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Synthesis of oxaspiro[*m.n*] skeletons based on the Nicholas reaction

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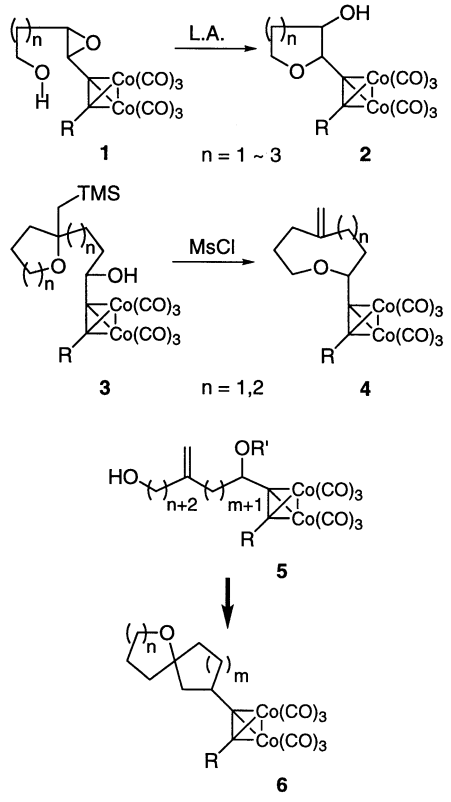
Abstract—Treatment of alkyne–$Co_2(CO)_6$ complexes possessing a methylidene moiety as well as a terminal hydroxy functionality with $SnCl_4$ at 0°C effected tandem ring-closure reactions resulting in the formation of 1-oxaspiro[4.4]nonane, 1-oxaspiro[4.5]decane, 6-oxaspiro-[4.5]decane, and 1-oxaspiro[5.5]undecane frameworks in high yields.

Alkyne–$Co_2(CO)_6$ complexes, which are easily prepared by reacting alkynes with commercially available dicobaltoctacarbonyl ($Co_2(CO)_8$), have been shown to liberate the corresponding propynyl cation species upon treatment with a suitable acid, such as a Lewis acid. The newly generated cation species are subsequently inter- or intramolecularly captured by various kinds of nucleophiles. This reaction is well known as the Nicholas reaction.[1] During the course of our studies on the development of an efficient method for constructing oxacycles based on the Nicholas reaction, we noted a highly stereoselective procedure for preparing five- to seven-membered oxacycles **2**[2] by taking advantage of *endo*-mode cyclization of the alkyne–cobalt complexes **1** with an epoxy functionality adjacent to the complexed alkyne moiety (Scheme 1). In addition, a procedure for the formation of medium-sized oxacycles **4** (eight or nine members)[3] was developed by combining the propynyl cation-stabilizing ability of alkyne–$Co_2(CO)_6$ complexes **3** with the β-effect of the trimethylsilyl group, as shown in Scheme 1. In this paper, we describe the use of alkyne–$Co_2(CO)_6$ complexes **5** to construct oxaspiro[4.4]nonane, oxaspiro[4.5]decane, and oxaspiro[5.5]undecane frameworks **6** via tandem ring-closure steps initiated by a Nicholas-type reaction.

At the inception of this program, we investigated ring construction of 1-oxaspiro[4.4]nonane derivative **13**. The required starting alkyne–$Co_2(CO)_6$ complex **11** for ring-closure experiments was synthesized as depicted in Scheme 2. Wittig reaction of the known 4-heptanone derivative **7**[3] with methylidenetriphenylphosphorane was followed by debenzylation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give the alcohol derivative **8** in 87% yield. An alkyne moiety was introduced by successive oxidation of **8** under Swern conditions and the addition of phenylacetylide to give the alkyne derivative **9** in 49% yield. Methylation of the propynyl alcohol moiety of **9** with methyl iodide was followed by desilylation to provide **10**, which was subsequently treated with $Co_2(CO)_8$ to give the alkyne–$Co_2(CO)_6$ complex **11** in 83% overall yield from **9**.



Scheme 1.

Keywords: oxaspiro[*m.n*] skeletons; Nicholas reaction; dicobaltoctacarbonyl.

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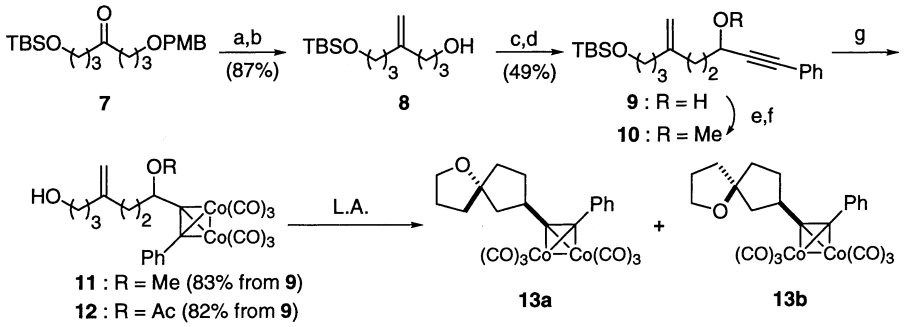
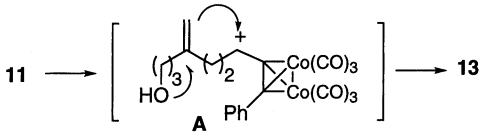


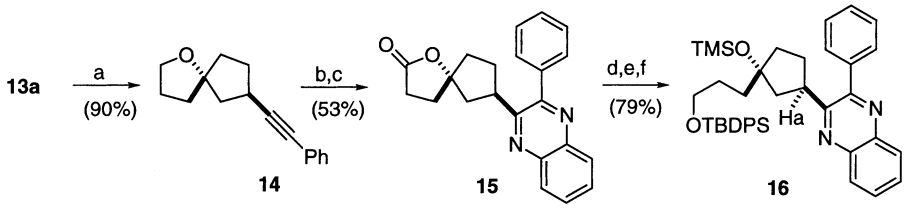
Starting Material	Lewis Acid	Equiv.	Yield (%)	13a : 13b
11	TMSOTf	1.1	—	—
11	$TiCl_4$	1.1	—	—
11	$BF_3{\cdot}OEt_2$	1.1	30	67 : 33
11	$SnCl_4$	2.0	53	87 : 13
12	$SnCl_4$	2.0	83	83 : 17

Scheme 2. *Reagents and conditions*: (a) Ph_3PCH_3Br, ^tBuOK, THF; (b) DDQ, CH_2Cl_2, H_2O; (c) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2; (d) phenylacetylene, ^nBuLi; (e) MeI, NaH, THF; (f) TBAF, THF; (g) $Co_2(CO)_8$, Et_2O; (h) Ac_2O, DMAP, CH_2Cl_2.

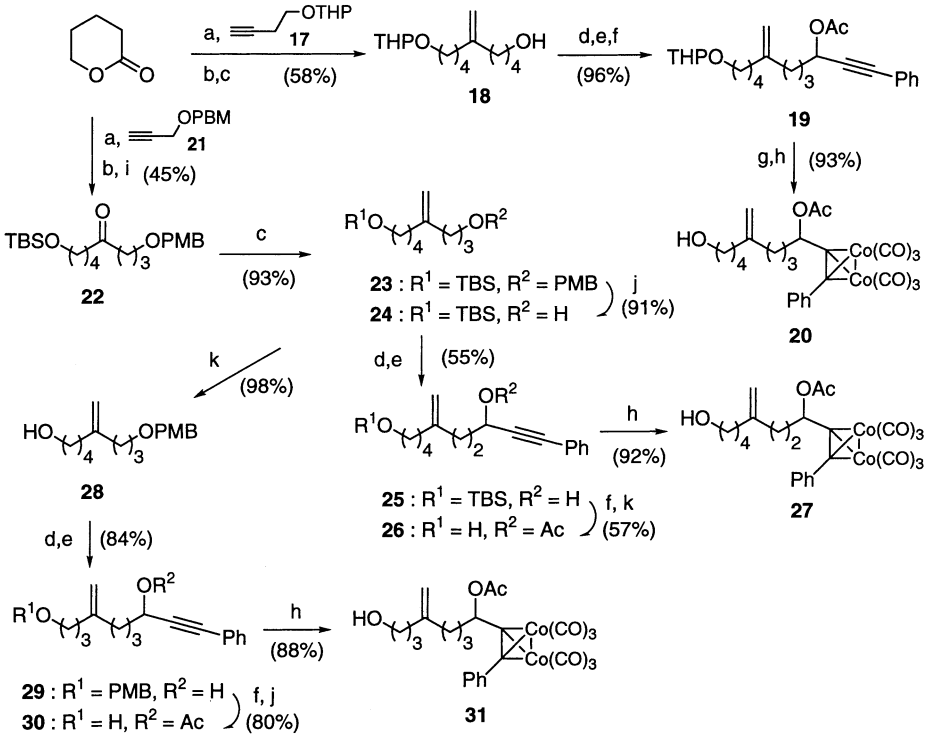


Alkyne–$Co_2(CO)_6$ complex **11** was then subjected to Lewis acid-catalyzed ring-formation reaction to obtain the 1-oxaspiro[4.4]nonane framework. Treatment of the methoxy derivative **11** with 1.1 equiv. of TMSOTf in CH_2Cl_2 at −40°C gave a complex mixture. Similar treatment with $TiCl_4$ again gave an intractable mixture. However, when complex **11** was exposed to $BF_3{\cdot}OEt_2$ at 0°C, the desired 1-oxaspiro derivatives **13a** and **13b** were obtained in 30% yield in a ratio of 67:33. After screening various Lewis acids,[4] $SnCl_4$ was found to be suitable for this ring-closure reaction. Thus, a mixture of **13a** and **13b** (**13a/13b**=87:13) was produced in 53% yield on exposure to 2 equiv. of $SnCl_4$ at 0°C for 1 h. Although 1-oxaspiro[4.4]nonane derivative **13** was obtained, the yield was far from satisfactory. A simple mechanistic explanation involves an initial generation of the propynyl cation species **A**,[1] which induces cationic olefin-cyclization with the methylene moiety anchimerically assisted by the terminal hydroxy group to give rise to the formation of the 1-oxaspiro skeleton. Consequently, we expected that changing the methoxy group at the propynyl position to a more powerful leaving group such as an acetoxy group would improve the chemical yield in this ring-closure reaction. Thus, alkyne–$Co_2(CO)_6$ complex **12** with an acetoxy group was prepared in 82% overall yield from **9** by successive acetylation, desilylation and cobalt complex formation (see Section 1). Alkyne–$Co_2(CO)_6$ complex **12** was then exposed to the best conditions identified thus far i.e. 2 equiv. of $SnCl_4$ in CH_2Cl_2 at 0°C for 1 h, and this resulted in the formation of **13a** and **13b** in 83% yield in a ratio of 83:17. Cobalt complexation is necessary for this tandem ring-closure reaction. In fact, no reaction took place when the acetyl derivative of uncomplexed alkyne **9** was exposed to the conditions used for the synthesis of **13**.

Regeneration of the triple bond from the alkyne–$Co_2(CO)_6$ moiety is already well established. Thus, **13a** was converted into alkyne derivative **14** (90% yield) by treatment with cerium(IV) ammonium nitrate (CAN)[5] in acetone at room temperature (Scheme 3). The stereochemistry of **13** was confirmed by an NOE experiment with the quinoxaline derivative **16**. Oxidation of **13** with ruthenium dioxide[6] in the presence of sodium periodate effected not only 1,2-dicarbonylation of the triple bond, but also conversion of the tetrahydrofuran ring into the γ-lactone to produce a labile 4-butanolide derivative with 1,2-dicarbonyl



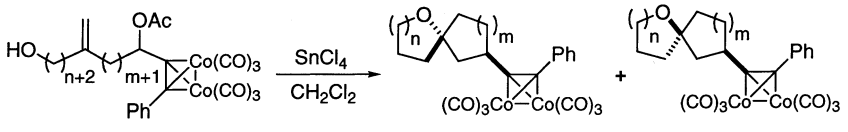
Scheme 3. *Reagents and conditions*: (a) CAN, acetone; (b) RuO_2, CCl_4, CH_3CN, H_2O; (c) *o*-phenylenediamine, CH_2Cl_2; (d) $LiAlH_4$, Et_2O; (e) TBDPSCl, Imid., DMF; (f) TMS-Imid., CH_2Cl_2.



Scheme 4. *Reagents and conditions*: (a) ^{n}BuLi, THF; (b) H_2, 5%Pd–C, AcOEt; (c) Ph_3PCH_3Br, ^{t}BuOK, THF; (d) Py·SO_3, Et_3N, DMSO, CH_2Cl_2; (e) phenylacetylene, nBuli; (f) Ac_2O, DMAP, CH_2Cl_2; (g) PPTS, MeoH; (h) $Co_2(CO)_8$, Et_2O; (i) Cl, Imid., DMF; (j) DDQ, CH_2Cl_2, H_2O; (k) TBAF, THF.

functionality. This compound was subsequently treated with *o*-phenylenediamine to give the quinoxaline derivative **15**[7] in 53% yield. Reduction of **15** with $LiAlH_4$ afforded the diol, the primary hydroxy group of which was first silylated with TBDPSCl. The resulting tertiary hydroxy moiety was then protected with a TMS group, resulting in the formation of **16** in an overall yield of 79%. Since an NOE experiment with **16** revealed 8.2% enhancement between the TMS group and Ha, stereochemistries of both **13** and **16** were confirmed as depicted in Schemes 2 and 3.

The next step in this program was to see whether this procedure could be used to prepare other oxaspiro frameworks. We chose δ-valerolactone as a common starting material for the synthesis of alkyne–$Co_2(CO)_6$ complexes **20**, **27**, and **31**, which would produce the oxaspiro[5.5]undecane and oxaspiro[4.5]decane skeletons. The starting cobalt complex **20** for the oxaspiro[5.5]undecane derivative was prepared as follows (Scheme 4). δ-Valerolactone was treated with the acetylide, adjusted from the reaction of **17** with ^{n}BuLi, to give the crude ring-opened product, which was then hydrogenated under a hydrogen atmosphere in the presence of 5% Pd–C to give the saturated 1-hydroxynonanone derivative. This compound was exposed to the Wittig conditions described for the conversion of **7** to **9**, and this resulted in the formation of **18** in 58% overall yield. Consecutive oxidation, addition of phenylacetylide, and acetylation of **18** provided **19** in 96% yield. A tetrahydropyranyl moiety of **19** was then removed by pyridinium *p*-toluenesulfonate (PPTS) in MeOH, and the resulting hydroxy compound was treated with $Co_2(CO)_8$ in Et_2O. Thus, the required alkyne–$Co_2(CO)_6$ complex **20** was obtained in 93% yield from **19**.



20 : n = 2, m = 2
27 : n = 2, m = 1
31 : n = 1, m = 2

32a : n = 2, m = 2
33a : n = 2, m = 1
34a : n = 1, m = 2

32b : n = 2, m = 2
33b : n = 2, m = 1
34a : n = 1, m = 2

Starting Material	Product	Yield (%)
20	**32a** : **32b** = 56 : 44	63
27	**33a** : **33b** = 49 : 51	81
31	**34a** : **34b** = 51 : 49	87

Scheme 5.

The two other alkyne–$Co_2(CO)_6$ complexes **27** and **31** for the ring-closure reaction were obtained in a manner similar to that described for the preparation of **20** (Scheme 4).

Treatment of the alkyne–$Co_2(CO)_6$ complex **20** with 2 equiv. of $SnCl_4$ in CH_2Cl_2 at 0°C nonstereoselectively afforded the ring-closed products, 1-oxaspiro[5.5]undecane derivatives **32a** and **32b** (56:44),[8] in 63% yield. The ring-closure of **20** proceeded as anticipated, but no significant stereoselectivity was observed. This is in sharp contrast to the case of **11**, where **13a** was predominantly formed (**13a/13b**=83:17). Similarly, the 6-oxaspiro[4.5]decane derivatives **33a** and **33b** (49:51)[8] were formed nonstereoselectively in 81% yield when **27** was exposed to $SnCl_4$. In addition, alkyne–$Co_2(CO)_6$ complex **31** underwent acid-catalyzed ring-closure, which gave rise to the formation of a mixture of 1-oxaspiro[4.5]decane compounds **34a** and **34b** in a ratio of 51:49 (Scheme 5).[8]

In summary, we have described here an alternative application of the Nicholas reaction to ring construction with which the 1-oxaspiro[4.4]nonane, 1-oxaspiro[4.5]decane, 6-oxaspiro[4.5]decane, and 1-oxaspiro[5.5]undecane frameworks were efficiently constructed by taking advantage of the propynyl cation species generated from alkyne–$Co_2(CO)_6$ complexes. Further studies on the scope and limitations of the *endo*-mode cyclization of alkyne–$Co_2(CO)_6$ are now in progress.

1. Experimental

1.1. General

Infrared spectra were measured with a Shimazu IR-460 spectrometer in $CHCl_3$, mass spectra with a Hitachi M-80 mass spectrometer, ^{1}H NMR spectra with JEOL JNM-EX270 and JNM-GSX500 spectrometers for samples in $CDCl_3$, using either tetramethylsilane (for compounds without a silyl group) or $CHCl_3$ (7.26 ppm)(for compounds with a silyl group) as an internal standard, and ^{13}C NMR spectra with JEOL JNM-EX270 and JNM-GSX500 spectrometers in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal reference. All reactions were carried out under a nitrogen atmosphere otherwise stated. Silica gel (Silica gel 60, 230–400 mesh, Merck) was used for chromatography. Organic extracts were dried over anhydrous $_2SO_4$.

1.1.1. 7-(*tert*-Butyldimethylsiloxy)-4-methyleneheptan-1-ol (8). To a suspension of ^{t}BuOK (3.45 g, 30.8 mmol) in THF (41.0 mL) was added methyltriphenylphosphonium bromide (11.0 g, 30.8 mmol) at 0°C and the THF solution was stirred for 15 min. A solution of **7** (3.90 g, 10.3 mmol) in THF (10.0 mL) was added to this THF solution of the resulting methylenetriphenylphosphorane at room temperature. After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was taken up in a combined solution of CH_2Cl_2 and H_2O (20:1, 50.0 mL), to which was added DDQ (3.49 g, 15.4 mmol). The reaction mixture was stirred at room temperature and quenched by addition of saturated aqueous $NaHCO_3$. The resulting precipitates were filtered off and the filtrate was extracted with Et_2O, which was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (4:1) to give **8** (2.31 g, 87%) as a colorless oil: IR 3456, 1645 cm^{-1}; ^{1}H NMR δ 4.75 (2H, s), 3.65 (2H, t, J=6.4 Hz), 3.61 (2H, t, J=6.4 Hz), 2.10 (2H, t, J=7.8 Hz), 2.07 (2H, t, J=7.8 Hz), 1.74–1.62 (4H, m), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR δ 149.0, 109.2, 62.8, 62.7, 32.4, 32.1, 30.9, 30.7, 25.9, 18.3, −5.3; MS m/z 201 ($M^+-{}^t$Bu, 28). Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.06; H, 11.70. Found: C, 64.75; H, 11.95.

1.1.2. 9-(*tert*-Butyldimethylsiloxy)-6-methylene-1-phenylnon-1-yn-3-ol (9). A solution of DMSO (0.80 mL, 11.3 mmol) in CH_2Cl_2 (4.00 mL) was added to a solution of oxalyl chloride (0.49 mL, 5.63 mmol) in CH_2Cl_2 (20.0 mL) at −78°C over a period of 5 min. After the mixture was stirred for 30 min, a solution of the alcohol **8** (726 mg, 2.81 mmol) in CH_2Cl_2 (4.00 mL) was added to the CH_2Cl_2 solution, and the reaction mixture was stirred at the same temperature for 1.5 h. Et_3N (3.92 mL, 28.1 mmol) was then added to the reaction mixture, which was gradually warmed to room temperature over a period of 1 h and diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed with water and brine, dried, and concentrated to leave the crude aldehyde. The crude aldehyde was used directly for the next reaction. To a solution of phenylacetylene (0.34 mL, 3.09 mmol) in THF (24.0 mL) was added ^{n}BuLi (1.42 M hexane solution, 2.20 mL, 3.09 mmol) at 0°C, and the reaction mixture was stirred for 30 min. A solution of the crude aldehyde in THF (4.00 mL) was then added to a solution of the acetylide in THF solution thus adjusted at 0°C, and stirring was continued for 1 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (20:1) to give **9** (491 mg, 49%) as a colorless oil: IR 3412, 1645 cm^{-1}; ^{1}H NMR δ 7.44–7.30 (5H, m), 4.81 (1H, s), 4.80 (1H, s), 4.62 (1H, t, J=6.4 Hz), 3.62 (2H, t, J=6.4 Hz), 2.27 (2H, t, J=7.3 Hz), 2.11 (2H, t, J=7.3 Hz), 1.97–1.92 (2H, m), 1.71–1.58 (2H, m), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR δ 148.5, 131.7, 128.4, 128.3, 122.6, 109.6, 89.9, 85.1, 62.8, 62.7, 35.9, 32.3, 31.6, 30.9, 26.0, 18.3, −5.3; MS m/z 301 ($M^+-{}^t$Bu, 1.3). Anal. Calcd for $C_{22}H_{34}O_2Si$: C, 73.69; H, 9.56. Found: C, 73.31; H, 9.71.

1.1.3. Hexacarbonyl-μ-[η^4-3-methoxy-6-methylene-1-phenylnon-1-yn-9-ol]dicobalt(Co–Co) (11). To a solution of **9** (1.00 g, 2.79 mmol) in THF (28.0 mL) was added NaH (134 mg, 3.35 mmol) and MeI (1.04 mL, 16.7 mmol) at 0°C. The reaction mixture was stirred at 0°C for 30 min and then at room temperature for 1 h, quenched by addition of water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to leave **10**. TBAF (1.00 M THF solution, 3.10 mL, 3.10 mmol) was added to a solution of the crude **10** in THF (28.0 mL) and the mixture was stirred at room temperature for 30 min. THF was evaporated off and the resulting oil was dissolved in Et_2O (28.0 mL). $Co_2(CO)_8$ (1.08 g, 4.18 mmol) was added to the Et_2O solution and the mixture was stirred at room temperature for 30 min. Et_2O was evaporated off and

the residue was chromatographed with hexane–AcOEt (3:1) to give **11** (1.26 g, 83%) as a reddish brown oil: IR 2091, 2054, 2029 cm^{-1}; ^1H NMR δ 7.50–7.26 (5H, m), 4.82 (1H, s), 4.78 (1H, s), 4.53 (1H, t, J=6.4 Hz), 3.67–3.61 (2H, m), 3.51 (3H, s), 2.39–2.19 (2H, m), 2.13–2.04 (2H, m), 1.98–1.90 (2H, m), 1.74–1.64 (2H, m); ^{13}C NMR δ 199.5, 148.2, 137.9, 129.4, 128.8, 127.7, 109.8, 98.5, 91.7, 81.3, 65.8, 62.5, 59.0, 36.1, 32.4, 30.7; MS m/z 544 (M^+, 5.6). Anal. Calcd for $C_{23}H_{22}Co_2O_8$: C, 50.75; H, 4.07. Found: C, 50.63; H, 4.20.

1.1.4. Hexacarbonyl-μ-[η⁴-3-acetoxy-6-methylene-1-phenylnon-1-yn-9-ol]dicobalt(Co–Co) (12). A solution of **9** (720 mg, 2.01 mmol), DMAP (736 mg, 6.03 mmol), and Ac_2O (0.28 mL, 3.02 mmol) in CH_2Cl_2 (20.0 mL) was allowed to stand at 0°C for 30 min. The mixture was washed with water and brine, dried, and concentrated to leave the crude acetate. According to the procedure described for the preparation of **11**, this crude acetate was successively treated with TBAF and $Co_2(CO)_8$ to afford, after purification by chromatography with hexane–AcOEt (3:1), **12** (948 mg, 82%) as a reddish brown oil: IR 2093, 2056, 2025, 1733 cm^{-1}; ^1H NMR δ 7.47–7.28 (5H, m), 6.40 (1H, m), 4.81 (1H, s), 4.74 (1H, s), 3.65–3.61 (2H, m), 2.20–1.96 (6H, m), 2.14 (3H, s), 1.68–1.65 (2H, m); ^{13}C NMR δ 198.8, 170.5, 147.4, 137.4, 129.4, 128.9, 128.0, 110.0, 96.2, 90.5, 73.8, 62.5, 35.5, 32.4, 32.2, 30.6, 20.7; MS m/z 571 (M^+-1, 3.5). Anal. Calcd for $C_{24}H_{22}Co_2O_9$: C, 50.37; H, 3.87. Found: C, 50.20; H, 3.97.

1.2. Ring closure of 11, 12, 20, 27, and 30 with $SnCl_4$

A solution of $SnCl_4$ in CH_2Cl_2 (0.10 M solution; 2.36 mL, 2.36×10^{-1} mmol) was added to a solution of **12** (67.5 mg, 1.18×10^{-1} mmol), in CH_2Cl_2 (11.8 mL) at 0°C for 30 min. The reaction mixture was stirred for 1 h and quenched by addition of water. The CH_2Cl_2 layer was separated, washed with water and brine, dried, and concentrated to dryness. Chromatography with hexane–AcOEt (100:1) afforded **13a** (41.6 mg, 72%) and **13b** (6.50 mg, 11%). Treatment of **11** with $SnCl_4$ also gave a mixture of **13a** and **13b**. Similar treatment of **20**, **27**, and **31** with $SnCl_4$ gave the corresponding oxaspiro derivatives **32**, **33**, and **34**, respectively. Chemical yields and ratio of diastereoisomers are summarized in Schemes 2 and 5.

1.2.1. Hexacarbonyl-μ-[η⁴-(5*R,7*S**)-7-phenylethynyl-1-oxaspiro[4.4]-nonane]dicobalt(Co–Co) (13a).** A reddish brown oil: IR 2090, 2050, 2023 cm^{-1}; ^1H NMR δ 7.56–7.29 (5H, m), 3.85–3.80 (2H, m), 3.52 (1H, m), 2.40–1.70 (10H, m); ^{13}C NMR δ 199.8, 138.2, 129.4, 128.8, 127.7, 104.3, 91.7, 90.8, 66.9, 47.7, 42.7, 38.0, 36.0, 34.0, 25.9; MS m/z 512 (M^+, 0.8). HRMS calcd for $C_{22}H_{18}Co_2O_7$ 511.9717, found 511.9707.

1.2.2. Hexacarbonyl-μ-[η⁴-(5*R,7*R**)-7-phenylethynyl-1-oxaspiro[4.4]-nonane]dicobalt(Co–Co) (13b).** A reddish brown oil: IR 2090, 2050, 2023 cm^{-1}; ^1H NMR δ 7.39–7.26 (5H, m), 3.84–3.77 (2H, m), 3.11 (1H, m), 2.24–2.17 (2H, m), 1.95–1.72 (8H, m); MS m/z 512 (M^+, 1.5). Anal. Calcd for $C_{22}H_{18}Co_2O_7$: C, 51.59; H, 3.54. Found: C, 51.70; H, 3.76.

1.2.3. (5*R,7*S**)-7-Phenylethynyl-1-oxaspiro[4.4]nonane (14).** CAN (103 mg, 1.87×10^{-1} mmol) was added to a solution of **13a** (23.9 mg, 4.67×10^{-2} mmol) in acetone (4.70 mL) at 0°C. After being stirred for 15 min, the reaction mixture was concentrated, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (40:1) to give **14** (9.50 mg, 90%) as a colorless oil: ^1H NMR δ 7.39–7.26 (5H, m), 3.82–3.77 (2H, m), 3.12 (1H, m), 2.22–2.17 (2H, m), 1.95–1.72 (8H, m); ^{13}C NMR δ 131.5, 128.1, 127.5, 124.6, 94.1, 90.5, 80.3, 66.7, 45.7, 37.5, 36.2, 32.3, 29.2, 25.9; MS m/z 226 (M^+, 91). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.56; H, 8.11.

1.2.4. (5*R,7*S**)-7-(2-Phenylquinoxalin-3-yl)-1-oxaspiro-[4.4]nonan-2-one (15).** $RuO_2\cdot(H_2O)_n$ (5.90 mg, 0.45×10^{-1} mmol) and $NaIO_4$ (715 mg, 3.35 mmol) was added to a two-phase solution of **14** (50.5 mg, 2.23×10^{-1} mmol) in CCl_4 (0.50 mL), CH_3CN (0.50 mL), and water (0.90 mL) under vigorous stirring. Stirring was continued for 12 h at room temperature. The reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The crude lactone derivative was dissolved in CH_2Cl_2 (2.20 mL), to which *o*-phenylenediamine (28.9 mg, 0.27 mmol) was added. The reaction mixture was stirred at room temperature for 15 min, diluted with water, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (3:1) gave **15** (41.0 mg, 53%) as a colorless oil: IR 1763 cm^{-1}; ^1H NMR δ 8.12–8.04 (2H, m), 7.76–7.71 (2H, m), 7.57–7.50 (5H, m), 3.99 (1H, tt, J=8.8, 7.5 Hz), 2.66–2.60 (2H, m), 2.57–1.99 (8H, m); ^{13}C NMR δ 176.5, 157.9, 154.9, 141.4, 140.7, 139.7, 129.7, 129.5, 129.2, 129.1, 128.7, 128.6, 128.5, 95.3, 45.1, 41.8, 38.3, 32.2, 32.0, 29.8; MS m/z 344 (M^+, 0.2). HRMS calcd for $C_{22}H_{20}N_2O_2$ 344.1525, found 344.1522.

1.2.5. (1′*R,3′*S**)-2-[1′-(1″-*tert*-Butyldiphenylsiloxy)propyl-1′-trimethylsiloxycyclopent-3′-yl]-3-phenylquinoxaline (16).** To a solution of **15** (33.5 mg, 0.97×10^{-1} mmol) in Et_2O (1.00 mL) was added $LiAlH_4$ (5.50 mg, 1.46×10^{-1} mmol) at 0°C. The reaction mixture was stirred at the same temperature for 30 min and quenched by addition of water. The precipitates were filtered off and the filtrate was dried and concentrated. The crude diol derivative was dissolved in DMF (0.10 mL), to which TBDPSCl (40.0 mg, 1.46×10^{-1} mmol) and imidazole (19.8 mg, 0.29 mmol). The reaction mixture was stirred at room temperature for 1 h, diluted with water, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. A solution of the crude product thus prepared and TMS–imidazole (20.5 mg, 1.46×10^{-1} mmol) in CH_2Cl_2 (1.00 mL) was allowed to stand for 10 min at room temperature. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (8:1) gave **16** (50.5 mg, 79%) as a colorless oil: ^1H NMR δ 8.12–8.05 (2H, m), 7.74–7.34 (17H, m), 3.90 (1H, m), 3.69 (2H, t, J=5.4 Hz), 2.12–1.89 (6H, m), 1.82–1.64 (4H, m), 1.06 (9H, s), −0.02 (9H, s); ^{13}C NMR δ 159.2, 155.1, 141.6,

140.4, 139.1, 139.0, 135.6, 134.1, 129.5, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 127.6, 85.8, 64.5, 47.2, 42.0, 39.6, 37.7, 31.8, 28.3, 26.9, 19.2, 2.1; FABMS *m/z* 659 (M^++1, 11). FABHRMS calcd for $C_{41}H_{51}N_2O_2Si_2$ 659.3489, found 659.3499.

1.2.6. 9-Tetrahydropyranyloxy-5-methylenenonan-1-ol (18). To a solution of **17** (7.64 g, 49.5 mmol) in THF (145 mL) was added ^{n}BuLi (1.34 M hexane solution, 36.9 mL, 49.5 mmol) at 0°C, and the reaction mixture was stirred for 30 min. A solution of δ-valerolactone (4.95 g, 49.5 mmol) in THF (20.0 mL) was then added to a solution of the acetylide in THF solution thus adjusted at 0°C over a period of 20 min, and stirring was continued for 30 min. The reaction was quenched by addition of saturated aqueous NH_4Cl, extracted with AcOEt, dried, and concentrated. A solution of the crude adduct in AcOEt (165 mL) in the presence of 5% Pd–C (760 mg) was hydrogenated under hydrogen atmosphere for 1 h. The catalyst was filtered off and the filtrated was concentrated to leave the crude nonanone derivative. According to the procedure described for conversion of **7** to **8**, this compound was exposed to methylenetriphenylphosphorane, prepared from ^{t}BuOK (16.6 g, 148.5 mmol) and methyltriphenylphosphonium bromide (53.0 g, 148.5 mmol), to give **18** (7.36 g, 58%) after purification by chromatography with hexane–AcOEt (3:1). Compound **18** was a colorless oil: IR 3449, 1643 cm^{-1}; ^{1}H NMR δ 4.75 (2H, s), 4.58 (1H, dd, *J*=4.4, 2.9 Hz), 3.87 (1H, ddd, *J*=11.2, 7.3, 2.9 Hz), 3.75 (1H, dt, *J*= 9.8, 6.8 Hz), 3.66 (2H, t, *J*=6.4 Hz), 3.50 (1H, m), 3.40 (1H, dt, *J*=9.8, 6.4 Hz), 2.04 (4H, t, *J*=7.4 Hz), 1.86–1.42 (14H, m); ^{13}C NMR δ 149.3, 109.0, 98.7, 67.4, 62.6, 62.2, 35.6, 32.4, 30.7, 29.3, 25.4, 24.3, 23.8, 19.5; FABMS *m/z* 257 (M^++1, 2.0). FABHRMS calcd for $C_{15}H_{29}O_3$ 257.2117, found 257.2124.

1.2.7. 3-Acetoxy-11-tetrahydropyranyloxy-7-methylene-1-phenylundec-1-yne (19). Sulfur trioxide pyridine complex (1.53 g, 9.60 mmol) was added to a solution of **18** (612 mg, 2.40 mmol), DMSO (4.80 mL, 67.6 mmol), and Et_3N (1.67 mL, 12.0 mmol) in CH_2Cl_2 (24.0 mL) at 0°C. The reaction mixture was stirred for 30 min at the same temperature, quenched by addition of water, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. According to the procedure described for conversion of **8** to **12**, the crude aldehyde was successively exposed to the acetylide, prepared from phenylacetylene (0.40 mL, 3.60 mmol) and ^{n}BuLi (1.44 M, hexane solution, 2.50 mL, 3.60 mmol), and acetylation conditions (Ac_2O (0.34 mL, 3.60 mmol), DMAP (880 mg, 7.20 mmol)) to produce **19** (918 mg, 96%) as a colorless oil: IR 1736, 1643 cm^{-1}; ^{1}H NMR δ 7.45–7.28 (5H, m), 5.61 (1H, t, *J*=6.6 Hz), 4.76 (2H, s), 4.57 (1H, t, *J*=3.0 Hz), 3.86 (1H, dd, *J*=10.9, 3.6 Hz), 3.74 (1H, dd, *J*= 9.9, 6.6 Hz), 3.49 (1H, m), 3.39 (1H, dt, *J*=9.9, 6.6 Hz), 2.11 (3H, s), 2.09–1.51 (18H, m); ^{13}C NMR δ 169.9, 148.7, 131.8, 128.5, 128.2, 122.2, 109.5, 98.7, 86.4, 85.2, 67.3, 64.4, 62.2, 35.6, 35.2, 34.4, 30.7, 29.4, 25.4, 24.3, 23.0, 21.0, 19.6; FABMS *m/z* 399 (M^++1, 0.6). Anal. Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60. Found: C, 75.24; H, 8.77.

1.2.8. Hexacarbonyl-μ-[η^4-3-acetoxy-7-methylene-1-phenylundec-1-yn-11-ol]dicobalt(Co–Co) (20). To a solution of **19** (602 mg, 1.51 mmol) in MeOH (15.0 mL) was added PPTS (38.9 mg, 1.51×10^{-1} mmol) and the reaction mixture was allowed to stand at room temperature for 1 day. MeOH was evaporated off and the residue was diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. According to the procedure described for conversion of **10** to **11**, the crude hydroxy compound was treated with $Co_2(CO)_8$ (775 mg, 2.23 mmol) to give **20** (843 mg, 93%) as a reddish brown oil: IR 2093, 2058, 2031, 1734 cm^{-1}; ^{1}H NMR δ 7.49–7.32 (5H, m), 6.41 (1H, t, *J*=6.6 Hz), 4.72 (1H, s), 4.68 (1H, s), 3.64 (2H, dt, *J*=10.9, 5.9 Hz), 2.13 (3H, s), 2.08–1.96 (4H, m), 1.89–1.81 (2H, m), 1.63–1.43 (6H, m); ^{13}C NMR δ 198.9, 170.6, 148.5, 137.4, 129.4, 128.9, 127.9, 109.7, 96.4, 90.5, 73.9, 62.7, 37.0, 35.5, 35.2, 32.4, 24.1, 23.8, 20.6; MS *m/z* 516 (M^+−84, 21). Anal. Calcd for $C_{26}H_{26}Co_2O_9$: C, 52.02; H, 4.37. Found: C, 51.82; H, 4.50.

1.2.9. 8-(*tert*-Butyldimethylsiloxy)-1-(4-methoxyphenyloxy)octan-4-one (22). According to the procedure described for preparation of **18**, δ-valerolactone (3.39 g, 33.9 mmol) was treated with the acetylide, derived from **21** (6.56 g, 37.3 mmol) and ^{n}BuLi (1.58 M hexane solution, 23.6 mL, 37.3 mmol), and the resulting acetylenic compound was hydrogenated in the presence of 5% Pd–C. The residue was dissolved in DMF (17.0 mL), to which a solution of imidazole (5.54 g, 81.3 mmol) and TBSCl (6.13 g, 40.7 mmol) in DMF (17.0 mL) was added. The reaction mixture was stirred at room temperature for 1 h, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (9:1) gave **22** (5.91 g, 45%) as a colorless oil: IR 1710 cm^{-1}; ^{1}H NMR δ 7.30–7.25 (2H, m), 6.93–6.88 (2H, m), 4.44 (2H, s), 3.84 (3H, s), 3.66 (2H, t, *J*=6.3 Hz), 3.48 (2H, t, *J*=6.3 Hz), 2.53 (2H, t, *J*=7.3 Hz), 2.45 (2H, t, *J*=7.3 Hz), 1.95–1.85 (2H, m), 1.73–1.47 (4H, m), 0.92 (9H, s), 0.08 (6H, s); ^{13}C NMR δ 210.7, 159.1, 130.5, 129.2, 113.7, 72.5, 69.0, 62.8, 55.2, 42.6, 39.3, 32.2, 25.9, 23.8, 20.3, 18.3, −5.4; FABMS *m/z* 395 (M^++1, 0.6). Anal. Calcd for $C_{22}H_{38}O_4Si$: C, 66.96; H, 9.71. Found: C, 66.72; H, 9.78.

1.2.10. 8-(*tert*-Butyldimethylsiloxy)-1-(4-methoxyphenyloxy)-4-methyleneoctane (23). According to the procedure described for conversion of **7** to **8**, **23** (2.91 g, 93%) was obtained from **22** (3.17 g, 8.02 mmol). Compound **23** was a colorless oil: IR 1643 cm^{-1}; ^{1}H NMR δ 7.28–7.25 (2H, m), 6.89–6.87 (2H, m), 4.71 (2H, s), 4.43 (2H, s), 3.81 (3H, s), 3.61 (2H, t, *J*=6.4 Hz), 3.45 (2H, t, *J*=6.4 Hz), 2.07 (2H, t, *J*=7.8 Hz), 2.02 (2H, t, *J*=7.8 Hz), 1.77–1.71 (2H, m), 1.56–1.43 (4H, m), 0.89 (9H, s), 0.05 (6H, s); ^{13}C NMR δ 159.0, 149.0, 130.7, 129.1, 113.7, 108.9, 72.5, 69.7, 62.9, 55.1, 35.7, 32.4, 32.4, 27.8, 25.9, 23.9, 18.3, −5.4; MS *m/z* 392 (M^+, 0.3). Anal. Calcd for $C_{23}H_{40}O_3Si$: C, 70.35; H, 10.27. Found: C, 70.11; H, 10.39.

1.2.11. 8-(*tert*-Butyldimethylsiloxy)-4-methyleneoctan-1-ol (24). According to the procedure described for conversion of **7** to **8**, **24** (938 mg, 91%) was obtained from **23** (1.49 g, 3.79 mmol). Compound **24** was a colorless oil: IR 3456, 1643 cm^{-1}; ^{1}H NMR δ 4.75 (1H, s), 4.74 (1H, s), 3.66

(2H, t, J=6.4 Hz), 3.61 (2H, t, J=6.4 Hz), 2.09 (2H, t, J=7.3 Hz), 2.04 (2H, t, J=7.8 Hz), 1.71 (2H, tt, J=7.3, 6.4 Hz), 1.55–1.43 (4H, m), 0.89 (9H, s), 0.05 (6H, s); ^{13}C NMR δ 159.0, 149.0, 130.7, 129.1, 113.7, 108.9, 72.5, 69.7, 62.9, 55.1, 35.7, 32.4, 32.4, 27.8, 25.9, 23.9, 18.3, −5.4; FABMS m/z 273 (M^++1, 12). FABHRMS calcd for $C_{15}H_{33}O_2Si$ 273.2250, found 273.2256.

1.2.12. 10-(*tert*-Butyldimethylsiloxy)-6-methylene-1-phenyldec-1-yn-3-ol (25). According to the procedure described for the preparation of **9**, **25** (5.20 g, 55%) was obtained from **24** (6.95 g, 25.5 mmol). Compound **25** was a colorless oil: IR 3453, 1684 cm^{-1}; ^{1}H NMR δ 7.44–7.29 (5H, m), 4.81 (1H, s), 4.78 (1H, s), 4.62 (1H, t, J=6.4 Hz), 3.62 (2H, t, J=6.4 Hz), 2.26 (2H, t, J=7.8 Hz), 2.07 (2H, t, J=7.3 Hz), 1.97–1.92 (2H, m), 1.55–1.48 (4H, m), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR δ 148.8, 131.6, 128.4, 128.2, 122.6, 109.5, 89.9, 85.1, 63.0, 62.6, 35.9, 35.8, 32.5, 31.5, 26.0, 23.9, 18.3, −5.3; MS m/z 372 (M^+, 0.5). Anal. Calcd for $C_{23}H_{36}O_2Si$: C, 74.14; H, 9.74. Found: C, 73.84; H, 10.01.

1.2.13. 3-Acetoxy-6-methylene-1-phenyldec-1-yn-10-ol (26). According to the procedure described for the preparation of **12**, **26** (52.2 mg, 57%) was obtained from **25** (112 mg, 0.29 mmol). Compound **26** was a colorless oil: IR 3460, 1734 cm^{-1}; ^{1}H NMR δ 7.45–7.28 (5H, m), 5.60 (1H, t, J=6.8 Hz), 4.76 (1H, s), 4.75 (1H, s), 3.66 (2H, t, J=6.8 Hz), 2.12–2.05 (4H, m), 2.11 (3H, s), 1.89–1.45 (6H, m); ^{13}C NMR δ 170.0, 147.8, 131.8, 128.6, 128.2, 122.2, 109.9, 86.3, 85.5, 64.2, 62.8, 35.7, 33.0, 32.4, 31.3, 23.8, 21.0; MS m/z 300 (M^+, 5.2). HRMS calcd for $C_{19}H_{24}O_3$ 300.1725, found 300.1730.

1.2.14. Hexacarbonyl-μ-[η^4-3-acetoxy-6-methylene-1-phenyldec-1-yn-10-ol]dicobalt(Co–Co) (27). According to the procedure described for the preparation of **12**, **27** (271 mg, 92%) was obtained from **26** (150 mg, 0.50 mmol). Compound **27** was a reddish brown oil: IR 2093, 2056, 2025, 1734 cm^{-1}; ^{1}H NMR δ 7.48–7.28 (5H, m), 6.39 (1H, t, J=6.3 Hz), 4.78 (1H, s), 4.72 (1H, s), 3.66–3.60 (2H, m), 2.19–1.94 (6H, m), 2.13 (3H, s), 1.62–1.37 (4H, m); ^{13}C NMR δ 198.8, 170.5, 147.7, 137.4, 129.4, 128.9, 127.9, 109.8, 96.3, 90.5, 73.8, 62.7, 35.9, 35.5, 32.3, 32.2, 23.8, 20.7; MS m/z 586 (M^+, 3.3). Anal. Calcd for $C_{25}H_{24}Co_2O_9$: C, 51.21; H, 4.13. Found: C, 51.06; H, 4.21.

1.2.15. 1-(4-Methoxyphenyloxy)-4-methyleneoctan-8-ol (28). According to the procedure described for the preparation of **10**, **28** (5.44 g, 98%) was obtained from **23** (7.85 g, 20.0 mmol). Compound **28** was a colorless oil: IR 3421, 1645 cm^{-1}; ^{1}H NMR δ 7.28–7.25 (2H, m), 6.89–6.86 (2H, m), 4.72 (2H, s), 4.43 (2H, s), 3.80 (3H, s), 3.65 (2H, t, J=6.4 Hz), 3.45 (2H, t, J=6.4 Hz), 2.08 (2H, t, J=7.8 Hz), 2.04 (2H, t, J=7.3 Hz), 1.77–1.71 (2H, m), 1.59–1.46 (4H, m); ^{13}C NMR δ 159.0, 158.9, 148.9, 130.6, 129.2, 113.7, 109.1, 72.5, 69.7, 62.6, 55.2, 35.7, 32.3, 27.8, 23.8; MS m/z 278 (M^+, 9.9). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 72.97; H, 9.69.

1.2.16. 10-(4-Methoxyphenyloxy)-7-methylene-1-phenyldec-1-yn-3-ol (29). According to the procedure described for the preparation of **9**, **29** (2.29 g, 84%) was obtained from **28** (2.00 g, 7.18 mmol). Compound **29** was a colorless oil: IR 3402, 1646 cm^{-1}; ^{1}H NMR δ 7.44–7.24 (7H, m), 6.90–6.85 (2H, m), 4.75 (2H, s), 4.60 (1H, dd, J=11.9, 6.3 Hz), 4.42 (2H, s), 3.80 (3H, s), 3.45 (2H, t, J=6.3 Hz), 2.10 (4H, t, J=7.6 Hz), 1.86–1.61 (6H, m); ^{13}C NMR δ 159.0, 148.6, 131.6, 130.5, 129.1, 128.2, 128.1, 122.6, 113.7, 109.3, 90.2, 84.7, 72.4, 69.6, 62.6, 55.1, 37.3, 35.5, 32.3, 27.7, 23.1; MS m/z 378 (M^+, 0.9). Anal. Calcd for $C_{25}H_{30}O_3$: C, 79.33; H, 7.99. Found: C, 79.49; H, 8.26.

1.2.17. 3-Acetoxy-7-methylene-1-phenyldec-1-yn-10-ol (30). According to the procedure described for acetylation and debenzylation (**25** to **26** and **23** to **24**), **30** (635 mg, 80%) was obtained from **29** (1.00 g, 2.64 mmol). Compound **30** was a colorless oil: IR 3444, 1733, 1644 cm^{-1}; ^{1}H NMR δ 7.47–7.43 (5H, m), 5.62 (1H, t, J=6.4 Hz), 4.79 (1H, s), 4.78 (1H, s), 3.68–3.64 (2H, m), 2.12–2.10 (4H, m), 2.11 (3H, s), 1.88–1.60 (6H, m); ^{13}C NMR δ 170.0, 148.4, 131.8, 128.5, 128.2, 122.2, 109.7, 86.4, 85.3, 64.3, 62.5, 35.3, 34.3, 32.0, 30.6, 22.9, 21.0; MS m/z 300 (M^+, 8.7). Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.68; H, 8.19.

1.2.18. Hexacarbonyl-μ-[η^4-3-acetoxy-7-methylene-1-phenyldec-1-yn-10-ol]dicobalt(Co–Co) (31). According to the procedure described for the preparation of **12**, **31** (139 mg, 88%) was obtained from **30** (80.7 mg, 0.27 mmol). Compound **31** was a reddish brown oil: IR 2093, 2056, 2025, 1732 cm^{-1}; ^{1}H NMR δ 7.48–7.31 (5H, m), 6.40 (1H, dd, J=7.8, 5.3 Hz), 4.79 (1H, s), 4.70 (1H, s), 3.65–3.61 (2H, m), 2.14 (3H, s), 2.09–2.03 (4H, m), 1.87–1.57 (6H, m); ^{13}C NMR δ 198.9, 170.6, 148.3, 137.4, 129.4, 128.9, 127.9, 109.9, 96.4, 90.5, 73.9, 62.7, 37.1, 35.3, 32.0, 30.7, 24.1, 20.7; MS m/z 530 (M^+−56, 0.8). Anal. Calcd for $C_{25}H_{24}Co_2O_9$: C, 51.21; H, 4.13. Found: C, 50.93; H, 4.19.

1.2.19. Hexacarbonyl-μ-[η^4-(6*R**,8*S**)-8-phenylethynyl-1-oxaspiro[5.5]-undecane]dicobalt(Co–Co) (32a). A reddish brown oil: IR 2087, 2050, 2023 cm^{-1}; ^{1}H NMR δ 7.54–7.26 (5H, m), 3.73–3.59 (2H, m), 3.31 (1H, tt, J=11.9, 3.3 Hz), 2.48–2.43 (1H, m), 2.14–1.98 (2H, m), 1.91–1.09 (11H, m); ^{13}C NMR δ 200.0, 138.4, 129.2, 128.8, 127.5, 106.5, 91.5, 71.9, 60.8, 42.2, 37.0, 36.4, 35.3, 34.8, 26.1, 21.0, 18.9; FABMS m/z 541 (M^++1, 0.8). FABHRMS calcd for $C_{24}H_{23}Co_2O_7$ 541.0108, found 541.0089.

1.2.20. Hexacarbonyl-μ-[η^4-(6*R**,8*R**)-8-phenylethynyl-1-oxaspiro[5.5]-undecane]dicobalt(Co–Co) (32b). A reddish brown oil: IR 2089, 2050, 2023 cm^{-1}; ^{1}H NMR δ 7.52–7.30 (5H, m), 3.74–3.70 (2H, m), 3.03 (1H, tt, J=11.9, 3.3 Hz), 2.40 (1H, m), 2.12–2.03 (2H, m), 1.88–1.25 (11H, m); ^{13}C NMR δ 199.7, 138.3, 129.2, 128.8, 127.6, 10.5.1, 91.1, 73.1, 61.2, 44.4, 38.5, 35.4, 35.2, 31.4, 26.2, 22.6, 19.1; FABMS m/z 541 (M^++1, 0.7). FABHRMS calcd for $C_{24}H_{23}Co_2O_7$ 541.0108, found 541.0140.

1.2.21. Hexacarbonyl-μ-[η^4-(2*R**,5*S**)-2-phenylethynyl-6-oxaspiro[4.5]-decane]dicobalt(Co–Co) (33a). A reddish brown oil: IR 2087, 2050, 2023 cm^{-1}; ^{1}H NMR δ 7.56–7.30 (5H, m), 3.74–3.45 (3H, m), 2.29 (1H, m), 2.20–2.02 (2H, m), 1.98–1.80 (2H, m), 1.73–1.43 (7H, m); ^{13}C NMR 199.8,

138.2, 129.5, 128.8, 127.6, 103.5, 91.4, 82.8, 62.8, 45.9, 43.4, 38.2, 36.2, 34.2, 25.9, 20.8; FABMS *m/z* 527 (M^++1, 1.2). Anal. Calcd for $C_{23}H_{20}Co_2O_7$: C, 52.49; H, 3.83. Found: C, 52.60; H, 3.90.

1.2.22. Hexacarbonyl-μ-[η⁴-(2*R,5*R**)-8-phenylethynyl-6-oxaspiro[4.5]-decane]dicobalt(Co–Co) (33b).** A reddish brown oil: IR 2087, 2050, 2023 cm^{-1}; ^1H NMR δ 7.54–7.30 (5H, m), 3.86–3.63 (3H, m), 2.49 (1H, m), 2.34 (1H, m), 2.11–2.00 (1H, m), 1.80 (1H, m), 1.69–1.42 (8H, m); ^{13}C NMR δ 199.8, 138.2, 129.4, 128.8, 127.7, 104.2, 91.7, 83.3, 62.6, 47.2, 42.0, 36.0, 35.8, 33.9, 26.0, 21.0; FABMS *m/z* 541 (M^++1, 1.3). Anal. Calcd for $C_{23}H_{20}Co_2O_7$: C, 52.49; H, 3.83. Found: C, 52.82; H, 3.93.

1.2.23. Hexacarbonyl-μ-[η⁴-(5*R,7*S**)-7-phenylethynyl-1-oxaspiro[4.5]-decane]dicobalt(Co–Co) (34a).** A reddish brown oil: IR 2089, 2050, 2023 cm^{-1}; ^1H NMR δ 7.53–7.29 (5H, m), 3.93–3.82 (2H, m), 3.39 (1H, tt, *J*=12.2, 3.3 Hz), 2.12–1.64 (8H, m), 1.45–1.26 (4H, m); ^{13}C NMR δ 199.8, 138.4, 129.2, 128.8, 127.6, 106.1, 91.1, 81.6, 66.9, 45.1, 38.3, 38.1, 36.1, 34.6, 25.2; MS *m/z* 526 (M^+, 0.3). Anal. Calcd for $C_{23}H_{20}Co_2O_7$: C, 52.49; H, 3.83. Found: C, 52.59; H, 3.89.

1.2.24. Hexacarbonyl-μ-[η⁴-(5*R,7*R**)-7-phenylethynyl-1-oxaspiro[4.5]-decane]dicobalt(Co–Co) (34b).** A reddish brown oil: IR 2089, 2050, 2023 cm^{-1}; ^1H NMR δ 7.50–7.30 (5H, m), 3.92–3.80 (2H, m), 2.97 (1H, tt, *J*=11.9, 3.0 Hz), 2.08–1.23 (12H, m); ^{13}C NMR δ 199.7, 138.3, 129.2, 128.8, 127.6, 104.7, 91.2, 82.9, 66.5, 46.4, 40.6, 36.9, 34.7, 34.4, 26.1; FABMS *m/z* 527 (M^++1, 1.1). Anal. Calcd for $C_{23}H_{20}Co_2O_7$: C, 52.49; H, 3.83. Found: C, 52.72; H, 4.04.

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