Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Efficient End-Group Functionalization and Diblock Copolymer Synthesis *via* Au(III) Polymer Reagents

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I. General Information

Unless otherwise stated, all materials were purchased and used as received from Fisher Scientific, Combi-Blocks, Alfa Aesar, Oakwood Chemicals, or Sigma Aldrich. Silver hexafluoroantimonate ($AgSbF_6$) was stored in a nitrogen atmosphere glovebox prior to use. Anhydrous triethylamine, DCM, and toluene were prepared by distillation over calcium hydride under an argon atmosphere. Anhydrous dioxane was purchased from Sigma-Aldrich. Caprolactone and MTBD were distilled under vacuum over activated 4 Å molecular sieves prior to use.

NMR spectra were recorded on the following: AV400 Bruker spectrometer at 400 (^{1}H), 376 ($^{19}F\{^{1}H\}$), 101 (^{13}C), and 121 MHz ($^{31}P\{^{1}H\}$), AV300 Bruker spectrometer at 300 (1H) and 75 MHz (^{13}C), and NEO600 Bruker spectrometer at 600 (^{1}H) and 243 ($^{31}P\{^{1}H\}$). Spectra are reported in δ (parts per million) relative to residual proteo-solvent signals for ^{1}H and H_3PO_4 (δ 0.00 ppm) for $^{31}P\{^{1}H\}$. All DOSY NMR spectra were recorded on a DRX 500 Bruker spectrometer at 500 MHz (^{1}H). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received for all NMR experiments.

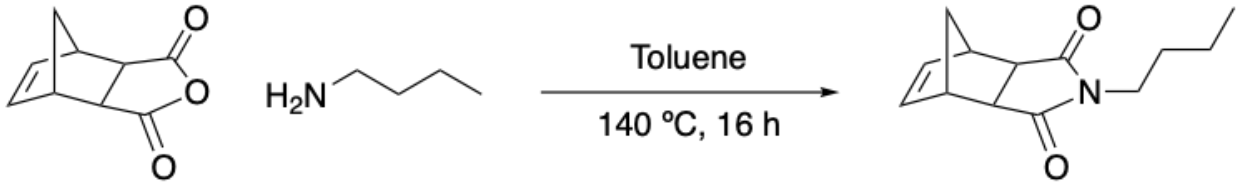
Column chromatography was performed on a Biotage Isolera One 3.0 autocolumn instrument using KP-Sil high-performance columns repacked using Silicycle silica (P60, particle size 40–63 μm, column sizes described in experimental). TLC was performed using Millipore Sigma silica plates (60F-254) using short-wave UV light or $KMnO_4$ as visualizing agents. Electrospray ionization (ESI) mass spectra were obtained using an Agilent 6530 QTOF-ESI in tandem with a 1260 Infinity LC. DART mass spectra were obtained using a Thermo Exactive Plus Orbitrap with IonSense ID-CUBE DART source. IR spectra were obtained using a PerkinElmer Spectrum One FT-IR Spectrometer.

DMF Size Exclusion Chromatography (SEC)/Gel Permeation Chromatography (GPC) was conducted on an Agilent 1260 Infinity II high performance liquid chromatography (HPLC) system with a Wyatt Optilab (RI and MALS detection), one Polymer Laboratories PLgel guard column, and two Polymer Laboratories PLgel 5 μm mixed D columns. The eluent was DMF (HPLC Grade, 99.7+%, Thermo Scientific Chemicals) containing LiBr (0.1 M) at 40 °C (Flow rate: 0.6 mL/min). THF SEC was conducted on a Shimadzu Prominence modular HPLC system with a Shimadzu Prominence-I LC 2030 C 3D autosampler, two MZ-Gel SDplus LS 5 μm, 300 × 8 mm linear columns, Wyatt DAWN HELOS-II, and a Wyatt Optilab T-rEX. The column temperature was set to 40 °C and flow rate was set to 0.7 mL/min. Molecular weight information was determined for data collected on either SEC instrument was obtained using a PMMA (Agilent Technologies, EasiVial PMMA, pre-weighed calibration kit) conventional calibration analysis.

MALDI-TOF spectra were obtained using a Bruker Ultraflex MALDI TOF-TOF. MALDI samples were prepared by combining 1 mg/mL solution of the polymer sample, 1 mg/mL dithranol, and NaTFA (100 mM) in a 5:25:1 v/v/v ratio. All solutions were prepared in THF.

II. Synthesis of monomers, catalysts, initiators, and terminating groups

Synthesis of *exo-n*-butylnorborneneimide (19)



A flame dried 250 mL round bottom flask was charged with a stir bar and equipped with a Dean-Stark apparatus. Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (2.0 g, 1 Eq, 12.2 mmol) was suspended in 60 mL of toluene, then *n*-butylamine (1.2 mL, 1 Eq, 12.2 mmol) was added to the flask, forming a light yellow suspension. This was heated at 140 ºC for 16 hours. The reaction was cooled to room temperature and further purified using flash column chromatography (100 g silica gel, 0-70% gradient of ethyl acetate against hexanes) to yield *exo-n*-butylnorborneneimide as an off white solid (2.52 g, 11.45 mmol, 94% yield).

Physical state: Off white solid
TLC ($KMnO_4$): R_f 0.77 (1:1 hexanes-ethyl acetate)
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.26 (t, *J* = 1.9 Hz, 2H), 3.49 – 3.39 (m, 2H), 3.25 (m, 2H), 2.65 (d, *J* = 1.4 Hz, 2H), 1.57 – 1.45 (m, 3H), 1.37 – 1.24 (m, 2H), 1.24 – 1.18 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 178.19, 137.93, 47.90, 45.27, 42.81, 38.60, 29.93, 20.32, 13.72.
HRMS (ESI/QTOF): $[M+H]^+$ calculated for $C_{13}H_{18}NO_2^+$ 220.1338, observed 220.1362.
IR (Film): 2960, 2876, 1768, 1689, 1435, 1394, 1358, 1341, 1286, 1263, 1190, 1137, 1103, 1017 cm^{-1}.

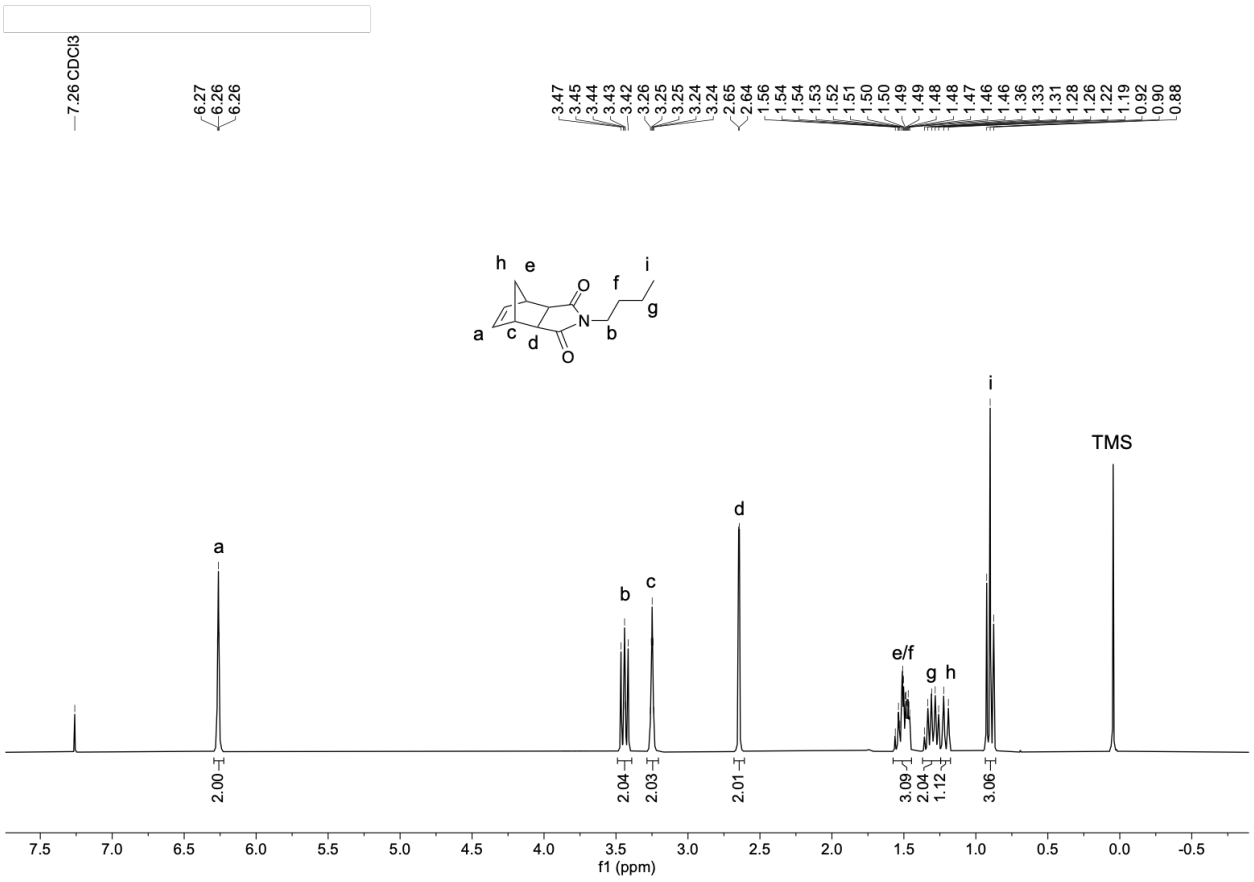


Figure S1. ^{1}H NMR spectrum of *exo-n*-butylnorborneneimide (**19**) in $CDCl_3$ at 25 ºC.

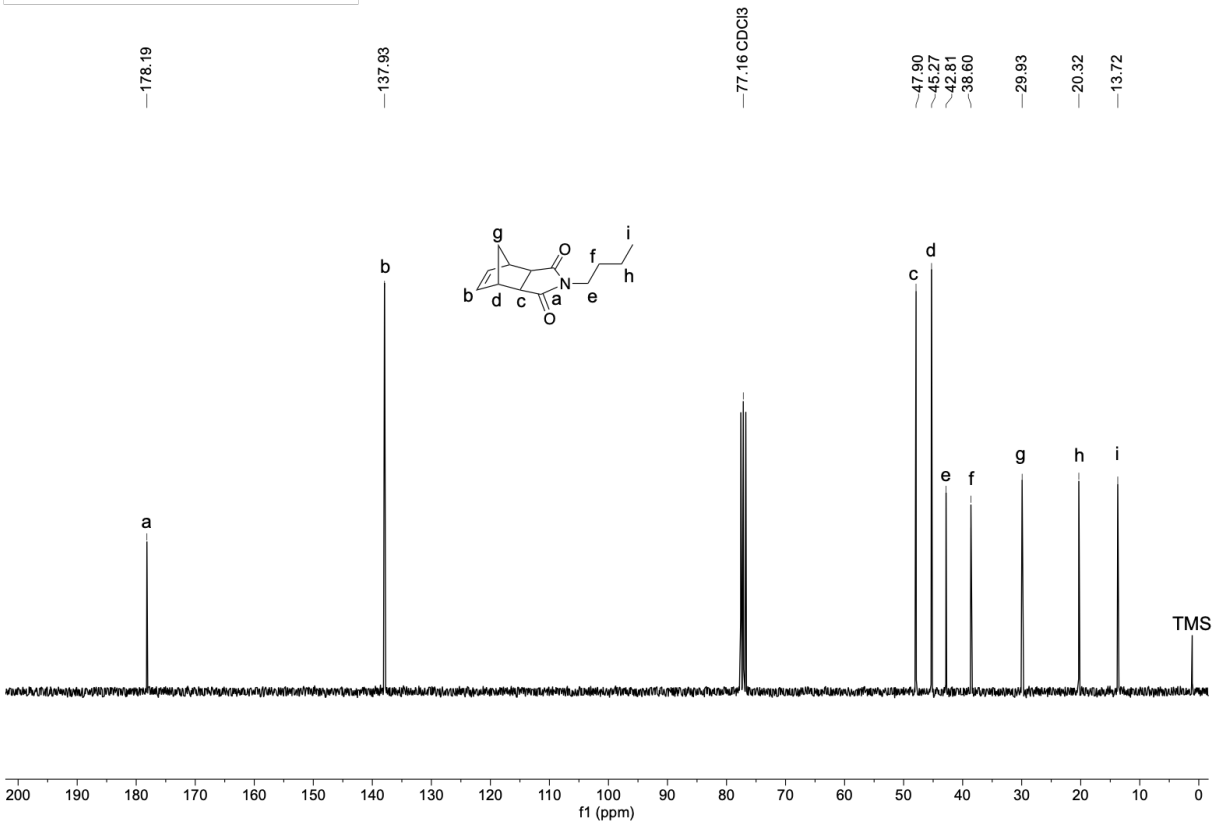
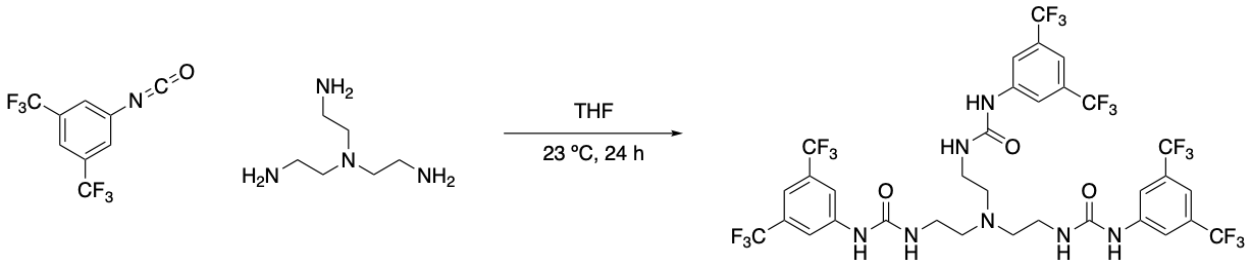


Figure S2. ^{13}C NMR spectrum of exo-n-butylnorborneneimide (**19**) in $CDCl_3$ at 25 ºC.

Synthesis of 3-O Trisurea (20)[1]



A flame dried two neck, 100 mL round bottom flask was charged with a stir bar and tris(2-aminoethyl)amine (400 mg, 1 Eq, 2.74 mmol) was dissolved in 20 mL of anhydrous THF. The 1-isocyanato-3,5-bis(trifluoromethyl)benzene (2.16 g, 1.18 mL, 3.1 Eq, 8.48 mmol) was dissolved in 5 mL of anhydrous THF and added to the round bottom flask at 23 ºC over 15 minutes *via* syringe pump. The reaction was left to stir at 23 ºC for 24 hours under an argon atmosphere. The reaction was subsequently concentrated under vacuum and purified using flash column chromatography (100 g silica gel, 0-10% gradient of methanol against DCM) to yield 3-O as a white solid (1.880 g, 2.137 mmol, 78% yield).

Physical state: White solid
TLC (UV): R_f 0.40 (9:1 DCM-methanol)
^{1}H NMR (400 MHz, Acetone-d_6): δ 8.80 (br s, 3H), 8.00 (d, *J* = 1.6 Hz, 6H), 7.41 (t, *J* = 1.6 Hz, 3H), 6.49 (t, *J* = 5.3 Hz, 3H), 3.36 (q, *J* = 5.5 Hz, 6H), 2.72 (d, *J* = 5.7 Hz, 6H).
^{19}F{^{1}H} NMR (376 MHz, Acetone-d_6): δ -63.74.
^{13}C NMR (101 MHz, Acetone-d_6): δ 156.31, 143.36, 132.28 (q, *J* = 32.9 Hz), 124.39 (q, *J* = 271.9 Hz), 118.34, 114.83, 55.71, 39.16.
HRMS (DART): $[M+H]^+$ calculated for $C_{33}H_{28}F_{18}N_7O_3^+$ 912.1966, observed 912.1965.

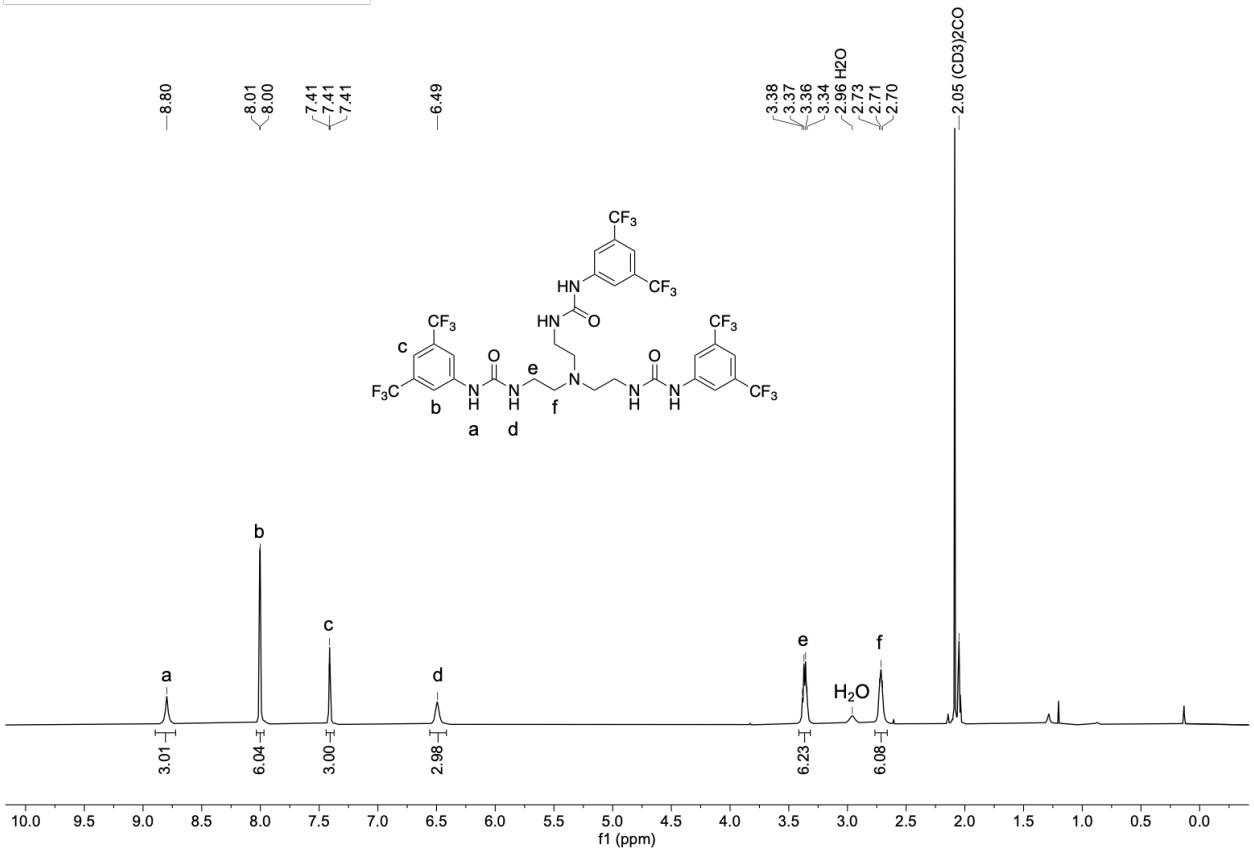


Figure S3. ^{1}H NMR spectrum of 3-O (**20**) in acetone-d_6 at 25 ºC.

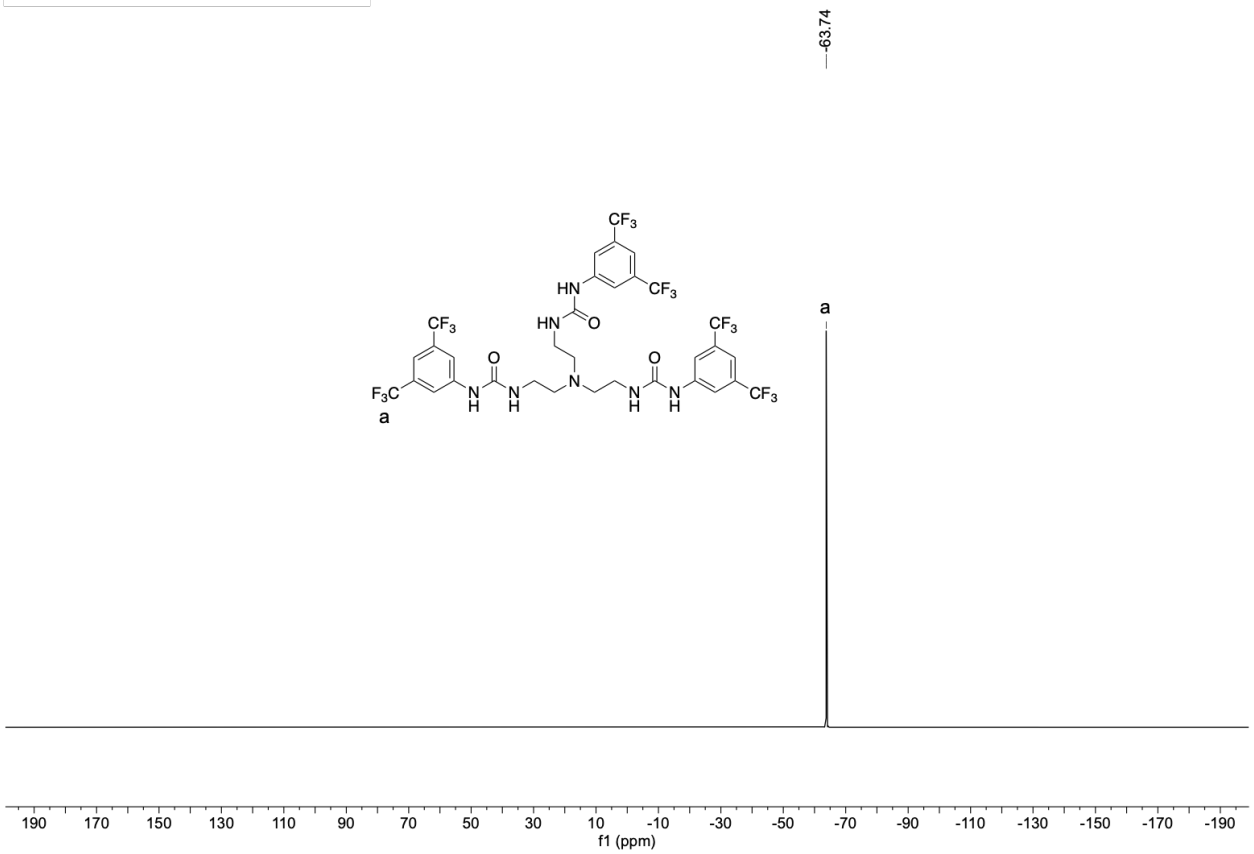


Figure S4. $^{19}F\{^{1}H\}$ NMR spectrum of 3-O (**20**) in acetone-d_6 at 25 ºC.

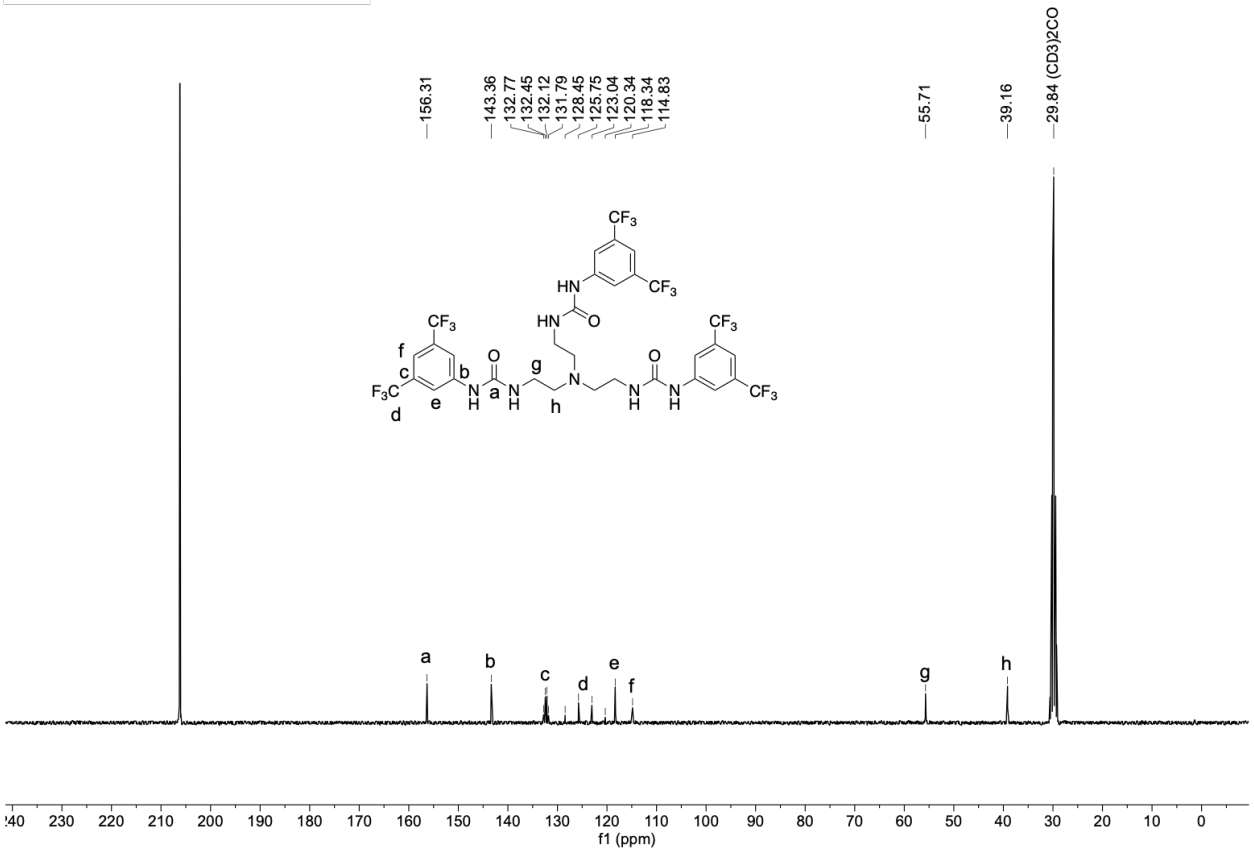
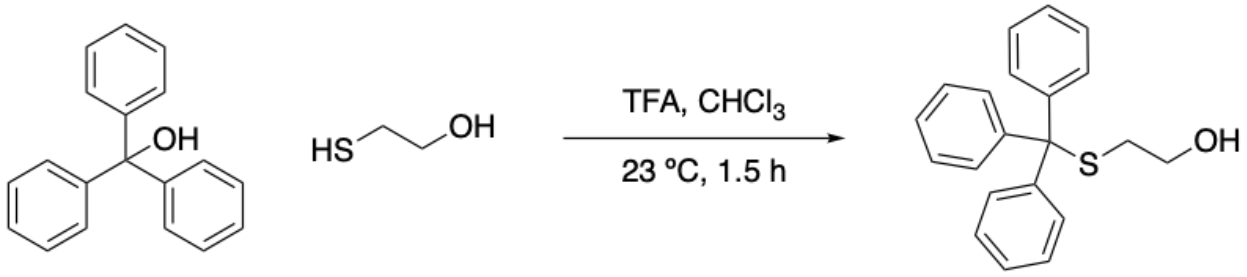


Figure S5. ^{13}C NMR spectrum of 3-O (**20**) in acetone-d_6 at 25 ºC.

Synthesis of 2-(tritylthio)ethan-1-ol (11)



A 100 mL round bottom flask was charged with a stir bar and 30 mL of chloroform was added to the flask followed by 2-mercaptoethan-1-ol (630.2 mg, 568 µL, 1.4 Eq, 8.066 mmol). This was left to stir at 23 ºC for a minute, then triphenylmethanol (1.500 g, 1 Eq, 5.762 mmol) was added as a solid to the flask, creating a light brown solution. Trifluoroacetic acid (7.400 g, 5.000 mL, 11.26 Eq, 64.90 mmol) was then added to the solution, immediately forming a bright yellow color. This was left to stir under an open atmosphere at 23 ºC for 90 minutes. The contents of the reaction were concentrated under vacuum, then the material was carefully neutralized with a saturated sodium bicarbonate solution. The material was transferred to a separatory funnel and extracted with ethyl acetate (200 mL) then washed with brine (50 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, then concentrated under vacuum. The product was further purified using flash column chromatography (100 g silica gel 0-60% gradient of ethyl acetate against hexanes) to afford 2-(tritylthio)ethan-1-ol as a white solid (1.197 g, 3.745 mmol, 65% yield).

Physical state: White solid
TLC (UV): R_f 0.32 (3:1 hexanes-ethyl acetate)
^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.47 – 7.40 (m, 6H), 7.34 – 7.19 (m, 9H), 3.36 (q, J = 6.2 Hz, 2H), 2.43 (t, J = 6.3 Hz, 2H), 1.59 (t, J = 6.1 Hz, 1H).
^{13}C NMR (75 MHz, CD_2Cl_2): δ 145.28, 129.97, 128.31, 127.12, 66.97, 61.19, 35.56.
HRMS (DART): $[M+H]^+$ calculated for $C_{21}H_{21}OS^+$ 321.1313, observed 321.1318.
IR (Film): 3357, 3056, 2948, 1595, 1488, 1443, 1183, 1034 cm^{-1}.

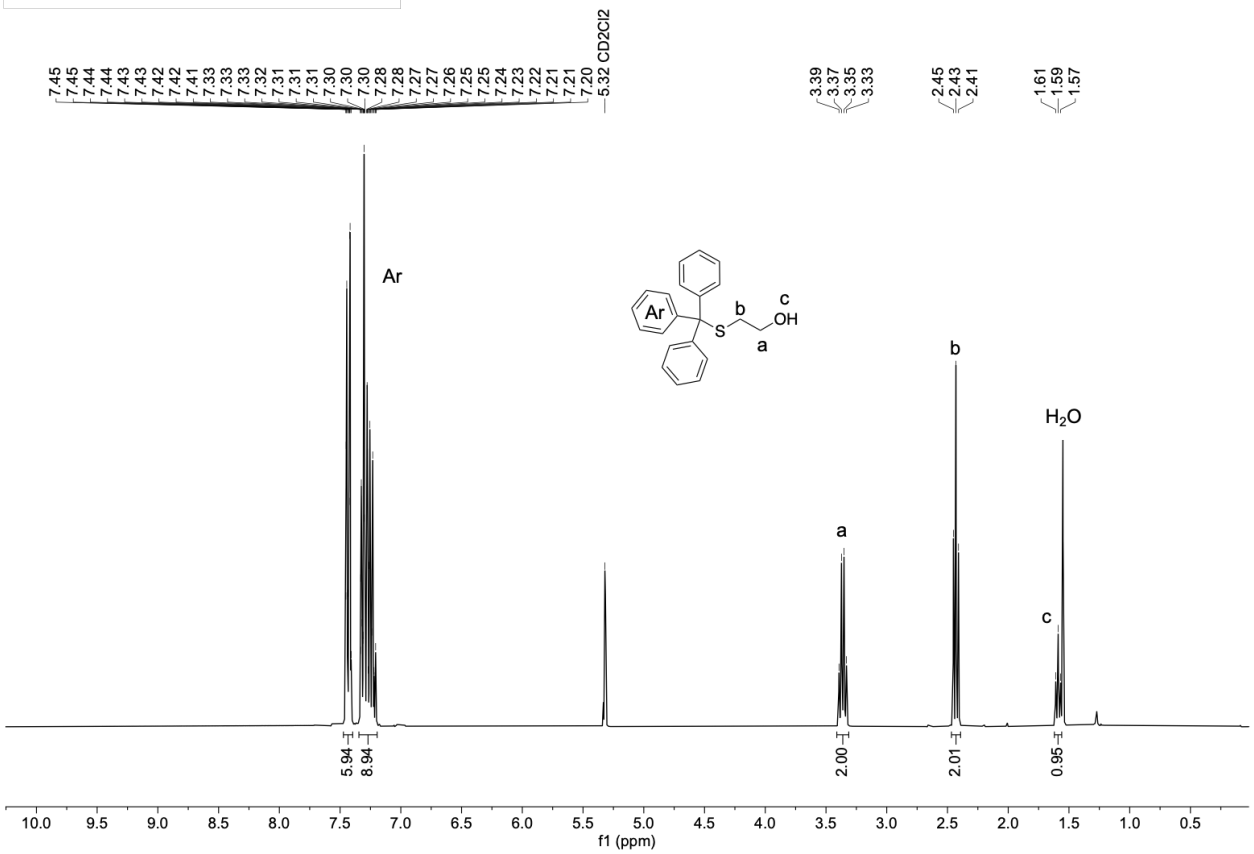


Figure S6. ^{1}H NMR spectrum of 2-(tritylthio)ethan-1-ol (**11**) in CD_2Cl_2 at 25 ºC.

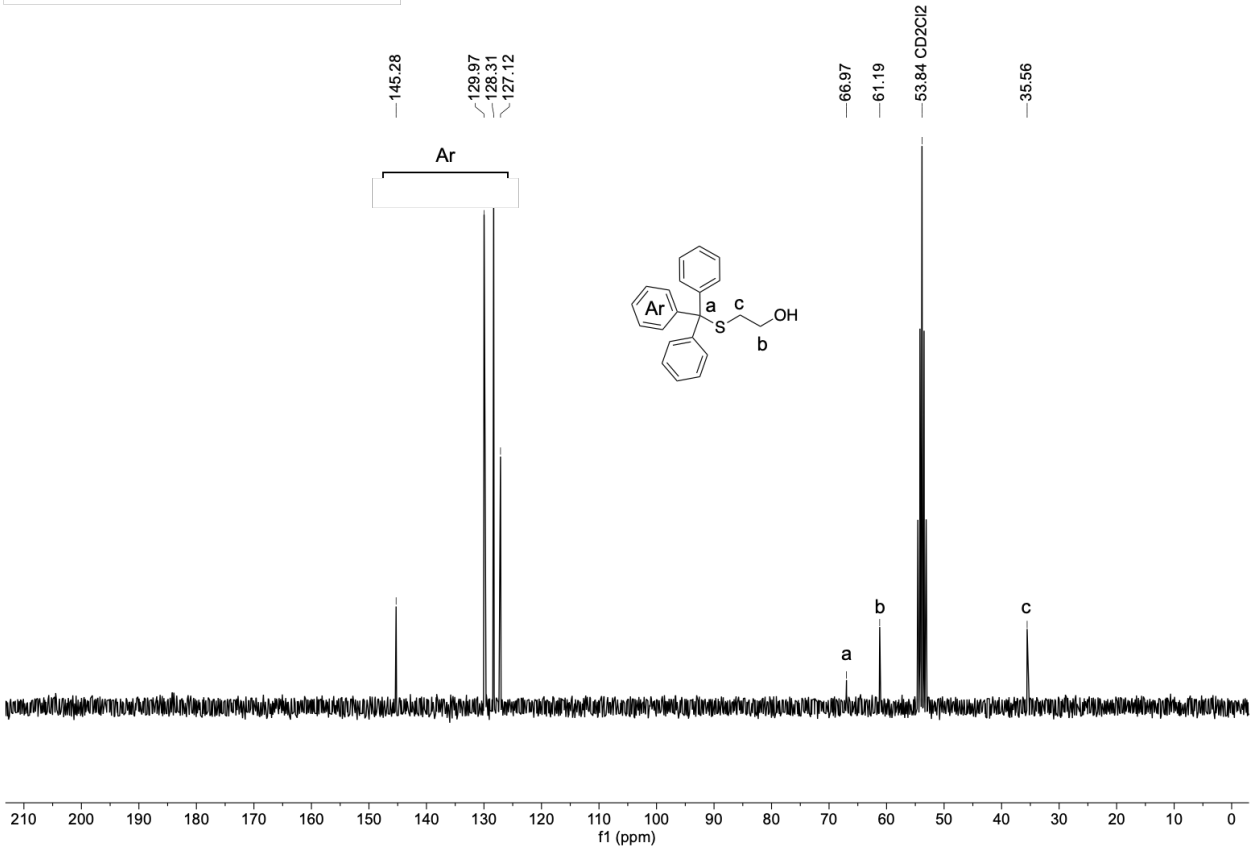
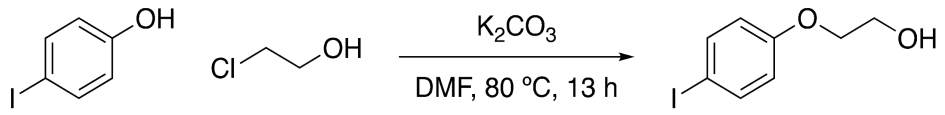


Figure S7. ^{13}C NMR spectrum of 2-(tritylthio)ethan-1-ol (**11**) in CD_2Cl_2 at 25 ºC.

Synthesis of 2-(4-iodophenoxy)ethan-1-ol (2)



A 50 mL round bottom flask was charged with a stir bar and 4-iodophenol (750.0 mg, 1 Eq, 3.409 mmol) and potassium carbonate (1.649 g, 3.5 Eq, 11.93 mmol) were added to the flask. The solids were dissolved in 10 mL of DMF, creating a white suspension. This mixture was headed at 50 ºC for five minutes, then 2-chloroethanol (274 µL, 1.2 Eq, 4.091 mmol) was added to the solution at 50 ºC. The solution was left to heat at 80 ºC for 13 hours. The contents of the reaction were cooled down and transferred to a separatory funnel with ethyl acetate (200 mL), then the organic layer was washed with water (50 mL), saturated sodium carbonate (50 mL), and brine (50 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The product was further purified using flash column chromatography (100 g silica gel, 0-60% gradient of ethyl acetate against hexanes) to afford 2-(4-iodophenoxy)ethan-1-ol as an off white solid (500 mg, 1.909 mmol, 56% yield).

Physical state: Off white solid
TLC (UV): R_f 0.42 (1:1 hexanes-ethyl acetate)
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 – 7.54 (m, 2H), 6.83 – 6.74 (m, 2H), 4.86 (t, *J* = 5.5 Hz, 1H), 3.95 (m, 2H), 3.74 – 3.64 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 158.60, 137.91, 117.29, 82.90, 69.65, 59.44.
HRMS (ESI/QTOF): $[M+H]^+$ calculated for $C_{12}H_{10}IO_2^+$ 264.9725, observed 264.9763.
IR (Film): 3303, 2937, 2863, 1585, 1485, 1456, 1285, 1244, 1175, 1083, 1051 cm^{-1}.

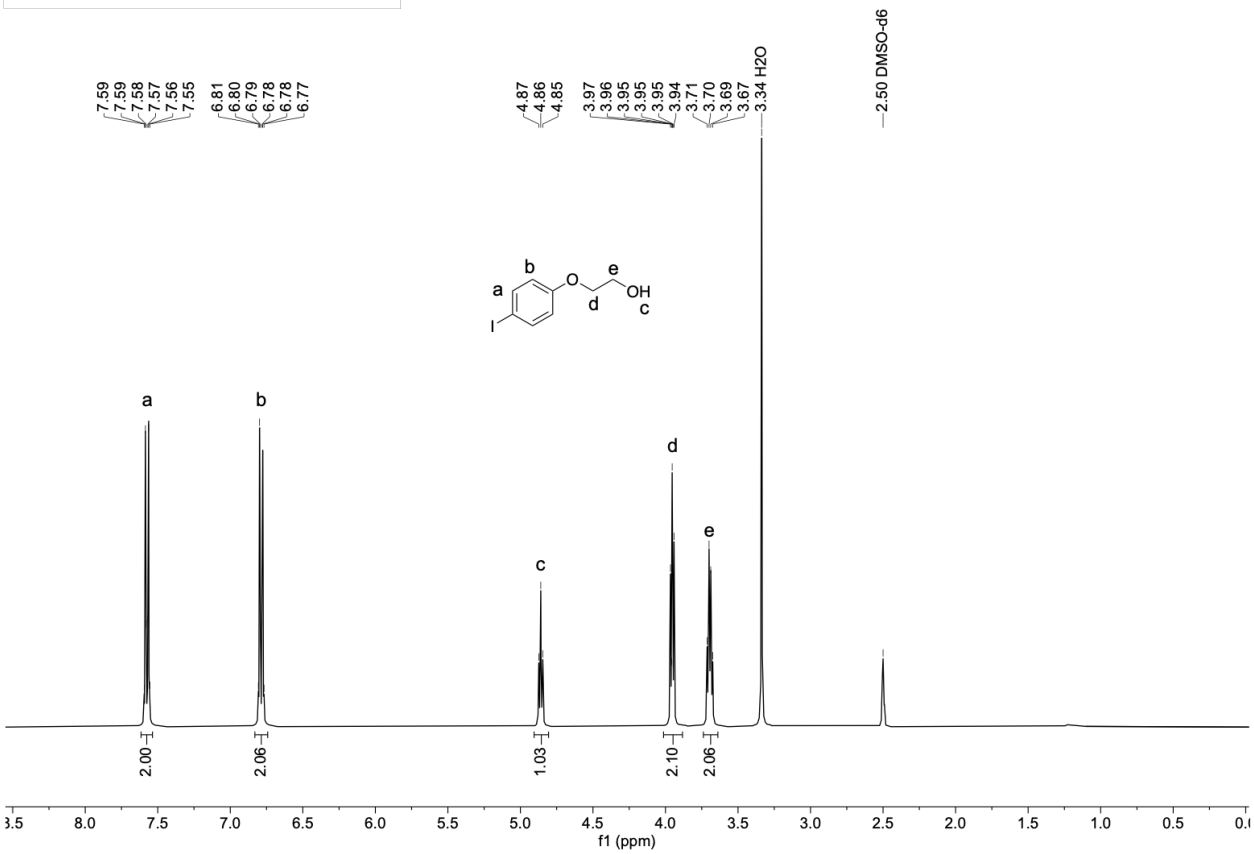


Figure S8. ^{1}H NMR spectrum of 2-(4-iodophenoxy)ethan-1-ol (**2**) in DMSO-d_6 at 25 ºC.

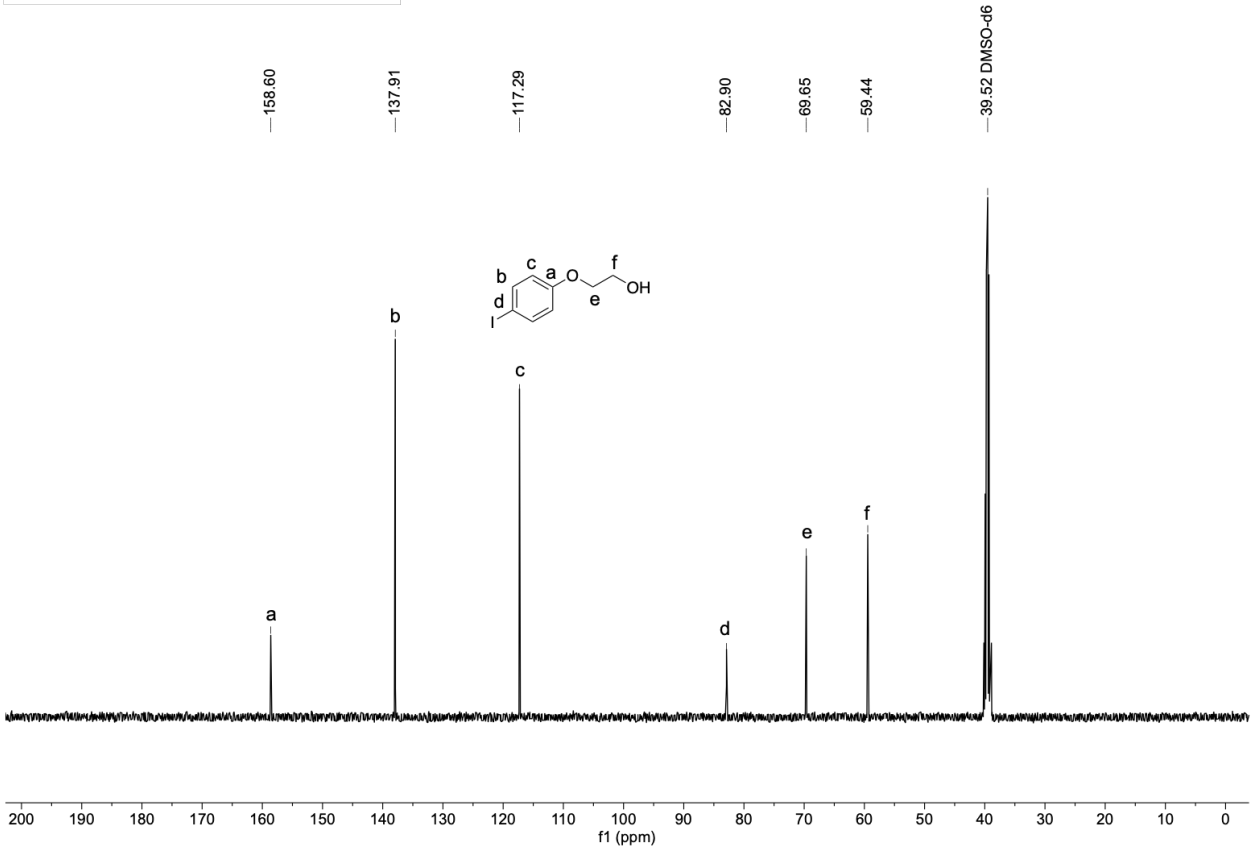
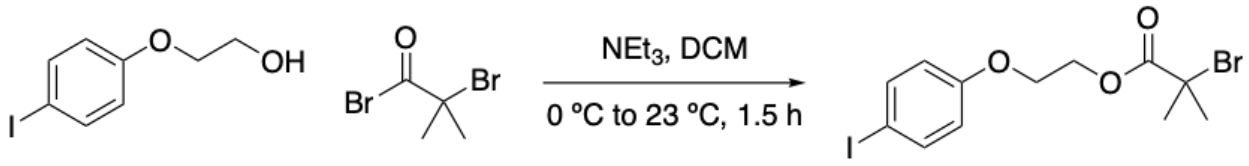


Figure S9. ^{13}C NMR spectrum of 2-(4-iodophenoxy)ethan-1-ol (**2**) in DMSO-d_6 at 25 ºC.

Synthesis of 2-(4-iodophenoxy)ethyl 2-bromo-2-methylpropanoate (5)



A flame dried two neck 50 mL round bottom flask was charged with a stir bar and 2-(4-iodophenoxy)ethan-1-ol (300 mg, 1 Eq, 1.14 mmol) was added to the flask and dissolved in 7 mL of anhydrous DCM, forming a clear solution. Anhydrous triethylamine (190 µL, 1.2 Eq, 1.36 mmol) was added to the flask, forming a light yellow solution. The solution was cooled to 0 ºC under an argon atmosphere. Separately, 2-bromo-2-methylpropanoyl bromide (181 µL, 1.2 Eq, 1.36 mmol) was dissolved in 3 mL of anhydrous DCM, then this was added to the solution *via* syringe pump over a period of 10 minutes with no color change. This was left to room up to 23 ºC where it was stirred for 90 minutes under an argon atmosphere. The contents of the reaction were transferred to a separatory funnel (150 mL DCM) where the organic layer was washed once with brine (50 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The product was further purified using flash column chromatography (50 g silica gel, 0-50% gradient of ethyl acetate against hexanes) to afford 2-(4-iodophenoxy)ethyl 2-bromo-2-methylpropanoate as a white solid (429 mg, 1.037 mmol, 91% yield).

Physical state: White solid
TLC (UV): R_f 0.67 (2:1 hexanes-ethyl acetate)
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.50 (m, 2H), 6.75 – 6.65 (m, 2H), 4.55 – 4.47 (m, 2H), 4.22 – 4.14 (m, 2H), 1.93 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 171.77, 158.52, 138.47, 117.30, 83.59, 65.89, 64.13, 55.55, 30.84.
HRMS (ESI/QTOF): $[M+Na]^+$ calculated for $C_{12}H_{14}BrINaO_3^+$ 434.9069, observed 434.9073.
IR (Film): 2970, 1735, 1586, 1485, 1461, 1388, 1371, 1275, 1242, 1161, 1108, 1073, 1058 cm^{-1}.

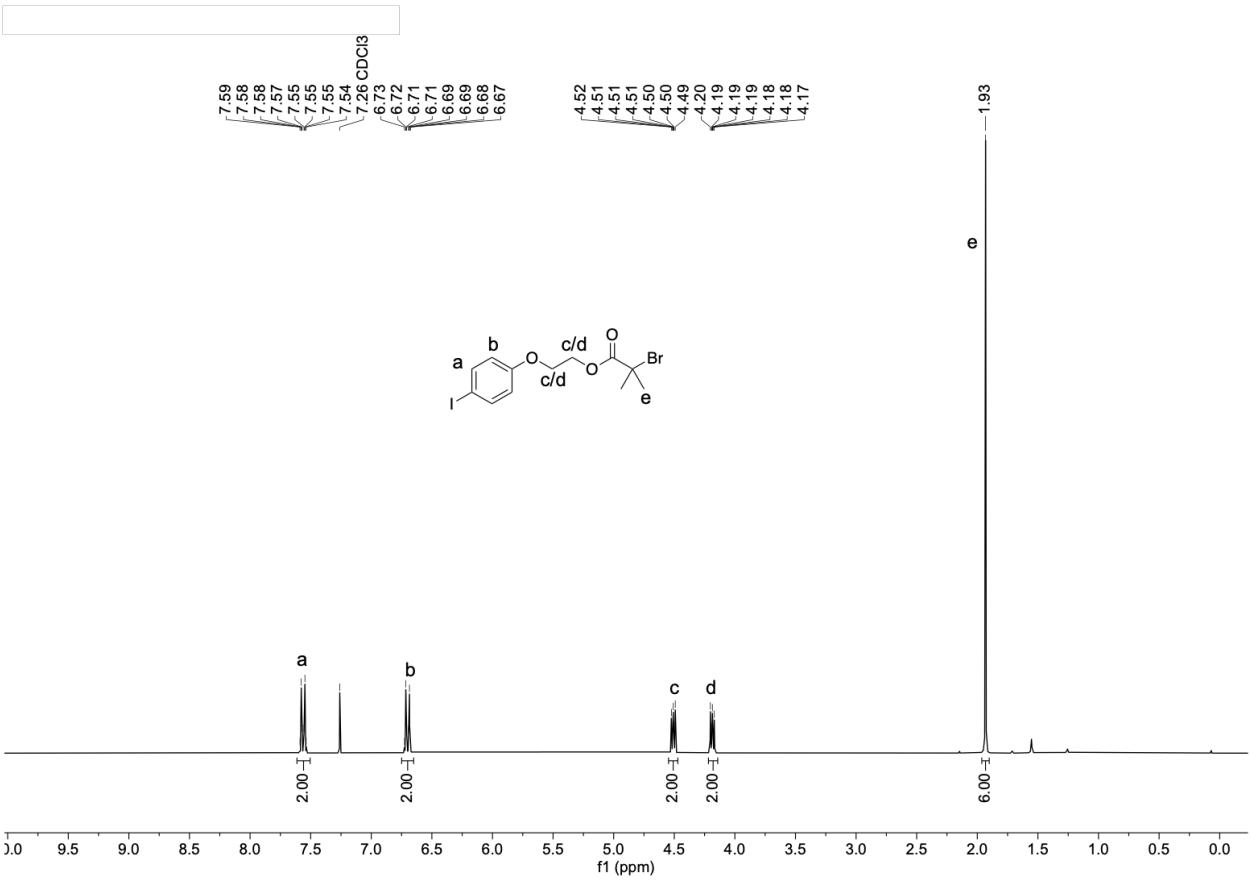


Figure S10. ^{1}H NMR spectrum of 2-(4-iodophenoxy)ethyl 2-bromo-2-methylpropanoate (**5**) in $CDCl_3$ at 25 ºC.

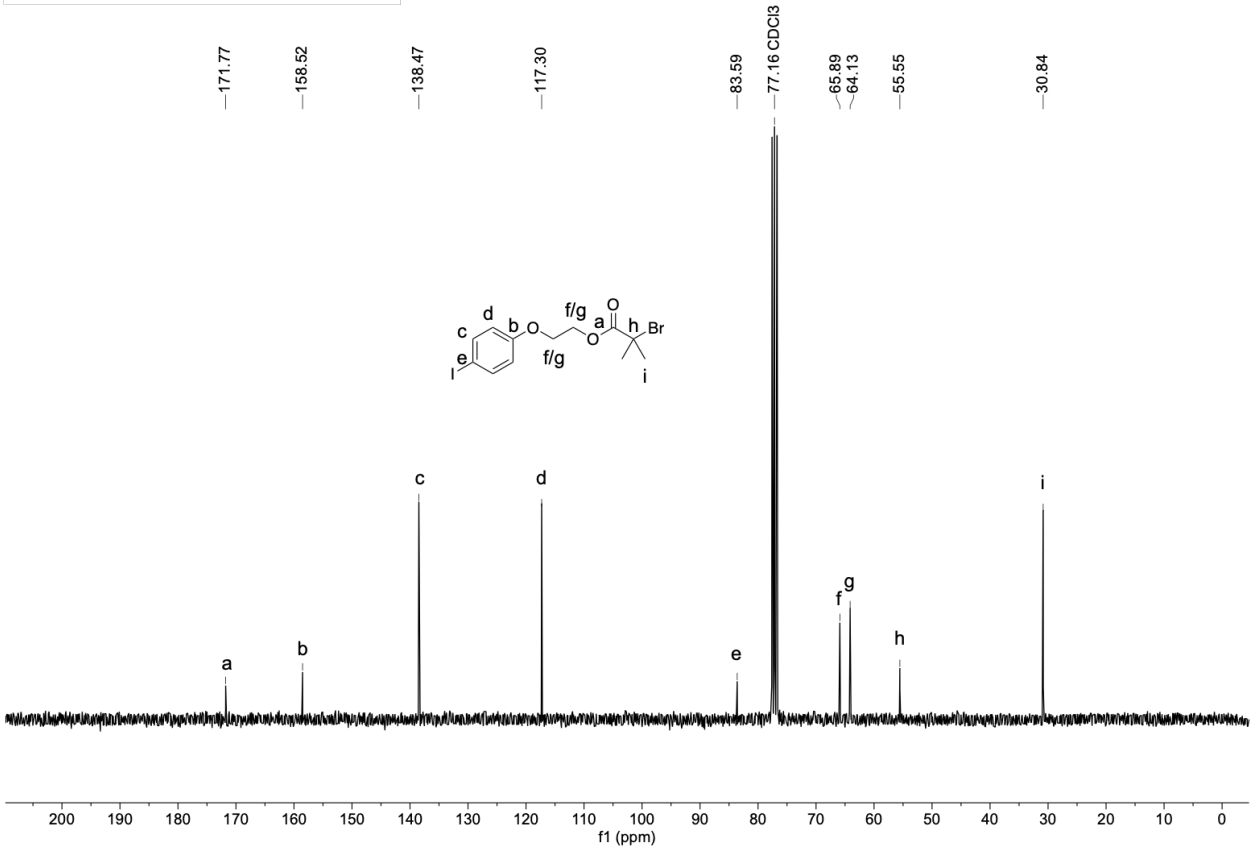
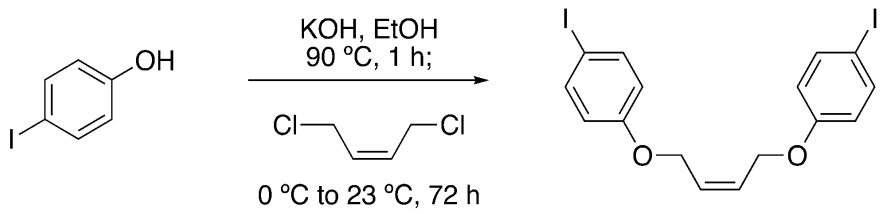


Figure S11. ^{13}C NMR spectrum of 2-(4-iodophenoxy)ethyl 2-bromo-2-methylpropanoate (**5**) in $CDCl_3$ at 25 ºC.

Synthesis of (*Z*)-1,4-bis(4-iodophenoxy)but-2-ene (4)



A one neck 250 mL round bottom flask was charged with a stir bar and 4-iodophenol (7.261 g, 3 Eq, 33.00 mmol) and potassium hydroxide (1.790 g, 2.9 Eq, 31.90 mmol) were added as solid to the flask. 40 mL of ethanol was added to the flask, and the solution was refluxed at 90 ºC for one hour. The flask was cooled to 0 ºC, then (Z)-1,4-dichlorobut-2-ene (1.157 mL, 1 Eq, 11.00 mmol) was added to the flask dropwise over three minutes. The solution was allowed to warm up to 23 ºC where it was left to stir for 72 hours (Product formation monitored by HPLC, near quantitative conversion after 72 hours). The contents of the reaction were diluted with ethyl acetate (300 mL) and transferred to a separatory funnel where the organic layer was washed with brine (2 x 100 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The product was further purified using flash column chromatography (350 g silica gel, 0-20% gradient of DCM against hexanes) to afford (Z)-1,4-bis(4-iodophenoxy)but-2-ene as a white solid (3.799 g, 7.700 mmol, 70% yield).

Physical state: White solid
TLC (UV): R_f 0.83 (1:1 hexanes-DCM)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.51 (m, 4H), 6.74 – 6.62 (m, 4H), 5.91 (m, 2H), 4.65 – 4.60 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.35, 138.46, 128.54, 117.20, 83.38, 64.38.
HRMS (DART): $[M]^+$ calculated for $C_{16}H_{14}I_2O_2^+$ 491.9083, observed 491.9087.
IR (Film): 3058, 2917, 2872, 1582, 1570, 1481, 1452, 1414, 1398, 1375, 1341, 1298, 1281, 1231, 1172, 1112, 1059, 1032 cm^{-1}.

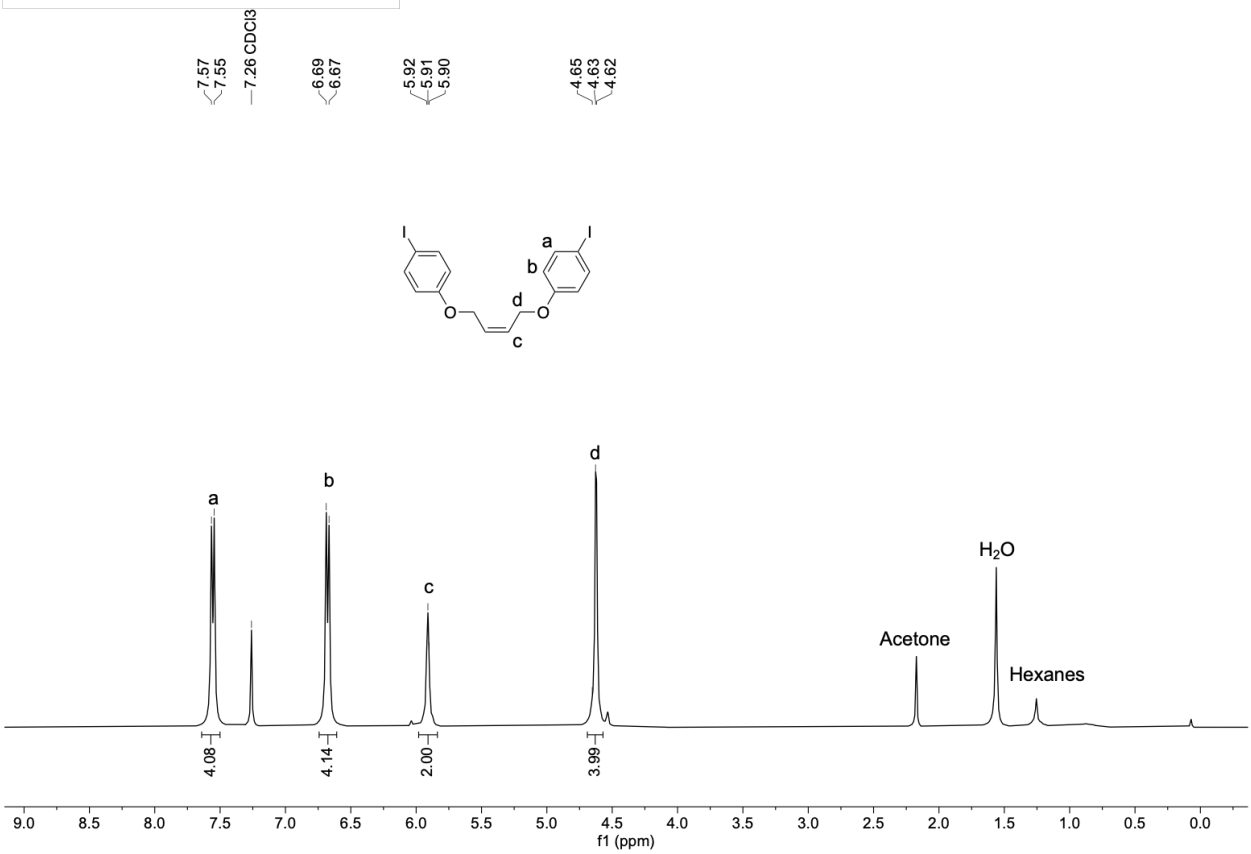


Figure S12. ^{1}H NMR spectrum of (*Z*)-1,4-bis(4-iodophenoxy)but-2-ene (**4**) in $CDCl_3$ at 25 ºC.

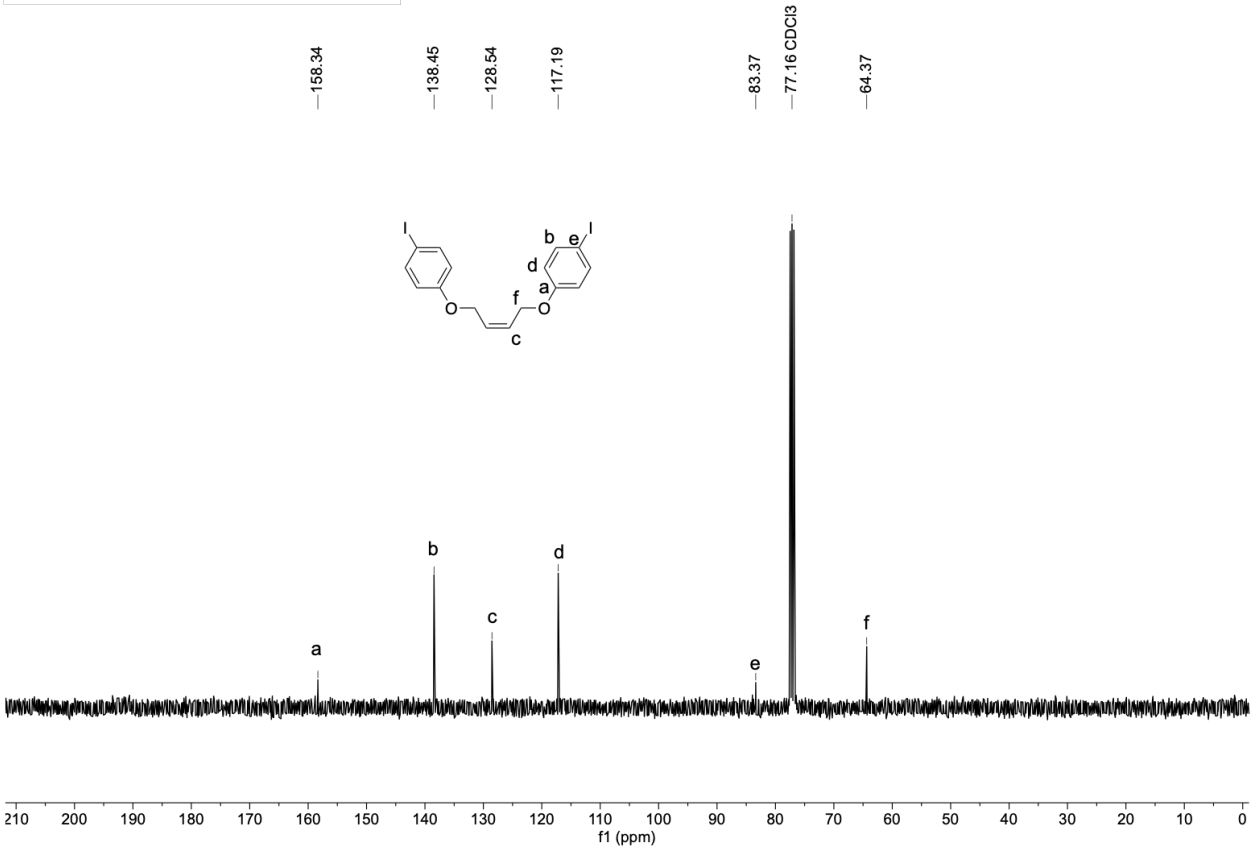
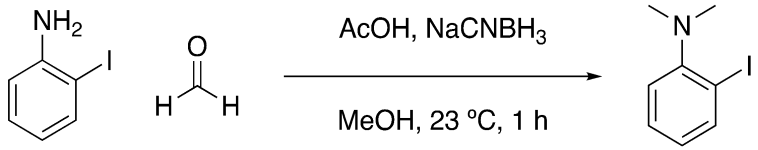


Figure S13. ^{13}C NMR spectrum of (*Z*)-1,4-bis(4-iodophenoxy)but-2-ene (**4**) in $CDCl_3$ at 25 ^{o}C.

III. Synthesis of (Me-DalPhos)Au^{I}Cl and thiol-containing small molecules

Synthesis of 2-iodo-*N*,*N*-dimethylaniline[2] (21)



A one neck 1 L round bottom flask was charged with a stir bar, then 2-iodoaniline (10.000 g, 1 Eq, 45.656 mmol) was dissolved in 400 mL of methanol. Formaldehyde (34.09 mL, 10 Eq, 456.56 mmol, 37 wt. % in water) and acetic acid (13.1 mL, 5 Eq, 228.28 mmol) were added to the flask and left to stir for ten minutes at 23 ºC. Sodium cyanoborohydride (11.48 g, 4 Eq, 182.62 mmol) was added in portions over a 15 minute period, then this was left to stir for one hour at 23 ºC. The reaction was concentrated under vacuum and carefully pH adjusted to pH 8.0 using 1 M $NaHCO_3$. The product was transferred to a separatory with ethyl acetate (300 mL), then the organic layer was washed with $NaHCO_3$ (2 x 75 mL) and brine (100 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The resulting product was further purified by vacuum distillation at 85 ºC to afford a clear liquid (9.445 g, 38.351 mmol, 84% yield).

Physical state: Clear liquid
TLC (UV): R_f 0.67 (5:1 hexanes-ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 (m, 1H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.77 (m, 1H), 2.77 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.10, 140.33, 129.19, 125.12, 120.61, 97.27, 45.12.
HRMS (ESI/QTOF): $[M+H]^+$ calculated for $C_8H_{11}IN^+$ 247.9936, observed 247.9963.
IR (Neat): 2981, 2939, 2857, 2826, 2777, 1579, 1468, 1450, 1314, 1183, 1157, 1110, 1094, 1045, 1011 cm^{-1}.

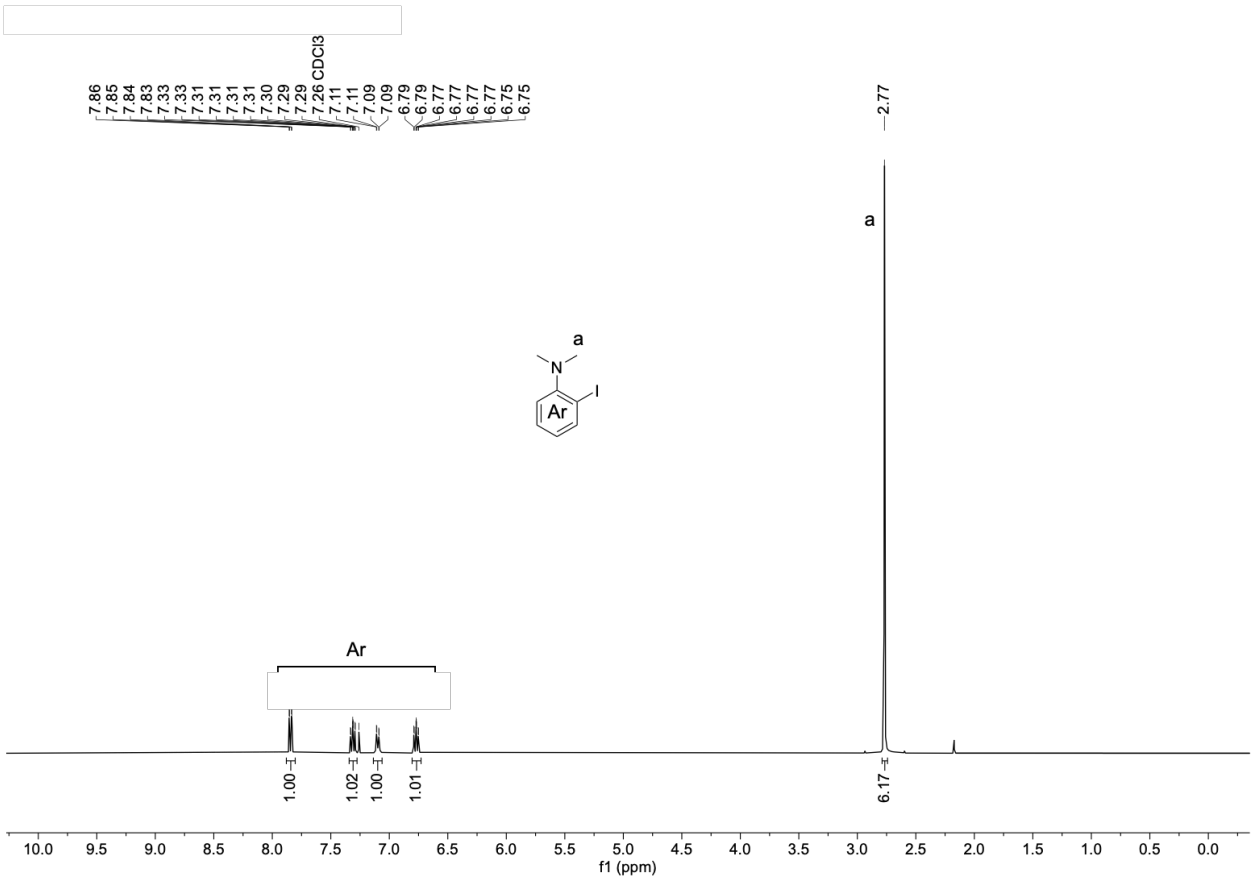


Figure S14. ^{1}H NMR spectrum of 2-iodo-*N*,*N*-dimethylaniline (**21**) in $CDCl_3$ at 25 ºC.

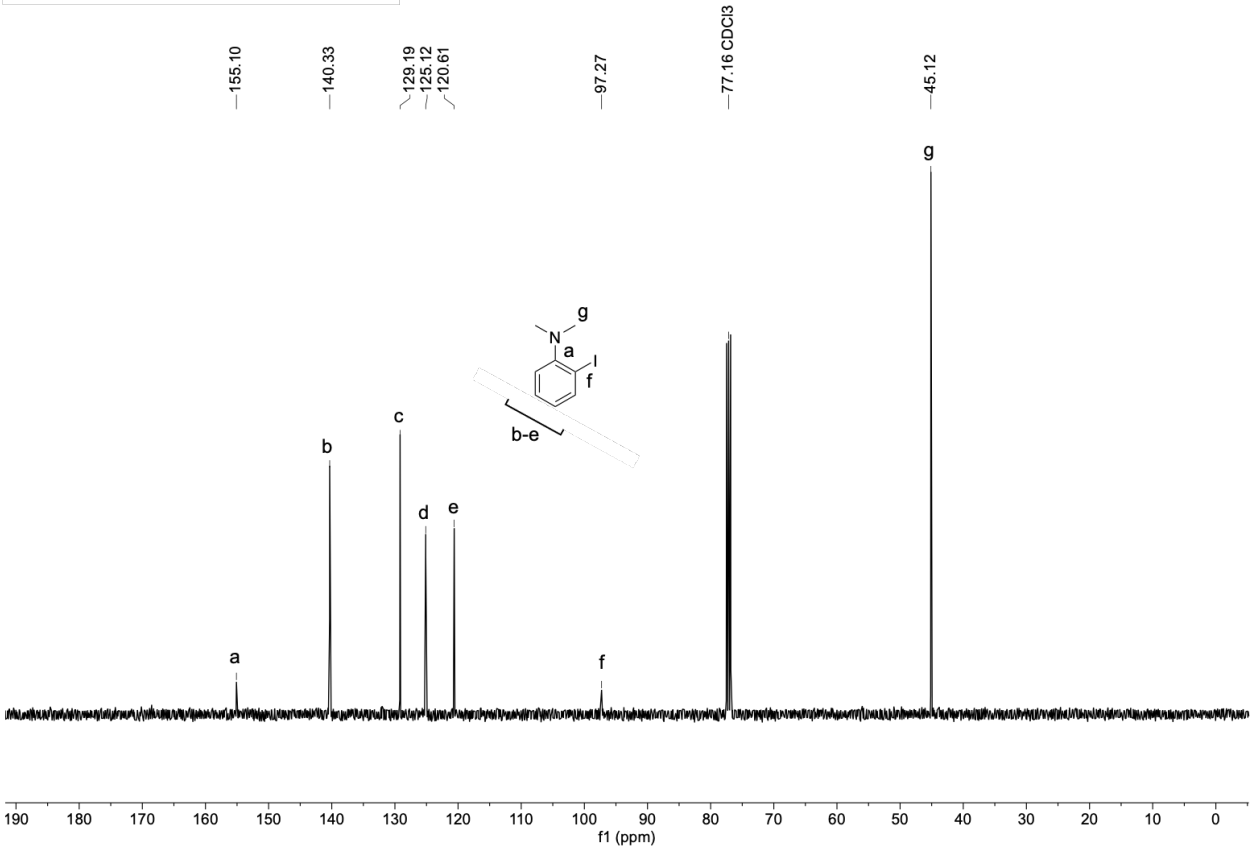
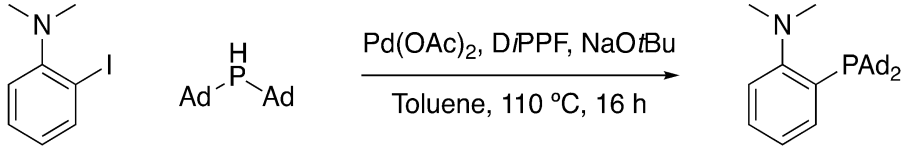


Figure S15. ^{13}C NMR spectrum of 2-iodo-*N*,*N*-dimethylaniline (**21**) in $CDCl_3$ at 25 ºC.

Synthesis of Me-DalPhos[3] (22)



Inside of a nitrogen atmosphere in a glovebox, $Pd(OAc)_2$ (16.7 mg, 0.025 Eq, 74.4 µmol) and D*i*PPF (37.3 mg, 0.030 Eq, 89.3 µmol) were added as solids to a one dram vial charged with a stir bar, then the solids were dissolved in 400 µL of anhydrous toluene and left to stir at 23 ºC for 15 minutes. Separately, di-1-adamantylphosphine (900 mg, 1 Eq, 2.98 mmol) and NaO*t*Bu (429 mg, 1.5 Eq, 4.46 mmol) were added as solids to a scintillation vial charged with a stir bar and subsequently dissolved in 8 mL of anhydrous toluene where this was left to stir for 15 minutes. 2-iodo-*N*,*N*-dimethylaniline (757 mg, 103 Eq, 3.07 mmol) was weighed out into a scintillation vial charged with a stir bar and diluted with 2 mL of anhydrous toluene. The $Pd(OAc)_2$/D*i*PPF solution was transferred to the scintillation vial containing the 2-iodo-*N*,*N*-diemethylaniline, then the $HPAd_2$/NaO*t*Bu suspension was transferred to the scintillation vial. Each vial was washed with 500 µL (1 mL total) of anhydrous toluene. The scintillation vial was sealed with electrical tape and removed from the glovebox where it was refluxed in a closed vial at 110 ºC for 16 hours. The reaction was cooled to 23 ºC and subsequently concentrated under vacuum. The solid was redissolved in chloroform and filtered through a plug of Celite, then the product was concentrated under vacuum. The product was suspended in cold hexanes and transferred to a medium grain fritted funnel where the product was rinsed with cold diethyl ether (2 x 5 mL), cold acetonitrile (2 x 5 mL), and cold diethyl ether (2 x 5 mL). The residual solid on the frit was then dried under vacuum to afford the product as a white solid (893 mg, 2.116 mmol, 71% yield).

Physical state: White solid
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 – 7.65 (m, 1H), 7.33 – 7.25 (m, 1H), 7.20 – 7.10 (m, 1H), 7.06 – 6.95 (m, 1H), 2.69 (s, 6H), 2.00 – 1.84 (m, 18H), 1.71 – 1.62 (m, 12H).
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 20.26.
HRMS (DART): $[M+H]^+$ calculated for $C_{28}H_{41}NP^+$ 422.2977, observed 422.2972.

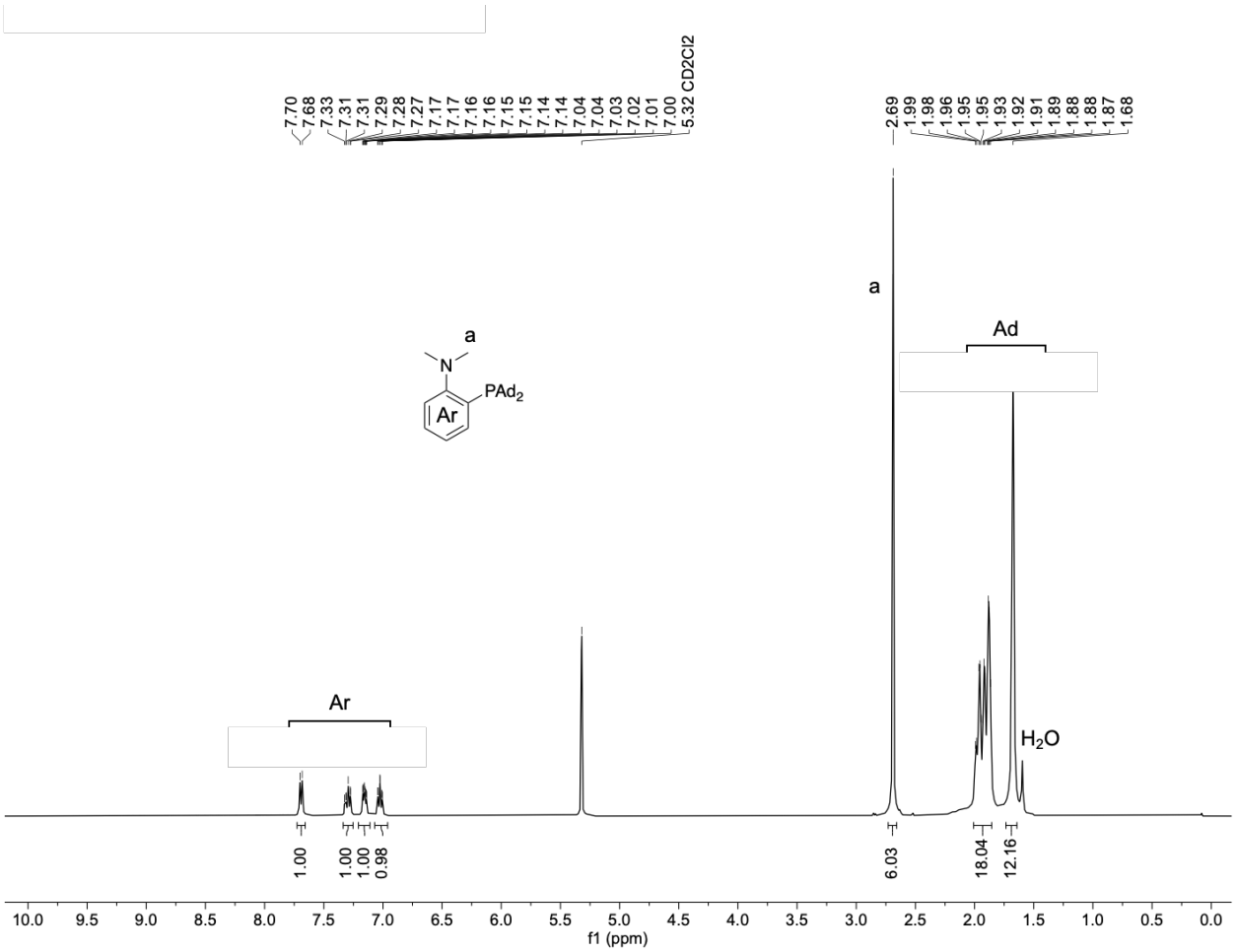


Figure S16. ^{1}H NMR spectrum of Me-DalPhos (**22**) in CD_2Cl_2 at 25 ºC.

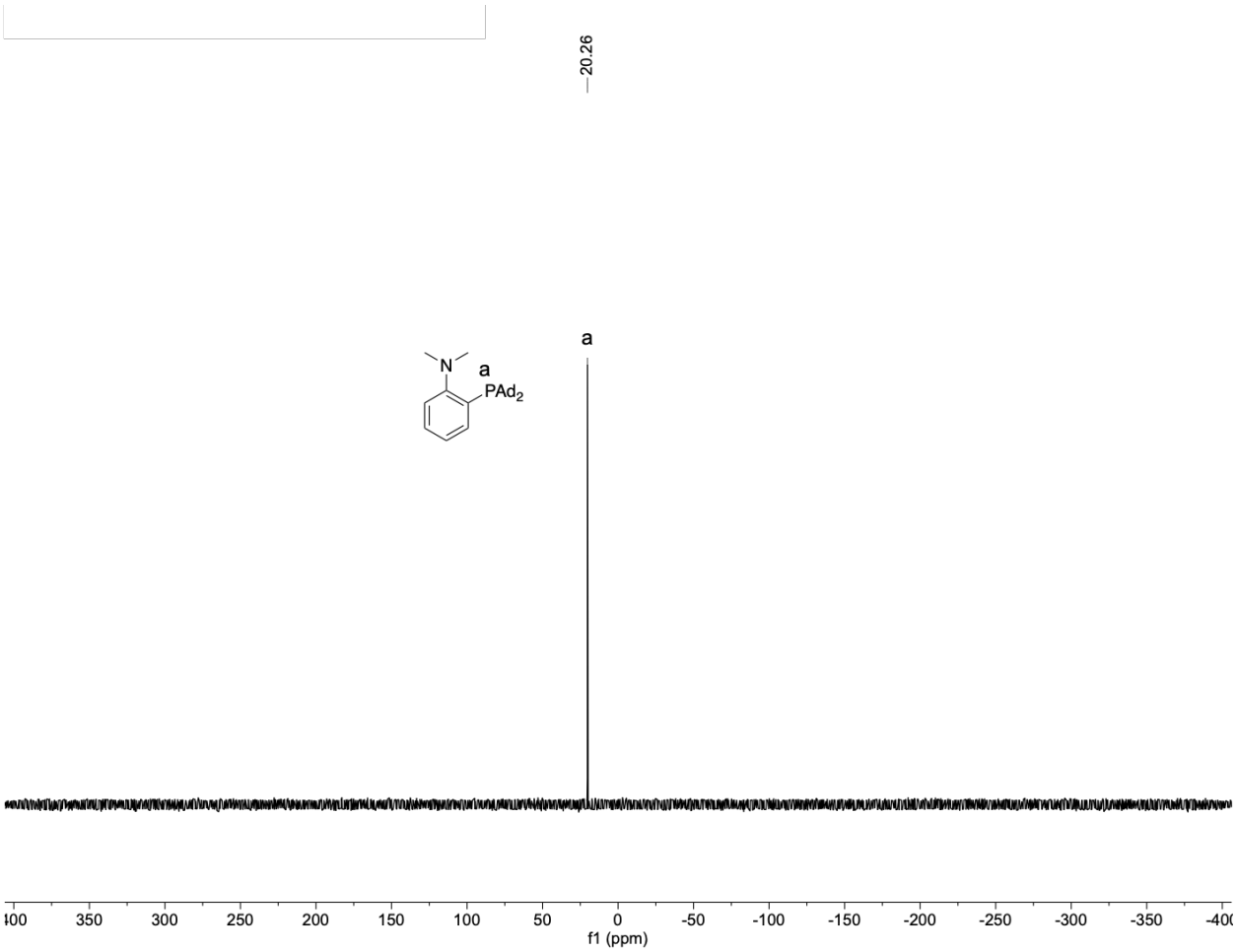
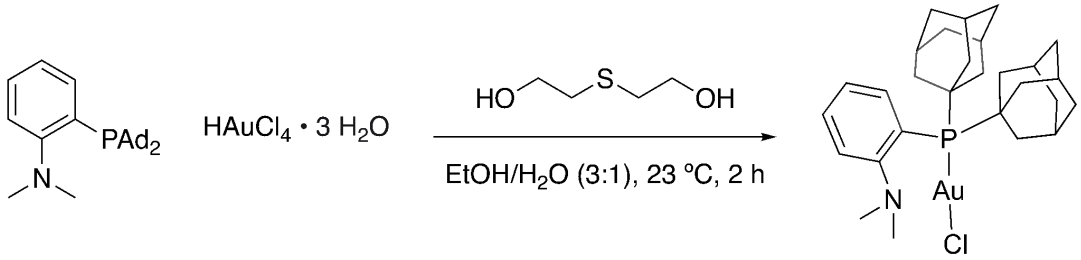


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of Me-DalPhos (**22**) in CD_2Cl_2 at 25 ºC.

Synthesis of (Me-DalPhos)Au^{I}Cl ^{4} (7)



A scintillation vial was charged with a stir bar and $HAuCl_4 \bullet 3H_2O$ (322.4 mg, 1 Eq, 818.6 µmol) was added as a solid to the flask, then it was dissolved in 2 mL of DI water. Separately, Me-DalPhos (345 mg, 1 Eq, 818.6 µmol) was suspended in 3 mL of ethanol in a dram vial, then this was added to the scintillation vial. The dram vial was washed with ethanol (3 x 1 mL) and transferred to the scintillation vial. This was stirred at 23 ºC for two hours. The contents of the reaction were then transferred onto a medium grain fritted funnel where the white solid was washed with methanol (3 x 5 mL). The white solid was dissolved in DCM and filtered through a plug of Celite to remove any nanoparticles that may have formed. The eluent was then concentrated under vacuum to afford the product as a white solid (482 mg, 736.7 µmol, 90% yield).

Physical state: White solid
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 – 7.72 (m, 1H), 7.59 – 7.51 (m, 2H), 7.34 – 7.27 (m, 1H), 2.57 (s, 6H), 2.26 – 2.17 (m, 6H), 2.12 – 2.04 (m, 6H), 2.01 – 1.94 (m, 6H), 1.72 – 1.64 (m, 12H).
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 56.70.
HRMS (DART): $[M+H]^+$ calculated for $C_{28}H_{41}NP^+$ 654.2331, observed 654.2325.

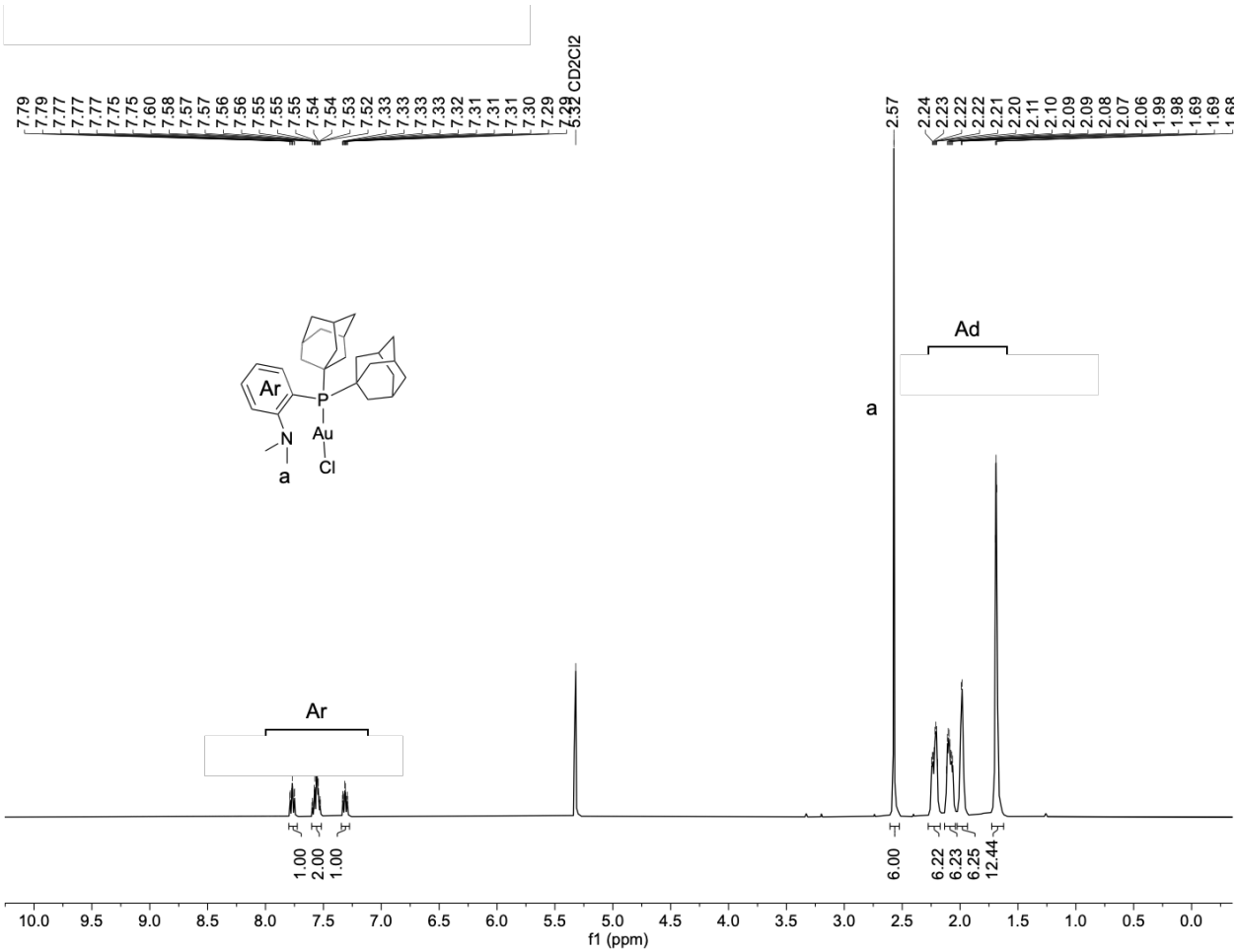


Figure S18. ^{1}H NMR spectrum of (Me-DalPhos)Au^{I}Cl (**7**) in CD_2Cl_2 at 25 ºC.

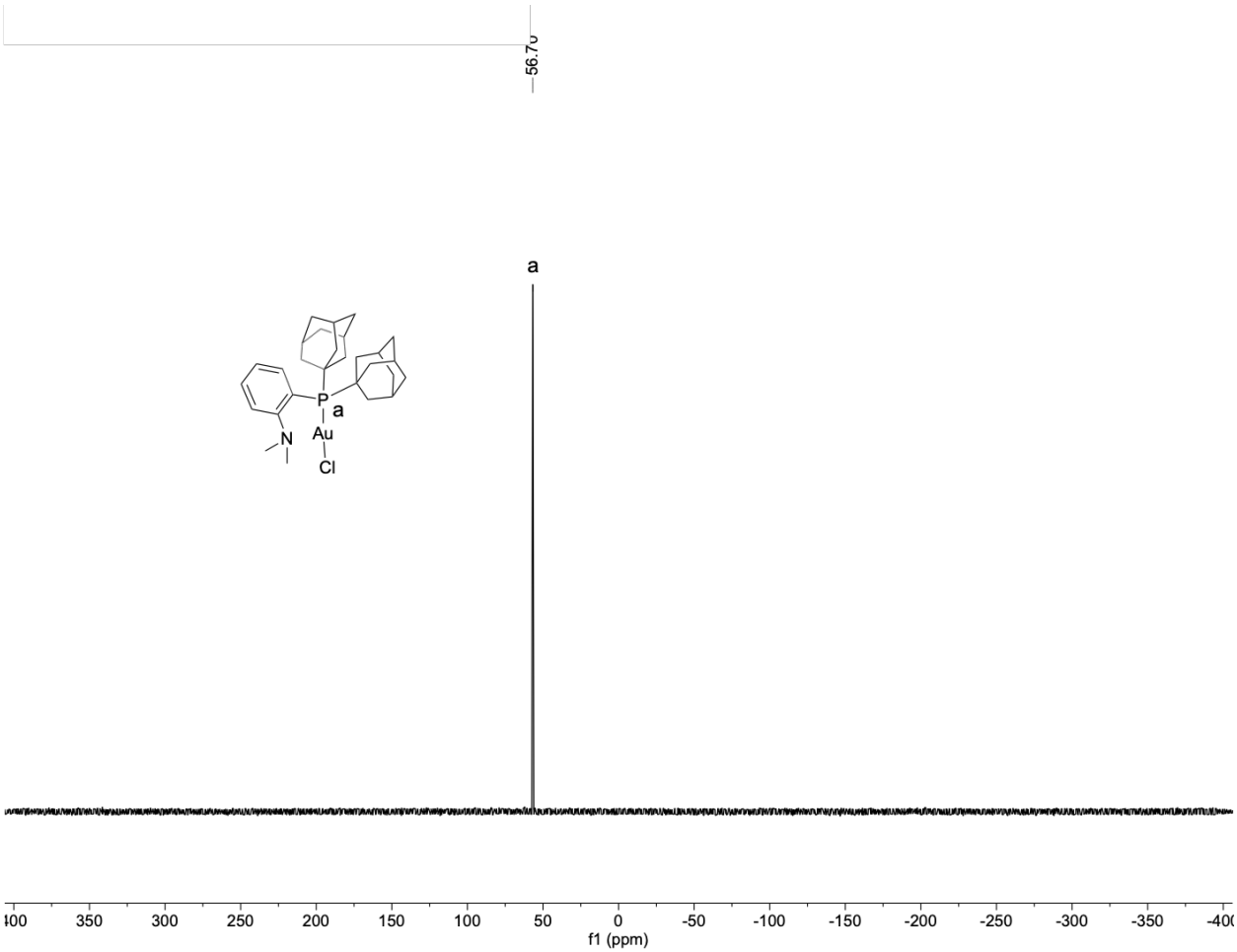
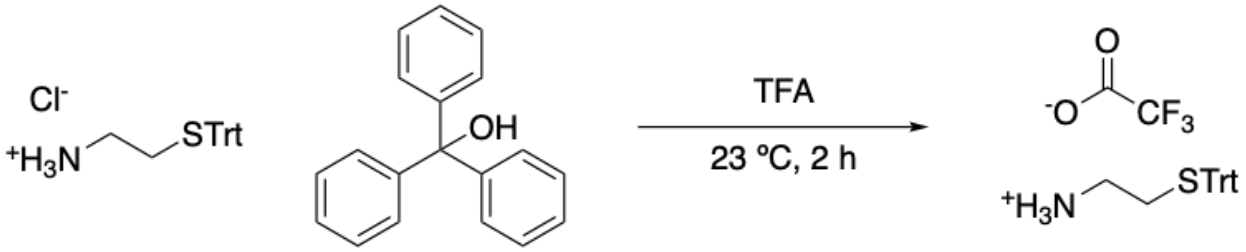


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of (Me-DalPhos)Au^{I}Cl (**7**) in CD_2Cl_2 at 25 ºC.

Synthesis of 2-(tritylthio)ethan-1-ammonium trifluoroacetate (23)



A 100 mL one neck RBF was charged with a stir bar and 2-aminoethane-1-thiol hydrochloride (1.920 g, 1.1 Eq, 16.90 mmol) and triphenylcarbinol (4.000 g, 1 Eq, 15.36 mmol) were added as solids to the flask. The materials were then dissolved in trifluoroacetic acid (22.20 g, 15.00 mL, 12.67 Eq, 194.7 mmol), turning the solution immediately yellow and then a dark brown color with a slight exotherm. The reaction was stirred at 23 ºC for two hours. After two hours, the reaction was dried under a stream of air. The reaction was then precipitated into diethyl ether (45 mL) upon which a white solid crashed out. The solid was filtered and washed with diethyl ether (3 x 25 mL) to yield 2-(tritylthio)ethan-1-ammonium trifluoroacetate as a white solid (3.900 g, 9.004 mmol, 59% yield).

Physical state: White solid
^{1}H NMR (400 MHz, MeOD): δ 7.45 – 7.38 (m, 6H), 7.29 – 7.25 (m, 6H), 7.24 – 7.18 (m, 3H), 2.40 – 2.39 (m, 2H), 2.37 – 2.31 (m, 2H).
^{13}C NMR (101 MHz, CD_3CN): δ 145.31, 130.28, 129.12, 127.98, 67.80, 39.34, 29.50.
HRMS (ESI/QTOF): $[M+Na]^+$ calculated for $C_{21}H_{21}NNaS^+$ 342.1292, observed 342.1289.

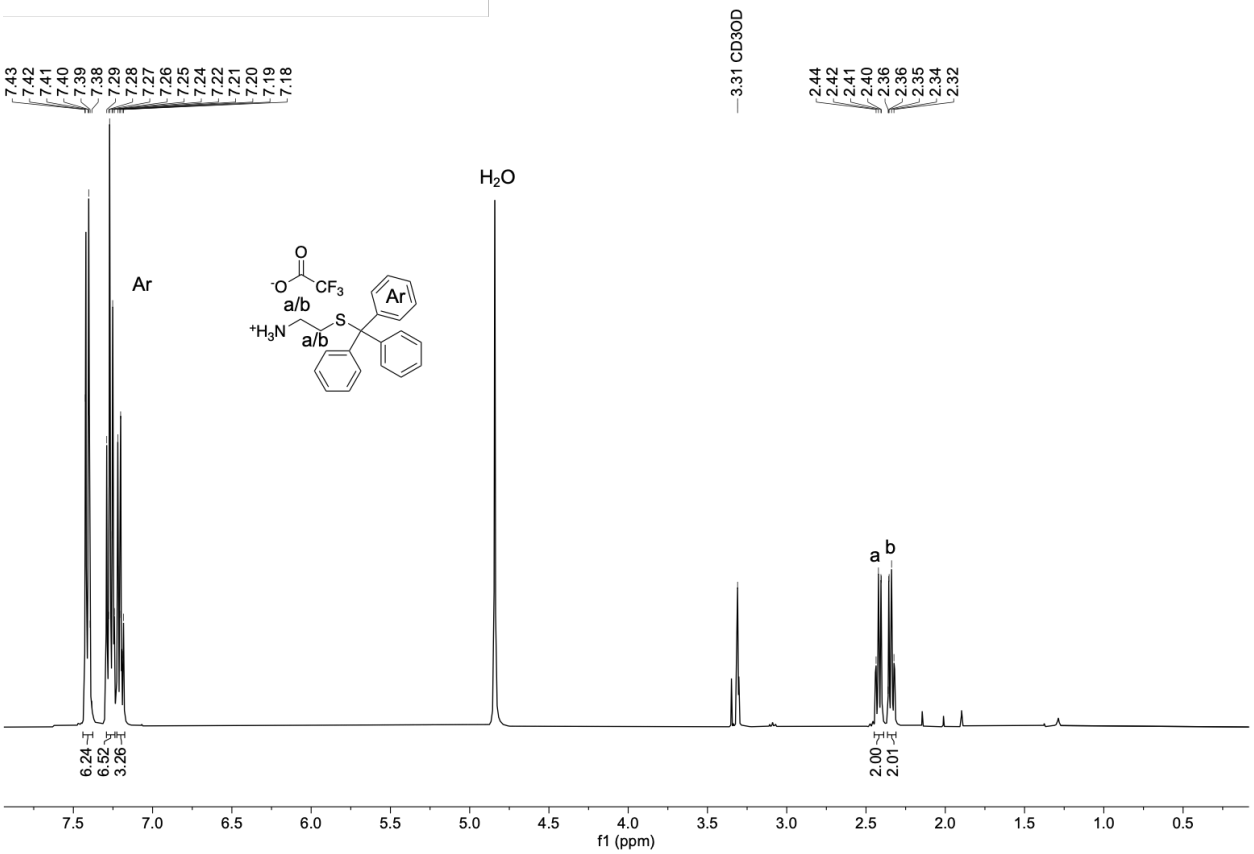


Figure S20. ^{1}H NMR spectrum of 2-(tritylthio)ethan-1-ammonium trifluoroacetate (**23**) in MeOD at 25 ºC.

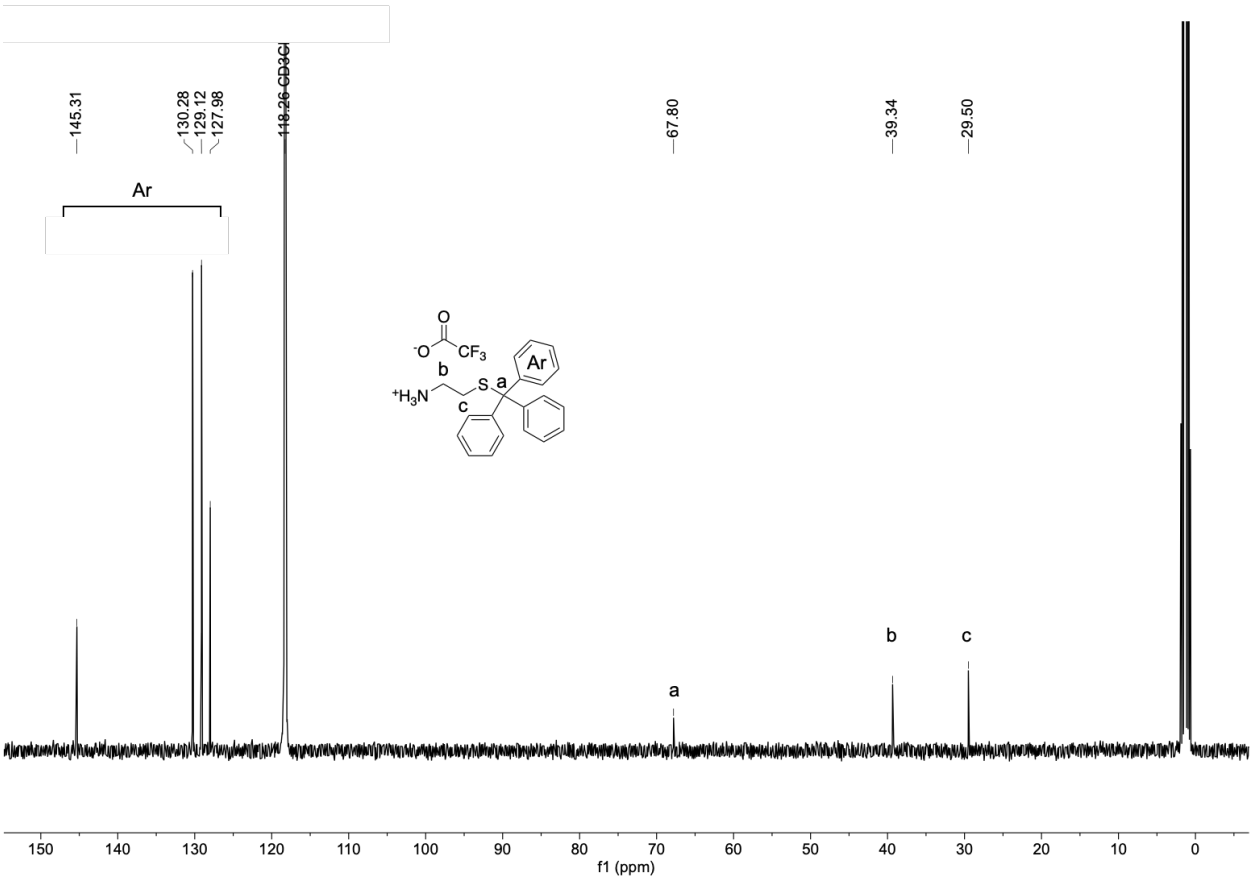
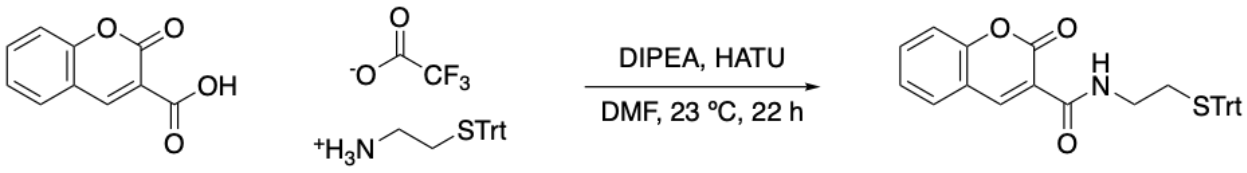


Figure S21. ^{13}C NMR spectrum of 2-(tritylthio)ethan-1-ammonium trifluoroacetate (**23**) in CD_3CN at 25 ºC.

*CD_3CN used to prevent overlap of the product signals with the solvent signals.

Synthesis of 2-oxo-N-(2-(tritylthio)ethyl)-2H-chromene-3-carboxamide (9)



A scintillation vial was charged with a stir bar, then 2-oxo-2H-chromene-3-carboxylic acid (200 mg, 1 Eq, 1.05 mmol) and HATU (520 mg, 1.3 Eq, 1.37 mmol) were added as solids and dissolved in 4 mL of DMF to create a clear solution. DIPEA (408 mg, 550 µL, 3 Eq, 3.16 mmol) was added to the flask upon which the reaction became a yellow suspension. This was left to stir under ambient conditions for 15 minutes. Separately, 2-(tritylthio)ethan-1-ammonium trifluoroacetate (545 mg, 1.2 Eq, 1.26 mmol) was added as a solid to a dram vial and dissolved in 2 mL of DMF. After 15 minutes, the activated solution had turned gold, so the amine was added to the vial with no color change or exotherm. The reaction was stirred at 23 ºC for 22 hours. The reaction mixture was then diluted with DCM (150 mL) and washed with brine (50 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The material was purified by flash column chromatography (50 g silica gel, 0-60% gradient of ethyl acetate against hexanes) to afford 2-oxo-N-(2-(tritylthio)ethyl)-2H-chromene-3-carboxamide as a white solid (236 mg, 483 µmol, 46% yield).

Physical state: White solid
TLC (UV): R_f 0.70 (1:1 hexanes-ethyl acetate)
^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.84 (s, 1H), 8.79 (br t, J = 5.8 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.47 – 7.36 (m, 8H), 7.30 (m, 6H), 7.25 – 7.19 (m, 3H), 3.29 (q, J = 6.7 Hz, 2H), 2.47 (t, J = 6.7 Hz, 2H).
^{13}C NMR (101 MHz, CD_2Cl_2): δ 161.68, 161.64, 154.94, 148.54, 145.21, 134.39, 130.26, 129.99, 128.36, 127.14, 125.61, 119.13, 118.92, 116.92, 67.13, 38.91, 32.15.
HRMS (ESI/QTOF): $[M+Na]^+$ calculated for $C_{31}H_{25}NNaO_3S^+$ 514.1453 Da, observed 514.1446 Da

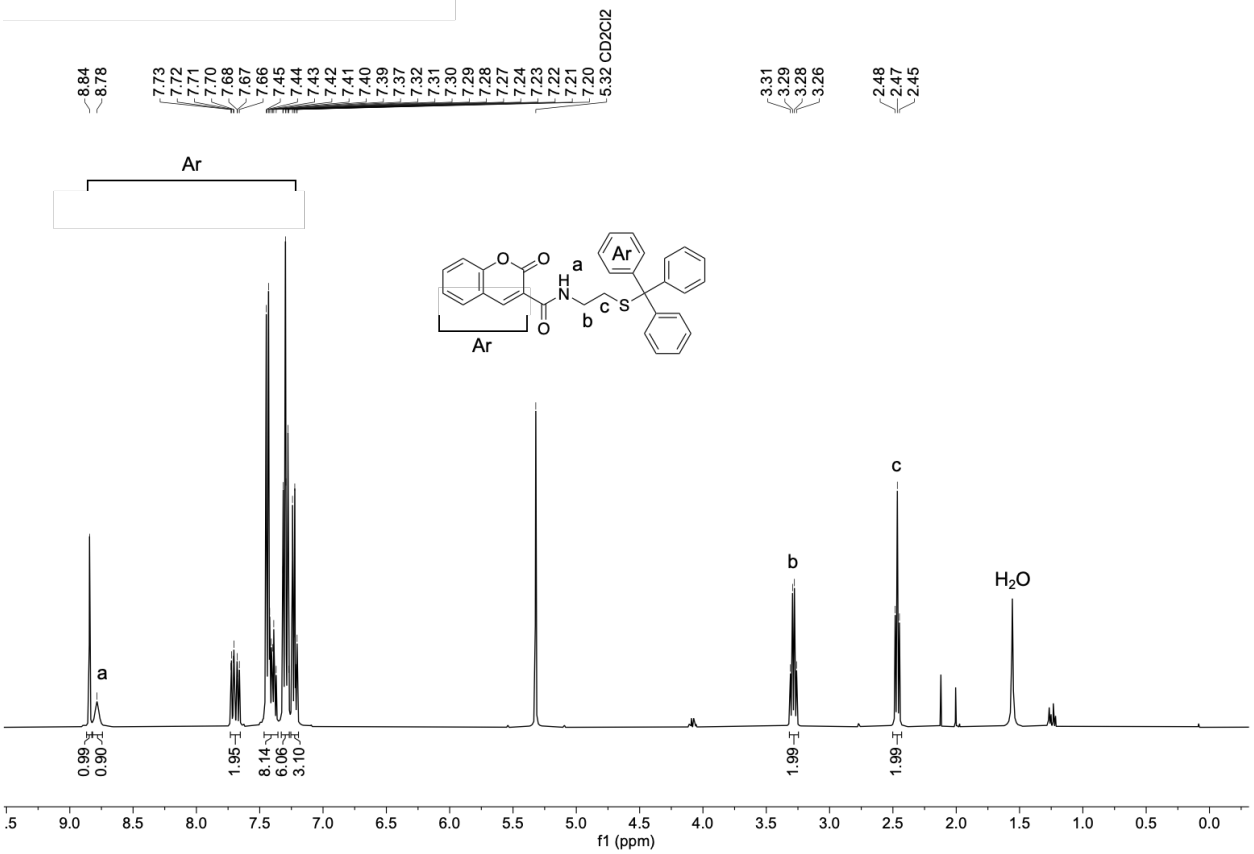


Figure S22. ^{1}H NMR spectrum of 2-oxo-N-(2-(tritylthio)ethyl)-2H-chromene-3-carboxamide (**9**) in CD_2Cl_2 at 25 ºC.

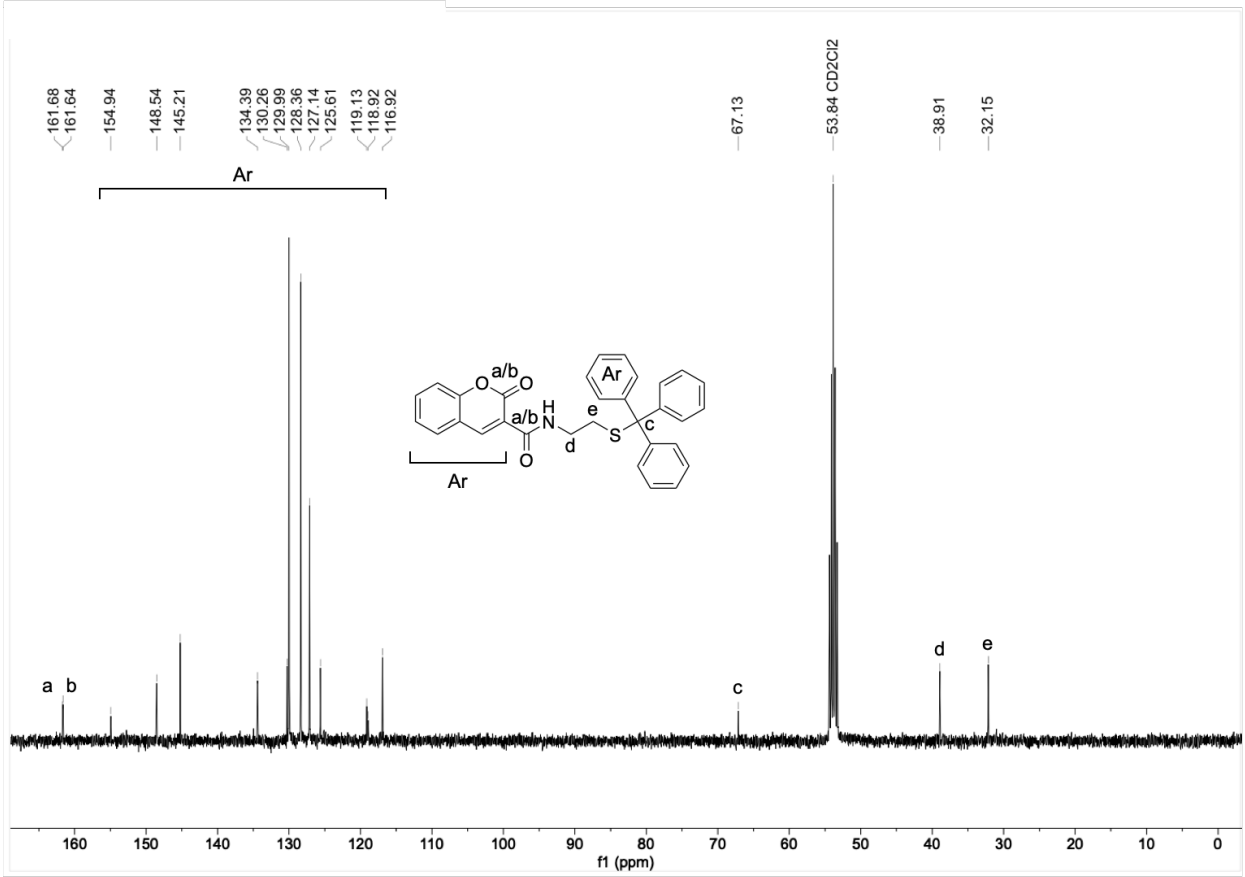
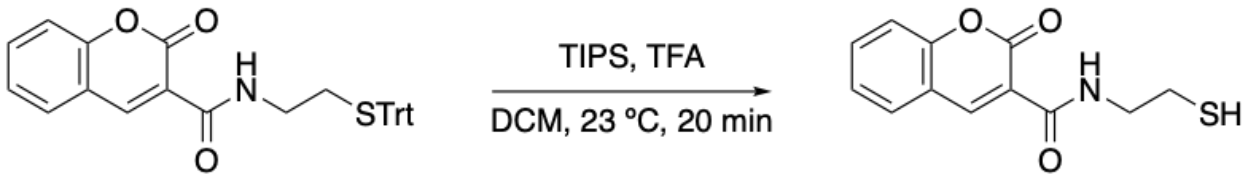


Figure S23. ^{13}C NMR spectrum of 2-oxo-N-(2-(tritylthio)ethyl)-2H-chromene-3-carboxamide (**9**) in CD_2Cl_2 at 25 ºC.

Synthesis of *N*-(2-mercaptoethyl)-2-oxo-2*H*-chromene-3-carboxamide (9a)



A scintillation vial was charged with a stir bar and 2-oxo-N-(2-(tritylthio)ethyl)-2H-chromene-3-carboxamide (90 mg, 1 Eq, 0.18 mmol) was added as a white solid to the flask. The solid was dissolved in 5 mL of 1:1 TFA-DCM (v/v), forming a golden solution. Subsequently, tris(propan-2-yl)silane (193 mg, 250 µL, 6.7 Eq, 1.22 mmol) was added to the solution with no observable exotherm and a color change from golden to clear and colorless. This was left to stir for 20 minutes at 23 ºC. After 20 minutes, the reaction was concentrated under vacuum. The product was purified by trituration with 8 mL of 3:1 hexanes-diethyl ether. This process was repeated three more times, then the residual white solid was concentrated under vacuum to yield N-(2-mercaptoethyl)-2-oxo-2H-chromene-3-carboxamide as a white solid (39 mg, 153 µmol, 85% yield).

Physical state: White solid
TLC (UV): R_f 0.45 (1:1 hexanes-ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.91 (s, 1H), 7.73 – 7.62 (m, 2H), 7.45 – 7.33 (m, 2H), 3.66 (q, J = 6.6 Hz, 2H), 2.78 (q, J = 8.5 Hz, 2H), 1.47 (t, J = 8.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 161.84, 161.54, 154.60, 148.69, 134.31, 129.97, 125.47, 118.73, 118.41, 116.80, 43.11, 24.42.
HRMS (ESI/QTOF): $[M+H]^+$ calculated for $C_{12}H_{12}NO_3S^+$ 250.0538 Da, observed 250.0567 Da.

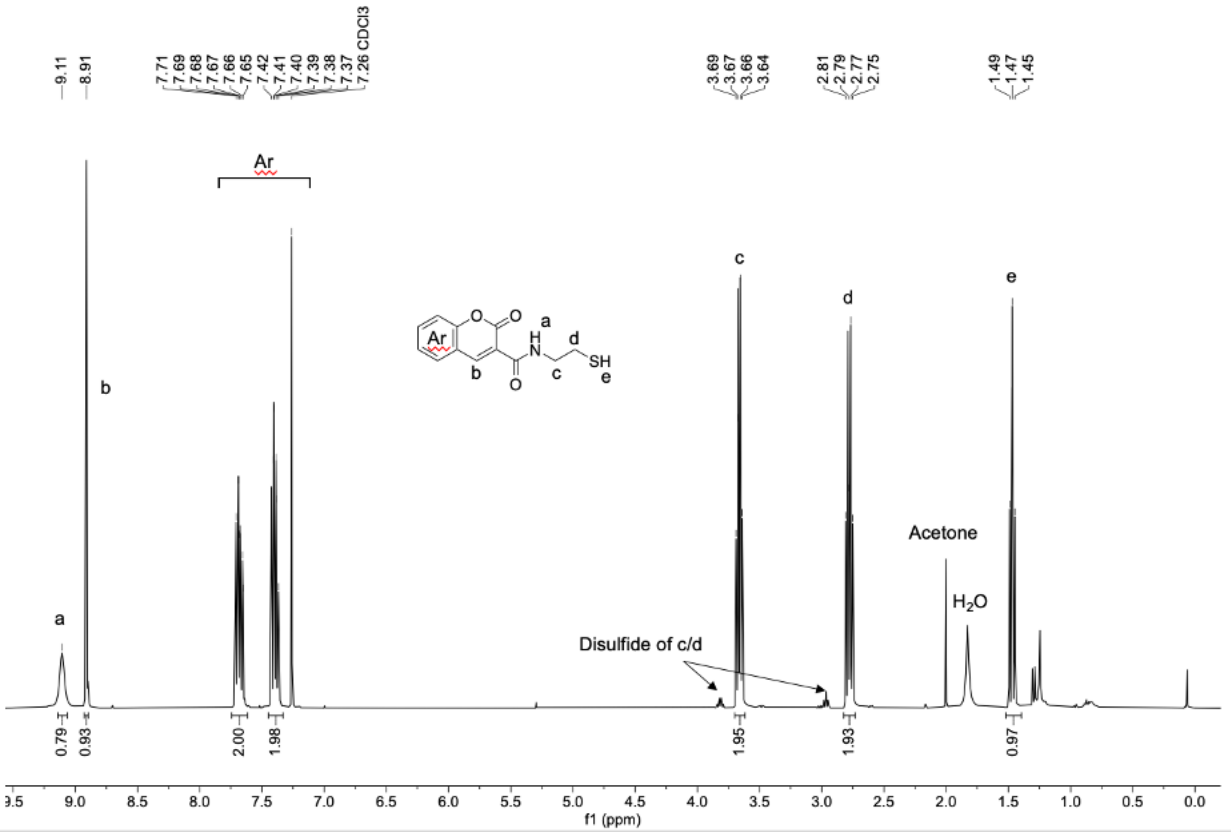


Figure S24. ^{1}H NMR spectrum of *N*-(2-mercaptoethyl)-2-oxo-2*H*-chromene-3-carboxamide (**9a**) in $CDCl_3$ at 25 ºC.

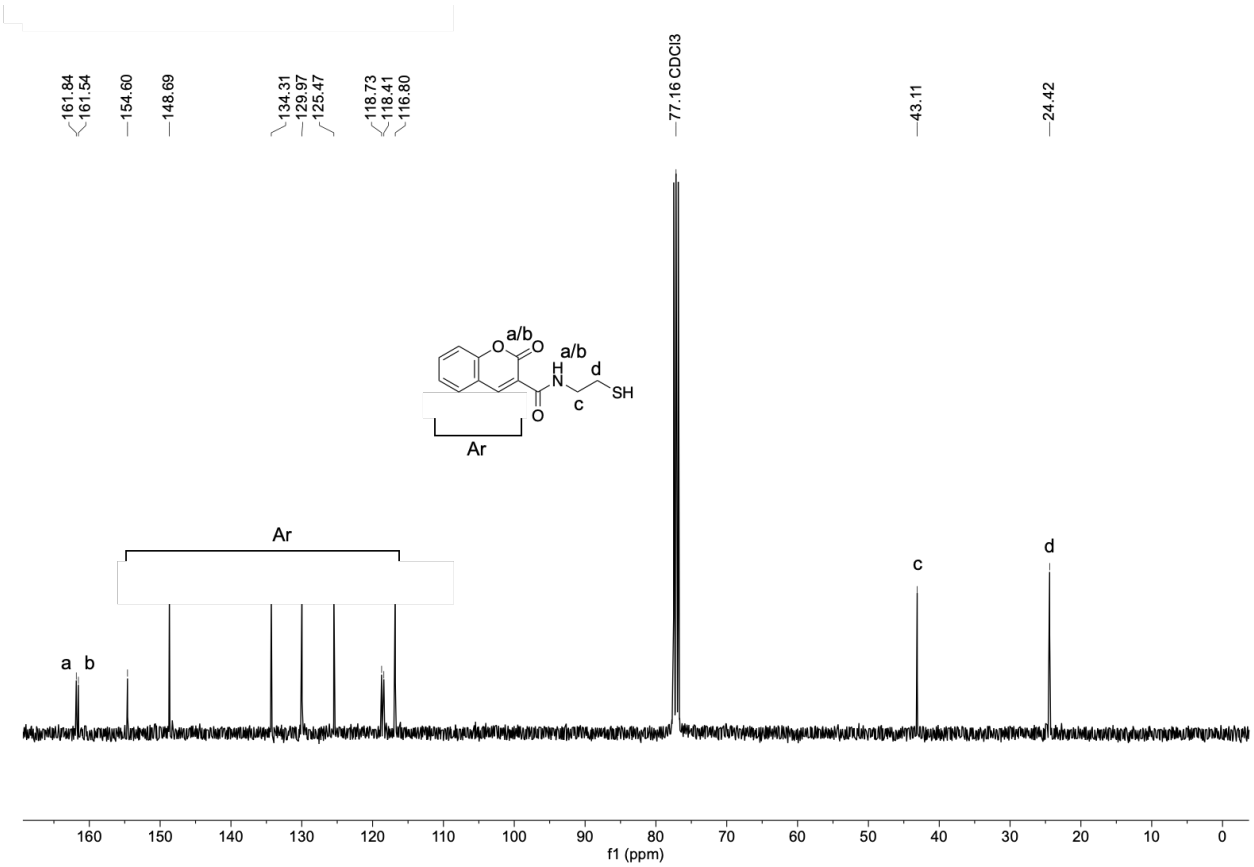
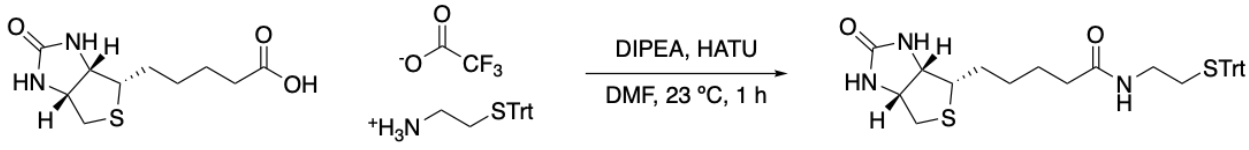


Figure S25. ^{13}C NMR spectrum of *N*-(2-mercaptoethyl)-2-oxo-2*H*-chromene-3-carboxamide (**9a**) in $CDCl_3$ at 25 ºC.

Synthesis of 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)-*N*-(2-(tritylthio)ethyl)pentanamide (8)



A one neck, 25 mL RBF was charged with a stir bar, then d-biotin (237 mg, 1.5 Eq, 969 µmol) and HATU (319 mg, 1.3 Eq, 840 µmol) were added as solids to the flask. These were dissolved in 4 mL of DMF to create a white suspension. After 5 minutes, DIPEA (250 mg, 338 µL, 3 Eq, 1.94 mmol) was added to the flask, creating a yellow suspension that came into solution over a few minutes. This was left to stir at 23 ºC for 15 minutes. Separately, 2-(tritylthio)ethan-1-ammonium trifluoroacetate (280 mg, 1 Eq, 646 µmol) was dissolved in 2 mL of DMF along with DIPEA (125 mg, 169 µL, 1.5 Eq, 970 µmol). After 15 minutes, the amine solution was added to the flask, retaining the yellow color. The reaction was stirred at 23 ºC for 1 hour. The reaction was then diluted with ethyl acetate (150 mL) and washed once with saturated sodium carbonate (50 mL) and once with brine (50 mL). The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The product was purified by reverse phase chromatography (25 g C18 column, 10-100% acetonitrile against water, both with 0.1% TFA additive) to yield 5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)-N-(2-(tritylthio)ethyl)pentanamide as a white solid (269 mg, 491 µmol, 76% yield).

Physical state: White solid

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.44 – 7.35 (m, 6H), 7.34 – 7.26 (m, 6H), 7.26 – 7.20 (m, 3H), 6.41 (s, 1H), 5.94 (s, 1H), 5.67 (s, 1H), 4.45 (dd, J = 7.9, 4.7 Hz, 1H), 4.27 (dd, J = 7.9, 4.5 Hz, 1H), 3.14 (td, J = 7.4, 4.5 Hz, 1H), 3.06 (q, J = 6.1 Hz, 2H), 2.88 (dd, J = 12.9, 4.9 Hz, 1H), 2.68 (d, J = 12.9 Hz, 1H), 2.45 – 2.34 (m, 2H), 2.21 – 2.04 (m, 2H), 1.76 – 1.54 (m, 4H), 1.48 – 1.34 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 173.50, 164.67, 145.14, 129.93, 128.36, 127.19, 67.12, 62.29, 60.92, 55.74, 40.83, 38.59, 35.96, 32.31, 28.23, 28.21, 25.86.

HRMS (ESI/QTOF): $[M+Na]^+$ calculated for $C_{31}H_{35}N_3NaO_2S_2^+$ 568.2068 Da, observed 568.2053 Da.

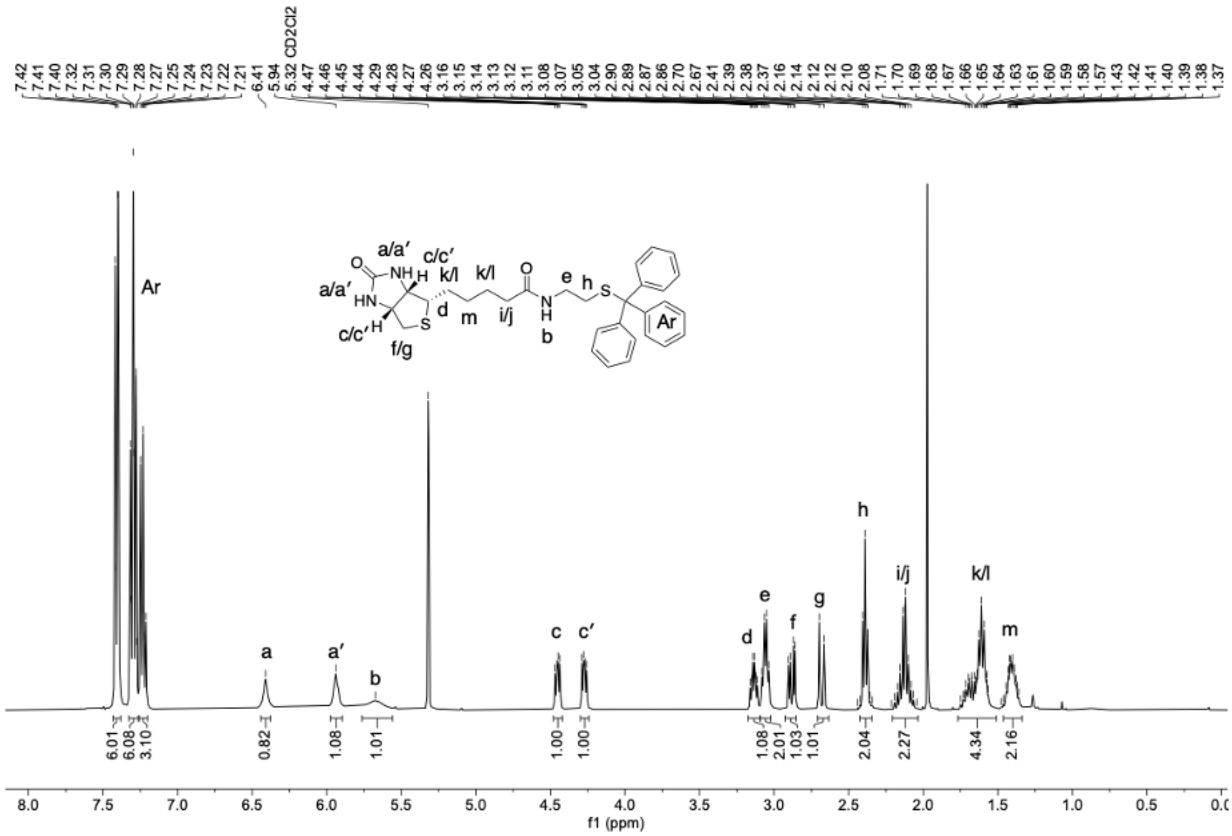


Figure S26. ^{1}H NMR spectrum of 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)-*N*-(2-(tritylthio)ethyl)pentanamide (**8**) in CD_2Cl_2 at 25 ºC.

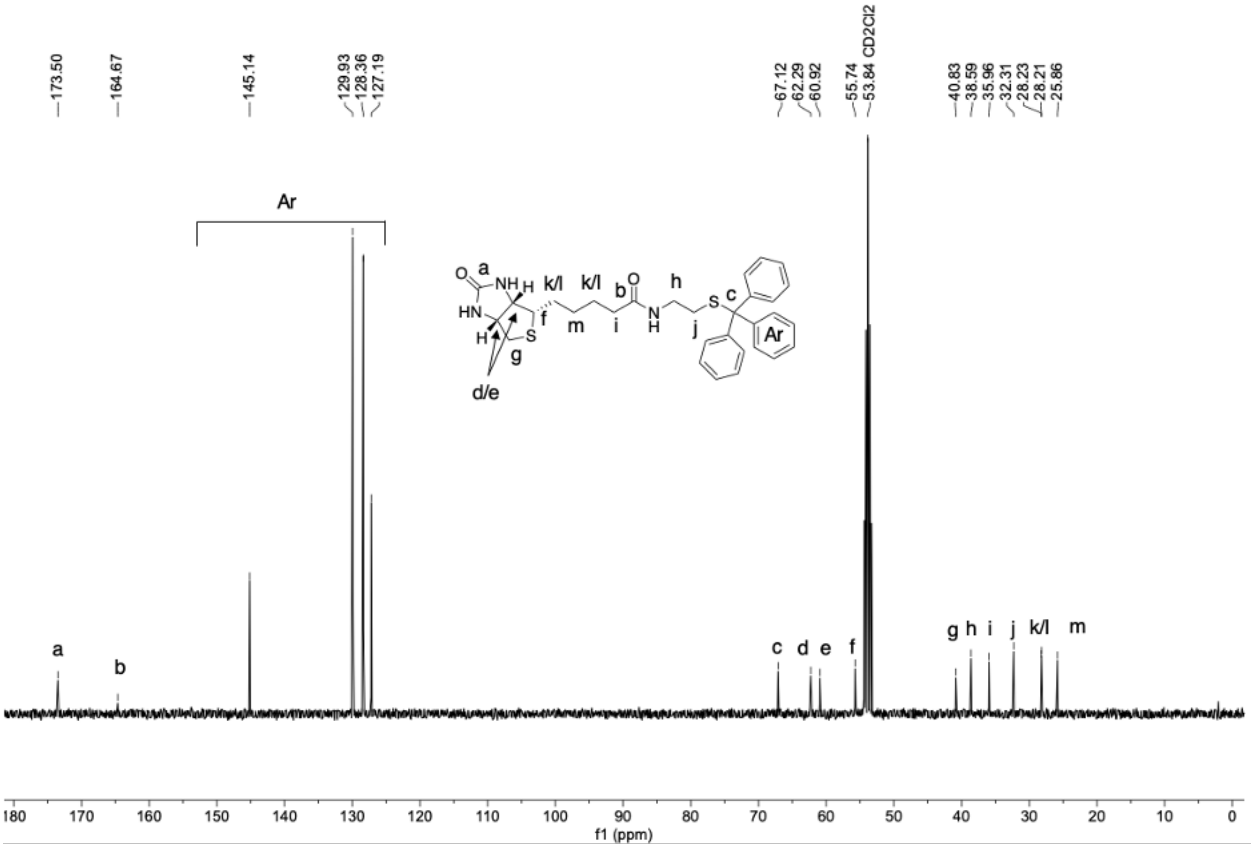
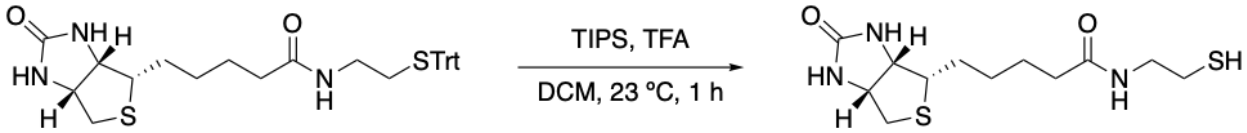


Figure S27. ^{13}C NMR spectrum of 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)-*N*-(2-(tritylthio)ethyl)pentanamide (**8**) in CD_2Cl_2 at 25 ºC.

Synthesis of N-(2-mercaptoethyl)-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide (8a)



A scintillation vial was charged with a stir bar and 5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)-N-(2-(tritylthio)ethyl)pentanamide (269 mg, 1 Eq, 493 µmol) was added. The solid was dissolved in 10 mL of 1:1 TFA-DCM (v/v), forming a bright yellow solution. Triisopropylsilane (387 mg, 500 µL, 4.95 Eq, 2.44 mmol) was then added to the solution upon which the solution turned white, then water (500 mg, 500 µL, 56.3 Eq, 27.7 mmol) was added. This was left to stir at 23 ºC for 1 hour. The reaction mixture was purified by reverse phase chromatography (25 g C18 column, 10-100% acetonitrile against water, both with 0.1% TFA) to yield N-(2-mercaptoethyl)-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide as a white powder (108 mg, 355 µmol, 72% yield).

Physical state: White solid

^{1}H NMR (400 MHz, MeOD): δ 4.50 (ddd, J = 7.9, 5.0, 1.0 Hz, 1H), 4.31 (dd, J = 7.9, 4.5 Hz, 1H), 3.34 (t, J = 6.8 Hz, 2H), 3.21 (ddd, J = 8.9, 5.8, 4.4 Hz, 1H), 2.93 (dd, J = 12.8, 5.0 Hz, 1H), 2.71 (d, J = 12.7 Hz, 1H), 2.60 (tt, J = 6.8, 1.2 Hz, 2H), 2.26 – 2.17 (m, 2H), 1.80 – 1.53 (m, 4H), 1.51 – 1.40 (m, 2H).

^{13}C NMR (101 MHz, MeOD): δ 176.20, 166.12, 63.40, 61.66, 56.98, 43.85, 41.02, 36.72, 29.75, 29.47, 26.83, 24.50.

HRMS (ESI/QTOF): $[M+H]^+$ calculated for $C_{12}H_{22}N_3O_2S_2^+$ 304.1153 Da, observed 304.1161 Da.

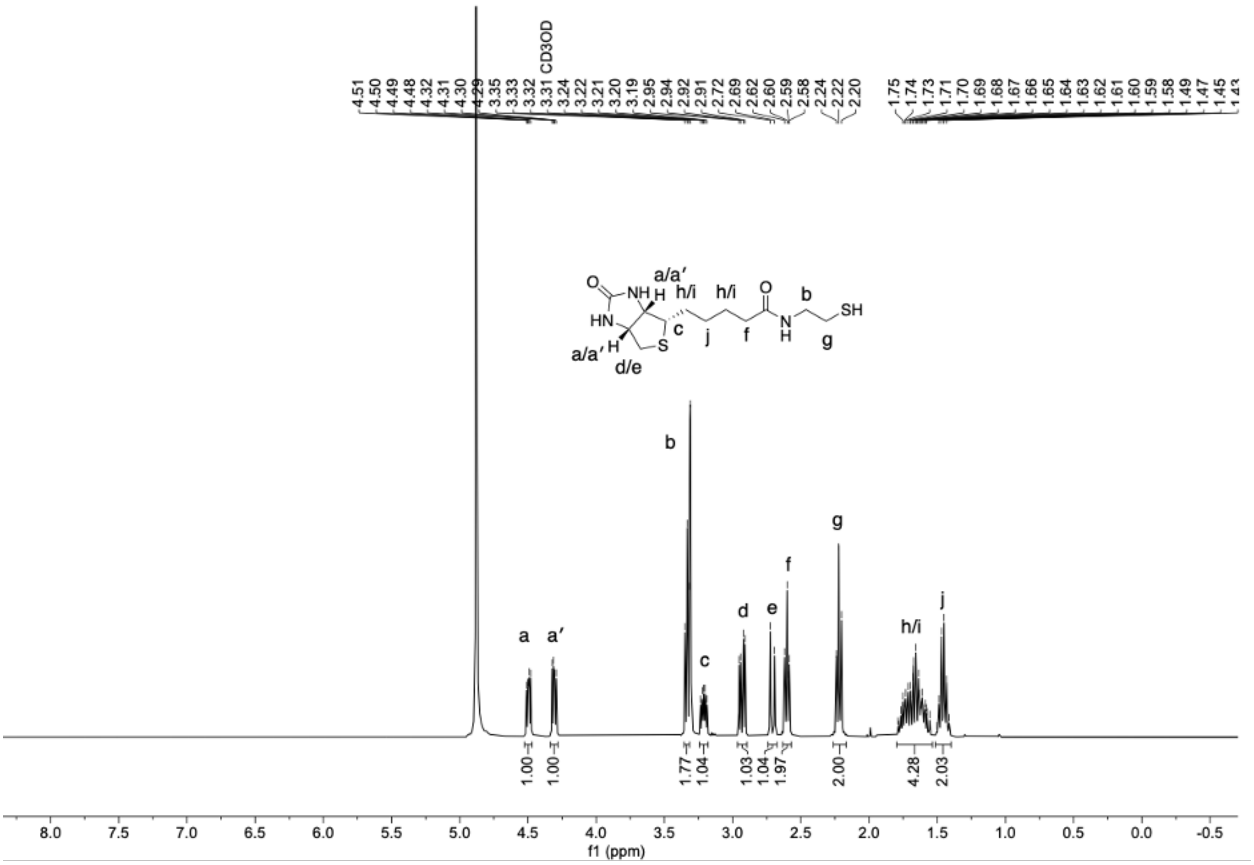


Figure S28. ^{1}H NMR spectrum of N-(2-mercaptoethyl)-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide (**8a**) in MeOD at 25 ºC.

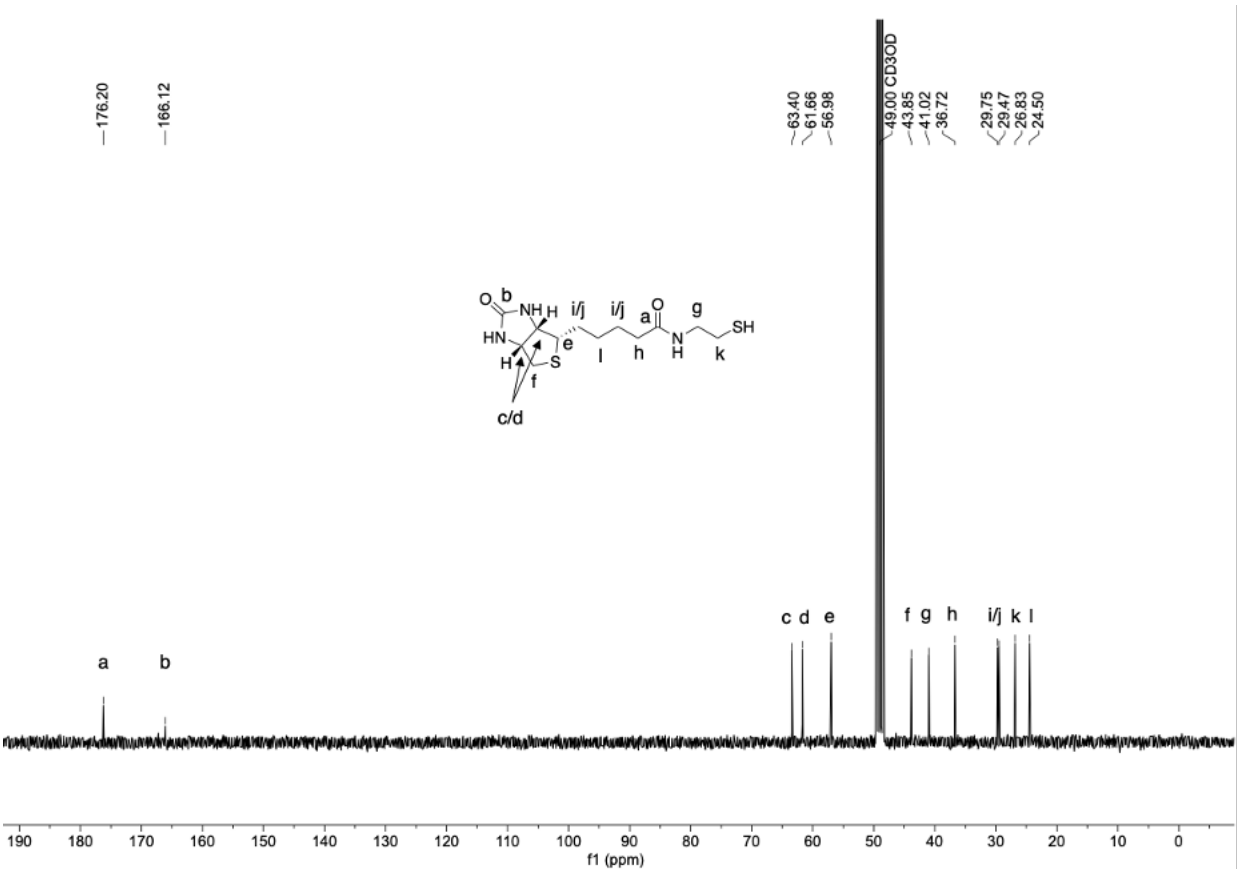


Figure S29. ^{13}C NMR spectrum of N-(2-mercaptoethyl)-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide (**8a**) in MeOD at 25 ºC.

IV. Synthesis of Polymer Precursors and Mono-telechelic End-Group Modified Polymers

Synthesis of p(CL)-aryl I *via* ROP (1)

General ROP procedure: This reaction was performed at 23ºC within a nitrogen filled glovebox. 3-O catalyst (**20**) (59.9 mg, 0.5 eq, 65.709 µmol) was weighed in a vial and a stir bar was added. Caprolactone (600 mg, 583 µL, 42 eq, 5.3 mmol) was added to a second vial. In a third vial, 2-(4-iodophenoxy)ethan-1-ol (33.1 mg, 1 Eq, 125.16 µmol) was measured and added to the 3-O vial using toluene to transfer. Next, MTBD (10.1 mg, 9.4 µL, 0.5 eq, 65.7 µmol) was added to the 3-O vial. Finally, the contents of the caprolactone vial were added to the 3-O reaction vial to initiate the reaction using toluene to transfer. A total of 2.5 mL toluene was added to the reaction mixture. After 60 min, the reaction was quenched with acetic acid outside of the glovebox and monomers were removed *via* precipitation with 45 mL of a cold MeOH/hexanes mixture (20:1 v/v) four times to produce a white powder. Yield: 92%

^{1}H NMR (300 MHz, CD_3CN): δ 7.59 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 4.39 – 4.29 (m, 2H), 4.18 – 4.11 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 99 H), 2.27 (t, *J* = 7.4 Hz, 100H), 1.67 – 1.50 (m, 200H), 1.46 – 1.22 (m, 101H).
SEC analysis: M_n is 8.2 kDa, M_w is 9.4 kDa, $Đ$ is 1.14.

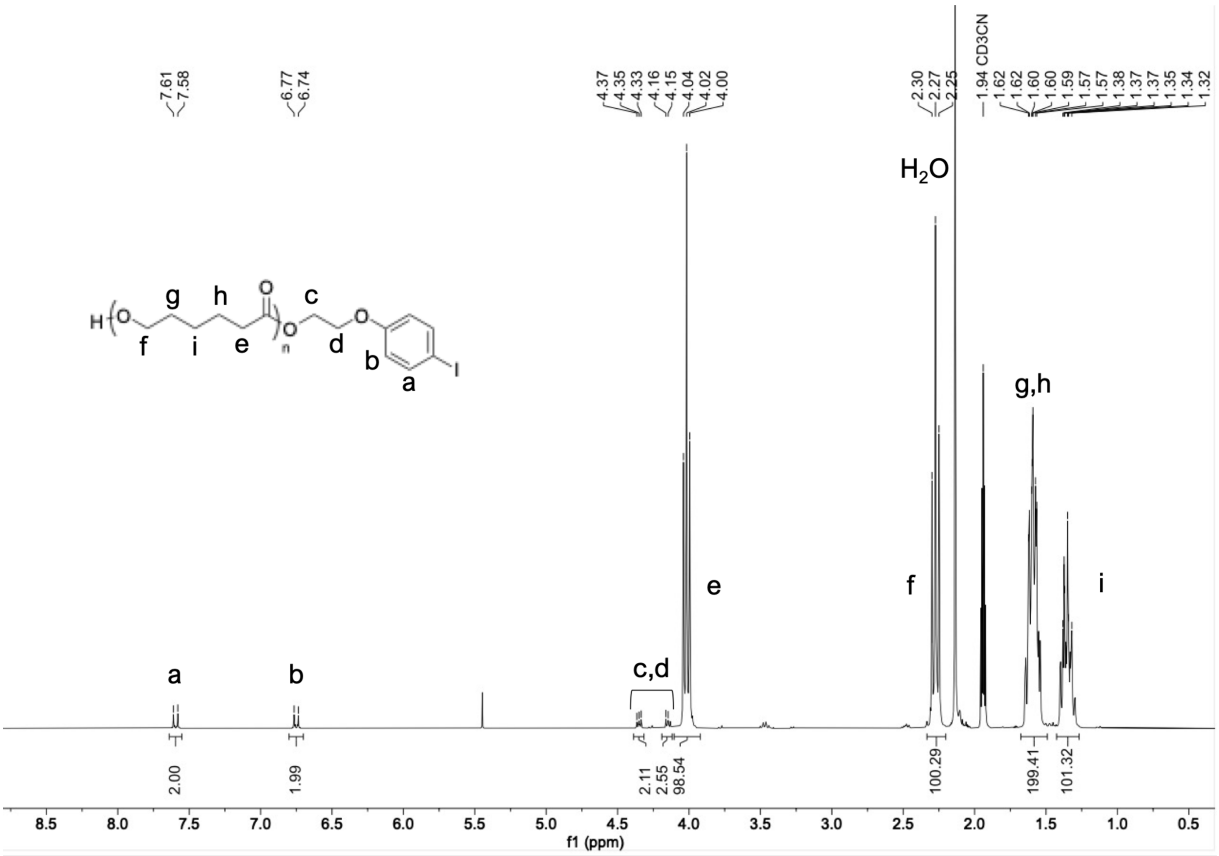


Figure S30. ^{1}H NMR spectrum of pCL-aryl iodide (**1**) in CD_3CN at 25 ºC.

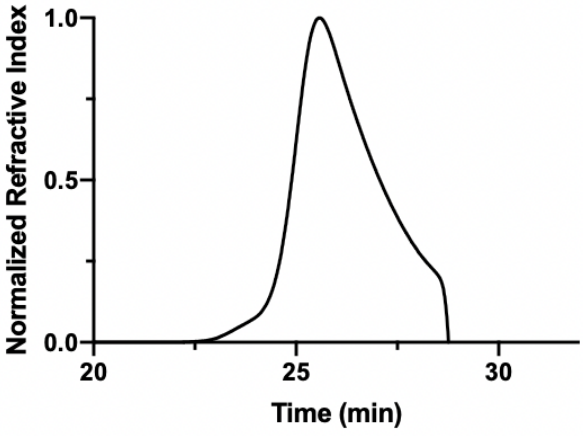
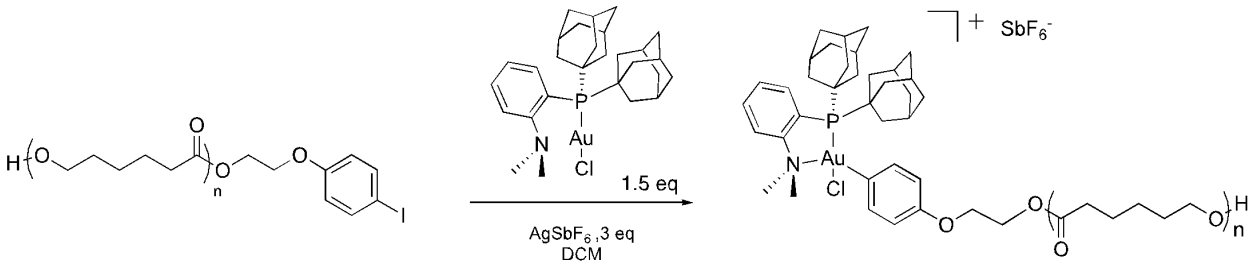


Figure S31. DMF SEC trace of pCL-aryl iodide (**1**).

Synthesis of p(CL)-Au(III) *via* oxidative addition (1a)



General Oxidative Addition Procedure[5,6]: For every oxidative addition, molecular weight of the precursor aryl iodide polymer was determined *via* ^{1}H NMR analysis. $AgSbF_6$ was removed from a glovebox with a nitrogen atmosphere, dissolved in DCM, blocked from the light with electrical tape, and placed in a -20 ºC freezer. Next, (Me-DalPhos)AuCl (18.5 mg, 1.5 eq, 28.2 µmol) was dissolved in 2 mL DCM and placed in a -20 ºC freezer. pCL-aryl iodide (103.5 mg, 1 eq, 18.8 µmol) was weighed into a dram vial, and the (Me-DalPhos)AuCl solution was added. Finally, the pCL-aryl iodide and (Me-DalPhos)AuCl mixture was added to the $AgSbF_6$ (9.1 mg, 1.4 eq, 26.4 µmol) dram vial and mixed. Precipitates immediately crashed out of solution and the solution became yellow. The reaction was stirred at room temperature for 30 minutes. Next, $AgSbF_6$ (3.2 mg, 0.5 eq, 9.4 µmol) was added and stirred for 30 minutes. Then, $AgSbF_6$ (3.9 mg, 0.6 eq, 11.3 µmol) was added and stirred for 30 minutes. Finally, AgSbF6 (3.2 mg, 0.5 eq, 9.4 µmol) was added and stirred for 15 hours. The reaction solution was run through a Celite plug with DCM, triturated with diethyl ether, and dried to produce a white or pale yellow powder. Complete conversion was determined by the disappearance of aryl-I peaks in the ^{1}H NMR. This reaction was carried forward without further purification. Product Yield: 61%. Product purity by weight was determined to be 93% based on ^{1}H NMR.

^{1}H NMR (300 MHz, CD_3CN): δ 8.06 – 7.88 (m, 2H), 7.73 – 7.63 (m, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.42 – 4.35 (m, 2H), 4.22 – 4.15 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 122H), 2.27 (t, *J* = 7.4 Hz, 137H), 1.71 – 1.46 (m, 244H), 1.42 – 1.23 (m, 126H).
^{31}P{^{1}H} NMR (121 MHz, CD_3CN): δ 75.31.

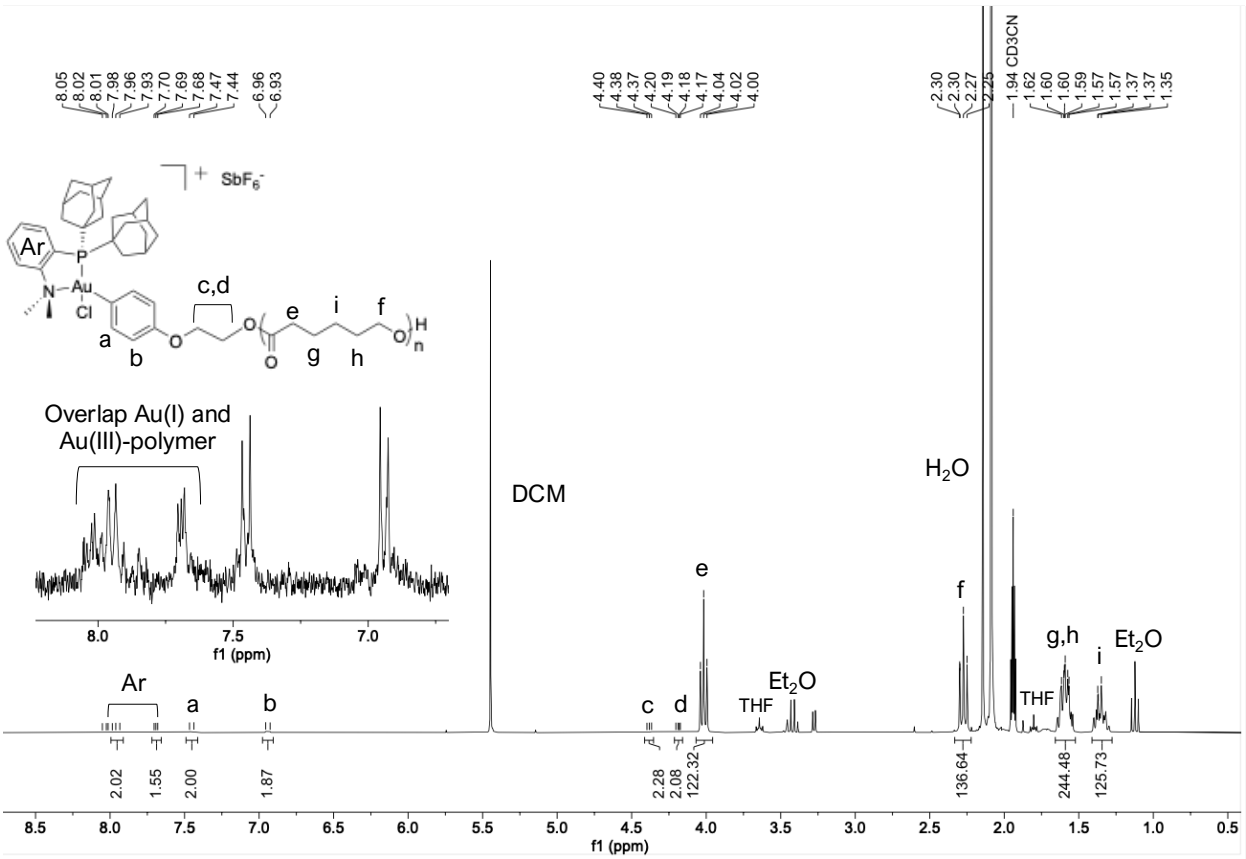


Figure S32. ^{1}H NMR spectrum of pCL-Au(III) (**1a**) in CD_3CN at 25 ºC.

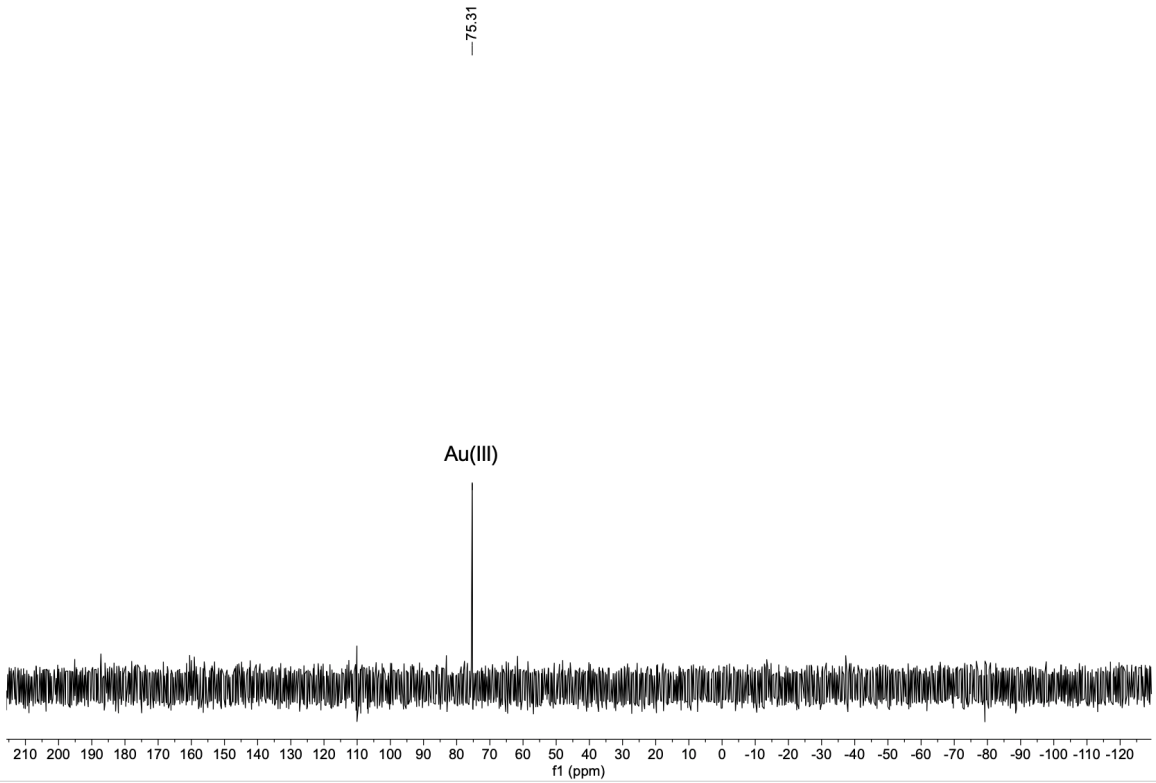
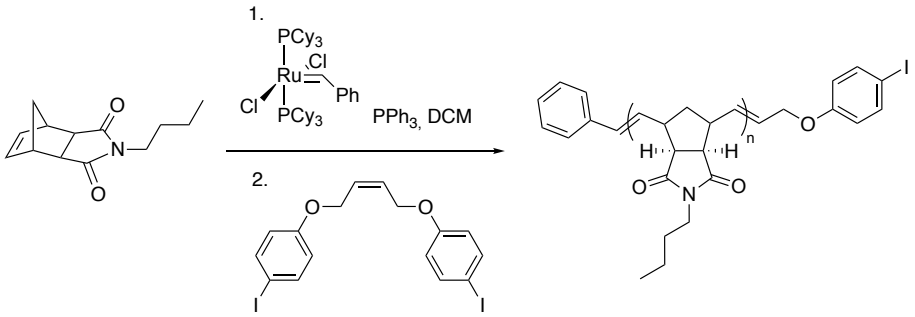


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of pCL-Au(III) (**1a**) in CD_3CN at 25 ºC.

Synthesis of p(BNI)-aryl I *via* ROMP (3)



General ROMP procedure: This reaction occurred within a nitrogen atmosphere glovebox. N-butylimide norbornene (295.8 mg, 37 eq, 1.3 mmol) was measured into a dram vial equipped with a stir bar in the glovebox and dissolved in DCM. Triphenylphosphine (9.6 mg, 1 eq, 36.5 µmol) was dissolved into DCM and added to the monomer vial. Grubbs' 1 catalyst (30.0 mg, 1 eq, 36.5 µmol) was measured and dissolved into a separate dram vial with DCM and then transferred to the monomer vial. The reaction solution was dark purple. The reaction stirred for 5 hours. Next, (Z)-1,4-bis(4-iodophenoxy)but-2-ene (179.4 mg, 10 eq, 364.5 µmol) was added and the reaction stirred for 16 hours. The polymer was precipitated four times in 45 mL of a diethylether/THF (2:1 v/v) and then dried to produce a tan powder. Yield: 51%

^{1}H NMR (400 MHz, CD_3CN): δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.45 – 7.21 (m, 5H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.77 – 5.48 (m, 97H), 4.50 (d, *J* = 5.3 Hz, 2H), 3.42 – 3.27 (m, 97H), 3.08 – 2.90 (m, 113H), 2.75 – 2.57 (m, 81H), 1.56 – 1.44 (m, 112H), 1.28 (q, *J* = 7.5 Hz, 100H), 0.90 (t, *J* = 7.3 Hz, 147H).
SEC analysis: M_n is 9.8 kDa, M_w is 11.8 kDa, $Đ$ is 1.21.

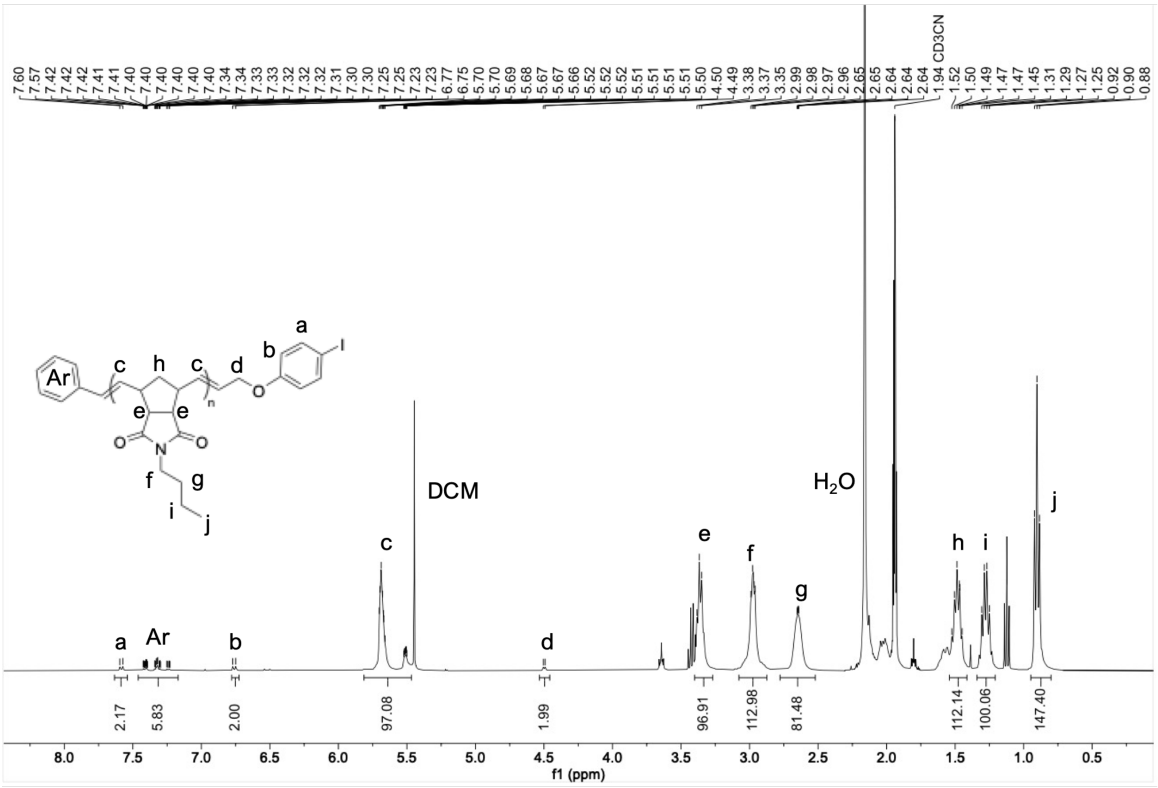


Figure S34. ^{1}H NMR spectrum of pBNI-aryl iodide (**3**) in CD_3CN at 25 ºC. Peak "c" contains both cis- and trans- alkene protons.

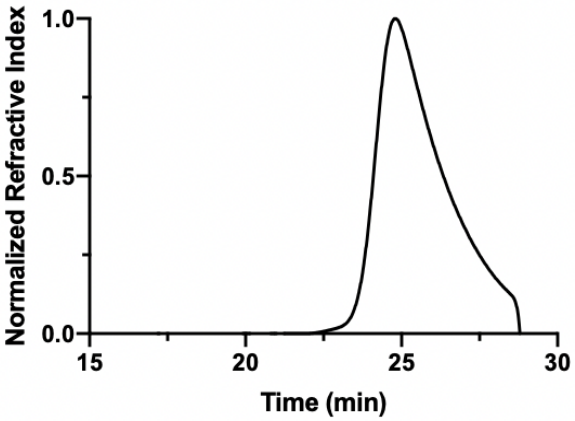
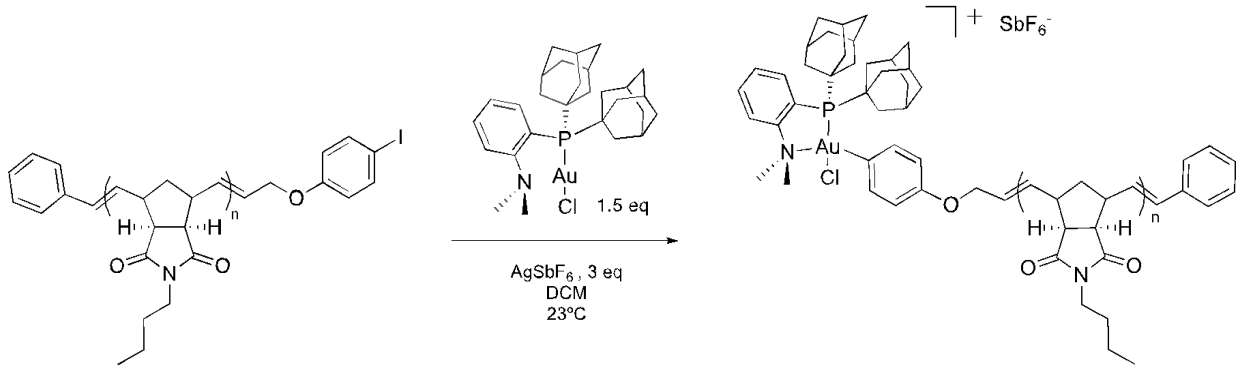


Figure S35. DMF SEC trace of pBNI-aryl iodide (**3**).

Synthesis of p(BNI)-Au(III) *via* oxidative addition (3a)



Following general oxidative addition procedure using $AgSbF_6$ (12.3 mg, 3 eq, 33.8 µmol) over four additions, (Me-DalPhos)AuCl (11.6 mg, 1.5 eq, 17.9 µmol), and p(BNI)-aryl I (100.0 mg, 1 eq, 11.3 µmol). The product is a yellow powder. Yield: 69%. Product purity by weight was determined to be 92% based on ^{1}H NMR.

^{1}H NMR (600 MHz, CD_3CN): δ 8.06 – 8.01 (m, 1H), 7.98 – 7.80 (m, 3H), 7.71 – 7.64 (m, 2H), 7.49 – 7.12 (m, 8H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.75 – 5.50 (m, 102H), 4.58 – 4.53 (m, 2H), 3.39 – 3.33 (m, 101H), 3.05 – 2.93 (m, 111H), 2.71 – 2.58 (m, 88H), 1.52 – 1.47 (m, 115H), 1.31 – 1.22 (m, 106H), 0.90 (t, *J* = 7.4 Hz, 153H).
^{31}P{^{1}H} NMR (243 MHz, CD_3CN): δ 75.11.

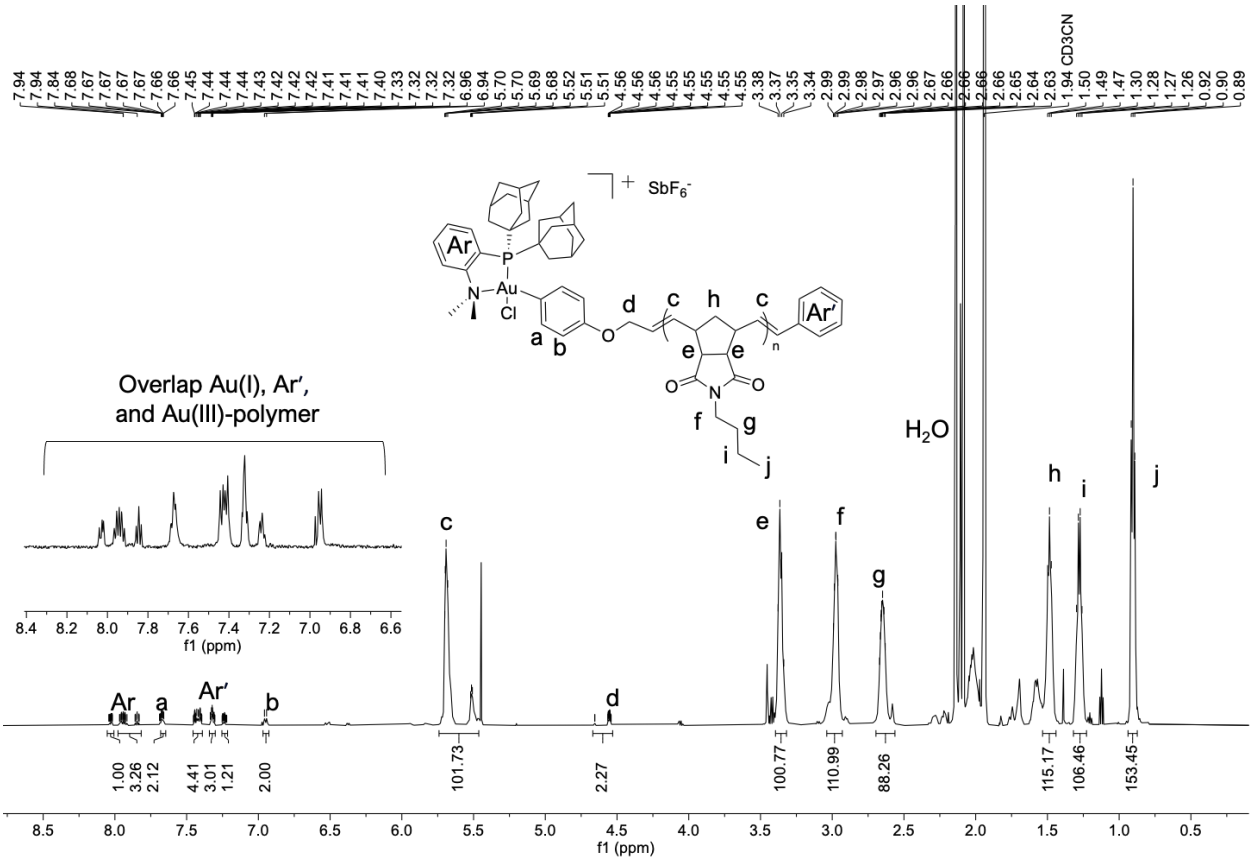


Figure S36. ^{1}H NMR spectrum of pBNI-Au(III) (**3a**) in CD_3CN at 25 ºC.

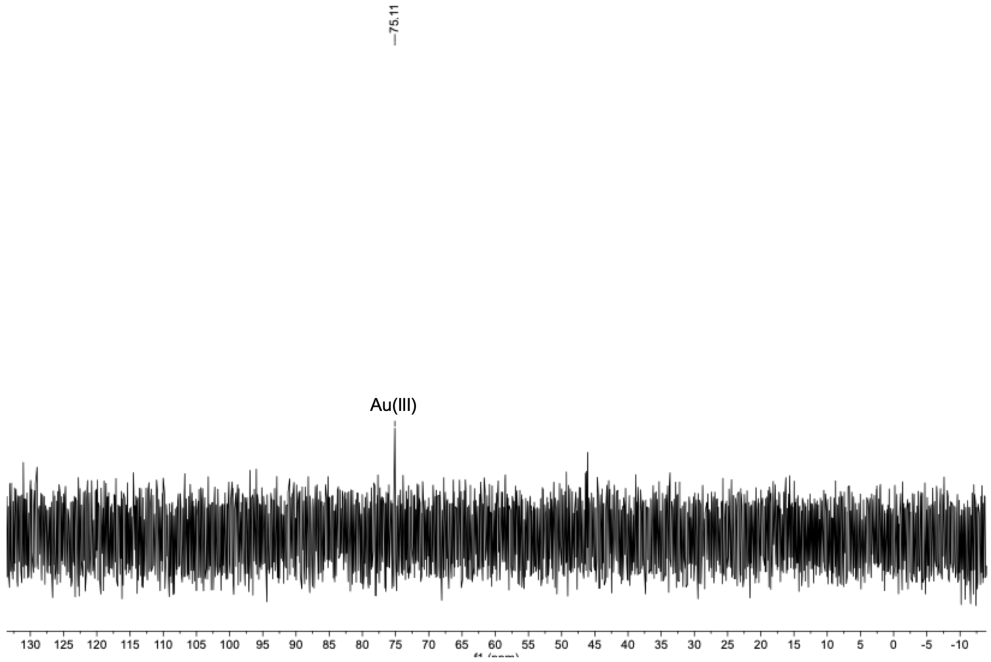
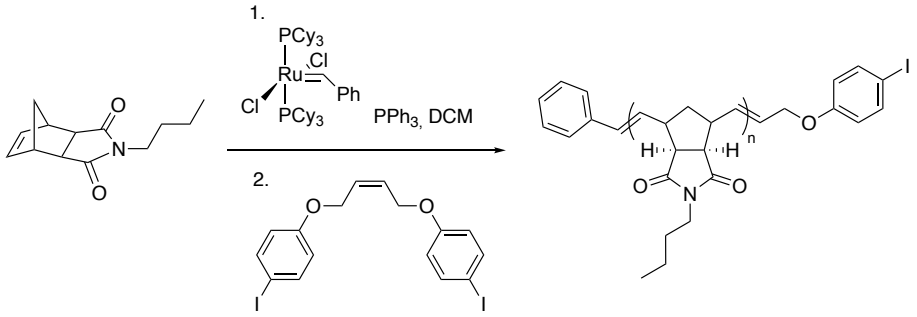


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of pBNI-Au(III) (**14a**) in CD_2Cl_2 at 25 ºC.

Synthesis of p(BNI)-aryl I *via* ROMP (16)



Following general ROMP procedure using N-butylimide norbornene (329 mg, 137 eq, 1.5 mmol), triphenylphosphine (2.87 mg, 1 eq, 10.9 µmol), 1st generation Grubbs Catalyst (9.0 mg, 1 eq, 10.9 µmol), and (Z)-1,4-bis(4-iodophenoxy)but-2-ene (53.8 mg, 10 eq, 109 µmol) to produce a tan powder. Yield: 89%

^{1}H NMR (400 MHz, CD_3CN): δ 7.58 (d, *J* = 9.0 Hz, 2H), 7.44 – 7.21 (m, 5H), 6.76 (d, *J* = 9.0 Hz, 2H), 5.74 – 5.48 (m, 276H), 4.50 (d, 2H), 3.41 – 3.30 (m, 275H), 3.01 – 2.93 (m, 325H), 2.72 – 2.57 (m, 227H), 1.54 – 1.43 (m, 317H), 1.28 (q, *J* = 7.5 Hz, 280H), 0.90 (t, *J* = 7.3 Hz, 416H).
SEC analysis: M_n is 27.2 kDa, M_w is 34.4 kDa, *Đ* is 1.27.

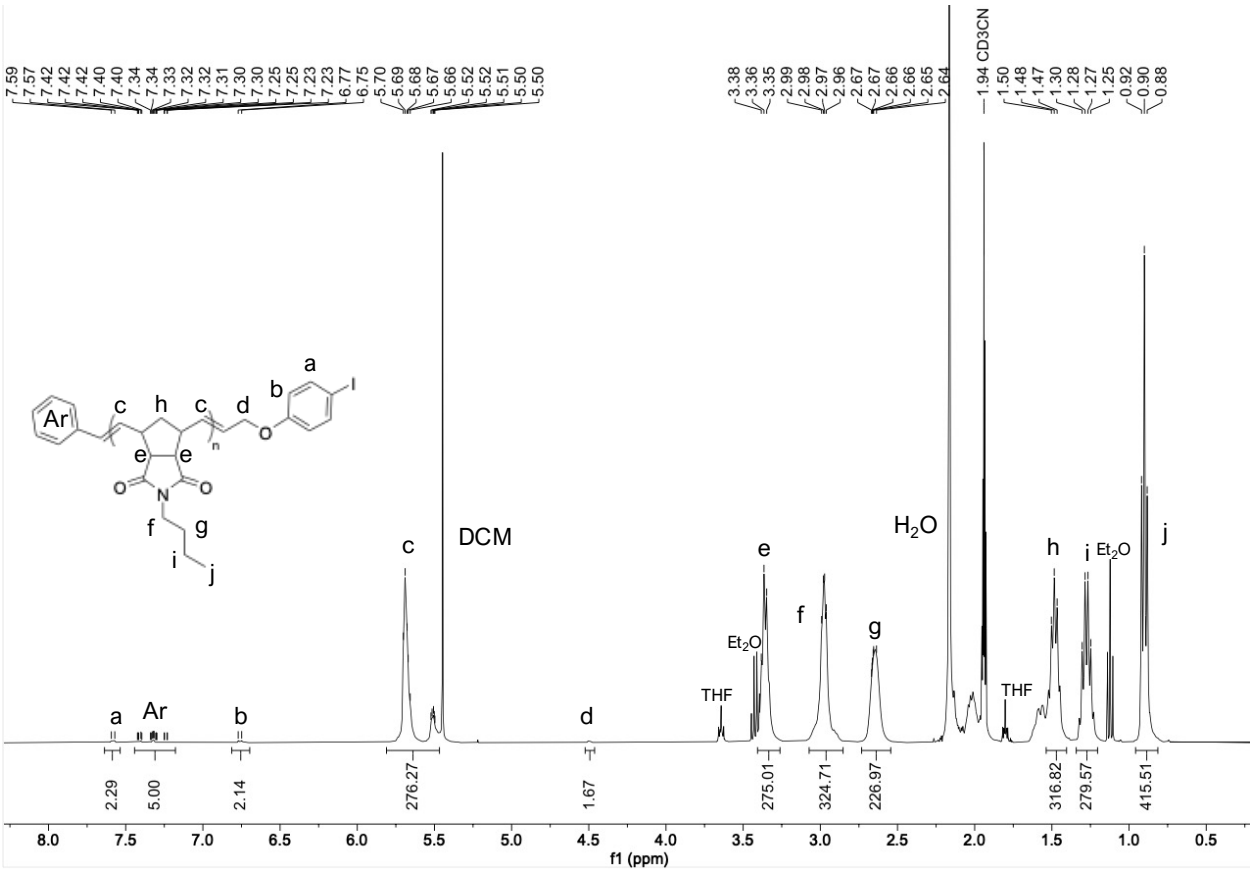


Figure S38. ^{1}H NMR spectrum of pBNI-aryl iodide (**16**) in CD_3CN at 25 ºC.

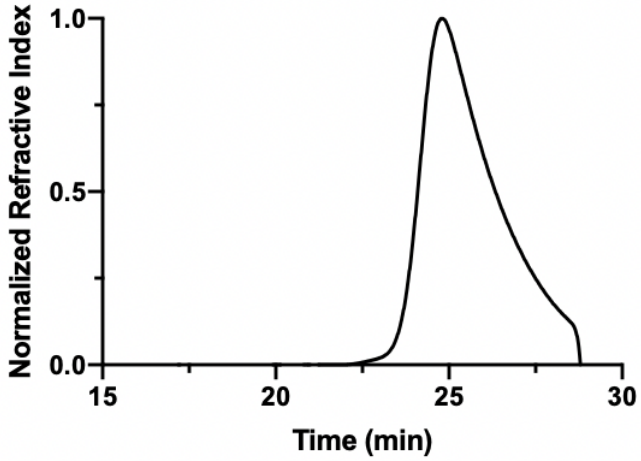
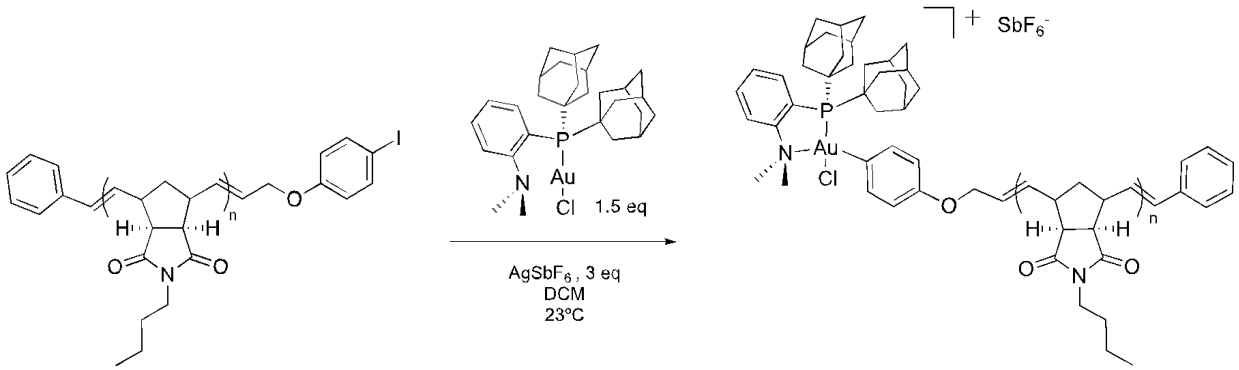


Figure S39. DMF SEC trace of pBNI-aryl iodide (**16**).

Synthesis of p(BNI)-Au(III) *via* oxidative addition (16a)



Following general oxidative addition procedure using $AgSbF_6$ (3.41 mg, 3 eq, 9.93 µmol) over four additions, (Me-DalPhos)AuCl (3.25 mg, 1.5 eq, 4.96 µmol), and p(BNI)-aryl I (100.0 mg, 1 eq, 3.31 µmol). The product is a yellow powder. Yield: 93%. Product purity by weight was determined to be 98% based on ^{1}H NMR.

^{1}H NMR (600 MHz, CD_3CN): δ 8.06 – 8.01 (m, 1H), 7.97 – 7.81 (m, 3H), 7.35 – 7.29 (m, 7H), 6.99 – 6.90 (m, 2H), 5.76 – 5.42 (m, 312H), 4.57 – 4.51 (m, 2H), 3.41 – 3.25 (m, 306H), 3.02 – 2.91 (m, 361H), 2.70 – 2.60 (m, 253H), 1.48 (t, *J* = 7.7 Hz, 343H), 1.28 (q, *J* = 7.5 Hz, 313H), 0.90 (t, *J* = 7.4 Hz, 466H).
^{31}P{^{1}H} NMR (243 MHz, CD_3CN): δ 75.11.

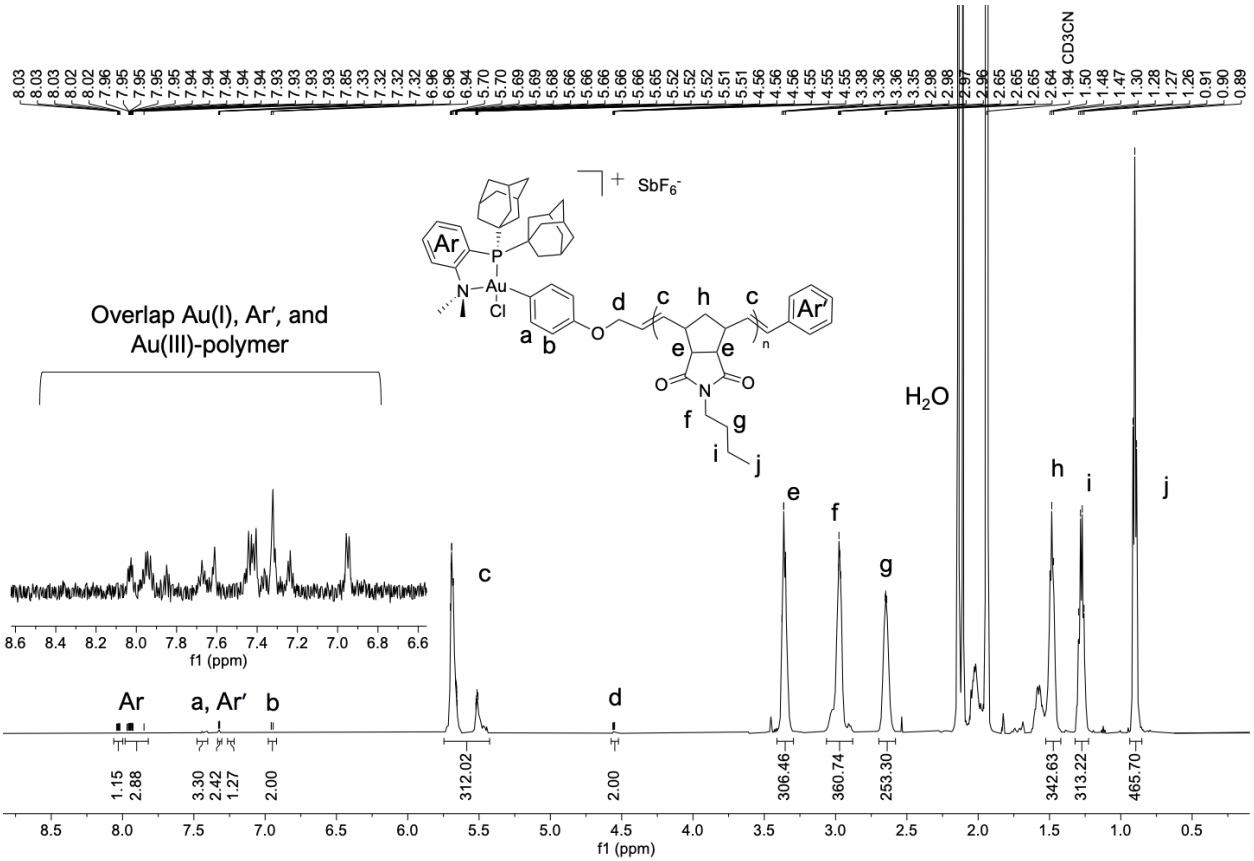


Figure S40. ^{1}H NMR spectrum of pBNI-Au(III) (**16a**) in CD_3CN at 25 ºC.

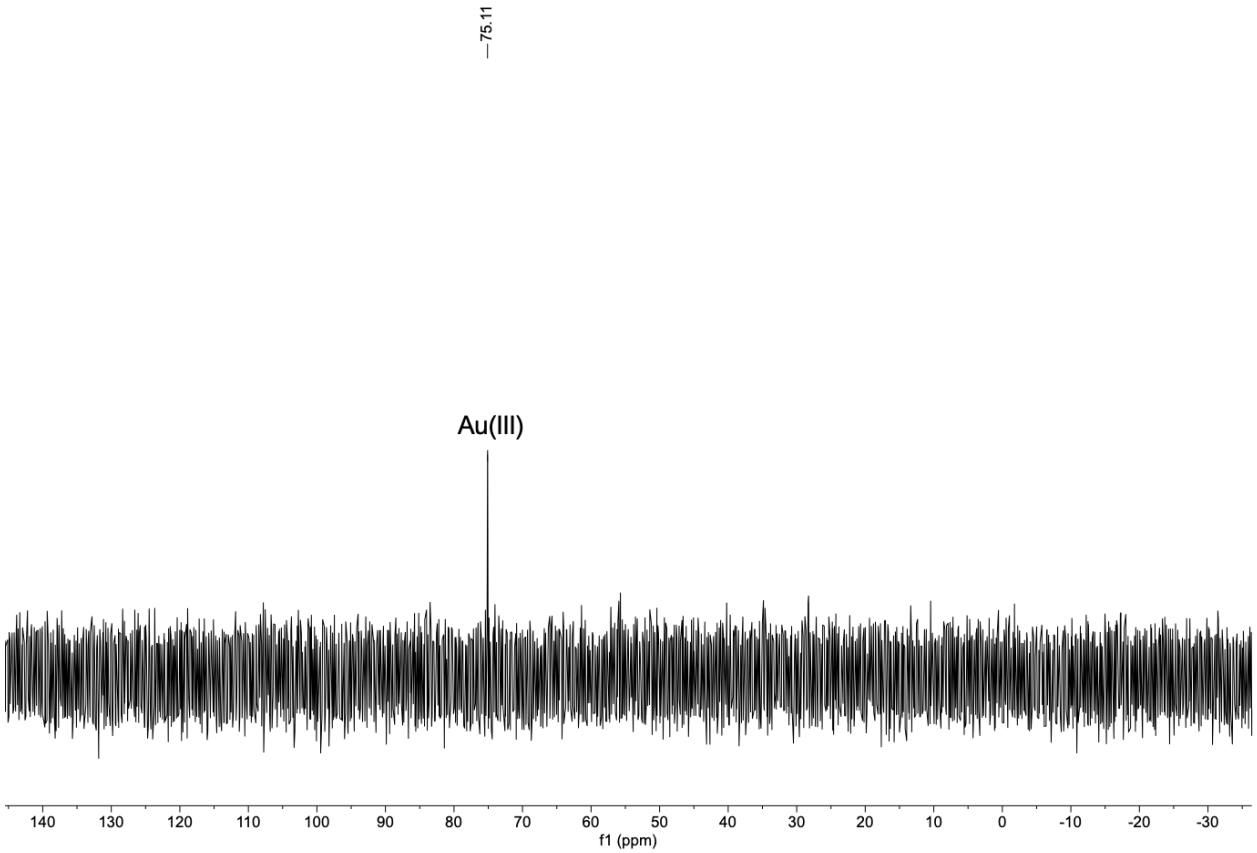
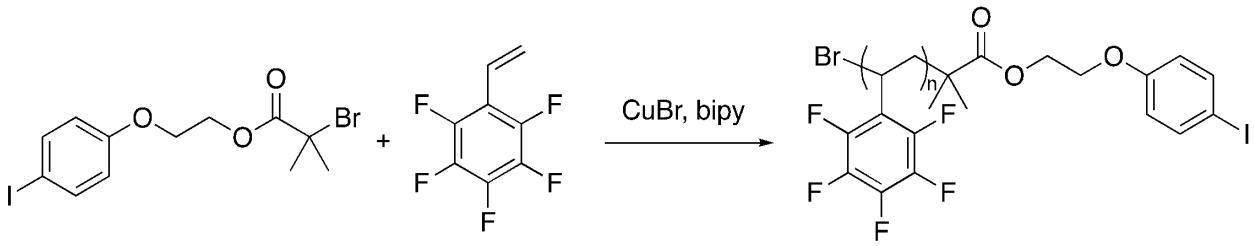


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of pBNI-Au(III) (**16a**) in CD_2Cl_2 at 25 ºC.

Synthesis of p(PFS)-aryl I *via* ATRP (6)



2,2'-Bipyridine (26.8 mg, 2 eq, 171.7 µmol), copper(I) bromide (12.3 mg, 1 eq, 85.9 µmol), neat 1,2,3,4,5-pentafluoro-6-vinylbenzene (500.0 mg, 353.9 µL, 30 eq, 2.6 mmol) and 2-(4-iodophenoxy)ethyl 2-bromo-2-methylpropanoate (35.5 mg, 1 eq, 85.9 µmol) were measured and added to a Schlenk flask. The reaction was freeze-pump-thawed 3 times. The reaction solution was blue/green. After 1 hour, the reaction was diluted in THF, filtered through a pad of neutral alumina, then precipitated in cold hexanes (45 mL) three times to produce a white solid. Yield: 54%

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.55 (d, 2H), 6.66 (d, 2H), 2.87 – 2.27 (m, 34H), 2.11 – 1.89 (m, 64H).
^{19}F NMR (376 MHz, Acetone-d_6): δ -140.24 – -146.85 (m), -155.50 – -160.20 (m), -162.64 – -166.37 (m).
SEC analysis: M_n is 5.7 kDa, M_w is 6.2 kDa, $Đ$ is 1.09.

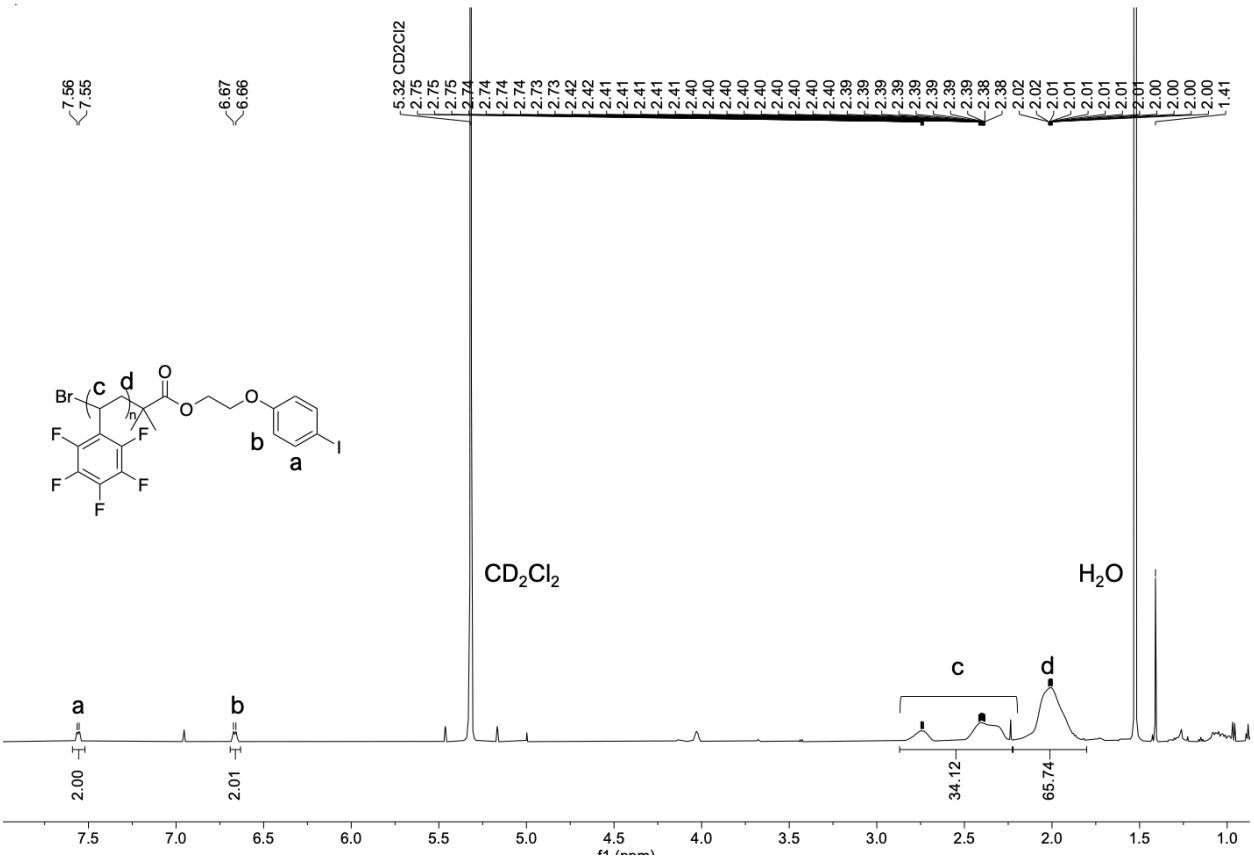


Figure S42. ^{1}H NMR spectrum of pPFS-aryl iodide (**6**) in CD_2Cl_2 at 25 ºC.

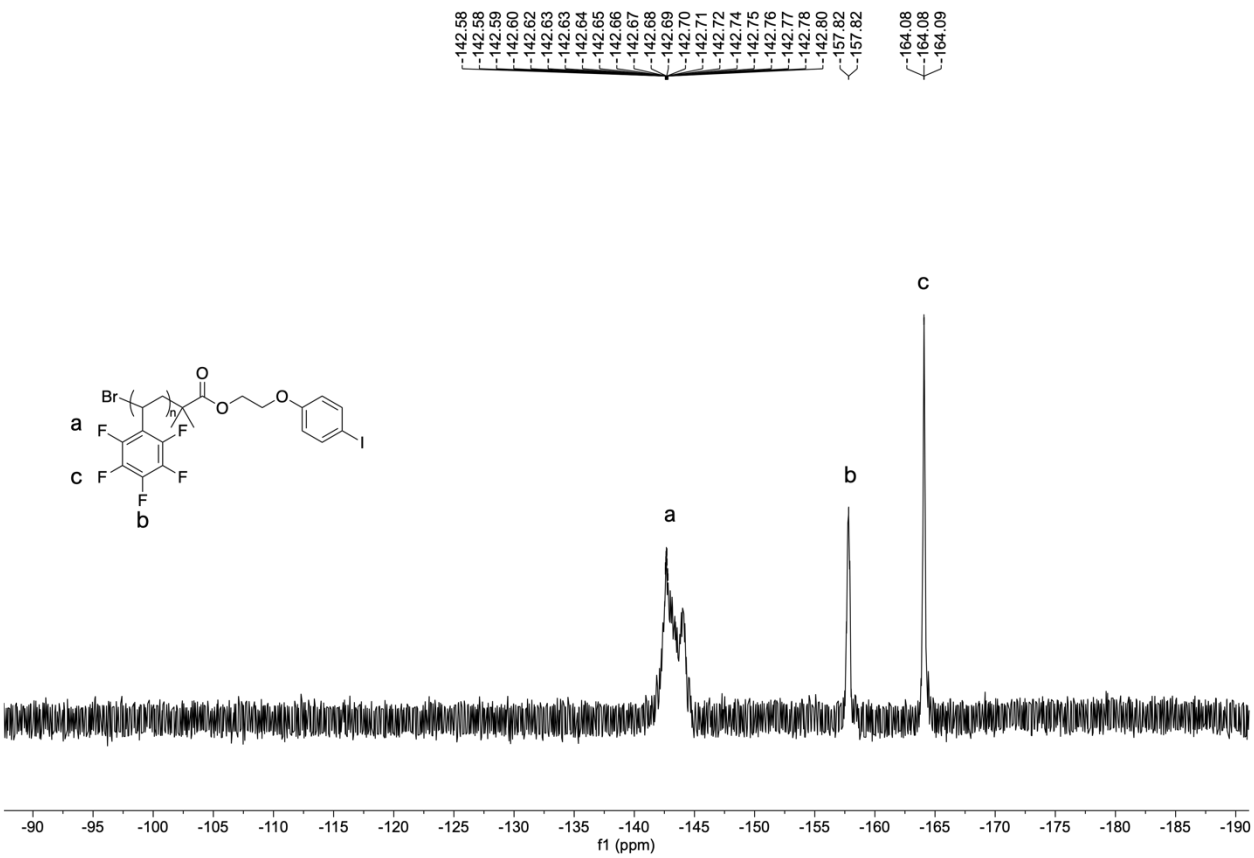


Figure S43. $^{19}F\{^{1}H\}$ NMR spectrum of pPFS-aryl iodide (**6**) in acetone-d_6 at 25 ºC.

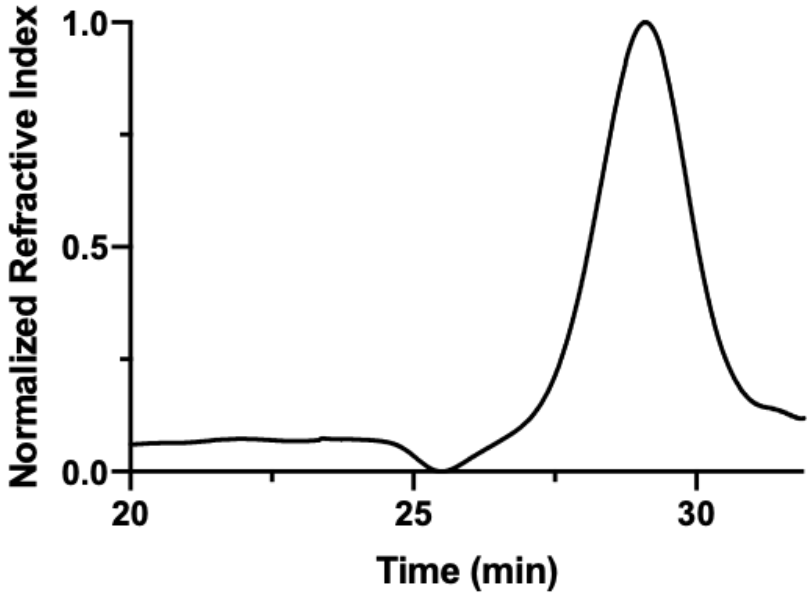
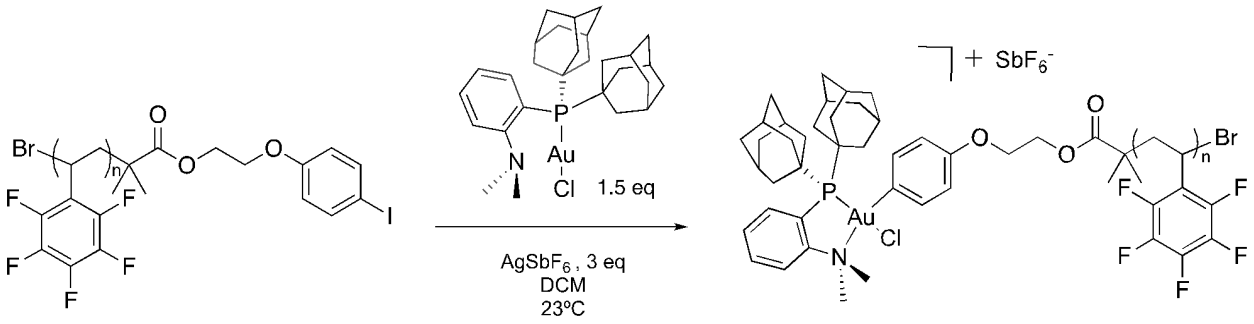


Figure S44. THF SEC trace of pPFS-aryl iodide (**6**).

Synthesis of p(PFS)-Au(III) *via* oxidative addition (6a)



Following general oxidative addition procedure using $AgSbF_6$ (16.1 mg, 3 eq, 46.8 μmol) over four additions, (Me-DalPhos)AuCl (15.3 mg, 1.5 eq, 23.4 μmol), and p(PFS)-aryl I (100.0 mg, 1 eq, 15.6 μmol). The product is a yellow powder. Yield: 58%. Product purity by weight was determined to be 94% based on ^{1}H NMR.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.07 – 7.68 (m, 4H), 7.33 (d, *J* = 1.2 Hz, 2H), 6.90 (d, *J* = 1.2 Hz, 2H), 2.84 – 2.25 (m, 54H), 2.14 – 1.88 (m, 90H).
^{19}F NMR (376 MHz, CD_2Cl_2): δ -143.47 (d, *J* = 329.6 Hz), -155.33, -162.09.
^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2): δ 74.53, 59.88, 57.44, 51.70.

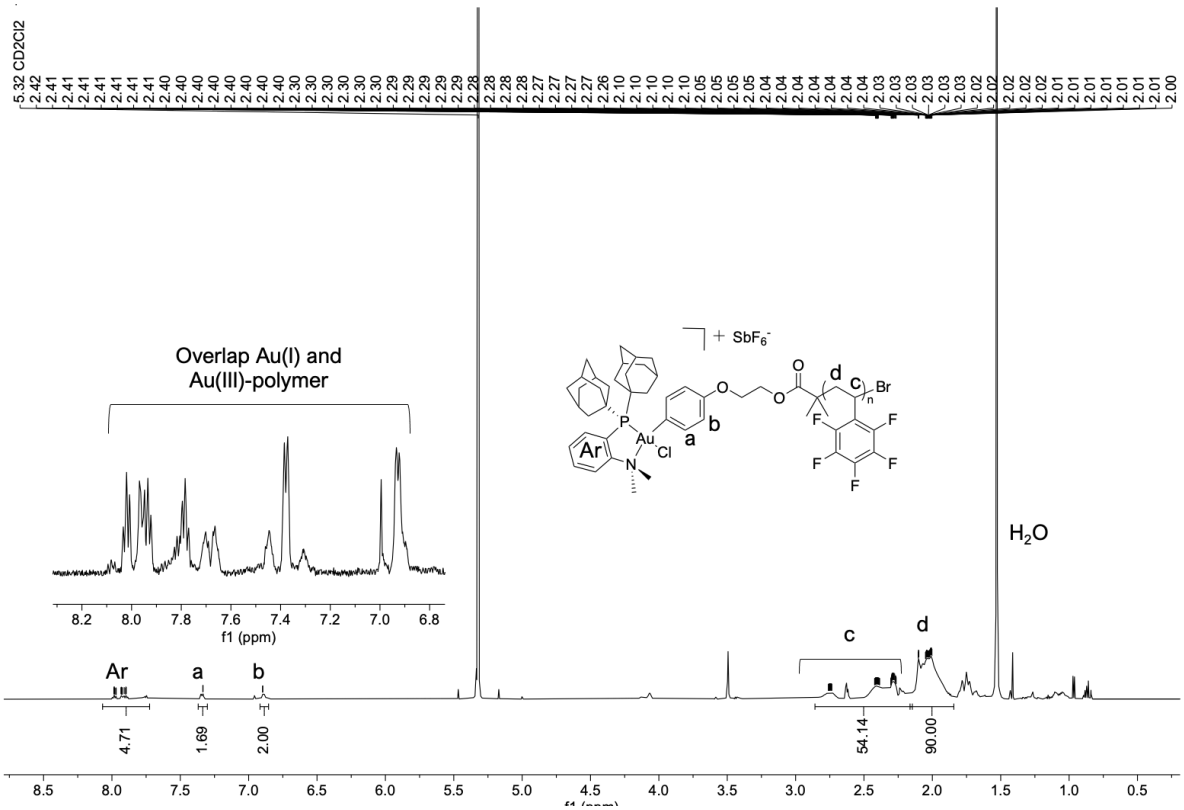


Figure S45. ^{1}H NMR spectrum of pPFS-Au(III) (**6a**) in CD_2Cl_2 at 25 ºC.

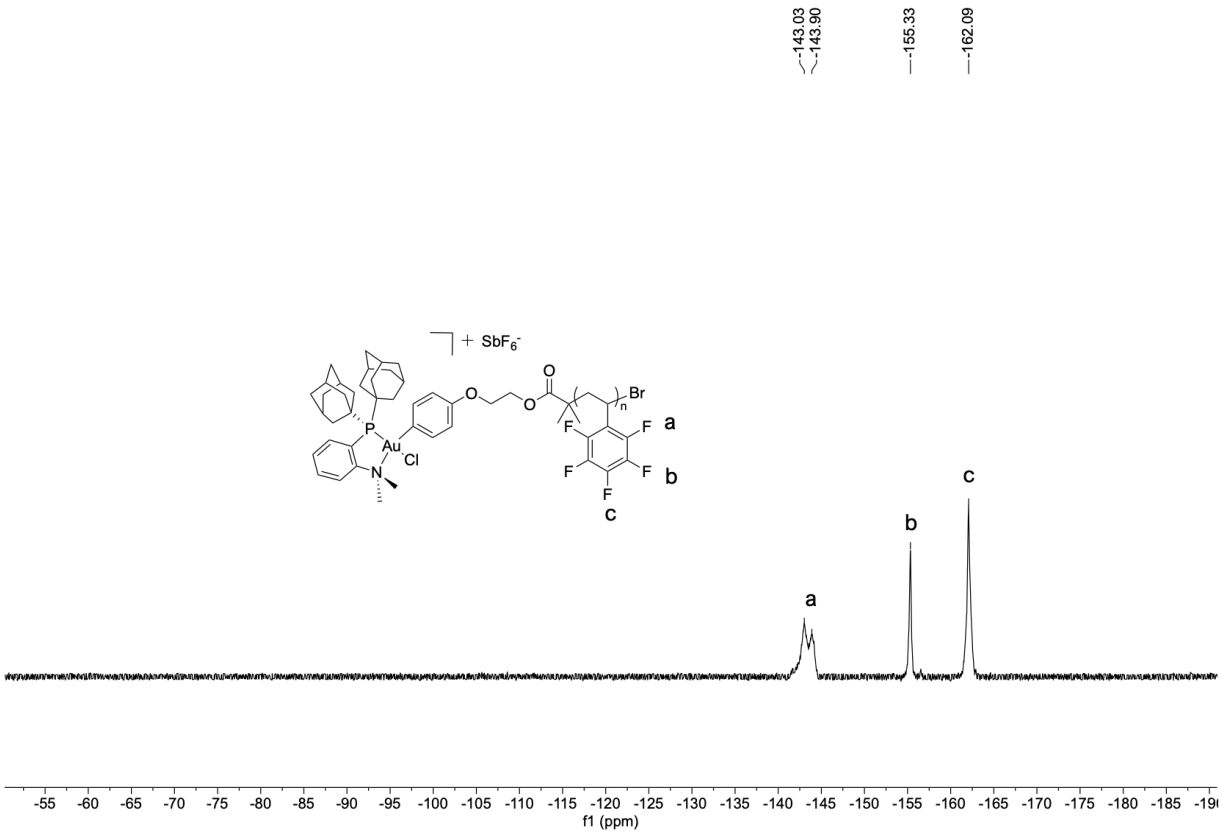


Figure S46. $^{19}F\{^{1}H\}$ NMR spectrum of pPFS-Au(III) (**6a**) in CD_2Cl_2 at 25 ºC.

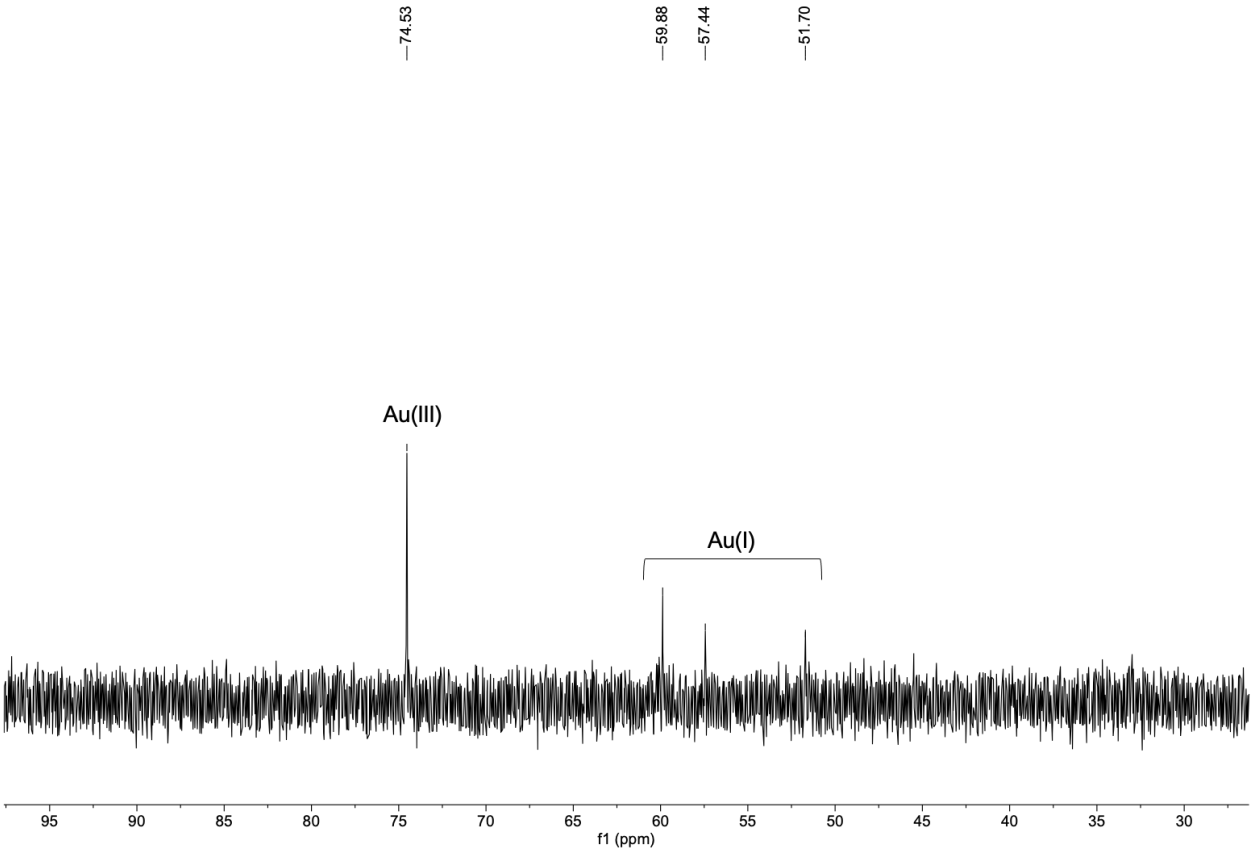
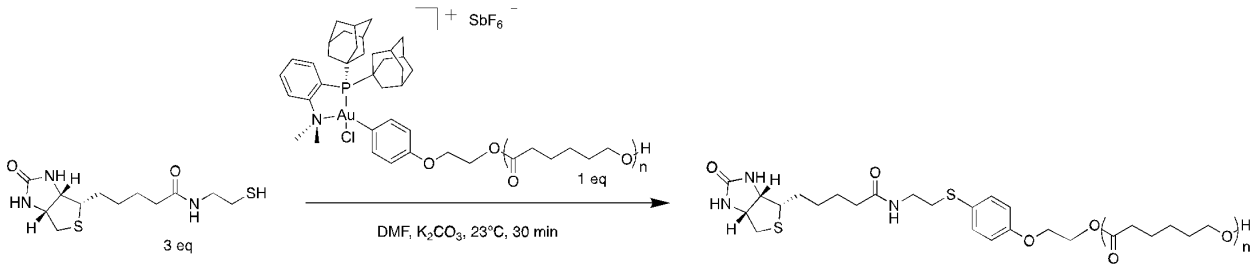


Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum of pPFS-Au(III) (**6a**) in CD_2Cl_2 at 25 ºC.

Synthesis of mono-telechelic biotin-p(CL) *via* reductive elimination (1a-8a)



General Small Molecule Reductive Elimination Procedure: Thiolated biotin (1.4 mg, 3 eq, 4.7 µmol), potassium carbonate (1.5 mg, 7 eq, 10.9 µmol), and pCL-Au(III) (**1a**) (10.3 mg, 93% wt, 1 eq, 1.6 µmol) was added to a vial with 500 µL DMF. The reaction proceeded for 30 minutes before one precipitation in 15 mL of cold methanol to produce a white powder. Yield: 47%.

^{1}H NMR (400 MHz, CD_3CN): δ 7.38 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.56 – 6.48 (m, 0H), 5.19 – 5.07 (m, 1H), 4.95 – 4.89 (m, 1H), 4.42 – 4.38 (m, 1H), 4.38 – 4.31 (m, 2H), 4.25 – 4.20 (m, 1H), 4.18 – 4.13 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 101H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.31 – 3.22 (m, 2H), 2.91 (s, 2H), 2.27 (t, *J* = 7.4 Hz, 105H), 1.72 – 1.46 (m, 217H), 1.45 – 1.28 (m, 110H).

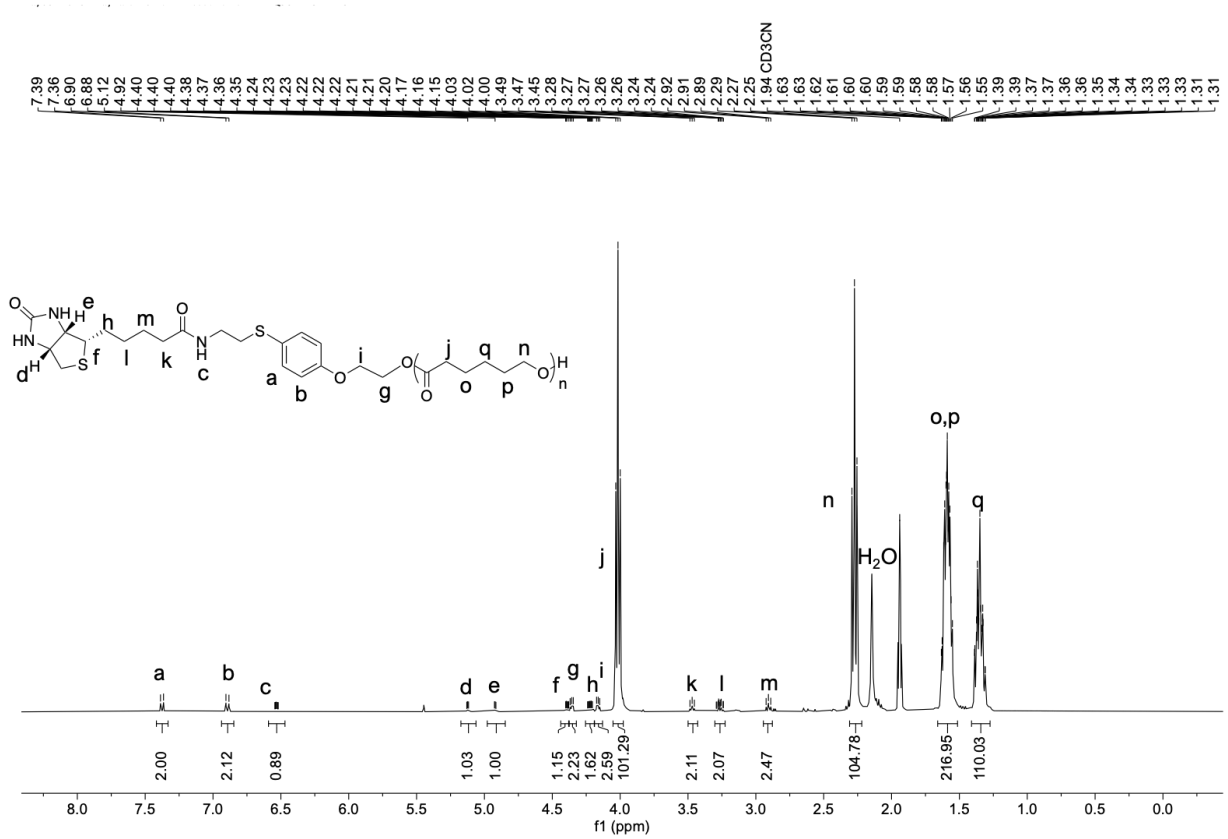


Figure S48. ^{1}H NMR spectrum of biotin-p(CL) (**1a-8a**) in CD_3CN at 25 ºC.

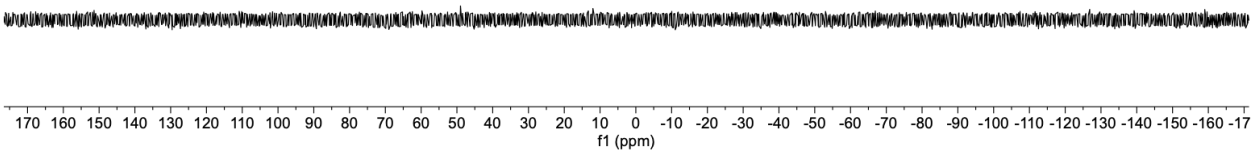


Figure S49*. ^{31}P{^{1}H} NMR spectrum of biotin-p(CL) (**1a-8a**) in CD_3CN at 25 ºC.

*No ^{31}P NMR peak is expected, indicating Au(III) is eliminated.

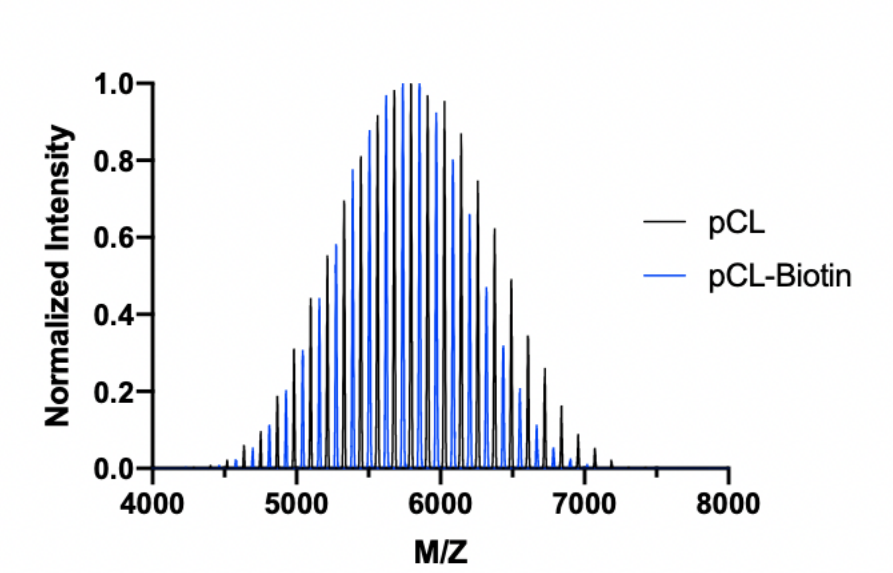
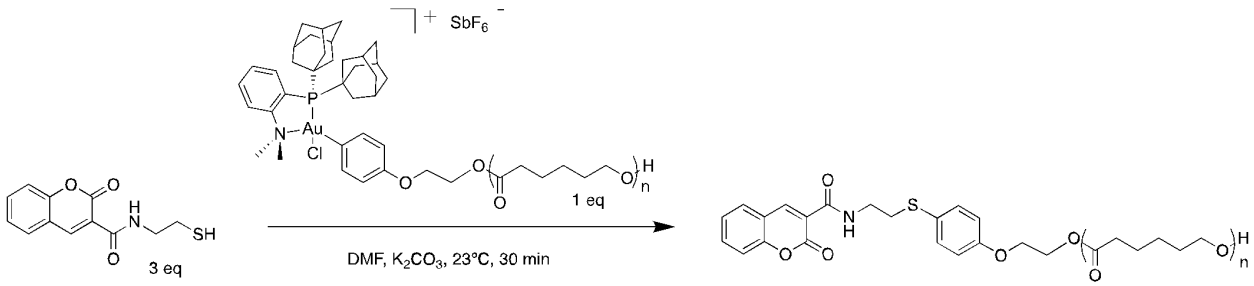


Figure S50. MALDI of biotin-p(CL) (**1a-8a**). This figure is also shown in the main text in Figure 2, shown larger here for easier viewing.

Synthesis of mono-telechelic coumarin-p(CL) *via* reductive elimination (1a-9a)



Following the general small molecule reductive elimination procedure with potassium carbonate (1.5 mg, 7 eq, 11.0 μmol), thiolated coumarin (1.2 mg, 3 eq, 4.7 μmol), pCL-Au(III) (**1a**) (10.4 mg, 93% wt, 1 eq, 1.6 μmol), and one precipitation in 15 mL of cold diethyl ether to produce a white powder. Yield: 82%.

^{1}H NMR (400 MHz, CD_3CN): δ 8.89 (d, *J* = 1.6 Hz, 1H), 8.82 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.66 (m, 1H), 7.48 – 7.30 (m, 4H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.38 – 4.22 (m, 2H), 4.09 (d, *J* = 4.8 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 134H), 3.59 – 3.51 (m, 2H), 3.51 – 3.42 (m, 2H), 3.06 (t, *J* = 6.7 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 113H), 1.71 – 1.50 (m, 230H), 1.44 – 1.21 (m, 116H).

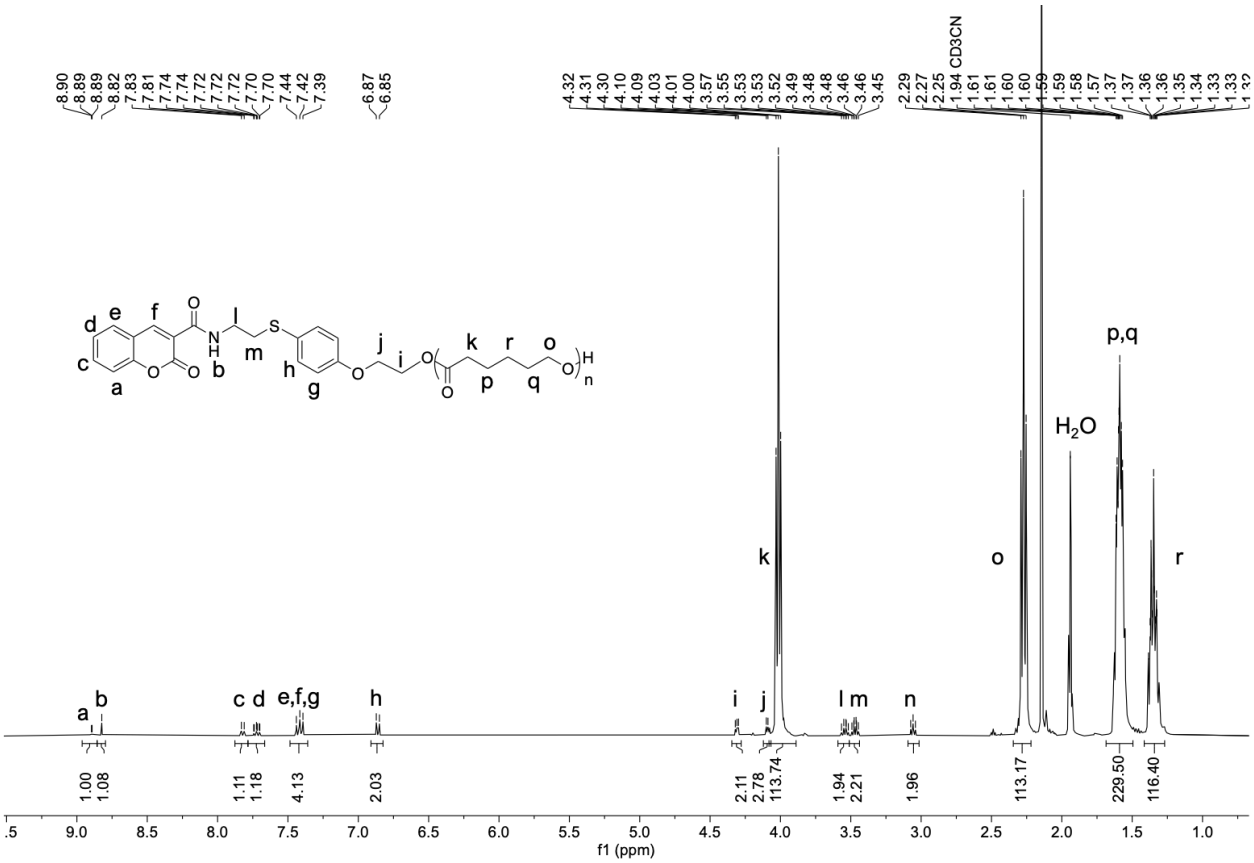


Figure S51. ^{1}H NMR spectrum of coumarin-pCL (**1a-9a**) in CD_3CN at 25 ºC.

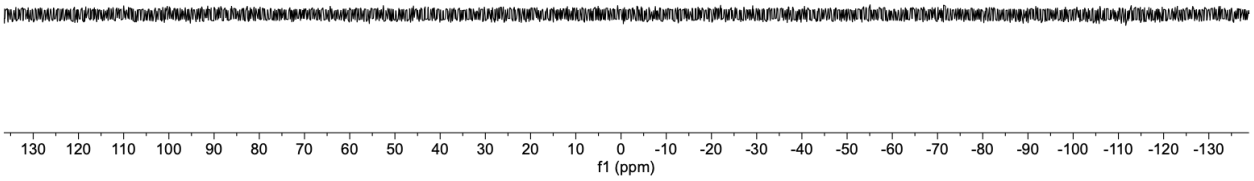
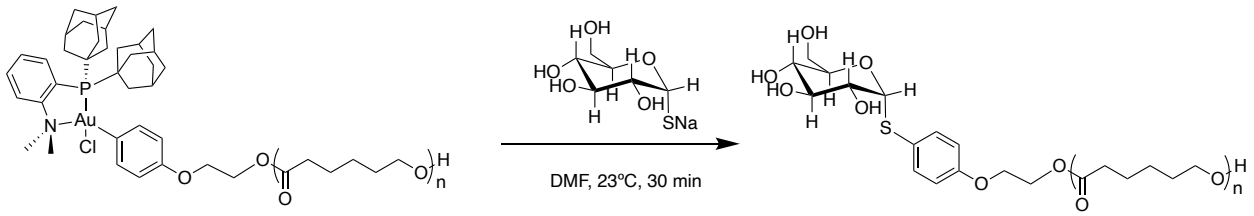


Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum of coumarin-p(CL) (**1a-9a**) in CD_3CN at 25 ºC.

Synthesis of mono-telechelic glucose-p(CL) *via* reductive elimination (1a-TG)



Following the general small molecule reductive elimination procedure with 1-Thio-b-D-glucose sodium salt dihydrate (1.0 mg, 3 eq, 4.7 μmol) and pCL-Au(III) (**1a**) (10.4 mg, 93% wt, 1 eq, 1.6 μmol) to produce a white powder. Potassium carbonate was not required with use of a thiol salt. Yield: 49%.

^{1}H NMR (400 MHz, CD_3CN): δ 7.49 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.72 – 5.67 (m, 1H), 4.43 (d, *J* = 9.7 Hz, 2H), 4.39 – 4.33 (m, 2H), 4.22 – 4.13 (m, 3H), 4.02 (t, *J* = 6.6 Hz, 141H), 3.87 – 3.80 (m, 1H), 3.76 – 3.70 (m, 1H), 3.62 – 3.53 (m, 1H), 3.33 – 3.28 (m, 1H), 3.10 – 3.01 (m, 1H), 2.27 (t, *J* = 7.4 Hz, 154H), 1.68 – 1.51 (m, 285H), 1.44 – 1.26 (m, 150H).

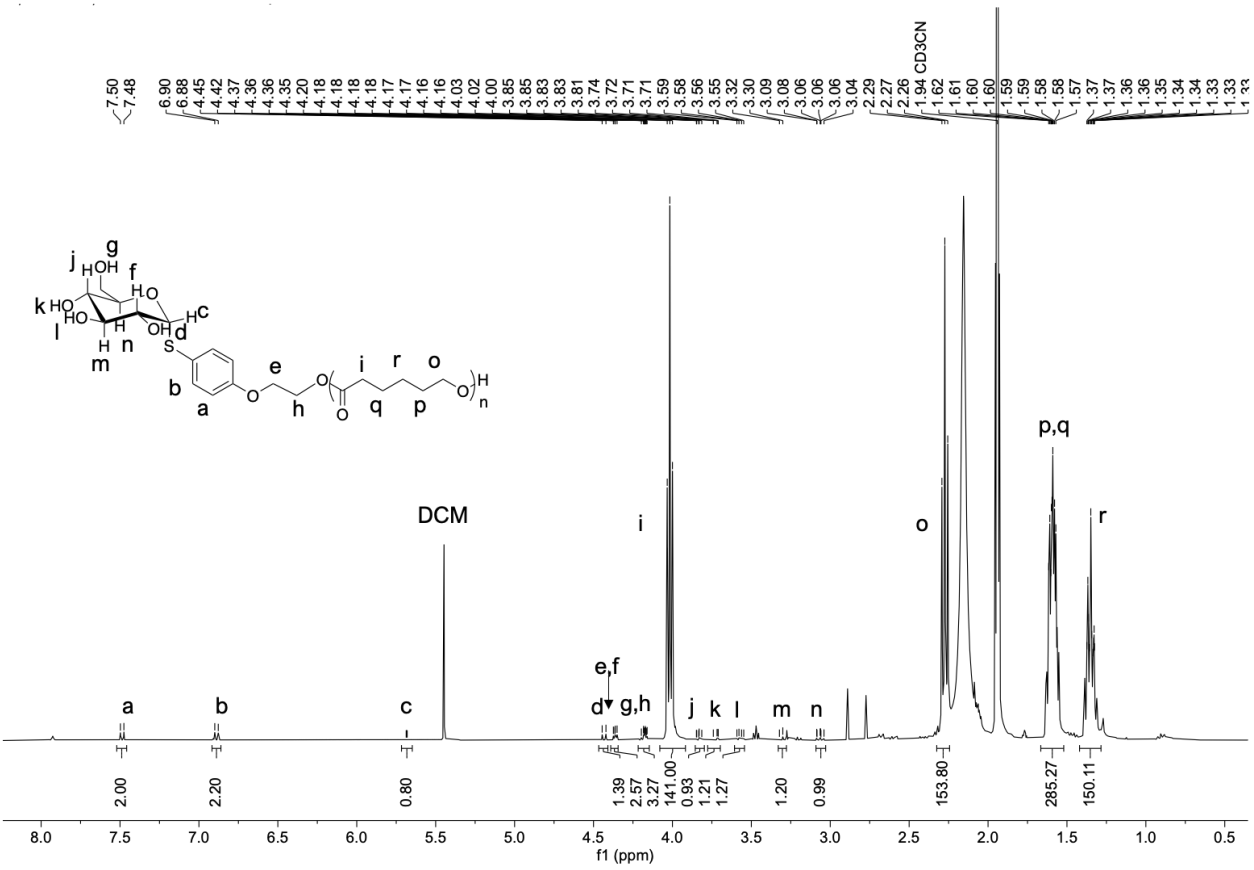


Figure S53. ^{1}H NMR spectrum of glucose-p(CL) (**1a-TG**) in CD_3CN at 25 ºC.

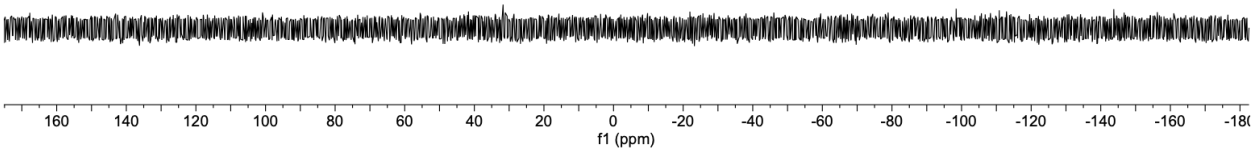
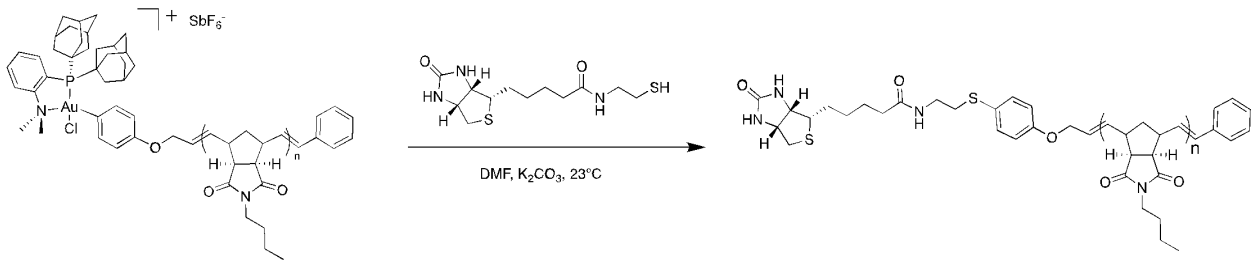


Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum of glucose-p(CL) (**1a-TG**) in CD_3CN at 25 ºC.

Synthesis of mono-telechelic biotin-p(BNI) *via* reductive elimination (3a-8a)



Following the general small molecule reductive elimination procedure with potassium carbonate (682 µg, 7 eq, 4.9 µmol), thiolated biotin (642 µg, 3 eq, 2.1 µmol), and pBNI-Au(III) (**2a**) (6.6 mg, 92% wt, 1 eq, 0.7 µmol) to produce a white powder. Yield: 62%.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.98 – 7.91 (m, 1H), 7.45 – 7.19 (m, 7H), 6.92 (d, 2H), 6.01 – 5.91 (m, 1H), 5.69 – 5.36 (m, 78H), 4.51 (d, *J* = 5.6 Hz, 2H), 4.36 – 4.27 (m, 1H), 4.15 – 4.10 (m, 1H), 3.11 – 2.96 (m, 87H), 2.70 – 2.58 (m, 64H), 2.03 – 1.93 (m, 36H), 1.54 – 1.49 (m, 27H), 1.43 (t, *J* = 7.3 Hz, 97H), 1.32 – 1.15 (m, 88H), 0.86 (t, *J* = 7.4 Hz, 123H).

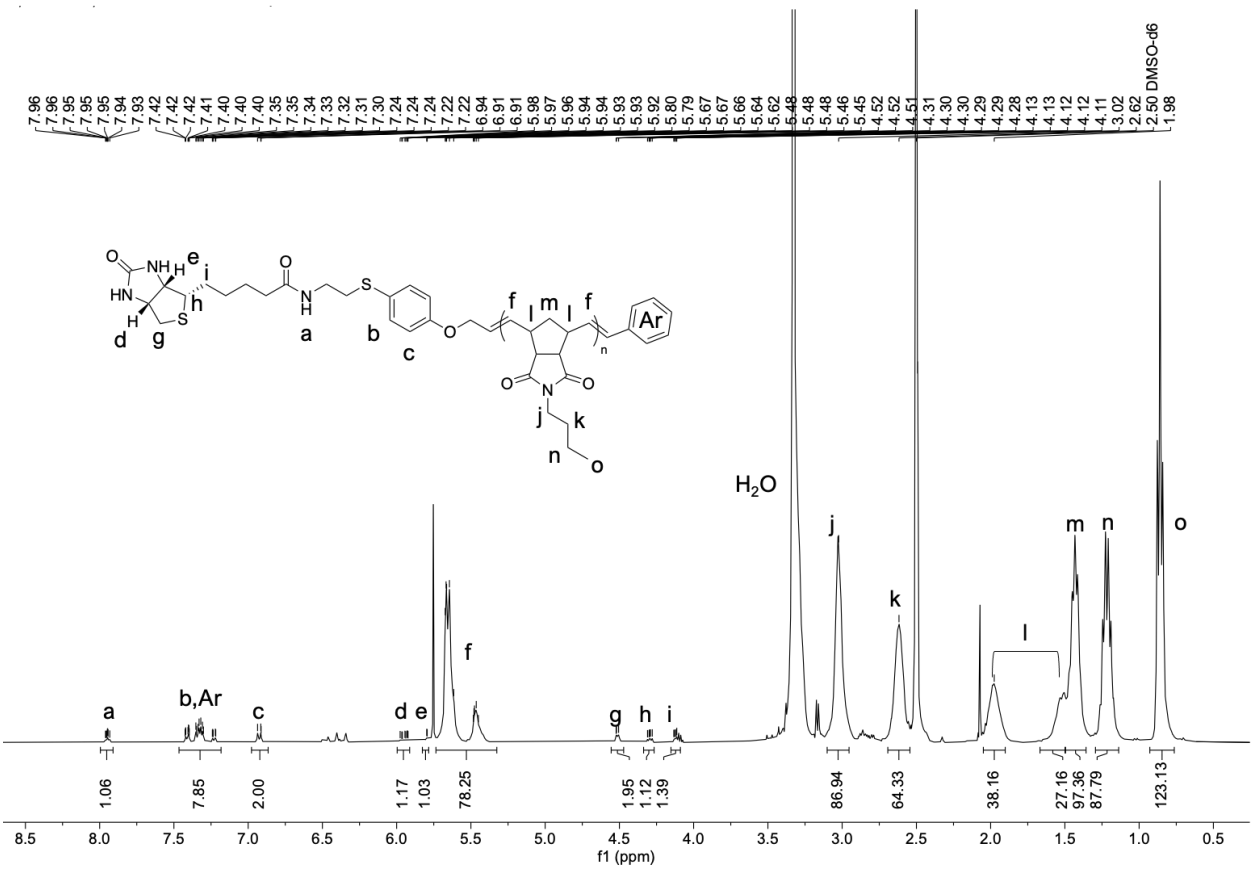


Figure S55. ^{1}H NMR spectrum of biotin-p(BNI) (**3a-8a**) in DMSO-d_6 at 25 ºC.

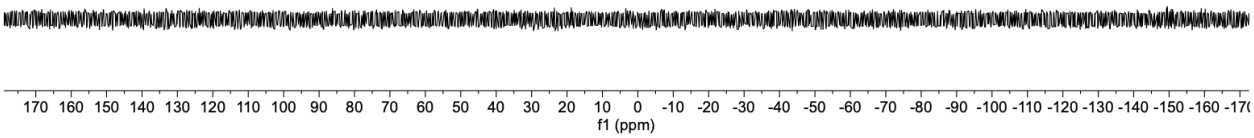
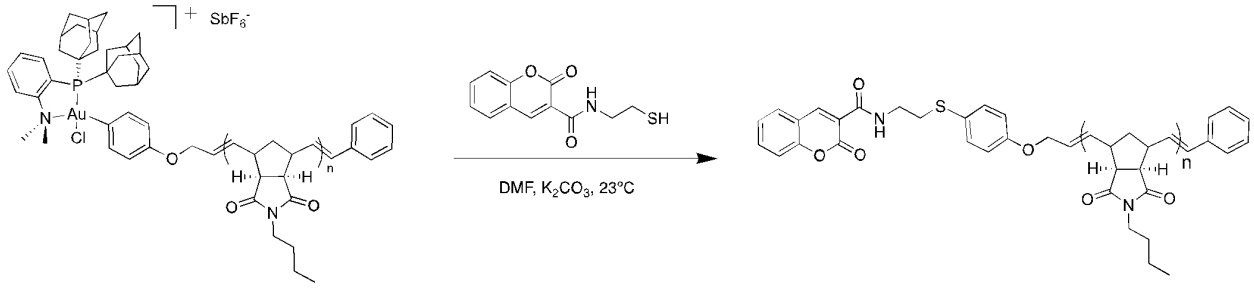


Figure S56. ^{31}P{^{1}H} NMR spectrum of biotin-p(BNI) (**3a-8a**) in DMSO-d_6 at 25 ºC.

Synthesis of mono-telechelic coumarin-p(BNI) *via* reductive elimination (3a-9a)



Following the general small molecule reductive elimination procedure with potassium carbonate (820 µg, 7 eq, 5.9 µmol), thiolated coumarin (634 µg, 3 eq, 2.5 µmol), pBNI-Au(III) (**2a**) (7.9 mg, 92% wt, 1 eq, 0.8 µmol), and one precipitation in 15 mL cold diethyl ether to produce a white powder. Yield: 40%.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.95 – 8.88 (m, 1H), 8.00 – 7.91 (m, 1H), 7.79 – 7.71 (m, 1H), 7.50 (d, 1H), 7.46 – 7.29 (m, 7H), 7.25 – 7.18 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.73 – 5.39 (m, 76H), 3.10 – 2.96 (m, 87H), 2.70 – 2.54 (m, 62H), 2.06 – 1.90 (m, 37H), 1.60 – 1.49 (m, 26H), 1.49 – 1.37 (m, 86H), 1.28 – 1.15 (m, 95H), 0.86 (t, *J* = 7.3 Hz, 122H).

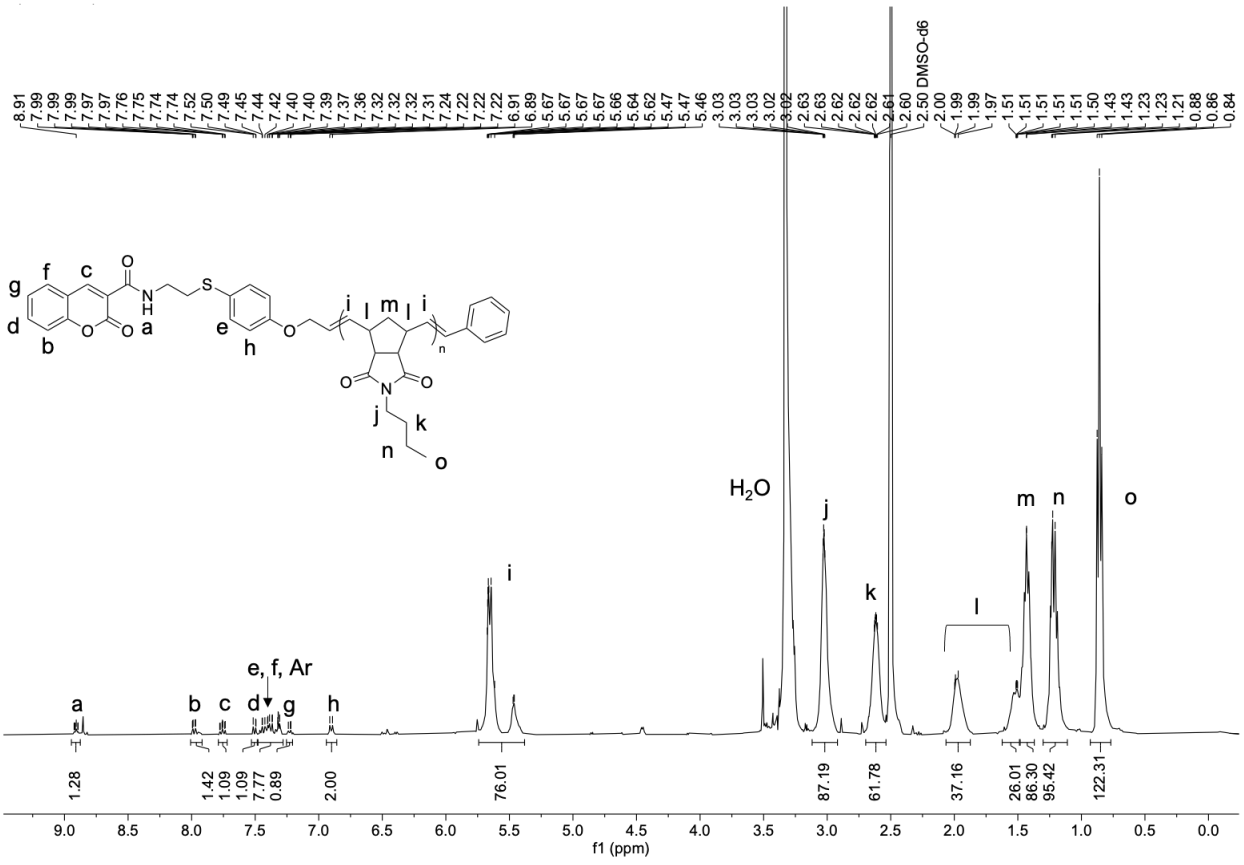


Figure S57. ^{1}H NMR spectrum of coumarin-p(BNI) (**3a-9a**) in DMSO-d$_6$ at 25 ºC.

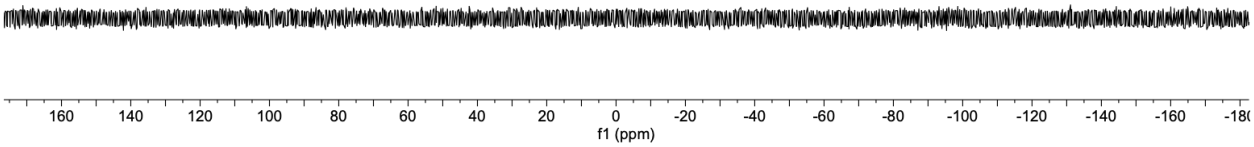
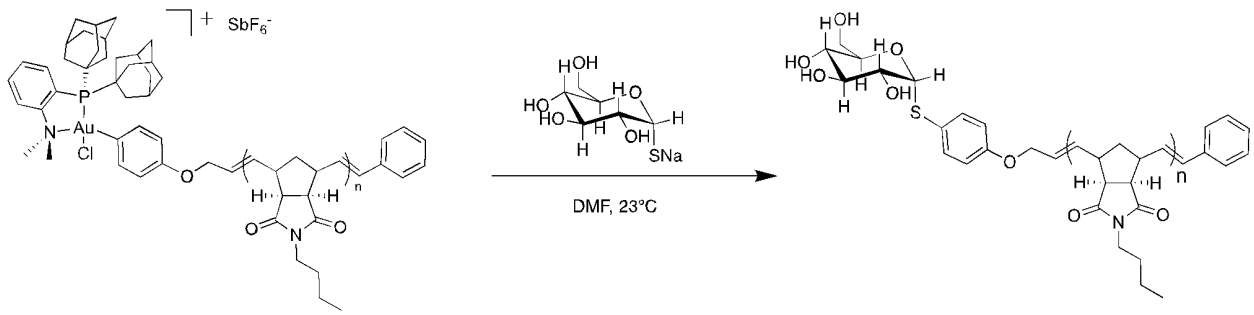


Figure S58. $^{31}P\{^{1}H\}$ NMR spectrum of coumarin-p(BNI) (**3a-9a**) in DMSO-d_6 at 25 ºC.

Synthesis of mono-telechelic glucose-p(BNI) *via* reductive elimination (3a-TG)



Following the general small molecule reductive elimination procedure 1-thio-b-D-glucose sodium salt dihydrate (528 µg, 3 eq, 2.4 µmol) and pBNI-Au(III) (**2a**) (7.5 mg, 92% wt, 1 eq, 0.8 µmol). Yield: 82%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.47 – 7.20 (m, 7H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.72 – 5.43 (m, 80H), 5.20 – 5.12 (m, 1H), 5.06 – 5.02 (m, 1H), 4.95 – 4.89 (m, 1H), 4.55 – 4.47 (m, 3H), 4.38 (d, *J* = 10.0 Hz, 1H), 3.70 – 3.63 (m, 2H), 3.06 – 2.99 (m, 95H), 2.69 – 2.57 (m, 65H), 2.02 – 1.93 (m, 50H), 1.67 – 1.49 (m, 28H), 1.48 – 1.39 (m, 97H), 1.22 (q, *J* = 7.2 Hz, 98H), 0.86 (t, *J* = 7.4 Hz, 131H).

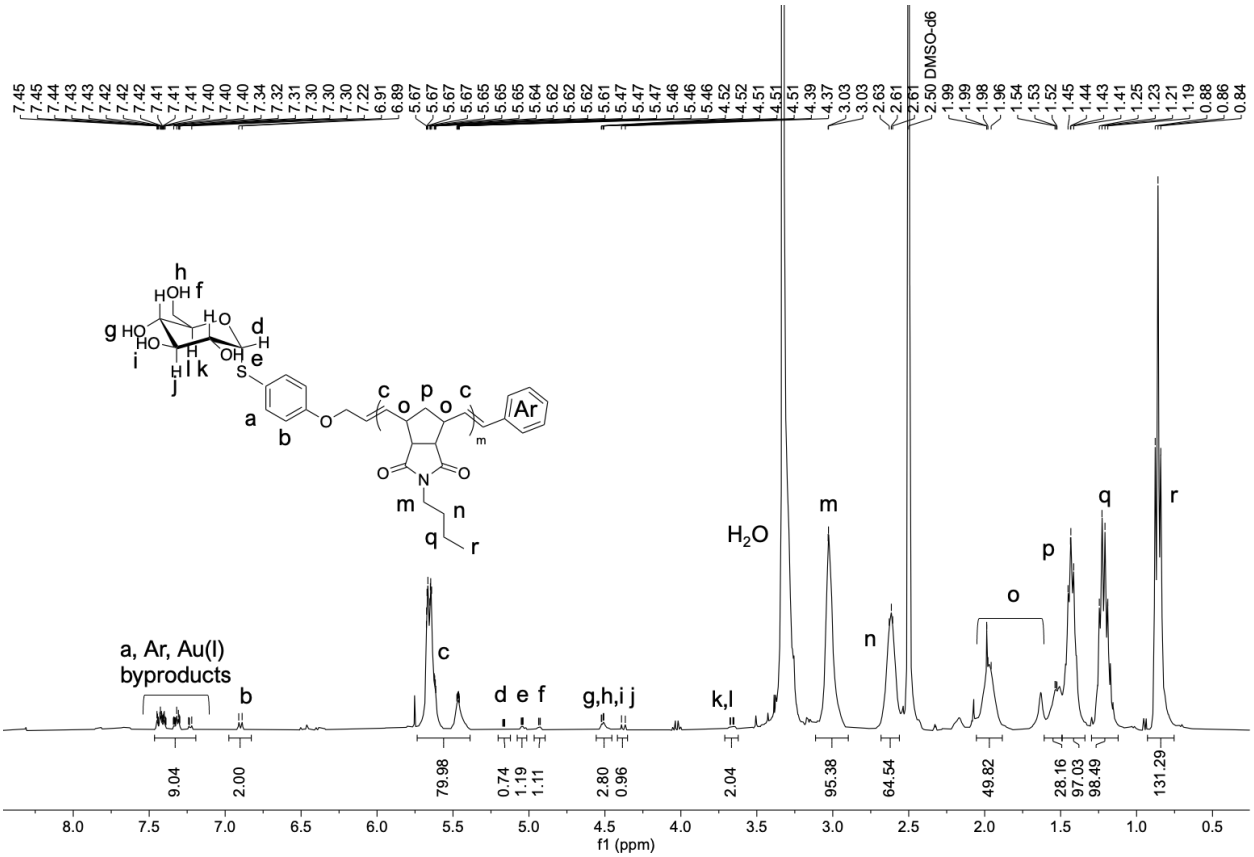


Figure S59. ^{1}H NMR spectrum of glucose-p(BNI) (**3a-TG**) in DMSO-d_6 at 25 ºC.

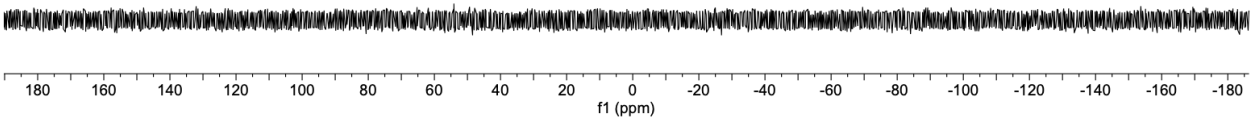
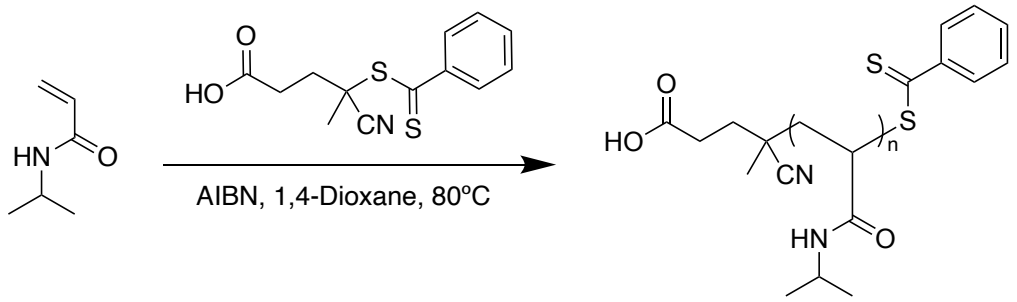


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of glucose-p(BNI) (**3a-TG**) in DMSO-d_6 at 25 ºC.

Synthesis of p(*N*-isopropylacrylamide) *via* RAFT (10)



N-Isopropylacrylamide (NIPAM) (700.0 mg, 140 eq, 6.2 mmol) and 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (12.3 mg, 1 eq, 44.2 µmol), and azobisisobutyronitrile (2.2 mg, 0.3 eq, 13.3 µmol) were dissolved in a Schlenk flask with 2 mL of anhydrous 1,4-dioxane. The reaction underwent three freeze-pump-thaw cycles to remove oxygen. The reaction was exposed to an argon atmosphere. The reaction progressed at 80 °C while stirring for 4 hours, at which time the reaction was precipitated into 45 mL of cold diethyl ether three times to produce a pink solid. Yield: 20%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (t, *J* = 8.2 Hz, 2H), 7.54 (t, 1H), 7.39 (t, 2H), 6.30 (s, 1H), 4.24 – 3.83 (m, 69H), 2.69 – 1.28 (m, 492H), 1.21 – 1.01 (m, 408H).
SEC analysis: M_n is 9.3 kDa, M_w is 10.4, $Đ$ is 1.11.

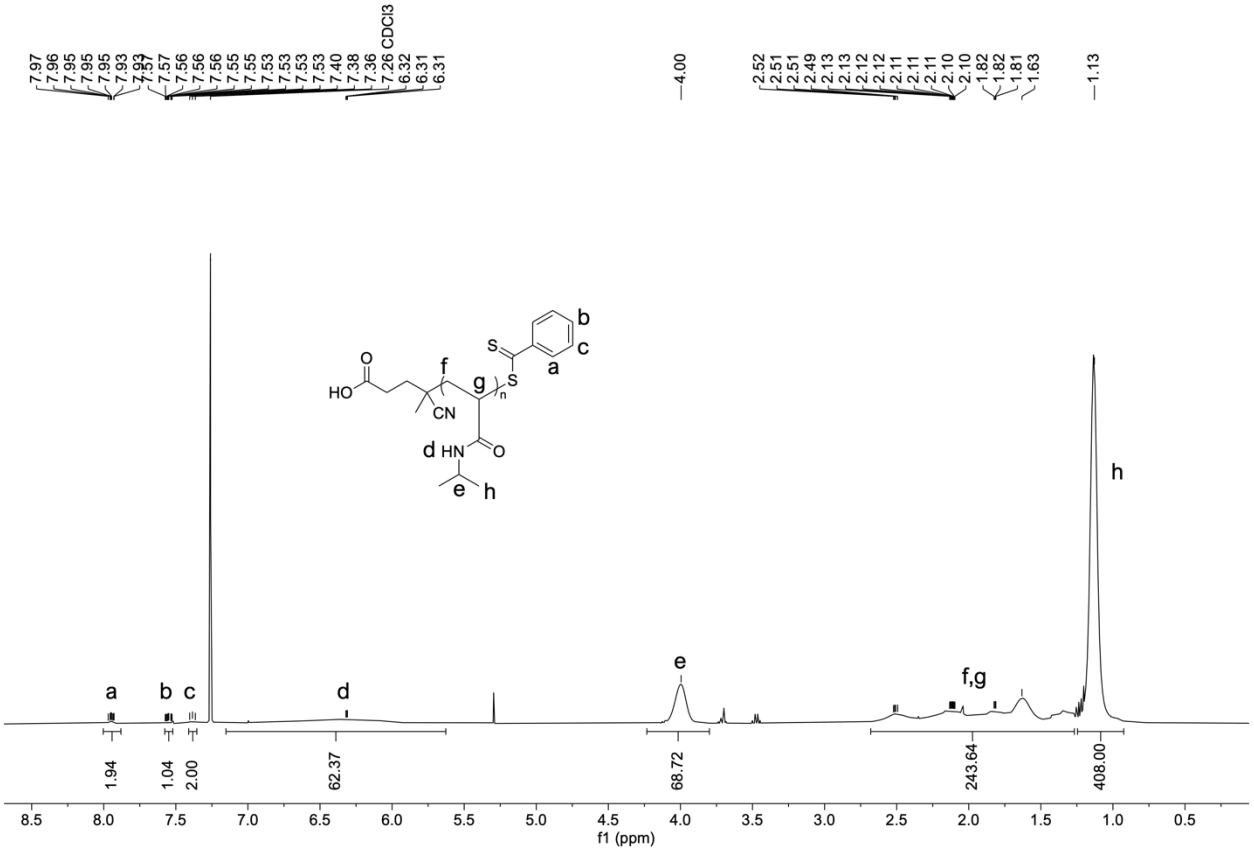


Figure S61. ^{1}H NMR spectrum of pNIPAM (**10**) in $CDCl_3$ at 25 ºC.

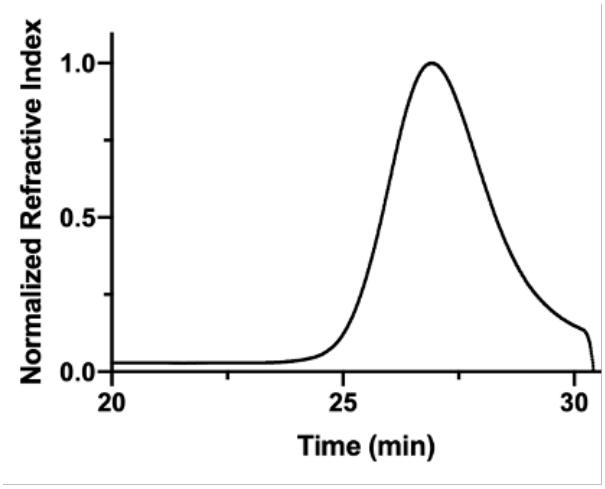
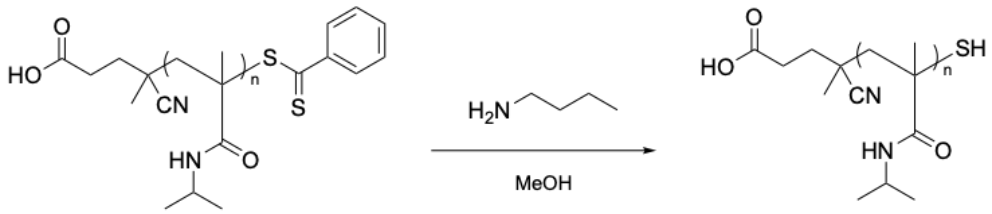


Figure S62. DMF SEC trace of pNIPAM (**10**).

Aminolysis of p(*N*-isopropylacrylamide) (10a)



p(*N*-isopropylacrylamide) (51.5 mg, 1 eq, 4.5 μmol) was added to a dram vial and dissolved in 500 μL of methanol. The reaction solution was pink and translucent. *n*-butylamine (13.2 mg, 17.9 μL, 40 eq, 181 μmol) was added to the dram vial and the reaction was stirred at 23 ºC for 30 minutes. The reaction became yellow, indicating that the dithioester end group had been cleaved. Next, the reaction was precipitated three times into cold diethyl ether (45 mL) to produce a white solid. Yield: 64%

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 – 6.03 (m, 67H), 4.22 – 3.76 (m, 69H), 2.57 – 1.29 (m, 278H), 1.30 – 0.96 (m, 401H).

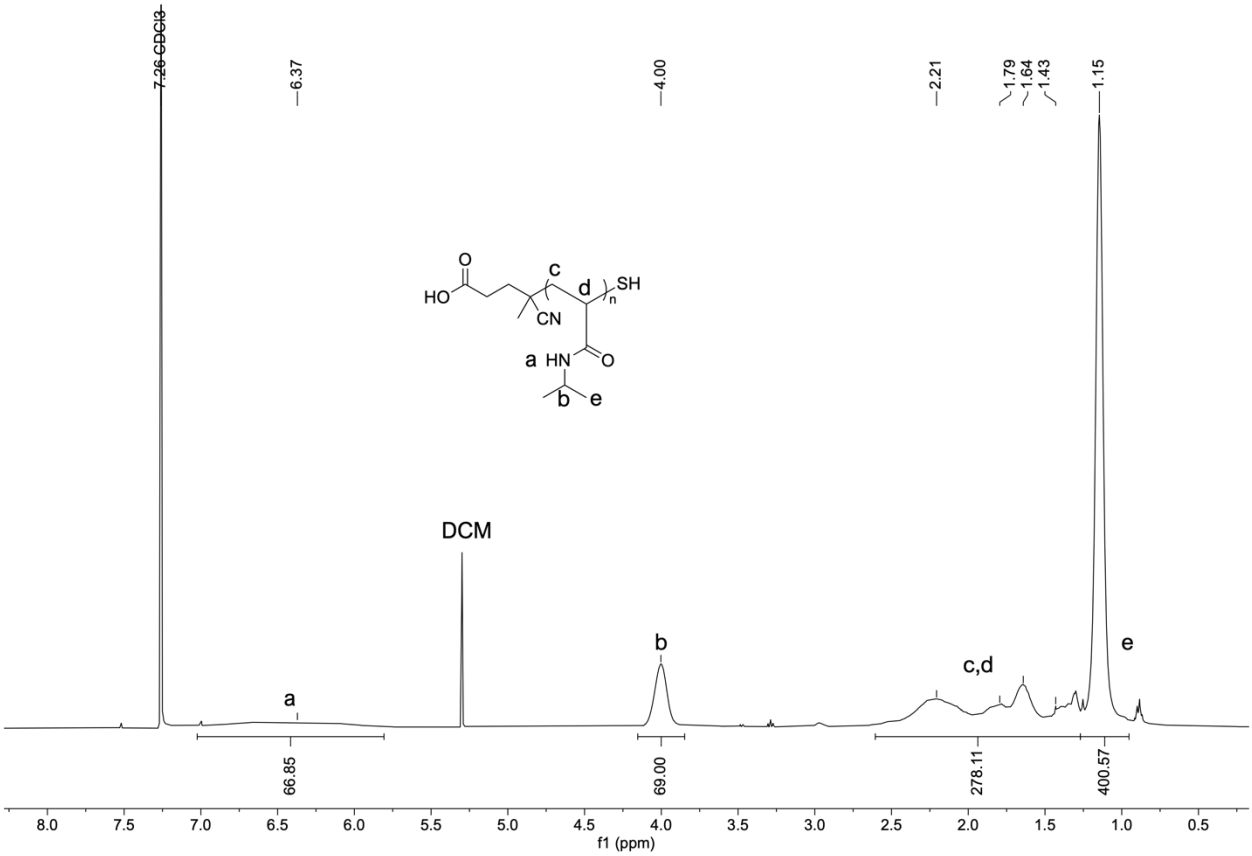


Figure S63. ^{1}H NMR spectrum of pNIPAM-SH (**10a**) in $CDCl_3$ at 25 ºC.

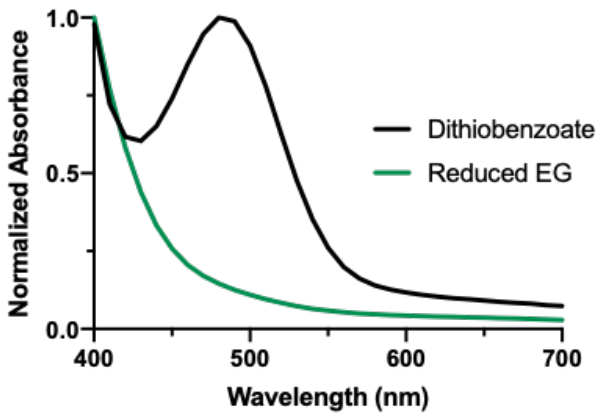
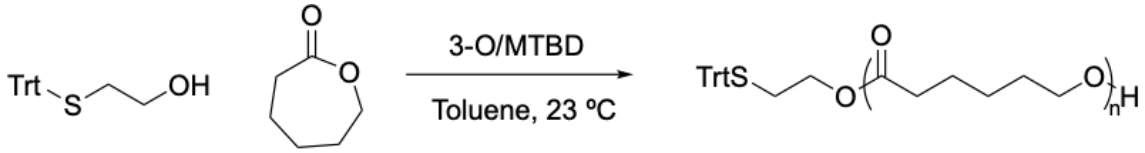


Figure S64. UV-vis spectroscopy of dithiobenzoate-containing p(NIPAM) (**10**) (black) and the resulting reduced thiol end-group pNIPAM-SH (**10a**) (green).

Synthesis of Trt-p(CL) *via* ROP (12)



Following the general ROP procedure, 3-O catalyst (9.983 mg, 1.1 eq, 10.951 µmol), caprolactone (100.0 mg, 97.0 µL, 88 eq, 876.1 µmol), 2-(tritylthio)ethan-1-ol (3.2 mg, 1 eq, 10.0 µmol), MTBD (1.7 mg, 1.6 µL, 1.1 eq, 11.0 µmol), and 1.75 mL toluene. Yield: 93%

^{1}H NMR (300 MHz, CD_3CN): δ 7.52 – 7.19 (m, 15H), 4.07 (t, *J* = 6.7 Hz, 168H), 2.32 (t, *J* = 7.5 Hz, 171H), 1.84 – 1.50 (m, 345H), 1.54 – 1.31 (m, 173H).
SEC analysis: M_n is 10.0 kDa, M_w is 12.0 kDa, $Đ$ is 1.20.

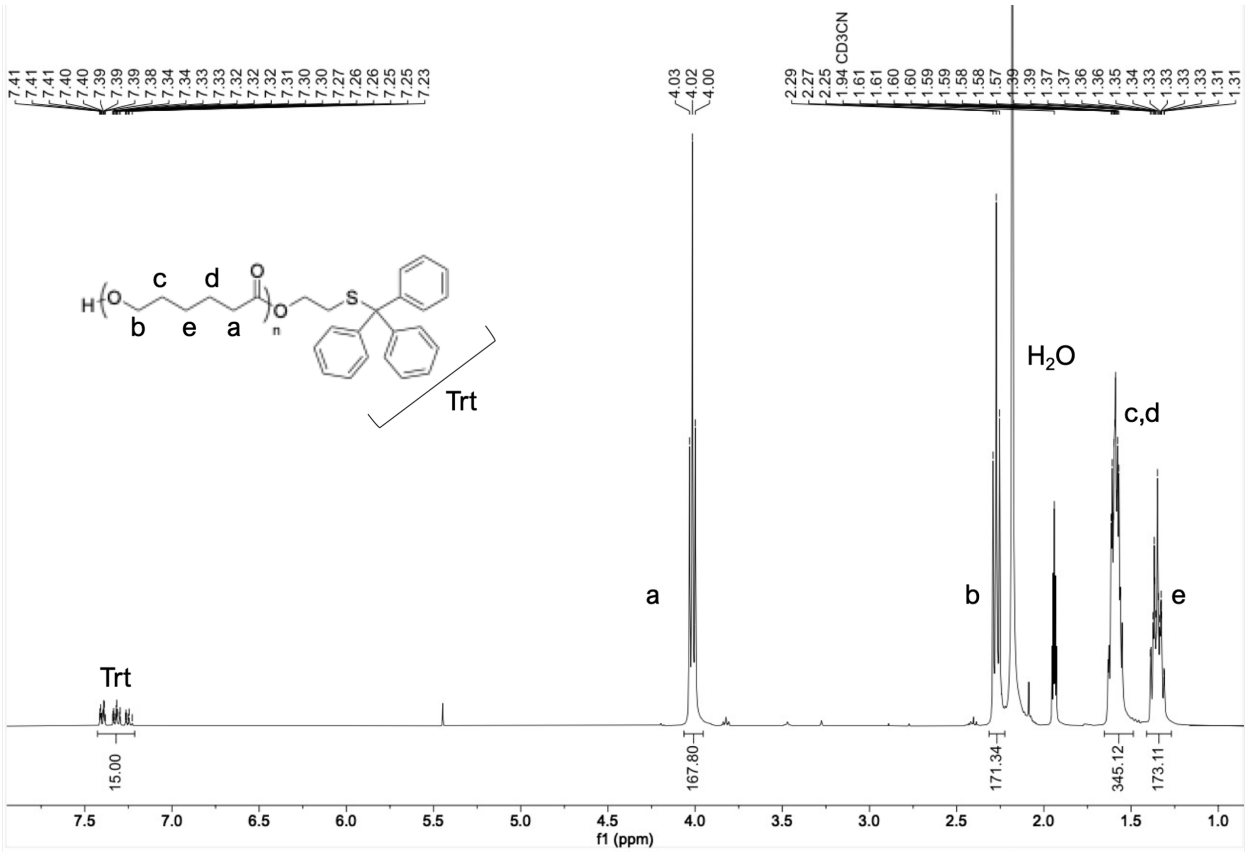


Figure S65. ^{1}H NMR spectrum of pCL-Trt (**12**) in CD_3CN at 25 ºC.

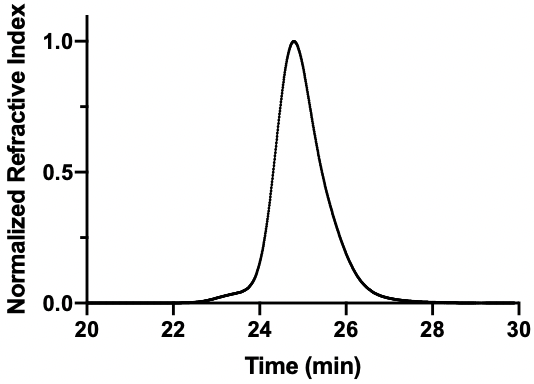
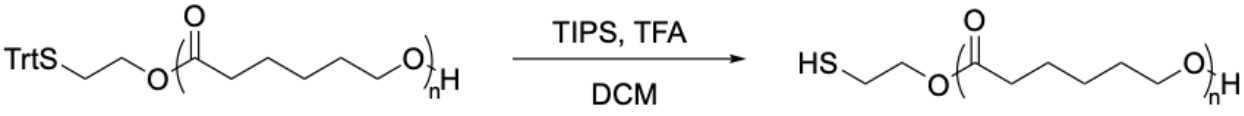


Figure S66. DMF SEC trace of pCL-Trt (**12**).

Deprotection of Trt-p(CL) (12a)



General Trt deprotection procedure: The polymer was dissolved in 0.5 mL DCM and TFA (0.7 g, 0.5 mL, 700 eq, 6 mmol) was added. The solution turned bright yellow. Next, tris(propan-2-yl)silane (70.9 mg, 91.9 µL, 45 eq, 448.0 µmol)was added and the reaction became clear and colorless. After 10 minutes, the reaction solution was precipitated into cold diethyl ether (45 mL) to produce a white powder. Yield: 85%

^{1}H NMR (300 MHz, CD_3CN): δ 4.07 (t, *J* = 6.6 Hz, 168H), 2.32 (t, *J* = 7.5 Hz, 181H), 1.78 – 1.56 (m, 337H), 1.52 – 1.30 (m, 171H).

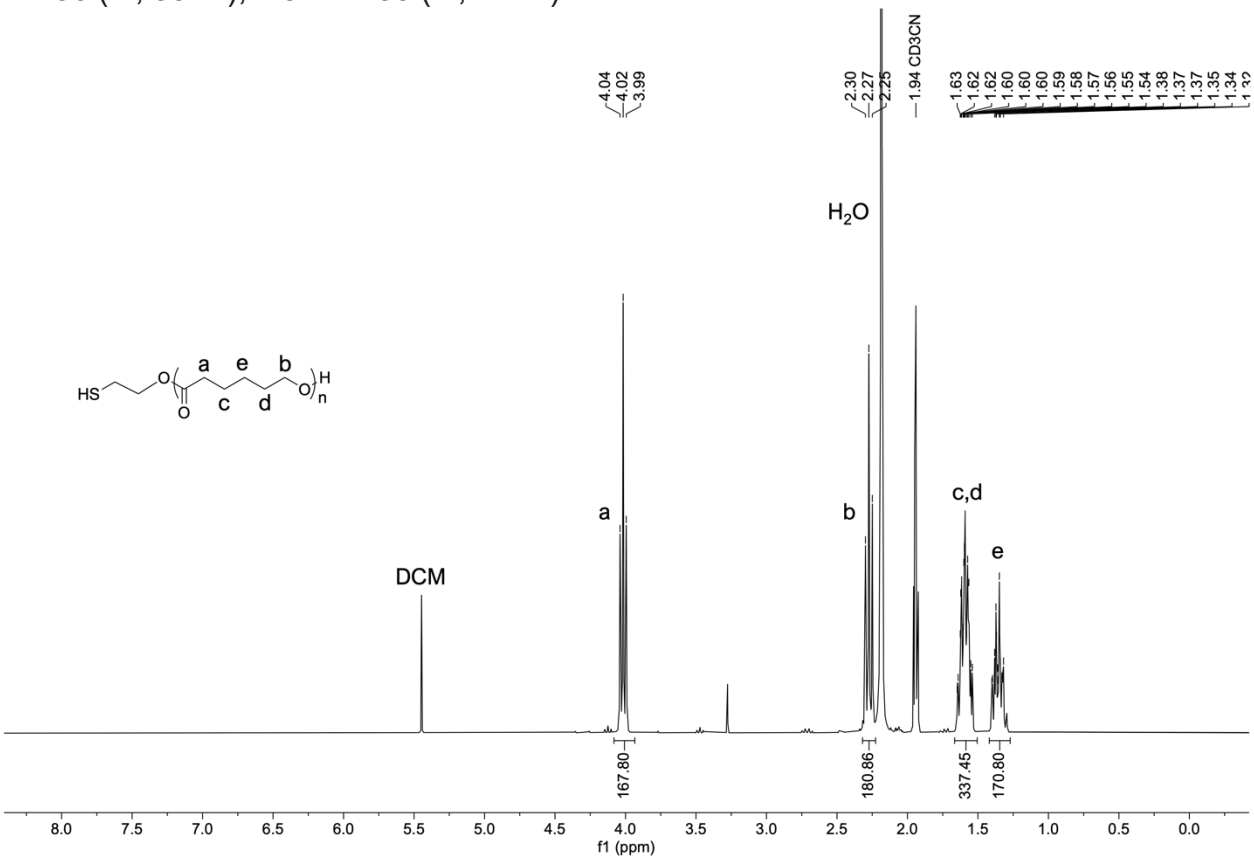
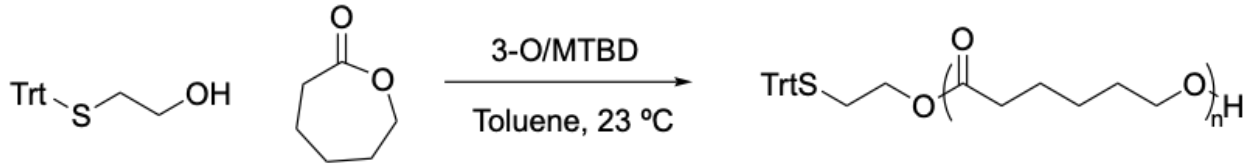


Figure S67. ^{1}H NMR spectrum of pCL-SH (**12a**) in CD_3CN at 25 ºC.

Synthesis of p(CL)-Trt *via* ROP (17)



Following general ROP procedure using 3-O catalyst (30.0 mg, 3.8 eq, 32.9 µmol), caprolactone (300 mg, 291 µL, 307 Eq, 2.6 mmol, 2-(tritylthio)ethan-1-ol (2.7 mg, 1 eq, 8.6 µmol) and MTBD (5.0 mg, 4.7 µL, 3.8 eq, 32.9 µmol). Yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.30 – 7.27 (m, 10H), 7.24 – 7.19 (m, 5H), 4.32 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.7 Hz, 708H), 2.29 (t, *J* = 7.5 Hz, 714H), 1.70 – 1.54 (m, 1450H), 1.43 – 1.29 (m, 718H).
SEC analysis: M_n is 37.4 kDa, M_w is 42.3 kDa, $Đ$ is 1.13.

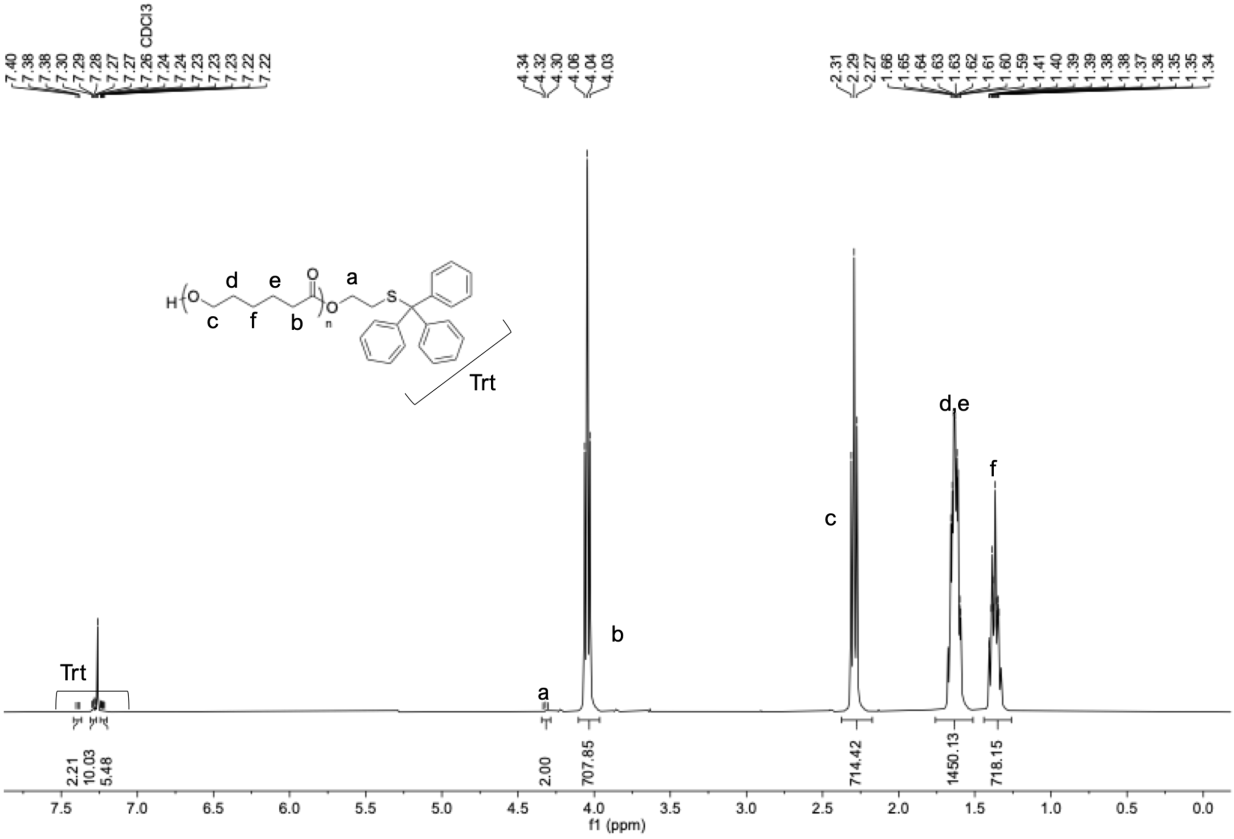


Figure S68. ^{1}H NMR spectrum of p(CL)-Trt (**17**) in $CDCl_3$ at 25 ºC.

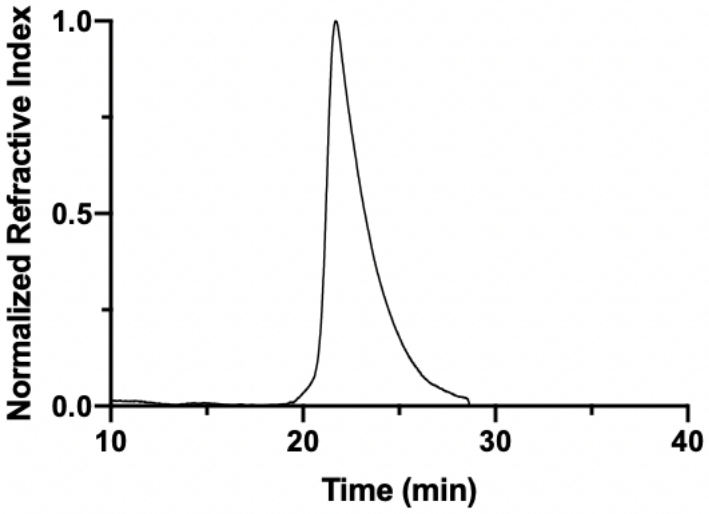
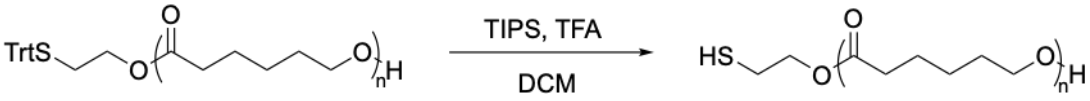


Figure S69. DMF SEC trace of p(CL)-Trt (**17**).

Deprotection of p(CL)-Trt (17a)



Following the general trityl deprotection procedure using pCL-Trt (**17**) (100.0 mg, 1 eq, 2.70 µmol)). TFA (92.4 mg, 62.5 µL, 300 eq, 810.8 µmol) and tris(propan-2-yl)silane (19.3 mg, 24.9 µL, 45 eq, 121.6 µmol) to produce a white powder. Yield: 87%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.06 (t, 708H), 2.30 (t, *J* = 7.5 Hz, 736H), 1.77 – 1.54 (m, 1464H), 1.44 – 1.29 (m, 776H).

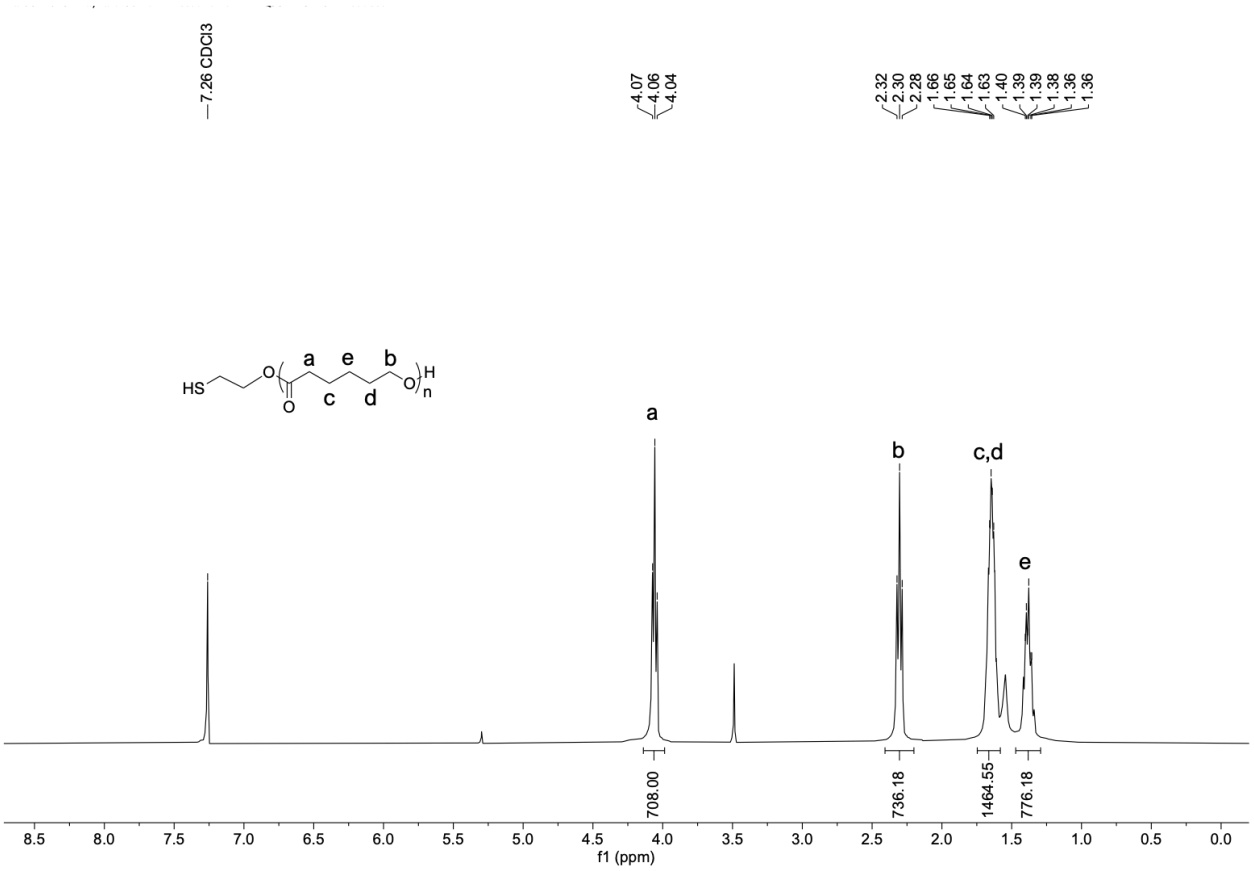
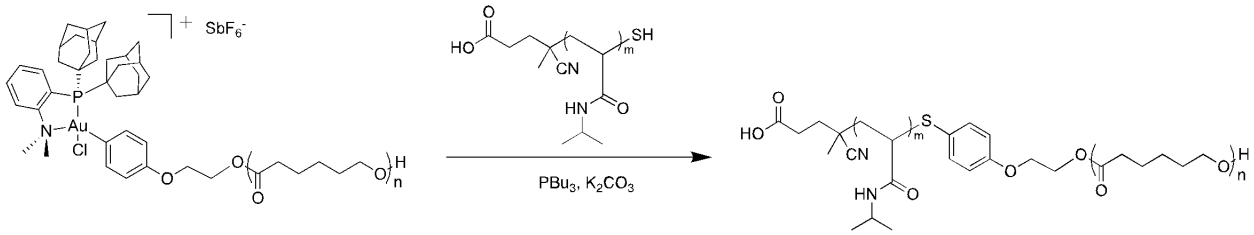


Figure S70. ^{1}H NMR spectrum of p(CL)-SH (**17a**) in $CDCl_3$ at 25 ºC.

V. Synthesis of Diblock copolymers

Synthesis of p(NIPAM)-*b*-p(CL) (13) *via* reductive elimination of pNIPAM-SH (10a) and pCL-Au(III) (1a)



General Polymer Reductive Elimination Procedure: For every reductive elimination, molecular weight of each precursor polymer was determined *via* ^{1}H NMR analysis. pNIPAM-SH (**10a**) (7.31 mg, 1 eq, 0.76 µmol) and a stir bar were added to a 1 mL vial and dissolved in 250 µL DMF. After preparation of a tributyl phosphine (PBu_3) solution, pNIPAM-SH was reduced with PBu_3 (308 µg, 2 eq, 1.52 µmol) for 20 minutes at room temperature. Next, potassium carbonate (1.9 mg, 10 eq, 13.7 µmol) was added to the vial. Finally, pCL-Au(III) (**1a**) (4.47 mg, 93% wt, 1 eq, 0.76 µmol) was dissolved with an additional 250 µL DMF and added to the solution. The reaction was stirred for 1 hour at room temperature, where it was then precipitated in 15 mL of cold diethyl ether and dried under vacuum to produce a white powder. Yield: 53%.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.51 (s, 73H), 4.03 (t, *J* = 6.7 Hz, 113H), 3.99 (s, 59H), 2.29 (t, *J* = 7.5 Hz, 100H), 2.11 – 1.78 (m, 163H), 1.67 – 1.57 (m, 308H), 1.46 – 1.29 (m, 166H), 1.13 (s, 495H), 0.99 – 0.86 (m, 75H).
SEC analysis: M_n is 11.9 kDa, M_w is 16.3 kDa, $Đ$ is 1.37

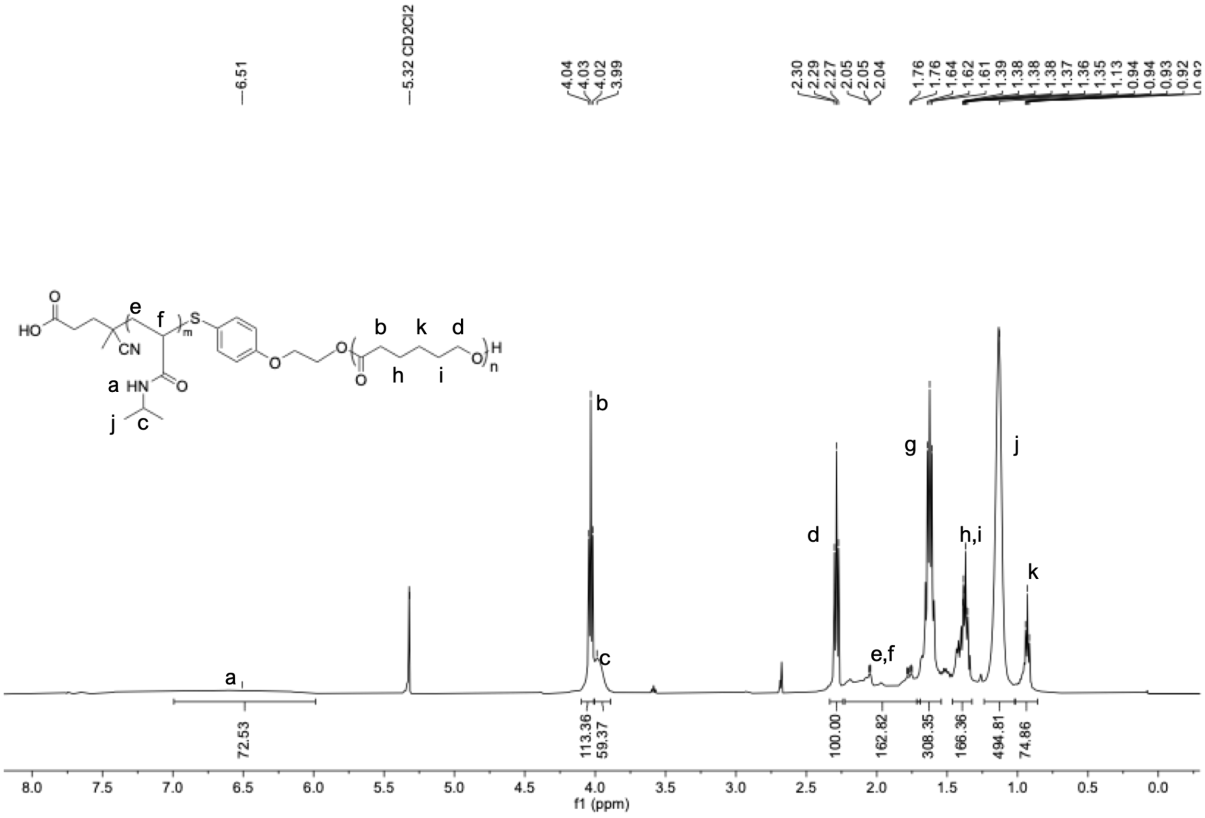


Figure S71. ^{1}H NMR spectrum of p(NIPAM)-*b*-p(CL) (**13**) in CD_2Cl_2 at 25 ºC.

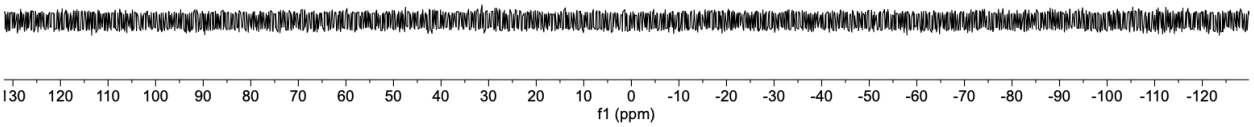


Figure S72. $^{31}P\{^{1}H\}$ NMR spectrum of p(NIPAM)-*b*-p(CL) (**13**) in CD_2Cl_2 at 25 ºC.

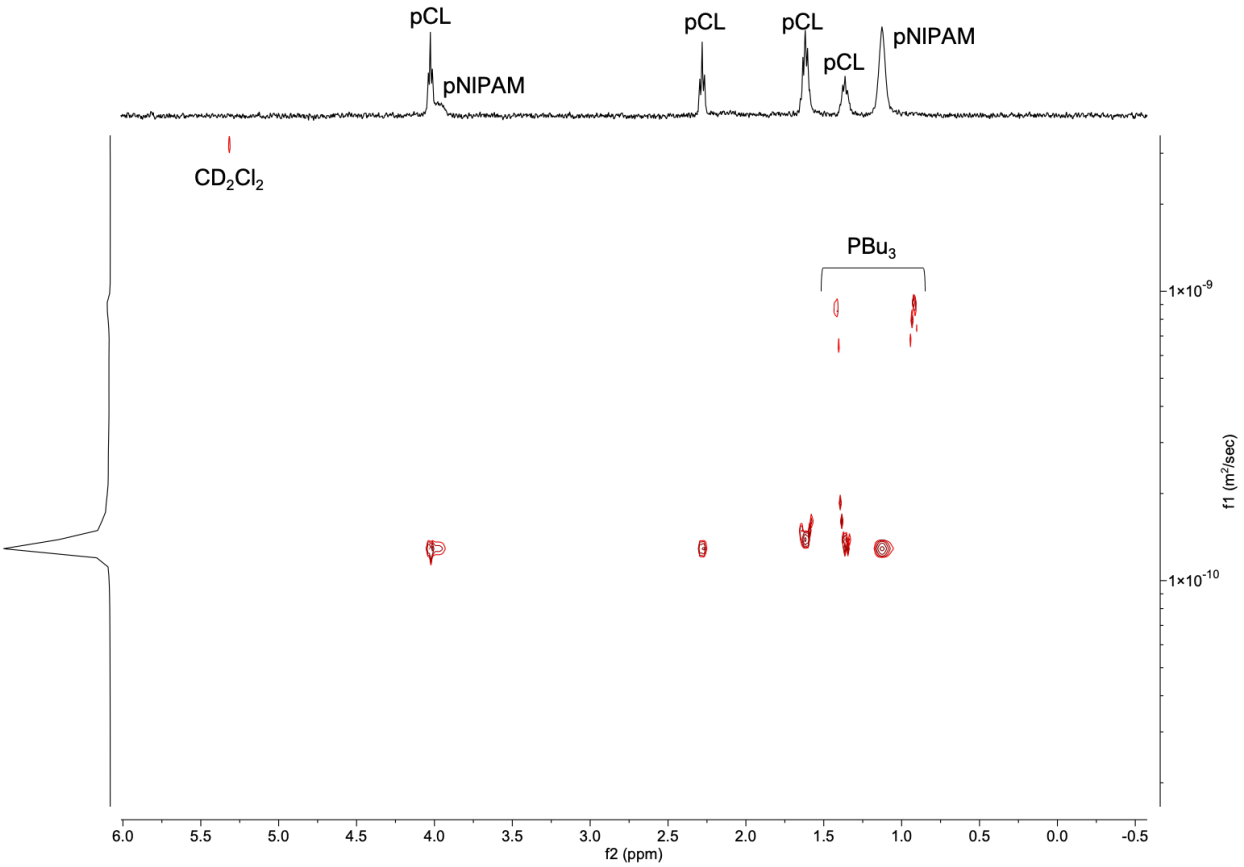


Figure S73. DOSY spectrum of p(NIPAM)-*b*-p(CL) (**13**) in CD_2Cl_2 at 25 ºC.

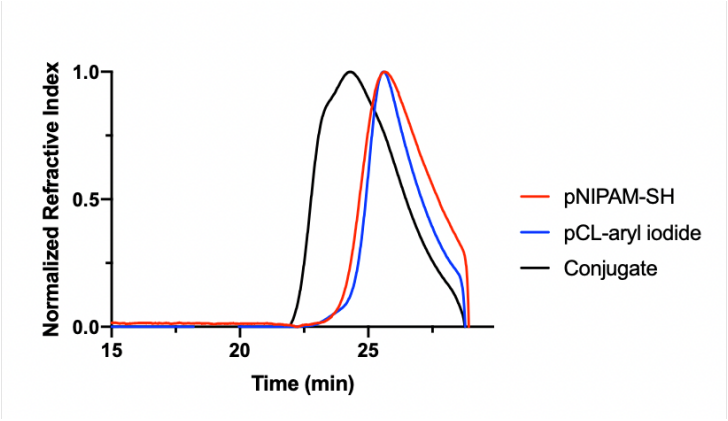
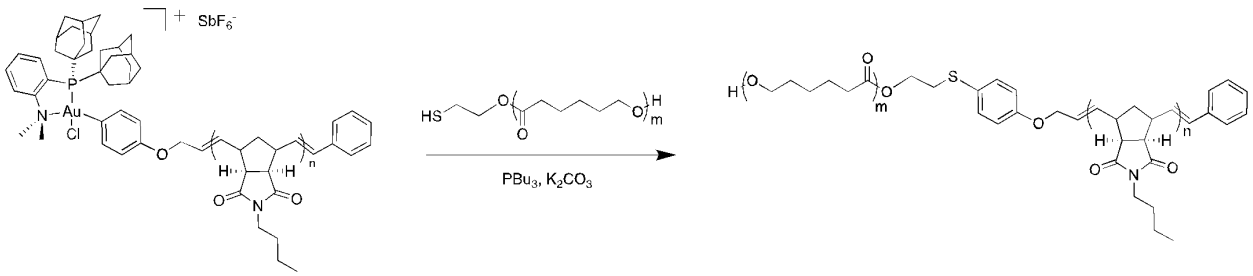


Figure S74. DMF SEC trace of p(NIPAM)-*b*-p(CL) (**13**).

Synthesis of p(CL)-*b*-p(BNI) (14) *via* reductive elimination of pCL-SH (12a) and pBNI-Au(III) (3a)



Following the general polymer reductive elimination procedure using pCL-SH (4.62 mg, 1 eq, 0.5 μmol) (**12a**), PBu_3 (187 μg, 2 eq, 0.9 μmol), potassium carbonate (447 μg, 7 eq, 3.2 μmol), and pBNI-Au(III) (**3a**) (4.30 mg, 92% wt, 1 eq, 0.5 μmol). The product is a white powder. Yield: 57%.

^{1}H NMR (500 MHz, CD_3CN): δ 5.72 – 5.46 (m, 102H), 4.52 – 4.49 (m, 2H), 4.01 (t, 256H), 3.42 – 3.32 (m, 104H), 3.04 – 2.94 (m, 119H), 2.69 – 2.61 (m, 88H), 2.27 (t, 268H), 1.65 – 1.53 (m, 556H), 1.52 – 1.46 (m, 120H), 1.40 – 1.32 (m, 266H), 1.31 – 1.23 (m, 101H), 0.91 (t, *J* = 7.4 Hz, 155H).
^{31}P{^{1}H} NMR (243 MHz, CD_3CN): δ 67.91, 57.32.
SEC analysis: M_n is 17.7 kDa, M_w is 22.5 kDa, ~~$Đ$~~ is 1.27.

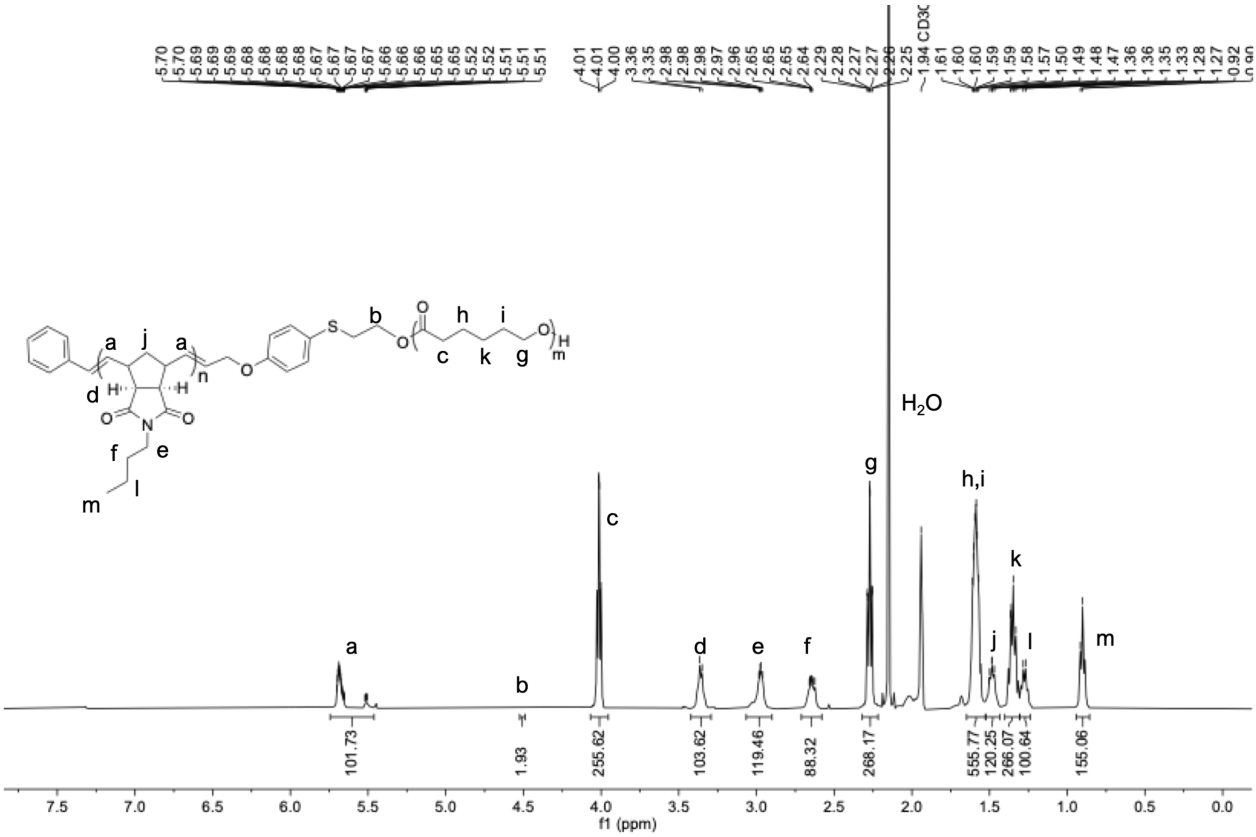


Figure S75. ^{1}H NMR spectrum of p(CL)-*b*-p(BNI) (**14**) in CD_3CN at 25 ºC.

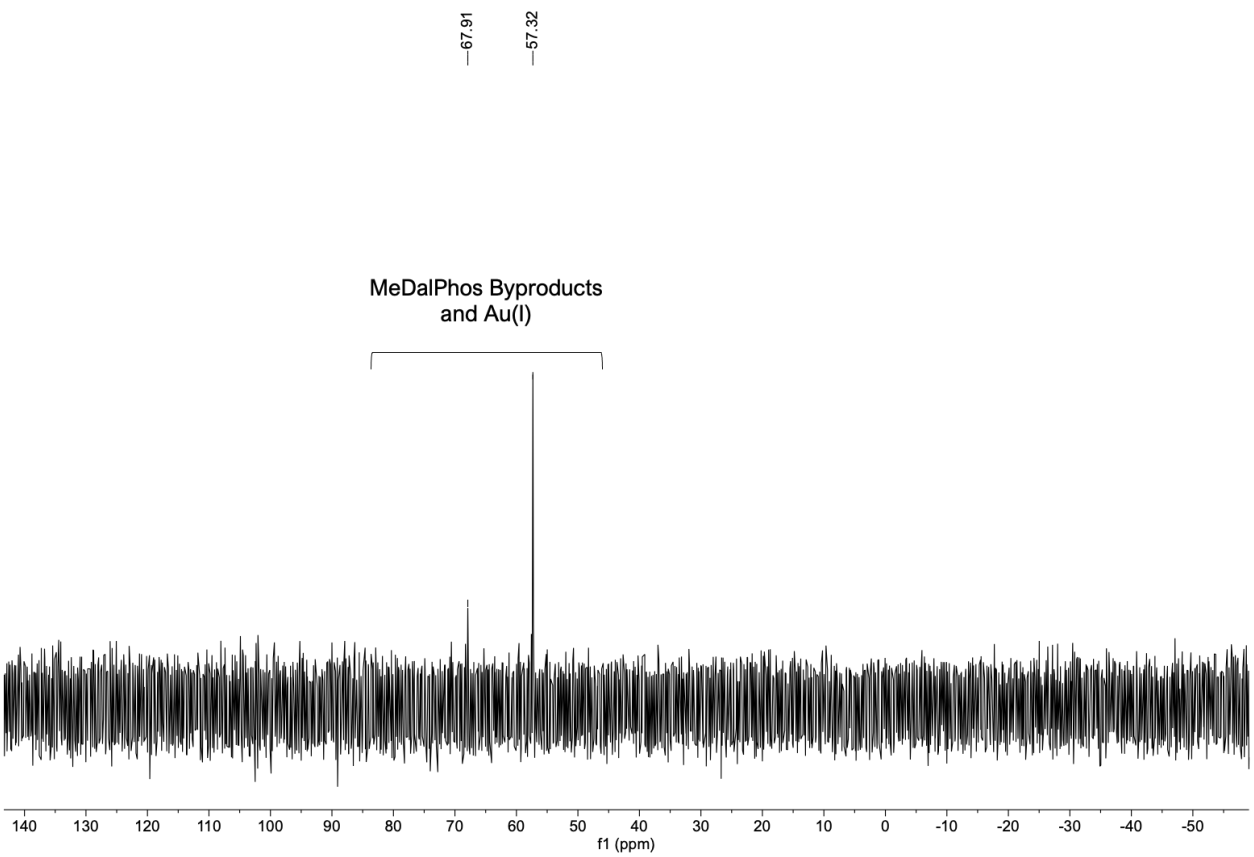


Figure S76. $^{31}P\{^{1}H\}$ NMR spectrum of p(CL)-*b*-p(BNI) (**14**) in CD_3CN at 25 ºC.

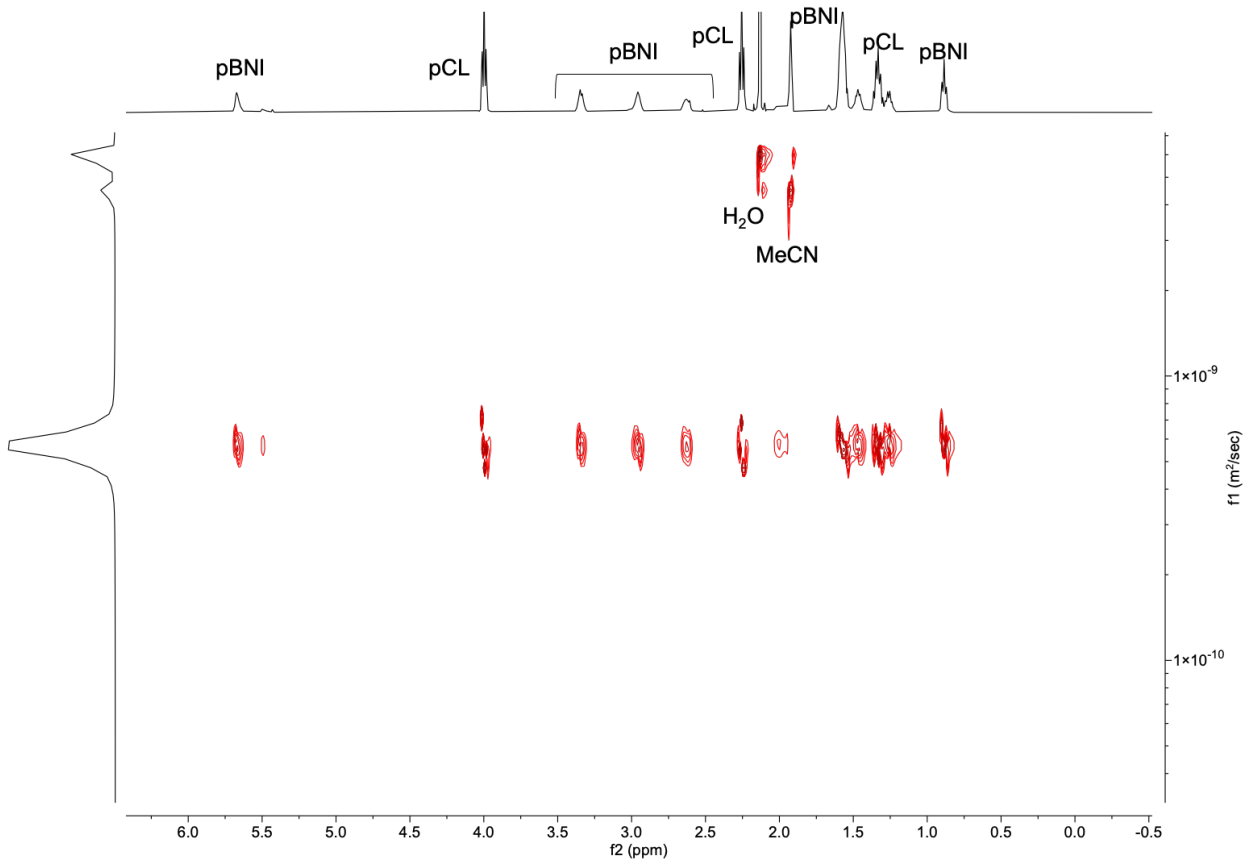


Figure S77. DOSY NMR spectrum of p(CL)-*b*-p(BNI) (**14**) in CD_3CN at 25 ºC.

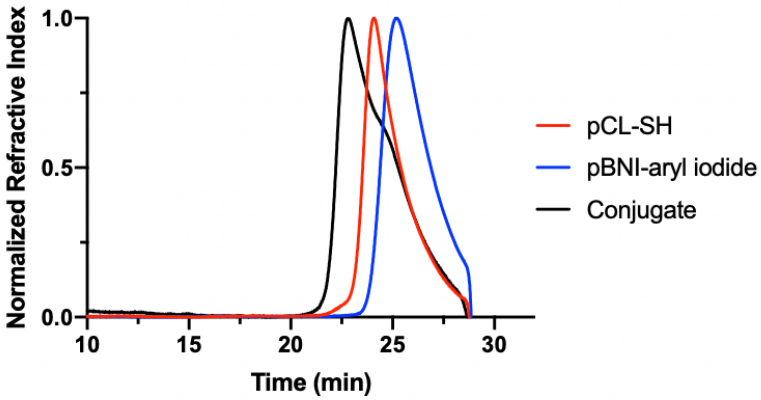
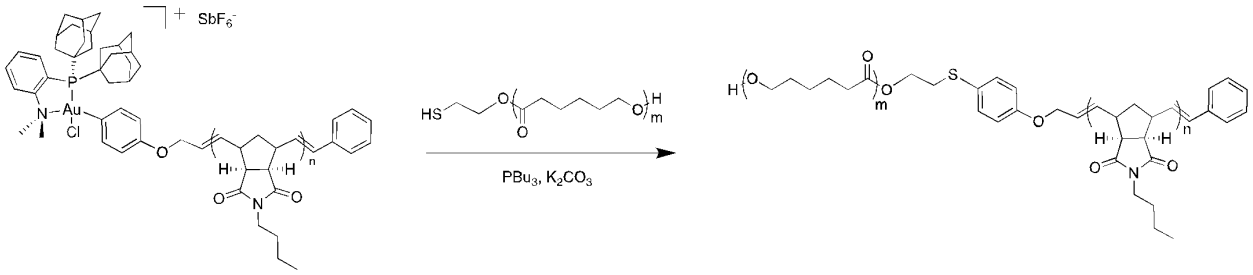


Figure S78. DMF SEC trace of p(CL)-*b*-p(BNI) (**14**).

Synthesis of p(CL)-*b*-p(BNI) (18) *via* reductive elimination of pCL-SH (17a) and pBNI-Au(III) (16a)



Following general polymer reductive elimination procedure using pCL-SH (10.0 mg, 1 eq, 0.3 μmol) (**17a**), PBu_3 (118 μg, 2 eq, 0.6 μmol), potassium carbonate (283 μg, 7 eq, 2.0 μmol), and pBNI-Au(III) (8.4 mg, 98% wt, 1 eq, 0.3 μmol) (**16a**). The product is a white powder. Yield: 85%.

^{1}H NMR (500 MHz, CD_3CN): δ 5.76 – 5.38 (m, 276H), 4.00 (t, *J* = 6.6 Hz, 745H), 3.40 – 3.28 (m, 271H), 3.04 – 2.87 (m, 332H), 2.63 (s, 232H), 2.26 (t, *J* = 7.4 Hz, 812H), 1.64 – 1.52 (m, 1568H), 1.47 (t, *J* = 7.6 Hz, 350H), 1.38 – 1.29 (m, 772H), 1.29 – 1.21 (m, 342H), 0.88 (t, *J* = 7.4 Hz, 408H).
^{31}P{^{1}H} NMR (243 MHz, CD_3CN): δ 61.78, 57.23.
SEC analysis: M_n is 42.3 kDa, M_w is 59.1 kDa, $Đ$ is 1.40.

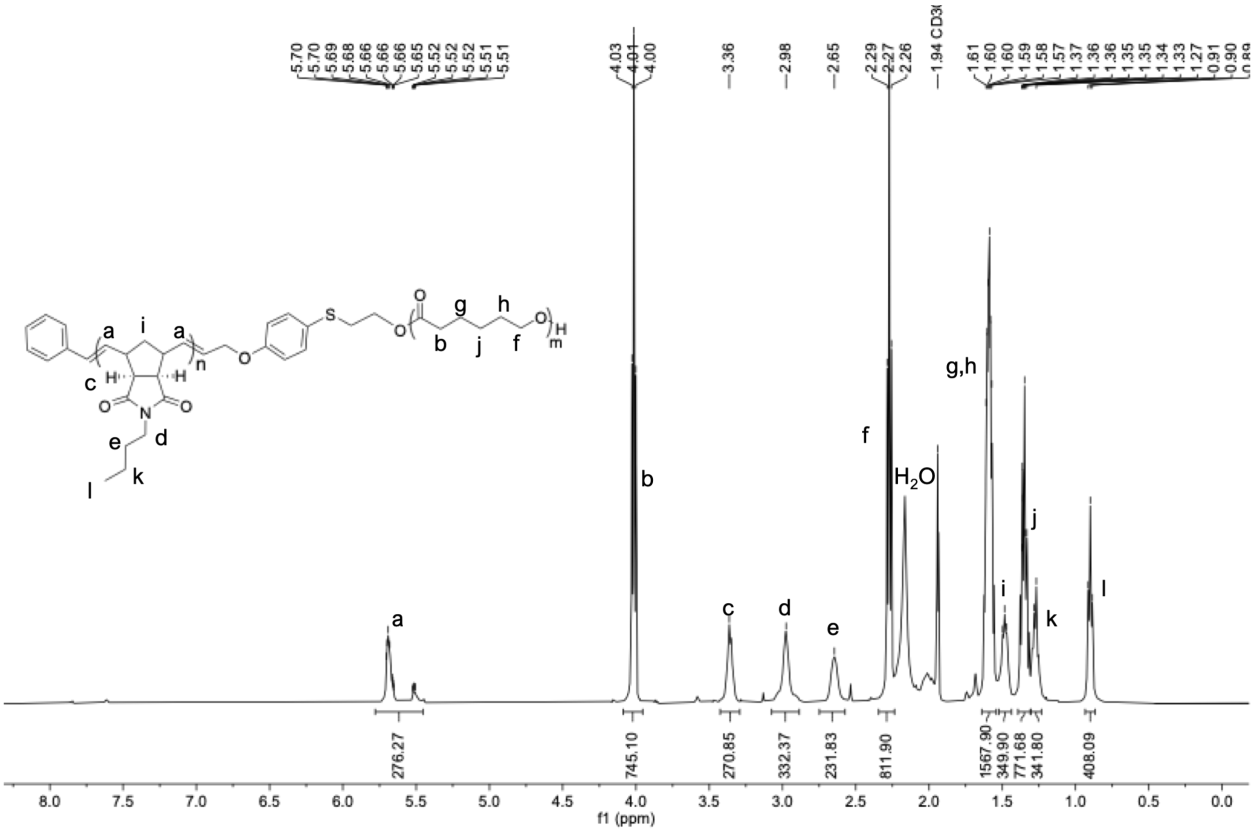


Figure S79. ^{1}H NMR spectrum of p(CL)-*b*-p(BNI) (**18**) in $CDCN_3$ at 25 ºC. Peak "a" contains both cis- and trans- alkene protons.

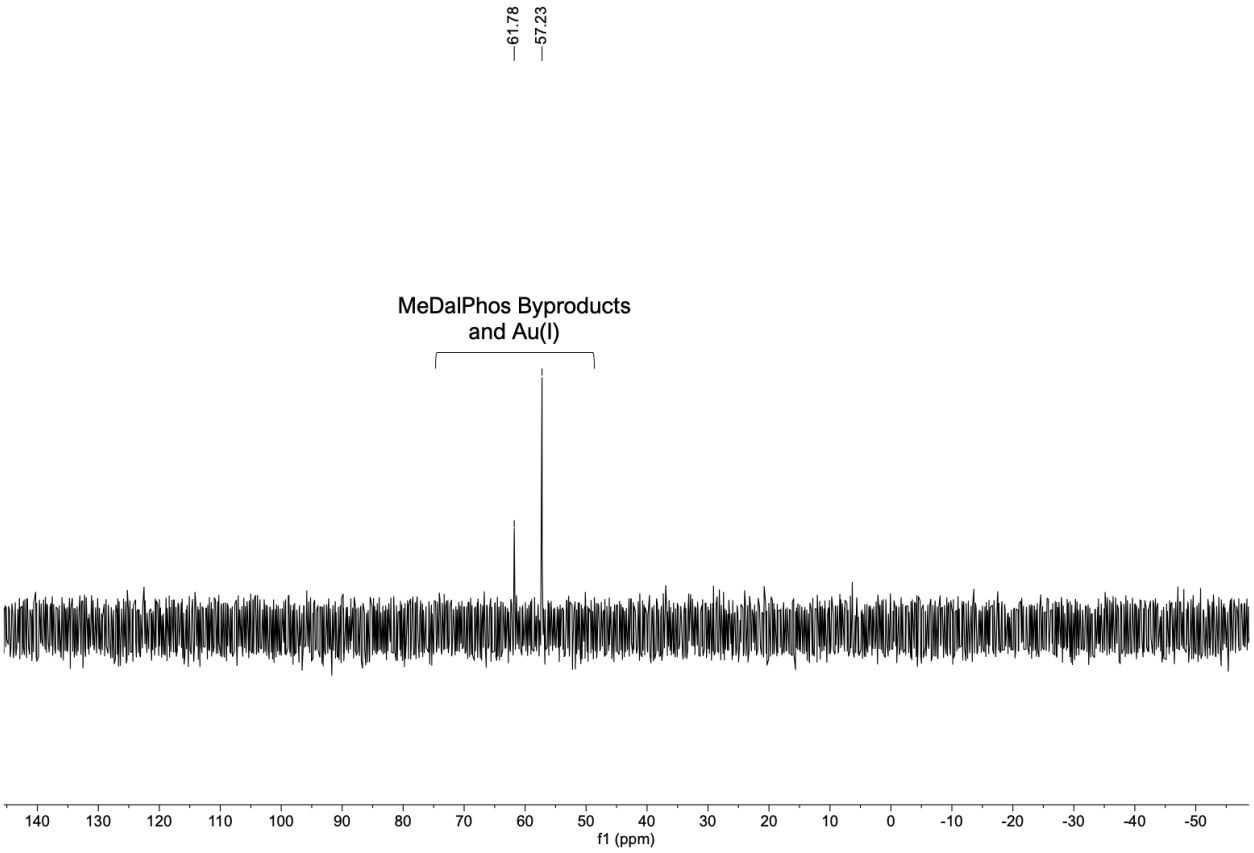


Figure S80. $^{31}P\{^{1}H\}$ NMR spectrum of p(CL)-*b*-p(BNI) (**18**) in $CDCN_3$ at 25 ºC.

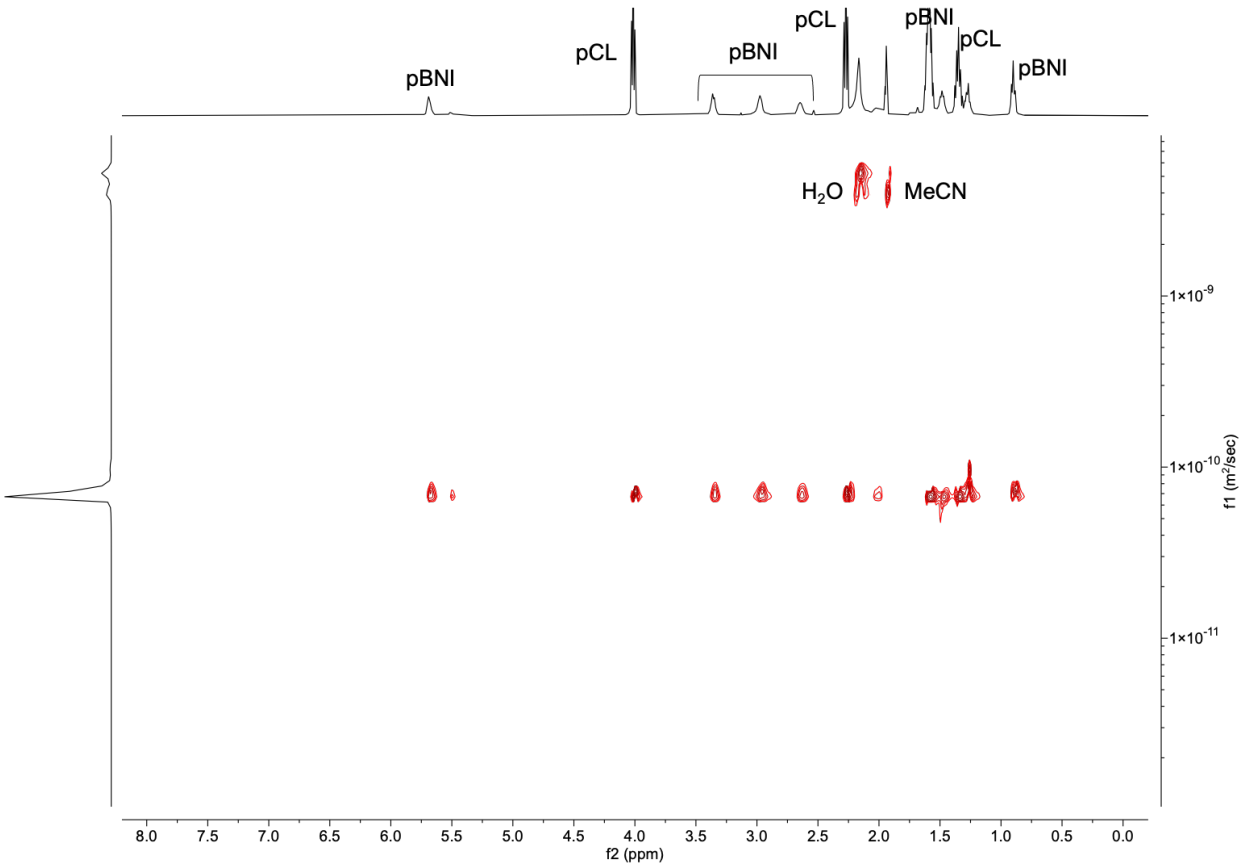


Figure S81. $^{31}P\{^{1}H\}$ NMR spectrum of p(CL)-*b*-p(BNI) (**18**) in $CDCN_3$ at 25 ºC.

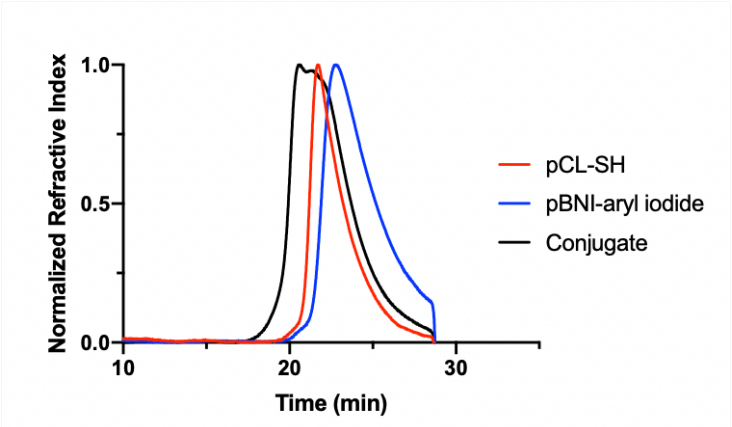
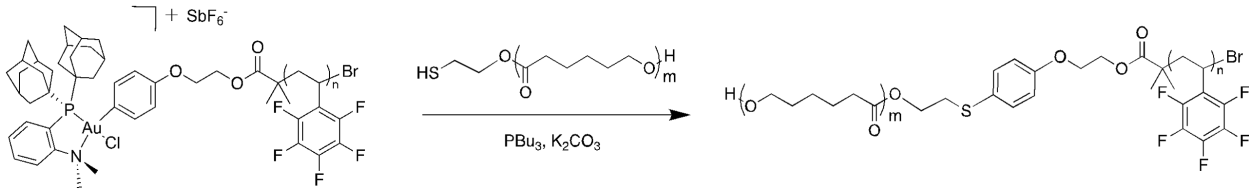


Figure S82. DMF SEC trace of p(CL)-*b*-p(BNI) (**18**).

Synthesis of p(CL)-*b*-p(PFS) (15) *via* reductive elimination of pBNI-SH (12a) and pPFS-Au(III) (6a)



Following general polymer reductive elimination procedure using pCL-SH (**12a**) (11.4 mg, 1 eq, 1.2 μmol), tributyl phosphine (967 μg, 1.19 μL, 4 eq, 4.8 μmol), potassium carbonate (1.7 mg, 10 eq, 11.9 μmol), and pPFS-Au(III) (**6a**) (9.1 mg, 94% wt, 1 eq, 1.2 μmol). The product is a white powder. Yield: 66%.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.07 (t, *J* = 6.7 Hz, 223H), 2.89 – 2.40 (m, 28H), 2.33 (t, *J* = 7.5 Hz, 231H), 2.19 – 1.92 (m, 71H), 1.74 – 1.52 (m, 545H), 1.50 – 1.37 (m, 235H).
^{19}F NMR (376 MHz, CD_3CN): δ -141.40 – -145.97 (m), -156.88 – -158.79 (m), -163.19 – -166.18 (m).
SEC analysis: M_n is 9.77 kDa, M_w is 15.6 kDa, and ~~$Đ$~~ is 1.60.

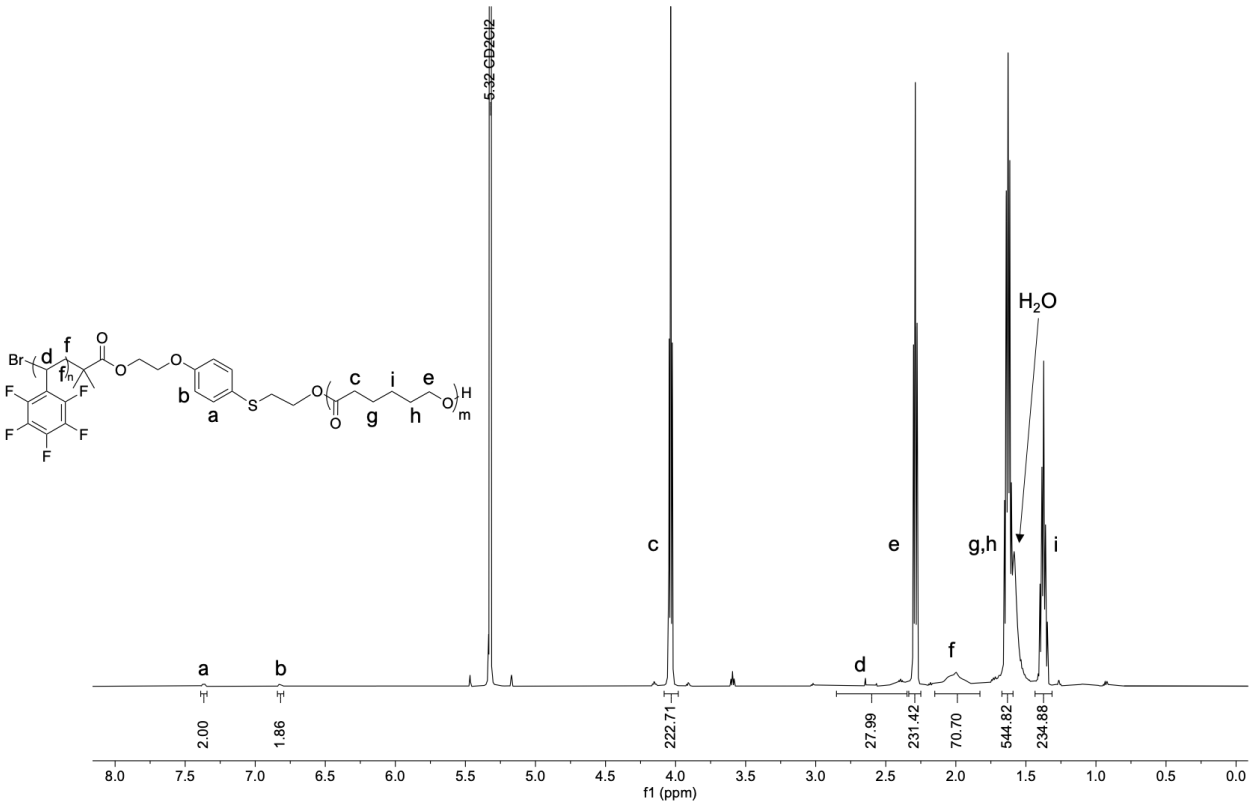


Figure S83. ^{1}H NMR spectrum of p(CL)-*b*-p(PFS) (**15**) in CD_2Cl_2 at 25 ºC.

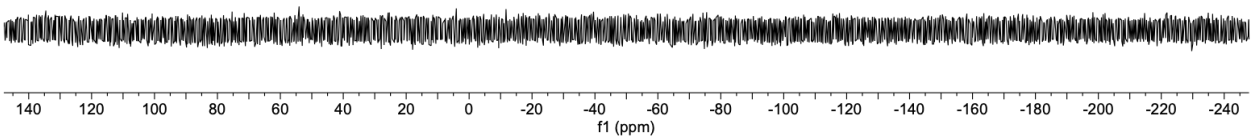


Figure 84. $^{31}P\{^{1}H\}$ NMR spectrum of p(CL)-*b*-p(PFS) (**15**) in CD_3CN at 25 ºC.

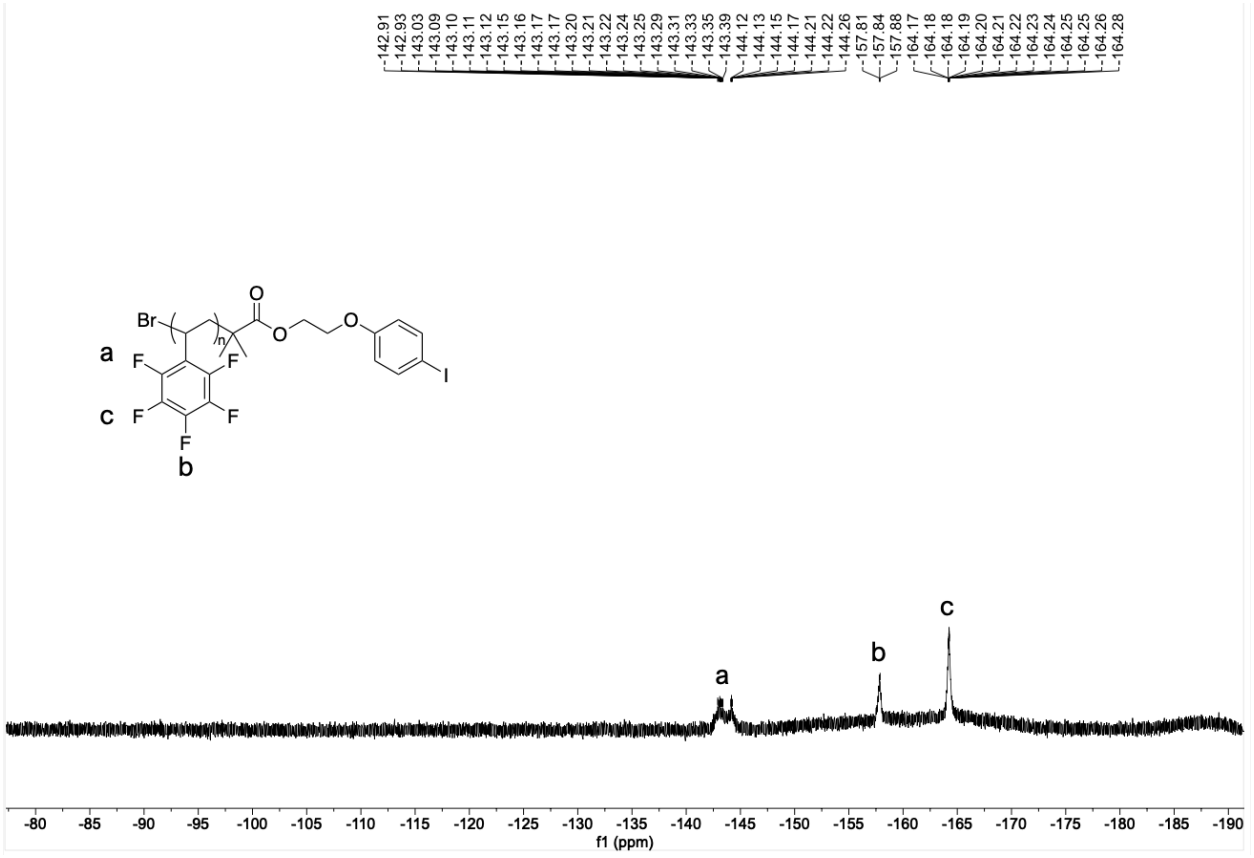


Figure S85. $^{19}F\{^{1}H\}$ NMR spectrum of p(CL)-*b*-p(PFS) (**15**) in CD_3CN at 25 ºC.

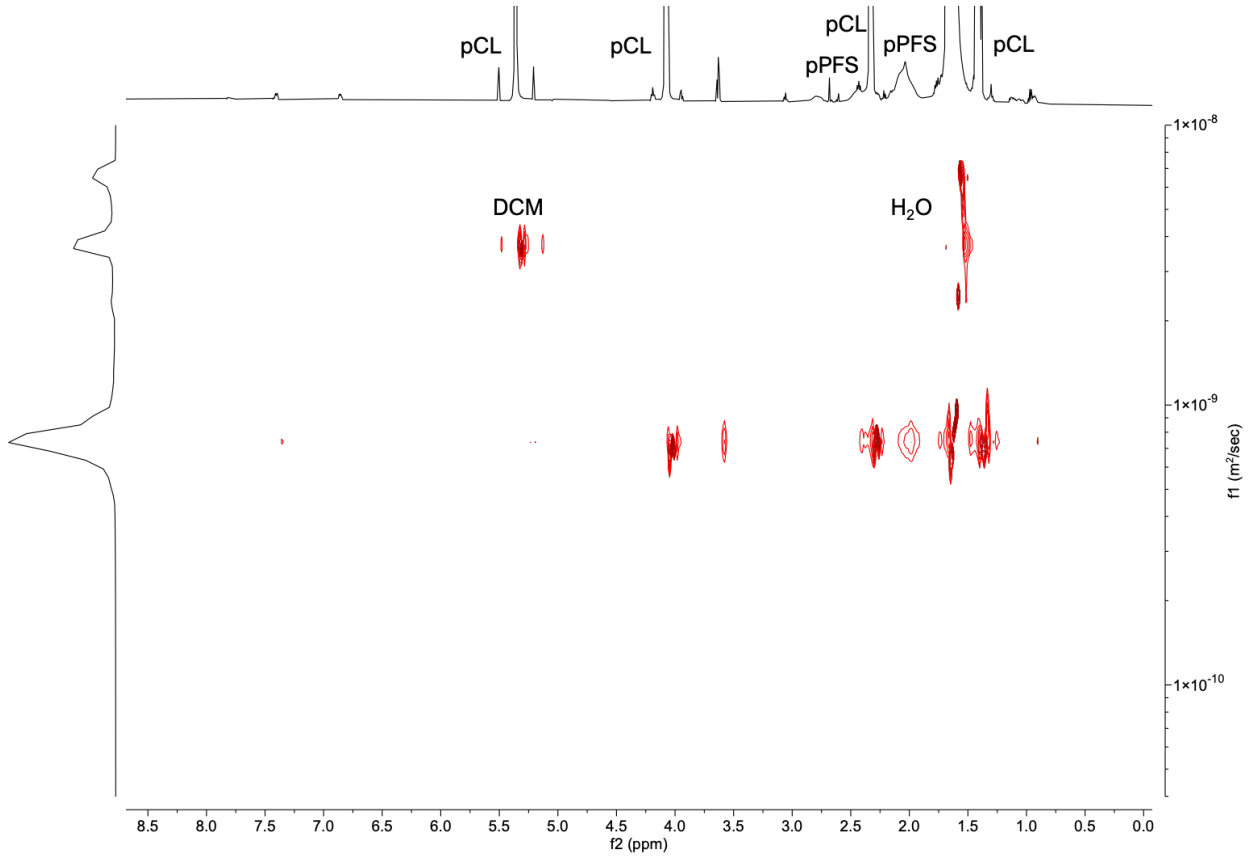


Figure S86. DOSY NMR spectrum of p(CL)-*b*-p(PFS) (**15**) in CD_2Cl_2 at 25 ºC.

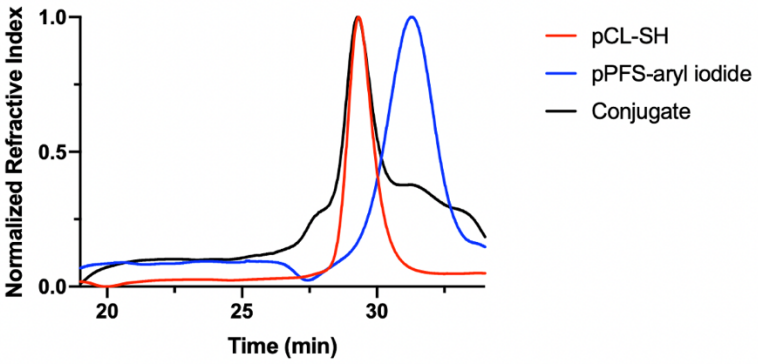


Figure S87. THF SEC trace of p(CL)-*b*-p(PFS) (**15**).

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