A thermomorphic approach to rhodium-catalyzed biphasic hydroformylation of higher olefins (C > 6) was developed based on the HRhCO(PPh3)3/P(OPh)3/propylene carbonate/n-heptane catalytic system. The catalyst system showed excellent selectivity toward the desired linear aldehyde (n/i ratio > 8) and high activity demonstrated by efficient recycling without significant loss of the catalyst activity. The effects of temp., the total pressure, ratio of CO/H2, reaction time, and type of ligand were studied.