

## Electronic Supplementary Information

**Table a:** Aqueous biphasic hydroformylation of 1-octene at different pressures over 8 hours.<sup>a</sup>

Entry	Cat.	Pressure (bars)	Conversion (%)	Aldehydes (%)	<i>iso</i> -octenes (%)	n:iso <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1	<b>5</b> /[RhCl(COD)] <sub>2</sub>	40	98	71	29	38:62	258
2	<b>6</b> /[RhCl(COD)] <sub>2</sub>	40	90	76	24	34:66	276
3	<b>7</b>	40	98	96	4	31:69	349
4	<b>8</b>	40	91	90	10	30:70	327

<sup>a</sup> Reactions carried out with (CO:H<sub>2</sub>) (1:1) at 95 °C in distilled H<sub>2</sub>O (5ml) and toluene (5ml) with 6.37 mmol of 1-octene and 2.87x10<sup>-3</sup> mmol Rh catalyst precursor (Error estimate: (**5**/ RhCl(COD))<sub>2</sub>) = ± 0.11; (**6**/ RhCl(COD))<sub>2</sub>) = ± 0.17; (**7**) = ± 0.10 and (**8**) = ± 0.11). GC conversions obtained using *n*-decane as an internal standard in relation to authentic standard *iso*-octenes and aldehydes. <sup>b</sup> Regioselectivity calculated at 2 hours. <sup>c</sup> TOF = (mol product/mol cat.) x h<sup>-1</sup>.