SUPPORTING INFORMATION

Contents:

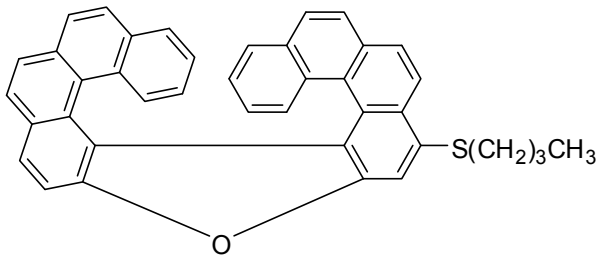
1. General Experimental Details

Analytical grade solvents and commercially available reagents were used without further purification. The flash column chromatography was carried out over silica gel (40-50 μm), purchased from Kanto Chemical Co., Inc. Purification was performed by a recycling preparative HPLC (Japan Analytical Industry Co, Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC, using $CHCl_3$ as an eluent). Melting points were determined on a Yanagimoto melting point apparatus and uncorrected. IR spectra was recorded on a JASCO IR-450, samples were prepared as KBr plates. ^{1}H NMR and ^{13}C NMR spectra were recorded at VARAIN NMR system using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. Mass spectra were measured with JEOL JMS-AX500. High resolution mass spectral (HRMS) analyze were also measured on an Agilent JEOL JMS-AX500 using EI techniques.

Typical Procedure for the synthesis of 9- thiobutoxy-11-oxa[9]helicene (2a)

Typical procedure: The helical quinone **1** (24.5 mg, 0.05 mmol) was added with butylthiol (3 eq) in chloroform (1 mL) in presence of concentrated HCl (4 eq) at room temperature for 0.5 h. The mixture was neutralized by 5% NaOH, washed with brine solution and extracted with chloroform (3 × 10 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (chloroform) to give 9-thiobutoxy-11-oxa[9]helicene and symmetrical oxa[9]helicene (82%, 1.5:1). They are separated by recrystallization with ethyl acetate.

2. Experimental characterization data for compounds



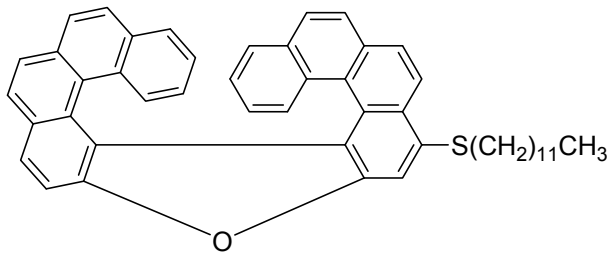
9-thiobutoxy-11-oxa[9]helicene (**2a**)

Yellow solid: Mp: 218-220 ºC. Isolated yield: 44%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.63 (1H, d, *J*= 8.5 Hz), 8.35 (1H, s), 8.28 (1H, d, *J*= 8.5 Hz), 8.23 (1H, d, *J*= 8.0 Hz), 7.98 (1H, d, *J*= 8.0 Hz), 7.62 (1H, d, *J*= 8.5 Hz), 7.59 (1H, d, *J*= 8.5 Hz), 7.58 (1H, d, *J*= 8.0 Hz), 7.54 (1H, d, *J*= 8.5 Hz), 7.40 (1H, d, *J*= 8.5 Hz), 7.38 (1H, d, *J*= 8.5 Hz), 7.33 (1H, d, *J*= 7.5 Hz), 7.28 (1H, d, *J*= 8.0 Hz), 6.79 (1H, t, *J*= 7.5 Hz), 6.74 (1H, t, *J*= 7.0 Hz), 6.22 (1H, d, *J*= 9.0 Hz), 6.18 (1H, d, *J*= 8.0 Hz), 5.75 (1H, t, *J*= 8.0 Hz), 5.72 (1H, t, *J*= 7.0 Hz), 3.19-3.29 (2H, m), 1.79-1.85 (2H, m), 1.55-1.62 (2H, m), 0 .98 (3H, t, *J*=7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 154.04, 153.53, 134.24, 129.94, 129.86, 129.56, 129.52, 129.49, 128.97, 127.59, 127.27, 127.25, 127.19, 126.99, 126.54, 126.51, 126.35, 126.24, 126.05, 125.55, 125.37, 125.33, 125.13, 125.04, 124.63, 124.37, 124.18, 124.15, 124.03, 122.85, 122.31, 122.29, 121, 120.03, 112.24, 110.87, 34.94, 31.21, 22.13, 13.76.

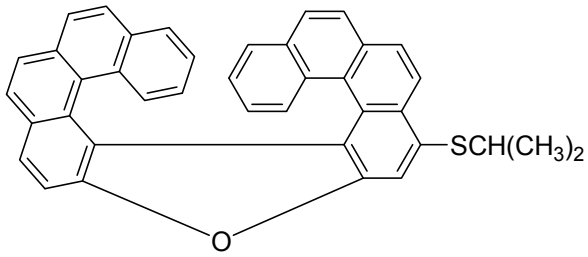
HRMS (EI) calcd for $C_{40}H_{28}OS$ $[M]^+$ 556.1861, found 556.1861.



9-thiododecyloxy-11-oxa[9]helicene (**2b**)

Pale yellow oil. Isolated yield: 32%.
^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.63 (1H, d, *J*= 8.5 Hz), 8.33 (1H, s), 8.24 (1H, d, *J*= 8.5 Hz), 8.20 (1H, d, *J*= 8.5 Hz), 7.95 (1H, d, *J*= 8.0 Hz), 7.60 (1H, d, *J*= 8.5 Hz), 7.55 (2H, d, *J*= 8.5 Hz), 7.51 (1H, d, *J*= 8.5 Hz), 7.37 (1H, d, *J*= 8.5 Hz), 7.34 (1H, d, *J*= 8.5 Hz), 7.30 (1H, d, *J*= 7.5 Hz), 7.25 (1H, d, *J*= 8.0 Hz), 6.77 (1H, t, *J*= 7.0 Hz), 6.71 (1H, t, *J*= 7.0 Hz), 6.21 (1H, d, *J*= 8.5 Hz), 6.18 (1H, d, *J*= 8.5 Hz), 5.74 (1H, t, *J*= 7.5 Hz), 5.72 (1H, t, *J*= 7.5 Hz), 3.25-3.15 (2H, m), 1.80-1.77 (2H, m), 1.56-1.52 (2H, m), 1.33-1.24 (18H, m), 0 .86 (3H, t, *J*=7.0 Hz).

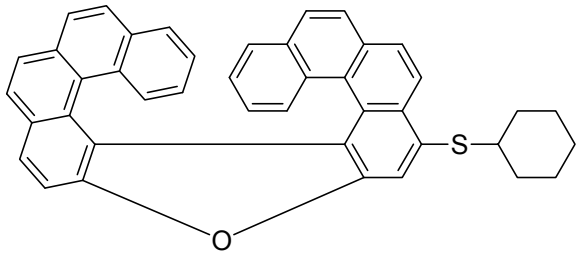
^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 154.04, 153.54, 134.30, 129.94, 129.87, 129.57, 129.53, 129.49, 128.99, 127.57, 127.29, 127.27, 127.18, 126.98, 126.54, 126.50, 126.36, 126.23, 126.06, 125.53, 125.38, 125.33, 125.14, 125.05, 124.62, 124.36, 124.18, 124.13, 124.02, 122.87, 122.31, 122.29, 121, 120.02, 112.23, 110.85, 35.24, 31.89, 29.64, 29.61, 29.59, 29.53, 29.33, 29.24, 29.13, 28.96, 22.67, 14.12.



9-thioisopropoxy-11-oxa[9]helicene (**2c**)

Pale yellow oil. Isolated yield: 50%.
^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.77 (1H, d, *J*= 8.5 Hz), 8.50 (1H, s), 8.29 (1H, d, *J*= 8.5 Hz), 8.24 (1H, d, *J*= 8.5 Hz), 7.98 (1H, d, *J*= 8.0 Hz), 7.63-7.53 (4H, m), 7.41-7.37 (2H, m), 7.33-7.29 (2H, m), 6.79 (1H, t, *J*= 7.0 Hz), 6.73 (1H, t, *J*= 7.0 Hz), 6.19 (1H, d, *J*= 9.0 Hz), 6.17 (1H, d, *J*= 8.5 Hz), 5.72 (1H, t, *J*= 7.0 Hz), 5.72 (1H, t, *J*= 7.0 Hz), 3.67-3.61 (1H, m), 1.47 (3H, d, *J*= 6.5 Hz), 1.37 (3H, d, *J*= 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm):154.29. 153.11, 132.37, 130.54, 129.99, 129.84, 129.57, 129.54, 129.48, 127.93, 127.25, 127.20, 127.03, 126.55, 126.52, 126.31, 126.24, 126.03, 125.65, 125.39, 125.11, 125.05, 124.62, 124.38, 124.25, 124.20, 124.05, 123.88, 122.33, 122.30, 121,21, 120.89, 116.40, 110.92, 40.24, 32.60, 23.05.

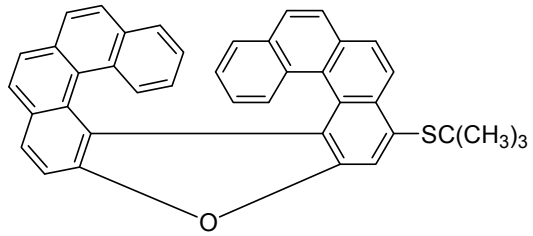


9-thiocyclohexyoxy-11-oxa[9]helicene (**2d**)

Yellow solid: Mp: 227-229 ºC, Isolated yield: 49%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.78 (1H, d, *J*=8.5 Hz), 8.50 (1H, s), 8.29 (1H, d, *J*=8.5 Hz), 8.24 (1H, d, *J*=8.5 Hz), 7.98 (1H, d, *J*=8.0 Hz), 7.63-7.54 (4H, m), 7.41 (1H, d, *J*=8.5 Hz), 7.38 (1H, d, *J*=8.0 Hz), 7.33 (1H, d, *J*=7.5 Hz), 7.28 (1H, d, *J*=8.0 Hz), 6.79 (1H, t, *J*=8.0 Hz), 6.74 (1H, t, *J*=8.0 Hz), 6.19 (1H, d, *J*=9.0 Hz), 6.17 (1H, d, *J*=9.0 Hz), 5.72 (1H, t, *J*=8.0 Hz), 5.71 (1H, t, *J*=8.0 Hz), 3.39-3.33 (1H, m), 2.18-2.14 (2H, m), 2.04-1.98 (2H, m), 1.91-1.77 (4H,m), 1.64-1.59 (2H, m).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 154.28, 153.13, 131.94, 130.65, 130.00, 129.86, 129.59, 129.49, 127.94, 127.28, 127.12, 126.97, 126.61, 126.54, 126.33, 126.23, 126.06, 125.55, 125.33, 125.18, 125.16, 125.07, 124.69, 124.33, 124.18, 124.12, 124.05, 123.93, 122.33, 121.15, 120.93, 116.49, 116.37, 110.89, 48.54, 33.76, 33.34, 26.18, 26.00, 25.81



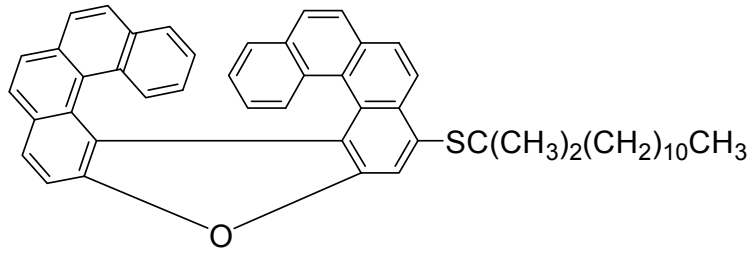
9-*t*-thiobutoxy-11-oxa[9]helicene (**2e**)

Yellow solid: Mp: 278-280 ºC, Isolated yield: 79%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm) : 8.99 (1H, d, *J*= 8.5 Hz), 8.63 (1H, s), 8.32 (1H, d, *J*= 8.5 Hz), 8.27 (1H, d, *J*= 8.5 Hz), 8.00 (1H, d, *J*= 8.5 Hz), 7.62 (1H, d, *J*= 8.5 Hz), 7.60 (1H, d, *J*= 8.0 Hz), 7.55 (1H, d, *J*= 8.5 Hz), 7.42 (1H, d, *J*= 8.5 Hz), 7.39 (1H, d, *J*= 8.0 Hz), 7.34 (1H, d, *J*= 7.5 Hz), 7.29 (1H, d, *J*= 8.0 Hz), 6.79 (1H, t, *J*= 7.5 Hz), 6.74 (1H, t, *J*= 7.0 Hz), 6.18 (1H, d, *J*= 8.5 Hz), 6.16 (1H, d, *J*= 8.5 Hz), 5.72 (1H, t, *J*= 7.0 Hz), 5.68 (1H, t, *J*= 7.0 Hz), 1.45 (9H, s).

^{13} C NMR (125 MHz, $CDCl_3$, δ/ppm) : 154.53, 152.56, 132.78, 130.02, 129.84, 129.75, 129.56, 129.52, 129.44, 128.31, 127.25, 127.22, 127.18, 127.09, 126.55, 126.52, 126.24, 126.11, 125.99, 125.54, 125.45, 125.29, 125.04, 124.9, 124.6, 124.41, 124.32, 124.23, 124.02, 122.32, 122.25, 121.17, 120.77, 110.98, 48.51, 31.37.

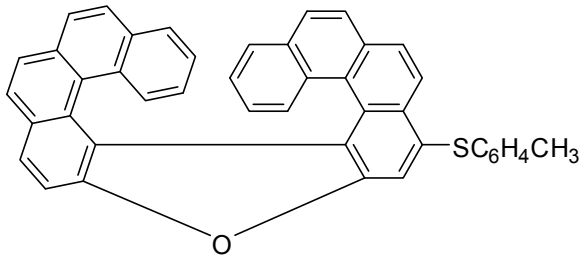
HRMS (EI) calcd for $C_{40}H_{28}OS$ $[M]^+$ 556.1861, found 556.1841.



Pale yellow oil. Isolated yield: 70%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm) : 9.00-8.99 (1H, m), 8.62-8.58 (1H, m), 8.32-8.25 (2H, m), 7.99 (1H, d, *J*= 8.0 Hz), 7.63-7.54 (4H, m), 7.42-7.37 (2H, m), 7.33 (1H, d, *J*= 8.0 Hz), 7.28 (1H, d, *J*= 8.0 Hz), 6.78 (1H, t, *J*= 7.0 Hz), 6.73 (1H, t, *J*= 7.0 Hz), 6.17 (1H, d, *J*= 7.0 Hz), 6.16 (1H, d, *J*= 7.5 Hz), 5.72-5.68 (2H, m), 1.36-0.81 (29H, m).

HRMS (EI) for $C_{50}H_{48}OS$ $[M]^+$ calcd 696.3425, found 696.3427.



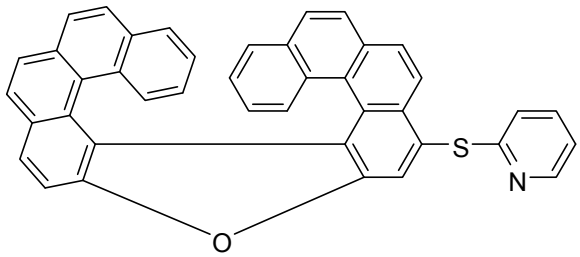
9-*p*-tolylthioxy-11-oxa[9]helicene (**2g**)

Yellow solid: Mp: 268-270 ºC, Isolated yield: 55%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm) : 8.61 (1H, d, *J*= 9.0 Hz), 8.29-8.27 (2H, m), 8.21 (1H, d, *J*= 8.5 Hz), 7.99 (1H, d, *J*= 8.5 Hz), 7.61-7.58 (4H, m), 7.55 (1H, d, *J*= 8.5 Hz), 7.41 (1H, d, *J*= 9.0 Hz), 7.37 (1H, d, *J*= 8.5 Hz), 7.33 (2H, d, *J*= 8.5 Hz), 7.29 (1H, d, *J*= 8.0 Hz), 7.16 (2H, d, *J*= 8.0 Hz), 6.79 (1H, t, *J*= 7.5 Hz), 6.75 (1H, t, *J*= 8.0 Hz), 6.23 (1H, d, *J*= 8.5 Hz), 6.18 (1H, d, *J*= 8.0 Hz), 5.78 (1H, t, *J*= 7.0 Hz), 5.73 (1H, t, *J*= 7.0 Hz), 2.36 (3H, s).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm) : 154.3, 153.44, 137.1, 132.54, 132.41, 130.61, 130.22, 130 , 129.89, 129.58, 129.55, 129.48, 129.1, 127.98, 127.28, 127.23, 127.21, 127.05, 126.59, 126.54, 126.25, 126.02, 125.41, 125.37, 125.1, 124.65, 124.41, 124.21, 124.19, 124.11, 123.14, 122.35, 122.31, 121.14, 120.83, 115.05, 110.89, 21.12.

HRMS (EI) calcd for $C_{43}H_{26}OS$ $[M]^+$ 590.1704, found 590.1707.



9-(2-pyridylthioxy)-11-oxa[9]helicene (**2h**)

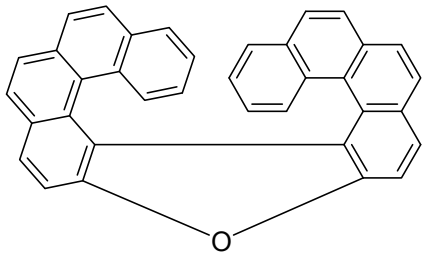
Yellow solid: Mp. 176-177 ºC, Isolated yield: 58%.

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm) : 8.75 (1H, s), 8.64 (1H, d, *J*= 8.5 Hz), 8.48 (1H, bs), 8.35 (1H, d, *J*= 8.5 Hz), 8.28 (1H, d, *J*= 8.5 Hz), 8.02 (1H, d, *J*= 8.5 Hz), 7.57-7.63 (4H, m), 7.43 (1H, d, *J*= 8.5 Hz), 7.29-7.38 (4H, m), 6.98 (1H, bs), 6.79 (1H, t, *J*= 8.0 Hz), 6.77 (1H, t, *J*= 8.0 Hz), 6.57 (1H, bd, *J*= 6.0 Hz), 6.23 (1H, d, *J*= 8.5 Hz), 6.19 (1H, d, *J*= 8.5 Hz), 5.76 (1H, t, *J*= 7.0 Hz), 5.75 (1H, t, *J*= 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm) : 154.81, 152.96, 130.71, 130.12, 129.92, 129.6, 129.53, 128.86, 127.53, 127.2, 127.18, 127.05, 126.84, 126.69, 126.64, 126.47, 126.32, 126.28, 125.95,

125.62, 125.37, 125.3, 125.12, 124.94, 124.7, 124.43, 124.31, 124.28, 124, 123.71, 123.43, 122.5, 122.29, 120.98, 120.52, 119.73, 111.06, 110.92.

HRMS (EI) calcd for $C_{41}H_{23}NOS$ $[M]^+$ 577.1500, found 577.1490.



11-oxa[9]helicene (**3**)

Yellow solid: Mp : 310- 314 ºC

IR (KBr disk) : 3040 (arom.C-H), 1250 (-O-) , 830, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, δ/ppm) : 8.30 (2H, d, *J* =8.5 Hz), 8.27 (2H, d, *J* =8.5 Hz), 8.01 (2H, d, *J* =8.5 Hz), 7.59 (2H, d, *J* =8.0 Hz), 7.57 (2H, d, *J* =8.5 Hz), 7.39 (2H, d, *J* =8.5 Hz), 7.30 (2H, d, *J* =8.0 Hz), 6.76 (2H, t, *J* = 7.5 Hz,), 6.19 (2H, d, *J* = 8.5 Hz,), 5.72 (2H, t, *J* =7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm) : 110.95, 121.02, 122.19, 124.03, 124.33, 124.62 , 125.15, 125.34, 126.20, 126.27, 126.50, 126.93, 127.29, 127.61, 129.45, 129.51, 129.94, 154.22.

HRMS (EI) calcd for $C_{36}H_{20}O$ $[M]^+$ 468.1514, found 468.1504.