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Enantioselective synthesis of planar-chiral metacyclophanes through cationic Rh(I)/modified-BINAP-catalyzed inter- and intramolecular alkyne cyclotrimerizations

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Abstract

We have achieved the first catalytic enantioselective synthesis of planar-chiral metacyclophanes by means of cationic Rh(I)/(*S*)-xyl-H_8-BINAP or (*R*)-H_8-BINAP complex-catalyzed inter- and intramolecular alkyne cyclotrimerizations. This highly enantioselective catalysis represents a versatile new method for the preparation of planar-chiral metacyclophanes.

Keywords: Alkyne; BINAP; Cyclotrimerization; Metacyclophanes; Rhodium

1. Introduction

Transition-metal-catalyzed enantioselective cycloadditions are powerful synthetic methods for the rapid construction of chiral cyclic frameworks.[1] Although a number of efficient enantioselective cycloadditions have been developed, enantioselective [2+2+2] cycloadditions have been accomplished in only a few examples at the time we started our project toward cationic Rh(I)/bisphosphine complex-catalyzed [2+2+2] cycloadditions in 2002.[2–5] In 1994, Sato, Mori, and co-workers reported an enantioselective desymmetrization of triynes leading to isoindoline and isoquinoline derivatives bearing a tertiary stereocenter through a Ni(0)-catalyzed [2+2+2] cycloaddition.[3] In 1999, Stará and co-workers reported a Ni(0)-catalyzed enantioselective [2+2+2] cycloaddition of triynes leading to a [6]helicene-like molecule.[4] These pioneering works clearly demonstrated the potential utility of enantioselective [2+2+2] cycloadditions for the asymmetric synthesis of chiral aromatic compounds. However, a lack of highly active transition-metal/chiral bisphosphine complexes, other than Ni(0) complexes, might strictly limit the further development of the enantioselective [2+2+2] cycloadditions.[3–5] We anticipated that Rh(I)/chiral bisphosphine complexes, having a rigid chiral environment and multiple free coordination sites, were potentially more suitable for enantioselective [2+2+2] cycloadditions than Ni(0) complexes.

In 2001, a highly active transition-metal/bisphosphine complex was discovered by Takeuchi and co-workers.[6a] They found that a neutral Ir(I)/dppe [1,2-bis(diphenylphosphino)-ethane] complex catalyzes [2+2+2] cycloadditions of tethered diynes with monoalkynes in high yields.[6] Furthermore in 2003, they reported that a neutral Ir(I)/dppe or $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ complex can also catalyze intermolecular cross [2+2+2] cycloadditions.[6b] On the other hand, pioneering works by Müller[7] and Grigg[8] demonstrated that a neutral Rh(I) complex, such as $RhCl(PPh_3)_3$, can catalyze an intramolecular [2+2+2] cycloaddition of tethered diynes at elevated temperature,[9] but such Rh(I) complexes generally react with untethered terminal alkynes to give linear dimers.[10] Independently, our research group discovered in 2003 that cationic Rh(I)/BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]-type bisphosphine complexes can catalyze both inter- and intramolecular cross [2+2+2] cycloadditions of tethered and untethered alkynes.[11] The combination of a cationic

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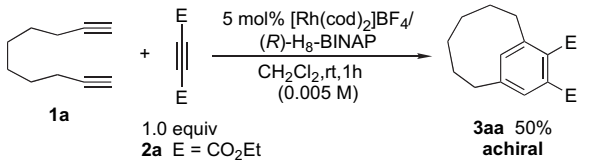
Rh(I) species and a BINAP-type bisphosphine ligand is essential for this reaction. A neutral Rh(I)/BINAP-type bisphosphine complex, and both cationic and neutral iridium(I)/BINAP-type bisphosphine complexes exhibit significantly decreased catalytic activity.

Fortunately, the cationic Rh(I)/BINAP-type bisphosphine complexes can be applied to a wide variety of [2+2+2] cycloadditions of various unsaturated compounds including not only alkynes[11,12] but also isocyanates,[13] isothiocyanates,[14] carbon disulfide,[14] nitriles,[15] aldehydes,[16] ketones,[16] and alkenes.[17] We have also developed a number of asymmetric variants of these reactions to construct axial[12a,c–e,g,j,15b,16] and central[12h,14,15a,17] chirality.[18] The most striking feature of our cationic Rh(I)/BINAP-type bisphosphine complex-catalyzed [2+2+2] cycloadditions is its applicability to cyclophane synthesis.[11,12b,f] Maryanoff and co-workers have developed highly efficient syntheses of pyridinophanes by Co(I)-catalyzed [2+2+2] cycloadditions,[19a–d] but synthesis of cyclophanes through alkyne cyclotrimerization has some room for improvement.[19a,e] By employing a cationic Rh(I)/H_8-BINAP [2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl][20] complex as a catalyst, [6]–[21]carba-[11,12b] and polyethercyclophanes[12f] can be synthesized in high yields through [2+2+2] cycloadditions of α,ω-diynes with dialkyl acetylenedicarboxylates. In this paper, we describe the first catalytic enantioselective synthesis of planar-chiral metacyclophanes by means of cationic Rh(I)/(*S*)-xyl-H_8-BINAP [2,2′-bis{di(3,5-dimethylphenyl)phosphino}-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl][20] or (*R*)-H_8-BINAP complex-catalyzed inter- and intramolecular alkyne cyclotrimerizations.[21]

2. Results and discussion

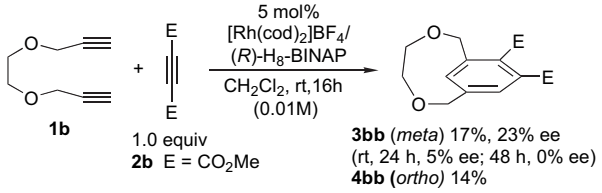
2.1. Enantioselective synthesis of planar-chiral metacyclophanes through cationic Rh(I)/modified-BINAP-catalyzed intermolecular alkyne cyclotrimerization

It is well established that certain cyclophanes having short ansa chains exhibit planar-chirality due to the restricted rotation of the aromatic ring.[22] In spite of the potential utility of the planar-chiral cyclophanes in areas of asymmetric synthesis, host–guest chemistry, and material science, the existing methods for their synthesis are based exclusively on the optical resolution of racemic compounds and methods for straightforward enantioselective synthesis have not been reported to date.[23–25] We have reported the one-step synthesis of [6]carbametacyclophane **3aa** from 1,9-decadiyne (**1a**) and diethyl acetylenedicarboxylate (**2a**) (Scheme 1).[11] At rt, if the ansa chain of **3aa** resides at one side of the aromatic ring, **3aa** can exhibit the planar-chirality.[26] However, broad signals of the benzylic protons of **3aa** were observed by ^{1}H NMR analysis at rt, which suggests rapid ring flipping.



Scheme 1. Synthesis of [6]metacyclophane **3aa** through Rh(I)$^+$/(*R*)-H_8-BINAP-catalyzed intermolecular alkyne cyclotrimerization.

Thus, the reaction of ether-linked terminal 1,9-diyne **1b** and dimethyl acetylenedicarboxylate (**2b**) was investigated to increase the steric strain of the ansa chain. The reaction gave the desired [6]ether metacyclophane **3bb** with 23% ee, but complete racemization of **3bb** proceeded at rt over 48 h (Scheme 2).

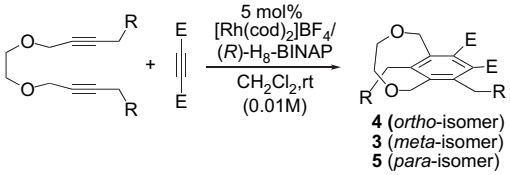


Scheme 2. Synthesis of [6]metacyclophane **3bb** through Rh(I)$^+$/(*R*)-H_8-BINAP-catalyzed intermolecular alkyne cyclotrimerization.

Consequently, we have gone onto employ internal diynes as the substrates to avoid racemization of the products. The expected metacyclophanes would possess stable planar-chirality since ring flipping would not be possible.[27] We first examined the reaction of methyl-substituted internal 1,9-diynes **1c** with **2b** in the presence of 5 mol % Rh(I)$^+$/(*R*)-H_8-BINAP, which led to a messy reaction (Table 1, entry 1). Although the reaction of **1c** with di-*t*-butyl acetylenedicarboxylate (**2c**) furnished [6]orthocyclophane **4cc** in 21% yield, the desired planar-chiral [6]metacyclophane **3cc** was obtained in <5% yield with only 8% ee (entry 2). On the other hand, the use of methoxymethyl-substituted internal 1,9-diyne **1d** furnished [6]metacyclophane **3dc** with good ee (68% ee, entry 3).

After screening of various modified-BINAP ligands, we were pleased to find that further improved ee (81% ee) could be obtained by using (*S*)-xyl-H_8-BINAP as a ligand (Table 2, entry 2). The use of 10 mol % Rh catalyst and a slight excess of **2c** (1.5 equiv) increased the yield of cyclophanes (entry 3). Interestingly, the enantioselectivity of this process is highly dependent on the reaction concentration (0.01–0.2 M, entries 3–5). Although the yield of [6]metacyclophane **3dc**

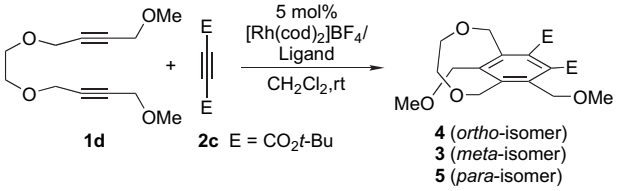
Table 1
Effect of substituents on yield and enantioselectivity of [6]metacyclophanes **3**



Entry	**1** (*R*)	**2** (*E*)	Yield[a] (%)			ee (%)
			4	**3**	**5**	**3**
1	**1c** (H)	**2b** (CO_2Me)	—	—	—	—
2	**1c** (H)	**2c** (CO_2*t*-Bu)	21	<5	0	8
3	**1d** (OMe)	**2c** (CO_2*t*-Bu)	7	7	0	68

[a] Isolated yield.

Table 2
Effect of ligands and concentration on yield and enantioselectivity of [6]metacyclophane **3dc**



Entry	Ligand	Concn (M)	Yield[a] (%)			ee (%)
			4	**3**	**5**	**3**
1	(*R*)-H_8-BINAP	0.01	7	7	0	68
2	(*S*)-Xyl-H_8-BINAP	0.01	7	9	0	81
3[b]	(*S*)-Xyl-H_8-BINAP	0.01	14	11	0	82
4[b]	(*S*)-Xyl-H_8-BINAP	0.05	8	10	0	89
5[b]	(*S*)-Xyl-H_8-BINAP	0.2	<5	9	0	95

[a] Isolated yield.
[b] Catalyst: 10 mol %.

decreased, the highest ee of **3dc** was obtained at the 0.2 M concentration (95% ee, entry 5).

A series of internal diynes **1d–m** was subjected to the above optimal reaction conditions as shown in Table 3. Although the formation of [8]metacyclophane **3fc** was inefficient (entry 3), the desired planar-chiral [6], [7], and [9]metacyclophanes were obtained as major isomers with high ee values (entries 1, 2, 4, and 8). On the other hand, although the reactions of diynes **1h–j** and **1l** with **2c** proceeded to give the desired planar-chiral [10]–[12]metacyclophanes, their ee values were lower than those of [6], [7], and [9]metacyclophanes (entries 5–7 and 9). Planar-chiral [15]metacyclophane **3mc** could not be obtained by the reaction of diyne **1m** with **2c** at all (entry 10).[28] In these reactions, the diynes **1** were consumed and a complex mixture not containing **3–5** was generated.

Figure 1 depicts possible intermediates **A–C** for the formation of metacyclophanes **3**. At high concentration, the formation of rhodacyclopentadienes **A** or **B**, through intermolecular coupling of the electron-deficient monoalkyne **2c** and the electron-rich diynes **1**, may be predominant, which provides planar-chiral metacyclophanes **3** with high enantioselectivity, due to the steric interaction between the chiral ligand and the tethering chains within **1**. On the other hand, the formation of rhodacyclopentadienes **C**, through intramolecular coupling of the electron-rich diynes **1**, may be increased at low concentration,[12f] which decreases the ee values of **3**, due to the small steric interaction between the chiral ligand and the tethering chains within **1**.

2.2. Enantioselective synthesis of planar-chiral metacyclophanes through cationic Rh(I)/modified-BINAP-catalyzed intramolecular alkyne cyclotrimerization

Although planar-chiral metacyclophanes can be synthesized with high enantioselectivity through intermolecular alkyne cyclotrimerization, their yields are not satisfactory. Therefore, we designed the intramolecular cyclotrimerization

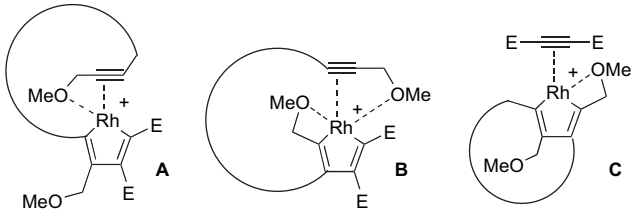
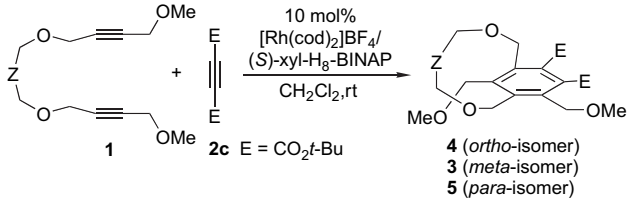


Figure 1. Possible intermediates **A–C** for the formation of metacyclophanes.

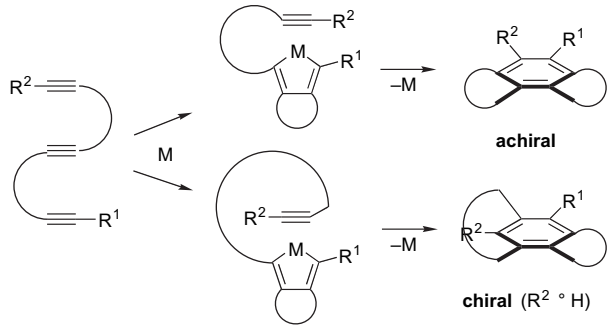
Table 3
Enantioselective synthesis of planar-chiral metacyclophanes **3** through Rh(I)$^+$/(*S*)-xyl-H_8-BINAP-catalyzed intermolecular alkyne cyclotrimerization



Entry	**1** (*Z*)	Concn (M)	Yield[a] (%)			ee (%)
			4	**3**	**5**	**3**
1	**1d** (—)	0.2	<5	9	0	95
2	**1e** (CH_2)	0.2	12	12	0	98
3	**1f** (CH_2CH_2)	0.2	0	<5	<5	—
4	**1g** ($CH_2CH_2CH_2$)	0.01	0	15	5	92
5[b]	**1h** ($CH_2CH_2CH_2CH_2$)	0.01	0	27	0	52
6[b]	**1i** ($CH_2CH_2CH_2CH_2CH_2$)	0.01	11[c]	9[c]	5[c]	56
7[b]	**1j** ($CH_2CH_2CH_2CH_2CH_2CH_2$)	0.01	7[c]	7[c]	<5	62
8	**1k** (CH_2OCH_2)	0.2	8	11	0	92
9[b]	**1l** ($CH_2OCH_2CH_2OCH_2$)	0.01	18	6	<5	80
10[b]	**1m** ($CH_2OCH_2CH_2OCH_2CH_2OCH_2$)	0.01	0	0	<5	—

[a] Isolated yield.
[b] Ligand: (*R*)-H_8-BINAP.
[c] Isolated as a mixture of isomers.

of triynes bearing substituents at two alkyne termini, which could furnish either achiral orthocyclophanes or chiral metacyclophanes, but the formation of achiral paracyclophanes could be eliminated (Scheme 3). Oshima and co-workers realized this type of macrocyclization using reactive triynes bearing hydrogens at two alkyne termini in an aqueous–organic biphasic system, which diminished the formation of undesired intermolecular reaction products.[19e] However, only [9] and [10]metacyclophanes were obtained as minor products along with the major orthocyclophanes, whilst [7] and [8]metacyclophanes possessing short ansa chains were not obtained.[19e,29] Furthermore, the intramolecular cyclotrimerization of less reactive triynes bearing substituents at two alkyne termini has not been realized to date.



Scheme 3. Enantioselective synthesis of planar-chiral metacyclophanes through intramolecular alkyne cyclotrimerization.

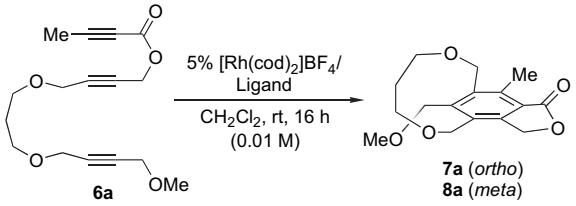
We first examined the reaction of methyl and methoxymethyl-substituted triyne **6a**, bearing an ester-linked 1,6-diyne moiety, with 5% $Rh(I)^+$/(*R*)-H_8-BINAP at rt, which furnished the desired [7]metacyclophane **8a** with excellent enantioselectivity (>98% ee), although **8a** was obtained as a minor isomer (Table 4, entry 1). The use of (*R*)-Segphos [(4,4′-bi-1,3-benzodioxole)-5,5′-diylbis(diphenylphosphine)],[30] (*R*)-BINAP, or (*R*)-xyl-BINAP as a ligand slightly or considerably decreased the ee values of the desired [7]metacyclophane **8a** (entries 2–4).

Thus, the reactions of a series of triynes **6a–j** with 5% $Rh(I)^+$/(*R*)-H_8-BINAP at rt were investigated as shown in Table 5. [7]–[10]Metacyclophanes **8a**, **8c–e**, and **8h** were obtained in 10–29% yields with high ee values (91 to >98% ees, entries 2–5 and 8). However, [12]metacyclophanes **8g** and **8i** were obtained with low to moderate ee values (32 and 68% ees, entries 7 and 9), and [6], [11], and [15]metacyclophanes were not obtained at all (entries 1, 6, and 10). The absolute configuration of [9]metacyclophane (−)-**8d** was determined to be *R* by X-ray crystallographic analysis (Fig. 2).

Next, we examined the reactions of a series of triynes **9a–j**, bearing an ether-linked 1,6-diyne moiety, with 5% $Rh(I)^+$/(*R*)-H_8-BINAP at rt as shown in Table 6. [7]–[10]Metacyclophanes **11b–e** and **11h** were obtained in improved yields with high ee values (21–33% yields, 88 to >94% ees, entries 2–5 and 8). [11] and [12]Metacyclophanes **11f** and **11g** were also obtained although lower ee values were observed (74 and 58% ees, entries 6 and 7). However, [6], [12], and [15]metapolyethercyclophanes **11a**, **11i**, and **11j** were not obtained at all (entries 1, 9, and 10). Increasing the catalyst loading to 10 mol % did not improve the yields of cyclophanes significantly (entry 4). In general, triynes bearing an ether-linked 1,6-diyne moiety furnished metacyclophanes in higher yields than those bearing an ester-linked 1,6-diyne moiety, but enantioselectivities of the former were lower than those of the latter. In the reactions shown in both Tables 5 and 6, the triynes **6** and **9** were consumed and a complex mixture not containing **7**, **8**, **10**, and **11** was generated.

A possible mechanism for the highly enantioselective formation of (*R*)-**8d** is shown in Scheme 4. Enantioselectivity would be determined by preferential formation of intermediate **D**, due to the high reactivity of the 1,6-diyne moiety to the

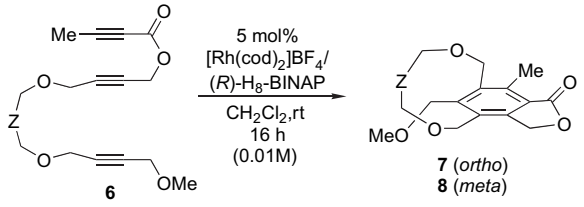
Table 4
Effect of ligands on yield and enantioselectivity of [7]metacyclophane



Entry	Ligand	Yield[a] (%)		ee (%)
		7a	**8a**	**8a**
1	(*R*)-H_8-BINAP	31	10	>98
2	(*R*)-Segphos	37	7	26
3	(*R*)-BINAP	25	9	91
4	(*R*)-Xyl-BINAP	13	15	83

[a] Isolated yield.

Table 5
Enantioselective synthesis of planar-chiral metacyclophanes through $Rh(I)^+$/(*R*)-H_8-BINAP-catalyzed intramolecular alkyne cyclotrimerization of **6**



Entry	**6** (*Z*)	Yield[a] (%)		ee (%)
		7	**8**	**8**
1	**6b** (—)	53	0	—
2	**6a** (CH_2)	31	10	>98
3	**6c** (CH_2CH_2)	15	13	>98
4	**6d** ($CH_2CH_2CH_2$)	40	10	98
5	**6e** ($CH_2CH_2CH_2CH_2$)	23	13	91
6	**6f** ($CH_2CH_2CH_2CH_2CH_2$)	24	0	—
7	**6g** ($CH_2CH_2CH_2CH_2CH_2CH_2$)	29	18	32
8	**6h** (CH_2OCH_2)	29[b]	29[b,c]	>98
9	**6i** ($CH_2OCH_2CH_2OCH_2$)	55	24	68
10	**6j** ($CH_2OCH_2CH_2OCH_2CH_2OCH_2$)	(ca. 40)[d]	0	—

[a] Isolated yield of a pure regioisomer.
[b] Isolated as a mixture of **7h** and **8h**.
[c] The corresponding chiral diol was isolated in pure form by treating **8h** with $LiAlH_4$.
[d] Product **7j** could not be isolated in a pure form (ca. 90% purity).

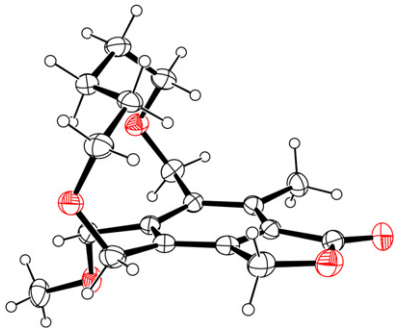
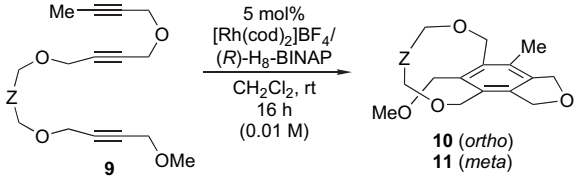


Figure 2. ORTEP diagram of (*R*)-(−)-**8d**.

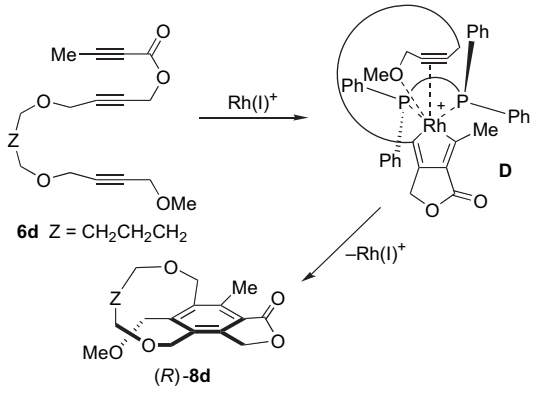
Table 6
Enantioselective synthesis of planar-chiral metacyclophanes through $Rh(I)^+$/(*R*)-H_8-BINAP-catalyzed intramolecular alkyne cyclotrimerization of **9**



Entry	**9** (*Z*)	Yield[a] (%)		ee (%)
		10	**11**	**11**
1	**9a** (—)	87	0	—
2	**9b** (CH_2)	37	25	90
3	**9c** (CH_2CH_2)	35	33	93
4	**9d** ($CH_2CH_2CH_2$)	15 (17[c])	21 (24[c])	94 (94[c])
5[b]	**9e** ($CH_2CH_2CH_2CH_2$)	23	30	93
6	**9f** ($CH_2CH_2CH_2CH_2CH_2$)	25	22	74
7	**9g** ($CH_2CH_2CH_2CH_2CH_2CH_2$)	27	19	58
8[b]	**9h** (CH_2OCH_2)	55[d]	30[d]	88
9	**9i** ($CH_2OCH_2CH_2OCH_2$)	0	0	—
10	**9j** ($CH_2OCH_2CH_2OCH_2CH_2OCH_2$)	90	0	—

[a] Isolated yield of a pure regioisomer.
[b] Reaction time: 40 h.
[c] Catalyst: 10 mol %.
[d] Isolated as a mixture of **10h** and **11h**.

$Rh(I)^+$/H_8-BINAP complex, the coordination of the terminal methoxy group to the cationic rhodium, and the steric interaction between the ansa chain of **6d** and the PPh_2 groups of (*R*)-H_8-BINAP.



Scheme 4. Possible mechanism for the formation of (*R*)-**8d**.

3. Conclusions

In conclusion, we have demonstrated that cationic rhodium(I)/(*S*)-xyl-H_8-BINAP or (*R*)-H_8-BINAP complex-catalyzed inter- and intramolecular alkyne cyclotrimerizations represent versatile new methods for the enantioselective synthesis of planar-chiral metacyclophanes. Applications of cationic rhodium(I)/modified-BINAP complex-catalyzed [2+2+2] cycloadditions to the synthesis of a variety of planar-chiral cyclophanes including paracyclophanes will be reported in due course.

4. Experimental

4.1. General

^1H NMR spectra were recorded on 300 MHz (JEOL AL 300). ^{13}C NMR spectra were obtained with complete proton decoupling on 75 MHz (JEOL AL 300). HRMS data were obtained on a JEOL JMS-T100LC. Infrared spectra were obtained on a JASCO A-302. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

4.2. Materials

Anhydrous CH_2Cl_2 (No. 27,099-7) was obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over molecular sieves 4 Å prior to use. Diyne **1b** was prepared according to a literature procedure.[31] All other reagents were obtained from commercial sources and used as received.

4.3. Synthesis of α,ω-diynes *1*

4.3.1. 1-(2-(But-2-ynyloxy)ethoxy)but-2-yne *1c*

A mixture of KOH (1.99 g, 35.4 mmol), ethylene glycol (1.00 g, 16.1 mmol), and DMSO (80 mL) was stirred at rt for 2 h. To this mixture was added 1-bromo-2-butyne (4.7 g, 35.4 mmol) at 0 °C, and the resulting mixture was stirred at rt for 16 h. The reaction was quenched by the addition of water and extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc=10:1) to afford **1c** (1.36 g, 8.17 mmol, 51% yield) as a pale yellow oil. IR (neat) 2850, 2200, 1350, 1140, 1090, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.16 (q, *J*=2.4 Hz, 4H), 3.69 (s, 4H), 1.85 (t, *J*=2.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.5, 74.9, 68.6, 58.8, 3.5; HRMS (ESI) calcd for $C_{10}H_{14}O_2Na$ $[M+Na]^+$ 189.0892, found 189.0881.

4.3.2. Representative procedure for synthesis of internal α,ω-diynes *1d–m*: synthesis of diyne *1d*

n-BuLi (1.6 M in hexane, 18.1 mL, 29.0 mmol) was added over 15 min to a cooled (−40 °C) solution of **1b**[31] (2.00 g, 14.5 mmol) in ether (25 mL). To this mixture was added a solution of bromomethyl methyl ether (2.90 g, 36.3 mmol) in

Et_2O (10 mL), and the resulting mixture was stirred at rt for 1 h. The reaction was quenched by the addition of ice water and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc=10:1) to afford **1d** (2.05 g, 62% yield) as a pale yellow oil. IR (neat) 2850, 1440, 1340, 1250, 1180, 1090, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.27 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.72 (s, 4H), 3.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.3, 82.2, 68.7, 59.8, 58.6, 57.5; HRMS (ESI) calcd for $C_{12}H_{18}O_4Na$ $[M+Na]^+$ 249.1102, found 249.1120.

4.3.3. Diyne *1e*

Pale yellow oil; IR (neat) 3250, 2900, 1440, 1340, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.19 (t, J=1.5 Hz, 4H), 4.15 (t, J=1.5 Hz, 4H), 3.60 (t, J=6.3 Hz, 4H), 3.39 (s, 6H), 1.90 (quint, J=6.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.6, 81.9, 66.9, 59.8, 58.3, 57.6, 29.7; HRMS (ESI) calcd for $C_{13}H_{20}O_4Na$ $[M+Na]^+$ 263.1259, found 263.1241.

4.3.4. Diyne *1f*

Colorless oil; IR (neat) 3250, 2850, 1440, 1340, 1180, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.19 (t, J=1.5 Hz, 4H), 4.14 (t, J=1.5 Hz, 4H), 3.57–3.50 (m, 4H), 3.39 (s, 6H), 1.68 (quint, J=2.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 81.8, 69.7, 59.8, 58.2, 57.6, 26.1; HRMS (ESI) calcd for $C_{14}H_{22}O_4Na$ $[M+Na]^+$ 277.1416, found 277.1429.

4.3.5. Diyne *1g*

Colorless oil; IR (neat) 2900, 1440, 1340, 1180, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.18 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.51 (t, J=6.6 Hz, 4H), 3.39 (s, 6H), 1.63 (quint, J=6.6 Hz, 4H), 1.50–1.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 81.8, 70.0, 59.9, 58.2, 57.6, 29.2, 22.7; HRMS (ESI) calcd for $C_{15}H_{24}O_4Na$ $[M+Na]^+$ 291.1572, found 291.1577.

4.3.6. Diyne *1h*

Pale yellow oil; IR (neat) 2850, 1440, 1340, 1180, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.18 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.50 (t, J=6.6 Hz, 4H), 3.39 (s, 6H), 1.66–1.51 (m, 4H), 1.42–1.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 81.8, 70.1, 59.9, 58.2, 57.6, 29.4, 25.9; HRMS (ESI) calcd for $C_{16}H_{26}O_4Na$ $[M+Na]^+$ 305.1729, found 305.1714.

4.3.7. Diyne *1i*

Pale yellow oil; IR (neat) 2850, 1440, 1340, 1180, 1090, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.18 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.50 (t, J=6.6 Hz, 4H), 3.39 (s, 6H), 1.65–1.50 (m, 4H), 1.40–1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 81.8, 70.2, 59.9, 58.2, 57.6, 29.4, 29.2, 26.0; HRMS (ESI) calcd for $C_{17}H_{28}O_4Na$ $[M+Na]^+$ 319.1885, found 319.1910.

4.3.8. Diyne *1j*

Pale yellow oil; IR (neat) 2850, 1440, 1340, 1180, 1090, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.18 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.50 (t, J=6.6 Hz, 4H), 3.39 (s, 6H), 1.65–1.50 (m, 4H), 1.40–1.25 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 81.8, 70.2, 59.9, 58.2, 57.6, 29.4, 29.2, 26.0; HRMS (ESI) calcd for $C_{18}H_{30}O_4Na$ $[M+Na]^+$ 333.2042, found 333.2043.

4.3.9. Diyne *1k*

Colorless oil; IR (neat) 2900, 1440, 1340, 1180, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.26 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.74–3.64 (m, 8H), 3.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.3, 82.2, 70.4, 69.0, 59.8, 58.6, 57.5; HRMS (ESI) calcd for $C_{14}H_{22}O_5Na$ $[M+Na]^+$ 293.1365, found 293.1366.

4.3.10. Diyne *1l*

Pale yellow oil; IR (neat) 2850, 1440, 1340, 1100, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.26 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.70–3.66 (m, 8H), 3.67 (s, 4H), 3.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.3, 82.2, 70.5, 70.4, 69.0, 59.8, 58.6, 57.6; HRMS (ESI) calcd for $C_{16}H_{26}O_6Na$ $[M+Na]^+$ 337.1627, found 337.1624.

4.3.11. Diyne *1m*

Pale yellow oil; IR (neat) 2850, 1440, 1340, 1100, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.26 (t, J=1.8 Hz, 4H), 4.14 (t, J=1.8 Hz, 4H), 3.71–3.64 (m, 8H), 3.67 (s, 8H), 3.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.4, 82.2, 70.6, 70.5, 70.4, 69.1, 59.9, 58.6, 57.6; HRMS (ESI) calcd for $C_{18}H_{30}O_7Na$ $[M+Na]^+$ 381.1889, found 381.1893.

4.4. Representative procedure for rhodium-catalyzed intermolecular alkyne cyclotrimerization (Table 3, entry 2)

(*S*)-Xyl-H_8-BINAP (22.3 mg, 0.03 mmol) and $[Rh(cod)_2]$-BF_4 (12.2 mg, 0.03 mmol) were dissolved in CH_2Cl_2 (3.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting mixture was concentrated to dryness. To this was added a solution of di-*tert*-butyl acetylenedicarboxylate (**2c**, 101.8 mg, 0.45 mmol) in CH_2Cl_2 (0.5 mL) at rt. To this solution was added a solution of diyne **1e** (72.1 mg, 0.30 mmol) in CH_2Cl_2 (1.0 mL) at rt. The mixture was stirred at rt for 48 h. The resulting solution was concentrated and purified by preparative TLC (pure **4ec** and crude **3ec** were obtained by hexane/triethylamine=5:1, and **3ec** was then obtained pure by hexane/ethyl acetate=2:1), to furnish [7]metacyclophane (−)-**3ec** (16.8 mg, 0.036 mmol, 12% yield, 98% ee) as a colorless oil and [7]orthocyclophane **4ec** (17.0 mg, 0.0364 mmol, 12% yield) as a colorless solid.

4.4.1. (−)-[7]Metacyclophane (−)-*3ec*

$[\alpha]_D^{25}$ −39.3 (*c* 0.440, $CHCl_3$, 98% ee); IR (neat) 2900, 1710, 1440, 1370, 1300, 1150, 1110, 1070, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.19 (d, J=13.8 Hz, 1H), 5.07

(d, J=13.8 Hz, 1H), 5.03 (d, J=9.6 Hz, 1H), 5.00 (d, J=9.6 Hz, 1H), 4.61 (d, J=12.6 Hz, 1H), 4.56 (d, J=12.6 Hz, 1H), 4.52 (d, J=13.8 Hz, 1H), 4.37 (d, J=13.8 Hz, 1H), 3.70–3.55 (m, 2H), 3.36 (s, 3H), 3.31 (s, 3H), 2.35–2.15 (m, 2H), 1.63–1.50 (m, 1H), 1.59 (s, 9H), 1.58 (s, 9H), 1.08–0.92 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 166.1, 146.8, 143.4, 139.9, 134.3, 132.5, 131.0, 82.6, 82.4, 73.2, 69.0, 68.8, 68.7, 68.6, 67.3, 58.7, 57.8, 32.9, 28.2, 28.0; HRMS (ESI) calcd for $C_{25}H_{38}O_8Na$ $[M+Na]^+$ 489.2464, found 489.2478. CHIRALPAK AD, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 9.8 min (minor isomer) and 12.6 min (major isomer).

4.4.2. [7]Orthocyclophane **4ec**

Mp 76.4–77.1 °C; IR (KBr) 2900, 1710, 1360, 1300, 1160, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.96 (s, 4H), 4.57 (s, 4H), 3.66 (t, J=5.6 Hz, 4H), 3.31 (s, 6H), 1.76 (quint, J=5.6 Hz, 2H), 1.59 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.3, 139.5, 134.5, 82.8, 77.2, 68.5, 67.8, 67.4, 57.9, 28.1; HRMS (ESI) calcd for $C_{25}H_{38}O_8Na$ $[M+Na]^+$ 489.2464, found 489.2482.

4.4.3. [6]Metacyclophane **3bb** (Scheme 2)

Colorless solid; mp 85.6–86.0 °C; IR (KBr) 2900, 1720, 1430, 1280, 1200, 1140, 1080, 1030, 840, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (s, 1H), 7.72 (s, 1H), 4.60–5.00 (m, 2H), 4.15–4.60 (m, 2H), 3.903 (s, 3H), 3.901 (s, 3H), 3.50–3.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 166.6, 140.7, 131.4, 72.4 (br), 52.8, 52.7; HRMS (ESI) calcd for $C_{14}H_{16}O_6$ $[M+Na]^+$ 303.0845, found 303.0863; CHIRALPAK AD, hexane/2-PrOH=80:20, 0.8 mL/min, retention times: 11.0 min (minor isomer) and 15.3 min (major isomer).

4.4.4. [6]Orthocyclophane **4bb** (Scheme 2)

Colorless solid; mp 33.7–35.6 °C; IR (KBr) 2900, 1720, 1260, 1100, 1020, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54 (s, 2H), 4.99 (s, 4H), 3.90 (s, 6H), 3.81 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 140.5, 131.3, 130.4, 72.4, 71.0, 52.7; HRMS (ESI) calcd for $C_{14}H_{16}O_6$ $[M+Na]^+$ 303.0845, found 303.0860.

4.4.5. (+)-[6]Metacyclophane (+)-**3cc** (Table 1, entry 2)

Colorless solid; mp 122.0–122.8 °C; $[\alpha]_D^{25}$ +6.3 (c 0.155, $CHCl_3$, 8% ee); IR (KBr) 2900, 1720, 1690, 1360, 1300, 1240, 1170, 1110, 1070, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.70 (d, J=5.8 Hz, 1H), 5.56 (d, J=5.8 Hz, 1H), 4.38 (d, J=12.7 Hz, 1H), 4.27 (d, J=12.7 Hz, 1H), 3.50–3.80 (m, 2H), 3.08–3.35 (m, 2H), 2.35 (s, 3H), 1.93 (s, 3H), 1.49 (s, 9H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.0, 163.4, 157.7, 149.2, 143.4, 138.3, 134.5, 110.2, 80.5, 79.7, 72.7, 68.7, 67.4, 63.3, 28.4, 28.0, 13.2, 12.2; HRMS (ESI) calcd for $C_{22}H_{32}O_6Na$ $[M+Na]^+$ 415.2097, found 415.2109. CHIRALPAK AD, hexane/2-PrOH=98:2, 1.0 mL/min, retention times: 7.4 min (major isomer) and 10.2 min (minor isomer).

4.4.6. [6]Orthocyclophane **4cc** (Table 1, entry 2)

Colorless solid; mp 81.2–82.0 °C; IR (KBr) 2900, 1710, 1360, 1300, 1220, 1150, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.95 (s, 4H), 3.76 (s, 4H), 2.35 (s, 6H), 1.60 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 136.8, 133.8, 131.9, 82.6, 69.7, 65.6, 28.2, 16.2; HRMS (ESI) calcd for $C_{22}H_{32}O_6Na$ $[M+Na]^+$ 415.2097, found 415.2091.

4.4.7. [6]Orthocyclophane **4dc** (Table 1, entry 3)

Colorless solid; mp 97.8–98.7 °C; IR (KBr) 2900, 1710, 1360, 1300, 1220, 1160, 1100, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.05 (s, 4H), 4.57 (s, 4H), 3.77 (s, 4H), 3.34 (s, 6H), 1.60 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.2, 138.8, 134.8, 134.2, 83.0, 69.8, 68.4, 64.6, 58.2, 28.2; HRMS (ESI) calcd for $C_{24}H_{36}O_8Na$ $[M+Na]^+$ 475.2308, found 475.2330.

4.4.8. (−)-[6]Metacyclophane (−)-**3dc** (Table 3, entry 1)

Colorless solid; mp 76.8–77.4 °C; $[\alpha]_D^{25}$ −41.8 (c 0.190, $CHCl_3$, 95% ee); IR (KBr) 2900, 1700, 1360, 1290, 1150, 1100, 1040, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.08 (d, J=13.2 Hz, 1H), 5.00 (d, J=7.2 Hz, 1H), 4.97 (d, J=7.2 Hz, 1H), 4.94 (d, J=13.2 Hz, 1H), 4.68 (d, J=13.2 Hz, 1H), 4.67 (d, J=12.9 Hz, 1H), 4.60 (d, J=12.9 Hz, 1H), 4.47 (d, J=13.2 Hz, 1H), 3.52–3.35 (m, 2H), 3.34 (s, 3H), 3.33 (s, 3H), 2.88–2.70 (m, 1H), 2.22–2.03 (m, 1H), 1.58 (s, 9H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.9, 165.5, 148.9, 143.8, 141.6, 134.2, 132.6, 131.5, 82.5, 82.3, 72.8, 70.6, 69.9, 69.3, 68.6, 68.4, 58.8, 58.1, 28.2, 28.0; HRMS (ESI) calcd for $C_{24}H_{36}O_8Na$ $[M+Na]^+$ 475.2308, found 475.2333. CHIRALPAK AD, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 16.1 min (minor isomer) and 24.2 min (major isomer).

4.4.9. (+)-[9]Metacyclophane (+)-**3gc** (Table 3, entry 4)

Colorless solid; mp 110.2–110.8 °C, $[\alpha]_D^{25}$ +12.0 (c 0.470, $CHCl_3$, 92% ee); IR (KBr) 2900, 1710, 1440, 1360, 1300, 1250, 1150, 1080, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.19 (d, J=11.7 Hz, 1H), 5.18 (d, J=13.5 Hz, 1H), 5.16 (d, J=11.7 Hz, 1H), 5.13 (d, J=13.5 Hz, 1H), 4.62 (d, J=13.5 Hz, 1H), 4.58 (d, J=12.0 Hz, 1H), 4.54 (d, J=12.0 Hz, 1H), 4.43 (d, J=13.5 Hz, 1H), 3.54–3.45 (m, 2H), 3.36 (s, 3H), 3.32 (s, 3H), 3.28–3.21 (m, 1H), 3.12–3.05 (m, 1H), 1.71–1.50 (m, 1H), 1.60 (s, 9H), 1.59 (s, 9H), 1.20–0.95 (m, 3H), 0.60–0.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.3, 167.2, 143.0, 142.9, 138.1, 133.9, 133.5, 132.4, 83.2, 82.9, 69.3, 68.7, 67.8, 67.3, 67.1, 66.5, 58.8, 57.9, 28.24, 28.16, 28.0, 20.3; HRMS (ESI) calcd for $C_{27}H_{42}O_8Na$ $[M+Na]^+$ 517.2777, found 517.2756. CHIRALPAK AD, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 6.6 min (minor isomer) and 7.9 min (major isomer).

4.4.10. [9]Paracyclophane **5gc** (Table 3, entry 4)

Colorless oil; IR (neat) 2900, 1710, 1360, 1300, 1150, 1100, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.87 (d, J=12.6 Hz, 2H), 4.82 (d, J=12.6 Hz, 2H), 4.75 (d, J=11.4 Hz, 2H), 4.58 (d, J=11.4 Hz, 2H), 3.45 (s, 6H),

3.34–3.27 (m, 4H), 1.58 (s, 18H), 0.92–0.60 (m, 5H), 0.60–0.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 140.0, 137.3, 135.0, 82.8, 67.9, 66.9, 66.3, 58.8, 28.7, 28.1, 21.0; HRMS (ESI) calcd for $C_{27}H_{42}O_8Na$ $[M+Na]^+$ 517.2777, found 517.2783.

*4.4.11. (−)-[10]Metacyclophane (−)-**3hc** (Table 3, entry 5)*

Colorless oil; $[\alpha]_D^{25}$ −5.8 (*c* 0.625, $CHCl_3$, 52% ee); IR (neat) 2900, 1710, 1420, 1360, 1300, 1150, 1090, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.12 (d, *J*=13.8 Hz, 1H), 5.03 (d, *J*=5.4 Hz, 1H), 5.02 (d, *J*=13.8 Hz, 1H), 5.01 (d, *J*=5.4 Hz, 1H), 4.64 (d, *J*=13.8 Hz, 1H), 4.61 (d, *J*=11.7 Hz, 1H), 4.55 (d, *J*=11.7 Hz, 1H), 4.40 (d, *J*=13.5 Hz, 1H), 3.57–3.47 (m, 2H), 3.35 (s, 3H), 3.32 (s, 3H), 3.09–2.90 (m, 2H), 1.600 (s, 9H), 1.595 (s, 9H), 1.45–1.30 (m, 2H), 1.30–1.12 (m, 2H), 1.12–0.96 (m, 2H), 0.75–0.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 167.4, 141.9, 141.5, 136.8, 134.3, 134.1, 132.5, 83.1, 82.8, 69.0, 68.8, 68.2, 68.0, 67.0, 65.5, 58.6, 57.9, 29.11, 29.07, 28.2, 28.1, 25.50, 25.46; HRMS (ESI) calcd for $C_{28}H_{44}O_8Na$ $[M+Na]^+$ 531.2934, found 531.2923; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 7.6 min (major isomer) and 10.7 min (minor isomer).

*4.4.12. [11]Orthocyclophane, (−)-[11]metacyclophane, and [11]paracyclophane [**4ic**/(−)-**3ic**/**5ic**=44:36:20, Table 3, entry 6]*

Colorless oil; IR (neat) 2900, 1710, 1430, 1360, 1300, 1150, 1090, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.18 (d, *J*=13.2 Hz, 1H, **3ic**), 5.09 (d, *J*=13.5 Hz, 1H, **3ic**), 5.07 (d, *J*=13.2 Hz, 2H, **5ic**), 5.04 (d, *J*=12.6 Hz, 1H, **3ic**), 4.997 (d, *J*=11.7 Hz, 2H, **5ic**), 4.995 (d, *J*=12.6 Hz, 1H, **3ic**), 4.69 (d, *J*=13.5 Hz, 1H, **3ic**), 4.597 (s, 4H, **4ic**), 4.596 (d, *J*=13.2 Hz, 2H, **5ic**), 4.58 (s, 4H, **4ic**), 4.57 (d, *J*=11.4 Hz, 1H, **3ic**), 4.51 (d, *J*=11.4 Hz, 1H, **3ic**), 4.44 (d, *J*=13.2 Hz, 1H, **3ic**), 4.43 (d, *J*=13.2 Hz, 2H, **5ic**), 3.60 (t, *J*=5.1 Hz, 4H, **4ic**), 3.50–3.20 (m, 2H, **5ic**; 4H, **3ic**), 3.42 (s, 6H, **5ic**), 3.37 (s, 3H, **3ic**), 3.34 (s, 3H, **3ic**), 3.30 (s, 6H, **4ic**), 3.15–2.90 (m, 2H, **5ic**), 1.60 (s, 18H, **3ic**), 1.58 (s, 18H, **5ic**; 18H, **4ic**), 2.00–0.16 (m, 10H, **5ic**; 10H, **4ic**; 10H, **3ic**); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 167.3, 141.4, 140.6, 140.55, 140.53, 138.9, 135.7, 135.6, 135.0, 134.7, 134.3, 134.1, 132.7, 119.5, 83.2, 83.1, 83.0, 82.5, 70.6, 68.8, 68.6, 67.8, 67.4, 66.6, 65.8, 64.7, 64.6, 64.0, 58.7, 58.5, 58.0, 57.9, 29.5, 28.14, 28.11, 28.1, 28.05, 27.3, 25.7, 25.5, 25.4, 24.9, 24.8, 22.8; HRMS (ESI) calcd for $C_{29}H_{46}O_8Na$ $[M+Na]^+$ 545.3090, found 545.3077; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 9.4 min (major isomer) and 18.4 min (minor isomer).

*4.4.13. (+)-[12]Metacyclophane and [12]orthocyclophane [(+)-**3jc**/**4jc**=50:50, Table 3, entry 7]*

Colorless solid; mp 115.0–117.0 °C; $[\alpha]_D^{25}$ +5.0 [*c* 0.640, $CHCl_3$ (calculated content of (+)-**3jc**), 62% ee]; IR (KBr) 2850, 1720, 1430, 1360, 1300, 1150, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.96 (d, *J*=13.8 Hz, 1H, **3jc**), 4.94 (d, *J*=11.7 Hz, 1H, **3jc**), 4.87 (d, *J*=13.5 Hz, 1H, **3jc**), 4.86 (d, *J*=11.7 Hz, 1H, **3jc**), 4.74 (d, *J*=13.5 Hz, 1H, **3jc**), 4.69 (d, *J*=11.4 Hz, 1H, **3jc**), 4.61 (d, *J*=11.4 Hz, 1H, **3jc**), 4.60 (s, 4H, **4jc**), 4.59 (s, 4H, **4jc**), 4.55 (d, *J*=13.8 Hz, 1H, **3jc**), 3.59 (t, *J*=5.4 Hz, 4H, **4jc**), 3.45–3.21 (m, 4H, **3jc**), 3.38 (s, 3H, **3jc**), 3.30 (s, 3H, **3jc**), 3.28 (s, 6H, **4jc**), 1.80–0.85 (m, 12H, **3jc**; 12H, **4jc**), 1.60 (s, 9H, **3jc**), 1.59 (s, 9H, **3jc**), 1.58 (s, 18H, **4jc**); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 167.44, 167.41, 140.4, 139.74, 139.72, 138.2, 135.8, 135.4, 135.0, 134.8, 133.9, 82.9, 82.6, 82.4, 69.8, 68.8, 68.7, 68.1, 67.6, 67.0, 66.0, 65.63, 65.61, 58.5, 57.92, 57.86, 29.0, 28.8, 28.2, 28.13, 28.05, 27.4, 27.2, 26.14, 26.13, 24.7, 24.4, 22.9; HRMS (ESI) calcd for $C_{30}H_{48}O_8Na$ $[M+Na]^+$ 559.3247, found 559.3240; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 6.1 min (major isomer) and 8.0 min (minor isomer).

*4.4.14. (+)-[9]Metacyclophane (+)-**3kc** (Table 3, entry 8)*

Colorless solid; mp 98.0–99.6 °C; $[\alpha]_D^{25}$ +28.4 (*c* 0.350, $CHCl_3$, 92% ee); IR (KBr) 2900, 1710, 1440, 1360, 1300, 1140, 1090, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.20 (d, *J*=13.5 Hz, 1H), 5.13 (d, *J*=14.1 Hz, 1H), 5.00 (d, *J*=12.9 Hz, 1H), 4.96 (d, *J*=12.9 Hz, 1H), 4.70 (d, *J*=14.1 Hz, 1H), 4.55 (d, *J*=11.7 Hz, 1H), 4.51 (d, *J*=11.7 Hz, 1H), 4.50 (d, *J*=13.5 Hz, 1H), 3.74–3.64 (m, 2H), 3.40–3.30 (m, 1H), 3.334 (s, 3H), 3.332 (s, 3H), 3.22–3.06 (m, 3H), 2.98–2.88 (m, 2H), 1.60 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.61, 167.59, 144.4, 140.3, 135.5, 133.8, 133.1, 131.4, 83.0, 82.7, 70.4, 70.2, 68.8, 68.3, 67.9, 67.5, 67.1, 58.6, 58.5, 57.9, 28.2; HRMS (ESI) calcd for $C_{26}H_{40}O_9Na$ $[M+Na]^+$ 519.2570, found 519.2597. CHIRALPAK AD, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 9.5 min (minor isomer) and 11.1 min (major isomer).

*4.4.15. [9]Orthocyclophane **4kc** (Table 3, entry 8)*

Colorless solid; mp 104.0–104.6 °C; IR (KBr) 2850, 1710, 1440, 1360, 1300, 1150, 1100, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.83 (s, 4H), 4.63 (s, 4H), 3.80–3.75 (m, 4H), 3.68–3.64 (m, 4H), 3.30 (s, 6H), 1.58 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 138.9, 134.9, 134.7, 82.6, 72.7, 69.7, 68.6, 66.6, 57.9, 28.1; HRMS (ESI) calcd for $C_{26}H_{40}O_9Na$ $[M+Na]^+$ 519.2570, found 519.2588.

*4.4.16. (+)-[12]Metacyclophane (+)-**3lc** (Table 3, entry 9)*

Colorless oil; $[\alpha]_D^{25}$ +5.3 (*c* 0.350, $CHCl_3$, 80% ee); IR (neat) 2800, 1700, 1360, 1300, 1140, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.085 (d, *J*=12.5 Hz, 1H), 5.082 (d, *J*=13.6 Hz, 1H), 5.01 (d, *J*=12.5 Hz, 1H), 5.00 (d, *J*=13.2 Hz, 1H), 4.73 (d, *J*=13.2 Hz, 1H), 4.61 (d, *J*=11.7 Hz, 1H), 4.54 (d, *J*=11.7 Hz, 1H), 4.49 (d, *J*=13.6 Hz, 1H), 3.74–3.37 (m, 12H), 3.35 (s, 3H), 3.31 (s, 3H), 1.60 (s, 9H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.60, 167.58, 141.6, 139.9, 135.3, 134.8, 134.0, 133.01, 82.9, 82.8, 70.7, 70.5, 70.4, 70.1, 69.2, 68.9, 68.5, 68.2, 67.1, 65.5, 58.4, 57.9, 28.13, 28.12; HRMS (ESI) calcd for $C_{28}H_{44}O_{10}Na$ $[M+Na]^+$ 563.2832, found 563.2808; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 16.0 min (minor isomer) and 19.8 min (major isomer).

4.4.17. [12]Orthocyclophane ***4lc*** *(Table 3, entry 9)*

Colorless oil; IR (neat) 2900, 1710, 1360, 1300, 1150, 1090, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.86 (s, 4H), 4.63 (s, 4H), 3.80–3.70 (m, 8H), 3.69 (s, 4H), 3.26 (s, 6H), 1.57 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 138.6, 135.2, 134.8, 82.3, 71.7, 69.9, 69.7, 68.5, 66.5, 57.7, 28.0; HRMS (ESI) calcd for $C_{28}H_{44}O_{10}Na$ $[M+Na]^+$ 563.2832, found 563.2807.

4.5. Synthesis of triynes *6*

4.5.1. Representative procedure for the synthesis of triynes *6*: synthesis of triyne *6b*

n-BuLi (1.6 M in hexane, 10.0 mL, 16.0 mmol) was added over 15 min to a cooled (−40 °C) solution of **1b**[31] (2.00 g, 14.5 mmol) in Et_2O (25 mL). To this solution was added a solution of chloromethyl methyl ether (1.28 g, 16.0 mmol) in Et_2O (5 mL), and the resulting solution was stirred at rt for 1 h. The reaction was quenched by the addition of ice water and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc=3:1) to give 1-methoxy-4-(2-(prop-2-ynyloxy)ethoxy)-but-2-yne (0.873 g, 4.79 mmol, 33% yield) as a pale yellow oil.

n-BuLi (1.6 M in hexane, 1.53 mL, 2.45 mmol) was added dropwise to a THF (2.0 mL) solution of 1-methoxy-4-(2-(prop-2-ynyloxy)ethoxy)but-2-yne (0.430 g, 2.36 mmol) at −78 °C and the resulting solution was stirred at −78 °C for 15 min. A THF (10 mL) suspension of paraformaldehyde (0.144 mg, 4.72 mmol) was added at −78 °C, and the resulting mixture was stirred at rt for 16 h. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane/EtOAc=1:1), which furnished 4-[2-(4-methoxybut-2-ynyloxy)ethoxy]-but-2-yn-1-ol (0.258 g, 1.07 mmol, 51% yield) as a pale yellow oil.

To a CH_2Cl_2 (2.0 mL) solution of 4-*N*,*N*-dimethylamimopyridine (7.0 mg, 0.057 mmol) and 4-[3-(4-methoxybut-2-ynyloxy)ethoxy]but-2-yn-1-ol (0.258 g, 1.07 mmol) was added dropwise a CH_2Cl_2 (3.0 mL) solution of 2-butynoic acid (0.108 g, 1.28 mmol). The resulting solution was cooled to 0 °C. *N*,*N*′-Dicyclohexylcarbodiimide (0.265 g, 1.28 mmol) was added at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h and then at rt for 24 h. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane/ethyl acetate=2:1), which furnished **6b** (0.247 g, 0.888 mmol, 83% yield) as a colorless solid. Mp 147.2–148.0 °C; IR (KBr) 2900, 2250, 1710, 1240, 1060, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.26 (t, J=1.8 Hz, 2H), 4.25 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.71 (s, 4H), 3.39 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.5, 86.8, 83.1, 82.2, 82.0, 79.5, 71.5, 68.7, 68.5, 59.6, 58.4, 58.3, 57.3, 53.0, 3.6; HRMS (ESI) calcd for $C_{15}H_{18}O_5Na$ $[M+Na]^+$ 301.1208, found 301.1199.

4.5.2. Triyne *6a*

Colorless oil; IR (neat) 2850, 2240, 1710, 1350, 1240, 1070, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.20 (t, J=1.8 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.15 (t, J=1.8 Hz, 2H), 3.60 (t, J=6.3 Hz, 2H), 3.59 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 2.01 (s, 3H), 1.89 (quint, J=6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 86.9, 83.7, 82.6, 81.9, 79.2, 71.7, 67.1, 66.9, 59.9, 58.4, 58.3, 57.6, 53.3, 29.7, 3.8; HRMS (ESI) calcd for $C_{16}H_{20}O_5Na$ $[M+Na]^+$ 315.1208, found 315.1199.

4.5.3. Triyne *6c*

Colorless oil; IR (neat) 2890, 2230, 1710, 1440, 1350, 1250, 1070, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.19 (t, J=1.8 Hz, 2H), 4.17 (t, J=1.8 Hz, 2H), 4.15 (t, J=1.8 Hz, 2H), 3.53 (t, J=6.3 Hz, 2H), 3.51 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 2.01 (s, 3H), 1.67 (quint, J=6.3 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 86.9, 83.8, 82.7, 81.9, 79.2, 71.7, 69.9, 69.8, 59.9, 58.3, 58.2, 57.7, 53.4, 26.2, 26.0, 3.9; HRMS (ESI) calcd for $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1365, found 329.1336.

4.5.4. Triyne *6d*

Colorless oil; IR (neat) 2900, 2280, 1710, 1440, 1360, 1250, 1070, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.16 (t, J=1.8 Hz, 2H), 4.15 (t, J=1.8 Hz, 2H), 3.51 (t, J=6.3 Hz, 2H), 3.49 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 2.01 (s, 3H), 1.71–1.49 (m, 4H), 1.58–1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 86.9, 83.8, 81.9, 79.1, 77.2, 71.7, 70.2, 70.0, 59.9, 58.3, 58.2, 57.6, 53.3, 29.3, 22.7, 3.8; HRMS (ESI) calcd for $C_{18}H_{24}O_5Na$ $[M+Na]^+$ 343.1521, found 343.1507.

4.5.5. Triyne *6e*

Pale yellow oil; IR (neat) 2900, 2250, 1700, 1430, 1350, 1240, 1080, 1020, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.25–4.09 (m, 6H), 3.50 (t, J=6.3 Hz, 2H), 3.48 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 2.00 (s, 3H), 1.73–1.49 (m, 4H), 1.49–1.27 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.7, 86.8, 83.8, 82.7, 81.8, 79.1, 71.7, 70.2, 70.0, 59.8, 58.2, 58.1, 57.5, 53.2, 29.4, 29.3, 25.9, 25.8, 3.72; HRMS (ESI) calcd for $C_{19}H_{26}O_5Na$ $[M+Na]^+$ 357.1678, found 357.1664.

4.5.6. Triyne *6f*

Orange oil; IR (neat) 2935, 2857, 2240, 1716, 1437, 1354, 1305, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.80 (t, J=1.8 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.16 (t, J=1.8 Hz, 2H), 4.15 (t, J=1.8 Hz, 2H), 3.50 (t, J=6.6 Hz, 2H), 3.48 (t, J=6.6 Hz, 2H), 3.39 (s, 3H), 2.00 (s, 3H), 1.63–1.51 (m, 3H), 1.40–1.30 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 86.8, 83.9, 82.8, 81.8, 79.1, 71.7, 70.3, 70.2, 59.9, 58.2, 58.1, 57.6, 53.3, 29.41, 29.39, 29.2, 25.99, 25.97, 3.80;

HRMS (ESI) calcd for $C_{20}H_{28}O_5Na$ $[M+Na]^+$ 371.1834, found 371.1799.

4.5.7. Triyne **6g**

Orange oil; IR (neat) 2934, 2858, 2242, 1717, 1249, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.80 (t, J=1.8 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.16 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.50 (t, J=6.6 Hz, 2H), 3.48 (t, J=6.6 Hz, 2H), 3.39 (s, 3H), 2.00 (s, 3H), 1.65–1.51 (m, 3H), 1.42–1.23 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 86.8, 83.9, 82.8, 81.8, 79.1, 71.7, 70.4, 70.3, 59.9, 58.2, 58.1, 57.6, 53.3, 29.5, 29.4, 29.3, 26.00, 25.98, 3.80; HRMS (ESI) calcd for $C_{21}H_{30}O_5Na$ $[M+Na]^+$ 385.1991, found 385.2027.

4.5.8. Triyne **6h**

Pale orange oil; IR (neat) 2900, 2350, 1710, 1440, 1350, 1240, 1070, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.79 (t, J=1.8 Hz, 2H), 4.26 (t, J=1.8 Hz, 2H), 4.24 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.76–3.63 (m, 8H), 3.39 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.1, 86.4, 83.0, 81.9, 81.8, 79.1, 71.2, 69.88, 69.87, 68.6, 68.5, 59.3, 58.1, 58.0, 57.0, 52.7, 3.2; HRMS (ESI) calcd for $C_{17}H_{22}O_6Na$ $[M+Na]^+$ 345.1314, found 345.1314.

4.5.9. Triyne **6i**

Orange oil; IR (neat) 2874, 2239, 1715, 1438, 1350, 1249, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.78 (t, J=1.8 Hz, 2H), 4.25 (t, J=1.8 Hz, 2H), 4.24 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.81–3.54 (m, 12H), 3.38 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 86.5, 83.1, 82.0, 81.9, 79.2, 71.3, 70.2, 70.1, 69.99, 69.98, 68.8, 68.7, 59.42, 58.2, 58.1, 57.09, 52.8, 3.36; HRMS (ESI) calcd for $C_{19}H_{26}O_7Na$ $[M+Na]^+$ 389.1576, found 389.1567.

4.5.10. Triyne **6j**

Orange oil; IR (neat) 2872, 2238, 1715, 1350, 1248, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.78 (t, J=1.8 Hz, 2H), 4.25 (t, J=1.8 Hz, 2H), 4.24 (t, J=1.8 Hz, 2H), 4.13 (t, J=1.8 Hz, 2H), 3.72–3.59 (m, 16H), 3.37 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 86.6, 83.2, 82.1, 81.9, 79.2, 71.4, 70.24, 70.21, 70.03, 70.01, 68.8, 68.7, 59.5, 58.2, 58.1, 57.2, 52.9, 3.41; HRMS (ESI) calcd for $C_{21}H_{30}O_8Na$ $[M+Na]^+$ 433.1838, found 433.1822.

4.6. Synthesis of triynes **9**

4.6.1. Representative procedure for the synthesis of triynes **9**: synthesis of triyne **9b**

To a THF (10 mL) solution of 4-[3-(4-methoxybut-2-ynyloxy)propoxy]but-2-yn-1-ol (0.450 g, 1.98 mmol), prepared from 3-(3-(prop-2-ynyloxy)propoxy)propyne[31] as following the synthesis of 4-[3-(4-methoxybut-2-ynyloxy)ethoxy]but-2-yn-1-ol described in the synthesis of **6b**, was added NaH (57.1 mg, 2.38 mmol). The resulting mixture was stirred at rt for 30 min. 1-Bromo-2-butyne (0.342 g, 2.57 mmol) was added and the resulting mixture was stirred at rt for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane/EtOAc=5:1), which furnished **9b** (0.415 g, 1.49 mmol, 75% yield) as a colorless oil. IR (neat) 2850, 1430, 1340, 1080, 890 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.19 (t, J=1.8 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.15 (t, J=1.8 Hz, 2H), 3.600 (t, J=6.3 Hz, 2H), 3.594 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 1.88 (quint, J=6.3 Hz, 2H), 1.86 (t, J=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.8, 82.6, 81.9, 81.6, 74.3, 69.99, 66.97, 59.9, 58.4, 57.6, 57.2, 56.6, 29.8, 3.6; HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$ 301.1416, found 301.1396.

4.6.2. Triyne **9a**

Colorless oil; IR (neat) 2898, 2855, 1444, 1348, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.31–4.24 (m, 6H), 4.20 (q, J=2.4 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.72 (s, 4H), 3.39 (s, 3H), 1.86 (t, J=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.2, 82.41, 82.38, 82.21, 81.99, 74.2, 68.83, 68.80, 59.9, 58.6, 57.6, 57.2, 57.1, 56.5, 3.57; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ $[M+Na]^+$ 287.1259, found 287.1233.

4.6.3. Triyne **9c**

Colorless oil; IR (neat) 2850, 1430, 1340, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.17 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.56–3.48 (m, 4H), 3.37 (s, 3H), 1.86 (t, J=2.4 Hz, 3H), 1.71–1.62 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.9, 82.7, 81.9, 81.5, 74.3, 69.8, 69.7, 59.9, 58.2, 57.7, 57.6, 57.1, 56.6, 26.2, 3.57; HRMS (ESI) calcd for $C_{17}H_{24}O_4Na$ $[M+Na]^+$ 315.1572, found 315.1564.

4.6.4. Triyne **9d**

Colorless oil; IR (neat) 2850, 1430, 1340, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.17 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.51 (t, J=6.3 Hz, 2H), 3.50 (t, J=6.3 Hz, 2H), 3.39 (s, 3H), 1.86 (t, J=2.4 Hz, 3H), 1.68–1.56 (m, 4H), 1.50–1.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.9, 82.7, 81.8, 81.5, 74.3, 70.02, 69.99, 59.9, 58.2, 57.6, 57.1, 56.6, 29.3, 22.7, 3.57; HRMS (ESI) calcd for $C_{18}H_{26}O_4Na$ $[M+Na]^+$ 329.1729, found 329.1717.

4.6.5. Triyne **9e**

Pale orange oil; IR (neat) 2850, 1420, 1340, 1260, 1080, 1020, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.27 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.17 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.50 (t, J=6.6 Hz, 2H), 3.49 (t, J=6.6 Hz, 2H), 3.39 (s, 3H), 1.85 (t, J=2.4 Hz, 3H), 1.64–1.53 (m, 4H), 1.43–1.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.9, 82.7, 81.8, 81.4, 74.3, 70.13, 70.11, 60.3, 59.9, 58.2, 57.6, 57.1, 56.6, 31.6, 29.4, 25.9, 26.6, 3.57; HRMS (ESI) calcd for $C_{19}H_{28}O_4Na$ $[M+Na]^+$ 343.1885, found 343.1864.

4.6.6. Triyne **9f**

Colorless oil; IR (neat) 2934, 2855, 1445, 1349, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.18 (t, J=1.8 Hz, 2H), 4.17 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.496 (t, J=6.6 Hz, 2H), 3.488 (t, J=6.6 Hz, 2H), 3.39 (s, 3H), 1.86 (t, J=2.4 Hz, 3H), 1.69–1.51 (m, 4H), 1.42–1.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 83.0, 82.8, 81.8, 81.4, 74.3, 70.20, 70.17, 59.9, 58.2, 57.6, 57.1, 56.6, 29.4, 29.2. 26.0, 3.57; HRMS (ESI) calcd for $C_{20}H_{30}O_4Na$ $[M+Na]^+$ 357.2042, found 357.2012.

4.6.7. Triyne **9g**

Colorless oil; IR (neat) 2926, 2855, 1446, 13489, 1260, 1097, 802 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.181 (t, J=1.8 Hz, 2H), 4.175 (t, J=1.8 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.50 (t, J=6.6 Hz, 2H), 3.49 (t, J=6.6 Hz, 2H), 3.39 (s, 3H), 1.86 (t, J=2.4 Hz, 3H), 1.67–1.49 (m, 4H), 1.43–1.20 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 83.0, 82.8, 81.8, 81.4, 74.3, 70.3, 70.2, 59.9, 58.2, 57.6, 57.1, 56.6, 29.5, 29.3, 26.0, 24.3, 3.57; HRMS (ESI) calcd for $C_{21}H_{32}O_4Na$ $[M+Na]^+$ 371.2198, found 371.2209.

4.6.8. Triyne **9h**

Pale yellow oil; IR (neat) 2900, 1260, 1070, 1020, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.27 (t, J=1.8 Hz, 2H), 4.26 (t, J=1.8 Hz, 2H), 4.25 (t, J=1.8 Hz, 2H), 4.20 (q, J=2.4 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.74–3.65 (m, 8H), 3.38 (s, 3H), 1.86 (t, J=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.6, 82.4, 82.2, 81.9, 74.3, 70.4, 69.09, 69.08, 59.9, 58.6, 57.6, 57.1, 56.5, 3.57; HRMS (ESI) calcd for $C_{17}H_{24}O_5Na$ $[M+Na]^+$ 331.1521, found 331.1510.

4.6.9. Triyne **9i**

Colorless oil; IR (neat) 2874, 1716, 1349, 1251, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.31–4.22 (m, 6H), 4.20 (q, J=2.4 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.77–3.60 (m, 12H), 3.38 (s, 3H), 1.86 (t, J=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.6, 82.4, 82.2, 81.8, 77.2, 74.2, 70.6, 70.4, 69.1, 59.9, 58.6, 57.6, 57.1, 56.5, 3.55; HRMS (ESI) calcd for $C_{19}H_{28}O_6Na$ $[M+Na]^+$ 375.1784, found 375.1770.

4.6.10. Triyne **9j**

Yellow oil; IR (neat) 2866, 1447, 1348, 1138, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.32–4.22 (m, 6H), 4.19 (q, J=2.4 Hz, 2H), 4.14 (t, J=1.8 Hz, 2H), 3.76–3.58 (m, 16H), 3.38 (s, 3H), 1.86 (t, J=2.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.1, 82.6, 82.4, 82.2, 81.8, 77.2, 74.2, 70.6, 70.5, 70.4, 69.1, 59.9, 58.6, 57.6, 57.1, 56.6, 3.56; HRMS (ESI) calcd for $C_{21}H_{32}O_7Na$ $[M+Na]^+$ 419.2046, found 419.2013.

4.7. Representative procedure for the rhodium-catalyzed intramolecular alkyne cyclotrimerization (Table 6, entry 2)

A CH_2Cl_2 (1.0 mL) solution of (*R*)-H_8-BINAP (7.9 mg, 0.012 mmol) was added to a CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (5.1 mg, 0.012 mmol) at rt. The mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting solution was concentrated to dryness and the residue was dissolved in CH_2Cl_2 (20 mL). To this solution was added dropwise over 10 min a CH_2Cl_2 (5.0 mL) solution of **9b** (69.6 mg, 0.25 mmol). The solution was stirred at rt for 16 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc=1:2), which furnished (−)-[7]metacyclophane **11b** (17.5 mg, 0.0629 mmol, 25% yield, 90% ee) as a colorless solid and [7]orthocyclophane **10b** (25.8 mg, 0.0927 mmol, 37% yield) as a colorless solid.

4.7.1. (−)-[7]Metacyclophane (−)-**11b**

Mp 90.1–90.9 °C; $[\alpha]_D^{25}$ −16.4 (*c* 0.250, acetone, 90% ee); IR (KBr) 3250, 2860, 2320, 1680, 1440, 1350, 1050, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.17 (m, 4H), 5.11 (d, J=12.6 Hz, 1H), 5.04 (d, J=12.6 Hz, 1H), 5.02 (d, J=12.0 Hz, 1H), 4.95 (d, J=12.0 Hz, 1H), 4.57 (d, J=12.6 Hz, 1H), 4.11 (d, J=12.6 Hz, 1H), 3.52–3.35 (m, 2H), 3.38 (s, 3H), 2.68–2.48 (m, 2H), 2.22 (s, 3H), 1.39–1.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1, 138.9, 138.6, 137.3, 131.4, 130.5, 73.4, 72.9, 72.3, 68.7, 67.2, 67.1, 66.6, 58.7, 32.9, 15.4; HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$ 301.1416, found 301.1390; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 16.1 min (major isomer) and 22.6 min (minor isomer).

4.7.2. [7]Orthocyclophane **10b**

Mp 98.8–99.0 °C; IR (KBr) 3280, 2820, 2300, 1640, 1440, 1030, 890 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.19–5.13 (m, 2H), 5.13–5.05 (m, 2H), 4.96 (s, 2H), 4.71 (s, 2H), 4.54 (s, 2H), 3.73 (t, J=5.4 Hz, 2H), 3.64 (t, J=5.4 Hz, 2H), 3.44 (s, 3H), 2.26 (s, 3H), 1.77 (quint, J=5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.38, 138.36, 136.4, 135.4, 131.1, 128.9, 73.8, 73.5, 69.4, 68.2, 67.8, 67.5, 67.2, 58.4, 30.9, 15.9; HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$ 301.1416, found 301.1411.

4.7.3. [6]Orthocyclophane **7b** (Table 5, entry 1)

Colorless solid; mp 147.2–148.0 °C; IR (KBr) 2900, 1760, 1100, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.27 (s, 2H), 5.14 (s, 2H), 4.90 (s, 2H), 4.55 (s, 2H), 3.81 (t, J=6.0 Hz, 2H), 3.80 (t, J=6.0 Hz, 2H), 3.46 (s, 3H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 147.3, 143.3, 139.9, 136.5, 128.8, 122.8, 71.1, 69.1, 67.5, 67.3, 66.7, 66.1, 58.7, 12.9; HRMS (ESI) calcd for $C_{15}H_{18}O_5Na$ $[M+Na]^+$ 301.1052, found 301.1081.

*4.7.4. (−)-[7]Metacyclophane (−)-**8a** (Table 5, entry 2)*

Colorless oil; $[\alpha]_D^{25}$ −17.0 (*c* 0.360, acetone, >98% ee); IR (neat) 2900, 1750, 1060, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.29 (d, *J*=15.3 Hz, 1H), 5.22 (d, *J*=15.3 Hz, 1H), 5.14 (d, *J*=12.9 Hz, 1H), 5.13 (d, *J*=12.9 Hz, 1H), 5.10 (d, *J*=12.9 Hz, 1H), 4.97 (d, *J*=12.9 Hz, 1H), 4.58 (d, *J*=12.9 Hz, 1H), 4.25 (d, *J*=12.9 Hz, 1H), 3.59−3.48 (m, 2H), 3.40 (s, 3H), 2.68 (s, 3H), 2.60−2.46 (m, 1H), 2.36−2.24 (m, 1H), 1.51−1.34 (m, 1H), 0.47−0.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 150.3, 146.5, 141.9, 137.6, 132.1, 77.2, 72.8, 67.6, 67.3, 67.1, 66.9, 59.0, 33.0, 12.8; HRMS (ESI) calcd for $C_{16}H_{20}O_5Na$ $[M+Na]^+$ 315.1208, found 315.1220; CHIRALCEL OD-H, hexane/2-PrOH=90:10, 1.0 mL/min, retention times: 26.8 min (major isomer) and 31.0 min (minor isomer).

*4.7.5. [7]Orthocyclophane **7a** (Table 5, entry 2)*

Colorless solid; mp 126.5−127.4 °C; IR (KBr) 2900, 1750, 1100, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.23 (s, 2H), 5.01 (s, 2H), 4.81 (s, 2H), 4.58 (s, 2H), 3.78 (t, *J*=5.7 Hz, 2H), 3.74 (t, *J*=5.7 Hz, 2H), 3.44 (s, 3H), 2.78 (s, 3H), 1.84 (quint, *J*=5.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 146.4, 143.7, 139.6, 137.2, 129.7, 122.5, 68.9, 68.7, 67.94, 67.86, 67.6, 67.0, 58.5, 30.0, 13.0; HRMS (ESI) calcd for $C_{16}H_{20}O_5Na$ $[M+Na]^+$ 315.1208, found 315.1227.

*4.7.6. (−)-[8]Metacyclophane (−)-**8c** (Table 5, entry 3)*

Colorless solid; $[\alpha]_D^{25}$ −24.1 (*c* 0.505, acetone, >98% ee); IR (neat) 2900, 1750, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.26 (s, 2H), 5.18 (d, *J*=13.2 Hz, 1H), 5.109 (d, *J*=13.2 Hz, 1H), 5.108 (d, *J*=13.2 Hz, 1H), 5.107 (d, *J*=13.2 Hz, 1H), 4.74 (d, *J*=13.2 Hz, 1H), 4.26 (d, *J*=13.2 Hz, 1H), 3.57−3.44 (m, 2H), 3.40 (s, 3H), 2.74 (s, 3H), 2.69−2.56 (m, 2H), 1.37−1.12 (m, 2H), 0.62−0.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 147.6, 146.6, 141.4, 138.5, 132.1, 122.0, 70.7, 67.5, 67.3, 67.1, 67.0, 66.6, 66.1, 59.0, 26.7, 13.0; HRMS (ESI) calcd for $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1365, found 329.1342; CHIRALPAK AD-H, hexane/2-PrOH=90:10, 1.0 mL/min, retention times: 25.0 min (major isomer) and 32.6 min (minor isomer).

*4.7.7. [8]Orthocyclophane **7c** (Table 5, entry 3)*

Colorless solid; mp 102.4−103.0 °C; IR (KBr) 2900, 1750, 1110, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.23 (s, 2H), 4.86 (s, 2H), 4.66 (s, 2H), 4.59 (s, 2H), 3.74 (t, *J*=5.7 Hz, 2H), 3.67 (t, *J*=5.7 Hz, 2H), 3.45 (s, 3H), 2.77 (s, 3H), 1.76 (quint, *J*=5.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.0, 148.0, 146.2, 143.9, 139.7, 137.2, 129.8, 70.9, 69.8, 67.5, 67.0, 66.43, 66.39, 58.5, 27.0, 26.6, 13.0; HRMS (ESI) calcd for $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1365, found 329.1382.

*4.7.8. (R)-(−)-[9]Metacyclophane (R)-(−)-**8d** (Table 5, entry 4)*

Colorless solid; mp 149.8−150.2 °C; $[\alpha]_D^{25}$ −16.6 (*c* 0.400, acetone, 98% ee); IR (KBr) 2900, 1750, 1090, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.27 (s, 2H), 5.200 (d, *J*=13.2 Hz, 1H), 5.199 (d, *J*=13.2 Hz, 1H), 5.16 (d, *J*=13.2 Hz, 1H), 5.11 (d, *J*=13.2 Hz, 1H), 4.70 (d, *J*=13.2 Hz, 1H), 4.10 (d, *J*=13.2 Hz, 1H), 3.67−3.50 (m, 2H), 3.44 (s, 3H), 3.07−2.97 (m, 1H), 2.93−2.86 (m, 1H), 2.77 (s, 3H), 1.58−1.40 (m, 1H), 1.33−0.98 (m, 3H), 0.62−0.24 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 146.7, 146.1, 141.4, 138.6, 132.6, 121.5, 69.2, 68.1, 67.5, 66.9, 65.9, 65.3, 59.2, 28.1, 28.0, 20.0, 13.2; HRMS (ESI) calcd for $C_{18}H_{24}O_5Na$ $[M+Na]^+$ 343.1521, found 343.1521; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 23.6 min (major isomer) and 25.8 min (minor isomer).

The absolute configuration of (−)-**8d** was determined to be *R* by X-ray crystallographic analysis. X-ray intensity data were collected using Cu Ka radiation up to $2q$=136.4°. The crystal structure model was refined based on 2994 reflections (1253 Friedel pairs) and gave final *R* factor of 0.0358. The Flack parameter for the assigned absolute configuration shown in Figure 1 is −0.03(18). The details of the refinement are shown in Crystallographic Information File (CIF) attached as Supplementary data.

*4.7.9. [9]Orthocyclophane **7d** (Table 5, entry 4)*

Colorless solid; mp 118.2−119.3 °C; IR (KBr) 2900, 1750, 1110, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.28 (s, 2H), 4.658 (s, 2H), 4.655 (s, 2H), 4.51 (s, 2H), 3.66 (t, *J*=5.4 Hz, 2H), 3.60 (t, *J*=5.4 Hz, 2H), 3.47 (s, 3H), 2.78 (s, 3H), 1.74−1.52 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.3, 146.9, 143.4, 140.4, 138.1, 129.8, 122.9, 69.6, 69.1, 67.8, 67.2, 65.8, 65.0, 58.7, 26.4, 25.6, 21.0, 13.1; HRMS (ESI) calcd for $C_{18}H_{24}O_5Na$ $[M+Na]^+$ 343.1521, found 343.1511.

*4.7.10. (−)-[10]Metacyclophane (−)-**8e** (Table 5, entry 5)*

Colorless oil; $[\alpha]_D^{25}$ −18.6 (*c* 0.385, acetone, 91% ee); IR (neat) 2850, 2350, 1740, 1450, 1080, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.30 (d, *J*=15.3 Hz, 1H), 5.24 (d, *J*=15.3 Hz, 1H), 5.09 (d, *J*=13.2 Hz, 1H), 5.05 (d, *J*=13.2 Hz, 1H), 5.01 (d, *J*=13.2 Hz, 1H), 4.99 (d, *J*=13.2 Hz, 1H), 4.69 (d, *J*=13.2 Hz, 1H), 4.17 (d, *J*=13.2 Hz, 1H), 3.59−3.37 (m, 2H), 3.43 (s, 3H), 3.00 (dt, *J*=9.6, 2.7 Hz, 1H), 2.90 (dt, *J*=9.6, 2.7 Hz, 1H), 2.78 (s, 3H), 1.50−1.24 (m, 2H), 1.18−0.89 (m, 4H), 0.65−0.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 146.7, 145.0, 140.1, 138.8, 131.4, 121.6, 68.8, 68.2, 67.7, 67.5, 66.0, 64.7, 59.0, 29.3, 29.1, 25.0, 24.8, 13.2; HRMS (ESI) calcd for $C_{19}H_{26}O_5Na$ $[M+Na]^+$ 357.1678, found 357.1693; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 17.4 min (minor isomer) and 18.9 min (major isomer).

*4.7.11. [10]Orthocyclophane **7e** (Table 5, entry 5)*

Colorless solid; mp 107.2−107.6 °C; IR (KBr) 2850, 2350, 1740, 1440, 1080, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.28 (s, 2H), 4.66 (s, 2H), 4.63 (s, 2H), 4.55 (s, 2H), 3.68 (t, *J*=5.4 Hz, 2H), 3.57 (t, *J*=5.4 Hz, 2H), 3.46 (s, 3H), 2.78 (s, 3H), 1.75−1.34 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 147.1, 142.8, 140.5, 138.1, 129.6, 123.1, 69.5, 69.4, 67.8, 67.3, 66.5, 66.1, 58.7, 30.9, 27.6, 27.5, 22.7, 13.0; HRMS (ESI) calcd for $C_{19}H_{26}O_5Na$ $[M+Na]^+$ 357.1678, found 357.1667.

4.7.12. [11]Orthocyclophane ***7f*** *(Table 5, entry 6)*

Colorless solid; mp 79.2–80.0 °C; IR (KBr) 2926, 2855, 2360, 1758, 1100, 1024 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.28 (s, 2H), 4.61 (s, 2H), 4.58 (s, 2H), 4.53 (s, 2H), 3.66 (t, J=5.1 Hz, 2H), 3.57 (t, J=5.1 Hz, 2H), 3.46 (s, 3H), 2.77 (s, 3H), 1.73–1.60 (m, 4H), 1.54–1.42 (m, 4H), 1.42–1.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 147.2, 142.4, 140.3, 138.1, 130.0, 123.3, 71.2, 70.6, 68.0, 67.4, 66.4, 66.0, 58.7, 27.6, 27.0, 25.53, 25.47, 25.45, 13.0; HRMS (ESI) calcd for $C_{20}H_{28}O_5Na$ $[M+Na]^+$ 371.1834, found 371.1833.

*4.7.13. (−)-[12]Metacyclophane (−)-****8g*** *(Table 5, entry 7)*

Colorless oil; $[\alpha]_D^{25}$ −3.7 (*c* 0.210, acetone, 32% ee); IR (neat) 2928, 2856, 2359, 2320, 1759, 1093, 1023 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.38 (d, J=15.3 Hz, 1H), 5.23 (d, J=15.3 Hz, 1H), 4.96 (d, J=10.8 Hz, 1H), 4.94 (d, J=13.5 Hz, 1H), 4.90 (d, J=13.5 Hz, 1H), 4.84 (d, J=10.8 Hz, 1H), 4.75 (d, J=13.5 Hz, 1H), 4.34 (d, J=13.5 Hz, 1H), 3.52–3.30 (m, 3H), 3.46 (s, 3H), 3.23 (dt, J=9.6, 4.2 Hz, 1H), 2.81 (s, 3H), 1.65–1.38 (m, 1H), 1.38–1.02 (m, 6H), 1.02–0.72 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 147.2, 143.2, 139.3, 138.9, 131.3, 122.6, 69.5, 68.1, 67.6, 67.3, 66.7, 64.7, 59.0, 29.0, 28.6, 27.3, 26.8, 24.7, 24.3, 13.4; HRMS (ESI) calcd for $C_{21}H_{30}O_5Na$ $[M+Na]^+$ 385.1991, found 385.1968; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 19.6 min (major isomer) and 21.9 min (minor isomer).

4.7.14. [12]Orthocyclophane ***7g*** *(Table 5, entry 7)*

Colorless solid; mp 109.6–110.0 °C; IR (KBr) 2926, 2859, 2360, 2325, 1759, 1103, 1021 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.32 (s, 2H), 4.63 (s, 2H), 4.59 (s, 2H), 4.56 (s, 2H), 3.65 (t, J=5.7 Hz, 2H), 3.62 (t, J=5.7 Hz, 2H), 3.46 (s, 3H), 2.77 (s, 3H), 1.36–1.26 (m, 4H), 1.26–1.17 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 147.2, 140.7, 139.6, 137.5, 130.4, 123.6, 69.9, 69.7, 68.7, 67.4, 66.0, 65.7, 58.7, 28.5, 26.7, 26.4, 25.1, 23.0, 22.0, 13.0; HRMS (ESI) calcd for $C_{21}H_{30}O_5Na$ $[M+Na]^+$ 385.1991, found 385.1980.

*4.7.15. (−)-[9]Metacyclophane (−)-****8h*** *and [9]orthocyclophane (−)-****7h*** *[(−)-****8h****/****7h****=50:50, Table 5, entry 8]*

Colorless solid; mp 112.5–114.1 and 159.8–161.0 °C; $[\alpha]_D^{25}$ −13.1 [*c* 2.105, acetone (calculated content of (−)-**8h**), >98% ee]; IR (KBr) 2880, 1750, 1440, 1350, 1100, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.29 (s, 2H, **8h**), 5.26 (d, J=13.8 Hz, 2H, **8h**), 5.21 (d, J=13.8 Hz, 1H, **8h**), 5.08 (d, J=13.8 Hz, 1H, **8h**), 4.94 (s, 2H, **7h**), 4.87 (s, 2H, **7h**), 4.81 (d, J=13.8 Hz, 1H, **8h**), 4.77 (s, 2H, **7h**), 4.65 (s, 2H, **7h**), 4.20 (d, J=13.8 Hz, 1H, **8h**), 3.81–3.68 (m, 4H, **8h**; 4H, **7h**), 3.68–3.61 (m, 1H, **8h**; 1H, **7h**), 3.46 (s, 3H, **8h**), 3.45 (s, 3H, **7h**), 3.36–3.13 (m, 1H, **8h**; 1H, **7h**), 3.18–2.98 (m, 1H, **8h**; 1H, **7h**), 2.98–2.87 (m, 1H, **8h**; 1H, **7h**), 2.78 (s, 3H, **8h**), 2.75 (s, 3H, **7h**); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 171.2, 148.6, 147.3, 146.2, 142.7, 140.2, 138.4, 138.1, 137.7, 129.9, 129.8, 123.1, 120.6, 72.9, 72.4, 70.8, 70.7, 70.4, 70.2, 69.1, 68.6, 67.9, 67.6, 67.5, 67.23, 67.21, 67.0, 66.8, 65.8, 58.9, 58.6, 13.2, 13.0; HRMS (ESI) calcd for $C_{17}H_{22}O_6Na$ $[M+Na]^+$ 345.1314, found 345.1314; CHIRALCEL OD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 46.8 min (major isomer) and 67.7 min (minor isomer). The corresponding chiral diol was isolated in a pure form by treating (−)-**8h** with $LiAlH_4$. Mp 149.8–150.2 °C; $[\alpha]_D^{25}$ +3.50 (*c* 0.535, acetone, >99% ee); IR (KBr) 3300, 2900, 1080, 1000 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.07 (d, J=13.8 Hz, 1H), 5.03 (d, J=13.8 Hz, 1H), 5.01 (d, J=13.8 Hz, 1H), 4.98 (d, J=13.8 Hz, 1H), 4.92 (d, J=13.8 Hz, 1H), 4.77 (d, J=13.8 Hz, 1H), 4.96–4.76 (m, 4H), 3.77–3.60 (m, 2H), 3.57–3.41 (m, 1H), 3.36 (s, 3H), 3.29–3.09 (m, 3H), 2.90–2.80 (m, 1H), 2.80–2.70 (m, 2H), 2.59–2.49 (m, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.6, 138.7, 137.3, 136.38, 136.35, 135.5, 71.1, 70.70, 70.66, 69.6, 68.5, 67.40, 67.38, 59.6, 59.1, 58.5, 15.7; HRMS (ESI) calcd for $C_{17}H_{26}O_6$ $[M+Na]^+$ 349.1627, found 349.1605.

*4.7.16. (−)-[12]Metacyclophane (−)-****8i*** *(Table 5, entry 9)*

Colorless oil; $[\alpha]_D^{25}$ −3.48 (*c* 0.815, acetone, 68% ee); IR (neat) 2868, 2359, 2320, 1751, 1095, 1022 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.31 (d, J=15.3 Hz, 1H), 5.23 (d, J=15.3 Hz, 1H), 5.08 (d, J=13.2 Hz, 1H), 5.04 (d, J=12.0 Hz, 1H), 4.99 (d, J=12.0 Hz, 1H), 4.96 (d, J=12.9 Hz, 1H), 4.77 (d, J=12.9 Hz, 1H), 4.31 (d, J=13.2 Hz, 1H), 3.81–3.47 (m, 8H), 3.42 (s, 3H), 3.47–3.28 (m, 4H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 146.8, 145.1, 138.7, 138.3, 130.6, 121.9, 70.7, 70.5, 70.4, 70.1, 69.2, 68.19, 68.18, 67.9, 66.7, 64.5, 58.8, 13.2; HRMS (ESI) calcd for $C_{19}H_{26}O_7Na$ $[M+Na]^+$ 389.1576, found 389.1545; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 65.9 min (major isomer) and 74.8 min (minor isomer).

4.7.17. [12]Orthocyclophane ***7i*** *(Table 5, entry 9)*

Colorless solid; mp 103.3–103.8 °C; IR (KBr) 2872, 2360, 2325, 1752, 1128, 1103, 1021 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.33 (s, 2H), 4.99 (s, 2H), 4.78 (s, 2H), 4.59 (s, 2H), 3.84–3.71 (m, 8H), 3.68 (s, 4H), 3.43 (s, 3H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 146.6, 140.9, 139.2, 137.1, 131.1, 123.3, 72.3, 71.0, 70.0, 69.83, 69.76, 69.3, 68.6, 68.5, 67.2, 66.4, 58.4, 12.9; HRMS (ESI) calcd for $C_{19}H_{26}O_7Na$ $[M+Na]^+$ 389.1576, found 389.1542.

4.7.18. [15]Orthocyclophane ***7j*** *(Table 5, entry 10)*

Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.34 (s, 2H), 4.92 (s, 2H), 4.75 (s, 2H), 4.58 (s, 2H), 3.82–3.51 (m, 16H), 3.38 (s, 3H), 2.77 (s, 3H); HRMS (ESI) calcd for $C_{21}H_{30}O_8Na$ $[M+Na]^+$ 433.1838, found 433.1801.

4.7.19. [6]Orthocyclophane ***10a*** *(Table 6, entry 1)*

Colorless solid; mp 104.8–105.2 °C; IR (KBr) 2897, 2360, 2325, 1100, 1044 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.22–5.16 (m, 2H), 5.16–5.08 (m, 2H), 5.04 (s, 2H), 4.76 (s, 2H), 4.52 (s, 2H), 3.85–3.69 (m, 4H), 3.45 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7, 138.4, 135.7, 134.8, 131.5, 128.6, 73.8, 73.4, 70.0, 69.6, 67.7, 67.4, 65.0, 58.5,

15.9; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ $[M+Na]^+$ 287.1259, found 287.1235.

*4.7.20. (−)-[8]Metacyclophane (−)-**11c** (Table 6, entry 3)*

Colorless solid; $[\alpha]_D^{25}$ −10.0 (*c* 1.100, acetone, 93% ee); mp 58.2–58.7 °C; IR (KBr) 3250, 2860, 2330, 1640, 1440, 1350, 1040, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.22–5.17 (m, 2H), 5.179 (d, *J*=12.9 Hz, 1H), 5.176 (d, *J*=12.6 Hz, 1H), 5.09 (d, *J*=12.6 Hz, 1H), 5.08 (d, *J*=12.6 Hz, 1H), 5.04 (d, *J*=11.4 Hz, 1H), 4.99 (d, *J*=11.4 Hz, 1H), 4.66 (d, *J*=12.9 Hz, 1H), 4.13 (d, *J*=12.6 Hz, 1H), 3.52–3.31 (m, 2H), 3.39 (s, 3H), 2.64 (t, *J*=6.0 Hz, 1H), 2.60 (dt, *J*=6.0 Hz, 1H), 2.24 (s, 3H), 1.31–1.11 (m, 2H), 0.73–0.55 (m, 1H), 0.55–0.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.6, 139.0, 138.4, 137.7, 131.1, 130.9, 73.7, 73.4, 70.4, 68.2, 66.4, 66.1, 58.7, 26.63, 26.55, 16.0; HRMS (ESI) calcd for $C_{17}H_{24}O_4Na$ $[M+Na]^+$ 315.1572, found 315.1602; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 25.0 min (major isomer) and 27.2 min (minor isomer).

*4.7.21. [8]Orthocyclophane **10c** (Table 6, entry 3)*

Colorless solid; mp 110.1–110.8 °C; IR (KBr) 3250, 2890, 2330, 1640, 1440, 1060, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.18–5.12 (m, 2H), 5.12–5.05 (m, 2H), 4.79 (s, 2H), 4.58 (s, 2H), 4.55 (s, 2H), 3.76 (t, *J*=5.4 Hz, 2H), 3.63 (t, *J*=5.4 Hz, 2H), 3.44 (s, 3H), 2.25 (s, 3H), 1.79–1.64 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.17, 138.15, 137.0, 134.9, 130.8, 129.0, 73.8, 73.5, 70.7, 69.1, 68.4, 67.5, 66.1, 58.3, 27.5, 26.6, 16.0; HRMS (ESI) calcd for $C_{17}H_{24}O_4Na$ $[M+Na]^+$ 315.1572, found 315.1541.

*4.7.22. (−)-[9]Metacyclophane (−)-**11d** (Table 6, entry 4)*

Colorless solid; $[\alpha]_D^{25}$ −2.8 (*c* 0.560, acetone, 94% ee); mp 51.0–51.6 °C; IR (KBr) 3280, 2880, 2340, 1620, 1440, 1350, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.18 (m, 2H), 5.19 (d, *J*=12.9 Hz, 1H), 5.17 (d, *J*=12.9 Hz, 1H), 5.12 (d, *J*=10.8 Hz, 1H), 5.10 (d, *J*=12.9 Hz, 1H), 5.08 (d, *J*=12.9 Hz, 1H), 5.06 (d, *J*=10.8 Hz, 1H), 4.58 (d, *J*=12.9 Hz, 1H), 4.00 (d, *J*=12.9 Hz, 1H), 3.59–3.44 (m, 2H), 3.42 (s, 3H), 3.11–2.94 (m, 2H), 2.25 (s, 3H), 1.59–1.39 (m, 1H), 1.39–1.22 (m, 1H), 1.22–0.81 (m, 2H), 0.53–0.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.8, 138.6, 138.4, 137.2, 131.6, 130.4, 74.0, 73.7, 69.1, 68.5, 67.3, 65.8, 65.7, 58.9, 28.3, 28.2, 20.2, 16.3; HRMS (ESI) calcd for $C_{18}H_{26}O_4Na$ $[M+Na]^+$ 329.1729, found 329.1703; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 21.3 min (minor isomer) and 23.1 min (major isomer).

*4.7.23. [9]Orthocyclophane **10d** (Table 6, entry 4)*

Colorless solid; mp 122.8–123.1 °C; IR (KBr) 3280, 2880, 2340, 1620, 1510, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.17 (m, 2H), 5.13–5.07 (m, 2H), 4.61 (s, 2H), 4.60 (s, 2H), 4.43 (s, 2H), 3.63 (t, *J*=5.4 Hz, 2H), 3.55 (t, *J*=5.4 Hz, 2H), 3.44 (s, 3H), 2.25 (s, 3H), 1.74–1.53 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.8, 138.5, 136.9, 135.8, 131.6, 128.7, 73.9, 73.7, 69.1, 68.9, 67.9, 67.8, 64.8, 58.5, 26.9, 25.5, 21.1, 15.9; HRMS (ESI) calcd for $C_{18}H_{26}O_4Na$ $[M+Na]^+$ 329.1729, found 329.1710.

*4.7.24. (−)-[10]Metacyclophane (−)-**11e** (Table 6, entry 5)*

Colorless solid; $[\alpha]_D^{25}$ −3.9 (*c* 0.365, acetone, 93% ee); mp 84.8–85.4 °C; IR (KBr) 3250, 2890, 2350, 1440, 1350, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.18 (m, 2H), 5.19 (d, *J*=12.0 Hz, 1H), 5.07 (d, *J*=12.0 Hz, 1H), 5.06 (d, *J*=13.2 Hz, 1H), 4.98 (d, *J*=11.1 Hz, 1H), 4.95 (d, *J*=13.2 Hz, 1H), 4.93 (d, *J*=11.1 Hz, 1H), 4.60 (d, *J*=13.2 Hz, 1H), 4.03 (d, *J*=13.2 Hz, 1H), 3.59–3.46 (m, 2H), 3.41 (s, 3H), 3.05 (dt, *J*=6.9, 2.7 Hz, 1H), 3.01 (dt, *J*=6.9, 2.7 Hz, 1H), 2.26 (s, 3H), 1.44–1.20 (m, 2H), 1.18–0.89 (m, 4H), 0.76–0.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7, 138.1, 137.5, 137.3, 130.8, 130.3, 74.0, 73.8, 68.7, 67.71, 67.67, 67.3, 65.2, 58.7, 29.5, 29.3, 24.9, 24.8, 16.3; HRMS (ESI) calcd for $C_{19}H_{28}O_4Na$ $[M+Na]^+$ 343.1885, found 343.1877; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 11.6 min (minor isomer) and 13.1 min (major isomer).

*4.7.25. [10]Orthocyclophane **10e** (Table 6, entry 5)*

Colorless solid; mp 106.3–106.8 °C; IR (KBr) 3250, 2850, 2330, 1510, 1350, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.17 (m, 2H), 5.12–5.06 (m, 2H), 4.59 (s, 2H), 4.58 (s, 2H), 4.56 (s, 2H), 3.66 (t, *J*=5.4 Hz, 2H), 3.51 (t, *J*=5.4 Hz, 2H), 3.44 (s, 3H), 2.25 (s, 3H), 1.76–1.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.1, 138.6, 136.7, 135.8, 131.7, 128.5, 73.9, 73.8, 68.9, 68.8, 68.2, 67.9, 66.3, 58.5, 27.8, 27.5, 22.5, 22.4, 15.9; HRMS (ESI) calcd for $C_{19}H_{28}O_4Na$ $[M+Na]^+$ 343.1885, found 343.1870.

*4.7.26. (−)-[11]Metacyclophane (−)-**11f** (Table 6, entry 6)*

Colorless oil; $[\alpha]_D^{25}$ −1.8 (*c* 0.220, acetone, 74% ee); IR (neat) 2929, 2855, 2359, 2324, 1098, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.22–5.18 (m, 2H), 5.15 (d, *J*=12.9 Hz, 1H), 5.14 (d, *J*=13.8 Hz, 1H), 5.09 (d, *J*=13.8 Hz, 1H), 5.04 (d, *J*=12.9 Hz, 1H), 4.96 (d, *J*=10.8 Hz, 1H), 4.90 (d, *J*=10.8 Hz, 1H), 4.61 (d, *J*=12.6 Hz, 1H), 4.00 (d, *J*=12.6 Hz, 1H), 3.44 (s, 3H), 3.37–3.22 (m, 2H), 3.06–2.88 (m, 2H), 2.25 (s, 3H), 1.93–1.75 (m, 2H), 1.44–1.28 (m, 2H), 1.28–1.09 (m, 4H), 0.65–0.43 (m, 1H), 0.43–0.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.4, 138.4, 137.0, 136.3, 131.2, 129.4, 74.1, 73.9, 67.3, 67.0, 64.2, 63.0, 62.5, 58.9, 28.34, 28.31, 24.89, 24.87, 22.9, 16.5; HRMS (ESI) calcd for $C_{20}H_{30}O_4Na$ $[M+Na]^+$ 357.2042, found 357.2036; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 14.7 min (minor isomer) and 16.2 min (major isomer).

*4.7.27. [11]Orthocyclophane **10f** (Table 6, entry 6)*

Colorless solid; mp 94.1–94.5 °C; IR (KBr) 2909, 2849, 2360, 2326, 1100, 1049 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.17 (m, 2H), 5.13–5.06 (m, 2H), 4.55 (s, 2H), 4.53 (s, 2H), 4.41 (s, 2H), 3.64 (t, *J*=5.1 Hz, 2H), 3.52 (t, *J*=5.1 Hz, 2H), 3.44 (s, 3H), 2.24 (s, 3H), 1.64–1.44 (m, 4H), 1.44–1.26 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz)

δ 139.1, 138.7, 136.3, 135.8, 131.6, 128.8, 73.9, 73.8, 70.6, 70.4, 68.0, 68.0, 66.1, 58.5, 27.5, 27.3, 25.7, 25.5, 25.4, 15.9; HRMS (ESI) calcd for $C_{20}H_{30}O_4Na$ $[M+Na]^+$ 357.2042, found 357.2033.

*4.7.28. (−)-[12]Metacyclophane (−)-**11g** (Table 6, entry 7)*

Colorless oil; $[\alpha]_D^{25}$ −3.0 (*c* 0.275, acetone, 58% ee); IR (neat) 2926, 2854, 2360, 2325, 1097, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.27 (dd, *J*=11.1, 2.4 Hz, 1H), 5.22 (d, *J*=11.1 Hz, 1H), 5.18 (d, *J*=11.1 Hz, 1H), 5.08 (dd, *J*=11.1, 2.4 Hz, 1H), 4.96 (d, *J*=13.2 Hz, 1H), 4.88–4.79 (m, 2H), 4.86 (d, *J*=13.2 Hz, 1H), 4.65 (d, *J*=13.2 Hz, 1H), 4.13 (d, *J*=13.2 Hz, 1H), 3.52–3.23 (m, 4H), 3.44 (s, 3H), 2.29 (s, 3H), 1.66–1.40 (m, 2H), 1.40–1.01 (m, 6H), 1.01–0.79 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.0, 138.2, 136.9, 136.7, 131.4, 129.5, 74.0, 73.9, 67.8, 67.71, 67.69, 67.59, 65.4, 58.7, 29.0, 28.9, 27.2, 27.1, 24.53, 24.49, 16.5; HRMS (ESI) calcd for $C_{21}H_{32}O_4Na$ $[M+Na]^+$ 371.2198, found 371.2195; CHIRALPAK AD-H, hexane/2-PrOH=97:3, 1.0 mL/min, retention times: 11.5 min (minor isomer) and 13.2 min (major isomer).

*4.7.29. [12]Orthocyclophane **10g** (Table 6, entry 7)*

Colorless solid; mp 104.2–104.5 °C; IR (KBr) 2895, 2861, 2360, 2325, 1103, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.28–5.16 (m, 2H), 5.13–5.04 (m, 2H), 4.73 (s, 2H), 4.71 (s, 2H), 4.55 (s, 2H), 3.77–3.53 (m, 16H), 3.41 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.2, 139.1, 135.4, 135.1, 131.3, 129.0, 74.1, 73.5, 69.5, 68.0, 67.2, 65.7, 58.4, 28.4, 27.3, 26.4, 25.6, 23.0, 22.5, 15.9; HRMS (ESI) calcd for $C_{21}H_{32}O_4Na$ $[M+Na]^+$ 371.2198, found 371.2172.

*4.7.30. (−)-[9]Metacyclophane (−)-**11h** and [9]orthocyclophane (−)-**10h** [(−)-**11h**/**10h**=35:65, Table 6, entry 8]*

Colorless solid; $[\alpha]_D^{25}$ −4.0 (*c* 2.575, acetone, 88% ee); mp 102.8–104.7 °C; IR (KBr) 2850, 1430, 1350, 1100, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.21 (d, *J*=12.3 Hz, 2H, **11h**), 5.23–5.17 (m, 2H, **11h**), 5.21–5.17 (m, 2H, **10h**), 5.06–5.12 (m, 2H, **10h**), 5.08 (d, *J*=12.3 Hz, 2H, **11h**), 4.94 (d, *J*=12.9 Hz, 1H, **11h**), 4.89 (d, *J*=12.9 Hz, 1H, **11h**), 4.82 (s, 2H, **10h**), 4.67 (d, *J*=12.9 Hz, 1H, **11h**), 4.63 (s, 2H, **10h**), 4.60 (s, 2H, **10h**), 4.09 (d, *J*=12.9 Hz, 1H, **11h**), 3.88–3.56 (m, 6H, **11h**; 6H, **10h**), 3.43 (s, 3H, **10h**), 3.40 (s, 3H, **11h**), 3.25–2.91 (m, 2H, **11h**; 2H, **10h**), 2.26 (s, 3H, **10h**), 2.22 (s, 3H, **11h**); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.4, 138.9, 138.6, 138.1, 136.3, 135.93, 135.90, 135.5, 131.5, 129.7, 129.1, 128.5, 74.0, 73.7, 73.63, 73.62, 72.5, 72.3, 70.7, 70.6, 69.8, 69.7, 69.3, 69.1, 68.6, 67.7, 66.9, 66.5, 66.2, 58.5, 58.3, 16.3, 15.8; HRMS (ESI) calcd for $C_{17}H_{24}O_5Na$ $[M+Na]^+$ 331.1521, found 331.1507; CHIRALPAK AD-H, hexane/2-PrOH=95:5, 1.0 mL/min, retention times: 19.8 min (minor isomer) and 21.6 min (major isomer).

*4.7.31. [15]Orthocyclophane **10j** (Table 6, entry 10)*

Colorless oil; IR (neat) 2871, 2360, 2326, 1102 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24–5.16 (m, 2H), 5.13–5.02 (m, 2H), 4.554 (s, 2H), 4.538 (s, 2H), 4.48 (s, 2H), 3.62 (t, *J*=5.4 Hz, 2H), 3.55 (t, *J*=5.4 Hz, 2H), 3.43 (s, 3H), 2.25 (s, 3H), 1.73–1.54 (m, 4H), 1.54–1.32 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.1, 138.9, 135.4, 135.1, 131.1, 129.6, 74.1, 73.4, 71.14, 71.08, 71.03, 70.94, 70.61, 70.55, 69.9, 69.6, 68.5, 68.0, 66.4, 58.2, 15.9; HRMS (ESI) calcd for $C_{21}H_{32}O_7Na$ $[M+Na]^+$ 419.2046, found 419.2083.

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Supplementary data

Crystallographic Information File (CIF) of (*R*)-(−)-**8d** is provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.10.085.

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