Supporting Information

Palladium-catalyzed polar solvent empowered synthesis of hyperbranched ethylene oligomers and their application

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1. General methods and materials:

Unless noted otherwise, all manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or M-Braun glove box. Toluene, diethyl ether, 1,4 dioxane, dimethoxyethane, and THF were distilled from sodium/benzophenone under an argon atmosphere. Acetonitrile, methylene chloride, and pyridine were distilled on calcium-hydride. Ethylene (3.5 grade) was supplied by Praxair India Ltd., India. 1-Naphthol, diisopropyl aniline, and m-chloroperbenzoic acid, were supplied by Loba chemie and were used as received. Sodium borohydride was supplied by Avra Synthesis Pvt. Ltd. and was used as received. p-Anisidine and paraformaldehyde were supplied by Alfa aesar and were used as received \([\text{Pd(temda)}_2]^1\), 1 hydroxy 2 naphthaldehyde,\(^2\) aniline derivative\(^3\) were synthesized following known procedures. The insertion polymerization was run in a Büchi glasuster cyclone 075 high-pressure reactor equipped with an overhead mechanical stirrer, heating/cooling jacket, and pressure regulators. The hydroformylation was carried-out in a Amar Equipment Pvt. Ltd. high-pressure reactor equipped with pressure regulators and a safety rupture valve.

Solution NMR spectra were recorded on Bruker Avance 200, 400 and 500 MHz instruments. Chemical shifts are referenced to external reference TMS (\(^1\)H and \(^13\)C). Coupling constants are given as absolute values. Multiplicities are given as follows: s: singlet, d: doublet, t: triplet, m: multiplet. Mass spectra were recorded on Thermo Scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150 x 4.6 mm diameter 8 μm particle size mobile phase used is 90% methanol + 10% water + 0.1% formic acid. Infrared (IR) spectra were recorded on a Bruker Alpha II instrument and Fourier transform infrared spectrometer as a thin film. GPC was performed on a system equipped with an isocratic pump (Viscotek VE 1122 pump) and a differential refractometer (DRI) detector (Viscotek VE 3580 RI). For SEC with THF as the eluent, separations were performed using serially connected size exclusion columns (two T6000M, General Mixed Organic 8 x 300 mm, from Viscotek) at 25 °C and at a flow rate of 1.0 mL/min, and molecular weights were determined from the calibration curve generated from narrow polystyrene standards. DSM MICRO 5 twin screw microcompounder
was used for compounding LLDPE, Nylon-6. Tensile specimen were prepared using a DSM micro injection molding machine. Tensile testing was done on a universal testing machine (Instron 33R4204). Single crystal X-ray diffraction measurement for Cat.1 was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (MoKα = 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. SEM data was recorded on Field Emission Scanning Electron Microscope (FESEM), FEI – NOVA NANO 450.

2. Synthesis of ligands:

2.1 Synthesis of 1-hydroxy-2-naphthaldehyde:

![Scheme S1: Synthesis of 1-hydroxy-2-naphthaldehyde](image)

In an oven-dried round bottom flask, 1-naphthol (13.8 mmol, 2 g), paraformaldehyde (138 mmol, 4.14 g), magnesium chloride (36 mmol, 3.43 g) and triethyl amine (63.4 mmol, 6.42 g), were added in 50 mL THF. The resultant reaction mixture was refluxed at 80 °C temperature for 6 hours, the reaction was monitored by TLC analysis. After completion, the reaction mixture was cooled to room temperature and 2N.HCl (30 mL) was added, and the compound was extracted using 50 × 3 mL of ethyl acetate. Solvents were evaporated by using a rotary evaporator and the product was purified by using column chromatography (ethyl acetate 3%: petroleum ether 97%) to produce 1.34 g (56%) of 1-hydroxy-2-naphthaldehyde (1).

\[ ^1\text{H NMR} \quad (200 \text{ MHz}, \text{CDCl}_3) \delta = 12.68 \text{ (s, 1 H)}, 9.97 \text{ (s, 1 H)}, 8.45 \text{ (d, 1 H)}, 7.79 \text{ (d, 1 H)}, 7.71 - 7.63 \text{ (m, 1 H)}, 7.59 - 7.53 \text{ (m, 1 H)}, 7.49 \text{ (d, 1 H)}, 7.38 \text{ (d, 1 H)}. \]
2.2 Synthesis of L1
In an oven-dried round bottom flask, 1-hydroxy-2-naphthaldehyde (0.5 g, 2.90 mmol) and aniline derivative (1.32 g, 2.90 mmol) was dissolved in 25 mL toluene, and a catalytic amount of PTSA (15 mg, 0.087 mmol) was added. The resulting reaction mixture was refluxed for 6 hours at 120 °C (bath temperature). The reaction mixture was cooled to room temperature, the solvent was evaporated, and the resultant residue was purified by column chromatography (1 % ethyl acetate and 99% Petroleum ether) to yield an orange-colored compound (1.22 g, 69%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 14.35$ (br. s., 1 H), 8.42 (d, $J = 7.6$ Hz, 1 H), 7.64 (d, $J = 7.9$ Hz, 1 H), 7.59 - 7.50 (m, 1 H), 7.50 - 7.43 (m, 1 H), 7.25 (d, $J = 7.6$ Hz, 1 H), 7.21 - 7.12 (m, 12 H), 7.01 (d, $J = 6.6$ Hz, 7 H), 6.92 (d, $J = 8.5$ Hz, 1 H), 6.65 (br. s., 1 H), 6.45 (s, 2 H), 6.18 (s, 1 H), 5.56 (br. s., 2 H), 3.53 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 168.0, 165.3, 156.8, 143.1, 138.9, 138.3, 136.4, 129.7, 129.6, 129.2, 128.6, 128.4, 127.6, 127.4, 126.8, 126.5, 125.3, 124.3, 116.9, 114.2, 110.8, 55.2, 52.7. ESI-MS: m/z = 610.27 [M+H]$^+$ (observed); 610.27 (calculated). IR (cm$^{-1}$) 1605.
Scheme S2: Synthesis of L1.

Figure S2: $^1$H NMR spectrum of the L1 in CDCl$_3$ (500 MHz, 298 K).
Figure S3: $^{13}$C NMR spectrum of L1 in CDCl$_3$ (125 MHz, 298 K).

Figure S4: $^{13}$C DEPT NMR spectrum of L1 in CDCl$_3$ (125 MHz, 298 K).
Figure S5: $^1$H-$^1$H COSY NMR spectrum of L1 in CDCl$_3$ (500 MHz, 298 K).
Figure S6: $^1$H-$^{13}$C HSQC NMR spectrum of the L1 in CDCl$_3$ (500 MHz, 298 K).
2.3 Synthesis of L2:
In an oven-dried round bottom flask 1-hydroxy-2-naphthaldehyde (1 g, 0.0058 mol) was dissolved in 30 mL toluene. To that 2,6 diisopropyl amine (1.02 g, 0.0058 mol) was added along with a catalytic amount of PTSA (10 mg, 0.058 mmol). The resultant reaction mixture was refluxed for 6 hours at 110 °C. The reaction mixture was cooled to room temperature, and
volatiles were evaporated. The resultant crude product was purified using column chromatography to yield yellowish coloured compound (872 mg, 50.57%).

$^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ = 14.61 (m, 1 H), 8.49 (d, $J$ = 8.0 Hz, 1 H), 8.16 (d, $J$ = 2.6 Hz, 1 H), 7.72 (d, $J$ = 8.1 Hz, 1 H), 7.58 (t, $J$ = 7.4 Hz, 1 H), 7.54 - 7.47 (m, 1 H), 7.25 - 7.15 (m, 5 H), 3.10 (td, $J$ = 6.8, 13.7 Hz, 2 H), 1.20 (d, $J$ = 6.9 Hz, 12 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 167.2, 165.0, 142.9, 140.9, 136.8, 129.8, 127.6, 127.6, 127.2, 126.6, 125.7, 124.6, 123.7, 117.5, 111.0, 28.5, 23.8. ESI-MS: m/z = 332.20 [M+H]$^+$ (observed); 332.20 (calculated). IR (cm$^{-1}$) 1604.

**Scheme 3:** Synthesis of L2.

**Figure S9:** $^1$H NMR spectrum of the L2 in CDCl$_3$ (400 MHz, 298 K).
Figure S10: $^{13}$C NMR spectrum of the L2 in CDCl$_3$ (100 MHz, 298 K).

Figure S11: $^{13}$C DEPT NMR spectrum of the L2 in CDCl$_3$ (100 MHz, 298 K).
Figure S12: ESI-MS data of L2; observed mass (top), simulated pattern (bottom).
3. Synthesis of Pd-Complex:

3.1 Synthesis of Cat.1:
In an oven-dried Schlenk flask, ligand L1 (200 mg, 0.328 mmol) and [Pd(TMEDA)Me2] (82.74 mg, 0.328 mmol) were dissolved in 5 mL pyridine. The resulting reaction mixture was stirred at room temperature for 2 hours. The pyridine was evaporated to dryness. Next, the second batch of pyridine (5 mL) was added to the above residue, and the content was stirred for another 1 hour. Pyridine was evaporated to dryness. The above step was performed again, and finally, the resultant residue was dried under a high vacuum to pull out excess pyridine. The thus obtained crude product was washed with hexane (5 mL × 2), and dried to produce pure yellow-colored Pd-complex Cat.1 (183 mg, 68.9%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.04$ (dd, $J = 1.5$, 6.4 Hz, 2 H), 8.35 (d, $J = 8.2$ Hz, 1 H), 7.92 (s, 1 H), 7.57 - 7.50 (m, 3 H), 7.48 (s, 1 H), 7.33 - 7.27 (m, 5 H), 7.25 - 7.19 (m, 6 H), 7.09 - 7.01 (m, 10 H), 6.51 (s, 2 H), 6.45 (d, $J = 8.5$ Hz, 1 H), 6.29 (s, 2 H), 5.94 (s, 1 H), 5.51 (d, $J = 8.9$ Hz, 1 H), 3.61 (s, 3 H), 0.44 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 167.8$, 166.8, 156.5, 152.8, 143.8, 143.8, 142.7, 139.7, 138.0, 137.6, 132.1, 130.1, 129.9, 129.7, 128.5, 128.3,
128.3, 127.1, 126.4, 125.7, 124.9, 123.8, 113.8, 112.4, 111.7, 55.2, 52.3, 1.9. **ESI-MS:** m/z = 809.20 [M+H]^+ (observed); 809.23 (calculated). **IR (cm⁻¹):** 1589.

**Scheme S4:** Synthesis of Cat.1.

**Figure S14:** ^1^H NMR spectrum of the Cat.1 in CDCl₃ (400 MHz, 298 K).
Figure S15: $^{13}$C NMR spectrum of the Cat.1 in CDCl$_3$ (100 MHz, 298 K).

Figure S16: $^{13}$C DEPT NMR spectrum of the Cat.1 in CDCl$_3$ (100 MHz, 298 K).
Figure S17: $^1$H-$^1$H NOESY NMR spectrum of the Cat.1 in CDCl$_3$ (400 MHz, 298 K).

Figure S18: $^1$H-$^{13}$C HSQC NMR spectrum of the Cat.1 in CDCl$_3$ (400 MHz, 298 K).
**Figure S19:** ESI MS data for Cat.1; observed (top), simulated (bottom).
Figure S20: IR data of Cat.1.

Figure S21: Molecular structure of Cat.1. H-atoms have been omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Important bond distances and angles; Pd1-N2 2.01 Å, Pd1-N1 2.03 Å, Pd1-O1 2.07 Å, N2-Pd1-O1 91.70 °, C6-Pd1-N1 90.55 °.
Table S1: Crystal data and structure refinement for Cat.1 (CCDC 2225185).

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<th>Reported</th>
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<td>3886.64 (18)</td>
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<td>P 21/n</td>
<td>P 21/n</td>
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<tr>
<td>Hall group</td>
<td>-P 2yn</td>
<td>-P 2yn</td>
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<tr>
<td>Moleity formula</td>
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<td>C50 H42 N2 O2 Pd</td>
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<tr>
<td>Sum formula</td>
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<td>C50 H42 N2 O2 Pd</td>
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<td>4</td>
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<tr>
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<td>0.521</td>
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<td>17, 27, 20</td>
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<td>9902</td>
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<tr>
<td>Tmin'</td>
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Correction method = # Reported T Limits: Tmin=0.682 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness = 0.981 Theta(max) = 28.747

R(reflections) = 0.0322 (8728)

\[ wR2(\text{reflections}) = 0.0808 (9902) \]

S = 1.046 Npar = 498

3.2 Synthesis of Cat.2:
In the Schlenk flask, ligand L2 (150 mg, 0.452 mmol) and [Pd(TMEDA)Me₂] (114.07 mg, 0.452 mmol) was dissolved in 5 mL pyridine. The resulting reaction mixture was stirred at room temperature for 2 hours. The pyridine was evaporated to dryness, again 5 mL pyridine was added and stirred for another 1 hour. Pyridine was evaporated to dryness. The above step was performed once again, and finally, the resultant residue was dried under a high vacuum to remove unreacted pyridine. The thus obtained crude product was washed with hexane (5 mL × 2), and dried to produce pure green colored Pd-complex Cat.2 (214 mg, 89.1%).

\(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta = 8.91-8.89 \text{ (m, 2 H), 8.35-8.33 \text{ (m, 1 H), 7.84 \text{ (tt, } J = 1.6, 7.7 \text{ Hz, 1 H)}, 7.75 \text{ (s, 1 H), 7.61 - 7.58 \text{ (m, 1 H), 7.48 \text{ (dt, } J = 1.4, 7.4 \text{ Hz, 1 H)}, 7.44 - 7.40 \text{ (m, 2 H), 7.33 - 7.28 \text{ (m, 1 H), 7.24 - 7.17 \text{ (m, 3 H), 7.09 - 7.04 \text{ (m, 1 H), 6.84 \text{ (d, } J = 8.5 \text{ Hz, 1 H), 3.68 - 3.54 \text{ (m, 2 H), 1.32 \text{ (d, } J = 6.7 \text{ Hz, 6 H), 1.11 \text{ (d, } J = 7.0 \text{ Hz, 6 H), 0.02 \text{ (s, 3 H).}}\text{\(^1\text{C}}\)
NMR (125 MHz, CDCl₃) δ = 167.7, 164.8, 152.7, 149.0, 141.6, 138.0, 137.6, 131.7, 130.2, 128.9, 127.3, 126.4, 125.8, 124.8, 124.3, 123.4, 113.1, 112.3, 27.9, 25.0, 22.9, 0.7. ESI-MS m/z = 531.16 (M+H)⁺ observed; 531.16 (M+H)⁺ calculated. IR (cm⁻¹) 1586.

Scheme S5: Synthesis of Cat.2.

Figure S22: ¹H NMR spectrum of the Cat.2 in CDCl₃ (500 MHz, 298 K).
Figure S23: $^{13}$C NMR spectrum of the Cat.2 in CDCl$_3$ (100 MHz, 298 K).

Figure S24: $^{13}$C DEPT NMR spectrum of the Cat.2 in CDCl$_3$ (100 MHz, 298 K).
Figure S25: $^1$H-$^1$H COSY NMR spectrum of the Cat.2 in CDCl$_3$ (500 MHz, 298 K).
Figure S26: $^1$H-$^1$H NOESY NMR spectrum of the Cat.2 in CDCl$_3$ (500 MHz, 298 K).
Figure S27: $^1$H-$^{13}$C HSQC NMR spectrum of the Cat.2 in CDCl$_3$ (500 MHz, 298 K).

Figure S28: $^1$H-$^{13}$C HMBC NMR spectrum of the Cat.2 in CDCl$_3$ (500 MHz, 298 K).
Figure S29: ESI-MS spectrum (top) and IR spectrum (bottom) of Cat.2.
4. Ethylene Oligomerization:
The oligomerization reaction was carried out in a 250 mL stainless steel high-pressure Büchi (GlasUster cyclone 075) reactor equipped with a heating/cooling jacket and mechanical stirrer. Prior to the experiment, the reactor was fully dried by heating it in vacuum at 90 °C for 1 hour, followed by cooling it to room temperature and filling it with argon. The reactor was maintained at the desired reaction temperature, and was purged with ethylene gas. To this, 100 mL of dried and freshly distilled solvent (toluene or other solvents) was added under positive ethylene pressure. Subsequently, the solvent was stirred under ethylene pressure for 30 minutes to dissolve ethylene. Suitable amount of catalyst was injected into the reactor using the syringe under positive ethylene pressure. Next, the reactor was pressurized to desired ethylene pressure with rapid stirring, and desired ethylene pressure was maintained throughout the reaction. After the completion of polymerization, excess ethylene was vented, and the solvent was evaporated under a high vacuum to yield highly viscous semi-solid ethylene oligomers. The yield is determined after subtracting the initial weight of the catalyst, and the resultant oligomers were characterized by various methods. Table S2 summarizes the most important runs using Cat.1 and Cat.2.

Table S2. Ethylene oligomerization using Cat.1 and Cat.2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Temperature °C</th>
<th>Pressure bar</th>
<th>Yield</th>
<th>Branches/1000 carbon atom</th>
<th>Mn (NMR)</th>
<th>Mn (GPC)</th>
<th>Mw (GPC)</th>
<th>PDI</th>
<th>TOF</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cat.1</td>
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<td>25</td>
<td>0.171</td>
<td>74</td>
<td>1350</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>301</td>
</tr>
<tr>
<td>2</td>
<td>Cat.1</td>
<td>70</td>
<td>25</td>
<td>0.206</td>
<td>67</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>363</td>
</tr>
<tr>
<td>3</td>
<td>Cat.1</td>
<td>80</td>
<td>25</td>
<td>0.385</td>
<td>71</td>
<td>1000</td>
<td>550</td>
<td>800</td>
<td>1.46</td>
<td>679</td>
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<tr>
<td>4</td>
<td>Cat.1</td>
<td>90</td>
<td>25</td>
<td>0.168</td>
<td>76</td>
<td>800</td>
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<td>Cat.1</td>
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<td>950</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Cat.1</td>
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<td>Cat.2</td>
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<td>-</td>
<td>-</td>
<td>340.7</td>
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<td>10</td>
<td>Cat.2</td>
<td>80</td>
<td>10</td>
<td>0.148</td>
<td>93</td>
<td>450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>261</td>
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<tr>
<td>11</td>
<td>Cat.2</td>
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<td>106</td>
<td>500</td>
<td>-</td>
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</table>
**Reaction conditions:** Toluene 100 mL, catalyst- 13.6 µmol., Time – 90 min, Ethylene pressure- 5 to 25 bar, TOF in (mol of PE / mol of Pd h⁻¹), (-) Not Determined, the reported yield is after subtracting catalyst quantity from the final weight of oligomer, Branches /1000 C-atoms was calculated using ¹H NMR spectroscopy.

### 4.1 Analysis of distribution of different branches by ¹³C NMR:

<table>
<thead>
<tr>
<th>Entry (Table 1)</th>
<th>Total branchesᵃ</th>
<th>Methyl (%)ᵇ</th>
<th>Ethyl (%)ᵇ</th>
<th>Propyl (%)ᵇ</th>
<th>Long chain branching (%)ᶜ</th>
<th>Sec-Butyl (%)ᵇ</th>
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<tr>
<td>Entry 8</td>
<td>78</td>
<td>51.3</td>
<td>19.9</td>
<td>15.7</td>
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<td>3.9</td>
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<tr>
<td>Entry 9</td>
<td>90</td>
<td>37.42</td>
<td>25.4</td>
<td>21.5</td>
<td>8.7</td>
<td>7.0</td>
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</tbody>
</table>

ᵃBranches per 1000 carbons calculated from ¹H NMR.ᵇCalculated by the relative intensities of the methyl resonances 1B₁, 1B₂, 1B₃, and sec-Bu.ᶜLCB = butyl and longer branches, calculated by the relative intensity of the methine resonance.

### 4.2 GC-MS analysis of low boiling ethylene oligomer:

Ethylene oligomerization reaction was performed at optimized reaction conditions (80 °C, 5 bar, 90 minutes, and 100 mL of Toluene solvent). To check the presence of low boiling compound after completion of ethylene polymerization reaction we cooled the reactor to 0 °C and excess ethylene was vented. The reactor was maintained at 0 °C and the sample was taken and immediately performed GC-MS analysis of the oligomerization reaction mixture.

**Method:** Headspace GC-MS analysis was performed on an Agilent 7890B GC system equipped with Agilent HP-5 column. Inlet temperature was maintained at 250 °C, column flow = 3 ml/min. split ratio 75:1. Detector temperature was maintained at 300 °C. Temperature program: starting at 40 °C with hold time of 5 mins. Ramp 1: @ 10 °C to 320 °C.

**GC chromatogram of ethylene oligomeric reaction mixture**
C7 Compound with olefin (Mass- 98.10) [5.9 minute].

C8 Compound with olefin (Mass- 112.12) [5.7, 5.8, 6.0, 6.1, 6.3, 6.8, 6.9 minute]
4.3 Mn and N_branch/1000C calculation: Calculation of Mn and N_branches/1000C from $^1$H is well established in literature. Literature reported method was adopted and the number of branches per 1000 C-atoms is calculated as under.\(^4\)

$H_1$ (vinylidene end group); $H_2$ (1,2-disubstituted olefin); $H_3$ (trisubstituted olefin); $H_4$ ($\alpha$-olefin); $H_5$ (alkyl methyl, alk-CH3); $H_6$ (allylic methyl); $H_7$ (alkyl methylene and methine, alk-CH and alk-CH2); $H_8$ (allylic methylene or methine).

In our case, more than <98% of polymeric chain ends were found to be of $H_2$ and $H_4$ type. Therefore, we modified the literature reported formula as under.

$$V = H_2 + (2/3)H_4$$

$$A = H_3 + H_6 + H_7 + H_8 - H_2 - (1/3)H_4$$

$$N_{av} = (2/V) \times (A) + 2$$

$$M_n = N_{av} \times 14.01$$

$N_{av}$ is number of methyl branches per 1000 C atoms.

$$Y = (H_5 + H_6)/3 \times (2/V)$$

$$X = [H_2 + (H_4/3)] \times (2/V)$$

$$N_{br} = (1000/N_{av}) \times (Y - X)$$

For Table S2, entry 3,

$$V = H_2 + (2/3)H_4$$

$$V = 6.27 + (0.66 \times 3.17) = 8.38$$

$$A = H_3 + H_6 + H_7 + H_8 - H_2 - (1/3)H_4$$

$$A = (603.02 - 6.27 - 1.05)/2$$

$$A = 297.85$$

$$N_{av} = (2/V) \times (A) + 2$$

$$N_{av} = (2/8.38) \times 297.85 + 2$$

$$N_{av} = 73.08$$

$$M_n = N_{av} \times 14.01$$
\[ M_n = 73.08 \times 14.01 = 1023 \sim 1000 \]

\[ Y = (H_5 + H_6)/3 \times (2/V) \]

\[ Y = (78.18 + 9.08)/3 \times (2/8.38) \]

\[ Y = 29.08 \times 0.238 = 6.94 \]

\[ X = [H_2 + (H_4/3)] \times (2/V) \]

\[ X = [6.27 + (3.17/3)] \times (2/8.38) \]

\[ X = 7.32 \times 0.238 = 1.74 \]

\[ N_{br} = (1000/N_{av}) \times (Y-X) \]

\[ N_{br} = (1000/73.08) \times (6.94 - 1.74) \]

\[ N_{br} = 13.68 \times 5.2 = 71.13 \sim 71 \]

4.4 Reactivity of Cat.1 with ethylene:

Cat.1 (3 mg, 3.7 mol) was dissolved in benzene-d6 (0.25mL) in a high-pressure NMR tube in a glove box, and the \(^1\)H NMR spectrum was recorded (figure S30 top.). The NMR tube was then connected to the vacuum line, and the argon gas was evacuated from inside the NMR tube. The NMR tube was instantly charged with 4 bar of ethylene gas, and a proton NMR was recorded after 20 minutes, 4 and 24 hours. As depicted in figure S30, the initial Pd-Me resonance at 1.00 ppm slowly disappears, with the concomitant appearance of methylene (-CH\(_2\)-) resonance at 1.47 ppm. These mechanistic investigations suggest that the ethylene inserts in a Pd-Me bond and Cat.1 is capable of ethylene insertion and oligomerization or polymerization, even at room temperature.
**Figure S30:** Stacked high-pressure $^1$H NMR spectra of Cat.1 in the presence of 4 bar ethylene at 0 (top) and 20 minutes, 4 and 24 hours (bottom) (at room temperature).

5. Ethylene Oligomer Characterization:

5.1 NMR Data:

The assignment of peaks of ethylene oligomer in $^1$H and $^{13}$C NMR was performed using a literature method.$^5$
Figure S31: $^1$H NMR spectrum of the oligomer in CDCl₃ (Table S2, entry 3, 298 K), expanded view in sets.
**Figure S32:** $^{13}$C NMR and HSQC spectra of the oligomer in CDCl₃ (top, middle), expanded view (bottom) (Table S2, entry 3, 298 K)
Figure S33: $^{13}$C DEPT NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 3, 298 K).

Figure S34: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 1, 298 K).
Figure S35: $^{13}$C NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 1, 298 K).

Figure S36: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 2, 298 K).
Figure S37: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 4, 298 K).

Figure S38: $^{13}$C NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 4, 298 K).
Figure S39: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 5, 298 K).

Figure S40: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 6, 298 K).
Figure S41: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 7, 298 K).
Figure S42: $^1$H NMR and $^{13}$C (quantitative) spectrum of the oligomer in CDCl$_3$ (Table S2, entry 8, 298 K).
Figure S43: $^1$H and $^{13}$C (quantitative) NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 9, 298 K).
Figure S44: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 10, 298 K).

Figure S45: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S2, entry 11, 298 K).
5.2 GPC Data:

Figure S46: Molecular weight (by GPC) of oligomer in THF (Table S2, entry 3).
Figure S47: Molecular weight (by GPC) of oligomer in THF (Table S2, entry 4).
**Figure S48:** Molecular weight (by GPC) of oligomer in THF (Table S2, entry 8).

**5.3 GC-MS Data:**

When the polymerization reaction was performed in toluene, the friedel craft alkylation was observed in the literature.\textsuperscript{6,7,8} To rule out that possibility we performed the GC-MS analysis for the oligomeric sample (Table S2 entries 6 and 8). No Friedel craft alkylation products were discovered in the GC-MS analysis, and when we compared our data to those in the published literature, we found no such compounds.

a. GC-MS graph (Table S2 entry 6):
b. GC-MS graph (Table S2 entry 8):
6. Effect of Polar Solvents:

6.1 Ethylene oligomerization in polar solvent:

Table S3. Ethylene oligomerization using Cat.1 in polar solvent.^[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat</th>
<th>Solvent</th>
<th>Yield g</th>
<th>Branches/1000 C-atoms</th>
<th>TOF</th>
<th>Mn NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cat.1</td>
<td>DME</td>
<td>0.655</td>
<td>78</td>
<td>1155.2</td>
<td>750</td>
</tr>
<tr>
<td>2</td>
<td>Cat.2</td>
<td>DME</td>
<td>0.466</td>
<td>86</td>
<td>821.8</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>Cat.1</td>
<td>1,4 dioxane</td>
<td>1.124</td>
<td>75</td>
<td>1982.3</td>
<td>650</td>
</tr>
<tr>
<td>4</td>
<td>Cat.2</td>
<td>1,4 dioxane</td>
<td>0.738</td>
<td>97</td>
<td>1301</td>
<td>350</td>
</tr>
<tr>
<td>5</td>
<td>Cat.1</td>
<td>Et₂O</td>
<td>0.812</td>
<td>100</td>
<td>1421.5</td>
<td>800</td>
</tr>
<tr>
<td>6[^b]</td>
<td>Cat.1</td>
<td>DCM</td>
<td>0.092</td>
<td>100</td>
<td>162.5</td>
<td>1250</td>
</tr>
<tr>
<td>7</td>
<td>Cat.1</td>
<td>ACN</td>
<td>0.141</td>
<td>99</td>
<td>248.6</td>
<td>400</td>
</tr>
<tr>
<td>8</td>
<td>Cat.1</td>
<td>THF</td>
<td>1.323</td>
<td>77</td>
<td>2333</td>
<td>650</td>
</tr>
<tr>
<td>9</td>
<td>Cat.2</td>
<td>THF</td>
<td>0.612</td>
<td>83</td>
<td>1079</td>
<td>350</td>
</tr>
</tbody>
</table>

^[a]Reaction conditions: Solvent-100 mL, catalyst-13.6 μmol., Time- 90 min, Ethylene pressure-5 bar, Temperature-80 °C, TOF in (mol of PE/mol of Pd h⁻¹), the reported yield is after subtracting catalyst quantity from the final weight of oligomers, Branches/1000 C-atoms was calculated using ¹H NMR spectroscopy,^[b] Reaction temperature was 45 °C.
Figure S49: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 1, 298 K) (DME).

Figure S50: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 2, 298 K) (DME).
Figure S51: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 3, 298 K) (1,4 dioxane).

Figure S52: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 4, 298 K) (1,4 dioxane).
Figure S53: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 5, 298 K) (Diethyl Ether)
Figure S54: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 6, 298 K) (DCM)

Figure S55: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 7, 298 K) (Acetonitrile).
Figure S56: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, entry 8, 298 K) (THF).

Figure S57: $^1$H NMR spectrum of the oligomer in CDCl$_3$ (Table S3, Entry 9, 298 K) (THF).
6.2 Understanding the role of polar solvent:

Figure S58: $^1$H NMR spectrum of the Cat.1 in C$_6$D$_6$ (298 K).

Figure S59: $^1$H NMR spectrum of Cat.1 + 50 eq. of THF in C$_6$D$_6$ (298 K).
Figure S60: $^1$H NMR spectrum of the Cat.1 + 2 eq B(C₆F₅)₃ + 50 eq. of THF in C₆D₆ (298 K).

Figure S61: $^{11}$B NMR spectrum of the Cat.1 + 2 eq B(C₆F₅)₃ + 50 eq. of THF in C₆D₆ (298 K).
6.3 *in-situ* Pd.THF complex synthesis and its usage in ethylene oligomerization study:

**Route I:** In an oven-dried Schlenk flask, ligand L1 (24.85 mg, 0.040 mmol) and [Pd(TMEDA)Me₂] (10.28 mg, 0.040 mmol) were dissolved in 5 mL THF. The resulting reaction mixture was stirred at room temperature for 1 hour. The THF was evaporated to dryness. Next, the second batch of THF (5 mL) was added to the above residue, and the content was stirred for another 3 hours. This reaction content was directly transferred to the polymerization reactor and polymerization was performed (Time 90 min., Temperature-80 °C, pressure 5 bar, solvent-THF). After completion of reaction solvent was evaporated which produced 2.155g of ethylene oligomer.

**Route II:** In an oven-dried Schlenk flask, ligand L1 (24.85 mg, 0.040 mmol) and NaH (1mg, 0.040 mmol) were dissolved in 2 mL THF and stirred for 3 hours at 25 °C. In another round bottom flask [Pd(COD)MeCl] (10.81 mg, 0.040 mmol) was dissolved in 2 mLTHF and transferred to the sodium salt of ligand. The reaction content was further stirred for 3 hours at room temperature and solvent was evaporated to the dryness, and again 2 mL of THF was added and further stirred for 1 hour. This reaction content was directly added to the polymerization reactor and polymerization was performed (Time 90 min., Temperature-80 °C, pressure 5 bar, solvent-THF). After completion of reaction solvent was evaporated which produced 2.42 g of ethylene oligomer.

![Chemical structure](image)

**Hyperbranched Ethylene Oligomer (HBOE)**

7. **Functionalization of Ethylene Oligomer:**

1. **Ozonolysis (F1):**

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Scheme S6: Ozonolysis of ethylene oligomers.

In a round bottom flask, ethylene oligomer (250 mg) was dissolved in 30 mL DCM and cooled to -78 °C by using acetone and dry ice. Ozone gas was bubbled in the reaction mixture for 5 minutes; after that RB was purged with argon and dimethyl sulfide was added drop wise to the reaction mixture with vigorous stirring. Reaction mixture was allowed to warm to ambient temperature, and DCM was evaporated by using a high vacuum pump to yield chain-end functionalized ethylene oligomer (228 mg). A single peak at 9.76 ppm was observed for the terminal aldehyde.

Figure S62: $^1$H NMR spectrum of the oligomer after ozonolysis (F1) in CDCl$_3$ (500 MHz, 298 K).
Figure S63: $^{13}$C NMR spectrum of the oligomer after ozonolysis (F1) in CDCl$_3$ (125 MHz, 298 K).

Figure S64: IR spectrum of oligomer after ozonolysis (F1).
Figure S65: GPC data of oligomer in THF after ozonolysis.

2. Hydroformylation (F2)\textsuperscript{10}

\[
\text{\begin{align*}
\text{F2}
\end{align*}}
\]

Scheme S7: Hydroformylation of ethylene oligomers.

Hydroformylation reaction was performed in a high-pressure Amar Equipment autoclave. Ethylene oligomer (1.19 g), [Rh(acac)(CO)\textsubscript{2}] (15 mg, 0.0581 mmol), and triphenylphosphine (30.4 mg, 0.116 mmol) were weighed in the vial, and 10 mL of toluene was added. The reaction vial was placed in the high-pressure autoclave, and the reactor was immediately pressurized
with syngas (15 bar) after purging three times. Finally, the reactor was pressurized with 10 bar of syngas, and the temperature was raised to 100 °C for 18 hours with constant stirring. After completion of the reaction, the reactor was cooled to room temperature, and excess syngas was released. Toluene was evaporated, and the resultant crude product was submitted for NMR analysis. 10 mL hexane was added to the above crude reaction mixture, and the content was stirred for 5 minutes. The resultant solution was filtered, and the filtrate was evaporated. This process was repeated twice to obtain a highly viscous compound F2 (1.2 gm).

Figure S66A: $^1$H NMR spectrum of the hydroformylated ethylene oligomer (F2) in CDCl$_3$ (500 MHz, 298 K).
Figure S66B: Stacked $^{13}$C NMR spectra of the olefinic product (top, red color line) and hydroformylated ethylene oligomer (bottom, blue color line) in CDCl$_3$ (125 MHz, 298 K). Expanded view in sets.
**Figure S67**: $^{13}$C NMR spectrum of the hydroformylated ethylene oligomer(F2) in CDCl$_3$ (125 MHz, 298 K).

**Figure S68**: GPC data of ethylene oligomer in THF after hydroformylation.

3. **Epoxidation using mCPBA (F3):**

![Epoxidation Scheme](image)

**Scheme S8**: Epoxidation of ethylene oligomers using mCPBA.
In a round bottom flask, 200 mg of ethylene oligomer was dissolved in 20 mL of dichloromethane. The reaction mixture was cooled to 0 °C, and mCPBA [50-55% (80 mg)] was added. Subsequently, the mixture was allowed to reach ambient temperature and was further stirred for 14 hours. A saturated sodium hydrogen carbonate solution was added to the reaction mixture and stirred for 10 minutes. The organic layer was washed three times with NaHCO₃ and dried over Na₂SO₄. DCM was evaporated using a rota evaporator to obtain colorless oil (176 mg).

Figure S69: \(^1\)H NMR spectrum of the epoxidation product (F3) of ethylene oligomer in CDCl₃ (500 MHz, 298 K).
Figure S70: $^{13}$C NMR spectrum of the epoxidation product (F3) of ethylene oligomer in CDCl$_3$ (125 MHz, 298 K).
Figure S71: $^{13}$C (DEPT) NMR spectrum of the epoxidation product (F3) of ethylene oligomer in CDCl$_3$ (125 MHz, 298 K).
**Figure S72:** IR spectrum of the epoxidation product of ethylene oligomer.

![IR Spectrum](image)

**Figure S73:** Molecular weight (by GPC) of ethylene oligomer in THF after epoxidation.

![GPC Results](image)

### 4. Synthesis of hydroxy functionalized oligomers (F4):

![Synthesis Scheme](image)

**Scheme S9:** Synthesis of hydroxy functionalized ethylene oligomers.

The hydroformylation product (1.2 g) obtained from the above (F2 from hydroformylation) reaction mixture was directly used in this step. Methanol (1:1) was added to the toluene solution
of functional ethylene oligomer F2, and the mixture was cooled to 0 °C. Next, sodium borohydride (NaBH₄) (110 mg) was added with vigorous stirring and was allowed to warm to room temperature. It was further stirred for 14 hours at room temperature. The solvent was evaporated, and 10 mL hexane was added; the resultant mixture was stirred for 5 minutes. The hexane layer was decanted in another round bottom flask, and hexane was evaporated to produce F4 (1.048 gm). The formation of hydroxyl functionalized ethylene oligomer was confirmed by ¹H NMR spectroscopy. It was found that the aldehyde peaks diminished, and new peaks appeared in the region of 3.6 ppm.

Figure S74: ¹H NMR spectrum of the hydroxyl functionalized ethylene oligomer (F4) in CDCl₃ (400 MHz, 298 K).
Figure S75: $^{13}$C NMR spectrum of the hydroxyl functionalized (F4) ethylene oligomer in CDCl$_3$ (100 MHz, 298 K).

Figure S76: $^{13}$C (DEPT) NMR spectrum of the hydroxyl functionalized (F4) ethylene oligomer in CDCl$_3$ (100 MHz, 298 K).
Figure S77: IR data of the hydroxyl functionalized (F4) ethylene oligomer.
Figure S78: Molecular weight (by GPC) data of oligomer in THF.

Table S4. Post functionalized ethylene oligomer, Mn, Mw and PDI as determined by GPC.

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Reaction</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ozonolysis (F1)</td>
<td>1600</td>
<td>3200</td>
<td>2.038</td>
</tr>
<tr>
<td>2.</td>
<td>Hydroformylation (F2)</td>
<td>1300</td>
<td>2650</td>
<td>2.017</td>
</tr>
<tr>
<td>3.</td>
<td>Epoxidation (F3)</td>
<td>1550</td>
<td>2800</td>
<td>1.801</td>
</tr>
<tr>
<td>4.</td>
<td>Hydroxy functionalized (F4)</td>
<td>1400</td>
<td>2700</td>
<td>1.921</td>
</tr>
</tbody>
</table>

8. References:
(1) De Graaf, W.; Boersma, J.; Smeets, W. J.; Spek, A. L.; Van Koten, G. Dimethyl (N, N, N', N'-tetramethylethanediamine) palladium (II) and dimethyl [1, 2-bis (dimethylphosphino) ethane] palladium (II): syntheses, x-ray crystal structures, and thermolysis, oxidative-addition and ligand-exchange reactions. *Organometallics* 1989, 8(12), 2907-2917


(4) Daugulis, O.; Brookhart, M. Polymerization of Ethylene with Cationic Palladium and Nickel Catalysts Containing Bulky Nonenolizable Imine- Phosphine Ligands. Organometallics 2002, 21(26), 5926-5934


