

## **Strong $\pi$ -Acceptor Sulfonated Phosphines in Biphasic Rhodium catalyzed Hydroformylation of Polar Alkenes**

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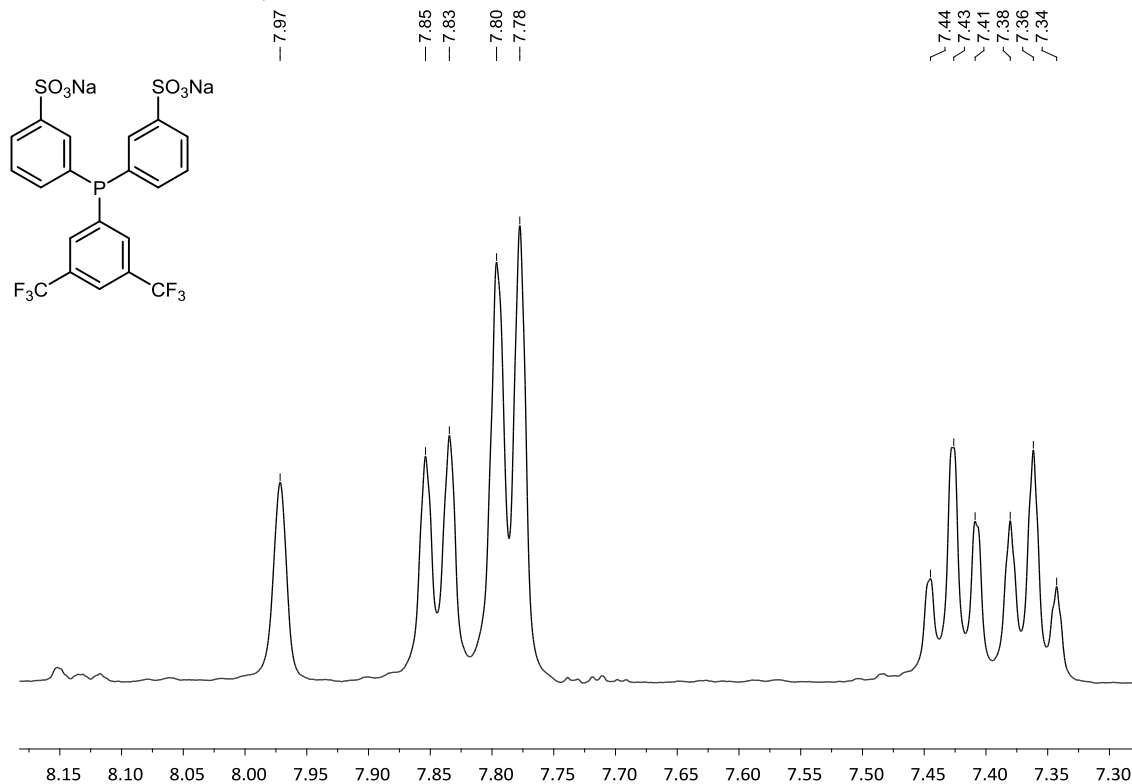
### **Table of Contents:**

<b>NMR spectra of Danphos type phosphines .....</b>	<b>2</b>
<b>IR spectra of Danphos type phosphines .....</b>	<b>8</b>
<b>HRMS spectra of Danphos type phosphines .....</b>	<b>9</b>
<b><math>^{31}\text{P}\{^1\text{H}\}</math> NMR spectra of Danphos selenides .....</b>	<b>11</b>
<b>Reaction profile of the biphasic hydroformylation of vinyl acetate using 4 equivalents of the sulfonated phosphines .....</b>	<b>13</b>
<b>Reaction profile of the biphasic hydroformylation of vinyl acetate using 20 equivalents of the sulfonated phosphines .....</b>	<b>13</b>
<b>Reaction profile of the recycling experiments of the biphasic hydroformylation of vinyl acetate using Danphos and <i>p</i>-Danphos .....</b>	<b>14</b>
<b>Reaction profile of the biphasic hydroformylation of allyl cyanide using 20 equivalents of the sulfonated phosphines .....</b>	<b>15</b>
<b>Reaction profile of the recycling experiments of the biphasic hydroformylation of allyl cyanide using Danphos and <i>p</i>-Danphos .....</b>	<b>16</b>

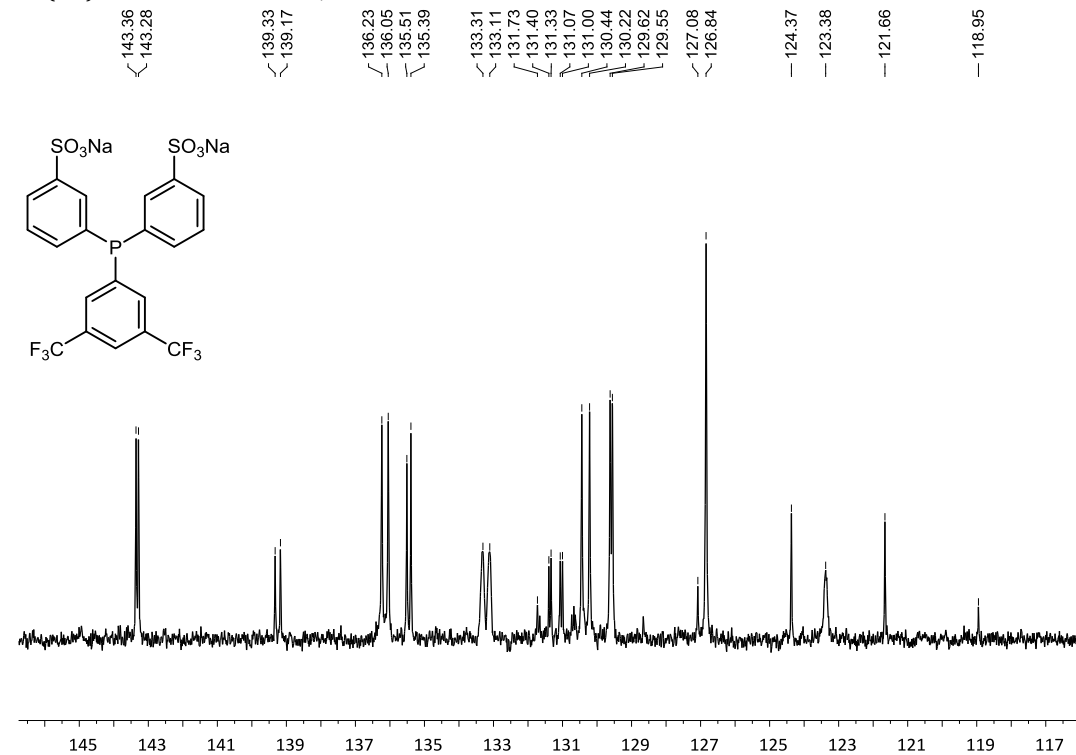
# NMR spectra of Danphos type phosphines

## Danphos

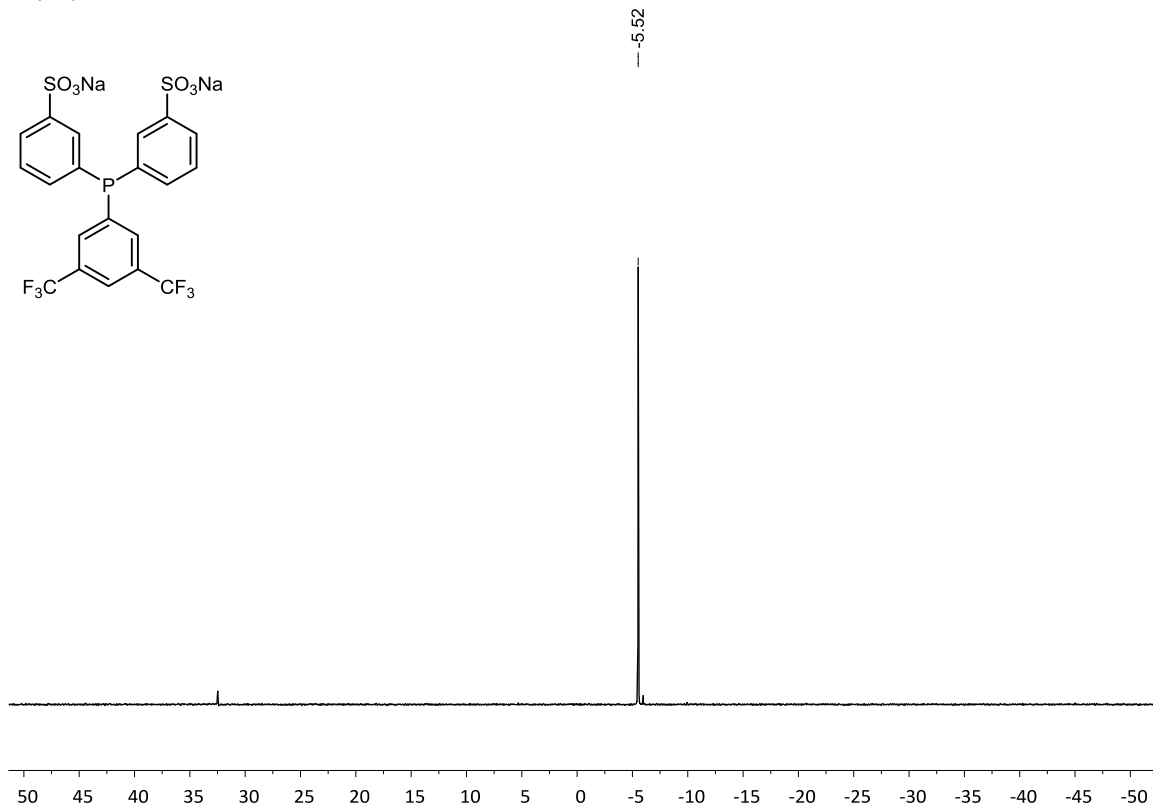
$^1\text{H}$  NMR: 400.13 MHz,  $\text{D}_2\text{O}$



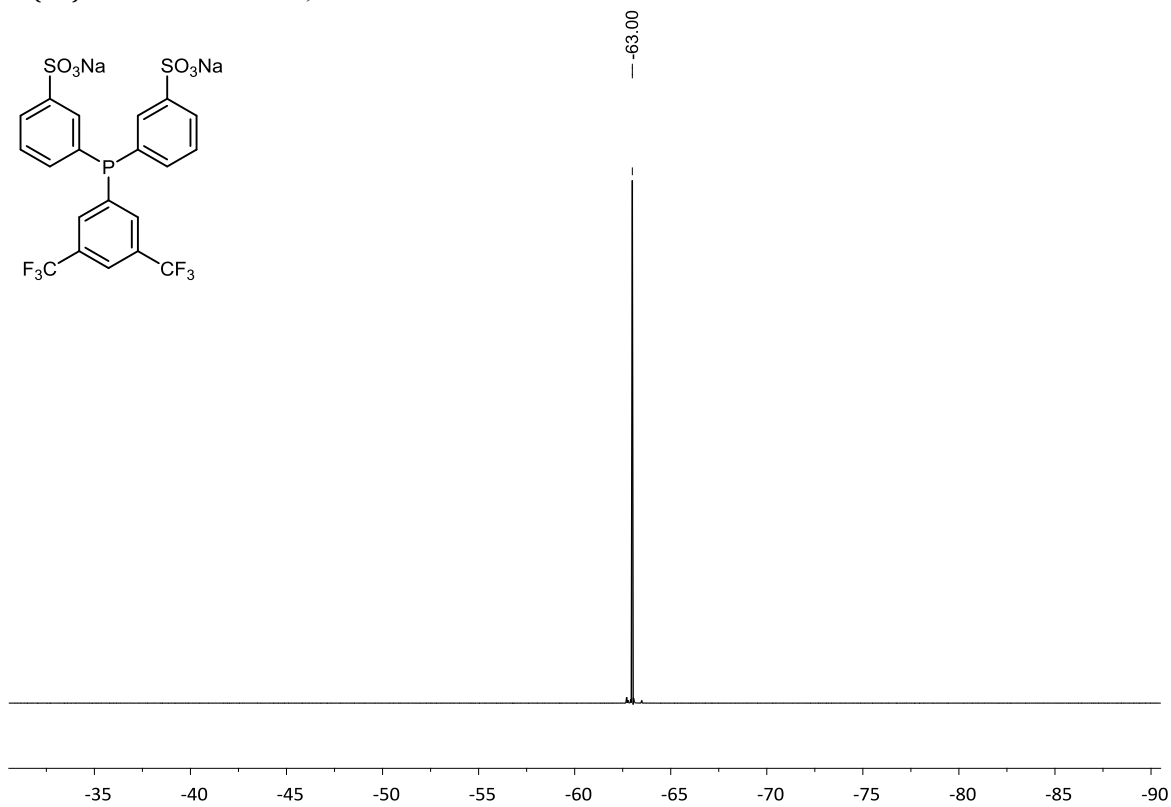
$^{13}\text{C}\{^1\text{H}\}$  NMR: 100.61 MHz,  $\text{D}_2\text{O}$



$^{31}\text{P}\{^1\text{H}\}$  NMR: 161.98 MHz,  $\text{D}_2\text{O}$

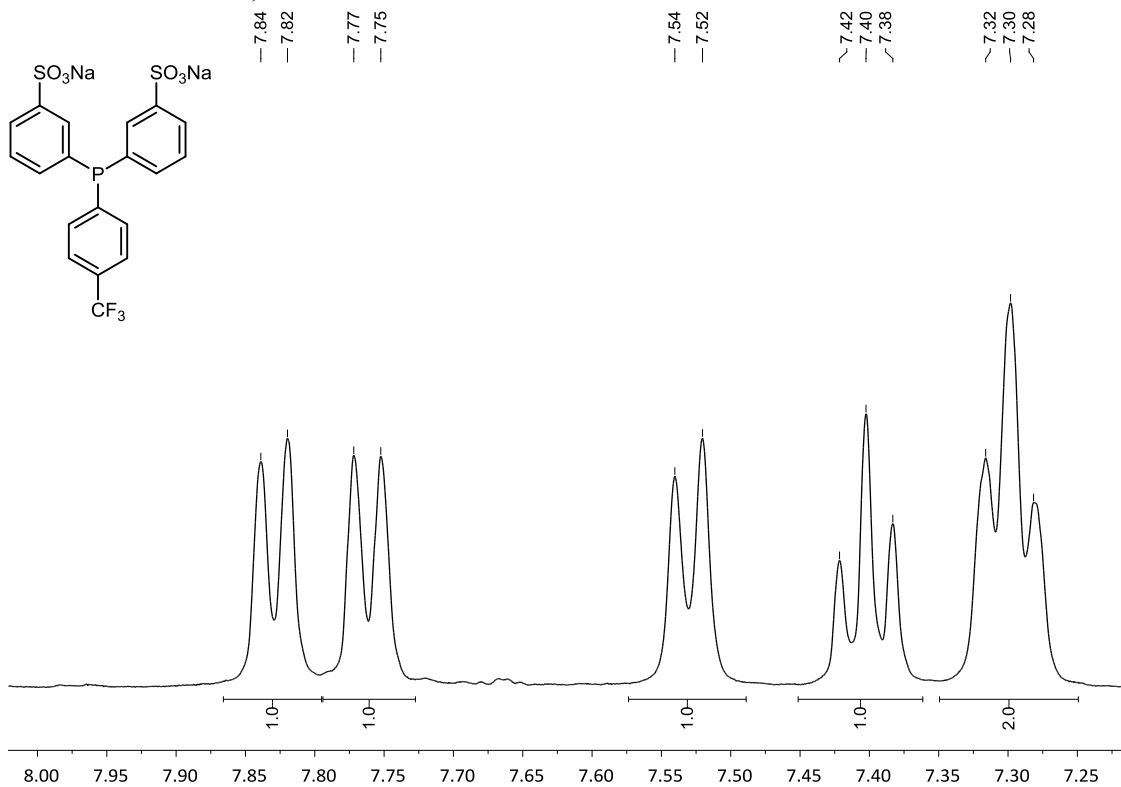


$^{19}\text{F}\{^1\text{H}\}$  NMR: 376.50 MHz,  $\text{D}_2\text{O}$

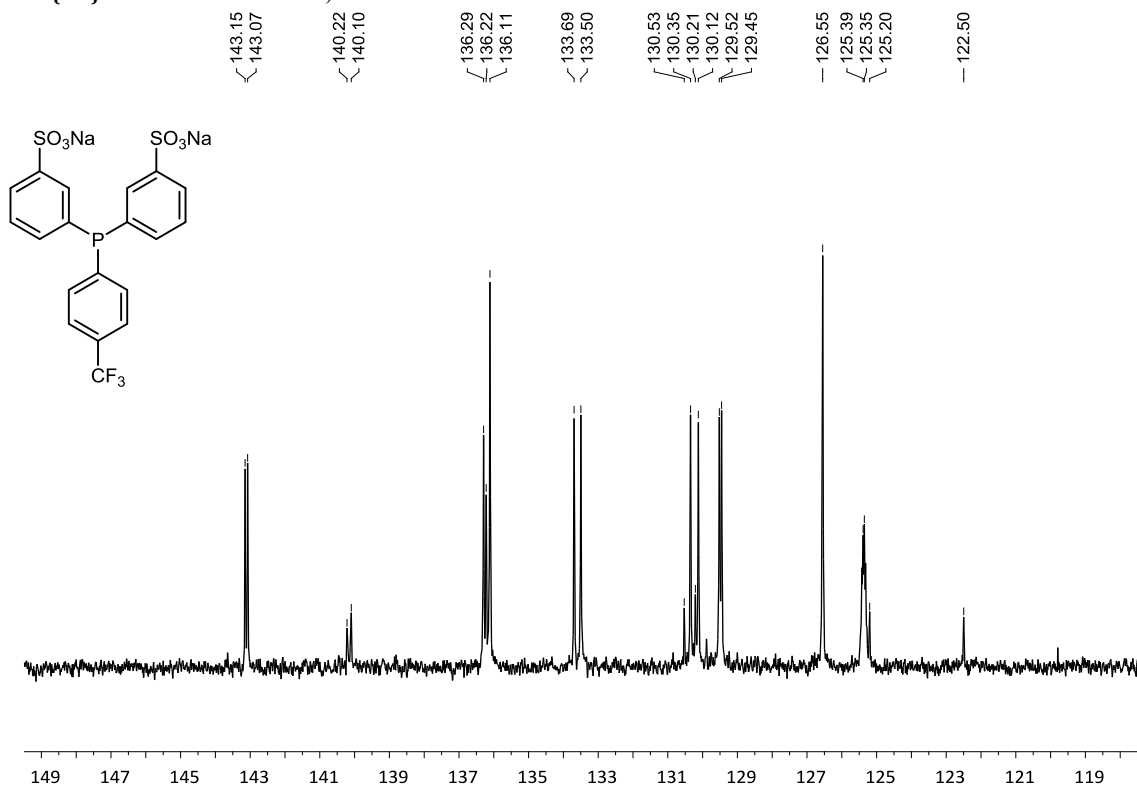


# *p*-Danphos

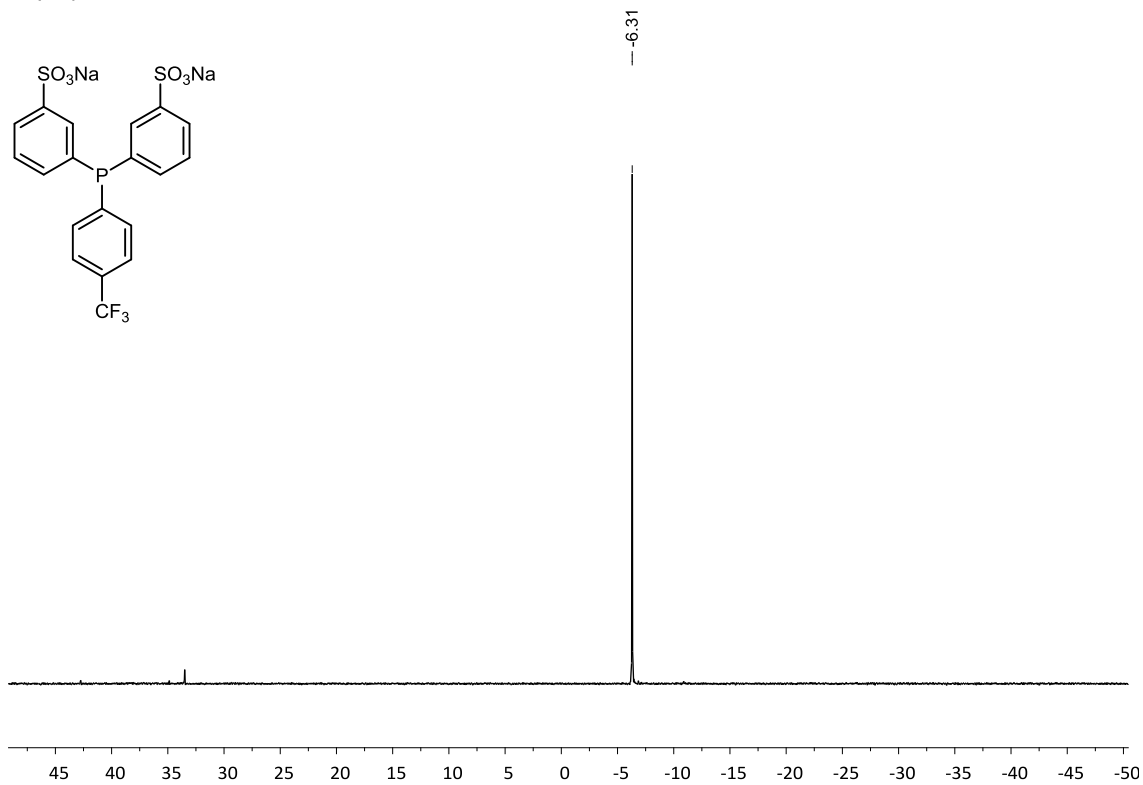
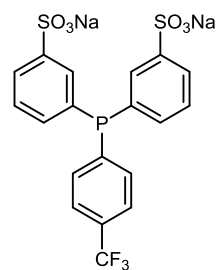
$^1\text{H}$  NMR: 400.13 MHz,  $\text{D}_2\text{O}$



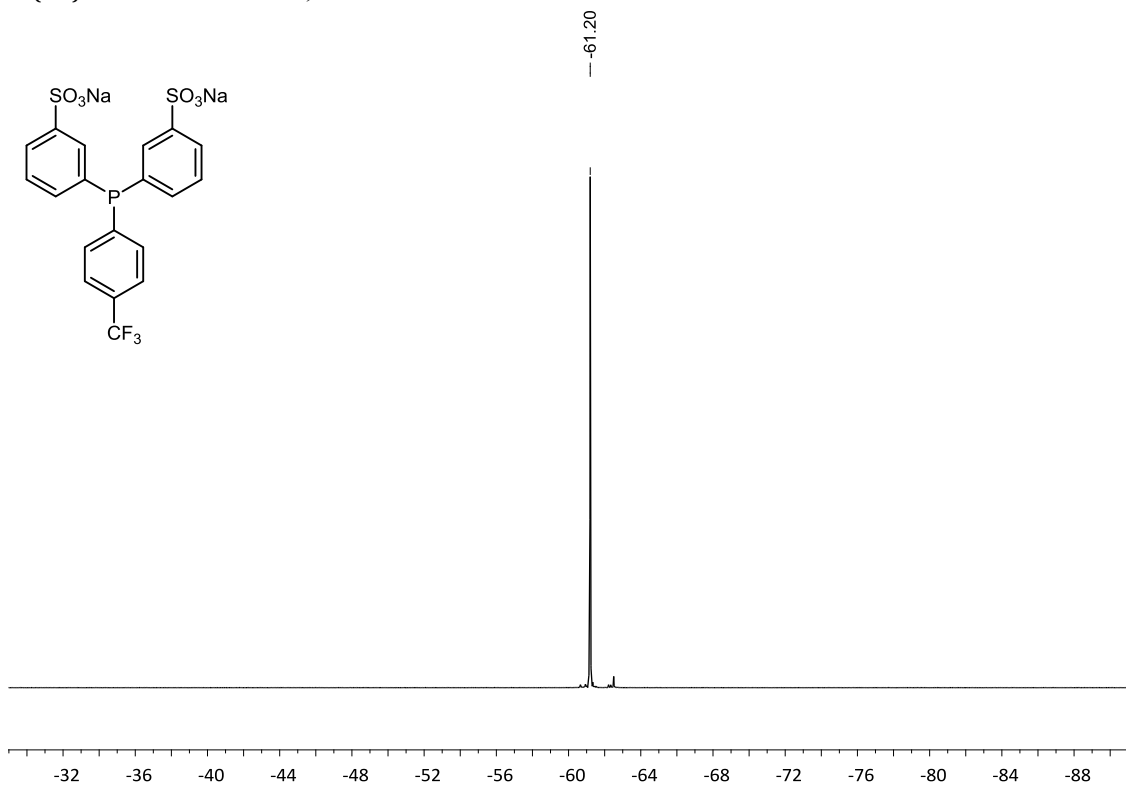
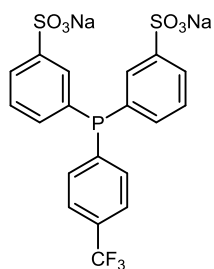
$^{13}\text{C}\{^1\text{H}\}$  NMR: 100.61 MHz,  $\text{D}_2\text{O}$



$^{31}\text{P}\{^1\text{H}\}$  NMR: 161.98 MHz,  $\text{D}_2\text{O}$

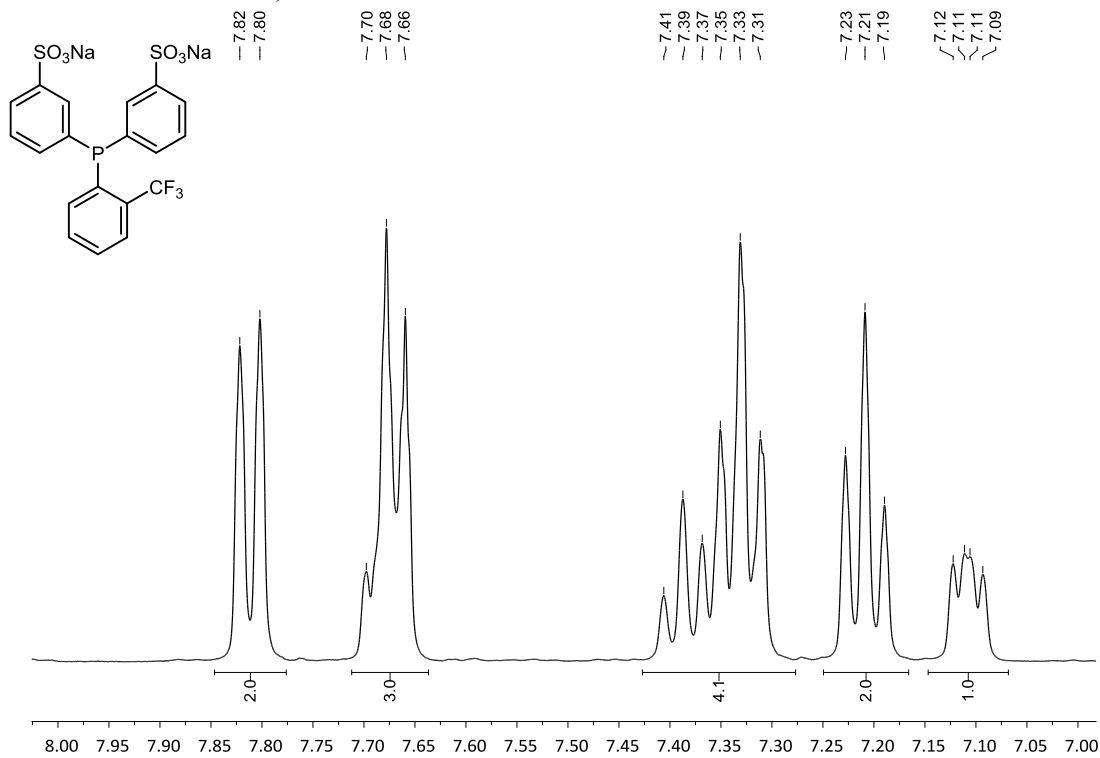


$^{19}\text{F}\{^1\text{H}\}$  NMR: 376.50 MHz,  $\text{D}_2\text{O}$

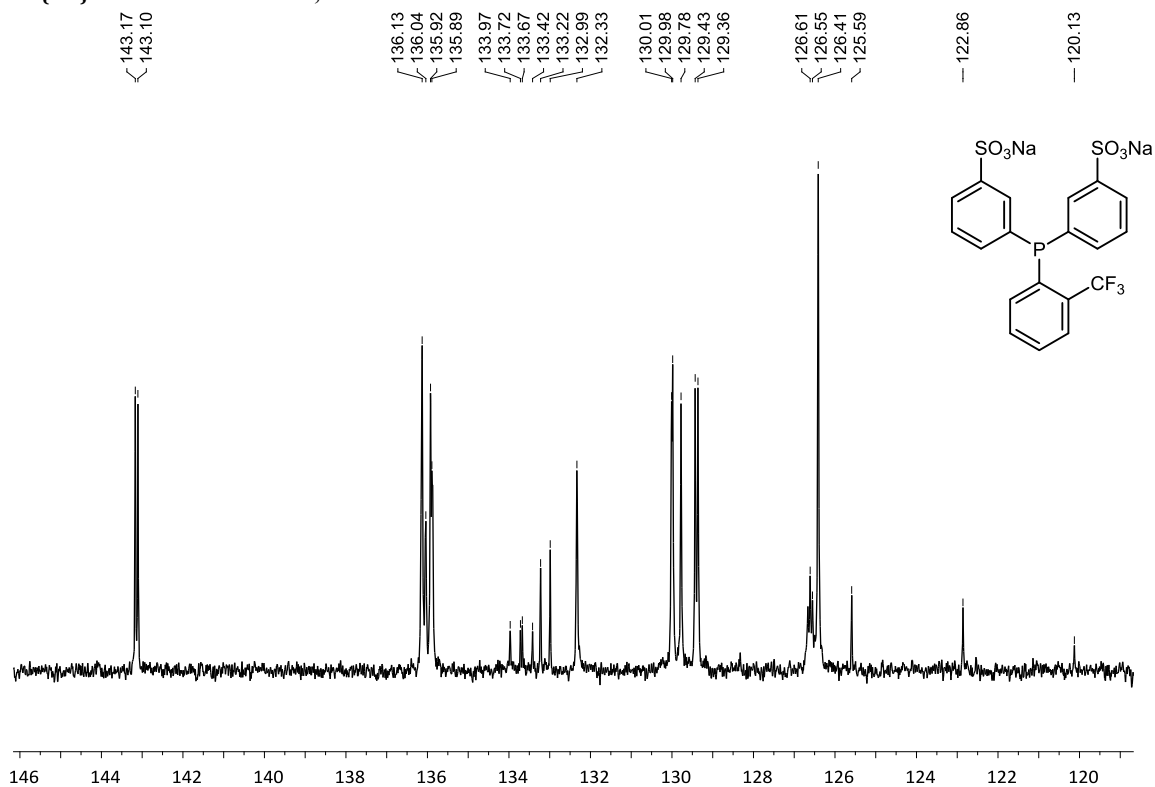


# *o*-Danphos

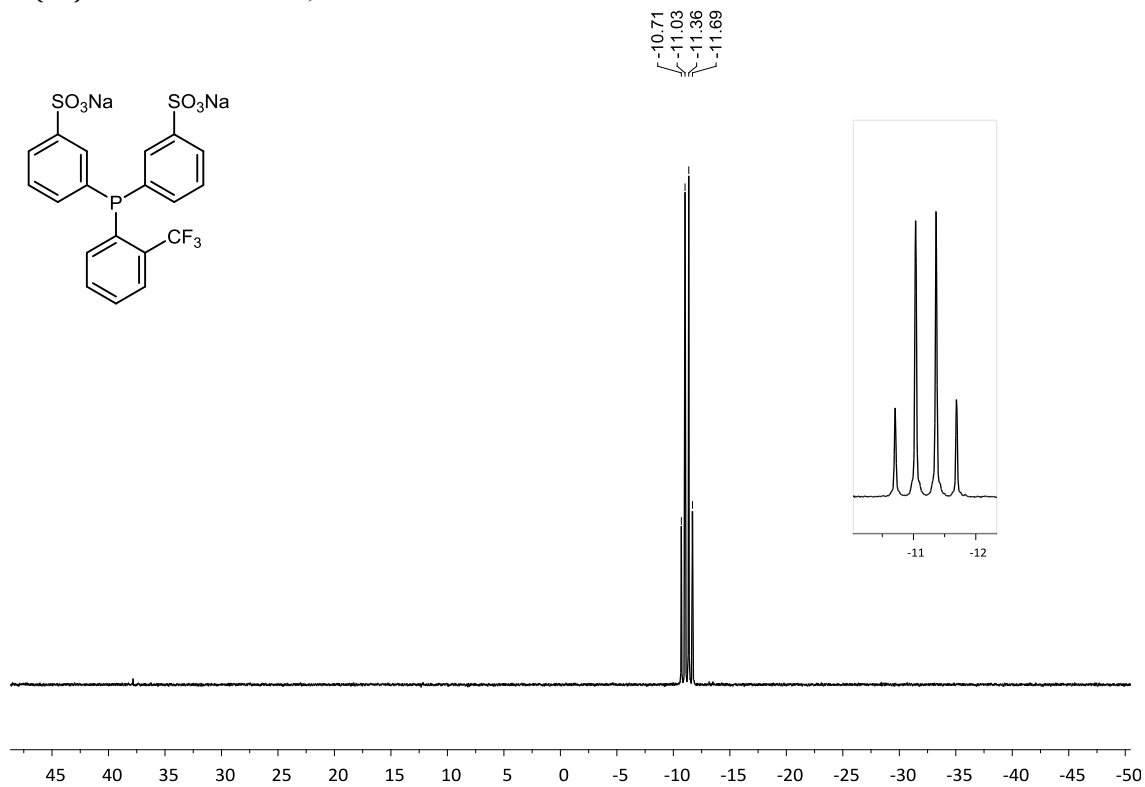
$^1\text{H NMR}$ : 400.13 MHz,  $\text{D}_2\text{O}$



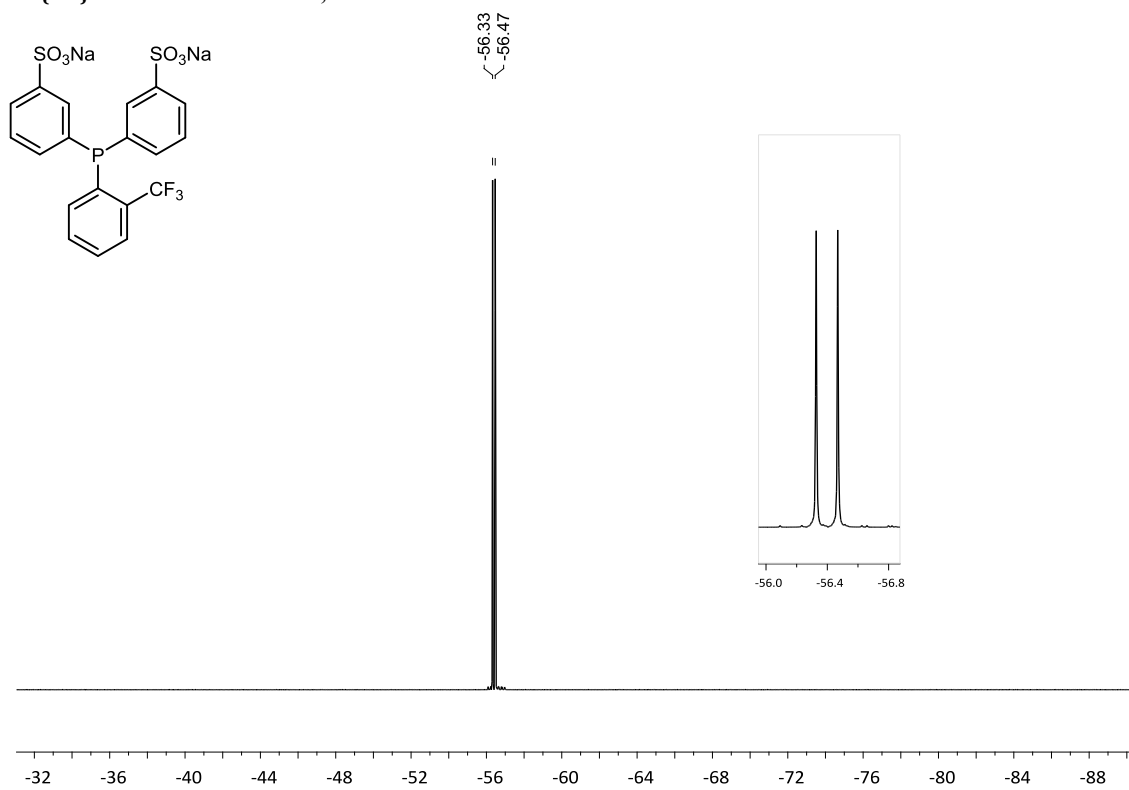
$^{13}\text{C}\{^1\text{H}\}$  NMR: 100.61 MHz,  $\text{D}_2\text{O}$



$^{31}\text{P}\{^1\text{H}\}$  NMR: 161.98 MHz,  $\text{D}_2\text{O}$

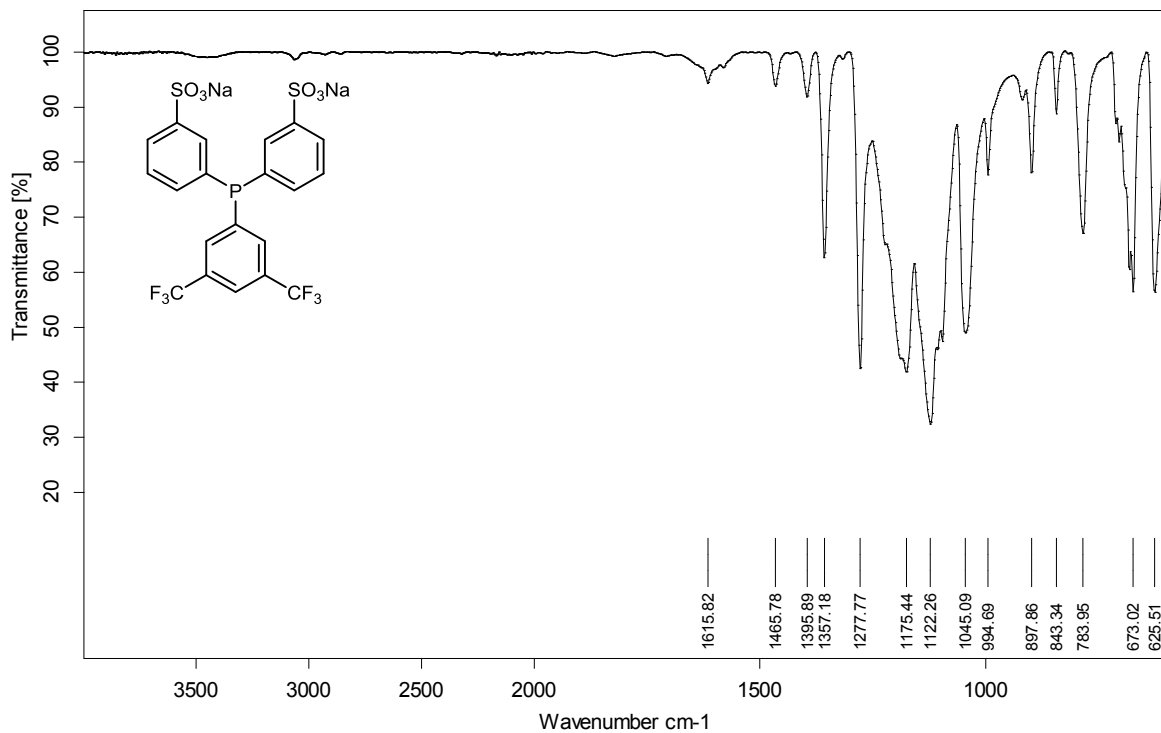


$^{19}\text{F}\{^1\text{H}\}$  NMR: 376.50 MHz,  $\text{D}_2\text{O}$

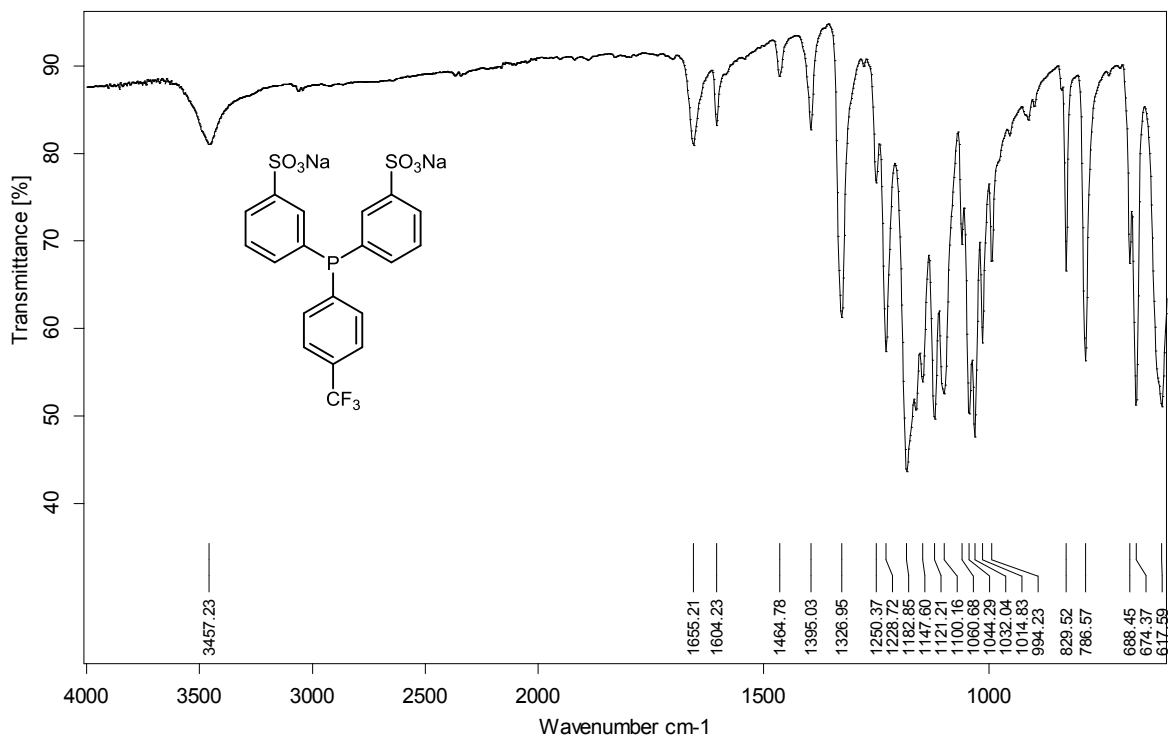


# IR(ATR) spectra of Danphos type phosphine

## Danphos

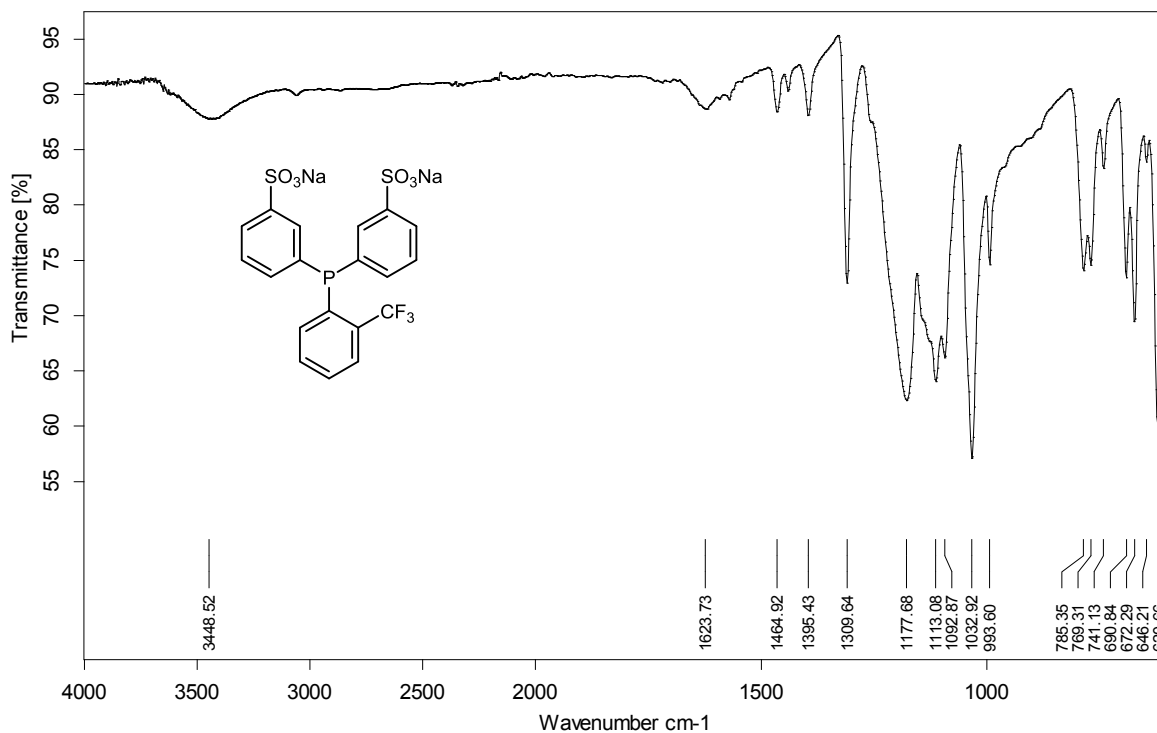


## *p*-Danphos





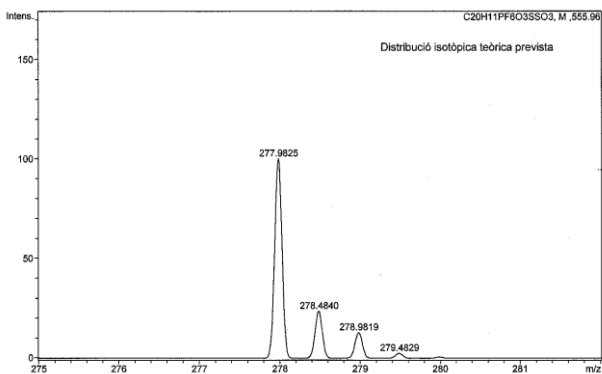
***o*-Danphos**



**HRMS spectra of Danphos type phosphines**

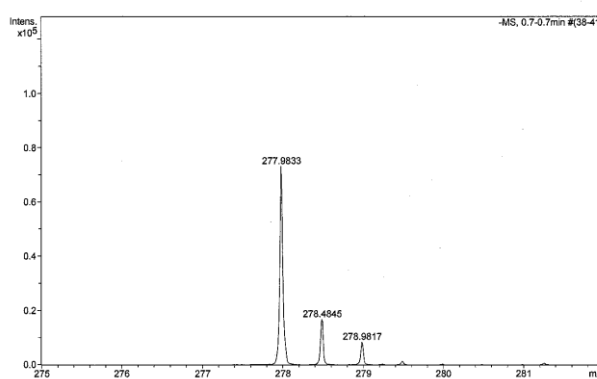
**Danphos: HRMS: ESI  $m/z$**

Theoretical Isotopic Distribution



#	$m/z$	I	I %
1	277.9825	100	100.0
2	278.4840	24	23.6
3	278.9819	13	12.9
4	279.4829	3	2.5
5	279.9818	1	0.6

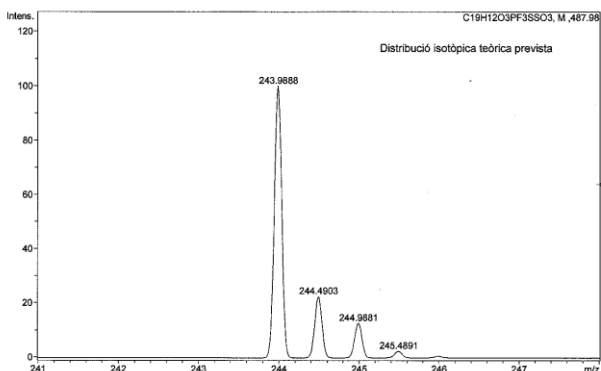
Experimental Isotopic Distribution



#	$m/z$	I	I %
1	277.9833	73047	100.0
2	278.4845	16662	22.8
3	278.9817	8308	11.4

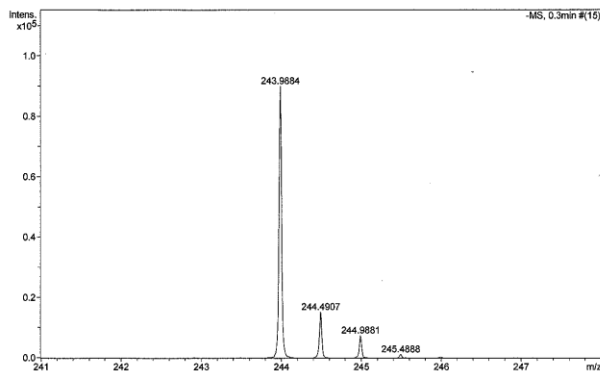
***p*-Danphos: HRMS: ESI  $m/z$**

Theoretical Isotopic Distribution



#	$m/z$	I	I%
1	243.9888	100	100.0
2	244.4903	23	22.5
3	244.9881	13	12.7
4	245.4891	2	2.4
5	245.9880	1	0.6

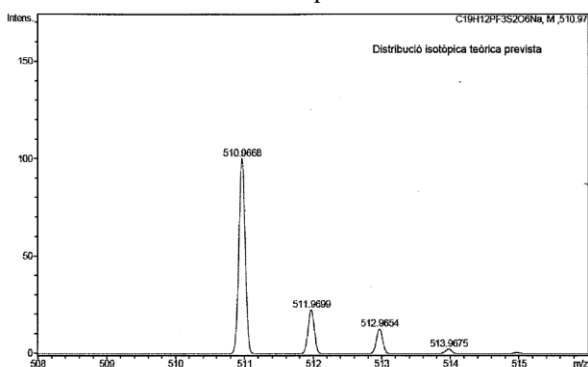
Experimental Isotopic Distribution



#	$m/z$	I	I%
1	243.9884	89853	100.0
2	244.4907	15196	16.9
3	244.9881	7458	8.3
4	245.4888	1187	1.3
5	245.9897	391	0.4

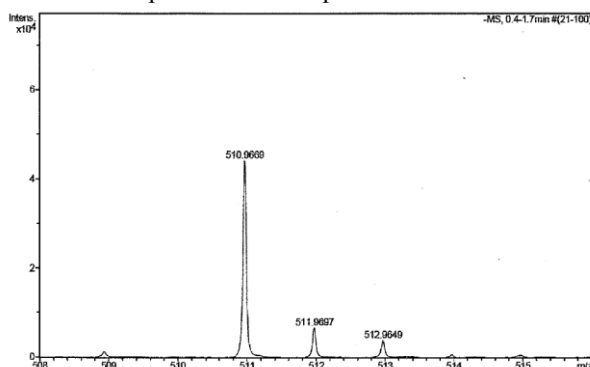
***o*-Danphos: HRMS: ESI  $m/z$**

Theoretical Isotopic Distribution



#	$m/z$	I	I%
1	510.9668	100	100.0
2	511.9699	23	22.5
3	512.9654	13	12.7
4	513.9675	2	2.4
5	514.9652	1	0.6

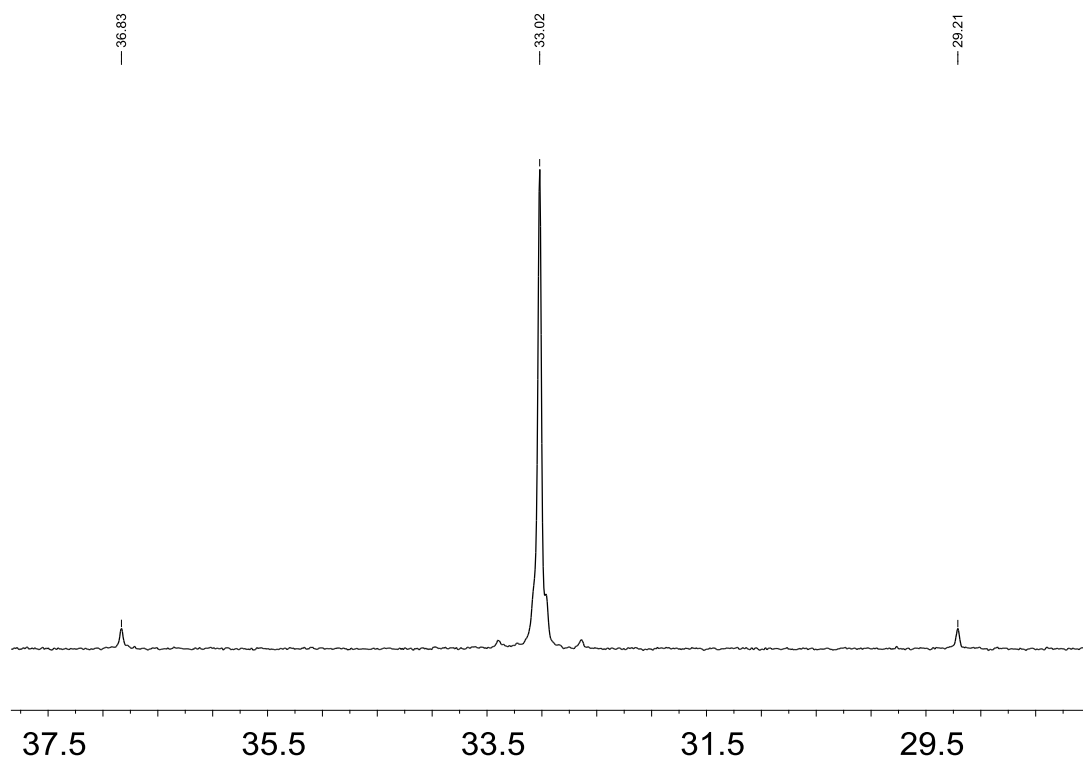
Experimental Isotopic Distribution



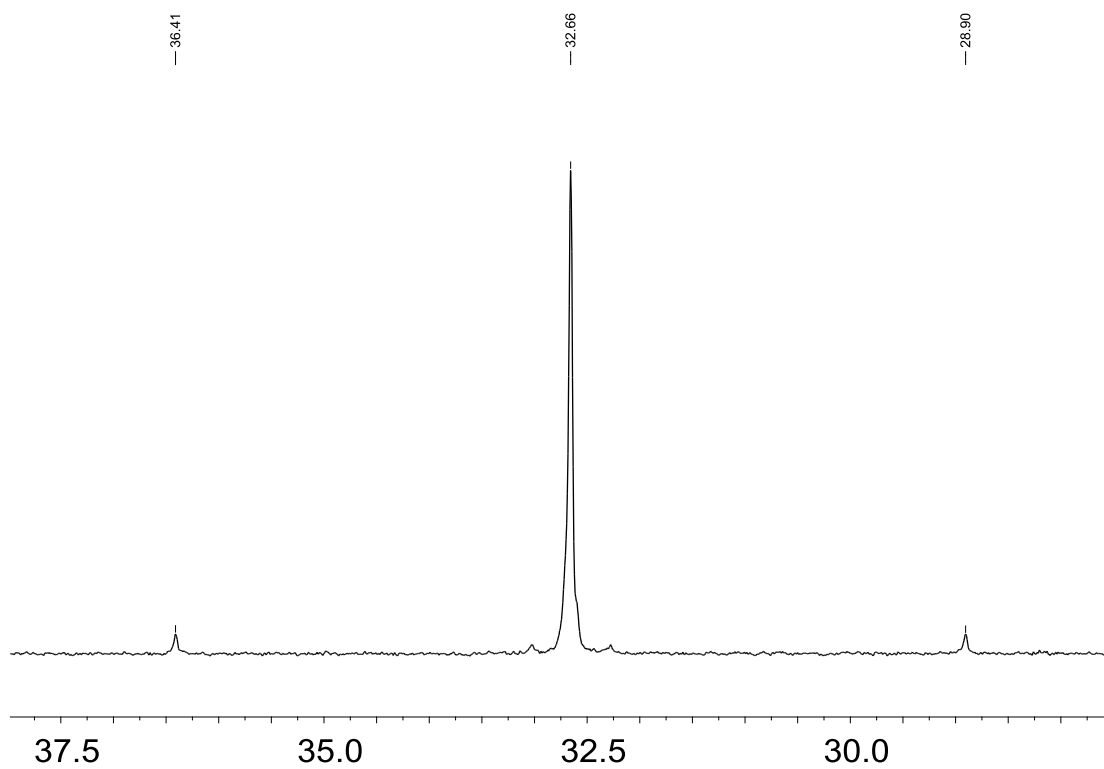
#	$m/z$	I	I%
1	510.9669	44152	100.0
2	511.9697	6600	14.9
3	512.9649	3870	8.8
4	513.9655	577	1.3

## $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of Danphos selenides

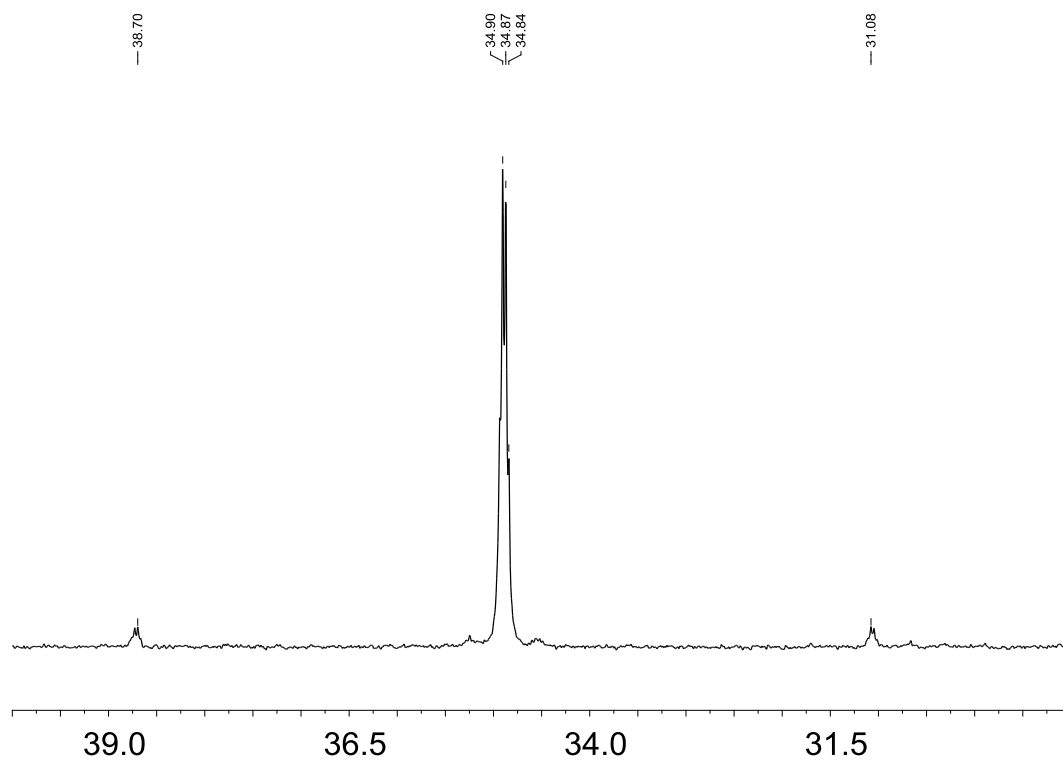
Danphos Selenide:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum



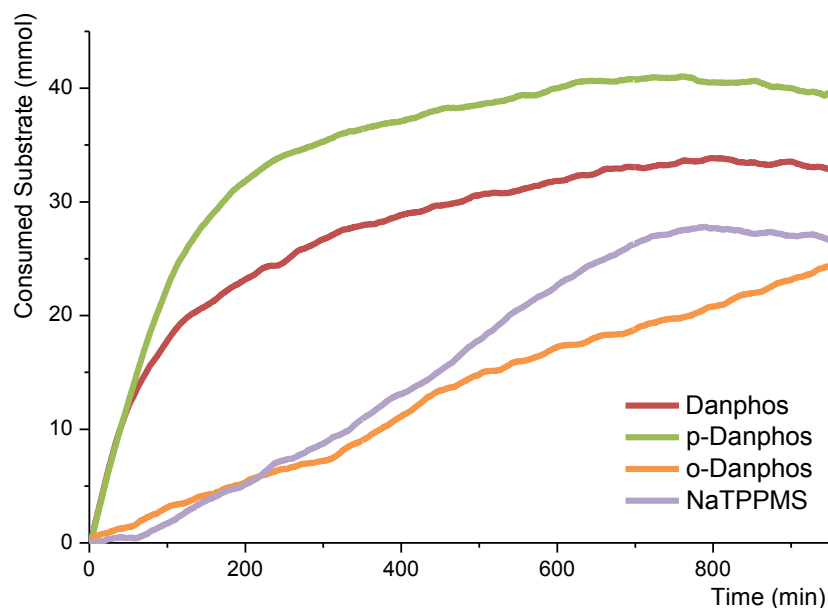
*p*-Danphos Selenide:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum



***o*-Danphos Selenide:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum**

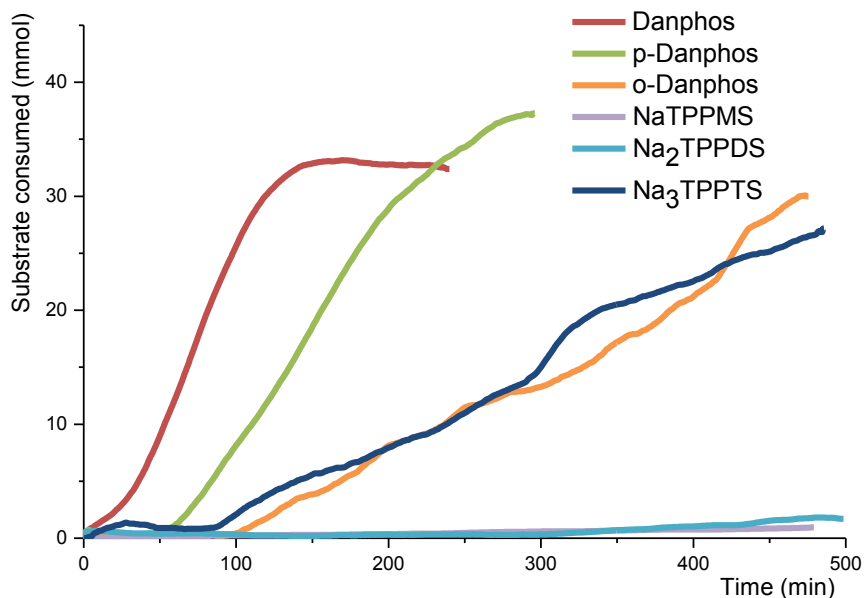


**Reaction profile of the biphasic hydroformylation of vinyl acetate using 4 equivalents of the sulfonated phosphines.**



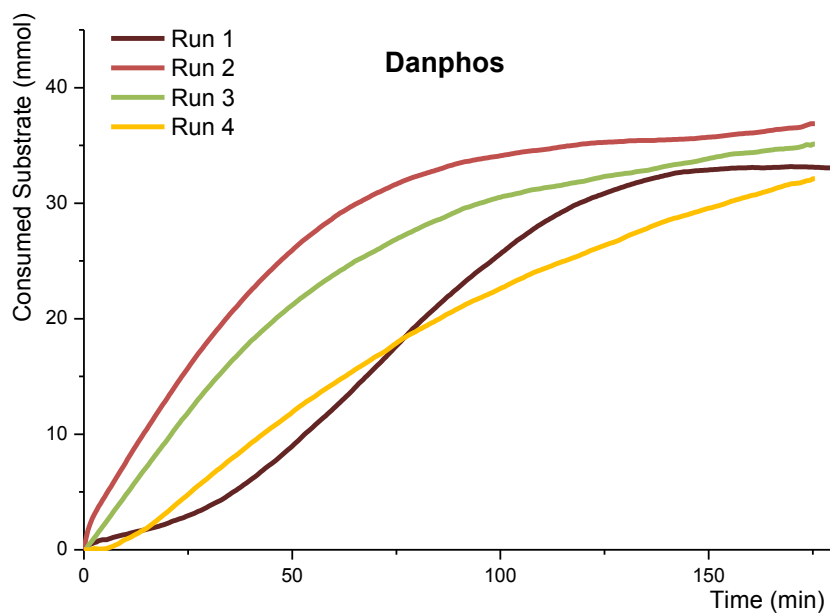
**Figure.** Substrate consumed (mmol) *versus* time (min) in the biphasic hydroformylation of vinyl acetate with sulfonated phosphines. Conditions: [Rh]:[L]:[substrate] = 1:4:2500 (43.4 mmol vinyl acetate), 2 ml H<sub>2</sub>O, 6 ml toluene, 80 °C, 30 bar CO:H<sub>2</sub> (1:1), 16h.

**Reaction profile of the biphasic hydroformylation of vinyl acetate using 20 equivalents of the sulfonated phosphines.**

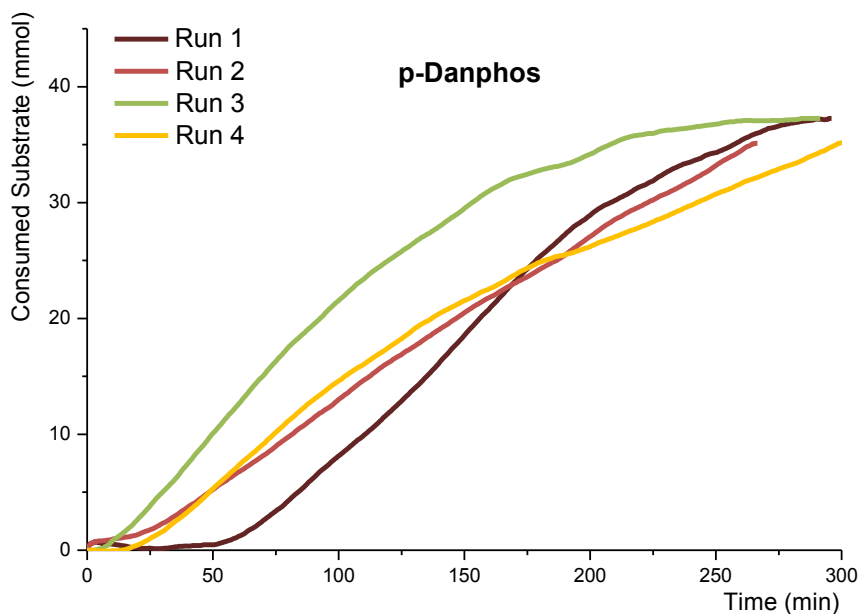


**Figure.** Substrate consumed (mmol) *versus* time (min) in the biphasic hydroformylation of vinyl acetate with sulfonated phosphines. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol vinyl acetate), 3 ml toluene, 5 ml H<sub>2</sub>O, 80 °C, 30 bar CO:H<sub>2</sub> (1:1).

## Reaction profile of the recycling experiments of the biphasic hydroformylation of vinyl acetate using Danphos and *p*-Danphos

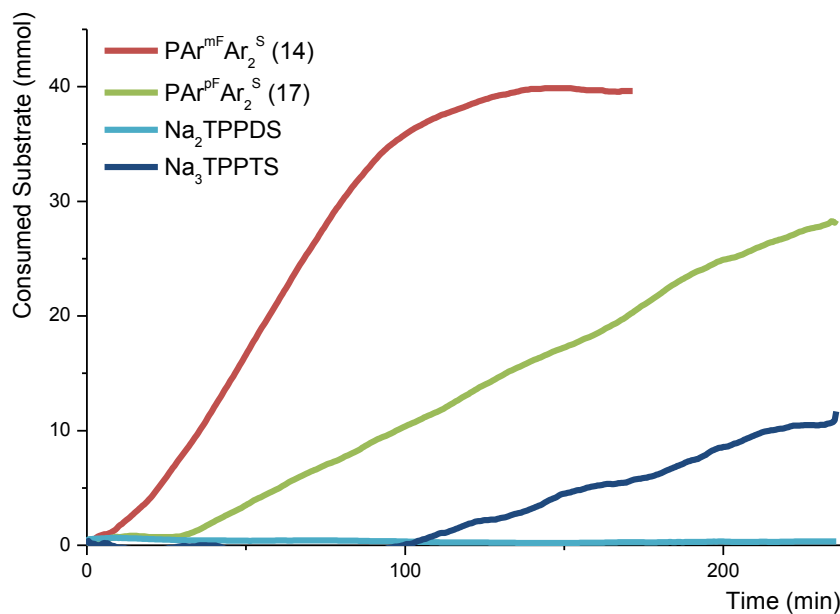


**Figure.** Substrate consumed (mmol) *versus* time (min) in the recycling experiments of the biphasic hydroformylation of vinyl acetate with Danphos phosphine. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol vinyl acetate), 3 ml toluene, 5 ml H<sub>2</sub>O, 80 °C, 30 bar CO:H<sub>2</sub> (1:1).



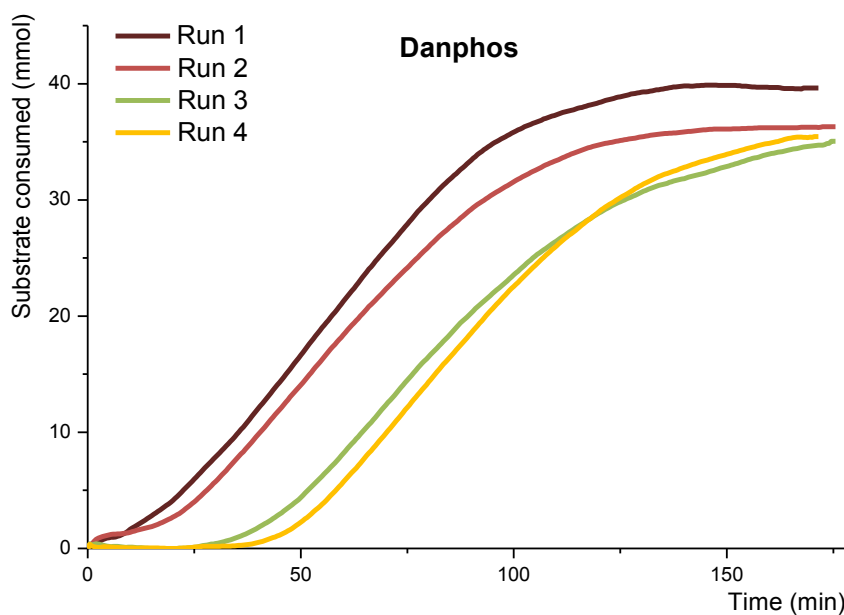
**Figure.** Substrate consumed (mmol) *versus* time (min) in the recycling experiments of the biphasic hydroformylation of vinyl acetate with *p*-Danphos phosphine. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol vinyl acetate), 3 ml toluene, 5 ml H<sub>2</sub>O, 80 °C, 30 bar CO:H<sub>2</sub> (1:1).

**Reaction profile of the biphasic hydroformylation of allyl cyanide using 20 equivalents of the sulfonated phosphines.**

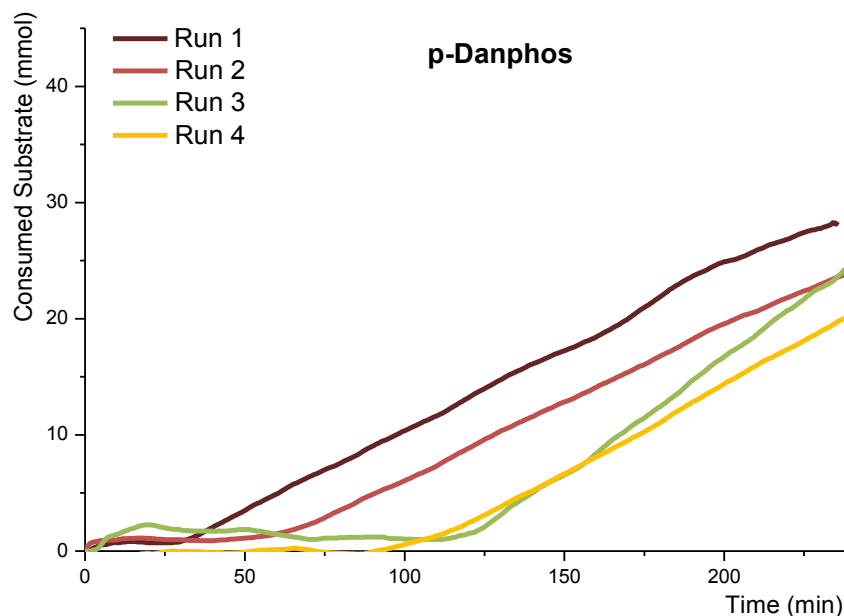


**Figure.** Substrate consumed (mmol) *versus* time (min) in the biphasic hydroformylation of allyl cyanide with sulfonated phosphines. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol allyl cyanide), 3 ml toluene, 5 ml H<sub>2</sub>O, 80°C, 30 bar CO:H<sub>2</sub> (1:1).

## Reaction profile of the recycling experiments of the biphasic hydroformylation of allyl cyanide using Danphos and *p*-Danphos



**Figure.** Substrate consumed (mmol) *versus* time (min) in the recycling experiments of the biphasic hydroformylation of allyl cyanide with Danphos phosphine. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol allyl cyanide), 3 ml toluene, 5 ml H<sub>2</sub>O, 80 °C, 30 bar CO:H<sub>2</sub> (1:1).



**Figure.** Substrate consumed (mmol) *versus* time (min) in the recycling experiments of the biphasic hydroformylation of allyl cyanide with *p*-Danphos phosphine. Conditions: [Rh]:[L]:[substrate] = 1:20:2500 (43.4 mmol allyl cyanide), 3 ml toluene, 5 ml H<sub>2</sub>O, 80 °C, 30 bar CO:H<sub>2</sub> (1:1).