
Biorenewable and circular polydiketoenamine plastics

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Supplementary Information

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Supplementary Methods

Materials

4-Hydroxy-6-methyl-2-pyrone (Triacetic Acid Lactone, 98%), suberic acid ($\geq 98\%$), azelaic acid (98%), dodecanedioic acid (99%), 4-dimethylaminopyridine (DMAP, $\geq 99\%$), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), and *tris*(2-aminoethyl)amine (TREN, 96%) were purchased from Sigma Aldrich. Bio-based sebacic acid (99%) was purchased from Arkema. 1,9-Nonanedicarboxylic acid (97%) was purchased from AmBeed. Anhydrous magnesium sulfate (MgSO_4 , 99%) was purchased from Arcos Organics. Tetrahydrofuran (THF, $\geq 99.9\%$), dichloromethane (DCM, $\geq 99.9\%$), acetonitrile (ACN, $>99.8\%$), ethanol (90%), hydrochloric acid (HCl, 36.5–38%), trifluoroacetic acid ($>99.8\%$), and formic acid (98–100%) were purchased from VWR. Chloroform-*d* (CDCl_3 , 99.8% D) was purchased from Cambridge Isotope Laboratories. All solvents and reagents were used without further purification.

LB broth (Miller), carbenicillin (100 mg mL^{-1} in ethanol–water, 0.2- μm filtered), isopropyl β -D-1-thiogalactopyranoside (IPTG, $>99\%$), dextrose (*D*-(+)-glucose), ethyl acetate ($>99.7\%$), HPLC Water, sodium selenite ($>98\%$) were purchased from Sigma Aldrich. MOPS EZ Rich Defined Medium Kit was purchased from Teknova, (M2105). The strain used for the fermentation is *E. coli* JBEI-3695 pBbA5a-bktB_Burk so.RF2-nonBP3 (registry.jbei.org/entry/148833).

Instrumentation

^1H and ^{13}C Solution State Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H and ^{13}C solution state NMR spectroscopy was carried out using a Bruker Avance II at 500 and 125 MHz, respectively. Chemical shifts are reported relative to the residual solvent signal (^1H : $\delta = 7.26$ ppm (CDCl_3); ^{13}C : $\delta = 77.16$ ppm (CDCl_3)). NMR data are reported as follows: chemical shift (multiplicity, coupling constants (where applicable), number of hydrogens). Splitting patterns are reported as s (singlet), d (doublet), t (triplet), and m (multiplet). All spectra were processed using Bruker TopSpin 4.1.1 software.

^{13}C Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy. Solid-state ^{13}C NMR spectra were carried out at 500.12 MHz (11.7 T) on a Bruker Avance spectrometer with a Bruker 4 mm narrow bore H/C/N magic angle spinning probe. Solid state ^{13}C NMR spectra were in general acquired by cross-polarization from ^1H with a contact time of 5 ms at a spinning rate of 10 kHz. Adamantane was used as an external reference.

Electrospray Ionization Mass Spectrometry (ESI-MS). ESI-MS was carried out using a Bruker microTOF-Q mass spectrometer using an acetonitrile/ H_2O (95:5 *v/v*) mixture containing 0.01% trifluoroacetic acid and 0.1% formic acid as the ionization medium.

Single Crystal X-Ray Diffraction (XRD). Single crystals for triketones TAL-TKs **1**, **3**, and **5** were selected, mounted on Mitegen® loops with Paratone oil, and placed in an Oxford Cryosystems Cryostream 800 plus at $T = 100$ K. Data were collected on beamline 12.2.1 at the Advanced Light Source (Berkeley, CA) with $\lambda = 0.7288$ Å using a Bruker D8 diffractometer with

a Bruker PHOTONII CPAD detector. Data reductions were performed and corrected for Lorentz and polarization effects using SAINT⁵⁴ v8.40a and were corrected for absorption and other effects using TWINABS 2012/1.⁵⁵ Structure solutions were performed by SHELXT⁵⁶ using the direct method and were refined by least-square refinement against F^2 by SHELXL.⁵⁷

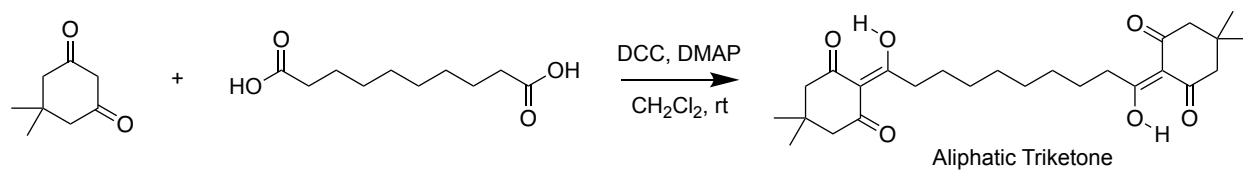
Powder X-Ray Diffraction (PXRD). PXRD patterns were collected using a Rigaku MiniFlex 6G X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The voltage and current were set at 40 kV and 15 mA, respectively. The scanning rate was $10^\circ \text{ min}^{-1}$ in the range of 2θ from 2° – 60° .

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR data were collected on a Nicolet iS50 spectrophotometer using a built-in ATR. Data was reported as an average of 16 scans over an energy range of $400\text{--}4000 \text{ cm}^{-1}$.

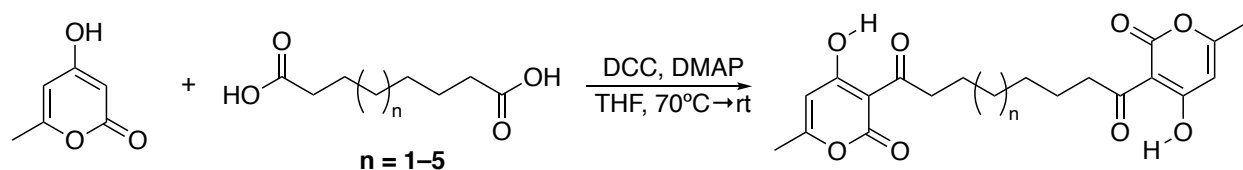
Differential Scanning Calorimetry (DSC). DSC data were acquired using a TA Instruments Q200 Differential Scanning Calorimeter. TAL-PDK samples were heated over a temperature range of $0\text{--}200^\circ \text{C}$ at a rate of $10^\circ \text{C min}^{-1}$ under a N_2 atmosphere. For each sample, data acquisition runs consisted of a heating step, a cooling step, and a second heating step. Glass transition temperatures (T_g) and melting temperatures (T_m) were interpreted and reported from the second heating curve.

Dynamic Mechanical Analysis (DMA). DMA data were acquired using a TA instruments DMA Q800 in tensile mode. All TAL-PDKs were fabricated as rectangular samples with dimensions of approximately $l = 20 \text{ mm}$, $w = 5 \text{ mm}$, $t = 1 \text{ mm}$. Each sample was tested at a frequency of 1 Hz with a displacement amplitude of $15 \text{ }\mu\text{m}$ and a preload force of 0.01 N. Heating ramps of $3^\circ \text{C min}^{-1}$ were applied from $40\text{--}200^\circ \text{C}$. The storage modulus and elastic modulus were reported at 40°C and 180°C , respectively. The T_g was reported as the temperature at which the maximum value of $\tan \delta$ was observed.

Thermogravimetric Analysis (TGA) was performed on a TA instruments TGA5500 Thermal Analyzer. Samples were heated under nitrogen at a rate of $10^\circ \text{C min}^{-1}$ from 20 to 800°C .



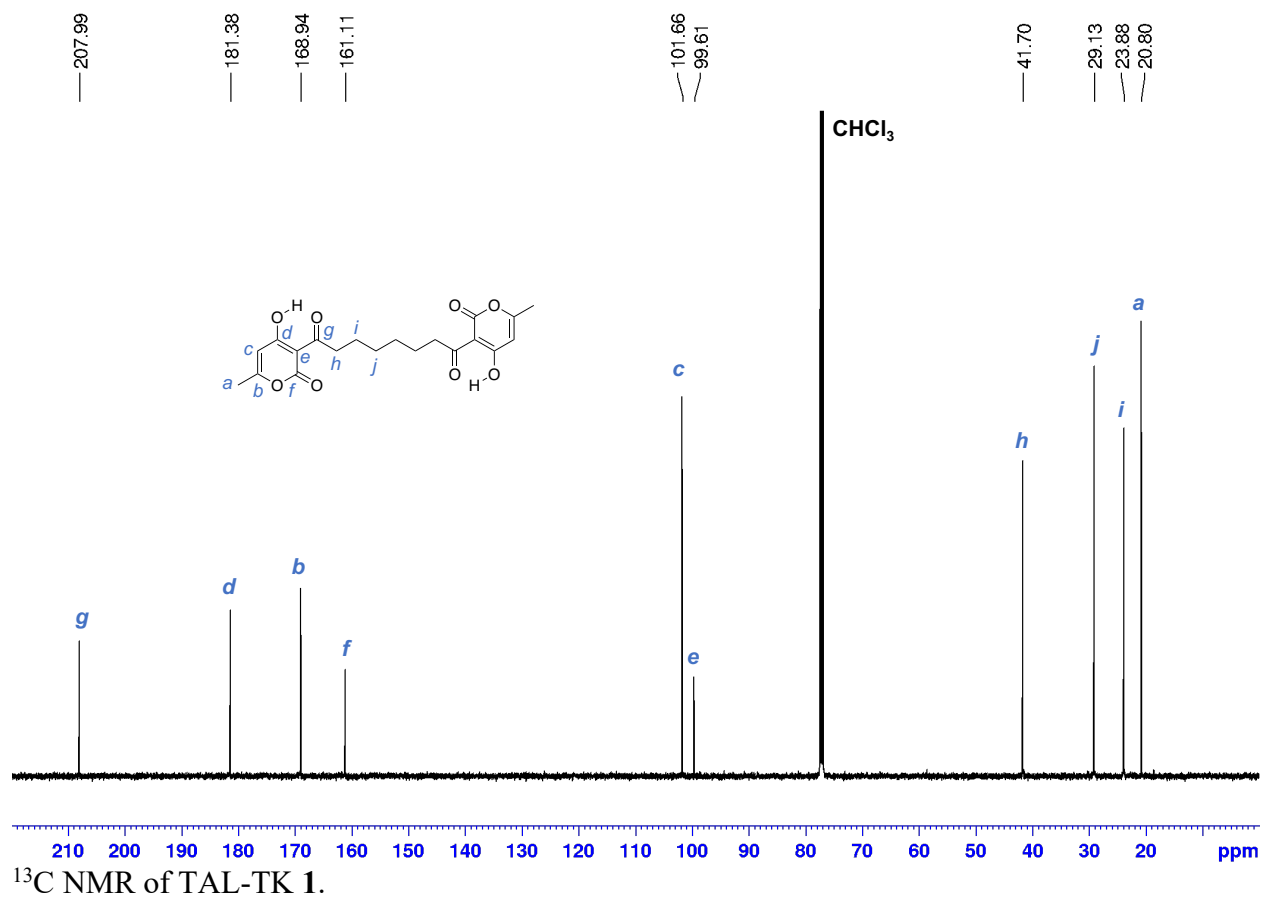
Synthesis of 1,10-bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)decane-1,10-dione (Aliphatic Triketone). The synthesis of Aliphatic Triketone monomer was synthesized from dimedone and sebacic acid (C₁₀ diacid), according to previously reported procedure in *Nat. Chem.* **11**, 442–448 (2019).

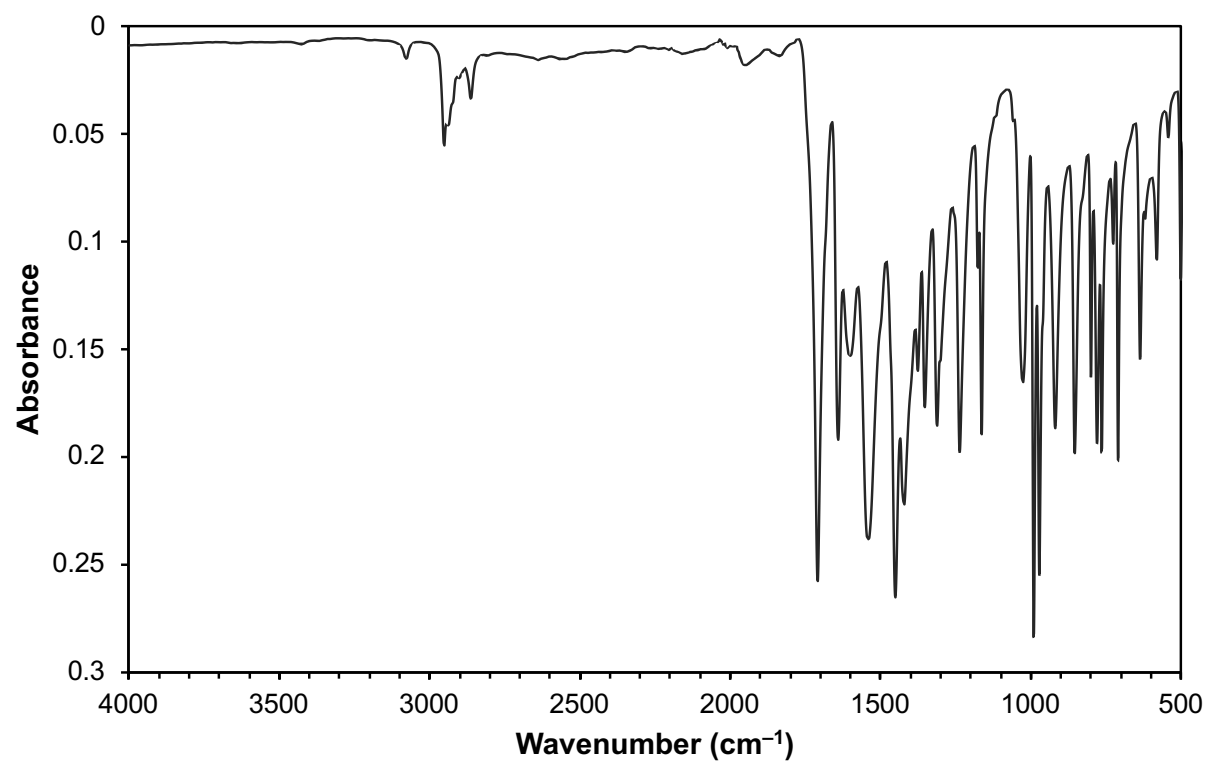


Synthesis of 1,8-bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)octane-1,8-dione (TAL-TK 1).

Triacetic acid lactone (10.10 g, 80.1 mmol), suberic acid (6.65 g, 38.2 mmol), and DMAP (14.04 g, 114.9 mmol) were solubilized in tetrahydrofuran (200 mL) upon heating at 70 °C. A separate solution of DCC (18.65 g, 90.4 mmol) in tetrahydrofuran (50 mL) was added slowly to the reaction mixture. The reaction mixture gradually turned yellow, accompanied by the formation of a white precipitate. After the complete addition of DCC, the reaction was allowed to cool to room temperature and pursued overnight (24 h). The mixture was filtered and washed with CH₂Cl₂ until the solid became colorless. The filtrate was concentrated and the recovered product, a dark red oil, was dissolved in CH₂Cl₂ (400 mL) and extracted with 2 M HCl (2 x 150 mL). The organic phase was dried over MgSO₄ and concentrated, leaving the crude product as an orange paste. The crude product was recrystallized from ethanol to yield TAL-TK **1** as light orange needles (6.00 g, 15.4 mmol, 40.2%). ¹H NMR (500 MHz, CDCl₃): δ 16.84 (s, 2H), 5.92 (s, 2H), 3.05–3.08 (t, *J* = 7.4 Hz, 4H), 2.26 (s, 6H), 1.65–1.67 (m, 4H), 1.40–1.43 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 207.99, 181.38, 168.94, 161.11, 101.66, 99.61, 41.70, 29.13, 23.88, 20.81 ppm; ESI-MS: *m/z* for (C₂₀H₂₂O₈)Na⁺ ([M+Na]⁺) calculated 413.1207, found 413.1350; FT-IR: 3076, 2951, 2860, 1711, 1643, 1601, 1540, 1451, 1421, 1377, 1354, 1313, 1237, 1164, 1027, 992, 972, 920, 855, 801, 781, 766, 711, 638, 582, 502, 484, 400 cm⁻¹. Crystallographic data for TAL-TK **1** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2223455.



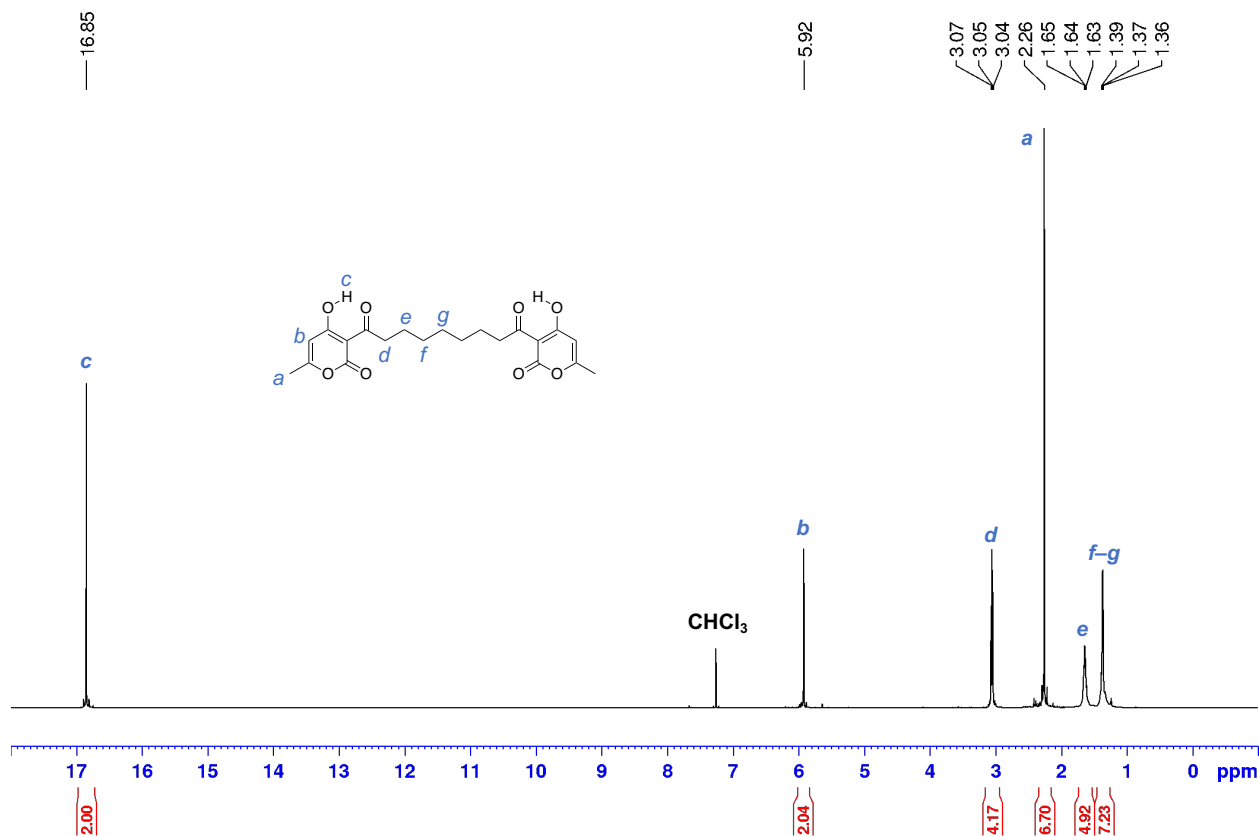


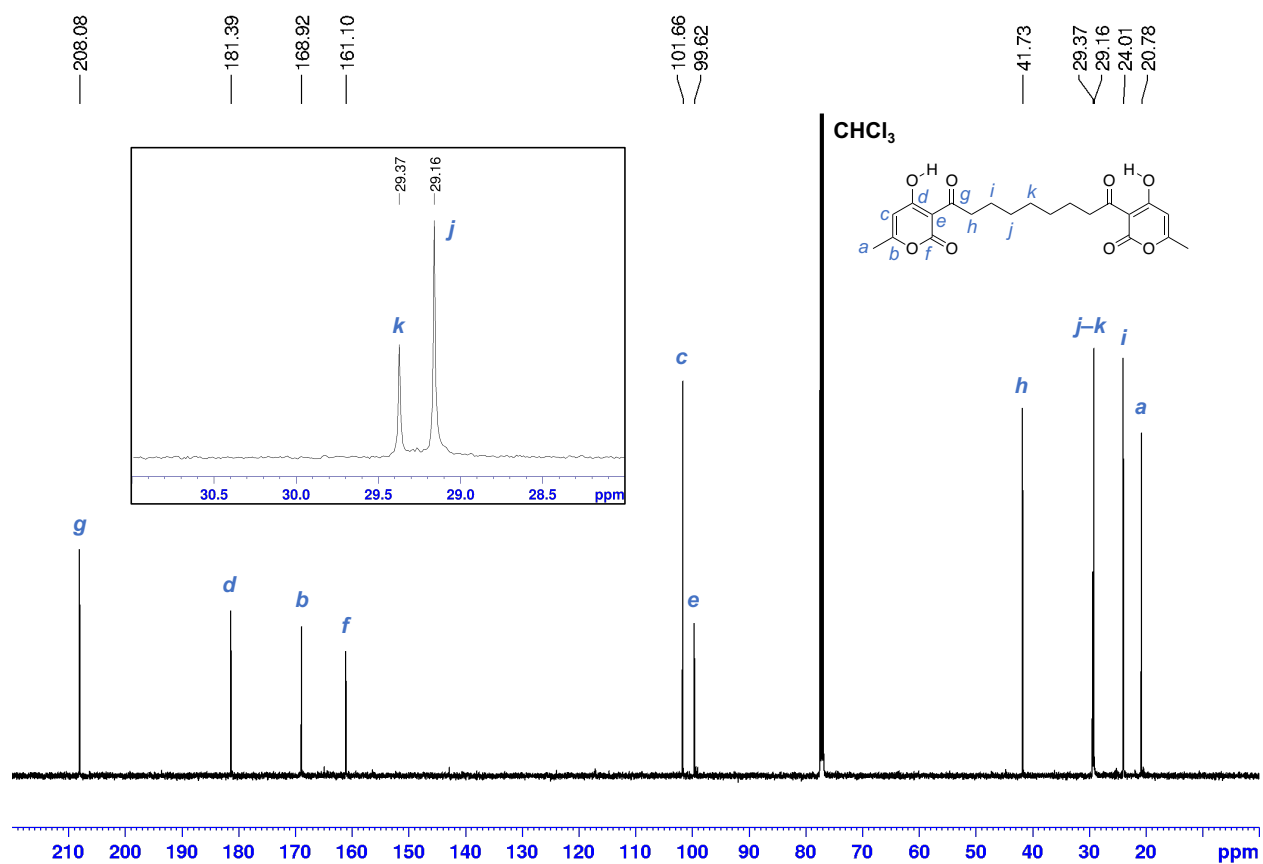


FT-IR of TAL-TK 1.

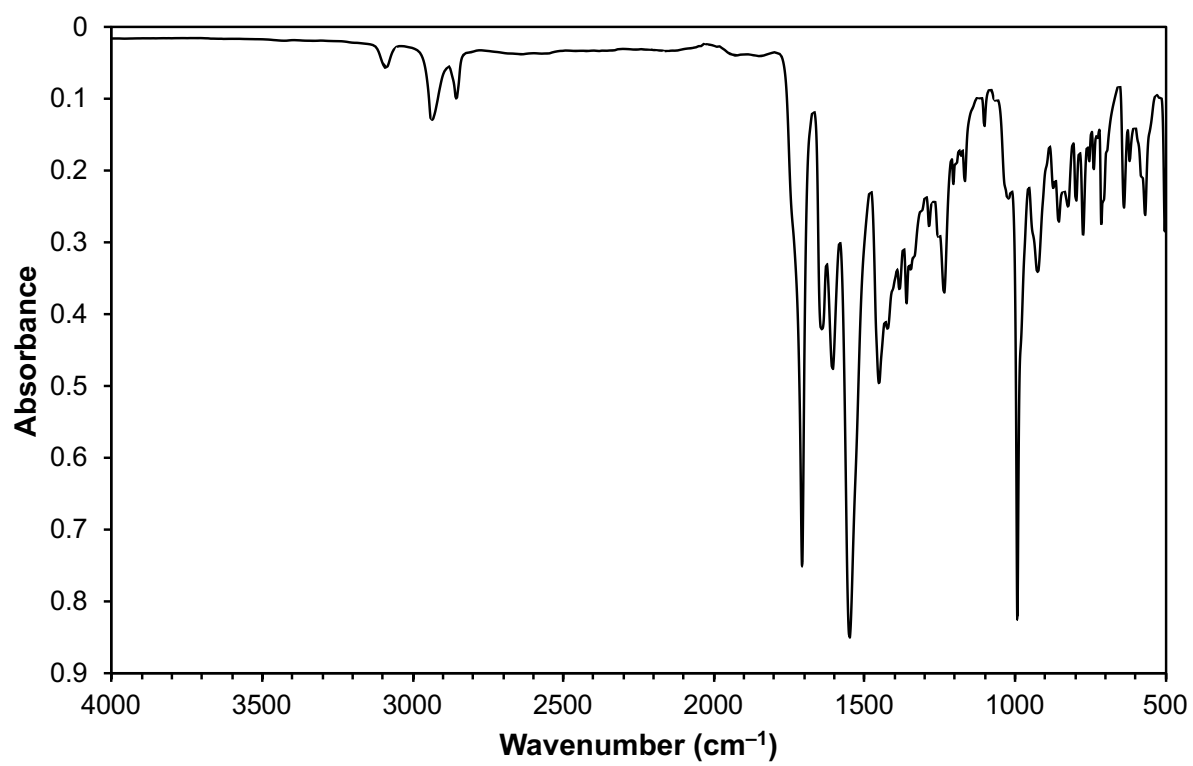
Synthesis of 1,9-bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)nonane-1,9-dione (TAL-TK 2).

Triacetic acid lactone (10.11 g, 80.2 mmol), azelaic acid (7.20 g, 38.3 mmol), and DMAP (14.01 g, 114.7 mmol) were solubilized in tetrahydrofuran (200 mL) upon heating at 70 °C. A separate solution of DCC (18.63 g, 90.3 mmol) in tetrahydrofuran (50 mL) was added slowly to the reaction mixture. The reaction mixture gradually turned orange, accompanied by the formation of a white precipitate. After the complete addition of DCC, the reaction was allowed to cool to room temperature and pursued overnight (25 h). The mixture was filtered and washed with CH₂Cl₂ until the solid became colorless. The filtrate was concentrated and the recovered product, a dark red oil, was dissolved in CH₂Cl₂ (450 mL) and extracted with 2 M HCl (2 x 150 mL). The organic phase was dried over MgSO₄ and concentrated, leaving the crude product as a yellow paste. The crude product was co-recrystallized from ethanol and H₂O to yield TAL-TK 2 as a yellow powder (6.64 g, 16.4 mmol, 42.9%). ¹H NMR (500 MHz, CDCl₃): δ 16.85 (s, 2H), 5.92 (s, 2H), 3.04–3.07 (t, *J* = 7.4 Hz, 4H), 2.26 (s, 6H), 1.63–1.65 (m, 4H), 1.36–1.39 (m, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 208.08, 181.39, 168.92, 161.10, 101.66, 99.62, 41.73, 29.37, 29.16, 24.01, 20.78 ppm; ESI-MS: *m/z* for (C₂₁H₂₄O₈)Na⁺ ([M+Na]⁺) calculated 427.1364, found 427.1519; FT-IR: 3087, 2934, 2854, 1707, 1639, 1604, 1548, 1450, 1234, 992, 924, 773, 713, 639, 567, 502, 401 cm⁻¹.



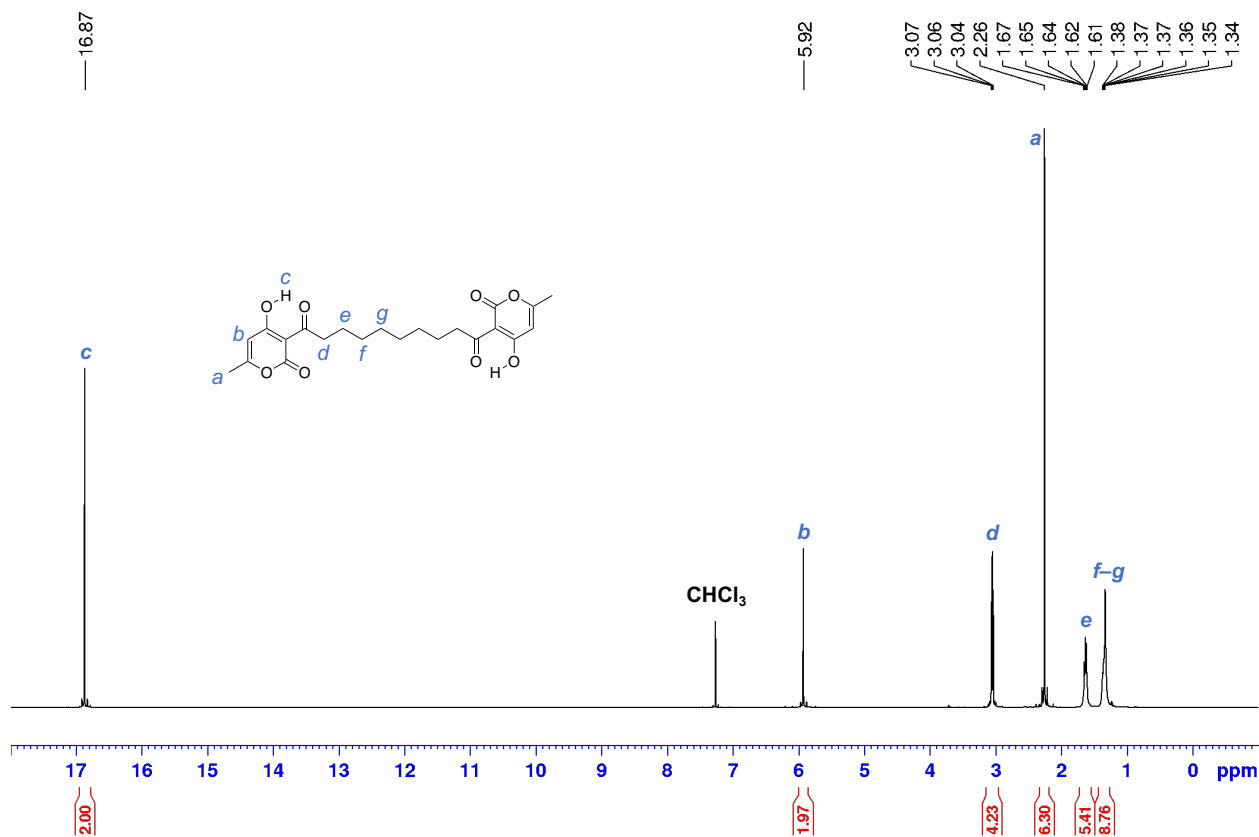


¹³C NMR of TAL-TK 2. Inset shows 28–31 ppm.

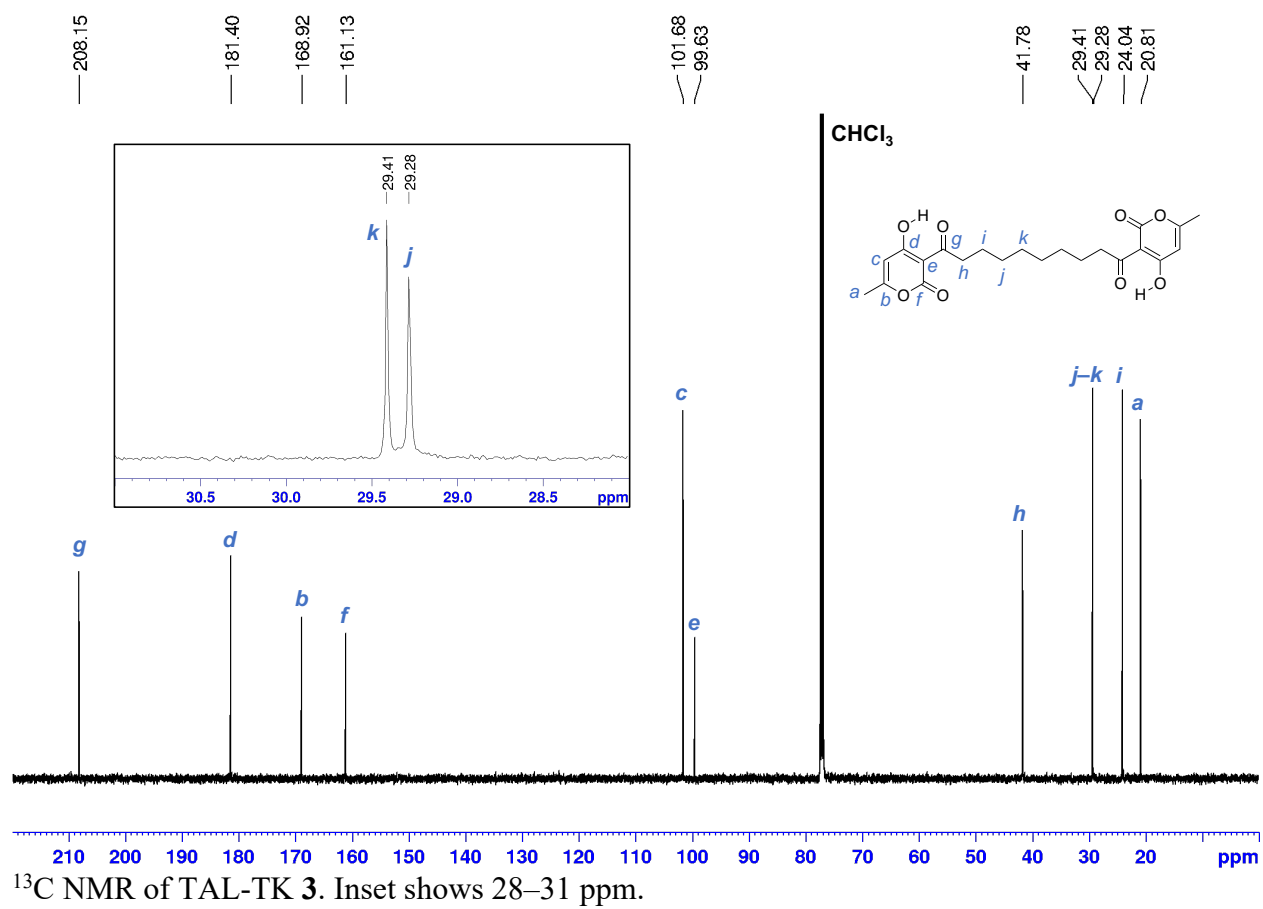


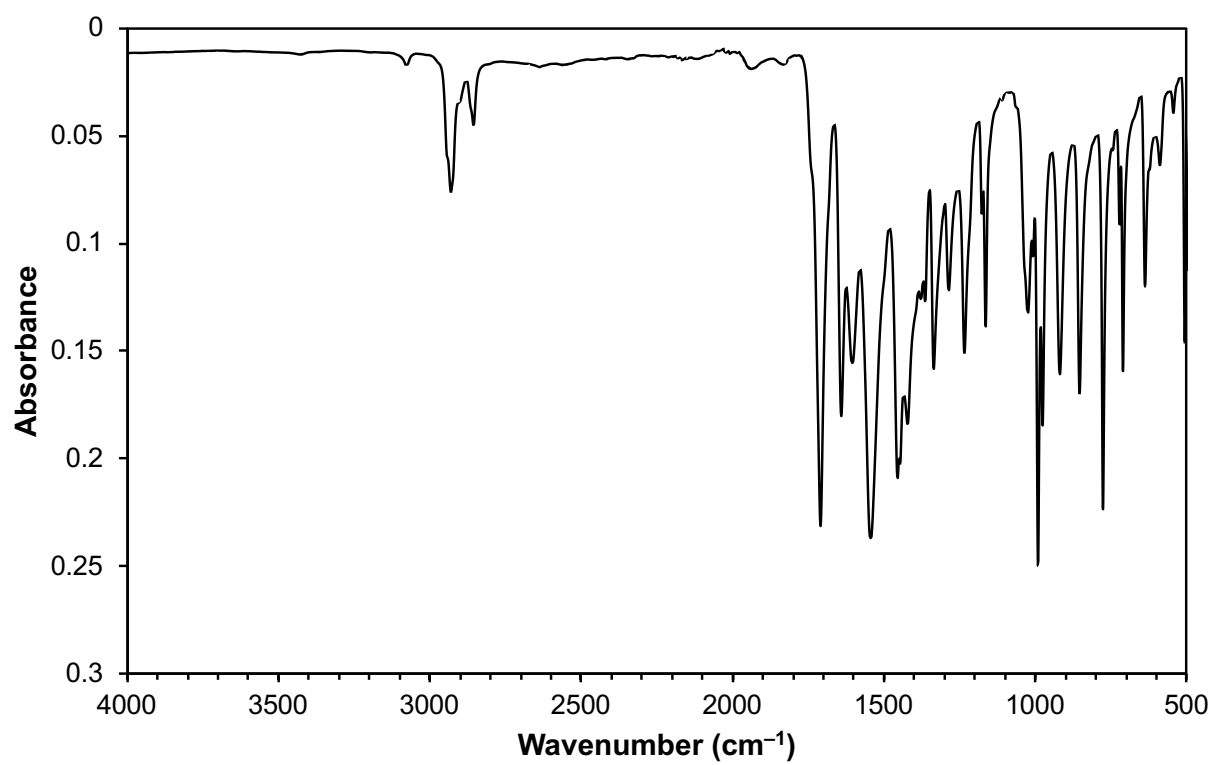
FT-IR of TAL-TK 2.

Synthesis of 1,10-bis(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)decane-1,10-dione (TAL-TK 3). Triacetic acid lactone (10.05 g, 79.7 mmol), sebacic acid (7.71 g, 38.1 mmol), and DMAP (14.01 g, 114.7 mmol) were solubilized in tetrahydrofuran (200 mL) upon heating at 70 °C. A separate solution of DCC (18.70 g, 90.6 mmol) in tetrahydrofuran (50 mL) was added slowly to the reaction mixture. The reaction mixture gradually turned orange, accompanied by the formation of a white precipitate. After the complete addition of DCC, the reaction was allowed to cool to room temperature and pursued overnight (24 h). The mixture was filtered and washed with CH₂Cl₂ until the solid became colorless. The filtrate was concentrated and the recovered product, a dark red oil, was dissolved in CH₂Cl₂ (450 mL) and extracted with 2 M HCl (2 x 150 mL). The organic phase was dried over MgSO₄ and concentrated, leaving the crude product as an orange paste. The crude product was recrystallized from ethanol to yield TAL-TK 3 as yellow-orange needles (6.48 g, 15.5 mmol, 40.6%). ¹H NMR (500 MHz, CDCl₃): δ 16.87 (s, 2H), 5.92 (s, 2H), 3.04–3.07 (t, *J* = 7.4 Hz, 4H), 2.26 (s, 6H), 1.61–1.67 (m, 4H), 1.34–1.38 (m, 8H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 208.15, 181.40, 168.92, 161.13, 101.68, 99.63, 41.78, 29.41, 29.28, 24.04, 20.81 ppm; ESI-MS: *m/z* for (C₂₂H₂₆O₈)Na⁺ ([M+Na]⁺) calculated 441.1520, found 441.1350; FT-IR: 3076, 2930, 2856, 1710, 1641, 1603, 1543, 1455, 1421, 1335, 1285, 1234, 1165, 1024, 992, 918, 853, 776, 710, 637, 506, 431, 400 cm⁻¹. Crystallographic data for TAL-TK 3 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2223456.



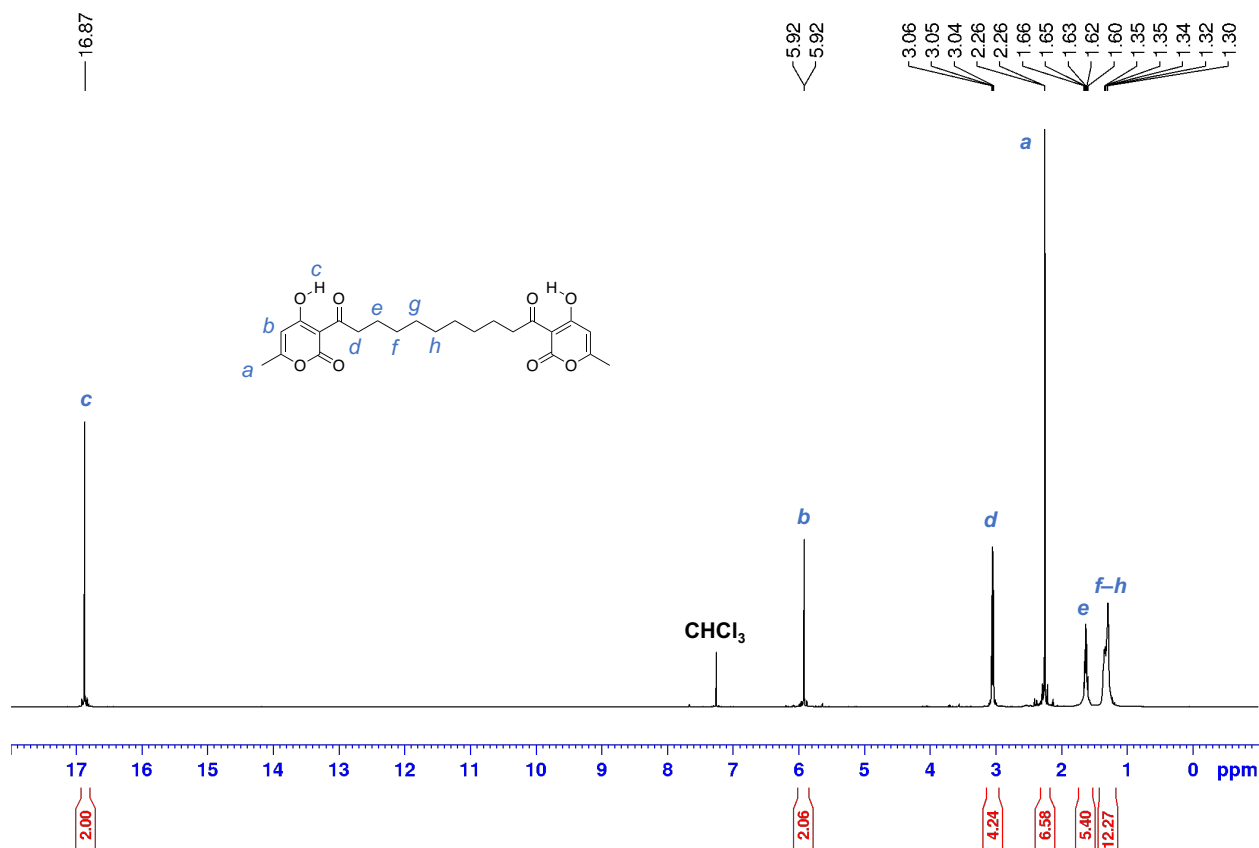
¹H NMR of TAL-TK 3.



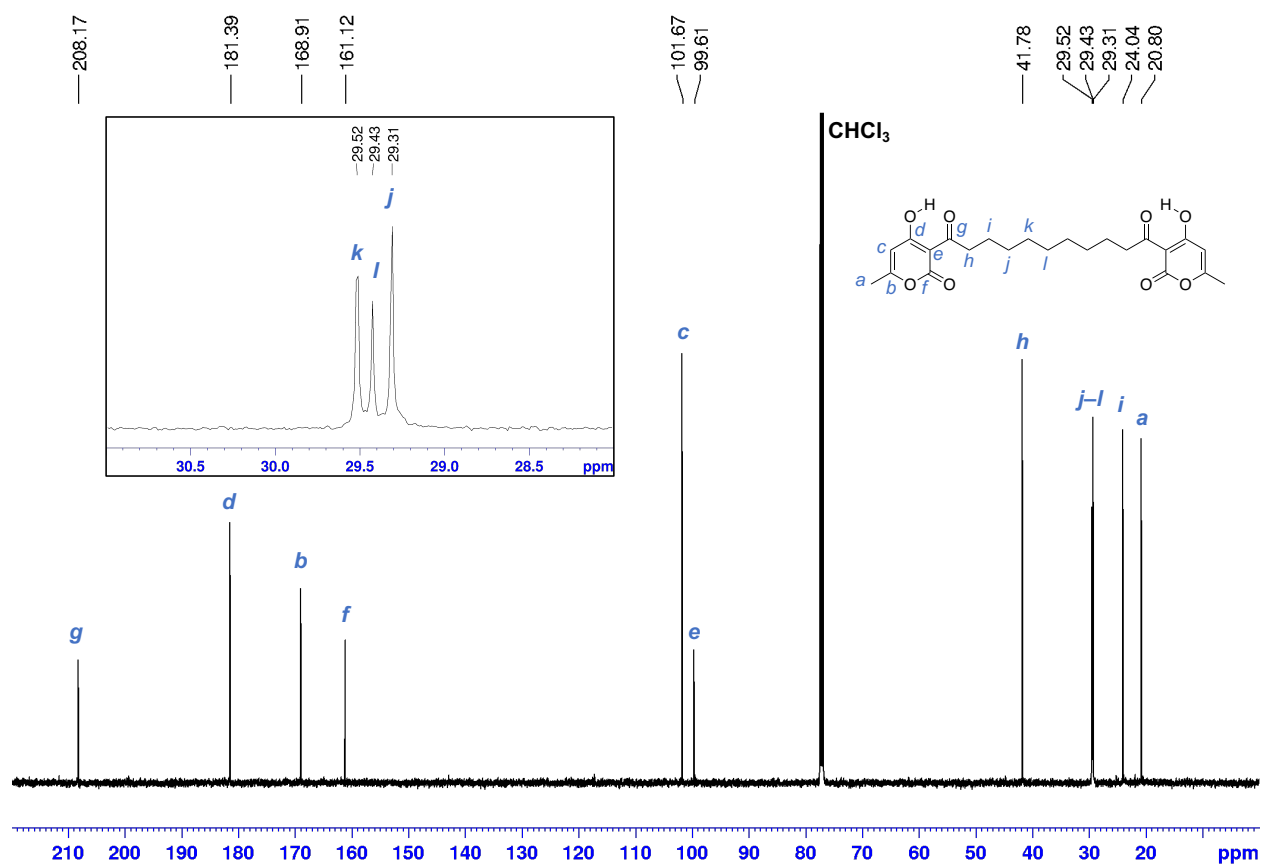


FT-IR of TAL-TK 3.

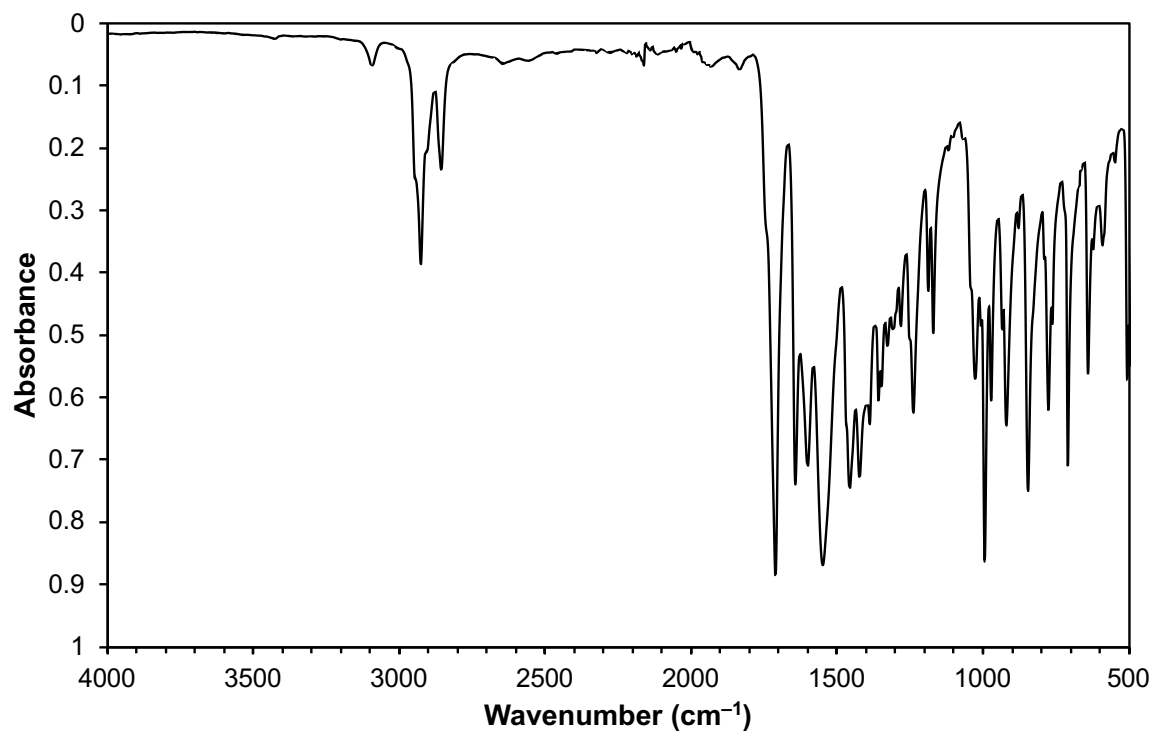
Synthesis of 1,11-bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)undecane-1,11-dione (TAL-TK 4). Triacetic acid lactone (9.82g, 77.9 mmol), 1,9-nonanedicarboxylic acid (8.03 g, 37.1 mmol), and DMAP (13.60 g, 111.3 mmol) were solubilized in tetrahydrofuran (200 mL) upon heating at 70 °C. A separate solution of DCC (18.36 g, 89.0 mmol) in tetrahydrofuran (50 mL) was added slowly to the reaction mixture. The reaction mixture gradually turned orange, accompanied by the formation of a white precipitate. After the complete addition of DCC, the reaction was allowed to cool to room temperature and pursued overnight (24 h). The mixture was filtered and washed with CH₂Cl₂ until the solid became colorless. The filtrate was concentrated and the recovered product, a dark red oil, was dissolved in CH₂Cl₂ (600 mL) and extracted with 2 M HCl (2 x 150 mL). The organic phase was dried over MgSO₄ and concentrated, leaving the crude product as an orange paste. The crude product was co-recrystallized from ethanol and H₂O to yield TAL-TK 4 as a yellow granules (7.69 g, 17.8 mmol, 47.9 %). ¹H NMR (500 MHz, CDCl₃): δ 16.87 (s, 2H), 5.92 (d, *J* = 0.65 Hz, 2H), 3.04–3.07 (t, *J* = 7.4 Hz, 4H), 2.26 (d, *J* = 0.55 Hz, 6H), 1.60–1.66 (m, 4H), 1.30–1.35 (m, 10H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 208.17, 181.39, 168.91, 161.12, 101.67, 99.61, 41.78, 29.52, 29.43, 29.31, 24.04, 20.80 ppm; ESI-MS: *m/z* for (C₂₃H₂₈O₈)Na⁺ ([M+Na]⁺) calculated 455.1676, found 455.1831; FT-IR: 3094, 2926, 2857, 1711, 1643, 1600, 1549, 1456, 1423, 1388, 1385 1238, 1187, 1171, 1025, 994, 972, 919, 846, 775, 709, 640, 590, 506, 447 cm⁻¹.



¹H NMR of TAL-TK 4.

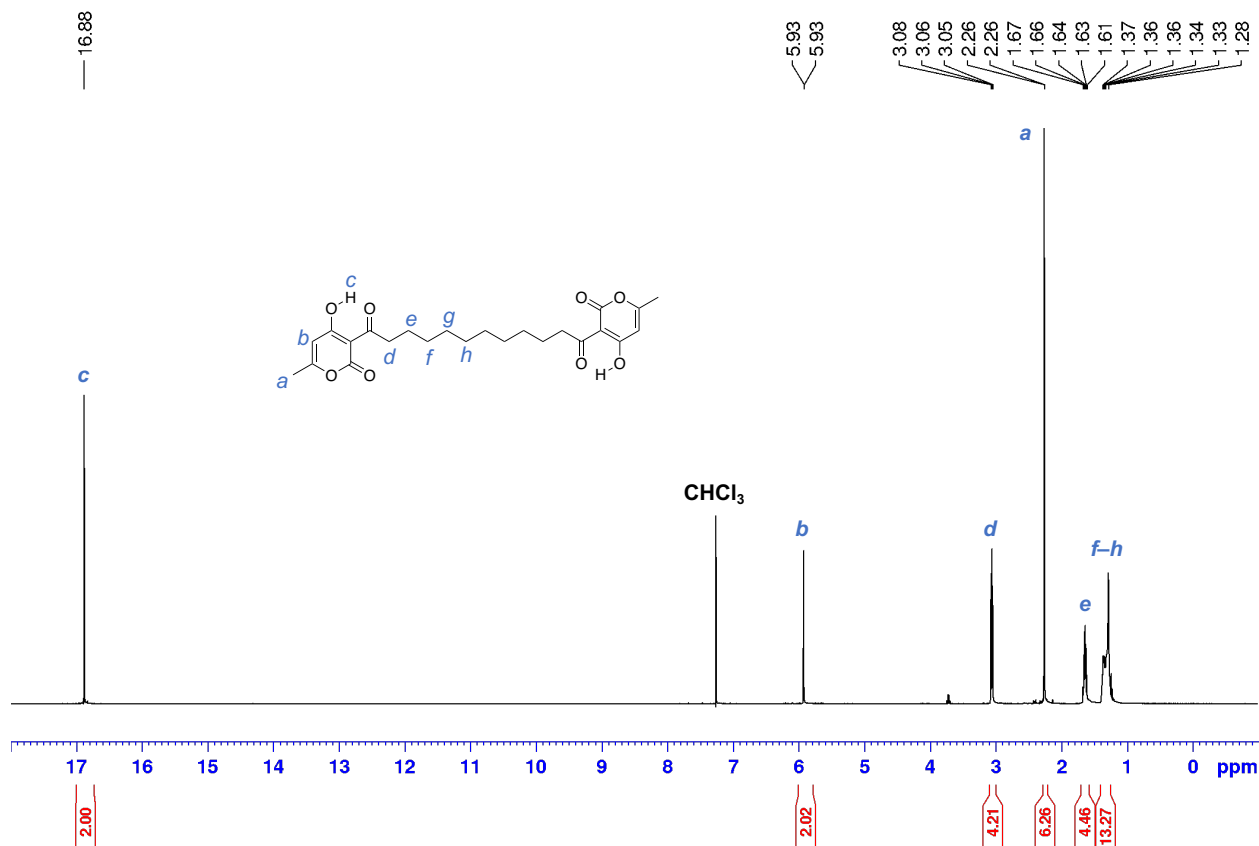


¹³C NMR of TAL-TK 4. Inset shows 28–31 ppm.

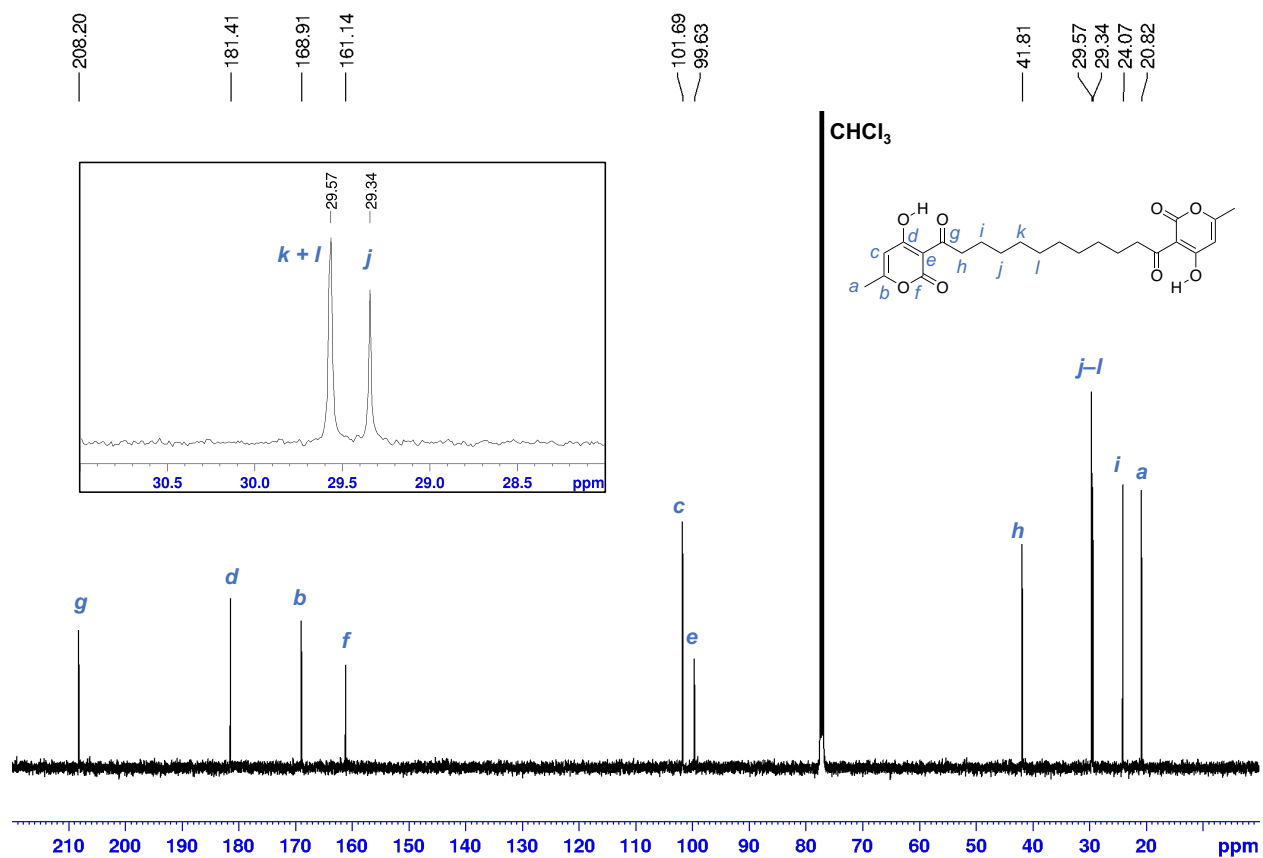


FT-IR of TAL-TK 4.

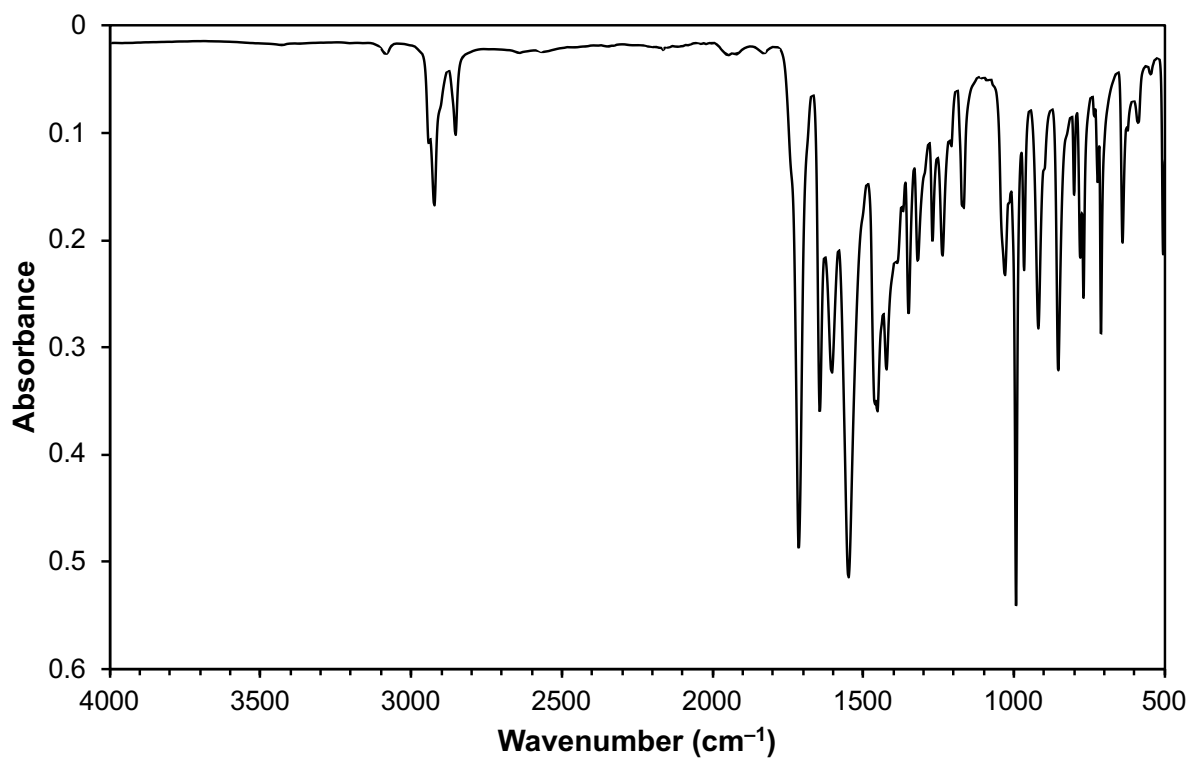
Synthesis of 1,12-bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)dodecane-1,12-dione (TAL-TK 5). Triacetic acid lactone (10.15 g, 80.5 mmol), dodecanedioic acid (8.79 g, 38.2 mmol), and DMAP (13.94 g, 114.0 mmol) were dissolved in tetrahydrofuran (200 mL) under refluxing conditions at 70 °C. A separate solution of DCC (17.78 g, 86.2 mmol) in tetrahydrofuran (100 mL) was added slowly to the reaction mixture. The reaction mixture gradually turned yellow, accompanied by the formation of a white precipitate. After the complete addition of DCC, the mixture was allowed to cool to room temperature and stirred overnight (23 h). The mixture was filtered and washed with CH₂Cl₂ until the solid became colorless. The filtrate was concentrated and the recovered product, an orange paste, was dissolved in CH₂Cl₂ (800 mL) and extracted with 2 M HCl (3 x 100 mL). The organic phase was dried over MgSO₄ and concentrated, leaving the crude product as an orange paste. The crude product was recrystallized from ethanol to yield TAL-TK 5 as yellow needles (10.58 g, 23.7 mmol, 62.1%). ¹H NMR (500 MHz, CDCl₃): δ 16.88 (s, 2H), 5.93 (d, *J* = 0.65 Hz, 2H), 3.05–3.08 (t, *J* = 7.4 Hz, 4H), 2.26 (d, *J* = 0.5 Hz, 6H), 1.61–1.67 (m, 4H), 1.28–1.36 (m, 12H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 208.21, 181.41, 168.91, 161.14, 101.69, 99.63, 41.81, 29.57, 29.34, 24.07, 20.82 ppm; ESI-MS: *m/z* for (C₂₄H₃₀O₈)Na⁺ ([M+Na]⁺) calculated 469.1833, found 469.1974; FT-IR: 2923, 2852, 1715, 1643, 1606, 1550, 1452, 1422, 1350, 1318, 1269, 1238, 1166, 1031, 993, 967, 919, 852, 768, 711, 640, 504, 416 cm⁻¹. Crystallographic data for TAL-TK 5 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2223457.



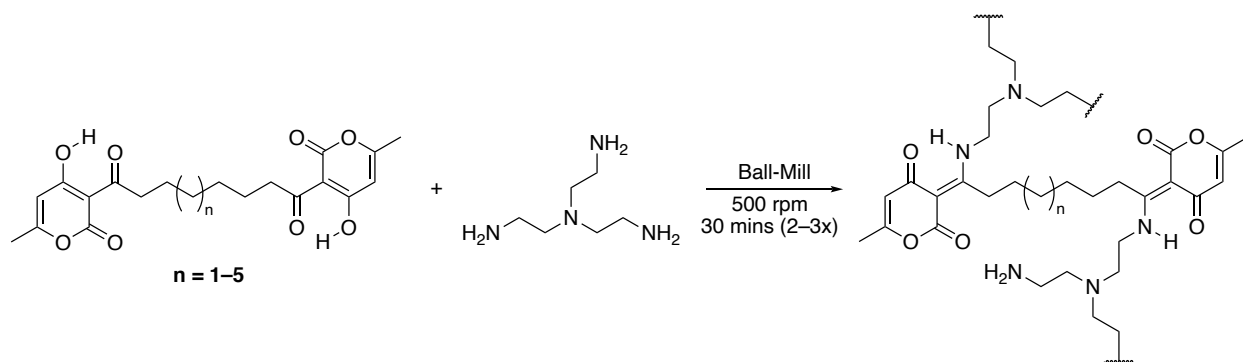
¹H NMR of TAL-TK 5.



¹³C NMR of TAL-TK 5. Inset shows 28–31 ppm, highlighting overlapping k and l peaks.



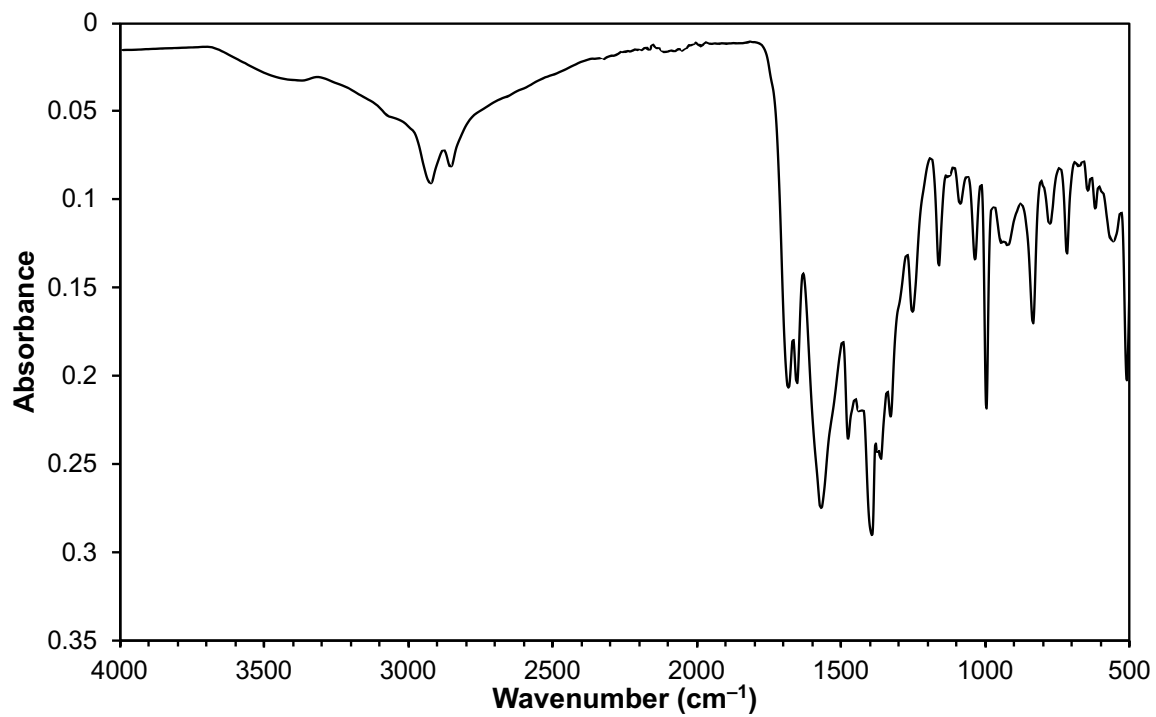
FT-IR of TAL-TK 5.



Synthesis of TAL-PDK Resins. Ball-milling was performed using a Retsch Planetary BallMill PM100. The container in which the reactions were carried out was a zirconium-coated cylinder either with an inner diameter of 4.5 cm and a height of 3.5 cm (reactor volume ~50 mL) or with an inner diameter of 10 cm and a height of 7 cm (reactor volume ~500 mL). All experiments reported herein used the same weight ratio of zirconium oxide ball bearings (5 mm diameter) to triketone monomer, with the ball bearings being 10 times the weight of triketone. The general procedure for all ball-milling reactions involved weighing out the appropriate amount of triketone monomer (2.0 or 10.0 g) and placing at the bottom of the ball mill, along with the ball bearings (20 or 100 g). To the triketone monomer was added *tris*(2-aminoethyl)amine (TREN) using a pre-calibrated micropipette such that the ratio of amine to triketone functional groups is 1.1 to 1. This was immediately followed by ball-milling the contents of the closed container for 30 min at 500 rpm with changes in spinning direction every 1 min. The reactor was opened to air and the reactor walls were scraped to bring together the reactants homogeneously. Ball-milling was resumed under identical conditions for an additional 30 min. For TAL-PDK **2**, the walls of the reactor were scraped again, followed by one more round of ball-milling for 30 min. The powders were recovered from the reactor and the residual water was removed under vacuum at 90 °C.

TAL-PDK 1:

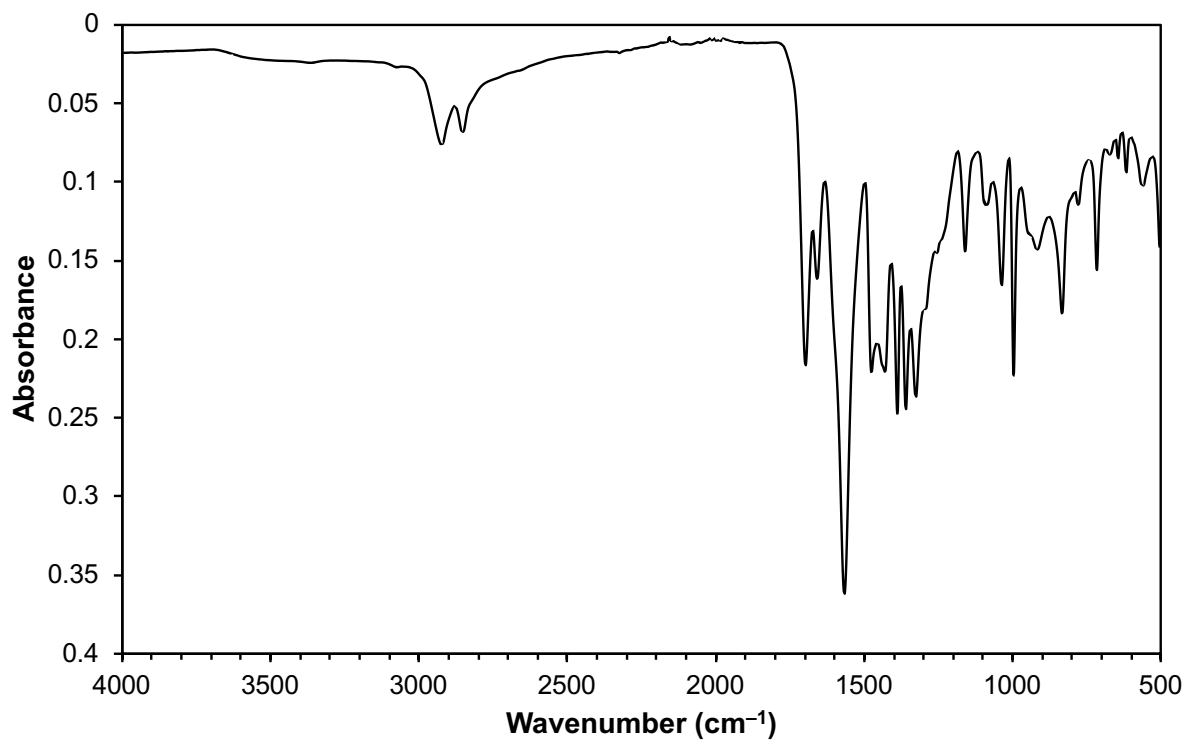
FT-IR: 2921, 2853, 1682, 1653, 1569, 1475, 1396, 1365, 1329, 1252, 1161, 1036, 997, 919, 835, 775, 719, 556, 511, 443 cm^{-1} .



FT-IR of TAL-PDK 1.

TAL-PDK 2:

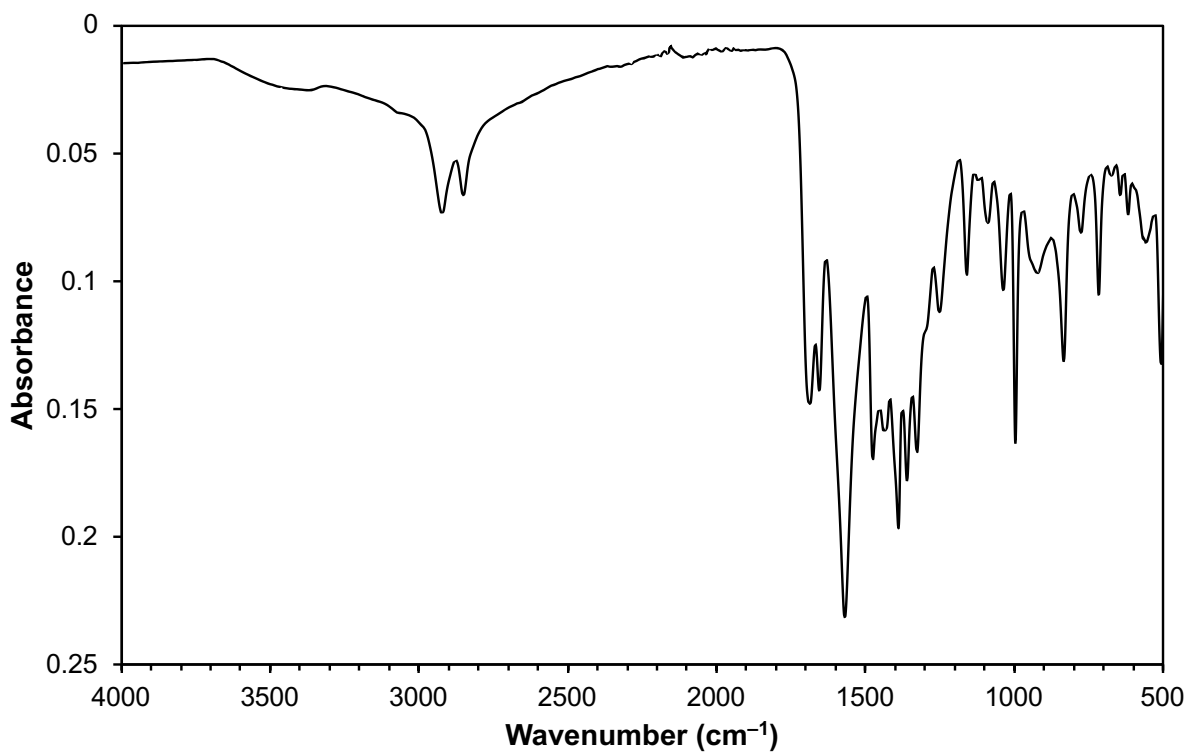
FT-IR: 2919, 2850, 1697, 1657, 1566, 1474, 1428, 1388, 1359, 1325, 1159, 1036, 997, 913, 833, 778, 716, 556, 503, 443 cm^{-1} .



FT-IR of TAL-PDK 2.

TAL-PDK **3**:

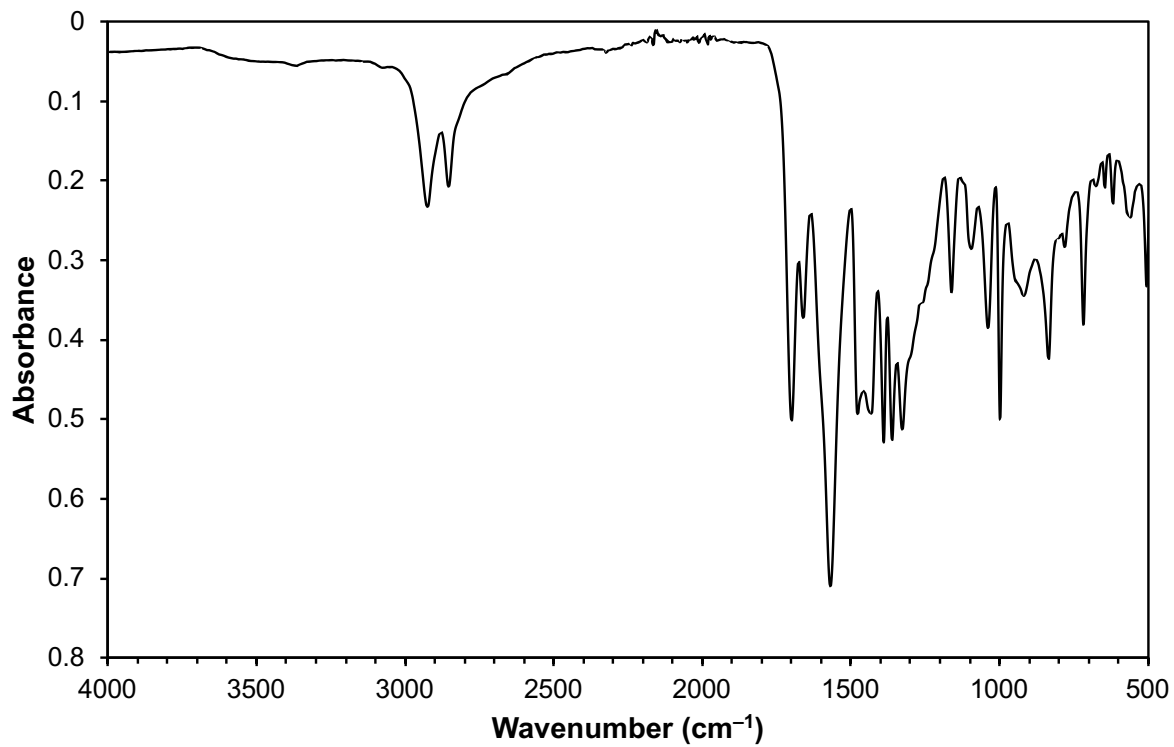
FT-IR: 2922, 2851, 1687, 1655, 1570, 1476, 1391, 1364, 1327, 1251, 1161, 1038, 998, 921, 835, 779, 717, 557, 510, 446 cm^{-1} .



FT-IR of TAL-PDK **3**.

TAL-PDK 4:

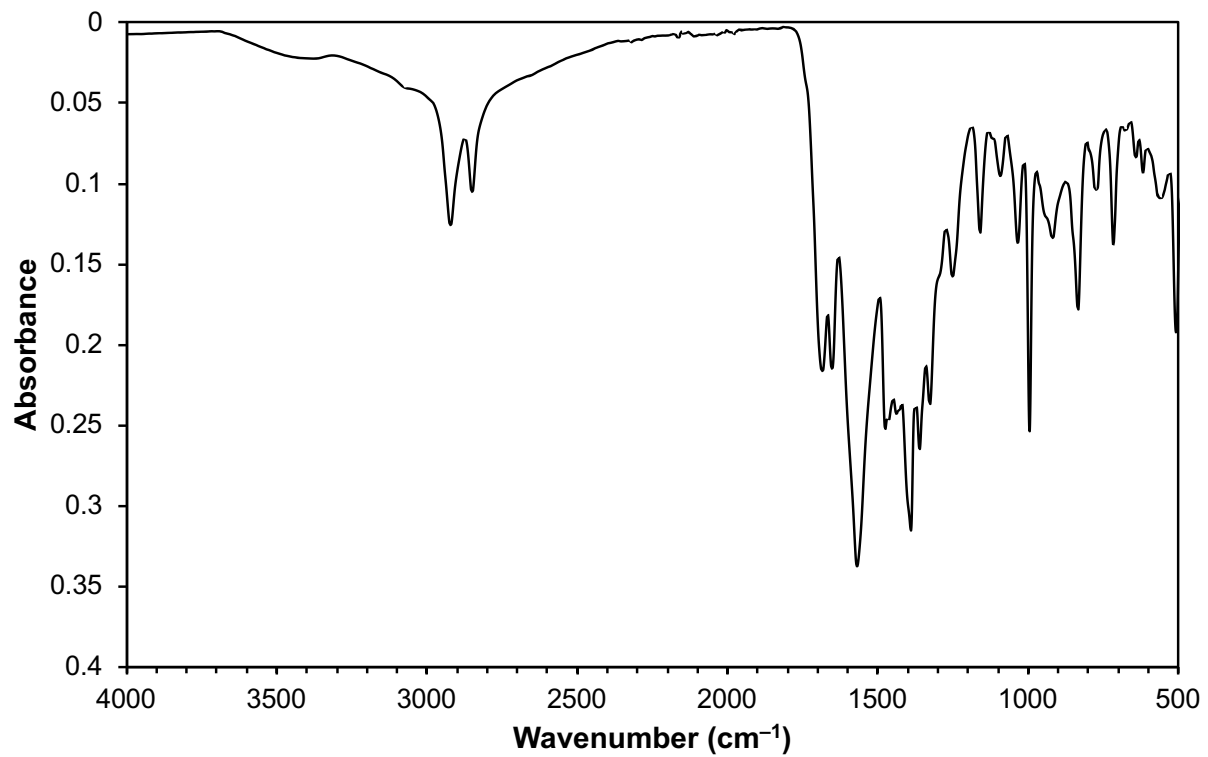
FT-IR: 2923, 2853, 1698, 1659, 1567, 1476, 1430, 1388, 1360, 1326, 1159, 1094, 1038, 997, 917, 834, 716, 617, 557, 504, 445 cm^{-1} .



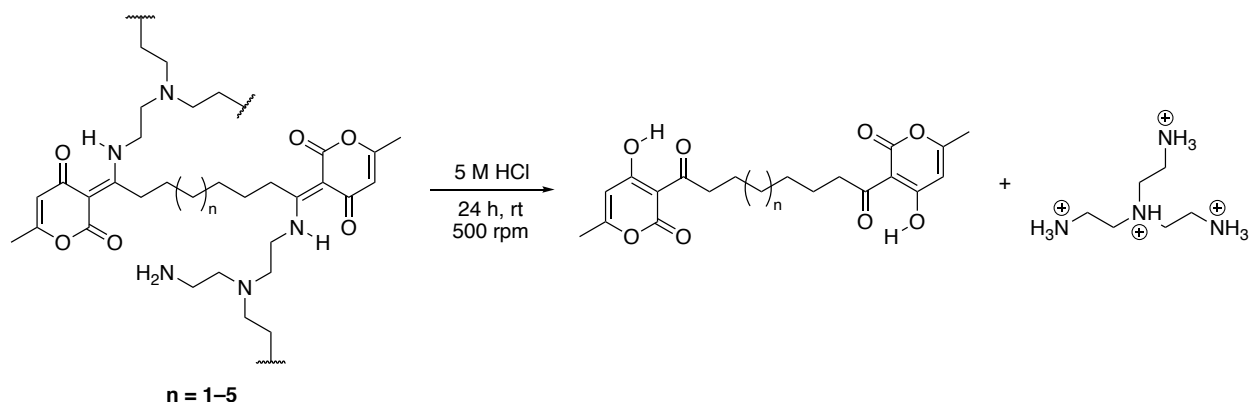
FT-IR of TAL-PDK 4.

TAL-PDK 5:

FT-IR: 2923, 2851, 1686, 1654, 1569, 1476, 1393, 1364, 1331, 1253, 1160, 1035, 997, 918, 837, 775, 718, 556, 509, 445 cm^{-1} .



FT-IR of TAL-PDK 5.



Acid-Catalyzed Hydrolysis of TAL-PDK Resins. TAL-PDK resins were placed in separate 40 mL vials along with 5.0 M HCl (15 mL) and a magnetic stirrer. Depolymerization reactions were conducted over 24 h at room temperature while stirring at 500 rpm. Triketones were isolated by extraction with CH₂Cl₂ and evaporation of the organic phase. Percent triketone recovery was calculated by the following equation:

$$\text{Percent TK Recovery} = \frac{\frac{\text{TK (g)}}{\text{PDK (g)}}}{1 + x - \frac{2(MW_{H_2O})}{MW_{TK}}} * 100\%$$

Where:

TK (g) is the mass of recovered triketone

PDK (g) is the mass of the TAL-PDK to be depolymerized

x is the mass ratio of TREN:Triketone used during TAL-PDK polymerization

MW_{H₂O} is the molecular weight of H₂O

MW_{TK} is the molecular weight of the triketone

TAL-PDK **1** (472 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a light brown suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give an orange-brown paste. The product was dried under vacuum at 80 °C to yield TAL-TK **1** (yield = 289 mg, 72.4%).

TAL-PDK **2** (320 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a light brown suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a dark red solid. The product was dried under vacuum at 80 °C to yield TAL-TK **2** (yield = 254 mg, 93.4%).

TAL-PDK **3** (487 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a dark yellow suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a yellow-orange paste. The product was dried under vacuum at 80 °C to yield TAL-TK **3** (yield = 376 mg, 90.3%).

TAL-PDK **4** (303 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a dark orange suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a dark red solid. The product was dried under vacuum at 80 °C to yield TAL-TK **4** (yield = 256 mg, 98.4%).

TAL-PDK **5** (527 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a brown suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a yellow-brown paste. The product was dried under vacuum at 80 °C to yield TAL-TK **5** (yield = 455 mg, 100%).

Preparation of TAL-PDK Plastics for Hydrolysis. TAL-PDK resins obtained from ball-milling were pressed into sheets of ~ 1 mm in thickness using a thermal press operating at 110°C for TAL-PDK **5**, 125°C for TAL-PDK **4**, 130°C for TAL-PDK **3**, 140°C for TAL-PDK **2**, and 150 °C for TAL-PDK **1** and 20,000 psi for 20 min. Small rectangular samples used for depolymerization studies were shaped with dimensions of $l = 20$ mm, $w = 5$ mm, $t = 1$ mm.

Acid-Catalyzed Hydrolysis of TAL-PDK Plastics. Plastic TAL-PDK samples were each placed in 40 mL vials containing 5.0 M HCl (15 mL) and a magnetic stirrer. Depolymerization reactions were conducted over 24 h at room temperature while stirring at 500 rpm. Crude triketones were isolated by extraction with CH₂Cl₂ and evaporation of the organic phase. Purified triketones were obtained by recrystallization in ethanol. Percent triketone recovery was calculated by the same equation as for TAL-PDK resin depolymerization.

TAL-PDK **1** (491 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a yellow-brown suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a yellow-brown paste (crude yield = 293 mg, 70.6%). The crude product was recrystallized from ethanol and dried under vacuum at 80 °C to yield pure TAL-TK **1** as a pale orange powder (yield = 182 mg, 43.8%).

TAL-PDK **2** (539 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a brown suspension. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a dark red solid (crude yield = 377 mg, 82.3%). The crude product was recrystallized from ethanol and dried under vacuum at 80 °C to yield pure TAL-TK **2** as brown granules (yield = 206 mg, 45.0%).

TAL-PDK **3** (527 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a yellow-brown precipitate. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a yellow-brown paste (crude yield = 437 mg, 97.1%). The crude product was recrystallized from ethanol and dried under vacuum at 80 °C to yield pure TAL-TK **3** as pale orange crystals (yield = 302 mg, 67.0%).

TAL-PDK **4** (469 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a dark yellow precipitate. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a red-brown solid (crude yield =

409 mg, 101.7%). The crude product was recrystallized from ethanol and dried under vacuum at 80 °C to yield pure TAL-TK **4** as a dark orange powder (yield = 198 mg, 49.3%).

TAL-PDK **5** (564 mg) was completely depolymerized in aqueous 5.0 M HCl (15 mL) over 24 h at room temperature, yielding a yellow precipitate. The mixture was extracted with CH₂Cl₂ (20 mL), and the organic layer was evaporated under vacuum to give a dark yellow paste (crude yield = 546 mg, 112.4%). The crude product was recrystallized from ethanol and dried under vacuum at 80 °C to yield TAL-TK **5** as dark yellow needles (yield = 427 mg, 87.8%).

Quantification of TAL production. 100 μ L cell culture was mixed with 100 μ L acetonitrile before the analysis. This sample was filtered (AcroPrep Advance Filter Plates for Ultrafiltration - 350 μ L, Omega 3K MWCO) at $4,000 \times g$ for 1 h. 5 μ L filtered sample was injected into the HPLC (Agilent Technologies) with a Diode-Array Detector (Agilent, G1315D) with a reverse phase column (Kinetex 5 μ m EVO C18, 150 x 4.6 mm) for analysis. The starting mobile phase was 20 % methanol, which increased to 72 % in 6.5 min. It was further increased to 95 % of methanol from 6.5 to 7.8 min. 95 % methanol was maintained for 1 min to 8.8 min and decreased to 20 % at 9 min. 20 % methanol was maintained until 11.2 min. 0.1 % formic acid was added in the mobile phase. TAL standards were prepared at 0.0625, 0.125, 0.25, 0.5, 1 g L⁻¹ under the same conditions for making the standard curve. The R square of the linear standard curve is > 0.99.

Purification of TAL. The pH of the 1-L broth supernatant was adjusted to pH <2 with HCl and extracted with 3 x 2 L ethyl acetate. The organic phases were separated and combined to 2 L extraction. This extraction was concentrated to 20 mL in rotavapor. Column chromatography was applied on CombiFlash NEXTGEN 300+ with a silica column (RediSep Rf Gold Silica Gel Disposable columns, Cat. No. 69-2203-349) to purify TAL. All fractions containing TAL were combined and dried. NMR is used to determine the purity of TAL, which was >99%.

Techno-Economic Analysis and Life Cycle Assessment of bioTAL Production System.

Biomass-to-TAL production process models used in this study were developed in a commercial process modeling software package—SuperPro Designer-V12.⁵⁸ The process parameters and assumptions for “this work” and optimized scenarios are shown in Supplementary Table 11. Additionally, description and major assumptions for each of the major biomass-to-TAL production system are presented below. For the intermediate and Cao *et al.* scenarios, the same assumptions and parameters were used as that used for the “this work” scenario, unless otherwise noted in relevant sections below.

Feedstock handling. Corn stover was assumed as a representative biomass feedstock for the simulated biorefinery. The biorefinery utilizes 2000 bone-dry metric tons of corn stover per day. The modeling parameters were obtained from Xu *et al.*⁵⁹ The feedstock handling process includes transportation from farm to refinery with shipping distance of 31 miles (50 km) and a handling dome. The milled biomass is routed to the biomass deconstruction unit for pretreatment and enzymatic hydrolysis. The greenhouse gas (GHG) emissions for the feedstock handling and supply of corn stover was assumed to be 83.8 kg CO_{2e} per metric ton of stover.⁶⁰

Corn stover composition

Corn stover composition	wt%
Acetate (bound)	1.81
Ash	4.93
Cellulose	35.05
Hemicellulose	19.53
Lignin	15.76
Other solids	22.93

Biomass Deconstruction. The biomass undergoes pre-treatment to break the cell wall made of recalcitrant lignin and that aids in further enzymatic hydrolysis to convert glucose into cellulose. Here, bio-based ionic liquid (IL) cholinium lysinate [Ch][Lys] is chosen as preferred option for pre-treatment. The biomass deconstruction stage includes pretreatment, enzymatic hydrolysis, solid-liquid separation, and ionic liquid recovery units. The biomass solids loading rate is maintained at 30% by supplying additional water to the biomass and IL mixture. The water is added to ensure better heat and mass transfer when utilizing a high solid loading rate and IL mixture.⁶¹ For all scenarios except optimistic scenario, the IL loading rate is maintained at 0.29 kg per kg of bone-dry corn stover feedstock.⁶² High IL recovery of 97% (99% for optimistic scenario) is assumed,⁵⁹ where IL is recovered post bioconversion through pervaporation technology. The lignin fraction on cellulose can inhibit enzyme accessible areas and overall sugar yields. Treatment with [Ch][Lys] rectifies this and results in dissolution of 31% (17% for optimistic scenario) of lignin fraction.⁶³ The pretreated biomass is sent to the enzymatic hydrolysis unit after pH adjustment using sulfuric acid.

Enzymatic Hydrolysis. Enzymatic hydrolysis releases fermentable sugars, including glucose from cellulose and xylose from xylan. Cellulose to glucose conversion is modeled at 84% and xylan to xylose conversion is considered to be 80%. The enzyme loading rate is maintained at 20 mg-protein/g-cellulose. Initial solids loading is at 20 wt%. Enzymatic hydrolysis is operated at a

temperature of 48 °C for 72 h. The liquid fraction consisting of glucose and xylose is sent to the bioconversion unit. The solid fraction primarily consisting of lignin is sent to on-site combustor for energy generation. The slurry is cooled to 32 °C for bioconversion with a heat exchanger.

Bioconversion. The currently modeled bioconversion process uses *E. coli*. The bioconversion time is assumed to be 74.5 h. Xylose to bioTAL conversion is assumed to be 90% of that of glucose to bioTAL conversion. The fermenter requires 10 vol% of inoculum, and the ratio is maintained by sending 10% of the slurry from enzymatic hydrolysis to the seed fermenters, and the rest to the main bioconversion tank. The seed bioconversion consists of five reactors and designed with the modeling assumptions consistent with Humbird *et al.*⁶⁴ and Yang *et al.*⁶¹ For both seed bioconversion and main bioconversion unit, the nutrient source is assumed to be corn steep liquor (CSL) and diammonium phosphate (DAP). CSL and DAP are used as a placeholder for a low-cost source of providing nitrogen, phosphorus, and other trace minerals and are not actually used in laboratory experiments. However, for production at scale, an alternate source of nutrients could be explored, which may be separate from both modeled source and media used in experiments.⁶⁴ Therefore, in future it is possible to lower the cost of media and obtain consistent yields. For the Cao *et al.*⁶⁵ scenario, the bioconversion time and temperature are assumed to be 120 h and 30 °C, respectively.

Product Separation and Recovery. BioTAL production is extracellular, and therefore the first step in product separation and recovery is separation through solids (cell biomass) from liquid (supernatant). Here, separation is modeled through a centrifuge, and the cell biomass solids are sent to the boiler for co-firing for heat and electricity generation. The supernatant stream undergoes solvent extraction using ethyl acetate. The stream is subsequently treated with sulfuric acid to reduce the pH to 2. The acidification is followed by second round of solvent extraction with ethyl acetate to extract bioTAL with limited contaminants. The ethyl acetate is recovered through distillation. The stream with bioTAL product undergoes drying using a drum (to simulate vacuum evaporation) and then column chromatography, to obtain a product with purity greater than 95%. Methanol used for column chromatography is also recovered through distillation. For both ethyl acetate and methanol used, a 95% of solvent recovery rate is assumed. For the scenario using yield data from Cao *et al.*,⁶⁵ crystallization is used to recover bioTAL instead of column chromatography.

Onsite Energy Generation. The onsite energy (heat and power) generation relies on a combination of unutilized biomass and supplemental natural gas (when needed). Any excess energy is sold to the grid for a credit based on average U.S. electricity prices. While solvent recovery and recycling increases the facility's on-site energy consumption, the cost associated with hazardous waste management is reduced by maximizing solvent recycling. The process model accounts for waste heat recovery.

List of equipment used in process modeling (costs derived from SuperPro)

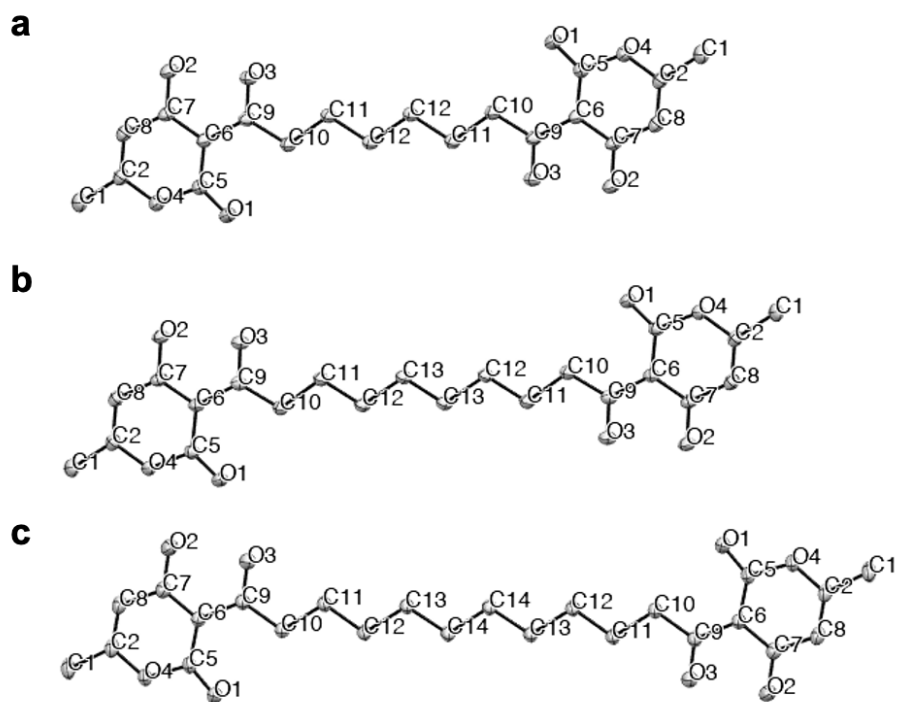
Name	Type	Units	Size (Capacity)	Unit	Unit Price (\$ per unit)	Total Price (\$)
SG-101	Steam generator	1	287.79	MT/h	36,025,000	36,025,000
R-101	Stirred reactor	1	944.27	m ³	6,590,000	6,590,000
S-104	Shredder	4	26.04	MT/h	4,815,000	19,260,000
ET-101	Extraction steam turbine-generator	2	21,718.53	kW	3,559,000	7,118,000
FR-102	Fermentor	2	3,045.40	m ³	2,137,000	8,548,000
FR-106	Fermentor	1	3,025.28	m ³	2,122,000	2,122,000
C-101	Pba column	2	3,141.59	L	2,108,000	4,216,000
DC-101	Decanter centrifuge	1	114,253.08	L/h	1,465,000	1,465,000
DC-102	Decanter centrifuge	1	105,688.66	L/h	1,370,000	1,370,000
CSP-110	Component splitter	1	174.12	MT/h	968,000	968,000
ST-207	Receiver tank	1	2,189.29	m ³	656,000	656,000

BT-205	Blending tank	1	79,413.06	L	441,000	441,000
V-109	Blending tank	2	44,349.91	L	362,000	724,000
D-403	Distillation column	1	40.09	m ³	346,000	346,000
V-101	Blending tank	1	29,357.65	L	320,000	320,000
ST-407	Flat bottom tank	1	596.2	m ³	272,000	272,000
BC-101	Belt conveyor	1	100.00	m	268,000	268,000
V-103	Flat bottom tank	4	753.06	m ³	257,000	1,028,000
RVF-101	Rotary vacuum filter	11	76.77	m ²	216,000	2,376,000
FR-105	Fermentor	1	302.56	m ³	212,000	212,000
ST-311	Flat bottom tank	1	363.66	m ³	180,000	180,000
UF-101	Ultrafilter	106	79.67	m ²	135,000	14,310,000
HX-111	Heat exchanger	4	92.52	m ²	116,000	464,000
DDR-101	Drum dryer	1	0.08	m ²	84,000	84,000
HX-104	Heat exchanger	2	53.29	m ²	83,000	166,000

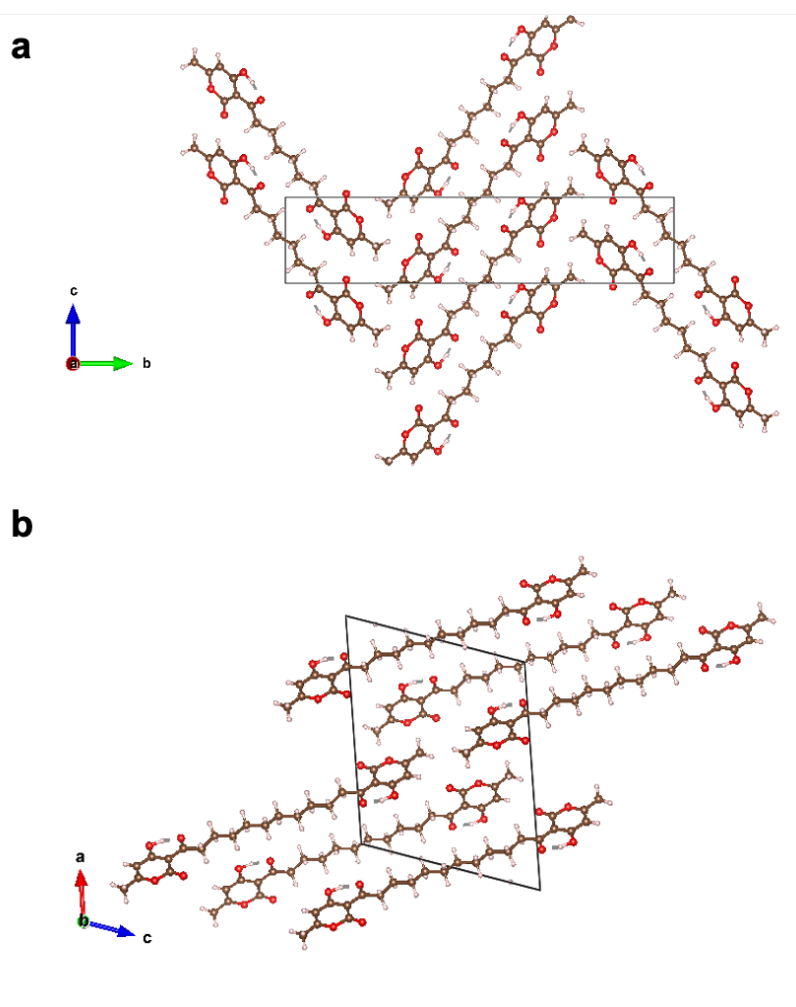
HX-101	Heat exchanger	1	48.45	m ²	79,000	79,000
PM-104	Centrifugal pump	1	6.70	kW	42,000	42,000
CT-101	Cooling tower	3	26,433.84	L	41,000	123,000
P-224	Centrifugal pump	1	6.26	kW	41,000	41,000
ST-302	Hopper	1	10.75	m ³	40,000	40,000
PM-105	Centrifugal pump	1	3.89	kW	33,000	33,000
PM-102	Centrifugal pump	1	3.47	kW	32,000	32,000
411P	Centrifugal pump	1	0.76	HP-E	30,000	30,000
HX-304	Heat exchanger	2	74.26	m ²	29,000	58,000
ST-301	Blending tank	1	43.46	m ³	24,000	24,000
PM-124	Centrifugal pump	1	86.01	kW	23,000	23,000
C-102	Distillation column	1	0.01	m ³	22,000	22,000
FR-104	Fermentor	1	30.29	m ³	21,000	21,000
PM-101	Centrifugal pump	1	1.14	kW	20,000	20,000

502P	Centrifugal pump	1	0.21	HP-E	19,000	19,000
P-300	Centrifugal pump	1	0.84	HP-E	15,000	15,000
P-720	Centrifugal pump	1	0.01	kW	9,000	9,000
PM-103	Centrifugal pump	1	0.00	kW	9,000	9,000
P-760	Centrifugal pump	1	0.00	kW	9,000	9,000
PM-108	Centrifugal pump	1	18.17	kW	8,000	8,000
HX-102	Heat exchanger	1	0.25	m ²	8,000	8,000
HX-105	Heat exchanger	1	0.24	m ²	8,000	8,000
PM-113	Centrifugal pump	1	18.17	kW	7,000	7,000
M-103	Centrifugal fan	33	8,943,502.02	L/h	7,000	215,000
512P	Centrifugal pump	1	0.00	HP-E	6,000	6,000
BT-303	Blending tank	1	615.24	L	6,000	6,000
P-302	Gear pump	1	0.30	kW	2,000	2,000
P-301	Gear pump	1	0.30	kW	2,000	2,000

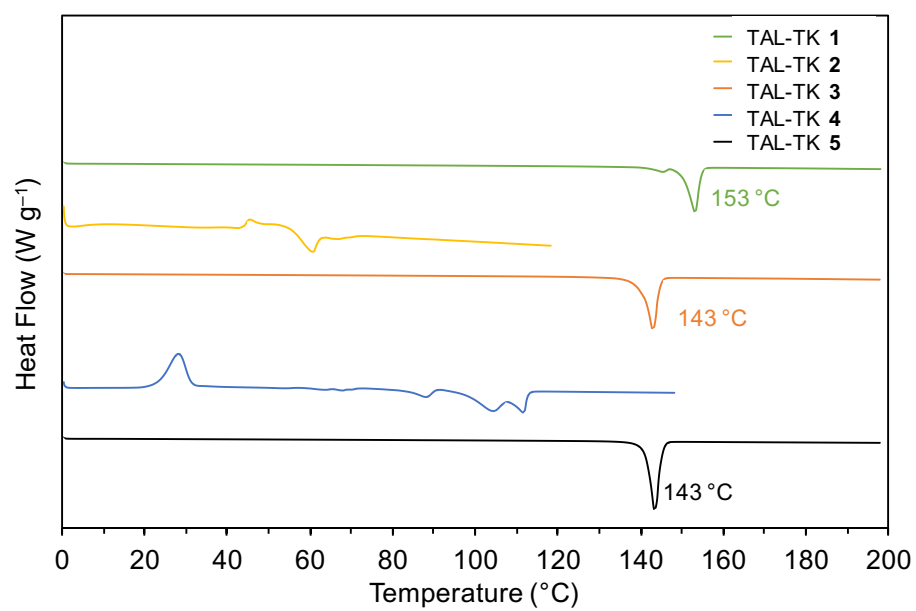
Supplementary Figures



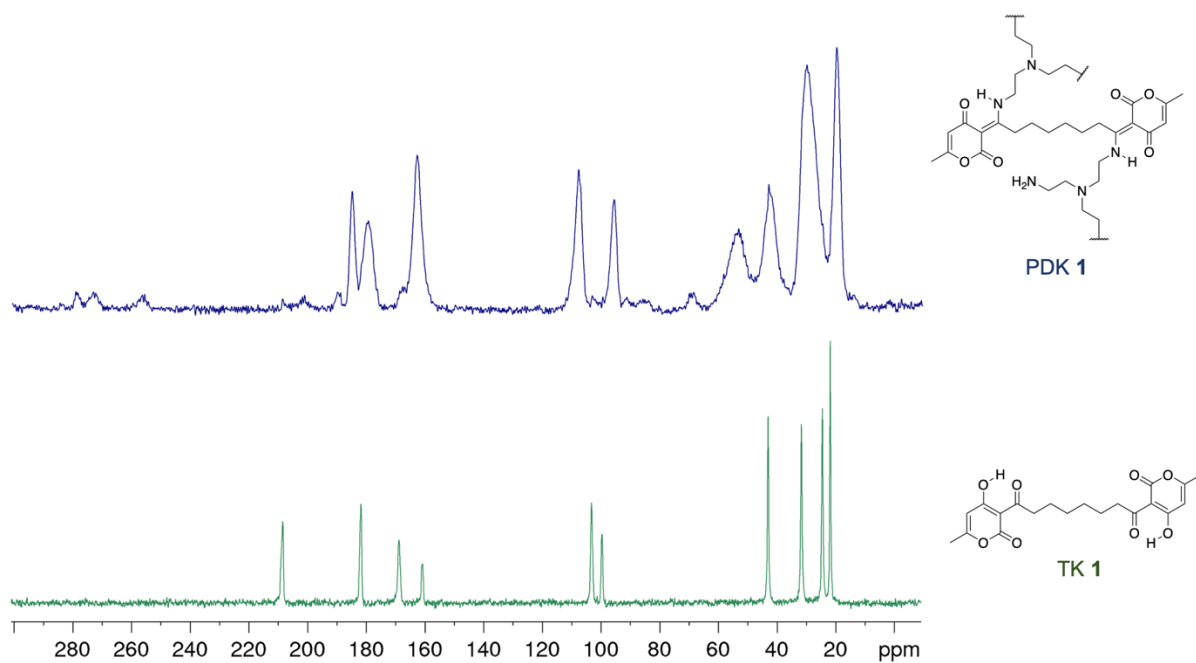
Supplementary Figure 1. Single-crystal XRD. **a**, TAL-TK 1. **b**, TAL-TK 3. **c**, TAL-TK 5. Crystallographic data for compounds TAL-TK 1, TAL-TK 3 and TAL-TK 5 are available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference numbers 2223455, 2223456 and 2223457, respectively.



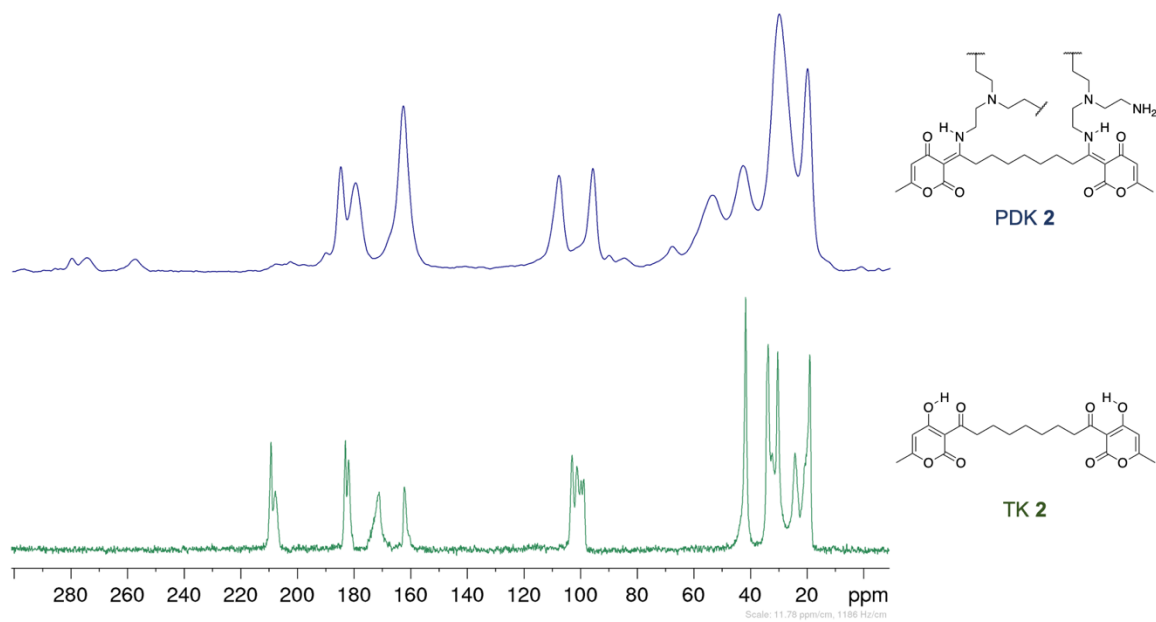
Supplementary Figure 2. Single-crystal XRD. **a**, TAL-TK **1**. **b**, TAL-TK **5**. Crystallographic data for compounds TAL-TK **1** and TAL-TK **5** are available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under reference numbers 2223455 and 2223457, respectively.



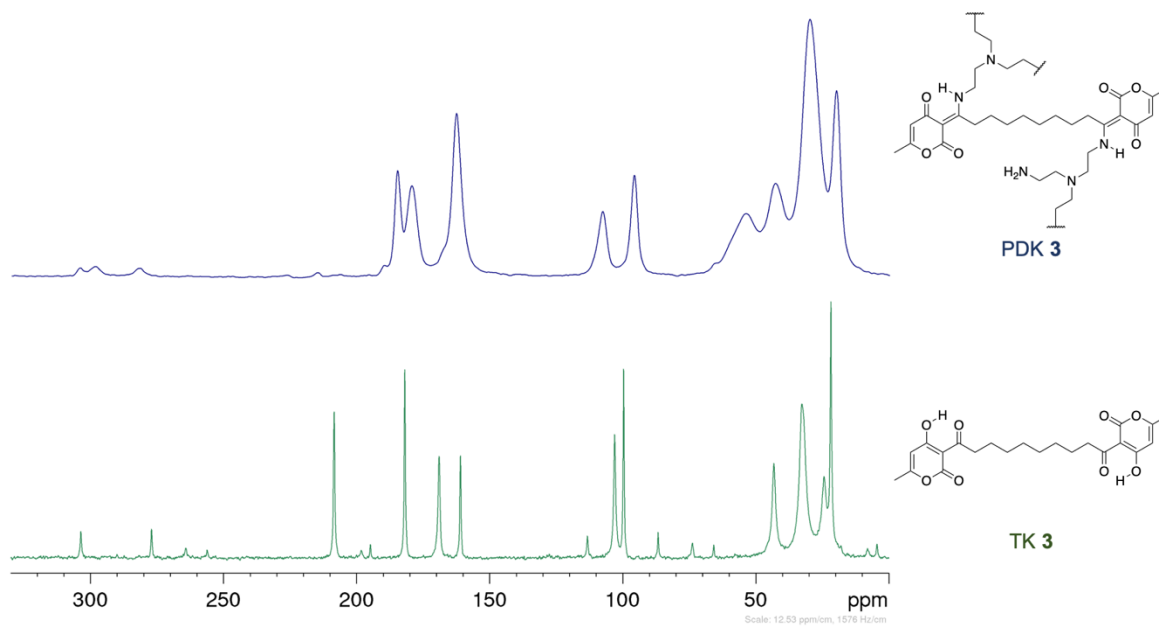
Supplementary Figure 3. DSC of TAL-TK 1–5.



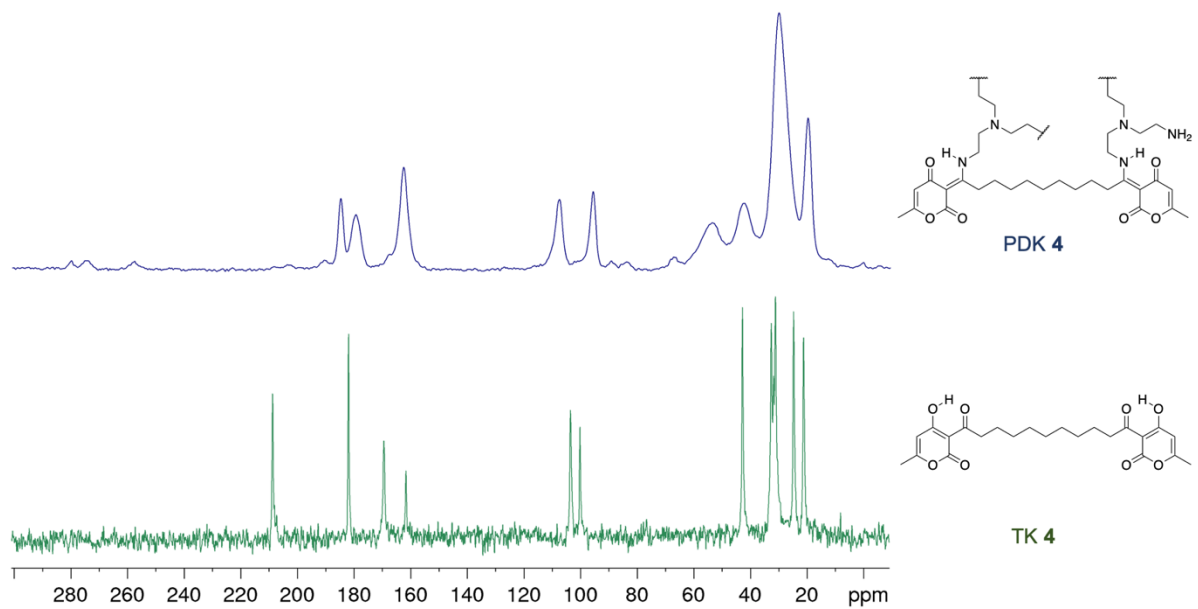
Supplementary Figure 4. Solid-state ^{13}C NMR spectra of TAL-TK 1 and TAL-PDK 1.



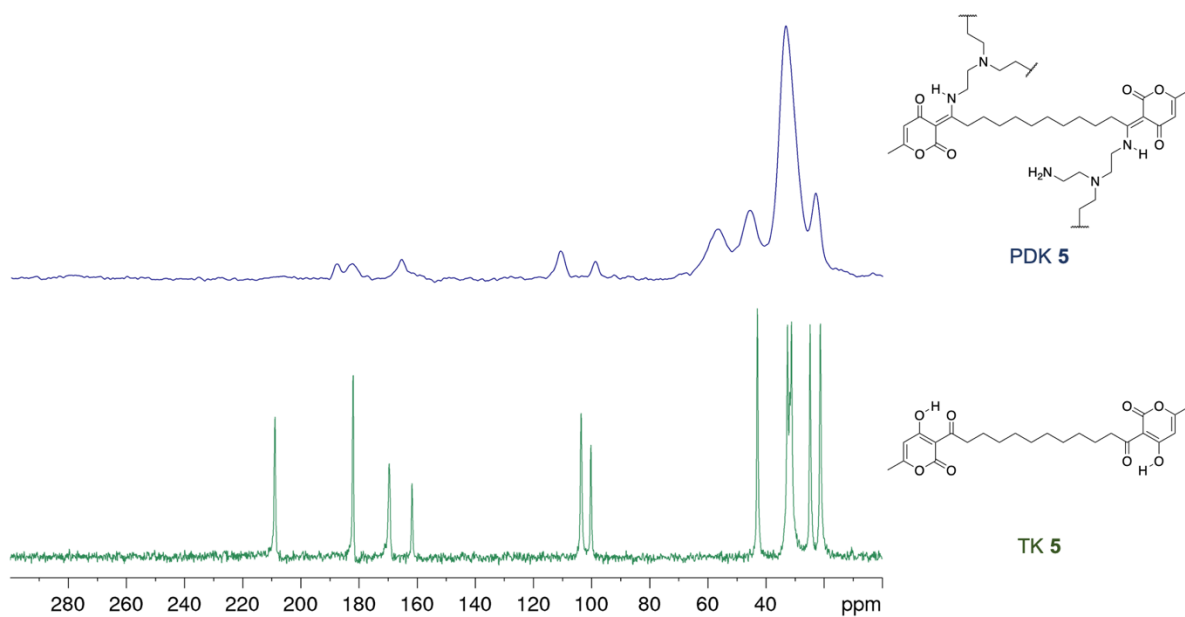
Supplementary Figure 5. Solid-state ^{13}C NMR spectra of TAL-TK 2 and TAL-PDK 2.



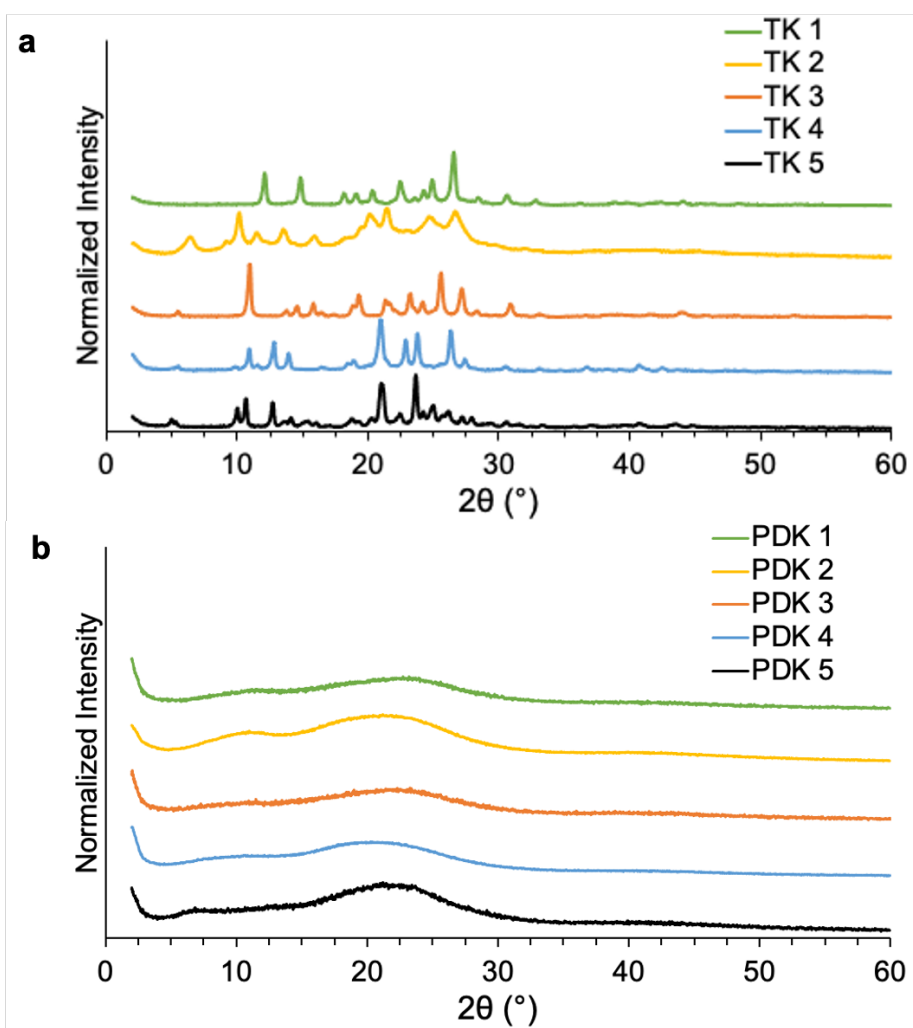
Supplementary Figure 6. Solid-state ^{13}C NMR spectra of TAL-TK 3 and TAL-PDK 3.



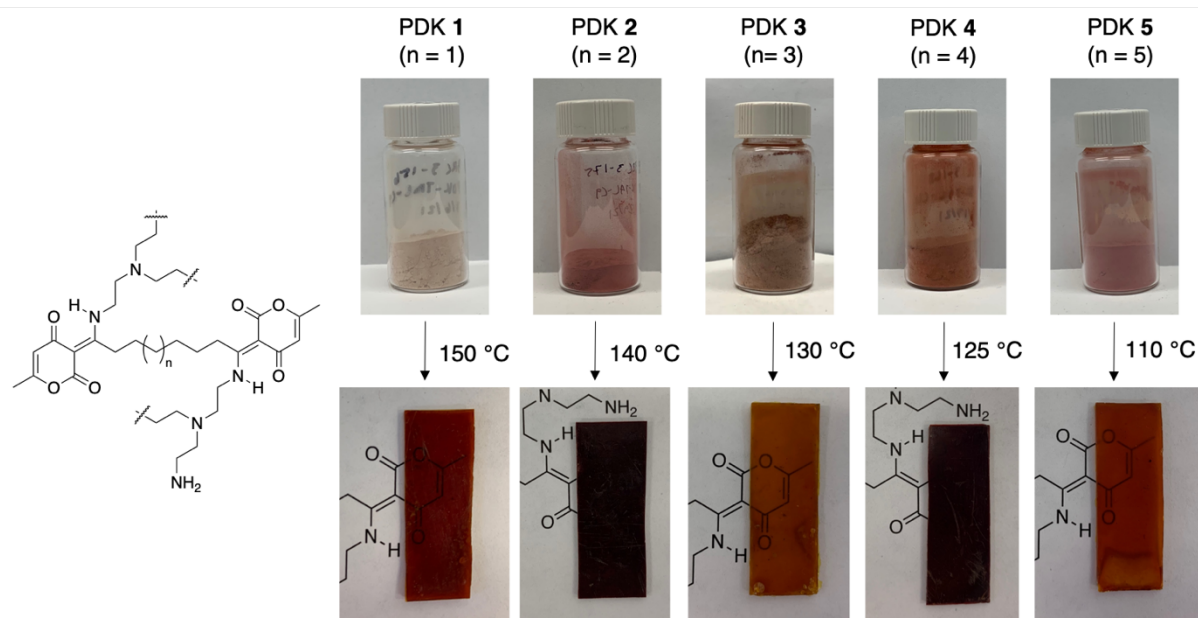
Supplementary Figure 7. Solid-state ^{13}C NMR spectra of TAL-TK 4 and TAL-PDK 4.



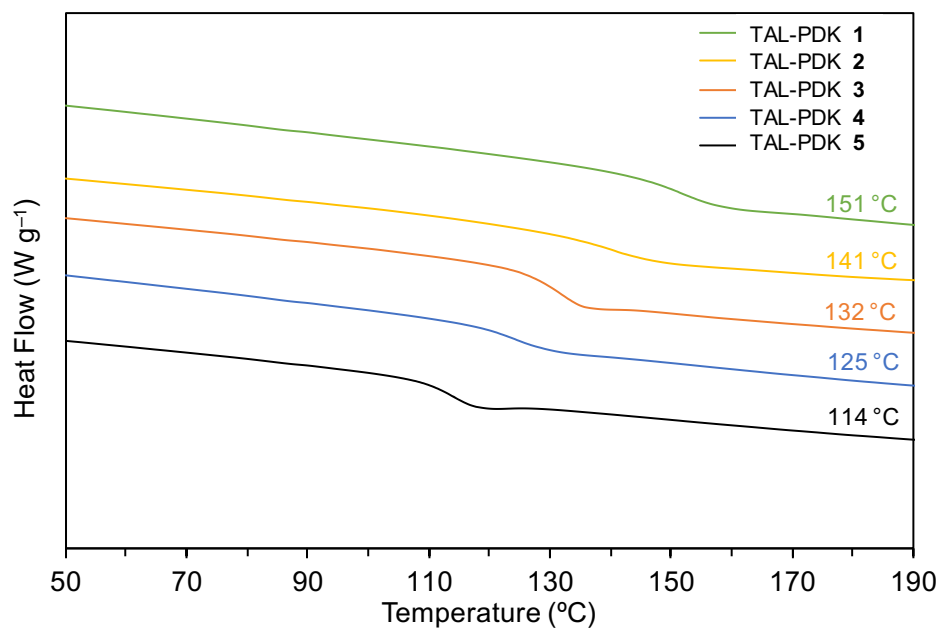
Supplementary Figure 8. Solid-state ^{13}C NMR spectra of TAL-TK 5 and TAL-PDK 5.



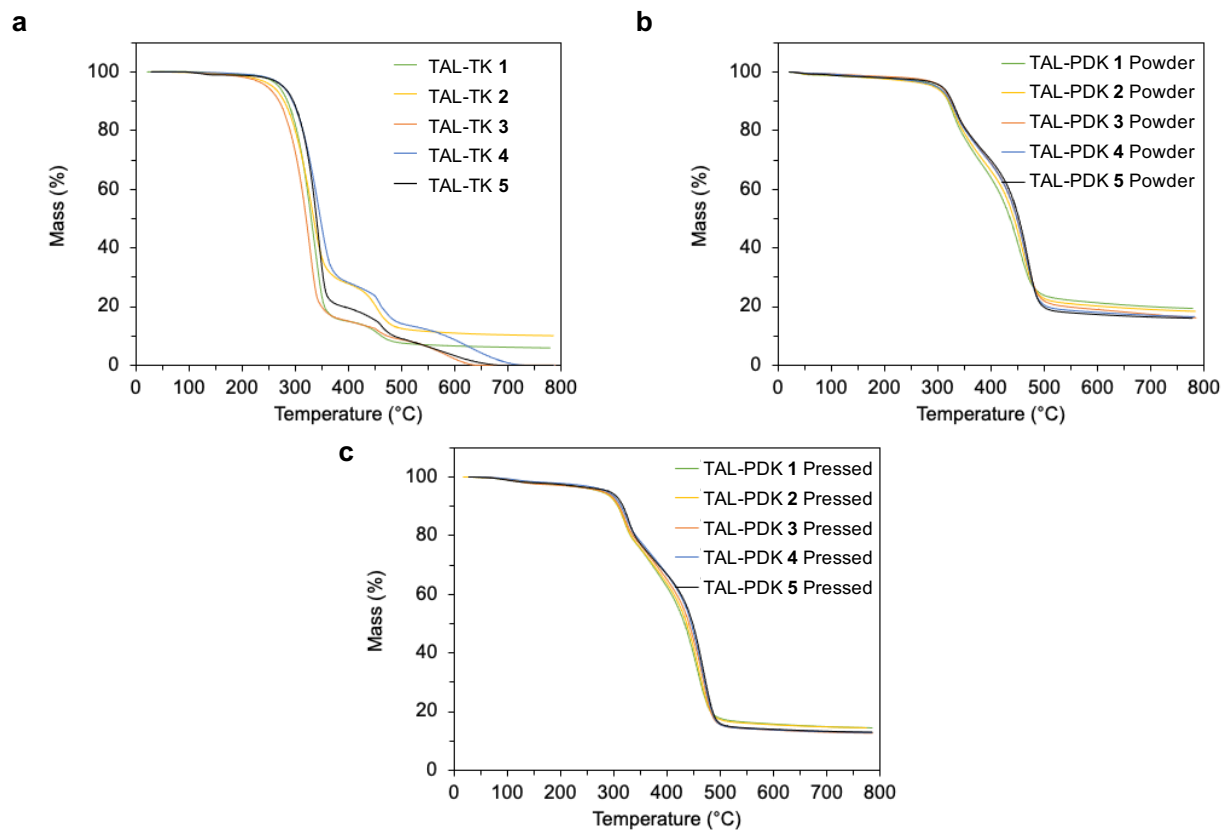
Supplementary Figure 9. PXRD of TAL-TK 1–5 and TAL-PDK 1–5.



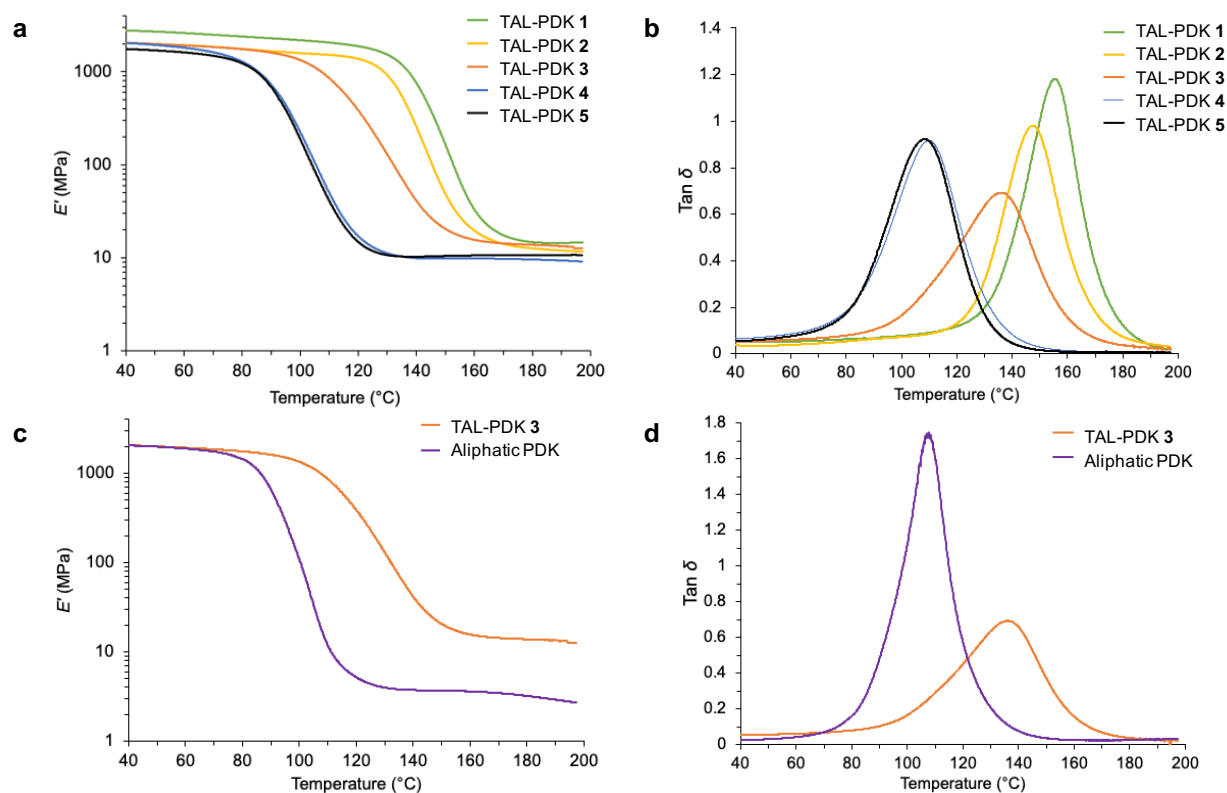
Supplementary Figure 10. Processing of TAL-PDK resins into solid bar samples.



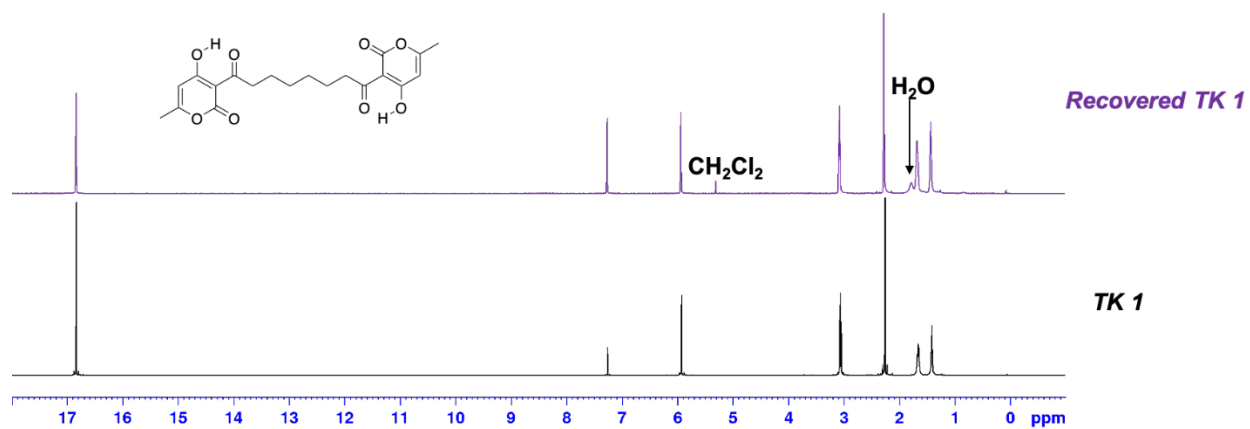
Supplementary Figure 11. DSC of TAL-PDK 1–5.



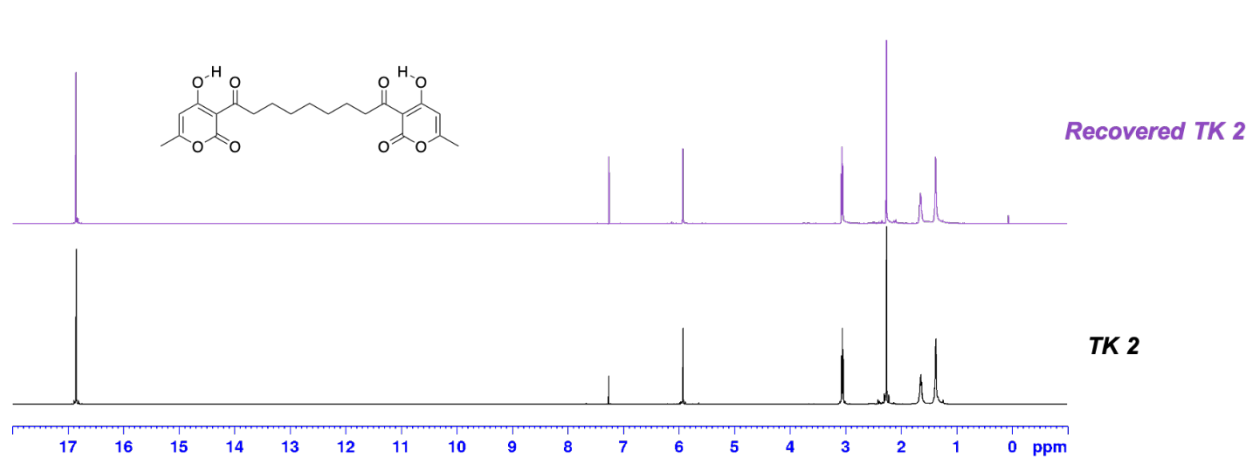
Supplementary Figure 12. TGA of TAL-TK 1–5 and powder and pressed TAL-PDK 1–5.



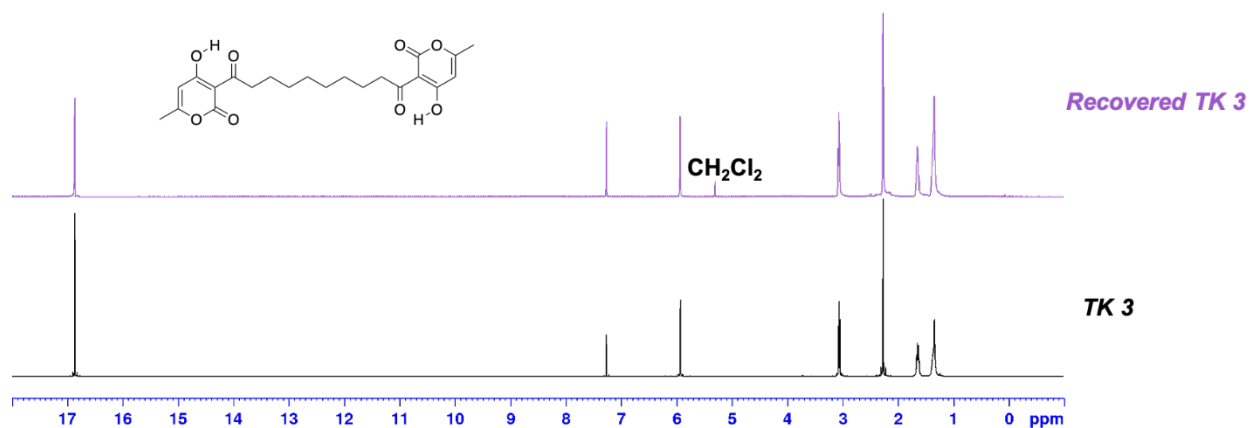
Supplementary Figure 13. DMA of TAL-PDK 1–5 and Aliphatic PDK.



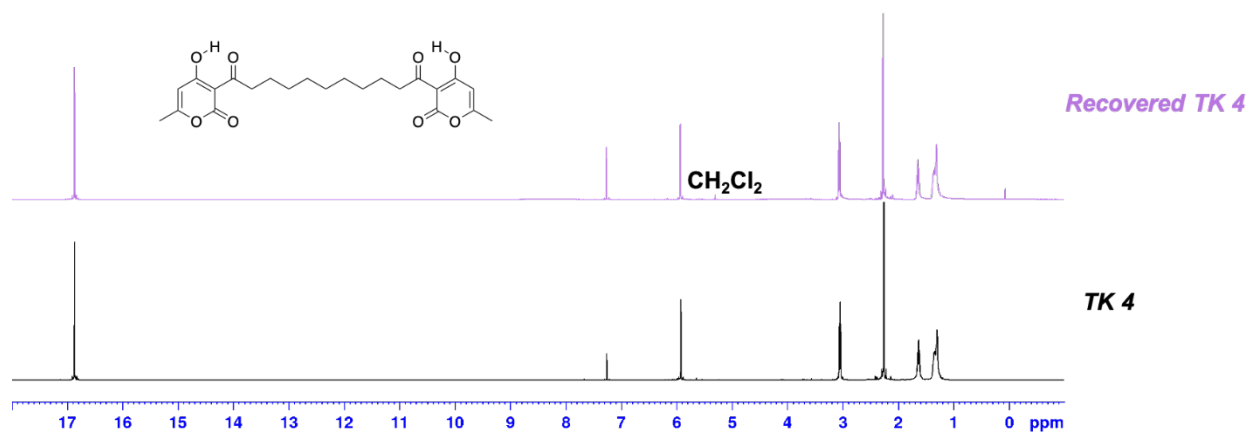
Supplementary Figure 14. ¹H NMR of TAL-TK **1** recovered from depolymerized TAL-PDK **1** resin (*top*) and original TAL-TK **1** monomer (*bottom*).



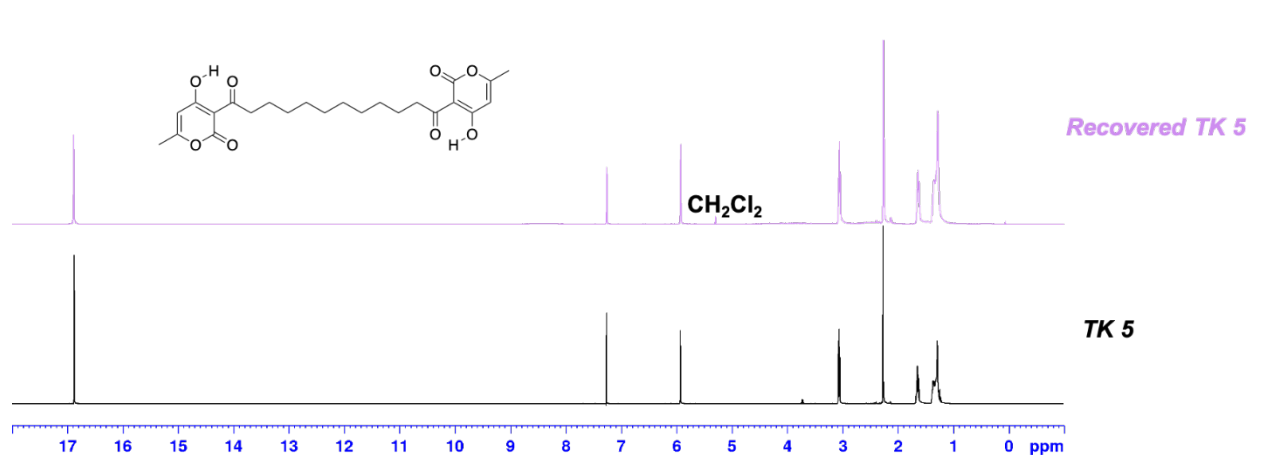
Supplementary Figure 15. ¹H NMR of TAL-TK **2** recovered from depolymerized TAL-PDK **2** resin (*top*) and original TAL-TK **2** monomer (*bottom*).



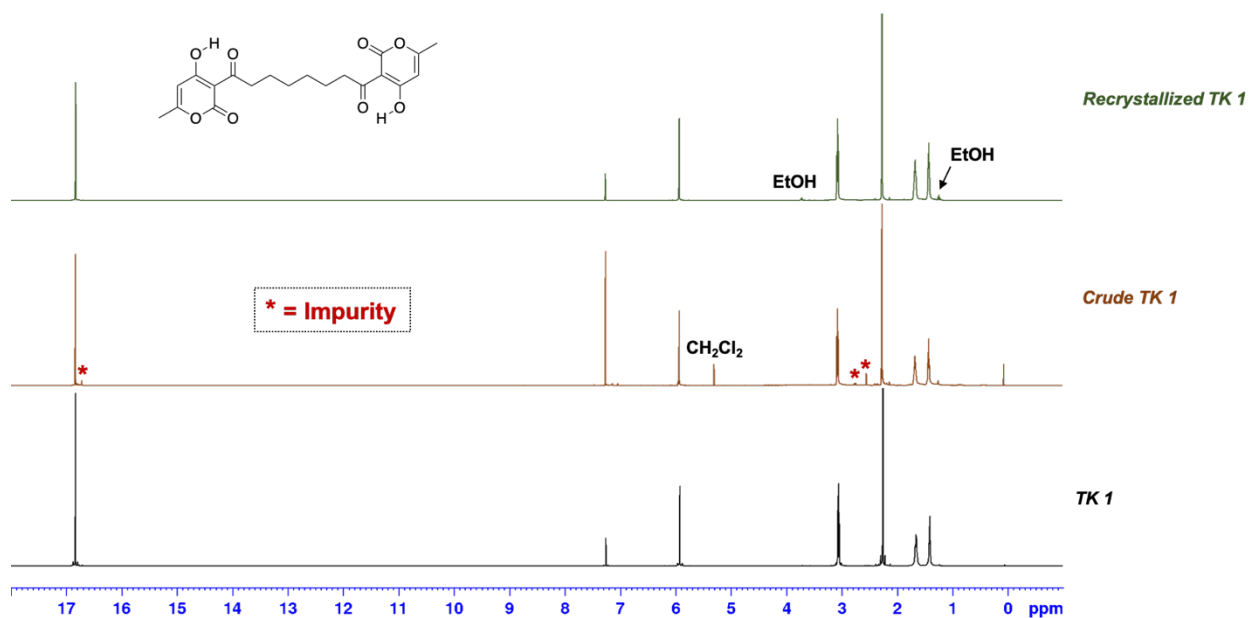
Supplementary Figure 16. ¹H NMR of TAL-TK 3 recovered from depolymerized TAL-PDK 3 resin (*top*) and original TAL-TK 3 monomer (*bottom*).



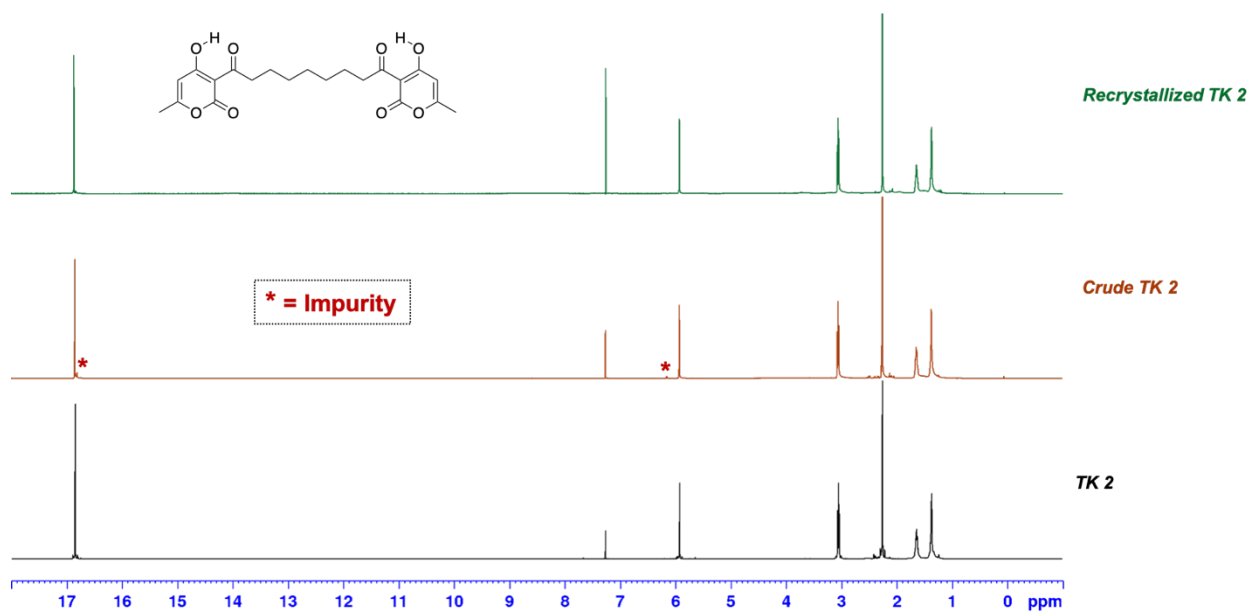
Supplementary Figure 17. ¹H NMR of TAL-TK 4 recovered from depolymerized TAL-PDK 4 resin (*top*) and original TAL-TK 4 monomer (*bottom*).



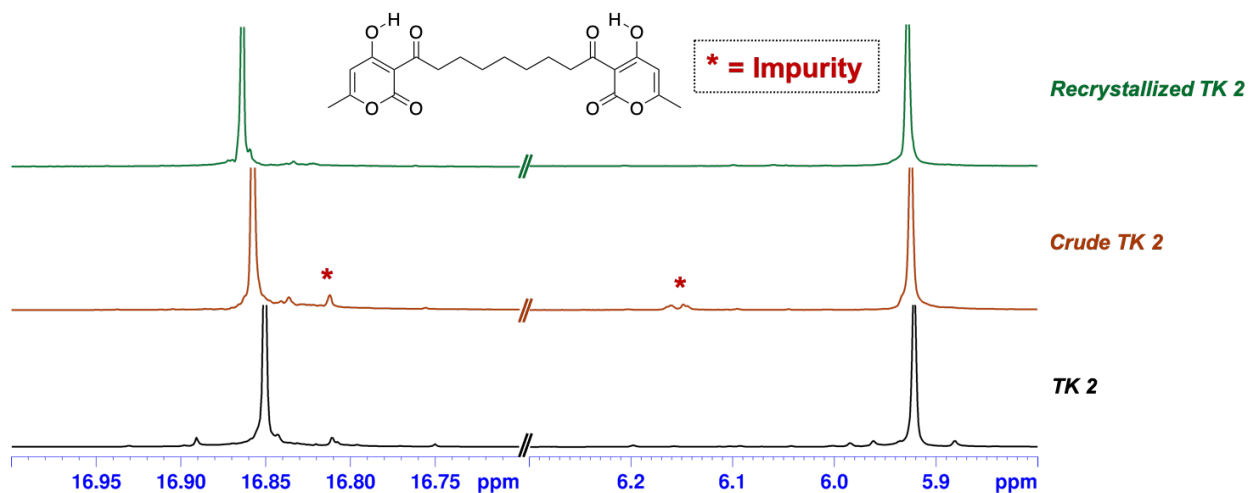
Supplementary Figure 18. ¹H NMR of TAL-TK **5** recovered from depolymerized TAL-PDK **5** resin (*top*) and original TAL-TK **5** monomer (*bottom*).



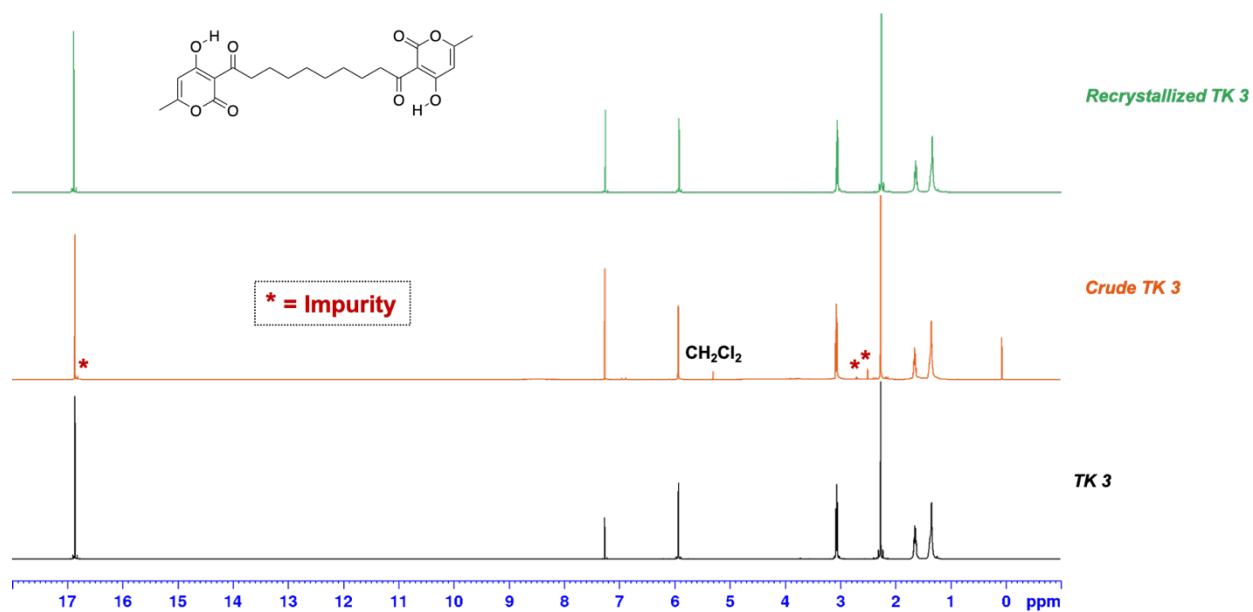
Supplementary Figure 19. ¹H NMR spectra of purified TAL-TK **1** recovered from depolymerized TAL-PDK **1** compression-molded plastics (*top*), crude TAL-TK **1** recovered from depolymerized TAL-PDK **1** compression-molded plastics (*middle*), and original TAL-TK **1** monomer (*bottom*). Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



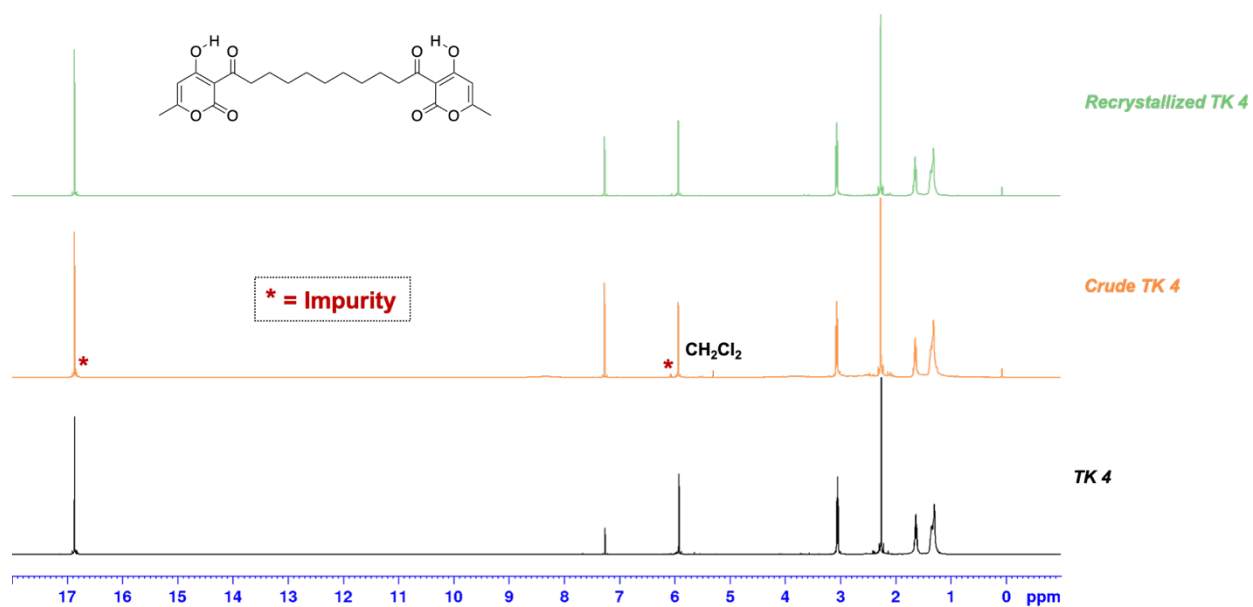
Supplementary Figure 20. ^1H NMR spectra of purified TAL-TK **2** recovered from depolymerized TAL-PDK **2** compression-molded plastics (*top*), crude TAL-TK **2** recovered from depolymerized TAL-PDK **2** compression-molded plastics (*middle*), and original TAL-TK **2** monomer (*bottom*). Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



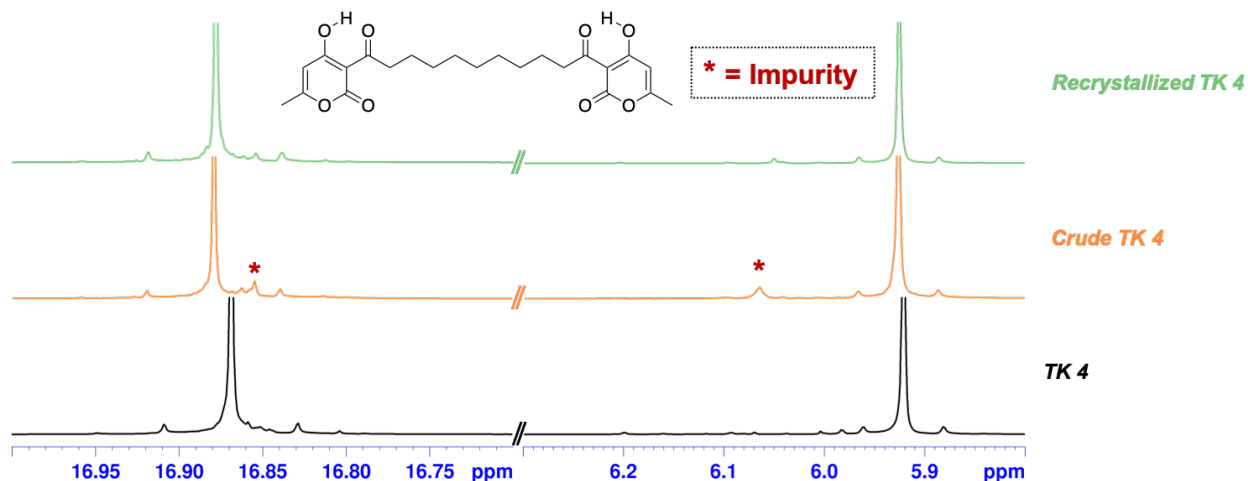
Supplementary Figure 21. ^1H NMR spectra of purified TAL-TK **2** recovered from depolymerized TAL-PDK **2** compression-molded plastics (*top*), crude TAL-TK **2** recovered from depolymerized TAL-PDK **2** compression-molded plastics (*middle*), and original TAL-TK **2** monomer (*bottom*) zoomed in on 5.8–6.3 ppm and 16.7–17.0 ppm. Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



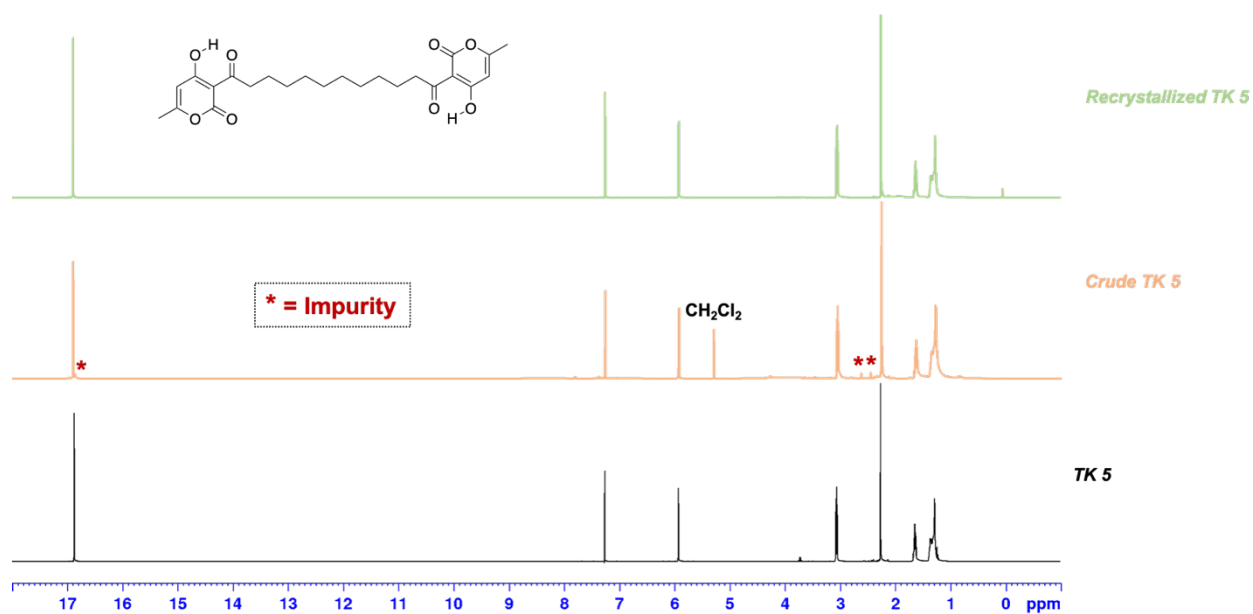
Supplementary Figure 22. ¹H NMR spectra of purified TAL-TK **3** recovered from depolymerized TAL-PDK **3** compression-molded plastics (*top*), crude TAL-TK **3** recovered from depolymerized TAL-PDK **3** compression-molded plastics (*middle*), and original TAL-TK **3** monomer (*bottom*). Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



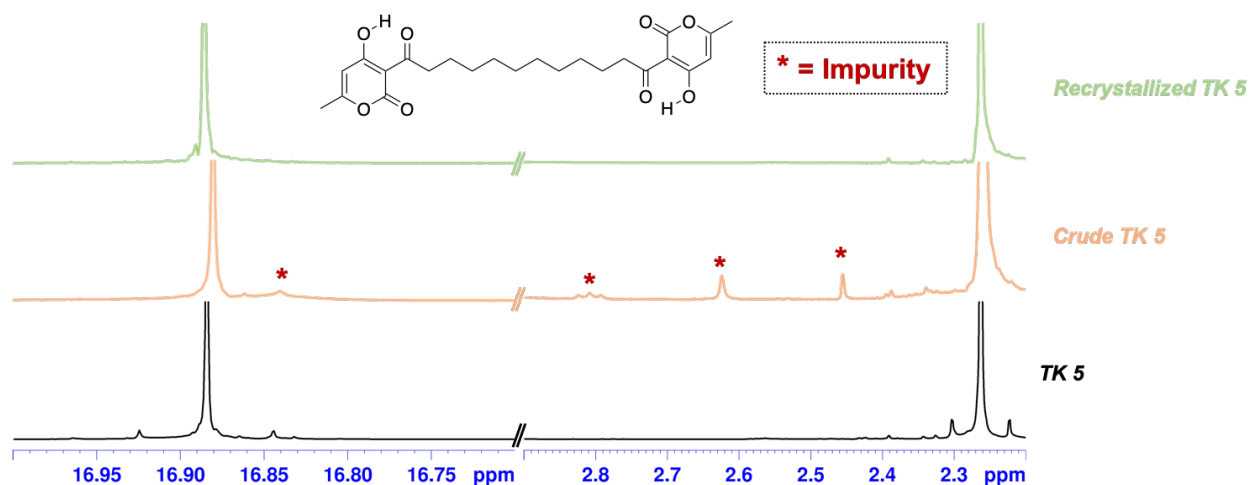
Supplementary Figure 24. ^1H NMR spectra of purified TAL-TK 4 recovered from depolymerized TAL-PDK 4 compression-molded plastics (*top*), crude TAL-TK 4 recovered from depolymerized TAL-PDK 4 compression-molded plastics (*middle*), and original TAL-TK 4 monomer (*bottom*). Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



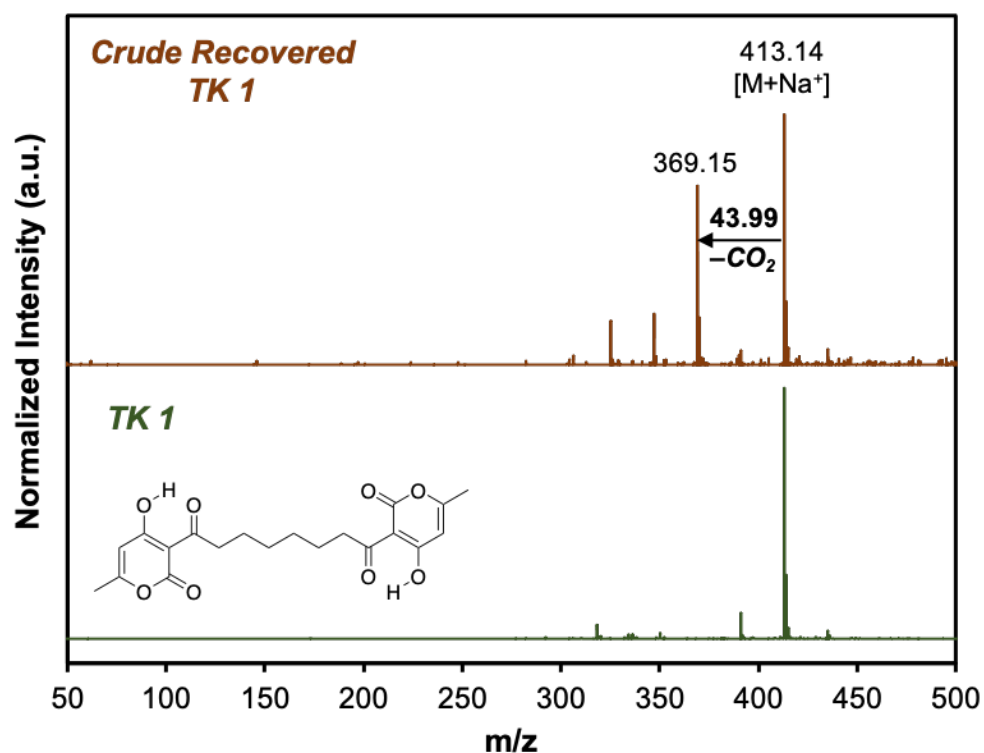
Supplementary Figure 25. ^1H NMR spectra of purified TAL-TK **4** recovered from depolymerized TAL-PDK **4** compression-molded plastics (*top*), crude TAL-TK **4** recovered from depolymerized TAL-PDK **4** compression-molded plastics (*middle*), and original TAL-TK **4** monomer (*bottom*) zoomed in on 5.8–6.3 ppm and 16.7–17.0 ppm. Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



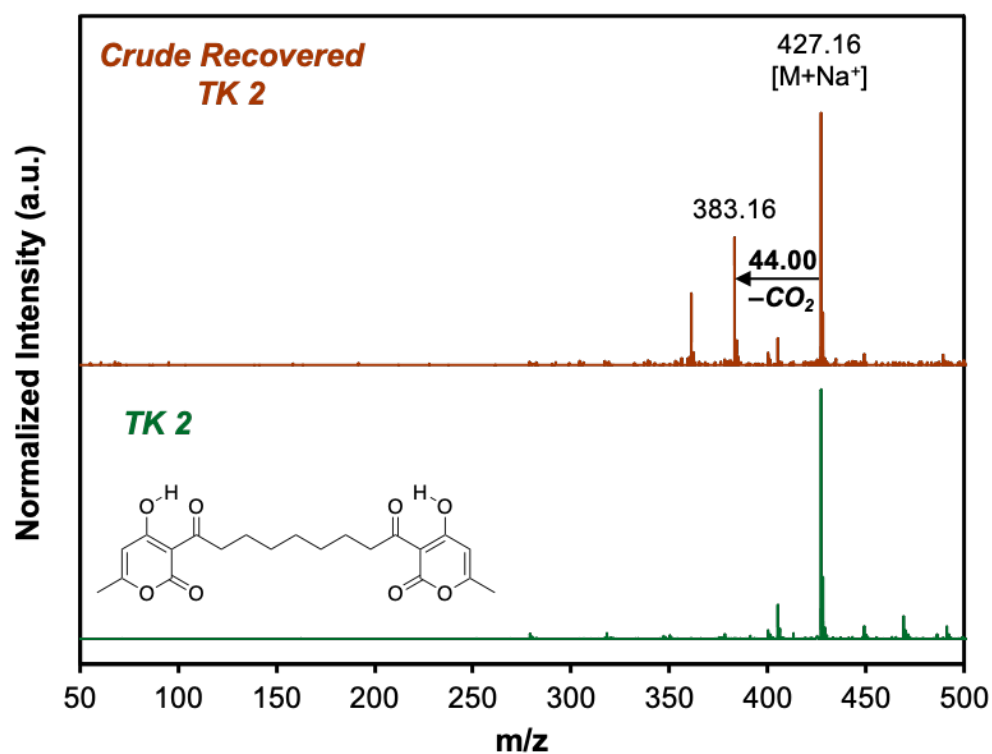
Supplementary Figure 26. ^1H NMR spectra of purified TAL-TK **5** recovered from depolymerized TAL-PDK **5** compression-molded plastics (*top*), crude TAL-TK **5** recovered from depolymerized TAL-PDK **5** compression-molded plastics (*middle*), and original TAL-TK **5** monomer (*bottom*). Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



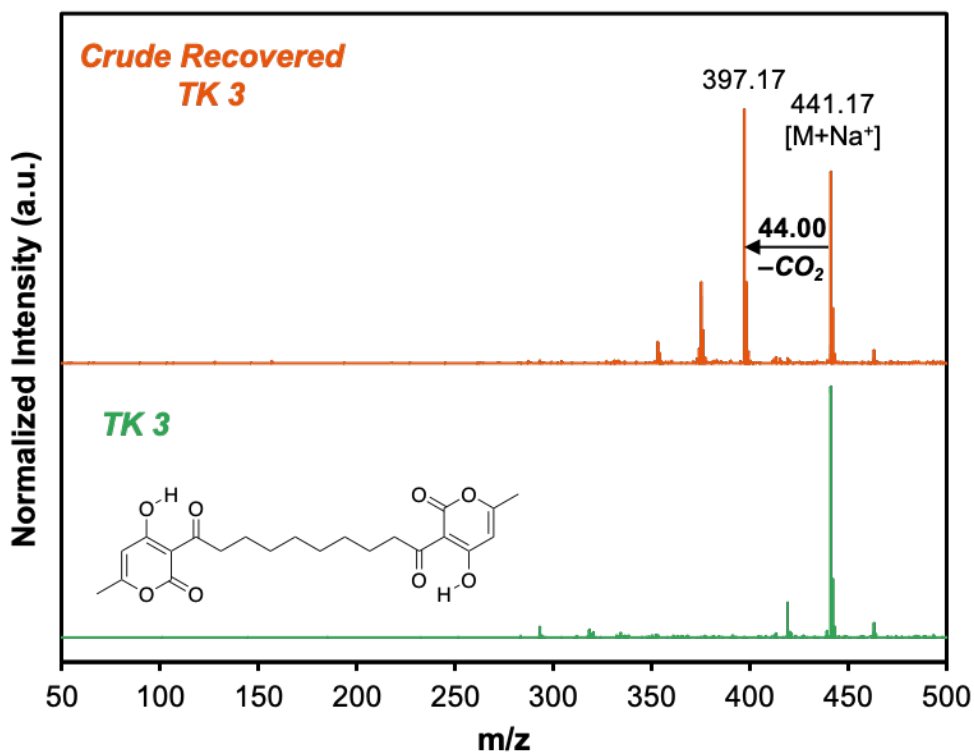
Supplementary Figure 27. ^1H NMR spectra of purified TAL-TK 5 recovered from depolymerized TAL-PDK 5 plastic (*top*), crude TAL-TK 5 recovered from depolymerized TAL-PDK 5 plastic (*middle*), and original TAL-TK 5 monomer (*bottom*) zoomed in on 2.2–2.9 ppm and 16.7–17.0 ppm. Notable impurities caused by parasitic side reactions are identified by a red asterisk (*).



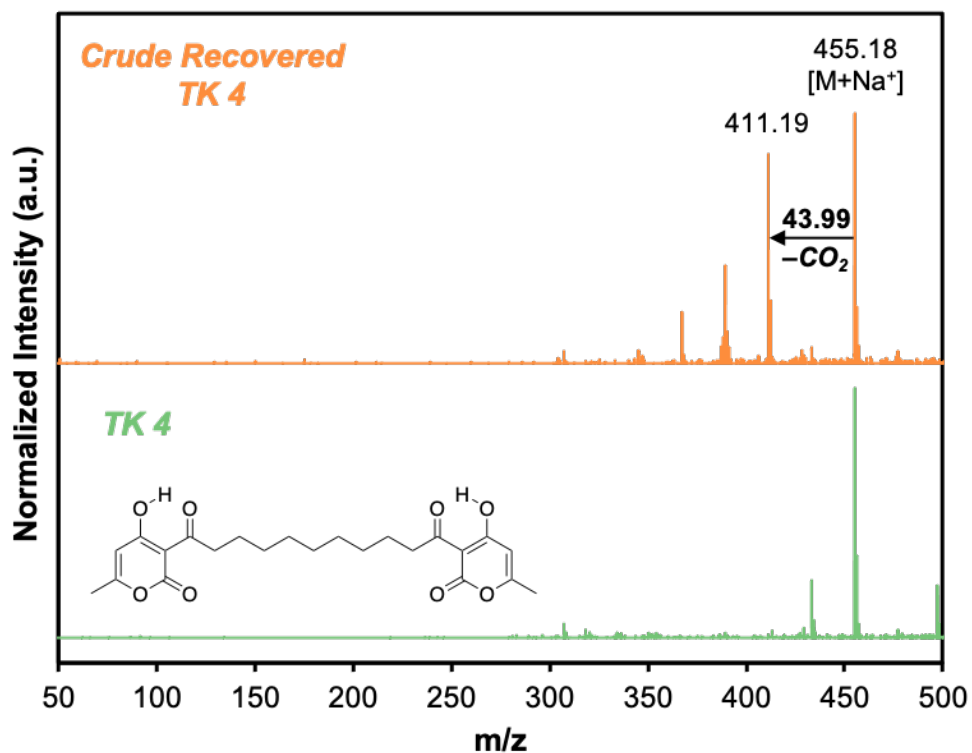
Supplementary Figure 28. ESI-MS spectra of crude recovered TAL-TK 1 from depolymerized TAL-PDK 1 compression-molded plastics (*top*) and original TAL-TK 1 monomer (*bottom*). The prevalent peak corresponding to a decarboxylated subproduct is identified.



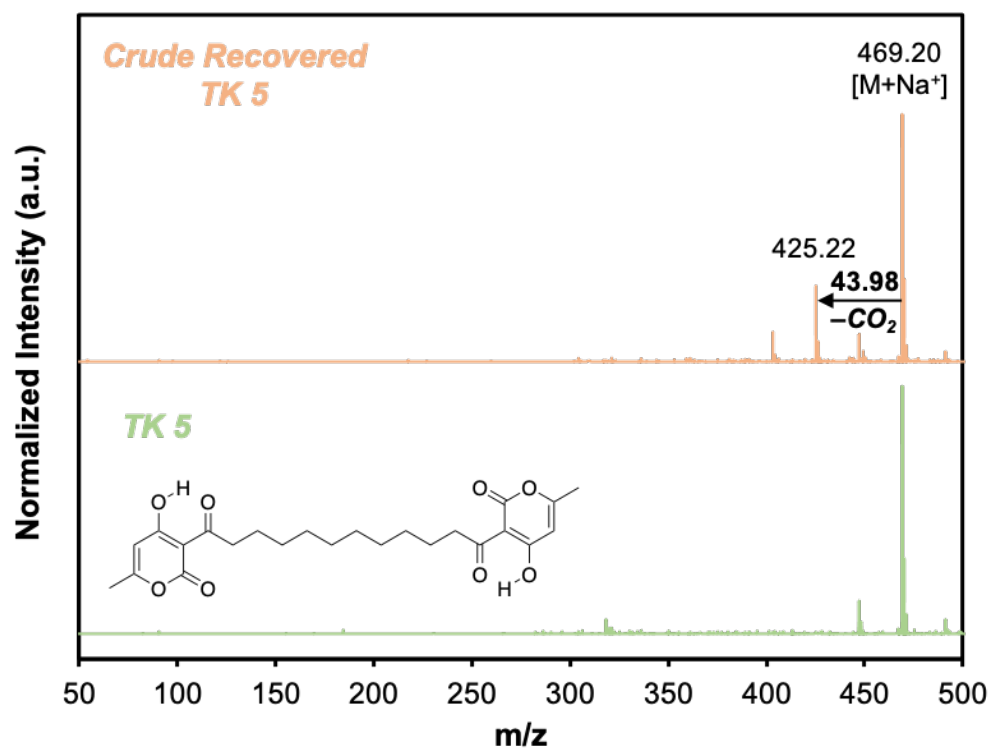
Supplementary Figure 29. ESI-MS spectra of crude recovered TAL-TK **2** from depolymerized TAL-PDK **2** compression-molded plastics (*top*) and original TAL-TK **2** monomer (*bottom*). The prevalent peak corresponding to a decarboxylated subproduct is identified.



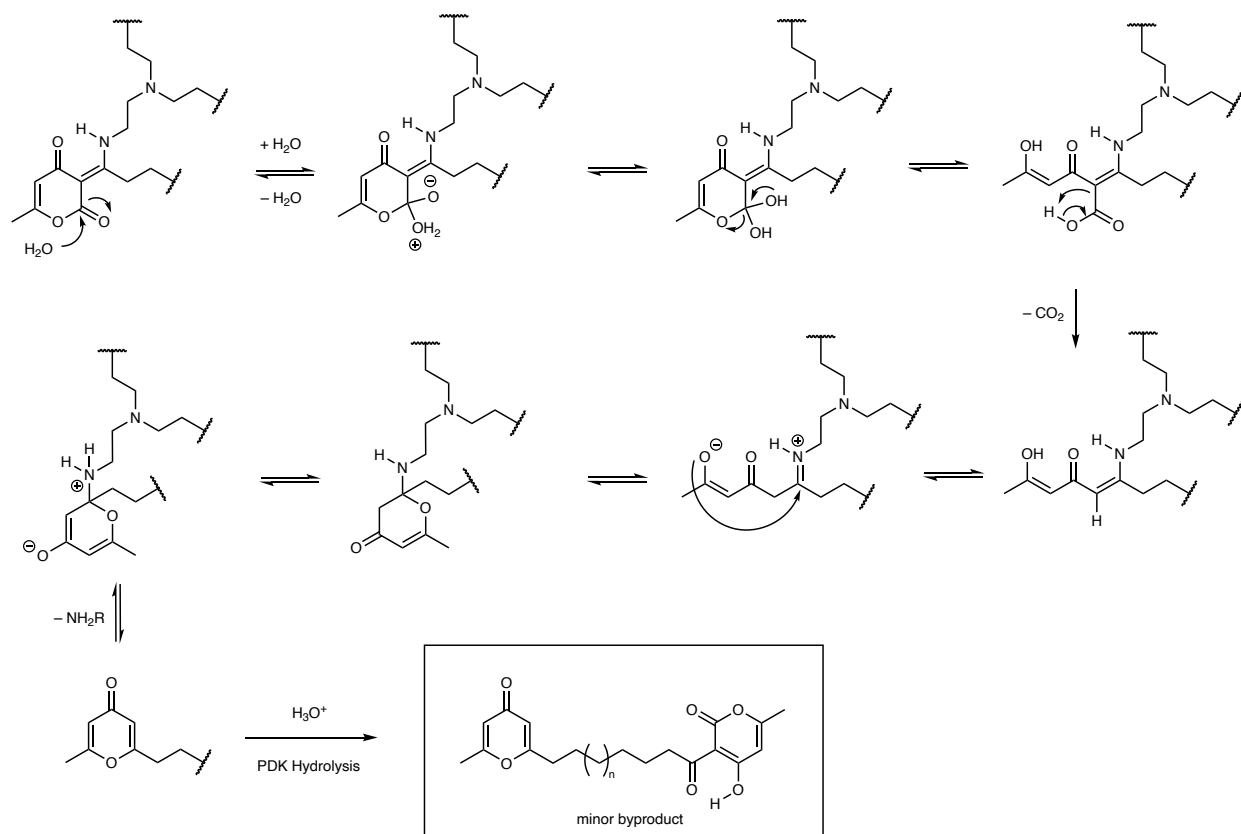
Supplementary Figure 30. ESI-MS spectra of crude recovered TAL-TK 3 from depolymerized TAL-PDK 3 compression-molded plastics (*top*) and original TAL-TK 3 monomer (*bottom*). The prevalent peak corresponding to a decarboxylated subproduct is identified.



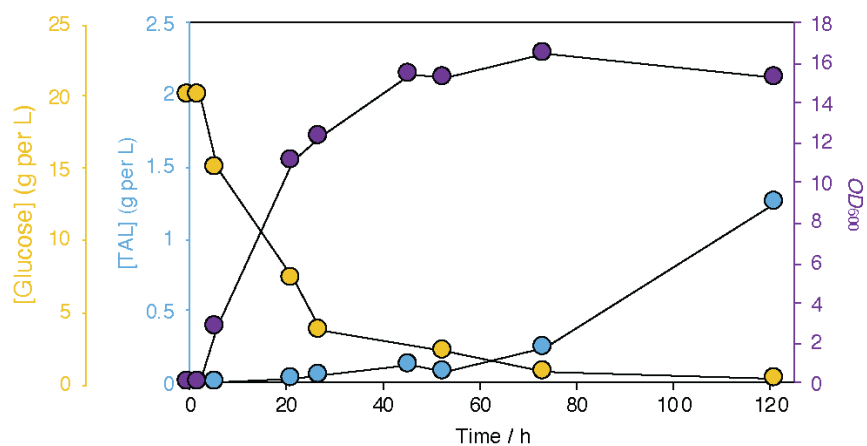
Supplementary Figure 31. ESI-MS spectra of crude recovered TAL-TK 4 from depolymerized TAL-PDK 4 compression-molded plastics (*top*) and original TAL-TK 4 monomer (*bottom*). The prevalent peak corresponding to a decarboxylated subproduct is identified.



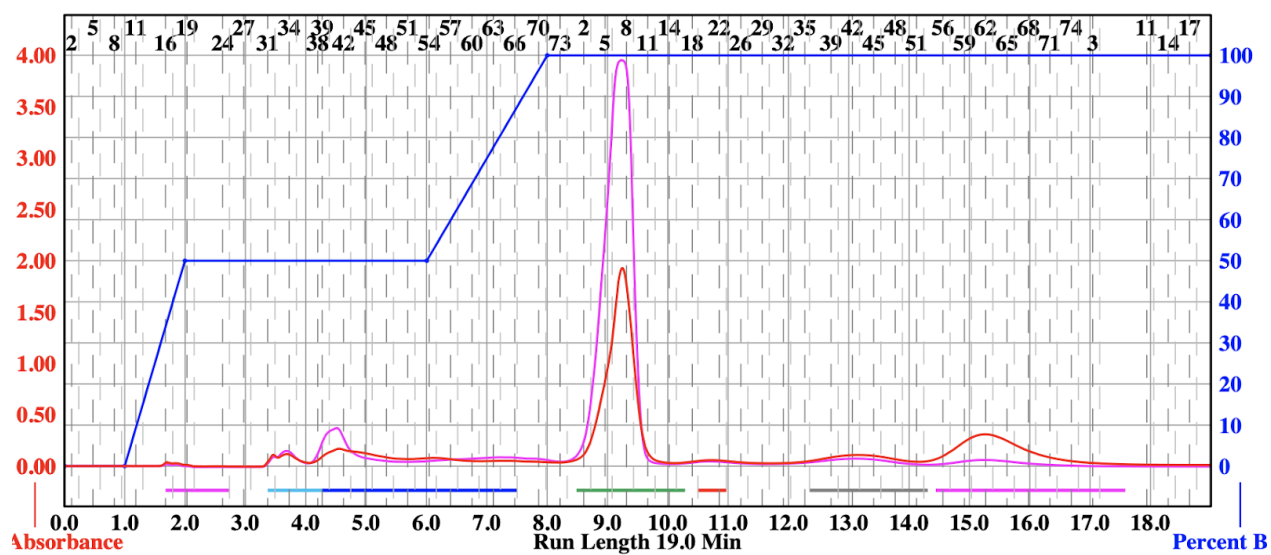
Supplementary Figure 32. ESI-MS spectra of crude recovered TAL-TK **5** from depolymerized TAL-PDK **5** compression-molded plastics (*top*) and original TAL-TK **5** monomer (*bottom*). The prevalent peak corresponding to a decarboxylated subproduct is identified.



Supplementary Figure 33. Mechanistic hypothesis of TAL-PDK degradation leading to pyrone-triketone monomer.



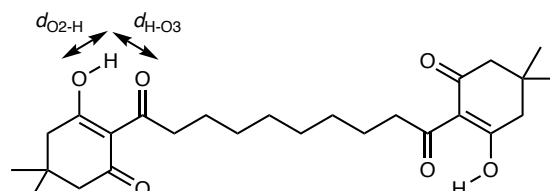
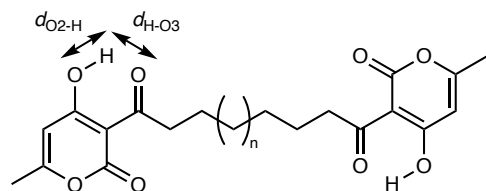
Supplementary Figure 34. 1-L fed batch fermentation of TAL production with *E. coli* JBEI-3695 pBbA5A-BktB. Cell growth (OD_{600}), TAL titer and glucose concentration during the 120-h production run.



Supplementary Figure 35. Dual-wavelength optical densities of eluent acquired during TAL purification by column chromatography. TAL was eluted at 8.5–9.7 min (i.e., the major component of the extracted material post-fermentation). Flow Rate: 110 mL min⁻¹, Solvent A: Hexane, Solvent B: Ethyl Acetate, Wavelength 1 (red): 254 nm, Wavelength 2 (purple): 280 nm.

Supplementary Tables

Supplementary Table 1. Selected O–H bond distances and calculated crystal density extracted from X-ray crystallography data for triketones TAL-TK **1**, **3**, and **5** as well as a dimedone-derived TAL-TK reference.



Triketone	$d_{\text{O2-H}}$ (Å)	$d_{\text{H-O3}}$ (Å)	Crystal ρ (mg m ⁻³)
TAL-TK 1 ($n = 1$)	1.03	1.47	1.476
TAL-TK 3 ($n = 3$)	0.99	1.50	1.426
TAL-TK 5 ($n = 5$)	1.03	1.45	1.354
Dimedone- derived TK	1.08	1.38	1.270

Supplementary Table 2. Densities of TAL-PDK **1–5** and a dimedone-derived PDK reference were determined by displacement via immersion of solid samples (~250 mg) in 5-mL volumetric flasks filled with water at 18 °C.

	ρ (g mL ⁻¹) at 18 °C
TAL-PDK 1	1.129
TAL-PDK 2	1.011
TAL-PDK 3	1.078
TAL-PDK 4	1.032
TAL-PDK 5	1.086
Dimedone-derived PDK	0.987

Supplementary Table 3. Summary of thermo-mechanical data for PDK plastics collected by DMA. T_g measured with $\tan \delta$ (DMA) is also compared with the T_g measured by DSC.

	Tensile Storage Modulus at 40 °C (GPa)	Tensile Elastic Modulus at 180 °C (MPa)	T_g (DMA) (°C)	T_g (DSC) (°C)
TAL-PDK 1	2.78	14.8	155	151
TAL-PDK 2	2.02	12.7	147	141
TAL-PDK 3	2.06	13.8	136	132
TAL-PDK 4	2.04	9.6	110	125
TAL-PDK 5	1.76	10.7	108	114
Dimedone-derived PDK	2.08	3.21	108	96

Supplementary Table 4. Crystal data and structure refinement for TAL-TK 1.

Identification code	TAL-TK 1	
Empirical formula	C ₂₀ H ₂₂ O ₈	
Formula weight	390.37	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 4.7046(3) Å	a = 90°.
	b = 29.1012(15) Å	b = 97.232(2)°.
	c = 6.4669(3) Å	g = 90°.
Volume	878.34(8) Å ³	
Z	2	
Density (calculated)	1.476 Mg/m ³	
Absorption coefficient	0.120 mm ⁻¹	
F(000)	412	
Crystal size	0.140 x 0.080 x 0.010 mm ³	
Theta range for data collection	2.871 to 33.558°.	
Index ranges	-7<=h<=7, -44<=k<=44, -9<=l<=9	
Reflections collected	30567	
Independent reflections	3200 [R(int) = 0.0348]	
Completeness to theta = 25.930°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.913	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3200 / 0 / 132	
Goodness-of-fit on F ²	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1075	
R indices (all data)	R1 = 0.0479, wR2 = 0.1141	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.395 and -0.194 e.Å ⁻³	

Supplementary Table 5. Crystal data and structure refinement for TAL-TK 3.

Identification code	TAL-TK 3	
Empirical formula	C ₂₂ H ₂₆ O ₈	
Formula weight	418.43	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 4.7597(2) Å	a = 90°.
	b = 32.0911(14) Å	b = 97.147(2)°.
	c = 6.4284(3) Å	g = 90°.
Volume	974.27(7) Å ³	
Z	2	
Density (calculated)	1.426 Mg/m ³	
Absorption coefficient	0.114 mm ⁻¹	
F(000)	444	
Crystal size	0.100 x 0.090 x 0.010 mm ³	
Theta range for data collection	2.603 to 29.974°.	
Index ranges	-6<=h<=6, -43<=k<=43, -8<=l<=8	
Reflections collected	15447	
Independent reflections	2640 [R(int) = 0.0363]	
Completeness to theta = 25.930°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.909	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2640 / 0 / 141	
Goodness-of-fit on F ²	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0945	
R indices (all data)	R1 = 0.0447, wR2 = 0.1002	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.351 and -0.192 e.Å ⁻³	

Supplementary Table 6. Crystal data and structure refinement for TAL-TK 5.

Identification code	TAL-TK 5	
Empirical formula	C ₂₄ H ₃₀ O ₈	
Formula weight	446.48	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 17.1106(11) Å	a = 90°.
	b = 4.8661(3) Å	b = 108.440(2)°.
	c = 13.8696(9) Å	g = 90°.
Volume	1095.52(12) Å ³	
Z	2	
Density (calculated)	1.354 Mg/m ³	
Absorption coefficient	0.106 mm ⁻¹	
F(000)	476	
Crystal size	0.310 x 0.020 x 0.010 mm ³	
Theta range for data collection	2.573 to 31.397°.	
Index ranges	-24 ≤ h ≤ 24, -6 ≤ k ≤ 6, -19 ≤ l ≤ 19	
Reflections collected	35253	
Independent reflections	3335 [R(int) = 0.0416]	
Completeness to theta = 25.930°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.907	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3335 / 0 / 150	
Goodness-of-fit on F ²	1.057	
Final R indices [I > 2σ(I)]	R1 = 0.0374, wR2 = 0.1098	
R indices (all data)	R1 = 0.0441, wR2 = 0.1152	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.356 and -0.188 e.Å ⁻³	

Supplementary Table 7. Recipe of the EZ-rich media.

Composition	Volume / μL
10x MOPS	1000
0.132 M K_2HPO_4	100
10x AGCU	1000
5x Supplement EZ	2000
100 g L^{-1} tryptone + 50 g L^{-1} yeast extract, autoclaved	1000
600 g L^{-1} glucose	330
Autoclaved water	4500
1.0 M Calcium pantothenate	50
100 mg mL^{-1} carbenicillin	10
5.0 mM sodium selenite	10
Total	10000

Supplementary Table 8. Material mass-balance for bioTAL production for the intermediate scenario

Material	Input (kg per year)	Output (kg per year)
Acetate (bound)	11,962,500	21,463
Ash	32,505,000	33,889,661
bioTAL	0	85,126,585
Cellulose	231,330,000	31,083,796
Ionic liquid	3,473,684	3,181,788
Corn steep liquor	2,591,164	0
Diammonium phosphate	324,507	0
<i>E. coli</i>	6	81,413,189
Ethyl acetate	8,595,738	8,595,738
Glucose	0	35,438,391
Hemicellulose	128,865,000	21,737,943
Hydrolase	4,626,600	752,604
Lactic acid	0	8,382,764
Lignin	104,032,500	128,793
Methane	1,188,000	0
Methanol	4,343	4,343
Other solids	151,305,000	1,340,004
Return cooling water	8,395,200,000	0
Soluble lignin	0	285,617
Sulfuric acid	132,387,595	128,416,213
Water	1,582,686,415	10,129,267,443
Xylose	0	19,316,246
TOTAL	10,791,078,052	10,588,382,581

*Only make-up amount is shown in the mass-balance stream. Solvent recycling is assumed to be 95% for the intermediate case.

Supplementary Table 9. Major costs and revenue for bioTAL production for different scenarios

Scenario	Inside Battery Limit (ISBL)	Total capital investment	Operating cost	MSP (\$ per kg)
<i>Cao et al.</i>	\$86,270,963	\$469,063,217	\$117,984,886	\$11.53
This work	\$81,911,313	\$ 448,460,310	\$107,876,774	\$9.24
Intermediate	\$97,154,363	\$512,976,541	\$123,403,858	\$2.98
Optimized	\$138,511,325	\$651,527,281	\$137,960,350	\$1.19

Supplementary Table 10. Material and energy inputs for bioTAL production (intermediate scenario)

Material input	Amount	Unit
Ionic liquid	0.04	kg per kg bioTAL
Ionic Liquid (recycle)	1.32	kg per kg bioTAL
Corn liquor	0.03	kg per kg bioTAL
Diammonium phosphate	0.0038	kg per kg bioTAL
<i>E. Coli</i>	0.0705	mg per kg bioTAL
Ethyl acetate	1.92	kg per kg bioTAL
Ethyl acetate (makeup)	0.10	kg per kg bioTAL
Hydrolase	0.05	kg per kg bioTAL
Methane	0.01	kg per kg bioTAL
Methanol	969.2	mg per kg bioTAL
Methanol (makeup)	51.0	mg per kg bioTAL
Stover	9.69	kg per kg bioTAL
Sulfuric acid	1.56	kg per kg bioTAL
Water	64.34	kg per kg bioTAL
Electricity required	3.24	kWh per kg bioTAL
Electricity generated	3.64, resulting in −0.4 kWh per kg credit	kWh per kg bioTAL

Supplementary Table 11. Process parameters and assumptions

Process Parameters	Units	This Work	Optimized	Source
Corn stover	bone-dry metric ton(bdt)/day	2000	2000	Xu, et al., 2016 ⁵⁵
Cost of corn stover	\$/bdt	87.83	71.26	Davis et al., 2018 ⁶⁶
Cellulose	wt%	28.04	35.1	Xu, et al., 2016 ⁵⁵
Hemicellulose	wt%	15.62	19.5	Humbird et al., 2011 ⁶⁰
Ionic liquid (IL) pre-treatment				
Solids loading rate	wt%	30	30	Baral et al. 2019 ⁶²
Ionic liquid ([Ch][Lys]) loading rate	kg/kg-dry biomass	0.29	0.125	Baral et al. 2019 ⁶²
Ionic liquid ([Ch][Lys]) cost	\$/kg	2	0.5	Xu et al.,2016 ⁵⁵
Sulfuric acid loading	kg/kg- IL	0.2	0.07	Magurudeniya et al., 2021 ⁵⁹
Sulfuric acid price	\$/kg	0.14	0.14	Alibaba
Lignin to soluble lignin	wt%	31	17	Magurudeniya et al., 2021 ⁵⁹
Pretreatment time	h	3	1	Magurudeniya et al., 2021 ⁵⁹
IL recovery rate	wt%	97	99	Xu et al.,2016 ⁵⁵
Enzymatic hydrolysis				
Solids loading rate	wt%	25	25	Baral et al. 2019 ⁶²
Enzyme loading rate	mg/g-glucan	20	10	Baral et al. 2019 ⁶²
Cellulose to glucose	wt%	84	95	Baral et al. 2019 ⁶²
Xylan to xylose	wt%	80	90	Baral et al. 2019 ⁶²
Temperature	°C	48	48	Humbird et al.,2011 ⁶⁰
Hydrolysis time	h	72	48	Baral et al. 2019 ⁶²
Enzyme (hydrolase) price	\$/kg-protein	4.29	4.29	Xu et al.,2016 ⁵⁵
Bioconversion				
Cost of corn steep liquor	\$/kg	0.1	0.1	Baral et al. 2019 ⁶²
Cost of diammonium phosphate	\$/kg	1	1	Baral et al. 2019 ⁶²

Aeration rate	vvm	0.5	0.5	Experimental results (this work)
Power consumption	kW/m ³	0.5	0.5	Baral et al. 2019 ⁶²
Power dissipation to heat	%	40	40	Baral et al. 2019 ⁶²
Temperature	°C	22	22	Experimental results (this work)
Bioconversion time	h	74.5 [*]	48 [†]	*Experimental results (this work). †Modeling assumption
Glucose to bioTAL	wt%	14.9	90	x% of theoretical yield, calculations
Xylose to bioTAL	g bioTAL/g xylose	0.094	0.567	Modeling assumption
Onsite energy generation				
Boiler heat loss		5%	5%	Vakkilainen et al. 2017 ⁶⁷

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