Supporting Information

A Straightforward Synthesis of Functionalized cis-Perhydroisoquinolin-1-ones

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I) Copies of $^1$H- and $^{13}$C-NMR spectra

![NMR Spectrum](image)

(400 MHz, CDCl$_3$)

![NMR Spectrum](image)

(100.6 MHz, CDCl$_3$)
3b
(400 MHz, CDCl$_3$)

3b
(100.6 MHz, CDCl$_3$)
4a
(300 MHz, CDCl₃)

4a
(100.6 MHz, CDCl₃)
\begin{align*}
\text{Me} & \\
\text{N} & \\
\text{O} & \\
\text{SPh} & \\
\end{align*}

\textbf{4b} \\
(400 MHz, CDCl$_3$)

\begin{align*}
\text{Me} & \\
\text{N} & \\
\text{O} & \\
\text{SPh} & \\
\end{align*}

\textbf{4b} \\
(100.6 MHz, CDCl$_3$)
5b
(400 MHz, CDCl₃)

5b
(100.6 MHz, CDCl₃)
6a
(400 MHz, CDCl₃)

6a
(100.8 MHz, CDCl₃)
6b
(400 MHz, CDCl₃)

6b
(100.6 MHz, CDCl₃)
$\text{Ts}$

\[
\begin{align*}
\text{N} & \text{O} \\
\text{SO}_2\text{Ph}
\end{align*}
\]

**6c**

$(400 \text{ MHz, CDCl}_3)$

---

$\text{Ts}$

\[
\begin{align*}
\text{N} & \text{O} \\
\text{SO}_2\text{Ph}
\end{align*}
\]

**6c**

$(100.6 \text{ MHz, CDCl}_3)$
(400 MHz, CDCl₃)

(100.6 MHz, CDCl₃)
$12b$

$(400 \text{ MHz, CDCl$_3$})$

$12b$

$(100.6 \text{ MHz, CDCl$_3$})$
14b

(400 MHz, CDCl₃)

14b

(100.6 MHz, CDCl₃)
\[ 16 \]

(400 MHz, CDCl\textsubscript{3})

\[ 16 \]

(100.6 MHz, CDCl\textsubscript{3})
18b

(400 MHz, CDCl₃)

18b

(100.6 MHz, CDCl₃)
II) Copies of NOE NMR spectra 13a, 14a, and 14b
NOE effect

14a

(400 MHz, CDCl₃)
NOE effect

14b

(400 MHz, CDCl₃)
III) X-ray crystallographic data for compounds 10a, 12a, and 12b

Table S1. Crystal data and structure refinement for compound 10a.

| Description                              | Value                  |
|------------------------------------------|------------------------|
| Identification code                      | Jb95                   |
| Empirical formula                        | C23 H29 N O8 S         |
| Formula weight                           | 479.53                 |
| Temperature                              | 294(2) K               |
| Wavelength                               | 0.71073 Å              |
| Crystal system                           | Orthorhombic           |
| Space group                              | P 21 21 21             |
| Unit cell dimensions                     | a = 7.948(3) Å         |
|                                          | b = 10.790(3) Å        |
|                                          | c = 27.749(9) Å        |
| Volume                                   | 2379.7(14) Å³          |
| Z                                        | 4                      |
| Density (calculated)                     | 1.338 Mg/m³            |
| Absorption coefficient                   | 0.184 mm⁻¹             |
| F(000)                                   | 1016                   |
| Crystal size                             | 0.45 x 0.27 x 0.15 mm³ |
| Theta range for data collection          | 1.47 to 24.96°         |
| Index ranges                             | 0<=h<=9, 0<=k<=12, 0<=l<=32 |
| Reflections collected                    | 2468                   |
| Independent reflections                  | 2398 [R(int) = 0.0534] |
| Completeness to theta = 24.96°          | 99.8 %                 |
| Max. and min. transmission               | 0.9729 and 0.9218      |
| Refinement method                        | Full-matrix least-squares on F² |
| Data / restraints / parameters            | 2398 / 0 / 304         |
| Goodness-of-fit on F²                    | 0.958                  |
| Final R indices [I>2sigma(I)]            | R1 = 0.0559, wR2 = 0.1214 |
| R indices (all data)                     | R1 = 0.1161, wR2 = 0.1470 |
| Absolute structure parameter             | -0.1(2)                |
| Largest diff. peak and hole              | 0.220 and -0.256 e Å³  |

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Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for jb95. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|   | x     | y     | z     | U(eq) |
|---|-------|-------|-------|-------|
| S(1)| 6582(2)| 1618(2)| 4083(1)| 57(1) |
| O(1)| 8167(6)| 1911(5)| 3856(2)| 75(2) |
| O(2)| 6553(7)| 1294(4)| 4584(2)| 76(2) |
| O(6)| 1414(6)| 5630(5)| 4169(2)| 79(2) |
| O(10)| 5358(6)| 3177(5)| 3147(2)| 68(2) |
| O(11)| 8107(8)| 4282(5)| 2805(2)| 89(2) |
| O(12)| 8266(7)| 6097(5)| 3187(2)| 70(1) |
| O(51)| 2924(7)| 6523(5)| 4904(2)| 80(2) |
| O(52)| 4939(7)| 5391(5)| 5234(2)| 68(1) |
| N(1)| 6969(7)| 4561(5)| 3565(2)| 53(2) |
| C(2)| 7303(8)| 5248(6)| 4012(2)| 53(2) |
| C(3)| 7099(8)| 4426(7)| 4449(2)| 53(2) |
| C(4)| 5357(8)| 3813(6)| 4450(2)| 46(2) |
| C(5)| 3927(8)| 4767(6)| 4474(2)| 47(2) |
| C(6)| 2625(9)| 4752(7)| 4167(3)| 58(2) |
| C(7)| 2348(8)| 3766(7)| 3807(3)| 60(2) |
| C(8)| 3301(8)| 2602(6)| 3921(2)| 48(2) |
| C(9)| 5178(8)| 2995(6)| 4001(2)| 45(2) |
| C(10)| 5832(9)| 3587(6)| 3526(3)| 51(2) |
| C(11)| 7818(10)| 4960(7)| 3146(3)| 62(2) |
| C(12)| 8442(11)| 6864(8)| 2359(3)| 99(3) |
| C(13)| 8442(11)| 6864(8)| 2359(3)| 99(3) |
| C(14)| 11002(9)| 6081(7)| 2780(3)| 77(2) |
| C(15)| 9630(11)| 7999(7)| 3075(3)| 85(3) |
| C(51)| 3888(9)| 5628(7)| 4873(3)| 59(2) |
| C(52)| 4860(11)| 6166(8)| 5662(3)| 94(3) |
| C(81)| 2539(9)| 1939(6)| 4356(3)| 62(2) |
| C(91)| 5719(9)| 355(7)| 3758(3)| 56(2) |
| C(92)| 5774(11)| 357(8)| 3271(3)| 80(3) |
| C(93)| 5130(16)| -661(12)| 3024(5)| 127(5) |
| C(94)| 4492(14)| -1639(14)| 3279(7)| 134(7) |
| C(95)| 4475(14)| -1643(11)| 3753(5)| 123(5) |
| C(96)| 5069(11)| -601(8)| 4020(4)| 92(3) |
Table S3. Bond lengths [Å] and angles [°] for j9b95.

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| S(1)-O(2)             | 1.436(5)   |           |
| S(1)-O(1)             | 1.444(5)   |           |
| S(1)-C(91)            | 1.771(7)   |           |
| S(1)-C(9)             | 1.871(6)   |           |
| O(6)-C(6)             | 1.350(8)   |           |
| O(10)-C(10)           | 1.204(7)   |           |
| O(11)-C(11)           | 1.218(8)   |           |
| O(12)-C(11)           | 1.282(8)   |           |
| O(12)-C(12)           | 1.488(8)   |           |
| O(51)-C(51)           | 1.236(8)   |           |
| O(52)-C(51)           | 1.329(8)   |           |
| O(52)-C(52)           | 1.453(8)   |           |
| N(1)-C(10)            | 1.391(8)   |           |
| N(1)-C(11)            | 1.412(9)   |           |
| N(1)-C(2)             | 1.469(7)   |           |
| C(2)-C(3)             | 1.509(8)   |           |
| C(3)-C(4)             | 1.534(9)   |           |
| C(4)-C(9)             | 1.534(9)   |           |
| C(4)-C(5)             | 1.535(9)   |           |
| C(5)-C(6)             | 1.341(9)   |           |
| C(5)-C(51)            | 1.446(9)   |           |
| C(6)-C(7)             | 1.475(9)   |           |
| C(7)-C(8)             | 1.500(9)   |           |
| C(8)-C(81)            | 1.528(8)   |           |
| C(8)-C(9)             | 1.567(8)   |           |
| C(9)-C(10)            | 1.553(9)   |           |
| C(12)-C(13)           | 1.488(10)  |           |
| C(12)-C(14)           | 1.504(10)  |           |
| C(12)-C(15)           | 1.540(10)  |           |
| C(91)-C(92)           | 1.352(10)  |           |
| C(91)-C(96)           | 1.364(11)  |           |
| C(92)-C(93)           | 1.392(13)  |           |
| C(93)-C(94)           | 1.368(18)  |           |
| C(94)-C(95)           | 1.315(17)  |           |
| C(95)-C(96)           | 1.427(14)  |           |
| O(2)-S(1)-O(1)        | 119.4(3)   |           |
| O(2)-S(1)-C(91)       | 107.5(4)   |           |
| O(1)-S(1)-C(91)       | 106.5(3)   |           |
| O(2)-S(1)-C(9)        | 107.5(3)   |           |
| O(1)-S(1)-C(9)        | 107.0(3)   |           |
| C(91)-S(1)-C(9)       | 108.6(3)   |           |
| C(11)-O(12)-C(12)     | 123.2(6)   |           |
| C(51)-O(52)-C(52)     | 118.5(6)   |           |
| C(10)-N(1)-C(11)      | 118.5(6)   |           |
Table S3. Cont.

| Bond                        | Distance (Å) |
|-----------------------------|--------------|
| C(10)-N(1)-C(2)            | 124.4(6)     |
| C(11)-N(1)-C(2)            | 117.1(6)     |
| N(1)-C(2)-C(3)             | 111.2(5)     |
| C(2)-C(3)-C(4)             | 110.7(5)     |
| C(9)-C(4)-C(3)             | 109.2(5)     |
| C(9)-C(4)-C(5)             | 110.7(5)     |
| C(3)-C(4)-C(5)             | 112.3(5)     |
| C(6)-C(5)-C(1)             | 118.6(6)     |
| C(6)-C(5)-C(4)             | 122.4(6)     |
| C(51)-C(5)-C(4)            | 118.7(6)     |
| C(5)-C(6)-O(6)             | 122.6(7)     |
| C(5)-C(6)-C(7)             | 123.6(7)     |
| O(6)-C(6)-C(7)             | 113.8(6)     |
| C(6)-C(7)-C(8)             | 112.7(6)     |
| C(7)-C(8)-C(9)             | 111.0(6)     |
| C(7)-C(8)-C(10)            | 106.5(5)     |
| C(81)-C(8)-C(9)            | 113.1(5)     |
| C(4)-C(9)-C(10)            | 114.9(5)     |
| C(4)-C(9)-C(8)             | 111.0(5)     |
| C(10)-C(9)-C(8)            | 108.1(5)     |
| C(4)-C(9)-S(1)             | 107.7(4)     |
| C(10)-C(9)-S(1)            | 103.3(4)     |
| C(8)-C(9)-S(1)             | 111.7(4)     |
| O(10)-C(10)-N(1)           | 123.3(6)     |
| O(10)-C(10)-C(9)           | 119.1(6)     |
| N(1)-C(10)-C(9)            | 117.6(6)     |
| O(11)-C(11)-O(12)          | 126.2(8)     |
| O(11)-C(11)-N(1)           | 123.2(7)     |
| O(12)-C(11)-N(1)           | 110.6(7)     |
| C(13)-C(12)-O(12)          | 110.5(6)     |
| C(13)-C(12)-C(14)          | 112.9(7)     |
| O(12)-C(12)-C(14)          | 109.9(6)     |
| C(13)-C(12)-C(15)          | 112.5(7)     |
| O(12)-C(12)-C(15)          | 101.3(6)     |
| C(14)-C(12)-C(15)          | 109.0(6)     |
| C(92)-C(91)-C(96)          | 123.1(8)     |
| C(92)-C(91)-S(1)           | 119.6(7)     |
| C(96)-C(91)-S(1)           | 117.2(7)     |
| C(91)-C(92)-C(93)          | 118.6(10)    |
| C(94)-C(93)-C(92)          | 119.4(13)    |
| C(95)-C(94)-C(93)          | 121.5(15)    |
### Table S3. Cont.

|                  | C(94)-C(95)-C(96) | C(91)-C(96)-C(95) |
|------------------|-------------------|-------------------|
|                  | 120.9(14)         | 116.4(10)         |

### Table S4. Anisotropic displacement parameters (Å² x 10³) for jβ95. The anisotropic displacement factor exponent takes the form: -2 \( \frac{h^2a^2U_{11} + \ldots + 2hkab^*U_{12}}{2} \)

|     |   U_{11}   |   U_{22}   |   U_{33}   |   U_{12}   |   U_{13}   |   U_{23}   |
|-----|------------|------------|------------|------------|------------|------------|
| S(1)|  51(1)     |  53(1)     |  66(1)     |  -1(1)     |  -10(1)    |   4(1)     |
| O(1)|  37(3)     |  78(4)     | 111(4)     |  -9(3)     |    2(3)    |  -2(3)     |
| O(2)|  96(4)     |  60(3)     |  72(3)     |   5(3)     |  -26(3)    |  18(3)     |
| O(6)|  43(3)     |  69(4)     | 125(5)     |  -7(3)     |  -6(3)     |  22(3)     |
| O(10)|  71(3)    |  77(4)     |  56(3)     |   2(3)     |  -7(3)     |  -29(3)    |
| O(11)|  93(4)    |  81(4)     |  94(4)     |  -14(3)    | 31(4)      |  -31(4)    |
| O(12)|  71(3)    |  55(3)     |  82(3)     |  10(3)     | 15(3)      |  -10(3)    |
| O(51)|  72(4)    |  63(3)     | 106(4)     |  -23(3)    |  -1(3)     |  13(3)     |
| O(52)|  65(3)    |  66(3)     |  72(3)     |  -17(3)    |   3(3)     |  -4(3)     |
| N(1)|  46(3)     |  61(4)     |  53(3)     |  -5(3)     |   6(3)     |  -13(3)    |
| C(2)|  44(4)     |  55(4)     |  60(5)     |  -3(4)     |  -2(4)     |  -7(4)     |
| C(3)|  38(4)     |  55(4)     |  67(5)     |  -10(4)    |  -3(3)     |   0(4)     |
| C(4)|  45(4)     |  46(4)     |  46(4)     |   5(3)     |  -2(3)     |   1(3)     |
| C(5)|  38(4)     |  50(4)     |  52(4)     |  -2(3)     |   3(3)     |   1(3)     |
| C(6)|  38(4)     |  52(5)     |  85(6)     |  -2(4)     |   1(4)     |  -2(4)     |
| C(7)|  33(4)     |  67(5)     |  78(5)     |   1(4)     |  -6(4)     |   7(4)     |
| C(8)|  35(3)     |  57(4)     |  52(4)     |   5(3)     |  -6(3)     |  -5(4)     |
| C(9)|  36(3)     |  43(4)     |  56(4)     |  14(3)     |  -5(3)     |   2(3)     |
| C(10)|  51(4)    |  54(5)     |  50(4)     |   4(4)     |  -2(4)     |   1(4)     |
| C(11)|  60(5)    |  60(5)     |  67(5)     |  -2(4)     |   2(4)     |  -9(4)     |
| C(12)|  52(4)    |  66(5)     |  68(5)     |  18(4)     |   3(4)     | -12(5)     |
| C(13)|  93(6)    | 128(8)     |  76(5)     |  38(6)     |  -11(6)    | -32(7)     |
| C(14)|  51(5)    |  79(6)     | 100(6)     |   0(5)     |   3(5)     |   3(5)     |
| C(15)|  89(6)    |  56(5)     | 109(7)     |   6(5)     |  26(6)     |   6(5)     |
| C(51)|  48(4)    |  62(5)     |  69(5)     |   2(4)     |  -1(4)     |  -8(4)     |
| C(52)|  82(6)    |  97(7)     | 105(7)     |  -48(6)    |  -6(6)     |   4(6)     |
| C(81)|  43(4)    |  67(5)     |  75(5)     |  10(4)     |   5(4)     |  -3(4)     |
| C(91)|  49(4)    |  52(5)     |  67(5)     |  -15(4)    |  -7(4)     |   6(4)     |
| C(92)|  79(6)    |  75(6)     |  86(6)     |  -9(5)     |  -4(5)     |  29(5)     |
| C(93)| 111(10)   | 124(10)    | 147(11)    |  -69(10)   |  -56(9)    |  58(9)     |
| C(94)|  63(7)    |  97(10)    | 242(19)    |  -73(14)   |  -36(11)   |  11(7)     |
| C(95)|  80(7)    |  68(7)     | 221(15)    |  -22(10)   |  28(10)    |   0(6)     |
| C(96)|  74(6)    |  58(5)     | 145(9)     |  -25(6)    |  21(7)     |   4(5)     |
Table S5. Crystal data and structure refinement for compound 12a.

| Property                              | Value                          |
|---------------------------------------|-------------------------------|
| Identification code                   | Jb94                          |
| Empirical formula                     | C_{19}H_{23}N_{6}O_{6}S       |
| Formula weight                        | 393.44                        |
| Temperature                           | 293(2) K                      |
| Wavelength                            | 0.71073 Å                     |
| Crystal system                        | Triclinic                     |
| Space group                           | P -1                          |
| Unit cell dimensions                  | a = 7.652(3) Å, b = 8.175(3) Å, c = 17.270(10) Å |
|                                      | = 80.94(4)°, = 79.28(4)°, = 62.69(4)° |
| Volume                                | 939.9(7) Å³                   |
| Z                                     | 2                             |
| Density (calculated)                  | 1.390 Mg/m³                   |
| Absorption coefficient                | 0.208 mm⁻¹                    |
| F(000)                                | 416                           |
| Crystal size                          | 0.45 x 0.39 x 0.21 mm³        |
| Theta range for data collection       | 1.20 to 24.97°                |
| Index ranges                          | -8<=h<=9, -9<=k<=9, 0<=l<=20   |
| Reflections collected                 | 3556                          |
| Independent reflections              | 3294 [R(int) = 0.0452]        |
| Completeness to theta = 24.97°        | 100.0 %                       |
| Refinement method                     | Full-matrix least-squares on F² |
| Data / restraints / parameters        | 3294 / 0 / 248                |
| Goodness-of-fit on F²                 | 1.054                         |
| Final R indices [I>2sigma(I)]         | R1 = 0.0451, wR2 = 0.1184     |
| R indices (all data)                  | R1 = 0.0607, wR2 = 0.1255     |
| Largest diff. peak and hole           | 0.314 and -0.267 e.Å⁻³        |
Table S6. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for jb94. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|   | x    | y    | z    | U(eq) |
|---|------|------|------|-------|
| S(1) | 3709(1) | 3363(1) | 2117(1) | 36(1) |
| O(1) | 3669(3) | 4156(2) | 2806(1) | 51(1) |
| O(2) | 5595(2) | 2370(2) | 1661(1) | 54(1) |
| O(6) | -656(3) | -921(3) | 3763(1) | 65(1) |
| O(10) | 2083(3) | 1508(2) | 1128(1) | 53(1) |
| O(11) | 1981(3) | -2493(3) | 4700(1) | 70(1) |
| O(12) | 4294(3) | -1486(2) | 4591(1) | 56(1) |
| N(1) | 4416(3) | -1052(3) | 1677(1) | 41(1) |
| C(1) | 4852(4) | -1984(4) | 963(2) | 57(1) |
| C(2) | 5500(3) | -2140(3) | 2337(2) | 44(1) |
| C(3) | 5560(3) | -933(3) | 2893(1) | 41(1) |
| C(4) | 3466(3) | 526(3) | 3162(1) | 34(1) |
| C(5) | 2184(3) | -372(3) | 3618(1) | 38(1) |
| C(6) | 434(4) | -59(3) | 3406(2) | 44(1) |
| C(7) | -535(4) | 1385(4) | 2776(2) | 48(1) |
| C(8) | 266(3) | 2822(3) | 2617(1) | 39(1) |
| C(9) | 2551(3) | 1748(3) | 2428(1) | 32(1) |
| C(10) | 3009(3) | 704(3) | 1690(1) | 37(1) |
| C(11) | 2787(4) | -1558(3) | 4340(2) | 47(1) |
| C(12) | 5003(5) | -2610(4) | 5303(2) | 77(1) |
| C(13) | -457(4) | 4021(3) | 3316(2) | 52(1) |
| C(14) | 2222(3) | 5159(3) | 1466(1) | 34(1) |
| C(15) | 820(3) | 6827(3) | 1746(1) | 39(1) |
| C(16) | -290(4) | 8206(3) | 1218(2) | 48(1) |
| C(17) | -6(4) | 7926(3) | 432(2) | 52(1) |
| C(18) | 1433(5) | 6285(4) | 157(2) | 62(1) |
| C(19) | 2573(4) | 4898(3) | 672(2) | 51(1) |
Table S7. Bond lengths [Å] and angles [°] for jß94.

| Bond                  | Length  |
|-----------------------|---------|
| S(1)-O(1)             | 1.4321(19) |
| S(1)-O(2)             | 1.437(2)  |
| S(1)-C(14)            | 1.771(2)  |
| S(1)-C(9)             | 1.868(2)  |
| O(6)-C(6)             | 1.335(3)  |
| O(10)-C(10)           | 1.226(3)  |
| O(11)-C(11)           | 1.222(3)  |
| O(12)-C(11)           | 1.333(3)  |
| O(12)-C(12)           | 1.444(3)  |
| N(1)-C(10)            | 1.343(3)  |
| N(1)-C(1)             | 1.456(3)  |
| N(1)-C(2)             | 1.462(3)  |
| C(2)-C(3)             | 1.501(3)  |
| C(3)-C(4)             | 1.533(3)  |
| C(4)-C(5)             | 1.521(3)  |
| C(4)-C(9)             | 1.545(3)  |
| C(5)-C(6)             | 1.354(3)  |
| C(5)-C(11)            | 1.459(3)  |
| C(6)-C(7)             | 1.489(3)  |
| C(7)-C(8)             | 1.525(3)  |
| C(8)-C(13)            | 1.533(4)  |
| C(8)-C(9)             | 1.551(3)  |
| C(9)-C(10)            | 1.540(3)  |
| C(14)-C(19)           | 1.378(3)  |
| C(14)-C(15)           | 1.385(3)  |
| C(15)-C(16)           | 1.382(3)  |
| C(16)-C(17)           | 1.374(4)  |
| C(17)-C(18)           | 1.374(4)  |
| C(18)-C(19)           | 1.379(4)  |
| O(1)-S(1)-O(2)        | 118.30(12) |
| O(1)-S(1)-C(14)       | 108.32(11) |
| O(2)-S(1)-C(14)       | 106.63(11) |
| O(1)-S(1)-C(9)        | 107.98(10) |
| O(2)-S(1)-C(9)        | 107.41(11) |
| C(14)-S(1)-C(9)       | 107.79(10) |
| C(11)-O(12)-C(12)     | 117.5(2)   |
| C(10)-N(1)-C(1)       | 118.1(2)   |
| C(10)-N(1)-C(2)       | 125.01(19) |
| C(1)-N(1)-C(2)        | 116.9(2)   |
| N(1)-C(2)-C(3)        | 111.79(18) |
| C(2)-C(3)-C(4)        | 110.79(18) |
| C(5)-C(4)-C(3)        | 111.12(18) |
| C(5)-C(4)-C(9)        | 111.53(17) |
| C(3)-C(4)-C(9)        | 108.73(18) |
Table S7. Cont.

| Bond                  | Angle (°) |
|-----------------------|-----------|
| C(6)-C(5)-C(11)       | 117.4(2)  |
| C(6)-C(5)-C(4)        | 122.8(2)  |
| C(11)-C(5)-C(4)       | 119.7(2)  |
| O(6)-C(6)-C(5)        | 124.1(2)  |
| O(6)-C(6)-C(7)        | 113.0(2)  |
| C(5)-C(6)-C(7)        | 122.8(2)  |
| C(6)-C(7)-C(8)        | 111.30(19)|
| C(7)-C(8)-C(13)       | 110.2(2)  |
| C(7)-C(8)-C(9)        | 106.62(18)|
| C(13)-C(8)-C(9)       | 115.0(2)  |
| C(10)-C(9)-C(4)       | 114.97(17)|
| C(10)-C(9)-C(8)       | 107.96(18)|
| C(4)-C(9)-C(8)        | 110.73(18)|
| C(10)-C(9)-S(1)       | 104.17(15)|
| C(4)-C(9)-S(1)        | 107.67(14)|
| C(8)-C(9)-S(1)        | 111.17(15)|
| O(10)-C(10)-N(1)      | 121.7(2)  |
| O(10)-C(10)-C(9)      | 118.9(2)  |
| N(1)-C(10)-C(9)       | 119.39(19)|
| O(11)-C(11)-O(12)     | 122.3(2)  |
| O(11)-C(11)-C(5)      | 124.5(2)  |
| O(12)-C(11)-C(5)      | 113.2(2)  |
| C(19)-C(14)-C(15)     | 121.0(2)  |
| C(19)-C(14)-S(1)      | 118.64(18)|
| C(15)-C(14)-S(1)      | 120.24(18)|
| C(16)-C(15)-C(14)     | 118.6(2)  |
| C(17)-C(16)-C(15)     | 120.6(2)  |
| C(16)-C(17)-C(18)     | 120.2(2)  |
| C(17)-C(18)-C(19)     | 120.1(3)  |
| C(14)-C(19)-C(18)     | 119.4(2)  |
**Table S8.** Anisotropic displacement parameters (Å²x 10³) for jb94. The anisotropic displacement factor exponent takes the form: -2 \[ h^2a^*U^{11} + ... + 2hk a^*b^* U^{12} \]

|        | U¹¹  | U²²  | U³³  | U²³  | U¹³  | U¹²  |
|--------|------|------|------|------|------|------|
| S(1)   | 36(1)| 30(1)| 42(1)| 4(1) | -14(1)| -13(1)|
| O(1)   | 71(1)| 44(1)| 51(1)| 5(1) | -31(1)| -32(1)|
| O(2)   | 33(1)| 42(1)| 74(1)| 5(1) | -2(1) | -11(1)|
| O(6)   | 58(1)| 64(1)| 81(2)| 20(1)| -17(1)| -38(1)|
| O(10)  | 68(1)| 51(1)| 42(1)| 3(1) | -30(1)| -22(1)|
| O(11)  | 83(2)| 62(1)| 66(1)| 28(1)| -20(1)| -40(1)|
| O(12)  | 75(1)| 53(1)| 44(1)| 14(1)| -31(1)| -28(1)|
| N(1)   | 41(1)| 36(1)| 44(1)| -10(1)| -7(1) | -14(1)|
| C(1)   | 60(2)| 59(2)| 60(2)| -24(1)| 3(1)  | -31(1)|
| C(2)   | 36(1)| 33(1)| 56(2)| 0(1)  | -8(1) | -9(1) |
| C(3)   | 32(1)| 36(1)| 49(1)| 9(1)  | -18(1)| -9(1) |
| C(4)   | 37(1)| 29(1)| 34(1)| 2(1)  | -16(1)| -11(1)|
| C(5)   | 42(1)| 32(1)| 37(1)| 2(1)  | -11(1)| -14(1)|
| C(6)   | 46(1)| 40(1)| 47(2)| 4(1)  | -10(1)| -21(1)|
| C(7)   | 37(1)| 53(2)| 54(2)| 8(1)  | -18(1)| -20(1)|
| C(8)   | 31(1)| 37(1)| 42(1)| 10(1) | -13(1)| -10(1)|
| C(9)   | 33(1)| 27(1)| 33(1)| 3(1)  | -13(1)| -10(1)|
| C(10)  | 41(1)| 39(1)| 37(1)| 0(1)  | -14(1)| -20(1)|
| C(11)  | 57(2)| 37(1)| 42(1)| 4(1)  | -15(1)| -17(1)|
| C(12)  | 104(3)| 69(2)| 57(2)| 22(2)| -49(2)| -31(2)|
| C(13)  | 46(1)| 38(1)| 55(2)| 0(1)  | 0(1)  | -7(1) |
| C(14)  | 37(1)| 26(1)| 37(1)| 2(1)  | -10(1)| -13(1)|
| C(15)  | 41(1)| 33(1)| 41(1)| 2(1)  | -6(1) | -15(1)|
| C(16)  | 39(1)| 32(1)| 64(2)| 7(1)  | -9(1) | -11(1)|
| C(17)  | 61(2)| 44(1)| 59(2)| 19(1) | -33(1)| -27(1)|
| C(18)  | 100(2)| 49(2)| 40(2)| 7(1)  | -24(2)| -35(2)|
| C(19)  | 75(2)| 36(1)| 38(1)| 0(1)  | -11(1)| -20(1)|

**Table S9.** Hydrogen bonds for jb94 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| O(6)-H(6)...O(11) | 0.82  | 1.84  | 2.553(3) | 145.3 |
Table S10. Crystal data and structure refinement for compound 12b.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Identification code                   | Jb96                                       |
| Empirical formula                     | C19 H23 N O6 S                             |
| Formula weight                        | 393.44                                     |
| Temperature                           | 294(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system                        | Orthorhombic                               |
| Space group                           | P 2 1 2 1                                  |
| Unit cell dimensions                  | a = 8.256(2) Å                             |
|                                       | b = 11.521(14) Å                           |
|                                       | c = 19.717(3) Å                            |
| Volume                                | 1875.4(6) Å                                |
| Z                                     | 4                                          |
| Density (calculated)                  | 1.393 Mg/m³                                |
| Absorption coefficient                | 0.209 mm⁻¹                                 |
| F(000)                                | 832                                        |
| Crystal size                          | 0.39 x 0.21 x 0.21 mm³                     |
| Theta range for data collection       | 2.05 to 24.97°                             |
| Index ranges                          | -9 <= h <= 9, 0 <= k <= 13, 0 <= l <= 23  |
| Reflections collected                 | 3689                                       |
| Independent reflections               | 3289 [R(int) = 0.0455]                     |
| Completeness to theta = 24.97°        | 100.0%                                     |
| Max. and min. transmission            | 0.9574 and 0.9230                          |
| Refinement method                     | Full-matrix least-squares on F²            |
| Data / restraints / parameters         | 3289 / 0 / 248                             |
| Goodness-of-fit on F²                 | 0.971                                      |
| Final R indices [I>2sigma(I)]         | R1 = 0.0492, wR2 = 0.0858                  |
| R indices (all data)                  | R1 = 0.0944, wR2 = 0.0962                  |
| Absolute structure parameter          | -0.05(12)                                  |
| Largest diff. peak and hole           | 0.159 and -0.189 e.Å⁻³                    |
Table S11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for jb96. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|     | x    | y    | z    | $U(\text{eq})$ |
|-----|------|------|------|---------------|
| S(1) | 2860(1) | 4807(1) | 6406(1) | 46(1)        |
| O(1) | 1504(3) | 4042(2) | 6520(1) | 59(1)        |
| O(2) | 3254(3) | 5645(2) | 6923(1) | 59(1)        |
| O(6) | 6615(4) | 4060(3) | 8239(1) | 83(1)        |
| O(10) | 3428(3) | 2795(2) | 5397(1) | 57(1)        |
| O(51) | 8625(4) | 5592(3) | 7879(1) | 92(1)        |
| O(52) | 8414(3) | 6362(3) | 6852(2) | 64(1)        |
| N(1) | 5486(3) | 3898(3) | 5030(1) | 39(1)        |
| C(2) | 6916(4) | 4605(3) | 5151(2) | 47(1)        |
| C(3) | 7538(4) | 4440(3) | 5864(2) | 43(1)        |
| C(4) | 6200(3) | 4734(3) | 6374(2) | 37(1)        |
| C(5) | 6791(4) | 4738(3) | 7103(2) | 46(1)        |
| C(6) | 6124(5) | 4054(4) | 7591(2) | 54(1)        |
| C(7) | 4768(5) | 3239(4) | 7467(2) | 60(1)        |
| C(8) | 4649(5) | 2872(3) | 6730(2) | 49(1)        |
| C(9) | 4712(4) | 3936(3) | 6249(2) | 36(1)        |
| C(10) | 4529(4) | 3481(3) | 5516(2) | 39(1)        |
| C(11) | 5115(4) | 3627(4) | 4322(2) | 55(1)        |
| C(51) | 8005(5) | 5566(4) | 7319(2) | 62(1)        |
| C(52) | 9650(5) | 7218(4) | 7051(2) | 87(2)        |
| C(81) | 5969(5) | 1973(3) | 6574(2) | 68(1)        |
| C(91) | 2523(4) | 5564(3) | 5638(2) | 43(1)        |
| C(92) | 1552(4) | 5088(4) | 5138(2) | 50(1)        |
| C(93) | 1327(5) | 5689(4) | 4537(2) | 59(1)        |
| C(94) | 2086(6) | 6726(4) | 4432(2) | 70(1)        |
| C(95) | 3048(5) | 7190(4) | 4921(3) | 71(1)        |
| C(96) | 3239(5) | 6624(4) | 5543(2) | 58(1)        |
Table S12. Bond lengths [Å] and angles [°] for jb96.

| Bond                  | Length  |
|-----------------------|---------|
| S(1)-O(1)             | 1.442(2) |
| S(1)-O(2)             | 1.442(2) |
| S(1)-C(91)            | 1.770(4) |
| S(1)-C(9)             | 1.855(3) |
| O(6)-C(6)             | 1.341(4) |
| O(10)-C(10)           | 1.227(4) |
| O(51)-C(51)           | 1.218(4) |
| O(52)-C(51)           | 1.343(5) |
| O(52)-C(52)           | 1.472(5) |
| N(1)-C(10)            | 1.332(4) |
| N(1)-C(2)             | 1.454(4) |
| N(1)-C(11)            | 1.462(4) |
| C(2)-C(3)             | 1.509(4) |
| C(3)-C(4)             | 1.531(4) |
| C(4)-C(5)             | 1.519(4) |
| C(4)-C(9)             | 1.554(4) |
| C(5)-C(6)             | 1.359(5) |
| C(5)-C(51)            | 1.448(5) |
| C(6)-C(7)             | 1.482(6) |
| C(7)-C(8)             | 1.517(5) |
| C(8)-C(81)            | 1.534(5) |
| C(8)-C(9)             | 1.550(5) |
| C(9)-C(10)            | 1.544(5) |
| C(91)-C(96)           | 1.370(5) |
| C(91)-C(92)           | 1.384(5) |
| C(92)-C(93)           | 1.385(5) |
| C(93)-C(94)           | 1.365(5) |
| C(94)-C(95)           | 1.358(6) |
| C(95)-C(96)           | 1.398(5) |
| O(1)-S(1)-O(2)        | 118.26(15) |
| O(1)-S(1)-C(91)       | 108.21(16) |
| O(2)-S(1)-C(91)       | 108.10(17) |
| O(1)-S(1)-C(9)        | 109.62(15) |
| O(2)-S(1)-C(9)        | 107.13(15) |
| C(91)-S(1)-C(9)       | 104.70(15) |
| C(51)-O(52)-C(52)     | 116.6(3)  |
| C(10)-N(1)-C(2)       | 124.4(3)  |
| C(10)-N(1)-C(11)      | 119.0(3)  |
| C(2)-N(1)-C(11)       | 116.6(3)  |
| N(1)-C(2)-C(3)        | 111.0(3)  |
| C(2)-C(3)-C(4)        | 109.8(3)  |
| C(5)-C(4)-C(3)        | 113.0(3)  |
| C(5)-C(4)-C(9)        | 113.9(3)  |
| C(3)-C(4)-C(9)        | 109.6(3)  |
| Bond                  | Angle (°)   |
|----------------------|-------------|
| C(6)-C(5)-C(51)      | 117.0(3)    |
| C(6)-C(5)-C(4)       | 122.6(3)    |
| C(51)-C(5)-C(4)      | 120.2(3)    |
| O(6)-C(6)-C(5)       | 123.3(4)    |
| O(6)-C(6)-C(7)       | 112.9(4)    |
| C(5)-C(6)-C(7)       | 123.8(3)    |
| C(6)-C(7)-C(8)       | 112.5(3)    |
| C(7)-C(8)-C(81)      | 109.5(3)    |
| C(7)-C(8)-C(9)       | 111.3(3)    |
| C(81)-C(8)-C(9)      | 112.8(3)    |
| C(10)-C(9)-C(8)      | 107.5(3)    |
| C(10)-C(9)-C(4)      | 115.2(3)    |
| C(8)-C(9)-C(4)       | 113.4(3)    |
| C(10)-C(9)-S(1)      | 105.0(2)    |
| C(8)-C(9)-S(1)       | 107.3(2)    |
| C(4)-C(9)-S(1)       | 107.8(2)    |
| O(10)-C(10)-N(1)     | 122.2(3)    |
| O(10)-C(10)-C(9)     | 118.1(3)    |
| N(1)-C(10)-C(9)      | 119.5(3)    |
| O(51)-C(51)-O(52)    | 120.0(4)    |
| O(51)-C(51)-C(5)     | 125.0(4)    |
| O(52)-C(51)-C(5)     | 115.0(3)    |
| C(96)-C(91)-C(92)    | 120.5(4)    |
| C(96)-C(91)-S(1)     | 119.2(3)    |
| C(92)-C(91)-S(1)     | 120.3(3)    |
| C(91)-C(92)-C(93)    | 119.2(4)    |
| C(94)-C(93)-C(92)    | 120.5(4)    |
| C(95)-C(94)-C(93)    | 120.3(4)    |
| C(94)-C(95)-C(96)    | 120.4(4)    |
| C(91)-C(96)-C(95)    | 119.1(4)    |
Table S13. Anisotropic displacement parameters (Å$^2$ x 10$^3$) for jb96. The anisotropic displacement factor exponent takes the form: -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) | 38(1) | 59(1) | 40(1) | -3(1) | 4(1) | 3(1) |
| O(1) | 38(1) | 81(2) | 58(2) | 6(2) | 11(1) | -8(2) |
| O(2) | 58(2) | 74(2) | 46(2) | -27(1) | -6(1) | 11(2) |
| O(6) | 95(3) | 119(3) | 34(2) | -2(2) | -14(2) | 16(2) |
| O(10) | 59(2) | 64(2) | 49(2) | -11(1) | 3(1) | -20(2) |
| O(51) | 91(2) | 128(3) | 56(2) | -20(2) | -30(2) | -6(2) |
| O(52) | 53(2) | 64(2) | 75(2) | -24(2) | -13(2) | -6(2) |
| N(1) | 38(2) | 49(2) | 30(2) | -3(2) | 2(1) | -5(2) |
| C(2) | 47(2) | 54(3) | 42(2) | -5(2) | 5(2) | -5(2) |
| C(3) | 37(2) | 50(2) | 43(2) | -5(2) | 0(2) | 1(2) |
| C(4) | 36(2) | 40(2) | 36(2) | -4(2) | 1(2) | 2(2) |
| C(5) | 43(2) | 57(3) | 37(2) | -11(2) | -6(2) | 8(2) |
| C(6) | 60(3) | 71(3) | 32(2) | -6(2) | -7(2) | 17(2) |
| C(7) | 71(3) | 72(3) | 38(2) | 10(2) | 8(2) | 5(3) |
| C(8) | 52(2) | 50(2) | 43(2) | 10(2) | 9(2) | 0(2) |
| C(9) | 37(2) | 39(2) | 31(2) | -1(2) | 2(2) | 1(2) |
| C(10) | 38(2) | 40(2) | 39(2) | -3(2) | -1(2) | 3(2) |
| C(11) | 56(3) | 75(3) | 34(2) | -7(2) | -1(2) | 0(2) |
| C(51) | 62(3) | 74(3) | 50(3) | -16(2) | -4(2) | 9(3) |
| C(52) | 57(3) | 90(4) | 114(4) | -48(3) | -3(3) | -13(3) |
| C(81) | 97(3) | 49(3) | 58(3) | 7(2) | 6(2) | 14(2) |
| C(91) | 35(2) | 45(2) | 48(2) | -2(2) | -2(2) | 5(2) |
| C(92) | 42(2) | 55(3) | 54(2) | -3(2) | -1(2) | 2(2) |
| C(93) | 61(3) | 66(3) | 51(3) | -5(2) | -12(2) | 15(2) |
| C(94) | 67(3) | 72(3) | 71(3) | 24(3) | -5(3) | 16(3) |
| C(95) | 64(3) | 45(3) | 105(4) | 19(3) | -9(3) | -1(3) |
| C(96) | 51(3) | 47(3) | 77(3) | -2(2) | -9(2) | 6(2) |