Supporting Information: Selective Trimerization of α-Olefins with Immobilized Chromium Catalyst for Lubricant Base Oils

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Oligomerization 1-octene with $[iPrN\{P(C_6H_4\text{-}p\text{-}SiR_3)_2\}_2CrCl_2]^+[B(C_6F_5)_4]^-$. A Schlenk flask (1 L) was charged with $[iPrN\{P(C_6H_4\text{-}p\text{-}SiR_3)_2\}_2CrCl_2]^+[B(C_6F_5)_4]^-$ (0.35 g), 1-octene (800 mL), and triisobutylaluminum (400 mg). After the resulting solution was stirred at 90 ℃ for 16 h, it was filtered over shot pad of silica gel to remove the catalyst. Unreacted octene was removed using a vacuum line to obtain a clear oil (341 g, 60%), which was analyzed with SimDis GC.

Table S1. 1-Octene trimerization at various temperatures (data for Figure 2).

reaction time (h)	conversion at rt (%)	conversion at 40 ℃ (%)	conversion at 60 ℃ (%)	conversion at 80 ℃ (%)	conversion at 60 ℃ with homogenous catalyst[a] (%)
1	3.8	2.7	12	16	20
2	4.2	3.5	17	19	27
3	5.6	6.1	22	24	31
5	7.9	13	28	26	31
7	12	16	32	30	
9	16	21	34	32	
12	17	22	36	35	
24	27	35	47	42	
30	31	39	51	44	
36	33	42	55	46	
48	37	48	60	52	
54	39	50	61	54	
72	44	59	64	56	

[a]Homogeneous catalyst was prepared by reacting (N,N',N''-tridodecyltriazacyclohexane)$CrCl_3$ (19 mg, 25 μmol-Cr) with MAO (1.5 g, 10 wt% in toluene, 2.5 mmol-Al) in toluene (5 mL).

Table S2. Trimer/dimer selectivity in 1-octene trimerization performed at various temperature (Figure 2).

reaction time (h)	conversion at rt (%)		conversion at 40 °C (%)		conversion at 60 °C (%)	
	Dimer	Trimer	Dimer	Trimer	Dimer	Trimer
1	0	3.8	0	2.7	0.02	12
2	0	4.2	0	3.5	0.03	17
3	0	5.6	0	6.1	0.04	22
5	0	7.9	0	13	0.08	28
7	0	12	0	16	0.11	32
9	0	16	0	21	0.16	34
12	0	17	0	22	0.17	36
24	0	27	0.02	35	0.36	47
30	0.02	31	0.02	39	0.38	51
36	0.02	33	0.02	42	0.48	55
48	0.02	37	0.04	48	0.62	60
54	0.02	39	0.04	50	0.62	61
72	0.02	44	0.07	59	0.87	64

Table S3. Trimerization of 1-octene, 1-decene, and 1-dodecene performed at 60 °C (Figure 4).

reaction time (h)	1-octene		1-decene		1-dodecene	
	Conversion (%)	TON	Conversion (%)	TON	Conversion (%)	TON
1	12	850	20	1100	23	1100
2	17	1200	29	1700	32	1500
3	22	1600	30	1700	36	1700
5	28	2000	37	2100	40	1900
7	32	2300	42	2400	47	2200
9	34	2400	46	2600	52	2500
12	36	2600	50	2800	57	2700
24	47	3300	60	3400	69	3300
30	51	3600	64	3700	71	3400
36	55	3900	71	4000	73	3500
48	60	4300	73	4200	76	3600
54	61	4400	75	4300	78	3700
72	64	4600	77	4400	80	3800

Table S4. SimDis GC data for 1-octene/1-dodecene mixed trimerization reactions.

	$C_{24}H_{50}$	$C_{28}H_{58}$	$C_{32}H_{66}$	$C_{36}H_{74}$
1-Octene/1-Dodecene (2 : 1 mole ratio)	26 wt% (30 mol%) (24 : 74 : 2)[a]	45 wt% (45 mol%) (23 : 75 : 2)[a]	24 wt% (21 mol%) (23 : 75 : 2)[a]	5.0 wt% (4.0 mol%) (25 : 73 : 2)[a]
1-Octene/1-Dodecene (1 : 1 mole ratio)	10 wt% (12 mol%) (24 : 74 : 2)[a]	35 wt% (37 mol%) (23 : 75 : 2)[a]	40 wt% (38 mol%) (22 : 76 : 2)[a]	15 wt% (13 mol%) (24 : 74 : 2)[a]
1-Octene/1-Dodecene (1 : 2 mole ratio)	3.0 wt% (4.0 mol%) (23 : 75 : 2)[a]	19 wt% (22 mol%) (23 : 75 : 2)[a]	44 wt% (44 mol%) (21 : 77 : 2)[a]	34 wt% (30 mol%) (23 : 75 : 2)[a]

[a]Ratio of the three signals in each fraction.

Figure S1. SimDis GC chart for 1-octene trimerization performed at 80 °C for 72 h.

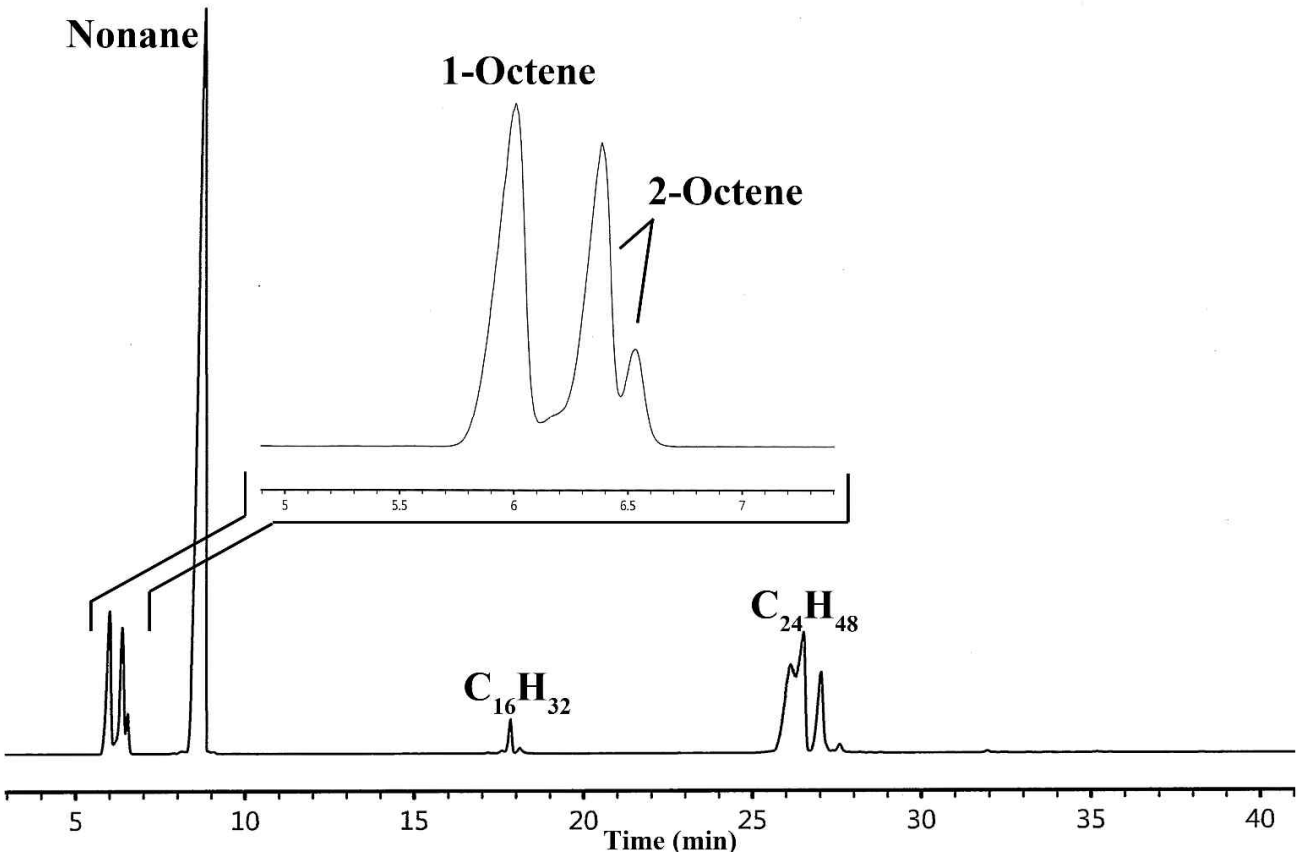

Figure S2. Conversion vs. time for 1-octene, 1-decene, and 1-dodecene trimerization performed at 60 °C.

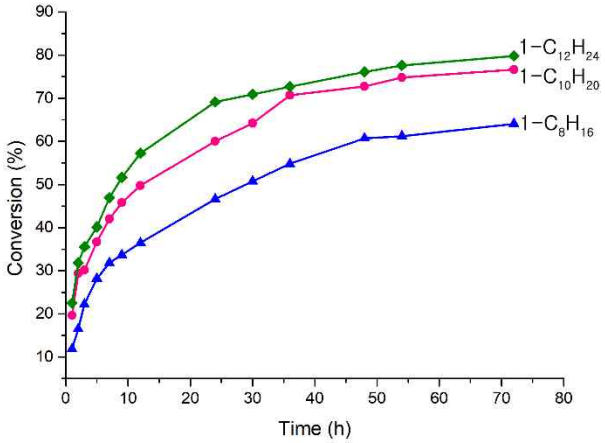

Figure S3. ^{1}H NMR spectra of 1-octene, 1-decene, and 1-dodecene trimers.

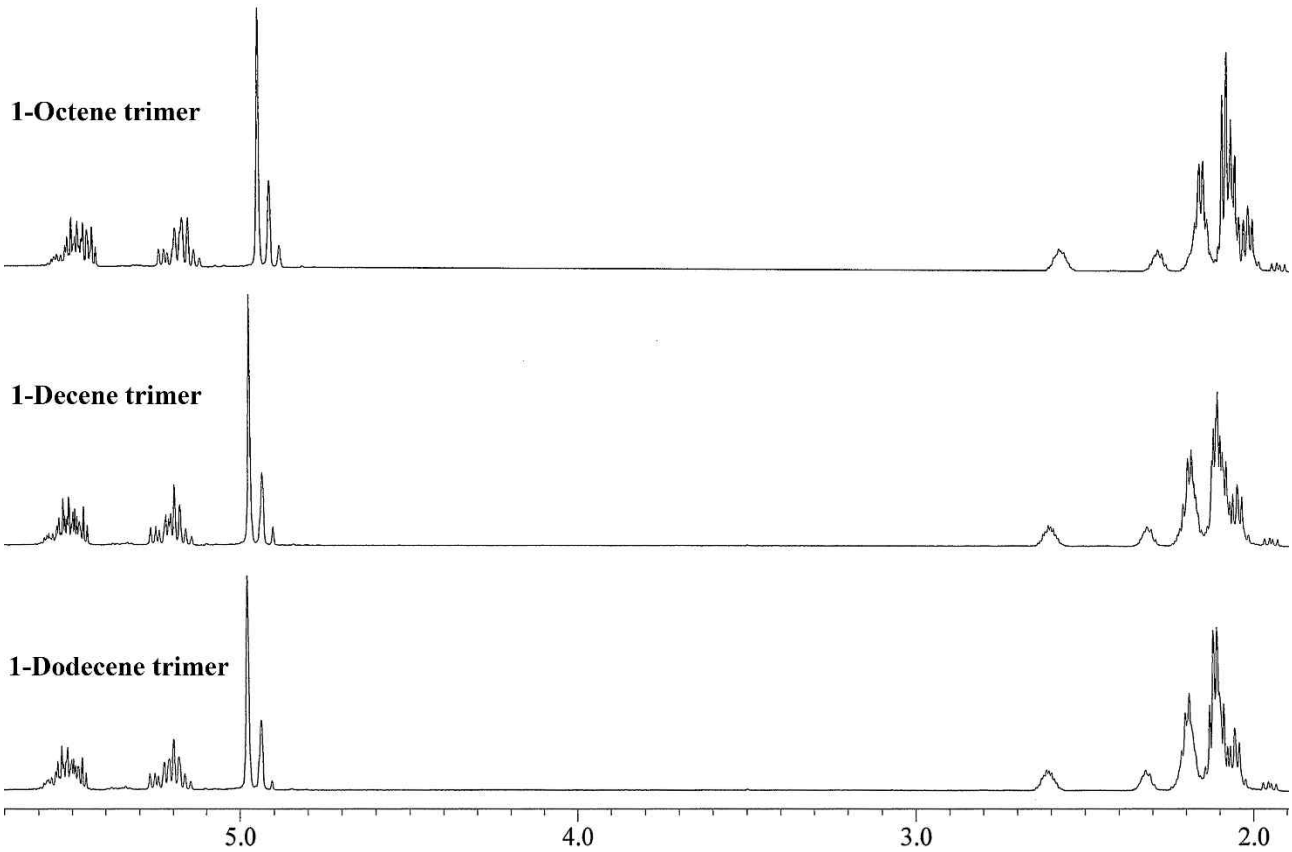

Figure S4. ^{1}H NMR spectra before and after hydrogenation of 1-octene trimer.