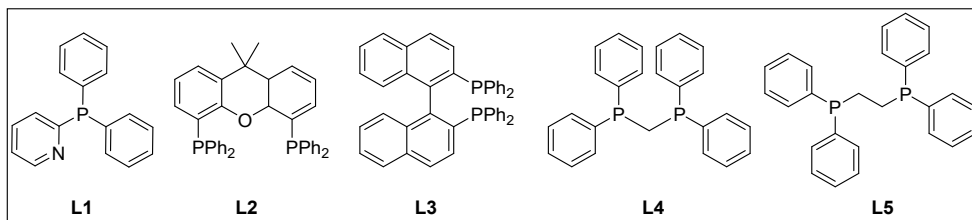


Supplementary Information

Selected screening data

S. Table 1 Ir-catalyzed tandem hydroformylation–acetalization of 1-hexene with different ligands.^[a]



Entry	Ligand	Conv. (%) ^[b]	S _{oxo} (%) ^[b, c]	P _{acetals} (%) ^[b, c]	S _{iso} (%) ^[b, c]	S _{hexane} (%) ^[b, c]	L/B ^[b]
1	PPh₃	100	87	88	10	3	2.6
2	L1	100	48	52	40	12	2.2
3	L2	100	48	54	41	11	2.0
4	L3	100	43	63	50	7	3.3
5	L4	100	31	61	64	5	2.7
6	L5	100	78	55	11	11	3.6
7	/	97	19	74	78	3	5.1

[a] 1-hexene 2.0 mmol, [Ir(COD)Cl]₂ 0.01 mmol (Ir 1 mol %), Ligand 0.02 mmol (P/Ir = 1 molar ratio), AlCl₃ 0.02 mmol (1 mol %), H₂O 0.2 g, methanol 70 mmol, *N*-methyl pyrrolidone (NMP) 1.5 mL, CO 4.0 MPa, React at 140 °C for 22 hours, then at 100 °C for 3 hours. [b] Determined by GC and GC-MS. [c] S_{oxo} = (aldehydes + acetals) / (aldehydes + acetals + iso-hexenes + hexane), P_{acetals} = acetals / (aldehydes + acetals), percentage of acetals in the total oxo-products, S_{iso} = iso-hexenes / (aldehydes + acetals + iso-hexenes + hexane), S_{hexane} = hexane / (aldehydes + acetals + iso-hexenes + hexane), L/B, the ratio of linear acetals to branched acetals.