

## Supporting Information

### Relating Norbornene Composition-to-Reactivity for Thiol-Ene Photopolymerizations and 3D Printing

**Authors:** Yutong Liu<sup>1</sup>, Henry L. Cater<sup>1</sup>, Elizabeth A. Recker<sup>2</sup>, and Zachariah A. Page<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemistry, The University of Texas at Austin; Austin, TX 78712, USA

<sup>2</sup>McKetta Department of Chemical Engineering, The University of Texas at Austin; Austin, TX, 78712, USA

\*Corresponding author. Email: zpage@utexas.edu

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## S1. Experimental Details

### S1.1. Materials

*Chemicals.* All reagents were used as received unless otherwise noted. Certified ACS certified solvents were used as received from Fisher Scientific unless otherwise noted. 5-Norbornene-2,3-dicarboxylic anhydride (*endo*, >97.0%), *N*-hydroxyethyl acrylamide (97%), and 2-ethylhexylamine (98%) were purchased from TCI. 5-Norbornene-2-carboxylic acid (98%, mixture of *endo* and *exo*, predominantly *endo*), iodomethane (99%), and acetic anhydride (99.5%) were purchased from Sigma-Aldrich. 5-Norbornene-*exo*-2,3-dicarboxylic anhydride (>97%), 5-Norbornene-2-methanol (98%), methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (99%, isomer mixture), 5-norbornen-2-ol (98%, isomer mixture), and lithium phenyl-2, 4,6-trimethylbenzoylphosphinate (97%) were purchased from Ambeed, Inc. 1,4-Dithio-DL-threitol (99%) was purchased from Chem Impex. CDCl<sub>3</sub> (D, 99.8%) and dimethyl sulfoxide-D<sub>6</sub> (D, 99.9%) were purchased from Cambridge Isotope Laboratories. *N*-Hydroxyethyl acrylamide (97%) was passed through inhibitor removal column (SDHR-4 from scientific polymer) before use.

Methyl 2-[(Ethoxycarbonothioyl)thio]propionate (XAN) was synthesized according to literature procedure<sup>S1</sup>. *N*-(Glycine)-*cis*-5-norbornene-*exo*-dicarboximide (*exo*-NbI-COOH) was synthesized according to literature procedure<sup>S2</sup>. Bis(2-Ethylhexyl) (1R,2R,3S,4S)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*exo*-NbI-dister) and bis(2-ethylhexyl) (1R,2S,3R,4S)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*endo*-Nb-EH-diester) were synthesized following prior procedures from our group<sup>S3</sup>.

*Non-Chemicals.* Dialysis membrane (MWCO: 3500 Da) was purchased from Spectra/Por.

### S1.2. Methods

*Nuclear Magnetic Resonance (NMR) Spectroscopy.* NMR spectra were recorded on an Agilent MR 400 MHz spectrometer utilizing CDCl<sub>3</sub> or DMSO-D<sub>6</sub> as solvents. <sup>1</sup>H-NMR were carried out coupled and referenced to the CDCl<sub>3</sub> chemical shift at 7.26 ppm or referenced to the DMSO-D<sub>6</sub> chemical shift at 2.50 ppm. <sup>13</sup>C-NMR were carried out decoupled and referenced to the CDCl<sub>3</sub> chemical shift at 77.16 ppm. The peak assignments for *endo*- and *exo*- isomers was estimated based on previous literatures reports.<sup>S4-8</sup>

*High Resolution Mass Spectrometry (HRMS):* HRMS was performed on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS using ESI, and the data was subsequently analyzed using Agilent Mass Hunter Qualitative Analysis Software.

*Size Exclusion Chromatography (SEC):* Size exclusion chromatography (a.k.a., gel permeation chromatography, GPC) was performed on a TOSOH EcoSEC Elite HLC-8420GPC equipped with a (RI) detector. The instrument was run with HPLC-grade DMF with 10 mM LiBr as the eluent at 0.4 mL/min flow rate at 60 °C. Prior to injection, all samples were fully dissolved in the mobile phase and passed through a 0.45 μm PTFE syringe filter from Aijiren. Molecular weight and molecular weight distributions for the samples were estimated vs. polystyrene (PSt) standards.

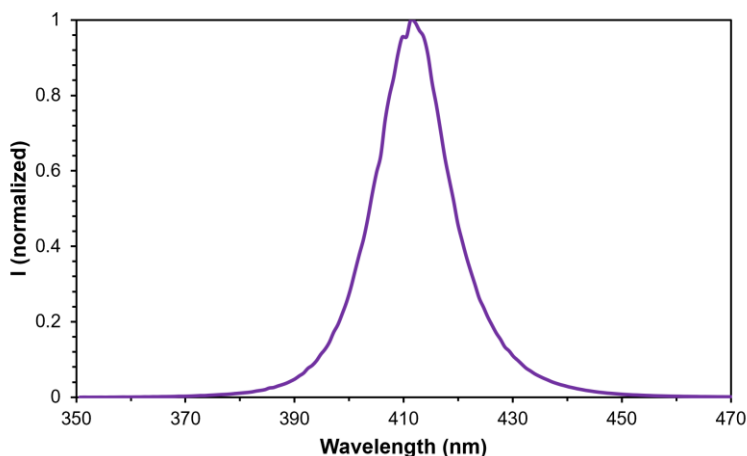
*Photo-Rheology:* Storage modulus  $G'$  and loss modulus  $G''$  measurements to estimate the time to gelation or “gel point” ( $G' = G''$ ) were carried out using a TA instrument Discovery Hybrid Rheometer (HR2). The rheometer was equipped with a “UV Light Guide” accessory (part # 546301.901, TA Instruments), a 20 mm diameter quartz bottom plate, and a 20 mm diameter geometry steel upper parallel plate. A liquid light guide was used to illuminate the samples with 405 nm LED, (LCS0405-12-22, Mightex Systems) connected to a driver from which light intensity could be controlled remotely through software (SLC-MA02-U, Mightex Systems). For a typical

photo-rheology measurement, the gap height was set to 100  $\mu\text{m}$  for each experiment to best match the printing conditions. The oscillation time sweep was used as the procedure with 1% strain and 10 rad/s frequency. The light intensity of the 405 nm LED was set to the desired value as measured at the top surface of quartz plate using a silicon photometer (Thorlabs, Model: S401C). The light was not turned on until 10 seconds into the oscillation time sweep step. The crossover of  $G'$  and  $G''$  (gel point) was determined using the “moduli cross” data analysis function in TRIOS.

*Viscosity:* Viscosity measurements were carried out using a TA instrument Discovery Hybrid Rheometer (HR2). The rheometer was equipped with a Peltier Plate and a 20 mm diameter geometry steel upper parallel plate. A flow sweep was performed with a logarithmic shear rate range from 1  $\text{s}^{-1}$  to 200  $\text{s}^{-1}$  at 25°C following a 30-second equilibration period at 100  $\mu\text{m}$  gap.

*Real-Time Fourier Transform Infrared (RT-FTIR) Spectroscopy (Transmission):* Resin formulations were injected between two 1 mm thick glass microscope slides (cat. no. 12-550-A3, Fisher Scientific) separated by  $\sim 100$   $\mu\text{m}$  polyester plastic shims (cat. no. 9513K66, McMaster-Carr) to maintain a constant sample thickness over the course of the photopolymerization. Each sample was placed in a horizontal transmission accessory (A043-N/Q, Bruker) equipped on the FTIR spectrometer (INVENIO-R, Bruker), which was controlled using OPUS spectroscopy software. Spectra were collected using a liquid nitrogen cooled (LN-MCTMid) detector from 2000 to 7000  $\text{cm}^{-1}$  at a rate of 1 scan every 0.36 s. All samples were monitored without degassing at room temperature. The light exposure was performed using the 405 nm LED light sources (LCS0405-12-22) from Mightex Systems, together with Lightguide Adapters. The functional group conversion upon light exposure was determined by monitoring the disappearance of the peak area centered at  $\sim 2580$   $\text{cm}^{-1}$  corresponding to the S–H stretch and the peak area centered at  $\sim 3050$   $\text{cm}^{-1}$  corresponding to the C=C–H stretch. Each sample was tested in triplicate at the same light intensity (1  $\text{mW}/\text{cm}^2$ ). The light was not turned on until 10 seconds after the measurement had started.

*Light Source:* For all experiments aside from 3D printing, a violet Type B LED (serial no. LCS-0405-12-22, Mightex Systems) was used with an emission centered at  $\sim 405$  nm. The LED was operated using a current-adjustable driver (SLC-MA02-U, Mightex Systems) for intensity control. Light was delivered via a 3 mm liquid light guide (LLG3-4H, ThorLabs). Irradiation intensity was measured with a ThorLabs PM100D photometer equipped with a silicon-based photodiode power sensor (S120VC and S130C).



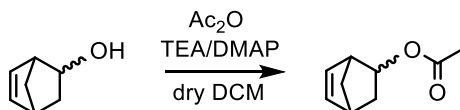
**Figure S1.** 405 nm LED emission profile used for photo-rheology and RT-FTIR spectroscopy.

*Digital Light Processing 3D Printer:* A custom digital light processing (DLP) 3D printer from Monoprinter equipped with a 405 nm LED was used for all fabrication and operated at a light intensity of 20 mW/cm<sup>2</sup>. Detailed information about the printer can be found in our previous reports<sup>S9,10</sup>. A transparent fluorinated polymer film (Teflon FEP film, McMaster-Carr, 127 μm thick) coated with a thin layer of fluorinated oil (Krytox by Chemours GLP 101 Industrial Oil) when needed was used as the base of the resin tank to provide a non-stick, high-temperature resistant, and flexible surface.

### S1.3. Synthesis

#### S1.3.1. Norbornene synthesis

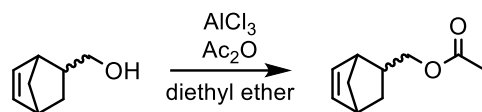
##### Scheme S1. Synthesis of bicyclo[2.2.1]hept-5-en-2-ol, 2-acetate (*mix-Nb-acetate*)



To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, 5-norbornen-2-ol (2.5 g, 22.7 mmol, 1 eq.), triethylamine (3 mL, 22 mmol, 1 eq.), 4-*N,N*-dimethylaminopyridine (3 mg, catalytic amount), and 20 mL of anhydrous dichloromethane were added. The reaction mixture was stirred under N<sub>2</sub> and placed in an ice bath. Acetic anhydride (3.5 mL, 37 mmol, 1.6 eq.) was added to the reaction mixture dropwise. After addition, the reaction mixture was allowed to warm to room temperature overnight with stirring. The reaction mixture was concentrated by rotary evaporation and purified via flash silica column chromatography with hexane:ethyl acetate = 5:2 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (2.57 g, 74%).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) (*endo:exo*=3:1) (*exo-isomer*) δ 6.23 (dd, 1H), 5.97 (dd, 1H), 4.66 (dt, 1H), 2.87 (br, 1H), 2.84 (s, 1H), 2.04 (s, 3H), 1.72-1.56 (m, 3H), 1.42-1.38 (1dt, 1H); (*endo-isomer*) δ 6.33 (dd, 1H), 5.97 (dd, 1H), 5.27 (dt, 1H), 3.13 (br, 1H), 2.84 (s, 1H), 2.13 (m, 1H), 1.97 (s, 3H), 1.47-1.45 (1H), 1.32-1.30 (1H), 0.94-0.90 (dt, 1H); <sup>13</sup>C NMR (400 MHz, Chloroform-*d*) (*exo-isomer*) δ 171.3, 141.2, 132.7, 75.2, 47.4, 46.3, 40.7, 34.7, 21.5; (*endo-isomer*) δ 171.5, 138.6, 131.6, 75.3, 47.8, 45.8, 42.3, 34.7, 21.3. ESI-HRMS: *m/z* = 153.0913 ([*M*+*H*]<sup>+</sup>), (calcd. 153.0910).

##### Scheme S2. Synthesis of bicyclo[2.2.1]hept-5-ene-2-methanol, 2-acetate (*mix-Nb-CH<sub>2</sub>-acetate*)

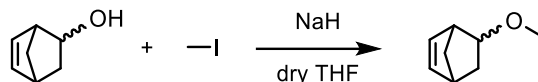


To a nitrogen flushed 50 mL round-bottom flask equipped with a magnetic stir bar, anhydrous AlCl<sub>3</sub> (50 mg 0.4 mmol, catalytic amount) and acetic anhydride (6 mL, 63.5 mmol, 4 eq.) were added, followed by the dropwise addition of 5-norbornene-2-methanol (2 g, 16 mmol, 1 eq.) dissolved in 5 mL of diethyl ether. The reaction mixture was stirring overnight at room temperature. The reaction mixture was diluted with 5 mL of diethyl ether, then transferred into separatory funnel and extracted with 10 wt% NaHCO<sub>3</sub> in deionized water. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to obtain the desired product as a colourless liquid (2.04 g, 77%).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) (*endo:exo*=3:2) (*exo-isomer*) δ 6.09 (m, 2H), 4.41 (dd, 1H), 3.95 (dd, 1H), 2.82 (m, 1H), 2.70 (s, 1H), 2.07-2.05 (m, 3H), 1.71 (m, 1H), 1.32-1.24 (3H), 1.16-

1.13 (dt, 1H); (*endo-isomer*)  $\delta$  6.15 (dd, 1H), 5.94 (dd, 1H), 3.84 (dd, 1H), 3.65 (dd, 1H), 2.88 (s, 1H), 2.82 (m, 1H), 2.38 (m, 1H), 2.07-2.05 (m, 3H), 1.84 (1H), 1.45-1.44 (m, 1H), 1.32-1.24 (m, 1H), 0.56-0.53 (qd, 1H);  $^{13}\text{C}$  NMR (400 MHz, Chloroform-d)  $\delta$  171.4, 171.3, 137.7, 137.1, 136.3, 132.3, 68.7, 68.1, 49.5, 45.1, 44.0, 43.8, 42.3, 41.7, 38.1, 37.9, 29.7, 29.1, 21.2, 21.1. ESI-HRMS:  $m/z = 167.1062$  ( $[\text{M}+\text{H}]^+$ ), (calcd. 167.1067).

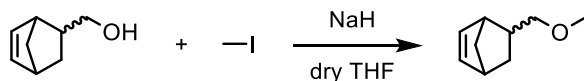
**Scheme S3. Synthesis of 5-methoxybicyclo[2.2.1]hept-2-ene (*mix-Nb-ether-CH<sub>3</sub>*)**



To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, sodium hydride (2.2 g of a 60% dispersion in mineral oil, which was removed by rinsing with pentane) and 10 mL of anhydrous tetrahydrofuran were added, followed by cooling the flask in an ice bath and dropwise adding 5-norbornen-2-ol (3 g, 24 mmol, 1 eq.) in 20 mL of anhydrous tetrahydrofuran, then the reaction mixture was stirring at room temperature. After 2 hours, the reaction mixture was placed in an ice bath, then methyl iodide (3 mL, 6.8 g, 48 mmol, 2 eq.) was added into the reaction mixture dropwise. The reaction mixture was allowed to stir for ~12 hours at room temperature and then quenched by adding methanol. The crude mixture was then diluted with 100 mL of diethyl ether and transferred into a separatory funnel. The organic phase was washed three times with water and dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure to afford the crude product. The crude product was purified via flash silica column chromatography with a gradient of hexanes:ethyl acetate = 10:1 to 4:1 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (1.36 g, 46%).

$^1\text{H}$  NMR (400 MHz, Chloroform-d) (*endo:exo=4:1*) (*exo-isomer*)  $\delta$  6.17 (dd, 1H), 5.91 (dd, 1H), 3.38-3.36 (m, 1H), 3.33 (s, 3H), 2.89 (s, 1H), 2.80 (s, 1H), 1.53 (m, 3H), 1.32-1.29 (dt, 1H); (*endo-isomer*)  $\delta$  6.32 (dd, 1H), 5.99 (dd, 1H), 4.06 (m, 1H), 3.28 (s, 3H), 3.11 (s, 1H), 2.80 (s, 1H), 1.97 (m, 1H), 1.45-1.42 (m, 1H), 1.24-1.21 (d, 1H), 0.88-0.85 (dt, 1H);  $^{13}\text{C}$  NMR (400 MHz, Chloroform-d)  $\delta$  (*exo-isomer*) 141.15, 132.71, 75.26, 47.35, 46.31, 40.70, 34.67, 21.51; (*endo-isomer*)  $\delta$  138.61, 131.64, 75.21, 47.75, 45.84, 42.30, 34.65, 21.25. ESI-HRMS:  $m/z = 125.0960$  ( $[\text{M}+\text{H}]^+$ ), (calcd. 125.0961).

**Scheme S4. Synthesis of 5-(methoxymethyl)bicyclo[2.2.1]hept-2-ene (*mix-Nb-CH<sub>2</sub>-ether-CH<sub>3</sub>*)**

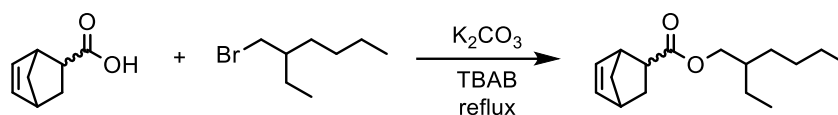


To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, sodium hydride (1 g of a 60% dispersion in mineral oil, which was removed by rinsing with pentane, 25.8 mmol, 2 eq.) and 30 mL of anhydrous tetrahydrofuran were added, followed by cooling the flask in an ice bath. 5-norbornene-2-methanol (1.6 g, 13 mmol, 1 eq.) in 10 mL of anhydrous tetrahydrofuran was added dropwise. After addition, the reaction mixture was stirred at room temperature for 30 min. Methyl iodide (1.7 mL, 25.8 mmol, 2 eq.) was dissolved in 5 mL of anhydrous tetrahydrofuran and then added dropwise into the reaction mixture that was in an ice bath and under a  $\text{N}_2$  atmosphere. The reaction mixture was stirred at room temperature for 2 h. The flask was placed in an ice bath and methanol was added dropwise to quench the reaction. Then 125 mL of diethyl ether was added into the reaction mixture and the contents were filtered before

transferring the filtrate into a separatory funnel and washing with deionized water (50 mL) 4 times. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was purified via silica column chromatography using hexane:ethyl acetate = 1:1 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (789 mg, 44%).

<sup>1</sup>H NMR (400 MHz, Chloroform-d) (*endo:exo*=3:2) (*exo-isomer*) δ 6.09 (dd, 1H), 6.05 (dd, 1H), 3.44-3.40 (dd, 1H), 3.35 (s, 3H), 3.31-3.27 (t, 1H), 2.79 (br, 1H), 2.72 (s, 1H), 1.68 (m, 1H), 1.30-1.25 (m, 3H), 1.12-1.09 (dt, 1H); (*endo-isomer*) δ 6.11 (dd, 1H), 5.93 (m, 1H), 3.30 (s, 3H), 3.10-3.06 (dd, 1H), 3.03-2.98 (t, 1H), 2.89 (s, 1H), 2.89 (1H), 2.79 (br, 1H), 1.81 (m, 1H), 1.43-1.42 (m, 1H), 1.30-1.25 (m, 1H), 0.51-0.47 (m, 1H); <sup>13</sup>C NMR (400 MHz, Chloroform-d) (*exo-isomer*) δ 136.7, 136.7, 77.7, 58.9, 45.2, 43.8, 41.7, 39.0, 29.8; (*endo-isomer*) δ 137.2, 132.6, 76.8, 58.9, 49.6, 44.1, 42.3, 38.8, 29.3. ESI-HRMS: *m/z* = 139.1115 ([M+H]<sup>+</sup>), (calcd. 139.1117).

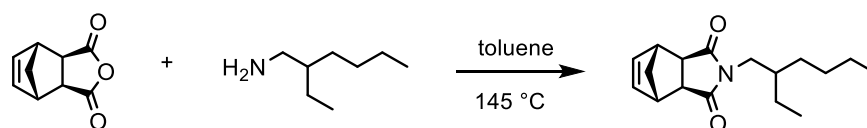
**Scheme S5. Synthesis of 2-ethylhexyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (*mix-Nb-ester-EH*)**



To a 100 mL round bottom flask equipped with a magnetic stir bar and condenser, 5-norbornene-2-carboxylic acid (1 g, 7.2 mmol, 1 eq.), 2-ethylhexyl bromide (1.6 mL, 9.1 mmol, 1.3 eq.), potassium carbonate (6.0 g, 43 mmol, 6 eq.), tetrabutylammonium bromide (5 mg, 0.015 mmol, 0.002 eq.), and acetone (25 mL) were added. The reaction mixture was refluxed overnight with magnetic stirring before allowing it to cool to room temperature. The precipitate was filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica flash column chromatography using dichloromethane as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (1.57 g, 87%).

<sup>1</sup>H NMR (400 MHz, Chloroform-d) (*endo:exo*=4:1) δ 6.18 (m, 1H<sub>endo</sub>), 6.12 (m, 2H<sub>exo</sub>), 5.91 (m, 1H<sub>endo</sub>), 4.0 (m, 2H<sub>exo</sub>), 3.92 (m, 2H<sub>endo</sub>), 3.21 (s, 1H<sub>endo</sub>), 3.04 (s, 1H<sub>exo</sub>), 2.96-2.90 (m, 2H<sub>exo&endo</sub>), 2.21-2.24 (m, 1H<sub>exo</sub>), 1.90 (m, 1H<sub>endo</sub>), 1.43-1.42 (m, 2H<sub>exo&endo</sub>), 1.35-1.28 (m, 10 H<sub>exo&endo</sub>) 0.91-0.87 (m, 6H<sub>exo & endo</sub>). <sup>13</sup>C NMR (400 MHz, Chloroform-d) δ (*exo-isomer*) 176.6, 138.1, 135.9, 67.0, 46.7, 46.5, 43.5, 41.8, 39.0, 30.6, 30.4, 29.1, 24.0, 23.1, 14.2, 11.2. (*endo-isomer*) 175.1, 137.9, 132.5, 66.7, 49.8, 45.9, 43.6, 42.7, 38.9, 30.6, 30.5, 29.2, 29.1, 24.0, 14.2, 11.1. ESI-HRMS: *m/z* = 273.1827 ([M+Na]<sup>+</sup>), (calcd. 273.1825).

**Scheme S6. Synthesis of (3aR,7aS)-2-(2-ethylhexyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (*exo-NBI-EH*)**

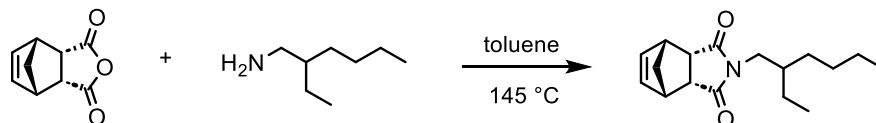


To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, Dean-Stark trap, and condenser, *exo-cis*-5-norbornene-2,3-dicarboxylic anhydride (2 g, 12.2 mmol, 1 eq.), 2-ethyl-1-hexylamine (2.2 mL, 13.4 mmol, 1.1 eq.) and toluene (40 mL) were added. The reaction mixture was refluxed at 145 °C overnight with stirring. After allowing to cool to room temperature, solvent was removed under reduced pressure, and the crude product was purified via silica flash

column using hexane:ethyl acetate = 5:1 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless oil (3.25 g, 96%).

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  6.28 (s, 2H), 3.37-3.35 (m, 2H), 3.27 (m, 2H), 2.67 (s, 2H), 1.70 (m, 1H), 1.52-1.50 (m, 1H), 1.33-1.17 (m, 9H), 0.90-0.86 (m, 6H);  $^{13}\text{C}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  178.5, 137.9, 47.9, 45.3, 42.9, 42.7, 37.9, 30.6, 28.5, 24.0, 23.1, 14.2, 10.5. ESI-HRMS:  $m/z$  = 298.1776 ( $[\text{M}+\text{Na}]^+$ ), (calcd. 298.1778).

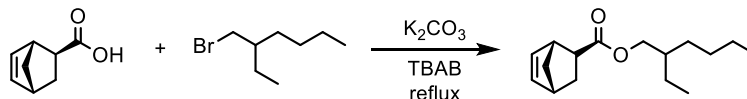
**Scheme S7. Synthesis of (3aR,7aS)-2-(2-Ethylhexyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (*endo*-NBI-EH)**



To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, Dean-Stark trap, and condenser, *endo*-cis-5-norbornene-2,3-dicarboxylic anhydride (2g, 12.2 mmol, 1 eq.), 2-ethyl-1-hexylamine (2.2 mL, 13.4 mmol, 1.1 eq.) and toluene (30 mL) were added. The reaction mixture refluxed at 145 °C overnight with stirring. After allowing to cool to room temperature, the solvent was removed under reduced pressure, and the crude product was purified via silica flash column using hexane:ethyl acetate = 2:1 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless oil (3.24 g, 96%).

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  6.10 (s, 2H), 3.38 (m, 2H), 3.24 (m, 2H), 3.22 (d, 2H), 1.74-1.72 (d, 2H), 1.55-1.52 (m, 2H), 1.28-1.16 (m, 8H), 0.89-0.83 (m, 6H);  $^{13}\text{C}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  178.2, 134.7, 52.5, 45.8, 45.0, 42.4, 37.8, 30.5, 28.6, 23.9, 23.2, 14.2, 10.5. ESI-HRMS:  $m/z$  = 298.1774 ( $[\text{M}+\text{Na}]^+$ ), (calcd. 298.1778).

**Scheme S8. Synthesis of 2-ethylhexyl *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (*exo*-Nb-ester-EH)**



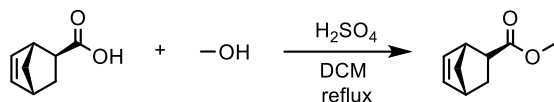
To a 25 mL round bottom flask equipped with a magnetic stir bar and condenser, *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (200 mg, 1.4 mmol, 1 eq.), 2-ethylhexyl bromide (0.32 mL, 1.8 mmol, 1.3 eq.), potassium carbonate (1.2 g, 8.6 mmol, 6 eq.), tetrabutylammonium bromide (1 mg, 0.003mmol, 0.002 eq.), and acetone (10 mL) were added. The reaction mixture was refluxed overnight with magnetic stirring before allowing it to cool to room temperature. The crude mixture was then diluted with 10 mL of DCM and transferred into a separatory funnel. The organic phase was extracted with deionized water and brine, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure to afford the crude product. The crude product was purified by silica flash column chromatography using 5% ethyl acetate in hexane as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (243.6 mg, 69%).

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  6.13 (m, 2H), 4.00 (m, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.93 (m, 1H), 1.60-1.51 (m, 2H), 1.36-1.29 (m, 10H), 0.91-0.87(t, 6H).  $^{13}\text{C}$  NMR



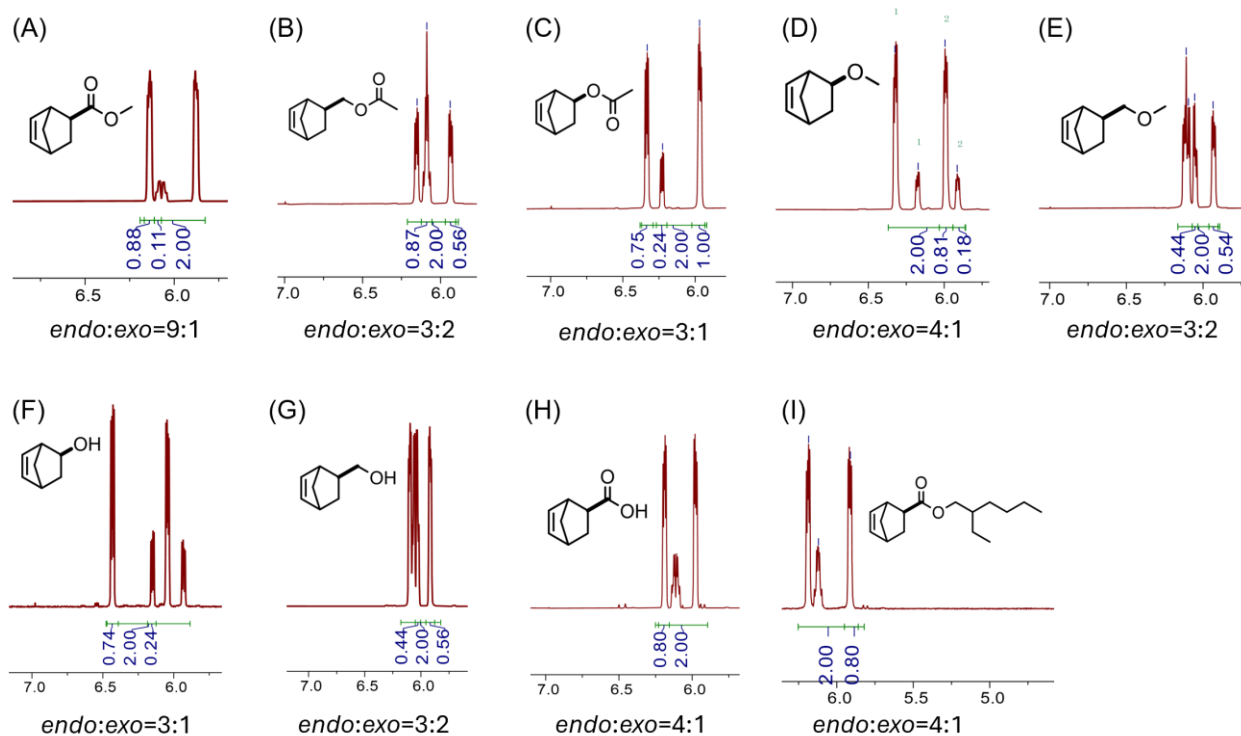
(400 MHz, Chloroform-d)  $\delta$  176.6, 138.2, 135.9, 67.0, 46.7, 46.5, 43.5, 41.8, 40.0, 30.6, 30.4, 29.1, 24.0, 23.1, 14.2, 11.2. ESI-HRMS:  $m/z = 273.1821$  ( $[M+Na]^+$ ), (calcd. 273.1825).

**Scheme S9. Synthesis of *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, methyl ester (*exo*-Nb-ester-CH3)**



To a 25 mL round bottom flask equipped with a magnetic stir bar and condenser, *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (250 mg, 1.8 mmol, 1 eq.), methanol (0.75 mL, 18 mmol, 10 eq.), H<sub>2</sub>SO<sub>4</sub> (1 drop, 25  $\mu$ L) and DCM (10 mL) were added. The reaction mixture was refluxed overnight with magnetic stirring before allowing it to cool to room temperature. The crude mixture was then diluted with 10 mL of DCM and transferred into a separatory funnel. The organic phase was extracted with deionized water and brine, and dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford the crude product. The crude product was purified by silica flash column chromatography using 0-20% ethyl acetate in hexane as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid (178.4 mg, 65%).

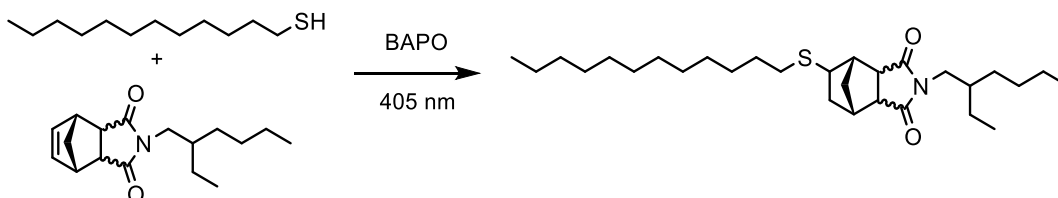
<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  6.14-6.10 (m, 2H), 3.69 (s, 3H), 3.03 (s, 1H), 2.92 (s, 1H), 2.23 (m, 1H), 1.93 (m, 1H), 1.51 (m, 1H), 1.37 (m, 2H). <sup>13</sup>C NMR (400 MHz, Chloroform-d)  $\delta$  176.9, 138.2, 135.9, 51.9, 46.7, 46.5, 43.1, 41.8, 30.5. ESI-HRMS:  $m/z = 153.0910$  ( $[M+H]^+$ ), (calcd. 153.0903).



**Figure S2.** <sup>1</sup>H-NMR spectra used to determine *endo* to *exo* ratios.

**Table S1. Summary of *endo* to *exo* ratios, determined via <sup>1</sup>H-NMR.**

Norbornene derivatives	<i>endo:exo</i>	Norbornene derivatives	<i>endo:exo</i>
Norbornene carboxylic acid ( <i>mix</i> -Nb-COOH)	75:25 (3:1)	<i>mix</i> -Nb-CH <sub>2</sub> -acetate	56:44 (~3:2)
5-Norbornen-2-ol ( <i>mix</i> -Nb-OH)	80:20 (4:1)	<i>mix</i> -Nb-ether-CH <sub>3</sub>	81:18 (~4:1)
5-Norbornene-2-methanol ( <i>mix</i> -Nb-CH <sub>2</sub> -OH)	56:44 (~3:2)	<i>mix</i> -Nb-CH <sub>2</sub> -ether-CH <sub>3</sub>	56:44 (~3:2)
<i>mix</i> -Nb-ester-CH <sub>3</sub>	88:12 (~9:1)	<i>mix</i> -Nb-ester-EH	80:20 (4:1)
<i>mix</i> -Nb-acetate	75:25 (3:1)	/	/

**Scheme S10. Reaction of *exo*-NbI-EH or *endo*-NbI-EH with 1-dodecanethiol**

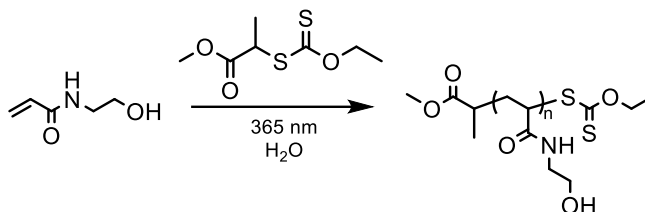
In a 4 mL glass vial equipped with a magnetic stir bar, *exo*-NbI-EH or *endo*-NbI-EH (550 mg, 2 mmol, 1 eq.), 1-dodecanethiol (405 mg, 2 mmol, 1 eq.), and BAPO (5 mg, 0.5 wt%) were added. The mixture was degassed with argon for 15 minutes and then placed in front of a 405 nm LED. The 405 nm LED was turned on for 10 minutes with an intensity of 20 mW/cm<sup>2</sup> as measured with a silicon photometer (Thorlabs, Model: S401C). After 10 minutes, an aliquot was removed and analysed using <sup>1</sup>H-NMR spectroscopy to determine the conversion. Then, the crude product was purified via silica column chromatography with hexane:ethyl acetate = 3:1 as the mobile phase, isolating the desired band and concentrating it under reduced pressure to afford the desired product as a colourless liquid.

*Exo*-isomer: <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 3.45 (t, 2H), 2.78 (m, 1H), 2.70-2.67 (m, 2H), 2.58 (m, 4H), 1.86 (m, 1H), 1.70-1.67 (d, 1H), 1.57-1.53 (m, 5H), 1.37-1.26 (m, 28H), 1.07-1.04 (d, 1H), 0.88 (d, 6H); <sup>13</sup>C NMR (500 MHz, Chloroform-d) δ 178.78, 178.40, 48.20, 48.14, 45.53, 45.20, 42.84, 39.56, 37.80, 37.79, 37.42, 32.74, 32.06, 30.61, 30.38, 29.79, 29.77, 29.73, 29.69, 29.66, 29.48, 29.38, 29.12, 28.52, 24.01, 23.10, 22.83, 14.26, 10.47. ESI-HRMS: m/z = 500.3533 ([M+Na]<sup>+</sup>), (calcd. 500.3533).

*Endo*-isomer: <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 3.37-3.35 (d, 2H), 3.13-3.08 (m, 1H), 2.76-2.67 (m, 3H), 2.49 (m, 2H), 2.04-2.01 (d, 1H), 1.78-1.70 (m, 2H), 1.59-1.51 (m, 3H), 1.25 (m, 28H), 0.89 (m, 9H); <sup>13</sup>C NMR (500 MHz, Chloroform-d) δ 178.10, 178.01, 48.42, 48.06, 44.83, 42.67, 41.90, 41.80, 39.50, 39.11, 37.99, 34.38, 32.79, 32.05, 30.78, 29.79, 29.77, 29.74, 29.58, 29.48, 29.36, 29.04, 28.62, 28.55, 24.10, 23.15, 22.82, 14.25, 10.48. ESI-HRMS: m/z = 500.3537 ([M+Na]<sup>+</sup>), (calcd. 500.3533).

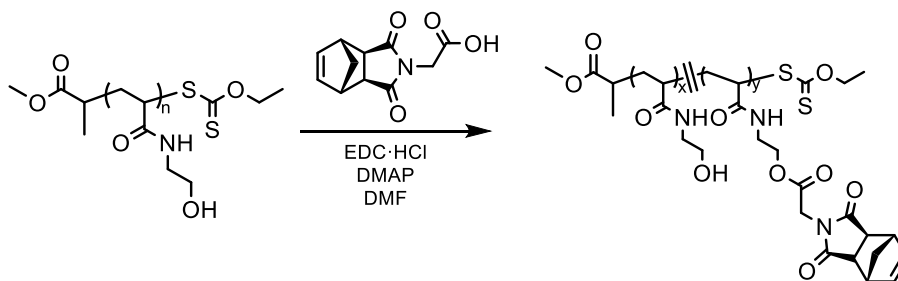
### S1.3.2. Polymer synthesis

#### Scheme S11. Polymerization of HEAA in aqueous solution via photoiniferter



In a 20 mL glass vial equipped with a magnetic stir bar, de-inhibited *N*-hydroxyethyl acrylamide (HEAA) (2.3 g, 20 mmol, 1000 eq.), 500  $\mu\text{L}$  of the stock solution of XAN CTA (4.2 mg, 0.02 mmol, 1 eq.) in DMSO, and 7.9 mL  $\text{H}_2\text{O}$  were added ([monomer] = 2 M). The mixture was degassed with argon for 15 min and then placed in a 365 nm photoreactor. The 365 nm LED was turned on for 10 minutes, providing an estimated intensity of  $9 \text{ mW}/\text{cm}^2$  by putting the photodiode at the centre of photoreactor and facing it towards LEDs. The reaction mixture became viscous during the polymerization. After 10 minutes, the light was turned off, and an aliquot was removed for  $^1\text{H-NMR}$  spectroscopy in deuterated DMSO to monitor the polymerization conversion. The reaction mixture was then transferred to dialysis tubing and placed in deionized water for 3 days with exchanging water roughly every 6 hours. Following this, the contents were transferred to a glass vial, and the water was removed via freeze drying (Labconco FreeZone,  $-80^\circ\text{C}$  and 0.5 mbar).

#### Scheme S12. Post-functionalization of PHEAA with *exo*-NBI



To a nitrogen flushed 100 mL round-bottom flask equipped with a magnetic stir bar, PHEAA (1.4 g, 12.2 mmol -OH), *exo*-NBI-COOH (168 mg, 1.2 mmol), DMAP (171 mg, 1.4 mmol), EDC·HCl (540 mg, 2.8 mmol), and DMF (30 mL) were added. The reaction mixture was stirred overnight and then transferred to dialysis tubing and placed in deionized water for 3 days with exchanging water roughly every 6 hours. Then, the reaction mixture was transferred to glass vial, and the water was removed via freeze drying (Labconco FreeZone,  $-80^\circ\text{C}$  and 0.5 mbar).

## S2. Supplementary Text

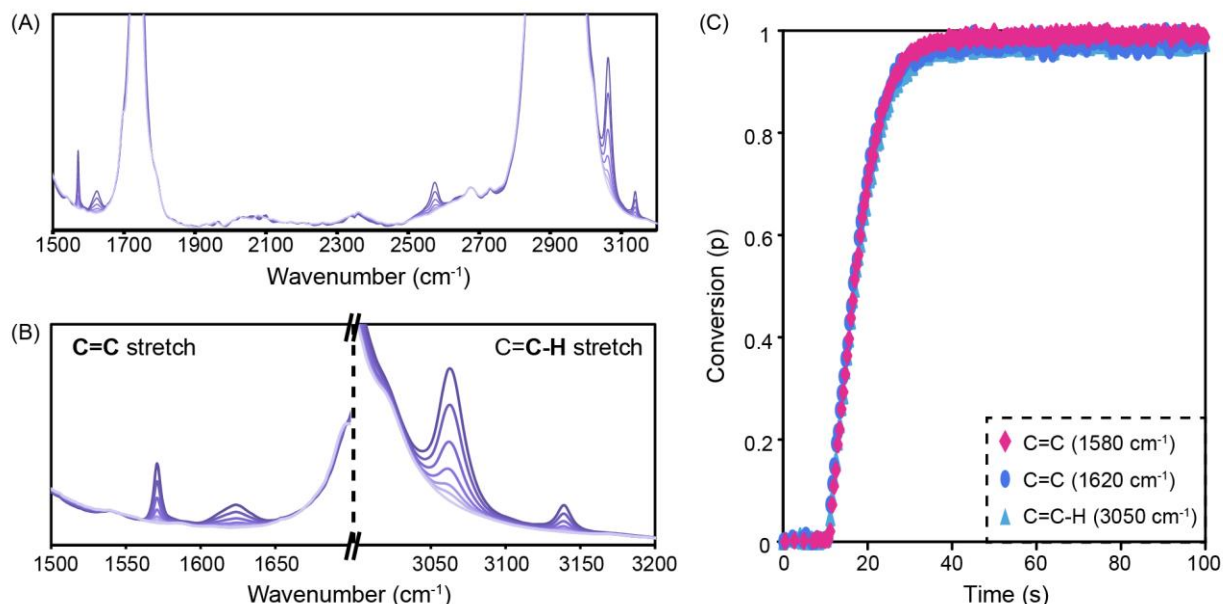
### S2.1. Real-time FTIR Spectroscopy

The reaction kinetics for different derivatives of norbornene with 1-dodecanethiol were characterized using real time Fourier transform infrared (FTIR) spectroscopy in a transmission configuration. All derivatives used in this study are liquid at room temperature. Equimolar amounts of Nb-derivatives and 1-dodecanthiol were mixed with 0.1 mol% BAPO (relative to total mol of Nb + thiol) as the photoinitiator. Take *exo*-NBI-EH as an example: *exo*-NBI-EH (1 mmol) was added into a 4 mL vial, and BAPO (0.002 mmol) in 1-dodecanethiol (1 mmol) stock solution was added to make the thiol and norbornene functionality stoichiometrically balanced, then the reaction mixture was homogenized using a vortex mixer. The thiol-Nb reaction rate was calculated from the initial slope of the conversion vs. time plots. Additionally,  $t_{50}$  was determined as the time required to reach 50% monomer (C=C–H) conversion, excluding the initial 10 seconds before LED was turned on.

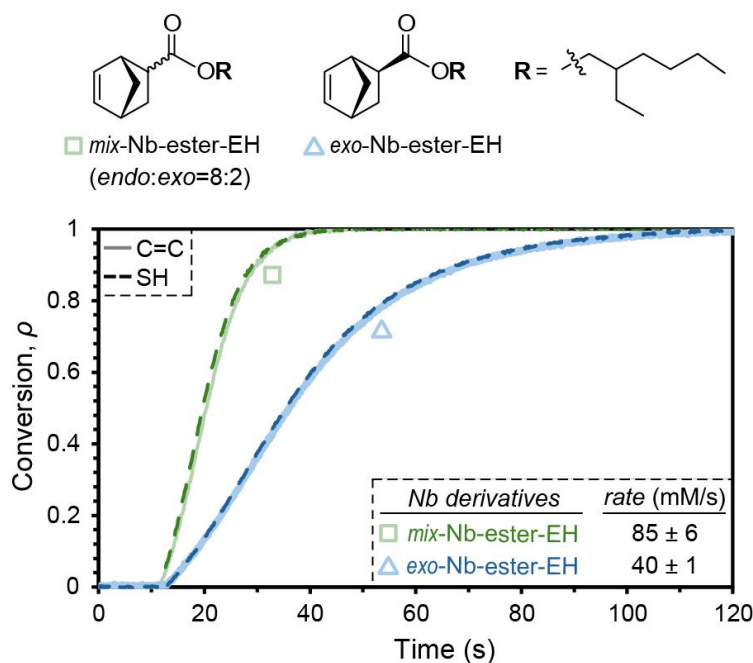
An unbalanced molar ratio of Nb:thiol was also conducted in this work to examine the influence of stoichiometry on reaction kinetics. By varying the ratio of norbornene to thiol, the observed changes in reaction rate reveal that the concentrations of norbornene and thiol have different effects on the rate depending on the specific compound. However, to extract explicit rate constants (e.g., addition, chain-transfer, and propagation) will require additional experimentation.

**Table S2. Summary of the kinetics of equimolar thiol-norbornene reactions for various norbornene derivatives. Values are averages ( $n \geq 3$ ) with  $\pm 1$  standard deviation from the mean provided.**

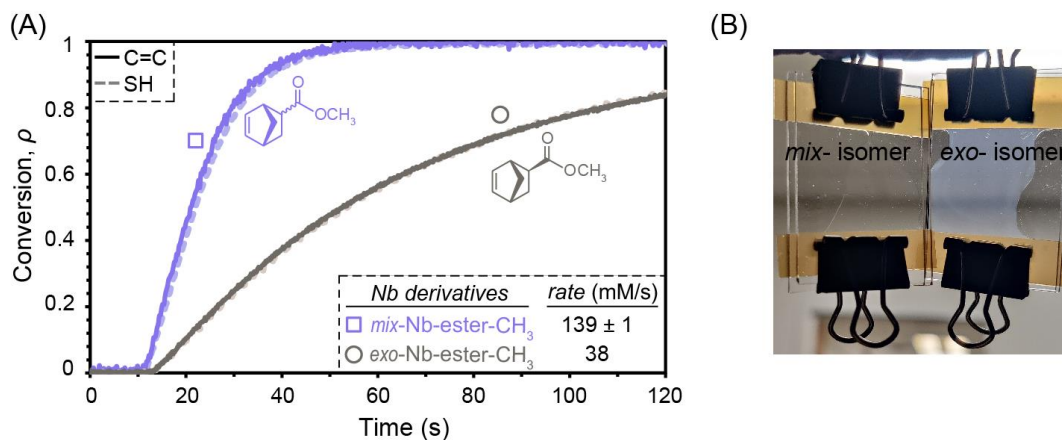
Nb derivative	Rate (%s <sup>-1</sup> ) (H–C=C)	Rate (%s <sup>-1</sup> ) (S–H)	Rate (mM/s) (H–C=C)	Rate (mM/s) (S–H)	$t_{50}$ (s)
Nb-ester-methyl	4.92 ± 0.05	5.0 ± 0.1	139 ± 1	141 ± 3	12.7 ± 0.1
Nb-acetate	6.1 ± 0.1	6.2 ± 0.2	171 ± 4	174 ± 5	10.4 ± 0.1
Nb-CH <sub>2</sub> -acetate	1.2 ± 0.1	1.3 ± 0.2	33 ± 4	35 ± 5	32 ± 3
Nb-ester-EH	3.9 ± 0.3	4.3 ± 0.5	85 ± 6	94 ± 11	10.9 ± 0.1
<i>exo</i> -Nb-diester-EH	2.03 ± 0.01	2.11 ± 0.06	42.5 ± 0.3	44 ± 1	23.3 ± 0.1
<i>endo</i> -Nb-diester-EH	0.81 ± 0.01	0.86 ± 0.03	17.0 ± 0.3	18.0 ± 0.6	56 ± 2
<i>exo</i> -NBI-EH	6.1 ± 0.2	6.0 ± 0.2	100 ± 3	99 ± 3	7.3 ± 0.2
<i>endo</i> -NBI-EH	0.65 ± 0.03	0.69 ± 0.08	10.7 ± 0.4	11 ± 1	79 ± 2
Nb-ether-methyl	4.4 ± 0.6	4.79 ± 0.75	133 ± 20	147 ± 23	12 ± 1
Nb-CH <sub>2</sub> -ether-methyl	1.13 ± 0.05	1.16 ± 0.16	33 ± 1	34 ± 5	24.0 ± 0.3
<i>exo</i> -Nb-ester-methyl	1.34	1.36	37.8	38.2	43.4
<i>exo</i> -Nb-ester-EH	1.82 ± 0.05	1.89 ± 0.45	40 ± 1	42 ± 10	26.1 ± 0.2



**Figure S3.** (A) A real-time FTIR spectra of *mix*-Nb-ester-CH<sub>3</sub> on sodium chloride salt plates with a 100  $\mu\text{m}$  spacer, along with its magnification (B) to show the C=C stretch at 1620  $\text{cm}^{-1}$  and C=C-H stretch at 3050  $\text{cm}^{-1}$  region. (C) A summary of alkene conversion as a function of irradiation time by monitoring distinct absorption bands, showing consistency in the results.

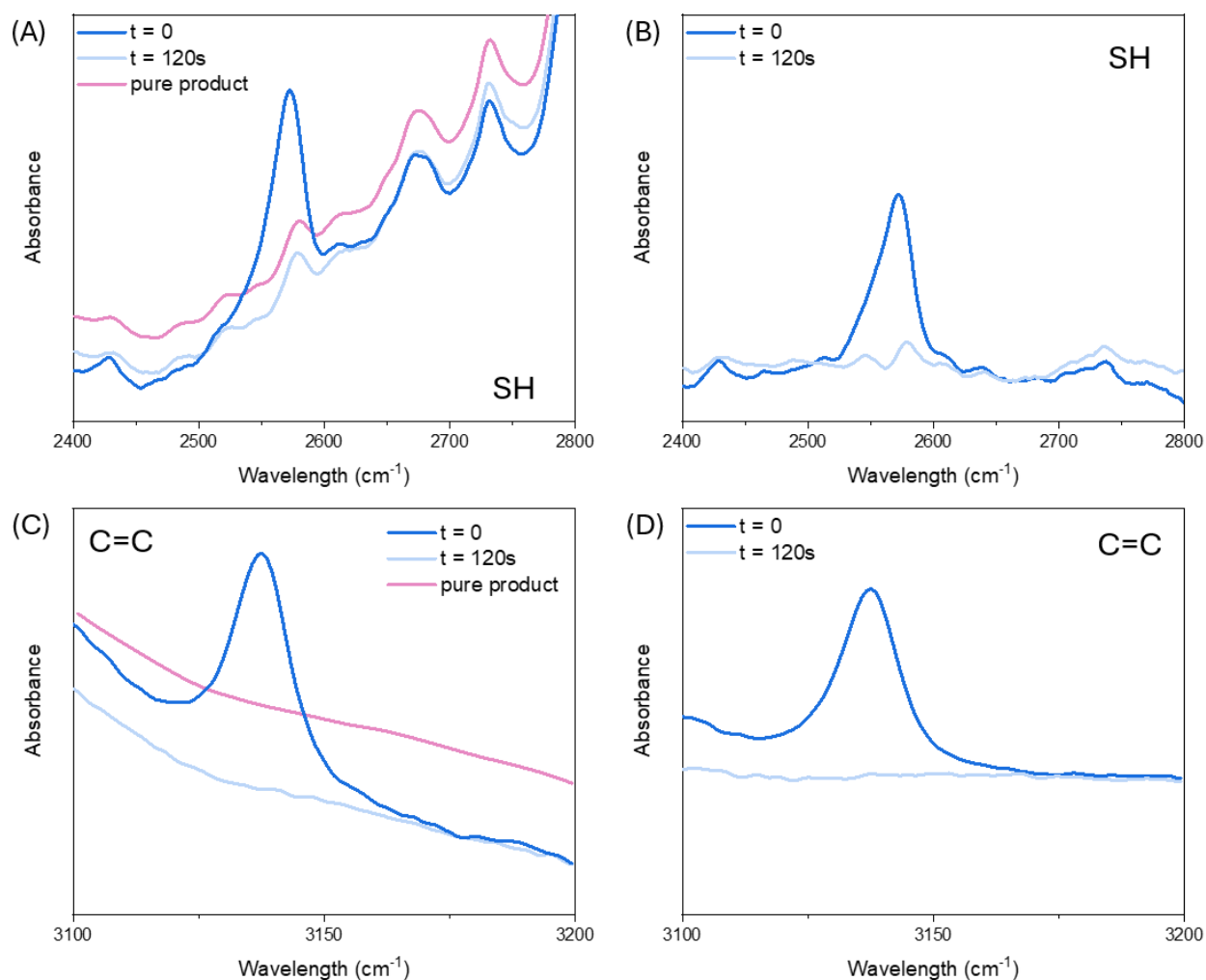


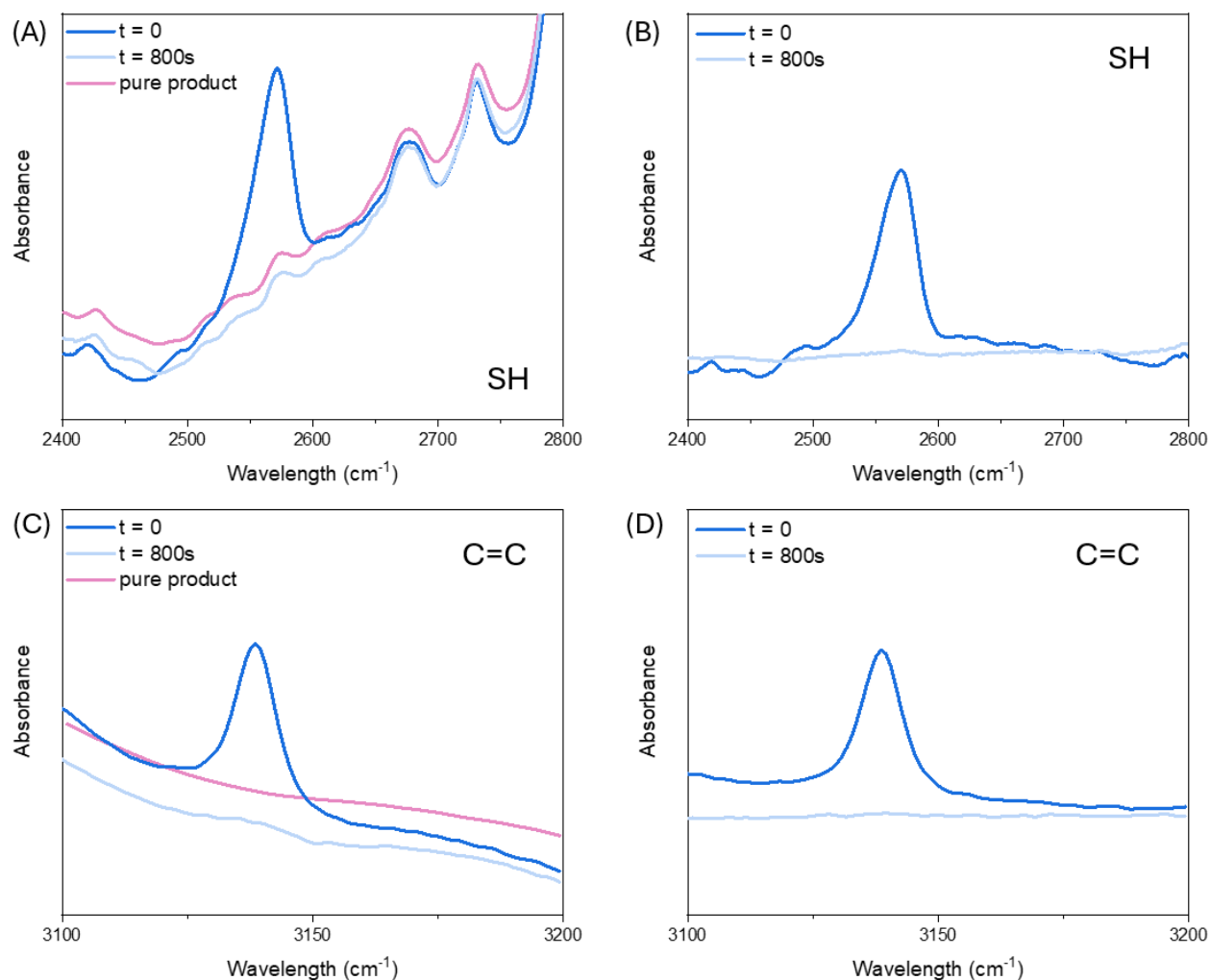
**Figure S4.** Summary of thiol-Nb reaction kinetics for Nb-ester-EH *exo*-isomer and *mixed*-isomers characterized via real-time FTIR spectroscopy. Samples were 100  $\mu\text{m}$  thick and irradiated with a 405 nm LED (1  $\text{mW}/\text{cm}^2$ ). Rates are averages ( $n = 3$ ) with  $\pm 1$  standard deviation from the mean provided.



**Figure S5.** (A) Summary of thiol-Nb reaction kinetics for Nb-ester- $\text{CH}_3$  *exo*-isomer and *mixed*-isomers characterized via real-time FTIR spectroscopy. Samples were 100  $\mu\text{m}$  thick and irradiated with a 405 nm LED ( $1 \text{ mW}/\text{cm}^2$ ). (B) Photograph of the samples after reaction showing opacity in the pure *exo*-isomer, which may contribute to the observed reduction in reaction rate relative to the samples containing the mixed-isomers.

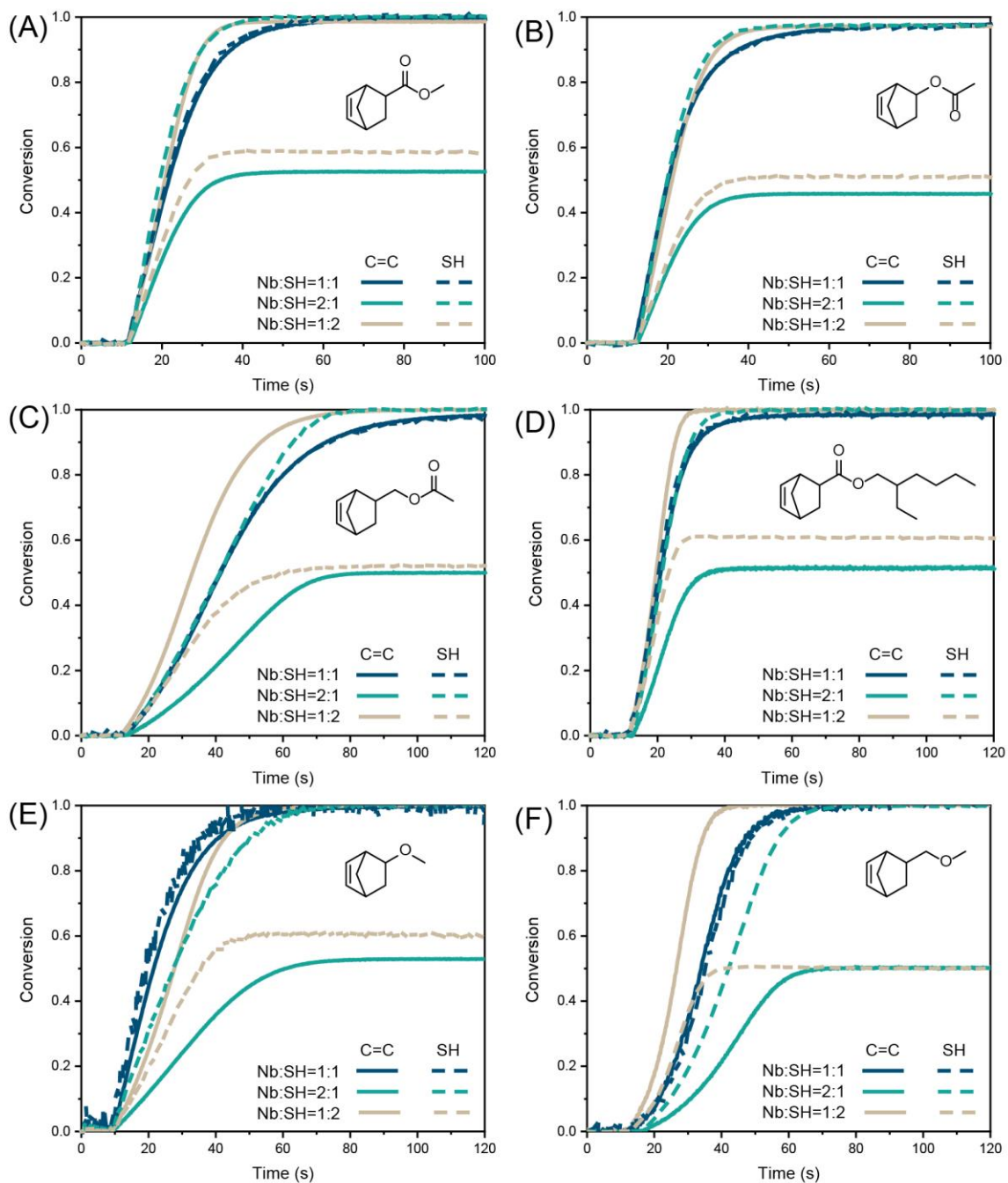
In attempting to quantify thiol conversion within norbornene imide (NbI) systems using a stoichiometrically balanced monothiol, we identified the presence of a residual peak at  $2580\text{-}2600 \text{ cm}^{-1}$ , which ultimately was attributed to the NbI compound itself. This attribution was indirectly supported by using an excess of monothiol (as noted below) and continuing to see the presence of the residual peak and by size exclusion chromatography showing the lack of high molecular weight oligomers or polymers that would arise from chain-growth. Furthermore, the thiol-ene product between NbI-EH (*exo* and *endo*) with  $\text{C}_{12}\text{H}_{25}\text{SH}$  was isolated and characterized, directly revealing the presence of a peak in the same regions as the thiol signal ( $2580\text{-}2600 \text{ cm}^{-1}$ ). Consequently, for NbI derivatives, this pure product (dodecyl-sulfide-NbI-EH) was employed as the background reference to remove the residual signature. The pure products, being viscous liquids, were used in their neat form and placed between glass slides with 100  $\mu\text{m}$  spacers for backgrounding.



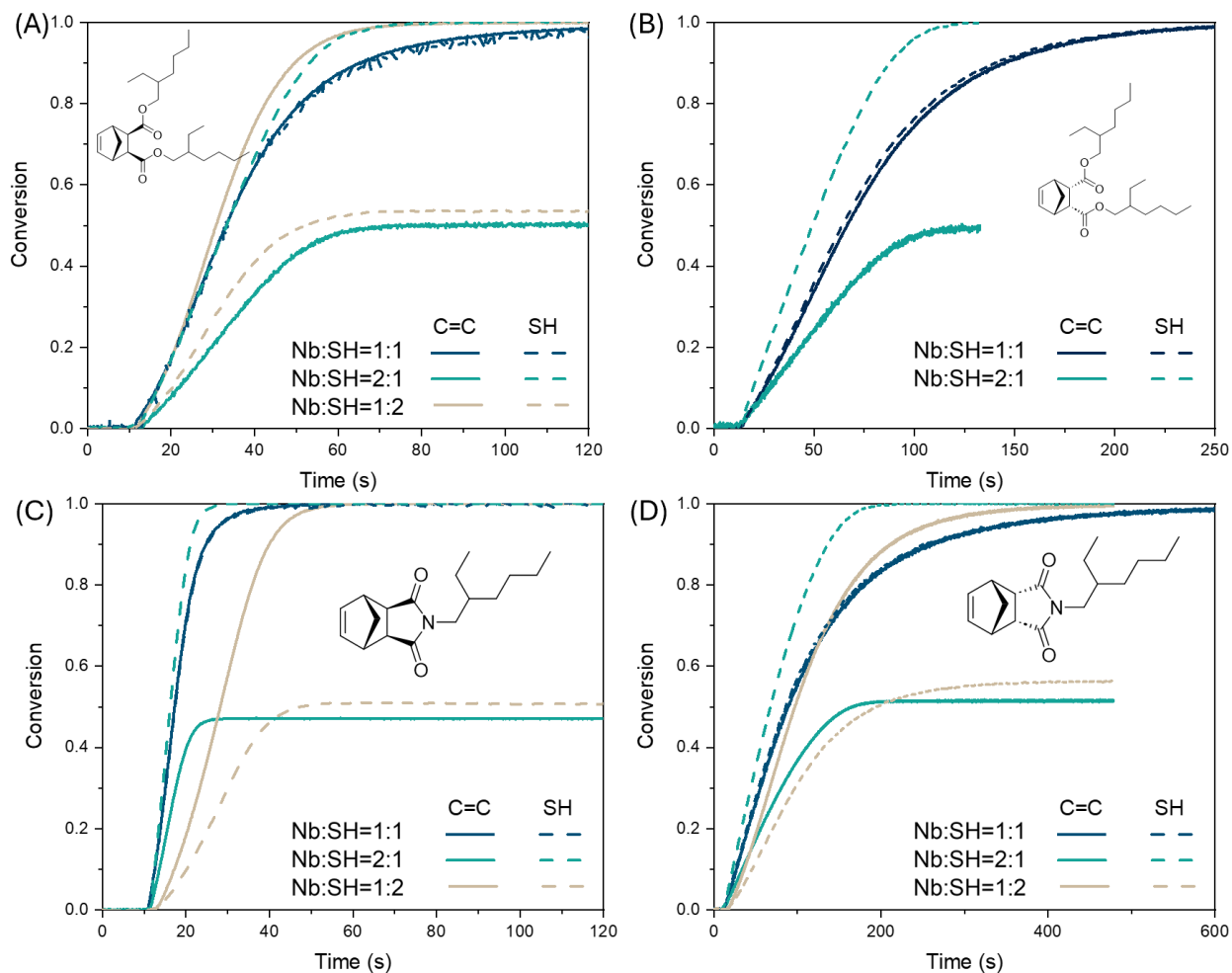


**Figure S7.** Representative FTIR spectra for the reaction between *endo*-NbI-EH and  $C_{12}H_{25}SH$  (stoichiometrically balanced) upon irradiating the samples with 405 nm light ( $1\text{ mW}/\text{cm}^2$ ) using 0.01 mol% (relative to total mol) of BAPO as a photoinitiator. (A) Traces in the region of the thiol signature ( $\sim 2580\text{ cm}^{-1}$ ) where glass slides were used for backgrounding. The “pure product” (pink line) represents the isolated thiol-ene product between *endo*-NbI-EH and  $C_{12}H_{25}SH$ . (B) Traces in the region of the thiol signature ( $\sim 2580\text{ cm}^{-1}$ ) where the isolated thiol-ene product between *endo*-NbI-EH and  $C_{12}H_{25}SH$  was used for backgrounding. (C) Traces in the region of the alkene signature ( $\sim 3135\text{ cm}^{-1}$ ) where glass slides were used for backgrounding. The “pure product” (pink line) represents the isolated thiol-ene product between *endo*-NbI-EH and  $C_{12}H_{25}SH$ . (D) Traces in the region of the alkene signature ( $\sim 3135\text{ cm}^{-1}$ ) where the isolated thiol-ene product between *exo*-NbI-EH and  $C_{12}H_{25}SH$  was used for backgrounding.





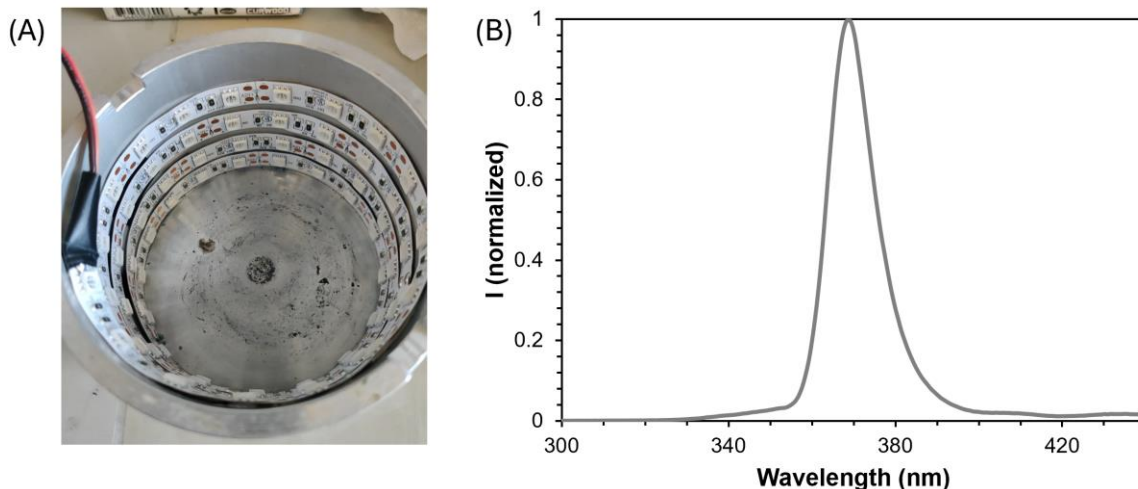
**Figure S8.** Data from real time FTIR spectroscopy showing alkene and thiol conversion for monofunctional Nb derivatives, where  $C_{12}H_{25}SH$  and 0.01 mol% (relative to whole system) BAPO under  $1mW/cm^2$  405nm LED were used.



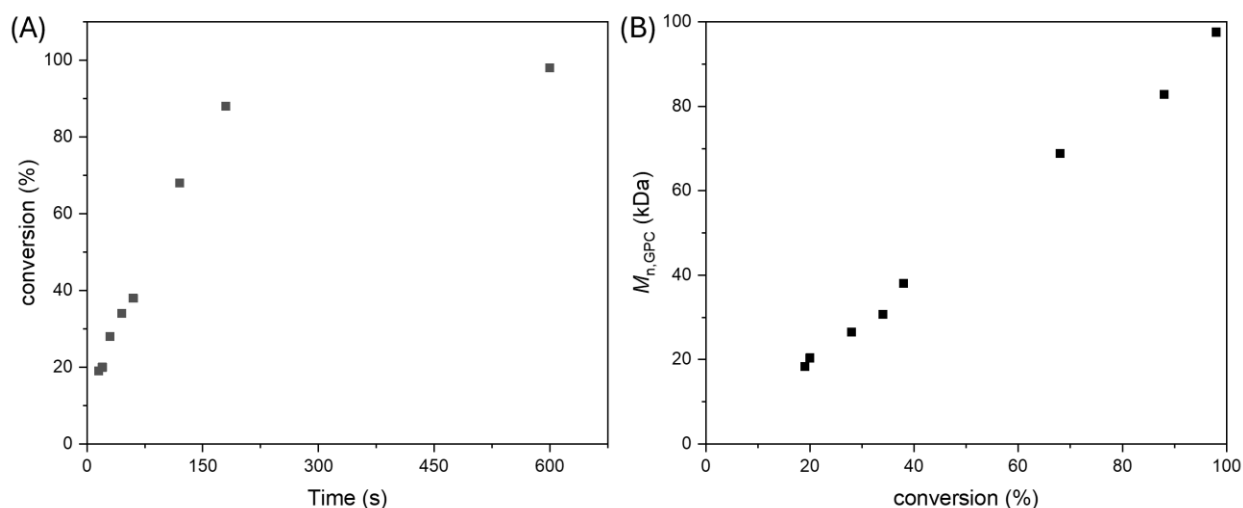
**Figure S9.** Data from real time FTIR spectroscopy showing alkene and thiol conversion for Nb-diesters (A/B) and NbI (C/D) derivatives, where  $C_{12}H_{25}SH$  and 0.01 mol% (relative to whole system) and BAPO were used under  $1mW/cm^2$  405nm LED irradiation.

## S2.2. Polymerization of HEAA via Photoiniferter Polymerization

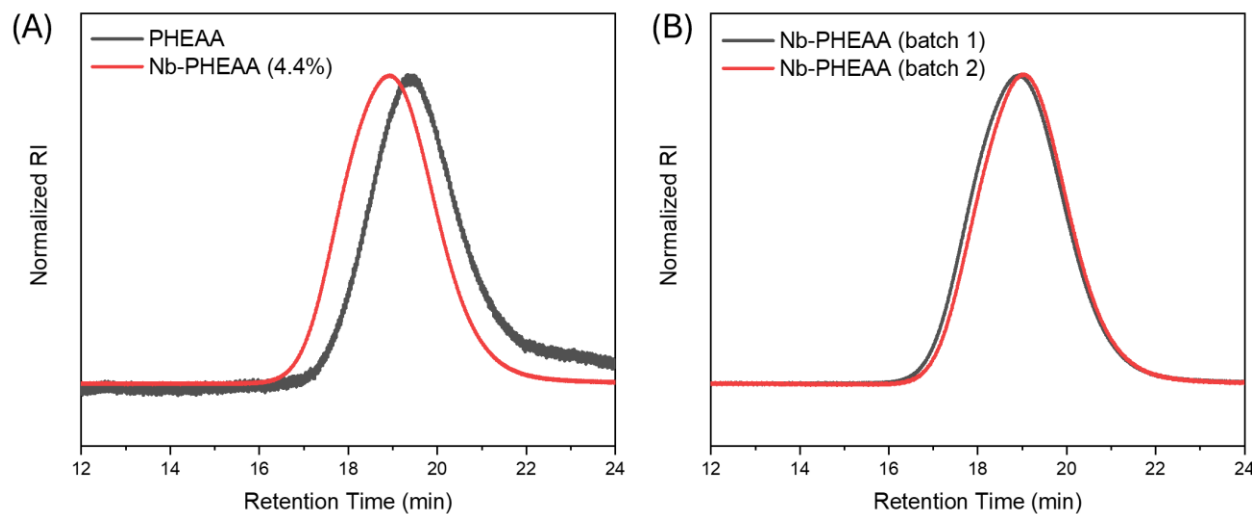
The polymerization of HEAA was conducted in a 20 mL glass vial placed in photo-reactor (365 nm, 9 mW/cm<sup>2</sup>).



**Figure S10.** (A) Images of photoreactor used for photoiniferter polymerizations. Irradiation was accomplished using UV LED strips (~365 nm, realUV™ LED Strip light from Waveform Lighting (part number: 7021.65.5M)) that provided an intensity of ~9 mW/cm<sup>2</sup> at the centre of the dish as measured using a silicon photometer (Thorlabs, Model: S401C) and digital power meter (Thorlabs, Model: PM100D). (B) Normalized emission profile of the UV LED strips.



**Figure S11.** Kinetic study of HEAA photoiniferter homopolymerizations, [M<sub>0</sub>]:[CTA]=1000:1. (A) Plot of conversion vs. time. (B) Plot of number average molecular weight vs. conversion plot, showing control through their linear relationship.



**Figure S12.** Representative SEC traces of (A) PHEAA before and after post-functionalization and (B) two different batches of *exo*-NbI-PHEAA to show reproducibility.

**Table S3. Summary of PHEAA and *exo*-NbI-PHEAA data obtained from SEC**

Polymer	$M_{n,RI}^a$ (kDa)	$D_{RI}$	$M_{n,theoro.}^b$ (kDa)	$Nb^c$ (%)
PHEAA	95	1.42	111	/
<i>exo</i> -NbI-PHEAA	117	1.70	120	4.4
<i>exo</i> -NbI-PHEAA (batch2)	112	1.62	120	4.0

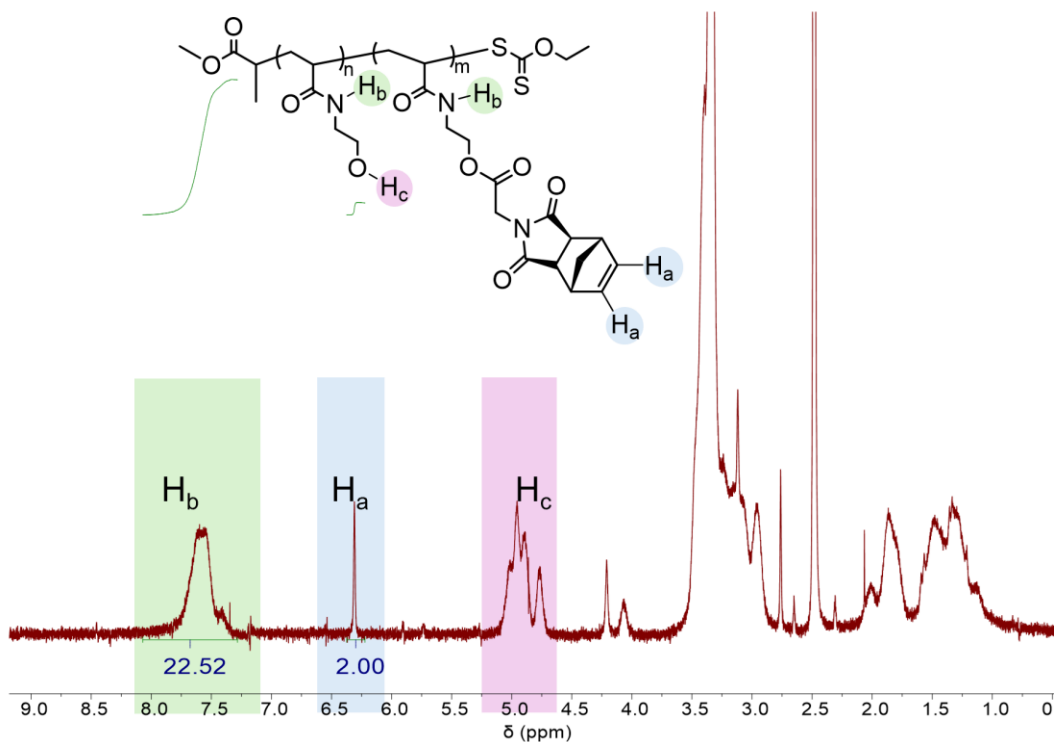
<sup>a</sup> $M_{n,RI}$  was determined relative to polystyrene standards

<sup>b</sup> $M_{n,theoro.}$  was calculated using conversion from <sup>1</sup>H NMR and target degree of polymerization

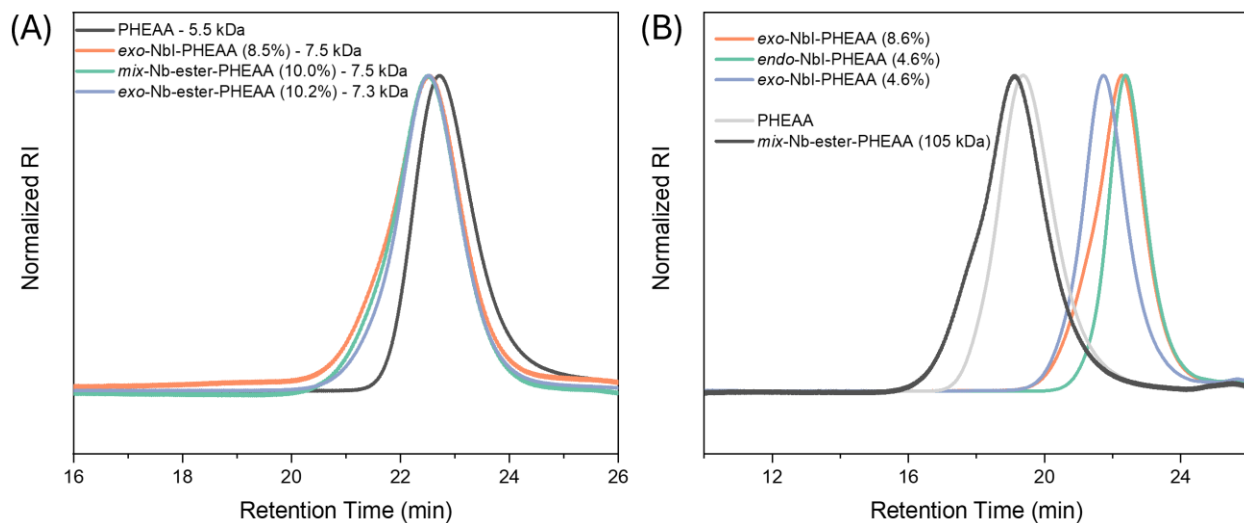
<sup>c</sup>NbI content was calculated using <sup>1</sup>H NMR

The percentage of norbornene was characterized using <sup>1</sup>H-NMR and the following equation:

$$Nb (\%) = \frac{H_a/2}{H_b} * 100\%$$



**Figure S13.** Representative  $^1\text{H-NMR}$  spectrum of *exo*-NbI-PHEAA (4.4 mol% Nb) in  $\text{DMSO-d}_6$ .



**Figure S14.** Representative SEC traces of (A) Nb-PHEAA with different Nb-functionality synthesized from same batch of PHEAA (B) different batches of *exo*-NbI-PHEAA and *mix*-Nb-PHEAA with varying Nb content and molecular weight.

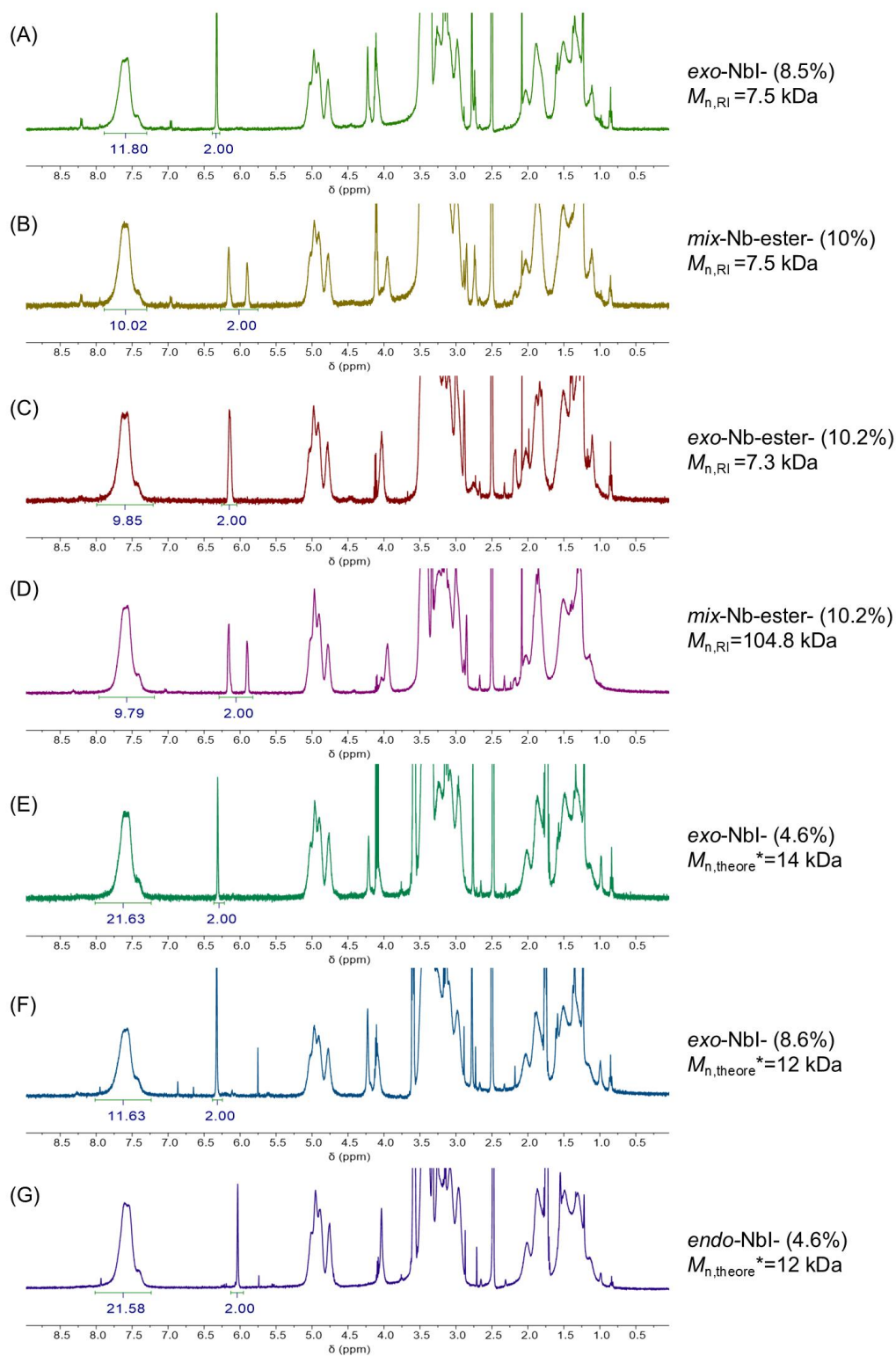
**Table S4. Summary of PHEAA and *exo*-Nb-ester-PHEAA data obtained from SEC**

Polymer	$M_{n,RI}^a$ (kDa)	$D_{RI}$	$M_{n,theor.}^b$ (kDa)	$Nb^c$ (%)
<i>exo</i> -NbI-PHEAA	7.5	1.63	9.8	8.5
<i>mix</i> -Nb-ester-PHEAA	7.5	1.63	9.4	10
<i>exo</i> -Nb-ester-PHEAA	7.3	1.55	9.4	10.2
<i>mix</i> -Nb-ester-PHEAA	105	1.86	109	10.2
<i>exo</i> -NbI-PHEAA	/	/	14	4.6
<i>exo</i> -NbI-PHEAA	/	/	12	8.6
<i>mix</i> -NbI-PHEAA	/	/	12	4.6

<sup>a</sup> $M_{n,RI}$  was determined relative to polystyrene standards

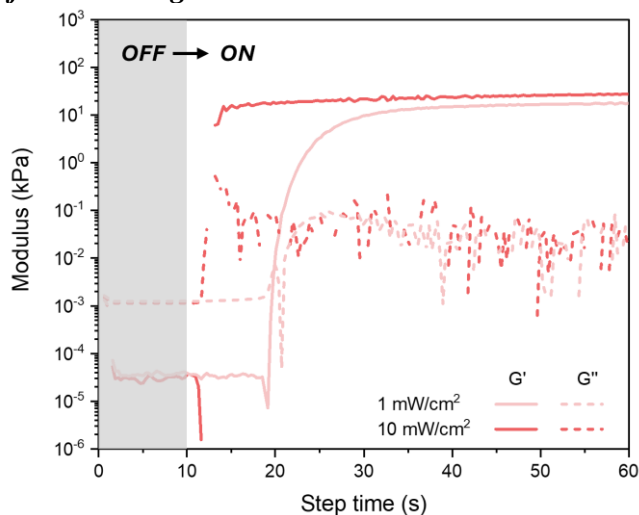
<sup>b</sup> $M_{n,theor.}$  was calculated using conversion from <sup>1</sup>H NMR and target degree of polymerization

<sup>c</sup>Nb content was calculated using <sup>1</sup>H NMR

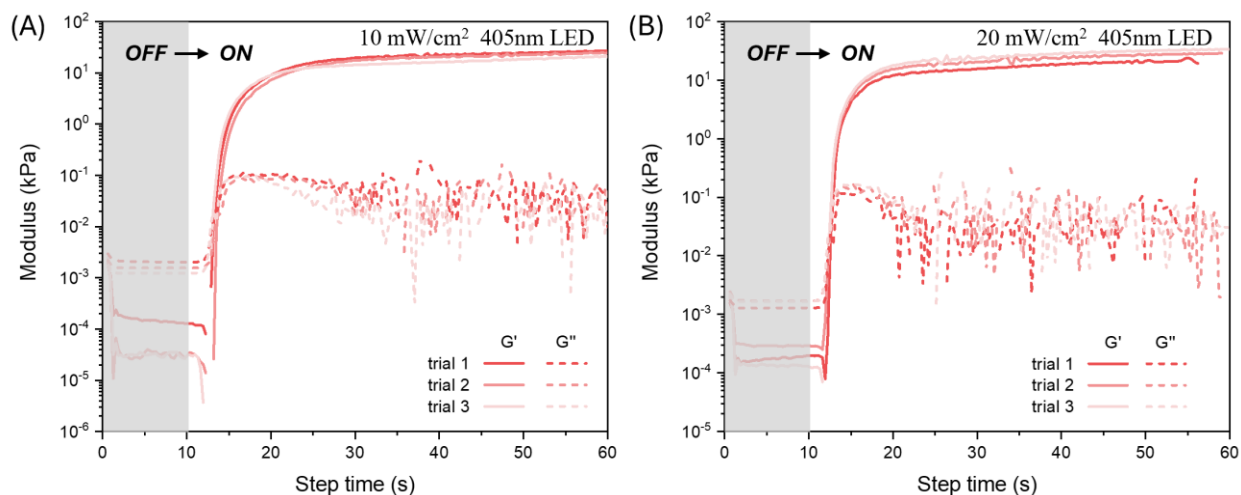


**Figure S15.**  $^1\text{H}$ -NMR spectra in  $\text{DMSO-d}_6$ . (A) Nb-PHEAA (*exo*-NbI-) (8.5 mol%) ( $M_{n,RI} = 7.5$  kDa) (B) Nb-PHEAA (*mix*-Nb-ester-) (10 mol%) ( $M_{n,RI} = 7.5$  kDa) (C) Nb-PHEAA (*exo*-Nb-ester-) (10.2 mol%) ( $M_{n,RI} = 7.3$  kDa) (D) Nb-PHEAA (*mix*-Nb-ester-) (10.2 mol%) ( $M_{n,RI} = 104.8$  kDa) (E) Nb-PHEAA (*exo*-NbI-) (4.6 mol%), and (F) Nb-PHEAA (*exo*-NbI-) (8.6 mol%) (G) Nb-PHEAA (*endo*-NbI-) (4.6 mol%).

### S2.3. Photo-Rheology of 3D Printing Resin



**Figure S16.** Photo-rheology to determine gel points as a function of 405 nm LED light intensity for resins comprising *exo*-NbI-PHEAA ( $M_n = 117$  kDa) with 4.4 mol% NbI installed, stoichiometrically balanced DTT, 0.5 wt% LAP, 0.05 wt% TEMPO, and 85 wt% water.



**Figure S17.** Photo-rheology to determine gel points as a function of 405 nm LED light intensity for resins comprising *exo*-NbI-PHEAA ( $M_n = 117$  kDa) with 4.4 mol% NbI installed, stoichiometrically balanced DTT, 0.5 wt% LAP, 0.05 wt% TEMPO, and 85wt% water with 1 drop ( $\sim 45 \mu\text{L}$ ) of a yellow 5 dye (tartrazine) solution from McCormick & Co. for every 3 mL of resin. (A) 10 mW/cm<sup>2</sup> 405 nm LED light exposure and (B) 20 mW/cm<sup>2</sup> 405 nm LED light exposure.

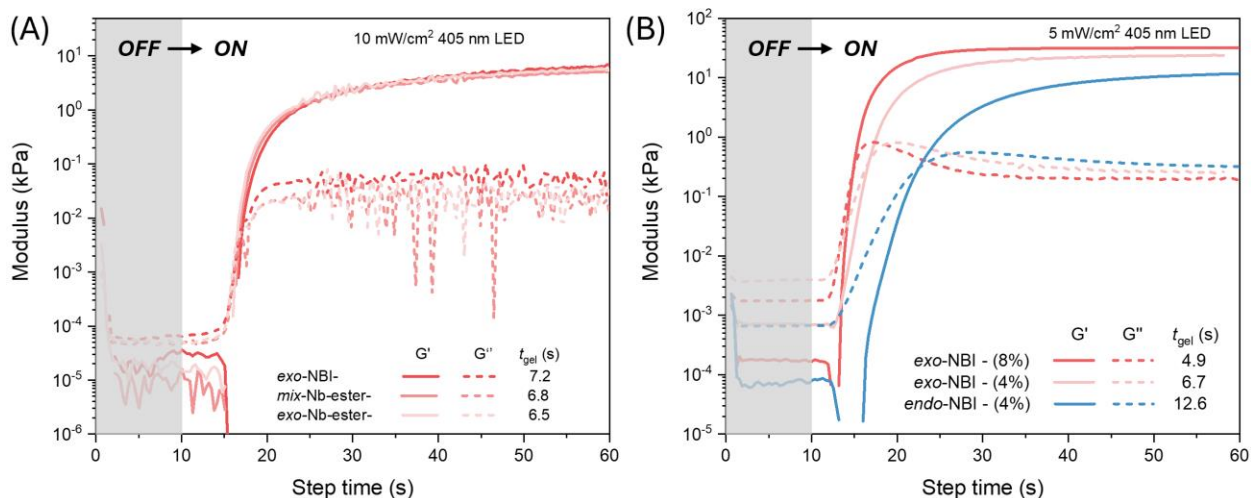
**Table S5. Summary of gel point and plateau storage moduli ( $G'$ ) values for 3D printing resins.**

Resin	LED intensity (mW/cm <sup>2</sup> )	$\tau_{\text{gel}}$ (s) <sup>a</sup>	Plateau $G'$ (kPa)
Printing resin (without yellow 5 dye)	1	9.9	18
	10	2.5	24
Printing resin (with yellow 5 dye)	10	$3.6 \pm 0.2$	$24 \pm 3$
	20	$2.5 \pm 0.1$	$24 \pm 4$

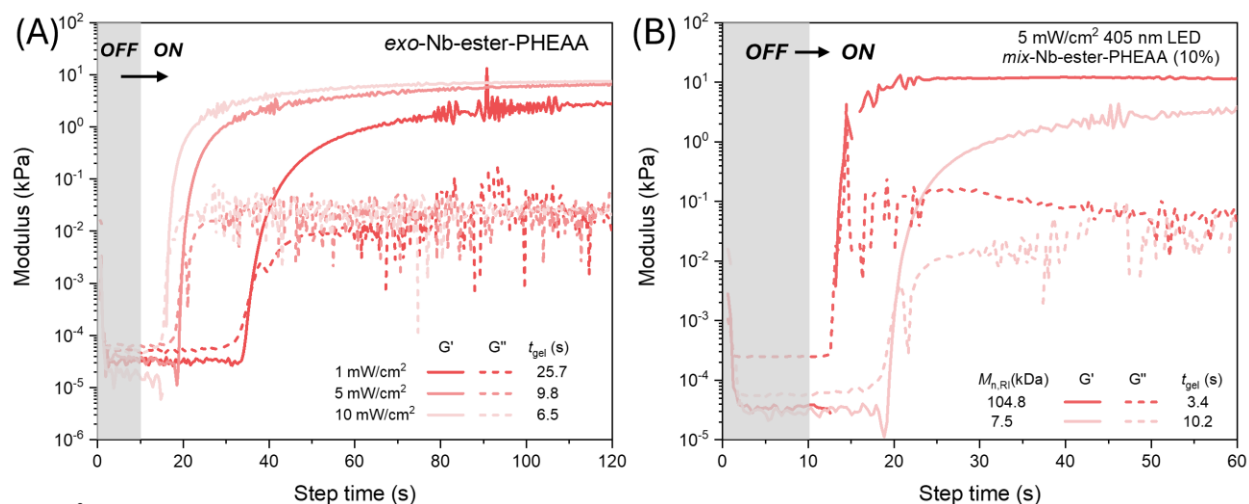


### S2.4. Photo-Rheology of Resins with Alternate Nb-PHEAA Prepolymers

Note that in this section various conditions and resin compositions were screened. Due to the changing conditions direct comparisons between different figures in this section cannot be made, while all traces within a single plot systematically change one variable and allow for direct comparisons between the traces. In all cases, the 405 nm LED was not turned on until 10 s after starting each measurement and the gel point ( $\tau_{gel}$ ) was estimated as the crossover of storage modulus ( $G'$ ) and loss modulus ( $G''$ ), subtracting 10 seconds for when the LED is off.



**Figure S18.** (A) Photo-rheology of Nb-functionalized PHEAA resins, varying Nb composition from the same batch of PHEAA ( $M_n = 5.5$ ,  $D = 1.4$ ). Comparison of *exo*-NbI (8.5 mol%), *mix*-Nb-ester (10 mol%), and *exo*-Nb-ester (10 mol%) installed on PHEAA, using DTT (equimolar by functionality with Nb), LAP (0.5 wt%) and 90 wt% water in the resin and 10 mW/cm<sup>2</sup> 405 nm LED exposure. (B) Comparison of *exo*-NbI (4 mol%) and *endo*-NbI (4 mol%) installed on PHEAA, using DTT (equimolar by functionality with Nb), LAP (1 wt%) and 80 wt% water in the resin, and 5 mW/cm<sup>2</sup> 405 nm LED exposure.

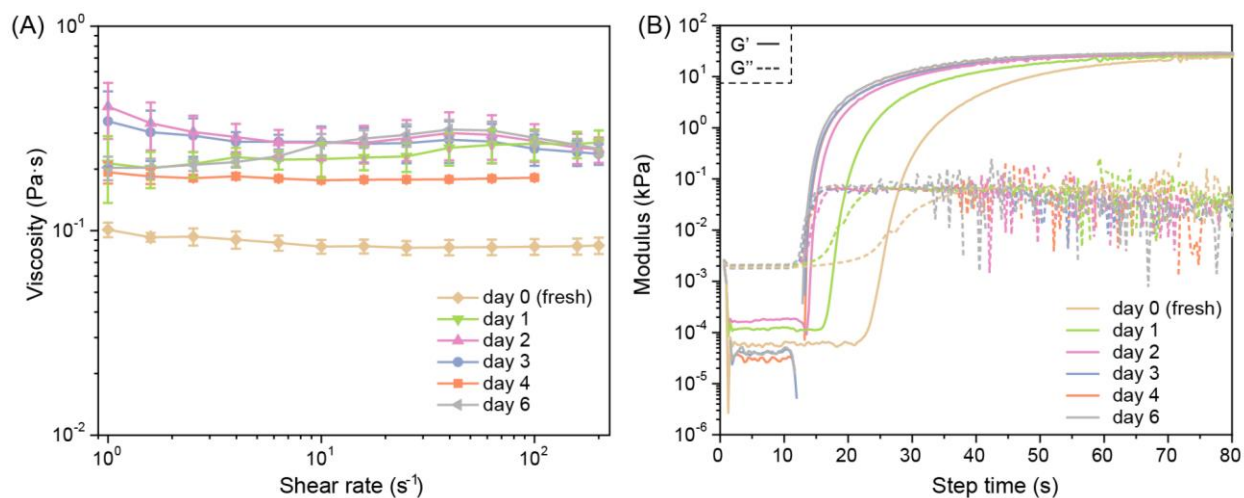


**Figure S19.** Photo-rheology of (A) *exo*-Nb-ester-PHEAA (10 mol% Nb) as a function of light intensity and (B) *mix*-Nb-ester PHEAA (10 mol% Nb) as a function of prepolymer molecular weight at a constant 5 mW/cm<sup>2</sup> 405 nm light intensity. Both resins comprised DTT (equimolar by functionality with Nb), LAP (0.5 wt%), and 90 wt% water.

**Table S6. Summary of gel point and plateau storage moduli ( $G'$ ) values from Figures S15-S16.**

Functionality (mol%)	PHEAA- $M_n$ (kDa)	water content (wt%)	LAP content (wt%)	LED intensity (mW/cm <sup>2</sup> )	$\tau_{gel}$ (s)	Plateau $G'$ (kPa)
<i>exo</i> -Nb-ester (10.2)	7.3	90	0.5	1	26	2.6
				5	10	6.4
				10	7	7.4
<i>mix</i> -Nb-ester (10)	7.5	90	0.5	10	7	6.6
				5	10	5.2
<i>exo</i> -NbI (8.5)	7.5	90	0.5	10	7	8.5
<i>mix</i> -Nb-ester (10.2)	104.8	90	0.5	5	3	11.5
<i>exo</i> -NbI (8.2)	12*	80	1	10	5	31.5
<i>exo</i> -NbI (4.3)	14*	80	1	5	7	23.2
<i>endo</i> -NbI (4.3)	12*	80	1	5	13	10.3

\*Estimated based on <sup>1</sup>H-NMR and conversion.



**Figure S20.** Resin stability tests using (photo)rheology. Samples were stored at  $-20$  °C and intermittently tested. (A) Summary of viscosity changes over time for resins that did not contain photoinitiator. (B) Summary of gelation kinetics estimated as the crossover between storage and loss moduli. Traces represent averages ( $n = 3$ ) with  $\pm 1$  standard deviation from the mean provided.

### S2.5. Thiol-Ene Hydrogel DLP 3D Printing

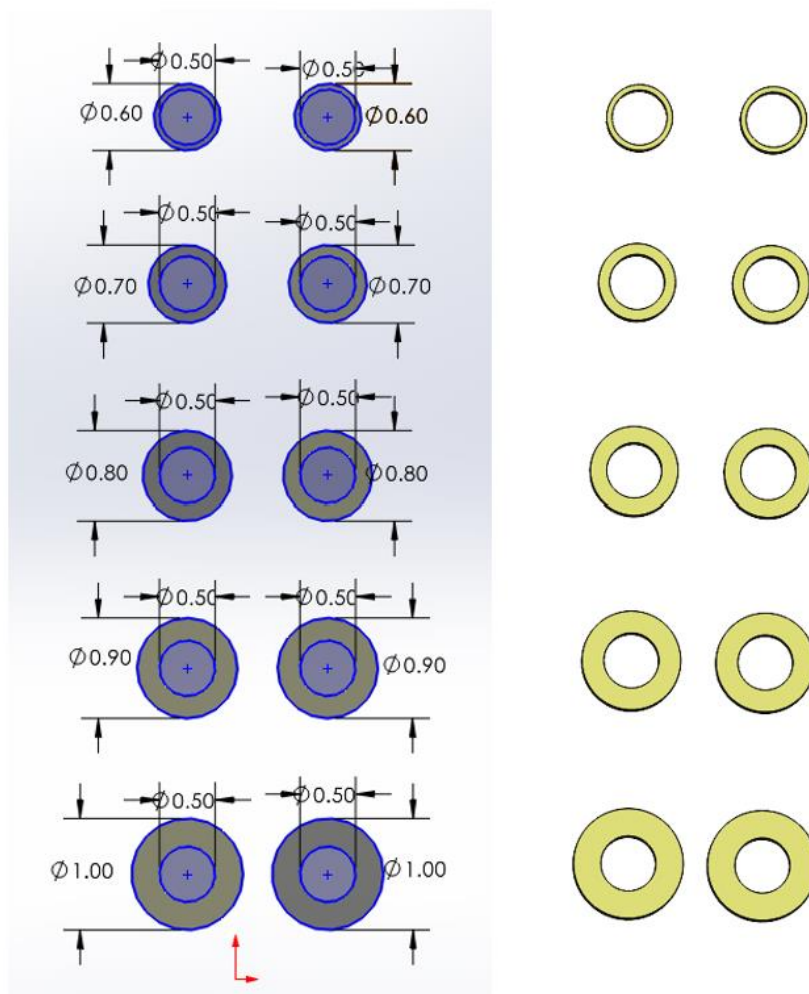
For context, representative examples of water-based resins comprising thiol and ene functionalized monomers that were implemented in DLP 3D printing of hydrogels are provided in the following Table. Notably, changes in composition, concentration of resin components, wavelength and intensity of light source all influence the build speed, and thus these results are primarily for qualitative reference and not quantitative comparisons.

**Table S7. Representative thiol-ene hydrogel DLP 3D printing metrics.**

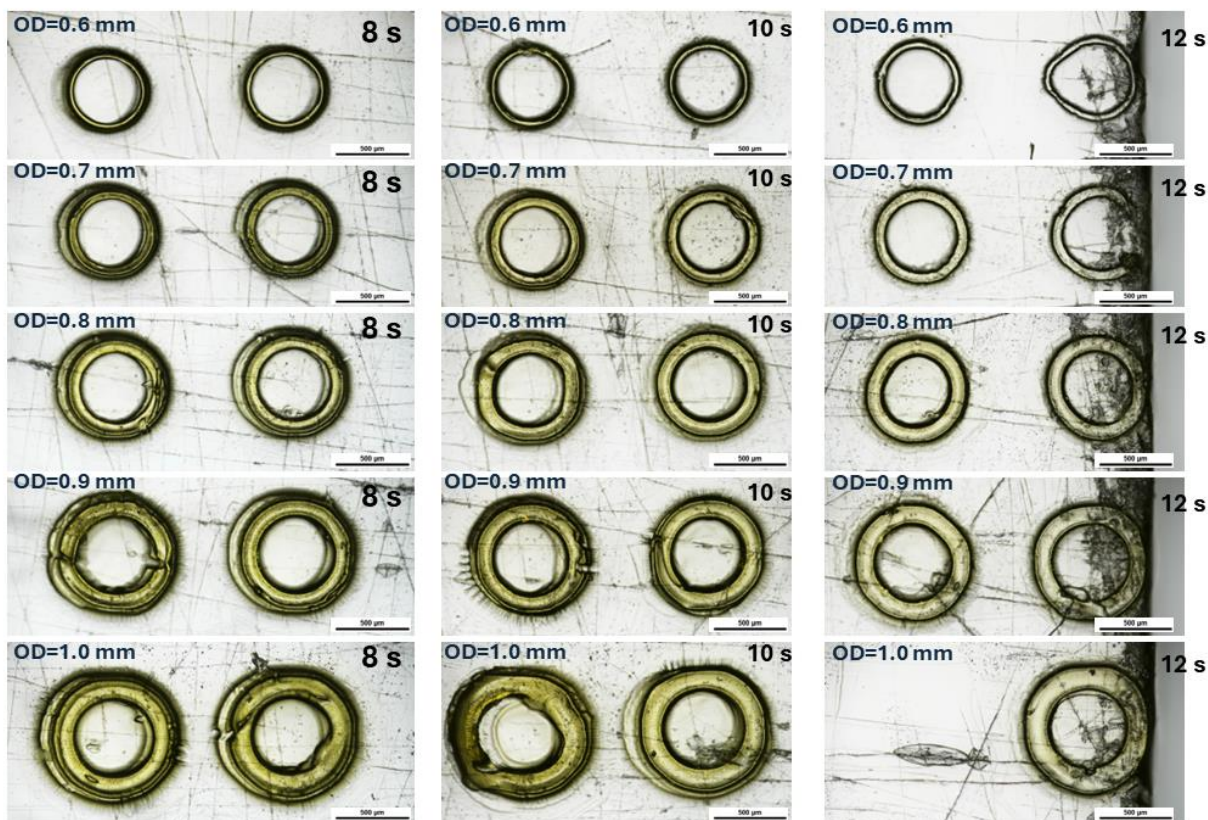
Ref	Composition	Total monomer content in water	Wave-length (nm)	Light intensity (mW/cm <sup>2</sup> )	Photo-initiator (I)	[I] (conv.)	Build speed (s / μm)
This work	NBI-PHEAA with DTT	15 wt%	405	20	LAP	0.5 wt%	8-12 / 100
S11	norbornene–alginate (SR-NOR)	10 wt%	405	35	LAP	1 wt%	4 / 50
S12	gelatin-norbornene with PEG4SH	6 wt%	405	24	LAP	~0.3 wt%	13 / 100
S13	HA-Nb (36-42%) with DTT	4% w/v	385	20	LAP	0.1 wt%	2 / 100
	HA-MA (40-47%) with DTT	4% w/v	385	20	LAP	0.1 wt%	10 / 100
S14	Norbornene modified hyaluronic acid (NorHA)	MeHA (0.6 wt%), NorHA (4.5 wt%)	405	15	LAP	~0.5 wt%	2.5-7.5 / 100
S15	PEG8NB and PEG4SH	5 wt% PEG8NB, 4 wt% PEG4SH	405	10-19	LAP	~0.3 wt%	5-20 / 100
S16	PEG-amide-norbornene-carboxylate and PEG4SH	5 wt% PEGaNB <sub>CA</sub>	400-500 filter	25 mW/cm <sup>2</sup> at 405 nm	LAP	~0.3 wt%	15 s per layer
S17	carbic anhydride - modified HA anhydride (NorHA <sub>CA</sub> )	NorHA <sub>CA</sub> (5 wt %, 40% mod.)	405	15	LAP	~0.5 wt%	6 / 100

### S2.6. Resolution Prints

The following print file was created to determine the minimum lateral feature sizes achievable with the present hydrogel prepolymer resin. The prints consisted of 3 repeating 100  $\mu\text{m}$  layers.

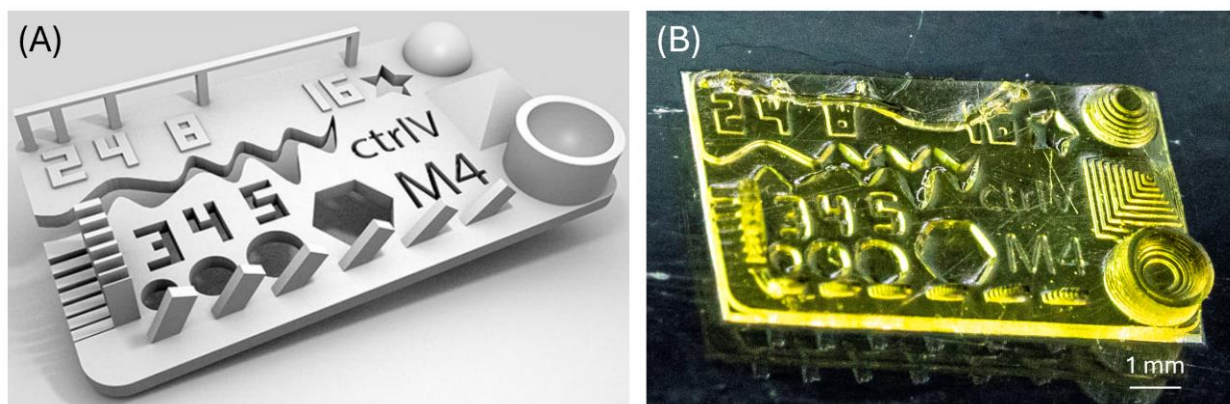


**Figure S21.** Dimensioned drawing of the disk resolution print (left) and digital rendering of the disk resolution print (right).

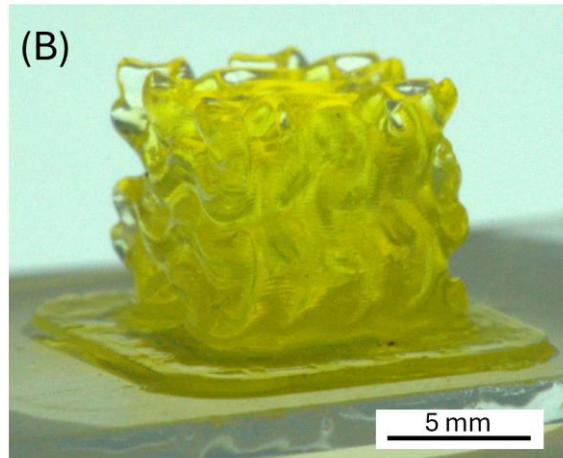
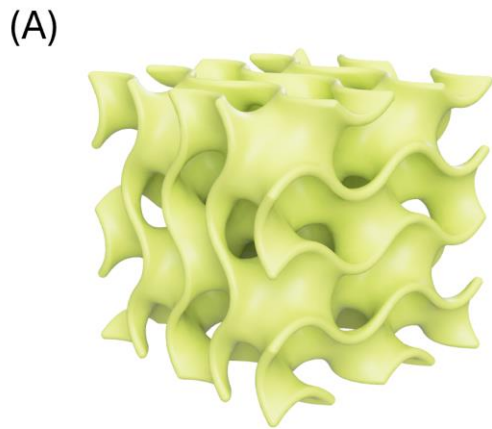


**Figure S22.** Stitched optical microscope images of resolution prints having a fixed inner diameter (ID) = 0.5 mm, and outer diameter (OD) varying from 0.6 mm to 1 mm using different light exposure times per 100 µm layer, varying from 8 s to 10 s to 12 s, with 3 layers in total per print.

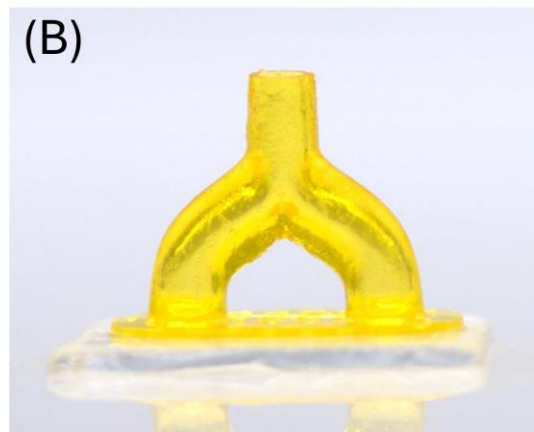
### S2.7. Additional 3D Prints



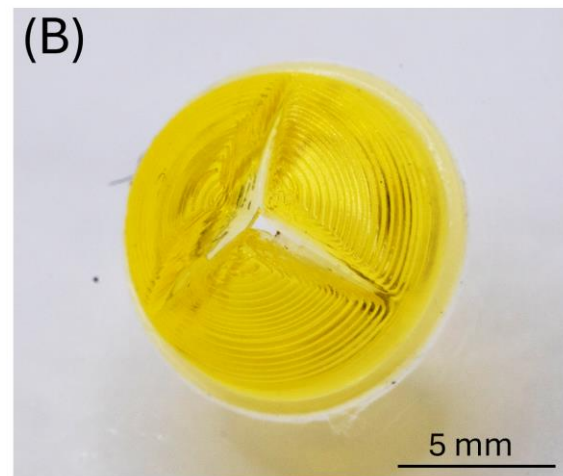
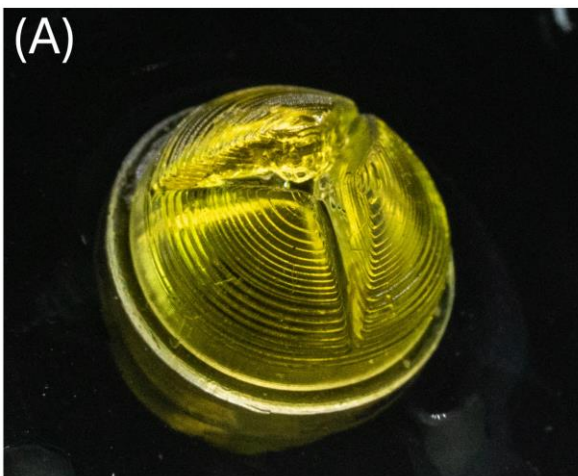
**Figure S23.** “Test your printer” Print.<sup>S18</sup> (A) Digital rendering of print file and (B) photograph of the print, which was created using 20 mW/cm<sup>2</sup> 405 nm LED, 7 s/100 µm layer and 4 base layers at 10 s/100 µm layer.



**Figure S24.** “Gyroid” Print.<sup>S19</sup> (A) Digital rendering of print file and (B) photograph of the print, which was created using 20 mW/cm<sup>2</sup> 405 nm LED, 6 s/100 μm layer and 4 base layers at 10 s/100 μm layer.



**Figure S25.** (A/B) Photographs of a blood vessel print, which was prepared using 20 mW/cm<sup>2</sup> 405 nm LED, 12 s/100 μm layer, and 4 base layers at 20 s/100 μm layer. Outer diameter = 3 mm, inner diameter = 2.3 mm.



**Figure S26.** (A/B) Photographs of a heart valve print, which was prepared using 20 mW/cm<sup>2</sup> 405 nm LED, 6 s/100 μm layer, and 5 base layers at 10 s/100 μm. Outer diameter = 11 mm.

S2.8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR and Mass Spectra

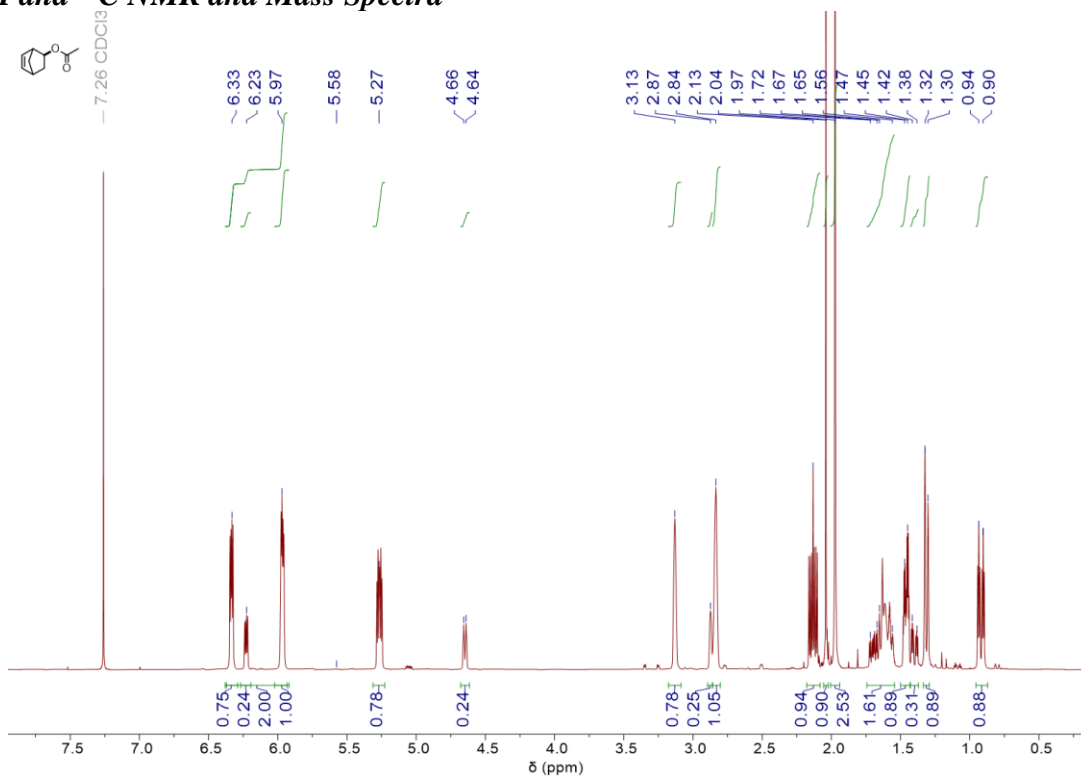


Figure S27.  $^1\text{H}$ -NMR spectrum (400 MHz) of *mix*-Nb-acetate in  $\text{CDCl}_3$ .

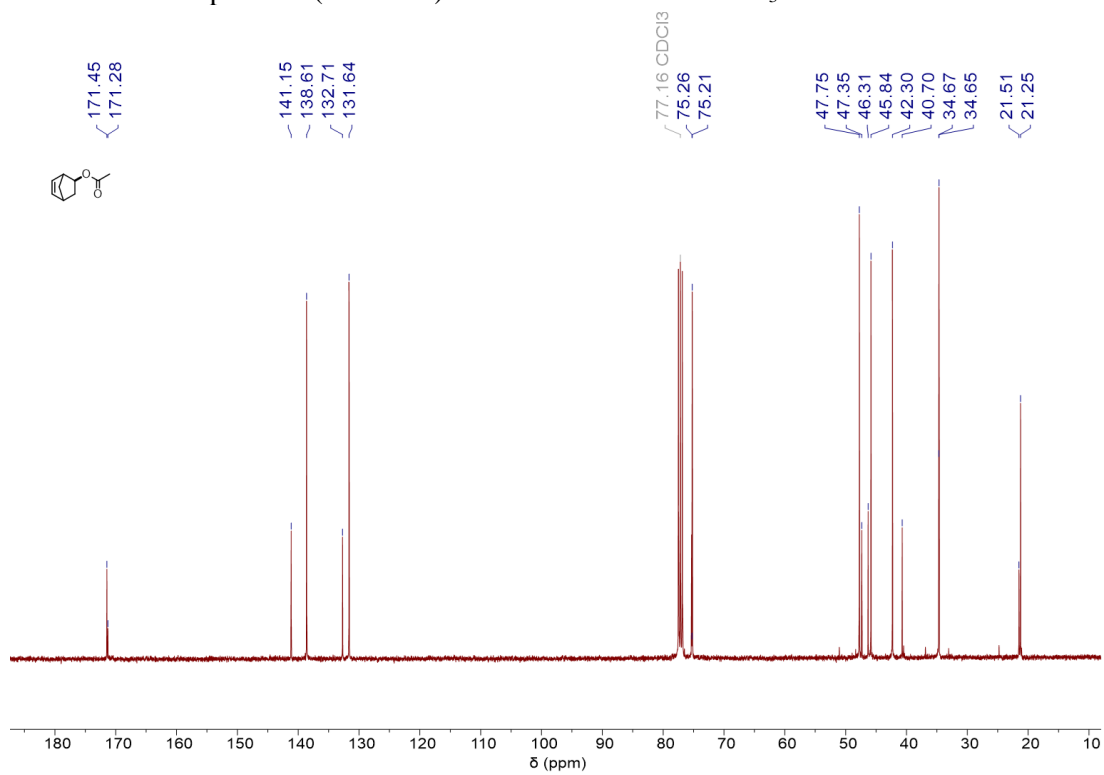


Figure S28.  $^{13}\text{C}$ -NMR spectrum (400 MHz) of *mix*-Nb-acetate in  $\text{CDCl}_3$ .

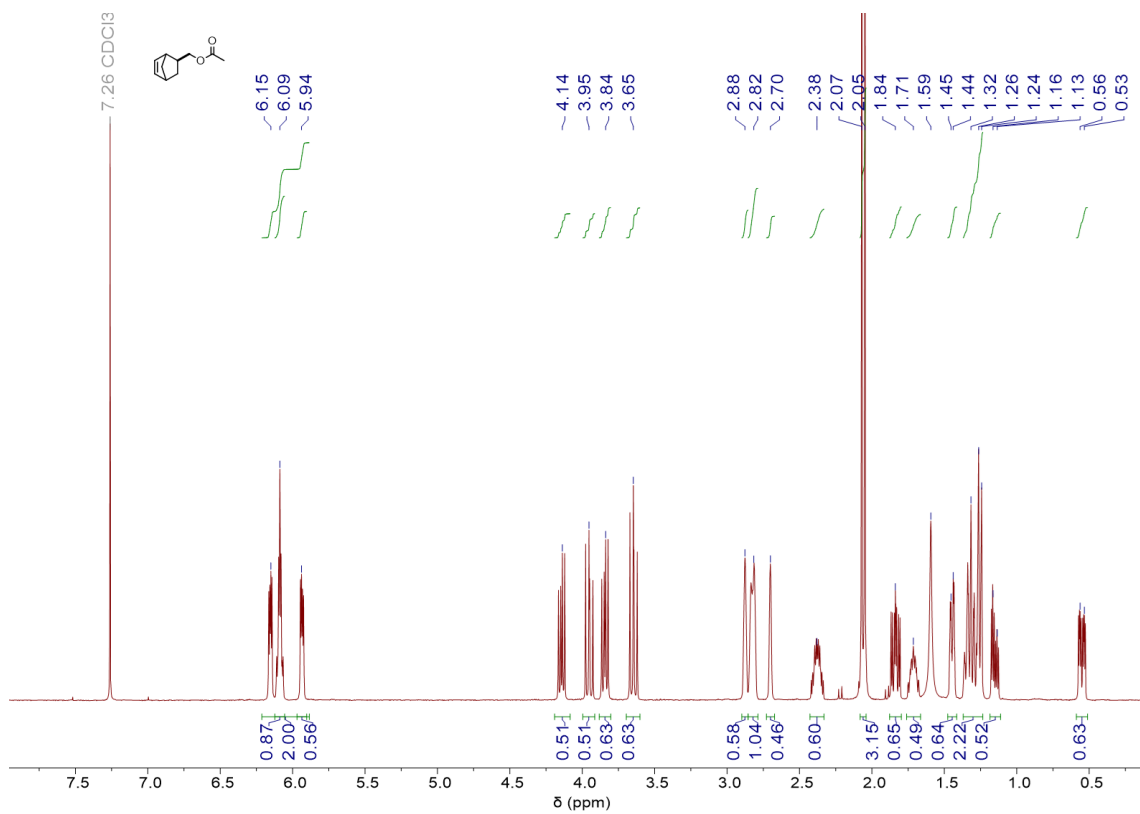


Figure S29. <sup>1</sup>H-NMR spectrum (400 MHz) of *mix*-Nb-CH<sub>2</sub>-acetate in CDCl<sub>3</sub>.

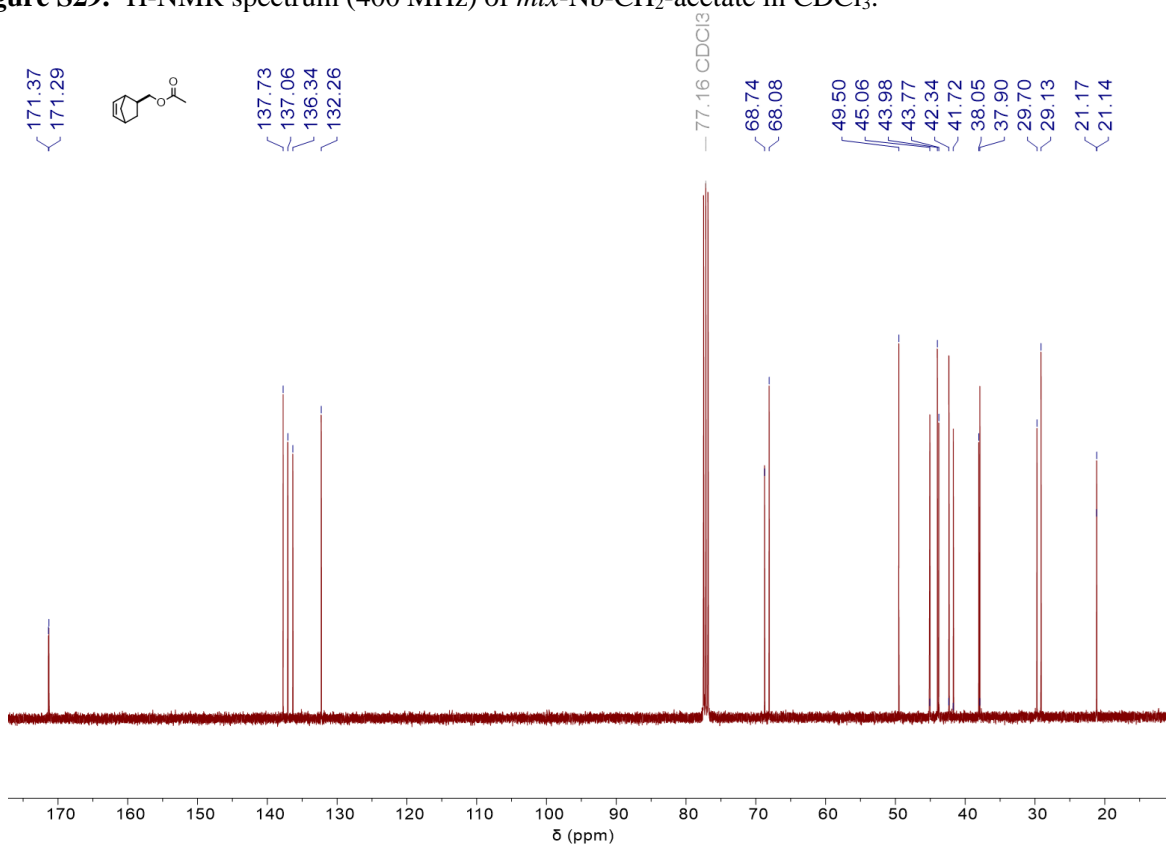


Figure S30. <sup>13</sup>C-NMR spectrum (400 MHz) of *mix*-Nb-CH<sub>2</sub>-acetate in CDCl<sub>3</sub>.



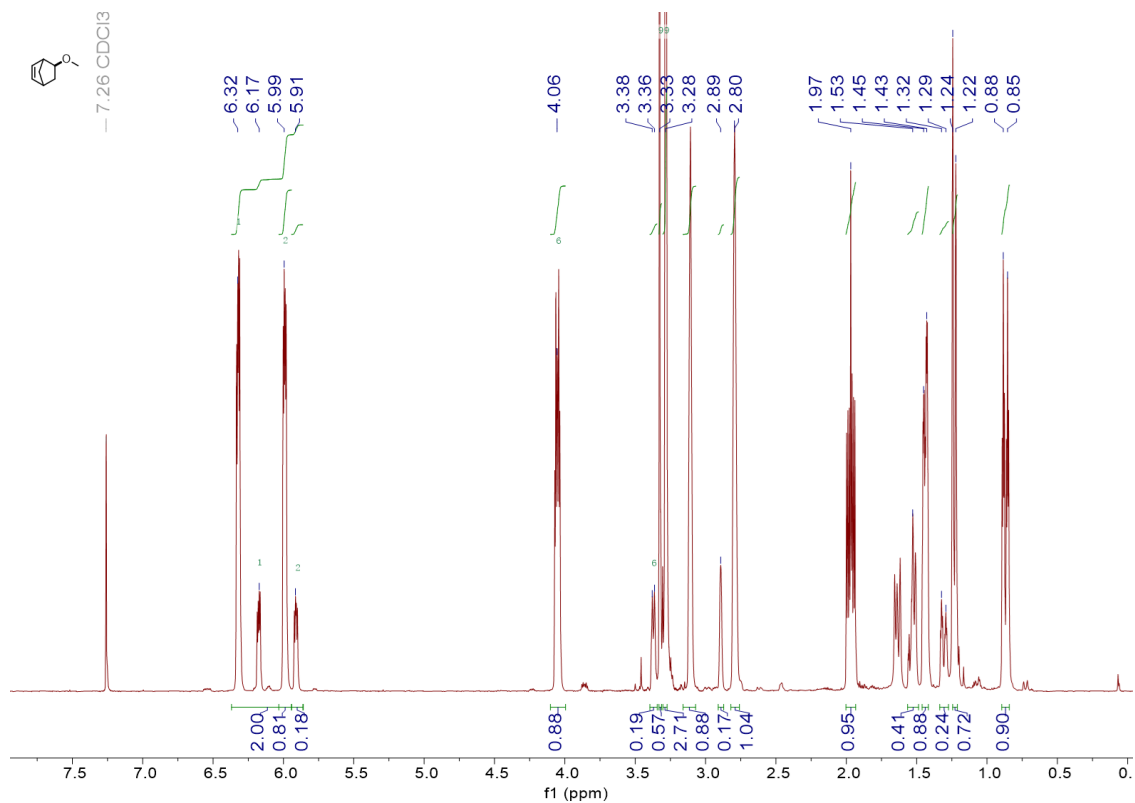


Figure S31. <sup>1</sup>H-NMR spectrum (400 MHz) of *mix*-Nb-ether-CH<sub>3</sub> in CDCl<sub>3</sub>.

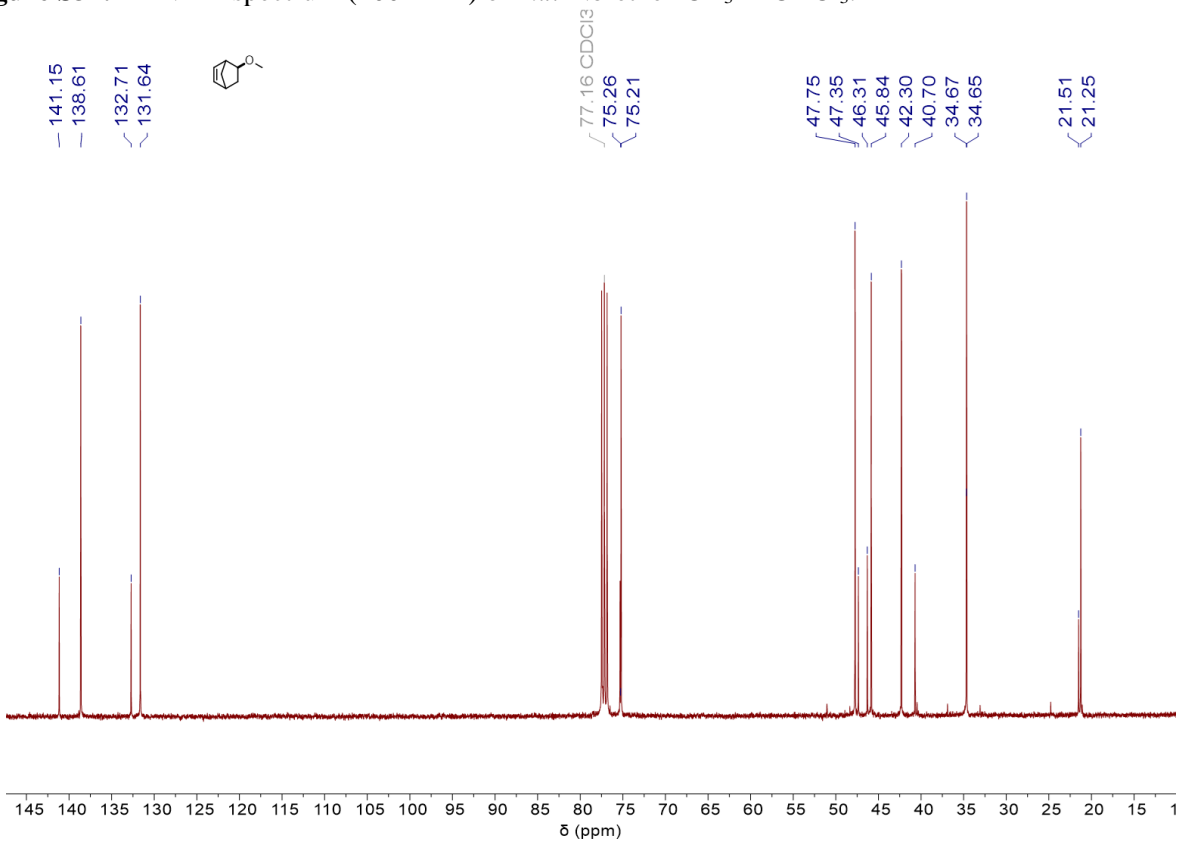


Figure S32. <sup>13</sup>C-NMR spectrum (400 MHz) of *mix*-Nb-ether-CH<sub>3</sub> in CDCl<sub>3</sub>.

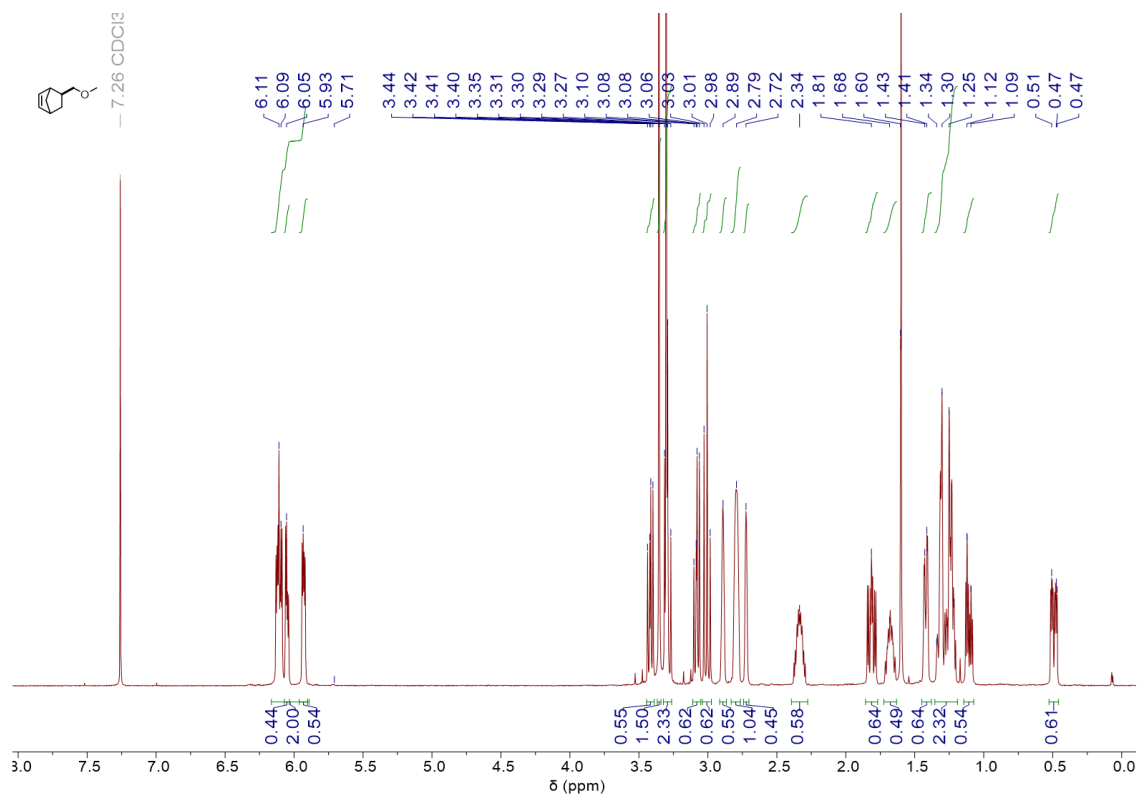


Figure S33. <sup>1</sup>H-NMR spectrum (400 MHz) of *mix*-Nb-CH<sub>2</sub>-ether-CH<sub>3</sub> in CDCl<sub>3</sub>.

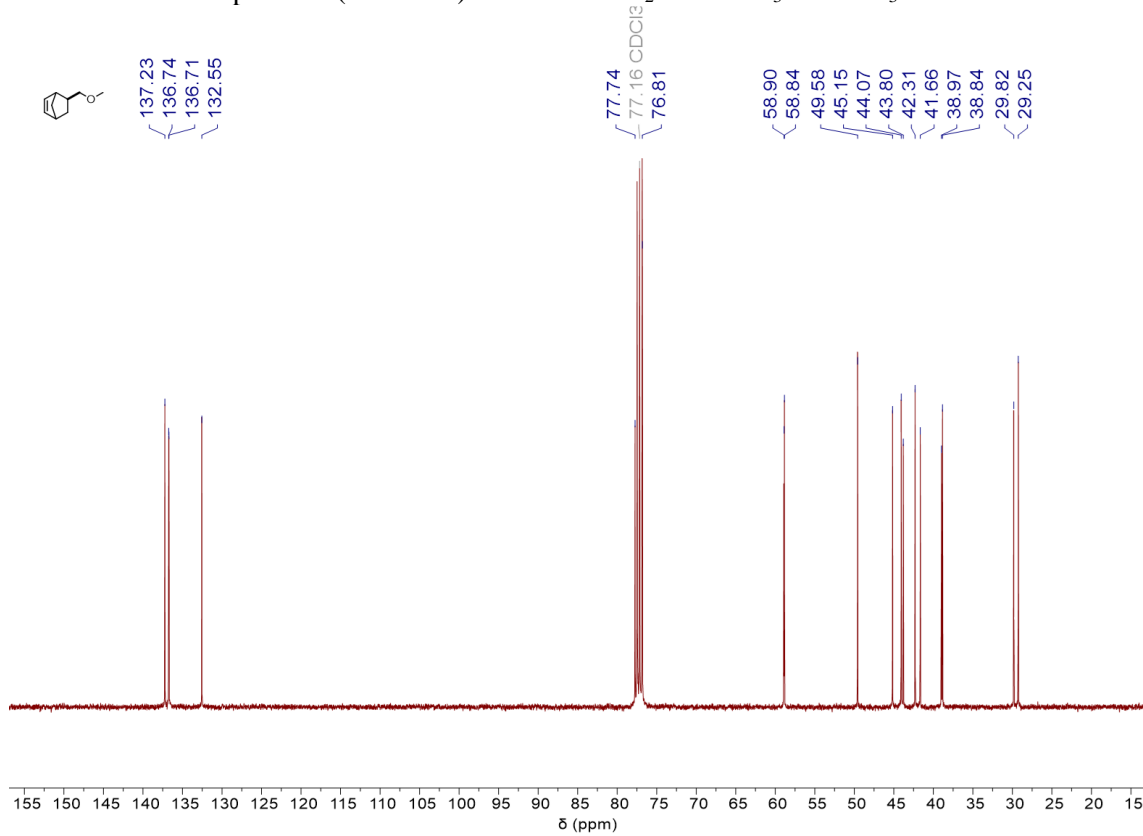


Figure S34. <sup>13</sup>C-NMR spectrum (400 MHz) of *mix*-Nb-CH<sub>2</sub>-ether-CH<sub>3</sub> in CDCl<sub>3</sub>.

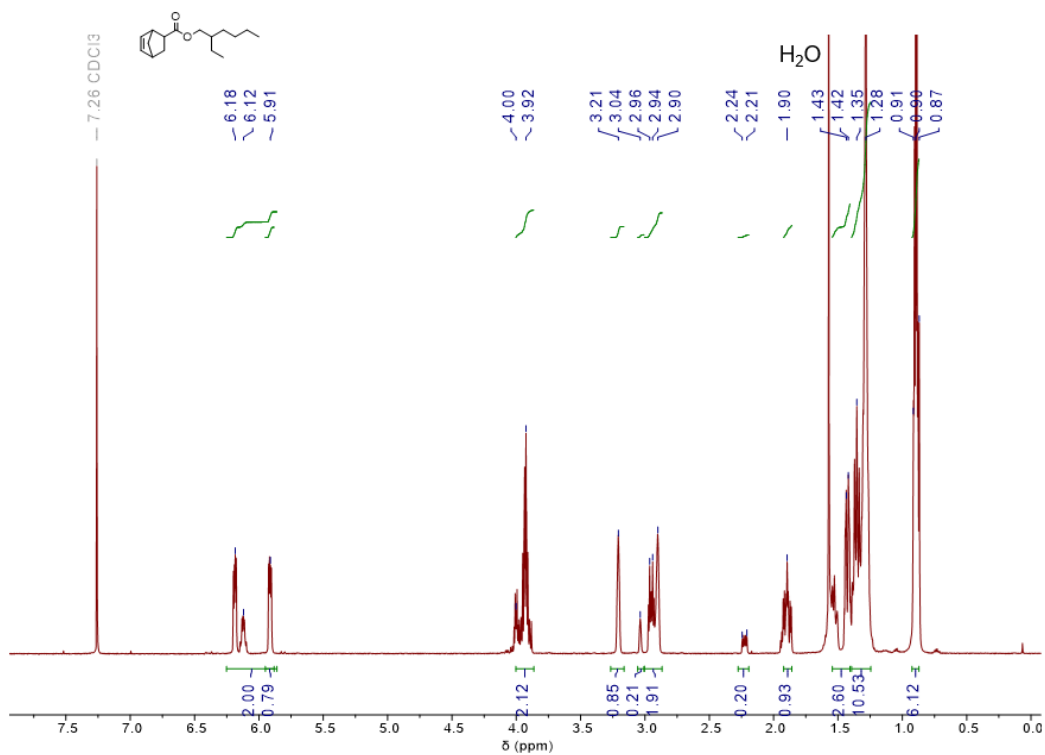


Figure S35. <sup>1</sup>H-NMR spectrum (400 MHz) of *mix-Nb-ester-EH* in CDCl<sub>3</sub>.

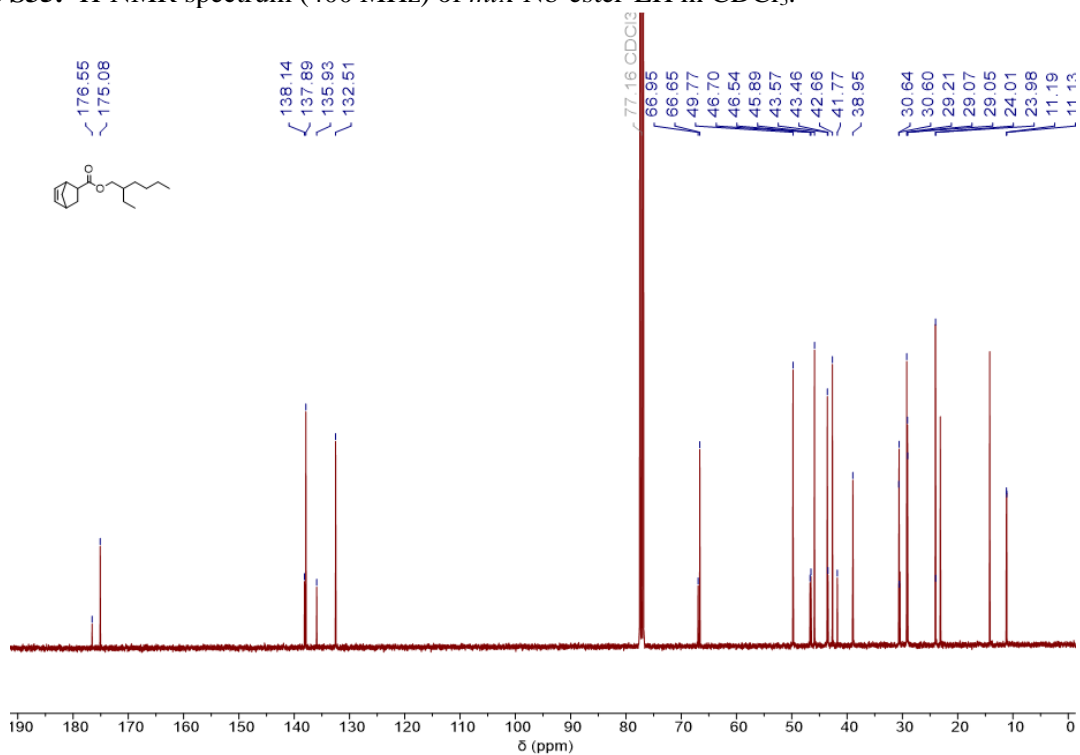
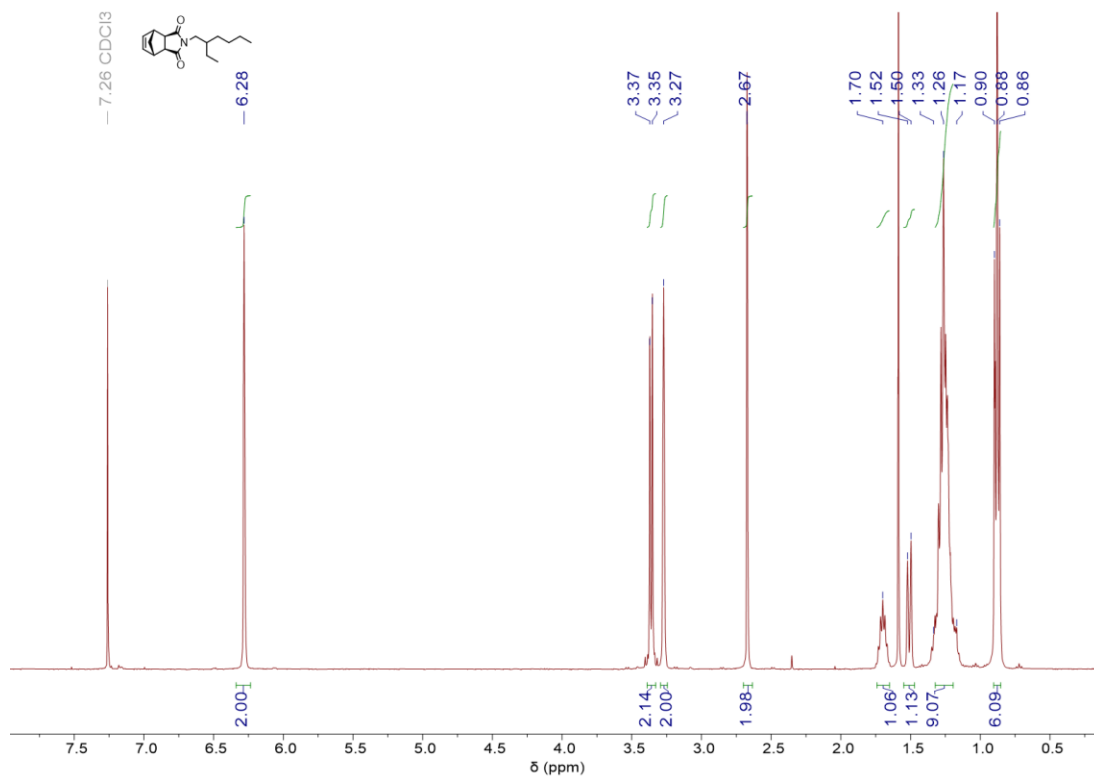
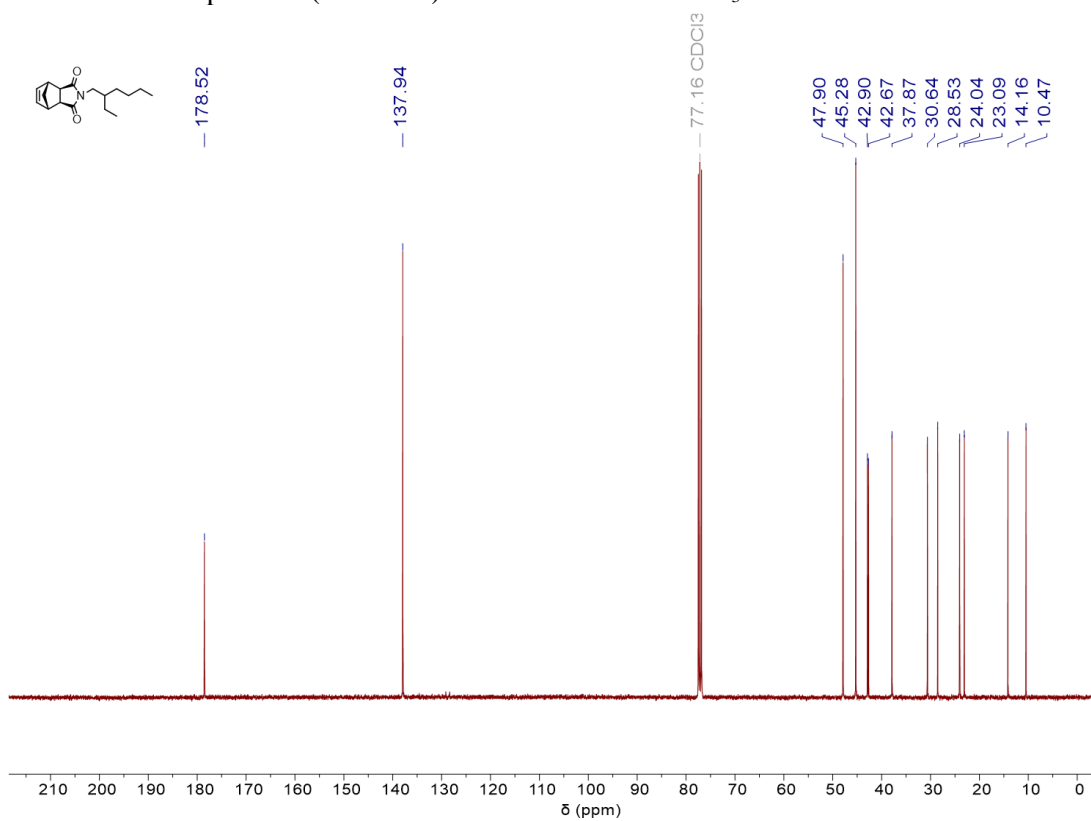


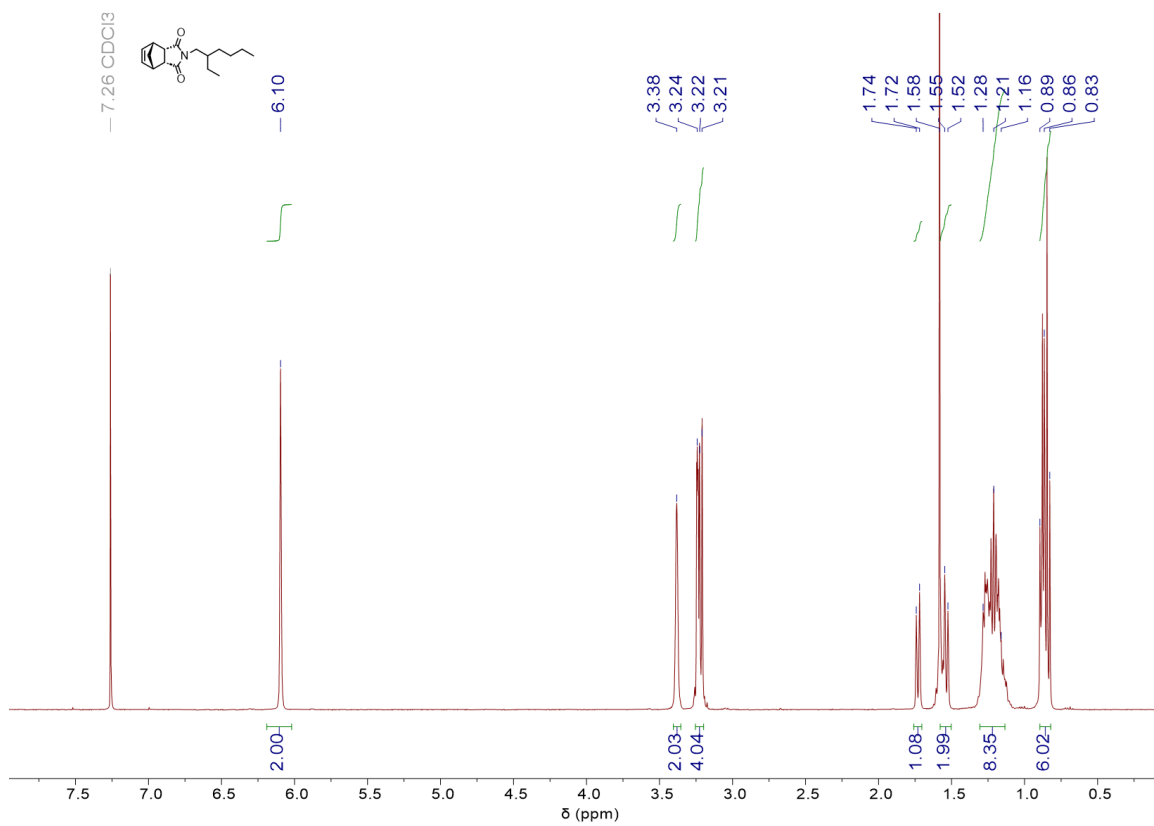
Figure S36. <sup>13</sup>C-NMR spectrum (400 MHz) of *mix-Nb-ester-EH* in CDCl<sub>3</sub>.



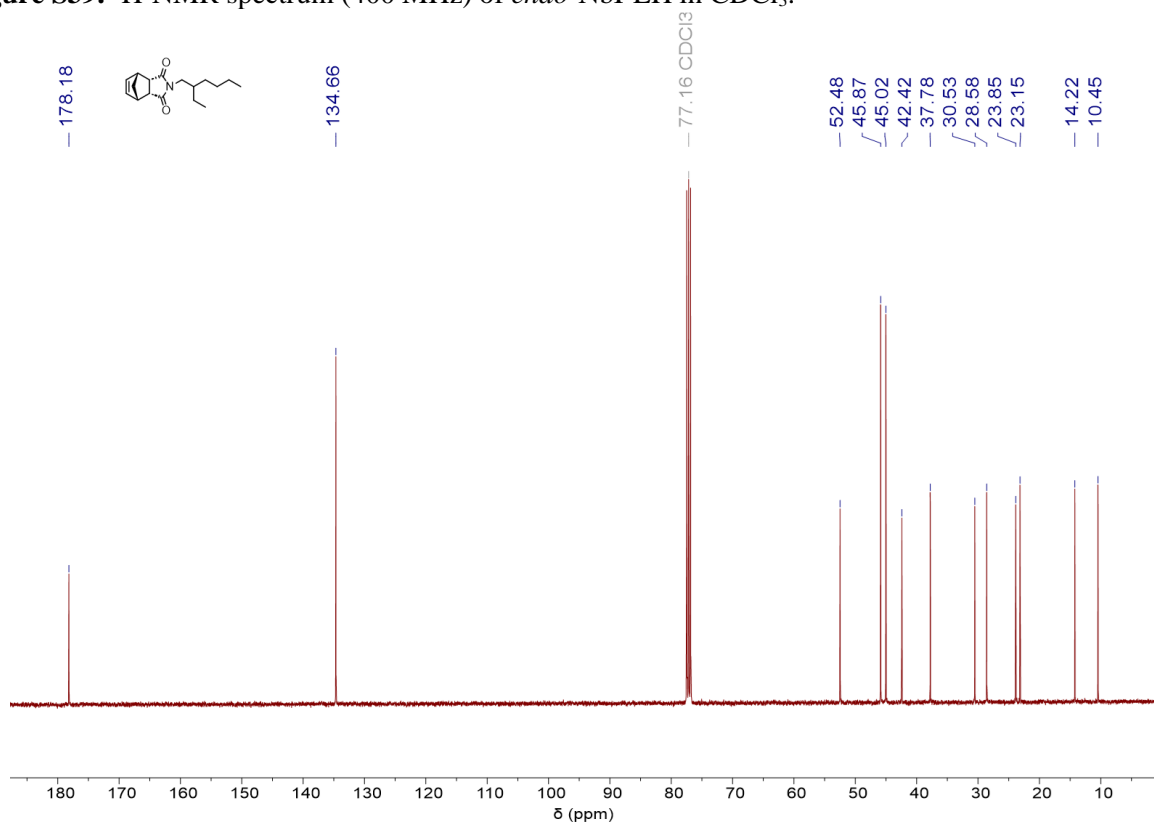
**Figure S37.**  $^1\text{H-NMR}$  spectrum (400 MHz) of *exo*-NbI-EH in  $\text{CDCl}_3$ .



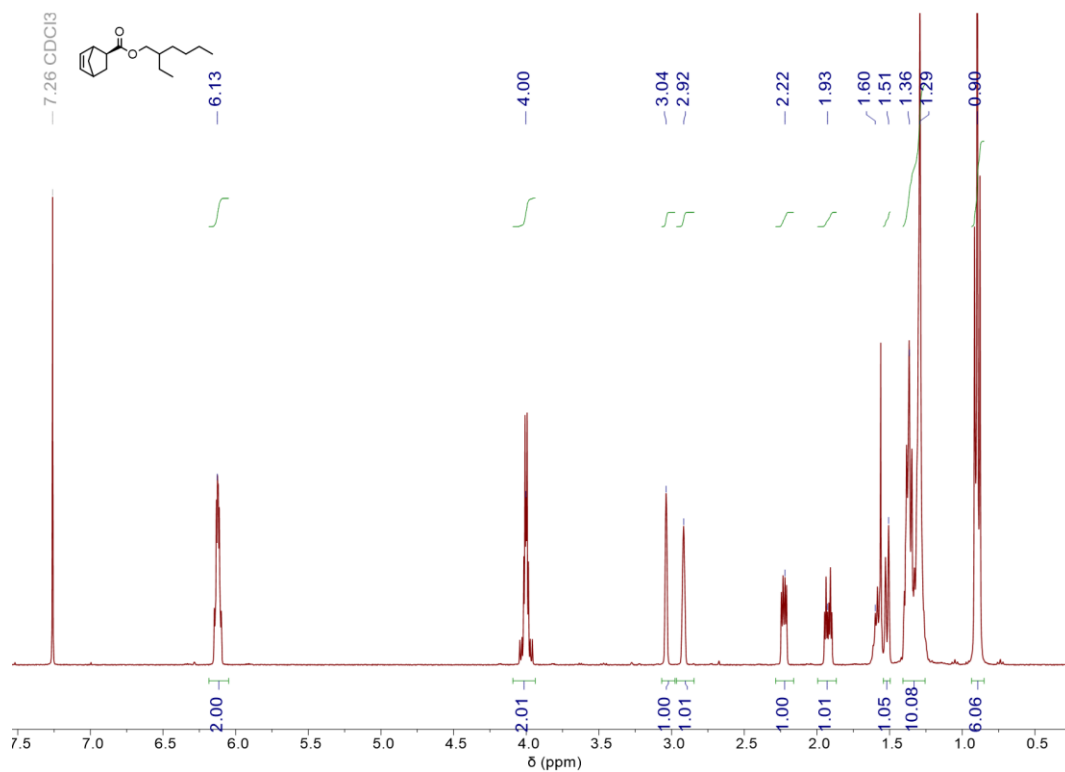
**Figure S38.**  $^{13}\text{C-NMR}$  spectrum (400 MHz) of *exo*-NbI-EH in  $\text{CDCl}_3$ .



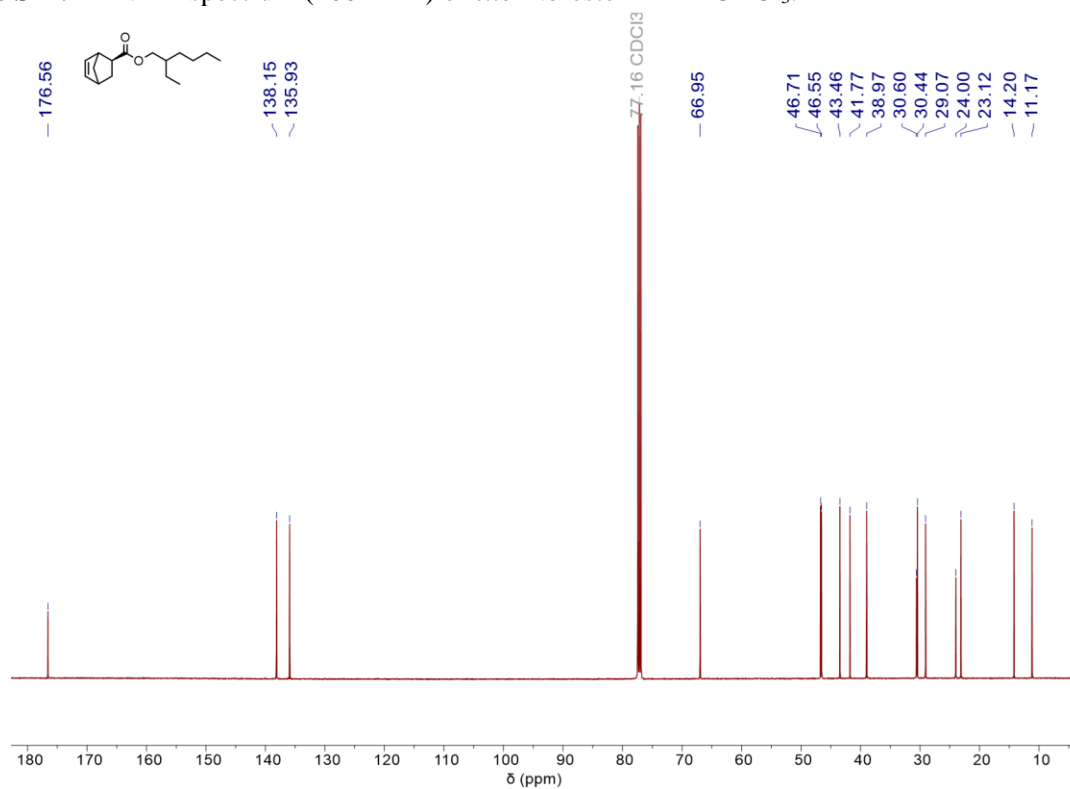
**Figure S39.** <sup>1</sup>H-NMR spectrum (400 MHz) of *endo*-NbI-EH in CDCl<sub>3</sub>.



**Figure S40.** <sup>13</sup>C-NMR spectrum (400 MHz) of *endo*-NbI-EH in CDCl<sub>3</sub>.



**Figure S41.** <sup>1</sup>H-NMR spectrum (400 MHz) of *exo*-Nb-ester-EH in CDCl<sub>3</sub>.



**Figure S42.** <sup>13</sup>C-NMR spectrum (400 MHz) of *exo*-Nb-ester-EH in CDCl<sub>3</sub>.

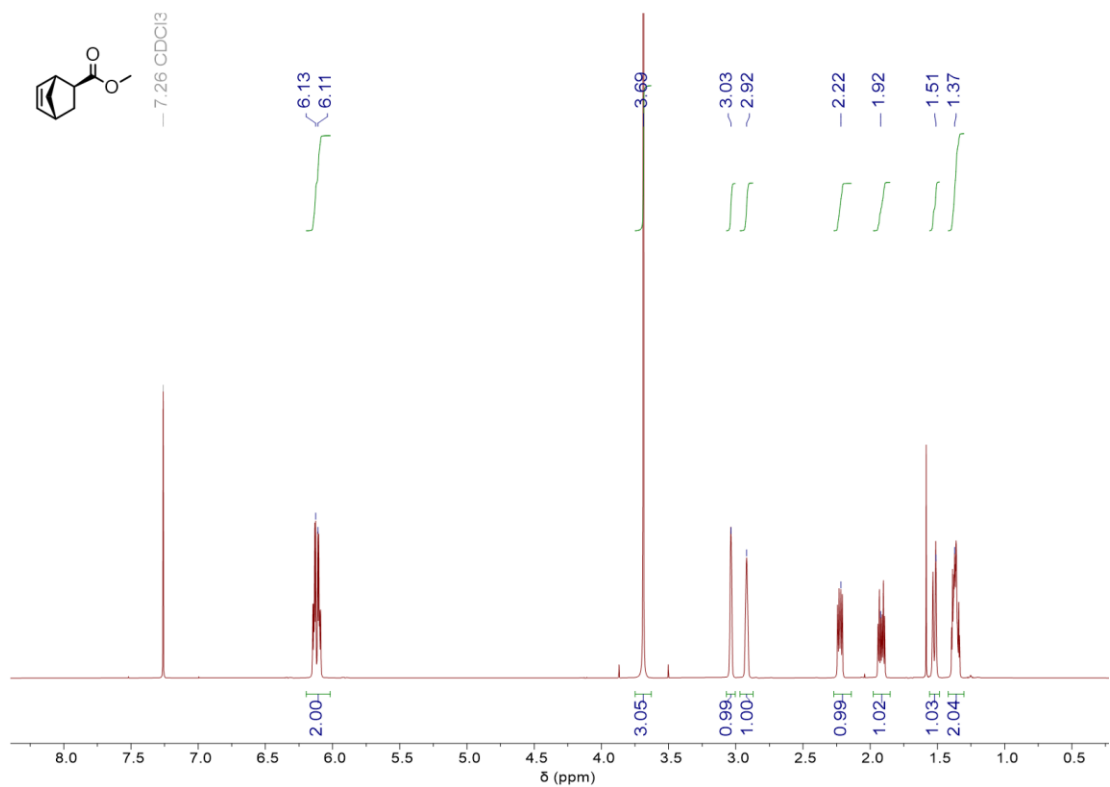


Figure S43. <sup>1</sup>H-NMR spectrum (400 MHz) of *exo*-Nb-ester-CH<sub>3</sub> in CDCl<sub>3</sub>.

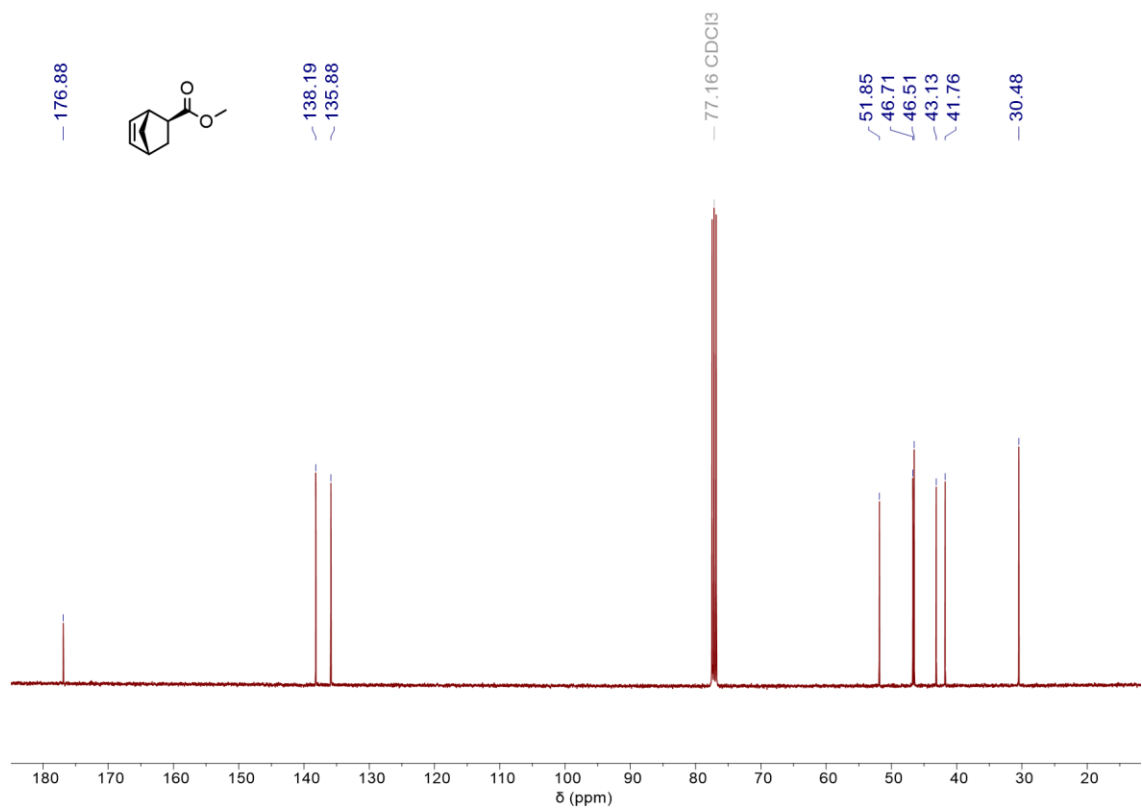
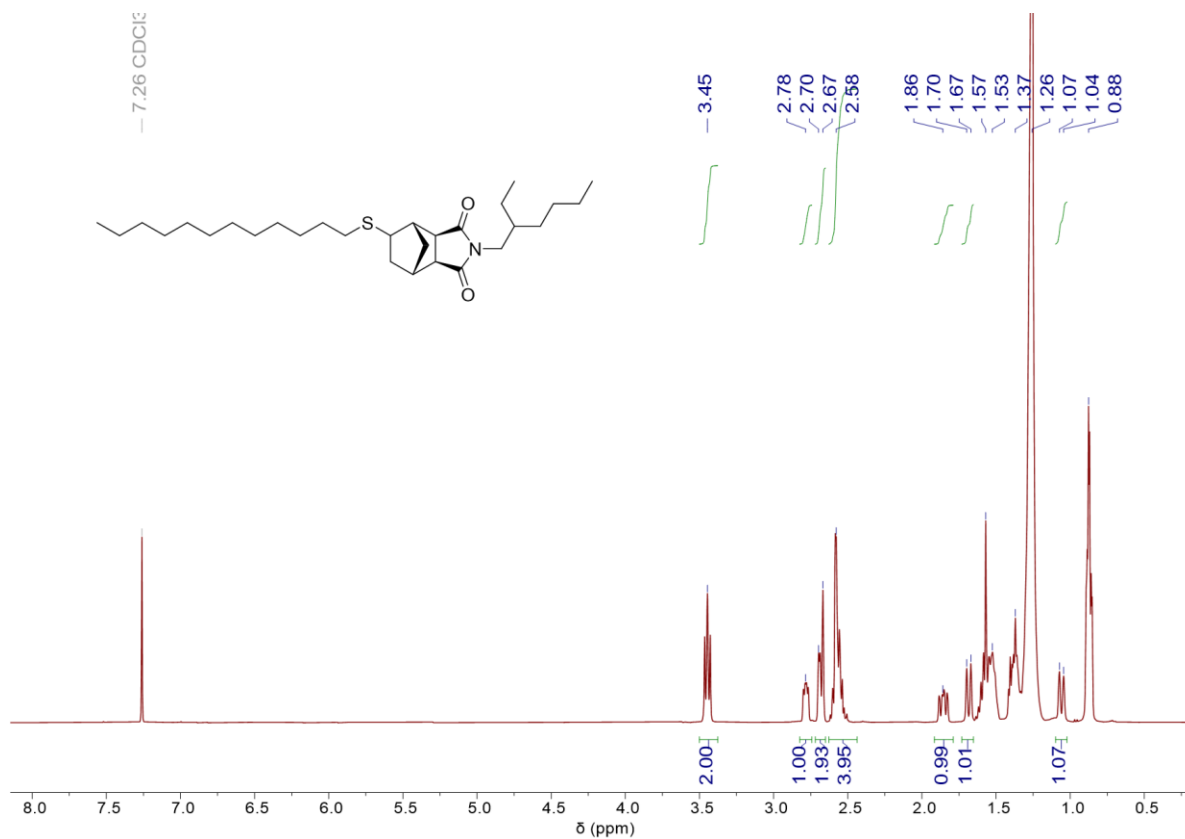
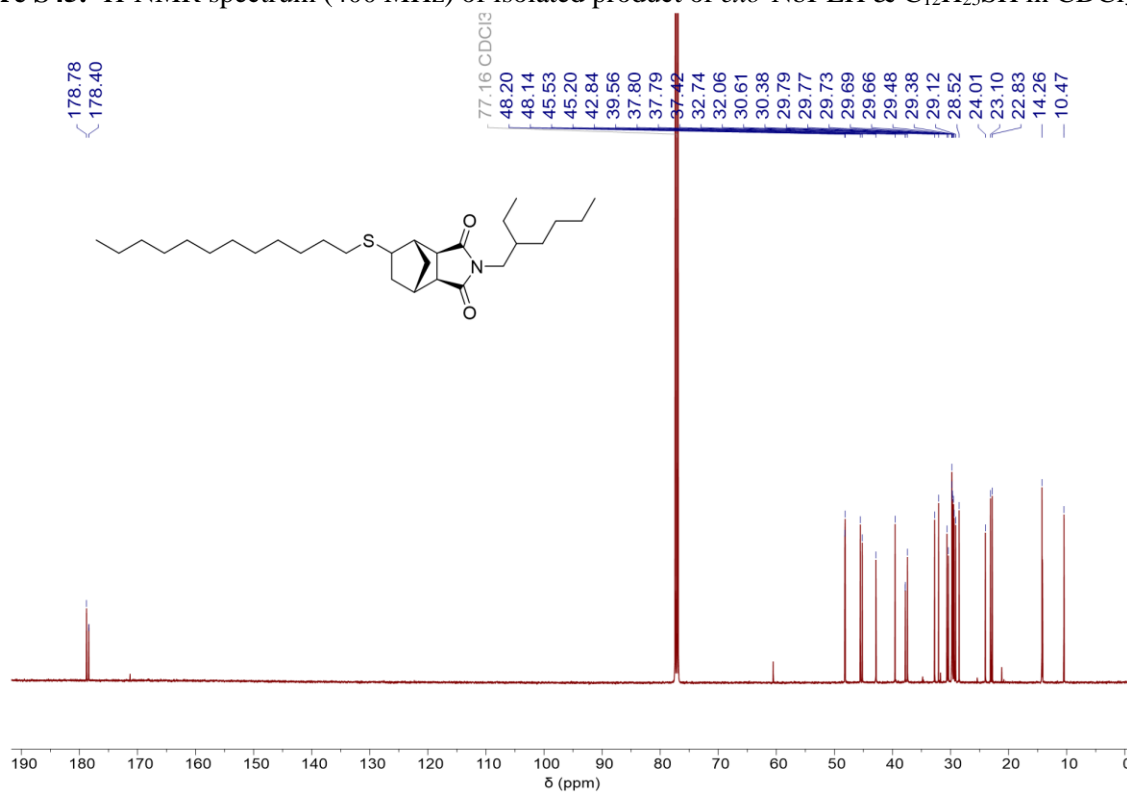


Figure S44. <sup>13</sup>C-NMR spectrum (400 MHz) of *exo*-Nb-ester-CH<sub>3</sub> in CDCl<sub>3</sub>.

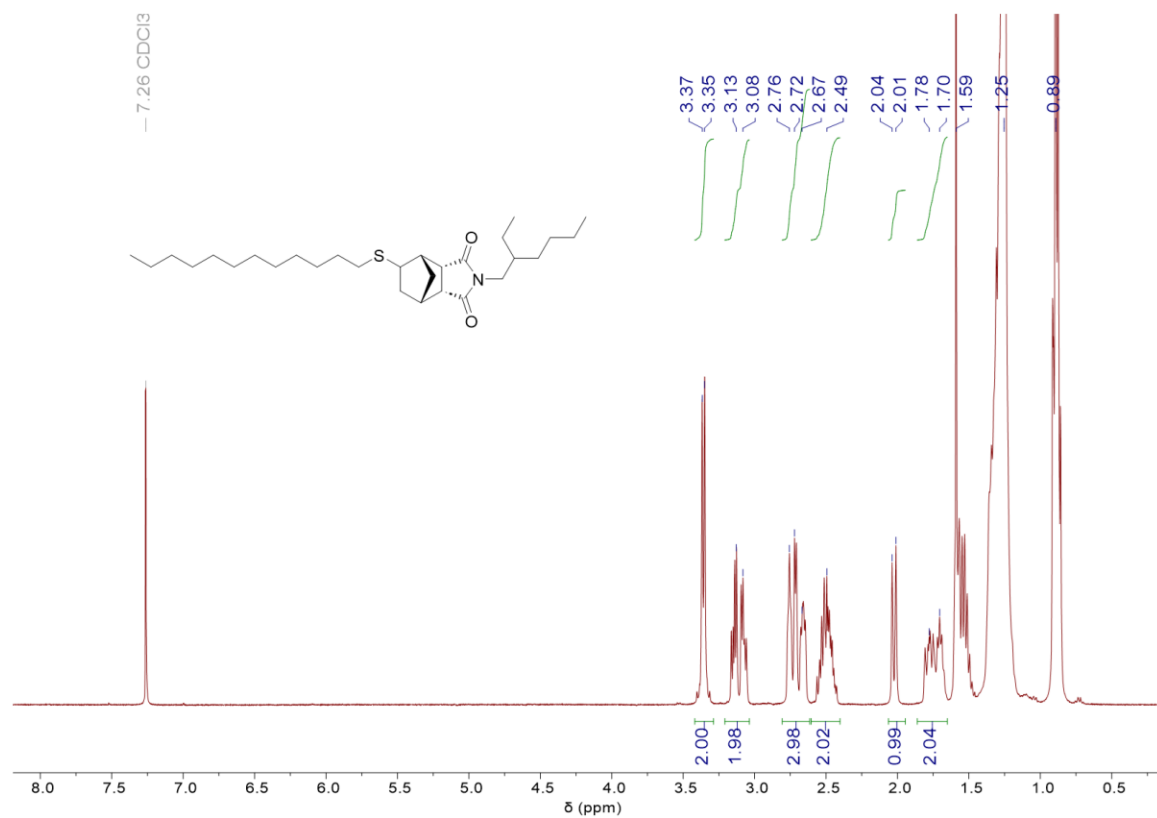


**Figure S45.** <sup>1</sup>H-NMR spectrum (400 MHz) of isolated product of *exo*-NbI-EH & C<sub>12</sub>H<sub>25</sub>SH in CDCl<sub>3</sub>.

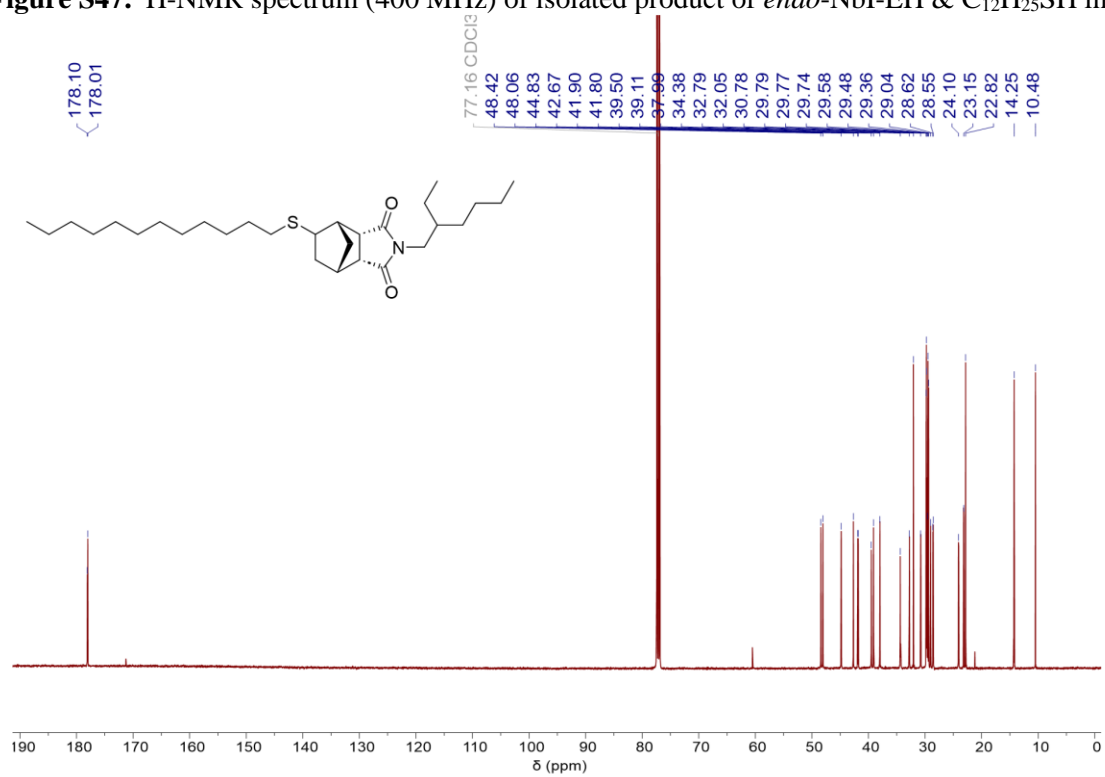


**Figure S46.** <sup>13</sup>C-NMR spectrum (500 MHz) of isolated product of *exo*-NbI-EH & C<sub>12</sub>H<sub>25</sub>SH in CDCl<sub>3</sub>.

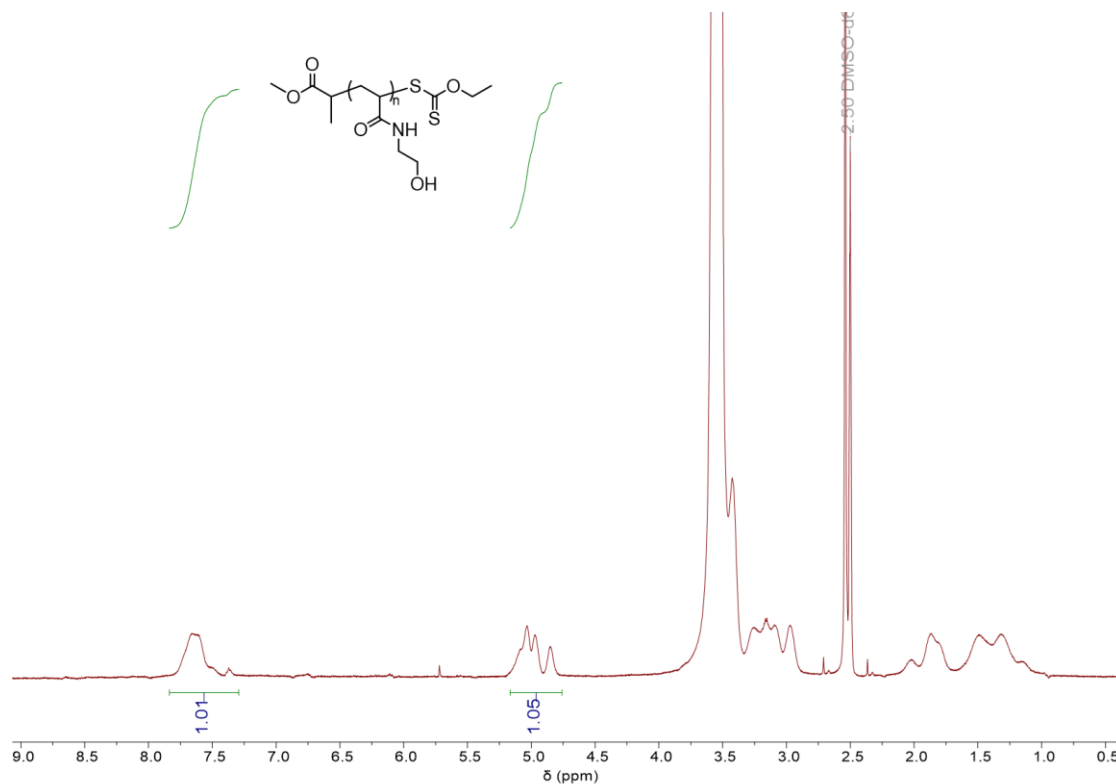




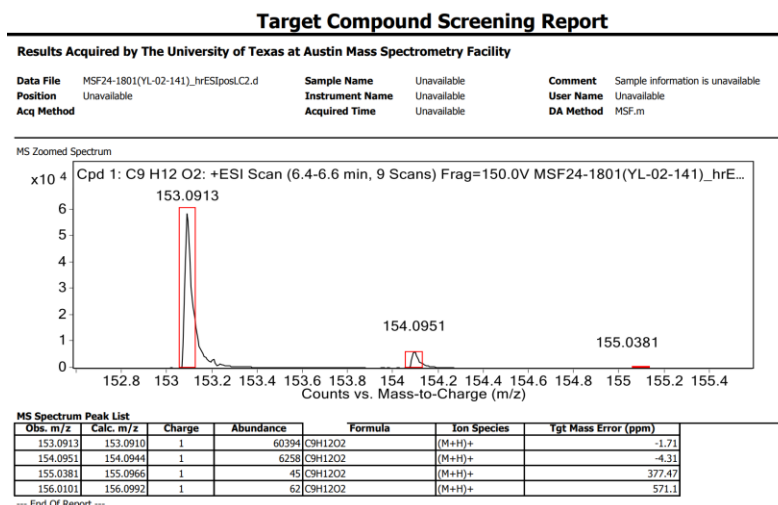
**Figure S47.**  $^1\text{H-NMR}$  spectrum (400 MHz) of isolated product of *endo*-NbI-EH &  $\text{C}_{12}\text{H}_{25}\text{SH}$  in  $\text{CDCl}_3$ .



**Figure S48.**  $^{13}\text{C-NMR}$  spectrum (500 MHz) of isolated product of *endo*-NbI-EH &  $\text{C}_{12}\text{H}_{25}\text{SH}$  in  $\text{CDCl}_3$ .



**Figure S49.**  $^1\text{H-NMR}$  spectrum (400 MHz) of isolated PHEAA via photoiniferter polymerization in  $\text{DMSO-d}_6$ .

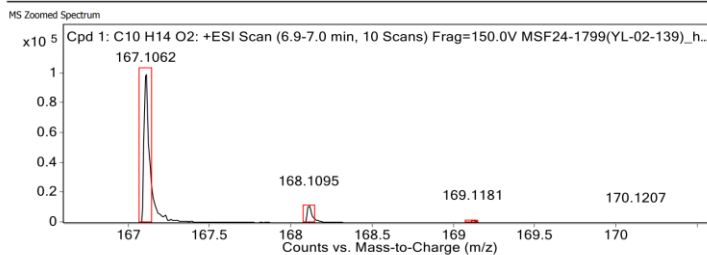


**Figure S50.** HRMS (ESI) of *mix*-Nb-acetate.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

**Data File** MSF24-1799(YL-02-139)\_hrESIpos.C2.d      **Sample Name** Unavailable      **Comment** Sample information is unavailable  
**Position** Unavailable      **Instrument Name** Unavailable      **User Name** Unavailable  
**Acq Method** Unavailable      **Acquired Time** Unavailable      **DA Method** MSF.m



Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
167.1062	167.1067	1	101944	C10H14O2	(M+H)+	2.61
168.1095	168.1101	1	11465	C10H14O2	(M+H)+	3.14
169.1181	169.1124	1	1954	C10H14O2	(M+H)+	-33.69
170.1207	170.1150	1	206	C10H14O2	(M+H)+	-33.29
249.1098			487678			

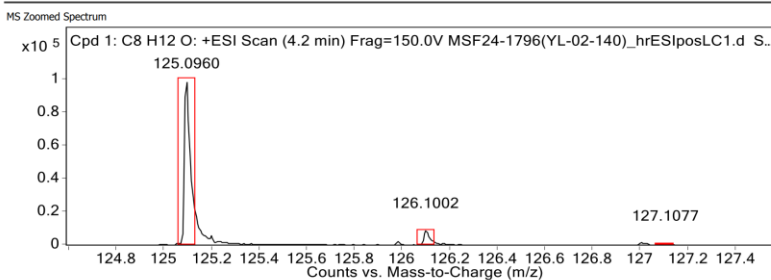
--- End Of Report ---

Figure S51. HRMS (ESI) of *mix*-Nb-CH<sub>2</sub>-acetate.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

**Data File** MSF24-1796(YL-02-140)\_hrESIposLC1.d      **Sample Name** 1796(YL-02-140)      **Comment** 1796(YL-02-140)  
**Position** P1-B7      **Instrument Name** Instrument 1      **User Name**      **Acq Method** LC\_C18\_pos\_jl.m      **Acquired Time** 9/10/2024 1:20:15 PM      **DA Method** MSF.m



Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
125.0960	125.0961	1	98931	C8H12O	(M+H)+	0.91
126.1002	126.0995	1	9026	C8H12O	(M+H)+	-5.23
127.1077	127.1020	1	1375	C8H12O	(M+H)+	-45.19
128.0478	128.1045	1	331	C8H12O	(M+H)+	442.76

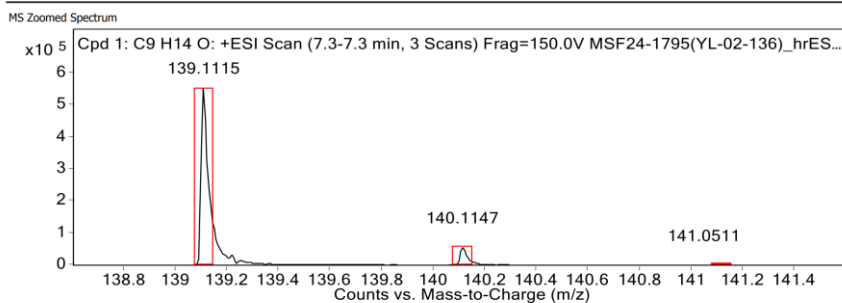
--- End Of Report ---

Figure S52. HRMS (ESI) of *mix*-Nb-ether-CH<sub>3</sub>.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

**Data File** MSF24-1795(YL-02-136)\_hrESIposLC1.d      **Sample Name** 1795(YL-02-136)      **Comment** 1795(YL-02-136)  
**Position** P1-B6      **Instrument Name** Instrument 1      **User Name**      **Acq Method** LC\_C18\_pos\_jl.m      **Acquired Time** 9/10/2024 12:39:04 PM      **DA Method** MSF.m



Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
139.1115	139.1117	1	550846	C9H14O	(M+H)+	1.59
140.1147	140.1152	1	56016	C9H14O	(M+H)+	3.41
141.0511	141.1178	1	342	C9H14O	(M+H)+	472.71
142.0612	142.1203	1	547	C9H14O	(M+H)+	416.06

--- End Of Report ---

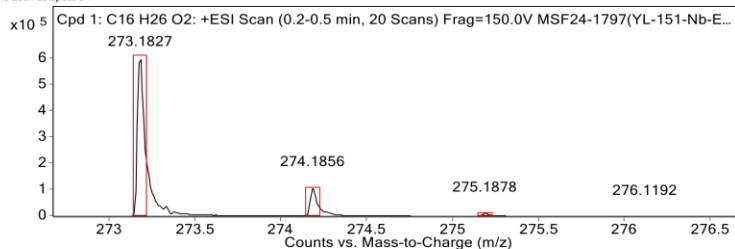
Figure S53. HRMS (ESI) of *mix*-Nb-CH<sub>2</sub>-ether-CH<sub>3</sub>.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF24-1797(YL-151-Nb-EH)\_hrES[post].d Sample Name 1797(YL-151-Nb-EH) Comment 1797(YL-151-Nb-EH)  
 Position P1-B8 Instrument Name Instrument 1 User Name  
 Acq Method FIA\_pos.m Acquired Time 9/10/2024 10:41:27 AM DA Method MSF.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
273.1827	273.1825	1	605969	C16H26O2	(M+Na)+	-0.75
274.1856	274.1859	1	110078	C16H26O2	(M+Na)+	1.22
275.1878	275.1888	1	12816	C16H26O2	(M+Na)+	3.62
276.1192	276.1915	1	477	C16H26O2	(M+Na)+	261.65
277.0850	277.1942	1	458	C16H26O2	(M+Na)+	394.3

--- End Of Report ---

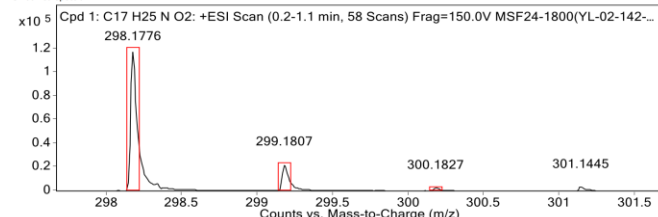
Figure S54. HRMS (ESI) of *mix*-Nb-ester-EH.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF24-1800(YL-02-142-exo-NbI-EH)\_hrES[post].d Sample Name 1800(YL-02-142-exo-NbI-EH) Comment 1800(YL-02-142-exo-NbI-EH)  
 Position P1-C2 Instrument Name Instrument 1 User Name  
 Acq Method FIA\_pos.m Acquired Time 9/10/2024 10:48:43 AM DA Method MSF.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
276.1956			126836			
298.1776	298.1778	1	117480	C17H25NO2	(M+Na)+	0.58
299.1807	299.1810	1	22479	C17H25NO2	(M+Na)+	1.1
300.1827	300.1839	1	2696	C17H25NO2	(M+Na)+	3.77
301.1445	301.1866	1	3463	C17H25NO2	(M+Na)+	139.57

--- End Of Report ---

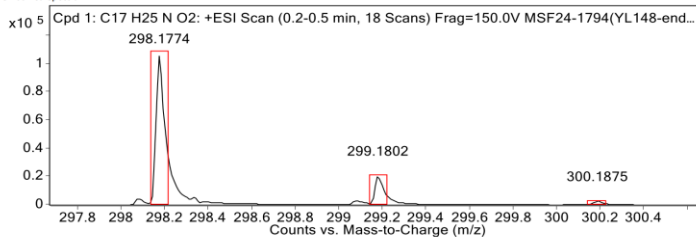
Figure S55. HRMS (ESI) of *exo*-NbI-EH.

### Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF24-1794(YL148-endo-NbI-EH)\_hrES[post].d Sample Name 1794(YL148-endo-NbI-EH) Comment 1794(YL148-endo-NbI-EH)  
 Position P1-B5 Instrument Name Instrument 1 User Name  
 Acq Method FIA\_pos.m Acquired Time 9/10/2024 10:36:22 AM DA Method MSF.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
298.1774	298.1778	1	106012	C17H25NO2	(M+Na)+	1.33
299.1802	299.1810	1	20706	C17H25NO2	(M+Na)+	2.61
300.1875	300.1839	1	2670	C17H25NO2	(M+Na)+	-12.17
301.1501	301.1866	1	2258	C17H25NO2	(M+Na)+	120.96
427.3293			134969			

--- End Of Report ---

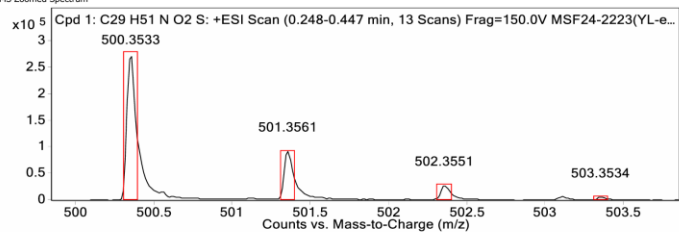
Figure S56. HRMS (ESI) of *endo*-NbI-EH.

### Target Compound Screening Report

#### Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF24-2223(YL-exo-Nbl-SH-product)\_hrESIpos1.d Sample Name 2223(YL-exo-Nbl-SH-product) Comment 2223(YL-exo-Nbl-SH-product)  
 Position P1-E2 Instrument Name 6530 User Name  
 Acq Method FIA\_pos.m Acquired Time 11/15/2024 9:57:31 AM DA Method MSF.m

#### MS Zoomed Spectrum



#### MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
500.3533	500.3533	1	276460	C29H51NO2S	(M+Na)+	-0.03
501.3561	501.3565	1	93130	C29H51NO2S	(M+Na)+	0.24
502.3551	502.3550	1	28597	C29H51NO2S	(M+Na)+	-0.24
503.3534	503.3557	1	6393	C29H51NO2S	(M+Na)+	4.46
504.3554	504.3573	1	1352	C29H51NO2S	(M+Na)+	3.81

--- End Of Report ---

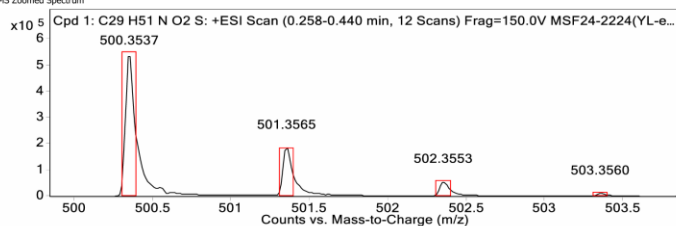
Figure S57. HRMS (ESI) of isolated product of *exo*-Nbl-EH & C<sub>12</sub>H<sub>25</sub>SH.

### Target Compound Screening Report

#### Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF24-2224(YL-endo-Nbl-SH-product)\_hrESIpos1.d Sample Name 2224(YL-endo-Nbl-SH-product) Comment 2224(YL-endo-Nbl-SH-product)  
 Position P1-E3 Instrument Name 6530 User Name  
 Acq Method FIA\_pos.m Acquired Time 11/15/2024 9:59:32 AM DA Method MSF.m

#### MS Zoomed Spectrum



#### MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
500.3537	500.3533	1	547420	C29H51NO2S	(M+Na)+	-0.94
501.3565	501.3565	1	185932	C29H51NO2S	(M+Na)+	-0.04
502.3553	502.3550	1	55793	C29H51NO2S	(M+Na)+	-0.71
503.3560	503.3557	1	11288	C29H51NO2S	(M+Na)+	-0.52
516.3485			638187			

--- End Of Report ---

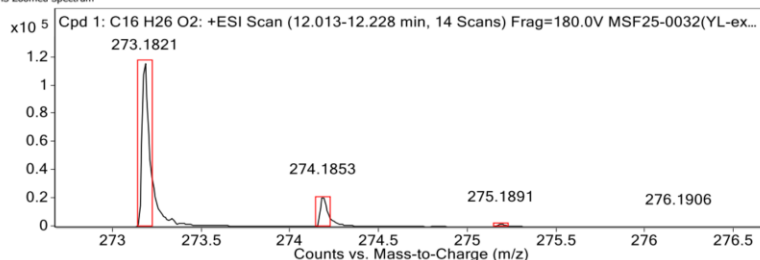
Figure S58. HRMS (ESI) of isolated product of *endo*-Nbl-EH & C<sub>12</sub>H<sub>25</sub>SH.

### Target Compound Screening Report

#### Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File MSF25-0032(YL-exo-Nb-ester-EH)\_hrESIpos1.C1.d Sample Name Unavailable Comment Sample information is unavailable  
 Position Unavailable Instrument Name Unavailable User Name Unavailable  
 Acq Method Unavailable Acquired Time Unavailable DA Method MSF.m

#### MS Zoomed Spectrum



#### MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
139.0749			212607			
273.1821	273.1825	1	116747	C16H26O2	(M+Na)+	1.57
274.1853	274.1859	1	21810	C16H26O2	(M+Na)+	2.27
275.1891	275.1888	1	2292	C16H26O2	(M+Na)+	-1.17
276.1906	276.1915	1	171	C16H26O2	(M+Na)+	3.18

--- End Of Report ---

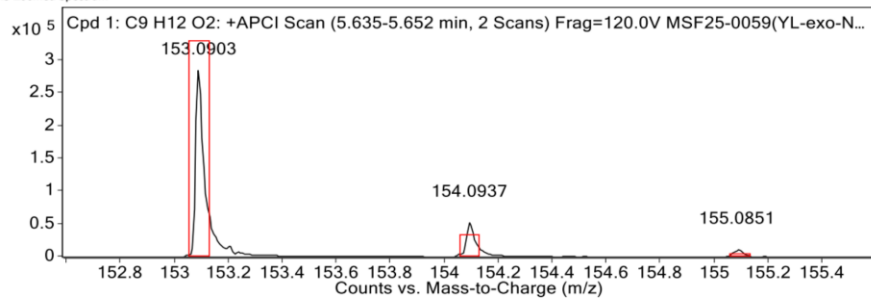
Figure S59. HRMS (ESI) of *exo*-Nb-ester-EH.

## Target Compound Screening Report

### Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

**Data File** MSF25-0059(YL-exo-Nb-ester-CH3)\_hrAPCIposLC1.d      **Sample Name** 0059(YL-exo-Nb-ester-CH3)      **Comment** 0059(YL-exo-Nb-ester-CH3)  
**Position** P1-D7      **Instrument Name** 6530      **User Name**  
**Acq Method** APCI\_LC\_C18\_MeOH\_pos\_II.m      **Acquired Time** 1/23/2025 10:59:54 AM      **DA Method** MSF.m

MS Zoomed Spectrum



#### MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
153.0903	153.0910	1	286421	C9H12O2	(M+H)+	4.71
154.0937	154.0944	1	53457	C9H12O2	(M+H)+	4.57
155.0851	155.0966	1	12244	C9H12O2	(M+H)+	74.29
156.0967	156.0992	1	12038	C9H12O2	(M+H)+	16.38
210.1122			381860			

--- End Of Report ---

**Figure S60.** HRMS (ESI) of *exo*-Nb-ester-CH<sub>3</sub>.

### S3. Movie Captions

All movies were recorded in real-time on a digital camera (Sony Alpha 7S (ILCE-7SM2, WW898259 equipped with a Sony Interchangeable Lens (FE 2.8/90 Macro G OSS, SEL90M28G)). Scale bars have been overlaid onto each movie.

**Movie S1.** 3D-printed hollow vessel, fabricated with *exo*-NbI-PHEAA and filled with leftover resin and methanol. The sample is tested by extracting liquid with a needle to confirm the hollow structure. Video highlights the liquid being drawn through the needle, demonstrating the internal permeability of the model. The test showcases the vessel's ability to hold and release liquid, confirming its structural integrity. Other images of this print are represented in **Figure 4E** of the main manuscript and Figure S21. Video is played at 4× speed.

**Movie S2.** 3D-printed heart valve model, fabricated with *exo*-NbI-PHEAA. The sample is tested by probing the valve flaps with a needle to demonstrate that the flaps remain flexible and unfused. This confirms the model's open geometry, mimicking a functional heart valve. Other images of this print are represented in **Figure 4E** of the main manuscript and Figure S22. Video is played at 1.5× speed.

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