A Novel Strategy for the Synthesis of Molecules with Helical Chirality. Intramolecular [2 + 2 + 2] Cycloisomerization of Triynes under Cobalt Catalysis†

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A straightforward synthetic approach to a new class of molecules with helical chirality has been developed involving an intramolecular [2 + 2 + 2] cycloisomerization of triynes under $CpCo(CO)_2$/PPh_3 catalysis. The cyclization reaction is promoted by visible light irradiation. Starting from 1,2-diarylacetylenes with two terminal or methyl-substituted tethered acetylene moieties (**1a**,**b**, **4**, **5**, and **7**), the target products (**8a**,**b**, **11**, **12**, and **14**) are obtained in 64−89% yield. The triynes bearing terminal trimethylsilyl groups (**1c**, **2**, and **3**) are less reactive and afford the products (**8c**, **9a**,**b**, and **10**) in 23−71% yield. The ability of the trimethylsilylated derivatives to cycloisomerize strongly depends on the tether length. The cyclized products (**8**−**14**) with five, six, and seven ortho-fused rings structurally resemble classical helicenes. Several representatives (**8b**, **11**, **12**, and **14**) have been resolved into enantiomers by HPLC on a chiral column. Thus, the methodology exhibits a considerable versatility and allows the preparation of a variety of helical objects.

Introduction

Helicenes, the most common representatives of small helical molecules,[1,2] are envisaged to play an important role as chiral building or functional entities in various branches of chemistry. However, only a few achievements in the application of helicenes, e.g., to stoichiometric asymmetric synthesis,[3] enantioselective catalysis,[4] chiral recognition,[7] and development of advanced material prototypes,[8] have been so far reported.

One of the reasons for the limited progress rests in difficult and laborious large-scale synthesis of helicenes by the classical method, i.e., via the intramolecular photocyclization of stilbene-type precursors.[9] Reflecting serious drawbacks of such a process,[10] several novel nonphotochemical strategies[11] have emerged recently as, namely, the elegant Diels−Alder approach[12] or the biaryl coupling methodology.[13]

Searching alternative synthetic routes toward small helical molecules, we have devised a novel strategy that is based on intramolecular [2 + 2 + 2] cycloisomerization of triynes. The proposed reaction scheme follows the well-known Vollhardt approach to the synthesis of planar achiral angular[n]phenylenes.[14] In contrast to the Vollhardt synthesis, incorporation of appropriate two- or three-atom linkers connecting an 1,2-bisarylacetylene central unit with tethered alkynes should result in formation of helical molecules (Scheme 1).

Results and Discussion

We report herein a novel synthetic approach to helical skeletons based on intramolecular [2 + 2 + 2] cycloisomerization of triynes[15] mediated by cobalt complexes. Exploiting the original Vollhardt protocol[16] in the initial experiment, triyne **1b**[17] was cyclized to **8b** in 41% yield and, under irradiation with a halogen lamp, in 47% yield (Table 1, entries 1 and 2). Hence, the reaction of **1b** demonstrated that the proposed synthetic methodology is feasible.

Tuning Reaction Conditions. Increased reaction temperature (120 °C, isooctane displaced by *n*-decane)

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Scheme 1

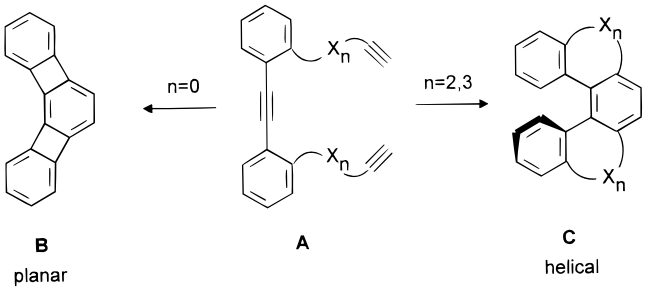
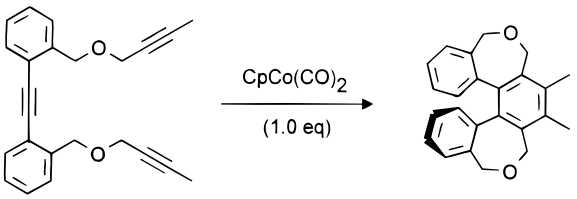


Table 1. Optimization of [2 + 2 + 2] Cycloisomerization[a,b]



entry	ligand (equiv)	solvent	time (h)	T (°C)	yield[c] (%)
1		isooctane	3.5[d]	99	41[e]
2		isooctane	3.5	99	47[e]
3		decane	1	120	64
4		chlorobenzene	0.5	120	48
5	CO [f]	decane	4	120	16
6	$P[OCH(CF_3)_2]_3$ (2)	decane	4	120	31
7	PPh_3 (2)	decane	2	120	70[e]
8	PPh_3 (2)	decane	1[g]	140	74[e]

[a] Only one enantiomer is shown. [b] Reaction performed under irradiation with a 250 W halogen lamp. [c] Calculated from GC analysis of the reaction mixture with *n*-nonadecane as internal standard. [d] Not irradiated. [e] Isolated. [f] Under 1 atm pressure. [g] Co/PPh_3 added in two portions within a 0.5 h period.

with a concomitant halogen lamp irradiation markedly promoted the formation of the target product **8b** and shortened the reaction period (64% yield; Table 1, entry 3). With varying solvents under otherwise identical conditions, the cyclization in chlorobenzene gave rise to the product **8b** in a still satisfactory yield (48%; Table 1, entry 4), but the use of coordinating solvents resulted in low yields (in diglyme, anisole, and amyl acetate) or cobalt complex decomposition (in benzonitrile, DMF, or in refluxing pyridine, *i*-$PrNO_2$, *n*-BuOH, and acetic acid).

In all runs, regardless of the yields, we observed a rapidly decreasing conversion rate. Thus, the moderate yields might be attributed to a gradual decomposition of $CpCo(CO)_2$ and the consequent loss of the reaction substrate due to concurrent polymerization. Therefore, we applied various ligands to increase the lifetime of an active cobalt complex. While carbon monooxide or $P[OCH(CF_3)_2]_3$ as strong π-acceptors[18] dramatically retarded the reaction and lowered conversion of the starting triyne **1b** (Table 1, entries 5 and 6), the use of PPh_3 led to improved yield of the cyclized product **8b** (Table 1, entry 7).

Although the role of PPh_3 in the cyclotrimerization mechanism is not entirely clear, the in situ formation of $CpCo(PPh_3)L$ and/or $CpCo(PPh_3)_2$ may be proposed to prevent rapid decomposition of short-lived partially or completely decarbonylated cobalt species as CpCo(CO) and CpCo, respectively, prior to entering the cycloisomerization process. Such phosphine cobalt complexes are assumed to be sufficiently labile to allow a ligand exchange between PPh_3 and alkyne moieties of triyne **1b** and to generate a CpCo complex with two coordinated alkynes, a precursor for the key cobaltacyclopentadiene intermediate.[16,19]

Finally, under the optimized conditions (1 equiv of $CpCo(CO)_2$, 1−2 equiv of PPh_3, *n*-decane, 140 °C, irradiation with a halogen lamp), the pentacyclic product **8b** could be obtained in 74% yield (Table 1, entry 8).

Triyne Variation. Encouraged by these results, we turned our attention to other substrates.[17] Upon treatment with $CpCo(CO)_2/PPh_3$ in *n*-decane and simultaneous irradiation at 140 °C, triynes with terminal or methyl-substituted acetylene moieties such as **1a**,**b**, **4**, **5**, and **7** afforded cleanly the products **8a**,**b**, **11**, **12**, and **14** in 64−89% yield (Table 2, entries 1−3, 7−10, and 12).

In a contrast, triyne **1c** with terminal trimethylsilyl groups reacted less readily and gave the product **8c** in low yield (23%; Table 2, entry 4). Steric hindrance apparently disallowed the completion of the stepwise process, and a cobalt complex arising from the starting material and the CpCo species was therefore isolated[20] along with the desired cyclized product. However, the reaction ability of triynes bearing bulky trimethylsilyl terminal substituents can be effectively controlled by the length of tethers. Shortening one three-atom linker to a two-atom one, triyne (±)-**2** underwent the cyclization reaction more smoothly than the derivative **1c** to afford a 7:3 mixture of diastereomers (M*,7*R**)-**9a** and (M*,7*S**)-**9b** in 37% yield (Table 2, entry 5). At last, the presence of only two-atom tethers in bis(trimethylsilyl)triyne **3** led to its markedly enhanced reactivity, and the cyclized product **10** was isolated in 71% yield (Table 2, entry 6). In both of the last cases, the [2 + 2 + 2] cycloisomerization of trimethylsilyl-substituted triynes (±)-**2** and **3** was accompanied by a cobalt complex formation.[20]

Reaction of the *p*-tosylamide derivative **6** gave only a very low yield of **13** (10%; Table 2, entry 11).

Catalysis and Reaction Scale. The [2 + 2 + 2] cycloisomerization of alkynes has been reported to be catalytic in cobalt.[16] In accordance with this fact, the triynes **1a**,**b** and **3**−**5** underwent the cyclization on treatment with only catalytic amount of $CpCo(CO)_2$ (40 mol %) to form the products **8a**,**b** and **10**−**12** (Table 2, entries 1, 2, 6, 7, and 9). Moreover, the reaction in the presence of a *substoichiometric* (method A, Table 2) as well as *stoichiometric* (method B, Table 2) amount of the cobalt complex provided similarly high yields (Table 2, cf. entries 2 and 3, 7 and 8).

The results presented in Table 2 were obtained performing the cycloisomerization on a scale of 0.2−0.5 mmol, i.e., with ca. 100 mg of triyne. To demonstrate the applicability of the [2 + 2 + 2] triyne cyclization methodology to a practically useful synthesis of helical molecules, a model experiment was scaled up. Starting from 2 g (5.8 mmol) of triyne **1b** and reducing further the amount of the $CpCo(CO)_2$ catalyst (to 20 mol %) and

(17) Triynes **1**−**7** are readily accessible by an acetylene−aryl halide coupling methodology. Manuscript in preparation.

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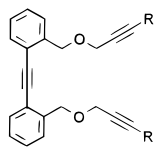
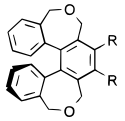
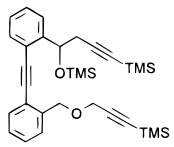
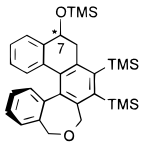
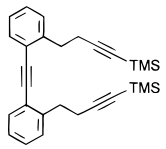
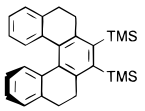
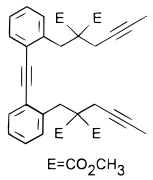
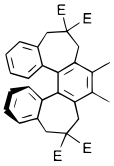
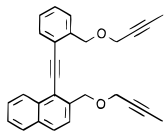
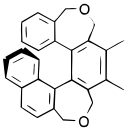
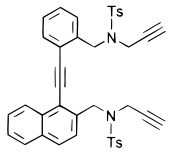
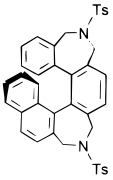
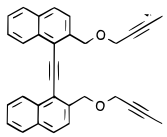
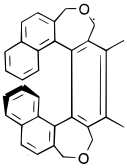
(20) The structure of cobalt complexes is under study.

Table 2. Results of [2 + 2 + 2] Cycloisomerization[a]

entry	substrate	cond.[b]	time (h)	product	yield (%)[c]
1					
	1a (R=H)	A	0.5	**8a** (R=H)	89
2	**1b** ($R=CH_3$)	A	1.5	**8b** ($R=CH_3$)	70
3	**1b**	B	1	**8b**	74
4	**1c** (R=TMS)	B	5.5	**8c** (R=TMS)	23[d]
5					
	(±)-**2**	B	4	($M^{\cdot}$,7R$^{\cdot}$)-**9a**+($M^{\cdot}$,7S$^{\cdot}$)-**9b** (7:3)[e]	37[d]
6					
	3	A	2.5	**10**	71[d]
7					
	4	A	1	**11**	72
8	**4**	B	1.3	**11**	83
9					
	5	A	2	**12**	80
10	**5**	B	2	**12**	71
11					
	6	B	3	**13**	10
12					
	7	B	3	**14**	64[d]

[a] Only one enantiomer is shown. [b] A, $CpCo(CO)_2$ (40 mol %), PPh_3 (80 mol %), decane, 140 °C, irradiation with a 250 W halogen lamp; B, $CpCo(CO)_2$ (1.0 equiv), PPh_3 (2.0 equiv), for further conditions see method A. In all runs, the catalyst/ligand was added in two portions within a 0.5 h period. [c] Isolated. [d] A complex arising from the starting material and the CpCo fragment was also detected. [e] Calculated from ^{1}H NMR integration.

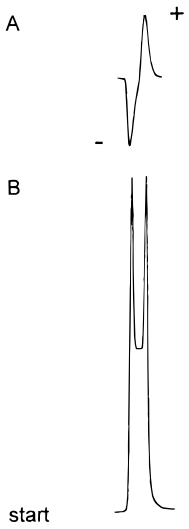


Figure 1. Resolution of **8b** into enantiomers by chiral HPLC on a (*R*,*R*)-Whelk-O1 column (250 mm × 4 mm, *n*-heptane−2-propanol 90:10, 1.6 mL/min, 27.2 °C). Key: A, polarimetric detector recording; B, UV detector recording. (−)-**8b**: 3.67 min. (+)-**8b**: 4.50 min.

PPh_3 (to 40 mol %), the reaction in *n*-decane (100 mL) under concomitant irradiation at 140 °C for 4 h afforded 1.36 g (68% yield)[21] of the target product **8b** (cf Table 2, entry 2).

Helical Arrangement. The compounds **8**−**14** have been assumed to possess a helical arrangement and to exist in the form of racemates. Therefore, we attempted to resolve the cyclized products into enantiomers. The use of chiral HPLC on a brush-type column (R,R)-Whelk-O1 enabled us to separate the racemic penta-, hexa-, and heptacyclic homologues **8b**, **12**, and **14** as well as the malonic acid derivative **11** on an analytical scale[22] (see, e.g., Figure 1).

In addition, semiempirical AM1 calculations[23] showed that the lowest-energy conformer of the heptacyclic product **14**, a typical representative of the newly synthesized helices, adopts the screwed primary structure of C_2 symmetry. The comparison of **14** with the analogous [7]helicene **15**[1] demonstrates their close structural resemblance (Figure 2).

Conclusions

In summary, we have developed a versatile methodology for the synthesis of a new class of molecules with helical chirality, which may find application to enantioselective catalysis and material science.

Experimental Section

General Procedure. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were measured at 500 or 200 MHz and ^{13}C NMR

(21) At the end of the cycloisomerization reaction, a substantial part of triphenylphosphine is bound in the form of insoluble cobalt complexes. Therefore, separation of a cyclized product from the rest of triphenylphosphine by means of flash chromatography on silica gel makes no problem. In addition, the lipophilic triphenylphosphine differs sufficiently in polarity from the products **8**−**14**.

(22) Computational as well as experimental estimation of racemization barriers for selected representatives of compounds **8**−**14** will be published separately.

(23) Molecular construction and energy minimization were made using the *Quantum CAChe for Windows 3.0* package: Oxford Molecular Group, Inc., 2105 South Bascom Ave., Suite 200, Campbell, CA 95008.

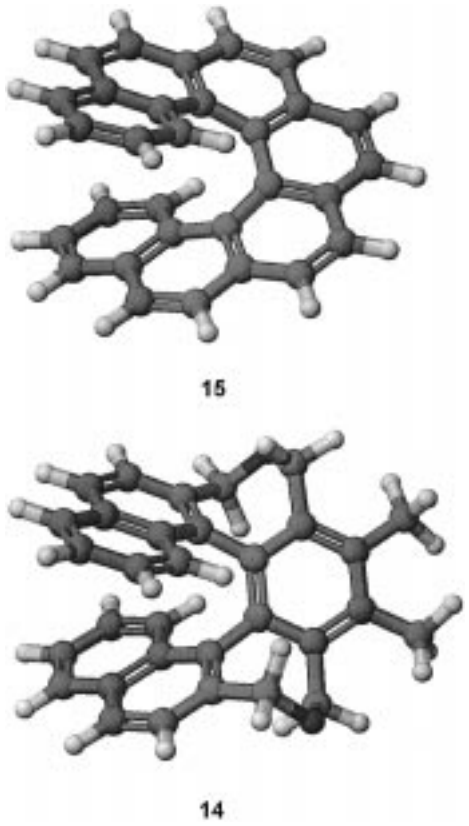


Figure 2. AM1 simulation of the lowest-energy conformers of [7]helicene **15** and its heptacyclic analogue **14**.

spectra at 125 MHz, in $CDCl_3$ with TMS as an internal standard or in acetone-d_6 (referenced relative to acetone). IR spectra were measured in CCl_4 or $CHCl_3$. EI MS spectra were determined at an ionizing voltage of 70 eV. HR MS spectra were obtained using the EI technique. All reactions were performed in Schlenk or double-necked flasks equipped with rubber septa and connected via rubber tubings to a standard vacuum/argon line. Irradiation of a reaction mixture (if indicated) was performed with a 250 W halogen lamp (Halo Star 64480, Osram, or KANDOlite JDD E27) placed outside the reaction vessel (if necessary, more lamps were used to achieve the desired reaction temperature). Solvents (isooctane, *n*-decane, and chlorobenzene) were distilled from calcium hydride under argon and degassed by three freeze−pump−thaw cycles before use. All chemicals were reagent-grade materials. $CpCo(CO)_2$ (Aldrich) was used as received. The starting triynes **1**−**7** were synthesized in our laboratory.[17] TLC was performed on silica gel 60 F_{254}-coated aluminum sheets (Merck), and spots were detected by ceric sulfate/phosphomolybdic acid/sulfuric acid solution. Flash chromatography was performed using Silpearl silica gel (Kavalier Votice, Czech Republic) or silica gel 60 (0.040−0.063 mm or <0.063 mm, Merck). Purification of selected products was accomplished by semipreparative HPLC on a silica gel column (Partisil M9, Whatman 10/50, 500 mm × 10 mm), and sample injections were repeated on a 10−20 mg scale. GLC analyses were performed on a wide-bore column (HP-17, 0.53 mm × 2.0 mm × 10 m, carrier gas hydrogen, flame ionization detector).

General Procedure for Cobalt-Catalyzed [2 + 2 + 2] Cycloisomerization of 1−7. Method A. Triyne **1**−**6** (0.20 mmol) and PPh_3 (0.08 mmol, 40 mol %) under argon were dissolved in *n*-decane (3−6 mL) at 140 °C. $CpCo(CO)_2$ (0.04 mmol, 20 mol %) was added via syringe, and the reaction mixture was irradiated from the bottom with a 250 W halogen lamp under stirring while the temperature was maintained at 140 °C (measured inside the mixture) for 0.5 h. A second portion of PPh_3 (0.08 mmol, 40 mol %) in *n*-decane (1 mL) and $CpCo(CO)_2$ (0.04 mmol, 20 mol %) was added, and the irradiation at 140 °C was prolonged for additional 0.5−5 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and directly flash chromatographed on a silica gel column. The product was eluted with a mixture of petroleum ether−ether−acetone (80:10:10 for **8a** and **12**, 85:5:10 for **8b**, 100:0:0 to 98:2:0 for **10**, 60:30:10 for **11**).

Method B. This method differs from method A in the amount of PPh_3 (0.4 mmol, 200 mol %, in two portions) and $CpCo(CO)_2$ (0.2 mmol, 100 mol %, in two portions) used. The product was eluted with a mixture of petroleum ether−ether−acetone (90:10:0 for **8c**, 95:5:0 for **9a** and **9b**, 50:30:20 for **13**, 80:10:10 for **14**). Analytical samples of **8c** and **13** were further purified via semipreparative HPLC using a petroleum ether−acetone mobile phase (99:1 for **8c**, 80:20 for **13**).

Resolution of 8b, 11, 12, and 14 into Enantiomers. Racemic **8b**, **11**, **12**, and **14** were resolved into enantiomers on an analytical scale by chiral HPLC on a brush-type column ((R,R)-Whelk-O1, 250 mm × 4 mm, Merck) in *n*-heptane−2-propanol (90:10) employing a UV detector (254 nm) along with a polarimetric one (Chiralyser, Knauer); flow rate 0.8−1.6 mL/min. The column was thermostated (±0.1 °C), and the analyses were run at 24−28 °C.

1,3,6,8-Tetrahydrobenzo[*c*]benzo[5′,6′]oxepino[3′,4′:5,6]benzo[*e*]oxepin (8a). Mp: 225 °C (subl; petroleum ether−ether−acetone). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.07 (2 H, d, J = 11.5 Hz), 4.47 (2 H, d, J = 11.2 Hz), 4.57 (2 H, d, J = 11.5 Hz), 4.65 (2 H, d, J = 11.2 Hz), 6.62 (2 H, bdd, J = 7.6, 1.2 Hz), 7.03 (2 H, dt, J = 7.6, 7.6, 1.2 Hz), 7.28 (2 H, dt, J = 7.6, 7.6, 1.2 Hz), 7.45 (2 H, dd, J = 7.6, 1.2 Hz), 7.47 (2 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 67.51 (t), 67.56 (t), 127.58 (d), 127.94 (d), 129.45 (d), 129.57 (d), 130.83 (d), 135.48 (s), 136.32 (s), 138.12 (s), 139.43 (s). IR ($CHCl_3$): 3066 w, 3009 s, 2967 m, 2926 m, 2863 s, 1605 w, 1573 w, 1484 w, 1465 m, 1078 vs, 1069 s, 1059 vs, 1043 s cm^{-1}. EI MS (*m*/*z*, rel intensity): 314 ($M^{\bullet+}$, 100), 277 (69), 267 (24), 253 (38), 239 (25), 215 (10), 201 (12), 183 (9), 165 (13), 152 (10), 126 (16), 84 (27), 57 (17). HR EI MS: calcd for $C_{22}H_{18}O_2$ 314.1307, found 314.1347.

4,5-Dimethyl-1,3,6,8-tetrahydrobenzo[*c*]benzo[5′,6′]-oxepino[3′,4′:5,6]benzo[*e*]oxepin (8b). Typical Large-Scale Experiment. A mixture of triyne **1b** (2.0 g, 5.84 mmol) and *n*-decane (100 mL) under argon was stirred and heated at 100 °C by means of irradiation with two 250 W halogen lamps to dissolve the educt. A hot solution of PPh_3 (613 mg, 2.34 mmol, 40 mol %) in *n*-decane (6 mL) was added, and the mixture was further irradiated to achieve 140 °C. $CpCo(CO)_2$ (210 mg, ca. 160 μL, 1.17 mmol, 20 mol %) was added via syringe, and the resulting orange-brown solution was irradiated under stirring while the temperature was maintained at 140 °C (measured inside the mixture) for 4 h. A brown-greenish solid gradually deposited on the flask surface. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and poured onto a silica gel column. The product was eluted with a mixture of petroleum ether−ether−acetone (90:10:0 to 80:10:10). Solvents were evaporated in vacuo to get **8b** (1.36 g, 68%) as a foam. Mp: 199−201 °C (*n*-heptane−2-propanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.52 (6 H, s), 3.82 (2 H, d, J = 12.2 Hz), 4.95 (2 H, d, J = 12.2 Hz), 4.42 (2 H, d, J = 11.0 Hz), 4.64 (2 H, d, J = 11.0 Hz), 6.51 (2 H, dd, J = 7.6, 1.2 Hz), 6.98 (2 H, dt, J = 7.6, 7.6, 1.4 Hz), 7.25 (2 H, dt, J = 7.6, 7.6, 1.2 Hz), 7.41 (2 H, dd, J = 7.6, 1.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 16.72 (q), 62.90 (t), 67.68 (t), 127.34 (d), 127.61 (d), 129.00 (d), 130.82 (d), 133.90 (s), 135.19 (s), 135.64 (s), 136.09 (s), 140.34 (s). IR ($CHCl_3$): 3067 w, 1603 w, 1581 w, 1569 w, 1559 w, 1483 m, 1462 s, 1372 s, 1292 m, 1158 w, 1081 s, 1054 vs, 1040 s, 1023 s, 948 m, 551 m cm^{-1}. EI MS (*m*/*z*, rel intensity): 342 ($M^{\bullet+}$, 100), 327 (8), 309 (19), 295 (12), 281 (27), 269 (12), 253 (20), 239 (10), 146 (10), 126 (9), 66 (10). HR EI MS: calcd for $C_{24}H_{22}O_2$ 342.1619, found 342.1578.

4,5-Bis(trimethylsilyl)-1,3,6,8-tetrahydrobenzo[*c*]benzo-[5′,6′]oxepino[3′,4′:5,6]benzo[*e*]oxepin (8c). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.53 (18 H, s), 3.95 (2 H, d, J = 12.0 Hz), 4.57 (2 H, d, J = 11.3 Hz), 4.66 (2 H, d, J = 11.3 Hz), 4.93 (2 H, d,

J = 12.0 Hz), 6.47 (2 H, bdd, J = 7.6, 1.2 Hz), 6.95 (2 H, dt, J = 7.6, 7.6, 1.4 Hz), 7.22 (2 H, dt, J = 7.6, 7.6, 1.2 Hz), 7.40 (2 H, dd, J = 7.6, 1.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 4.16 (q), 66.40 (t), 67.13 (t), 127.47 (d), 127.81 (d), 128.61 (d), 131.25 (d), 135.38 (s), 138.55 (s), 140.05 (s), 141.19 (s), 151.08 (s). IR ($CHCl_3$): 3092 vw, 3068 w, 2901 w, 1604 vw, 1577 vw, 1484 w, 1461 w, 1254 s, 1092 m, 1074 s, 1064 m, 860 vs, 850 vs cm^{-1}. EI MS (*m*/*z*, rel intensity): 458 ($M^{\bullet+}$, 100), 443 (55), 429 (6), 413 (15), 385 (7), 369 (9), 353 (16), 341 (12), 325 (10), 280 (22), 265 (21), 252 (13), 147 (16), 111 (6), 97 (11), 73 (90). HR EI MS: calcd for $C_{28}H_{34}O_2Si_2$ 458.2097, found 458.2159.

(M*,7*R)-4,5-Bis(trimethylsilyl)-7-[(trimethylsilyl)oxy]-1,3,6,7-tetrahydrobenzo[*c*]phenathro[4,3-*e*]oxepin (9a).** ^{1}H NMR (200 MHz, $CDCl_3$) in a mixture with (M*,7*S**)-**9b** δ: 0.34 (9 H, s), 0.50 (9 H, s), 0.53 (9 H, s), 2.67 (1 H, dd, J = 14.9, 13.1 Hz), 3.50 (1 H, dd, J = 14.9, 4.4 Hz), 3.87 (1 H, d, J = 13.0 Hz), 4.61 (1 H, d, J = 11.2 Hz), 4.73 (1 H, d, J = 11.2 Hz), 4.85 (1 H, d, J = 13.0 Hz), 5.23 (1 H, dd, J = 13.1, 4.4 Hz), 6.48−7.60 (8 H, m).

(M*,7*S)-4,5-Bis(trimethylsilyl)-7-[(trimethylsilyl)oxy]-1,3,6,7-tetrahydrobenzo[*c*]phenathro[4,3-*e*]oxepin (9b).** ^{1}H NMR (200 MHz, $CDCl_3$) in a mixture with (M*,7*R**)-**9a** δ: 0.11 (9 H, s), 0.50 (9 H, s), 0.53 (9 H, s), 2.77 (1 H, bd, J = 16.5 Hz), 3.85 (1 H, dd, J = 16.5, 3.0 Hz), 3.89 (1 H, d, J = 13.0 Hz), 4.63 (1 H, d, J = 11.3 Hz), 4.74 (1 H, d, J = 11.3 Hz), 4.87 (1 H, d, J = 13.0 Hz), 5.07 (1 H, t, J = 3.0 Hz), 6.48−7.60 (8 H, m).

3,4-Bis(trimethylsilyl)-1,2,5,6-tetrahydropentahelicene (10). Mp: 191−193 °C ($CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.41 (18 H, s), 2.47 (2 H, dd, J = 15.4, 13.9 Hz), 2.79 (2 H, bd, J = 13.0 Hz), 2.93 (2 H, dd, J = 15.2, 13.0 Hz), 3.29 (2 H, bd, J = 15.7 Hz), 6.86 (2 H, dt, J = 7.7, 7.7, 1.4 Hz), 7.00 (2 H, dd, J = 7.8, 1.3 Hz), 7.07 (2 H, dt, J = 7.4, 7.4, 1.3 Hz), 7.24 (2 H, dd, J = 7.5, 1.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 4.00 (q), 29.89 (t), 30.47 (t), 125.27 (d), 126.45 (d), 126.85 (d), 131.01 (d), 131.52 (s), 135.14 (s), 139.26 (s), 144.15 (s), 147.06 (s). IR ($CHCl_3$): 3093 vw, 3068 w, 2951 m, 2899 m, 2839 w, 1601 vw, 1520 vw, 1486 w, 1471 w, 1252 s, 1160 vw, 1113 w, 1040 w, 947 w, 852 vs, 628 m, 585 w, 496 w, 424 w cm^{-1}. EI MS (*m*/*z*, rel intensity): 426 ($M^{\bullet+}$, 78), 411 (11), 395 (9), 354 (98), 338 (12), 279 (75), 265 (10), 131 (6), 73 (100), 59 (29). HR EI MS: calcd for $C_{28}H_{34}Si_2$ 426.2199, found 426.2159.

Tetramethyl 4,5-Dimethyl-1,2,3,6,7,8-hexahydrobenzo[*a*]benzo[3′,4′]cyclohepta[5,6]benzo[*c*]cycloheptene-2,2,7,7-tetracarboxylate (11). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.24 (6 H, s), 2.67 (2 H, d, J = 14.8 Hz), 3.18 (2 H, bd, J = 13.5 Hz), 3.29 (2 H, d, J = 13.5 Hz), 3.48 (2 H, bd, J = 14.8 Hz), 3.767 (6 H, s), 3.770 (6 H, s), 6.35 (2 H, dd, J = 7.5, 1.4 Hz), 6.81 (2 H, dt, J = 7.5, 7.5, 1.4 Hz), 7.02 (2 H, dt, J = 7.5, 7.5, 1.4 Hz), 7.06 (2 H, dd, J = 7.5, 1.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 16.64 (q), 33.31 (t), 36.93 (t), 52.65 (q), 52.75 (q), 63.53 (s), 126.31 (d), 126.73 (d), 128.04 (d), 131.24 (d), 132.47 (s), 134.63 (s), 135.66 (s), 136.55 (s), 140.20 (s), 171.25 (s), 171.41 (s). IR ($CHCl_3$): 3064 w, 1744 s, 1732 vs, 1488 w, 1435 m, 1329 w, 1279 s, 1241 m, 1069 w cm^{-1}. EI MS (*m*/*z*, rel intensity): 570 ($M^{\bullet+}$, 100), 539 (11), 510 (66), 495 (21), 479 (19), 451 (74), 438 (61), 419 (45), 391 (60), 377 (23), 365 (45), 331 (40), 317 (50), 303 (44), 149 (15), 111 (13), 97 (18), 83 (23), 69 (35), 57 (45), 43 (29). HR EI MS: calcd for $C_{34}H_{34}0_8$ 570.2254, found 570.2206.

4,5-Dimethyl-1,3,6,8-tetrahydrobenzo[*c*]naphtho[1″,2″:5′,6′]oxepino [3′,4′:5,6]benzo[*e*]oxepin (12). Mp: 205−208 °C (acetone). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.56 (3 H, s), 2.59 (3 H, s), 3.85 (1 H, d, J = 12.4 Hz), 3.87 (1 H, d, J = 12.2 Hz), 4.46 (1 H, d, J = 11.2 Hz), 4.61 (1 H, d, J = 11.1 Hz), 4.72 (1 H, d, J = 11.2 Hz), 4.77 (1 H, d, J = 11.1 Hz), 4.98 (1 H, d, J = 12.4 Hz), 4.99 (1 H, d, J = 12.2 Hz), 6.23 (1 H, dd, J = 7.6, 1.2 Hz), 6.56 (1 H, dt, J = 7.6, 7.6, 1.4 Hz), 6.90 (1 H, ddd, J = 8.5, 6.8, 1.4 Hz), 6.93 (1 H, dt, J = 7.6, 7.6, 1.2 Hz), 7.13 (1 H, dq, J = 8.5, 1.0, 1.0, 1.0 Hz), 7.16 (1 H, ddd, J = 8.1, 6.8, 1.2 Hz), 7.21 (1 H, dd, J = 7.6, 1.4 Hz), 7.53 (1 H, d, J = 8.1 Hz), 7.66 (1 H, bd, J = 8.1 Hz), 7.83 (1 H, bd, J = 8.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 16.64 (q), 16.94 (q), 62.73 (t), 63.11 (t), 67.90 (t), 68.00 (t), 125.08 (d), 125.31 (d), 125.89 (d), 126.68 (d), 126.82 (d), 127.50 (d), 127.63 (d), 128.66 (d), 128.87 (d), 128.96 (d), 130.10 (s), 132.23 (s), 133.15 (s), 133.74 (s), 133.95 (s), 134.25 (s, two carbon atoms), 135.42 (s, two carbon atoms), 137.10 (s), 137.15 (s), 140.44 (s). IR (CCl_4): 3055 w, 3008 m, 2962 m, 2924 m, 2858 s, 1569 w, 1510 w, 1468 w, 1462 m, 1086 m, 1075 m, 1058 vs, 1049 s cm^{-1}. EI MS (*m*/*z*, rel intensity): 392 ($M^{\bullet+}$, 67), 377 (12), 331 (13), 303 (14), 149 (18), 111 (18), 97 (30), 83 (36), 69 (61), 57 (100), 43 (87), 28 (45). HR EI MS: calcd for $C_{28}H_{24}O_2$ 392.1776, found 392.1773.

2,7-Bis[(4-methylphenyl)sulfonyl]-1,2,3,6,7,8-hexahydrobenzo[5′,6′]azepino[4′,3′:3,4]benzo[*c*]naphtho-[1,2-*e*]azepine (13). ^{1}H NMR (200 MHz, acetone-d_6) δ: 2.37 (3 H, s), 2.38 (3 H, s), 3.40 (1 H, d, J = 14.0 Hz), 3.44 (1 H, d, J = 12.0 Hz), 3.89 (1 H, d, J = 12.0 Hz), 4.10 (1 H, d, J = 14.0 Hz), 4.73 (2 H, d, J = 14.0 Hz), 4.79 (1 H, d, J = 12.0 Hz), 4.91 (1 H, d, J = 12.0 Hz), 6.20 (1 H, dd, J = 8.0, 2.0 Hz), 6.50 (1 H, dt, J = 8.0, 8.0, 2.0 Hz), 6.79 (1 H, dt, J = 8.0, 8.0, 2.0 Hz), 6.99−7.22 (4 H, m), 7.31−7.44 (7 H, m), 7.66−7.86 (6 H, m). EI MS (*m*/*z*, rel intensity): 670 ($M^{\bullet+}$, 69), 515 (78), 499 (9), 486 (55), 359 (39), 343 (21), 332 (59), 315 (41), 303 (100), 289 (21), 155 (19), 91 (72), 57 (43). HR EI MS: calcd for $C_{40}H_{34}N_2O_4S_2$ 670.1960, found 670.2068.

10,11-Dimethyl-7,9,12,14-tetrahydronaphtho[2,1-*c*]naphtho[1″,2″:5′,6′]oxepino[3′,4′:5,6]benzo[*e*]oxepin (14). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.66 (6 H, s), 3.95 (2 H, d, J = 12.0 Hz), 4.64 (2 H, d, J = 11.2 Hz), 4.84 (2 H, d, J = 11.2 Hz), 5.04 (2 H, d, J = 12.0 Hz), 6.70 (2 H, ddd, J = 8.0, 6.7, 1.2 Hz), 6.95 (2 H, bd, J = 8.0 Hz), 6.99 (2 H, ddd, J = 8.3, 6.7, 1.2 Hz), 7.29 (2 H, d, J = 8.0 Hz), 7.33 (2 H, bd, J = 8.0 Hz), 7.44 (2 H, bd, J = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 16.93 (q), 63.10 (t), 68.31 (t), 124.44 (d), 124.86 (d), 125.88 (d), 126.88 (d, two carbon atoms), 128.50 (d), 129.45 (s), 131.58 (s), 132.63 (s), 134.98 (s), 135.65 (s), 135.96 (s), 137.44 (s). IR ($CHCl_3$): 3055 w, 2966 m, 2920 w, 2866 m, 1623 vw, 1594 w, 1565 w, 1511 w, 1381 m, 1254 w, 1080 w, 1068 m, 1050 s, 1029 w, 895 m, 886 m, 870 w, 822 vs cm^{-1}. EI MS (*m*/*z*, rel intensity): 442 ($M^{\bullet+}$, 32), 383 (4), 367 (4), 353 (6), 256 (8), 213 (7), 185 (8), 163 (7), 149 (16), 129 (15), 111 (22), 97 (41), 83 (48), 69 (100), 57 (97), 43 (64). HR EI MS: calcd for $C_{32}H_{26}O_2$ 442.1933, found 442.1976.

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Supporting Information Available: Copies of ^{1}H NMR spectra of **8**−**14** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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