Supplementary Information

Photoinduced Iron-Catalyzed C−H Alkylation of Polyolefins

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Table of Contents

General information

(1) Materials:

Chlorobenzene (PhCl) was purchased from Sinopharm without purification, acetonitrile (MeCN) and dichloromethane (DCM) were purified by a Vigor solvent purification system. Anhydrous $FeCl_3$ was purchased from Energy Chemical. TBACl (tetrabutylammonium chloride) was purchased from TCI. $TBAFeCl_4$ was prepared by mixing $FeCl_3$ and TBACl (1:1 ratio) in MeCN in the glovebox. LDPE, LLDPE, PP, and PIB were purchased from Macklin. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise.

(2) Starting materials:

The electron deficient alkenes including **14**[1], **15**[1], **12**[2], **13**[2], **9**[3] are known and were prepared according to the known literature.

(3) Setting-up of the photo-induced reactions:

The LED light (100 W, emitting area: 30 × 30 mm) was assembled using the 390-395 nm chips purchased from GuangHong Chips. The emission spectrum of the LED light is shown below (**Figure S1**) and wavelength of peak intensity is 390-395 nm. The material of the reaction vessels is regular borosilicate glass. The distance from the light source to the reaction vessel is 5 cm (**Figure S2**).

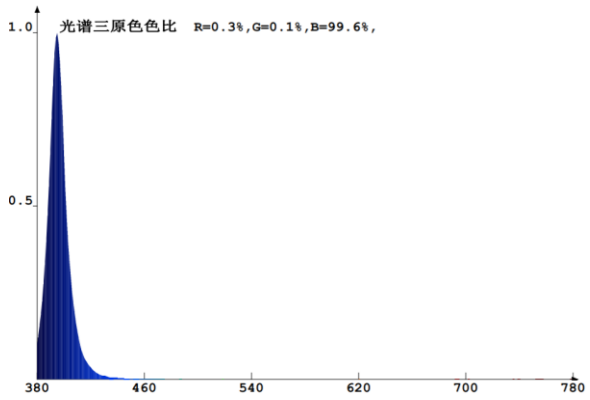


Figure S1. The emission spectrum of the LED light.

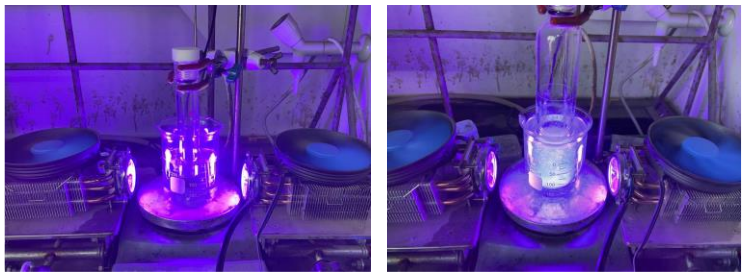


Figure S2. The setting-up reactions. Left is for 2-10 mmol scale; right is for > 100 mmol scale.

(4) IR:

Infrared spectra were recorded on a Nicolet iS5 using neat thin film technique.

(5) NMR:

^{1}H NMR spectra were recorded on JNM-ECZ400S/L1 or Bruker-600 MHz spectrometer at 400 or 600 MHz, ^{13}C NMR spectra were recorded at 101 or 151 MHz, ^{19}F NMR spectra were recorded at 376 MHz, and ^{31}P NMR spectra were recorded at 162 MHz. Spectra were acquired in $CDCl_3$, $C_2D_2Cl_4$, or acetone-d_6. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent [($CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C)), ($C_2D_2Cl_4$, δ = 6.00 ppm (^{1}H)) and (acetone-d_6, δ = 2.05 ppm (^{1}H) and 206.00 ppm (^{13}C))]. Coupling constants were reported in Hertz (Hz). Data for NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, coupling constant (Hz), and integration.

(6) GPC:

M_w, M_n, and $Đ$ of PS and **PS-5** were determined by an Agilent 1260 infinity II gel permeation chromatography (GPC) equipped with a refractive index (RI) detector. 5.0 mg of sample was dissolved in 1 mL of DMF containing 0.1% LiBr, and then filtered through a 0.22 μm filter. GPC columns (PolarGel-M Gard, 50 mm × 7.5 mm, and PolarGel-M, 300 mm × 7.5 mm, two in series) were eluted with DMF (plus 0.1% LiBr) at a flow rate of 1 mL/min at 50 °C. GPC column were calibrated with linear poly(methyl methacrylate) (PMMA) standards.

M_w, M_n, and $Đ$ of PIB and **PIB-5** were determined by an Agilent 1260 infinity II gel permeation chromatography (GPC) equipped with a refractive index (RI) detector. 5.0 mg of sample was dissolved in 1 mL of THF, and then filtered through a 0.22 μm filter. GPC columns (PolarGel-M Gard, and Plgel 5 μm MIXED-C, 300 mm × 7.5 mm) were eluted with THF at a flow rate of 1 mL/min at 40 °C. GPC column were calibrated with linear polystyrene (PS) standards.

(7) HT-GPC:

M_w, M_n, and $Đ$ of LDPE, LLDPE, PP, functionalized-LDPE, functionalized-LDPE, and functionalized-PP were determined by an Agilent 1260 infinity II high temperature system gel permeation chromatography (GPC) equipped with a refractive index (RI) detector. 5.0 mg of sample was dissolved in 1 mL of 1,2,4-trichlorobenzene (TCB), and then filtered through a 0.22 μm filter. GPC columns (PolarGel-M Gard, 50 mm × 7.5 mm, and mix-B 2.50 mm × 300 mm, two in series) were eluted with TCB at a flow rate of 1 mL/min at 140 °C. GPC column were calibrated with linear polystyrene (PS) standards.

(8) DSC:

The melting temperature (T_m) were evaluated. Heating (1-10 mg of sample) at a rate of 10 °C/min from 30 to160 °C, 160 to 30 °C, and 30 to160 °C under N_2. Data was taken from the last heating cycle.

(9) TGA:

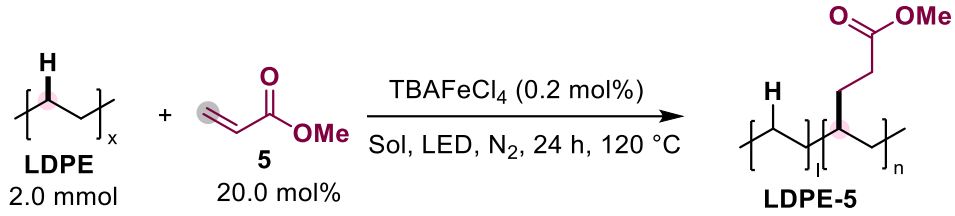
The melting temperature (T_m) and decomposition onset temperature (T_d) were evaluated with METTLER TOLEDO TGA/DSC. Heating (1-10 mg of sample) at a rate of 10 °C/min from 35-800 °C under N_2.

(10) Definition of the level of functionalization (LOF)

The level of functionalization (LOF) = $n_{(\text{polar alkene in polymer})}/n_{(\text{monomer})} = A_{(\text{equivalent of functional group in polymer})}/ A_{(\text{equivalent of monomer})}$.

n: mole number; A: integral area by ^{1}H NMR.

Solvent effect of the Fe-catalyzed C–H bond alkylation of LDPE with 5



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LDPE (56.7 mg, 2.0 mmol, M_n = 30423 g/mol, $Đ$ = 5.84), **5** (34.4 mg, d = 0.956 g/mL, 36 μL, 0.4 mmol), and solvent (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours, the level of the functionalization was then determined by ^{1}H NMR.

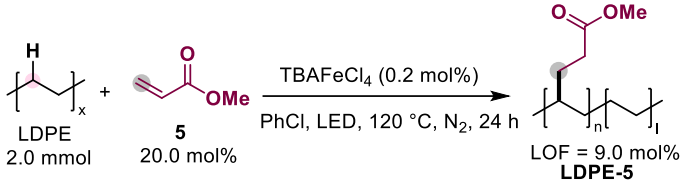
Table S1. Solvent effect for C–H alkylation reaction

entry	solvent	the level of functionalization (LOF mol%)
1	MeCN	-[a]
2	DMF	-[a]
3	$PhCF_3$	4.2 mol%
4	**PhCl**	**9.0 mol%**

[a] The LOF was not determined due to the low solubility in $CDCl_3$.

When PhCl was used as solvent, the product **LDPE-5** was obtained as a white solid (54.2 mg, LOF = 9.0 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, **3.00 H**), 2.62-2.13 (m, 1.89 H), 1.86-0.68 (m, **45.64 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. IR ν (neat, cm^{-1}) 2820, 1742, 1463, 1375, 1165.

Characterization of LDPE-5



LDPE in $CDCl_3$ **LDPE-5 in $CDCl_3$**

Typical Procedure 1: To a 35 mL sealed tube were added $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LDPE (56.7 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **5** (34.4 mg, d = 0.956 g/mL, 36 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LDPE-5** was obtained as a white solid (54.2 mg, LOF = 9.0 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, **3.00 H**), 2.62-2.13 (m, 1.89 H), 1.86-0.68 (m, **45.64 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2820, 1742, 1463, 1375, 1165. **GPC (TCB, 140 °C)** M_n = 35944 g/mol, M_w = 228129 g/mol, $Đ$ = 6.35. **TGA (°C)** LDPE T_d = 420, **LDPE-5** T_d = 360. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-5** T_m = 88 with 12% crystallinity (DH = 34 J/g).

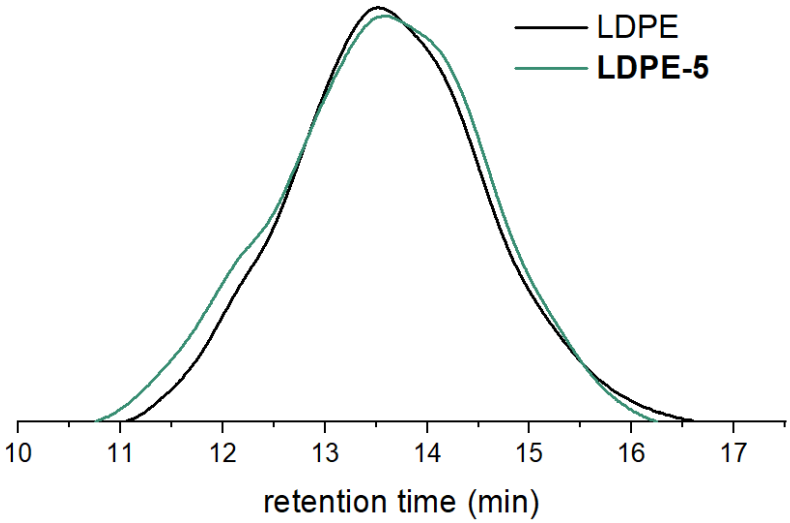


Figure S3. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-5** (green), M_n = 35944 g/mol, M_w = 228129 g/mol, $Đ$ = 6.35.

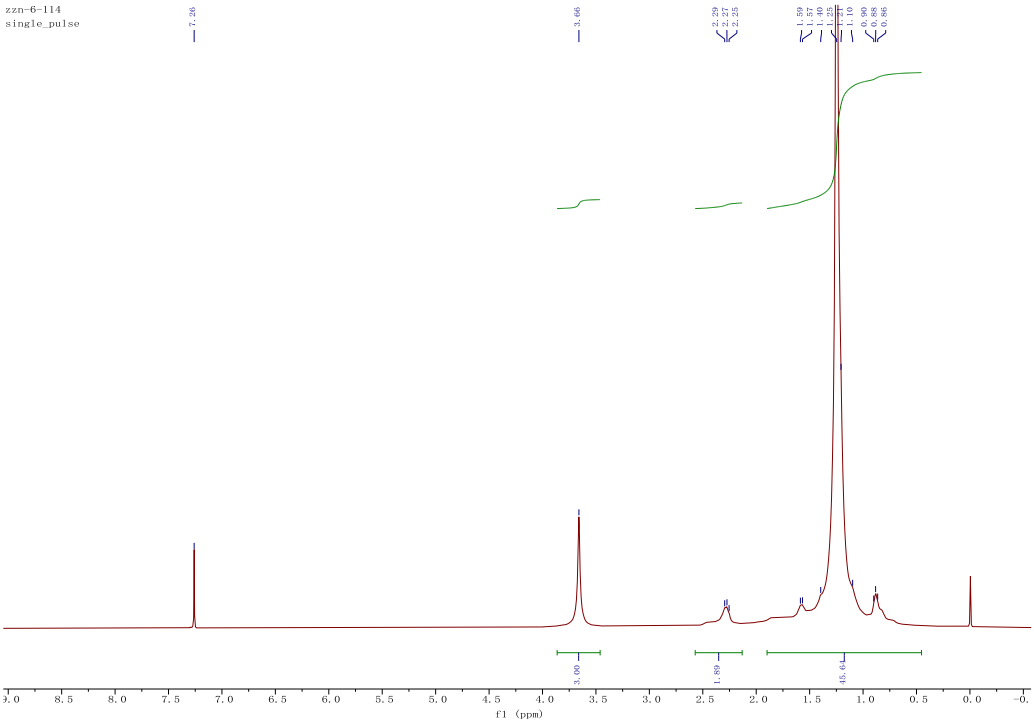


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-5**

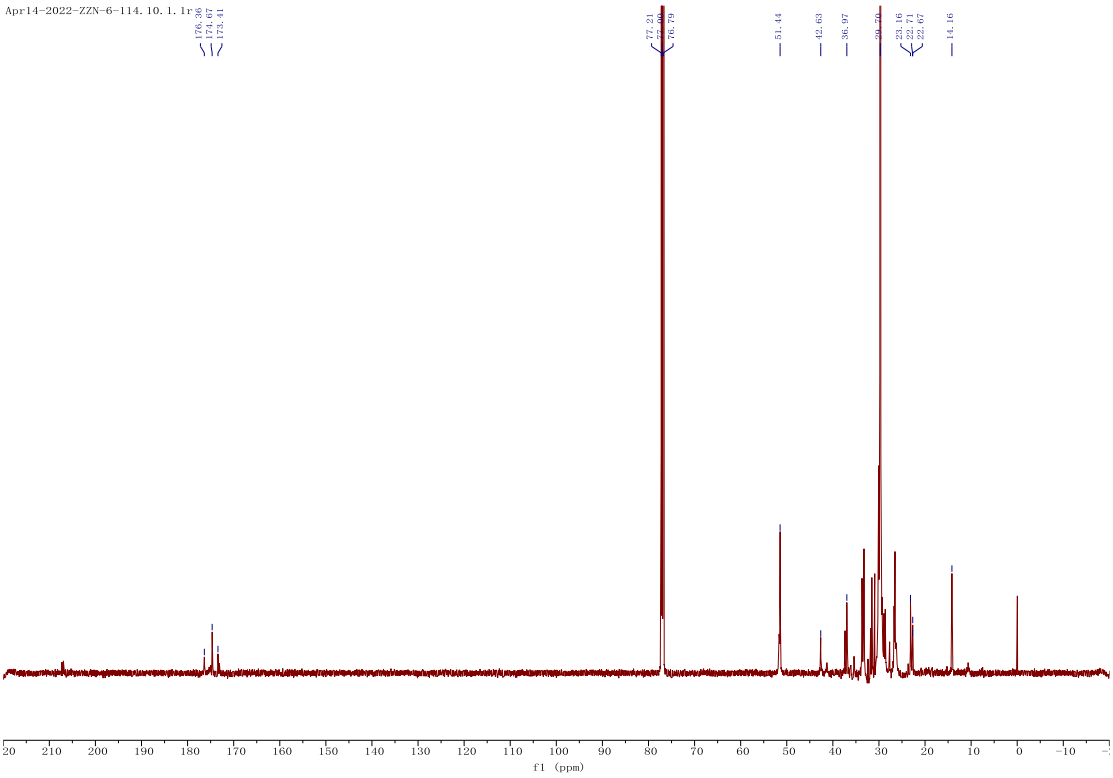


Figure S5.^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-5**

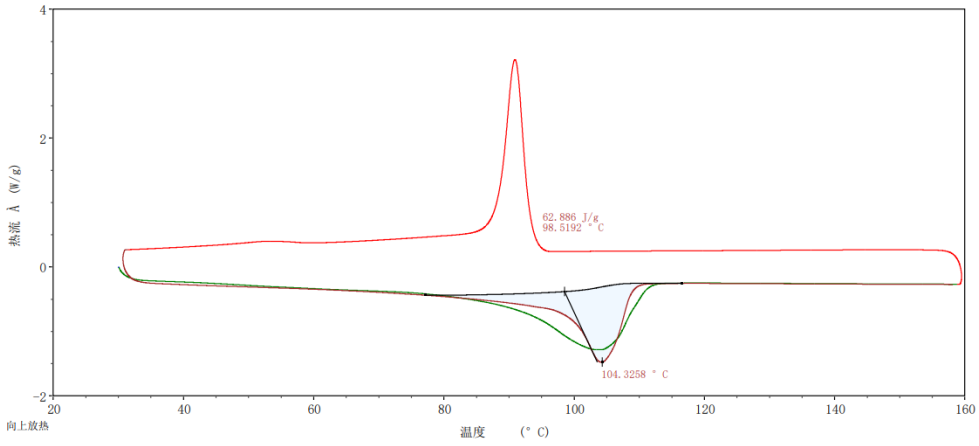


Figure S6. The DSC trace of LDPE

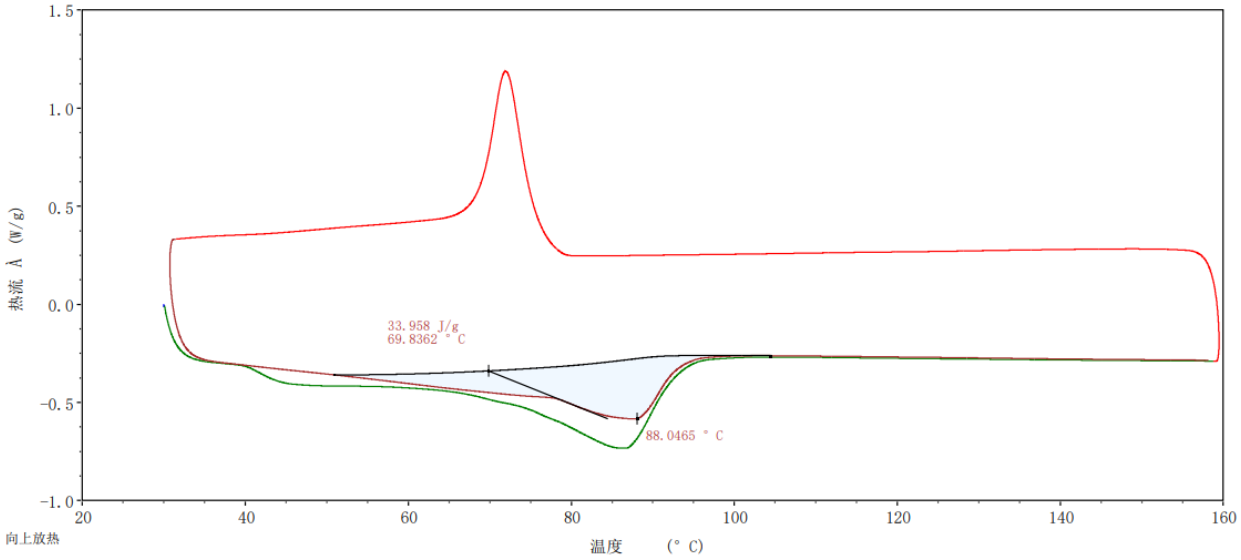
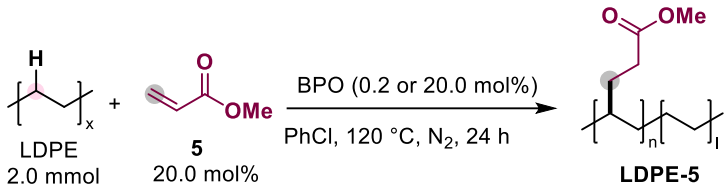


Figure S7. The DSC trace of **LDPE-5**

Comparable result using BPO as a radical initiator



To a 35 mL sealed tube were added BPO (127.5mg, 0.4 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 36500 g/mol, M_w = 227734 g/mol $Đ$ = 6.24), **5** (34.4 mg, d = 0.956 g/mL, 36 μL, 0.4 mmol), and solvent (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. The resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LDPE-5** was obtained as a white solid (20.0 mol% BPO: 55.2 mg, LOF = 2.2 mol%). **GPC (TCB, 140 °C)** 20.0 mol% BPO: M_n = 14049 g/mol, M_w = 52513 g/mol, $Đ$ = 3.74. The level of functionalization was determined by ^{1}H NMR. Notably, when the loading of BPO was decreased to 0.2 mol%, no detectable C-H functionalization was observed.

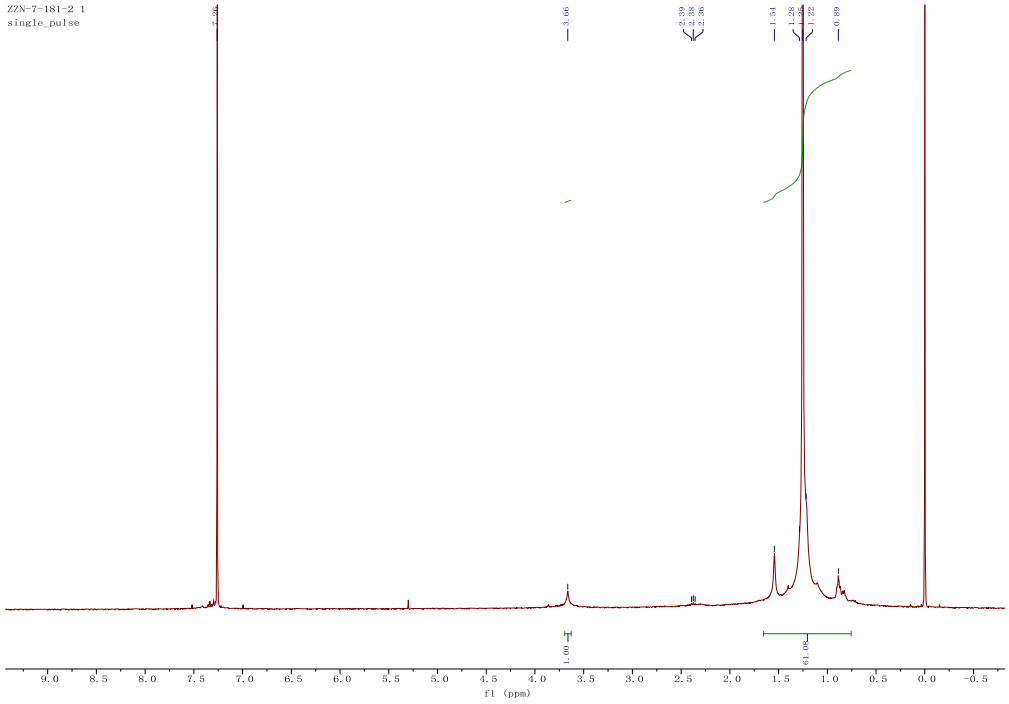


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-5-2.2 mol%**

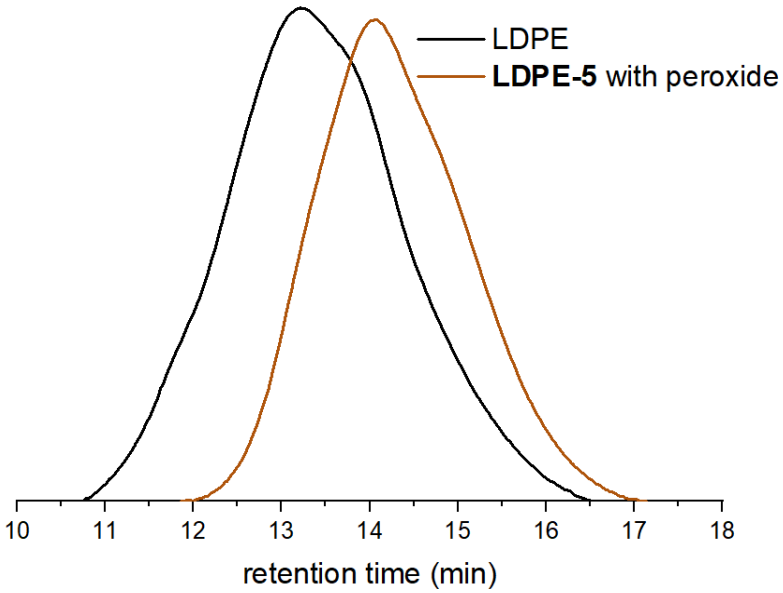
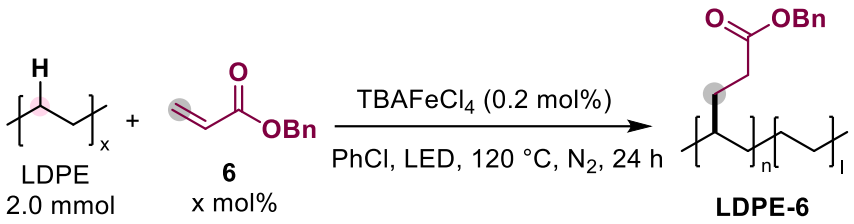


Figure S9. The HT-GPC traces of comparable result using BPO as a radical initiator

The C–H alkylation of LDPE by controlling the reaction time and loading of 6

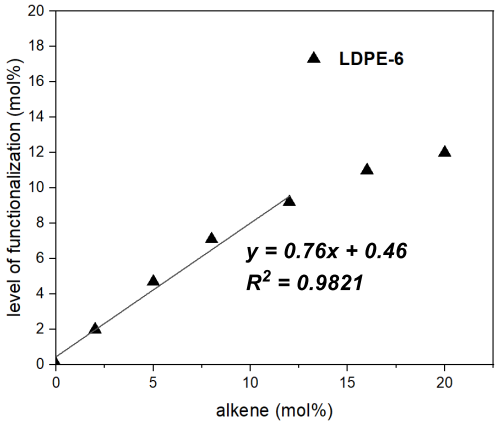
(1) The level of functionalization (LOF) using various amount of alkenes



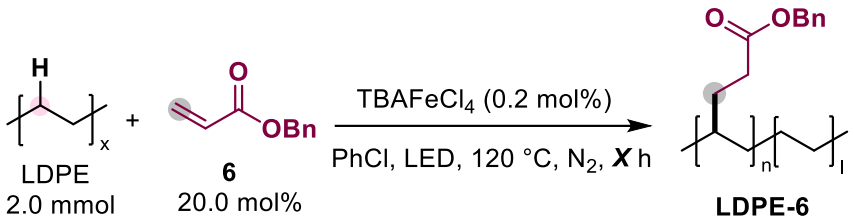
To a 35 mL sealed tube were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 30423 g/mol, $Đ$ = 5.84), **6** [(6.5 mg, d = 1.080 g/mL, 6 μL, 0.04 mmol, 2.0 mol%), (16.5 mg, d = 1.080 g/mL, 15 μL, 0.1 mmol, 5.0 mol%), (25.9 mg, d = 1.080 g/mL, 24 μL, 0.16 mmol, 8.0 mol%), (38.9 mg, d = 1.080 g/mL, 36 μL, 0.24 mmol, 12.0 mol%), (51.8 mg, d = 1.080 g/mL, 48 μL, 0.32 mmol, 16.0 mol%), or (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol, 20.0 mol%)], and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 ºC for 12 hours. The compound **LDPE-6** was obtained as white solid (38.6-64.1 mg). The level of functionalization was determined by ^{1}H NMR. When less than 12 mol% of **6** was used in the 24-hours reactions, the LOFs depended on the usage of alkene (mol%) in terms of a linear function y = 0.76x + 0.46 with R^2 = 0.98.

Table S2. The LOF using various amount of **6**

6 (mol%)	LOF (mol%)
0	0
2.0	2.0
5.0	4.7
8.0	7.1
12.0	9.2
16.0	11.0
20.0	12.0



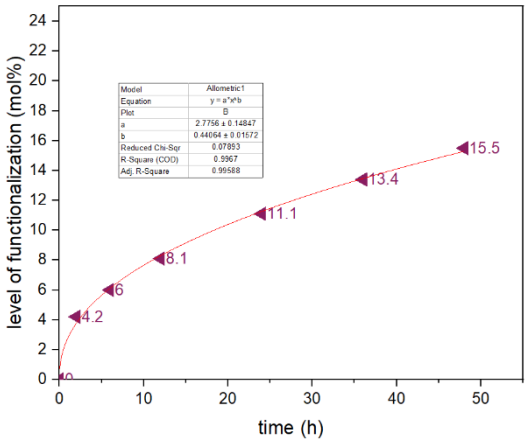
(2) The time-dependent experiment of the C–H alkylation of LDPE with **6**



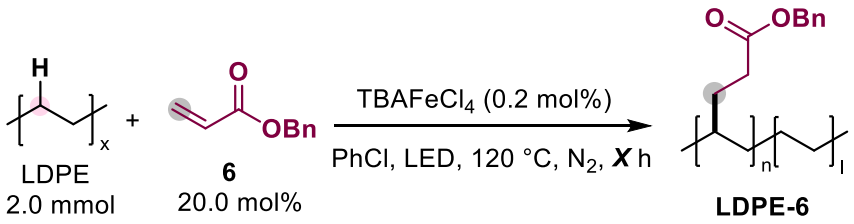
To a 4 mL vial were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 30423 g/mol, $Đ$ = 5.84), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 2, 6, 12, 24, 36 or 48 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours, the level of the functionalization was then determined by ^{1}H NMR. The compound **LDPE-6** was obtained as white solid (56.6-78.4 mg). The level of functionalization was determined by ^{1}H NMR.

Table S3. The LOF vs various reaction time

Time (h)	LOF (mol%)
0	0
2	4.2
6	6.0
12	8.1
24	11.1
36	13.4
48	15.5



(3) The reaction order with **6** in the C–H alkylation of LDPE



To a 4 mL vial were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 30423 g/mol, $Đ$ = 5.84), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 2, 6, 8, 12, 20 or 24 hours at 120 °C. After cooling to rt, the resulting mixture was transformed to 20 mL vial with dodecane as internal standard, EtOH (10.0 mL) was added to precipitate the product. The amount of **6** in the liquid phase was then determined by GC using standard calibration curves.

Table S4. The kinetics experiment for **6**

Time (h)	n_i (mmol)	A_i	A_6	**6** (mmol)	[**6**] (mol/L)	1/[**6**]	ln(1/[**6**])
0	-	-	-	0.400	0.133	7.519	2.017
2	0.214	5226	3110	0.170	0.057	17.544	2.865
6	0.212	5316	1795	0.100	0.033	30.303	3.411
8	0.218	5264	1359	0.075	0.025	40.000	3.689
12	0.217	5502	559.4	0.030	0.010	100.00	4.605
20	0.212	5229	55.6	0.0030	0.001	1000.0	6.908
24	0.221	6382	25.3	0.0012	0.0004	2500.0	7.824

n_i: the amount of dodecane as internal standard. A_i: the area of dodecane as internal standard determined by GC. A_6: the area of **6** determined by GC.

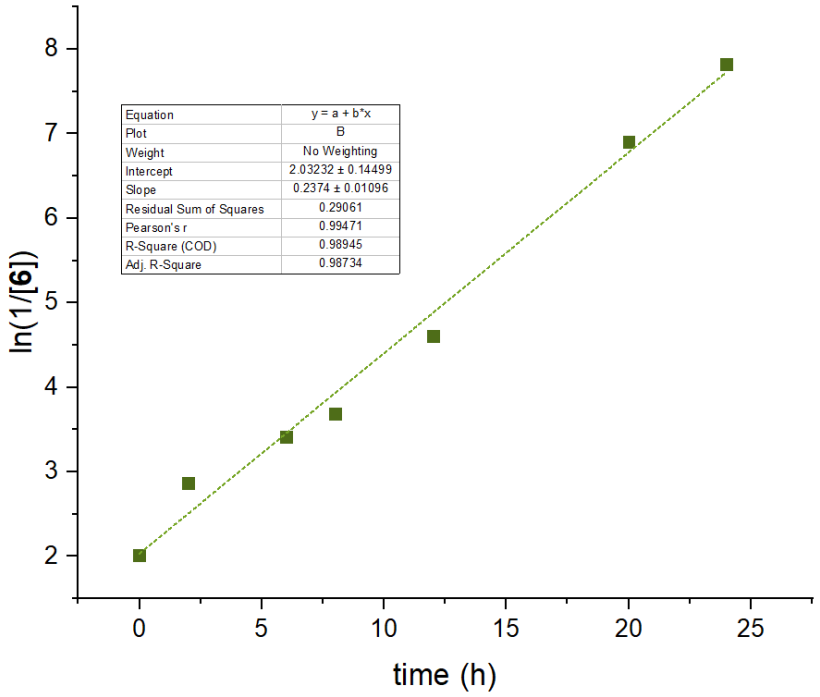
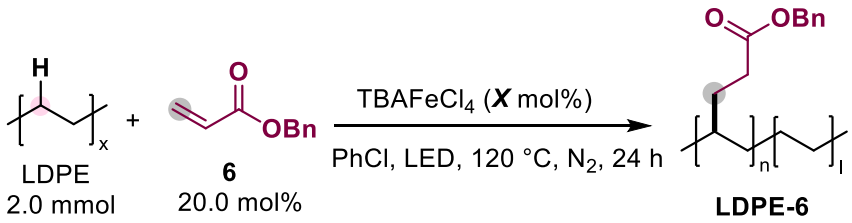


Figure S10. A linear relationship was observed for ln(1/[**6**]) vs reaction time, indicating a first order dependence of the reaction rate with alkene **6**.

(4) The screening of the catalyst loading



To a 4 mL vial were added $TBAFeCl_4$ (44.0 mg, 0.1 mmol or 88.0 mg, 0.2 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 40897 g/mol, $Đ$ = 6.68), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours, the level of the functionalization was then determined by ^1H NMR. The compound **LDPE-6** was obtained as oil (131.2 mg, 19.9 mol% LOF or 122.4 mg, 17.5 mol% LOF). **GPC (TCB, 140 °C)** with 5.0 mol% $TBAFeCl_4$: M_n = 39764 g/mol, M_w = 230205 g/mol, $Đ$ = 5.79. **GPC (TCB, 140 °C)** with 10.0 mol% $TBAFeCl_4$: M_n = 35774 g/mol, M_w =

227393 g/mol, $Đ$ = 6.36. The level of functionalization was determined by ^{1}H NMR.

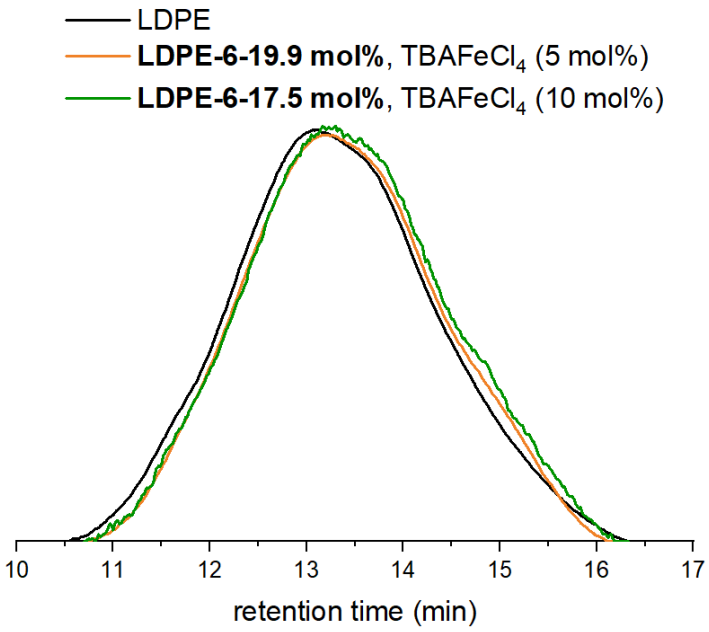


Figure S11. The HT-GPC traces of LDPE, **LDPE-6-19.9 mol%**, and **LDPE-6-17.5 mol%**

Determination of quantum yield

(1) Determination of the light intensity at 390 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry (referred to the reported procedure: M. A. Cismesia, et al., *Chem. Sci.* **2015**, *6*, 5426-5434). A 0.006 M solution of ferrioxalate was prepared by dissolving 88.4 mg of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 5.0 mL of the ferrioxalate solution was placed in a 10 mL quartz reaction tube (V = 5.0 mL) and irradiated for 30.0 seconds with a commercial 100 W 390 nm laser. After irradiation, the solution was shielded with aluminum foil and 0.88 mL of the phenanthroline solution was added. The solution was then allowed to rest for 1 h to allow the ferrous ions to coordinate to the phenanthroline completely. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$mol\ Fe^{2+} = (V \cdot \Delta A)/(l \cdot \varepsilon) \qquad (1)$$

Where V is the total volume (0.00588 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

$$Photon\ flux = (mol\ Fe^{2+})/(\Phi \cdot t \cdot f) \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.19 for a 0.006 M solution at λ = 390 nm), t is the time (30.0 s), and f is the fraction of light absorbed at λ = 390 nm (A = 2.1761, see Figure S11). The photon flux was calculated to be 0.60×10^{-8} einstein s^{-1}.

$$mol\ Fe^{2+} = (0.00588\ L \cdot 0.4006)/(1.000\ cm \cdot 11100\ L\ mol^{-1} cm^{-1}) = 2.12 \times 10^{-7}\ mol$$

$$Photon\ flux = (2.12 \times 10^{-7}\ mol)/(1.18 \cdot 30.0\ s \cdot 0.9933) = 0.60 \times 10^{-8}\ einstein\ s^{-1}$$

(2) Determination of fraction of light absorbed at 390 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 390 nm was measured to be 2.1761. The fraction of light absorbed (*f*) by this solution was calculated using eq 3, where A is the measured absorbance at 390 nm.

$$f = 1 - 10^{-A} \qquad (3)$$

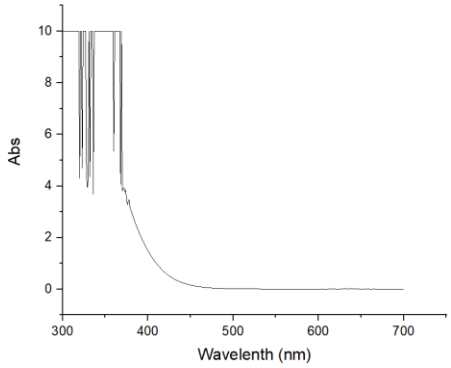
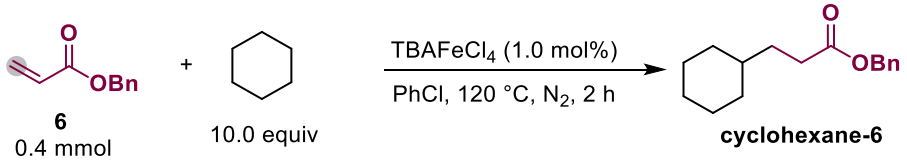


Figure S12. Absorbance of the ferrioxalate actinometer solution.

(3) Determination of quantum yield

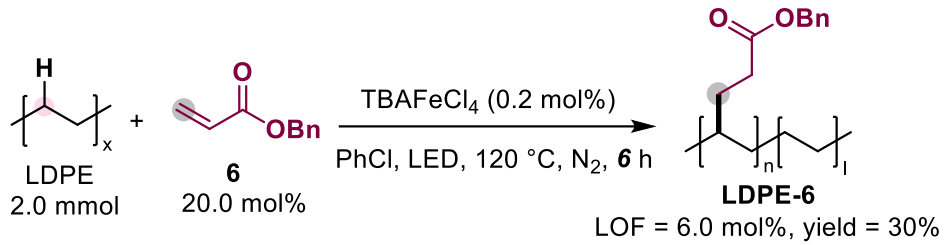
The reaction sample was prepared following the general procedure, and subsequently the sample was irradiated with a commercial 100 W 390 nm laser. After irradiation, the yield of **cyclohexane-6** was detected by ^{1}H NMR spectrum of crude product with an internal standard of CH_2Br_2. The quantum yield was determined using eq 4.

$$\Phi = mol\ product/(flux \bullet t \bullet f) \qquad (4)$$



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), cyclohexane (336.0 mg, d = 0.779 g/mL, 431 μL, 4.0 mmol), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (4.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 100 W 390 nm LEDs, the resulting mixture was stirred for 2 hours (7200 s) at 120 °C. After cooling to rt, the resulting mixture was concentrated in vacuo. Yield: 1.4 %, Φ = 0.131.

$$\Phi = (4 \times 10^{-4}\ mol \times 1.4\ \%)/\ (0.60 \times 10^{-8}\ einstein\ s^{-1} \bullet 7200\ s \bullet 0.9933) = 0.131$$



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LDPE (56.0 mg, 2.0 mmol, M_n = 30423 g/mol, $Đ$ = 5.84), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (4.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 100 W 390 nm LEDs, the resulting mixture was stirred for 6 hours (21600 s) at 120 °C. After cooling to rt, the resulting mixture was concentrated in vacuo. Yield: 30 %, Φ = 0.932.

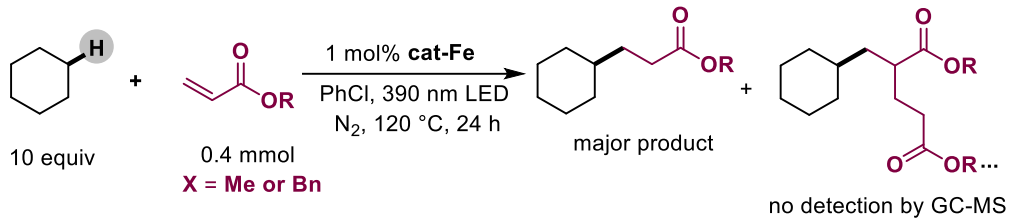
$$\Phi = (4 \times 10^{-4}\ mol \times 30\ \%)/\ (0.60 \times 10^{-8}\ einstein\ s^{-1} \bullet 21600\ s \bullet 0.9933) = 0.932$$

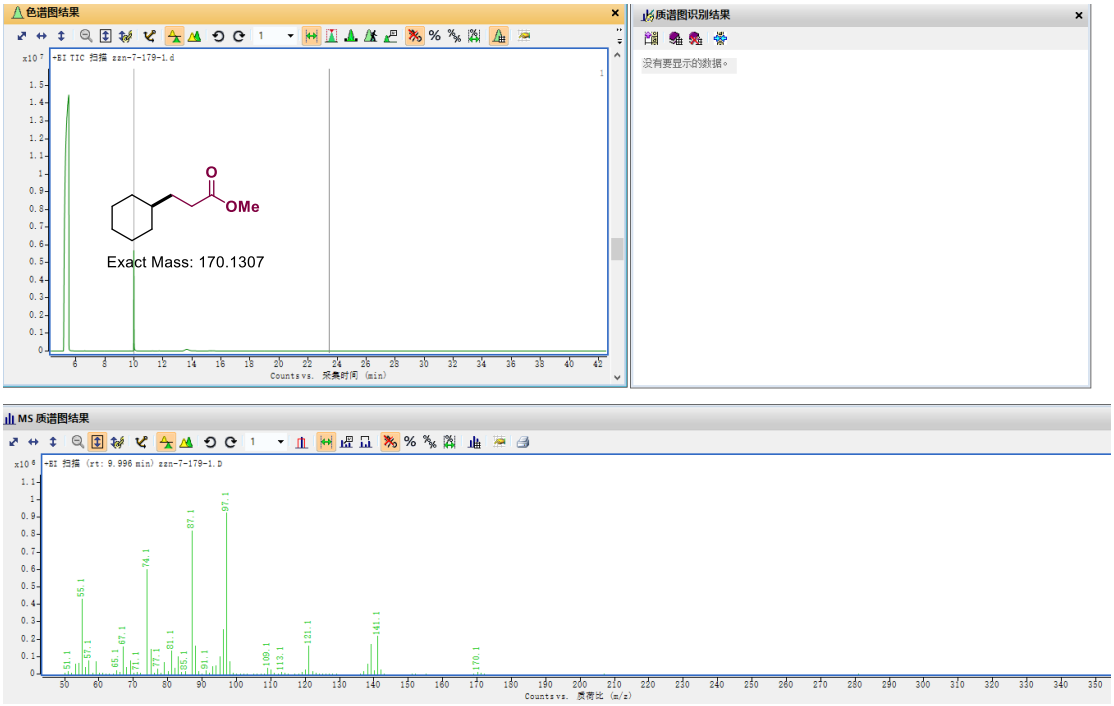
Concern on multiple peaks in the ^{13}C NMR carbonyl region of LDPE-5 and LDPE-6

One concern in this reaction was arisen by the multiple peaks in the ^{13}C NMR carbonyl region of **LDPE-5** and **LDPE-6**, which could be yielded by either the incorporation of the alkenes via multiple C-H functionalization or alkene trimer- and oligomer-grafting.

To address this concern, a series of experiments were then conducted.

Firstly, we have conducted the reaction of cyclohexane with acrylates **5** and **6** as model reactions under the conditions. The reaction of cyclohexane, acrylate **5** or **6**, $TBAFeCl_4$, and PhCl in an N_2 glovebox was conducted under irradiation at 390 nm LEDs for 24 hours at 120 °C. We only observed one cross coupling product, in which only one acrylate was attached to cyclohexane. These results could be confirmed by TLC, ^{1}H NMR, and GC-MS. This result highly suggested that the oligomer-grafted product be not easy to prepare under the standard conditions. The ^{1}H NMR spectrum was matching with the known literature.[4]





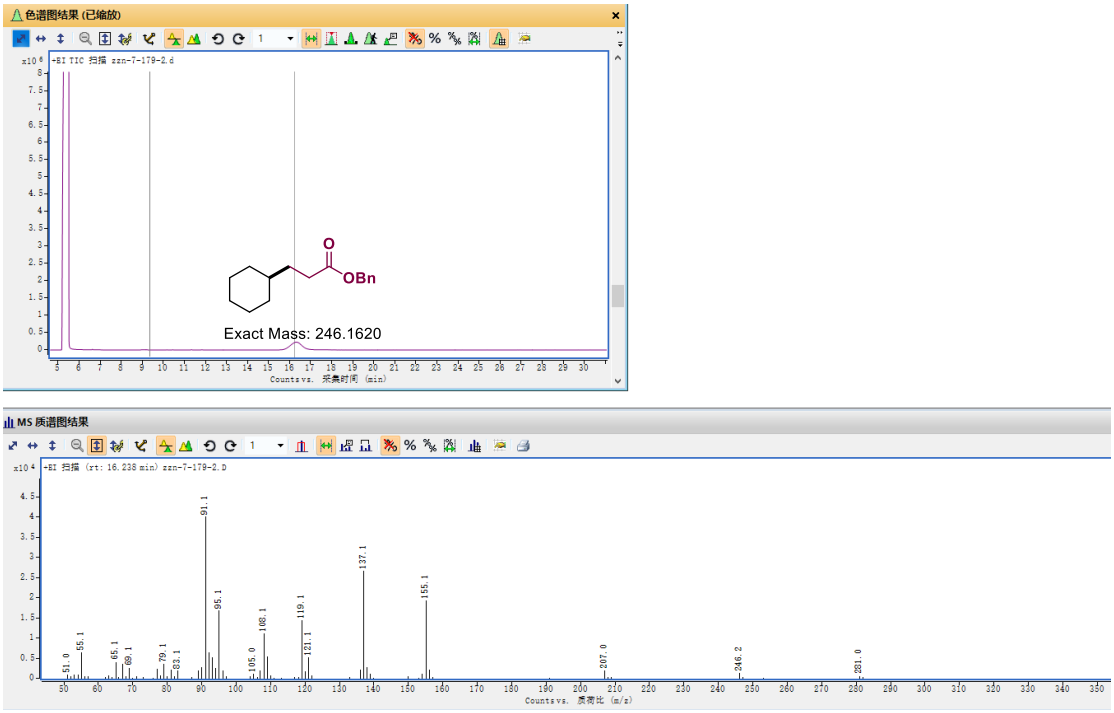


Figure S13. The detection of cross-coupling product by GC-MS.

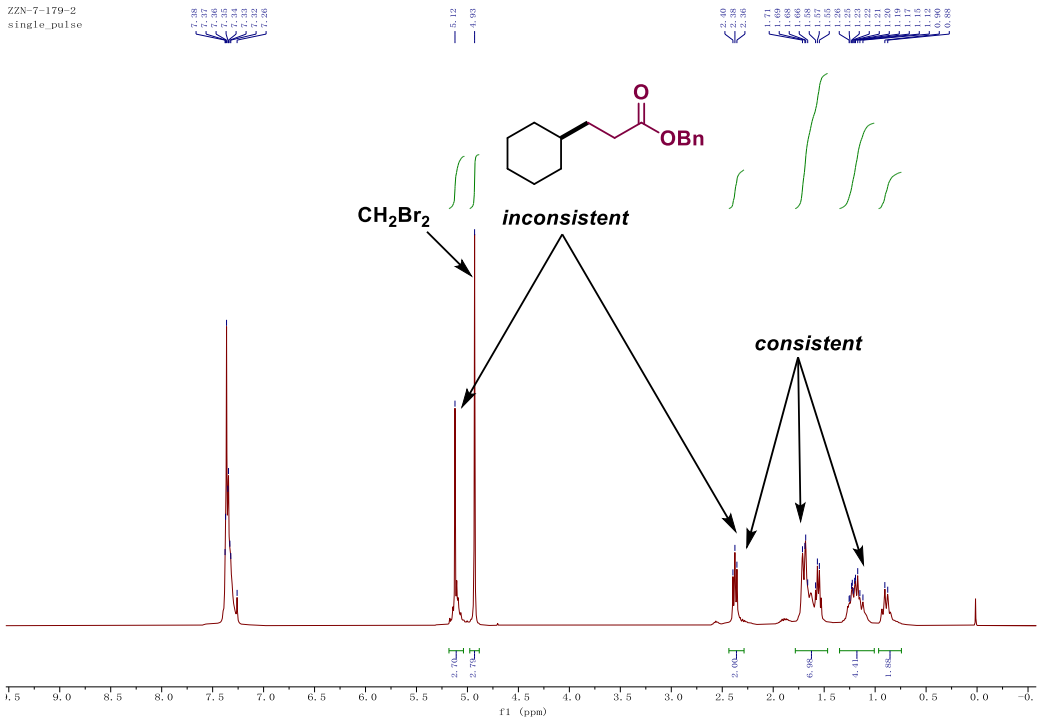
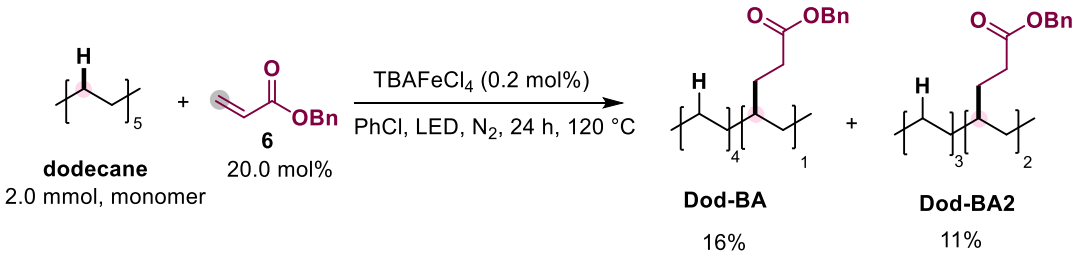


Figure S14. Crude ^{1}H NMR

Moreover, as a better model reaction than that of cyclohexane, the reaction of dodecane (0.4 mmol, accounting for 2.0 mmol of ethylene monomer) with acrylics **6** (20 mol% based on ethylene monomer) was examined for 24 hours at 120 °C. Evaporation and flash chromatography on silica gel (PE/EA = 30/1) afforded the less polar mono-alkylation product, which could be determined by NMRs: **Dod-MA** (17.6 mg, 16%): ^{1}H NMR and ^{13}C NMR spectra see below. **IR ν (neat, cm^{-1})** 2924, 2853, 1738, 1454, 1163. **HRMS (ESI) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{37}O_2$ 333.2788; found 333.2798.

Dod-MA2 (17.9 mg, 11%): ^{1}H NMR and ^{13}C NMR spectra see below. **IR ν (neat, cm^{-1})** 2926, 2853, 1737, 1454, 1154. **HRMS (ESI) m/z**: $[M + H]^+$ Calcd for $C_{32}H_{47}O_4$ 495.3469; found 495.3466.



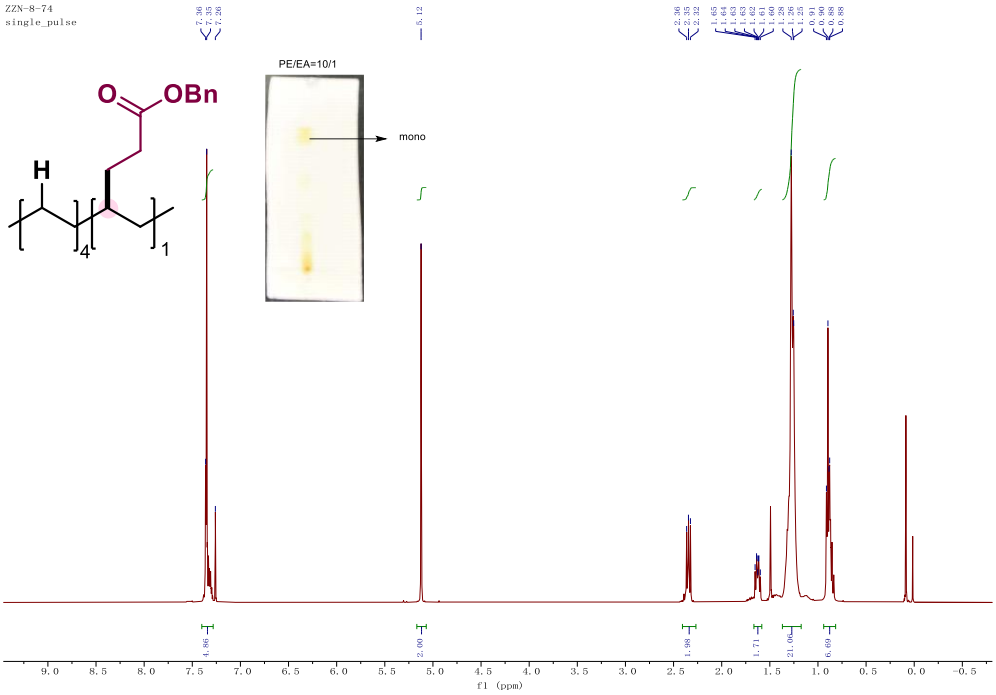
The ^{1}H NMR of **Dod-MA** and **Dod-MA2** clearly showed the incorporation of the acrylate **6**. Interestingly, while the corresponding ^{13}C NMR of **Dod-MA** disclosed that the acrylate group should be randomly incorporated into the main chain since over 40 peaks were observed in the alkyl group region, however, only one major peak was observed in the carbonyl region. The position of the acrylate in the main chain did not significantly affect the chemical shift of the carbonyl group in ^{13}C NMR. This conclusion is very important.

The ^{13}C NMR of the di-alkylation product **Dod-MA2** was also measured and showed multiple peaks in the ^{13}C NMR carbonyl region, which are quite similar as **LDPE-6**. This result clearly disclosed that the incorporation of two acrylate randomly into a long chain alkane (such as dodecane) would observe the multiple peaks in the ^{13}C NMR carbonyl region. The reasons might be explained by the diverse regio- and diastereoisomers. And it is reasonable to assume that the incorporation of more than two acrylate molecules would observed similar multiple peaks in the ^{13}C NMR carbonyl region.

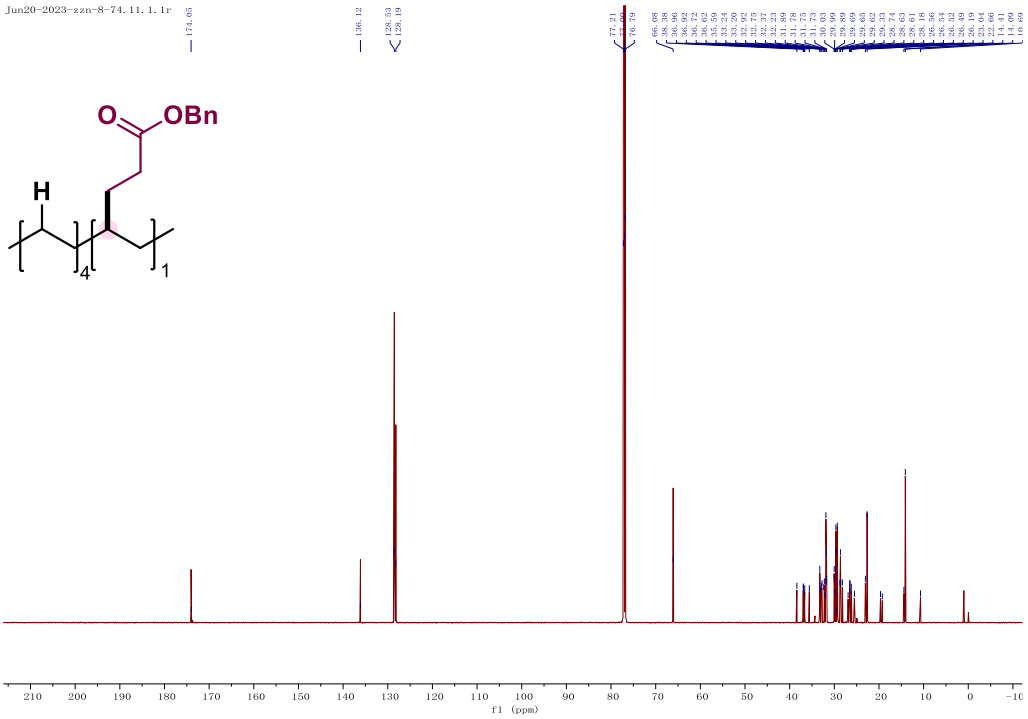
Alternatively, according to the known literature (*Organometallics*, **2012**, *31*, 8388-8406) and the conclusion we obtained above, the structure of the dimerization product (probably also the trimers) of acrylate **6** might present only two peaks in the ^{13}C NMR carbonyl region, which would

be much less than that of **Dod-MA2**. Therefore, although we cannot rule out the possibility on the existence of the dimerization of acrylate, the installation of two acylates by double C-H bond functionalization would be the major process during the transformation.

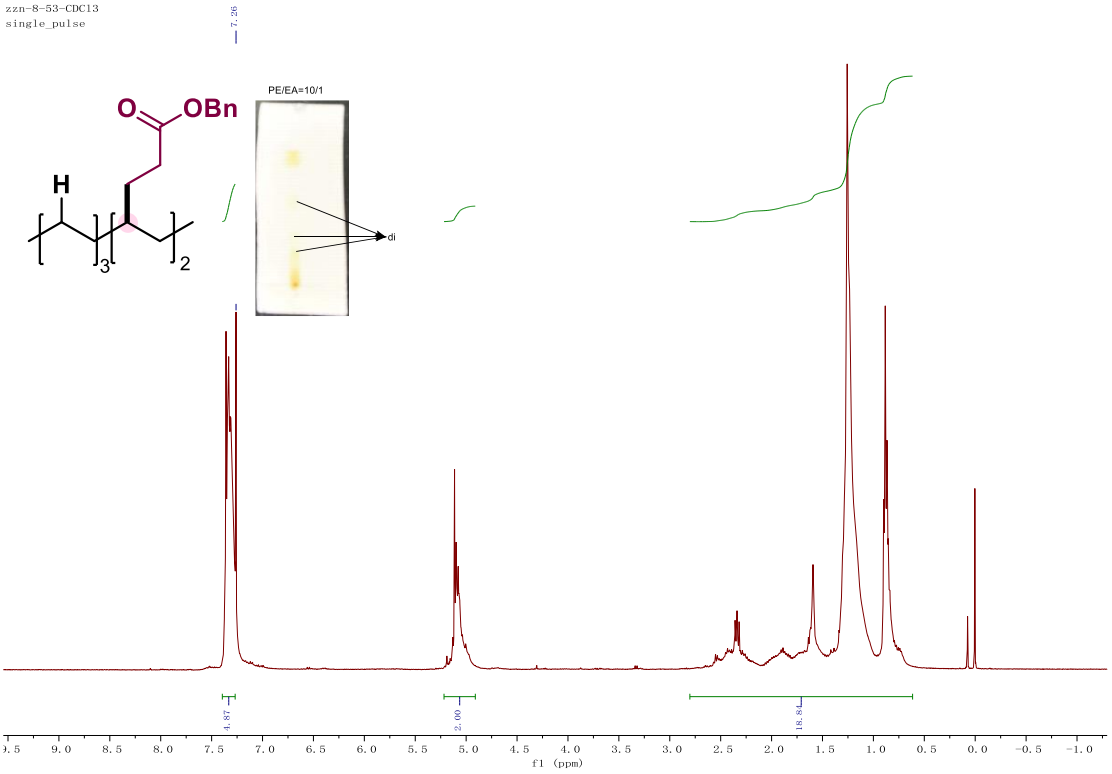
^{1}H NMR of mono-alkylation product **Dod-MA**:



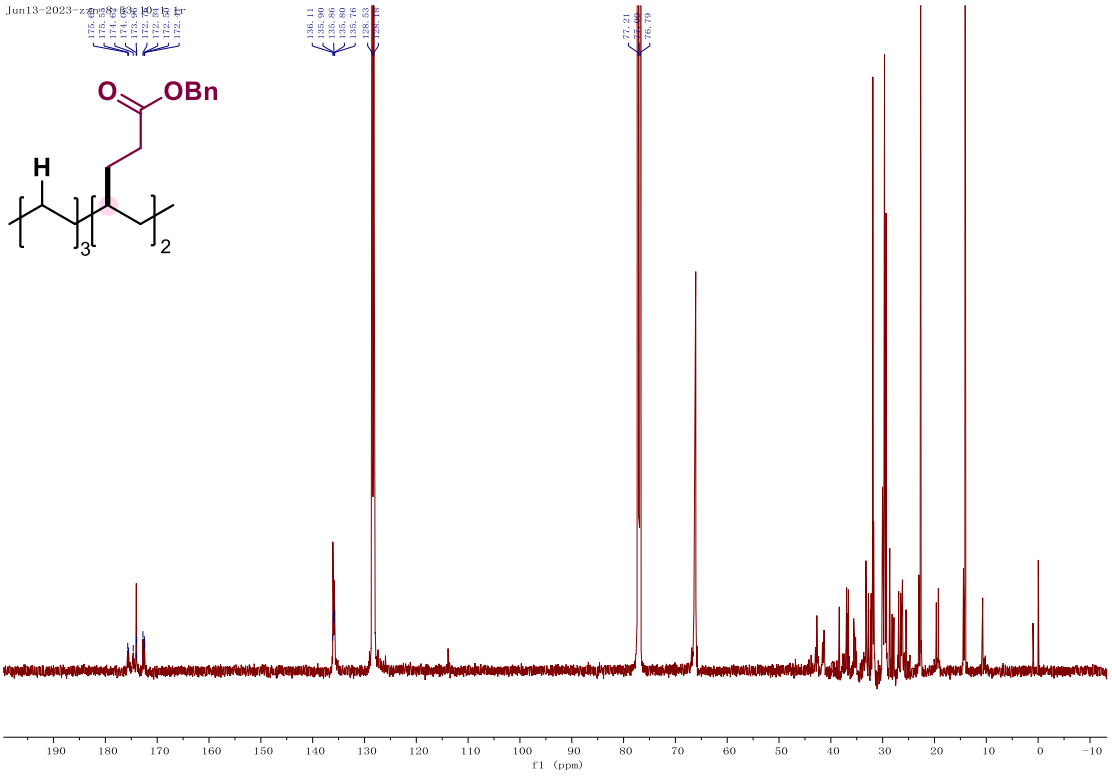
^{13}C NMR of mono-alkylation product **Dod-MA**:



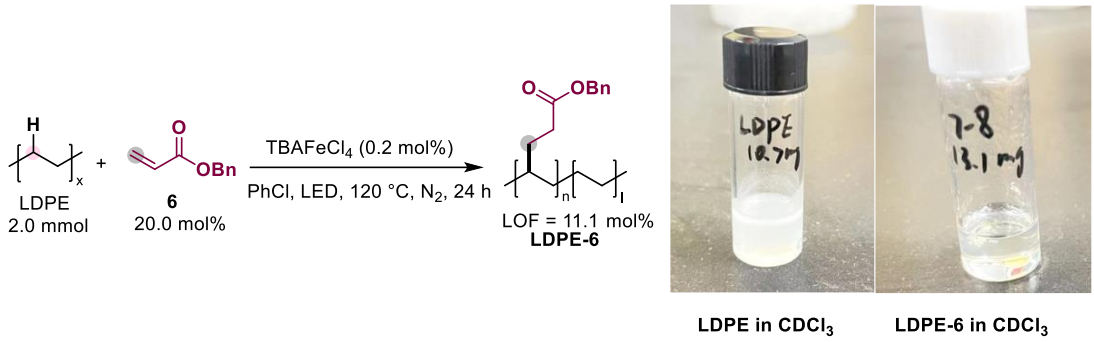
^{1}H NMR of di-alkylation product **Dod-MA2**:



^{13}C NMR of di-alkylation product **Dod-MA2**:


O
OBn
H
3
2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

The C–H bond functionalization of the LDPE



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LDPE (56.4 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-6** as a white solid (69.4 mg, LOF = 11.1 mol%). The level of functionalization was determined by ^{1}H NMR. Moreover, the heteronuclear multiple bond correlation (HMBC) and diffusion ordered NMR spectroscopy (DOSY) spectra of **LDPE-6** confirmed the small molecule is covalently linked onto LDPE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.27 (m, 5.36 H, Ar-H), 5.25-4.78 (m, **2.00 H**), 2.35-2.12 (m, 1.82 H), 1.75-0.60 (m, **37.06 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2919, 1737, 1587, 1454, 1157. **GPC (TCB, 140 °C)** M_n = 38373 g/mol, M_w = 161595 g/mol, $Đ$ = 4.21. **TGA (°C)** LDPE T_d = 420, **LDPE-6** T_d = 340. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-6** no recorded melting point.

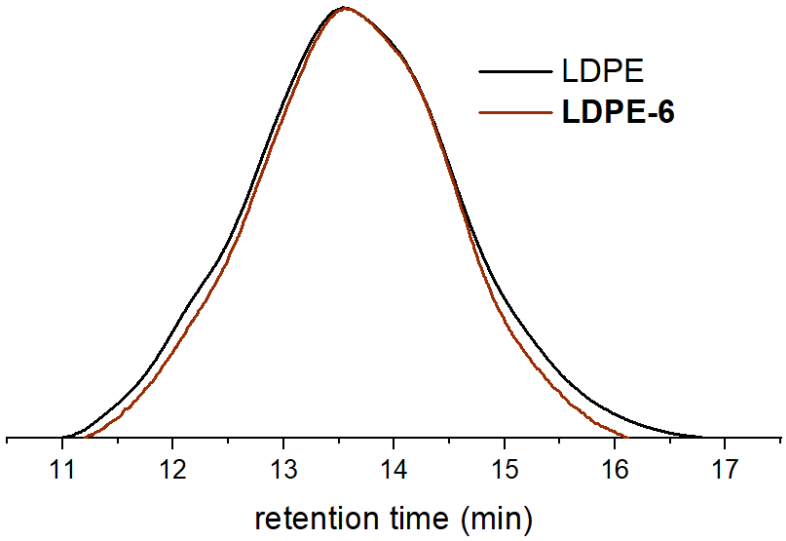


Figure S15. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-6** (red), M_n = 38373 g/mol, M_w = 161595 g/mol, $Đ$ = 4.21.

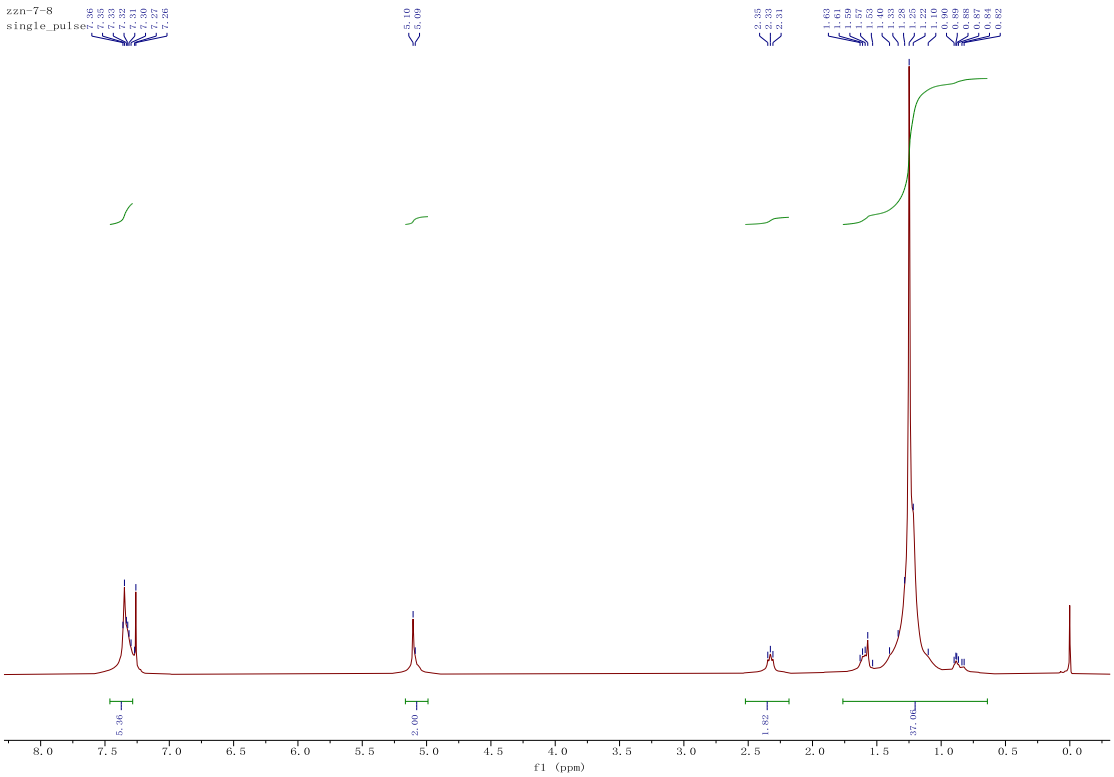


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-6**

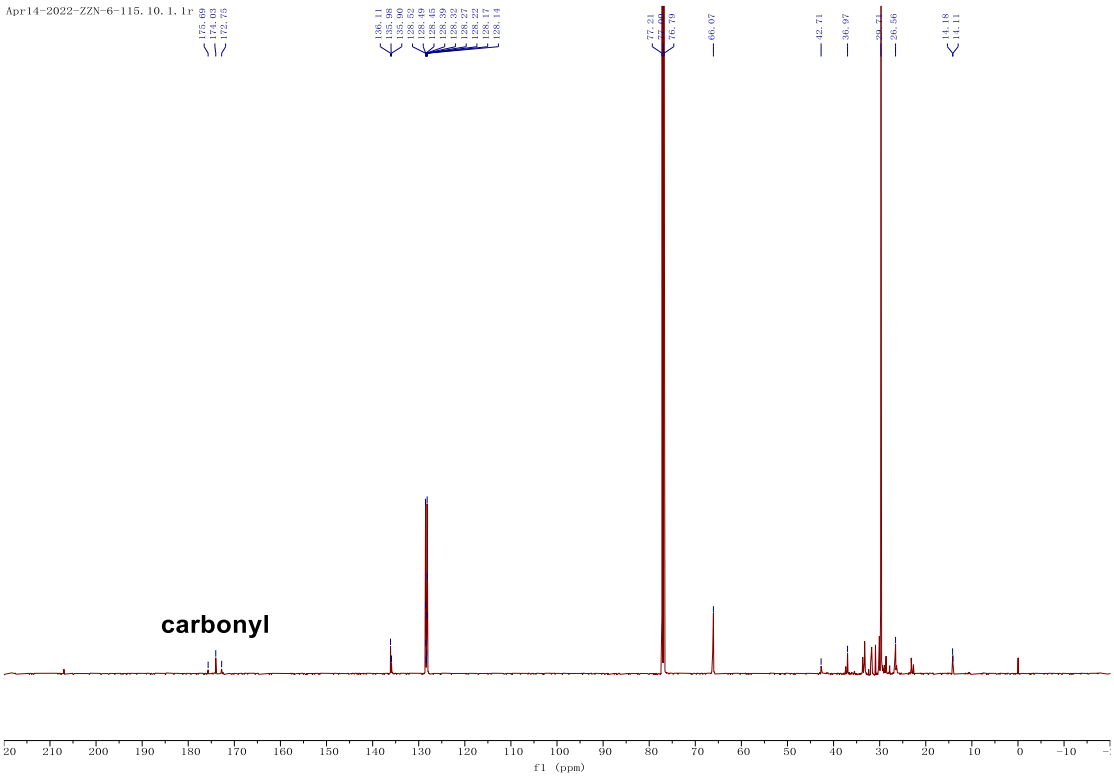


Figure S17.^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-6**

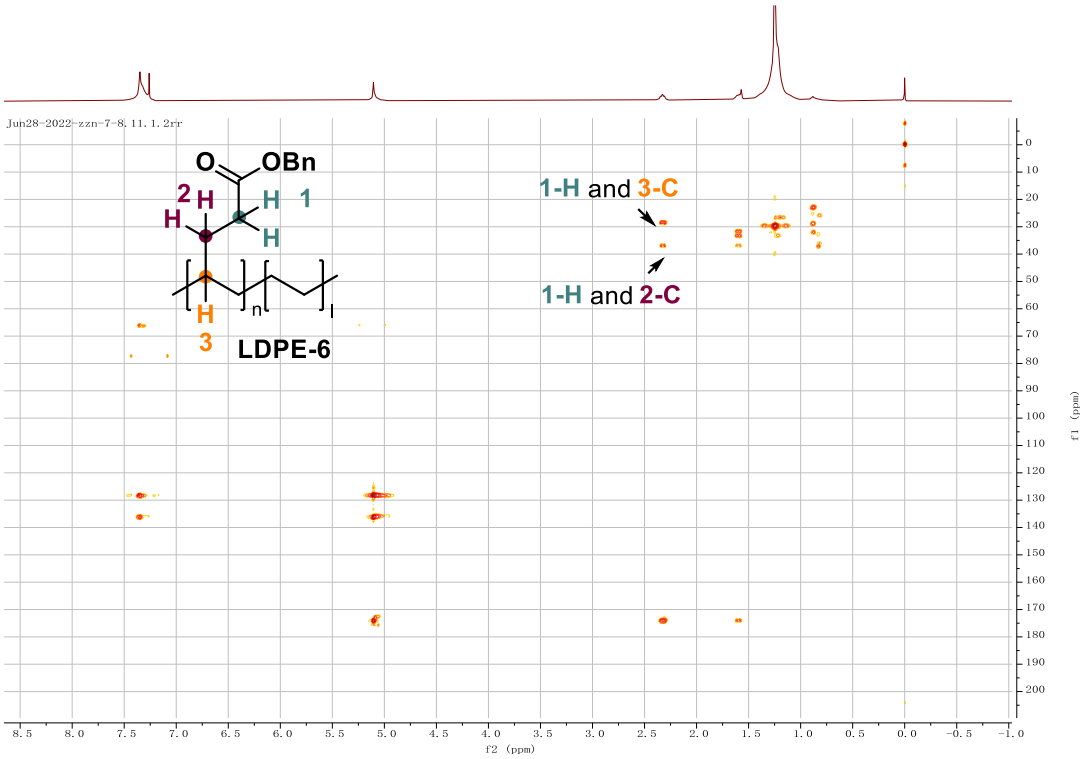


Figure S18. Heteronuclear multiple bond correlation (HMBC) spectroscopy of **LDPE-6**.

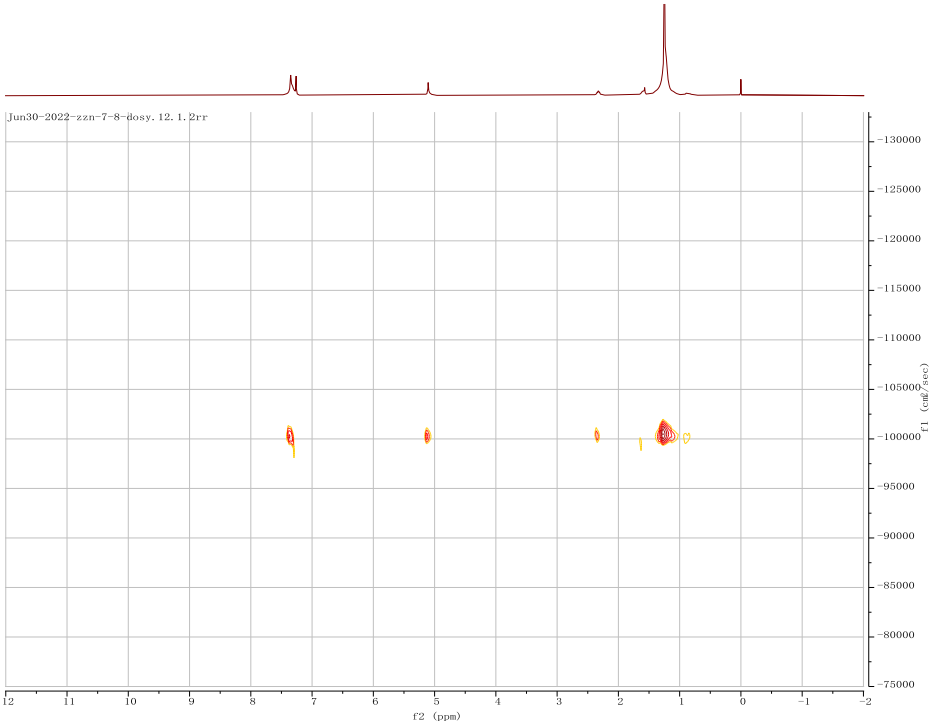
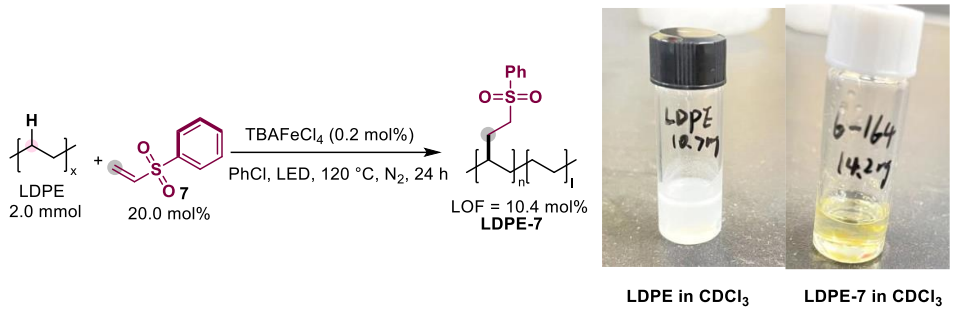


Figure S19. Diffusion ordered NMR spectroscopy (DOSY) of **LDPE-6** presented that the all protons of **LDPE-6** had the same diffusion coefficient, indicating the small molecule is covalently linked onto LDPE.



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LDPE (56.3 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **7** (67.3 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-7** as a yellow solid (73.0 mg, LOF = 10.4 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-7.28 (m, 5.00 H), 3.25-2.89 (m, **2.00 H**), 2.25-0.61 (m, **41.40 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2919, 1464, 1306, 1147, 1087. **GPC (TCB, 140 °C)** M_n = 26789 g/mol, M_w = 94167 g/mol, $Đ$ = 3.52. **TGA (°C)** LDPE T_d = 420, **LDPE-7** T_d = 370. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-7** T_m = 84 with 10% crystallinity (DH = 26 J/g).

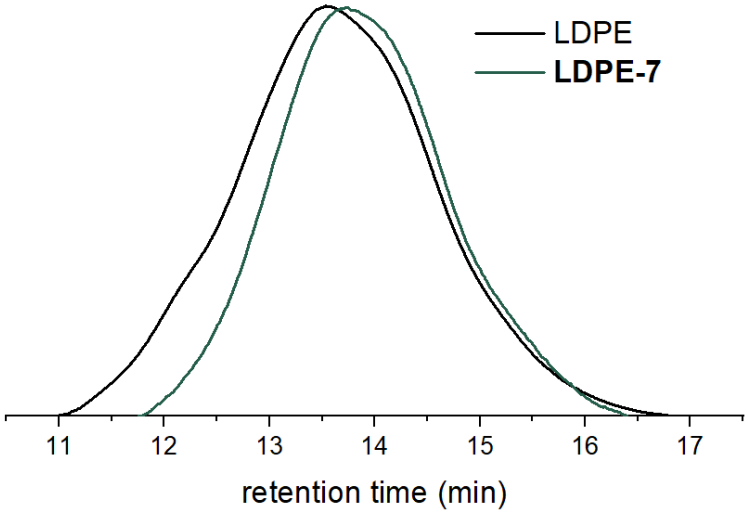


Figure S20. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-7** (green), M_n = 94167 g/mol, $Đ$ = 3.52.

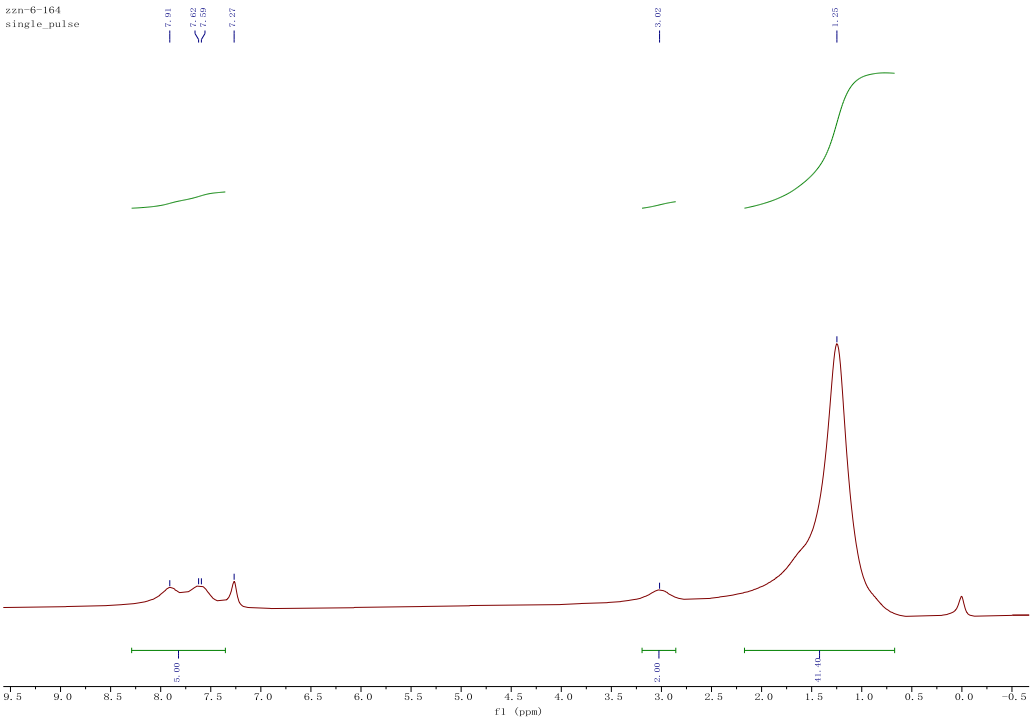


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-7**

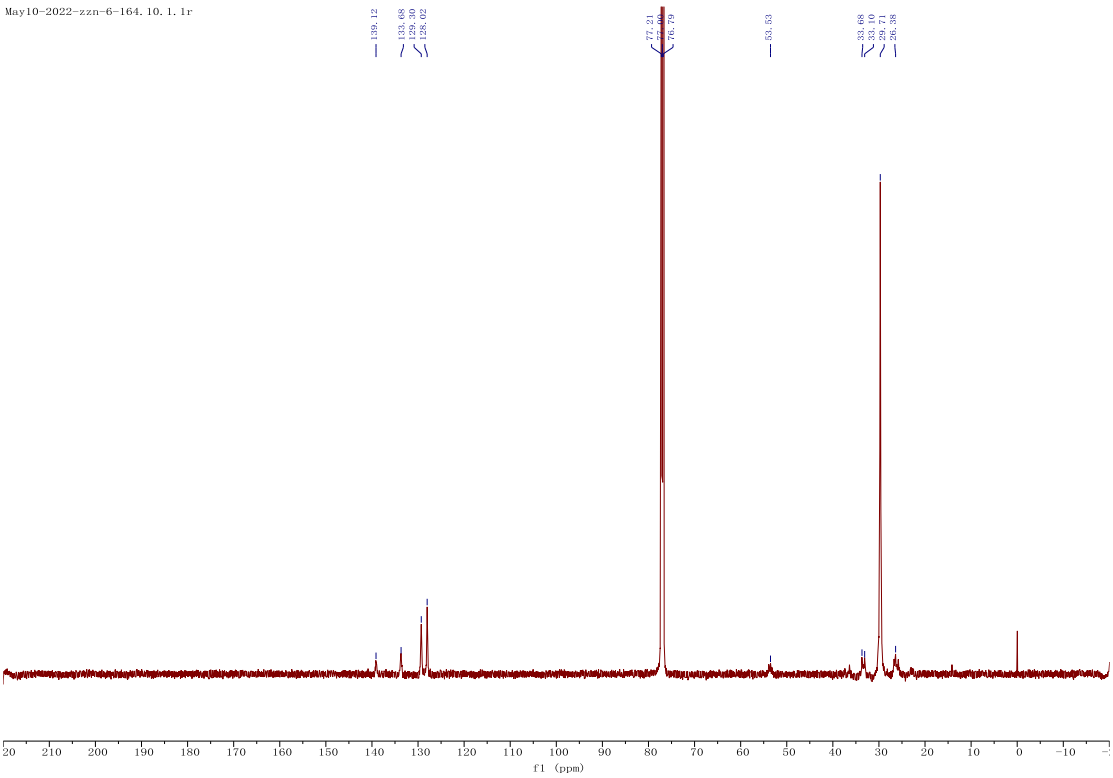


Figure S22.^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-7**

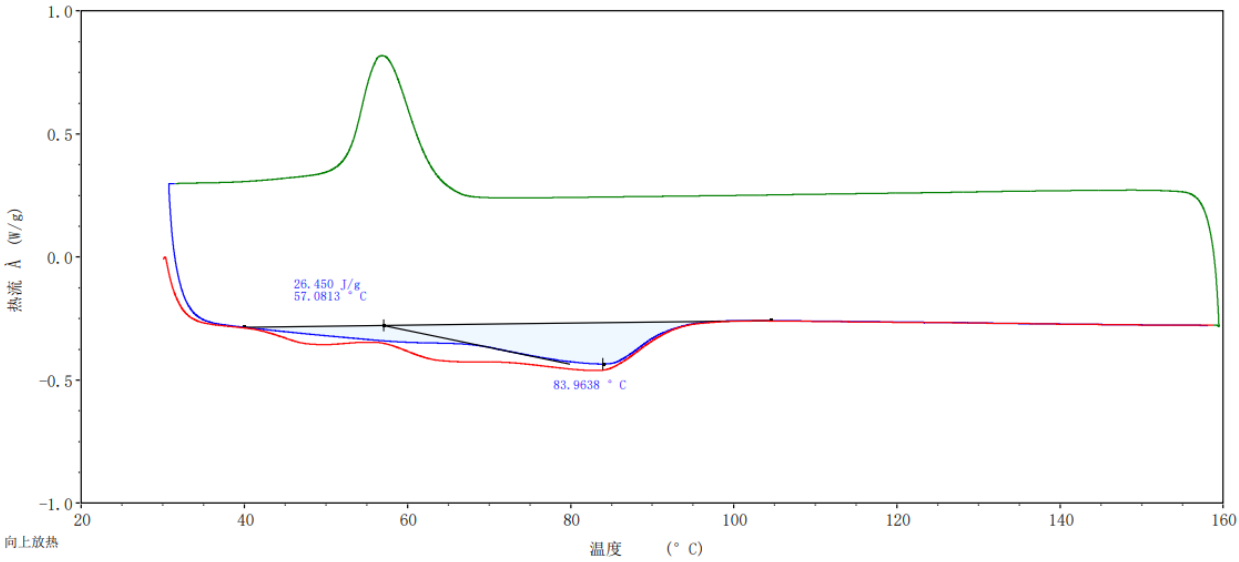
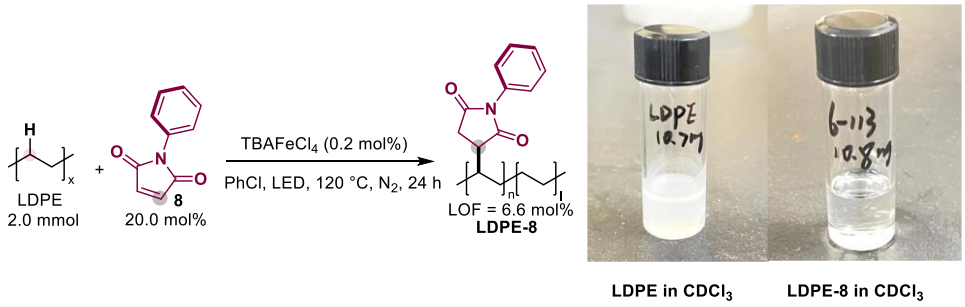


Figure S23. The DSC trace of **LDPE-7**



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LDPE (56.8 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **8** (69.5 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-8** as a white solid (60.5 mg, LOF = 6.6 mol%). The level of functionalization was determined by ^{1}H NMR. Moreover, the heteronuclear multiple bond correlation (HMBC) and diffusion ordered NMR spectroscopy (DOSY) spectra of **LDPE-8** confirmed the small molecule is covalently linked onto LDPE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.23 (m, 5.52 H, Ar-H), 3.24-3.06 (m, **1.00 H**), 2.80-2.75 (m, 1.09 H), 2.72-2.55 (m, 0.99 H), 1.68-0.61 (m, **60.44 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2918, 1714, 1369, 1176. **GPC (TCB, 140 °C)** M_n = 50547 g/mol, M_w = 187854 g/mol, $Đ$ = 3.72. **TGA (°C)** LDPE T_d = 420, **LDPE-8** T_d = 380. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-8** T_m = 78 with 5% crystallinity (DH = 13 J/g).

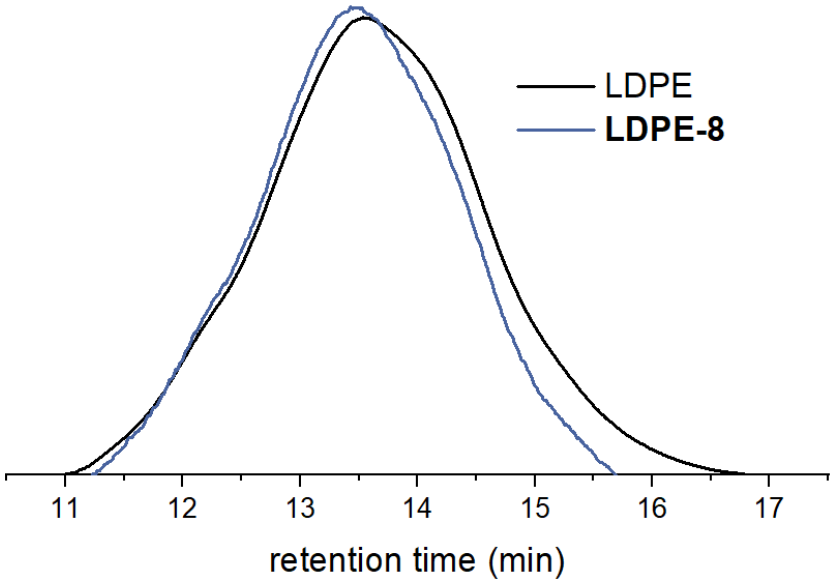


Figure S24. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-8** (blue), M_n = 50547 g/mol, M_w = 187854 g/mol, $Đ$ = 3.72.

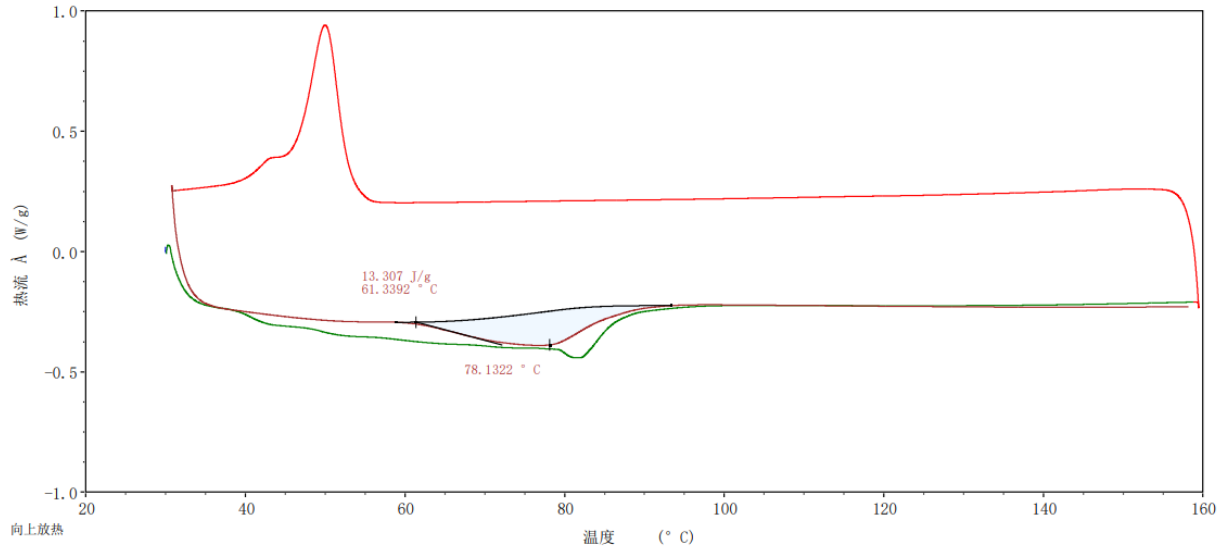


Figure S25. The DSC trace of **LDPE-8**

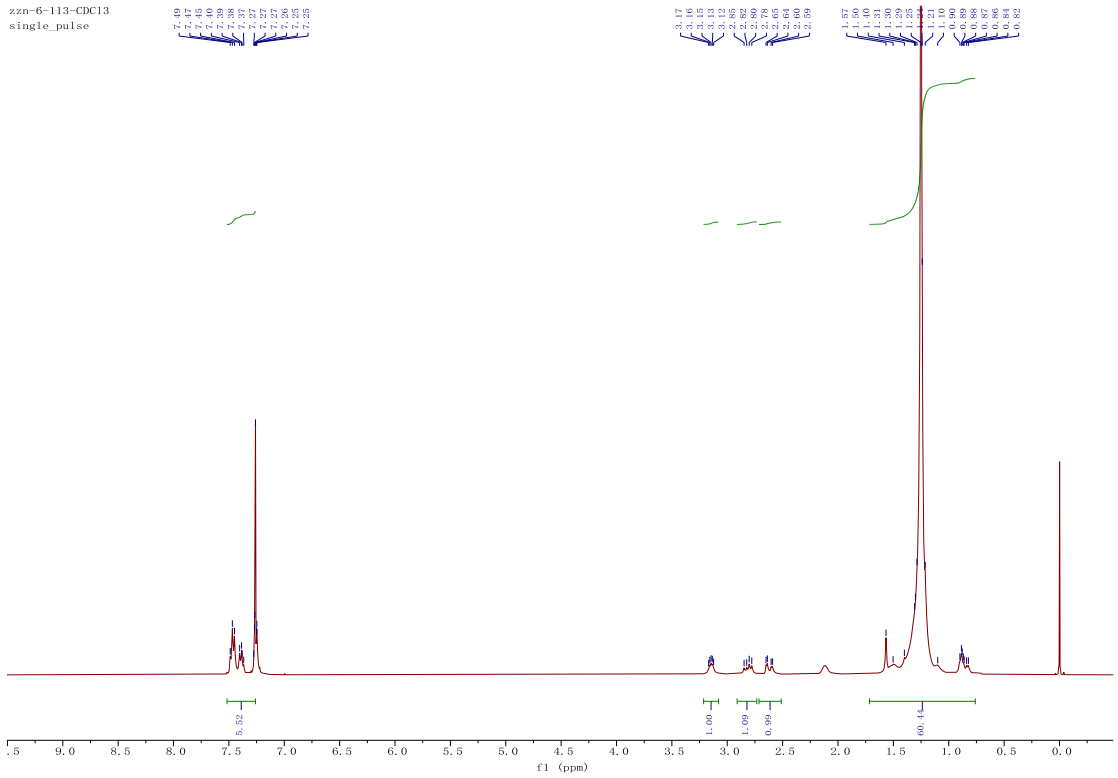


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-8**

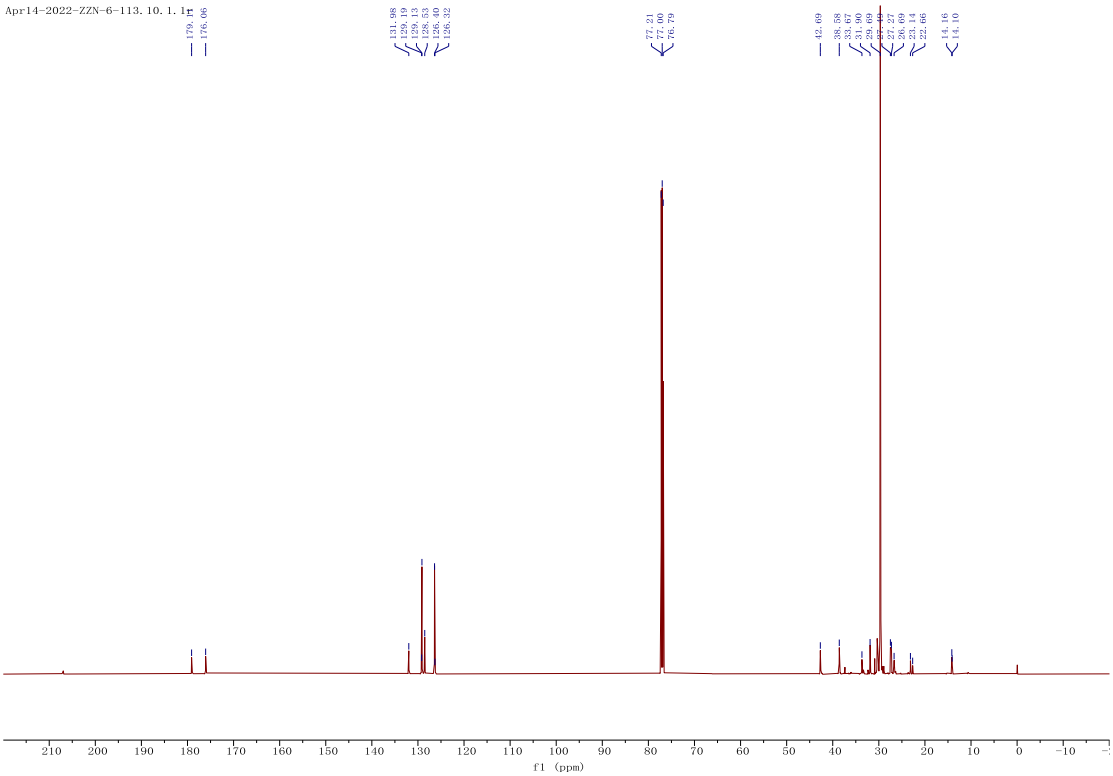


Figure S27. ^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-8**

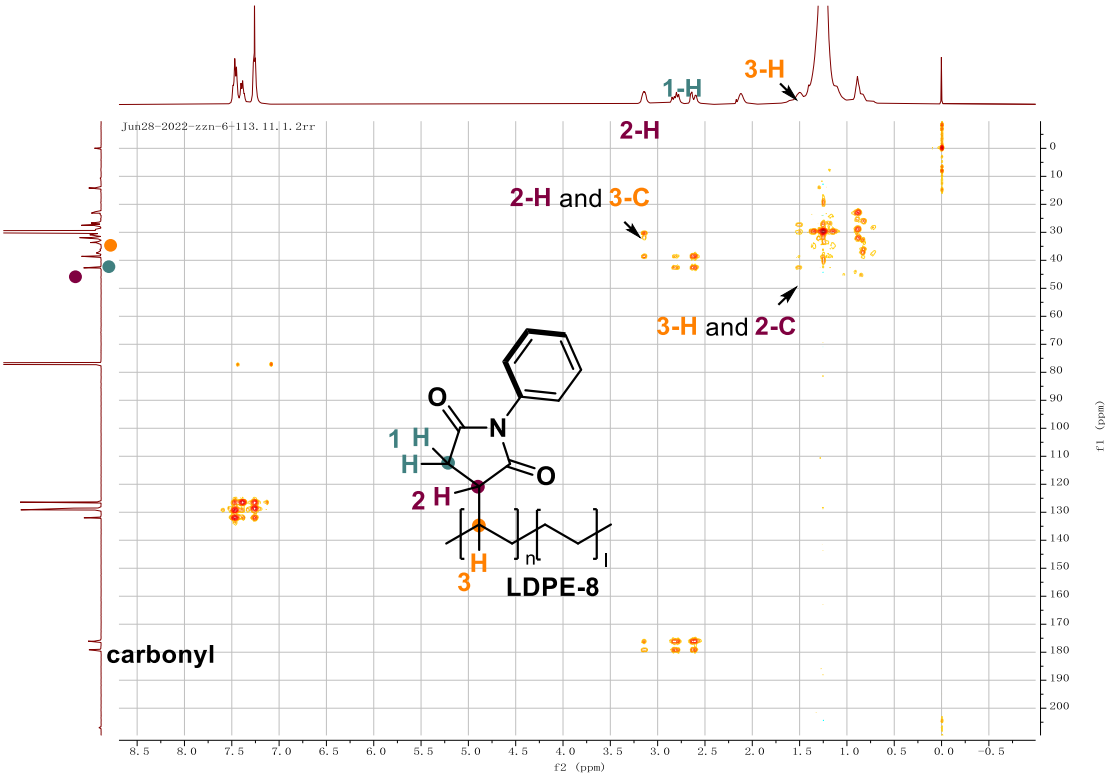


Figure S28. Heteronuclear multiple bond correlation (HMBC) spectroscopy of **LDPE-8**

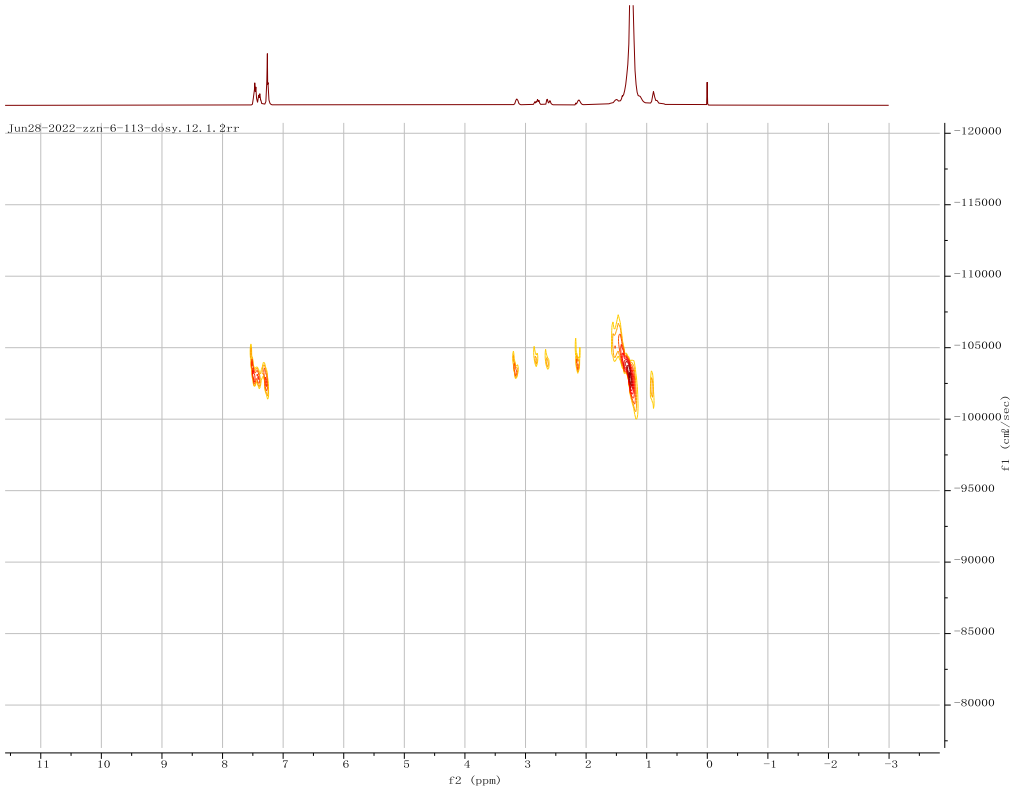
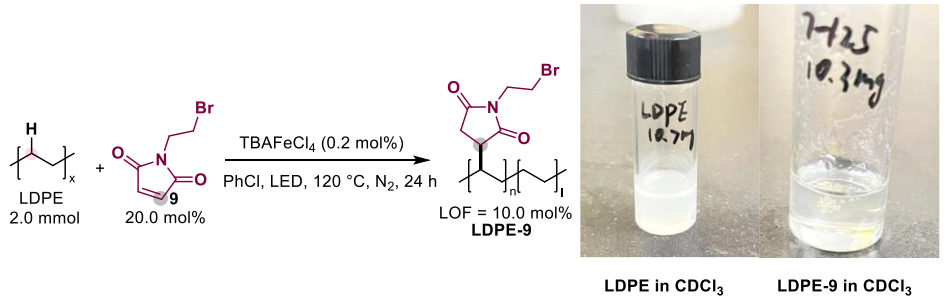


Figure S29. Diffusion ordered NMR spectroscopy (DOSY) of **LDPE-8** presented that the all

protons of **LDPE-8** had the same diffusion coefficient, indicating the small molecule is covalently linked onto LDPE.



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LDPE (56.3 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **9** (81.5 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-9** as a white solid (70.0 mg, LOF = 10.0 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02-3.80 (m, **2.00 H**), 3.68-2.85 (m, 2.05 H), 3.18-2.85 (m, 0.86 H), 2.75-2.45 (m, 1.77 H), 1.72-0.58 (m, **38.26 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2920, 1703, 1397, 1145. **GPC (TCB, 140 °C)** M_n = 40501 g/mol, M_w = 138482 g/mol, $Đ$ = 3.42. **TGA (°C)** LDPE T_d = 420, **LDPE-9** T_d = 320. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-9** no recorded melting point.

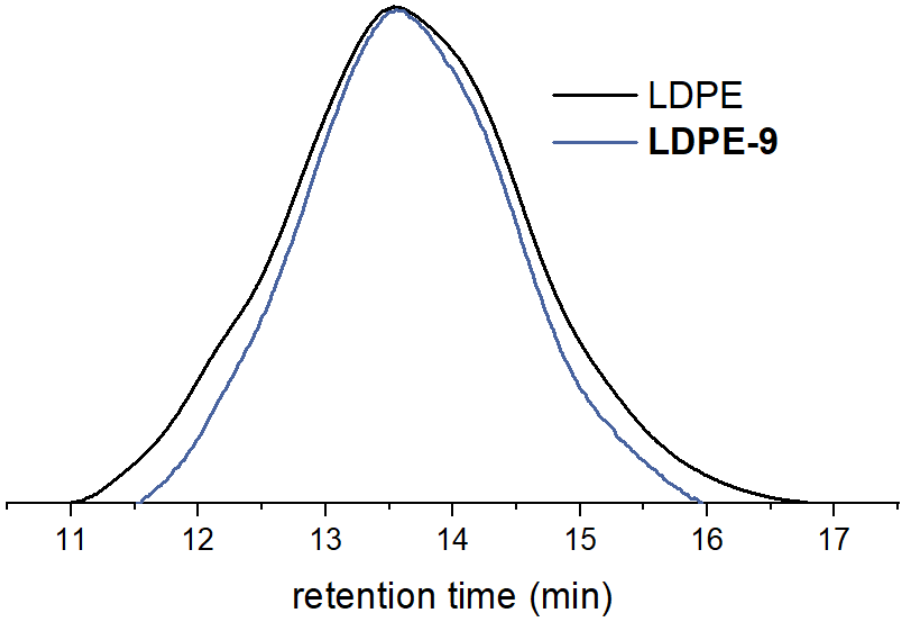


Figure S30. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-9** (blue), M_n = 40501 g/mol, M_w = 138482 g/mol, $Đ$ = 3.42.

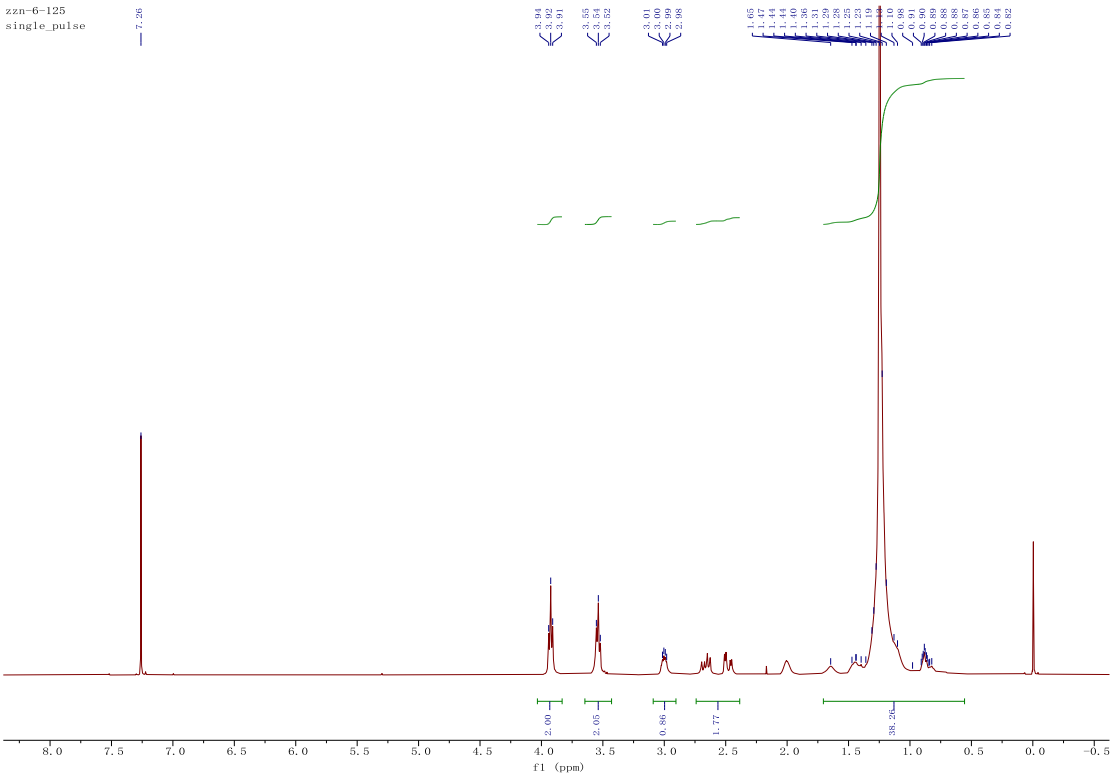


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-9**

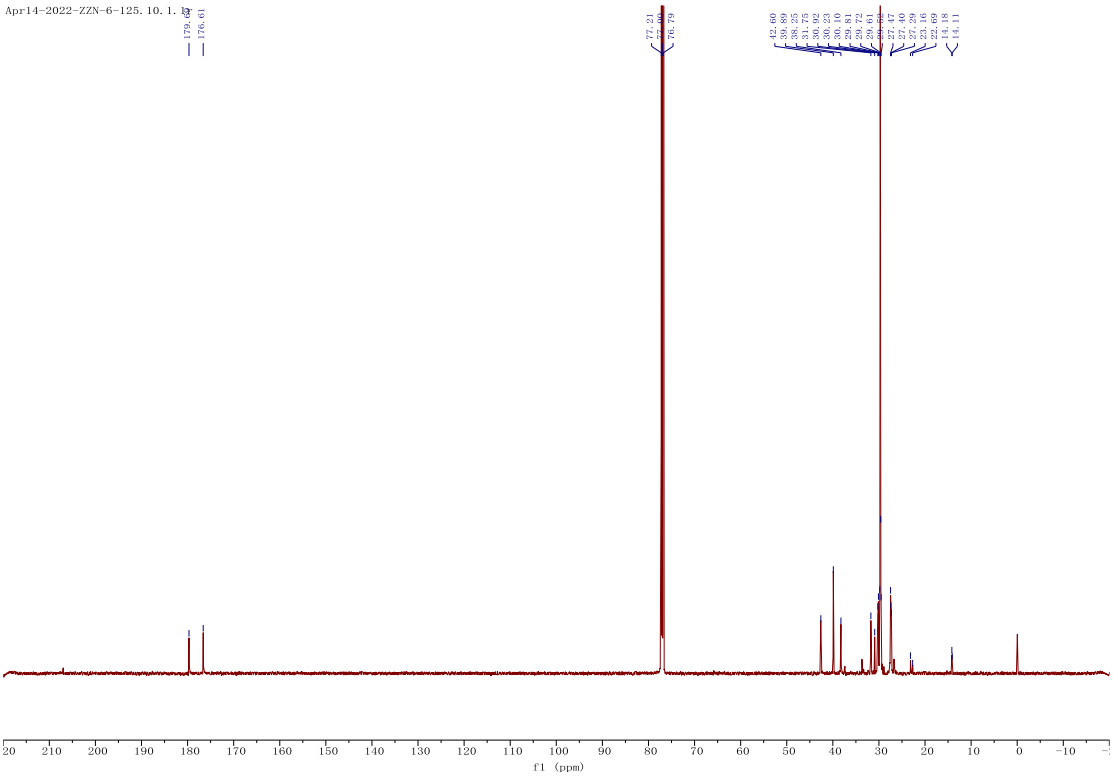
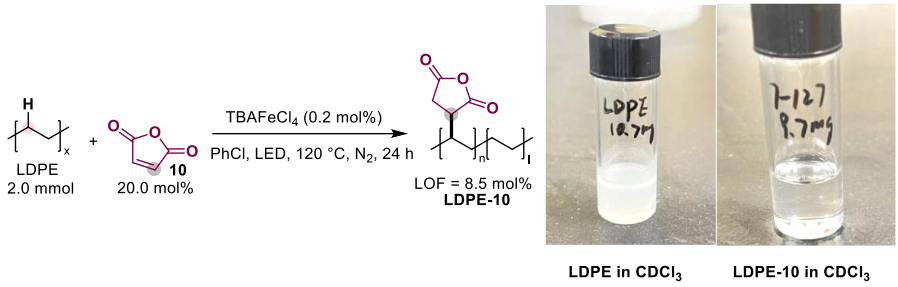


Figure S32. ^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-9**



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LDPE (56.3 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **10** (38.7 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-10** as a white solid (70.1 mg, LOF = 8.5 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50-3.24 (m, **1.00 H**), 3.12-2.85 (m, 1.22 H), 2.83-2.63 (m, 1.03 H), 1.76-0.58 (m, **44.56 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2915, 1774, 1705, 1461, 1143. **GPC (TCB, 140 °C)** M_n = 12199 g/mol, M_w = 37383 g/mol, $Đ$ = 3.06. **TGA (°C)** LDPE T_d = 420, **LDPE-10** T_d = 220. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-10** no recorded melting point.

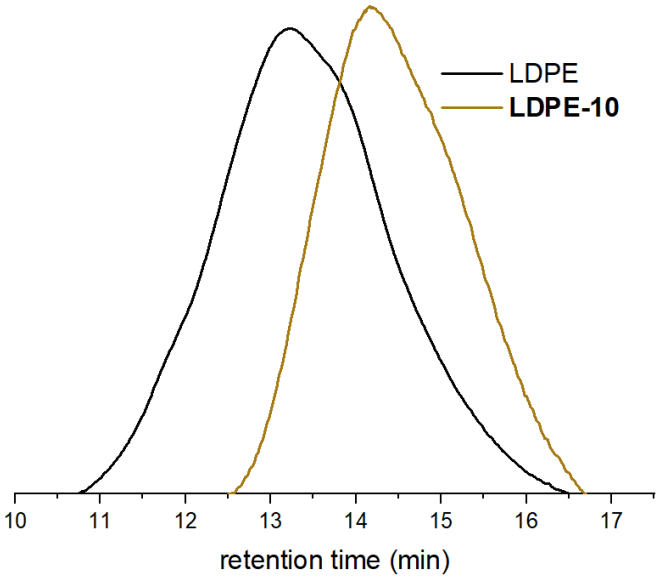


Figure S33. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-10** (yellow), M_n = 12199 g/mol, M_w = 37383 g/mol, $Đ$ = 3.06.

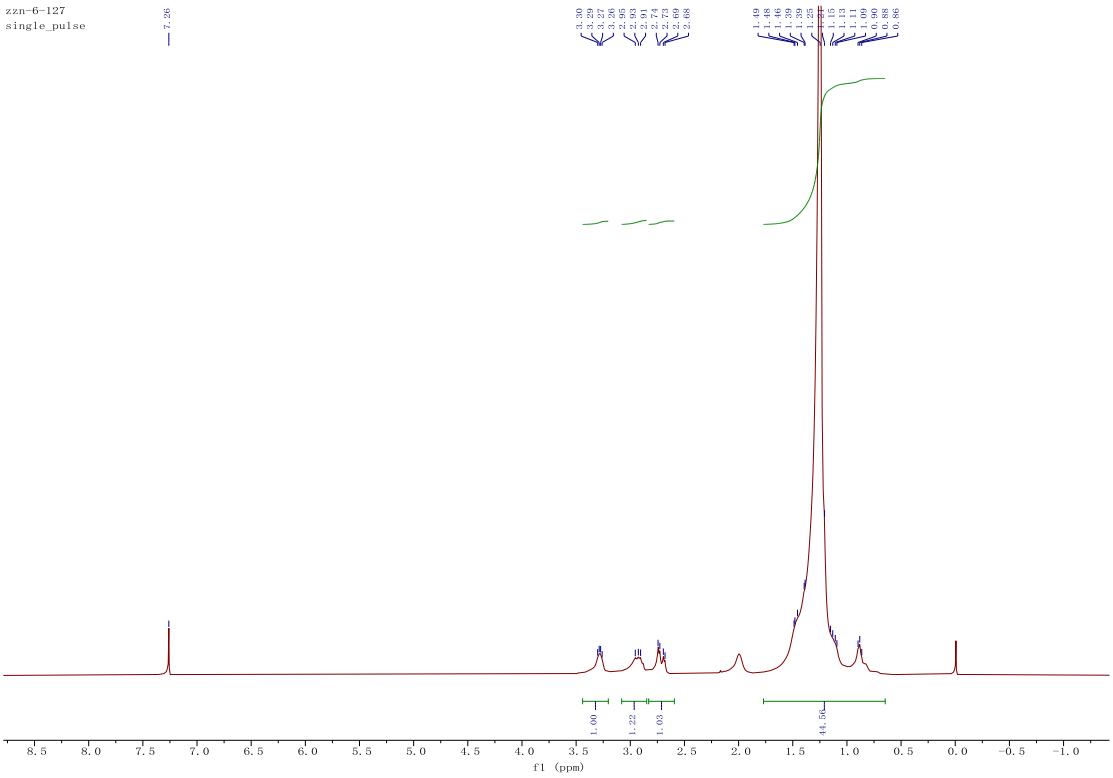


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-10**

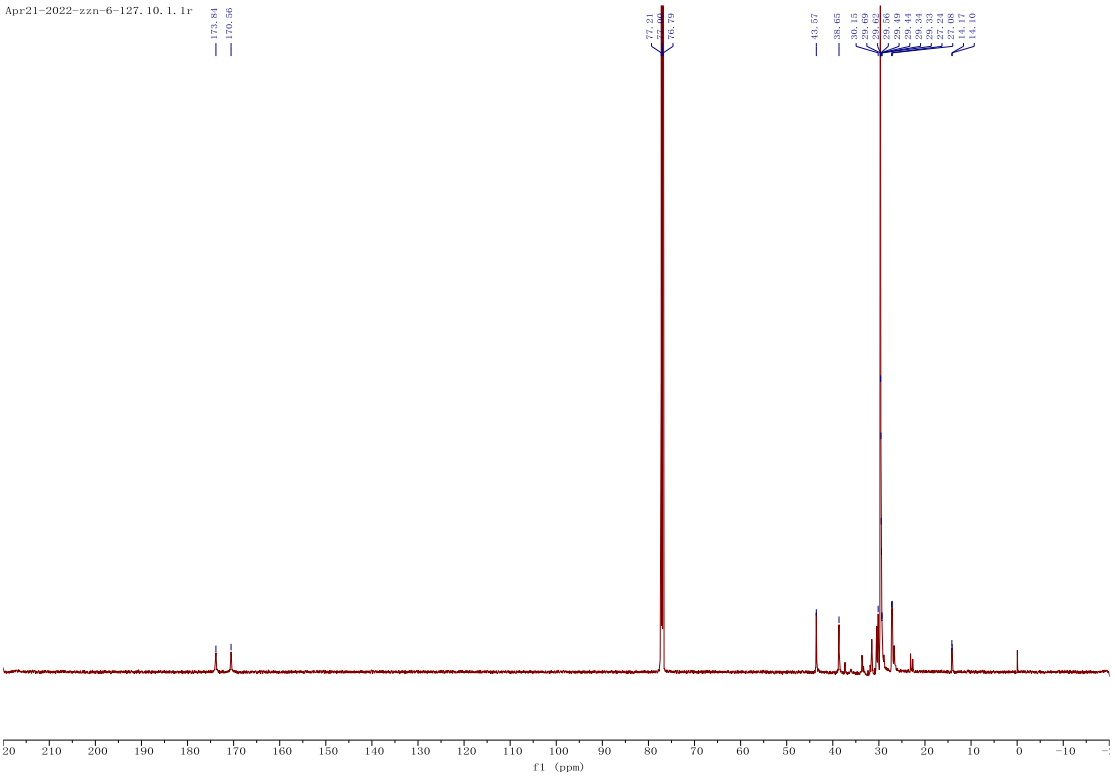
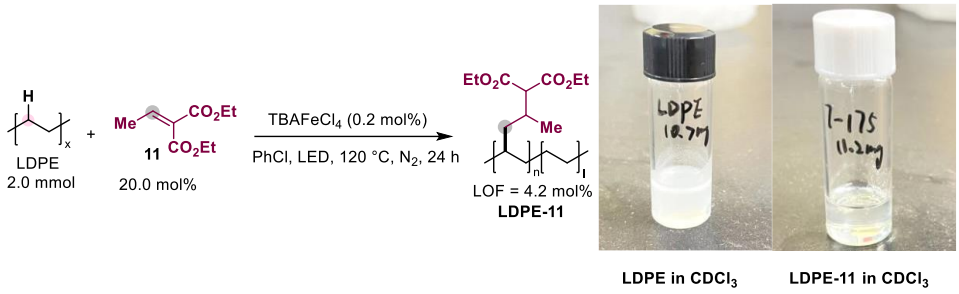


Figure S35. ^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-10**



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LDPE (56.5 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **17** (73.9 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-11** as a white solid (70.7 mg, LOF = 4.2 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25-4.18 (m, **4.00 H**), 3.34 (d, *J* = 10.4 Hz, 0.83 H), 2.50-2.36 (m, 0.83 H) 1.50-0.65 (m, **104.11 H** including **9.00 H** from di-ester moiety). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2917, 1736, 1461, 1373, 1174. **GPC (TCB, 140 °C)** M_n = 26867 g/mol, M_w = 147230 g/mol, $Đ$ = 5.48. **TGA (°C)** LDPE T_d = 420, **LDPE-11** T_d = 320. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-11** no recorded melting point.

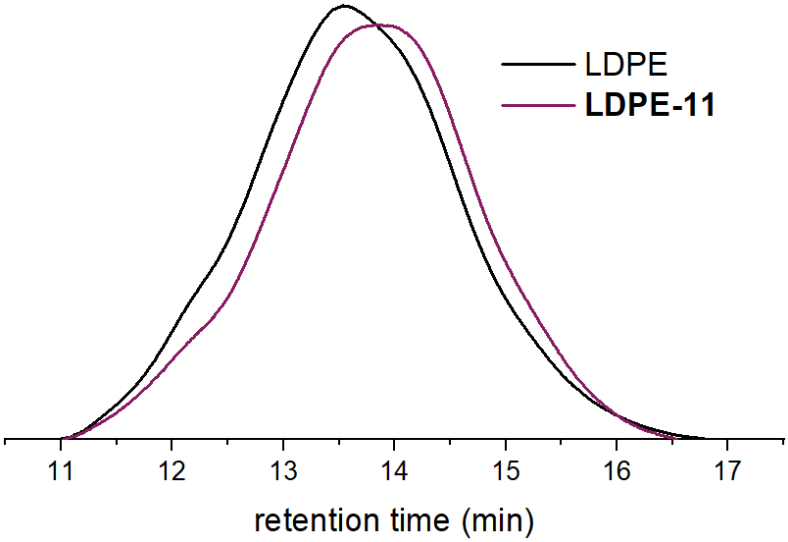


Figure S36. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-11** (purple), M_n = 26867 g/mol, M_w = 147230 g/mol, $Đ$ = 5.48.

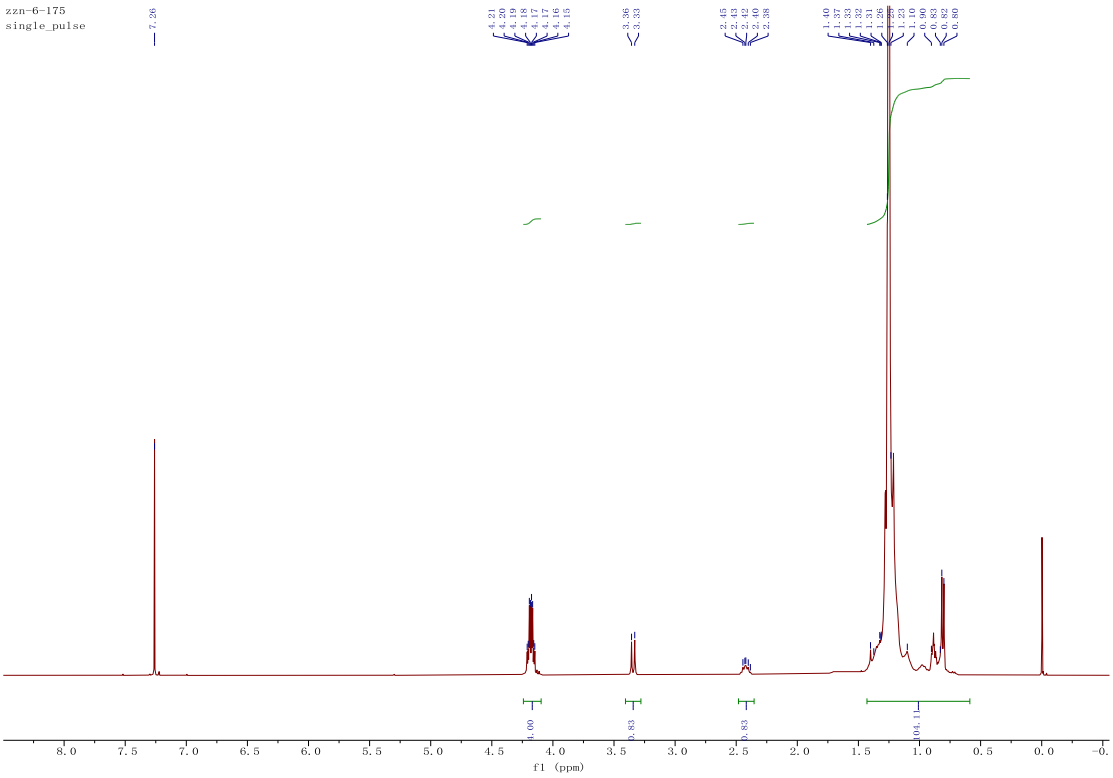


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-11**

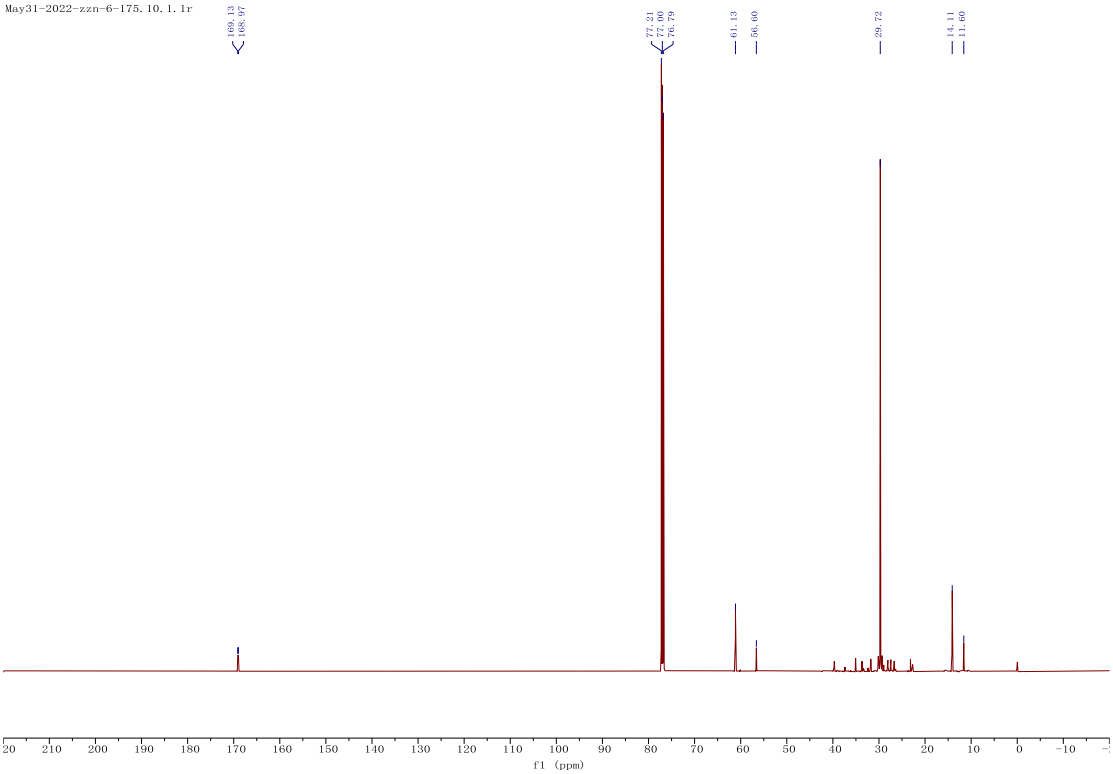


Figure S38. ^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-11**

Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LDPE (56.3 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **12** (62.8 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-12** as a yellow solid (56.3 mg, LOF = 4.1 mol%, 21%). The 21% yield was determined as LOF/amount of alkene. The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, **1.00 H**, Ar-H), 7.27-7.19 (m, 1.47 H, Ar-H), 7.18-7.03 (m, 0.92 H, Ar-H), 4.15-4.02 (m, 0.89 H), 3.36-3.25 (m, 0.91 H), 1.57-0.60 (m, **97.25 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2917, 2329, 1572, 1464, 1085. **GPC (TCB, 140 °C)** M_n = 27632 g/mol, M_w = 80165 g/mol, $Đ$ = 2.90. **TGA (°C)** LDPE T_d = 420, **LDPE-12** T_d = 310. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-12** T_m = 75 with 5% crystallinity (DH = 14 J/g).

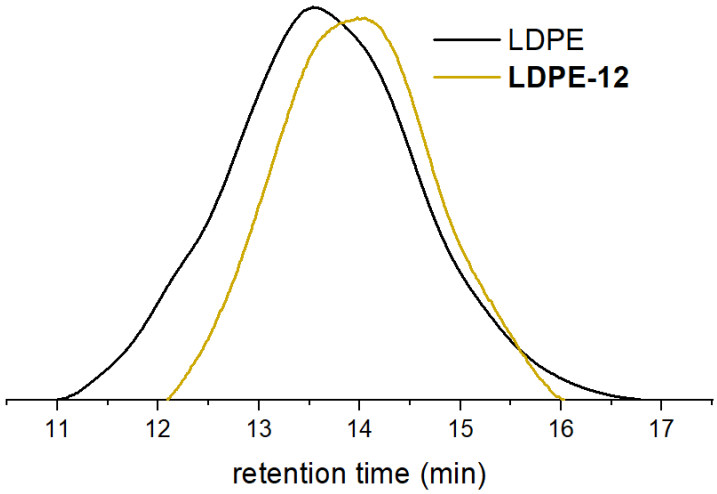


Figure S39. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-12** (yellow), M_n = 27632 g/mol, M_w = 80165 g/mol, $Đ$ = 2.90.

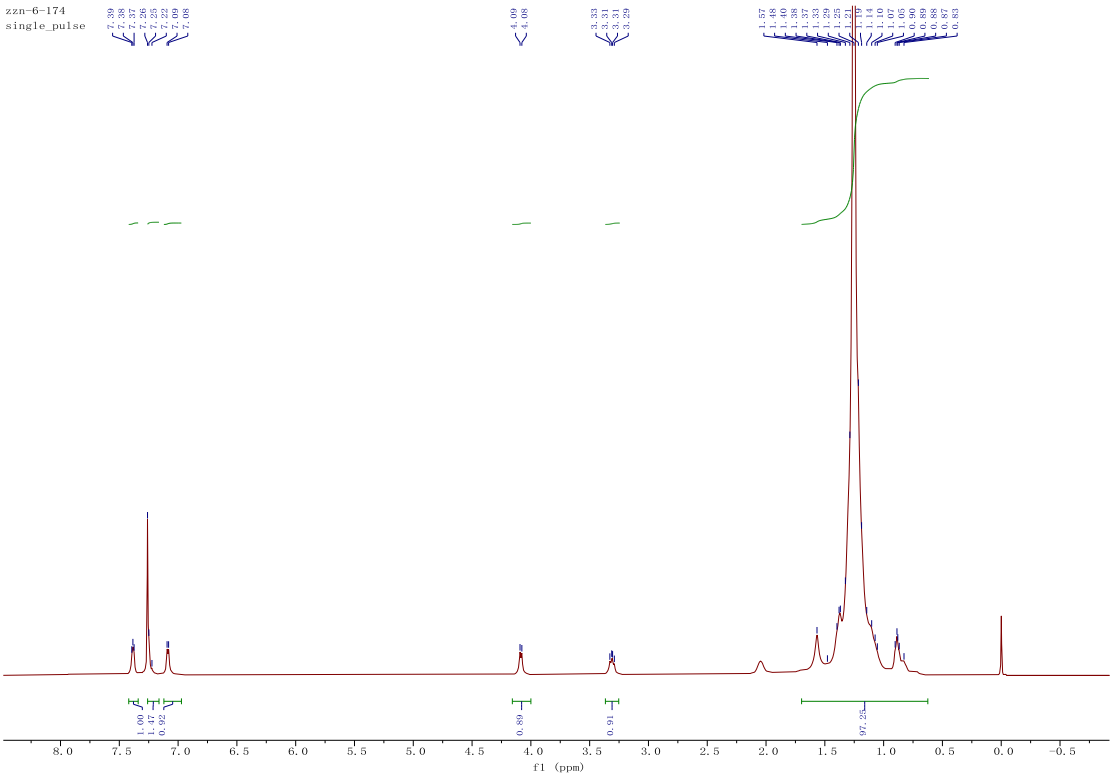


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of **LDPE-12**

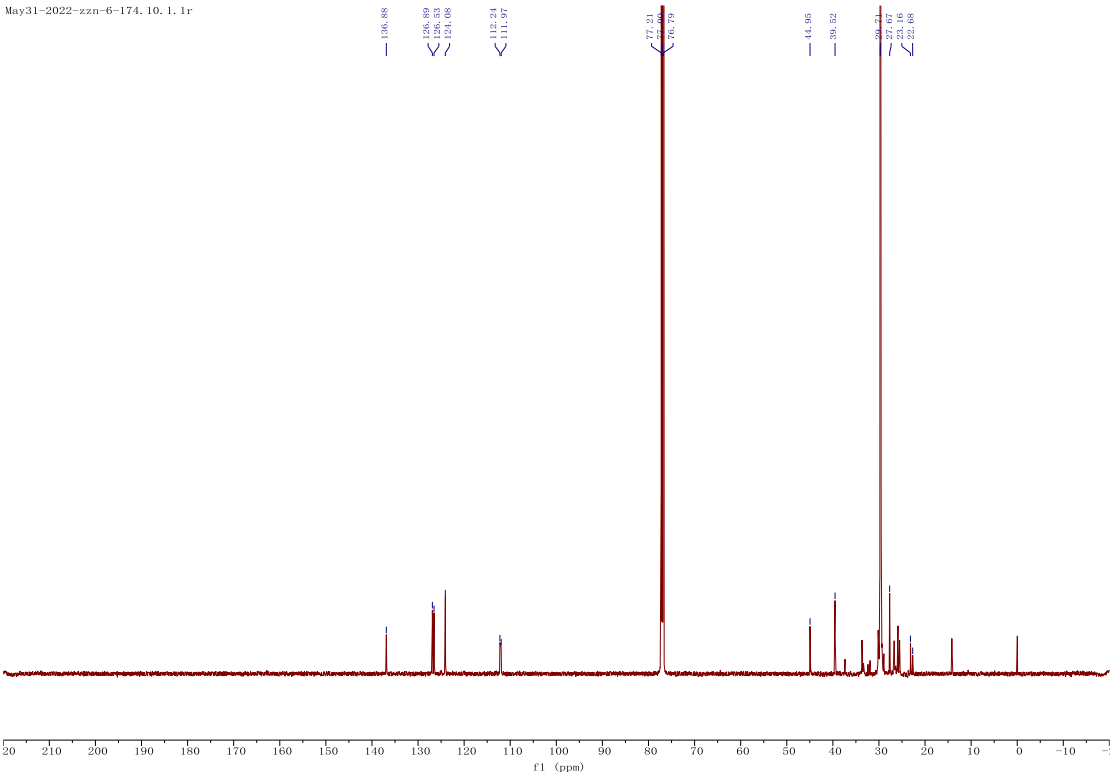


Figure S41. ^{13}C NMR (151 MHz, $CDCl_3$) of **LDPE-12**

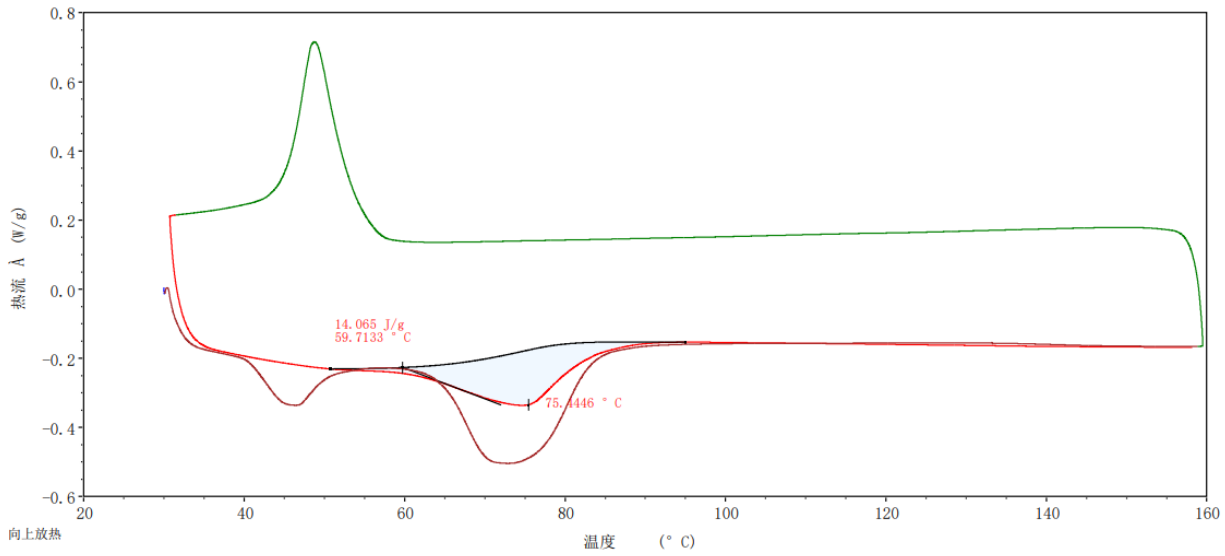
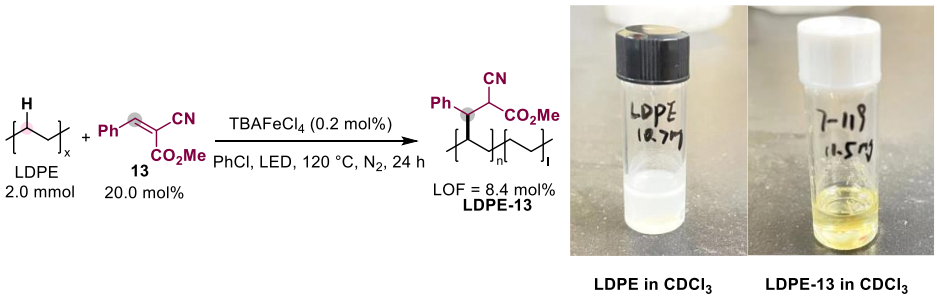


Figure S42. The DSC trace of **LDPE-12**



Following Typical Procedure 1, the reaction of $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LDPE (56.8 mg, 2.0 mmol, M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84), **13** (74.3 mg, 0.4 mmol), and PhCl (3.0 mL) afforded **LDPE-13** as a brown solid (51.5 mg, LOF = 8.4 mol%). The level of functionalization was determined by ^{1}H NMR. Moreover, the heteronuclear multiple bond correlation (HMBC) and diffusion ordered NMR spectroscopy (DOSY) spectra of **LDPE-13** confirmed the small molecule is covalently linked onto LDPE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.15 (m, 5.36 H, Ar-H), 4.23-3.06 (m, **5.00 H**), 1.69-0.61 (m, **46.28 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2922, 2247, 1747, 1275. **GPC (TCB, 140 °C)** M_n = 26949 g/mol, M_w = 109311 g/mol, $Đ$ = 4.06. **TGA (°C)** LDPE T_d = 420, **LDPE-133** T_d = 300. **DSC (°C)** LDPE T_m = 104 with 23% crystallinity (DH = 63 J/g), **LDPE-13** no recorded melting point.

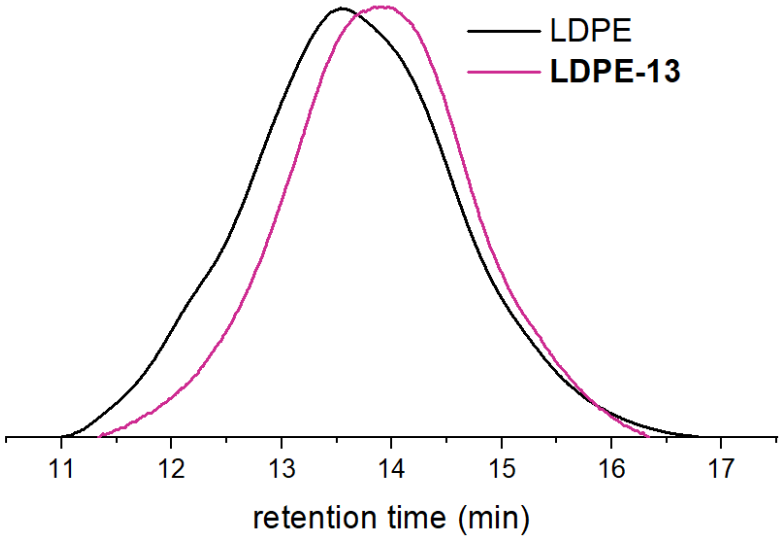


Figure S43. The HT-GPC traces. LDPE (black), M_n = 30423 g/mol, M_w = 177700 g/mol, $Đ$ = 5.84; **LDPE-13** (purple), M_n = 26949 g/mol, M_w = 109311 g/mol, $Đ$ = 4.06.

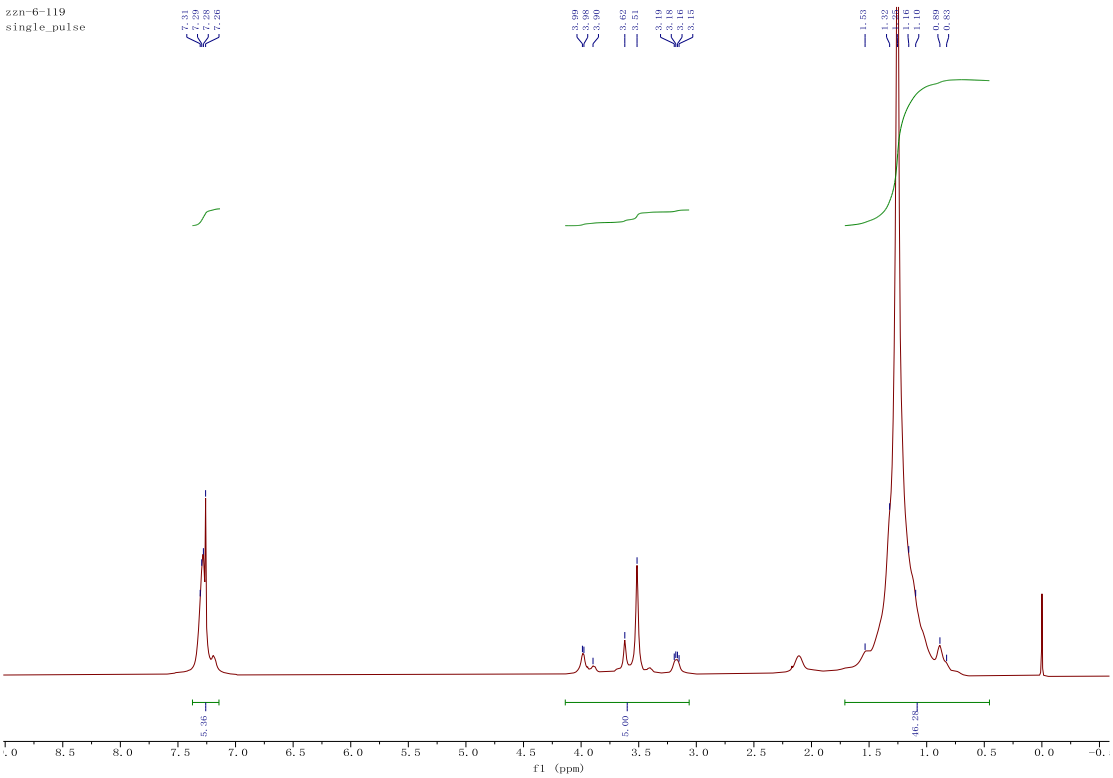


Figure S44.[1]H NMR (400 MHz, $CDCl_3$) of **LDPE-13**

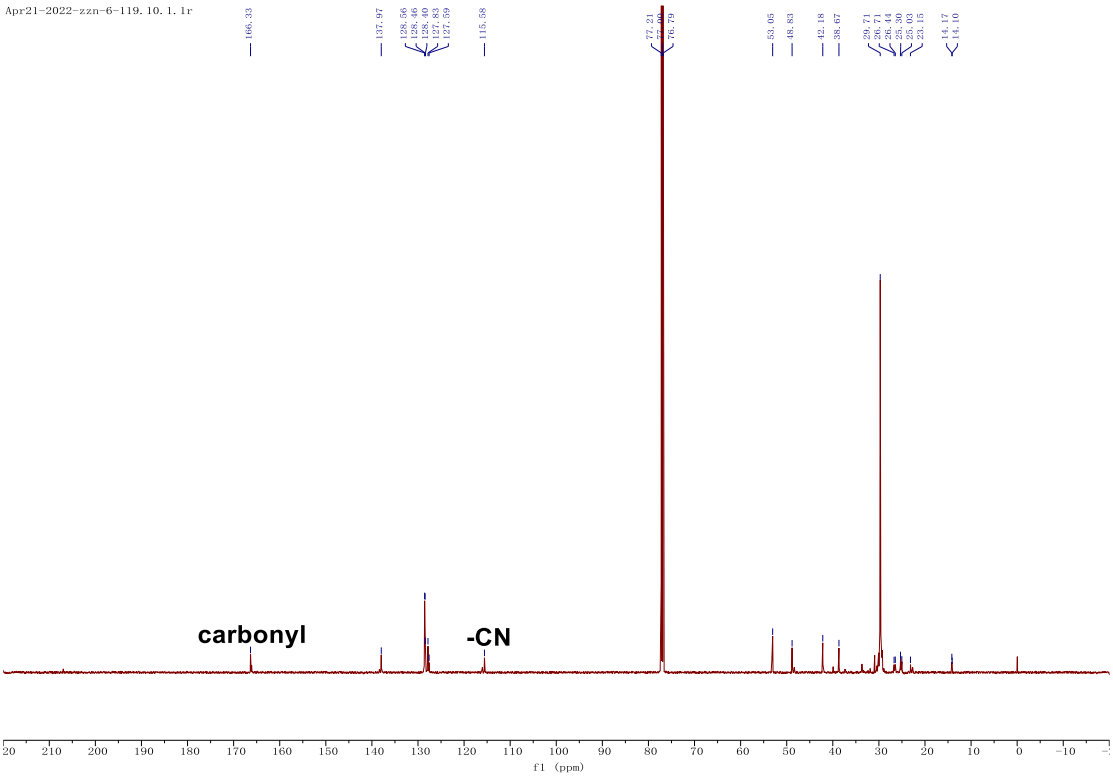


Figure S45.[13]C NMR (151 MHz, $CDCl_3$) of **LDPE-13**

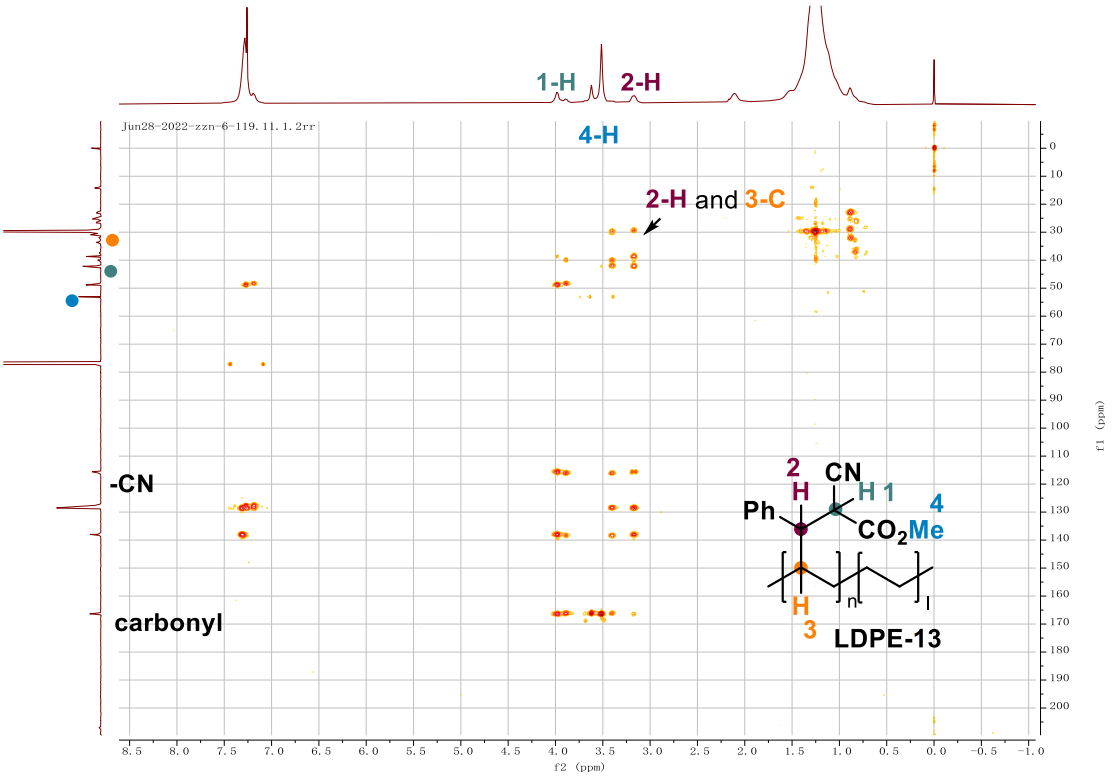


Figure S46. Heteronuclear multiple bond correlation (HMBC) spectroscopy of **LDPE-13**

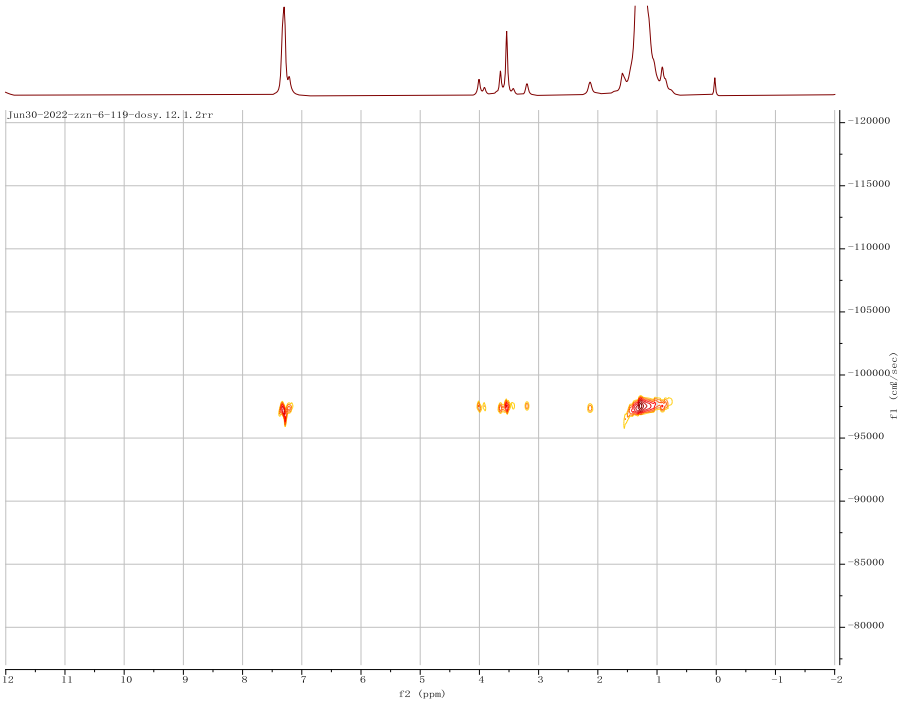
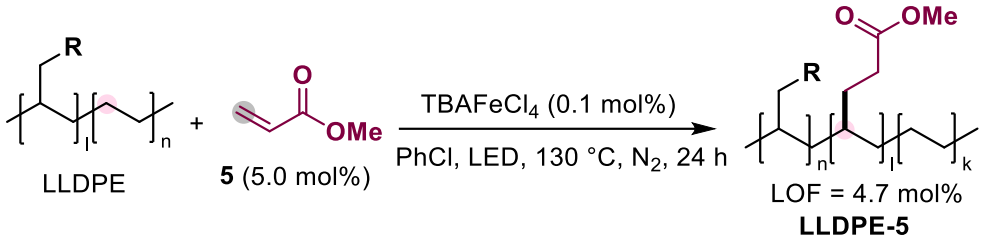


Figure S47. Diffusion ordered NMR spectroscopy (DOSY) of **LDPE-13** presented that the all protons of **LDPE-13** had the same diffusion coefficient, indicating the small molecule is covalently linked onto LDPE.

The C–H bond functionalization of polyolefins



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.8 mg, 0.1 mmol), LLDPE (2.8025 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (430.0 mg, d = 0.956 g/mL, 450 μL, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-5** was obtained as a white solid (3.0641 g, LOF = 4.7 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3.34 H), 2.50-2.25 (m, **2.00 H**), 2.12-0.75 (m, **83.73 H**). **GPC (TCB, 140 °C)** M_n = 64342 g/mol, M_w = 210306 g/mol $Đ$ = 3.27. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5** T_d = 410. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5** T_m = 106 with 18% crystallinity (DH = 50 J/g).

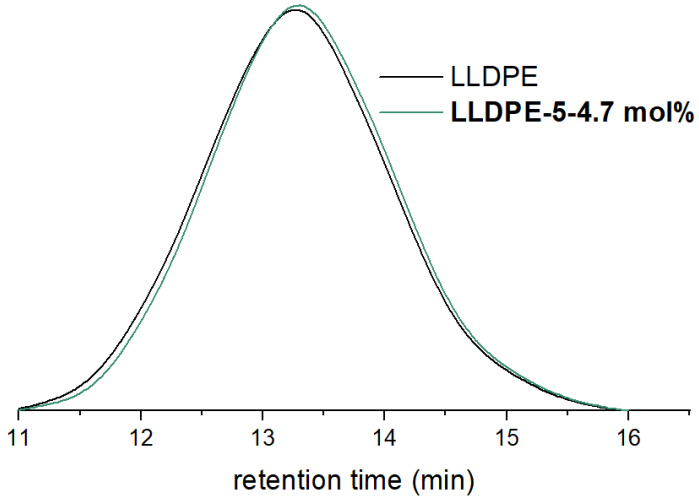


Figure S48. The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol $Đ$ = 3.37; **LLDPE-5** (green), M_n = 64342 g/mol, M_w = 210306 g/mol $Đ$ = 3.27.

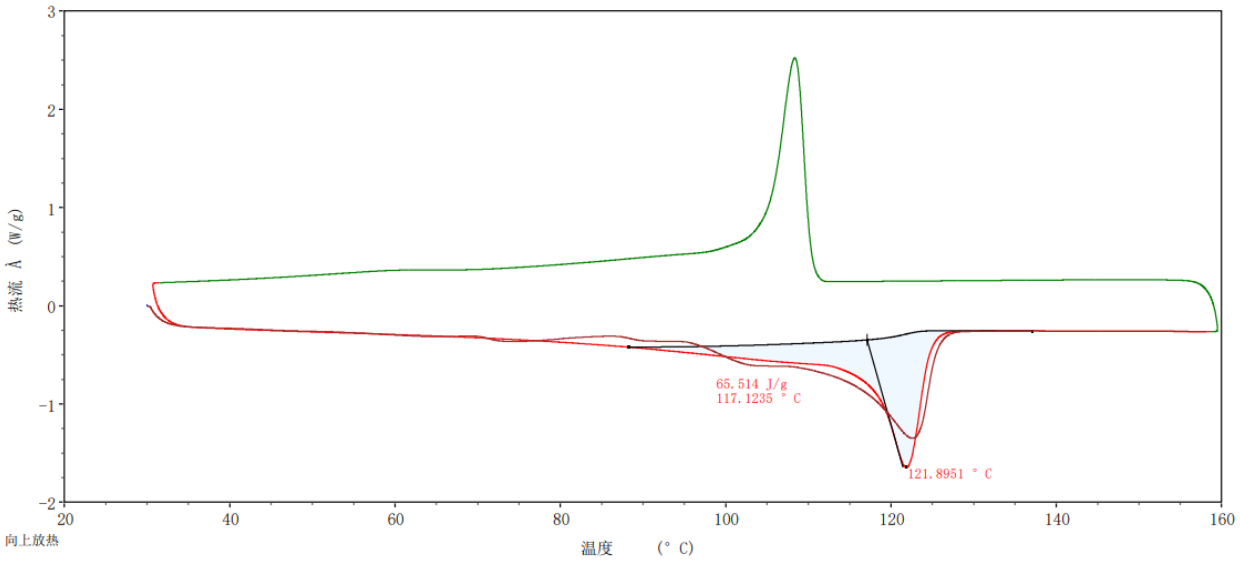


Figure S49. The DSC trace of LLDPE

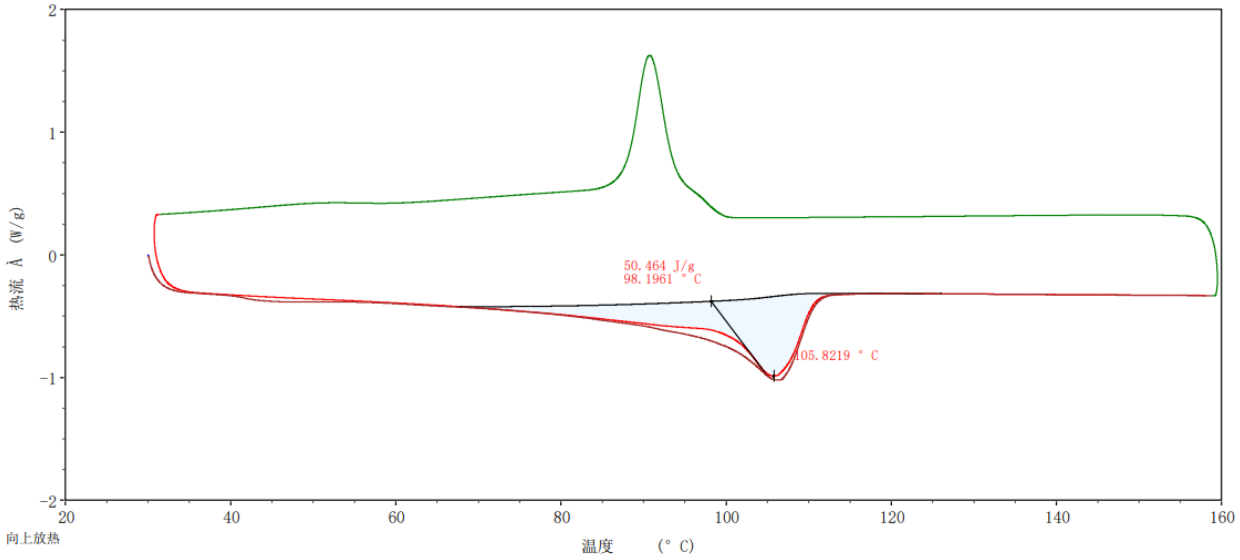
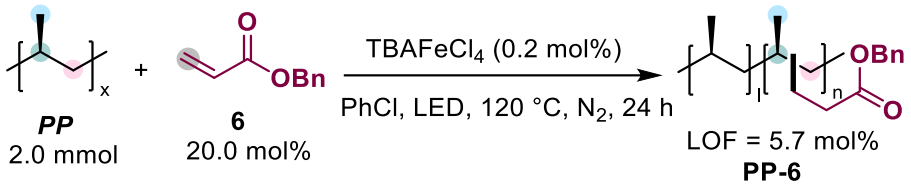


Figure S50. The DSC trace of **LLDPE-5**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), PP (84.5 mg, 2.0 mmol, M_n = 12122 g/mol, M_w = 27466 g/mol, $Đ$ = 2.27), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **PP-6** was obtained as a white solid (81.2 mg, LOF = 5.7 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.26 (m, 5.39 H), 5.25-5.02 (m, **2.00 H**), 2.39-2.25 (m, 1.29 H), 1.72-1.40 (m, **20.77 H**), 1.27-1.02 (m, **16.26 H**), 1.00-0.61 (m, **67.68 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2953, 1736, 1455, 1374, 1155. **GPC (TCB, 140 °C)** M_n = 13899 g/mol, M_w = 28876 g/mol, $Đ$ = 2.08. **TGA (°C)** PP T_d = 410, **PP-6** T_d = 352. **DSC (°C)** PP T_m = 151 with 59% crystallinity (DH = 111 J/g), **PP-6** no recorded melting point.

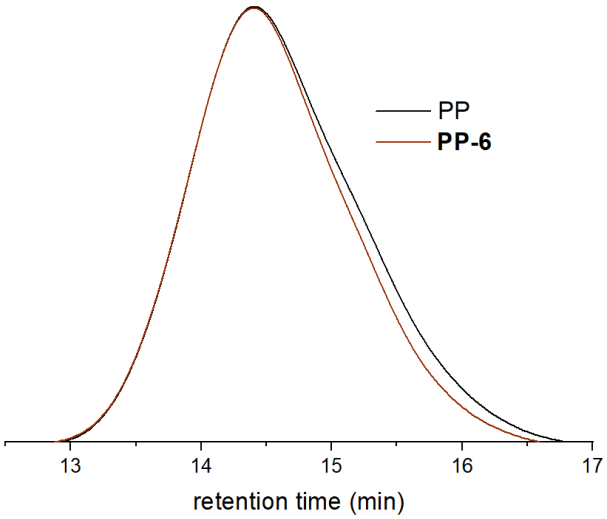


Figure S51. The HT-GPC traces. PP (black), M_n = 12122 g/mol, M_w = 27466 g/mol, $Đ$ = 2.27; **PP-6** (red), M_n = 13899 g/mol, M_w = 28876 g/mol, $Đ$ = 2.08.

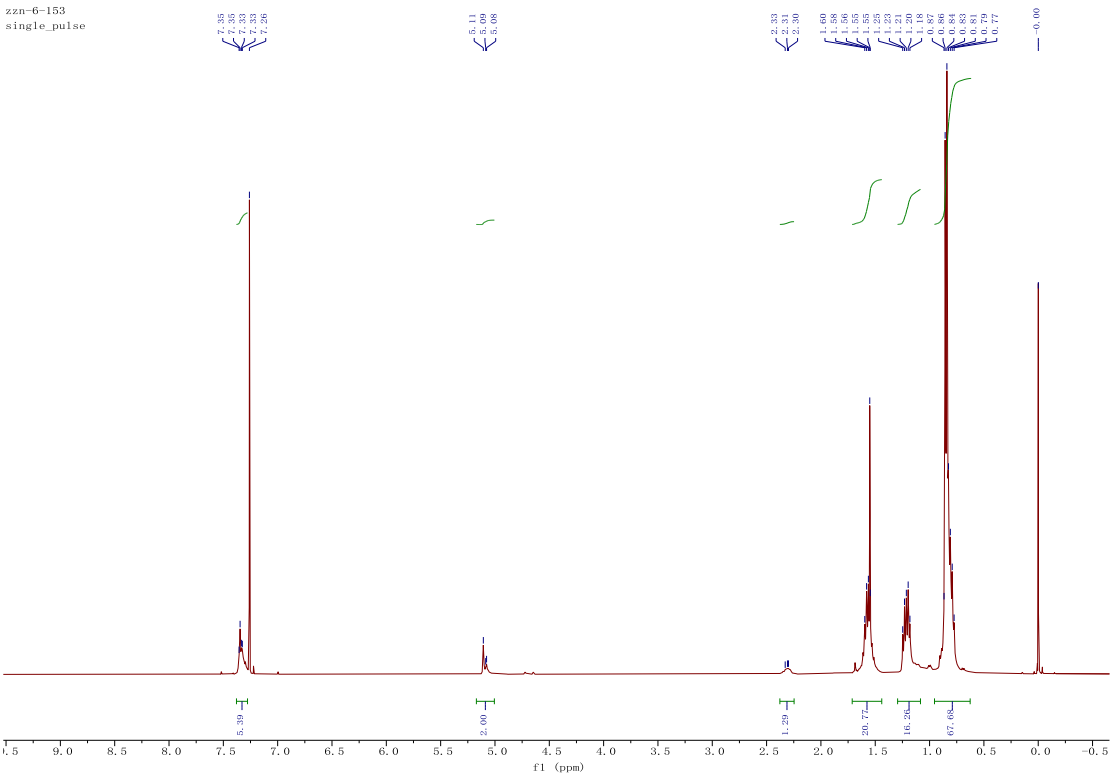


Figure S52.[1]H NMR (400 MHz, $CDCl_3$) of **PP-6**

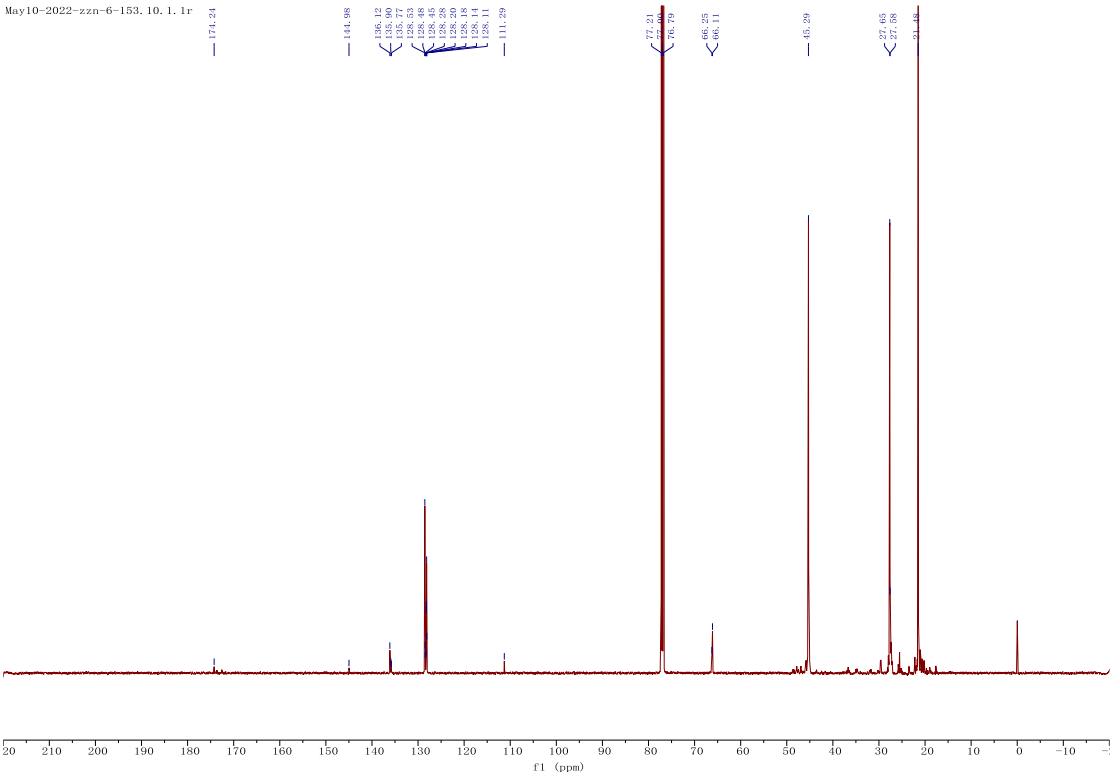


Figure S53. [13]C NMR (151 MHz, $CDCl_3$) of **PP-6**

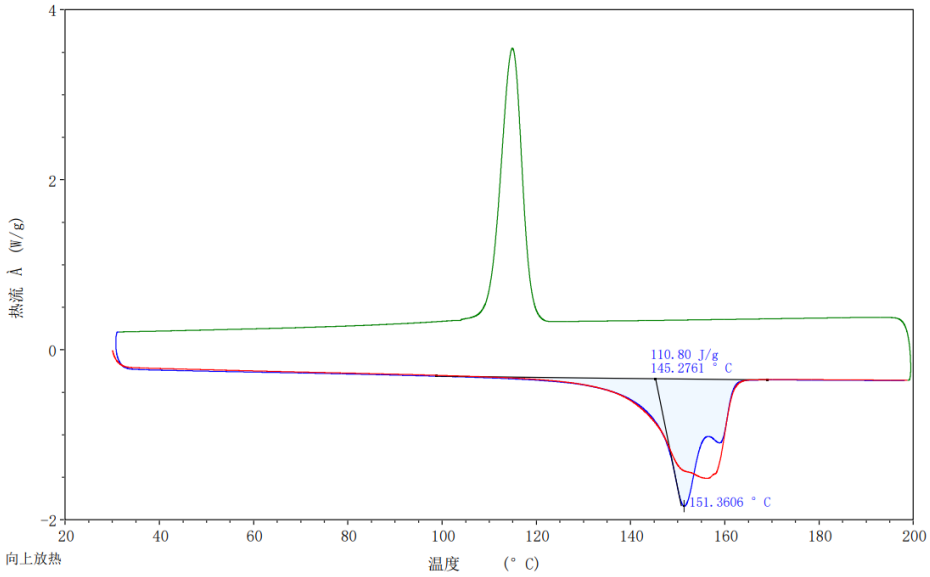
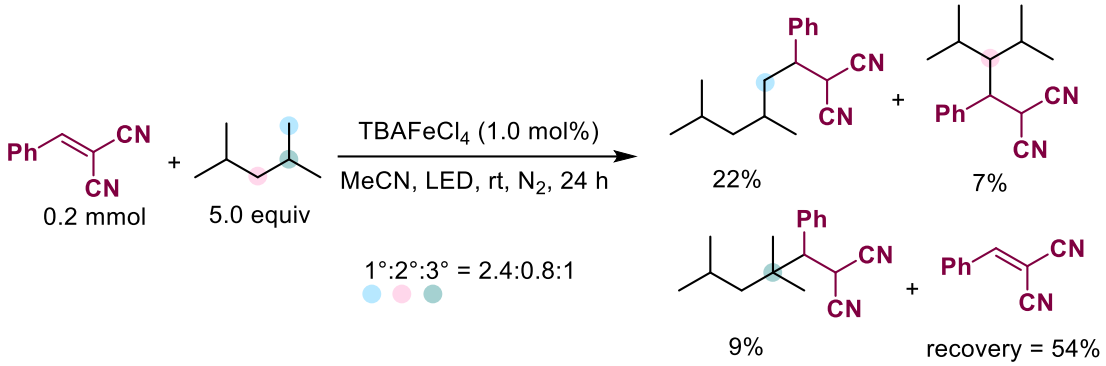


Figure S54. The DSC trace of PP

The regioselectivity was determined using the model reaction of benzalmalononitrile with 2,4-dimethylpentane and PP.



To a 4 mL vial were added benzalmalononitrile (30.9 mg, 0.20 mmol), 2,4-dimethylpentane (100.0 mg, d = 0.673 g/mL, 149 μL, 1.0 mmol), and $TBAFeCl_4$ (1.2 mg, 0.002 mmol) in MeCN (1.0 mL) in an N_2 glovebox. The vial was sealed and transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at rt. Evaporation and flash chromatography on silica gel afforded the alkylation product (19.3 mg, 38%) (eluent: PE/EA = 20/1): oil. A mixture was afforded and the ratio of 1°, 2°, 3° C–H alkylation was determined as 2.4:0.8:1.

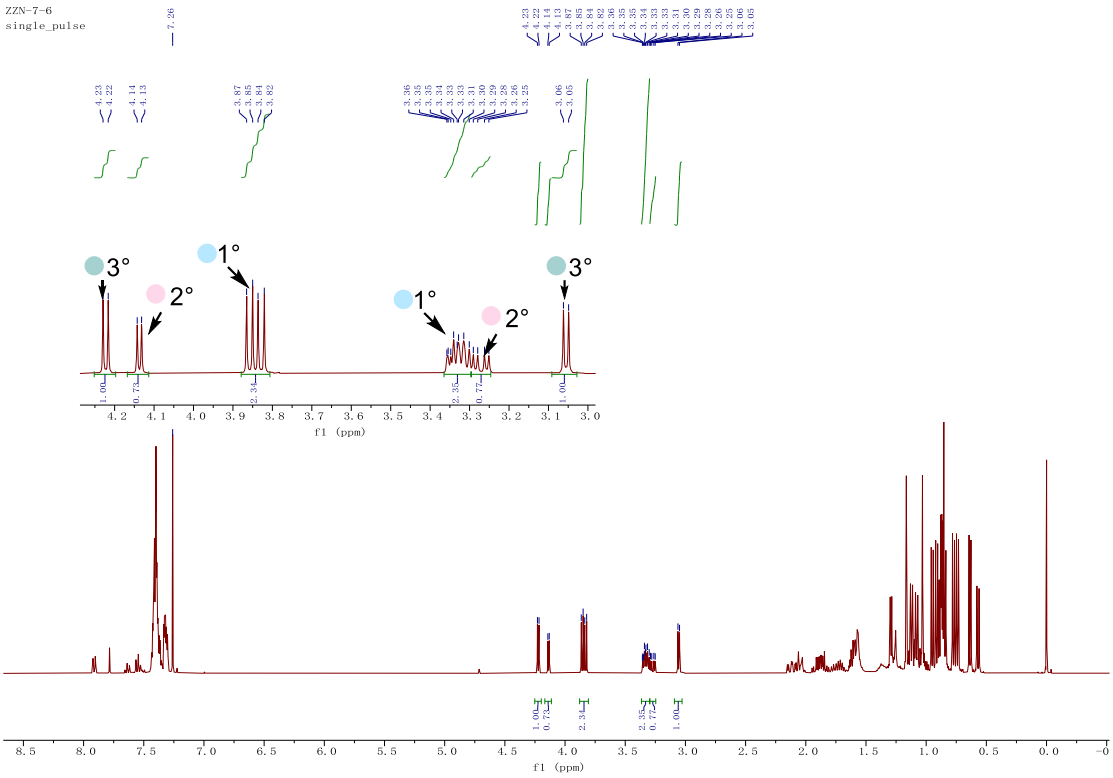
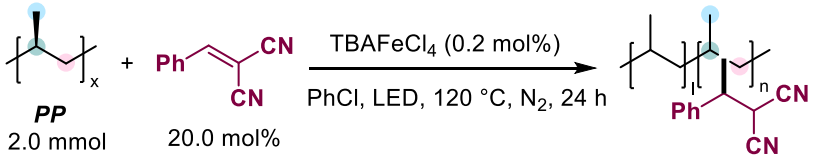


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with 2,4-dimethylpentane



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.7 mg, 0.004 mmol), PP (85.0 mg, 2.0 mmol, M_n = 12122 g/mol, M_w = 27466 g/mol, $Đ$ = 2.27), benzalmalononitrile (61.2 mg, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooling to rt, EtOH (8.0 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5.0 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound was obtained as a white solid (89.1 mg).

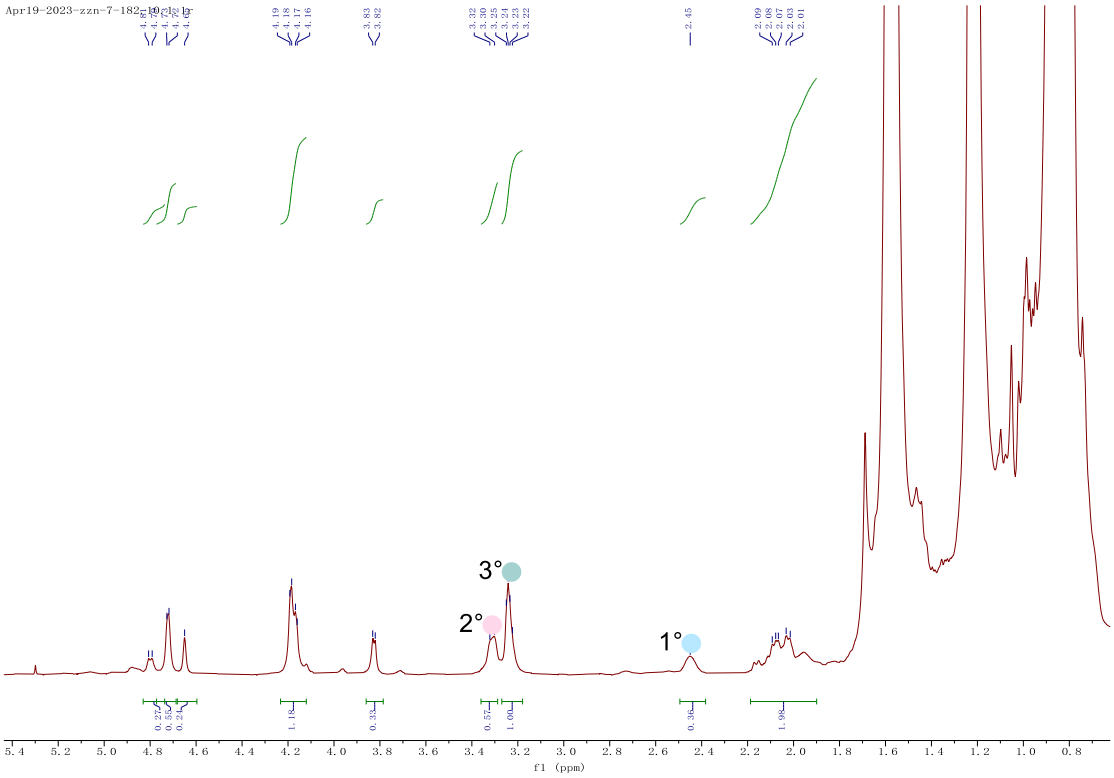


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with PP.

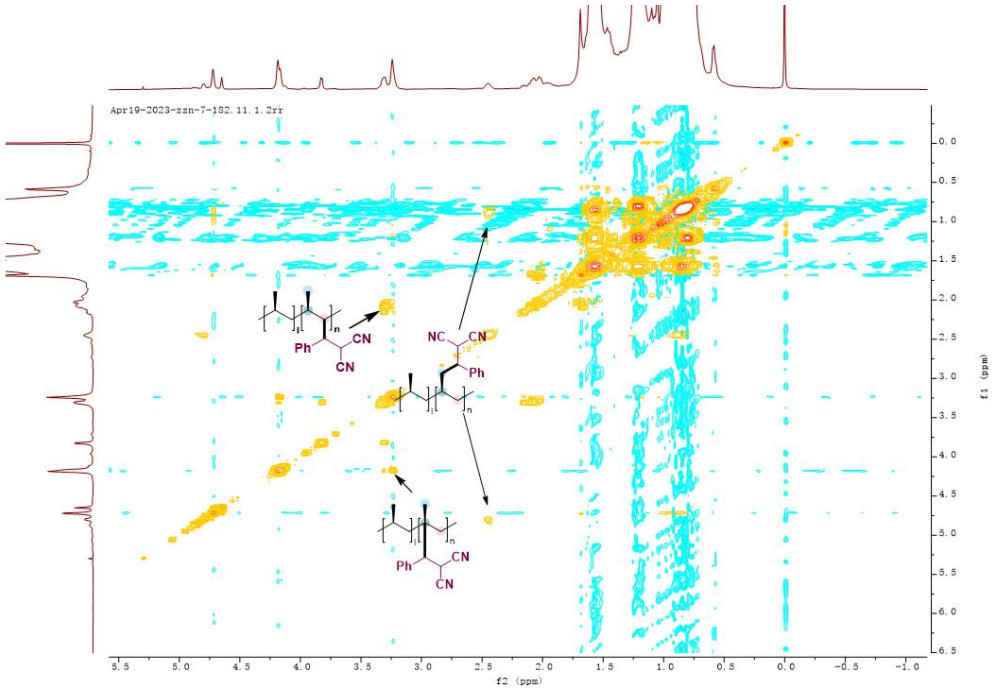
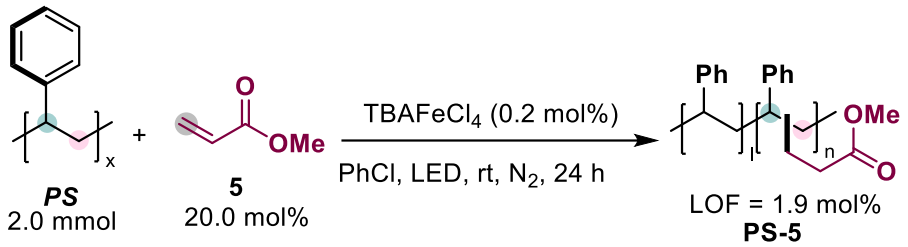


Figure S57. COSY of benzalmalononitrile alkylation products with PP.



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), PS (207.3 mg, 2.0 mmol, M_n = 130714 g/mol, M_w = 265657 g/mol, $Đ$ = 2.03), **5** (34.4 mg, d = 0.956 g/mL, 36 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at rt. EtOH (8.0 mL) was added to the resulting mixture precipitated. Then, the resulting mixture was precipitated 2 times using DCM and EtOH (DCM/EtOH = 1:8) until the small molecules were removed completely. The compound **PS-5** was obtained as a yellow solid (150.7 mg, LOF = 1.9 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) 7.26-6.25 (m, 260.29 H), 3.85-3.25 (m, **3.00 H**), 2.38-0.74 (m, **160.93 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 3024, 2922, 1737, 1600, 1028. **GPC (DMF, 50 °C)** M_n = 129038 g/mol, M_w = 249576 g/mol, $Đ$ = 1.93. **TGA (°C)** PS T_d = 370, **PS-5** T_d = 355. **DSC (°C)** PS no recorded melting point, **PS-5** no recorded melting point.

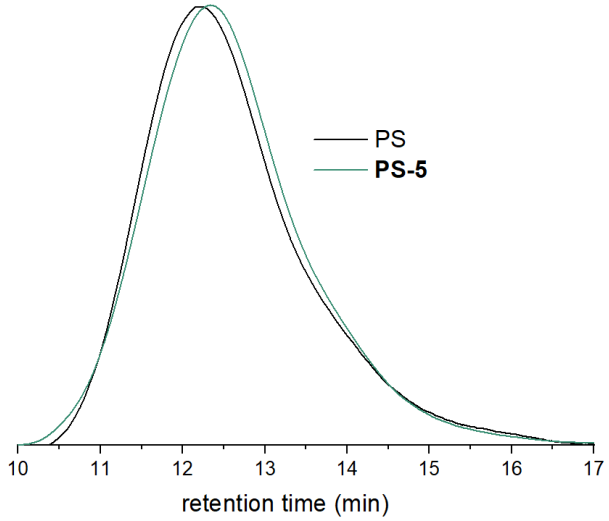


Figure S58. The GPC traces. PS (black), M_n = 130714 g/mol, M_w = 265657 g/mol, $Đ$ = 2.03; **PS-5** (green), M_n = 129038 g/mol, M_w = 249576 g/mol, $Đ$ = 1.93.

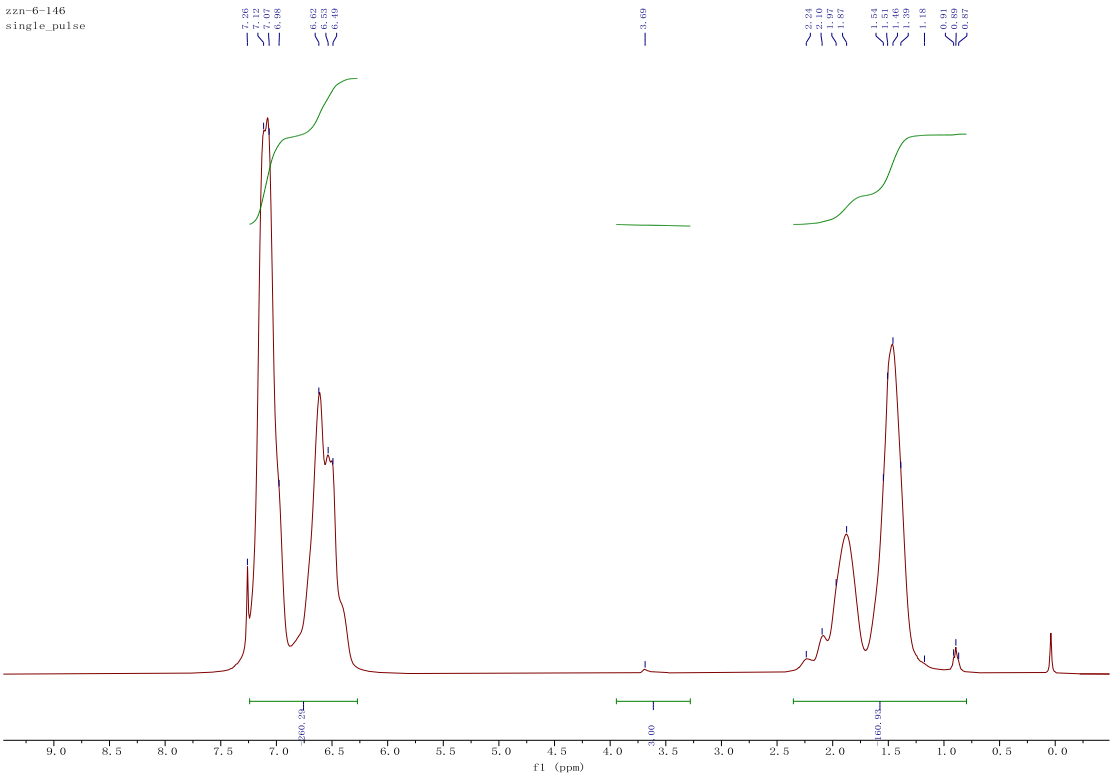


Figure S59.[1]H NMR (400 MHz, $CDCl_3$) of **PS-5**

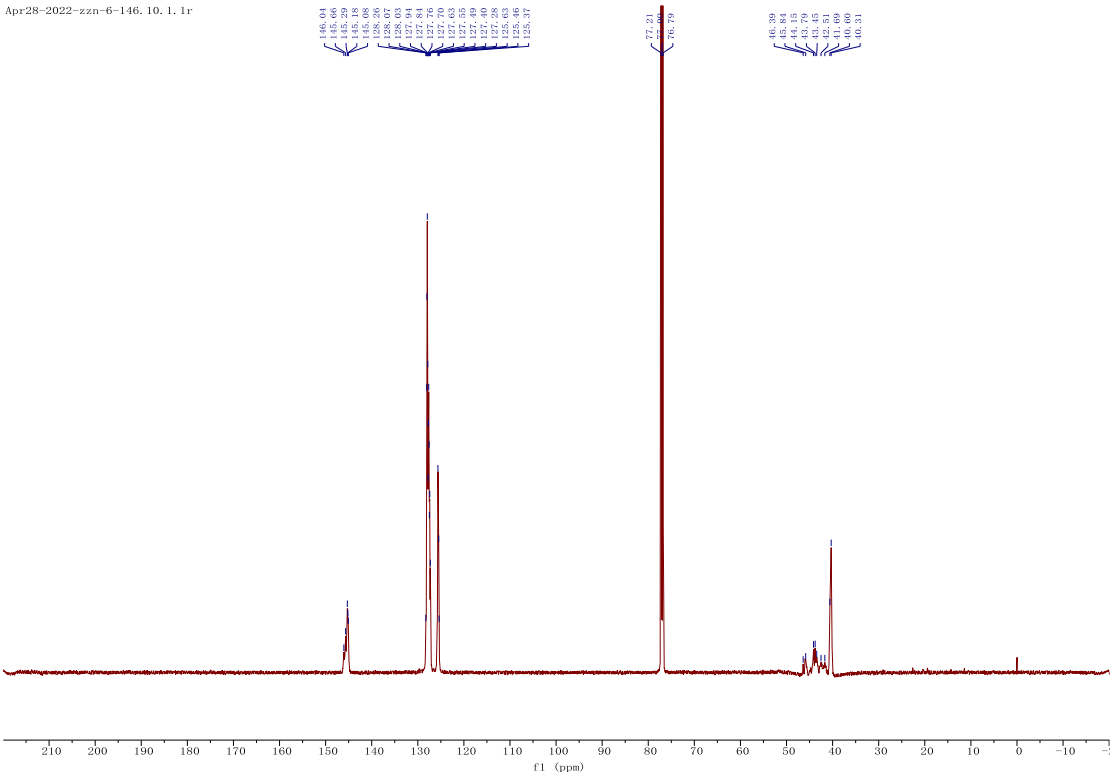
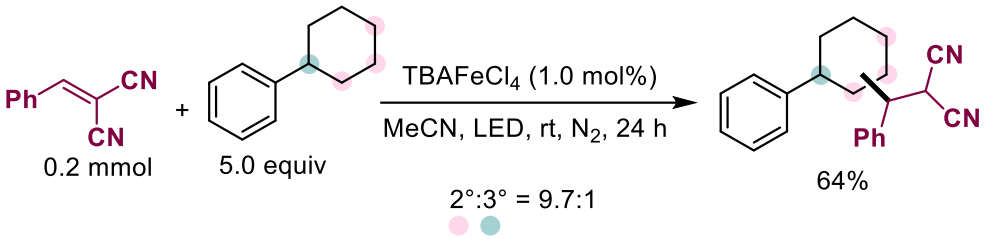


Figure S60.[13]C NMR (151 MHz, $CDCl_3$) of **PS-5**

The regioselectivity was determined using the model reaction of benzalmalononitrile with

cyclohexylbenzene and PS.



To a 4 mL vial were added benzalmalononitrile (30.6 mg, 0.20 mmol), cyclohexylbenzene (160.0 mg, d = 0.950 g/mL, 168 μL, 1.0 mmol), and $TBAFeCl_4$ (1.1 mg, 0.002 mmol) in MeCN (1.0 mL) in an N_2 glovebox. The vial was sealed and transferred out of glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at rt. Evaporation and flash chromatography on silica gel afforded a less polar mixture (27.5 mg, 44%) and a more polar mixture (12.4 mg, 20%) (eluent: PE/EA = 20/1): oil. The ratio of 2° and 3° C–H alkylation was determined as 9.7:1 by analyzing the ^1H NMRs.

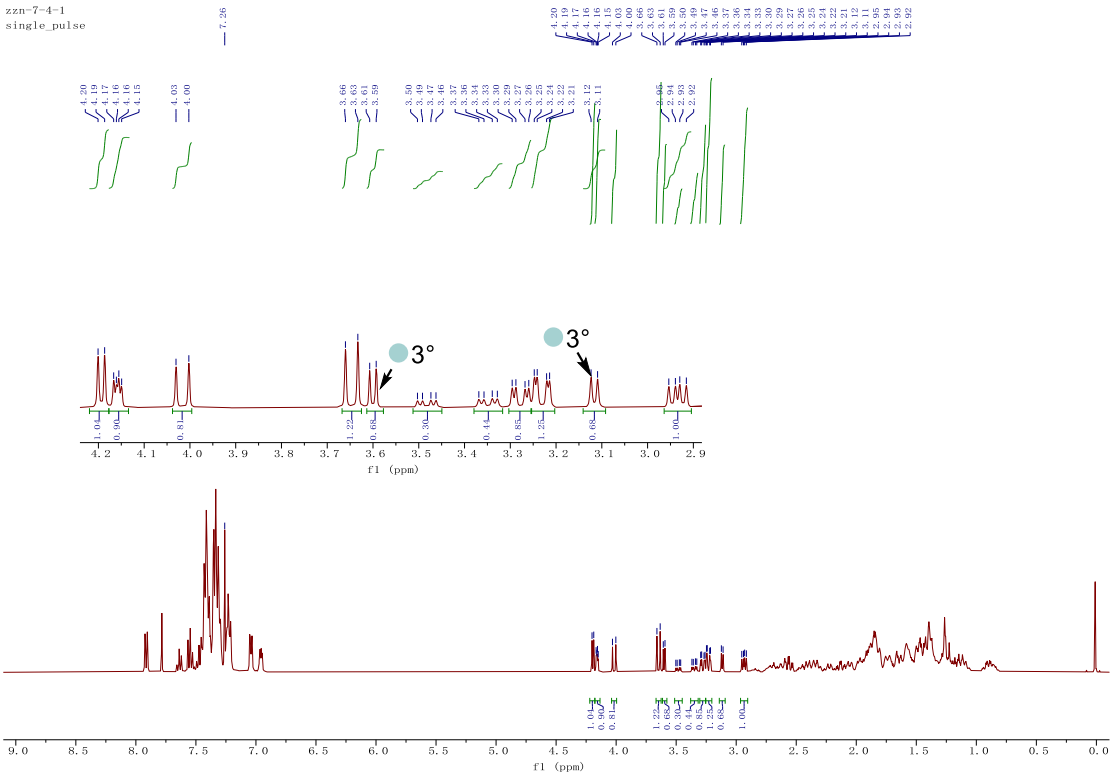


Figure S61. ^1H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with cyclohexylbenzene (less polar mixture)

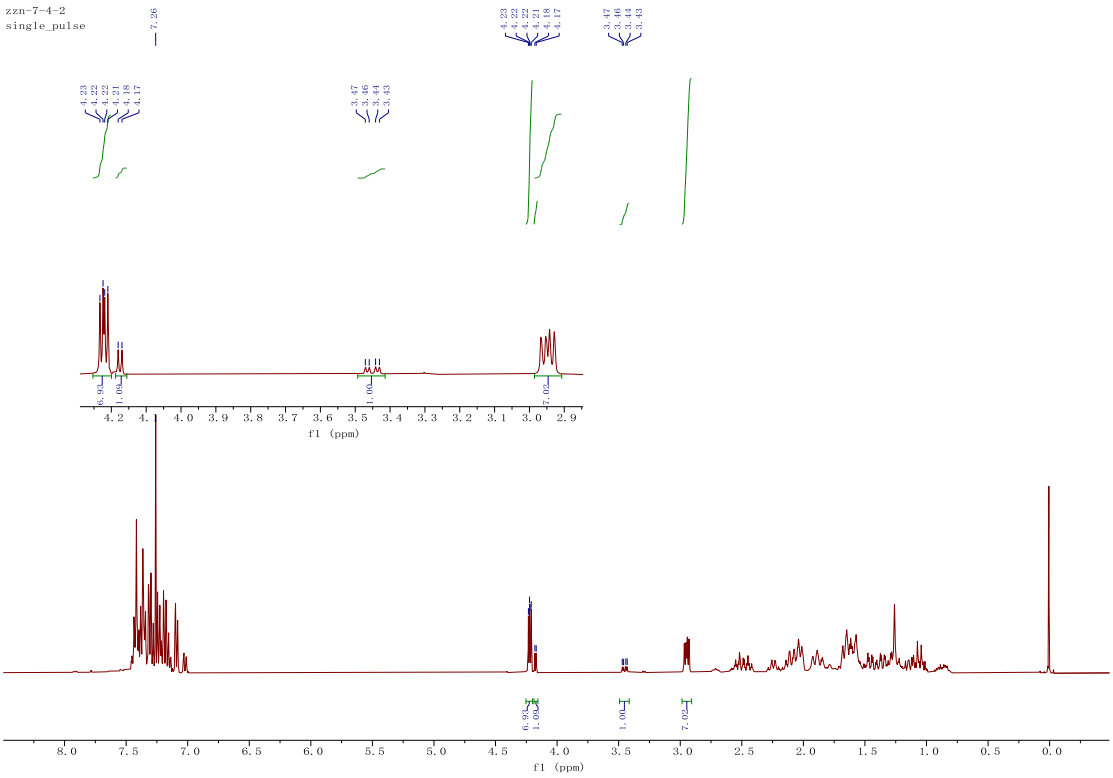
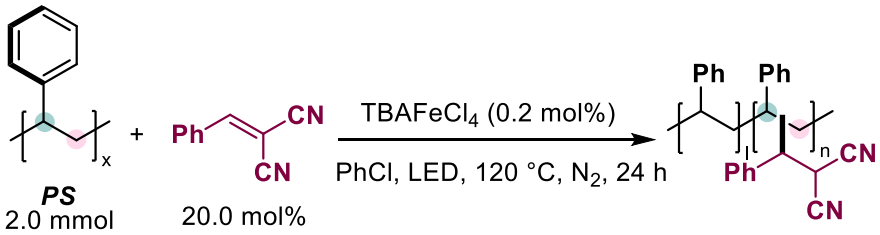


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with cyclohexylbenzene (more polar mixture)



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.6 mg, 0.004 mmol), PS (209.1 mg, 2.0 mmol, M_n = 130714 g/mol, M_w = 265657 g/mol, $Đ$ = 2.03), benzalmalononitrile (61.6 mg, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at rt. EtOH (8.0 mL) was added to the resulting mixture precipitated. Then, the resulting mixture was precipitated 2 times using DCM and EtOH (DCM/EtOH = 1:8) until the small molecules were removed completely. The compound was obtained as a yellow solid (206.3 mg).

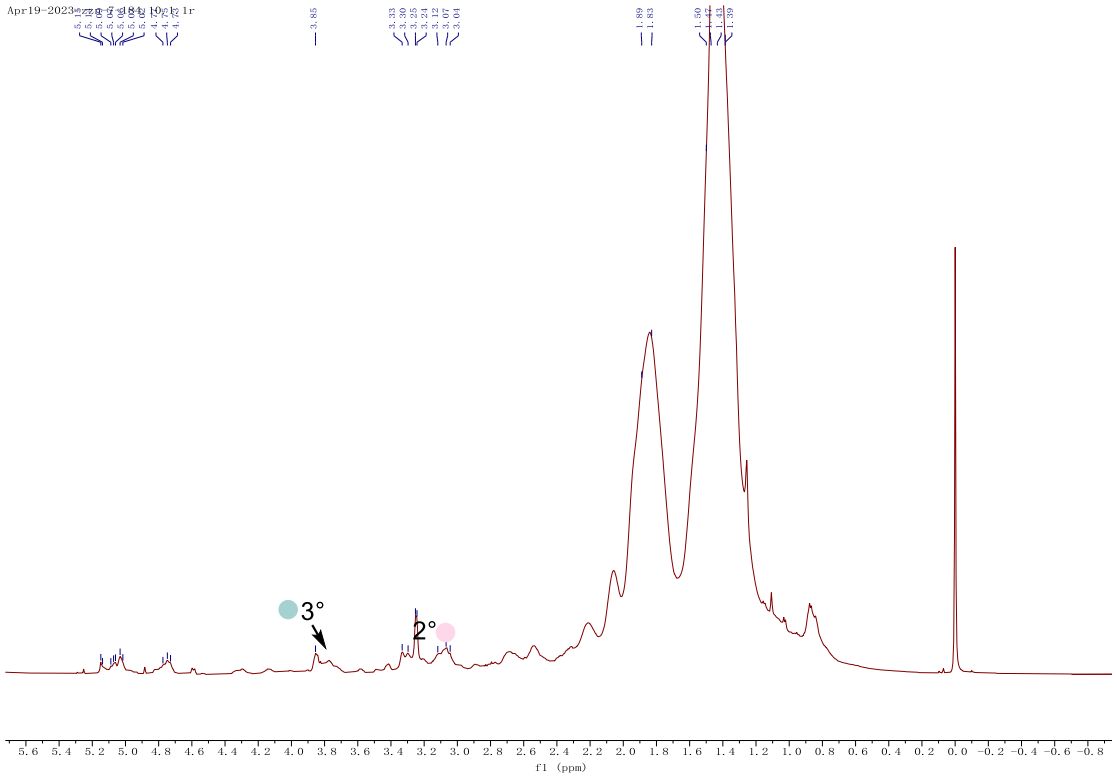


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with PS.

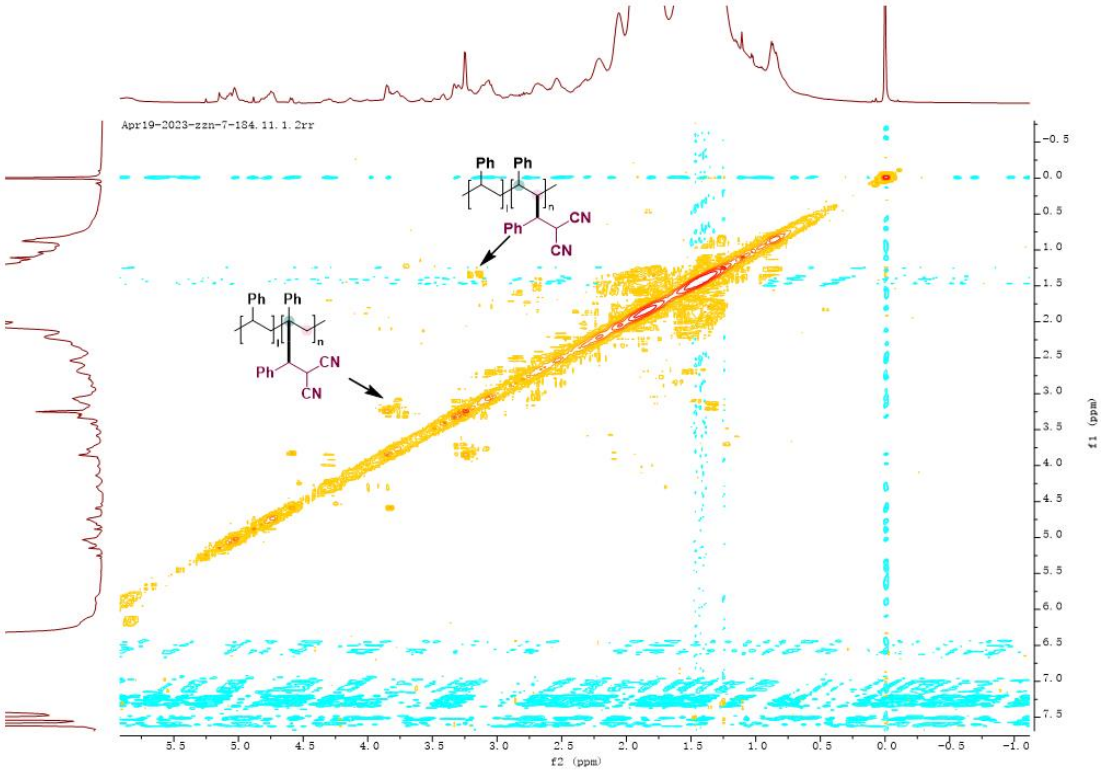
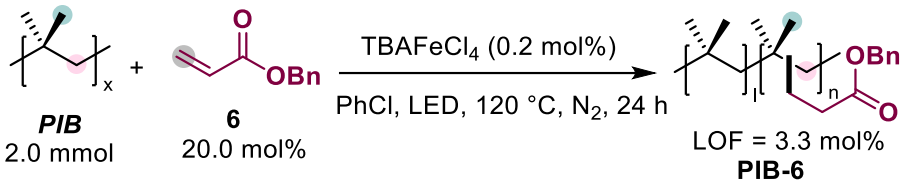


Figure S64. COSY of benzalmalononitrile alkylation products with PS.



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), PIB (112.9 mg, 2.0 mmol, M_n = 2497 g/mol, M_w = 12770 g/mol, $Đ$ = 5.11), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooled to rt, EtOH (8.0 mL) was added to the resulting mixture precipitated. Then, the resulting mixture was precipitated 2 times using DCM and EtOH (DCM/EtOH = 1:8) until the small molecules were removed completely. The compound **PIB-6** was obtained as a colorless gel (93.1 mg, LOF = 3.3 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) 7.48-7.27 (m, 6.52 H), 5.25-5.03 (m, **2.00 H**), 1.78-0.58 (m, **427.30 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2951, 1738, 1470, 1230, 1158. **GPC (THF, 40 °C)** M_n = 3502 g/mol, M_w = 5369 g/mol, $Đ$ = 1.53. **TGA (°C)** PIB T_d = 342, **PIB-6** T_d = 330. **DSC (°C)** PIB no recorded melting point, **PIB-6** no recorded melting point.

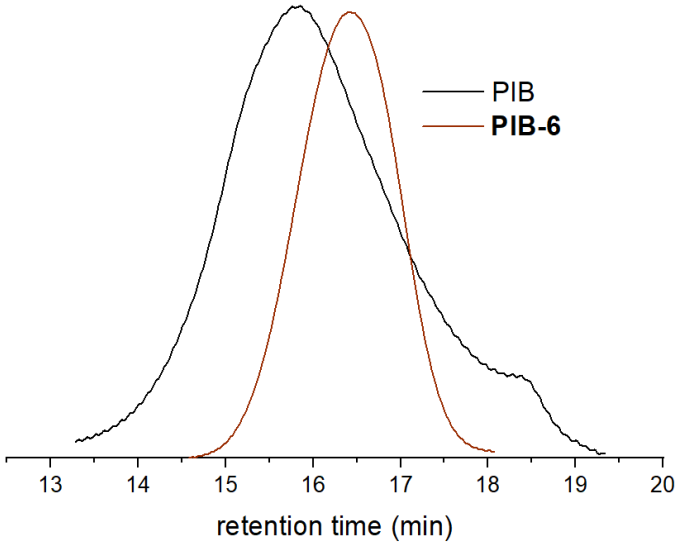


Figure S65. The GPC traces. PIB (black), M_n = 2497 g/mol, M_w = 12770 g/mol, $Đ$ = 5.11; **PIB-6** (red), M_n = 3502 g/mol, M_w = 5369 g/mol, $Đ$ = 1.53.

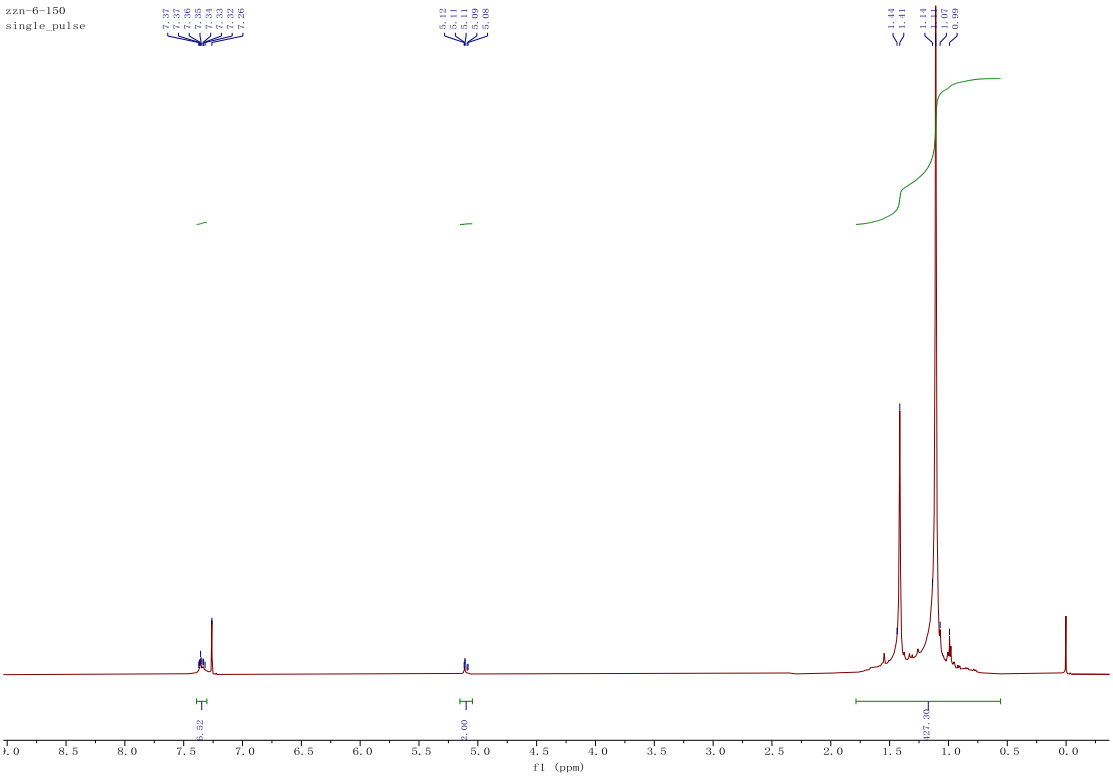


Figure S66.[1]H NMR (400 MHz, $CDCl_3$) of **PIB-6**

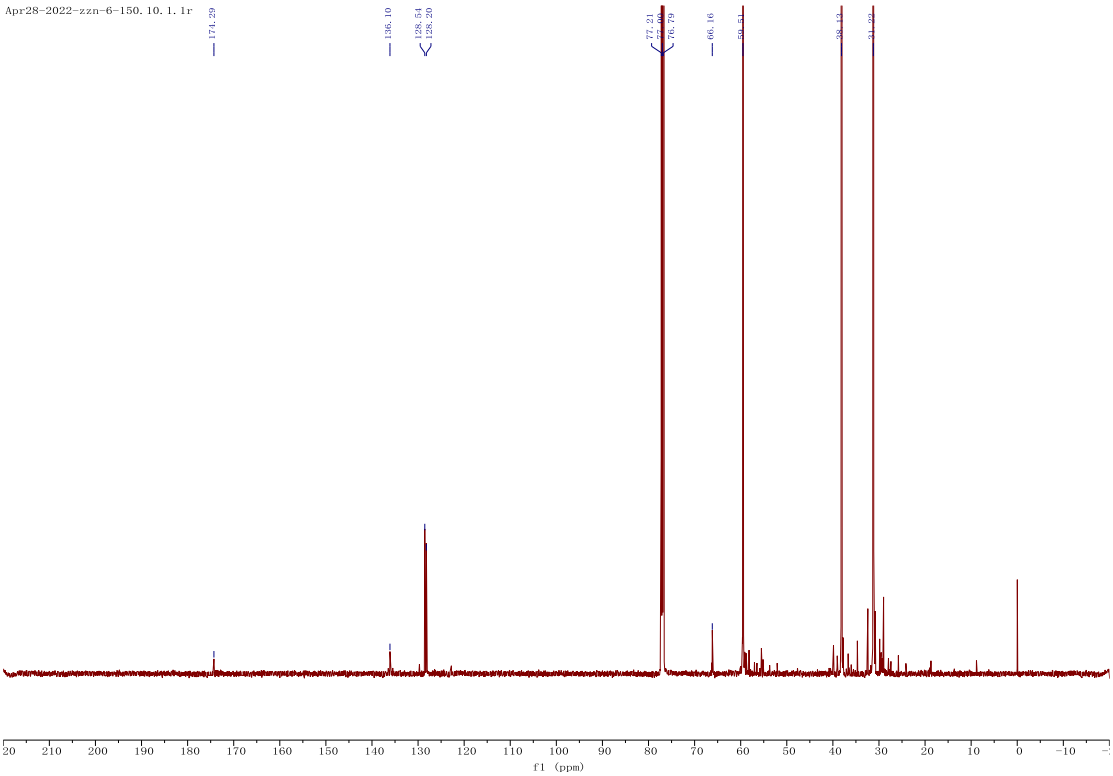
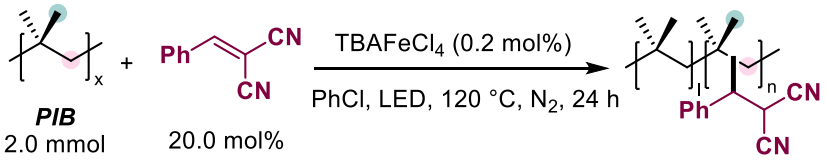


Figure S67. [13]C NMR (151 MHz, $CDCl_3$) of **PIB-6**

The regioselectivity was determined using the model reaction of benzalmalononitrile with PIB.



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), PIB (114.5 mg, 2.0 mmol, M_n = 2497 g/mol, M_w = 12770 g/mol, $Đ$ = 5.11), benzalmalononitrile (61.7 mg, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 120 °C. After cooled to rt, EtOH (8.0 mL) was added to the resulting mixture precipitated. Then, the resulting mixture was precipitated 2 times using DCM and EtOH (DCM/EtOH = 1:8) until the small molecules were removed completely. The compound was obtained as a colorless gel (112.0 mg).

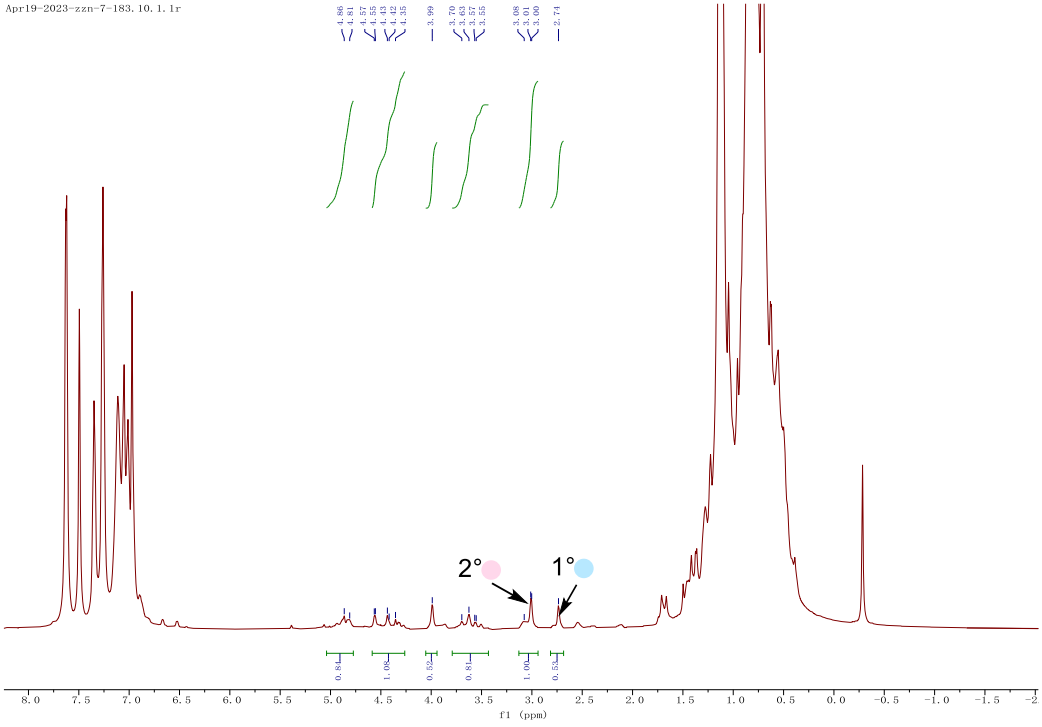


Figure S68. ^1H NMR (400 MHz, $CDCl_3$) of benzalmalononitrile alkylation products with PIB.

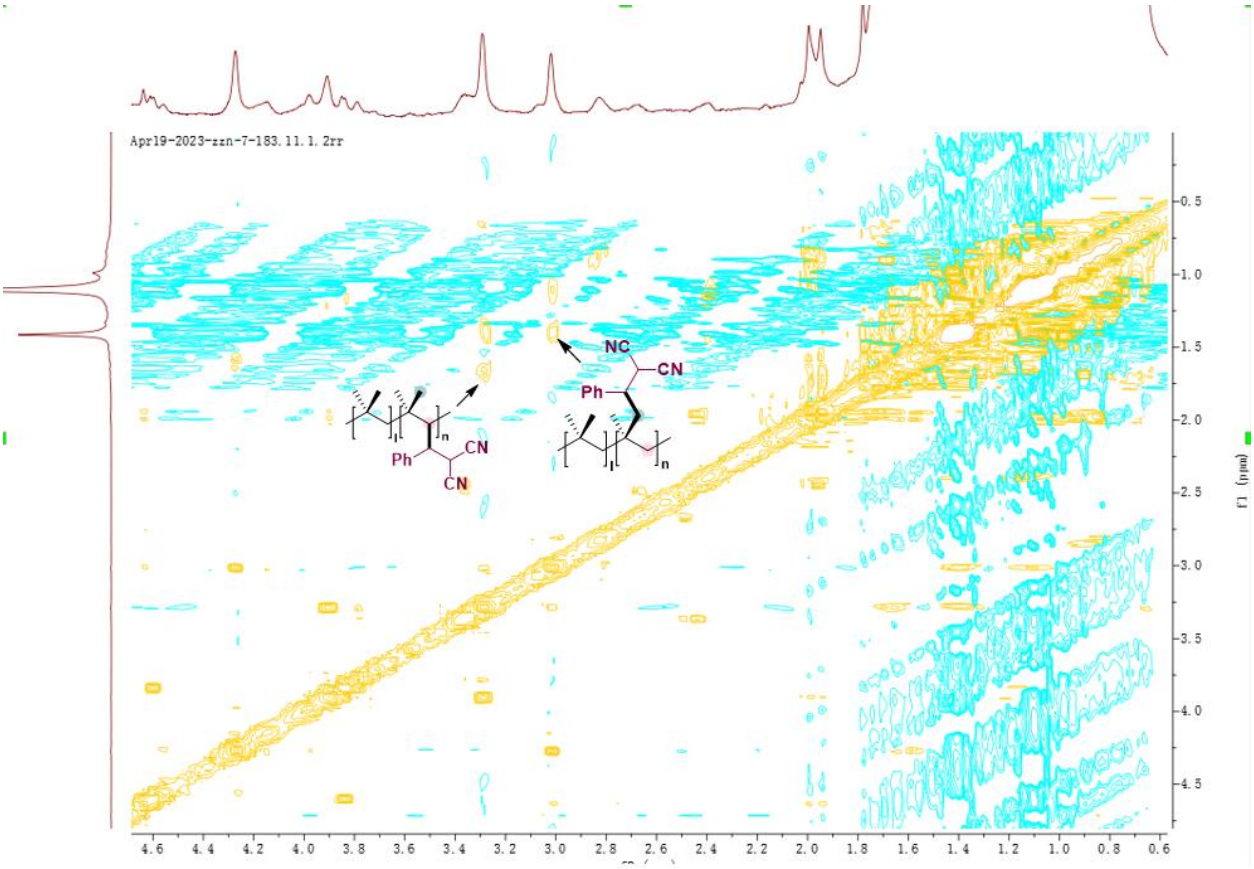
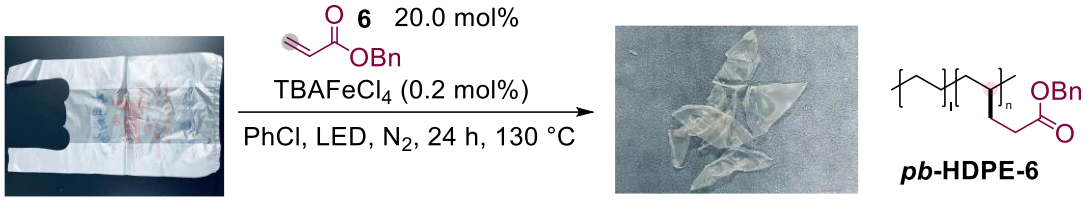


Figure S69. COSY of benzalmalononitrile alkylation products with PIB.

Concerting plastic waste into the potentially valuable materials



plastic bag
HDPE

LOF = 11.0 mol%

To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), plastic bag (HDPE) (57.1 mg, 2.0 mmol), **6** (64.8 mg, d = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (10 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound ***pb*-HDPE-6** was obtained as a white solid (74.1 mg, LOF = 11.0 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.26 (m, 5.32 H), 5.23-5.00 (m, **2.00 H**), 2.50-2.24 (m, 1.72 H), 1.75-1.02 (m, **36.30 H**).

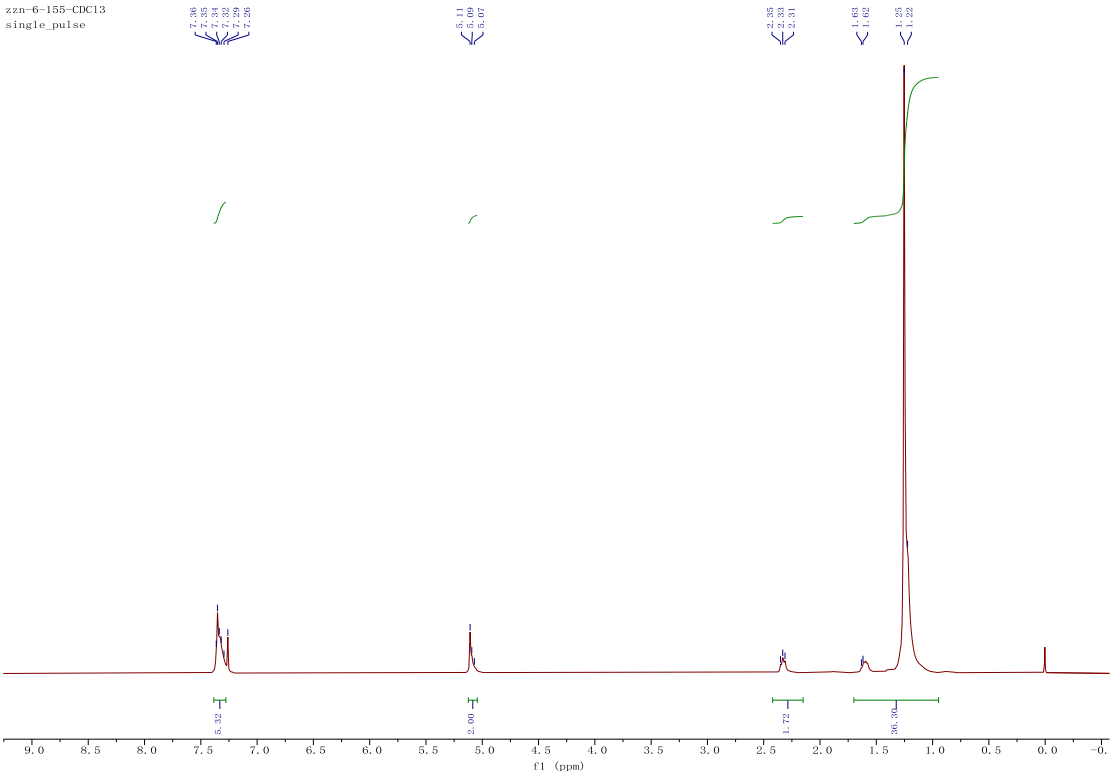


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of ***pb*-HDPE-6**

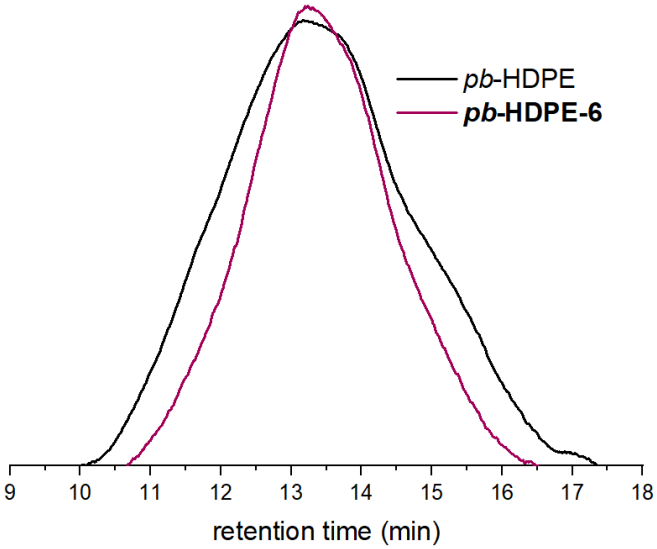
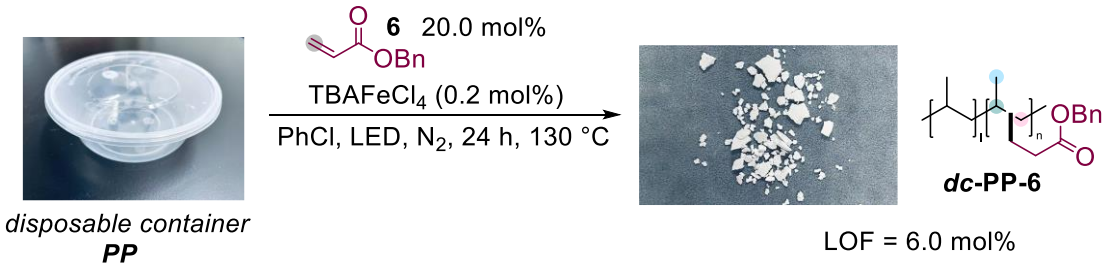


Figure S71. The GPC traces. *pb*-HDPE (black), M_n = 19250g/mol, M_w = 378866 g/mol, $Đ$ = 19.68; ***pb*-HDPE-6** (purple), M_n = 35727 g/mol, M_w = 239292 g/mol, $Đ$ = 6.70.



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), single-use container (PP) (84.3 mg, 2.0 mmol), **6** (64.8 mg, *d* = 1.080 g/mL, 60 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (10 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound ***dc*-PP-6** was obtained as a white solid (101.8 mg, LOF = 6.0 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.27 (m, 5.95 H), 5.31-4.75 (m, **2.00 H**), 2.41-2.24 (m, 1.67 H), 1.75-0.58 (m, **99.26 H**).

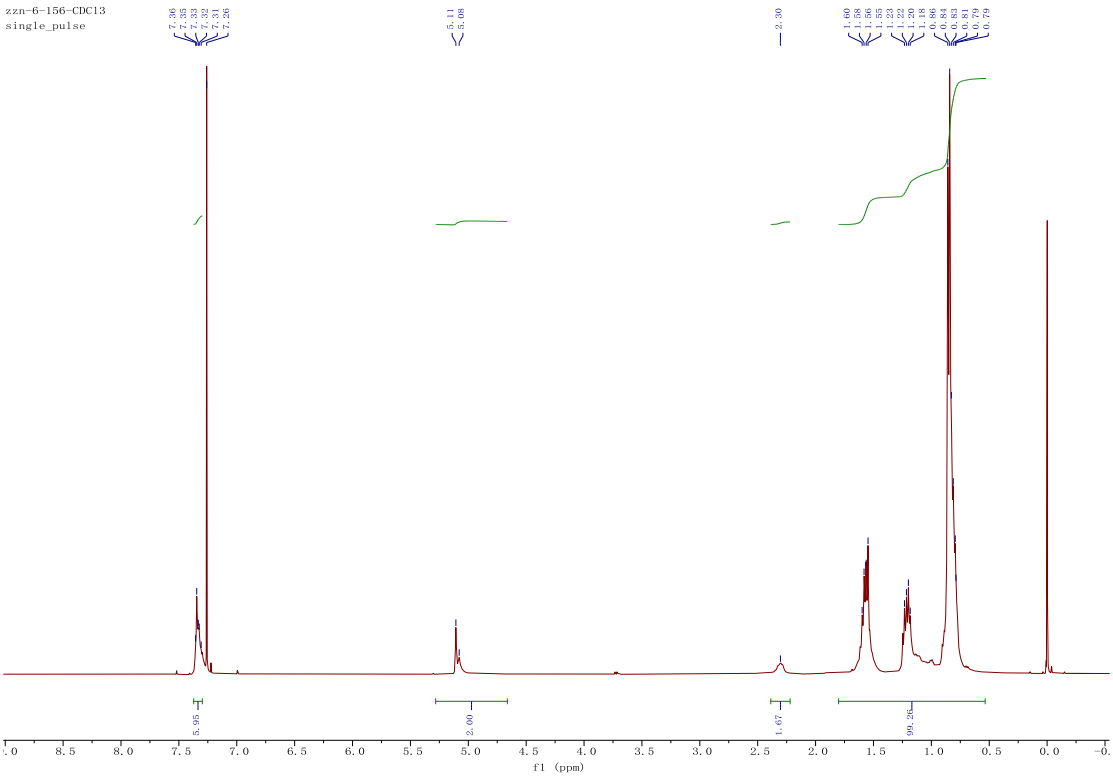


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of ***dc*-PP-6**

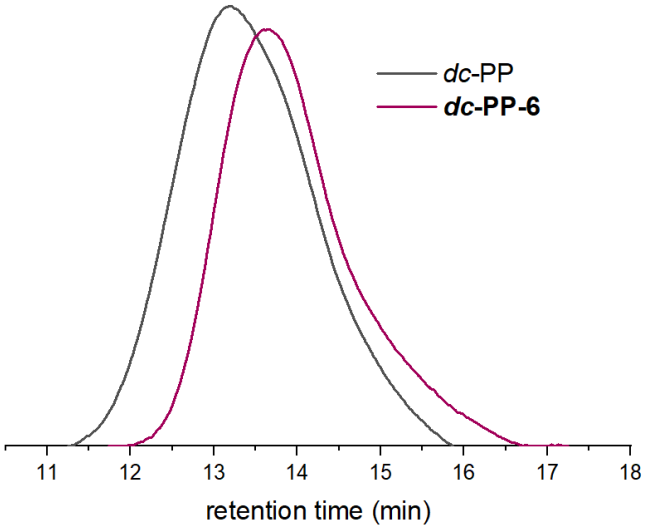
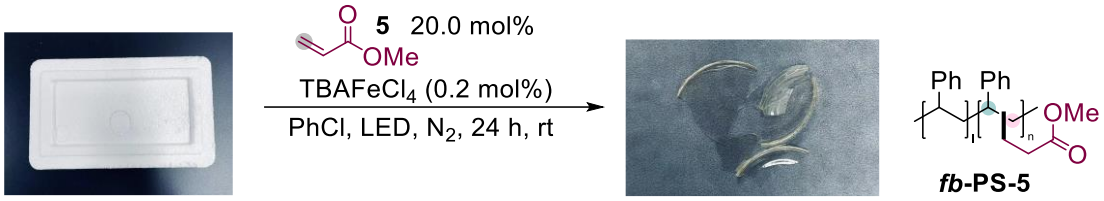


Figure S73. The GPC traces. *dc*-PP (black), M_n = 50218 g/mol, M_w = 163591 g/mol, $Đ$ = 3.26; ***dc*-PP-6** (purple), M_n = 22551 g/mol, M_w = 75962 g/mol, $Đ$ = 3.37.



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), foam box (PS) (209.1 mg, 2.0 mmol), **5** (34.4 mg, *d* = 0.956 g/mL, 36 μL, 0.4 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at rt. EtOH (8.0 mL) was added to the resulting mixture precipitated. Then, the resulting mixture was precipitated 2 times using DCM and EtOH (DCM/EtOH = 1:8) until the small molecules were removed completely. The compound ***foam*-PS-5** was obtained as a yellow solid (200.4 mg, LOF = 0.2 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.26-6.24 (m, 2455.36 H), 3.25-3.16 (m, **3.00 H**), 2.75-0.74 (m, **1506.53 H**).

^{1}H NMR (400 MHz, $CDCl_3$) of ***foam*-PS-5**

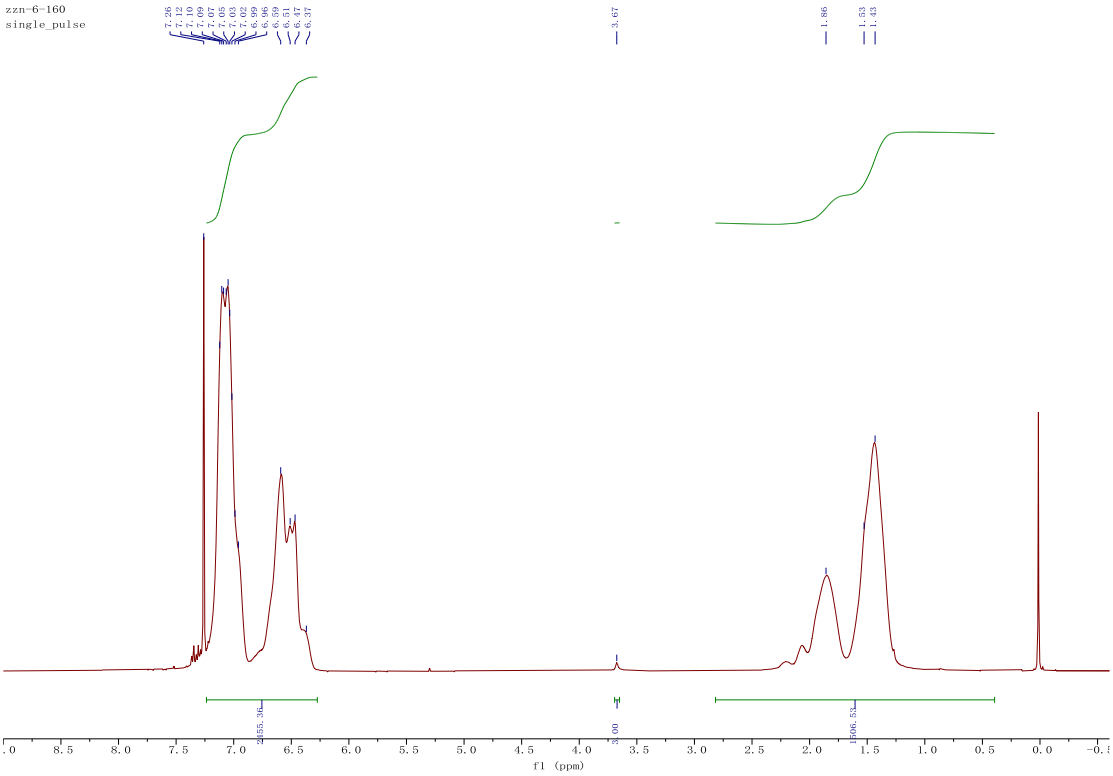


Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of ***foam*-PS-5**

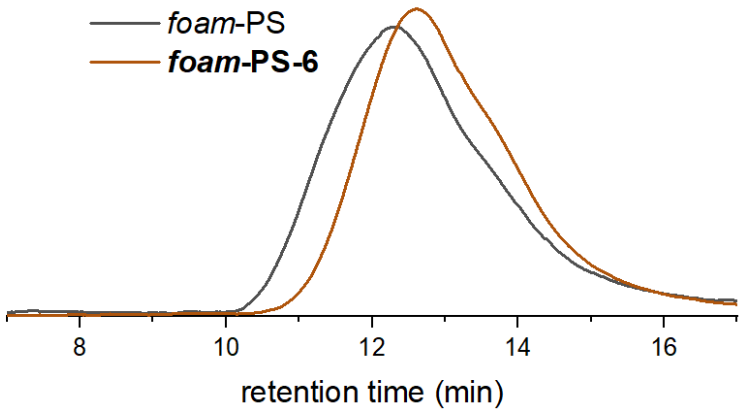
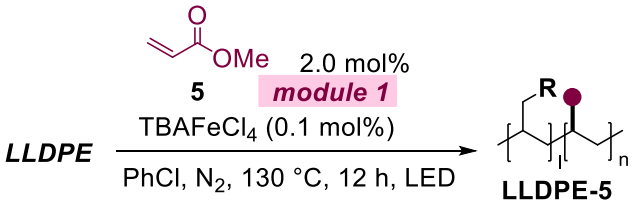


Figure S75. The GPC traces. *foam*-PS (black), M_n = 114458 g/mol, M_w = 261570 g/mol, $Đ$ = 2.29; ***foam*-PS-6** (brown), M_n = 85031 g/mol, M_w = 176373 g/mol, $Đ$ = 2.07.

Modular synthesis of multi-polar polyolefins from LLDPE and deficient alkenes

(1) LOF-controllable multi-incorporation of the polar groups.

Entry 1:



To a 100 mL sealed tube were added $TBAFeCl_4$ (2.3 mg, 0.005 mmol), LLDPE (141.1 mg, 5.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol $Đ$ = 3.37), **5** (8.6 mg, d = 0.956 g/mL, 9 μL, 0.1 mmol), and PhCl (4.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 12 hours at 130 °C. After EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5** was obtained as a white solid (142.4 g, LOF = 1.9 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, **3.00 H**), 2.50-2.25 (m, 2.43 H), 2.12-0.75 (m, **207.08 H**). The level of functionalization was determined by ^{1}H NMR.

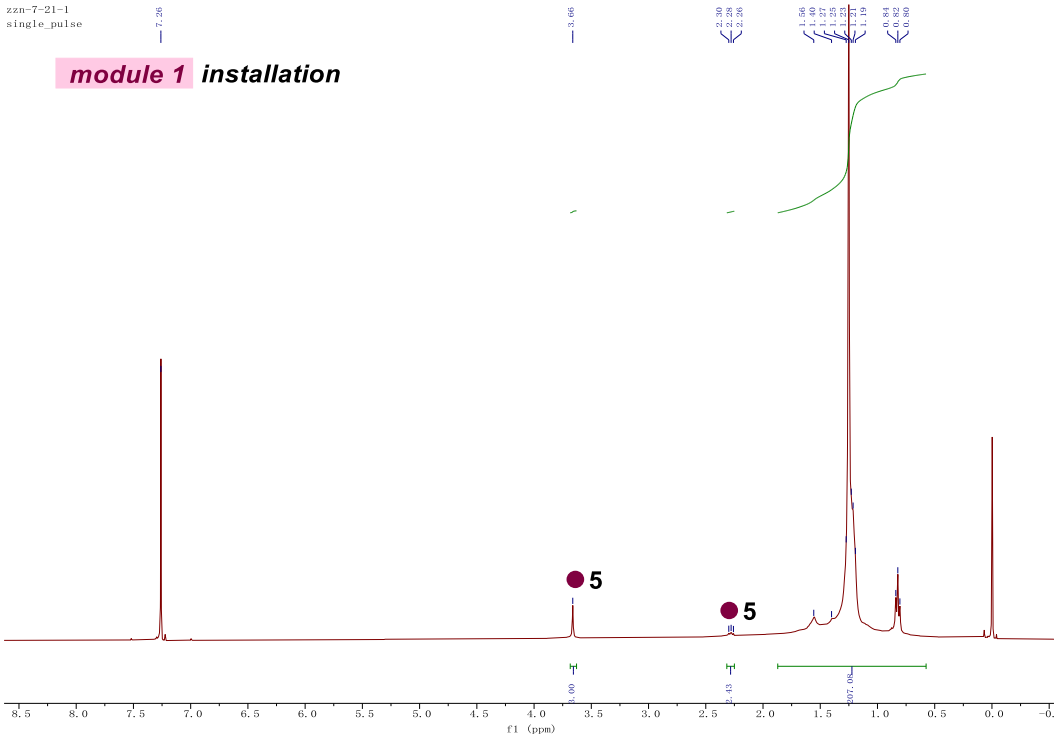
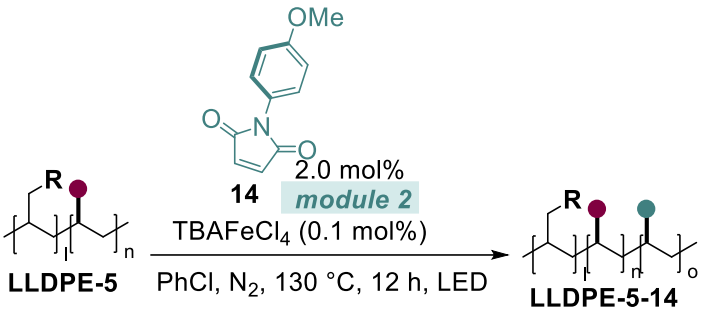


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.006 mmol), **LLDPE-5** (112.5 mg, 4.0 mmol), **14** (16.4 mg, 0.08 mmol), and PhCl (4.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14** was obtained as a yellow solid (119.4 mg, LOF = **1.6 mol%** for **14**).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.80 (m, 3.50 H), 3.82 (s, **3.00 H**), 1.78-0.71 (m, **243.21 H**).

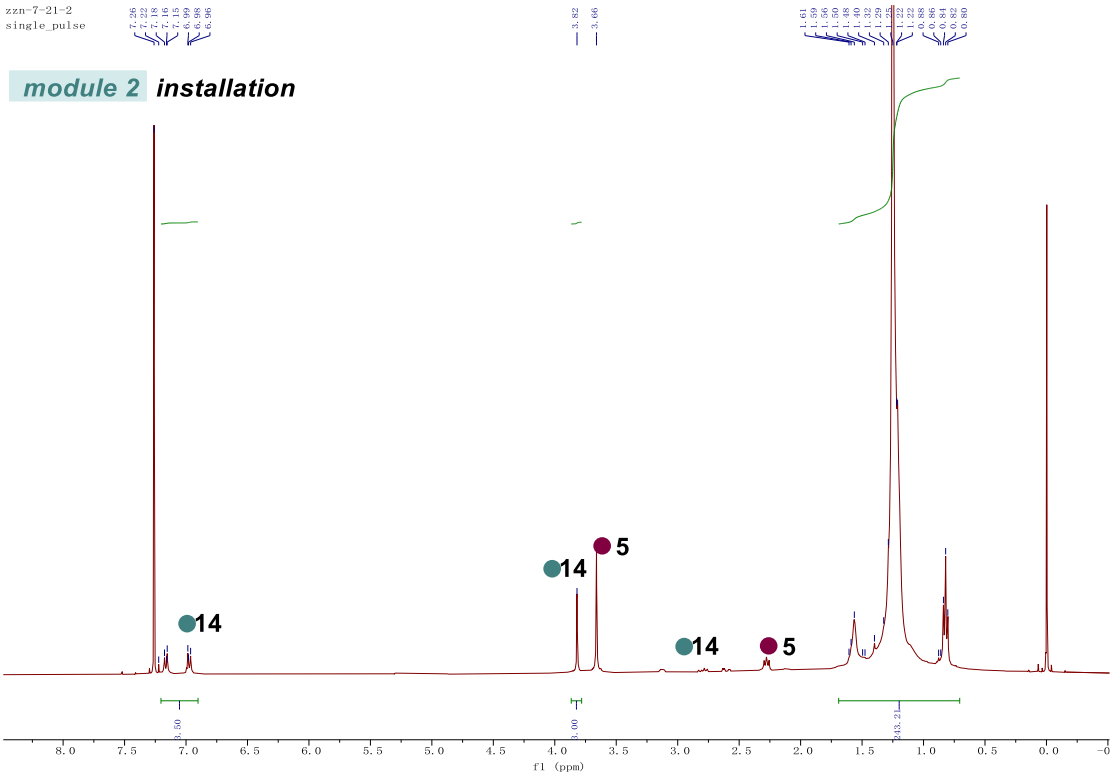
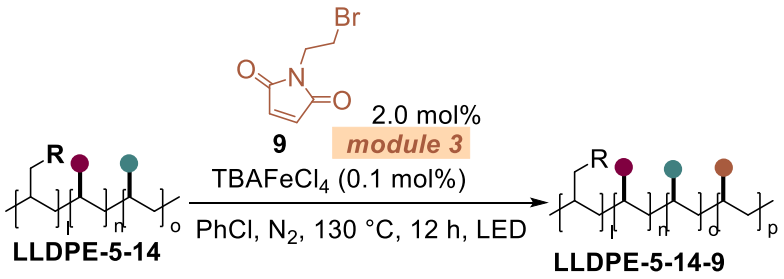


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.4 mg, 0.003 mmol), **LLDPE-5-14** (84.5 mg, 3.0 mmol), **9** (12.3 mg, 0.06 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9** was obtained as a white solid (87.9 mg, LOF = **1.7 mol%** for **9**). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR δ (400 MHz, $CDCl_3$) 4.01-3.78 (m, **2.00 H**), 3.60-3.48 (m, 2.06 H), 1.78-0.71 (m, **236.36 H**). **GPC (TCB, 140 °C)** M_n = 69558 g/mol, M_w = 337594 g/mol, $Đ$ = 4.85. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-13-15** T_d = 325. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9** no recorded melting point.

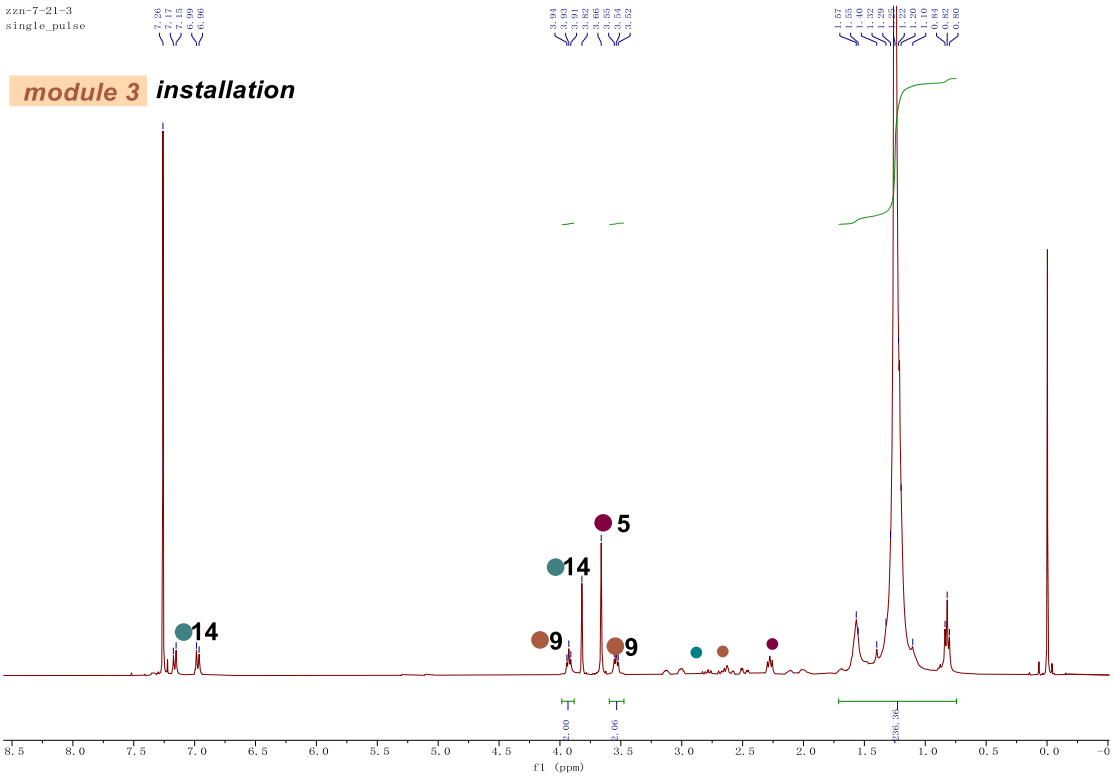


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9**

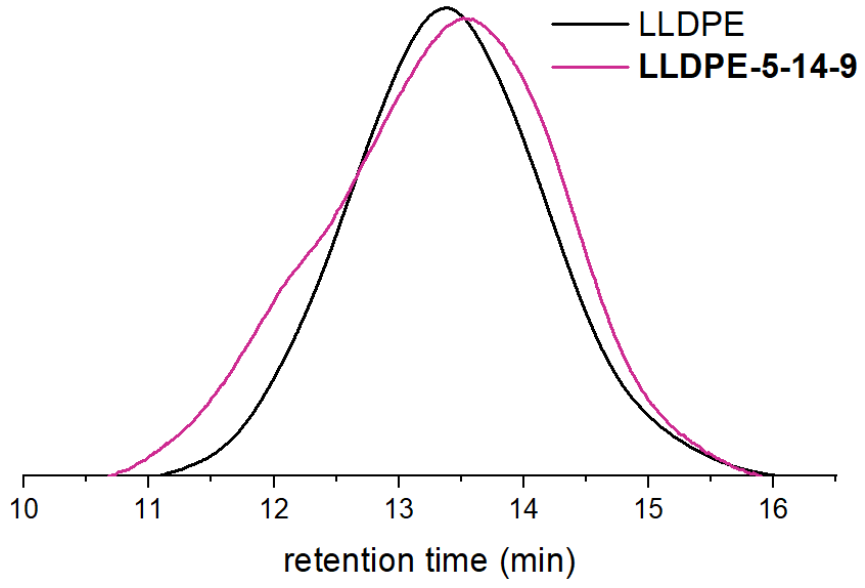
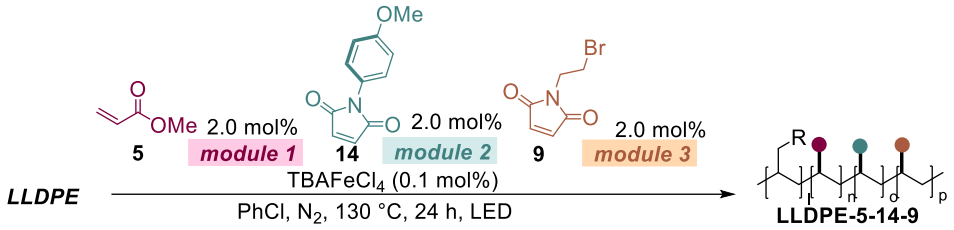


Figure S79.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5-14-9** (purple), M_n = 69588 g/mol, M_w = 337594 g/mol, $Đ$ = 4.85 for entry 1.

Entry 2:



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LLDPE (112.5 mg, 4.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (6.9 mg, d = 0.956 g/mL, 7 μL, 0.08 mmol), **14** (16.3 mg, 0.08 mmol), **9** (16.5 mg, 0.08 mmol) and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9** was obtained as a white solid (139.0 mg, LOF = 1.2/1.8/1.9 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.80 (m,4.00 H), δ 3.94-3.83 (m, **2.33 H**), δ 3.82 (s, **3.27 H**), δ 3.66 (s, **2.22 H**), δ 3.57-3.50 (m, 2.36 H), 1.75-0.70 (m, **245.73 H**). **GPC (TCB, 140 °C)** M_n = 66103 g/mol, M_w = 194904 g/mol, $Đ$ = 2.95. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9** T_d = 330. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9** no recorded melting point.

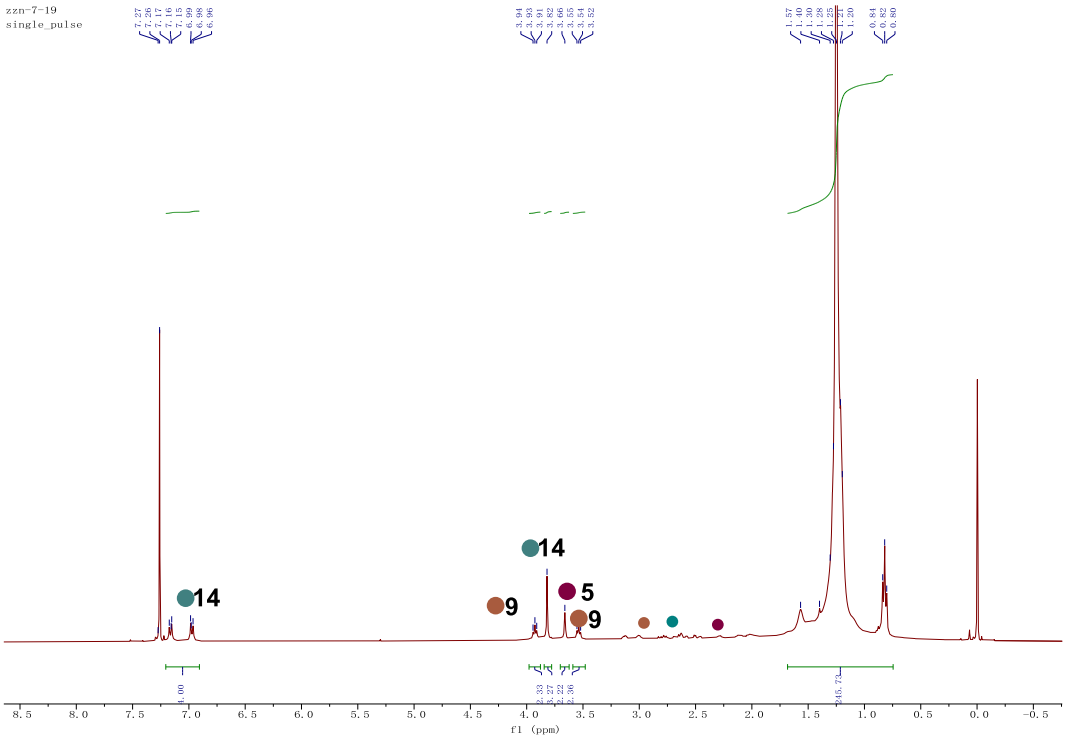


Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9**

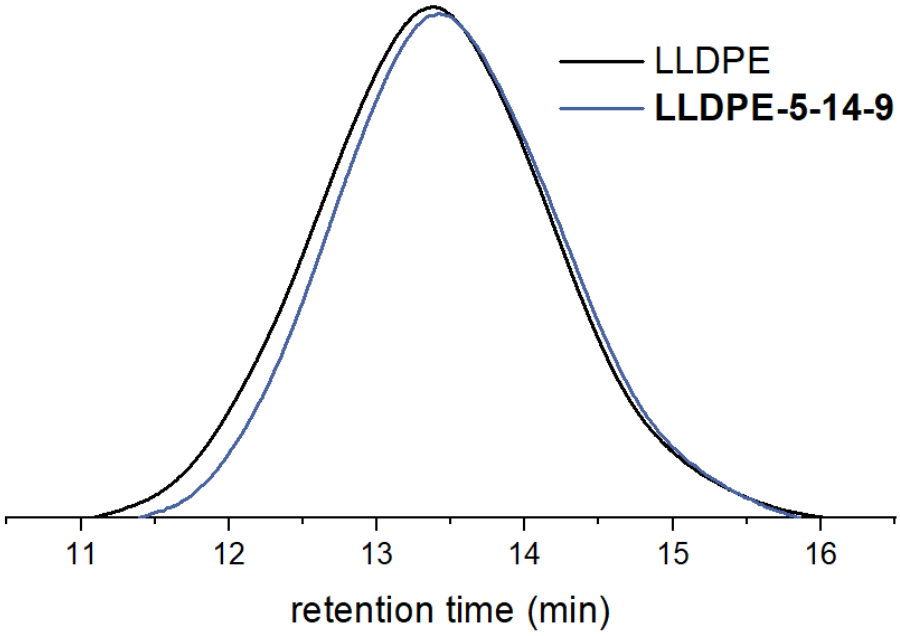
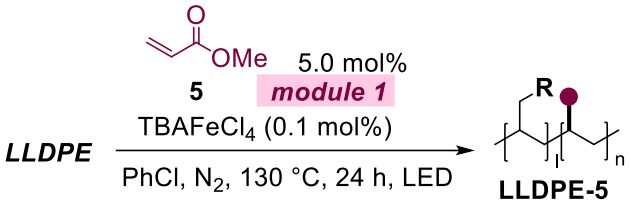


Figure S81.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5-14-9** (blue), M_n = 66103 g/mol, M_w = 194904 g/mol, $Đ$ = 2.95 for entry 2.

Entry 3:



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.8 mg, 0.1 mmol), LLDPE (2.8025 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (430.0 mg, d = 0.956 g/mL, 450 μL, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-5** was obtained as a white solid (3.0641 g, LOF = 4.7 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3.34 H), 2.50-2.25 (m, **2.00 H**), 2.12-0.75 (m, **83.73 H**). The level of functionalization was determined by ^{1}H NMR.

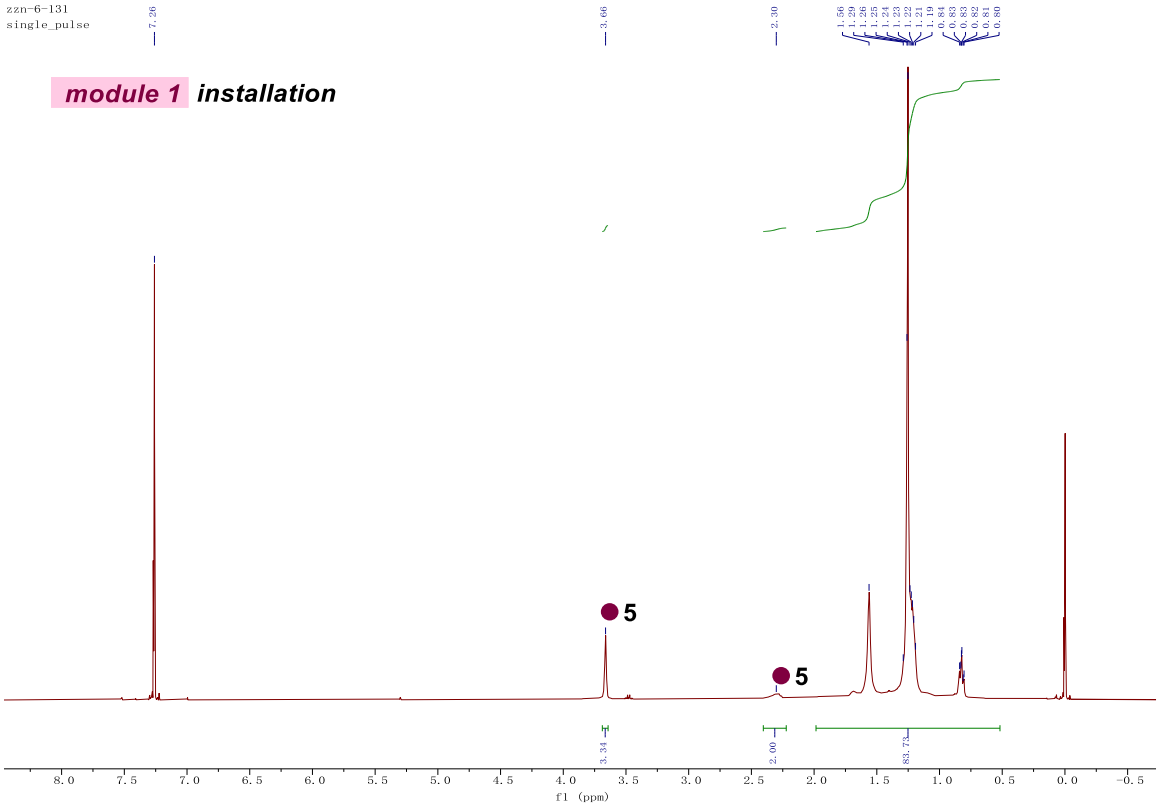
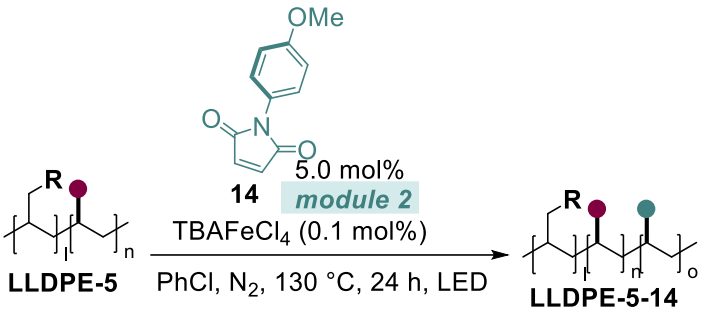


Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), **LLDPE-5** (112.3 mg, 4.0 mmol), **14** (40.4 mg, 0.2 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14** was obtained as a white solid (132.7 mg, LOF = **3.7 mol%** for **14**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.80 (m, **4.00** H), 3.82 (m, 3.17 H), 1.78-0.71 (m, **109.32 H**).

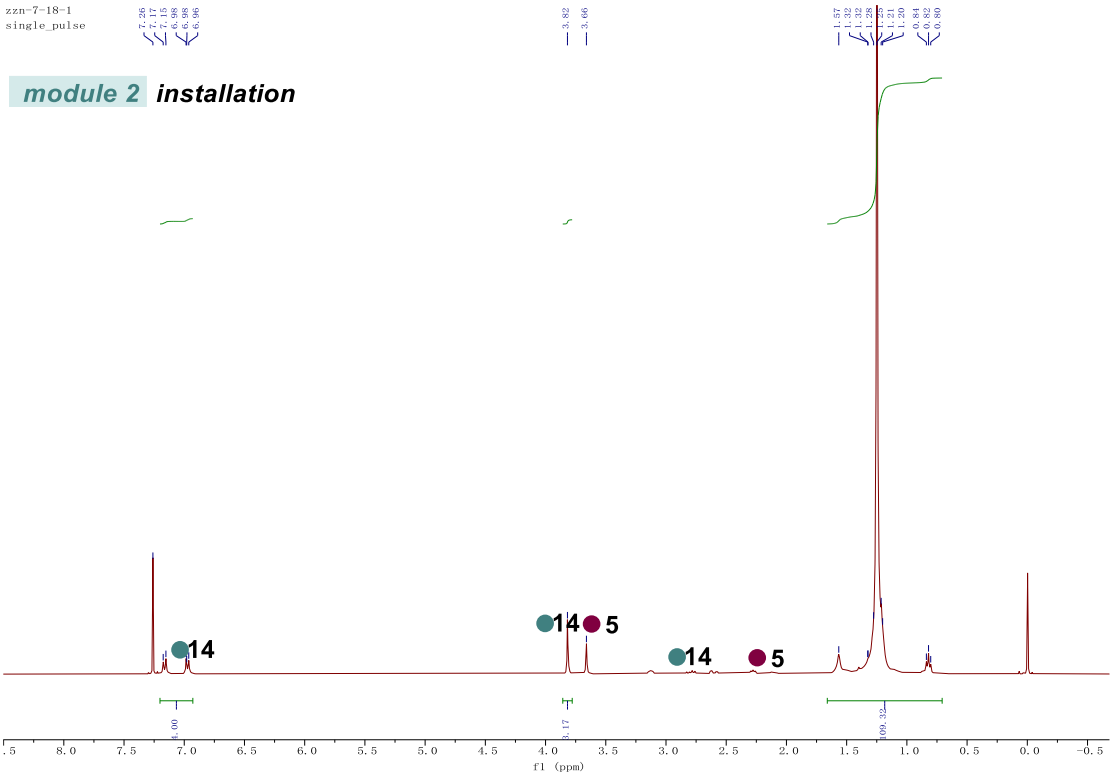
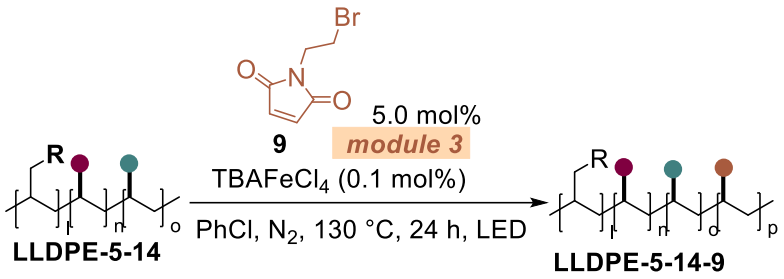


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.5 mg, 0.003 mmol), **LLDPE-5-14** (84.2 mg, 3.0 mmol), **9** (30.8 mg, 0.15 mmol), and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9** was obtained as a yellow solid (104.7 mg, LOF = **4.6 mol%** for **9**). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR δ (400 MHz, $CDCl_3$) 4.01-3.78 (m, **2.00 H**), 3.60-3.48 (m, 2.06 H), 1.85-0.71 (m, **86.05 H**). **GPC (TCB, 140 °C)** M_n = 64821 g/mol, M_w = 162946 g/mol, $Đ$ = 2.51. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9** T_d = 300. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9** no recorded melting point.

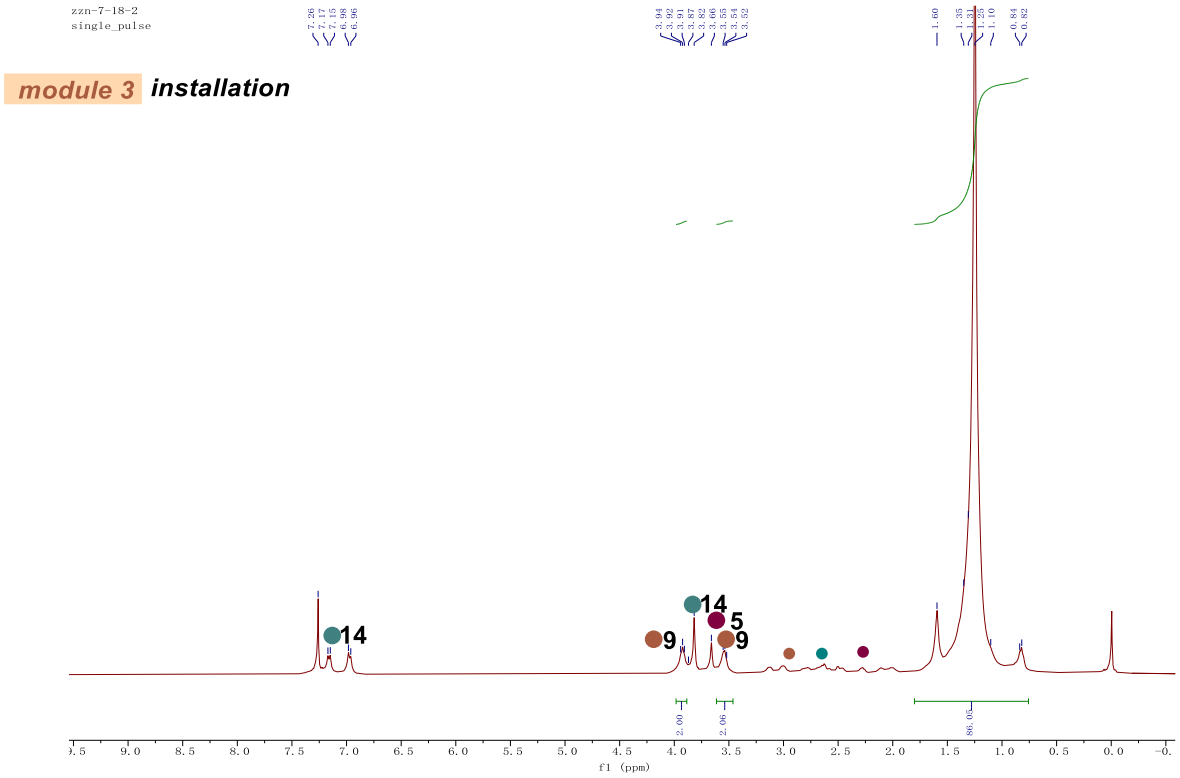


Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9**

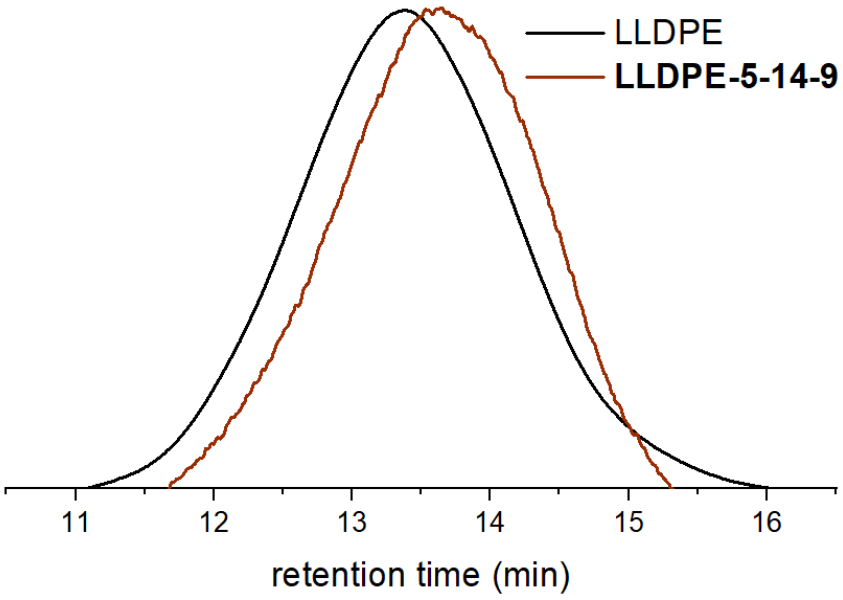
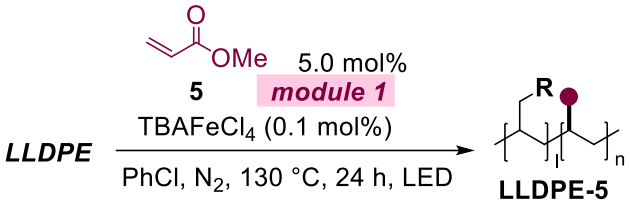


Figure S85.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5-14-9** (brown), M_n = 64821 g/mol, M_w = 162946 g/mol, $Đ$ = 2.51 for entry 3.

Entry 4:



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.8 mg, 0.1 mmol), LLDPE (2.8025 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (430.0 mg, d = 0.956 g/mL, 450 μL, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5** was obtained as a white solid (3.0641 g, LOF = 4.7 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3.34 H), 2.50-2.25 (m, **2.00 H**), 2.12-0.75 (m, **83.73 H**). The level of functionalization was determined by ^{1}H NMR.

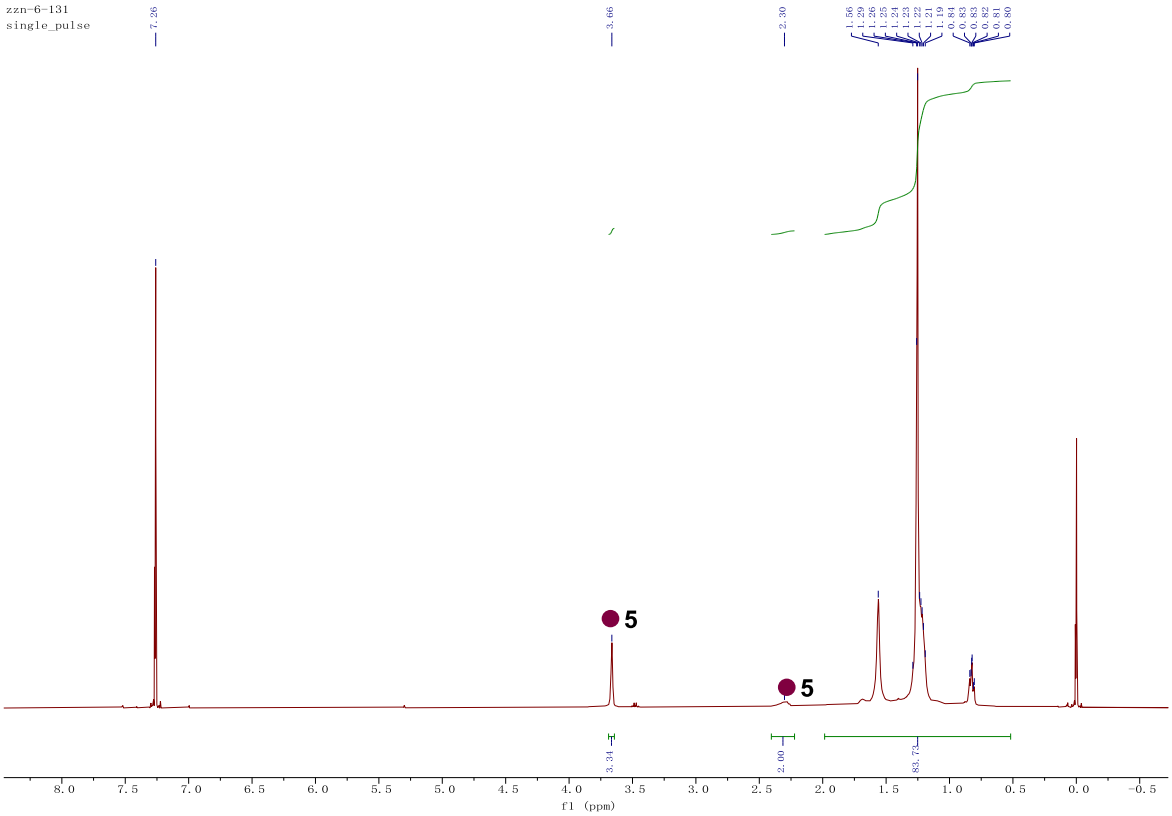
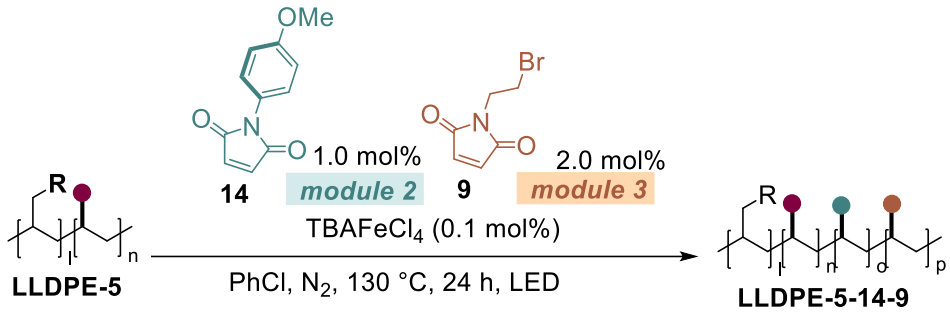


Figure S86. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5**



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), **LLDPE-5** (111.7 mg, 4.0 mmol), **14** (8.2 mg, 0.04 mmol), **9** (16.2 mg, 0.08 mmol) and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9** was obtained as a yellow solid (123.9 mg, LOF = 1.0/1.4 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94-3.83 (m, 2.71 H), δ 3.82 (m, **3.00 H**), δ 3.57-3.50 (m, **3.02** H), 1.68-0.70 (m, **388.0 H**). **GPC (TCB, 140 °C)** M_n = 67668 g/mol, M_w = 229527 g/mol, $Đ$ = 3.39. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9** T_d = 331. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9** no recorded melting point.

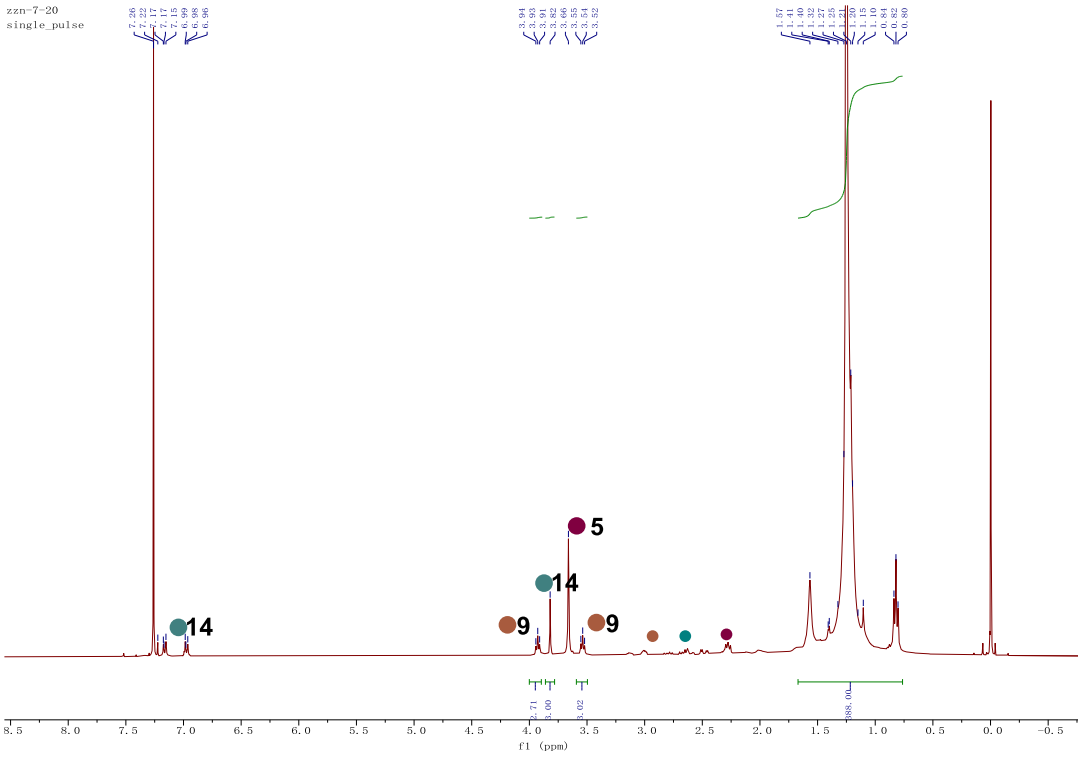


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9**

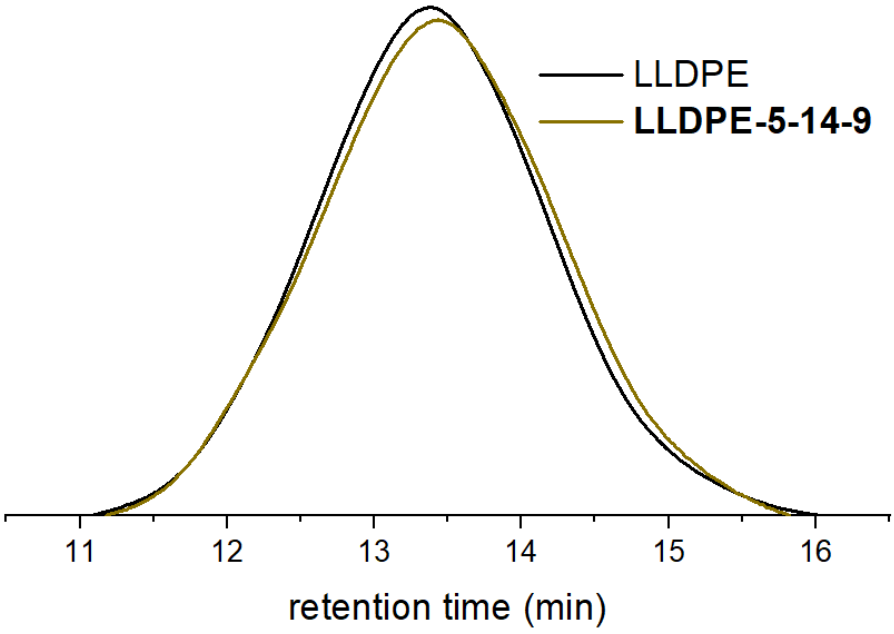
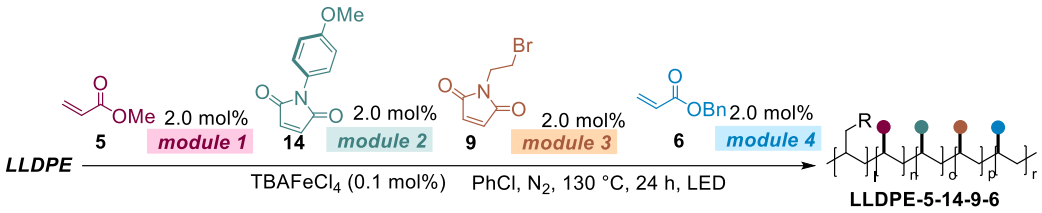


Figure S88.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5-14-9** (gold), M_n = 67668 g/mol, M_w = 229527 g/mol, $Đ$ = 3.39 for entry 4.

Entry 5:



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.7 mg, 0.004 mmol), LLDPE (112.5 mg, 4.0 mmol, M_n = 56845 g/mol, M_w = 193809 g/mol, $Đ$ = 3.41), **5** (6.9 mg, d = 0.956 g/mL, 7 μL, 0.08 mmol), **14** (16.3 mg, 0.08 mmol), **9** (16.5 mg, 0.08 mmol), **6** (13.0 mg, d = 1.080 g/mL, 12 μL, 0.08 mmol) and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9-6** was obtained as a white solid (141.3 mg, LOF = 0.6/1.7/1.2/1.2 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 6.58 H), 7.25-6.80 (m, 6.10 H), 5.25-5.02 (m, **2.00** H), δ 3.94-3.83 (m, 2.55 **H**), δ 3.82 (s, **5.07 H**), δ 3.66 (s, **1.65 H**), δ 3.57-3.50 (m, **2.66** H), 1.75-0.70 (m, **387.71 H**). **GPC (TCB, 140 °C)** M_n = 57238 g/mol, M_w = 186614 g/mol $Đ$ = 3.26. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9-6** T_d = 335. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9-6** no recorded melting point.

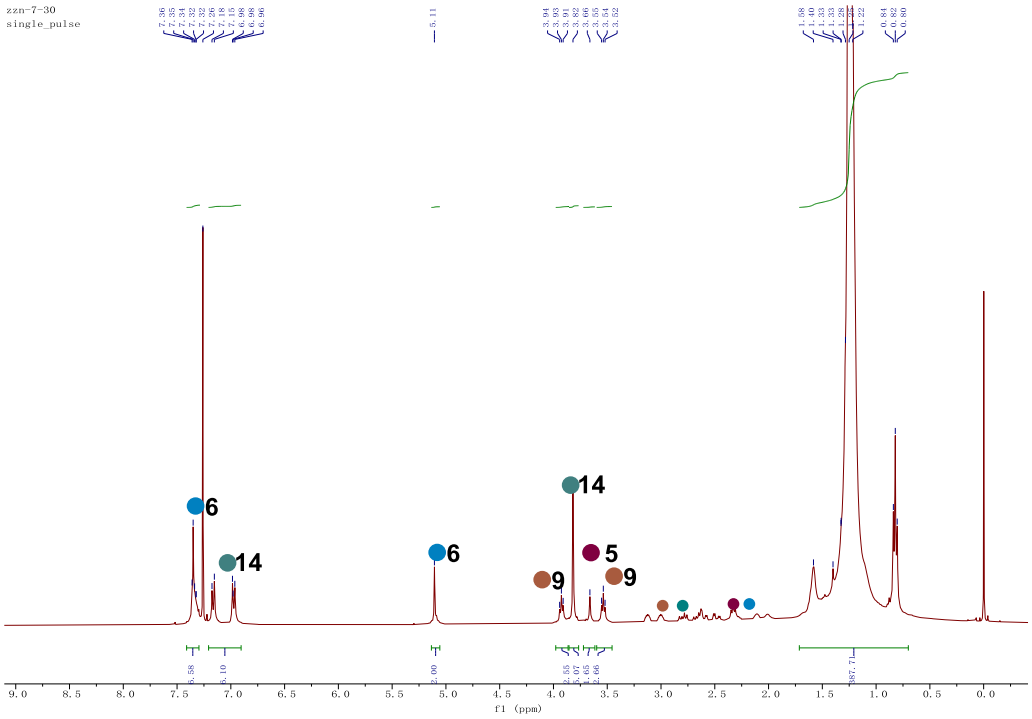


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9-6**

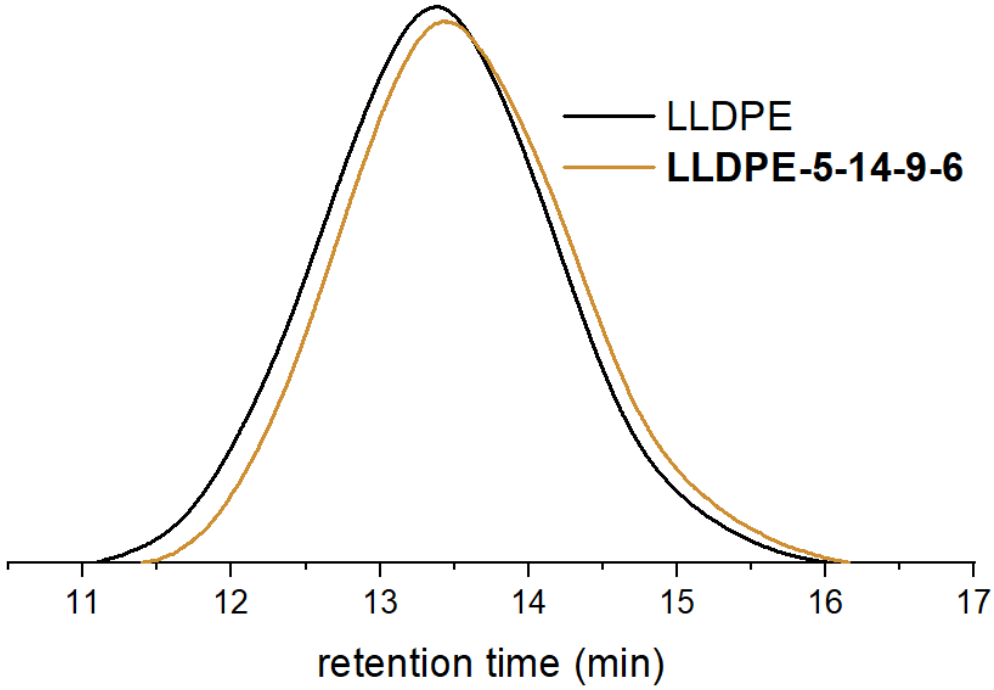
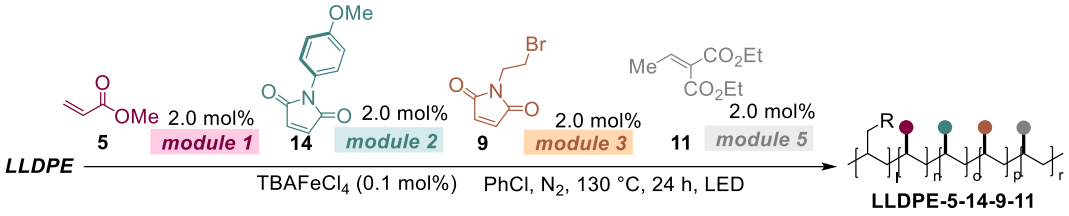


Figure S90.The HT-GPC traces. LLDPE (black), M_n = 56845 g/mol, M_w = 193809 g/mol $Đ$ = 3.41; **LLDPE-5-14-9-6** (orange), M_n = 57238 g/mol, M_w = 186614 g/mol $Đ$ = 3.26 for entry 5.

Entry 6:



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.8 mg, 0.004 mmol), LLDPE (112.1 mg, 4.0 mmol, M_n = 56845 g/mol, M_w = 193809 g/mol $Đ$ = 3.41), **5** (6.9 mg, d = 0.956 g/mL, 7 μL, 0.08 mmol), **14** (16.5 mg, 0.08 mmol), **9** (16.2 mg, 0.08 mmol), **11** (15.5 mg, 0.08 mmol) and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9-11** was obtained as a white solid (141.6 mg, LOF = 1.1/1.7/1.6/0.3 mol%). The level of functionalization was determined

^{1}H NMR (400 MHz, $CDCl_3$) δ7.25-6.80 (m, **4.00** H), 4.26-4.10 (m, **0.87** H), δ 3.94-3.83 (m, 2.10 **H**), δ 3.82 (s, **3.47 H**), δ 3.66 (s, **2.26 H**), δ 3.57-3.50 (m, **2.20** H), 1.75-0.70 (m, **269.51 H**). by ^{1}H NMR. **GPC (TCB, 140 °C)** M_n = 47723 g/mol, M_w = 159958 g/mol $Đ$ = 3.35. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9-11** T_d = 345. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9-11** no recorded melting point.

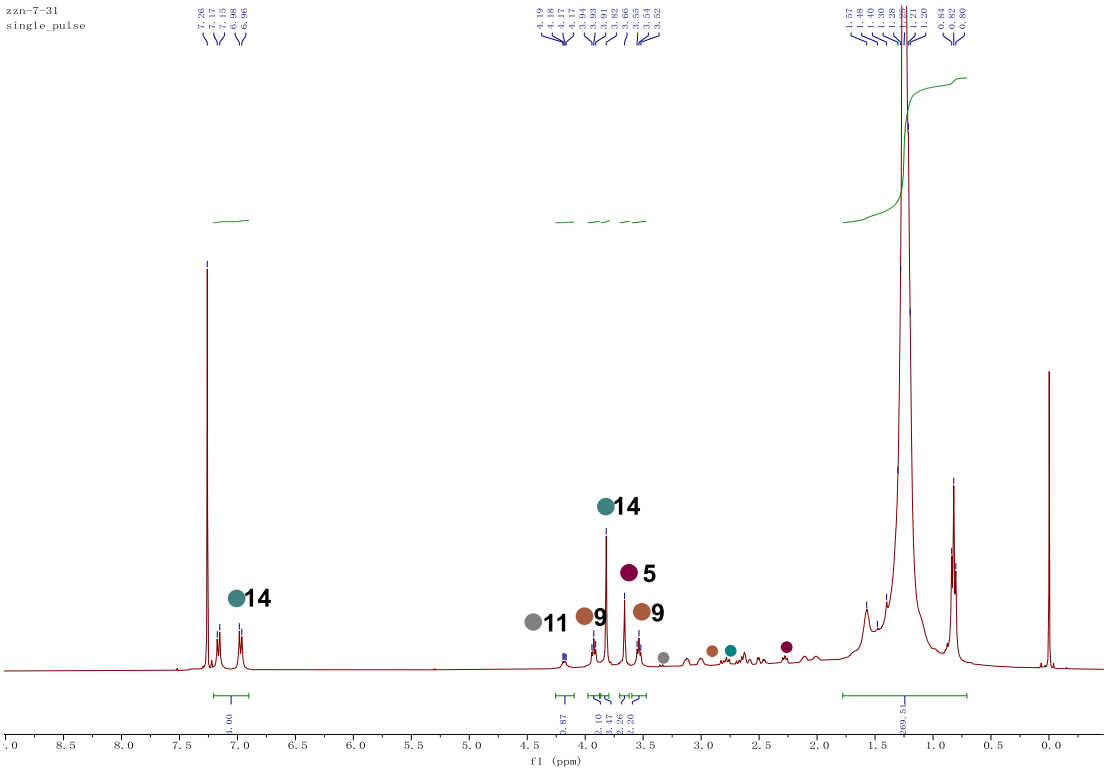


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9-11**

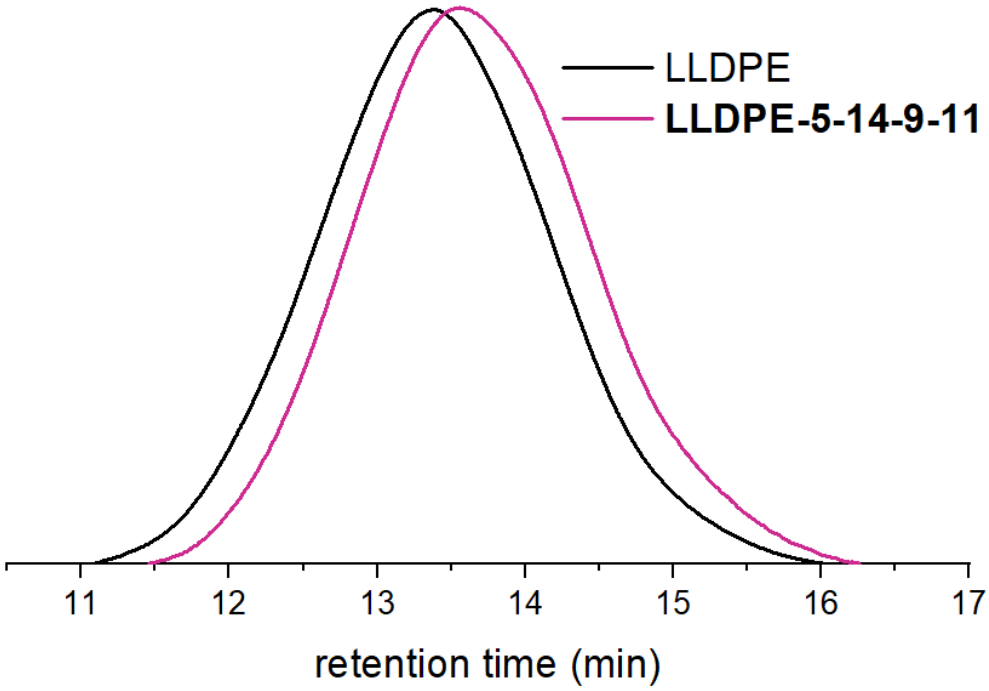
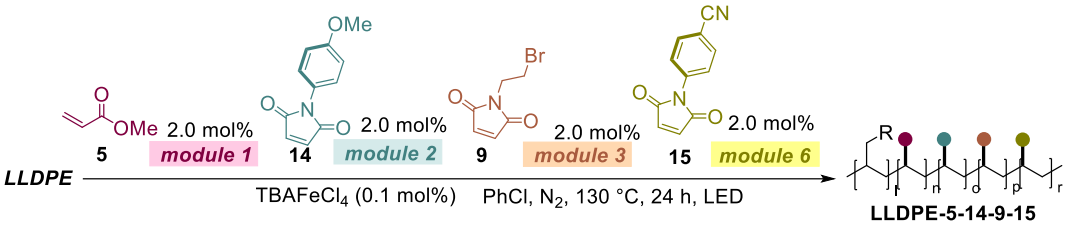


Figure S92.The HT-GPC traces. LLDPE (black) M_n = 56845 g/mol, M_w = 193809 g/mol $Đ$ = 3.41; **LLDPE-5-14-9-11** (purple), M_n = 47723 g/mol, M_w = 159958 g/mol $Đ$ = 3.35 for entry 6.

Entry 7:



To a 35 mL sealed tube were added $TBAFeCl_4$ (1.9 mg, 0.004 mmol), LLDPE (112.0 mg, 4.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (6.9 mg, d = 0.956 g/mL, 7 μL, 0.08 mmol), **14** (16.3 mg, 0.08 mmol), **9** (16.4 mg, 0.08 mmol), **15** (15.9 mg, 0.08 mmol) and PhCl (3.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After cooling to rt, EtOH (10 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (5 mL × 3) until the small molecules were removed completely. After drying under vacuum at 50 °C for 12 hours. The compound **LLDPE-5-14-9-15** was obtained as a white solid (147.9 mg, LOF = 0.4/1.7/1.2/1.2 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.42 (m, **4.00** H), 7.25-6.80 (m, 4.70 H), δ 3.94-3.83 (m, 1.84 **H**), δ 3.82 (s, **4.14 H**), δ 3.66 (s, **0.92 H**), δ 3.57-3.50 (m, **2.00** H), 1.75-0.70 (m, **333.58 H**). **GPC (TCB, 140 °C)** M_n = 55542 g/mol, M_w = 194723 g/mol $Đ$ = 3.51. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5-14-9-15** T_d = 340. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5-14-9-15** no recorded melting point.

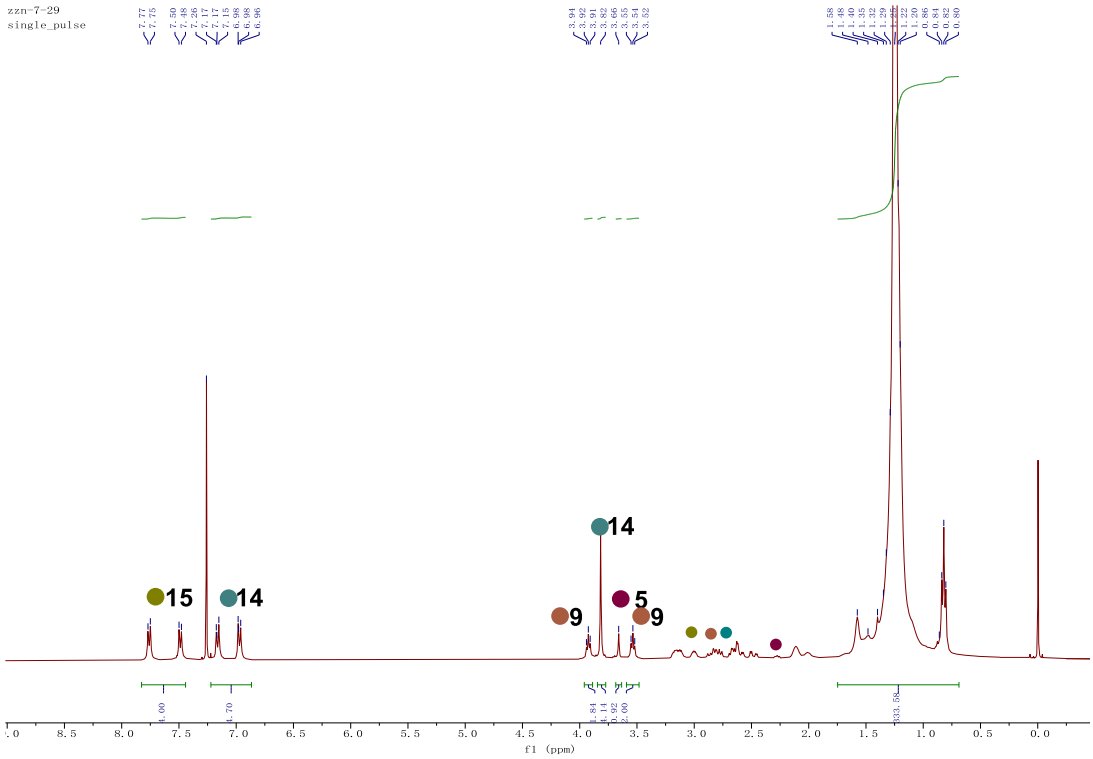


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-5-14-9-15**

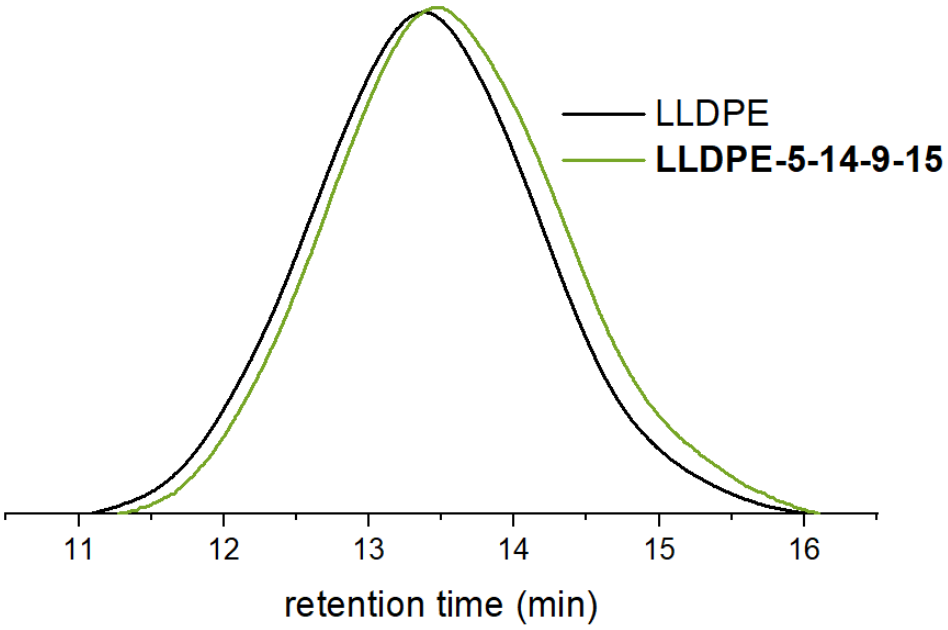
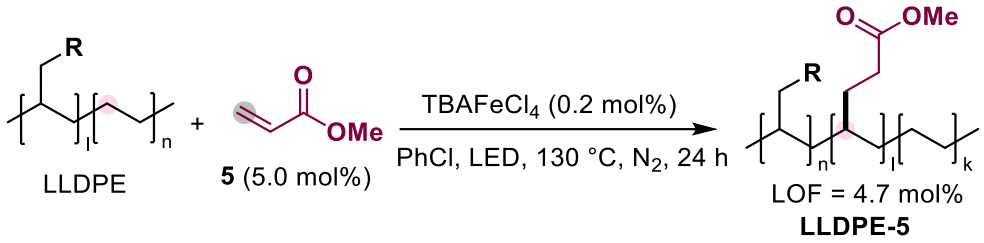


Figure S94.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5-14-9-15** (green), M_n = 55542 g/mol, M_w = 194723 g/mol, $Đ$ = 3.51 for entry 7.

Physical properties of various grafted-LLDPE



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.8 mg, 0.1 mmol), LLDPE (2.8025 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **5** (430.0 mg, d = 0.956 g/mL, 450 μL, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-5** was obtained as a white solid (3.0641 g, LOF = 4.7 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3.34 H), 2.50-2.25 (m, **2.00 H**), 2.12-0.75 (m, **83.73 H**). **GPC (TCB, 140 °C)** M_n = 64342 g/mol, M_w = 210306 g/mol, $Đ$ = 3.27. **TGA (°C)** LLDPE T_d = 420, **LLDPE-5** T_d = 410. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-5** T_m = 106 with 18% crystallinity (DH = 50 J/g).

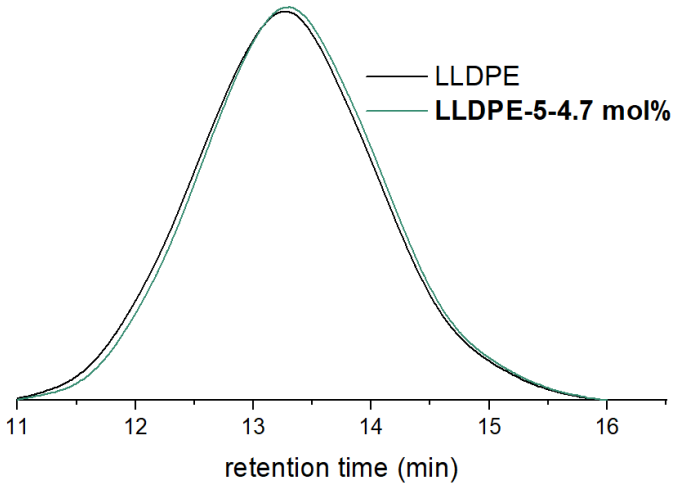
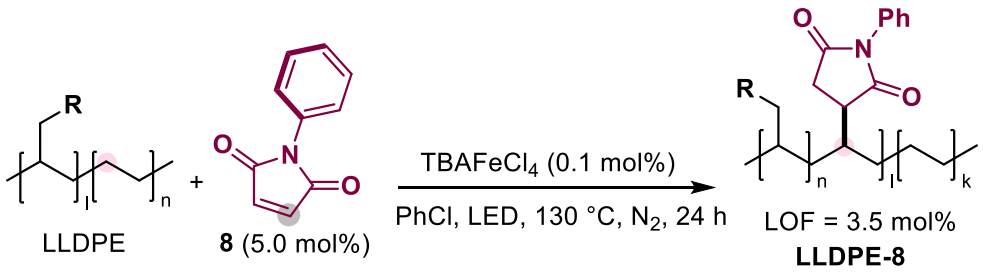


Figure S95.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-5** (green), M_n = 64342 g/mol, M_w = 210306 g/mol, $Đ$ = 3.27.



To a 100 mL sealed tube were added $TBAFeCl_4$ (43.8 mg, 0.1 mmol), LLDPE (2.8003 g, 100.0 mmol, M_n = 56845 g/mol, M_w = 193809 g/mol, $Đ$ = 3.41), **8** (863.2 mg, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-8** was obtained as a white solid (3.2489 g, LOF = 3.5 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.30 (m, 3.20 H), 7.28-7.26 (m, 2.31 H), 7.25-7.16 (m, 0.85 H), 3.23-3.12 (m, **1.00 H**), 2.83-2.75 (m, 1.12 H), 2.61-2.55 (m, 1.11 H), 2.18-2.05 (m, 1.07 H), 1.75-0.72 (m, **114.09 H**). **GPC (TCB, 140 °C)** M_n = 46914 g/mol, M_w = 134479 g/mol, $Đ$ = 2.87. **TGA (°C)** LLDPE T_d = 420, **LLDPE-8** T_d = 410. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-8** T_m = 92 with 11% crystallinity (DH = 29 J/g).

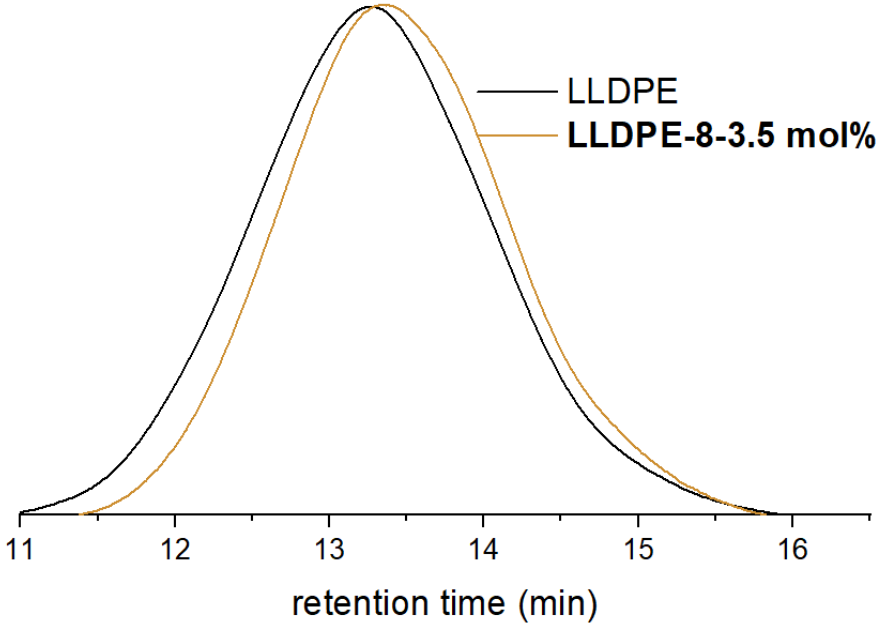


Figure S96.The HT-GPC traces. LLDPE (black), M_n = 56845 g/mol, M_w = 193809 g/mol, $Đ$ =

3.41; **LLDPE-8** (orange), M_n = 46914 g/mol, M_w = 134479 g/mol, $Đ$ = 2.87.

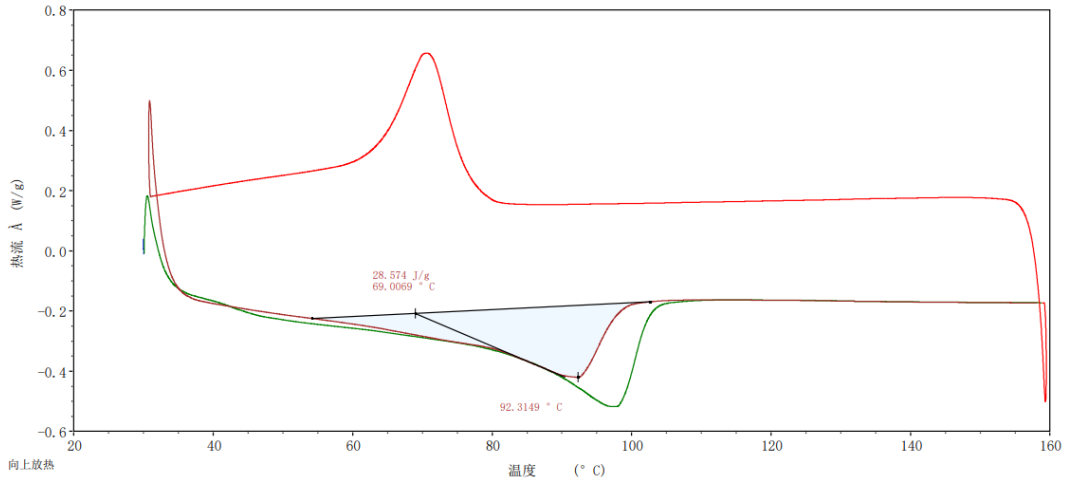
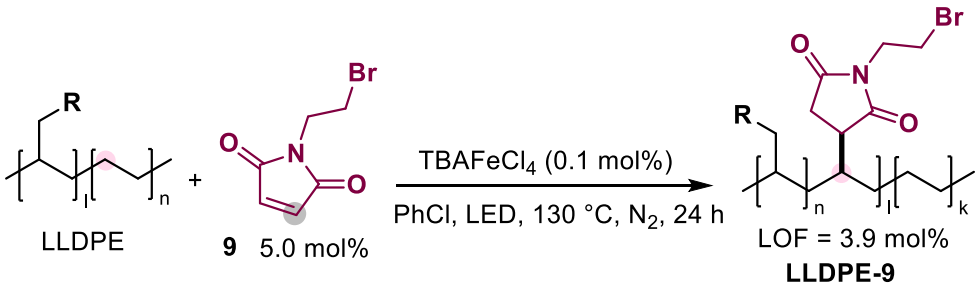


Figure S97. The DSC trace of **LLDPE-8**



To a 100 mL sealed tube were added $TBAFeCl_4$ (43.5 mg, 0.1 mmol), LLDPE (2.8003 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **9** (1.0232 g, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-9** was obtained as a white solid (3.5702 g, LOF = 3.9 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00-3.82 (m, **2.00 H**), 3.62-3.47 (m, 2.31 H), 3.10-2.95 (m, 1.09 H), 2.67-2.55 (m, 1.14 H), 2.53-2.45 (m, 1.10 H), 2.12-1.98 (m, 1.11 H), 1.62-0.73 (m, **103.60 H**). **GPC (TCB, 140 °C)** M_n = 71463 g/mol, M_w = 269291 g/mol, $Đ$ = 3.77. **TGA (°C)** LLDPE T_d = 420, **LLDPE-9** T_d = 310. **DSC (°C)** LLDPE T_m = 122 with 24% crystallinity (DH = 66 J/g), **LLDPE-9** T_m = 95 with 11% crystallinity (DH = 30 J/g).

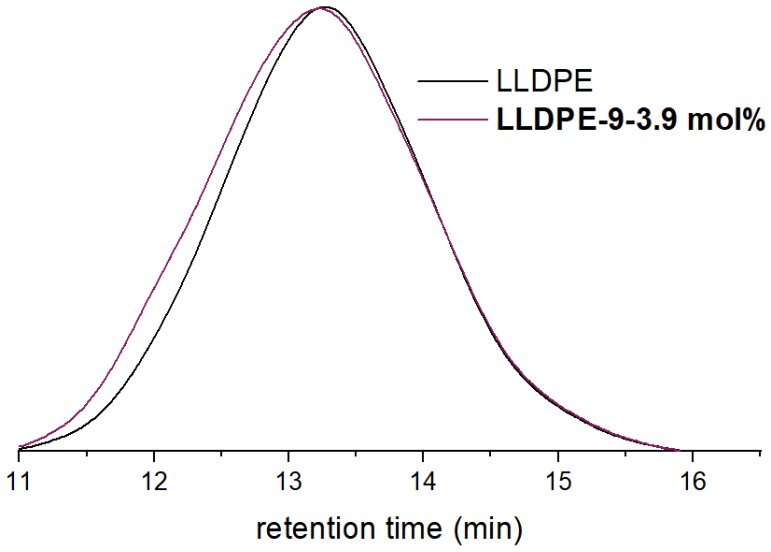


Figure S98.The HT-GPC traces. LLDPE (black), M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37; **LLDPE-9** (purple), M_n = 71463 g/mol, M_w = 269291 g/mol, $Đ$ = 3.77.

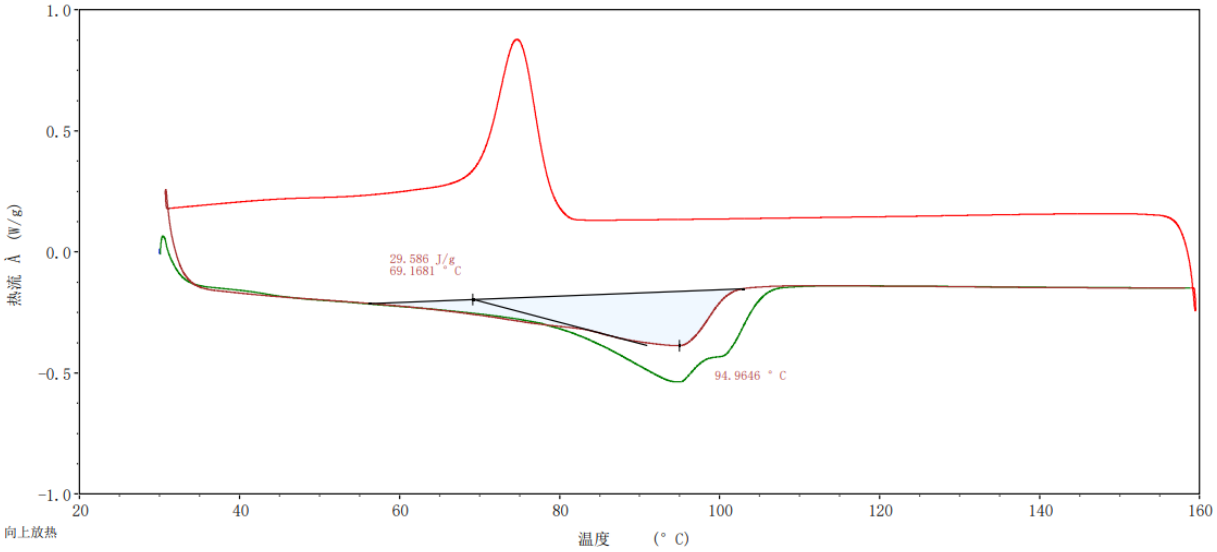
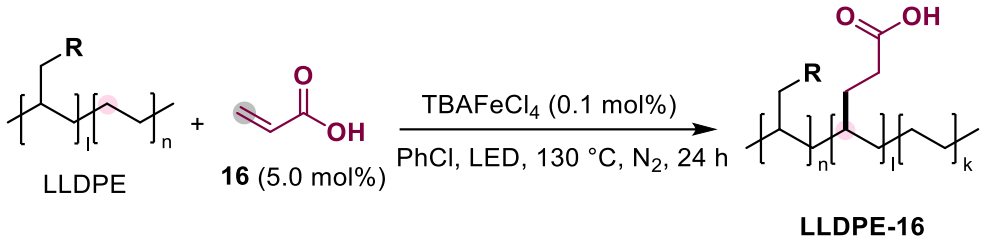


Figure S99. The DSC trace of **LLDPE-9**

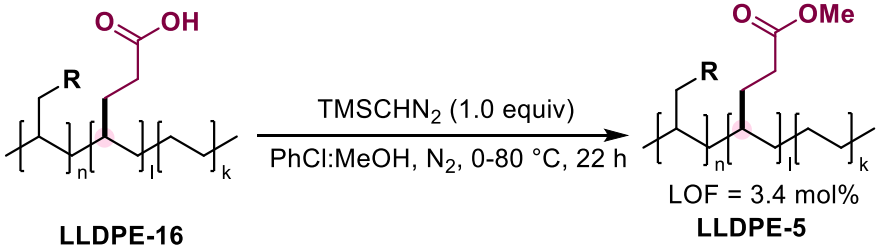
Synthesis of the ionomers

(1) Preparation of ***ion*-LLDPE-9** and ***ion*-LLDPE-15** in gram scale



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.8 mg, 0.1 mmol), LLDPE (2.8025 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **16** (430.0 mg, d = 0.956 g/mL, 450 μL, 5.0 mmol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. After drying under vacuum at 70 °C for 12 hours. The compound **LLDPE-16** was obtained as a white solid.

The level of functionalization (LOF) of compound **LLDPE-16** was not able to be determined due to the low solubility. However, such a LOF could be determined after the methylation with $TMSCHN_2$.



To a 100 mL Schlenk tube were added **LLDPE-16** (57.2 mg, 2.0 mmol), PhCl/MeOH = 10/1 (5.0 mL), and $TMSCHN_2$ (2.0 M, 1.0 mL, 2.0 mmol) were added at 0 ℃. The resulting mixture was warmed to 80 ℃ and stirred for 22 hours under N_2. After MeOH (10 mL) was added to precipitate the product. After filtration, the product was washed with MeOH (5 mL × 3) until the small molecules were removed completely. The compound **LLDPE-16** was obtained as a white solid (59.0 mg, LOF = 3.4 mol%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, **3.00 H**), 2.50-2.25 (m, 1.76 H), 2.12-0.75 (m, **118.54 H**).

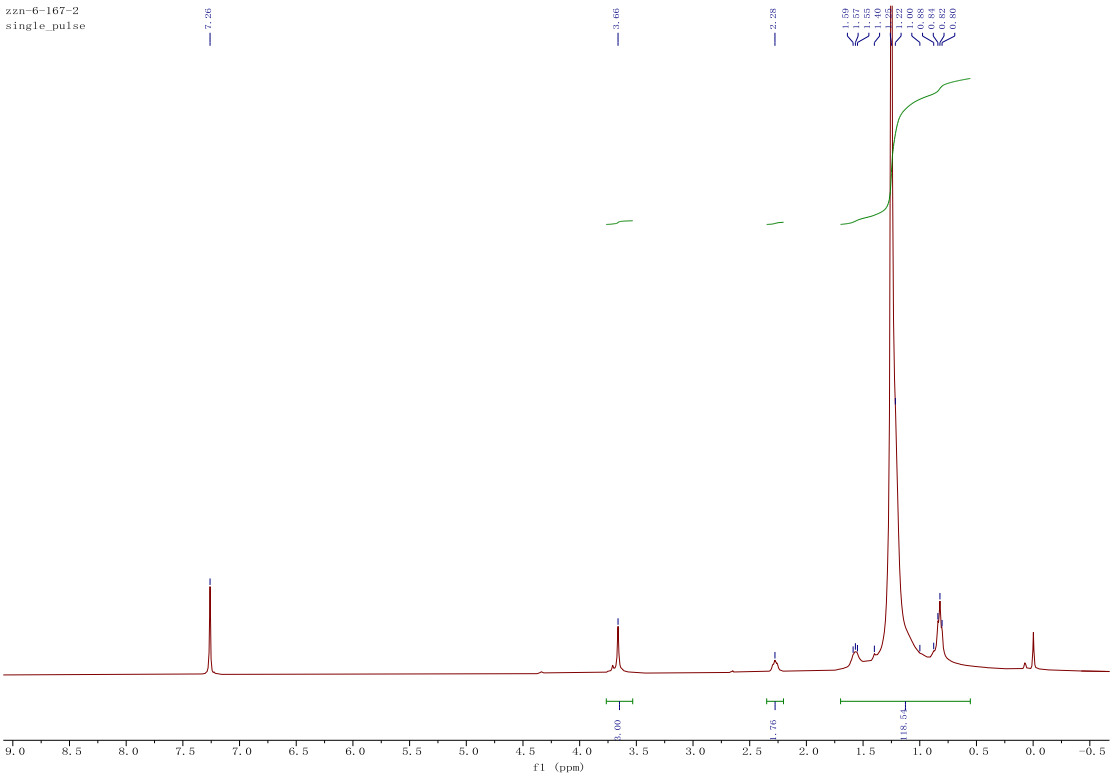
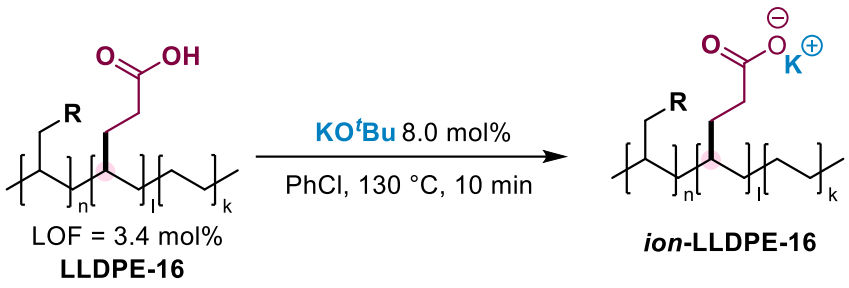
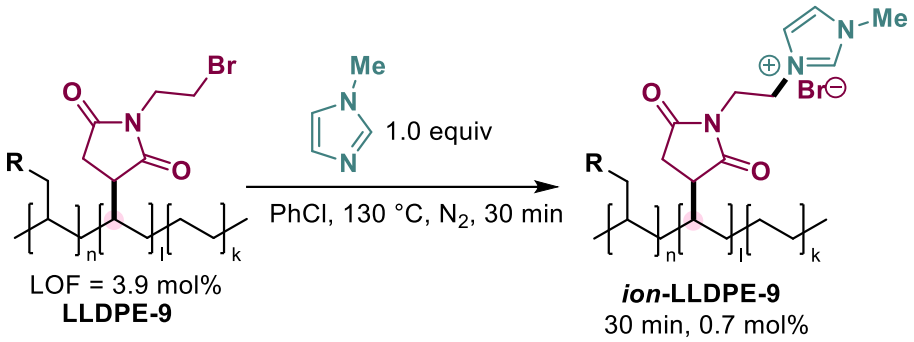


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-16-3.4 mol%**



To a solution of **LLDPE-16** (1.4279 g, about 50.0 mmol) in PhCl (30.0 mL) at 130 °C was added KO^{t}Bu (449.1 mg, 4.0 mmol) under a N_2 atmosphere. The resulting mixture was stirred for 10 min at 130 °C to precipitate a yellow solid. After adding of EtOH (100.0 mL), the product was filtrated and washed with EtOH (50.0 mL × 3) until the small molecules were removed completely. The compound ***ion*-LLDPE-16** was obtained as a yellow solid (1.1529 g).



To a 250 mL Schlenk flask with condenser were added **LLDPE-9** (1.4032 g, about 50.0 mmol), 1-methylimidazole (4.1000 g, *d* = 1.030 g/mL, 4.0 mL, 50.0 mmol), and PhCl (25.0 mL) in an N_2 atmosphere. The resulting mixture was stirred at 130 °C for **30 min**. After adding of acetone (100 mL), the product was precipitated, filtrated, and then washed with acetone (50 mL × 3) until the small molecules were removed completely. The compound ***ion*-LLDPE-9-0.7 mol%** was obtained as a yellow solid (1.4164 g, LOI = 0.7 mol%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.65 (s, **2.00 H**), 4.18-4.12 (m, 4.94 H), 4.12-4.02 (m, 2.27 H), 3.97-3.82 (m, 5.55 H), 3.65-3.53 (m, 5.49 H), 1.68-0.75 (m, **556.73 H**). IR ν (neat, cm^{-1}) 2917, 1773, 1702, 1465, 1398.

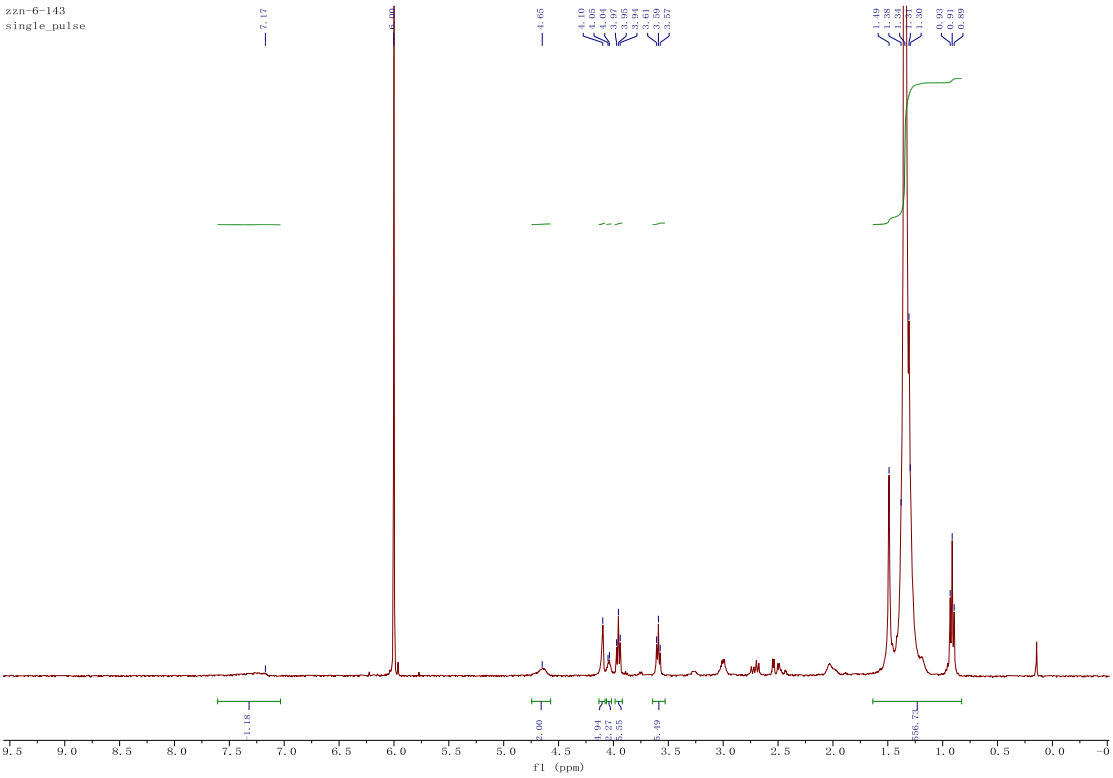
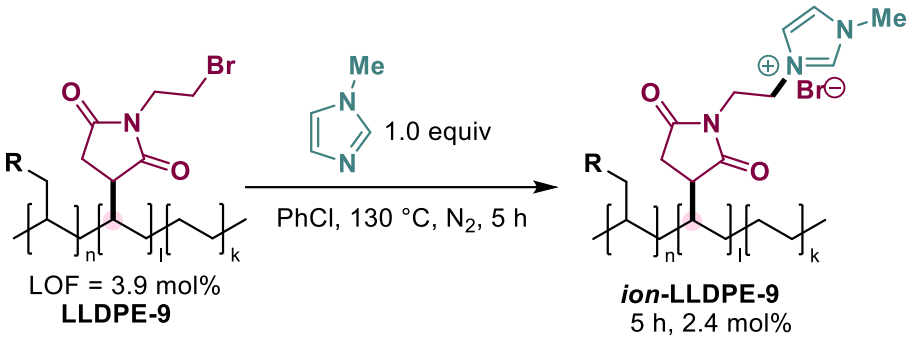


Figure S101. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 110 °C) of ***ion*-LLDPE-9-0.7 mol%**



To a 250 mL Schlenk flask with condenser were added **LLDPE-9** (1.4053 g, about 50.0 mmol), 1-methylimidazole (4.1000 g, *d* = 1.030 g/mL, 4.0 mL, 50.0 mmol), and PhCl (30.0 mL) in an N_2 atmosphere. the resulting mixture was stirred for **5 h** at 130 °C and brown solid was precipitated. After acetone (50 mL) was added to precipitate the product. After filtration, the product was washed with acetone (30 mL × 3) until the small molecules were removed completely. The compound ***ion*-LLDPE-9-2.4 mol%** was obtained as a yellow solid (1.4670 g, LOI = 2.4 mol%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.69 (s, **2.00 H**), 4.25-3.96 (m, 6.05 H), 1.65-0.78 (m, **164.30 H**). IR ν (neat, cm^{-1}) 2917, 1771, 1700, 1465, 1399.

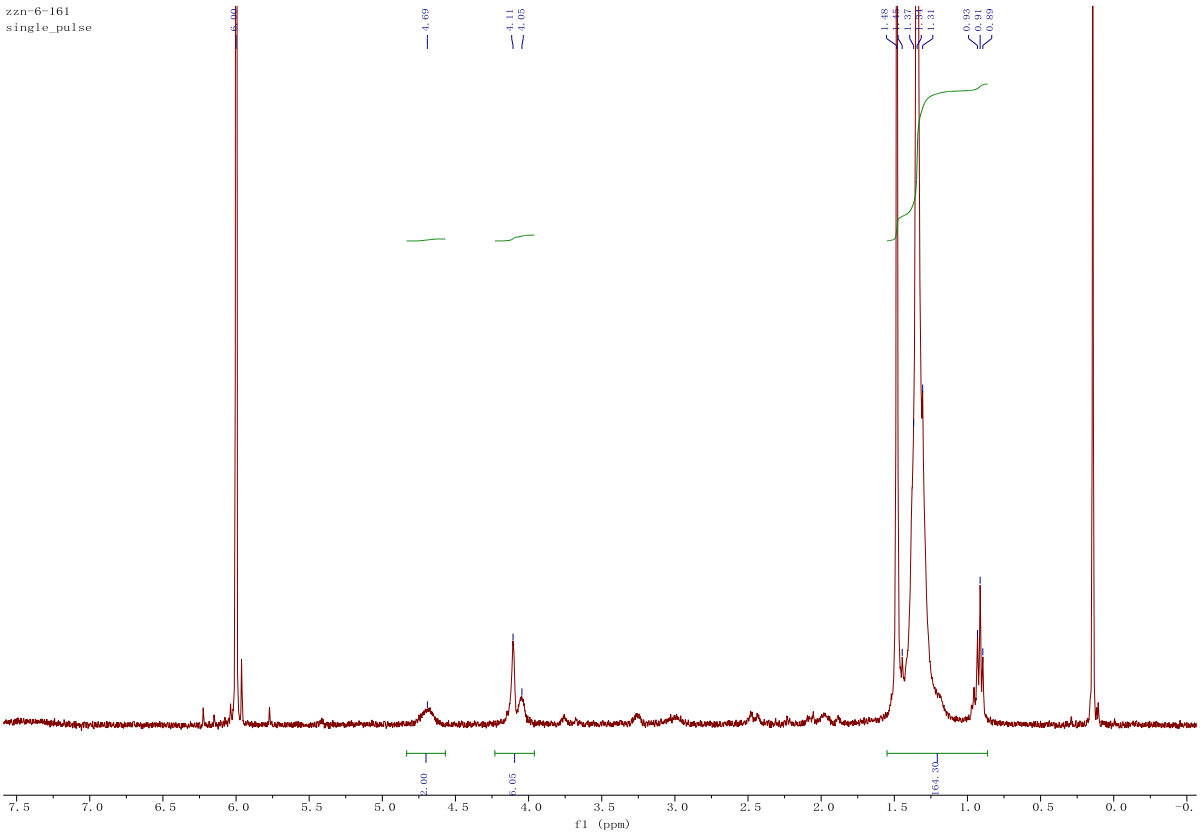


Figure S102. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 110 °C) of ***ion*-LLDPE-9-2.4 mol%**

(2) The clarities of LLDPE and ionized-LLDPEs

Polymer films were prepared by melt pressing using a Manual Compression Press.

LLDPE and ***ion*-LLDPE-9-0.7 mol%** samples were placed between two Kapton films and steel plates to be heated at 120 °C and pressed at 1.0 ± 0.1 MPa for 2 minutes.

***ion*-LLDPE-9-2.4 mol%** samples were placed between two Kapton films and steel plates to be heated at 150 °C and pressed at 5.0 ± 0.1 MPa for 2 minutes.

***ion*-LLDPE-16** samples were placed between two Kapton films and steel plates to be heated at 145 °C and pressed at 4.0 ± 0.1 MPa for 5 minutes.

Ionomers are hygroscopic and demonstrate slow crystallization kinetics, the films were staged for 4-7 days in N_2 glovebox before tensile testing.

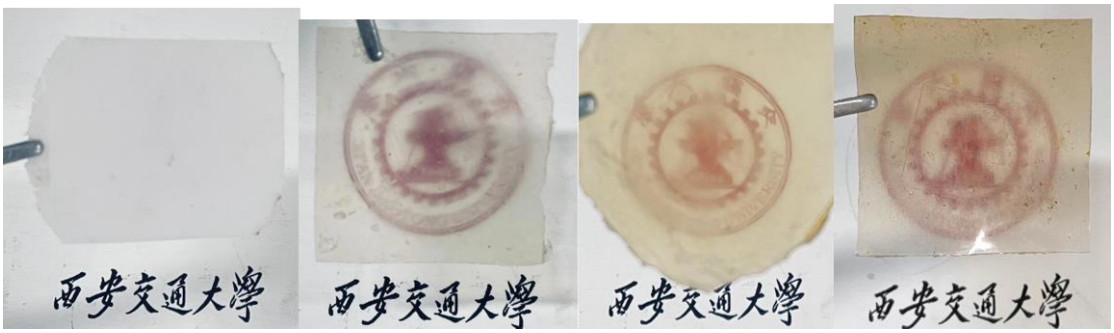
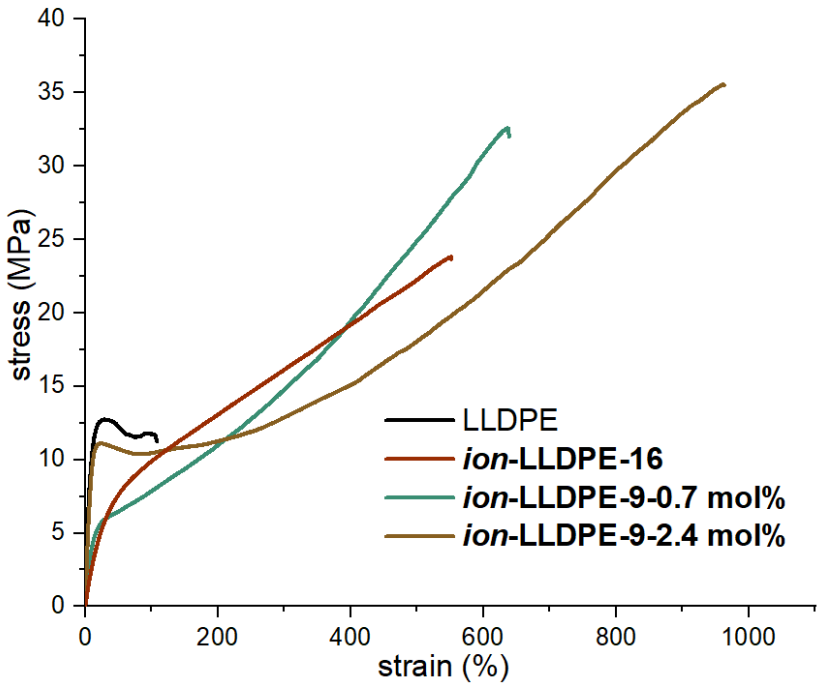


Figure S103. Images of LLDPE, ***ion*-LLDPE-16**, ***ion*-LLDPE-9-0.7 mol%**, and ***ion*-LLDPE-9-2.4 mol%** films. Comparing with LLDPE, the clarity of ionized-LLDPE is enhanced.

(3) Tensile test

Specimens for analysis were cut into dog-bone. Sample thickness at the bridge was measured using calipers. Test specimens were affixed on an CMT-1503 electromechanical tester (SUST Inc., China). Tensile stress and strain were measured at room temperature using an extension rate of 10 mm/min. Measurements were repeated for at least 3 specimens.

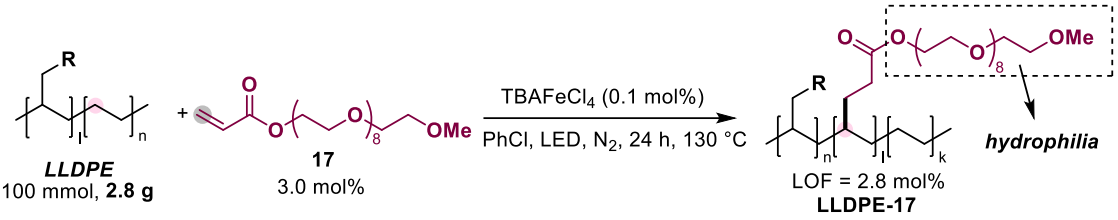
Figure S104. Images of LLDPE, ***ion*-LLDPE-9-0.7 mol%**, ***ion*-LLDPE-9-2.4 mol%**, and ***ion*-LLDPE-16** dog-bones for tensile test.



Entry	Polymers	σ_b (MPa)	ε_b	E (MPa)
1	LLDPE	13 ± 3	135 ± 18%	92 ± 3
2	***ion*-LLDPE-16**	24 ± 2	552 ± 50%	27 ± 1
3	***ion*-LLDPE-9-0.7 mol%**	33 ± 2	639 ± 65%	38 ± 2
4	***ion*-LLDPE-9-2.4 mol%**	36 ± 2	963± 110%	93 ± 5

Table S5. Tensile test data of LLDPE, ***ion*-LLDPE-9-0.7 mol%**, ***ion*-LLDPE-9-2.4 mol%**, and ***ion*-LLDPE-16**

Contact angles of LLDPE and LLDPE-17



To a 100 mL sealed tube were added $TBAFeCl_4$ (44.1 mg, 0.1 mmol), LLDPE (2.8003 g, 100.0 mmol, M_n = 68110 g/mol, M_w = 229639 g/mol, $Đ$ = 3.37), **17** (1.4001g, 3.0 mmol, M_n = 480 g/mol), and PhCl (40.0 mL) in an N_2 glovebox. The tube was then sealed and transferred out of the glovebox. Under irradiation at 390 nm LEDs, the resulting mixture was stirred for 24 hours at 130 °C. After EtOH (100 mL) was added to precipitate the product. After filtration, the product was washed with EtOH (50 mL × 3) until the small molecules were removed completely. The compound **LLDPE-17** was obtained as a yellow solid (3.6738 g, LOF = 2.8 mol%). The level of functionalization was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.25 (m, **40.0 H**), 1.82-0.74 (m, **139.37 H**). The ^{13}C NMR (151 MHz, $CDCl_3$) spectrum is very complicated, which is attached in the spectra part directly. **IR ν (neat, cm^{-1})** 2916, 1737, 1464, 1251, 1107.

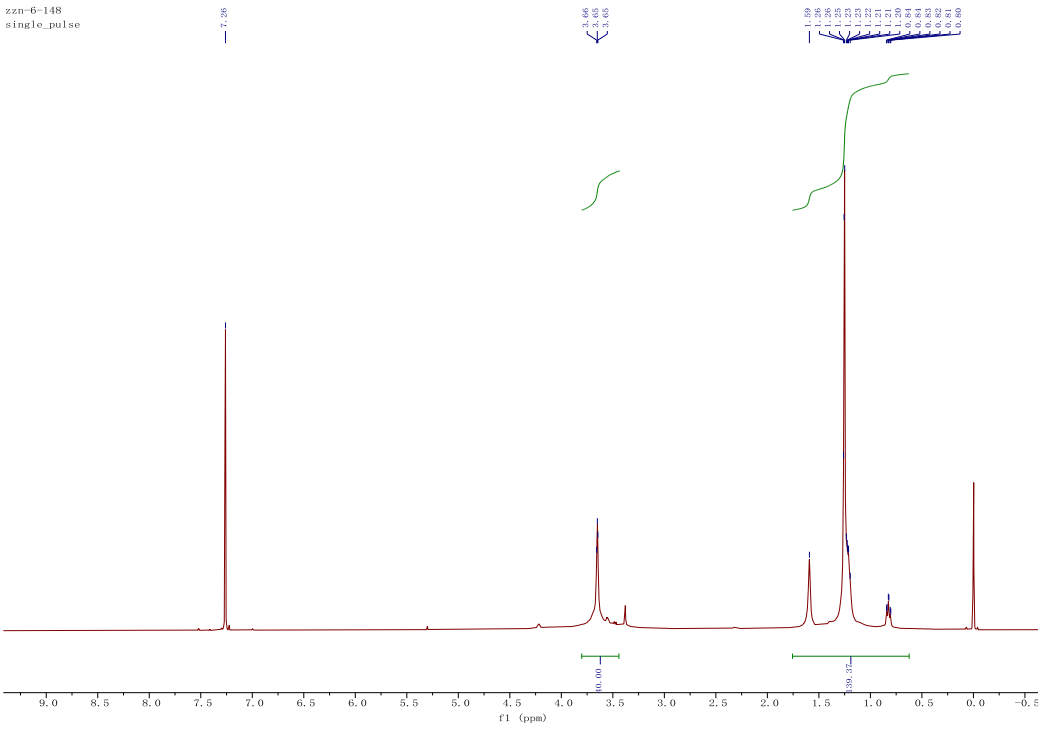


Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$) of **LLDPE-17**

^{13}C NMR (151 MHz, $CDCl_3$) of **LLDPE-17**

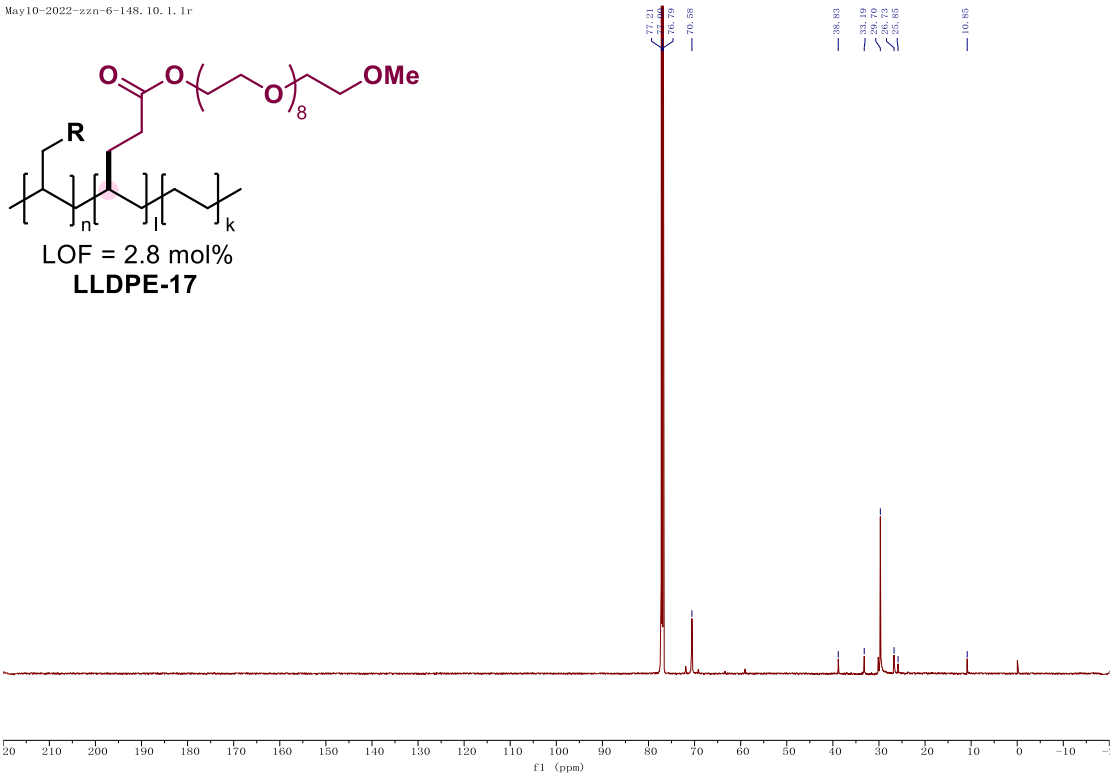


Figure S106. ^{13}C NMR (151 MHz, $CDCl_3$) of **LLDPE-17**

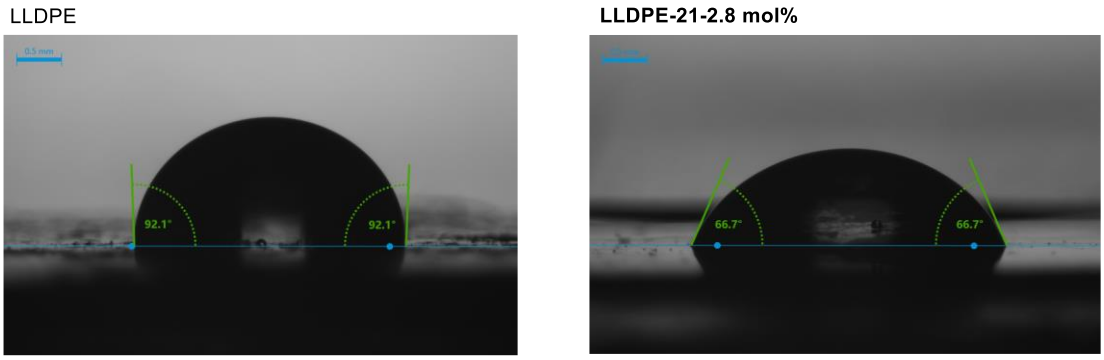


Figure S107. Polymer films from LLDPE and **LLDPE-17-2.8 mol%** were prepared by hot pressing. Static water contact angles were measured with deionized water by KRUSS DSA100.

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