

Supplementary Information

Orthogonal *O,S*-CKA Monomer for the Introduction of Thioesters and/or Thionoester Functionalities by Radical Polymerization

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1. Materials

The following chemicals were used as received: 2-methylbenzoic acid (97%, AmBeed), *N*-bromosuccinimide (NBS, >99%, Glentham Life Sciences), 2,2'-azobis(2-methylproprionitrile) (AIBN, >98%, Sigma Aldrich), potassium thioacetate (>98%, Glentham Life Sciences), lithium aluminium hydride (LiAlH₄, 95%, powder, Sigma-Aldrich), cobalt (II) chloride anhydrous (pure p. a., Chempur), trimethylsilyl chloride (TMSCl, 98%, Thermo Scientific), chloroacetaldehyde dimethyl acetal (98%, Sigma Aldrich), potassium tert-butoxide (>98%, Thermo Scientific), conc. H₂SO₄ (pure p. a., Chempur), sodium bicarbonate (pure p. a., Eurochem), ammonium chloride (pure p. a., Eurochem), anhydrous sodium sulfate (pure p. a., Eurochem), acrylamide (AM, 98%, Glentham Life Sciences), allyl acetate (AAc, 99%, Thermo Scientific), potassium permanganate (KMnO₄, pure p. a., Chempur), chloroform-*d* (CDCl₃, 99.8%, Deutero), acetone-*d*6 (99.0%, Deutero) and dimethylsulfoxide-*d*6 (DMSO-*d*6, 99.8%, Deutero).

Styrene (Sty, 99%, Alfa Aesar), methyl acrylate (MA, 99% Thermo Scientific), methyl methacrylate (MMA, 99%, Alfa Aesar), *N,N*-dimethyl acrylamide (DMAA, 99%, Sigma-Aldrich), and vinyl acetate (VAc, >99%, TCI) were purified shortly before use by passing through a column of basic Al₂O₃.

The following solvents were used as received: ethyl acetate (EtOAc, pure p. a., Chempur), hexane (pure p. a., POCH) chloroform (pure p. a., Chempur, for reaction with AlCl₃) and anhydrous dimethylformamide (99.8%, Sigma Aldrich). The following solvents were further dried using molecular sieves (3 or 4 Å beads, Honeywell): ethanol (pure p. a., POCH), chloroform (pure p. a., Chempur; for reaction with AIBN and NBS), tetrahydrofuran (THF, pure p. a. Chempur), acetonitrile (MeCN, pure p. a., Chempur), *tert*-butanol (*t*BuOH, > 99%, TCI), and diethyl ether (Et₂O, pure p.a., POCH).

Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-sheets (Merck TLC Silicagel 60 F₂₅₄) and visualized by ultraviolet irradiation or KMnO₄ stain. For flash chromatography (FC) silica gel (60, 63-200 μm, Merck KGaA) was used.

2. Instrumentations and Analysis

NMR spectra characterization

Nuclear magnetic resonance spectroscopy (^1H NMR) was used to determine the chemical structure of synthesized compound and polymers, as well as for examining monomer conversion during the polymerization reactions. NMR spectra were recorded at 25 °C on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^1H NMR and 176 MHz for ^{13}C NMR, respectively, or on JEOL JNM-ECZL 400R, running at 400 MHz for ^1H NMR. CDCl_3 , acetone- d_6 and $\text{DMSO-}d_6$ were used as the solvents. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl_3 : 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). The resonance multiplicities are described as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet) or m (multiplet).

GPC characterization

Gel permeation chromatography (GPC) was used to determine number average molecular weights (M_n) of the synthesized polymers and their dispersity (\mathcal{D}). The GPC measurements were performed with a Wyatt (Wyatt, Dernbach, Germany) instrument equipped with two Perfect Separation Solutions (PSS) columns and one guard column (GRAM Linear, 10 μm , M_n from 800 to 1,000,000 g/mol), utilizing a differential refractometer (RI) and a multi-angle light scattering (MALS) detector. The measurements were performed in DMF, containing 50 mmol LiBr, as eluent at a flow rate of 1 mL/min. Linear poly(methyl methacrylate) (M_n from 545 to 2,000,000 g/mol) and polystyrene standards (M_n from 435 to 2,300,000 g/mol) were used as standards. The samples were filtered through nylon filters of 0.22 μm pore size before the measurement.

FT-IR characterization

Fourier transform infrared spectroscopy (FT-IR) was used for the characterization of specific chemical functional groups in the samples. The experiments were performed with the use of Nicolet is50 FT-IR spectrometer (Thermo Fischer Scientific Instruments, Waltham, MA, USA) equipped with diamond Smart Orbit ATR sampling accessory. The data were collected in the mid-infrared region of 500–4000 cm^{-1} with spectral resolution 2 cm^{-1} and averaging of 64 scans.

Mass Spectroscopy

Ultra-performance liquid chromatograph (UPLC) Acquity (Waters Ltd.) equipped with photodiode array detector and combined with LCT Premier XE (Waters Ltd.) mass spectrometer with TOF-analyzer (ultimate instrument spectral resolution of 11,000 FWHM) was used for the chromatographic separation and identification of products **5** and **7**. Separation was performed on a reversed-phase C18 UPLC column (Waters Acquity UPLC BEH C 18 1.7mm, 50 \times 2.1 mm) equilibrated with a water/acetonitrile (90/10 v/v) mobile phase containing 0.1% (v/v) trifluoroacetic acid (TFA) at a flow rate of 0.3 mL/min. The injection volume was 2 μL , the sample temperature was 20 °C, and the column temperature was 40 °C. The electrospray source was operated at positive ion mode using the following

parameters: capillary voltage 2.8 kV, sample cone voltage 60 V, desolvation temp. 350 °C, source temp. 100 °C, desolvation gas flow 800 L/h, and cone gas flow 50 L/h. The MCP detector voltage was 2.5 kV.

3. Experimental Procedures

3.1 – Synthesis of monomer *O,S*-BMDO (5,6-benzo-2-methylene-1,3-oxthiepane) (**8**)

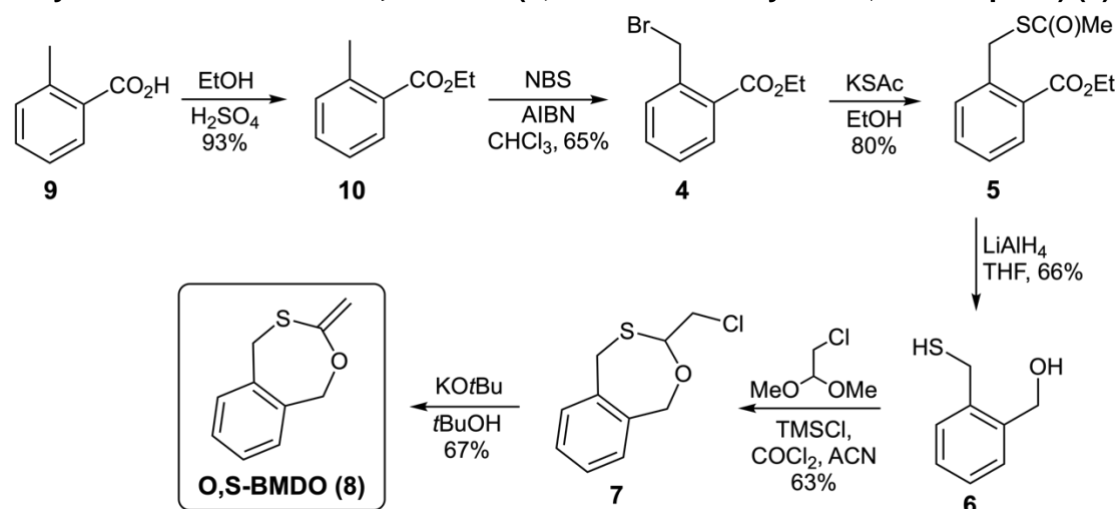


Figure S1. Synthesis of monomer *O,S*-BMDO (**8**).

Ethyl 2-methylbenzoate (**10**)

2-Methylbenzoic acid (**9**) (10.0 g, 73.4 mmol) was dissolved in ethanol (100 mL). To this mixture, 3 Å molecular sieves (6.5 g) and conc. H₂SO₄ (3.0 ml) were added, and the mixture refluxed for 40 h. Then, ca. 60% of the volume of the reaction mixture was removed under reduced pressure, followed by pouring the mixture into crushed ice with subsequent neutralization with NaHCO₃. The mixture was then extracted with EtOAc (2 x 100 mL). The organic fractions were combined, dried over Na₂SO₄, and concentrated to give 11.2 g of ethyl 2-methylbenzoate (**10**) (93% yield) as colorless oil. Spectroscopic data were consistent with the literature (Bioorg. Med. Chem. Lett., 2011, 21, 7246–7250).

2-Ethoxycarbonylbzyl bromide (**4**)

Ethyl 2-methylbenzoate (**9**) (11.2 g, 68.3 mmol) was dissolved in anhydrous CHCl₃ (120 mL). The mixture was then purged with nitrogen for 10 min before *N*-bromosuccinimide (13.4 g, 75.1 mmol) and AIBN (1.23 g, 7.51 mmol) were added. The mixture was then stirred at reflux for 16 h under nitrogen. The mixture was then cooled and filtered, and the filter cake washed with chloroform (50 mL). After concentration of the filtrate under reduced pressure the resulting crude product was then purified by silica gel column chromatography (hexane:ethyl acetate = 19:1) to provide 10.8 g of 2-ethoxycarbonylbzyl bromide (**4**) as a yellow oil (65% yield). Spectroscopic data were consistent with the literature (Bioorg Med Chem Lett, 2011, 21, 7246–7250).

Ethyl 2-(acetylsulfanylmethyl)benzoate (**5**)

2-Ethoxycarbonylbzyl bromide (**4**) (10.8 g, 44.3 mmol) was dissolved in ethanol (100 mL) and potassium thioacetate (5.06 g, 44.3 mmol) was added in portions. The reaction mixture was stirred at RT overnight. When analysis by TLC indicated complete consumption of the starting material, the formed precipitate was filtered and washed with ethanol. The filtrate

was then concentrated *in vacuo* and purified by passage through a silica plug (hexane/chloroform = 1:1). The solution was concentrated to ca. 30 mL and then cooled overnight to allow crystals to form which were then filtered, washed with hexane and dried to give 8.45 g of ethyl 2-(acetylsulfanylmethyl)benzoate (**5**) (80% yield) as colorless crystals.

MP: 44-45 °C.

IR (neat): ν (cm⁻¹): 2986, 2976, 1705, 1678, 1269, 1074, 721.

¹H NMR (400 MHz, CDCl₃): δ 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (td, *J* = 7.7, 1.4 Hz, 1H), 4.48 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃): δ 195.76, 167.08, 139.98, 132.51, 131.72, 131.08, 129.13, 127.52, 77.34, 77.16, 76.98, 61.21, 32.37, 30.25, 14.33.

HRMS: [M + H]⁺ Calc. mass.: 239.0742; Found: 239.0760.

(2-(Mercaptomethyl)phenyl)methanol (6)

Ethyl 2-(acetylsulfanylmethyl)benzoate (**6**) (8.45 g, 35.4 mmol) was dissolved in anhydrous THF (90 mL) and cooled in an ice-bath. To the stirred solution, LiAlH₄ (6.73 g, 177.0 mmol) was added in portions. After 10 minutes, the ice-bath was removed, and the mixture was stirred at room temperature for 3 h. Then, the mixture was chilled again with an ice-bath and quenched by the dropwise addition of sat. aqueous NH₄Cl while being vigorously stirred. The resulting suspension was then extracted with EtOAc (3 x 100 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated. The resulting crude product was purified by silica gel column chromatography (hexane/EtOAc = from 19:1 to 3:2) to give 3.6 g of (2-(mercaptomethyl)phenyl)methanol (**6**) (66% yield) as a yellow oil. Spectroscopic data were consistent with the literature (K. E. Giesler, D. C. Liotta J. Med. Chem. 2016, 59, 10244-10252).

5,6-Benzo-2-(chloromethyl)-1,3-oxthiepane (7)

To the solution of (2-(mercaptomethyl)phenyl)methanol (**6**) (3.60 g, 23.4 mmol) in anhydrous acetonitrile (280 mL) was added cobalt chloride (760 mg, 5.85 mmol) and trimethylsilyl chloride (2.97 ml, 23.4 mmol). This was then followed by a dropwise addition of chloroacetaldehyde dimethyl acetal (2.66 ml, 23.4 mmol) in acetonitrile (10 mL). The mixture was stirred at RT for 16 h and then poured into 5% aqueous NaHCO₃ (250 mL). This mixture was then extracted with EtOAc (3 x 200 mL). The organic layers were combined and washed with aqueous NaHCO₃ (250 mL), dried over Na₂SO₄, filtered and condensed under reduced pressure. The resulting solid crude was triturated with small amount of Et₂O (2 x 5 mL) to give 5,6-benzo-2-(chloromethyl)-1,3-oxthiepane (**7**) (63% yield) as gray solid.

MP: 94 °C.

IR (neat): ν (cm⁻¹): 3015, 2961, 1452, 1439, 1242, 1057, 761.

¹H NMR (400 MHz, CDCl₃): δ 7.17–7.25 (m, 5H), 5.21 (dd, *J* = 7.5, 4.1 Hz), 5.01 (d, *J* = 14.0 Hz), 4.95 (d, *J* = 14.0 Hz), 4.10 (d, *J* = 15.1 Hz), 3.97 (d, *J* = 15.1 Hz), 3.75 (dd, *J* = 11.7, 7.5 Hz, 1H), 3.70 (dd, *J* = 11.7, 4.1 Hz, 1H).

^{13}C NMR (176 MHz, CDCl_3): δ 140.15, 137.37, 129.35, 128.56, 127.57, 88.33, 74.41, 46.23, 34.70.

HRMS: $[\text{M} + \text{H}]^+$ Calc. mass: 215.0297; Found: 215.0302.

5,6-Benzo-2-methylene-1,3-oxthiepane (**8**)

Benzo-2-(chloromethyl)-1,3-oxthiepane (**7**) (500 mg, 2.32 mmol) was placed in a screw-cap glass tube and dissolved in *t*BuOH (1 mL) under nitrogen. Then, potassium tert-butoxide (313 mg, 2.79 mmol) was added and the mixture was sealed and stirred at 120 °C for 18 h. The mixture was then cooled to RT and diluted with diethyl ether (10 ml), followed by being filtered to remove the KCl precipitate, with subsequent concentration under reduced pressure. This process was repeated three times. To the combined fractions was then added diethyl ether (30 mL) and the mixture again filtered. The resulting solution was concentrated under reduced pressure to give 277 mg of 5,6-benzo-2-methylene-1,3-oxthiepane (**8**) (67% yield) as a brown oil.

IR (neat): ν (cm^{-1}): 3019, 2915, 1604, 1158, 1036, 742.

^1H NMR (400 MHz, CDCl_3): δ 7.20–7.24 (m, 2H), 7.09–7.15 (m, 2H), 5.20 (s), 4.78 (d, $J = 1.1$ Hz, 1H), 4.63 (d, $J = 1.1$ Hz, 1H), 4.02 (s, 2H).

^{13}C NMR (176 MHz, CDCl_3): δ 157.86, 136.86, 136.66, 129.06, 128.10, 127.85, 127.32, 96.86, 73.07, 35.49.

3.2 – Polymerization procedures

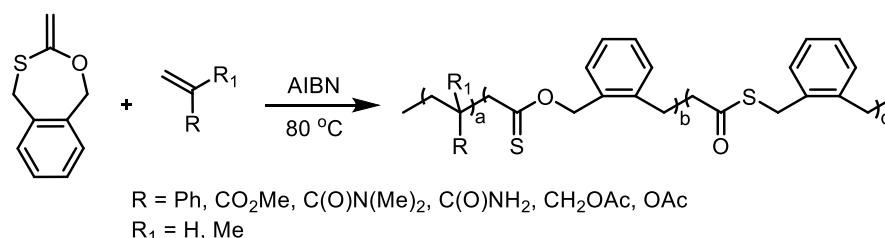


Figure S2. Scheme of bulk polymerization of O,S-BMDO (**8**) and comonomer.

Typical bulk polymerization procedure for 20% of O,S-BMDO and 80% of comonomer

O,S-BMDO (**8**) (71 mg, 0.4 mmol), comonomer (Sty, MMA, MA, DMAA, AAc, VAc; 1.6 mmol) and AIBN (9.85 mg, 0.06 mmol) were homogenized in a rounded vial and then closed with a bimetal crimp cap with a PTFE/silicone septum. The mixture was purged with nitrogen in an ice-bath for 20 min and then placed in a pre-heated oil bath at 80 °C. After 18 hours the vessels were cooled to room temperature and opened. The reaction mixtures were dissolved in chloroform (1.5 mL) and then precipitated with hexane. The samples were then dissolved in CDCl_3 to obtain ^1H and ^{13}C NMR spectra.

In the case of the copolymerization of O,S-BMDO with acrylamide (MP: 84.5 °C), the monomers and initiator were placed in a rounded vial with a bimetal crimp cap with a PTFE/silicone septum and dissolved in tetrahydrofuran (1 mL) under nitrogen. The solution was purged with nitrogen for 20 min. Then, the solvent was removed under reduced pressure at 20 °C and the thick mixture placed in a pre-heated oil bath at 80 °C. The reaction mixture

was then dissolved in acetone (1.5 mL) and precipitated in hexane. The sample was then dissolved in DMDO-*6d* to measure ^1H NMR.

In the case of the conversion studies: monomer(s) and initiator were homogenized in a rounded vial closed with a bimetal crimp cap with a PTFE/silicone septum and purged with nitrogen in an ice-bath for 20 minutes. Then, the mixture was distributed in equal portions to 6 to 8 vessels with bimetal crimp caps with PTFE/silicone septums under nitrogen. At various times during the polymerization the vessels were removed, put into ice, and then opened. The reaction mixtures were dissolved in CDCl_3 to obtain ^1H NMR spectra.

3.3 – Chemical degradation

Poly(Sty-*co-O,S*-BMDO) or poly(*O,S*-BMDO) (35-38 mg) and KOH (45 mg, 17.8 mmol) were suspended in EtOH/H₂O (4:1; 0.4 mL) and stirred under nitrogen at 80 °C for 18 h. The mixture was then diluted with H₂O (3 mL) and acidified with 1M HCl to pH = ca. 6 followed by extraction with EtOAc. The organic fractions were dried over Na₂SO₄, filtered, and then concentrated.

Poly(Sty-*co-O,S*-BMDO) or poly(*O,S*-BMDO) (26-30 mg) were dissolved in TFA (1.0 mL). The mixture was stirred at room temperature for 5 h and then concentrated under reduced pressure.

Poly(Sty-*co-O,S*-BMDO) or poly(*O,S*-BMDO) (30 mg) were dissolved in chloroform (1 mL). Then, AlCl₃ was added (for poly(*O,S*-BMDO) = 44 mg of AlCl₃); (for poly(Sty_{82.7}-*co-O,S*-BMDO_{17.3}) = 12 mg of AlCl₃). The mixture was stirred at room temperature for 4h and then diluted with chloroform (5 mL) and filtered, followed by concentration under reduced pressure.

4. ^1H and ^{13}C NMR spectra

4.1 – Monomers & intermediates

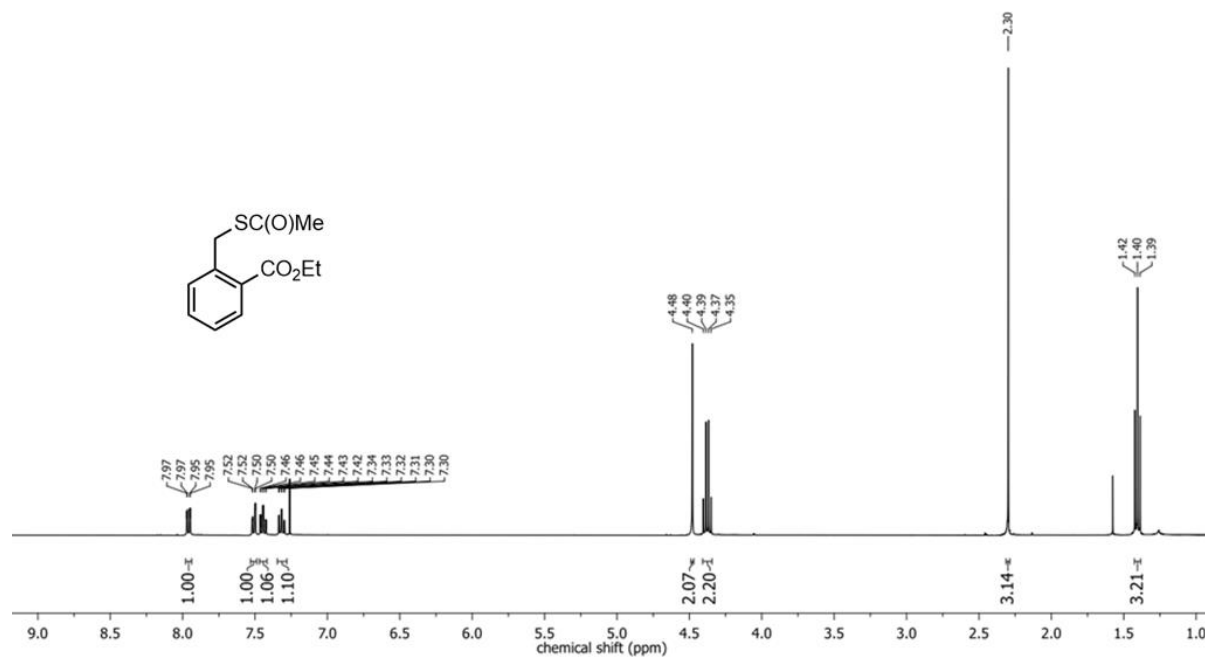


Figure S3. ^1H NMR (CDCl₃, 700 MHz) of ethyl 2-(acetylsulfanylmethyl)benzoate (5).

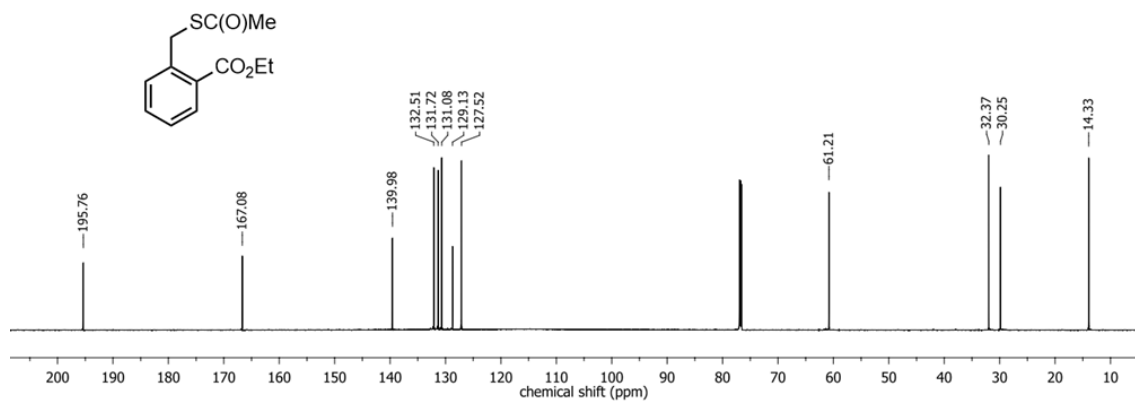


Figure S4. ^{13}C NMR (CDCl₃, 176 MHz) of ethyl 2-(acetylsulfanylmethyl)benzoate (5).

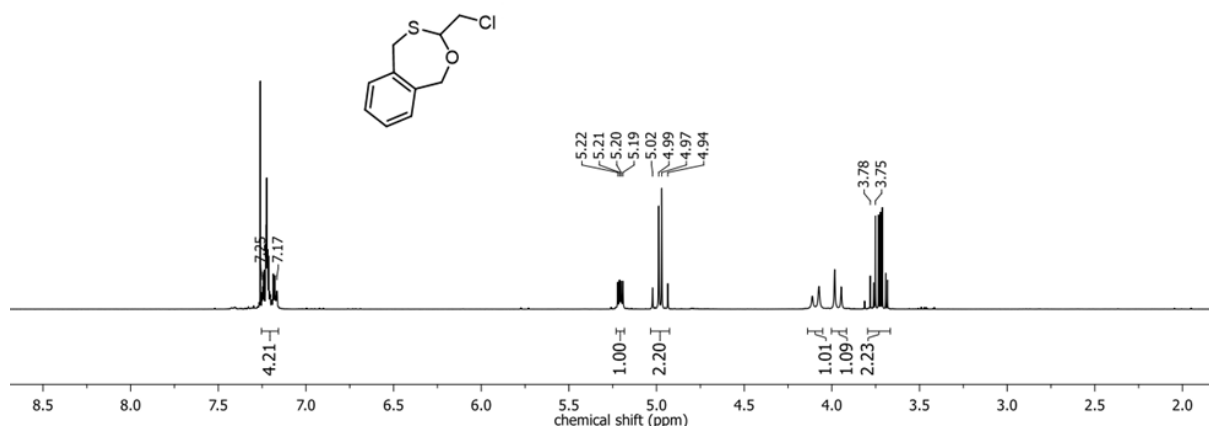


Figure S5. $^1\text{H NMR}$ (CDCl₃, 700 MHz) of 5,6-benzo-2-(chloromethyl)-1,3-oxthiepane (**7**).

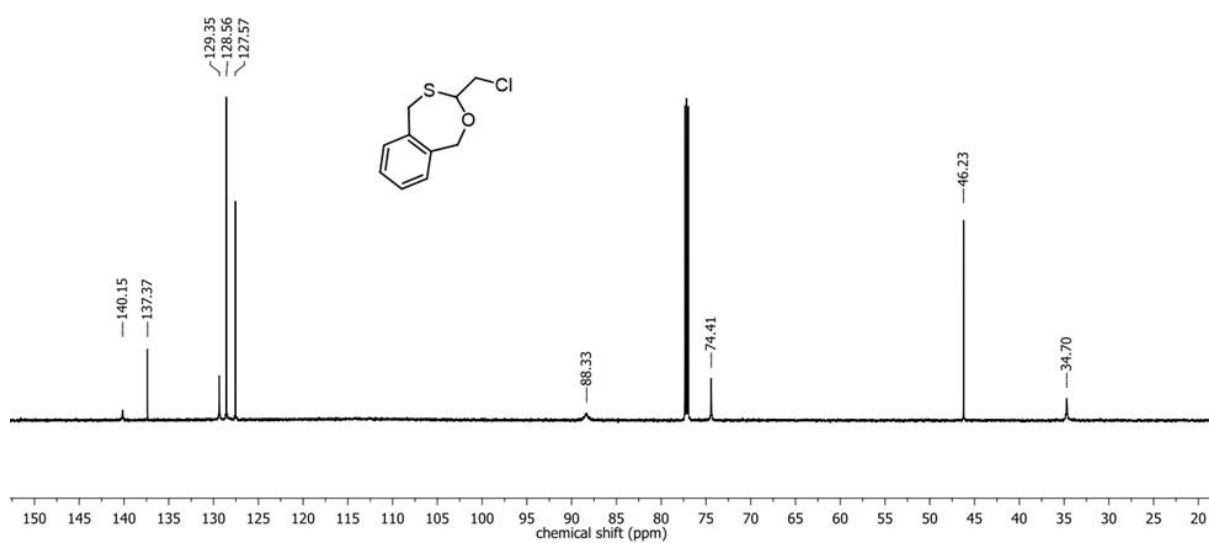


Figure S6. $^{13}\text{C NMR}$ (CDCl₃, 176 MHz) of 5,6-benzo-2-(chloromethyl)-1,3-oxthiepane (**7**).

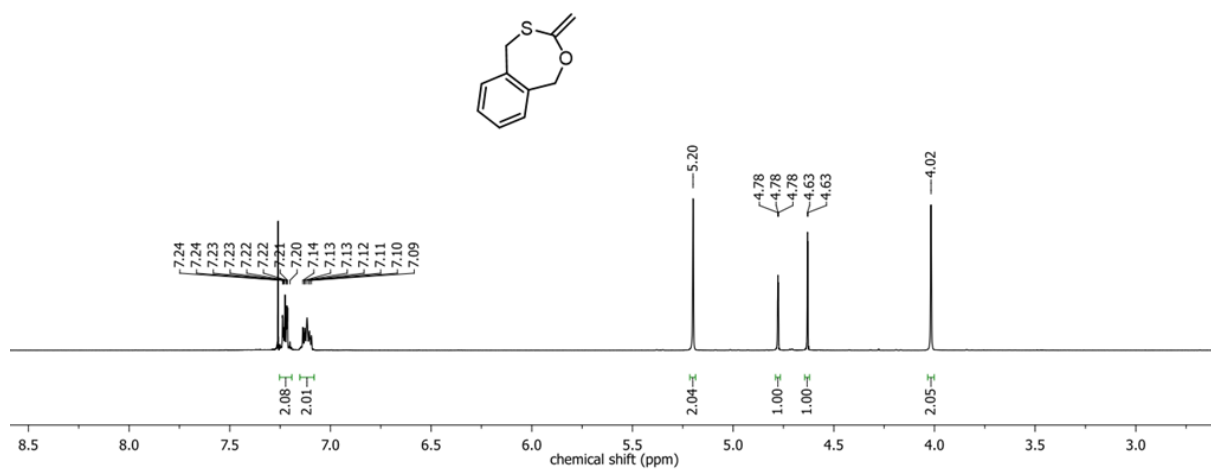


Figure S7. ¹H NMR (CDCl₃, 700 MHz) of 5,6-benzo-2-methylene-1,3-oxthiepane (**8**).

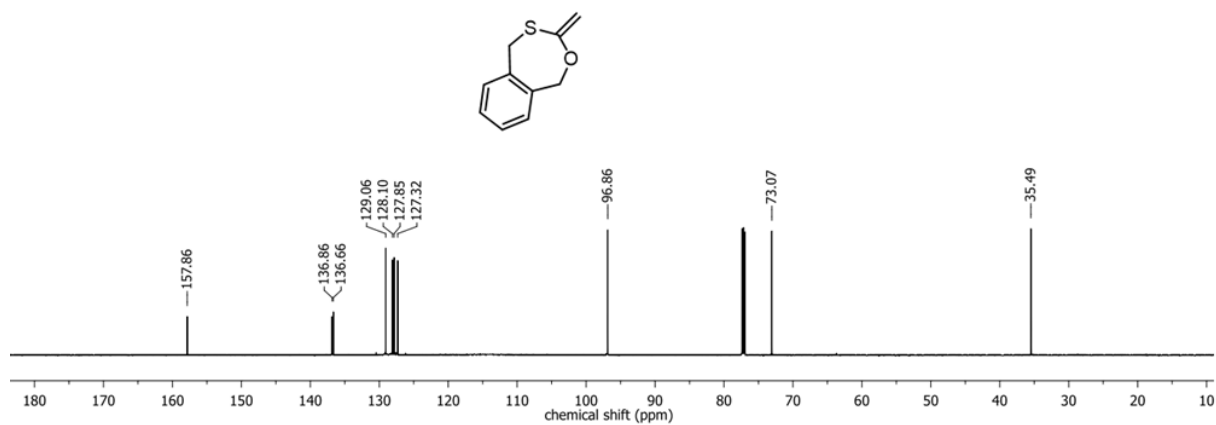


Figure S8. ¹³C NMR (CDCl₃, 176 MHz) of 5,6-benzo-2-methylene-1,3-oxthiepane (**8**).

4.2 – Polymers

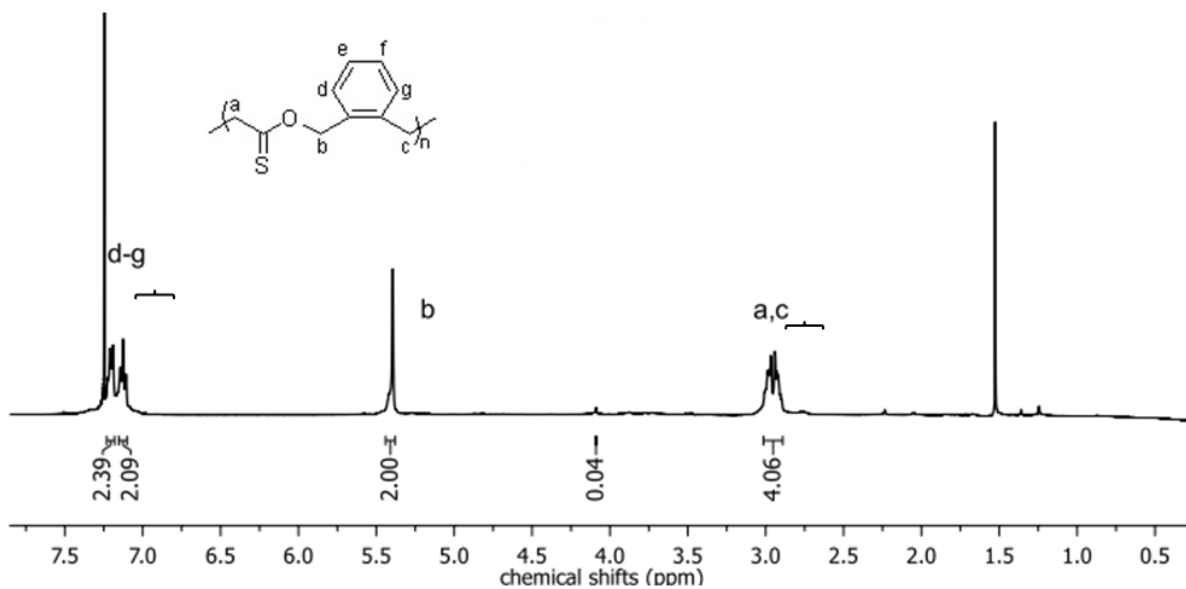


Figure S9. ^1H NMR (CDCl_3 , 700 MHz) of poly(*O,S*-BMDO).

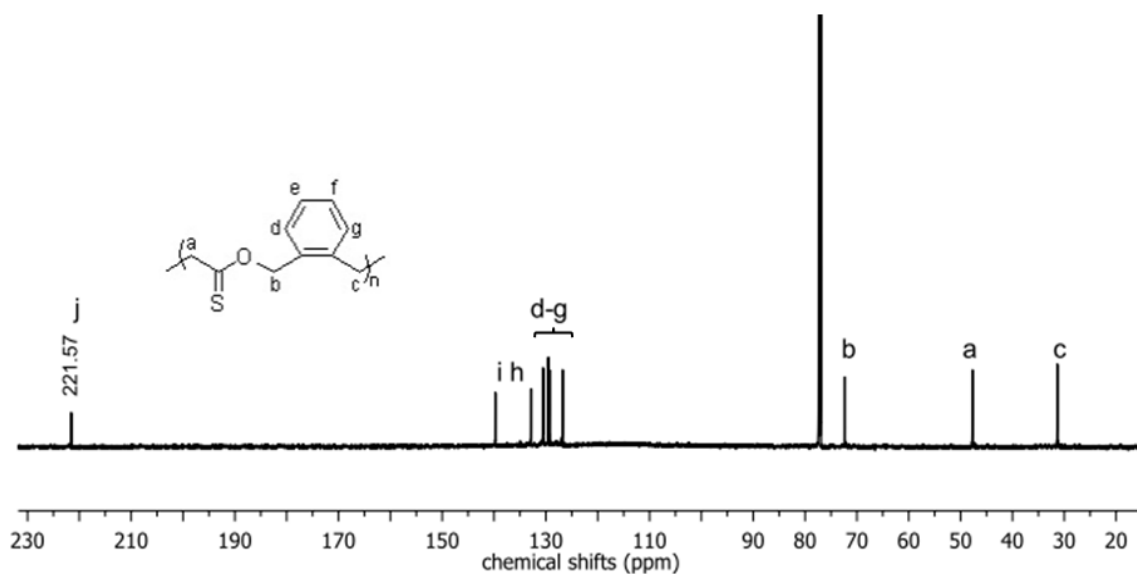


Figure S10. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(*O,S*-BMDO).

Poly(Sty_{59.5}-co-O,S-BMDO_{40.5}) – an example of almost exclusive S-side ring-opening

The copolymer composition was determined by taking the total peak areas of the aromatic protons of O,S-BMDO and the Sty units together (I_{Ar}) and that of C(S)OCH₂ protons of O,S-BMDO at 5.0–5.5 ppm (I_{BMDO}) using the following formula:

a:b = molar ratio of O,S-BMDO : molar ratio of Sty

$I_{BMDO} = 2a$, $I_{Ar} = 4a + 5b$, thus $a = I_{BMDO}/2$ and $b = (I_{Ar} - 2*I_{BMDO})/5$.

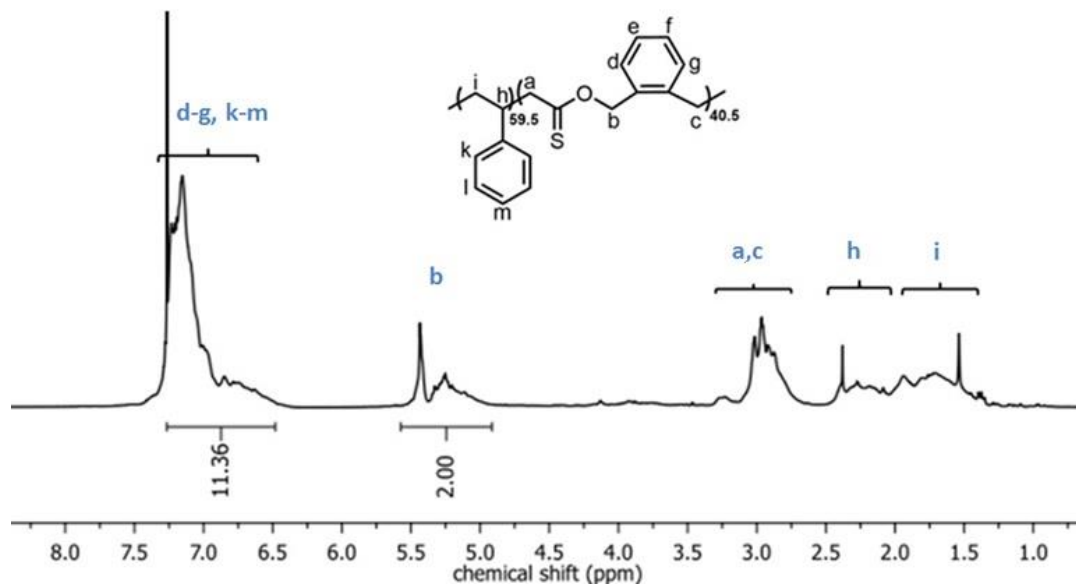


Figure S11. ¹H NMR (CDCl₃, 700 MHz) of poly(Sty-co-O,S-BMDO)

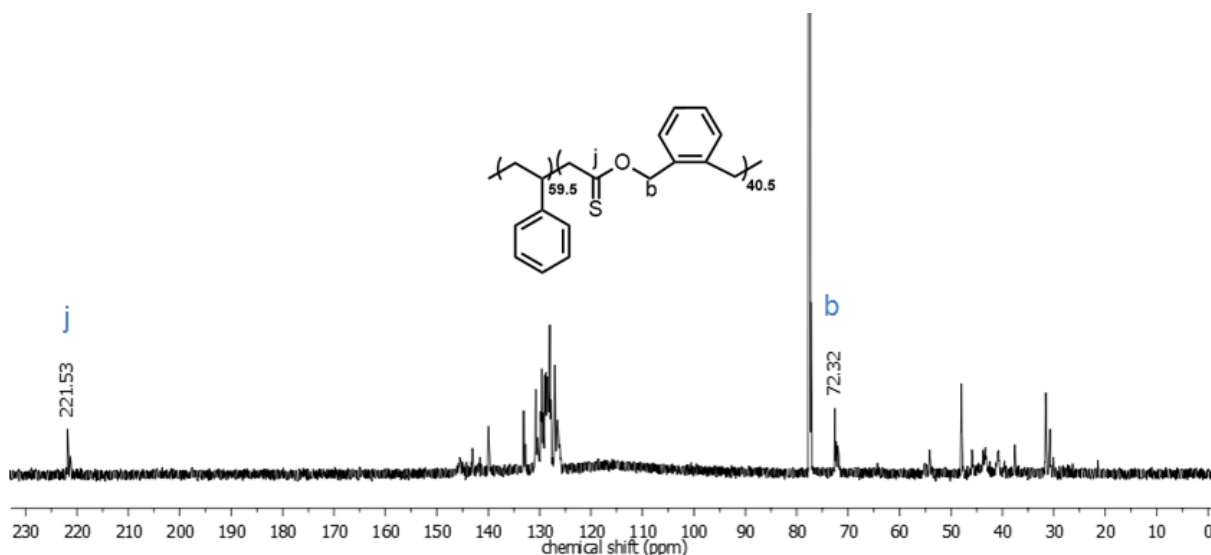


Figure S12. ¹³C NMR (CDCl₃, 176 MHz) of poly(Sty-co-O,S-BMDO).

Poly(MMA_{48.5}-co-O,S-BMDO_{51.5}) – an example of mixed O-side and S-side ring-opening

Poly(MMA-co-O,S-BMDO) revealed similar complexity to that obtained for poly(MMA-co-BMDO), as analysed by Wickel *et al.* (Macromolecules 2003, 36, 2397-2403). Thus, for the previously published copolymer the methoxy group of the MMA was observed as four peaks at 3.4–3.8 ppm in all copolymer samples, in contrast to a single peak in the PMMA homopolymer. Similarly, the methyl group attached to carbon α showed complex resonance signals at 0.83–1.33 ppm. As stated by the authors, these signals have high chemical shift variation due to the presence of compositional and tacticity effects. Furthermore, many overlapping resonance signals in the region 1.48–3.0 ppm were assigned to BMDO and MMA-main chain protons.

After careful analysis of samples of poly(MMA-co-O,S-BMDO) with different compositions, *ca.* 5 peaks at 3.25–3.75 ppm were assigned to the methoxy group of MMA. The copolymer composition was then determined by taking the sum of the C(S)OCH₂ protons and C(O)SCH₂ protons of O,S-BMDO at 5.25–5.55 ppm and at 4.0–4.2 ppm (*I*_{BMDO}), respectively, and the sum of O–CH₃ protons at 3.25–3.75 ppm (*I*_{MMA}) and applying the following formula:

a:*b* = molar ratio of O,S-BMDO : molar ratio of MMA.

*I*_{BMDO} = 2*a*, *I*_{MMA} = 3*b*, thus $a = I_{\text{BMDO}}/2$ and $b = I_{\text{MMA}}/3$.

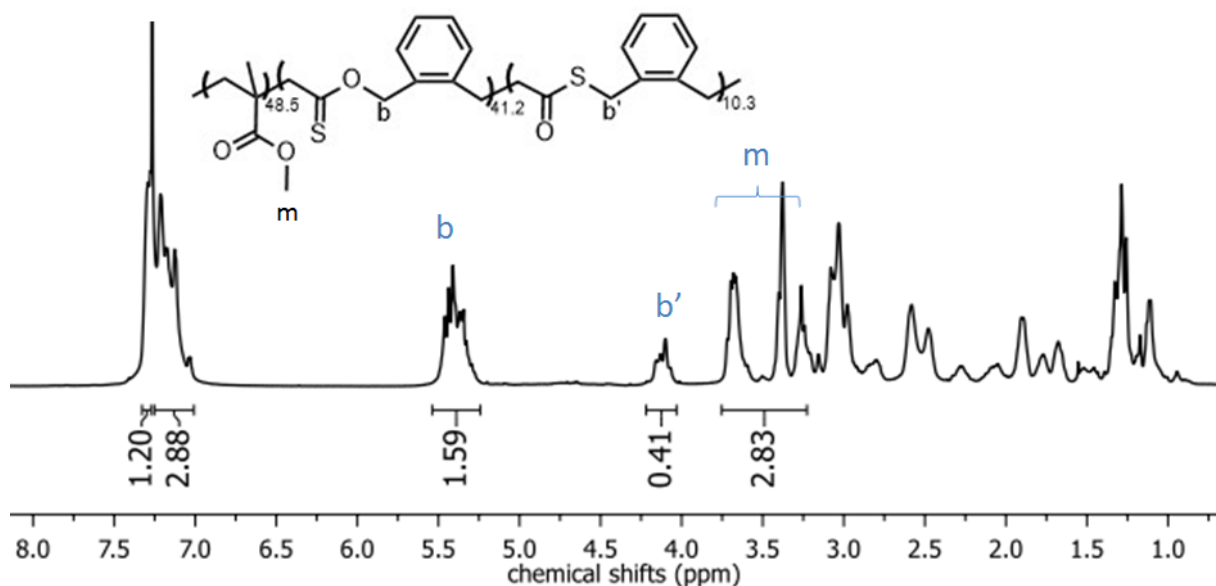


Figure S13. ¹H NMR (CDCl₃, 700 MHz) of poly(MMA-co-O,S-BMDO).

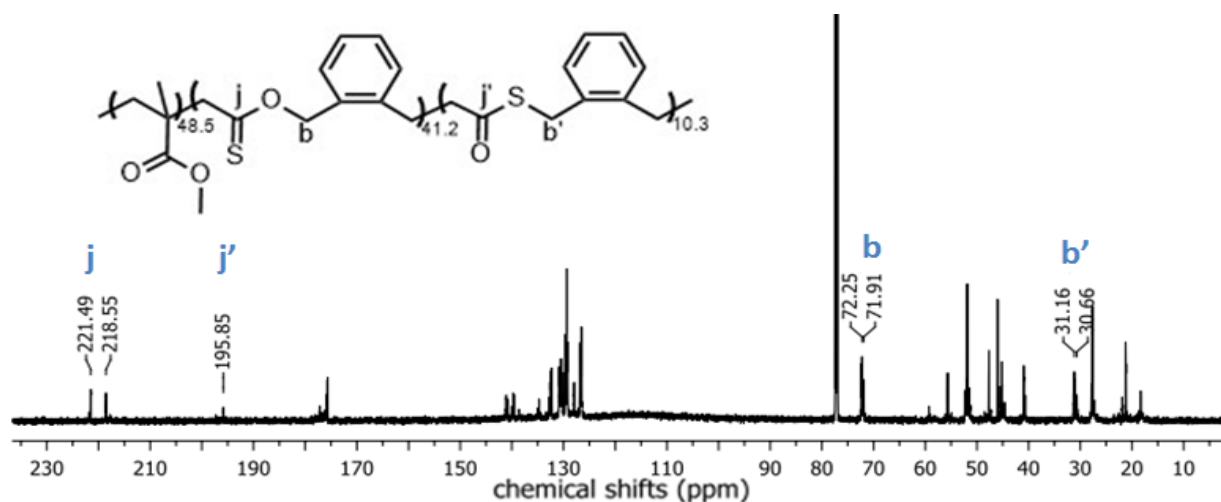


Figure S14. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(MMA-*co*-O,S-BMDO).

Poly(DMAA_{57.4}-*co*-O,S-BMDO_{42.6}) – an example of almost exclusive O-side ring opening

The copolymer composition was determined by taking the sum of the C(S)OCH₂ protons and C(O)SCH₂ protons of O,S-BMDO at 5.4–5.5 ppm and at 4.0–4.25 ppm (= I_{BMDO}), respectively, and the sum of all protons at ca. 1.5–2.00 ppm and ca. 2.5–3.30 ppm – 2*I_{BMDO} (= I_{DMAA}) and using the following formula:

a:b = molar ratio of O,S-BMDO : molar ratio of DMAA.

I_{BMDO} = 2a, I_{DMAA} = 9b, thus $a = I_{\text{BMDO}}/2$ and $b = I_{\text{DMAA}}/9$.

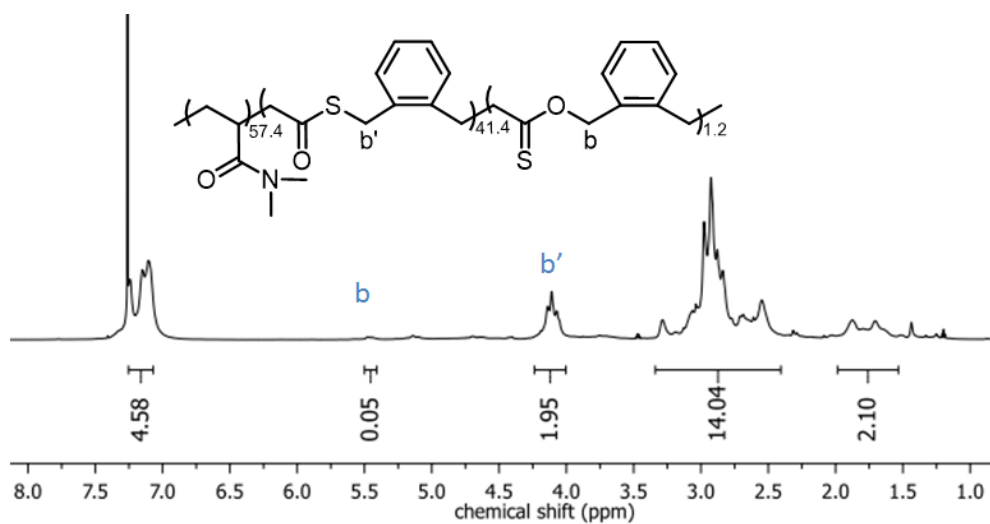


Figure S15. ^1H NMR (CDCl_3 , 700 MHz) of poly(DMAA-*co*-O,S-BMDO).

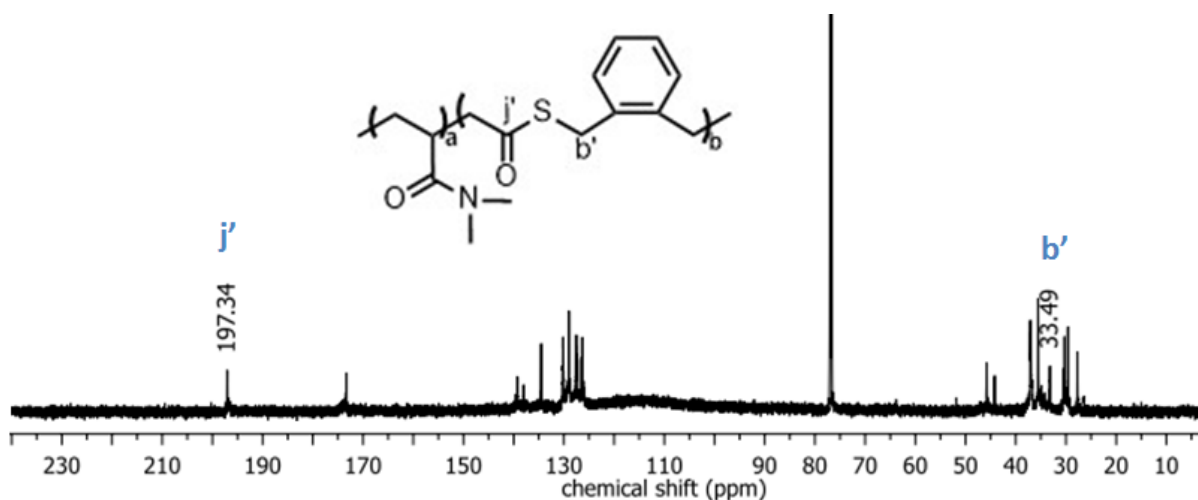


Figure S16. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(DMAA-co-O,S-BMDO).

Poly(MA_{55.7}-co-O,S-BMDO_{44.3}) (^1H NMR) and poly(MA_{30.0}-co-O,S-BMDO_{70.0}) (^{13}C NMR)

The copolymer composition was determined by taking the sum of the $\text{C}(\text{S})\text{OCH}_2$ protons and $\text{C}(\text{O})\text{SCH}_2$ protons of O,S-BMDO at 5.35–5.50 ppm and at 4.05–4.15 ppm (I_{BMDO}), respectively, and the integration of $\text{O}-\text{CH}_3$ protons at 3.45–3.70 ppm (I_{MA}) and applying the following formula:

a:b = molar ratio of O,S-BMDO : molar ratio of MA.

$I_{\text{BMDO}} = 2a$, $I_{\text{MA}} = 3b$, thus $a = I_{\text{BMDO}}/2$ and $b = I_{\text{MA}}/3$.

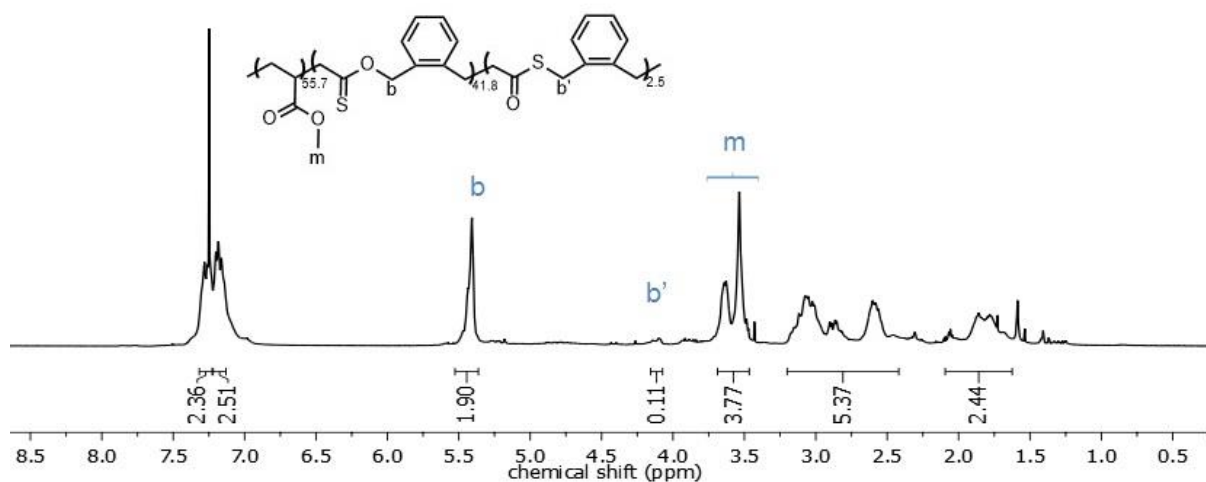


Figure S17. ^1H NMR (CDCl_3 , 700 MHz) of poly(MA-co-O,S-BMDO).

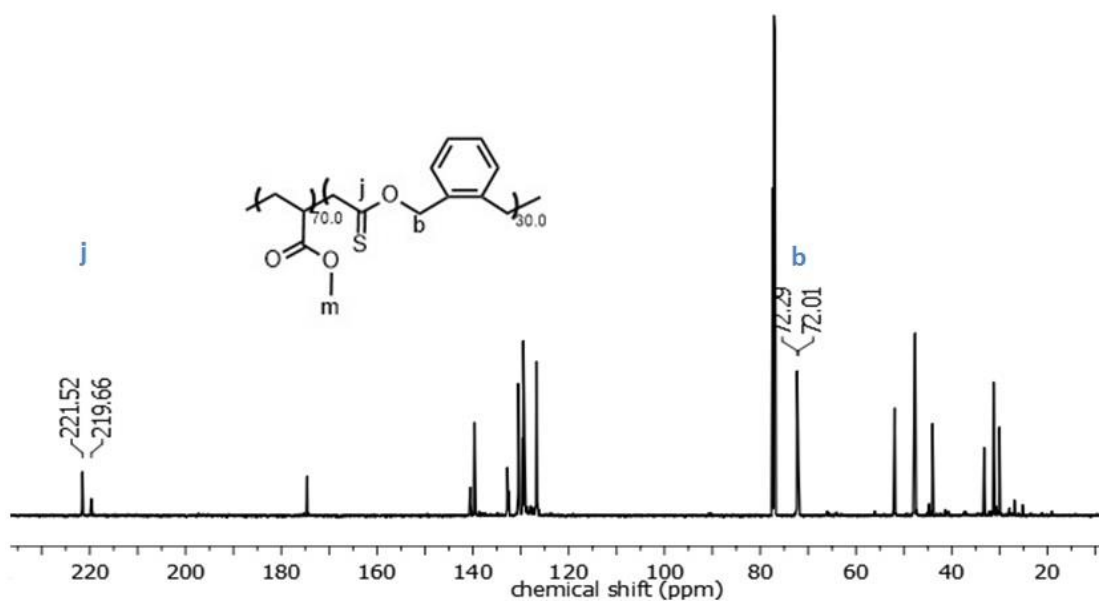


Figure S18. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(MA-*co*-O,S-BMDO).

Poly(AAc_{36.7}-*co*-O,S-BMDO_{63.3})

The copolymer composition was determined by taking the sum of the C(S)OCH₂ protons and C(O)SCH₂ protons of O,S-BMDO at 5.40–5.55 ppm and at 4.10–4.20 ppm (*I*_{BMDO}), respectively, and the integration of C(O)CH₃ protons at 2.0–2.10 ppm (*I*_{AAc}) and applying the following formula:

a:b = molar ratio of O,S-BMDO : molar ratio of AAc.

*I*_{BMDO} = 2a, *I*_{AAc} = 3b, thus $a = I_{\text{BMDO}}/2$ and $b = (I_{\text{AAc}}/3)$.

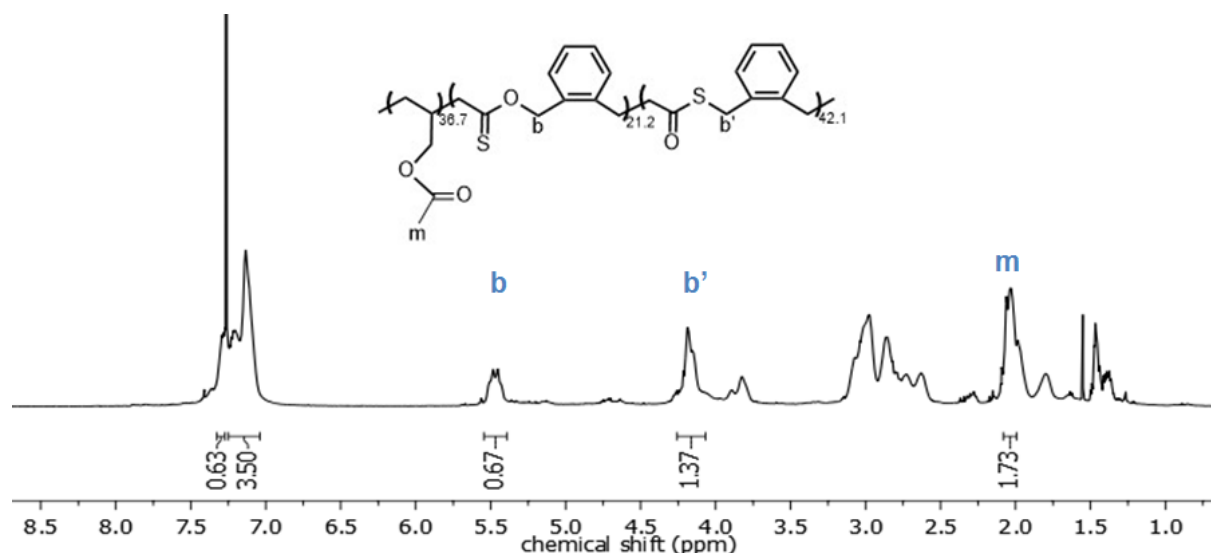


Figure S19. ^1H NMR (CDCl_3 , 700 MHz) of poly(AAc-*co*-O,S-BMDO).

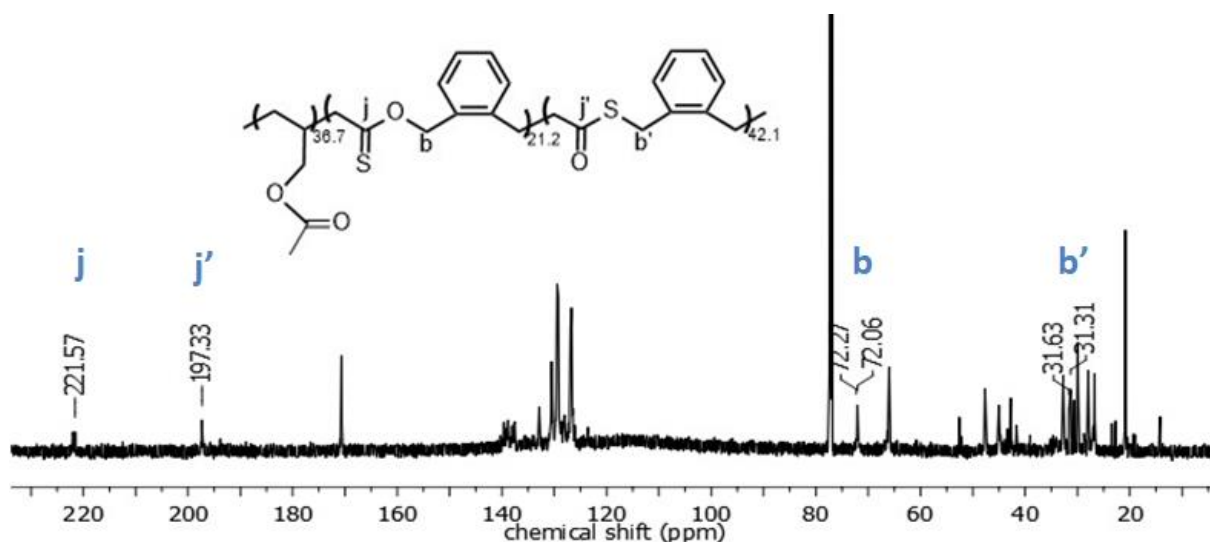


Figure S20. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(AAc-*co*-O,S-BMDO).

Poly(VAc_{22.3}-*co*-O,S-BMDO_{77.7})

The copolymer composition was determined by taking the sum of integrations of the C(S)OCH₂ protons and C(O)SCH₂ protons of O,S-BMDO at 5.35–5.55 ppm and at 4.10–4.25 ppm (*I*_{BMDO}), respectively, and the integration of C(O)CH₃ protons at 1.95–2.10 ppm (*I*_{VAc}) and applying the following formula:

a:b = molar ratio of O,S-BMDO : molar ratio of VAc.

*I*_{BMDO} = 2a, *I*_{VAc} = 3b, thus $a = I_{\text{BMDO}}/2$ and $b = (I_{\text{VAc}}/3)$.

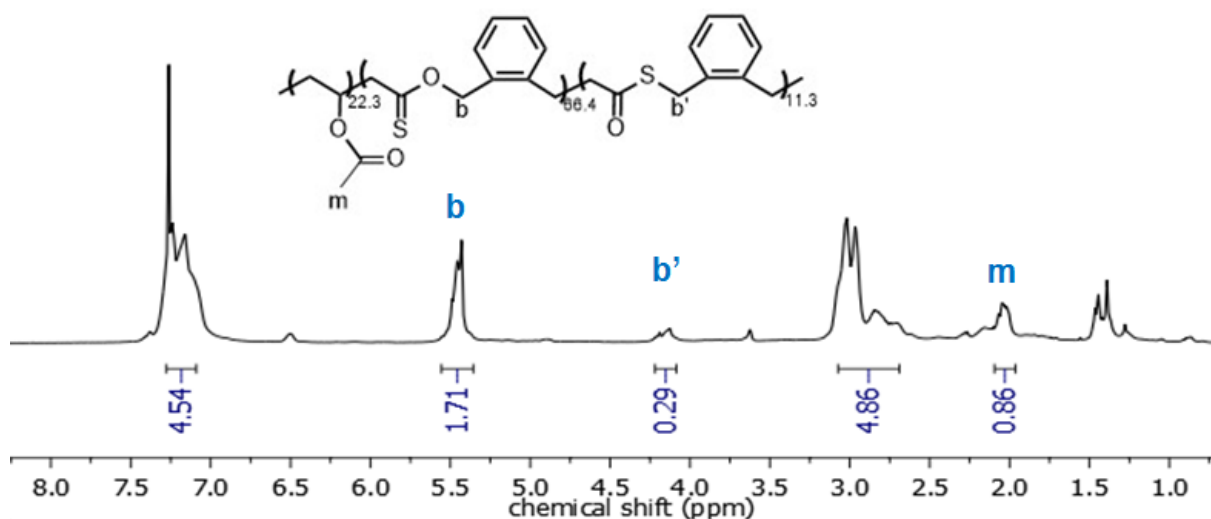


Figure S21. ^1H NMR (CDCl_3 , 700 MHz) of poly(VAc-*co*-O,S-BMDO).

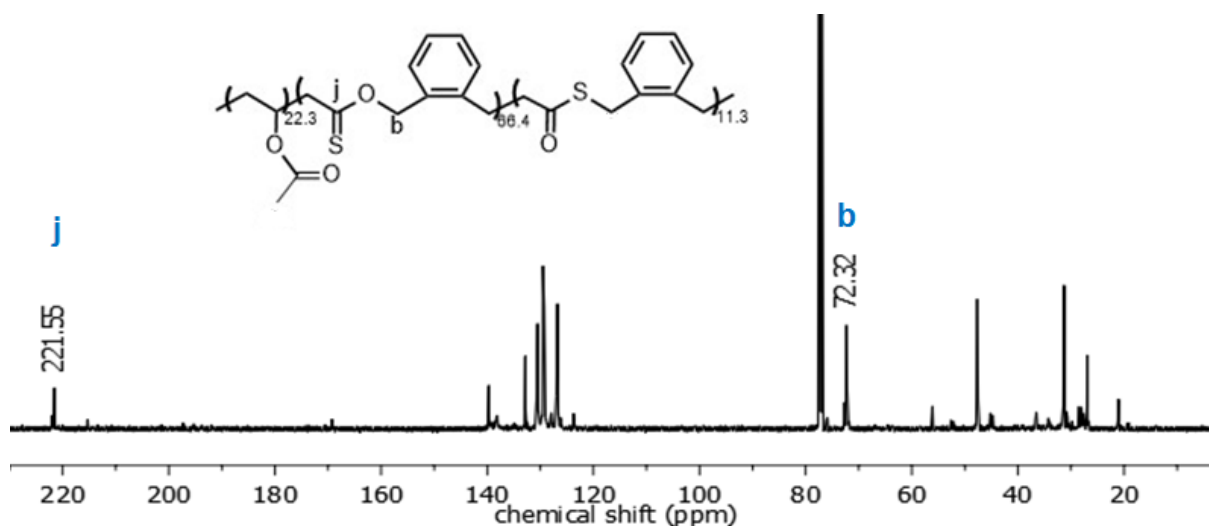


Figure S22. ^{13}C NMR (CDCl_3 , 176 MHz) of poly(VAc-co-O,S-BMDO).

Poly(AM_{88.6}-co-O,S-BMDO_{11.4})

The copolymer composition was then determined by taking the sum of the $\text{C}(\text{S})\text{OCH}_2$ protons and $\text{C}(\text{O})\text{SCH}_2$ protons of O,S-BMDO at 5.40–5.50 ppm and at 4.00–4.10 ppm (I_{BMDO}), respectively, and the integration of $\text{CHC}(\text{O})\text{NH}_2$ protons at 2.05–2.25 ppm (I_{AM}) and applying the following formula:

$a:b$ = molar ratio of O,S-BMDO : molar ratio of AM.

$I_{\text{BMDO}} = 2a$, $I_{\text{AM}} = b$, thus $a = I_{\text{BMDO}}/2$.

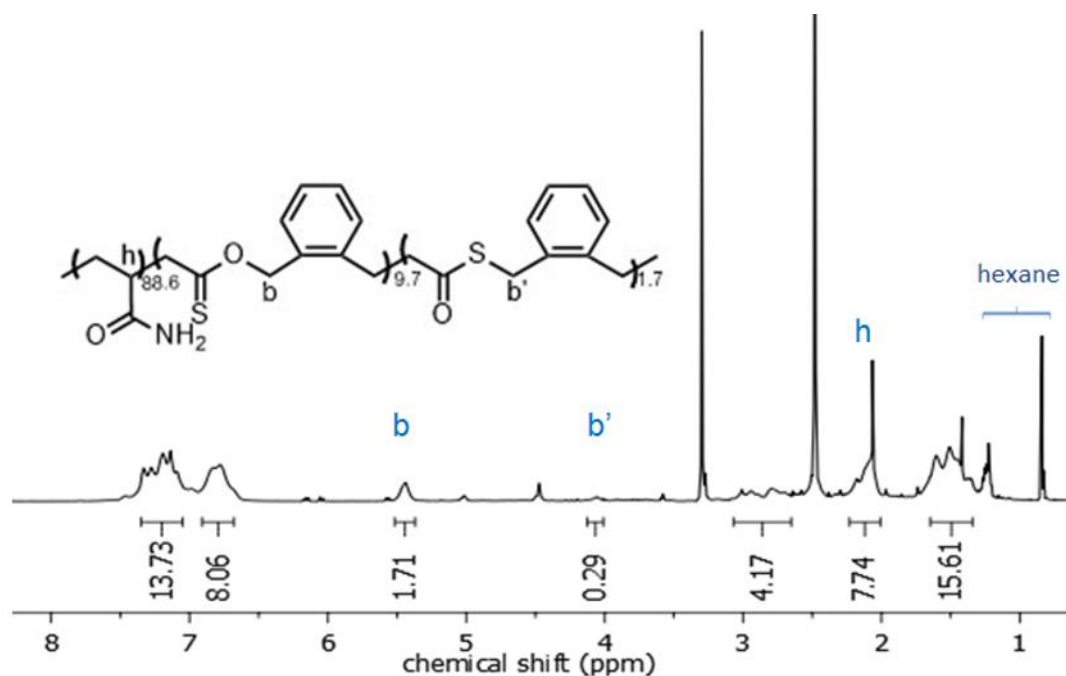


Figure S23. ^1H NMR (DMSO-d_6 , 700 MHz) of poly(AM-co-O,S-BMDO).

5. GPC of Styrene and *O,S*-BMDO copolymers

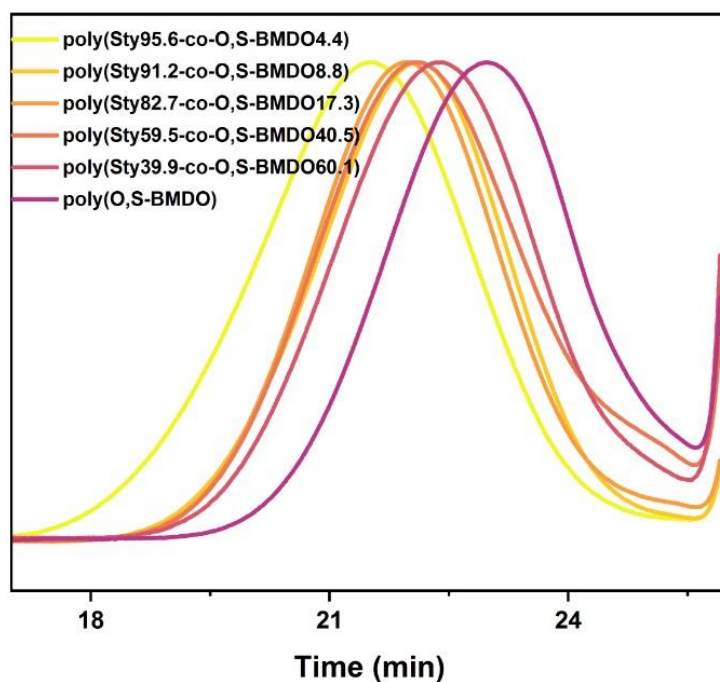


Figure S24. GPC traces of different compositions of polymers obtained from styrene/*O,S*-BMDO, and the homopolymer of *O,S*-BMDO. In most cases, the M_n decreased with increased *O,S*-BMDO (**8**) in the feed.

Copolymer	M_n (kg/mol)	\bar{D}
poly(Sty _{95.6} -co- <i>O,S</i> -BMDO _{4.4})	12.2	2.4
poly(Sty _{91.2} -co- <i>O,S</i> -BMDO _{8.8})	8.54	2.1
poly(Sty _{82.7} -co- <i>O,S</i> -BMDO _{17.3})	8.76	2.1
poly(Sty _{59.5} -co- <i>O,S</i> -BMDO _{40.5})	6.53	2.5
poly(Sty _{39.1} -co- <i>O,S</i> -BMDO _{60.9})	5.97	2.5
poly(<i>O,S</i> -BMDO)	3.62	2.6

Table S1. SEC results for copolymers of Sty/*O,S*-BMDO, and poly(*O,S*-BMDO).

6. Conversion

Conversion of styrene in the homopolymerization, as well as the conversion of styrene and *O,S*-BMDO (**8**) in the copolymerization, were calculated based on ^1H NMR.

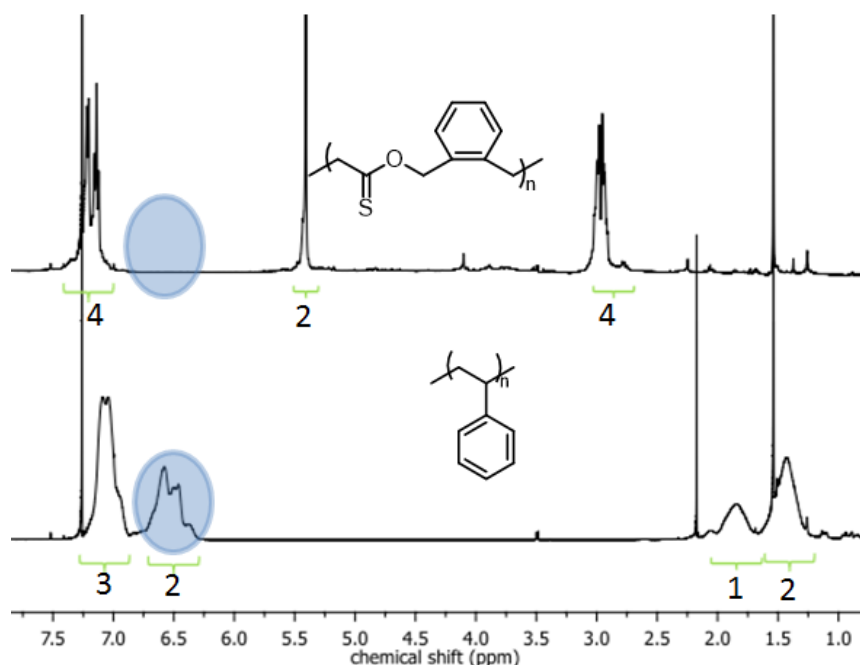


Figure S25. ^1H NMR spectra of poly(*O,S*-BMDO) and polystyrene with highlighted aromatic signals. For polystyrene, in the region at ca. 6.25–6.75 ppm the integration of the multiplet = 2.0. This region is empty in the ^1H NMR of *O,S*-BMDO and poly(*O,S*-BMDO). Therefore, these signals were used to calculate the amount of styrene monomer that underwent polymerization.

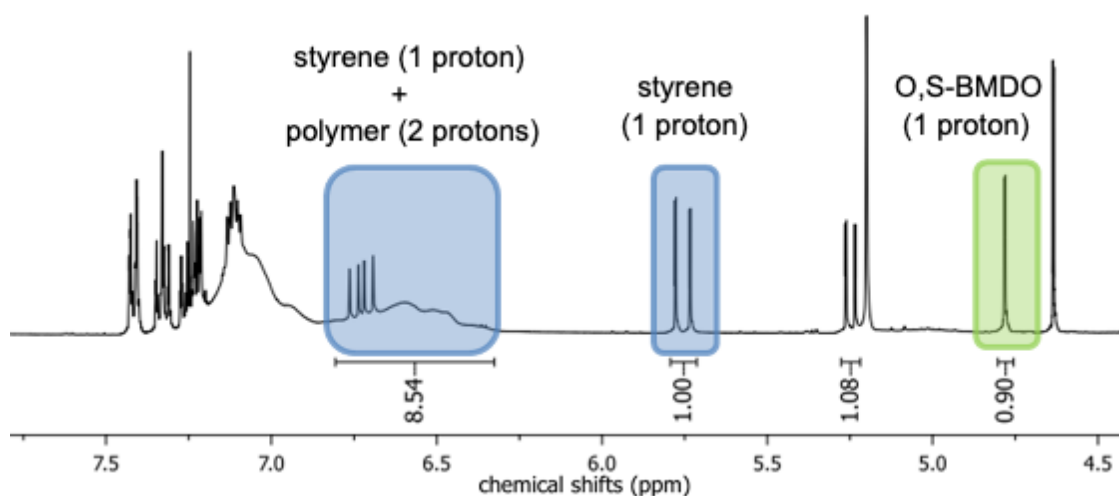


Figure S26. Example of ^1H NMR taken to determine the conversion of the monomers in the copolymerization (75 min).

Time (min)	Homopolymerization	Copolymerization		
	Conversion of Sty (%)	Conversion of Sty (%) (Sty_{conv})	Conversion of O,S-BMDO (%) ($O,S-BMDO_{conv}$)	Total Conversion (%)
0	0	0	0	0.0
15	12.5	15.2	5.1	13.2
30	34.9	29.9	10.2	25.9
45	56.2	63.9	13.5	53.9
60	68.9	71.1	16.8	60.2
75	77.2	79.0	24.5	68.1
90	90.0	91.8	32.0	79.8
105	-	92.5	37.6	81.6
120	-	93.1	43.4	83.2

Table S2. Conversion of styrene in the homopolymerization as well as conversion of styrene and O,S-BMDO (**8**) in copolymerization calculated based on 1H NMR. Total conversion = $a(Sty_{conv.}) + b(O,S-BMDO_{conv.})$ where a and b are the fractional composition of monomers (0.8 and 0.2 respectively).

7. Reactivity Ratio (Fineman-Ross, Kelen-Tüdös and Mayo-Lewis Methods)

In the Fineman-Ross method, G was plotted against H for each experiment yielding a straight line with slope r_1 and intercept r_2 . The G and H were calculated based on equations listed below (1-3). F refers to monomer feed, and f to copolymer composition:

$$G = r_1 H - r_2 \quad (1)$$

$$G = \frac{F_1}{F_2} \left(1 - \frac{f_2}{f_1} \right) \quad (2)$$

$$H = \left(\frac{F_1}{F_2} \right)^2 \left(\frac{f_2}{f_1} \right) \quad (3)$$

Entry	F ₁	F ₂	f ₁	f ₂	H	G	r ₁	r ₂
1	10	90	4.4	95.6	0.27	-2.30	0.96±0.17	2.52±0.32
2	20	80	8.8	91.2	0.65	-2.34		
3	30	70	17.3	82.7	0.88	-1.62		
4	50	50	40.5	59.5	1.47	-0.47		
5	70	30	60.1	39.9	3.61	0.78		

Table S3. Finemann-Ross method: F₁, f₁ and r₁ refers to O,S-BMDO and F₂, f₂ and r₂ refers to styrene.

Intercept -2,51573 ± 0,31593

Slope 0,96395 ± 0,17399

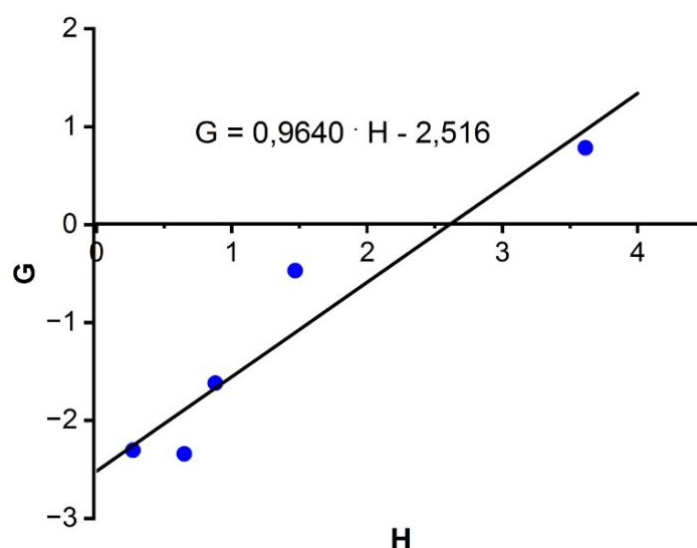


Figure S27. The Fineman-Ross plot for poly(Sty-co-O,S-BMDO).

In the Kelen-Tüdös method, arbitrary constant (α) is introduced. The previously defined values, G and H are modified, giving values ξ and η where r_1 and r_2 are the reactivity ratios of styrene and O,S-BMDO and G and H are variables defined from the Fineman-Ross technique. H_{\min} and H_{\max} are the minimum and maximum values of H determined from the data. Reactivity ratios r_1 and r_2 can be calculated by plotting ξ versus η for each experiment. See equation, table, and plot below:

$$\eta = \left(\frac{r_1+r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (4)$$

$$\eta = \frac{G}{\alpha+H} \quad (5)$$

$$\xi = \frac{H}{\alpha+H} \quad (6)$$

$$\alpha = (H_{\min}H_{\max})^{\frac{1}{2}} \quad (7)$$

Entry	F1	F2	f1	f2	α	ξ	η	r_1	r_2
1	10	90	4.4	95.6	0.970	0.214	-1.84	1.09±0.23	2.67±0.25
2	20	80	8.8	91.2		0.397	-1.43		
3	30	70	17.3	82.7		0.471	-0.87		
4	50	50	40.5	59.5		0.599	-0.191		
5	70	30	60.1	39.9		0.786	0.171		

Table S4. Kelen-Tüdös method: F₁, f₁ and r₁ refers to O,S-BMDO and F₂, f₂ and r₂ refers to styrene.

Intercept -2,70663 ± 0,25672

Slope 3,7985 ± 0,48489

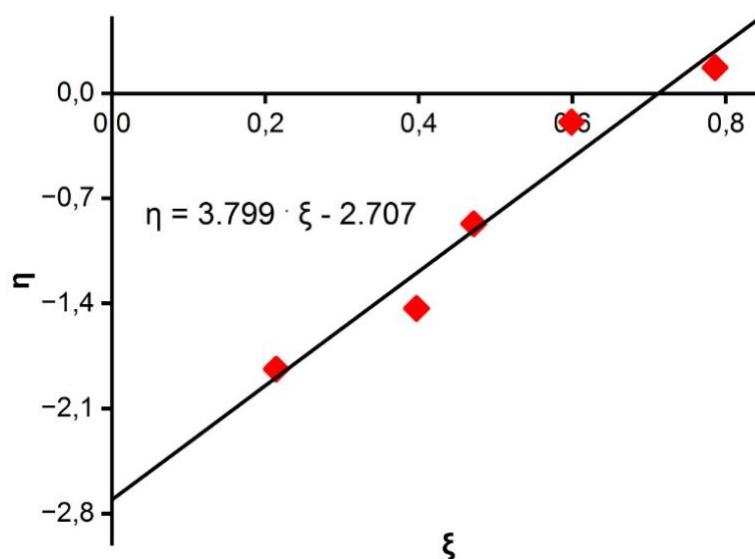


Figure S28. The Kelen-Tüdös plot for poly(Sty-co-O,S-BMDO).

The Mayo-Lewis method calculations were based on the equation:

$$r_2 = \frac{F_1}{F_2} \left[\frac{f_2}{f_1} \left(1 + \frac{F_1 r_1}{F_2} \right) - 1 \right] \quad (8)$$

For each different monomer composition, a line was generated using arbitrary r_1 and r_2 values. Then the point where the most lines were intersecting (entry 1, 3 and 5) r_1 and r_2 for the system was defined. See table and graph below:

Entry	F_1	F_2	f_1	f_2	$r_2 = ar_1 + b$ calculated from equation (8)	r_1	r_2
1	10	90	4.4	95.6	$r_2 = 0.268 r_1 + 2.30$	0.99 ±0.11	2.50±0.1
2	20	80	8.8	91.2	$r_2 = 0.6475 r_1 + 2.34$		
3	30	70	17.3	82.7	$r_2 = 0.880 r_1 + 1.62$		
4	50	50	40.5	59.5	$r_2 = 1.469 r_1 + 0.469$		
5	70	30	60.1	39.9	$r_2 = 3.613 r_1 - 0.784$		

Table S5. Mayo-Lewis method: F_1 , f_1 and r_1 refers to O,S-BMDO and F_2 , f_2 and r_2 refers to styrene.

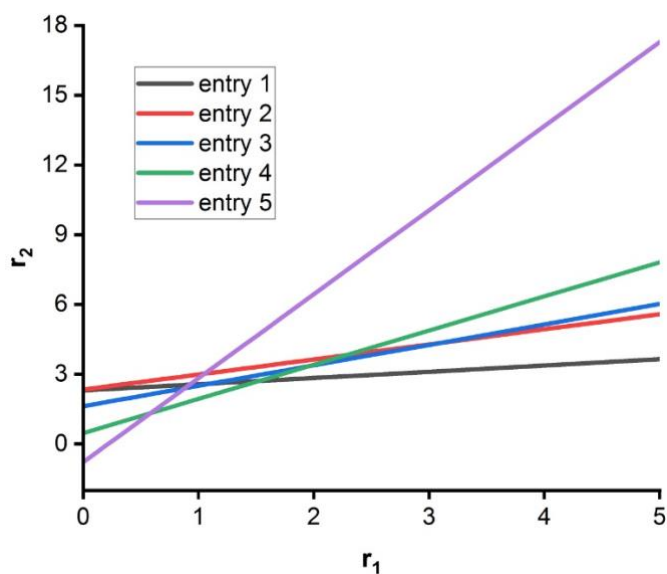


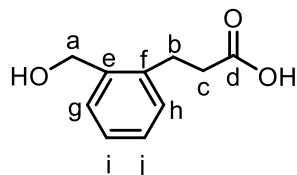
Figure S29. Line generated in Mayo-Lewis method for poly(Sty-co-O,S-BMDO)s.

8. Degradation

Degradation of poly(*O,S*-BMDO) – KOH.

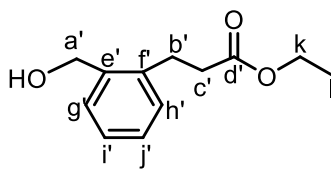
Degradation was performed by the addition of 2M KOH in EtOH/H₂O (4:1) at 80 °C for 18 h followed by dilution with water and lowering the pH value to ca. 6 by the dropwise addition of 1M HCl, followed by extraction with EtOAc.

Main product:

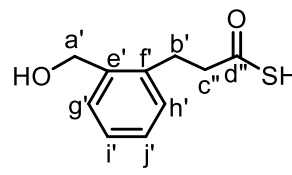


A

Other products:



B



C

Figure S30. Structural formulas of the putative products of alkaline hydrolysis.

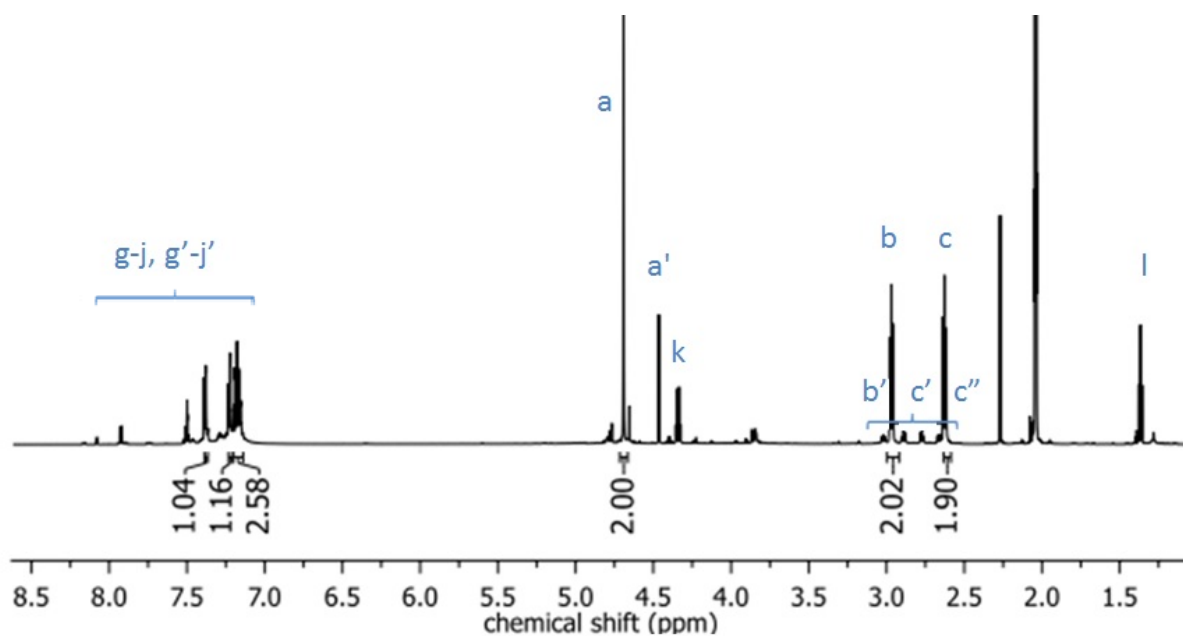


Figure S31. ¹H NMR (acetone-*d*₆, 700 MHz) of poly(*O,S*-BMDO) after alkaline hydrolysis.

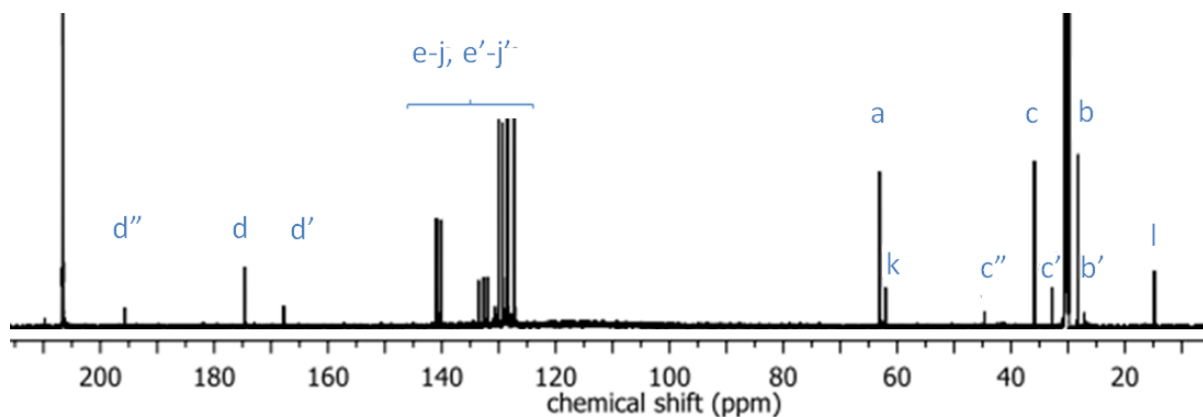


Figure S32. ¹³C NMR (CDCl₃, 176 MHz) of poly(*O,S*-BMDO) after alkaline hydrolysis.

Rearrangement and degradation of poly(Sty-co-O,S-BMDO) – AlCl₃.

Reaction: AlCl₃ (2.0 eq in relation to –C(S)O-) in chloroform, rt, 4 h.

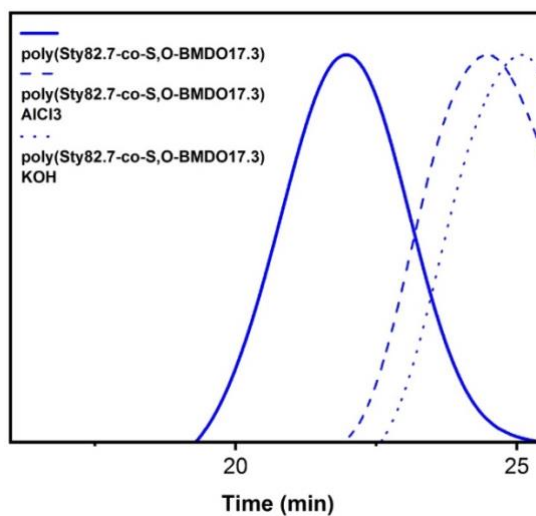


Figure S33. Changes in the GPC trace of poly(Sty_{82.7}-co-O,S-BMDO_{17.3}) after treatment with KOH or AlCl₃.

Polymer	<i>M_n</i> (kg/mol) ^a
poly(Sty _{82.7} -co-O,S-BMDO _{17.3})	8.76
poly(Sty _{82.7} -co-O,S-BMDO _{17.3}) - AlCl ₃ , chloroform, rt	<1.30 ^a
poly(Sty _{82.7} -co-O,S-BMDO _{17.3}) – KOH, EtOH, H ₂ O, 80 °C	<1.00 ^a

Table S6: Molecular weights of the copolymer samples treated with AlCl₃. ^a Difficult to accurately measure due to the overlapping of polymer and solvent signals.

9. Cartesian Coordinates and Energies (a.u.) of Stationary Points

R...M5

-1070.820381

S	0.09917400	-0.16508600	1.93227800
C	0.87671200	1.05588700	0.82564900
C	1.34845900	-1.77363400	-0.29367800
O	-0.00920400	-1.33095900	-0.45968200
H	1.04289500	1.95791600	1.43683900
H	0.12651100	1.31798000	0.05570800
H	1.43484000	-2.33560900	0.65576500
H	1.52994700	-2.48109200	-1.12025400
C	-0.71639100	-1.11691800	0.68983100
C	-1.97515600	-1.56789800	0.81895700
H	-2.40530400	-2.22982000	0.06301900
H	-2.59004000	-1.25433600	1.66421100
C	2.38124300	-0.66299800	-0.35771500
C	2.18539100	0.61891700	0.19710800
C	3.23473400	1.55173300	0.14052200
H	3.07894300	2.54466000	0.57780800
C	3.61215100	-0.96520700	-0.96215800
H	3.75086100	-1.95931400	-1.40313600
C	4.46111000	1.23777700	-0.45380600
H	5.26157700	1.98281300	-0.48239400
C	4.65181500	-0.03153100	-1.00996400
H	5.60207900	-0.29339800	-1.48420400
C	-3.52445200	0.91613900	-0.66895500
C	-2.56936900	1.01509700	-1.82001300
C	-3.25827100	1.71716400	0.56983800
C	-4.60196200	0.02834400	-0.71727300
N	-5.50938300	-0.71962500	-0.75575200
H	-1.60465400	0.54115900	-1.54761700
H	-2.94813100	0.52238400	-2.72648300
H	-2.35472700	2.07508500	-2.04577000
H	-2.23314100	1.51085500	0.93508700
H	-3.30645000	2.79901700	0.34496600
H	-3.96877300	1.49089700	1.37767300

TS (RM5)

-1070.80466

S	-0.01042500	1.03965200	1.51031400
C	0.97684800	1.42371600	0.02437200
C	1.17717200	-1.59450200	0.62826000
O	-0.12106500	-1.23002800	0.12598400
H	1.21416300	2.49827600	0.08888400
H	0.30707400	1.28616400	-0.84532300
H	1.15686700	-1.55689100	1.73439600
H	1.31997600	-2.64593600	0.32821800
C	-0.84235400	-0.37115500	0.90330300
C	-2.20166800	-0.57867300	1.04660800
H	-2.57941300	-1.59770900	0.91397200
H	-2.75557400	0.08151800	1.71846200
C	2.32667500	-0.76520700	0.08531300

C	2.25536800	0.62589900	-0.13528400
C	3.40693500	1.30646800	-0.56557900
H	3.34669100	2.38826900	-0.73082000
C	3.54069900	-1.43211000	-0.14640600
H	3.58404600	-2.51569100	0.01447000
C	4.61453600	0.63540100	-0.78241200
H	5.49614000	1.19040200	-1.11604400
C	4.68209900	-0.74580300	-0.57190300
H	5.61605000	-1.28897200	-0.74248800
C	-3.26005500	0.17992600	-0.71795100
C	-2.50491200	-0.47109600	-1.85411900
C	-3.10763700	1.67563200	-0.56539800
C	-4.52544200	-0.37178000	-0.38666200
N	-5.53111400	-0.86224900	-0.03714500
H	-1.46423300	-0.10398400	-1.85737400
H	-2.48609300	-1.56861600	-1.75745000
H	-2.95707700	-0.21427100	-2.83075400
H	-2.03480700	1.93386000	-0.54703700
H	-3.56611700	2.21035100	-1.41888600
H	-3.57416800	2.04446000	0.36205100

RM5

-1070.83542

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C	-0.96258900	1.44352000	0.06130300
C	-1.15763500	-1.54679200	-0.74235300
O	0.14350700	-1.24286400	-0.21727600
H	-1.20964000	2.51821600	0.05183200
H	-0.29942200	1.26205900	0.92812300
H	-1.13521900	-1.42176500	-1.84258700
H	-1.31713000	-2.61619300	-0.52495600
C	0.86402100	-0.30583000	-0.90809500
C	2.34687400	-0.46629800	-0.85792400
H	2.58365300	-1.54062400	-0.97764100
H	2.80197600	0.08258900	-1.70203600
C	-2.30122400	-0.74945100	-0.13812600
C	-2.23468300	0.62647000	0.17065200
C	-3.38892200	1.27261900	0.64551800
H	-3.33253800	2.34254600	0.87669900
C	-3.51321300	-1.43272500	0.05756700
H	-3.55370200	-2.50421200	-0.17103200
C	-4.59352700	0.58531800	0.82483100
H	-5.47584600	1.11543500	1.19520200
C	-4.65609500	-0.78033300	0.52965200
H	-5.58684000	-1.33770200	0.66946800
C	3.04992000	0.03225100	0.46547000
C	2.43875600	-0.64284700	1.71120600
C	2.97663800	1.56774200	0.59958500
C	4.46765000	-0.36412400	0.35134900
N	5.57912000	-0.68663600	0.23527500
H	1.40189200	-0.28776800	1.83319000
H	2.42061700	-1.73927200	1.60232200
H	3.01087800	-0.37703700	2.61406200
H	1.92610700	1.86752600	0.74016300
H	3.55484700	1.90543400	1.47450100
H	3.36551700	2.06611400	-0.30324100

TS (RM5-Oopening)
-1070.80967

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C	-1.35742900	1.50785400	0.28825200
C	-1.21271500	-1.48836500	-0.61291700
O	0.15866400	-0.82623300	0.48399100
H	-1.70387800	2.55344900	0.25145200
H	-0.95184400	1.33248000	1.30215300
H	-0.74598900	-1.17117000	-1.55055200
H	-1.17167200	-2.56734900	-0.43226600
C	0.86449200	0.02580600	-0.15805600
C	2.22629800	-0.30531800	-0.71650800
H	2.22511600	-1.36662400	-1.03128200
H	2.44409200	0.32348300	-1.60071400
C	-2.44826500	-0.80988200	-0.20831400
C	-2.54305800	0.58546300	0.05238700
C	-3.81305700	1.13782100	0.29018700
H	-3.88698800	2.21388100	0.48459000
C	-3.61970600	-1.59544200	-0.12326500
H	-3.53115100	-2.67420600	-0.29387800
C	-4.97139900	0.35365000	0.31705300
H	-5.94239500	0.82059900	0.50565500
C	-4.87047900	-1.02972800	0.12804500
H	-5.76055800	-1.66423000	0.16800200
C	3.37496100	-0.09328200	0.32924900
C	3.18313700	-1.00331600	1.56137300
C	3.44720200	1.38742600	0.76135500
C	4.63817000	-0.45802400	-0.34376700
N	5.62625800	-0.74763300	-0.88380000
H	2.26082900	-0.70203100	2.08334900
H	3.09028600	-2.06028400	1.26385400
H	4.03441500	-0.89670500	2.25215600
H	2.51917800	1.64162100	1.30051800
H	4.30397600	1.55364800	1.43292100
H	3.53940500	2.05263400	-0.11308300

TS (RM5-Sopening)
-1070.8099

S	-0.14809900	0.92029600	1.72216100
C	1.04105700	1.47324000	-0.30907800
C	1.16324900	-1.52155800	0.61729300
O	-0.20525100	-1.26860500	0.25183100
H	1.14749600	2.56338000	-0.33154000
H	0.18622500	1.08653900	-0.86588500
H	1.23553000	-1.41698900	1.71822000
H	1.31021400	-2.58403100	0.36077400
C	-0.89556000	-0.33830200	0.95385800
C	-2.38524400	-0.52566200	0.81878900
H	-2.60186700	-1.60981200	0.83427600
H	-2.87893000	-0.05469000	1.68413900
C	2.28402400	-0.71431800	-0.02219800
C	2.26060600	0.68298300	-0.29366600
C	3.48564200	1.32603900	-0.59313600
H	3.46521000	2.40599700	-0.77792700
C	3.49462900	-1.40963500	-0.16161400

H	3.50438600	-2.48935900	0.03052100
C	4.68402400	0.62296500	-0.69690700
H	5.60874400	1.15108000	-0.94734700
C	4.68790600	-0.76316000	-0.49921900
H	5.61376800	-1.33746200	-0.59363400
C	-3.03041800	0.07166600	-0.48340800
C	-2.40600800	-0.52905800	-1.76070800
C	-2.93686900	1.61237500	-0.50188400
C	-4.45814800	-0.31026900	-0.43566600
N	-5.57823200	-0.61651300	-0.38869700
H	-1.36136000	-0.19252200	-1.85716600
H	-2.41184600	-1.63033300	-1.72428600
H	-2.96566600	-0.19675900	-2.64942400
H	-1.88228600	1.92109900	-0.57366400
H	-3.48386400	2.01513700	-1.36939100
H	-3.35986700	2.04458800	0.41925300

RM5-Oopened
-1070.86

S	0.05298600	-0.72661100	-0.27909600
C	1.34615700	-0.64125800	1.00693500
C	2.17297400	2.04780300	0.01357600
O	-1.05198600	1.09371600	1.31068500
H	1.34904300	-1.60784800	1.53415200
H	1.01639400	0.14312300	1.70975200
H	2.49146500	3.01979700	-0.36998500
H	1.18641700	1.98580200	0.47391000
C	-1.15438700	0.43143100	0.29555300
C	-2.35855300	0.50498300	-0.63902800
H	-2.52860200	1.56734000	-0.88728700
H	-2.14411200	-0.04709900	-1.57061200
C	3.04975700	0.94369100	-0.07431100
C	2.70294300	-0.36824400	0.40526300
C	3.62559000	-1.40953400	0.29619900
H	3.34502800	-2.40169800	0.66831800
C	4.34650200	1.11346600	-0.65388400
H	4.61757900	2.11027100	-1.01935500
C	4.89443800	-1.21264500	-0.27244900
H	5.59851600	-2.04622000	-0.34184200
C	5.24779700	0.06150800	-0.75156900
H	6.23270600	0.22570900	-1.19886900
C	-3.65043800	-0.08270400	0.02007700
C	-4.16318400	0.79265300	1.18537200
C	-3.41485100	-1.53212800	0.50128100
C	-4.68140100	-0.09618300	-1.03957600
N	-5.49414500	-0.10616400	-1.87033300
H	-3.43277900	0.76755700	2.00722100
H	-4.30247100	1.83699700	0.86404500
H	-5.12477000	0.39946200	1.55154700
H	-2.69729800	-1.51695200	1.33920100
H	-4.35781700	-1.97481100	0.85729800
H	-3.00224100	-2.15925600	-0.30573700

RM5-Sopened
-1070.82932

S	-1.24442000	2.60592400	-0.51069500
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C	1.85983000	0.67933600	1.92838500
C	0.73509700	-0.81382600	-0.38896600
O	0.14639100	0.47973500	-0.72898000
H	2.29184700	1.22852700	2.76737600
H	0.77514800	0.56672900	1.91729000
H	0.25937000	-1.23780000	0.50864900
H	0.54726800	-1.48372000	-1.24378400
C	-0.93509400	1.02314400	-0.17842100
C	-1.86902100	0.20967300	0.70350300
H	-1.32991100	-0.52757900	1.32239100
H	-2.36800500	0.91803000	1.38137700
C	2.21346000	-0.60402800	-0.19628700
C	2.70443400	0.13448600	0.93622600
C	4.11988100	0.30737400	1.04396200
H	4.50513200	0.87094800	1.90065400
C	3.10705000	-1.12336500	-1.13146300
H	2.71006400	-1.67952300	-1.98820100
C	4.99265000	-0.22330500	0.10271000
H	6.07078200	-0.07555100	0.21587400
C	4.49379900	-0.94845600	-0.99407200
H	5.17589500	-1.36775900	-1.73822200
C	-2.98497500	-0.55309000	-0.10266500
C	-2.39642000	-1.57097500	-1.10301300
C	-3.93588000	0.41388900	-0.84158400
C	-3.76687100	-1.28918100	0.91348100
N	-4.37971100	-1.87022300	1.71178400
H	-1.80597700	-1.02949400	-1.86182800
H	-1.75619600	-2.31325700	-0.60087700
H	-3.21159600	-2.10210800	-1.61822800
H	-3.39678000	0.88937200	-1.67550100
H	-4.78961600	-0.14983800	-1.24948100
H	-4.30749500	1.20186200	-0.16778600

R...Sty

-519.946423

C	-0.30255100	1.42455400	0.76670000
C	0.77622500	1.03324300	1.46854100
H	1.60353400	1.72144300	1.66227500
H	0.89053500	0.01809400	1.86567100
H	-0.33810300	2.45905700	0.39642400
C	-1.63470400	-0.73847600	0.80027500
C	-2.77366000	-1.45906400	0.43936700
C	-3.79104300	-0.85116600	-0.31354100
C	-3.65605200	0.48627600	-0.70280700
C	-2.51360500	1.20754600	-0.34010400
C	-1.48347000	0.61250900	0.41655000
H	-0.85023400	-1.23054700	1.38508900
H	-2.87281800	-2.50468000	0.74685600
H	-4.68228200	-1.42044700	-0.59351600
H	-4.44233300	0.97034400	-1.29001300
H	-2.40634400	2.25573300	-0.64264000
C	2.65725200	-0.33206200	-0.74866700
C	2.69199900	0.80118000	-1.72808400
C	1.58446700	-1.37145700	-0.88003500
C	3.57673500	-0.39627800	0.30098100
N	4.34064200	-0.44809100	1.19439400

H	1.75576000	1.38751100	-1.63838000
H	3.54758400	1.47206700	-1.56985000
H	2.72500000	0.41328100	-2.76269000
H	0.61718200	-0.87715300	-1.08535700
H	1.79346000	-2.04081900	-1.73621200
H	1.48500900	-1.98806900	0.02653000

TS (RSty)

-519.926989

C	0.07752200	0.94798100	-0.98689300
C	-1.07240200	0.26267000	-1.32742900
H	-1.88285400	0.79652100	-1.83205700
H	-1.06941000	-0.82388100	-1.46418600
H	0.04719500	2.04563000	-1.01142400
C	1.56079600	-1.02138000	-0.42201800
C	2.78378300	-1.51235900	0.03039200
C	3.81429600	-0.63155200	0.39984000
C	3.60573300	0.75202200	0.31057000
C	2.38155500	1.24676800	-0.14068000
C	1.32914900	0.37521400	-0.51677800
H	0.77198600	-1.72509000	-0.70617400
H	2.94158600	-2.59331400	0.09566800
H	4.77219100	-1.02373000	0.75336500
H	4.40202200	1.44645600	0.59523300
H	2.21593000	2.32798100	-0.21100000
C	-2.32286600	0.09381900	0.53265000
C	-2.53359800	1.54555000	0.88808300
C	-1.42971800	-0.71618400	1.43848700
C	-3.39378200	-0.58517200	-0.10266400
N	-4.23799700	-1.14308200	-0.69380800
H	-1.55429700	2.02042000	1.06988600
H	-3.05558500	2.09280200	0.08748500
H	-3.13044600	1.63808300	1.81515600
H	-0.48097500	-0.17582600	1.59693400
H	-1.90456900	-0.85814500	2.42823200
H	-1.20959600	-1.71060500	1.01817500

RSty

-519.959852

C	0.06469100	0.97002500	-0.67829000
C	-1.19543600	0.22825800	-0.99432400
H	-1.74421800	0.75986700	-1.79449900
H	-0.98921200	-0.79222800	-1.36266900
H	0.01364600	2.06500100	-0.68730800
C	1.55930500	-1.01408900	-0.28670300
C	2.82252400	-1.51562700	0.01455400
C	3.90486100	-0.64883400	0.24430000
C	3.70330700	0.74153400	0.16933300
C	2.44642500	1.25260200	-0.13066600
C	1.32917000	0.39330600	-0.37129100
H	0.73377100	-1.71156200	-0.45584000
H	2.97155300	-2.59837200	0.07369700
H	4.89356100	-1.05186100	0.48037500
H	4.53927000	1.42509600	0.34746400
H	2.28959200	2.33570800	-0.19035900
C	-2.17189200	0.11094900	0.23521200

C	-2.53286600	1.50789900	0.78446800
C	-1.55303700	-0.75847600	1.34987500
C	-3.40203000	-0.54382700	-0.25220000
N	-4.36280200	-1.06208200	-0.65305900
H	-1.62516200	1.96573300	1.21107300
H	-2.91950100	2.16104900	-0.01493700
H	-3.29075000	1.42816600	1.57944200
H	-0.61609300	-0.28553500	1.68916600
H	-2.24090700	-0.83587500	2.20682300
H	-1.32606700	-1.77293800	0.98338000

RSty...M5
-1380.019841

C	1.17550900	1.32277400	0.22933800
H	0.16570000	1.27676000	0.68263000
H	1.76434100	2.05288900	0.81234600
C	4.16246400	0.62778400	0.75623600
C	5.48064300	0.25207300	0.99983500
C	5.85419100	-1.10307700	1.00016700
C	4.88154100	-2.08820500	0.74835800
C	3.56316700	-1.72402500	0.50381500
C	3.15614500	-0.35330600	0.50147000
H	3.89857200	1.68965300	0.75356800
H	6.23368900	1.02301700	1.19111200
H	6.89210100	-1.38851800	1.19235000
H	5.16343200	-3.14571100	0.74447600
H	2.80277300	-2.48988600	0.30698500
C	0.98975100	1.89386000	-1.22595900
C	0.18763200	0.90515500	-2.09988500
C	2.35546800	2.20566400	-1.87101100
C	0.21096100	3.14158600	-1.09679500
N	-0.41088400	4.11683500	-0.97411900
H	0.79102300	-0.00350700	-2.26649000
H	-0.74957800	0.61601900	-1.59589300
H	-0.05090100	1.35359500	-3.07744200
H	2.93788400	1.27047100	-1.92979200
H	2.22341200	2.60373400	-2.88970200
H	2.92168300	2.93842200	-1.27266400
S	-3.00924600	1.26808400	0.86218000
C	-3.83198300	0.04778900	-0.21207200
C	-1.64333800	-1.40714100	1.40117100
O	-2.79765000	-1.04237900	2.16834100
H	-4.33137900	0.62521000	-1.00650100
H	-4.61694100	-0.43973100	0.39002700
H	-0.84826000	-0.64937600	1.55747700
H	-1.28321000	-2.35269500	1.84242700
C	-2.98795900	0.30081300	2.33987000
C	-1.88878800	-1.62410400	-0.08346800
C	-2.87811500	-0.95333500	-0.83179200
C	-2.96224900	-1.19099400	-2.21452600
H	-3.72819300	-0.66074800	-2.79178200
C	-1.02264000	-2.51481400	-0.73987000
H	-0.26608500	-3.04551400	-0.14683800
C	-2.08101800	-2.06224400	-2.86267400
H	-2.16220500	-2.22008400	-3.94201100
C	-1.09901400	-2.72725400	-2.11962100

H	-0.40414100	-3.41676200	-2.60762200
C	-3.17584200	0.82393900	3.56184500
H	-3.46483300	1.86865000	3.67713200
H	-3.04769800	0.20139200	4.44996500
C	1.79251200	-0.03849500	0.24647600
H	1.12990400	-0.88210200	0.01800500

TS (RStyM5)
-1379.993448

C	-1.74781800	1.28658500	-0.51043200
H	-0.77590800	1.46660200	-1.00739200
H	-2.52522900	1.45931200	-1.27478300
C	-4.23238200	-0.56024700	-0.61503400
C	-5.36456800	-1.37458300	-0.53397700
C	-5.35545400	-2.54321400	0.24138400
C	-4.18767100	-2.89176400	0.93992000
C	-3.05712700	-2.08138100	0.86348400
C	-3.04666500	-0.88845500	0.09089500
H	-4.27752700	0.34575500	-1.22644800
H	-6.26863700	-1.09157300	-1.08263500
H	-6.24610500	-3.17499100	0.30088300
H	-4.16372000	-3.80137000	1.54847100
H	-2.14355200	-2.35698200	1.40601200
C	-1.88309000	2.38699700	0.60075100
C	-0.66443200	2.35576500	1.55126400
C	-3.19678100	2.23667100	1.39717400
C	-1.89463600	3.68922500	-0.09599600
N	-1.90432500	4.70508300	-0.66221900
H	-0.69004700	1.42815400	2.14675600
H	0.27929500	2.38749600	0.97830400
H	-0.68937300	3.20953600	2.24675800
H	-3.16883900	1.28401800	1.95192400
H	-3.31219800	3.06258100	2.11700300
H	-4.06887300	2.22220300	0.72266900
S	1.60010200	0.41084800	-1.78593300
C	3.24792100	-0.36856700	-1.83573300
C	1.93343100	-0.98321300	0.87965000
O	1.34181200	-1.71525100	-0.20847400
H	3.81850000	0.18281200	-2.60049000
H	3.09975000	-1.39725700	-2.20773000
H	1.36338900	-0.04368300	1.03562100
H	1.79214400	-1.61439400	1.77362900
C	0.70970300	-0.95938000	-1.15917700
C	3.41224500	-0.68535800	0.71155800
C	4.00658600	-0.35324200	-0.52374400
C	5.37336000	-0.02819400	-0.55381300
H	5.82932000	0.23435700	-1.51532800
C	4.20416700	-0.69667200	1.87101500
H	3.73671300	-0.97033500	2.82428800
C	6.15195800	-0.03159600	0.60795600
H	7.21372400	0.22630000	0.55531100
C	5.56287400	-0.36902300	1.83101500
H	6.15735100	-0.38334800	2.74908500
C	-0.62246800	-1.21119000	-1.43449500
H	-1.06499400	-0.78100300	-2.33778600
H	-1.02966400	-2.16329900	-1.08060400

C	-1.81108500	-0.12236500	0.01549200
H	-1.09978800	-0.35885000	0.81978700

RStyM5

-1380.024226

C	2.01689300	1.06401900	0.79129500
H	1.19415300	1.26814700	1.50345600
H	2.93426800	0.91515500	1.38952600
C	3.71607200	-1.56307900	0.79792200
C	4.82483200	-2.38448800	0.56668800
C	5.17325900	-2.74422500	-0.74223000
C	4.40179200	-2.28033200	-1.81430900
C	3.29104300	-1.46077400	-1.57618200
C	2.93614500	-1.08589300	-0.27073100
H	3.44989100	-1.28969600	1.82647500
H	5.41968600	-2.74552900	1.41145600
H	6.04252200	-3.38311200	-0.92442300
H	4.66483600	-2.55586300	-2.84034100
H	2.68738600	-1.09772900	-2.41739800
C	2.19913600	2.33584000	-0.08800600
C	0.85736400	2.77088600	-0.72354900
C	3.27625500	2.13332200	-1.17781400
C	2.64491800	3.41713300	0.81642000
N	2.99383600	4.26303800	1.53386700
H	0.52251300	2.00612000	-1.44301000
H	0.08007100	2.88662800	0.05177200
H	0.97305200	3.72556000	-1.26108900
H	2.90651300	1.40924700	-1.92210200
H	3.48951600	3.08235000	-1.69493300
H	4.20979800	1.73988200	-0.74202700
S	-1.89471200	-0.78094900	2.00901100
C	-3.02609600	-1.72345100	0.91824600
C	-2.25770200	0.95778300	-0.41373600
O	-1.17058500	0.02387700	-0.41774100
H	-3.57761200	-2.42562400	1.56494100
H	-2.38474300	-2.32361000	0.24792400
H	-2.18153100	1.58744900	0.49578600
H	-2.09354000	1.60977600	-1.28991200
C	-0.69465600	-0.34199800	0.81336400
C	-3.63395200	0.32477400	-0.51848800
C	-4.00351400	-0.87196100	0.13347800
C	-5.33141000	-1.31945300	0.02683000
H	-5.61468100	-2.24513500	0.54093400
C	-4.59759100	1.01881000	-1.26885300
H	-4.29839200	1.93917700	-1.78406400
C	-6.28654600	-0.61422500	-0.71232300
H	-7.31299800	-0.98705800	-0.77666500
C	-5.91630400	0.56500200	-1.36726700
H	-6.64700100	1.12738300	-1.95575700
C	0.62535500	-1.05512100	0.73626400
H	0.96570000	-1.27958500	1.76379900
H	0.50233300	-2.03534800	0.22028400
C	1.70406100	-0.22702300	-0.01177400
H	1.27535500	0.04103300	-0.99541200

TS (RStyM5-Opening)

-1380.000693

C	-1.43371700	0.92894300	-0.79636900
H	-0.40512800	1.00928700	-1.20065700
H	-2.10163300	0.86031200	-1.67616800
C	-3.89932100	-0.99911800	-0.78145900
C	-5.20393800	-1.44485900	-0.54020500
C	-5.62170900	-1.72909900	0.76674300
C	-4.72145600	-1.57317900	1.82797700
C	-3.41732300	-1.12754000	1.58096000
C	-2.99305200	-0.82262000	0.27828000
H	-3.58392500	-0.78865500	-1.81034700
H	-5.89741600	-1.57213500	-1.37727500
H	-6.64237000	-2.07464300	0.95557700
H	-5.03529900	-1.79705700	2.85228500
H	-2.71388000	-0.99837000	2.41290000
C	-1.74367500	2.26476500	-0.04762200
C	-0.66140200	2.60771100	1.00253600
C	-3.13502400	2.28610500	0.62544300
C	-1.71737800	3.32512900	-1.07934600
N	-1.69510200	4.15523800	-1.89313700
H	-0.61419000	1.80617400	1.75920600
H	0.33008400	2.71904700	0.53501200
H	-0.91528900	3.54916900	1.51542700
H	-3.12022000	1.62094600	1.50335200
H	-3.37090300	3.30668600	0.96695200
H	-3.92369900	1.94205300	-0.06332300
S	1.62541300	-0.94816600	-1.98236900
C	3.27073500	-1.39657100	-1.36250200
C	1.89848500	0.02153300	1.05324300
O	1.22630300	-1.62522200	0.51343400
H	3.90592100	-1.45000300	-2.26175700
H	3.16486400	-2.42727100	-0.97573100
H	1.32269600	0.60045600	0.32581500
H	1.54292200	0.11980600	2.08573100
C	0.66286600	-1.52754700	-0.63358500
C	3.34976600	-0.02627500	0.85851200
C	3.96640100	-0.53706100	-0.31768000
C	5.35801400	-0.40118700	-0.45563300
H	5.83385200	-0.78760100	-1.36425100
C	4.16859200	0.51155000	1.87618900
H	3.68492300	0.87545600	2.78966200
C	6.15014800	0.18059900	0.54043300
H	7.23090300	0.26807300	0.39626600
C	5.55150600	0.62323900	1.72620800
H	6.15586000	1.06142400	2.52571900
C	-0.83962300	-1.53242000	-0.77189400
H	-1.13250200	-1.48133200	-1.83822300
H	-1.21338400	-2.49560700	-0.37523800
C	-1.55707300	-0.38231500	0.01438900
H	-1.04444700	-0.27915100	0.99373800

TS (RStyM5-Sopening)

-1380.001382

C	-2.04086000	1.09117700	-0.72519200
H	-1.25905600	1.27023200	-1.48828600
H	-3.00746300	1.04226800	-1.25817400

C	-3.78279600	-1.50071500	-0.95087200
C	-4.92414400	-2.29578600	-0.80491000
C	-5.34684400	-2.69162000	0.47173400
C	-4.61819900	-2.28997400	1.59730600
C	-3.47263100	-1.49787700	1.44533000
C	-3.04346300	-1.09004200	0.17299900
H	-3.45839300	-1.19226200	-1.95266500
H	-5.48725100	-2.60737400	-1.69006700
H	-6.24192600	-3.31002100	0.58711300
H	-4.94125400	-2.59325900	2.59798600
H	-2.90037700	-1.18571600	2.32770000
C	-2.06325000	2.32588800	0.22312000
C	-0.65698800	2.60635400	0.80306000
C	-3.10272900	2.15861100	1.35511400
C	-2.45482600	3.48879200	-0.60145200
N	-2.76292500	4.39919700	-1.25563800
H	-0.34436900	1.76435900	1.44392700
H	0.08121900	2.72401400	-0.00923700
H	-0.66382000	3.52054800	1.41763000
H	-2.77227500	1.36221100	2.04180500
H	-3.20167500	3.09130800	1.93267800
H	-4.08824000	1.88024100	0.94589500
S	1.57013600	0.16168300	-1.91466700
C	3.24779000	-1.47355500	-1.40428400
C	2.25951400	0.32570100	0.98130700
O	1.14769300	-0.50626100	0.60292700
H	3.69932200	-1.77772700	-2.35485800
H	2.44632100	-2.12716400	-1.05374500
H	2.13664000	1.30279200	0.47403400
H	2.11879200	0.48108000	2.06400000
C	0.65849200	-0.40925200	-0.65369200
C	3.67476000	-0.17892900	0.74147900
C	4.13212300	-0.86488100	-0.42036300
C	5.52994100	-0.98570200	-0.61604700
H	5.87819700	-1.49104700	-1.52383800
C	4.61704700	0.25517800	1.68732200
H	4.25782000	0.76659100	2.58818300
C	6.45209700	-0.52170400	0.32097800
H	7.52398700	-0.64899500	0.14307700
C	5.99285800	0.08797500	1.49573100
H	6.69799000	0.44424800	2.25193200
C	-0.68890000	-1.07044700	-0.75437900
H	-0.96710900	-1.17916600	-1.81568100
H	-0.62515700	-2.07962300	-0.30037900
C	-1.78063200	-0.25624100	0.00487900
H	-1.37532600	-0.06646800	1.01668900

RStyM5-Oopened

-1380.063408

C	-1.24659400	0.80931000	-0.24869700
H	-0.14901800	0.66131500	-0.23133200
H	-1.53228600	0.86584500	-1.31500100
C	-3.54151900	-0.89490100	-1.52727100
C	-4.81038300	-1.19406000	-2.03653400
C	-5.91108200	-1.28734900	-1.17477100
C	-5.73194400	-1.08468700	0.19908900

C	-4.46024200	-0.78678700	0.70327300
C	-3.35123100	-0.68063400	-0.15109900
H	-2.68689300	-0.83280800	-2.21175500
H	-4.93968600	-1.35603000	-3.11106800
H	-6.90361200	-1.51779900	-1.57304000
H	-6.58475200	-1.15609100	0.88115800
H	-4.32116700	-0.62217900	1.77910000
C	-1.53424700	2.19053400	0.41314900
C	-0.92759500	2.28998600	1.83339800
C	-3.04491900	2.50673000	0.46008200
C	-0.84832900	3.19593800	-0.42724600
N	-0.28599800	3.97390800	-1.08380000
H	-1.39549200	1.54492500	2.49575600
H	0.15842000	2.10684500	1.81524400
H	-1.11204600	3.29140700	2.25431700
H	-3.52439400	1.83915200	1.19481000
H	-3.21291200	3.54807600	0.77737700
H	-3.51930500	2.34346300	-0.52201900
S	1.61465100	-2.03082700	-0.01156000
C	3.07783300	-1.63354200	1.00699600
C	2.61779100	1.25546000	0.46494900
O	0.36226400	-0.94914700	2.06931400
H	3.55126300	-2.58376500	1.29829900
H	2.68788200	-1.14076100	1.91437600
H	1.91915100	0.75214500	1.13318100
H	2.42765400	2.30615300	0.22634300
C	0.25781000	-1.46927600	0.97353500
C	3.76981500	0.60853100	-0.03561600
C	4.04993500	-0.77851400	0.22883900
C	5.21705700	-1.35348600	-0.27583400
H	5.41589700	-2.41098400	-0.06680900
C	4.71060000	1.33640700	-0.82843000
H	4.49966800	2.39163200	-1.03440100
C	6.13165900	-0.61104200	-1.04053600
H	7.04022400	-1.08664800	-1.41976400
C	5.86594000	0.74157900	-1.31891700
H	6.56911100	1.32647000	-1.91927500
C	-1.08187700	-1.65984100	0.26844100
H	-0.92137100	-1.90258800	-0.79863300
H	-1.58796300	-2.52646300	0.73250900
C	-1.96438100	-0.39465600	0.41607900
H	-2.07346800	-0.20646800	1.50040800

RStyM5-Sopened
-1380.039294

C	-1.82521400	1.36509900	-0.16364800
H	-1.43326600	1.93031900	-1.02965000
H	-2.92087900	1.50609600	-0.16268800
C	-3.89404900	-0.93073300	-0.64022000
C	-4.96754200	-1.77617300	-0.34185400
C	-4.83746700	-2.75245600	0.65551700
C	-3.62707000	-2.87834200	1.34717600
C	-2.55316400	-2.03234700	1.04144900
C	-2.67406600	-1.04709800	0.04935600
H	-4.00321300	-0.16810400	-1.42135900
H	-5.90979900	-1.67272700	-0.88866700

H	-5.67802200	-3.41140200	0.89244400
H	-3.51676900	-3.63670000	2.12841000
H	-1.60412200	-2.13257400	1.58245400
C	-1.24597200	2.01637800	1.12711700
C	0.30045400	2.06244100	1.08739600
C	-1.73807200	1.29264500	2.40131000
C	-1.74325900	3.40823100	1.15795900
N	-2.13679200	4.50202200	1.17687300
H	0.70699900	1.03962900	1.14946400
H	0.65206300	2.52773900	0.14834200
H	0.69602300	2.63775100	1.93984300
H	-1.30172500	0.28101500	2.43895000
H	-1.42181700	1.83777200	3.30462700
H	-2.83691900	1.19998500	2.40108200
S	0.51611600	1.37315700	-3.21425400
C	3.40846800	-2.45854000	-1.09657200
C	2.57442600	0.38906700	-1.26353300
O	1.24527700	-0.20149500	-1.21478300
H	3.73747800	-3.49772800	-1.02895800
H	2.82386300	-2.16887700	-1.97033200
H	3.01512500	0.14487900	-2.24815200
H	2.47242300	1.48604300	-1.19590500
C	0.30777800	0.22984100	-2.05101300
C	3.36011100	-0.16203400	-0.10574800
C	3.74848700	-1.54645600	-0.07277300
C	4.51071100	-1.98958700	1.05311900
H	4.81328300	-3.04197100	1.08789300
C	3.72732700	0.68952000	0.93637300
H	3.41862900	1.74139100	0.89020600
C	4.86806900	-1.12237800	2.07786000
H	5.45319600	-1.49248700	2.92512500
C	4.47951000	0.22861300	2.02921300
H	4.75794600	0.91525900	2.83286800
C	-1.00363200	-0.46568700	-1.74662800
H	-1.75757100	-0.15516000	-2.48708600
H	-0.84574700	-1.55677900	-1.83349000
C	-1.49496500	-0.14844300	-0.30254400
H	-0.66491000	-0.41542000	0.37692200

RMAM5

-1377.1793216

C	1.84489900	0.74284500	0.76427000
H	0.83042400	0.96393500	1.14745500
H	2.50860600	0.62208700	1.64060200
C	3.22702600	-1.18947700	-0.09744300
C	2.31648300	1.97535800	-0.06823800
C	1.25793100	2.39370200	-1.11485800
C	3.67158000	1.73240400	-0.77115600
C	2.47729200	3.09884400	0.88012000
N	2.59825400	3.98508600	1.62180900
H	1.09519500	1.57231600	-1.83421300
H	0.29953300	2.64023700	-0.62887200
H	1.60284800	3.27761100	-1.67521400
H	3.54191100	0.97110800	-1.56142100
H	4.02201900	2.66148600	-1.24823300
H	4.43513700	1.38353000	-0.05806400

S	-1.37843800	-0.62099600	1.95324600
C	-3.03637800	-1.20014800	1.47082300
C	-1.53988100	-0.26041700	-1.05173000
O	-1.04251900	-1.50584600	-0.54070200
H	-3.65934300	-1.14450400	2.37880300
H	-2.92595900	-2.26628600	1.20295300
H	-0.95702500	0.56849900	-0.60046800
H	-1.33329900	-0.26845100	-2.13798000
C	-0.49011100	-1.45528400	0.71563300
C	-3.02415900	-0.03580100	-0.82704700
C	-3.69758300	-0.41553500	0.35375100
C	-5.05676200	-0.08931700	0.49067800
H	-5.57541800	-0.38001600	1.41172700
C	-3.73453000	0.63783000	-1.83222300
H	-3.20616700	0.91479800	-2.75250700
C	-5.75292700	0.59276800	-0.51153400
H	-6.81122800	0.83382600	-0.37528000
C	-5.08679800	0.95890200	-1.68435000
H	-5.61603100	1.48693300	-2.48284000
C	0.98776200	-1.66566700	0.78872400
H	1.32494600	-1.68051000	1.84095500
H	1.21822300	-2.65685700	0.34624300
C	1.82848200	-0.59426300	0.00752500
H	1.40340900	-0.50353600	-1.01063000
O	4.04720300	-1.18967300	0.79379800
C	4.68995200	-2.43738800	-1.43146100
H	5.50394900	-1.70117300	-1.32852300
H	4.81774500	-3.21557100	-0.66238100
H	4.68903000	-2.87842000	-2.43673600
O	3.41594800	-1.79158500	-1.28670700

RDMMAM5

-1396.5957811

C	2.47159700	0.51105300	0.65531700
H	1.74449500	0.63641000	1.48029700
H	3.40958300	0.14200400	1.10893800
C	3.04420300	-1.43453600	-0.86799200
C	2.72554300	1.91077300	0.02714800
C	1.39497200	2.57643200	-0.39610500
C	3.69622500	1.82773600	-1.17160000
C	3.34079700	2.74530900	1.08154600
N	3.82344400	3.39616700	1.91462100
H	0.94375300	2.01930700	-1.23374700
H	0.68053900	2.58345100	0.44587900
H	1.57004000	3.61377800	-0.72322600
H	3.23098300	1.25516900	-1.99052300
H	3.94170700	2.83665200	-1.53966000
H	4.63208700	1.31916800	-0.88439400
S	-1.57371500	-1.06674700	1.81315100
C	-2.86570800	-1.70311200	0.67942000
C	-1.88518500	1.05582800	-0.28909400
O	-0.90904600	0.03230700	-0.51430900
H	-3.45256300	-2.44073900	1.25225100
H	-2.33754600	-2.25118600	-0.12203800
H	-1.69152900	1.52047500	0.69908900
H	-1.69874800	1.81971200	-1.06544000

C	-0.40896700	-0.57068200	0.60914900
C	-3.32665800	0.59077600	-0.38854300
C	-3.78889000	-0.64707400	0.10691000
C	-5.16180600	-0.93415800	0.03614800
H	-5.51699000	-1.89410200	0.42891400
C	-4.24818900	1.48573700	-0.95464900
H	-3.87860300	2.43912300	-1.35088100
C	-6.07333400	-0.03041000	-0.51732100
H	-7.13722100	-0.28175900	-0.55791300
C	-5.61243700	1.19009300	-1.01897000
H	-6.30869100	1.90768600	-1.46250300
C	0.81710200	-1.39231300	0.32724500
H	1.19025500	-1.81749900	1.27434500
H	0.55758700	-2.25359000	-0.33167200
C	1.92335300	-0.54292700	-0.34502800
H	1.49361400	-0.05478000	-1.23466600
O	3.46938200	-1.44575200	-2.00136400
C	4.59424200	-3.09328500	-0.28297100
H	4.26826800	-3.76783100	-1.09076000
H	5.45128300	-2.50091300	-0.64172500
H	4.86477600	-3.66366000	0.61521500
O	3.51930100	-2.22949700	0.11164600

TS (RDMAAM5-Oopening)

-1396.557415

C	-1.78047700	1.10544400	-0.76359300
H	-0.78637800	1.35738100	-1.18507200
H	-2.51083900	1.14823600	-1.59094500
C	-3.15994800	-0.93528000	-0.12075900
C	-2.13955100	2.20346600	0.28743800
C	-1.00191800	2.41916900	1.31276000
C	-3.45532100	1.91079000	1.04308800
C	-2.30330300	3.46866900	-0.46151400
N	-2.42230400	4.46611400	-1.04569900
H	-0.84698300	1.49972400	1.90384700
H	-0.05743400	2.68673100	0.81106900
H	-1.26844700	3.23083700	2.00879500
H	-3.32637700	1.00418600	1.66181700
H	-3.69370900	2.75177000	1.71426000
H	-4.29099200	1.74569600	0.34809200
S	1.48428600	-0.35445500	-2.20705200
C	3.12256200	-0.88324800	-1.63239400
C	1.61938300	-0.07129900	0.96551300
O	1.02765100	-1.57989800	0.06239600
H	3.78976200	-0.72579100	-2.49614500
H	3.03720000	-1.97536200	-1.47848600
H	1.04673800	0.63586700	0.35737800
H	1.22540500	-0.21056600	1.97990100
C	0.50788600	-1.25206100	-1.06359100
C	3.07730800	-0.03029000	0.83023200
C	3.75302300	-0.25193400	-0.40119400
C	5.14096400	-0.04549900	-0.44824600
H	5.66230500	-0.20842900	-1.39873600
C	3.83870000	0.29852600	1.97247900
H	3.31013600	0.44048600	2.92203800

C	5.87489500	0.32966000	0.68167100
H	6.95543200	0.48129700	0.60520800
C	5.21958100	0.48411700	1.90822800
H	5.77858200	0.75717300	2.80786500
C	-0.98816800	-1.25971600	-1.25726600
H	-1.25946000	-0.95199500	-2.28359900
H	-1.33815400	-2.30405700	-1.13058400
C	-1.74610900	-0.34021600	-0.24061400
H	-1.22234100	-0.38267700	0.73277100
O	-4.07369900	-0.53500200	-0.83308400
N	-3.34289300	-1.95114800	0.78774500
C	-4.65509300	-2.58432100	0.85929800
H	-5.42435300	-1.87885600	0.52341300
H	-4.69742900	-3.49063400	0.22402000
H	-4.84614000	-2.88582000	1.90346000
C	-2.29081800	-2.71839400	1.44229200
H	-2.27696300	-3.75230700	1.04204000
H	-1.29304700	-2.28854300	1.29140000
H	-2.49190200	-2.78412700	2.52725000

TS (RDMAAM5-Sopening)

-1396.557466

C	-2.33185500	1.06840400	-0.72550400
H	-1.52366600	1.55472500	-1.30305300
H	-3.22676300	1.02434400	-1.36902300
C	-3.11825200	-1.33360500	-0.41089400
C	-2.62678900	1.94923900	0.52210000
C	-1.32669800	2.24807200	1.30803500
C	-3.68664700	1.28686100	1.43343700
C	-3.16598400	3.23813100	0.03936300
N	-3.58435800	4.25511600	-0.33593900
H	-0.91188500	1.31557600	1.73130300
H	-0.56806900	2.69572700	0.64218400
H	-1.52345400	2.94274000	2.14053700
H	-3.27061900	0.36469700	1.87993000
H	-3.97432000	1.96290600	2.25429300
H	-4.58414800	1.01866600	0.85220300
S	1.40244100	0.80114000	-1.88424500
C	3.24335500	-0.74501700	-1.74417500
C	1.93627200	0.13264100	0.97366800
O	0.95528100	-0.65287600	0.27367900
H	3.76674800	-0.70268200	-2.70543800
H	2.50781700	-1.54747000	-1.66303900
H	1.71195300	1.20002300	0.77426700
H	1.72933600	-0.07007200	2.03882200
C	0.50910700	-0.20481500	-0.92759900
C	3.41317500	-0.11858400	0.71083900
C	4.00234700	-0.36997400	-0.56107100
C	5.41042100	-0.27176800	-0.67238700
H	5.85855100	-0.44036700	-1.65804900
C	4.25092400	0.11274100	1.81225100
H	3.79142900	0.28812100	2.79261600
C	6.22471800	-0.01122100	0.42772100
H	7.31055500	0.03985800	0.30487300
C	5.64291500	0.16372800	1.68912900
H	6.26416500	0.35221800	2.56914300

C	-0.78661400	-0.87819400	-1.28958100
H	-1.04300800	-0.66500300	-2.33908900
H	-0.67114400	-1.97565000	-1.17122200
C	-1.92035400	-0.36662400	-0.35086500
H	-1.50624400	-0.37855200	0.67039100
O	-4.07467900	-1.12497700	-1.14706800
N	-3.02101900	-2.46576400	0.36461500
C	-2.00000300	-2.67224300	1.38661100
H	-0.98779500	-2.44128700	1.02024400
H	-2.19041100	-2.06751400	2.29781700
H	-2.01954300	-3.73406300	1.67774000
C	-4.14913500	-3.38975300	0.41390300
H	-4.85533700	-3.13534800	-0.38486900
H	-3.79035500	-4.42522900	0.28087800
H	-4.66544000	-3.32536900	1.39093900

TS (RMAM5-Opening)

-1377.142781

C	1.83491100	0.70580000	0.80617200
H	0.82650900	0.88934400	1.22390100
H	2.51719600	0.55428300	1.66349700
C	3.23997300	-1.14890100	-0.17810700
C	2.27694500	1.98394700	0.02746800
C	1.21117800	2.43202800	-0.99917900
C	3.63481000	1.80159900	-0.68883100
C	2.41923300	3.06462200	1.02727200
N	2.52507100	3.91674400	1.81009800
H	1.05449500	1.63774200	-1.74956100
H	0.25076200	2.65203900	-0.50532200
H	1.54840700	3.33987000	-1.52481700
H	3.51714400	1.07902700	-1.51643700
H	3.96448600	2.76014200	-1.12013200
H	4.40783200	1.43324900	0.00375600
S	-1.34404700	-0.94441200	1.98535400
C	-3.02291300	-1.24696000	1.36625300
C	-1.55370400	0.05824700	-1.04851500
O	-1.01936500	-1.64234900	-0.51718800
H	-3.65764100	-1.26060100	2.26790600
H	-3.00191000	-2.27700600	0.96385600
H	-0.92305900	0.58581800	-0.32696100
H	-1.19977900	0.12148000	-2.08440100
C	-0.44865000	-1.59700800	0.62600100
C	-3.00179200	0.13851700	-0.84284200
C	-3.65073300	-0.32091800	0.33629800
C	-5.02221700	-0.06118900	0.48830600
H	-5.52234200	-0.40784600	1.40017500
C	-3.77876500	0.75165800	-1.84936500
H	-3.27300500	1.07538400	-2.76618600
C	-5.76827400	0.59413000	-0.49657200
H	-6.83523500	0.77817600	-0.34120300
C	-5.14395600	0.98617700	-1.68571900
H	-5.71412000	1.48050900	-2.47754000
C	1.05021800	-1.72117000	0.75640200
H	1.36338200	-1.71058800	1.81650700
H	1.34298700	-2.69995900	0.32864300
C	1.82775900	-0.59887100	-0.00922700

H	1.36665300	-0.47961100	-1.00879900
O	4.07858400	-1.17433500	0.69525600
C	4.70997100	-2.26855400	-1.61275800
H	5.50190800	-1.51227800	-1.48518400
H	4.88053000	-3.08437900	-0.89258000
H	4.69914400	-2.65136500	-2.64147900
O	3.41964900	-1.67443700	-1.40335800

TS (RMAM5-Sopening)
-1377.142182

C	2.50037600	0.53669600	0.62477200
H	1.81265600	0.59839500	1.48981200
H	3.49610700	0.27726000	1.02997800
C	3.20209600	-1.43987400	-0.76297100
C	2.57995200	1.94572700	-0.02997100
C	1.17147300	2.45641100	-0.41214200
C	3.51737700	1.95153000	-1.25783700
C	3.13772400	2.85763900	0.99183200
N	3.57936700	3.56968500	1.79698400
H	0.73893000	1.81404600	-1.19897800
H	0.50063300	2.44135600	0.46441800
H	1.22730200	3.48550100	-0.80149400
H	3.09872300	1.31788700	-2.05633500
H	3.63544900	2.97638500	-1.64435500
H	4.51142700	1.55379600	-0.99436800
S	-1.14141400	-0.22480400	1.84622100
C	-3.02890800	-1.55410400	1.16325100
C	-1.96454500	0.54803400	-0.91459600
O	-0.93142600	-0.44335400	-0.77787800
H	-3.46168200	-1.98204300	2.07406700
H	-2.32349100	-2.20838700	0.64712100
H	-1.71549800	1.38918900	-0.23773800
H	-1.85906800	0.89869200	-1.95557800
C	-0.37464600	-0.63621200	0.44095900
C	-3.41332800	0.14767400	-0.68261400
C	-3.88737300	-0.68980700	0.36709900
C	-5.27839500	-0.70365600	0.63023900
H	-5.63696200	-1.32970600	1.45504300
C	-4.34535600	0.83829300	-1.47171000
H	-3.97512600	1.46759100	-2.29001100
C	-6.18673400	0.01291900	-0.14628400
H	-7.25649300	-0.03712500	0.07706600
C	-5.72002700	0.77713100	-1.22239600
H	-6.41674400	1.33353100	-1.85558100
C	0.89622800	-1.43442500	0.32324100
H	1.21800000	-1.76835100	1.32119400
H	0.70072700	-2.32808600	-0.30367100
C	2.01343800	-0.58471600	-0.34008100
H	1.61101500	-0.15410000	-1.27237100
O	3.79172700	-1.35004800	-1.81621000
C	4.69787100	-3.10659000	-0.07206300
H	4.52177700	-3.72113700	-0.96916300
H	5.57903400	-2.46878200	-0.24694600
H	4.84557100	-3.74063000	0.81177100
O	3.54612700	-2.29937700	0.21475500

RMAM5-Sopened
-1377.1922882

C	-1.35808500	-0.61051900	0.89393300
H	-0.54476600	-0.20124100	1.52010700
H	-2.26278700	-0.65269200	1.52610700
C	-3.00002300	0.16907000	-0.92925100
C	-0.95450900	-2.05694200	0.47833600
C	0.46386600	-2.09111000	-0.13599100
C	-1.96825900	-2.67686000	-0.51054300
C	-0.94131200	-2.86690000	1.71539400
N	-0.92955000	-3.49914400	2.69044300
H	0.48527800	-1.49153700	-1.06132900
H	1.21246000	-1.68059700	0.56212700
H	0.74800700	-3.12580500	-0.38902600
H	-1.88551400	-2.17028100	-1.48700300
H	-1.75396100	-3.74696700	-0.65837100
H	-3.00324100	-2.57296000	-0.13982500
S	0.08724100	3.81553900	1.20452200
C	2.22862700	0.70797200	-2.40519600
C	2.17216800	1.83025900	0.34386800
O	0.77361200	1.48163000	0.16251800
H	1.66464400	1.63099900	-2.26794800
H	2.24916700	0.27396800	-3.40723800
H	2.38524800	2.70607800	-0.29824300
H	2.33185700	2.13119700	1.39311700
C	-0.16754400	2.34878200	0.52704600
C	2.96297500	0.60233200	-0.01437000
C	2.94201200	0.08593300	-1.35576600
C	3.65266700	-1.12850100	-1.60406400
H	3.63567500	-1.53618200	-2.62103600
C	3.67204200	-0.07021300	0.97963900
H	3.66935200	0.33809400	1.99676300
C	4.34387600	-1.78794700	-0.59570200
H	4.87346300	-2.71934600	-0.81736400
C	4.36661100	-1.25968400	0.70686100
H	4.91019800	-1.77325300	1.50403900
C	-1.55735000	1.81980100	0.19442200
H	-2.20026500	1.96025200	1.08155300
H	-1.96614300	2.49414000	-0.58163400
C	-1.62534900	0.34931000	-0.28536400
H	-0.89586900	0.20193200	-1.10134100
O	-3.20689600	0.13177100	-2.12107300
C	-5.29765700	-0.05347900	-0.53529300
H	-5.55326400	0.78438600	-1.20290400
H	-5.35893000	-0.99423800	-1.10748300
H	-5.96858600	-0.08161700	0.33299700
O	-3.97541100	0.11200200	-0.00260400

RMAM5-Oopened
-1377.2110144

C	-3.01889300	0.32245300	-0.90720100
H	-2.93901900	0.62822800	-1.96784500
H	-3.71449500	-0.53607800	-0.87237200
C	-1.68325600	-0.99128200	0.85703700
C	-3.63608600	1.51553200	-0.11841400
C	-2.84946700	2.82348200	-0.36404400

C	-3.72194600	1.23397600	1.39819600
C	-5.00486200	1.69653900	-0.64932100
N	-6.07792100	1.83563600	-1.07301900
H	-1.83003700	2.72902700	0.04437200
H	-2.78607400	3.05118400	-1.44046200
H	-3.34381600	3.66687500	0.14370500
H	-2.70978500	1.26047000	1.83335500
H	-4.33542100	2.00171300	1.89517200
H	-4.16836600	0.24356100	1.59458900
S	1.67515200	-0.61321000	-1.80750300
C	3.13007000	-1.22806700	-0.89091600
C	2.07237900	0.09931700	1.55408600
O	0.47769600	-2.46587500	-0.31631700
H	3.79832600	-1.72127800	-1.61431300
H	2.73917500	-1.99151500	-0.19536500
H	1.52867100	-0.78353500	1.22128500
H	1.66961900	0.62258900	2.42428100
C	0.35077400	-1.55707300	-1.11349600
C	3.27793400	0.53709100	0.96200000
C	3.84577100	-0.09231600	-0.20077900
C	5.05159700	0.37796200	-0.72154800
H	5.46900600	-0.11373800	-1.60842100
C	3.98760000	1.64303400	1.52397200
H	3.56006700	2.12783700	2.40883500
C	5.73393100	1.45758700	-0.13944100
H	6.68004100	1.80178700	-0.56598200
C	5.18700100	2.09250000	0.98891900
H	5.70729500	2.93876100	1.44769400
C	-1.00944700	-1.03019100	-1.55536100
H	-0.91409100	-0.41905300	-2.46990400
H	-1.67585400	-1.88809300	-1.75317400
C	-1.63167200	-0.15728300	-0.42775100
H	-0.95114200	0.68914400	-0.21348000
O	-1.06385700	-0.74959700	1.86784500
C	-2.44299400	-2.99146400	1.79222700
H	-1.41276100	-3.36341800	1.91642800
H	-2.77079200	-2.50797000	2.72662300
H	-3.12441100	-3.80566100	1.51372500
O	-2.48430300	-2.05699200	0.70265300

RDMMAM5-Oopened

-1396.630207

C	-0.96344400	0.93209200	-0.82090600
H	-0.00253100	0.51632400	-1.18131000
H	-1.51162100	1.31708200	-1.69801900
C	-3.30855900	0.06114000	-0.30157200
C	-0.61553900	2.10603500	0.13972500
C	0.25728100	1.61954000	1.32547100
C	-1.88512700	2.81626800	0.65779600
C	0.18871400	3.06558000	-0.64761500
N	0.83115600	3.81126900	-1.26622000
H	-0.37120300	1.11443600	2.07767400
H	1.02746700	0.91002600	0.98131700
H	0.75530600	2.47181100	1.81604300
H	-2.46408300	2.11011500	1.27999300
H	-1.61507600	3.68150400	1.28472600

H	-2.52399400	3.14945700	-0.17487100
S	1.08534100	-2.22893400	-1.70188400
C	2.65448300	-2.22843800	-0.78045200
C	3.38156300	-1.67081500	2.12545400
O	0.32758100	-1.92037300	0.80503300
H	3.40536900	-2.57973200	-1.51016200
H	2.57209200	-2.98858700	0.00716800
H	2.98791900	-2.67149100	1.95766600
H	3.71075600	-1.42852900	3.13811700
C	-0.01900600	-1.91332000	-0.36016800
C	3.41669200	-0.66446700	1.13226000
C	3.02780400	-0.85773000	-0.23939500
C	3.04338800	0.23298600	-1.11563200
H	2.72658400	0.07650400	-2.15390000
C	3.84949900	0.64869400	1.51127200
H	4.15808200	0.79784000	2.55224400
C	3.44092400	1.51307300	-0.70743500
H	3.41579700	2.34674600	-1.41345900
C	3.85837600	1.71139600	0.62151900
H	4.17776700	2.70373800	0.95371200
C	-1.43897100	-1.55308200	-0.79062200
H	-1.52101800	-1.49782000	-1.89121700
H	-2.11876000	-2.34807100	-0.43279500
C	-1.79520500	-0.18250100	-0.15773800
H	-1.52738100	-0.24505200	0.90968300
O	-3.75396400	0.79106800	-1.17916800
N	-4.13196600	-0.58767800	0.58987700
C	-5.57685500	-0.46631900	0.43811800
H	-5.80219400	0.32110200	-0.28989400
H	-6.01192100	-1.42386400	0.09226200
H	-6.03008400	-0.21892500	1.41472000
C	-3.73786600	-1.57692500	1.58207100
H	-4.08416100	-2.58638600	1.28011700
H	-2.65279500	-1.61748500	1.73638900
H	-4.21794300	-1.33772900	2.54850800

RDMAM5-Sopened
-1396.

C	2.61928800	0.25754900	0.25008200
H	2.72013100	1.28246700	0.65040200
H	3.48070300	-0.33285600	0.60591900
C	1.51333300	-1.90843800	0.99757900
C	2.64441200	0.34568900	-1.30398100
C	1.65099000	1.42070600	-1.80524500
C	2.34152400	-1.02493800	-1.95494800
C	4.00374600	0.76315200	-1.70695300
N	5.06892100	1.09642500	-2.03023400
H	0.62415200	1.15067600	-1.49834100
H	1.89308800	2.40706400	-1.37592500
H	1.67401100	1.49198900	-2.90507200
H	1.28575400	-1.29979000	-1.77192500
H	2.49604100	-0.97881000	-3.04466900
H	2.98891000	-1.81018100	-1.53070600
S	0.65162600	3.07733200	1.75795300
C	-3.94002000	0.09645900	1.42775400
C	-1.89594800	1.99360200	0.40363200

O	-1.08026600	1.13871200	1.24142200
H	-3.50422900	0.78632100	2.15063200
H	-4.67569500	-0.62268600	1.79437500
H	-2.54461700	2.60894400	1.05451000
H	-1.23800700	2.66741400	-0.17300600
C	0.10110700	1.53965100	1.72164400
C	-2.64572400	1.04027200	-0.49476700
C	-3.59655000	0.11293800	0.05731100
C	-4.18617100	-0.83645700	-0.83352200
H	-4.90871700	-1.54944100	-0.42069700
C	-2.34803500	0.99872000	-1.85686400
H	-1.63090900	1.72155900	-2.26268700
C	-3.86457200	-0.86706800	-2.18469100
H	-4.33160600	-1.60863000	-2.83970700
C	-2.94679900	0.05797900	-2.71165700
H	-2.69776700	0.04761900	-3.77599300
C	0.86914200	0.29206000	2.11374500
H	1.73834900	0.53875000	2.74079600
H	0.19166700	-0.38164300	2.67166000
C	1.32842700	-0.39121300	0.78384300
H	0.51052100	-0.24225400	0.05961900
O	2.59830500	-2.37797700	1.31978200
N	0.39605500	-2.68469800	0.81315100
C	-0.91812900	-2.16469400	0.43856500
H	-1.24608600	-1.34778100	1.09998000
H	-0.95671200	-1.79290800	-0.60820600
H	-1.64666200	-2.98543200	0.52707400
C	0.49999600	-4.13281000	0.95561200
H	1.53884100	-4.39479500	1.18812800
H	-0.16031700	-4.49021500	1.76670300
H	0.19387400	-4.62962000	0.01699500

Table S7: Cartesian coordinates and energies (a.u.) of stationary points calculated at PCM(THF@353.2K)/uMN15L/def2-TZVP, scale factor = 0.9797, R = AIBN, M5 = O,S-BMDO

X	opening side	$\Delta G^\ddagger(\text{forward})$	$\Delta G^\ddagger(\text{reverse})$	ΔG_r
-	O	12.4	38.4	-26.0
	S	13.3	14.5	-1.2
Sty	O	14.9	39.4	-24.5
	S	14.3	23.8	-9.5
MA	O	13.0	21.8	-8.8
	S	14.0	9.7	4.3
DMMA	O	13.1	24.2	-11.1
	S	13.6	8.7	4.9

Table S8: Activation and reaction Gibbs free energies (kcal/mol) of AIBNXO,S-BMDO ring-opening.

10. Elemental Composition Reports

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -0.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 4

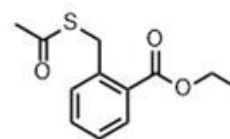
Monoisotopic Mass, Even Electron Ions

131 formula(e) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-500 H: 0-1000 O: 0-200 S: 0-6

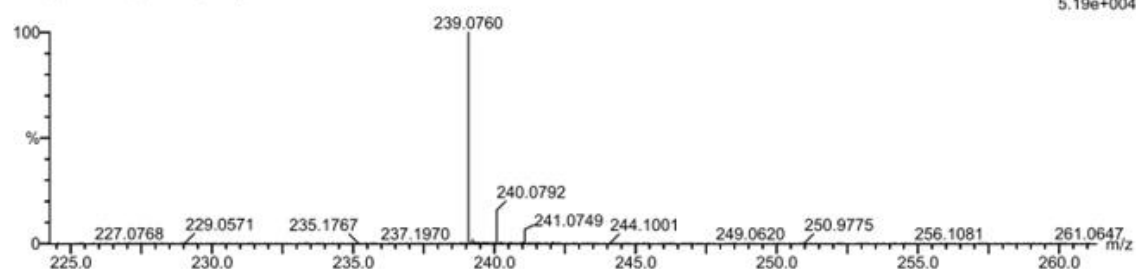
MP65_06062023_1 349 (2.308)



Chemical Formula: C₁₂H₁₄O₃S

Exact Mass: 238.07

m/z: 238.07 (100.0%), 239.07 (14.1%),
240.06 (4.5%), 240.07 (1.5%)



1: TOF MS ES+
5.19e+004

Minimum: -0.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
239.0760	239.0742	1.8	7.5	5.5	612.5	0.0	C12 H15 O3 S
	239.0776	-1.6	-6.7	0.5	623.9	11.4	C9 H19 O3 S2
	239.0767	-0.7	-2.9	1.5	631.8	19.3	C8 H15 O8

Figure S34. Elemental composition report for ethyl 2-(acetylsulfanylmethyl)benzoate (5).

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -0.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 4

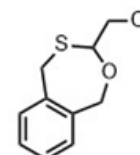
Monoisotopic Mass, Even Electron Ions

159 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-500 H: 0-1000 O: 0-200 S: 1-6 Cl: 0-8

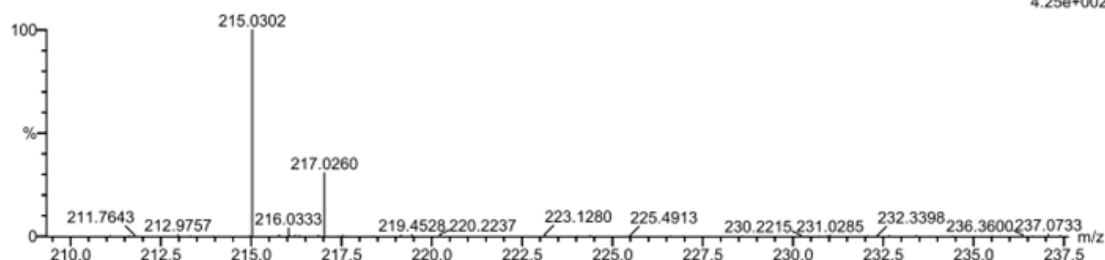
MP93_06062023_1 333 (2.195) Cm (329:336-(340:351+320:327))



Chemical Formula: C₁₀H₁₁ClOS

Exact Mass: 214.02

m/z: 214.02 (100.0%), 216.02 (36.6%),
215.03 (11.0%), 217.02 (4.2%),
218.01 (1.4%)



1: TOF MS ES+
4.25e+002

Minimum: -0.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
215.0302	215.0297	0.5	2.3	4.5	26.9	0.4	C10 H12 O S Cl
	215.0331	-2.9	-13.5	-0.5	27.6	1.1	C7 H16 O S2 Cl

Figure S35. Elemental composition report for 5,6-benzo-2-(chloromethyl)-1,3-oxthiepane (7).