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An efficient synthesis of fused tricycles with a benzene core via intramolecular double ring-closing enyne metathesis

Zhiqiang Liang,[a,b] Shengming Ma,[a,*] Jihong Yu[b] and Ruren Xu[b]

[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China*
[b]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, PR China*

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Abstract—A double enyne metathesis reaction has been developed for the efficient synthesis of tricyclic products with a benzene core in good yields. By this protocol, bisannulated benzenes with different ring sizes may be simultaneously constructed from the corresponding precursors in just 'one shot'.

1. Introduction

During the past decade, olefin metathesis has become a very important and effective method for the construction of many functionalized carbocycles and heterocycles[1] with the development of the highly active ruthenium[2] and molybdenum[3] carbene complexes. Enyne metathesis is also very interesting and useful in synthetic organic chemistry[4] because the carbon–carbon double and triple bonds are cleaved forming a new conjugated 1,3-diene moiety,[4d] which is very useful for various cycloadditions.[5] Thus, enyne metathesis has received more and more attention in recent years.

On the other hand, chromenes have received increasing attention due to their biological properties such as phototoxicity,[6] anti-microbial activity,[7] anti-juvenile hormone,[8] anti-tumor,[9] insecticidal,[7] and anti-feedant activities.[10] Recently, we reported bicyclic carbopalladation[11] and triple cyclic Heck reactions[12] affording fused bicyclic and tetracyclic compounds with a benzene core, respectively. In our previous study, we also used double RCM reaction to construct bicyclic quinolizidine alkaloids and their analogues.[13] Here, we wish to report an efficient and versatile method for the synthesis of benzodipyrans and their analogues via double metathesis.

2. Results and discussion

Diiodide **1**[14a] and dibromide **9**[14b] were used as the key building blocks for the synthesis of the starting materials. We first tried to synthesize compound **3** by a Sonogashira coupling of the diiodide **1** with 1-hexyne directly, but the yields were very low. So we protected the hydroxy groups in the form of acetates, then a Sonogashira coupling with 1-hexyne followed by hydrolysis gave **3** in good yield. Then substrates **4a–c** were prepared by the treatment of **3** with allyl bromide, homoallyl bromide, and 5-bromo-1-pentene in the presence of K_2CO_3 in DMF, respectively. Compound with different C=C bond **6** was obtained from compound **5**, which was prepared by the stepwise monoallylation of **3** (Scheme 1). Using the same method, substrates **8a–c**, **12a**,**b**, and **14** were easily synthesized as depicted in Schemes 2 and 3.

All the prepared substrates were reacted with the second generation Grubbs' catalyst **15**. Compound **4a** was used as a model to study the double enyne ring-closing metathesis reaction. Temperature, solvent, and protecting atmosphere were compared in the presence of 5 mol % Ru catalyst **15**, and some of the most meaningful results are summarized in Table 1.

As shown in Table 1, when a mixture of **4a** and 5 mol % Ru catalyst **15** in CH_2Cl_2 was stirred at rt for 8 h under argon, the desired tricyclic compound **16a** was formed in a trace amount (entry 1, Table 1). However, product **16a** was formed in good yield in refluxing CH_2Cl_2 for 8 h under argon (entry 2, Table 1). Mori et al. observed that ethylene gas has profound effects on the rates and efficiency of enyne metathesis.[15] So we performed the reaction of substrate **4a** in refluxing CH_2Cl_2 under ethylene gas, but the yield is not improved (entry 3, Table 1). The result in toluene was not better (entry 4, Table 1). We chose the conditions listed in entry 2 of Table 1 as the standard conditions.

Having established the standard reaction conditions for the double enyne ring-closing metathesis of **4a**, we tried

Keywords: Double RCM; Enynes; Ruthenium; Tricyclic compounds.
* Corresponding author. Tel.: +86 21 54925147; fax: +86 21 64167510; e-mail: masm@mail.sioc.ac.cn

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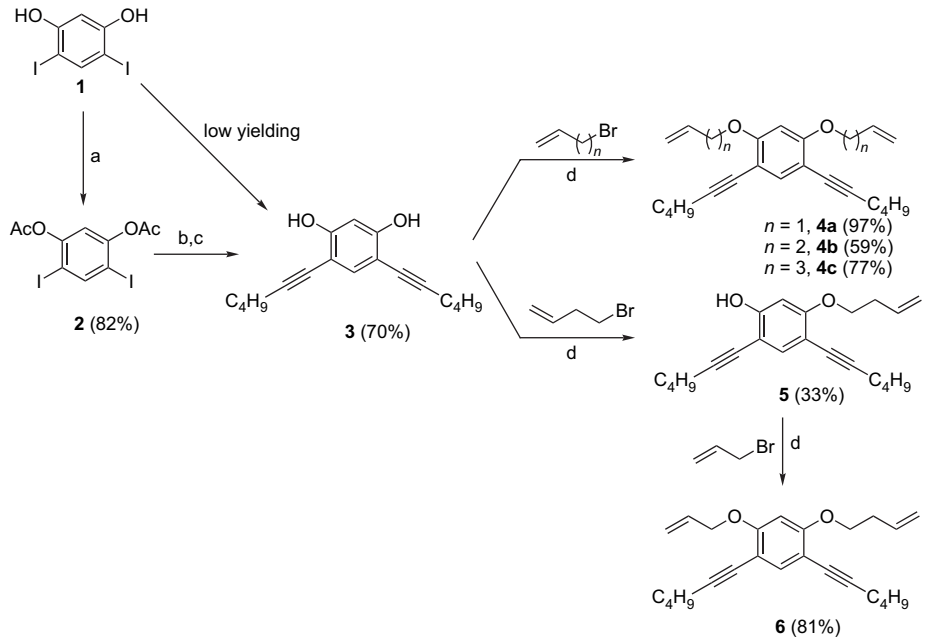
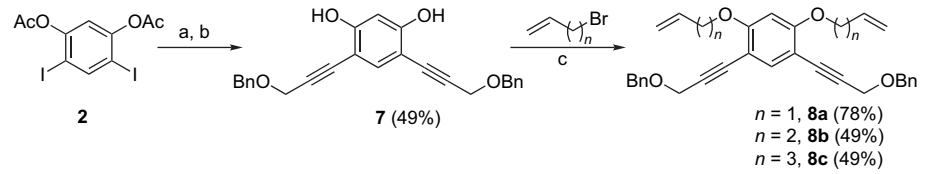
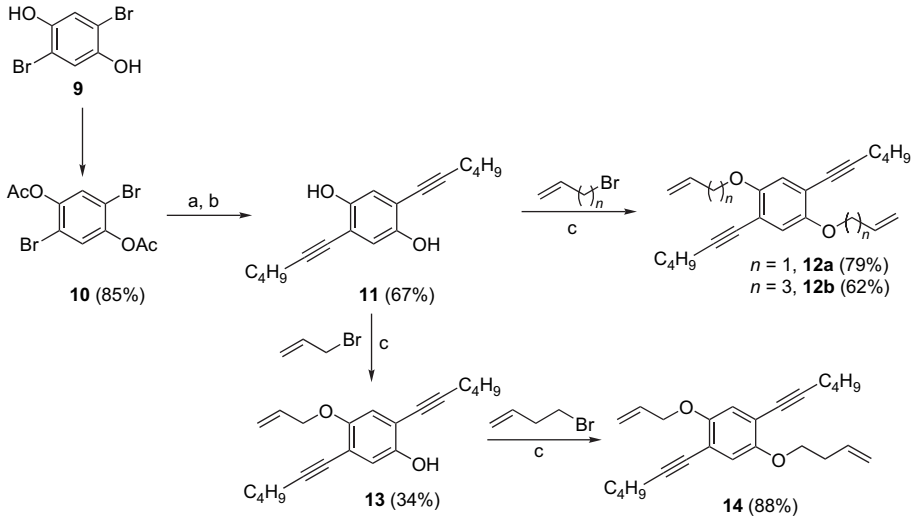


Scheme 1. (a) AcCl, Py, Et_2O; (b) 1-hexyne, $Pd(PPh_3)_2Cl_2$, CuI, DMF, Et_3N, 50 °C; (c) LiOH, THF/MeOH/H_2O, 0 °C; (d) K_2CO_3, DMF, rt.



Scheme 2. (a) $Pd(PPh_3)_2Cl_2$, CuI, toluene, Et_3N, rt; (b) LiOH, THF/MeOH/H_2O, 0 °C; (c) K_2CO_3, DMF, rt.

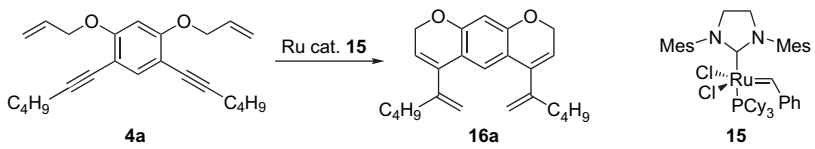


Scheme 3. (a) 1-Hexyne, $Pd(PPh_3)_2Cl_2$, CuI, DMF, Et_3N, 70 °C; (b) NaOH, THF/MeOH/H_2O, 0 °C; (c) K_2CO_3, DMF, rt.

to investigate the scope and cyclization patterns of this reaction. Some typical examples are summarized in Table 2.

From Table 2, it is obvious that a series of tricyclic compounds could be efficiently prepared from their corresponding precursors in moderate to good yields under the standard conditions, i.e., tricyclic compounds **16a**, **17a**, and **18a** were prepared in 76, 78, and 83% yields, respectively (entries 1, 4 and 7, Table 2). Tricyclic compounds **16b** and **17b** containing seven-membered rings were prepared in 88 and 57% yields (entries 2 and 5, Table 2). The synthesis of the tricyclic products with two different rings was demonstrated by the treatment of **6** and **14** with 5 mol % Ru catalyst **15**

Table 1. Double enyne RCM of **4a** under different reaction conditions



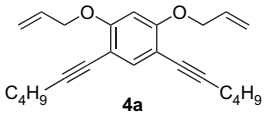
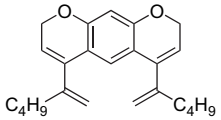
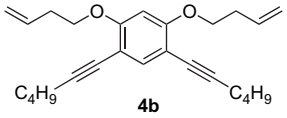
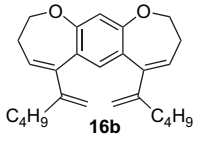
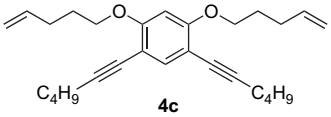
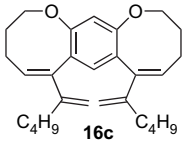
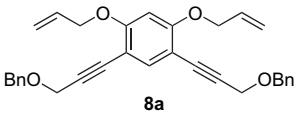
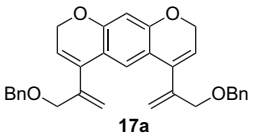
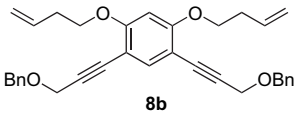
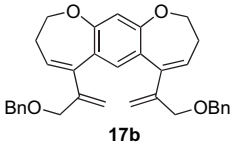
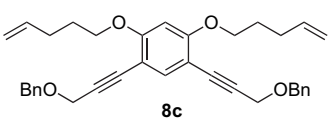
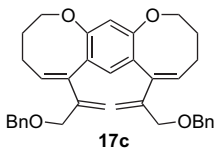
Entry	Solvent	Atmosphere	Temperature	Time (h)	Yield (%)
1	CH_2Cl_2	Ar	rt	8	30[a]
2	CH_2Cl_2	Ar	Reflux	8	76
3	CH_2Cl_2	Ethylene	Reflux	4	76
4	Toluene	Ar	80 °C	8	33[b]

[a] Not completed.
[b] Forty-four percent of monocyclic compound was formed.

to give tricyclic fused compounds **19** and **20** in 85 and 73% yield, respectively (entries 9 and 10, Table 2).

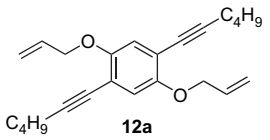
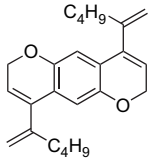
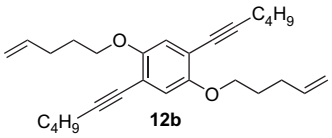
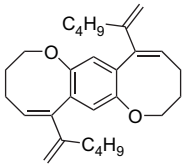
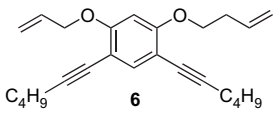
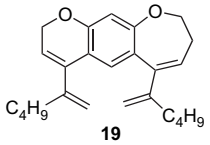
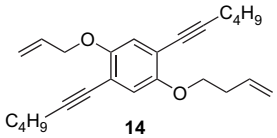
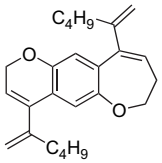
In general, synthesis of eight-membered cyclic compounds is difficult.[16] First, the reaction of substrate **4c** was conducted under the standard conditions, but did not go to completion. Probably due to the fact that the eight-membered ring formed may undergo ring-opening metathesis reaction in the presence of ethylene gas. So we changed the protecting atmosphere to argon, which led to a complete reaction smoothly when 10 mol % of Ru catalyst **15** was added in two portions (entries 3, 6, and 8, Table 2). Thus, it should be noted that the application of ethylene gas should be avoided. As reported by Mori,[17] two heteroatoms were needed to improve the eight-membered ring synthesis, and the monocyclic eight-membered rings containing single heteroatom were formed in low yield. But under the current conditions, eight-membered rings containing single heteroatom **16c**, **17c**, and **18b** were prepared in high yields.

Table 2. Double enyne RCM reaction of substrates

Entry	Substrates	Products	Yield (%)
1	 **4a**	 **16a**	76
2	 **4b**	 **16b**	88[a]
3	 **4c**	 **16c**	73[b]
4	 **8a**	 **17a**	78
5	 **8b**	 **17b**	57
6	 **8c**	 **17c**	49[b]

(*continued*)

Table 2. (*continued*)

Entry	Substrates	Products	Yield (%)
7	 **12a**	 **18a**	83
8	 **12b**	 **18b**	75[b]
9	 **6**	 **19**	85[a]
10	 **14**	 **20**	73[a]

[a] Conducted in toluene at 80 °C under ethylene.
[b] Ru catalyst **15** (10 mol %) was added in two portions (5 mol % each) under Ar.

In conclusion, we have developed an efficient synthesis of fused tricycles with a benzene core via intramolecular double enyne ring-closing metathesis. Due to the easy availability of the starting materials and the potential application of the products, this methodology will show its utility in organic synthesis. Further studies in this area are being conducted in our laboratory.

3. Experimental

3.1. Synthesis of starting materials

3.1.1. 1,5-Diacetoxy-2,4-diiodobenzene (2). To a solution of **1** (4.13 g, 11.5 mmol) and pyridine (2.70 g, 34.4 mmol) in CH_2Cl_2 (40 mL) was added acetyl chloride (2.70 g, 34.4 mmol) at 0 °C. The reaction was stirred at rt for 30 min, quenched with water, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) gave **2** (4.19 g, 82%) as a white solid, mp 85–86 °C (ethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 6.96 (s, 1H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 151.9, 147.4, 117.9, 87.9, 21.1; MS (ESI) *m/z* (%): 478.7 [M+Na$^+$]; IR (neat) ν (cm^{-1}): 1768, 1454, 1359, 1185. Anal. Calcd for $C_{10}H_8I_2O_4$: C, 26.93; H, 1.81. Found: C, 26.63; H, 2.07.

3.1.2. 2,4-Bis(hex-1′-ynyl)-1,5-dihydroxybenzene (3). Typical procedure A. To a solution of **2** (3.00 g, 6.8 mmol) in DMF (8 mL) were added sequentially Et_3N (8 mL), 1-hexyne (2.3 g, 28 mmol), $PdCl_2(PPh_3)_2$ (190 mg, 0.27 mmol), and CuI (129 mg, 0.68 mmol) under Ar. After being stirred at 50 °C under Ar for 19 h, the reaction mixture was quenched with water, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) gave the coupling product 2,4-bis(hex-1′-ynyl)-1,5-diacetoxybenzene **3′** (2.076 g, 87%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 6.86 (s, 1H), 2.39 (t, *J*=6.6 Hz, 4H), 2.29 (s, 6H), 1.60–1.39 (m, 8H), 0.93 (t, *J*=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 150.8, 136.7, 116.6, 116.0, 95.8, 74.3, 30.6, 21.8, 20.7, 19.1, 13.5; MS (EI) *m/z* (%): 354 (M$^+$, 3.5), 43 (100.0); IR (neat) ν (cm^{-1}): 2958, 2934, 2234, 1774, 1494. HRMS Calcd for $C_{22}H_{26}O_4Na$ [M+Na$^+$]: 377.1723. Found: 377.1729. To this product (1.46 g, 4.1 mmol) dissolved in a mixed solvent (MeOH/THF/H_2O=1:1:1, 50 mL) was added LiOH (300 mg, 12.5 mmol) at 0 °C and the resulting solution was stirred at this temperature for 80 min as monitored by TLC. The mixture was neutralized with aq HCl, extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) gave **3** (0.885 g, 80%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.52 (s, 1H), 5.92 (s, 2H), 2.45 (t, *J*=6.9 Hz, 4H), 1.62–1.56 (m, 4H), 1.54–1.40 (m, 4H), 0.95 (t, *J*=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 134.0, 103.1, 100.6, 96.7, 73.6, 30.8, 22.0, 19.2, 13.6; MS (EI) *m/z* (%): 270 (M$^+$, 100.0), 227 (94.8); IR (neat) ν (cm^{-1}): 3498, 2959, 1629, 1686, 1493. HRMS Calcd for $C_{18}H_{23}O_2$ [M+H$^+$]: 271.1693. Found: 271.1703.

3.1.3. 1,5-Bis(allyloxy)-2,4-bis(hex-1′-ynyl)benzene (4a). Typical procedure B. To a solution of **3** (62 mg, 0.23 mmol) in DMF (4 mL) were added K_2CO_3 (190 mg, 1.38 mmol) and allyl bromide (164 mg, 1.36 mmol). The reaction mixture was stirred at rt for 9 h as monitored by TLC, then quenched with water, extracted with ether, washed with brine, and dried over $MgSO_4$. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) gave **4a** (78 mg, 97%) as a white solid, mp 38 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.37 (s, 1H), 6.09–5.98 (m, 2H), 5.45 (dm, J=17.4 Hz, 2H), 5.28 (dm, J=10.5 Hz, 2H), 4.57 (dt, J_1=5.1 Hz, J_2=1.8 Hz, 4H), 2.43 (t, J=6.6 Hz, 4H), 1.61–1.44 (m, 8H), 0.93 (t, J=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 137.8, 132.8, 117.5, 106.4, 98.5, 93.3, 75.7, 69.6, 30.9, 21.9, 19.3, 13.9; MS (EI) *m/z* (%): 350 (M^+, 61.9), 309 (20.6), 41 (100.0); IR (neat) ν (cm^{-1}): 2958, 2931, 1604, 1498, 1406. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 81.94; H, 8.88.

The following compounds were prepared according to procedure B.

3.1.4. 1,5-Bis(but-3′-enyloxy)-2,4-di(hex-1′-ynyl)benzene (4b). The reaction of **3** (190 mg, 0.17 mmol), K_2CO_3 (580 mg, 4.20 mmol), and 3-butenyl bromide (570 mg, 4.22 mmol) in DMF (5 mL) afforded **4b** (158 mg, 59%) as a white solid after being stirred for 17 h at rt: mp 51–52 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.33 (s, 1H), 6.00–5.86 (m, 2H), 5.18 (dm, J=17.1 Hz, 2H), 5.10 (dm, J=10.8 Hz, 2H), 4.03 (t, J=6.9 Hz, 4H), 2.62–2.54 (m, 4H), 2.42 (t, J=6.6 Hz, 4H), 1.59–1.47 (m, 8H), 0.93 (t, J=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 137.5, 134.2, 117.2, 106.1, 97.8, 93.0, 75.7, 68.2, 33.6, 30.8, 21.9, 19.3, 13.6; MS (EI) *m/z* (%): 378 (M^+, 63.6), 55 (100.0); IR (neat) ν (cm^{-1}): 2957, 2930, 1606, 1500, 1415, 1309, 905. Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.18; H, 9.05.

3.1.5. 2,4-Bis(hex-1′-ynyl)-1,5-bis(pent-4′-enyloxy)benzene (4c). The reaction of **3** (162 mg, 0.60 mmol), K_2CO_3 (332 mg, 2.4 mmol), and 5-bromo-1-pentene (358 mg, 2.40 mmol) in DMF (5 mL) afforded **4c** (188 mg, 77%) as a white solid after being stirred for 12 h at rt: mp 34–35 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.32 (s, 1H), 5.93–5.80 (m, 2H), 5.08 (dm, J=17.1 Hz, 2H), 5.00 (dm, J=10.2 Hz, 2H), 4.00 (t, J=6.3 Hz, 4H), 2.42 (t, J=6.6 Hz, 4H), 2.28 (q, J=7.2 Hz, 4H), 1.97–1.87 (m, 4H), 1.60–1.45 (m, 8H), 0.94 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 137.8, 137.4, 115.2, 105.9, 97.5, 92.8, 75.8, 68.0, 30.9, 30.0, 28.3, 21.9, 19.3, 13.6; MS (EI) *m/z* (%): 406 (M^+, 28.4), 41 (100.0); IR (neat) ν (cm^{-1}): 2956, 2934, 1604, 1499. HRMS Calcd for $C_{28}H_{38}O_2Na^+$ [M+Na^+]: 429.2764. Found: 429.2765.

3.1.6. 5-(But-3′-enyloxy)-2,4-bis(hex-1′-ynyl)phenol (5). A mixture of **3** (300 mg, 1.11 mmol), K_2CO_3 (167 mg, 1.21 mmol), and 3-butenyl bromide (165 mg, 1.22 mmol) in DMF (3 mL) was stirred for 11 h, and then again 120 mg of 3-butenyl bromide was added. After 22 h, the reaction afforded **5** (119 mg, 33%), as an oil, and **3** (50 mg, 17% recovered). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 1H), 6.43 (s, 1H), 6.00–5.85 (m, 1H), 5.88 (s, 1H), 5.17 (dm, J=17.4 Hz, 1H), 5.10 (dm, J=10.2 Hz, 1H), 4.00 (t, J=6.6 Hz, 2H), 2.58 (q, J=6.6 Hz, 2H), 2.43 (q, J=7.2 Hz, 4H), 1.63–1.40 (m, 8H), 0.940 (t, J=7.2 Hz, 3H), 0.935 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 157.2, 135.6, 134.1, 117.1, 106.0, 102.3, 98.6, 96.6, 92.7, 75.6, 73.6, 67.9, 33.4, 30.8, 30.7, 21.9, 21.8, 19.22, 19.17, 13.6, 13.5; MS (EI) *m/z* (%): 324 (M^+, 74.5), 55 (100.0); IR (neat) ν (cm^{-1}): 3498, 2957, 2932, 2872, 1616, 1571, 1498. HRMS Calcd for $C_{22}H_{28}O_2$: 324.2089. Found: 324.2092.

3.1.7. 1-Allyloxy-5-(but-3′-enyloxy)-2,4-bis(hex-1′-ynyl)-benzene (6). The reaction of **5** (110 mg, 0.34 mmol), K_2CO_3 (187 mg, 1.36 mmol), and allyl bromide (190 mg, 1.57 mmol) in DMF (3 mL) afforded **6** (103 mg, 81%) as a white solid after being stirred for 4.3 h at rt: mp 53–54 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36, (s, 1H), 6.35 (s, 1H), 6.11–5.86 (m, 2H), 5.46 (dm, J=17.4 Hz, 1H), 5.29 (dm, J=10.5 Hz, 1H), 5.19 (dm, J=17.1 Hz, 1H), 5.11 (dm, J=10.2 Hz, 1H), 4.58 (dt, J_1=4.8 Hz, J_2=1.2 Hz, 2H), 4.02 (t, J=6.6 Hz, 2H), 2.62–2.54 (m, 2H), 2.43 (t, J=6.9 Hz, 2H), 2.42 (t, J=6.9 Hz, 2H), 1.62–1.42 (m, 8H), 0.93 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 159.5, 137.6, 134.1, 132.8, 117.4, 117.2, 106.2, 106.1, 98.1, 93.1, 93.0, 75.7, 75.6, 69.5, 68.2, 33.6, 30.9, 30.8, 21.90, 21.86, 19.30, 19.26, 13.6; MS (EI) *m/z* (%): 364 (M^+, 100.0); IR (neat) ν (cm^{-1}): 2957, 2933, 1408, 1308, 1237. Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85. Found: C, 82.13; H, 8.71.

3.1.8. 2,4-Bis(3′-benzyloxyprop-1′-ynyl)-1,5-dihydroxy-benzene (7). This compound was prepared according to procedure A. The reaction of **2** (3.00 g, 6.76 mmol), Et_3N (10 mL), 3-benzyloxyprop-1-yne (4.00 g, 27.4 mmol), $PdCl_2(PPh_3)_2$ (95 mg, 0.14 mmol), and CuI (52 mg, 0.27 mmol) in toluene (15 mL) afforded the coupling product 2,4-bis(3′-benzyloxypropyl-1′-ynyl)-1,5-diacetoxybenzene **7′** (2.46 g, 75%) as an oil after being stirred at rt for 12 h under Ar. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.40–7.26 (m, 10H), 6.98 (s, 1H), 4.65 (s, 4H), 4.39 (s, 4H), 2.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 151.8, 137.1, 136.9, 128.4, 128.0, 127.9, 117.1, 114.8, 90.6, 80.0, 71.4, 57.5, 20.7; MS (ESI) *m/z* (%): 483.2 (M+H^+); IR (neat) ν (cm^{-1}): 2855, 1774, 1493. HRMS Calcd for $C_{30}H_{26}O_6Na^+$ [M+Na^+]: 505.1622. Found: 505.1622. The reaction of this product **7′** (0.929 g, 1.93 mmol) and LiOH (185 mg, 7.71 mmol) in the mixed solvent (MeOH/THF/H_2O=1:1:1, 20 mL) afforded **7** (0.497 g, 65%) as yellow oil after being stirred at 0 °C for 30 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.27 (m, 11H), 6.53 (s, 1H), 6.29–6.25 (br s, 2H), 4.66 (s, 4H), 4.43 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 137.0, 135.6, 128.5, 128.13, 128.06, 102.0, 101.6, 91.1, 79.9, 71.9, 57.8; MS (EI) *m/z* (%): 398 (M^+, 7.73), 91 (100.0); IR (neat) ν (cm^{-1}): 3470, 2853, 1625, 1454. HRMS Calcd for $C_{26}H_{22}O_4Na^+$ [M+Na^+]: 421.1410. Found: 421.1406.

The following compounds were prepared according to procedure B.

3.1.9. 1,5-Bis(allyloxy)-2,4-bis(3′-benzyloxyprop-1′-ynyl)-benzene (8a). The reaction of **7** (67 mg, 0.17 mmol), K_2CO_3 (139 mg, 1.01 mmol), and allyl bromide (122 mg,

1.01 mmol) in DMF (3 mL) afforded **8a** (63 mg, 78%) as a yellow oil after being stirred for 5 h at rt. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.44–7.31 (m, 10H), 6.42 (s, 1H), 6.13–5.99 (m, 2H), 5.50 (dm, J=17.4 Hz, 2H), 5.33 (dm, J=10.5 Hz, 2H), 4.72 (s, 4H), 4.62 (dt, J_1=4.8 Hz, J_2=1.2 Hz, 4H), 4.45 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 138.1, 137.5, 132.4, 128.3, 128.2, 127.7, 117.9, 104.9, 97.8, 88.1, 81.9, 71.2, 69.5, 57.9; MS (ESI) *m/z* (%):501.2 [M+Na$^+$]; IR (neat) ν (cm^{-1}): 2852, 2226, 1604, 1562, 1498, 1072. Anal. Calcd for $C_{32}H_{30}O_4Na^+$ [M+Na$^+$]: 501.2036. Found: 501.2028.

3.1.10. 1,5-Bis(but-3′-enyloxy)-2,4-bis(3′-benzyloxyprop-1′-ynyl)benzene (8b). The reaction of **7** (294 mg, 0.79 mmol), K_2CO_3 (650 mg, 4.71 mmol), and 3-butenyl bromide (424 mg, 3.14 mmol) in DMF (5 mL) afforded **8b** (186 mg, 49%) as a yellow oil after being stirred for 9 h at rt. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.36–7.20 (m, 10H), 6.32 (s, 1H), 5.94–5.78 (m, 2H), 5.12 (dm, J=17.1 Hz, 2H), 5.04 (dm, J=10.2 Hz, 2H), 4.63 (s, 4H), 4.35 (s, 4H), 4.00 (t, J=6.6 Hz, 4H), 2.54 (q, J=6.6 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 138.0, 137.6, 133.9, 128.3, 128.1, 127.7, 117.4, 104.7, 97.1, 87.9, 81.9, 71.1, 68.2, 57.9, 33.5; MS (ESI) *m/z* (%): 529.1 [M+Na$^+$]; IR (neat) ν (cm^{-1}): 2926, 2854, 2222, 1604, 1499, 1027. HRMS Calcd for $C_{34}H_{34}O_4Na^+$ [M+Na$^+$]: 529.2349. Found: 529.2349.

3.1.11. 2,4-Bis(3′-benzyloxyprop-1′-ynyl)-1,5-bis(pent-4′-enyloxy)benzene (8c). The reaction of **7** (313 mg, 0.79 mmol), K_2CO_3 (625 mg, 4.53 mmol), and 5-bromo-1-pentene (449 mg, 3.01 mmol) in DMF (5 mL) afforded **8c** (204 mg, 49%) as a white solid after being stirred for 10 h at rt: mp 51–52 °C (ethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.42–7.27 (m, 10H), 6.37 (s, 1H), 5.90–5.76 (m, 2H), 5.10–4.96 (m, 4H), 4.70 (s, 4H), 4.42 (s, 4H), 4.04 (t, J=6.3 Hz, 4H), 2.32–2.21 (m, 4H), 1.99–1.90 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 138.1, 137.6, 137.5, 128.4, 128.2, 127.8, 115.1, 104.5, 97.0, 87.8, 82.1, 71.1, 68.0, 57.9, 29.9, 28.2; MS (ESI) *m/z* (%): 557.1 [M+Na$^+$]; IR (neat) ν (cm^{-1}): 2942, 2227, 1604, 1500, 1070. HRMS Calcd for $C_{36}H_{38}O_4Na^+$ [M+Na$^+$]: 557.2662. Found: 557.2671.

3.1.12. 1,4-Diacetoxy-2,5-dibromobenzene (10). To a solution of **9** (7.00 g, 26 mmol) in CH_2Cl_2 (30 mL) and Et_2O (80 mL) were added sequentially Et_3N (10.50 g, 104 mmol) at −40 °C and acetyl chloride (8.20 g, 104 mmol) at <0 °C. After being stirred at rt for 90 min, the reaction mixture was quenched with water and the white solid was collected by filtration. The organic layer was washed with brine. Evaporation of the solvent afforded additional solid, which was washed with Et_2O (10 mL). In this way, **10** (7.85 g, 85%) was obtained as a white solid: mp 153–154 °C (acetone). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 2H), 2.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 146.3, 127.7, 115.3, 20.6; MS (EI) *m/z* (%): 354 (M$^+$, 2×^{81}Br, 0.17), 352 (M$^+$, 1×^{81}Br, 1×^{79}Br, 0.38), 350 (M$^+$, 2×^{79}Br, 0.26), 43 (100.0); IR (neat) ν (cm^{-1}): 1759, 1475, 1203. Anal. Calcd for $C_{10}H_8Br_2O_4$: C, 34.12; H, 2.29. Found: C, 34.63; H, 2.55.

3.1.13. 2,5-Bis(hex-1′-ynyl)-1,4-dihydroxybenzene (11). This compound was prepared according to procedure A except that NaOH was used instead of LiOH. The reaction of **10** (5.00 g, 14.2 mmol), 1-hexyne (4.66 g, 56.8 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol), CuI (54 mg, 0.28 mmol), and Et_3N (10 mL) in DMF (10 mL) afforded the coupling product 2,5-bis(hex-1′-ynyl)-1,4-diacetoxybenzene **11′** (4.20 g, 84%) as a white solid after being stirred at 80 °C for 24 h under Ar: mp 54–55 °C (ethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H), 2.40 (t, J=6.3 Hz, 4H), 2.28 (s, 6H), 1.60–1.39 (m, 8H), 0.93 (t, J=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 148.6, 126.0, 118.3, 97.4, 74.7, 30.4, 21.7, 20.5, 19.0, 13.4; MS (EI) *m/z* (%): 354 (M$^+$, 9.5), 270 (100.0); IR (neat) ν (cm^{-1}): 2958, 2229, 1767, 1497, 1198. Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.32; H, 7.38. The reaction of this product **11′** (550 mg, 1.55 mmol) and NaOH (248 mg, 6.2 mmol) in a mixed solvent (MeOH/THF/H_2O=1:1:1, 50 mL) afforded **11** (337 mg, 80%) as a white solid after being stirred at 0 °C for 20 min: mp 104–105 °C (ethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.43 (s, 2H), 2.47 (t, J=6.9 Hz, 4H), 1.64–1.55 (m, 4H), 1.51–1.40 (m, 4H), 0.95 (t, J=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 116.2, 111.2, 99.0, 74.5, 30.6, 22.0, 19.3, 13.6; MS (EI) *m/z* (%): 270 (M$^+$, 100.0), 227 (92.6); IR (neat) ν (cm^{-1}): 3281, 2948, 2926, 2222, 1422, 1191. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.72; H, 8.01.

The following compounds were prepared according to procedure B.

3.1.14. 1,4-Bis(allyloxy)-2,5-di(hex-1′-ynyl)benzene (12a). The reaction of **11** (70 mg, 0.26 mmol), K_2CO_3 (143 mg, 1.04 mmol), and allyl bromide (125 mg, 1.03 mmol) in DMF (3 mL) afforded **12a** (71 mg, 79%) as a yellow oil after being stirred for 9 h at rt. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.11–5.97 (m, 2H), 5.43 (dm, J=17.4 Hz, 2H), 5.25 (dm, J=10.5 Hz, 2H), 4.57–4.48 (m, 4H), 2.45 (t, J=6.0 Hz, 4H), 1.64–1.40 (m, 8H), 0.93 (t, J=8.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 133.1, 117.6, 117.1, 114.0, 95.9, 76.5, 70.0, 30.7, 21.9, 19.4, 13.6; MS (EI) *m/z* (%): 350 (M$^+$, 64.5), 41 (100.0); IR (neat) ν (cm^{-1}): 2957, 2929, 1500, 1406, 1205. HMRS Calcd for $C_{24}H_{30}O_2$: 350.2246. Found: 350.2242.

3.1.15. 2,5-Bis(hex-1′-ynyl)-1,4-bis(pent-4′-enyloxy)-benzene (12b). The reaction of **11** (177 mg, 0.66 mmol), K_2CO_3 (546 mg, 3.96 mmol), and 5-bromo-1-pentene (390 mg, 2.62 mmol) in DMF (5 mL) afforded **12b** (166 mg, 62%) as a white solid after being stirred for 23 h at rt: mp 35–36 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H), 5.93–5.78 (m, 2H), 5.06 (dm, J=17.4 Hz, 2H), 4.99 (dm, J=10.2 Hz, 2H), 3.95 (t, J=6.3 Hz, 4H), 2.46 (t, J=6.3 Hz, 4H), 2.27 (q, J=7.0 Hz, 4H), 1.93–1.83 (m, 4H), 1.65–1.46 (m, 8H), 0.94 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 137.2, 117.2, 115.0, 113.8, 95.6, 76.7, 68.6, 30.8, 30.1, 28.4, 21.9, 19.4, 13.6; MS (EI) *m/z* (%): 406 (M$^+$, 11.3), 41 (100.0); IR (neat) ν (cm^{-1}): 2933, 2222, 1634, 1500, 1410, 1204. Anal. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42. Found: C, 82.76; H, 9.37.

3.1.16. 4-Allyloxy-2,5-bis(hex-1′-ynyl)phenol (13). The reaction of **11** (310 mg, 1.15 mmol), K_2CO_3 (169 mg,

1.22 mmol), and allyl bromide (147 mg, 1.21 mmol) in DMF (5 mL) afforded **12a** (115 mg, 29%), **13** (120 mg, 34%), and **11** (114 mg, 37% recovered) after being stirred for 19 h at rt. Compound **13**: mp 41–42 °C (ethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.76 (s, 1H), 6.11–5.98 (m, 1H), 5.44 (dm, J=17.1 Hz, 1H), 5.41 (s, 1H), 5.26 (dm, J=10.2 Hz, 1 Hz), 4.50 (d, J=4.8 Hz, 2H), 2.47 (q, J=7.2 Hz, 4H), 1.66–1.43 (m, 8H), 0.95 (t, J=6.9 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 150.5, 133.2, 118.8, 117.2, 115.6, 115.5, 109.7, 98.8, 96.2, 76.3, 74.6, 70.3, 30.71, 30.69, 22.1, 21.9, 19.4, 19.3, 13.62, 13.59; MS (EI) m/z (%): 310 (M^+, 39.6), 41 (100.0); IR (neat) ν (cm^{-1}): 3514, 2958, 2931, 2229, 1494. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.42; H, 8.73.

3.1.17. 1-Allyloxy-4-(but-3′-enyloxy)-2,5-bis(hex-1′-ynyl)-benzene (14). The reaction of **13** (120 mg, 0.39 mmol), K_2CO_3 (215 mg, 1.56 mmol), and 3-butenyl bromide (210 mg, 1.56 mmol) in DMF (3 mL) afforded **14** (124 mg, 88%) as an oil after being stirred for 10.5 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.85 (s, 1H), 6.11–5.85 (m, 2H), 5.44 (dm, J=17.1 Hz, 1H), 5.26 (dm, J=10.8 Hz, 1H), 5.16 (dm, J=17.1 Hz, 1H), 5.09 (dm, J=10.5 Hz, 1H), 4.52 (d, J=5.1 Hz, 2H), 3.99 (t, J=6.9 Hz, 2H), 2.55 (q, J=6.8 Hz, 2H), 2.46 (t, J=6.6 Hz, 2H), 2.45 (t, J=6.6 Hz, 2H), 1.65–1.45 (m, 8H), 0.94 (t, J=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 153.0, 134.5, 133.2, 117.6, 117.5, 117.1, 116.9, 114.06, 113.97, 95.9, 95.8, 77.0, 76.6 (overlap with the signal of $CDCl_3$), 70.1, 68.8, 33.8, 30.8, 30.7, 22.0, 21.9, 19.44, 19.41, 13.6; MS (EI) m/z (%): 364 (M^+, 18.7), 55 (100.0); IR (neat) ν (cm^{-1}): 2957, 2932, 2222, 1500, 1405. HRMS Calcd for $C_{25}H_{32}O_2Na^+$ [M+Na^+]: 387.2295. Found: 387.2302.

3.2. Intramolecular double ring-closing enyne metathesis

3.2.1. 4,6-Bis(1′-butylethenyl)-2,8-dihydrobenzo-[1,2-*b*:5,4-*b*′]dipyran (16a). Typical procedure C. To a solution of **4a** (63 mg, 0.18 mmol) in CH_2Cl_2 (6 mL) was added the catalyst **15** (8 mg, 0.009 mmol). After being refluxed with stirring under Ar for 8 h, the reaction was complete (monitored by TLC). Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=100:1) gave **16a** (48 mg, 76%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.38 (s, 1H), 5.51 (t, J=4.2 Hz, 2H), 5.11–5.07 (m, 2H), 5.01–4.98 (m, 2H), 4.71 (d, J=3.9 Hz, 4H), 2.20 (t, J=6.6 Hz, 4H), 1.41–1.21 (m, 8H), 0.88 (t, J=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 147.1, 137.6, 122.6, 116.5, 115.6, 114.3, 104.2, 65.4, 35.5, 30.2, 22.3, 13.9; MS (EI) m/z (%): 350 (M^+, 100.0), 307 (93.7), 293 (64.7); IR (neat) ν (cm^{-1}): 2957, 2930, 1619, 1490, 1159. HRMS Calcd for $C_{24}H_{30}O_2$: 350.2246. Found: 350.2242.

The following compounds were prepared according to procedure C.

3.2.2. 5,7-Bis(1′-butylethenyl)-2,3,9,10-tetrahydro-1,11-dioxabenzo[1,2-*b*:5,4-*b*′]dicycloheptene (16b). A solution of **4b** (40 mg, 0.11 mmol) and the catalyst **15** (10 mg, 0.012 mmol) in toluene (10 mL) was stirred at 80 °C for 13 h under ethylene. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=50:1) gave **16b** (35 mg, 88%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.66 (s, 1H), 5.94 (t, J=5.7 Hz, 2H), 4.93–4.90 (m, 2H), 4.86–4.84 (m, 2H), 4.30 (t, J=6.0 Hz, 4H), 2.36 (q, J=5.8 Hz, 4H), 2.07 (t, J=6.9 Hz, 4H), 1.34–1.16 (m, 8H), 0.80 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 151.0, 141.6, 132.9, 125.4, 125.3, 114.2, 113.5, 75.9, 35.0, 30.2, 30.1, 22.3, 14.0; MS (EI) m/z (%): 378 (M^+, 87.2), 335 (95.6), 321 (100.0); IR (neat) ν (cm^{-1}): 2958, 2931, 1602, 1493, 1125. HRMS Calcd for $C_{26}H_{34}O_2$: 378.2559. Found: 378.2546.

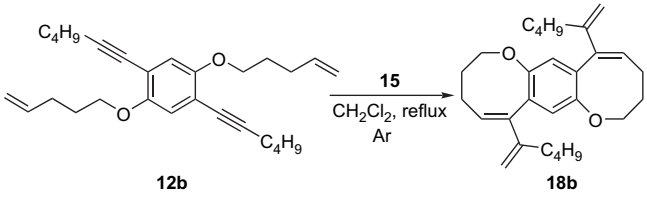
3.2.3. 6,8-Bis(1′-butylethenyl)-2,3,4,10,11,12-hexahydro-1,13-dioxabenzo[1,2-*b*:5,4-*b*′]-dicyclooctene (16c). A solution of **4c** (55 mg, 0.14 mmol) and the catalyst **15** (6 mg, 0.007 mmol) in CH_2Cl_2 (7 mL) was refluxed for 17 h under Ar, then extra amount of **15** (9 mg, 0.11 mmol) was added, which was followed by stirring under refluxing for another 10 h. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=100:1) gave **16c** (40 mg, 73%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 1H), 6.80 (s, 1H), 6.00 (t, J=7.8 Hz, 2H), 4.92 (s, 2H), 4.76 (d, J=1.5 Hz, 2H), 4.22–4.10 (br s, 4H), 2.22 (t, J=7.5 Hz, 4H), 2.16–2.00 (m, 4H), 1.74–1.64 (m, 4H), 1.47–1.39 (m, 4H), 1.37–1.25 (m, 4H), 0.88 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 149.5, 138.4, 132.1, 127.0, 126.6, 115.0, 113.8, 73.8, 33.9, 30.3, 26.8, 26.5, 22.4, 13.9; MS (EI) m/z (%): 406 (M^+, 21.8), 363 (34.7), 84 (100.0); IR (neat) ν (cm^{-1}): 2954, 2931, 1601, 1492, 1148. HRMS Calcd for $C_{28}H_{39}O_2$ [M+H^+]: 407.2945. Found: 407.2959.

3.2.4. 4,6-Bis(1′-benzyloxymethylethenyl)-2,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dipyran (17a). A solution of **8a** (55 mg, 0.12 mmol) and the catalyst **15** (6 mg, 0.007 mmol) in CH_2Cl_2 (5 mL) was refluxed for 6 h under Ar. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=10:1) gave **17a** (43 mg, 78%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.21 (m, 10H), 6.97 (s, 1H), 6.43 (s, 1H), 5.64 (t, J=3.6 Hz, 2H), 5.75 (s, 2H), 5.22 (s, 2H), 4.73 (d, J=3.9 Hz, 4H), 4.53 (s, 4H), 4.09 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 142.7, 138.1, 134.9, 128.3, 127.5, 122.0, 117.0, 116.4, 116.3, 104.4, 72.1, 71.8, 65.3; MS (MALDI) m/z (%): 478.1 (M^+); IR (neat) ν (cm^{-1}): 1619, 1493, 1159. HRMS Calcd for $C_{32}H_{30}O_4Na^+$ [M+Na^+]: 501.2036. Found: 501.2054.

3.2.5. 5,7-Bis(1′-benzyloxymethylethenyl)-2,3,9,10-tetrahydro-1,11-dioxabenzo-[1,2-*b*:5,4-*b*′] dicycloheptene (17b). A solution of **8b** (70 mg, 0.14 mmol) and the catalyst **15** (6 mg, 0.006 mmol) in CH_2Cl_2 (5 mL) was refluxed for 12 h under Ar. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=10:1) gave **17b** (40 mg, 57%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.18 (m, 10H), 7.07 (s, 1H), 6.72 (s, 1H), 6.09 (t, J=6.6 Hz, 2H), 5.26 (s, 2H), 5.06 (s, 2H), 4.44 (s, 4H), 4.33 (t, J=6.0 Hz, 4H), 4.03 (s, 4H), 2.34 (q, J=6.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 146.1, 139.0, 138.3, 132.0, 128.3, 127.6, 127.5, 126.7, 125.6, 115.7, 114.9, 76.5, 72.0, 71.7, 29.7; MS (ESI) m/z (%): 524.1 (M+NH_4^+); IR (neat) ν (cm^{-1}): 1605, 1499, 1453, 1123, 1092. Anal. Calcd for $C_{34}H_{34}O_4Na^+$ [M+Na^+]: 529.2349. Found: 529.2346.

3.2.6. 6,8-Bis(1′-benzyloxymethylethenyl)-2,3,4,10,11,12-hexahydro-1,13-dioxabenzo-[1,2-*b*:5,4-*b*′]dicyclooctene (17c). A solution of **8c** (76 mg, 0.14 mmol) and the catalyst **15** (7 mg, 0.008 mmol) in CH_2Cl_2 (5 mL) was refluxed for 17 h under Ar. Then extra amount of **15** (7 mg, 0.008 mmol) was added, which was followed by stirring under reflux for another 4 h. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=10:1) gave **17c** (37 mg, 49%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.21 (m, 10H), 6.92 (s, 1H), 6.83 (s, 1H), 6.08 (t, J=7.8 Hz, 2H), 5.25 (s, 2H), 4.99 (s, 2H), 4.52 (s, 4H), 4.22 (s, 8H), 2.19–2.04 (br s, 4H), 1.80–1.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 145.2, 138.3, 136.3, 132.1, 128.3, 128.2, 127.7, 127.5, 125.3, 116.1, 115.0, 73.4, 71.9, 71.5, 26.6, 26.3; MS (ESI) m/z (%): 552.1 ($M+NH_4^+$); IR (neat) ν (cm^{-1}): 1603, 1493, 1454, 1078. Anal. Calcd for $C_{36}H_{38}O_4Na^+$ [$M+Na^+$]: 557.2662. Found: 557.2661.

3.2.7. 4,9-Bis(1′-butylethenyl)-2,7-dihydrobenzo[1,2-*b*:4,5-*b*′]dipyran (18a). A solution of **12a** (84 mg, 0.24 mmol) and the catalyst **15** (11 mg, 0.013 mmol) in CH_2Cl_2 (8 mL) was refluxed for 6 h under ethylene. Evaporation and flash column chromatography on silica gel (petroleum ether) gave **18a** (70 mg, 83%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (s, 2H), 5.67 (t, J=3.6 Hz, 2H), 5.12–5.09 (m, 2H), 5.02–4.99 (m, 2H), 4.66 (d, J=3.9 Hz, 4H), 2.24 (t, J=6.9 Hz, 4H), 1.41–1.21 (m, 8H), 0.88 (t, J=6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 146.7, 137.6, 123.5, 119.0, 114.7, 112.7, 65.1, 35.5, 30.2, 22.2, 13.9; MS (EI) m/z (%): 350 (M^+, 61.8), 307 (100.0), 293 (54.6); IR (neat) ν (cm^{-1}): 2957, 2929, 1629, 1490, 1421, 1183, 1075. HRMS Calcd for $C_{24}H_{31}O_2^+$ [$M+H^+$]: 351.2319. Found: 351.1317.



12b 18b

3.2.8. 6,13-Bis(1′-butylethenyl)-2,3,4,9,10,11-hexahydro-1,8-dioxabenzo[1,2-*b*:4,5-*b*′]-dicyclooctene (18b). A solution of **12b** (60 mg, 0.14 mmol) and the catalyst **15** (6 mg, 0.007 mmol) in CH_2Cl_2 (7 mL) was refluxed for 10 h under Ar. Then extra amount of **15** (6 mg, 0.07 mmol) was added, which was followed by stirring under reflux for another 12 h. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=100:1) gave **18b** (45 mg, 75%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 2H), 6.04 (t, J=8.4 Hz, 2H), 4.95 (s, 2H), 4.83 (d, J=2.1 Hz, 2H), 4.20–4.01 (br s, 4H), 2.25 (t, J=7.5 Hz, 4H), 2.08 (t, J=4.8 Hz, 4H), 1.72–1.62 (m, 4H), 1.51–1.40 (m, 4H), 1.39–1.25 (m, 4H), 0.89 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 149.5, 138.0, 132.6, 127.6, 123.3, 113.9, 74.5, 34.0, 30.4, 26.73, 26.67, 22.5, 13.9; MS (EI) m/z (%): 406 (M^+, 15.0), 349 (42.2), 84 (100.0); IR (neat) ν (cm^{-1}): 2931, 2858, 1492, 1038. HRMS Calcd for $C_{28}H_{38}O_2$: 406.2872. Found: 406.2873.

3.2.9. 4,6-Bis(1′-butylethenyl)-2,8,9-trihydro-1,10-dioxacyclohepta[*b*]naphthalene (19). A solution of **6** (79 mg, 0.22 mmol) and the catalyst **15** (9 mg, 0.011 mmol) in toluene (7 mL) was stirred at 80 °C for 12 h under ethylene. Evaporation and flash column chromatography on silica gel (petroleum ether/ethyl ether=40:1) gave **19** (67 mg, 85%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.55 (s, 1H), 5.98 (t, J=6.3 Hz, 1H), 5.55 (t, J=3.6 Hz, 1H), 5.08–4.93 (m, 4H), 4.74 (d, J=3.6 Hz, 2H), 4.35 (t, J=6.0 Hz, 2H), 2.41 (q, J=6.0 Hz, 2H), 2.22–2.12 (m, 4H), 1.41–1.21 (m, 8H), 0.87 (t, J=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 154.5, 151.0, 147.1, 141.5, 137.5, 127.6, 124.9, 123.4, 118.3, 116.6, 114.3, 113.5, 109.1, 76.2, 65.4, 35.4, 34.9, 30.22, 30.17, 30.0, 22.33, 22.27, 14.0, 13.9; MS (EI) m/z (%): 364 (M^+, 32.0), 321 (27.3), 84 (100.0); IR (neat) ν (cm^{-1}): 2956, 2930, 1610, 1492, 1160, 1138. HRMS Calcd for $C_{25}H_{32}O_2$: 364.2402. Found: 364.2405.

3.2.10. 4,10-Bis(1′-butylethenyl)-2,7,8-trihydro-1,6-dioxacyclohepta[*b*]naphthalene (20). A solution of **14** (90 mg, 0.25 mmol) and the catalyst **15** (11 mg, 0.013 mmol) in toluene (7 mL) was stirred at 80 °C for 7 h under ethylene. Evaporation and flash column chromatography on silica gel (petroleum ether) gave **20** (66 mg, 73%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.71 (s, 1H), 6.09 (t, J=6.0 Hz, 1H), 5.66 (t, J=3.6 Hz, 1H), 5.11 (m, 1H), 5.05–4.97 (m, 3H), 4.70 (d, J=3.9 Hz, 2H), 4.32 (t, J=6.3 Hz, 2H), 2.37 (q, J=6.0 Hz, 2H), 2.28–2.16 (m, 4H), 1.43–1.20 (m, 8H), 0.88 (t, J=7.2 Hz, 3H), 0.87 (t, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 150.1, 149.9, 146.7, 141.7, 137.5, 131.8, 126.3, 122.9, 118.9, 118.1, 117.2, 114.6, 114.1, 76.6, 65.2, 35.5, 34.8, 30.22, 30.16, 29.6, 22.3, 22.2, 13.94, 13.91; MS (EI) m/z (%): 364 (M^+, 78.3), 55 (100.0); IR (neat) ν (cm^{-1}): 2956, 2930, 2860, 1620, 1490, 1410, 1180. Anal. Calcd for $C_{25}H_{32}O_2Na^+$ [$M+Na^+$]: 387.2295. Found: 387.2302.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.11.016.

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