Chiral Self-sorting Process with Ditopic Ligands: Alternate- or Block-Metallopolymers Assembly as Function of the Metal Ion

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Supporting Information
1. General remarks

Solvents were purified and degassed by standard procedures. All reagents were used without further purification. MeOH was purchased with Aldrich without any purification. Pyridine employed during complexation reactions was distilled from calcium hydride and carefully stored under argon. \(^1\)H and \(^13\)C NMR spectra were recorded by using a Bruker Avance 300 spectrometer using the residual solvent peak as a reference (CDCl\(_3\): \(\delta\) H = 7.26 ppm; \(\delta\) C = 77.16 ppm) at 298 K. Positive mode electrospray ionization mass spectra (ESI-MS) were recorded on microTOF, Bruker Daltonics. X-ray diffraction studies were carried out by Dr. Lydia Brelot at Institut de Chimie X-ray Facility of the University of Strasbourg. Crystal data were collected at 173 K using a MoK\(\alpha\) graphite monochromated (\(\lambda = 0.71073\) Å) radiation on a Nonius KappaCCD diffractometer. The structures were solved using direct methods with SHELXS97552 and refined against F2 using the SHELXL97 software. 553 Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Density Functional Theory (DFT) and time dependent (TD-) DFT calculations have been performed with the Gaussian 09 software using the hybrid B3-LYP functional and the polarizable continuum model for methanol at a qualitative level of accuracy in order to assess possible ligand conformations and how they are affected by metal chelation, to identify the optical transitions of interest and to gauge their optical activity.
2 Generic procedure for the synthesis of monotopic & ditopic VinylBox

2.1 2.1 Synthesis of DiVinylBox:

N,N'-bis[(1S)-1-isopropyl-2-hydroxyethyl]malonide (1)
Dimethylmalonate (38.18 mmol, 4.4 mL) and (S)-Valinol (77.5 mmol, 8 g) were put in a Schlenk. Then, and under argon, a catalytic amount of NaH was added. The mixture was stirred overnight at 140°C. The next day, MeOH is evaporated under vacuo. The yellowish solid was then dissolved in a minimum of dichloromethane and precipitated with ether. A white powder was obtained (29 mmol, 7.9g, 76%). 1H NMR (300 MHz, DMSO-d6): δ = 7.73 (d, J= 9.2 Hz, 2H; -NH), 4.60 (bs, 2H; -C-H2OH), 3.60-3.52 (m, 4H; C-H2OH), 3.10 (s, 2H; -C-H2CO), 1.84-1.73 (m, 2H; -C-H(CH3)2), 0.82 (dd, J= 6.8 Hz, J= 2.4 Hz, 12 H; -C-H(CH3)2).

N,N'-bis[(1S)-1-isopropyl-2-chloro]malonide (2)
Compound 1 (29 mmol, 7.924 g) was dissolved in toluene (250 mL) and stirred for 10 min. A light yellow solution was obtained. Then, SOCl2 (63.8 mL, 4.6 mL) was added dropwise. The resulting mixture was stirred and heated for 4h at 90 °C. After this time, the mixture was left to cool down at r.t and poured onto an ice cold 20% KOH solution. Then, it was extracted with dichloromethane (3x150 mL) and the organic phase washed with NaHCO3. The solution was dried over Na2SO4 and reduced under pressure. A yellow/orange solid was obtained (26.2 mmol, 8.2 g, 90%). 1H NMR (300 MHz, CDCl3): δ = 6.98 (d, J= 8.7 Hz, 2H; -NH), 4.01-3.94 (m, 2H; -C-H2OH), 3.72-3.66 (m, 4H; C-H2OH), 3.27 (s, 2H; -C-H2CO), 2.02-1.94 (m, 2H; -C-H(CH3)2), 0.96 (dd, J= 6.8 Hz, J= 1.5 Hz, 12 H; -C-H(CH3)2).

1,1-bis[(4S)-4-isopropyl-4,5-dihydrooxazol-2-yl]methane (S,S)-Box [1]
To compound 2 obtained (26.2 mmol, 8.152 g) was added KOH (65.5 mmol, 3.675 g) and the whole was dissolved in MeOH (250 mL). The orange solution was heated at reflux for 3h. Then, it was let to cool down at r.t and the mixture was poured onto water (260 mL), extracted with dichloromethane (3x130 mL), washed with brine, dried over Na2SO4 and reduced under pressure. An orange oil was obtained and then, distilled under vacuo to afford a yellow crystalline solid (15 mmol, 3.4 g, 57%). 1H NMR (300 MHz, CDCl3): δ = 4.26 (t, J= 7.7 Hz, 2H; -NH), 4.03-3.92 (m, 4H; -C-H2CO), 3.34 (s, 2H; -C-H2), 1.80-1.73 (m, 2H; -C-H(CH3)2), 0.91 (d, J= 6.8 Hz, 12 H; -C-H(CH3)2); 13C{1H} NMR (300 MHz, CDCl3): δ =161.5 (-C-O), 72.2 (-CHN), 70.5 (-C-H2O), 32.3 (-C-H(CH3)2), 28.3 (-C-H2), 18.6, 17.9 (-C-H(CH3)2);MS (ESI +): m/z (%): 239.17 [M+H]+; elemental analysis calcd (%) for C13H22N2O2 (238.33): C 65.51, H 9.30, N11.75; found C 62.06, H 8.95, N 11.26.

Figure S1. Synthesis of bisoxazoline unit (S,S)-Box.

2 equiv NaH (cat.) 140 °C overnight

N,N'-bis[(1S)-1-isopropyl-2-hydroxyethyl]malonide (1)

Dimethylmalonate (38.18 mmol, 4.4 mL) and (S)-Valinol (77.5 mmol, 8 g) were put in a Schlenk. Then, and under argon, a catalytic amount of NaH was added. The mixture was stirred overnight at 140°C. The next day, MeOH is evaporated under vacuo. The yellowish solid was then dissolved in a minimum of dichloromethane and precipitated with ether. A white powder was obtained (29 mmol, 7.9g, 76%). 1H NMR (300 MHz, DMSO-d6): δ = 7.73 (d, J= 9.2 Hz, 2H; -NH), 4.60 (bs, 2H; -CH2OH), 3.60-3.52 (m, 4H; CH2OH), 3.10 (s, 2H; -CH2CO), 1.84-1.73 (m, 2H; -CH(CH3)2), 0.82 (dd, J= 6.8 Hz, J= 2.4 Hz, 12 H; -CH2(CH3)2).

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Figure S1. Synthesis of bisoxazoline unit (S,S)-Box.
Synthesis of 1,4-bis(2,2-bis((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)vinyl)benzene (S,S,S,S) DiVinylBox

![Chemical structure of DiVinylBox](image)

**Figure S2.** Synthesis of DiVinylBox ligands through Knoevenagel condensation

**Thermic conditions:**
1,1-bis[(4S)-4-isopropyl-4,5-dihydrooxazol-2-yl]methane (0.84 mmol, 200 mg), piperidinium acetate (0.17 mmol, 24.22 mg) and terephthaldehyde (0.42 mmol, 56.33 mg) were put together in a Schlenk. Pyridine (3 mL) was added and the mixture was heated and stirred at 65 °C for 72h. After this time, the solvent was evaporated trap to trap. The resulting yellow-orange solid was purified by silica gel column chromatography (AcOEt/MeOH, 95:5) yielding a white solid (0.30 mmol, 174.8 mg, 71%).

**Microwave assisted conditions:**
1,1-bis[(4S)-4-isopropyl-4,5-dihydrooxazol-2-yl]methane (0.839 mmol, 200 mg, 2 equiv), 1,4-Phthalaldehyde (0.461 mmol, 62 mg, 1.1 equiv) and freshly made piperidinium acetate (0.168 mmol, 24 mg) were suspended in dry pyridine (4 mL). The mixture was then stirred for 2 min before being subjected to microwave irradiation for 4 hours at 70 °C. After cooling to r.t., the pyridine was removed under vacuum giving a yellow oil, which was purified by silica-gel column chromatography (AcOEt/MeOH, 95:5) to yield a white solid (150 mg, 62%). \([\alpha]_{D}^{20} = -154 \text{ cm}^2\text{g}^{-1}\text{dm}^{-1} \text{ (c = 0.02 in MeOH)}; \) \(^1\text{H} \text{NMR (300 MHz, CDCl}_3\) } \delta 7.53 (s, 2H), 7.44 (s, 4H), 4.28-4.41 (m, CH-N, 4H), 4.19-3.96 (m, CH2-O, 8H), 1.74-1.89 (m, CH(CH3)2, 4H), 1.07-0.77 (m, 6 x CH3, 24H). \(^1^C\text{NMR (101 MHz, CDCl}_3\) } \delta = 161.8 (2 x N-CO), 160.4 (2 x N=CO), 139.9 (2 x HC=C), 135.4 (2 x C=O), 129.6 (4 x CH=O), 120.0 (2 x C=CH), 73.1 (2 x N=CH), 73.1 (2 x NCH), 70.6 (2 x OCH2), 70.4 (2 x OCH2), 33.1 (2 x CH(CH3)2), 32.6 (2 x CH(CH3)2), 19.2, 18.9, 18.7 and 18.4 (8 x CH3). IR (KBr): \(\tilde{\nu} = 1674 \text{ cm}^{-1} \text{ (s, C=N)}; \) MS (ESI+): \([m/z] = 239.18 [C_{13}H_{22}N_2O_2]^+, 327.19 [C_{20}H_{26}N_2O_2]^+, 597.34 [M+Na]^+, 813.52 [M+C_{13}H_{22}N_2O_2]^+; \) elemental analysis calcd (%) for C34H46N4O4 (574.75): C 71.05, H 8.07, N 9.75; found C 70.78, H 8.11, N 9.48.
2.2 Synthesis of VinylBox:

\[
\begin{align*}
\text{O} & \quad (S) \\
\text{N} & \quad (S) \\
\text{O} & \quad (S) \\
\text{O} & \quad (S)
\end{align*}
\]

+ 0.4 equiv Piperidinium acetate

Pyridine, 70 °C MW, 4h

Figure S3. Synthesis of DiVinylBox ligands through Knoevenagel condensation

Synthesis of (S,S)-VinylBOX
Using the same procedure depicted for ditopic ligand. 1,1-bis[(4S)-4-isopropyl-4,5-dihydrooxazol-2-yl]methane (0.839 mmol, 200 mg, 1 equiv), freshly distilled benzaldehyde (0.461 mmol, 62 mg, 1 equiv) and freshly made piperidinium acetate (0.168 mmol, 24 mg, 5 equiv) were suspended in dry pyridine (4 mL). The mixture was then stirred for 2 min before being subjected to microwave irradiation for 4 hours at 70 °C. After cooling to r.t., the pyridine was removed under vacuum giving yellow oil. The crude material was then taken up on DCM, washed with a NaHCO₃, dry with Na₂SO₄ and concentrate under vacuum. The yellow oil was purified by silica-gel column chromatography deactivated by small amount of trimethylamine (first pure DCM and then pure AcOEt) to yield a white soft-solid (192 mg, 70 %).

\[
[\alpha]_D^{20} = -12.46 \text{ cm}^2\text{g}^{-1}\text{dm}^{-1} (c = 0.35 \text{ in CHCl}_3); \quad ^1H \text{NMR (300 MHz,CDCl}_3); \quad \delta 7.57 (s, 1H, ArHC} = \text{C}), 7.46–7.49 (m, 2H, H\text{Ar}), 7.32–7.34 (m, 3H, H\text{Ar}), 4.29–4.39 (m, 2H, CH), 4.04–4.17 (m, 4H, CH₂), 1.73–1.88 (m, 2H, CH(CH₃)₂), 0.99 (s, 3H, CH(CH₃)₂), 0.97 (s, 3H, CH(CH₃)₂), 0.94 (s, 3H, CH(CH₃)₂), 0.89 (s, 3H, CH(CH₃)₂) ppm. \quad ^{13}C \text{NMR (75 MHz,CDCl}_3); \quad \delta 161.8, 160.4, 140.8, 134.2, 129.43, 129.35, 128.35, 119.0, 72.87, 72.85, 70.23, 70.16, 32.88, 32.36, 18.93, 18.75, 18.43 and 18.21 ppm.
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These data are in agreement with the one reported in literature. [1]
3 Titration experiments of rac DivinylBox with copper metal salt

Figure S4. Titration of racemic DivinylBox ligand concentration of 2.5 $10^{-5}$ M in MeOH with Cu(BF$_4$)$_2$ followed by UV-vis spectroscopy. The spectra corresponding to 0 and 1 eq. of Cu$^{2+}$ added are displayed as black and red trace, respectively. Black arrow indicates the variation of the spectra features upon addition of the salt. The insets show the change in absorbance at 328 nm as a function of added Cu$^{2+}$. 
4 CD titration experiments of (S) DivinylBox with zinc metal salt

Figure S5. CD spectral changes in the titration of (S) DivinylBox solution (MeOH, c=5×10^{-5} M) with Zn(BF₄)₂: 0 equiv. (blue line, bottom) to 2 equiv. of zinc ion (orange line, top).
5 Circular Dichroism of enantiopure DivinylBox metallopolymers

Figure S6. Mirror image of the CD spectra of enantiopure metallopolymers generated from Cu(BF$_4$)$_2$ and (S) and (R) DiVinylBox; [Cu] = 2.5 $10^{-5}$ M (blue and red lines, respectively) (solvent: MeOH).
6. **$^1$H NMR AND $^{13}$C-NMR SPECTRA OF ALL NOVEL COMPOUNDS**

(S,S,S,S)-DiVinylBOX

![Chemical Structure](image)

**Figure S7.** $^1$H NMR (300 MHz) CDCl$_3$

**Figure S8.** $^{13}$C NMR (126 MHz) CDCl$_3$
(5,5)-VinylBOX

Figure S9. $^1$H NMR (300 MHz) CDCl$_3$

Figure S10. $^{13}$C NMR (126 MHz) CDCl$_3$
7 Density Functional Theory (DFT) and time dependent (TD) DFT calculations

DFT geometries of the free DiVinylBox ditopic ligand and of its bimetallic complexes with copper and zinc have been optimized using the hybrid B3-LYP functional along with the 6-31G(d,p) basis set while using the polarizable continuum model (PCM) for methanol as implemented in the Gaussian 09 software. The TD-DFT calculations have been run either at the same level of precision or, in the case of the free ligand, also with the larger 6-311+G(d,p) basis set to gauge the level of basis set dependency of the resulting excited states (the convergence of 32 roots has routinely been asked for, except for the syn+ form of the Cu complex for which it has also been pushed to 48 roots but the results showed no significant changes).

7.1 Free DiVinylBox ligand in solution in methanol:

Even when not taking into consideration all the possible orientations of the isopropyl steric groups, DFT geometry optimizations of the free ligand converge to several conformational structures differing in the positioning of the two non-conjugated oxazolines with respect to their nearest phenyl hydrogen atom. On either end, the heterocyclic atom closest to a phenyl H atom may be the oxygen or the nitrogen. That these conformations are indeed stable has been tested by running normal mode calculations where the lowest frequencies have always been found to be positive. The conformation shown below is the one that resembles the X-ray crystal structure the most: it combines the two situations mentioned above for the positioning of the out-of-plane oxazolines. For this set of orientations of the isopropyl groups with respect to their oxazoline rings it is also the configuration with the lowest DFT+PCM energy. The one aspect were X-ray and DFT structures differ is in the exact orientation of the out-of-plane five membered rings which are held orthogonally to the phenyl plane in the crystal while the calculated geometries allow for some departure from orthogonality.

![Figure S11. The stable DFT geometry of DiVinylBox most similar to the conformation adopted in the crystal.](image)

TTD-DFT (B3-LYP, 6-32G(d,p)) results for the transitions to the first excited singlet states for the above geometry are summarized in the following table.

| Transition | 6-31G(d,p) | 6-311+G(d,p) |
|------------|------------|--------------|
|            | wavelength (nm) | oscillator strength | rotary strength (cgs) | wavelength (nm) | oscillator strength | rotary strength (cgs) |
| S1 ← S0   | 360.6      | 1.6380       | -65.80             | 365.5      | 1.6400       | -68.66             |
| S2 ← S0   | 328.7      | 0.0117       | -0.78              | 328.8      | 0.0096       | -2.05              |
| S3 ← S0   | 327.5      | 0.0194       | 2.69               | 327.1      | 0.0152       | 2.35               |
| S4 ← S0   | 309.4      | 0.0009       | 1.90               | 310.1      | 0.0017       | 4.12               |
| S5 ← S0   | 294.6      | 0.0198       | 1.34               | 298.1      | 0.0182       | 2.03               |
| S6 ← S0   | 287.6      | 0.0715       | 27.26              | 288.8      | 0.0538       | 23.42              |

Table S1. TD-DFT results (B3-LYP).

The rotary strengths indicated are given in units of $10^{-40}$ erg.esu.cm/Gauss. The marked blue shift and the width of the experimental absorption band as well as the absence of detectable levels of circular dichroism for free ligands in methanol together with the possibility to find several stable geometries in the DFT calculations are indications that the DiVinylBox
compound is a highly labile entity in solution, at least as far as the librations of the individual oxazolines as well as those of the head groups as a whole are concerned.

7.2 Bimetallic complex of Cu(II) with a DiVinylBox and MeOH ligands:

Geometries for a fully coordinated ditopic ligand have been obtained with two Cu(II) ions by completing their coordination spheres with methanol molecules. To allow for the proper left-right correlation of the odd d-electron on the copper atoms, calculations for the Cu(II) bimetallic complex have been carried out by running the calculations in the unrestricted scheme and asking for a triplet multiplicity both for the ground (DFT geometry optimization) and for the excited states (TD-DFT optical transitions).

Figure S12. Three conformations of the bimetallic copper complex. Top: boat with positive optical activity (OA), middle: chair with low negative OA, and bottom: boat with negative OA.
The total energy of formation of the copper complex in its first *boat* conformation above is computed at $E = -5586.3491856$ Ha. This makes it more stable by 1.26 kJ/mol than the *chair* configuration which is computed at $E = -5586.3487068$ Ha. The second *boat* conformation has a total energy of $E = -5586.3490559$ Ha, only 0.34 kJ/mol above that of the first *boat* structure and 0.92 kJ/mol below that of the *chair* geometry. The fully allowed ligand centered optical transition is obtained as the 14th or the 16th root of the TD-DFT calculations and while contributions of excitations out of methanol centered orbitals are found in the lower energy transitions, including the #11 root which happens also to be of LMCT character, the optical transitions of interest turn out to be largely uncontaminated by such contributions and is a DiVinylBox centered $\pi-\pi^*$ transition.

| Cu(II) complex form | Excited state # | wavelength (nm) | oscillator strength | rotary power (cgs) |
|---------------------|----------------|-----------------|---------------------|-------------------|
| *Boat*+             | (root #11)     | 468.65          | 0.1273              | -90.94            |
| (root #14)          | 410.33         | 1.2882          |                     | 248.66            |
| (root #16)          | 407.00         | 0.1849          |                     | 70.91             |
| *Chair*             | (root #16)     | 404.01          | 1.3723              | 35.12             |
| (root #16)          | 473.05         | 0.2022          |                     | -182.66           |
| (root #16)          | 403.02         | 1.2893          |                     | -258.29           |

**Table S2.** Calculated wavelength and rotary power for Cu complexes.

As opposed to what is seen in experiment, the main absorption is red shifted upon complexation with metal ions in the DFT calculations. This can be attributed to the enlargement of the pi electron system not compensated by the resulting increase in dihedral angle of the vinyl groups with respect to the phenyl plane in the optimal geometries. Of course, allowance must also be made for the coordination spheres which poorly reproduce the real situation. The rotary powers obtained illustrate the fact that the *chair* form gives rise to a pseudo inversion center for the $\pi$-electron system which is located in the center of the phenyl ring while the *boat* conformations result in a pseudo helical axis corresponding to the phenyl’s six-fold symmetry axis. The detection of a positive CD in titration experiments indicates that entropic factors must dominate over internal energies for the links in the polymer strands to mostly adopt the *boat*+ conformation.

### 7.3 Bimetallic complex of Zn(II) with a DiVinylBox and MeOH ligands:

Again, the geometries for a fully coordinated ditopic ligand have been obtained with two Zn(II) ions by completing their coordination spheres with methanol molecules. Because of the full d shell, all calculations have been performed for a closed shell singlet. The first *boat* conformation shown below is computed to have a total energy of formation of $E = -5864.0923684$ Ha, the *chair* configuration to have $E = -5864.0945766$ Ha (i.e. lower by 5.8 kJ/mol) and the second *boat* geometry to have $E = -5864.0956603$ Ha (lower again by 2.8 kJ/mol). Although such small energy differences may be compensated by entropic factors, it is of interest to note that, in contrast to the previous complexes, the first *boat* conformation is not favored here by the energetics obtained at the DFT level with the PCM solvation model for methanol. It may be of interest to mention that running the same DFT and TD-DFT calculations without the use of the solvation model leads to little changes in transition energies but noticeable increases in oscillator strengths as well as decreases in rotary strengths showing that the possible stable conformations of the complex are more strongly bent out of conjugation when the interaction of the local atomic net charges and polarities are allowed to interact with a polarizable dielectric environment.
Figure S13. Three conformations of the bimetallic zinc complex. Top: syn with positive optical activity (OA), middle: anti with low negative OA, and bottom: syn with negative OA.

The fully allowed ligand centered optical transition corresponds to the first singlet transition obtained in TD-DFT and it is chiefly of (π* ← π, DiVinylBox centered) HOMO-LUMO type:

| Zn(II) complex form | Wavelength (nm) | oscillator strength | rotary strength (cgs) |
|---------------------|----------------|---------------------|-----------------------|
| Syn+                | 404.17         | 1.4232              | 299.71                |
| Anti                | 395.57         | 1.4706              | -69.76                |
| Syn-                | 398.78         | 1.3946              | -410.43               |

Table S3. Calculated wavelength and rotary power for Zn complexes.
8 X-ray tables of DivinylBOX ligand

Single crystals of \((S,S,S,S)\)-DiVinylBOX were grown in chloroform. The crystals were placed in oil, and a colourless plate single crystal of dimensions 0.40 x 0.25 x 0.15 mm was selected, mounted on a glass fibre and placed in a low-temperature N\(_2\) stream.

X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N\(_2\) device, using Cu-K\(\alpha\) radiation \((\lambda = 1.54178 \text{ Å})\). The crystal-detector distance was 40mm. The cell parameters were determined (APEX2 software) \([4]\) from reflections taken from three sets of 20 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-2013 \([5]\). The refinement and all further calculations were carried out using SHELXL-2013 \([3]\). The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F\(^2\). A semi-empirical absorption correction was applied using SADABS in APEX2 \([6]\); transmission factors: T\(_{\text{min}}\)/T\(_{\text{max}}\) = 0.6699/0.7528. The methyl group C28 is disordered over two positions with a 0.6/0.4 ratio. The H-atom H26 is also disordered over two positions with the same ratio.

![Figure S14. Ortep views of \((S,S,S,S)\)-DiVinylBOX ligand X-ray structure.](image-url)
| Identification   | sblta160205            |
|------------------|------------------------|
| Empirical formula| C_{34}H_{46}N_{4}O_{4} |
| Formula weight   | 574.75                 |
| Temperature      | 173(2)K                |
| Wavelength       | 1.54178 Å              |
| Crystal system   | Triclinic              |
| space group      | P 1                    |

| Unit cell dimensions |                          |
|----------------------|--------------------------|
| a (Å)                | 5.4629(2)                |
| b (Å)                | 10.0985(3)               |
| c (Å)                | 15.3132(5)               |
| α (°)                | 90.204(2)                |
| β (°)                | 96.2270(10)              |
| γ (°)                | 103.0290(10)             |
| Volume (Å³)          | 817.838                  |
| Z                    | 1                        |
| Calculated density (Mg/m³) | 1.167            |

| Absorption coefficient (mm⁻¹) | 0.611 |
|-------------------------------|-------|
| F(000)                        | 310   |
| Crystal size (mm)             | 0.400 x 0.250 x 0.150 |
| Theta range (°)               | 4.496 to 66.908         |
| Limiting indices              | -6<=h<=4, -12<=k<=11, -18<=l<=18 |
| Reflections collected / unique / R_{int} | 12957 / 4089 / 0.0269 |
| Completeness to theta         | 67.679; 97.0 %           |
| Absorption correction         | Semi-empirical from equivalents |
| Max. and min. transmission    | 0.7528 and 0.6699         |
| Refinement method             | Full-matric least-square on F² |
| Data / restraints / parameters | 4089 / 3 / 391          |
| Goodness-of-fit on F₂         | 1.048 |
Final R indices $R_I$, $wR_2$

$(I>2\sigma(I))$

$R_I$, $wR_2$ (all data) 0.0382; 0.0969

Absolute structure parameter -0.04(12)

Largest diff. peak and hole (e.$\text{Å}^{-3}$) 0.212; -0.169

Extinction coefficient n/a

| Table S5. Bond lengths [Å] |
|----------------------------|
| C1-C2 1.398(4) | C19-H19A 0.979 |
| C1-C6 1.394(4) | C19-H19B 0.980 |
| C1-C7 1.471(3) | C19-H19C 0.981 |
| C2-H2 0.950 | C20-H20A 0.981 |
| C2-C3 1.382(4) | C20-H20B 0.980 |
| C3-H3 0.950 | C20-H20C 0.980 |
| C3-C4 1.402(4) | C21-H21 0.950 |
| C4-C5 1.400(4) | C21-C22 1.344(4) |
| C4-C21 1.469(3) | C22-C23 1.487(3) |
| C5-H5 0.950 | C22-C29 1.466(3) |
| C5-C6 1.385(4) | C23-N3 1.263(3) |
| C6-H6 0.950 | C23-O3 1.353(4) |
| C7-H7 0.950 | C24-H24A 0.990 |
| C7-C8 1.342(4) | C24-H24B 0.990 |
| C8-C9 1.466(3) | C24-C25 1.512(5) |
| C8-C15 1.485(3) | C24-O3 1.447(3) |
| C9-N1 1.265(3) | C25-H25 1.000 |
| C9-O1 1.359(3) | C25-C26 1.527(4) |
| C10-H10A 0.990 | C25-N3 1.483(4) |
| C10-H10B 0.991 | C26-H26 0.999 |
| C10-C11 1.540(4) | C26-C27 1.524(5) |
| C10-O1 1.443(3) | C26-C28 1.610(7) |
| C11-H11 1.000 | C27-H27A 0.980 |
| C11-C12 1.523(4) | C27-H27B 0.980 |
| C11-N1 1.470(3) | C27-H27C 0.980 |
| C12-H12 0.999 | C28-H28A 0.980 |
| C12-C13 1.521(4) | C28-H28B 0.980 |
| C12-C14 1.521(4) | C28-H28C 0.980 |
| C13-H13A 0.979 | C29-N4 1.272(3) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C13-H13B             | 0.980        | C29-O4               | 1.356(3)     |
| C13-H13C             | 0.981        | C30-H30A             | 0.990        |
| C14-H14A             | 0.981        | C30-H30B             | 0.990        |
| C14-H14B             | 0.980        | C30-C31              | 1.523(4)     |
| C14-H14C             | 0.980        | C30-O4               | 1.456(3)     |
| C15-N2               | 1.251(4)     | C31-H31              | 0.999        |
| C15-O2               | 1.368(3)     | C31-C32              | 1.525(4)     |
| C16-H16A             | 0.991        | C31-N4               | 1.486(3)     |
| C16-H16B             | 0.990        | C32-H32              | 1.000        |
| C16-C17              | 1.534(5)     | C32-C33              | 1.531(4)     |
| C16-O2               | 1.441(4)     | C32-C34              | 1.510(4)     |
| C17-H17              | 1.000        | C33-H33A             | 0.981        |
| C16-C18              | 1.526(5)     | C33-H33B             | 0.979        |
| C17-N2               | 1.478(4)     | C33-H33C             | 0.980        |
| C18-H18              | 1.000        | C34-H34A             | 0.980        |
| C18-C19              | 1.529(4)     | C34-H34B             | 0.980        |
| C18-C20              | 1.515(5)     | C34-H34C             | 0.980        |

### Table S6. Angles [deg]

| Angle                  | Value (deg) | Angle                  | Value (deg) |
|------------------------|-------------|------------------------|-------------|
| C2-C1-C6               | 118.0(2)    | C18-C20-H20B           | 109.5       |
| C2-C1-C7               | 117.7(2)    | C18-C20-H20C           | 109.4       |
| C2-C1-C3               | 121.7(3)    | H20A-C20-H20B          | 109.5       |
| C6-C1-H2              | 119.1       | H20A-C20-H20C          | 109.5       |
| C1-C2-C3              | 119.8       | C4-C21-H21            | 115.6       |
| C2-C3-H3              | 119.8       | C4-C21-H22            | 128.8(2)    |
| C2-C3-C4              | 120.3(2)    | H21-C21-C22           | 115.6       |
| C3-C3-C4              | 119.8       | C21-C22-C23           | 124.1(2)    |
| C3-C4-C5              | 117.8(2)    | C21-C22-C29           | 120.9(2)    |
| C3-C4-C21             | 123.8(2)    | C23-C22-C29           | 115.1(2)    |
| C5-C4-C21             | 118.4(2)    | C22-C23-N3            | 125.0(2)    |
| C4-C5-H5              | 119.2       | C22-C23-O3            | 115.6(2)    |
| C4-C5-C6              | 121.6(3)    | N3-C23-O3             | 119.4(2)    |
| H5-C5-C6              | 119.2       | H24A-C24-H24B         | 108.8       |
| C1-C6-C5              | 120.4(3)    | C24A-C24-C24          | 110.7       |
| C1-C6-C6              | 119.8       | H24A-C24-O3           | 110.8       |
| C5-C6-C6              | 119.8       | H24B-C24-C25          | 110.7       |
| C1-C7-H7              | 115.1       | H24B-C24-O3           | 110.7       |
| C1-C7-C8              | 129.6(2)    | C25-C24-O3            | 105.2(3)    |
| H7-C7-C8              | 115.2       | C24-C25-H25           | 108.5       |
| C7-C8-C9              | 121.0(2)    | C24-C25-C26           | 115.3(3)    |
| C7-C8-C15             | 125.5(2)    | C24-C25-N3            | 104.4(2)    |
| C9-C8-C15             | 113.5(2)    | H25-C25-C26           | 108.5       |
| Bond | Bond Angle | Bond Length |
|------|------------|-------------|
| C8-C9-N1 | 125.0(2) | H25-C25-N3 | 108.5 |
| C8-C9-O1 | 116.1(2) | C26-C25-N3 | 111.4(3) |
| N1-C9-O1 | 118.9(2) | C25-C26-H26 | 109.9 |
| H10A-C10-H10B | 108.9 | C25-C26-C27 | 111.3(3) |
| H10A-C10-C11 | 110.8 | C25C26C28 | 107.1(3) |
| H10A-C10-O1 | 110.8 | H26-C26-C27 | 109.9 |
| H10B-C10-C11 | 110.8 | H26-C26-C28 | 109.9 |
| H10B-C10-O1 | 110.8 | C27-C26-C28 | 108.8(3) |
| C11-C10-O1 | 104.6(2) | C26-C27-H27A | 109.5 |
| C10-C11-H11 | 108.6 | C26-C27-H27B | 109.5 |
| C10-C11-C12 | 114.1(2) | C26-C27-H27C | 109.5 |
| C10-C11-N1 | 103.9(2) | H27A-C27-H27B | 109.5 |
| H11-C11-C12 | 108.6 | H27A-C27-H27C | 109.5 |
| H11-C11-N1 | 108.6 | H27B-C27-H27C | 109.4 |
| C12-C11-N1 | 112.9(2) | C26-C28-H28A | 109.5 |
| C11-C12-H12 | 108.2 | C26-C28-H28B | 109.4 |
| C11-C12-C13 | 109.7(2) | C26-C28-H28C | 109.5 |
| C11-C12-C14 | 111.1(2) | H28A-C28-H28B | 109.5 |
| H12-C12-C13 | 108.2 | H28A-C28-H28C | 109.5 |
| H12-C12-C14 | 108.2 | H28B-C28-H28C | 109.4 |
| C13-C12-C14 | 111.3(3) | C22-C29-N4 | 124.7(2) |
| C12-C13-H13A | 109.5 | C22-C29-O4 | 116.4(2) |
| C12-C13-H13B | 109.5 | N4-C29-O4 | 118.8(2) |
| C12-C13-H13C | 109.4 | H30A-C30-H30B | 109.0 |
| H13A-C13-H13B | 109.5 | H30A-C30-C31 | 111.0 |
| H13A-C13-H13C | 109.5 | 30A-C30-O4 | 111.0 |
| H13B-C13-H13C | 109.4 | H30B-C30-C31 | 111.0 |
| C12-C14-H14A | 109.5 | H30B-C30-O4 | 111.0 |
| C12-C14-H14B | 109.5 | C31-C30-O4 | 103.8(2) |
| C12-C14-H14C | 109.5 | C30-C31-H31 | 108.3 |
| H14A-C14-H14B | 109.4 | C30-C31-C32 | 114.3(2) |
| H14A-C14-H14C | 109.4 | C30-C31-N4 | 103.9(2) |
| H14B-C14-H14C | 109.5 | H31-C31-C32 | 108.4 |
| C8-C15-N2 | 127.6(2) | H31-C31-N4 | 108.4 |
| C8-C15-O2 | 113.4(2) | C32-C31-N4 | 113.4(2) |
| N2-C15-O2 | 119.0(2) | C31-C32-H32 | 108.2 |
| H16A-C16-C16B | 108.8 | C31-C32-C33 | 109.7(2) |
| H16A-C16-C17 | 110.8 | C31-C32-C34 | 111.1(2) |
| H16A-C16-O2 | 110.7 | H32-C32-C33 | 108.2 |
| H16B-C16-C17 | 110.8 | H32-C32-C34 | 108.2 |
| H16B-C16-O2 | 110.8 | C33-C32-C34 | 111.3(3) |
| C17-C16-O2 | 104.9(2) | C32-C33-H33A | 109.5 |
| C16-C17-H17 | 108.9 | C32-C33-H33B | 109.5 |
| C16-C17-C18 | 115.6(3) | C32-C33-H33C | 109.5 |
| C6C1C2H2 | -177.0 | C17C18C19H19C | -60.4 |
| C6C1C2C3 | 2.9(4) | C17C18C19H19A | 62.0 |
| C7C1C2H2 | 2.9 | H18C18C19H19B | -58.0 |
| C7C1C2C3 | -177.1(2) | H18C18C19H19C | -178.0 |
| C2C1C6C5 | -2.6(4) | C20C18C19H19A | -55.5 |
| C2C1C6H6 | 177.5 | C20C18C19H19B | -175.5 |
| C7C1L6C5 | 177.4(2) | C20C18C19H19C | 64.5 |
| C7C1L6H6 | -2.5 | C17C18C20H20A | -46.5 |
| C2C1L7H7 | -27.1 | C17C18C20H20B | -166.5 |
| C2C1L7C8 | 152.8(3) | C17C18C20H20C | 73.4 |
| C6C1C7H7 | 152.8 | H18C18C20H20A | 71.7 |
| C6C1C7C8 | -27.2(4) | H18C18C20H20B | -48.3 |
| C1C2C3H3 | 177.8 | H18C18C20H20C | -168.4 |
| C1C2C3C4 | -2.2(4) | C19C18C20H20A | -170.9 |
| H2C2C3H3 | -2.2 | C19C18C20H20B | 69.2 |
| H2C2C3C4 | 177.8 | C19C18C20H20C | -50.9 |
| C2C3C4C5 | 1.0(4) | C4C21C22C23 | 5.0(4) |
| C2C3C4C21 | 178.6(3) | C4C21C22C29 | -176.1(2) |
| H3C3C4C5 | -179.0 | H21C21C22C23 | -175.0 |
| Bond                        | Distance (Å) | Angle (°) |
|-----------------------------|--------------|-----------|
| H3C3C4C21                   | -1.4         | H21C21C22C29 3.8 |
| C3C4C5H5                   | 179.3        | C21C22C23N3 81.2(4) |
| C3C4C5C6                   | -0.7(4)      | C21C22C23O3 -97.9(3) |
| C21C4C5H5                  | 1.6          | C29C22C23N3 -97.8(3) |
| C21C4C5C6                  | -178.4(3)    | C29C22C23O3 83.2(3) |
| C3C4C21H21                 | -157.1       | C21C22C29N4 175.3(3) |
| C3C4C21C22                 | 22.8(4)      | C21C22C29O4 -3.7(4) |
| C5C4C21H21                 | 20.4         | C23C22C29N4 -5.7(4) |
| C5C4C21C22                 | -159.7(3)    | C23C22C29O4 175.2(2) |
| C4C5C6C1                   | 1.6(4)       | C22C23N3C25 179.4(2) |
| C4C5C6H6                   | -178.5       | O3C23N3C25 -1.5(3) |
| H5C5C6C1                   | -178.4       | C22C23O3C24 -178.7(2) |
| H5C5C6H6                   | 1.5          | N3C23O3C24 2.2(3) |
| C1C7C8C9                   | -178.7(2)    | H24AC24C25H25 5.1 |
| C1C7C8C15                  | -1.8(4)      | H24AC24C25C26 -116.8 |
| H7C7C8C9                   | 1.3          | H24AC24C25N3 120.6 |
| H7C7C8C15                  | 178.2        | H24BC24C25H25 125.8 |
| C7C8C9N1                   | -171.3(2)    | H24BC24C25C26 3.9 |
| C7C8C9O1                   | 9.5(3)       | H24BC24C25N3 -118.6 |
| C15C8C9N1                  | 11.5(4)      | O3C24C25H25 -114.6 |
| C15C8C9O1                  | -167.8(2)    | O3C24C25C26 123.5(3) |
| C7C8C15N2                  | 87.3(4)      | O3C24C25N3 1.0(3) |
| C7C8C15O2                  | -93.7(3)     | H24AC24O3C23 -121.4 |
| C9C8C15N2                  | -95.6(3)     | H24BC24O3C23 117.8 |
| C9C8C15O2                  | 83.4(3)      | C25C24O3C23 -1.7(3) |
| C8C9N1C11                  | -177.1(2)    | C24C25C26H26 -173.9 |
| O1C9N1C11                  | 2.1(3)       | C24C25C26C27 64.2(4) |
| C8C9O1C10                  | -178.9(2)    | C24C25C26C28 -54.6(4) |
| N1C9O1C10                  | 1.8(3)       | H25C25C26H26 64.2 |
| H10AC10C11H11              | 9.8          | H25C25C26C27 -57.7 |
| H10AC10C11C12              | -111.5       | H25C25C26C28 -176.5 |
| H10AC10C11N1               | 125.2        | N3C25C26H26 -55.2 |
| H10BC10C11H11              | 130.8        | N3C25C26C27 -177.1(3) |
| H10BC10C11C12              | 9.5          | N3C25C26C28 64.2(4) |
| H10BC10C11N1               | -113.8       | C24C25N3C23 0.2(3) |
| O1C10C11H11                | -109.7       | H25C25N3C23 115.7 |
| O1C10C11C12                | 129.0(2)     | C26C25N3C23 -124.9(3) |
| O1C10C11N1                 | 5.7(3)       | C25C26C27H27A 60.8 |
| Bond/Angle/Distance     | Value       |
|-------------------------|-------------|
| H10AC1001C9             | -124.1      |
| H10BC1001C9             | 114.9       |
| C11C1001C9              | -4.6(3)     |
| C10C11C12H12            | -57.3       |
| C10C11C12C13            | 60.6(3)     |
| C10C11C12C14            | -175.9(2)   |
| H11C11C12H12            | -178.5      |
| H11C11C12C13            | -60.6       |
| H11C11C12C14            | 62.9        |
| N1C11C12H12             | 61.0        |
| N1C11C12C13             | 178.9(2)    |
| N1C11C12C14             | -57.6(3)    |
| C10C11N1C9              | -4.8(3)     |
| H11C11N1C9              | 110.6       |
| H11C11N1C9              | 178.9(2)    |
| C11C12C13H13A           | -128.9(2)   |
| C11C12C13H13B           | -58.6       |
| C11C12C13H13C           | 61.4        |
| H12C12C13H13A           | 59.2        |
| H12C12C13H13B           | -60.8       |
| H12C12C13H13C           | 179.3       |
| C14C12C13H13A           | 178.0       |
| C14C12C13H13B           | 58.0        |
| C14C12C13H13C           | -61.9       |
| C11C12C14H14A           | -60.1       |
| C11C12C14H14B           | 179.9       |
| C11C12C14H14C           | 59.9        |
| H12C12C14H14A           | 178.8       |
| H12C12C14H14B           | 61.2        |
| H12C12C14H14B           | -58.8       |
| C13C12C14H14A           | 62.4        |
| C13C12C14H14B           | -57.6       |
| C13C12C14H14C           | -177.6      |
| C8C15N2C17              | 177.4(2)    |
| O2C15N2C17              | -1.6(3)     |
| C8C15O2C16              | -177.5(2)   |
| N2C15O2C16              | 1.6(3)      |
| H16AC16C17H17           | 3.7         |

| Dist. to Other Atoms    | Value       |
|-------------------------|-------------|
| C25C26C27H27B           | -59.3       |
| H26C26C27H27C           | 59.0        |
| C25C26C27H27A           | -61.1       |
| H26C26C27H27B           | 178.9       |
| C28C26C27H27A           | 178.5       |
| H28C26C27H27B           | 58.5        |
| C28C26C27H27C           | -61.4       |
| C25C26C28H28A           | -51.6       |
| C25C26C28H28B           | -171.5      |
| C25C26C28H28C           | 68.5        |
| H26C26C28H28A           | 67.7        |
| H26C26C28H28B           | -52.2       |
| H26C26C28H28C           | -172.2      |
| C27C26C28H28A           | -171.9      |
| C27C26C28H28B           | 68.1        |
| C27C26C28H28C           | -51.9       |
| C22C29N4C31             | -176.9(2)   |
| O4C29N4C31              | 2.1(3)      |
| C22C29O4C30             | -172.0(2)   |
| N4C29O4C30              | 8.9(3)      |
| H30AC30C31H31           | 20.5        |
| H30AC30C31C32           | -100.4      |
| H30AC30C31N4            | 135.6       |
| H30BC30C31H31           | 141.9       |
| H30BC30C31C32           | 21.0        |
| H30BC30C31N4            | -103.0      |
| O4C30C31H31             | -98.7       |
| O4C30C31C32             | 140.4(2)    |
| O4C30C31N4              | 16.3(3)     |
| H30AC30O4C29            | -134.4      |
| H30BC30O4C29            | 104.2       |
| C31C30O4C29             | -15.2(3)    |
| C30C31H32               | -56.4       |
| C30C31C32C33            | 61.4(3)     |
| C30C31C32C34            | -175.1(3)   |
| H31C31H32               | -177.3      |
| H31C31C32C33            | -59.4       |
| Bond                        | Distance (Å) | Bond                        | Distance (Å) |
|-----------------------------|--------------|-----------------------------|--------------|
| H16AC16C17C18               | -119.2       | H31C31C32C34               | 64.1         |
| H16AC16C17N2               | 119.5        | N4C31C32H32                | 62.4         |
| H16BC16C17H17              | 124.6        | N4C31C32C33               | -179.8(2)    |
| H16BC16C17C18              | 1.7          | N4C31C32C34               | -56.3(3)     |
| H16BC16C17N2               | -119.6       | C30C31N4C29               | -11.7(3)     |
| O2C16C17H17                | -115.8       | H31C31N4C29               | 103.3        |
| O2C16C17C18                | 121.3(3)     | C32C31N4C29               | -136.3(2)    |
| O2C16C17N2                 | 0.0(3)       | C31C32C33H33A             | 62.9         |
| H16AC16O2C15               | -120.3       | C31C32C33H33B             | -57.0        |
| H16BC16O2C15               | 118.9        | C31C32C33H33C             | -177.1       |
| C17C16O2C15                | -0.8(3)      | H32C32C33H33A             | -179.2       |
| C16C17C18H18               | -173.4       | H32C32C33H33B             | 60.8         |
| C16C17C18C19               | 69.0(4)      | H32C32C33H33C             | -59.2        |
| C16C17C18C20               | -55.2(4)     | C34C32C33H33A             | -60.5        |
| H17C17C18H18               | 63.7         | C34C32C33H33B             | 179.6        |
| H17C17C18C19               | -53.9        | C34C32C33H33C             | 59.5         |
| H17C17C18C20               | -178.1       | C31C32C34H34A             | 176.4        |
| N2C17C18H18                | -55.9        | C31C32C34H34B             | 56.3         |
| N2C17C18C19                | -173.4(3)    | C31C32C34H34C             | -63.7        |
| N2C17C18C20                | 62.3(4)      | H32C32C34H34A             | 57.7         |
| C16C17N2C15                | 0.8(3)       | H32C32C34H34B             | -62.4        |
| H17C17N2C15                | 116.7        | H32C32C34H34C             | 177.6        |
| C18C17N2C15                | -123.7(3)    | C33C32C34H34A             | -61.1        |
| C17C18C19H19A              | 179.5        | C33C32C34H34B             | 178.9        |
| C17C18C19H19B              | 59.5         | C33C32C34H34C             | 58.9         |
9 References

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