Supporting Information

for

A study of the photochemical behavior of terarylenes containing allomaltol and pyrazole fragments

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Experimental procedures, characterization data of all products, copies of $^1$H, $^{13}$C, 2D NMR, HRMS spectra of all new compounds, and X-ray crystallographic data
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1. General information.

Unless otherwise stated, all starting chemicals were commercially available and were used as received. Starting compounds 19a,b, 20a,b\textsuperscript{1} and 12a,f,h,i\textsuperscript{2} were prepared according to a procedure described previously.

NMR spectra were recorded with Bruker AM 300 (300 MHz) and Bruker DRX 500 (500 MHz) spectrometers in DMSO-\textit{d}_6. Chemical shifts (ppm) are given relative to solvent signals (DMSO-\textit{d}_6: 2.50 ppm (\textit{^1}H NMR) and 39.52 ppm (\textit{^{13}}C NMR)). High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The melting points were determined on a Kofler hot stage.

UV-irradiation was carried out with a Vilber Lourmat VL-6.LM lamp (365 nm). Photochemical reactions were performed in common borosilicate glassware at 27 °C. The distance from the light source to the irradiation vessel was 4 cm.
2. All synthesized starting compounds

The synthesis of compounds 19 and 20:

\[ \text{Ar-} \xrightarrow{\text{EtOH, reflux, 10 h}} \xrightarrow{\text{DMF-DMA, reflux, 10 min}} \]

\[ \text{19} \rightarrow \text{20} \]

a New compounds
The synthesis of compounds 12:

\[
\text{R}^1\text{NHNH}_{2}, \quad \text{EtOH, reflux, 3 h} \quad \rightarrow \quad \text{R}^2\text{NHNNH}_2, \quad \text{EtOH, reflux, 3 h}
\]

\[
\begin{align*}
12a & \quad 12b^a & \quad 12c^a & \quad 12d^a & \quad 12e^a \\
12f & \quad 12g^a & 12h & \quad 12i & \quad 12j^a \\
12k^a & \quad 12l^a & 12m^a & \quad 12n^a & \quad 12o^a
\end{align*}
\]

\(^a\) New compounds

The synthesis of compound 16:

\[
\text{Me}, \quad \text{K}_2\text{CO}_3, \quad \text{acetone, 2 h, reflux}
\]

\[
\begin{align*}
12a & \quad 16
\end{align*}
\]
3. Characterization data of compounds 19, 20, 12 and 16.

2-(2-(4-Chlorophenyl)-2-oxoethyl)-3-hydroxy-6-methyl-4H-pyran-4-one (19c)
Yellow powder; yield 31% (0.86 g); mp 201-203 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 9.01 (br. s, 1H), 8.04 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 6.23 (s, 1H), 4.43 (s, 2H), 2.22 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 193.53, 173.37, 164.59, 145.49, 142.88, 138.73, 134.46, 130.18, 128.97, 111.47, 38.63, 19.20. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{14}$H$_{11}$ClO$_2$ 279.0419; Found 279.0424.

3-Hydroxy-6-methyl-2-(2-oxo-2-(p-tolyl)ethyl)-4H-pyran-4-one (19d)
Yellow powder; yield 33% (0.85 g); mp 180-182 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.98 (br.s, 1H), 7.93 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 7.9$ Hz, 2H), 6.23 (s, 1H), 4.38 (s, 2H), 2.38 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 193.99, 173.47, 164.65, 145.99, 144.37, 142.85, 133.38, 129.47, 128.43, 111.49, 38.54, 21.25, 19.26. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{15}$H$_{14}$O$_4$ 259.0965; Found 259.0964.

3-Hydroxy-6-methyl-2-(2-oxo-2-(thiophen-2-yl)ethyl)-4H-pyran-4-one (19e)
Yellow powder; yield 27% (0.68 g); mp 122-124 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 9.04 (br.s, 1H), 8.09 (d, $J = 3.9$ Hz, 1H), 8.06 (d, $J = 4.9$ Hz, 1H), 7.33 – 7.22 (m, 1H), 6.23 (s, 1H), 4.37 (s, 2H), 2.22 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 187.37, 173.46, 164.66, 145.33, 142.92, 142.71, 135.81, 134.39, 128.96, 111.52, 38.82, 19.25. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{12}$H$_{10}$O$_4$S 251.0373; Found 251.0386.

2-(3-(4-Chlorophenyl)-1-(dimethylamino)-3-oxoprop-1-en-2-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (20c)
Yellow powder; yield 70% (0.23 g); mp 189-191 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.61 (br.s, 1H), 7.52 (s, 1H), 7.43 – 7.31 (m, 4H), 6.16 (s, 1H), 3.16 (s, 3H), 2.72 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$
2-(1-(Dimethylamino)-3-oxo-3-(p-tolyl)prop-1-en-2-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (20d)

Yellow powder; yield 82% (0.26 g); mp 174-176 °C. 

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.41 (br.s, 1H), 7.46 (s, 1H), 7.29 (d, $J = 7.7$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 6.15 (s, 1H), 3.73 – 3.10 (m, 6H), 2.29 (s, 3H), 2.15 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 190.65, 173.45, 164.22, 154.51, 146.41, 142.99, 139.64, 138.41, 129.52, 128.32, 127.66, 111.11, 98.68, 20.96, 19.49. HRMS (ESI-TOF) m/z: [M-H]$^+$ Calcld for C$_{18}$H$_{19}$NO$_4$ 312.1230; Found 312.1228.

2-(1-(Dimethylamino)-3-oxo-3-(thiophen-2-yl)prop-1-en-2-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (20e)

Brown powder; yield 77% (0.23 g); mp 167-169 °C. 

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.56 (br.s, 1H), 7.77 – 7.56 (m, 2H), 7.16 (s, 1H), 7.03 (s, 1H), 6.27 (s, 1H), 3.02 (s, 6H), 2.23 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 180.49, 173.51, 164.61, 154.33, 146.29, 145.12, 143.81, 131.09, 129.55, 127.47, 111.54, 97.49, 19.60. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcld for C$_{15}$H$_{15}$NO$_4$S 304.0638; Found 304.0632.

2-(1-(tert-Butyl)-5-phenyl-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12b)

White powder; yield 74% (0.72 g); mp 246-248 °C. 

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.68 (br.s, 1H), 8.01 (s, 1H), 7.53 – 7.42 (m, 3H), 7.43 – 7.33 (m, 2H), 5.99 (s, 1H), 1.55 (s, 3H), 1.48 – 1.38 (m, 9H). 

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 173.07, 162.84, 140.23, 136.50, 133.07, 130.62, 128.62, 127.70, 113.09, 110.19, 61.94, 30.71, 18.05. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcld for C$_{19}$H$_{20}$N$_2$O$_3$ 325.1547; Found 325.1546.
2-(1-(tert-Butyl)-5-(4-chlorophenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12c)

White powder; yield 70% (0.75 g); mp 263-265 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.79 (br.s, 1H), 8.02 (s, 1H), 7.52 (d, $J$ = 8.5 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 6.02 (s, 1H), 1.62 (s, 3H), 1.48 – 1.36 (m, 9H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 173.04, 162.79, 140.31, 138.82, 136.53, 133.60, 132.50, 131.95, 129.29, 127.79, 113.30, 110.28, 62.01, 30.70, 17.98. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{19}$H$_{19}$ClN$_2$O$_3$ 359.1157; Found 359.1148.

2-(1-(tert-Butyl)-5-(p-tolyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12d)

White powder; yield 68% (0.69 g); mp 207-209 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 9.01 (br.s, 1H), 7.99 (s, 1H), 7.33 – 7.19 (m, 4H), 6.00 (s, 1H), 2.37 (s, 3H), 1.53 (s, 3H), 1.39 (s, 9H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 172.71, 162.85, 142.16, 140.24, 139.85, 137.77, 136.26, 130.12, 129.62, 127.79, 112.72, 109.64, 61.54, 30.37, 20.33, 17.63. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{20}$H$_{22}$N$_2$O$_3$ 339.1703; Found 339.1700.

2-(1-(tert-Butyl)-5-(thiophen-2-yl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12e)

Grey powder; yield 56% (0.55 g); mp 237-239 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 9.17 (br.s, 1H), 8.01 (s, 1H), 7.85 – 7.71 (m, 1H), 7.25 (s, 1H), 7.20 – 7.12 (m, 1H), 6.08 (s, 1H), 1.71 (s, 3H), 1.58 – 1.34 (m, 9H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 173.13, 163.12, 141.77, 140.77, 136.60, 132.54, 131.69, 131.11, 128.79, 126.83, 115.21, 110.37, 62.29, 30.38, 18.39. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{17}$H$_{18}$N$_2$O$_3$S 331.1111; Found 331.1114.

2-(1-(4-Bromophenyl)-5-phenyl-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12g)

White powder; yield 75% (0.95 g); mp 245-247 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.28 (s, 1H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.47 – 7.35 (m, 3H),
7.35 – 7.27 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 6.11 (s, 1H), 1.73 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 173.29, 163.44, 141.45, 140.99, 140.54, 140.02, 138.29, 131.87, 130.19, 129.77, 128.93, 128.18, 127.30, 120.81, 112.99, 110.62, 18.35. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{21}$H$_{15}$BrN$_2$O$_3$ 423.0339; Found 423.0331.

A mixture of 3-hydroxy-6-methyl-2-(5-phenyl-1H-pyrazol-4-yl)-4H-pyran-4-one and 3-hydroxy-6-methyl-2-(3-phenyl-1H-pyrazol-4-yl)-4H-pyran-4-one isomers (12j)

Yellow powder; yield 59% (0.47 g); mp 233-240 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 13.64 – 13.31 (m, 1H), 9.14 (br.s, 1H), 8.23 (br.s, 0.5 H), 8.03 (br.s, 0.5 H) 7.56 – 7.28 (m, 5H), 6.21 (s, 1H), 1.92 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 173.40, 163.71, 142.68, 140.66, 140.08, 134.10, 129.63, 128.70, 128.30, 127.92, 127.67, 110.83, 108.90, 108.51, 18.76. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{15}$H$_{12}$N$_2$O$_3$ 269.0921; Found 269.0917.

A mixture of 2-(5-(4-chlorophenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one and 2-(3-(4-chlorophenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one isomers (12k)

Yellow powder; yield 61% (0.55 g); mp 285-287 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 13.48 (br.s, 1H), 9.13 (br.s, 1H), 8.18 (br.s, 1H), 7.59 – 7.38 (m, 4H), 6.22 (s, 1H), 1.98 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 173.35, 163.77, 142.33, 140.64, 131.15, 130.00, 128.02, 110.82, 18.79. HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{15}$H$_{11}$ClN$_2$O$_3$ 303.0531; Found 303.0530.
A mixture of \(3\)-hydroxy-\(6\)-methyl-\(2\)-(5-(p-tolyl)-1H-pyrazol-4-yl)-4H-pyran-4-one and \(3\)-hydroxy-\(6\)-methyl-\(2\)-(3-(p-tolyl)-1H-pyrazol-4-yl)-4H-pyran-4-one isomers (12l)

Pale yellow powder; yield 63\% (0.53 g); mp 253-255 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 13.37 (br.s, 1H), 9.04 (br.s, 1H), 8.09 (br.s, 1H), 7.38 (d, \(J = 7.7\) Hz, 2H), 7.23 (d, \(J = 7.7\) Hz, 2H), 6.21 (s, 1H), 2.33 (s, 3H), 1.96 (s, 3H). \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 173.42, 163.79, 148.29, 142.78, 140.72, 140.13, 138.30, 137.83, 136.91, 131.08, 128.86, 128.53, 128.16, 126.44, 110.82, 108.67, 108.34, 20.90, 18.86. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for \(C_{16}H_{14}N_2O_3\) 283.1077; Found 283.1078.

\[2-(1-Benzyl-3-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12m)\]

White powder; yield 68\% (0.79 g); mp 194-196 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 9.19 (br.s, 1H), 8.34 (s, 1H), 7.47 – 7.24 (m, 7H), 6.95 (d, \(J = 8.7\) Hz, 2H), 6.21 (s, 1H), 5.43 (s, 2H), 3.76 (s, 3H), 1.95 (s, 3H). \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 173.30, 163.66, 159.01, 148.91, 142.30, 140.52, 137.05, 132.52, 129.52, 128.65, 127.82, 125.96, 113.32, 110.87, 108.88, 55.02, 55.14, 18.87. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for \(C_{23}H_{20}N_2O_4\) 389.1496; Found 389.1503.

\[2-(1-Benzyl-3-phenyl-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12n)\]

Pale brown powder; yield 63\% (0.68 g); mp 156-158 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 9.24 (br.s, 1H), 8.39 (s, 1H), 7.52 – 7.44 (m, 2H), 7.41 – 7.25 (m, 8H), 6.21 (s, 1H), 5.46 (s, 2H), 1.89 (s, 3H). \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 173.26, 163.54, 149.08, 142.08, 140.48, 136.97, 133.61, 132.52, 128.63, 128.30, 127.82, 127.79, 110.84, 109.23, 55.04, 18.67. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for \(C_{22}H_{18}N_2O_3\) 359.1390; Found 359.1384.
2-(1-Benzyl-3-(p-tolyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (12o)

White powder; yield 72% (0.8 g); mp 211-213 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 9.18 (br.s, 1H), 8.35 (s, 1H), 7.43 – 7.26 (m, 7H), 7.19 (d, $J = 7.9$ Hz, 2H), 6.21 (s, 1H), 5.45 (s, 2H), 2.32 (s, 3H), 1.93 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 173.26, 163.61, 149.05, 142.16, 140.53, 137.01, 132.52, 130.69, 128.62, 128.40, 128.10, 127.79, 110.84, 109.02, 55.00, 20.83, 18.77.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{23}$H$_{20}$N$_2$O$_3$ 373.1547; Found 373.1542.

Experimental procedure and characterization data of compound 16.

A mixture of compound 12a (1 mmol, 0.35 g), K$_2$CO$_3$ (2 mmol, 0.27 g) and MeI (3 mmol, 0.43 g) in acetone (10 ml) was refluxed for 2 h. Then the solvent was removed under reduced pressure, H$_2$O (20 ml) was added, and the mixture was left overnight. The resulting precipitate was filtered off and washed H$_2$O (3 x 10 ml) to give the corresponding product 16.

2-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-methoxy-6-methyl-4H-pyran-4-one (16)

White powder; yield 94% (0.35 g); mp 149-151 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.96 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 6.01 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.58 (s, 3H), 1.41 (s, 9H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 174.39, 163.16, 159.59, 151.33, 142.08, 141.44, 136.70, 131.76, 124.34, 113.32, 113.22, 112.38, 61.98, 58.92, 55.25, 30.67, 17.99. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{21}$H$_{24}$N$_2$O$_4$ 369.1809; Found 369.1809.
4. Experimental procedure and characterization data of compounds 14a, 15 and 18.

*Experimental procedure for the synthesis of photoproduct 14a*

A solution of compound 12a (0.5 mmol, 0.18 g) in AcOH (25 ml) was irradiated in common glassware with a Vilber Lourmat VL-6.LM (365 nm, 6 W) for 24 h. Then the solvent was removed under reduced pressure and the residue was triturated with Et₂O (10 ml) to give the corresponding photoproduct 14a.

![5-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-5-hydroxy-4-methylcyclopent-3-ene-1,2-dione (14a)](image_url)

5-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-5-hydroxy-4-methylcyclopent-3-ene-1,2-dione (14a)

Orange powder; yield 47% (0.08 g); mp 161-163 °C. ¹H NMR (300 MHz, DMSO-ᴅ6) δ 7.62 (s, 1H), 7.02 (dd,  Jazeera 8.5, 2.2 Hz, 1H), 6.86 (dd,  Jazeera 8.4, 2.7 Hz, 1H), 6.68 (dd,  Jazeera 8.4, 2.2 Hz, 1H), 6.52 – 6.41 (m, 2H), 3.75 (s, 3H), 1.94 (s, 3H), 1.30 (s, 9H). ¹³C NMR (75 MHz, DMSO-ᴅ6) δ 201.02, 186.03, 176.73, 159.64, 137.56, 135.47, 135.23, 132.70, 132.25, 122.48, 119.40, 113.47, 72.41, 61.14, 55.21, 30.55, 14.57. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C₂₀H₂₂N₂O₄ 355.1652; Found 355.1655.

*Experimental procedure for the synthesis of compounds 15.*

A solution of compounds 12 (0.5 mmol) in AcOH (25 ml) was irradiated in common glassware with a Vilber Lourmat VL-6.LM (365 nm, 6 W) for 24 h. 1,2-Phenylendiamine (0.6 mmol, 0.07 g) was added to reaction mixture and obtained solution was refluxed for 2 h. Then the solvent was removed under reduced pressure and the residue was recrystallized from EtOH (5 ml). The resulting precipitate was filtered off and washed EtOH (3 x 5 ml) to give the corresponding product 15.

![1-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15a)](image_url)

1-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15a)

White powder; yield 81% (0.17 g); mp 243-245 °C. ¹H NMR (300 MHz, DMSO-ᴅ6) δ 7.98 – 7.90 (m, 1H), 7.82 – 7.75 (m, 1H), 7.73 (s, 1H), 7.71
\[ \text{7.59 (m, 2H), 6.86 (dd, } J = 8.5, 2.2 \text{ Hz, 1H), 6.69 (dd, } J = 8.5, 2.7 \text{ Hz, 1H), 6.21 (s, 1H), 6.08 (s, 1H), 5.86 (dd, } J = 8.5, 2.2 \text{ Hz, 1H), 5.70 (dd, } J = 8.5, 2.7 \text{ Hz, 1H), 3.52 (s, 3H), 1.88 (s, 3H), 1.25 (s, 9H).} \]
\[ \text{13C NMR (75 MHz, DMSO-\text{d}_6) } \delta 164.62, 162.14, 158.69, 157.04, 141.52, 139.10, 136.85, 136.10, 131.90, 131.38, 128.89, 128.79, 127.99, 127.79, 125.86, 122.67, 120.24, 113.35, 111.02, 78.12, 60.76, 54.84, 30.57, 12.99. \]
\[ \text{HRMS (ESI-TOF) } m/z: [M+H]^+ \text{ Calcd for } C_{26}H_{26}N_4O_2 427.2129; \text{ Found 427.2128.} \]

**1-(1-(tert-Butyl)-5-phenyl-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15b)**

Pale yellow powder; yield 72% (0.14 g); mp 255-257 °C. \(^1\)H NMR (300 MHz, DMSO-\text{d}_6) \( \delta 7.99 - 7.90 \) (m, 1H), 7.80 (s, 1H), 7.04 - 6.95 (m, 2H), 6.28 - 6.21 (m, 1H), 6.14 (d, \( J = 1.7 \) Hz, 1H), 6.10 (s, 1H), 5.95 (d, \( J = 8.0 \) Hz, 1H), 1.89 (s, 3H), 1.24 (s, 9H). \(^{13}\)C NMR (75 MHz, DMSO-\text{d}_6) \( \delta 164.54, 162.10, 157.11, 141.53, 139.11, 137.15, 136.31, 131.09, 130.56, 130.40, 129.11, 128.89, 128.15, 127.94, 127.45, 126.09, 119.90, 78.14, 61.08, 30.64, 13.13. \) HRMS (ESI-TOF) \( m/z: [M+H]^+ \) Calcd for \( C_{25}H_{24}N_4O \) 397.2023; Found 397.2013.

**1-(1-(tert-Butyl)-5-(4-chlorophenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15c)**

Pale yellow powder; yield 74% (0.16 g); mp 228-230 °C. \(^1\)H NMR (300 MHz, DMSO-\text{d}_6) \( \delta 7.99 - 7.88 \) (m, 1H), 7.03 (d, \( J = 7.8 \) Hz, 1H), 6.26 (s, 1H), 6.03 (d, \( J = 7.6 \) Hz, 1H), 1.91 (s, 3H), 1.24 (s, 9H). \(^{13}\)C NMR (75 MHz, DMSO-\text{d}_6) \( \delta 164.29, 162.38, 156.99, 141.58, 138.99, 136.34, 135.73, 133.14, 132.53, 132.09, 129.88, 129.14, 128.85, 128.06, 128.01, 127.46, 126.19, 125.97, 120.08, 78.06, 61.14, 30.62, 13.04. \) HRMS (ESI-TOF) \( m/z: [M+H]^+ \) Calcd for \( C_{25}H_{23}ClN_4O \) 431.1633; Found 431.1634.
1-(1-(tert-Butyl)-5-(p-tolyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15d)

White powder; yield 78% (0.16 g); mp 243-245 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.91 (s, 1H), 7.84 – 7.72 (m, 2H), 7.70 – 7.60 (m, 2H), 6.95 (d, $J$ = 7.7 Hz, 1H), 6.83 (d, $J$ = 7.9 Hz, 1H), 6.19 (s, 1H), 6.09 (s, 1H), 5.97 (d, $J$ = 7.8 Hz, 1H), 5.86 (d, $J$ = 7.9 Hz, 1H), 2.04 (s, 3H), 1.89 (s, 3H), 1.24 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 164.52, 162.24, 157.06, 141.66, 139.12, 137.45, 137.16, 136.26, 130.73, 130.04, 129.02, 128.87, 127.94, 126.74, 125.97, 119.98, 78.18, 60.97, 30.65, 20.76, 13.08.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{26}$H$_{28}$N$_4$O$_4$ 411.2179; Found 411.2189.

1-(1-(tert-Butyl)-5-(thiophen-2-yl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15e)

Grey powder; yield 61% (0.12 g); mp 235-237 °C. A mixture of isomers: $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.95 (d, $J$ = 6.8 Hz, 1H), 7.86 (s, 1H), 7.83 – 7.76 (m, 1H), 7.73 – 7.59 (m, 2H), 7.47 (br.s, 1H), 7.22 (br.s, 0.5 H), 6.90 (br.s, 0.5 H), 6.28 (s, 1H), 6.23 – 6.12 (m, 1.5 H), 5.59 (br.s, 0.5 H), 1.88 (s, 3H), 1.32 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 157.30, 141.54, 139.26, 136.64, 130.60, 129.74, 129.05, 128.88, 128.63, 128.21, 127.88, 126.37, 77.98, 61.41, 30.23, 13.20.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{23}$H$_{22}$N$_4$O$_2$ 403.1587; Found 403.1596

1-(5-(4-Methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15f)

Pale brown powder; yield 69% (0.15 g); mp 213-215 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.06 (s, 1H), 7.88 (dd, $J$ = 7.8, 1.9 Hz, 1H), 7.81 (dd, $J$ = 7.9, 1.8 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.29 – 7.16 (m, 3H), 7.16 – 7.08 (m, 2H), 6.48 – 6.36 (m, 3H), 6.32 – 6.23 (m, 3H), 3.48 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 164.00, 162.52, 158.79, 157.29, 141.59, 139.97, 139.57, 139.08, 137.94, 130.94, 129.13, 128.90, 128.70, 128.13, 127.97, 127.09, 126.40, 124.58, 121.07, 120.59, 112.86, 78.01, 54.86, 13.18.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{28}$H$_{22}$N$_4$O$_2$ 447.1816; Found 447.1825.
1-(1-(4-Bromophenyl)-5-phenyl-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15g)

Beige powder; yield 73% (0.18 g); mp 228-230 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.11 (s, 1H), 7.89 (dd, \(J = 7.6, 2.0\) Hz, 1H), 7.81 (dd, \(J = 7.7, 1.9\) Hz, 1H), 7.71 – 7.57 (m, 2H), 7.42 (d, \(J = 8.8\) Hz, 2H), 7.07 (d, \(J = 8.8\) Hz, 2H), 7.01 – 6.92 (m, 1H), 6.84 – 6.74 (m, 2H), 6.54 (d, \(J = 7.5\) Hz, 2H), 6.40 (d, \(J = 1.7\) Hz, 1H), 6.35 (s, 1H), 1.95 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 163.95, 162.25, 157.26, 141.55, 140.40, 138.99, 138.65, 138.11, 131.63, 129.62, 129.22, 128.89, 128.34, 128.20, 128.00, 127.47, 126.56, 126.42, 120.78, 119.97, 77.91, 13.16. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for C\(_{27}\)H\(_{19}\)BrN\(_4\)O 495.0815; Found 495.0817.

1-(1-(4-Bromophenyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15h)

Pale brown powder; yield 80% (0.21 g); mp 193-195 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.08 (s, 1H), 7.92 – 7.78 (m, 2H), 7.73 – 7.57 (m, 2H), 7.44 (d, \(J = 8.4\) Hz, 2H), 7.08 (d, \(J = 8.7\) Hz, 2H), 6.52 – 6.38 (m, 3H), 6.35 – 6.25 (m, 3H), 3.49 (s, 3H), 1.96 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 163.91, 162.48, 158.95, 157.29, 141.60, 140.41, 139.79, 139.09, 138.80, 138.04, 131.69, 130.95, 129.21, 128.93, 128.16, 128.03, 126.44, 121.00, 120.76, 119.93, 113.03, 77.99, 54.91, 13.20. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for C\(_{28}\)H\(_{21}\)BrN\(_4\)O\(_2\) 525.0921; Found 525.0916.

1-(5-(4-Methoxyphenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15i)

Pale brown powder; yield 65% (0.12 g); mp 222-224 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 12.81 (s, 1H), 7.92 – 7.73 (m, 3H), 7.73 – 7.55 (m, 2H), 6.76 (d, \(J = 8.2\) Hz, 2H), 6.56 (s, 1H), 6.49 (d, \(J = 8.1\) Hz, 2H), 6.16 (s, 1H), 3.58 (s, 3H), 1.89 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 164.41, 163.13, 158.97, 158.64, 141.64, 139.11, 129.88, 129.21, 128.93, 128.24, 128.06, 126.51, 116.87, 112.75, 78.22, 55.01, 13.25. HRMS (ESI-TOF) \(m/z\): [M+H]\(^+\) Calcd for C\(_{22}\)H\(_{18}\)N\(_4\)O\(_2\) 371.1503; Found 371.1496.
2-Methyl-1-(5-phenyl-1H-pyrazol-4-yl)-1H-cyclopenta[b]quinoxalin-1-ol (15j)

Pale brown powder; yield 61% (0.1 g); mp 282-284 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 12.53 (br.s, 1H), 7.93 – 7.79 (m, 3H), 7.72 – 7.56 (m, 2H), 7.11 – 7.01 (m, 1H), 6.99 – 6.77 (m, 4H), 6.53 (s, 1H), 6.19 (s, 1H), 1.89 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 164.46, 163.02, 157.59, 141.64, 139.10, 129.30, 128.95, 128.67, 128.31, 128.13, 127.53, 127.27, 126.65, 117.05, 78.23, 13.26. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₂₁H₁₆N₄O 341.1397; Found 341.1394.

1-(5-(4-Chlorophenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15k)

Beige powder; yield 68% (0.13 g); mp 275-277 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 13.00 (s, 1H), 8.04 – 7.76 (m, 3H), 7.71 – 7.53 (m, 2H), 7.24 – 6.86 (m, 4H), 6.63 (s, 1H), 6.21 (s, 1H), 1.93 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 164.19, 163.06, 157.36, 141.60, 138.96, 130.48, 129.28, 128.87, 128.24, 128.11, 127.16, 126.63, 117.16, 78.15, 13.22. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₂₁H₁₅ClN₄O 375.1007; Found 375.1001.

2-Methyl-1-(5-(p-tolyl)-1H-pyrazol-4-yl)-1H-cyclopenta[b]quinoxalin-1-ol (15l)

Pale brown powder; yield 63% (0.11 g); mp 278-280 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 12.86 (s, 1H), 8.07 – 7.81 (m, 2H), 7.77 – 7.53 (m, 3H), 6.87 – 6.50 (m, 5H), 6.16 (s, 1H), 2.09 (s, 3H), 1.89 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 164.35, 162.99, 157.56, 141.66, 139.08, 129.17, 128.92, 128.44, 128.23, 128.01, 127.82, 126.56, 78.17, 20.63, 13.23. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₂₂H₁₈N₄O 355.1553; Found 355.1548.

1-(1-Benzyl-3-(4-methoxyphenyl)-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15m)

Brown powder; yield 83% (0.19 g); mp 167-169 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 8.02 (s, 1H), 7.87 (d, J = 7.9 Hz, 2H), 7.73 – 7.56
(m, 2H), 7.47 – 7.26 (m, 5H), 6.69 (d, J = 8.1 Hz, 2H), 6.55 (s, 1H), 6.41 (d, J = 8.2 Hz, 2H), 6.20 (s, 1H), 5.36 (s, 2H), 3.55 (s, 3H), 1.88 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 164.17, 162.62, 158.25, 157.53, 147.94, 141.62, 139.05, 137.39, 131.49, 129.65, 129.14, 128.90, 128.58, 128.19, 127.72, 126.70, 125.99, 118.11, 112.43, 78.09, 54.87, 13.13. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{29}$H$_{24}$N$_4$O$_2$ 461.1972; Found 461.1966.

1-(1-Benzyl-3-phenyl-1H-pyrazol-4-yl)-2-methyl-1H-cyclopenta[b]quinoxalin-1-ol (15n)

Brown powder; yield 69% (0.15 g); mp 162-164 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.05 (s, 1H), 7.91 – 7.81 (m, 2H), 7.73 – 7.54 (m, 2H), 7.45 – 7.26 (m, 5H), 7.03 – 6.92 (m, 1H), 6.92 – 6.81 (m, 2H), 6.78 (d, J = 7.5 Hz, 2H), 6.53 (d, J = 2.0 Hz, 1H), 6.22 (s, 1H), 5.38 (s, 2H), 1.87 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 164.16, 162.52, 157.55, 148.17, 141.59, 139.00, 137.34, 133.68, 131.65, 129.20, 128.90, 128.60, 128.45, 128.23, 127.96, 127.76, 127.06, 126.97, 126.78, 118.13, 78.07, 54.96, 13.12. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{28}$H$_{22}$N$_4$O 431.1866; Found 431.1872.

Experimental procedure for the synthesis of compound 18.

A mixture of compound 12a (1 mmol, 0.35 g) and NaBH$_3$CN (5 mmol, 0.31 g) in MeOH$_{abs}$ (10 ml) was stirred for 24 h at room temperature. The obtained mixture was poured into
H₂O (100 ml) and AcOH (10 mmol, 0.6 g) was added. Then solution was extracted with CHCl₃ (3×25 ml). The combined CHCl₃ extract was dried over Na₂SO₄. The organic layer was evaporated in vacuum and the residue was recrystallized from Et₂O (5 ml). The resulting precipitate was filtered off and washed Et₂O (3 x 5 ml) to give the corresponding product 18.

4-(1-(tert-Butyl)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-4,5-dihydroxy-3-methylcyclopent-2-en-1-one (18).

White powder; yield 67% (0.24 g); mp 170-172 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 7.39 (s, 1H), 7.09 (dd, J = 8.4, 2.3 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.84 (dd, J = 8.4, 2.8 Hz, 1H), 6.72 (dd, J = 8.5, 2.7 Hz, 1H), 5.52 (s, 1H), 5.37 – 5.29 (m, 2H), 3.96 (s, 1H), 3.76 (s, 3H), 1.77 (s, 3H), 1.27 (s, 9H). ¹³C NMR (75 MHz, DMSO-d₆) δ 202.56, 173.37, 159.13, 138.16, 136.39, 133.43, 131.95, 127.54, 124.42, 120.25, 112.52, 112.23, 82.17, 80.73, 60.61, 55.05, 30.77, 14.68. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C₂₀H₂₄N₂O₄ 357.1809; Found 357.1807.
5. Copies of $^1$H and $^{13}$C NMR spectra for compounds 19, 20, 12 and 16.

$^1$H NMR spectrum (300 MHz) of 19c in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 19c in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 19d in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 19d in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 19e in DMSO-$d_6$

$^{13}$C $\{^1$H$\}$ NMR spectrum (75 MHz) of 19e in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 20c in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 20c in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 20d in DMSO-d$_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 20d in DMSO-d$_6$
$^1$H NMR spectrum (300 MHz) of 20e in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 20e in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12b in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 12b in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12c in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12c in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12d in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (126 MHz) of 12d in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12e in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12e in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12g in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12g in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12j in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 12j in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12k in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12k in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12I in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12I in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12m in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 12m in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12n in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 12n in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 12o in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 12o in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 16 in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 16 in DMSO-$d_6$
6. Copies of $^1$H and $^{13}$C NMR spectra for compounds 14a, 15 and 18.

$^1$H NMR spectrum (300 MHz) of 14a in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 14a in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15a in DMSO-$d_6$

$^{13}$C \{^1$H$\} NMR spectrum (75 MHz) of 15a in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15b in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 15b in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15c in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 15c in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15d in DMSO-$_d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 15d in DMSO-$_d_6$
$^1$H NMR spectrum (300 MHz) of 15e in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 15e in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15f in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 15f in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15g in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 15g in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15h in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 15h in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15i in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15j in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 15j in DMSO-$d_6$
$^{1}H$ NMR spectrum (300 MHz) of 15k in DMSO-$d_6$

$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of 15k in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15i in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 15i in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15m in DMSO-$d_6$

$^{13}$C {^1}H NMR spectrum (75 MHz) of 15m in DMSO-$d_6$
$^1$H NMR spectrum (300 MHz) of 15n in DMSO-$d_6$

$^{13}$C {$^1$H} NMR spectrum (75 MHz) of 15n in DMSO-$d_6$
\(^1\)H NMR spectrum (300 MHz) of 15o in DMSO-\(d_6\)

\(^{13}\)C \{{^1}\}H NMR spectrum (75 MHz) of 15o in DMSO-\(d_6\)
$^1$H NMR spectrum (300 MHz) of 18 in DMSO-$d_6$

$^{13}$C ($^1$H) NMR spectrum (75 MHz) of 18 in DMSO-$d_6$
7. Copies of HRMS for all compounds.

HRMS for compound 19c
HRMS for compound 19d
HRMS for compound 19e
HRMS for compound 20c
HRMS for compound 20d
HRMS for compound 20e
HRMS for compound 12b
HRMS for compound 12c
HRMS for compound 12d
HRMS for compound 12e
HRMS for compound 12g
HRMS for compound 12\text{j}

| Acquisition Parameter | Value |
|------------------------|-------|
| Source Type            | ESI   |
| Focus                  | Not active |
| Scan Begin             | 50 m/z |
| Scan End               | 1600 m/z |
| Ion Polarity           | Positive |
| Set Nebulizer          | 0.4 Bar |
| Set Dry Heater         | 185 °C |
| Set Dry Gas            | 4.0 l/min |
| Set End Plate Offset   | -300 V |
| Set Diver Valve        | Waste |

![Mass Spectrogram](https://via.placeholder.com/150)

Bruker Compass DataAnalysis 4.0

Printed: 17.03.2022 16:53:19
HRMS for compound 121

Acquisition Parameter

Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 1600 m/z

Ion Test: Positive
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Divert Valve: Waste

Intensities:

- MS, 0.5-1.0 min (35-56)

- C16H14N2O3, M+H+, 283.11

- C16H14N2O3, M+Na+, 305.09

Printed: 08.02.2022 17:39:59
HRMS for compound 12m
HRMS for compound 12n
HRMS for compound 12o
HRMS for compound 16

![HRMS Graph]

**Acquisition Parameter**
- **Source Type**: ESI
- **Ion Polarity**: Positive
- **Set Nebulizer**: 0.4 Bar
- **Set Dry Heater**: 100 °C
- **Set Capillary**: 4500 V
- **Set End Plate Offset**: -500 V
- **Set Dry Gas**: 4.0 l/min
- **Set Divert Valve**: Waste

**Mass Spectra**:
- 369.1809
- 230.2402, 622.0298, 922.0126
- 1521.9762
- 2121.6486
- 391.1624
- 407.1367
- C21H24N2O4, M+H+, 369.18
- C21H24N2O4, M+Na+, 391.16
- 407.14
- 407.368
HRMS for compound 14a
HRMS for compound 145a
HRMS for compound 15b
HRMS for compound 15c
HRMS for compound 15d
HRMS for compound 15e

[Image of a mass spectrometry chart showing molecular ions and their intensities.]
HRMS for compound 15f
HRMS for compound 15g
HRMS for compound 15h
HRMS for compound 15i
HRMS for compound 15j
HRMS for compound 15k
HRMS for compound 15I
HRMS for compound 15m
HRMS for compound 15n
HRMS for compound 15o
HRMS for compound 18
8. 2D NMR spectra for compound 14a

Table S1. Assignment of NMR signals and 2D NMR (HMBC) correlations for compound 13a

| №  | \(^1\)H          | \(^{13}\)C        | HMBC       |
|----|------------------|-------------------|------------|
| 1  |                  | 201.1             | 3, 19      |
| 2  |                  | 186.1             | 3, 6       |
| 3  | 6.47 (q, J = 1.4 Hz, 1H) | 135.3             | 6          |
| 4  |                  | 176.8             | 3, 6       |
| 5  |                  | 72.43             | 3, 6, 19   |
| 6  | 1.94 (d, J = 1.3 Hz, 3H) | 14.6              | 2, 3, 4, 5 |
| 7  | 7.62 (s, 1H)     | 135.5             | ----       |
| 8  |                  | 119.4             | 7, 19      |
| 9  |                  | 137.6             | 7, 13, 17, 19 |
| 10 |                  | 61.2              | 11         |
| 11 | 1.30 (s, 9H)     | 30.6              | 11         |
| 12 |                  | 122.5             | 14, 16     |
| 13 | 7.02 (dd, J = 8.5, 2.3 Hz, 1H) | 132.3             | 17         |
| 14 | 6.86 (dd, J = 8.5, 2.8 Hz, 1H) | 113.5             | 16         |
HMBC spectrum for compound 14a
HSQC spectrum for compound 14a
COSY spectrum for compound 14a
9. X-ray crystallographic data and refinement details

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

X-ray crystallographic data for compound 15a:

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless \( \omega \)-scan technique), using monochromatized Cu K\( \alpha \)-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program\(^3\). The structure was solved by direct methods using SHELXT\(^4\) and refined on \( F^2 \) using SHELXL-2018\(^5\) in the OLEX2 program.\(^5\) All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Locations of hydrogen atoms at oxygen atoms O1, O3, O5 and O6 were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. Site occupancies for peroxide molecules are 0.882(7) for O5-O6 and 0.103(6) for O7-O8.
Table S2. Crystal data and structure refinement for 15a.

| Identification code | 15a |
|---------------------|-----|
| Empirical formula   | C26 H26.99 N4 O2.99 |
| Formula weight      | 443.26 |
| Temperature         | 100.0(1) K |
| Wavelength          | 1.54184 Å |
| Crystal system      | Triclinic |
| Space group         | P T |
| Unit cell dimensions| a = 6.59886(6) Å, β = 64.7444(15)°. |
|                     | b = 19.0031(3) Å, γ = 85.5729(9)°. |
|                     | c = 20.1060(3) Å, δ = 88.7649(9)°. |
| Volume              | 2273.28(6) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.295 g/cm³ |
| Absorption coefficient | 0.696 mm⁻¹ |
| F(000)              | 939.5 |
| Crystal size        | 0.468 x 0.074 x 0.061 mm³ |
| Theta range for data collection | 2.437 to 78.973°. |
| Index ranges        | -8≤h≤7, -24≤k≤24, -25≤l≤25 |
| Reflections collected | 11269 |
| Independent reflections | 11269 [R(int) = 0] |
| Observed reflections | 9934 |
| Completeness to theta = 67.684° | 99.9 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.964 and 0.767 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 11269 / 7 / 642 |
| Goodness-of-fit on F² | 1.088 |
| Final R indices [I>2sigma(I)] | R1 = 0.0650, wR2 = 0.1804 |
| R indices (all data) | R1 = 0.0716, wR2 = 0.1839 |
| Largest diff. peak and hole | 0.392 and -0.352 e.Å⁻³ |
| CCDC                | 2159683 |
Table S3. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å² x $10^3$) for 15a. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|   | x     | y     | z     | U(eq) |
|---|-------|-------|-------|-------|
| O(1) | 7420(3) | 1558(1) | 4321(1) | 22(1) |
| O(2) | 13803(4) | 180(2) | 7865(2) | 59(1) |
| N(1) | 7382(4) | 2752(1) | 5833(1) | 27(1) |
| N(2) | 6291(4) | 3091(1) | 5234(1) | 28(1) |
| N(3) | 10631(3) | -440(1) | 6155(1) | 22(1) |
| N(4) | 6679(3) | 261(1) | 5896(1) | 22(1) |
| C(1) | 8382(4) | 2110(1) | 5826(1) | 24(1) |
| C(2) | 7850(4) | 2041(1) | 5204(1) | 22(1) |
| C(3) | 6571(4) | 2665(1) | 4860(1) | 25(1) |
| C(4) | 8562(4) | 1437(1) | 4939(1) | 21(1) |
| C(5) | 10869(4) | 1494(1) | 4738(1) | 23(1) |
| C(6) | 11814(4) | 834(1) | 5147(1) | 23(1) |
| C(7) | 10330(4) | 269(1) | 5664(1) | 20(1) |
| C(8) | 8893(4) | -822(1) | 6576(1) | 22(1) |
| C(9) | 9070(4) | -1570(2) | 7148(1) | 26(1) |
| C(10) | 7367(4) | -1971(2) | 7566(1) | 27(1) |
| C(11) | 5434(4) | -1639(2) | 7417(2) | 29(1) |
| C(12) | 5219(4) | -903(2) | 6869(1) | 26(1) |
| C(13) | 6941(4) | -481(1) | 6439(1) | 22(1) |
| C(14) | 8358(4) | 610(1) | 5544(1) | 20(1) |
| C(15) | 11821(4) | 2231(2) | 4171(2) | 27(1) |
| C(16) | 7538(5) | 3180(2) | 6303(2) | 33(1) |
| C(17) | 8198(6) | 2645(2) | 7063(2) | 47(1) |
| C(18) | 9038(7) | 3846(2) | 5904(2) | 55(1) |
| C(19) | 5418(6) | 3490(2) | 6400(2) | 49(1) |
| C(20) | 9747(4) | 1594(2) | 6386(1) | 27(1) |
| C(21) | 11822(5) | 1769(2) | 6306(2) | 35(1) |
| C(22) | 13116(5) | 1279(2) | 6809(2) | 44(1) |
| C(23) | 12374(5) | 608(2) | 7398(2) | 42(1) |
| C(24) | 10330(6) | 418(2) | 7483(2) | 40(1) |
| C(25) | 9027(5) | 913(2) | 6972(2) | 32(1) |
| C(26) | 13131(7) | -550(2) | 8449(2) | 60(1) |
| O(3) | 2434(3) | 3486(1) | 10777(1) | 23(1) |
| O(4) | -1002(4) | 5140(1) | 6826(1) | 41(1) |
| N(5) | 2161(4) | 1961(1) | 9590(1) | 33(1) |
| N(6) | 2811(4) | 1611(1) | 10279(1) | 38(1) |
|  |  |  |  |  |
|---|---|---|---|---|
| N(7) | -437(3) | 5391(1) | 8784(1) | 22(1) |
| N(8) | 3386(3) | 4614(1) | 9146(1) | 23(1) |
| C(27) | 1555(4) | 2709(2) | 9423(1) | 26(1) |
| C(28) | 1867(4) | 2839(1) | 10036(1) | 23(1) |
| C(29) | 2639(5) | 2141(2) | 10544(2) | 32(1) |
| C(30) | 1314(4) | 3543(1) | 10176(1) | 22(1) |
| C(31) | -1002(4) | 3561(1) | 10343(1) | 23(1) |
| C(32) | -1823(4) | 4218(1) | 9867(1) | 23(1) |
| C(33) | -250(4) | 4709(1) | 9334(1) | 21(1) |
| C(34) | 1349(4) | 5704(1) | 8354(1) | 22(1) |
| C(35) | 1272(4) | 6407(2) | 7718(1) | 26(1) |
| C(36) | 3014(4) | 6734(2) | 7277(2) | 28(1) |
| C(37) | 4881(4) | 6360(2) | 7469(2) | 30(1) |
| C(38) | 5002(4) | 5675(2) | 8087(2) | 28(1) |
| C(39) | 3231(4) | 5326(1) | 8540(1) | 22(1) |
| C(40) | 1657(4) | 4322(1) | 9504(1) | 21(1) |
| C(41) | -2093(4) | 2889(2) | 10952(2) | 29(1) |
| C(42) | 2122(6) | 1501(2) | 9145(2) | 43(1) |
| C(43) | -86(7) | 1446(2) | 8987(3) | 56(1) |
| C(44) | 3450(9) | 1895(3) | 8434(3) | 71(2) |
| C(45) | 2852(11) | 687(2) | 9600(3) | 71(2) |
| C(43A) | 800(50) | 1820(20) | 8489(15) | 56(1) |
| C(44A) | 4346(19) | 1500(30) | 8900(20) | 71(2) |
| C(45A) | 1410(60) | 697(12) | 9698(18) | 71(2) |
| C(46) | 840(4) | 3284(2) | 8712(1) | 27(1) |
| C(47) | -1204(4) | 3470(2) | 8611(2) | 29(1) |
| C(48) | -1766(5) | 4085(2) | 7977(2) | 33(1) |
| C(49) | -294(5) | 4530(2) | 7427(2) | 31(1) |
| C(50) | 1735(5) | 4347(2) | 7509(2) | 34(1) |
| C(51) | 2273(5) | 3731(2) | 8151(2) | 32(1) |
| C(52) | 481(6) | 5618(2) | 6258(2) | 49(1) |
| O(5) | 4353(6) | 4494(2) | 4421(2) | 62(1) |
| O(6) | 4730(5) | 4398(2) | 3735(2) | 52(1) |
| O(7) | 6880(40) | 9545(14) | 8207(13) | 55(6) |
| O(8) | 7100(40) | 9892(14) | 8725(13) | 55(6) |
Table S4. Bond lengths [Å] and angles [°] for 15a.

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| O(1)-H(1O)            | 0.89(3) | C(16)-C(18)           | 1.513(5) |
| O(1)-C(4)             | 1.434(3)| C(16)-C(19)           | 1.538(4) |
| O(2)-C(23)            | 1.373(4)| C(17)-H(17A)          | 0.9800  |
| O(2)-C(26)            | 1.433(5)| C(17)-H(17B)          | 0.9800  |
| N(1)-N(2)             | 1.354(3)| C(17)-H(17C)          | 0.9800  |
| N(1)-C(1)             | 1.377(3)| C(18)-H(18A)          | 0.9800  |
| N(1)-C(16)            | 1.498(3)| C(18)-H(18B)          | 0.9800  |
| N(2)-C(3)             | 1.323(3)| C(18)-H(18C)          | 0.9800  |
| N(3)-C(7)             | 1.309(3)| C(19)-H(19A)          | 0.9800  |
| N(3)-C(8)             | 1.386(3)| C(19)-H(19B)          | 0.9800  |
| N(4)-C(13)            | 1.384(3)| C(19)-H(19C)          | 0.9800  |
| N(4)-C(14)            | 1.296(3)| C(20)-C(21)           | 1.397(4) |
| C(1)-C(2)             | 1.385(4)| C(20)-C(25)           | 1.388(4) |
| C(1)-C(20)            | 1.489(4)| C(21)-H(21)           | 0.9500  |
| C(2)-C(3)             | 1.394(3)| C(21)-C(22)           | 1.383(4) |
| C(2)-C(4)             | 1.511(3)| C(22)-H(22)           | 0.9500  |
| C(3)-H(3)             | 0.9500  | C(22)-C(23)           | 1.384(5) |
| C(4)-C(5)             | 1.538(3)| C(23)-C(24)           | 1.382(5) |
| C(4)-C(14)            | 1.523(3)| C(24)-H(24)           | 0.9500  |
| C(5)-C(6)             | 1.343(4)| C(24)-C(25)           | 1.399(4) |
| C(5)-C(15)            | 1.490(3)| C(25)-H(25)           | 0.9500  |
| C(6)-H(6)             | 0.9500  | C(26)-H(26A)          | 0.9800  |
| C(6)-C(7)             | 1.458(3)| C(26)-H(26B)          | 0.9800  |
| C(7)-C(14)            | 1.432(3)| C(26)-H(26C)          | 0.9800  |
| C(8)-C(9)             | 1.404(3)| O(3)-H(3O)            | 0.85(4) |
| C(8)-C(13)            | 1.422(3)| O(3)-C(30)            | 1.428(3) |
| C(9)-H(9)             | 0.9500  | O(4)-C(49)            | 1.376(3) |
| C(9)-C(10)            | 1.377(4)| O(4)-C(52)            | 1.438(4) |
| C(10)-H(10)           | 0.9500  | N(5)-N(6)             | 1.355(3) |
| C(10)-C(11)           | 1.406(4)| N(5)-C(27)            | 1.372(3) |
| C(11)-H(11)           | 0.9500  | N(5)-C(42)            | 1.496(4) |
| C(11)-C(12)           | 1.375(4)| N(6)-C(29)            | 1.324(4) |
| C(12)-H(12)           | 0.9500  | N(7)-C(33)            | 1.307(3) |
| C(12)-C(13)           | 1.406(4)| N(7)-C(34)            | 1.388(3) |
| C(15)-H(15A)          | 0.9800  | N(8)-C(39)            | 1.390(3) |
| C(15)-H(15B)          | 0.9800  | N(8)-C(40)            | 1.299(3) |
| C(15)-H(15C)          | 0.9800  | C(27)-C(28)           | 1.386(4) |
| C(16)-C(17)           | 1.521(4)| C(27)-C(46)           | 1.487(4) |
|          |          |          |
|----------|----------|----------|
| C(28)-C(29) | 1.399(4) | C(43A)-H(43F) | 0.9800 |
| C(28)-C(30) | 1.512(3) | C(44A)-H(44D) | 0.9800 |
| C(29)-H(29) | 0.9500   | C(44A)-H(44E) | 0.9800 |
| C(30)-C(31) | 1.542(3) | C(44A)-H(44F) | 0.9800 |
| C(30)-C(40) | 1.526(3) | C(45A)-H(45D) | 0.9800 |
| C(31)-C(32) | 1.342(4) | C(45A)-H(45E) | 0.9800 |
| C(31)-C(41) | 1.489(3) | C(45A)-H(45F) | 0.9800 |
| C(32)-H(32) | 0.9500   | C(46)-C(47)   | 1.395(4) |
| C(32)-C(33) | 1.454(3) | C(46)-C(51)   | 1.392(4) |
| C(33)-C(40) | 1.433(3) | C(47)-H(47)   | 0.9500  |
| C(34)-C(35) | 1.404(3) | C(47)-C(48)   | 1.382(4) |
| C(34)-C(39) | 1.415(4) | C(48)-H(48)   | 0.9500  |
| C(35)-H(35) | 0.9500   | C(48)-C(49)   | 1.398(4) |
| C(35)-C(36) | 1.377(4) | C(49)-C(50)   | 1.380(4) |
| C(36)-H(36) | 0.9500   | C(50)-H(50)   | 0.9500  |
| C(36)-C(37) | 1.404(4) | C(50)-C(51)   | 1.387(4) |
| C(37)-H(37) | 0.9500   | C(51)-H(51)   | 0.9500  |
| C(37)-C(38) | 1.370(4) | C(52)-H(52A)  | 0.9800  |
| C(38)-H(38) | 0.9500   | C(52)-H(52B)  | 0.9800  |
| C(38)-C(39) | 1.411(4) | C(52)-H(52C)  | 0.9800  |
| C(41)-H(41A)| 0.9800   | O(5)-H(5O)    | 0.90(7) |
| C(41)-H(41B)| 0.9800   | O(5)-O(6)     | 1.468(4) |
| C(41)-H(41C)| 0.9800   | O(6)-H(6O)    | 0.95(6) |
| C(42)-C(43) | 1.531(6) | O(7)-H(7O)    | 0.8400  |
| C(42)-C(44) | 1.514(6) | O(7)-O(8)     | 1.468(5) |
| C(42)-C(45) | 1.513(5) | O(8)-H(8O)    | 0.8400  |
| C(42)-C(43A)| 1.531(7) | C(4)-O(1)-H(1O)| 108(2) |
| C(42)-C(44A)| 1.515(7) | C(23)-O(2)-C(26)| 116.6(3) |
| C(43)-H(43A)| 0.9800   | N(2)-N(1)-C(1)| 110.6(2) |
| C(43)-H(43B)| 0.9800   | N(2)-N(1)-C(16)| 116.9(2) |
| C(43)-H(43C)| 0.9800   | C(1)-N(1)-C(16)| 131.8(2) |
| C(44)-H(44A)| 0.9800   | C(3)-N(2)-N(1)| 106.1(2) |
| C(44)-H(44B)| 0.9800   | C(7)-N(3)-C(8)| 114.4(2) |
| C(44)-H(44C)| 0.9800   | C(14)-N(4)-C(13)| 114.0(2) |
| C(45)-H(45A)| 0.9800   | N(1)-C(1)-C(2)| 106.4(2) |
| C(45)-H(45B)| 0.9800   | N(1)-C(1)-C(20)| 126.3(2) |
| C(45)-H(45C)| 0.9800   | C(2)-C(1)-C(20)| 127.3(2) |
| C(43A)-H(43D)| 0.9800   | C(1)-C(2)-C(3)| 105.3(2) |
| C(43A)-H(43E)| 0.9800   | C(1)-C(2)-C(4)| 127.5(2) |
| Bond                  | Angle (°)  |
|-----------------------|------------|
| C(3)-C(2)-C(4)        | 127.3(2)   |
| N(2)-C(3)-C(2)        | 111.5(2)   |
| N(2)-C(3)-H(3)        | 124.2      |
| C(2)-C(3)-H(3)        | 124.2      |
| O(1)-C(4)-C(2)        | 106.31(19) |
| O(1)-C(4)-C(5)        | 112.24(19) |
| O(1)-C(4)-C(14)       | 112.96(19) |
| C(2)-C(4)-C(5)        | 111.8(2)   |
| C(2)-C(4)-C(14)       | 112.7(2)   |
| C(14)-C(4)-C(5)       | 100.90(19) |
| C(6)-C(5)-C(4)        | 112.0(2)   |
| C(6)-C(5)-C(15)       | 127.3(2)   |
| C(15)-C(5)-C(4)       | 120.6(2)   |
| C(5)-C(6)-H(6)        | 125.2      |
| C(5)-C(6)-C(7)        | 109.6(2)   |
| C(7)-C(6)-H(6)        | 125.2      |
| N(3)-C(7)-C(6)        | 128.7(2)   |
| N(3)-C(7)-C(14)       | 123.0(2)   |
| C(14)-C(7)-C(6)       | 108.3(2)   |
| N(3)-C(8)-C(9)        | 118.9(2)   |
| N(3)-C(8)-C(13)       | 121.8(2)   |
| C(9)-C(8)-C(13)       | 119.4(2)   |
| C(8)-C(9)-H(9)        | 119.9      |
| C(10)-C(9)-C(8)       | 120.3(2)   |
| C(10)-C(9)-H(9)       | 119.9      |
| C(9)-C(10)-H(10)      | 119.9      |
| C(9)-C(10)-C(11)      | 120.2(2)   |
| C(11)-C(10)-H(10)     | 119.9      |
| C(10)-C(11)-H(11)     | 119.6      |
| C(12)-C(11)-C(10)     | 120.8(2)   |
| C(12)-C(11)-H(11)     | 119.6      |
| C(11)-C(12)-C(13)     | 119.9(2)   |
| C(13)-C(12)-H(12)     | 120.0      |
| N(4)-C(13)-C(8)       | 121.9(2)   |
| N(4)-C(13)-C(12)      | 118.6(2)   |
| C(12)-C(13)-C(8)      | 119.5(2)   |
| N(4)-C(14)-C(4)       | 126.1(2)   |
| N(4)-C(14)-C(7)       | 124.7(2)   |
| C(7)-C(14)-C(4)       | 109.2(2)   |
| C(5)-C(15)-H(15A)     | 109.5      |
| C(5)-C(15)-H(15B)     | 109.5      |
| C(5)-C(15)-H(15C)     | 109.5      |
| H(15A)-C(15)-H(15B)   | 109.5      |
| H(15A)-C(15)-H(15C)   | 109.5      |
| H(15B)-C(15)-H(15C)   | 109.5      |
| N(1)-C(16)-C(17)      | 111.4(2)   |
| N(1)-C(16)-C(18)      | 107.8(2)   |
| N(1)-C(16)-C(19)      | 107.8(2)   |
| C(17)-C(16)-C(19)     | 108.2(3)   |
| C(18)-C(16)-C(17)     | 111.1(3)   |
| C(18)-C(16)-C(19)     | 110.5(3)   |
| C(16)-C(17)-H(17A)    | 109.5      |
| C(16)-C(17)-H(17B)    | 109.5      |
| C(16)-C(17)-H(17C)    | 109.5      |
| H(17A)-C(17)-H(17B)   | 109.5      |
| H(17A)-C(17)-H(17C)   | 109.5      |
| H(17B)-C(17)-H(17C)   | 109.5      |
| C(16)-C(18)-C(17)     | 109.5      |
| C(16)-C(18)-C(19)     | 109.5      |
| C(16)-C(18)-H(18C)    | 109.5      |
| H(18A)-C(18)-H(18B)   | 109.5      |
| H(18A)-C(18)-H(18C)   | 109.5      |
| H(18B)-C(18)-H(18C)   | 109.5      |
| C(16)-C(19)-H(19A)    | 109.5      |
| C(16)-C(19)-H(19B)    | 109.5      |
| C(16)-C(19)-H(19C)    | 109.5      |
| H(19A)-C(19)-H(19B)   | 109.5      |
| H(19A)-C(19)-H(19C)   | 109.5      |
| H(19B)-C(19)-H(19C)   | 109.5      |
| C(21)-C(20)-C(1)      | 119.9(3)   |
| C(25)-C(20)-C(1)      | 121.5(3)   |
| C(25)-C(20)-C(21)     | 118.5(3)   |
| C(20)-C(21)-H(21)     | 119.8      |
| C(22)-C(21)-C(20)     | 120.5(3)   |
| C(22)-C(21)-H(21)     | 119.8      |
| C(21)-C(22)-H(22)     | 119.8      |
| C(21)-C(22)-C(23)     | 120.5(3)   |
| C(23)-C(22)-H(22)     | 119.8      |
| O(2)-C(23)-C(22)      | 114.9(3)   |

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| O(2)-C(23)-C(24) | 125.0(3) | C(31)-C(32)-H(32) | 125.1 |
| O(24)-C(23)-C(22) | 120.1(3) | C(31)-C(32)-C(33) | 109.8(2) |
| C(23)-C(24)-H(24) | 120.4 | C(33)-C(32)-H(32) | 125.1 |
| C(23)-C(24)-C(25) | 119.3(3) | N(7)-C(33)-C(32) | 128.4(2) |
| C(25)-C(24)-H(24) | 120.4 | N(7)-C(33)-C(40) | 123.2(2) |
| C(20)-C(25)-C(24) | 121.2(3) | C(40)-C(33)-C(32) | 108.4(2) |
| C(20)-C(25)-H(25) | 119.4 | N(7)-C(34)-C(35) | 119.0(2) |
| C(24)-C(25)-H(25) | 119.4 | N(7)-C(34)-C(39) | 121.3(2) |
| O(2)-C(26)-H(26A) | 109.5 | C(35)-C(34)-C(39) | 119.7(2) |
| O(2)-C(26)-H(26B) | 109.5 | C(35)-C(35)-H(35) | 119.7 |
| O(2)-C(26)-H(26C) | 109.5 | C(35)-C(36)-H(36) | 120.3 |
| H(26A)-C(26)-H(26B) | 109.5 | C(35)-C(36)-C(37) | 119.5(2) |
| H(26A)-C(26)-H(26C) | 109.5 | C(35)-C(36)-H(36) | 120.3 |
| C(30)-O(3)-H(3O) | 112(2) | C(36)-C(37)-H(37) | 119.4 |
| C(49)-O(4)-C(52) | 117.3(3) | C(38)-C(37)-C(36) | 121.2(3) |
| N(6)-N(5)-C(27) | 111.5(2) | C(38)-C(37)-H(37) | 119.4 |
| N(6)-N(5)-C(42) | 118.7(2) | C(37)-C(38)-H(38) | 119.9 |
| C(27)-N(5)-C(42) | 129.8(2) | C(37)-C(38)-C(39) | 120.1(3) |
| C(29)-N(6)-N(5) | 105.5(2) | C(39)-C(38)-H(38) | 119.9 |
| C(33)-N(7)-C(34) | 114.8(2) | N(8)-C(39)-C(34) | 122.2(2) |
| C(40)-N(8)-C(39) | 114.1(2) | N(8)-C(39)-C(38) | 118.9(2) |
| N(5)-C(27)-C(28) | 106.1(2) | C(38)-C(39)-C(34) | 118.9(2) |
| N(5)-C(27)-C(46) | 127.2(2) | N(8)-C(40)-C(30) | 126.7(2) |
| C(28)-C(27)-C(46) | 126.6(2) | N(8)-C(40)-C(33) | 124.2(2) |
| C(27)-C(28)-C(29) | 105.2(2) | C(33)-C(40)-C(30) | 109.1(2) |
| C(27)-C(28)-C(30) | 128.7(2) | C(31)-C(41)-H(41A) | 109.5 |
| C(29)-C(28)-C(30) | 125.9(2) | C(31)-C(41)-H(41B) | 109.5 |
| N(6)-C(29)-C(28) | 111.7(2) | C(31)-C(41)-H(41C) | 109.5 |
| N(6)-C(29)-H(29) | 124.2 | H(41A)-C(41)-H(41B) | 109.5 |
| C(28)-C(29)-H(29) | 124.2 | H(41B)-C(41)-H(41C) | 109.5 |
| O(3)-C(30)-C(28) | 106.32(19) | N(5)-C(42)-C(43) | 107.9(3) |
| O(3)-C(30)-C(31) | 112.54(19) | N(5)-C(42)-C(44) | 110.0(3) |
| O(3)-C(30)-C(40) | 112.5(2) | N(5)-C(42)-C(45) | 108.8(3) |
| C(28)-C(30)-C(31) | 110.3(2) | N(5)-C(42)-C(43A) | 116.1(15) |
| C(28)-C(30)-C(40) | 114.6(2) | N(5)-C(42)-C(44A) | 102.3(17) |
| C(40)-C(30)-C(31) | 100.75(19) | N(5)-C(42)-C(45A) | 104.3(17) |
| C(32)-C(31)-C(30) | 111.9(2) | C(44)-C(42)-C(43) | 110.8(4) |
| Bond | Angle (deg) |
|------|------------|
| C(45)-C(42)-C(43) | 108.3(4) |
| C(45)-C(42)-C(44) | 111.0(4) |
| C(44A)-C(42)-C(43A) | 111.3(15) |
| C(45A)-C(42)-C(43A) | 111.4(15) |
| C(45A)-C(42)-C(44A) | 110.8(15) |
| C(42)-C(43)-H(43A) | 109.5 |
| C(42)-C(43)-H(43B) | 109.5 |
| C(42)-C(43)-H(43C) | 109.5 |
| H(43A)-C(43)-H(43B) | 109.5 |
| H(43A)-C(43)-H(43C) | 109.5 |
| C(42)-C(44)-H(44A) | 109.5 |
| C(42)-C(44)-H(44B) | 109.5 |
| C(42)-C(44)-H(44C) | 109.5 |
| H(44A)-C(44)-H(44B) | 109.5 |
| H(44A)-C(44)-H(44C) | 109.5 |
| C(42)-C(45)-H(45A) | 109.5 |
| C(42)-C(45)-H(45B) | 109.5 |
| C(42)-C(45)-H(45C) | 109.5 |
| H(45A)-C(45)-H(45B) | 109.5 |
| H(45A)-C(45)-H(45C) | 109.5 |
| C(42)-C(46)-C(47) | 122.8(3) |
| C(46)-C(47)-C(48) | 119.7 |
| C(46)-C(47)-C(49) | 120.6(3) |
| C(46)-C(47)-C(48) | 119.7 |
| C(46)-C(47)-C(49) | 120.4(3) |
| O(4)-C(49)-C(48) | 116.1(3) |
| C(49)-C(48)-C(47) | 119.8 |
| C(49)-C(50)-C(51) | 118.8(3) |
| C(49)-C(50)-H(50) | 120.6 |
| C(49)-C(50)-H(51) | 118.8 |
| C(50)-C(50)-H(50) | 120.6 |
| C(50)-C(51)-H(50) | 118.8 |
| C(50)-C(51)-C(51) | 122.5(3) |
| C(50)-C(51)-H(51) | 118.8 |
| H(52A)-C(52)-H(52B) | 109.5 |
| H(52A)-C(52)-H(52C) | 109.5 |
| H(52B)-C(52)-H(52C) | 109.5 |
| O(5)-O(6)-H(5O) | 98(4) |
| O(5)-O(6)-H(6O) | 102(3) |
| O(5)-O(7)-H(7O) | 109.5 |
| O(5)-O(8)-H(8O) | 109.5 |
Table S5. Anisotropic displacement parameters (Å\(^2\) x 10\(^3\)) for 15a. The anisotropic displacement factor exponent takes the form: -2\(e^{-2[h^2a^*2U^{11} + ... + 2hka^*b^*U^{12}]}\)

|     | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{23}\)  | \(U^{13}\)  | \(U^{12}\)  |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O(1) | 24(1)       | 21(1)       | 21(1)       | -9(1)       | -6(1)       | 4(1)        |
| O(2) | 67(2)       | 59(2)       | 61(2)       | -32(1)      | -39(1)      | 33(1)       |
| N(1) | 32(1)       | 24(1)       | 27(1)       | -13(1)      | -4(1)       | 4(1)        |
| N(2) | 32(1)       | 24(1)       | 29(1)       | -12(1)      | -6(1)       | 7(1)        |
| N(3) | 22(1)       | 23(1)       | 22(1)       | -9(1)       | -3(1)       | 3(1)        |
| N(4) | 20(1)       | 22(1)       | 23(1)       | -9(1)       | -3(1)       | 1(1)        |
| C(1) | 25(1)       | 23(1)       | 25(1)       | -11(1)      | 0(1)        | 2(1)        |
| C(2) | 22(1)       | 21(1)       | 21(1)       | -7(1)       | -1(1)       | 0(1)        |
| C(3) | 27(1)       | 23(1)       | 24(1)       | -10(1)      | -4(1)       | 3(1)        |
| C(4) | 21(1)       | 22(1)       | 18(1)       | -7(1)       | -4(1)       | 2(1)        |
| C(5) | 26(1)       | 24(1)       | 21(1)       | -11(1)      | -1(1)       | 3(1)        |
| C(6) | 21(1)       | 24(1)       | 22(1)       | -10(1)      | -1(1)       | 1(1)        |
| C(7) | 19(1)       | 22(1)       | 22(1)       | -11(1)      | -4(1)       | 1(1)        |
| C(8) | 23(1)       | 22(1)       | 22(1)       | -10(1)      | -2(1)       | 0(1)        |
| C(9) | 27(1)       | 24(1)       | 26(1)       | -9(1)       | -5(1)       | 4(1)        |
| C(10)| 36(1)       | 22(1)       | 20(1)       | -5(1)       | -2(1)       | 0(1)        |
| C(11)| 30(1)       | 26(1)       | 27(1)       | -9(1)       | 2(1)        | -4(1)       |
| C(12)| 24(1)       | 29(1)       | 25(1)       | -11(1)      | -3(1)       | 0(1)        |
| C(13)| 24(1)       | 22(1)       | 21(1)       | -10(1)      | -5(1)       | 2(1)        |
| C(14)| 21(1)       | 21(1)       | 22(1)       | -11(1)      | -5(1)       | 2(1)        |
| C(15)| 26(1)       | 26(1)       | 27(1)       | -9(1)       | 1(1)        | -2(1)       |
| C(16)| 42(2)       | 30(1)       | 33(1)       | -20(1)      | -4(1)       | 5(1)        |
| C(17)| 71(2)       | 46(2)       | 35(2)       | -27(2)      | -12(2)      | 14(2)       |
| C(18)| 76(3)       | 52(2)       | 48(2)       | -34(2)      | 9(2)        | -23(2)      |
| C(19)| 58(2)       | 50(2)       | 51(2)       | -34(2)      | -6(2)       | 17(2)       |
| C(20)| 30(1)       | 31(1)       | 26(1)       | -17(1)      | -7(1)       | 7(1)        |
| C(21)| 31(1)       | 46(2)       | 37(2)       | -25(1)      | -6(1)       | 5(1)        |
| C(22)| 31(2)       | 61(2)       | 51(2)       | -32(2)      | -15(1)      | 14(2)       |
| C(23)| 51(2)       | 46(2)       | 45(2)       | -31(2)      | -27(2)      | 26(2)       |
| C(24)| 65(2)       | 31(1)       | 27(1)       | -15(1)      | -13(1)      | 12(1)       |
| C(25)| 39(2)       | 32(1)       | 29(1)       | -15(1)      | -8(1)       | 7(1)        |
| C(26)| 85(3)       | 53(2)       | 49(2)       | -27(2)      | -30(2)      | 35(2)       |
| O(3) | 28(1)       | 21(1)       | 22(1)       | -10(1)      | -7(1)       | 5(1)        |
| O(4) | 57(1)       | 32(1)       | 31(1)       | -10(1)      | -13(1)      | 8(1)        |
| N(5) | 45(1)       | 26(1)       | 31(1)       | -15(1)      | -9(1)       | 9(1)        |
|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| N(6) | 58(2) | 27(1) | 32(1) | -13(1) | -14(1) | 13(1) |
| N(7) | 23(1) | 21(1) | 23(1) | -9(1) | -3(1) | 2(1) |
| N(8) | 21(1) | 23(1) | 25(1) | -9(1) | -3(1) | 1(1) |
| C(27) | 29(1) | 23(1) | 26(1) | -9(1) | -2(1) | 3(1) |
| C(28) | 26(1) | 21(1) | 22(1) | -8(1) | -3(1) | 3(1) |
| C(29) | 47(2) | 25(1) | 26(1) | -11(1) | -10(1) | 7(1) |
| C(30) | 24(1) | 21(1) | 19(1) | -7(1) | -3(1) | 1(1) |
| C(31) | 27(1) | 23(1) | 20(1) | -9(1) | -1(1) | 2(1) |
| C(32) | 22(1) | 24(1) | 23(1) | -9(1) | -2(1) | 0(1) |
| C(33) | 20(1) | 22(1) | 21(1) | -10(1) | -3(1) | 2(1) |
| C(34) | 24(1) | 23(1) | 21(1) | -10(1) | -1(1) | 0(1) |
| C(35) | 30(1) | 22(1) | 26(1) | -9(1) | -4(1) | 4(1) |
| C(36) | 39(2) | 21(1) | 23(1) | -6(1) | -1(1) | 3(1) |
| C(37) | 29(1) | 30(1) | 27(1) | -10(1) | 3(1) | -6(1) |
| C(38) | 24(1) | 29(1) | 30(1) | -12(1) | -3(1) | 0(1) |
| C(39) | 23(1) | 22(1) | 22(1) | -8(1) | -2(1) | 0(1) |
| C(40) | 21(1) | 20(1) | 21(1) | -8(1) | -2(1) | 2(1) |
| C(41) | 29(1) | 26(1) | 27(1) | -8(1) | 2(1) | -4(1) |
| C(42) | 67(2) | 32(2) | 39(2) | -22(1) | -9(2) | 7(2) |
| C(43) | 77(3) | 41(2) | 63(3) | -32(2) | -22(2) | 1(2) |
| C(44) | 102(4) | 69(3) | 62(3) | -50(3) | 17(3) | -7(3) |
| C(45) | 122(5) | 43(2) | 71(3) | -42(2) | -41(3) | 35(3) |
| C(43A) | 77(3) | 41(2) | 63(3) | -32(2) | -22(2) | 1(2) |
| C(44A) | 102(4) | 69(3) | 62(3) | -50(3) | 17(3) | -7(3) |
| C(45A) | 122(5) | 43(2) | 71(3) | -42(2) | -41(3) | 35(3) |
| C(46) | 34(1) | 26(1) | 24(1) | -12(1) | -5(1) | 3(1) |
| C(47) | 34(1) | 29(1) | 30(1) | -16(1) | -4(1) | 1(1) |
| C(48) | 35(2) | 33(1) | 37(2) | -20(1) | -9(1) | 6(1) |
| C(49) | 47(2) | 25(1) | 25(1) | -14(1) | -11(1) | 5(1) |
| C(50) | 42(2) | 32(1) | 25(1) | -10(1) | -1(1) | -3(1) |
| C(51) | 33(1) | 36(2) | 26(1) | -11(1) | -4(1) | 1(1) |
| C(52) | 74(3) | 34(2) | 31(2) | -6(1) | -10(2) | 0(2) |
| O(5) | 88(3) | 47(2) | 55(2) | -25(2) | -30(2) | 37(2) |
| O(6) | 47(2) | 62(2) | 37(2) | -12(1) | -9(1) | 12(1) |
| O(7) | 47(11) | 57(12) | 60(12) | -21(9) | -18(8) | 6(8) |
| O(8) | 47(11) | 57(12) | 60(12) | -21(9) | -18(8) | 6(8) |
Table S6. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2\times 10^3$) for 15a.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| H(1O) | 7760(50) | 1190(20) | 4169(18) | 33    |
| H(3)  | 5974  | 2770  | 4412  | 29    |
| H(6)  | 13232 | 748   | 5106  | 27    |
| H(9)  | 10370 | -1799 | 7246  | 31    |
| H(10) | 7497  | -2474 | 7955  | 33    |
| H(11) | 4264  | -1926 | 7699  | 34    |
| H(12) | 3909  | -680  | 6781  | 31    |
| H(15A)| 13195 | 2126  | 4016  | 41    |
| H(15B)| 11894 | 2610  | 4379  | 41    |
| H(15C)| 11000 | 2441  | 3743  | 41    |
| H(17A)| 8090  | 2920  | 7380  | 70    |
| H(17B)| 9610  | 2491  | 7018  | 70    |
| H(17C)| 7319  | 2181  | 7280  | 70    |
| H(18A)| 9104  | 4157  | 6186  | 82    |
| H(18B)| 8596  | 4175  | 5413  | 82    |
| H(18C)| 10385 | 3638  | 5856  | 82    |
| H(19A)| 5447  | 3731  | 6744  | 73    |
| H(19B)| 4428  | 3059  | 6596  | 73    |
| H(19C)| 5027  | 3879  | 5922  | 73    |
| H(21) | 12348 | 2227  | 5904  | 42    |
| H(22) | 14524 | 1404  | 6750  | 53    |
| H(24) | 9816  | -43   | 7885  | 47    |
| H(25) | 7624  | 781   | 7027  | 39    |
| H(26A)| 14246 | -786  | 8764  | 89    |
| H(26B)| 12707 | -898  | 8238  | 89    |
| H(26C)| 11980 | -464  | 8743  | 89    |
| H(30) | 2110(50) | 3840(20) | 10916(19) | 35    |
| H(29) | 2996  | 2057  | 11021 | 39    |
| H(32) | -3223 | 4344  | 9877  | 28    |
| H(35) | 8     | 6660  | 7591  | 31    |
| H(36) | 2953  | 7209  | 6846  | 34    |
| H(37) | 6081  | 6587  | 7164  | 35    |
| H(38) | 6282  | 5435  | 8211  | 33    |
| H(41A) | -3500 | 3033  | 11024 | 43    |
| H(41B) | -1413 | 2747  | 11407 | 43    |
|        |       |       |       |       |
|--------|-------|-------|-------|-------|
| H(41C) | -2084 | 2445  | 10824 | 43    |
| H(43A) | -162  | 1125  | 8715  | 83    |
| H(43B) | -584  | 1968  | 8690  | 83    |
| H(43C) | -927  | 1208  | 9453  | 83    |
| H(44A) | 3604  | 1549  | 8186  | 107   |
| H(44B) | 4789  | 2012  | 8545  | 107   |
| H(44C) | 2815  | 2380  | 8111  | 107   |
| H(45A) | 2865  | 384   | 9309  | 106   |
| H(45B) | 1936  | 436   | 10045 | 106   |
| H(45C) | 4229  | 714   | 9739  | 106   |
| H(43D) | 884   | 1480  | 8236  | 83    |
| H(43E) | -613  | 1849  | 8664  | 83    |
| H(43F) | 1288  | 2345  | 8145  | 83    |
| H(44D) | 4505  | 1205  | 8593  | 107   |
| H(44E) | 4833  | 2032  | 8603  | 107   |
| H(44F) | 5138  | 1248  | 9327  | 107   |
| H(45D) | 1344  | 356   | 9447  | 106   |
| H(45E) | 2369  | 485   | 10083 | 106   |
| H(45F) | 61    | 731   | 9921  | 106   |
| H(47)  | -2218 | 3172  | 8981  | 35    |
| H(48)  | -3163 | 4206  | 7915  | 39    |
| H(50)  | 2745  | 4638  | 7134  | 41    |
| H(51)  | 3670  | 3610  | 8210  | 39    |
| H(52A) | -212  | 6018  | 5855  | 73    |
| H(52B) | 1286  | 5294  | 6069  | 73    |
| H(52C) | 1380  | 5866  | 6463  | 73    |
| H(5O)  | 4920(100) | 4050(40) | 4730(30) | 92 |
| H(6O)  | 3510(90) | 4590(30) | 3500(30) | 78 |
| H(7O)  | 5905  | 9754  | 7947  | 83    |
| H(8O)  | 6778  | 9561  | 9157  | 83    |
Table S7. Torsion angles [°] for 15a.

| Bond                  | Value   |
|-----------------------|---------|
| O(1)-C(4)-C(5)-C(6)   | -120.7(2) |
| O(1)-C(4)-C(5)-C(15)  | 61.6(3)  |
| O(1)-C(4)-C(14)-N(4)  | -58.6(3) |
| O(1)-C(4)-C(14)-C(7)  | 121.0(2) |
| O(2)-C(23)-C(24)-C(25)| 179.0(3) |
| N(1)-N(2)-C(3)-C(2)   | -0.1(3)  |
| N(1)-C(1)-C(2)-C(3)   | 1.1(3)   |
| N(1)-C(1)-C(2)-C(4)   | 179.1(2) |
| N(1)-C(1)-C(20)-C(21) | -88.8(3) |
| N(1)-C(1)-C(20)-C(25) | 94.6(3)  |
| N(2)-N(1)-C(1)-C(2)   | -1.3(3)  |
| N(2)-N(1)-C(1)-C(20)  | 179.2(2) |
| N(2)-N(1)-C(16)-C(17) | 162.1(3) |
| N(2)-N(1)-C(16)-C(18) | -75.8(3) |
| N(2)-N(1)-C(16)-C(19) | 43.5(3)  |
| N(3)-C(7)-C(14)-N(4)  | -0.7(4)  |
| N(3)-C(7)-C(14)-C(4)  | 179.8(2) |
| N(3)-C(8)-C(9)-C(10)  | -178.6(2) |
| N(3)-C(8)-C(13)-N(4)  | -2.5(4)  |
| N(3)-C(8)-C(13)-C(12) | 178.1(2) |
| C(1)-N(1)-N(2)-C(3)   | 0.9(3)   |
| C(1)-N(1)-C(16)-C(17) | -28.4(4) |
| C(1)-N(1)-C(16)-C(18) | 93.7(4)  |
| C(1)-N(1)-C(16)-C(19) | -147.0(3) |
| C(1)-C(2)-C(3)-N(2)   | -0.6(3)  |
| C(1)-C(2)-C(4)-O(1)   | 173.8(2) |
| C(1)-C(2)-C(4)-C(5)   | -63.4(3) |
| C(1)-C(2)-C(4)-C(14)  | 49.5(3)  |
| C(1)-C(20)-C(21)-C(22) | -177.7(3) |
| C(1)-C(20)-C(25)-C(24) | 178.0(2) |
| C(2)-C(1)-C(20)-C(21) | 91.8(3)  |
| C(2)-C(1)-C(20)-C(25) | -84.8(4) |
| C(2)-C(4)-C(5)-C(6)   | 119.9(2) |
| C(2)-C(4)-C(5)-C(15)  | -57.8(3) |
| C(2)-C(4)-C(14)-N(4)  | 62.0(3)  |
| C(2)-C(4)-C(14)-C(7)  | -118.5(2) |
| C(3)-C(2)-C(4)-O(1)   | -8.6(3)  |
| C(3)-C(2)-C(4)-C(5)   | 114.2(3) |
| C(3)-C(2)-C(4)-C(14)  | -132.9(3) |
| C(4)-C(2)-C(3)-N(2)   | -178.6(2) |
| C(4)-C(5)-C(6)-C(7)   | -0.6(3)  |
| C(5)-C(4)-C(14)-N(4)  | -178.6(2) |
| C(5)-C(4)-C(14)-C(7)  | 1.0(2)   |
| C(5)-C(6)-C(7)-N(3)   | -180.0(2) |
| C(5)-C(6)-C(7)-C(14)  | 1.3(3)   |
| C(6)-C(7)-C(14)-N(4)  | 178.2(2) |
| C(6)-C(7)-C(14)-C(4)  | -1.4(3)  |
| C(7)-N(3)-C(8)-C(9)   | -176.4(2) |
| C(7)-N(3)-C(8)-C(13)  | 4.5(3)   |
| C(8)-N(3)-C(7)-C(6)   | 178.4(2) |
| C(8)-N(3)-C(7)-C(14)  | -3.0(3)  |
| C(8)-C(9)-C(10)-C(11) | 0.8(4)   |
| C(9)-C(8)-C(13)-C(12) | -1.0(4)  |
| C(9)-C(10)-C(11)-C(12)| -1.8(4)  |
| C(10)-C(11)-C(12)-C(13)| 1.4(4)  |
| C(11)-C(12)-C(13)-N(4)| -179.3(2) |
| C(11)-C(12)-C(13)-C(8)| 0.0(4)   |
| C(13)-N(4)-C(14)-C(4) | -177.8(2) |
| C(13)-N(4)-C(14)-C(7) | 2.8(3)   |
| C(13)-C(8)-C(9)-C(10)| 0.5(4)   |
| C(14)-N(4)-C(13)-C(8)| -1.2(3)  |
| C(14)-N(4)-C(13)-C(12)| 178.2(2) |
| C(14)-C(4)-C(5)-C(6)  | -0.2(3)  |
| C(14)-C(4)-C(5)-C(15)| -177.9(2) |
| C(15)-C(5)-C(6)-C(7)  | 176.9(2) |
| C(16)-N(1)-N(2)-C(3)  | 172.5(2) |
| C(16)-N(1)-C(1)-C(2)  | -171.2(3) |
| C(16)-N(1)-C(1)-C(20)| 9.3(5)    |
| C(20)-C(1)-C(2)-C(3)  | -179.4(3) |
| C(20)-C(1)-C(2)-C(4)  | -1.4(4)  |
| C(20)-C(21)-C(22)-C(23)| 0.1(5)  |
| C(21)-C(20)-C(25)-C(24)| 1.4(4)  |
| C(21)-C(22)-C(23)-O(2)| -178.7(3) |
| C(21)-C(22)-C(23)-C(24)| 0.6(5)  |
| C(22)-C(23)-C(24)-C(25)| -0.3(5) |
| Bond                  | Distance (Å) |
|----------------------|--------------|
| C(23)-C(24)-C(25)-C(20) | 0.7(4)      |
| C(25)-C(20)-C(21)-C(22) | -1.1(4)     |
| C(26)-O(2)-C(23)-C(22) | -175.3(3)   |
| C(26)-O(2)-C(23)-C(24) | 5.4(5)      |
| O(3)-C(30)-C(31)-C(32) | 119.7(2)    |
| O(3)-C(30)-C(31)-C(41) | -62.7(3)    |
| O(3)-C(30)-C(40)-N(8)  | 58.0(3)     |
| O(3)-C(30)-C(40)-C(33) | -120.0(2)   |
| O(4)-C(49)-C(50)-C(51) | 178.1(3)    |
| N(5)-N(6)-C(29)-C(28)  | 0.3(4)      |
| N(5)-C(27)-C(28)-C(29) | -0.6(3)     |
| N(5)-C(27)-C(28)-C(30) | -174.9(3)   |
| N(5)-C(27)-C(46)-C(47) | 103.8(3)    |
| N(5)-C(27)-C(46)-C(51) | -84.6(4)    |
| N(6)-N(5)-C(27)-C(28)  | 0.8(3)      |
| N(6)-N(5)-C(27)-C(46)  | 177.0(3)    |
| N(6)-N(5)-C(42)-C(43)  | 117.9(3)    |
| N(6)-N(5)-C(42)-C(44)  | -121.2(4)   |
| N(6)-N(5)-C(42)-C(45)  | 0.6(5)      |
| N(6)-N(5)-C(42)-C(43A) | 161.9(17)   |
| N(6)-N(5)-C(42)-C(44A) | -76.7(18)   |
| N(6)-N(5)-C(42)-C(45A) | 38.9(18)    |
| N(7)-C(33)-C(40)-N(8)  | 1.8(4)      |
| N(7)-C(33)-C(40)-C(30) | 179.9(2)    |
| N(7)-C(34)-C(35)-C(36) | -179.9(2)   |
| N(7)-C(34)-C(39)-N(8)  | 2.1(4)      |
| N(7)-C(34)-C(39)-C(38) | -179.3(2)   |
| C(27)-N(5)-N(6)-C(29)  | -0.7(4)     |
| C(27)-N(5)-C(42)-C(43) | -59.5(4)    |
| C(27)-N(5)-C(42)-C(44) | 61.4(5)     |
| C(27)-N(5)-C(42)-C(45) | -176.8(4)   |
| C(27)-N(5)-C(42)-C(43A) | -15.5(18)   |
| C(27)-N(5)-C(42)-C(44A) | 105.9(18)   |
| C(27)-N(5)-C(42)-C(45A) | -138.5(18)  |
| C(27)-C(28)-C(29)-N(6) | 0.2(3)      |
| C(27)-C(28)-C(30)-O(3) | -164.4(3)   |
| C(27)-C(28)-C(30)-C(31) | 73.3(3)     |
| C(27)-C(28)-C(30)-C(40) | -39.5(4)    |
| C(27)-C(46)-C(47)-C(48) | 170.8(2)    |
| C(27)-C(46)-C(51)-C(50) | -171.5(3)   |
| C(28)-C(27)-C(46)-C(47) | -80.7(4)    |
| C(28)-C(27)-C(46)-C(51) | 90.8(4)     |
| C(28)-C(30)-C(31)-C(32) | -121.7(2)   |
| C(28)-C(30)-C(31)-C(41) | 55.9(3)     |
| C(28)-C(30)-C(40)-N(8)  | -63.6(3)    |
| C(28)-C(30)-C(40)-C(33) | 118.4(2)    |
| C(29)-C(28)-C(30)-O(3)  | 22.4(3)     |
| C(29)-C(28)-C(30)-C(31) | -99.9(3)    |
| C(29)-C(28)-C(30)-C(40) | 147.3(3)    |
| C(30)-C(28)-C(29)-N(6)  | 174.6(3)    |
| C(30)-C(31)-C(32)-C(33) | 0.5(3)      |
| C(31)-C(30)-C(40)-N(8)  | 178.0(2)    |
| C(31)-C(30)-C(40)-C(33) | 0.0(2)      |
| C(31)-C(32)-C(33)-N(7)  | 179.9(2)    |
| C(32)-C(33)-C(40)-N(8)  | -0.4(3)     |
| C(32)-C(33)-C(40)-C(40) | -177.8(2)   |
| C(33)-N(7)-C(34)-C(35)  | 175.1(2)    |
| C(33)-N(7)-C(34)-C(39)  | -4.3(3)     |
| C(34)-N(7)-C(33)-C(32)  | -177.9(2)   |
| C(34)-N(7)-C(33)-C(40)  | 2.6(3)      |
| C(34)-C(35)-C(36)-C(37) | -0.3(4)     |
| C(35)-C(34)-C(39)-N(8)  | -177.4(2)   |
| C(35)-C(34)-C(39)-C(34) | 1.4(3)      |
| C(39)-N(8)-C(40)-C(30)  | 178.2(2)    |
| C(39)-N(8)-C(40)-C(33)  | -4.1(3)     |
| C(39)-C(34)-C(35)-C(36) | -0.4(3)     |
| C(40)-N(8)-C(39)-C(34)  | 2.1(3)      |
| C(40)-N(8)-C(39)-C(38)  | -176.4(2)   |
| C(40)-C(30)-C(31)-C(32) | -0.3(3)     |
| C(40)-C(30)-C(31)-C(41) | 177.3(2)    |
| C(41)-C(31)-C(32)-C(33) | -177.0(2)   |
| C(42)-N(5)-N(6)-C(29)   | -178.6(3)   |
| C(42)-N(5)-C(27)-C(28)  | -5.4(5)     |
| C(46)-C(27)-C(28)-C(29) | -176.8(3)   |
Table S8. Hydrogen bonds for 15a [Å and °].

| D-H...A     | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|-------------|--------|----------|----------|--------|
| O(1)-H(1O)...N(3)#1 | 0.89(3) | 2.05(4)  | 2.917(3) | 163(3) |
| O(3)-H(3O)...N(7)#2 | 0.85(4) | 2.07(4)  | 2.894(3) | 162(3) |
| O(5)-H(5O)...N(2)   | 0.90(7) | 1.91(7)  | 2.805(4) | 170(6) |
| O(6)-H(6O)...O(4)#3 | 0.95(6) | 1.81(6)  | 2.754(4) | 172(5) |
| O(7)-H(7O)...O(2)#4 | 0.84    | 1.57     | 2.33(2)  | 148.8  |
| O(8)-H(8O)...N(6)#5 | 0.84    | 2.05     | 2.70(3)  | 134.5  |

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1  #2 -x,-y+1,-z+2  
#3 -x,-y+1,-z+1  #4 x-1,y+1,z  #5 -x+1,-y+1,-z+2

X-ray crystallographic data for compound 15m:

X-ray diffraction data were collected at 100K on a Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu Kα-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program. The structure was solved by direct methods using SHELXT and refined on Fl using SHELXL-2018 in the OLEX2 program. Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters.
Table S9. Crystal data and structure refinement for 15m.

| Identification code | 15m          |
|---------------------|--------------|
| Empirical formula   | C29 H24 N4 O2|
| Formula weight      | 460.52       |
| Temperature         | 100.0(1) K   |
| Wavelength          | 1.54184 Å    |
| Crystal system      | Monoclinic   |
| Space group         | P2₁/n        |
| Unit cell dimensions|             |
| a = 15.06336(14) Å  |             |
| b = 7.17340(5) Å    | =109.6165(10)°. |
| c = 22.2144(2) Å    | = 90°.      |
| Volume              | 2261.07(4) Å³|
| Z                   | 4            |
| Density (calculated)| 1.353 g/cm³  |
| Absorption coefficient| 0.694 mm⁻¹  |
| F(000)              | 968          |
| Crystal size        | 0.05 x 0.04 x 0.01 mm³|
| Theta range for data collection | 3.122 to 79.505°. |
| Index ranges        | -19<=h<=19, -8<=k<=9, -28<=l<=28 |
| Reflections collected | 32034     |
| Independent reflections | 4916 [R(int) = 0.0239] |
| Observed reflections | 4630        |
| Completeness to theta = 67.684° | 100.0 %   |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.93109 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 4916 / 0 / 412 |
| Goodness-of-fit on F² | 1.055     |
| Final R indices [I>2sigma(I)] | R1 = 0.0382, wR2 = 0.0990 |
| R indices (all data) | R1 = 0.0400, wR2 = 0.1004 |
| Largest diff. peak and hole | 0.303 and -0.238 e.Å⁻³ |
| CCDC                 | 2159682     |
Table S10. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 15m. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| O(1)| 9252(1)| 10460(1)| 3488(1)| 29(1) |
| O(2)| 5538(1)| 3309(1)| 4358(1)| 24(1) |
| N(1)| 4706(1)| 8736(1)| 4195(1)| 19(1) |
| N(2)| 5395(1)| 9588(1)| 4030(1)| 20(1) |
| N(3)| 8743(1)| 3984(1)| 4910(1)| 22(1) |
| N(4)| 7254(1)| 5050(1)| 5390(1)| 20(1) |
| C(1)| 5996(1)| 8224(2)| 4016(1)| 19(1) |
| C(2)| 5687(1)| 6495(2)| 4171(1)| 19(1) |
| C(3)| 4853(1)| 6882(2)| 4279(1)| 19(1) |
| C(4)| 3942(1)| 9842(2)| 4288(1)| 21(1) |
| C(5)| 3115(1)| 10145(2)| 3682(1)| 19(1) |
| C(6)| 3225(1)| 11078(2)| 3161(1)| 22(1) |
| C(7)| 2460(1)| 11360(2)| 2609(1)| 24(1) |
| C(8)| 1572(1)| 10717(2)| 2570(1)| 25(1) |
| C(9)| 1451(1)| 9807(2)| 3088(1)| 24(1) |
| C(10)| 2223(1)| 9529(2)| 3643(1)| 21(1) |
| C(11)| 6869(1)| 8692(2)| 3879(1)| 20(1) |
| C(12)| 6863(1)| 8946(2)| 3255(1)| 25(1) |
| C(13)| 7671(1)| 9498(2)| 3135(1)| 27(1) |
| C(14)| 8504(1)| 9804(2)| 3644(1)| 23(1) |
| C(15)| 8530(1)| 9486(2)| 4266(1)| 24(1) |
| C(16)| 7712(1)| 8942(2)| 4378(1)| 23(1) |
| C(17)| 10077(1)| 10946(2)| 4014(1)| 28(1) |
| C(18)| 6171(1)| 4626(2)| 4250(1)| 19(1) |
| C(19)| 6493(1)| 4090(2)| 3685(1)| 21(1) |
| C(20)| 7429(1)| 3833(2)| 3868(1)| 22(1) |
| C(21)| 7856(1)| 4137(2)| 4553(1)| 20(1) |
| C(22)| 7117(1)| 4642(2)| 4797(1)| 19(1) |
| C(23)| 5799(1)| 3896(2)| 3029(1)| 26(1) |
| C(24)| 8917(1)| 4368(2)| 5550(1)| 22(1) |
| C(25)| 9848(1)| 4197(2)| 5977(1)| 25(1) |
| C(26)| 10046(1)| 4545(2)| 6618(1)| 28(1) |
| C(27)| 9330(1)| 5116(2)| 6851(1)| 27(1) |
| C(28)| 8415(1)| 5315(2)| 6443(1)| 25(1) |
| C(29)| 8190(1)| 4922(2)| 5787(1)| 21(1) |
Table S11. Bond lengths [Å] and angles [°] for 15m.

| Bond                  | Length [Å]  | Angle [°]    |
|-----------------------|-------------|--------------|
| O(1)-C(14)            | 1.3682(14)  |              |
| O(1)-C(17)            | 1.4329(16)  |              |
| O(2)-H(2)             | 0.93(2)     |              |
| O(2)-C(18)            | 1.4195(13)  |              |
| N(1)-N(2)             | 1.3574(13)  |              |
| N(1)-C(3)             | 1.3511(14)  |              |
| N(1)-C(4)             | 1.4682(14)  |              |
| N(2)-C(1)             | 1.3404(14)  |              |
| N(3)-C(21)            | 1.3106(15)  |              |
| N(3)-C(24)            | 1.3845(15)  |              |
| N(4)-C(22)            | 1.2972(15)  |              |
| N(4)-C(29)            | 1.3924(15)  |              |
| C(1)-C(2)             | 1.4075(15)  |              |
| C(1)-C(11)            | 1.4833(15)  |              |
| C(2)-C(3)             | 1.3833(15)  |              |
| C(2)-C(18)            | 1.5088(15)  |              |
| C(3)-H(3)             | 0.933(15)   |              |
| C(4)-H(4A)            | 0.978(16)   |              |
| C(4)-H(4B)            | 1.006(15)   |              |
| C(4)-C(5)             | 1.5114(15)  |              |
| C(5)-C(6)             | 1.3941(16)  |              |
| C(5)-C(10)            | 1.3898(16)  |              |
| C(6)-H(6)             | 0.972(16)   |              |
| C(6)-C(7)             | 1.3876(17)  |              |
| C(7)-H(7)             | 0.982(15)   |              |
| C(7)-C(8)             | 1.3895(17)  |              |
| C(8)-H(8)             | 0.987(15)   |              |
| C(8)-C(9)             | 1.3864(18)  |              |
| C(9)-H(9)             | 1.017(16)   |              |
| C(9)-C(10)            | 1.3960(17)  |              |
| C(10)-H(10)           | 0.978(16)   |              |
| C(11)-C(12)           | 1.3964(17)  |              |
| C(11)-C(16)           | 1.3890(16)  |              |
| C(12)-H(12)           | 1.009(16)   |              |
| C(12)-C(13)           | 1.3877(17)  |              |
| C(13)-H(13)           | 0.983(18)   |              |
| C(13)-C(14)           | 1.3957(17)  |              |
| C(14)-C(15)           | 1.3891(17)  |              |
| C(14)-O(1)-C(17)     | 116.11(10)  |              |
| C(15)-H(15)           | 0.999(17)   |              |
| C(15)-C(16)           | 1.3922(16)  |              |
| C(16)-H(16)           | 0.970(17)   |              |
| C(17)-H(17A)         | 0.990(17)   |              |
| C(17)-H(17B)         | 0.990(17)   |              |
| C(17)-H(17C)         | 1.020(16)   |              |
| C(18)-C(19)           | 1.5380(16)  |              |
| C(18)-C(22)           | 1.5322(15)  |              |
| C(19)-C(20)           | 1.3416(16)  |              |
| C(19)-C(23)           | 1.4877(16)  |              |
| C(20)-H(20)           | 1.013(15)   |              |
| C(20)-C(21)           | 1.4547(16)  |              |
| C(21)-C(22)           | 1.4382(15)  |              |
| C(23)-H(23A)         | 0.993(18)   |              |
| C(23)-H(23B)         | 0.992(18)   |              |
| C(23)-H(23C)         | 1.4108(16)  |              |
| C(24)-C(25)           | 1.4227(16)  |              |
| C(25)-H(25)           | 0.953(16)   |              |
| C(25)-C(26)           | 1.3762(18)  |              |
| C(26)-H(26)           | 0.999(17)   |              |
| C(26)-C(27)           | 1.4051(19)  |              |
| C(27)-H(27)           | 0.990(18)   |              |
| C(27)-C(28)           | 1.3788(18)  |              |
| C(28)-H(28)           | 0.988(16)   |              |
| C(28)-C(29)           | 1.4081(17)  |              |
| C(14)-O(1)-C(17)     | 116.11(10)  |              |
| C(18)-O(2)-H(2)      | 111.1(11)   |              |
| N(2)-N(1)-C(4)       | 120.10(9)   |              |
| C(3)-N(1)-N(2)       | 112.05(9)   |              |
| C(3)-N(1)-C(4)       | 127.79(10)  |              |
| C(1)-N(2)-N(1)       | 105.15(9)   |              |
| C(21)-N(3)-C(24)     | 114.05(10)  |              |
| C(22)-N(4)-C(29)     | 114.21(10)  |              |
| N(2)-C(1)-C(2)       | 110.86(10)  |              |
| N(2)-C(1)-C(11)      | 119.43(10)  |              |
| C(2)-C(1)-C(11)      | 129.65(10)  |              |
| Bond                  | Distance (Å)  |
|----------------------|--------------|
| C(1)-C(2)-C(18)      | 128.65(10)   |
| C(3)-C(2)-C(1)       | 105.08(10)   |
| C(3)-C(2)-C(18)      | 126.15(10)   |
| N(1)-C(3)-C(2)       | 106.87(10)   |
| N(1)-C(3)-H(3)       | 122.2(9)     |
| C(2)-C(3)-H(3)       | 131.0(9)     |
| N(1)-C(4)-H(4A)      | 107.8(9)     |
| N(1)-C(4)-H(4B)      | 106.7(8)     |
| N(1)-C(4)-C(5)       | 113.75(9)    |
| H(4A)-C(4)-H(4B)     | 109.8(12)    |
| C(5)-C(4)-H(4A)      | 109.3(9)     |
| C(5)-C(4)-H(4B)      | 109.4(8)     |
| C(6)-C(5)-C(4)       | 121.05(10)   |
| C(10)-C(5)-C(4)      | 119.99(10)   |
| C(10)-C(5)-C(6)      | 118.95(11)   |
| C(5)-C(6)-H(6)       | 119.5(9)     |
| C(7)-C(6)-C(5)       | 120.55(11)   |
| C(7)-C(6)-H(6)       | 119.9(9)     |
| C(6)-C(7)-H(7)       | 121.0(9)     |
| C(6)-C(7)-C(8)       | 120.17(11)   |
| C(8)-C(7)-H(7)       | 118.8(9)     |
| C(7)-C(8)-H(8)       | 120.3(9)     |
| C(9)-C(8)-C(7)       | 119.82(11)   |
| C(9)-C(8)-H(8)       | 119.9(9)     |
| C(8)-C(9)-H(9)       | 121.6(9)     |
| C(8)-C(9)-C(10)      | 119.85(11)   |
| C(10)-C(9)-H(9)      | 118.5(9)     |
| C(5)-C(10)-C(9)      | 120.65(11)   |
| C(5)-C(10)-H(10)     | 120.2(9)     |
| C(9)-C(10)-H(10)     | 119.1(9)     |
| C(12)-C(11)-C(1)     | 121.56(10)   |
| C(16)-C(11)-C(1)     | 120.05(10)   |
| C(16)-C(11)-C(12)    | 118.36(11)   |
| C(11)-C(12)-H(12)    | 119.7(9)     |
| C(13)-C(12)-C(11)    | 120.98(11)   |
| C(13)-C(12)-H(12)    | 119.3(9)     |
| C(12)-C(13)-H(13)    | 120.8(10)    |
| C(12)-C(13)-C(14)    | 119.84(11)   |
| C(14)-C(13)-H(13)    | 119.3(10)    |
| O(1)-C(14)-C(13)     | 116.23(11)   |
| O(1)-C(14)-C(15)     | 123.94(11)   |
| C(15)-C(14)-C(13)    | 119.81(11)   |
| C(14)-C(15)-H(15)    | 121.9(9)     |
| C(14)-C(15)-C(16)    | 119.59(11)   |
| C(16)-C(15)-H(15)    | 118.5(9)     |
| C(11)-C(16)-C(15)    | 121.34(11)   |
| C(11)-C(16)-H(16)    | 119.5(10)    |
| C(15)-C(16)-H(16)    | 119.1(10)    |
| O(1)-C(17)-H(17A)    | 106.1(10)    |
| O(1)-C(17)-H(17B)    | 111.5(10)    |
| O(1)-C(17)-H(17C)    | 111.4(9)     |
| H(17A)-C(17)-H(17B)  | 109.5(13)    |
| H(17A)-C(17)-H(17C)  | 110.4(13)    |
| H(17B)-C(17)-H(17C)  | 107.9(13)    |
| O(2)-C(18)-C(19)     | 106.52(9)    |
| O(2)-C(18)-C(22)     | 112.77(9)    |
| O(2)-C(18)-C(19)     | 111.66(9)    |
| C(2)-C(18)-C(19)     | 113.59(9)    |
| C(2)-C(18)-C(22)     | 111.73(9)    |
| C(22)-C(18)-C(19)    | 100.67(9)    |
| C(20)-C(19)-C(18)    | 111.95(10)   |
| C(20)-C(19)-C(23)    | 127.29(11)   |
| C(23)-C(19)-C(18)    | 120.76(10)   |
| C(19)-C(20)-H(20)    | 125.3(9)     |
| C(19)-C(20)-C(21)    | 110.31(10)   |
| C(21)-C(20)-H(20)    | 124.4(9)     |
| C(22)-C(21)-C(20)    | 107.83(10)   |
| N(3)-C(21)-C(20)     | 128.55(11)   |
| N(3)-C(21)-C(22)     | 123.61(11)   |
| C(22)-C(21)-C(20)    | 107.83(10)   |
| N(4)-C(22)-C(18)     | 126.61(10)   |
| N(4)-C(22)-C(21)     | 124.17(11)   |
| C(21)-C(22)-C(18)    | 109.22(10)   |
| C(19)-C(23)-H(23A)   | 111.2(10)    |
| C(19)-C(23)-H(23B)   | 110.1(10)    |
| C(19)-C(23)-H(23C)   | 111.3(10)    |
| H(23A)-C(23)-H(23B)  | 107.5(14)    |
| H(23A)-C(23)-H(23C)  | 109.2(14)    |
| H(23B)-C(23)-H(23C)  | 107.4(14)    |
| N(3)-C(24)-C(25)     | 118.44(11)   |
| N(3)-C(24)-C(29)     | 122.21(10)   |
\[
\begin{align*}
\text{C(25)-C(24)-C(29)} & \quad 119.35(11) & \text{C(28)-C(27)-C(26)} & \quad 120.54(12) \\
\text{C(24)-C(25)-H(25)} & \quad 117.3(9) & \text{C(28)-C(27)-H(27)} & \quad 120.1(10) \\
\text{C(26)-C(25)-C(24)} & \quad 120.06(12) & \text{C(27)-C(28)-H(28)} & \quad 122.1(9) \\
\text{C(26)-C(25)-H(25)} & \quad 122.6(9) & \text{C(27)-C(28)-C(29)} & \quad 120.05(12) \\
\text{C(25)-C(26)-H(26)} & \quad 119.1(10) & \text{C(29)-C(28)-H(28)} & \quad 117.8(9) \\
\text{C(25)-C(26)-C(27)} & \quad 120.56(12) & \text{N(4)-C(29)-C(24)} & \quad 121.69(10) \\
\text{C(26)-C(27)-H(27)} & \quad 119.4(10) & \text{N(4)-C(29)-C(28)} & \quad 118.90(11) \\
\text{N(4)-C(29)-C(24)} & \quad 121.69(10) & \text{C(28)-C(29)-C(24)} & \quad 119.40(11)
\end{align*}
\]

**Table S12.** Anisotropic displacement parameters \((\AA^2 \times 10^3)\) for 15m. The anisotropic displacement factor exponent takes the form: 

\[-2\pi^2 \left[ h^2 a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} \right] \]

|       | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{23}\) | \(U_{13}\) | \(U_{12}\) |
|-------|------------|------------|------------|------------|------------|------------|
| O(1)  | 23(1)      | 35(1)      | 32(1)      | 1(1)       | 13(1)      | -4(1)      |
| O(2)  | 25(1)      | 15(1)      | 34(1)      | -2(1)      | 14(1)      | -3(1)      |
| N(1)  | 17(1)      | 17(1)      | 22(1)      | 0(1)       | 6(1)       | 0(1)       |
| N(2)  | 19(1)      | 17(1)      | 24(1)      | 1(1)       | 7(1)       | -1(1)      |
| N(3)  | 22(1)      | 20(1)      | 25(1)      | -2(1)      | 7(1)       | 1(1)       |
| N(4)  | 23(1)      | 16(1)      | 22(1)      | 1(1)       | 8(1)       | 0(1)       |
| C(1)  | 18(1)      | 16(1)      | 20(1)      | 0(1)       | 4(1)       | 1(1)       |
| C(2)  | 18(1)      | 16(1)      | 20(1)      | -1(1)      | 5(1)       | -1(1)      |
| C(3)  | 19(1)      | 16(1)      | 20(1)      | -1(1)      | 6(1)       | -1(1)      |
| C(4)  | 20(1)      | 20(1)      | 22(1)      | -1(1)      | 7(1)       | 2(1)       |
| C(5)  | 20(1)      | 15(1)      | 21(1)      | -1(1)      | 6(1)       | 2(1)       |
| C(6)  | 21(1)      | 21(1)      | 27(1)      | 0(1)       | 10(1)      | -1(1)      |
| C(7)  | 29(1)      | 20(1)      | 23(1)      | 3(1)       | 10(1)      | 3(1)       |
| C(8)  | 24(1)      | 24(1)      | 24(1)      | -1(1)      | 4(1)       | 3(1)       |
| C(9)  | 21(1)      | 24(1)      | 27(1)      | -2(1)      | 7(1)       | -2(1)      |
| C(10)| 23(1)      | 18(1)      | 23(1)      | 0(1)       | 9(1)       | -1(1)      |
| C(11)| 21(1)      | 14(1)      | 27(1)      | 1(1)       | 8(1)       | 1(1)       |
| C(12)| 22(1)      | 27(1)      | 25(1)      | 0(1)       | 6(1)       | -1(1)      |
| C(13)| 27(1)      | 32(1)      | 24(1)      | 1(1)       | 11(1)      | -1(1)      |
| C(14)| 22(1)      | 20(1)      | 31(1)      | 0(1)       | 13(1)      | 0(1)       |
| C(15)| 21(1)      | 22(1)      | 28(1)      | 1(1)       | 6(1)       | 0(1)       |
| C(16)| 22(1)      | 21(1)      | 24(1)      | 2(1)       | 8(1)       | 0(1)       |
| C(17)| 23(1)      | 28(1)      | 36(1)      | 0(1)       | 11(1)      | -3(1)      |
| C(18)| 20(1)      | 15(1)      | 24(1)      | 0(1)       | 8(1)       | -1(1)      |
| C(19)| 23(1)      | 15(1)      | 24(1)      | -1(1)      | 8(1)       | -1(1)      |
Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å² x 10^3) for 15m.

|     | x      | y      | z      | U(eq) |
|-----|--------|--------|--------|-------|
| H(2) | 5628(12)| 2130(30)| 4213(9)| 43(5) |
| H(3) | 4436(10)| 6100(20)| 4389(7)| 22(3) |
| H(4A) | 4204(11)| 11050(20)| 4464(7)| 27(4) |
| H(4B) | 3724(10)| 9150(20)| 4607(7)| 22(3) |
| H(6) | 3842(11)| 11550(20)| 3189(7)| 29(4) |
| H(7) | 2532(10)| 12020(20)| 2241(7)| 25(4) |
| H(8) | 1028(11)| 10910(20)| 2177(7)| 27(4) |
| H(9) | 809(11)| 9340(20)| 3077(7)| 28(4) |
| H(10) | 2129(11)| 8890(20)| 4005(8)| 29(4) |
| H(12) | 6263(11)| 8740(20)| 2884(8)| 29(4) |
| H(13) | 7662(12)| 9700(30)| 2696(9)| 40(5) |
| H(15) | 9116(11)| 9680(20)| 4641(8)| 32(4) |
| H(16) | 7729(11)| 8760(20)| 4815(8)| 31(4) |
| H(17A) | 10516(12)| 11530(20)| 3824(8)| 35(4) |
| H(17B) | 10378(11)| 9830(20)| 4261(8)| 31(4) |
| H(17C) | 9920(11)| 11850(20)| 4319(7)| 29(4) |
| H(20) | 7793(10)| 3500(20)| 3574(7)| 26(4) |
| H(23A) | 6101(12)| 3310(30)| 2727(9)| 42(5) |
| H(23B) | 5554(12)| 5140(20)| 2855(8)| 35(4) |
| H(23C) | 5252(12)| 3130(20)| 3029(8)| 38(4) |
| H(25) | 10323(11)| 3860(20)| 5801(7)| 28(4) |
| H(26) | 10706(12)| 4390(20)| 6916(8)| 36(4) |
| H(27) | 9489(12)| 5400(20)| 7312(8)| 36(4) |
|     |         |         |         |         |        |
|-----|---------|---------|---------|---------|--------|
| H(28) | 7899(11) | 5710(20) | 6595(7) | 27(4)   |        |

Table S14. Torsion angles [°] for 15m.

| Bond | Torsion Angle ° | Bond | Torsion Angle ° |
|------|-----------------|------|-----------------|
| O(1)-C(14)-C(15)-C(16) | 175.45(11) | C(3)-N(1)-C(4)-C(5) | -95.30(13) |
| O(2)-C(18)-C(19)-C(20) | -118.63(11) | C(3)-C(2)-C(18)-O(2) | 8.76(15) |
| O(2)-C(18)-C(19)-C(23) | 60.90(14) | C(3)-C(2)-C(18)-C(19) | 133.52(11) |
| O(2)-C(18)-C(22)-N(4) | -61.42(14) | C(3)-C(2)-C(18)-C(22) | -113.42(12) |
| O(2)-C(18)-C(22)-C(21) | 118.91(10) | C(4)-N(1)-N(2)-C(1) | 176.90(9) |
| N(1)-N(2)-C(1)-C(2) | 0.18(12) | C(4)-N(1)-C(3)-C(2) | -176.55(10) |
| N(1)-N(2)-C(1)-C(11) | -177.21(9) | C(4)-C(5)-C(6)-C(7) | -179.52(11) |
| N(1)-C(4)-C(5)-C(6) | -60.79(14) | C(4)-C(5)-C(10)-C(9) | 179.68(10) |
| N(1)-C(4)-C(5)-C(10) | 120.78(11) | C(5)-C(6)-C(7)-C(8) | 0.17(18) |
| N(2)-N(1)-C(3)-C(2) | 0.55(13) | C(6)-C(7)-C(8)-C(9) | 1.21(17) |
| N(2)-N(1)-C(4)-C(5) | 87.81(12) | C(7)-C(8)-C(9)-C(10) | 0.61(18) |
| N(2)-C(1)-C(2)-C(3) | 0.14(13) | C(8)-C(9)-C(10)-C(5) | -0.45(18) |
| N(2)-C(1)-C(2)-C(18) | -176.04(10) | C(10)-C(5)-C(6)-C(7) | -1.07(17) |
| N(2)-C(1)-C(11)-C(12) | -81.58(14) | C(11)-C(1)-C(2)-C(3) | 177.19(11) |
| N(2)-C(1)-C(11)-C(16) | 96.42(13) | C(11)-C(1)-C(2)-C(18) | 1.0(2) |
| N(3)-C(21)-C(22)-N(4) | 2.02(18) | C(11)-C(12)-C(13)-C(14) | 0.05(19) |
| N(3)-C(21)-C(22)-C(18) | -178.31(10) | C(12)-C(11)-C(16)-C(15) | 1.78(17) |
| N(3)-C(24)-C(25)-C(26) | -179.25(11) | C(12)-C(13)-C(14)-O(1) | -175.94(11) |
| N(3)-C(24)-C(29)-N(4) | 2.19(17) | C(12)-C(13)-C(14)-C(15) | 2.45(19) |
| N(3)-C(24)-C(29)-C(28) | -179.17(11) | C(13)-C(14)-C(15)-C(16) | -2.81(18) |
| C(1)-C(2)-C(3)-N(1) | -0.40(12) | C(14)-C(15)-C(16)-C(11) | 0.68(18) |
| C(1)-C(2)-C(18)-O(2) | -175.81(11) | C(16)-C(11)-C(12)-C(13) | -2.14(18) |
| C(1)-C(2)-C(18)-C(19) | -51.05(16) | C(17)-O(1)-C(14)-C(13) | 174.08(11) |
| C(1)-C(2)-C(18)-C(22) | 62.00(15) | C(17)-O(1)-C(14)-C(15) | -4.24(17) |
| C(1)-C(11)-C(12)-C(13) | 175.90(11) | C(18)-C(2)-C(3)-N(1) | 175.90(10) |
| C(1)-C(11)-C(16)-C(15) | -176.29(11) | C(18)-C(19)-C(20)-C(21) | 0.21(14) |
| C(2)-C(1)-C(11)-C(12) | 101.59(15) | C(19)-C(18)-C(22)-N(4) | 178.67(11) |
| C(2)-C(1)-C(11)-C(16) | -80.41(16) | C(19)-C(18)-C(22)-C(21) | -1.00(11) |
| C(2)-C(18)-C(19)-C(20) | 120.05(11) | C(19)-C(20)-C(21)-N(3) | 178.58(11) |
| C(2)-C(18)-C(19)-C(23) | -60.42(14) | C(19)-C(20)-C(21)-C(22) | -0.87(13) |
| C(2)-C(18)-C(22)-N(4) | 57.77(14) | C(20)-C(21)-C(22)-N(4) | -178.50(10) |
| C(2)-C(18)-C(22)-C(21) | -121.89(10) | C(20)-C(21)-C(22)-C(18) | 1.18(12) |
| C(3)-N(1)-N(2)-C(1) | -0.46(12) | | | |
Table S15. Hydrogen bonds for 15m [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| O(2)-H(2)...N(2)#1 | 0.93(2) | 1.87(2)  | 2.7564(13) | 156.8(16) |

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z

X-ray crystallographic data for compound 18:

X-ray diffraction data were collected at 100K on a Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu Kα-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program. The structure was solved by direct methods using SHELXT and refined on $F^2$ using SHELXL-2018 in the OLEX2 program. Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters.
Table S16. Crystal data and structure refinement for 18.

| Identification code | 18 |
|---------------------|----|
| Empirical formula   | C20 H24 N2 O4 |
| Formula weight      | 356.41 |
| Temperature         | 100.0(1) K |
| Wavelength          | 1.54184 Å |
| Crystal system      | Triclinic |
| Space group         | P T |
| Unit cell dimensions| a = 7.0064(2) Å, b = 10.6340(4) Å, c = 13.5148(5) Å |
|                     | □=101.528(3)°, □=101.535(3)°, □=108.514(3)° |
| Volume              | 897.17(6) Å³ |
| Z                   | 2 |
| Density (calculated)| 1.319 g/cm³ |
| Absorption coefficient| 0.753 mm⁻¹ |
| F(000)              | 380 |
| Crystal size        | 0.167 x 0.042 x 0.024 mm³ |
| Theta range for data collection | 3.480 to 79.797° |
| Index ranges        | -8<=h<=6, -13<=k<=13, -16<=l<=17 |
| Reflections collected| 15589 |
| Independent reflections | 3705 [R(int) = 0.0454] |
| Observed reflections | 3149 |
| Completeness to theta = 67.684° | 98.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.70049 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 3705 / 0 / 332 |
| Goodness-of-fit on F² | 1.032 |
| Final R indices [I>2sigma(I)] | R1 = 0.0484, wR2 = 0.1218 |
| R indices (all data) | R1 = 0.0566, wR2 = 0.1266 |
| Extinction coefficient | 0.0026(7) |
| Largest diff. peak and hole | 0.370 and -0.330 e.Å⁻³ |
| CCDC                | 2159684 |
Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 18. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

|     | x      | y      | z      | U(eq)  |
|-----|--------|--------|--------|--------|
| O(1)| 10633(2)| 8091(1)| 4950(1)| 24(1)  |
| O(2)| -774(2)| 2873(1)| 1740(1)| 19(1)  |
| O(3)| 3453(2)| 3802(1)| 815(1) | 20(1)  |
| O(4)| 6112(2)| 3356(2)| 2507(1)| 24(1)  |
| N(1)| -205(2)| 6544(2)| 966(1) | 18(1)  |
| N(2)| 1790(2)| 7320(2)| 1576(1)| 16(1)  |
| C(1)| 2636(3)| 6558(2)| 2101(1)| 16(1)  |
| C(2)| 1119(3)| 5226(2)| 1790(1)| 15(1)  |
| C(3)| -596(3)| 5289(2)| 1093(1)| 17(1)  |
| C(4)| 2730(3)| 8813(2)| 1606(2)| 20(1)  |
| C(5)| 4875(3)| 9109(2)| 1393(2)| 27(1)  |
| C(6)| 2903(3)| 9715(2)| 2679(2)| 25(1)  |
| C(7)| 1292(3)| 9100(2)| 745(2) | 27(1)  |
| C(8)| 4751(3)| 7067(2)| 2862(1)| 16(1)  |
| C(9)| 6388(3)| 6783(2)| 2537(2)| 18(1)  |
| C(10)| 8318(3)| 7141(2)| 3254(2)| 20(1)  |
| C(11)| 8671(3)| 7792(2)| 4311(2)| 19(1)  |
| C(12)| 7066(3)| 8092(2)| 4652(2)| 19(1)  |
| C(13)| 5124(3)| 7722(2)| 3921(1)| 18(1)  |
| C(14)| 11065(3)| 8740(2)| 6049(2)| 24(1)  |
| C(15)| 1248(3)| 3961(2)| 2093(1)| 16(1)  |
| C(16)| 2706(3)| 3329(2)| 1611(1)| 17(1)  |
| C(17)| 4509(3)| 3554(2)| 2553(2)| 18(1)  |
| C(18)| 3918(3)| 3967(2)| 3503(2)| 19(1)  |
| C(19)| 2161(3)| 4228(2)| 3277(1)| 17(1)  |
| C(20)| 1087(3)| 4696(2)| 4039(2)| 20(1)  |
Table S18. Bond lengths [Å] and angles [°] for 18.

| Bond                  | Length  | Angle      |
|-----------------------|---------|------------|
| O(1)-C(11)            | 1.370(2)|            |
| O(1)-C(14)            | 1.431(2)|            |
| O(2)-H(2)             | 0.86(3) |            |
| O(2)-C(15)            | 1.429(2)|            |
| O(3)-H(3)             | 0.97(3) |            |
| O(3)-C(16)            | 1.399(2)|            |
| O(4)-C(17)            | 1.218(2)|            |
| N(1)-N(2)             | 1.360(2)|            |
| N(1)-C(3)             | 1.329(2)|            |
| N(2)-C(1)             | 1.370(2)|            |
| N(2)-C(4)             | 1.502(2)|            |
| C(1)-C(2)             | 1.393(2)|            |
| C(1)-C(8)             | 1.485(2)|            |
| C(2)-C(3)             | 1.399(2)|            |
| C(2)-C(15)            | 1.507(2)|            |
| C(3)-H(3A)            | 0.99(3) |            |
| C(4)-C(5)             | 1.533(3)|            |
| C(4)-C(6)             | 1.529(3)|            |
| C(4)-C(7)             | 1.527(3)|            |
| C(5)-H(5A)            | 0.97(3) |            |
| C(5)-H(5B)            | 0.96(3) |            |
| C(5)-H(5C)            | 1.04(3) |            |
| C(6)-H(6A)            | 1.05(3) |            |
| C(6)-H(6B)            | 0.95(3) |            |
| C(6)-H(6C)            | 1.01(3) |            |
| C(7)-H(7A)            | 0.98(2) |            |
| C(7)-H(7B)            | 1.02(3) |            |
| C(7)-H(7C)            | 0.99(3) |            |
| C(8)-C(9)             | 1.403(2)|            |
| C(8)-C(13)            | 1.392(3)|            |
| C(9)-H(9)             | 0.96(2) |            |
| C(9)-C(10)            | 1.383(3)|            |
| C(10)-H(10)           | 0.95(2) |            |
| C(10)-C(11)           | 1.391(3)|            |
| C(11)-C(12)           | 1.399(3)|            |
| C(12)-H(12)           | 0.96(3) |            |
| C(12)-C(13)           | 1.396(2)|            |
| C(13)-H(13)           | 0.99(2) |            |
| C(14)-H(14A)          | 1.00(2) |            |
| C(14)-H(14B)          | 0.99(2) |            |
| C(14)-H(14C)          | 1.00(2) |            |
| C(15)-C(16)           | 1.564(2)|            |
| C(15)-C(19)           | 1.531(2)|            |
| C(16)-H(16)           | 0.98(2) |            |
| C(16)-C(17)           | 1.523(2)|            |
| C(17)-C(18)           | 1.454(3)|            |
| C(18)-H(18)           | 0.97(3) |            |
| C(18)-C(19)           | 1.337(3)|            |
| C(19)-C(20)           | 1.489(2)|            |
| C(20)-H(20A)          | 0.98(3) |            |
| C(20)-H(20B)          | 0.97(3) |            |
| C(20)-H(20C)          | 1.01(2) |            |
| C(11)-O(1)-C(14)      | 117.78(15)|         |
| C(15)-O(2)-H(2)       | 114(2) |            |
| C(16)-O(3)-H(3)       | 106.9(18)|          |
| C(3)-N(1)-N(2)        | 105.68(14)|          |
| N(1)-N(2)-C(1)        | 111.12(14)|          |
| N(1)-N(2)-C(4)        | 119.22(14)|          |
| C(1)-N(2)-C(4)        | 129.65(15)|          |
| N(2)-C(1)-C(2)        | 106.59(15)|          |
| N(2)-C(1)-C(8)        | 126.37(16)|          |
| C(2)-C(1)-C(8)        | 127.04(16)|          |
| C(1)-C(2)-C(3)        | 104.87(15)|          |
| C(1)-C(2)-C(15)       | 129.02(15)|          |
| C(3)-C(2)-C(15)       | 126.10(15)|          |
| N(1)-C(3)-C(2)        | 111.72(15)|          |
| N(1)-C(3)-H(3A)       | 119.7(14)|          |
| C(2)-C(3)-H(3A)       | 128.6(14)|          |
| N(2)-C(4)-C(5)        | 109.52(15)|          |
| N(2)-C(4)-C(6)        | 108.82(15)|          |
| N(2)-C(4)-C(7)        | 109.01(15)|          |
| C(6)-C(4)-C(5)        | 111.73(16)|          |
| C(7)-C(4)-C(5)        | 108.56(17)|          |
| C(7)-C(4)-C(6)        | 109.17(16)|          |
| C(4)-C(5)-H(5A)       | 109.3(15)|          |
| Bond                                    | Angle (°)   |
|-----------------------------------------|------------|
| C(4)-C(5)-H(5B)                        | 113.2(14)  |
| C(4)-C(5)-H(5C)                        | 107.8(13)  |
| H(5A)-C(5)-H(5B)                       | 108(2)     |
| H(5A)-C(5)-H(5C)                       | 110(2)     |
| H(5B)-C(5)-H(5C)                       | 109(2)     |
| C(4)-C(6)-H(6A)                        | 108.8(15)  |
| C(4)-C(6)-H(6B)                        | 111.5(16)  |
| C(4)-C(6)-H(6C)                        | 108.0(14)  |
| H(6A)-C(6)-H(6B)                       | 110(2)     |
| H(6A)-C(6)-H(6C)                       | 107(2)     |
| H(6B)-C(6)-H(6C)                       | 111(2)     |
| C(4)-C(7)-H(7A)                        | 110.3(14)  |
| C(4)-C(7)-H(7B)                        | 108.5(14)  |
| C(4)-C(7)-H(7C)                        | 112.5(15)  |
| H(7A)-C(7)-H(7B)                       | 110(2)     |
| H(7A)-C(7)-H(7C)                       | 110(2)     |
| H(7B)-C(7)-H(7C)                       | 106(2)     |
| C(9)-C(8)-C(1)                         | 119.73(16) |
| C(13)-C(8)-C(1)                        | 121.75(15) |
| C(13)-C(8)-C(9)                        | 118.28(16) |
| C(8)-C(9)-H(9)                         | 120.4(13)  |
| C(10)-C(9)-C(8)                        | 120.66(17) |
| C(10)-C(9)-H(9)                        | 118.9(13)  |
| C(9)-C(10)-H(10)                       | 120.4(14)  |
| C(9)-C(10)-C(11)                       | 120.57(16) |
| C(11)-C(10)-H(10)                      | 119.1(14)  |
| O(1)-C(11)-C(10)                       | 115.62(16) |
| O(1)-C(11)-C(12)                       | 124.61(17) |
| C(10)-C(11)-C(12)                      | 119.77(16) |
| C(11)-C(12)-H(12)                      | 120.6(14)  |
| C(13)-C(12)-C(11)                      | 119.11(17) |
| C(13)-C(12)-H(12)                      | 120.3(14)  |
| C(8)-C(13)-C(12)                       | 121.60(16) |
| C(8)-C(13)-H(13)                       | 119.6(14)  |
| C(12)-C(13)-H(13)                      | 118.8(14)  |
| O(1)-C(14)-H(14A)                      | 110.8(14)  |
| O(1)-C(14)-H(14B)                      | 103.7(14)  |
| O(1)-C(14)-H(14C)                      | 111.9(14)  |
| H(14A)-C(14)-H(14B)                    | 107.8(19)  |
| H(14A)-C(14)-H(14C)                    | 110.7(19)  |
| H(14B)-C(14)-H(14C)                    | 111.6(19)  |
| O(2)-C(15)-C(2)                        | 110.43(13) |
| O(2)-C(15)-C(16)                       | 105.24(13) |
| O(2)-C(15)-C(19)                       | 109.37(14) |
| C(2)-C(15)-C(16)                       | 114.87(14) |
| C(2)-C(15)-C(19)                       | 113.59(14) |
| C(19)-C(15)-C(16)                      | 102.76(13) |
| O(3)-C(16)-H(16)                       | 111.7(13)  |
| O(3)-C(16)-C(17)                       | 111.14(14) |
| C(15)-C(16)-H(16)                      | 105.8(13)  |
| C(17)-C(16)-C(15)                      | 104.52(14) |
| C(17)-C(16)-H(16)                      | 103.4(13)  |
| O(4)-C(17)-C(16)                       | 125.42(17) |
| O(4)-C(17)-C(18)                       | 126.58(17) |
| C(18)-C(17)-C(16)                      | 107.91(14) |
| C(17)-C(18)-H(18)                      | 124.3(15)  |
| C(19)-C(18)-C(17)                      | 110.93(17) |
| C(19)-C(18)-H(18)                      | 124.7(15)  |
| C(18)-C(19)-C(20)                      | 112.41(15) |
| C(18)-C(19)-C(20)                      | 126.81(17) |
| C(20)-C(19)-C(15)                      | 120.77(15) |
| C(19)-C(20)-H(20A)                     | 109.8(15)  |
| C(19)-C(20)-H(20B)                     | 112.1(15)  |
| C(19)-C(20)-H(20C)                     | 109.8(14)  |
| H(20A)-C(20)-H(20B)                    | 110(2)     |
| H(20A)-C(20)-H(20C)                    | 105(2)     |
| H(20B)-C(20)-H(20C)                    | 110(2)     |
Table S19. Anisotropic displacement parameters (Å² x 10³) for 18. The anisotropic displacement factor exponent takes the form: -2π²( h² a*² U₁₁ + ... + 2 h k a* b* U₁₂ )

|        | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|--------|------|------|------|------|------|------|
| O(1)   | 15(1)| 28(1)| 24(1)| 4(1) | 0(1) | 8(1) |
| O(2)   | 12(1)| 19(1)| 24(1)| 3(1) | 4(1) | 6(1) |
| O(3)   | 18(1)| 26(1)| 18(1)| 7(1) | 6(1) | 10(1) |
| O(4)   | 16(1)| 34(1)| 28(1)| 10(1)| 7(1) | 15(1) |
| N(1)   | 13(1)| 21(1)| 17(1)| 3(1) | 1(1) | 8(1) |
| N(2)   | 16(1)| 17(1)| 17(1)| 3(1) | 2(1) | 8(1) |
| C(1)   | 16(1)| 18(1)| 17(1)| 4(1) | 6(1) | 9(1) |
| C(2)   | 12(1)| 19(1)| 15(1)| 2(1) | 4(1) | 8(1) |
| C(3)   | 13(1)| 20(1)| 17(1)| 3(1) | 3(1) | 8(1) |
| C(4)   | 22(1)| 16(1)| 21(1)| 4(1) | 4(1) | 8(1) |
| C(5)   | 28(1)| 25(1)| 31(1)| 12(1)| 11(1)| 10(1)|
| C(6)   | 29(1)| 22(1)| 22(1)| 3(1) | 3(1) | 11(1)|
| C(7)   | 31(1)| 21(1)| 26(1)| 7(1) | -1(1)| 12(1)|
| C(8)   | 14(1)| 15(1)| 21(1)| 6(1) | 4(1) | 6(1) |
| C(9)   | 17(1)| 19(1)| 20(1)| 5(1) | 6(1) | 8(1) |
| C(10)  | 15(1)| 20(1)| 26(1)| 6(1) | 8(1) | 9(1) |
| C(11)  | 14(1)| 18(1)| 24(1)| 7(1) | 2(1) | 6(1) |
| C(12)  | 17(1)| 19(1)| 17(1)| 3(1) | 3(1) | 6(1) |
| C(13)  | 14(1)| 18(1)| 21(1)| 6(1) | 6(1) | 7(1) |
| C(14)  | 22(1)| 24(1)| 22(1)| 6(1) | 0(1) | 6(1) |
| C(15)  | 11(1)| 17(1)| 18(1)| 2(1) | 3(1) | 5(1) |
| C(16)  | 16(1)| 18(1)| 19(1)| 4(1) | 5(1) | 8(1) |
| C(17)  | 16(1)| 16(1)| 22(1)| 6(1) | 5(1) | 6(1) |
| C(18)  | 17(1)| 20(1)| 20(1)| 6(1) | 3(1) | 6(1) |
| C(19)  | 15(1)| 16(1)| 18(1)| 5(1) | 5(1) | 6(1) |
| C(20)  | 20(1)| 24(1)| 19(1)| 6(1) | 6(1) | 12(1) |
Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 18.

|       | x       | y       | z       | U(eq)  |
|-------|---------|---------|---------|--------|
| H(2)  | -1740(50)| 3120(30)| 1920(20)| 43(8)  |
| H(3)  | 2240(50)| 3510(30)| 200(30) | 49(8)  |
| H(3A) | -1980(40)| 4540(30)| 710(20) | 29(6)  |
| H(5A) | 4710(40)| 8500(30)| 720(20) | 33(6)  |
| H(5B) | 5880(40)| 8970(20)| 1920(20)| 26(6)  |
| H(5C) | 5440(40)| 10130(30)| 1370(20)| 29(6)  |
| H(6A) | 3460(40)| 10750(30)| 2680(20)| 38(7)  |
| H(6B) | 3800(40)| 9570(30)| 3230(20)| 34(7)  |
| H(6C) | 1440(40)| 9490(30)| 2770(20)| 30(6)  |
| H(7A) | 1120(40)| 8500(20)| 50(20)  | 24(6)  |
| H(7B) | 1950(40)| 10120(30)| 770(20) | 32(6)  |
| H(7C) | -100(40)| 8970(30)| 860(20) | 32(6)  |
| H(9)  | 6170(30)| 6310(20)| 1815(19)| 19(5)  |
| H(10) | 9410(40)| 6940(20)| 3032(18)| 21(5)  |
| H(12) | 7300(40)| 8560(20)| 5380(20)| 25(6)  |
| H(13) | 3990(40)| 7920(20)| 4168(19)| 24(6)  |
| H(14A)| 11140(40)| 9720(30)| 6171(19)| 25(6)  |
| H(14B)| 12490(40)| 8770(20)| 6359(19)| 25(6)  |
| H(14C)| 10010(40)| 8200(20)| 6364(19)| 24(6)  |
| H(16) | 1950(30)| 2320(20)| 1386(17)| 18(5)  |
| H(18) | 4710(40)| 4060(30)| 4200(20)| 32(6)  |
| H(20A)| 1280(40)| 5660(30)| 4110(20)| 29(6)  |
| H(20B)| 1590(40)| 4580(30)| 4730(20)| 30(6)  |
| H(20C)| -480(40)| 4180(20)| 3752(19)| 26(6)  |
Table S21. Torsion angles [°] for 18.

| Bond Sequence | Torsion Angle |
|---------------|---------------|
| O(1)-C(11)-C(12)-C(13) | -179.45(17) |
| O(2)-C(15)-C(16)-O(3) | 110.52(17) |
| O(2)-C(15)-C(16)-C(17) | -124.85(14) |
| O(2)-C(15)-C(19)-C(18) | 116.85(16) |
| O(2)-C(15)-C(19)-C(20) | -61.92(2) |
| O(3)-C(16)-C(17)-O(4) | -41.5(2) |
| O(3)-C(16)-C(17)-C(18) | 141.63(15) |
| O(4)-C(17)-C(18)-C(19) | 173.76(18) |
| N(1)-N(2)-C(1)-C(2) | 1.39(19) |
| N(1)-N(2)-C(1)-C(8) | -177.96(16) |
| N(1)-N(2)-C(4)-C(5) | -128.98(17) |
| N(1)-N(2)-C(4)-C(6) | 108.63(17) |
| N(1)-N(2)-C(4)-C(7) | -10.3(2) |
| N(2)-N(1)-C(3)-C(2) | 0.46(19) |
| N(2)-C(1)-C(2)-C(3) | -1.03(18) |
| N(2)-C(1)-C(2)-C(15) | 177.56(16) |
| N(2)-C(1)-C(8)-C(9) | -101.2(2) |
| N(2)-C(1)-C(8)-C(13) | 84.5(2) |
| C(1)-N(2)-C(4)-C(5) | 52.1(2) |
| C(1)-N(2)-C(4)-C(6) | -70.3(2) |
| C(1)-N(2)-C(4)-C(7) | 170.72(17) |
| C(1)-C(2)-C(3)-N(1) | 0.36(19) |
| C(1)-C(2)-C(15)-O(2) | 170.12(16) |
| C(1)-C(2)-C(15)-C(16) | -71.1(2) |
| C(1)-C(2)-C(15)-C(19) | 46.8(2) |
| C(1)-C(8)-C(9)-C(10) | -174.29(17) |
| C(1)-C(8)-C(13)-C(12) | 174.37(16) |
| C(2)-C(1)-C(8)-C(9) | 79.6(2) |
| C(2)-C(1)-C(8)-C(13) | -94.8(2) |
| C(2)-C(15)-C(19)-C(18) | -119.29(17) |
| C(2)-C(15)-C(19)-C(20) | 61.9(2) |
| C(3)-N(1)-N(2)-C(1) | -1.15(19) |
| C(3)-N(1)-N(2)-C(4) | 179.73(15) |
| C(3)-C(2)-C(15)-O(2) | -11.6(2) |
| C(3)-C(2)-C(15)-C(16) | 107.23(19) |
| C(3)-C(2)-C(15)-C(19) | -134.86(17) |
| C(4)-N(2)-C(1)-C(2) | -179.61(16) |
| C(4)-N(2)-C(1)-C(8) | 1.0(3) |
| C(8)-C(1)-C(2)-C(3) | 178.31(16) |
| C(8)-C(9)-C(10)-C(11) | -3.1(3) |
| C(9)-C(8)-C(13)-C(12) | -0.1(3) |
| C(9)-C(10)-C(11)-O(1) | 179.65(16) |
| C(9)-C(10)-C(11)-C(12) | -0.3(3) |
| C(10)-C(11)-C(12)-C(13) | 0.4(3) |
| C(11)-C(12)-C(13)-C(8) | -0.3(3) |
| C(13)-C(8)-C(9)-C(10) | 0.3(3) |
| C(14)-O(1)-C(11)-C(10) | -178.95(16) |
| C(14)-O(1)-C(11)-C(12) | 0.9(3) |
| C(15)-C(2)-C(3)-N(1) | -178.28(16) |
| C(15)-C(16)-C(17)-O(4) | -170.92(17) |
| C(15)-C(16)-C(17)-C(18) | 12.22(18) |
| C(16)-C(15)-C(19)-C(18) | 5.43(19) |
| C(16)-C(15)-C(19)-C(20) | -173.34(15) |
| C(17)-C(18)-C(19)-C(15) | -9.4(2) |
| C(17)-C(18)-C(19)-C(20) | 2.3(2) |
| C(17)-C(18)-C(19)-C(20) | -179.01(17) |
| C(19)-C(15)-C(16)-O(3) | -135.02(15) |
| C(19)-C(15)-C(16)-C(17) | -10.39(17) |
Table S22. Hydrogen bonds for 18 [Å and °].

| D-H...A          | d(D-H) | d(H...A) | d(D...A)      | <(DHA) |
|------------------|--------|----------|---------------|--------|
| O(2)-H(2)...O(4)#1 | 0.86(3)| 1.90(3)  | 2.7390(18)    | 166(3) |
| O(3)-H(3)...N(1)#2 | 0.97(3)| 1.88(3)  | 2.8333(19)    | 165(3) |

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z  #2 -x,-y+1,-z
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