Chemo- and Regioselective Intermolecular Cyclotrimerization of Terminal Alkynes Catalyzed by Cationic Rhodium(I)/Modified BINAP Complexes: Application to One-Step Synthesis of Paracyclophanes

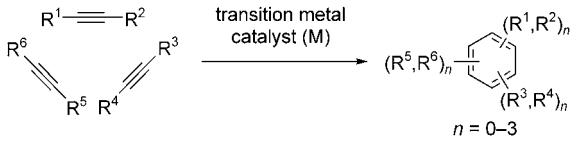
Ken Tanaka,* Kazuki Toyoda, Azusa Wada, Kaori Shirasaka, and Masao Hirano[a]

Abstract: A highly regioselective intermolecular cyclotrimerization of terminal alkynes has been developed based on the use of the cationic rhodium(I)/DTBM-Segphos complex. This method can be applied to a variety of terminal alkynes to provide 1,2,4-trisubstituted benzenes in high yield and with high regioselectivity. A chemo- and regioselective intermolecular crossed-cyclotrimerization of dialkyl acetylenedicarboxylates with a variety of terminal alkynes has also been developed based on the use of the cationic rhodium(I)/H8-BINAP complex, furnishing 3,6-disubstituted phthalates in high yields. It constitutes a highly efficient new method for intermolecular crossed-cyclotrimerization of two different monoynes in terms of catalytic activity, chemo- and regioselectivity, scope of substrates, and ease of operation. The versatility of this new crossed-alkyne cyclotrimerization procedure is demonstrated through its application to one-step synthesis of a [6]metacyclophane and [7]–[12]paracyclophanes from the corresponding terminal α,ω-diynes. Mechanistic studies have revealed that the chemo- and regioselectivity of this crossed-alkyne cyclotrimerization are determined by the preferential formation of a specific rhodium metallacycle derived from a terminal alkyne and a dialkyl acetylenedicarboxylate.

Keywords: alkynes · cyclotrimerization · N ligands · paracyclophane · rhodium

Introduction

The transition-metal-catalyzed cyclotrimerization of alkynes has received much attention as a useful method for the construction of substituted benzenes.[1] Compared with conventional substitution methods of benzenes, the alkyne cyclotrimerization strategy is considerably advantageous for the synthesis of substituted benzenes due to its high atom economy and convergent nature.[2] Although various transition metals catalyze alkyne cyclotrimerization, it has been difficult to carry out intermolecular reactions in a highly regioselective manner.[3,4] In particular, intermolecular crossed-cyclotrimerization of two or three different alkynes leads to complex mixtures of products, which severely limits its application to organic synthesis (Scheme 1). In general, either a partially intramolecular reaction between an α,ω-diyne and an excess of a monoyne, or a completely intramolecular reaction of a triyne, has been employed to overcome this problem.[5,6] Recently, a strategy of temporarily connecting monoynes by means of a cleavable tether group, such as a boron[7] or silyl[8] group, was employed to allow highly chemo- and regioselective crossed-cyclotrimerization of three different alkynes. However, without the use of such tether groups, simultaneous control of both chemo- and regioselectivity in wholly intermolecular crossed-cyclotrimerizations of two or three different alkynes has not yet been accomplished.[9,10]



Scheme 1. Intermolecular crossed-cyclotrimerization of three different alkynes.

Herein, we describe regioselective intermolecular cyclotrimerization of terminal alkynes, as well as chemo- and regioselective intermolecular crossed-cyclotrimerization of terminal alkynes and dialkyl acetylenedicarboxylates, as catalyzed

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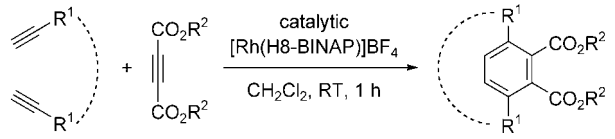
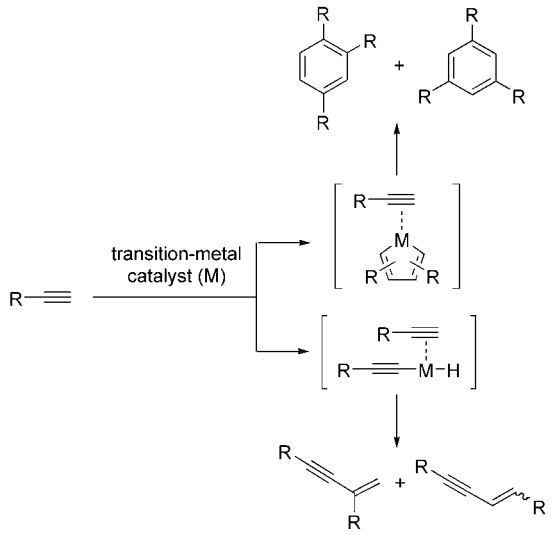
by cationic rhodium(I)/modified BINAP complexes.[11] Furthermore, we also describe application of this new crossed-alkyne cyclotrimerization procedure to a one-step synthesis of a [6]metacyclophane and [7]–[12]paracyclophanes from the corresponding α,ω-diynes (Scheme 2).



Scheme 2. Cationic rhodium(I)/H8-BINAP complex catalyzed chemo- and regioselective intermolecular crossed-cyclotrimerization of terminal alkynes and dialkyl acetylenedicarboxylates.

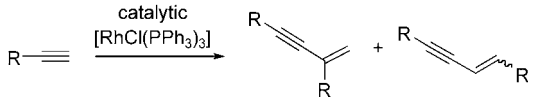
Results and Discussion

Intermolecular cyclotrimerization of terminal alkynes: Various transition metals have been found to catalyze intermolecular cyclotrimerization of terminal alkynes.[1] There have been several reports of highly regioselective cyclotrimerization of terminal alkynes, but a general protocol applicable to a wide variety of terminal alkynes is still lacking.[4] Besides the problem of regioselectivity, intermolecular reactions of terminal alkynes are also prone to a competition between dimerization through C–H activation and cyclotrimerization through a metallacyclopentadiene (Scheme 3).[12,13]



Scheme 3. Transition metal catalyzed dimerization and cyclotrimerization of terminal alkynes.

Indeed, although a neutral rhodium(I) complex, such as $[RhCl(PPh_3)_3]$, is an effective catalyst for partially or completely intramolecular cyclotrimerization of diynes or triynes,[14] it generally reacts with terminal monoynes to give linear dimers (Scheme 4).[15] It has been well documented that cationic rhodium(I) complexes are the effective catalysts

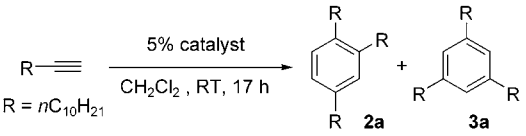


Scheme 4. $[RhCl(PPh_3)_3]$-catalyzed dimerization of terminal monoynes.

in transition metal catalyzed intermolecular cycloaddition processes involving alkynes.[16] However, the application of a cationic rhodium(I) complex to the cyclotrimerization of terminal alkynes remains unexplored.[17]

With this background in mind, we began to explore the application of a cationic rhodium(I) complex to the cyclotrimerization of terminal alkynes. We first examined the reaction of 1-dodecyne (**1a**) using 5 mol% of $[Rh(PPh_3)_2]BF_4$ at room temperature. The reaction was sluggish, but a small amount of cyclotrimerization products was detected (Table 1, entry 1). Although the catalytic activities were low,

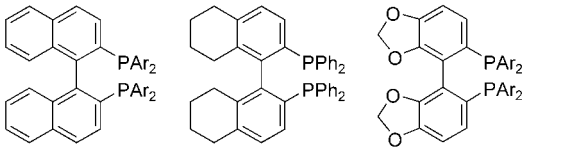
Table 1. Screening of catalysts for intermolecular cyclotrimerization of 1-dodecyne (**1a**).[a]



Entry	Catalyst	Yield [%][b] **2a**+**3a**	Ratio of **2a**:**3a**[b]
1[c]	$[Rh(Ph_3P)_2]BF_4$	3	–
2[c]	$[Rh(nBu_3P)_2]BF_4$	5	–
3[c]	$[Rh(dppe)]BF_4$	<2	–
4[c]	$[Rh(dcpe)]BF_4$	3	–
5[c]	$[Rh(dppf)]BF_4$	<2	–
6[c]	$[Rh(Tol\text{-}BINAP)]BF_4$	>95	64:36
7[c]	[Rh(Tol-BINAP)Cl]	<2	–
8[c]	$[Ir(Tol\text{-}BINAP)]BF_4$	<2	–
9[c]	[Ir(Tol-BINAP)Cl]	0	–
10	$[Rh(cod)(Tol\text{-}BINAP)]BF_4$	3	–

[a] Catalyst (0.0050 mmol), **1a** (0.10 mmol), and CH_2Cl_2 (1.0 mL) were employed. [b] Determined by ^1H NMR spectroscopy. [c] The active catalysts were prepared by hydrogenation (1 atm, RT, 0.5 h).

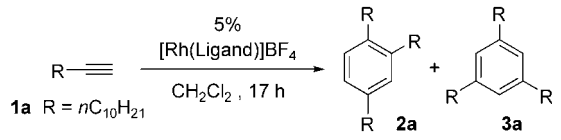
the use of cationic rhodium(I) complexes with various monodentate or bidentate phosphine ligands (Ph_3P, nBu_3P, dppe, dcpe, dppf) furnished cyclotrimerization products (rather than dimerization products) as major products (Table 1, entries 1–5). Surprisingly, the use of Tol-BINAP dramatically improved the catalytic activity and cyclotrimerization products were obtained in almost quantitative yield with moderate regioselectivity (entry 6). The use of a cationic rhodium(I) complex is essential for this reaction. The neutral rhodium(I)/Tol-BINAP complex and both cationic and neutral iridium(I)/Tol-BINAP complexes did not show any catalytic activity (Table 1, entries 7–9). Treatment of the catalyst with hydrogen (removal of the cod ligand) proved to be effective for this reaction. The catalytic activity of $[Rh(cod)(Tol\text{-}BINAP)]BF_4$ (without treatment with hydrogen) was very low (Table 1, entry 10).



BINAP (Ar = Ph) H8-BINAP Segphos (Ar = Ph)
Tol-BINAP (Ar = 4-MeC_6H_4) DTBM-Segphos
DM-BINAP (Ar = 3,5-$Me_2C_6H_4$) (Ar = 4-MeO-3,5-$tBu_2C_6H_2$)

Scheme 5. Structures of modified BINAP ligands.

Table 2. Screening of modified BINAP ligands for intermolecular cyclotrimerization of 1-dodecyne (**1a**).[a]



1a R = $nC_{10}H_{21}$ **2a** **3a**

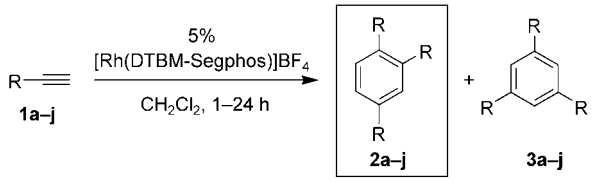
Entry	Ligand	Temp. [°C]	Yield [%][b] **2a+3a**	Ratio of **2a**:**3a**[b]
1	Tol-BINAP	RT	>95	64:36
2	BINAP	RT	>95	52:48
3	DM-BINAP	RT	90	51:49
4	H8-BINAP	30	88	76:24
5	Segphos	30	>95	80:20
6	DTBM-Segphos	30	>95	83:17

[a] $[Rh(cod)_2]BF_4$ (0.0050 mmol), modified BINAP (0.0050 mmol), 1-dodecyne (**1a**, 0.10 mmol), and CH_2Cl_2 (1.0 mL) were employed. The active catalysts were prepared by mixing $[Rh(cod)_2]BF_4$ and phosphines in CH_2Cl_2 followed by hydrogenation (1 atm, RT, 0.5 h). [b] Determined by ^1H NMR spectroscopy.

To improve regioselectivity, a variety of cationic rhodium(I) complexes having modified BINAP ligands (Scheme 5) were screened, as shown in Table 2. The use of BINAP and DM-BINAP did not improve the regioselectivity significantly (Table 2, entries 2 and 3). Although the catalytic activity was slightly lower than that seen with Tol-BINAP, the use of H8-BINAP[18] showed good regioselectivity (Table 2, entry 4). Both high catalytic activity and regioselectivity were achieved using cationic rhodium(I)/Segphos[19] or DTBM-Segphos[19] complexes (Table 2, entries 5 and 6). In particular, the use of the cationic rhodium(I)/DTBM-Segphos complex at 30°C showed the highest regioselectivity (Table 2, entry 6).

A series of terminal alkynes was subjected to the above optimal reaction conditions, as summarized in Table 3. Alkyl- (**1a** and **1b**, Table 3, entries 1 and 2), benzyl- (**1c**, Table 3, entry 3), and chloroalkyl- (**1d**, Table 3, entry 4) substituted terminal alkynes cleanly furnished the corresponding 1,2,4-trisubstituted benzenes **2a–d** in high yield and with high regioselectivity. Not only alkyl-substituted terminal alkynes but also alkenyl- and aryl-substituted terminal alkynes proved to be suitable substrates, yielding 1,2,4-trisubstituted benzenes **2e** and **2f** in high yield and with high regioselectivity (Table 3, entries 5 and 6). For the reaction of **1f**, excellent regioselectivity was obtained by the use of H8-BINAP as a ligand (Table 3, entry 7). Methoxymethyl- (**1g**, entry 8), acetoxymethyl- (**1h**, Table 3, entry 9), and ethoxycarbonyl-

Table 3. Cationic rhodium(I)/DTBM-Segphos complex catalyzed intermolecular cyclotrimerization of terminal alkynes.[a]



1a–j **2a–j** **3a–j**

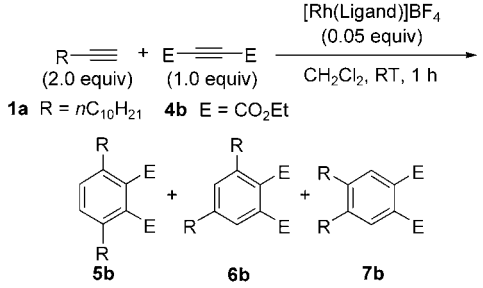
Entry	R	Temp. [°C]	Major product	Yield [%][b] **2a+3a**	Ratio of **2a**:**3a**[b]
1	$nC_{10}H_{21}$ (**1a**)	30	**2a**	91	83:17[e]
2	nC_6H_{13} (**1b**)	30	**2b**	81	82:18[e]
3	Bn (**1c**)	30	**2c**	94	82:18[f]
4	$(CH_2)_3Cl$ (**1d**)	30	**2d**	90	86:14[e]
5	1-cyclohexenyl (**1e**)	30	**2e**	89	97:3[e]
6	Ph (**1f**)	30	**2f**	93	83:17[f]
7[c,d]	Ph (**1f**)	RT	**2f**	94[e]	97:3[f]
8	CH_2OMe (**1g**)	RT	**2g**	94	86:14[f]
9	CH_2OAc (**1h**)	RT	**2h**	90	100:0[e]
10	CO_2Et (**1i**)	RT	**2i**	99	93:7[e]
11	Me_3Si (**1j**)	30	**2j**	74	70:30[f]
12[c]	Me_3Si (**1j**)	RT	**2j**	84	83:17[f]

[a] $[Rh(cod)_2]BF_4$ (0.050 mmol), DTBM-Segphos (0.050 mmol), terminal alkyne (1.0 mmol), and CH_2Cl_2 (3.0 mL) were employed. The active catalyst was prepared by mixing $[Rh(cod)_2]BF_4$ and DTBM-Segphos in CH_2Cl_2 followed by hydrogenation (1 atm, RT, 0.5 h). [b] Yield of isolated product. [c] H8-BINAP was used. [d] Catalyst (1.5%) was used. [e] Determined by ^1H NMR spectroscopy. [f] Determined by GC.

(**1i**, Table 3, entry 10) substituted terminal alkynes proved to be highly reactive substrates, yielding 1,2,4-trisubstituted benzenes **2g–i** in high yield and with high regioselectivity at room temperature (20–25°C). In particular, alkyne **1h** furnished **2h** with complete regioselectivity (Table 3, entry 9). The reaction of sterically demanding trimethylsilyl acetylene (**1j**) also proceeded to give **2j** in good yield and with moderate regioselectivity (Table 3, entry 11). Higher regioselectivity was obtained by the use of H8-BINAP as a ligand (Table 3, entry 12). To the best of our knowledge, the use of this catalyst system constitutes one of the most general methods for the regioselective cyclotrimerization of terminal alkynes.[10]

Intermolecular crossed-cyclotrimerization of terminal alkynes and dialkyl acetylenedicarboxylates: Encouraged by the above results, we subsequently investigated rhodium-catalyzed intermolecular crossed-cyclotrimerization of two different alkynes. After screening combinations of 1-dodecyne (**1a**) and various terminal or internal alkynes in the presence of the cationic rhodium(I)/Tol-BINAP complex, we were pleased to discover that this complex catalyzes chemoselective intermolecular crossed-cyclotrimerization of **1a** and diethyl acetylenedicarboxylate (DEAD, **4b**) furnishing a mixture of disubstituted phthalates **5b**/**6b**/**7b** with moderate regioselectivity (Table 4, entry 1). To improve the regioselectivity, a variety of cationic rhodium(I) complexes having modified BINAP ligands (Scheme 5) were screened, as shown in Table 4. The use of BINAP and DM-BINAP did not improve the regioselectivity significantly (Table 4, en-

Table 4. Screening of modified BINAP ligands for intermolecular crossed-cyclotrimerization of 1-dodecyne (**1a**) and diethyl acetylenedicarboxylate (**4b**).[a]



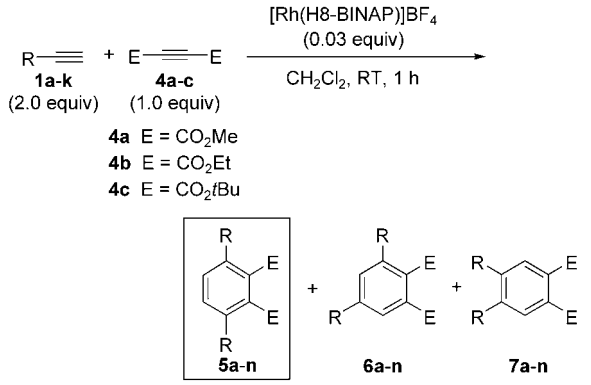
Entry	Ligand	Yield [%][b] **5+6+7**	Ratio of **5**:**6**:**7**[b]
1	Tol-BINAP	82	46:22:32
2	BINAP	84	54:26:20
3	DM-BINAP	80	49:19:32
4	Segphos	82	81:17:2
5	DTBM-Segphos	69	32:62:6
6	H8-BINAP	93	92:6:2

[a] $[Rh(cod)_2]BF_4$ (0.005 mmol), modified BINAP (0.005 mmol), **1a** (0.2 mmol), **4b** (0.1 mmol), and CH_2Cl_2 (1.0 mL) were employed. The active catalysts were prepared by mixing $[Rh(cod)_2]BF_4$ and modified BINAP in CH_2Cl_2, followed by hydrogenation (1 atm, RT, 0.5 h). [b] Determined by ^1H NMR spectroscopy.

tries 2 and 3). Although the overall yield of phthalates was slightly lower than that obtained using Tol-BINAP, the use of Segphos[19] showed good regioselectivity and gave 3,6-disubstituted phthalate **5b** as the major isomer (Table 4, entry 4). A sterically demanding Segphos derivative, DTBM-Segphos,[19] was not so effective, leading to decreased yield and regioselectivity (Table 4, entry 5). Both high yield and regioselectivity were achieved by using the cationic rhodium(I)/H8-BINAP[18] complex, which yielded **5b** with 92% regioselectivity and an overall phthalate yield of 93% (Table 4, entry 6).

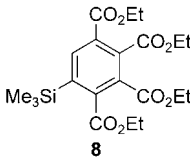
Two molecules of a wide variety of terminal alkynes **1a–k** cleanly reacted with one molecule of DEAD (**4b**) to give 3,6-disubstituted diethyl phthalates **5** in high yield and with high regioselectivity upon treatment with a catalytic amount (3%) of the cationic rhodium(I)/H8-BINAP complex (Table 5). Alkyl- (**1a**, Table 5, entry 2), chloroalkyl- (**1d**, Table 5, entry 5), alkenyl- (**1e**, Table 5, entry 7), and aryl- (**1f**, Table 5, entry 9; **1k**, Table 5, entry 11) substituted terminal alkynes proved to be suitable substrates for this reaction. The respective reactions of methyl propargyl ether (**1g**) and propargyl acetate (**1h**) furnished **5l** and **5m** in moderate yields due to homo-cyclotrimerization of these alkynes yielding **2g** and **2h** as by-products (Table 5, entries 13 and 14). Though the reaction of sterically demanding trimethylsilyl acetylene (**1j**) furnished **5n** in only moderate yield due to the formation of a 1:2 (= **1j**:**4b**) crossed-cyclotrimerization product **8**, excellent regioselectivity was observed (Table 5, entry 15). Interestingly, the ester group of **4** affected the yield and regioselectivity of phthalates **5–7**. The use of dimethyl acetylenedicarboxylate (DMAD, **4a**) led to a

Table 5. Cationic rhodium(I)/H8-BINAP complex-catalyzed intermolecular crossed-cyclotrimerization of terminal alkynes and dialkyl acetylenedicarboxylates.[a]



Entry	R	**4**	Major product	Yield [%][b] **5+6+7**	Ratio of **5**:**6**:**7**[c]
1	$nC_{10}H_{21}$ (**1a**)	**4a**	**5a**	78	91:8:1
2	$nC_{10}H_{21}$ (**1a**)	**4b**	**5b**	88	92:6:2
3	$nC_{10}H_{21}$ (**1a**)	**4c**	**5c**	94	94:4:2
4[d]	$nC_{10}H_{21}$ (**1a**)	**4c**	**5c**	93	93:4:3
5	$(CH_2)_3Cl$ (**1d**)	**4b**	**5d**	92	91:8:1
6	$(CH_2)_3Cl$ (**1d**)	**4c**	**5e**	95	95:4:1
7	1-cyclohexenyl (**1e**)	**4b**	**5f**	90	91:4:5
8	1-cyclohexenyl (**1e**)	**4c**	**5g**	92	94:4:2
9	Ph (**1f**)	**4b**	**5h**	90	89:9:2
10	Ph (**1f**)	**4c**	**5i**	90	90:10:0
11	*o*-Tol (**1k**)	**4b**	**5j**	77	89:9:2
12	*o*-Tol (**1k**)	**4c**	**5k**	90	88:12:0
13	$MeOCH_2$ (**1g**)	**4b**	**5l**	61(30[e])	86:10:4
14	$AcOCH_2$ (**1h**)	**4b**	**5m**	63(28[e])[f]	87:10:3
15	Me_3Si (**1j**)	**4b**	**5n**	57(33[g])	99:1:0

[a] $[Rh(cod)_2]BF_4$ (0.0090 mmol), H8-BINAP (0.0090 mmol), terminal alkyne (0.60 mmol), dialkyl acetylenedicarboxylate (0.30 mmol), and CH_2Cl_2 (3.0 mL) were employed. The catalyst was prepared by mixing $[Rh(cod)_2]BF_4$ and H8-BINAP in CH_2Cl_2 followed by hydrogenation (1 atm, RT, 0.5 h). [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] Catalyst (0.005 equiv) was used. Reaction time was 19 h. [e] Yield of homo-cyclotrimerization products. [f] Isolated as a mixture with homo-cyclotrimerization products. [g] Yield of 1:2 (= **1j**:**4b**) crossed-cyclotrimerization product **8** based on **4b**.



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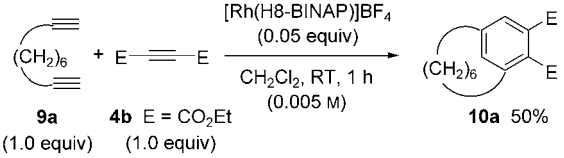
lower yield of **5a** (entry 1). On the other hand, the use of sterically demanding di-*tert*-butyl acetylenedicarboxylate (**4c**) improved both the yield and regioselectivity of **5c** (Table 5, entry 3). By employing **4c** with alkynes **1d**, **1e**, **1f**, and **1k**, the corresponding 3,6-disubstituted phthalates **5e**, **5g**, **5i**, and **5k** were obtained in higher yields and with higher regioselectivities than the phthalates **5d**, **5f**, **5h**, and **5j** obtained from **4a** (Table 5, entries 6, 8, 10, and 12 vs. entries 5, 7, 9, and 11). To demonstrate the practical utility of this reaction, the use of a lower catalyst loading was investigated. The reaction of **1a** and **4c** could be carried out in the

presence of 0.005 equivalent of the catalyst without erosion of the yield or regioselectivity (Table 5, entry 4).

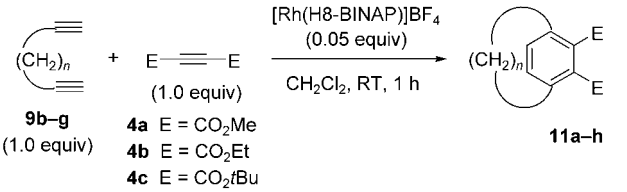
Intermolecular crossed-cyclotrimerization of terminal α,ω-diynes and dialkyl acetylenedicarboxylates: **Application to one-step synthesis of paracyclophanes**: The successful crossed-cyclotrimerization of two molecules of a terminal alkyne and one molecule of a dialkyl acetylenedicarboxylate to yield a 3,6-disubstituted phthalate prompted us to investigate the synthesis of paracyclophanes using terminal α,ω-diynes instead of two molecules of a terminal alkyne.[20] Maryanoff et al. reported cobalt-catalyzed macrocyclizations to form pyridinophanes through [2+2+2] cycloaddition of α,ω-diynes with nitriles[21] or isocyanates.[22] Yamamoto et al. reported palladium-catalyzed macrocyclizations to form exo-methylene paracyclophanes based on intramolecular benzannulation of conjugated enynes.[23] Wullf et al. reported benzannulation reactions of Fischer carbene complexes with alkynes to form meta- and paracyclophanes.[24] Shinokubo and Oshima et al. reported $[RhCl(PPh_3)_3]$-catalyzed macrocyclizations to form ortho- and metacyclophanes by intramolecular [2+2+2] cycloaddition of triynes in an aqueous/organic biphasic system.[14n] On the other hand, the formation of cyclophanes by intermolecular crossed-cyclotrimerization of α,ω-diynes and alkynes has not hitherto been reported. For the test reaction, commercially available 1,9-decadiyne (**9a**) was chosen as an α,ω-diyne. In this case, a [6]metacyclophane would be obtained due to the instability of a [6]paracyclophane at room temperature.[25] We were pleased to find that the reaction of **9a** and **4b** under dilute conditions (0.005 M) furnished [6]metacyclophane **10a** in 50% yield (Scheme 6). This is the shortest (one-step) synthesis of a [6]metacyclophane starting from commercially available reagents.[25]



Scheme 6. Synthesis of a [6]metacyclophane by intermolecular crossed-cyclotrimerization of 1,9-decadiyne and DEAD.

Next, we investigated the reaction of 1,10-undecadiyne (**9b**), which was synthesized in one step from the corresponding dibromide and lithium acetylide.[26] The effect of concentration on the yield of [7]cyclophane was investigated (Table 6, entries 1–3). The highest yield of [7]cyclophane was obtained at a concentration of 0.01 M (Table 6, entry 2). The reactions of **9b** with various dialkyl acetylenedicarboxylates **4a–c** were investigated at concentrations of 0.01 M, which revealed that the desired highly strained [7]paracyclophanes were obtained along with [7]metacyclophanes (Table 6, entries 1, 4, and 5).[27] The highest yield of [7]paracyclophane was obtained by the use of **4a** (Table 6, entry 1).

Table 6. Cationic rhodium(I)/H8-BINAP complex catalyzed crossed-cyclotrimerization of terminal α,ω-diynes and dialkyl acetylenedicarboxylates.[a]

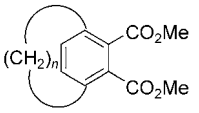


Entry	*n*	4	Conc. [M]	Paracyclophane	Yield [%][b]
1	7 (**9b**)	**4a**	0.01	**11a**	23[c](1:0.8[d])
2	7 (**9b**)	**4a**	0.02[e]	**11a**	14[c](1:0.9[d])
3	7 (**9b**)	**4a**	0.10[f]	**11a**	0
4	7 (**9b**)	**4b**	0.01	**11b**	20[c](1:0.8[d])
5	7 (**9b**)	**4c**	0.01	**11c**	17[c](1:0.8[d])
6	8 (**9c**)	**4a**	0.01	**11d**	46
7	9 (**9d**)	**4a**	0.01	**11e**	53
8	10 (**9e**)	**4a**	0.01	**11f**	36
9	11 (**9f**)	**4a**	0.01	**11g**	45
10	12 (**9g**)	**4a**	0.01	**11h**	35

[a] $[Rh(cod)_2]BF_4$ (0.0125 mmol), H8-BINAP (0.0125 mmol), α,ω-diyne (0.25 mmol), dialkyl acetylenedicarboxylate (0.25 mmol), and CH_2Cl_2 (25 mL) were employed. A mixture of the α,ω-diyne and the dialkyl acetylenedicarboxylate was added dropwise over 10 min. The active catalyst was prepared by mixing $[Rh(cod)_2]BF_4$ and H8-BINAP in CH_2Cl_2 followed by hydrogenation (1 atm, RT, 0.5 h). [b] Yield of isolated product. [c] Isolated as a mixture of meta- and paracyclophanes. [d] Ratio of paracyclophane:metacyclophane. [e] CH_2Cl_2 (12.5 mL) was used. [f] CH_2Cl_2 (2.5 mL) was used.

The reactions of **4a** with α,ω-diynes **9c–g** having different lengths of the carbon chain furnished the corresponding [8]–[12]paracyclophanes in fair to good yields (Table 6, entries 6–10). Importantly, the formation of [8]–[12]paracyclophanes predominated and the corresponding [8]–[12]meta- or orthocyclophanes were generated either in very low yield (<5%) or not at all.

Table 7. ^{1}H NMR chemical shifts of methylene protons of paracyclophanes at highest field.

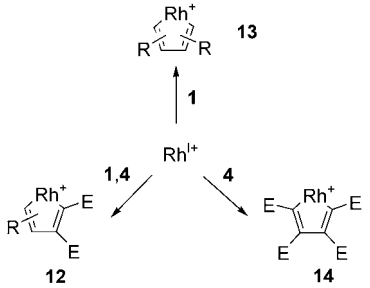


Compound	Chemical shift [ppm]
11a (n = 7)	−1.88 (1H)
11d (n = 8)	−0.10 (2H)
11e (n = 9)	0.10 (2H)
11f (n = 10)	0.30 (2H)
11g (n = 11)	0.90 (10H)
11h (n = 12)	1.00 (4H)

The chemical shifts of the methylene protons appearing at highest field for each paracyclophane are shown in Table 7. The higher field shift of the methylene protons clearly supports the formation of paracyclophanes.

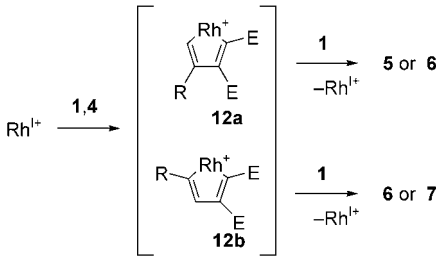
Mechanistic consideration regarding the intermolecular crossed-cyclotrimerization of terminal alkynes and dialkyl

acetylenedicarboxylates: It is difficult to achieve sufficient control to ensure both high chemo- and regioselectivity in the intermolecular cyclotrimerization of alkynes, and successful examples are quite limited. Our study realized a successful control of both high chemo- and regioselectivity in the intermolecular crossed-cyclotrimerization of alkynes. The high chemo- and regioselectivity observed in this crossed-cyclotrimerization indicate that the intermediate, a rhodium metallacycle, was formed in a highly chemo- and regioselective manner from two different alkynes. Scheme 7 depicts the possible formation of rhodium metallacycles

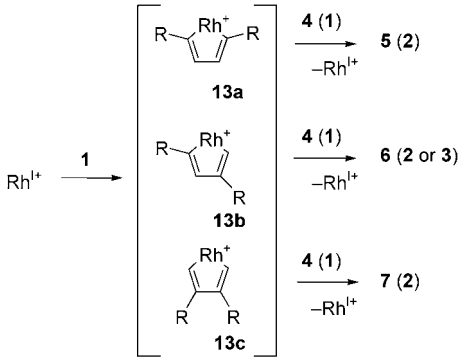


Scheme 7. Possible formation of rhodium metallacycles from **1** and **4**.

from terminal alkyne **1** and dialkyl acetylenedicarboxylate **4**. The crossed-cyclotrimerization products **5**–**7** may be obtained from metallacycles **12** or **13**. Metallacycle **12a** could produce isomers **5** and **6**, while metallacycle **12b** could produce isomers **6** and **7** (Scheme 8). Alternatively, metallacycles **13a**, **13b**, and **13c** could produce isomers **5**, **6**, and **7**, respectively (Scheme 9). Because the major isomer of the



Scheme 8. Correlation of cyclotrimerization products with rhodium metallacycles **12a** and **12b**.

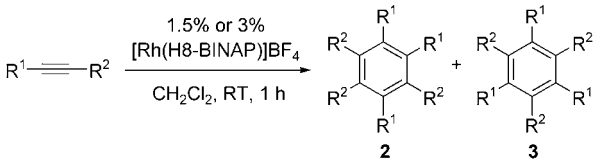


Scheme 9. Correlation of cyclotrimerization products with rhodium metallacycles **13a**–**c**.

crossed-cyclotrimerization product is **5**, metallacycle **12a** or **13a** should be a major intermediate. On the other hand, homo-cyclotrimerization product **2** could be obtained from metallacycle **13a**, **13b**, or **13c**, and homo-cyclotrimerization product **3** could be obtained from metallacycle **13b** (Scheme 8). Because the **3a**:**2a** ratio using Rh^{I+}/H8-BINAP was 24:76 (Table 2, entry 4), the ratio of **13b** to **13a**+**13c** should be >24:76. However, crossed-cyclotrimerization product **6b**, which would be derived from metallacycle **13b**, only constituted 6% of the total product (Table 5, entry 2). Thus, the formation of **5b** from metallacycle **13a** is at least a minor pathway, and the major intermediate should be metallacycle **12a**.

To confirm the formation of metallacycle **12a** as the major intermediate of this crossed-cyclotrimerization, homo-cyclotrimerization of various alkynes in the presence of Rh^{I+}/H8-BINAP was investigated at room temperature for 1 h, as summarized in Table 8. Though it takes less than 1 h

Table 8. Reactivity of various alkynes in the presence of the cationic rhodium(I)/H8-BINAP complex.[a]



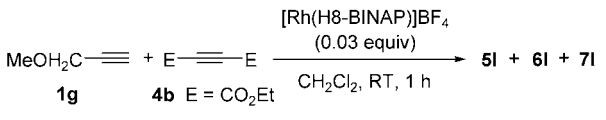
Entry	R^1	R^2		Cat. [%]	Yield [%][b] **2**+**3**	Ratio of **2**:**3**[c]
1	*n*-$C_{10}H_{21}$	H	(**1a**)	1.5	6	–
2	Me_3Si	H	(**1j**)	1.5	36	83:17
3	Ph	H	(**1f**)	1.5	94	97:3
4	CH_2OMe	H	(**1g**)	1.5	95	85:15
5[d]	CO_2Me	CO_2Me	(**4a**)	3.0	68	–
6[d]	CO_2Et	CO_2Et	(**4b**)	3.0	78[e]	–
7[d]	CO_2tBu	CO_2tBu	(**4c**)	3.0	0	–

[a] $[Rh(cod)_2]BF_4$ (0.0090 mmol), H8-BINAP (0.0090 mmol), alkyne (0.60 mmol), and CH_2Cl_2 (3.0 mL) were employed. The active catalyst was prepared by mixing $[Rh(cod)_2]BF_4$ and H8-BINAP in CH_2Cl_2 followed by hydrogenation (1 atm, RT, 0.5 h). [b] Determined by ^1H NMR spectroscopy. [c] Determined by GC. [d] Alkyne (0.30 mmol) was used. [e] Yield of isolated product.

for the Rh^{I+}/H8-BINAP-catalyzed crossed-cyclotrimerization of **1a** and **4** to proceed to completion at room temperature, the reactions of terminal alkynes **1a** and **1j** were slow (Table 8, entries 1 and 2). On the other hand, the reactions of DMAD (**4a**) and DEAD (**4b**) furnished the corresponding cyclotrimerization products in good yields (Table 8, entries 5 and 6). Thus, the formation of **5** from metallacycle **13a** is unlikely. The homo-cyclotrimerization of di-*tert*-butyl acetylenedicarboxylate **4c** in the presence of Rh^{I+}/H8-BINAP did not proceed at all, which accounts for the high yield of crossed-cyclotrimerization products **5c**.

The reactions of terminal alkynes **1f** and **1g** bearing aryl and oxymethylene substituents furnished the corresponding cyclotrimerization products in good yields at room temperature (Table 8, entries 3 and 4). The reaction of **1f** and **4b**

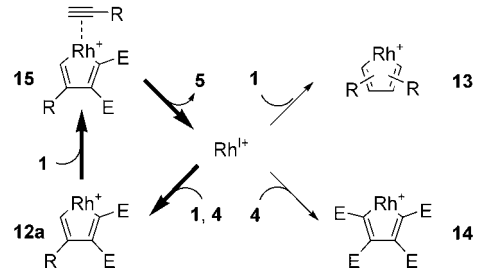
furnished the crossed-cyclotrimerization product **5h** in high yield and did not furnish the homo-cyclotrimerization products (Table 5, entry 9). Thus, the major intermediate would be **12a**. On the other hand, the reaction of **1g** and **4b** furnished the corresponding homo-cyclotrimerization products as by-products due to competitive formation of metallacycle **13** rather than **12**. A slightly lower regioselectivity was also observed in this reaction (Table 5, entry 14). We assume that **5l–7l** were partially derived from metallacycle **13**. To confirm this hypothesis, we carried out the reaction using excess **4b** (Scheme 10). The yield and regioselectivity were improved, presumably due to the formation of metallacycle **12** being favored by the use of excess **4b**.



1g (equiv)	**4b** (equiv)	**5l+6l+7l**	**5l:6l:7l**
2.0	1.0	61%	86:10:4
1.0	2.0	74%	91:7:2
		(based on **1g**)	

Scheme 10. Crossed-cyclotrimerization of **1g** with excess **4b**.

Thus, a plausible mechanism for the cationic rhodium(I)/H8-BINAP complex-catalyzed intermolecular crossed-cyclotrimerization of **1** and **4** is illustrated in Scheme 11. Chemo- and regioselectivity are determined by the preferential formation of metallacycle **12a** rather than **13** and **14**, followed by the coordination of terminal alkynes **1** to form complex **15**. Reductive elimination of rhodium gives **5** and regenerates the rhodium catalyst. The formation of metallacycle **12a** clearly accounts for the selective generation of a [6]metacyclophane **10a** and [7]–[12]paracyclophanes **11** when α,ω-diynes **9** are used instead of two molecules of **1**.



Scheme 11. Plausible mechanism for intermolecular crossed-cyclotrimerization of **1** and **4** catalyzed by the cationic rhodium(I)/H8-BINAP complex.

The sterically unfavorable coordination of terminal monoynes to form complex **15** occurs under electronic control. The electronegative carbon atom in the 2-position of **1** coordinates to the carbon atom α to the carbonyl and rhodium of **12a**, giving rise to the observed regioselectivity. Indeed, the reaction of sterically demanding trimethylsilyl acetylene **1j** with **4b** also furnished the sterically unfavorable product **5n** with excellent regioselectivity due to the carbon atom α to the silicon atom being highly electronegative as a result of the polarization of the silicon–carbon bond.[28] The effect of modified BINAP ligands on the regioselectivity is not clearly understood, although their electronic character would seem to be more important than their steric character (Table 4). The use of more electron-rich BINAP ligands, such as H8-BINAP and Segphos, significantly improved the regioselectivity in favor of **5** compared with the use of BINAP itself (Table 4, entries 4 and 6 versus entry 2). On the other hand, no correlation was observed between the dihedral angles of the ligands and the regioselectivity of the cyclotrimerization products (dihedral angle: H8-BINAP > BINAP > Segphos,[19b,29] regioselectivity: H8-BINAP > Segphos ≫ BINAP).

Conclusion

In conclusion, we have discovered that the cationic rhodium(I)/DTBM-Segphos complex is a widely applicable catalyst for highly regioselective intermolecular cyclotrimerization of terminal alkynes, providing 1,2,4-trisubstituted benzenes in high yield and with high regioselectivity. A chemo- and regioselective intermolecular crossed-cyclotrimerization of dialkyl acetylenedicarboxylates with a variety of terminal alkynes has also been developed based on the use of the cationic rhodium(I)/H8-BINAP complex, providing 3,6-disubstituted phthalates in high yields. This catalytic process is a noteworthy example of intermolecular crossed-cyclotrimerization of two different alkynes in terms of catalytic activity, chemo- and regioselectivity, scope of substrates, and ease of operation. This versatile new crossed-alkyne cyclotrimerization procedure has been successfully applied to a one-step synthesis of a [6]metacyclophane and [7]–[12]paracyclophanes from the corresponding terminal α,ω-diynes. Because 1,10- to 1,15-diynes can be synthesized in one-step from the commercially available corresponding dibromides, the present method allows a two-step synthesis of [7]–[12]paracyclophanes starting from commercially available reagents. The successful application to the synthesis of the highly strained [6]metacyclophane and [7]paracyclophane is particularly noteworthy. Mechanistic studies have revealed that the chemo- and regioselectivity of this crossed-alkyne cyclotrimerization are determined by preferential formation of the rhodium metallacycle **12a** derived from terminal alkyne **1** and dialkyl acetylenedicarboxylate **4**.

Experimental Section

General methods: ^{1}H NMR spectra were recorded at 300 MHz (JEOL AL 300). ^{13}C NMR spectra were obtained with complete proton decoupling at 75 MHz (JEOL AL 300). Product isomer distributions were determined by ^{1}H NMR or GC (HP5890 A). HRMS data were obtained on a JEOL JMS-700. Infrared spectra were obtained on a JASCO A-302. Anhydrous CH_2Cl_2 was obtained from Aldrich (No. 27,099–7) and was

used as received. Tol-BINAP, DM-BINAP, H8-BINAP, Segphos, and DTBM-Segphos were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and were used as received. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. α,ω-Diynes **9b**, **9c**, **9d**, **9e**, **9f**, and **9g** were prepared according to the literature.[26]

General procedure for intermolecular cyclotrimerization of terminal monoynes (Table 3, entry 1): Under an argon atmosphere, a solution of DTBM-Segphos (59.0 mg, 0.050 mmol) in CH_2Cl_2 (1.0 mL) was added to a solution of $[Rh(cod)_2]BF_4$ (20.3 mg, 0.050 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. The mixture was stirred at room temperature for 5 min, and then H_2 was introduced into the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness and the residue was redissolved in CH_2Cl_2 (2.0 mL). A solution of 1-dodecyne (**1a**) (166.4 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was then added dropwise to this solution over 1 min, and any substrate remaining in the syringe was rinsed into the reaction mixture with further CH_2Cl_2 (0.5 mL). The mixture was stirred at room temperature (20–25 °C) for 24 h. The resulting solution was concentrated and the residue was purified by preparative TLC (hexane), which furnished a mixture of 1,2,4-tridecylbenzene (**2a**) and 1,3,5-tridecylbenzene (**3a**) (151.9 mg, 0.913 mmol, 91 %, **2a**:**3a** = 83:17).

1,2,4-Tridecylbenzene (2a, 83 % regioselectivity):[4f] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.04 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.92 (d, J = 7.5 Hz, 1H), 2.48–2.61 (m, 6H), 1.45–1.65 (m, 6H), 1.20–1.43 (m, 42H), 0.88 ppm (t, J = 6.6 Hz, 9H); aryl protons of minor isomer **3a**: δ = 6.80 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.7, 140.3, 140.2, 137.7, 129.2, 128.9, 125.8, 125.7, 36.0, 35.6, 32.8, 32.4, 31.9, 31.63, 31.62, 31.4, 29.9, 29.7, 29.65, 29.59, 29.56, 29.49, 29.38, 22.7, 14.1 ppm.

1,2,4-Trihexylbenzene (2b, 82 % regioselectivity):[30] Reaction time: 18 h. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.03 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.92 (d, J = 7.5 Hz, 1H), 2.43–2.63 (m, 6H), 1.45–1.70 (m, 6H), 1.20–1.45 (m, 18H), 0.78–0.98 ppm (m, 9H); aryl protons of minor isomer **3b**: δ = 6.80 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.7, 140.3, 140.1, 137.7, 129.2, 128.9, 125.8, 125.7, 36.0, 35.6, 32.8, 32.4, 31.8, 31.59, 31.57, 31.4, 29.5, 29.1, 22.7, 22.6, 14.1 ppm.

1,2,4-Tribenzylbenzene (2c, 82 % regioselectivity):[10a] Reaction time: 16 h. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.94–7.34 (m, 18H), 3.92 (s, 2H), 3.90 (s, 2H), 3.88 ppm (s, 2H), aryl protons of minor isomer **3c**: δ = 6.86 ppm (s, 3H), benzyl protons of minor isomer **3c**: δ = 3.88 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 141.3, 141.2, 141.1, 140.6, 140.5, 139.3, 138.9, 136.8, 131.3, 130.7, 128.9, 128.8, 128.7, 128.6, 128.39, 128.35, 128.34, 127.5, 127.1, 125.96, 125.94, 125.90, 41.8, 41.5, 39.0, 38.6 ppm.

1,2,4-Tris(3-chloropropyl)benzene (2d, 86 % regioselectivity):[4f] Reaction time: 16 h. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.09 (d, J = 6.9 Hz, 1H), 7.00 (s, 1H), 6.98 (d, J = 6.9 Hz, 1H), 3.44–3.65 (m, 6H), 2.64–2.85 (m, 6H), 1.96–2.16 ppm (m, 6H); aryl protons of minor isomer **3d**: δ = 6.87 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 141.1, 138.7, 136.3, 129.65, 129.56, 126.5, 44.5, 44.2, 34.00, 33.95, 33.82, 33.79, 32.6, 32.3, 29.5, 29.1 ppm.

1,2,4-Tris(1-cyclohexenyl)benzene (2e, 97 % regioselectivity):[31] Reaction time: 18 h. Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19 (dd, J = 8.1, 2.1 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.06–6.14 (m, 1H), 5.64–5.72 (m, 2H), 2.04–2.48 (m, 12H), 1.51–1.82 ppm (m, 12H); aryl protons of minor isomer **3e**: δ = 7.23 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.5, 141.0, 140.6, 139.8, 139.1, 136.3, 128.4, 126.2, 125.3, 124.1, 123.4, 122.9, 29.59, 29.54, 29.48, 27.4, 25.88, 25.77, 25.76, 25.73, 23.3, 23.1, 22.2 ppm.

1,2,4-Triphenylbenzene (2f, 83 % regioselectivities):[4e] Reaction time: 16 h (1 h using H8-BINAP). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.11–7.80 ppm (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.3, 141.5, 141.11, 141.07, 140.95, 140.55, 140.3, 139.5, 131.1, 129.89, 129.85, 129.4, 128.83, 128.81, 127.92, 127.89, 127.5, 127.4, 127.3, 127.1, 126.6, 126.5, 126.1, 125.2 ppm.

1,2,4-Tris(methoxymethyl)benzene (2g, 86 % regioselectivity):[4e] Reaction time: 15 h. Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19–7.43 (m, 3H), 4.52 (s, 2H), 4.51 (s, 2H), 4.45 (s, 2H), 3.39 (s, 3H), 3.373 (s, 3H), 3.366 ppm (s, 3H); methylene protons of minor isomer **3g**: δ = 4.45 ppm (s, 6H); methyl protons of minor isomer **3g**: δ = 3.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.5, 137.7, 136.4, 135.6, 128.8, 127.9, 126.9, 126.1, 74.4, 74.3, 72.0, 71.9, 58.2, 58.13, 58.05, 57.99 ppm.

Acetic acid 2,4-bis(acetoxymethyl)benzyl ester (2h, 100 % regioselectivity):[32] Reaction time: 24 h. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz); δ = 7.28–7.46 (m, 3H), 5.20 (s, 2H), 5.19 (s, 2H), 5.11 (s, 2H), 2.11 (s, 3H), 2.10 (s, 3H), 2.09 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.7, 170.5, 136.5, 134.8, 134.4, 130.0, 129.4, 128.3, 65.6, 65.5, 63.5, 63.4, 31.9, 20.9, 20.8 ppm.

Benzene 1,2,4-tricarboxylic acid triethyl ester (2i, 93 % regioselectivity):[33] Reaction time: 16 h. Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.41 (dd, J = 1.8, 0.3 Hz, 1H), 8.20 (dd, J = 7.8, 1.8 Hz, 1H), 7.76 (dd, J = 7.8, 0.3 Hz, 1H), 4.31–4.52 (m, 6H), 1.30–1.50 ppm (m, 9H); aryl protons of minor isomer **3i**: δ = 8.85 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.0, 166.5, 164.9, 164.8, 136.1, 134.3, 132.5, 131.9, 131.8, 131.3, 129.9, 128.7, 61.9, 61.8, 61.5, 14.2, 14.1, 14.0, 13.9 ppm.

1,2,4-Tris(trimethylsilyl)benzene (2j, 70 % regioselectivity):[33] Reaction time: 24 h (24 h using H8-BINAP). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 0.37 (s, 9H), 0.36 (s, 9H), 0.27 ppm (s, 9H); aryl protons of minor isomer **3j**: δ = 7.69 ppm (s, 3H); trimethylsilyl protons of minor isomer **3j**: δ = 0.28 ppm (s, 27H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.6, 144.8, 140.0, 139.3, 138.8, 138.3, 134.3, 132.8, 1.96, 1.86, −1.06, −1.22 ppm.

General procedure for the intermolecular crossed-cyclotrimerization of dialkyl acetylenedicarboxylates and terminal monoynes (Table 5, entry 2): Under an Ar atmosphere, H8-BINAP (5.7 mg, 0.009 mmol) and $[Rh(cod)_2]BF_4$ (3.7 mg, 0.009 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred for 5 min. H_2 was then introduced into the resulting solution in a Schlenk tube. After stirring for 0.5 h at room temperature, the resulting solution was concentrated to dryness and the residue was redissolved in CH_2Cl_2 (2.0 mL). A solution of 1-dodecyne (**1a**) (99.8 mg, 0.60 mmol) and diethyl acetylenedicarboxylate (**4b**) (51.0 mg, 0.30 mmol) in CH_2Cl_2 (0.5 mL) was then added dropwise to this solution over 1 min, and any substrates remaining in the syringe were rinsed into the reaction mixture with further CH_2Cl_2 (0.5 mL). The mixture was stirred at room temperature (20–25 °C) for 1 h. The resulting solution was then concentrated and the residue was purified by preparative TLC (hexane/ethyl acetate, 10:1), which furnished a mixture of diethyl 3,6-didecylphthalate (**5b**), diethyl 3,5-didecylphthalate (**6b**), and diethyl 4,5-didecylphthalate (**7b**) (133 mg, 0.264 mmol, 88 %, **5b**:**6b**:**7b** = 92:6:2). This mixture could be purified by preparative TLC (hexane/ethyl acetate, 10:1), which furnished pure 3,6-didecylphthalic acid diethyl ester (**5b**) (120 mg, 0.238 mmol, 79 %).

Diethyl 3,6-didecylphthalate (5b): Colorless solid; m.p. 42–44 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20 (s, 2H), 4.32 (q, J = 7.2 Hz, 4H), 2.67 (t, J = 7.8 Hz, 4H), 1.50–1.62 (m, 4H), 1.36 (t, J = 7.2 Hz, 6H), 1.18–1.40 (m, 28H), 0.88 ppm (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 139.0, 131.8, 131.6, 61.3, 33.5, 31.9, 31.6, 29.6, 29.63, 29.60, 29.5, 29.3, 22.7, 14.12, 14.10 ppm; IR (neat): $\tilde{\nu}$ = 2750, 1670, 1230, 1160, 1060 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{54}O_4$: C 76.45, H 10.83; found: C 76.73, H 11.09.

Dimethyl 3,6-didecylphthalate (5a, 91 % regioselectivity): Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.21 (s, 2H), 3.85 (s, 6H), 2.67 (t, J = 7.5 Hz, 4H), 1.50–1.62 (m, 4H), 1.20–1.37 (m, 28H), 0.88 ppm (t, J = 6.6 Hz, 6H); aryl protons of minor isomer **6a**: δ = 7.63 (d, J = 1.8 Hz, 1H), 7.20 ppm (d, J = 1.8 Hz, 1H); aryl protons of minor isomer **7a**: δ = 7.49 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.9, 139.1, 131.7, 131.5, 52.2, 33.4, 31.8, 31.4, 29.6, 29.5, 29.45, 29.36, 29.3, 22.6, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 2900, 1820, 1720, 1420, 1260, 1190 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{50}O_4$: C 75.90, H 10.62; found: C 75.59, H 10.68.

Di-*tert*-butyl 3,6-didecylphthalate (5c, 94 % regioselectivity): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.12 (s, 2H), 2.64 (t, J = 7.8 Hz, 4H), 1.46–1.68 (m, 18H), 1.18–1.60 (m, 32H), 0.88 ppm (t, J = 6.6 Hz,

6H); aryl protons of minor isomer **6c**: δ = 7.41 (d, J = 1.8 Hz, 1H), 7.12 ppm (d, J = 1.8 Hz, 1H); aryl protons of minor isomer **7c**: δ = 7.38 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.3, 137.7, 133.1, 130.7, 82.1, 33.7, 31.9, 31.7, 29.9, 29.6, 29.5, 29.3, 28.1, 22.7, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 2910, 1850, 1710, 1450, 1360, 1290, 1150, 1125 cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{62}O_4$: C 77.37, H 11.18; found: C 77.11, H 11.25.

Diethyl 3,6-bis(3-chloropropyl)phthalate (5d, 91% regioselectivity): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (s, 2H), 4.34 (q, J = 7.2 Hz, 4H), 3.54 (t, J = 6.3 Hz, 4H), 2.86 (t, J = 7.5 Hz, 4H), 2.02–2.11 (m, 4H), 1.37 ppm (t, J = 7.2 Hz, 6H); aryl protons of minor isomer **6d**: δ = 7.68 (d, J = 1.5 Hz, 1H), 7.28 ppm (d, J = 1.5 Hz, 1H); aryl protons of minor isomer **7d**: δ = 7.53 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.1, 137.6, 132.4, 132.0, 61.7, 44.3, 34.0, 30.6, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 2800, 1680, 1230, 1150, 990 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{24}Cl_2O_4$: C 57.61, H 6.45; found: C 57.89, H 6.51.

Di-*tert*-butyl 3,6-bis(3-chloropropyl)phthalate (5e, 95% regioselectivity): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19 (s, 2H), 3.55 (t, J = 6.9 Hz, 4H), 2.83 (t, J = 6.9 Hz, 4H), 2.08 (m, 4H), 1.60 ppm (s, 18H); aryl protons of minor isomer **6e**: δ = 7.42 (s, 1H), 7.25 ppm (s, 1H); aryl protons of minor isomer **7e**: δ = 7.56 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.1, 136.5, 133.9, 131.3, 82.9, 44.5, 33.9, 30.7, 28.2 ppm; IR (neat): $\tilde{\nu}$ = 2950, 1710, 1370, 1290, 1160, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{32}Cl_2O_4$: C 61.25, H 7.48; found: C 60.89, H 7.49.

Diethyl 3,6-bis(1-cyclohexenyl)phthalate (5f, 91% regioselectivity): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.18 (s, 2H), 5.57–5.62 (m, 2H), 4.26 (q, J = 7.2 Hz, 4H), 2.03–2.33 (m, 8H), 1.55–1.80 (m, 8H), 1.33 ppm (t, J = 7.2 Hz, 6H); aryl protons of minor isomer **6f**: δ = 7.83 (d, J = 1.8 Hz, 1H), 7.33 ppm (d, J = 1.8 Hz, 1H); aryl protons of minor isomer **7f**: δ = 7.46 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.7, 141.7, 137.3, 131.3, 129.5, 126.7, 61.4, 29.8, 25.5, 23.1, 21.9, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 3200, 2750, 1660, 1180, 770 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{30}O_4$: C 75.36, H 7.91; found: C 75.07, H 7.97.

Di-*tert*-butyl 3,6-bis(1-cyclohexenyl)phthalate (5g, 94% regioselectivity): Colorless solid; m.p. 138.5–143.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.10 (s, 2H), 5.55–5.65 (m, 2H), 2.22–2.32 (m, 4H), 2.04–2.14 (m, 4H), 1.60–1.80 (m, 8H), 1.53 ppm (s, 18H); aryl protons of minor isomer **6g**: δ = 7.61 (m, 1H), 7.24 ppm (m, 1H); aryl protons of minor isomer **7g**: δ = 7.35 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.0, 140.7, 137.3, 132.4, 128.6, 126.3, 81.6, 36.7, 28.0, 25.3, 22.9, 21.8 ppm; IR (neat): $\tilde{\nu}$ = 2850 (br), 1700, 1290, 1220, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{38}O_4$: C 76.68, H 8.73; found: C 76.46, H 8.98.

Diethyl 3,6-diphenylphthalate (5h, 89% regioselectivity): Colorless solid; m.p. 99–105 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.47 (s, 2H), 7.32–7.66 (m, 10H), 4.07 (q, J = 7.2 Hz, 4H), 0.97 ppm (t, J = 6.9 Hz, 6H); aryl protons of minor isomer **6h**: δ = 8.21 (d, J = 2.1 Hz, 1H), 7.74 ppm (d, J = 2.1 Hz, 1H); aryl protons of minor isomer **7h**: δ = 7.79 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.3, 139.9, 132.3, 131.5, 129.0, 128.4, 128.3, 127.7, 61.5, 13.5 ppm; IR (neat): $\tilde{\nu}$ = 1680, 1200, 1110, 1040, 740, 670 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{22}O_4$: C 76.99, H 5.92; found: C 76.82, H 6.01.

Di-*tert*-butyl 3,6-diphenylphthalate (5i, 90% regioselectivity):[34] Colorless solid; m.p. 183.5–185.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34–7.44 (m, 12H), 1.24 ppm (s, 18H); *tert*-butyl protons of minor isomer **6i**: δ = 1.31 (s, 9H), 1.24 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.4, 140.3, 139.4, 133.3, 130.8, 128.9, 128.1, 127.4, 82.3, 27.5 ppm.

Diethyl 3,6-di-*o*-tolylphthalate (5j, 89% regioselectivity): Colorless solid; m.p. 103–108 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (s, 2H), 7.07–7.29 (m, 8H), 3.98 (q, J = 7.2 Hz, 1.6H), 3.97 (q, J = 7.2 Hz, 2.4H), 2.21 (s, 3.5H), 2.17 (s, 2.5H), 0.88 (t, J = 7.2 Hz, 2.5H), 0.87 ppm (t, J = 7.2 Hz, 3.5H); aryl protons of minor isomer **6j**: δ = 7.99 (d, J = 2.1 Hz, 1H), 7.38 ppm (d, J = 2.1 Hz, 1H); aryl protons of minor isomer **7j**: δ = 7.69 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.9, 139.9, 139.8, 139.5, 136.2, 135.9, 132.6, 129.3, 127.9, 125.2, 61.2, 20.4, 13.4 ppm; IR (neat): $\tilde{\nu}$ = 2800, 1680, 1380, 1200, 1100, 730 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{26}O_4$: C 77.59, H 6.51; found: C 77.41, H 6.47.

Di-*tert*-butyl 3,6-di-*o*-tolylphthalate (5k, 88% regioselectivity): Yellow solid; m.p. 50.0–52.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.16–7.30 (m, 10H), 2.21 (s, 3.5H), 2.17 (s, 2.5H), 1.15 (s, 7.5H), 1.14 ppm (s, 10.5H); methyl protons of minor isomer **6k**: δ = 2.29 (s, 3.5H), 2.16 ppm (s, 2.5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.3, 167.2, 165.4, 141.9, 140.2, 139.93, 139.89, 139.88, 139.0, 138.9, 136.5, 136.4, 136.3, 135.3, 134.3, 133.8, 133.7, 133.6, 130.7, 130.5, 130.3, 129.8, 129.63, 129.62, 129.60, 129.55, 129.45, 128.9, 127.85, 127.83, 127.6, 125.9, 125.1, 125.0, 81.8, 81.74, 81.70, 81.6, 60.3, 28.09, 28.05, 27.5, 27.2, 21.0, 20.4, 20.3, 20.2, 20.1, 14.2 ppm; IR (neat): $\tilde{\nu}$ = 2850, 1700, 1360, 1300, 1240, 1140 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{34}O_4$: C 78.57, H 7.47; found: C 78.83, H 7.57.

Diethyl 3,6-bis(methoxymethyl)phthalate (5l, 86% regioselectivity): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.54 (s, 2H), 4.59 (s, 4H), 4.33 (q, J = 7.2 Hz, 4H), 3.35 (s, 6H), 1.36 ppm (t, J = 7.2 Hz, 6H); aryl protons of minor isomer **6l**: δ = 7.85–7.87 (m, 1H), 7.61–7.63 ppm (m, 1H); aryl protons of minor isomer **7l**: δ = 7.77 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.5, 136.6, 131.2, 129.8, 71.8, 61.5, 58.5, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 2750, 1660, 1220, 1070, 990 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{22}O_4$: C 61.92, H 7.15; found: C 61.60, H 6.95.

Diethyl 3,6-bis(acetoxymethyl)phthalate (5m, 87% regioselectivity): Isolated as a mixture of **5m** (63% yield) and **2h**/**3h** (28% yield), these yields being determined on the basis of ^{1}H NMR integrals. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.52 (s, 2H), 5.26 (s, 4H), 4.37 (q, J = 7.2 Hz, 4H), 2.07 (s, 6H), 1.37 ppm (t, J = 7.2 Hz, 6H); aryl protons of minor isomer **6m**: δ = 7.92 (d, J = 1.5 Hz, 1H), 7.60 ppm (d, J = 1.5 Hz, 1H); aryl protons of minor isomer **7m**: δ = 7.76 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.3, 167.0, 134.8, 132.2, 130.9, 63.6, 61.9, 20.7, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 2900, 1700 (br), 1360, 1050 cm^{-1}; HRMS (EI): calcd for $C_{16}H_{19}O_6$: 307.1181, found: 307.1133 [M−OAc]$^+$.

Diethyl 3,6-bis(trimethylsilyl)phthalate (5n, 99% regioselectivity): Colorless solid; m.p. 65–68 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (s, 2H), 4.32 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.2 Hz, 6H), 0.30 ppm (s, 18H); aryl protons of minor **6n**: δ = 8.00 (d, J = 1.2 Hz, 1H), 7.87 ppm (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.3, 140.4, 137.7, 135.8, 61.9, 14.3, 0.3 ppm; IR (neat): $\tilde{\nu}$ = 2770, 1660, 1200, 1130, 1070, 790 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{30}O_4Si_2$: C 58.97, H 8.25; found: C 59.10, H 8.36.

Tetraethyl 5-(trimethylsilyl)benzene-1,2,3,4-tetracarboxylate (8): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.20 (s, 1H), 4.25–4.44 (m, 8H), 1.29–1.43 (m, 12H), 0.34 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.7, 167.5, 166.9, 165.9, 142.7, 141.9, 138.3, 135.2, 131.4, 130.4, 62.8, 62.62, 62.55, 62.53, 14.6, 14.5, 14.42, 14.41, 0.0 ppm; IR (neat): $\tilde{\nu}$ = 3000, 1740, 1390, 1240 (br), 1040, 860 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{30}O_8Si$: C 57.51, H 6.90; found: C 57.46, H 6.91.

General procedure for the intermolecular crossed-cyclotrimerization of dialkyl acetylenedicarboxylates and terminal α,ω-diynes (Table 6, entry 6): Under an argon atmosphere, H8-BINAP (5.1 mg, 0.0125 mmol) and $[Rh(cod)_2]BF_4$ (7.9 mg, 0.0125 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred for 5 min. H_2 was then introduced into the resulting solution in a Schlenk tube. After stirring for 0.5 h at room temperature, the resulting solution was concentrated to dryness and the residue was redissolved in CH_2Cl_2 (20 mL). A solution of 1,11-dodecadiyne (**9c**) (40.6 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (**4a**; 35.5 mg, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was then added dropwise to this solution over 1 min, and any substrates remaining in the syringe were rinsed into the reaction mixture with further CH_2Cl_2 (2.0 mL). The mixture was stirred at room temperature for 1 h. The resulting solution was concentrated and the residue was purified by preparative TLC (hexane/ethyl acetate, 6:1), which furnished [8]paracyclophane **11d** (34.8 mg, 0.114 mmol, 46%).

Dimethyl [8]paracyclophane-10,11-dicarboxylate (11d):[35] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (s, 2H), 3.86 (s, 6H), 3.15 (dt, J = 13.0, 5.3 Hz, 2H), 2.51 (ddd, J = 14.1, 9.0, 5.1 Hz, 2H), 1.57–1.70 (m, 2H), 1.38–1.49 (m, 2H), 1.00–1.15 (m, 2H), 0.75–0.90 (m, 2H), 0.40–0.60 (m, 2H), −0.15–0.10 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.4, 140.6, 132.8, 132.1, 52.3, 33.9, 30.3, 29.2, 25.4 ppm; IR (neat): $\tilde{\nu}$ = 2880, 2820, 1705, 1420, 1280, 1190, 1100 cm^{-1}; HRMS (EI): calcd for $C_{18}H_{24}O_4$: 273.1491, found: 273.1469 [M−OMe]$^+$.

Diethyl [6]metacyclophane-8,9-dicarboxylate (10a): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50 (d, J = 1.2 Hz, 1H), 7.45 (d, J = 1.2 Hz, 1H), 4.29–4.43 (m, 4H), 2.54–2.84 (m, 4H), 1.72–1.91 (m, 2H), 1.16–1.48 (m, 4H), 1.36 (t, J = 7.2 Hz, 6H), 0.20–0.65 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.9, 166.7, 144.2, 141.1, 139.3, 130.6, 129.5, 125.6, 61.3, 61.2, 34.3, 32.6, 32.4, 32.3, 27.8, 27.5, 14.13, 14.11 ppm; IR (neat): $\tilde{\nu}$ = 2800, 1670, 1420, 1230, 750 cm^{-1}; HRMS (FAB): calcd for $C_{18}H_{24}O_4$: 305.1753, found 305.1779 $[M+H]^+$; elemental analysis calcd (%) for $C_{18}H_{24}O_4$: C 71.03, H 7.95; found: C 71.29, H 7.96.

Dimethyl [7]paracyclophane-9,10-dicarboxylate (11a) and dimethyl[7]-metacyclophane-9,10-dicarboxylate (10b) (11a:10b = 1:0.8):[27] Colorless solid; m.p. 60–63 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.67 (d, J = 1.5 Hz, 1H; **10b**), 7.62 (d, J = 1.5 Hz, 1H; **10b**), 7.23 (s, 2H; **11a**), 3.92 (s, 3H; **10b**), 3.88 (s, 3H; **10b**), 3.87 (s, 6H; **11a**), 3.34 (ddd, J = 12.9, 6.3, 1.8 Hz, 2H), 2.70–2.76 (m, 4H), 2.40 (ddd, J = 18.0, 11.4, 6.6 Hz, 2H), 1.26–1.70 (m, 13H), 0.93–1.07 (m, 2H), 0.48–0.67 (m, 1H), 0.21–0.33 (m, 2H), −0.15–0.15 (m, 1H), −1.99 to −1.77 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.0, 168.2, 166.6, 143.8, 141.1, 140.1, 136.3, 132.8, 132.3, 131.7, 128.9, 126.8, 52.4, 52.34, 52.30, 37.0, 34.9, 30.4, 30.0, 29.5, 29.2, 29.0, 28.8, 28.5, 27.3, 26.9 ppm; IR (neat): $\tilde{\nu}$ = 2900, 1710, 1420, 1260, 1190 cm^{-1}; HRMS (EI): calcd for $C_{17}H_{22}O_4$: 290.1518, found: 290.1526 $[M]^+$.

Diethyl [7]paracyclophane-9,10-dicarboxylate (11b) and diethyl [7]metacyclophane-9,10-dicarboxylate (10c) (11b:10c = 1:1.2): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.67 (d, J = 1.5 Hz, 1H; **10c**), 7.62 (d, J = 1.5 Hz, 1H; **10c**), 7.21 (s, 2H; **11a**), 4.28–4.43 (m, 8H), 3.36 (ddd, J = 12.9, 6.3, 1.8 Hz, 2H), 2.65–2.82 (m, 4H), 2.39 (ddd, J = 17.7, 11.4, 6.3 Hz, 2H), 1.26–1.70 (m, 19H), 0.95–1.10 (m, 2H), 0.48–0.68 (m, 1H), 0.20–0.35 (m, 2H), −0.15–0.15 (m, 1H), −1.98 to −1.72 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.3, 167.8, 166.2, 143.6, 140.9, 138.8, 136.2, 132.7, 132.6, 131.9, 131.5, 126.7, 61.3, 42.3, 37.0, 34.9, 31.4, 30.5, 30.0, 29.4, 29.1, 28.9, 28.6, 28.4, 27.4, 26.6, 14.2, 14.14, 14.08 ppm; IR (neat): $\tilde{\nu}$ = 2870, 1700 (br), 1260, 1190 cm^{-1}; HRMS (EI): calcd for $C_{19}H_{26}O_4$: 318.1831, found: 318.1783 $[M]^+$.

Di-*tert*-butyl [7]paracyclophane-9,10-dicarboxylate (11c) and di-*tert*-butyl [7]metacyclophane-9,10-dicarboxylate (10d) (11c:10d = 1:0.8): Colorless solid; m.p. 90–93 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.58 (d, J = 1.5 Hz, 1H; **10d**), 7.41 (d, J = 1.5 Hz, 1H; **10d**), 7.26 (s, 2H; **11c**), 3.35 (ddd, J = 12.6, 6.3, 1.8 Hz, 2H), 2.66–2.85 (m, 4H), 2.36 (ddd, J = 18.0, 11.4, 6.6 Hz, 2H), 1.59 (s, 18H; **11c**), 1.58 (s, 18H; **10d**), 1.25–1.70 (m, 13H), 0.95–1.30 (m, 2H), 0.48–0.67 (m, 1H), 0.19–0.34 (m, 2H), −0.15–0.15 (m, 1H), −1.95 to −1.70 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.3, 165.5, 142.3, 140.0, 139.7, 135.5, 134.1, 132.9, 132.1, 131.3, 126.1, 81.7, 81.6, 81.2, 65.8, 37.0, 35.0, 34.8, 30.0, 29.5, 29.3, 28.2, 28.14, 28.09, 27.9, 27.4, 26.7, 15.2 ppm; IR (neat): $\tilde{\nu}$ = 2900, 1695, 1360, 1270, 1140 cm^{-1}; HRMS (EI): calcd for $C_{23}H_{34}O_4$: 244.1099, found: 244.1086 $[M-t\mathrm{Bu}_2\mathrm{O}]^+$.

Dimethyl [9]paracyclophane-11,12-dicarboxylate (11e): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.27 (s, 2H), 3.86 (s, 6H), 3.00 (ddd, J = 12.7, 7.7, 4.6 Hz, 2H), 2.37 (ddd, J = 12.8, 7.9, 5.1 Hz, 2H), 1.50–1.65 (m, 2H), 1.35–1.50 (m, 2H), 0.75–1.15 (m, 4H), 0.48–0.68 (m, 4H), −0.05–0.17 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.5, 139.9, 132.8, 131.9, 52.2, 33.1, 28.4, 27.4, 25.7, 23.0 ppm; IR (neat): $\tilde{\nu}$ = 2880, 2820, 1710, 1420, 1260, 1190, 1140 cm^{-1}; HRMS (EI): calcd for $C_{19}H_{26}O_4$: 318.1832, found: 318.1830 $[M]^+$.

Dimethyl [10]paracyclophane-12,13-dicarboxylate (11f):[36] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.25 (s, 2H), 3.86 (s, 6H), 3.16 (dt, J = 13.2, 5.0 Hz, 2H), 2.47 (ddd, J = 15.8, 10.5, 5.3 Hz, 2H), 1.67–1.80 (m, 2H), 1.42–1.57 (m, 2H), 1.17–1.37 (m, 2H), 0.95–1.08 (m, 2H), 0.65–0.90 (m, 6H), 0.20–0.37 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 139.2, 132.9, 132.1, 52.2, 33.4, 28.0, 27.9, 26.8, 24.9 ppm; IR (neat): $\tilde{\nu}$ = 2880, 2820, 1710, 1420, 1260, 1190, 1150 cm^{-1}; HRMS (EI): calcd for $C_{20}H_{28}O_4$: 332.1988, found: 332.1968 $[M]^+$.

Dimethyl [11]paracyclophane-13,14-dicarboxylate (11g): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (s, 2H), 3.85 (s, 6H), 3.00 (ddd, J = 13.8, 7.2, 4.8 Hz, 2H), 2.52 (ddd, J = 12.3, 7.8, 4.8 Hz, 2H), 1.55–1.70 (m, 4H), 1.15–1.35 (m, 4H), 0.65–0.95 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.7, 139.7, 132.4, 132.0, 52.2, 33.2, 28.5, 28.0, 27.4, 26.6, 25.6 ppm; IR (neat): $\tilde{\nu}$ = 2870, 1710, 1420, 1260, 1090 cm^{-1}; HRMS (EI): calcd for $C_{21}H_{30}O_4$: 346.2144, found: 346.2147 $[M]^+$.

Dimethyl [12]paracyclophane-14,15-dicarboxylate (11h): Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.24 (s, 2H), 3.85 (s, 6H), 2.95–3.15 (m, 2H), 2.45–2.65 (m, 2H), 1.52–1.72 (m, 4H), 0.90–1.20 (m, 12H), 0.75–0.90 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.8, 139.4, 132.1, 131.9, 52.2, 32.7, 29.3, 27.4, 27.3, 26.4, 25.2 ppm; IR (neat): $\tilde{\nu}$ = 2870, 2820, 1710, 1420, 1260, 1190 cm^{-1}; HRMS (EI): calcd for $C_{22}H_{32}O_4$: 360.2301, found: 360.2306 $[M]^+$.

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