

Expedient Synthesis and Ring-Opening Metathesis Polymerization of Pyridinonornbornenes

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General Reagent Information

All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Dry acetonitrile (MeCN), dichloromethane (DCM), tetrahydrofuran (THF), and toluene were obtained by passing the previously degassed solvents through activated alumina columns. Anhydrous 1,2-dichloroethane (DCE) was purchased from Sigma-Aldrich and was degassed under an inert nitrogen atmosphere in an ultrasonicator for 1 hour prior to its transfer into a nitrogen-filled glove box (SG1800/750TS-F, VIGOR). Cesium fluoride (CsF) was obtained from Oakwood Chemical, dried at 105 °C *in vacuo* for 48 h, and then stored in the nitrogen-filled glove box. Syntheses of polymers using ruthenium metathesis catalysts were carried out in a nitrogen-filled glove box, unless otherwise stated. **Ru-2** was purchased from Sigma-Aldrich and stored in the nitrogen-filled glove box. **Ru-1** was synthesized according to literature procedure (*Angew. Chem. Int. Ed.* **2002**, *41*, 4035) from **Ru-2**, and was stored in the nitrogen-filled glove box.

Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 250 μm SiliCycle SiliaPlate™ silica plates (F254), using UV light as the visualizing agent and aqueous solution of KMnO₄ and heat as developing agents. Flash silica gel chromatography was performed using SiliCycle SiliaFlash® Irregular Silica Gel (60 Å, particle size 40–63 μm). Polymers were isolated after precipitation using an Eppendorf 5804 centrifuge.

General Analytical Information

Proton and Carbon (¹H and ¹³C) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 MHz instrument and were calibrated using residual undeuterated solvent as an internal reference (CDCl₃ @ 7.26 ppm ¹H-NMR, 77.16 ppm ¹³C-NMR; d₂-DCM @ 5.32 ppm ¹H-NMR, 54.00 ppm ¹³C-NMR). Fluorine (¹⁹F) NMR spectra were recorded using a Varian Inova 500 MHz instrument and calibrated by a solution of CFC₃ in CDCl₃ (@ 0.65 ppm ¹⁹F NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) and electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a Thermo Scientific Q

Exactive Focus. Sample was injected into a 10 μL loop and methanol was used as a mobile phase at a flow rate of 600 $\mu\text{L}/\text{min}$. The Q Exactive Focus source was operated in full MS in positive mode. The mass resolution was tuned to 70000 FWHM at m/z 200. The discharge current of APCI was set at 5 μA . The spray voltage for ESI was set to 3.5 kV. Sheath gas and auxiliary gas flow rates were set to 40 and 10 arbitrary units, respectively. Auxiliary gas temperature was set to 300 $^{\circ}\text{C}$ for APCI. The transfer capillary temperature was held at 320 $^{\circ}\text{C}$ and the S-Lens RF level was set at 50 v. Exactive Series 2.11 /Xcalibur 4.02.47 software was used for data acquisition and processing.

Melting points were recorded on a Fisher-Johns 13-144 melting point apparatus and are uncorrected.

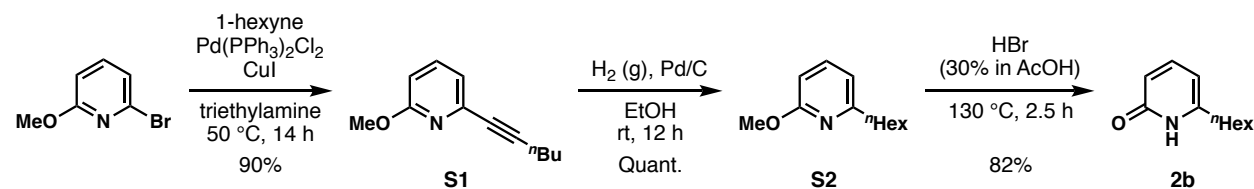
All polymer samples were analyzed using a TosohEcoSEC HLC 8320 GPC system with a TSKgel SuperHM-M and a Super H-RC column at a flow rate of 0.35 mL/min at 40 $^{\circ}\text{C}$. THF stabilized with BHT was used as the eluent and all number-average molar masses (M_n), weight-average molar masses (M_w), and dispersities (D) for polymers were calculated from refractive index (RI) against TSKgel polystyrene standards.

Matrix assisted laser desorption ionization (MALDI) experiments were performed using a Bruker Microflex MALDI-TOF mass spectrometer (Bruker Daltonics) operated using FlexControl software version 3.4 under optimized conditions in positive linear mode. Trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix.

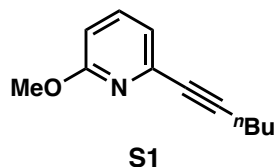
Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 5500 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC 2500.

Monomer Synthesis

Preparation of pyridine precursors 2b and 2c:



Scheme S1. Synthesis of *n*-hexyl pyridone **2b**.



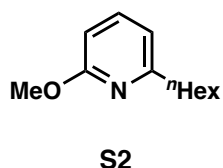
Pyridine S1 was prepared according to a modified procedure (*Bioorg. Med. Chem.* **2001**, *9*, 2863). To a flame-dried 250 mL round-bottom flask equipped with a stir bar was charged with CuI (51 mg, 0.27 mmol, 0.050 equiv) and Pd(PPh₃)₂Cl₂ (93 mg, 0.13 mmol, 0.025 equiv). Triethylamine (21 mL) was added under a nitrogen atmosphere followed by 2-bromo-6-methoxypyridine (0.65 mL, 5.32 mmol, 1.0 equiv). The mixture was then degassed by sparging vigorously with argon for 30 min while sonicating. The degassed solution was then cooled to 0 °C and stirred for 10 min. 1-Hexyne (0.69 mL, 6.01 mmol, 1.1 equiv) was added dropwise to the reaction mixture, and the solution was stirred at 0 °C for 1 h. The reaction mixture was allowed to warm to rt over 10 min and then stirred at 50 °C for 12 h. The mixture was cooled to rt and then filtered through celite. The solvent was removed under reduced pressure and the resulting dark brown oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 90:10 hexanes:EtOAc) to yield a light brown oil (0.95 g, 95% yield).

R_f = 0.36 (19:1 hexanes:EtOAc)

¹H NMR (CDCl₃, 500 MHz) δ: 7.47 (dd, *J* = 8.2, 7.4 Hz, 1 H), 6.98 (d, *J* = 7.3 Hz, 1 H), 6.65 (d, *J* = 8.3 Hz, 1 H), 3.94 (s, 3H), 2.44 (t, *J* = 7.1 Hz, 2 H), 1.66–1.59 (m, 2 H), 1.53–1.44 (m, 2 H), 0.95 (t, *J* = 7.4 Hz, 3 H) ppm.

¹³C NMR (CDCl₃, 126 MHz) δ: 163.9, 141.0, 138.5, 120.4, 110.5, 90.5, 80.6, 53.6, 30.6, 22.2, 19.3, 13.7 ppm.

HRMS (+APCI): calc'd. for C₁₂H₁₅NO [M+H]⁺ 190.1226, found 190.1225.

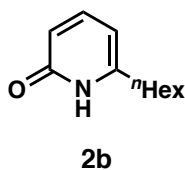


Pyridine S2. In a 100 mL round bottom flask equipped with a stir bar was added **S1** (1.25 g, 6.61 mmol) and 10% Pd on carbon (140 mg). EtOH (26 mL) was added to the mixture, and the solution was flushed with H₂. The reaction was stirred at rt under a hydrogen atmosphere (maintained with a balloon) over 14 h. The solution was filtered through celite, and the solvent was evaporated under reduced pressure to afford **S2** as a light brown oil that was used without further purification (1.27 g, >99% yield).

^1H NMR (CDCl_3 , 500 MHz) δ : 7.47 (dd, $J = 8.1, 7.4$ Hz, 1 H), 6.71 (d, $J = 7.3$ Hz, 1 H), 6.55 (d, $J = 8.2$ Hz, 1 H), 3.94 (s, 3 H), 2.70 (t, $J = 7.7$ Hz, 2 H), 1.78–1.69 (m, 2 H), 1.43–1.27 (m, 6 H), 0.91 (t, $J = 7.1$ Hz, 3 H) ppm.

^{13}C NMR (CDCl_3 , 126 MHz) δ : 163.8, 160.6, 138.7, 115.1, 107.2, 53.2, 38.1, 31.9, 29.5, 29.2, 22.7, 14.2 ppm.

HRMS (+APCI): calc'd. for $\text{C}_{12}\text{H}_{19}\text{NO}$ $[\text{M}+\text{H}]^+$ 194.1539, found 194.1538.



***n*-Hexyl pyridone 2b. S2** (5.46 g, 28.2 mmol, 1.0 equiv) was placed in a 250 mL round-bottom flask. To the flask was slowly added HBr dropwise (30% in AcOH, 130 mL). The flask was fitted with a condenser equipped with a connector at the top and a tubing to bubble acidic fumes through an aqueous solution of NaOH ($C = 6$ M, 25 mL) cooled to 0 °C with an ice bath. The mixture was stirred for 2.5 h at 130 °C and allowed to cool to rt. The solution was diluted with Et_2O (100 mL), and the acidic mixture was slowly neutralized by addition of sat. NaHCO_3 until the pH reaches ~ 8 using a pH strip. The product mixture was extracted with Et_2O (2 \times 50 mL), then the organic extracts were washed with water (100 mL), followed by brine (100 mL), and dried using MgSO_4 . Evaporation of solvent under reduced pressure left a brown oil which was further purified by column chromatography (SiO_2 , gradient from 100:0 to 30:70 hexanes:EtOAc) to furnish **2b** as a light brown solid (4.14 g, 82% yield).

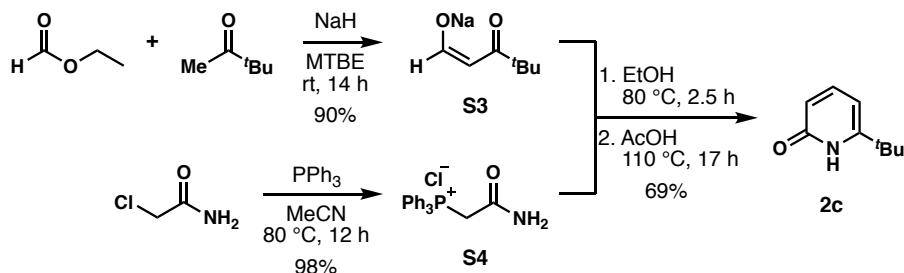
$R_f = 0.49$ (3:7 hexanes:EtOAc)

^1H NMR (CDCl_3 , 126 MHz) δ : 13.0 (br s, 1 H), 7.35 (dd, $J = 9.1, 6.9$ Hz, 1 H), 6.39 (d, $J = 9.0$ Hz, 1 H), 6.03 (d, $J = 7.0$ Hz, 1 H), 2.59 (t, $J = 7.7$ Hz, 2 H), 1.72–1.62 (m, 2 H), 1.40–1.23 (m, 6 H), 0.86 (t, $J = 7.0$ Hz, 3 H) ppm.

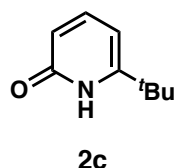
^{13}C NMR (CDCl_3 , 126 MHz) δ : 166.1, 150.5, 141.8, 116.8, 105.1, 33.2, 31.6, 28.7, 28.5, 22.6, 14.1 ppm.

HRMS (+ESI): calc'd. for $\text{C}_{11}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$ 180.1383, found 180.1383.

m.p.: 51–52 °C



Scheme S2. Synthesis of *tert*-butyl pyridone **2c**.



tert-Butyl pyridone **2c** was prepared according to literature procedure (*Chem. – Eur. J.* **2009**, *15*, 7167). A flame dried 1000 mL round-bottom flask equipped with a stir bar was charged with sodium hydride (5.20 g, 60%, 130 mmol, 1.3 equiv) and methyl *tert*-butyl ether (MTBE, 120 mL). The flask was then submerged in a water-bath at rt for external cooling to maintain the reaction temperature around rt. Using a syringe pump, a solution of ethyl formate (9.70 mL, 120 mmol, 1.2 equiv) and 3,3-dimethylbutan-2-one (12.5 mL, 100 mmol, 1.0 equiv) was added dropwise over 2 h. Upon completion of the addition, the mixture was allowed to stir for an additional 12 h. The suspension was then diluted with hexanes (120 mL). The solid was filtered and washed with additional hexanes, and then dried under high vacuum to afford keto-aldehyde salt **S3** (13.5 g, 90% yield).

To a 250 mL round-bottom flask equipped with a stir bar was added 2-chloroacetamide (9.33 g, 100 mmol, 1.0 equiv), triphenylphosphine (26.2 g, 100 mmol, 1.0 equiv), and MeCN (53 mL). A condenser was fitted to the flask, and the suspension was heated to 80 °C. The solids dissolved over 10 min, and the product started to precipitate after ~1 h. The mixture was allowed to stir for 12 h at 80 °C before cooling to rt. The suspension was then diluted with MTBE (50 mL). Filtration and washing with excess MTBE afforded an MeCN-solvate, which was dried under reduced pressure in an oven at 100 °C, leaving the phosphonium salt **S4** as a colorless solid. (34.7 g, 98% yield).

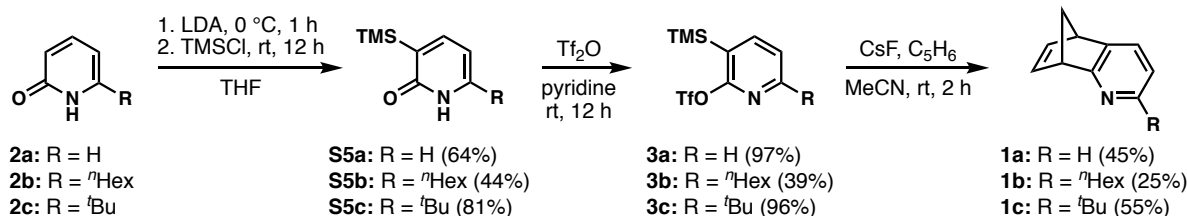
A 500 mL round bottom flask equipped with a stir bar was loaded with keto-aldehyde salt **S3** (13.5 g, 90 mmol, 1.0 equiv) and phosphonium salt **S4** (32.0 g, 90 mmol, 1.0 equiv). To the mixture was added EtOH (145 mL), and the flask was adapted with a condenser. The mixture was heated at 80 °C for 2.5 h, and then AcOH (56 mL) was slowly added at 80 °C. The mixture was then stirred at 110 °C for 17 h. After cooling to rt, and removal of majority of solvent under reduced pressure,

the crude mixture was redissolved in EtOAc (200 mL) and washed with sat. NaHCO₃ (300 mL) to remove residual AcOH. The aqueous layer was extracted with EtOAc (2×100 mL), and the combined organic phases were dried under reduced pressure. The solid residues were then deposited onto silica gel by the careful evaporation of solvent from a suspension of the crude solid and silica gel in DCM. Dry-packed column chromatography (2:1 Hexanes:EtOAc + 0.5% AcOH) afforded pure fractions containing the product that were combined and washed with sat. NaHCO₃ to remove residual AcOH. The aqueous layer was extracted with EtOAc (2×100 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL) and dried with Na₂SO₄. Evaporation of solvent gave **2c** as a pale light yellow solid (9.37 g, 69% yield).

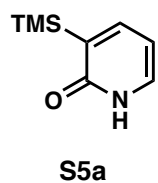
The spectroscopic data for this compound were identical to those reported in the literature (*Chem. Eur. J.* **2009**, *15*, 7167).

¹H NMR (CDCl₃, 500 MHz) δ: 10.21 (br s, 1 H), 7.43 (dd, *J* = 9.1, 7.1 Hz, 1 H), 6.46 (d, *J* = 9.1 Hz, 1 H), 6.19 (d, *J* = 7.0 Hz, 1 H), 1.34 (s, 9 H) ppm.

Synthesis of monomers 1a–c and norbornene diimide 4:



Scheme S3. Synthesis of monomers **1a**, **1b**, and **1c**.

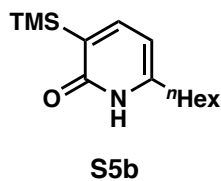


TMS pyridone S5a was prepared according to a known procedure (*J. Med. Chem.* **2007**, *50*, 6383). In a flame-dried 250 mL round-bottom flask equipped with a stir bar, *n*-butyl lithium (C = 2.5 M in hexanes, 46 mL, 0.12 mol, 2.2 equiv) was added dropwise to a solution of diisopropylamine (16 mL, 0.12 mol, 2.2 equiv) in THF (58 mL) at –78 °C over 10 min. The solution was stirred for 15 min at –78 °C. To a flame-dried 1000 mL round-bottom flask equipped with a stir bar, was added pyridone **2a** (5.0 g, 0.053 mol, 1.0 equiv) and the flask was placed under an atmosphere of nitrogen. THF (125 mL) was added and the solution was stirred at 0 °C until the dissolution of **2a** was complete. The lithium diisopropylamide (LDA) solution was transferred dropwise via cannula to the reaction solution

over 20 min with continued stirring of the reaction solution at 0 °C. Stirring was continued at 0 °C for 1 h. To the reaction solution was added TMSCl (7.3 mL, 0.058 mol, 1.1 equiv) dropwise at 0 °C over 5 min. Stirring was continued for 10 min at 0 °C, followed by 12 h at rt. The solvent was evaporated under reduced pressure. The residues were suspended in EtOAc (150 mL) and the suspension was cooled to 0 °C for 15 min, followed by filtration over a plug of silica gel (~3 cm, eluted with EtOAc). Evaporation of solvent under reduced pressure afforded a brown oil. The brown oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 20:80 hexanes:EtOAc) to yield **S5a** as an off-white solid (5.61 g, 64% yield).

The spectroscopic data for this compound were identical to those reported in the literature (*J. Med. Chem.* **2007**, *50*, 6383).

¹H NMR (CDCl₃, 500 MHz) δ: 12.06 (br s, 1 H), 7.55 (dd, *J* = 6.4, 2.2 Hz, 1 H), 7.34 (dd, *J* = 6.4, 2.2 Hz, 1 H), 6.24 (t, *J* = 6.5 Hz, 1 H), 0.27 (s, 9 H) ppm.



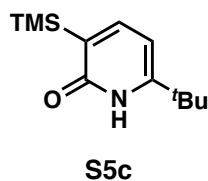
TMS *n*-hexyl pyridone S5b. In a flame-dried 100 mL round-bottom flask equipped with a stir bar, *n*-butyl lithium (*C* = 2.5 M in hexanes, 18.6 mL, 0.046 mol, 2.2 equiv) was added dropwise to a solution of diisopropylamine (6.4 mL, 0.046 mol, 2.2 equiv) in THF (30 mL) at -78 °C over 10 min. The solution was stirred for 15 min at -78 °C. To a flame-dried 250 mL round-bottom flask equipped with a stir bar was added **2b** (3.80 g, 0.021 mol, 1.0 equiv) and the flask was placed under an atmosphere of nitrogen. THF (55 mL) was added and solution was stirred at 0 °C until the dissolution of **2b** was complete. The LDA solution was transferred dropwise via cannula to the reaction solution over 15 min with continued stirring of the reaction solution at 0 °C. Stirring was continued at 0 °C for 1 h. To the reaction solution was added TMSCl (3.2 mL, 0.025 mol, 1.2 equiv) dropwise at 0 °C over 5 min. Stirring was continued for 10 min at 0 °C, followed by 12 h at rt. The solvent was evaporated under reduced pressure afforded a brown oil. The oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 80:20 hexanes:EtOAc) to yield **S5b** as a pale yellow oil (2.34 g, 44% yield).

R_f = 0.59 (4:1 hexanes:EtOAc)

¹H NMR (CDCl₃, 126 MHz) δ: 13.10 (br s, 1 H), 7.44 (d, *J* = 6.7 Hz, 1 H), 6.01 (d, *J* = 6.7 Hz, 1 H), 2.54 (t, *J* = 7.9 Hz, 2 H), 1.76–1.65 (m, 2 H), 1.41–1.23 (m, 6 H), 0.88 (t, *J* = 7.1 Hz, 3 H), 0.25 (s, 9 H) ppm.

¹³C NMR (CDCl₃, 500 MHz) δ: 168.7, 151.5, 147.7, 126.9, 105.3, 33.6, 31.7, 29.1, 29.0, 22.8, 14.2, –1.6 ppm.

HRMS (+): calc'd. for C₁₄H₂₅NOSi [M+H]⁺ 252.1778, found 252.1778.



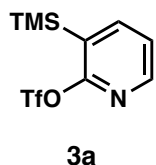
TMS *tert*-butyl pyridone S5c. In a flame-dried 500 mL round-bottom flask equipped with a stir bar, *n*-butyl lithium (C = 2.5 M in hexanes, 144 mL, 2.5 M, 0.36 mol, 2.4 equiv) was added dropwise to a solution of diisopropylamine (49 mL, 0.36 mol, 2.4 equiv) in THF (200 mL) at –78 °C over 10 min. The solution was stirred for 15 min at –78 °C. To flame-dried 2000 mL round-bottom flask equipped with a stir bar, was added **2c** (22.7 g, 0.15 mol, 1.0 equiv) and the flask was placed under an atmosphere of nitrogen. THF (400 mL) was added and the solution was stirred at 0 °C until the dissolution of **2b** was complete. The LDA solution was transferred dropwise via cannula to the reaction solution over 30 min with continued stirring of the reaction solution at 0 °C for 1 h. To the reaction solution was added TMSCl (23 mL, 0.18 mmol, 1.2 equiv) dropwise at 0 °C over 5 min. Stirring was continued at 0 °C for 10 min, followed by 12 h at rt. The solvent was evaporated under reduced pressure. Cold MeOH (250 mL) was added to the residues, which resulted in the precipitation of the desired product. The solid was filtered, washed with MeOH, and then dried under high vacuum to afford **S5c** as an off-white solid (27.2 g, 81% yield).

¹H NMR (CDCl₃, 500 MHz) δ: 12.65 (br s, 1 H), 7.46 (d, *J* = 6.9 Hz, 1 H), 6.09 (d, *J* = 6.9 Hz, 1 H), 1.38 (s, 9 H), 0.26 (s, 9 H) ppm.

¹³C NMR (CDCl₃, 126 MHz) δ: 168.4, 158.5, 147.6, 127.5, 101.7, 35.1, 29.0, –1.6 ppm.

HRMS (+ESI): calc'd. for C₁₂H₂₁NOSi [M+H]⁺ 224.1465, found 224.1463.

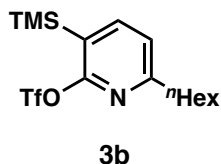
m.p.: sublimation around 127 °C



2,3-Pyridyne precursor 3a. In a flame-dried 100 mL round-bottom flask equipped with a stir bar, Tf₂O (6.1 mL, 36.1 mmol, 1.1 equiv) was added dropwise to a solution of **S5a** (5.44 g, 32.5 mmol, 1.0 equiv) in pyridine (32 mL) over 5 min at 0 °C. The solution was stirred at 0 °C for 15 min and then at rt for 12 h. The mixture was diluted with Et₂O (50 mL), and HCl (C = 6 M, 70 mL) was added slowly. The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 20 mL). The combined organic phases were washed with water (30 mL), brine (30 mL), then dried over MgSO₄. The solvent was removed under reduced pressure. The resulting yellow oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 95:5 hexanes:EtOAc) to yield **3a** as a clear, colorless oil (9.48 g, 97% yield).

The spectroscopic data for this compound were identical to those reported in the literature (*J. Med. Chem.* **2007**, *50*, 6383).

¹H NMR (CDCl₃, 500 MHz) δ: 8.32 (dd, *J* = 4.8, 2.0 Hz, 1 H), 7.92 (dd, *J* = 7.2, 2.1 Hz, 1 H), 7.30 (dd, *J* = 7.2, 4.8 Hz, 1 H), 0.37 (s, 9 H) ppm.



***n*-Hexyl 2,3-pyridyne precursor 3b.** In a flame-dried 100 mL round-bottom flask equipped with a stir bar, Tf₂O (1.7 mL, 10.1 mmol, 1.1 equiv) was added dropwise to a solution of **S5b** (2.32 g, 9.23 mmol, 1.0 equiv) in pyridine (13 mL) over 5 min at 0 °C. The solution was stirred at 0 °C for 15 min and then at rt for 12 h. The mixture was diluted with Et₂O (100 mL) and HCl (C = 3 M, 80 mL) was added slowly. The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 25 mL). The combined organic phases were washed with water (100 mL), brine (100 mL), then dried over MgSO₄. The solvent was removed under reduced pressure. The resulting yellow oil was further purified by column chromatography (SiO₂, eluted with hexanes) to yield **3b** as a clear, colorless oil (1.39 g, 39% yield).

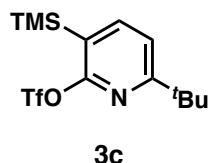
R_f = 0.35 (hexanes)

¹H NMR (CDCl₃, 500 MHz) δ: 7.78 (d, *J* = 7.3 Hz, 1 H), 7.12 (d, *J* = 7.3 Hz, 1 H), 2.74 (t, *J* = 7.6 Hz, 2 H), 1.75–1.68 (m, 2 H), 1.38–1.26 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.35 (s, 9 H) ppm.

¹³C NMR (CDCl₃, 126 MHz) δ: 163.6, 160.6, 146.9, 122.3, 121.3, 118.8 (q, *J* = 321 Hz), 37.3, 31.8, 28.9, 28.8, 22.7, 14.2, –1.3 ppm.

^{19}F NMR (CDCl_3 , 470 MHz) δ : -72.4 (s, 3 F) ppm.

HRMS (+): calc'd. for $\text{C}_{15}\text{H}_{24}\text{F}_3\text{NO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$ 384.1271, found 384.1267.



tert-Butyl 2,3-pyridyne precursor 3c. In a flame-dried 100 mL round-bottom flask equipped with a stir bar, Tf_2O (6.3 mL, 37.6 mmol, 1.1 equiv) was added dropwise to a solution of **S5c** (7.57 g, 33.9 mmol, 1.0 equiv) in pyridine (45 mL) over 5 min at 0°C . The solution was stirred for 15 min and then stirred at rt for 12 h. The reaction was diluted with Et_2O (100 mL) and HCl ($C = 6\text{ M}$, 100 mL) was added slowly. The layers were separated, and the aqueous layer was extracted with Et_2O ($3 \times 40\text{ mL}$). The combined organic phases were washed with water (150 mL), brine (150 mL), then dried over MgSO_4 . The solvent was removed under reduced pressure. Hexanes (100 mL) was added to the resulting yellow oil and the solution was filtered over a plug of silica gel ($\sim 3\text{ cm}$, eluted with hexanes). The solvent was removed under reduced pressure to yield **3c** as a clear, colorless oil (11.6 g, 96% yield).

$R_f = 0.32$ (DCM)

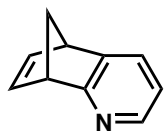
^1H NMR (CDCl_3 , 500 MHz) δ : 7.83 (d, $J = 7.5\text{ Hz}$, 1 H), 7.30 (d, $J = 7.5\text{ Hz}$, 1 H), 1.34 (s, 9 H), 0.36 (s, 9 H) ppm.

^{13}C NMR (CDCl_3 , 126 MHz) δ : 170.7, 160.2, 147.3, 121.3, 118.8 (q, $J = 321\text{ Hz}$), 118.5, 37.6, 29.8, -1.3 ppm.

^{19}F NMR (CDCl_3 , 470 MHz) δ : -72.5 (s, 3 F) ppm.

HRMS (+APCI): calc'd. for $\text{C}_{13}\text{H}_{20}\text{F}_3\text{NO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$ 356.0958, found 356.0949.

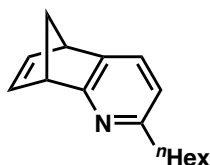
Cyclopentadiene was purified as follows: a 100 mL round-bottom flask equipped with a stir bar was attached to a Vigreux column. The column was connected to a short-path distillation head, which was connected to a 25 mL Schlenk tube. The apparatus was flame-dried and cooled to rt under an atmosphere of nitrogen. Once cooled, the round-bottom flask was charged with dicyclopentadiene (50 g) and the apparatus was purged with nitrogen. The round-bottom flask was heated to 220°C . After 2.5 h, $\sim 20\text{ mL}$ of cyclopentadiene was collected in the Schlenk tube, which was submerged in a -78°C bath (dry ice/acetone). The distillate was stored under an atmosphere of nitrogen at -20°C and was used within one week's time.

**1a**

Pyridinonorbornene 1a. CsF stored in a nitrogen-filled glovebox (254 mg, 1.67 mmol, 5.0 equiv) was added to a flame-dried 5 mL reaction vial equipped with a stir bar. Outside the glovebox, traces of water were removed from the CsF using a heat gun under high vacuum. The vial was allowed to cool to rt under nitrogen. To the reaction vial was added MeCN (5.6 mL) and cyclopentadiene (140 μ L, 1.67 mmol, 5.0 equiv). The flask was lowered into a pre-heated oil bath set at 30 $^{\circ}$ C. A solution of **3a** (100 mg, 0.33 mmol, 1.0 equiv) in MeCN (1.0 mL) was added dropwise to the flask *via* syringe pump over 2 h. Upon completion of the addition of the **3a** solution, the mixture was allowed to stir for an additional 1 h at 30 $^{\circ}$ C. The resulting suspension was filtered over a plug of silica gel (~3 cm, eluted with EtOAc) and concentrated under reduced pressure. The resulting dark brown oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 70:30 Hexanes:EtOAc) to yield **1a** as a light brown oil (22 mg, 45% yield).

The spectroscopic data for this compound was identical to that reported in the literature (*J. Org. Chem.* **1987**, 52, 5218).

¹H NMR (CDCl₃, 500 MHz) δ : 7.99 (dd, J = 5.3, 1.5 Hz, 1 H), 7.36 (ddd, J = 7.1, 1.3, 0.5 Hz, 1 H), 6.84 (m, 2 H), 6.78 (dd, J = 7.2, 5.4 Hz, 1 H), 3.88 (m, 2 H), 2.46 (dt, J = 7.6, 1.7 Hz, 1 H), 2.38 (dt, J = 7.5, 1.6 Hz, 1 H) ppm.

**1b**

Hexyl pyridinonorbornene 1b. CsF stored in a nitrogen-filled glovebox (198 mg, 1.30 mmol, 5.0 equiv) was added to a flame-dried 25 mL round-bottom flask equipped with a stir bar. Outside the glovebox, traces of water were removed from the CsF using a heat gun under high vacuum. The flask was

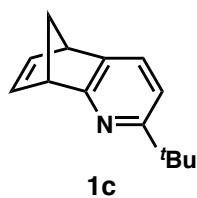
allowed to cool to rt under nitrogen. To the flask was added MeCN (4.2 mL) and cyclopentadiene (110 μ L, 1.30 mmol, 5.0 equiv). The flask was lowered into a pre-heated oil bath set at 30 $^{\circ}$ C. A solution of **3b** (100 mg, 0.26 mmol, 1.0 equiv) in DCM (1.0 mL) was added dropwise to the flask *via* syringe pump over 2 h. Upon completion of the addition of the solution of **3b**, the mixture was allowed to stir for an additional 1 h at 30 $^{\circ}$ C. The resulting suspension was filtered over a plug of silica gel (~3 cm, eluted with EtOAc) and concentrated under reduced pressure. The resulting dark brown oil was further purified by column chromatography (SiO₂, gradient from 100:0 to 90:10 hexanes:EtOAc) to yield **1b** as a light brown oil (15 mg, 25% yield).

R_f = 0.44 (9:1 hexanes:EtOAc)

¹H NMR (CD₂Cl₂, 500 MHz) δ: 7.27 (d, *J* = 7.3 Hz, 1 H), 6.86–6.80 (m, 2 H), 6.62 (d, *J* = 7.3 Hz, 1 H), 3.89–3.82 (m, 1 H), 3.80–3.74 (m, 1 H), 2.64 (t, *J* = 7.7 Hz, 2 H), 2.43 (dt, *J* = 7.4, 1.5 Hz, 1 H), 2.34–2.30 (m, 1 H), 1.69–1.61 (m, 2 H), 1.40–1.24 (m, 6 H), 0.88 (t, *J* = 7.0 Hz, 3 H) ppm.

¹³C NMR (CD₂Cl₂, 126 MHz) δ: 175.4, 156.9, 144.3, 142.8, 142.1, 128.3, 117.5, 69.7, 52.7, 49.0, 38.5, 32.4, 30.8, 29.7, 23.2, 14.4 ppm.

HRMS (+ESI): calc'd. for C₁₆H₂₁N [M+H]⁺ 228.1747, found 228.1747.



tert-Butyl pyridinonorbornene 1c. CsF stored in a nitrogen-filled glovebox (214 mg, 1.40 mmol, 5.0 equiv) was added to a flame-dried 25 mL round-bottom flask equipped with a stir bar. Outside the glovebox, traces of water were removed from the CsF using a heat gun under high vacuum. The flask was

allowed to cool to rt under nitrogen. To the flask was added MeCN (4.6 mL) and cyclopentadiene (120 μL, 1.40 mmol, 5.0 equiv). The flask was lowered into a pre-heated oil bath set at 30 °C. A solution of **3c** (100 mg, 0.28 mmol, 1.0 equiv) in MeCN (1.0 mL) was added dropwise to the flask *via* syringe pump over 2 h. Upon completion of the addition of the solution of **3c**, the mixture was allowed to stir for an additional 1 h at 30 °C. The resulting suspension was filtered over a plug of silica gel (~3 cm, eluted with EtOAc) and concentrated under reduced pressure. The resulting dark brown oil was further purified by column chromatography (SiO₂, gradient from 90:10 to 70:30 hexanes:DCM) to yield **1c** as a light brown oil (31 mg, 55% yield).

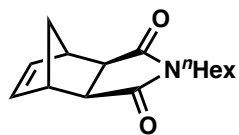
Note: It is important to only increase the solvent gradient for the column chromatography by no more than 2% of DCM at a time otherwise the product will not elute purely.

R_f = 0.39 (DCM)

¹H NMR (CD₂Cl₂, 500 MHz) δ: 7.29 (d, *J* = 7.6 Hz, 1 H), 6.89–6.79 (m, 3 H), 3.88–3.84 (m, 1 H), 3.81–3.76 (m, 1 H), 2.44 (dt, *J* = 7.4, 1.6 Hz, 1 H), 2.34–2.31 (m, 1 H), 1.31 (s, 9 H) ppm.

¹³C NMR (CD₂Cl₂, 126 MHz) δ: 174.7, 164.0, 144.2, 142.9, 141.6, 128.1, 113.8, 69.7, 52.8, 48.9, 37.5, 30.8 ppm.

HRMS (+ESI): calc'd. for C₁₄H₁₇N [M+H]⁺ 200.1434, found 200.1428.



4

N-Hexyl *exo*-norbornene diimide **4**. Prepared according to literature procedures (*Macromolecules* **2013**, *46*, 5905; *Macromolecules* **2019**, *52*, 3426). *exo*-Norbornene anhydride prepared from *endo*-norbornene anhydride according to literature procedure (*J. Am. Chem. Soc.* **2008**, *130*, 6731) and

recrystallized 6 times (1.0 g, 6.1 mmol, 1.0 equiv) was added to a flame-dried 100 mL round-bottom flask followed by and hexylamine (2.0 mL, 15.2 mmol, 2.5 equiv). To the flask was added toluene (20 mL), and the flask was fitted with a Dean-Stark trap and a condenser. The flask was stirred at 120 °C under reflux for 14 h. The mixture was cooled to rt and washed with HCl (C= 0.1 M, 30 mL). The organic layer was washed with water (30 mL), brine (30 mL), and dried over MgSO₄. The solvent was then removed under reduced pressure. DCM (30 mL) was added to the resulting yellow oil was filtered over a plug of silica gel (~3 cm, eluted with DCM). Removal of the solvent under reduced pressure afforded **4** as a clear, colorless oil (1.42 g, 94% yield).

The spectroscopic data for this compound was identical to that reported in the literature (*Macromolecules* **2013**, *46*, 5905; *Macromolecules* **2019**, *52*, 3426).

¹H NMR (CDCl₃, 500 MHz) δ: 6.28 (s, 2 H), 3.45 (t, *J* = 7.6 Hz, 2 H), 3.27 (s, 2 H), 2.66 (s, 2 H), 1.59–1.47 (m, 3 H), 1.33–1.21 (m, 7 H), 0.86 (t, *J* = 6.7 Hz, 3 H).

ROMP Procedures

ROMP of 1a (50 equiv) catalyzed by Ru-1:

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1a** (14 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was sealed, and the mixture was stirred at rt for 22 h. The polymerization was then quenched with ethyl vinyl ether (EVE, 20 μL) and stirred for an additional 30 min. An aliquot (~20 μL) was taken to determine monomer conversion via ¹H NMR spectroscopy.

ROMP of 1b (50 equiv) catalyzed by Ru-1:

Polymerization at rt:

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1b** (23 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was sealed, and the mixture was stirred at rt for 22 h. The polymerization was quenched

with EVE (20 μ L) and stirred at rt for an additional 30 min. An aliquot (\sim 20 μ L) was taken to determine monomer conversion via ^1H NMR spectroscopy. No to very little conversion was observed by NMR.

Polymerization at 60 $^\circ\text{C}$:

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1b** (23 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was hermetically sealed and taken out of the glovebox. The mixture was stirred at rt for 5 min and placed into a preheated oil bath at 60 $^\circ\text{C}$ for 8 h. Once cooled to rt, the polymerization was quenched with EVE (20 μ L) and stirred at rt for an additional 30 min. An aliquot (\sim 20 μ L) was taken to determine monomer conversion via ^1H NMR spectroscopy. The remaining solution was diluted to \sim 1.5 mg/mL with THF, filtered (0.45 μm), and injected into the SEC instrument directly. The remaining polymer was precipitated into methanol, and the solid was isolated by centrifugation and decantation. The resulting polymer was dried under high vacuum.

ROMP of 1c (50 equiv) catalyzed by Ru-1:

Polymerization at rt:

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was sealed, and the mixture was stirred at rt for 5 h. The polymerization was then quenched with EVE (20 μ L) and stirred for an additional 30 min. An aliquot (\sim 20 μ L) was taken to determine monomer conversion via ^1H NMR spectroscopy. The remaining solution was diluted to \sim 1.5 mg/mL with THF, filtered (0.45 μm), and injected into the SEC instrument directly. The remaining polymer was precipitated into methanol, and the solid was isolated by centrifugation and decantation. The resulting polymer was dried under high vacuum.

Polymerization at 40 or 60 $^\circ\text{C}$:

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was hermetically sealed and taken out of the glovebox. The mixture was stirred at rt for 5 min and placed into a preheated oil bath at 60 $^\circ\text{C}$ for 1 h or 40 $^\circ\text{C}$ for 2 h. Once cooled to rt, the polymerization was then quenched with EVE (50 μ L) and stirred for an additional 30 min. An aliquot (\sim 20 μ L) was taken to determine monomer conversion via ^1H NMR spectroscopy. The

remaining solution was diluted to ~1.5 mg/mL with THF, filtered (0.45 μm), and injected into the SEC instrument directly. The remaining polymer was precipitated into methanol, and the solid was isolated by centrifugation and decantation. The resulting polymer was dried under high vacuum.

The standard procedures described above were slightly modified to investigate the effect of the catalyst, the solvent, and temperature on the ROMP of **1c**. The results are summarized below:

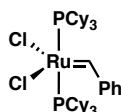


Figure S1. Structure of Grubbs 1st generation catalyst **Ru-S**.

Table S1. ROMP attempts of **1c** with catalysts **Ru-1**, **Ru-2**, and **Ru-S**

Entry	Catalyst	Time (h)	Conv. (%)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	\bar{D}
1	Ru-1	4	89	9.0	8.8	1.13
2	Ru-2	4	85	8.6	8.3	1.30
3	Ru-S	4	trace	—	—	—

M_n 's and \bar{D} 's were determined by SEC (THF) using polystyrene standards (RI detection)

Table S2. Solvent screen for ROMP of **1c** catalyzed by **Ru-1**

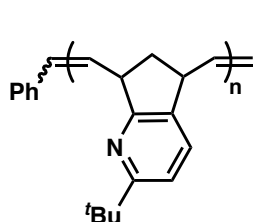
Entry	Solvent	Time (h)	Conv. (%)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	\bar{D}
1	DCE	4	89	9.0	8.8	1.13
2	DCM	4	81	8.2	9.0	1.22
3	THF	4	91	9.2	9.1	1.37
4	PhMe	4	88	8.9	8.3	1.14
5	Chlorobenzene	4	88	8.9	8.6	1.13
6	MeCN	4	47	4.8	3.1	1.22

M_n 's and \bar{D} 's were determined by SEC (THF) using polystyrene standards (RI detection)

Table S3. Temperature screen for ROMP of **1c** catalyzed by **Ru-1**

Entry	Temperature		Conv. (%)	M_n^{theo}	M_n^{exp}	\bar{D}
	(°C)	Time (h)		(kg/mol)	(kg/mol)	
1	23 (rt)	5	>99	10.1	9.7	1.07
2	40	2	>99	10.1	9.4	1.22
3	60	1	>99	10.1	9.6	1.22

Spectroscopic data for poly-**1c**:



^1H NMR (CDCl_3 , 500 MHz) δ : 8.22–7.95 and 7.69–7.29 (br m, 1 H), 7.22–6.97 (br s, 1 H), 6.29–5.20 (br m, 2 H), 4.61–3.50 (br m, 2 H), 2.96–2.42 (br s, 1 H), 1.91–1.57 (br s, 1 H), 1.45–1.16 (br m, 9 H) ppm.

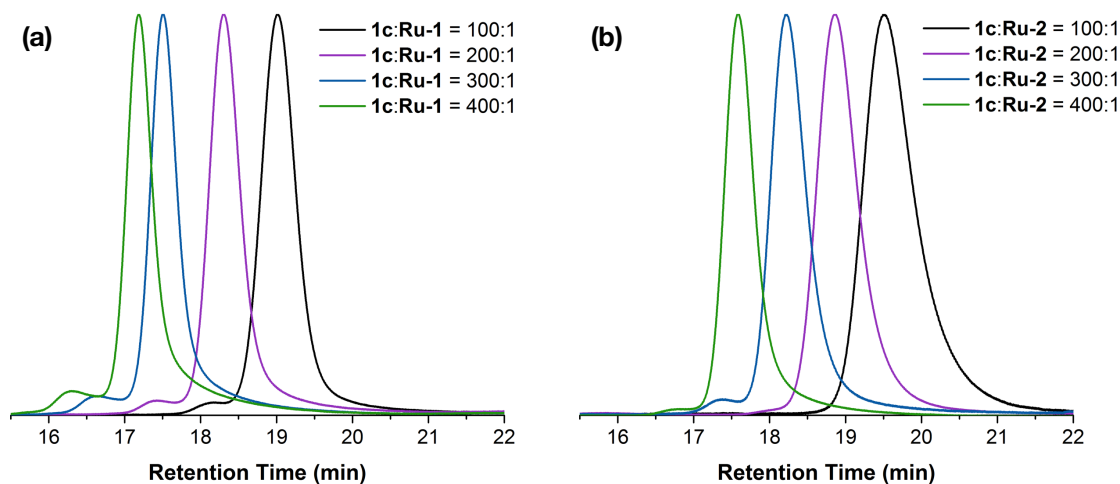
^{13}C NMR (CDCl_3 , 126 MHz) δ : 168.5, 165.1, 135.8, 133.3, 131.6, 116.8, 44.2, 41.2, 40.3, 37.6, 30.7 ppm.

ROMP of 1c targeting different DPs using Ru-1 and Ru-2:

In a nitrogen-filled glove box, a solution of **Ru-1** or **Ru-2** (see Table S4 for concentration) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (0.10 mmol) and a stir bar. The vial was sealed, and the mixture was stirred at rt for a specified amount of time (see Table S4). The polymerization was then quenched with EVE (10 equiv with respect to **Ru**) and stirred for an additional 30 min. An aliquot (~20 μL) was taken to determine monomer conversion via ^1H NMR spectroscopy. The remaining solution was diluted to ~1.5 mg/mL with THF, filtered (0.45 μm), and injected into the SEC instrument directly. The remaining polymer was precipitated into methanol, and the solid was isolated by centrifugation and decantation. The resulting polymer was dried under high vacuum.

Table S4. ROMP of **1c** catalyzed by **Ru-1** and **Ru-2**

Entry	Catalyst	1c:Ru	[Ru] (mM)	Time (h)	Conv. (%)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	\bar{D}
1	Ru-1	100:1	5.0	10	>99	20.0	22.0	1.07
2	Ru-2	100:1	5.0	11	85	17.0	16.7	1.17
3	Ru-1	200:1	2.5	20	88	35.3	50.1	1.07
4	Ru-2	200:1	2.5	25	90	36.0	29.7	1.12
5	Ru-1	300:1	1.7	31	81	48.5	89.3	1.08
6	Ru-2	300:1	1.7	37	93	55.7	49.8	1.11
7	Ru-1	400:1	1.3	41	82	65.4	109.7	1.11
8	Ru-2	400:1	1.3	42	87	69.4	77.6	1.12

**Figure S2.** (a) SEC traces of poly-**1c** catalyzed by **Ru-1** (THF eluent, RI detection). (b) SEC traces of poly-**1c** catalyzed by **Ru-2** (THF eluent, RI detection).

¹H NMR Investigation of the Chain Termination of Poly-1c with EVE

In a nitrogen-filled glove box, a solution of **Ru-1** (1.8 mg, 0.002 mmol, 1 equiv) in DCM (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 50 equiv) and a stir bar. The vial was sealed, and the mixture was stirred at rt for 20 min. The polymerization was then quenched either by addition of EVE (20 μL) to the well-stirred mixture or with, first, a solution of DMAP (2.5 mg, 0.02 mmol, 10 equiv), followed by EVE (20 μL), 5 min after the addition of DMAP. Mesitylene (10 μL, 0.7 equiv) was added to both quenched reaction mixture as an internal standard. Aliquots (~20 μL) were taken for ¹H NMR analysis immediately after quenching, after 1 h, and after 5 h (Figures S3 and S4). The results summarized in Table S5 clearly indicate that the monomer kept reacting after quenching with EVE, however quenching with DMAP and EVE successfully halted polymerization within minutes.

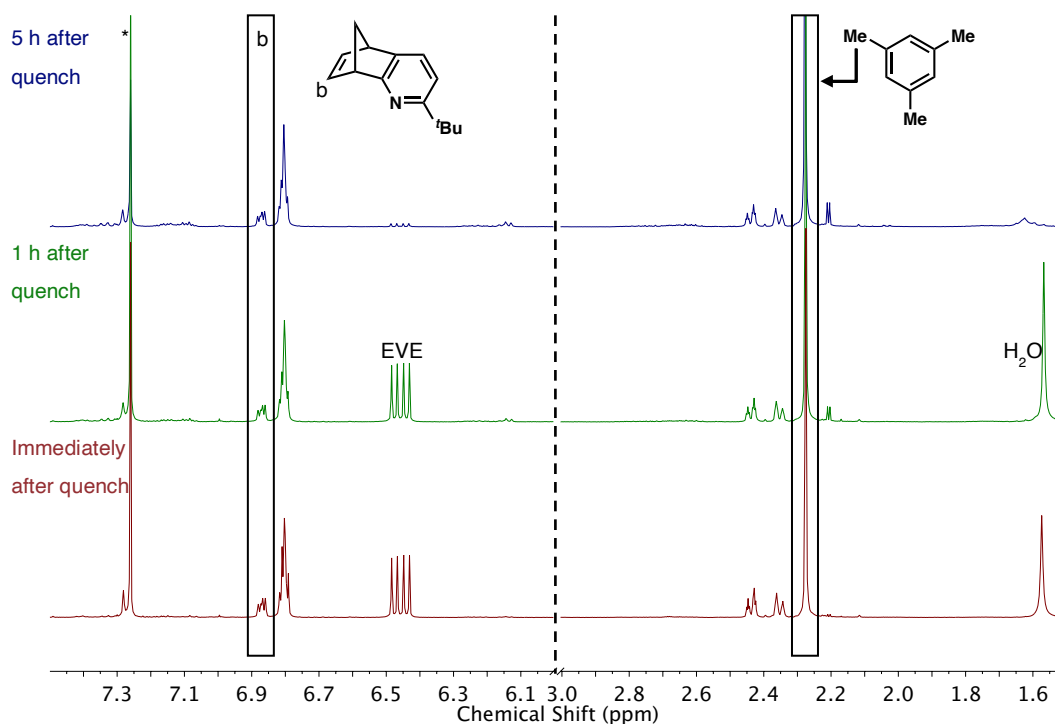


Figure S3. Monitoring the concentration of **1c** over time after quenching with only EVE using ¹H NMR (500 MHz, CDCl₃) [showing regions 7.5–6.0 and 3.0–1.5 ppm for sake of clarity].

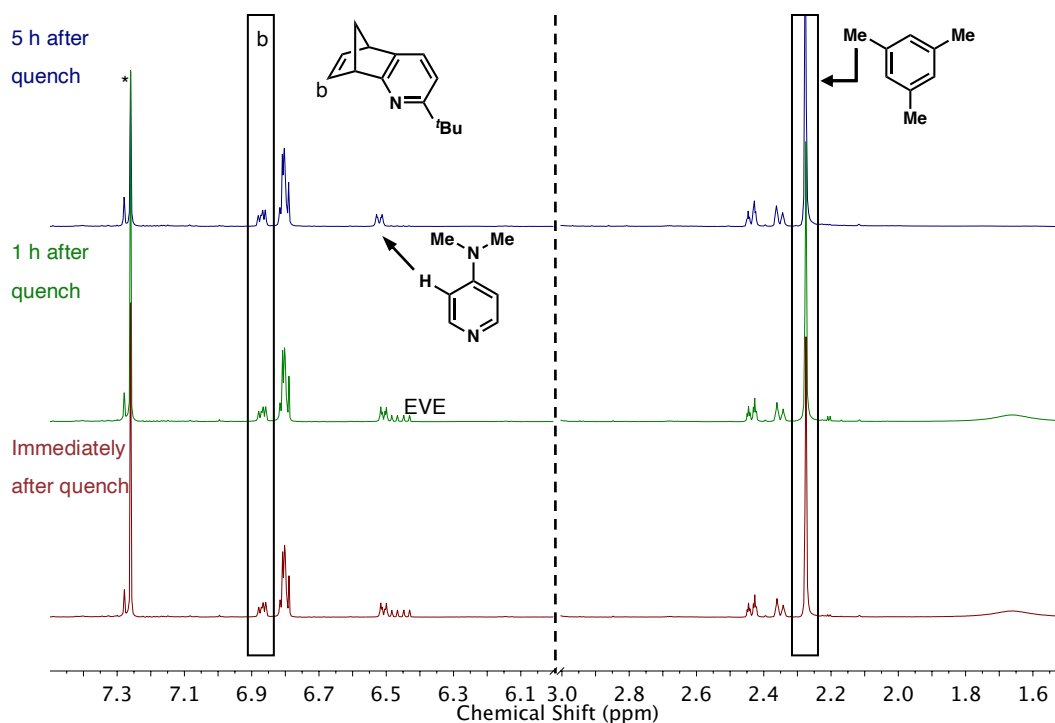


Figure S4. Monitoring the concentration of **1c** over time after quenching with DMAP then EVE using ^1H NMR (500 MHz, CDCl_3) [showing regions 7.5–6.0 and 3.0–1.5 ppm for sake of clarity].

Table S5. Monitoring **1c** concentration over time after different quenching techniques

Time after Quenching	1c :Mesitylene Ratio	1c :Mesitylene Ratio
	(Quench with EVE only)	(Quench with DMAP + EVE)
—	0.17	0.18
1 h	0.14	0.18
5 h	0.12	0.18

Kinetics Study of the ROMP of **1c** Catalyzed by **Ru-1**

Investigation of the rate of propagation (Figure 4a):

A solution of **1c** (0.25 mmol) and **Ru-1** (10 mM) in CD_2Cl_2 (0.5 mL) was prepared in a nitrogen-filled glovebox and transferred to a J. Young tube kept at rt without stirring. The sample was then inserted into a Bruker Avance 500 MHz instrument set at 32 °C and remained within the instrument until data collection was complete. Conversion of **1c** was monitored by ^1H NMR using the integration ratio of the olefinic proton in **1c** at 6.86 ppm in CD_2Cl_2 to the proton in poly-**1c** at 7.20

ppm. Plotting $\ln([M_0]/[M_t])$ as a function of time revealed a linear fit and a k_p^{app} value of 0.00959 min^{-1} based on the following equations

$$\frac{-d[M]}{dt} = k_p^{app} [M_t] \quad (1)$$

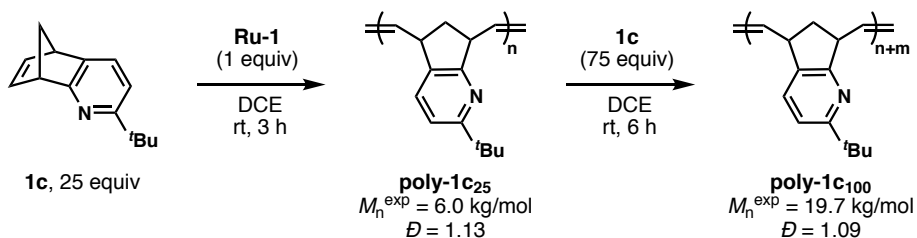
$$k_p^{app} = k_p [C_t] \quad (2)$$

where $[M_t]$ is the concentration of the monomer **1c** at time t , k_p^{app} the apparent propagation rate constant, k_p the propagation rate constant, and $[C_t]$ the concentration of **Ru-1** at time t .

Molar mass and \bar{D} vs monomer conversion comparison (Figure 4b):

In a nitrogen-filled glove box, a solution of **Ru-1** (8.9 mg, 0.01 mmol, 1 equiv) in DCM (1.0 mL) was added to a 1-dram vial containing monomer **1c** (100 mg, 0.50 mmol, 50 equiv) and a stir bar. The mixture was stirred at rt and 80 μL aliquots were sampled from the reaction solution over time. Each aliquot was transferred to a separate 1-dram vial. To each aliquot was added 10 μL of a DMAP solution (0.9 M) in DCM, and was allowed to stir at rt for 5 min. Then, to quench the polymerization, EVE (10 μL) was added to the aliquot, and the solution was stirred for an additional 30 min at rt. The M_n and \bar{D} were determined by SEC analysis (THF eluent, RI detection) for each aliquot, and the monomer conversion was monitored by ^1H NMR.

Chain-extension of Poly-1c with Additional 1c



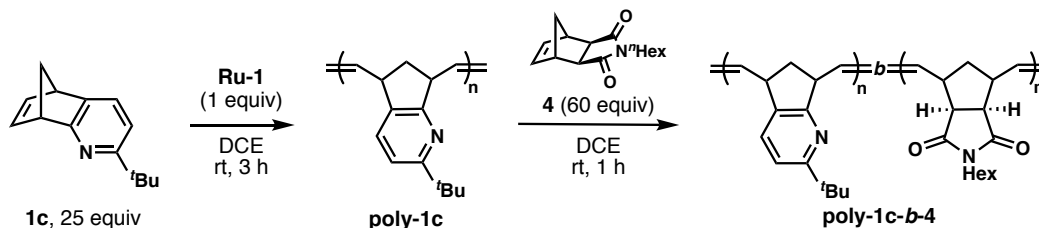
Scheme S4. Synthesis of poly-**1c**₁₀₀ via chain-extension of poly-**1c**₂₅.

In a nitrogen-filled glove box, a solution of **Ru-1** (3.5 mg, 0.004 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 25 equiv) and a stir bar. The mixture was stirred at rt for 3 h until full monomer conversion. Half of the mixture (0.1 mL) was transferred to another 1-dram vial charged with a solution of monomer **1c** (30 mg, 0.15 mmol, 75 equiv) in DCE (0.3 mL) and a stir bar and was stirred at rt for 6 h. The remainder of the original mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min at rt. Then the second mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min

at rt. The M_n and D were determined by SEC analysis (THF eluent, RI detection) for each aliquot, and the monomer conversion was determined via ^1H NMR spectroscopy.

Synthesis of Block Copolymer Poly-1c-b-4

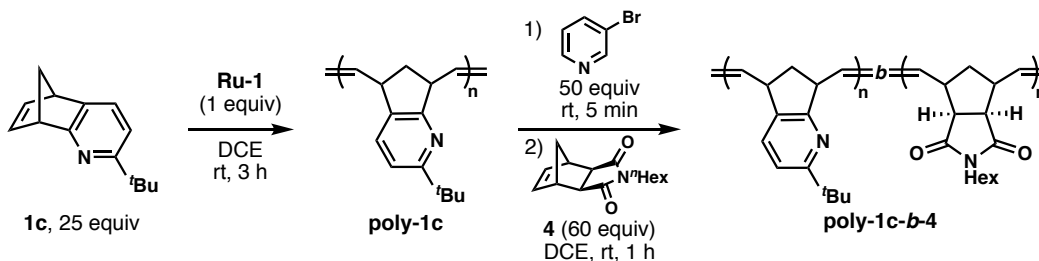
Without 3-bromopyridine additive (Figure 5b, top):



Scheme S5. Synthesis of poly-1c-b-4 without 3-bromopyridine additive.

In a nitrogen-filled glove box, a solution of **Ru-1** (3.5 mg, 0.004 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 25 equiv) and a stir bar. The mixture was stirred at rt for 3 h until full monomer conversion. Half of the mixture (0.1 mL) was transferred to another 1-dram vial charged with a solution of monomer **4** (30 mg, 0.12 mmol, 60 equiv) in DCE (0.24 mL) and a stir bar and was stirred at rt for 1 h. The remainder of the original mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min at rt. Then the second mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min at rt. The M_n and D were determined by SEC analysis (THF eluent, RI detection) for each aliquot, and the monomer conversion was determined via ^1H NMR spectroscopy (Table S6, entry 1).

With 3-bromopyridine additive:



Scheme S6. Synthesis of poly-1c-b-4 with 3-bromopyridine additive.

In a nitrogen-filled glove box, a solution of **Ru-1** (3.5 mg, 0.004 mmol, 1 equiv) in DCE (0.2 mL) was added to a 1-dram vial containing monomer **1c** (20 mg, 0.10 mmol, 25 equiv) and a stir bar. The mixture was stirred at rt for 3 h until full monomer conversion. To the vial was added 3-

bromopyridine (20 μL , 0.20 mmol, 50 equiv) and was allowed to stir for 5 min at rt. Half of the mixture (0.1 mL) was transferred to another 1-dram vial charged with a solution of monomer **4** (30 mg, 0.12 mmol, 60 equiv) in DCE (0.24 mL) and a stir bar and was stirred at rt for 1 h. The remainder of the original mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min at rt. Then the second mixture was quenched with EVE (50 μL) and allowed to stir for an additional 30 min at rt. The molecular weight (M_n) and dispersity values (\mathcal{D}) were determined by SEC analysis (THF eluent, RI detection) for each aliquot, and the monomer conversion was determined via ^1H NMR spectroscopy (Table S6, entry 2). A DOSY NMR experiment confirmed the chain extension of the initial block (Figure S44).

Table S6. Synthesis of poly-**1c-b-4** via chain extension of poly-**1c** catalyzed by **Ru-1**

Entry	3-bromo	n, m	1 st Block	1 st Block	\mathcal{D}	2 nd Block	2 nd Block	\mathcal{D}
	pyridine (equiv)		M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)		M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	
1	—	25, 60	5.0	5.6	1.12	20.0	23.3	3.25
2	50	25, 60	5.0	6.1	1.10	20.0	24.5	1.15

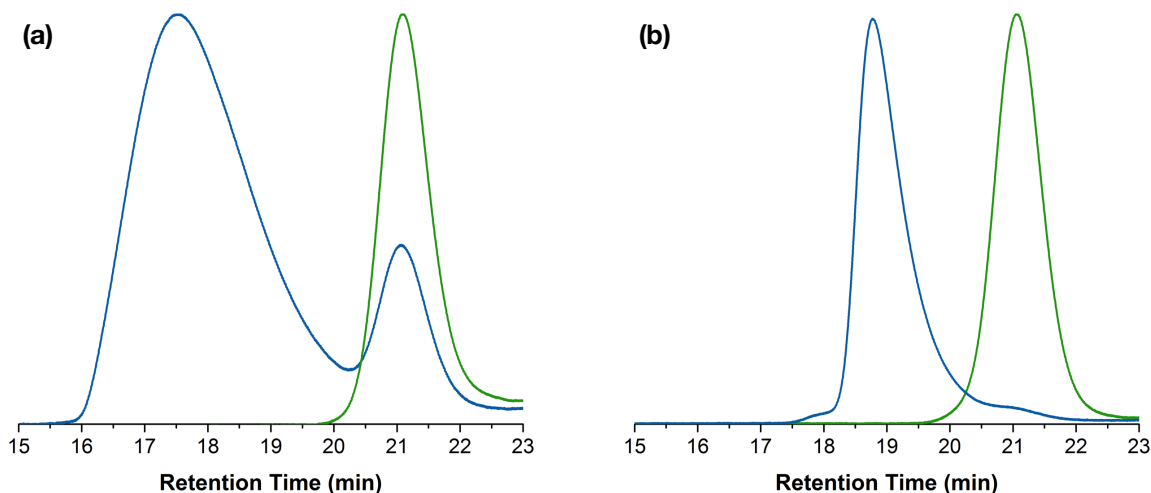


Figure S5. (a) SEC traces of poly-**1c** (green) and poly-**1c-b-4** (blue) from Table S6, entry 1. (b) SEC traces of poly-**1c** (green) and poly-**1c-b-4** (blue) from Table S6, entry 2. [Traces are duplicates from Figure 5b].

Investigation of the rate of propagation of monomer 4 in the chain extension of poly-1c:

Preparation of poly-1c-b-4:

In a nitrogen-filled glove box, a solution of **Ru-1** (7.1 mg, 0.008 mmol, 1 equiv) in DCE (0.4 mL) was added to a 1-dram vial containing monomer **1c** (40 mg, 0.20 mmol, 25 equiv) and a stir bar. The mixture was stirred at rt for 3 h until full monomer conversion. To the vial was added 3-bromopyridine (48 μ L, 0.40 mmol, 50 equiv) and the solution was allowed to stir for 5 min at rt. Half of the mixture (0.2 mL) was transferred to another 1-dram vial charged with a solution of monomer **4** (60 mg, 0.24 mmol, 60 equiv) in DCE (0.48 mL) and a stir bar and was stirred at rt. \sim 50 μ L aliquots were sampled from the reaction solution over time. Each aliquot was transferred to a separate 1-dram vial and was subsequently quenched with EVE (10 μ L). For each aliquot, the conversion of **4** was monitored by ^1H NMR spectroscopy (Table S7).

Preparation of homopolymer poly-4:

In a nitrogen-filled glove box, a solution of **Ru-1** (3.0 mg, 0.003 mmol, 1 equiv) in DCE (0.57 mL) was added to a 1-dram vial containing monomer **4** (50 mg, 0.20 mmol, 60 equiv) and a stir bar. The mixture was stirred at rt and \sim 50 μ L aliquots were sampled from the reaction solution over time. Each aliquot was transferred to a separate 1-dram vial and was subsequently quenched with EVE (10 μ L). For each aliquot, the conversion of **4** was monitored by ^1H NMR spectroscopy (Table S7).

Table S7. Monitoring conversion of **4** over time in the preparation of poly-1c-b-4 and poly-4

Time after Addition of 4	Conversion of 4 (poly-1c-b-4)	Conversion of 4 (poly-4)
2 min	22%	>99%
5 min	41%	—
10 min	53%	—
20 min	75%	—
60 min	>99%	—

Random Copolymerization of Monomers **1c** and **4**

In a nitrogen-filled glove box, a solution of monomer **4** (20 mg, 0.08 mmol, 20 equiv) in DCM (0.5 mL) was added to a 1-dram vial containing monomer **1c** (60 mg, 0.30 mmol, 75 equiv), 1,2,4,5-tetramethylbenzene (7.0 mg, 0.05 mmol, 13 equiv, internal standard), and a stir bar. To the monomer mixture was added a solution of **Ru-1** (3.6 mg, 0.004 mmol, 1 equiv) in DCE (0.26 mL). The mixture was stirred at rt and ~50 μ L aliquots were sampled from the reaction solution over time. Each aliquot was transferred to a separate 1-dram vial. To each aliquot was added 10 μ L of a DMAP solution (0.25 M) in DCM, and the mixture was stirred at rt for 5 min. EVE (10 μ L) was then added to the aliquot, and the solution was stirred for an additional 30 min at rt. For each aliquot, the conversion of **1c** and **4** was monitored by ^1H NMR spectroscopy, and the M_n and \mathcal{D} were determined by SEC analysis (THF eluent, RI detection) (Table S8, Figure S6).

Table S8. Random copolymerization of **1c** and **4** catalyzed by **Ru-1**

Time (min)	1c Conv. (%)	4 Conv. (%)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	\mathcal{D}
2	14	4	2.4	— ^a	— ^a
5	16	6	2.6	— ^a	— ^a
10	24	9	4.0	— ^a	— ^a
20	32	15	5.4	4.0	1.15
60	42	28	7.6	8.1	1.10
300	87	80	17.0	19.2	1.08
600	98	96	19.5	21.5	1.10

^a M_n and \mathcal{D} could not be determined because of overlap with peaks corresponding to species with low molar masses.

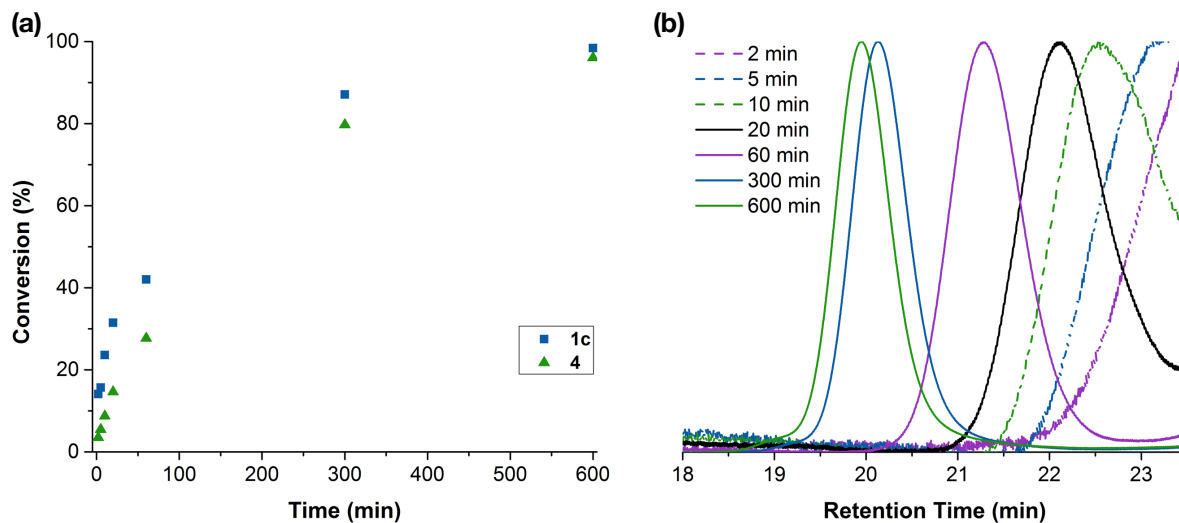


Figure S6. (a) Monomer conversion vs time for the random copolymerization of **1c** (blue squares) and **4** (green triangles) (Table S8). (b) SEC traces of poly-**1c-r-4** (Table S8).

Thermal Properties of Poly-1c

TGA curve of purified poly-**1c** samples were obtained in a nitrogen atmosphere at a heating rate of 10 °C/min.

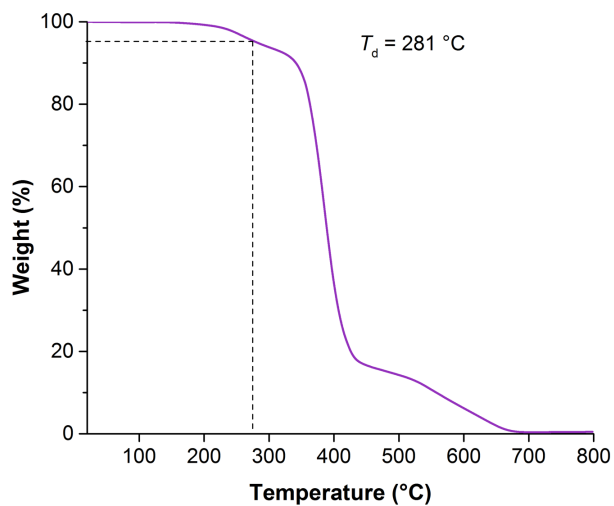


Figure S7. TGA of poly-**1c** ($M_n^{\text{SEC}} = 19.4\text{ kg/mol}$, $D = 1.12$).

DSC analysis of purified poly-**1c** was performed under nitrogen flow (20 °C to 225 °C, heating rate = 10 °C/min, cooling rate = 10 °C/min). Only the second heating cycle is displayed. A glass transition temperature (T_g) was found at 157 °C.

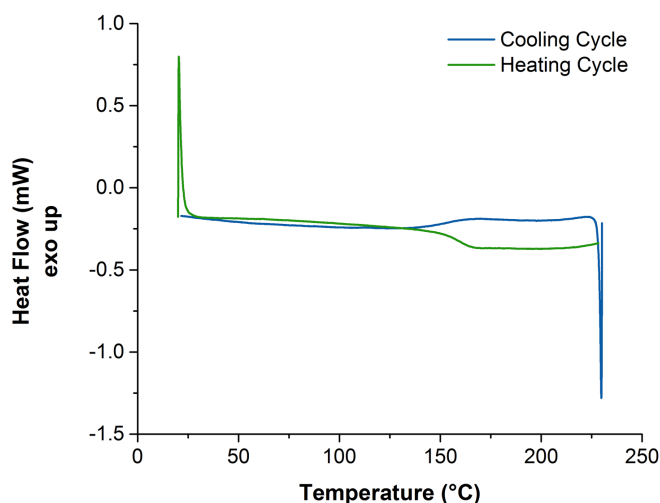


Figure S8. DSC of poly-1c ($M_n^{\text{exp}} = 19.4$ kg/mol, $D = 1.12$).

Estimation of the Ring Strain of 1a–c Using an Isodesmic Reaction

Computational methods. All the calculations were carried out using Psi 4 (*J. Chem. Theory Comput.*, 2017, **13**, 3185) with the standard grid size (75,302). All of the geometry optimizations and frequency analysis were performed at the B3LYP-D/6-311++G(d,p) level of theory in the gas phase. The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). Electronic and thermal energies were calculated for all structures. Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). Strain energies were calculated using isodesmic reactions based on total energies (with zero-point energy and thermal corrections) for optimized structures. Gibbs free energies were determined using vibrational frequency calculations.

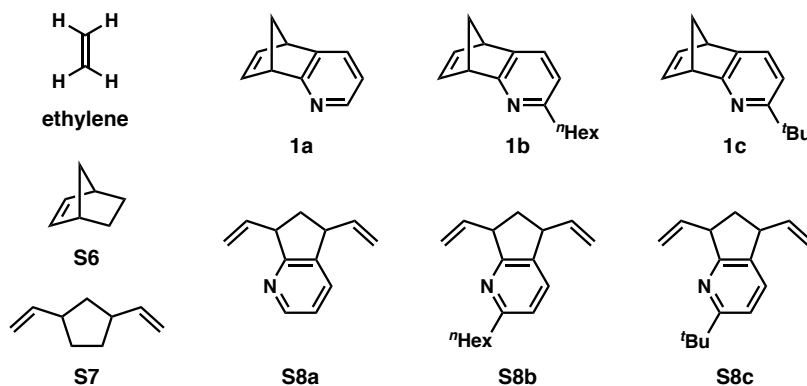
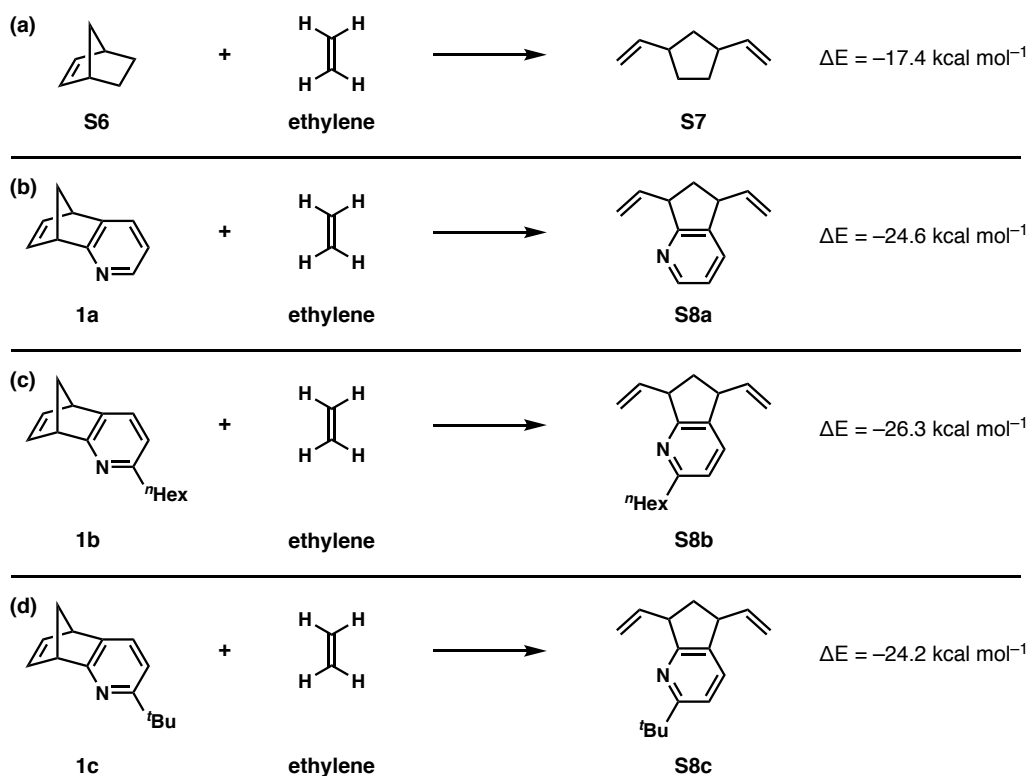


Figure S9. Structures calculated in this study.

Table S9. Energies calculated for optimized structures using B3LYP-D/6-311++G(d,p).

Compound	Total Energy (au)	Total Energy [ZPE Correction] (au)	Total Energy [ZPE and Thermal Corrections] (au)	Gibbs Free Energy (au)	Total Energy (kcal mol ⁻¹)	Total Energy [ZPE and Thermal Corrections] (kcal mol ⁻¹)	Gibbs Free Energy (kcal mol ⁻¹)
ethylene	-78.617194	-78.566622	-78.563576	-78.587495	-49330.366	-49296.722	-49311.731
S6	-272.818558	-272.667075	-272.661810	-272.695618	-171186.970	-171088.615	-171109.828
S7	-351.467569	-351.262770	-351.253129	-351.298444	-220537.301	-220402.744	-220431.179
1a	-441.314347	-441.151083	-441.143857	-441.182895	-276913.956	-276806.977	-276831.473
S8a	-519.975051	-519.758302	-519.746670	-519.797264	-326271.623	-326128.319	-326160.066
1b	-677.290916	-676.959634	-676.944703	-677.002474	-424983.479	-424766.239	-424802.489
S8b	-755.953261	-755.568543	-755.550116	-755.616217	-474342.176	-474089.212	-474130.689
1c	-598.638458	-598.363977	-598.351217	-598.402324	-375630.986	-375450.749	-375482.818
S8c	-677.298336	-677.970681	-677.953421	-677.016239	-424988.135	-424771.710	-424811.126

**Figure S10.** Ring strain energies determined from ring-opening metathesis reactions between: (a) norbornene (**S6**) and ethylene, (b) **1a** and ethylene, (c) **1b** and ethylene, and (d) **1c** and ethylene.

Ethylene

Energy: -78.617194 au

Energy including zero-point energy and thermal corrections: -78.563576 au

Geometry:

C	-0.664338000000	-0.000000000000	0.000000000000
C	0.664338000000	0.000000000000	0.000000000000
H	1.234677000000	-0.922817000000	0.000000000000
H	1.234677000000	0.922817000000	0.000000000000
H	-1.234677000000	-0.922817000000	0.000000000000
H	-1.234677000000	0.922817000000	0.000000000000

S6

Energy: -272.818558 au

Energy including zero-point energy and thermal corrections: -272.661810 au

Geometry:

C	0.128516600618	0.304512475548	1.129130992529
C	1.125255427484	-0.750894159300	0.669456101732
C	1.125255427484	-0.750894159300	-0.669456101732
C	0.128516600618	0.304512475548	-1.129130992529
C	-1.295202620143	-0.256819641283	-0.781330566686
C	-1.295202620143	-0.256819641283	0.781330566686
H	-1.453475758229	-1.251007207194	1.204109769868
H	-2.068476408177	0.409232738439	1.174434920185
H	-2.068476408177	0.409232738439	-1.174434920185
H	-1.453475758229	-1.251007207194	-1.204109769868
C	0.294096099090	1.350253236197	0.000000000000
H	-0.491551605984	2.113423033635	0.000000000000
H	1.279507931623	1.822112236173	0.000000000000

S7

Energy: -351.467569 au

Energy including zero-point energy and thermal corrections: -351.253129 au

Geometry:

C	-1.396302132408	0.958207900918	0.170764518991
C	-0.073469282882	1.693499899224	0.522855170557
C	0.984778469943	0.573716617423	0.731063839814
C	0.461863677778	-0.570286889174	-0.144530913785
C	-1.054157028274	-0.559273808226	0.130270523874
C	-1.859950006209	-1.324867505129	-0.871447342998
C	-2.657279916781	-2.354205198001	-0.593347632312
H	-3.216940076498	-2.868342088114	-1.367604618800
H	-2.772557314914	-2.713048758254	0.426122186829
H	-1.764909821865	-0.983535335069	-1.902585588489
H	-1.223966018455	-0.989028504969	1.124368105331
H	0.923820339506	-1.535528524144	0.077036426537

1a

Energy: -441.314347 au

Energy including zero-point energy and thermal corrections: -441.143857 au

Geometry:

C	1.205539125832	0.417353856702	1.106378140495
C	2.131242553010	-0.650726950357	0.493716174202
C	2.082498107837	-0.518325815406	-0.834587643020
C	1.119450721260	0.644223497746	-1.153168147092
C	-0.269139788068	0.172796310317	-0.719452753307
C	-0.214250528597	0.029135683496	0.683082763001
N	-1.206501272490	-0.375782904929	1.450548654332
C	-2.357276187961	-0.668004466051	0.800763303391
C	-2.520256154074	-0.560893411304	-0.574759456265
C	-1.444068987095	-0.125846502074	-1.371907540832
H	-1.548746863814	-0.030302193386	-2.448058588684
H	-3.474924468821	-0.811017390841	-1.022761206872

H	-3.181765368541	-1.000348785819	1.424146968482
C	1.444665160712	1.562328439176	0.070542569923
H	0.744572917560	2.395867467633	0.179831060622
H	2.476749130983	1.920465459390	0.067008452931
H	1.190772707218	1.077295185278	-2.150368035277
H	2.548670951950	-1.148028961188	-1.580998344455
H	2.644794388137	-1.412784992685	1.064717272679
H	1.332373063323	0.633767334457	2.165062029717

S8a

Energy: -519.975051 au

Energy including zero-point energy and thermal corrections: -519.746670 au

Geometry:

C	0.537521154691	0.588943909660	1.393978429302
C	-0.630572995537	-0.083967822012	0.694060490014
C	-0.663821901450	0.235398073653	-0.666093940311
C	0.462050496448	1.175609633815	-1.044272774477
C	0.964346092486	1.666105876706	0.352931258391
H	0.460438668383	2.606275977177	0.592078965743
H	2.040510322905	1.848957149150	0.360829613730
H	0.092040290009	2.017817441605	-1.637577927922
C	1.522936133986	0.465503667426	-1.844289509088
C	1.901463130586	0.815931117289	-3.071011489788
H	2.668904896579	0.268953677413	-3.608091588578
H	1.451879361789	1.668302549883	-3.573659267153
H	1.984805378760	-0.393154043437	-1.361272541952
C	-1.647861220176	-0.336404889130	-1.461577340323
C	-2.566313049753	-1.185487713006	-0.842232283498
C	-2.448765875312	-1.428756929230	0.528606620265
N	-1.491918400748	-0.896917804574	1.301080599591
H	-3.157561065335	-2.083851708585	1.027471222906

H	-3.363802004882	-1.654509033521	-1.406689564484
H	-1.701793228809	-0.130459705952	-2.525781872370
H	0.209068439753	1.044504458434	2.331893282490
C	1.630033926611	-0.402712832927	1.697455156066
C	2.070827239169	-0.687452706085	2.919360703038
H	2.859466871818	-1.413850975408	3.084086016232
H	1.645537337642	-0.203743152260	3.794134888993
H	2.063079294936	-0.909012214052	0.836788392448

1b

Energy: -677.290916 au

Energy including zero-point energy and thermal corrections: -676.944703 au

Geometry:

C	3.793576437070	0.629690390857	-0.514809462374
C	4.301069290517	-0.384653190185	-1.556987506148
C	3.907318951320	0.037640591519	-2.761654605772
C	3.119968145567	1.349398365359	-2.562509009767
C	1.847670500217	0.968194802767	-1.805102538720
C	2.265530775208	0.518137566707	-0.535650405833
N	1.475277003038	0.080026311658	0.419829110747
C	0.143604483398	0.067367547627	0.144788387586
C	-0.364285494545	0.493547917517	-1.079999200908
C	0.502603699488	0.958074410030	-2.088517358932
H	0.109359494586	1.294054868853	-3.043007839204
H	-1.431673657976	0.469359980065	-1.256059923775
C	-0.731288845488	-0.438280355299	1.268750251174
C	-2.235485823237	-0.470167769813	1.000047468183
C	-3.024540856004	-0.998254326678	2.199310494042
C	-4.533463614545	-1.036159921316	1.952948988086
C	-5.325663314504	-1.563998436269	3.151257792052
C	-6.834360071162	-1.596258788345	2.891246558406

H	-7.209822233749	-0.592227433710	2.664391318122
H	-7.066176842001	-2.239615067159	2.035173957749
H	-7.384564931327	-1.975360107822	3.758158327351
H	-4.970839961997	-2.571983678026	3.399386193621
H	-5.113834487840	-0.936012045733	4.025489247557
H	-4.886003912685	-0.026718048006	1.702710256665
H	-4.742762048788	-1.663535153669	1.076321995231
H	-2.671981250346	-2.007198887531	2.449587123821
H	-2.815428582580	-0.371005083772	3.075539741222
H	-2.589756199628	0.537715502092	0.750529526705
H	-2.443517234049	-1.099190145906	0.125628413460
H	-0.385020881375	-1.444812922553	1.533836617113
H	-0.529999173088	0.180530162298	2.151926195692
C	3.935320218452	1.934407500990	-1.362817917176
H	3.455594814225	2.802784368297	-0.901792491929
H	4.972249960233	2.157269792538	-1.624733655032
H	2.987318396880	1.976631092808	-3.443411049000
H	4.023671314089	-0.468169017343	-3.711224872745
H	4.806271013904	-1.309549312296	-1.312378298523
H	4.249523129469	0.594549987189	0.472417036012

S8b

Energy: -755.953261 au

Energy including zero-point energy and thermal corrections: -755.550116 au

Geometry:

C	0.980658691375	2.503637225752	0.797039465462
C	0.639656714605	1.358658628805	-0.141783790719
C	0.532836115259	1.797586292498	-1.462958475761
C	0.767429685434	3.289484642329	-1.576686822259
C	0.675179069894	3.750498337313	-0.085053189209
H	-0.348174093677	4.079975776298	0.113269098543

H	1.345225569436	4.585553680005	0.128481508110
H	-0.012464460320	3.770462529019	-2.175850482184
C	2.100453084290	3.588955423414	-2.211264049851
C	2.262558420232	4.300577202572	-3.324166521983
H	3.245457615231	4.484663774167	-3.744536925753
H	1.408878830283	4.723486129316	-3.847406034885
H	2.969316397658	3.172284849864	-1.705688021282
C	0.275237153861	0.855950480383	-2.449883923026
C	0.115055021475	-0.471514979718	-2.053690693577
C	0.228764795888	-0.814483518728	-0.699549249009
N	0.497019046027	0.097205318327	0.251230049970
C	0.013376058016	-2.229284528793	-0.229978096553
C	-1.336417211616	-2.394805624340	0.486810499790
C	-1.544945531175	-3.811028359562	1.023584362457
C	-2.886738648320	-3.986568476776	1.736585072417
C	-3.098900870822	-5.401431948872	2.280030552238
H	-3.027899238630	-6.117904121625	1.452165292805
H	-2.283845620560	-5.645044520327	2.972729156513
C	-4.446249689140	-5.563183086955	2.989556806394
H	-4.581046207359	-6.580028500430	3.371586839028
H	-4.524208302838	-4.870554299635	3.834924499163
H	-5.273291383652	-5.346229477667	2.304348830362
H	-2.954477812032	-3.267086276669	2.563068705362
H	-3.701579666056	-3.739368978660	1.043205835598
H	-1.477527001482	-4.530151479456	0.196320324553
H	-0.730229630841	-4.057697736818	1.716751360593
H	-1.382057520256	-1.673258016023	1.309477617339
H	-2.148317197245	-2.140475161050	-0.206223021040
H	0.063886164466	-2.917015536877	-1.081036731412
H	0.816730560603	-2.495060456321	0.465296546214
H	-0.095401524517	-1.246366260707	-2.782068829274

H	0.201837572118	1.140116475697	-3.494902154998
H	0.342648543868	2.473164774525	1.684427270968
C	2.419365283751	2.430473351504	1.236577431983
C	2.816485870601	2.298521951762	2.498944698404
H	3.867699412020	2.245938104871	2.761690035129
H	2.094606960198	2.231561592615	3.308027770676
H	3.160698953258	2.483859571765	0.441403717266

1c

Energy: -598.638458 au

Energy including zero-point energy and thermal corrections: -598.35127 au

Geometry:

C	2.314329840238	0.659289473346	0.544634413128
C	3.191860105255	-0.379260173601	-0.179426127398
C	3.124185022875	-0.126935543907	-1.489488084327
C	2.194370895127	1.088976108510	-1.683866138220
C	0.799445693624	0.624989193266	-1.263469337669
C	0.874422764612	0.355474696900	0.117920667976
N	-0.111910933976	-0.086532622929	0.865292822819
C	-1.303457390040	-0.298237127187	0.244962334899
C	-1.472190395048	-0.057788827561	-1.117028091792
C	-0.400678453955	0.415496313301	-1.899523494726
H	-0.535282121875	0.604970552787	-2.960008355355
H	-2.432211009141	-0.232768385806	-1.582502803886
C	-2.422154174099	-0.810407268891	1.151825214709
C	-3.738559345635	-1.034808667943	0.395949830292
H	-3.620805688612	-1.777824081951	-0.399311990714
H	-4.496295736024	-1.401790431123	1.094341487275
H	-4.107993776152	-0.104973244301	-0.048308184374
C	-2.661471195768	0.220302858030	2.273699487072
H	-1.738335208575	0.392866557625	2.830761649211

H	-3.001832780284	1.173839557162	1.856271246740
H	-3.429620724479	-0.151924233051	2.960077330650
C	-1.977354436938	-2.145315267354	1.783041484171
H	-1.043375469849	-2.010487812258	2.332287060001
H	-2.749872845191	-2.503598139628	2.471864732740
H	-1.821855322168	-2.905274396755	1.010028504490
C	2.572357357820	1.883762258472	-0.390853158175
H	1.902088457972	2.725693794539	-0.194158877873
H	3.615481646308	2.208208601810	-0.383968849701
H	2.263396639347	1.607363370843	-2.639599080777
H	3.555082694272	-0.702640516496	-2.298103915452
H	3.688850232641	-1.205689581533	0.310967315966
H	2.468267766642	0.776739455186	1.615293447891

S8c

Energy: -677.298336 au

Energy including zero-point energy and thermal corrections: -676.953421 au

Geometry:

C	1.273104908736	1.293339747527	1.224447850062
C	0.205253305298	0.546855234487	0.443172934679
C	-0.014138433352	1.125992312740	-0.803436444712
C	0.859866954756	2.343596194667	-1.017951580051
C	1.386725691326	2.627065894679	0.427378048833
H	0.737033293801	3.372591588920	0.893404317055
H	2.403969395325	3.023412337390	0.422371917044
H	0.276505704963	3.193163955330	-1.387557328663
C	1.959643523045	2.060945841623	-2.008021093267
C	2.145384557648	2.733529395902	-3.141304877514
H	2.951335113153	2.487401338253	-3.824380278314
H	1.491625497571	3.556959812194	-3.416910644524
H	2.624483051219	1.237886621663	-1.753290272223

C	-0.931953923806	0.519669219016	-1.654373375201
C	-1.589472289781	-0.616181046419	-1.194958493319
C	-1.310643639016	-1.124429690644	0.086506792662
N	-0.411493565044	-0.544941070480	0.892611388570
C	-2.037848634822	-2.373272245130	0.587530747597
C	-1.592573781287	-2.751778531690	2.005925284604
H	-0.519088320858	-2.950171056166	2.039422826343
H	-1.800688180011	-1.942968846039	2.710152101809
H	-2.133917618095	-3.649502426312	2.322188925574
C	-1.733977589803	-3.550774150587	-0.361877004974
H	-0.659794457813	-3.758563072162	-0.384977693160
H	-2.253748468456	-4.449200447890	-0.012952311166
H	-2.065827573192	-3.337561286031	-1.382281575414
C	-3.557717460361	-2.109733443220	0.594582807412
H	-4.084738984065	-3.001567403286	0.949451103287
H	-3.800724537827	-1.275922607729	1.260509449534
H	-3.927071447809	-1.869734933068	-0.406790526220
H	-2.318543643661	-1.115771903342	-1.820653255966
H	-1.130396014229	0.916871132504	-2.644885301040
H	0.944326632144	1.466830854077	2.252758527351
C	2.561272238472	0.513620353051	1.256558703568
C	3.148404064283	0.071353843289	2.364959188822
H	4.075391887328	-0.491222058830	2.331856844481
H	2.709972263232	0.256144994782	3.341627279555
H	3.013244021591	0.306974054523	0.288052696657

^1H , ^{13}C , ^{19}F , and 2D NMR Spectra

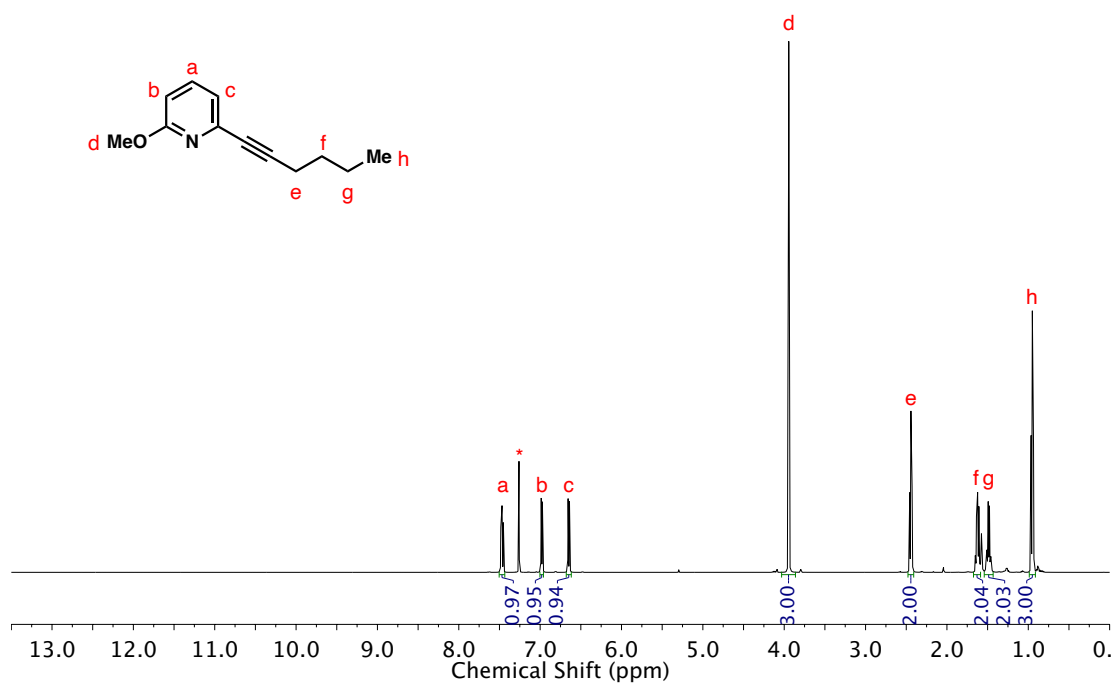


Figure S11. ^1H NMR (500 MHz, CDCl_3) of S1.

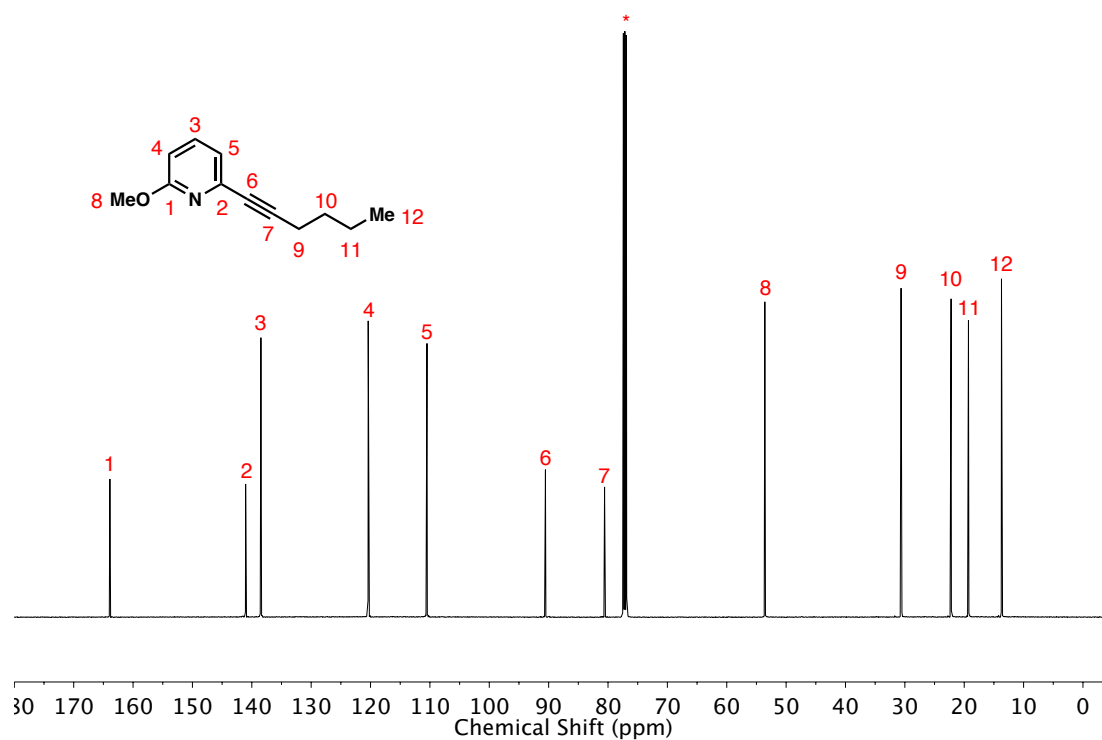


Figure S12. ^{13}C NMR (126 MHz, CDCl_3) of S1.

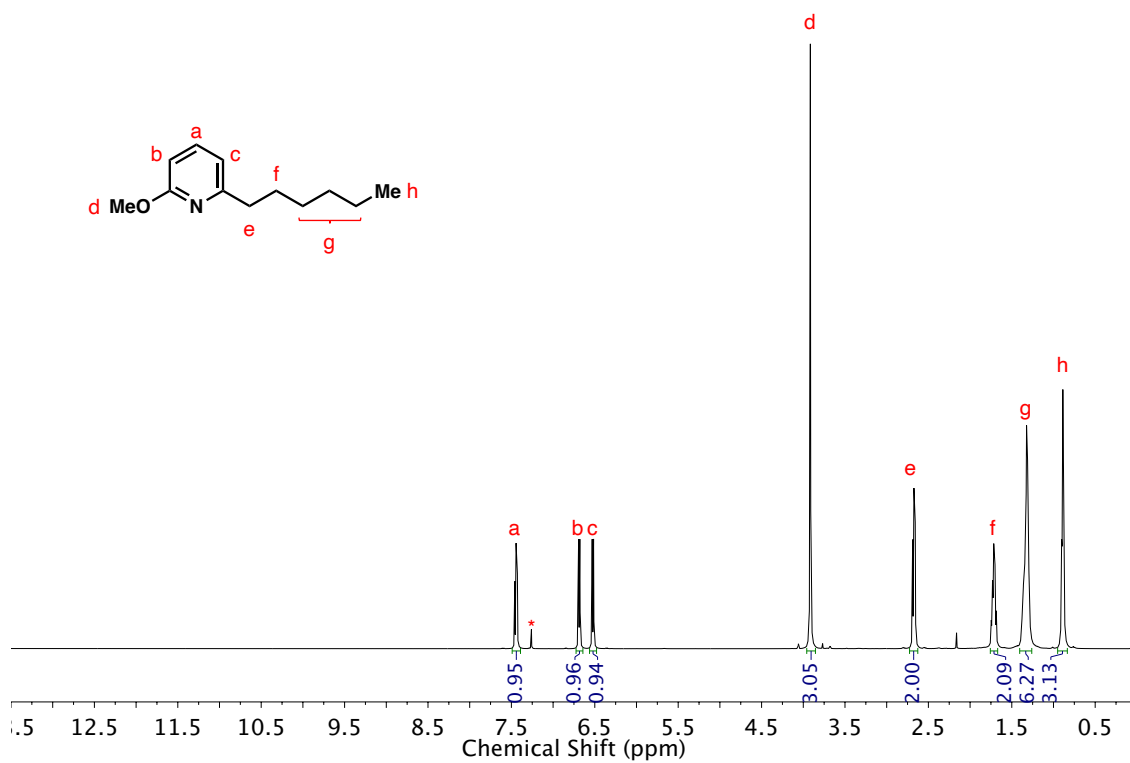


Figure S13. ¹H NMR (500 MHz, CDCl₃) of S2.

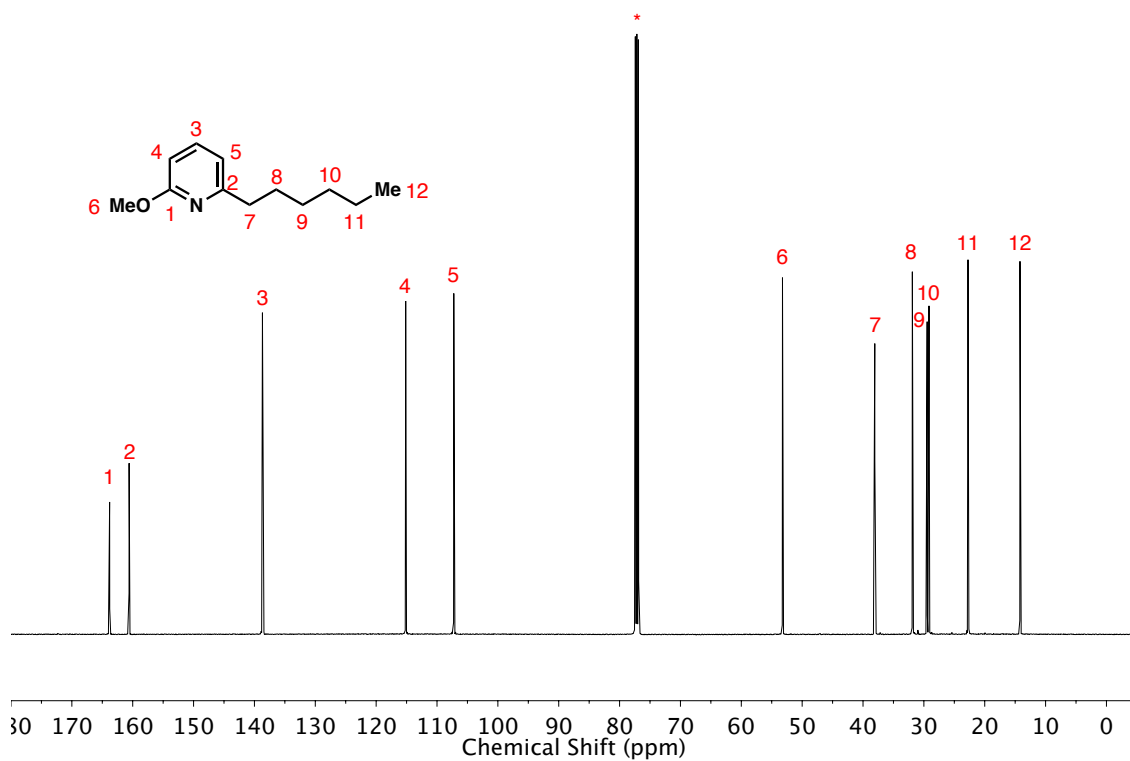


Figure S14. ¹³C NMR (126 MHz, CDCl₃) of S2.

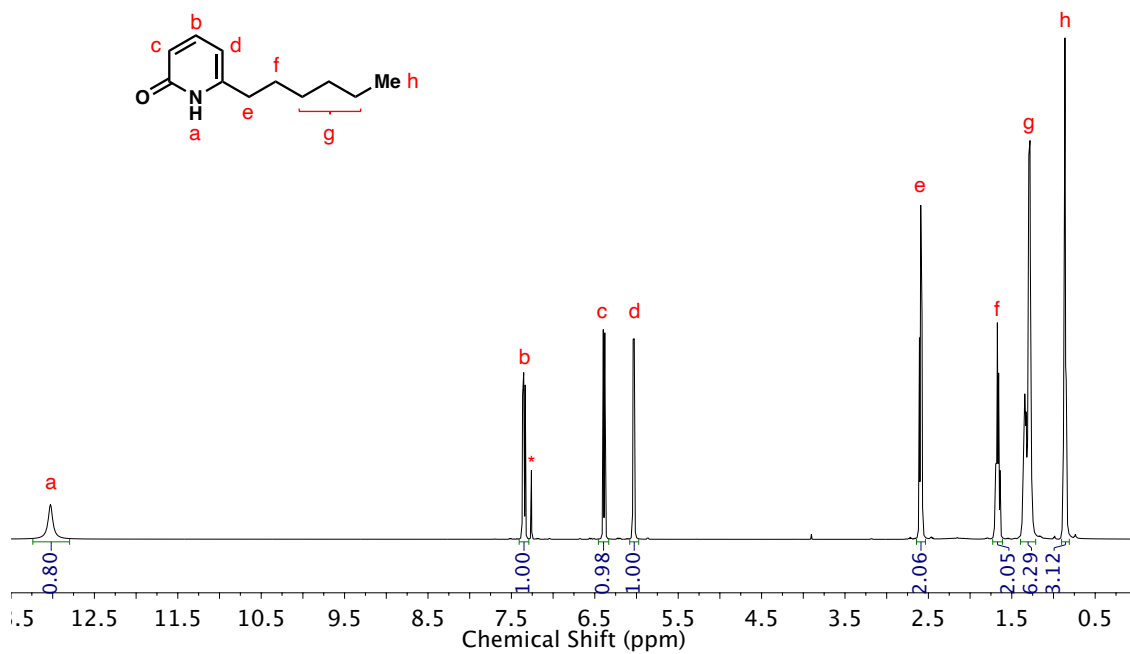


Figure S15. ¹H NMR (500 MHz, CDCl₃) of **2b**.

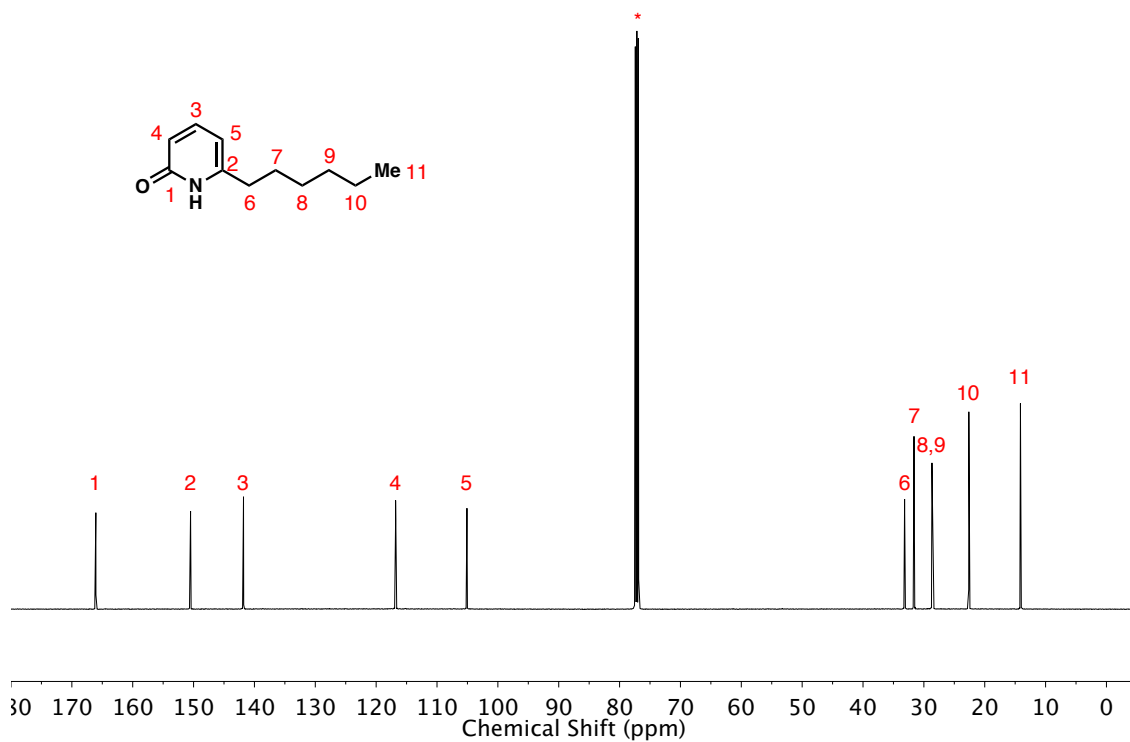


Figure S16. ¹³C NMR (126 MHz, CDCl₃) of **2b**.

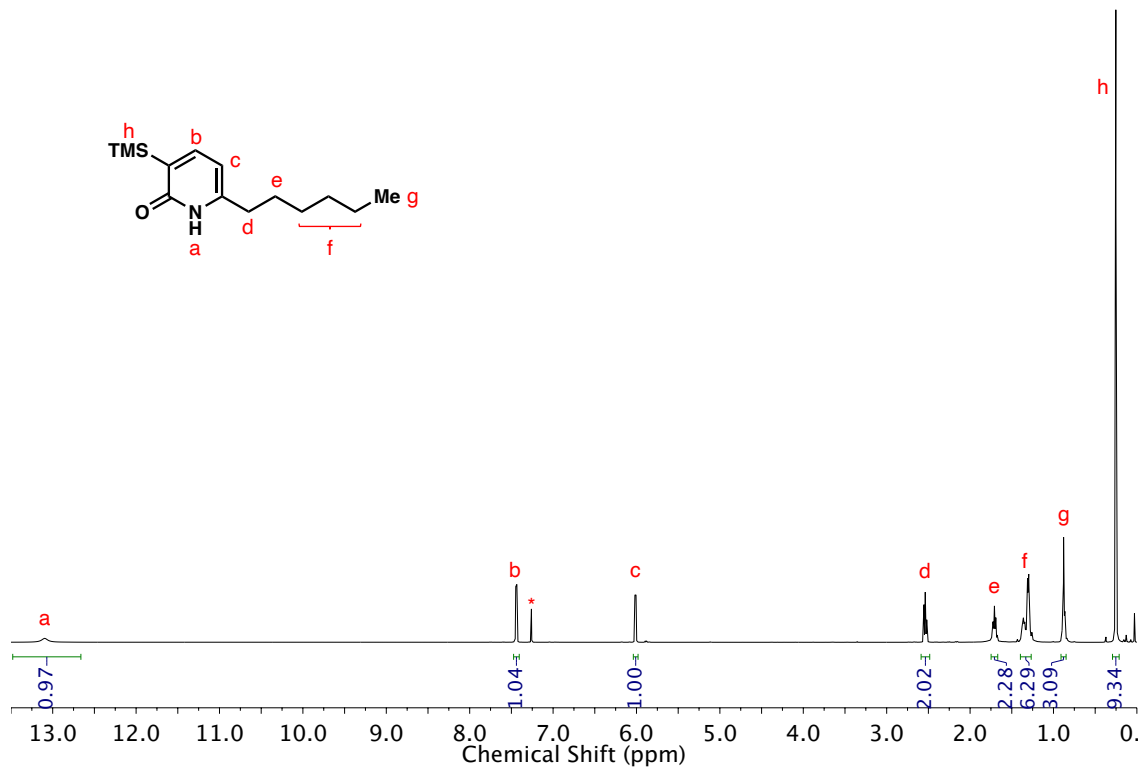


Figure S17. ¹H NMR (500 MHz, CDCl₃) of S5b.

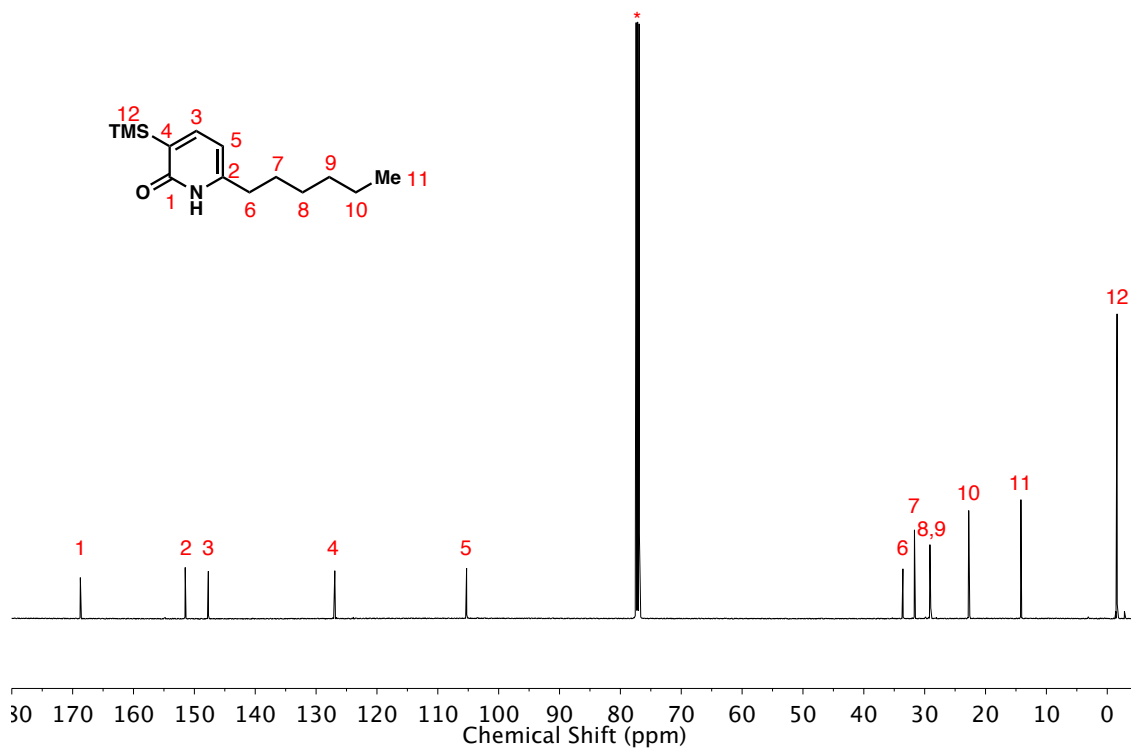


Figure S18. ¹³C NMR (126 MHz, CDCl₃) of S5b.

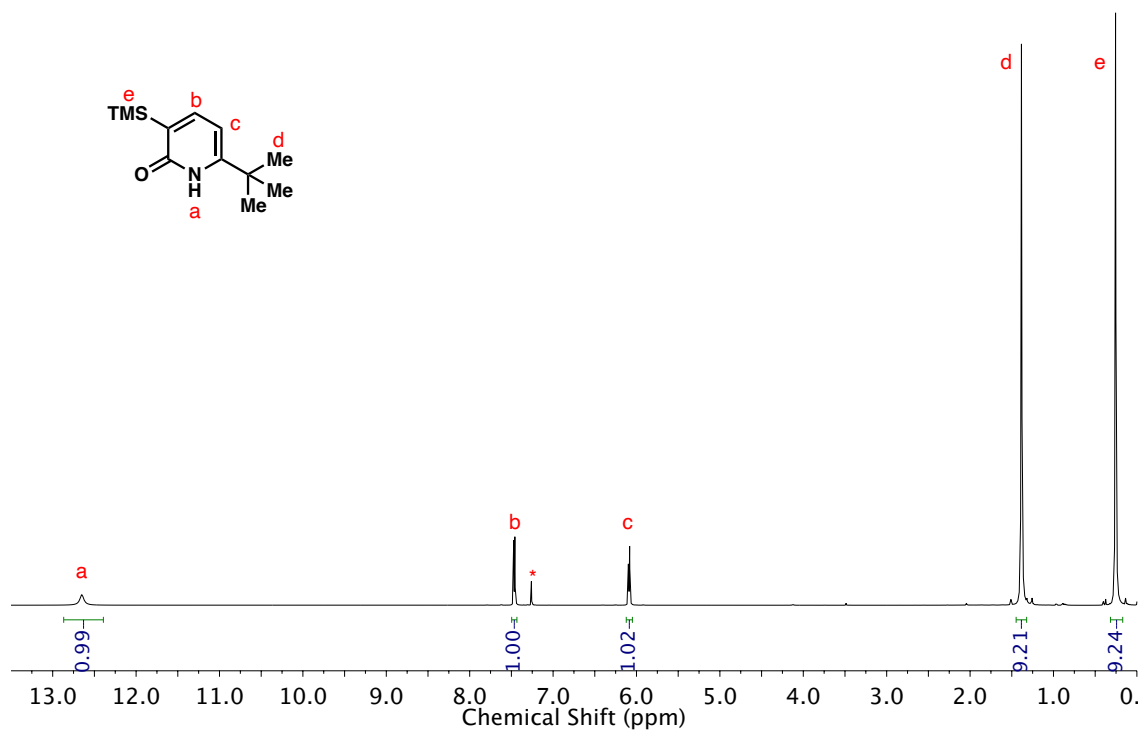


Figure S19. ^1H NMR (500 MHz, CDCl_3) of S5c.

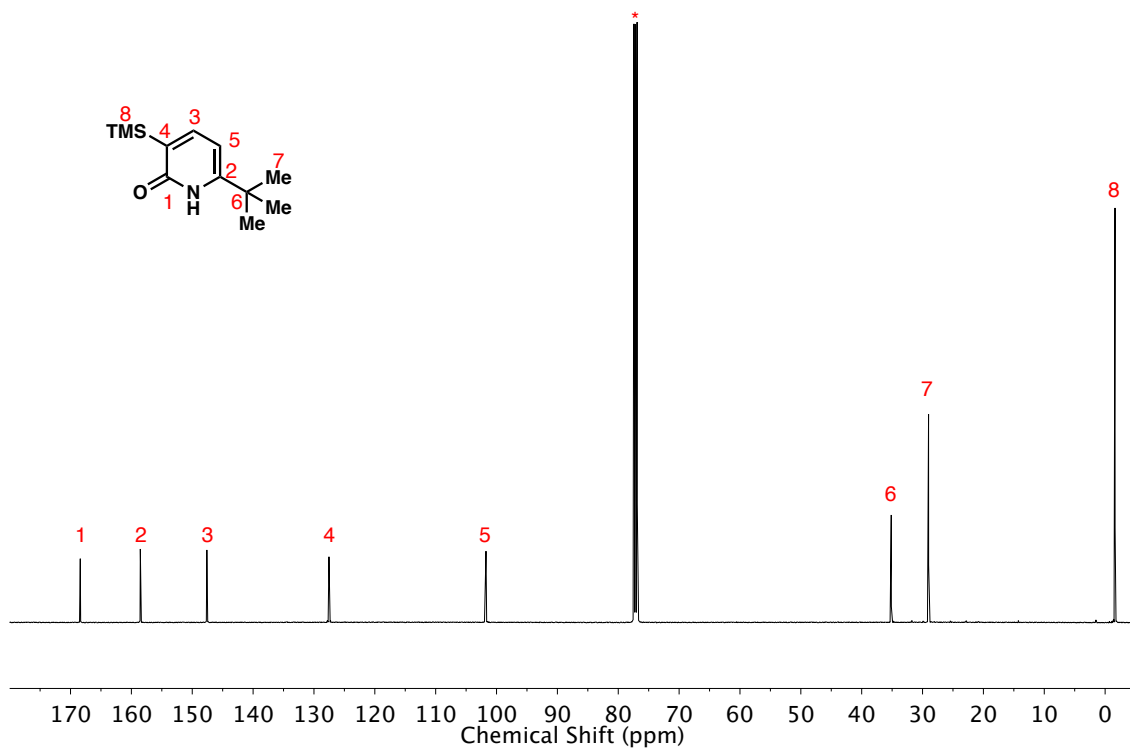


Figure S20. ^{13}C NMR (126 MHz, CDCl_3) of S5c.

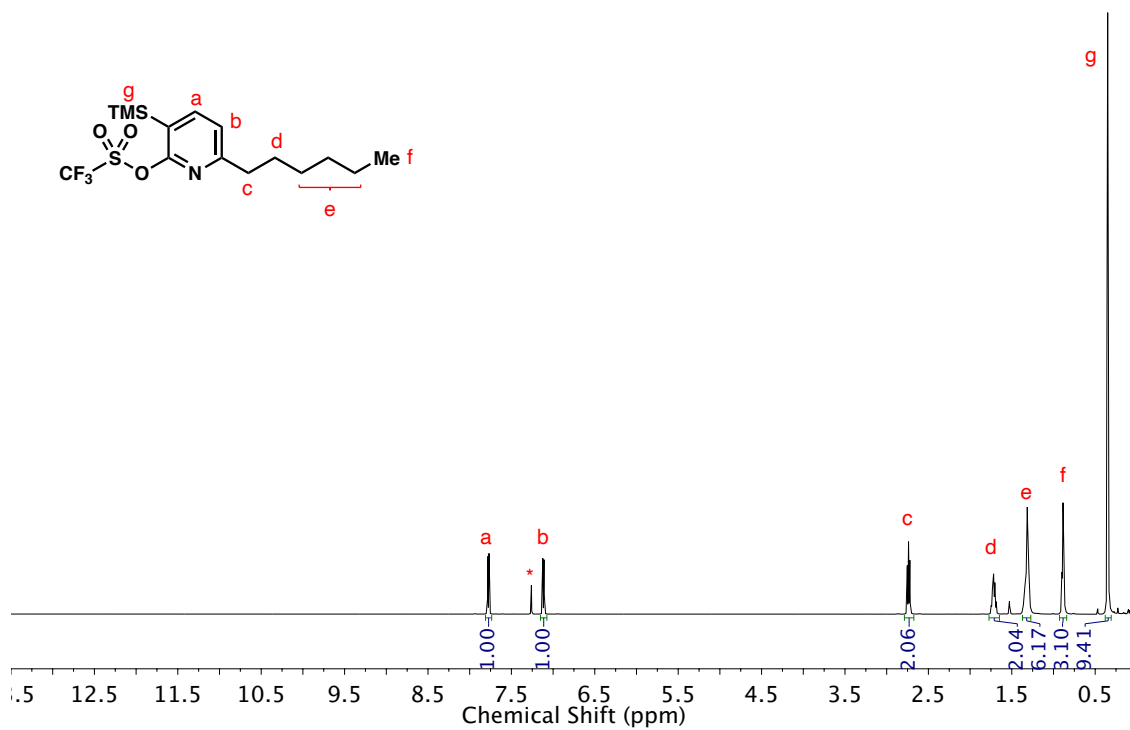


Figure S21. ¹H NMR (500 MHz, CDCl₃) of **3b**.

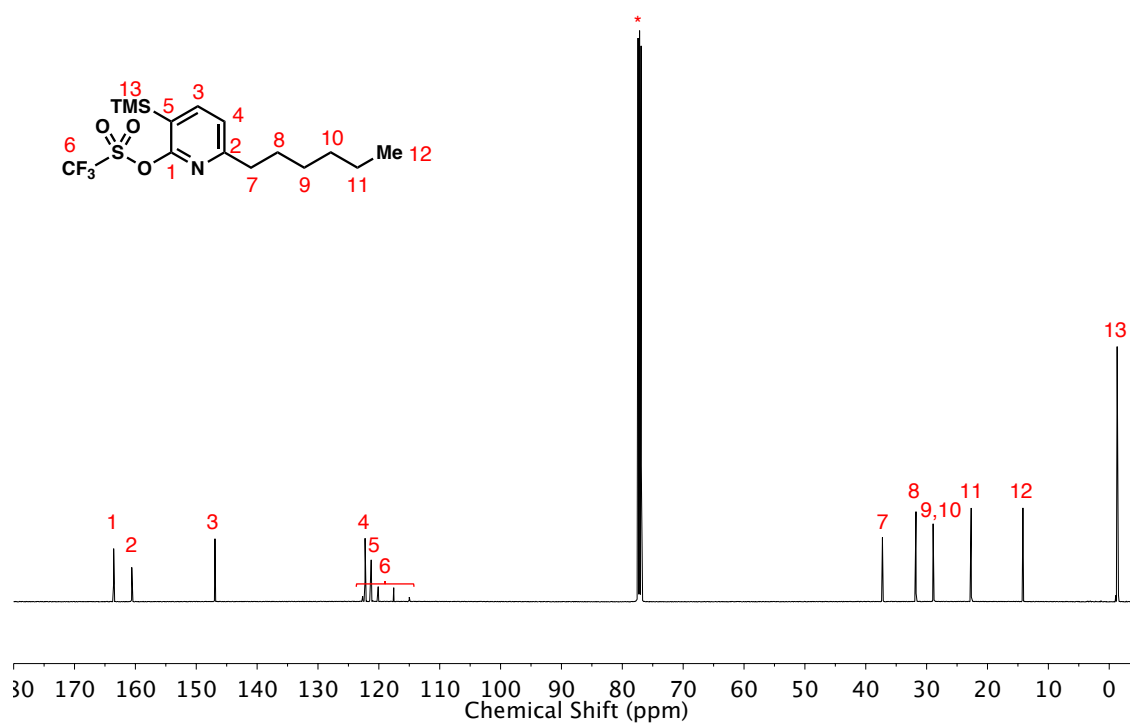


Figure S22. ¹³C NMR (126 MHz, CDCl₃) of **3b**.

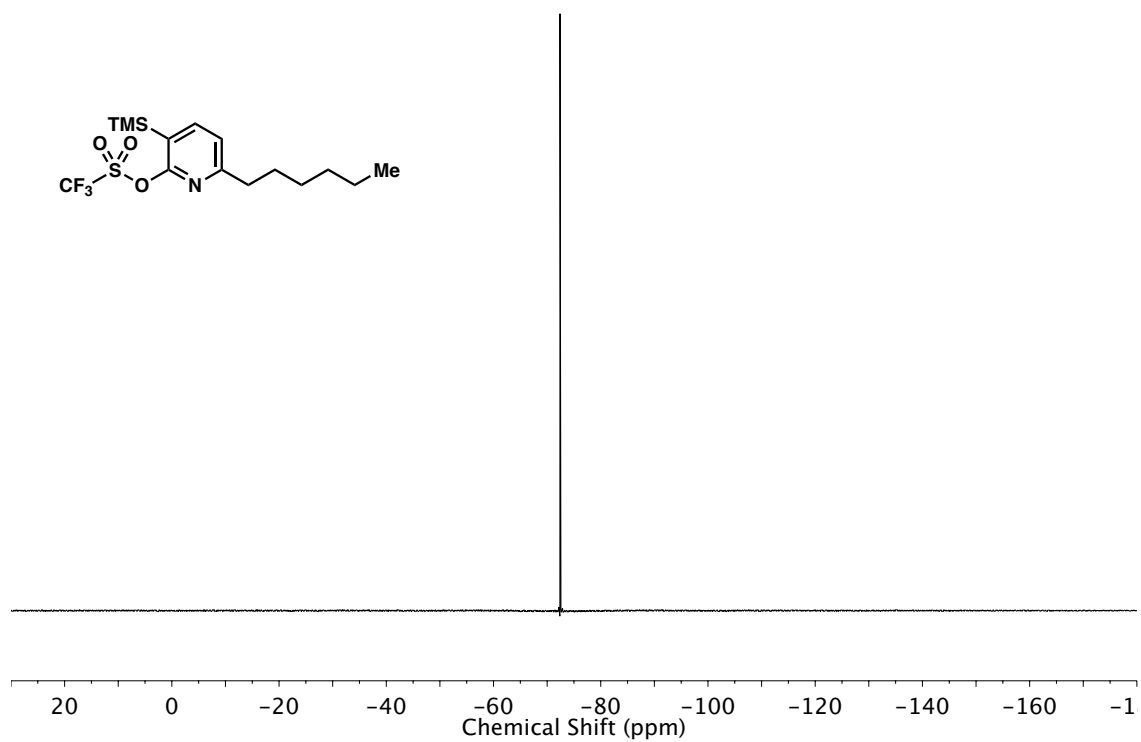


Figure S23. ^{19}F NMR (470 MHz, CDCl_3) of **3b**.

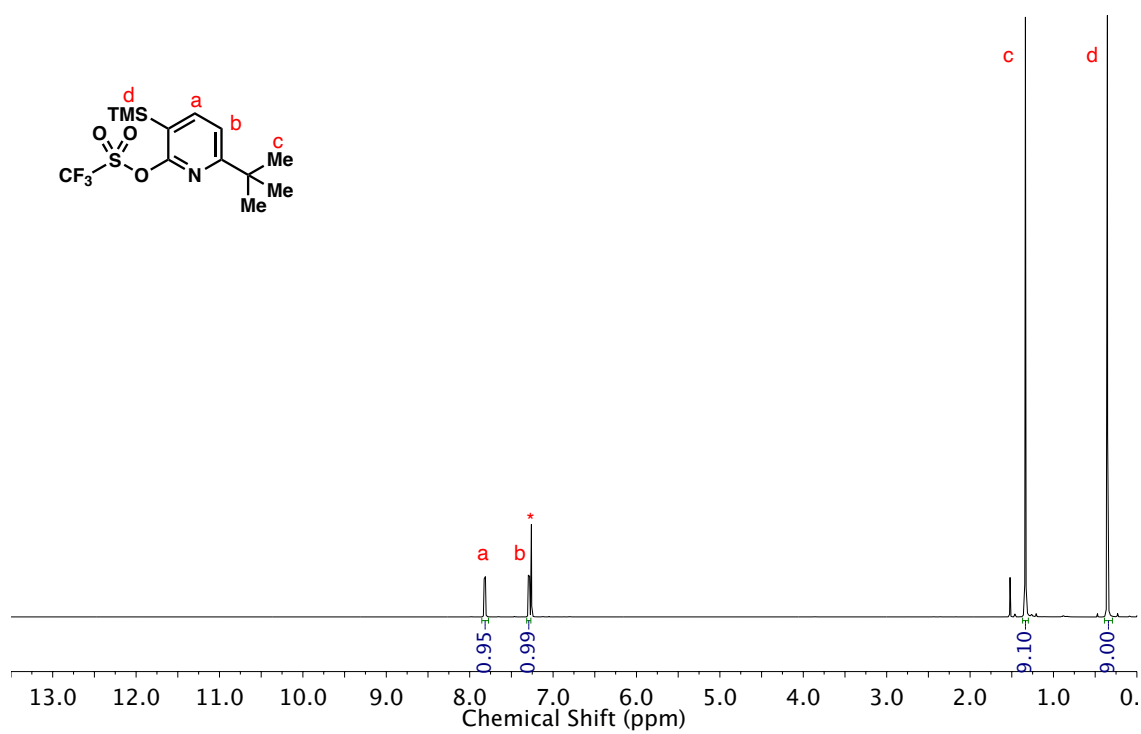
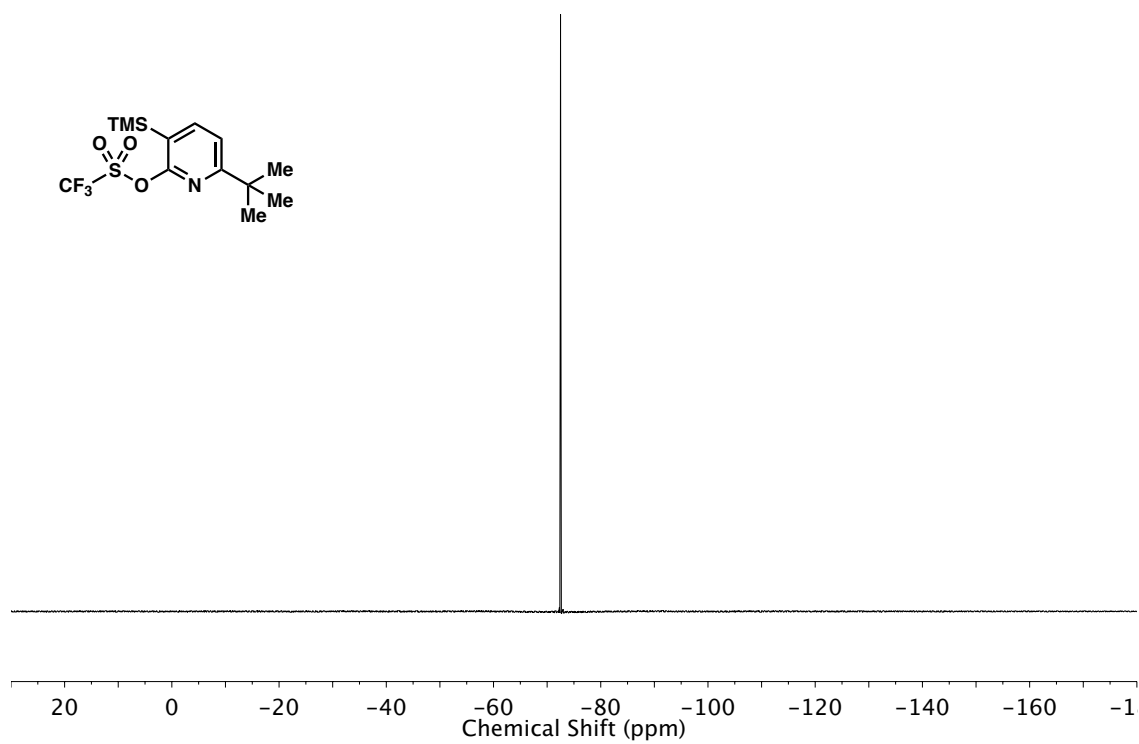
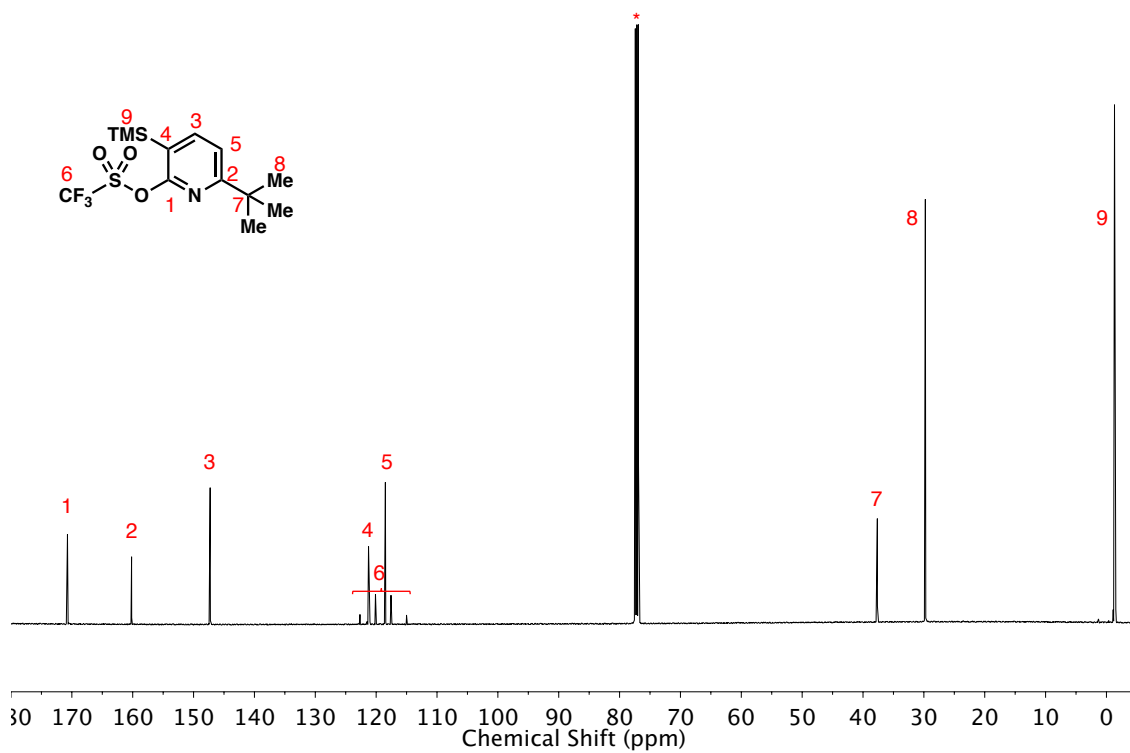


Figure S24. ^1H NMR (500 MHz, CDCl_3) of **3c**.



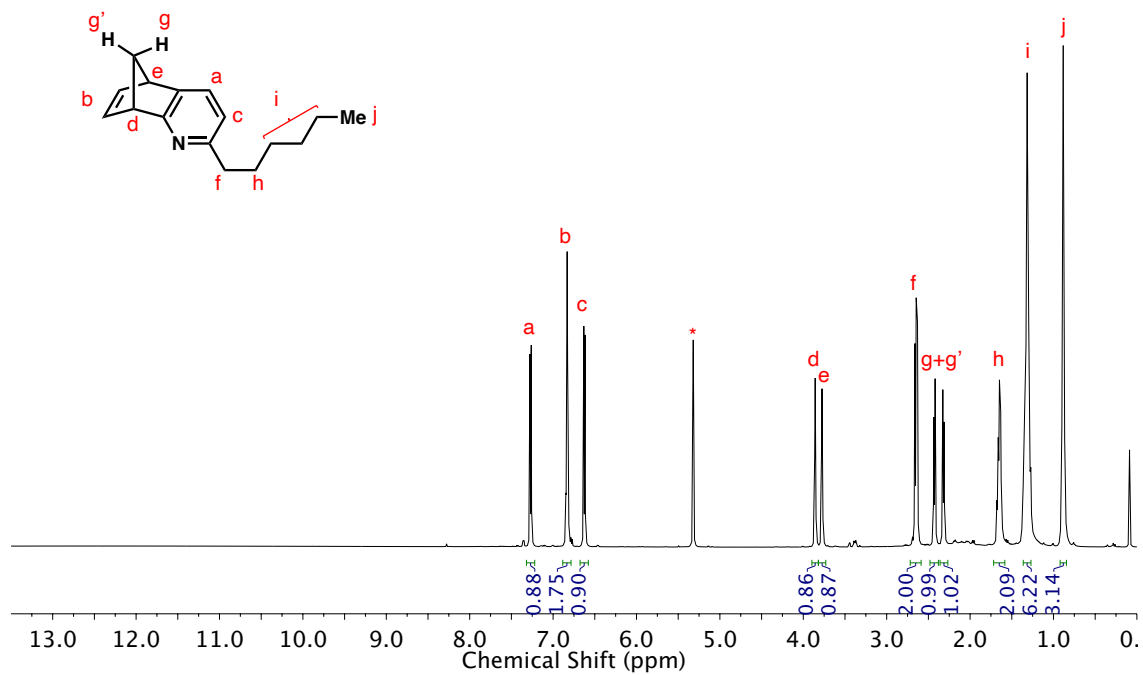


Figure S27. ^1H NMR (500 MHz, CD_2Cl_2) of **1b**.

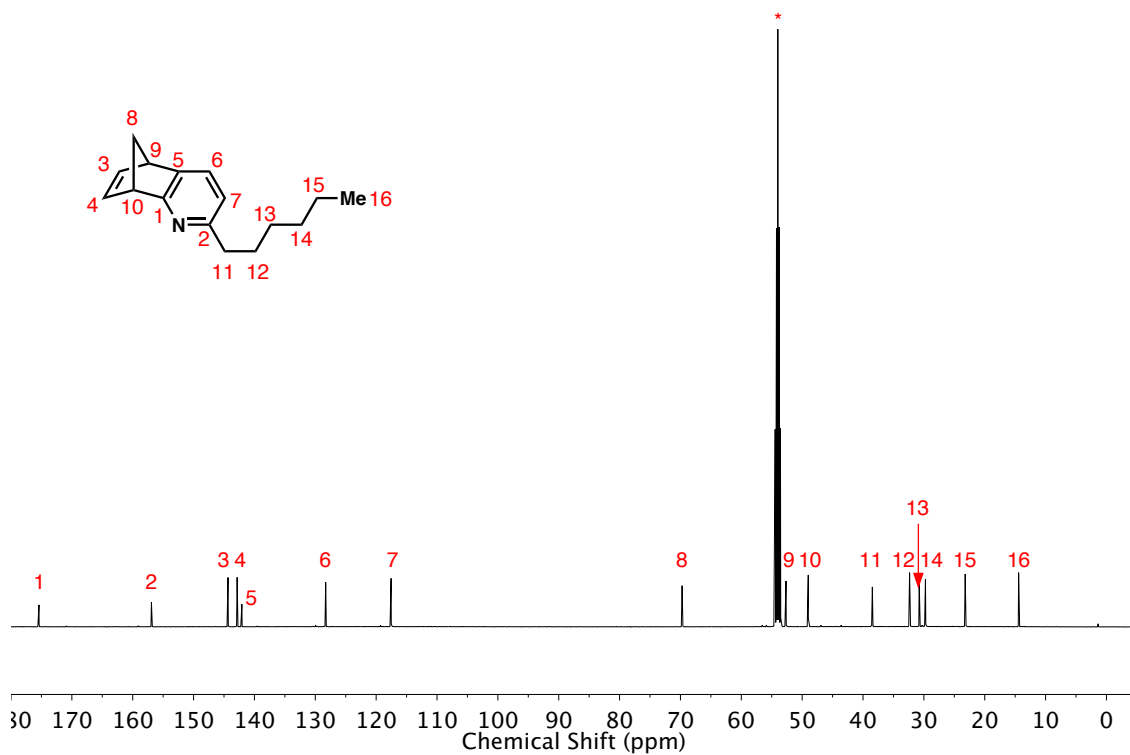


Figure S28. ^{13}C NMR (126 MHz, CD_2Cl_2) of **1b**.

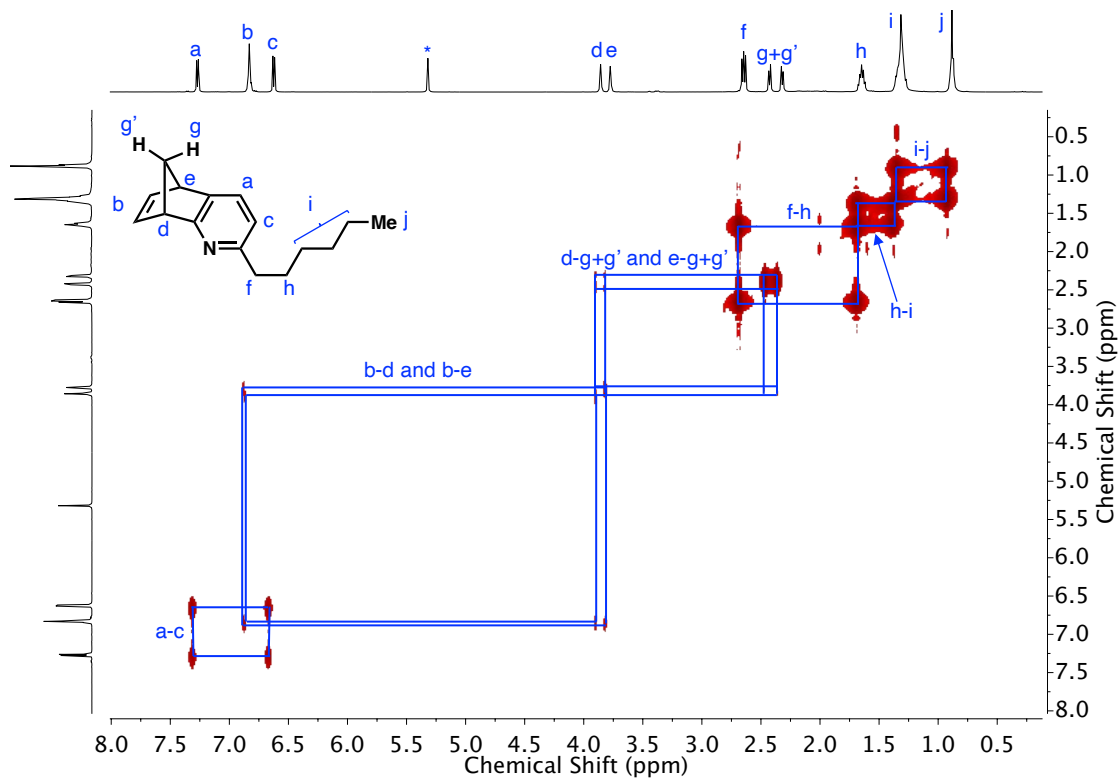


Figure S29. ^1H COSY (500 MHz, CD_2Cl_2) of **1b**.

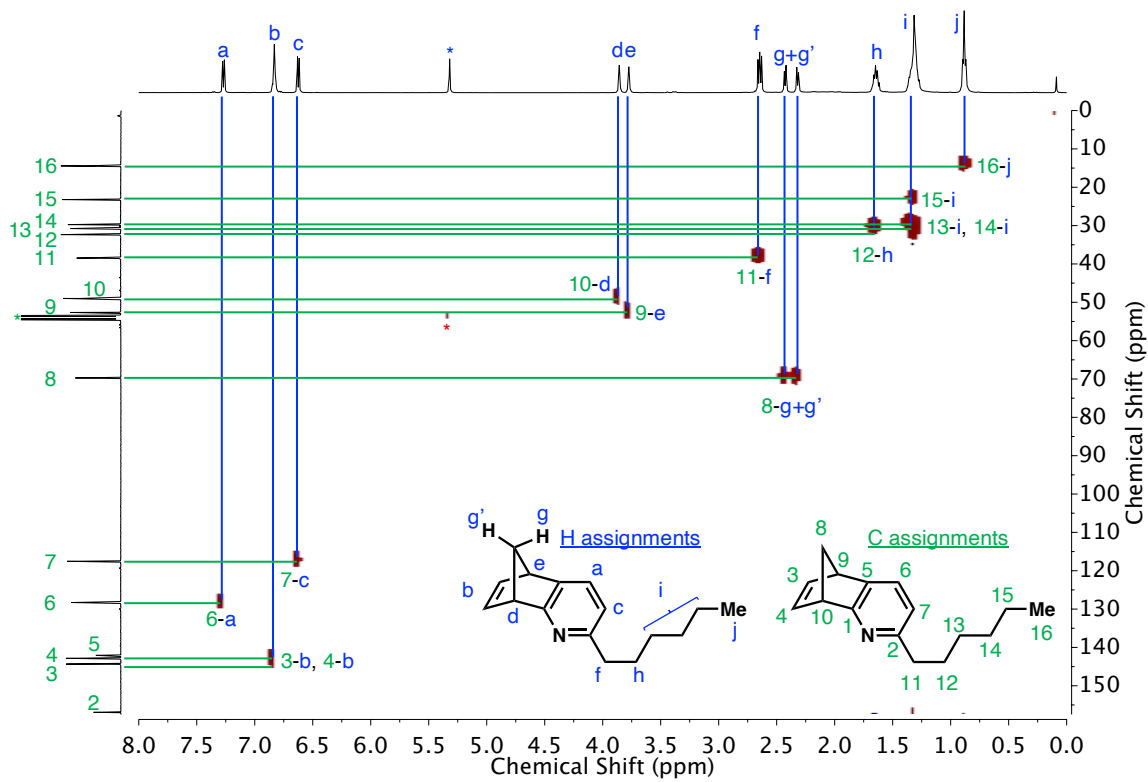


Figure S30. HSQC (500 MHz, CD_2Cl_2) of **1b**.

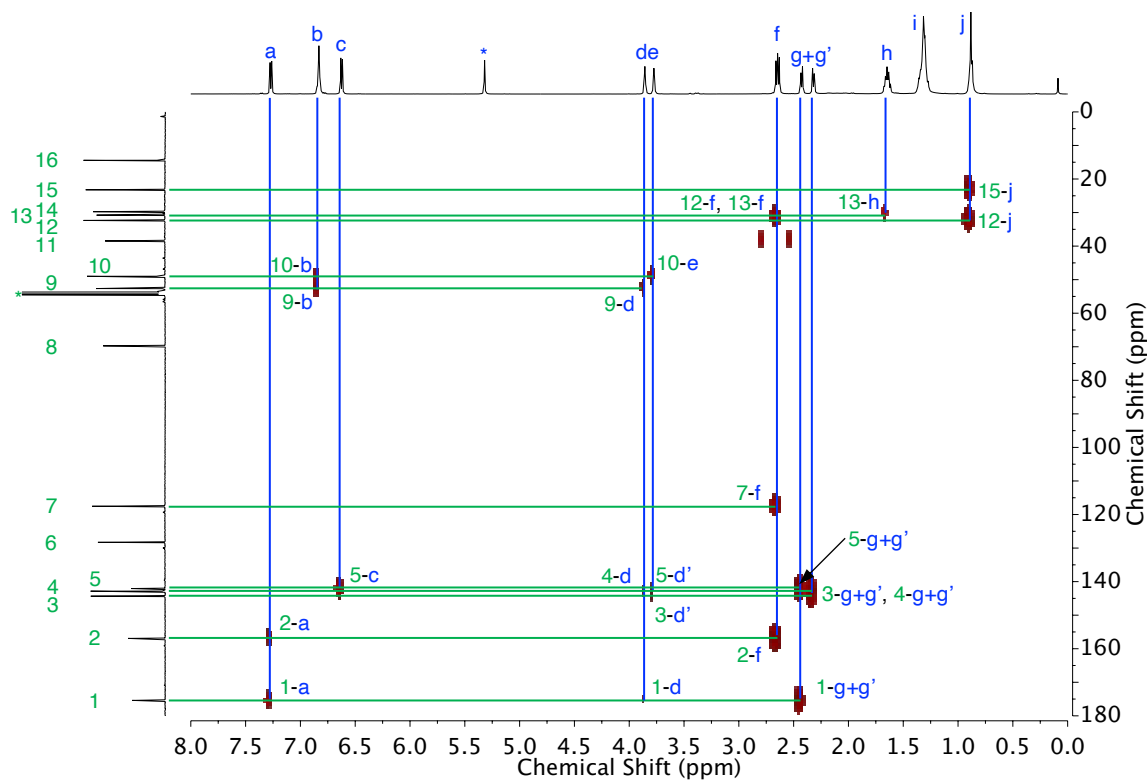


Figure S31. HMBC (500 MHz, CD₂Cl₂) of 1b.

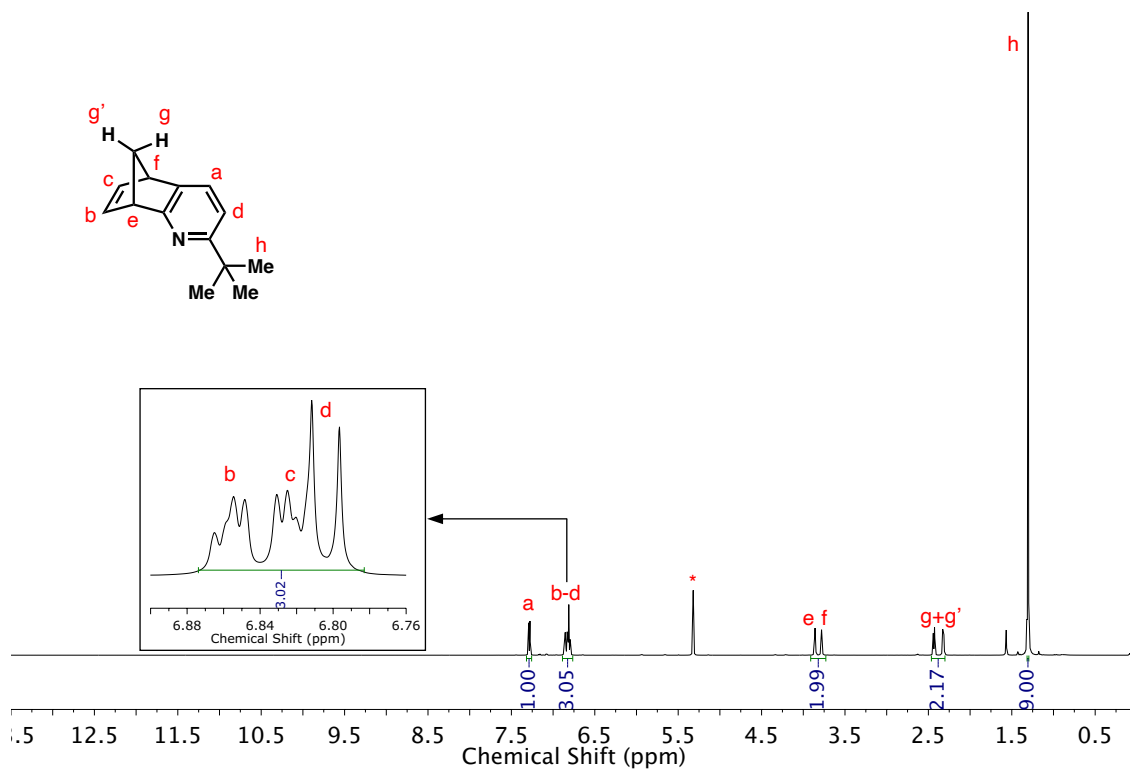


Figure S32. ¹H NMR (500 MHz, CD₂Cl₂) of 1c.

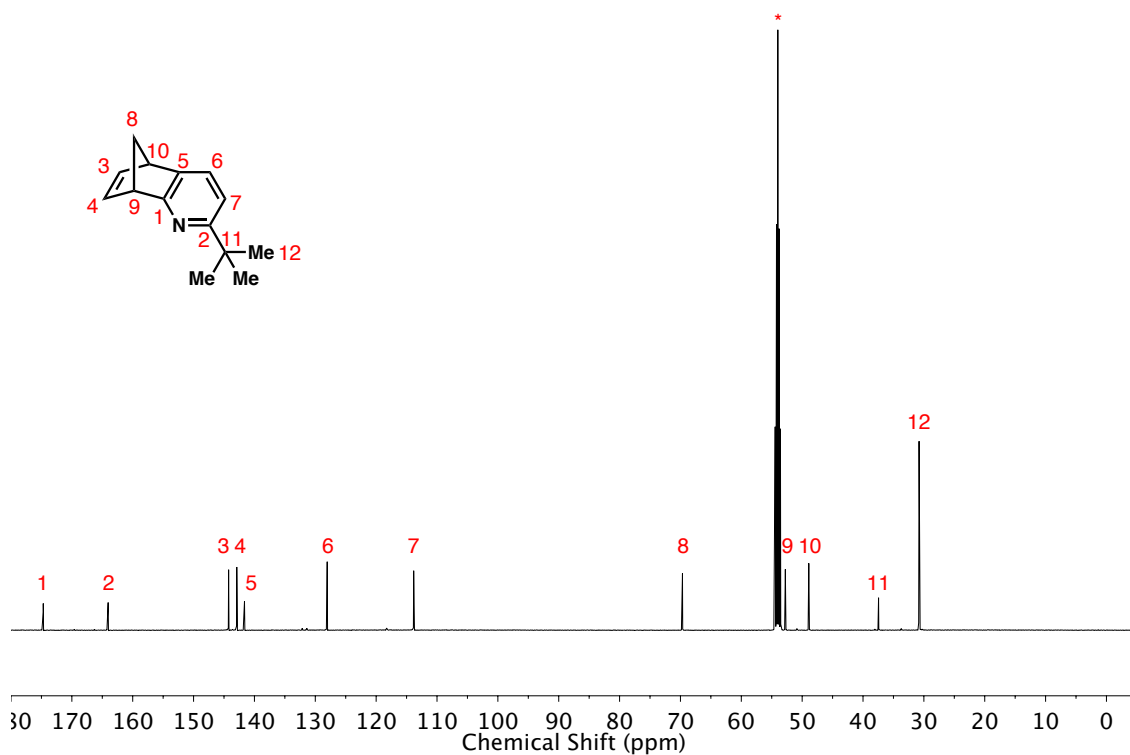


Figure S33. ^{13}C NMR (126 MHz, CD_2Cl_2) of **1c**.

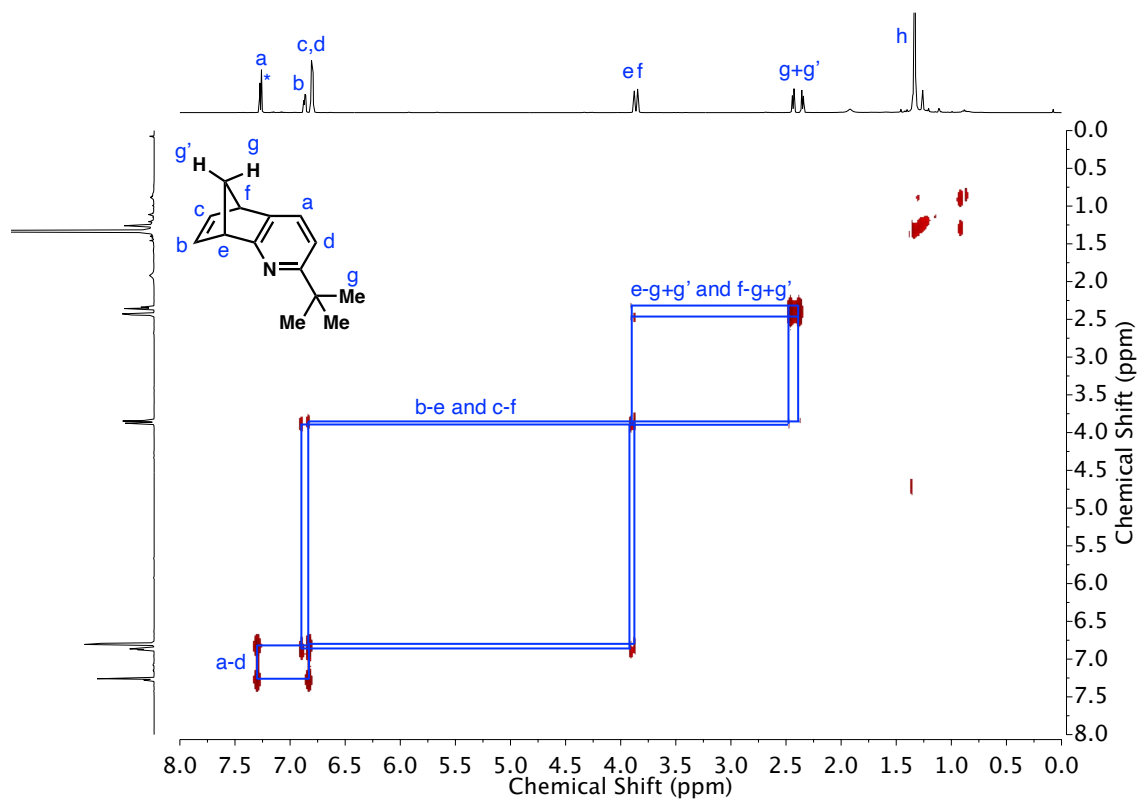
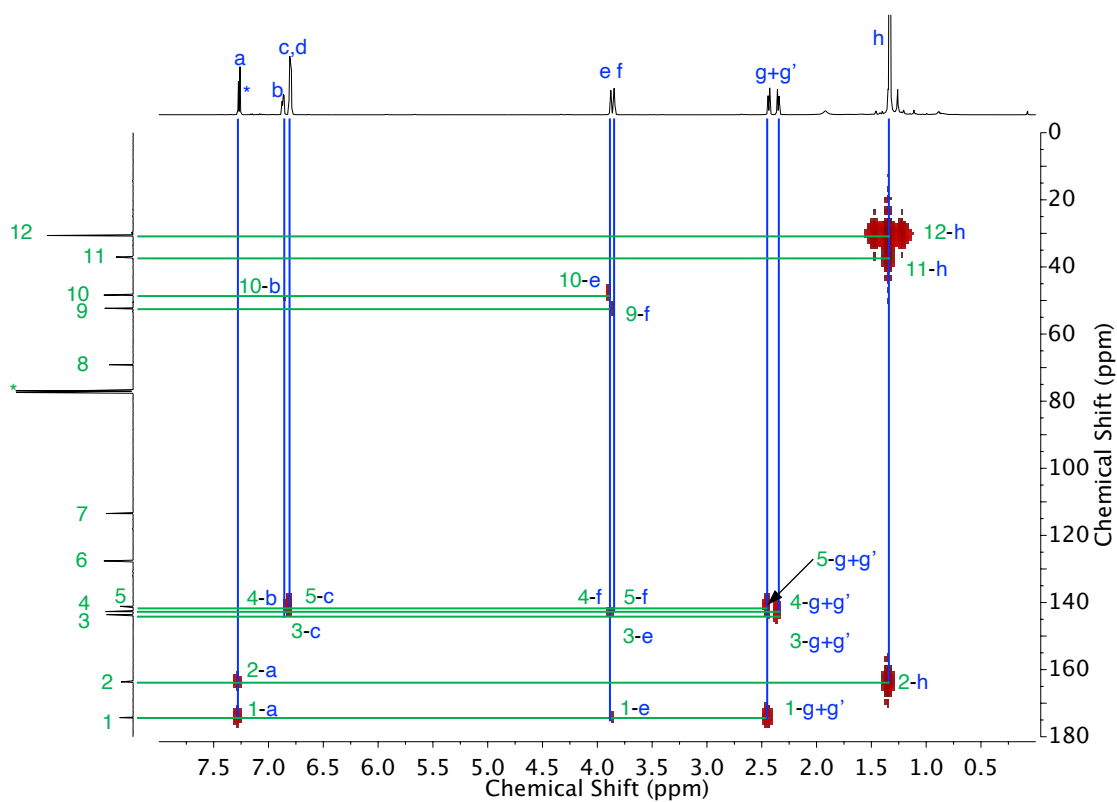
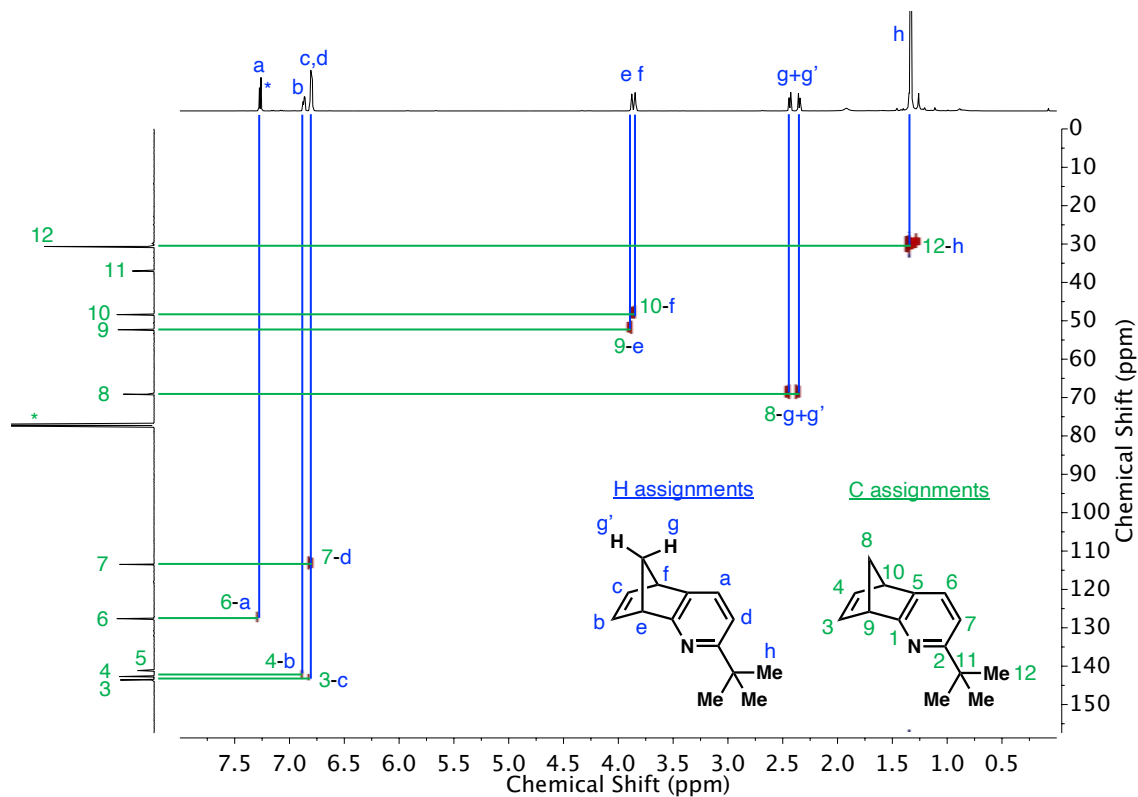


Figure S34. ^1H COSY (500 MHz, CDCl_3) of **1c**.



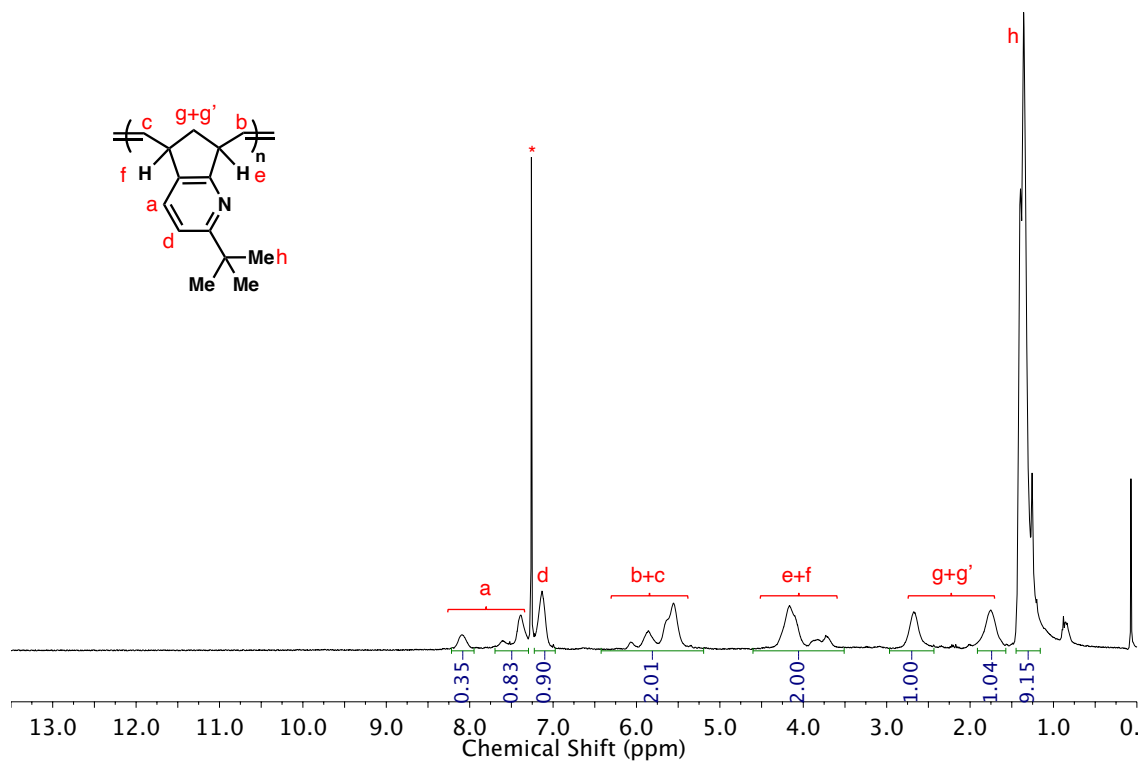


Figure S37. ¹H NMR (500 MHz, CDCl₃) of poly-1c.

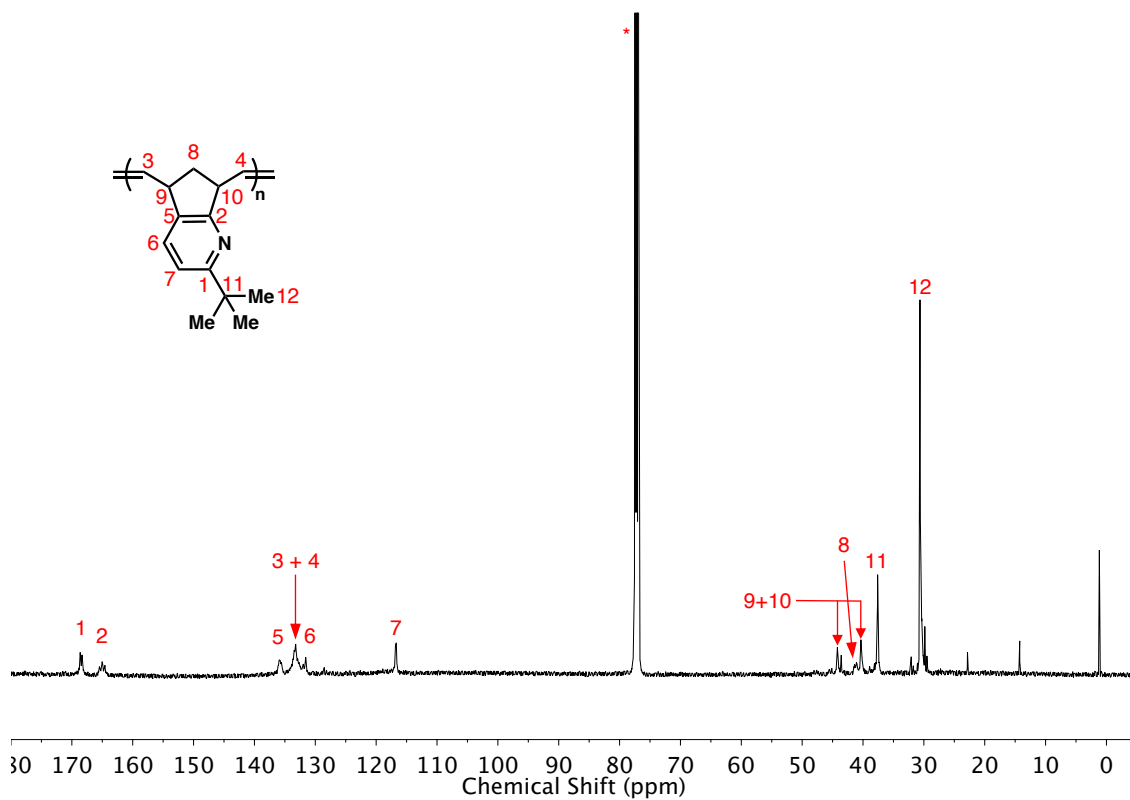
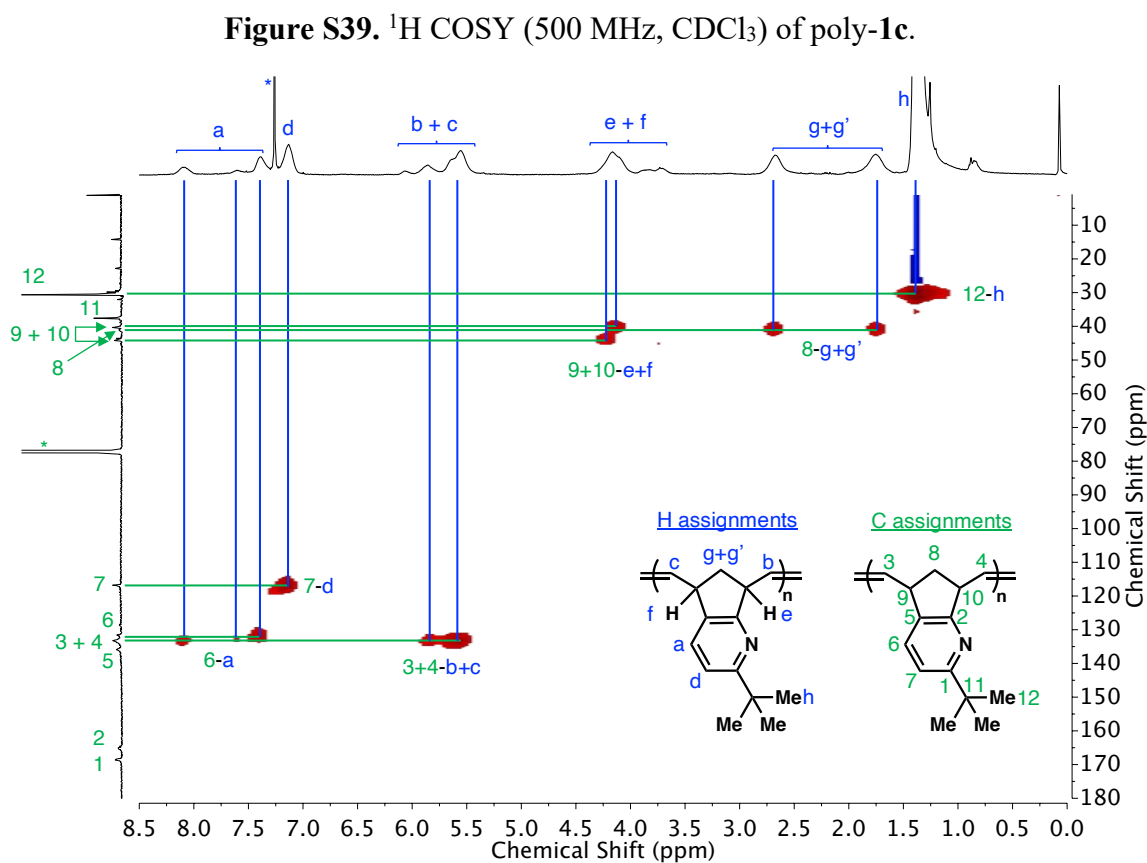
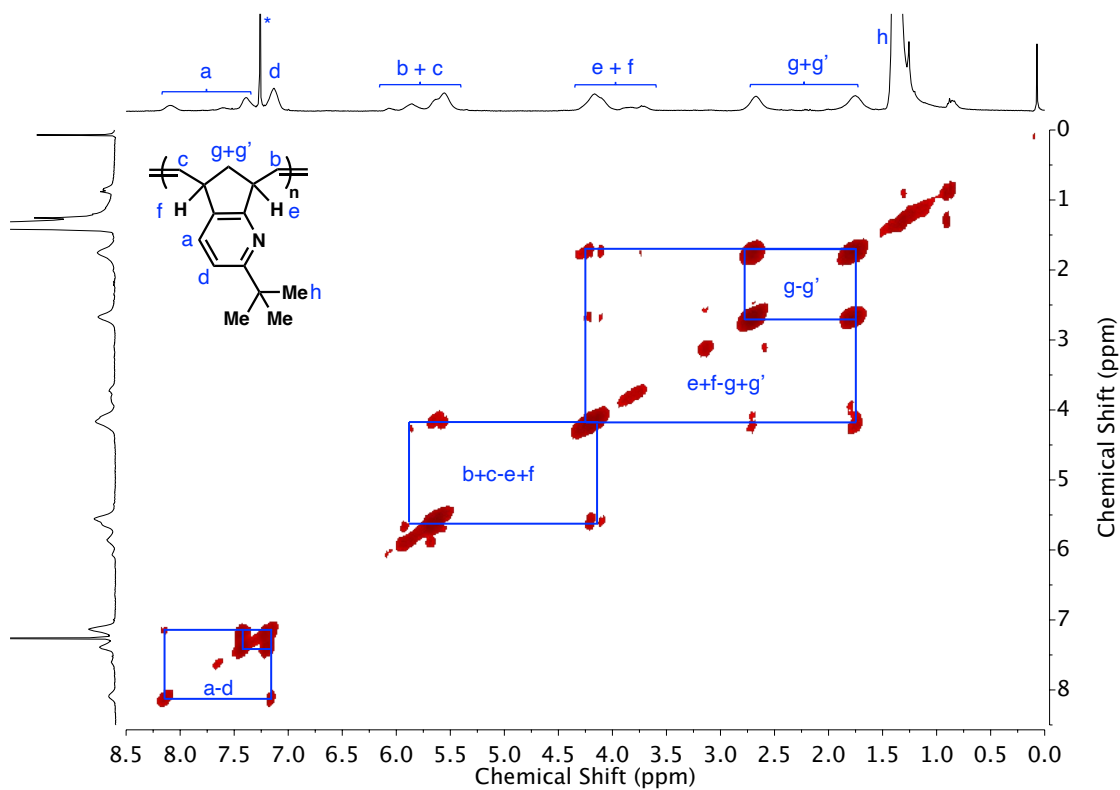


Figure S38. ¹³C NMR (126 MHz, CDCl₃) of poly-1c.



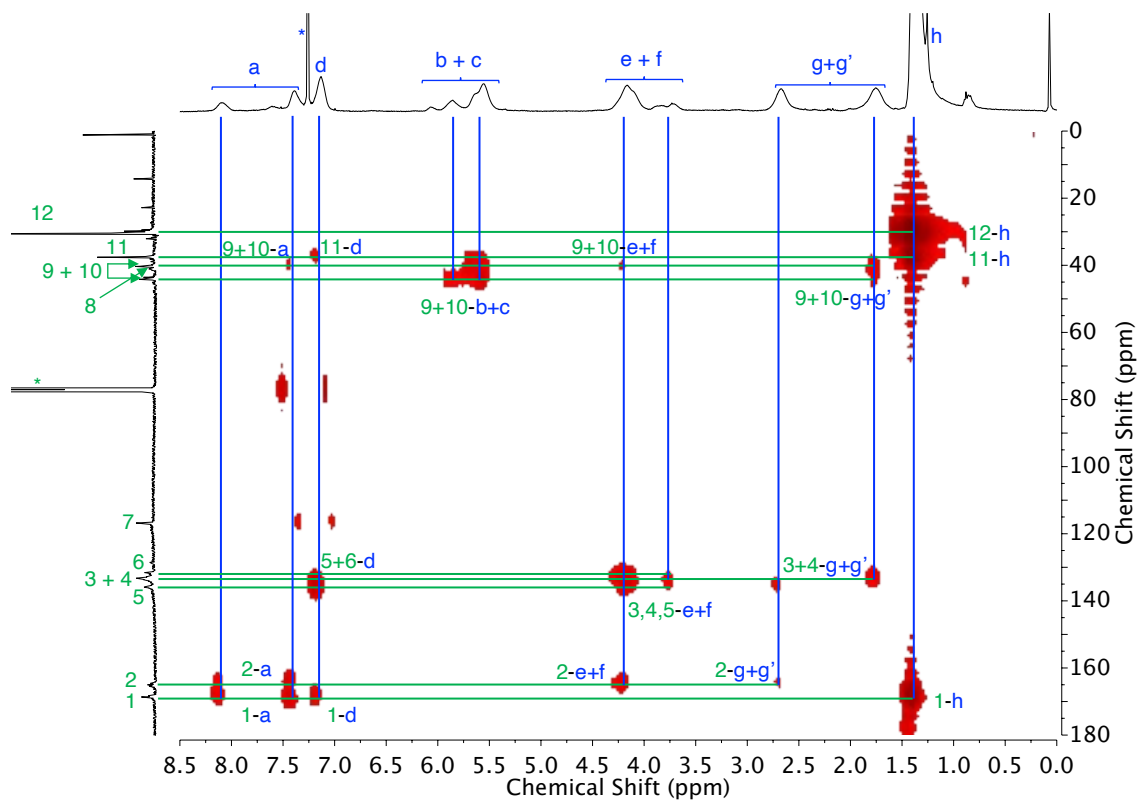


Figure S41. HMBC (500 MHz, CDCl₃) of poly-1c.

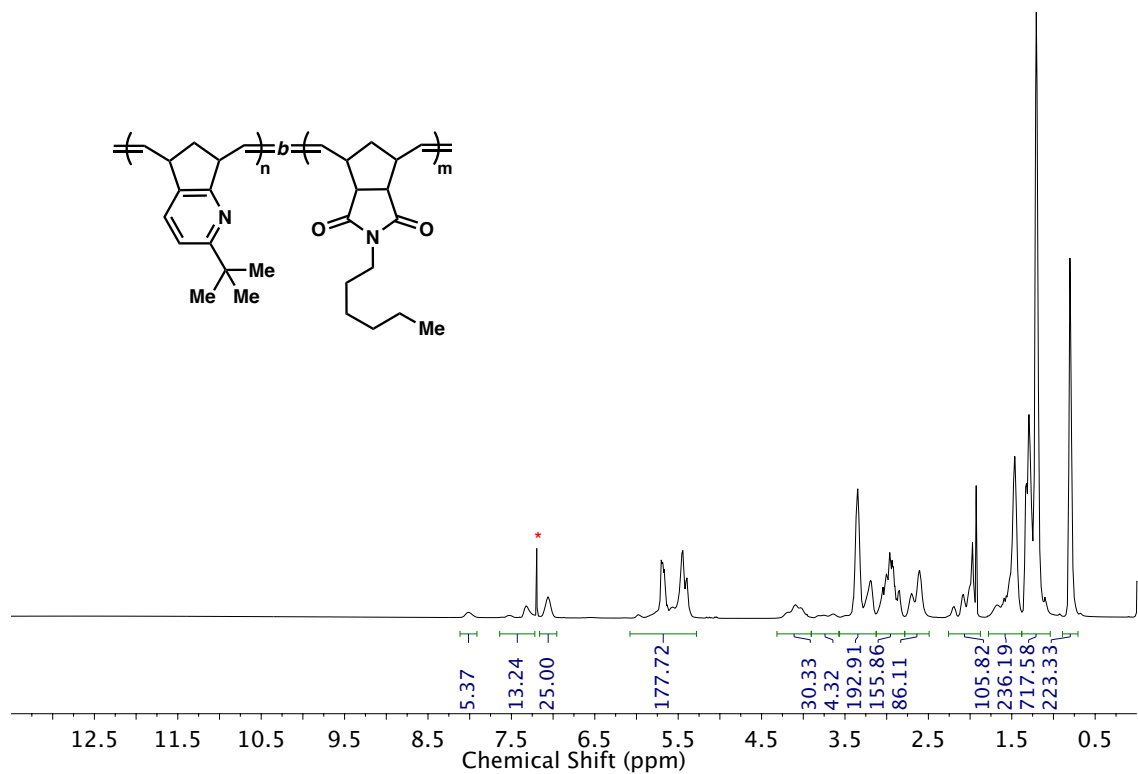


Figure S42. ¹H NMR (500 MHz, CDCl₃) of poly-1c-b-4.

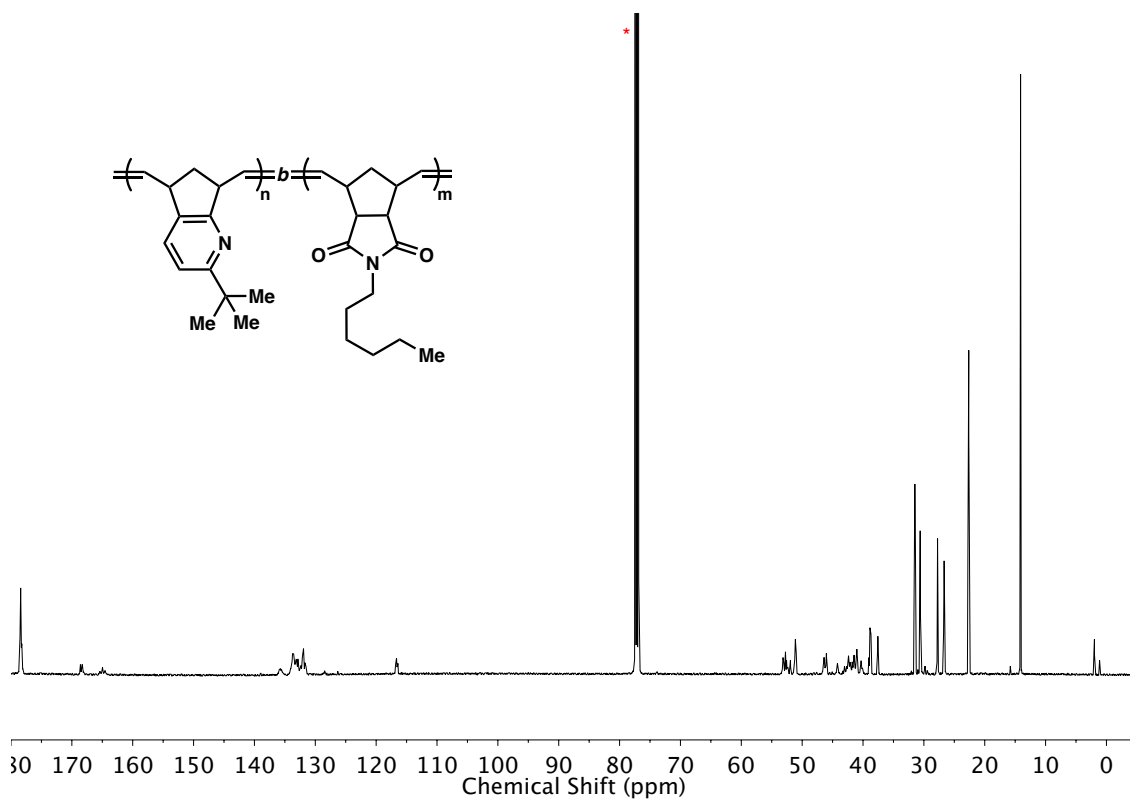


Figure S43. ^{13}C NMR (126 MHz, CDCl_3) of poly-**1c-b-4**.

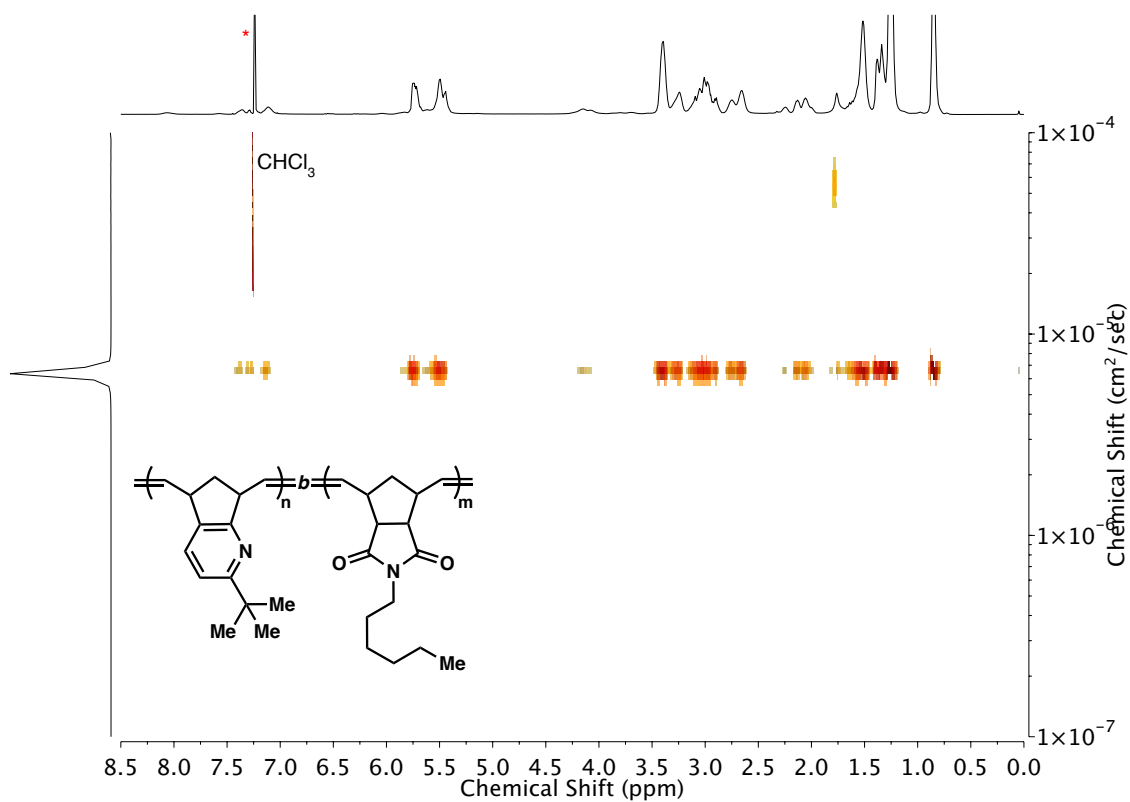


Figure S44. DOSY (500 MHz, CDCl_3) of poly-**1c-b-4**.