# $n \rightarrow \pi^*$ Interactions Engender Chirality in Carbonyl Groups

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**General Experimental.** Commercial chemicals were of reagent grade or better, and were used without further purification. Anhydrous THF, DMF, and $CH_2Cl_2$ were obtained from CYCLE-TAINER® solvent delivery systems (J. T. Baker, Phillipsburg, NJ). Other anhydrous solvents were obtained in septum-sealed bottles. Reactions were monitored by thin-layer chromatography with visualization by UV light or staining with $KMnO_4$, or $I_2$. In all reactions involving anhydrous solvents, glassware was either oven- or flame-dried. Flash chromatography was performed with columns of silica gel 60, 230–400 mesh (Silicycle, Québec City, Canada). The removal of solvents and other volatile materials "under reduced pressure" refers to the use of a rotary evaporator at water-aspirator pressure (<20 torr) and a water bath of <45 °C. All reported yields are unoptimized.

**Instrumentation.** NMR spectra were acquired at ambient temperature with a Bruker DMX-400 Avance spectrometer ($^1$H, 400 MHz; $^{13}$C, 100.6 MHz) at the National Magnetic Resonance Facility at Madison (NMRFAM). Carbon-13 spectra were proton-decoupled. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) at the Mass Spectrometry Facility in the Department of Chemistry, UW-Madison. X-Ray data were collected in the Molecular Structure Laboratory of the Department of Chemistry at the University of Wisconsin–Madison.

*N*-Acetyl–(2*S*,4*R*)-4-acetoxyproline methyl ester, *N*-acetyl–(2*S*,4*S*)-4-acetoxyproline methyl ester, *N*-acetyl–(2*S*,4*R*)-4-methoxyproline methyl ester, and *N*-acetyl–(2*S*,4*S*)-4-acetoxyproline methyl ester were synthesized using previously reported procedures.[1] Deprotection of acetoxy group of **5*R*** and **5*S*** to generate **2*R*** and **2*S***, respectively, was carried out following procedure reported previously.[2]

**Typical Procedure for synthesis of thioamides (4*R*, 4*S*, 5*R*, and 5*S*):** A solution of the required amide (2.9 mmol) and the Lawesson's reagent (0.74 g, 1.83 mmol) in anhydrous toluene (20 mL) was refluxed for 30 min. The reaction mixture was filtered, evaporated, and chromatographed using hexane/EtOAc to afford the desired thioamide as a white solid.

***N*-Thioacetyl–(2*S*,4*R*)-4-hydroxyproline methyl ester (2*R*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz, 6.7:1 mixture of two rotamers): $\delta$ 5.08–4.98 (m, 0.86H), 4.80–4.73 (m, 0.15H), 4.73–4.56 (m, 1H), 4.04–3.88 (m, 1H), 3.82–3.68 (m, 4H) 2.64 and 2.53 (s, 3H), 2.42–2.20 (m, 2H), 2.08–1.82 (brs, 1H).
**$^{13}$C NMR** ($CDCl_3$, 100.6 MHz, 6.7:1 mixture of two rotamers): $\delta$ 199.6, 199.2, 171.4, 171.0, 69.8, 68.2, 63.9, 61.9, 59.4, 53.2, 52.7, 40.1, 38.2, 33.0, 32.1.
**ESI–MS**: $[M + H]^+$ calcd 204.0689 ; found 204.0690 (< 1 ppm).

***N*-Thioacetyl–(2*S*,4*S*)-4-hydroxyproline methyl ester (2*S*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz, 4.3:1 mixture of two rotamers): $\delta$ 5.06–4.98 and 4.74–4.66 (m, 1H), 4.60–4.50 (m, 1H), 4.10–4.04 (m, 0.31H), 4.00–3.78 (m, 4.60H), 3.66 and 3.64 (s, 1H), 2.65 and 2.60 (s, 3H), 2.54–2.40 (m, 1H), 2.62–2.18 (m, 1H), 1.25 (brs, 1H).
**$^{13}$C NMR** ($CDCl_3$, 100.6 MHz, 4.3:1 mixture of two rotamers): $\delta$ 200.0, 199.7, 173.5, 171.5, 71.8, 69.2, 64.2, 63.0, 62.0, 60.7, 53.3, 53.1, 39.9, 37.5, 33.0, 32.8.
**ESI–MS**: $[M + Na]^+$ calcd 226.0509 ; found 226.0516 (3.1 ppm).

***N*-Thioacetyl–(2*S*,4*R*)-4-methoxyproline methyl ester (4*R*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 5.02–4.98 (m, 1H), 4.22–4.12 (m, 1H), 3.98–3.88 (m, 1H), 3.84–3.70 (m, 4H), 3.35 (s, 3H), 2.63 and 2.52 (s, 3H), 2.50–2.15 (m, 2H).

**$^{13}$C NMR** ($CDCl_3$, 6.0:1 mixture of two rotamers): $\delta$ 199.5, 199.0, 171.1, 171.0, 78.5, 63.8, 61.8, 58.4, 57.2, 57.0, 56.5, 53.1, 52.6, 37.6, 34.8, 33.0, 32.2.
**ESI–MS**: $[M + Na]^+$ calcd 240.0665 ; found 240.0668 (1.2 ppm).

***N*-Thioacetyl–(2*S*,4*S*)-4-methoxyproline methyl ester (4*S*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz, 1.4:1 mixture of two rotamers): $\delta$ 5.26–5.19 (m, 0.54H), 4.70–4.66 (m, 0.40H), 4.16–3.70 (m, 6H), 3.36–3.22 (m, 3H), 2.80–2.22 (m, 5H).
**$^{13}$C NMR** ($CDCl_3$, 100.6 MHz, 1.4:1 mixture of two rotamers): $\delta$ 199.2, 170.0, 79.1, 63.4, 61.8, 59.1, 56.7, 56.6, 56.2, 52.9, 52.4, 36.3, 34.3, 32.9, 32.6.
**ESI–MS**: $[M + Na]^+$ calcd 240.0665 ; found 240.0667 (< 1 ppm).

***N*-Thioacetyl–(2*S*,4*R*)-4-acetoxyproline methyl ester (5*R*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 5.43–5.35 (m, 1H), 5.04–4.96 (m, 1H), 4.12–4.02 (m, 1H), 3.88–3.72 (m, 4H), 2.68–2.30 (m, 5H), 2.09 and 2.07 (s, 3H).
**$^{13}$C NMR** ($CDCl_3$, 100.6 MHz): $\delta$ 199.4, 170.7, 170.4, 72.4, 63.6, 56.7, 52.7, 35.3, 33.1, 21.1.
**ESI–MS**: $[M + Na]^+$ calcd 268.0614 ; found 268.0609 (1.9 ppm).

***N*-Thioacetyl–(2*S*,4*S*)-4-acetoxyproline methyl ester (5*S*)**
**$^1$H NMR** ($CDCl_3$, 400 MHz, 2.0:1 mixture of two rotamers): $\delta$ 5.43–5.33 (m, 1H), 5.31–5.24 (m, 0.68H), 4.77–4.70 (m, 0.35H), 4.22–3.72 (m, 5H), 2.72–2.34 (m, 5H), 2.05 and 1.99 (s, 3H).
**$^{13}$C NMR** ($CDCl_3$, 100.6 MHz, 2.0:1 mixture of two rotamers): $\delta$ 199.6, 199.5, 170.2, 169.9, 169.8, 169.7, 72.9, 71.3, 63.5, 61.8, 59.5, 56.7, 53.0, 52.4, 37.3, 35.0, 32.9, 32.7, 20.9.
**ESI–MS**: $[M + Na]^+$ calcd 268.0615 ; found 268.0613 (<1 ppm).

**Crystal structure determination of 2*R*, 2*S*, 4*R*, 4*S*, 5*R*, and 5*S*.** Each compound was dissolved in hexane with minimal amount of EtOAc. Slow evaporation afforded crystals suitable for X-ray analysis after ~4 d. X-ray intensity data were collected on a Bruker CCD-1000 diffractometer with Mo $K_\alpha$ ($\lambda$ = 0.71073 Å) radiation at 105(2) K with the diffractometer to crystal distance of 4.9 cm. Preliminary indexing was carried out for determination of cell constants. This consisted three series of ω scans at different initial angles with each series consisting of 20 frames at intervals of 0.3° with the exposure time of 10 s per frame. The reflections were indexed by an automated indexing routine built in the SMART program. The data were collected by using the full-sphere data collection routine to a resolution of 0.80 Å. The intensity data was then corrected for absorption and Lorentz and polarization effects. Structure solution and refinement was carried out using SHELXTL V.6.10.[3]

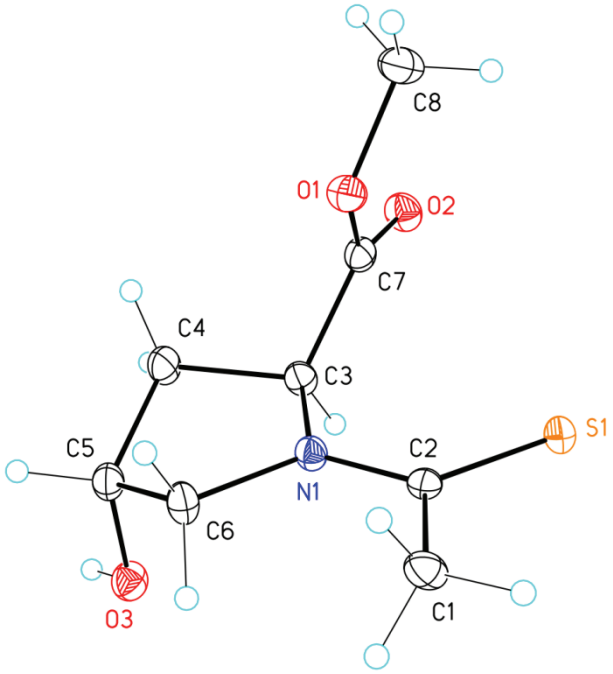


**Figure S1.** Molecular drawing of **2*R*** drawn at 50% probability ellipsoids.

**Table S1.** Crystal data and structure refinement for **2*R***.

| | | |
|---|---|---|
| Identification code | raines17 | |
| Empirical formula | $C_8H_{13}NO_3S$ | |
| Formula weight | 203.25 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | $a$ = 6.4374(4) Å | $\alpha$ = 90° |
| | $b$ = 11.8996(7) Å | $\beta$ = 90° |
| | $c$ = 12.6886(7) Å | $\gamma$ = 90° |
| Volume | 971.98(10) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.389 mg/m$^3$ | |
| Absorption coefficient | 0.308 mm$^{-1}$ | |
| $F_{000}$ | 432 | |
| Crystal size | 0.44 × 0.33 × 0.33 mm$^3$ | |
| Theta range for data collection | 2.35–30.03° | |
| Index ranges | $-9 \le h \le 8$, $-16 \le k \le 16$, $-17 \le l \le 17$ | |
| Reflections collected | 14496 | |
| Independent reflections | 2773 [$R_{int}$ = 0.0237] | |
| Completeness to theta = 30.03° | 99.0% | |
| Absorption correction | Empirical with SADABS | |
| Max. and min. transmission | 0.9051 and 0.8763 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2773 / 0 / 122 | |
| Goodness-of-fit on $F^2$ | 1.047 | |
| Final $R$ indices [$I > 2\sigma_I$] | $R1$ = 0.0233, $wR2$ = 0.0641 | |
| $R$ indices (all data) | $R1$ = 0.0237, $wR2$ = 0.0645 | |
| Absolute structure parameter | –0.01(5) | |
| Largest diff. peak and hole | 0.343 and –0.171 e.Å$^{-3}$ | |

**Table S2.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2*R***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S(1) | 7375(1) | 4056(1) | 6258(1) | 16(1) |
| O(1) | 7760(1) | 2846(1) | 8667(1) | 17(1) |
| O(3) | 7740(1) | -267(1) | 5888(1) | 19(1) |
| O(2) | 4336(1) | 2779(1) | 8287(1) | 19(1) |
| N(1) | 8733(1) | 2023(1) | 6702(1) | 13(1) |
| C(2) | 9145(2) | 3021(1) | 6281(1) | 13(1) |
| C(3) | 6734(2) | 1750(1) | 7199(1) | 14(1) |
| C(6) | 10124(2) | 1032(1) | 6663(1) | 16(1) |
| C(4) | 7082(2) | 551(1) | 7627(1) | 18(1) |
| C(8) | 7319(2) | 3579(1) | 9554(1) | 21(1) |
| C(5) | 8672(2) | 51(1) | 6864(1) | 16(1) |
| C(7) | 6130(2) | 2541(1) | 8088(1) | 15(1) |
| C(1) | 11283(2) | 3179(1) | 5831(1) | 17(1) |

**Table S3.** Bond lengths [Å] and angles [°] for **2*R***.

| | |
|---|---|
| S(1)-C(2) | 1.6777(9) |
| O(1)-C(7) | 1.3311(12) |
| O(1)-C(8) | 1.4521(12) |
| O(3)-C(5) | 1.4275(12) |
| O(3)-H(3) | 0.8400 |
| O(2)-C(7) | 1.2155(12) |
| N(1)-C(2) | 1.3289(12) |
| N(1)-C(3) | 1.4696(12) |
| N(1)-C(6) | 1.4815(12) |
| C(2)-C(1) | 1.5019(13) |
| C(3)-C(7) | 1.5198(13) |
| C(3)-C(4) | 1.5427(13) |
| C(3)-H(3A) | 1.0000 |
| C(6)-C(5) | 1.5178(14) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(4)-C(5) | 1.5289(14) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(5)-H(5) | 1.0000 |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| | |
| C(7)-O(1)-C(8) | 115.94(8) |
| C(5)-O(3)-H(3) | 109.5 |
| C(2)-N(1)-C(3) | 123.05(8) |
| C(2)-N(1)-C(6) | 125.24(8) |
| C(3)-N(1)-C(6) | 111.55(7) |

| | |
|---|---|
| N(1)-C(2)-C(1) | 116.60(8) |
| N(1)-C(2)-S(1) | 121.81(7) |
| C(1)-C(2)-S(1) | 121.60(7) |
| N(1)-C(3)-C(7) | 113.89(8) |
| N(1)-C(3)-C(4) | 103.21(8) |
| C(7)-C(3)-C(4) | 110.44(8) |
| N(1)-C(3)-H(3A) | 109.7 |
| C(7)-C(3)-H(3A) | 109.7 |
| C(4)-C(3)-H(3A) | 109.7 |
| N(1)-C(6)-C(5) | 103.58(7) |
| N(1)-C(6)-H(6A) | 111.0 |
| C(5)-C(6)-H(6A) | 111.0 |
| N(1)-C(6)-H(6B) | 111.0 |
| C(5)-C(6)-H(6B) | 111.0 |
| H(6A)-C(6)-H(6B) | 109.0 |
| C(5)-C(4)-C(3) | 103.58(7) |
| C(5)-C(4)-H(4A) | 111.0 |
| C(3)-C(4)-H(4A) | 111.0 |
| C(5)-C(4)-H(4B) | 111.0 |
| C(3)-C(4)-H(4B) | 111.0 |
| H(4A)-C(4)-H(4B) | 109.0 |
| O(1)-C(8)-H(8A) | 109.5 |
| O(1)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| O(1)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| O(3)-C(5)-C(6) | 108.46(8) |
| O(3)-C(5)-C(4) | 111.76(9) |
| C(6)-C(5)-C(4) | 102.66(8) |
| O(3)-C(5)-H(5) | 111.2 |
| C(6)-C(5)-H(5) | 111.2 |
| C(4)-C(5)-H(5) | 111.2 |
| O(2)-C(7)-O(1) | 124.80(9) |
| O(2)-C(7)-C(3) | 122.78(9) |
| O(1)-C(7)-C(3) | 112.14(8) |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |

**Table S4.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2*R***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 19(1) | 12(1) | 16(1) | 1(1) | 0(1) | 2(1) |
| O(1) | 17(1) | 18(1) | 16(1) | -2(1) | 0(1) | 1(1) |
| O(3) | 21(1) | 16(1) | 20(1) | 0(1) | -2(1) | -2(1) |
| O(2) | 16(1) | 19(1) | 22(1) | 0(1) | 4(1) | 2(1) |
| N(1) | 12(1) | 12(1) | 15(1) | 1(1) | 2(1) | 1(1) |
| C(2) | 15(1) | 13(1) | 11(1) | -1(1) | 0(1) | 0(1) |
| C(3) | 13(1) | 13(1) | 16(1) | 0(1) | 3(1) | 0(1) |
| C(6) | 14(1) | 13(1) | 21(1) | 2(1) | 1(1) | 2(1) |
| C(4) | 22(1) | 13(1) | 20(1) | 3(1) | 6(1) | 0(1) |
| C(8) | 25(1) | 22(1) | 17(1) | -4(1) | 1(1) | -1(1) |
| C(5) | 17(1) | 13(1) | 17(1) | 2(1) | 0(1) | 1(1) |
| C(7) | 17(1) | 13(1) | 15(1) | 2(1) | 2(1) | 0(1) |
| C(1) | 18(1) | 16(1) | 19(1) | -2(1) | 6(1) | -3(1) |

**Table S5.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2*R***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(3) | 6946 | -817 | 5987 | 28 |
| H(3A) | 5614 | 1740 | 6653 | 17 |
| H(6A) | 11211 | 1079 | 7213 | 19 |
| H(6B) | 10798 | 966 | 5965 | 19 |
| H(4A) | 7634 | 570 | 8355 | 22 |
| H(4B) | 5774 | 114 | 7620 | 22 |
| H(8A) | 6613 | 4258 | 9303 | 32 |
| H(8B) | 8623 | 3788 | 9901 | 32 |
| H(8C) | 6423 | 3185 | 10058 | 32 |
| H(5) | 9428 | -595 | 7192 | 19 |
| H(1A) | 12317 | 3100 | 6393 | 26 |
| H(1B) | 11392 | 3930 | 5519 | 26 |
| H(1C) | 11536 | 2610 | 5287 | 26 |

**Table S6.** Torsion angles [°] for **2*R***.

| | |
|---|---|
| C(3)-N(1)-C(2)-C(1) | 178.29(8) |
| C(6)-N(1)-C(2)-C(1) | -6.68(13) |
| C(3)-N(1)-C(2)-S(1) | -1.35(12) |
| C(6)-N(1)-C(2)-S(1) | 173.68(7) |
| C(2)-N(1)-C(3)-C(7) | -56.32(11) |
| C(6)-N(1)-C(3)-C(7) | 128.04(9) |
| C(2)-N(1)-C(3)-C(4) | -176.08(9) |
| C(6)-N(1)-C(3)-C(4) | 8.28(9) |
| C(2)-N(1)-C(6)-C(5) | -159.35(9) |
| C(3)-N(1)-C(6)-C(5) | 16.18(10) |
| N(1)-C(3)-C(4)-C(5) | -29.32(9) |
| C(7)-C(3)-C(4)-C(5) | -151.42(9) |
| N(1)-C(6)-C(5)-O(3) | 84.50(9) |
| N(1)-C(6)-C(5)-C(4) | -33.89(9) |
| C(3)-C(4)-C(5)-O(3) | -76.67(9) |
| C(3)-C(4)-C(5)-C(6) | 39.38(10) |
| C(8)-O(1)-C(7)-O(2) | -4.36(14) |
| C(8)-O(1)-C(7)-C(3) | -178.33(8) |
| N(1)-C(3)-C(7)-O(2) | 147.77(9) |
| C(4)-C(3)-C(7)-O(2) | -96.64(11) |
| N(1)-C(3)-C(7)-O(1) | -38.11(11) |
| C(4)-C(3)-C(7)-O(1) | 77.48(10) |

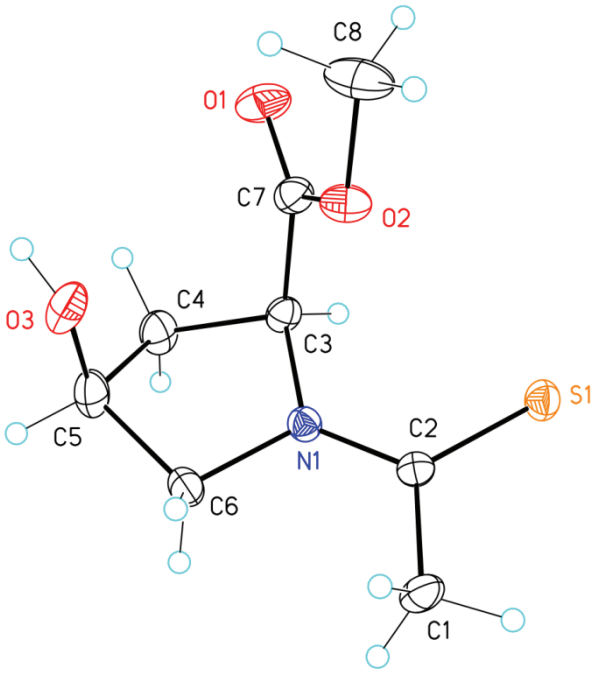


**Figure S2.** Molecular drawing of **2*S*** drawn at 50% probability ellipsoids.

**Table S7.** Crystal data and structure refinement for **2*S***.

| | | |
|---|---|---|
| Identification code | raines18 | |
| Empirical formula | $C_8H_{13}NO_3S$ | |
| Formula weight | 203.25 | |
| Temperature | 105(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | $a$ = 7.9045(5) Å | $\alpha$ = 90° |
| | $b$ = 10.8117(7) Å | $\beta$ = 90° |
| | $c$ = 11.4208(8) Å | $\gamma$ = 90° |
| Volume | 976.03(11) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.383 mg/m$^3$ | |
| Absorption coefficient | 0.307 mm$^{-1}$ | |
| $F_{000}$ | 432 | |
| Crystal size | 0.41 × 0.38 × 0.28 mm$^3$ | |
| Theta range for data collection | 2.59–29.16° | |
| Index ranges | $-10 \le h \le 10$, $-14 \le k \le 14$, $-15 \le l \le 15$ | |
| Reflections collected | 14299 | |
| Independent reflections | 2637 [$R_{int}$ = 0.0328] | |
| Completeness to theta = 29.16° | 100.0% | |
| Absorption correction | Empirical with SADABS | |
| Max. and min. transmission | 0.9190 and 0.8844 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2637 / 0 / 122 | |
| Goodness-of-fit on $F^2$ | 1.054 | |
| Final $R$ indices [$I > 2\sigma_I$] | $R1$ = 0.0307, $wR2$ = 0.0761 | |
| $R$ indices (all data) | $R1$ = 0.0352, $wR2$ = 0.0797 | |
| Absolute structure parameter | –0.03(6) | |
| Largest diff. peak and hole | 0.352 and –0.183 e.Å$^{-3}$ | |

**Table S8.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2*S***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S(1) | 350(1) | 4610(1) | 6890(1) | 19(1) |
| O(1) | 5653(2) | 5413(1) | 5620(1) | 29(1) |
| N(1) | 3203(2) | 4167(1) | 8019(1) | 15(1) |
| O(2) | 4078(2) | 3696(1) | 5812(1) | 22(1) |
| O(3) | 6797(1) | 3425(1) | 7783(1) | 27(1) |
| C(7) | 4708(2) | 4767(1) | 6179(1) | 19(1) |
| C(4) | 5583(2) | 5444(1) | 8198(1) | 23(1) |
| C(3) | 4084(2) | 5157(1) | 7386(1) | 16(1) |
| C(6) | 4313(2) | 3604(1) | 8918(1) | 19(1) |
| C(1) | 935(2) | 2822(1) | 8588(1) | 21(1) |
| C(2) | 1597(2) | 3867(1) | 7853(1) | 15(1) |
| C(8) | 4652(3) | 3292(2) | 4674(1) | 33(1) |
| C(5) | 6034(2) | 4167(1) | 8671(2) | 23(1) |

**Table S9.** Bond lengths [Å] and angles [°] for **2*S***.

| | |
|---|---|
| S(1)-C(2) | 1.6811(14) |
| O(1)-C(7) | 1.2053(18) |
| N(1)-C(2) | 1.3236(18) |
| N(1)-C(3) | 1.4679(17) |
| N(1)-C(6) | 1.4821(18) |
| O(2)-C(7) | 1.3281(18) |
| O(2)-C(8) | 1.4442(18) |
| O(3)-C(5) | 1.427(2) |
| O(3)-H(3) | 0.8400 |
| C(7)-C(3) | 1.524(2) |
| C(4)-C(5) | 1.525(2) |
| C(4)-C(3) | 1.535(2) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(3)-H(3A) | 1.0000 |
| C(6)-C(5) | 1.517(2) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(1)-C(2) | 1.5019(19) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(5)-H(5) | 1.0000 |
| | |
| C(2)-N(1)-C(3) | 124.30(11) |
| C(2)-N(1)-C(6) | 124.51(11) |
| C(3)-N(1)-C(6) | 111.08(11) |
| C(7)-O(2)-C(8) | 115.47(13) |
| C(5)-O(3)-H(3) | 109.5 |

| | |
|---|---|
| O(1)-C(7)-O(2) | 124.76(13) |
| O(1)-C(7)-C(3) | 121.31(13) |
| O(2)-C(7)-C(3) | 113.91(12) |
| C(5)-C(4)-C(3) | 102.24(11) |
| C(5)-C(4)-H(4A) | 111.3 |
| C(3)-C(4)-H(4A) | 111.3 |
| C(5)-C(4)-H(4B) | 111.3 |
| C(3)-C(4)-H(4B) | 111.3 |
| H(4A)-C(4)-H(4B) | 109.2 |
| N(1)-C(3)-C(7) | 113.39(11) |
| N(1)-C(3)-C(4) | 102.50(11) |
| C(7)-C(3)-C(4) | 110.61(12) |
| N(1)-C(3)-H(3A) | 110.0 |
| C(7)-C(3)-H(3A) | 110.0 |
| C(4)-C(3)-H(3A) | 110.0 |
| N(1)-C(6)-C(5) | 103.73(11) |
| N(1)-C(6)-H(6A) | 111.0 |
| C(5)-C(6)-H(6A) | 111.0 |
| N(1)-C(6)-H(6B) | 111.0 |
| C(5)-C(6)-H(6B) | 111.0 |
| H(6A)-C(6)-H(6B) | 109.0 |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| N(1)-C(2)-C(1) | 115.99(12) |
| N(1)-C(2)-S(1) | 122.58(10) |
| C(1)-C(2)-S(1) | 121.43(11) |
| O(2)-C(8)-H(8A) | 109.5 |
| O(2)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| O(2)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| O(3)-C(5)-C(6) | 106.57(12) |
| O(3)-C(5)-C(4) | 110.84(13) |
| C(6)-C(5)-C(4) | 102.70(12) |
| O(3)-C(5)-H(5) | 112.1 |
| C(6)-C(5)-H(5) | 112.1 |
| C(4)-C(5)-H(5) | 112.1 |

**Table S10.** Anisotropic displacement parameters (Å$^2$ × 10$^3$) for **2*S***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 16(1) | 20(1) | 22(1) | 2(1) | -2(1) | 1(1) |
| O(1) | 32(1) | 25(1) | 30(1) | 7(1) | 11(1) | -4(1) |
| N(1) | 15(1) | 15(1) | 15(1) | 1(1) | -1(1) | 0(1) |
| O(2) | 28(1) | 19(1) | 18(1) | -1(1) | 5(1) | 0(1) |
| O(3) | 15(1) | 28(1) | 37(1) | 1(1) | 1(1) | 0(1) |
| C(7) | 18(1) | 18(1) | 20(1) | 4(1) | 2(1) | 2(1) |
| C(4) | 21(1) | 20(1) | 27(1) | 1(1) | -4(1) | -5(1) |
| C(3) | 16(1) | 14(1) | 20(1) | 1(1) | 1(1) | -2(1) |
| C(6) | 19(1) | 21(1) | 17(1) | 3(1) | -4(1) | 0(1) |
| C(1) | 18(1) | 18(1) | 26(1) | 6(1) | 5(1) | -1(1) |
| C(2) | 16(1) | 14(1) | 15(1) | -1(1) | 2(1) | 1(1) |
| C(8) | 51(1) | 28(1) | 19(1) | -1(1) | 11(1) | 7(1) |
| C(5) | 19(1) | 24(1) | 27(1) | 1(1) | -7(1) | -2(1) |

**Table S11.** Hydrogen coordinates (×10$^4$) and isotropic displacement parameters (Å$^2$ × 10$^3$) for **2*S***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(3) | 7698 | 3761 | 7558 | 40 |
| H(4A) | 6539 | 5810 | 7758 | 27 |
| H(4B) | 5248 | 6013 | 8836 | 27 |
| H(3A) | 3335 | 5899 | 7317 | 20 |
| H(6A) | 4346 | 2692 | 8836 | 23 |
| H(6B) | 3922 | 3815 | 9717 | 23 |
| H(1A) | 1609 | 2077 | 8442 | 31 |
| H(1B) | -249 | 2661 | 8385 | 31 |
| H(1C) | 1014 | 3045 | 9418 | 31 |
| H(8A) | 4471 | 3955 | 4102 | 49 |
| H(8B) | 4013 | 2557 | 4436 | 49 |
| H(8C) | 5859 | 3091 | 4712 | 49 |
| H(5) | 6750 | 4217 | 9392 | 28 |

**Table S12.** Torsion angles [°] for **2*S***.

| | |
|---|---|
| C(8)-O(2)-C(7)-O(1) | 2.4(2) |
| C(8)-O(2)-C(7)-C(3) | -179.58(13) |
| C(2)-N(1)-C(3)-C(7) | -81.63(16) |
| C(6)-N(1)-C(3)-C(7) | 102.04(13) |
| C(2)-N(1)-C(3)-C(4) | 159.12(13) |
| C(6)-N(1)-C(3)-C(4) | -17.21(14) |
| O(1)-C(7)-C(3)-N(1) | -169.54(14) |
| O(2)-C(7)-C(3)-N(1) | 12.32(17) |
| O(1)-C(7)-C(3)-C(4) | -55.05(18) |
| O(2)-C(7)-C(3)-C(4) | 126.81(13) |
| C(5)-C(4)-C(3)-N(1) | 36.20(14) |
| C(5)-C(4)-C(3)-C(7) | -84.98(13) |
| C(2)-N(1)-C(6)-C(5) | 174.82(13) |
| C(3)-N(1)-C(6)-C(5) | -8.86(15) |
| C(3)-N(1)-C(2)-C(1) | 179.88(12) |
| C(6)-N(1)-C(2)-C(1) | -4.28(19) |
| C(3)-N(1)-C(2)-S(1) | -0.68(18) |
| C(6)-N(1)-C(2)-S(1) | 175.17(10) |
| N(1)-C(6)-C(5)-O(3) | -85.14(13) |
| N(1)-C(6)-C(5)-C(4) | 31.45(14) |
| C(3)-C(4)-C(5)-O(3) | 71.37(15) |
| C(3)-C(4)-C(5)-C(6) | -42.12(14) |

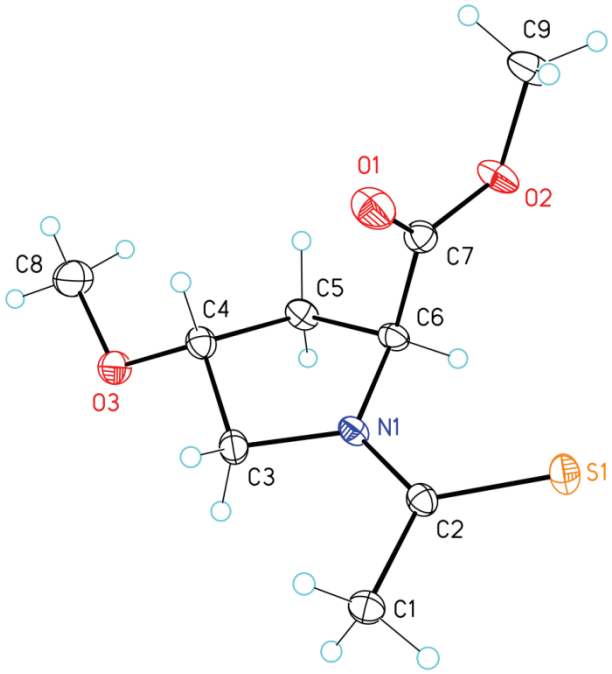


**Figure S3.** Molecular drawing of **4*R*** drawn at 50% probability ellipsoids.

**Table S13.** Crystal data and structure refinement for **4*R***.

| | | |
|---|---|---|
| Identification code | raines20 | |
| Empirical formula | $C_9H_{15}NO_3S$ | |
| Formula weight | 217.28 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1$ | |
| Unit cell dimensions | $a$ = 6.3034(9) Å | $\alpha$ = 90° |
| | $b$ = 6.8102(9) Å | $\beta$ = 99.245(2)° |
| | $c$ = 12.5634(17) Å | $\gamma$ = 90° |
| Volume | 532.31(13) Å$^3$ | |
| $Z$ | 2 | |
| Density (calculated) | 1.356 mg/m$^3$ | |
| Absorption coefficient | 0.286 mm$^{-1}$ | |
| $F_{000}$ | 232 | |
| Crystal size | 0.42 × 0.39 × 0.07 mm$^3$ | |
| Theta range for data collection | 3.27 to 30.01° | |
| Index ranges | $-8 \le h \le 8$, $-9 \le k \le 9$, $-17 \le l \le 17$ | |
| Reflections collected | 7824 | |
| Independent reflections | 2923 [$R_{int}$ = 0.0247] | |
| Completeness to theta = 30.01° | 97.6% | |
| Absorption correction | Empirical with SADABS | |
| Max. and min. transmission | 0.9802 and 0.8892 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2923 / 1 / 131 | |
| Goodness-of-fit on $F^2$ | 1.069 | |
| Final $R$ indices [$I > 2\sigma_I$] | $R1$ = 0.0350, $wR2$ = 0.0817 | |
| $R$ indices (all data) | $R1$ = 0.0422, $wR2$ = 0.0862 | |
| Absolute structure parameter | –0.14(6) | |
| Largest diff. peak and hole | 0.388 and –0.204 e.Å$^{-3}$ | |

**Table S14.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4*R***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S(1) | -1208(1) | 9673(1) | 6124(1) | 18(1) |
| C(4) | 4063(2) | 4608(3) | 7543(1) | 16(1) |
| C(1) | 2754(2) | 9597(3) | 5434(1) | 18(1) |
| N(1) | 1884(2) | 7095(2) | 6646(1) | 14(1) |
| C(6) | 529(3) | 5997(2) | 7278(1) | 14(1) |
| C(3) | 3996(3) | 6167(3) | 6665(1) | 17(1) |
| C(2) | 1217(2) | 8701(2) | 6092(1) | 14(1) |
| C(5) | 1691(3) | 4032(2) | 7474(1) | 16(1) |
| O(2) | -1482(2) | 6614(2) | 8658(1) | 21(1) |
| O(3) | 5442(2) | 3081(2) | 7315(1) | 21(1) |
| O(1) | 1761(2) | 8060(2) | 8826(1) | 25(1) |
| C(7) | 381(3) | 7055(2) | 8327(1) | 16(1) |
| C(9) | -1796(3) | 7406(3) | 9689(2) | 25(1) |
| C(8) | 5865(3) | 1705(3) | 8175(2) | 28(1) |

**Table S15.** Bond lengths [Å] and angles [°] for **4*R***.

| | |
|---|---|
| S(1)-C(2) | 1.6725(16) |
| C(4)-O(3) | 1.414(2) |
| C(4)-C(3) | 1.527(2) |
| C(4)-C(5) | 1.535(2) |
| C(4)-H(4) | 1.0000 |
| C(1)-C(2) | 1.501(2) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| N(1)-C(2) | 1.328(2) |
| N(1)-C(6) | 1.4619(19) |
| N(1)-C(3) | 1.470(2) |
| C(6)-C(7) | 1.519(2) |
| C(6)-C(5) | 1.526(2) |
| C(6)-H(6) | 1.0000 |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| O(2)-C(7) | 1.341(2) |
| O(2)-C(9) | 1.446(2) |
| O(3)-C(8) | 1.423(2) |
| O(1)-C(7) | 1.201(2) |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| | |
| O(3)-C(4)-C(3) | 108.17(12) |

| | |
|---|---|
| O(3)-C(4)-C(5) | 115.16(15) |
| C(3)-C(4)-C(5) | 102.92(13) |
| O(3)-C(4)-H(4) | 110.1 |
| C(3)-C(4)-H(4) | 110.1 |
| C(5)-C(4)-H(4) | 110.1 |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| C(2)-N(1)-C(6) | 122.86(14) |
| C(2)-N(1)-C(3) | 124.91(13) |
| C(6)-N(1)-C(3) | 112.18(12) |
| N(1)-C(6)-C(7) | 110.57(13) |
| N(1)-C(6)-C(5) | 103.26(12) |
| C(7)-C(6)-C(5) | 111.76(13) |
| N(1)-C(6)-H(6) | 110.4 |
| C(7)-C(6)-H(6) | 110.4 |
| C(5)-C(6)-H(6) | 110.4 |
| N(1)-C(3)-C(4) | 103.34(12) |
| N(1)-C(3)-H(3A) | 111.1 |
| C(4)-C(3)-H(3A) | 111.1 |
| N(1)-C(3)-H(3B) | 111.1 |
| C(4)-C(3)-H(3B) | 111.1 |
| H(3A)-C(3)-H(3B) | 109.1 |
| N(1)-C(2)-C(1) | 116.46(14) |
| N(1)-C(2)-S(1) | 121.83(12) |
| C(1)-C(2)-S(1) | 121.71(13) |
| C(6)-C(5)-C(4) | 102.86(13) |
| C(6)-C(5)-H(5A) | 111.2 |
| C(4)-C(5)-H(5A) | 111.2 |
| C(6)-C(5)-H(5B) | 111.2 |
| C(4)-C(5)-H(5B) | 111.2 |
| H(5A)-C(5)-H(5B) | 109.1 |
| C(7)-O(2)-C(9) | 116.53(14) |
| C(4)-O(3)-C(8) | 112.13(13) |
| O(1)-C(7)-O(2) | 124.24(16) |
| O(1)-C(7)-C(6) | 125.67(16) |
| O(2)-C(7)-C(6) | 109.98(14) |
| O(2)-C(9)-H(9A) | 109.5 |
| O(2)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| O(2)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| O(3)-C(8)-H(8A) | 109.5 |
| O(3)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| O(3)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |

**Table S16.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4*R***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 14(1) | 17(1) | 24(1) | 1(1) | 4(1) | 2(1) |
| C(4) | 16(1) | 15(1) | 17(1) | -2(1) | 4(1) | 2(1) |
| C(1) | 17(1) | 18(1) | 19(1) | 4(1) | 5(1) | -1(1) |
| N(1) | 13(1) | 15(1) | 14(1) | 0(1) | 5(1) | -1(1) |
| C(6) | 13(1) | 17(1) | 13(1) | 0(1) | 5(1) | -3(1) |
| C(3) | 13(1) | 18(1) | 21(1) | 4(1) | 4(1) | 2(1) |
| C(2) | 13(1) | 16(1) | 14(1) | -2(1) | 3(1) | -1(1) |
| C(5) | 19(1) | 14(1) | 18(1) | -1(1) | 7(1) | -1(1) |
| O(2) | 21(1) | 25(1) | 19(1) | -4(1) | 12(1) | -5(1) |
| O(3) | 23(1) | 20(1) | 20(1) | 3(1) | 6(1) | 8(1) |
| O(1) | 22(1) | 31(1) | 22(1) | -10(1) | 5(1) | -6(1) |
| C(7) | 16(1) | 15(1) | 16(1) | 1(1) | 4(1) | 0(1) |
| C(9) | 32(1) | 26(1) | 20(1) | -3(1) | 15(1) | 0(1) |
| C(8) | 35(1) | 25(1) | 24(1) | 4(1) | 8(1) | 13(1) |

**Table S17.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **4*R***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(4) | 4610 | 5193 | 8265 | 19 |
| H(1A) | 4081 | 9972 | 5909 | 27 |
| H(1B) | 2098 | 10765 | 5060 | 27 |
| H(1C) | 3088 | 8641 | 4902 | 27 |
| H(6) | -937 | 5801 | 6851 | 17 |
| H(3A) | 5172 | 7133 | 6850 | 21 |
| H(3B) | 4111 | 5563 | 5960 | 21 |
| H(5A) | 1242 | 3110 | 6870 | 20 |
| H(5B) | 1418 | 3422 | 8154 | 20 |
| H(9A) | -864 | 6712 | 10268 | 38 |
| H(9B) | -3301 | 7235 | 9779 | 38 |
| H(9C) | -1436 | 8807 | 9719 | 38 |
| H(8A) | 6457 | 2394 | 8842 | 42 |
| H(8B) | 6903 | 728 | 8007 | 42 |
| H(8C) | 4525 | 1046 | 8270 | 42 |

**Table S18.** Torsion angles [°] for **4*R***.

| | |
|---|---|
| C(2)-N(1)-C(6)-C(7) | -76.40(18) |
| C(3)-N(1)-C(6)-C(7) | 105.99(15) |
| C(2)-N(1)-C(6)-C(5) | 163.91(14) |
| C(3)-N(1)-C(6)-C(5) | -13.70(17) |
| C(2)-N(1)-C(3)-C(4) | 171.49(15) |
| C(6)-N(1)-C(3)-C(4) | -10.96(18) |
| O(3)-C(4)-C(3)-N(1) | 153.20(13) |
| C(5)-C(4)-C(3)-N(1) | 30.89(17) |
| C(6)-N(1)-C(2)-C(1) | -176.68(14) |
| C(3)-N(1)-C(2)-C(1) | 0.6(2) |
| C(6)-N(1)-C(2)-S(1) | 3.3(2) |
| C(3)-N(1)-C(2)-S(1) | -179.42(13) |
| N(1)-C(6)-C(5)-C(4) | 32.52(15) |
| C(7)-C(6)-C(5)-C(4) | -86.35(15) |
| O(3)-C(4)-C(5)-C(6) | -156.98(12) |
| C(3)-C(4)-C(5)-C(6) | -39.51(16) |
| C(3)-C(4)-O(3)-C(8) | 171.02(15) |
| C(5)-C(4)-O(3)-C(8) | -74.52(19) |
| C(9)-O(2)-C(7)-O(1) | -0.5(3) |
| C(9)-O(2)-C(7)-C(6) | 175.86(14) |
| N(1)-C(6)-C(7)-O(1) | -31.2(2) |
| C(5)-C(6)-C(7)-O(1) | 83.2(2) |
| N(1)-C(6)-C(7)-O(2) | 152.42(14) |
| C(5)-C(6)-C(7)-O(2) | -93.15(16) |

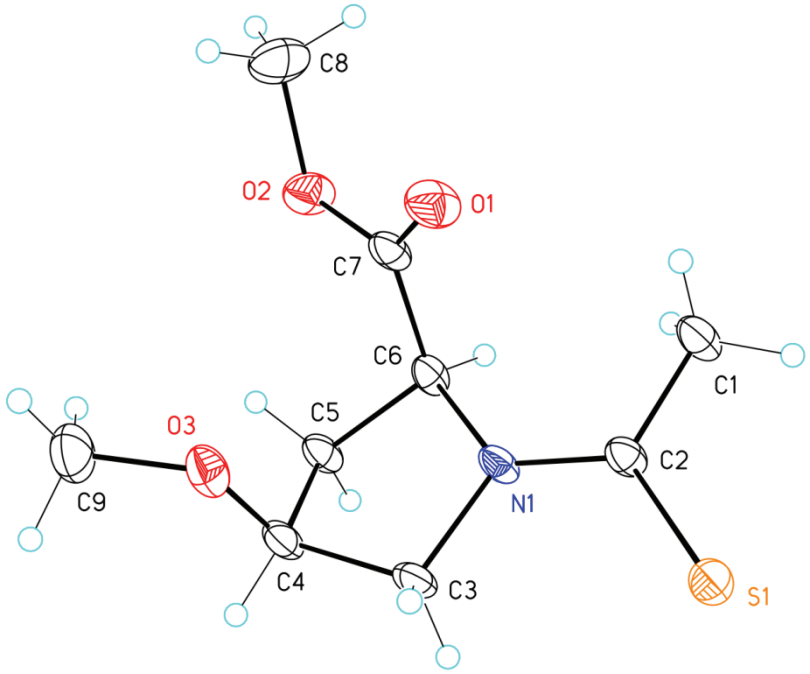


**Figure S4.** Molecular drawing of **4*S*** drawn at 50% probability ellipsoids.

**Table S19.** Crystal data and structure refinement for **4*S***.

| | | |
|---|---|---|
| Identification code | raines37 | |
| Empirical formula | $C_9H_{15}NO_3S$ | |
| Formula weight | 217.28 | |
| Temperature | 273(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2 | |
| Unit cell dimensions | $a$ = 14.493(6) Å | $\alpha$ = 90° |
| | $b$ = 6.393(3) Å | $\beta$ = 96.568(6)° |
| | $c$ = 11.849(5) Å | $\gamma$ = 90° |
| Volume | 1090.6(8) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.323 mg/m$^3$ | |
| Absorption coefficient | 0.279 mm$^{-1}$ | |
| $F_{000}$ | 464 | |
| Crystal size | 0.50 × 0.45 × 0.40 mm$^3$ | |
| Theta range for data collection | 2.83 to 28.18°. | |
| Index ranges | $-19 \le h \le 19$, $-8 \le k \le 8$, $-15 \le l \le 14$ | |
| Reflections collected | 6025 | |
| Independent reflections | 2611 [$R_{int}$ = 0.0502] | |
| Completeness to theta = 28.18° | 99.3% | |
| Absorption correction | Empirical with SADABS | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2611 / 1 / 131 | |
| Goodness-of-fit on $F^2$ | 0.765 | |
| Final $R$ indices [$I > 2\sigma_I$] | $R1$ = 0.0486, $wR2$ = 0.1245 | |
| $R$ indices (all data) | $R1$ = 0.0538, $wR2$ = 0.1317 | |
| Absolute structure parameter | 0.01(10) | |
| Largest diff. peak and hole | 0.803 and –0.403 e.Å$^{-3}$ | |

**Table S20.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4*S***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S(1) | 7939(1) | 5692(1) | 8936(1) | 22(1) |
| O(3) | 5072(1) | 2871(3) | 6665(1) | 24(1) |
| O(2) | 6202(1) | -1936(3) | 6529(2) | 26(1) |
| C(6) | 6509(1) | 442(4) | 8022(2) | 17(1) |
| C(2) | 7678(2) | 3217(4) | 8564(2) | 18(1) |
| N(1) | 6813(1) | 2586(3) | 8287(2) | 18(1) |
| C(5) | 5483(1) | 472(4) | 8236(2) | 19(1) |
| O(1) | 7177(1) | 689(4) | 6243(1) | 27(1) |
| C(1) | 8442(2) | 1629(4) | 8537(2) | 23(1) |
| C(4) | 5182(2) | 2675(4) | 7860(2) | 21(1) |
| C(3) | 6010(2) | 4004(4) | 8311(2) | 20(1) |
| C(9) | 4212(2) | 2067(5) | 6153(2) | 32(1) |
| C(8) | 6425(2) | -2992(5) | 5512(2) | 34(1) |
| C(7) | 6670(2) | -187(4) | 6824(2) | 19(1) |

**Table S21.** Bond lengths [Å] and angles [°] for **4*S***.

| | |
|---|---|
| S(1)-C(2) | 1.674(2) |
| O(3)-C(4) | 1.413(3) |
| O(3)-C(9) | 1.418(3) |
| O(2)-C(7) | 1.334(3) |
| O(2)-C(8) | 1.449(3) |
| C(6)-N(1) | 1.463(3) |
| C(6)-C(5) | 1.537(3) |
| C(6)-C(7) | 1.519(3) |
| C(6)-H(6) | 0.9800 |
| C(2)-N(1) | 1.323(3) |
| C(2)-C(1) | 1.505(3) |
| N(1)-C(3) | 1.478(3) |
| C(5)-C(4) | 1.525(3) |
| C(5)-H(5A) | 0.9700 |
| C(5)-H(5B) | 0.9700 |
| O(1)-C(7) | 1.202(3) |
| C(1)-H(1A) | 0.9600 |
| C(1)-H(1B) | 0.9600 |
| C(1)-H(1C) | 0.9600 |
| C(4)-C(3) | 1.517(3) |
| C(4)-H(4) | 0.9800 |
| C(3)-H(3A) | 0.9700 |
| C(3)-H(3B) | 0.9700 |
| C(9)-H(9A) | 0.9600 |
| C(9)-H(9B) | 0.9600 |
| C(9)-H(9C) | 0.9600 |
| C(8)-H(8A) | 0.9600 |
| C(8)-H(8B) | 0.9600 |
| C(8)-H(8C) | 0.9600 |
| | |
| C(4)-O(3)-C(9) | 112.94(19) |

| | |
|---|---|
| C(7)-O(2)-C(8) | 116.9(2) |
| N(1)-C(6)-C(5) | 103.05(18) |
| N(1)-C(6)-C(7) | 111.96(18) |
| C(5)-C(6)-C(7) | 114.32(18) |
| N(1)-C(6)-H(6) | 109.1 |
| C(5)-C(6)-H(6) | 109.1 |
| C(7)-C(6)-H(6) | 109.1 |
| N(1)-C(2)-C(1) | 117.9(2) |
| N(1)-C(2)-S(1) | 122.18(17) |
| C(1)-C(2)-S(1) | 119.93(17) |
| C(2)-N(1)-C(6) | 126.33(19) |
| C(2)-N(1)-C(3) | 122.3(2) |
| C(6)-N(1)-C(3) | 111.14(17) |
| C(4)-C(5)-C(6) | 102.34(18) |
| C(4)-C(5)-H(5A) | 111.3 |
| C(6)-C(5)-H(5A) | 111.3 |
| C(4)-C(5)-H(5B) | 111.3 |
| C(6)-C(5)-H(5B) | 111.3 |
| H(5A)-C(5)-H(5B) | 109.2 |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(3)-C(4)-C(5) | 111.73(19) |
| O(3)-C(4)-C(3) | 107.29(19) |
| C(5)-C(4)-C(3) | 103.07(18) |
| O(3)-C(4)-H(4) | 111.5 |
| C(5)-C(4)-H(4) | 111.5 |
| C(3)-C(4)-H(4) | 111.5 |
| N(1)-C(3)-C(4) | 104.05(18) |
| N(1)-C(3)-H(3A) | 110.9 |
| C(4)-C(3)-H(3A) | 110.9 |
| N(1)-C(3)-H(3B) | 110.9 |
| C(4)-C(3)-H(3B) | 110.9 |
| H(3A)-C(3)-H(3B) | 109.0 |
| O(3)-C(9)-H(9A) | 109.5 |
| O(3)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| O(3)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| O(2)-C(8)-H(8A) | 109.5 |
| O(2)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| O(2)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| O(1)-C(7)-O(2) | 124.6(2) |
| O(1)-C(7)-C(6) | 125.5(2) |
| O(2)-C(7)-C(6) | 109.81(19) |

**Table S22.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4*S***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 18(1) | 14(1) | 35(1) | -1(1) | 4(1) | -2(1) |
| O(3) | 16(1) | 22(1) | 32(1) | 3(1) | 2(1) | 0(1) |
| O(2) | 28(1) | 16(1) | 35(1) | -5(1) | 9(1) | -4(1) |
| C(6) | 12(1) | 12(1) | 27(1) | 2(1) | 4(1) | -1(1) |
| C(2) | 15(1) | 13(1) | 25(1) | 2(1) | 5(1) | 1(1) |
| N(1) | 12(1) | 11(1) | 29(1) | 1(1) | 5(1) | 2(1) |
| C(5) | 13(1) | 17(1) | 29(1) | 1(1) | 7(1) | 0(1) |
| O(1) | 25(1) | 26(1) | 32(1) | -2(1) | 13(1) | -4(1) |
| C(1) | 15(1) | 16(1) | 40(1) | 1(1) | 8(1) | 1(1) |
| C(4) | 12(1) | 19(1) | 32(1) | -3(1) | 5(1) | 2(1) |
| C(3) | 15(1) | 14(1) | 32(1) | -3(1) | 5(1) | 4(1) |
| C(9) | 19(1) | 33(2) | 41(2) | -2(1) | -2(1) | -3(1) |
| C(8) | 44(2) | 23(1) | 37(1) | -10(1) | 9(1) | -3(1) |
| C(7) | 15(1) | 13(1) | 31(1) | -1(1) | 5(1) | 2(1) |

**Table S23.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **4*S***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(6) | 6852 | -515 | 8564 | 20 |
| H(5A) | 5128 | -580 | 7785 | 23 |
| H(5B) | 5417 | 248 | 9032 | 23 |
| H(1A) | 8262 | 344 | 8869 | 35 |
| H(1B) | 9000 | 2147 | 8960 | 35 |
| H(1C) | 8552 | 1384 | 7764 | 35 |
| H(4) | 4619 | 3102 | 8186 | 25 |
| H(3A) | 6067 | 5215 | 7830 | 24 |
| H(3B) | 5955 | 4475 | 9079 | 24 |
| H(9A) | 4165 | 615 | 6345 | 48 |
| H(9B) | 4180 | 2211 | 5343 | 48 |
| H(9C) | 3711 | 2829 | 6425 | 48 |
| H(8A) | 6079 | -2371 | 4858 | 51 |
| H(8B) | 6267 | -4446 | 5551 | 51 |
| H(8C) | 7078 | -2856 | 5454 | 51 |

**Table S24.** Torsion angles [°] for **4*S***.

| | |
|---|---|
| C(1)-C(2)-N(1)-C(6) | 4.3(3) |
| S(1)-C(2)-N(1)-C(6) | -175.79(17) |
| C(1)-C(2)-N(1)-C(3) | 178.5(2) |
| S(1)-C(2)-N(1)-C(3) | -1.5(3) |
| C(5)-C(6)-N(1)-C(2) | 158.3(2) |
| C(7)-C(6)-N(1)-C(2) | -78.4(3) |
| C(5)-C(6)-N(1)-C(3) | -16.5(2) |
| C(7)-C(6)-N(1)-C(3) | 106.8(2) |
| N(1)-C(6)-C(5)-C(4) | 34.8(2) |
| C(7)-C(6)-C(5)-C(4) | -87.0(2) |
| C(9)-O(3)-C(4)-C(5) | 80.1(2) |
| C(9)-O(3)-C(4)-C(3) | -167.6(2) |
| C(6)-C(5)-C(4)-O(3) | 74.5(2) |
| C(6)-C(5)-C(4)-C(3) | -40.4(2) |
| C(2)-N(1)-C(3)-C(4) | 176.3(2) |
| C(6)-N(1)-C(3)-C(4) | -8.6(2) |
| O(3)-C(4)-C(3)-N(1) | -87.7(2) |
| C(5)-C(4)-C(3)-N(1) | 30.4(2) |
| C(8)-O(2)-C(7)-O(1) | 8.9(4) |
| C(8)-O(2)-C(7)-C(6) | -167.6(2) |
| N(1)-C(6)-C(7)-O(1) | 17.4(3) |
| C(5)-C(6)-C(7)-O(1) | 134.1(3) |
| N(1)-C(6)-C(7)-O(2) | -166.06(18) |
| C(5)-C(6)-C(7)-O(2) | -49.4(3) |

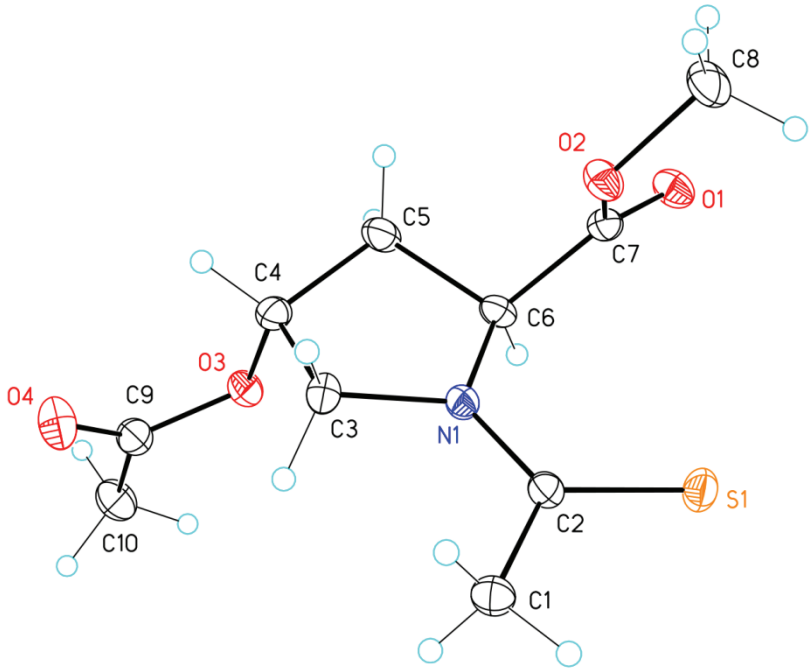


**Figure S5.** Molecular drawing of **5*R*** drawn at 50% probability ellipsoids.

**Table S25.** Crystal data and structure refinement for **5*R***.

| | | |
|---|---|---|
| Identification code | raines12 | |
| Empirical formula | $C_{10}H_{15}NO_4S$ | |
| Formula weight | 245.29 | |
| Temperature | 273(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | $a$ = 6.5056(6) Å | $\alpha$ = 90° |
| | $b$ = 8.2425(8) Å | $\beta$ = 90° |
| | $c$ = 21.780(2) Å | $\gamma$ = 90° |
| Volume | 1167.9(2) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.395 mg/m$^3$ | |
| Absorption coefficient | 0.276 mm$^{-1}$ | |
| $F_{000}$ | 520 | |
| Crystal size | 0.50 × 0.46 × 0.28 mm$^3$ | |
| Theta range for data collection | 1.87–28.28° | |
| Index ranges | $-8 \le h \le 8$, $-10 \le k \le 10$, $-29 \le l \le 27$ | |
| Reflections collected | 16028 | |
| Independent reflections | 2887 [$R_{int}$ = 0.0386] | |
| Completeness to theta = 28.28° | 99.9% | |
| Absorption correction | Empirical with SADABS | |
| Max. and min. transmission | 0.9267 and 0.8743 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2887 / 0 / 149 | |
| Goodness-of-fit on $F^2$ | 0.548 | |
| Final R indices [$I > 2\sigma_I$] | $R1$ = 0.0248, $wR2$ = 0.0678 | |
| $R$ indices (all data) | $R1$ = 0.0259, $wR2$ = 0.0696 | |
| Absolute structure parameter | 0.00(5) | |
| Largest diff. peak and hole | 0.323 and –0.180 e.Å$^{-3}$ | |

**Table S26.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5*R***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| C(7) | -1890(2) | 10090(1) | 9241(1) | 15(1) |
| S(1) | -2635(1) | 10341(1) | 7872(1) | 20(1) |
| O(1) | -3566(1) | 10000(1) | 9480(1) | 20(1) |
| O(3) | 2154(1) | 5726(1) | 8877(1) | 17(1) |
| O(4) | 5546(1) | 5429(1) | 8709(1) | 25(1) |
| C(2) | -177(2) | 9760(1) | 7932(1) | 15(1) |
| O(2) | -687(1) | 11401(1) | 9254(1) | 18(1) |
| N(1) | 530(1) | 9041(1) | 8437(1) | 14(1) |
| C(4) | 2581(2) | 7372(1) | 9073(1) | 17(1) |
| C(9) | 3831(2) | 4867(2) | 8705(1) | 18(1) |
| C(1) | 1329(2) | 10022(2) | 7418(1) | 19(1) |
| C(3) | 2678(2) | 8517(1) | 8528(1) | 16(1) |
| C(6) | -791(2) | 8639(1) | 8964(1) | 15(1) |
| C(8) | -1568(2) | 12840(2) | 9530(1) | 23(1) |
| C(10) | 3296(2) | 3159(2) | 8537(1) | 23(1) |
| C(5) | 731(2) | 7942(2) | 9441(1) | 20(1) |

**Table S27.** Bond lengths [Å] and angles [°] for **5*R***.

| | |
|---|---|
| C(7)-O(1) | 1.2101(14) |
| C(7)-O(2) | 1.3344(14) |
| C(7)-C(6) | 1.5193(15) |
| S(1)-C(2) | 1.6744(11) |
| O(3)-C(9) | 1.3533(14) |
| O(3)-C(4) | 1.4488(13) |
| O(4)-C(9) | 1.2078(15) |
| C(2)-N(1) | 1.3314(14) |
| C(2)-C(1) | 1.5035(15) |
| O(2)-C(8) | 1.4479(14) |
| N(1)-C(6) | 1.4714(14) |
| N(1)-C(3) | 1.4759(14) |
| C(4)-C(3) | 1.5194(16) |
| C(4)-C(5) | 1.5202(17) |
| C(4)-H(4) | 0.9800 |
| C(9)-C(10) | 1.4957(18) |
| C(1)-H(1A) | 0.9600 |
| C(1)-H(1B) | 0.9600 |
| C(1)-H(1C) | 0.9600 |
| C(3)-H(3A) | 0.9700 |
| C(3)-H(3B) | 0.9700 |
| C(6)-C(5) | 1.5465(17) |
| C(6)-H(6) | 0.9800 |
| C(8)-H(8A) | 0.9600 |
| C(8)-H(8B) | 0.9600 |
| C(8)-H(8C) | 0.9600 |
| C(10)-H(10A) | 0.9600 |
| C(10)-H(10B) | 0.9600 |
| C(10)-H(10C) | 0.9600 |

| | |
|---|---|
| C(5)-H(5A) | 0.9700 |
| C(5)-H(5B) | 0.9700 |
| | |
| O(1)-C(7)-O(2) | 124.71(10) |
| O(1)-C(7)-C(6) | 123.11(10) |
| O(2)-C(7)-C(6) | 111.71(9) |
| C(9)-O(3)-C(4) | 114.66(9) |
| N(1)-C(2)-C(1) | 117.03(10) |
| N(1)-C(2)-S(1) | 121.45(8) |
| C(1)-C(2)-S(1) | 121.52(8) |
| C(7)-O(2)-C(8) | 116.09(9) |
| C(2)-N(1)-C(6) | 122.85(9) |
| C(2)-N(1)-C(3) | 124.61(9) |
| C(6)-N(1)-C(3) | 112.52(9) |
| O(3)-C(4)-C(3) | 111.01(9) |
| O(3)-C(4)-C(5) | 107.06(10) |
| C(3)-C(4)-C(5) | 104.69(9) |
| O(3)-C(4)-H(4) | 111.3 |
| C(3)-C(4)-H(4) | 111.3 |
| C(5)-C(4)-H(4) | 111.3 |
| O(4)-C(9)-O(3) | 122.79(11) |
| O(4)-C(9)-C(10) | 125.29(11) |
| O(3)-C(9)-C(10) | 111.88(10) |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| N(1)-C(3)-C(4) | 104.28(9) |
| N(1)-C(3)-H(3A) | 110.9 |
| C(4)-C(3)-H(3A) | 110.9 |
| N(1)-C(3)-H(3B) | 110.9 |
| C(4)-C(3)-H(3B) | 110.9 |
| H(3A)-C(3)-H(3B) | 108.9 |
| N(1)-C(6)-C(7) | 114.10(9) |
| N(1)-C(6)-C(5) | 103.54(9) |
| C(7)-C(6)-C(5) | 109.03(9) |
| N(1)-C(6)-H(6) | 110.0 |
| C(7)-C(6)-H(6) | 110.0 |
| C(5)-C(6)-H(6) | 110.0 |
| O(2)-C(8)-H(8A) | 109.5 |
| O(2)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| O(2)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(9)-C(10)-H(10A) | 109.5 |
| C(9)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(9)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| C(4)-C(5)-C(6) | 105.49(9) |
| C(4)-C(5)-H(5A) | 110.6 |
| C(6)-C(5)-H(5A) | 110.6 |

| | |
|---|---|
| C(4)-C(5)-H(5B) | 110.6 |
| C(6)-C(5)-H(5B) | 110.6 |
| H(5A)-C(5)-H(5B) | 108.8 |

**Table S28.** Anisotropic displacement parameters (Å$^2$ × 10$^3$) for **5*R***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\, ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(7) | 17(1) | 15(1) | 12(1) | 0(1) | 0(1) | 1(1) |
| S(1) | 15(1) | 25(1) | 19(1) | 4(1) | 0(1) | 5(1) |
| O(1) | 18(1) | 22(1) | 20(1) | -3(1) | 6(1) | -1(1) |
| O(3) | 18(1) | 14(1) | 18(1) | -1(1) | 2(1) | 2(1) |
| O(4) | 18(1) | 21(1) | 36(1) | -1(1) | 2(1) | 2(1) |
| C(2) | 15(1) | 14(1) | 15(1) | -1(1) | 1(1) | 1(1) |
| O(2) | 17(1) | 14(1) | 22(1) | -4(1) | 2(1) | 0(1) |
| N(1) | 13(1) | 16(1) | 13(1) | 0(1) | 2(1) | 1(1) |
| C(4) | 20(1) | 15(1) | 15(1) | -2(1) | -2(1) | 3(1) |
| C(9) | 20(1) | 17(1) | 17(1) | 3(1) | 1(1) | 3(1) |
| C(1) | 19(1) | 22(1) | 15(1) | 2(1) | 4(1) | 1(1) |
| C(3) | 14(1) | 16(1) | 19(1) | 1(1) | -2(1) | 1(1) |
| C(6) | 18(1) | 14(1) | 13(1) | 0(1) | 4(1) | 0(1) |
| C(8) | 23(1) | 15(1) | 30(1) | -7(1) | -2(1) | 2(1) |
| C(10) | 26(1) | 17(1) | 26(1) | -2(1) | 4(1) | 2(1) |
| C(5) | 29(1) | 19(1) | 13(1) | 1(1) | 2(1) | 9(1) |

**Table S29.** Hydrogen coordinates (×10$^4$) and isotropic displacement parameters (Å$^2$ × 10$^3$) for **5*R***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(4) | 3843 | 7425 | 9318 | 20 |
| H(1A) | 2513 | 10587 | 7571 | 28 |
| H(1B) | 692 | 10656 | 7100 | 28 |
| H(1C) | 1742 | 8992 | 7253 | 28 |
| H(3A) | 3559 | 9437 | 8615 | 19 |
| H(3B) | 3194 | 7962 | 8166 | 19 |
| H(6) | -1793 | 7808 | 8846 | 18 |
| H(8A) | -2666 | 13236 | 9277 | 34 |
| H(8B) | -528 | 13661 | 9568 | 34 |
| H(8C) | -2094 | 12578 | 9930 | 34 |
| H(10A) | 4176 | 2800 | 8210 | 35 |
| H(10B) | 1890 | 3112 | 8404 | 35 |
| H(10C) | 3479 | 2469 | 8888 | 35 |
| H(5A) | 1129 | 8769 | 9734 | 25 |
| H(5B) | 114 | 7043 | 9662 | 25 |

**Table S30.** Torsion angles [°] for **5*R***.

| | |
|---|---|
| O(1)-C(7)-O(2)-C(8) | -5.58(16) |
| C(6)-C(7)-O(2)-C(8) | -177.96(10) |
| C(1)-C(2)-N(1)-C(6) | -177.04(10) |
| S(1)-C(2)-N(1)-C(6) | 2.73(16) |
| C(1)-C(2)-N(1)-C(3) | 1.14(17) |
| S(1)-C(2)-N(1)-C(3) | -179.09(8) |
| C(9)-O(3)-C(4)-C(3) | 84.93(12) |
| C(9)-O(3)-C(4)-C(5) | -161.37(9) |
| C(4)-O(3)-C(9)-O(4) | -0.63(16) |
| C(4)-O(3)-C(9)-C(10) | 177.30(9) |
| C(2)-N(1)-C(3)-C(4) | -164.45(10) |
| C(6)-N(1)-C(3)-C(4) | 13.89(12) |
| O(3)-C(4)-C(3)-N(1) | 87.78(11) |
| C(5)-C(4)-C(3)-N(1) | -27.41(12) |
| C(2)-N(1)-C(6)-C(7) | -58.04(15) |
| C(3)-N(1)-C(6)-C(7) | 123.59(10) |
| C(2)-N(1)-C(6)-C(5) | -176.41(10) |
| C(3)-N(1)-C(6)-C(5) | 5.21(12) |
| O(1)-C(7)-C(6)-N(1) | 148.53(11) |
| O(2)-C(7)-C(6)-N(1) | -38.96(13) |
| O(1)-C(7)-C(6)-C(5) | -96.28(13) |
| O(2)-C(7)-C(6)-C(5) | 76.24(12) |
| O(3)-C(4)-C(5)-C(6) | -86.81(11) |
| C(3)-C(4)-C(5)-C(6) | 31.11(12) |
| N(1)-C(6)-C(5)-C(4) | -22.35(12) |
| C(7)-C(6)-C(5)-C(4) | -144.18(10) |

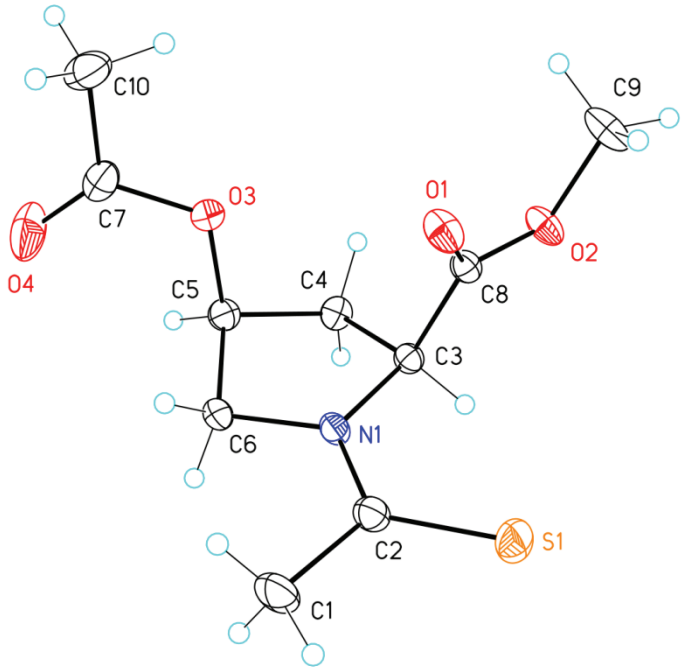


**Figure S6.** Molecular drawing of **5*S*** drawn at 50% probability ellipsoids.

**Table S31.** Crystal data and structure refinement for **5*S***.

| | | |
|---|---|---|
| Identification code | raines19 | |
| Empirical formula | $C_{10}H_{15}NO_4S$ | |
| Formula weight | 245.29 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | $a$ = 8.4606(3) Å | $\alpha$ = 90° |
| | $b$ = 9.8014(3) Å | $\beta$ = 90° |
| | $c$ = 14.3985(5) Å | $\gamma$ = 90° |
| Volume | 1194.01(7) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.365 mg/m$^3$ | |
| Absorption coefficient | 0.270 mm$^{-1}$ | |
| $F_{000}$ | 520 | |
| Crystal size | 0.45 × 0.24 × 0.23 mm$^3$ | |
| Theta range for data collection | 2.51–30.00° | |
| Index ranges | $-11 \le h \le 11$, $-13 \le k \le 13$, $-19 \le l \le 19$ | |
| Reflections collected | 17885 | |
| Independent reflections | 3407 [$R_{int}$ = 0.0277] | |
| Completeness to theta = 30.00° | 98.9% | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9405 and 0.8881 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3407 / 0 / 149 | |
| Goodness-of-fit on $F^2$ | 1.075 | |
| Final $R$ indices [$I > 2\sigma_I$] | $R1$ = 0.0315, $wR2$ = 0.0791 | |
| $R$ indices (all data) | $R1$ = 0.0353, $wR2$ = 0.0828 | |
| Absolute structure parameter | 0.01(6) | |
| Largest diff. peak and hole | 0.387 and –0.163 e.Å$^{-3}$ | |

**Table S32.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5*S***. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S(1) | 3836(1) | 5697(1) | 10194(1) | 28(1) |
| O(3) | 2386(1) | 6958(1) | 6579(1) | 18(1) |
| O(2) | 2541(1) | 3286(1) | 7974(1) | 20(1) |
| O(1) | 4508(1) | 4807(1) | 7787(1) | 22(1) |
| C(8) | 3192(1) | 4534(1) | 8025(1) | 15(1) |
| N(1) | 2630(1) | 6821(1) | 8692(1) | 16(1) |
| C(4) | 690(1) | 5894(1) | 7692(1) | 17(1) |
| C(5) | 1242(1) | 7254(1) | 7299(1) | 16(1) |
| C(6) | 2063(2) | 7964(1) | 8105(1) | 17(1) |
| C(3) | 1952(1) | 5508(1) | 8417(1) | 14(1) |
| C(7) | 2585(2) | 7953(1) | 5937(1) | 22(1) |
| O(4) | 1860(2) | 9006(1) | 5954(1) | 39(1) |
| C(2) | 3451(2) | 6990(1) | 9475(1) | 19(1) |
| C(9) | 3517(2) | 2229(1) | 7562(1) | 26(1) |
| C(1) | 3967(2) | 8427(1) | 9688(1) | 29(1) |
| C(10) | 3817(2) | 7565(2) | 5238(1) | 31(1) |

**Table S33.** Bond lengths [Å] and angles [°] for **5*S***.

| | |
|---|---|
| S(1)-C(2) | 1.6687(13) |
| O(3)-C(7) | 1.3529(15) |
| O(3)-C(5) | 1.4483(14) |
| O(2)-C(8) | 1.3426(15) |
| O(2)-C(9) | 1.4517(15) |
| O(1)-C(8) | 1.1955(15) |
| C(8)-C(3) | 1.5275(16) |
| N(1)-C(2) | 1.3340(15) |
| N(1)-C(3) | 1.4636(14) |
| N(1)-C(6) | 1.4828(15) |
| C(4)-C(5) | 1.5215(17) |
| C(4)-C(3) | 1.5404(16) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.5205(16) |
| C(5)-H(5) | 1.0000 |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(3)-H(3) | 1.0000 |
| C(7)-O(4) | 1.2018(18) |
| C(7)-C(10) | 1.4984(19) |
| C(2)-C(1) | 1.5064(18) |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(10)-H(10A) | 0.9800 |

| | |
|---|---|
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |

| | |
|---|---|
| C(7)-O(3)-C(5) | 115.33(10) |
| C(8)-O(2)-C(9) | 116.03(10) |
| O(1)-C(8)-O(2) | 124.78(11) |
| O(1)-C(8)-C(3) | 127.26(11) |
| O(2)-C(8)-C(3) | 107.94(10) |
| C(2)-N(1)-C(3) | 122.78(10) |
| C(2)-N(1)-C(6) | 123.84(10) |
| C(3)-N(1)-C(6) | 112.49(9) |
| C(5)-C(4)-C(3) | 104.74(9) |
| C(5)-C(4)-H(4A) | 110.8 |
| C(3)-C(4)-H(4A) | 110.8 |
| C(5)-C(4)-H(4B) | 110.8 |
| C(3)-C(4)-H(4B) | 110.8 |
| H(4A)-C(4)-H(4B) | 108.9 |
| O(3)-C(5)-C(6) | 109.43(10) |
| O(3)-C(5)-C(4) | 107.21(9) |
| C(6)-C(5)-C(4) | 104.89(9) |
| O(3)-C(5)-H(5) | 111.7 |
| C(6)-C(5)-H(5) | 111.7 |
| C(4)-C(5)-H(5) | 111.7 |
| N(1)-C(6)-C(5) | 103.76(9) |
| N(1)-C(6)-H(6A) | 111.0 |
| C(5)-C(6)-H(6A) | 111.0 |
| N(1)-C(6)-H(6B) | 111.0 |
| C(5)-C(6)-H(6B) | 111.0 |
| H(6A)-C(6)-H(6B) | 109.0 |
| N(1)-C(3)-C(8) | 112.37(9) |
| N(1)-C(3)-C(4) | 103.85(9) |
| C(8)-C(3)-C(4) | 112.27(9) |
| N(1)-C(3)-H(3) | 109.4 |
| C(8)-C(3)-H(3) | 109.4 |
| C(4)-C(3)-H(3) | 109.4 |
| O(4)-C(7)-O(3) | 122.82(12) |
| O(4)-C(7)-C(10) | 125.92(13) |
| O(3)-C(7)-C(10) | 111.25(12) |
| N(1)-C(2)-C(1) | 116.05(11) |
| N(1)-C(2)-S(1) | 122.14(10) |
| C(1)-C(2)-S(1) | 121.79(9) |
| O(2)-C(9)-H(9A) | 109.5 |
| O(2)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| O(2)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| C(7)-C(10)-H(10A) | 109.5 |
| C(7)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |

| | |
|---|---|
| C(7)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |

**Table S34.** Anisotropic displacement parameters (Å$^2$ × 10$^3$) for **5*S***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12} \,]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 37(1) | 23(1) | 24(1) | 2(1) | -14(1) | 1(1) |
| O(3) | 22(1) | 18(1) | 16(1) | 0(1) | 2(1) | 1(1) |
| O(2) | 15(1) | 13(1) | 32(1) | -4(1) | 3(1) | -1(1) |
| O(1) | 16(1) | 17(1) | 32(1) | -1(1) | 5(1) | 0(1) |
| C(8) | 15(1) | 14(1) | 17(1) | -1(1) | -1(1) | 0(1) |
| N(1) | 18(1) | 12(1) | 17(1) | -1(1) | -2(1) | 1(1) |
| C(4) | 14(1) | 19(1) | 18(1) | 1(1) | -1(1) | 0(1) |
| C(5) | 15(1) | 18(1) | 17(1) | 0(1) | 0(1) | 3(1) |
| C(6) | 21(1) | 13(1) | 17(1) | 0(1) | 0(1) | 3(1) |
| C(3) | 14(1) | 14(1) | 15(1) | 0(1) | 0(1) | 0(1) |
| C(7) | 23(1) | 24(1) | 19(1) | 3(1) | -3(1) | -6(1) |
| O(4) | 38(1) | 34(1) | 44(1) | 21(1) | 5(1) | 8(1) |
| C(2) | 21(1) | 17(1) | 19(1) | -2(1) | -3(1) | 1(1) |
| C(9) | 19(1) | 16(1) | 43(1) | -10(1) | 2(1) | 2(1) |
| C(1) | 39(1) | 19(1) | 28(1) | -8(1) | -11(1) | -1(1) |
| C(10) | 38(1) | 34(1) | 21(1) | -4(1) | 8(1) | -13(1) |

**Table S35.** Hydrogen coordinates (×10$^4$) and isotropic displacement parameters (Å$^2$ × 10$^3$) for **5*S***.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H(4A) | 627 | 5195 | 7197 | 20 |
| H(4B) | -362 | 5986 | 7986 | 20 |
| H(5) | 337 | 7806 | 7056 | 20 |
| H(6A) | 2957 | 8528 | 7883 | 20 |
| H(6B) | 1315 | 8551 | 8451 | 20 |
| H(3) | 1427 | 5077 | 8966 | 17 |
| H(9A) | 3613 | 2390 | 6893 | 39 |
| H(9B) | 3029 | 1336 | 7669 | 39 |
| H(9C) | 4569 | 2247 | 7847 | 39 |
| H(1A) | 4545 | 8799 | 9156 | 43 |
| H(1B) | 4657 | 8423 | 10235 | 43 |
| H(1C) | 3037 | 8993 | 9813 | 43 |
| H(10A) | 3354 | 7579 | 4615 | 46 |
| H(10B) | 4210 | 6646 | 5375 | 46 |
| H(10C) | 4695 | 8216 | 5267 | 46 |

**Table S36.** Torsion angles [°] for **5*S***.

| | |
|---|---|
| C(9)-O(2)-C(8)-O(1) | -2.53(18) |
| C(9)-O(2)-C(8)-C(3) | 176.45(10) |
| C(7)-O(3)-C(5)-C(6) | -89.46(12) |
| C(7)-O(3)-C(5)-C(4) | 157.30(10) |
| C(3)-C(4)-C(5)-O(3) | 83.65(11) |
| C(3)-C(4)-C(5)-C(6) | -32.63(12) |
| C(2)-N(1)-C(6)-C(5) | 178.77(11) |
| C(3)-N(1)-C(6)-C(5) | -11.76(12) |
| O(3)-C(5)-C(6)-N(1) | -87.60(11) |
| C(4)-C(5)-C(6)-N(1) | 27.13(12) |
| C(2)-N(1)-C(3)-C(8) | -77.08(14) |
| C(6)-N(1)-C(3)-C(8) | 113.32(10) |
| C(2)-N(1)-C(3)-C(4) | 161.35(11) |
| C(6)-N(1)-C(3)-C(4) | -8.25(12) |
| O(1)-C(8)-C(3)-N(1) | -13.57(17) |
| O(2)-C(8)-C(3)-N(1) | 167.48(9) |
| O(1)-C(8)-C(3)-C(4) | 103.06(14) |
| O(2)-C(8)-C(3)-C(4) | -75.89(12) |
| C(5)-C(4)-C(3)-N(1) | 25.00(11) |
| C(5)-C(4)-C(3)-C(8) | -96.64(11) |
| C(5)-O(3)-C(7)-O(4) | -0.64(19) |
| C(5)-O(3)-C(7)-C(10) | 178.60(10) |
| C(3)-N(1)-C(2)-C(1) | -175.77(11) |
| C(6)-N(1)-C(2)-C(1) | -7.35(18) |
| C(3)-N(1)-C(2)-S(1) | 2.39(17) |
| C(6)-N(1)-C(2)-S(1) | 170.80(9) |

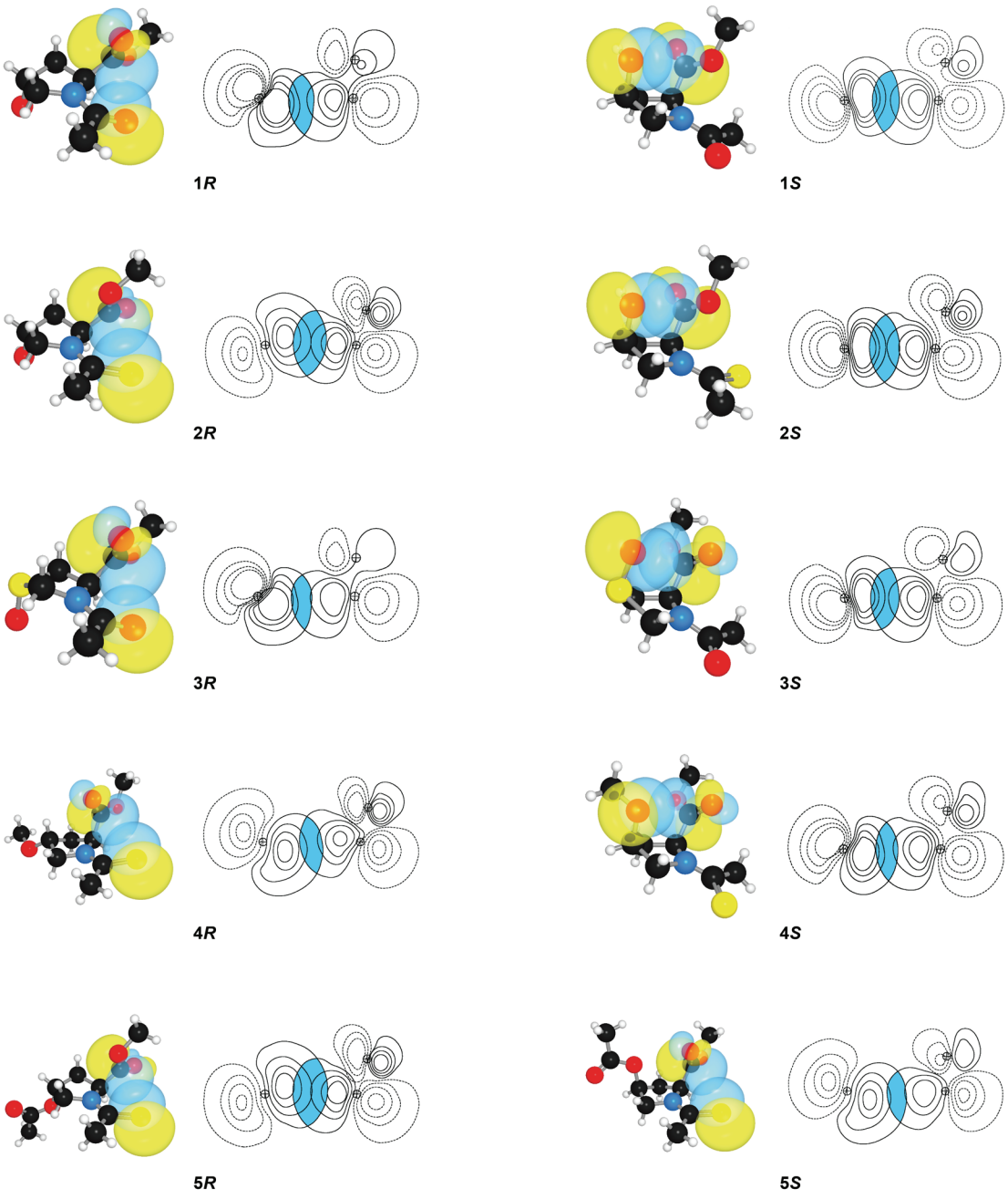


**Figure S7.** Calculated overlap between *n* and $\pi^*$ orbitals in the crystalline structures of diastereomers **1**–**5** as calculated with Natural Bond Orbital analysis[4] and depicted with NBOView 1.1.[5]

**Table S37.** Calculated energy and overlap integral for the $n \rightarrow \pi^*$ interaction in diastereomers **1**–**5** as calculated with Natural Bond Orbital analysis.[4]

| Compound | $E_{n \rightarrow \pi^*}$ (kcal/mol) | Overlap Integral |
|---|---|---|
| **1*R*** | 0.91 | 0.0924 |
| **1*S*** | 0.94 | 0.1102 |
| **2*R*** | 2.77 | 0.1488 |
| **2*S*** | 1.38 | 0.1305 |
| **3*R*** | 0.43 | 0.0746 |
| **3*S*** | 1.22 | 0.1006 |
| **4*R*** | 1.02 | 0.1015 |
| **4*S*** | 0.75 | 0.0762 |
| **5*R*** | 3.35 | 0.1542 |
| **5*S*** | 0.56 | 0.0855 |

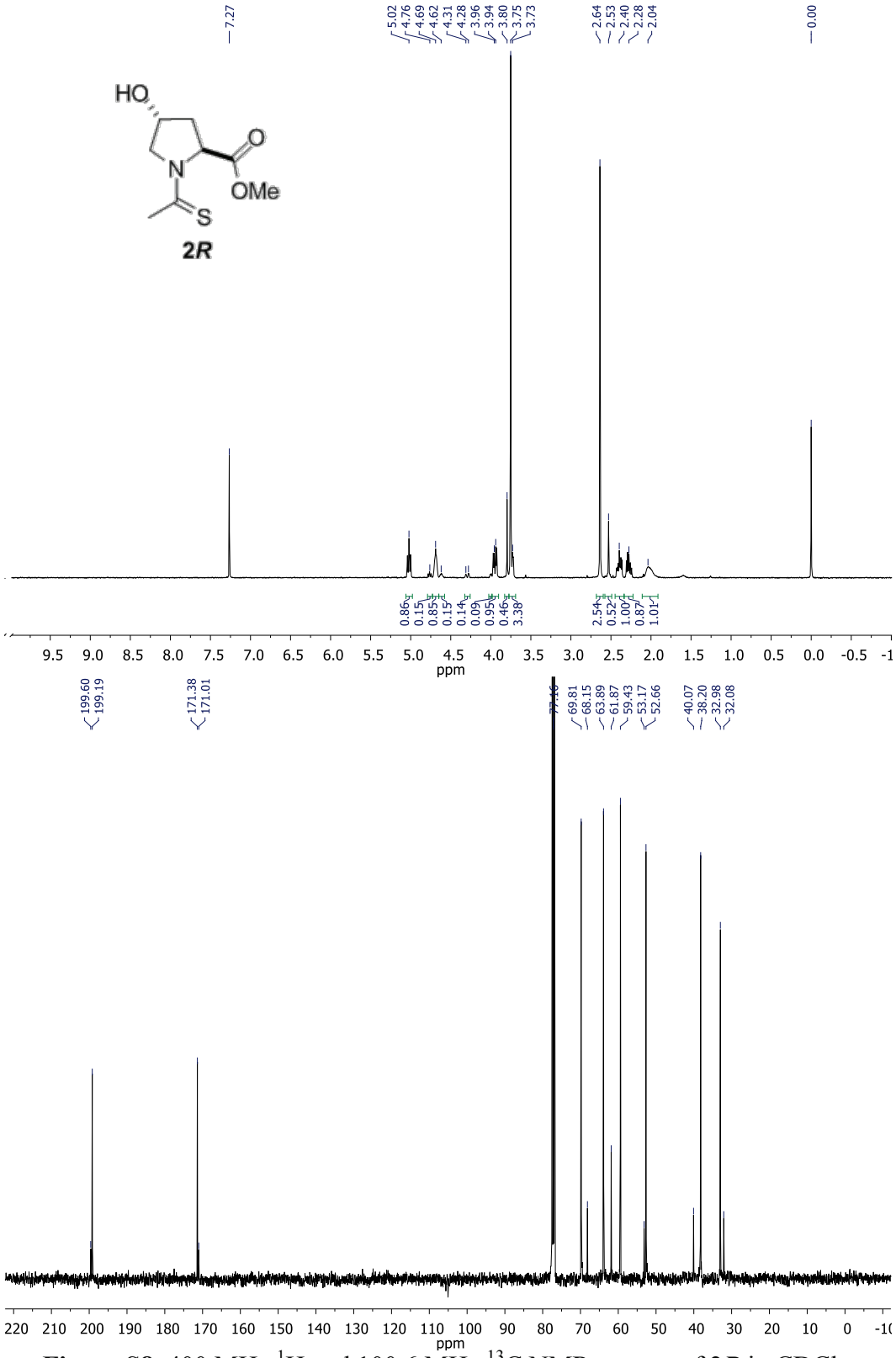


**Figure S8.** 400 MHz $^{1}$H and 100.6 MHz $^{13}$C NMR spectra of **2*R*** in $CDCl_3$.

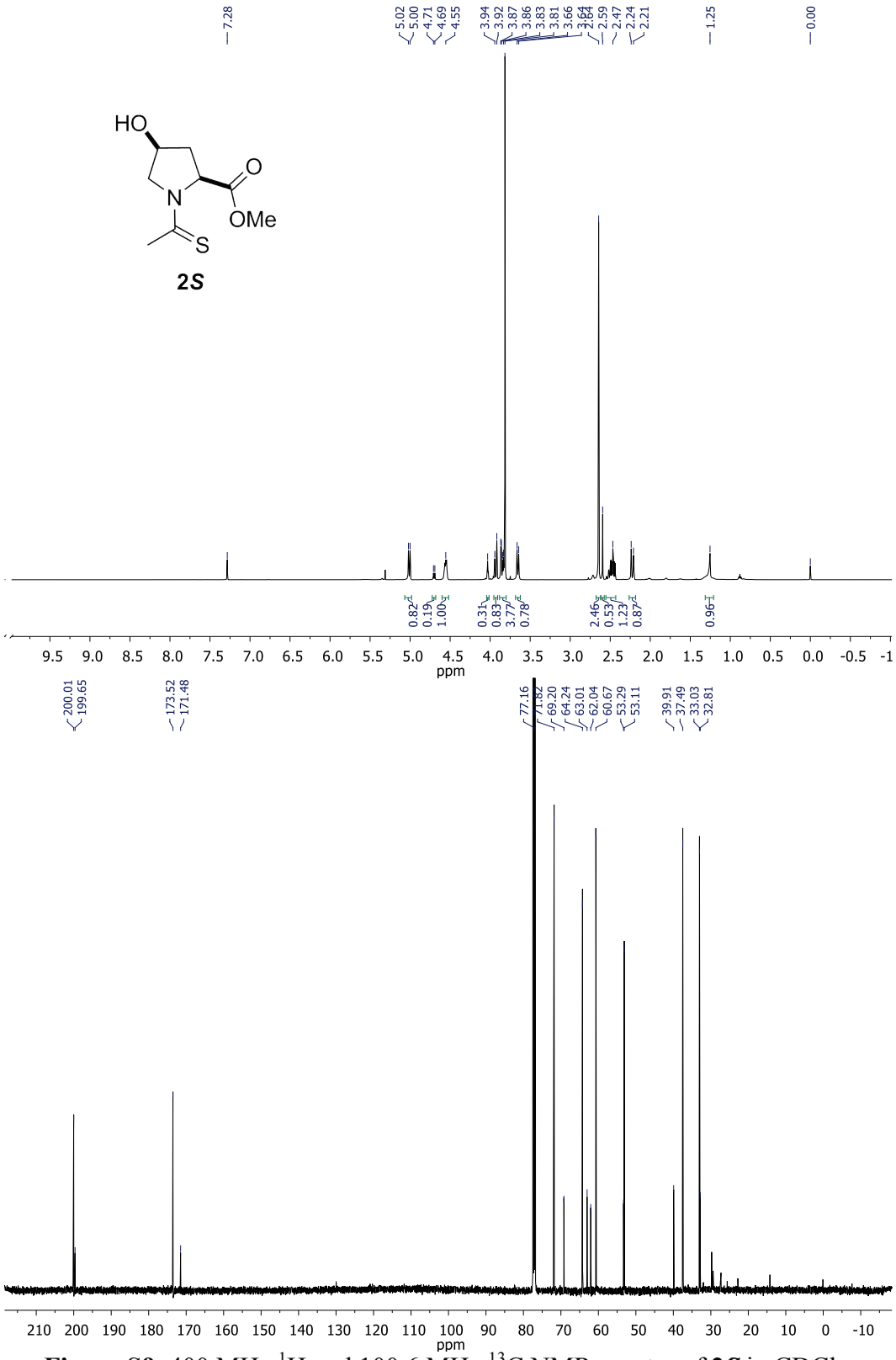


**Figure S9.** 400 MHz $^{1}$H and 100.6 MHz $^{13}$C NMR spectra of **2*S*** in $CDCl_3$.

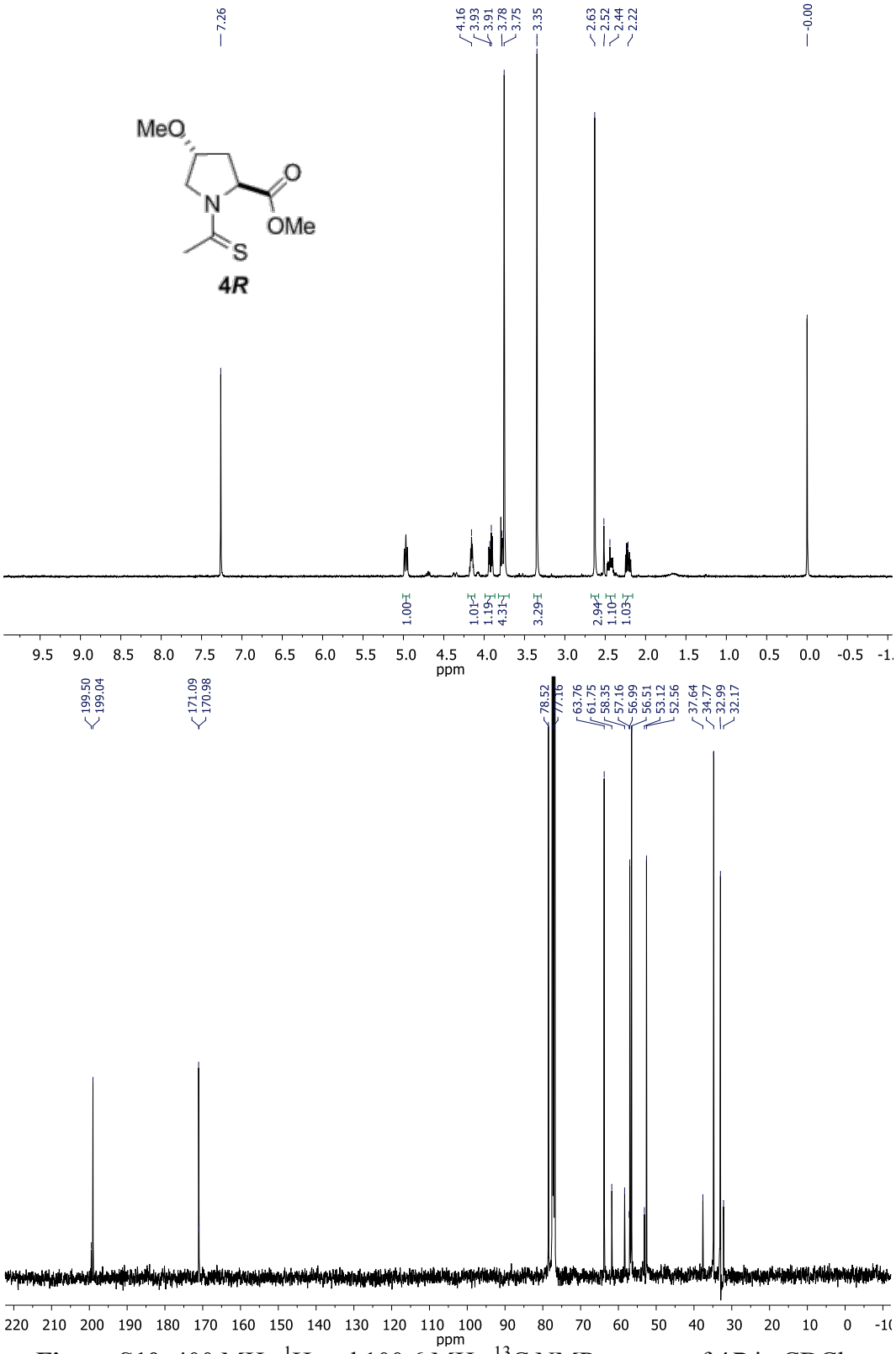


**Figure S10.** 400 MHz $^{1}$H and 100.6 MHz $^{13}$C NMR spectra of ***4R*** in $CDCl_3$.

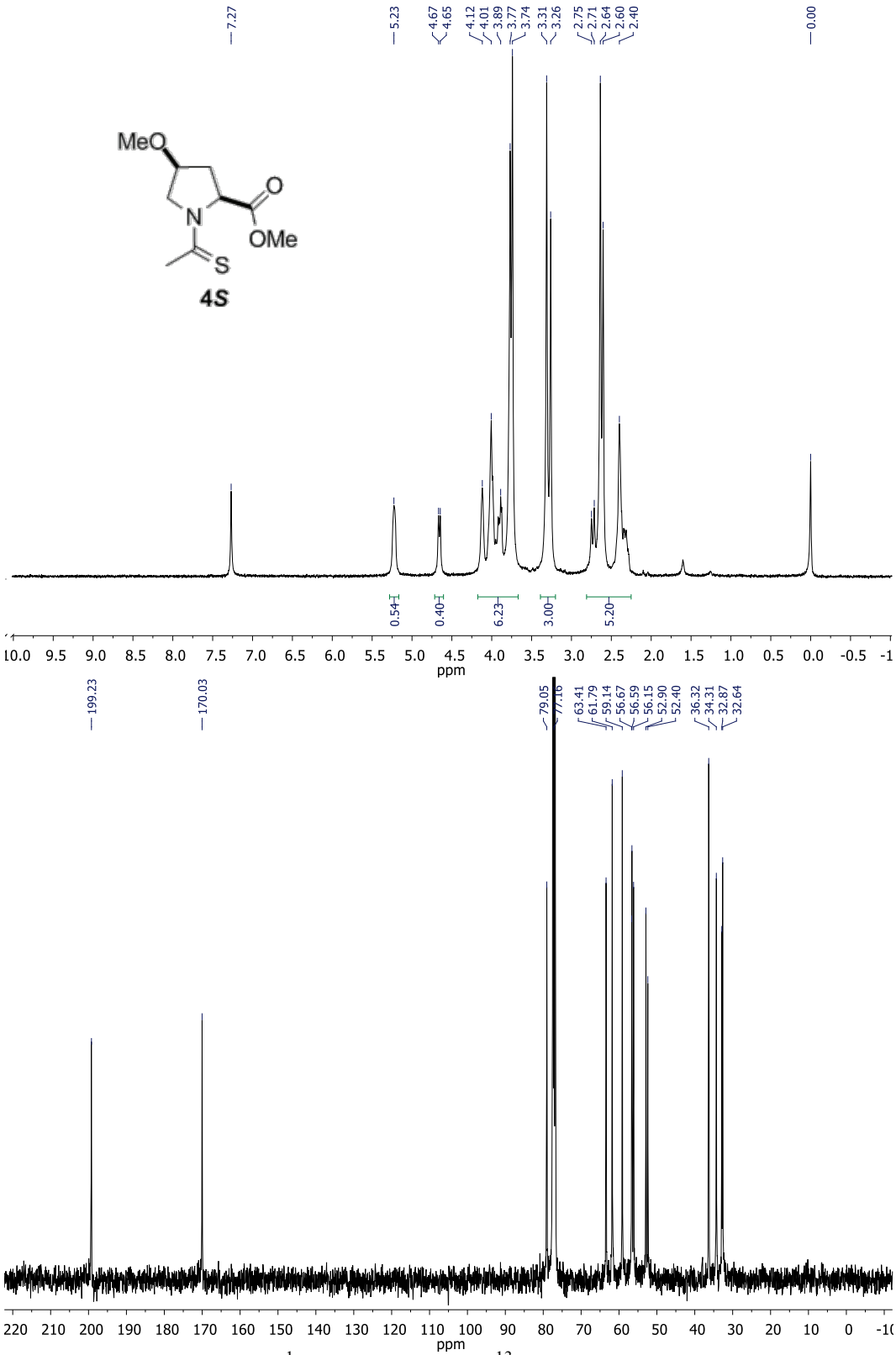


**Figure S11.** 400 MHz $^{1}$H and 100.6 MHz $^{13}$C NMR spectra of 4***S*** in $CDCl_3$.

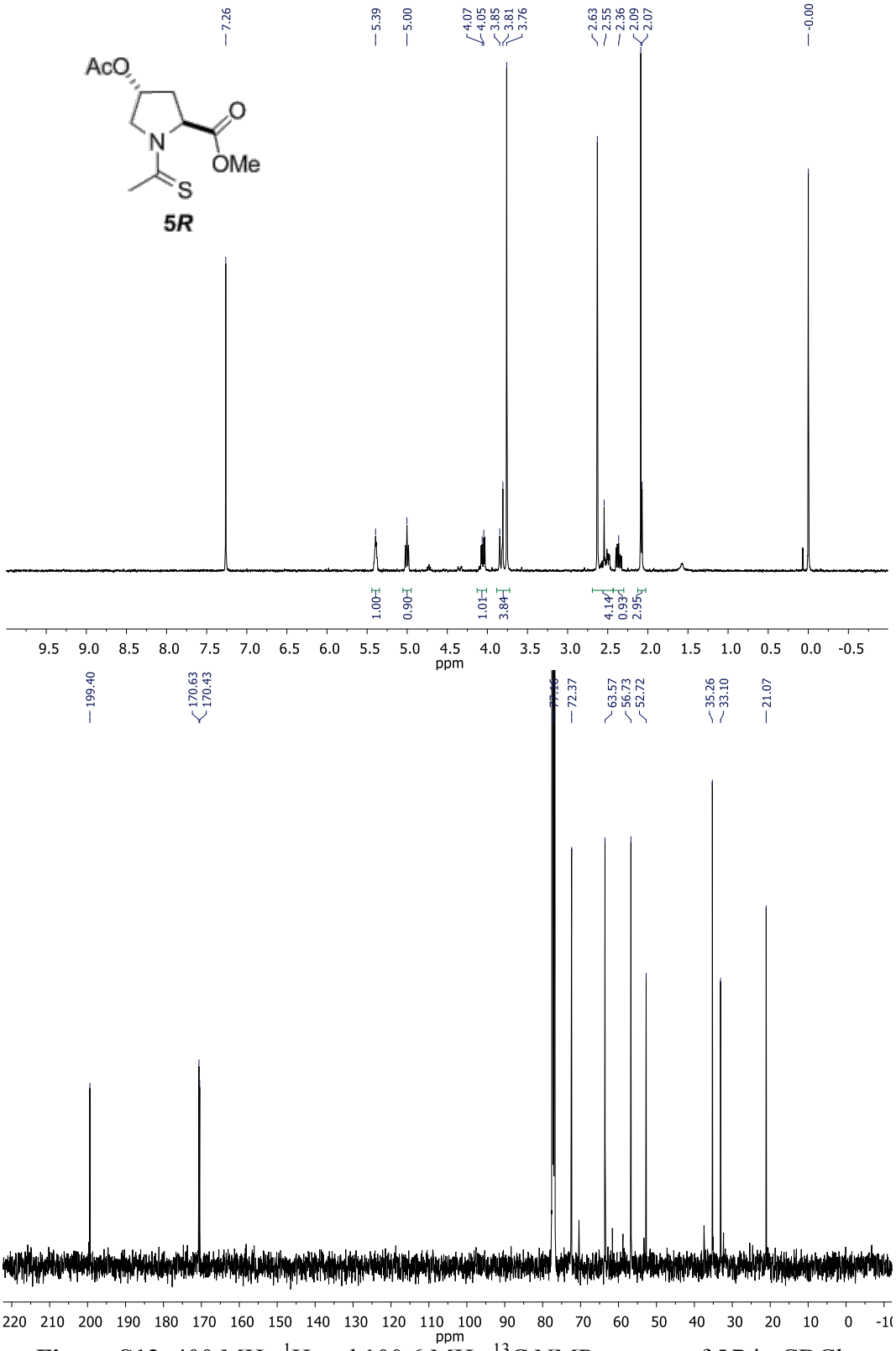


**Figure S12.** 400 MHz $^{1}$H and 100.6 MHz $^{13}$C NMR spectra of 5***R*** in $CDCl_3$.

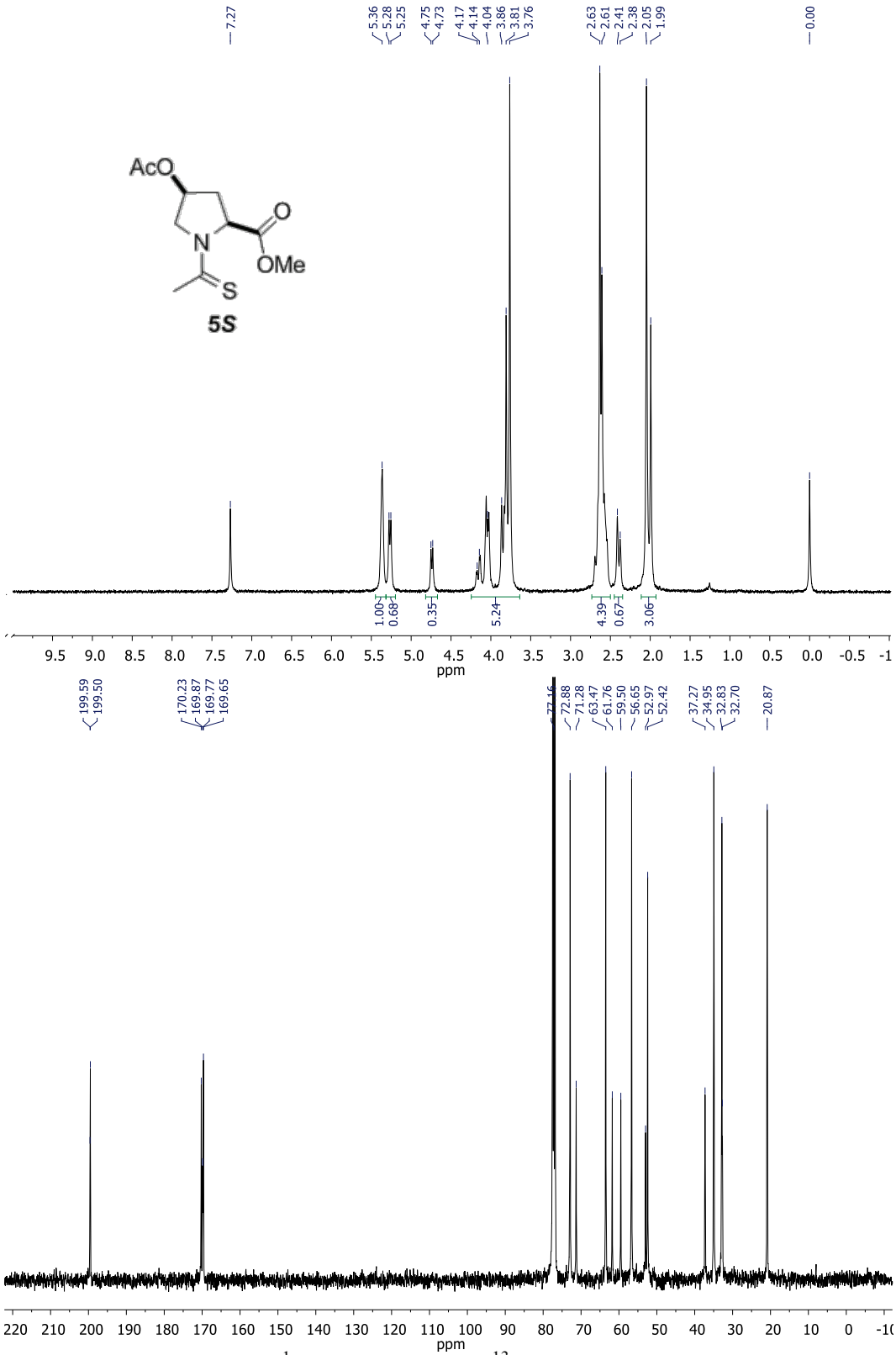


**Figure S13.** 400MHz $^{1}H$ and 100.6 MHz $^{13}C$ NMR spectra of 5***S*** in $CDCl_3$.

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