Supporting Information For:

Synthesis and study of 7,12,17-trioxa[11]helicene

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Experimental Section:

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc. All solvents that were used were stored on oven dried molecular sieves (4Å). All commercial products were used without further purification. Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using SRL silica gel (60-120 mesh). All reactions were carried out under an inert atmosphere (nitrogen) unless other conditions are specified. ^1H and ^{13}C NMR spectra are recorded on a 400 MHz Bruker Avance 400 Spectrometer (100 MHz for ^{13}C respectively) spectrometer with CDCl_3 as solvent and TMS as internal standard. Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), quartet of triplets (qt), septet (sept) and multiplet (m). Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

Experimental Procedures:

7, 12, 17-trioxa[11]helicene (1)

Compound **2** was refluxed in toluene (20 mL) in the presence of p-TsOH (80 mg w/w) for 24 h. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. The combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over Na_2SO_4 and evaporated to obtained crude solid. The crude product was purified by column chromatography over silica gel using light petroleum ether/ethyl acetate as eluent (100:00 to 98:2) furnishing a yellow solid (36 mg, 37%)

M.p. 345 °C

^1H NMR (CDCl_3 , 400 MHz) δ 8.06 (d, J = 8.8 Hz, 1H, ArH), 8.01 (d, J = 8.4 Hz, 1H, ArH), 7.67 (d, J = 8.8 Hz, 1H, ArH), 7.61 (d, J = 8.4 Hz, 1H, ArH), 7.58 (d, J = 8.8 Hz, 1H, ArH), 7.36 (d, J = 8.8 Hz, 1H, ArH), 7.08 (d, J = 8.8 Hz, 1H, ArH), 7.07 (d, J = 8.4 Hz, 1H, ArH), 6.95 (td, J = 6.8, 1.2 Hz, 1H, ArH), 6.26 (td, J = 6.8, 1.2 Hz, 1H, ArH)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 154.97 (2 $\times$ Cq), 154.58 (2 $\times$ Cq), 152.27 (2 $\times$ Cq), 130.45 (2 $\times$ Cq), 129.26 (2 $\times$ CH), 128.73 (2 $\times$ Cq), 128.66 (2 $\times$ CH), 128.51 (2 $\times$ CH), 127.54 (2 $\times$ Cq), 127.05 (2 $\times$ CH), 125.06 (2 $\times$ CH), 124.65 (2 $\times$ CH), 123.68 (2 $\times$ Cq), 123.20 (2 $\times$ CH), 121.07 (2 $\times$ Cq), 120.58 (2 $\times$ Cq), 118.66 (2 $\times$ Cq), 110.78 (2 $\times$ CH), 110.64 (2 $\times$ CH), 110.39 (2 $\times$ CH)

IR (KBr) ν 1671, 1568, 1551, 1519, 1441, 1379, 1220, 1074, 1004, 840, 809

MS (EI) m/z , (%) 548 (100)

HRMS [ESI^+] calcd for $\text{C}_{40}\text{H}_{20}\text{O}_3$ [M] $^+$ 548.1412, found 548.1422

2-hydroxy-7-oxa[5]helicene (3)

dinaphtho[2,1-b:1',2'-d]furan-2-ol compound (**4**) (1 g, 3.31 mmol) was refluxed in toluene (20 mL) in the presence of *p*-TsOH (0.63 g 3.31 mmol) for 24 h. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. The combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over Na_2SO_4 and evaporated to obtained crude solid. The crude product was purified by column chromatography over silica gel using light petroleum ether/ethyl acetate as eluent (100:00 to 90:10) furnishing a white solid (0.58 g, 62%) M.pt.180-182 $^\circ\text{C}$

^1H NMR (CDCl_3 , 400 MHz) δ 9.12 (d, J = 8.8 Hz, 1H, ArH), 8.50 (d, J = 2.4 Hz, ArH), 8.09 (d, J = 8.8 Hz, 1H, ArH), 7.99 (d, J = 8.4 Hz, 1H, ArH), 7.97 (d, J = 8.4 Hz, 1H, ArH), 7.90 (d, J = 8.8 Hz, 1H, ArH), 7.85 (d, J = 8.8 Hz, 1H, ArH), 7.77 (td, J = 6.8, 1.2 Hz, 1H, ArH), 7.71 (d, J = 8.8 Hz, 1H, ArH), 7.61 (td, J = 6.8, 1.2 Hz, 1H, ArH), 7.20 (dd, J = 8.8, 2.4 Hz, 1H, ArH), 5.37 (s, 1H, OH)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 155.05 (Cq), 154.13 (Cq), 154.05 (Cq), 131.43 (CH), 131.21 (Cq), 130.04 (Cq), 129.55 (CH), 128.75 (Cq), 128.49 (Cq), 128.28 (CH), 128.10 (CH), 126.36 (Cq), 126.10 (CH), 125.58 (CH), 124.34 (CH), 118.46 (Cq), 115.54 (CH), 112.37 (CH), 110.37 (CH), 109.08 (CH)

IR (KBr) ν 3535, 3230 (OH), 3050, 1621, 1447, 1375, 1236, 1202, 1030, 996, 829, 803

Mass (EI) m/z , (%) (M+1) 285 (21), (M) 284 (99), (M-H) 283 (100) and (ESI^{ve}) [M] 284.3

HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2$ (M) $^+$ 284.0837, found 284.0839

Representative Procedure for the compound 4

A solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (42.18 g, 156.08 mmol) in 200 mL water was added drop wise for 1 h at 100 °C to the solution of 2,7-dihydroxynaphthalene **6** (10 g, 62.43 mmol) and 2-naphthalene **5** (13.5 g, 93.65 mmol) in 500 mL of water. After the addition the reaction mixture was refluxed for 24 h, completion of the reaction the 2, 7-dihydroxynaphthalene reaction mixture was cooled to room temperature and extracted with ethyl acetate (2 x 500 mL) the solvent dried over sodium sulphate and concentrated under reduced pressure to obtain the crude black mass. Purification of compound by column chromatography on silica gel using gradient petroleum ether: ethyl acetate 100:00 to 70:30 as eluent to obtained binaphthol derivatives. Yield of **4** & **7** was calculated based on **5** and yield of **4** & **8** was calculated based on **6**.

2-Napthalol (**5**): Yield = 3.20 g, 24% (recovered)

Binol (**7**): Yield = 3.60 g, 34% (M.pt. = 216-218 °C Lit.¹ 218°C)

Tetrol (**8**): Yield = 5.11 g, 51% (M.pt. = 122-124 °C ²)

Triol (**4**): Yield = 7.15 g, 38% (M.pt. = 172-174 °C)

¹H NMR (CDCl_3 , 400 MHz) δ 7.96 (d, J = 9.2 Hz, 1H, ArH), 7.91-7.87 (d, J = 8.4 Hz, 2H merged, ArH), 7.78 (d, J = 8.8 Hz, 1H, ArH), 7.42-7.39 (m, 1H, ArH), 7.37 (d, J = 9.2 Hz, 1H, ArH), 7.34-7.28 (m, 1H, ArH), 7.22 (d, J = 8.8 Hz, 1H, ArH), 7.18 (d, J = 8.4 Hz, 1H, ArH), 6.97 (dd, J = 8.8, 2.4 Hz, 1H, ArH), 6.41 (d, J = 2.4 Hz, 1H, ArH), 5.13 (s, 1H, ArOH), 5.05 (s, 1H, ArOH), 4.83 (s, 1H, ArOH)

¹³C NMR (CDCl_3 , 100.6 MHz) δ 154.9 (Cq), 153.5 (Cq), 152.7 (Cq), 134.9 (Cq), 133.3 (Cq), 131.5 (CH), 131.3 (CH), 130.5 (CH), 129.5 (Cq), 128.4 (CH), 127.6 (CH), 124.8 (CH), 124.2 (Cq), 124.1 (CH), 117.7 (CH), 115.6 (CH), 115.3 (CH), 110.9 (Cq), 109.4 (Cq), 106.4 (CH).

IR (KBr) ν 3492 (OH), 3391 (OH), 1620, 1593, 1560, 1470, 1216, 1150, 838, 820

Mass (EI) m/z , (%) 301.88 (100) and (ESI) $[\text{M}+1]$ 303.4

HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{O}_3$ ($\text{M} + 1$)⁺ 303.1012, found 303.1022

Synthesis of Compound (9)

Copper (II) chloride dihydrate (0.60 g, 3.52 mmol) and TEMED (0.43 g, 3.69 mmol) were taken in methanol (2 ml) under a nitrogen atmosphere. The solution was allowed to stand for 30 min at room temperature. After the solution had been purged with nitrogen for 5

min, a solution of 2-hydroxy-7-oxa[5]helicene **3** (0.1 g, 0.35 mmol) in degassed methanol (5 ml) was added, and the mixture was stirred at room temperature for 24 h under nitrogen. The reaction mixture was poured into the mixed solvent of 1 M hydrochloric acid solution and ethyl acetate. The organic layer was separated, washed successively with water and brine, and dried over sodium sulfate, and the solvent was evaporated to give a residue. The residue was purified by column chromatography on silica gel using light petroleum ether:ethyl acetate (100:0 to 95:5) as eluent to obtain an orange solid **9** (33 mg, 27%), M.p. 190-192 °C. And using ethyl acetate to collect impure **2** compound which was without purification convert to **1** compound.

¹H NMR (CDCl₃, 400 MHz) δ 9.62 (d, *J* = 8.8 Hz, 1H, ArH), 8.04 (d, *J* = 8.8 Hz, 1H ArH), 7.98 (dd, *J* = 8, 1.2 Hz, 1H, ArH), 7.77 (d, *J* = 8 Hz, 1H, ArH), 7.75 (d, *J* = 8 Hz, 1H, ArH), 7.70-7.67 (m, 1H, ArH), 7.58 (d, *J* = 10 Hz, 1H, ArH), 7.57 – 7.55 (m, 1H, ArH), 7.48 (d, *J* = 8.4 Hz, 1H, ArH), 6.26 (d, *J* = 10 Hz, 1H), 3.22 (s, 6H, OCH₃)

¹³C NMR (CDCl₃, 100.6 MHz) δ 194.71 (C=O), 158.01 (Cq), 156.17 (Cq), 147.75 (CH), 133.35 (Cq), 131.62 (CH), 131.26 (Cq), 129.95 (Cq), 129.49 (CH), 129.08 (CH), 128.38 (CH), 127.74 (Cq), 125.76 (CH), 125.04 (Cq), 124.49 (CH), 122.71 (CH), 117.43 (Cq), 113.56 (CH=CH), 112.07 (CH=CH), 97.64 [C(OCH₃)₂], 51.87 (2 × OCH₃)

IR (KBr) ν 3043, 1759, 1681, 1600, 1541, 1394, 1222, 1084, 998, 887, 800, 743, 624

Mass (EI): *m/z*, (%) 344 (100)

HRMS [ESI⁺] calcd for C₂₂H₁₆O₄Na [M+Na]⁺ 367.0946, found 367.0951.

Spectral Data:

¹H-NMR Spectrum of 7,12,17-trioxa[11]helicene] (1) in CDCl₃ (400 MHz)

¹³C-NMR spectrum of 7,12,17-trioxa[11]helicene] (1) in CDCl₃ on 100.6 MHz

¹³C-NMR spectrum of 2-hydroxy-7-oxa[5]helicene (3) in CDCl₃ on 100.6 MHz

HRMS spectrum of 2-hydroxy-7-oxa[5]helicene (3)

¹³C-NMR spectrum of 1,1'-binaphthalenyl-2,2',7-triol (4) in CDCl₃ on 100.6 MHz

HRMS spectrum of 1,1'-binaphthalenyl-2,2',7-triol (4)

¹H-NMR Spectrum of (9) in CDCl₃ (400 MHz)

¹³C-NMR spectrum of (9) in CDCl₃ on 100.6 MHz

HPLC analysis for 7,12,17-trioxa[11]helicene (1):

Observed two peaks of separated enantiomers at 1) R_t – 11.15 min and 2) R_t – 12.95 min.

Solvent System: Hexane: *Iso*-propanol (90:10), Flow rate: 0.5 mL/min.

Chiral Column: CHIRAL PAK IC, UV: 233nm.

Figure 1: DSC thermogram of 7, 12, 17-trioxa[11]helicene (**1**) flow rate 10°C/min to 385°C

X-ray Crystal Data

Crystallographic data for the structures of compounds **1** (CCDC No. 999892) and **9** (CCDC No. 999893) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained from <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

1). For Compound 7,12,17-trioxa[11]helicene (**1**):

Figure 2: ORTEP diagram of **1** with atom numbering scheme 50% probability factor for the thermal ellipsoids.

Figure 3: Stacking of **1** in the crystal, with a helical pitch of 7.637 Å. The rods represent the position of helical axis, yellow for 'P' and purple for 'M' isomer.

Figure 4: Interplanar angle of **1**

Table 1 Crystal data and structure refinement for 7,12,17-trioxa[11]helicene(1):

Empirical formula	C ₄₀ H ₂₀ O ₃
Formula weight	548.56
Temperature/K	293
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	7.63737(19)
b/Å	22.5914(7)
c/Å	15.1095(4)
α/°	90
β/°	99.906(3)
γ/°	90
Volume/Å ³	2568.11(12)
Z	4
ρ _{calc} /g/cm ³	1.4188
μ/mm ⁻¹	0.704
F(000)	1136.0
Crystal size/mm ³	0.29 × 0.26 × 0.22
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.12 to 150.94
Index ranges	-8 ≤ h ≤ 9, -28 ≤ k ≤ 27, -18 ≤ l ≤ 11
Reflections collected	12179
Independent reflections	5333 [R _{int} = 0.0203, R _{sigma} = 0.0261]
Data/restraints/parameters	5333/0/396
Goodness-of-fit on F ²	1.052
Final R indexes [I > 2σ (I)]	R ₁ = 0.0427, wR ₂ = 0.1124
Final R indexes [all data]	R ₁ = 0.0522, wR ₂ = 0.1209
Largest diff. peak/hole / e Å ⁻³	0.22/-0.20

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 7,12,17-trioxa[11]helicene(1). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	1122.6 (15)	4716.8 (5)	2838.5 (8)	58.3 (3)
O2	-5665.1 (14)	4387.2 (5)	1784.1 (7)	55.7 (3)
O3	-1065 (2)	1641.2 (5)	2493.0 (8)	66.5 (3)
C4	-2584.8 (17)	3920.9 (6)	3732.4 (9)	40.2 (3)
C5	474.6 (17)	3733.8 (7)	2590.7 (9)	40.4 (3)
C6	-481.9 (17)	4077.5 (6)	1841.5 (9)	39.9 (3)
C7	-1491.9 (17)	3954.0 (6)	971.6 (9)	40.0 (3)
C8	-1711.8 (19)	3385.3 (7)	587.2 (9)	42.5 (3)
C9	659.0 (18)	3128.7 (7)	2865.6 (9)	41.9 (3)
C10	-3591.3 (17)	3936.8 (6)	2841.4 (9)	39.6 (3)
C11	-3994.1 (18)	2892.2 (7)	1974.8 (9)	41.8 (3)

C12	-535 (2)	2640.9 (7)	2622.8 (9)	44.4 (3)
C13	-4282.2 (17)	3502.2 (7)	2162.9 (9)	40.2 (3)
C14	-1954.5 (19)	3396.3 (7)	4181.6 (9)	44.0 (3)
C15	1495.5 (19)	4151.9 (8)	3127.2 (10)	49.3 (4)
C16	-4435 (2)	4461.3 (7)	2550.8 (10)	49.4 (3)
C17	-5629.5 (19)	3796.2 (8)	1593.1 (10)	48.3 (3)
C18	-2423 (2)	2545.1 (6)	2249.2 (9)	42.8 (3)
C19	-72 (2)	4662.1 (7)	2051.8 (11)	50.3 (4)
C20	-2592 (3)	1934.8 (7)	2142.3 (11)	55.3 (4)
C21	-5450 (2)	2598.4 (8)	1411.8 (10)	53.1 (4)
C22	-2217 (2)	4446.7 (7)	440.9 (11)	52.7 (4)
C23	-2350 (2)	4465.9 (7)	4216.2 (11)	51.2 (4)
C24	-6867 (2)	2929.7 (10)	921.1 (11)	62.3 (5)
C25	2245 (2)	2990.2 (9)	3496.7 (10)	54.6 (4)
C26	-783 (3)	3942.5 (9)	5513.6 (11)	66.7 (5)
C27	-1073 (2)	3405.8 (8)	5050.7 (10)	56.5 (4)
C28	-6920 (2)	3527.5 (10)	954.5 (10)	60.3 (5)
C29	-2659 (2)	3301.4 (8)	-256.4 (10)	55.7 (4)
C30	140 (2)	2071.8 (8)	2803.5 (11)	57.3 (4)
C31	-4170 (3)	5001.1 (8)	2999.6 (13)	62.7 (4)
C32	2866 (2)	4023.2 (10)	3840.0 (11)	62.2 (5)
C33	3275 (2)	3443.8 (10)	3971.5 (10)	63.0 (5)
C34	-5461 (3)	1973.6 (9)	1312.7 (12)	66.1 (5)
C35	-3107 (3)	4999.0 (8)	3817.7 (13)	64.2 (5)
C36	-1416 (3)	4455.6 (9)	5109.1 (11)	64.3 (5)
C37	-3232 (3)	4337.3 (9)	-417.8 (12)	66.9 (5)
C38	-4078 (3)	1634.3 (8)	1695.6 (12)	68.0 (5)
C39	-3451 (2)	3781.7 (10)	-758.2 (11)	66.7 (5)
C40	1797 (3)	1931.5 (10)	3297.2 (13)	72.9 (6)
C41	2782 (3)	2391.7 (11)	3667.8 (12)	71.4 (6)
C42	-1845 (3)	5036.6 (8)	754.1 (14)	69.6 (5)
C43	-735 (3)	5148.1 (8)	1534.3 (14)	68.3 (5)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7,12,17-trioxa[11]helicene(1). The Anisotropic displacement factor exponent takes the form: - $2\pi^2[\text{h}^2\text{a}^{*2}\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	54.9 (6)	58.2 (7)	63.4 (7)	-15.4 (5)	14.9 (5)	-18.4 (5)
O2	48.7 (6)	62.7 (7)	56.5 (6)	13.0 (5)	10.9 (5)	10.0 (5)
O3	96.6 (10)	41.6 (6)	64.7 (7)	7.7 (6)	23.7 (7)	3.9 (5)
C4	37.2 (6)	43.3 (7)	42.7 (7)	-5.8 (5)	14.3 (5)	-4.9 (5)
C5	32.9 (6)	52.7 (8)	37.1 (6)	-1.4 (6)	9.7 (5)	-3.9 (6)
C6	35.8 (6)	40.3 (7)	45.5 (7)	-1.1 (5)	12.8 (5)	-0.6 (5)

C7	35.0 (6)	44.0 (7)	42.6 (7)	-0.0 (5)	11.0 (5)	4.6 (6)
C8	41.2 (7)	46.7 (8)	40.1 (7)	0.6 (6)	8.8 (5)	2.4 (6)
C9	37.4 (7)	54.8 (8)	34.6 (6)	6.4 (6)	9.5 (5)	2.5 (6)
C10	36.4 (6)	40.9 (7)	44.4 (7)	-1.0 (5)	14.5 (5)	-0.8 (5)
C11	42.5 (7)	49.1 (8)	35.4 (6)	-9.7 (6)	11.3 (5)	-4.1 (5)
C12	50.1 (8)	46.8 (8)	37.6 (6)	6.7 (6)	11.7 (6)	4.3 (6)
C13	34.0 (6)	51.3 (8)	36.9 (6)	-3.6 (5)	10.1 (5)	0.6 (5)
C14	43.8 (7)	48.3 (8)	41.6 (7)	-5.4 (6)	12.7 (6)	-1.9 (6)
C15	40.6 (7)	63.3 (10)	46.3 (7)	-8.8 (7)	14.0 (6)	-9.5 (7)
C16	47.1 (8)	49.1 (8)	55.1 (8)	6.1 (6)	17.7 (6)	4.6 (7)
C17	39.8 (7)	62.0 (9)	44.6 (7)	3.9 (6)	12.1 (6)	5.2 (7)
C18	53.2 (8)	41.5 (7)	36.3 (6)	-4.1 (6)	14.6 (5)	-2.0 (5)
C19	48.5 (8)	46.2 (8)	58.6 (9)	-7.4 (6)	16.2 (7)	-7.9 (7)
C20	77.3 (11)	42.6 (8)	49.8 (8)	-3.8 (8)	22.1 (8)	-1.9 (6)
C21	51.5 (8)	68.6 (10)	41.7 (7)	-18.7 (7)	15.1 (6)	-11.5 (7)
C22	52.5 (8)	49.5 (9)	57.0 (9)	4.2 (7)	11.4 (7)	11.7 (7)
C23	52.5 (8)	49.0 (8)	55.8 (8)	-11.8 (7)	19.8 (7)	-10.5 (7)
C24	42.3 (8)	98.3 (15)	46.0 (8)	-17.5 (8)	6.3 (6)	-11.9 (9)
C25	39.7 (7)	84.0 (12)	41.5 (7)	8.8 (7)	10.7 (6)	11.2 (7)
C26	72.3 (11)	86.7 (14)	40.4 (8)	-27.1 (10)	7.5 (7)	-5.8 (8)
C27	56.8 (9)	67.9 (11)	44.9 (8)	-6.7 (8)	9.4 (7)	6.0 (7)
C28	38.1 (7)	98.8 (15)	43.4 (8)	1.1 (8)	5.4 (6)	3.0 (8)
C29	56.7 (9)	63.6 (10)	45.7 (8)	-2.9 (8)	5.8 (7)	-6.1 (7)
C30	72.1 (11)	51.7 (9)	51.1 (8)	13.5 (8)	19.4 (8)	8.0 (7)
C31	72.0 (11)	43.4 (8)	77.4 (11)	10.7 (8)	26.2 (9)	2.6 (8)
C32	41.5 (8)	101.9 (15)	44.0 (8)	-19.5 (9)	9.6 (6)	-15.2 (9)
C33	36.8 (7)	109.5 (16)	42.1 (8)	-2.3 (9)	4.7 (6)	7.8 (9)
C34	75.8 (12)	70.6 (12)	55.2 (9)	-33.1 (10)	20.2 (8)	-20.8 (8)
C35	77.5 (12)	42.3 (8)	78.9 (12)	-5.7 (8)	30.5 (10)	-14.9 (8)
C36	76.0 (11)	67.0 (11)	53.0 (9)	-26.7 (9)	19.9 (8)	-19.4 (8)
C37	67.2 (11)	72.4 (12)	58.3 (10)	11.2 (9)	3.2 (8)	24.2 (9)
C38	98.5 (15)	49.7 (10)	61.5 (10)	-26.2 (10)	29.5 (10)	-13.8 (8)
C39	65.4 (10)	86.8 (14)	43.8 (8)	2.3 (10)	-2.0 (7)	6.6 (8)
C40	79.1 (13)	71.1 (13)	70.5 (12)	32.7 (11)	19 (1)	22.5 (10)
C41	56.4 (10)	100.6 (16)	57.7 (10)	30.4 (10)	11.4 (8)	28.3 (10)
C42	79.5 (12)	44.1 (9)	85.2 (13)	7.4 (8)	14.6 (10)	17.8 (9)
C43	79.6 (12)	36.7 (8)	91.3 (13)	-5.4 (8)	22.6 (10)	-2.1 (8)

Table 4 Bond Lengths for 7,12,17-trioxa[11]helicene(1):

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C15	1.363 (2)	C14	C27	1.369 (2)
O1	C19	1.3738 (19)	C15	C32	1.397 (2)
O2	C16	1.3705 (19)	C16	C31	1.393 (2)

O2	C17	1.367(2)	C17	C28	1.394(2)
O3	C20	1.367(2)	C18	C20	1.392(2)
O3	C30	1.366(2)	C19	C43	1.392(2)
C4	C10	1.4312(19)	C20	C38	1.393(3)
C4	C14	1.409(2)	C21	C24	1.416(3)
C4	C23	1.4274(19)	C21	C34	1.419(3)
C5	C6	1.4607(19)	C22	C37	1.414(2)
C5	C9	1.429(2)	C22	C42	1.426(2)
C5	C15	1.393(2)	C23	C35	1.424(2)
C6	C7	1.4324(19)	C23	C36	1.414(2)
C6	C19	1.382(2)	C24	C28	1.352(3)
C7	C8	1.408(2)	C25	C33	1.411(3)
C7	C22	1.427(2)	C25	C41	1.423(3)
C8	C29	1.367(2)	C26	C27	1.398(2)
C9	C12	1.437(2)	C26	C36	1.360(3)
C9	C25	1.4413(19)	C29	C39	1.400(2)
C10	C13	1.4517(19)	C30	C40	1.391(3)
C10	C16	1.384(2)	C31	C35	1.357(3)
C11	C13	1.432(2)	C32	C33	1.352(3)
C11	C18	1.434(2)	C34	C38	1.352(3)
C11	C21	1.4405(19)	C37	C39	1.356(3)
C12	C18	1.471(2)	C40	C41	1.347(3)
C12	C30	1.394(2)	C42	C43	1.352(3)
C13	C17	1.3915(19)			

Table 5 Bond Angles for 7,12,17-trioxa[11]helicene(1):

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	O1	C15	105.29(12)	C20	C18	C11	116.87(14)
C17	O2	C16	105.19(12)	C20	C18	C12	104.81(14)
C30	O3	C20	105.49(13)	C6	C19	O1	112.06(14)
C14	C4	C10	123.92(12)	C43	C19	O1	122.56(15)
C23	C4	C10	117.38(13)	C43	C19	C6	125.36(16)
C23	C4	C14	118.45(13)	C18	C20	O3	112.32(15)
C9	C5	C6	138.18(13)	C38	C20	O3	121.40(16)
C15	C5	C6	104.22(13)	C38	C20	C18	126.20(18)
C15	C5	C9	117.54(13)	C24	C21	C11	120.55(16)
C7	C6	C5	136.56(13)	C34	C21	C11	120.69(17)
C19	C6	C5	105.47(13)	C34	C21	C24	118.72(16)
C19	C6	C7	117.53(13)	C37	C22	C7	118.55(15)
C8	C7	C6	124.29(13)	C42	C22	C7	120.42(16)
C22	C7	C6	117.35(13)	C42	C22	C37	120.95(16)
C22	C7	C8	118.21(13)	C35	C23	C4	120.46(15)
C29	C8	C7	121.19(14)	C36	C23	C4	118.22(16)

C12	C9	C5	129.28 (12)	C36	C23	C35	121.27 (15)
C25	C9	C5	115.45 (14)	C28	C24	C21	122.27 (15)
C25	C9	C12	115.25 (14)	C33	C25	C9	120.69 (16)
C13	C10	C4	135.93 (13)	C41	C25	C9	120.63 (17)
C16	C10	C4	117.73 (13)	C41	C25	C33	118.66 (16)
C16	C10	C13	105.20 (13)	C36	C26	C27	120.06 (16)
C18	C11	C13	128.21 (12)	C26	C27	C14	120.18 (17)
C21	C11	C13	115.55 (14)	C24	C28	C17	115.99 (16)
C21	C11	C18	116.19 (14)	C39	C29	C8	120.50 (16)
C18	C12	C9	138.38 (13)	C12	C30	O3	112.64 (15)
C30	C12	C9	117.39 (14)	C40	C30	O3	121.28 (17)
C30	C12	C18	104.15 (14)	C40	C30	C12	125.93 (19)
C11	C13	C10	137.87 (13)	C35	C31	C16	117.03 (16)
C17	C13	C10	104.73 (13)	C33	C32	C15	115.98 (16)
C17	C13	C11	117.34 (13)	C32	C33	C25	122.28 (15)
C27	C14	C4	121.33 (15)	C38	C34	C21	121.93 (16)
C5	C15	O1	112.55 (13)	C31	C35	C23	121.59 (16)
C32	C15	O1	121.95 (15)	C26	C36	C23	121.67 (16)
C32	C15	C5	125.28 (17)	C39	C37	C22	121.47 (16)
C10	C16	O2	112.20 (14)	C34	C38	C20	116.25 (17)
C31	C16	O2	122.64 (15)	C37	C39	C29	119.91 (16)
C31	C16	C10	125.06 (16)	C41	C40	C30	116.01 (18)
C13	C17	O2	112.03 (13)	C40	C41	C25	122.32 (16)
C28	C17	O2	122.26 (15)	C43	C42	C22	121.52 (17)
C28	C17	C13	125.44 (17)	C42	C43	C19	117.11 (16)
C12	C18	C11	138.32 (13)				

Table 6 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7,12,17-trioxa[11]helicene(1):

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H24	-7792 (2)	2729.4 (10)	563.4 (11)	74.8 (6)
H26	-157 (3)	3948.7 (9)	6098.7 (11)	80.0 (6)
H27	-665 (2)	3054.3 (8)	5333.9 (10)	67.8 (5)
H28	-7768 (2)	3746.3 (10)	574.4 (10)	72.4 (5)
H29	-2779 (2)	2922.2 (8)	-499.2 (10)	66.8 (5)
H31	-4698 (3)	5347.4 (8)	2749.7 (13)	75.2 (5)
H32	3461 (2)	4318.2 (10)	4202.3 (11)	74.6 (6)
H33	4270 (2)	3340.9 (10)	4389.4 (10)	75.6 (6)
H34	-6448 (3)	1792.4 (9)	974.4 (12)	79.4 (6)
H35	-2867 (3)	5354.3 (8)	4125.4 (13)	77.1 (6)
H36	-1230 (3)	4808.6 (9)	5428.0 (11)	77.1 (6)
H37	-3762 (3)	4653.6 (9)	-756.7 (12)	80.2 (6)
H38	-4117 (3)	1223.3 (8)	1662.6 (12)	81.7 (6)

H39	-4126 (2)	3719.7 (10)	-1324.2 (11)	80.0 (6)
H40	2201 (3)	1543.2 (10)	3367.4 (13)	87.4 (7)
H41	3850 (3)	2315.7 (11)	4048.8 (12)	85.7 (7)
H42	-2377 (3)	5351.7 (8)	413.8 (14)	83.5 (6)
H43	-428 (3)	5532.9 (8)	1717.3 (14)	81.9 (6)
H8	-1150 (20)	3054 (7)	927 (11)	46 (4)
H14	-2190 (20)	3028 (7)	3888 (10)	45 (4)

2). For Compound (9):

Figure 5: ORTEP diagram of **9** with atom numbering scheme 50% probability factor for the thermal ellipsoids.

Table 7 Crystal data and structure refinement for compound (9)

Empirical formula	$C_{44}H_{33}O_6$
Formula weight	657.70
Temperature/K	293(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	23.0883(10)
b/Å	8.2485(4)

c/Å	17.6035(8)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	90.00
Volume/Å ³	3352.5(3)
Z	4
ρ_{calc} /mg/mm ³	1.303
μ /mm ⁻¹	0.086
F(000)	1380.0
2 θ range for data collection	6.5 to 58.06°
Index ranges	-29 ≤ h ≤ 30, -11 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	19835
Independent reflections	7464[R(int) = 0.0318]
Data/restraints/parameters	7464/1/455
Goodness-of-fit on F ²	1.056
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0856, wR ₂ = 0.2314
Final R indexes [all data]	R ₁ = 0.1102, wR ₂ = 0.2554
Largest diff. peak/hole / e Å ⁻³	0.82/-0.26
Flack parameter	-0.3(18)

Table 8 Bond Lengths for compound (9)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O24	C10	1.406(5)	C18	C19	1.394(8)
O24	C25	1.444(5)	O48	C45	1.395(5)
O22	C10	1.404(4)	O48	C49	1.431(5)
O22	C23	1.443(6)	O46	C45	1.413(5)
C11	C6	1.401(6)	O46	C47	1.426(7)
C11	C12	1.413(6)	C27	C45	1.513(8)
C11	C10	1.526(6)	C27	C28	1.453(10)
C2	C3	1.366(6)	C27	C41	1.398(8)
C2	C1	1.355(6)	C30	C31	1.351(7)
C13	C14	1.442(6)	C30	C29	1.414(8)
C13	C12	1.491(6)	C30	C35	1.489(8)
C13	C1	1.394(6)	C45	C44	1.556(8)
O26	C9	1.218(6)	C31	C32	1.406(8)
C6	C7	1.451(7)	C29	C28	1.487(9)
C6	C5	1.400(7)	C29	C37	1.487(11)
C14	C15	1.415(6)	C28	C39	1.580(11)
C14	C19	1.437(6)	C44	O50	1.252(9)
C3	C12	1.411(6)	C44	C43	1.507(13)
C3	C4	1.364(7)	C39	C38	1.252(14)
C10	C9	1.562(6)	C39	C40	1.99(2)
C7	C8	1.326(8)	C35	C36	1.917(17)
C4	C5	1.367(8)	C35	C34	1.410(11)
C15	C16	1.346(7)	C38	C37	1.327(12)
C21	C1	1.396(7)	C33	C32	1.370(10)

C21	C20	1.341(8)	C33	C34	1.292(11)
C9	C8	1.450(8)	C36	C37	1.700(18)
C17	C16	1.386(8)	C40	C41	1.787(18)
C17	C18	1.379(8)	C41	C42	1.375(16)
C20	C19	1.402(7)	C42	C43	1.310(15)

Table 9 Bond Angles for compound (9)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O24	C25	114.6 (3)	C4	C5	C6	121.3 (4)
C10	O22	C23	118.5 (3)	C45	O48	C49	113.9 (3)
C6	C11	C12	119.3 (4)	C45	O46	C47	117.6 (4)
C6	C11	C10	117.4 (4)	C28	C27	C45	123.9 (4)
C12	C11	C10	123.3 (3)	C41	C27	C45	118.7 (7)
C1	C2	C3	106.5 (3)	C41	C27	C28	117.4 (7)
C14	C13	C12	138.9 (3)	C31	C30	C29	126.4 (5)
C1	C13	C14	116.6 (4)	C31	C30	C35	115.5 (5)
C1	C13	C12	104.3 (4)	C29	C30	C35	117.9 (5)
C11	C6	C7	121.3 (4)	O48	C45	O46	108.7 (4)
C5	C6	C11	121.0 (4)	O48	C45	C27	111.3 (4)
C5	C6	C7	117.6 (4)	O48	C45	C44	109.2 (4)
C15	C14	C13	126.0 (4)	O46	C45	C27	104.5 (4)
C15	C14	C19	116.6 (4)	O46	C45	C44	105.6 (4)
C19	C14	C13	117.2 (4)	C27	C45	C44	117.1 (5)
C2	C3	C12	111.9 (4)	C30	C31	C32	122.9 (5)
C4	C3	C2	121.3 (4)	C30	C29	C28	139.8 (4)
C4	C3	C12	126.8 (5)	C30	C29	C37	113.8 (6)
C11	C12	C13	141.0 (4)	C37	C29	C28	106.2 (6)
C3	C12	C11	115.0 (4)	C27	C28	C29	139.4 (4)
C3	C12	C13	104.0 (3)	C27	C28	C39	121.1 (7)
O24	C10	C11	112.4 (3)	C29	C28	C39	99.5 (7)
O24	C10	C9	108.8 (3)	O50	C44	C45	117.5 (5)
O22	C10	O24	109.3 (3)	O50	C44	C43	128.4 (7)
O22	C10	C11	104.9 (3)	C43	C44	C45	114.1 (7)
O22	C10	C9	106.0 (3)	C28	C39	C40	93.4 (9)
C11	C10	C9	115.0 (4)	C38	C39	C28	110.7 (8)
C8	C7	C6	124.2 (4)	C38	C39	C40	155.9 (8)
C3	C4	C5	116.2 (5)	C30	C35	C36	101.3 (6)
C16	C15	C14	121.4 (4)	C34	C35	C30	117.9 (6)
C20	C21	C1	117.5 (5)	C34	C35	C36	140.5 (7)
O26	C9	C10	119.2 (4)	C39	C38	C37	114.6 (7)
O26	C9	C8	123.9 (4)	C34	C33	C32	120.9 (7)
C8	C9	C10	116.7 (4)	C33	C32	C31	119.7 (7)
C18	C17	C16	117.4 (5)	C37	C36	C35	97.1 (4)
C7	C8	C9	119.6 (4)	C33	C34	C35	122.9 (6)
C2	C1	C13	113.0 (4)	C41	C40	C39	101.0 (4)
C2	C1	C21	121.8 (4)	C29	C37	C36	109.5 (7)

C13	C1	C21	125.2 (5)	C38	C37	C29	108.7 (9)
C21	C20	C19	122.0 (4)	C38	C37	C36	141.8 (9)
C15	C16	C17	122.8 (5)	C27	C41	C40	106.7 (9)
C17	C18	C19	122.4 (5)	C42	C41	C27	120.0 (9)
C20	C19	C14	121.0 (4)	C42	C41	C40	133.3 (8)
C18	C19	C14	119.2 (4)	C43	C42	C41	128.0 (8)
C18	C19	C20	119.7 (4)	C42	C43	C44	119.7 (8)

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