Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Rearrangement of thiazolidine derivatives – a synthesis of chiral fused oxathiane-γ-lactam bicyclic system

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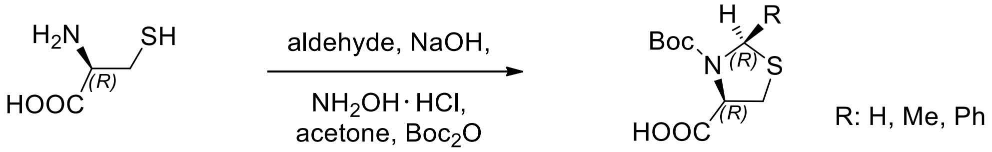
1. General

All commercially available reagents were purchased from Merck and used without further purifications. ^1H and ^{13}C spectra were recorded using 400 MHz Jeol 400yh (Jeol Ltd., Tokyo, Japan) and 600 MHz Bruker Avance II 600 instruments (Bruker, Billerica, MA, USA). If not stated otherwise, reference solvent residual peaks were used for calibration (chloroform-*d*, δ (^1H) = 7.28 ppm, δ (^{13}C) = 77.00 ppm and acetonitrile-d δ (^1H) = 1.94 ppm, δ (^{13}C) = 1.32, 118.26 ppm). The reported *J* values are those observed from the splitting patterns in the spectrum and may not reflect the true coupling constant value. IR spectra were obtained either as potassium bromide pellets or as liquid films with a Perkin Elmer 2000 FTIR spectrometer (PerkinElmer, Waltham, MA, USA). High resolution mass spectra were recorded (Waters LCT Premier XE TOF spectrometer, Waters Corporation, Milford, MA, USA) utilizing electrospray ionization mode. Melting points are determined by the open capillary method using Apotec® Schmelzpunktbestimmer melting point apparatus (WEPA Apothekenbedarf GmbH & Co. KG., Hillscheid, Germany). The optical rotation was measured on an automatic polarimeter model AA-5 (Optical Activity, Ltd., Ramsey, UK, $[\alpha]^D_{20}$ values are expressed in 10^{-1} deg cm^2 g^{-1}). Liquid chromatography purifications were performed on silica gel 60 (70– 230 mesh). Thin layer chromatography was carried out using silica gel 60 precoated plates (Merck).

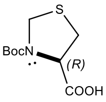
2. Synthesis

2.1. Synthesis of aldehyde-derived Boc-protected carboxylic acids (2-4)



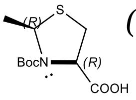
General procedure A (compounds 2-4), according to [1].

To a 100 ml round-bottom flask containing L-cysteine (3.63 g, 30 mmol), NaOH (2 M, 1.20 g in 15 mL H_2O, 30 mmol, 1.0 eq.) was added at 0°C, followed by aldehyde (3 mmol, 0.1 eq.). The reaction mixture was stirred for 24 h at the same temperature. Then, acetone (17.5 mL), NaOH (1.2 M, 0.12 g in 2.5 mL H_2O, 3 mmol, 0.1 eq.) and hydroxylamine hydrochloride (0.21 g, 3 mmol, 0.1 eq.) were added. After stirring for 15 minutes at 0°C, $(Boc)_2O$ (7.20 g, 33 mmol, 1.1 eq.) was introduced and stirring was continued for 3 h at room temperature. The mixture was diluted with water, followed by washing with diethyl ether (2 × 100 mL). The aqueous phase was quenched with 20% citric acid solution and extracted with ethyl acetate (2 × 100 mL). The organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. After purification by column chromatography (silica gel, *n*–hexane/EtOAc = 6:1), the desired Boc-protected products **2-4** were obtained.



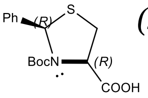
*(R)-3-(tert-butoxycarbonyl)thiazolidine-4-carboxylic acid (**2**)*

Prepared according to the **General procedure A** from L-cysteine (30 mmol) and formaldehyde (3 mmol, 0.1 eq.), product **2** was obtained as a white crystalline solid (6.28 g, 26.9 mmol, 90% yield). Mp. 132 – 134 °C, $[\alpha]_D^{20}$ = -130.8 (*c* 0.50, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (br s, 1H), 4.87 – 4.41 (m, 3H), 3.35 – 3.27 (m, 2H), 1.46 (s, 9H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 175.0, 154.0, 153.2, 82.0, 81.7, 61.4, 49.0, 48.4, 34.5, 32.9, 28.3, ppm. IR (KBr): 3433, 2971, 2935, 1746, 1635, 1419, 1217, 1197 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_9H_{15}NO_4SNa)^+$ 256.0620; found 256.0621.



*(2R,4R)-3-(tert-butoxycarbonyl)-2-methylthiazolidine-4-carboxylic acid (**3**)*

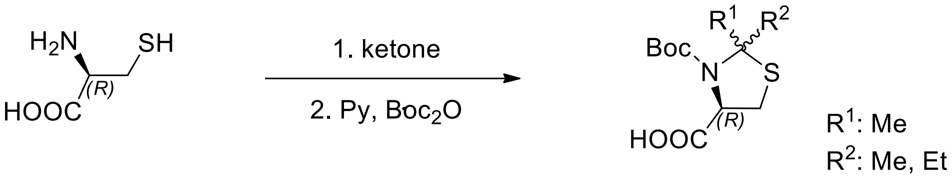
Prepared according to the **General procedure A** from L-cysteine (30 mmol) and acetaldehyde (3 mmol, 0.1 eq.), product **3** was obtained as white needles (6.23 g, 25.2 mmol, 84% yield). Mp. 119 – 121 °C, $[\alpha]_D^{20}$ = -95.2 (*c* 0.69, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.38 (br s, 1H), 5.20 – 5.14 (m, 1H), 4.85 – 4.67 (m, 1H), 3.40 – 3.31 (m, 2H), 1.57 (d, *J* = 5.2 Hz, 3H), 1.47 (s, 9H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.2, 175.6, 153.7, 152.4, 81.8, 63.9, 60.3, 59.5, 33.1, 32.0, 28.3, 23.6 ppm. IR (KBr): 2976, 2611, 1728, 1621, 1428, 1351, 1286, 1270, 1235, 1216, 1142, 1043, 861, 839 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{10}H_{17}NO_4SNa)^+$ 270.0776; found 270.0781.



*(2R,4R)-3-(tert-butoxycarbonyl)-2-phenylthiazolidine-4-carboxylic acid (**4**)*

Prepared according to the **General procedure A** from L-cysteine (30 mmol) and benzaldehyde (3 mmol, 0.1 eq.), product **4** was obtained as a white solid (8.81 g, 28.5 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.21 (m, 5H), 5.93 (s, 1H), 4.90 (s, 1H), 3.48 – 3.45 (m, 1H), 3.32 (dd, *J* = 11.8, 6.7 Hz, 1H), 1.32 (s, 9H) ppm. The spectroscopic data are in agreement with the literature data [5].

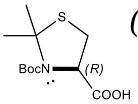
2.2. Synthesis of ketone-derived Boc-protected carboxylic acids (5-6)



General procedure B (compounds 5-6), according to [2-3].

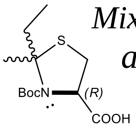
Step 1: To a 250 ml round-bottom flask containing L-cysteine (2.42 g, 20 mmol), 200 ml of ketone was added under argon atmosphere. The resulting suspension was refluxed for 3h. The reaction mixture was cooled to room temperature and the product was separated from the unreacted ketone and side products by filtration. Obtained carboxylic acid was used directly in the next step, without additional purification.

Step 2: In a 100 ml round-bottom flask under argon, carboxylic acid (20 mmol) was dissolved in pyridine (25 ml) and $(Boc)_2O$ (4.80 g, 22 mmol, 1.1 eq.) was added at -25°C. The reaction mixture was stirred for 72h at room temperature. Then, it was diluted with toluene and extracted with 2 N ice-cold NaOH solution (3 × 80ml). The aqueous layers were combined and washed with toluene (3 × 100ml) and hexane (100ml). After bringing pH down to 3 with solid citric acid, extraction with DCM (3 × 100ml) was performed. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product. Purification by column chromatography (silica gel, *n* – hexane/EtOAc: 9:1 → 1:1) yielded in pure Boc-protected carboxylic acid **5-6**.



*(R)-3-(tert-butoxycarbonyl)-2,2-dimethylthiazolidine-4-carboxylic acid (**5**)*

Prepared according to the **General procedure B** from L-cysteine (20 mmol) and acetone (200 ml), product **5** was obtained as a white solid (3.65 g, 14.0 mmol, 70% yield over two steps). ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (br s, 1H), 5.02 – 4.75 (m, 1H), 3.32 – 3.10 (m, 2H), 1.85 (s) and 1.78 (s, 6H), 1.49 (s) and 1.41 (s) (9H) ppm. The spectroscopic data are in agreement with the literature data [3].

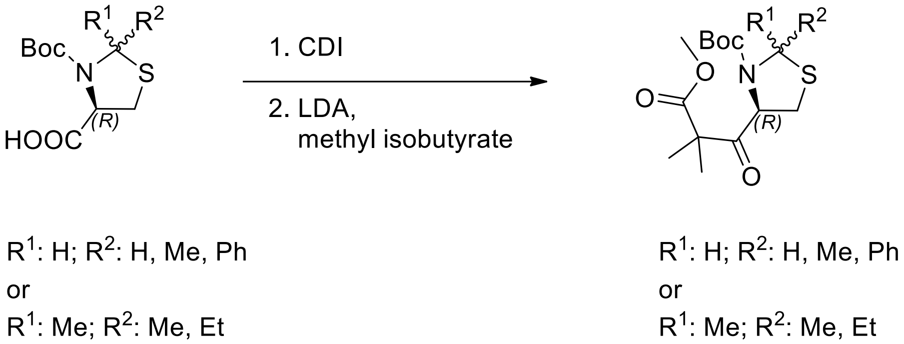


*Mixture of (2S,4R)-3-(tert-butoxycarbonyl)-2-ethyl-2-methylthiazolidine-4-carboxylic acid and (2R,4R)-3-(tert-butoxycarbonyl)-2-ethyl-2-methylthiazolidine-4-carboxylic acid (**6**)*

Prepared according to the **General procedure B** from L-cysteine (20 mmol) and 2-butanone (200 ml), a mixture of products **6** was obtained as a colorless oil (3.85 g, 14.0 mmol, 70% yield over two steps). ^1H NMR (400 MHz, $CDCl_3$): δ 9.38 (br s, 1H), 4.96-4.88 (m, 1H), 3.32-3.17

(m,2H), 2.20-2.08 (m, 2H), 1.72 (s, 3H), 1.41 (s, 9H), 0.98 (t, *J* = 8.0 Hz, 3H) (major diastereoisomer); 9.38 (br s, 1H), 4.83-4.76 (m, 1H), 3.16-3.08 (m,2H), 2.34-2.21 (m, 2H), 1.72 (s, 3H), 1.49 (s, 9H), 0.95 (t, *J* = 8.0 Hz, 3H) (minor diastereoisomer) ppm. The spectroscopic data are in agreement with the literature data [2].

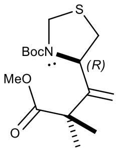
2.3. Synthesis of ketones (7-11)



General procedure C (compounds 7-11), according to [4].

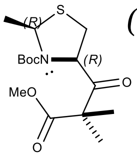
Step 1: Carboxylic acid **2-6** (12 mmol) was dissolved in dry THF (20 ml) at 0°C and CDI (1.95 g, 12 mmol, 1.0 eq.) was added. After stirring for 30min, ice bath was removed and the reaction mixture was stirred for another 2h at room temperature. The mixture was briefly dried under reduced pressure. The residue transferred to a separating funnel, diluted utilizing EtOAc and washed with distilled water and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated to obtain activated carboxylic acid.

Step 2: LDA solution was prepared at -78°C under argon atmosphere, by adding DIPA (2.52 ml, 18 mmol, 1.5 eq.) to a solution of n-BuLi (2.5 M, 7.2 ml, 18 mmol, 1.5 eq.) in dry THF (15 ml). After stirring for 30 min at the same temperature, methyl isobutyrate (2.89 ml, 25.2 mmol, 2.1 eq.) was added dropwise over a period of 10 min at -78°C and stirred at that temperature for another 30 min. Then, acylimidazole was dissolved in dry THF (10 ml) and added dropwise over 25 min. It was kept stirring for 30 min at the same temperature. The unreacted reagents were deactivated with 10% citric acid solution, followed by extraction with EtOAc (2 × 80ml). Then, the organic extracts were combined and washed with water and brine. After drying it over anhydrous Na_2SO_4 and filtering, solvent evaporation *in vacuo* was performed to give crude product **7-11**, which was then purified by column chromatography (silica gel, *n* – hexane/EtOAc = 9:1).



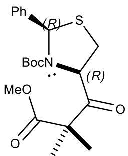
*(R)-tert-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)thiazolidine-3-carboxylate (**7**)*

Prepared according to the **General procedure C** from carboxylic acid **2** (2.80 g, 12 mmol), product **7** was obtained as a crystalline solid (1.45 g, 4.57 mmol, 38% yield over two steps). Mp. 66 – 68 °C, $[\alpha]_D^{20}$ = -114.0 (*c* 0.39, DCM). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.16 (br s, 1H), 4.75 – 4.66 (m, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.19 (br s, 1H), 3.04 (dd, *J* = 11.6, 4.8 Hz, 1H), 1.49 (s, 3H), 1.42 (m, 12H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 205.6, 173.6, 153.2, 128.1, 128.0, 81.3, 63.3, 52.7, 49.6, 33.3, 28.4, 22.9, 22.7 ppm. IR (KBr): 2980, 2938, 1741, 1720, 1390, 1368, 1288, 1254, 1203, 1153 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{14}H_{23}NO_5SNa)^+$ 340.1195; found 340.1196.



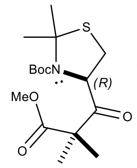
*(2R,4R)-tert-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-methylthiazolidine-3-carboxylate (**8**)*

Prepared according to the **General procedure C** from carboxylic acid **3** (2.97 g, 12 mmol), product **8** was obtained as a colorless oil (2.67 g, 8.06 mmol, 67% yield over two steps). $[\alpha]_D^{20}$ = +55.3 (*c* 0.60, DCM). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.13 – 5.09 (m, 2H), 3.73 (s, 3H), 3.44 – 3.39 (m, 1H), 2.98 (m, 1H), 1.53 (d, 3H), 1.51 (s, 3H), 1.42 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 205.9, 173.0, 151.8, 79.9, 63.7, 58.2, 51.6, 29.9, 29.6, 27.3, 24.0, 22.3 ppm. IR (KBr): 3442, 2978, 2931, 1743, 1721, 1699, 1459, 1366, 1267, 1173, 1153, 772 cm $^{-1}$. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{15}H_{25}NO_5SNa)^+$ 354.1351; found 354.1347.



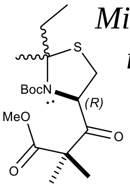
*(2R,4R)-tert-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-phenylthiazolidine-3-carboxylate (**9**)*

Prepared according to the **General procedure C** from carboxylic acid **4** (3.71 g, 12 mmol), product **9** was obtained as white crystals (3.07 g, 7.80 mmol, 65% yield over two steps). Mp. 73 – 74 °C. $[\alpha]_D^{20}$ = +62.9 (*c* 0.86, DCM). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.66 – 7.68 (m, 2H), 7.32 – 7.35 (m, 2H), 7.23 – 7.26 (m, 1H), 5.96 (s, 1H), 5.16 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.28-3.18 (m, 1H), 3.04 – 3.00 (m, 1H), 1.62 (s, 3H), 1.50 (s, 3H), 1.19 (s, 9H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 204.8, 173.8, 153.1, 142.6, 128.3, 127.6, 126.5, 81.2, 65.8, 55.7, 52.7, 33.2, 31.7, 28.1, 23.1, 14.2 ppm. IR (KBr): 3502, 2981, 2926, 1717, 1700, 1683, 1381, 1120, 696 cm $^{-1}$. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{20}H_{27}NO_5S)^+$ 394.1688; found 394.1694.



*(R)-tert-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2,2-dimethylthiazolidine-3-carboxylate (**10**)*

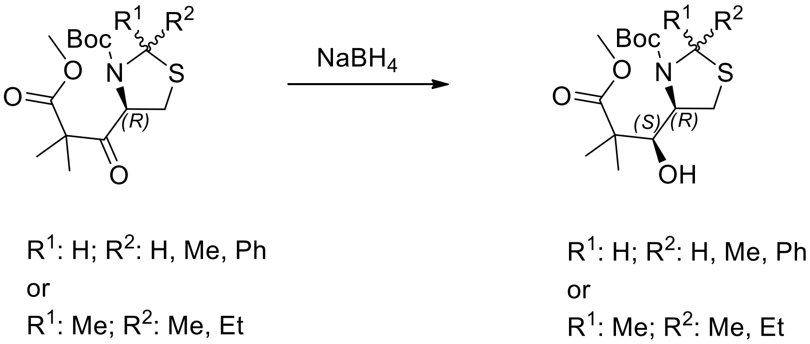
Prepared according to the **General procedure C** from carboxylic acid **5** (3.14 g, 12 mmol), product **10** was obtained as a crystalline solid (3.07 g, 8.89 mmol, 74% yield over two steps). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.26 (br s, 1H), 3.72 (s, 3H), 3.21 (br s, 1H), 2.91 (dd, J = 12.3, 4.0 Hz, 1H), 1.84 (br s, 3H), 1.75 (s, 3H), 1.53 (s, 3H), 1.44 (s, 3H), 1.42 (s, 9H) ppm. The spectroscopic data are in agreement with the literature data [4].



*Mixture of (2S,4R)-tert-butyl 2-ethyl-4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-methylthiazolidine-3-carboxylate and (2R,4R)-tert-butyl 2-ethyl-4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-methylthiazolidine-3-carboxylate (**11**)*

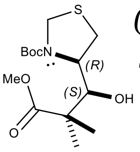
Prepared according to the **General procedure C** from carboxylic acid **6** (3.30 g, 12 mmol), a mixture of products **11** was obtained as a colorless oil (2.58 g, 7.18 mmol, 60% yield over two steps). ^{1}H NMR (400 MHz, Acetonitrile-d$_3$) δ (major diastereomer) 5.25 – 5.16 (m, 1H), 3.69 (s, 3H), 3.36 – 3.16 (m, 1H), 2.96-2.80 (m, 1H), 2.30 – 2.08 (m, 2H), 1.69 (s, 3H), 1.49 (s, 3H), 1.41 (s, 9H), 1.40 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H) ppm; (minor diastereomer) 5.35 – 5.27 (m, 1H), 3.69 (s, 3H), 3.36 – 3.16 (m, 1H), 3.07-2.98 (m, 1H), 2.30 – 2.08 (m, 2H), 1.71 (s, 3H), 1.44 (s, 3H), 1.41 (s, 9H), 1.40 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H) ppm. HRMS (ESI - TOF): m/z [M+Na]$^+$ calcd for (C$_{17}$H$_{29}$NO$_5$SNa)$^+$ 382.1664; found 382.1671.

2.4. Synthesis of alcohols (12-16)



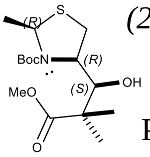
General procedure D (compounds 12-16), according to [4].

A solution of ketone **7-11** (3.5 mmol) in EtOH (15 ml) was prepared at 0°C and NaBH$_4$ (0.132 g, 3.5 mmol, 1.0 eq.) was added in small portions. The reaction mixture was stirred for 48 h at room temperature. It was then carefully transferred to a separating funnel containing ice-cold NH$_4$Cl solution, before being extracted with EtOAc (2 × 50ml). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated *in vacuo* to obtain crude product. Purification by column chromatography (silica gel, DCM) resulted in alcohol **12-16** and over-reduced diol **13'-15'**.



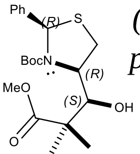
*(R)-tert-butyl 4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)thiazolidine-3-carboxylate (**12**)*

Prepared according to the **General procedure D** from ketone **7** (1.11 g, 3.5 mmol), product **12** was obtained as a crystalline solid (0.54 g, 1.69 mmol, 48% yield). Mp. 96 – 98 °C, $[\alpha]_D^{20}$ = -38.6 (*c* 0.45, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.79 (br s, 1H), 4.61 – 4.57 (m, 1H), 4.17 (d, *J* = 9.6 Hz, 1H), 3.68 (s, 3H), 3.63 (dd, *J* = 6.0, 8.0 Hz, 1H), 3.11 (dd, *J* = 7.2, 11.2 Hz, 1H), 2.84 (dd, *J* = 3.2, 11.2 Hz, 1H), 1.46 (s, 9H), 1.30 (s, 3H), 1.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 81.6, 79.4, 60.1, 52.2, 49.8, 46.3, 34.8, 28.4, 22.7, 21.8 ppm. IR (KBr): 3435, 2986, 2948, 1728, 1677, 1401, 1368, 1253, 1162, 1133, 1117 cm^{-1}. HRMS (ESI - TOF): m/z [M+H]$^+$ calcd for $(C_{14}H_{25}NO_5S)^+$ 320.1532; found 320.1539.



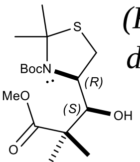
*(2R,4R)-tert-butyl 4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate (**13**)*

Prepared according to the **General procedure D** from ketone **8** (1.16 g, 3.5 mmol), product **13** was obtained as a colorless oil (0.76 g, 2.28 mmol, 65% yield). $[\alpha]_D^{20}$ = -10.6 (*c* 0.87, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.17 (q, *J* = 6.0 Hz, 1H), 4.48 (m, 1H), 3.82 (m, 1H), 3.69 (s, 3H), 3.08 (dd, *J* = 6.8, 12.0 Hz, 1H), 2.68 (dd, *J* = 2.8, 12.0 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.47 (s, 9H), 1.30 (s, 3H), 1.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 81.7, 78.1, 62.4, 58.9, 52.1, 47.1, 33.7, 28.4, 24.0, 22.7, 20.3 ppm. IR (KBr): 3465, 2978, 1728, 1697, 1456, 1389, 1369, 1260, 1168, 860, 773 cm^{-1}. HRMS (ESI - TOF): m/z [M+H]$^+$ calcd for $(C_{15}H_{27}NO_5S)^+$ 334.1688; found 334.1680.



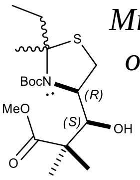
*(2R,4R)-tert-butyl 4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-phenylthiazolidine-3-carboxylate (**14**)*

Prepared according to the **General procedure D** from ketone **9** (1.38 g, 3.5 mmol), product **14** was obtained as a colorless oil (0.49 g, 1.24 mmol, 35% yield). $[\alpha]_D^{20}$ = +93.8 (*c* 0.54, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 – 7.52 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 5.97 (s, 1H), 4.58 – 4.53 (m, 1H), 4.04 (t, *J* = 8.8 Hz, 1H), 3.67 (s, 3H), 3.18 (dd, *J* = 6.4, 12.4 Hz, 1H), 2.59 (dd, *J* = 2.4, 12.4 Hz, 1H), 1.36 (s, 3H), 1.28 (s, 3H), 1.20 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 140.7, 128.5, 127.9, 126.7, 82.1, 78.2, 66.3, 63.6, 52.0, 47.4, 34.0, 28.0, 23.4, 19.7 ppm. IR (KBr): 3440, 2979, 2951, 1729, 1665, 1386, 1368, 1261, 1163, 1132, 858, 732 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{20}H_{29}NO_5S)^+$ 396.1845; found 396.1852.



*(R)-tert-butyl 4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2,2-dimethylthiazolidine-3-carboxylate (**15**)*

Prepared according to the **General procedure D** from ketone **10** (1.21 g, 3.5 mmol), product **15** was obtained as a crystalline solid (0.73 g, 2.10 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (dd, *J* = 8.9, 5.5 Hz, 1H), 3.88 (dd, *J* = 9.9, 8.9 Hz, 1H), 3.68 (s, 3H), 3.15 (dd, *J* = 12.3, 5.5 Hz, 1H), 2.36 (d, *J* = 12.3 Hz, 1H), 1.76 (s, 6H), 1.46 (s, 9H), 1.29 (s, 3H), 1.23 (s, 3H) ppm. The spectroscopic data are in agreement with the literature data [4].



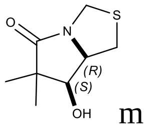
*Mixture of (2S,4R)-tert-butyl 2-ethyl-4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate and (2R,4R)-tert-butyl 2-ethyl-4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate (**16**)*

Prepared according to the **General procedure D** from ketone **11** (1.26 g, 3.5 mmol), a mixture of products **16** was obtained as a colorless oil (0.57 g, 1.58 mmol, 45% yield). *De* = 35%. ^{1}H NMR (400 MHz, CD_3CN): δ (major diastereomer) 4.48 (dd, *J* = 4.0, 8.0 Hz, 1H), 3.71 (t, *J* = 4,0Hz, 1H), 3.56 (s, 3H), 3.30-3.28 (m, 1H), 3.10 (dd, *J* = 4.0, 8.0 Hz, 1H), 2.32 (d, *J* = 12.0 Hz, 1H), 2.03 (q, *J* = 8.0 Hz, 2H), 1.67 (s, 3H), 1.38 (s, 9H), 1.16 (s, 3H), 1.11 (s, 3H), 0.93 (t, *J* = 8.0 Hz, 3H) ppm; (minor diastereomer) 4.53 (dd, *J* = 4.0, 8.0 Hz, 1H), 3.74 (t, *J* = 4,0Hz, 1H), 3.57 (s, 3H), 3.05 (dd, *J* = 4.0, 8.0 Hz, 1H), 2.98-2.96 (m, 1H), 2.26 (d, *J* = 12.0 Hz, 1H), 1.99 (q, *J* = 8.0 Hz, 2H), 1.63 (s, 3H), 1.37 (s, 9H), 1.17 (s, 3H), 1.12 (s, 3H), 0.86 (t, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ (major diastereomer) 176.9, 81.0, 75.1, 77.4, 64.6, 51.3, 47.4, 32.8, 30.8, 28.0, 27.7, 21.9, 20.1, 9.52 ppm; (minor diastereomer) 176.9, 81.0, 75.1, 64.6, 51.4, 47.4, 34.9, 32.7, 30.8, 27.8, 27.6, 21.5, 20.5, 8.9 ppm. HRMS (ESI - TOF): m/z $[M+Na]^+$ calcd for $(C_{17}H_{31}NO_5SNa)^+$ 384.1821; found 384.1814.

2.5. Synthesis of bicyclic products (20-24)

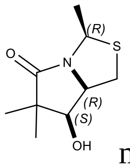
General procedure E (compounds 20-24),

To a solution of alcohol **12-16** or diol **13'-15'** (0.65 mmol) in dry DCM (1.0 ml), TFA (1.0 ml, 13.0 mmol, 20 eq) was added dropwise at 0°C under argon atmosphere. Reaction mixture was then stirred for 30 minutes at room temperature and subsequently ammonia solution was added portionwise (pH>7). Neutralized mixture was washed with DCM (3 × 10ml) and the combined organic phases were dried over Na$_2$SO$_4$. Solvent was removed under reduced pressure, products **23**, **24** were purified using column chromatography (silica gel, *n* – hexane/EtOAc: 4:1 → 1:1) and products **21'-23'** were purified by crystalization from petroelum ether. Crude intermediates **17-19** were refluxed in toluene (20ml) for 48 hours and after solvent evaporation, purified by column chromatography (silica gel, *n* – hexane/EtOAc: 4:1 → 1:1) to give products **20-22**.



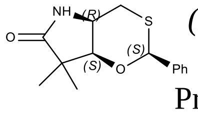
*(7S,7aR)-7-hydroxy-6,6-dimethyltetrahydropyrrolo[1,2-c]thiazol-5(3H)-one (**20**)*

Prepared according to the **General procedure E** from alcohol **12** (0.208 g, 0.65 mmol), product **20** was obtained as a crystalline solid (0.122 g, 0.65 mmol, 100% yield). Mp. 102 – 104 °C, $[\alpha]_D^{20}$ = +40.4 (*c* 0.45). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.81 (d, J = 9.6 Hz, 1H), 4.33 – 4.28 (m, 1H), 4.02 (d, J = 4.4 Hz, 1H), 3.98 (d, J = 9.2 Hz, 1H), 3.28 (dd, J = 6.8, 10.8 Hz, 1H), 2.96 (dd, J = 7.2, 11.2 Hz, 1H), 2.77 (br s, 1H), 1.25 (s, 3H), 1.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 177.8, 76.1, 64.8, 50.1, 44.8, 29.4, 23.6, 18.1 ppm. IR (KBr): 3429, 2969, 2932, 1666, 1467, 1437, 1292, 1270, 1096 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_8H_{13}NO_2S)^+$ 188.0745; found 188.0739.



*(3S,7S,7aR)-7-hydroxy-3,6,6-trimethyltetrahydropyrrolo[1,2-c]thiazol-5(3H)-one (**21**)*

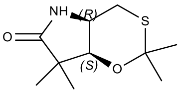
Prepared according to the **General procedure E** from alcohol **13** (0.217 g, 0.65 mmol), product **21** was obtained as white needles (0.071 g, 0.35 mmol, 54% yield). Mp. 93 – 95 °C. $[\alpha]_D^{20}$ = -90.2 (*c* 0.41, DCM). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.22 (q, J = 6.4 Hz, 1H), 4.41 – 4.36 (m, 1H), 4.02 – 4.00 (m, 1H), 3.27 (dd, J = 8.0, 10.8 Hz, 1H), 2.97 (dd, J = 6.4, 10.8 Hz, 1H), 2.32 (br s, 1H), 1.47 (d, J = 6.4 Hz, 3H), 1.22 (s, 3H), 1.14 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 176.4, 75.3, 64.3, 54.8, 49.9, 29.9, 23.7, 23.4, 18.2 ppm. IR (KBr): 3410, 2921, 1664, 1418, 1341, 1265, 1209, 1103, 870 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_9H_{15}NO_2S)^+$ 202.0902; found 202.0904.



*(2S,4aR,7aS)-7,7-dimethyl-2-phenyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one (**22**)*

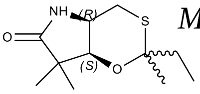
Prepared according to the **General procedure E** from alcohol **14** (0.257 g, 0.65 mmol), product **22** was obtained as a white solid (0.065 g, 0.25 mmol, 38% yield). Mp. 196 – 198 °C. $[\alpha]_D^{20}$ = -19.4 (*c* 0.41, DCM). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.43 (dd, J = 1.6, 8.4 Hz, 2H), 7.30 – 7.37 (m, 3H), 5.80 (br s, 1H), 5.80 (br s, 1H), 4.04 (dd, J = 1.2, 3.6 Hz, 1H), 3.90

(q, *J* = 4.0 Hz, 1H), 3.42 (dd, *J* = 4.0, 14.4 Hz, 1H), 3.00 (dd, *J* = 4.4, 14.8 Hz, 1H), 1.62 (m, 2H), 1.25 (s, 3H), 1.22 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.6, 139.4, 128.6, 125.9, 81.9, 46.5, 46.4, 31.0, 29.5, 22.2, 17.5 ppm. IR (KBr): 3430, 2921, 1699, 1660, 1447, 1306, 1238, 1096, 1087, 712 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{14}H_{17}NO_2S)^+$ 264.1058; found 264.1039.



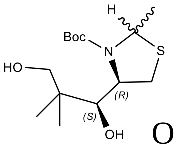
*(4aR,7aS)-2,2,7,7-tetramethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one (**23**)*

Prepared according to the **General procedure E** from alcohol **15** (0.226 g, 0.65 mmol), product **23** was obtained as a white crystalline solid (0.098 g, 0.455 mmol, 70% yield). Mp. 137-139°C, $[\alpha]_D^{20}$ = +49.5 (*c* 0.41, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 1H), 3.89 – 3.79 (m, 1H), 2.85 (dd, *J* = 13.3, 6.4 Hz, 1H), 2.55 (dd, *J* = 13.3, 8.8 Hz, 1H), 1.52 (s, 1H), 1.45(s, 1H), 1.11(s, 1H), 1.06 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 180.85, 80.43, 75.75, 50.41, 43.04, 30.24, 26.54, 25.28, 23.19, 16.46 δ ppm. IR (KBr): 3405, 3313, 3240, 2981, 2935, 2886, 1709, 1692, 1640, 1383, 1327, 1292, 1052 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{10}H_{18}NO_2S)^+$ 216.1058; found 216.1059.



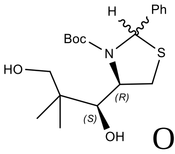
*Mixture of (2S,4aR,7aS)-2-ethyl-2,7,7-trimethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one and (2R,4aR,7aS)-2-ethyl-2,7,7-trimethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one (**24**)*

Prepared according to the **General procedure E** from alcohol **16** (0.235 g, 0.65 mmol), a mixture of products **24** was obtained as a colorless oil (0.107 g, 0.467 mmol, 72% yield). *De* = 35 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 6.37-6.31 (m, 1H), 3.97-3.95 (m, 1H), 3.88-3.86 (m, 1H), 2.86 (dd, *J* = 8.0, 16.0 Hz, 1H), 2.59 (dd, *J* = 8.0, 16.0 Hz, 1H) 1.87-1.77 (m, 1H), 1.72-1.67 (m, 1H), 1.45 (s, 3H), 1.17 (s, 3H), 1.11 (s, 3H), 0.97 (t, *J* = 8.0 Hz, 3H) ppm; (minor diastereomer) 6.37-6.31 (m, 1H), 3.91-3.87 (m, 2H), 2.88 (dd, *J* = 8.0, 16.0 Hz, 1H), 2.58 (dd, *J* = 8.0, 16.0 Hz, 1H), 2.03-1.93 (m, 1H), 1.72-1.67 (m, 1H), 1.51 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 0.91 (t, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): (major diastereomer) 181.9, 84.8, 76.5, 51.8, 44.3, 36.8, 27.8, 24.5, 17.7, 8.7 ppm; (minor diastereomer) 181.9, 85.1, 76.4, 51.9, 44.1, 31.4, 27.4, 24.5, 23.6, 17.6, 8.6 ppm. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{11}H_{19}NO_2)^+$ 230,1215; found 230.1219.



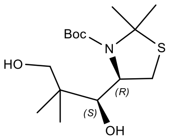
*Mixture of (2S,4R)-tert-butyl 4-((S)-1,3-dihydroxy-2,2-dimethylpropyl)-2-methylthiazolidine-3-carboxylate and (2R,4R)-tert-butyl 4-((S)-1,3-dihydroxy-2,2-dimethylpropyl)-2-methylthiazolidine-3-carboxylate **(13')***

Obtained as a side product from ketone **8** according to the **General procedure D**. White solid. Yield ~ 15%. Mp. 94-95°C, $[\alpha]_D^{20}$ = (*c* , DCM). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.12 (q, *J* = 6.1 Hz, 1H), 4.64 (t, *J* = 7.1 Hz, 1H), 3.61 – 3.48 (m, 2H), 3.44 (d, *J* = 8.0 Hz, 1H), 3.18 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.04 (br s, 1H), 2.70 (dd, *J* = 11.6, 1.7 Hz, 1H), 1.55 (d, *J* = 6.1 Hz, 3H), 1.46 (s, 9H), 1.01 (s, 3H), 0.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.34, 81.70, 71.49, 61.57, 58.86, 39.11, 35.79, 28.43, 23.57, 20.06. IR (KBr): 3369, 2976, 2965, 2924, 2874, 1661, 1476, 1410, 1364, 1327, 1264, 1123, 1074, 1040 cm^{-1}. HRMS (ESI - TOF): m/z [M+H]$^+$ calcd for $(C_{14}H_{27}NO_4S)^+$ 328.1559; found 328.1555.



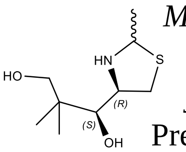
*Mixture of (2S,4R)-tert-butyl 4-((S)-1,3-dihydroxy-2,2-dimethylpropyl)-2-phenylthiazolidine-3-carboxylate and (2R,4R)-tert-butyl 4-((S)-1,3-dihydroxy-2,2-dimethylpropyl)-2-phenylthiazolidine-3-carboxylate **(14')***

Obtained as a side product from ketone **9** according to the **General procedure D**. Crystalline solid. Yield ~ 15%. Mp. 117-119°C, $[\alpha]_D^{20}$ = +43.6 (*c* 0.62, DCM). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.61 – 7.56 (m, 2H), 7.35 – 7.25 (m, 3H), 5.90 (br s, 1H), 4.67 (ddd, *J* = 8.4, 6.3, 1.8 Hz, 1H), 3.67 – 3.58 (m, 2H), 3.54 (d, *J* = 11.4 Hz, 1H), 3.31 (dd, *J* = 12.0, 6.3 Hz, 1H), 2.80 (dd, *J* = 12.0. 1.8 Hz, 1H), 1.18 (s, 9H), 1.06 (s, 3H), 1.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.53, 140.70, 128.42, 128.07, 127.15, 82.06, 80.28, 71.76, 66.52, 62.89, 39.49, 35.91, 28.03, 23.56, 19.92 ppm. IR (KBr): 3458, 2976, 2932, 1667, 1477, 1456, 1387, 1367, 1311, 1259, 1165, 1117, 1076, 1046 cm^{-1}. HRMS (ESI - TOF): m/z [M+H]$^+$ calcd for $(C_{19}H_{29}NO_4S)^+$ 368.1895; found 368.1889.



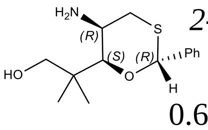
*(R)-tert-butyl 4-((S)-1,3-dihydroxy-2,2-dimethylpropyl)-2,2-dimethylthiazolidine-3-carboxylate **(15')***

Obtained as a side product from ketone **10** according to the **General procedure D**. White solid. Yield ~ 15%. Mp. 129°C, ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.76 – 4.64 (m, 1H), 3.63 – 3.52 (m, 2H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.27 (dd, *J* = 11.9, 5.3 Hz, 1H), 2.46 (d, *J* = 11.9 Hz, 1H), 1.78 (s) and 1.78 (s) (6H), 1.49 (s, 9H), 1.04 (s, 3H), 0.96 (s, 3H) ppm. HRMS (ESI - TOF): m/z [M+H]$^+$ calcd for $(C_{15}H_{29}NO_4S)^+$ 320.1895; found 320.1895. Spectroscopic data is consistent with literature [4].



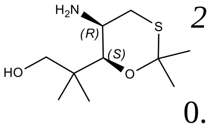
*Mixture of epimers (S)-2,2-dimethyl-1-((2R,4R)-2-methylthiazolidin-4-yl)propane-1,3-diol and (S)-2,2-dimethyl-1-((2S,4R)-2-methylthiazolidin-4-yl)propane-1,3-diol (**21'**)*

Prepared according to the **General procedure E** from alcohol **13'** (0.199 g, 0.65 mmol), a mixture of products **21'** was obtained as a crystalline solid (0.113 g, 0.55 mmol, 85% yield). Mp. 139-140°C, $[\alpha]_D^{20}$ = +17.9 (*c* 0.55, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.54 (q, *J* = 8.0 Hz, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.44 (s, 1H), 3.37 – 3.33 (m, 1H), 3.03 – 2.97 (m, 4H), 2.93 – 2.56 (m, 2H), 1.53 (d, *J* = 8.0 Hz, 3H), 1.00 (s, 3H), 0.89 (s, 3H) ppm (major epimer); 4.72 (q, *J* = 8.0 Hz, 1H), 3.67 (d, *J* = 12.0 Hz, 1H), 3.57 – 3.53 (m, 1H), 3.48 (s, 1H), 3.03 – 2.97 (m, 4H), 2.93 – 2.56 (m, 2H), 1.44 (d, *J* = 8.0 Hz, 3H), 1.00 (s, 3H), 0.90 (s, 3H) ppm (minor epimer). IR (KBr): 3401, 2926, 2854, 1475, 1307, 1219, 1135, 1093, 1048, 916 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_9H_{20}NO_2S)^+$ 206.1215; found 206.1218.



*2-((2R,5R,6S)-5-amino-2-phenyl-1,3-oxathian-6-yl)-2-methylpropan-1-ol (**22'**)*

Prepared according to the **General procedure E** from alcohol **14'** (0.239 g, 0.65 mmol), product **22'** was obtained as a white crystalline solid (0.104 g, 0.39 mmol, 60% yield). Mp. 175-176°C, $[\alpha]_D^{20}$ = -42.2 (*c* 0.51, DCM).^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 – 7.43 (m, 2H), 7.39 – 7.30 (m, 3H), 5.87 (s, 1H), 3.87 (d, *J* = 11.7 Hz, 1H), 3.51 (dd, *J* = 13.5, 1.9 Hz, 1H), 3.33 (s, 1H), 3.16 (ddd, *J* = 4.0, 1.9, 1.1 Hz, 1H), 2.94 (d, *J* = 11.9 Hz, 1H), 2.70 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.05 (s, 3H), 0.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.09, 128.50, 125.74, 90.76, 85.45, 64.99, 40.66, 40.49, 40.28, 26.15, 21.25 ppm. IR (KBr): 3435, 3345, 2959, 2911, 2864, 1504, 1475, 1370, 1309, 1243, 1075, 1038, 1024, 1002, 979, 730, 699 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{14}H_{21}NO_2S)^+$ 268.1371; found 268.1363.



*2-((5R,6S)-5-amino-2,2-dimethyl-1,3-oxathian-6-yl)-2-methylpropan-1-ol (**23'**)*

Prepared according to the **General procedure E** from alcohol **15'** (0.208 g, 0.65 mmol), product **23'** was obtained as a white crystalline solid (0.125 g, 0.57 mmol, 87% yield). Mp. 115-117°C, $[\alpha]_D^{20}$ = +29.2 (*c* 0.59, DCM). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.94 (s, 2H), 3.73 (d, *J* = 11.5 Hz, 1H), 3.45 – 3.31 (m, 2H), 3.09 – 2.96 (m, 1H), 2.85 (d, *J* = 11.6 Hz, 1H), 2.56 (dd, *J* = 13.7, 4.0 Hz, 1H), 1.62 (s, 3H), 1.53 (s, 3H), 1.32 (s, 1H), 1.01 (s, 3H), 0.81 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 80.92, 64.58, 40.19, 39.52, 36.83, 31.56, 25.98, 25.87, 21.37 ppm. IR (KBr): 3435, 3338, 3272, 2958, 2924, 2853, 1512, 1456, 1377, 1363, 1172, 1132, 1071, 1045, 993 cm^{-1}. HRMS (ESI - TOF): m/z $[M+H]^+$ calcd for $(C_{10}H_{22}NO_2S)^+$ 220.1371; found 220.1370.

3. Copies of NMR spectra

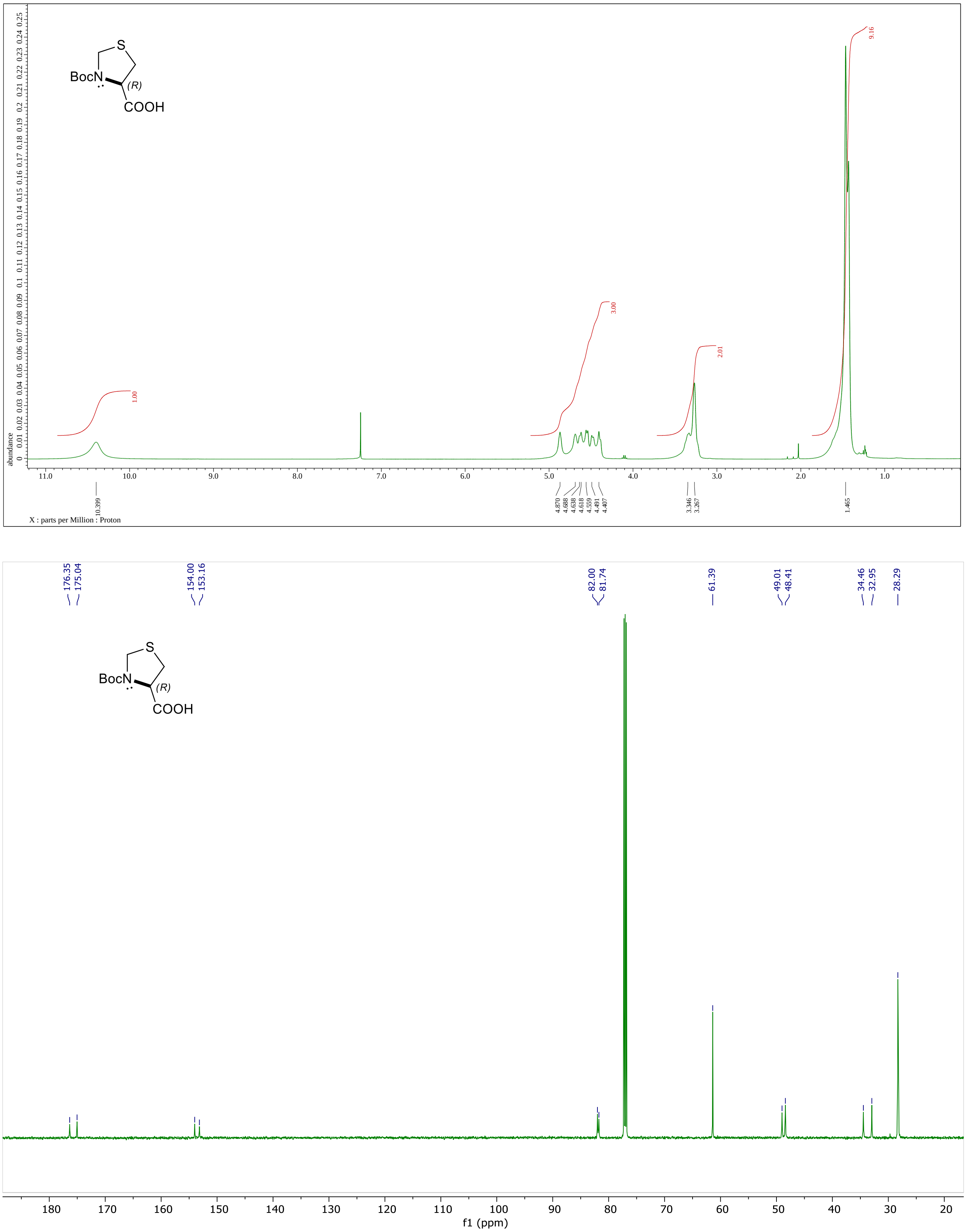


Figure S1. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-3-(*tert*-butoxycarbonyl)thiazolidine-4-carboxylic acid (**2**)

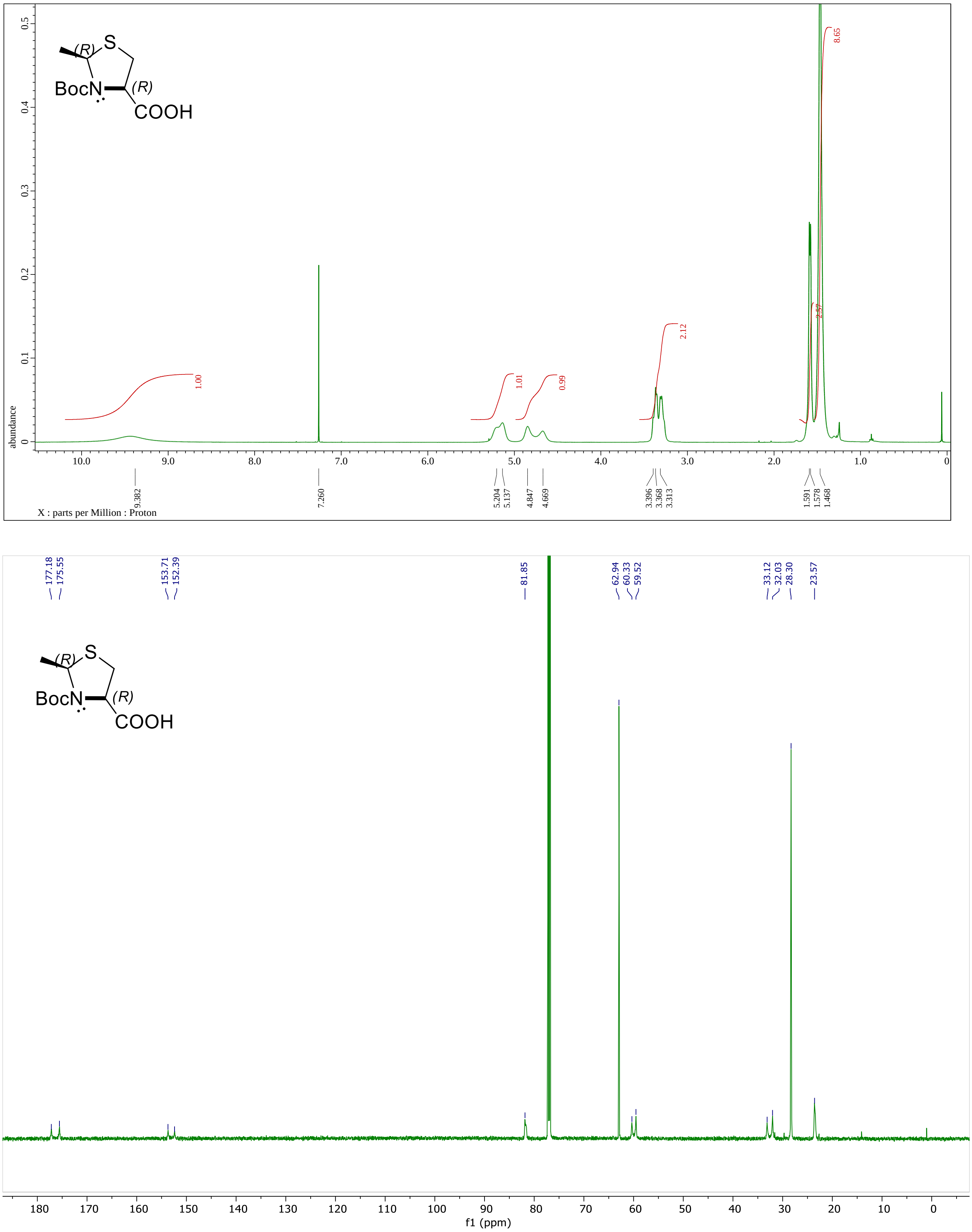


Figure S2. (Top) ^{1}H NMR spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of (2*R*,4*R*)-3-(*tert*-butoxycarbonyl)-2-methylthiazolidine-4-carboxylic acid (**3**)

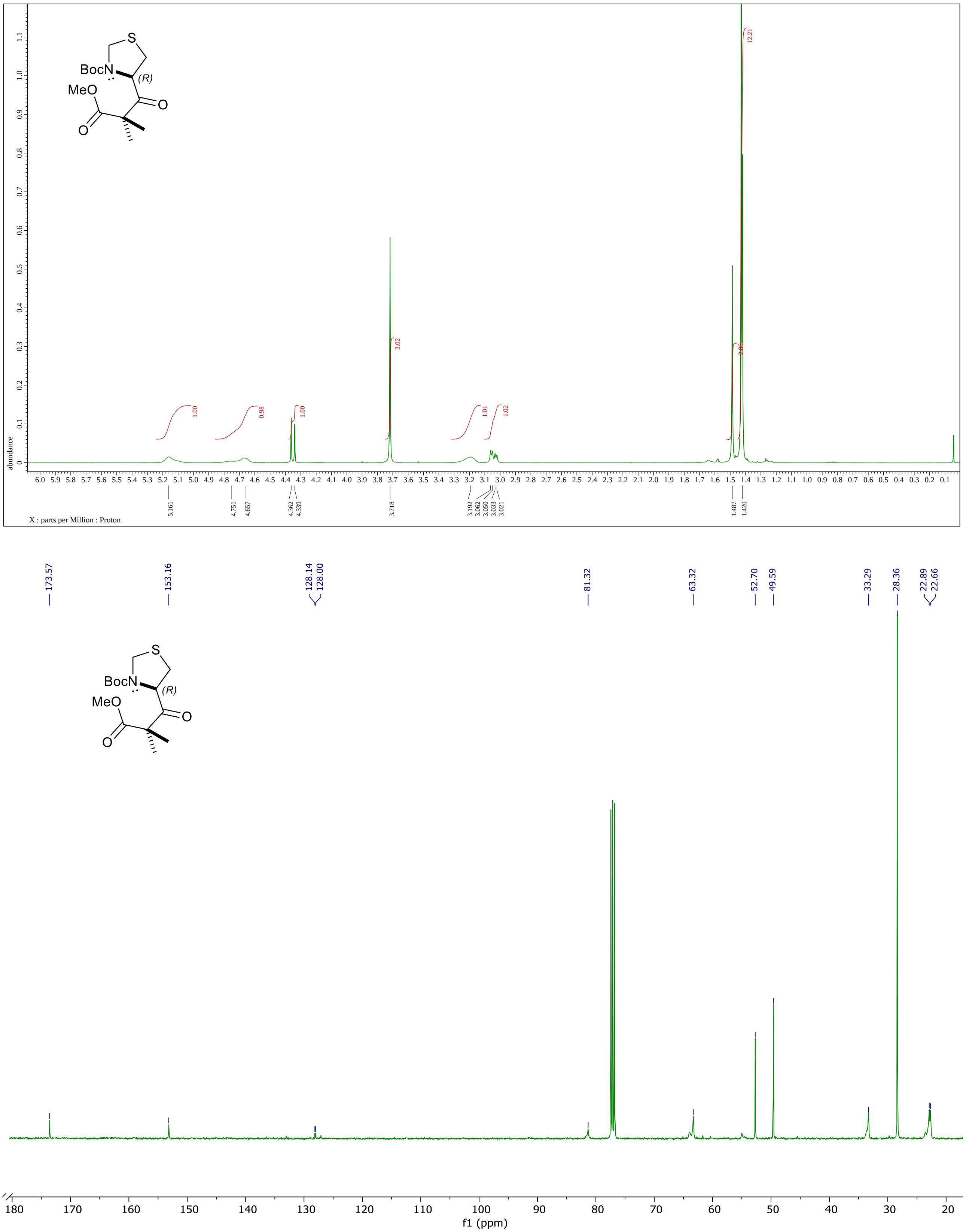


Figure S3. (Top) ^{1}H NMR spectrum (400 MHz, CDCl$_3$), (bottom) ^{13}C NMR spectrum (150 MHz, CDCl$_3$) of (*R*)-*tert*-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)thiazolidine-3-carboxylate (**7**)

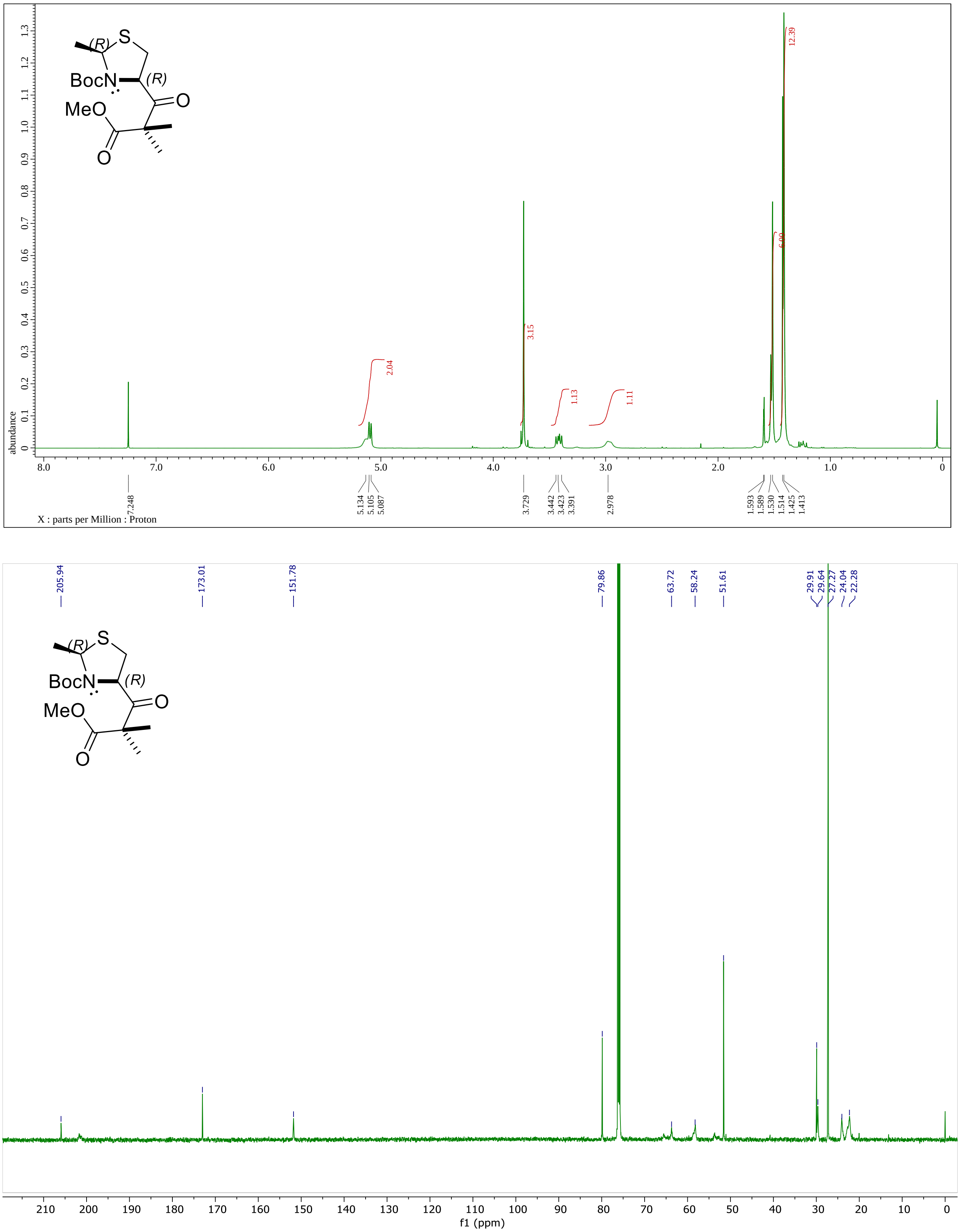


Figure S4. (Top) ^{1}H NMR spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of (2*R*,4*R*)-*tert*-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-methylthiazolidine-3-carboxylate (**8**)

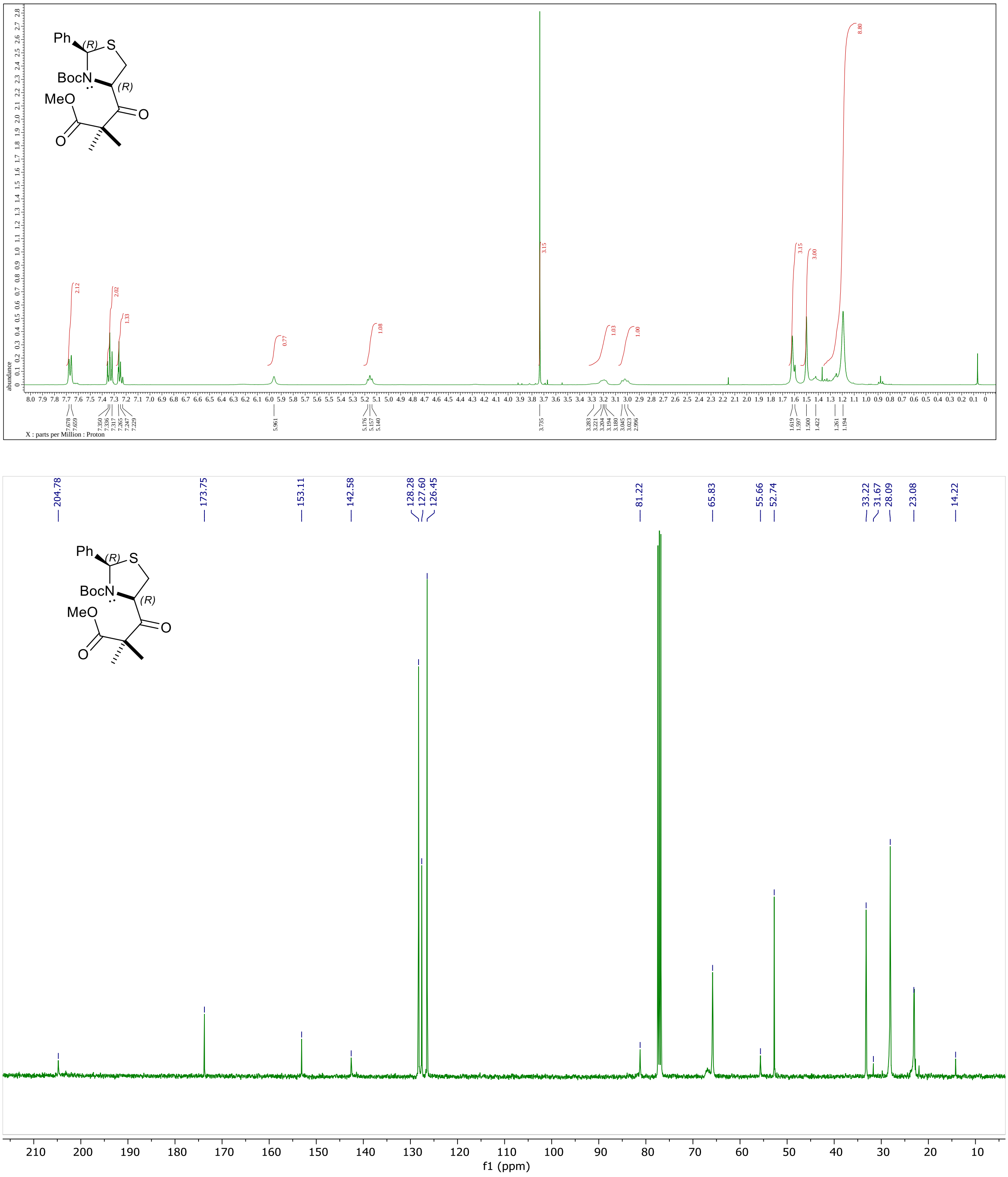


Figure S5. (Top) ^{1}H NMR spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of (2*R*,4*R*)-*tert*-butyl 4-(3-methoxy-2,2-dimethyl-3-oxopropanoyl)-2-phenylthiazolidine-3-carboxylate (**9**)

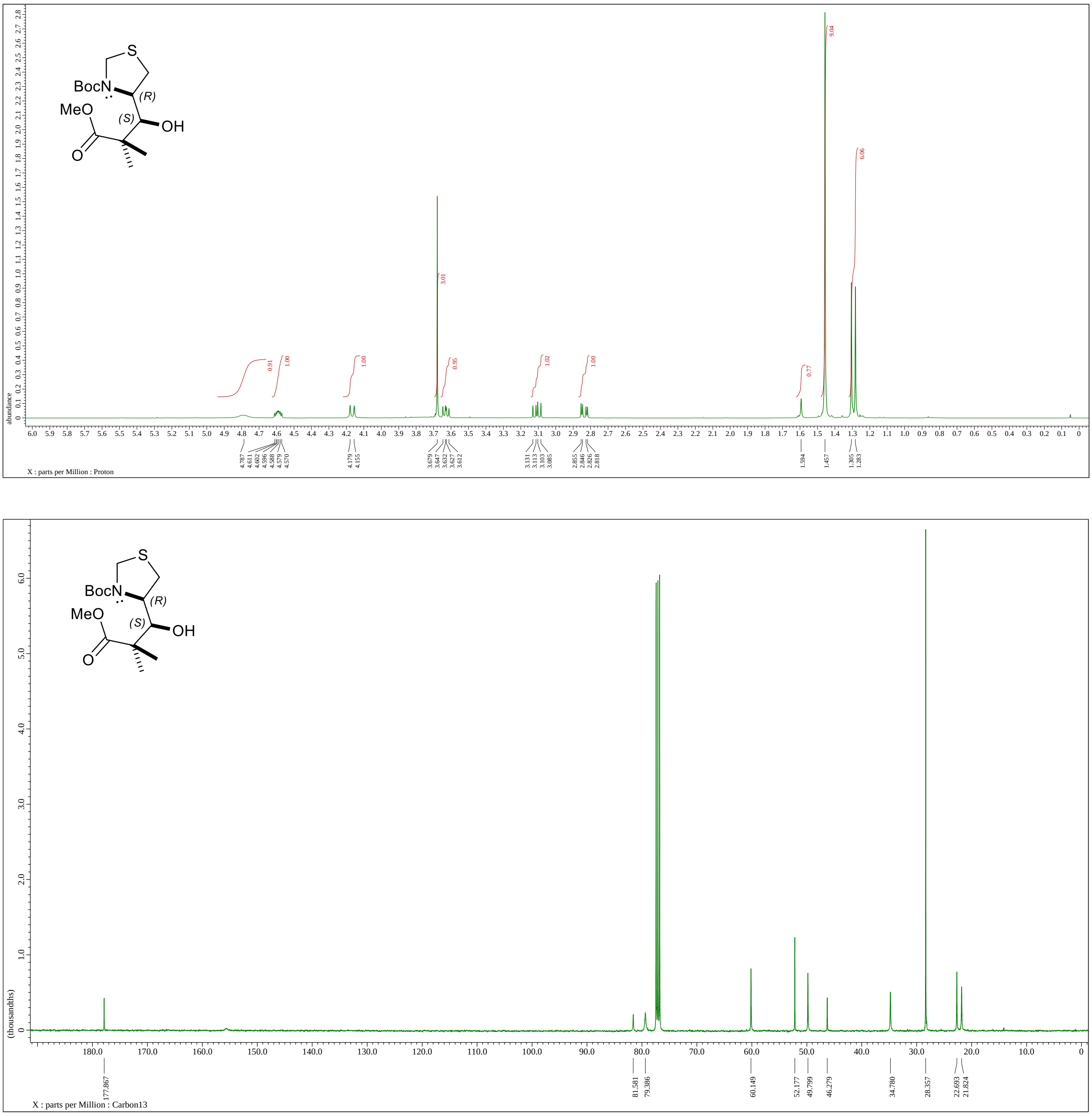


Figure S6. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-*tert*-butyl 4-((*S*)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)thiazolidine-3-carboxylate (**12**)

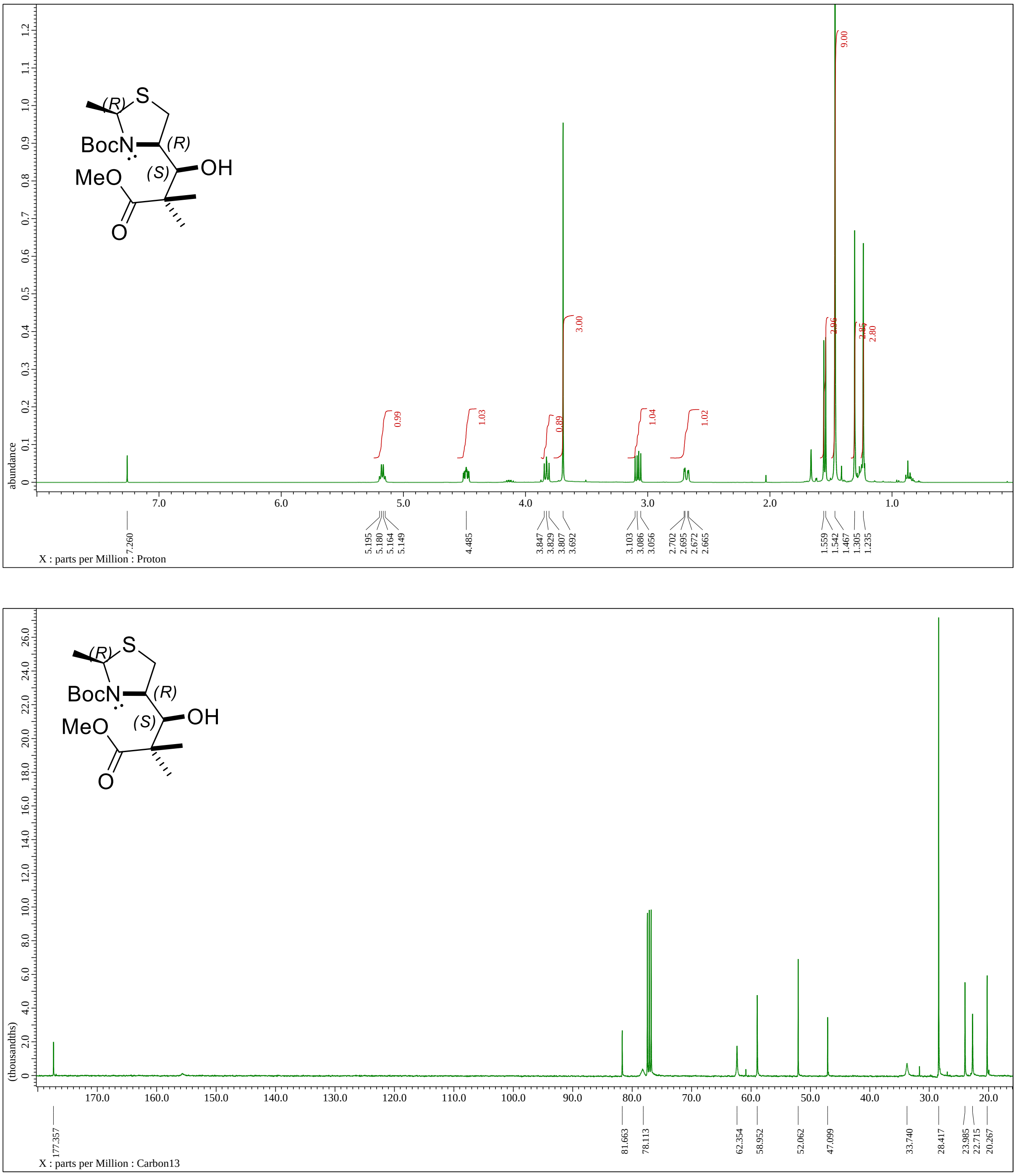


Figure S7. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2*R*,4*R*)-*tert*-butyl 4-((*S*)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate (**13**)

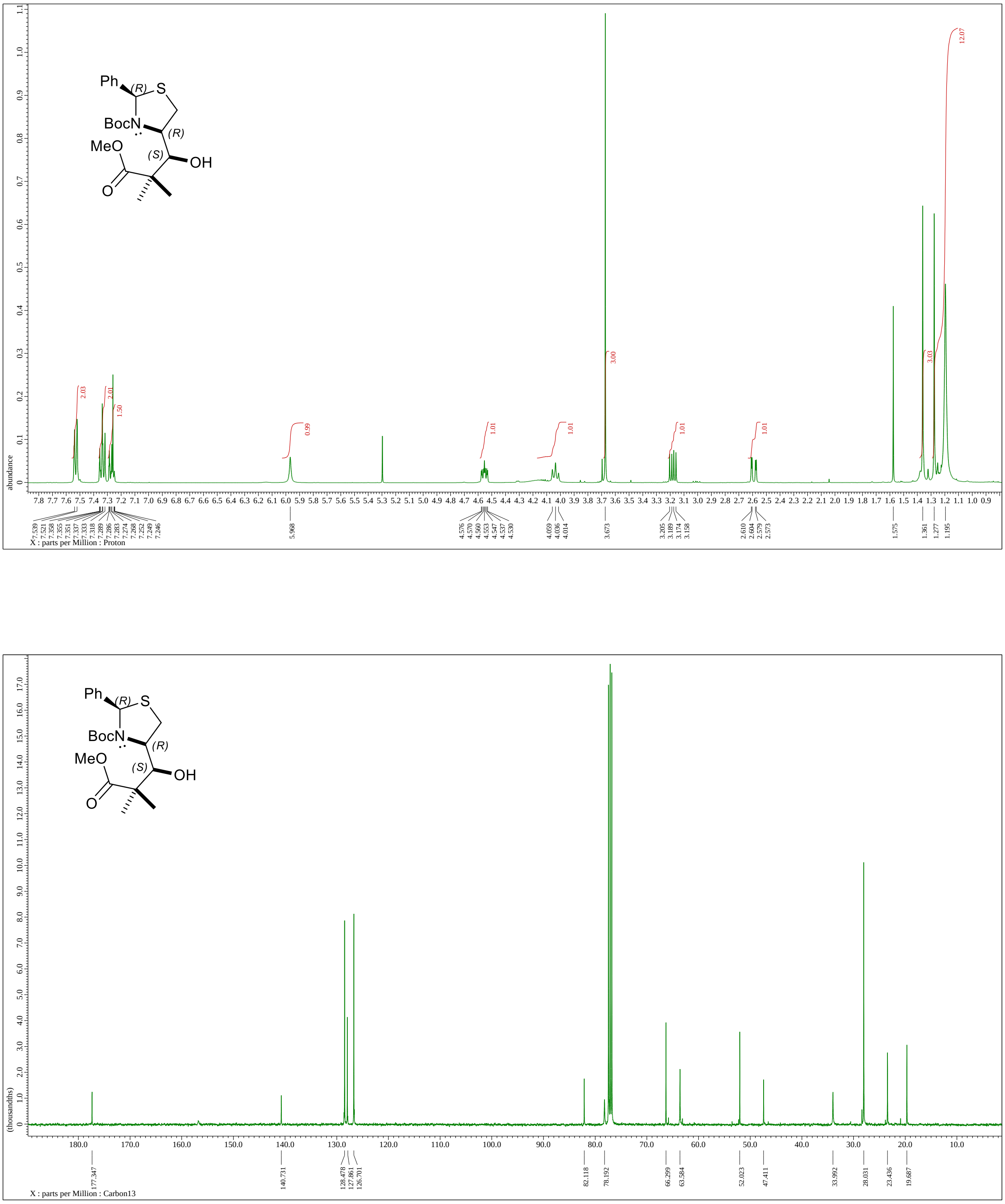
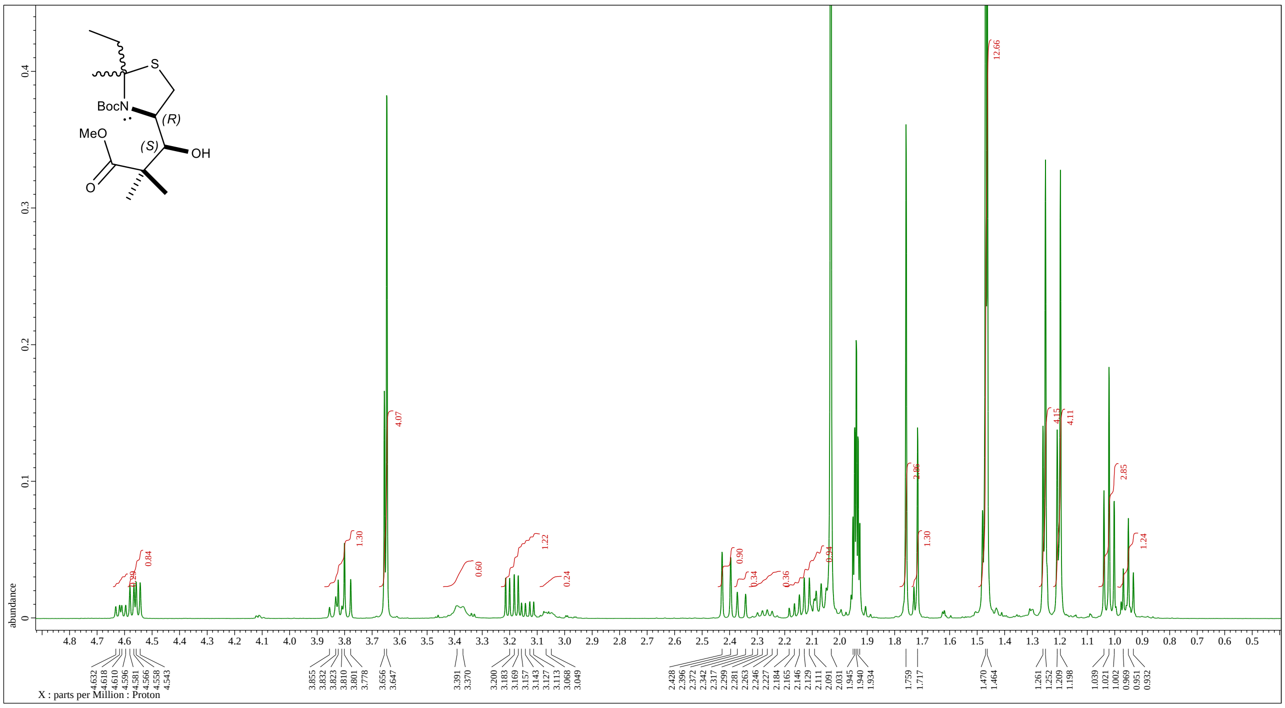


Figure S8. (Top) ^{1}H NMR Spectrum (400 MHz, CDCl$_3$), (bottom) ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of (2*R*,4*R*)-*tert*-butyl 4-((*S*)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-phenylthiazolidine-3-carboxylate (**14**)



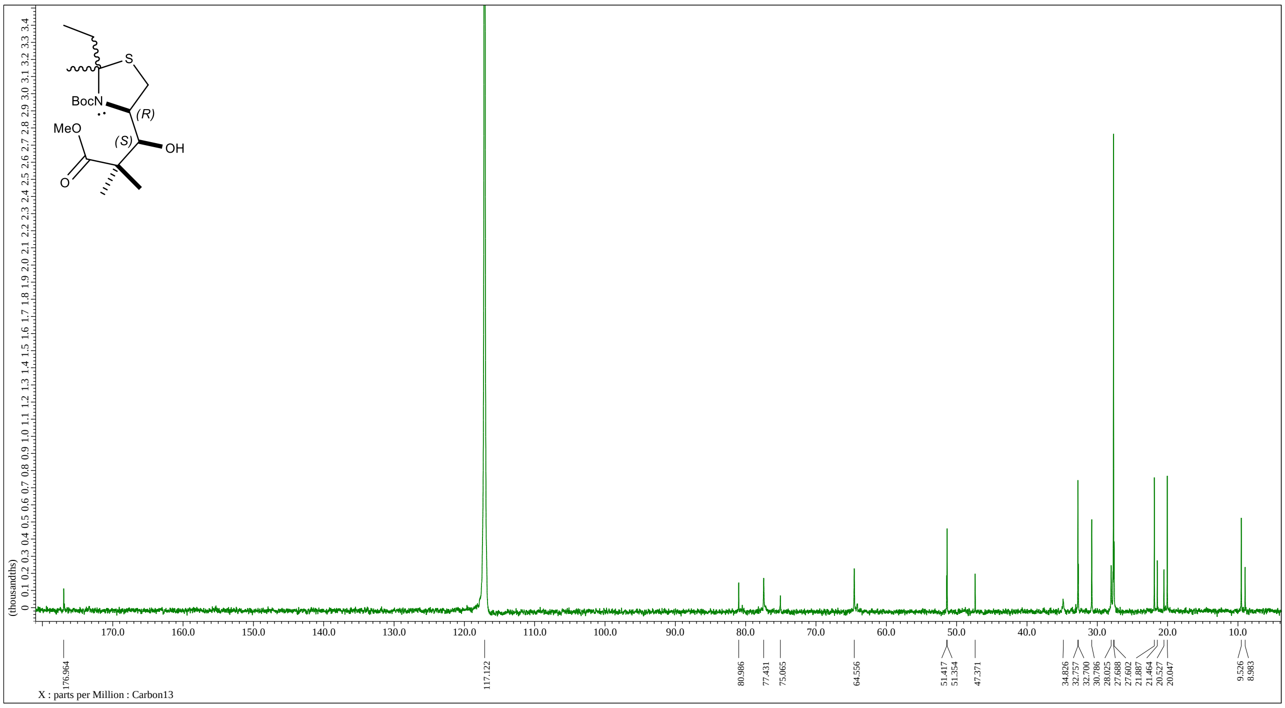


Figure S9. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of a mixture of (2*S*,4*R*)-*tert*-butyl 2-ethyl-4-((*S*)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate and (2*R*,4*R*)-*tert*-butyl 2-ethyl-4-((S)-1-hydroxy-3-methoxy-2,2-dimethyl-3-oxopropyl)-2-methylthiazolidine-3-carboxylate (**16**)

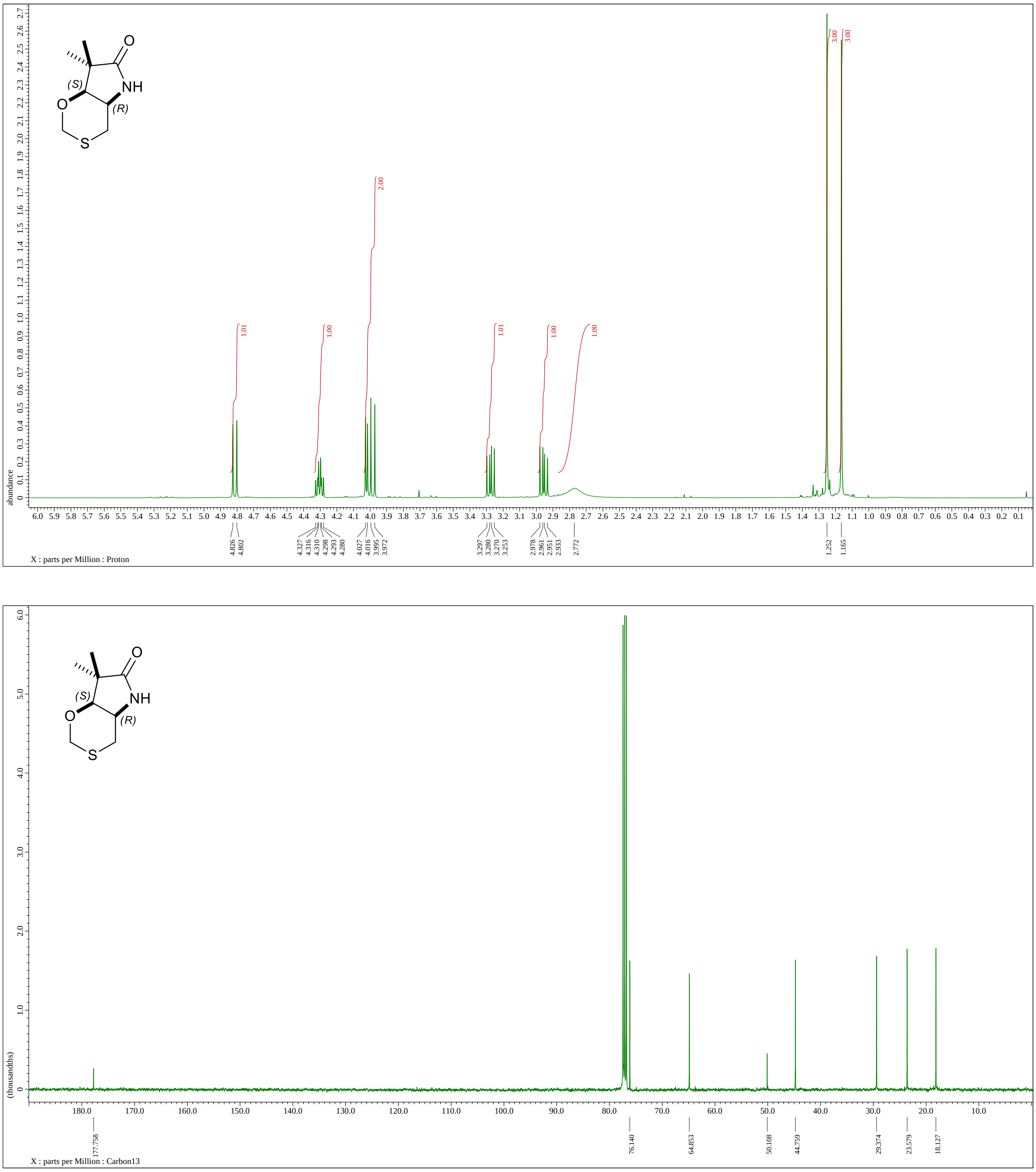


Figure S10. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (7*S*,7*aR*)-7-hydroxy-6,6-dimethyltetrahydropyrrolo[1,2-c]thiazol-5(3*H*)-one (**20**)

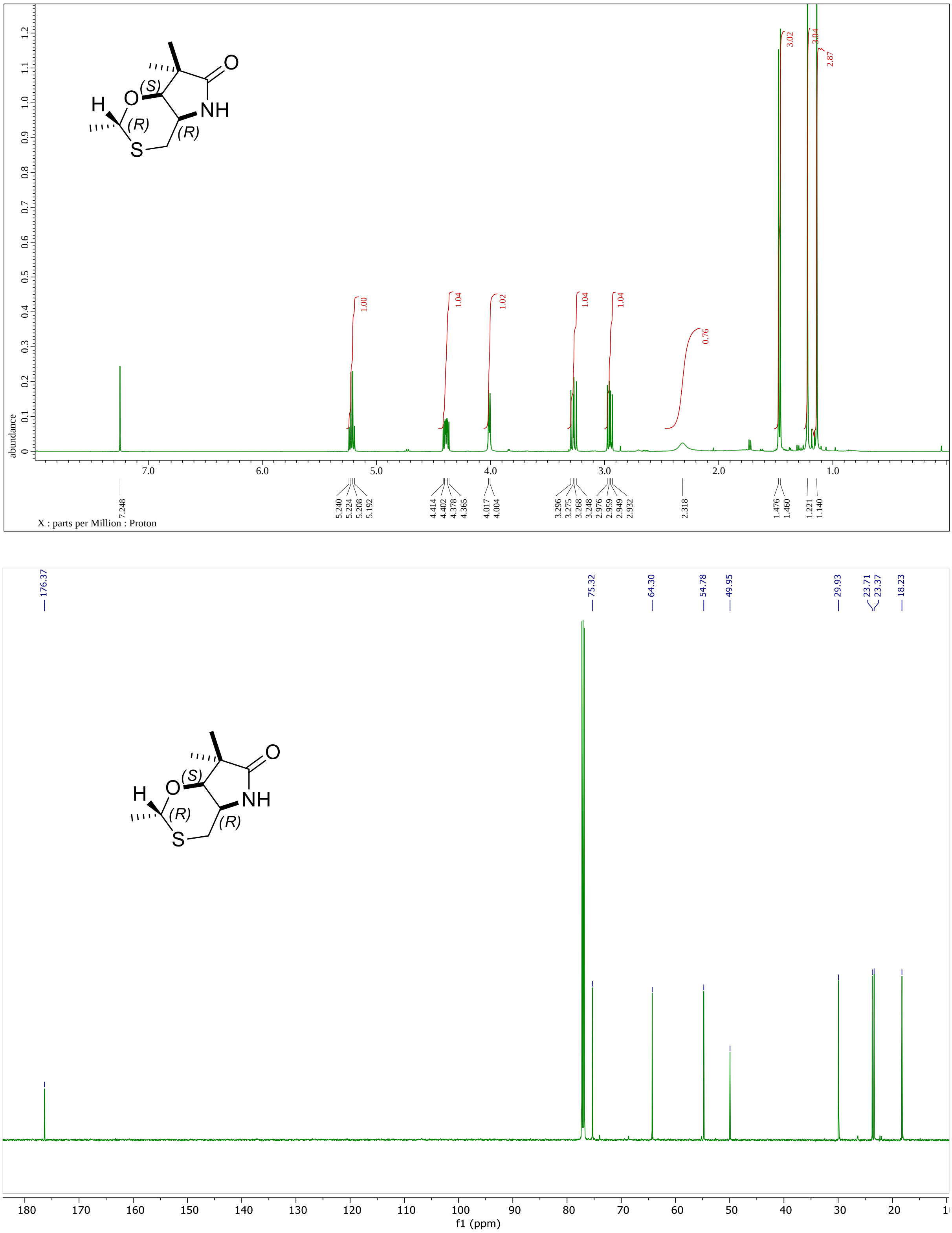


Figure S11. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of (3*S*,7*S*,7*aR*)-7-hydroxy-3,6,6-trimethyltetrahydropyrrolo[1,2-c]thiazol-5(3*H*)-one (**21**)

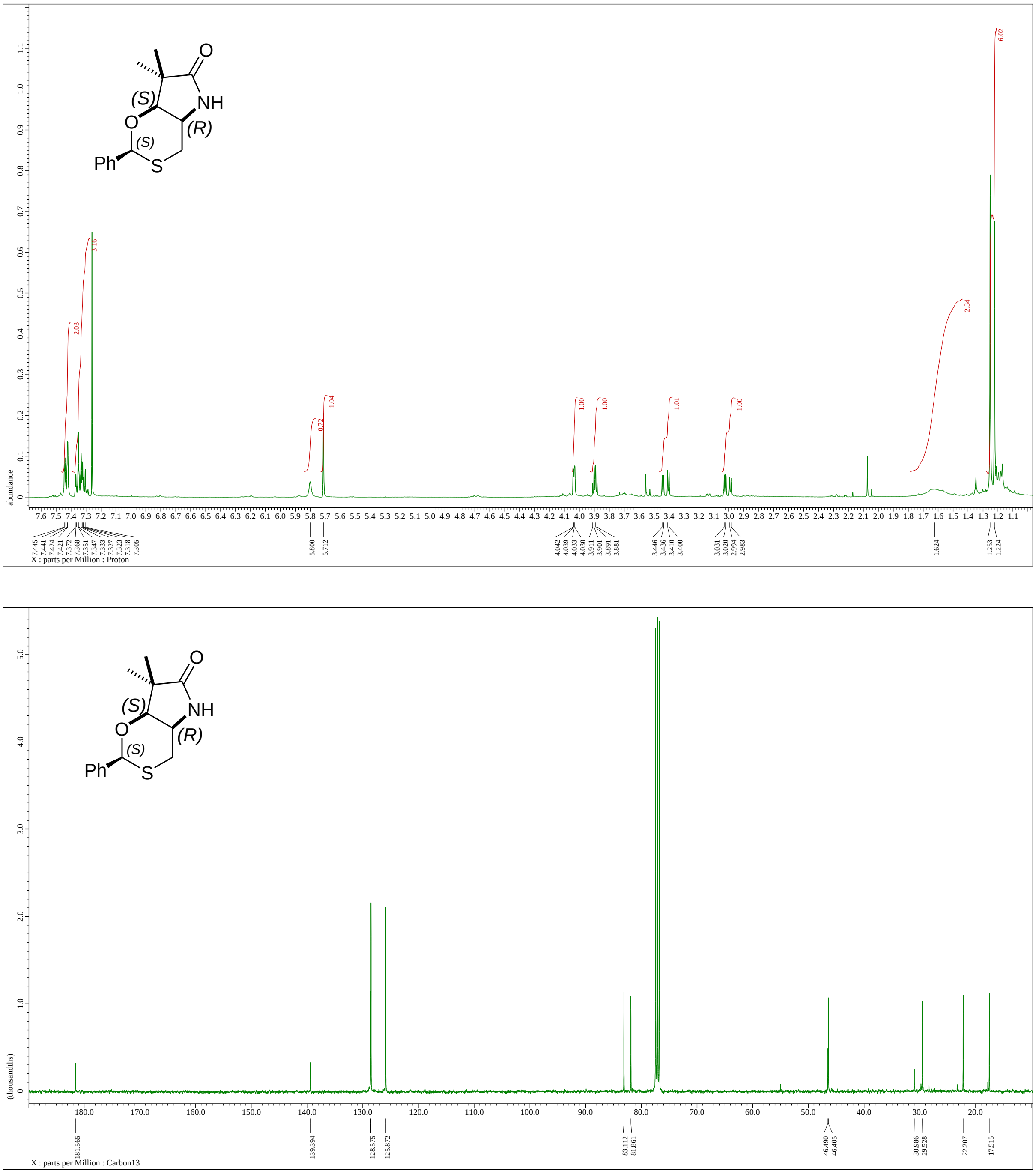


Figure S12. (Top) ^{1}H NMR Spectrum (400 MHz, CDCl$_3$), (bottom) ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of (2*S*,4*aR*,7*aS*)-7,7-dimethyl-2-phenyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4*H*)-one (**22**)

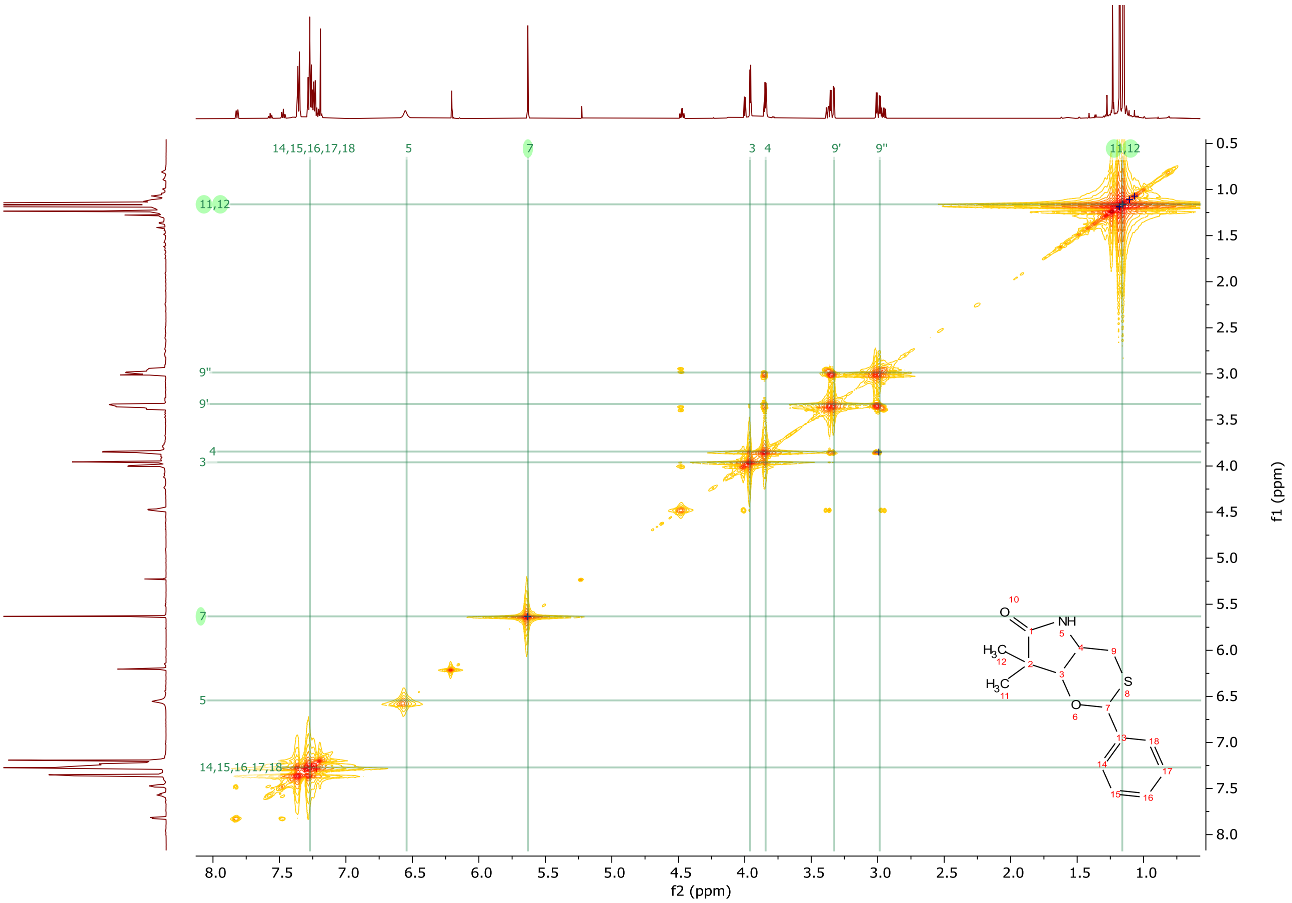


Figure S13. ^1H-^1H COSY spectrum ($CDCl_3$), of compound **22**

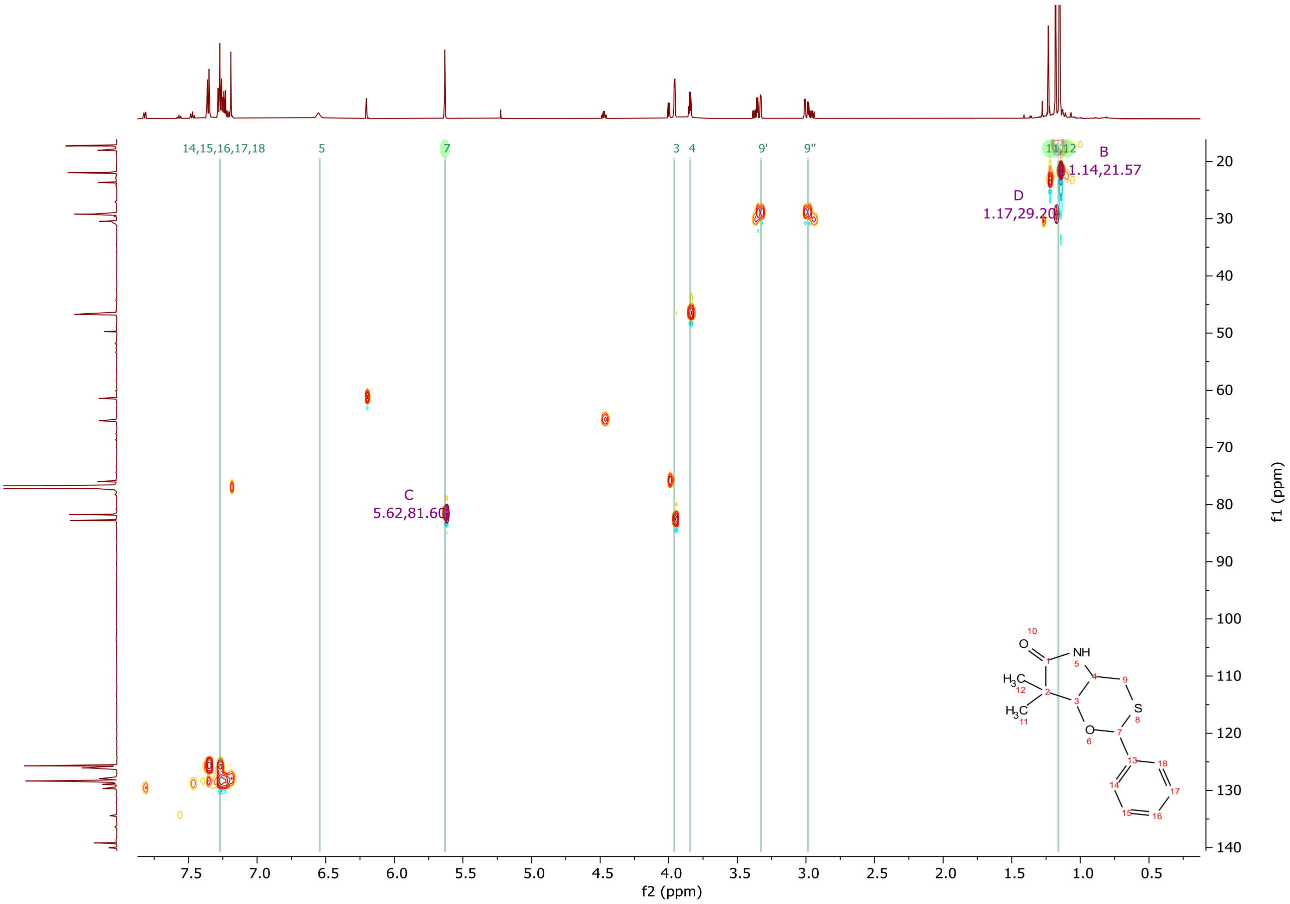


Figure S14. ^{1}H-^{13}C HSQC spectrum (CDCl$_3$), of compound **22**

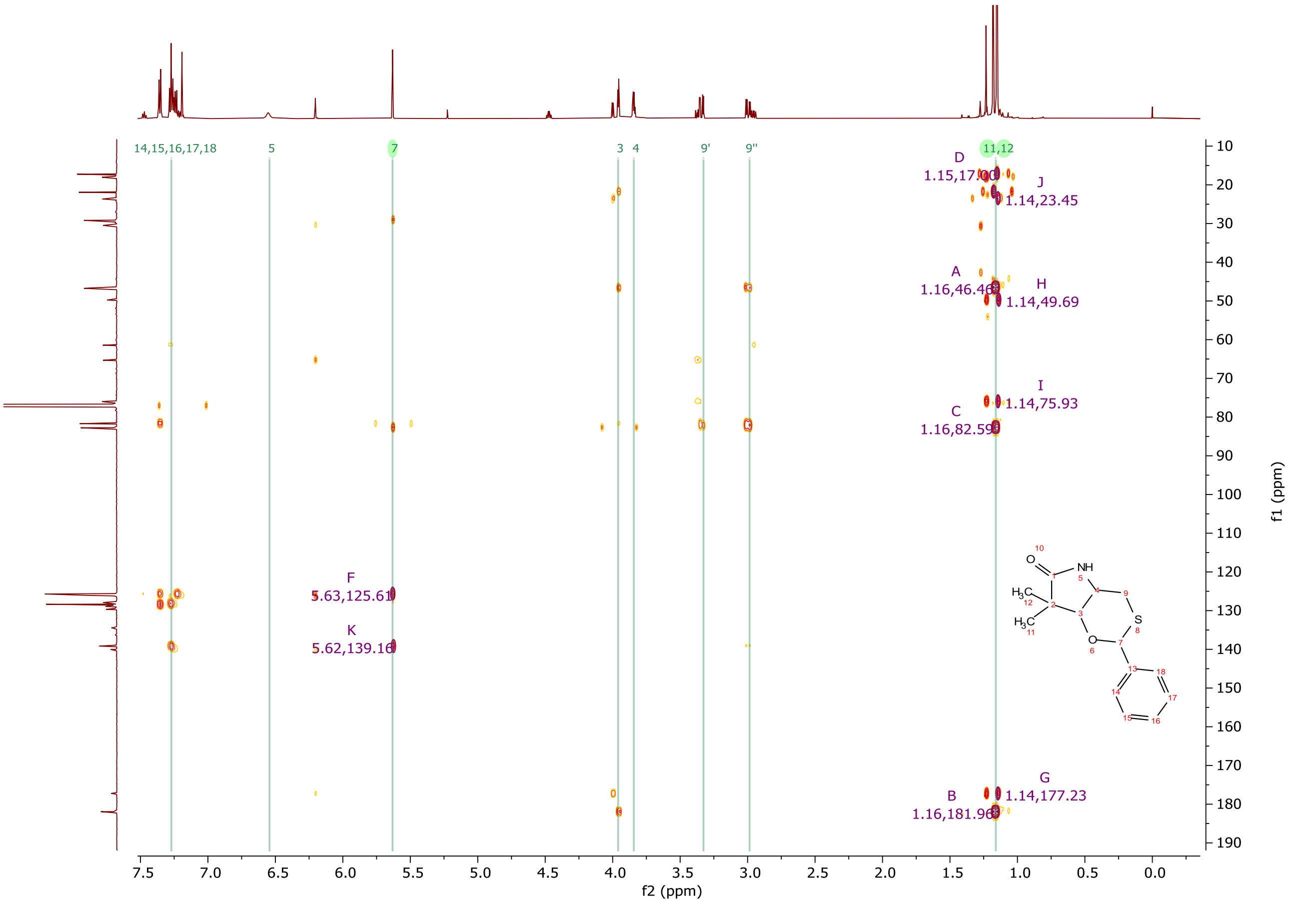


Figure S15. ^{1}H-^{13}C HMBC spectrum (CDCl$_3$) of **22**

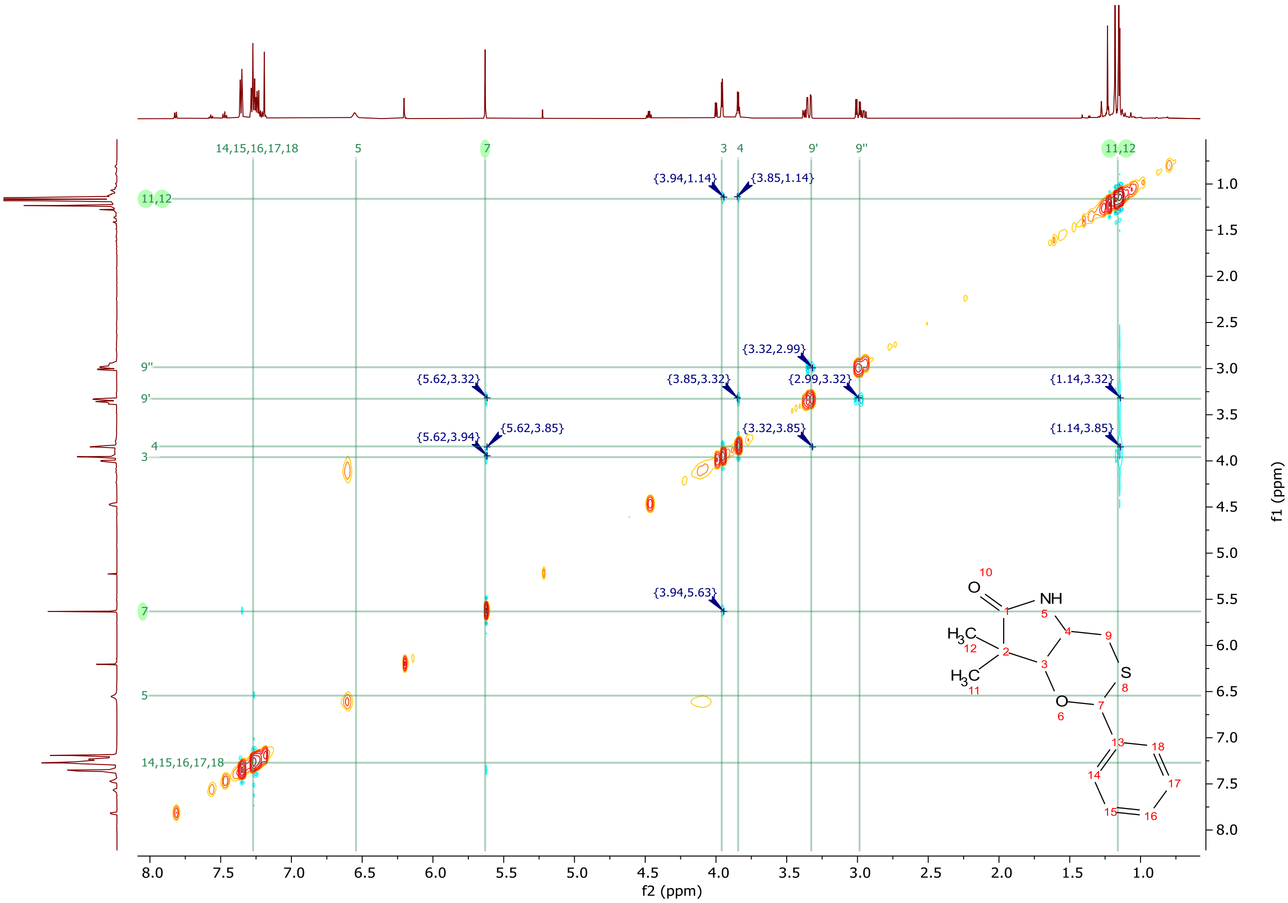


Figure S16. ^{1}H-^{1}H NOESY spectrum (CDCl$_3$) of **22**

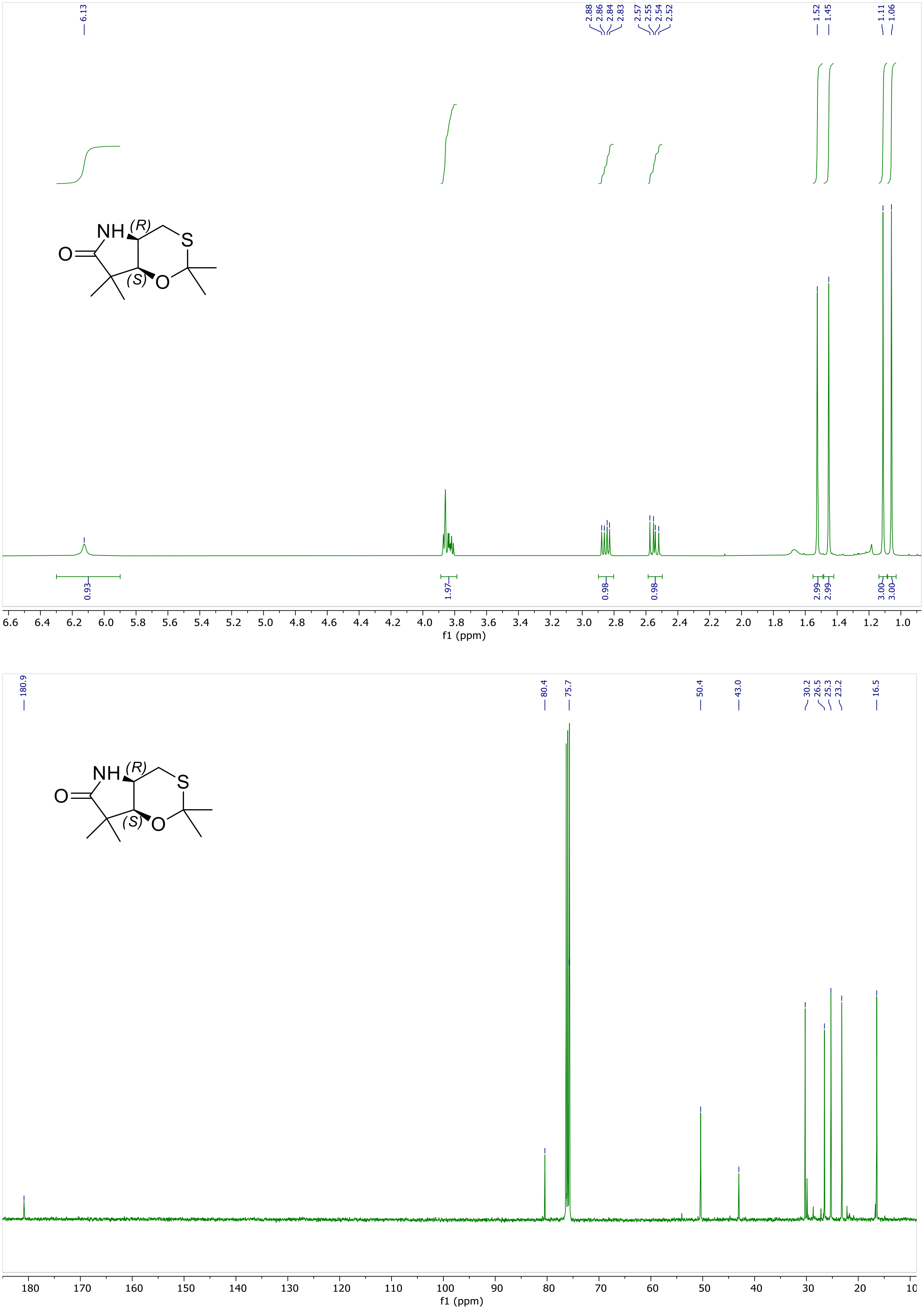


Figure S17. (Top) ^{1}H NMR Spectrum (400 MHz, CDCl$_3$), (bottom) ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of (4*aR*,7*aS*)-2,2,7,7-tetramethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4*H*)-one (**23**)

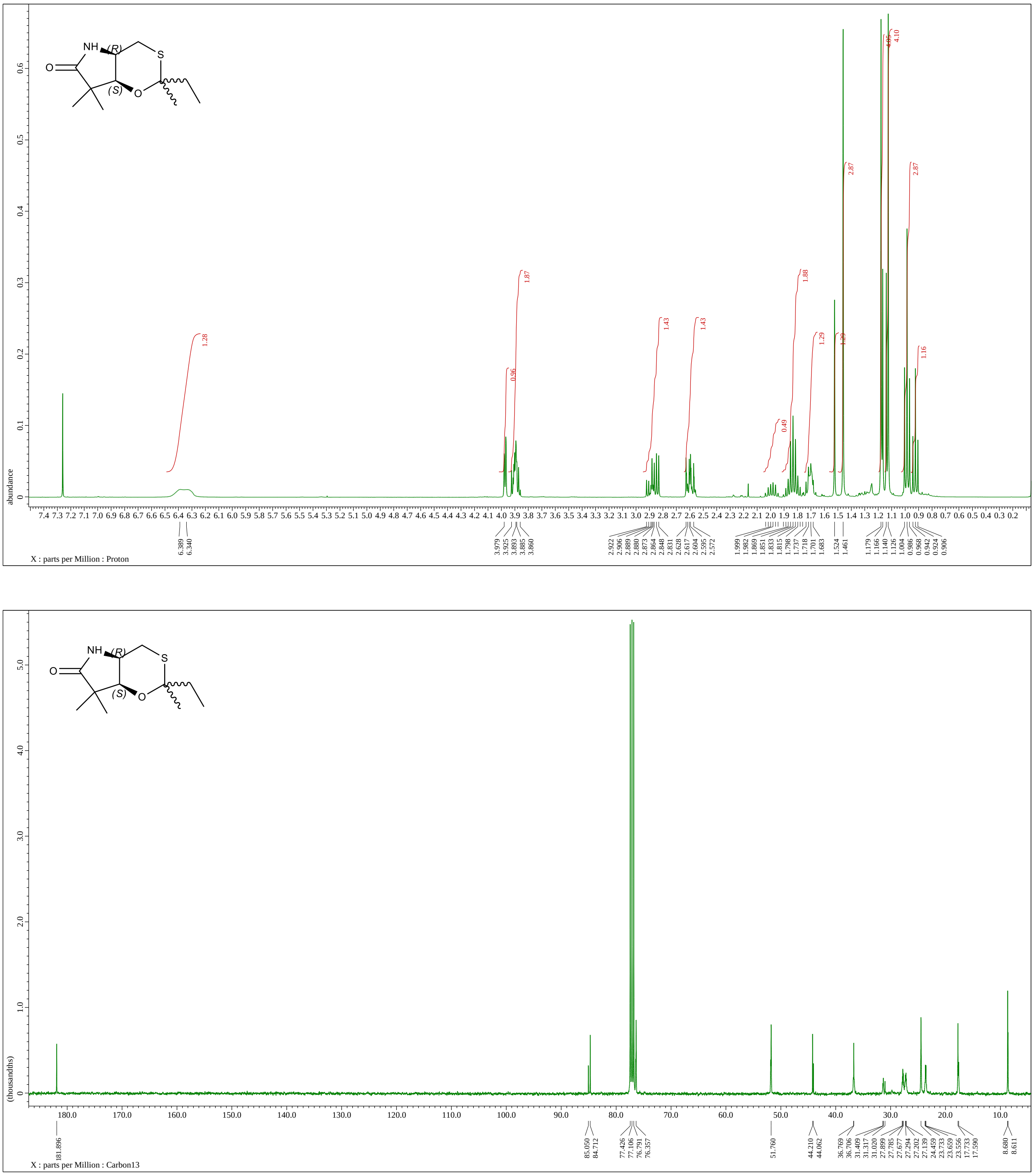


Figure S18. (Top) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$), (bottom) ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of a mixture of (2*S*,4*aR*,7*aS*)-2-ethyl-2,7,7-trimethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one and (2*R*,4*aR*,7*aS*)-2-ethyl-2,7,7-trimethyltetrahydro-[1,3]oxathiino[5,6-b]pyrrol-6(4H)-one (**24**)

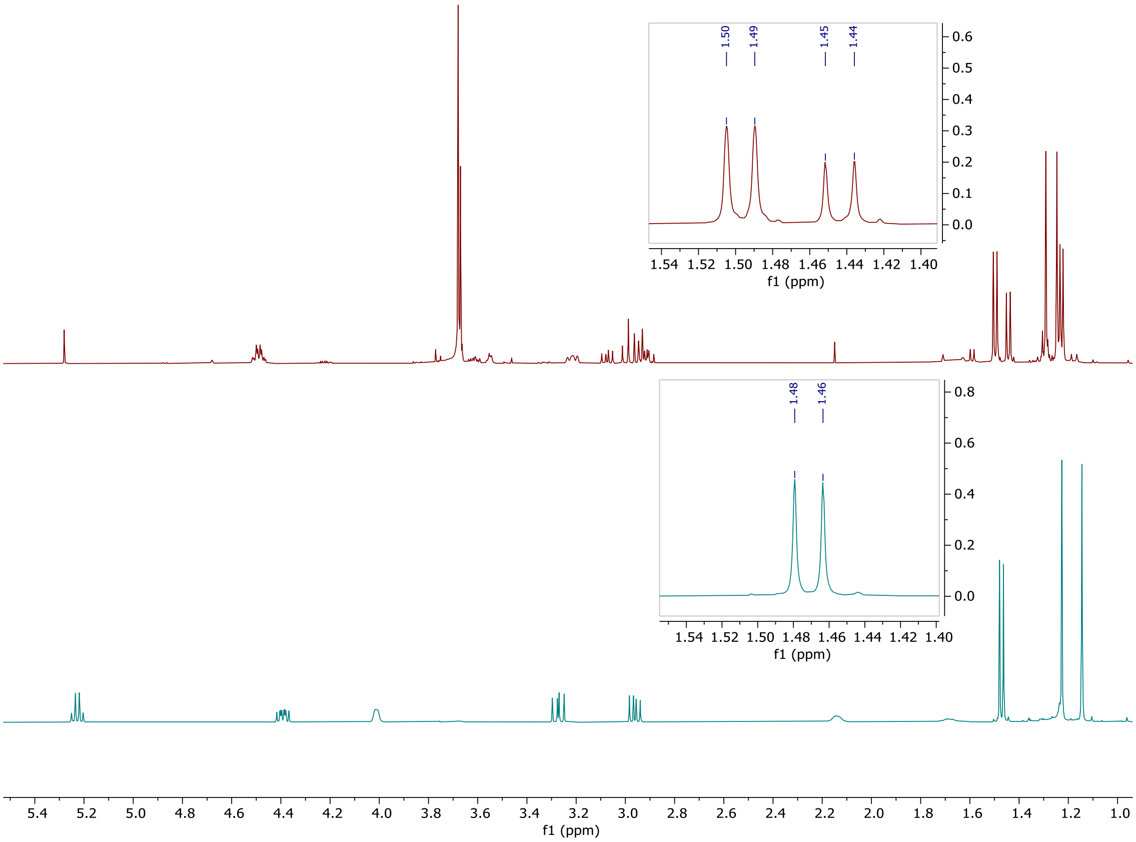


Figure S19. Comparison of ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compounds **18** (top), and **21** (bottom).

4. Single crystal X-ray diffraction studies

The data were collected on an Oxford Diffraction four-circle single crystal diffractometer equipped with a CCD detector using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The raw data were treated with the CrysAlis Data Reduction Program (version 1.171.39.46). The intensities of the reflection were corrected for Lorentz and polarization effects. The crystal structure were solved by direct methods using SHELXS-2018/3 and refined by full-matrix least-squares method using SHELXL-2018/3 program [6,7]. Crystal structure of compound **23'** was refined as a three component twin with the respective domain contribution 0.56, 0.23 and 0.21. Non-hydrogen atoms were refined using anisotropic displacement parameters. H-atoms were placed by geometry and allowed to refine "riding on" the parent atom with U_{iso} = 1.2 U_{eq}(N/C) for NH, CH and CH_2 groups and U_{iso} = 1.5 U_{eq}(C/O) for CH_3 and OH groups. Crystal data and structure refinement details are presented in Table S1. Visualization of the structures were made with Mercury, Diamond 3.2k and CrystalExplorer programs [8-10]. CCDC 2180921-2180926 and 2237944-2237947 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

4.1. A comment on the crystal structure of compounds 3, 4, 7, 20, 21, 21', 22, 22', 23 and 23'.

The compounds crystallize in non-centrosymmetric space groups (Table S1). The symmetry independent part of the unit cell contain one molecule for all the structures with the exception of **21** and **23**, where Z' is 2 and 3, respectively. X-ray analysis reveals that the chiral center of the *S* configuration of the basic reagent L-cysteine is inherited in the crystalline products of the reactions studied in this work and therefore the inversion center is absent in the crystal structures (Figures S20 and S21). Apart of that one chiral center, the new ones are formed during the syntheses and the only one type of the stereoisomer is present in the crystals with the exception of structure **21'** (Figure S21a). Here, a disorder of the five-membered ring is observed which cannot be interpreted as a dynamical hopping of the atoms between two positions, because C1A and C1B atoms has the opposite configuration *R* vs. *S*, respectively. Thus, two diastereoisomers are statistically located in the crystal structure of **21'**.

The bond lengths collected in Table S2 are normal for such type of organic compounds. Particularly, the C–O bond lengths unambiguously indicate carbonyl and hydroxyl groups in the obtained compounds. In the studied crystals, the molecules are assembled around two-fold or screw axes, and they interact to each other by hydrogen bonds. However, the d_{norm} parameter mapped on the Hirshfeld surface [11,12] is relatively poor of strong or medium interactions. The important ones are created by the OH and NH groups (Figure S22). The donor···acceptor distance for the O–H···O hydrogen bonds lies in the range of 2.609(2)–2.788(8) Å, and they are shorter than N–H···O hydrogen bonds, 2.8094(16)–3.442 (5) Å. Nevertheless, the map of the d_{norm} parameter is depicted in blue in most extent indicating large value of this parameter. So, the most intermolecular interactions possess weak nature in the studied crystal structures, *e.g.* see C–H···O interactions in Table S3.

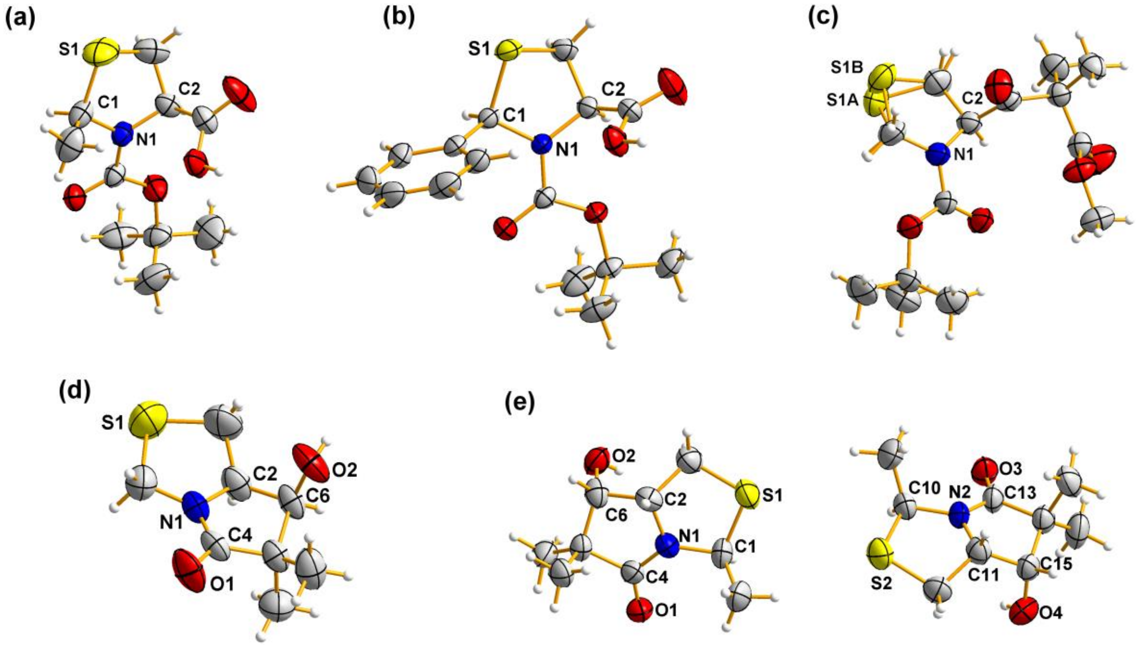


Figure S20. Molecular structure of compounds (a) **3**, (b) **4**, (c) **7**, (d) **20**, (e) **21**.

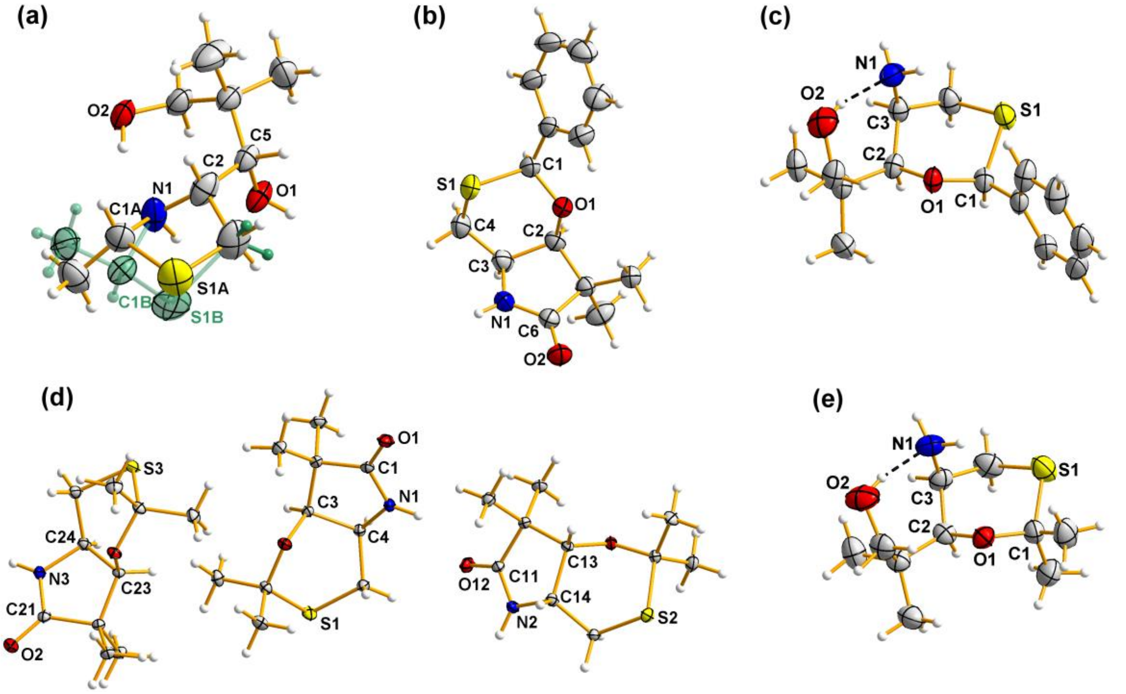


Figure S21. Molecular structure of symmetry independent molecules of compounds (a) **21’**, (b) **22**, (c) **22’**, (d) **23** and (e) **23’**.

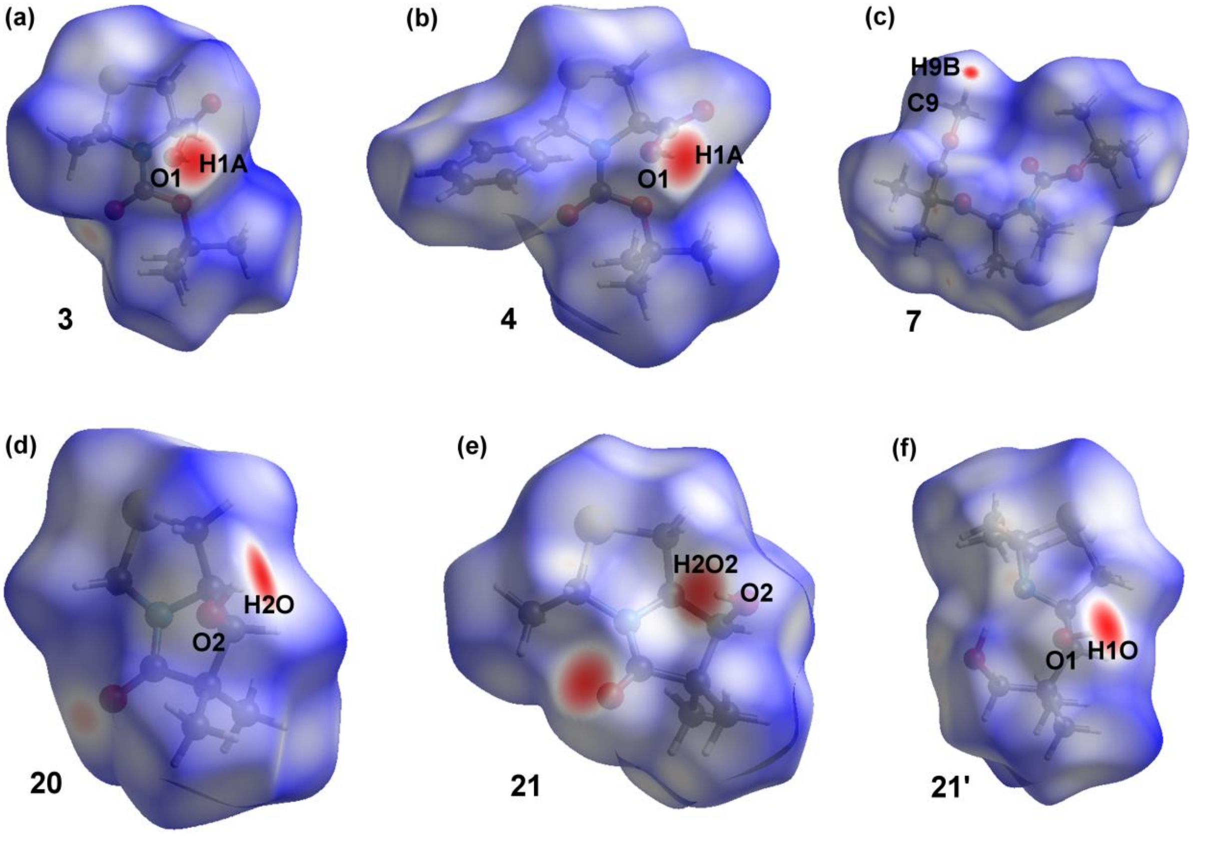


Figure S22. The d_{norm} parameter mapped on the Hirshfeld surface for compounds (a) **3**, (b) **4**, (c) **7**,(d) **20**, (e) **21** and (f) **21’**.

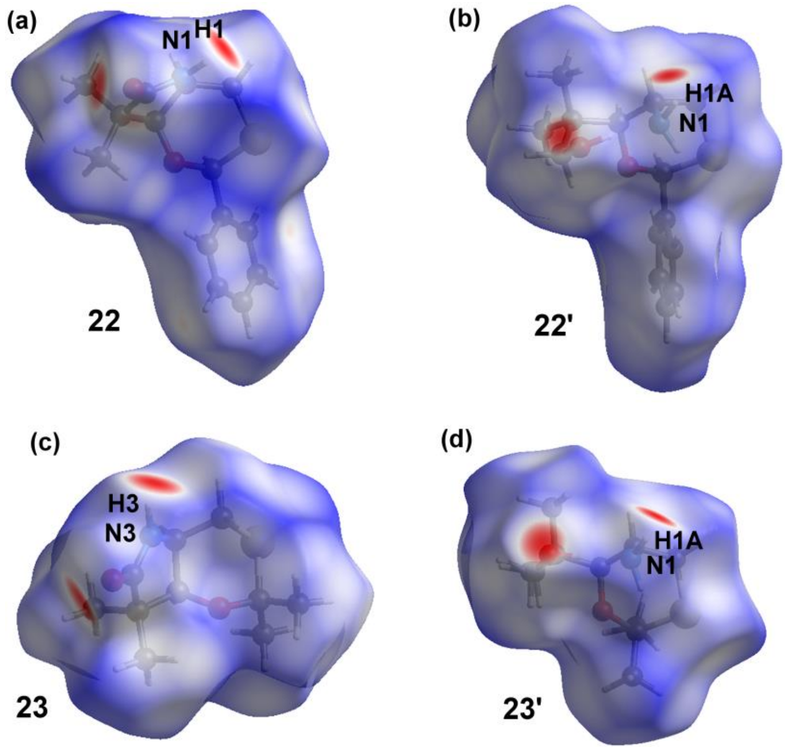


Figure S23. The d_{norm} parameter mapped on the Hirshfeld surface for compounds (a) **22**, (b) **22’**, (c) **23** and (d) **23’**.

Table S1. Crystal data and structure refinement details for compounds **3**, **4**, **7**, **20** and **21**.

Compound	**3**	**4**	**7**	**20**	**21**
Chemical formula	$C_{10}H_{17}NO_4S$	$C_{15}H_{19}NO_4S$	$C_{14}H_{23}NO_5S$	$C_8H_{13}NO_2S$	$C_9H_{15}NO_2S$
M_r	247.30	309.37	317.39	187.25	201.28
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $C2$	Monoclinic, $C2$
Temperature (K)	295	295	295	295	295
a, b, c (Å)	6.5356 (2), 9.8260 (3), 20.5497 (6)	10.3124 (4), 6.3748 (3), 12.1798 (6)	10.0040 (3), 6.04477 (15), 14.4466 (4)	10.0224 (6), 6.6552 (3), 14.9401 (9)	19.872 (3), 6.6196 (7), 16.260 (2)
α, β, γ (°)	90, 90, 90	90, 100.745 (5), 90	90, 105.076 (3), 90	90, 107.562 (6), 90	90, 108.918 (16), 90
V (Å^3)	1319.67 (7)	786.66 (7)	843.54 (4)	950.07 (9)	2023.4 (5)
Z	4	2	2	4	8
μ (mm^{-1})	0.25	0.22	0.21	0.30	0.29
Crystal size (mm)	0.47 × 0.23 × 0.18	0.70 × 0.26 × 0.16	0.60 × 0.26 × 0.12	0.31 × 0.28 × 0.11	0.55 × 0.08 × 0.03
$T_{\min}$, $T_{\max}$	0.926, 0.964	0.908, 0.978	0.912, 0.978	0.935, 0.971	0.957, 0.993
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39826, 3480, 2745	11226, 3558, 3116	22584, 3942, 3443	6887, 2137, 1788	5194, 3217, 1916
R_{int}	0.031	0.022	0.019	0.024	0.071
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.693	0.658	0.658	0.649	0.633
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.133, 1.02	0.033, 0.078, 1.04	0.035, 0.096, 1.02	0.042, 0.115, 1.04	0.075, 0.208, 1.03
No. of refl. / par. / restr.	3480 / 151 / 0	3558 / 195 / 1	3942 / 206 / 1	2137 / 113 / 1	3217 / 244 / 2
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.42, -0.25	0.13, -0.17	0.16, -0.12	0.16, -0.19	0.44, -0.38
Absolute structure parameter	-0.005 (17)	-0.04 (2)	-0.007 (16)	-0.03 (3)	-0.1 (2)

Table S1 cont. Crystal data and structure refinement details for compounds **21’**, **22**, **22’**, **23** and **23’**.

Compound	**21’**	**22**	**22’**	**23**	**23**
Chemical formula	$C_9H_{19}NO_2S$	$C_{14}H_{17}NO_2S$	$C_{14}H_{21}NO_2S$	$C_{10}H_{17}NO_2S$	$C_{10}H_{21}NO_2S$
M_r	205.31	263.34	267.38	215.30	219.34
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	295	295	295	100	295
a, b, c (Å)	6.2757 (4), 10.0567 (8), 18.9671 (16)	5.6555 (3), 8.2434 (3), 14.8956 (7)	9.9519 (5), 5.9259 (3), 12.0663 (6)	14.7795 (2), 8.01466 (11), 15.0100 (3)	5.9251 (4), 11.4025 (8), 18.0255 (14)
α, β, γ (°)	90, 90, 90	90, 100.631 (5), 90	90, 90.859 (4), 90	90, 107.4776 (18), 90	90, 90, 90
V (Å^3)	1197.06 (16)	682.52 (6)	711.51 (6)	1695.89 (5)	1217.81 (15)
Z	4	2	2	6	4
μ (mm^{-1})	0.25	0.23	0.22	0.26	0.25
Crystal size (mm)	0.50 × 0.09 × 0.05	0.54 × 0.32 × 0.04	0.66 × 0.11 × 0.04	0.53 × 0.26 × 0.15	0.46 × 0.09 × 0.06
$T_{\min}$, $T_{\max}$	0.937, 0.990	0.903, 0.990	0.919, 0.991	0.925, 0.969	0.901, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8475, 2504, 1382	8211, 3249, 2608	6822, 3003, 2732	57514, 10359, 9890	7693, 7693, 3609
R_{int}	0.035	0.023	0.028	0.030	?
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.632	0.690	0.633	0.714	0.628
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.130, 1.00	0.039, 0.089, 1.06	0.036, 0.093, 1.05	0.025, 0.064, 1.06	0.054, 0.139, 0.83
No. of refl. / par. / restr	2504 / 152 / 1	3249 / 165 / 1	3003 / 172 / 1	10359 / 400 / 1	7693 / 140 / 2
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.13, -0.11	0.14, -0.21	0.28, -0.28	0.34, -0.19	0.24, -0.22
Absolute structure parameter	-0.07 (6)	0.06 (3)	0.00 (3)	0.006 (12)	0.35 (11)

Table S2. Selected geometric parameters (Å) for compounds **3**, **4**, **7**, **20**, **21**, **21'**, **22**, **22'**, **23** and **23'**.

Compound **3**			
S1—C1	1.817 (3)	N1—C2	1.447 (3)
S1—C3	1.801 (4)	N1—C1	1.475 (3)
O1—C5	1.300 (3)	C1—C4	1.503 (4)
O2—C5	1.197 (3)	C2—C3	1.522 (4)
O3—C6	1.331 (3)	C2—C5	1.527 (4)
O3—C7	1.485 (3)	C7—C10	1.496 (5)
O4—C6	1.231 (3)	C7—C9	1.517 (5)
N1—C6	1.340 (3)	C7—C8	1.519 (5)
Compound **4**			
S1—C1	1.821 (2)	C2—C10	1.516 (3)
S1—C3	1.799 (2)	C2—C3	1.532 (3)
O1—C10	1.309 (3)	C4—C5	1.385 (4)
O2—C10	1.199 (3)	C4—C9	1.385 (4)
O3—C11	1.329 (3)	C5—C6	1.388 (4)
O3—C12	1.480 (3)	C6—C7	1.365 (5)
O4—C11	1.224 (3)	C7—C8	1.379 (5)
N1—C11	1.346 (3)	C8—C9	1.386 (3)
N1—C2	1.459 (3)	C12—C15	1.510 (3)
N1—C1	1.479 (3)	C12—C14	1.510 (4)
C1—C4	1.504 (3)	C12—C13	1.515 (4)
Compound **7**			
S1B—C1B	1.710 (5)	O5—C10	1.338 (2)
S1B—C3B	1.831 (5)	O5—C11	1.478 (3)
S1A—C1A	1.816 (4)	N1—C10	1.361 (3)
S1A—C3A	1.779 (3)	N1—C2	1.461 (3)
C1A—N1	1.440 (3)	C2—C4	1.530 (3)
C3A—C2	1.545 (3)	C4—C5	1.535 (3)
C1B—N1	1.440 (3)	C5—C7	1.535 (3)
C3B—C2	1.545 (3)	C5—C6	1.535 (3)
O1—C4	1.208 (2)	C5—C8	1.536 (3)
O2—C7	1.185 (3)	C11—C12	1.503 (4)
O3—C7	1.317 (3)	C11—C14	1.506 (4)
O3—C9	1.443 (3)	C11—C13	1.512 (4)
O4—C10	1.203 (2)		
Compound **20**			
S1—C1	1.807 (4)	C2—C6	1.538 (4)
S1—C3	1.816 (5)	O2—C6	1.408 (3)
O1—C4	1.235 (3)	C4—C5	1.523 (4)

C1—N1	1.438 (4)	C5—C8	1.522 (4)
N1—C4	1.327 (4)	C5—C7	1.535 (4)
N1—C2	1.462 (3)	C5—C6	1.546 (4)
C2—C3	1.511 (5)		
Compound **21**			
S1—C1	1.806 (9)	C5—C8	1.527 (12)
S1—C3	1.800 (9)	C5—C6	1.533 (11)
S2—C10	1.825 (9)	O3—C13	1.205 (10)
S2—C12	1.803 (9)	O4—C15	1.406 (11)
O1—C4	1.221 (9)	N2—C13	1.354 (10)
O2—C6	1.410 (10)	N2—C11	1.454 (10)
N1—C4	1.333 (10)	N2—C10	1.456 (9)
N1—C2	1.450 (11)	C10—C16	1.506 (13)
N1—C1	1.470 (10)	C11—C12	1.516 (12)
C1—C7	1.477 (13)	C11—C15	1.526 (11)
C2—C3	1.520 (12)	C13—C14	1.513 (11)
C2—C6	1.549 (11)	C14—C17	1.522 (13)
C4—C5	1.543 (11)	C14—C18	1.531 (12)
C5—C9	1.495 (11)	C14—C15	1.556 (12)
Compound **21’**			
S1B—C1B	1.841 (14)	C2—C3B	1.537 (6)
S1B—C3B	2.031 (13)	N1—C1B	1.519 (15)
S1A—C1A	1.840 (9)	N1—C1A	1.539 (9)
S1A—C3A	1.723 (7)	C1A—C4A	1.450 (19)
O1—C5	1.415 (4)	C1B—C4B	1.58 (3)
O2—C7	1.407 (4)	C5—C6	1.534 (5)
C2—N1	1.475 (6)	C6—C7	1.519 (5)
C2—C5	1.512 (5)	C6—C9	1.540 (6)
C2—C3A	1.537 (6)	C6—C8	1.552 (6)
Compound **22**			
S1—C1	1.816 (2)	C3—C4	1.519 (4)
S1—C4	1.812 (3)	C5—C8	1.520 (3)
O1—C1	1.417 (3)	C5—C6	1.531 (3)
O1—C2	1.427 (3)	C5—C7	1.535 (3)
O2—C6	1.232 (3)	C9—C14	1.383 (4)
N1—C6	1.338 (3)	C9—C10	1.391 (4)
N1—C3	1.451 (3)	C10—C11	1.383 (4)
C1—C9	1.500 (3)	C11—C12	1.364 (5)
C2—C5	1.539 (3)	C12—C13	1.369 (5)
C2—C3	1.540 (3)	C13—C14	1.382 (4)
Compound **22’**			
S1—C1	1.825 (3)	C5—C10	1.387 (4)

S1—C4	1.821 (3)	C5—C6	1.394 (4)
O1—C1	1.420 (3)	C6—C7	1.402 (5)
O1—C2	1.444 (3)	C7—C8	1.372 (6)
O2—C14	1.408 (3)	C8—C9	1.368 (5)
N1—C3	1.459 (4)	C9—C10	1.382 (4)
C1—C5	1.505 (3)	C11—C12	1.528 (3)
C2—C3	1.525 (3)	C11—C13	1.534 (4)
C2—C11	1.546 (3)	C11—C14	1.535 (3)
C3—C4	1.532 (4)		
Compound **23**			
S1—C5	1.8060 (14)	O12—C11	1.2365 (18)
S1—C6	1.8593 (15)	C12—C18	1.526 (2)
S2—C15	1.8039 (14)	C12—C11	1.5320 (19)
S2—C16	1.8645 (15)	C12—C17	1.544 (2)
S3—C25	1.8099 (15)	C12—C13	1.5483 (19)
S3—C26	1.8583 (15)	C13—C14	1.5532 (19)
O1—C1	1.2352 (18)	C14—C15	1.522 (2)
C1—N1	1.3411 (19)	C16—C20	1.518 (2)
C1—C2	1.532 (2)	C16—C19	1.528 (2)
N1—C4	1.4622 (18)	O2—C21	1.2331 (18)
O4—C3	1.4311 (17)	O5—C23	1.4265 (16)
O4—C6	1.4322 (17)	O5—C26	1.4335 (17)
C4—C5	1.530 (2)	C6—C9	1.523 (2)
C4—C3	1.5453 (19)	C6—C10	1.527 (2)
C2—C7	1.529 (2)	C22—C27	1.527 (2)
C2—C8	1.538 (2)	C22—C21	1.536 (2)
C2—C3	1.539 (2)	C22—C28	1.541 (2)
N2—C11	1.3376 (19)	C22—C23	1.541 (2)
N2—C14	1.4558 (18)	C25—C24	1.526 (2)
N3—C21	1.3387 (19)	C24—C23	1.545 (2)
N3—C24	1.4588 (18)	C30—C26	1.521 (2)
O3—C16	1.4283 (17)	C29—C26	1.525 (2)
O3—C13	1.4288 (17)		
Compound **23’**			
S1—C1	1.845 (7)	C1—C6	1.525 (9)
S1—C4	1.804 (7)	C2—C3	1.520 (9)
O1—C1	1.423 (8)	C2—C7	1.527 (9)
O1—C2	1.429 (8)	C3—C4	1.524 (9)
O2—C8	1.410 (8)	C7—C9	1.521 (9)
N1—C3	1.475 (9)	C7—C10	1.527 (10)
C1—C5	1.514 (9)	C7—C8	1.541 (10)

Table S3. Selected hydrogen-bond parameters for compounds **3**, **4**, **7**, **20**, **21**, **21'**, **22**, **22'**, **23** and **23'**.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
Compound **3**				
O1—H1A···O4$^{\mathrm{i}}$	0.78	1.87	2.648 (3)	175.0
C2—H2···O2$^{\mathrm{ii}}$	0.98	2.58	3.370 (4)	138.1
C9—H9B···O4$^{\mathrm{iii}}$	0.96	2.53	3.462 (4)	163.3
C10—H10B···O4	0.96	2.53	3.068 (4)	115.7
Compound **4**				
O1—H1A···O4$^{\mathrm{iv}}$	0.87	1.74	2.609 (2)	173.5
C14—H14B···O4	0.96	2.44	2.953 (3)	113.4
C15—H15C···O4	0.96	2.48	3.032 (3)	116.6
Compound **7**				
C3Bb—H3BBb···O1$^{\mathrm{v}}$	0.97	2.68	3.605 (3)	160.3
C3Aa—H3ABa···O1$^{\mathrm{v}}$	0.97	2.69	3.605 (3)	157.2
C9—H9B···O2$^{\mathrm{iv}}$	0.96	2.61	3.545 (4)	165.4
Compound **20**				
O2—H2O···O1$^{\mathrm{iv}}$	0.74	2.06	2.731 (3)	150.9
C1—H1AB···O2$^{\mathrm{vi}}$	0.97	2.60	3.269 (4)	126.1
C2—H2···O1$^{\mathrm{vii}}$	0.98	2.49	3.437 (4)	162.0
Compound **21**				
O2—H2O2···O1$^{\mathrm{viii}}$	0.82	1.97	2.788 (8)	174.7
O4—H4O4···O3$^{\mathrm{ix}}$	0.82	1.95	2.764 (8)	171.0
C2—H2···S1$^{\mathrm{x}}$	0.98	3.03	3.829 (9)	139.8
Compound **21'**				
O1—H1O···O2$^{\mathrm{i}}$	0.82	1.87	2.685 (3)	172.0
O2—H2O···N1	0.82	1.92	2.701 (4)	158.9
N1—H1···O2$^{\mathrm{xi}}$	1.18	2.37	3.442 (5)	150.3
C4Bb—H4BAb···S1Bb$^{\mathrm{xii}}$	0.96	2.99	3.52 (2)	115.7
Compound **22**				
N1—H1···O2$^{\mathrm{xiii}}$	0.86	2.09	2.917 (3)	162.1
C7—H7C···O2$^{\mathrm{xii}}$	0.96	2.53	3.390 (4)	148.8
C8—H8C···S1$^{\mathrm{iv}}$	0.96	2.98	3.722 (3)	134.6
Compound **22'**				
O2—H2O···N1	0.82	1.90	2.698 (3)	165.7
N1—H1A···O2$^{\mathrm{xiv}}$	0.84 (4)	2.34 (4)	3.016 (3)	138 (4)
Compound **23**				
N1—H1···O12	0.87 (2)	2.03 (2)	2.8497 (16)	155.4 (19)
N2—H2···O1$^{\mathrm{iv}}$	0.86 (2)	2.04 (2)	2.8390 (17)	154.2 (19)
N3—H3···O2$^{\mathrm{xv}}$	0.83 (2)	2.02 (2)	2.8094 (16)	159 (2)
C4—H4···O12$^{\mathrm{xvi}}$	0.98	2.59	3.5243 (18)	160.2

C14—H14···O2$^{\mathrm{xvii}}$	0.98	2.62	3.5029 (18)	150.3
C15—H15A···S1$^{\mathrm{xviii}}$	0.97	2.96	3.9294 (15)	177.2
C24—H24···S2$^{\mathrm{xix}}$	0.98	2.82	3.7065 (14)	151.2
Compound **23’**				
O2—H2A···N1	0.82	1.88	2.683 (9)	164.6
N1—H1A···O2$^{\mathrm{ii}}$	0.88 (4)	2.16 (6)	2.962 (8)	150 (7)

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) *x*+1/2, -*y*+3/2, -*z*+1; (iii) -*x*+2, *y*+1/2, -*z*+3/2; (iv) *x*, *y*-1, *z*; (v) -*x*+1, *y*+1/2, -*z*+1; (vi) *x*+1/2, *y*+1/2, *z*; (vii) *x*+1/2, *y*-1/2, *z*; (viii) -*x*+1/2, *y*+1/2, -*z*+1; (ix) -*x*+1/2, *y*-1/2, -*z*; (x) -*x*+1, *y*, -*z*+1; (xi) *x*-1/2, -*y*+1/2, -*z*; (xii) *x*+1, *y*, *z*; (xiii) -*x*, *y*+1/2, -*z*; (xiv) -*x*+2, *y*+1/2, -*z*; (xv) -*x*, *y*+1/2, -*z*+1; (xvi) -*x*+1, *y*+1/2, -*z*; (xvii) -*x*+1, *y*-1/2, -*z*+1; (xviii) -*x*+1, *y*-1/2, -*z*; (xix) *x*-1, *y*+1, *z*.

5. Calculations

5.1. Methods

The conformational analysis of the studied systems was performed using the Conflex program [13-15], in which the MMFF94s force field was applied and the 1 kcal/mol energy window. In the next step, the MMFF94s structures were optimized using the DFT B3LYP functional [16-18] combined with the def2-TZVP basis set [19]. All stationary points (minima and transition structures) were characterized by calculating the harmonic vibrational frequencies. The transition structures (TS) were found by using the quadratic synchronous transit-guided quasi-Newton (QST3) method [20]. In some cases, the intrinsic reaction coordinate (IRC) calculations [21,22] were performed for both forward and reverse directions of the vibrational mode calculations to confirm that the found transition states connect the appropriate minima. However, in most cases, one imaginary frequency with a high value and appropriate vibrational mode was enough to state that the found TS structure is the proper one. Structures minima were confirmed by ascertaining that all harmonic frequencies were real.

The duplicate conformers have been removed, and the relative abundances were calculated based on the ΔE and ΔG values referred to the value of the most stable conformer. The natural bond analysis (NBO) [23] was performed to estimate the charge distribution. All calculations were performed using the *Gaussian 16* package [24], and the structures were visualized using *GaussView* [25]. The computational data were processed with the help of the *Tesliper* software [26].

5.2. Results

To model the mechanisms proceeding through the iminium and sulfonium ions, the starting structures corresponding to compounds **13** (with R^1 = H, R^2 = Me) and **16** (R^1 = Me, R^2 = Et), though with Boc already replaced by COOH group were considered, respectively. In some calculations, also the R^1 = H, R^2 = Ph derivatives corresponding to compound **14** were addressed. In every reaction step, both epimers (differing by configuration on C-2) were taken into account. The studied structures are presented in Scheme S1, their energetic data are gathered in Tables S4-S17, and the Cartesian coordinates of the most stable conformers can be found in Tables S18-S20.

Despite conformational flexibility, only one or two conformers dominated in each of the reaction step due to the intermolecular hydrogen bond (HB) interactions (Tables S4-S17). Figures S24-S27 show the reaction mechanisms based on the computational results. The calculated energetic data of the molecule with R^1 = H, R^2 = Me substituents show that if the substrate has (2*R*)-configuration, the intermediate product **18** contains some amount of (*S*)-epimer due to the opening of thiazolidine ring.

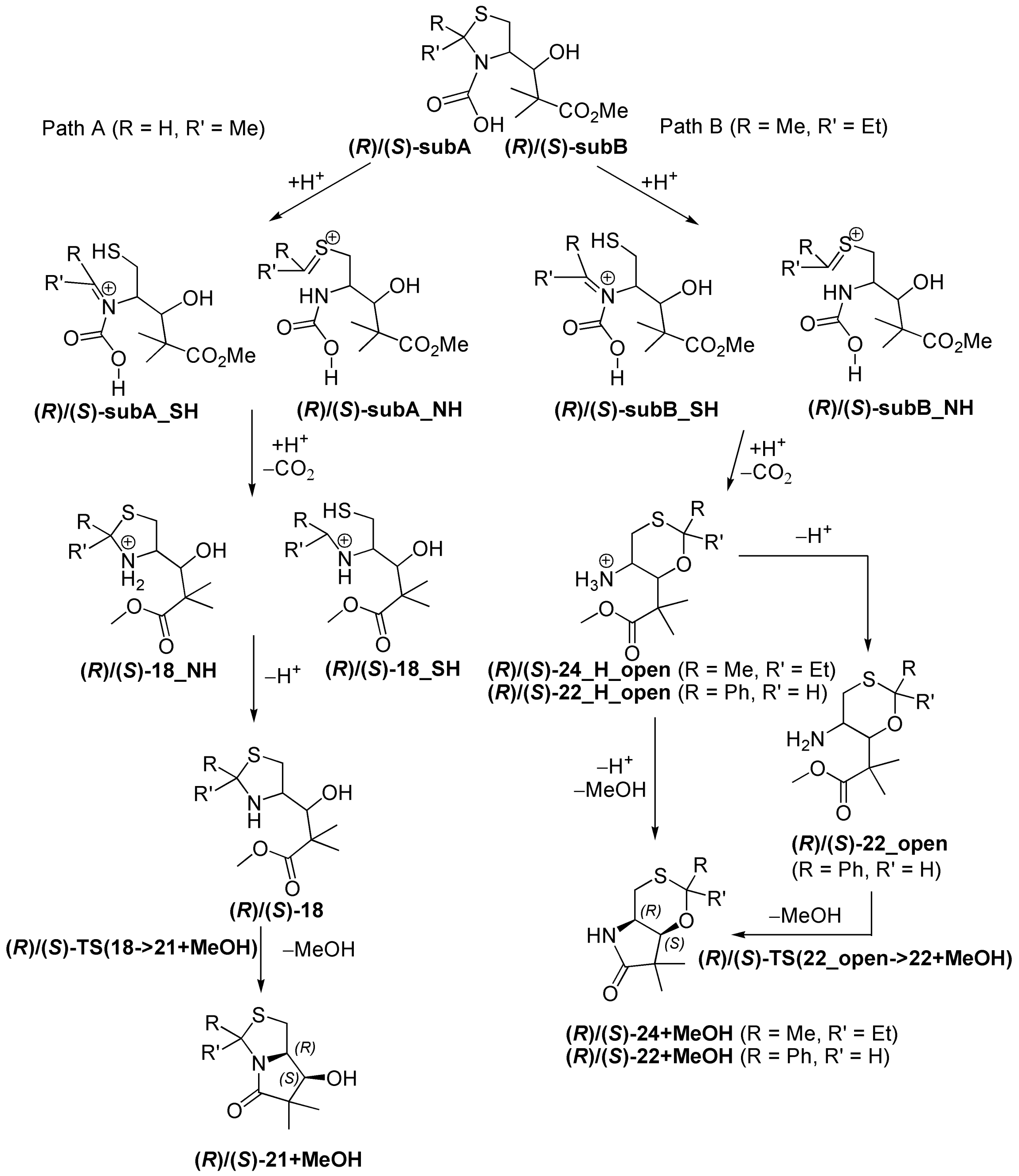
In case of product **21** conformers with (2*S*)-configuration have lower energy (Tables S4-S10). Thus, reactants and products in the iminium pathway have reverse configurations at the C2 atom. On the other hand, an epimeric mixture is obtained at every step of the sulfonium ion path (R^1 = H, R^2 = Et) with a slight domination of (*S*)-forms (Tables S11-S14). Finally, in case of compound **22** (R^1 = H, R^2 = Ph) the reaction mechanism is more complicated, however, (2*R*)-configuration of the product is preferred, while the substrate has (2*S*) configuration (Tables S15-S17). Thus, the energetic computational results are concordant with the experiment.

Two main issues arise within this study: 1. What determines the choice of the iminium and sulfonium ion paths? 2. Why products **21**, **22** have an inverted configuration on C-2 in comparison to the substrate?

The presence of two substituents at the C2 atom (R^1 = Me, and R^2 = Et, path B) leads to formation of very stable structure in which protonation takes place at the N atom and the C2-N bond is broken (Fig. S20). Simple rotation about the single C-S bond leads to the closure of the 1,3-oxathiane ring (Fig. S20). Since this rotation can take place in both directions, no preferential configuration is found at the C2 atom. However, the 1,3-oxathiane ring may adopt chair or boat conformations. The former dominates in (*S*)-**24**_H_open-c8 and (*S*)-**22**_H_open-c3 structures (Figs. S20 and S21). During closure of the γ-lactam ring, the chair conformation is changed to the boat one, but only in **24**.

According to the calculations, in path A (R^1 = H, R^2 = Me), the carbocation formation with the C2-S bond breaking takes place during the protonation and CO_2 release (**18**-SH-c9(r), Fig. S22). This step is necessary for epimerization to occur at the C-2 position in the thiazolidine ring. Indeed, rotation about the single N-C bond would yield (*R*)- or (*S*)-**18** formation. The bicyclic product **21** has an inverted configuration on C2 compared to the substrate. This is because in the (*R*)-subA structure, the -CH_3 group at C2 in the *cis* orientation to OH. The *trans* arrangement in the (*S*)-**21** product is more stable than the *cis* one due to the steric hindrance in the latter. Thus, the (*S*)-configuration of **21** is thermodynamically and kinetically favorable than the (*R*)-one (Fig. S23).

The X-ray geometries of **21** (R^1 = H, R^2 = Me), **22** (R^1 = H, R^2 = Ph), and **23** (R^1,R^2 = Me) were very well reproduced by the calculated structures **21**, **22**, and **24** (R^1 = Me, R^2 = Et) interacting with one MeOH molecule, respectively (Fig. S24). Interaction of **21** with MeOH (proton acceptor and proton donor, Fig. S22) directed the hydroxyl group as in the experiment. Notice that in **22** and **24**, the proper conformation of the 1,3-oxathiane ring was also reproduced (Fig. S24).



Scheme S1. Numbering of the computationally studied structures proceeding through the iminium (left) and sulfonium (right) ion paths. Configurations indicated in the compound name are at the C2 atom. The remaining chiral centers do not change during the reaction; thus, they are only shown in the product structures.

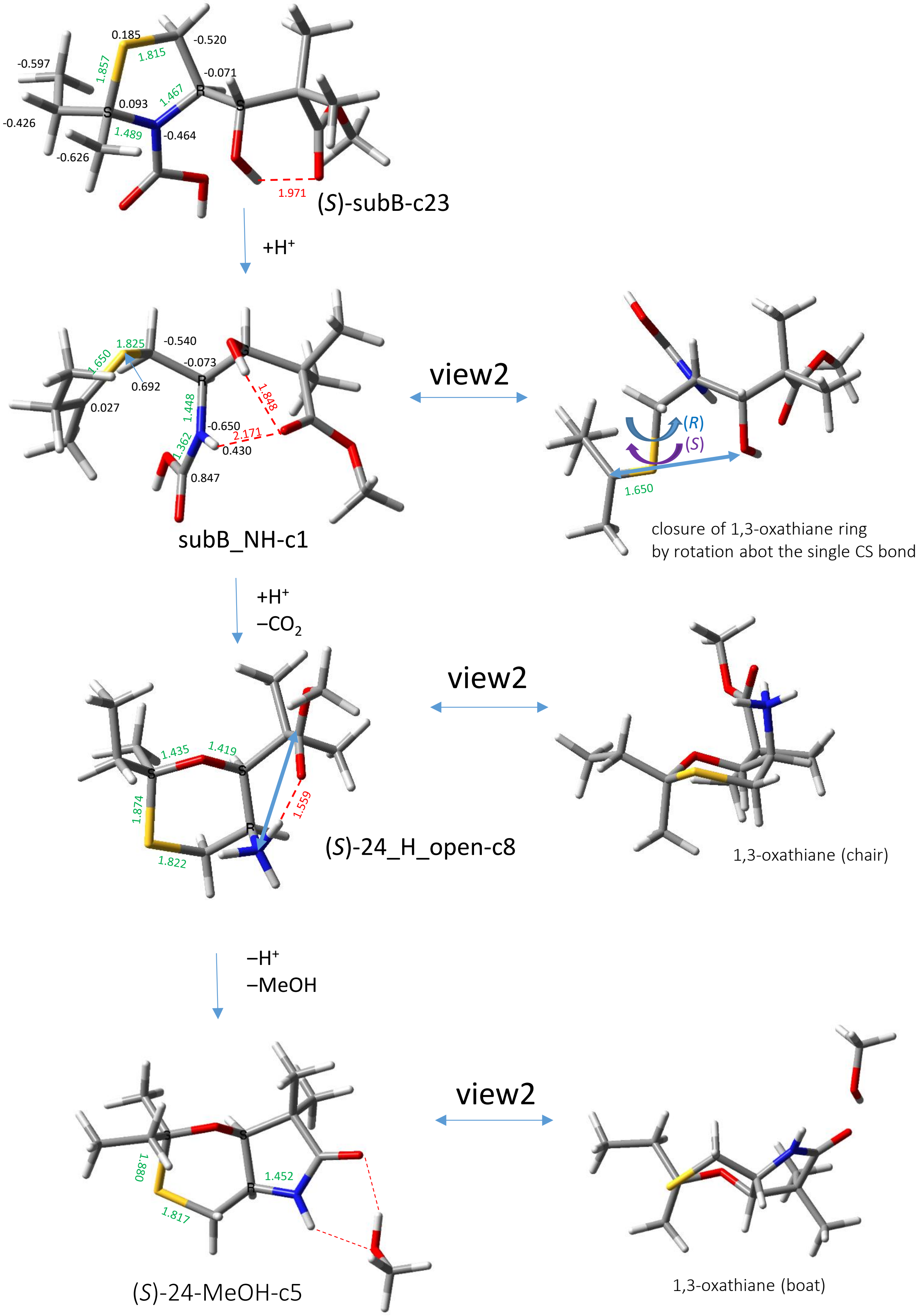


Figure S24. Structures of the most stable conformers in the sulfonium ion path (R^1 = Me, R^2 = Et) calculated at the B3LYP/def2TZVP level. Black, green, and red values corresponds to NBO charges, bond lengths (Å), and intramolecular HB distances (Å), respectively.

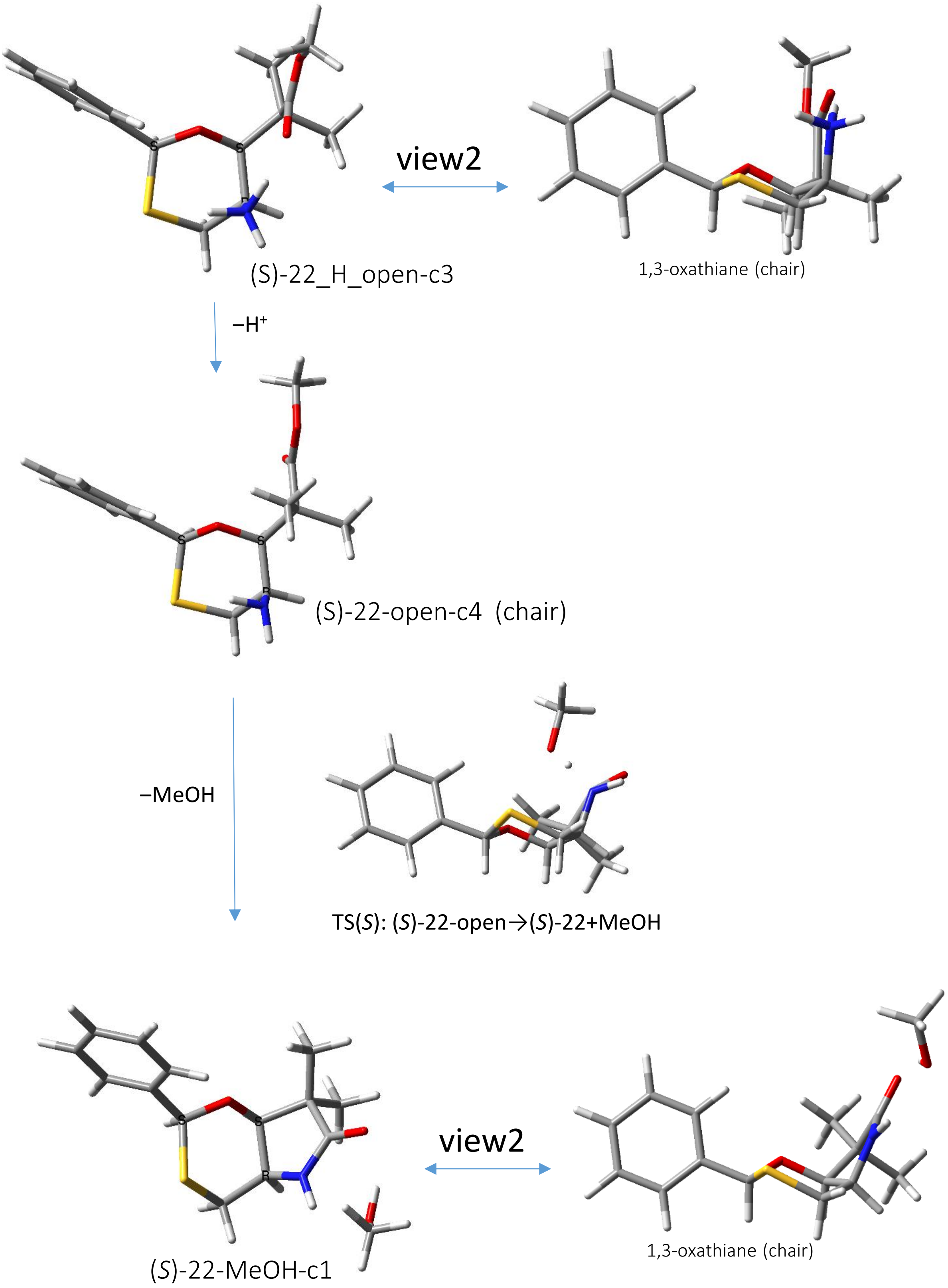


Figure S25. Structures of the most stable conformers in the last reaction steps of (R^1 = H, R^2 = Ph) calculated at the B3LYP/def2TZVP level.

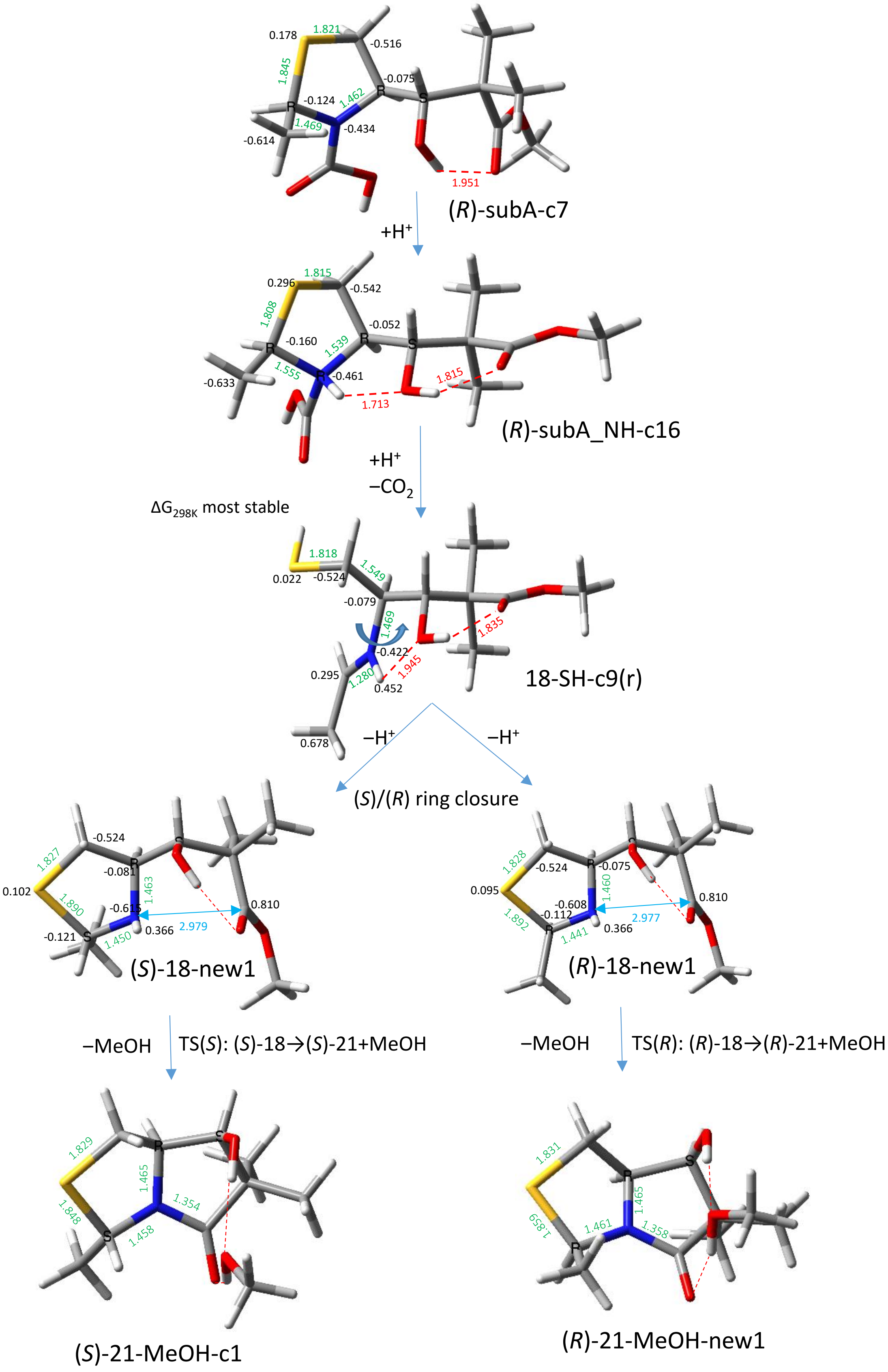


Figure S26. Structures of the most stable conformers in the iminium ion path calculated at the B3LYP/def2TZVP level. Black, green, and red values correspond to NBO charges, bond lengths (Å), and intramolecular HB distances (Å), respectively.

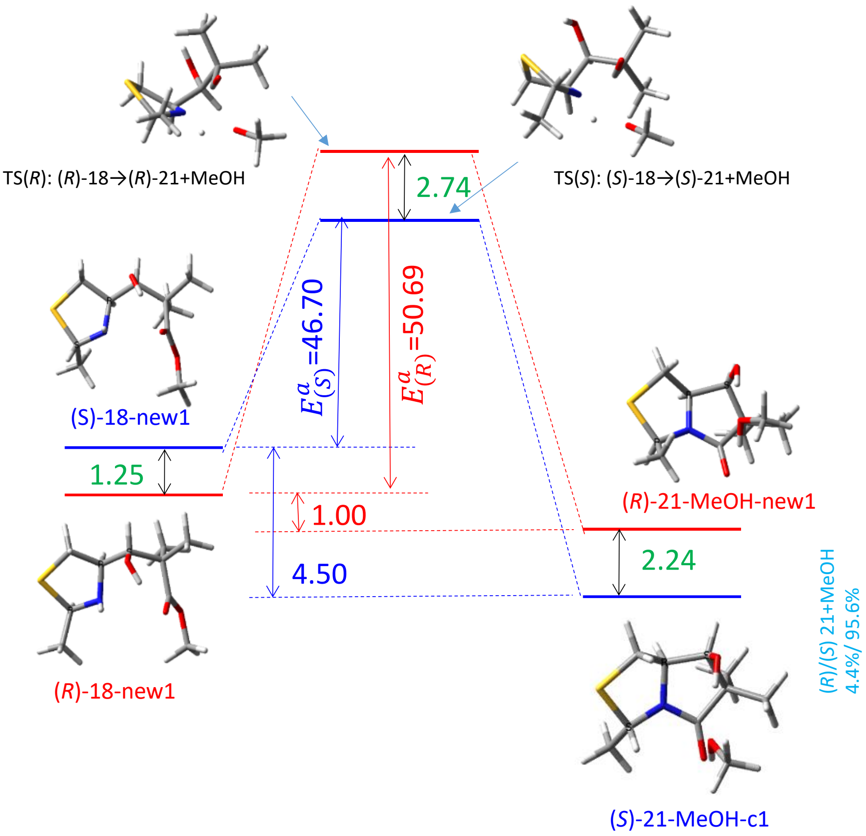
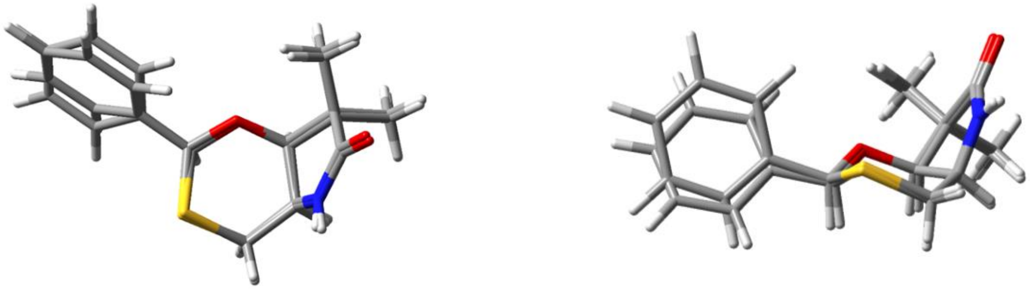


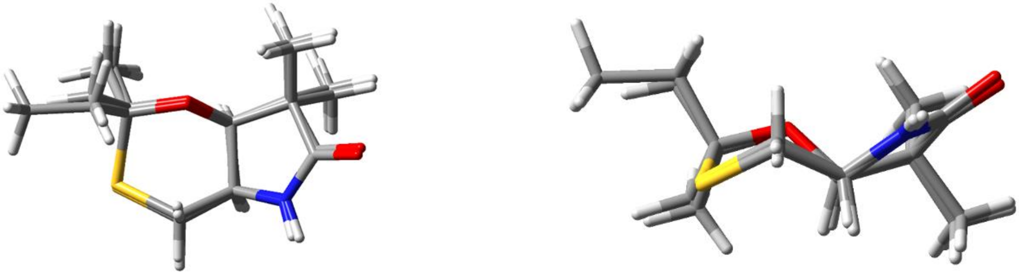
Figure S27. Energetics of the γ-lactam ring closure with the simultaneous release of methanol (last step of the iminium ion path mechanism, R^1 = H, R^2 = Me). The B3LYP/def2TZVP calculation results.

view 1 view 2

21 (R^1 = H, R^2 = Me) **21** (R^1 = H, R^2 = Me)



22 (R^1 = H, R^2 = Ph) **22** (R^1 = H, R^2 = Ph)



23 (R^1,R^2 = Me) *vs* (*S*)-**24** (R^1 = Me, R^2 = Et) **23** (R^1,R^2 = Me) *vs* (*S*)-**24** (R^1 = Me, R^2 = Et)

Figure S28. Superposition of the X-ray **21** (R^1 = H, R^2 = Me), **22** (R^1 = H, R^2 = Ph), and **23** (R^1,R^2 = Me) structures with the calculated most stable conformers of (*S*)-**21**, (*S*)-**22**, and (*S*)-**24** (R^1 = Me, R^2 = Et) interacting with one MeOH molecule (which was omitted for clarity).

Table S4. Energetic data of (*R*)/(*S*)-**subA** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(*S*)-subA-c1	-1260.078533	-1259.821606	1.95	2.12	1.21	0.84
(S)-subA-c10	-1260.077051	-1259.819937	2.88	3.17	0.25	0.14
(S)-subA-c11	-1260.070097	-1259.812637	7.25	7.75	0.00	0.00
(S)-subA-c3	-1260.078084	-1259.821085	2.24	2.45	0.75	0.48
(S)-subA-c4	-1260.077360	-1259.821982	2.69	1.89	0.35	1.25
(S)-subA-c5	-1260.078850	-1259.821419	1.76	2.24	1.69	0.69
(S)-subA-c6	-1260.075119	-1259.818601	4.10	4.01	0.03	0.03
(S)-subA-c7	-1260.074548	-1259.817550	4.46	4.67	0.02	0.01
(S)-subA-c8	-1260.072227	-1259.815903	5.91	5.70	0.00	0.00
(S)-subA-c9	-1260.072207	-1259.815245	5.92	6.11	0.00	0.00
		∑(S)-ent			*4.31%*	*3.46%*
(R)-subA-c1	-1260.080266	-1259.824505	0.87	0.30	7.59	18.14
(R)-subA-c11	-1260.076574	-1259.819703	3.18	3.32	0.15	0.11
(R)-subA-c12	-1260.079006	-1259.823732	1.66	0.79	2.00	8.00
(R)-subA-c13	-1260.075075	-1259.818484	4.12	4.08	0.03	0.03
(R)-subA-c14	-1260.072251	-1259.814406	5.90	6.64	0.00	0.00
(R)-subA-c16	-1260.078765	-1259.823559	1.81	0.90	1.55	6.66
(R)-subA-c18	-1260.072606	-1259.814916	5.67	6.32	0.00	0.00
(R)-subA-c19	-1260.075595	-1259.817678	3.80	4.59	0.05	0.01
(R)-subA-c2	-1260.079598	-1259.823360	1.29	1.02	3.74	5.40
(R)-subA-c20	-1260.070941	-1259.814456	6.72	6.61	0.00	0.00
(R)-subA-c22	-1260.064097	-1259.806417	11.01	11.65	0.00	0.00
(R)-subA-c3	-1260.081470	-1259.824123	0.11	0.54	27.17	12.10
(R)-subA-c4	-1260.080664	-1259.823870	0.62	0.70	11.56	9.26
(R)-subA-c5	-1260.079907	-1259.822892	1.09	1.32	5.19	3.29
(R)-subA-c6	-1260.079253	-1259.822491	1.50	1.57	2.59	2.15
(R)-subA-c7	-1260.081648	-1259.824988	0.00	0.00	**32.79**	**30.26**
(R)-subA-c8	-1260.078576	-1259.821878	1.93	1.95	1.27	1.12
		∑(R)-ent			*95.69%*	*96.54%*

Table S5. Energetic data of (*R*)/(*S*)-**subA_Hp** conformers calculated at the B3LYP/def2TZVP level (NH and SH mean protonation on N or S atom, respectively). Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold. However, in most of them, the NC or SC bond is not broken; thus, the C2 center is chiral. The structures with broken NC or SC bonds are denoted by "a," and in such structures, the C2 is not a chiral center.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-subA-NH-c1	-1260.411966	-1260.142721	14.28	15.59	0.00	0.00
(R)-subA-NH-c11	-1260.424197	-1260.155039	6.61	7.86	0.00	0.00
(R)-subA-NH-c12	-1260.427944	-1260.160438	4.26	4.47	0.07	0.04
(R)-subA-NH-c13	-1260.424763	-1260.155341	6.25	7.67	0.00	0.00
(R)-subA-NH-c14	-1260.427380	-1260.159276	4.61	5.20	0.04	0.01
(R)-subA-NH-c14a	-1260.410616	-1260.148421	15.13	12.01	0.00	0.00
(R)-subA-NH-c16	-1260.434730	-1260.166242	0.00	0.83	**97.15**	**19.52**
subA-NH-c16a	-1260.430117	-1260.167567	2.89	0.00	0.73	**79.43**
(R)-subA-NH-c17	-1260.417321	-1260.155501	10.92	7.57	0.00	0.00
(R)-subA-NH-c18	-1260.417555	-1260.155795	10.78	7.39	0.00	0.00
(R)-subA-NH-c19	-1260.417350	-1260.147854	10.91	12.37	0.00	0.00
(R)-subA-NH-c1a	-1260.399318	-1260.135667	22.22	20.02	0.00	0.00
(R)-subA-NH-c2	-1260.422295	-1260.153854	7.80	8.61	0.00	0.00
(R)-subA-NH-c20	-1260.422569	-1260.152831	7.63	9.25	0.00	0.00
subA-NH-c20a	-1260.418518	-1260.154738	10.17	8.05	0.00	0.00
(R)-subA-NH-c3	-1260.430839	-1260.163387	2.44	2.62	1.58	0.95
(R)-subA-NH-c4	-1260.412265	-1260.143097	14.10	15.36	0.00	0.00
(R)-subA-NH-c6	-1260.423513	-1260.156115	7.04	7.19	0.00	0.00
(R)-subA-NH-c7	-1260.416433	-1260.145752	11.48	13.69	0.00	0.00
		∑(R)-ent-NH			*99.58%*	*99.96%*
(R)-subA-SH-c1	-1260.417233	-1260.151956	10.98	9.80	0.00	0.00
(R)-subA-SH-c11	-1260.415013	-1260.148227	12.37	12.14	0.00	0.00
(R)-subA-SH-c12	-1260.411826	-1260.147009	14.37	12.90	0.00	0.00
(R)-subA-SH-c14	-1260.403726	-1260.137725	19.46	18.73	0.00	0.00
(R)-subA-SH-c16	-1260.416866	-1260.151775	11.21	9.91	0.00	0.00
(R)-subA-SH-c17	-1260.405076	-1260.138287	18.61	18.37	0.00	0.00
(R)-subA-SH-c19	-1260.406188	-1260.139368	17.91	17.70	0.00	0.00
(R)-subA-SH-c20	-1260.410378	-1260.143719	15.28	14.96	0.00	0.00
(R)-subA-SH-c22	-1260.398148	-1260.131084	22.96	22.89	0.00	0.00
(R)-subA-SH-c3	-1260.419281	-1260.152947	9.69	9.17	0.00	0.00
(R)-subA-SH-c4	-1260.413283	-1260.148906	13.46	11.71	0.00	0.00
(R)-subA-SH-c5	-1260.415160	-1260.149547	12.28	11.31	0.00	0.00
(R)-subA-SH-c6	-1260.423278	-1260.156815	7.19	6.75	0.00	0.00
subA-SH-c6a	-1260.408110	-1260.147632	16.70	12.51	0.00	0.00
(R)-subA-SH-c7	-1260.416859	-1260.151637	11.21	10.00	0.00	0.00
(R)-subA-SH-c8	-1260.421217	-1260.155057	8.48	7.85	0.00	0.00
subA-SH-c8a	-1260.413285	-1260.151438	13.46	10.12	0.00	0.00
		∑(R)-ent-SH			*0.00%*	*0.00%*
(S)-subA-NH-c1	-1260.417457	-1260.148858	10.84	11.74	0.00	0.00
(S)-subA-NH-c10	-1260.416472	-1260.146921	11.46	12.96	0.00	0.00
(S)-subA-NH-c16	-1260.429578	-1260.160301	3.23	4.56	0.41	0.04
(S)-subA-NH-c5	-1260.418317	-1260.149618	10.30	11.26	0.00	0.00
(S)-subA-NH-c8	-1260.401518	-1260.131331	20.84	22.74	0.00	0.00
(S)-subA-NH-c9	-1260.415486	-1260.145962	12.08	13.56	0.00	0.00
		∑(S)-ent-NH			*0.41%*	*0.04%*
(S)-subA-SH-c1	-1260.416265	-1260.151540	11.59	10.06	0.00	0.00
(S)-subA-SH-c10	-1260.409563	-1260.145841	15.79	13.63	0.00	0.00
(S)-subA-SH-c11	-1260.410376	-1260.149966	15.28	11.04	0.00	0.00

(S)-subA-SH-c4	-1260.416533	-1260.151880	11.42	9.84	0.00	0.00
(S)-subA-SH-c5	-1260.416017	-1260.154930	11.74	7.93	0.00	0.00
(S)-subA-SH-c6	-1260.416542	-1260.152094	11.41	9.71	0.00	0.00
(S)-subA-SH-c7	-1260.408342	-1260.143852	16.56	14.88	0.00	0.00
subA-SH-c7a	-1260.414606	-1260.154036	12.63	8.49	0.00	0.00
(S)-subA-SH-c8	-1260.409604	-1260.142714	15.77	15.60	0.00	0.00
(S)-subA-SH-c9	-1260.395949	-1260.129834	24.34	23.68	0.00	0.00
		∑*(S)-ent-SH*			*0.00%*	*0.00%*

Table S6. Energetic data of **protonated** (*R*)**-18** conformers calculated at the B3LYP/def2TZVP level (NH and SH mean protonation on N or S atom, respectively). Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold. Protonation at the S atom causes the SC bond breakage; in such a case, the C2 atom is not chiral. (r) means that the input geometry was from the (*R*)-conformer.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-18-NH-c1	-1071.795595	-1071.536773	4.52	6.94	0.03	0.00
(R)-18-NH-c11	-1071.797173	-1071.538566	3.53	5.81	0.19	0.00
(R)-18-NH-c12	-1071.799858	-1071.540779	1.85	4.42	3.19	0.03
(R)-18-NH-c13	-1071.798049	-1071.539736	2.98	5.08	0.47	0.01
(R)-18-NH-c14	-1071.802802	-1071.542725	0.00	3.20	**72.07**	0.21
(R)-18-NH-c17	-1071.791526	-1071.531893	7.08	10.00	0.00	0.00
(R)-18-NH-c19	-1071.797408	-1071.537356	3.38	6.57	0.24	0.00
(R)-18-NH-c2	-1071.792581	-1071.534395	6.41	8.43	0.00	0.00
(R)-18-NH-c27	-1071.793654	-1071.533541	5.74	8.97	0.00	0.00
(R)-18-NH-c29	-1071.794657	-1071.536606	5.11	7.04	0.01	0.00
(R)-18-NH-c3	-1071.798542	-1071.539694	2.67	5.10	0.79	0.01
(R)-18-NH-c30	-1071.795588	-1071.536864	4.53	6.88	0.03	0.00
(R)-18-NH-c31	-1071.782703	-1071.523778	12.61	15.09	0.00	0.00
(R)-18-NH-c33	-1071.797596	-1071.539116	3.27	5.47	0.29	0.00
(R)-18-NH-c36	-1071.793929	-1071.534034	5.57	8.66	0.01	0.00
(R)-18-NH-c9	-1071.801508	-1071.542187	0.81	3.54	18.30	0.12
18-SH-c1(r)	-1071.764201	-1071.510475	24.22	23.44	0.00	0.00
18-SH-c17(r)	-1071.795017	-1071.543569	4.89	2.67	0.02	0.50
18-SH-c18(r)	-1071.795492	-1071.544438	4.59	2.13	0.03	1.26
18-SH-c2(r)	-1071.797261	-1071.545952	3.48	1.18	0.20	6.28
18-SH-c27(r)	-1071.791557	-1071.538960	7.06	5.56	0.00	0.00
18-SH-c31(r)	-1071.756123	-1071.501631	29.29	28.99	0.00	0.00
18-SH-c33(r)	-1071.772619	-1071.519749	18.94	17.62	0.00	0.00
18-SH-c36(r)	-1071.790419	-1071.539378	7.77	5.30	0.00	0.01
18-SH-c8a(r)	-1071.796798	-1071.546285	3.77	0.97	0.12	8.93
18-SH-c8(r)	-1071.798009	-1071.547127	3.01	0.44	0.45	21.79
18-SH-c9b(r)	-1071.798487	-1071.546773	2.71	0.66	0.75	14.98
18-SH-c9a(r)	-1071.794364	-1071.542075	5.29	3.61	0.01	0.10
18-SH-c9(r)	-1071.799729	-1071.547828	1.93	0.00	2.78	**45.78**

Table S7. Energetic data of **protonated** (*S*)-**18** conformers calculated at the B3LYP/def2TZVP level (NH and SH means protonation on N or S atom, respectively). Total (E, hartree) and Gibbs free energies (G hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold. Protonation at the S atom causes the SC bond breakage; in such a case, the C2 atom is not chiral. (s) means that the input geometry was from the (*S*)-conformer.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(S)-18-NH-c1	-1071.805208	-1071.545006	2.92	3.60	0.71%	0.23%
(S)-18-NH-c11	-1071.795918	-1071.537307	8.75	8.43	0.00%	0.00%
(S)-18-NH-c13	-1071.793587	-1071.535855	10.22	9.34	0.00%	0.00%
(S)-18-NH-c18	-1071.797582	-1071.538809	7.71	7.48	0.00%	0.00%
(S)-18-NH-c19	-1071.795846	-1071.537179	8.80	8.51	0.00%	0.00%
(S)-18-NH-c2	-1071.793798	-1071.535063	10.08	9.84	0.00%	0.00%
(S)-18-NH-c21	-1071.796790	-1071.537785	8.21	8.13	0.00%	0.00%
(S)-18-NH-c23	-1071.804379	-1071.544565	3.44	3.87	0.30%	0.14%
(S)-18-NH-c26	-1071.789443	-1071.529737	12.82	13.18	0.00%	0.00%
(S)-18-NH-c3	-1071.790660	-1071.532590	12.05	11.39	0.00%	0.00%
(S)-18-NH-c32	-1071.797552	-1071.538594	7.73	7.62	0.00%	0.00%
(S)-18-NH-c35	-1071.794952	-1071.535586	9.36	9.51	0.00%	0.00%
(S)-18-NH-c39	-1071.792863	-1071.533335	10.67	10.92	0.00%	0.00%
(S)-18-NH-c4	-1071.800263	-1071.541654	6.03	5.70	0.00%	0.01%
(S)-18-NH-c41	-1071.781507	-1071.522330	17.80	17.83	0.00%	0.00%
(S)-18-NH-c43	-1071.783107	-1071.523847	16.79	16.87	0.00%	0.00%
(S)-18-NH-c44	-1071.795748	-1071.535693	8.86	9.44	0.00%	0.00%
(S)-18-NH-c47	-1071.782303	-1071.523668	17.30	16.99	0.00%	0.00%
(S)-18-NH-c48	-1071.792329	-1071.532227	11.01	11.62	0.00%	0.00%
(S)-18-NH-c7	-1071.809868	-1071.550737	0.00	0.00	**98.99%**	**99.60%**
18-SH-c1(s)	-1071.763578	-1071.509274	29.05	26.02	0.00%	0.00%
18-SH-c11(s)	-1071.765955	-1071.510550	27.56	25.22	0.00%	0.00%
18-SH-c13(s)	-1071.758971	-1071.503985	31.94	29.34	0.00%	0.00%
18-SH-c18(s)	-1071.794364	-1071.542072	9.73	5.44	0.00%	0.01%
18-SH-c19(s)	-1071.790746	-1071.539352	12.00	7.14	0.00%	0.00%
18-SH-c2(s)	-1071.759911	-1071.505991	31.35	28.08	0.00%	0.00%
18-SH-c21(s)	-1071.791400	-1071.540137	11.59	6.65	0.00%	0.00%
18-SH-c23(s)	-1071.767338	-1071.512443	26.69	24.03	0.00%	0.00%
18-SH-c26(s)	-1071.756684	-1071.502280	33.37	30.41	0.00%	0.00%
18-SH-c32(s)	-1071.790396	-1071.538695	12.22	7.56	0.00%	0.00%
18-SH-c35(s)	-1071.786616	-1071.535201	14.59	9.75	0.00%	0.00%
18-SH-c39(s)	-1071.786285	-1071.533640	14.80	10.73	0.00%	0.00%
18-SH-c4(s)	-1071.787153	-1071.536458	14.25	8.96	0.00%	0.00%
18-SH-c41(s)	-1071.787238	-1071.534276	14.20	10.33	0.00%	0.00%
18-SH-c43(s)	-1071.777563	-1071.526052	20.27	15.49	0.00%	0.00%
18-SH-c44(s)	-1071.789039	-1071.537796	13.07	8.12	0.00%	0.00%
18-SH-c8(s)	-1071.790802	-1071.539699	11.96	6.93	0.00%	0.00%

Table S8. Energetic data of (*R*)/(*S*)-**18** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-18-c1	-1071.422550	-1071.176831	2.51	2.30	0.78	0.96
(R)-18-c11	-1071.420476	-1071.176540	3.81	2.48	0.09	0.70
(R)-18-c12	-1071.420167	-1071.174610	4.00	3.69	0.06	0.09
(R)-18-c13	-1071.417623	-1071.172835	5.60	4.81	0.00	0.01
(R)-18-c14	-1071.418574	-1071.173385	5.00	4.46	0.01	0.02
(R)-18-c15	-1071.419334	-1071.174547	4.53	3.73	0.03	0.09
(R)-18-c16	-1071.418344	-1071.173397	5.15	4.46	0.01	0.03
(R)-18-c17	-1071.412529	-1071.167105	8.80	8.40	0.00	0.00
(R)-18-c18	-1071.416652	-1071.171664	6.21	5.54	0.00	0.00
(R)-18-c19	-1071.413210	-1071.168011	8.37	7.84	0.00	0.00
(R)-18-c2	-1071.422415	-1071.176554	2.59	2.47	0.68	0.71
(R)-18-c20	-1071.414246	-1071.168369	7.72	7.61	0.00	0.00
(R)-18-c21	-1071.412280	-1071.168337	8.95	7.63	0.00	0.00
(R)-18-c22	-1071.412761	-1071.166480	8.65	8.80	0.00	0.00
(R)-18-c23	-1071.411336	-1071.166251	9.55	8.94	0.00	0.00
(R)-18-c24	-1071.409933	-1071.166609	10.43	8.71	0.00	0.00
(R)-18-c25	-1071.412029	-1071.168671	9.11	7.42	0.00	0.00
(R)-18-c27	-1071.412152	-1071.165801	9.03	9.22	0.00	0.00
(R)-18-c28	-1071.409933	-1071.166608	10.43	8.72	0.00	0.00
(R)-18-c29	-1071.413716	-1071.168267	8.05	7.67	0.00	0.00
(R)-18-c3	-1071.419172	-1071.174711	4.63	3.63	0.02	0.10
(R)-18-c30	-1071.412059	-1071.167247	9.09	8.31	0.00	0.00
(R)-18-c31	-1071.414660	-1071.168849	7.46	7.31	0.00	0.00
(R)-18-c32	-1071.409290	-1071.163392	10.83	10.73	0.00	0.00
(R)-18-c33	-1071.410948	-1071.167588	9.79	8.10	0.00	0.00
(R)-18-c34	-1071.408157	-1071.162880	11.54	11.05	0.00	0.00
(R)-18-c35	-1071.412059	-1071.167258	9.09	8.31	0.00	0.00
(R)-18-c36	-1071.407556	-1071.161857	11.92	11.70	0.00	0.00
(R)-18-c4	-1071.419703	-1071.175394	4.30	3.20	0.04	0.21
(R)-18-c5	-1071.420931	-1071.177365	3.52	1.97	0.14	1.68
(R)-18-c6	-1071.414970	-1071.171469	7.27	5.67	0.00	0.00
(R)-18-c7	-1071.415546	-1071.170849	6.90	6.05	0.00	0.00
(R)-18-c8	-1071.420261	-1071.174796	3.95	3.58	0.07	0.11
(R)-18-c9	-1071.425981	-1071.180497	0.36	0.00	**29.70**	**46.38**
(R)-18-new1	-1071.426548	-1071.180162	0.00	0.21	**54.14**	**32.53**
(R)-18-new2	-1071.417846	-1071.172743	5.46	4.87	0.01	0.01
(R)-18-new3	-1071.423142	-1071.177355	2.14	1.97	1.47	1.66
(R)-18-new5	-1071.411728	-1071.167471	9.30	8.17	0.00	0.00
(R)-18-new6	-1071.416047	-1071.171072	6.59	5.91	0.00	0.00
		∑(R)-ent			*87.25%*	*85.3%*
(S)-18-c1	-1071.422128	-1071.177009	2.77	2.19	0.50	1.15
(S)-18-c10	-1071.420753	-1071.175724	3.64	3.00	0.12	0.30
(S)-18-c11	-1071.420000	-1071.174991	4.11	3.46	0.05	0.14
(S)-18-c12	-1071.424007	-1071.178334	1.59	1.36	**3.67**	**4.69**
(S)-18-c13	-1071.418225	-1071.172597	5.22	4.96	0.01	0.01
(S)-18-c16	-1071.418424	-1071.174376	5.10	3.84	0.01	0.07
(S)-18-c17	-1071.422344	-1071.175975	2.64	2.84	0.63	0.39
(S)-18-c18	-1071.418137	-1071.172426	5.28	5.06	0.01	0.01
(S)-18-c19	-1071.417757	-1071.172222	5.52	5.19	0.00	0.01
(S)-18-c2	-1071.420614	-1071.174842	3.72	3.55	0.10	0.12
(S)-18-c20	-1071.419726	-1071.174529	4.28	3.74	0.04	0.08

(S)-18-c21	-1071.416495	-1071.171345	6.31	5.74	0.00	0.00
(S)-18-c22	-1071.415799	-1071.170833	6.75	6.06	0.00	0.00
(S)-18-c23	-1071.415590	-1071.169637	6.88	6.81	0.00	0.00
(S)-18-c24	-1071.420469	-1071.175204	3.81	3.32	0.09	0.17
(S)-18-c25	-1071.412543	-1071.168075	8.79	7.79	0.00	0.00
(S)-18-c26	-1071.410582	-1071.165245	10.02	9.57	0.00	0.00
(S)-18-c27	-1071.411066	-1071.166736	9.72	8.64	0.00	0.00
(S)-18-c28	-1071.413631	-1071.168607	8.11	7.46	0.00	0.00
(S)-18-c29	-1071.410965	-1071.167170	9.78	8.36	0.00	0.00
(S)-18-c3	-1071.420449	-1071.174634	3.83	3.68	0.08	0.09
(S)-18-c30	-1071.411479	-1071.166959	9.46	8.50	0.00	0.00
(S)-18-c31	-1071.415090	-1071.171744	7.19	5.49	0.00	0.00
(S)-18-c32	-1071.411140	-1071.165697	9.67	9.29	0.00	0.00
(S)-18-c33	-1071.415372	-1071.169790	7.01	6.72	0.00	0.00
(S)-18-c34	-1071.412174	-1071.166066	9.02	9.06	0.00	0.00
(S)-18-c35	-1071.409327	-1071.163939	10.81	10.39	0.00	0.00
(S)-18-c37	-1071.410629	-1071.164254	9.99	10.19	0.00	0.00
(S)-18-c38	-1071.409173	-1071.164271	10.90	10.18	0.00	0.00
(S)-18-c39	-1071.410138	-1071.163637	10.30	10.58	0.00	0.00
(S)-18-c4	-1071.421685	-1071.176736	3.05	2.36	0.31	0.86
(S)-18-c40	-1071.411890	-1071.166308	9.20	8.90	0.00	0.00
(S)-18-c41	-1071.408435	-1071.163682	11.37	10.55	0.00	0.00
(S)-18-c42	-1071.410222	-1071.165326	10.24	9.52	0.00	0.00
(S)-18-c43	-1071.412683	-1071.166710	8.70	8.65	0.00	0.00
(S)-18-c44	-1071.407331	-1071.161454	12.06	11.95	0.00	0.00
(S)-18-c45	-1071.404652	-1071.159294	13.74	13.31	0.00	0.00
(S)-18-c46	-1071.406204	-1071.160801	12.77	12.36	0.00	0.00
(S)-18-c47	-1071.402953	-1071.158348	14.81	13.90	0.00	0.00
(S)-18-c48	-1071.405587	-1071.159963	13.15	12.89	0.00	0.00
(S)-18-c5	-1071.420580	-1071.177544	3.75	1.85	0.10	2.03
(S)-18-c6	-1071.417603	-1071.173308	5.61	4.51	0.00	0.02
(S)-18-c7	-1071.421114	-1071.175202	3.41	3.32	0.17	0.17
(S)-18-c8	-1071.421584	-1071.176833	3.12	2.30	0.28	0.96
(S)-18-c9	-1071.418896	-1071.175293	4.80	3.27	0.02	0.19
(S)-18-new1	-1071.424553	-1071.177974	1.25	1.58	**6.54**	**3.21**
(S)-18-new4-new	-1071.417257	-1071.172422	5.83	5.07	0.00	0.01
(S)-18-new5	-1071.409482	-1071.165511	10.71	9.40	0.00	0.00
(S)-18-Rent-c1	-1071.422550	-1071.176831	2.51	2.30	0.78	0.96
(S)-18-Rent-c11	-1071.420476	-1071.176540	3.81	2.48	0.09	0.70
		∑(S)-ent			*12.75%*	*14.68%*

Table S9. Energetic data of (*R*/*S*)-**21** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(*R*)-21-c1	-955.639177	-955.443417	1.82	1.78	2.46	2.37
(*R*)-21-c2	-955.640185	-955.444065	1.18	1.37	7.14	4.71
(*R*)-21-c3	-955.638530	-955.442725	2.22	2.21	1.24	1.14
		∑(R)-ent			*10.83%*	*8.22%*
(*S*)-21-c1	-955.640751	-955.445430	0.83	0.52	13.01	19.99
(*S*)-21-c2	-955.642071	-955.446252	0.00	0.00	**52.66**	**47.74**
(*S*)-21-c3	-955.640403	-955.444829	1.05	0.89	9.00	10.58
(*S*)-21-c4	-955.640854	-955.445057	0.76	0.75	14.50	13.47
		∑(S)-ent			*89.17%*	*91.78%*

Table S10. Energetic data of (*R*)/(*S*)-**21+MeOH** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-21-MeOH-c1	-1071.425748	-1071.185553	3.75	2.48	0.14	0.28
(R)-21-MeOH-c2	-1071.426932	-1071.186576	3.00	1.84	0.49	0.87
(R)-21-MeOH-c3	-1071.425957	-1071.185975	3.61	2.21	0.18	0.35
(R)-21-MeOH-c4	-1071.427721	-1071.187116	2.51	1.50	1.14	1.80
(R)-21-MeOH-c5	-1071.425485	-1071.185308	3.91	2.63	0.11	0.22
(R)-21-MeOH-c6	-1071.425542	-1071.185688	3.87	2.39	0.11	0.24
(R)-21-MeOH-new1	-1071.428140	-1071.184587	2.24	3.09	**1.78**	**1.27**
(R)-21-MeOH-oh-c1	-1071.425640	-1071.186126	3.81	2.12	0.13	0.24
(R)-21-MeOH-oh-c2	-1071.425956	-1071.186703	3.61	1.76	0.18	0.35
(R)-21-MeOH-oh-c3	-1071.423183	-1071.183746	5.35	3.61	0.01	0.02
(R)-21-MeOH-oh-c4	-1071.421902	-1071.182645	6.16	4.30	0.00	0.01
(R)-21-MeOH-oh-c5	-1071.423405	-1071.183626	5.22	3.69	0.01	0.02
(R)-21-MeOH-oh-c6	-1071.421941	-1071.181869	6.13	4.79	0.00	0.01
(R)-21-MeOH-oh	-1071.422174	-1071.184159	5.99	3.35	0.00	0.01
(R)-21-MeOH-oh2-c1	-1071.424838	-1071.186653	4.32	1.79	0.05	0.12
(R)-21-MeOH-oh2-c2	-1071.424957	-1071.186616	4.24	1.81	0.06	0.13
(R)-21-MeOH-oh2-c5	-1071.421791	-1071.180307	6.23	5.77	0.00	0.01
		∑*(R)-ent*			4.39%	10.29%
(S)-21-MeOH-c1	-1071.431717	-1071.188916	0.00	0.37	**78.44**	**63.10**
(S)-21-MeOH-c10	-1071.421890	-1071.184393	6.17	3.21	0.00	0.01
(S)-21-MeOH-c11	-1071.426828	-1071.187380	3.07	1.33	0.44	0.85
(S)-21-MeOH-c12	-1071.423425	-1071.182917	5.20	4.13	0.01	0.03
(S)-21-MeOH-c2	-1071.427794	-1071.186640	2.46	1.80	1.23	1.89
(S)-21-MeOH-c3	-1071.429552	-1071.189504	1.36	0.00	7.92	13.26
(S)-21-MeOH-c4	-1071.427623	-1071.188190	2.57	0.82	1.03	2.16
(S)-21-MeOH-c6	-1071.423976	-1071.184272	4.86	3.28	0.02	0.05
(S)-21-MeOH-c7	-1071.427431	-1071.187995	2.69	0.95	0.84	1.83
(S)-21-MeOH-c8	-1071.427375	-1071.188094	2.72	0.88	0.79	1.69
(S)-21-MeOH-c9	-1071.427785	-1071.187829	2.47	1.05	1.22	2.00
(S)-21-meoh-from-qst3-C17	-1071.421102	-1071.185085	6.66	2.77	0.00	0.01
(S)-21-MeOH-new1-res2	-1071.428822	-1071.189271	1.82	0.15	3.66	7.20
		∑*(S)-ent*			95.61%	89.71%

Table S11. Energetic data of (*R*)/(*S*)-**subB** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-subB-c1	-1338.731976	-1338.422523	1.39	0.67	3.07%	7.58%
(R)-subB-c2	-1338.728173	-1338.417100	3.78	4.07	0.05%	0.02%
(R)-subB-c3	-1338.732376	-1338.421698	1.14	1.19	4.70%	3.16%
(R)-subB-c4	-1338.733456	-1338.423058	0.46	0.34	14.74%	13.36%
(R)-subB-c5	-1338.727319	-1338.416503	4.32	4.45	0.02%	0.01%
(R)-subB-c6	-1338.728119	-1338.418301	3.81	3.32	0.05%	0.09%
(R)-subB-c7	-1338.731278	-1338.421026	1.83	1.61	1.47%	1.55%
(R)-subB-c8	-1338.727205	-1338.416358	4.39	4.54	0.02%	0.01%
(R)-subB-c9	-1338.726435	-1338.416322	4.87	4.56	0.01%	0.01%
(R)-subB-c10	-1338.722483	-1338.411970	7.35	7.29	0.00%	0.00%
(R)-subB-c11	-1338.732269	-1338.422663	1.21	0.58	4.19%	8.79%
(R)-subB-c12	-1338.722358	-1338.411770	7.43	7.42	0.00%	0.00%
(R)-subB-c13	-1338.726040	-1338.416148	5.12	4.67	0.01%	0.01%
(R)-subB-c14	-1338.725106	-1338.415394	5.70	5.14	0.00%	0.00%
(R)-subB-c15	-1338.727260	-1338.418158	4.35	3.41	0.02%	0.07%
(R)-subB-c16	-1338.730305	-1338.419799	2.44	2.38	0.52%	0.42%
(R)-subB-c17	-1338.730804	-1338.420868	2.13	1.71	0.89%	1.31%
(R)-subB-c18	-1338.723703	-1338.413227	6.58	6.50	0.00%	0.00%
(R)-subB-c19	-1338.722726	-1338.412861	7.20	6.73	0.00%	0.00%
(R)-subB-c20	-1338.722440	-1338.411940	7.38	7.31	0.00%	0.00%
(R)-subB-c21	-1338.726030	-1338.416144	5.12	4.67	0.01%	0.01%
(R)-subB-c22	-1338.723210	-1338.413227	6.89	6.50	0.00%	0.00%
(R)-subB-c23	-1338.720434	-1338.411289	8.64	7.72	0.00%	0.00%
(R)-subB-c24	-1338.719752	-1338.408586	9.06	9.42	0.00%	0.00%
(R)-subB-c25	-1338.719682	-1338.408762	9.11	9.31	0.00%	0.00%
(R)-subB-c26	-1338.718910	-1338.408299	9.59	9.60	0.00%	0.00%
(R)-subB-c27	-1338.717926	-1338.407263	10.21	10.25	0.00%	0.00%
(R)-subB-c28	-1338.717202	-1338.405568	10.66	11.31	0.00%	0.00%
(R)-subB-c29	-1338.717635	-1338.406560	10.39	10.69	0.00%	0.00%
(R)-subB-c30	-1338.717154	-1338.407748	10.69	9.94	0.00%	0.00%
(R)-subB-c31	-1338.731813	-1338.421894	1.50	1.07	2.59%	3.89%
(R)-subB-c32	-1338.718121	-1338.407887	10.09	9.86	0.00%	0.00%
(R)-subB-c33	-1338.722716	-1338.411361	7.20	7.68	0.00%	0.00%
(R)-subB-c34	-1338.716778	-1338.407041	10.93	10.39	0.00%	0.00%
(R)-subB-c35	-1338.715230	-1338.404940	11.90	11.70	0.00%	0.00%
(R)-subB-c36	-1338.711315	-1338.401048	14.36	14.15	0.00%	0.00%
(R)-subB-c37	-1338.727844	-1338.419203	3.99	2.75	0.04%	0.23%
(R)-subB-c38	-1338.731603	-1338.420880	1.63	1.70	2.07%	1.33%
(R)-subB-c39	-1338.731443	-1338.421062	1.73	1.59	1.75%	1.61%
(R)-subB-c40	-1338.727262	-1338.418133	4.35	3.43	0.02%	0.07%
(R)-subB-c41	-1338.729853	-1338.419302	2.73	2.69	0.32%	0.25%
		∑(R)-ent			36.57%	43.81%
(S)-subB-c1	-1338.732743	-1338.422651	0.91	0.59	6.93%	8.68%
(S)-subB-c2	-1338.731343	-1338.421044	1.79	1.60	1.57%	1.58%
(S)-subB-c3	-1338.726260	-1338.416000	4.98	4.76	0.01%	0.01%
(S)-subB-c4	-1338.726912	-1338.416231	4.57	4.62	0.01%	0.01%
(S)-subB-c5	-1338.725753	-1338.415401	5.30	5.14	0.00%	0.00%
(S)-subB-c6	-1338.722514	-1338.413263	7.33	6.48	0.00%	0.00%
(S)-subB-c7	-1338.725825	-1338.415665	5.25	4.97	0.00%	0.01%
(S)-subB-c8	-1338.731124	-1338.420762	1.93	1.78	1.25%	1.17%
(S)-subB-c9	-1338.721727	-1338.411385	7.82	7.66	0.00%	0.00%

(S)-subB-c10	-1338.722708	-1338.412549	7.21	6.93	0.00%	0.00%
(S)-subB-c11	-1338.723627	-1338.413290	6.63	6.46	0.00%	0.00%
(S)-subB-c12	-1338.732554	-1338.422663	1.03	0.58	5.67%	8.79%
(S)-subB-c13	-1338.724024	-1338.413801	6.38	6.14	0.00%	0.00%
(S)-subB-c14	-1338.719557	-1338.409100	9.19	9.09	0.00%	0.00%
(S)-subB-c15	-1338.718342	-1338.408754	9.95	9.31	0.00%	0.00%
(S)-subB-c16	-1338.725301	-1338.414876	5.58	5.47	0.00%	0.00%
(S)-subB-c17	-1338.719208	-1338.408629	9.40	9.39	0.00%	0.00%
(S)-subB-c18	-1338.711691	-1338.401071	14.12	14.13	0.00%	0.00%
(S)-subB-c19	-1338.711555	-1338.400883	14.21	14.25	0.00%	0.00%
(S)-subB-c20	-1338.732291	-1338.421891	1.20	1.07	4.29%	3.88%
(S)-subB-c21	-1338.732114	-1338.421840	1.31	1.10	3.56%	3.68%
(S)-subB-c22	-1338.732767	-1338.422013	0.90	0.99	7.11%	4.42%
(S)-subB-c23	-1338.734196	-1338.423592	0.00	0.00	**32.27%**	**23.51%**
(S)-subB-c24	-1338.730221	-1338.419240	2.49	2.73	0.48%	0.23%
(S)-subB-c25	-1338.726694	-1338.416515	4.71	4.44	0.01%	0.01%
(S)-subB-c26	-1338.729662	-1338.419087	2.85	2.83	0.27%	0.20%
		∑*(S)-ent*			63.43%	56.19%

Table S12. Energetic data of **protonated subB** conformers calculated at the B3LYP/def2TZVP level (NH and SH mean protonation on N or S atom, respectively). Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold. In all structures, protonation at the N atom causes the NC bond breakage; in such a case, the C2 atom is not chiral. The molecules protonated at the S atom are less stable by at least 11 kcal/mol, thus, they are not shown in this table.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
subB_NH-c1	-1339.100856	-1338.784169	0.00	0.00	**61.00**	**47.06**
subB_NH-c2	-1339.099810	-1338.782908	0.66	0.79	20.16	12.38
subB_NH-c3	-1339.099512	-1338.783798	0.84	0.23	14.70	31.77
subB_NH-c4	-1339.098234	-1338.782380	1.65	1.12	3.80	7.08
subB_NH-c5	-1339.095129	-1338.780044	3.59	2.59	0.14	0.60
subB_NH-c6	-1339.094952	-1338.780009	3.70	2.61	0.12	0.57
subB_NH-c7	-1339.093924	-1338.778897	4.35	3.31	0.04	0.18
subB_NH-c8	-1339.093737	-1338.778940	4.47	3.28	0.03	0.19
subB_NH-c9	-1339.092765	-1338.777600	5.08	4.12	0.01	0.04
subB_NH-c10	-1339.091570	-1338.776586	5.83	4.76	0.00	0.02
subB_NH-c11	-1339.091340	-1338.778278	5.97	3.70	0.00	0.09
subB_NH-c12	-1339.091072	-1338.776500	6.14	4.81	0.00	0.01
subB_NH-c13	-1339.090808	-1338.774044	6.31	6.35	0.00	0.00
subB_NH-c14	-1339.089765	-1338.776022	6.96	5.11	0.00	0.01
subB_NH-c15	-1339.089663	-1338.776042	7.02	5.10	0.00	0.01
subB_NH-c16	-1339.089448	-1338.775585	7.16	5.39	0.00	0.01
subB_NH-c17	-1339.088571	-1338.772682	7.71	7.21	0.00	0.00
subB_NH-c18	-1339.088552	-1338.775326	7.72	5.55	0.00	0.00
subB_NH-c19	-1339.088029	-1338.773665	8.05	6.59	0.00	0.00
subB_NH-c20	-1339.087704	-1338.771991	8.25	7.64	0.00	0.00
subB_NH-c21	-1339.085615	-1338.769734	9.56	9.06	0.00	0.00
subB_NH-c22	-1339.085386	-1338.769566	9.71	9.16	0.00	0.00
subB_NH-c23	-1339.085325	-1338.771605	9.75	7.88	0.00	0.00
subB_NH-c24	-1339.084499	-1338.768707	10.26	9.70	0.00	0.00
subB_NH-c25	-1339.084158	-1338.769479	10.48	9.22	0.00	0.00
subB_NH-c26	-1339.084127	-1338.769884	10.50	8.96	0.00	0.00
subB_NH-c27	-1339.084027	-1338.771140	10.56	8.18	0.00	0.00
subB_NH-c28	-1339.083667	-1338.769761	10.79	9.04	0.00	0.00
subB_NH-c29	-1339.083649	-1338.769844	10.80	8.99	0.00	0.00
subB_NH-c30	-1339.083629	-1338.769454	10.81	9.23	0.00	0.00
subB_NH-c31	-1339.083612	-1338.768216	10.82	10.01	0.00	0.00
subB_NH-c32	-1339.083429	-1338.768487	10.94	9.84	0.00	0.00
subB_NH-c33	-1339.082962	-1338.767823	11.23	10.26	0.00	0.00
subB_NH-c34	-1339.082070	-1338.767182	11.79	10.66	0.00	0.00
subB_NH-c35	-1339.080621	-1338.766109	12.70	11.33	0.00	0.00
subB_NH-c36	-1339.080296	-1338.765126	12.90	11.95	0.00	0.00
subB_NH-c37	-1339.078144	-1338.764512	14.25	12.33	0.00	0.00
subB_NH-c38	-1339.077781	-1338.763623	14.48	12.89	0.00	0.00
subB_NH-c39	-1339.077778	-1338.764887	14.48	12.10	0.00	0.00
subB_NH-c40	-1339.076287	-1338.760830	15.42	14.65	0.00	0.00
subB_NH-c41	-1339.075888	-1338.759179	15.67	15.68	0.00	0.00
subB_NH-c42	-1339.074508	-1338.751904	16.53	20.25	0.00	0.00
subB_NH-c43	-1339.074397	-1338.758212	16.60	16.29	0.00	0.00
subB_NH-c44	-1339.073236	-1338.758639	17.33	16.02	0.00	0.00
subB_NH-c45	-1339.065734	-1338.744178	22.04	25.09	0.00	0.00
subB_NH-c46	-1339.054118	-1338.739761	29.33	27.87	0.00	0.00

Table S13. Energetic data of **protonated** (*R/S*)-**24_H_open** conformers calculated at the B3LYP/def2TZVP level (NH and SH means protonation on N or S atom, respectively). Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(S)-24_H_open-c1	-1150.449879	-1150.136735	10.64	10.09	0.00	0.00
(S)-24_H_open-c12	-1150.445785	-1150.132514	13.21	12.74	0.00	0.00
(S)-24_H_open-c13[1,2]	-1150.466762	-1150.152814	0.04	0.00	**23.58**	**27.69**
(S)-24_H_open-c14	-1150.452668	-1150.138601	8.89	8.92	0.00	0.00
(S)-24_H_open-c16	-1150.444921	-1150.132183	13.75	12.95	0.00	0.00
(S)-24_H_open-c17	-1150.445983	-1150.132576	13.08	12.70	0.00	0.00
(S)-24_H_open-c19	-1150.445301	-1150.132132	13.51	12.98	0.00	0.00
(S)-24_H_open-c2	-1150.450035	-1150.136867	10.54	10.01	0.00	0.00
(S)-24_H_open-c22	-1150.452235	-1150.138559	9.16	8.95	0.00	0.00
(S)-24_H_open-c27	-1150.449170	-1150.134811	11.08	11.30	0.00	0.00
(S)-24_H_open-c29	-1150.449553	-1150.135785	10.84	10.69	0.00	0.00
(S)-24_H_open-c3	-1150.450000	-1150.136927	10.56	9.97	0.00	0.00
(S)-24_H_open-c32	-1150.451335	-1150.138982	9.72	8.68	0.00	0.00
(S)-24_H_open-c34	-1150.435311	-1150.122095	19.78	19.28	0.00	0.00
(S)-24_H_open-c35	-1150.452167	-1150.140129	9.20	7.96	0.00	0.00
(S)-24_H_open-c39	-1150.453150	-1150.140620	8.59	7.65	0.00	0.00
(S)-24_H_open-c4	-1150.456704	-1150.142447	6.36	6.51	0.00	0.00
(S)-24_H_open-c41	-1150.450934	-1150.137586	9.98	9.56	0.00	0.00
(S)-24_H_open-c5[1,2]	-1150.466631	-1150.152596	0.13	0.14	**20.52**	**21.98**
(S)-24_H_open-c51	-1150.430571	-1150.118820	22.75	21.33	0.00	0.00
(S)-24_H_open-c53	-1150.433450	-1150.118696	20.95	21.41	0.00	0.00
(S)-24_H_open-c6	-1150.456880	-1150.142495	6.25	6.48	0.00	0.00
(S)-24_H_open-c7	-1150.446641	-1150.133872	12.67	11.89	0.00	0.00
(S)-24_H_open-c8[1,2]	-1150.466832	-1150.152646	0.00	0.11	**25.41**	**23.18**
(S)-24_H_open-c9	-1150.446964	-1150.133984	12.47	11.82	0.00	0.00
		∑(S)-ent			69.51%	72.86%
(R)-24_H_open-c1	-1150.448978	-1150.135548	11.20	10.83	0.00	0.00
(R)-24_H_open-c10	-1150.445991	-1150.132535	13.08	12.73	0.00	0.00
(R)-24_H_open-c11	-1150.445138	-1150.131737	13.61	13.23	0.00	0.00
(R)-24_H_open-c13	-1150.443096	-1150.129921	14.90	14.37	0.00	0.00
(R)-24_H_open-c15	-1150.444829	-1150.131779	13.81	13.20	0.00	0.00
(R)-24_H_open-c16	-1150.451265	-1150.137399	9.77	9.67	0.00	0.00
(R)-24_H_open-c17	-1150.444279	-1150.130815	14.15	13.80	0.00	0.00
(R)-24_H_open-c18	-1150.452360	-1150.138417	9.08	9.03	0.00	0.00
(R)-24_H_open-c2	-1150.449947	-1150.136634	10.60	10.15	0.00	0.00
(R)-24_H_open-c23	-1150.449364	-1150.135143	10.96	11.09	0.00	0.00
(R)-24_H_open-c25	-1150.449973	-1150.136077	10.58	10.50	0.00	0.00
(R)-24_H_open-c28	-1150.460990	-1150.146833	3.67	3.75	0.05	0.05
(R)-24_H_open-c29	-1150.451722	-1150.139104	9.48	8.60	0.00	0.00
(R)-24_H_open-c3	-1150.455936	-1150.141915	6.84	6.84	0.00	0.00
(R)-24_H_open-c30	-1150.452400	-1150.139748	9.06	8.20	0.00	0.00
(R)-24_H_open-c31	-1150.446572	-1150.132520	12.71	12.73	0.00	0.00
(R)-24_H_open-c36	-1150.449942	-1150.136948	10.60	9.96	0.00	0.00
(R)-24_H_open-c4	-1150.456929	-1150.142538	6.21	6.45	0.00	0.00
(R)-24_H_open-c42	-1150.435852	-1150.122823	19.44	18.82	0.00	0.00
(R)-24_H_open-c44	-1150.430950	-1150.118674	22.52	21.42	0.00	0.00
(R)-24_H_open-c5[2]	-1150.466758	-1150.152556	0.05	0.16	**23.48**	**21.07**
(R)-24_H_open-c50	-1150.433548	-1150.118831	20.89	21.32	0.00	0.00
(R)-24_H_open-c6	-1150.465609	-1150.151373	0.77	0.90	6.95	6.02
(R)-24_H_open-c7	-1150.446622	-1150.133685	12.68	12.00	0.00	0.00
(R)-24_H_open-c53	-1150.433717	-1150.119265	20.78	21.05	0.00	0.00
		∑(R)-ent			30.49%	27.14%

[1] differ by the conformation of the Et group. [2] Chair conformation of the 1,3-oxathiane ring.

Table S14. Energetic data of (*R/S*)-**24+MeOH** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol). and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(S)-24-MeOH-c1	-1150.088405	-1149.792458	0.24	0.40	17.86	13.33
(S)-24-MeOH-c2	-1150.082576	-1149.789179	3.90	2.45	0.04	0.41
(S)-24-MeOH-c3	-1150.085517	-1149.789846	2.05	2.03	0.84	0.84
(S)-24-MeOH-c4	-1150.088329	-1149.792771	0.29	0.20	16.47	18.57
(S)-24-MeOH-c5	-1150.088786	-1149.793088	0.00	0.00	**26.74**	**25.98**
(S)-24-MeOH-c6	-1150.085248	-1149.789382	2.22	2.33	0.63	0.51
(S)-24-MeOH-c7	-1150.078268	-1149.783615	6.60	5.94	0.00	0.00
(S)-24-MeOH-c8	-1150.078779	-1149.784193	6.28	5.58	0.00	0.00
(S)-24-MeOH-c9	-1150.077588	-1149.783893	7.03	5.77	0.00	0.00
(S)-24-MeOH-c10	-1150.076329	-1149.782361	7.82	6.73	0.00	0.00
(S)-24-MeOH-c11	-1150.075765	-1149.782370	8.17	6.73	0.00	0.00
		∑*(S)-ent*			62.58%	59.64%
(R)-24-MeOH-c1	-1150.088530	-1149.792952	0.16	0.09	**20.38**	**22.49**
(R)-24-MeOH-c2	-1150.088223	-1149.792617	0.35	0.30	14.73	15.77
(R)-24-MeOH-c3	-1150.085522	-1149.789582	2.05	2.20	0.84	0.63
(R)-24-MeOH-c4	-1150.085429	-1149.789475	2.11	2.27	0.76	0.57
(R)-24-MeOH-c5	-1150.085320	-1149.789440	2.18	2.29	0.68	0.55
(R)-24-MeOH-c6	-1150.079613	-1149.783347	5.76	6.11	0.00	0.00
(R)-24-MeOH-c7	-1150.082352	-1149.789006	4.04	2.56	0.03	0.34
(R)-24-MeOH-c8	-1150.078699	-1149.783825	6.33	5.81	0.00	0.00
(R)-24-MeOH-c9	-1150.078391	-1149.783557	6.52	5.98	0.00	0.00
(R)-24-MeOH-c10	-1150.074961	-1149.780595	8.68	7.84	0.00	0.00
(R)-24-MeOH-c11	-1150.075581	-1149.781103	8.29	7.52	0.00	0.00
(R)-24-MeOH-c12	-1150.075856	-1149.782730	8.11	6.50	0.00	0.00
		∑*(R)-ent*			37.42%	40.36%

Table S15. Energetic data of **protonated** (*R/S*)-**22_H_open** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-22_H_open-c1	-1263.591419	-1263.282960	14.11	14.44	0.00%	0.00%
(R)-22_H_open-c11	-1263.596514	-1263.289827	10.91	10.13	0.00%	0.00%
(R)-22_H_open-c12	-1263.592658	-1263.284125	13.33	13.71	0.00%	0.00%
(R)-22_H_open-c16	-1263.579157	-1263.273302	21.80	20.50	0.00%	0.00%
(R)-22_H_open-c2	-1263.599108	-1263.289675	9.28	10.22	0.00%	0.00%
(R)-22_H_open-c22	-1263.586415	-1263.277662	17.25	17.76	0.00%	0.00%
(R)-22_H_open-c23	-1263.594309	-1263.287199	12.30	11.78	0.00%	0.00%
(R)-22_H_open-c24	-1263.585975	-1263.278183	17.53	17.44	0.00%	0.00%
(R)-22_H_open-c26	-1263.580307	-1263.274432	21.08	19.79	0.00%	0.00%
(R)-22_H_open-c27	-1263.573412	-1263.267214	25.41	24.32	0.00%	0.00%
(R)-22_H_open-c3	-1263.608351	-1263.299109	3.49	4.30	0.28%	0.07%
(R)-22_H_open-c4	-1263.585047	-1263.276889	18.11	18.25	0.00%	0.00%
(R)-22_H_open-c8	-1263.595705	-1263.288086	11.42	11.22	0.00%	0.00%
(R)-22_H_open-c9	-1263.589172	-1263.281140	15.52	15.58	0.00%	0.00%
(R)-22_H_open-c5	-1263.594073	-1263.284913	12.44	13.21	0.00%	0.00%
		∑(R)-ent			0.28%	0.07%
(S)-22_H_open-c1	-1263.596908	-1263.289995	10.67	10.02	0.00%	0.00%
(S)-22_H_open-c13	-1263.578656	-1263.271600	22.12	21.57	0.00%	0.00%
(S)-22_H_open-c15	-1263.598636	-1263.290248	9.58	9.87	0.00%	0.00%
(S)-22_H_open-c17	-1263.594174	-1263.287278	12.38	11.73	0.00%	0.00%
(S)-22_H_open-c2	-1263.604055	-1263.296031	6.18	6.24	0.00%	0.00%
(S)-22_H_open-c20	-1263.583943	-1263.275471	18.80	19.14	0.00%	0.00%
(S)-22_H_open-c22	-1263.577501	-1263.269719	22.84	22.75	0.00%	0.00%
(S)-22_H_open-c23	-1263.558066	-1263.248314	35.04	36.18	0.00%	0.00%
(S)-22_H_open-c24	-1263.573517	-1263.262923	25.34	27.01	0.00%	0.00%
(S)-22_H_open-c3	-1263.613905	-1263.305969	0.00	0.00	**99.72%**	**99.93%**
(S)-22_H_open-c4	-1263.593362	-1263.286885	12.89	11.98	0.00%	0.00%
(S)-22_H_open-c8	-1263.592050	-1263.285402	13.71	12.91	0.00%	0.00%
(S)-22_H_open-c9	-1263.592175	-1263.284211	13.64	13.65	0.00%	0.00%
(S)-22_H_open-c5	-1263.598858	-1263.291494	9.44	9.08	0.00%	0.00%
		∑(S)-ent			99.72%	99.93%

Table S16. Energetic data of (*R/S*)-**22_open** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(S)-22-open-c1	-1263.219355	-1262.926881	**27.84%**	**24.24%**	0.14	0.25
(S)-22-open-c11	-1263.210688	-1262.917866	0.00%	0.00%	5.58	5.91
(S)-22-open-c12	-1263.208829	-1262.916251	0.00%	0.00%	6.75	6.92
(S)-22-open-c13	-1263.208164	-1262.915716	0.00%	0.00%	7.17	7.26
(S)-22-open-c14	-1263.207167	-1262.914860	0.00%	0.00%	7.79	7.80
(S)-22-open-c15	-1263.208527	-1262.915728	0.00%	0.00%	6.94	7.25
(S)-22-open-c18	-1263.207542	-1262.914608	0.00%	0.00%	7.56	7.95
(S)-22-open-c19	-1263.203280	-1262.910878	0.00%	0.00%	10.23	10.29
(S)-22-open-c2	-1263.218054	-1262.925759	7.02%	7.39%	0.96	0.96
(S)-22-open-c20	-1263.204843	-1262.912031	0.00%	0.00%	9.25	9.57
(S)-22-open-c22	-1263.205017	-1262.913083	0.00%	0.00%	9.14	8.91
(S)-22-open-c24	-1263.184751	-1262.890620	0.00%	0.00%	21.86	23.01
(S)-22-open-c3	-1263.218235	-1262.925901	8.50%	8.59%	0.85	0.87
(S)-22-open-c4	-1263.219586	-1262.927283	**35.54%**	**37.11%**	0.00	0.00
(S)-22-open-c5	-1263.217551	-1262.924642	4.12%	2.26%	1.28	1.66
(S)-22-open-c6	-1263.217253	-1262.925682	3.01%	6.81%	1.46	1.00
(S)-22-open-c7	-1263.217219	-1262.924153	2.90%	1.35%	1.49	1.96
(S)-22-open-c8	-1263.218479	-1262.926236	11.01%	12.24%	0.69	0.66
(S)-22-open-c9	-1263.209782	-1262.916585	0.00%	0.00%	6.15	6.71
(S)-22-open-c10	-1263.208074	-1262.916051	0.00%	0.00%	7.22	7.05
			99.95%	99.99%		
(R)-22-open-c1	-1263.212333	-1262.918843	0.02%	0.00%	4.55	5.30
(R)-22-open-c11	-1263.210411	-1262.917326	0.00%	0.00%	5.76	6.25
(R)-22-open-c12	-1263.204854	-1262.911293	0.00%	0.00%	9.24	10.03
(R)-22-open-c13	-1263.206292	-1262.913593	0.00%	0.00%	8.34	8.59
(R)-22-open-c14	-1263.208694	-1262.915431	0.00%	0.00%	6.83	7.44
(R)-22-open-c16	-1263.207535	-1262.915961	0.00%	0.00%	7.56	7.10
(R)-22-open-c17	-1263.206261	-1262.913567	0.00%	0.00%	8.36	8.61
(R)-22-open-c19	-1263.204899	-1262.911661	0.00%	0.00%	9.22	9.80
(R)-22-open-c2	-1263.211239	-1262.917970	0.01%	0.00%	5.24	5.84
(R)-22-open-c20	-1263.206043	-1262.912783	0.00%	0.00%	8.50	9.10
(R)-22-open-c21	-1263.207534	-1262.914393	0.00%	0.00%	7.56	8.09
(R)-22-open-c22	-1263.206313	-1262.912300	0.00%	0.00%	8.33	9.40
(R)-22-open-c24	-1263.206229	-1262.912826	0.00%	0.00%	8.38	9.07
(R)-22-open-c25	-1263.201178	-1262.909077	0.00%	0.00%	11.55	11.42
(R)-22-open-c26	-1263.201878	-1262.908688	0.00%	0.00%	11.11	11.67
(R)-22-open-c27	-1263.202035	-1262.909917	0.00%	0.00%	11.01	10.90
(R)-22-open-c29	-1263.195323	-1262.900813	0.00%	0.00%	15.23	16.61
(R)-22-open-c3	-1263.211752	-1262.917562	0.01%	0.00%	4.92	6.10
(R)-22-open-c4	-1263.211911	-1262.917699	0.01%	0.00%	4.82	6.01
(R)-22-open-c5	-1263.210883	-1262.916768	0.00%	0.00%	5.46	6.60
(R)-22-open-c6	-1263.210345	-1262.918340	0.00%	0.00%	5.80	5.61
(R)-22-open-c7	-1263.210063	-1262.915968	0.00%	0.00%	5.98	7.10
(R)-22-open-c8	-1263.208118	-1262.915193	0.00%	0.00%	7.20	7.59
(R)-22-open-c9	-1263.208176	-1262.915394	0.00%	0.00%	7.16	7.46
			0.05%	0.01%		

Table S17. Energetic data of (*R/S*)-**22+MeOH** conformers calculated at the B3LYP/def2TZVP level. Total (E, hartree) and Gibbs free energies (G, hartee), relative energies (ΔE, ΔG; kcal/mol), and abundances (%) referred to the value of the most stable conformer. The most stable conformers are highlighted in bold.

Structure	E	G	ΔE	ΔG	ΔE(%)	ΔG(%)
(R)-22-MeOH-c1	-1263.228258	-1262.938381	3.39	3.49	0.20%	0.15%
(R)-22-MeOH-c2	-1263.228635	-1262.937492	3.16	4.04	0.30%	0.06%
(R)-22-MeOH-c3	-1263.230873	-1262.940841	1.75	1.94	3.20%	1.97%
(R)-22-MeOH-c4	-1263.222335	-1262.933137	7.11	6.78	0.00%	0.00%
		∑*(R)-ent*			3.70%	2.17%
(S)-22-MeOH-c1	-1263.233665	-1262.943935	0.00	0.00	**61.60%**	**52.08%**
(S)-22-MeOH-c2	-1263.232735	-1262.943144	0.58	0.50	23.00%	22.53%
(S)-22-MeOH-c3	-1263.232089	-1262.943141	0.99	0.50	11.61%	22.46%
(S)-22-MeOH-c4	-1263.227540	-1262.939937	3.84	2.51	0.09%	0.75%
		∑*(S)-ent*			96.30%	97.83%

Table S18. Cartesian coordinates of the most stable structures in the iminium ion path (R^1=H, R^2=Me) calculated at the B3LYP/def2TZVP level.

(*R*)-subA-c7			
C	2.90398400	0.02254000	-0.03887800
C	1.14394200	-1.28011200	-1.53941000
C	0.48561500	-0.24090900	-0.62293400
H	3.63137500	0.59237400	-0.61648700
H	1.28846300	-0.87139800	-2.53978900
H	0.57512500	-2.20257600	-1.61689700
H	-0.22186100	0.35540800	-1.19741900
S	2.74640300	-1.66536200	-0.76600400
C	3.35080700	-0.04517000	1.41502800
H	2.60981700	-0.55411600	2.02852000
H	4.30098700	-0.57860500	1.48511700
H	3.49718000	0.96621800	1.79510600
N	1.58781300	0.64133200	-0.24506100
C	1.50465800	1.99022400	-0.16105100
O	2.42963500	2.73624500	0.08742000
O	0.24336000	2.45579300	-0.39974800
H	0.30552100	3.41538100	-0.29509100
C	-0.24981700	-0.88622700	0.60857700
H	0.20512000	-1.86523100	0.78380500
O	-0.03523100	-0.15698300	1.79417600
H	-0.67428700	0.57415700	1.82056200
C	-1.77809000	-1.14590100	0.35528900
C	-2.01039300	-2.03802800	-0.87078900
H	-1.47132700	-2.97919300	-0.74707200
H	-3.06920000	-2.27401300	-0.97313100
H	-1.69208800	-1.57441400	-1.80279300
C	-2.36446700	-1.85301000	1.59703500
H	-2.22422200	-1.26007600	2.49689300
H	-3.43128200	-2.04188100	1.46176700
H	-1.86649200	-2.81414600	1.73688200
C	-2.48715000	0.20624300	0.23938500
O	-3.22556200	0.34400400	-0.86930800
O	-2.40669300	1.07739800	1.07843700
C	-3.92629300	1.59382600	-1.01460400
H	-3.21901100	2.42097500	-1.04229100
H	-4.46494500	1.51553900	-1.95457400
H	-4.61685200	1.73955600	-0.18532600

(*R*)-subA-c3			
C	2.72834600	0.41155800	0.21357800
C	1.59239400	-0.76555300	-1.86045700
C	0.55169000	-0.18804100	-0.88894000
H	3.34017000	1.24737300	-0.12380000
H	1.80592400	-0.05799700	-2.66134900
H	1.27692800	-1.70893400	-2.30229800
H	-0.17787200	0.37435700	-1.46360200
S	3.09421000	-1.04563800	-0.86166000
C	3.03755500	0.12509400	1.67465600
H	2.40698100	-0.67374900	2.06099300
H	4.08515100	-0.16178800	1.78574300
H	2.87126000	1.03122000	2.25811600
N	1.31971900	0.75530600	-0.05841700
C	0.99243000	2.06701100	0.09086000
O	1.70806100	2.91266000	0.58654900
O	-0.25918400	2.35724500	-0.36479800
H	-0.38095200	3.30120800	-0.19072000
C	-0.22480900	-1.30682900	-0.14209500
H	-0.55301600	-1.97842100	-0.94489300
O	0.57590600	-2.02468900	0.78558100
H	1.45089100	-2.17562700	0.39394600
C	-1.52269600	-0.90124800	0.61595300
C	-2.23410300	-2.20984000	1.04845100
H	-1.59645900	-2.75835000	1.73926000
H	-3.17605300	-1.98014300	1.54730100
H	-2.44250300	-2.84903500	0.18863800
C	-1.25790900	-0.05278400	1.86924300
H	-0.93183600	0.95524300	1.62707600
H	-2.16549500	0.02914500	2.46544400
H	-0.49045600	-0.53530200	2.47188300
C	-2.47984100	-0.22503000	-0.36417400
O	-3.41003000	0.51742500	0.25994400
O	-2.46386500	-0.37617800	-1.56323600
C	-4.40305700	1.12284300	-0.58251500
H	-4.96481200	0.36007200	-1.12073500
H	-5.05535300	1.67624400	0.08751700
H	-3.93498100	1.79276600	-1.30271300

(*R*)-subA-c4			
C	-2.86369200	-0.06268700	0.10099200
C	-1.26162600	1.48644100	-1.33168200
C	-0.50256400	0.35261100	-0.63100100
H	-3.61867900	-0.56336200	-0.50479800
H	-1.49111700	1.21204300	-2.36141700
H	-0.71848000	2.42678600	-1.33313700
H	0.15880200	-0.13604200	-1.34546700
S	-2.79095100	1.71609500	-0.37216200
C	-3.20545300	-0.22432500	1.57590100
H	-2.43222700	0.21234800	2.20552900
H	-4.15786900	0.26455100	1.79034200
H	-3.30505100	-1.28419900	1.81133400
N	-1.55166600	-0.60631000	-0.28122500
C	-1.43355100	-1.94994600	-0.37735400
O	-2.32473000	-2.75209200	-0.18841100
O	-0.17011200	-2.34788500	-0.72440600
H	-0.22928200	-3.31067800	-0.80045900
C	0.33116600	0.83903000	0.60813800
H	-0.13751900	1.75214300	0.98356800
O	0.25231400	-0.07083000	1.68527100
H	0.83483300	-0.82002000	1.50031500
C	1.81534800	1.21727000	0.25998900
C	1.88124600	2.36166600	-0.76033000
H	1.32234400	3.22353100	-0.39170900
H	2.91618800	2.66965400	-0.90796200
H	1.49541900	2.07580300	-1.73658300
C	2.52655900	1.66802400	1.55290300
H	2.49929300	0.90117600	2.32166700
H	3.56772500	1.92193200	1.34479100
H	2.03512400	2.56042300	1.94509100
C	2.55853800	0.01308000	-0.32963200
O	2.63477000	-1.01964200	0.54444800
O	3.03657200	-0.04231200	-1.43260000
C	3.30935200	-2.19918900	0.07009400
H	4.34244100	-1.96557800	-0.18212600
H	3.26779000	-2.90928600	0.89135300
H	2.80469100	-2.59433400	-0.80967800

(*R*)-subA-NH-c16			
C	-2.96618100	-0.73444100	-0.29084500
C	-1.21600400	-1.28327600	1.48460300
C	-0.72453100	-0.04413400	0.73536000
H	-3.69995500	-0.42965900	0.45483400
H	-1.85318000	-1.01694800	2.32788400
H	-0.38613700	-1.88190800	1.85136200
H	-0.58971100	0.79197200	1.41498200
S	-2.14390100	-2.24797400	0.25896000
C	-3.57647200	-0.82578400	-1.67346700
H	-2.83434900	-1.12033000	-2.41598900
H	-4.36682900	-1.57637700	-1.66186800
H	-4.02454700	0.12313800	-1.97051500
C	-2.44712300	1.70173600	-0.02255900
O	-2.60384400	2.44932900	-0.92761400
O	-2.76851000	1.85418900	1.25492900
H	-3.18229400	2.72556600	1.38157900
C	0.56098200	-0.28348100	-0.11442300
H	0.67457100	-1.36515400	-0.24248300
O	0.32353300	0.30758400	-1.38323700
H	1.12279800	0.12209200	-1.91953300
C	1.86275000	0.26235700	0.54648100
C	1.84501000	1.79869300	0.68886500
H	1.10421700	2.11540900	1.42569400
H	2.81325800	2.15038600	1.04285900
H	1.62473700	2.28892300	-0.25864000
C	2.09654000	-0.39747300	1.91471900
H	2.13992000	-1.48605300	1.84147500
H	3.03752500	-0.05922600	2.34175800
H	1.30651400	-0.12766500	2.61816200
C	3.01363000	-0.08194400	-0.42151600
O	4.19971600	-0.05003200	0.16067800
O	2.85481900	-0.31953400	-1.60362000
C	5.35571800	-0.28899400	-0.68257900
H	5.40128000	0.46050100	-1.46984200
H	6.21098700	-0.20979000	-0.01984900
H	5.29435800	-1.28189000	-1.12261200
N	-1.85596200	0.35304900	-0.22965100

(*R*)-subA-NH-c16a			
C	-3.53200400	-1.30857400	-0.18621400
C	-1.63563500	-0.43453200	1.58764000
C	-0.63077100	0.47651700	0.82515800
H	-3.83623600	-0.27544200	-0.05189500
H	-2.50508500	0.14167700	1.89742700
H	-1.17284600	-0.87444000	2.47150900
H	-0.40114400	1.27378700	1.53117500
S	-2.23362600	-1.85970100	0.62160400
C	-4.30213800	-2.15061900	-1.11910900
H	-3.93468600	-3.17240200	-1.18688800
H	-5.35395500	-2.15228400	-0.81237800
H	-4.28314000	-1.68637900	-2.11209800
C	-2.00992400	2.17394600	-0.41057500
O	-2.46134900	2.64219900	-1.42385000
O	-2.22699300	2.68446500	0.83000600
H	-2.74518300	3.49523100	0.71385200
C	0.64674200	-0.30196500	0.48663500
H	0.93419600	-0.83066600	1.40485600
O	0.24493900	-1.24882900	-0.49660200
H	1.03509100	-1.80409600	-0.65938900
C	1.90918600	0.51786600	0.06802600
C	1.76644200	1.25331200	-1.28181400
H	1.05901800	2.07728100	-1.20303400
H	2.72806200	1.67443200	-1.57324800
H	1.43718300	0.58204200	-2.07537300
C	2.27843800	1.51607700	1.17730100
H	2.36805400	1.02957300	2.15128600
H	3.23028700	1.99331800	0.95742800
H	1.52732100	2.30327600	1.25124100
C	3.03402500	-0.52009900	-0.12217600
O	4.24322000	0.01388700	-0.07361700
O	2.83683300	-1.70170600	-0.33706600
C	5.36533500	-0.86896900	-0.32084300
H	5.28292200	-1.30559500	-1.31404800
H	6.24483400	-0.23804100	-0.24583600
H	5.38873100	-1.65889500	0.42682400
N	-1.24138700	1.04357800	-0.35486600
H	-1.00706900	0.63992100	-1.24815000

18-SH-c9(r)			
C	-2.70542700	1.49615300	0.36311200
C	-2.06450000	-1.55616100	-0.38424500
C	-1.18235800	-0.42052600	0.19109700
H	-3.05512200	1.10049900	1.30940500
H	-1.63592700	-2.50914100	-0.07978300
H	-2.03943000	-1.51862100	-1.47348500
H	-1.18762200	-0.47221300	1.27756400
S	-3.82167100	-1.51089500	0.07948900
C	-3.32260000	2.72195300	-0.17593000
H	-4.39699600	2.55403000	-0.29452400
H	-3.21878500	3.53088800	0.55320900
H	-2.89475000	3.02779000	-1.12905100
N	-1.74526100	0.87305000	-0.21104000
C	0.25551400	-0.51978100	-0.38175400
H	0.45522500	-1.58526000	-0.54055900
O	0.18419200	0.13918000	-1.63618200
H	1.06538300	0.03223500	-2.04469300
C	1.39679000	0.01180500	0.53761000
C	1.22191000	1.49586000	0.91218900
H	0.35312600	1.63032900	1.55930500
H	2.09108300	1.84966100	1.46436900
H	1.10368300	2.12384600	0.02841100
C	1.48957300	-0.85394500	1.80710800
H	1.62174300	-1.91079900	1.56674900
H	2.33383300	-0.54310500	2.41791800
H	0.59172900	-0.75279000	2.41908000
C	2.70978100	-0.11936300	-0.26258100
O	3.78156200	0.05368900	0.49482600
O	2.76487800	-0.33448600	-1.45709300
C	5.07151600	-0.00852100	-0.16429900
H	5.13504700	0.76169400	-0.93011300
H	5.80011600	0.16316700	0.62106500
H	5.21023700	-0.98823000	-0.61631300
H	-1.35631200	1.19885100	-1.10059700
H	-3.67892900	-1.98177500	1.33123700

18-SH-c8(r)			
C	1.85119800	1.78008300	-0.52374700
C	2.38129700	-1.15116900	0.58690000
C	1.21102600	-0.57155100	-0.24130300
H	2.65665600	1.45689500	-1.17307500
H	2.36769400	-2.23553400	0.48847000
H	2.22936200	-0.92318900	1.63945900
H	1.40458400	-0.73931300	-1.30069200
S	4.04558400	-0.53536500	0.18865600
C	1.68243900	3.21964000	-0.24526500
H	2.59780300	3.59827700	0.21989000
H	1.57503300	3.76222800	-1.18867300
H	0.83224800	3.42663000	0.40165200
N	1.08824500	0.87960200	-0.02855200
C	-0.09453800	-1.30992800	0.14275500

18-SH-c9b(r)			
C	-2.69407400	1.50355300	0.34851600
C	-2.05424000	-1.59043000	-0.30370700
C	-1.18114700	-0.42065200	0.21736500
H	-3.03520300	1.13235600	1.30823900
H	-1.63792600	-2.50872900	0.10861100
H	-1.98845100	-1.65559800	-1.38757300
H	-1.18325600	-0.43216300	1.30480700
S	-3.80258300	-1.54012800	0.20894300
C	-3.30211000	2.72620900	-0.20912400
H	-4.38369800	2.58489700	-0.28734800
H	-3.15487400	3.55283900	0.49264300
H	-2.89693100	2.99563300	-1.18297700
N	-1.74870700	0.85671600	-0.22410500
C	0.25411400	-0.53649300	-0.35787700

(*R*)-18-NH-c14			
C	-3.13607200	0.74294600	0.46051200
C	-1.61505900	-1.19552300	1.11414100
C	-0.72847300	-0.05529900	0.59961700
H	-3.35409800	0.96892700	1.50550200
H	-1.78886100	-1.11932500	2.18801500
H	-1.17843800	-2.16879000	0.90596700
H	-0.06358100	0.30815900	1.38038800
S	-3.18482100	-1.05034000	0.20867500
C	-4.03502300	1.53217600	-0.46880600
H	-5.07432200	1.26441600	-0.28094000
H	-3.93499900	2.60445400	-0.29015500
H	-3.81013100	1.31976400	-1.51473800
N	-1.66932600	1.09516900	0.25819500
C	0.08027100	-0.40457600	-0.70328800

H	0.10208300	-2.34377300	-0.16289500	H	0.45483900	-1.60636100	-0.48252500	H	-0.41035100	-1.26151300	-1.16829500
O	-0.20512400	-1.23047600	1.55625700	O	0.17473800	0.08039800	-1.63354800	O	-0.04182100	0.65318900	-1.64732600
H	-0.73601300	-1.95939100	1.89495700	H	1.05579700	-0.03510000	-2.04057700	H	0.64484800	1.30847800	-1.41334500
C	-1.44341400	-0.92650900	-0.55684700	C	1.39902200	0.02654400	0.53765400	C	1.55971600	-0.79387700	-0.43399400
C	-1.24303000	-0.59204400	-2.05033800	C	1.22248300	1.52119000	0.86675500	C	1.65525600	-1.95694900	0.56807900
H	-0.74491900	-1.42100300	-2.55710000	H	0.35763200	1.67338000	1.51520700	H	1.09486100	-2.81676500	0.19654700
H	-2.20766000	-0.44661100	-2.53609400	H	2.09412200	1.89415100	1.40220600	H	2.69188400	-2.26414400	0.68522600
H	-0.65490300	0.31317600	-2.20309700	H	1.09723700	2.12120500	-0.03535900	H	1.28180000	-1.69963200	1.56072700
C	-2.37647900	-2.14861000	-0.44762800	C	1.50009400	-0.79900200	1.83306200	C	2.21009800	-1.22821600	-1.76872700
H	-2.57950900	-2.42166700	0.58939300	H	1.63697500	-1.86205000	1.62502800	H	2.16792500	-0.44089200	-2.51968500
H	-3.33548800	-1.95436600	-0.92083200	H	2.34461600	-0.46518400	2.43124900	H	3.25154100	-1.50161600	-1.60619400
H	-1.91956000	-3.00456600	-0.94645700	H	0.60349400	-0.68395200	2.44430300	H	1.68722800	-2.10045300	-2.16406500
C	-2.07401300	0.30690300	0.11452700	C	2.70802000	-0.12595700	-0.26511700	C	2.32148300	0.43898100	0.06817400
O	-3.39049800	0.25162400	0.15926100	O	3.78347200	0.06863200	0.48149300	O	3.49017600	0.14523100	0.60501600
O	-1.45023100	1.27207300	0.52550200	O	2.75722900	-0.37387800	-1.45368900	O	1.90425100	1.57970200	-0.05185700
C	-4.09076400	1.39238300	0.71730100	C	5.07017400	-0.01138700	-0.18202900	C	4.33292500	1.25083000	1.02027600
H	-3.88363400	2.28076000	0.12437500	H	5.12957200	0.73731600	-0.96921700	H	3.83470300	1.82706200	1.79693300
H	-5.14218700	1.12992600	0.66799000	H	5.80253300	0.18224300	0.59468100	H	5.23783600	0.78931300	1.40087000
H	-3.77642800	1.55228300	1.74622000	H	5.20711200	-1.00323300	-0.60732000	H	4.55038800	1.89079000	0.16791400
H	4.18865300	-1.16767500	-0.99014500	H	-1.36495900	1.15704300	-1.12481900	H	-1.45311700	1.28826900	-0.74319300
H	0.22364100	1.16456800	0.48173900	H	-4.31388100	-1.09632500	-0.95065000	H	-1.42429000	1.93483000	0.78380200
(*R*)-18-NH-c9				(*S*)-18-NH-c7				(*R*)-18-new1			
C	-3.20616800	0.77744000	0.27221500	C	-2.62503600	1.15270900	-0.42033800	C	-2.28605800	1.07123700	0.42850000
C	-2.00975800	-1.61403800	0.15628000	C	-2.27004800	-1.44173500	0.18120400	C	-2.17500900	-1.56093200	-0.01636900
C	-1.06985500	-0.44824200	0.48139200	C	-0.99904400	-0.60698500	0.23765800	C	-0.87944600	-0.82051900	0.39366900
H	-3.24800200	1.02962600	1.33256500	H	-2.35770200	-2.08045400	1.05805600	H	-2.25513900	1.23936300	1.50625000
H	-1.96166500	-2.36445500	0.94254900	H	-2.29732400	-2.06107700	-0.71558700	H	-2.36564400	-2.41688900	0.63103100
H	-1.74155800	-2.07363900	-0.79304800	H	-0.86978200	-0.19152500	1.23360000	H	-2.11367800	-1.89845800	-1.04923300
H	-1.01342700	-0.29447400	1.55641400	S	-3.65953800	-0.25231200	0.18708000	H	-0.82077500	-0.84602700	1.48419200
S	-3.71946700	-0.95681200	0.01446700	N	-1.26916800	0.55552600	-0.67996500	S	-3.52121200	-0.33679200	0.16025300
C	-4.00046400	1.77038400	-0.55106400	C	0.26982000	-1.35992200	-0.21930200	C	-2.71349200	2.33704200	-0.28551000
H	-5.05119500	1.71385600	-0.26739000	H	0.14270100	-2.38888900	0.13330500	H	-3.69960600	2.65616300	0.05268000
H	-3.66562200	2.79302500	-0.36378000	O	0.22144100	-1.32738800	-1.64358400	H	-2.00488200	3.14255700	-0.07902200
H	-3.92829600	1.55003700	-1.61679700	H	0.71381400	-2.06264000	-2.02314900	H	-2.76449200	2.17662700	-1.36416800
N	-1.74569300	0.78062100	-0.08961400	C	1.64982100	-0.91270000	0.35134700	N	-1.00087700	0.57984000	0.00048200
C	0.32369900	-0.61141800	-0.15971700	C	1.63537400	-1.01292500	1.89509400	C	0.38063300	-1.48970500	-0.18033300
H	0.55093800	-1.68317100	-0.13389100	H	1.33873800	-2.01747700	2.20254800	H	0.36392900	-2.52912400	0.16561700
O	0.13864200	-0.19056200	-1.50073400	H	2.63323800	-0.82788700	2.29024200	O	0.32185900	-1.54535700	-1.59637000
H	0.97701500	-0.38145300	-1.96279800	H	0.95849600	-0.29539200	2.35958600	H	0.79658300	-0.76862900	-1.93980800
C	1.50075100	0.10810200	0.56511900	C	2.71671500	-1.88001700	-0.19764100	C	1.73445300	-0.89891000	0.33998400
C	1.27637700	1.62476300	0.71489400	H	2.85048600	-1.77790900	-1.27502700	C	1.76521300	-0.87580500	1.87316800
H	0.48249100	1.82973600	1.44038400	H	3.68238300	-1.69374000	0.26506600	H	1.49356500	-1.86020900	2.26098800
H	2.17206600	2.10612000	1.10326300	H	2.43296100	-2.91060200	0.02613200	H	2.76625700	-0.64032700	2.23305600
H	1.03591300	2.09588300	-0.24029500	C	1.99558100	0.54116100	0.00539700	H	1.08385000	-0.13783200	2.29131900
C	1.73400100	-0.53613800	1.94460000	O	3.29389000	0.76228700	-0.00825900	C	2.88476400	-1.79702100	-0.17176800
H	1.92227700	-1.60807100	1.86103200	O	1.18003200	1.43257100	-0.17624500	H	2.87284400	-1.88369200	-1.25598500
H	2.59283600	-0.08287400	2.43443000	C	3.74548600	2.12179100	-0.23846000	H	3.85214000	-1.39699600	0.13750500
H	0.87229700	-0.39272200	2.59891500	H	3.36001400	2.77694400	0.53972800	H	2.78167100	-2.79675800	0.25443600
C	2.75774300	-0.11179800	-0.30402600	H	4.82826400	2.06911800	-0.20090100	C	1.96222300	0.48244600	-0.27499200
O	3.86046200	0.30399200	0.29766200	H	3.40649200	2.46388800	-1.21372700	O	2.38842800	1.40059400	0.59287200
O	2.74280600	-0.60070300	-1.41520600	H	-1.20160500	0.19220600	-1.63461800	O	1.83356400	0.71543500	-1.46152700
C	5.10528900	0.16294500	-0.43423900	C	-2.55387200	2.31296600	0.55374900	C	2.63577800	2.71432100	0.06094200
H	5.05630300	0.72901100	-1.36200200	H	-1.96983700	3.13633900	0.13586400	H	1.71644700	3.13086200	-0.34763500
H	5.86870400	0.56199300	0.22524000	H	-3.56162000	2.68057500	0.74491400	H	2.98464400	3.30597500	0.90244900
H	5.28913800	-0.88668700	-0.65267100	H	-2.12577100	2.01306200	1.51033700	H	3.39179200	2.67273000	-0.72174300
H	-1.59886800	0.73583500	-1.10781800	H	-3.01041700	1.48516000	-1.38263100	H	-0.93914300	0.64216000	-1.01289100
H	-1.28497900	1.63324100	0.23502100	H	-0.46844200	1.21279700	-0.55480300				
(*S*)-18-new1				TS: (*R*)-18-new1 → (R)-21-MeOH-R-new1 (img freq -616 cm^{-1})				TS: (*S*)-18-new1 → (R)-21-MeOH-c1 (img freq -760 cm^{-1})			
C	-2.28034200	1.21341500	-0.29613500	6	1.823406	1.135131	-0.352314	6	-1.529988	1.078615	-0.460182
C	-2.24784100	-1.44886600	-0.01376700	6	1.85118	1.455409	-0.675428	6	-2.144838	-0.927114	1.079191
C	-0.96324900	-0.67077000	0.33394900	6	0.551396	-0.77169	-1.172549	6	-0.645468	-0.635152	1.130803
H	-2.52502800	-2.14402000	0.77876700	1	2.251696	1.32857	-1.339895	1	-2.683443	-0.408376	1.871217
H	-2.12640000	-1.99633300	-0.94695800	1	2.46863	1.7452	-1.52331	1	-2.346968	-1.993846	1.147428
H	-1.00070100	-0.42999500	1.39763300	1	1.657105	-2.352736	-0.0929	1	-0.337188	-0.43792	2.158143
S	-3.55119800	-0.18044800	-0.18368600	1	0.605553	-0.692619	-2.258671	16	-2.698512	-0.333704	-0.556554
N	-0.97879100	0.58630000	-0.41393100	16	2.745859	-0.266815	0.383405	7	-0.379827	0.584836	0.32132
C	0.31130800	-1.49020500	0.06618600	6	1.910199	2.402045	0.480341	6	0.265468	-1.750411	0.543293
H	0.21421400	-2.41225200	0.64981300	1	2.946649	2.742245	0.483039	1	0.544055	-2.443741	1.338104
O	0.37786900	-1.88943800	-1.29334400	1	1.295284	3.187662	0.039701	8	-0.3845	-2.55427	-0.421143
H	0.92880600	-1.23953500	-1.76338500	1	1.578567	2.243237	1.501429	1	-0.898183	-2.000119	-1.028494
C	1.63945300	-0.82292100	0.56000400	7	0.472537	0.597424	-0.606346	6	1.539057	-1.016309	0.027738
C	1.53129300	-0.42086700	2.03594000	6	-0.799416	-1.44378	-0.791474	6	2.518929	-0.834837	1.197132
H	1.17806800	-1.27126200	2.62355700	1	-1.522943	-1.14498	-1.547295	1	2.882419	-1.817502	1.507173
H	2.50571100	-0.12816200	2.42572400	8	-0.758663	-2.854641	-0.853622	1	3.367944	-0.227472	0.89149
H	0.85154900	0.41445700	2.19008400	1	-0.357426	-3.203802	-0.050585	1	2.070742	-0.338091	2.055303
C	2.78572200	-1.84904900	0.40208400	6	-1.252727	-0.83579	0.552329	6	2.237312	-1.778203	-1.101936
H	2.86881700	-2.20225800	-0.62337200	6	-2.775844	-0.841981	0.694302	1	1.589786	-1.91548	-1.96364
H	3.73947400	-1.40941800	0.69968400	1	-3.13989	-1.870807	0.725842	1	3.120436	-1.226987	-1.425844
H	2.59478400	-2.70841500	1.04765300	1	-3.074101	-0.343822	1.617877	1	2.550973	-2.761713	-0.748856
C	1.99051200	0.35624600	-0.34811300	1	3.237933	-0.325807	-0.144229	6	0.973757	0.307987	-0.535974
O	2.37378000	1.45249600	0.30648200	6	-0.624302	-1.534994	1.77601	8	1.602029	1.727421	0.696057
O	1.98738200	0.28807000	-1.56235500	1	0.466312	-1.524577	1.764029	8	1.015698	0.701428	-1.66887
C	2.72979500	2.58700400	-0.50372400	1	-0.939003	-1.018143	2.68186	6	2.111184	2.839173	0.021226
H	1.87255700	2.90794700	-1.09344300	1	-0.975608	-2.567117	1.850628	1	2.039265	2.70599	-1.069458
H	3.02503500	3.36195100	0.19781200	6	-0.702509	0.590427	0.527774	1	1.562948	3.75656	0.277049
H	3.55302000	2.33591500	-1.17087900	8	-1.666748	1.346496	-1.065804	1	3.167247	3.003147	0.272732
H	-0.80202600	0.37027300	-1.38991900	8	-0.692158	1.395188	1.411977	1	0.242298	1.396278	0.806343
C	-2.39118400	2.14672600	0.90024000	6	-2.373721	2.51048	-0.759695	6	-2.136943	2.335105	0.149077
H	-1.69675900	2.98264200	0.78462300	1	-2.127706	3.322744	-1.456677	1	-1.385849	3.126819	0.198641
H	-3.40399900	2.54330300	0.98244000	1	-3.458711	2.345374	-0.813601	1	-2.963496	2.685472	-0.468439
H	-2.16236000	1.62790000	1.83158100	1	-2.137856	2.865653	0.255968	1	-2.516385	2.15438	1.156039
H	-2.48908900	1.76700800	-1.21117700	1	-0.245528	1.218225	-1.19946	1	-1.168247	1.278267	-1.469858
(*S*)-21-c2				(*S*)-21-MeOH-c1				(*R*)-21-MeOH-new1			
C	-1.75525500	0.82662400	-0.39236100	C	-1.81580200	0.40845300	0.84403600	C	1.88422100	0.44529800	-1.02024200
C	-1.34124800	-1.77577100	0.10131800	C	-1.57070900	0.06648100	-1.79073000	C	1.90623900	-0.47319200	1.49754300
C	-0.26060200	-0.86767200	0.68206700	C	-0.73583300	-0.92583000	-0.99159400	C	0.90961000	-1.19087800	0.60605300
H	-1.61342500	-2.58306600	0.77926300	H	-2.03227500	-0.39237400	-2.66339300	H	2.41209700	-1.15137000	2.18240700

H	-1.03593900	-2.19151800	-0.85424500	H	-0.97602100	0.91964700	-2.10684700	H	1.43367900	0.32649000	2.06261900
H	-0.42169700	-0.76969200	1.76105400	H	-1.21212100	-1.91058100	-1.03137000	H	1.33087100	-2.16052800	0.31823900
S	-2.79327500	-0.68022200	-0.10168000	S	-2.89726700	0.58581200	-0.64337900	S	3.14436600	0.18734900	0.32199200
N	-0.42236900	0.42345400	0.02347600	N	-0.71130200	-0.42457800	0.38520000	N	0.73598800	-0.34060000	-0.57461800
C	1.22048900	-1.22398100	0.41513000	C	0.77667200	-1.05057800	-1.33291500	C	-0.54642600	-1.37873800	1.09694500
H	1.65442100	-1.74183500	1.27735900	H	0.95034900	-1.86095200	-2.04236700	H	-0.65789800	-2.31848100	1.64001600
O	1.27446500	-2.06560900	-0.72827400	O	1.30129600	0.11026000	-1.93623500	O	-0.96168900	-0.36416500	1.98456600
H	2.19678500	-2.23466000	-0.94673200	H	1.33323800	0.84452000	-1.29499400	H	-1.09419800	0.47574900	1.50822400
C	1.89479800	0.16212700	0.19431300	C	1.40393600	-1.35867400	0.05982000	C	-1.32999200	-1.38875000	-0.24635700
C	2.31614600	0.76688200	1.54630500	C	1.20422000	-2.84174600	0.43193200	C	-1.19566800	-2.75384200	-0.95299800
H	3.14374200	0.19783600	1.97596700	H	1.80380300	-3.47515400	-0.22500300	H	-1.71093000	-3.52488000	-0.37660100
H	2.64480700	1.79778400	1.41014300	H	1.52832100	-3.01769500	1.45871400	H	-1.65428600	-2.70681100	-1.94163400
H	1.49738800	0.76996000	2.26845100	H	0.16351800	-3.15843100	0.35199800	H	-0.15817700	-3.06425200	-1.08236100
C	3.08298300	0.14675400	-0.76333300	C	2.88043900	-0.99823900	0.18723700	C	-2.80869700	-1.03347100	-0.12809800
H	2.80877400	-0.23322600	-1.74735500	H	3.07608000	0.04043200	-0.06879400	H	-2.96869400	-0.09439400	0.39574200
H	3.45032000	1.16314700	-0.90321600	H	3.21102800	-1.16167500	1.21349300	H	-3.24528900	-0.94716200	-1.12363800
H	3.90262700	-0.45639300	-0.36196300	H	3.47979100	-1.62593500	-0.47484600	H	-3.34023100	-1.81606600	0.41669400
C	0.73869700	1.00901800	-0.37202100	C	0.50680900	-0.50162700	0.97222500	C	-0.52973600	-0.35250900	-1.06556800
O	0.83795100	2.03067600	-1.02415900	O	1.37091000	2.21116600	0.11574900	O	-1.48013100	2.10006000	0.42963000
C	-2.30200700	2.02933000	0.36365100	O	0.82565700	0.04328100	2.02231000	O	-0.96388700	0.33445100	-1.98062600
H	-1.68180400	2.90193300	0.15320100	C	2.15317500	3.40018300	0.15907500	C	-2.48984100	3.06454700	0.71216600
H	-3.32227500	2.24721500	0.04252800	H	2.13330800	3.83531900	-0.83884600	H	-2.41877700	3.30209200	1.77229900
H	-2.31151600	1.84194300	1.43767900	H	1.73688500	4.12484800	0.86441600	H	-2.33603000	3.98162800	0.13680300
H	-1.72656800	1.04953500	-1.46052700	H	3.19245800	3.19234600	0.43092100	H	-3.49182200	2.67631900	0.50546700
				H	1.35267100	1.79055700	0.98968500	H	-1.50578800	1.86265100	-0.50957000
				C	-2.58057700	-0.18015300	2.02043400	C	1.58654100	1.91807700	-1.26522500
				H	-1.91954900	-0.25318100	2.88521400	H	2.51453500	2.43184800	-1.51793700
				H	-3.42146100	0.46353200	2.28487900	H	0.88569000	2.02961600	-2.09209600
				H	-2.96662700	-1.16987300	1.77571700	H	1.16318000	2.38272500	-0.37493400
				H	-1.41489800	1.38643700	1.11738300	H	2.30844600	-0.00058700	-1.92315400

Table S19. Cartesian coordinates of the most stable structures in the sulfonium ion path (R^1=Me, R^2=Et) calculated at the B3LYP/def2TZVP level.

(*S*)-subB-c23			
C	-2.55240500	-0.19952200	-0.33024800
C	-0.84842800	-1.41735000	1.32323800
C	-0.16249000	-0.33128000	0.49355200
H	-1.14526200	-1.03250300	2.29859300
H	-0.22196500	-2.29284800	1.46809000
H	0.43242500	0.30439400	1.14838900
S	-2.29683200	-1.91172800	0.34891600
C	-2.80382700	-0.32127000	-1.83598200
H	-3.01057700	0.66275800	-2.25552900
H	-3.66786100	-0.96368300	-2.01573500
N	-1.26526500	0.48479100	-0.02669600
C	-1.09831200	1.78451000	-0.37720200
O	-1.92004000	2.50290800	-0.90814500
O	0.13891300	2.25804600	-0.03458800
H	0.15161900	3.17239400	-0.35009100
C	0.75796900	-0.93601000	-0.63381900
H	0.38836900	-1.94402700	-0.84176400
O	0.64027700	-0.23862500	-1.85217600
H	1.26584300	0.50382900	-1.84504200
C	2.26123800	-1.09962600	-0.20221100
C	2.40370000	-1.93505400	1.07642500
H	1.95186600	-2.91733000	0.92628000
H	3.45688000	-2.08895100	1.31120200
H	1.94448800	-1.46892700	1.94593700
C	3.01597300	-1.81468100	-1.34369400
H	2.94979100	-1.25966100	-2.27545600
H	4.06925700	-1.94129600	-1.08543200
H	2.58512600	-2.80514500	-1.50018000
C	2.87697600	0.29477100	-0.06226900
O	3.35932300	0.56132800	1.15857000
O	2.93162900	1.09299500	-0.97259000
C	3.94516100	1.86387300	1.33979500
H	3.19936100	2.63848300	1.16935000
H	4.29236400	1.88438900	2.36884600
H	4.77541800	2.00580200	0.64966200
C	-3.75600400	0.48104000	0.35500900
H	-3.92206700	1.43394600	-0.14808000
H	-4.62603000	-0.14613000	0.14434100
C	-3.64605600	0.70800200	1.85843700
H	-3.52872400	-0.23285900	2.39917200
H	-2.80574100	1.35824800	2.10795600
H	-4.55203100	1.19085300	2.22884600
H	-1.93816100	-0.74524800	-2.33989000

subB_NH-c1			
C	3.34639500	-0.01418500	0.21551600
C	1.32406100	-0.03152400	-1.77148500
C	-0.09615900	0.32223800	-1.25694800
H	1.86654500	0.87052600	-2.03974100
H	1.25754300	-0.66567800	-2.65726100
H	-0.51709700	0.95752200	-2.03712500
S	2.34727700	-1.01999400	-0.62794700
C	4.29111300	-0.66910300	1.17610500
H	4.17044100	-0.13709700	2.12873500
H	5.29398600	-0.37736400	0.83465900
C	0.17137200	2.42274900	0.08401300
O	0.25644900	3.01972500	1.13019400
O	0.32134100	3.01111000	-1.13271600
H	0.42353200	3.96111700	-0.97130400
C	-0.95985300	-0.95551800	-1.15745100
H	-0.99166500	-1.35626900	-2.17501400
O	-0.28468500	-1.93632100	-0.38089300
H	-0.57785600	-1.81497100	0.54233700
C	-2.44962900	-0.76262500	-0.74263300
C	-3.10747300	0.33949700	-1.58750200
H	-2.95021700	0.13582700	-2.64873400
H	-4.18038100	0.36395100	-1.41061600
H	-2.71463700	1.33112200	-1.36251900
C	-3.19160100	-2.10096400	-0.98686600
H	-2.72820900	-2.92513500	-0.44665800
H	-4.23261900	-2.01822100	-0.67682900
H	-3.17404500	-2.33793400	-2.05184800
C	-2.56828800	-0.48004500	0.75756900
O	-3.71254400	0.08373100	1.09213400
O	-1.71578400	-0.79142500	1.57690100
C	-3.95792100	0.31146800	2.50305500
H	-3.21300000	0.99599500	2.90315200
H	-4.94975300	0.74847100	2.55030900
H	-3.92131800	-0.63209200	3.04322900
C	3.38506800	1.46849000	0.16114000
H	2.76203300	1.86651100	0.97194000
H	4.40198800	1.81685000	0.34578200
H	3.01939300	1.89128100	-0.77005400
C	4.21854500	-2.17653000	1.38461800
H	4.42031200	-2.72806600	0.46567000
H	4.97078100	-2.47038300	2.11551100
H	3.24580900	-2.48837300	1.76704100
N	-0.05198600	1.08330500	-0.02610900
H	-0.22609200	0.61094000	0.84953000

(S)-24_H_open-c8			
C	1.92288000	0.72038700	0.14154300
C	1.98721800	-2.07953900	0.09449000
H	2.35347400	-2.98045700	-0.40037000
H	2.25671300	-2.15987100	1.14713300
S	2.83440500	-0.67978600	-0.70759000
O	0.50945800	0.47630500	0.07654000
C	2.18085600	1.95761800	-0.72510900
H	3.26276800	2.06727100	-0.83560800
H	1.78204400	1.75370300	-1.72079700
C	0.46565500	-1.94635300	-0.03719800
C	-0.01393100	-0.68120200	0.70817100
C	-1.53746200	-0.44143000	0.94905500
H	-0.02189200	-2.82818700	0.37551200
H	0.40023300	-0.79313100	1.71551900
C	-1.66635800	0.59499300	2.07936000
H	-2.71065700	0.79836200	2.30337000
H	-1.19800300	0.20620600	2.98487200
H	-1.18600600	1.53544000	1.81665700
C	-2.23842600	-1.74812500	1.38541500
H	-1.72560800	-2.18028000	2.24674200
H	-3.26328900	-1.53624200	1.68912300
H	-2.27795100	-2.49375600	0.59083300
C	-2.24583500	0.02780500	-0.32832600
O	-2.08555200	-0.48960900	-1.42847800
O	-3.10986700	0.99483700	-0.13466600
C	-3.88726600	1.44683400	-1.27500300
H	-4.47780600	0.62280600	-1.66908400
H	-4.52549600	2.23256200	-0.88555700
H	-3.22197400	1.82978700	-2.04536900
C	2.41745400	0.88553400	1.57516300
H	3.45032600	1.23073300	1.56468900
H	1.80985000	1.62536500	2.09715200
H	2.39428700	-0.04048500	2.14815600
C	1.58213000	3.25803200	-0.18816000
H	1.75755200	4.06068100	-0.90473300
H	0.50520600	3.17201100	-0.04264000
H	2.03451100	3.56212100	0.75583200
N	0.11647500	-1.87649200	-1.49905800
H	-0.82837100	-1.39286300	-1.61078700
H	0.10836400	-2.79737100	-1.93407700
H	0.84211700	-1.30198100	-1.95529100

(R)-24_H_open-c5			
C	-1.79995900	-0.69820900	-0.41704200
C	-1.80613600	1.93804600	0.53695100
H	-2.10937400	2.97246200	0.36744500
H	-2.17470600	1.65245900	1.52163000
S	-2.59479900	0.95823900	-0.78196800
O	-0.38039800	-0.51820300	-0.25854700
C	-2.41704800	-1.36973600	0.81922700
H	-1.79741400	-2.24630100	1.03192800
H	-2.33033000	-0.71221800	1.68675800
C	-1.95128500	-1.53275800	-1.67868800
H	-2.99486900	-1.60702800	-1.97988600
H	-1.38364300	-1.09076600	-2.49582900
C	-3.87881400	-1.79360400	0.67807600
H	-4.23493400	-2.19957100	1.62504700
H	-4.51882800	-0.94991500	0.41738600
H	-4.00817400	-2.56840000	-0.07702800
H	-1.57256500	-2.53941500	-1.49513200
C	-0.28143300	1.78604400	0.49454900
C	0.10249400	0.31819900	0.78114200
C	1.59218600	-0.06891300	1.04213400
H	0.17853000	2.44119000	1.23281600
H	-0.39869000	0.09314100	1.72779000
C	1.59507700	-1.44363200	1.73390600
H	2.60961200	-1.76406700	1.95778600
H	1.04755800	-1.37879700	2.67542800
H	1.12775200	-2.20454200	1.11193500
C	2.27277200	0.96165700	1.97163800
H	1.68983600	1.08512100	2.88627300
H	3.26117200	0.60541500	2.26076800
H	2.39883000	1.93772300	1.50227300
C	2.40929200	-0.09242000	-0.25613700
O	2.36104900	0.78547400	-1.11118100
O	3.23635700	-1.10552600	-0.34708200
C	4.10830000	-1.16635300	-1.50678100
H	4.74547200	-0.28532200	-1.53629900
H	4.69550600	-2.06778600	-1.36904100
H	3.51067500	-1.22430000	-2.41354100
N	0.20466500	2.21829600	-0.86220500
H	1.14696500	1.75633700	-1.06060400
H	0.27146800	3.23164800	-0.93909200
H	-0.48445700	1.87914300	-1.55125600

(S)-24_H_open-c5			
C	1.88541400	0.62121600	0.67786400
C	2.02612200	-1.89993000	-0.53038200
H	2.44331500	-2.50974100	-1.33328000
H	2.23491200	-2.41568600	0.40634500
S	2.88399800	-0.29450500	-0.61783100
O	0.48430000	0.42605900	0.43780600
C	2.15201300	2.12045400	0.50102100
H	1.65819500	2.61654000	1.34135900
H	3.22394400	2.28140300	0.63841500
C	0.51220400	-1.72101200	-0.69068600
C	-0.04136200	-0.89061100	0.48812300
C	-1.58077700	-0.77854200	0.71940700
H	0.02438400	-2.69402100	-0.72148900
H	0.32073900	-1.41807500	1.37667100
C	-1.79335200	-0.29926100	2.16659000
H	-2.85257200	-0.21869300	2.39777700
H	-1.35235400	-1.01960200	2.85728700
H	-1.33306100	0.67200700	2.33720000
C	-2.26330800	-2.15427300	0.54129900
H	-1.77995300	-2.89859900	1.17690600
H	-3.30742100	-2.09318900	0.84693700
H	-2.24191700	-2.50778200	-0.48999600
C	-2.24413600	0.16903100	-0.28793300
O	-1.99783100	0.17497300	-1.48928800
O	-3.17124100	0.93528700	0.23429100
C	-3.91492200	1.80496900	-0.65985700
H	-4.43520700	1.20904200	-1.40635800
H	-4.61715700	2.32942900	-0.02098000
H	-3.23525900	2.50057100	-1.14656700
C	2.29509700	0.17178500	2.07782200
H	3.32696200	0.46388000	2.26545600
H	1.65720800	0.65977100	2.81730300
H	2.23366200	-0.90545500	2.22642600
C	1.69051900	2.75540300	-0.80804300
H	1.89267500	3.82653900	-0.78414200
H	2.21767400	2.34565800	-1.67043500
H	0.61931200	2.62449500	-0.96027700
N	0.24681100	-1.03713300	-2.00416900
H	0.28874600	-1.68622900	-2.78789000
H	0.98186800	-0.32346000	-2.12677700
H	-0.70324100	-0.55271000	-1.95923000

(S)-24-MeOH-c5			
C	-2.42970200	-0.02925000	0.18954700
C	-0.47487500	-1.58020900	-0.96674300
H	-0.31603400	-1.94705700	0.04693200
H	-0.19640300	-2.37161500	-1.66218200
S	-2.23959200	-1.24219300	-1.23483400
O	-1.15991800	0.52497400	0.52509400
C	-2.87565200	-0.74828900	1.46886200
H	-2.12826400	-1.51065900	1.69824400
H	-2.82005300	-0.01014300	2.27533000
C	0.34178600	-0.30978800	-1.20752000
C	-0.31268600	0.93379800	-0.53937300
C	0.87158000	1.76507500	0.01298000
H	0.42580600	-0.14524400	-2.28714100
H	-0.88230500	1.50767100	-1.27156000
C	0.61427600	2.44876500	1.35428100
H	1.52719200	2.94556400	1.68297600
H	-0.17538900	3.19613800	1.25879900
H	0.31560200	1.73548200	2.11943100
C	1.30794500	2.80640300	-1.03693300
H	0.54231600	3.57774600	-1.14133100
H	2.23835900	3.28228600	-0.72663700
H	1.47217000	2.35494500	-2.01793300
N	1.65320500	-0.36314200	-0.58690700
H	2.31944100	-1.12146900	-0.69815500
C	2.00224600	0.73368900	0.11853200
O	3.06583800	0.89871800	0.70456600
C	4.92522600	-2.31942400	0.85619400
H	5.07214400	-3.29024500	0.38231900
H	4.31514900	-2.46145100	1.75565400
H	5.90488200	-1.93319600	1.15767500
O	4.29559900	-1.47140100	-0.08933300
H	4.12302300	-0.59879500	0.31732400
C	-3.41189300	1.05264000	-0.24884300
H	-4.35164200	0.61237800	-0.58283400
H	-3.61981500	1.72092600	0.58963200
H	-3.01357900	1.63896300	-1.07548300
C	-4.26511500	-1.37779500	1.43463200
H	-4.35773200	-2.09224000	0.61515800
H	-4.45217700	-1.91475800	2.36587000
H	-5.05261600	-0.63015600	1.32729800

Table S20 Cartesian coordinates of the most stable structures in the sulfonium ion path (R^1 = H, R^2 = Ph) calculated at the B3LYP/def2TZVP level.

(S)-22_H_open-c3 (chair)			
S	-1.49336100	2.25385700	-0.57205200
O	-0.05404000	0.13144100	0.30131500
O	2.44773900	-0.67039000	-1.43672100
C	-1.30796100	0.76570000	0.52526700
C	1.08228000	0.88896300	0.68950600
H	0.90187900	1.34180800	1.67358100
C	1.25455000	2.10209800	-0.25414600
H	2.18738300	2.61703000	-0.02914700
C	0.07127400	3.06455100	-0.09199700
H	0.18068600	3.94357000	-0.72905500
H	0.02513200	3.41448000	0.93964900
C	2.26113400	-0.10238200	0.93094600
C	2.47322300	-1.03739400	-0.26638000
C	3.58955800	0.66181900	1.13271800
H	4.37143500	-0.02968700	1.44528500
H	3.47777500	1.40718200	1.92237700
H	3.93368100	1.16110600	0.22634100
C	1.93601700	-0.89276800	2.21158500
H	2.72819500	-1.60027200	2.44321800
H	1.00279800	-1.44428400	2.11358800
H	1.84576800	-0.20241600	3.05175300
C	3.06166800	-3.21124000	-0.99686200
H	2.19712600	-3.31095300	-1.64900000
H	3.27835000	-4.14650500	-0.49225800
H	3.92120600	-2.86580900	-1.56689800
O	2.76600100	-2.26992200	0.06869600
C	-2.43751700	-0.18631900	0.27060400
C	-3.49918000	-0.24256600	1.17239000
C	-2.45414900	-1.00059300	-0.86251100
C	-4.56734200	-1.10122800	0.94452500
H	-3.49322600	0.38522800	2.05556700
C	-3.51868900	-1.86332600	-1.08425500
H	-1.63172100	-0.96888800	-1.56500300
C	-4.57770500	-1.91296200	-0.18326800
H	-5.38708100	-1.13878300	1.64975800
H	-3.52451300	-2.49616800	-1.96215200
H	-5.40786700	-2.58428300	-0.35998900
H	-1.34309600	1.13430200	1.55476900
H	1.75277000	2.35656700	-2.28827400
H	1.83860500	0.72687500	-1.74283900
H	0.34460400	1.51303000	-2.00437000
N	1.31618900	1.65742700	-1.68987500

(S)-22-open-c4 (chair)			
C	-1.13807800	-0.52543500	-0.60214600
C	0.06605900	-2.95922700	-0.89504400
H	0.02667900	-4.03767200	-0.73457200
H	0.23704900	-2.78773700	-1.96126300
S	-1.57901500	-2.31760100	-0.43246100
O	-0.00414500	-0.20832700	0.16716500
C	1.20215300	-2.33515200	-0.05473400
C	1.21291200	-0.81385700	-0.29213200
C	2.37643400	0.01974500	0.30166900
H	2.13702500	-2.72531900	-0.46767000
H	1.26901600	-0.67521600	-1.37762100
C	3.73129600	-0.64535600	-0.02466100
H	4.55078600	0.01840200	0.25535200
H	3.84148500	-1.56771500	0.54527000
H	3.82505200	-0.86793500	-1.08898200
C	2.26265000	0.23925900	1.81735600
H	2.27167000	-0.72344300	2.32254700
H	3.10027500	0.83705600	2.17391700
H	1.34248200	0.76086200	2.07411500
N	1.16742500	-2.68734500	1.36019500
H	1.20147600	-3.69455300	1.47196700
H	0.29188300	-2.37616900	1.76837400
C	2.36987300	1.35163500	-0.47646600
O	2.14126600	1.44952700	-1.65779600
O	2.71368400	2.40422100	0.28308400
C	2.78657700	3.66992100	-0.39219700
H	1.81899100	3.92824000	-0.82045100
H	3.07236400	4.39015400	0.36961000
H	3.53010600	3.63664300	-1.18788800
C	-2.31490800	0.30816600	-0.17660400
C	-3.25241900	0.71420600	-1.12487600
C	-2.49986500	0.66390700	1.15865600
C	-4.36067100	1.46201200	-0.74658600
H	-3.11322800	0.44448800	-2.16516000
C	-3.60479500	1.41714000	1.53569200
H	-1.77133000	0.35709500	1.89626100
C	-4.53905200	1.81609300	0.58589100
H	-5.08045000	1.77292900	-1.49329300
H	-3.73683200	1.69282100	2.57455200
H	-5.39967800	2.40256500	0.88211600
H	-0.91798600	-0.35418000	-1.66170900

TS: (S)-22-open-c4 → (S)-22-MeOH-c1 (img freq -1003 cm^{-1})			
6	1.264171	-1.000148	0.344576
6	-0.555706	-2.602536	-0.871354
1	-0.962356	-3.032964	-1.78763
1	-0.343528	-3.43213	-0.191593
16	0.996722	-1.768713	-1.317267
8	0.175164	-0.194178	0.713228
6	-1.576567	-1.68543	-0.207125
6	-1.051511	-0.848444	0.983815
6	-2.15127	0.213458	1.231199
1	-2.378486	-2.322135	0.178749
1	-0.924875	-1.499871	1.85865
6	-1.642157	1.504876	1.870321
1	-2.474281	2.202338	1.97897
1	-1.235257	1.30231	2.863289
1	-0.876106	1.967347	1.257615
6	-3.254615	-0.392384	2.123486
1	-2.865726	-0.566251	3.128441
1	-4.093155	0.299026	2.186878
1	-3.642063	-1.33823	1.739581
7	-2.188469	-0.677973	-1.086301
1	-2.902562	-1.024659	-1.718511
6	-2.787053	0.464522	-0.158498
8	-3.891492	0.888095	-0.386905
6	-1.992314	2.582663	-1.793388
1	-3.082075	2.627455	-1.649589
1	-1.801706	2.512043	-2.872063
1	-1.562279	3.527029	-1.436735
8	-1.444047	1.494864	-1.103982
1	-1.537902	0.171093	-1.516407
6	2.508446	-0.158366	0.287873
6	2.460136	1.12678	-0.253421
6	3.720067	-0.664331	0.75269
6	3.616451	1.893368	-0.320965
1	1.51525	1.516635	-0.60967
6	4.8765	0.10333	0.678926
1	3.760561	-1.661732	1.175051
6	4.825811	1.384511	0.142328
1	3.57335	2.891786	-0.737776
1	5.813496	-0.297183	1.044841
1	5.724812	1.985563	0.087449
1	1.387286	-1.823717	1.059331

(S)-22-MeOH-c1 (chair)			
C	-1.53823800	-0.22892300	0.86612400
C	0.52997800	0.53364700	2.41673200
H	1.17674000	1.32824900	2.79169300
H	0.14276800	-0.00234100	3.28676900
S	-0.85310200	1.33804500	1.55104400
O	-0.58647000	-0.87247900	0.05040700
C	1.33680700	-0.44190600	1.56528300
C	0.52856300	-1.45414800	0.71297900
C	1.54633300	-1.88070800	-0.37195500
H	1.94323300	-1.02450800	2.27283000
H	0.18552700	-2.29653500	1.32605000
C	0.93193600	-2.31946600	-1.69919800
H	1.73077000	-2.52191200	-2.41273200
H	0.34431900	-3.23005600	-1.56682400
H	0.28363500	-1.55410700	-2.11791300
C	2.47344900	-2.99012400	0.16324700
H	1.91290800	-3.91812600	0.29194600
H	3.27788500	-3.17180400	-0.54963800
H	2.93007000	-2.73294800	1.12074700
N	2.19067700	0.16966200	0.56563400
H	2.74235100	1.01198100	0.69721600
C	2.38898300	-0.60177300	-0.52668800
O	3.14253400	-0.34899500	-1.45795500
C	4.28610700	3.17336800	-1.11634800
H	4.48150800	3.98899100	-0.41990900
H	3.32809500	3.36336700	-1.61313800
H	5.07775500	3.17112800	-1.87329100
O	4.27135500	1.96712500	-0.37015700
H	4.06751400	1.21944500	-0.96590800
C	-2.77323800	0.07571300	0.06433200
C	-2.67347900	0.59714500	-1.22548500
C	-4.03392100	-0.14090700	0.61640200
C	-3.82093100	0.89104700	-1.95066700
H	-1.69634600	0.76653800	-1.65690500
C	-5.18194100	0.15861000	-0.10756500
H	-4.11889300	-0.54633800	1.61788800
C	-5.07724200	0.67434200	-1.39390100
H	-3.73424900	1.29196300	-2.95272300
H	-6.15618900	-0.01541000	0.33148000
H	-5.97018700	0.90504800	-1.96107700
H	-1.79266200	-0.86968000	1.71918100

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