

Supporting Information

On-demand degradable and acid generating polymers using phenacyl ester derivatives

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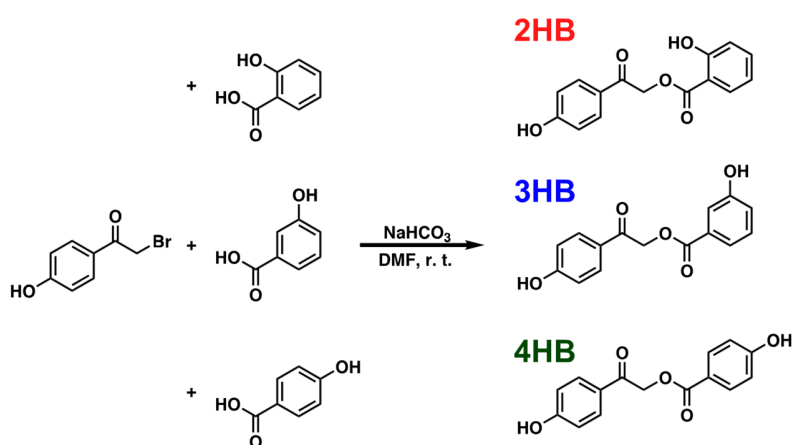
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1. Synthesis and characterization of xHB small molecules

1.1 Synthesis of phenacyl ester regioisomers

2-Bromo-4'-hydroxyacetophenone (1.6 g, 7.4 mmol, 1.0 equiv.) was dissolved in 10 ml of DMF, followed by adding sodium bicarbonate (0.688 g, 8.2 mmol, 1.1 equiv.) to the solution. After stirring for 30 minutes, hydroxybenzoic acid (1.02 g, 7.4 mmol, 1.0 equiv.) was added and further stirred for 3 hours. The reaction mixture was precipitated in 200 ml of deionized water and collected by filtering. The precipitates were vacuum dried for more than 24 hours to yield as a white solid.



Scheme S1. Synthesis of dihydroxy phenacyl ester regio-isomers (**xHBs**).

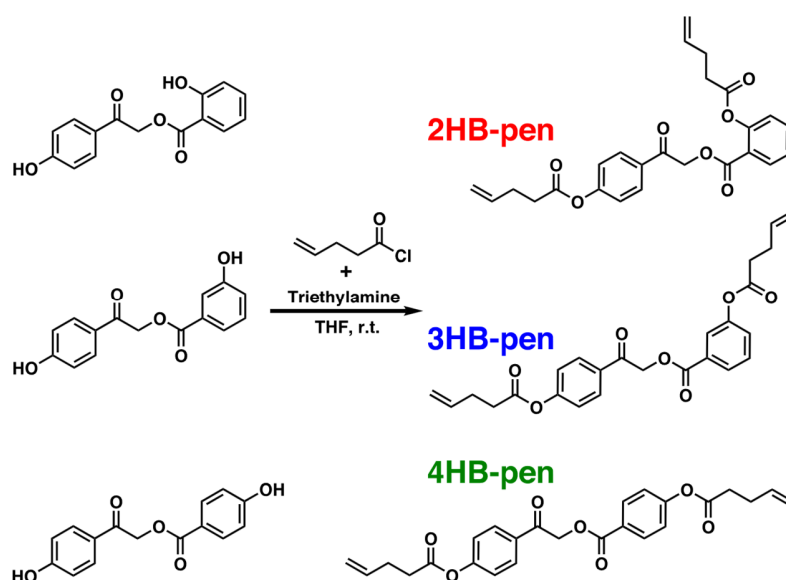
2-(4-hydroxyphenyl)-2-oxoethyl 2-hydroxybenzoate (2HB): Yield 96%. ¹H NMR (400 MHz, DMSO-d₆) δ 10.39 (s, 2H), 7.99 – 7.85 (m, 3H), 7.65 – 7.53 (m, 1H), 7.12 – 6.97 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.71 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 190.70, 168.47, 163.42, 160.62, 136.39, 130.94, 130.77, 125.67, 119.98, 118.00, 116.05, 113.23, 67.43.

2-(4-hydroxyphenyl)-2-oxoethyl 3-hydroxybenzoate (3HB): Yield 72%. ¹H NMR (400 MHz, DMSO-d₆) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 191.09, 165.81, 163.22, 158.04, 131.02, 130.85, 130.37, 125.93, 121.07, 120.54, 116.28, 116.00, 67.09.

2-(4-hydroxyphenyl)-2-oxoethyl 4-hydroxybenzoate (4HB): Yield 80%. ¹H NMR (400 MHz, DMSO) δ 10.49 (s, 2H), 7.95 – 7.82 (m, 4H), 6.89 (dd, *J* = 8.8, 0.9 Hz, 4H), 5.56 (s, 2H). ¹³C (101 MHz, DMSO) δ 191.41, 165.56, 163.10, 162.67, 132.16, 130.82, 126.02, 120.39, 115.95, 115.89, 66.69.

1.2 Synthesis of bis-alkene functionalized HBs (**xHB-pen**)

xHB (200 mg, 0.73 mmol, 1.0 equiv.) and triethylamine (0.254 mL, 1.83 mmol, 2.5 equiv.) were dissolved in 5 ml of THF. After the solution was cooled to 0 °C, 4-pentenoyl chloride (0.185 mL, 1.68 mmol, 2.3 equiv.) was added dropwise and stirred for 6 hours at room temperature. The reaction mixture was filtered to remove salts and the residual solvent was completely removed. The crude product was re-dissolved in CH₂Cl₂, washed with NH₄Cl solution, brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting solid was purified by column chromatography (25% EtOAc:Hex) to yield as a white solid.



Scheme S2. Synthesis of bis-alkene functionalized **xHBs**

2-oxo-2-(4-(pent-4-enoyloxy)phenyl)ethyl 2-(pent-4-enoyloxy)benzoate (2HB-pen) : Yield 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 5.93 (td, *J* = 16.1, 6.8 Hz, 2H), 5.52 (s, 2H), 5.23 – 5.02 (m, 4H), 2.80 – 2.69 (m, 4H), 2.54 (p, *J* = 7.0 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 190.55, 171.67, 170.85, 163.77, 155.02, 150.93, 136.64, 136.05, 134.24, 132.06, 131.77, 129.51, 126.07, 123.91, 122.64, 122.21, 116.19, 115.65, 66.29, 33.64, 33.42, 28.75, 28.55.

2-oxo-2-(4-(pent-4-enoyloxy)phenyl)ethyl 3-(pent-4-enoyloxy)benzoate (3HB-pen): Yield

55%. ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 7.99 (m, 3H), 7.90 – 7.84 (m, 1H), 7.51 (t, $J = 7.9$ Hz, 1H), 7.36 (ddd, $J = 8.1, 2.4, 1.0$ Hz, 1H), 7.28 – 7.23 (m, 2H), 5.93 (ddtd, $J = 16.8, 10.2, 6.4, 1.3$ Hz, 2H), 5.57 (s, 2H), 5.23 – 5.08 (m, 4H), 2.72 (td, $J = 7.2, 5.2$ Hz, 4H), 2.54 (q, $J = 6.8$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.65, 171.27, 170.85, 165.11, 155.03, 150.71, 136.19, 136.05, 131.76, 130.86, 130.26, 129.54, 129.51, 127.40, 126.83, 123.21, 122.21, 122.17, 116.19, 116.09, 66.49, 33.64, 33.58, 28.81, 28.75.

2-oxo-2-(4-(pent-4-enoyloxy)phenyl)ethyl 4-(pent-4-enoyloxy)benzoate (4HB-pen): Yield 35%. ^1H NMR (400 MHz, CDCl_3) δ 8.22 – 8.17 (m, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.28 – 7.20 (m, 4H), 5.99 – 5.87 (m, 2H), 5.57 (s, 2H), 5.22 – 5.09 (m, 4H), 2.73 (td, $J = 7.3, 2.5$ Hz, 4H), 2.55 (q, $J = 7.0$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.84, 170.93, 170.86, 165.23, 155.01, 154.75, 136.12, 136.05, 131.79, 131.61, 129.51, 126.86, 122.20, 121.74, 116.18, 116.13, 77.24, 66.41, 33.66, 33.64, 28.78, 28.75.

1.3 Molar extinction coefficients (ϵ) of xHBs

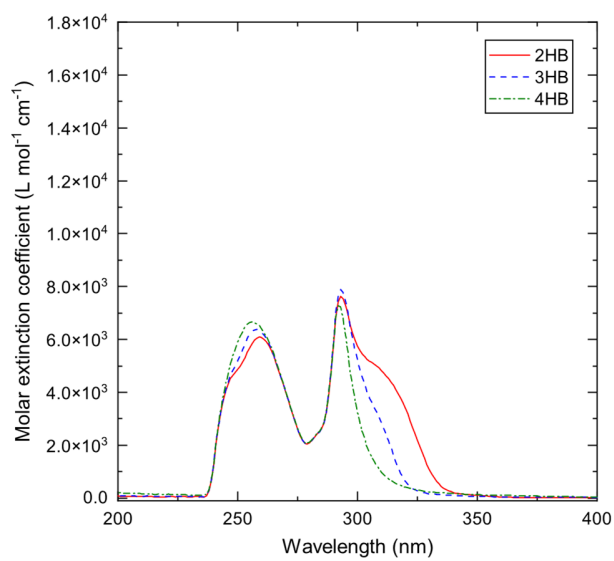


Figure S1. Molar extinction coefficients of **2HB** (red, solid), **3HB** (blue, dash), and **4HB** (green, dash dot).

1.4 UV degradation tests of small molecules

Each regio-isomer of phenacyl ester was dissolved in isopropanol (IPA) with an internal standard (3,5-bis(trifluoromethyl)benzoic acid) with concentrations of 50 mM and 20 mM, respectively. HB-incorporated linear polymers were dissolved in a THF/IPA (4:1 v/v) mixture at a concentration of 12 mg mL⁻¹. A mercury lamp was used as the UV light source and the samples were exposed to UV light through a bandpass filter of 312 nm (**Figure S1**). The average intensity of the UV light is around 4.3 mW cm⁻².

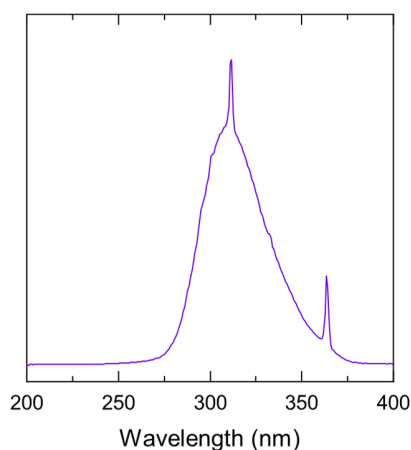


Figure S2. The spectrum of the mercury UV lamp used for UV degradation.

1.5 UV degradation of xHBs

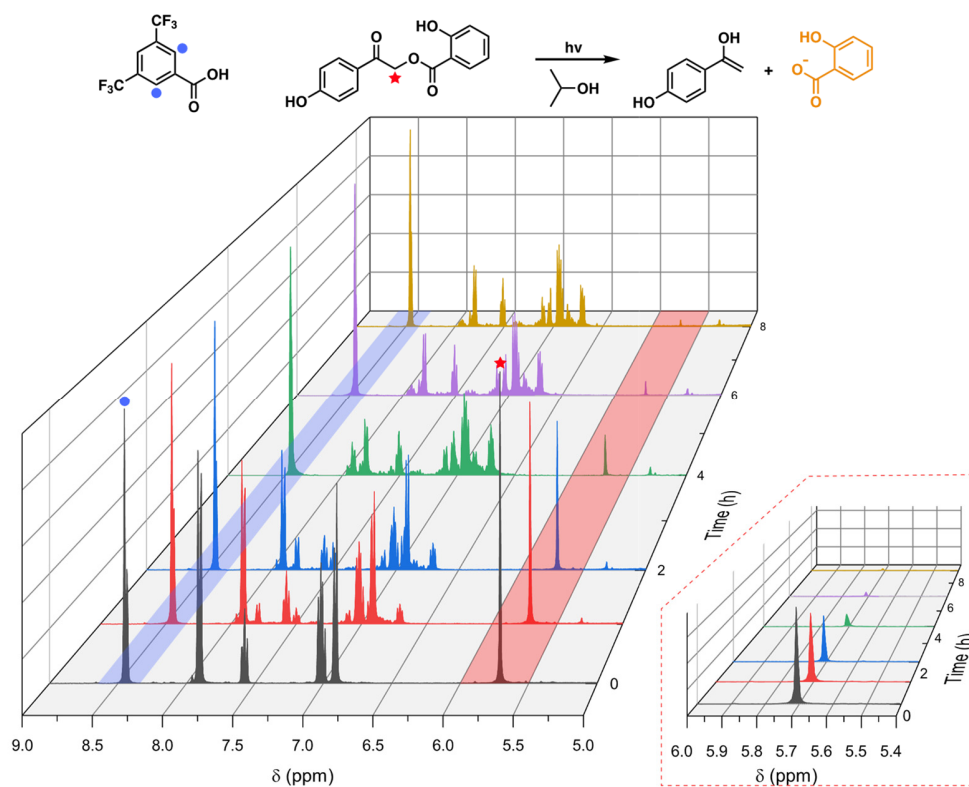


Figure S3. UV degradation of 2HB.

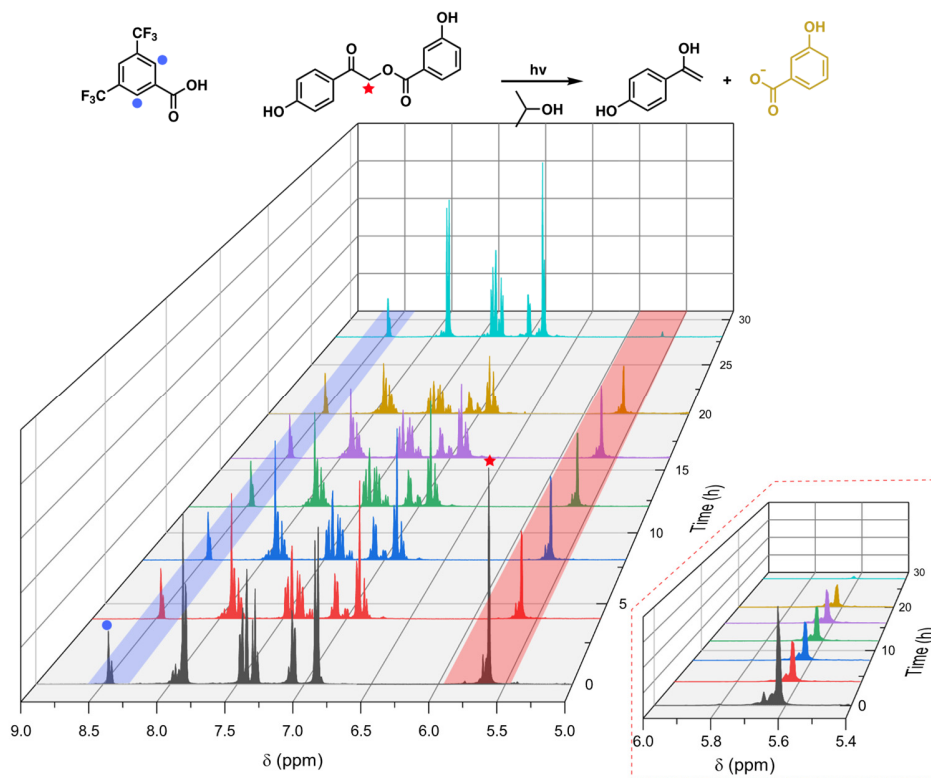


Figure S4. UV degradation of 3HB.

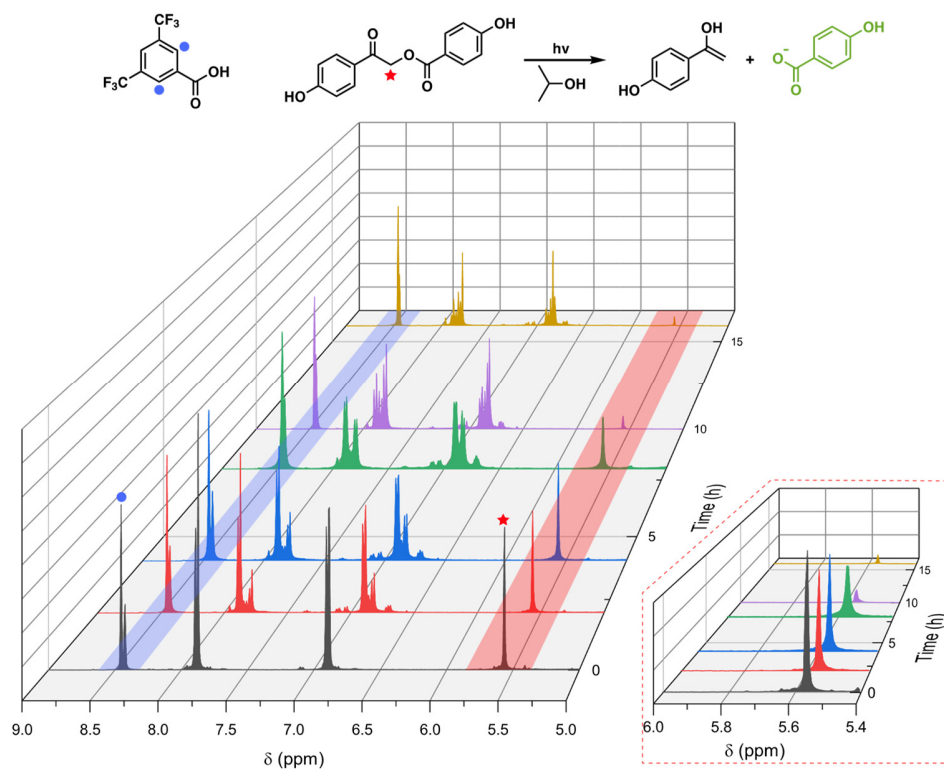


Figure S5. UV degradation of 4HB.

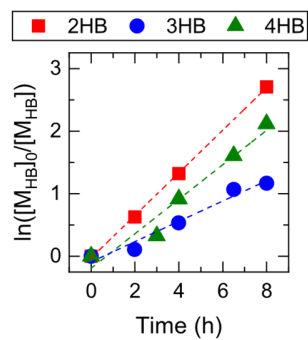


Figure S6. The average degradation rate constant (k) for 2HB, 3HB, and 4HB in a THF/IPA (4/1 v/v) mixture. Error bars represent one standard deviation of the data.

1.6 Acid generation of **xHBs** after UV decomposition

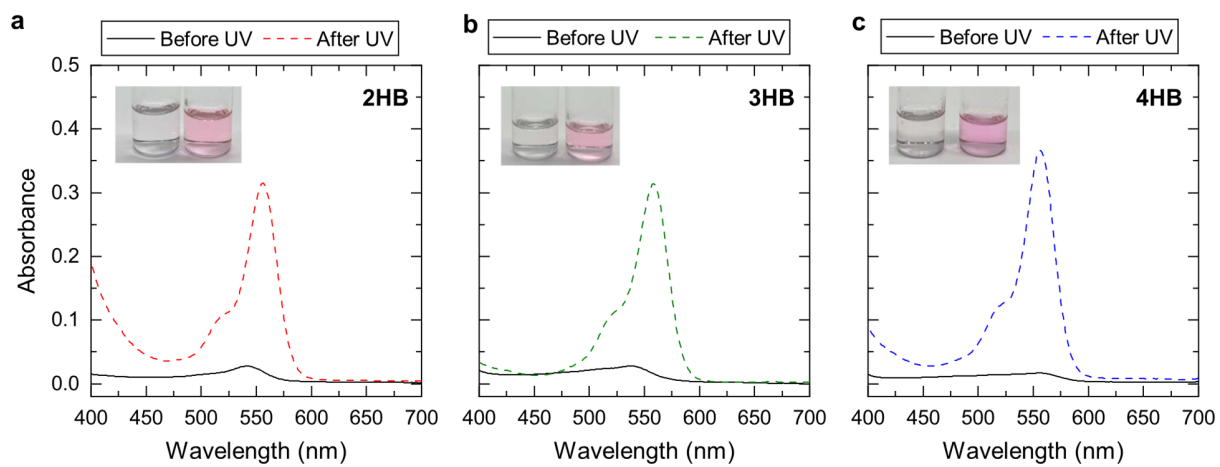


Figure S7. The change in absorbance before and after UV exposure for (a) **2HB**, (b) **3HB**, and (c) **4HB**.

2. Simulation models

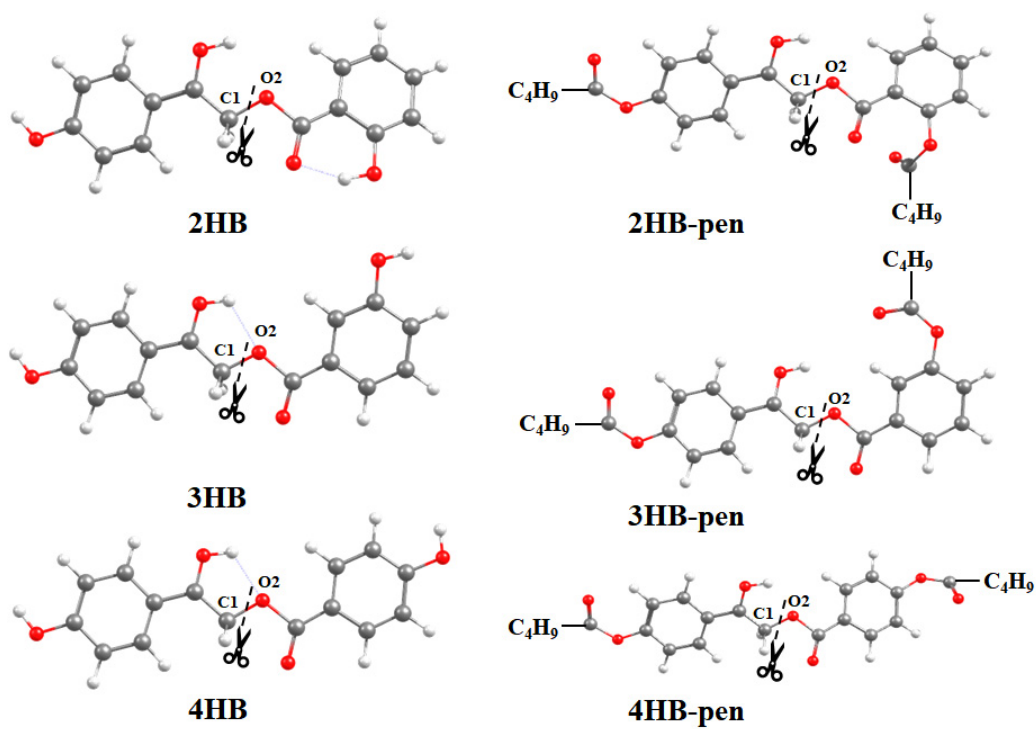


Figure S8. Optimized structures of xHB and xHB-pen series in the radical form.

3. Characterization of xHB-incorporated copolymer (P-xHB) and control sample

3.1 NMR spectra and GPC results of P-xHBs

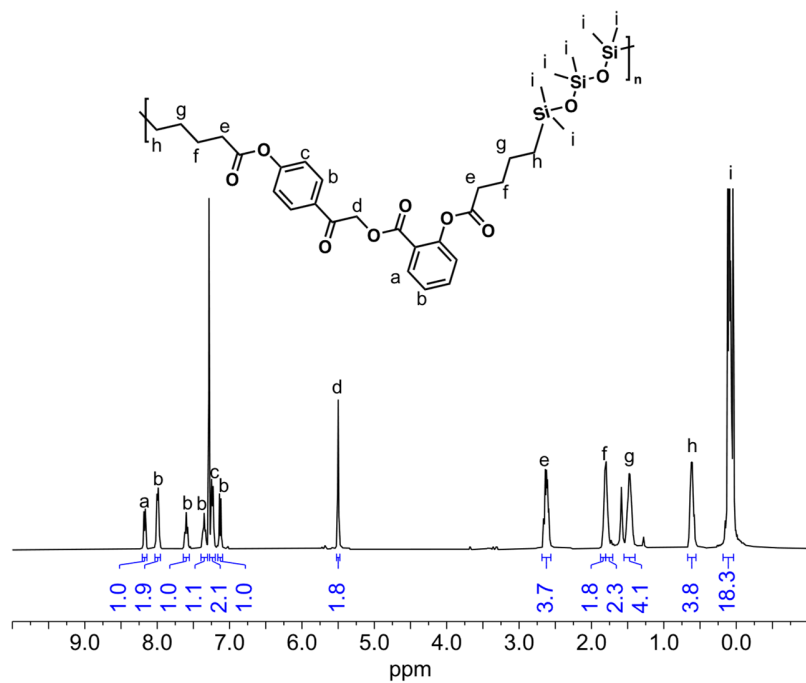


Figure S9. NMR spectrum of P-2HB.

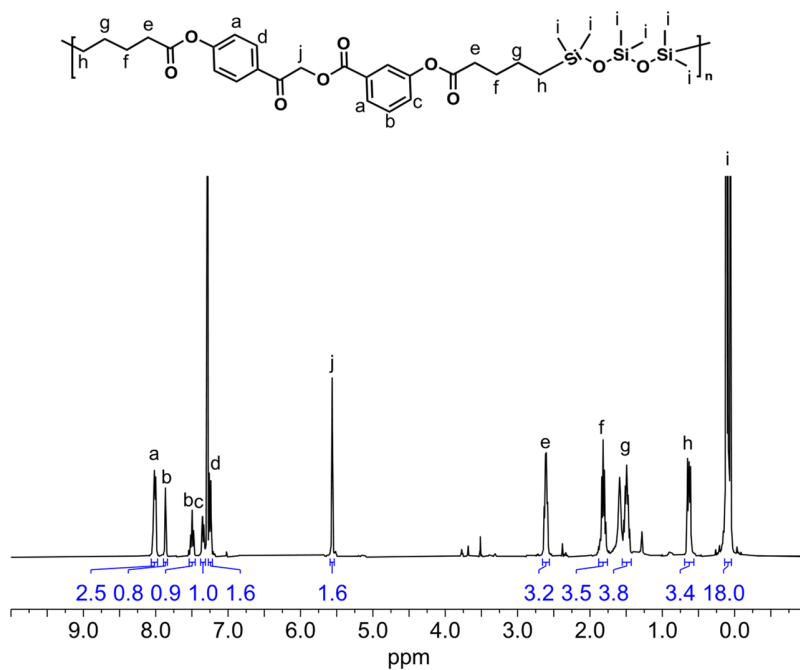


Figure S10. NMR spectrum of P-3HB.

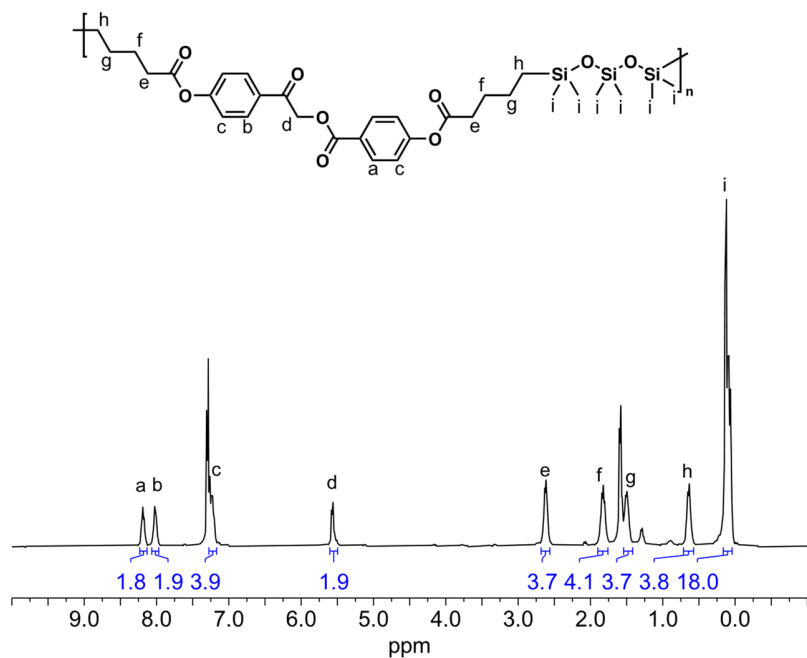


Figure S11. NMR spectrum of P-4HB.

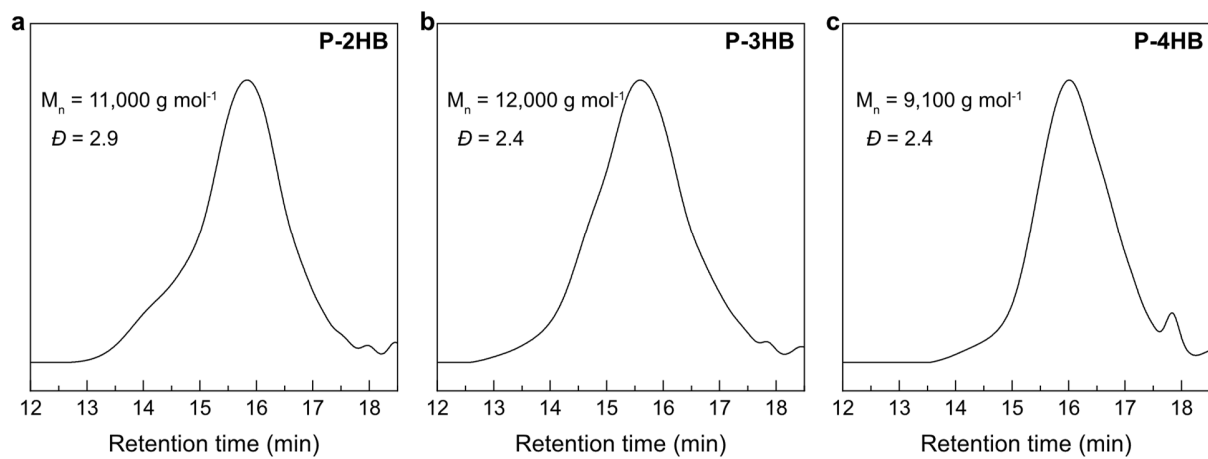


Figure S12. GPC results of P-xHBs.

3.2 UV degradation of P-xHBs

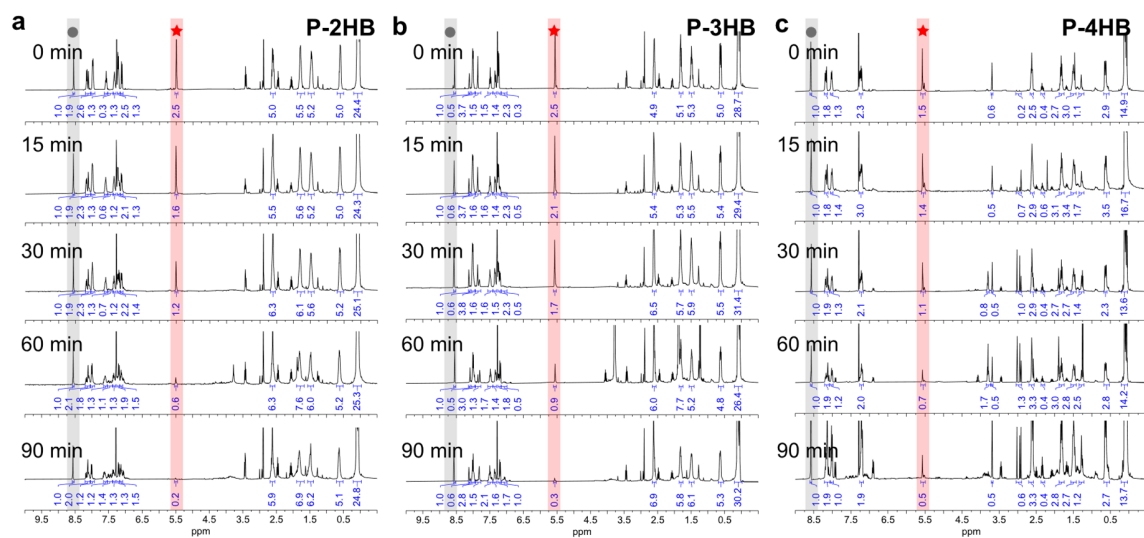


Figure S13. NMR spectra of HB-incorporated linear polymers with different UV exposure time. (a) P-2HB, (b) P-3HB, and (c) P-4HB.

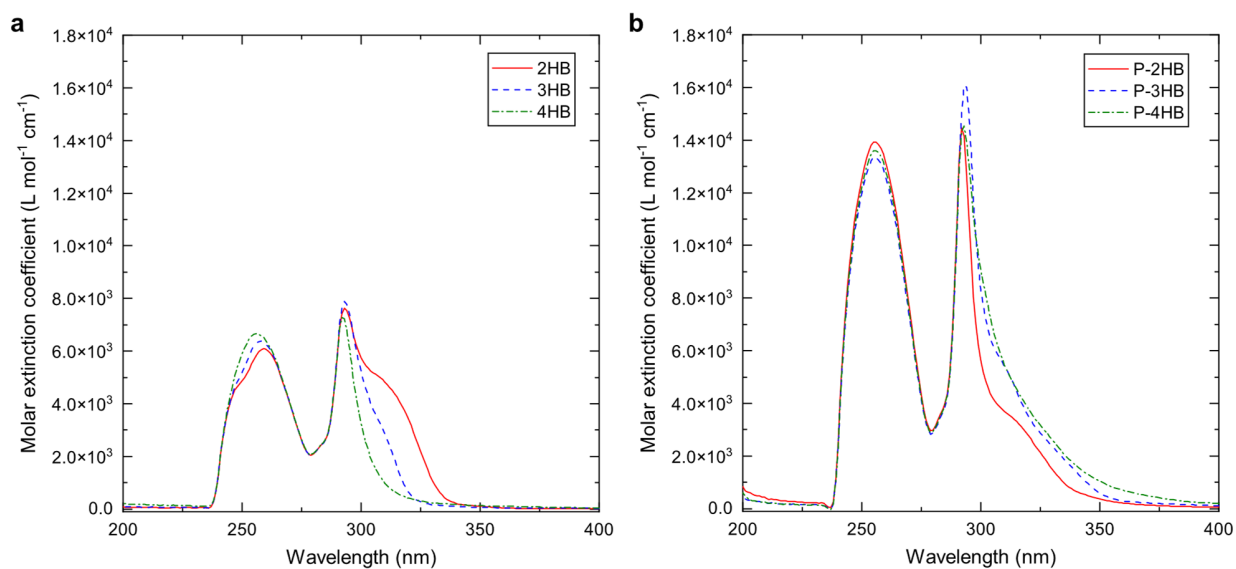


Figure S14. Molar extinction coefficients of (a) xHBs and (b) P-xHBs.

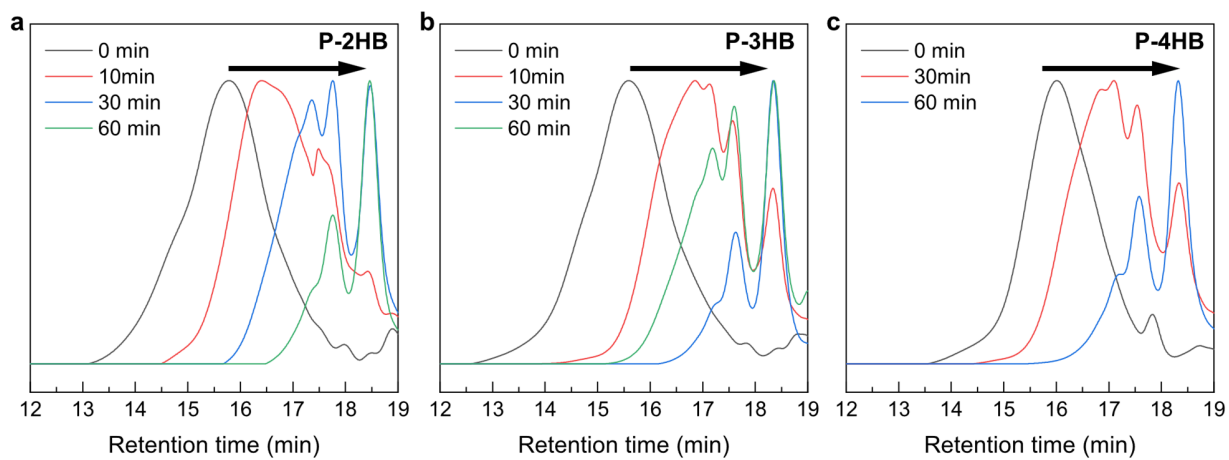


Figure S15. The change in molecular weight with UV exposure time for (a) **P-2HB**, (b) **P-3HB**, and (c) **P-4HB**.

3.3 Control samples

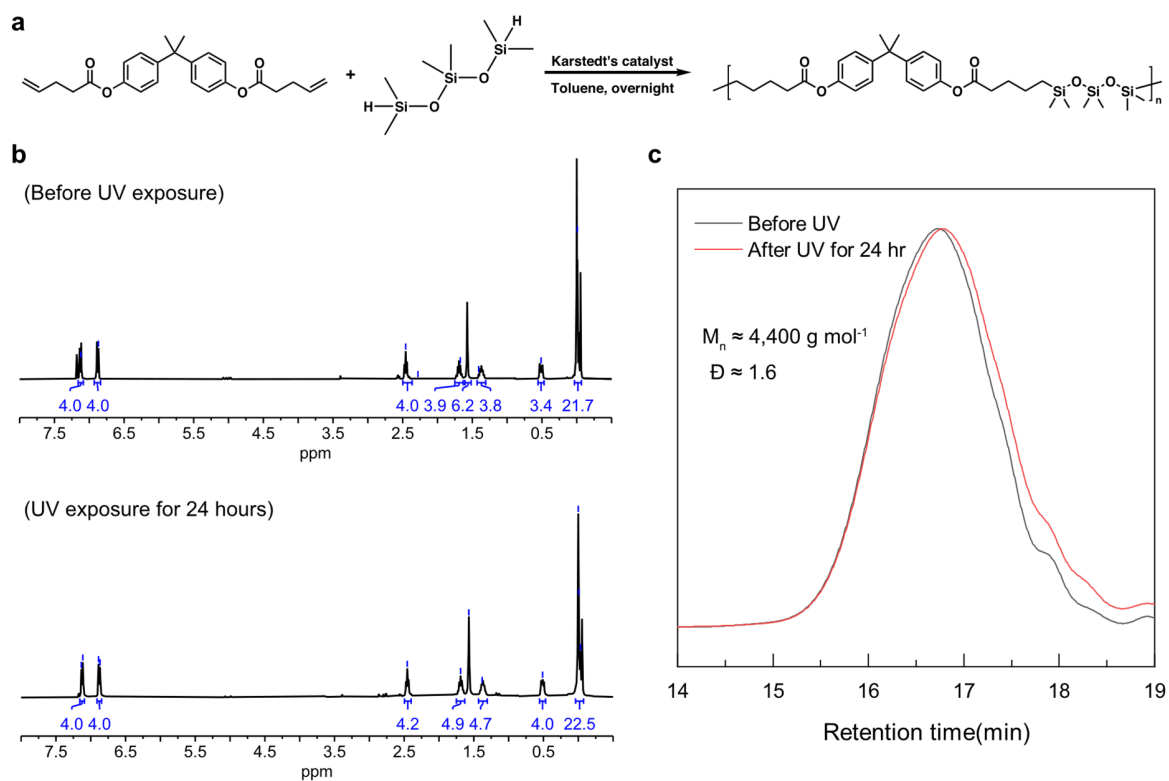


Figure S16. (a) Synthetic scheme of bisphenol A incorporated polymers, (b) their NMR spectra, and (c) the change in their molecular weights before and after UV exposure.

3.4 Acid generation of P-3HB and P-4HB after UV decomposition

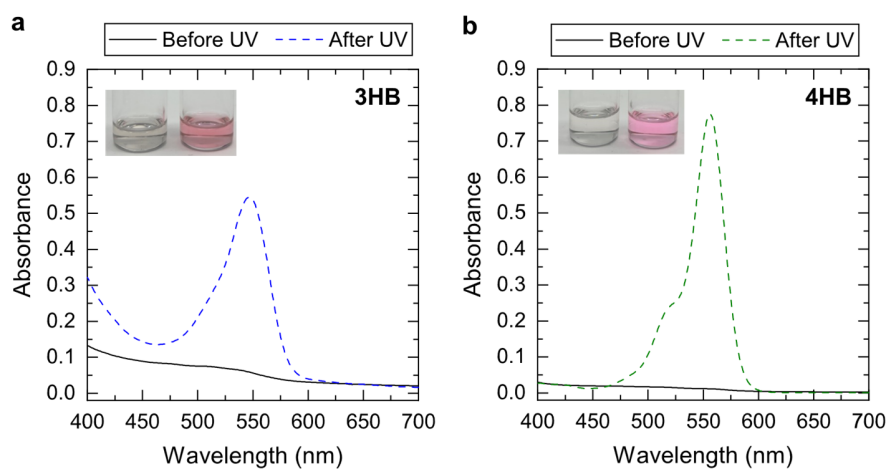
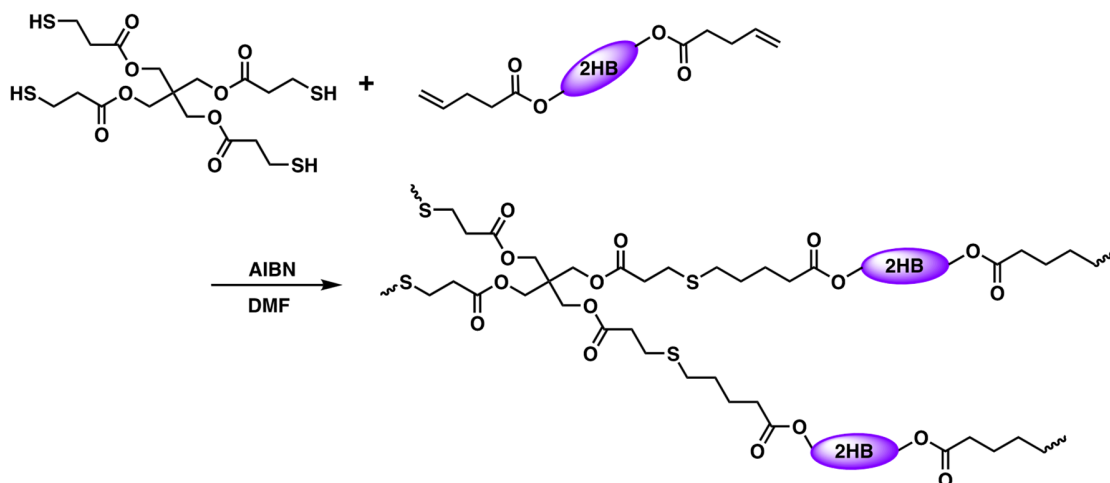


Figure S17. The change in absorbance before and after UV exposure for (a) P-3HB and (b) P-4HB.

4. 2HB-incorporated cross-linked polymers and composites

4.1 Synthetic scheme



Scheme S3. Synthesis of **2HB**-incorporated crosslinked polymer.

4.2 Weight change of CF and CFRP composites under UV exposure

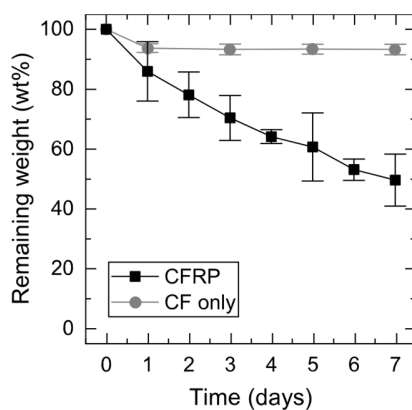


Figure S18. Remaining weights of pristine CF (gray circle) and **2HB-pen** incorporated CFRP composites (black square) with UV exposed time

4.3 Tensile properties of pristine and recycled CFRPs

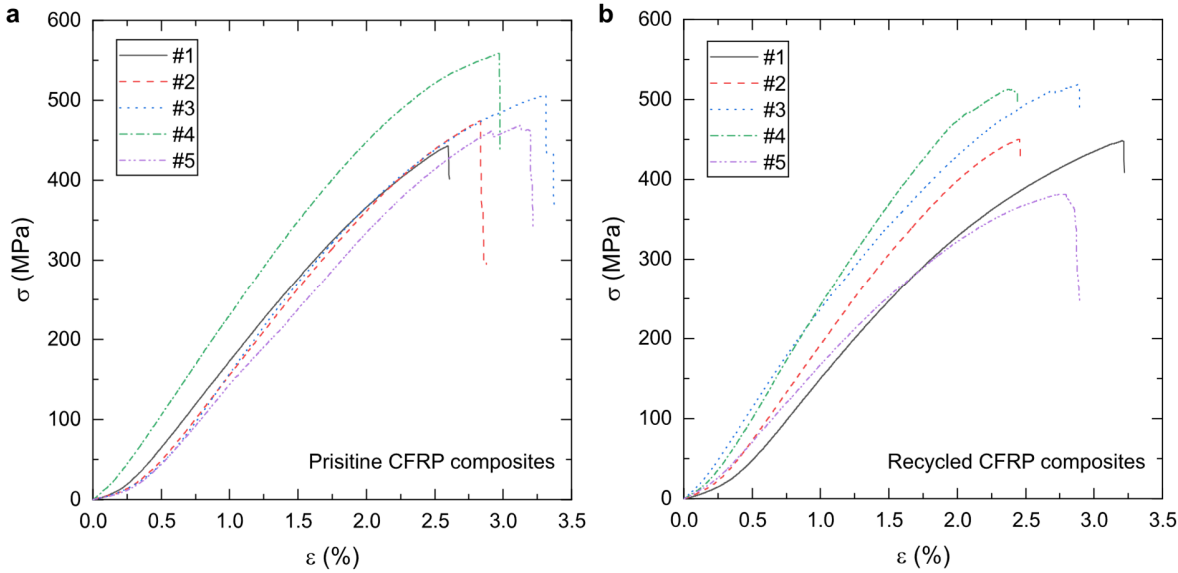
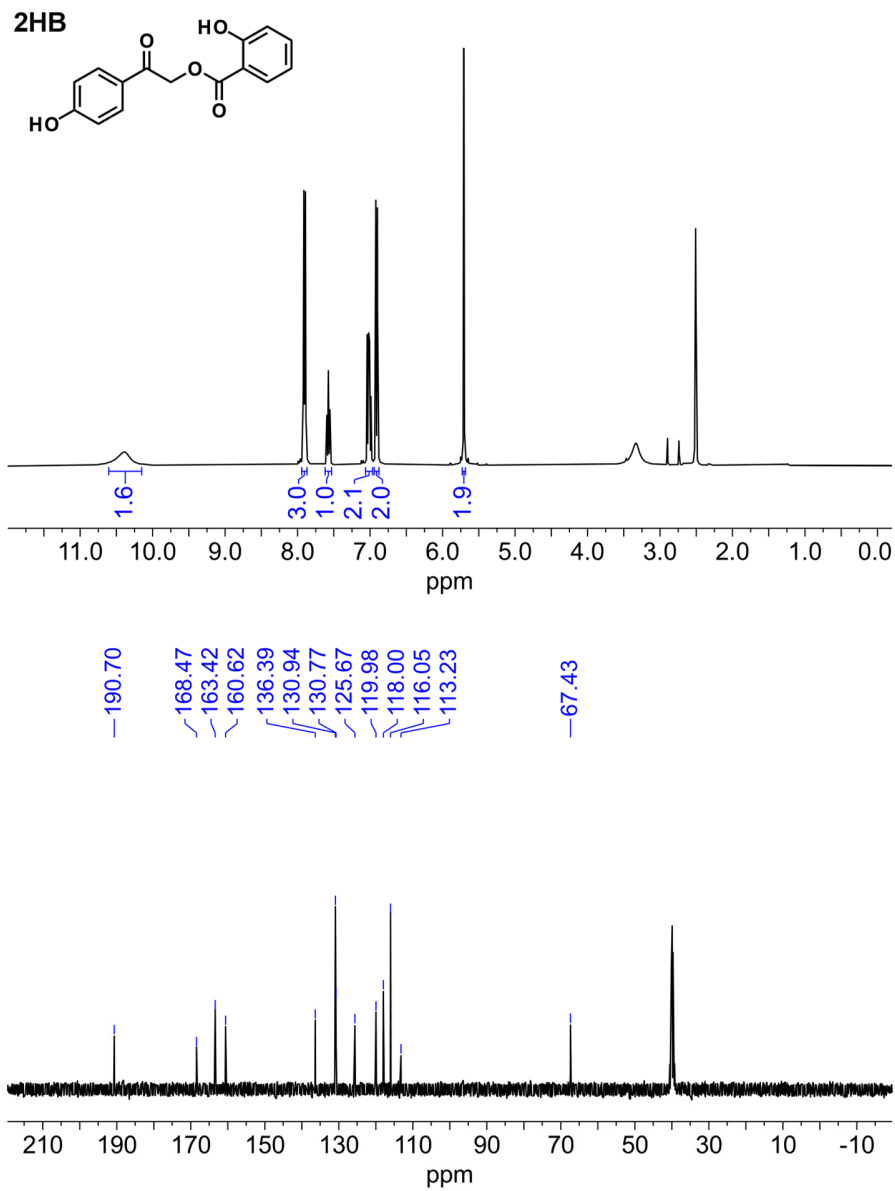
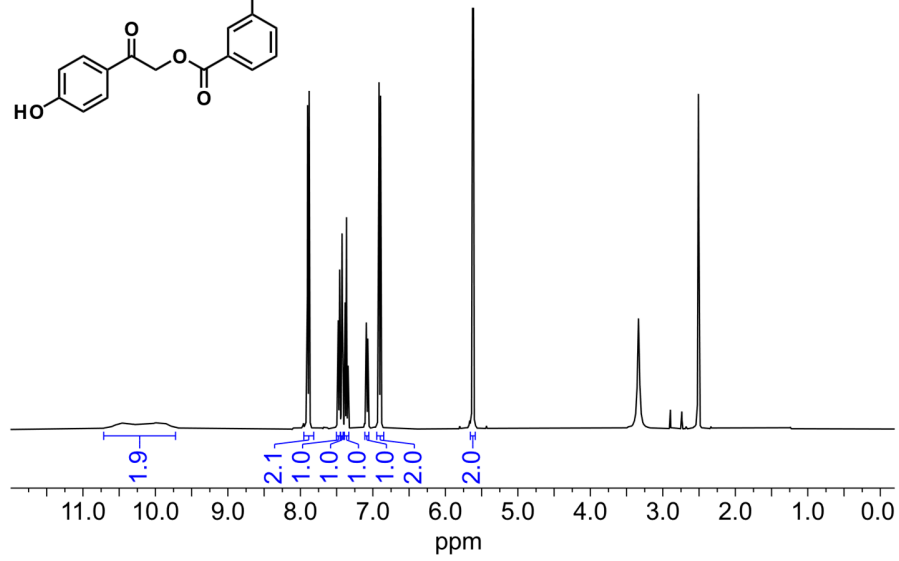
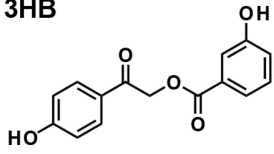


Figure S19. Engineering stress (σ) and strain (ϵ) curved for pristine (a) and recycled CFRP composites.

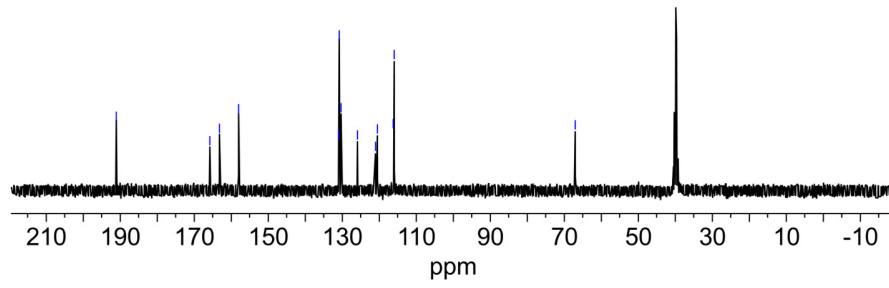
5. ^1H , ^{13}C spectra of small molecules

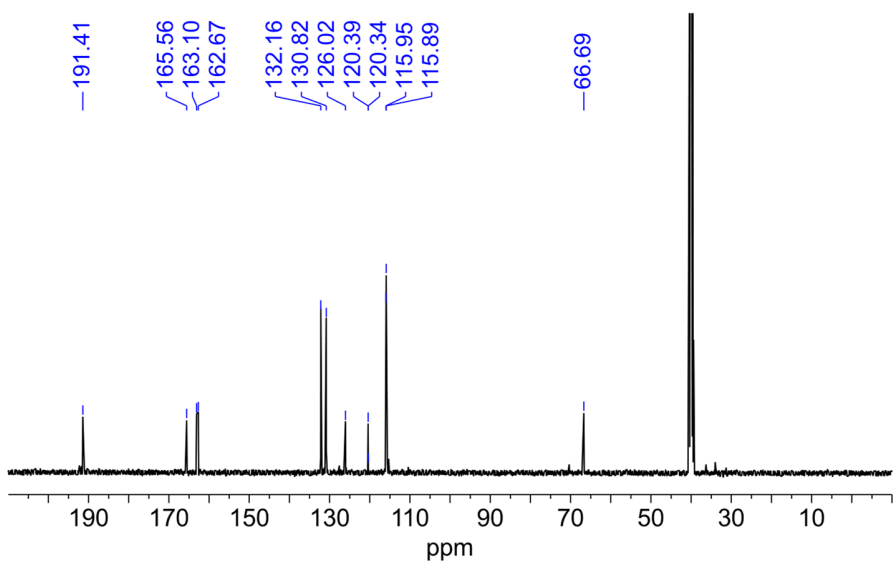
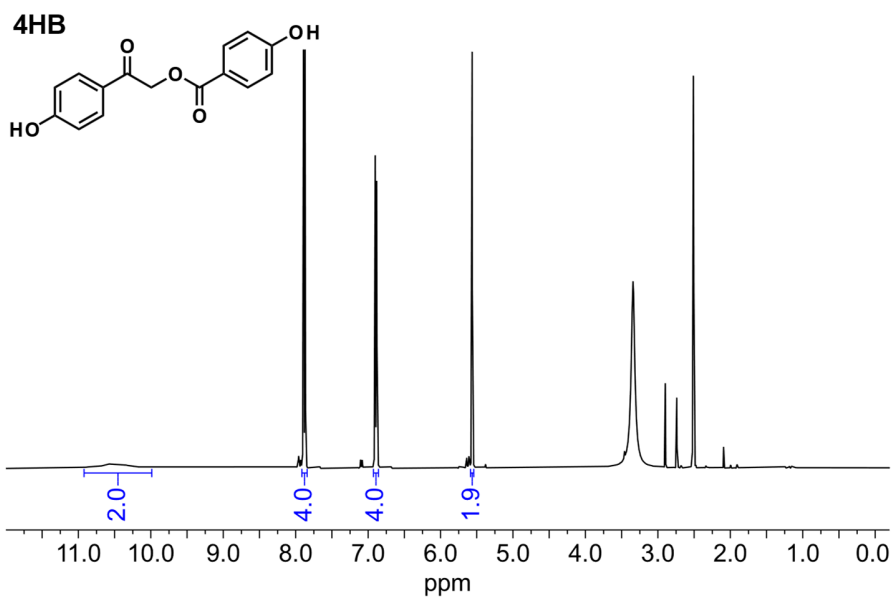


3HB

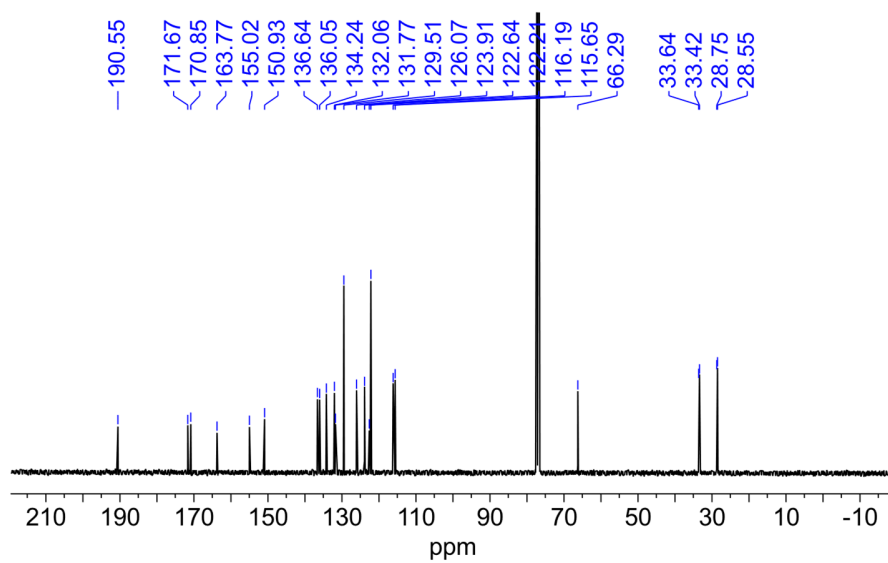
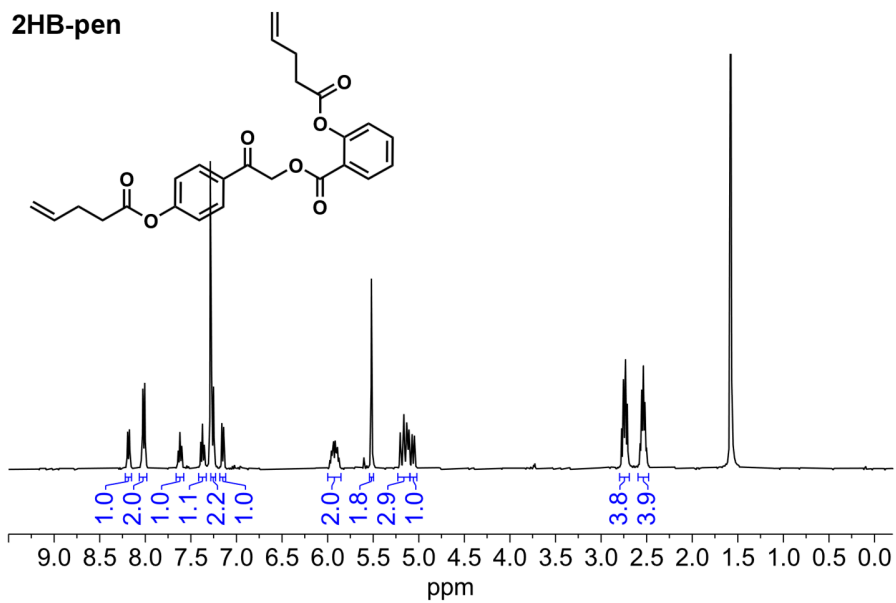


191.09
165.81
163.22
158.04
131.02
130.85
130.37
125.93
121.07
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116.28
116.00
67.09

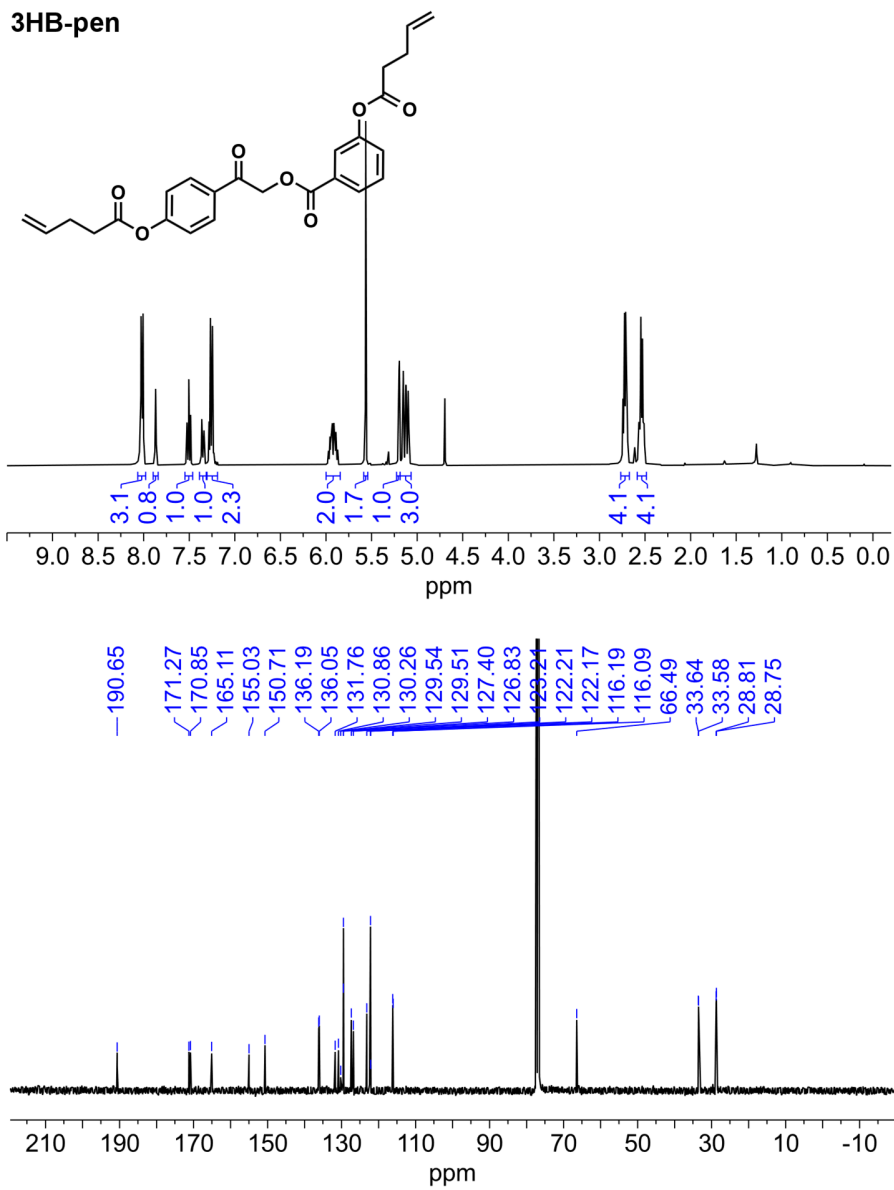




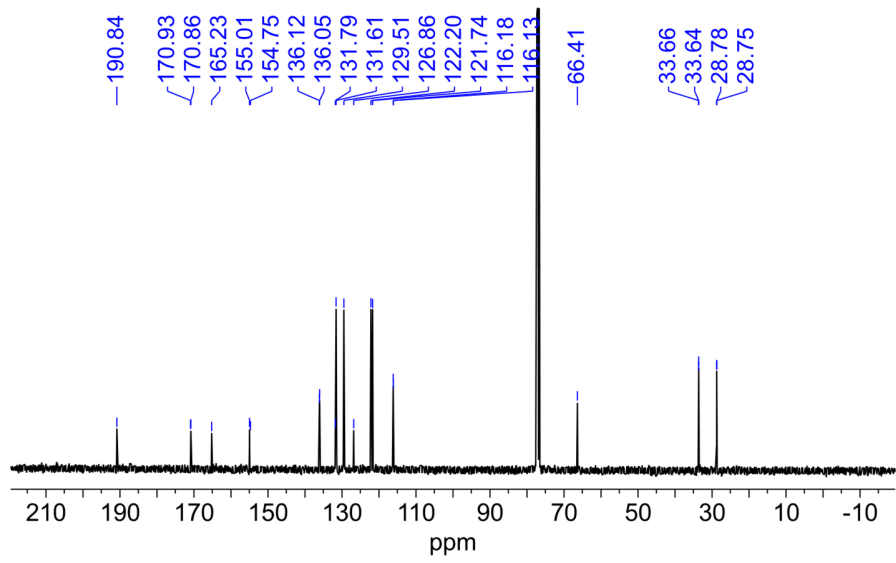
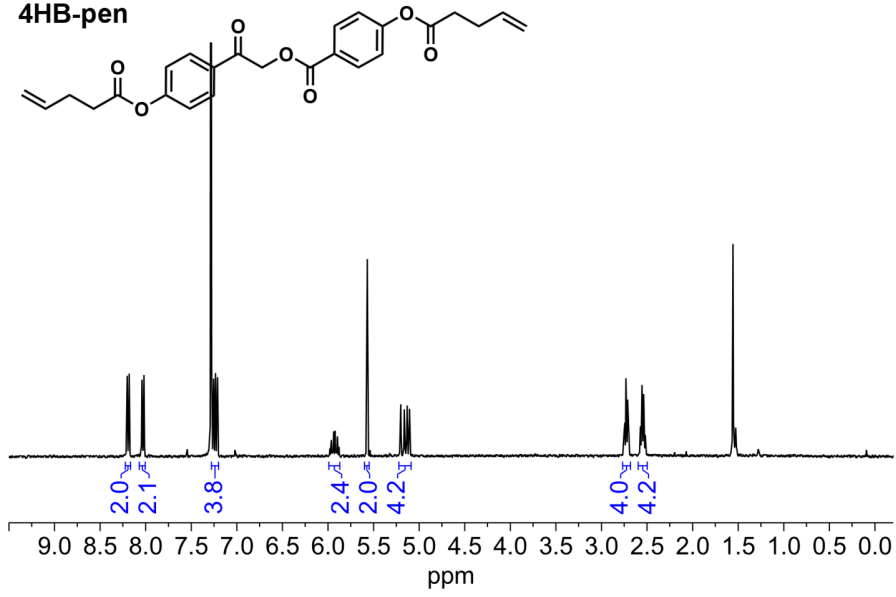
2HB-pen



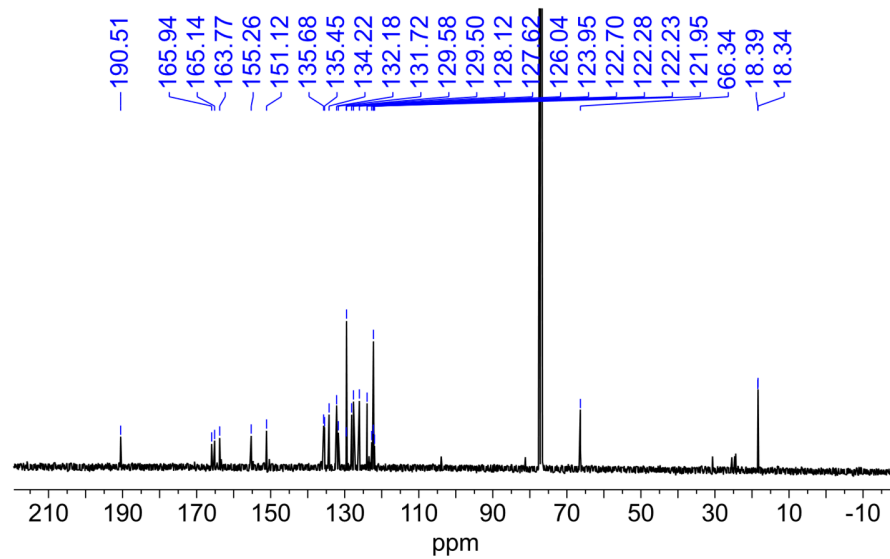
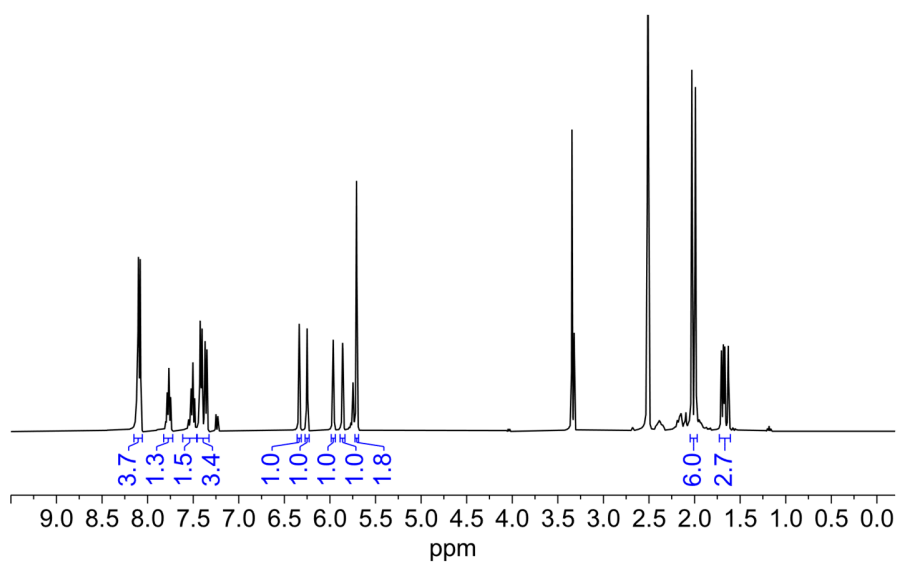
3HB-pen



4HB-pen



2HB-MA



SP-pen

