

## Supplementary Materials for

### **Efficient and selective degradation of polyethylenes into liquid fuels and waxes under mild conditions**

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## Supplementary Materials and Methods

### 1. General Considerations

All air-sensitive manipulations were carried out using standard Schlenk technique, or in an argon glovebox. Toluene and *n*-pentane were purified with solvent purification system. *n*-Hexane and *n*-octane were purchased from Alfa-Aesar, dried with Na, and distilled under argon. Petroleum ether was purchased from Acros and dried with LiAlH<sub>4</sub>, and distilled under argon.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was purchased from Strem, and calcined as previously reported (23). Ammonium perchlorate was purchased from Alfa-Aesar and used as received. [Ir(cod)Cl]<sub>2</sub> (35), [Ir(coe)<sub>2</sub>Cl]<sub>2</sub> (36), (*t*-BuPCP)IrH<sub>2</sub> (37), (*t*-Bu<sub>2</sub>PO-*t*-BuPOCOP)Ir(C<sub>2</sub>H<sub>4</sub>) (23), and 5 wt% Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (18) were prepared as previously reported.

NMR spectra were recorded on Varian 300 or 400 MHz and Agilent 400 MHz spectrometer at ambient temperature. The residual peak of deuterated solvent was used as a reference for <sup>1</sup>H and <sup>13</sup>C chemical shifts. <sup>31</sup>P NMR chemical shifts were referenced to an external 85% H<sub>3</sub>PO<sub>4</sub> standard. GC analysis was acquired on Agilent 7820A or 7890A gas chromatograph equipped with a flame-ionization detector. GC yields were calculated using mesitylene as an internal standard. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). High temperature gel permeation chromatography (GPC) was performed on Agilent PL-GPC 220 using GPC method A (SIOC) or GPC method B (UCI). GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) (stabilized with BHT) with a flow rate of 1.00 mL/min. The samples were prepared as 1.0 mg/mL in TCB. GPC data were calibrated with narrow polyethylene standards.

#### 1.1. GC Method

Column: Agilent HP-5, 100% dimethylpolysiloxane; 30 m length x 0.32 mm ID x 0.25 $\mu$ m film thickness.

Detector: FID

Starting temperature: 40 °C

Time at starting temperature: 5 min

Ramp: 20 °C/min

Ending temperature: 320 °C

Flow rate: 1 mL/min (N<sub>2</sub>)

Split ratio: 196

Inlet temperature: 250 °C

Detector temperature: 300 °C

## 1.2. GPC Method A

Column: MIXEDB + 2MIXEDD

Solvent: 1,2,4-trichlorobenzene

Flow rate: 1.00 mL/min

Detector: RI

Temperature: 135 °C

## 1.3. GPC Method B

Column: 2MIXEDC

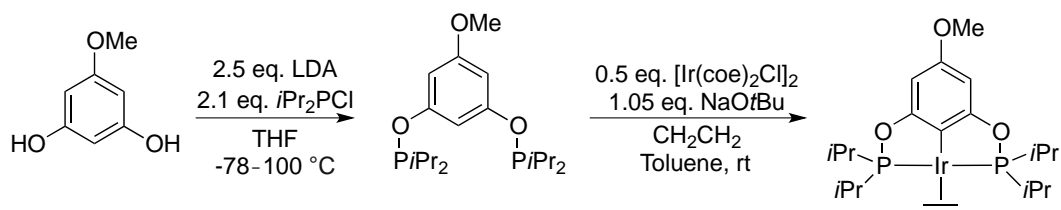
Solvent: 1,2,4-trichlorobenzene

Flow rate: 1.00 mL/min

Detector: RI

Temperature: 140 °C

## 2. Synthesis of (MeO-<sup>i</sup>PrPOCOP)Ir(C<sub>2</sub>H<sub>4</sub>) (3)



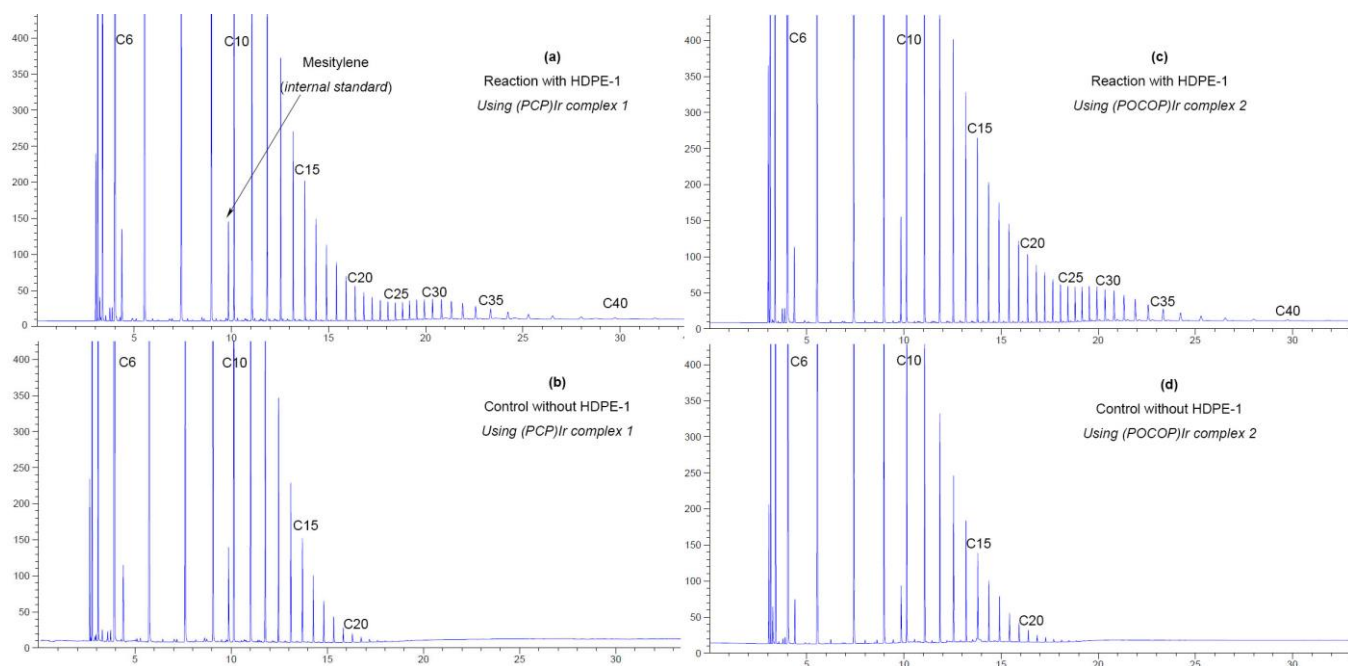
**((5-methoxy-1,3-phenylene)bis(oxy))bis(diisopropylphosphine) (MeO-<sup>i</sup>PrPOCOP):** A 100 mL Kontes flask was charged with 5-methoxybenzene-1,3-diol (1 g, 7.1 mmol) and 30 mL THF. Lithium diisopropylamide (9 mL, 2 M, 18 mmol) was added slowly to the solution at -78 °C. The solution stirred for 1 h, and *i*Pr<sub>2</sub>PCl (2.4 mL, 15 mmol) was added slowly at -78 °C. The flask was then sealed with a Teflon plug and heated at 100 °C for 3 h. After that, the solution was cooled to room temperature and the volatiles were removed under vacuum. The residue was treated with 30 mL of hexane, and the solution was cannula transferred and filtered through a pad of Celite. After removal of hexane under vacuum, the flask was heated at 70 °C for 1 h under vacuum to remove the remaining di-*iso*-propylchlorophosphine. The product was obtained as colorless viscous oil (2.0 g, 75% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.14 (s, 1H), 6.71 (s, 2H), 3.30 (s, 3H), 1.74 (m, 4H), 1.13 (dd, *J* = 10.5, 7.0 Hz, 12H), 0.97 (dd, *J* = 15.8, 7.2 Hz, 12H). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ 146.8. These spectroscopic data correspond to the reported data (38).

**(MeO-<sup>i</sup>PrPOCOP)Ir(C<sub>2</sub>H<sub>4</sub>) (3):** A 100 mL Kontes flask was charged with MeO-<sup>i</sup>PrPOCOP (0.299 g, 0.63 mmol), [Ir(coe)<sub>2</sub>Cl]<sub>2</sub> (0.284 g, 0.315 mmol), NaOtBu (67 mg, 0.69 mmol), and toluene (30 mL). The flask was sealed with a

Teflon plug and stirred at 25 °C for 24 h under an ethylene atmosphere. Following that, the solution was filtered and the filtrate was collected. The removal of the solvent gave the crude product **3**, which was recrystallized in hexane to afford pure product **3** (186 mg, 50% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.69 (s, 2H), 3.39 (s, 3H), 2.73 (t, *J* = 2.6 Hz, 4H), 2.27 (m, 4H), 1.15-1.00 (m, 24H). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ 182.6. <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 166.8 (t, *J* = 9.8 Hz), 160.3, 134.2 (m), 91.7 (t, *J* = 6.8 Hz), 55.0, 34.0, 32.4 (t, *J* = 14.3 Hz), 30.7 (t, *J* = 15.9 Hz), 17.8 (t, *J* = 2.7 Hz), 17.2. Elemental analysis calcd for C<sub>19</sub>H<sub>33</sub>IrO<sub>3</sub>P<sub>2</sub> (564.15): C, 42.63; H, 6.30. Found: C, 42.59; H, 6.57.

### 3. Procedure for Table 1

A 10 mL thick-wall Kontes flask was charged with iridium complex (20 μmol), *n*-hexane (3.0 mL, 7.7 M), and γ-Al<sub>2</sub>O<sub>3</sub> (506 mg). The solution was stirred and after the solution turned colorless, 5 wt% Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (546 mg, 57 μmol Re<sub>2</sub>O<sub>7</sub>), HDPE-1 (120 mg) and mesitylene (20 μL) as internal standard were added. In entries 2 and 4, HDPE-1 was not added. In entries 1 and 2, *tert*-butylethylene (40 μmol) was added as the hydrogen acceptor. The flask was sealed with a Teflon plug and then heated at 150 °C for 3 days. After that, an aliquot was removed from the flask and analyzed by GC. The concentrations of soluble products were calculated for each aliquot. The residual solution was filtered at 160 °C and washed with *n*-octane. The filtrates were combined and cooled to room temperature. The wax products precipitated from the solution and were separated by centrifugation.



**fig. S1.** GC traces for the reactions of HDPE-1 with Ir complex 1 or 2, and the control experiments without HDPE-1. The GC traces for (a) the reaction with HDPE-1 and (PCP)Ir complex 1 (Table 1, entry 1); (b) the control with (PCP)Ir complex 1 in the absence of HDPE-1 (Table 1, entry 2); (c) the reaction with HDPE-1 and (POCOP)Ir complex 2 (Table 1, entry 3); (d) the control with (POCOP)Ir complex 2 in the absence of HDPE-1 (Table 1, entry 4) after 3 days at 150 °C.

### 3.1. Testing the Recyclability of Olefin Metathesis Catalyst

The olefin metathesis catalyst ( $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) can be recycled after the degradation reaction. After completion of the polyethylene degradation reaction and separation of the wax products, the remaining  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  and adsorbed iridium catalyst was collected. The solid was washed with toluene, ultrasonicated and reactivated at high temperature following a literature procedure (5). To test the activity of the recycled catalyst, a 10 mL thick-wall Kontes flask was charged with  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (100 mg), 1-octene (200  $\mu\text{L}$ ), toluene (1 mL) as solvent, and mesitylene (10  $\mu\text{L}$ ) as an internal standard. The flask was sealed with a Teflon plug and then heated at 175  $^\circ\text{C}$  for 12 h. After that, an aliquot was removed from the flask, and analyzed by GC. GC analysis indicated there was a 97% conversion of 1-octene into the metathesis products (fig. S2).

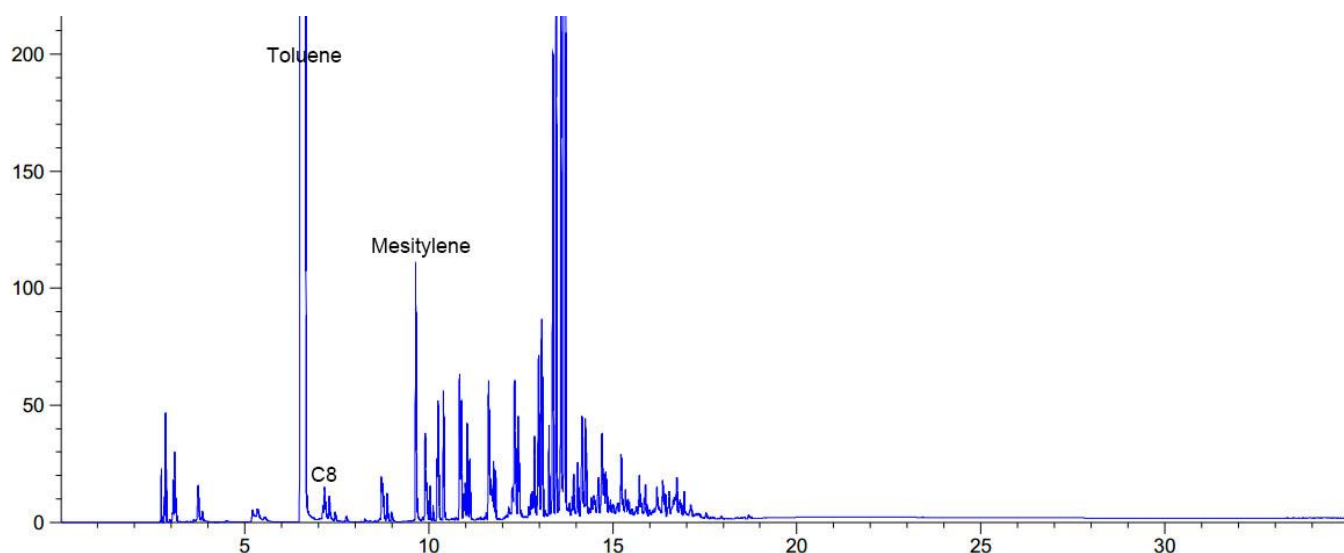


fig. S2. GC trace for the reaction of 1-octene with recycled  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  in toluene after 12 hours at 175  $^\circ\text{C}$ .

### 3.2. Testing the Recyclability of Alkane Dehydrogenation Catalyst

The alkane dehydrogenation catalyst (POCOP)Ir complex **2** could be recycled after the degradation reaction. A 10 mL thick-wall Kontes flask was charged with iridium complex **2** (4.2  $\mu\text{mol}$ ), *n*-octane (2.5 mL), 5 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (546 mg), HDPE-2 (*M*<sub>w</sub>: 124,000, 120 mg), and mesitylene (20  $\mu\text{L}$ ) as an internal standard. The flask was sealed with a Teflon plug and then heated at 175  $^\circ\text{C}$  for 2 days. After that, the catalysts were easily separated by removal of the solution with syringe and the solid was washed 5 times with *n*-octane under Ar. After removal of volatiles under vacuum, fresh cyclooctane (COA, 16.8 mmol) and *t*-butylethylene (TBE 8.4 mmol) were added (Note that the transfer dehydrogenation

between COA and TBE is a benchmark reaction for testing the activity of an alkene dehydrogenation catalyst. See ref. 25, 27). The flask was sealed with a Teflon plug and then heated at 200 °C for 8 h. After that, an aliquot was removed from the flask, and analyzed by GC, which indicated a 21% conversion of TBE into *t*-butylethane (TBA, the hydrogen acceptor), corresponding to 420 turnovers relative to Ir. As a comparison, the reaction using fresh catalyst (POCOP)Ir complex **2** (4.2  $\mu$ mol), Al<sub>2</sub>O<sub>3</sub> (546 mg), COA (16.8 mmol) and TBE (8.4 mmol) gave 940 turnovers after the same reaction time. These results showed that the Al<sub>2</sub>O<sub>3</sub>-supported pincer Ir catalyst is recyclable, albeit with reduced catalytic activity.

#### 4. Procedure for the Degradation of Various Polyethylenes

A 10 mL thick-wall Kontes flask was charged with iridium complex (4.2  $\mu$ mol), *n*-octane (2.5 mL or 4.0 mL), 5 wt% Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (546 mg), polyethylene (120 mg), and mesitylene (20  $\mu$ L) as an internal standard. The flask was sealed with a Teflon plug and then heated at 175 °C for 4 days. After that, an aliquot was removed from the flask, and analyzed by GC. The distributions of soluble products were calculated for each aliquot. The residual solution was filtered at 160 °C and washed with *n*-octane. The filtrates were combined and cooled to room temperature. The wax products precipitated from the solution and were separated by centrifugation.

##### 4.1. Control Experiments

###### (a) Control experiment in the absence of any catalyst

A 10 mL thick-wall Kontes flask was charged with polyethylene HDPE-1 ( $M_n$ : 2080, PDI: 1.6) (120 mg), *n*-octane (2.5 mL), and mesitylene (20  $\mu$ L) as internal standard. The flask was sealed with a Teflon plug and then heated in an oil bath at 175 °C for 4 days. After that, an aliquot was removed from the flask, and analyzed by GC (fig. S3a). We did not detect any compound except for *n*-octane and mesitylene. The molecular weight of the residual solid is very close to the starting PE materials. These data indicated that polyethylene did not undergo degradation at 175 °C in the absence of the iridium complex and Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>.

###### (b) Control experiment in the absence of the iridium catalyst

A 10 mL thick-wall Kontes flask was charged with 5 wt% Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (546 mg, 57  $\mu$ mol), *n*-octane (2.5 mL), polyethylene HDPE-1 ( $M_n$ : 2080, PDI: 1.6) (120 mg), and mesitylene (20  $\mu$ L) as an internal standard. The flask was sealed with a Teflon plug and then heated in an oil bath at 175 °C for 4 days. After that, an aliquot was removed from the flask, and analyzed by GC (fig. S3b). We did not detect any compound except for *n*-octane and mesitylene. The molecular weight of the residual solid is very close to the starting PE materials. These data indicated that polyethylene

did not undergo degradation at 175 °C in the presence of only the metathesis catalyst  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ .

### (c) Control experiment in the absence of the olefin metathesis catalyst

A 10 mL thick-wall Kontes flask was charged with the iridium complex **2** ( $4.2 \mu\text{mol}$ ), *n*-octane (2.5 mL), polyethylene HDPE-1 ( $M_n$ : 2080, PDI: 1.6) (120 mg), and mesitylene ( $20 \mu\text{L}$ ) as an internal standard. The flask was sealed with a Teflon plug and then heated at in an oil bath at 175 °C for 4 days. After that, an aliquot was removed from the flask, and analyzed by GC (fig. S3c). We did not detect any compound except for *n*-octane, and mesitylene. The data indicated that polyethylene did not undergo degradation at 175 °C in the presence of only the iridium catalyst.

#### 4.1.1. The GC Traces for the Control Experiments

GC traces for the control experiments in the absence of one of the dual catalysts or in the absence of both catalysts. (S3a - S3c)

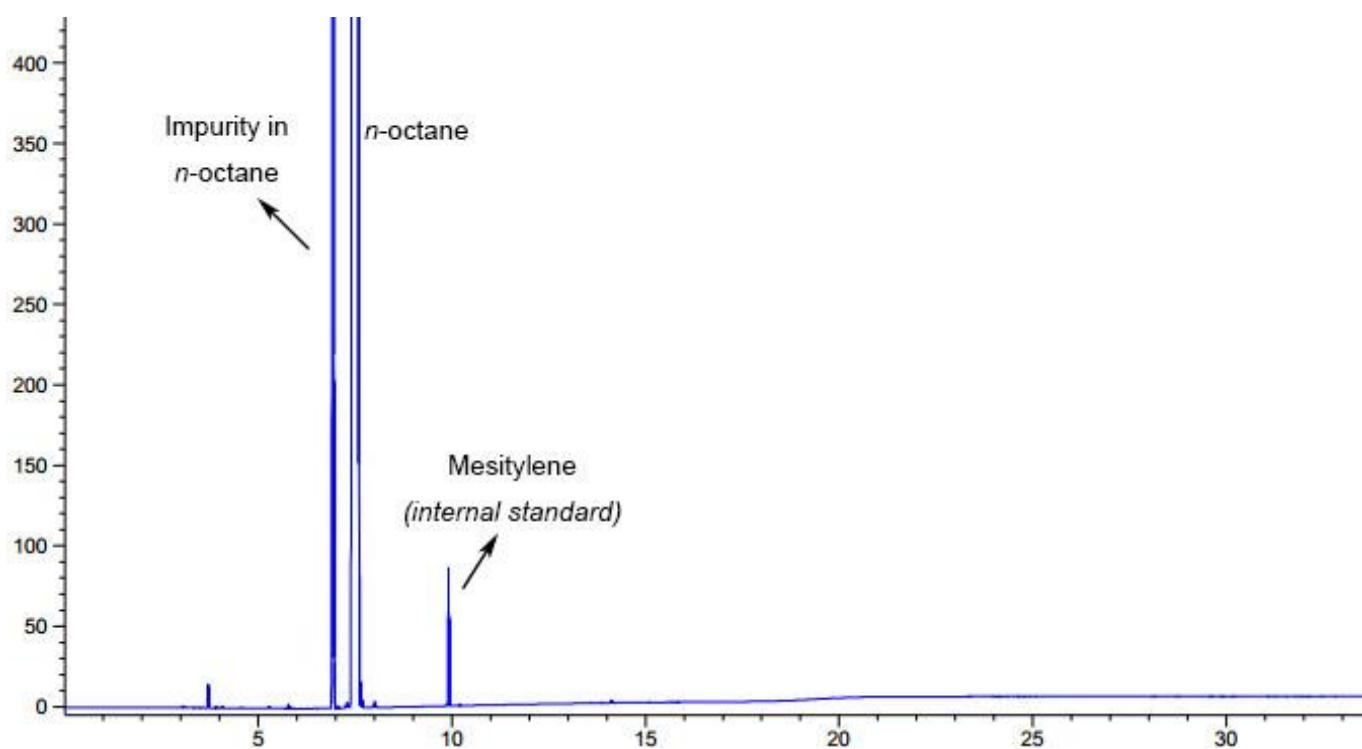
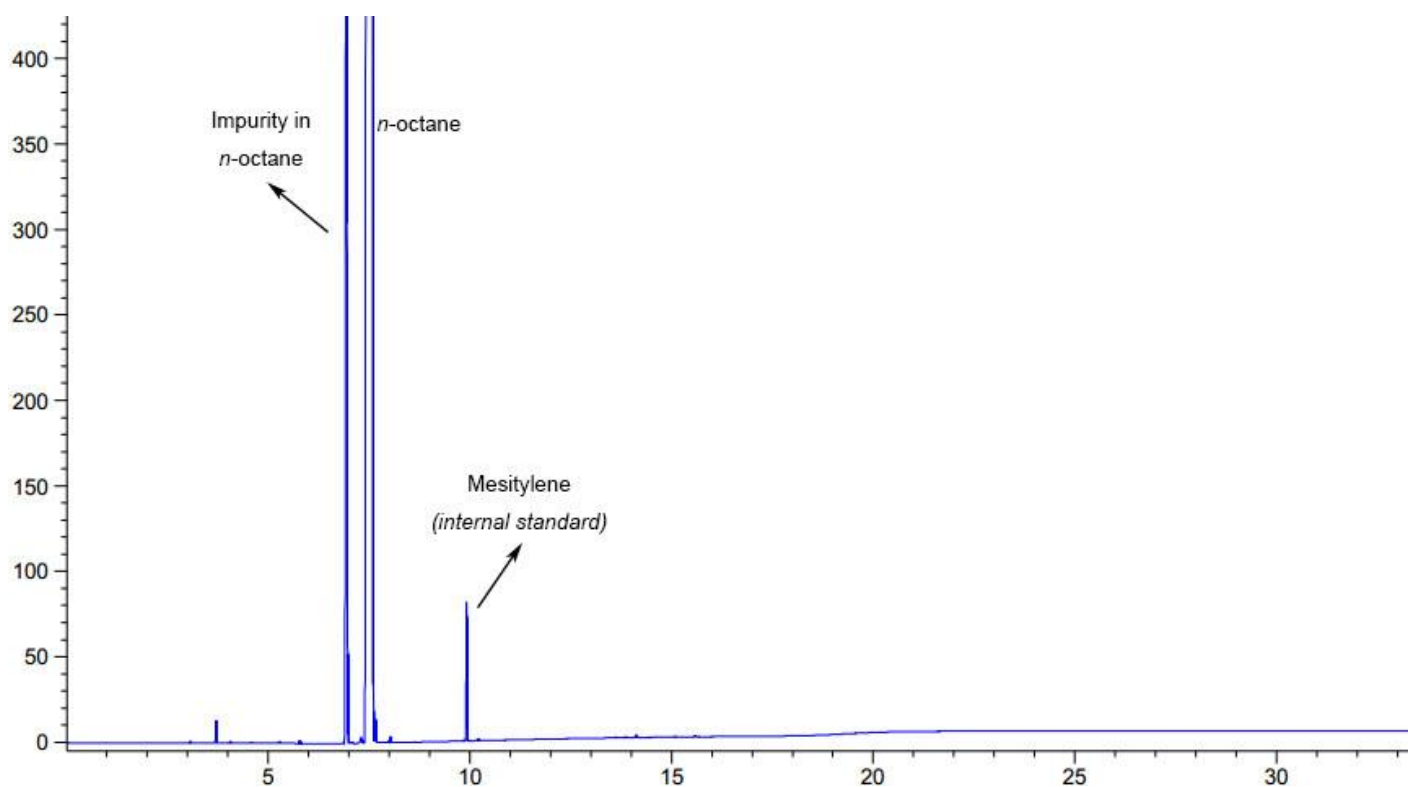
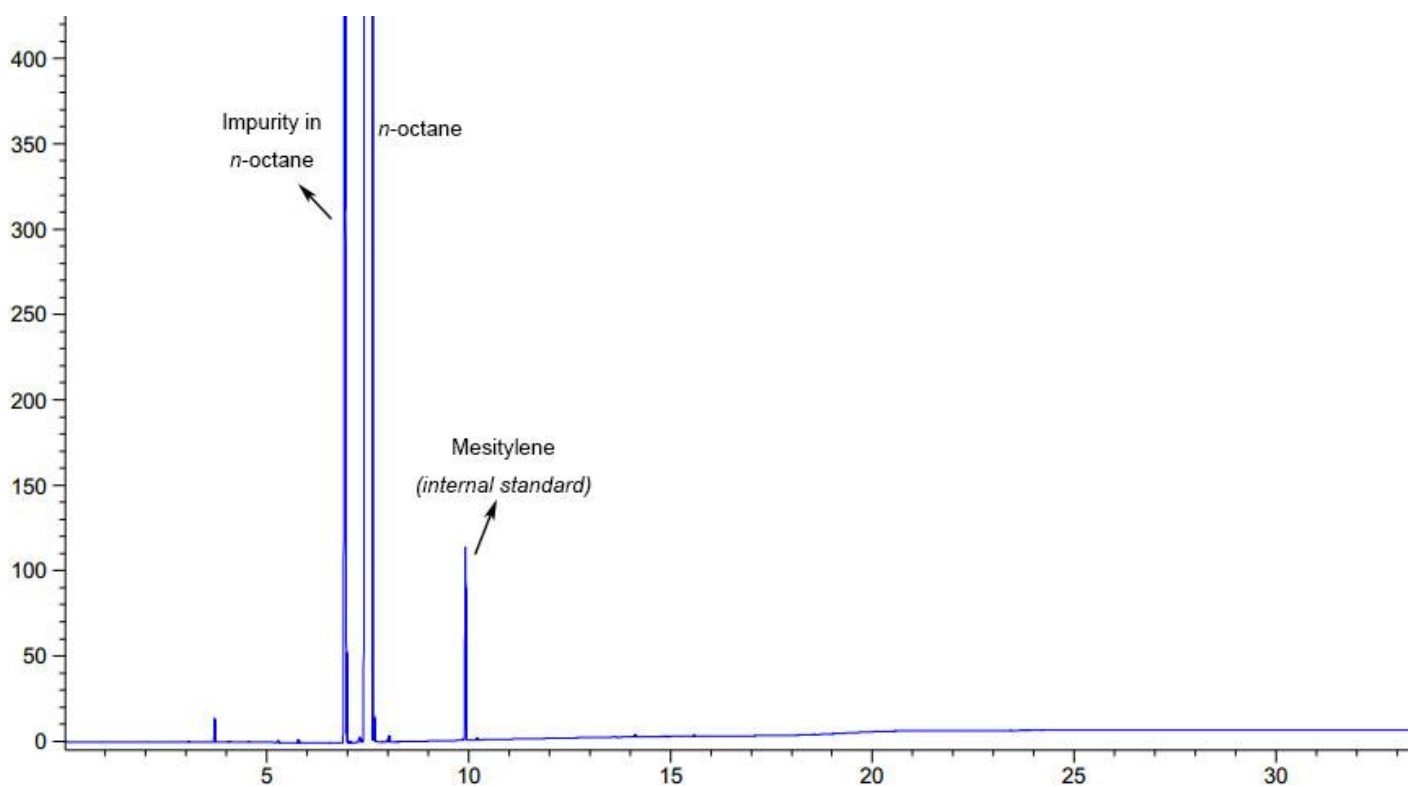


fig. S3a. The GC trace for the control experiment in the absence of any catalyst.



**fig. S3b.** The GC trace for the control experiment in the absence of the iridium catalyst.



**fig. S3c.** The GC trace for the control experiment in the absence of the olefin metathesis catalyst.



## 4.2. The Polyethylene Degradation Products Distributions

**table S1.** Degradation of various grades of polyethylene with *n*-octane (2.5 or 4.0 mL) by [Ir] (4.2  $\mu$ mol) and Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (57  $\mu$ mol Re<sub>2</sub>O<sub>7</sub>): the distribution of *n*-alkane products and conversion of PE to oil products after 4 days at 175 °C.

Entry	Ir. cat.	PE type (quantity in mg)	$M_w$ ( $M_n$ ) [PDI]	Mass (mg)/concentration (mM) of soluble products					Total soluble prod. (g)/(M)	Residual solid (mg)	$M_w$ ( $M_n$ ) [PDI]	Total conv. of PE (percent of PE to oils)
				C <sub>3-7</sub>	C <sub>9-13</sub>	C <sub>14-19</sub>	C <sub>20-25</sub>	>C <sub>25</sub>				
1 <sup>a</sup>	2	HDPE-1 powder (120)	3350 (2080) [1.6]	305/	220/	65/	22/	27/	0.64/	18	680 (500) [1.4]	100% (85%)
				1539	603	117	28	24	2.31			
2 <sup>b</sup>	2	HDPE-2 <sup>c</sup> pellet (120)	12.4 $\times$ 10 <sup>4</sup> (3.2 $\times$ 10 <sup>4</sup> ) [3.9]	312/	289/	81/	23/	31/	0.74/	34	780 (580) [1.3]	100% (72%)
				957	495	91	19	18	1.58			
Added additional 2 (4.2 $\mu$ mol) and Re <sub>2</sub> O <sub>7</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (28 $\mu$ mol Re <sub>2</sub> O <sub>7</sub> )				404/	388/	149/	66/	31/	1.04/	17	630 (470) [1.4]	100% (86%)
				1218	667	165	53	20	2.12			
3 <sup>b</sup>	3	HDPE-2 <sup>c</sup> pellet (120)	12.4 $\times$ 10 <sup>4</sup> (3.2 $\times$ 10 <sup>4</sup> ) [3.9]	208/	245/	79/	21/	17/	0.57/	61	2020 (920) [2.2]	100% (47%)
				624	419	89	17	10	1.16			
4 <sup>b</sup>	2	HDPE-3 <sup>c</sup> pellet (117)	36.5 $\times$ 10 <sup>4</sup> (2.8 $\times$ 10 <sup>4</sup> ) [13.0]	262/	264/	79/	22/	29/	0.66	44	780 (660) [1.2]	100% (62%)
				796	452	89	18	16	1.37			
5 <sup>b</sup>	2	HDPE-4 powder (120)	$M_n$ : 1.74 $\times$ 10 <sup>6</sup>	269/	271/	81/	21/	26/	0.67/	59	890 (690) [1.3]	100% (51%)
				818	464	91	17	15	1.41			
Added additional 2 (4.2 $\mu$ mol) and Re <sub>2</sub> O <sub>7</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (28 $\mu$ mol Re <sub>2</sub> O <sub>7</sub> )				335/	329/	108/	42/	33/	0.85/	34	780 (580) [1.3]	100% (72%)
				1005	563	121	33	20	1.74			
6 <sup>b</sup>	2	LDPE <sup>c</sup> film (120)	9.2 $\times$ 10 <sup>4</sup> (5.1 $\times$ 10 <sup>3</sup> ) [17.9]	281/	252/	54/	15/	22/	0.62/	17	4320 (1070) [4.0]	100% (86%)
				857	434	61	12	13	1.38			
7 <sup>a</sup>	2	LLDPE <sup>c</sup> pellet (120)	7.4 $\times$ 10 <sup>4</sup> (2.5 $\times$ 10 <sup>4</sup> ) [3.0]	271/	236/	71/	22/	31/	0.63/	26	790 (590) [1.3]	100% (77%)
				1335	646	128	28	28	2.16			
8 <sup>a</sup>	3	LLDPE <sup>c</sup> pellet (112)	7.4 $\times$ 10 <sup>4</sup> (2.5 $\times$ 10 <sup>4</sup> ) [3.0]	263/	215/	80/	24/	21/	0.60/	51	2450 (1170) [2.1]	100% (54%)
				1283	584	143	32	19	2.06			
9 <sup>b</sup>	2	Used PE bottle (120)	10.9 $\times$ 10 <sup>4</sup> (1.6 $\times$ 10 <sup>4</sup> ) [6.8]	314/	283/	77/	21/	29/	0.72/	40	860 (640) [1.3]	100% (67%)
				966	485	86	17	16	1.57			
10 <sup>b</sup>	3	Used PE bottle (118)	10.9 $\times$ 10 <sup>4</sup> (1.6 $\times$ 10 <sup>4</sup> ) [6.8]	228/	228/	70/	19/	16/	0.56/	60	1940 (910) (2.1)	100% (49%)
				687	390	79	15	9	1.18			

11 <sup>b</sup>	2	Used PE	21.6×10 <sup>4</sup>	305/	290/	80/	21/	30/	0.73/	34	810	100%
		film	(1.7×10 <sup>4</sup> )	927	498	91	17	17	1.55		(700)	
			[12.7]									
12 <sup>b</sup>	3	Used PE	21.6×10 <sup>4</sup>	231/	225/	66/	17/	14/	0.55/	51	2420	100%
		film	(1.7×10 <sup>4</sup> )	694	385	75	14	8	1.17		(1200)	
			[12.7]									

<sup>a</sup> *n*-Octane (2.5 mL); <sup>b</sup> *n*-Octane (4.0 mL); <sup>c</sup> Polymers contain 1000 ppm of antioxidant 1010, antioxidant 168, and zinc stearate respectively.

#### 4.3. The GPC traces for the wax products (fig. S4a – S4n)

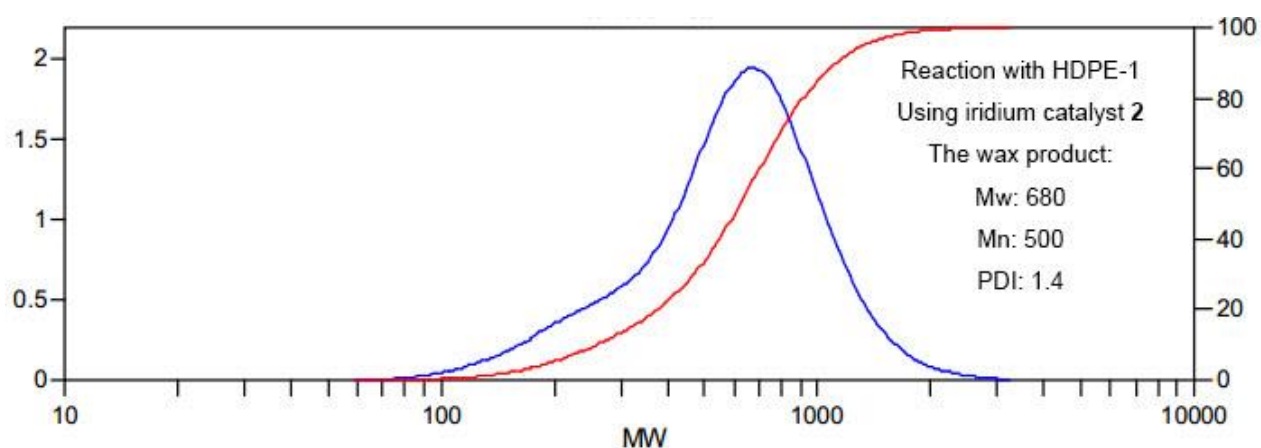


fig. S4a. The GPC trace for the wax product in the entry 1 of table S1 (corresponding to Fig. 2A).

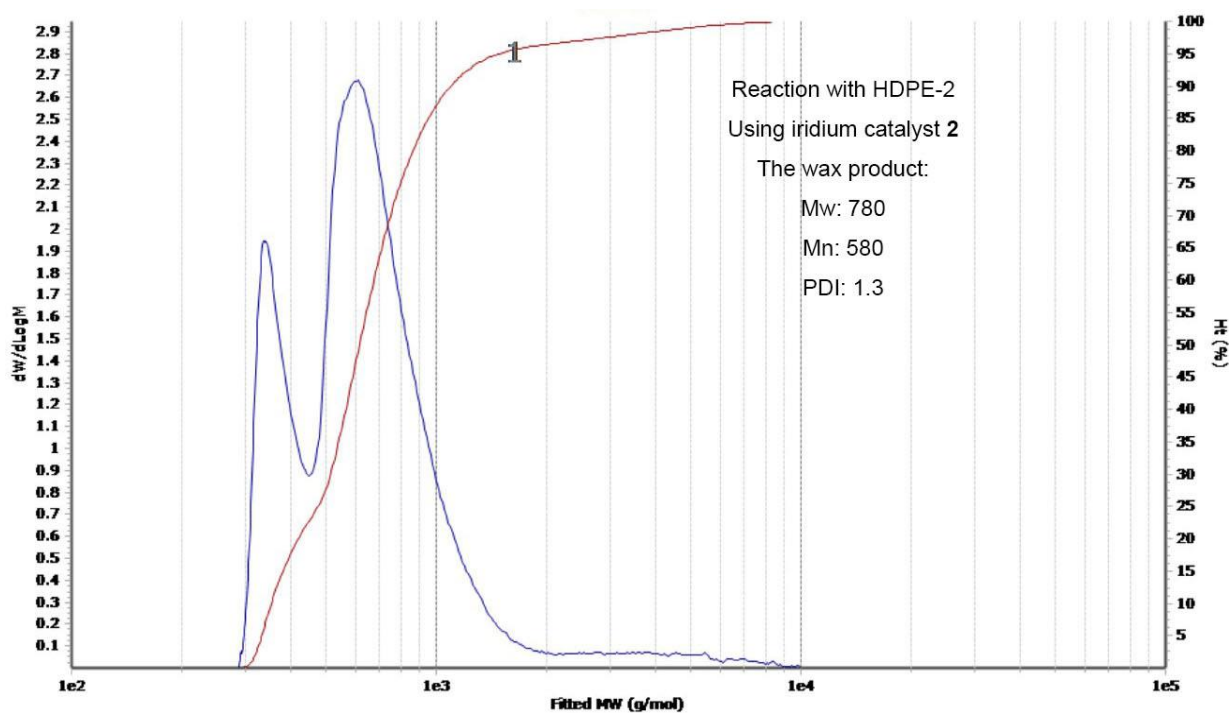


fig. S4b. The GPC trace for the wax product in the entry 2 (under normal conditions) of table S1 (corresponding to Fig. 2B).

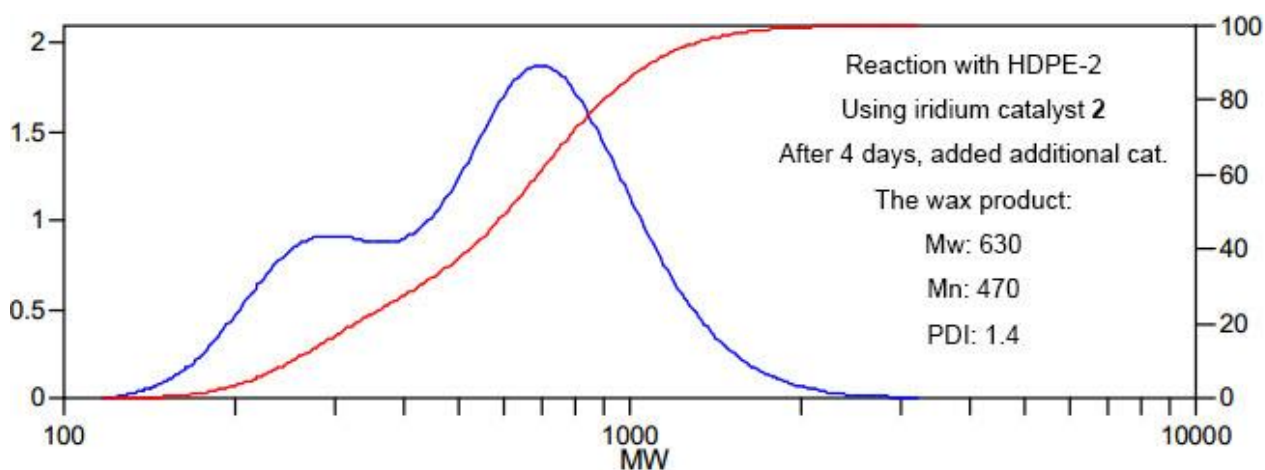


fig. S4c. The GPC trace for the wax product in the entry 2 of table S1 (after 4 days, added additional iridium complex 2 and  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ).

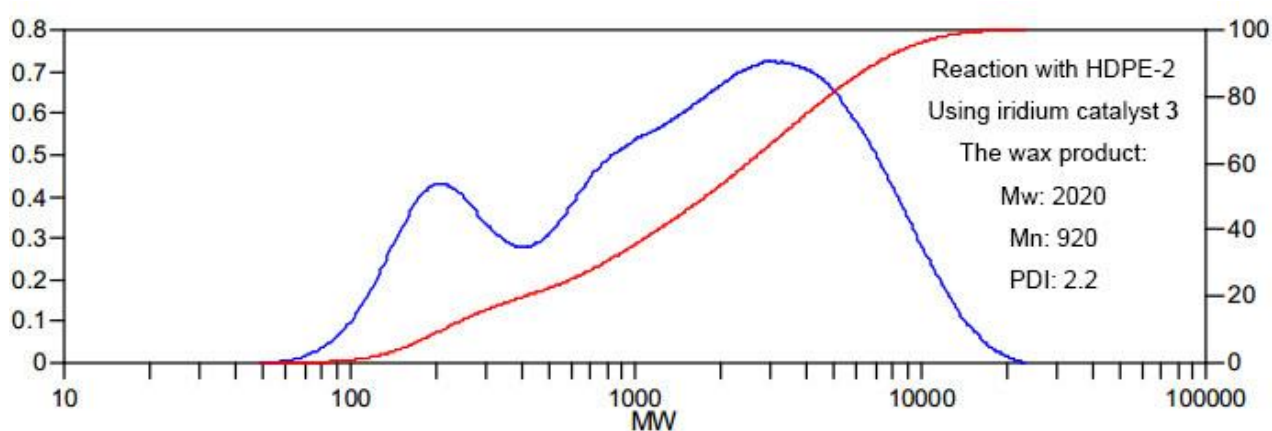


fig. S4d. The GPC trace for the wax product in the entry 3 of table S1.

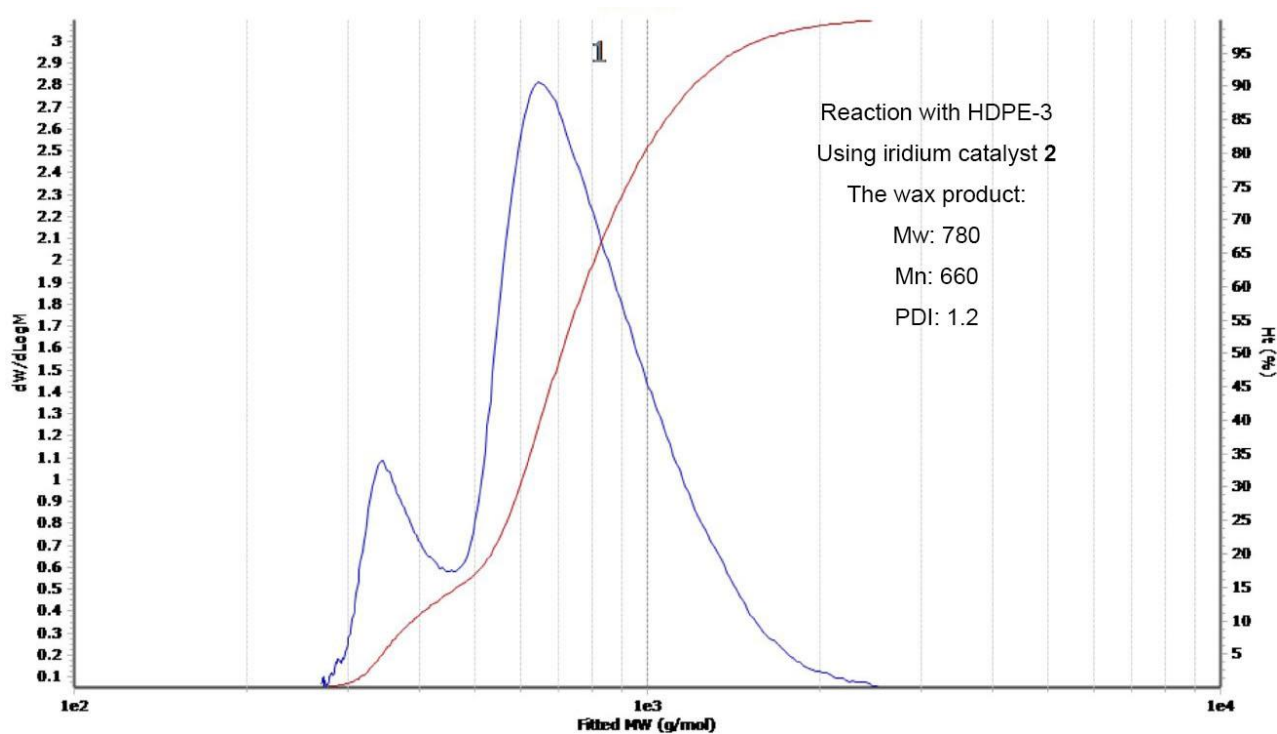


fig. S4e. The GPC trace for the wax product in the entry 4 of table S1 (corresponding to Fig. 2C).

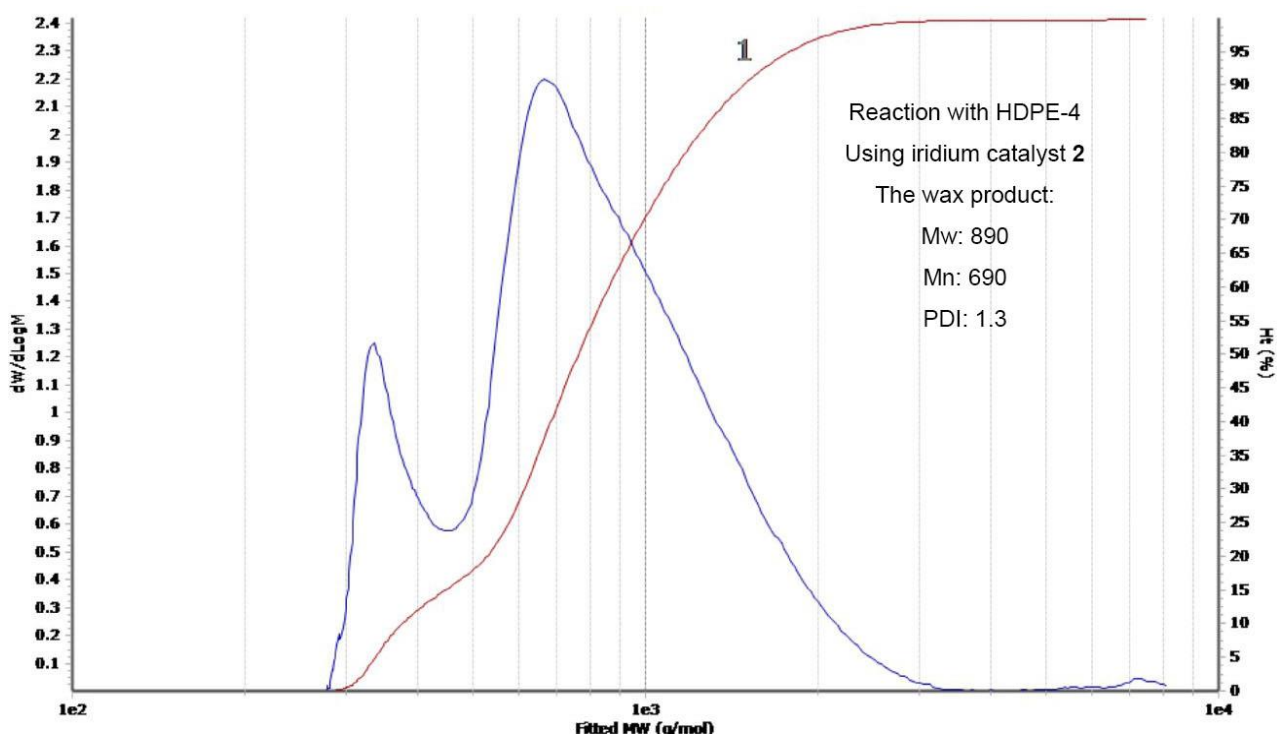


fig. S4f. The GPC trace for the wax product in the entry 5 (under normal conditions) of table S1 (corresponding to Fig. 2D).

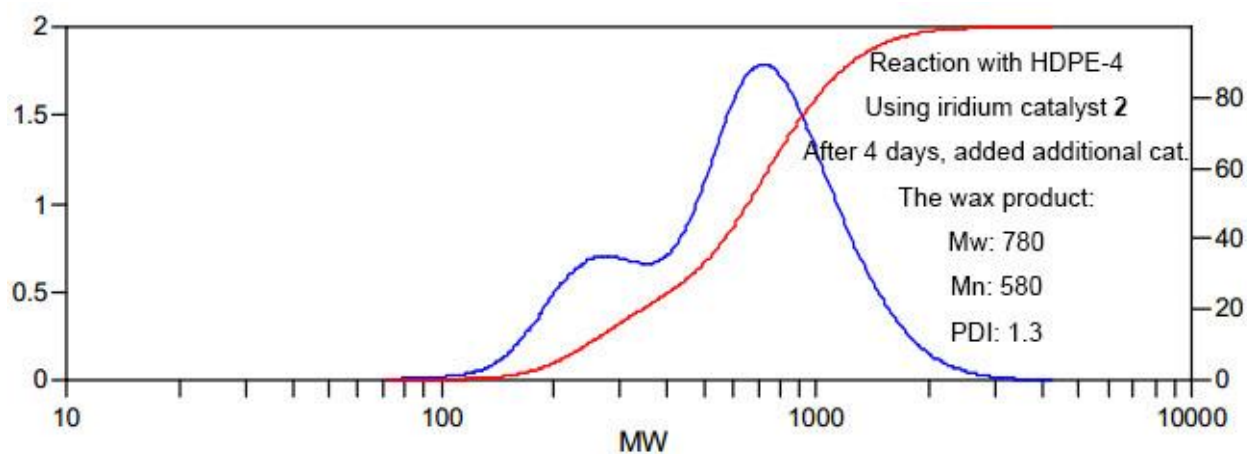


fig. S4g. The GPC trace for the wax product in the entry 5 of table S1 (after 4 days, added additional iridium complex 2 and  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ).

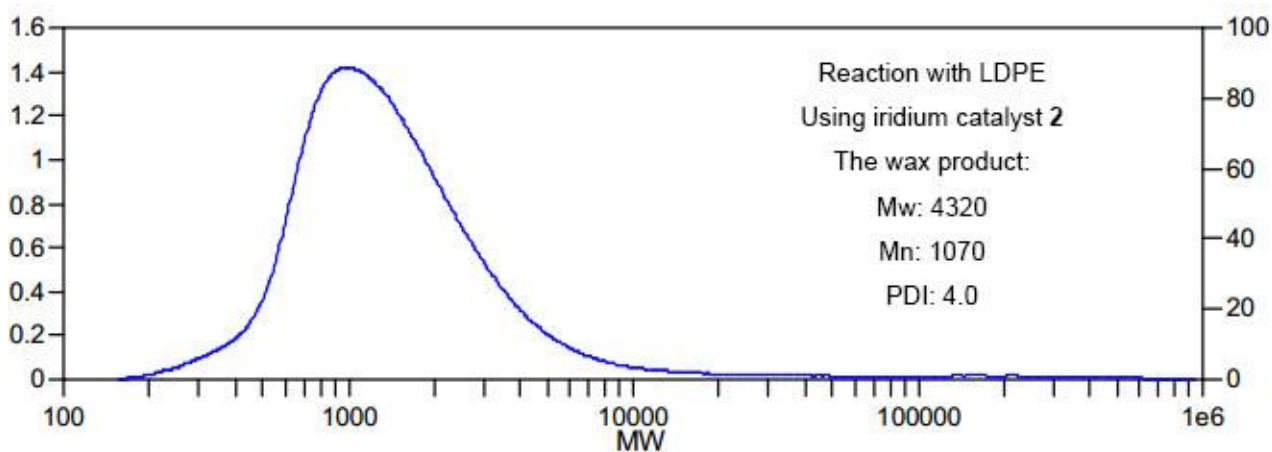


fig. S4h. The GPC trace for the wax product in the entry 6 of table S1 (corresponding to Fig. 2E).

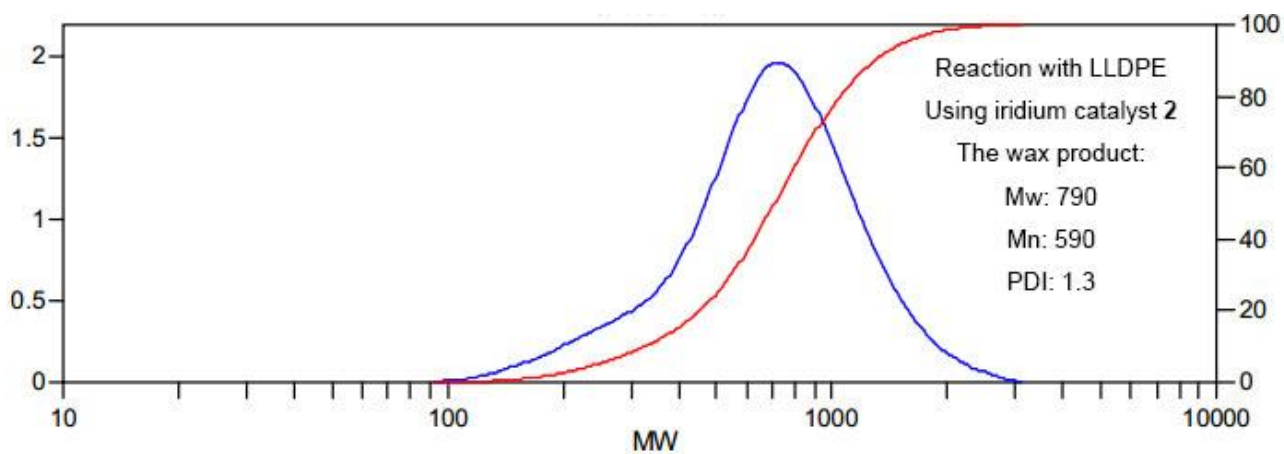


fig. S4i. The GPC trace for the wax product in the entry 7 of table S1 (corresponding to Fig. 2F).

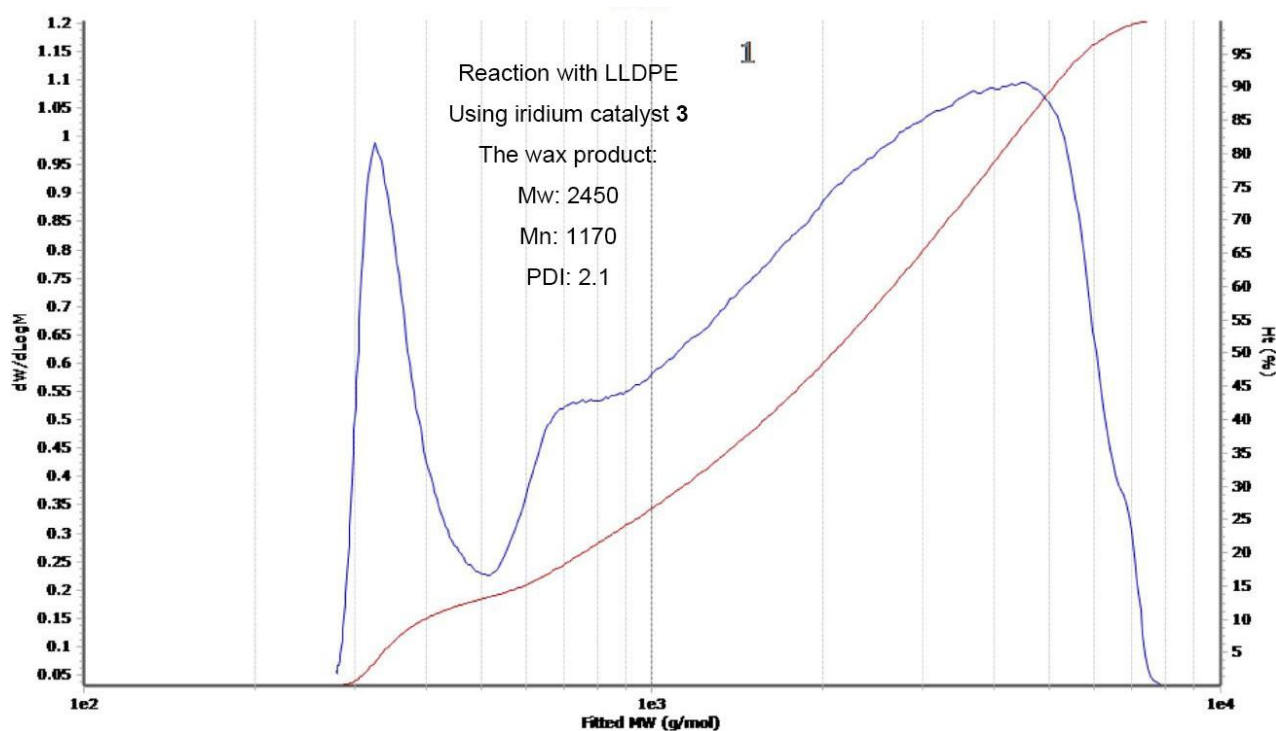


fig. S4j. The GPC trace for the wax product in the entry 8 of table S1.



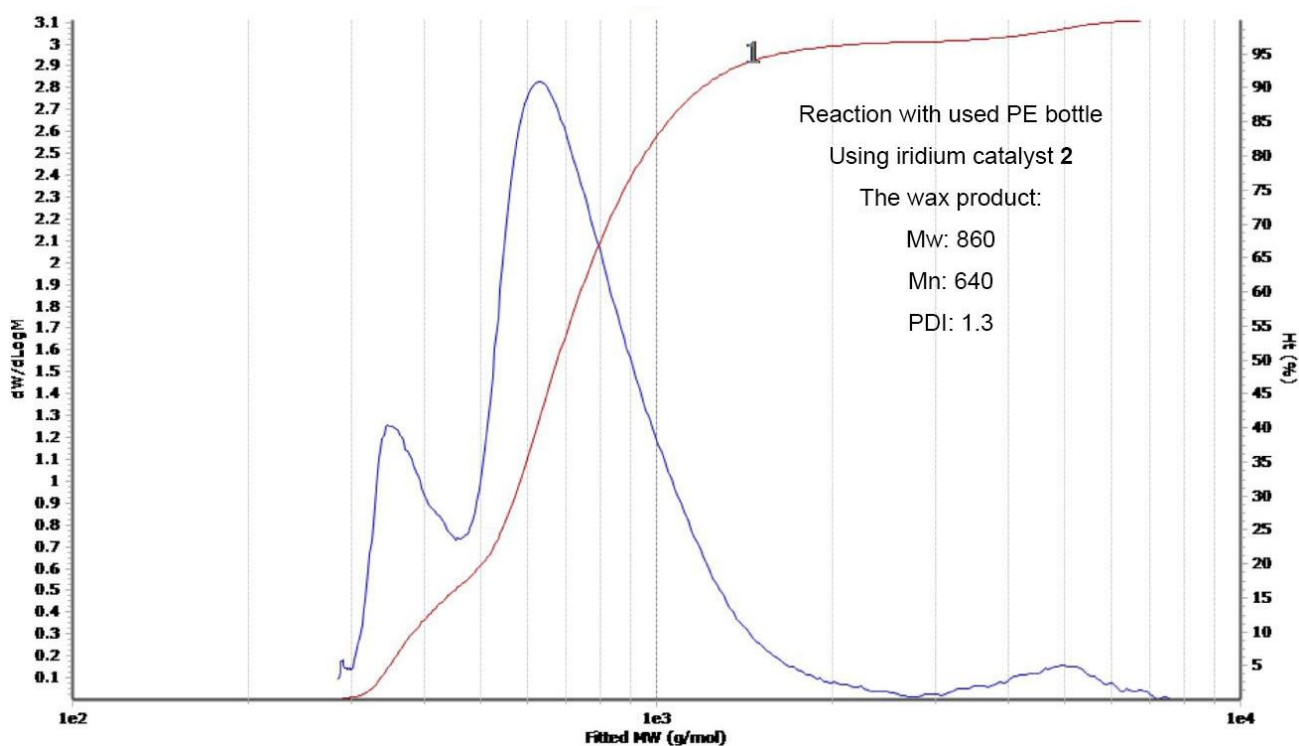


fig. S4k. The GPC trace for the wax product in the entry 9 of table S1 (corresponding to Fig. 2G).

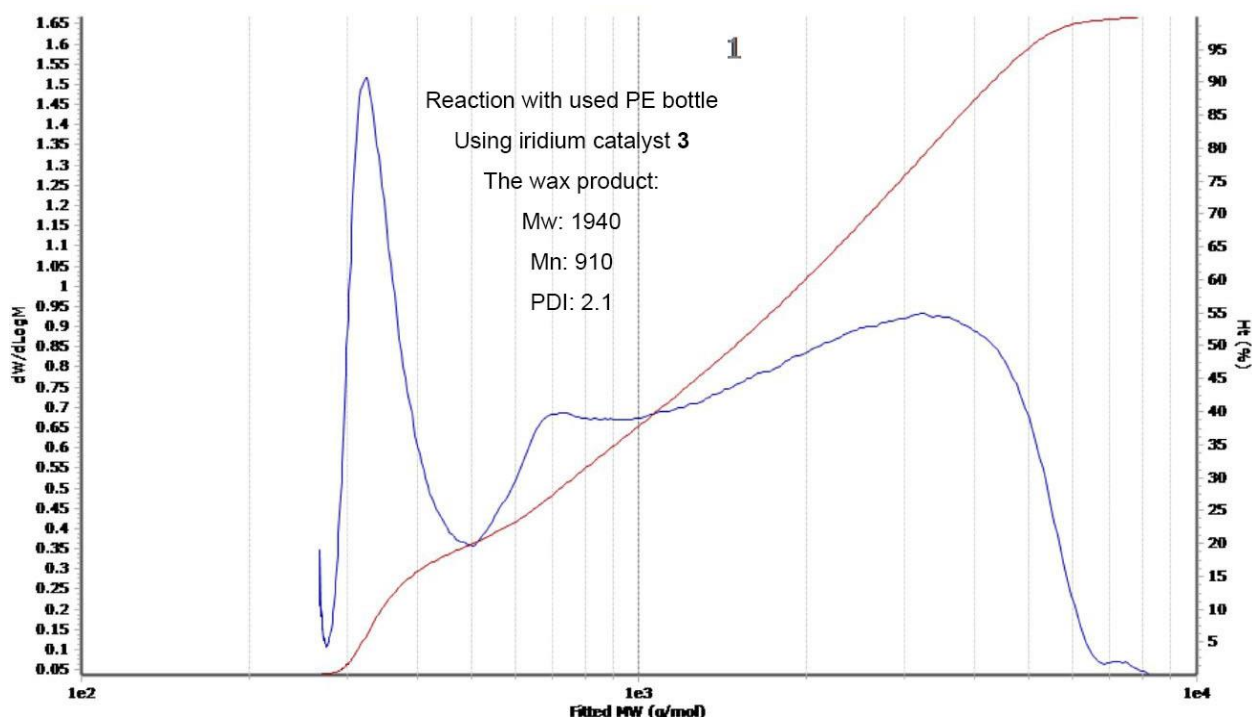


fig. S4l. The GPC trace for the wax product in the entry 10 of table S1.

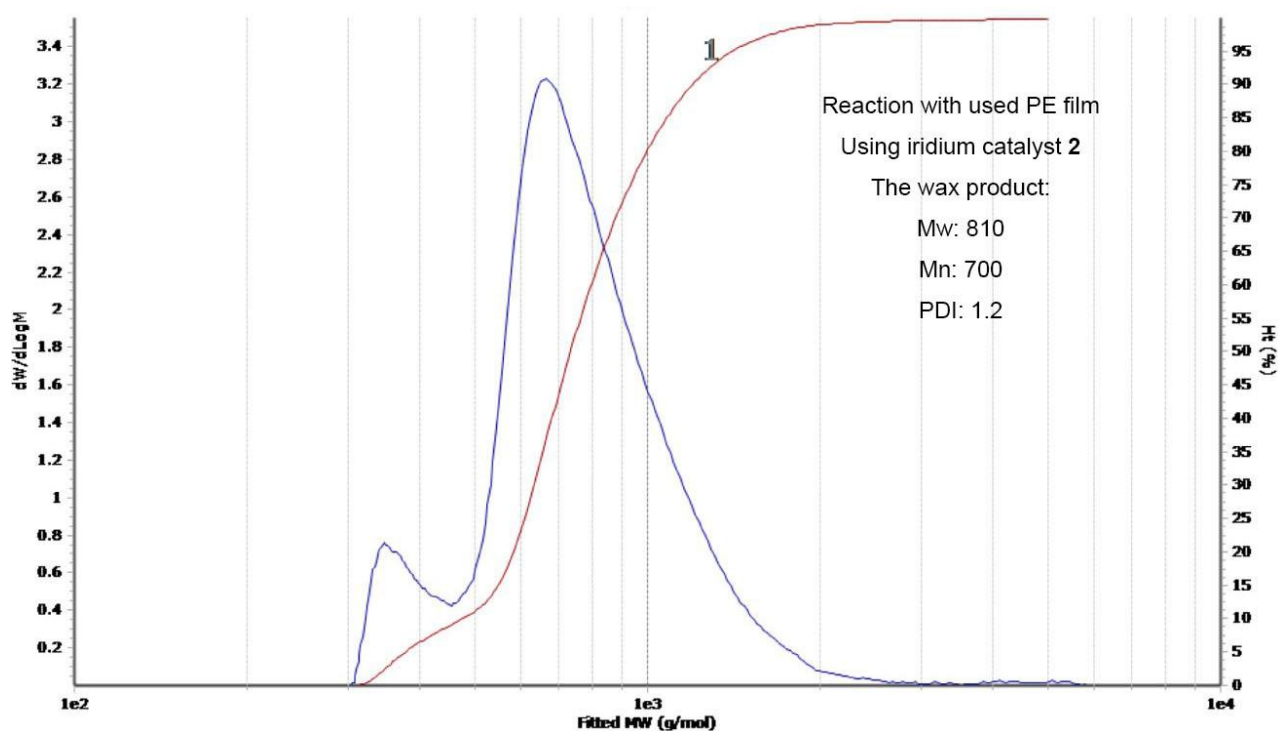


fig. S4m. The GPC trace for the wax product in the entry 11 of table S1 (corresponding to Fig. 2H).

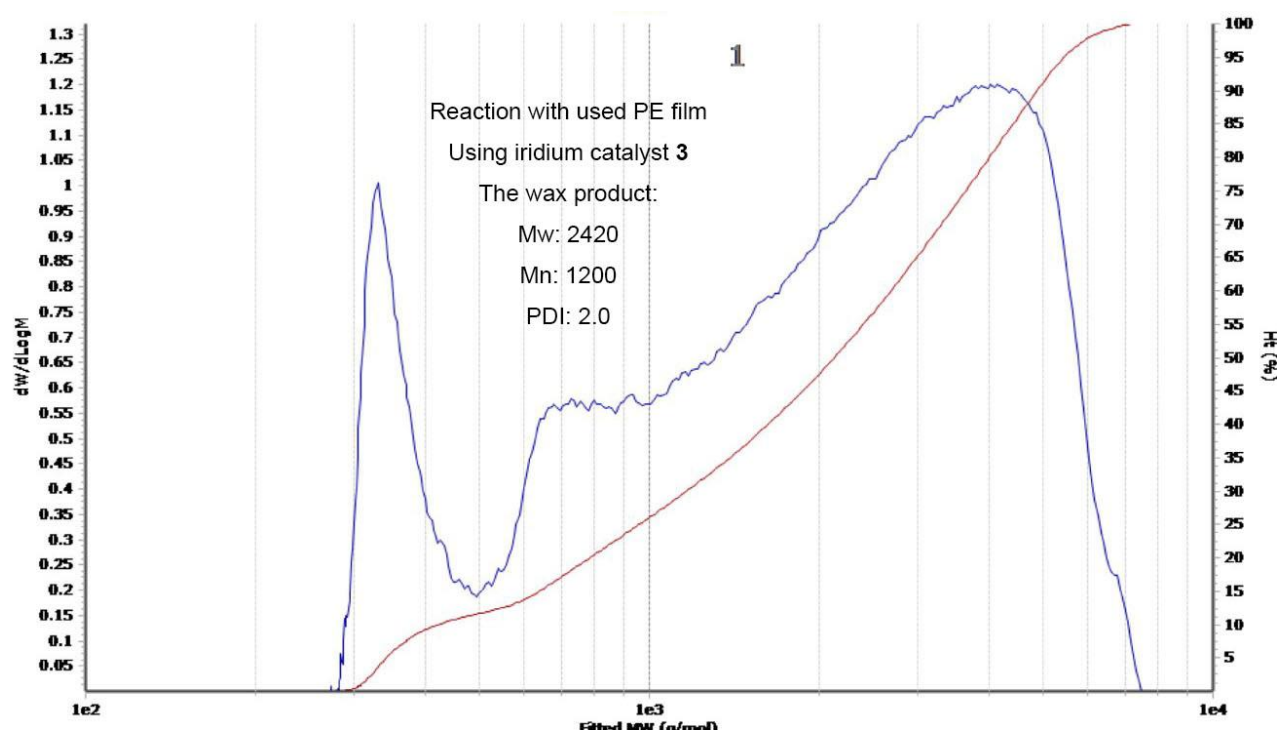


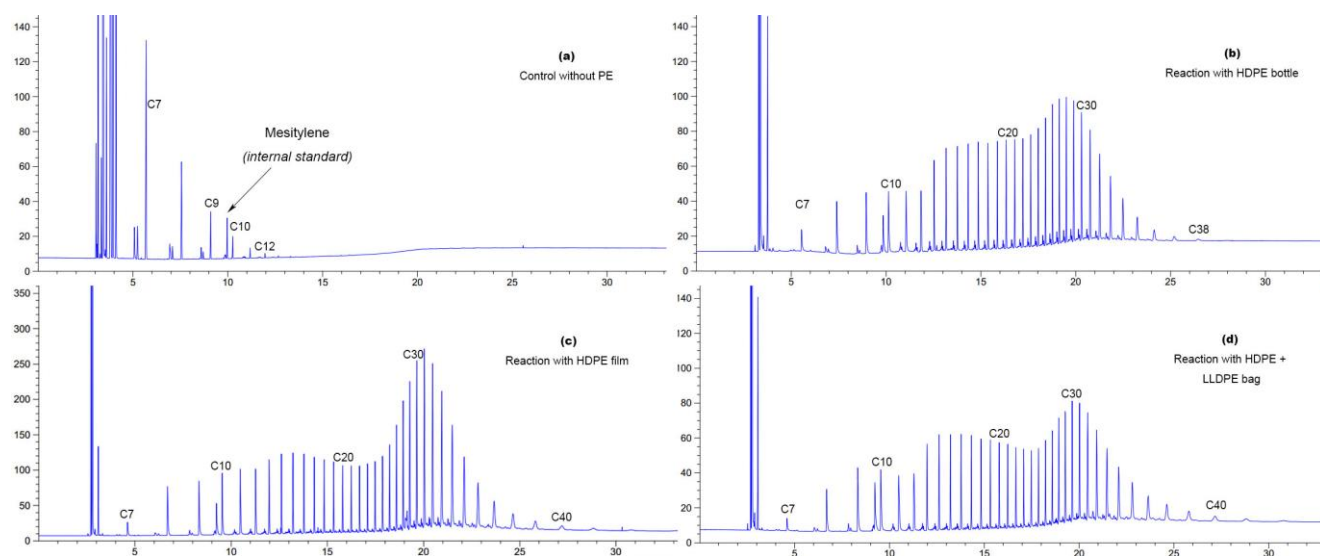
fig. S4n. The GPC trace for the wax product in the entry 12 of table S1 (corresponding to Fig. 2I).

#### 4.4. Experimental procedure for Fig. 3

A 10 mL thick-wall Kontes flask was charged with iridium complex **2** (10  $\mu\text{mol}$ ), petroleum ether (35-60  $^{\circ}\text{C}$  fraction, 8.0 mL), 5 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (819 mg, 86  $\mu\text{mol}$   $\text{Re}_2\text{O}_7$ ), HDPE bottle waste, HDPE film, or grocery shopping bag (LLDPE + HDPE) (0.3 g each), and mesitylene (20  $\mu\text{L}$ ) as an internal standard. The flask was sealed with a Teflon plug and then

heated at 175 °C for 4 days. The solution was filtered at room temperature and washed with *n*-pentane. The filtrates were combined and the volatile C3-C6 alkanes, and part of C7-C8 alkanes were removed by evaporation, and the alkane products in the diesel range and higher alkanes were collected and analyzed by GC.

The residual wax products were separated from the heterogeneous catalysts and alumina by extraction with *n*-octane at 160 °C. The filtrates were combined. The wax products precipitated from the solution at room temperature and were separated by centrifugation.



**fig. S5.** GC traces for the oil products from the degradation of the PE plastic bottle, film, and bag. The GC traces for (a) the reaction liquid of the control experiment with iridium complex **2**,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  and petroleum ether in the absence of polyethylene; (b) the oil products of the reaction with iridium complex **2**,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ , petroleum ether and HDPE bottle; (c) the oil products of the reaction with iridium complex **2**,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ , petroleum ether and HDPE film; (d) the oil products of the reaction with iridium complex **2**,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ , petroleum ether and HDPE + LLDPE bag.

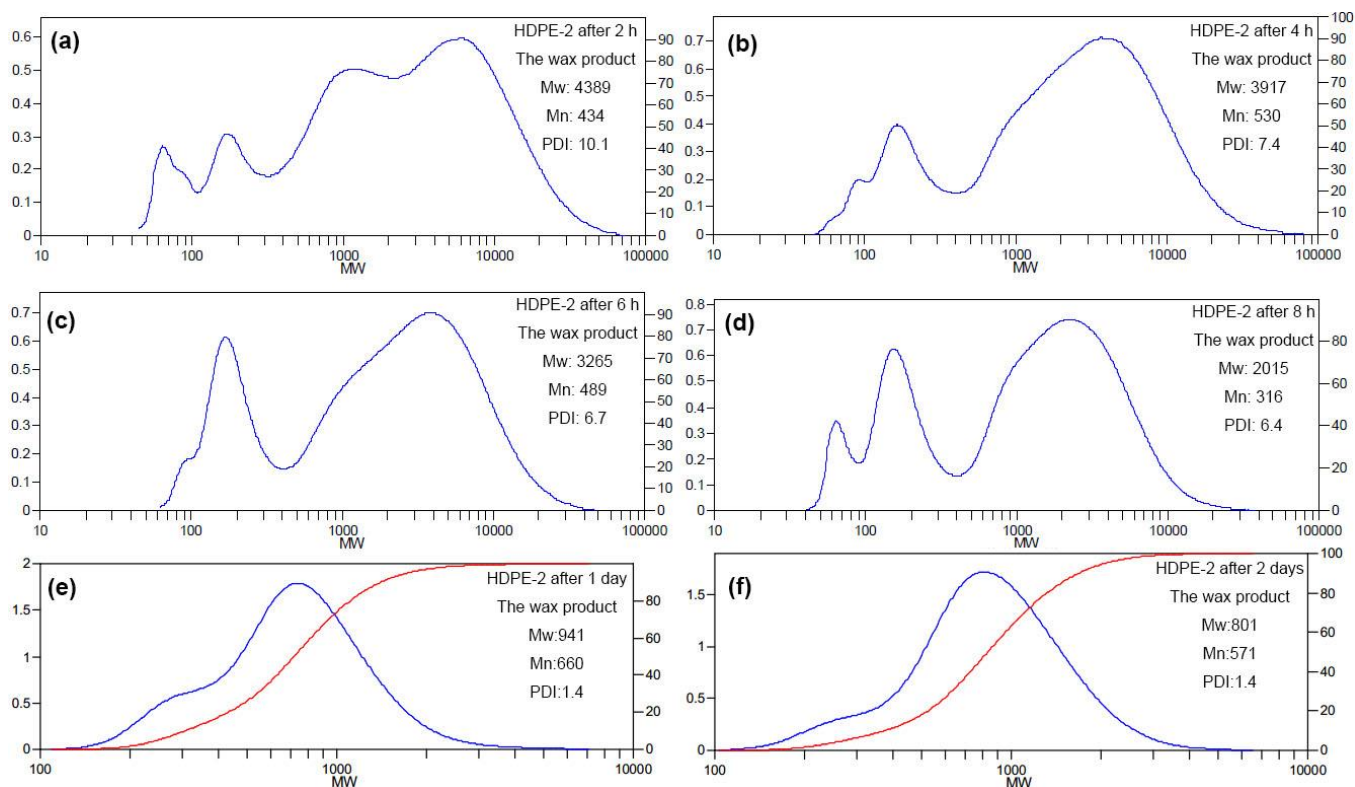


#### 4.5. The Polyethylene Degradation Product Distributions at Different Time Intervals

**table S2.** Degradation of HDPE-2 at different time intervals: the distribution of *n*-alkane products and conversion of PE to oil products.

Entry	Time	PE type (mg)	$M_w$ ( $M_n$ ) [PDI]	Mass (mg)/concentration (mM) of soluble products					Total soluble prod. (g)/(M)	Solid (mg)	$M_w$ ( $M_n$ ) [PDI]	Conv. of PE to oils
				C <sub>3-7</sub>	C <sub>9-13</sub>	C <sub>14-19</sub>	C <sub>20-25</sub>	>C <sub>25</sub>				
1	2 h	HDPE-2 120	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	42/	33/	12/	4/	1/	0.09	97	4389 (434) [10.1]	19%
				130	57	13	3	1	0.20			
2	4 h	HDPE-2 127	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	59/	54/	20/	7/	2/	0.14/	104	3917 530 [7.4]	19%
				177	92	22	6	1	0.30			
3	6 h	HDPE-2 126	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	77/	61/	22/	7/	2/	0.17/	100	3265 (489) [6.7]	21%
				237	106	24	6	1	0.37			
4	8 h	HDPE-2 128	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	123/	110/	37/	10/	4/	0.28/	98	2015 (316) [6.4]	23%
				378	187	42	8	3	0.62			
5	1 d	HDPE-2 132	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	195/	245/	75/	23/	24/	0.56/	63	941 (660) [1.4]	52%
				567	420	48	19	14	1.10			
6	2 d	HDPE-2 135	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	311/	294/	85/	29/	35/	0.76/	49	801 (571) [1.4]	64%
				944	504	90	19	15	1.57			
7	4 d	HDPE-2 120	12.4×10 <sup>4</sup> (3.2×10 <sup>4</sup> ) [3.9]	312/	289/	81/	23/	31/	0.74/	34	780 (580) [1.3]	72%
				957	495	91	19	18	1.58			

*n*-Octane (4.0 mL), 175 °C.



**fig. S6. GPC traces for the wax products obtained from the reaction with HDPE-2 after 2, 4, 6, 8, 24, 48, and 96 hours.** The GPC traces for the wax products in the reaction with HDPE-2 at 175°C (a) after 2 h; (b) after 4 h; (c) after 6 h; (d) after 8 h; (e) after 1 day; (f) after 2 days.