Supporting Information for:

Tricyclononenes and Tricyclononadienes as Efficient Monomers for Controlled ROMP: Understanding Structure–Propagation Rate Relationships and Enabling Facile Post-Polymerization Modification

Landon J. Kilgallon,¹ Timothy P. McFadden,² Matthew S. Sigman,² Jeremiah A. Johnson^{1,3,4}

Affiliations

¹Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

²Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, United States

³Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, 500 Main Street, Cambridge, MA 02139, U.S.A.

⁴Broad Institute of MIT and Harvard, Cambridge, MA, 02142, USA

Corresponding Author's Email: jaj2109@mit.edu

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Section 1: Materials and Methods

Instrumentation: ¹H and ¹³C, and NMR spectra were recorded either a 400 MHz Bruker Avance-III Nanobay, 400 MHz Bruker Avance Neo, or 500 MHz Bruker Avance Neo NMR spectrometer. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent peak (CDCl₃, 7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR). High resolution mass spectra were recorded on a JEOL AccuTOF 4G LC-plus equipped with an ionSense DART (Direct Analysis in Real-Time). Microwave reactions were performed in a Biotage Initiator+ microwave synthesizer. Size Exclusion Chromatography (SEC) analysis was performed on an Agilent 1260 Infinity HPLC stack with two Agilent PL1110-6500 columns (held at 60 °C) in tandem and a DMF (with 0.025 M LiBr) mobile phase. A Wyatt Dawn Heleos-II multi-angle light scattering (MALS) detector and a Wyatt Optilab T-rEX differential refractive index (dRI) detector were used to calculate absolute molecular weight using Wyatt's ASTRA software. Melting points were measured with differential scanning calorimetry (TA Instruments DSC 250 equipped with a RCS 90 cooler) as the onset temperature of the melting transition (scanning rate of 10 °C/min).

Reagents and Solvents: All solvents used in this work were non-dry, HPLC grade solvents purchased form Sigma-Aldrich unless otherwise noted. Grubbs 3rd generation initiator was prepared according to literature procedure from Grubbs 2nd generation catalyst.¹ Grubbs 2nd generation catalyst (C848) was purchased from Materia and used as-is. 4,4'-Bis(diethylamino)-benzophenone (ethyl Michler's ketone), benzylamine, hexylamine, cyclohexylamine, *exo*-5-norbornene-2-carboxylic acid, cis-5-Norbornene-exo-2,3-dicarboxylic anhydride, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), methyl thioglycolate, 1-methyl-3-mercaptopropionate, methyl propiolate, 2-naphthalenethiol, and 1-hexanethiol were purchased from Sigma-Aldrich and

vacuum distilled before use. Norbornadiene was purchased from Thermo Fisher Scientific and vacuum distilled before use. Maleic anhydride (pastilles) and thiophenol were purchased from Thermo Fisher Scientific and used as-is. 1-dodecanethiol was purchased from Beantown chemical and used as-is. 4-tert-butylthiophenol was purchased from TCI America and used as-is.

Deuterated chloroform (CDCl₃) for ROMP kinetic studies was prepared as follows: CDCl₃ was stored in an amber vial in the presence of 5Å molecular sieves to adsorb any trace water and acid (i.e. DCl) present in the chloroform. To degas the dry chloroform for use inside a nitrogenfilled glovebox, the chloroform was transferred to a Schlenk flask, cooled with an acetone/dry ice bath, and high vacuum was applied, along with mechanical agitation (i.e. swirling, shaking) while it was still in the liquid state. High vacuum was maintained for ≥15 minutes until the vigorous bubbling (dissolved gases escaping) significantly slowed down. Some evaporative loss of CDCl₃ (~10%) was typical in this degassing procedure due to its non-negligible volatility under these conditions. If any DCl remained in the chloroform after treatment with 5Å molecular sieves, we anticipated that it would be removed in this degassing step due to the high volatility of DCl relative to CDCl₃. While the freezing point of CDCl₃ is ~-64 C°, the CDCl₃ typically did not completely freeze during the duration of the degassing procedure. Once the degassing was complete, the Schlenk flask valve was closed while the contents were still under vacuum, and the solvent was transferred into a nitrogen-filled glovebox before opening the valve.

Section 2: Synthesis Experimental Details



Quadricyclane: Freshly vacuum-distilled norbornadiene (18.19 g, 197.7 mmol, 1 equiv) was added to a 20mL vial containing a stir-bar. Ethyl Michler's ketone (1.00 g, 3.1 mmol, 1.6 mol%) was added to the vial and stirred/vortexed to dissolve it into the neat norbornadiene. The vial was then wrapped in aluminum foil, shiny-side in, and a small window was scratched off one of the sides to enable light to pass into the vessel. The vial was then taped down to a small magnetic stirring plate, and a 365nm LED (1W) was positioned as close to the side of the vial as possible. The vial was irradiated and monitored by crude NMR for norbornadiene conversion. After 17 hours, the norbornadiene was 44% converted to quadricyclane. After 41 hours, the norbornadiene was 93% converted to quadricyclane. A few more hours after this crude NMR, irradiation was stopped, and the contents of the vial were transferred to a 100 mL round-bottom flask. The crude quadricyclane (17.22 g, 187.2 mmol, 95% yield). The quadricyclane was contaminated with 2 mol% of norbornadiene as measured by ¹H NMR of the distilled product. Storage under nitrogen in the freezer (-20 °C) is recommended to extend its shelf-life.

The product's ¹H NMR spectrum matched that of quadricyclane's previously reported ¹H NMR spectrum.² ¹H NMR (500 MHz, CDCl₃) δ 2.02 (2H), 1.49 ppm (4H), 1.36 (2H).



1: To a 100 mL flask containing a stir bar was added quadricyclane (12.37 g, 134.5 mmol, 1.1 equiv). A reflux condenser was added to the flask in the case of thermal runaway of the reaction. The quadricyclane was heated to 50 °C and stirred vigorously, and then maleic anhydride (pastilles, 11.98 g, 122.2 mmol, 1 equiv) was slowly added, one or two pastilles at a time, waiting in-between additions to allow any possible exothermic reactions to calm down. Once the addition of maleic anhydride was complete, the reaction was stirred at 50 °C until it solidified (indicating the formation of solid product). The reaction was then heated to 120 °C for 1-2 hours to drive it to completion. Once it cooled back to room temperature, it was transferred to a 500 mL Erlenmeyer flask for crystallization. The crude product was crystallized from boiling EtOAc/Hexanes (~1:2 EtOAc:Hexanes) to afford **1** (15.97 g, 84.0 mmol, 69% yield) as white needles. The *anti:syn* ratio of the crude product (before crystallization) was 67:33, and was enhanced to 78:22 after the crystallization.

Caution! This cycloaddition is highly exothermic, and caution should be taken when performing the reaction neat due to the tendency for thermal runaway to occur. Do not conduct this reaction in a closed system. This neat mixture of reagents is slow-reacting and stable at room temperature but will begin thermal runaway at ~50-60 °C if not properly stirred and immersed in a bath (water or oil) to thermally equilibrate and dissipate heat.



NB-NBn: Synthesized in accordance with the literature.³ The product was re-purified by crystallization from hot methanol before use.

Melting point: 101.6 °C



TCN-NBnanti and TCN-NBnsyn: To a 100 mL flask containing a stir-bar was added maleic anhydride (868 mg, 8.86 mmol, 1 equiv) and toluene (10 mL). The flask was stirred to dissolve the maleic anhydride. Once dissolved, quadricyclane (997 µL, 10.63 mmol, 1.2 equiv) was slowly added to the flask. A reflux condenser was fitted onto the flask, and the reaction was then heated at 100 °C for 3 hours to form 1 in-situ at a ~67:33 anti:syn ratio. Benzylamine (1.159 mL, 10.63 mmol, 1.2 equiv) was then slowly added to the flask (an exotherm occurs upon addition of benzylamine due to its fast reaction with anhydride 1). After heating and stirring at 100 °C for another 4 hours, the reaction was then cooled to room temperature. The contents of the flask were then vacuum filtered through a silica plug, collecting the filtrate in another flask, and washed with more toluene. The polar intermediate amic acid adsorbs to the silica gel, while the imide product elutes and is collected in the filtrate. The flask containing the toluene filtrate was removed and replace with a new flask. The silica plug was then washed with acetone to elute the amic acid, and the acetone filtrate was collected. Each of the filtrates were evaporated. NMR of the imide-containing filtrate, which crystallized upon evaporation, revealed that the imide product's anti:syn ratio was 96:4. Crystallization from hot methanol (~10 mL, 50 °C \rightarrow -20 °C, seeded at 30 °C) afforded TCN-NBnanti (900 mg, 3.22 mmol, 36% yield from maleic anhydride) as a white crystalline solid with an *anti:syn* ratio of >98:2.

After evaporating the acetone filtrate, the residue was re-dissolved in toluene (~10 mL), and vigorously refluxed for 6 hours. The reaction was cooled, and filtered through a silica plug and washed with more toluene. The filtrate (containing more imide product) was evaporated, and analysis by NMR revealed that its *anti:syn* ratio was 43:57. A single crystallization from hot methanol afforded **TCN-NBn**_{syn} (96 mg, 0.34 mmol, 4% yield from maleic anhydride) as a light brown crystalline solid with an *anti:syn* ratio of <2:98.

TCN-NBnanti melting point: 111.7 °C

TCN-NBn_{syn} melting point: 157.4 °C



NB-NCy: Synthesized in accordance with the literature. ⁴ The product was re-purified by crystallization from hot methanol before use.

Melting point: 133.7 °C



TCN-NCy: To a 100 mL flask containing a stir-bar, **1** (1.01 g, 5.3 mmol, 1 equiv) (78:22 *anti:syn*) and toluene (~10 mL) were added, and the contents were stirred to dissolve **1**. After dissolution, cyclohexylamine (668 μL, 5.8mmol, 1.1 equiv) was slowly added. A reflux condenser was fitted on the flask, and the reaction was then refluxed for 16 hours. The reaction was cooled, and then the solution was concentrated by rotary evaporation. The crude product was then transferred to a 50 mL Erlenmeyer flask for crystallization. The crude material was crystallized from hot methanol to afford **TCN-NCy** (0.49 g, 1.9 mmol, 34% yield) (>98:2 *anti:syn*).

Melting point: 144.0 °C



NB-NHex: Synthesized in accordance with the literature.⁴ The product was re-purified by microscale vacuum distillation with a Hickmann head before use.

Melting point: <-60 °C. Broad thermal transition at roughly -70 °C.



TCN-NHex: To a 100 mL flask containing a stir-bar, **1** (571 mg, 3.00 mmol, 1 equiv) and toluene (~10 mL) were added, and the contents were stirred to dissolve **1**. After dissolution, hexylamine (434 μ L, 3.30 mmol, 1.1 equiv) was slowly added. A reflux condenser was fitted on the flask, and the reaction was refluxed for 2 hours. The reflux condenser was then swapped out for a distillation head, and most of the toluene was removed (~7 mL) by atmospheric pressure distillation. The flask was then cooled to ~40-50 °C, and the distillation apparatus was replaced with a vacuum adapter. The remaining volatiles were removed under high vacuum with stirring. After a few minutes of drying, the product began to solidify/crystallize. The residue was then transferred to a 50 mL Erlenmeyer flask, and the crude product was crystallized from hot methanol/water (~2:1 methanol/water) to afford **TCN-NHex** (640 mg, 2.34 mmol, 78% yield) (>98:2 *anti:syn*) as a white crystalline solid.

Melting point: 74.0 °C



NB-(CO₂Me)₂: Synthesized in accordance with the literature.⁵ The product was re-purified by short-path vacuum distillation before use.

Melting point: <-75 °C



TCN-(CO₂Me)²: To a 40 mL vial containing a stir-bar was added **1** (3.01g, 15.8 mmol, 1 equiv) (78:22 *anti:syn*), followed by ~25 mL of a 98:2 v:v solution of MeOH:conc. H₂SO₄. The vial was capped, stirred, and heated overnight at 60 °C. The reaction was then cooled and transferred to a separatory funnel. ~50 mL of saturated NaHCO_{3 (aq)} was added to neutralize it, and then water and ethyl acetate (~20 mL of each) were added to partition the mixture. The organic layer was reserved, and the aqueous phase was extracted 2x more with ethyl acetate. The combined organic extracts were then washed with sat. NaHCO_{3 (aq)}, brine, and dried with anhydrous sodium sulfate. The organic extract was then concentrated by rotary evaporation, and the crude product crystallized in the flask upon evaporation of the solvent. The solid crude product was then

transferred to a 50 mL Erlenmeyer flask and was crystallized from hot methanol (~15 mL) to afford **TCN-(CO₂Me)**₂ (2.01g, 8.5 mmol, 54% yield) (>98:2 *anti:syn*) as a white, crystalline solid. Melting point: 90.0 °C



TCND-(CO₂Me)²: To a 100 mL flask containing a stir bar was added freshly distilled dimethylacetylenedicarboxylate (4.00g, 28.2 mmol, 1 equiv) and quadricyclane (3.17 mL, 33.8 mmol, 1.2 equiv). The flask was then fitted with a reflux condenser in the case of an exothermic reaction. The reaction was heated at 75 °C overnight, and allowed to cool to room temperature the following morning. The reaction was then stirred at room temperature for ~2 more days (due to the lack of time for the experimenter to work-up the reaction). Crude NMR of the reaction showed exclusively product, the excess quadricyclane, and a small amount of norbornadiene with <1% of unknown species. The flask was then fitted with a short-path vacuum distillation head. The crude product was then vacuum distilled to isolate **TCND-(CO₂Me)**² (5.68g, 24.2 mmol, 86% yield) as a clear, colorless oil.

Melting point: 13.6 °C



TCND-(CO₂Me)₂ Oxidized Impurity: After storage for >6 months in a fridge under air, a new product was generated in the TCND-(CO₂Me)₂, which was observable by ¹H NMR. A small amount (~10 mg) was isolated by column chromatography (EtOAc/Hexanes). ¹H and ¹³C NMR was not sufficient to identify its structure, other than the fact that it did not display olefinic resonances, and that the peak shape (sharp singlets) of the rest of the protons indicated that it still maintained a rigid, carbocyclic structure. To unambiguously determine its structure, we opted to use X-Ray crystallography. However, this compound was liquid at room temperature, which complicated its crystallization. To convert the impurity to a solid derivative, we saponified it by treating it with aqueous NaOH and then acidifying it with HCl_(aq). The new, saponified product was soluble in water, so the water was evaporated under a stream of nitrogen, and the solid remains (NaCl and product) were triturated with CDCl₃ to obtain a solution of the saponified product. Finally, this solution was used to grow crystals of the saponified impurity via vapor diffusion with pentane, and a single crystal was analyzed by X-Ray diffraction (Supporting information section 11). The structure contained an exo-epoxide where the norbornene olefin once was. For this reason, we assign the structure of the TCND-(CO₂Me)₂ Oxidized Impurity to the exo-epoxide of **TCND-(CO₂Me)**₂, presumably generated by aerobic oxidation. ¹H NMR, ¹³C NMR, and HRMS support this structure assignment (Supporting information section 10)



NB-CO₂Me: *exo*-5-norbornene-2-carboxylic acid (505 mg, 3.7 mmol, 1 equiv.) was dissolved in ~10 mL of a solution of 95:5 v:v MeOH:conc. H₂SO₄ in a 20 mL microwave tube. The solution was then heated in a microwave reactor at 90 °C for 1 hour. The reaction was cooled and transferred to a separatory funnel. ~50 mL of saturated NaHCO_{3 (aq)} was then added to neutralize the solution, followed by ~10 mL of ethyl acetate to partition the layers. The layers were separated and the organic extract reserved, and the aqueous layer was extracted 2x more with ethyl acetate. The combined organic extracts were then washed with brine and dried with anhydrous sodium sulfate. The solution was concentrated by rotary evaporation, and the residue was transferred to a smaller flask (~10 mL) for a vacuum Hickmann head distillation. The crude product was vacuum distilled to isolate **NB-CO₂Me** (192 mg, 1.3 mmol, 34% yield) as a clear, colorless oil. Due to the high volatility of the product under high vacuum, some product was lost due to evaporation to after condensation in the Hickmann head. The product is extremely odorous and smells sickeningly sweet and fruity, reminiscent of melons.

Melting point: -34.5 °C



TCND-CO₂Me: To a 50 mL flask containing a stir bar was added methyl propiolate (574 μ L, 6.5 mmol, 1 equiv) and quadricyclane (717 mg, 7.8 mmol, 1.2 equiv). The flask was then fitted with a water-cooled reflux condenser, and the reaction was heated until vigorously refluxing. After 4

hours, heating was stopped and the reaction was cooled to room temperature. The reaction was stopped early to allow for isolation of the product on the same day; methyl propiolate conversion was measured to be 36% by crude NMR. Higher conversion may be achieved by extended reaction times. Upon cooling to room temperature, the reflux condenser was replaced with a vacuum adapter. High vacuum was applied to evaporate unreacted quadricyclane and methyl propiolate to the vacuum cold trap. Once it stopped bubbling/boiling, the flask was back-filled with nitrogen and then fitted with a Hickmann head for vacuum distillation. The crude product was then vacuum distilled to isolate **TCND-CO₂Me** (259 mg, 1.5 mmol, 23% yield) as a clear, colorless oil. Like **NB-CO₂Me**, this ester was also extremely odorous and smelled sickeningly sweet and fruity, reminiscent of melons.

Melting point: -81.7 °C



Dimethyl 2,3-dimethylmaleate: 2,3-dimethylmaleic anhydride (693 mg, 5.5 mmol, 1 equiv) was dissolved in ~10 mL a mixture of 98:2 v:v MeOH:conc H₂SO₄ in a 20mL microwave tube. This solution was heated in a microwave reactor at 100 °C for 30 minutes. After cooling to room temperature, the solution was transferred to a separatory funnel, and ~20 mL of saturated NaHCO_{3 (aq)} was added to neutralize the solution. Then, 10mL of ethyl acetate was added to partition the mixture. The layers were separated and the organic extract reserved, and the aqueous layer was extracted 3x more with ethyl acetate. The combined organic extracts were then washed twice with water, once with brine, then dried with anhydrous sodium sulfate. The solution was concentrated via rotary evaporation, and then the residue was transferred to a

smaller round-bottom flask (~10 mL) for a Hickmann-head vacuum distillation. The product was vacuum distilled to isolate dimethyl 2,3-dimethylmaleate (196 mg, 1.1 mmol, 21% yield) as a clear, colorless oil.

The product's ¹H NMR (CDCl₃) spectrum matched that of dimethyl 2,3-dimethylmaleate's previously reported NMR spectrum.⁶ ¹H NMR (400 MHz, CDCl₃) δ 3.76 (6H), 1.94 (6H).

Section 3: TCN and TCND Monomer ROMP Experimental Details

TCN/TCND Monomer ROMP Procedure (for all but TCND-CO2Me): All materials and reagents were brought into a nitrogen-filled glovebox for sample preparation and polymerization. The desired monomer was dissolved in degassed CDCl₃ to make a 100 mM solution in a vial with a pierceable septum (10 mg to 14 mg monomer, ~400 µL to 550 µL monomer solution). Then, a solution of Grubbs 3rd generation (G3) initiator in CDCl₃ (10 mM) was prepared in a separate vial. Then, for each polymerization, G3 initiator solution was withdrawn into a 100 µL Hamilton syringe such that the monomer:G3 ratio is 200 (target DP of 200). The withdrawn G3 solution was then rapidly injected into the monomer vial, and the vial was vigorously shaken for a few seconds to encourage good mixing. After 15 minutes of polymerization, the vial was removed from the glovebox and guenched by the addition of a drop of ethyl vinyl ether. To precipitate and isolate the polymer, the polymer solution was diluted ≥8-fold with room-temperature MeOH to precipitate the polymer. The vial was then centrifuged and the supernatant decanted. The residue was dissolved once more in CDCl₃ (~200 µL) and diluted 10-20 fold with room temperature MeOH to precipitate it again. The polymer was isolated by centrifugation and vacuum drying until constant weight. The yield was then measured before analyzing the sample by SEC and NMR.

TCND-CO₂Me ROMP and Isolation Procedure: All materials and reagents were brought into a nitrogen-filled glovebox for sample preparation and polymerization. **TCND-CO₂Me** (10.0 mg) was dissolved in degassed CDCl₃ (568 μ L) to make a 100 mM solution in a vial with a pierceable cap. Then, a solution of Grubbs 3rd generation initiator in CDCl₃ (10 mM) was prepared in a separate vial. Then G3 initiator solution was withdrawn into a 100 μ L Hamilton syringe such that the **TCND-CO₂Me**:G3 ratio is 200 (target DP of 200). The withdrawn G3 solution was then rapidly injected into the monomer vial, and the vial was vigorously shaken for a few seconds to encourage good mixing. After 15 minutes of polymerization, the vial was removed from the glovebox and quenched by the addition of a drop of ethyl vinyl ether. Shortly thereafter, ~50 µL of pyridine was added to the vial. Then, the polymer solution was diluted ≥8-fold with roomtemperature MeOH to precipitate the polymer. The vial was then centrifuged and the supernatant decanted. The residue was dissolved once more in CDCl₃ (~200 µL), and another aliquot of pyridine was added (~50 µL) was added before diluting 10-20 fold with room temperature MeOH to precipitate it again. The polymer was isolated by centrifugation and vacuum drying until constant weight. p(**TCND-CO₂Me**) (7.5 mg, 75% yield) was then analyzed by SEC and NMR.

Polymer ¹**H NMR Spectra:** The p(TCN) and p(TCND) NMR spectra were recorded using the final, vacuum dried polymers synthesized by the above methods. The p(NB) NMR spectra shown here are the final spectra of the NMR kinetics studies, and are therefore contaminated with a trace amount of monomer, Grubbs 3^{rd} generation initiator, and mesitylene (δ 6.78 (s, 3H), 2.26 (s, 9H)), the internal standard used during the NMR kinetics study.



Figure S1: ¹H NMR spectrum of p(NB-NBn).



Figure S2: ¹H NMR spectrum of p(TCN-NBnanti).



Figure S3: ¹H NMR spectrum of p(NB-NCy).



Figure S4: ¹H NMR spectrum of p(TCN-NCy).



Figure S5: ¹H NMR spectrum of p(NB-NHex).



Figure S6: ¹H NMR spectrum of p(TCN-NHex).





Figure S8: ¹H NMR spectrum of p(TCN-(CO₂Me)₂).



Figure S10: ¹H NMR spectrum of p(NB-CO₂Me).



Figure S11: ¹H NMR spectrum of p(**TCND-CO₂Me**).

Section 4: NMR ROMP Kinetics Experimental Details and Data

NMR Kinetics Experimental Procedure: All materials and reagents were brought into a nitrogen-filled glovebox for sample preparation before removing from inert atmosphere for NMR analysis. A stock solution of monomer (100 mM) was prepared in degassed CDCI₃. A drop of mesitylene was added to the monomer stock solution as an NMR internal standard. To 3 NMR tubes, 600 or 700 µL of the stock solution was added, and the tubes were capped with a pierceable septum. Then, a solution of pyridine (Py) (50 mM) in degassed CDCl₃ was prepared, and this solution was used to make a stock solution of G3 initiator (10 mM), such that the molar ratio of G3:Py = 1:5. Usually more pyridine is used (e.g. 10 equiv) to slow down polymerizations for real-time NMR analysis,⁷ but 5 equiv was found to provide a good trade-off between sample throughput ($t_{1/2} \approx 1 - 10$ min for most monomers) and data quality; faster kinetics ($t_{1/2} <<1$ min) are not viable for real-time NMR analysis, and slower ($t_{1/2} > 10$ min) would significantly extend the time required per experiment. A precisely measured amount of this solution was withdrawn into a 100 uL Hamilton syringe (30 or 35 µL), such that the target degree of polymerization of the polymer is 200. Then, an NMR tube of monomer/ISTD and G3/Py containing syringe were removed from the glovebox and brought to the NMR spectrometer. First, the monomer/ISTD solution NMR tube was inserted into the spectrometer, and the signal was locked, tuned, shimmed, and the gain was adjusted. Then, an initial scan was taken to measure the initial ratio of monomer:ISTD. Then, the sample was ejected from the NMR spectrometer, and the G3/Py solution was injected into the NMR tube, the tube was vigorously shaken, and then re-inserted into the spectrometer for real-time analysis. The small increase in sample volume (5 vol%) after initiator injection is important, because the initial shim is maintained well. A larger volume change may have deleterious effects on the shim, resulting in poor peak shape. One scan was then

taken at intervals ranging from 20 seconds to 60 seconds. The interval was chosen by changing the relaxation delay; a 16 second delay resulted in a 20 second total scan time, a 56 second delay resulted in a 60 second total scan time, etc. It was estimated that the time delay between the injection of the initiator and the insertion into the spectrometer was 40 seconds. Monomer conversion was calculated by comparison of the monomer:ISTD integration ratio versus the initial monomer:ISTD integration ratio before the injection of initiator. The only exception is monomer **TCND-CO₂Me**, whose polymer signals overlapped with those belonging to the internal standard mesitylene. In this case, the relative integration of the monomer:polymer backbone was used to calculate monomer conversion. All polymerizations were run in triplicate.

NMR Kinetics Data: Both the raw and linearized data for each monomer is shown below. Error bars are shown in the raw data plots as \pm standard deviation. The linearized plots were made by using the average conversion value of each time point from the triplicate runs. For the linearized plots, the raw data at >98% conversion (ln([M]₀/[M]) \approx 3.8) was not included due to the poor S/N ratio of NMR at this low monomer concentration regime. Monomer k_{ρ} values were measured by fitting the linearized data using the "linear fit" function in Origin software; the slope is k_{ρ} and the error of k_{ρ} is the standard error of the slope calculated by the Origin software.



Figure S12: (left) Raw real-time NMR kinetic data for the ROMP of **NB-NBn**. (right) Linearized kinetic data for the ROMP of **NB-NBn**. Linear fit reveals that $k_p = 0.157 \pm 0.0006$ min⁻¹.



Figure S13: (left) Raw real-time NMR kinetic data for the ROMP of **TCN-NBn**anti. (right) Linearized kinetic data for the ROMP of **TCN-NBn**anti. Linear fit reveals that $k_p = 0.117 \pm 0.0005$ min⁻¹.



Figure S14: (left) Raw real-time NMR kinetic data for the ROMP of **TCN-NBn**_{syn}. (right) Linearized kinetic data for the ROMP of **TCN-NBn**_{syn}. Linear fit reveals that $k_{\rho} = 0.122 \pm 0.0013$ min⁻¹.



Figure S15: (left) Raw real-time NMR kinetic data for the ROMP of **NB-NCy**. (right) Linearized kinetic data for the ROMP of **NB-NCy**. Linear fit reveals that $k_p = 0.183 \pm 0.0009 \text{ min}^{-1}$.



Figure S16: (left) Raw real-time NMR kinetic data for the ROMP of **TCN-NCy**. (right) Linearized kinetic data for the ROMP of **TCN-NCy**. Linear fit reveals that $k_{\rho} = 0.101 \pm 0.0004$ min⁻¹.



Figure S17: (left) Raw real-time NMR kinetic data for the ROMP of **NB-NHex**. (right) Linearized kinetic data for the ROMP of **NB-NHex**. Linear fit reveals that $k_p = 0.140 \pm 0.0009 \text{ min}^{-1}$.



Figure S18: (left) Raw real-time NMR kinetic data for the ROMP of **TCN-NHex**. (right) Linearized kinetic data for the ROMP of **TCN-NHex**. Linear fit reveals that $k_p = 0.094 \pm 0.0004$ min⁻¹.



Figure S19: (left) Raw real-time NMR kinetic data for the ROMP of **NB-(CO₂Me)**₂. (right) Linearized kinetic data for the ROMP of **NB-(CO₂Me)**₂. Linear fit reveals that $k_{\rho} = 0.225 \pm 0.0008$ min⁻¹.



Linearized kinetic data for the ROMP of **TCN-(CO₂Me)**₂. Linear fit reveals that $k_p = 0.342 \pm 0.0014$ min⁻¹.



Figure S21: (left) Raw real-time NMR kinetic data for the ROMP of **TCND-(CO₂Me)**₂. (right) Linearized kinetic data for the ROMP of **TCND-(CO₂Me)**₂. Linear fit reveals that $k_p = 0.622 \pm 0.0073 \text{ min}^{-1}$.



Figure S22: (left) Raw real-time NMR kinetic data for the ROMP of **NB-CO₂Me**. (right) Linearized kinetic data for the ROMP of **NB-CO₂Me**. Linear fit reveals that $k_p = 1.259 \pm 0.0142$ min⁻¹.



Figure S23: (left) Raw real-time NMR kinetic data for the ROMP of **TCND-CO₂Me**. (right) Linearized kinetic data for the ROMP of **TCND-CO₂Me**. Linear fit reveals that $k_{\rho} = 0.564 \pm 0.0099$ min⁻¹.

Monomer	<i>k</i> _p (min⁻¹)	<i>t</i> _{1/2} (min)
NB-NBn	0.157 ± 0.0006	4.4
TCN-NBnanti	0.117 ± 0.0005	5.9
TCN-NBn _{syn}	0.122 ± 0.0013	5.7
NB-NCy	0.183 ± 0.0009	3.8
TCN-NCy	0.101 ± 0.0004	6.9
NB-NHex	0.140 ± 0.0009	5.0
TCN-NHex	0.094 ± 0.0004	7.4
NB-(CO ₂ Me) ₂	0.225 ± 0.0008	3.1
TCN-(CO ₂ Me) ₂	0.342 ± 0.0014	2.0
TCND-(CO ₂ Me) ₂	0.622 ± 0.0073	1.1
NB-CO ₂ Me	1.259 ± 0.0142	0.6
TCND-CO₂Me	0.564 ± 0.0099	1.2

Table S1: ROMP propagation rates and half-lives of all monomers in this study.



Section 5: Block Copolymerization Experimental Details

Block copolymerization procedure: All materials and reagents were brought into a nitrogenfilled glovebox for sample preparation. TCN-NBnanti (13.6 mg) and TCN-NHex (12.4 mg) were dissolved in degassed CDCl₃ at 100 mM in separate vials with pierceable caps. Then, a solution of G3 initiator was prepared in CDCl₃ (10 mM), and an aliquot was withdrawn into a 100 µL Hamilton syringe to target a degree of polymerization of the first block, p(**TCN-NBn**anti), of 100. The aliquot was rapidly injected into the 100 mM stock solution of **TCN-NBn**anti, and the vial was shaken vigorously to facilitate good mixing. After reacting for 6 minutes, half of the volume was withdrawn and transferred to a separate vial as an aliquot of the first block for later isolation and analysis. Then, a volume of the **TCN-NHex** stock solution was added to the living polymerization to target a degree of polymerization of 100, and the vial was again shaken vigorously to encourage good mixing. After reacting for another 6 minutes, both vials (aliguot of the first block and the diblock polymer) were removed from the glovebox and guenched with a drop of ethyl vinvl ether. Each block was then purified by 2 precipitations from methanol and dried under vacuum until constant weight. The dried polymers were then analyzed by SEC with 100% mass recovery methods.



Figure S24: SEC analysis of the first and second blocks of the block copolymerization of **TCN-NBn**anti (DP 100) with **TCN-NHex** (DP 100).

Section 6: Living Polymerization Experimental Details



Living polymerization of TCN-NBnanti procedure: All materials and reagents were brought into a nitrogen-filled glovebox for sample preparation. A solution of TCN-NBnanti (137.8 mg) in degassed CDCI₃ (987 µL, 500 mM) was prepared in a 4 mL vial with a pierceable cap. Then, a solution of pyridine in degassed CDCl₃ (50 mM) was prepared, and this solution was used to dissolve a sample of Grubbs 3rd generation initiator at 10 mM, such that the ratio of G3:Py is 1:5. An aliquot of this solution (49 µL) was withdrawn into a 100 µL Hamilton syringe to target a degree of polymerization of 500. Then, the vial of monomer solution and initiator-filled syringe were removed from the glovebox. To initiate the polymerization, the syringe of initiator solution was rapidly injected into the vial, and the vial was shaken vigorously for a few seconds to facilitate good mixing. The headspace of the vial was then supplied with nitrogen from a needle connected to a Schlenk line. Approximately 100 µL aliquots were withdrawn from the polymerization via syringe at 2, 4, 6, 8, 10, 15, and 30 minutes after the addition of the initiator. Upon removal from the polymerization vial, they were immediately quenched by injecting into vials containing ~500 µL of a 1:4 v:v ethyl vinyl ether/dichloromethane solution. This solvent mixture was used to maintain the solubility of the monomer and polymer upon quenching to ensure that the polymerization was completely quenched all at once. Once all aliquots were taken, the aliquots were evaporated under a stream of nitrogen and re-dissolved in CDCl₃ for NMR analysis. Conversion was measured by comparison of the integration ratio of monomer to
polymer backbone peak. The NMR samples were then retrieved, and the solvent again removed under a stream of nitrogen. The residue was re-dissolved in the SEC instrument solvent (DMF) and syringe filtered before analysis by SEC. The dn/dc value of p(**TCN-NBn**anti) was measured by isolating the remaining polymer from the reaction (quench with ethyl vinyl ether, precipitate 2x from MeOH, vacuum dry until constant weight) and analyzing it via SEC with a 100% mass recovery method.

<u>Table S2</u>: Conversion, M_n , and D data for the aliquots taken from the living polymerization of **TCN-NBn**_{anti}.

Time	Monomer Conversion	M _n (SEC-MALS)	Ъ
(min)	(¹ H NMR)	(kDa)	Ð
0	0	0	N/A
2	0.167	48.8	1.04
4	0.275	82.4	1.01
6	0.379	112	1.01
8	0.457	123	1.05
10	0.524	144	1.04
15	0.667	175	1.05
30	0.884	220	1.06



Figure S25: (a) Plot of $M_{n, \text{SEC}}$ and \mathcal{D} as a function of conversion for the living polymerization of **TCN-NBn**_{anti} with G3. (b) Plot of ln([**TCN-NBn**_{anti}]/[**TCN-NBn**_{anti}]₀) versus time for the polymerization.





A stock solution (200 mM) of conjugate acceptor (dimethyl 2,3-dimethylmaleate (DDM), dimethyl maleate (DM) TCND-CO₂Me, or TCND-(CO₂Me)₂) in either CDCl₃ or DMF-d₇ was prepared. A drop of internal standard (mesitylene) was added to this stock solution. A stock solution (200 mM) of 1-dodecanethiol was also prepared in the same solvent. Equal volumes of both stock solutions were added to an NMR tube under air (~300 µL of each) and capped with a pierceable septum to make an NMR sample containing 100 mM of both the conjugate acceptor and dodecanethiol. The desired amount of catalytic DBU (1, 2.5, or 10 mol%) was withdrawn into a 10 µL syringe and reserved for addition to the NMR sample later. The NMR sample was then inserted into the NMR spectrometer and locked, tuned, shimmed, and gain-adjusted. An initial spectrum was taken to measure the initial ratio of internal standard (mesitylene) to conjugate acceptor. The sample was removed from the spectrometer, the catalytic DBU was injected into the NMR tube, and the tube was rapidly shaken for a few seconds to encourage good mixing. The NMR tube was then re-inserted into the spectrometer, and one spectrum was taken every 60 seconds (56 second relaxation was used for a total scan time of 60 seconds) for 30 minutes using the same shim, lock, tune, and gain settings that set for the initial sample. Conjugate acceptor conversion was monitored by comparing the conjugate acceptor/internal standard integration ratio versus the initial ratio. The conjugate acceptor conversion after the 30 min reaction is reported in the following table.

<u>**Table S3:**</u> Conditions and conversion for the reaction of various conjugate acceptors with dodecanethiol for 30 minutes.

Entry	Conjugate Acceptor	Solvent	DBU (mol %)	Conversion (after 30 min)
1	TCND-(CO ₂ Me) ₂	CDCl ₃	10%	47%
2	TCND-(CO ₂ Me) ₂	CDCl ₃	2.5%	19%
3	TCND-(CO ₂ Me) ₂	DMF-d7	1%	87%
4	DDM	CDCl ₃	10%	0%
5	DDM	CDCl ₃	2.5%	0%
6	DM	CDCl ₃	10%	79%
7	DM	CDCl ₃	2.5%	51%
8	TCND-CO ₂ Me	CDCl ₃	10%	3%

Section 8: Optimization of p(TCND-(CO₂Me)₂) Post-polymerization Functionalization with Dodecanethiol Experimental Details and Data

p(TCND-(CO₂Me)₂) (DP100) was prepared using the polymerization methodology described above in Section 3. p(**TCND-(CO₂Me)**₂) (~4 - 10 mg) was dissolved in DMF at a concentration of 50 mg/mL (80 - 200 µL) in a 4mL vial containing a stir-bar. The desired amount of 1dodecanethiol (1.1 – 5 equiv relative to reactive sites in the p(TCND-(CO₂Me)₂) backbone) was then added to the vial with a 10 µL Hamilton syringe, and the solution was stirred. A 1:9 v:v DBU:DMF solution was then prepared. This diluted DBU solution was used to introduce the catalytic DBU to the reaction due to the very small amounts required; measuring such small amounts of neat DBU would result in significant error. Then, the required amount of DBU (2.5 -20 mol% relative to reactive sites in the p(TCND-(CO₂Me)₂) backbone) was added to the vial with a 10 µL Hamilton syringe. Soon after addition, the solution became cloudy and a precipitate formed, indicating the plummeting solubility of the resulting functionalized polymer. The solution was then stirred at room temperature for 1 hour. To stop the reaction, the reaction was diluted with 10-20 volumes of MeOH to precipitate any polymer remaining in solution. The solution was then centrifuged, and the supernatant discarded by decantation. The polymer was precipitated once more from MeOH and isolated by centrifugation. The polymer was then dried to constant weight under vacuum before analysis by ¹H NMR spectroscopy.

Conversion was measured by comparing the integration of the polymer's olefinic peaks to the integrated of the well-resolved triplet belonging to the newly introduced dodecanethiol sidechain. The following two NMR spectra show the differences between unmodified p(**TCND**-(**CO**₂**Me**)₂) and dodecanethiol functionalized p(**TCND**-(**CO**₂**Me**)₂). This functionalized sample is >95% conversion due to the near-ideal integration ratio (2:3) of 2:2.87 for the olefinic resonances:dodecanethiol chain-end resonances. By dividing 2.87/3 we find that the conversion is 96.7%. The high conversion is also supported by the additional non-olefinic resonances that have been added to the structure. The ideal ratio of olefinic resonances to all others for dodecane functionalized $p(TCND-(CO_2Me)_2)$ is 2:38, and the observed ratio is 2:37.08.

<u>Table S4</u>: Optimization of post-polymerization modification of p(**TCND-(CO₂Me)**₂) with dodecanethiol.

$$\begin{array}{c} Ph & \begin{array}{c} H_{25}C_{12}SH \\ MeO_2C & CO_2Me \end{array} \begin{array}{c} H_{25}C_{12}SH \\ \hline cat. DBU \\ DMF \\ p(\textbf{TCND-(CO_2Me)_2)} \end{array} \begin{array}{c} Ph & \begin{array}{c} H_{25}C_{12}SH \\ MeO_2C & CO_2Me \\ H_{25}C_{12} \end{array} \begin{array}{c} Ph & \begin{array}{c} H_{25}C_{12}SH \\ H_{25}C_{12} \end{array} \end{array}$$

Entry	$H_{25}C_{12}SH$	DBU	Conversion	
Enuy	equiv	equiv	(¹ H NMR)	
1	5	20 mol%	>95%	
2	2	20 mol%	>95%	
3	2	5 mol%	>95%	
4	1.5	5 mol%	>95%	
5	1.1	5 mol%	95%	
6	1.1	2.5 mol%	93%	
7	1.2	5 mol%	>95%	



Figure S26: Representative ¹H NMR spectra stack comparing the spectrum of unfunctionalized $p(TCND-(CO_2Me)_2)$ (top) to dodecanethiol functionalized $p(TCND-(CO_2Me)_2)$ (>95% conversion) (bottom).

Section 9: Post-polymerization Functionalization of p(TCND-(CO₂Me)₂) Experimental Details and Data

p(TCND-(CO₂Me)₂) (DP100) was prepared using the polymerization methodology described above in Section 3. p(**TCND-(CO₂Me)**₂) (~5 - 10 mg) was dissolved in DMF at a concentration of 50 mg/mL (100 – 200 µL) in a 4mL vial containing a stir-bar. 1.2 equiv of the desired thiol was added to the solution with a 10 µL Hamilton syringe, and the solution was stirred. A 1:9 v:v DBU:DMF solution was then prepared. This diluted DBU solution was used to introduce the catalytic DBU to the reaction due to the very small amounts required; measuring such small amounts of neat DBU would result in significant error. Before adding the DBU, the vial was optionally evacuated and back-filled with N₂ three times to run the reaction under an atmosphere of nitrogen. Then, 5 mol% of DBU/DMF solution was injected into the vial with a 10 µL Hamilton syringe to begin the functionalization reaction. All of the polymer functionalization reactions remained homogenous throughout functionalization. After 1 hour, the reaction was stopped by diluting 10-20 fold with MeOH to precipitate the polymer product. The vial was then centrifuged, the solvent decanted, and the polymer was then re-dissolved in CDCl₃ and precipitated once more by diluting 10-20 fold with MeOH. The polymer was isolated by centrifugation and dried to constant weight under vacuum. Once dry, the polymer was redissolved in the appropriate solvent for SEC and ¹H NMR analysis.

We estimated functionalization conversion by two methodologies, SEC-MALS and ¹H NMR, where applicable. Comparing the product's measured M_n by SEC-MALS with the theoretical M_n for 100% functionalization allowed for estimation based on molecular weight gain. This method is more error-prone, because of the relatively low expected mass increase of the polymer (only ~50-70% increase in M_n for 100% conversion for the thiols studied) and error associated with

measuring polymer molecular weight via SEC-MALS with 100% mass recovery methods. If any of the protons in the thiol appendage were well-resolved from polymer signals belonging to the original poly(**TCND-(CO₂Me)**₂) backbone (olefinic protons) in ¹H NMR, the relative integration of the two peaks was used to calculate the conversion. In the case that the peaks of interest overlapped with the CDCl₃ solvent peak, the integration of the well-resolved ¹³C coupling satellite peak was used to calculate the contribution of the parent CDCl₃ peak's contribution to the total integration of the polymer + CDCl₃. These two methods for estimating conversion agreed within ~15% conversion in all cases except for the hexanethiol functionalization, where the measured M_n of the product exceeded that of the expected value from 100% functionalization (40.6 kDa) by 4.8 kDa. <u>Table S5:</u> Post-polymerization modification of poly(TCND-(CO₂Me)₂) with a variety of thiols.



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Entry	Thiol	Atmosphere	<i>M_n</i> Initial	<i>M_n</i> Final	Conversion	
					(IVIn)	
1	SH	Air	27.0 kDa	33.4 kDa	33%	45%
2	SH	Air	27.0 kDa	32.4 kDa	29%	16%
3	SH	N ₂	27.0 kDa	39.7 kDa	66%	64%
4	SH	N2	27.0 kDa	33.2 kDa	34%	36%
5	O SH	Air	27.0 kDa	41.4 kDa	118%	N/A
6	O SH	N2	27.0 kDa	40.0 kDa	106%	N/A
7	O SH	Air	27.0 kDa	39.4 kDa	90%	N/A
8	SH	Air	27.0 kDa	45.4 kDa	135%	>95%





Figure S27: SEC traces of p(**TCND-(CO₂Me)**₂) before and after functionalization with 4-tertbutylthiophenol under an atmosphere of air (left) or nitrogen (right).



Figure S28: SEC traces of p(**TCND-(CO₂Me)**₂) before and after functionalization with 2naphthalenethiol under an atmosphere of air (left) or nitrogen (right).



Figure S29: SEC traces of p(**TCND-(CO₂Me)**₂) before and after functionalization with methyl thioglycolate under an atmosphere of air (left) or nitrogen (right).



Figure S30: SEC traces of p(TCND-(CO₂Me)₂) before and after functionalization with methyl

thiopropiolate under an atmosphere of air.



Figure S31: SEC traces of p(**TCND-(CO₂Me)**₂) before and after functionalization with hexanethiol under an atmosphere of air.

¹H NMR Data for p(TCND-(CO₂Me)₂) Before and After Functionalization with Thiol Nucleophiles:



Figure S32: ¹H NMR spectrum of p(**TCND-(CO₂Me)**₂) before functionalization with thiol nucleophiles.



Figure S33: ¹H NMR spectrum of 4-tert-butylthiophenol functionalized $p(TCND-(CO_2Me)_2)$ (under an atmosphere of air). The key peaks are integrated (olefinic backbone peaks of $p(TCND-(CO_2Me)_2)$ and the newly introduced aromatic peaks from 4-tert-butylthiophenol).







Figure S35: ¹H NMR spectrum of methyl thioglycolate functionalized $p(TCND-(CO_2Me)_2)$ (under an atmosphere of air). The total integration of the non-olefinic peaks (~18 protons) agrees well with the anticipated value of 18 protons for a 100% functionalized polymer. A similar spectrum was observed for methyl thioglycolate functionalized $p(TCND-(CO_2Me)_2)$ when the reaction was ran under an atmosphere of nitrogen.



Figure S36: ¹H NMR spectrum of 4-tert-butylthiophenol functionalized $p(TCND-(CO_2Me)_2)$ (under an atmosphere of nitrogen). The key peaks are integrated (olefinic backbone peaks of $p(TCND-(CO_2Me)_2)$ and the newly introduced aromatic peaks from 4-tert-butylthiophenol).



<u>Figure S37:</u> ¹H NMR spectrum of 2-naphthalenethiol functionalized $p(TCND-(CO_2Me)_2)$ (under an atmosphere of nitrogen). The key peaks are integrated (olefinic backbone peaks of $p(TCND-(CO_2Me)_2)$ and the newly introduced aromatic peaks from 2-naphthalenethiol).



Figure S38: ¹H NMR spectrum of 1-methyl-3-mercaptopropionate functionalized p(**TCND-**(**CO**₂**Me**)₂) (under an atmosphere of air). The total integration of the non-olefinic peaks (~21 protons) agrees well with the anticipated value of 20 protons for a 100% functionalized polymer. The integration is slightly overestimated due to the overlapping trace DMF solvent peaks.



<u>Figure S39:</u> ¹H NMR spectrum of 1-hexanethiol functionalized p(**TCND-(CO₂Me)**₂) (under an atmosphere of air). The key peaks are integrated (olefinic backbone peaks of p(**TCND-(CO₂Me)**₂) and the well-resolved peak at ~0.9 ppm belonging to the -CH₃ group of 1-hexanethiol.

Section 10: Small Molecule Characterization Data



Figure S40: ¹H NMR spectrum of 1 (~73:27 anti:syn):

Anti isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.07 (t, *J* = 1.7 Hz, 2H), 3.03 (s, 2H), 2.96 – 2.94 (m, 2H), 2.33 (s, 2H), 1.57 – 1.53 (m, 1H), 1.51 (dt, *J* = 10.3, 1.5 Hz, 1H).

Syn isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.07 (t, *J* = 1.7 Hz, 2H), 3.56 – 3.52 (m, 2H), 3.07 (s, 2H), 2.56 – 2.50 (m, 2H), 1.57 – 1.53 (m, 1H), 1.41 (dp, *J* = 11.7, 1.4 Hz, 1H).



Figure S41: ¹³C{¹H} NMR spectrum of **1** (~73:27 *anti:syn*):

Anti isomer: ¹³C{¹H} NMR (126 MHz, CDCl3) δ 172.8, 135.5, 44.2, 41.2, 40.9, 40.3.

Syn isomer: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 172.0, 136.9, 41.8, 40.3, 38.1, 37.3.



Figure S42: HRMS spectrum for 1: (M+H)⁺ calc'd for C₁₁H₁₁O₃:191.0708. Found: 191.0693

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Figure S43: ¹H NMR spectrum of **TCN-NBn**anti: ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.24 (m, 3H), 6.03 (t, *J* = 1.7 Hz, 2H), 4.67 (s, 2H), 2.96 (s, 2H), 2.70 (s, 2H), 2.11 (s, 2H), 1.58 (d, *J* = 9.7 Hz, 1H), 1.49 (dp, *J* = 9.7, 1.3 Hz, 1H).



Figure S44: ¹³C{¹H} NMR spectrum of **TCN-NBn**anti: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 178.7, 136.1, 135.8, 128.8, 128.6, 128.0, 44.4, 42.5, 41.4, 41.0, 40.8.



Figure S45: HRMS spectrum for **TCN-NBn**anti: (M+H)⁺ calc'd for C₁₈H₁₈NO₂: 280.1338. Found: 280.1334



Figure S46: ¹H NMR spectrum of TCN-NBn_{syn}: ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.23 (m, 3H), 6.00 (t, J = 1.9 Hz, 2H), 4.60 (s, 2H), 3.30 – 3.24 (m, 2H), 2.96 (s, 2H), 2.45 – 2.38 (m, 2H), 0.99 (dp, J = 11.0, 1.6 Hz, 1H), 0.91 (d, J = 10.9 Hz, 1H).



Figure S47: ¹³C{¹H} NMR spectrum of **TCN-NBn**_{syn}: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 177.6, 137.2, 135.3, 129.5, 128.7, 128.1, 42.7, 42.2, 41.0, 37.6, 36.7.



Figure S48: HRMS spectrum for **TCN-NBn**_{syn}: (M+H)⁺ calc'd for C₁₈H₁₈NO₂: 280.1338. Found: 280.1348



Figure S49: ¹H NMR spectrum of **TCN-NCy**: ¹H NMR (500 MHz, CDCl₃) δ 6.03 (t, *J* = 1.8 Hz, 2H), 3.96 (tt, *J* = 12.3, 3.9 Hz, 1H), 2.96 (t, *J* = 1.9 Hz, 2H), 2.70 – 2.53 (m, 2H), 2.17 (qd, *J* = 12.5, 3.4 Hz, 2H), 2.10 (s, 2H), 1.87 – 1.75 (m, 2H), 1.69 – 1.62 (m, 1H), 1.62 – 1.53 (m, 3H), 1.47 (dp, *J* = 9.8, 1.5 Hz, 1H), 1.39 – 1.15 (m, 3H).



<u>Figure S50:</u> ¹³C{¹H} NMR spectrum of **TCN-NCy**: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.4, 135.8, 51.8, 44.4, 41.6, 40.8, 40.6, 28.8, 26.0, 25.2.



Figure S51: HRMS spectrum for TCN-NCy: (M+H)⁺ calc'd for C₁₇H₂₂NO₂: 272.1651. Found: 272.1664.



Figure S52: ¹H NMR spectrum of TCN-NHex: ¹H NMR (500 MHz, CDCl₃) δ 6.01 (t, J = 1.8 Hz, 2H), 3.51 (t, J = 7.4 Hz, 2H), 2.96 (s, 2H), 2.76 – 2.55 (m, 2H), 2.14 (s, 2H), 1.61 – 1.51 (m, 3H), 1.48 (d, J = 9.8 Hz, 1H), 1.37 – 1.20 (m, 6H), 0.95 – 0.76 (m, 3H).



Figure S53: ¹³C{¹H} NMR spectrum of **TCN-NHex:** ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.2, 135.8, 44.4, 41.5, 40.9, 40.8, 39.0, 31.5, 27.8, 26.6, 22.6, 14.1.



Figure S54: HRMS spectrum for **TCN-NHex**: (M+H)⁺ calc'd for C₁₇H₂₄NO₂: 274.1807. Found: 274.1821.


Figure S55: ¹H NMR spectrum of **TCN-(CO₂Me)**₂: ¹H NMR (500 MHz, CDCl₃) δ 6.00 (t, *J* = 1.8 Hz, 2H), 3.67 (s, 6H), 2.85 – 2.67 (m, 4H), 2.41 – 2.32 (m, 2H), 1.53 (d, *J* = 9.7 Hz, 1H), 1.40 (dp, *J* = 9.8, 1.6 Hz, 1H).



<u>Figure S56</u>: ¹³C{¹H} NMR spectrum of **TCN-(CO₂Me)**₂: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 173.5, 135.6, 52.0, 43.6, 41.04, 40.4, 38.0.



Intensity [%]

Figure S57: HRMS spectrum for **TCN-(CO₂Me)**₂: (M+H)⁺ calc'd for C₁₃H₁₇O₄: 237.1127. Found: 237.1139.



Figure S58: ¹H NMR spectrum of **TCND-(CO₂Me)**₂: ¹H NMR (500 MHz, CDCl₃) δ 6.17 (t, *J* = 1.9 Hz, 2H), 3.80 (s, 6H), 2.70 (p, *J* = 1.7 Hz, 2H), 2.56 (s, 2H), 1.40 (d, *J* = 9.7 Hz, 1H), 1.33 (d, *J* = 9.7 Hz, 1H).



<u>Figure S59</u>: ¹³C{¹H} NMR spectrum of **TCND-(CO₂Me)**₂: ¹³C{¹H} NMR (126 MHz, CDCI₃) δ 161.9, 145.2, 136.1, 52.0, 44.4, 39.7, 38.4.



Intensity [%]

Figure S60: HRMS spectrum for **TCND-(CO₂Me)**₂: (M+H)⁺ calc'd for C₁₃H₁₅O₄: 235.0970. Found: 235.0986.

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Figure S61: ¹H NMR spectrum of **TCND-(CO₂Me)**² **Oxidized Impurity**: ¹H NMR (500 MHz, CDCl₃) δ 3.77 (s, 6H), 3.17 (s, 2H), 2.85 (s, 2H), 2.57 (s, 2H), 1.31 (d, *J* = 11.2 Hz, 1H), 0.96 (d, *J* = 11.3 Hz, 1H).



Figure S62: ¹³C{¹H} NMR spectrum of **TCND-(CO₂Me)**₂ **Oxidized Impurity**: ¹³C{¹H} NMR (126 MHz, CDCI₃) δ 161.2, 142.3, 52.1, 51.2, 44.4, 34.8, 18.4.



Figure S63: HRMS spectrum for TCND-(CO_2Me)₂ Oxidation Product: (M+H)⁺ calc'd for C₁₃H₁₅O₅: 251.0914. Found: 251.0928.



Figure S64: ¹H NMR spectrum of **NB-CO**₂**Me**: ¹H NMR (500 MHz, CDCl₃) δ 6.13 (dd, J = 5.6, 2.9 Hz, 1H), 6.10 (dd, J = 5.6, 3.1 Hz, 1H), 3.69 (s, 3H), 3.06 – 3.01 (m, 1H), 2.95 – 2.89 (m, 1H), 2.26 – 2.19 (m, 1H), 1.90 (dt, J = 11.8, 3.9 Hz, 1H), 1.54 – 1.50 (m, 1H), 1.40 – 1.33 (m, 2H).



Figure S65: ¹³C{¹H} NMR spectrum of **NB-CO**₂**Me**: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 176.9, 138.2, 135.9, 51.9, 46.7, 46.5, 43.1, 41.8, 30.5.



Figure S66: HRMS spectrum for **NB-CO₂Me**: (M+H)⁺ calc'd for C₉H₁₃O₂: 153.0916. Found: 153.0903.



Figure S67: ¹H NMR spectrum of TCND-CO₂Me: ¹H NMR (500 MHz, CDCl₃) δ 7.01 (s, 1H),
6.20 - 6.13 (m, 2H), 3.74 (s, 6H), 2.66 - 2.60 (m, 2H), 2.52 - 2.46 (m, 1H), 2.39 - 2.34 (m, 1H), 1.40 - 1.30 (m, 2H).



Figure S68: ¹³C{¹H} NMR spectrum of **TCND-CO₂Me**: ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.9, 148.9, 141.2, 136.2, 136.2, 51.4, 45.9, 43.6, 39.8, 38.5, 37.9.



Figure S69: HRMS spectrum for **TCND-CO₂Me**: (M+H)⁺ calc'd for C₁₁H₁₃O₂: 177.0916. Found: 177.0918.

Section 11: Crystal Structure Information



Figure S70: Crystal structure of TCN-NBnanti. Grey is carbon, red is oxygen, and blue is nitrogen. Thermal ellipsoids are shown at the 50% probability level. Hydrogens omitted for clarity.

Formula: C₁₈H₁₇NO₂ Formula Weight: 279.33 Da

Crystal System: Monoclinic Space Group: P 21

Crystal Color: Colorless

Unit Cell Parameters: a = 5.9523, b = 13.5277, c = 9.0395, α = 90, β = 104.324, γ = 90

Temperature of Data Collection: 100 K

Z: 2

R: 0.0276

GOF: 1.053

Crystal preparation: **TCN-NBn**_{anti} was dissolved in trifluoroethanol (10 mg/mL) and syringe filtered into a small vial. Then, syringe filtered water was carefully layered on top of the trifluoroethanol solution, and the vial was left undisturbed for 1 week while the crystals formed by slow diffusion of the solvent.



Figure S71: Crystal structure of TCN-NBn_{syn}. Grey is carbon, red is oxygen, and blue is nitrogen. Thermal ellipsoids are shown at the 50% probability level. Hydrogens omitted for clarity.

Formula: C₁₈H₁₇NO₂ Formula Weight: 279.33 Da

Crystal System: Monoclinic Space Group: P 21/m

Crystal Color: Colorless

Unit Cell Parameters: a = 7.5018, b = 10.4685, c = 9.0020, α = 90, β = 108.336, γ = 90

Temperature of Data Collection: 100 K

Z: 2

R: 0.0478

GOF: 1.071

Crystal preparation: **TCN-NBn**_{syn} was dissolved in trifluoroethanol (5 mg/mL) and syringe filtered into a small vial. Then, syringe filtered water was carefully layered on top of the trifluoroethanol solution, and the vial was left undisturbed for 1 week while the crystals formed by slow diffusion of the solvent.



Figure S72: Crystal structure of saponified TCND-(CO₂Me)₂ Oxidation Product. Grey is carbon and red is oxygen. Thermal ellipsoids are shown at the 50% probability level. Hydrogens omitted for clarity.

Formula: C11H10O5 Formula Weight: 222.20 Da

Crystal System: Monoclinic Space Group: P 2₁/c

Crystal Color: Colorless

Unit Cell Parameters: a = 7.985, b = 11.749, c = 10.383, α = 90, β = 103.89, γ = 90

Temperature of Data Collection: 100 K

Z: 4

R: 0.0469

GOF: 1.028

Crystal preparation: Crystallized via vapor diffusion with CDCl₃ (good solvent) and pentane (antisolvent) at room temperature.

Section 12: DFT Calculation Procedure for HOMO/LUMO Levels and Coordinates

Geometry Optimization and HOMO/LUMO Calculations: DFT calculations of HOMO/LUMO were performed with the ORCA 5.0.4 software package The chemical structure of interest was first drawn in Chem3D, and its structure roughly optimized with the "Minimize MM2" function. The structure was then exported to Avogadro, and an input Orca file was generated from it. The input file was then modified based on the desired level of theory for geometry optimization and single point energy calculation.

First, the geometry was roughly optimized with the BP86/def2-TZVP level of theory with the Orca input:

! RI BP86 def2-TZVP def2/J D3BJ TIGHTSCF Opt

Then, the output coordinates from this initial optimization were then used as the input to further finely optimize the structure with the M06-2X/def2-TZVP level of theory with CPCM solvation (chloroform) with the Orca input:

! M062X def2-TZVP CPCM(Chloroform) Opt

HOMO and LUMO levels were extracted from the Orca output files.

Monomer HOMO Energy Levels

Table S6: Monomer HOMO energy levels that were extracted from their DFT output files (M06-

2X/def2-TZVP level of theory with CPCM solvation for chloroform):

	HOMO Energy	
wonomer	(kcal/mol)	
NB-NBn	-191.9	
TCN-NBnanti	-190.7	
TCN-NBn _{syn}	-191.0	
NB-NCy	-193.2	
TCN-NCy	-190.8	
NB-NHex	-193.8	
TCN-NHex	-191.0	
NB-(CO2Me)2	-192.0	
TCN-(CO ₂ Me) ₂	-189.4	
TCND-(CO ₂ Me) ₂	-185.4	
NB-CO₂Me	-188.8	
TCND-CO₂Me	-182.9	

Table S7: Calculated LUMO levels of conjugate acceptors.

Conjugate Acceptor	LUMO (kcal/mol)
TCND-(CO ₂ Me) ₂	-30
TCND-CO2Me	-10
Dimethyl 2,3-dimethylmaleate	-8
Dimethyl maleate	-17
Ethenolysed TCND-(CO ₂ Me) ₂	-32



Figure S73: Plot of $ln(k_p)$ versus HOMO energy level of the M06-2X/def2-TZVP optimized geometries of each monomer.

Monomer Coordinates: The following are the optimized geometry coordinates found in the

Orca output files after M06-2X/def2-TZVP optimization for all structures of interest.

NB-NBn:

С	-3.92011129909832	1.48900785617874	1.06170372872249
С	-3.66711870480617	0.40223528958832	1.78928461500886
С	-2.80398715157880	-0.52115628678706	0.94949455422479
С	-1.41058681987744	0.18463144319891	0.88084338193434
С	-1.69970652609547	1.44701099107548	0.04673203819006
С	-3.22574819122926	1.31571481807833	-0.27673167479587
С	-3.34975587762219	-0.20817059710583	-0.45550623356510
С	-0.42673874716289	-0.60781340664410	0.05028617528538
С	-1.83845724401825	-2.83399310307087	-4.75205518033193
С	-0.84667972491517	1.29290514113006	-1.19159452672046
С	-1.15049245803157	-3.42451321160931	-3.69914233769229
С	-0.33161348128852	-2.65455898904422	-2.88299989921128
С	0.65384836748247	-0.44065103186134	-2.19708211739679
С	-0.19399546489553	-1.28835608739843	-3.11413547040363
С	-0.88339744943516	-0.70215081974784	-4.17287359242966
С	-1.70342593100239	-1.47128019890595	-4.98837335977577
Н	-4.42845709952845	2.38964166714822	1.37724449777521
Н	-3.92401495933456	0.22707647126606	2.82481107098284
Н	-2.75086960090939	-1.56183495553975	1.25611831715050
Н	-0.98976433026468	0.36392277534958	1.86815880380497
Н	-1.46396565631752	2.39198422173766	0.53181563806354
Н	-3.55576877943279	1.95390565008850	-1.09143023876207
Н	-2.74364795316111	-0.61330094034923	-1.27012969876099
Н	-4.38295775958877	-0.52648494697638	-0.57775729795010
Н	1.08198278815889	0.40603214320989	-2.73072514334374
Н	1.45413244151754	-1.02825575086115	-1.75074559156343
Н	-0.77522161111841	0.36073377174020	-4.35366231157817
Н	-2.23367078082577	-1.00679633453374	-5.81008684051881
Н	-2.47515125396270	-3.43570281305591	-5.38799843131668
Н	-1.24929474798813	-4.48672967555926	-3.51450186724886
Н	0.20316820115475	-3.11096110329062	-2.05876308637922
Ν	-0.14668794842359	0.10126588888304	-1.10444428976542
0	-0.78050248753803	2.04908645713274	-2.13003100238136
0	0.03765824113735	-1.69244433346469	0.30627737074864

TCN-NBnanti:

С	-1.07330498461831	-0.95686013346615	-3.78169958059849
С	-2.28758512584294	-0.61848795181261	-3.34671298460754
С	-2.55162581641650	-1.39691186456505	-2.06912917892421
С	-1.61350987485946	-0.72821292928470	-1.03236807352201
С	-0.19259214217971	-1.12384380352911	-1.54079970292778
С	-0.50080415449795	-1.96841618316426	-2.80350567846901
С	-1.35526324123455	-1.53072655065553	0.27542517613660
С	0.04279744104455	-1.92686853365864	-0.22755844181929
С	-1.79022118310440	-2.69698152445278	-2.38325077611694
С	1.00067735267224	-1.23377579883190	0.70430180968886
С	2.38338168382438	4.04943959906107	0.93452194854026
С	-1.10492655251721	-0.62125910160047	1.44903536464042
С	3.14674658120498	3.32808678399056	1.84266956498758
С	2.66393601475928	2.13441422111481	2.36446862913270
С	0.88382196125802	0.37775121309666	2.59604873062285
С	1.41490123841727	1.65491948576996	1.98848743630917
С	0.65378769961235	2.38070888528298	1.07574380704823
С	1.13638577898564	3.57079072032752	0.54911535590401
Н	-0.52555182073205	-0.51608355001728	-4.60336346731352
Н	-2.93497909665699	0.15245974101072	-3.74173940624236
Н	-3.58727643832104	-1.48412252110927	-1.75006209258319
Н	-1.83405398373306	0.32765308112762	-0.88491234957677
Н	0.52909263877017	-0.33078501619711	-1.72896389729401
Н	0.33075872716732	-2.57585272459514	-3.15218056765627
Н	-2.08387715688726	-2.30045444756512	0.52152530307214
Н	0.29975527761135	-2.97740558057011	-0.34616616509393
Н	-2.24003414893163	-3.24492440818239	-3.20910434793527
Н	-1.67033454188144	-3.36303770907491	-1.52857922550813
Н	0.11807272841622	0.59533756292628	3.34151247839911
Н	1.69117797379561	-0.17290407857963	3.07736768084292
Н	-0.32339734343777	2.01702896478135	0.77615396051482
Н	0.53648847247166	4.12836822530697	-0.15890331192953
Н	2.75906570884736	4.97880737510866	0.52576626894820
Н	4.12167242657053	3.69068187465312	2.14269360132881
Н	3.26470991619107	1.56468119369449	3.06387316644817
Ν	0.26376445142910	-0.48980929661297	1.61206440451768
0	2.20686573315285	-1.26007763745502	0.68384549390386
0	-1.92652220034967	-0.05032758227259	2.12437906713180

TCN-NBn_{syn}:

С	-3.55509938049837	-2.59026747568033	-1.51500977060420
С	-2.61090481416520	-3.08079358384338	-2.31914061213952
С	-1.27406217702650	-2.50843609815984	-1.86753890125438
С	-1.38255306802803	-1.02689621425569	-2.31771004456125
С	-2.48354314215304	-0.45399611671099	-1.37609335440555
С	-2.87529596764324	-1.67650370347297	-0.50490349883303
С	-1.54125932395444	-2.43087842222522	-0.35239593942532
С	-0.39923612055168	0.08292664224417	-1.81997981461691
С	-1.47858059169879	0.63744539698698	-0.88562415740996
С	0.75536279490370	-0.27761064102409	-0.92205273831800
С	3.54076323807139	3.39146434982473	2.48651498668528
С	-0.88525397298550	0.54501248805055	0.49596006631784
С	2.36986041625200	3.10424282969341	3.17610373923707
С	1.28907719258126	-0.13714241780031	1.52005712278303
С	1.64721039223975	1.95669215062823	2.87301952331384
С	2.09134449806680	1.08824246019729	1.88115766130690
С	3.26898168926007	1.37820335822327	1.19651862467437
С	3.99077307805909	2.52516891188871	1.49697533562932
Н	-4.62563290893270	-2.70601048946018	-1.61602036900509
Н	-2.75370253176767	-3.67842773352042	-3.20909926375655
Н	-0.38041395390988	-3.03367725921702	-2.19441672916885
Н	-1.56906317063811	-0.94490014895398	-3.38507315073052
Н	-3.34922158393534	-0.01139893297782	-1.86112192602722
Н	-3.43080562294922	-1.44641903318926	0.40040176742257
Н	-0.77954603169923	-1.92091060355239	0.22974493129751
Н	-1.69129051639809	-3.42064145651849	0.07557252728559
Н	-0.04249737280904	0.73146856030962	-2.61707929039521
Н	-1.82135758921091	1.65570639578933	-1.05660674667094
Н	0.64768450588530	-0.43646820345006	2.34856908565963
Н	1.94367775064472	-0.96607233370152	1.25239454817669
Н	3.61801340352185	0.69855895949243	0.42743383092811
Н	4.90541913581705	2.74214900117815	0.96002838048490
Н	4.10473878236547	4.28472580028195	2.72299932704690
Н	2.01792414620339	3.77390792354528	3.95057182601292
Н	0.73217425604271	1.73052000733115	3.40787371341724
Ν	0.42542210244519	0.10394827855325	0.37125541205311
0	1.79910284632179	-0.80245395012666	-1.22531878227151
0	-1.41221038772654	0.79652130362210	1.55203267986118

NB-NCy:

С	-4.50637131488507	-0.36020843747032	0.58642087718503
С	-4.17402542967557	-1.63262704427537	0.37594974598013
С	-2.67714792512603	-1.75770270459011	0.59639714324359
С	-2.03157205852110	-1.01531435415089	-0.61842739492871
С	-2.41716532484406	0.45276217702071	-0.37791280607081
С	-3.23846058557994	0.39145674259568	0.95115845166447
С	-2.47454008723438	-0.71141620879383	1.70694542859550
С	-0.51949799203248	-1.03109984265358	-0.56110268312812
С	4.23594511970951	0.19197904040639	-0.03096357990646
С	-1.09853034826818	1.17062092162990	-0.20618519700208
С	3.40897336983276	0.46058292185676	1.22463068139286
С	1.96799931391000	-0.01660512696026	1.05016544284732
С	1.34449510109142	0.63991295957091	-0.18047410013983
С	2.15532606126392	0.36349648845075	-1.44452616851285
С	3.59400101054614	0.84203124614480	-1.25485684146827
Н	3.40958022522459	1.53619819291718	1.43092293620616
Н	1.95186571025818	-1.10184324513288	0.92574078567306
Н	1.37034854460108	0.22762946602838	1.93164987571362
Н	-5.47076607089177	0.10252043161574	0.42854023046174
Н	-4.80951147067802	-2.42738630480163	0.01035288664977
Н	-2.28273022867837	-2.75688005691393	0.75802024690663
Н	-2.35494102276207	-1.43103031242641	-1.57082639177298
Н	-2.97607733317165	0.92665375338736	-1.18251800732851
Н	-3.35750367016770	1.35602770425401	1.43625027676969
Н	-2.96547851357241	-0.99335094738209	2.63612635662730
Н	-1.42707392915209	-0.47126982317753	1.90178178151692
Н	1.31441031611542	1.71994466607069	-0.01805644377561
Н	2.14766239093858	-0.70944996065765	-1.64965690914139
Н	1.68799163066709	0.86955245418948	-2.29196936306412
Н	4.17488625601650	0.62432819452168	-2.15272500805974
Н	3.59815705041335	1.92974333223964	-1.12679028003654
Н	4.30636207448618	-0.88887820524212	-0.19202650558265
Н	5.25375360922704	0.56386102065727	0.10247366670969
Н	3.85691962259416	-0.03078614039105	2.08992830549053
Ν	-0.06135027200113	0.25841529432266	-0.34234749334010
0	-0.94445565217627	2.34461585575786	0.03053731800486
0	0.18652182252237	-2.00548414861821	-0.66862726438009

TCN-NCy:

С	-2.36005061443316	-3.30100026934072	2.54518475871863
С	-2.98312090293433	-3.58001700402319	1.39935481868568
С	-1.93199261876776	-3.61614075968539	0.30324520222232
С	-1.53462264777254	-2.12776794288828	0.12673415592028
С	-0.80158682619350	-1.80295718416975	1.46629482490733
С	-0.88067316046503	-3.14454716049257	2.23794647164684
С	-0.73336208179141	-4.16725799439961	1.09701702566559
С	-0.21143637920081	-1.86156458450493	-0.64604758033327
С	0.51283684465161	-1.55327917323946	0.67095632662050
С	-0.23348964457251	-0.55116860226599	-1.38760795925381
С	1.33053469995134	4.60748400802536	-0.78052269707263
С	0.87465889866571	-0.09345196150554	0.58573591795242
С	0.50835281333874	1.81108928539861	-1.03683947527858
С	-0.12732079892481	4.19081657790141	-0.59564836777197
С	-0.22795441573946	2.75359998460630	-0.08622592518307
С	1.96886092733152	2.21485690750087	-1.23260556210326
С	2.05152207163876	3.65603217152886	-1.73319741993824
Н	-0.64787612224158	4.27069990971125	-1.55590458824224
Н	0.21711451087692	2.68440473924810	0.90869709427029
Н	-1.27216335838254	2.44274020075624	-0.00712148908707
Н	-2.81416345487468	-3.09843027242538	3.50557274741574
Н	-4.04932597625988	-3.65016803024253	1.23244904751523
Н	-2.20161226771859	-4.12368011690211	-0.61979722001747
Н	-2.37392359776459	-1.50138868288409	-0.17010047695531
Н	-1.15006317287347	-0.95574354353605	2.05426153458032
Н	-0.19302093257373	-3.22285320638054	3.07652521964658
Н	0.21723645520625	-4.11386715825080	0.56600141497975
Н	-0.90119501439758	-5.18750363963940	1.43760640986706
Н	0.14315831218178	-2.66532763442721	-1.28842140407280
Н	1.37440002634578	-2.14722508045654	0.96935160670852
Н	0.00890752496042	1.84228046292624	-2.00813454467130
Н	2.49656730981735	2.12692768113267	-0.28043217331286
Н	2.43970530647227	1.52920555953584	-1.94060188389407
Н	3.09731838492694	3.94663459748517	-1.84725783889159
Н	1.59020447326382	3.72349148357225	-2.72419066225027
Н	1.83346215813347	4.59052392743123	0.19224386807762
Н	1.38634585906712	5.63150212600061	-1.15459515759162
Н	-0.63303195916663	4.86350780079038	0.09922701105572
Ν	0.39256100875151	0.41416060634741	-0.61138186517378
0	1.46131818987540	0.55102305039435	1.42248567624027
0	-0.73407982840820	-0.33964107863302	-2.46625684160148

NB-NHex:

1.80110278700146	-4.73770573945846	1.96247220656233
1.27759190434275	-5.25043260173233	0.85030453469982
1.31473526340257	-4.16879434058766	-0.21523076172578
0.23705767607330	-3.12969044695961	0.23852019661046
0.84626174435276	-2.53461245269036	1.52214200044658
2.19984593371035	-3.30345161044845	1.66343800122624
2.60831227259180	-3.43613489601178	0.18498213680093
0.11805958930211	-1.95612157610274	-0.70868162478673
-1.67846611600801	3.59433914023506	-0.62726895569193
1.04400410247690	-1.06853699730114	1.20754190306049
-1.56922888051863	5.00902868828174	-1.18467793709938
-2.76769320161206	5.87811302199316	-0.82333690727903
0.66202354958077	0.48957207888903	-0.70232204147061
-0.57012903800522	1.32346973737917	-0.37760774240123
-0.47293034144672	2.72560315438213	-0.96499764475724
-2.66892802059076	6.88448036194464	-1.23217747495750
-3.69179810452726	5.44585882753545	-1.21317566653379
-2.87172205515996	5.96341102401516	0.26030580729414
1.84938379019148	-5.19572435301402	2.94068825250227
0.80723662401667	-6.21621228931636	0.72715721349617
1.20892368595315	-4.49062894436197	-1.24733670286539
-0.74366035689102	-3.58596955558906	0.35907278530385
0.22887032852383	-2.62531574816306	2.41379154417502
2.90120150345979	-2.83464531455849	2.34778557756265
3.49173467866831	-4.05782825456869	0.05563911652173
2.75357943804954	-2.48042296765175	-0.32233335670920
1.56428235130402	0.98086861837185	-0.33660550661884
0.75620989021346	0.33608500000322	-1.77731903633391
-1.45702272389479	0.81434215004396	-0.76562855964375
-0.67813192811593	1.38457548376684	0.70898148459364
0.43614352508442	3.20835826308884	-0.59094816257248
-0.36664046647176	2.65865527540497	-2.05281156330648
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C 0.13899206872838	0.69320132714921	-0.53538208975972					
C 2.00083422992398	0.4091/09882/321	1.32/9///49103/4					
C 4.30420645528791	0.78087019200191	1.13238401193317					
C = 0.57402327977545	1.01400091900100	-1.91307313033133					
U = 2.33091945572099	1.4300/390109030	-3.30322007731090					
$\Pi -3.74003013207371$	-0.70990100070201	0.00901700044040					
$\Pi -2.27703402962027$ $\Pi -0.02254111292177$	-2.32730372740931	2.04000401431970					
$\square -0.02234111202177$	-1.00002924743112	2.21074042042309					
H = -1.92270353596311 H = -1.07350617001428	1 2//035032/6556	-0.2156/052002055					
H -1 568/20770/8575	-1 11635120/11705	-1 60/6357/67/72/					
H = 5.21067635049219	-1 32621376759527	-1 31300205245808					
H -3 74756403299808	-1 52567743918642	-2 42960081989271					
H -3 66844720955729	-0.85127216658575	3 84146780971511					
H -2.72302660742864	0.49984261275780	3.02019432594849					
H -0.13229543064963	-2.19798176828277	-0.08107306375189					
H -1.65816949658992	-2.89891242183312	0.44246721544849					
H 3.41918472345442	1.51012490312413	-3.31452973714552					
H 2.05319346602397	0.62965604852413	-4.05941300751483					
H 1.91137939807581	2.37325239178618	-3.73609288668776					
H 4.98472123308686	1.14702742047976	0.36784041255901					
H 4.33712543371972	1.42788893041003	2.01157188033051					
H 4.55318355552294	-0.23443196097530	1.41665251078145					
O 2.13215265575760	0.12915472452927	2.48255229691962					
O -0.22266725615921	1.13373362598953	-2.81245309939235					
O 1.88341838845205	1.14939511442998	-2.05872618431631					
O 3.00053037408688	0.82541305102711	0.54163466763157					

Section 13: DFT Calculation of Monomer Steric Parameters

A conformer ensemble⁸ for each monomer was generated from SMILES using AQME⁹ with rdkit.¹⁰

Density functional theory (DFT) geometry optimizations for all conformers were performed at the B3LYP/def2-SVP level in gas phase with Gaussian16. Single points were used to determine Energies and molecular features at the M062X/def2-TZVP level. The following properties required these gaussian keywords: Density Pop=NBO7 Pop=Hirshfeld Pop=(ChelpG,ReadRadii) Polar Prop=(Potential,EFG) Volume EmpiricalDispersion = GD3.

Molecular descriptors were collected and processed into ensembles using an in-house Python (Jupyter notebook) script. General atom labels for the common monomer core shown in Figure S74 were used to obtain molecular descriptors when required. Single-point corrected Gibbs free energies were obtained using Paton's GoodVibes Python Script.¹¹ Conformers with energy above $\Delta G = 4.2$ kcal/mol were dropped from the dataset. MORFEUS was used to collect buried volume and Sterimol values.¹² All other descriptors were extracted from the Gaussian .log files. The ensembles are based on the feature value: maximum (max), minimum (min), range (max – min), Boltzmann-weighted average (Boltz), and on specific conformers: lowest energy (low_E), minimum percent buried volume (V_{bur-min}), HOMO_{min}. The ensemble properties (sheet = ensemble_properties) , conformer properties (sheet = conformer_correlations) can be found in the SI_Monomer_spreadsheet.xlsx. The coordinates can be found in the document SI coordinates.pdf


Figure S74: Atom numbering for molecular descriptors using a common core with example of the common core match.



Figure S75: Plot of Sterimol B_5 (along the C₂-H₂ axis) versus the molar volume for the V_{bur-min} conformers of the monomers. Note that the two are colinear.

Representative Correlation Plots of Steric Parameters:

The following plots show the three strongest correlations found between the calculated steric parameters and the measured monomer k_p values.



Figure S76: Plot of $ln(k_p)$ versus the molar volume of the V_{bur-min} conformer of each monomer.



Figure S77: Plot of $ln(k_p)$ versus the solvent accessible surface area (SASA) volume of the V_{bur-min} conformer of each monomer.



Figure S78: Plot of $ln(k_p)$ versus the solvent accessible surface area (SASA) volume of the max conformer of each monomer.

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