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Enantioselective catalysis 107: new optically active deltacyclenes as building blocks for the synthesis of expanded phosphanes

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Summary — The cobalt-catalyzed homo Diels–Alder reaction of norbornadiene and terminal acetylenes yields chiral deltacyclenes. We tried to extend the scope of this reaction to acetylenes containing a heteroatom (i) in the propargylic position, (ii) in the *ortho* position of phenylacetylene or (iii) directly bonded to the triple bond. The synthesis of nine new substituted deltacyclenes with cobalt catalysts derived from CoI_2 and zinc powder or $Co(acac)_3$ and Et_2AlCl is described. Using Norphos as a cocatalyst, the products are obtained in high enantiomeric excess.

enantioselective homogeneous catalysis / homo Diels–Alder reaction / deltacyclene / terminal acetylene

Résumé — Catalyse énantiosélective 107. Nouveaux deltacyclènes optiquement actifs comme précurseurs dans la synthèse de phosphanes étendues. La réaction d'homo-Diels–Alder entre le norbornadiène et les acétyléniques vrais, catalysée par le cobalt conduit aux deltacyclènes. Nous avons tenté d'étendre le champ de cette réaction aux acétyléniques contenant un hétéroatome en position propargylique, en position *ortho* du phénylacétylène ou directement lié sur la triple liaison. La synthèse de neuf nouveaux deltacyclènes substitués, par une catalyse au cobalt, dérivé de CoI_2 et du zinc en poudre ou dérivé de $Co(acac)_3$ et de Et_2AlCl, a été décrite. Par l'utilisation de Norphos comme cocatalyseur, les produits ont été obtenus avec de bons excès énantiomériques.

catalyse homogène énantiosélective / réaction d'homo-Diels–Alder / deltacyclène / acétylène vrai

Introduction

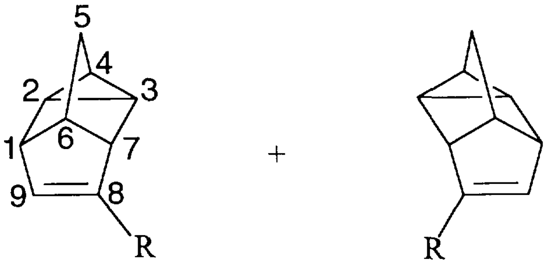
This paper is the sequel in a continuing series of articles [1].

In the presence of transition metal catalysts norbornadiene reacts with acetylenes to give deltacyclenes [2]. Two catalyst systems have proven to be the best:

System *A*: Catalyst: $Co(acac)_3/Et_2AlCl$/phosphane; solvent: THF; catalyst/substrate ratio = 1:500.

System *B*: Catalyst: CoI_2/zinc powder/phosphane; solvent: CH_2Cl_2; catalyst/substrate ratio = 1:40.

Using terminal acetylenes two enantiomers are formed (scheme 1). With chiral phosphanes as cocatalysts high enantiomeric excesses can be obtained [3-8]. Except a couple of aliphatic alkynol derivatives, up to now only acetylenes could be applied, which were hydrocarbons without any functional groups. The reason is, that the deltacyclene formation is very sensitive to hetero atoms in the acetylenic component. Catalyst system *A* tolerates only silicon substituents or oxygen-containing groups, which are further than three bonds away from the triple bond [9]. System *B* additionally accepts derivatives of propargylic alcohol, but it requires a higher catalyst concentration [7]. In this paper we describe the synthesis of new substituted deltacyclenes by enantioselective catalysis, suitable as building blocks for the synthesis of expanded phosphorus-based chelating ligands. Actually, we plan to use the double bonds in the deltacyclene systems for P–H addition reactions to attach phosphorus atoms which are able to coordinate to a metal center. In addition, there should be another functional group which allows the connection to further units in dendrizyme syntheses.



Scheme 1

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[*] Correspondence and reprints

$HC{\equiv}C{-}CH_2{-}R$

	1	2	3	4	5	6	7
R	Br	$SiMe_3$	OH	$OSiMe_3$	OPh	*O*-tetrahydropyranyl	*O*-benzoyl

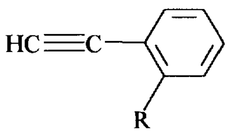
Scheme 2

The synthesis of the terminal acetylenes 1–21

The synthesis of terminal acetylenes is well known in organic chemistry [10–23]. To serve as building blocks for the construction of expanded ligands the deltacyclenes and hence the terminal acetylenes used in their preparation must contain a functional group for subsequent derivatization.

A first location of the functionality is the propargylic position (scheme 2). The acetylenes **1**, **3** and **6** were purchased from Aldrich or Merck, **2** was made as described in the literature [10], **4** and **7** were synthesized from propargylic alcohol and trimethylsilyl chloride or benzoyl chloride and **5** was prepared from phenol and **1**.

The second place that we have selected for the hetero atom, is the *ortho* position in the ring of phenylacetylene (acetylenes **8**–**13** in scheme 3). Compounds **8** [11] and **10** [12] were synthesized as reported in the literature. **9** had been prepared either via double deprotonation of phenylacetylene and subsequent bromination of the aromatic ring [13] or via palladium- and copper-catalyzed coupling of 2-bromoiodobenzene and trimethylsilylacetylene **14** (scheme 4) [14].



	8	9	10	11	12	13
R	Cl	Br	NO_2	OMe	*O*-benzyl	*O*-(2-methoxyethyl)

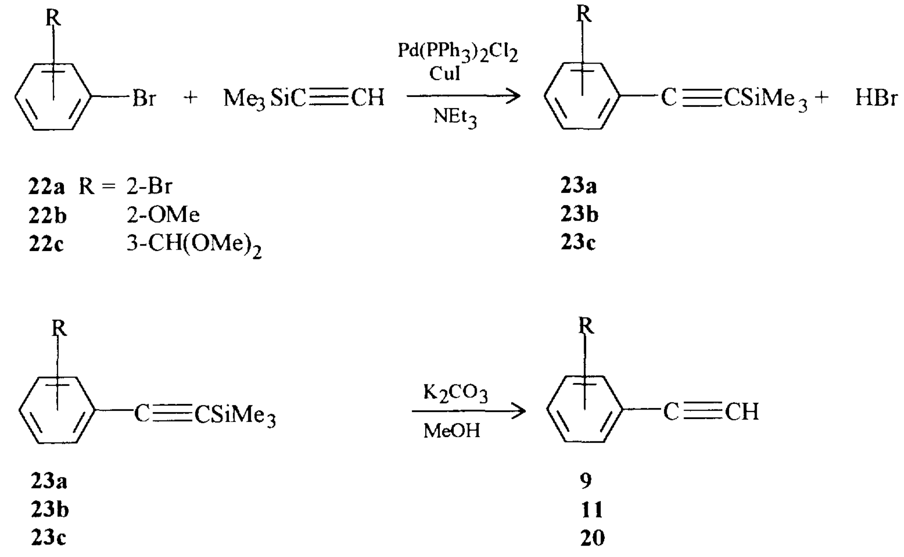
Scheme 3

$HC{\equiv}C{-}R$

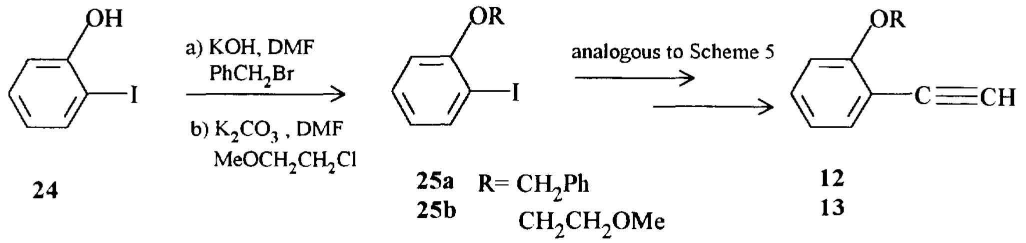
	14	15	16	17	18
R	$SiMe_3$	$SiMe_2Ph$	$SiPh_3$	Sn^nBu_3	$B(N^iPr_2)_2$
	19		20		21
R	2-pyridinyl		3-(dimethoxymethyl)phenyl		ferrocenyl

Scheme 4

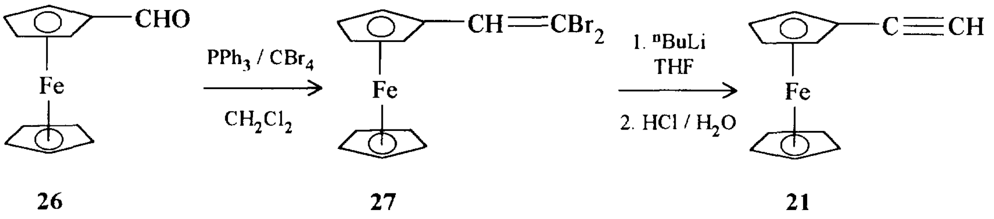
We used the metal-catalyzed coupling reaction between **14** and the cheaper 1,2-dibromobenzene **22a** (scheme 5). **22a** was dissolved in NEt_3 and treated with 2 mol% $Pd(PPh_3)_2Cl_2$ and 1 mol% CuI. Then, one equivalent of **14** was slowly added at 80 °C. After flash chromatography on silica gel, **23a** was obtained, which was treated with K_2CO_3 in MeOH to split off the protecting TMS group. After another flash chromatography on silica gel, **9** was isolated in 55% yield. **11** was prepared starting from the bromo derivative **22b** by the metal catalyzed coupling reaction (scheme 5). Former procedures had used the corresponding iodo compound [15]. After refluxing **22b** and **14** for 2 days, followed by the treatment described before (scheme 5), **11** was obtained in 61% yield.



Scheme 5



Scheme 6



Scheme 7

Acetylenes **12** and **13** were made via the coupling reaction of scheme 6 starting from the iodo compound **24**, which was transferred into the corresponding ethers **25a** and **25b** by either deprotonation with KOH in DMF and subsequent treatment with benzyl bromide or by reaction with (2-chloroethyl-methyl)ether in the presence of K_2CO_3 in refluxing DMF. **25a** and **25b** were converted into the terminal acetylenes **12** and **13** in 62 and 68% yield, respectively, using the method of scheme 5.

As acetylenes with the functional group connected directly to the triple bond, which should be stable during the deltacyclene formation, we choose the silyl, stannyl and boryl derivatives **14**–**18** (scheme 4). Alkynes **14** [16], **15** [17], **17** [18] and **18** [19] were made as described in the literature. Compound **16** was purchased from Aldrich.

Acetylenes **19**–**21** (scheme 4) cannot be assigned to one of the three groups mentioned above. **19** was prepared as reported in the literature [20]. Compound **20** was synthesized in 71% yield using the coupling reaction of scheme 5 starting from **22c**.

21 is a known compound [21, 22]. Here we report a new preparation, applying the method developed by Corey and Fuchs [23] (scheme 7). Ferrocenecarbaldehyde **26** was reacted with a mixture of triphenylphosphane and tetrabromomethane. After flash chromatography **27** was obtained as a red-brown solid. Treatment with two equiv of n-BuLi and subsequent acidification gave **21** as an orange-brown solid in 66% yield.

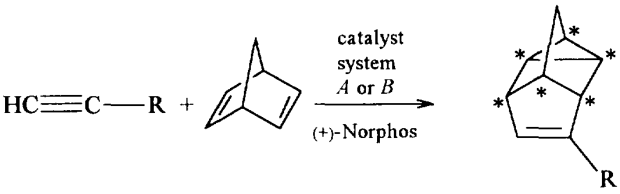
The formation of the new deltacyclenes 28–36

The reaction between acetylenes and 1,4-dienes is called a [2 + 2 + 2] homo Diels–Alder reaction. As this reaction requires a special arrangement of the π-orbitals of the unsaturated bonds, examples are rare. The products derived from norbornadiene, optimal for homo Diels–Alder reactions, are called deltacyclenes. Without any catalyst deltacyclenes are formed only with activated acetylenes [24]. Transition metal complexes also enable the reaction with unactivated acetylenes, in particular the two cobalt systems mentioned above. Using terminal acetylenes, two enantiomers arise (scheme 1). With chiral phosphane ligands, an asymmetric induction can be achieved [3–8].

The deltacyclene formation is very sensitive to several parameters. A variety of side products is possible, and it depends on the phosphane, the transition metal and the reaction conditions which polycyclic product is formed [8]. Yield and enantiomeric excess vary drastically with the chiral phosphane. In our experiments Norphos [25] was the best of all the ligands tested [5]. With phenylacetylene a quantitative yield and an enantiomeric excess up to 99% could be obtained. Therefore, in this study we use only Norphos to prepare the enantiomerically enriched deltacyclenes, functionalized by heteroatoms.

In 1989 Lautens et al failed to prepare deltacyclenes under achiral conditions from derivatives of propargylic alcohol using catalyst system *A*, but they succeeded in the formation of deltacyclenes from acetylenes, in which the oxygen atom and the acetylenic function were separated by more than one carbon atom [9]. In 1995 Buono et al published the enantioselective preparation of deltacyclene derivatives of propargylic and homopropargylic alcohol [7], attaining 53% yield and 78% ee for propargylic alcohol and 99% yield and 96% ee for homopropargylic alcohol derivatives.

In this paper we report the enantioselective [2 + 2 + 2] homo Diels–Alder reaction of norbornadiene with the acetylenes **1**–**21** (schemes 2–4) using (+)- and (−)-Norphos as the chiral phosphane in the catalyst systems *A* and *B* (table I). With (+)-Norphos universally the (+)-deltacyclenes **28**–**35** are obtained. The absolute stereochemistry shown in scheme 8 is proven for *R* = phenyl [4, 26]. We assume the same stereochemistry for all the compounds **28**–**36** in schemes 8 and 9.



1-21

28	**R = CH₂OPh**
29	**CH₂O-benzoyl**
30	**2 -chlorophenyl**
31	**2 -bromophenyl**
32	**2 -methoxyphenyl**
33	**2 -benzyloxyphenyl**
34	**2 -(2 -methoxyethyl)-oxyphenyl**
35	**ferrocenyl**

Scheme 8

In this study we started to carry out the cycloadditions with the alkynes **1**, **2** and **4**–**7** (table I), derivatized in the propargylic position. Compound **3** was not applied here, because meanwhile Buono et al had published its use in the deltacyclene formation [7]. However, they had obtained only 59.7% ee, which is too low for an application in dendrizyme synthesis. The reaction of **1** and norbornadiene did not yield a deltacyclene neither with catalyst system *A* nor *B*. **1** decomposed in the reaction mixture. In the homo Diels–Alder reactions of **2** and **4** with norbornadiene, the corresponding deltacyclenes were formed as the main components in a mixture of products isolated in 18 and 14% yield, respectively. These yields were not encouraging for an application in phosphane synthesis. Therefore, these reactions were not further investigated. The reaction of **6** and norbornadiene gave a mixture of products. The main constituent was an aromatic compound, which probably resulted from a cyclotrimerization of the alkyne. Here we report the successful synthesis of the new deltacyclenes **28** and **29** from **5** and **7** in 50 and 47% yield, respectively. **28** is formed in 88% ee and **29** in 93% ee, using catalyst system *B* (table I).

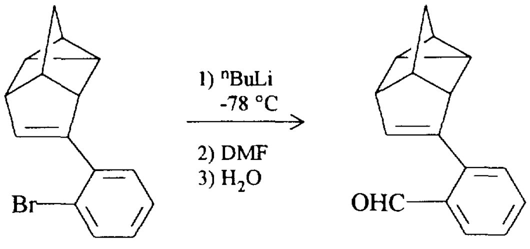
The substituted phenylacetylenes **8**, **9**, **11**, **12** and **13**, which allowed the formation of the deltacyclenes **30**–**34**, gave very high optical inductions from 93 to 98% ee and good yields using catalyst system *A* (table I). All these new deltacyclenes are oils, except **33**, which is a crystalline compound. Acetylene **10** decomposed under the reaction conditions. Thus, no product could be isolated from its reaction with norbornadiene.

With the acetylenes **14**–**18**, directly derivatized at the triple bond, no new deltacyclenes could be obtained as pure compounds. 8-(Trimethylsilyl)deltacyclene, derived from **14**, is well known [5, 9]. However, there is still no analytical method to measure the enantiomeric excess. The homo Diels–Alder reaction of **15** and norbornadiene yielded 40% of a product mixture, which contained 60% of the desired deltacyclene. However, due to the difficult product separation, this reaction was not further investigated. The acetylenes **16**–**18** decomposed during the attempted deltacyclene formation.

The acetylenes **19** and **20** are good chelating ligands. They blocked the catalyst in the homo Diels–Alder reaction and were isolated unchanged after the reactions. **35**, derived from acetylene **21**, could be synthesized in 98% ee and 54% yield using catalyst system *A* (table I). It is a crystalline compound. Thus, its ee could be increased by one recrystallization from methanol/pentane to nearly 100% ee.

Reaction of **31** with *n*-BuLi at low temperature, subsequent treatment with DMF and final hydrolysis with water gave the deltacyclene-substituted benzaldehyde **36** in 67% yield (scheme 9). Because no optically active center is involved in this reaction sequence, **36** should have 98% ee like **31**. The new deltacyclenes were identified by IR, ^{1}H NMR, ^{13}C NMR and EI mass spectroscopy.

Besides the signals of the substituents, the ^{1}H NMR spectra show the signals of the protons of the deltacyclene backbone. The spectra are very complicated because of many small couplings, which could not be assigned and therefore were neglected. The olefinic proton 9-CH (numbering scheme: see scheme 1) appears as a doublet of a doublet at 6.0–6.5 ppm, due to its ^3J and ^4J coupling with the protons 1-CH and 7-CH in the allylic positions (established by the COSY spectra). The



31 **36**

Scheme 9

^4J coupling is not observed in the spectrum of compound **32**, in which the olefinic signal 9-CH is a doublet. The three methine protons 1-CH, 6-CH and 7-CH of the cyclopentene ring occur at 2.0–3.1 ppm. The signal at lowest field, in all cases a broad singlet, belongs to the proton 7-CH adjacent to the substituted position (established by the COSY spectra). The signal at highest field, also in all cases a broad singlet, is assigned to the 6-CH group directly bonded to the CH_2 bridge (established by the COSY spectra). The signal in the middle of these low-field and high-field methine resonances, in all cases a doublet, is assigned to the proton 1-CH adjacent to the olefinic proton, to which it is coupled. The signals of the methylene bridge 5-CH_2 are observed between 1.52 and 1.63 ppm. The three methine protons of the cyclopropane ring appear at 1.29–1.85 ppm as multiplets. The group 4-CH directly bonded to the CH_2 bridge resonates at lower field than 5-CH_2 and the two other groups 2-CH and 3-CH, which come at higher field.

The signals of the ^{13}C NMR spectra could be assigned by CH correlation (see below). In the EI mass spectra of the new deltacyclenes the molecular ions are detected, besides the typical fragmentation patterns.

Table I. Enantioselective homo Diels–Alder reactions of 2,5-norbornadiene and the acetylenes **1**–**21** using catalyst systems *A* and *B* with (+)-Norphos as the chiral phosphane.

Acetylene	*Catalyst system*[a]	*Reaction time*[b] *(h)*	*Yield*[c] *(%)*	*ee*[d] *(%)*
1	*A* or *B*	12–60	no[e]	–
2	*B*	12	18[f],[9]	–
3[7],[g]	*B*	24	24	60
4	*B*	12	14[f]	–
5	*B*	12	50[h]	88
6	*B*	12	44[f]	–
7	*B*	60	47[h]	93
8	*A*	12	63[h]	97
9	*A*	12	60[h]	98
10	*A* or *B*	12–60	no[e]	–
11	*A*	24[i]	65[h]	93
12	*A*	60[i]	83[h]	97
13	*A*	60[i]	69[h]	96
14	*A*	24	28[5,9]	–
15	*B*	60	40[f]	–
16	*A* or *B*	12–60	no[e]	–
17	*A* or *B*	12–60	no[e]	–
18	*A* or *B*	12–60	no[e]	–
19	*A* or *B*	12–60	no[e]	–
20	*A* or *B*	12–60	no[e]	–
21	*A*	60[i]	54[h]	98

[a] System *A*: Acetylene (10 mmol); norbornadiene (1 mL, 10 mmol); THF (1 mL); $Co(acac)_3$ (7.1 mg, 0.2 mol%); Norphos (9.3 mg, 0.2 mol%); 5 mL of a 1 M solution of Et_2AlCl in hexane. System *B*: Acetylene (10 mmol); norbornadiene (1 mL, 10 mmol); CH_2Cl_2 (5 mL); CoI_2 (77.2 mg, 2.5 mol%); Norphos (115.6 mg, 2.5 mol%); zinc dust (81.8 mg, 25 mol%). Because system *B* needs more catalyst, system *A* was tested first. System *B* was only applied, if system *A* failed. [b] All the reactions were carried out at room temperature, unless indicated otherwise. [c] The yields given were determined by weighing after purification of the products either by bulb to bulb distillation or by chromatography (see Experimental section). [d] The enantiomeric excess was measured by gas chromatography or HPLC using various chiral columns (see Experimental section). For each enantiomerically enriched deltacyclene a racemic sample for reference was prepared using triphenylphosphane, as a cocatalyst instead of (+)-Norphos. In the case of acetylenes **13** and **21** racemic samples of Norphos had to be used to synthesize the racemic references. [e] no ≡ no deltacyclene formation (either no reaction or no evidence for a deltacyclene in the product mixture). [f] The deltacyclene was part of a product mixture, which was not separated. Therefore, the ee was not measured. [g] Buono et al used (+)-ValNOP as the chiral cocatalyst. [h] Only the pure deltacyclene was isolated. [i] This reaction was carried out at 40 °C.

Experimental section

All reactions were performed under nitrogen by using standard Schlenk techniques. Solvents were purified and dried by standard procedures. The bromo- and iodoarenes and the CoI_2 were purchased from Aldrich, Fluka or Merck.

^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker WM 250 instrument ($T = 24$ °C) using TMS as internal standard. EI mass spectra were obtained on a Finnigan Mat 112 S spectrometer and IR spectra on a Beckman IR 4240 instrument. Melting points were measured on a Büchi Smp 20 instrument. The optical rotations were determined on a Perkin-Elmer polarimeter 241 using CH_2Cl_2 Uvasol from Merck. The ee's of the deltacyclenes were measured by gas chromatography on a Hewlett Packard 5890 (FID detection) using various columns or by HPLC on a Merck-Hitachi L-6200 A instrument (UV detection on a Merck L-400 A), see individual compounds.

2-Bromo-1-ethynylbenzene **9**

A mixture of **22a** (10 mL, 83.9 mmol), $Pd(PPh_3)_2Cl_2$ (1.10 g, 2 mol%), CuI (160 mg, 1 mol%) and 80 mL of NEt_3 was heated to reflux. Then, a solution of **14** (11.6 mL, 84.0 mmol) in 20 mL of NEt_3 was added during 2 h. Heating to reflux was continued for 1 h. The resulting triethylammonium bromide was filtered off through a layer of a few centimeters of silica gel. The solvent was evaporated and the crude product was dissolved in 80 mL of methanol and treated with K_2CO_3 (1.16 g, 10 mol%). After stirring at room temperature for 1 h, the solvent was removed and the residue was dissolved in ether, washed with water, dried over $MgSO_4$ and filtered. Then, the solvent was evaporated and the crude product was purified by bulb to bulb distillation (45 °C/3 torr). **9** was obtained as a colorless, light-sensitive oil in 55% yield. Spectroscopic data were as described in the literature [13, 14].

1-Ethynyl-2-methoxybenzene **11**

A mixture of **22b** (21.7 mL, 175 mmol), **14** (34.6 mL, 250 mmol), $Pd(PPh_3)_2Cl_2$ (2.46 g, 2 mol%), CuI (330 mg, 1 mol%) and 150 mL of NEt_3 was heated to reflux for 2 d. Workup was carried out as for **9**. After bulb to bulb distillation (65 °C/0.05–0.1 torr), **11** was obtained in 61% yield as a colorless oil. Spectroscopic data were as described in the literature [15].

2-Benzyloxy-1-ethynylbenzene **12**

A mixture of **25a** (12.4 g, 40 mmol), **14** (6.92 mL, 50 mmol), $Pd(PPh_3)_2Cl_2$ (492 mg, 2 mol%), CuI (66 mg, 1 mol%) and 50 mL of NEt_3 was heated to reflux for 2 d. Workup was carried out as for **9**. The crude product was purified by chromatography on silica gel using petroleum ether/ether (10:1). **12** was obtained as a light orange oil in 76% yield.

IR (film): ν 3 280, 3 040, 3 020, 2 930, 2 835, 2 080, 1 580, 1 560 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.50–6.87 (m, 9H, ArH); 5.18 (s, 2H, CH$_2$O); 3.30 (s, 1H, ≡CH).

MS (EI): m/z 208.0 (25%, M$^+$); 91.0 (100%, [C$_7$H$_7$]$^+$).

Anal calc for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.36; H, 6.05.

1-Ethynyl-2-(2-methoxyethoxy)benzene **13**

A mixture of **25b** (9.5 g, 34 mmol), **14** (5.53 mL, 40 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (477 mg, 2 mol%), CuI (65 mg, 1 mol%) and 50 mL of NEt$_3$ was heated to reflux for 2 d. Workup was carried out as for **9**. The crude product was purified by chromatography on silica gel using petroleum ether/ether (10:1). **13** was obtained as a light orange oil, which solidified over night, in 75% yield (Mp: 38 °C).

IR (film): ν 3 280, 3 060, 3 020, 2 960, 2 940, 2 905, 2 090, 1 590, 1 565 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.47–6.88 (m, 4H, ArH); 4.20 (pseudo t, ^3J = 5.0 Hz, 2H, CH_2OAr); 3.80 (pseudo t, ^3J = 5.0 Hz, 2H, MeOCH_2); 3.48 (s, 3H, MeO); 3.26 (s, 1H, ≡CH).

MS (EI): m/z 175.9 (52%, M$^+$); 130.8 (22%, [M – CH$_3$OCH$_2$]$^+$); 117.8 (35%, [M–CH$_3$OCH=CH$_2$]$^+$); 59.0 (100%, [CH$_3$OCH$_2$CH$_2$]$^+$).

Anal calc for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.96; H, 6.94.

Ethynylferrocene **21**

PPh$_3$ (7.7 g, 29.3 mmol) was dissolved in 30 mL of CH$_2$Cl$_2$ and the solution was cooled to 0 °C. Then, CBr$_4$ (4.9 g, 14.67 mmol) and 15 min later **26** (1.57 g, 7.33 mmol) were added at 0 °C and the mixture was allowed to warm up to room temperature during 1 h. After addition of 30 mL of petroleum ether, the whole suspension was put on silica gel and extracted with petroleum ether/ether (10:1). After evaporation of the solvent, **27** was obtained as an orange-red solid. It was dissolved in 30 mL of THF and cooled to –78 °C. Then 9.2 mL of a 1.6 M solution of n-BuLi in hexane were added. The mixture was allowed to warm up to room temperature (2 h) and treated with 25 mL of 2 N HCl. The product was extracted three times with 30 mL of petroleum ether and the combined organic layers were dried over CaCl$_2$ and filtered. After evaporation of the solvent, the crude product was purified by chromatography on aluminum oxide using petroleum ether as eluent. **21** was obtained as an orange-brown solid in 66% yield. Spectroscopic data were as described in the literature [21, 22].

General procedure for the preparation of the deltacyclenes using catalyst system A

Co(acac)$_3$ (7.1 mg, 0.02 mmol, 0.2 mol%) and Norphos (9.3 mg, 0.02 mmol, 0.2 mol%) were dissolved in 1 mL of dry THF. Then, norbornadiene (1 mL, 10 mmol) and 10 mmol of the acetylene were added. The reaction was started by adding 5 mL of a 1 M solution of Et$_2$AlCl in hexane. The mixture was stirred at room temperature for the reaction times given in table I. Then, 5 mL of isopropanol was added dropwise. The resulting solution was passed through a layer of a few centimeters of silica gel and the solvent was evaporated. The resulting crude product was either purified by bulb to bulb distillation (**30–32**) or by chromatography on silica gel (**33**) or aluminum oxide (**34**, **35**), using petroleum ether/ether as eluent (see individual compounds).

General procedure for the preparation of the deltacyclenes using catalyst system B

To CoI$_2$ (77.2 mg, 0.25 mmol, 2.5 mol%) were added Norphos (115.6 mg, 0.25 mmol, 2.5 mol%) and Zn-dust (163.5 mg, 2.5 mmol; a sample of zinc dust <10 μ obtained from Aldrich was used, zinc dust <60 μ obtained from Merck was not effective), avoiding a high light intensity. The solids were dissolved in 5 mL of CH$_2$Cl$_2$ and norbornadiene (1 mL, 10 mmol) and 10 mmol of the acetylene were dissolved in the mixture. The suspension was stirred for the reaction times given in table I in a water bath at room temperature, because the reaction can be exothermic. The crude product was isolated via flash chromatography on silica gel, using petroleum ether/ether as eluent (see individual compounds). Purification was achieved by bulb to bulb distillation (**28**, **29**).

• *8-(Phenoxymethyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene* **28**

28 was prepared using catalyst system B with (+)-Norphos and obtained after bulb to bulb distillation (80–90 °C/0.05 torr) as a colorless oil in 50% yield (99% purity by GC).

$[\alpha]_D^{rt}$ = +17.5 (c 1; CH$_2$Cl$_2$); 88% ee (by GC; column: Lipodex C (50 m, Machery und Nagel); p = 2 bar H$_2$; T = 111 °C; retention times: (–)-**28** 181 min, (+)-**28** 184 min).

IR (film): ν 3 040, 2 940, 1 610, 1 590 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.29–6.88 (m, 5H, ArH); 6.01 (dd, ^3J = 2.8 Hz, ^4J = 1.3 Hz, 1H, =CH); 4.61 (s, 2H, CH$_2$O); 2.67 (s(br), 1H); 2.59 (d, ^3J = 2.8 Hz, 1H); 2.02 (s(br), 1H); 1.73–1.68 (m, 1H); 1.52 (pseudo t, ^3J = 1.4 Hz, 2H); 1.50–1.45 (m, 1H); 1.31 (m, 1H).

MS (EI): m/z 224.0 (21%, M$^+$); 131.1 (100%, [M – C$_6$H$_5$O]$^+$); 115.9 (18%, C$_9$H$_8^+$).

Anal calc for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.92; H, 7.07.

• *8-(Benzoyloxymethyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene* **29**

29 was prepared using catalyst system B with (+)-Norphos and obtained after bulb to bulb distillation (110 °C/0.05 torr) as a colorless oil in 47% yield (97% purity by GC).

$[\alpha]_D^{rt}$ = + 19.3 (c 1; CH$_2$Cl$_2$); 93% ee (by GC; column: Chirasil Dex-CB (25 m, Chrompak); p = 1.2 bar He; T = 170 °C; retention times: (–)-**29** 33.7 min, (+)-**29** 34.4 min).

IR (film): ν 3 035, 2 920, 1 700, 1 580, 1 560 cm^{-1}.

^{1}H NMR (250 MHz): δ 8.09–8.05 (m, 2H, o-ArH); 7.58–7.52 (m, 1H, p-ArH); 7.47–7.40 (m, 2H, m-ArH); 6.06 (dd, ^3J = 4.7 Hz, ^4J = 1.3 Hz, 1H, =CH); 4.99–4.87 (m, 2H, CH$_2$O); 2.66 (s(br), 1H); 2.60 (d, ^3J = 4.7 Hz, 1H); 2.04 (s(br), 1H); 1.75–1.69 (m, 1H); 1.54 (pseudo t, ^3J = 1.5 Hz, 2H); 1.39–1.29 (m, 2H).

^{13}C NMR (63 MHz): δ 22.7, 23.5, 26.0, 32.8, 48.8, 50.0, 57.6, 63.5, 128.3 (double intensity), 129.6 (double intensity), 130.6, 132.8 (double intensity), 144.5, 166.4.

MS (EI): m/z 252.2 (17%, M$^+$); 128.9 (49.7%, [M – C$_6$H$_5$O]$^+$); 104.9 (100%, PhCO$^+$).

Anal calc for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.97; H, 6.37.

• *8-(2-Chlorophenyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene* **30**

30 was prepared using catalyst system A with (+)-Norphos and obtained after bulb to bulb distillation (85–90 °C/0.05 torr) as a colorless oil in 63% yield (98% purity by GC).

$[\alpha]_D^{rt}$ = +97.2 (*c* 1; CH_2Cl_2); 88% ee (by GC; column: Lipodex C (50 m, Machery und Nagel); *p* = 2 bar H_2; *T* = 98 °C; retention times: (−)-**30** 376 min, (+)-**30** 381 min).

IR (film): ν 3 030, 2 930, 1 575, 1 565 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.36–7.07 (m, 4H, ArH); 6.47 (dd, ^3J = 3.2 Hz, ^4J = 0.9 Hz, 1H, =CH); 3.03 (s(br), 1H); 2.74 (d, ^3J = 3.2 Hz, 1H); 2.16 (s(br), 1H); 1.78–1.73 (m, 1H); 1.59 (s(br), 2H); 1.59–1.51 (m, 1H); 1.47–1.38 (m, 1H).

MS (EI): *m/z* 227.9 (81%, M^+); 192.9 (100%, $[M–Cl]^+$); 178.1 (84%, $[M–Cl–CH_2]^+$]); 114.9 (76%, $C_9H_7^+$).

Anal calc for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.26; H, 5.61; Cl, 15.61.

• *8-(2-Bromophenyl)tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene* **31**

31 was prepared using catalyst system *A* with (−)-Norphos and obtained after bulb to bulb distillation (90–95 °C/ 0.05 torr) as a pale yellow oil in 60% yield (94% purity by GC).

$[\alpha]_D^{rt}$ = −55.38 (*c* 1; CH_2Cl_2); 98% ee (by GC; column: B-PH (10 m, Astec); *p* = 4 bar H_2; *T* = 110 °C; retention times: (−)-**31** 133 min, (+)-**31** 138 min).

IR (film): ν 3 040, 2 940, 1 575, 1 565 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.57–6.99 (m, 4H, ArH); 6.41 (dd, ^3J = 3.2 Hz, ^4J = 0.9 Hz, 1H, =CH); 3.02 (s(br), 1H); 2.74 (d, ^3J = 3.2 Hz, 1H); 2.20 (s(br), 1H); 1.78–1.73 (m, 1H); 1.59 (s(br), 2H); 1.58–1.52 (m, 1H); 1.44–1.38 (m, 1H).

MS (EI): *m/z* 271.9 (45%, M^+); 192.9 (100%, $[M–Br]^+$); 178.1 (96%, $[M–Br–CH_2]^+$]); 114.9 (66%, $C_9H_7^+$).

• *8-(2-Methoxyphenyl)tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene* **32**

32 was prepared using catalyst system *A* with (−)-Norphos and obtained after bulb to bulb distillation (105 °C/ 0.05 torr) as a pale yellow oil in 65% yield (94% purity by GC).

$[\alpha]_D^{rt}$ = −66.83 (*c* 1; CH_2Cl_2); 93% ee (by GC; column: Chirasil-Dex CB (25 m, Chrompak); *p* = 1.2 bar He; *T* = 155 °C; retention times: (−)-**32** 33.5 min, (+)-**32** 35.0 min).

IR (film): ν 3 040, 2 940, 1 585, 1 545 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.35–6.84 (m, 4H, ArH); 6.58 (d, ^3J = 2.7 Hz, 1H, =CH); 3.84 (s, 3H, MeO); 3.07 (s(br), 1H); 2.71 (d, ^3J = 2.7 Hz, 1H); 2.07 (s(br), 1H); 1.75–1.70 (m, 1H); 1.59 (s(br), 2H); 1.50–1.45 (m, 1H); 1.41–1.36 (m, 1H).

MS (EI): *m/z* 224.1 (100%, M^+); 209.2 (29%, $[M–CH_3]^+$); 193.3 (22%, $[M–MeO]^+$); 115.2 (29%, $C_9H_7^+$).

Anal calc for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.76; H, 6.90.

• *8-[2-(Benzyloxy)phenyl]tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]-non-8-ene* **33**

33 was prepared using catalyst system *A* with (+)-Norphos and obtained after chromatography on silica gel using a mixture of petroleum ether and ether (10:1) as a pale yellow oil, which solidified after 1 d (Mp: 53 °C) in 83% yield (96% purity by GC).

$[\alpha]_D^{rt}$ = +35.4 (*c* 1; CH_2Cl_2); 97% ee (by HPLC: pre column: Chiralpak AD (50 mm × 4.6 mm, 20 μm, Daicel); column: Chiralpak AD (250 mm × 4.6 mm, 10 μm, Daicel); solvent: 2-propanol; flow: 0.35 mL/min; detection: UV 220 nm; retention times: (−)-**33** 26.7 min, (+)-**33** 66.4 min).

IR (film): ν 3 045, 2 940, 2 840, 1 590 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.48–6.90 (m, 9H, ArH); 6.59 (dd, ^3J = 3.2 Hz, ^4J = 1.0 Hz, 1H, =CH); 5.13 (s, 2H, CH_2O); 3.09 (s(br), 1H); 2.67 (d, ^3J = 3.2 Hz, 1H); 2.07 (s(br), 1H); 1.71–1.66 (m, 1H); 1.57 (pseudo dd, ^3J = 1.6 Hz, ^3J = 3.2 Hz, 2H); 1.41–1.33 (m, 2H).

^{13}C NMR (63 MHz): δ 22.5, 24.1, 25.3, 32.8, 49.5, 51.9, 56.4, 70.4, 112.4, 120.8, 126.7, 127.3, 127.7 (double intensity), 127.8, 128.2, 128.5 (double intensity), 133.8, 137.3, 145.0, 156.3.

MS (EI): *m/z* 300.2 (55%, M^+); 209.0 (78%, $[M–C_7H_7]^+$); 91.0 (100%, $C_7H_7^+$).

Anal calc for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.69; H, 6.52.

• *8-{2-[(2-Methoxyethyl)oxy]phenyl}tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene* **34**

34 was prepared using catalyst system *A* with (+)-Norphos and obtained after chromatography on aluminum oxide with petroleum ether/ether (10:1) as a pale yellow oil in 57% yield (99% purity by GC).

$[\alpha]_D^{rt}$ = +62.11 (*c* 0.5; CH_2Cl_2); 96% ee (by GC; column: Chirasil-Dex CB (25 m, Chrompak); *p* = 1.2 bar He; *T* = 170 °C; retention times: (−)-**34** 43.5 min, (+)-**34** 44.2 min).

IR (film): ν 3 020, 2 950, 2 920, 2 890, 1 570, 1 550 cm^{-1}.

^{1}H NMR (250 MHz): δ 7.33 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1H, ArH); 7.14 (ddd, ^3J = 8.2 Hz, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1H, ArH); 6.91 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, ArH); 6.85 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, ArH); 6.60 (dd, ^3J = 3.2 Hz, ^4J = 1.0 Hz, 1H, =CH); 4.15 (pseudo t, ^3J = 5.0 Hz, 2H, CH_2OAr); 3.80 (pseudo t, ^3J = 5.0 Hz, 2H, MeOCH_2); 3.45 (s, 3H, MeO); 3.09 (s(br), 1H); 2.70 (d, ^3J = 3.2 Hz, 1H); 2.07 (s(br), 1H); 1.74–1.70 (m, 1H); 1.59 (pseudo dd, ^3J = 3.2 Hz, ^3J = 1.6 Hz, 2H); 1.52–1.49 (m, 1H); 1.43–1.36 (m, 1H).

^{13}C NMR (63 MHz): δ 22.4, 24.0, 25.3, 32.8, 49.4, 51.8, 56.3, 59.0, 67.3, 71.2, 112.0, 120.8, 126.6, 127.3, 128.0, 133.5, 145.4, 156.3.

MS (EI): *m/z* 268.1 (100%, M^+); 210.0 (23%, $[M - CH_2CH_2OMe]^+$); 59.0 (89%, $[CH_2{=}CHOMe]^+$).

Anal calc for $C_{18}H_{20}O_2$: C, 80.57; H, 7.51. Found: C, 80.31; H, 7.64.

• *8-(Ferrocenyl)tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene* **35**

35 was prepared using catalyst system *A* with (+)-Norphos and obtained after chromatography on aluminum oxide using petroleum ether and additional recrystallization from MeOH/pentane as orange-red needles (Mp: 55–57 °C) in 54% yield (99% purity by HPLC).

$[\alpha]_D^{rt}$ = +38.4 (*c* 1; CH_2Cl_2); 98% ee (before crystallization by HPLC; precolumn: Chiralpak AD (50 mm × 4.6 mm, 20 μm, Daicel); column: Chiralpak AD (250 mm × 4.6 mm, 10 μm, Daicel); solvent: 70% EtOH, 30% hexane; flow: 0.4 mL/min; detection: UV 220 and 301 nm; retention times: (−)-**35** 14.3 min, (+)-**35** 15.6 min).

IR (film): ν 3 060, 2 920, 2 830, 1 440 cm^{-1}.

^{1}H NMR (250 MHz): δ 5.95 (dd, ^3J = 3.1 Hz, ^4J = 0.9 Hz, 1H, =CH); 4.32–4.18 (m, 4H, C_5H_4); 4.08 (s, 5H, C_5H_5); 2.79 (s(br), 1H); 2.61 (d, ^3J = 3.1 Hz, 1H); 2.05 (s(br), 1H); 1.74–1.69 (m, 1H); 1.58 (s(br), 2H); 1.43–1.32 (m, 2H).

^{13}C NMR (63 MHz): δ 22.3, 23.7, 25.1, 32.7, 49.2, 51.0, 56.8, 65.3, 66.2, 68.28, 68.34, 69.2 (fivefold intensity), 82.3, 125.9, 146.4.

MS (EI): m/z 302.2 (100%, M^+); 120.8 (21%, $[CpFe]^+$).

Anal calc for $C_{19}H_{18}Fe$: C, 75.52; H, 6.00. Found: C, 75.23; H, 6.27.

- *8-(2-Formylphenyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene* **36**

(−)-**31** (4.2 g, 15.4 mmol) was dissolved in 40 mL of THF and the mixture was cooled to −70 °C. Then 11.5 mL (7.19 mmol) of a 1.6 M solution of n-BuLi in hexane was added. After 20 min the reaction mixture was added dropwise to 5 mL of DMF in 20 mL of THF at −70 °C. After warming up to room temperature, 10 mL of H_2O were added. The THF was removed and the residue was extracted with ether. The organic layer was separated and dried over $CaCl_2$. The solvent was removed and the crude product was purified by chromatography on aluminum oxide with petroleum ether/ether as eluent. **36** was obtained as a pale yellow oil in 63% yield.

$[\alpha]_D^{rt} = -135.8$ (c 1; CH_2Cl_2); 98% ee.

IR (film): ν 3 045, 2 950, 2 920, 2 840, 1 685, 1 595, 1 580, 1 560 cm^{-1}.

^{1}H NMR (250 MHz): δ 10.20 (d, ^4J = 0.7 Hz, 1H, ArCHO); 7.91–7.29 (m, 4H, ArH); 6.05 (dd, ^3J = 3.1 Hz, ^4J = 0.9 Hz, 1H, =CH); 2.93 (s, 1H); 2.87 (d, ^3J = 3.1 Hz, 1H); 2.25 (s, 1H); 1.85–1.80 (m, 1H); 1.63 (s, 2H); 1.57–1.52 (m, 1H); 1.48–1.43 (m, 1H).

MS (EI): m/z 222.1 (100%, M^+); 206.1 (24%, $[M\text{–}O]^+$); 193.0 (23%, $[M\text{–}CHO]^+$); 115.0 (44%, $C_9H_7^+$).

Anal calc for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.64; H, 6.59.

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