Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information (ESI) for

Synthesis of ROS-responsive Poly(thioacetal)s with Narrow Molecular Weight Distributions *via* Lactone Ring-Opening Polymerization

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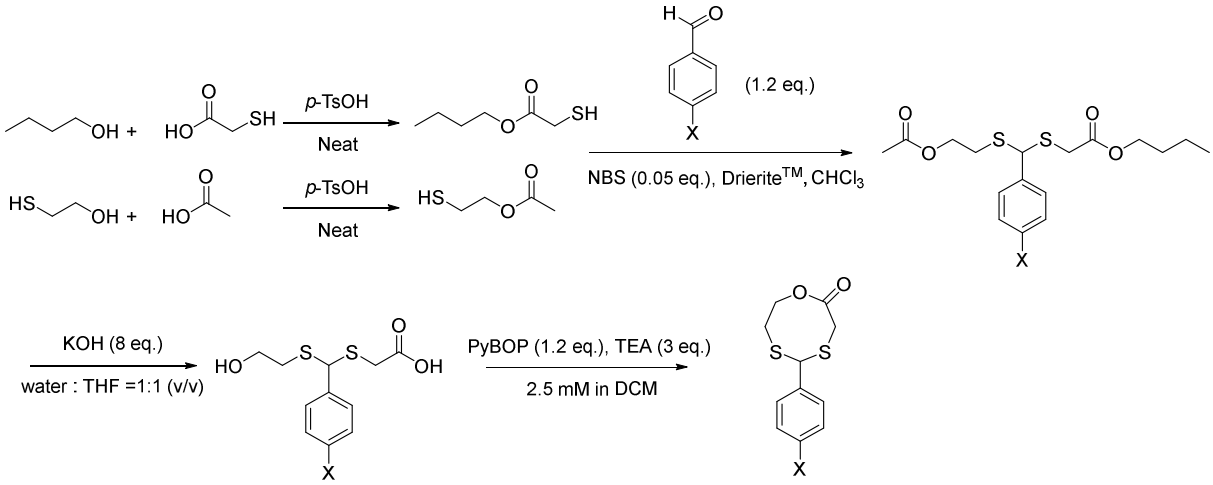
1. General

^{1}H-NMR spectra were recorded on a Varian (500 MHz) spectrometer. ^{1}H chemical shifts were measured with the reference peak of tetramethylsilane (0.00 ppm). ^{13}C-NMR spectra were recorded on a Bruker (125 MHz) spectrometer with complete proton decoupling. ^{13}C chemical shifts measured with the reference peak of $CDCl_3$ (77.16 ppm). ^{31}P-NMR spectra were recorded on a Bruker (200 MHz) spectrometer with complete proton decoupling. MALDI-MS spectra were recorded on a Bruker Daltonics Microflex LT and a Bruker Daltonics UltrafleXtreme TOF/TOF using dithranol as a matrix and sodium trifluoroacetate as a cation source. Size exclusion chromatography (SEC) was performed on a Waters Alliance HPLC-RI system equipped with a Shodex KF-803 SEC column. Tetrahydrofuran (THF) was used for the eluent of SEC, temperature of detector and column oven was maintained at 35 °C. Samples were diluted to 1-5 mg/ml with THF or *N*,*N*-dimethylformamide (DMF) and filtered through a 0.20 μm-PTFE filter before injection into the SEC system. HPLC analysis was perfomed on a Shimazu Prominence system equipped with a Eclipse XDB-C18 4.6x250 mm 5μ analytical column. Thermogravimetric analysis (TGA) was carried out under N_2 gas at a scan rate of 10 °C/min with a Q50 model device from TA Instruments. Differential scanning calorimetry (DSC) was carried out under N_2 gas at a scan rate of 10 °C/min from range of -40 °C to 150 °C with a Q10 model device from TA Instruments. 2-Mercaptoethanol, 2-thioglycolic acid, *p*-toluenesulfonic acid monohydrate (*p*-TsOH), *N*-bromosuccinimide (NBS), diphenylphosphate (DPP), 1-pyrenebutanol (PyBuOH), phosphorus(V) oxychloride ($POCl_3$), propargyl alcohol, benzoic acid, 2-propanol, poly(ethylene oxide) methyl ether (mPEO-OH, M_n ~2000 Da), dithranol, *p*-tolualdehyde, THF (anhydrous), dichloromethane (DCM, anhydrous) and toluene (anhydrous) were purchased from Sigma Aldrich (USA). Benzotriazol-1-yloxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) was purchased from Beadtech (Korea). Bromotrimethylsilane, aluminum(III) chloride, 4-nitrobenzaldehyde and *p*-anisaldehyde were purchased from TCI (Japan). Trifluoroacetic acid, 3,5-bis(trifluoromethyl)phenyl isothiocyanate, 4-fluorobenzaldehye, 4-(trifluoromethyl)benzaldehyde, Drierite (without indicator, 8 mesh) and *p*-xylene were purchased from Thermo scientific (USA). Magnesium sulfate, hydrogen peroxide (30.0 ~35.5 % in water), ethyl acetate, methanol, 1,2-dichloroethane (DCE), DCM, chloroform, 1-naphthol, diethyl ether, acetic acid, potassium hydroxide, triethylamine (TEA), Acetonitrile (HPLC grade), THF (HPLC grade), DMF (HPLC grade), *n*-pentane, *n*-hexane, petroleum ether and sodium bicarbonate were purchased from Samchun Chemicals (Korea). *n*-Butanol was purchased from Daejung chemicals & metals (Korea).

2. Experimental procedures

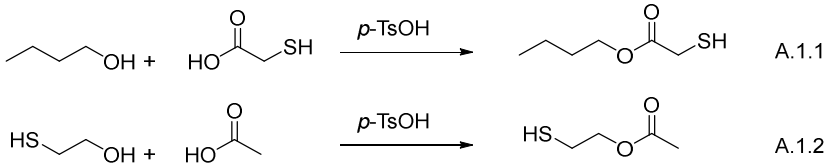
A. Synthesis of 5-phenyl-1,4,6-oxadithiocan-2-one (PTO) and its analogues

5-phenyl-1,4,6-oxadithiocan-2-one (PTO) and its analogues were synthesized as described below.



Scheme S1. Synthetic scheme of PTO and its analogues.

A.1. Synthesis of capped thiols



Scheme S2. Synthetic scheme of thiols.

A.1.1. Synthesis of butyl 2-mercaptoacetate

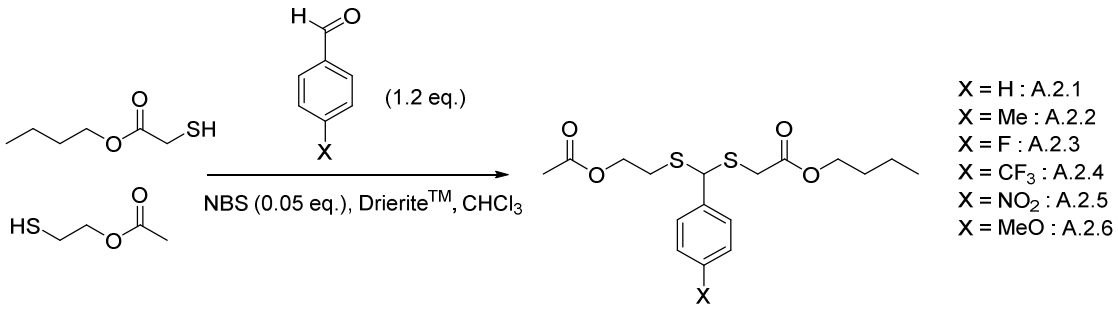
To 18.3 ml of *n*-butanol (200 mmol), 14.0 ml of 2-thioglycolic acid (200 mmol, 1.0 eq.) and 1.9 g of *p*-toluenesulfonic acid (10.0 mmol, 0.050 eq.) was added. The reaction mixture was sealed and stirred for 3 days at room temperature. The crude mixture was dissolved in 200 ml of DCM and washed carefully with 200 ml of aq. sodium bicarbonate (distilled water : saturated $NaHCO_3$ in water = 9 :1) three times and then, with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The product was clear oil and used without further purification. (15.2 g, 51.3 %) ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 (t, *J* = 6.7 Hz, 2H), 3.26 (d, *J* = 8.2 Hz, 2H), 2.00 (t, *J* = 8.2 Hz, 1H), 1.64 (m, 2H), 1.40 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H).

A.1.2. Synthesis of 2-mercaptoethyl acetate

To 14.1 ml of 2-mercaptoethanol (200 mmol), 11.4 ml of acetic acid (200 mmol, 1.0 eq.) and 1.90 g of *p*-toluenesulfonic acid (10.0 mmol, 0.050 eq.) was added. The reaction mixture was sealed and stirred for 3 days at room temperature. The crude mixture was dissolved in 200 ml of DCM and washed

carefully with 200 ml of aq. sodium bicarbonate (distilled water : saturated $NaHCO_3$ in water = 9 :1) three times and then, with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The product was clear oil and used without further purification. (11.3 g, 47.0 %) ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (t, *J* = 6.7 Hz, 2H), 2.74 (dt, *J* = 7.0, 7.7 Hz, 2H), 2.08 (s, 3H), 1.49 (t, *J* = 8.5 Hz, 1H).

A-2. Synthesis of linear thioacetals



Scheme S3. Synthetic scheme of linear thioacetals.

Thioacetals were synthesized *via* catalytic dehydration of NBS.[S1]

Reaction mixtures often include some impurities of disulfides which not affect the next reaction.

A.2.1. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(phenyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 0.980 ml of benzaldehyde (9.6 mmol, 1.2 eq.) were dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(phenyl)methyl)thio)acetate as clear oil. (1.22 g, 42.8%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 4.21 (m, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.37 (d, *J* = 15.1 Hz, 1H), 3.12 (d, *J* = 15.1 Hz, 1H), 2.93 (m, 1H), 2.78 (m, 1H), 2.06 (s, 3H), 1.62 (m, 2H), 1.39 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

A.2.2. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(*p*-tolyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 1.13 ml of *p*-tolualdehyde (9.6 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to

obtain butyl 2-((((2-acetoxyethyl)thio)(*p*-tolyl)methyl)thio)acetate as a clear oil. (1.02 g, 34.4%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.18 (s, 1H), 4.20 (m, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.35 (d, *J* = 15.1 Hz, 1H), 3.11(d, *J* = 15.1 Hz, 1H), 2.92 (m, 1H), 2.77 (m, 1H), 2.34 (s, 3H), 2.05 (s, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

A.2.3. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(4-fluorophenyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 1.03 ml of 4-fluorobenzaldehyde (9.6 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(4-fluorophenyl)methyl)thio)acetate as a clear oil. (794 mg, 26.5%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 6.8 Hz, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 5.21 (s, 1H), 4.21 (m, 2H), 4.10 (t, 2H), 3.36 (d, *J* = 15.1 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.93 (m, 1H), 2.77 (m, 1H), 2.06 (s, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

A.2.4. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 1.31 ml of 4-(trifluoromethyl)benzaldehyde (9.6 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate as a clear oil. (1.50 g, 43.8%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 8.6 Hz, 2H), 5.27 (s, 1H), 4.27 (m, 1H), 4.20 (m, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.37 (d, *J* = 15.2 Hz, 1H), 3.10 (d, *J* = 15.2 Hz, 1H), 2.95 (m, 1H), 2.78 (m, 1H), 2.06 (s, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

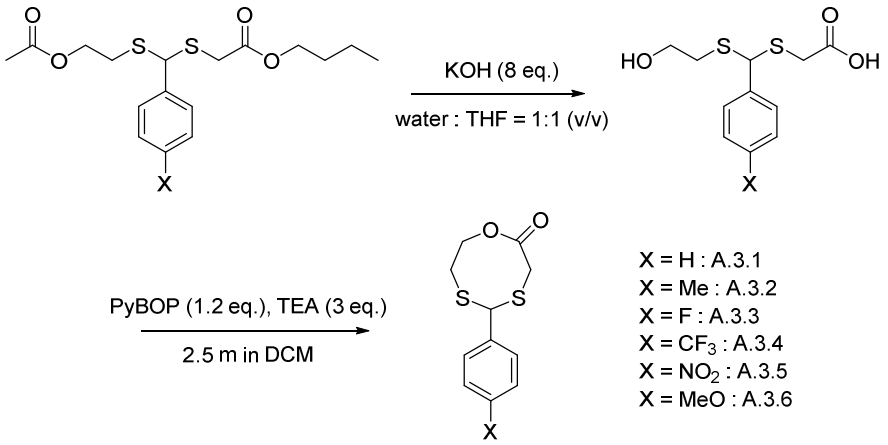
A.2.5. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(4-nitrophenyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 1.45 g of 4-nitrobenzaldehyde (9.6 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(4-nitrophenyl)methyl)thio)acetate as a clear oil. (1.21 g, 37.5%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 5.32 (s, 1H), 4.28 (m, 1H), 4.20 (m, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.39 (d, *J* = 15.2 Hz, 1H), 3.11 (d, *J* = 15.2 Hz, 1H), 2.96 (m, 1H), 2.78 (m, 1H), 2.07 (s, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

A.2.6. Synthesis of butyl 2-((((2-acetoxyethyl)thio)(4-methoxyphenyl)methyl)thio)acetate

961 mg of 2-mercaptoethyl acetate, (8.0 mmol) 1.19 g of butyl 2-mercaptoacetate, (8.0 mmol) 1.22 ml of trifluoroacetic acid (16 mmol, 2.0 eq.) and 1.17 ml of *p*-anisaldehyde (9.6 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 2 g of Drierite followed by 71.2 mg of NBS (0.40 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 200 ml of DCM and washed with 200 ml of distilled water three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(4-methoxyphenyl)methyl)thio)acetate as a clear oil. (1.32 g, 42.7%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.18 (s, 1H), 4.20(m, 2H), 4.10(t, *J* = 6.7 Hz, 2H), 3.81 (s, 3H), 3.35 (d, *J* = 15.1 Hz, 1H), 3.11 (d, *J* = 15.1 Hz, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 2.06 (s, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

A-3. Synthesis of thioacetal monomers



Scheme S4. Synthetic scheme of cyclic thioacetal monomers.

A.3.1. Synthesis of 5-phenyl-1,4,6-oxadithiocan-2-one (PTO)

891 mg of butyl 2-((((2-acetoxyethyl)thio)(phenyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 h until the solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain PTO as a white solid. (467 mg, 77.9%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.32 (m, 4H), 7.28 (m, 1H), 5.44 (s, 1H), 5.02 (m, 1H), 4.15 (m, 1H), 3.74 (d, *J* = 11.8 Hz, 1H) 3.22–3.08 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.35, 141.64, 129.13, 128.29, 126.40, 66.20, 60.39, 36.85, 36.57. MS (MALDI-MS) calculated for $C_{11}H_{12}NaO_2S_2$ $[M+Na]^+$: 263.02, found: 263.11.

A.3.2. Synthesis of 5-(*p*-tolyl)-1,4,6-oxadithiocan-2-one (Me-PTO)

926 mg of butyl 2-((((2-acetoxyethyl)thio)(*p*-tolyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 h until the solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain Me-PTO as a white solid. (554 mg, 87.1%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.42 (s, 1H), 5.02 (m, 1H), 4.15 (m, 1H), 3.74 (d, *J* = 11.9 Hz, 1H) 3.20–3.08 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.41,

138.72, 138.18, 129.76, 126.28, 66.25, 60.16, 36.72, 36.61, 21.28. MS (MALDI-MS) calculated for $C_{12}H_{14}NaO_2S_2$ $[M+Na]^+$: 277.03, found: 277.11.

A.3.3. Synthesis of 5-(4-fluorophenyl)-1,4,6-oxadithiocan-2-one (F-PTO)

936 mg of butyl 2-((((2-acetoxyethyl)thio)(4-fluorophenyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 hours until solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain F-PTO as a white solid. (485 mg, 72.1%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.45 (s, 1H), 5.02 (m, 1H), 4.15 (m, 1H), 3.73 (d, *J* = 11.8 Hz, 1H), 3.15 (d, 1H), 3.14 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.17, 163.35, 161.38, 137.56, 137.54, 128.34, 128.27, 116.09, 115.91, 66.28, 59.49, 36.65, 36.64. MS (MALDI-MS) calculated for $C_{11}H_{12}FNaO_2S_2$ $[M+Na]^+$: 281.01, found: 281.11.

A.3.4. Synthesis of 5-(4-(trifluoromethyl)phenyl)-1,4,6-oxadithiocan-2-one (CF_3-PTO)

1.06 g of butyl 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 hours until solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain CF_3-PTO as a white solid. (443 mg, 57.5%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 5.48 (s, 1H), 5.04 (m, 1H), 4.17 (m, 1H), 3.75 (d, *J* = 11.8 Hz, 1H), 3.24–3.11 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.00, 145.29, 130.78, 130.51, 130.26, 130.00, 126.92, 126.21, 126.19, 126.16, 126.13, 125.05, 122.88, 66.09, 59.65, 36.96, 36.47. MS (MALDI-MS) calculated for $C_{12}H_{11}F_3NaO_2S_2$ $[M+Na]^+$: 331.01, found: 331.16.

A.3.5. Synthesis of 5-(4-nitrophenyl)-1,4,6-oxadithiocan-2-one (NO_2-PTO)

1.00 g of butyl 2-((((2-acetoxyethyl)thio)(4-nitrophenyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 hours until solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml

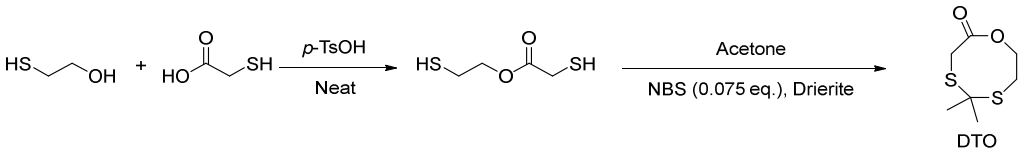
of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography. The obtained solid was once again washed with ether to obtain NO_2-PTO as an off-white solid. (167 mg, 23.4%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 5.51 (s, 1H), 5.05 (m, 1H), 4.18 (m, 1H), 3.76 (d, *J* = 11.8 Hz, 1H), 3.27–3.11 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.77, 148.20, 147.47, 127.53, 124.48, 66.02, 59.26, 37.07, 36.40. MS (MALDI-MS) calculated for $C_{11}H_{11}NNaO_4S_2$ $[M+Na]^+$: 308.00, found: 308.35.

A.3.6. Synthesis of 5-(4-methoxyphenyl)-1,4,6-oxadithiocan-2-one (MeO-PTO)

966 mg of butyl 2-((((2-acetoxyethyl)thio)(4-methoxyphenyl)methyl)thio)acetate (2.5 mmol) was dissolved in THF (60 ml) then 60 ml of a 0.33 M aqueous KOH solution was added. The reaction mixture was stirred vigorously at room temperature for 18 hours until solution became homogeneous. The reaction was quenched with 200 ml of a 0.1 M aqueous HCl solution. Then, the resulting turbid solution was diluted with additional 200 ml of water. The aqueous phase was extracted with 200 ml of DCM 3 times. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure then placed under high vacuum overnight. The resulting mixture was dissolved in 1 L of DCM followed by addition of 1.56 g of PyBOP (3.0 mmol, 1.2 eq.). After stirring for 10 min, 1.05 ml of TEA (7.5 mmol, 3.0 eq.) was added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain MeO-PTO as a white solid. (555 mg, 82.1%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 1H), 5.01 (m, 1H), 4.14 (m, 1H), 3.79 (s, 3H), 3.73 (d, *J* = 11.8 Hz, 1H), 3.17–3.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.35, 159.45, 133.84, 127.73, 114.41, 66.37, 59.81, 55.47, 36.70, 36.54. MS (MALDI-MS) calculated for $C_{12}H_{14}NaO_3S_2$ $[M+Na]^+$: 293.03, found: 293.07.

B. Synthesis of 5,5-dimethyl-1,4,6-oxadithiocan-2-one (DTO)

5,5-dimethyl-1,4,6-oxadithiocan-2-one (DTO) was synthesized as described below.



Scheme S5. Synthetic scheme of DTO.

B.1. Synthesis of 2-mercaptoethyl 2-mercaptoacetate

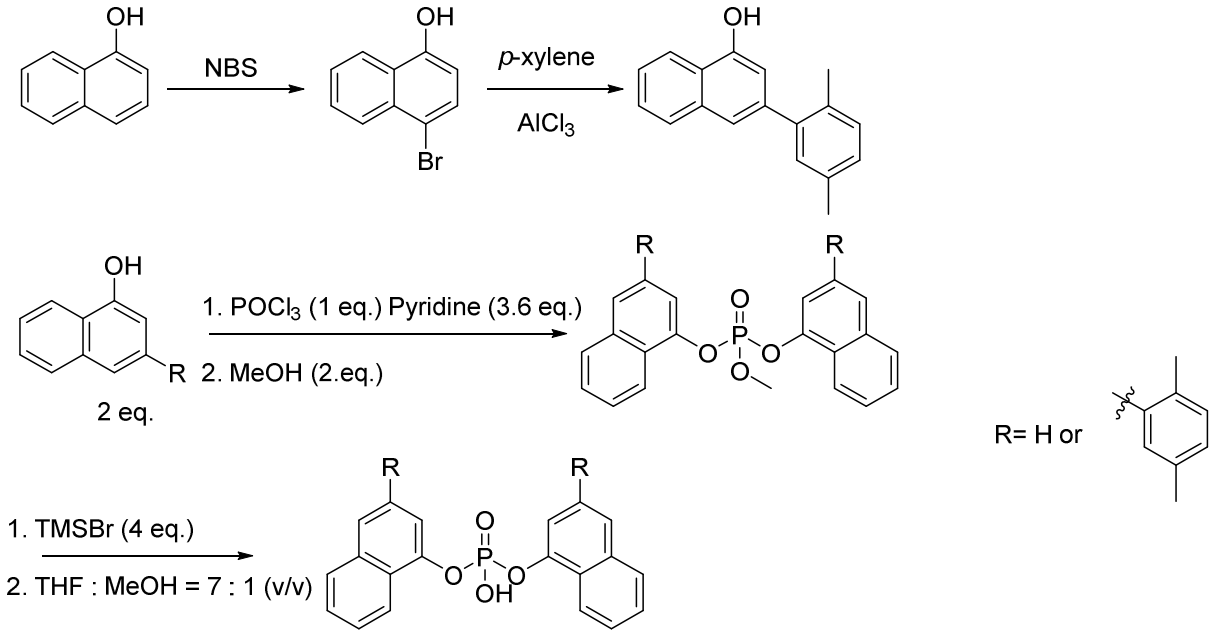
To 14.1 ml of 2-mercaptoethanol (200 mmol), 14.0 ml of 2-thioglycolic acid (200 mmol, 1.0 eq.) and 1.9 g of *p*-TsOH (10.0 mmol, 0.050 eq.) were added. The reaction mixture was sealed and stirred at room temperature for 3 days. The crude mixture was dissolved in 200 ml of DCM and washed in care with 200 ml of aq. sodium bicarbonate (distilled water : saturated $NaHCO_3$ in water = 9 :1) three times and then, with 200 ml of distilled water three times. The resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The product was clear oil and used without further purification. (17.4 g, 57.2%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27(t, *J* = 6.6 Hz, 2H), 3.29 (d, *J* = 8.3 Hz, 2H), 2.78 (dt, *J* = 13.9, 6.7 Hz, 2H), 2.03 (t, *J* = 8.3 Hz, 1H), 1.53 (t, *J* = 8.5 Hz, 1H).

B.2. Synthesis of 5,5-dimethyl-1,4,6-oxadithiocan-2-one (DTO)

761 mg of 2-mercaptoethyl 2-mercaptoacetate (5.0 mmol) was dissolved in 2 L of acetone followed by addition of 20 g of Drierite. After stirring for 1 hour, the solution become turbid due to ground power of Drierite, then 67 mg of NBS (0.38 mmol, 0.075 eq.) was added. The reaction vessel was sealed and stirred overnight. To the mixture, 0.1 ml of pyridine was added, then the solution was filtered and evaporated under reduced pressure. The crude mixture was further purified with silica gel column chromatography and the purified product was recrystallized in ether to obtain 5,5-dimethyl-1,4,6-oxadithiocan-2-one (DTO) as white solid. (33.0%, 317 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.49 (br, 2H), 3.38 (s, 2H), 3.04 (br 2H), 1.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.00, 66.63, 55.85, 34.80, 33.72, 31.28. MS (MALDI-MS) calculated for $C_7H_{12}NaO_2S_2$ $[M+Na]^+$: 215.02, found: 215.02.

C. Synthesis of catalysts

Diarylphosphates are synthesized as described below.



Scheme S6. Synthetic scheme of diarylphosphates.

C.1.1 Synthesis of methyl di(naphthalen-1-yl) phosphate

865 mg of 1-naphthol (6.0 mmol, 2 eq.) was dissolved in 60 ml of anhydrous toluene. To the solution, 280 µl of $POCl_3$ (3.0 mmol, 1 eq.) and 870 µl of pyridine (10.8 mmol, 3.6 eq.) were added sequentially and the reaction mixture was stirred at 60 °C. After confirming the full consumption of 1-naphthol by TLC, 243 µl of anhydrous methanol (6.0 mmol, 2.0 eq.) was added and the reaction mixture was stirred overnight. The solution was cooled to room temperature and diluted with 200 ml of DCM. The organic layer was washed with 200 ml of a 0.01 M aqueous HCl solution 3 times, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain methyl di(naphthalen-1-yl) phosphate as clear oil. (636 mg, 58.2%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49 (m, *J* = 7.9 Hz, 4H), 7.41 (t, 2H), 4.01 (d, 3H).

C.1.2 Synthesis of di(naphthalen-1-yl) phosphate (DNP)

636 mg of methyl di(naphthalen-1-yl) phosphate (1.75 mmol) was dissolved in 20 ml of anhydrous chloroform. To the solution, 920 µl of TMSBr (7.0 mmol, 4.0 eq.) was added dropwise under inert atmosphere and the reaction mixture was stirred overnight. After confirming the full conversion of methyl di(naphthalen-1-yl) phosphate, the solvent and remaining TMSBr was evaporated under reduced pressure to obtain yellowish oil. To the crude oil, 20 ml of MeOH/THF (1/7; v/v) was added and the mixture was stirred overnight. The solvent was removed under reduced pressure once again and the resulting solid was washed with the 1 : 1 solution of ether and petroleum

ether to obtain DNP as a white solid (440 mg, 71.8%). DNP could be further recrystallized in a mixture of ether and petroleum ether to obtain needle-shaped crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.55, 146.49, 134.86, 127.72, 126.81, 126.59, 126.51, 126.46, 125.54, 125.47, 125.46, 121.83, 115.40, 115.37. ^{31}P NMR (200 MHz, $CDCl_3$) δ -8.82. MS (MALDI-MS) calculated for $C_{20}H_{14}O_4P$ $[M-H]^-$: 349.06, found: 349.31.

C.2.1 Synthesis of 4-bromo-1-naphthol

2.88 g 1-naphthol (20 mmol) was dissolved in 80 ml of acetonitrile. Then 3.92 g of NBS (22 mmol, 1.1 eq.) was added to the solution portionwise. After stirring for 4 h, the solvent was evaporated under reduced pressure and the remaining product was dissolved into 100 ml of ether. The organic layer was washed three times with 100 ml of water and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting solid was recrystallized with DCE to obtain 4-bromo-1-naphthol as pale brown needle-shaped crystal. (2.41 g, 54.0%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.62 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.51 (s, 1H).

C.2.2 Synthesis of 3-(2,5-dimethylphenyl)naphthalen-1-ol

p-Xylene was stored with 4 Å molecular sieves before use. To 40 ml of pre-dried *p*-xylene, 2.00 g of $AlCl_3$ was added (15 mmol, 3.4 eq.) Then, 982 mg of 4-bromo-1-napthol (4.4 mmol) was added and the mixture was stirred under inert atmosphere for 2 h at 80 °C. The solution was cooled to room temperature and slowly poured into a mixture of conc. HCl (15 ml) and ice (100 g) in a separatory funnel. After 10 min, 200 ml of water was added to the mixture and the aqueous layer was extracted with 200 ml of ether 3 times. The organic layer was combined, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel chromatography to obtain 3-(2,5-dimethylphenyl)naphthalen-1-ol as a pale brown oil (680 mg, 62%). Because 3-(2,5-dimethylphenyl)naphthalen-1-ol can be easily oxidized under aerobic conditions, it was used for next reaction immediately. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.80 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.49 (m, 2H), 7.35 (s, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 1.3 Hz, 1H), 2.36 (s, 3H) 2.26 (s, 3H).

C.2.3 Synthesis of bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) methyl phosphate

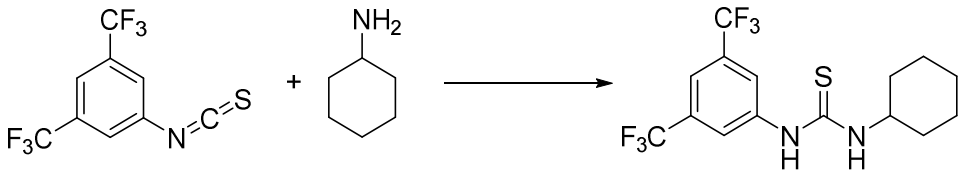
680 mg of 3-(2,5-dimethylphenyl)naphthalen-1-ol (2.74 mmol, 2.0 eq.) was dissolved in 30 ml of anhydrous toluene. To the solution, 130 µl of $POCl_3$ (1.37 mmol, 1 eq.) and 400 µl of pyridine (4.97 mmol, 3.6 eq.) were added sequentially and the mixture was stirred at 60 °C. After confirming the full consumption of bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) methyl phosphate by TLC, 110 µl of anhydrous methanol (2.74 mmol, 2.0 eq.) was added and the mixture was stirred overnight. The solution was cooled to room temperature and diluted with 200 ml of DCM. The organic layer was washed three times with 200 ml of a 0.01 M aqueous HCl solution, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain of bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) methyl phosphate as clear oil. (330 mg, 42.1%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 2H), 7.54 (s, 2H), 7.51 (td, *J* = 7.5, 1.1 Hz, 2H), 7.44 (td, *J* = 7.5, 1.1 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.08 (s, 2H) 4.04 (d, *J* = 11.6 Hz, 3H), 2.34 (s, 6H), 2.21 (s, 6H).

C.2.4 Synthesis of bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) phosphate (XNP)

240 mg of bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) methyl phosphate (0.42 mmol) was dissolved in 4 ml of anhydrous chloroform. To the solution, 330 µl of TMSBr (2.5 mmol, 6.0 eq.) was added dropwise under inert atmosphere and the mixture was stirred overnight. After confirming the full conversion of methyl di(naphthalen-1-yl) phosphate, the solvent and remaining TMSBr was evaporated under reduced pressure to obtain yellowish oil. To the mixture, 10 ml of MeOH/THF (1/7; v/v) was added and stirred overnight. The solvent was removed under reduced pressure once again then the resulting solid was washed with ice-cold *n*-hexane then *n*-pentane to obtain XNP as a white solid. (210 mg, 89.5%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 2H), 7.43 (s, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.08–6.99 (m, 6H), 2.27 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.96, 145.89, 140.65, 139.61, 139.60, 135.33, 134.60, 132.49, 130.65, 130.46, 128.40, 127.76, 127.00, 126.39, 125.40, 125.23, 125.18, 121.68, 117.49, 117.46, 21.00, 20.01.^{31}P NMR (200 MHz, $CDCl_3$) δ -8.38. MS (MALDI-MS) calculated for $C_{36}H_{30}O_4P$ $[M-H]^-$: 557.19, found: 557.55.

C.3.1 Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea

1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea was synthesized as described below.



Scheme S7. Synthetic scheme of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea.

910 µl of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (5.0 mmol, 1.0 eq.) was dissolved in 25 ml of anhydrous DCM. Then, 630 µl of cyclohexylamine (5.5 mmol, 1.1 eq.) and 770 µl of TEA (5.5 mmol, 1.1 eq.) were added. The reaction mixture was stirred under inert atmosphere for 2 h and the solution was washed with 30 ml of a 0.01 M aqueous HCl solution 3 times. The resulting mixture was recrystallized with *n*-hexane and chloroform to obtain 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea as white solid. (1.45 g, 78.3%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (br, 1H), 7.75 (s, 2H), 7.72 (s, 1H), 6.02 (br, 1H), 4.22 (br, 1H), 2.17–2.00 (m, 2H), 1.81–1.68 (m, 2H), 1.68–1.58 (m, 1H), 1.51–1.35 (m, 2H), 1.30–1.10 (m, 3H).

D. Procedures for polymerization

D.1 General procedure for homopolymerization of PTO, DTO, F-PTO, and CF_3-PTO (**P1**–**P10**, **P12**, **P14** and **P15**) using diarylphosphate as the catalyst and with various initiators

All reactions were conducted in the glove box. Monomers were dissolved in anhydrous toluene at a concentration of 0.50 M. To the solution, the initiator was added and stirred vigorously. After 2 min, diarylphosphate (0.020 eq., 5.0 mol% of the monomer) was added. Reaction progress of the polymerization was determined with small aliquots taken from the reaction mixture. Aliquots were quenched immediately with an excess of pyridine. Finally, the reaction mixtures were quenched with an excess of pyridine (> 5 eq.) and precipitated into cold methanol. The precipitates were collected by centrifugation at 3000 rpm and dried *in vacuo* to afford white greasy solid regardless of the initial [M]/[I] ratio and type of monomers. The dried polymers were stored at -20 °C.

D.2 General procedure for homopolymerization of PTO using thiourea and 1,8-diazabicyclo(5.4.0)undec-7-ene(DBU) as a catalyst

Reaction was conducted in the glove box. PTO (96.1 mg, 0.40 mmol) was dissolved in anhydrous THF at a concentration of 0.5 M. To the solution, 1-pyrenebutanol (2.7 mg, 0.010 mmol) was added and the mixture was stirred vigorously. After 2 min, 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (7.4 mg, 0.020 mmol) and DBU (3.0 µl, 0.020 mmol) were added. For the control reaction, only DBU (14.9 µl, 0.10 mmol) was added to PTO (96.1 mg, 0.40 mmol) without addition of thiourea and 1-pyrenebutanol. Aliquots were quenched after 18 h with an excess of benzoic acid and analyzed with ^{1}H NMR (**Figure S1**).

D.3 Procedure for polymerization of PTO using mPEO-OH (2 kDa) as an initiator (**P11**)

Reaction was conducted in the glove box. PTO (96.1 mg, 0.40 mmol) was dissolved in a mixture of anhydrous toluene and DCM (4 : 1 in v/v) to adjust the concentration as 0.50 M. To the solution, mPEO-OH (20 mg, 0.010 mmol) was added and the mixture was stirred vigorously. After 2 min, XNP (11.2 mg, 5.0 mol% of PTO) was added. Reaction progress of the polymerization was determined with small aliquots taken from the reaction mixture. Aliquots were quenched immediately with an excess of pyridine. Finally, the reaction mixtures were also quenched with an excess of pyridine (> 5 eq.) and precipitated into cold ether. The precipitates were collected by centrifugation at 3000 rpm and dried *in vacuo* to afford white solid. The dried polymer was stored at -20 °C.

D.4 Procedure for homopolymerization of Me-PTO (**P13**)

Reaction was conducted in the glove box. Me-PTO (102 mg, 0.40 mmol) was dissolved in anhydrous toluene and DCM (4 : 1 in v/v) to adjust the concentration as 0.50 M. To the solution, 1-pyrenebutanol (2.7 mg, 0.010 mmol) was added and the mixture was stirred vigorously. After 2 min, XNP (11.2 mg, 5.0 mol% of the monomer) was added. Reaction progress of the polymerization was determined with small aliquots taken from the reaction mixture. Aliquots were quenched immediately with an excess of pyridine. Finally, the reaction mixtures were also quenched with an excess of pyridine (> 5 eq.) and precipitated into cold methanol. The precipitates were collected by centrifugation at 3000 rpm and dried *in vacuo* to afford white greasy solid. The dried polymer was stored at -20 °C.

D.5 Procedure for homopolymerization of NO_2-PTO (**P16**)

Reaction was conducted in the glove box. NO_2-PTO (85.6 mg, 0.30 mmol) was dissolved in anhydrous DCM to adjust the concentration as 0.40 M. To the solution, 1-pyrenebutanol (2.7 mg, 0.010 mmol) was added and the mixture was stirred vigorously. After 2 min, XNP (11.2 mg, 5.0 mol% of the monomer) was added. Reaction progress of the polymerization was determined with small aliquots taken from the reaction mixture. Aliquots were quenched immediately with an excess of pyridine. Finally, the reaction mixtures were also quenched with an excess of pyridine (> 5 eq.) and precipitated into cold methanol. The precipitates were collected by centrifugation at 3000 rpm and dried *in vacuo* to afford pale-yellow greasy solid. The dried polymer was stored at -20 °C.

^{1}H, ^{13}C NMR characterization of representative polymers from different monomers and initiators

$\overline{DP}$ was calculated from the ratio of the peaks corresponding to C(O)OC***H***$_2$-CH_2- in backbone and C***H***$_2$-OH at the chain end, respectively.

P6, I = PyBuOH, target [PTO]/[I] = 40, $\overline{DP}$ = 37 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–7.82 (pyrene, 9H), 7.63–7.20 (br, 185H), 5.19 (s, 37H), 4.38–3.94 (br, 74H), 3.71 (br, 2H), 3.42–3.27 (d, *J* = 15.1 Hz, 39H), 3.14–3.02 (d, 15.1 Hz 37H), 2.96–2.65 (br, 74H), 2.21 (br, 1H), 1.92 (m, 2H), 1.80 (m, 2H).

P9, I = propargyl alcohol, target [PTO]/[I] = 40, $\overline{DP}$ = 38 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.20 (br, 190H), 5.19 (s, 38H), 4.67 (m, 2H), 4.38–3.94 (br, 76H), 3.71 (br, 2H), 3.42–3.27 (d, *J* = 15.1 Hz 40H), 3.14–3.02 (d, *J* = 15.1 Hz 38H), 2.96–2.65 (br, 76H), 2.52 (s, 1H), 2.21 (br, 1H).

P10, I = 2-propanol, target [PTO]/[I] = 40, $\overline{DP}$ = 37 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.20 (br, 185H), 5.19 (s, 37H), 5.00 (m, 1H), 4.38–3.94 (br, 74H), 3.71 (br, 2H), 3.42–3.27 (d, *J* = 15.1 Hz, 39H), 3.14–3.02 (d, *J* = 15.1 Hz, 37H), 2.96–2.65 (br, 74H), 2.20 (br, 1H), 1.23 (d, 6H).

P12, I = PyBuOH, target [DTO]/[I] = 40, $\overline{DP}$ = 37 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–7.82 (pyrene, 9H), 4.28 (t, *J* = 6.7 Hz 72H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.80 (br, 2H), 3.43 (s, 74H), 3.39 (br, 2H), 2.88 (t, *J* = 6.7 Hz, 74H), 2.15 (b, 1H), 1.96 (m, 2H), 1.84 (m, 2H), 1.62 (s, 222H).

P13, I = PyBuOH, target [Me-PTO]/[I] = 40, $\overline{DP}$ = 35 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–7.82 (pyrene, 9H), 7.35–7.24 (br, 70H), 7.16–7.01 (br, 70H), 5.16 (s, 37H), 4.40–3.95 (br, 70H), 3.71 (br, 2H), 3.37 (br, 2H), 3.36–3.26 (d, *J* = 15.1 Hz, 35H), 3.14–3.02 (d, *J* = 15.1 Hz, 35H), 2.96–2.66 (br, 70H), 2.39–2.28 (s, 102H), 2.27 (s, 3H), 1.92 (m, 2H), 1.81 (m, 2H).

P14, I = PyBuOH, target [F-PTO]/[I] = 40, $\overline{DP}$ = 37 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–7.82 (pyrene, 9H), 7.51–7.33 (br, 74H), 7.10–6.91 (br, 74H) 5.19 (s, 37H), 4.40–4.00 (br, 74H), 3.74 (br, 2H), 3.38–3.27 (d, *J* = 15.3 Hz, 39H), 3.14–3.01 (d, *J* = *J* = 15.3 Hz, 37H), 3.00–2.67 (br, 74H), 2.23 (br, 1H), 1.92 (m, 2H), 1.81 (m, 2H).

P15, I = PyBuOH, target [CF_3-PTO]/[I] = 40, $\overline{DP}$ = 39 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–7.82 (pyrene, 9H), 7.63–7.20 (br, 156H), 5.24(s, 39H), 4.46–3.98 (br, 78H), 3.76 (br, 2H), 3.41–3.26 (d, *J* = 15.3 Hz, 41H), 3.17–3.00 (d, 14.4 Hz, 39H), 2.96–2.65 (d, 78H), 2.21 (br, 1H), 1.92 (m, 2H), 1.80 (m, 2H).

P16, I = PyBuOH, target [NO_2-PTO]/[I] = 30, $\overline{DP}$ = 30 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (pyrene, d, 1H), 8.22–8.10 (Br, 60H), 8.13–8.06 (pyrene, 4H), 8.02 (pyrene, s, 2H), 7.98 (pyrene, t, 1H), 7.84 (pyrene, d, 1H), 7.70–7.50 (br, 30H), 5.29 (s, 30H), 4.40–4.00 (br, 60H), 3.79 (br, 2H), 3.44 (d, *J* = 15.0 Hz, 2H), 3.43–3.30 (d, *J* = 15.3 Hz, 30H), 3.18–3.02 (d, *J* = 15.3 Hz, 30H), 3.01–2.68 (d, 60H), 2.25 (br, 1H), 1.93 (m, 2H), 1.82 (m, 2H).

$\overline{DP}$ was calculated from peak from the ratio of C(O)OC***H***$_2$-CH_2- in backbone and C***H***$_2$-O- in chain end and mPEO

P11, I = mPEO-OH (2 kDa), target [PTO]/[I] = 40, $\overline{DP}$ = 33 in ^{1}H NMR analysis

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.20 (br, 165H), 5.19 (s, 33H), 4.38–3.94 (br, 66H), 3.82–3.48 (br, 182H), 3.42–3.27 (d, *J* = 15.1 Hz, 35H), 3.14–3.02 (d, *J* = 15.1 Hz, 33H), 2.96–2.65 (br, 66H).

^{13}C NMR peaks from the polymer backbone of poly(PTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.90, 138.92, 128.90, 128.58, 127.99, 63.98, 53.44, 33.80, 31.01.

^{13}C NMR peaks from the polymer backbone of poly(DTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.44, 64.55, 57.20, 33.14, 30.82, 29.06.

^{13}C NMR peaks from the polymer backbone of poly(Me-PTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.95, 138.40, 135.88, 129.56, 127.90, 64.02, 53.27, 33.84, 31.01, 21.32.

^{13}C NMR peaks from the polymer backbone of poly(F-PTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.82, 163.58, 161.61, 134.73, 129.82, 129.76, 115.94, 115.77, 63.91, 52.28, 33.76, 31.05.

^{13}C NMR peaks from the polymer backbone of poly(CF_3-PTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.71, 142.99, 131.15, 130.89, 130.63, 130.37, 128.44, 125.95, 125.02, 122.86, 63.85, 52.73, 33.67, 31.06.

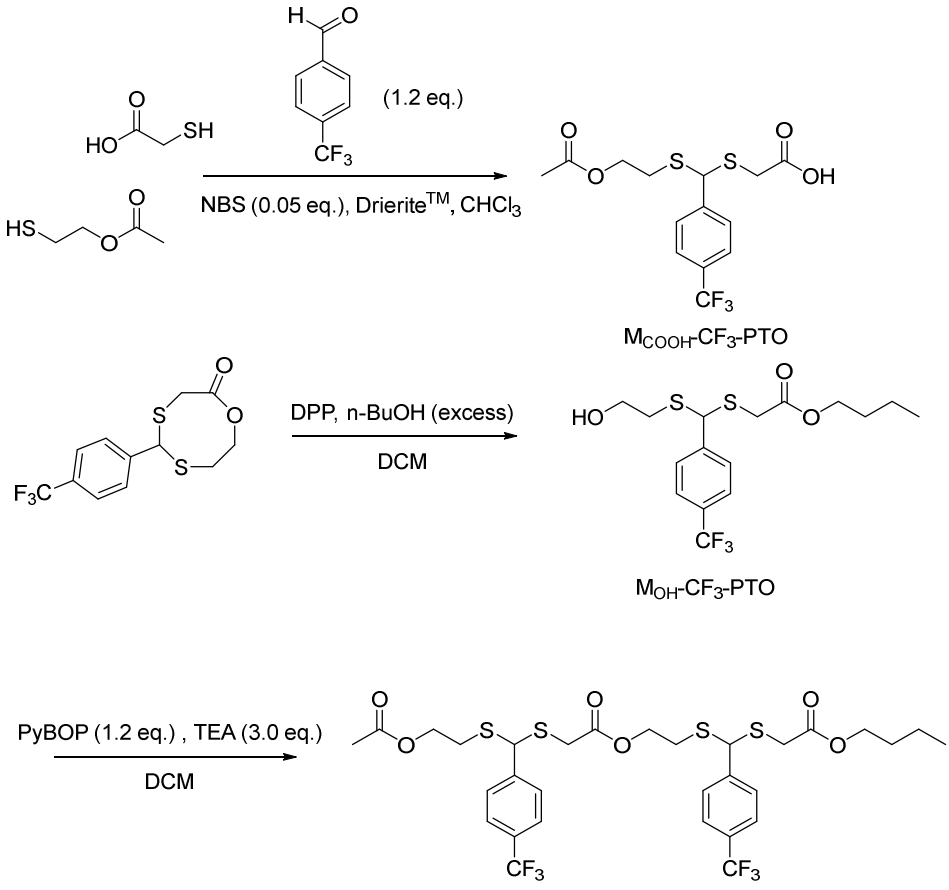
^{13}C NMR peaks from the polymer backbone of poly(NO_2-PTO)

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.59, 147.82, 146.28, 129.03, 124.22, 63.88, 52.48, 33.68, 31.13.

E. Procedure for the degradation test of polymers

4.8 mg of **P6**, 5.1 mg of **P13** and 6.2 mg of **P15** were dissolved in 3.8 ml of THF, respectively. 30% hydrogen peroxide in water (approx. 10 M) was diluted to 4 M with distilled water, and 200 µl each of the diluted hydrogen peroxide was added to each polymer solution. For the negative control, 200 µl of distilled water was added to the polymer solution instead. All solutions were stirred at 37°C, and analyzed with SEC at each time point. (Final concentration: [thioacetal groups in polymers] = 5 mM, [H_2O_2] = 200 mM)

F. Synthesis of model dimer of P15



Model dimer of **P15** (D-CF_3-PTO)

F.1. Synthesis of 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetic acid (M_{COOH}-CF_3-PTO)

240 mg of 2-mercaptoethyl acetate, (2.0 mmol) 140 µl of thioglycolic acid, (2.0 mmol) 306 µl of trifluoroacetic acid (4.0 mmol, 2.0 eq.) and 330 µl of 4-(trifluoromethyl)benzaldehyde (2.4 mmol, 1.2 eq.) was dissolved in 80 ml of chloroform. Then, 500 mg of Drierite followed by 17.8 mg of NBS (0.10 mmol, 0.050 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 100 ml of DCM and washed with 100 ml of the 0.01 M aqueous HCl solution water three times. Resulting organic layer was dried over anhydrous $MgSO_4$,

filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography using EA, hexane and small portion of acetic acid to obtain 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetic acid (M_{COOH}-CF_3-PTO) as a clear oil. (227 mg, 30.8%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (Aromatic, 4H), 5.30 (s, 1H), 4.25 (m, 2H), 3.43 (d, *J* = 15.3 Hz, 1H), 3.15 (d, *J* = 15.4 Hz, 1H), 2.97 (m, 1H), 2.78 (m, 1H), 2.07 (s, 3H).

F.2. Synthesis of butyl 2-((((2-hydroxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate (M_{OH}-CF_3-PTO)

154 mg of CF_3-PTO (0.50 mmol) was dissolved in 4.0 ml of 3:1 (v/v) solution of DCM and n-butanol, Then, 25 mg of DPP (0.10 mmol, 0.2 eq.) was added to the solution. The reaction mixture was sealed and stirred overnight at room temperature. The solution was diluted with 50 ml of DCM and washed with 50 ml of the saturated aqueous sodium bicarbonate solution three times. Resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was further purified with silica gel column chromatography to obtain butyl 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate as a clear oil. (174 mg, 91.0%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (Aromatic, 4H), 5.27 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.81 (q, *J* = 5.8 Hz, 2H), 3.41 (d, *J* = 15.0 Hz, 1H), 3.10 (d, *J* = 15.0 Hz, 1H), 2.91 (m, 1H), 2.75 (m, 1H), 2.17 (t, *J* = 6.2 Hz, 1H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

F.3. Synthesis model dimer of **P15** (D-CF_3-PTO)

147 mg of M_{COOH}-CF_3-PTO (0.40 mmol) and 153 mg of M_{OH}-CF_3-PTO (0.40 mmol) were dissolved in 8 ml of DCM. Then, 260 mg of PyBOP (0.50 mmol, 1.2 eq.) and 167 µl of TEA (1.2 mmol, 3.0 eq.) were added. The reaction mixture was stirred overnight and quenched with passing through a short silica plug. The filtrate was concentrated under reduced pressure and further purified with silica gel column chromatography to obtain D-CF_3-PTO as a clear oil. (250 mg, 85.3%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.47 (Aromatic, 8H), 5.29 (s, 1H), 5.26 (s, 1H), 4.32 (m, 1H), 4.28 – 4.15 (m, 3H), 4.09 (m, 2H), 3.41 (dd, *J* = 15.2, 3.4 Hz, 1H), 3.34 (d, *J* = 15.0 Hz, 1H), 3.16 – 3.06 (m, 2H), 2.99 (m, 1H), 2.91 (m, 1H), 2.86 – 2.69 (m, 2H), 2.05 (s, 3H), 1.60 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

3. Supporting figures

A. DBU/thiourea catalyzed polymerization of PTO

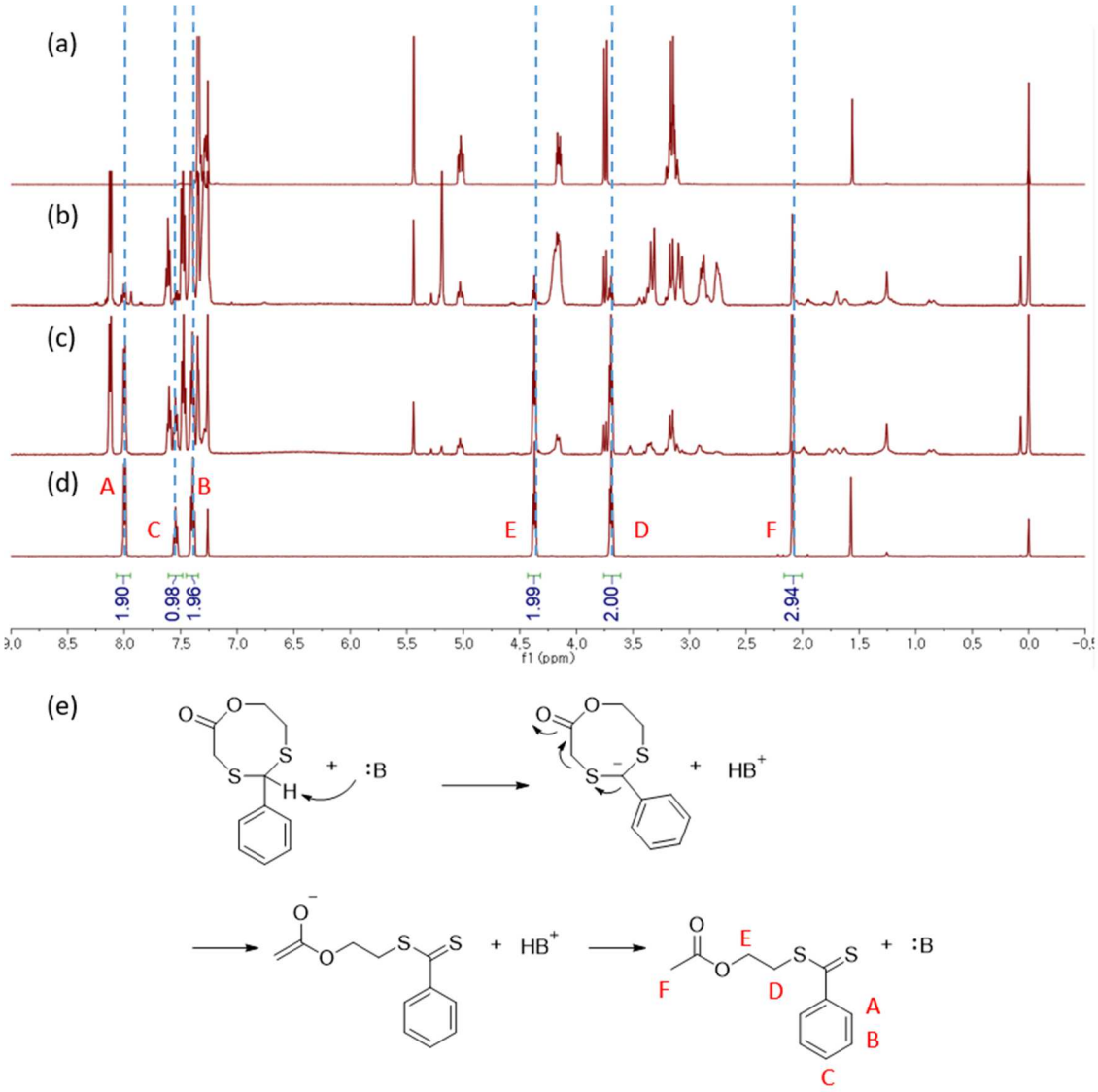
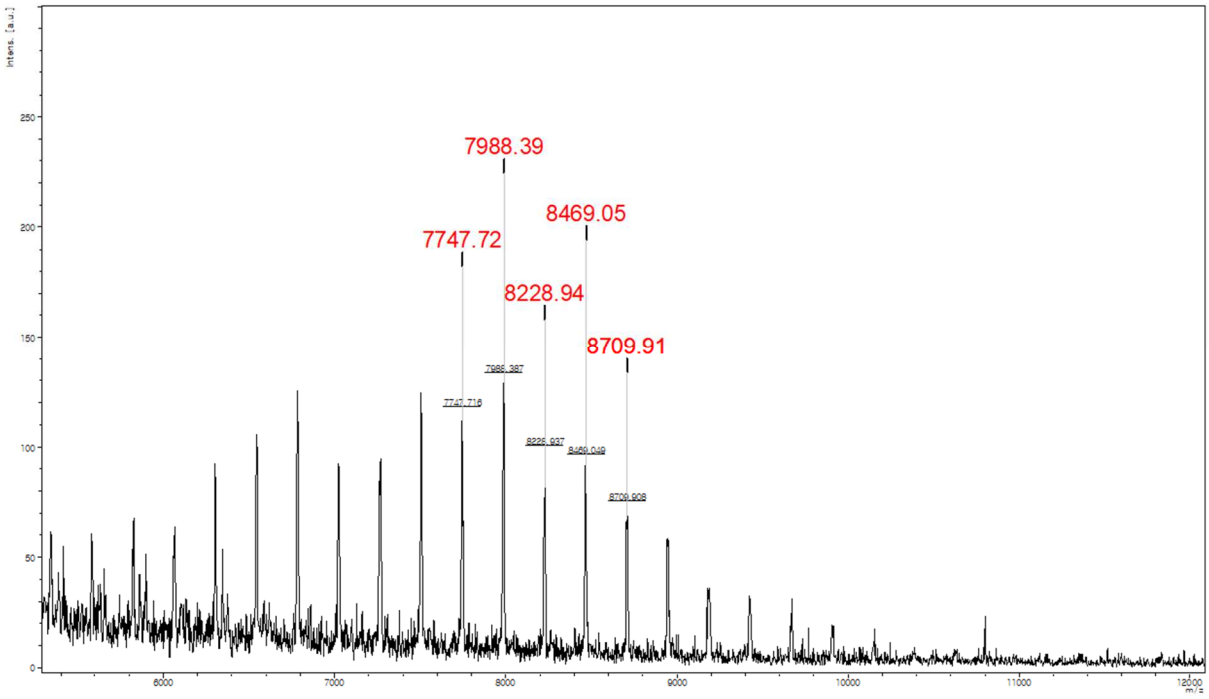
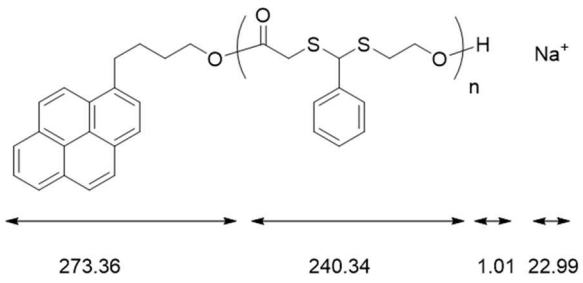


Figure S1. **Thiourea/DBU-catalyzed polymerization of PTO.** ^{1}H NMR spectra of (a) PTO monomer, (b) the sample after 18 h-polymerization and quenching with excess benzoic acid, (c) PTO monomer after 18 h-treatment with DBU in THF, and (d) the majour product isolated from (c). (e) A proposed mechanism for generation of (d)

B. Structure characterization of poly(PTO)





	Theoretical value	Detected
1	7747.89	7747.72
2	7988.23	7988.39
3	8228.57	8228.94
4	8468.91	8469.05
5	8709.25	8709.91

Figure S2. **MALDI-MS analysis of P6**. A 2:1 mixture of dithranol and sodium trifluoroacetate was used for the matrix.

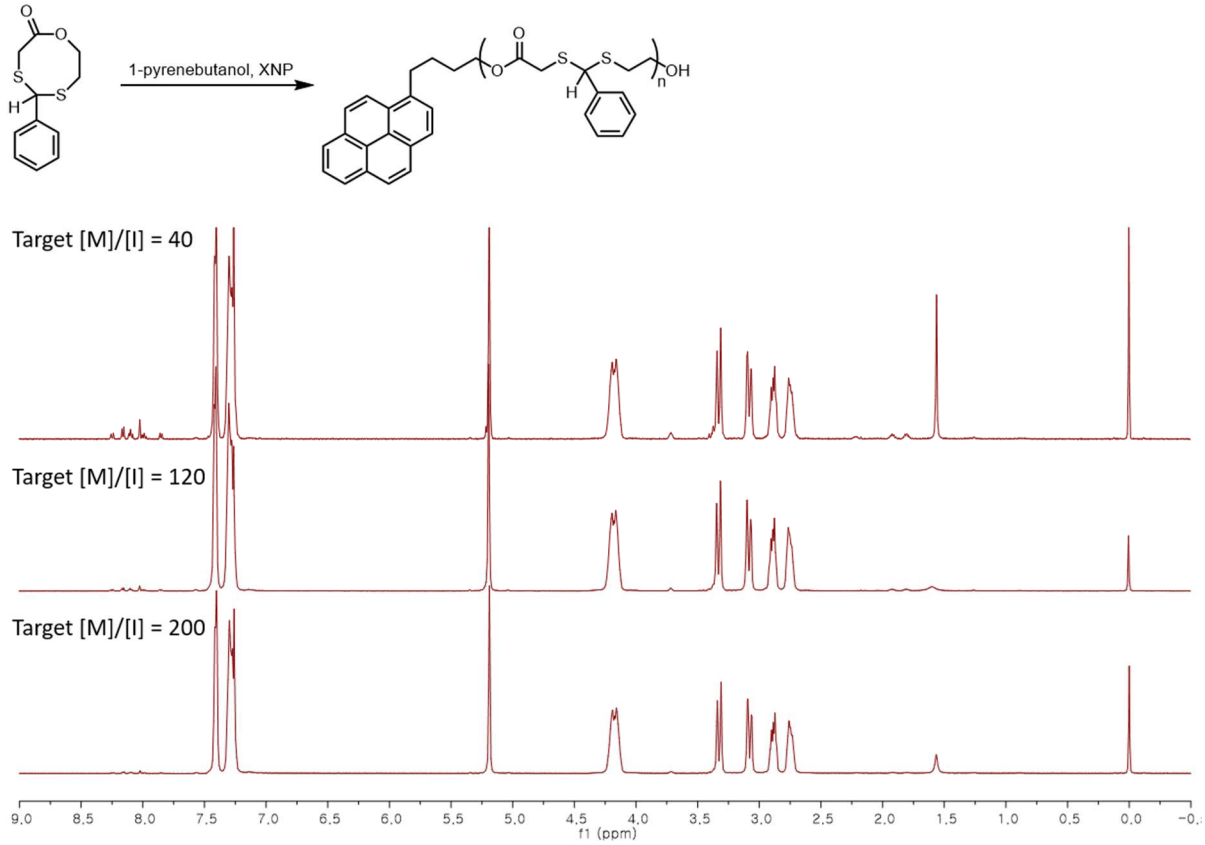


Figure S3. **NMR spectra of poly(PTO)s at various [M]/[I] ratios. P6** (top), **P7** (middle) and **P8** (bottom). Change of the peaks in the polymeric backbone or generation of new peaks were not observed during increase of the [M]/[I] ratio.

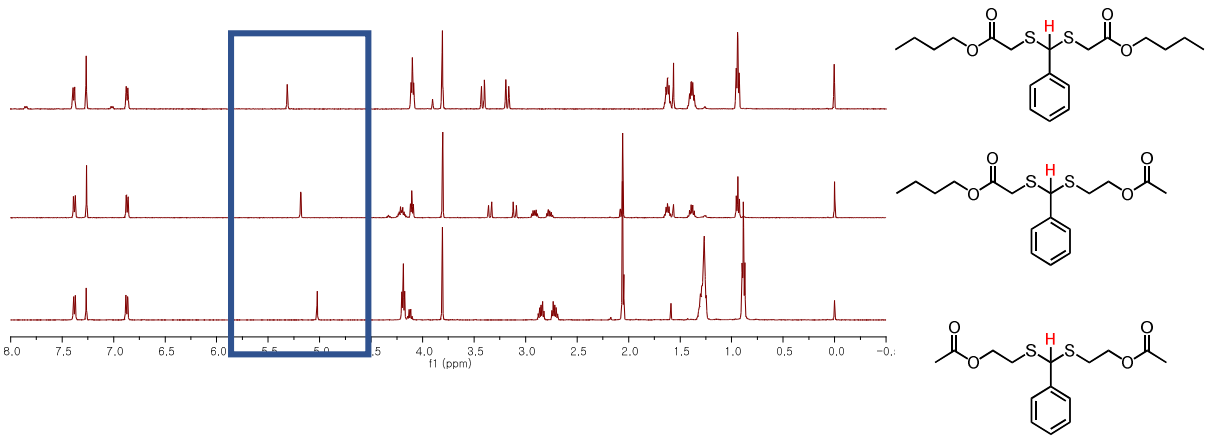


Figure S4. **Comparison of ^{1}H NMR spectra of three model thioacetals.** Model thioacetals based on diacid (top), hydroxyl acid (middle) and diol (bottom) which may be generated from rearrangement of the esters in the poly(PTO) backbone. Highlighted proton peaks appears as a singlet in the area inside the blue box. Compared with the peaks in **Figure S3**, we confirmed that the head-to-tail structure of the poly(PTO) backbone maintained during the increase of the [M]/[I] ratio.

C. SEC chromatograms of polymers

Shodex KF-803 column was used for the SEC with THF eluent at the flow rate of 0.7 ml/min. RI detector and column oven were maintained at 35 °C. Polystyrene standards were used for the calibration.

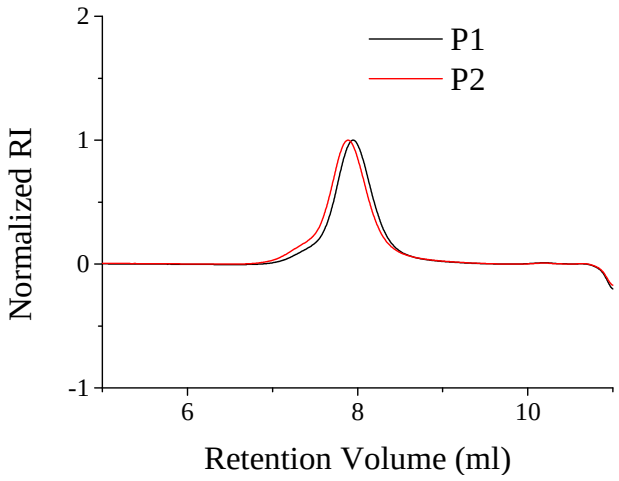


Figure S5. The SEC chromatograms of **P1** (black) and **P2** (red).

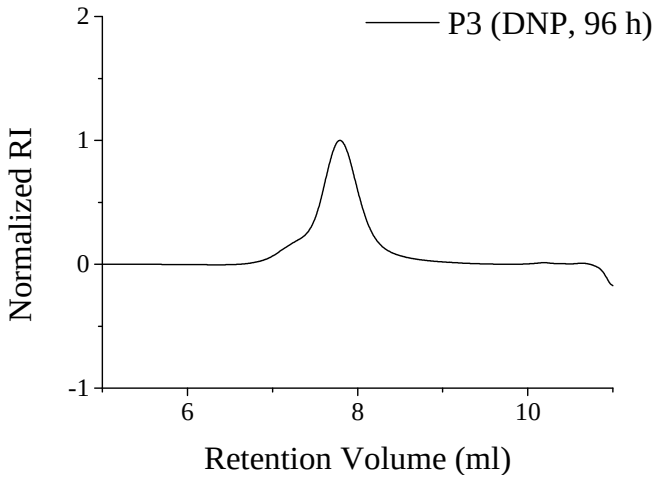


Figure S6. The SEC chromatogram of **P3**.

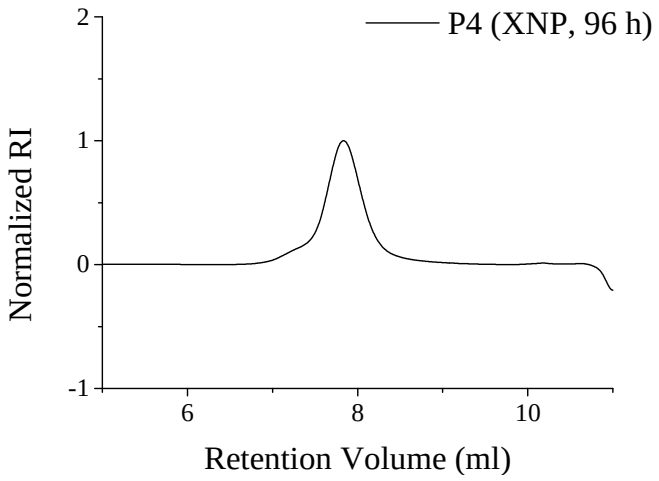


Figure S7. The SEC chromatogram of **P4**.

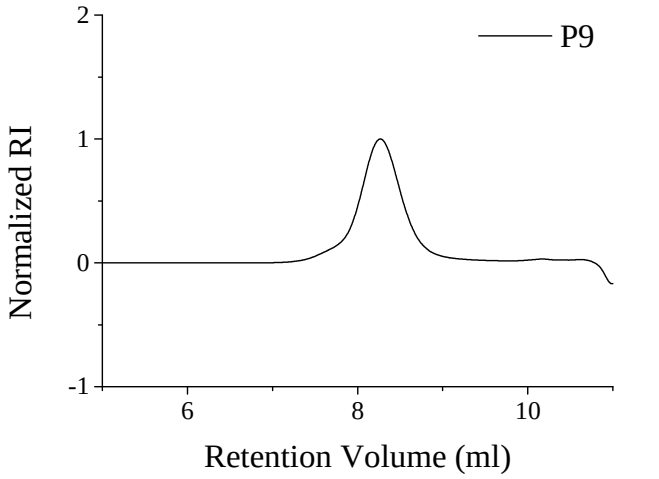


Figure S8. The SEC chromatogram of **P9**.

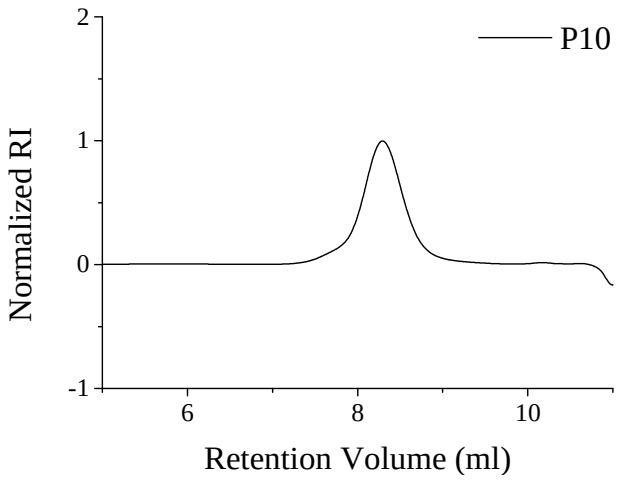


Figure S9. The SEC chromatogram of **P10**.

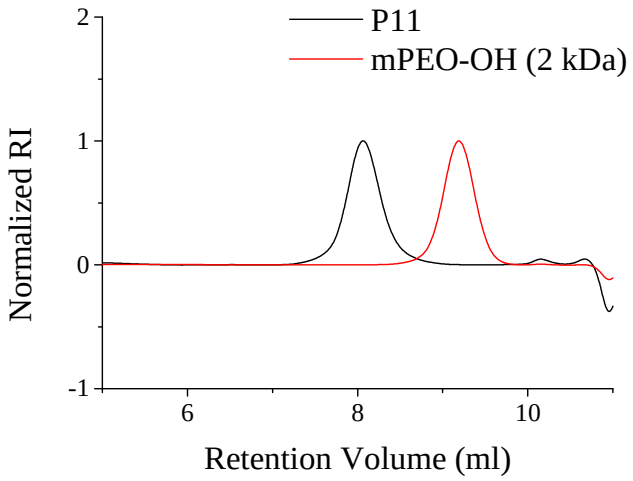


Figure S10. The SEC chromatograms of mPEO-OH (red, M_n ~ 2 kDa), the macroinitiator, and **P11** (black).

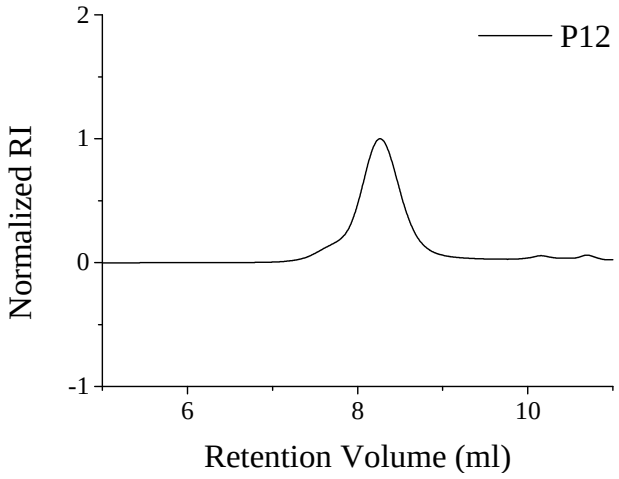


Figure S11. The SEC chromatogram of **P12**.

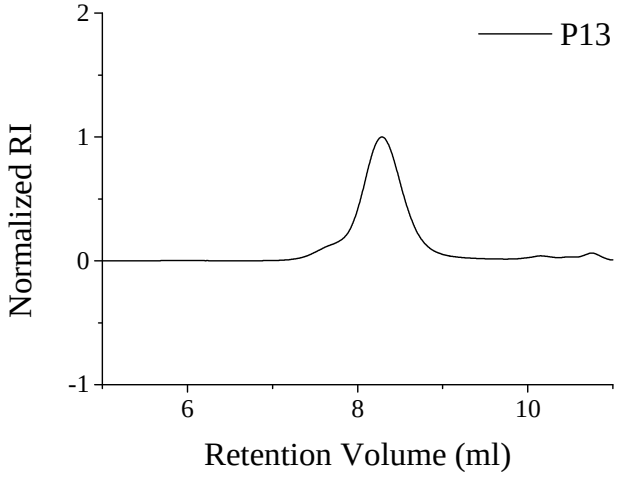


Figure S12. The SEC chromatogram of **P13**.

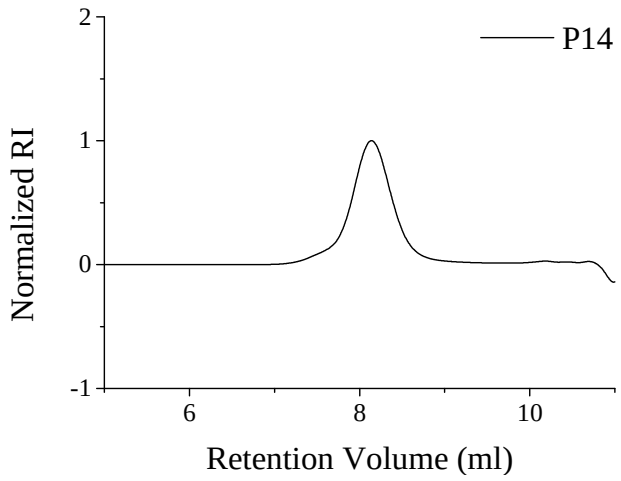


Figure S13. The SEC chromatogram of **P14**.

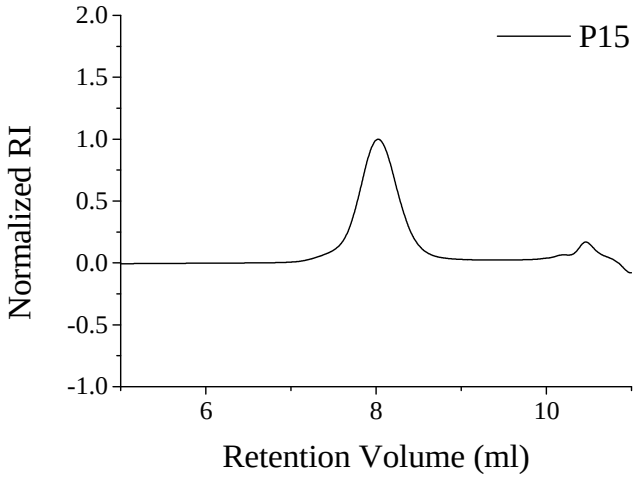


Figure S14. The SEC chromatogram of **P15**.

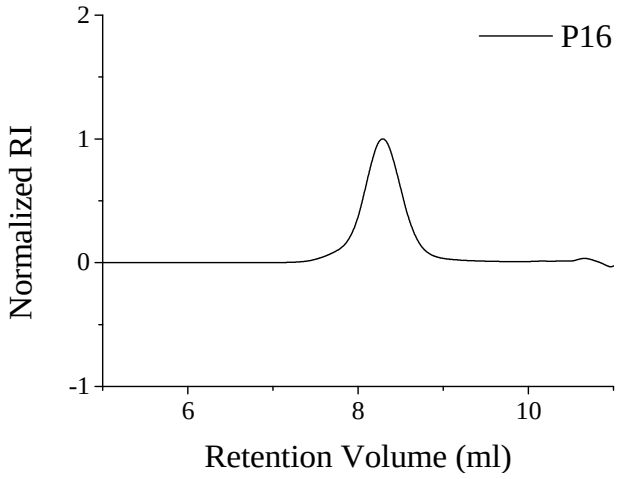


Figure S15. The SEC chromatogram of **P16**.

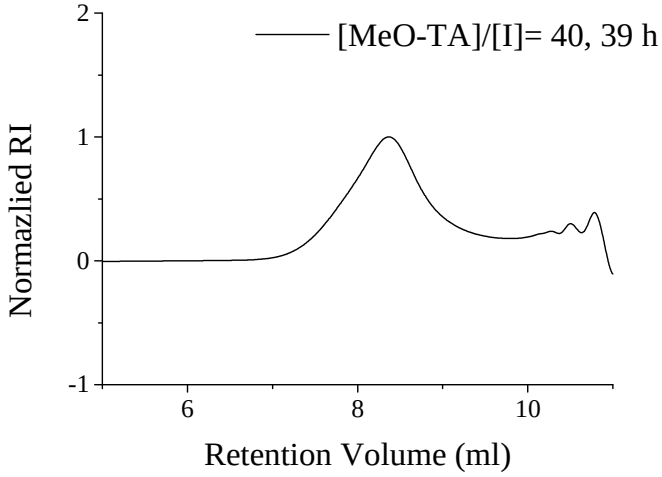


Figure S16. The SEC chromatogram of the polymerization product of MeO-TA. (39h, ~80% conversion)

D. ^{1}H NMR spectra of the polymerization mixture during the kinetics test

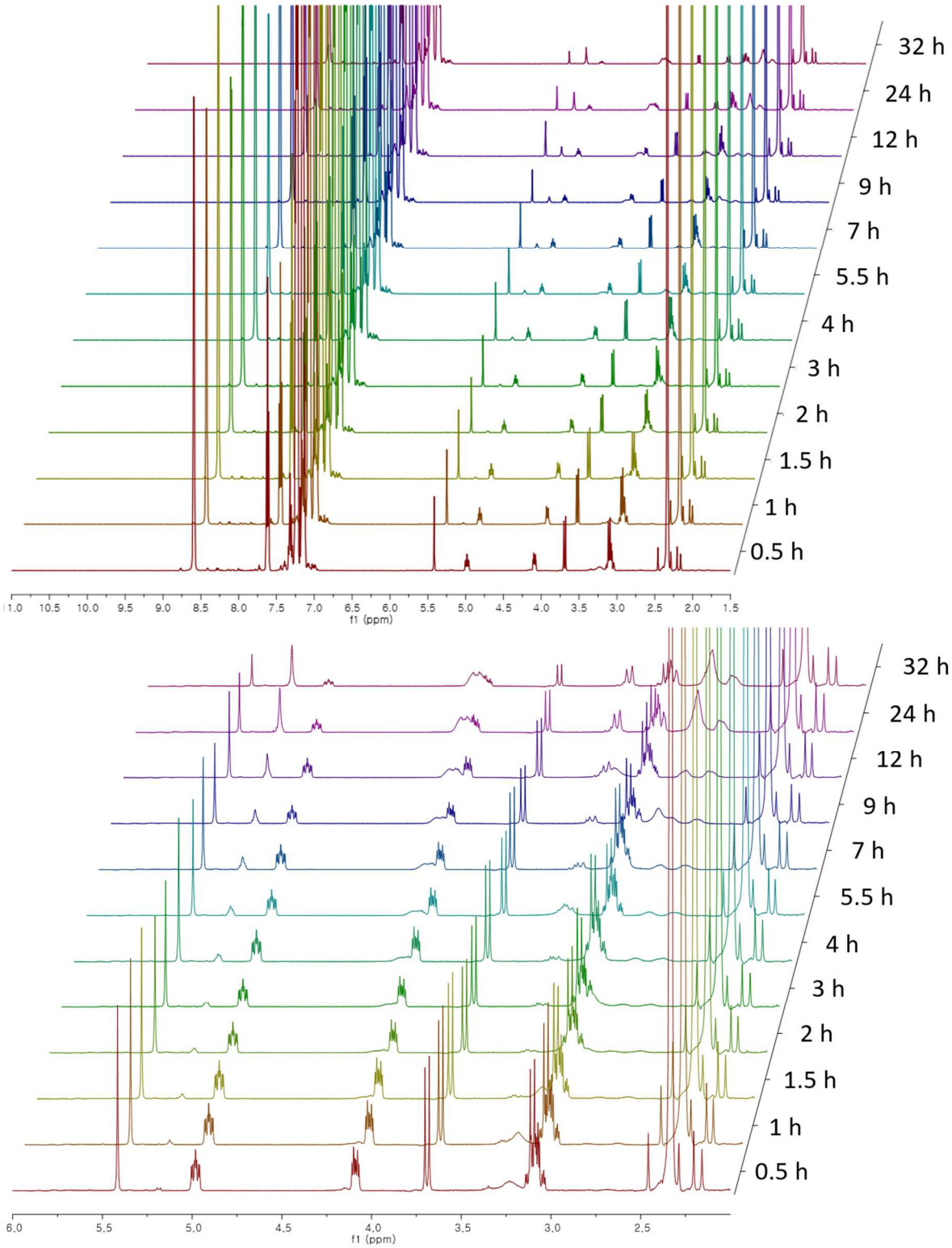


Figure S17. Change in ^{1}H NMR spectra during the polymerization in the range of 1.5–11.0 ppm (up) and 2.0–6.0 ppm (down)

E. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data of P6

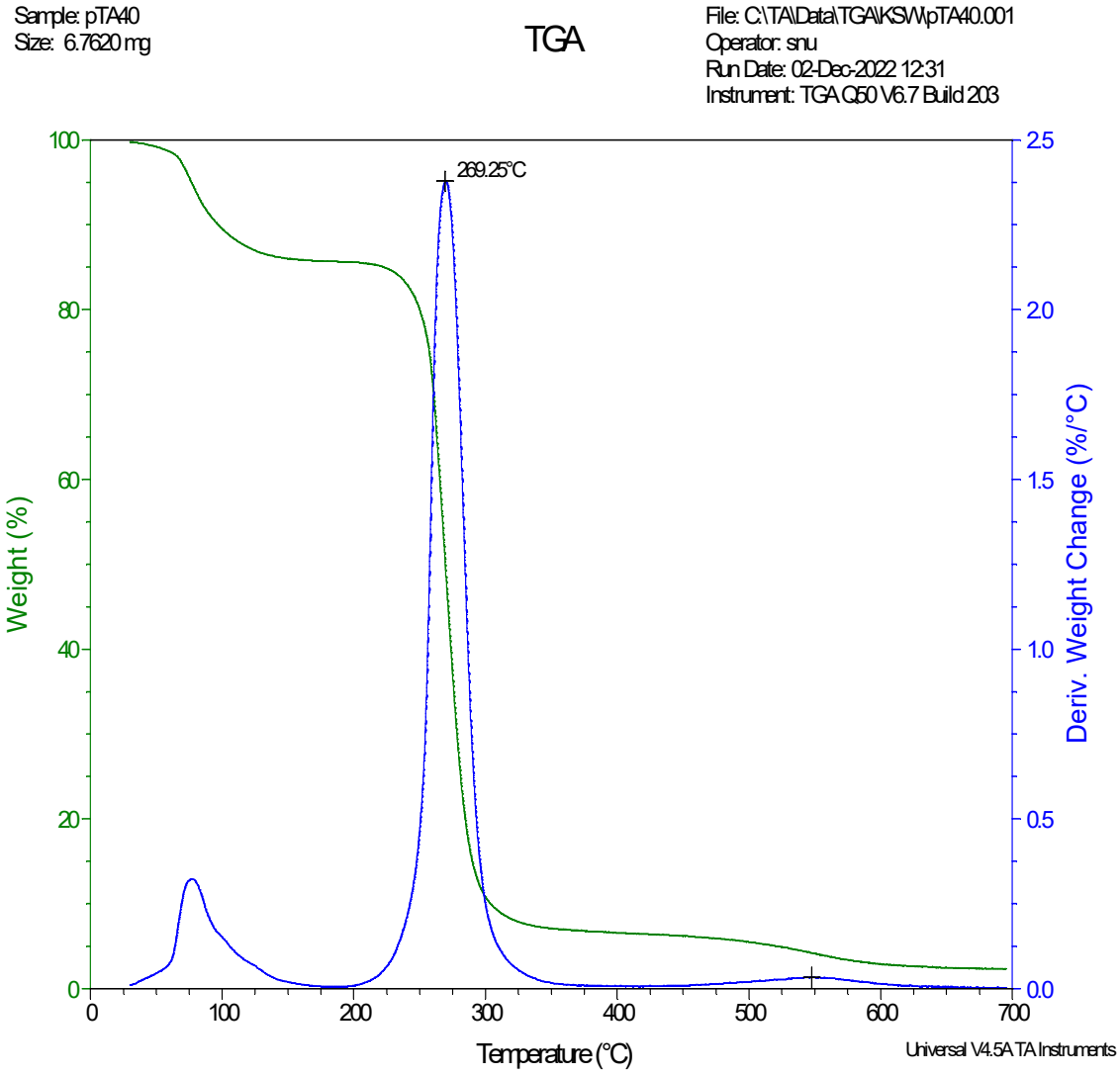


Figure S18. Thermogravimetric analysis data of **P6**.

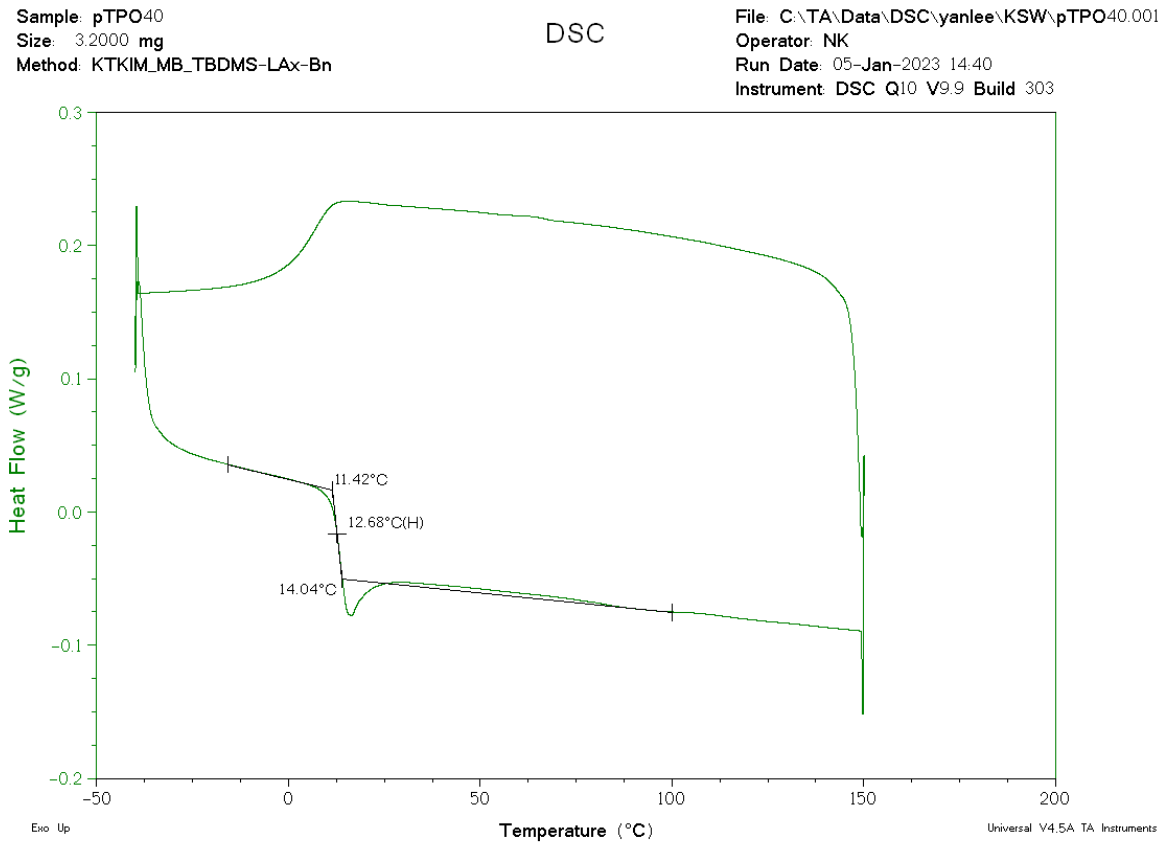


Figure S19. Differential scanning calorimetry data of **P6**.

F. Supplementary data for the degradation test

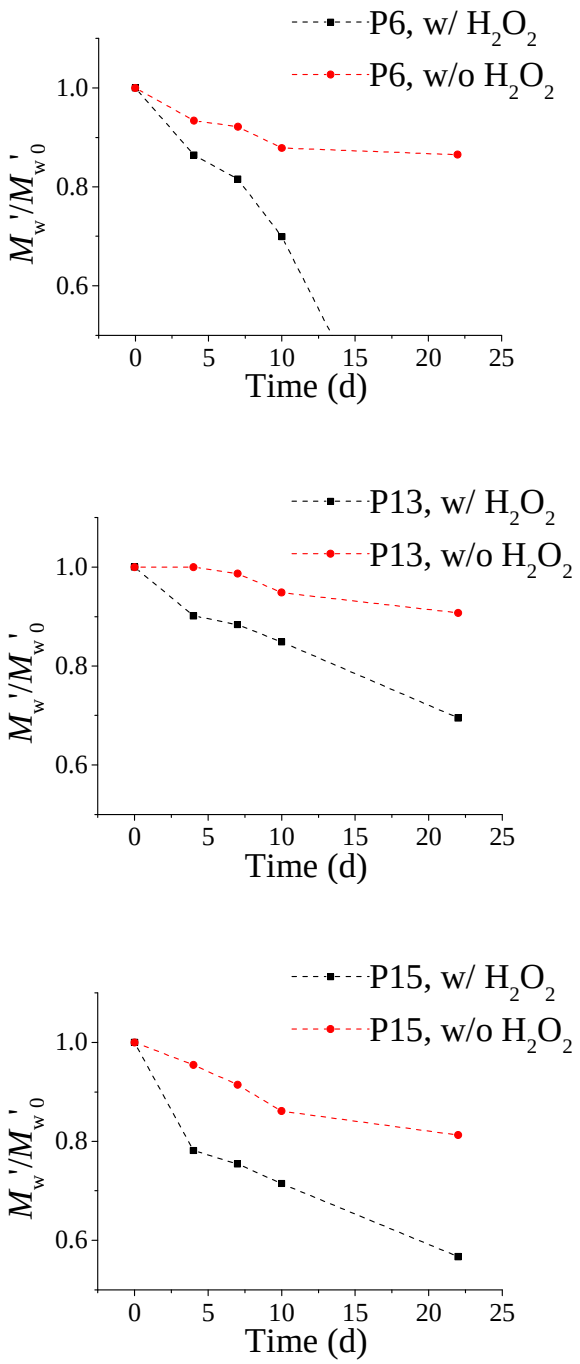


Figure S20. Molecular weight change of **P6** (top), **P13** (center) and **P15** (bottom) during 22 days of incubation with H_2O_2 (black) and without H_2O_2 (red). M_w' was calculated as the weight-average molecular weight of the degraded products in the range > 3 kDa in the SEC chromatograms to minimize the effect of ghost peaks or solvent peaks in the off-calibration area. $M_w'_0$ means the M_w' before the incubation. The $M_w'/M_w'_0$ of **P6** at the time point of 22 day is not shown in the graph because the value is too small ($M_w'/ M_w'_0 << 0.1$).

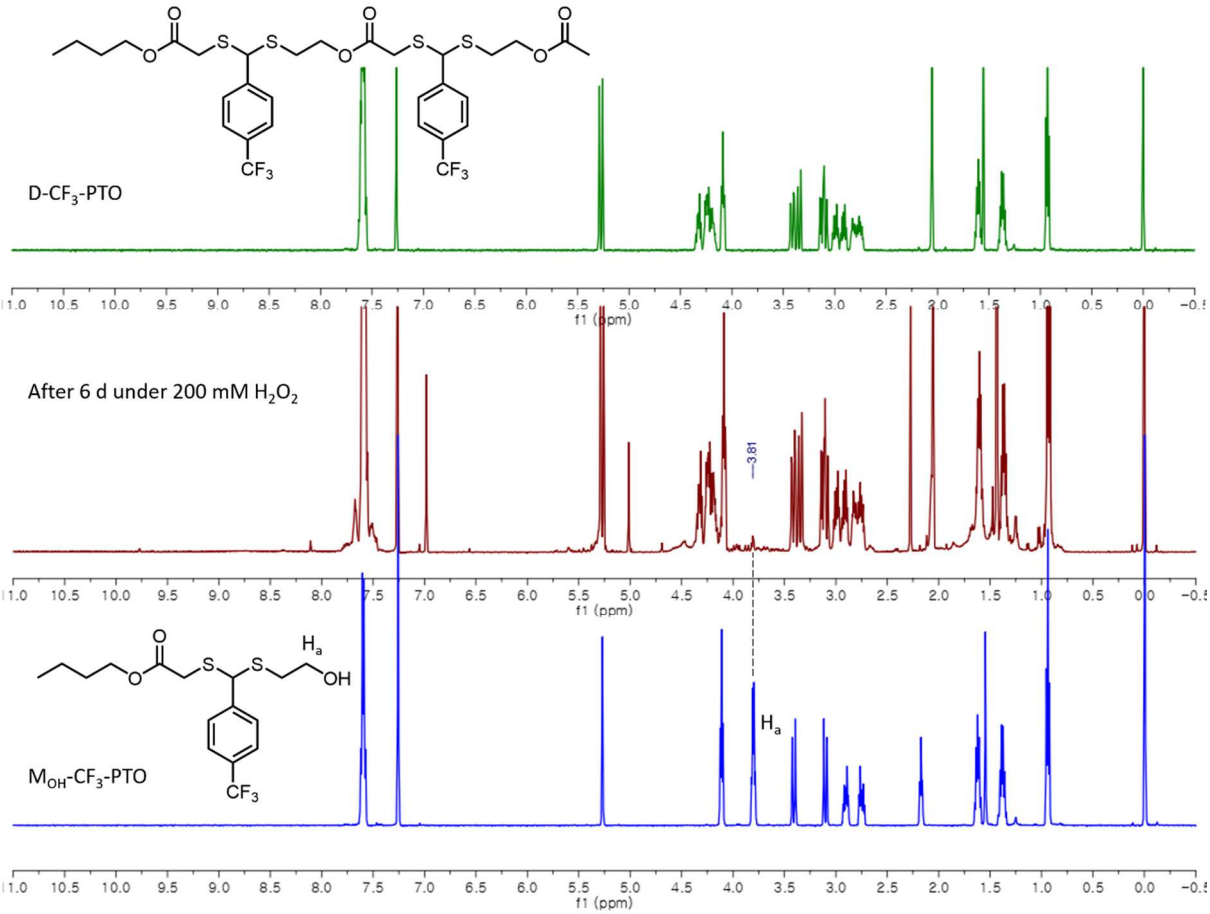


Figure S21. ^{1}H NMR spectra (11.00 to -0.50 ppm, $CDCl_3$, 500 MHz) of D-CF_3-PTO (top, green) D-CF_3-PTO after 6 days of incubation under 200 mM H_2O_2 (center, red) and M_{OH}-CF_3-PTO (bottom, blue). After 6-day incubation of D-CF_3-PTO under 200 mM H_2O_2, a peak emerged at 3.81 ppm which corresponds to -C*H*$_2$-OH peak of M_{OH}-CF_3-PTO, while no peak appearance observed at 10.09 ppm, which corresponds to aldehyde peak of 4-(trifluoromethyl)benzaldehyde[S2] that should be observed when thioacetal group is degraded and aldehyde was released.

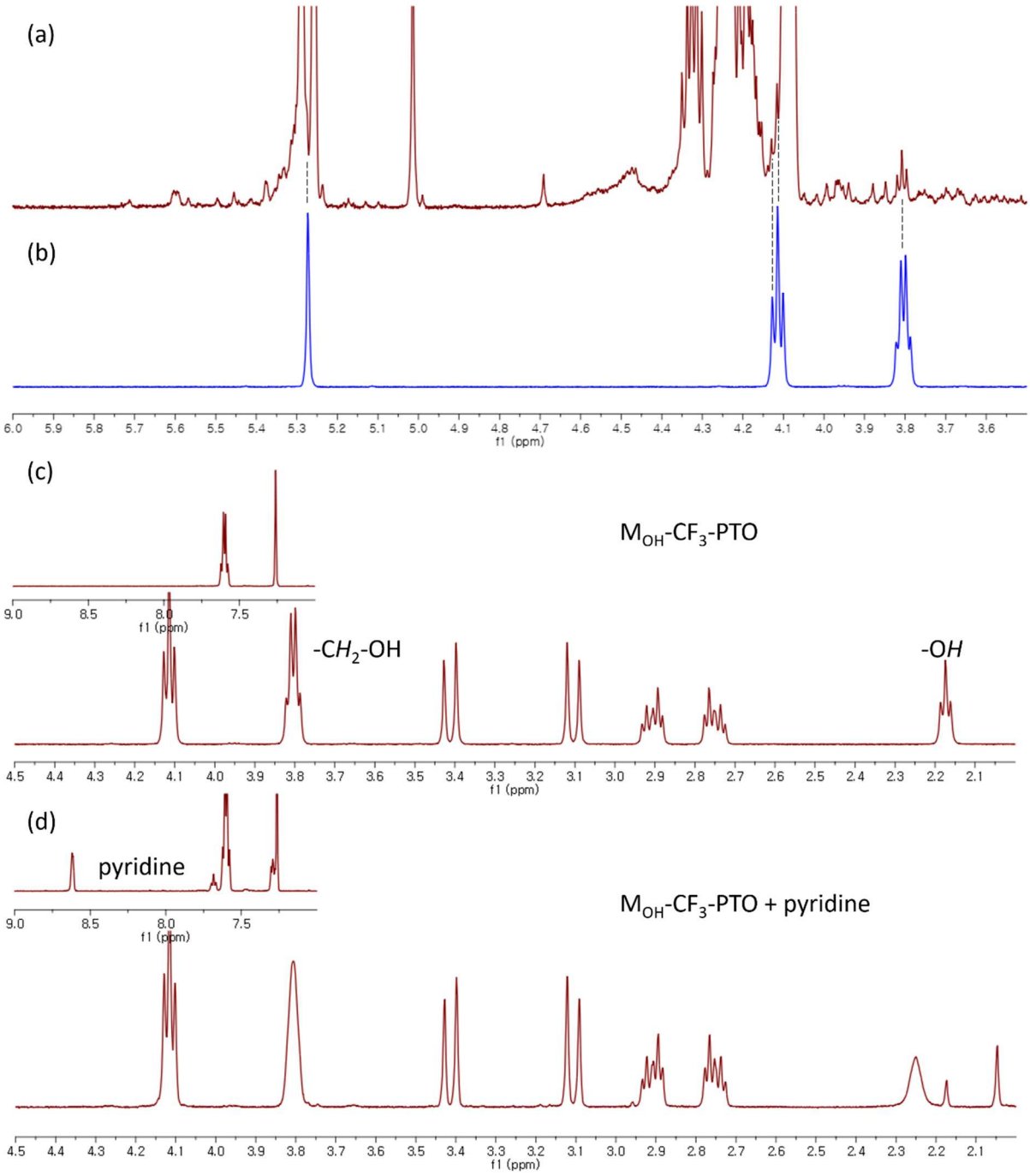


Figure S22. ^{1}H NMR spectra of (a) D-CF_3-PTO after 6 days of incubation under 200 mM H_2O_2 (6.00 to 3.50 ppm) (b) M_{OH}-CF_3-PTO (6.00 to 3.50 ppm), (c) M_{OH}-CF_3-PTO (9.00−7.00, 4.50−2.00 ppm) and (d) M_{OH}-CF_3-PTO mixed with small amount of pyridine. (9.00−7.00, 4.50−2.00 ppm)

After 6 days of incubation, we could not find any aldehyde peak that corresponds to 4-(trifluoromethyl) benzaldehyde that should be present if thioacetal group is degraded while noticeable peak at 3.81 ppm appeared. (**Figure S21**) In addition, we could find the overlapped but clearly existing peaks that corresponds to M_{OH}-CF_3-PTO. (**Figure S22(a) and S22(b)**) However, multiplicity of peak at 3.81 ppm is not identical, therefore, we added small amount of pyridine to pure M_{OH}-CF_3-PTO to confirm multplicity of -CH_2-OH can be changed with the surrounding condition while the chemical shift of -CH_2-OH remains

unchanged. (**Figure S22(c) and S22(d)**) To obtain additional evidence, we analyzed degradation product with HPLC (**Figure S23**) and found M_{OH}-CF_3-PTO, which is the hydrolyzed product of D-CF_3-PTO was generated during the incubation.

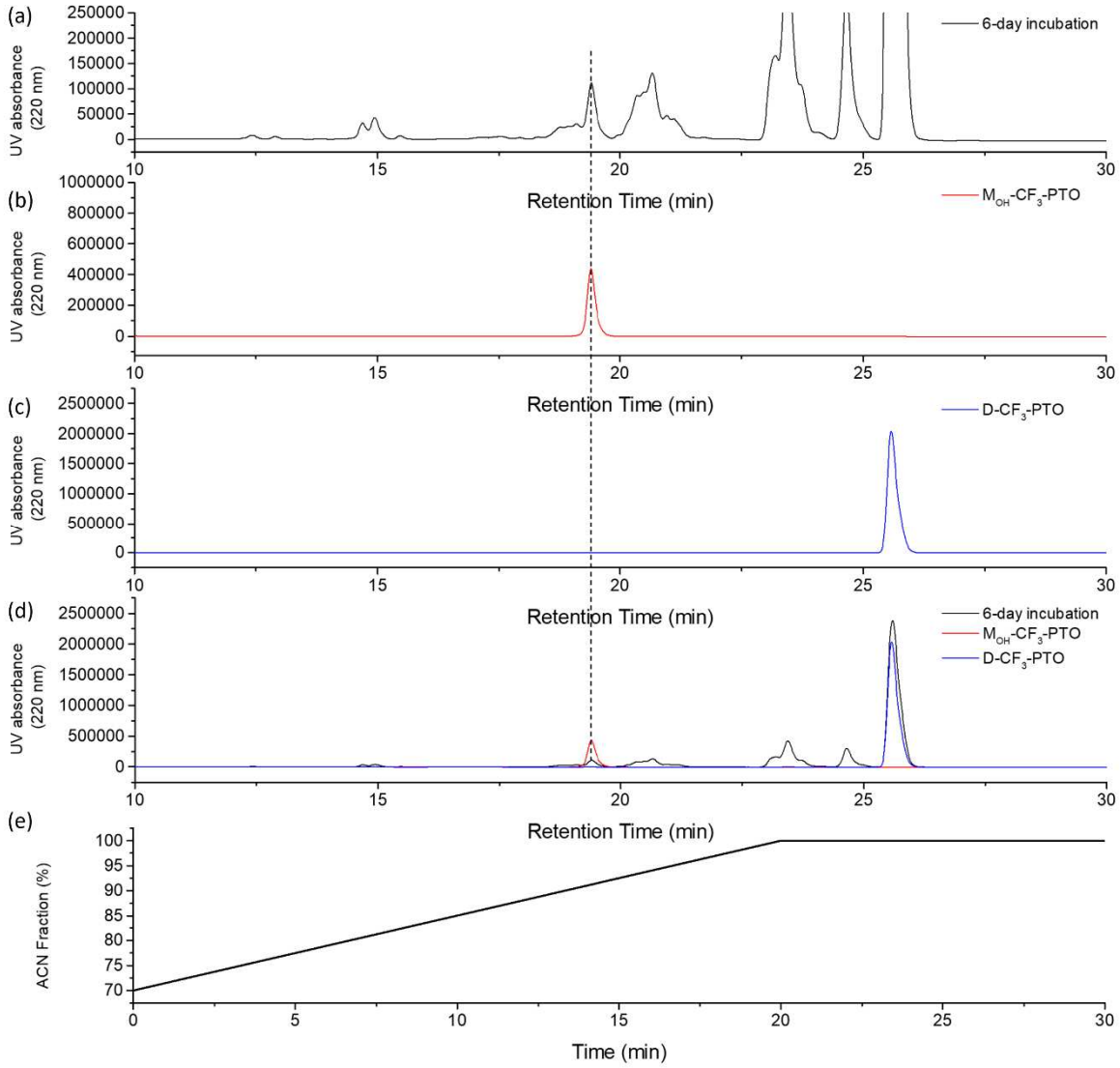
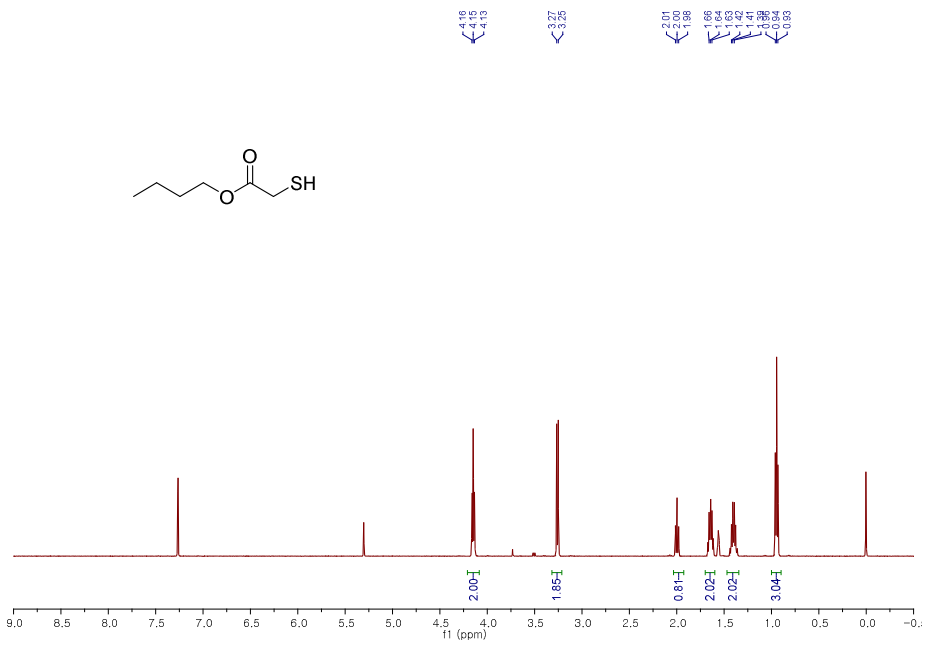


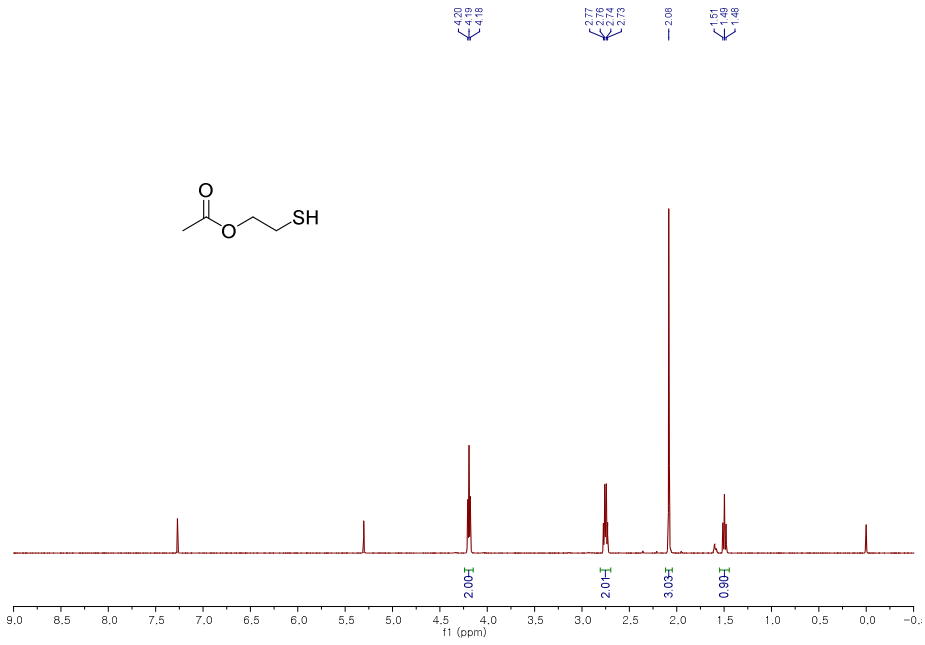
Figure S23. HPLC Chromatogram of (a) D-CF_3-PTO after 6 days of incubation under 200 mM H_2O_2, (b) M_{OH}-CF_3-PTO, (c) D-CF_3-PTO and (d) overlapped chromatogram of (a), (b) and (c). Acetonitirle and water was used for the eluent and the eluent condition is shown in (e). Shimazu Prominence system equipped with a Eclipse XDB-C18 4.6x250 mm 5µ analytical column was used. UV absorbance at λ = 220 nm was recorded during the experiment.

4. NMR spectra of compounds

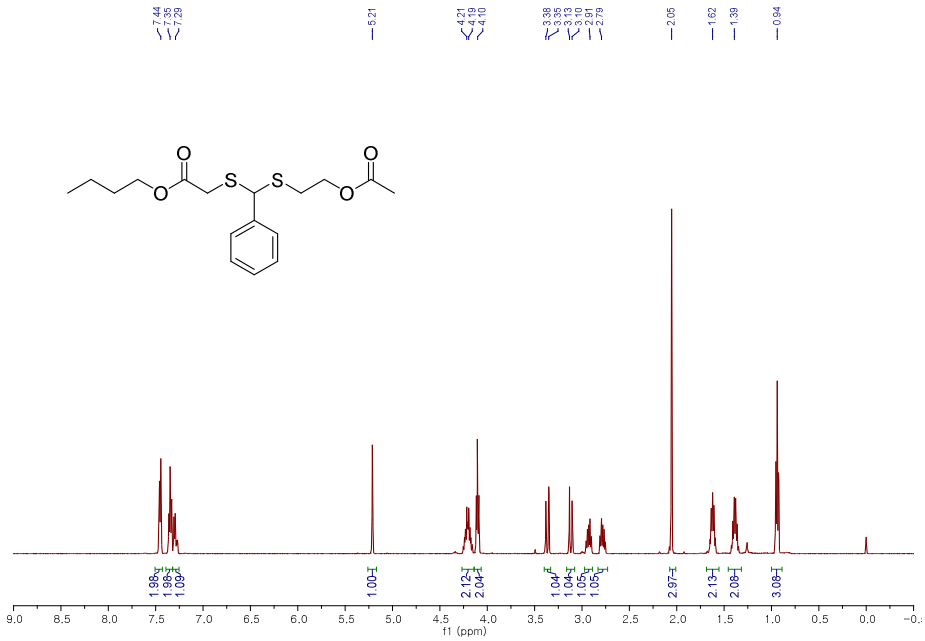
Butyl-2-mercaptoacetate (^{1}H NMR, 500 MHz, $CDCl_3$)



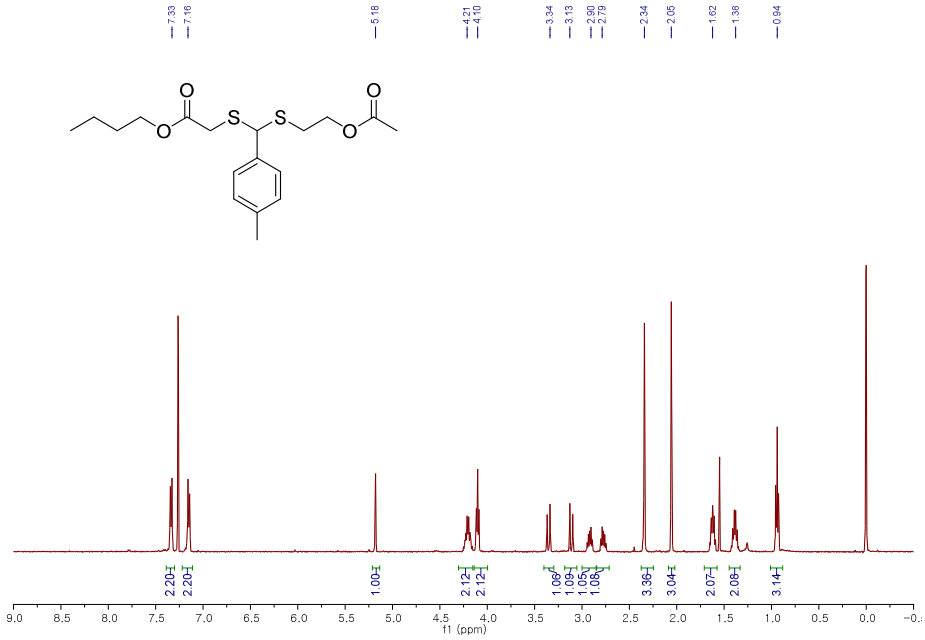
2-Mercaptoethyl acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



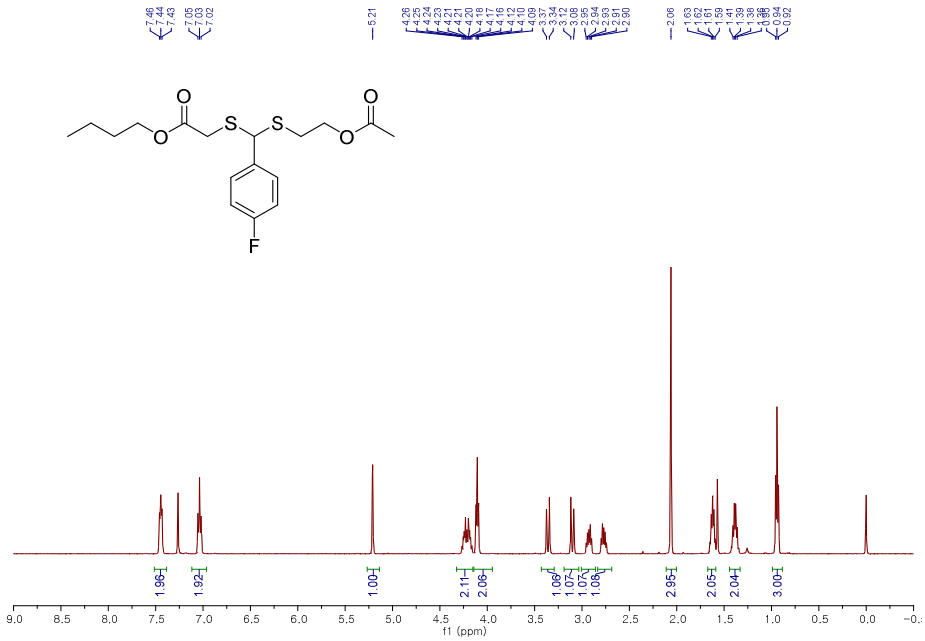
Butyl 2-((((2-acetoxyethyl)thio)(phenyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



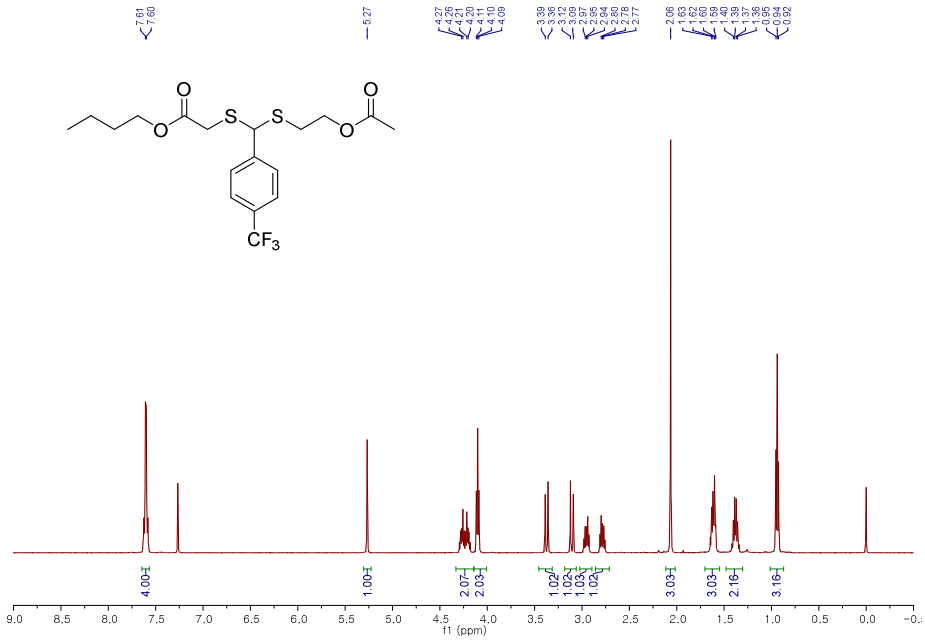
Butyl 2-((((2-acetoxyethyl)thio)(*p*-tolyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



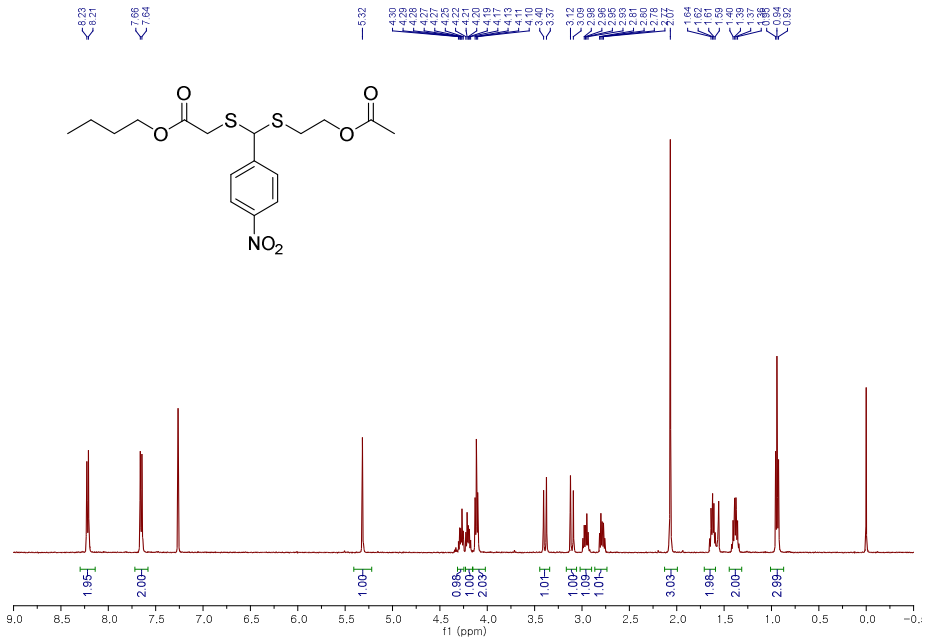
Butyl 2-((((2-acetoxyethyl)thio)(4-fluorophenyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



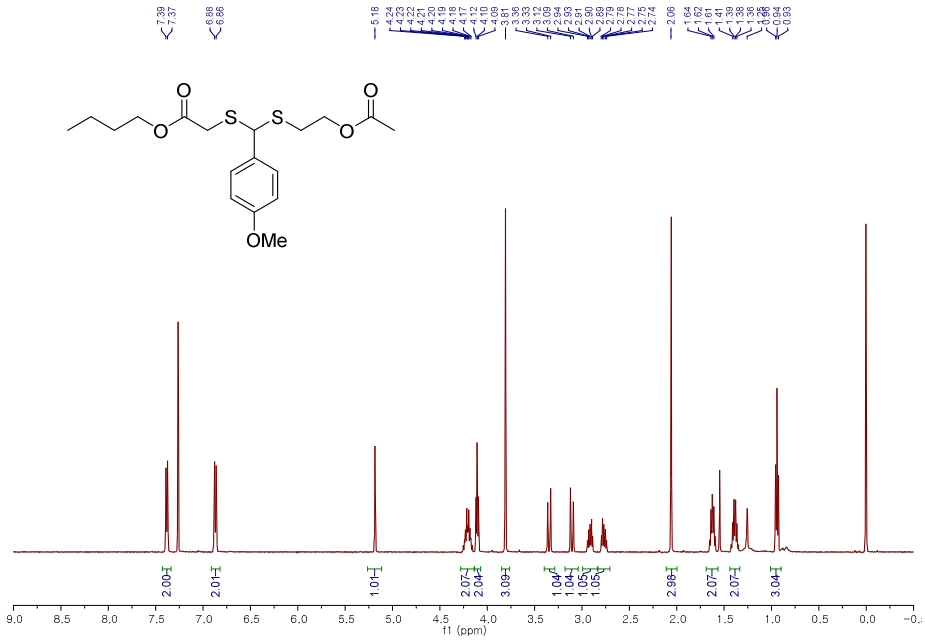
Butyl 2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



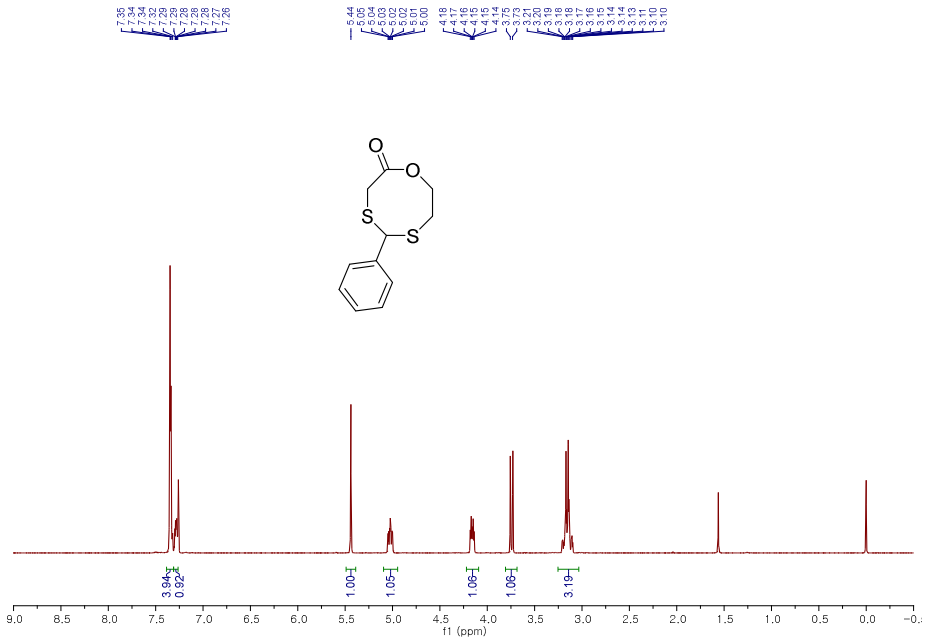
Butyl 2-((((2-acetoxyethyl)thio)(4-nitrophenyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



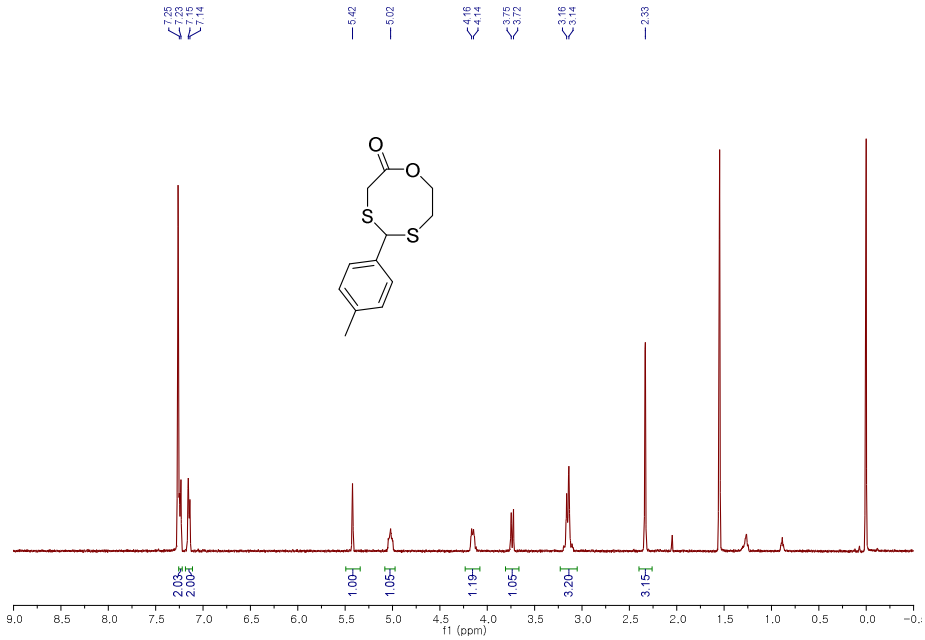
Butyl 2-((((2-acetoxyethyl)thio)(4-methoxyphenyl)methyl)thio)acetate (^{1}H NMR, 500 MHz, $CDCl_3$)



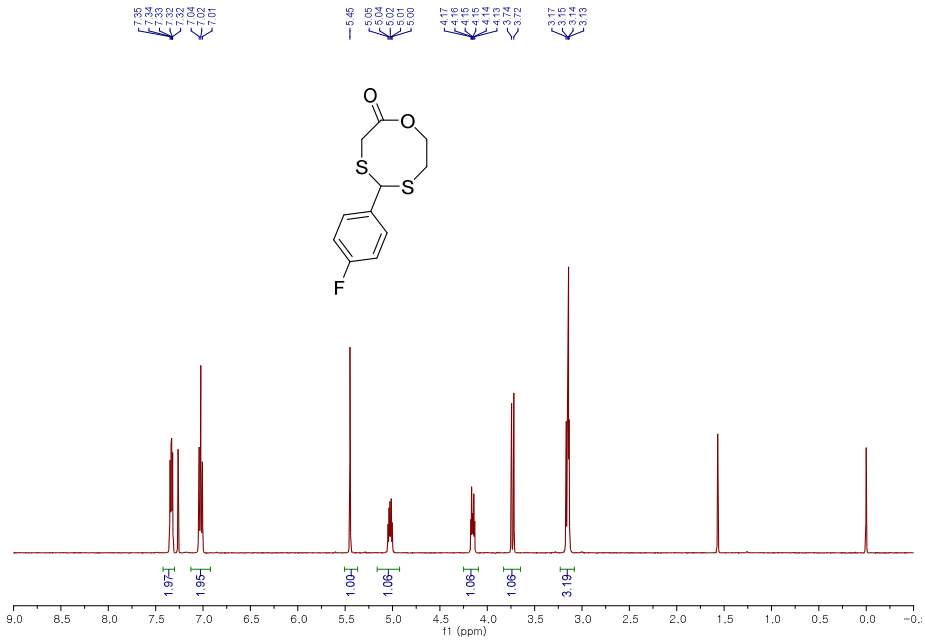
5-Phenyl-1,4,6-oxadithiocan-2-one (PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



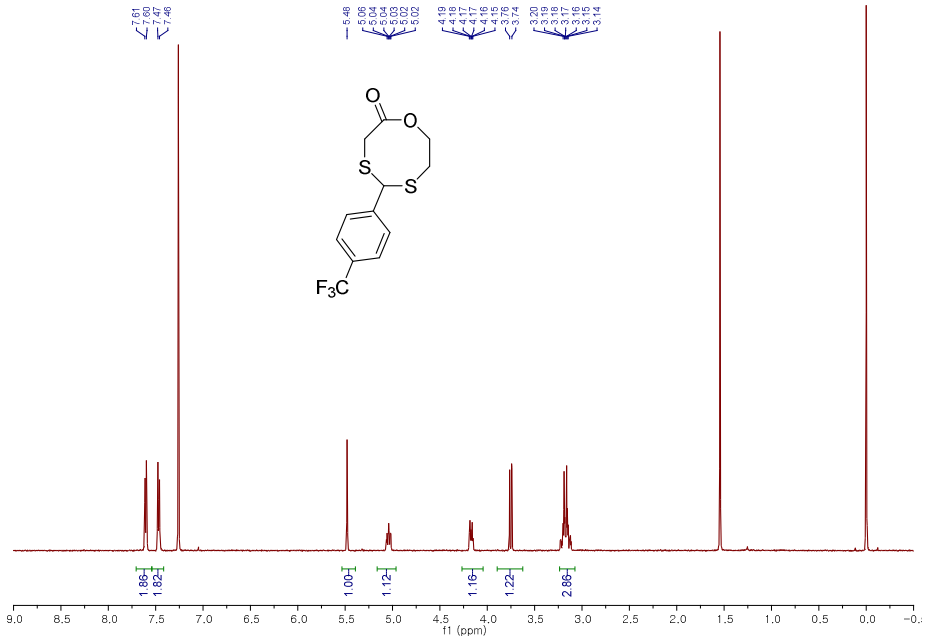
5-(*p*-Tolyl)-1,4,6-oxadithiocan-2-one (Me-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



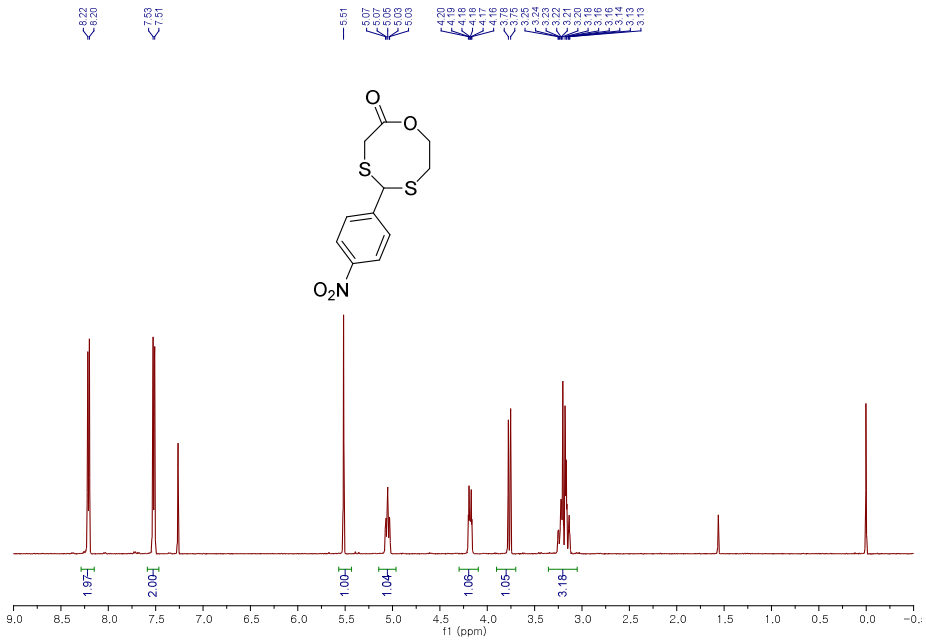
5-(4-Fluorophenyl)-1,4,6-oxadithiocan-2-one (F-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



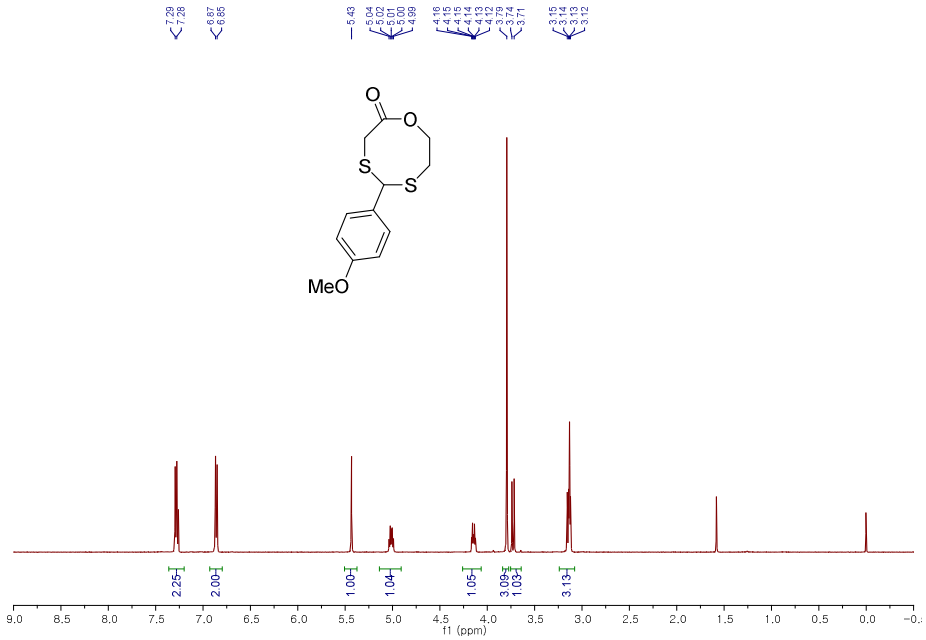
5-(4-(Trifluoromethyl)phenyl)-1,4,6-oxadithiocan-2-one (CF_3-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



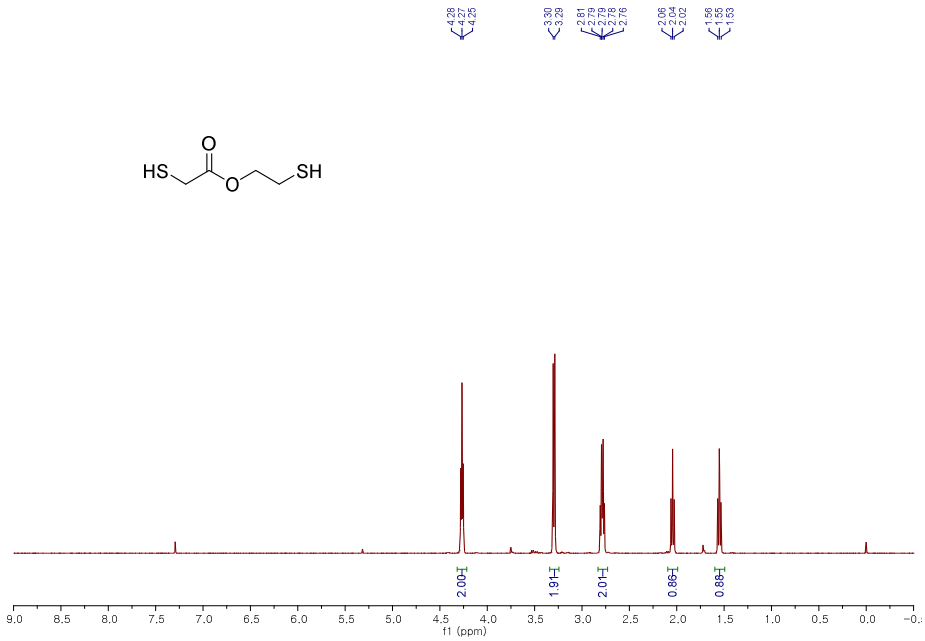
5-(4-Nitrophenyl)-1,4,6-oxadithiocan-2-one (NO_2-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



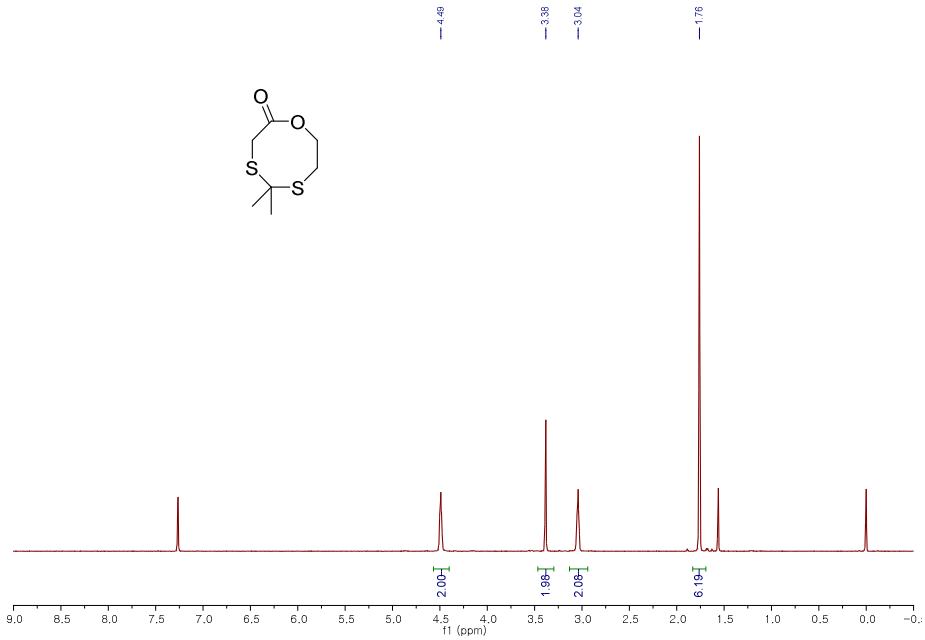
5-(4-Methoxyphenyl)-1,4,6-oxadithiocan-2-one (MeO-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



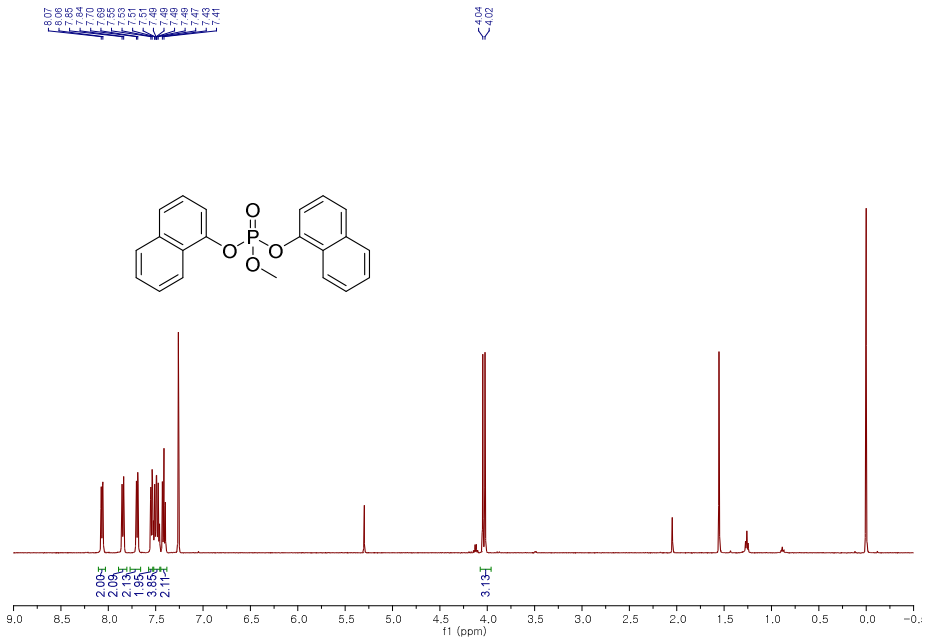
2-Mercaptoethyl 2-mercaptoacetate (^{1}H NMR, 500 MHz, $CDCl_3$)



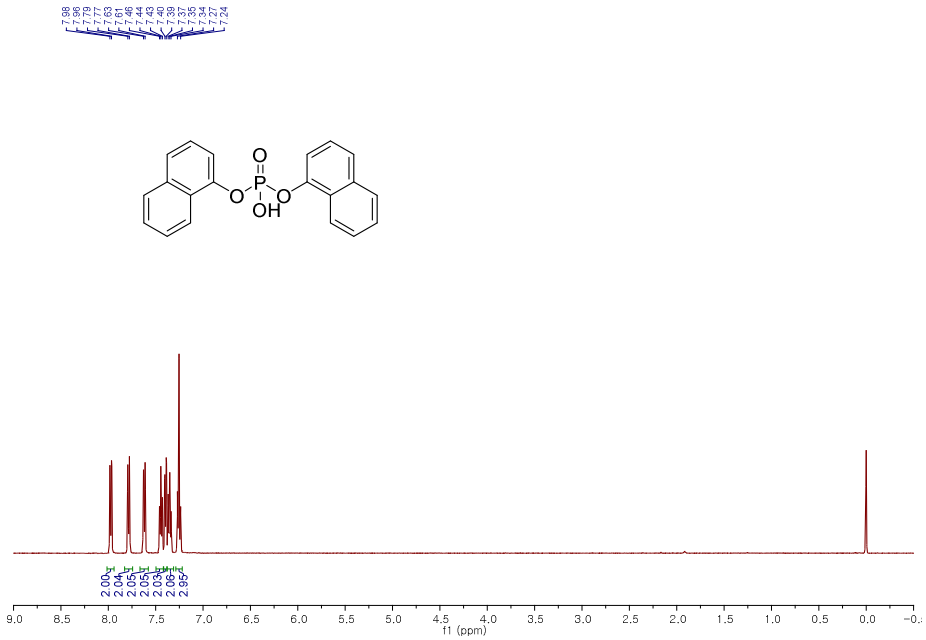
5,5-Dimethyl-1,4,6-oxadithiocan-2-one (DTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



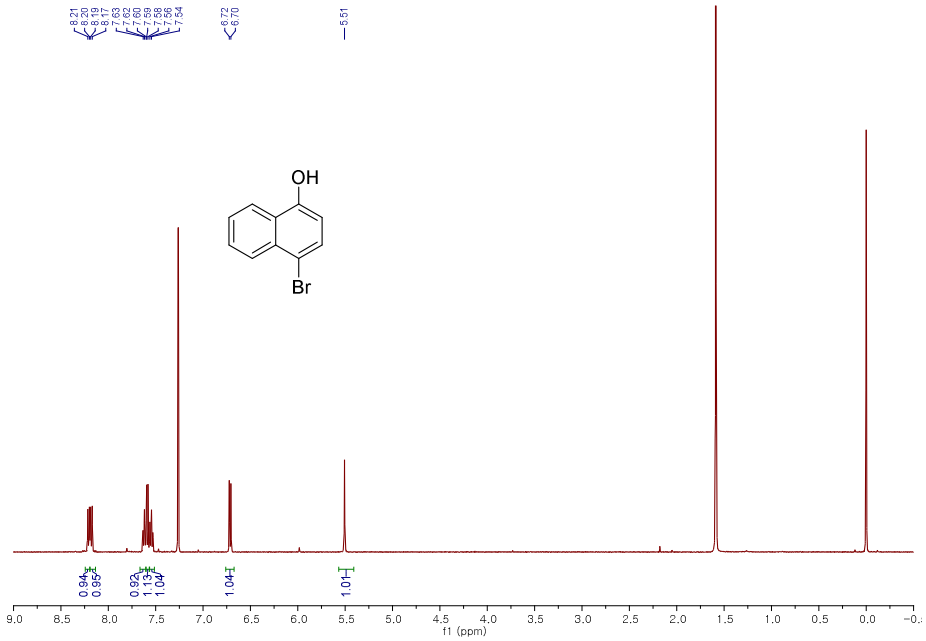
Methyl di(naphthalen-1-yl) phosphate (^{1}H NMR, 500 MHz, $CDCl_3$)



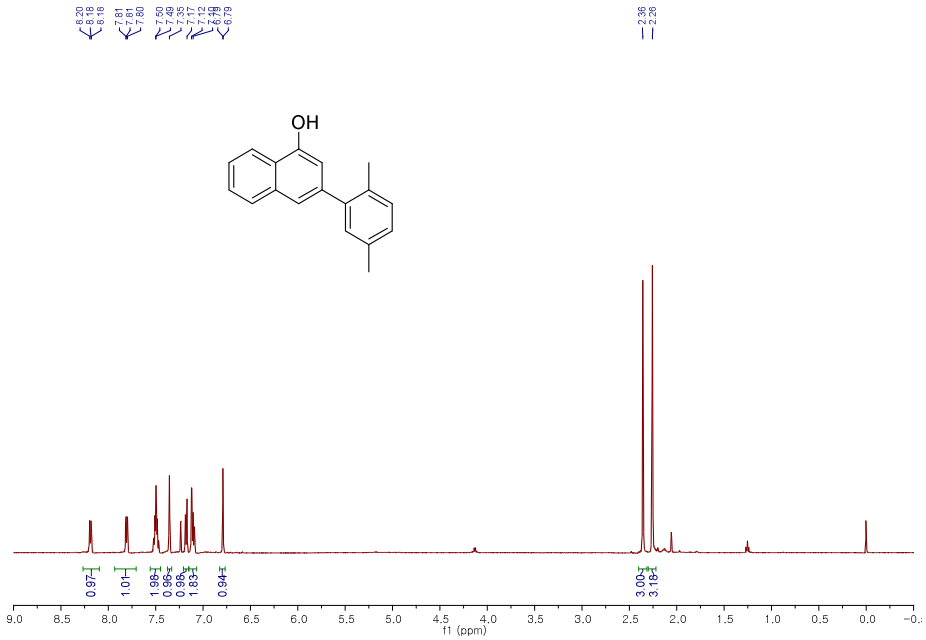
Di(naphthalen-1-yl) phosphate (DNP) (^{1}H NMR, 500 MHz, $CDCl_3$)



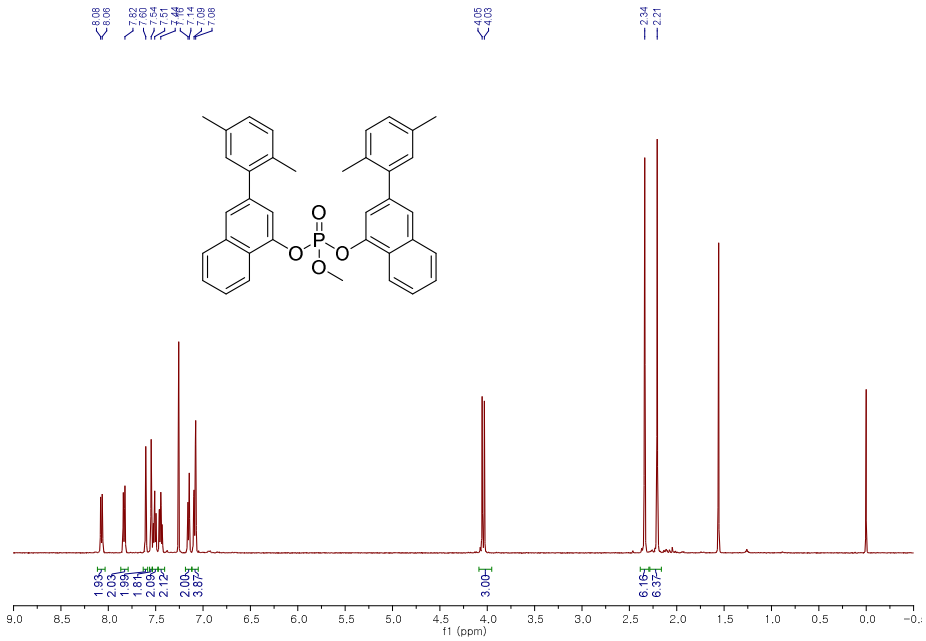
4-Bromo-1-naphthol (^{1}H NMR, 500 MHz, $CDCl_3$)



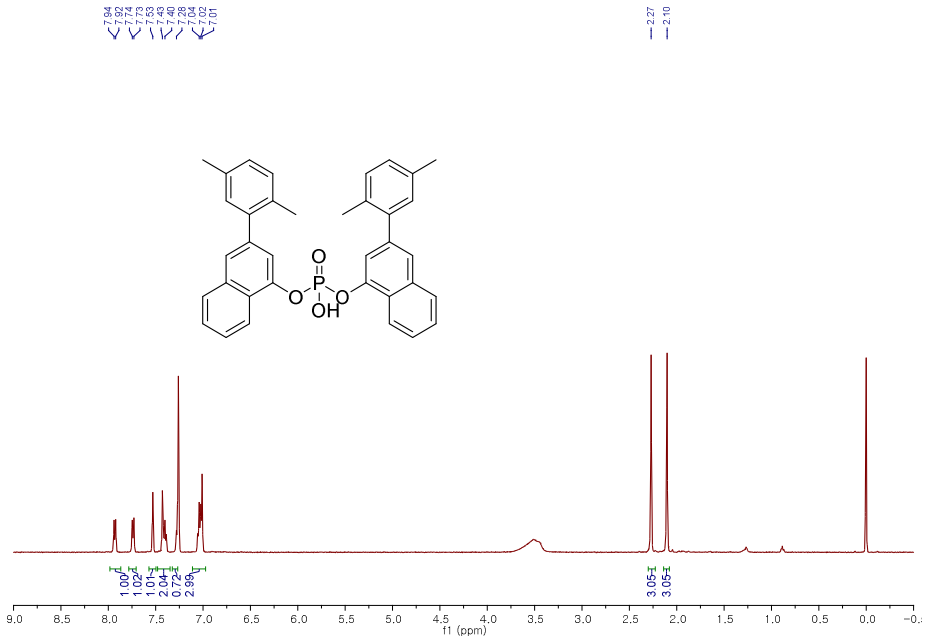
3-(2,5-Dimethylphenyl)naphthalen-1-ol (^{1}H NMR, 500 MHz, $CDCl_3$)



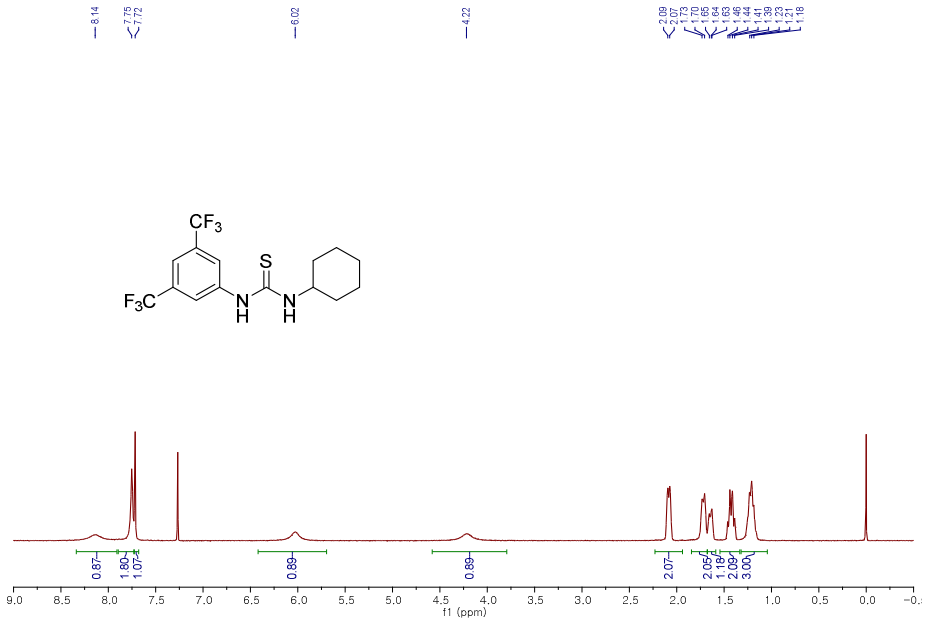
Bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) methyl phosphate (^{1}H NMR, 500 MHz, $CDCl_3$)



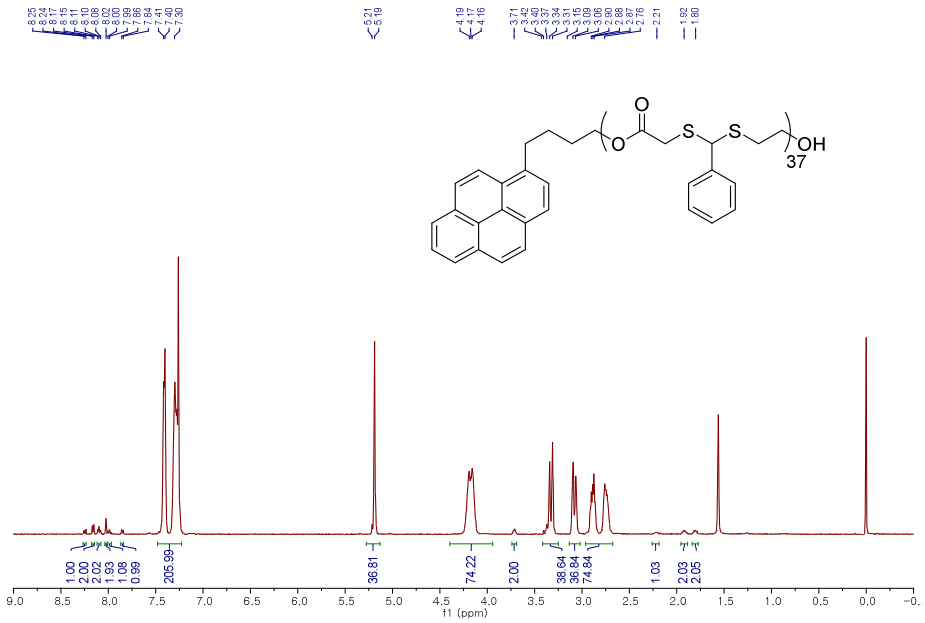
Bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) phosphate (XNP) (^{1}H NMR, 500 MHz, $CDCl_3$)



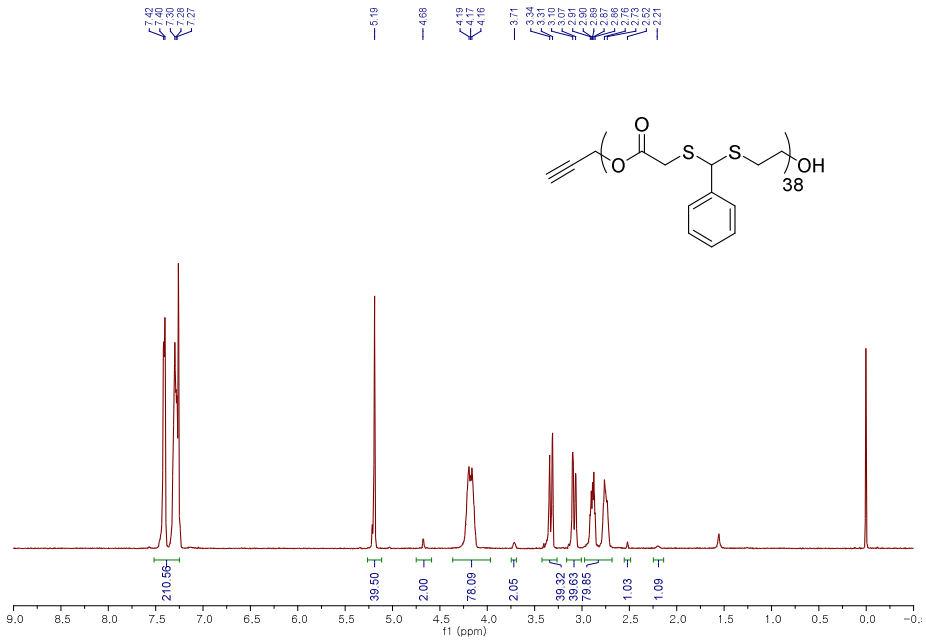
1-(3,5-Bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (^{1}H NMR, 500 MHz, $CDCl_3$)



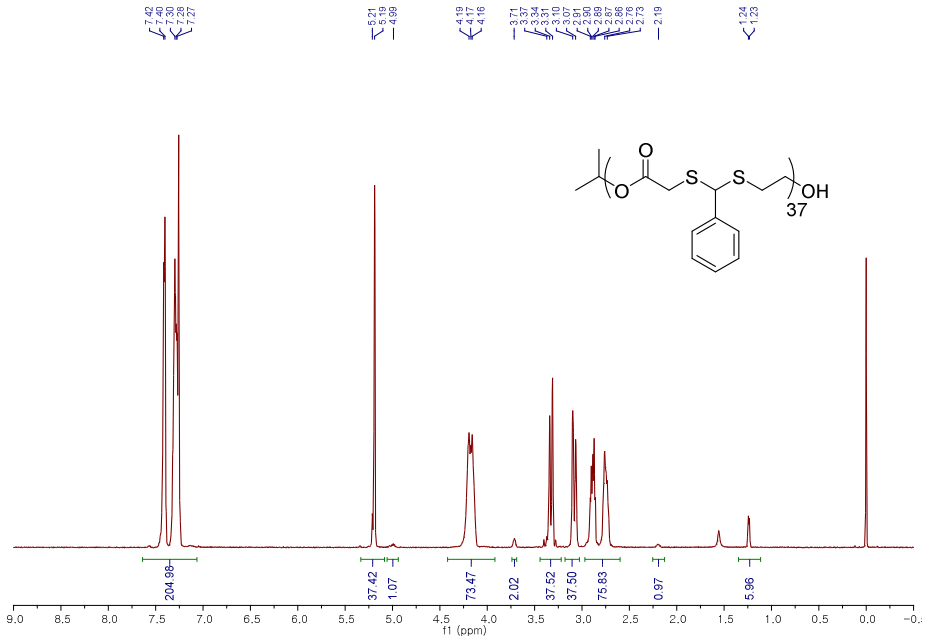
P6 (^{1}H NMR, 500 MHz, $CDCl_3$)



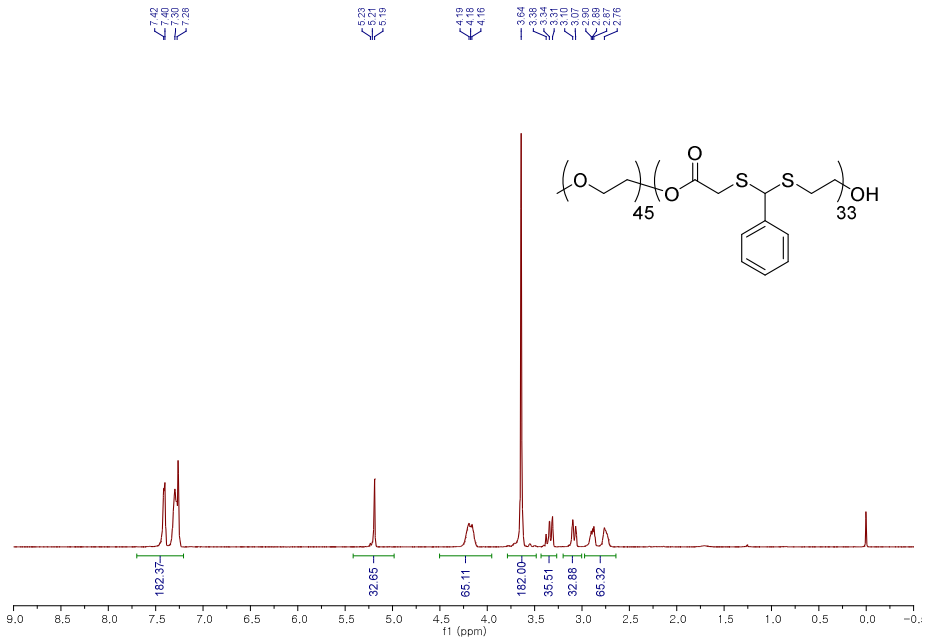
P9 (^{1}H NMR, 500 MHz, $CDCl_3$)



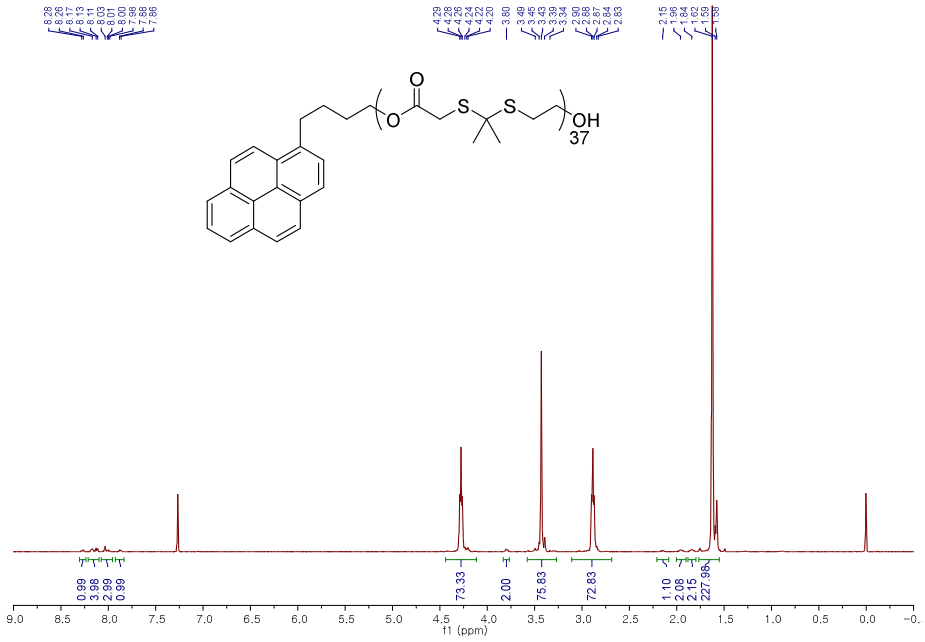
P10 (^{1}H NMR, 500 MHz, $CDCl_3$)



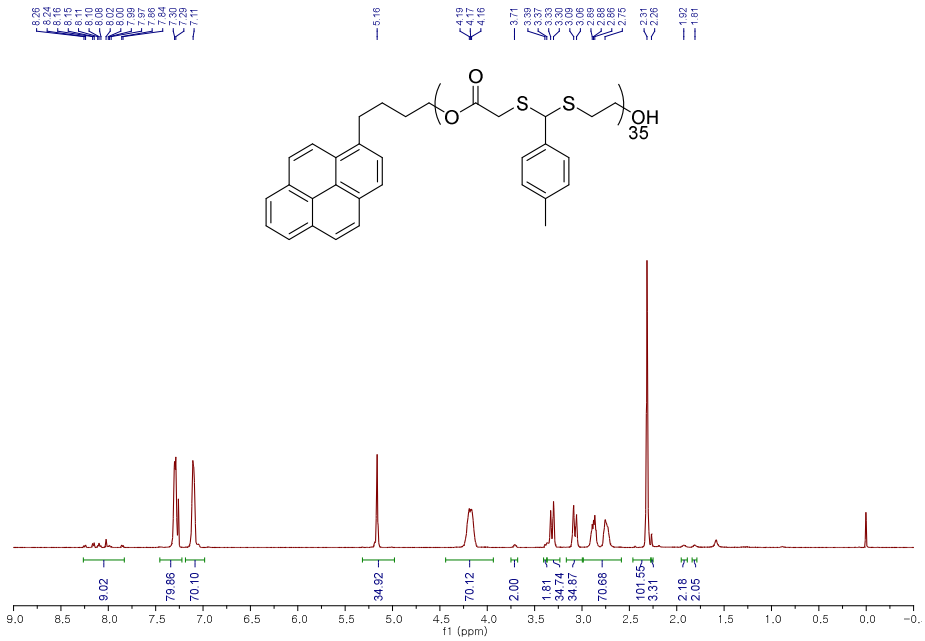
P11 (^{1}H NMR, 500 MHz, $CDCl_3$)



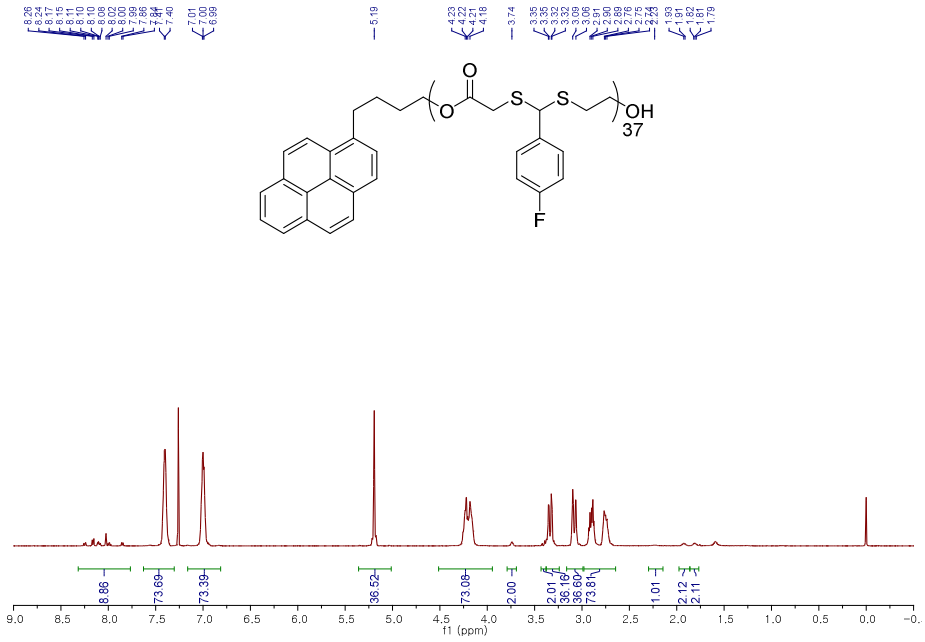
P12 (^{1}H NMR, 500 MHz, $CDCl_3$)



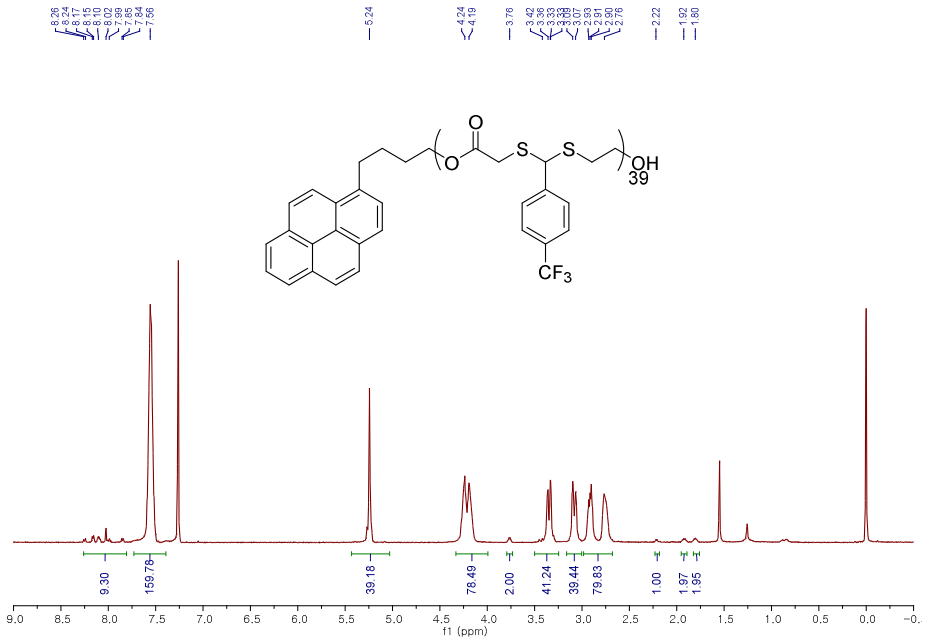
P13 (^{1}H NMR, 500 MHz, $CDCl_3$)



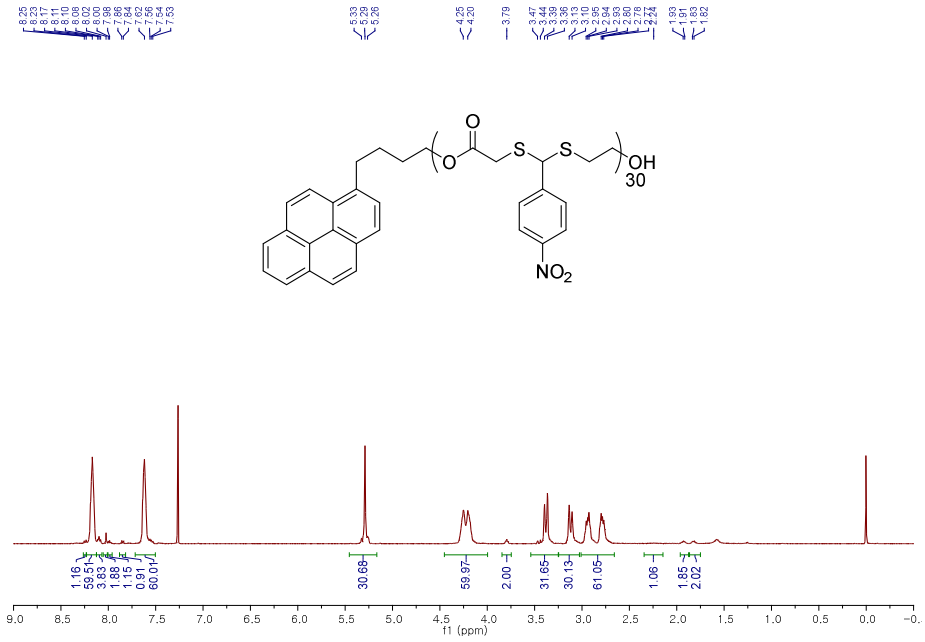
P14 (^{1}H NMR, 500 MHz, $CDCl_3$)



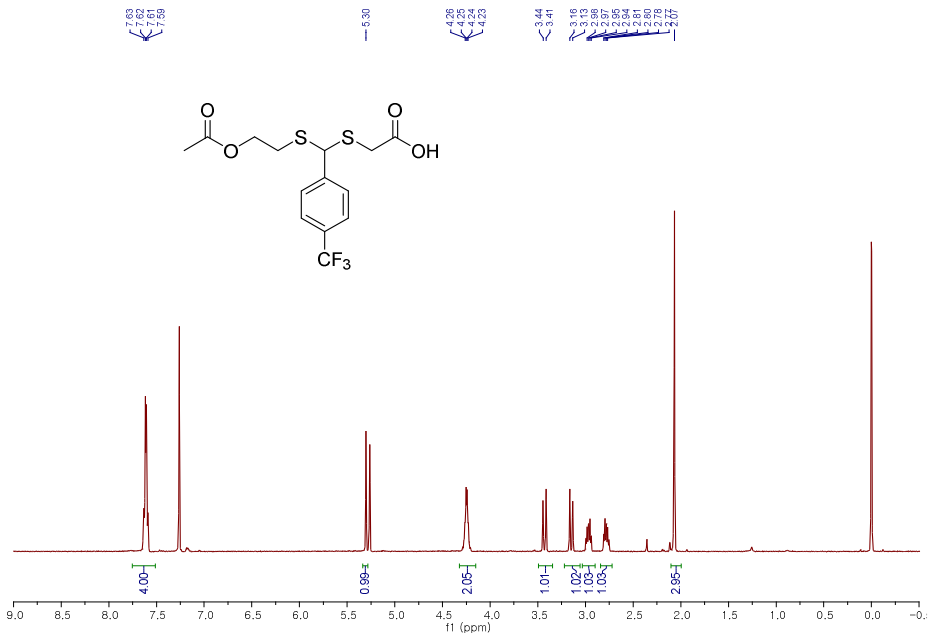
P15 (^{1}H NMR, 500 MHz, $CDCl_3$)



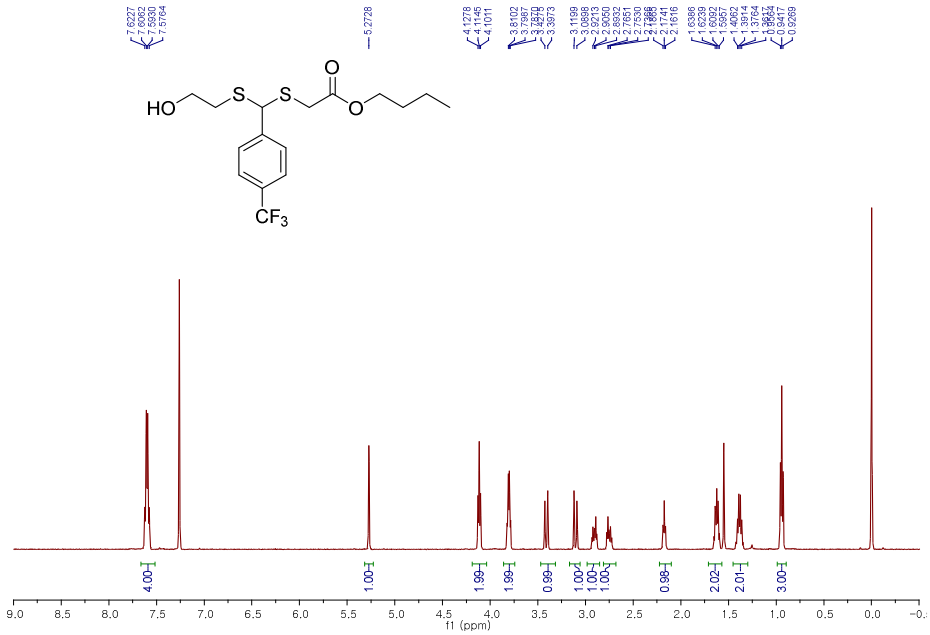
P16 (^{1}H NMR, 500 MHz, $CDCl_3$)



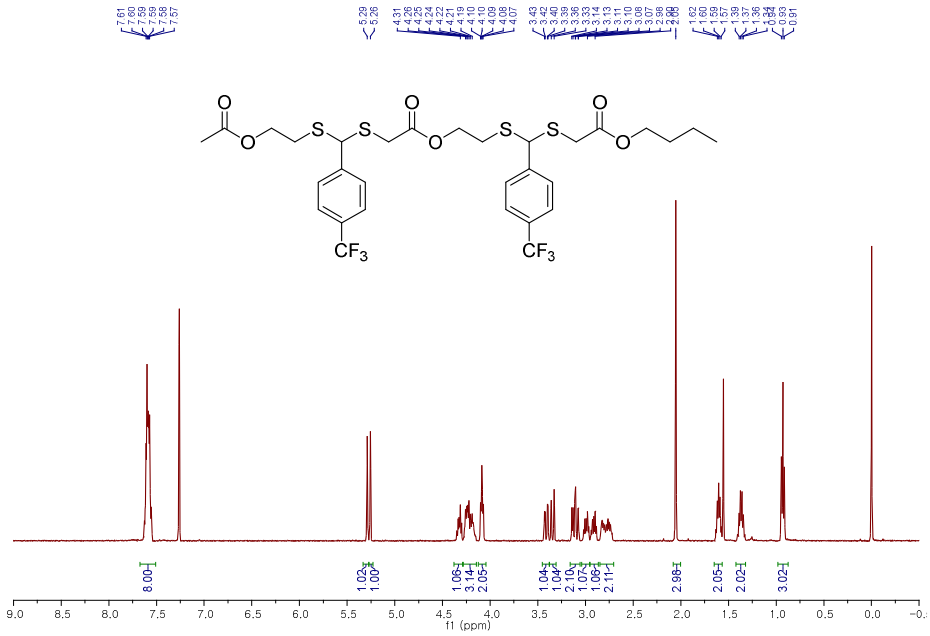
2-((((2-acetoxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetic acid (M_{COOH}-CF_3-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



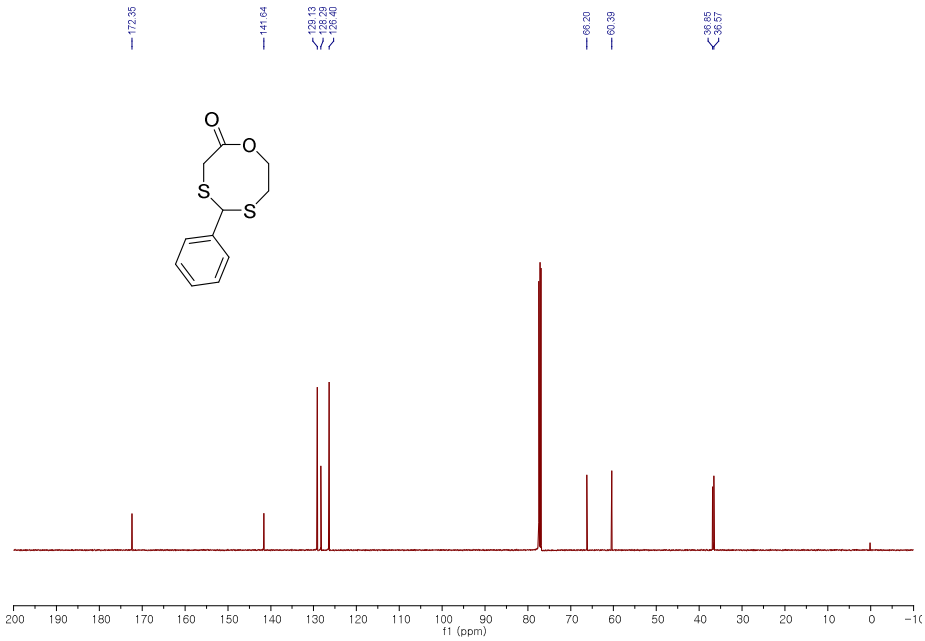
2-((((2-hydroxyethyl)thio)(4-(trifluoromethyl)phenyl)methyl)thio)acetate (M_{OH}-CF_3-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



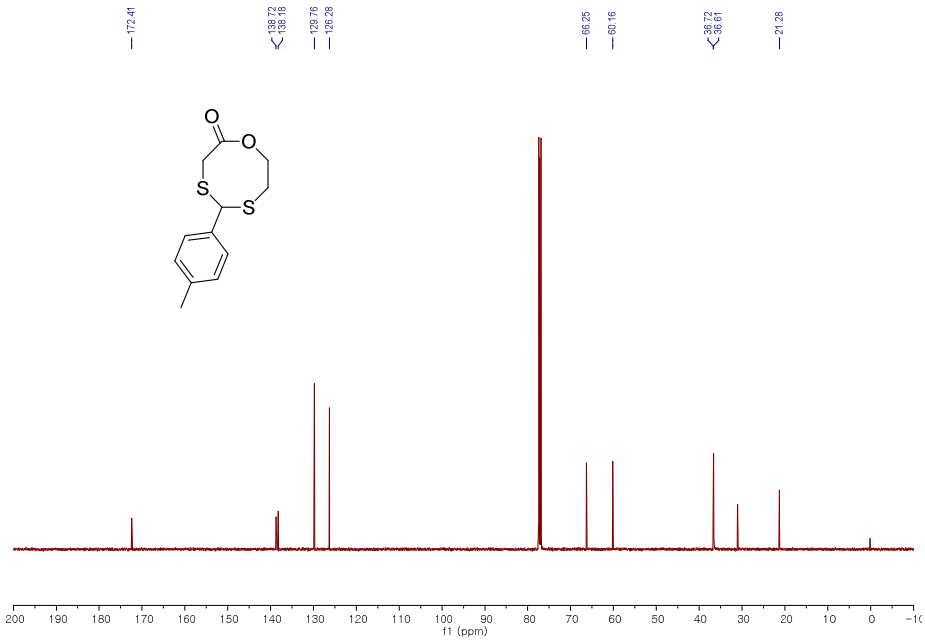
Model dimer of **P15** (D-CF_3-PTO) (^{1}H NMR, 500 MHz, $CDCl_3$)



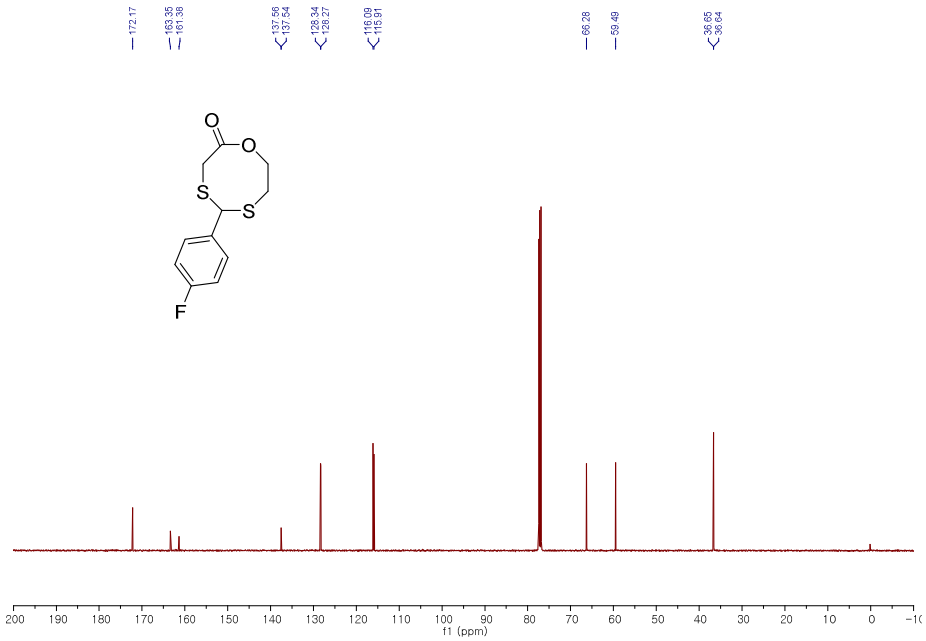
5-Phenyl-1,4,6-oxadithiocan-2-one (PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



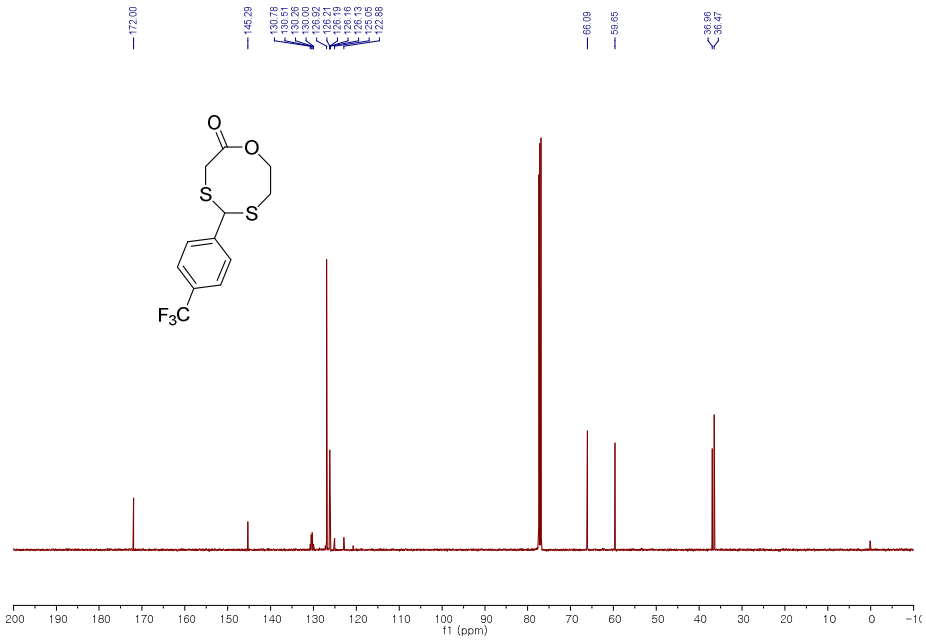
5-(*p*-Tolyl)-1,4,6-oxadithiocan-2-one (Me-PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



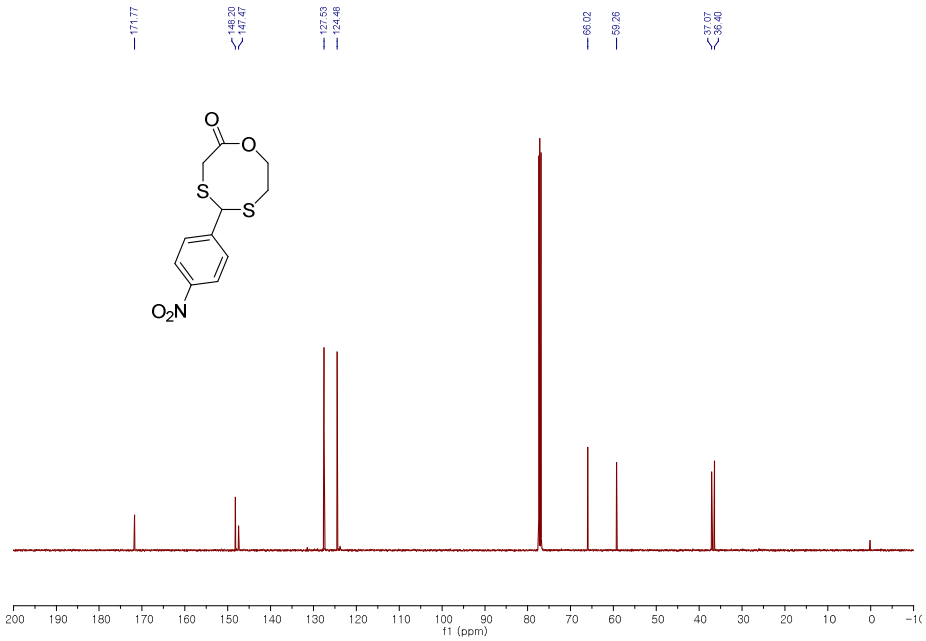
5-(4-Fluorophenyl)-1,4,6-oxadithiocan-2-one (F-PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



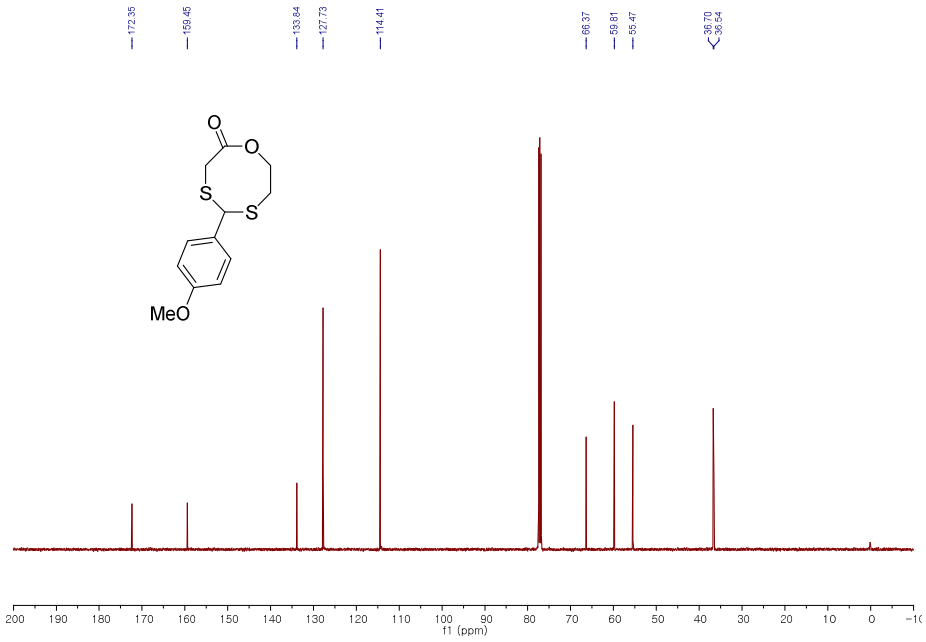
5-(4-(Trifluoromethyl)phenyl)-1,4,6-oxadithiocan-2-one (CF_3-PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



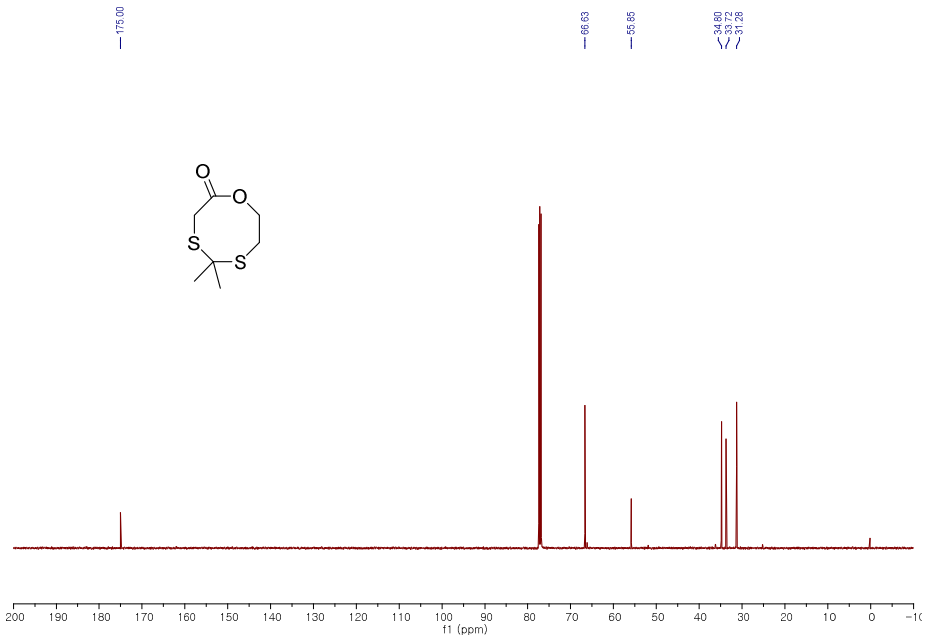
5-(4-Nitrophenyl)-1,4,6-oxadithiocan-2-one (NO_2-PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



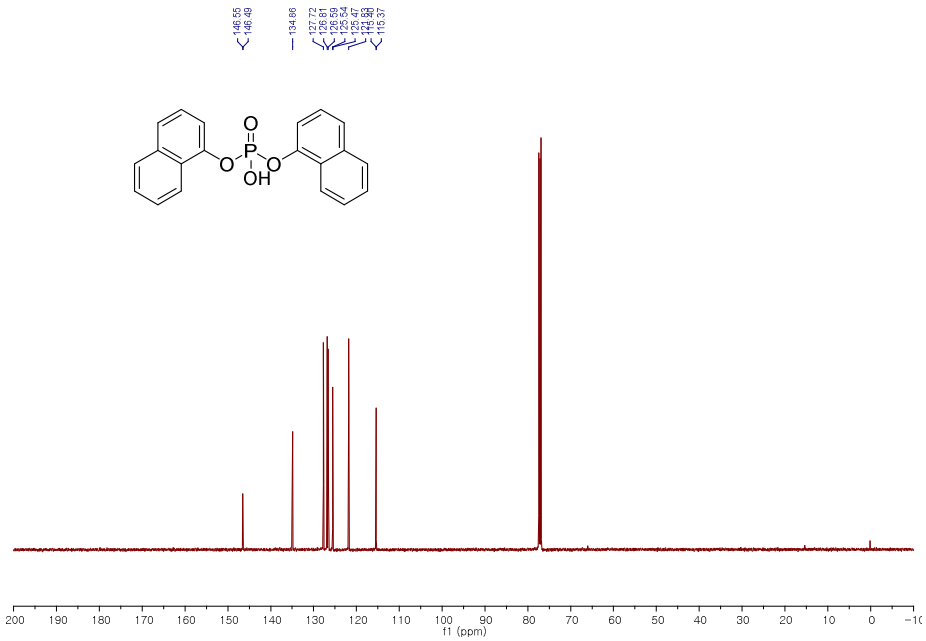
5-(4-Methoxyphenyl)-1,4,6-oxadithiocan-2-one (MeO-PTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



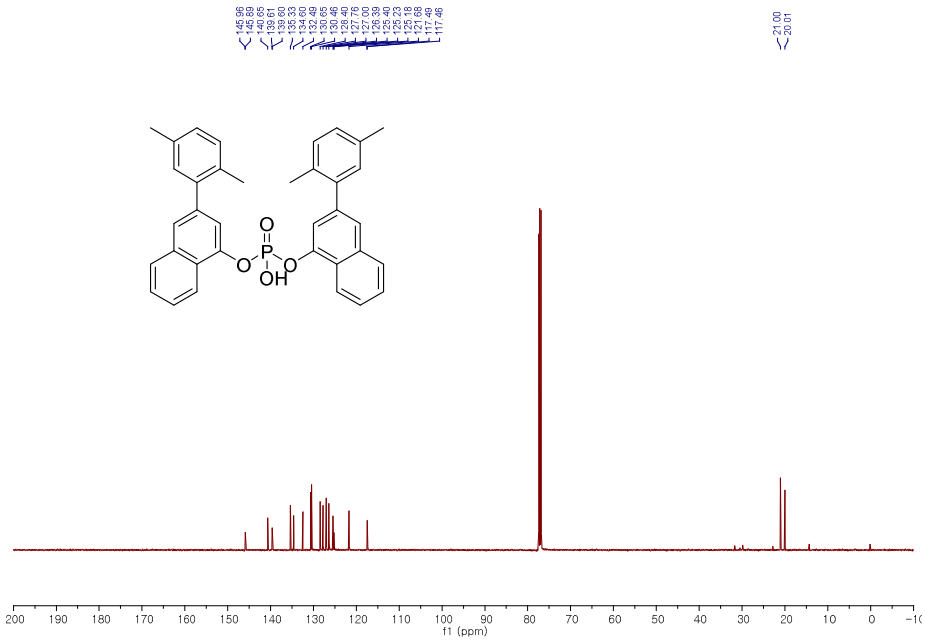
5,5-Dimethyl-1,4,6-oxadithiocan-2-one (DTO) (^{13}C NMR, 125 MHz, $CDCl_3$)



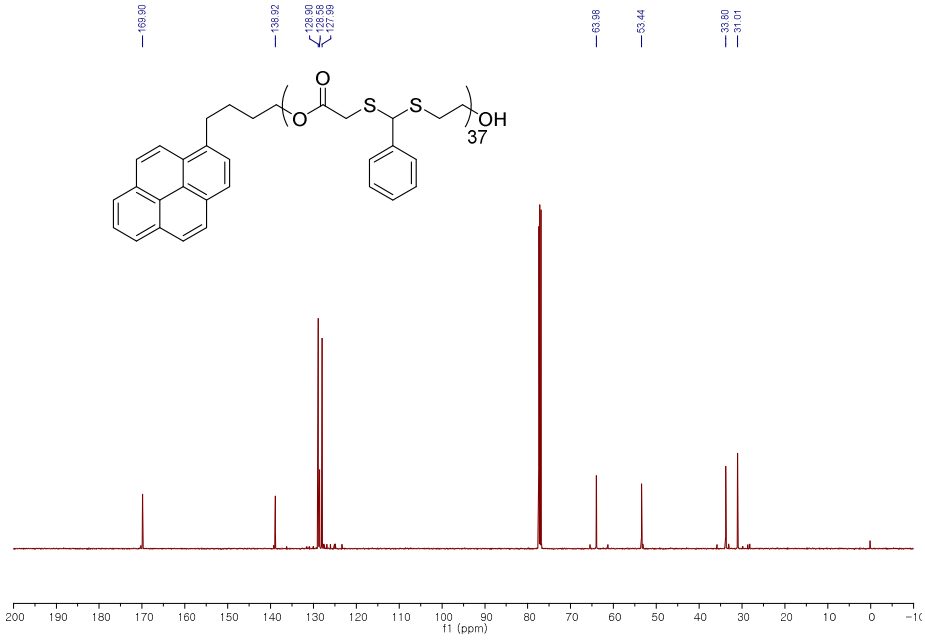
Di(naphthalen-1-yl) phosphate (DNP) (^{13}C NMR, 125 MHz, $CDCl_3$)



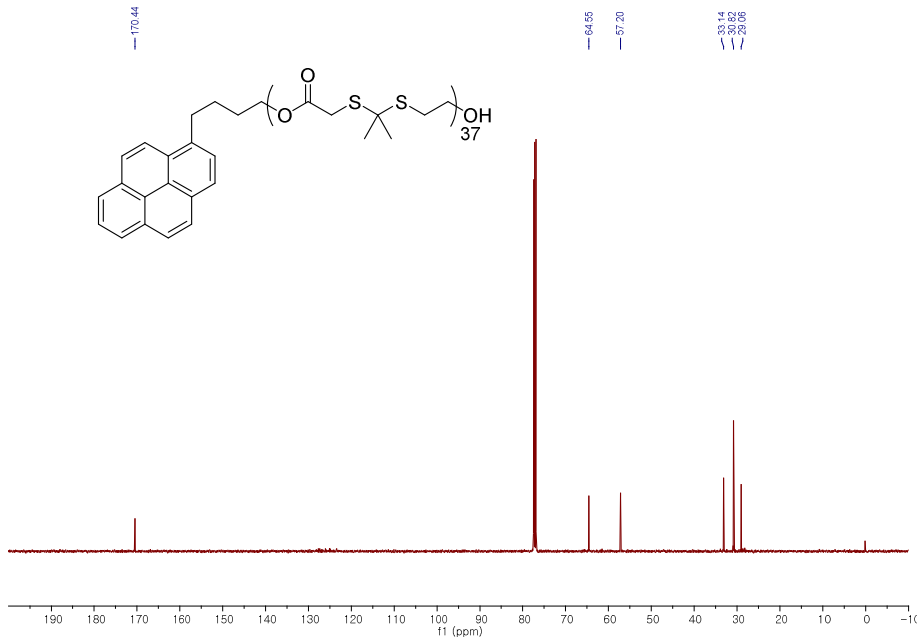
Bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) phosphate (XNP) (^{13}C NMR, 125 MHz, $CDCl_3$)



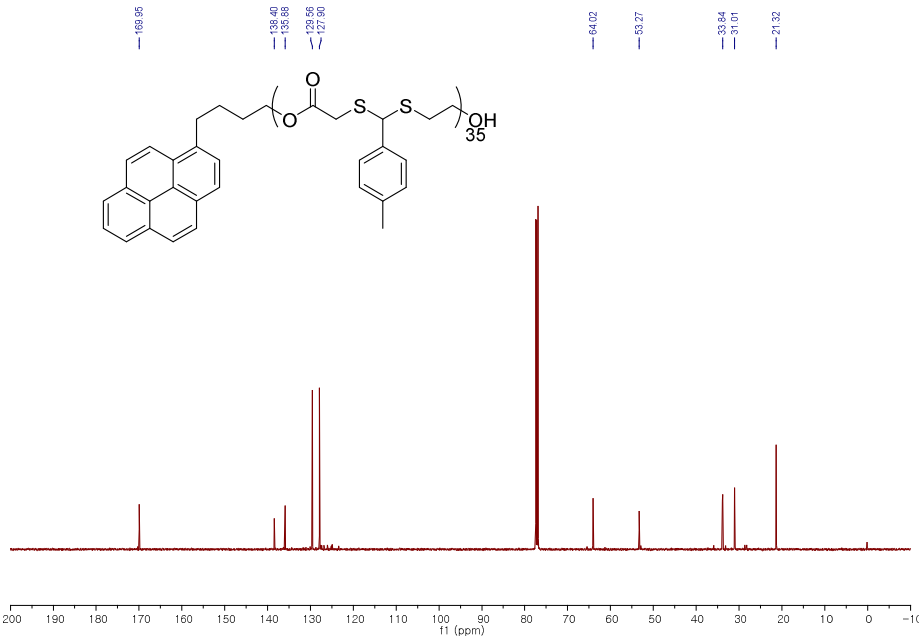
P6 (^{13}C NMR, 125 MHz, $CDCl_3$)



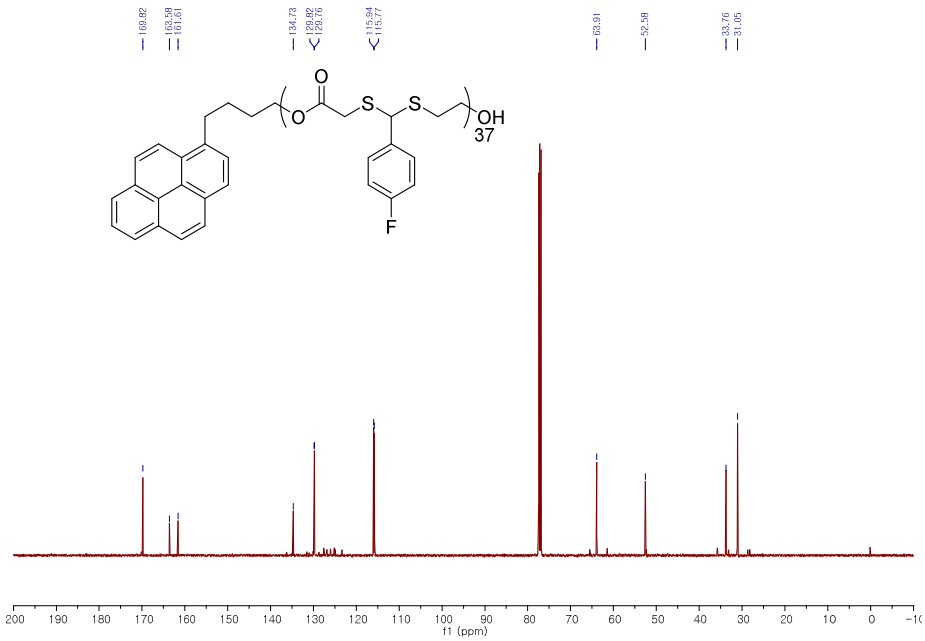
P12 (^{13}C NMR, 125 MHz, $CDCl_3$)



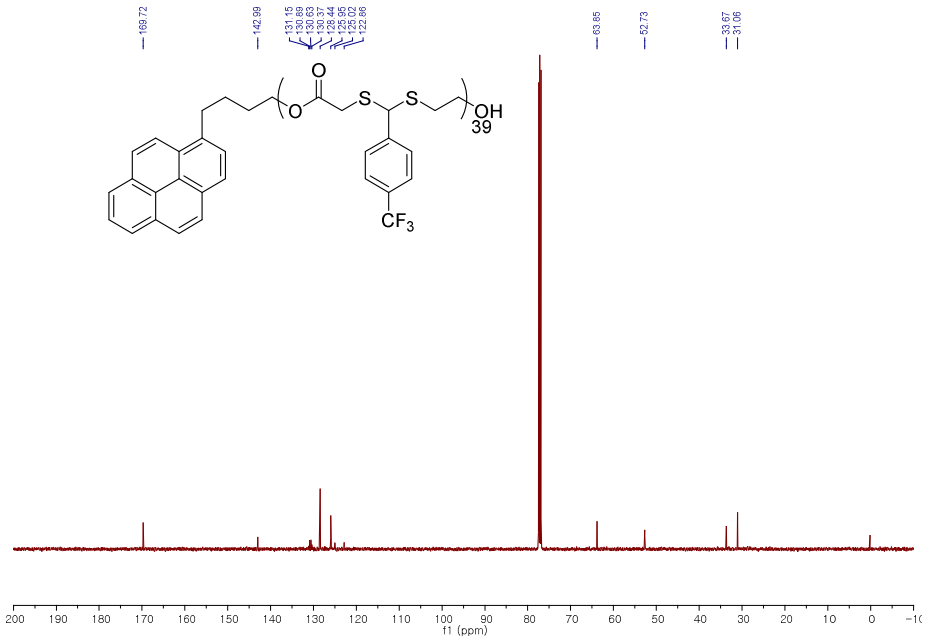
P13 (^{13}C NMR, 125 MHz, $CDCl_3$)



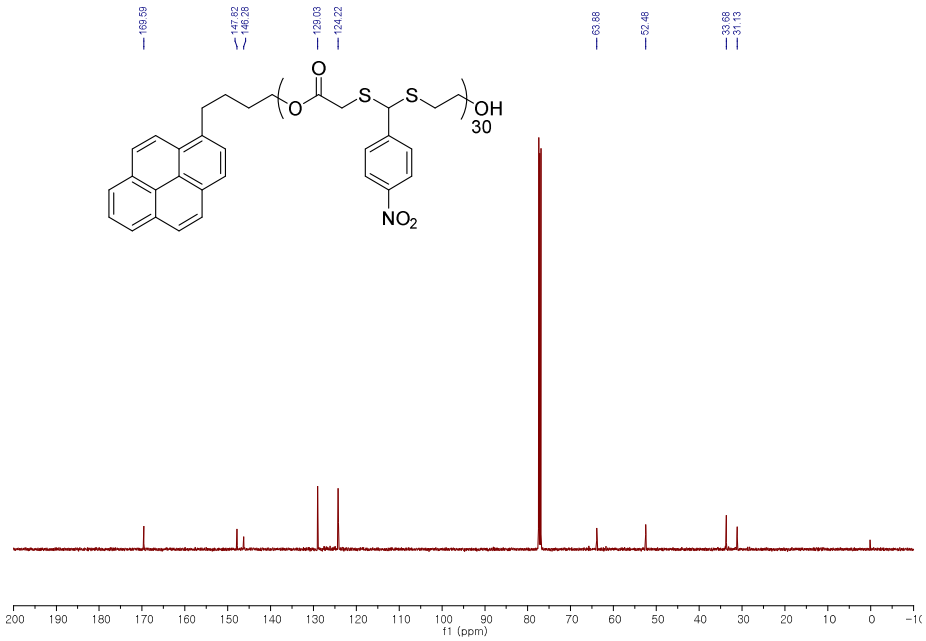
P14 (^{13}C NMR, 125 MHz, $CDCl_3$)



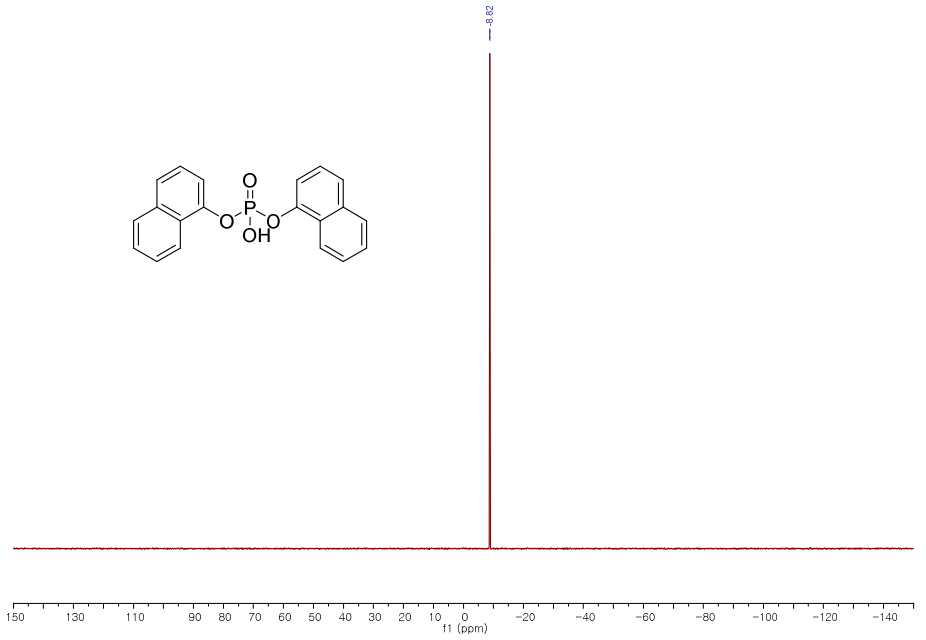
P15 (^{13}C NMR, 125 MHz, $CDCl_3$)



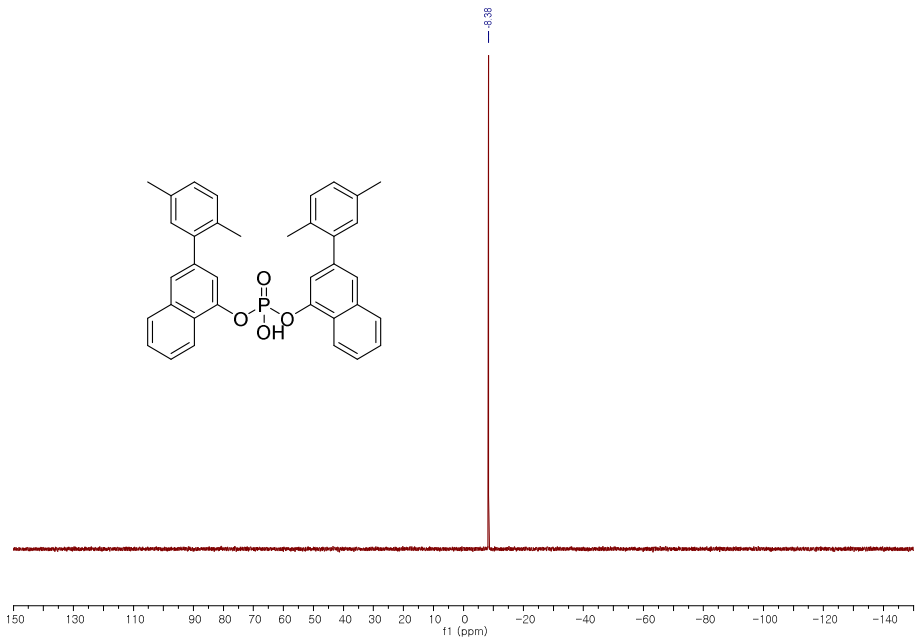
P16 (^{13}C NMR, 125 MHz, $CDCl_3$)



Di(naphthalen-1-yl) phosphate (DNP) (^{31}P NMR, 200 MHz, $CDCl_3$)



Bis(3-(2,5-dimethylphenyl)naphthalen-1-yl) phosphate (XNP) (^{31}P NMR, 200 MHz, $CDCl_3$)



5. References

S1. A. Kamal and G. Chouhan, *Synlett*, 2002, 0474–0476.

S2. C.-P. Zhang, J. Cai, C.-B. Zhou, X.-P. Wang, X. Zheng, Y.-C. Gu and J.-C. Xiao, *Chem. Commun.*, 2011, **47**, 9516–9518.