SYNTHESIS OF HELICENE SCAFFOLDS *via* [2+2+2] CYCLOISOMERIZATION OF AROMATIC TRIYNES

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Dedicated to the memory of Professor Otakar Červinka who deceased on May 24, 2002.

Triynes R–C≡C–CH_2CH_2–Ar–C≡C–Ar′–CH_2CH_2–C≡C–R were subjected to Co(I)- or Ni(0)-mediated intramolecular [2+2+2] cycloisomerization to provide corresponding tetrahydropentahelicene, tetrahydrohexahelicene, and tetrahydroheptahelicene in good to moderate yields. The reaction tolerates various substituents at pendant acetylene moieties (R = H, CH_3, trimethylsilyl, not triisopropylsilyl) and fluorine in an aromatic part. By contrast, under Rh(I) or Pd(0) catalysis, triyne with the CH_2OCH_2 tether lost pendant propargyl moieties and an aromatic spiroketal was formed preferentially.

Keywords: Alkynes; Arenes; Cobalt catalysis; Helical chirality; Helicenes; Nickel catalysis; Palladium catalysis; Rhodium catalysis; Spiroketals; Tetrahydrohelicenes; Triyne cyclotrimerization.

Helically chiral materials such as nucleic acids, proteins, and polysaccharides play an essential role in nature. By contrast, within the realms of small chiral organic molecules[1], the “screw-like” structural motif[2] is less frequent. Thus, most examples of small helices can be taken from the families of artificial molecules such as helicates[3] and helicenes[4]. The latter compounds have been applied or at least theoretically studied in diverse areas ranging from asymmetric catalysis[5] to nonlinear optics[6] and molecular wires[7] to provide promising results. In spite of this, there has still been a noticeable discrepancy between the number of original papers devoted to helicene synthesis published during the last two decades and the number of helicene exploitations. The reason for this is obvious: the current methods for helicene synthesis have been laborious or suitable only for preparing individual structure types. In addition, no helicene derivative is so far com-

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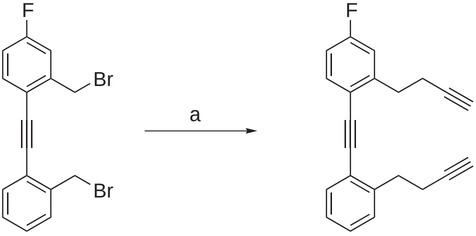
mercially available in multigram quantities. Hence, a general, modular, and really efficient synthetic methodology for preparing helicenes and their substituted derivatives in a non-racemic form is required.

Recently, Katz has contributed substantially to the solution of the helicenes availability problem[8]. However, a niche in this area of organic synthesis has still remained[9]. In our preliminary communication[10] we published an alternative route to tetrahydrohelicene scaffolds, which relied on intramolecular [2+2+2] cycloisomerization of aromatic triynes under Co(I) or Ni(0) catalysis. Herein, we report the cyclization procedure in full details being accompanied by further examples. This approach relates to the synthesis of helicene-like molecules from aromatic triynes[11] and it is complementary to our nonphotochemical synthesis of parent helicenes from aromatic *cis*,*cis*-dienetriynes[12].

RESULTS AND DISCUSSION

Synthesis of Aromatic Triynes

The synthesis of aromatic triynes **1**, **4**–**6**, and **8**–**11** (Scheme 2, Tables I–III) have been published elsewhere[13]. Fluorinated triyne **7** was prepared from dibromide[13] **21** by a one-pot procedure (Scheme 1). Treatment of **21** with $LiCH_2C{\equiv}CTMS$ (generated *in situ* from $CH_3C{\equiv}CTMS$ and butyllithium) followed by the TMS group removal with tetrabutylammonium fluoride led to triyne **7** in good overall yield. Diol[14] **2** and its TMS derivative[13] **3** were prepared earlier.



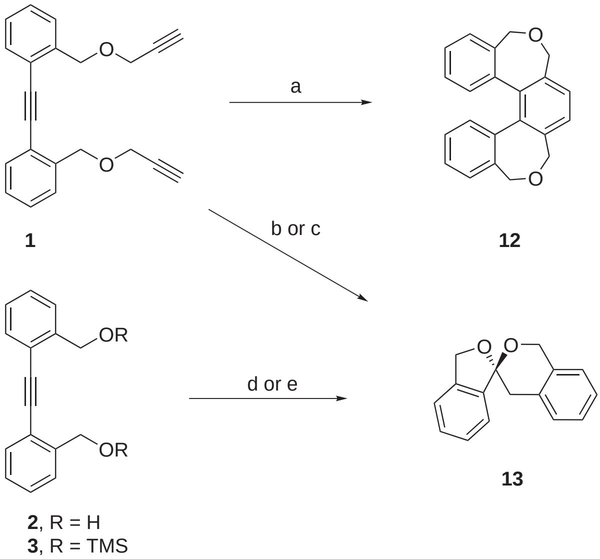
21 **7**

(a) $LiCH_2C{\equiv}CTMS$ (2.1 equiv.), THF, –78 °C, 1 h, then n-Bu_4NF (10.0 equiv.), rt, overnight, 76%

SCHEME 1
Synthesis of triyne **7**

[2+2+2] Cycloisomerization of Aromatic Triynes

The results of our attempts to pursue [2+2+2] cycloisomerization of aromatic triynes **1**, **4**–**11** are summarized in Scheme 2 and Tables I–III. We have already published that triyne **1** underwent a smooth cyclization under the cobalt(I) catalysis to afford **12** with a helical scaffold[11] (Scheme 2). To explore the catalytic efficiency of other transition metal complexes in this process, we paid attention to nickel(0), rhodium(I), and palladium(0) catalysis. Displacing Co(I) by Ni(0), the starting material **1** was partially consumed but a complex mixture was formed. Most astonishingly, the Wilkinson's catalyst[15] promoted the formation of an unexpected spiroketal[16] **13** instead of giving rise to the helicene-like derivative **12**. The yield was low but spiroketal **13** was the only product detected in the reaction mixture. Similarly, the application of palladium on charcoal with chloro(trimethyl)silane[17] led to spiroketal **13**, which was produced, contrary to



(a) $CpCo(CO)_2$ (40 mole %), PPh_3 (80 mole %), decane, 140 °C, 0.5 h, irradiated with a halogen lamp, 89% (ref.[11]);

(b) $Rh(PPh_3)_3Cl$ (10 mole %), ethanol, 120 °C, 3 h, in a sealed tube, 22%;

(c) 10% Pd/C (5 mole %), TMSCl (300%), tetrahydrofuran, 120 °C, 3 h, in a sealed tube, 95%;

(d) **2**, 10% Pd/C (5 mole %), TMSCl (300%), tetrahydrofuran, 120 °C, 10 h, in a sealed tube, 42%;

(e) **3**, 10% Pd/C (5 mole %), TMSCl (300%), tetrahydrofuran, 120 °C, 10 h, in a sealed tube, 66%

SCHEME 2
Cyclization of **1**, **2**, and **3**

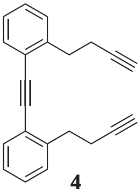
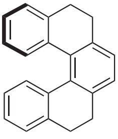
the previous run, in high yield. Apparently, both propargyl moieties in **1** are lost to afford spiroketal **13**. We hypothesize a competitive Rh- or Pd-mediated propargyl ether-to-allenyl ether isomerization operates at **1** instead of entering the desired [2+2+2] cycloisomerization catalytic cycle. The allenyl ether moiety might be cleaved with the assistance of a transition metal Lewis acid or hydrogen chloride (generated *in situ* from TMSCl and remnant water in the reaction medium) to produce diol **2** or its TMS derivative **3**. Then a double intramolecular addition of oxygen nucleophiles across the triple bond takes place. There is a common sense the reaction is catalyzed by transition metals, particularly by palladium[18], *via* electrophilic activation of a multiple carbon–carbon bond towards nucleophilic addition. To validate the occurrence of an inferred hydroxy or silyloxy intermediate, we subjected diol **2** and silyl ether **3** to the reaction in the presence of Pd/C and TMSCl. Indeed, both **2** and **3** were cyclized to spiroketal **13** in moderate and good yield, respectively.

Triyne **4** was cyclized under Co(I) catalysis to tetrahydro[5]helicene **14** in good yield (Table I, entry 1). In comparison with triyne **1** (Scheme 2), which differs only in the presence of the oxygen atom in the tether between pendant acetylene units and the core diphenylacetylene moiety, triyne **4** is more susceptible to [2+2+2] cycloisomerization. This difference emerged profoundly when decreasing the reaction temperature. While triyne **1** required heating at 140 °C to accomplish the conversion, triyne **4** could be cyclized even at 50 °C without any irradiation to provide **14** in still reasonable yield (Table I, entry 2). However, the presence of triphenylphosphine was essential to keep a cobalt(I) catalyst active throughout the long reaction period. In the absence of triphenylphosphine, triyne **4** furnished **14** in a very low yield (Table I, entry 3). As regards the catalytic system, nickel(0) was found to be superior to cobalt(I) in terms of reactivity and mildness of reaction conditions used. In the sharp contrast to triyne **1**, Ni(0)-catalyzed cyclization of **4** proceeded smoothly to afford **14** in good yield (Table I, entry 4). Despite the known activity of $TaCl_5$ in cycloisomerization of alkynes[19], it was found to be ineffective in the case of **4** (Table I, entry 5).

Our next goal was to explore the reactions potential for the synthesis of substituted tetrahydro[5]helicenes. In the presence of a Ni(0) complex, triyne **5** possessing only non-terminal acetylene units furnished the tetrahydro[5]helicene derivative **15** in acceptable yield (Table II, entry 1). Triyne **6** with more bulky TMS groups at the pendant alkyne units provided under Co(I) or Ni(0) catalysis the corresponding derivative **16** in good yields[20] (Table II, entries 2 and 3). In order to examine the accessibility of helicenes with modulated electronic properties, we attempted the synthesis of a model fluoro derivative. The Co(I)-catalyzed cyclization of **7** led to fluorotetrahydro[5]helicene **17** in moderate yield (Table II, entry 4).

As the general approach to tetrahydro[5]helicenes has been proved to be feasible, the next challenge was to synthesize higher homologues. Triyne **8** with the unsymmetrical naphthyl(phenyl)acetylene core provided under Co(I) catalysis tetrahydro[6]helicene **18** in good yield (Table III, entry 1). The triyne **8** was reactive enough to undergo cyclization at 50 °C (without irradiation) but the preparative yield was lower in comparison with the analogous experiment in a tetrahydro[5]helicene series (*cf.* Table III, entry 2 and Table I, entry 2). In the presence of a Ni(0) complex, triyne **8** was immediately cyclized to tetrahydro[6]helicene **18** in good yield (Table III, entry 3). The attempt to apply a Ni(0) catalyst generated *in situ* from nickelocene and triphenylphosphine[21] failed and no cyclized product **18** was observed (Table III, entry 4). The analogous dimethyl derivative **9** was cyclized under Co(I) catalysis to **19** in good yield (Table III, entry 5). Ex-

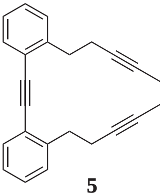
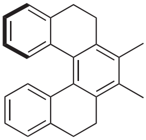
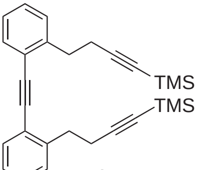
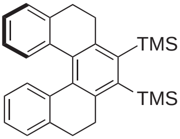
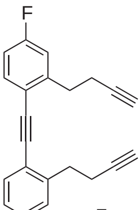
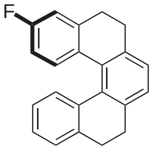
TABLE I
Cyclization of model substrate **4**

Entry	Starting material	ML$_n$ (mole %) Ligand (mole %)	Conditions[a] °C, h	Product	Yield[b] %
1	 **4**	CpCo(CO)$_2$ (20) PPh$_3$ (40)	140, 1[c]	 **14**	72
2	**4**	CpCo(CO)$_2$ (100) PPh$_3$ (200)	50, 72	**14**	63
3	**4**	CpCo(CO)$_2$ (100)	50, 8 days	**14**	8[d]
4	**4**	Ni(cod)$_2$ (20) PPh$_3$ (40)	r.t., 0.5	**14**	66
5	**4**	TaCl$_5$ (100)	reflux, 24	no reaction[e]	

[a] The reactions were run in decane (Co catalysis), tetrahydrofuran (Ni catalysis), or benzene (Ta catalysis) until the starting material disappeared or no progress was monitored. [b] Isolated. [c] The reaction mixture was irradiated by a 250 W halogen lamp. [d] The starting material was recovered (58%). [e] The starting material remained unchanged.

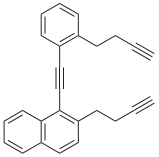
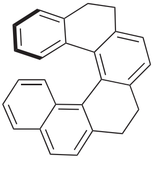
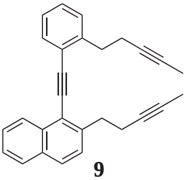
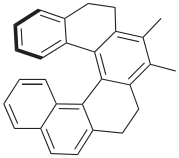
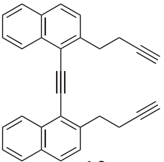
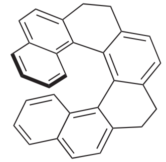
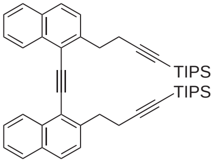
tending the triyne core to a dinaphthylacetylene as in **10**, led to successful cycloisomerization under Co(I) catalysis giving tetrahydro[7]helicene **20** again in good yield (Table III, entry 6). In the case of **10**, the Ni(0)-catalyzed reaction produced **20** in low yield and most of the starting material polymerized in contrast to the formation of lower homologues **14** and **18** (*cf*. Table III, entry 7 *versus* Table I, entry 4 and Table II, entry 3). Not surprisingly, the attempt at cyclization of triyne **11** bearing bulky TIPS groups was unsuccessful and starting material remained (Table III, entry 8).

TABLE II
Cyclization of model substrates **5**–**7**

Entry	Starting material	ML_n (mole %) Ligand (mole %)	Conditions[a] °C, h	Product	Yield[b] %
1	 **5**	$Ni(cod)_2$ (100) PPh_3 (200)	r.t., 20	 **15**	42
2	 **6**	$CpCo(CO)_2$ (40) PPh_3 (80)	140, 2.5[c]	 **16**	71
3	**6**	$Ni(cod)_2$ (100) PPh_3 (200)	r.t., 20	**16**	70
4	 **7**	$CpCo(CO)_2$ (40) PPh_3 (80)	140, 3[c]	 **17**	33

[a] The reactions were run in decane (Co catalysis) or tetrahydrofuran (Ni catalysis) until the starting material disappeared or no progress was monitored. [b] Isolated. [c] The reaction mixture was irradiated by a 250 W halogen lamp.

TABLE III
Cyclization of model substrates **8–11**

Entry	Starting material	ML$_n$ (mole %) Ligand (mole %)	Conditions^a °C, h	Product	Yield^b %
1	 **8**	CpCo(CO)$_2$ (20) PPh$_3$ (40)	140, 0.5^c	 **18**	64
2	**8**	CpCo(CO)$_2$ (20) PPh$_3$ (40)	50, 4 days	**18**	26
3	**8**	Ni(cod)$_2$ (200)	reflux, 0.1	**18**	75
4	**8**	Cp$_2$Ni (120) PPh$_3$ (120)	50, 12	no reaction^d	
5	 **9**	CpCo(CO)$_2$ (20) PPh$_3$ (40)	140, 1.0^c	 **19**	68
6	 **10**	CpCo(CO)$_2$ (20) PPh$_3$ (40)	140, 2.0^c	 **20**	64
7	**10**	Ni(cod)$_2$ (200)	reflux, 0.1	**20**	24
8	 **11**	Ni(cod)$_2$ (100) PPh$_3$ (200)	r.t., 2	no reaction^d	

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[a] The reactions were run in decane (Co catalysis) or tetrahydrofuran (Ni catalysis) until the starting material disappeared or no progress was monitored. [b] Isolated. [c] The reaction mixture was irradiated by a 250 W halogen lamp. [d] The starting material remained unchanged.

CONCLUSION

Model aromatic triynes **1** and **4**–**10** have been shown to undergo Co(I)- or Ni(0)-catalyzed intramolecular [2+2+2] cycloisomerization affording tetrahydrohelicenes. The reaction can be used to construct penta-, hexa- or heptacyclic helical scaffolds and displays reasonable tolerance towards substituents and conditions. The use of other transition metal catalysts is limited – Ta(V) is inactive and Rh(I) or Pd(0) can promote, in an individual case, a concurrent reaction channel to deliver a spiroketal product. The study has established a novel methodology for preparing helicene congeners in a nonphotochemical way and illustrates clearly its efficiency. Transformation of tetrahydrohelicenes to parent helicenes is underway and will be published separately.

EXPERIMENTAL

^{1}H NMR spectra were measured at 200.0, 499.8 or 500.13 MHz, ^{13}C NMR spectra at 125.7 MHz, in $CDCl_3$ with TMS as an internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants J are given in Hz. HMBC experiments were setup for J_{CH} = 5 Hz. For correct assignment of both ^{1}H and ^{13}C NMR spectra of key compounds, the HCOSY and HMQC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. IR spectra (ν, cm^{-1}) were measured in $CHCl_3$. EI MS spectra were determined at an ionizing voltage of 70 eV, *m/z* values are given along with their relative intensities (%). FAB MS spectrum was measured using the bis(2-hydroxyethyl) disulfide matrix. HR MS spectra were obtained by the EI technique. Reagent grade materials purchased from Sigma–Aldrich, Fluka, and Merck were used as received. The syntheses of triynes **1**, **4**–**6**, and **8**–**11** (ref.[13]), diol **2** (ref.[14]) and its TMS derivative **3** (ref.[13]) were published previously. A stock solution of $Ni(cod)_2$ in tetrahydrofuran (*ca* 0.06 mol/l) was stored at –78 °C under argon and reused within two weeks. Tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen; benzene was distilled from calcium hydride under argon; decane and UV grade ethanol were degassed by three freeze-pump-thaw cycles before use. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2 \cdot 4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on Silica gel 60 (0.040–0.063 mm or <0.063 mm, Merck).

General Procedures for the Cyclization of Triynes **1**, **4**–**11**

Procedure A. Cobalt catalysis with halogen lamp irradiation. A mixture of triyne (0.100 mmol) and decane (3 ml) under argon was stirred and heated at 100 °C by two 250 W halogen lamps to dissolve the starting material. A hot solution of triphenylphosphine (10.5 mg, 0.040 mmol, 40 mole %) in decane (1 ml) was added and the mixture was further irradiated to achieve 140 °C. $CpCo(CO)_2$ (*ca* 2.7 μl, 0.020 mmol, 20 mole %) in decane (0.1 ml) was added *via* syringe and the resulting orange-brown solution was irradiated under stirring at 140 °C (measured inside the reaction vessel) until the starting material disappeared or no reaction progress was monitored. The reaction mixture was cooled to room temperature, poured onto a silica gel column, and the product was eluted. Stoichiometric version or a reaction without halogen lamp irradiation was performed analogously.

Procedure B. Nickel catalysis. In a Schlenk flask, triphenylphosphine (10.5 mg, 0.040 mmol, 40 mole %) was dissolved in tetrahydrofuran (1 ml) under argon, a stock solution of Ni(cod)$_2$ (0.06 M in tetrahydrofuran, 330 μl, 0.020 mmol, 20 mole %) was added and the mixture was stirred at room temperature for 5 min. Triyne (0.100 mmol) in tetrahydrofuran (2 ml) was added and the mixture was stirred at room temperature or under reflux until the starting material disappeared or no reaction progress was monitored. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel to obtain the product. Stoichiometric version was performed analogously.

2-But-3-yn-1-yl-1-[(2-but-3-yn-1-ylphenyl)ethynyl]-4-fluorobenzene (**7**)

Butyllithium (1.6 M solution in hexanes, 480 μl, 0.768 mmol, 2.1 equiv.) was added dropwise over a 2-min period to a solution of trimethyl(prop-1-yn-1-yl)silane (115 μl, 0.777 mmol, 2.1 equiv.) in tetrahydrofuran (2 ml) at –78 °C under argon. After stirring at –78 °C for 3 h, dibromide[13] **21** (140 mg, 0.366 mmol) in tetrahydrofuran (1 ml) was added dropwise. The mixture was stirred at –78 °C for 1 h and then warmed to room temperature. Tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran, 3.65 ml, 3.65 mmol, 10.0 equiv.) was added and the mixture was stirred at room temperature overnight. The solution was evaporated *in vacuo* to dryness and the residue was chromatographed on silica gel (hexane–ether 97:3) to get triyne **7** (83.1 mg, 76%) as an amorphous solid. The product was immediately subjected to the Co-catalyzed cyclization. IR: 3308 s, 3071 w, 2960 s, 2928 vs, 2873 m, 2856 s, 2207 w, 2118 w, 1608 s, 1580 s, 1496 s, 1485 m (sh), 1452 m, 1432 m, 1416 w, 1340 w, 1304 m (sh), 1278 s, 1263 s, 1184 m, 1161 m, 1137 m, 1104 m, 954 m, 874 m, 822 m, 640 s, 542 w, 495 w, 453 w. ^{1}H NMR (200 MHz): 1.99 (1 H, t, J = 2.4, $CH_2CH_2C{\equiv}C\mathbf{H}$); 2.00 (1 H, t, J = 2.4, $CH_2CH_2C{\equiv}C\mathbf{H}$); 2.55–2.64 (4 H, m, $CH_2C\mathbf{H}_2C{\equiv}CH$); 3.07 (2 H, t, J = 7.1, $C\mathbf{H}_2CH_2C{\equiv}CH$); 3.11 (2 H, t, J = 7.1, $C\mathbf{H}_2CH_2C{\equiv}CH$); 6.95–7.74 (7 H, m, arom.). EI MS: 300 ($M^{\bullet+}$, 2), 299 (7), 283 (10), 260 (99), 246 (19), 239 (100), 233 (24), 133 (30), 115 (17), 109 (21), 98 (10), 87 (8), 81 (10), 75 (13), 63 (19), 57 (27), 51 (24), 39 (57). HR EI MS: calculated for $C_{22}H_{16}F$ (M – 1) 299.1236; found 299.1240.

1,4-Dihydro-3′*H*-spiro[2-benzopyran-3,1′-isobenzofuran] (**13**)

A sealed tube was charged with triyne **1** (21 mg, 0.067 mmol) and $Rh(PPh_3)_3Cl$ (6.5 mg, 0.007 mmol, 10 mole %) and flushed with argon. Ethanol (3 ml) was added, the tube was tightly closed and heated at 120 °C for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and the residue was chromatographed on silica gel (petroleum ether–ether–acetone 80:10:10) to obtain spiroketal[16] **13** (3.5 mg, 22%) as an oil.

Cyclization of **1** under Pd catalysis was carried out analogously: **1** (20 mg, 0.064 mmol), 10% Pd on charcoal (3.4 mg, 0.003 mmol, 5 mole %), chloro(trimethyl)silane (24 μl, 0.189 mmol, 300 mole %), tetrahydrofuran (3 ml), 120 °C, 3 h. Flash chromatography afforded spiroketal **13** (14.5 mg, 95%).

Cyclization of **2** under Pd catalysis was carried out analogously: **2** (27.1 mg, 0.114 mmol), 10% Pd on charcoal (6.3 mg, 0.006 mmol, 5 mole %), chloro(trimethyl)silane (43 μl, 0.339 mmol, 300 mole %), tetrahydrofuran (2 ml), 120 °C, 10 h. Flash chromatography afforded spiroketal **13** (11.4 mg, 42%).

Cyclization of **3** under Pd catalysis was carried out analogously: **3** (24 mg, 0.063 mmol), 10% Pd on charcoal (3.3 mg, 0.003 mmol, 5 mole %), chloro(trimethyl)silane (24 μl, 0.189 mmol, 300 mole %), tetrahydrofuran (2 ml), 120 °C, 10 h. Flash chromatography afforded spiroketal **13** (9.9 mg, 66%). IR: 2948 w, 2867 w, 1602 w, 1590 w, 1496 w, 1484 w, 1459 w, 1375 m, 1197 w, 1114 w, 1098 w, 1062 s, 1037 w, 1008 s, 939 w, 886 m, 865 vw, 591 vw. ^{1}H NMR (200 MHz): 3.08 (1 H, d, *J* = 16.2, Ph-CH_2-C); 3.58 (1 H, d, *J* = 16.2, Ph-CH_2-C); 4.87 (1 H, d, *J* = 14.5, Ph-CH_2-O); 5.07 (1 H, d, *J* = 12.4, Ph-CH_2-O); 5.17 (1 H, d, *J* = 14.5, Ph-CH_2-O); 5.26 (1 H, d, *J* = 12.4, Ph-CH_2-O); 7.04–7.40 (8 H, m, arom.). FAB MS: 239 ($(M + H)^+$), 238, 221, 179, 149, 147, 95, 81, 73, 69, 55.

5,6,9,10-Tetrahydropentahelicene (**14**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **4** (72 mg, 0.255 mmol), $CpCo(CO)_2$ (7 μl, 0.053 mmol, 20 mole %), triphenylphosphine (26.7 mg, 0.102 mmol, 40 mole %), decane (3 ml), 140 °C, 1 h. Flash chromatography on silica gel (petroleum ether) afforded **14** (52 mg, 72%) as an amorphous solid. Procedure *A* – Stoichiometric without halogen lamp irradiation. Triyne **4** (49 mg, 0.174 mmol), $CpCo(CO)_2$ (23 μl, 0.174 mmol, 100 mole %), triphenylphosphine (91 mg, 0.347 mmol, 200 mole %), decane (3 ml), 50 °C, 72 h. Flash chromatography afforded **14** (30.7 mg, 63%). Procedure *A* – Stoichiometric without halogen lamp irradiation and without triphenylphosphine. Triyne **4** (50 mg, 0.178 mmol), $CpCo(CO)_2$ (24 μl, 0.181 mmol, 100 mole %), decane (2 ml), 50 °C, 8 days. Flash chromatography afforded **14** (4 mg, 8%) and recovered **4** (29 mg, 58%). Procedure *B* – Catalytic. Triyne **4** (40 mg, 0.142 mmol), $Ni(cod)_2$ (0.06 M in tetrahydrofuran, 470 μl, 0.028 mmol, 20 mole %), triphenylphosphine (14.8 mg, 0.056 mmol, 40 mole %), tetrahydrofuran (5 ml), room temperature, 30 min. Flash chromatography afforded **14** (26.2 mg, 66%). IR: 3100, 3064, 2942, 2901, 2841, 1601, 1570, 1489, 1436, 1427, 1410, 824. ^{1}H NMR (500 MHz): 2.62–3.00 (8 H, m, H-5, 6, 9, 10); 6.91 (2 H, dt, *J* = 7.7, 7.7, 1.5, H-2, 13); 7.10 (2 H, s, H-7, 8); 7.10 (2 H, dt, *J* = 7.5, 7.5, 1.3, H-3, 12); 7.22 (2 H, dd, *J* = 7.9, 1.5, H-1, 14); 7.25 (2 H, dd, *J* = 7.5, 1.3, H-4, 11). ^{13}C NMR: 29.8 (t, C-5, 10), 30.2 (t, C-6, 9), 125.4 (d, C-2, 13), 126.6 (d, C-7, 8), 126.7 (d, C-3, 12), 127.3 (d, C-4, 11), 130.2 (d, C-1, 14), 132.7 (s, C-14b, 14c), 134.8 (s, C-14a, 14d), 138.9 (s, C-4a, 10a), 139.2 (s, C-6a, 8a). EI MS: 282 ($M^{\bullet+}$, 100), 265 (15), 254 (9), 239 (8), 138 (5), 126 (10), 69 (9). HR EI MS: calculated for $C_{22}H_{18}$ 282.1409; found 282.1470.

7,8-Dimethyl-5,6,9,10-tetrahydropentahelicene (**15**)

Procedure *B* – Stoichiometric. Triyne **5** (77 mg, 0.248 mmol), $Ni(cod)_2$ (0.06 M in tetrahydrofuran, 4.0 ml, 0.240 mmol, 100 mole %), triphenylphosphine (130 mg, 0.496 mmol, 200 mole %), tetrahydrofuran (4 ml), room temperature, 20 h. Flash chromatography on silica gel (petroleum ether) afforded **13** (32.5 mg, 42%) as an amorphous solid. IR: 3098 w, 3073 m, 3059 m, 3031 w, 3018 w, 3003 w, 2940 m, 2896 m, 2840 m, 1602 w, 1586 w, 1558 vw, 1489 m, 1480 m, 1456 w (sh), 1435 s, 1420 w (sh), 1378 vw, 1281 w, 1182 w, 1156 w, 1111 w, 1089 w, 1070 w, 1028 m, 1000 w, 973 w, 720 w, 617 w, 431 w. ^{1}H NMR (500 MHz): 2.31 (6 H, brs, 2 × CH_3); 2.86–2.91 (8 H, m, 2 × CH_2CH_2); 6.86 (2 H, dt, *J* = 7.6, 7.6, 1.4, H-2, 13); 7.06 (2 H, dt, *J* = 7.3, 7.3, 1.3, H-3, 12); 7.08 (2 H, brdd, *J* = 7.1, 1.3, H-1, 14); 7.24 (2 H, ddq, *J* = 7.3, 1.4, 0.8, 0.8, 0.8, H-4, 11). ^{13}C NMR: 16.3 (q, 2 × CH_3), 27.0 (t, C-6, 9), 29.8 (t, C-5, 10), 125.3 (d, C-2, 13), 126.1 (d, C-3, 12), 126.8 (d, C-4, 11), 130.7 (d, C-1, 14), 131.0 (s, C-14b, 14c), 132.8 (s, C-7, 8), 135.7 (s, C-14a, 14d), 137.3 (s, C-4a, 10a), 138.1 (s, C-6a, 8a). EI MS: 310 ($M^{\bullet+}$, 21), 262 (100), 183 (54), 152 (7), 108 (26), 69 (8), 55 (12), 43 (13). HR EI MS: calculated for $C_{24}H_{22}$ 310.1722; found 310.1723.

7,8-Bis(trimethylsilyl)-5,6,9,10-tetrahydropentahelicene (**16**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **6** (102 mg, 0.239 mmol), $CpCo(CO)_2$ (13 µl, 0.098 mmol, 40 mole %), triphenylphosphine (50 mg, 0.191 mmol, 80 mole %), decane (4 ml), 140 °C, 2.5 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded **16** (72.4 mg, 71%) as a solid and a more polar unstable cobalt complex as an oil. Procedure *B* – Stoichiometric. Triyne **6** (72 mg, 0.169 mmol), $Ni(cod)_2$ (0.06 M in tetrahydrofuran, 2.8 ml, 0.168 mmol, 100 mole %), triphenylphosphine (89 mg, 0.339 mmol, 200 mole %), tetrahydrofuran (4 ml), room temperature, 20 h. Flash chromatography afforded **14** (50.7 mg, 70%), m.p. 191–193 °C (chloroform). IR: 3093 vw, 3068 w, 2951 m, 2899 m, 2839 w, 1601 vw, 1520 vw, 1516 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. ^1H NMR (500 MHz): 0.41 (18 H, s, 2 × $(CH_3)_3Si$); 2.47 (2 H, dd, *J* = 15.4, 13.9, H-5, 10); 2.79 (2 H, brd, *J* = 13.0, H-6, 9); 2.93 (2 H, dd, *J* = 15.2, 13.0, H-6, 9); 3.29 (2 H, brd, *J* = 15.7, H-5, 10); 6.86 (2 H, dt, *J* = 7.7, 7.7, 1.4, H-2, 13); 7.00 (2 H, dd, *J* = 7.8, 1.3, H-1, 14); 7.07 (2 H, dt, *J* = 7.4, 7.4, 1.3, H-3, 12); 7.24 (2 H, brdd, *J* = 7.5, 1.1, H-4, 11). ^{13}C NMR: 4.0 (q, 2 × $(CH_3)_3Si$), 29.9 (t, C-5, 10), 30.5 (t, C-6, 9), 125.3 (d, C-2, 13), 126.5 (d, C-3, 12), 126.9 (d, C-4, 11), 131.0 (d, C-1, 14), 131.5 (s, C-14b, 14c), 135.1 (s, C-14a, 14d), 139.3 (s, C-4a, 10a), 144.2 (s, C-6a, 8a), 147.1 (s, C-7, 8). EI MS: 426 ($M^{\bullet+}$, 78), 411 (11), 395 (9), 354 (98), 338 (12), 279 (75), 265 (10), 131 (6), 73 (100), 59 (29), 45 (12). HR EI MS: calculated for $C_{28}H_{34}Si_2$ 426.2199; found 426.2159.

3-Fluoro-5,6,9,10-tetrahydropentahelicene (**17**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **7** (70 mg, 0.233 mmol), $CpCo(CO)_2$ (13 µl, 0.098 mmol, 40 mole %), triphenylphosphine (49 mg, 0.187 mmol, 80 mole %), decane (4 ml), 140 °C, 3 h. Flash chromatography on silica gel (hexane) afforded **17** (22.7 mg, 33%) as an amorphous solid. IR: 3100 vw, 3064 w, 3037 w, 2943 s, 2903 m, 2843 m, 1625 w (sh), 1610 m, 1595 m, 1584 m, 1571 m, 1495 vs, 1485 m (sh), 1467 w, 1436 vs, 1419 m, 1404 w, 1348 w, 1318 vw, 1294 m, 1279 m, 1258 w, 1235 w, 1188 m, 1164 s, 1130 w (sh), 1121 m, 1110 w, 1029 w, 948 w, 886 s, 824 vw, 812 w (sh), 703 m, 695 m, 628 m, 587 w, 542 s, 529 w, 508 w, 485 w, 451 w, 432 w. ^1H NMR (500 MHz): 2.60–2.96 (8 H, m, 2 × CH_2CH_2); 6.80 (1 H, dt, *J* = 8.4, 8.4, 2.6, H-2); 6.90 (1 H, dd, *J* = 10.8, 2.6, H-4); 6.95 (1 H, dt, *J* = 7.6, 7.6, 1.4, H-13); 7.11 (1 H, d, *J* = 7.5, H-8); 7.13 (1 H, d, *J* = 7.5, H-7); 7.13 (1 H, dt, *J* = 7.5, 7.5, 1.4, H-12); 7.20 (1 H, dd, *J* = 8.3, 5.6, H-1); 7.20 (1 H, dd, *J* = 7.5, 1.4, H-14); 7.27 (1 H, brdd, *J* = 7.7, 1.3, H-11). ^{13}C NMR: 29.1 (t, C-5), 29.8 (t, C-10), 30.1 (t, C-6), 30.3 (t, C-9), 113.4 (dd, J_{CF} = 21.5, C-2), 116.6 (dd, J_{CF} = 22.9, C-4), 125.6 (d, C-13), 126.6 (d, C-12), 127.1 (d, C-7, 8), 127.5 (d, C-11), 128.4 (dd, J_{CF} = 8.3, C-1), 130.1 (d, C-14), 132.1 (s, C-14c), 132.2 (d, J_{CF} = 9.7, C-4a), 133.0 (s, C-14b), 134.1 (s, C-14a), 134.4 (d, J_{CF} = 1.0, C-14d), 139.0 (s, C-10a), 139.1 (s, C-8a), 139.3 (s, C-6a), 160.8 (d, J_{CF} = 241.2, C-3). EI MS: 300 ($M^{\bullet+}$, 100), 283 (14), 270 (9), 257 (6), 201 (5), 183 (4), 135 (10), 77 (12), 71 (13), 57 (22), 51 (10), 43 (19). HR EI MS: calculated for $C_{22}H_{17}F$ 300.1314; found 300.1322.

5,6,9,10-Tetrahydrohexahelicene (**18**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **8** (67 mg, 0.202 mmol), $CpCo(CO)_2$ (5 μl, 0.038 mmol, 20 mole %), triphenylphosphine (21 mg, 0.080 mmol, 40 mole %), decane (3 ml), 140 °C, 30 min. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded **18** (42.9 mg, 64%) as an amorphous solid. Procedure *A* – Catalytic without halogen lamp irradiation. Triyne **8** (91 mg, 0.274 mmol), $CpCo(CO)_2$ (7 μl, 0.053 mmol, 20 mole %), triphenylphosphine (29 mg, 0.111 mmol, 40 mole %), decane (3 ml), 50 °C, 4 days. Flash chromatography afforded **18** (23.7 mg, 26%). Procedure *B* – Stoichiometric. Triyne **8** (33 mg, 0.099 mmol), $Ni(cod)_2$ (0.06 M in tetrahydrofuran, 3.30 ml, 0.198 mmol, 200 mole %), tetrahydrofuran (4 ml), refluxed, 5 min. Flash chromatography afforded **18** (24.8 mg, 75%). IR: 3098 w, 3055 m, 2942 s, 2837 m, 1619 w, 1603 w, 1595 w, 1587 w, 1570 w, 1560 w, 1509 m, 1489 m, 1436 s, 1425 m, 1416 w, 1250 w, 1159 w, 1113 w, 1037 w, 1027 w, 946 w, 865 w, 846 vs, 819 s, 589 w, 505 w. ^{1}H NMR (500 MHz): 2.66 (1 H, ddt, *J* = 15.0, 4.3, 1.4, 1.4, H-10); 2.69 (1 H, ddt, *J* = 15.2, 4.4, 1.4, 1.4, H-9); 2.75 (1 H, ddt, *J* = 15.2, 4.4, 1.4, 1.4, H-10); 2.86 (1 H, ddd, *J* = 14.8, 4.3, 2.2, H-5); 2.88 (1 H, ddt, *J* = 14.1, 4.1, 2.0, 2.0, H-6); 2.91 (1 H, ddd, *J* = 15.2, 4.5, 2.1, H-9); 3.01 (1 H, brddd, *J* = 14.7, 10.1, 4.2, H-5); 3.04 (1 H, brddd, *J* = 14.2, 10.0, 4.4, H-6); 6.34 (1 H, ddt, *J* = 7.8, 6.8, 1.2, 1.2, H-2); 6.36 (1 H, dd, *J* = 7.8, 1.9, H-1); 6.81 (1 H, ddd, *J* = 7.4, 6.8, 1.9, H-3); 6.84 (1 H, ddd, *J* = 8.3, 6.8, 1.3, H-15); 7.10 (1 H, ddd, *J* = 8.0, 6.8, 1.2, H-14); 7.15 (1 H, dq, *J* = 7.3, 0.8, 0.8, 0.8, H-4); 7.20 (1 H, dd, *J* = 7.4, 1.0, H-7); 7.25 (1 H, dd, *J* = 7.4, 1.0, H-8); 7.47 (1 H, d, *J* = 8.0, H-11); 7.47 (1 H, dq, *J* = 8.5, 1.0, 1.0, 1.0, H-16); 7.64 (1 H, brd, *J* = 8.1, H-13); 7.70 (1 H, brd, *J* = 8.2, H-12). ^{13}C NMR: 29.9 (t, C-6), 30.0 (t, C-5), 30.6 (t, C-9), 31.1 (t, C-10), 124.2 (d, C-14), 124.7 (d, C-15), 125.1 (d, C-2), 126.0 (d, C-11), 126.1 (d, C-8, 16), 126.2 (d, C-3), 126.3 (d, C-7), 127.0 (d, C-4), 127.51 (d, C-12), 127.53 (d, C-13), 128.1 (d, C-1), 129.4 (s, C-16a), 131.0 (s, C-16c), 132.1 (s, C-16b), 133.0 (s, C-12a), 134.3 (s, C-16d), 135.4 (s, C-16e), 137.8 (s, C-4a), 138.0 (s, C-6a, 10a), 140.6 (s, C-8a). EI MS: 332 ($M^{\bullet+}$, 100), 315 (11), 256 (12), 197 (9), 150 (8), 83 (6), 69 (9), 57 (8). HR EI MS: calculated for $C_{26}H_{20}$ 332.1565; found 332.1492.

7,8-Dimethyl-5,6,9,10-tetrahydrohexahelicene (**19**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **9** (80 mg, 0.241 mmol), $CpCo(CO)_2$ (6 μl, 0.045 mmol, 20 mole %), triphenylphosphine (25 mg, 0.095 mmol, 40 mole %), decane (5 ml), 140 °C, 1 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded **19** (54 mg, 68%) as an amorphous solid. IR: 3056 m, 3007 vs, 1620 w, 1603 w, 1595 w, 1586 w, 1572 w (sh), 1560 w, 1509 m, 1488 m, 1480 m (sh), 1436 vs, 1376 m, 1260 w, 1142 w, 1135 vw, 1090 w, 1034 m, 1028 m, 999 w, 974 w, 866 w, 815 vs, 700 s, 610 m, 572 w, 539 s, 459 m, 430 m. ^{1}H NMR (500 MHz): 2.39 (3 H, s, CH_3); 2.40 (3 H, s, CH_3); 2.40–2.52 (2 H, m, H-9, 10); 2.91–3.03 (4 H, m, H-5, 6, 9, 10); 3.15 (1 H, ddd, *J* = 14.9, 3.9, 2.7, H-5); 3.21 (1 H, ddd, *J* = 15.5, 4.6, 2.6, H-6); 6.31–6.36 (2 H, m, H-1, 2); 6.77 (1 H, m, H-3); 6.86 (1 H, ddd, *J* = 8.6, 6.7, 1.4, H-15); 7.08 (1 H, ddd, *J* = 8.0, 6.7, 1.2, H-14); 7.12 (1 H, brdq, *J* = 7.2, 0.9, 0.9, 0.9, H-4); 7.47 (1 H, d, *J* = 8.1, H-11); 7.51 (1 H, ddt, *J* = 8.6, 1.2, 0.9, 0.9, H-16); 7.61 (1 H, ddt, *J* = 8.0, 1.4, 0.8, 0.8, H-13); 7.68 (1 H, brd, *J* = 8.1, H-12). ^{13}C NMR: 16.4 (q, CH_3), 16.7 (q, CH_3), 26.7 (t, C-6), 29.9 (t, C-5), 27.1 (t, C-9), 31.0 (t, C-10), 124.0 (d, C-14), 124.7 (d, C-15), 125.0 (d, C-2), 125.7 (d, C-11), 125.8 (d, C-3), 125.9 (d, C-16), 126.5 (d, C-4), 127.1 (d, C-12), 127.5 (d, C-13), 128.3 (d, C-1), 129.0 (s, C-16c), 129.7 (s, C-16a), 132.7 (s, C-16b), 132.4 (s, C-7), 132.7 (s, C-16d), 132.90 (s, C-8), 132.94 (s, C-12a), 135.7 (s, C-6a), 136.2 (s, C-16e), 137.21 (s, C-10a), 137.24 (s, C-4a), 138.7 (s, C-8a). EI MS: 360 ($M^{\bullet+}$, 15), 262 (100), 183 (71), 152 (9), 108 (37), 77 (15), 51 (26). HR EI MS: calculated for $C_{28}H_{24}$ 360.1878; found 360.1874.

7,8,11,12-Tetrahydroheptahelicene (**20**)

Procedure *A* – Catalytic with halogen lamp irradiation. Triyne **10** (80 mg, 0.209 mmol), $CpCo(CO)_2$ (5 μl, 0.038 mmol, 20 mole %), triphenylphosphine (22 mg, 0.084 mmol, 40 mole %), decane (5 ml), 140 °C, 2 h. Flash chromatography on silica gel (petroleum ether-ether 100:0 to 96:4) afforded **20** (51 mg, 64%) as an amorphous solid. Procedure *B* – Stoichiometric. Triyne **10** (28 mg, 0.073 mmol), $Ni(cod)_2$ (0.06 M in tetrahydrofuran, 2.40 ml, 0.144 mmol, 200 mole %), tetrahydrofuran (4 ml), refluxed, 5 min. Flash chromatography afforded **20** (6.7 mg, 24%). IR: 3054 w, 3009 m, 2929 vs, 2856 m, 1620 vw, 1595 w, 1580 vw, 1566 vw, 1512 w, 1467 w, 1436 w, 1422 vw (sh), 1377 w, 1329 vw, 1309 vw, 1261 w, 1244 w, 1159 w, 1024 w, 866 w, 823 m, 811 m, 683 w, 504 w, 454 w. ^1H NMR (500 MHz): 2.76 (2 H, dddd, *J* = 15.8, 14.9, 4.1, 1.3, H-7, 12); 2.96 (2 H, ddd, *J* = 14.8, 4.1, 2.0, H-8, 11); 2.99 (2 H, ddd, *J* = 15.8, 4.2, 2.0, H-7, 12); 3.10 (2 H, ddd, *J* = 14.9, 14.8, 4.2, H-8, 11); 6.53 (2 H, ddd, *J* = 8.6, 6.8, 1.3, H-2, 17); 6.82 (2 H, ddd, *J* = 8.1, 6.8, 1.2, H-3, 16); 6.96 (2 H, dddd, *J* = 8.6, 1.3, 1.2, 0.7, H-1, 18); 7.20 (2 H, ddd, *J* = 8.1, 1.3, 0.7, H-4, 15); 7.33 (2 H, dd, *J* = 8.2, 1.0, H-5, 14); 7.34 (2 H, s, H-9, 10); 7.34 (2 H, d, *J* = 8.2, H-6, 13). ^{13}C NMR: 30.4 (t, C-7, 12), 31.0 (t, C-8, 11), 123.5 (d, C-6, 13), 123.8 (d, C-1, 18), 123.9 (d, C-2, 17), 125.8 (d, C-4, 15), 125.9 (d, C-3, 16), 126.6 (d, C-5, 14), 127.2 (d, C-9, 10), 128.9 (s, C-18a, 18f), 132.2 (s, C-18c, 18d), 132.7 (s, C-18b, 18e), 132.8 (s, C-4a, 14a), 137.5 (s, C-6a, 12a), 139.6 (s, C-8a, 10a). EI MS: 382 ($M^{\bullet+}$, 100), 365 (4), 354 (7), 276 (3), 239 (4), 175 (4), 97 (6), 83 (9), 71 (14), 69 (17), 57 (36), 55 (28), 43 (43). HR EI MS: calculated for $C_{30}H_{22}$ 382.1722; found 382.1710.

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