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A concise synthesis of functionalized 7-oxa-[5]-helicenes

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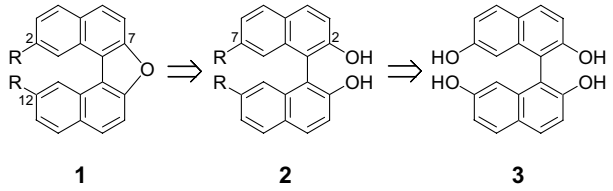
Dedicated to Professor Yodhathai Thebtaranonth on the occasion of his 60th birthday

Abstract—A practical procedure for the preparation of functionalized 7-oxa-[5]-helicenes from 2,7-dihydroxynaphthalene is described.

Although helicenes, conjugated molecules exhibiting a helical nonplanar skeleton, have long been known,[1] it was not until recently that their unique structural and electronic features were revealed, which prompted chemists to explore their potential as candidates for applications in materials and catalytic sciences.[2] Such studies are made possible due to the development of practical large scale syntheses, one of the most revolutionary and highly effective routes being via Katz's Diels–Alder approach.[3]

Reports have shown that the incorporation of heteroatoms such as nitrogen, oxygen or sulfur into the helicene skeleton markedly alters its electronic character, thus resulting in novel properties.[2a] Preparations of heterohelicenes have thus been extensively studied.[4] However, practical multi-gram scale synthesis is still limited. We therefore wish to report here a concise, practical and easily scalable synthesis of 2,12-disubstituted-7-oxa-[5]-helicenes **1**, from commercially available and low cost starting materials.

Scheme 1 depicts the retrosynthetic approach, the key steps in which are (1) the regioselective derivatization at the 7 and 7′-dihydroxy groups of binaphthol **3**, obtained from typical oxidative coupling of 2,7-dihydroxynaphthalene **4**, and (2) the acid catalyzed cyclization of binaphthol **2**.



Scheme 1. Retrosynthetic scheme of 7-oxa-[5]-helicene derivatives.

Thus, as shown in Scheme 2, the reaction of 2,7-dihydroxynaphthalene **4** with $FeCl_3$ in boiling H_2O[5] for 4 h gave 7,7′-dihydroxy-2,2′-binaphthol **3** in 96% yield. Upon treatment with alcohols or thiols in the presence of *p*-TsOH or H_2SO_4 in refluxing toluene, binaphthol **3** was readily and regioselectively converted into 7,7′-dialkoxy- or dialkylthio-2,2′-binaphthol **2** in good yields. Remarkably, under the stated reaction conditions, only the desired disubstituted binaphthol **2** was exclusively formed. Finally the cyclization step was achieved when binaphthol **2** was refluxed in toluene with *p*-TsOH for 12 h.[6] Yields for the regioselective ether/sulfide formation as well as for the cyclization are as reported in Table 1.

The mechanism of the regioselective derivatization of binaphthol **3** can be envisioned as involving the keto tautomer of the phenolic hydroxy group, as shown in Scheme 3.[8] Although both phenolic groups at positions 2 and 7 can tautomerize, preferential reaction with the external nucleophile was observed for the tautomer at position 7, possibly due to less steric congestion. Finally rearomatization upon loss of H_2O yielded, exclusively, the disubstituted binaphthol **2**.

Keywords: Helicene; Substituted binaphthol; Acid catalyzed cyclization; Phenol tautomerization.

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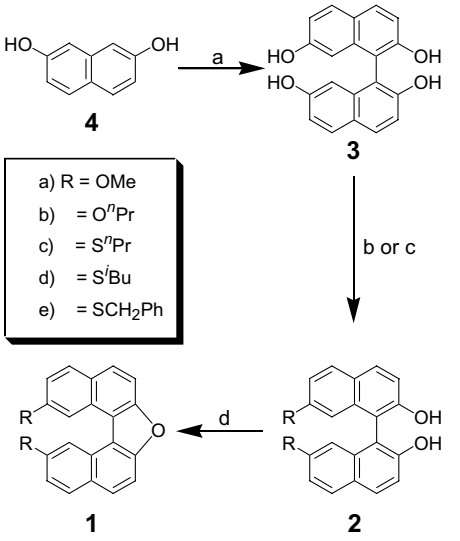
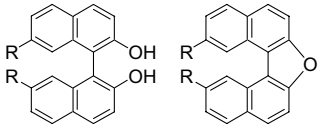


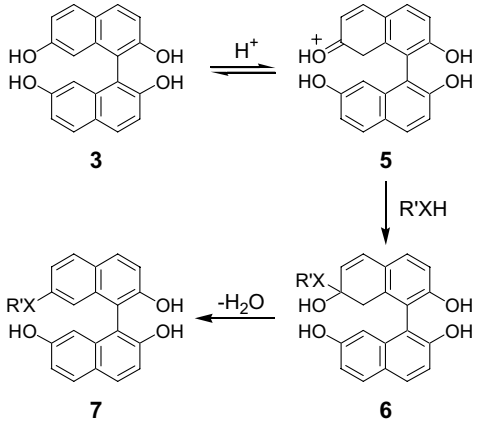
Scheme 2. Reagents and conditions: (a) $FeCl_3$, H_2O, reflux 4 h. (b) R′SH (3 equiv), *p*-TsOH (1 equiv), toluene, reflux, overnight. (c) R′OH (excess), H_2SO_4 (1 equiv), rt, 3 d. (d) *p*-TsOH (1 equiv), toluene, reflux, overnight. Synthesis of 2,12-disubstituted-7-oxa-[5]-helicenes.

Table 1. Yields of the binaphthols **2** and helicenes **1**[7]



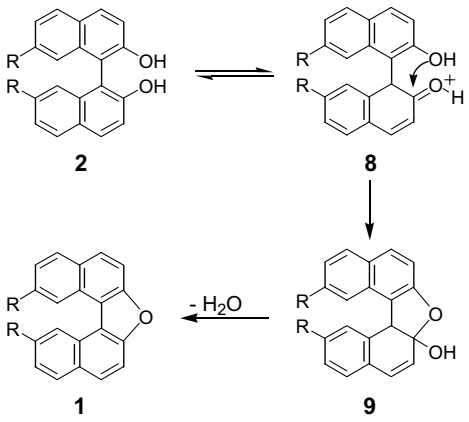
2a-d **1a-d**

Entry	R	**2** (%)	**1** (%)
a	OMe	68	70
b	O^{n}Pr	63	90
c	S^{n}Pr	66	88
d	S^{i}Bu	68	97
e	SCH$_2$Ph	69	71



Scheme 3. Proposed mechanism of the regioselective derivatization.

The cyclization step, likewise, could occur via tautomerization of the remaining phenol followed by an intramolecular nucleophilic addition of the proximal hydroxy group to the keto moiety to provide the 5-membered cyclic hemiacetal **9**, which upon dehydration, would yield the helicene **1** (Scheme 4). Interestingly, the cyclization process required a much longer reaction time, as compared to the ether/sulfide formation. This implies greater difficulty for the cyclization reaction, which could be attributable to the unfavorable entropic requirement of forcing the perpendicular structure of the binaphthol to become more planar.



Scheme 4. Proposed mechanism for the cyclization.

In conclusion, derivatives of 2,12-disubstituted-7-oxa-[5]-helicene were successfully synthesized, starting from 2,7-dihydroxynaphthalene. The procedure reported is straightforward, with all starting materials commercially available at low cost. Most importantly, this method can easily be scaled up and thus is suitable for the preparation of a variety of oxa-helicenes in large quantities.[9]

General procedure

Synthesis of 7,7′-dimethoxy-[1,1′]-binaphthalenyl-2,2′-diol 2a

To a solution of 7,7′-dihydroxy-1,1′-binaphthalenyl-2,2′-diol **3** (1.13 g, 3.55 mmol) in MeOH (30 mL) was added concentrated H_2SO_4 (0.35 mL, 3.55 mmol). The reaction mixture was allowed to gently reflux for 3 days. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. Column chromatography (silica gel; 8:2 hexane–ethyl acetate as eluent) followed by crystallization from ethyl acetate–hexane provided 7,7′-dimethoxy-[1,1′]-binaphthalenyl-2,2-diol **2a** (0.79 g, 68%) as white crystals.

Synthesis of 2,12-dimethoxy-7-oxa-[5]-helicene 1a

7,7′-Dimethoxy-1,1′-binaphthalenyl-2,2-diol **2a** (0.13 g, 0.39 mmol) was refluxed in toluene (20 mL) in the presence of *p*-TsOH (80 mg, 0.39 mmol) for 12 h. After quenching with saturated potassium carbonate solution,

the crude product was extracted with ethyl acetate. Column chromatography purification (silica gel; hexane as eluent) followed by crystallization from dichloromethane–methanol provided 2,12-dimethoxy-7-oxa-[5]-helicene **1a** (90 mg, 70% yield) as a white powder.

Acknowledgements

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References and notes

1. (a) Newman, M. S.; Lutz, W. B.; Lednicer, D. *J. Am. Chem. Soc.* **1955**, *77*, 3420–3421; (b) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770.
2. For some selected examples, see: (a) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. *J. Am. Chem. Soc.* **2001**, *123*, 11899–11907; (b) Katz, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1921–1923; (c) Weix, D. J.; Dreher, S. D.; Katz, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10027–10032; (d) Murguly, E.; McDonald, R.; Branda, N. R. *Org. Lett.* **2000**, *2*, 3169–3172; (e) Verbiest, T.; Van Elshcoht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913–915; (f) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541–9544; (g) Owens, L.; Thilgen, C.; Diederich, F.; Knobler, C. B. *Helv. Chim. Acta* **1993**, *76*, 2757–2774.
3. For selected examples of helicene synthesis based on the Diels–Alder approach, see: (a) Dreher, S. D.; Weix, D. J.; Katz, T. J. *J. Org. Chem.* **1999**, *64*, 3671–3678; (b) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456–7462; (c) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054.
4. (a) Maiorana, S.; Papagni, A.; Licandro, E.; Annunziata, R.; Paravidino, P.; Perdicchia, D.; Giannini, C.; Bencini, M.; Clays, K.; Persoons, A. *Tetrahedron* **2003**, *59*, 6481–6488; (b) Field, J. E.; Hill, T. J.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 6071–6078; (c) Cossu, S.; De Lucchi, O.; Fabbri, D.; Valle, G.; Painter, G. F.; Smith, R. A. J. *Tetrahedron* **1997**, *53*, 6073–6084; (d) Tanaka, K.; Kume, T.; Takimoto, T.; Kitahara, Y.; Suzuki, H.; Osuga, H.; Kawai, Y. *Chem. Lett.* **1997**, 501–502; (e) Arai, S.; Ishikura, M.; Yamagishi, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1561–1567.
5. Vogel, A. I. *Textbook of Practical Organic Chemistry*, 5th ed.; Longman, 1991; pp 1053–1054.
6. (a) Similar transformations have also been achieved by using H_2SO_4 Cui, Y.; Ngo, H. L.; Lin, B. *Inorg. Chem.* **2002**, *41*, 1033–1035; (b) using zeolite Arienti, A.; Bigi, F.; Maggi, R.; Moggi, P.; Rastelli, M.; Sartori, G.; Trere, A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1391–1393.
7. Compound characterization. 7,7′-Dimethoxy-[1,1′]-binaphthalenyl-2,2,-diol **2a**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.54 (s, 6H, OCH_3); 5.12 (s, 2H, OH); 6.46 (d, $J = 2.48$ Hz, 2H, Ar–H); 7.00 (dd, $J = 2.44$, 8.90 Hz, 2H, Ar–H); 7.20 (d, $J = 8.80$ Hz, 2H, Ar–H); 7.44 (d, $J = 8.93$ Hz, 2H, Ar–H); 7.82 (d, $J = 8.85$, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 159.0, 153.3, 134.7, 131.0, 129.9, 124.7, 116.0, 115.1, 110.1, 103.1, 55.1. IR (nujol-mull, ν/cm^{-1}): 3505 (m, O–H st); 2926 (s, C–H st); 1620 (s, Ar C–C st); 1511(s, Ar C–C st); 1459 (s, Ar C–C, st); 1221(m, C–O–C st). MS (EI [70 eV], m/z (%)): 346 (100) [M$^+$]. UV (CH_3CN): λ_{max} nm(ε): 235 (105,188); 300 (7913); 328 (7047). CHN: required for $C_{22}H_{18}O_4$, C 76.29, H 5.24; found, C 76.14, H 5.39. Mp: 144–146 °C. 7,7′-Di-*n*-propoxy-[1,1′]-binaphthalenyl-2,2,-diol **2b**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.81 (t, $J = 7.40$ Hz, 6H, CH_3); 1.58 (m, 4H, CH_2); 3.60 (m, 4H, CH_2); 4.95 (s, 2H, OH); 6.40 (d, $J = 2.44$ Hz, 2H, Ar–H); 6.96 (dd, $J = 2.45$, 8.93 Hz, 2H, Ar–H); 7.13 (d, $J = 8.82$ Hz, 2H, Ar–H); 7.70 (d, $J = 8.88$ Hz, 2H, Ar–H); 7.78 (d, $J = 8.83$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 158.6, 153.2, 134.7, 131.0, 129.9, 124.7, 116.3, 115.0, 110.0, 104.0, 69.2, 22.3, 10.4. IR (KBr, ν/cm^{-1}): 3481 (s, O–H st); 2964 (m, C–H st); 1619 (s, ArC–C st); 1515 (s, ArC–C st); 1218 (s, C–O–C st). MS (EI [70 eV], m/z (%)): 402 (37) [M$^+$]; 360 (15) [{M$-C_3H_6$}$^+$]; 318 (33) [{M$-2C_3H_6$}$^+$]; 300 (25) [{M$-2C_3H_6$, H_2O}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 236 (115,576); 300 (7958); 329 (7266). CHN: required for $C_{26}H_{26}O_4$, C 77.59, H 6.51; found C 77.99, H 6.41. Mp: 143–145 °C. 7,7′-Bis-*n*-propylsulfanyl-[1,1′]-binaphthalenyl-2,2,-diol **2c**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.80 (t, $J = 7.41$ Hz, 6H, CH_3); 1.44 (m, 4H, CH_2); 2.70 (t, $J = 7.43$ Hz, 4H, CH_2); 5.10 (s, 2H, OH); 6.94 (d, $J = 1.73$ Hz, 2H, Ar–H); 7.30 (dd, $J = 1.85$, 8.63 Hz, 2H, Ar–H); 7.32 (d, $J = 8.89$ Hz, 2H, Ar–H); 7.80 (d, $J = 8.63$ Hz, 2H, Ar–H); 7.90 (d, $J = 8.88$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 153.3, 137.0, 133.8, 131.2, 128.7, 127.4, 124.7, 121.4, 117.0, 110.0, 34.5, 22.2, 13.3. IR (nujol-mull, ν/cm^{-1}): 3472 (m, O–H st); 2956 (s, C–H st); 1608 (m, ArC–C st); 1499 (m, ArC–C st); 1181 (m, ArC–O st). MS (EI [70 eV], m/z (%)): 434 (83) [M$^+$]; 392 (51) [{M$-C_3H_6$}$^+$]; 350 (100) [{M$-2C_3H_6$}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 226 (64,686); 259 (92,283); 312 (11,075); 326 (9555); 342 (9000). CHN: required for $C_{26}H_{26}O_2S_2$, C 71.85, H 6.03; found C 72.07, H 5.90. Mp: 104–108 °C. 7,7′-Bis-isobutylsulfanyl-[1,1′]-binaphthalenyl-2,2,-diol **2d**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.74 (d, $J = 6.58$ Hz, 6H, CH_3); 0.84 (d, $J = 6.59$ Hz, 6H, CH_3); 1.60 (m, 2H, CH); 2.50 (m, 4H, CH_2); 5.10 (s, 2H, OH); 6.91 (d, $J = 1.00$ Hz, 2H, Ar–H); 7.28 (dd, $J = 1.81$, 8.50 Hz, 2H, Ar–H); 7.31 (d, $J = 8.68$ Hz, 2H, Ar–H); 7.77 (d, $J = 8.52$ Hz, 2H, Ar–H); 7.90 (d, $J = 8.90$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 153.2, 137.4, 133.8, 131.2, 128.6, 127.2, 124.6, 120.8, 116.8, 109.7, 41.2, 27.8, 21.8. IR (KBr, ν/cm^{-1}): 3500 (s, O–H st); 2956 (s, C–H st); 1610 (s, ArC–C st); 1499 (s, ArC–C st); 1171 (s, ArC–O st). MS (EI [70 eV], m/z (%)): 462 (100) [M$^+$]; 444 (44) [{M$-H_2O$}$^+$] UV (CH_3CN): λ_{max} nm(ε): 226 (65,275); 259 (86,049); 299 (11,510); 312 (114,43); 326 (9713); 342 (9221). CHN: required for $C_{28}H_{30}O_2S_2$, C 72.69, H 6.54; found C 73.23, H 6.34 Mp: 87–88 °C. 7,7′-Bis-benzylsulfanyl-[1,1′]-binaphthalenyl-2,2,-diol **2e**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.90 (s, 4H, CH_2); 5.00 (s, 2H, OH); 6.9–7.1 (m, 12H, Ar–H); 7.32 (m, 4H, Ar–H); 7.80 (d, $J = 8.58$ Hz, 2H, Ar–H); 7.92 (d, $J = 8.87$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 153.3, 136.8, 136.6, 133.7, 131.2, 128.42 128.3, 127.5, 127.0, 124.9, 121.6, 117.2, 109.8, 37.6. IR (KBr, ν/cm^{-1}): 3474 (s, O–H st); 3058 (w, ArC–H, st); 1610 (s, ArC–C st); 1499 (s, ArC–C st); 1172 (s, ArC–O st). MS (EI [70 eV], m/z (%)): 530 (37) [M$^+$]; 439 (32) [{M$-PhCH_2$}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 226 (58,253); 259 (70 323); 326 (8750); 342 (8398).

CHN: required for $C_{34}H_{26}S_2O_2$, C 76.95, H 4.94; found C 77.05, H 4.99. Mp: 122–125 °C. 2,12-Dimethoxy-7-oxa-[5]-helicene **1a**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.69 (s, 6H, OCH_3); 7.16 (dd, $J = 2.36$, 8.93 Hz, 2H, Ar–H); 7.60 (d, $J = 8.66$ Hz, 2H, Ar–H); 7.80 (d, $J = 8.84$ Hz, 2H, Ar–H); 7.90 (d, $J = 8.93$ Hz, 2H, Ar–H); 8.41 (d, $J = 2.31$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 158.0, 154.8, 130.9, 129.8, 127.8, 126.3, 118.7, 115.0, 110.3, 107.2, 55.7. IR (nujol-mull, ν/cm^{-1}): 2925 (s, C–H st); 1625 (m, ArC–C st); 1524 (w, ArC–C st); 1468 (m, ArC–C, st); 1230 (m, C–O–C st). MS (EI [70 eV], m/z (%)): 328 (100) [M$^+$]; 313 (7) [{M−CH_3}$^+$]; 298 (23) [{M−CH_2O}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 212 (74,192); 247 (56,817); 316 (14,158); 351 (22,665); 336 (23,194). CHN: required for $C_{22}H_{16}O_3$, C 80.47, H 4.91; found C 80.23, H 4.98. Mp: 160–165 °C. 2,12-Dipropoxy-7-oxa-[5]-helicene **1b**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.10 (t, $J = 7.45$ Hz, 6H, CH_3); 1.90 (m, 4H, CH_2); 4.10 (t, $J = 6.40$ Hz, 4H, CH_2); 7.18 (dd, $J = 2.43$, 8.84 Hz, 2H, Ar–H); 7.58 (d, $J = 9.06$ Hz, 2H, Ar–H); 7.76 (d, $J = 8.84$ Hz, 2H, Ar–H); 7.88 (d, $J = 9.00$ Hz, 2H, Ar–H); 8.44 (d, $J = 1.87$ Hz, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 157.5, 154.8, 130.8, 129.9, 127.8, 126.2, 118.7, 115.3, 110.1, 108.0, 69.9, 22.8, 10.7. IR (KBr,ν/cm^{-1}): 2925 (m, C–H st); 1628 (m, ArC–C st); 1231 (s, C–O–C st). MS (EI [70 eV], m/z (%)): 384 (100) [M$^+$]; 342 (28) [{M−C_3H_6}$^+$]; 300 (72) [{M−$2C_3H_6$}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 212 (65,441); 247 (48,230); 353 (19,744). CHN: required for $C_{26}H_{24}O_3$, C 81.82, H 6.29; found C 81.51, H 6.14. Mp: 96–99 °C. 2,12-Bis-propylsulfanyl-7-oxa-[5]-helicene **1c**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.10 (t, $J = 7.35$ Hz, 6H, CH_3); 1.80 (m, 4H, CH_2); 3.25 (t, $J = 7.16$ Hz, 4H, CH_2); 7.54 (d, $J = 8.55$ Hz, 2H, Ar–H); 7.71 (d, $J = 8.87$ Hz, 2H, Ar–H); 7.91 (d, $J = 8.87$ Hz, 2H, Ar–H); 7.96 (d, $J = 8.56$ Hz, 2H, Ar–H); 9.02 (s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 154.8, 136.0, 129.7, 129.1, 129.0, 128.1, 125.2, 124.0, 118.5, 112.0, 35.6, 22.4, 13.5. IR (nujol-mull, ν/cm^{-1}): 2925 (s, C–H st); 1611 (m, ArC–C st); 1235 (m, C–O–C st). MS (EI [70 eV], m/z (%)): 416 (100) [M$^+$]; 374 (33) [{M−C_3H_6}$^+$]; 332 (39) [{M−$2C_3H_6$}$^+$] UV (CH_3CN): λ_{max} nm(ε): 206 (57,056); 264 (55,652); 297 (20,120); 337 (13,487); 352 (22,606); 369 (22,053). CHN: required for $C_{26}H_{24}S_2O$, C 74.96, H 5.81; found C 74.70, H 6.25. Mp: 105–106 °C. 2,12-Bis-isobutylsulfanyl-7-oxa-[5]-helicene **1d**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.00 (d, $J = 6.67$ Hz, 12H, CH_3); 1.90 (m, 2H, CH); 3.02 (d, $J = 6.66$ Hz, 4H, CH_2); 7.44 (d, $J = 8.80$ Hz, 2H, Ar–H); 7.67 (d, $J = 8.80$ Hz, 2H, Ar–H); 7.80 (d, $J = 8.80$ Hz, 2H, Ar–H); 7.87 (d, $J = 8.55$ Hz, 2H, Ar–H); 8.90 (s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 154.8, 136.4, 129.7, 129.0, 129.0, 128.0, 125.2, 123.7, 118.4, 111.9, 64.3, 42.3, 28.3, 22.1. IR (KBr, ν/cm^{-1}): 2957 (s, C–H st); 1610 (m, ArC–C st); 1501 (w, ArC–C st); 1234 (s, C–O–C st). MS (EI [70 eV], m/z (%)): 444 (100) [M$^+$]; 388 (15) [{M−^{i}-C_4H_9}$^+$]; 332 (52) [{M−2^i-C_4H_9}$^+$]. UV (CH_3CN): λ_{max} nm(ε): 206 (58,508); 264 (56,424); 297 (20,646); 337 (13,684); 352 (22,398); 369 (21,387). CHN: required for $C_{28}H_{28}S_2O$, C 75.63, H 6.35; found C 75.28, H 6.36. Mp: 88–90 °C. 2,12-Bis-benzylsulfanyl-7-oxa-[5]-helicene **1e**. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 4.31 (s, 4H, $2CH_2$); 7.13 (m, 6H, Ar–H); 7.24 (m, 4H, Ar–H); 7.38 (d, $J = 8.62$ Hz, 2H, Ar–H); 7.66 (d, $J = 8.45$ Hz, 2H, Ar–H); 7.78 (d, $J = 8.69$ Hz, 2H, Ar–H); 7.84 (d, $J = 8.68$ Hz, 2H, Ar–H); 8.95 (s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 154.8, 136.7, 135.6, 129.8, 129.3, 129.1, 128.9, 128.5, 128.1, 127.2, 125.3, 124.4, 118.6, 112.3, 38.7. IR (KBr, ν/cm^{-1}): 3450 (m, ArC–H st); 2923 (w, C–H st); 1608 (m, ArC–C st); 1234 (m, C–O–C st). MS (EI [70 eV], m/z (%)): 512 (100) [M$^+$]; 421 (82) [{M−$PhCH_2$}$^+$]; 388 (66) [{M−$PhCH_2SH$}$^+$]. UV (Cyclohexane): λ_{max} nm(ε): 266 (72,852); 299 (28,588); 323 (13,059); 339 (18,114); 354 (29,837); 372 (29,600). CHN: required for $C_{34}H_{24}S_2O$ C 79.65 H 4.72; found C 79.84, H 4.82. Mp: 179–184 °C.

8. Charoonniyomporn, P.; Thongpanchang, T.; Wittayakran, S.; Thebtaranonth, Y.; Phillips, K. E. S.; Katz, T. J. *Tetrahedron Lett.* **2004**, *45*, 457–459.
9. For example, 7.47 g of helicene **1d** could be prepared in a single run.