>+</sup> 151 (31.06), [M + 2]<sup>+</sup> 150 (27.86), [M + 1]<sup>+</sup> 149 (12.82), [M]<sup>+</sup> 148 (2.28), [M - 42]<sup>+</sup> 107 (100). Calculated for (C<sub>10</sub>H<sub>12</sub>O): 150 (0.7), 149 (11.0), 148 (100).

**X-ray Crystallography of ((2S,4S)-BDPP)Pt(SnCl<sub>3</sub>)Cl (**1**).** A colorless needle-shaped crystal of **1** with dimensions of 0.25 x 0.88 x 0.08 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker SMART ccd area detector<sup>9</sup> mounted on a Bruker Platform goniometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The sample was cooled to 133K. The intensity data, which nominally covered one and a half hemispheres of reciprocal space, were measured as a series of  $2\theta$  oscillation frames each of 0.3 ° for 45 sec / frame. The detector was operated in 512 x 512 mode and was positioned 5.00 cm from the sample. Coverage of unique data was 98.8% complete to 25.00 degrees in  $2\theta$ . Cell parameters were determined from a non-linear least squares fit of 8192 peaks in the range  $3.0 < 2\theta < 25.0$  °. The first 50 frames were repeated at the end of data collection and yielded a total of 377 peaks showing a variation of -0.10% during the data collection. A total of 42876 reflections were measured in the range  $4.70 < 2\theta < 26.58$  °. The data were corrected for absorption by the empirical method<sup>10</sup> giving minimum and maximum transmission factors of 0.537 and 0.894. The data were merged to form a set of 18166 independent reflections with R(int) = 0.1228.

The orthorhombic space group P2(1)2(1)2(1) was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full matrix least-squares methods on F<sup>2</sup>.<sup>11</sup> Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 1025 parameters were refined against 3753 restraints and 18166 reflections to give wR(F<sup>2</sup>) = 0.2040 and S = 0.981 for weights of w = 1/[ $\sigma^2(F^2) + (0.0740 P)^2$ ], where P = [ $F_O^{-2} + 2F_C^{-2}] / 3$ . The final R(F) was 0.0856 for the 8021 observed [F > 4σ(F)] reflections. The largest shift / s.u. was 0.039 in the final refinement

cycle. The final difference map had maxima and minima of 2.868 and -2.666 e / Å<sup>3</sup>, respectively. The absolute structure was determined by refinement of the Flack parameter.<sup>12</sup>

**Comment:** The displacement ellipsoids were drawn at the 50% probability level. There are three formula units per asymmetric unit of the cell. The SnCl<sub>3</sub> group of one molecule was disordered and modeled in two orientations with occupancies of 0.627(5) for the (C) group and 0.373(5) for the (D) group. Because the intensities were so weak, restraints were applied to the positional parameters and displacement parameters of the carbons and the disordered atoms.

**Figure 8.** ORTEP of [2*S*,4*S*-BDDP]Pt(SnCl<sub>3</sub>)Cl (**1**)

**Table 5.** Crystal data and structure refinement for (**1**).

Identification code	n98048	
Empirical formula	C29 H30 Cl4 P2 Pt Sn	
Formula weight	896.05	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.4421(12) Å b = 18.289(2) Å c = 55.173(7) Å	□= 90° □= 90° □= 90°
Volume	9528(2) Å <sup>3</sup>	
Z	12	
Density (calculated)	1.874 Mg/m <sup>3</sup>	
Wavelength	0.71073 Å	
Temperature	133(2) K	
F(000)	5160	
Absorption coefficient	5.642 mm <sup>-1</sup>	
Absorption correction	Empirical	
Max. and min. transmission	0.894 and 0.537	
Theta range for data collection	4.70 to 26.58°.	
Reflections collected	42876	
Independent reflections	18166 [R(int) = 0.1228]	
Data / restraints / parameters	18166 / 3753 / 1025	
wR(F <sup>2</sup> all data)	wR2 = 0.2040	
R(F obsd data)	R1 = 0.0856	
Goodness-of-fit on F <sup>2</sup>	0.981	
Observed data [I > 2s(I)]	8021	
Absolute structure parameter	-0.012(9)	
Largest and mean shift / s.u.	0.039 and 0.001	
Largest diff. peak and hole	2.868 and -2.666 e/Å <sup>3</sup>	

**Table 6.** Atomic coordinates and equivalent isotropic displacement parameters for (**1**). U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Pt(1A)	0.14069(10)	0.87881(7)	0.897318(16)	0.0724(4)
Sn(1A)	0.10031(15)	0.95862(10)	0.85934(2)	0.0471(5)
P(1A)	0.1354(7)	0.7905(5)	0.92720(11)	0.081(3)
P(2A)	0.3769(7)	0.8801(5)	0.89518(14)	0.088(3)
Cl(1A)	-0.1073(6)	0.8857(4)	0.89893(9)	0.076(2)
Cl(2A)	-0.0909(5)	0.9217(3)	0.83437(8)	0.0423(14)
Cl(3A)	0.0382(6)	1.0822(4)	0.86100(10)	0.065(2)
Cl(4A)	0.2752(5)	0.9631(4)	0.82855(10)	0.0584(18)
C(1A)	0.300(4)	0.7053(17)	0.9591(6)	0.126(8)
C(2A)	0.305(3)	0.7792(18)	0.9451(6)	0.120(6)
C(3A)	0.440(3)	0.7840(17)	0.9305(6)	0.119(6)
C(4A)	0.478(4)	0.8599(16)	0.9218(6)	0.119(6)
C(5A)	0.446(4)	0.9225(17)	0.9401(6)	0.121(8)
C(6A)	0.0936(12)	0.7093(17)	0.9126(5)	0.117(6)
C(7A)	0.090(2)	0.7006(17)	0.8876(5)	0.119(6)
C(8A)	0.055(2)	0.6321(16)	0.8785(6)	0.117(6)
C(9A)	0.019(2)	0.5654(18)	0.8889(5)	0.121(6)
C(10A)	0.022(3)	0.5745(18)	0.9140(6)	0.122(6)
C(11A)	0.059(2)	0.6426(16)	0.9233(7)	0.120(6)
C(12A)	-0.011(3)	0.8023(14)	0.9467(5)	0.120(6)
C(13A)	-0.131(3)	0.7584(17)	0.9482(5)	0.119(6)
C(14A)	-0.234(3)	0.7780(16)	0.9650(5)	0.121(6)
C(15A)	-0.208(3)	0.8407(15)	0.9785(5)	0.121(6)
C(16A)	-0.089(3)	0.8853(17)	0.9778(5)	0.124(6)
C(17A)	0.013(3)	0.8636(16)	0.9610(4)	0.124(6)
C(18A)	0.4479(15)	0.9658(10)	0.88576(17)	0.047(3)
C(19A)	0.3759(19)	1.0302(9)	0.8906(3)	0.048(3)
C(20A)	0.4232(17)	1.0990(10)	0.8840(3)	0.049(3)
C(21A)	0.5504(16)	1.1042(10)	0.8714(2)	0.047(3)
C(22A)	0.6247(19)	1.0402(9)	0.8668(3)	0.044(3)
C(23A)	0.5759(17)	0.9714(10)	0.8735(2)	0.046(3)
C(24A)	0.450(4)	0.8115(14)	0.8728(5)	0.130(6)
C(25A)	0.591(4)	0.7916(15)	0.8755(6)	0.131(6)
C(26A)	0.643(4)	0.7411(16)	0.8590(5)	0.134(6)
C(27A)	0.554(3)	0.7142(17)	0.8411(6)	0.135(6)
C(28A)	0.412(4)	0.7307(16)	0.8370(6)	0.133(6)
C(29A)	0.369(4)	0.7811(15)	0.8543(5)	0.131(6)
Pt(1B)	0.15666(10)	0.93779(6)	0.228235(15)	0.0538(3)
Sn(1B)	0.12913(17)	1.00706(10)	0.18740(3)	0.0578(5)

P(1B)	0.1416(6)	0.8640(4)	0.26161(9)	0.0433(15)
P(2B)	0.3947(6)	0.9395(3)	0.22955(10)	0.0440(16)
Cl(1B)	-0.0913(7)	0.9426(5)	0.22619(12)	0.089(3)
Cl(2B)	-0.0538(6)	0.9667(4)	0.16166(11)	0.0637(19)
Cl(3B)	0.0687(8)	1.1296(4)	0.18936(10)	0.081(2)
Cl(4B)	0.3026(7)	1.0119(5)	0.15625(10)	0.082(2)
C(1B)	0.256(2)	0.8349(12)	0.3076(4)	0.062(5)
C(2B)	0.275(2)	0.8856(13)	0.2852(4)	0.060(4)
C(3B)	0.427(2)	0.8818(12)	0.2766(4)	0.059(4)
C(4B)	0.474(2)	0.9465(10)	0.2614(4)	0.058(4)
C(5B)	0.431(3)	1.0219(11)	0.2722(4)	0.063(5)
C(6B)	0.144(2)	0.7789(17)	0.2515(5)	0.118(6)
C(7B)	0.075(3)	0.7497(18)	0.2314(5)	0.125(6)
C(8B)	0.067(3)	0.6804(17)	0.2211(6)	0.127(6)
C(9B)	0.148(3)	0.6289(19)	0.2335(5)	0.125(6)
C(10B)	0.222(3)	0.6495(17)	0.2541(5)	0.121(6)
C(11B)	0.217(3)	0.7215(16)	0.2619(6)	0.119(6)
C(12B)	-0.0128(18)	0.8722(10)	0.2799(2)	0.060(4)
C(13B)	-0.1030(18)	0.8148(12)	0.2858(3)	0.061(4)
C(14B)	-0.221(2)	0.8267(12)	0.3003(3)	0.064(4)
C(15B)	-0.253(2)	0.8954(10)	0.3095(3)	0.063(4)
C(16B)	-0.1634(18)	0.9526(12)	0.3035(3)	0.064(4)
C(17B)	-0.046(2)	0.9412(12)	0.2888(3)	0.063(4)
C(18B)	0.4701(14)	1.0157(10)	0.2134(2)	0.041(3)
C(19B)	0.4105(18)	1.0848(8)	0.2153(3)	0.042(3)
C(20B)	0.4696(16)	1.1431(11)	0.2027(3)	0.046(3)
C(21B)	0.5882(16)	1.1341(10)	0.1880(3)	0.050(3)
C(22B)	0.644(2)	1.0640(9)	0.1867(3)	0.051(3)
C(23B)	0.5887(16)	1.0043(11)	0.1990(2)	0.046(3)
C(24B)	0.470(3)	0.8575(17)	0.2185(4)	0.131(6)
C(25B)	0.598(3)	0.8285(16)	0.2260(5)	0.129(6)
C(26B)	0.655(4)	0.7637(16)	0.2170(5)	0.130(6)
C(27B)	0.584(3)	0.7235(18)	0.1994(5)	0.134(6)
C(28B)	0.457(3)	0.7549(18)	0.1925(6)	0.136(6)
C(29B)	0.395(4)	0.8192(16)	0.2009(5)	0.135(6)
Pt(1C)	0.58700(9)	0.62792(7)	0.445159(16)	0.0632(4)
Sn(1C)	0.5885(3)	0.53380(19)	0.48144(5)	0.0340(8)
Sn(1D)	0.5542(5)	0.5750(3)	0.48790(8)	0.0339(12)
P(1C)	0.5596(5)	0.7020(4)	0.41155(9)	0.0488(18)
P(2C)	0.8232(6)	0.6229(4)	0.44170(9)	0.0522(19)
Cl(1C)	0.3441(6)	0.6312(5)	0.45286(10)	0.079(2)
Cl(2C)	0.5182(14)	0.5869(8)	0.5180(2)	0.124(5)
Cl(3C)	0.4195(11)	0.4431(6)	0.4783(2)	0.078(3)
Cl(4C)	0.7711(10)	0.4579(6)	0.49662(19)	0.072(3)
Cl(2D)	0.4430(19)	0.6305(11)	0.5215(3)	0.111(5)
Cl(3D)	0.4048(16)	0.4731(8)	0.4847(3)	0.063(4)

Cl(4D)	0.7369(14)	0.5161(9)	0.5100(3)	0.064(4)
C(1C)	0.677(2)	0.7184(12)	0.3634(3)	0.047(5)
C(2C)	0.7047(18)	0.6861(12)	0.3891(3)	0.041(3)
C(3C)	0.8531(18)	0.7023(12)	0.3981(3)	0.042(3)
C(4C)	0.8875(18)	0.7031(12)	0.4249(3)	0.042(3)
C(5C)	1.0496(17)	0.7173(12)	0.4269(4)	0.045(5)
C(6C)	0.5422(15)	0.7927(11)	0.41864(15)	0.045(3)
C(7C)	0.647(2)	0.8442(9)	0.4142(2)	0.046(3)
C(8C)	0.6212(19)	0.9163(10)	0.4207(3)	0.048(3)
C(9C)	0.4985(16)	0.9430(11)	0.4316(2)	0.052(3)
C(10C)	0.398(2)	0.8888(9)	0.4356(3)	0.049(3)
C(11C)	0.4167(19)	0.8162(10)	0.4292(2)	0.048(3)
C(12C)	0.4035(16)	0.6798(8)	0.3923(2)	0.044(3)
C(13C)	0.3365(15)	0.7341(10)	0.3791(2)	0.043(3)
C(14C)	0.2200(16)	0.7158(10)	0.3650(3)	0.041(3)
C(15C)	0.1760(18)	0.6439(8)	0.3644(3)	0.041(3)
C(16C)	0.2420(16)	0.5895(10)	0.3777(3)	0.043(3)
C(17C)	0.3584(16)	0.6077(9)	0.3919(3)	0.043(3)
C(18C)	0.890(3)	0.5386(10)	0.4254(2)	0.126(6)
C(19C)	0.795(2)	0.4872(15)	0.4163(4)	0.129(6)
C(20C)	0.846(3)	0.4255(13)	0.4044(4)	0.131(6)
C(21C)	0.991(3)	0.4152(11)	0.4015(3)	0.130(6)
C(22C)	1.085(2)	0.4666(15)	0.4106(4)	0.128(6)
C(23C)	1.035(3)	0.5283(12)	0.4225(4)	0.126(6)
C(24C)	0.9166(17)	0.6372(9)	0.4707(4)	0.070(4)
C(25C)	1.0251(19)	0.5913(12)	0.4782(4)	0.072(4)
C(26C)	1.094(2)	0.6037(12)	0.5002(3)	0.073(4)
C(27C)	1.046(2)	0.6636(10)	0.5133(4)	0.074(4)
C(28C)	0.938(2)	0.7112(12)	0.5071(4)	0.074(4)
C(29C)	0.875(2)	0.6959(11)	0.4850(3)	0.073(4)

**Table 7.** Bond lengths [Å] and angles [°] for (1).

Pt(1A)-P(2A)	2.234(7)	Pt(1B)-Cl(1B)	2.345(6)
Pt(1A)-P(1A)	2.309(7)	Pt(1B)-Sn(1B)	2.5976(16)
Pt(1A)-Cl(1A)	2.347(6)	Sn(1B)-Cl(3B)	2.315(8)
Pt(1A)-Sn(1A)	2.5821(18)	Sn(1B)-Cl(2B)	2.355(6)
Sn(1A)-Cl(3A)	2.336(8)	Sn(1B)-Cl(4B)	2.376(6)
Sn(1A)-Cl(2A)	2.369(5)	P(1B)-C(6B)	1.65(3)
Sn(1A)-Cl(4A)	2.370(6)	P(1B)-C(12B)	1.78(2)
P(1A)-C(6A)	1.74(3)	P(1B)-C(2B)	1.85(2)
P(1A)-C(12A)	1.77(4)	P(2B)-C(24B)	1.77(4)
P(1A)-C(2A)	1.89(3)	P(2B)-C(18B)	1.802(19)
P(2A)-C(18A)	1.78(2)	P(2B)-C(4B)	1.91(2)
P(2A)-C(4A)	1.79(3)	C(1B)-C(2B)	1.557(14)
P(2A)-C(24A)	1.89(4)	C(2B)-C(3B)	1.513(13)
C(1A)-C(2A)	1.559(14)	C(3B)-C(4B)	1.515(13)
C(2A)-C(3A)	1.513(13)	C(4B)-C(5B)	1.556(14)
C(3A)-C(4A)	1.513(14)	C(6B)-C(11B)	1.385(7)
C(4A)-C(5A)	1.557(14)	C(6B)-C(7B)	1.393(7)
C(6A)-C(7A)	1.387(7)	C(7B)-C(8B)	1.393(7)
C(6A)-C(11A)	1.394(7)	C(8B)-C(9B)	1.393(7)
C(7A)-C(8A)	1.391(7)	C(9B)-C(10B)	1.388(7)
C(8A)-C(9A)	1.388(7)	C(10B)-C(11B)	1.387(7)
C(9A)-C(10A)	1.394(7)	C(12B)-C(17B)	1.389(7)
C(10A)-C(11A)	1.392(7)	C(12B)-C(13B)	1.391(7)
C(12A)-C(13A)	1.388(7)	C(13B)-C(14B)	1.390(7)
C(12A)-C(17A)	1.388(7)	C(14B)-C(15B)	1.389(7)
C(13A)-C(14A)	1.394(7)	C(15B)-C(16B)	1.388(7)
C(14A)-C(15A)	1.390(7)	C(16B)-C(17B)	1.390(7)
C(15A)-C(16A)	1.385(7)	C(18B)-C(19B)	1.388(7)
C(16A)-C(17A)	1.393(7)	C(18B)-C(23B)	1.388(7)
C(18A)-C(19A)	1.386(7)	C(19B)-C(20B)	1.391(7)
C(18A)-C(23A)	1.389(7)	C(20B)-C(21B)	1.390(7)
C(19A)-C(20A)	1.384(7)	C(21B)-C(22B)	1.389(7)
C(20A)-C(21A)	1.390(7)	C(22B)-C(23B)	1.387(7)
C(21A)-C(22A)	1.388(7)	C(24B)-C(25B)	1.389(7)
C(22A)-C(23A)	1.390(7)	C(24B)-C(29B)	1.390(7)
C(24A)-C(25A)	1.389(7)	C(25B)-C(26B)	1.392(7)
C(24A)-C(29A)	1.390(7)	C(26B)-C(27B)	1.388(7)
C(25A)-C(26A)	1.390(7)	C(27B)-C(28B)	1.391(7)
C(26A)-C(27A)	1.390(7)	C(28B)-C(29B)	1.393(7)
C(27A)-C(28A)	1.389(7)	Pt(1C)-P(2C)	2.240(6)
C(28A)-C(29A)	1.387(7)	Pt(1C)-P(1C)	2.311(6)
Pt(1B)-P(2B)	2.249(6)	Pt(1C)-Cl(1C)	2.334(6)
Pt(1B)-P(1B)	2.287(5)	Pt(1C)-Sn(1D)	2.567(4)

Pt(1C)-Sn(1C)	2.640(3)	C(9C)-C(10C)	1.388(7)
Sn(1C)-Cl(3C)	2.309(10)	C(10C)-C(11C)	1.385(7)
Sn(1C)-Cl(2C)	2.337(11)	C(12C)-C(17C)	1.386(7)
Sn(1C)-Cl(4C)	2.366(9)	C(12C)-C(13C)	1.386(7)
Sn(1D)-Cl(3D)	2.345(13)	C(13C)-C(14C)	1.389(7)
Sn(1D)-Cl(2D)	2.358(14)	C(14C)-C(15C)	1.379(7)
Sn(1D)-Cl(4D)	2.372(12)	C(15C)-C(16C)	1.384(7)
P(1C)-C(6C)	1.71(2)	C(16C)-C(17C)	1.391(7)
P(1C)-C(12C)	1.861(19)	C(18C)-C(19C)	1.3900
P(1C)-C(2C)	1.869(19)	C(18C)-C(23C)	1.3900
P(2C)-C(24C)	1.84(2)	C(19C)-C(20C)	1.3900
P(2C)-C(4C)	1.84(2)	C(20C)-C(21C)	1.3900
P(2C)-C(18C)	1.89(2)	C(21C)-C(22C)	1.3900
C(1C)-C(2C)	1.559(14)	C(22C)-C(23C)	1.3900
C(2C)-C(3C)	1.516(13)	C(24C)-C(29C)	1.388(7)
C(3C)-C(4C)	1.511(13)	C(24C)-C(25C)	1.389(7)
C(4C)-C(5C)	1.557(14)	C(25C)-C(26C)	1.392(7)
C(6C)-C(7C)	1.388(7)	C(26C)-C(27C)	1.386(7)
C(6C)-C(11C)	1.389(7)	C(27C)-C(28C)	1.384(7)
C(7C)-C(8C)	1.388(7)	C(28C)-C(29C)	1.389(7)
C(8C)-C(9C)	1.394(7)		
P(2A)-Pt(1A)-P(1A)	93.8(3)	C(3A)-C(2A)-C(1A)	110(3)
P(2A)-Pt(1A)-Cl(1A)	176.2(3)	C(3A)-C(2A)-P(1A)	116(2)
P(1A)-Pt(1A)-Cl(1A)	89.4(2)	C(1A)-C(2A)-P(1A)	109(2)
P(2A)-Pt(1A)-Sn(1A)	95.7(2)	C(4A)-C(3A)-C(2A)	115(3)
P(1A)-Pt(1A)-Sn(1A)	166.39(19)	C(3A)-C(4A)-C(5A)	115(3)
Cl(1A)-Pt(1A)-Sn(1A)	81.55(15)	C(3A)-C(4A)-P(2A)	109(2)
Cl(3A)-Sn(1A)-Cl(2A)	96.2(2)	C(5A)-C(4A)-P(2A)	106(2)
Cl(3A)-Sn(1A)-Cl(4A)	99.8(2)	C(7A)-C(6A)-C(11A)	108(3)
Cl(2A)-Sn(1A)-Cl(4A)	97.13(19)	C(7A)-C(6A)-P(1A)	124(3)
Cl(3A)-Sn(1A)-Pt(1A)	123.50(15)	C(11A)-C(6A)-P(1A)	127(2)
Cl(2A)-Sn(1A)-Pt(1A)	115.03(15)	C(6A)-C(7A)-C(8A)	118(3)
Cl(4A)-Sn(1A)-Pt(1A)	119.87(16)	C(9A)-C(8A)-C(7A)	134(3)
C(6A)-P(1A)-C(12A)	102.0(13)	C(8A)-C(9A)-C(10A)	107(3)
C(6A)-P(1A)-C(2A)	109.9(12)	C(11A)-C(10A)-C(9A)	119(4)
C(12A)-P(1A)-C(2A)	111.0(11)	C(10A)-C(11A)-C(6A)	133(4)
C(6A)-P(1A)-Pt(1A)	105.8(10)	C(13A)-C(12A)-C(17A)	124(4)
C(12A)-P(1A)-Pt(1A)	111.5(5)	C(13A)-C(12A)-P(1A)	127(3)
C(2A)-P(1A)-Pt(1A)	115.5(10)	C(17A)-C(12A)-P(1A)	109(2)
C(18A)-P(2A)-C(4A)	102.7(11)	C(12A)-C(13A)-C(14A)	118(4)
C(18A)-P(2A)-C(24A)	104.9(7)	C(15A)-C(14A)-C(13A)	116(4)
C(4A)-P(2A)-C(24A)	101.8(14)	C(16A)-C(15A)-C(14A)	128(4)
C(18A)-P(2A)-Pt(1A)	113.6(6)	C(15A)-C(16A)-C(17A)	114(4)
C(4A)-P(2A)-Pt(1A)	119.2(12)	C(12A)-C(17A)-C(16A)	120(4)
C(24A)-P(2A)-Pt(1A)	112.9(10)	C(19A)-C(18A)-C(23A)	117.1(19)

C(19A)-C(18A)-P(2A)	120.5(13)	C(11B)-C(6B)-C(7B)	106(3)
C(23A)-C(18A)-P(2A)	122.4(14)	C(11B)-C(6B)-P(1B)	126(3)
C(20A)-C(19A)-C(18A)	124(2)	C(7B)-C(6B)-P(1B)	129(3)
C(19A)-C(20A)-C(21A)	118.2(19)	C(6B)-C(7B)-C(8B)	134(4)
C(22A)-C(21A)-C(20A)	118.1(19)	C(9B)-C(8B)-C(7B)	113(3)
C(21A)-C(22A)-C(23A)	123(2)	C(10B)-C(9B)-C(8B)	120(3)
C(18A)-C(23A)-C(22A)	119.1(19)	C(11B)-C(10B)-C(9B)	120(4)
C(25A)-C(24A)-C(29A)	120(4)	C(6B)-C(11B)-C(10B)	127(4)
C(25A)-C(24A)-P(2A)	117(3)	C(17B)-C(12B)-C(13B)	118(2)
C(29A)-C(24A)-P(2A)	123(3)	C(17B)-C(12B)-P(1B)	117.4(15)
C(24A)-C(25A)-C(26A)	116(4)	C(13B)-C(12B)-P(1B)	124.8(16)
C(25A)-C(26A)-C(27A)	119(4)	C(12B)-C(13B)-C(14B)	120(2)
C(28A)-C(27A)-C(26A)	129(4)	C(15B)-C(14B)-C(13B)	122(2)
C(29A)-C(28A)-C(27A)	108(4)	C(16B)-C(15B)-C(14B)	117(2)
C(28A)-C(29A)-C(24A)	128(4)	C(15B)-C(16B)-C(17B)	121(2)
P(2B)-Pt(1B)-P(1B)	92.6(2)	C(12B)-C(17B)-C(16B)	121(2)
P(2B)-Pt(1B)-Cl(1B)	176.9(2)	C(19B)-C(18B)-C(23B)	120.6(18)
P(1B)-Pt(1B)-Cl(1B)	90.0(2)	C(19B)-C(18B)-P(2B)	120.4(12)
P(2B)-Pt(1B)-Sn(1B)	96.95(15)	C(23B)-C(18B)-P(2B)	119.0(13)
P(1B)-Pt(1B)-Sn(1B)	168.43(15)	C(18B)-C(19B)-C(20B)	119.8(19)
Cl(1B)-Pt(1B)-Sn(1B)	80.79(15)	C(21B)-C(20B)-C(19B)	121.5(19)
Cl(3B)-Sn(1B)-Cl(2B)	98.7(2)	C(22B)-C(21B)-C(20B)	116.5(19)
Cl(3B)-Sn(1B)-Cl(4B)	99.6(3)	C(23B)-C(22B)-C(21B)	124(2)
Cl(2B)-Sn(1B)-Cl(4B)	94.6(2)	C(22B)-C(23B)-C(18B)	117.6(19)
Cl(3B)-Sn(1B)-Pt(1B)	117.15(16)	C(25B)-C(24B)-C(29B)	118(4)
Cl(2B)-Sn(1B)-Pt(1B)	116.33(16)	C(25B)-C(24B)-P(2B)	125(3)
Cl(4B)-Sn(1B)-Pt(1B)	125.2(2)	C(29B)-C(24B)-P(2B)	118(3)
C(6B)-P(1B)-C(12B)	106.3(7)	C(24B)-C(25B)-C(26B)	124(4)
C(6B)-P(1B)-C(2B)	115.4(13)	C(27B)-C(26B)-C(25B)	121(4)
C(12B)-P(1B)-C(2B)	98.0(7)	C(26B)-C(27B)-C(28B)	113(4)
C(6B)-P(1B)-Pt(1B)	106.5(8)	C(27B)-C(28B)-C(29B)	128(4)
C(12B)-P(1B)-Pt(1B)	117.3(5)	C(24B)-C(29B)-C(28B)	116(4)
C(2B)-P(1B)-Pt(1B)	113.4(7)	P(2C)-Pt(1C)-P(1C)	93.8(2)
C(24B)-P(2B)-C(18B)	109.0(6)	P(2C)-Pt(1C)-Cl(1C)	174.34(19)
C(24B)-P(2B)-C(4B)	102.6(12)	P(1C)-Pt(1C)-Cl(1C)	91.2(2)
C(18B)-P(2B)-C(4B)	104.5(7)	P(2C)-Pt(1C)-Sn(1D)	100.55(17)
C(24B)-P(2B)-Pt(1B)	112.2(10)	P(1C)-Pt(1C)-Sn(1D)	160.8(2)
C(18B)-P(2B)-Pt(1B)	113.0(4)	Cl(1C)-Pt(1C)-Sn(1D)	73.97(17)
C(4B)-P(2B)-Pt(1B)	114.8(7)	P(2C)-Pt(1C)-Sn(1C)	91.87(16)
C(3B)-C(2B)-C(1B)	109.2(18)	P(1C)-Pt(1C)-Sn(1C)	172.38(16)
C(3B)-C(2B)-P(1B)	114.5(15)	Cl(1C)-Pt(1C)-Sn(1C)	83.35(17)
C(1B)-C(2B)-P(1B)	110.8(15)	Sn(1D)-Pt(1C)-Sn(1C)	19.73(10)
C(2B)-C(3B)-C(4B)	114.4(18)	Cl(3C)-Sn(1C)-Cl(2C)	99.6(4)
C(3B)-C(4B)-C(5B)	113.9(18)	Cl(3C)-Sn(1C)-Cl(4C)	96.2(4)
C(3B)-C(4B)-P(2B)	110.0(15)	Cl(2C)-Sn(1C)-Cl(4C)	98.3(4)
C(5B)-C(4B)-P(2B)	108.1(14)	Cl(3C)-Sn(1C)-Pt(1C)	114.1(3)

Cl(2C)-Sn(1C)-Pt(1C)	112.5(4)	C(18C)-C(19C)-C(20C)	120.0
Cl(4C)-Sn(1C)-Pt(1C)	130.9(3)	C(19C)-C(20C)-C(21C)	120.0
Cl(3D)-Sn(1D)-Cl(2D)	97.6(6)	C(20C)-C(21C)-C(22C)	120.0
Cl(3D)-Sn(1D)-Cl(4D)	96.6(5)	C(23C)-C(22C)-C(21C)	120.0
Cl(2D)-Sn(1D)-Cl(4D)	96.6(5)	C(22C)-C(23C)-C(18C)	120.0
Cl(3D)-Sn(1D)-Pt(1C)	107.7(5)	C(29C)-C(24C)-C(25C)	120(2)
Cl(2D)-Sn(1D)-Pt(1C)	127.8(6)	C(29C)-C(24C)-P(2C)	117.9(16)
Cl(4D)-Sn(1D)-Pt(1C)	123.7(4)	C(25C)-C(24C)-P(2C)	121.8(17)
C(6C)-P(1C)-C(12C)	105.4(6)	C(24C)-C(25C)-C(26C)	120(2)
C(6C)-P(1C)-C(2C)	111.9(9)	C(27C)-C(26C)-C(25C)	116(2)
C(12C)-P(1C)-C(2C)	99.7(6)	C(28C)-C(27C)-C(26C)	127(3)
C(6C)-P(1C)-Pt(1C)	113.3(3)	C(27C)-C(28C)-C(29C)	114(2)
C(12C)-P(1C)-Pt(1C)	114.7(5)	C(24C)-C(29C)-C(28C)	122(2)
C(2C)-P(1C)-Pt(1C)	111.0(6)	—	—
C(24C)-P(2C)-C(4C)	99.6(6)	—	—
C(24C)-P(2C)-C(18C)	111.6(9)	—	—
C(4C)-P(2C)-C(18C)	107.4(8)	—	—
C(24C)-P(2C)-Pt(1C)	113.3(5)	—	—
C(4C)-P(2C)-Pt(1C)	109.8(6)	—	—
C(18C)-P(2C)-Pt(1C)	113.9(9)	—	—
C(3C)-C(2C)-C(1C)	112.4(15)	—	—
C(3C)-C(2C)-P(1C)	115.5(12)	—	—
C(1C)-C(2C)-P(1C)	114.8(13)	—	—
C(4C)-C(3C)-C(2C)	121.3(15)	—	—
C(3C)-C(4C)-C(5C)	106.5(15)	—	—
C(3C)-C(4C)-P(2C)	114.5(14)	—	—
C(5C)-C(4C)-P(2C)	114.8(13)	—	—
C(7C)-C(6C)-C(11C)	118(2)	—	—
C(7C)-C(6C)-P(1C)	123.3(14)	—	—
C(11C)-C(6C)-P(1C)	118.5(14)	—	—
C(8C)-C(7C)-C(6C)	118(2)	—	—
C(7C)-C(8C)-C(9C)	126(2)	—	—
C(10C)-C(9C)-C(8C)	113(2)	—	—
C(11C)-C(10C)-C(9C)	124(2)	—	—
C(10C)-C(11C)-C(6C)	121(2)	—	—
C(17C)-C(12C)-C(13C)	122.2(18)	—	—
C(17C)-C(12C)-P(1C)	117.4(13)	—	—
C(13C)-C(12C)-P(1C)	120.4(12)	—	—
C(12C)-C(13C)-C(14C)	118.9(18)	—	—
C(15C)-C(14C)-C(13C)	118.8(19)	—	—
C(14C)-C(15C)-C(16C)	122.5(19)	—	—
C(15C)-C(16C)-C(17C)	118.9(18)	—	—
C(12C)-C(17C)-C(16C)	118.7(18)	—	—
C(19C)-C(18C)-C(23C)	120.0	—	—
C(19C)-C(18C)-P(2C)	120.5(17)	—	—
C(23C)-C(18C)-P(2C)	119.5(17)	—	—

**Table 8.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for (1). The anisotropic displacement factor exponent takes the form:  $-2 p^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Pt(1A)	44(1)	137(1)	36(1)	25(1)	-24(1)	-37(1)
Sn(1A)	27(1)	91(1)	23(1)	2(1)	-5(1)	-12(1)
P(1A)	49(5)	158(8)	37(4)	29(5)	-20(3)	-30(5)
P(2A)	52(5)	118(7)	94(6)	31(6)	-45(4)	-36(5)
Cl(1A)	47(4)	150(7)	30(3)	20(4)	-11(3)	-43(4)
Cl(2A)	32(3)	70(4)	25(3)	-4(3)	-10(2)	-3(3)
Cl(3A)	42(3)	109(6)	44(3)	-31(4)	3(3)	-26(3)
Cl(4A)	28(3)	99(5)	48(4)	-5(4)	6(2)	-3(3)
C(1A)	124(9)	129(9)	126(9)	3(5)	-3(5)	-1(5)
C(2A)	119(7)	123(7)	119(7)	3(4)	-4(4)	1(4)
C(3A)	117(7)	122(7)	118(7)	3(4)	-4(4)	0(4)
C(4A)	117(7)	122(7)	119(7)	2(4)	-5(4)	0(4)
C(5A)	119(9)	126(9)	119(9)	4(5)	-6(5)	-1(5)
C(6A)	118(6)	118(6)	116(6)	0(4)	2(4)	-2(4)
C(7A)	120(6)	120(6)	117(6)	1(4)	0(4)	-2(4)
C(8A)	118(6)	119(7)	116(6)	-1(4)	0(4)	-2(4)
C(9A)	122(6)	123(7)	119(6)	-2(4)	-2(4)	1(4)
C(10A)	123(6)	124(7)	120(6)	0(4)	-1(4)	1(4)
C(11A)	121(6)	120(7)	119(6)	0(4)	0(4)	1(4)
C(12A)	122(7)	121(7)	118(7)	1(4)	0(4)	2(4)
C(13A)	118(7)	122(7)	117(7)	0(4)	0(4)	2(4)
C(14A)	120(7)	124(7)	120(7)	0(4)	-1(4)	3(4)
C(15A)	120(7)	123(7)	119(7)	1(4)	0(4)	3(4)
C(16A)	124(7)	125(7)	122(7)	1(4)	2(4)	3(4)
C(17A)	125(7)	124(7)	122(7)	1(4)	2(4)	1(4)
C(18A)	45(4)	51(5)	45(4)	-5(4)	-7(4)	-3(4)
C(19A)	45(4)	53(5)	46(4)	-4(4)	-3(4)	-3(4)
C(20A)	46(4)	52(5)	48(4)	-6(4)	-3(4)	-3(4)
C(21A)	46(4)	49(5)	45(4)	-5(4)	-3(4)	-3(4)
C(22A)	43(4)	48(5)	42(4)	-6(4)	-5(4)	-1(4)
C(23A)	43(4)	50(5)	45(4)	-5(4)	-7(4)	-1(4)
C(24A)	129(7)	130(7)	131(7)	-1(4)	-1(4)	-1(4)
C(25A)	129(7)	131(7)	133(7)	-2(4)	-2(4)	0(4)
C(26A)	132(7)	133(7)	136(7)	-3(4)	-3(4)	0(4)
C(27A)	134(7)	134(7)	138(7)	-4(4)	-2(4)	0(4)
C(28A)	132(7)	133(7)	136(7)	-3(4)	-1(4)	0(4)
C(29A)	130(7)	131(7)	132(7)	-3(4)	0(4)	-2(4)
Pt(1B)	38(1)	95(1)	29(1)	26(1)	-15(1)	-25(1)

Sn(1B)	48(1)	97(2)	29(1)	27(1)	-18(1)	-32(1)
P(1B)	44(3)	59(4)	27(3)	10(3)	-13(3)	-13(3)
P(2B)	40(4)	59(4)	33(3)	-4(3)	-18(3)	-5(3)
Cl(1B)	44(4)	159(7)	64(4)	66(5)	-16(3)	-41(4)
Cl(2B)	60(4)	75(5)	56(4)	16(4)	-32(3)	-13(3)
Cl(3B)	99(5)	102(6)	42(3)	12(4)	-28(3)	-41(5)
Cl(4B)	72(5)	146(7)	28(3)	6(4)	0(3)	-47(5)
C(1B)	62(7)	66(7)	58(7)	2(5)	-5(5)	0(5)
C(2B)	60(5)	62(5)	58(5)	-1(4)	-6(4)	0(4)
C(3B)	59(5)	61(5)	58(5)	1(4)	-6(4)	0(4)
C(4B)	57(5)	61(5)	57(5)	1(4)	-7(4)	0(4)
C(5B)	62(7)	66(7)	59(6)	-3(5)	-7(5)	-3(5)
C(6B)	120(7)	119(7)	116(7)	-1(4)	-3(4)	0(4)
C(7B)	128(7)	123(7)	125(7)	0(4)	-4(4)	2(4)
C(8B)	129(7)	125(7)	126(7)	-2(4)	-4(4)	2(4)
C(9B)	127(7)	123(7)	124(7)	-1(4)	-4(4)	2(4)
C(10B)	123(7)	121(7)	120(7)	0(4)	-5(4)	2(4)
C(11B)	121(7)	120(7)	117(7)	-2(4)	-4(4)	1(4)
C(12B)	59(5)	61(5)	60(5)	1(4)	0(4)	-1(4)
C(13B)	58(5)	64(5)	62(5)	2(4)	0(4)	0(4)
C(14B)	61(5)	65(5)	65(5)	1(4)	0(4)	-2(4)
C(15B)	60(5)	65(5)	64(5)	-1(4)	-2(4)	-1(4)
C(16B)	63(5)	65(5)	64(5)	-2(4)	0(4)	-1(4)
C(17B)	62(5)	64(5)	62(5)	-1(4)	0(4)	-1(4)
C(18B)	40(4)	45(4)	37(4)	1(4)	-2(3)	-3(4)
C(19B)	41(4)	47(4)	38(4)	2(4)	-1(4)	-2(4)
C(20B)	45(4)	50(4)	45(4)	1(4)	0(4)	-2(4)
C(21B)	49(4)	54(4)	48(4)	0(4)	-1(4)	-3(4)
C(22B)	48(4)	55(4)	49(4)	0(4)	-2(4)	-2(4)
C(23B)	45(4)	50(4)	44(4)	-2(4)	-1(4)	-3(4)
C(24B)	129(7)	131(7)	132(7)	-4(4)	-4(4)	2(4)
C(25B)	128(7)	129(7)	131(7)	-2(4)	-3(4)	2(4)
C(26B)	129(7)	130(7)	132(7)	-3(4)	-3(4)	1(4)
C(27B)	133(7)	133(7)	137(7)	-4(4)	-4(4)	3(4)
C(28B)	135(7)	135(7)	139(7)	-5(4)	-5(4)	3(4)
C(29B)	134(7)	134(7)	137(7)	-6(4)	-5(4)	4(4)
Pt(1C)	25(1)	128(1)	37(1)	31(1)	-9(1)	-29(1)
Sn(1C)	34(1)	40(2)	29(1)	-1(1)	-4(1)	11(1)
Sn(1D)	36(2)	41(3)	25(2)	5(2)	1(2)	-1(2)
P(1C)	19(3)	100(6)	27(3)	16(3)	-5(2)	-12(3)
P(2C)	31(3)	97(6)	28(3)	24(4)	-12(2)	-20(4)
Cl(1C)	21(3)	171(7)	46(3)	38(4)	-8(3)	-28(4)
Cl(2C)	132(5)	127(5)	113(5)	-2(3)	-7(3)	16(3)
Cl(3C)	77(4)	77(4)	80(4)	12(3)	0(3)	-7(3)
Cl(4C)	67(4)	71(4)	77(4)	12(3)	-4(3)	3(3)
Cl(2D)	113(6)	114(6)	106(6)	-1(3)	-2(3)	6(3)

Cl(3D)	66(5)	62(5)	61(5)	-1(3)	3(3)	-4(3)
Cl(4D)	63(5)	66(5)	62(5)	5(3)	0(3)	3(3)
C(1C)	47(6)	53(6)	42(6)	0(5)	1(5)	3(5)
C(2C)	39(5)	46(5)	39(5)	3(4)	3(4)	-1(4)
C(3C)	38(4)	45(5)	42(4)	4(4)	3(4)	-1(4)
C(4C)	36(5)	45(5)	44(5)	5(4)	1(4)	-2(4)
C(5C)	42(6)	48(6)	46(6)	0(5)	4(5)	1(5)
C(6C)	45(4)	51(5)	39(4)	4(4)	-1(4)	-1(4)
C(7C)	46(4)	51(5)	41(4)	2(4)	0(4)	1(4)
C(8C)	49(4)	52(5)	44(4)	2(4)	-1(4)	1(4)
C(9C)	53(4)	56(5)	46(4)	2(4)	-1(4)	2(4)
C(10C)	51(4)	54(5)	44(4)	3(4)	0(4)	1(4)
C(11C)	49(4)	53(5)	43(4)	4(4)	-1(4)	-1(4)
C(12C)	42(4)	49(4)	39(4)	1(4)	-1(4)	1(4)
C(13C)	41(4)	48(4)	38(4)	1(4)	-1(4)	-1(4)
C(14C)	39(4)	47(4)	38(4)	4(4)	-2(3)	-2(4)
C(15C)	37(4)	47(4)	38(4)	-1(4)	-3(3)	-2(4)
C(16C)	40(4)	47(4)	41(4)	0(4)	-5(3)	-1(4)
C(17C)	41(4)	49(4)	39(4)	0(4)	-3(3)	1(4)
C(18C)	124(7)	124(7)	129(7)	-1(4)	-3(4)	0(4)
C(19C)	129(7)	129(7)	130(7)	-2(4)	-3(4)	2(4)
C(20C)	130(7)	130(7)	132(7)	-4(4)	-2(4)	3(4)
C(21C)	130(7)	130(7)	132(7)	-2(4)	-2(4)	1(4)
C(22C)	128(7)	128(7)	129(7)	-1(4)	-1(4)	1(4)
C(23C)	125(7)	125(7)	127(7)	-2(4)	-1(4)	1(4)
C(24C)	69(5)	74(5)	68(5)	2(4)	-5(4)	-2(4)
C(25C)	71(5)	77(5)	68(5)	3(4)	-4(4)	-2(4)
C(26C)	72(5)	78(5)	70(5)	2(4)	-3(4)	-3(4)
C(27C)	75(5)	78(5)	71(5)	1(4)	-4(4)	-3(4)
C(28C)	75(5)	78(5)	70(5)	0(4)	-4(4)	-5(4)
C(29C)	72(5)	77(5)	70(5)	2(4)	-7(4)	-3(4)

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**Table 9.** Hydrogen coordinates and isotropic displacement parameters for (**1**).

	x	y	z	U(eq)
H(1AA)	0.3769	0.7034	0.9711	0.189
H(1AB)	0.3119	0.6653	0.9474	0.189
H(1AC)	0.2089	0.7002	0.9674	0.189
H(2A)	0.3075	0.8192	0.9574	0.144
H(3AA)	0.5191	0.7653	0.9406	0.143
H(3AB)	0.4317	0.7515	0.9162	0.143
H(4A)	0.5813	0.8611	0.9175	0.143
H(5AA)	0.4719	0.9080	0.9566	0.182
H(5AB)	0.3458	0.9356	0.9395	0.182
H(5AC)	0.5036	0.9648	0.9352	0.182
H(7A)	0.1109	0.7403	0.8771	0.143
H(8A)	0.0552	0.6306	0.8613	0.141
H(9A)	-0.0025	0.5216	0.8805	0.145
H(10A)	-0.0010	0.5351	0.9245	0.147
H(11A)	0.0620	0.6438	0.9406	0.144
H(13A)	-0.1417	0.7166	0.9382	0.143
H(14A)	-0.3182	0.7500	0.9672	0.146
H(15A)	-0.2796	0.8547	0.9896	0.145
H(16A)	-0.0783	0.9270	0.9878	0.149
H(17A)	0.0979	0.8906	0.9593	0.149
H(19A)	0.2882	1.0269	0.8989	0.058
H(20A)	0.3701	1.1415	0.8879	0.058
H(21A)	0.5856	1.1502	0.8661	0.056
H(22A)	0.7130	1.0435	0.8586	0.053
H(23A)	0.6294	0.9289	0.8698	0.055
H(25A)	0.6482	0.8115	0.8880	0.157
H(26A)	0.7386	0.7251	0.8599	0.161
H(27A)	0.5947	0.6801	0.8302	0.162
H(28A)	0.3542	0.7108	0.8245	0.160
H(29A)	0.2736	0.7967	0.8533	0.157
H(1BA)	0.3138	0.8530	0.3211	0.093
H(1BB)	0.2864	0.7853	0.3034	0.093
H(1BC)	0.1563	0.8343	0.3124	0.093
H(2B)	0.2568	0.9369	0.2906	0.072
H(3BA)	0.4392	0.8367	0.2669	0.071
H(3BB)	0.4894	0.8781	0.2909	0.071
H(4B)	0.5791	0.9451	0.2600	0.070
H(5BA)	0.4332	1.0191	0.2900	0.094
H(5BB)	0.3344	1.0342	0.2669	0.094
H(5BC)	0.4965	1.0598	0.2667	0.094

H(7B)	0.0204	0.7851	0.2229	0.150
H(8B)	0.0117	0.6694	0.2071	0.152
H(9B)	0.1526	0.5799	0.2278	0.150
H(10B)	0.2765	0.6143	0.2627	0.145
H(11B)	0.2707	0.7326	0.2761	0.143
H(13B)	-0.0837	0.7670	0.2799	0.074
H(14B)	-0.2818	0.7867	0.3040	0.077
H(15B)	-0.3334	0.9029	0.3196	0.076
H(16B)	-0.1825	1.0003	0.3095	0.077
H(17B)	0.0130	0.9815	0.2847	0.075
H(19B)	0.3295	1.0923	0.2252	0.050
H(20B)	0.4279	1.1902	0.2041	0.056
H(21B)	0.6289	1.1738	0.1794	0.061
H(22B)	0.7249	1.0564	0.1768	0.061
H(23B)	0.6306	0.9572	0.1977	0.056
H(25B)	0.6504	0.8542	0.2380	0.155
H(26B)	0.7437	0.7468	0.2230	0.156
H(27B)	0.6197	0.6791	0.1928	0.161
H(28B)	0.4047	0.7292	0.1804	0.164
H(29B)	0.3061	0.8360	0.1950	0.162
H(1CA)	0.7571	0.7085	0.3527	0.071
H(1CB)	0.6625	0.7713	0.3648	0.071
H(1CC)	0.5911	0.6958	0.3567	0.071
H(2C)	0.7042	0.6320	0.3865	0.049
H(3CA)	0.9170	0.6661	0.3905	0.050
H(3CB)	0.8800	0.7508	0.3916	0.050
H(4C)	0.8389	0.7468	0.4319	0.050
H(5CA)	1.0760	0.7569	0.4158	0.068
H(5CB)	1.1019	0.6728	0.4226	0.068
H(5CC)	1.0727	0.7314	0.4436	0.068
H(7C)	0.7341	0.8305	0.4069	0.055
H(8C)	0.6940	0.9507	0.4174	0.058
H(9C)	0.4849	0.9928	0.4358	0.062
H(10C)	0.3115	0.9024	0.4431	0.059
H(11C)	0.3429	0.7820	0.4322	0.058
H(13C)	0.3696	0.7831	0.3797	0.051
H(14C)	0.1716	0.7520	0.3558	0.049
H(15C)	0.0974	0.6312	0.3545	0.049
H(16C)	0.2084	0.5406	0.3771	0.051
H(17C)	0.4059	0.5715	0.4012	0.052
H(19C)	0.6964	0.4943	0.4182	0.155
H(20C)	0.7811	0.3904	0.3981	0.157
H(21C)	1.0251	0.3731	0.3934	0.157
H(22C)	1.1843	0.4596	0.4087	0.154
H(23C)	1.0996	0.5634	0.4288	0.151
H(25C)	1.0528	0.5513	0.4684	0.086

H(26C)	1.1678	0.5730	0.5059	0.088
H(27C)	1.0936	0.6731	0.5282	0.089
H(28C)	0.9101	0.7509	0.5171	0.089
H(29C)	0.8007	0.7266	0.4794	0.088

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- (2) The initial paragraph of this preparation is a variation of a procedure by Stefan Bräse, Ph.D. Thesis, Universität Göttingen, 1997.
- (3) For this experiment, GC samples of the aliquots were run at 150 °C and 80 mL/min N<sub>2</sub>.  
Retention times (min): 0.88, benzene; 1.26, toluene; 1.90, ethylbenzene; 2.17, styrene; 5.78, (*R*)- and (*S*)-2-phenylpropanal; 6.89, 3-phenylpropanal.
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- (6) The 3:1 (*Z*)-□-deuteriostyrene : phenylacetylene-*d*<sub>1</sub> mixture was prepared with phenylacetylene-*d*<sub>1</sub> and DIBAL-H. Phenylacetylene-*d*<sub>1</sub> was prepared by deprotonation of phenylacetylene with EtMgBr in ether and quenching with D<sub>2</sub>O, as reported by Wood, J. T.; Arney, J. S.; Cortés, D.; Berson, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3855. <sup>1</sup>H NMR of (*Z*)-□-deuteriostyrene (300 MHz, CDCl<sub>3</sub>): □ 7.37 - 7.42 (m, 2 H, Ar), 7.19 - 7.34 (m, 3 H, Ar), 6.70 (dt, 1 H, *J*<sub>trans</sub> = 17.5 Hz, *J*<sub>HD</sub> = 1.5 Hz, =CH), 5.72 (d, 0.07 H, *J*<sub>trans</sub> = 17.5 Hz, =CHD), 5.23 (d, 1 H, *J*<sub>cis</sub> = 11.0 Hz). Phenylacetylene appears at □ 7.44 - 7.48 (0.63 H, m, Ph), 7.2-7.4 (m, Ph, coincident with styrene Ph), 3.04 (s, 0.18 H, CCH).
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