Supplementary Information

“First Catalytic Reductive Coupling of 1,3-Diynes to Carbonyl Partners: A New Regio- and Enantioselective C-C Bond Forming Hydrogenation”

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Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloroethane (DCE) was distilled from calcium hydride. All Products exhibited spectral properties consistent with literature reports and syn/anti ratios of the products were determined by proton nuclear magnetic resonance (^1H NMR) spectra according to previous papers. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F₂₅₄). Preparative column chromatography employing silica gel was performed according to the method of Still.¹ Solvents for chromatography are listed as volume/volume ratios. ^1H NMR spectra were recorded with a Varian Gemini (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

Racemic Representative Procedure

To a solution of glyoxal (100 mol%) and diphenylbutadiyne (200 mol%) in DCE (0.1 M) at ambient temperature was added $\text{Rh}(\text{COD})_2\text{OTf}$ (5 mol%) and Ph_3P (10 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 25 °C under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product purified by silica gel chromatography.

Enantioselective Representative Procedure

To a solution of glyoxal (100 mol%) and diphenylbutadiyne (200 mol%) in DCE (0.1 M) at ambient temperature was added $\text{Rh}(\text{COD})_2\text{OTf}$ (5 mol%) and (R)-(+)-5,5'-Dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl [(R)-Cl-MeO-BIPHEP] (5 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 25 °C under 1 atm of hydrogen until complete consumption of substrate, at which point the reaction mixture was evaporated onto silica gel and the product purified by silica gel chromatography.

(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

¹H NMR (CDCl₃, 400 MHz) δ 7.84 (m, 2H), 7.53 (m, 3H), 7.35 (m, 5H), 7.23 (m, 5H), 6.15 (s, 1H), 5.83 (d, *J* = 5.8 Hz, 1H), 4.62 (d, *J* = 5.8 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ 198.4, 150.1, 137.3, 134.3, 133.8, 131.7, 129.2, 128.9, 128.9, 128.7, 128.7, 128.5, 128.3, 123.3, 112.6, 95.6, 87.4, 78.0.

HRMS calcd for C₂₄H₁₈O₂ [*M*+1] 339.1385, found 339.1384.

FTIR (NaCl) 3676, 3452, 3056, 2986, 2935, 2305, 2194, 1681, 1598, 1492, 1265, 1092, 1073, 966, 896, 737 cm⁻¹.

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 90/10 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

Chromatogram showing a major peak at 10.00 minutes and a minor peak at 33.79 minutes. The y-axis is labeled 'Abundance' and the x-axis is labeled 'Time (min)'.

¹H NMR (CDCl₃, 400 MHz) δ 8.26 (d, *J* = 1.0, 1H), 7.92 (dd, *J* = 1.71, 8.5 Hz, 1H), 7.83 (m, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.50 (m, 4H), 7.35 (m, 3H), 7.24 – 7.19 (m, 5H), 6.18 (s, 1H), 5.95 (d, *J* = 5.8 Hz, 1H), 4.67 (d, *J* = 5.8 Hz).

¹³C NMR (CDCl₃, 100 MHz) δ 198.1, 150.3, 137.5, 136.2, 132.3, 131.7, 131.6, 131.0, 130.0, 129.4, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.2, 124.3, 123.3, 112.4, 95.6, 87.4, 78.0.

HRMS calcd for C₂₈H₂₀O₂ [M+1] 389.1542, found 389.1538

FTIR (NaCl) 3367, 3060, 2956, 2927, 2873, 1678, 1629, 1467, 1378, 1161, 1130, 1107, 953, 817, 742, 698cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 90/10 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

Racemic Sample

Enantioselective Sample: 90% e.e.

¹H NMR (CDCl₃, 400 MHz) δ 7.76 – 7.74 (m, 2H), 7.45 – 7.26 (m, 8H), 5.93 (s, 1H), 5.30 (d, *J* = 7.2 Hz, 1H), 4.21 (d, *J* = 7.2 Hz, 1H), 1.15 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz) δ 214.9, 149.0, 137.7, 131.8, 128.8, 128.7, 128.6, 128.6, 128.4, 123.3, 111.6, 95.8, 87.5, 77.7, 43.4, 27.4.

HRMS calcd for C₂₂H₂₁O₂ [M+1] 318.1620, found 318.1619

FTIR (NaCl) 3436, 2952, 2929, 2873, 1701, 1490, 1466, 1378, 1103, 1054, 984, 754, 697cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralpak AD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 98/2 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

Racemic Sample

Enantioselective Sample: 95% e.e.

¹H NMR (CDCl₃, 400 MHz) δ 7.51 (m, 2 H), 7.36 (m, 3H), 7.24 (m, 5H), 6.82 (m, 2H), 6.15 (s, 1H), 6.07 (dd, *J* = 2.4, 4.1 Hz, 1H), 5.51 (d, *J* = 6.2 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 1H), 3.86 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ 189.9, 151.8, 137.8, 132.5, 131.7, 129.0, 128.5, 128.5, 128.5, 128.2, 128.0, 123.7, 121.4, 111.6, 109.2, 95.2, 87.8, 77.7, 37.8.

HRMS calcd for C₂₃H₁₉O₂ [M+1] 342.1494, found 342.1499.

FTIR (NaCl) 3390, 2959, 2927, 2873, 2861, 1647, 1465, 1379, 1161, 1130, 1107, 952, 817, 754, 738, 697 cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 90/10 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm

Racemic Sample

Enantioselective Sample: 86% e.e.

¹H NMR (CDCl₃, 400 MHz) δ 7.54 (m, 1H), 7.50 (m, 2H), 7.38 – 7.27 (m, 3H), 7.26 – 7.20 (m, 5H), 7.17 (d, J = 3.4 Hz, 1H) 6.48 (dd, J = 1.4, 3.4 Hz, 1H), 6.19 (s, 1H), 5.59 (s, 1H), 4.26 (br, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ 186.5, 150.2, 149.7, 147.9, 137.0, 131.7, 128.9, 128.6, 128.5, 128.3, 123.3, 120.3, 112.9, 112.4, 95.4, 87.4, 77.8.

HRMS calcd for C₁₉H₁₆O₂ 328.1099, found 328.1099.

FTIR (NaCl) 3445, 3056, 2986, 2305, 2194, 1761, 1671, 1570, 1465, 1266, 1082, 897, 736, 705, 593 cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 100/0 Hexane:IPA to 90/10 Hexane:IPA gradient over 25minutes; Flow Rate: 1.5ml/min; Detection Wavelength: 254nm.

Racemic Sample

Enantioselective Sample: 91% e.e.

¹H NMR (CDCl₃, 400 MHz) δ 7.62 (m, 2H), 7.56 (dd, *J* = 1.7, 7.7 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.30 – 7.21 (m, 5H), 7.02 (dd, *J* = 4.1, 4.8 Hz, 1H), 6.25 (s, 1H), 5.63 (s, 1H), 4.47 (br, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ 190.7, 150.2, 139.7, 136.9, 135.6, 134.4, 131.8, 129.0, 128.8, 128.7, 128.6, 128.4, 123.2, 112.9, 95.7, 87.4, 78.8.

HRMS calcd for C₂₂H₁₆O₂ [M+1] 345.0949, found 345.0952.

FTIR (NaCl) 3429, 2966, 2927, 2872, 1659, 1465, 1443, 1413, 1379, 1354, 1265, 1128, 951, 817, 755 cm⁻¹.

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 90/10 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

Racemic Sample

Enantioselective Sample: 93% e.e.

Deuterio-6b

¹H NMR (CDCl₃, 400 MHz) δ 7.84 (m, 2H), 7.53 (m, 3H), 7.35 (m, 5H), 7.23 (m, 5H), 5.83 (d, *J* = 5.6 Hz, 1H), 4.62 (d, *J* = 5.6 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ 198.4, 150.1, 137.3, 134.3, 133.8, 131.7, 129.2, 128.9, 128.9, 128.7, 128.7, 128.5, 128.3, 123.3, 95.6, 87.4, 78.0.

HRMS calcd for C₂₄H₁₇DO₂ [M+1] 340.1448, found 340.1444.

0.65 : 0.35 (under the racemic condition)

¹H NMR (CDCl₃, 400 MHz) δ 7.98 (m, 0.33x1H), 7.77 (m, 0.67x1H), 7.41 (m, 9H), 6.02 (d, *J* = 0.4 Hz, 0.35x1H), 5.86 (q, *J* = 2.4 Hz, 0.65x1H), 5.68 (d, *J* = 5.6 Hz, 0.65x1H), 5.47 (d, *J* = 5.6 Hz, 0.35x1H), 4.44 (d, *J* = 6.4 Hz, 0.65x1H), 4.36 (d, *J* = 6.0 Hz, 0.35x1H), 1.80 (d, *J* = 1.2 Hz, 0.35x3H), 1.77 (d, *J* = 2.4 Hz, 0.65x3H)

¹³C NMR (CDCl₃, 100 MHz) δ 198.7, 198.2, 148.1, 147.6, 136.8, 134.2, 133.8, 133.4, 133.3, 131.2, 128.72, 128.68, 128.4, 128.3, 128.2, 127.9, 127.86, 123.0, 113.0, 111.7, 95.2, 92.4, 86.0, 78.0, 77.7, 76.7, 14.4, 4.4

HRMS calcd for C₁₉H₁₆O₂ [M+1] 277.1229, found 277.1228

FTIR (NaCl) 3444, 3058, 3031, 2915, 2218, 1682, 1598, 1578, 1494, 1448, 1377, 1261, 1090, 968, 698 cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 90/10 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

NOE experiment

Racemic Sample

Enantioselective Sample: 88% e.e. for major compound, 83 % e.e. for minor compound
Regiomer ratio = 6.1 :1

0.59:0.41 (under the racemic condition)

¹H NMR (CDCl₃, 400 MHz) δ 7.97 (m, 1Hx0.8), 7.78 (m, 1Hx1.2), 7.41 (m, 8H), 5.93 (s, 1Hx0.41), 5.88 (t, *J* = 2.2 Hz, 1Hx0.59), 5.69 (d, *J* = 5.6 Hz, 1Hx0.59), 5.48 (d, *J* = 5.6 Hz, 1Hx0.41), 4.43 (d, *J* = 6.0 Hz, 1Hx0.59), 4.27 (d, *J* = 6.0 Hz, 1Hx0.41), 2.29 (m, 2Hx0.41), 2.13 (dt, *J* = 2.4, 7.2 Hz, 2Hx0.59), 1.50 (m, 2Hx0.41), 1.36 (sextet, *J* = 7.2 Hz, 2Hx0.59), 0.90 (t, *J* = 7.2 Hz, 3Hx0.41), 0.79 (t, *J* = 7.6 Hz, 3Hx0.59)

¹³C NMR (CDCl₃, 100 MHz) δ 199.1, 198.2, 152.1, 148.2, 136.9, 134.1, 133.8, 133.7, 133.5, 131.2, 128.77, 128.75, 128.5, 128.4, 128.24, 128.21, 127.9, 127.8, 123.1, 113.1, 112.0, 96.9, 95.5, 86.2, 77.8, 77.6, 77.5, 32.2, 22.1, 21.7, 21.4, 14.3, 13.2

HRMS calcd for C₂₁H₂₀O₂ [M+1] 305.1542, found 305.1550

FTIR (NaCl) 3437, 2959, 2936, 1685, 1604, 1452, 1266, 1095, 966 cm⁻¹

Racemic sample spectrum

Separation condition : OD column, Hexane:IPA = 95:5

Chiral sample spectrum

Separation condition : OD column, Hexane:IPA = 95:5

Regiomer ratio = 4 :1

85 % ee for the major compound, 89 % ee for the minor compound

¹H NMR (CDCl₃, 400 MHz) δ 7.92 (m, 2H), 7.58 (m, 1H), 7.47 (m, 2H), 7.35 (m, 2H), 7.28 (m, 3H), 5.54 (m, 2H), 3.94 (d, *J* = 6.0 Hz, 1H), 1.47 (s, 9H)

¹³C NMR (CDCl₃, 100 MHz) δ 200.1, 159.5, 133.93, 133.91, 130.9, 128.9, 128.8, 128.4, 128.3, 123.3, 111.5, 99.5, 87.3, 76.4, 36.9, 30.0

HRMS calcd for C₂₂H₂₂O₂ [M+1] 319.1698, found 319.1685

FTIR (NaCl) 3457, 2963, 2878, 1685, 1600, 1499, 1456, 1266, 1223, 966 cm⁻¹

Racemic sample spectrum

Separation condition : OD column, Hexane:IPA = 95:5

Chiral sample spectrum

Separation condition : OD column, Hexane:IPA = 95:5

Regiomer ratio = 99:1

98 % ee for the major compound

10b

0.83 : 0.17 (under the racemic condition)

¹H NMR (CDCl₃, 400 MHz) δ 7.61 (m, 2H), 7.45 – 7.28 (m, 3H), 5.89 (br, .17x1H), 5.64 (q, *J* = 2.4 Hz, .83x1H), 5.16 (d, *J* = 7.2 Hz, .83x1H), 4.96 (d, *J* = 6.5 Hz, .17x1H), 4.03 (d, *J* = 7.2 Hz, 1H), 1.88 (d, *J* = 2.4 Hz, .83x3H), 1.82 (d, *J* = 1.0 Hz, .17x3H), 1.22 (s, .17x9H), 1.10 (s, .83x9H).

¹³C NMR (CDCl₃, 100 MHz) δ 215.3, 215.0, 147.4, 147.4, 137.7, 131.7, 129.4, 128.6, 128.6, 128.5, 128.3, 123.4, 112.5, 112.2, 95.7, 93.1, 86.3, 77.8, 77.2, 43.8, 43.3, 27.4, 27.2, 14.7, 4.9.

HRMS calcd for C₁₇H₂₀O₂ [M] 256.1463, found 256.1467

FTIR (NaCl) 3463, 3082, 2969, 2934, 2217, 1698, 1640, 1478, 1442, 1367, 1100, 1052, 983, 779, 732, 689 cm⁻¹

HPLC Conditions Column: Chiral Technologies Chiralcel OD; Column Size: 250 x 4.6mm analytical; Mobile Phase: 97/3 Hexane:IPA; Flow Rate: 1ml/min; Detection Wavelength: 254nm.

Racemic Sample

Enantioselective Sample: 90% e.e. major, 93% e.e. minor

Crystallographic Material for **1b**.

X-ray Experimental.

Table 1. Crystallographic Data for **1b**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) for the non-hydrogen atoms of **1b**.

Table 3. Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for the non-hydrogen atoms of **1b**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **1b**.

Table 5. Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the hydrogen atoms of **1b**.

Table 6. Torsion Angles ($^\circ$) for the non-hydrogen atoms of **1b**.

Figure 1. View of **1b** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 2. Unit cell packing diagram for **1b**. The view is approximately down the **a** axis.

X-ray Experimental for $\text{C}_{24}\text{H}_{18}\text{O}_2$: Crystals grew as pale yellow lathes by slow evaporation from ether/hexane. The data crystal was cut from a long lathe and had approximate dimensions;

0.55 x 0.11 x 0.11 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073\text{\AA}$). A total of 359 frames of data were collected using ω -scans with a scan range of 1.1° and a counting time of 150 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms were observed in a ΔF map and refined with isotropic displacement parameters.

The crystal was formed from a racemic mixture which spontaneously resolved into separate enantiomorphic crystals. The absolute configuration was assigned arbitrarily and could not be determined from the X-ray results.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.019 \cdot P)^2 + (0.823 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.118, with $R(F)$ equal to 0.0657 and a goodness of fit, S , = 1.14. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were corrected for secondary extinction effects. The correction takes the form: $F_{\text{corr}} = kF_c/[1 + (3.1(2) \times 10^{-5}) \cdot F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

- 1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, 276: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 2) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. J. Appl. Cryst. 32, 115-119.
- 3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \sum(|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 6) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 7) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

SIR97 - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. (1999) J. Appl. Cryst. 32, 115-119.

Table 1. Crystal data and structure refinement for 1.

Empirical formula

C₂₄ H₁₈ O₂

Formula weight	338.38	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 5.7781(2) Å	$\alpha = 90^\circ$.
	b = 15.2090(4) Å	$\beta = 90^\circ$.
	c = 20.4982(7) Å	$\gamma = 90^\circ$.
Volume	1801.36(10) Å ³	
Z	4	
Density (calculated)	1.248 Mg/m ³	
Absorption coefficient	0.078 mm ⁻¹	
F(000)	712	
Crystal size	0.55 x 0.11 x 0.11 mm	
Theta range for data collection	3.27 to 27.47°.	
Index ranges	-7<=h<=7, -19<=k<=19, -26<=l<=26	
Reflections collected	4102	
Independent reflections	4102 [R(int) = 0.0000]	
Completeness to theta = 27.47°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4102 / 0 / 308	
Goodness-of-fit on F ²	1.143	
Final R indices [I>2sigma(I)]	R1 = 0.0657, wR2 = 0.0966	
R indices (all data)	R1 = 0.1221, wR2 = 0.1175	
Absolute structure parameter	1(2)	
Extinction coefficient	3.1(2)x10 ⁻⁵	
Largest diff. peak and hole	0.210 and -0.212 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1b. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O1	4182(3)	6237(2)	8460(1)	51(1)
O2	9651(3)	6662(1)	8324(1)	39(1)
C1	6081(4)	6112(2)	8704(1)	35(1)
C2	8150(4)	5914(2)	8254(1)	32(1)
C3	7327(4)	5797(2)	7558(1)	33(1)
C4	7879(5)	6379(2)	7093(1)	37(1)
C5	7051(5)	6341(2)	6436(2)	40(1)
C6	6283(5)	6341(2)	5891(2)	39(1)
C7	5290(5)	6331(2)	5253(1)	36(1)
C8	3143(5)	5937(2)	5143(2)	47(1)
C9	2211(6)	5921(2)	4519(2)	56(1)
C10	3379(7)	6300(2)	4008(2)	62(1)
C11	5469(7)	6702(2)	4115(2)	56(1)
C12	6431(6)	6718(2)	4731(2)	44(1)
C13	6442(4)	6190(2)	9416(1)	32(1)
C14	4716(5)	6585(2)	9792(1)	38(1)
C15	4978(6)	6683(2)	10453(2)	43(1)
C16	6967(6)	6383(2)	10758(2)	44(1)
C17	8681(5)	5981(2)	10393(2)	43(1)
C18	8436(5)	5890(2)	9724(1)	37(1)
C19	5840(5)	5017(2)	7431(1)	34(1)
C20	6567(6)	4169(2)	7591(1)	40(1)
C21	5187(6)	3448(2)	7433(2)	47(1)
C22	3101(6)	3560(2)	7117(2)	50(1)
C23	2351(6)	4399(2)	6975(2)	48(1)
C24	3687(5)	5126(2)	7128(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for 1b.

O1-C1	1.221(3)	C12-H12	0.99(4)
O2-C2	1.437(3)	C13-C18	1.391(4)
O2-H2O	0.99(4)	C13-C14	1.396(4)
C1-C13	1.479(4)	C14-C15	1.372(4)
C1-C2	1.540(4)	C14-H14	0.97(3)
C2-C3	1.513(4)	C15-C16	1.386(4)
C2-H2	1.08(2)	C15-H15	0.99(3)
C3-C4	1.339(4)	C16-C17	1.384(4)
C3-C19	1.488(4)	C16-H16	1.00(3)
C4-C5	1.431(4)	C17-C18	1.386(4)
C4-H4	1.07(3)	C17-H17	1.00(3)
C5-C6	1.201(4)	C18-H18	0.96(3)
C6-C7	1.428(4)	C19-C20	1.397(4)
C7-C12	1.388(4)	C19-C24	1.400(4)
C7-C8	1.396(4)	C20-C21	1.393(4)
C8-C9	1.389(5)	C20-H20	1.05(3)
C8-H8	0.94(3)	C21-C22	1.378(5)
C9-C10	1.373(5)	C21-H21	0.92(3)
C9-H9	0.96(3)	C22-C23	1.379(5)
C10-C11	1.372(5)	C22-H22	1.08(4)
C10-H10	1.04(4)	C23-C24	1.384(4)
C11-C12	1.380(5)	C23-H23	0.97(3)
C11-H11	0.98(4)	C24-H24	1.04(3)
C2-O2-H2O	105(2)	C19-C3-C2	116.1(2)
O1-C1-C13	121.3(3)	C3-C4-C5	124.4(3)
O1-C1-C2	118.8(3)	C3-C4-H4	116.5(16)
C13-C1-C2	119.8(2)	C5-C4-H4	119.1(16)
O2-C2-C3	112.1(2)	C6-C5-C4	176.9(3)
O2-C2-C1	104.7(2)	C5-C6-C7	177.9(3)
C3-C2-C1	110.1(2)	C12-C7-C8	118.7(3)
O2-C2-H2	112.2(13)	C12-C7-C6	120.7(3)
C3-C2-H2	111.8(12)	C8-C7-C6	120.6(3)
C1-C2-H2	105.5(12)	C9-C8-C7	120.0(3)
C4-C3-C19	122.6(2)	C9-C8-H8	123(2)
C4-C3-C2	121.2(2)	C7-C8-H8	117(2)

C10-C9-C8	120.4(3)	C16-C17-C18	120.4(3)
C10-C9-H9	118.4(19)	C16-C17-H17	118.1(15)
C8-C9-H9	121.2(19)	C18-C17-H17	121.4(15)
C11-C10-C9	119.8(4)	C17-C18-C13	120.1(3)
C11-C10-H10	125(3)	C17-C18-H18	121.3(17)
C9-C10-H10	115(3)	C13-C18-H18	118.6(17)
C10-C11-C12	120.6(4)	C20-C19-C24	118.7(3)
C10-C11-H11	118(2)	C20-C19-C3	121.5(3)
C12-C11-H11	121(2)	C24-C19-C3	119.8(3)
C11-C12-C7	120.4(3)	C21-C20-C19	120.0(3)
C11-C12-H12	121(2)	C21-C20-H20	121.9(16)
C7-C12-H12	118(2)	C19-C20-H20	118.2(16)
C18-C13-C14	118.9(3)	C22-C21-C20	120.8(3)
C18-C13-C1	122.6(2)	C22-C21-H21	125.8(19)
C14-C13-C1	118.6(2)	C20-C21-H21	113(2)
C15-C14-C13	120.9(3)	C21-C22-C23	119.3(3)
C15-C14-H14	123.2(17)	C21-C22-H22	118(2)
C13-C14-H14	115.9(17)	C23-C22-H22	123(2)
C14-C15-C16	120.1(3)	C22-C23-C24	121.0(3)
C14-C15-H15	122.4(16)	C22-C23-H23	119(2)
C16-C15-H15	117.5(16)	C24-C23-H23	120(2)
C17-C16-C15	119.7(3)	C23-C24-C19	120.1(3)
C17-C16-H16	119.9(19)	C23-C24-H24	121(2)
C15-C16-H16	120.5(19)	C19-C24-H24	119(2)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1b. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	27(1)	77(2)	49(1)	-13(1)	-10(1)	11(1)
O2	26(1)	40(1)	50(1)	-8(1)	-6(1)	-1(1)
C1	26(1)	35(2)	42(2)	-2(1)	-1(1)	1(1)
C2	25(1)	32(2)	38(2)	-4(1)	-5(1)	0(1)
C3	26(1)	35(2)	37(2)	-6(1)	-1(1)	0(1)
C4	39(2)	32(2)	40(2)	-3(1)	1(1)	-1(1)
C5	41(2)	34(2)	46(2)	-1(1)	-1(2)	-2(1)
C6	43(2)	32(2)	43(2)	-4(1)	-1(2)	0(1)
C7	37(2)	33(2)	39(2)	-2(1)	-1(1)	5(1)
C8	40(2)	40(2)	61(2)	-2(2)	2(2)	5(2)
C9	43(2)	47(2)	78(3)	-20(2)	-21(2)	6(2)
C10	74(3)	55(2)	57(2)	-8(2)	-22(2)	20(2)
C11	74(3)	49(2)	45(2)	0(2)	-2(2)	12(2)
C12	47(2)	41(2)	42(2)	1(2)	1(2)	5(2)
C13	30(1)	29(2)	36(2)	1(1)	-3(1)	-2(1)
C14	35(2)	37(2)	42(2)	0(1)	4(1)	3(1)
C15	47(2)	43(2)	39(2)	-3(2)	8(2)	-4(2)
C16	52(2)	45(2)	35(2)	4(2)	0(2)	-8(2)
C17	43(2)	42(2)	43(2)	5(2)	-10(2)	-1(2)
C18	35(2)	40(2)	37(2)	-1(1)	-2(1)	3(1)
C19	33(2)	36(2)	33(2)	-3(1)	5(1)	-5(1)
C20	45(2)	37(2)	36(2)	-2(1)	6(2)	-7(2)
C21	63(2)	37(2)	42(2)	-1(2)	11(2)	-10(2)
C22	57(2)	54(2)	40(2)	-4(2)	6(2)	-21(2)
C23	41(2)	65(2)	38(2)	-7(2)	-2(2)	-18(2)
C24	32(2)	52(2)	38(2)	-4(2)	-1(1)	-6(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 1b.

	x	y	z	U(eq)
H2O	11220(70)	6410(30)	8373(18)	92(13)
H2	8920(40)	5320(16)	8443(11)	23(6)
H4	9100(50)	6880(20)	7224(14)	55(9)
H8	2400(60)	5690(20)	5507(15)	58(10)
H9	750(60)	5640(20)	4433(15)	55(10)
H10	2580(80)	6230(30)	3560(20)	119(16)
H11	6250(60)	6980(20)	3744(18)	73(12)
H12	7970(70)	6990(20)	4810(16)	75(11)
H14	3340(50)	6768(18)	9558(14)	44(8)
H15	3780(50)	6963(17)	10730(14)	39(8)
H16	7180(60)	6460(20)	11240(16)	61(9)
H17	10130(50)	5785(17)	10624(13)	39(7)
H18	9620(50)	5619(19)	9464(13)	44(8)
H20	8170(60)	4095(18)	7826(13)	47(8)
H21	5850(50)	2920(20)	7537(15)	45(9)
H22	2090(80)	2980(30)	7007(19)	97(13)
H23	870(60)	4470(20)	6756(15)	59(10)
H24	3120(60)	5760(20)	7012(16)	69(11)

Table 6. Torsion angles [°] for 1b.

O1-C1-C2-O2	113.5(3)	C4-C3-C19-C20	126.2(3)
C13-C1-C2-O2	-63.5(3)	C2-C3-C19-C20	-55.2(3)
O1-C1-C2-C3	-7.2(4)	C4-C3-C19-C24	-52.0(4)
C13-C1-C2-C3	175.8(2)	C2-C3-C19-C24	126.6(3)
O2-C2-C3-C4	-3.8(4)	C24-C19-C20-C21	1.8(4)
C1-C2-C3-C4	112.3(3)	C3-C19-C20-C21	-176.5(3)
O2-C2-C3-C19	177.6(2)	C19-C20-C21-C22	0.1(4)
C1-C2-C3-C19	-66.3(3)	C20-C21-C22-C23	-1.8(5)
C19-C3-C4-C5	2.5(4)	C21-C22-C23-C24	1.7(5)
C2-C3-C4-C5	-176.0(3)	C22-C23-C24-C19	0.2(4)
C3-C4-C5-C6	103(6)	C20-C19-C24-C23	-1.9(4)
C4-C5-C6-C7	-66(12)	C3-C19-C24-C23	176.3(3)
C5-C6-C7-C12	168(8)		
C5-C6-C7-C8	-11(9)		
C12-C7-C8-C9	1.4(4)		
C6-C7-C8-C9	-179.2(3)		
C7-C8-C9-C10	-0.7(5)		
C8-C9-C10-C11	-0.6(5)		
C9-C10-C11-C12	1.1(5)		
C10-C11-C12-C7	-0.3(5)		
C8-C7-C12-C11	-0.9(4)		
C6-C7-C12-C11	179.7(3)		
O1-C1-C13-C18	167.1(3)		
C2-C1-C13-C18	-15.9(4)		
O1-C1-C13-C14	-13.1(4)		
C2-C1-C13-C14	163.8(2)		
C18-C13-C14-C15	0.5(4)		
C1-C13-C14-C15	-179.2(3)		
C13-C14-C15-C16	-0.6(5)		
C14-C15-C16-C17	-0.2(5)		
C15-C16-C17-C18	1.0(5)		
C16-C17-C18-C13	-1.1(4)		
C14-C13-C18-C17	0.3(4)		
C1-C13-C18-C17	-180.0(3)		