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NEW APPROACH TO CYCLOPHANES CONTAINING ETHYLENEOXY BRIDGE BY GLASER–EGLINTON COUPLING†

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†This paper is dedicated to Prof. Isao Kuwajima on the occasion of his 77th birthday.

Abstract – Three strategies have been explored to generate cyclophane derivatives. In this regard, we identified alkyne metathesis, Diels–Alder reaction, and Glaser–Eglinton coupling as key steps. To this end, cyclophane derivatives containing ethyleneoxy bridge were successfully synthesized in four steps involving Glaser–Eglinton coupling and catalytic hydrogenation sequence.

Among macrocycles, crown ethers play a critical role in molecular recognition,[1-7] metal ion transportation,[8] and also in drug design.[9,10] Synthesis of cyclophanes containing crown ether moiety is a difficult task because the synthetic processes leads to the formation of oligomers and the required products are formed in low yield.[11,12] Among other macrocycles, cyclophane[13-21] synthesis is of great interest because of the presence of aromatic rings that are linked together by aliphatic chains in a cyclic manner. Due to this structural sophistication, cyclophanes with a defined cavity size is useful in encapsulating and also stabilizing selective guest molecules. For this reason, larger cyclophanes provide a cavity fit for complex metal ions, or they can accommodate bulky guest molecules. To this end, design of new synthetic methods to cyclophanes of varying cavity size and shape is an important exercise. Moreover, introducing diverse functional groups or hetero atoms at an appropriate site(s) of the cyclophane moiety can bring structural variations desirable for molecular recognition. In connection with a major program aimed at designing new routes to cyclophanes,[22-27] we have shown that the crown containing compound **1** is useful to generate the diene **2** by cross-enyne metathesis sequence (**Figure 1**). Later the diene **2** was found to be useful starting material to various cyclophane derivatives via the Diels–

Alder (DA) strategy.[28,29] Here, we identified *o*-xylylene intermediate **3** containing crown ether moiety and the dialkyne building block **4** for further synthetic exploration. In this short paper, we report our results in this direction.

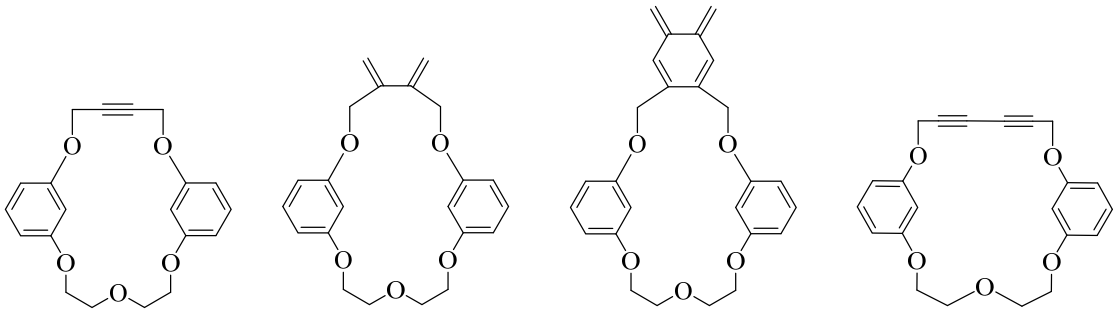


Figure 1. Useful crown containing building blocks

To design functionalized cyclophanes, we conceived three different strategies. The first one involves alkyne metathesis of **6** and the second one deals with the DA reaction of the *o*-xylylene intermediate such as **3** (**Figure 2**). The third route relies on Glaser–Eglinton coupling[30] reaction of dialkyne **6** to generate the cyclophane derivatives **4**.

Alkyne metathesis[31-38] is a valuable strategy to prepare macrocycles. To explore new routes to cyclophane derivatives, initially we attempted the alkyne metathesis of **8** to assemble macrocyclic compound **1**. In this regard, bisphenol **5** was reacted with propargyl bromide under K_2CO_3/acetone reflux condition to generate the dipropargylated compound **6** in 86% yield (**Scheme 1**). Then, the acidic hydrogens present on terminal alkyne portion of **6** were replaced with methyl groups by using *n*-BuLi/MeI/THF conditions to generate the dimethyl compound **8** in 68% yield.

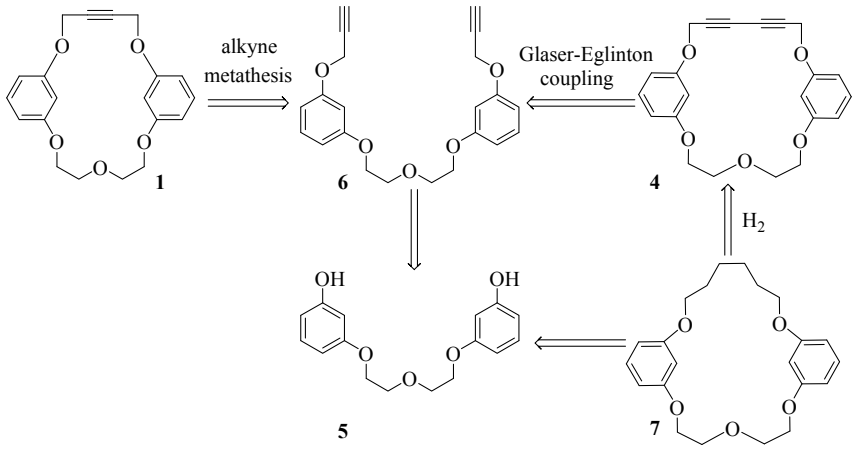
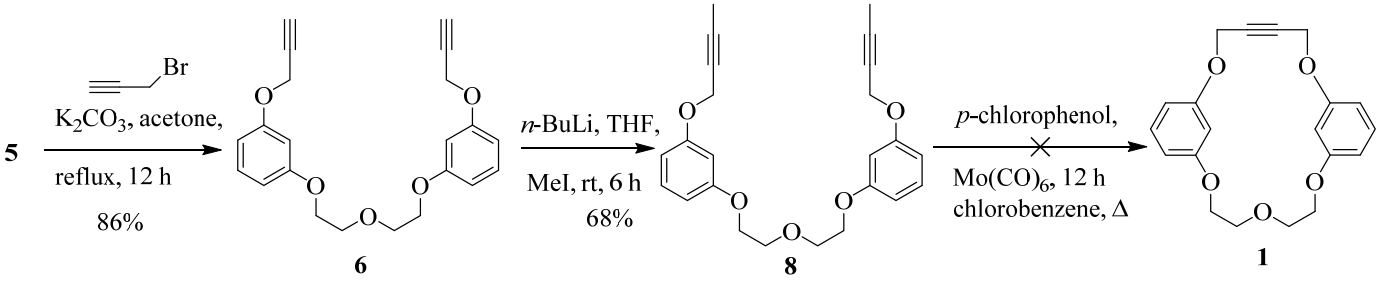


Figure 2. Retrosynthetic analysis to *meta*-cyclophane derivative **7**

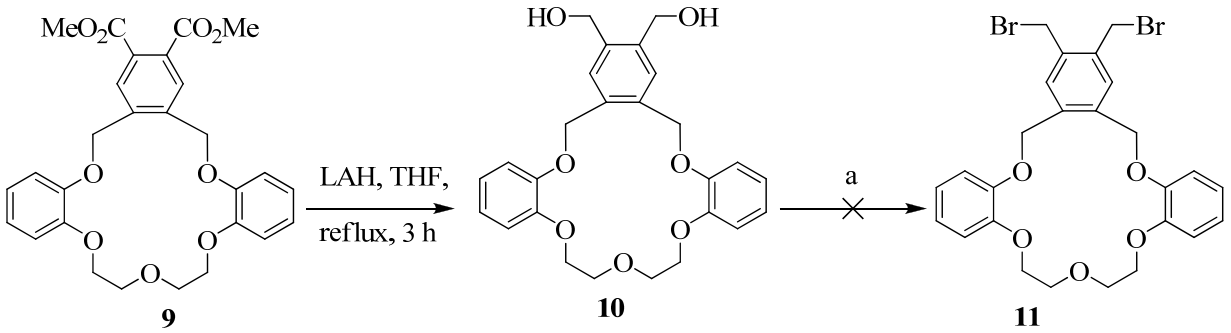
Next, the diacetylene derivative **8** was subjected to alkyne metathesis in the presence of homogeneous catalyst such as $Mo(CO)_6$/4-chlorophenol in refluxing chlorobenzene for 12 h. However, our attempts to

generate the corresponding metathesis product **1** were unsuccessful, and the starting material **8** was recovered.



Scheme 1. Alkyne metathesis approach towards to macrocycle **1**

Another approach to produce catechol-type crownophane derivatives such as **15** involve treatment of the dibromide **11**[39] with rongalite[40-44] to generate sulfone **14**, which can undergo a DA reaction with a suitable dienophiles followed by aromatization sequence. In this regard, the diester **9**[28] was reduced with an excess amount of lithium aluminium hydride (LAH) in dry THF under reflux conditions to deliver the diol **10** (62% yield). Later, conversion of the diol **10** to the corresponding dibromide **11** was attempted using various brominating reagents such as PBr_3 in dry DCM. Unfortunately, durene tetrabromide was obtained in 76% yield instead of the expected dibromide **11** (**Scheme 2**). Alternatively, when the diol **10** was subjected to using $BF_3{\cdot}OEt_2$/NaBr bromination conditions, only mono-bromoderivative was obtained and all other attempts to convert the monobromide to the dibromide **11** were unsuccessful.

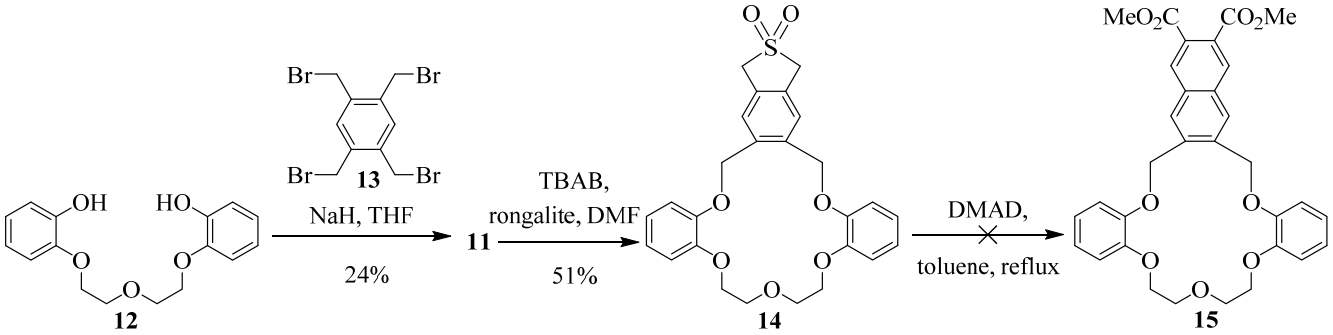


(a) (i) PBr_3, DCM, rt; (ii) $BF_3{\cdot}OEt_2$, NaBr, MeCN, reflux

Scheme 2. Attempts to prepare dibromide **11** from **9**

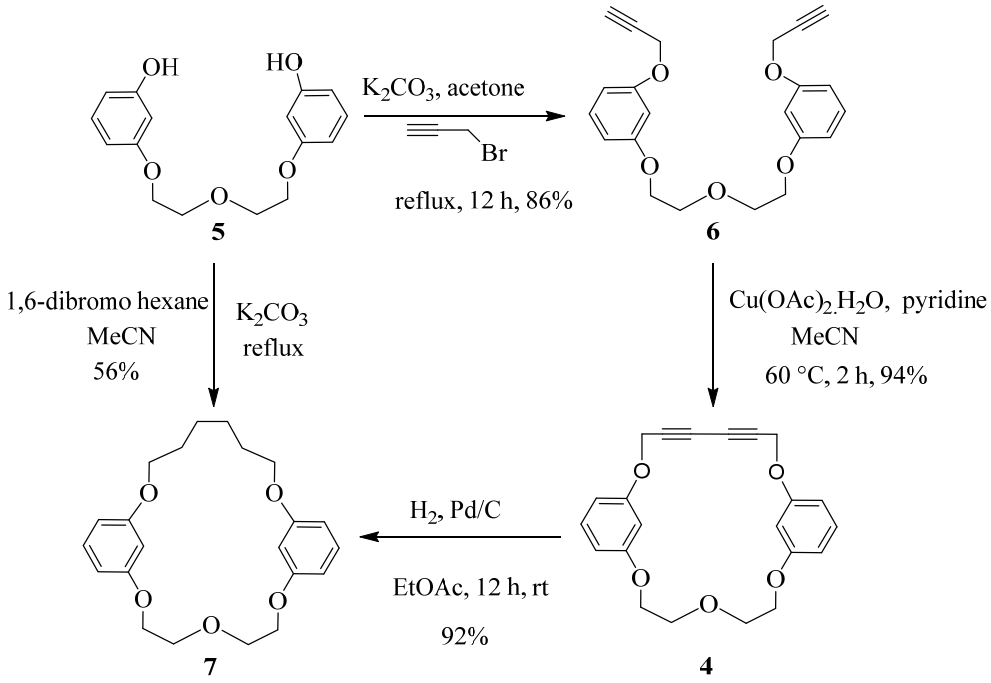
Next, we prepared the dibromide **11** by adopting the known procedure.[39] The yield of the dibromo compound **11** is 24% and later the dibromide **11** was treated with rongalite in the presence of phase-transfer catalyst (PTC) such as tetra-*n*-butylammonium bromide (TBAB) to generate the sulfone **14** in 51% yield. Subsequently, the sulphone **14** was treated with dimethylacetylene dicarboxylate (DMAD) under toluene reflux conditions to generate the DA adduct. However, under these condition no DA

product was obtained and the starting material was recovered. Even under forcing reaction conditions no DA product was obtained. Further, when the DA reaction of **14** with DMAD was attempted under microwave conditions no desired DA adduct was obtained (**Scheme 3**).



Scheme 3. Attempted synthesis of cyclophane **15**

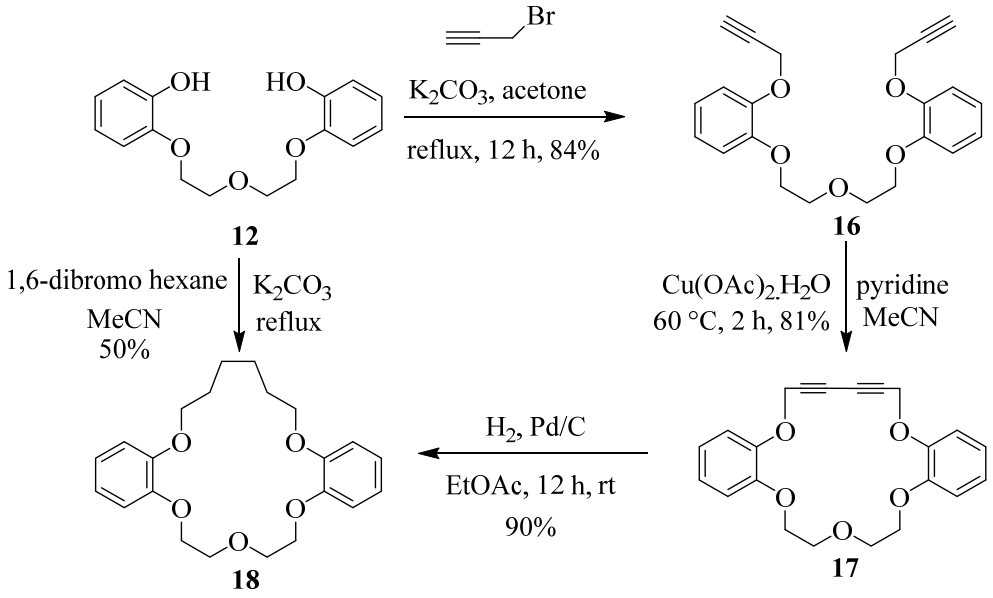
Our next route to prepare cyclophanes involves, *O*-propargylation followed by Glaser–Eglinton coupling and hydrogenation reaction sequences. In this regard, the dipropargylated compound **6** was subjected to Glaser–Eglinton coupling strategy to generate the macrocyclic bis-acetylene derivative **4** in 94% yield (**Scheme 4**).



Scheme 4. Synthesis of cyclophane **7** via Glaser–Eglinton coupling and hydrogenation

Finally, the diyne **4** was subjected to hydrogenation sequence with 10% Pd/C under 1 atm. pressure of H_2 to generate the cyclophane derivative **7** in 92% yield. Alternatively, the cyclophane **7** was also obtained by treatment of the bisphenol **5** with 1,6-dibromohexane in the presence of K_2CO_3 under acetonitrile reflux condition in 56% yield.

Along similar lines, bisphenol derivative **12**,[45] was converted to the corresponding *O*-propargylated compound **16** in 84% yield on reaction with propargyl bromide in the presence of K_2CO_3 under acetone reflux condition (**Scheme 5**). Further, the dipropargyl derivative **16** was reacted with Cu-II salt in the presence of pyridine to generate a cyclic conjugated macrocycle **17** in 81% yield. Hydrogenation of the dialkyne **17** in the presence of 10% Pd/C under H_2 atmosphere gave the cyclophane derivative **18** in 90% yield. In another route, bisphenol **12** was alkylated with 1,6-dibromohexane in the presence of K_2CO_3 to deliver **18** in 50% yield.



Scheme 5. Synthesis of cyclophane **18** by Glaser–Eglinton coupling

In conclusion, we have designed a simple strategy for the synthesis of cyclophane derivatives **7** and **18** by using Glaser–Eglinton coupling and catalytic hydrogenation as key steps. Synthesis of **7** and **18** was carried under normal concentration without using high dilution conditions. This may be due to the presence of ethyleneonxy linkage which provide close proximity for *O*-propargyl group and help for Glaiser–Eglinton coupling. This protocol may be extended to variety of other cyclophane derivatives by varying the length of alkynyl moiety attached to bisphenols **12** (or **5**). Several intermediates prepared here (e.g. **4** and **17**) may play an influential role in exploring new strategies to cyclophane derivatives containing ethyleneoxy bridge of varying chain length.

EXPERIMENTAL

Synthesis of sulfone 14

To a suspension of rongalite (1.18 g, 9.5 mmol) in DMF (15 mL) were added TBAB (305 mg, 0.95 mmol) and dibromide compound **11** (550 mg, 0.95 mmol) at 0 ^{o}C, and the stirring was continued for 4 h

at 0 °C. Then, the reaction mixture was brought to rt, and the stirring was continued for an additional 4 h. After completion of the reaction (TLC monitoring), the reaction mixture was diluted with EtOAc and washed with water (3-4 times). The aqueous layer was again extracted with 30 mL of EtOAc and the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, and the product was purified by silica gel column chromatography. Elution of the column with 70% EtOAc/ petroleum ether gave **14**.

Compound **14** colorless solid: $\mathbf{R_f}$ = 0.3 in (70% EtOAc/ petroleum ether mixture): (234 mg, 51% yield); **mp** 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (t, *J* = 4.08 Hz, 4H), 4.15 (t, *J* = 4.00 Hz, 4H), 4.40 (s, 4H), 5.21 (s, 4H), 7.04–6.87 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.13, 67.95, 69.67, 70.45, 113.15, 119.46, 121.25, 123.71, 125.56, 130.63, 137.16, 148.00, 150.84; HRMS (Q-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{26}O_7SNa$ 505.1296 found 505.1298; IR (KBr): υ_{max} 1265, 1422, 1602, 2305, 2986, 3434 cm^{-1}.

General procedure for *O*-propargylation

To a stirred solution of bisphenol (**5**/**12**) (1 mmol) in acetone (15 mL) was added K_2CO_3 (5 mmol) and the resultant suspension was stirred for 30 min. Then, propargyl bromide (3 mmol) was added dropwise over a period of 10 min. Further, the crude reaction mixture was stirred for 12 h at reflux. At the conclusion of the reaction (TLC monitoring), the crude mixture was filtered through celite pad (washed with CH_2Cl_2) and concentrated under reduced pressure. The crude product was purified by column chromatography.

Following the general procedure, 1 mmol (290 mg) of bisphenol **5** was subjected to *O*-propargylation to generate compound **6** (314 mg, 86% yield). Compound **6** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **6** $\mathbf{R_f}$ = 0.4 in (10% EtOAc/ petroleum ether mixture): colorless solid: **mp** 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (t, *J* = 2.5 Hz, 2H), 3.91-3.93 (m, 4H), 4.13-4.15 (m, 4H), 4.65 (d, *J* = 2.5 Hz, 4H), 6.90-7.25 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.01, 67.68, 70.07, 75.69, 78.71, 102.28, 107.49, 107.95, 130.08, 158.91, 160.11; HRMS (Q- TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{22}O_5Na$ 389.1359 found 389.1357; IR (KBr): υ_{max} 740, 1265, 1422, 1602, 2305, 2986, 3434 cm^{-1}.

Following the general procedure, 1 mmol (290 mg) of bisphenol **12** was subjected for *O*-propargylation to generate compound **16** (307 mg, 84% yield). Compound **16** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **16** $\mathbf{R_f}$ = 0.4 in (10% EtOAc/ petroleum ether mixture): colorless solid: **mp** 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (t, *J* = 2.5 Hz, 2H), 3.94-3.97 (m, 4H), 4.18-4.21 (m, 4H), 4.18 (d, *J* = 2.5 Hz, 4H), 6.90-7.25 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.32, 68.97, 70.07, 75.71, 79.11, 114.77, 116.09, 121.56, 122.74, 147.65, 149.44; HRMS (Q- TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{22}O_5Na$

389.1359 found 389.1358; IR (KBr): υ_{max}: 740, 1265, 1499, 2305, 2987, 3420 cm^{-1}.

Synthesis of compound 8

Solution of dipropargylated compound **6** (366 mg, 1 mmol) in dry THF (15 mL) was maintained at -78 ^{o}C and *n*-BuLi (1.6 M solution in hexanes) was added to the reaction mixture. The reaction mixture was stirred for 3 h at the same temperature, and MeI (158 mg, 3 mmol) was added dropwise over a period of 10 min. Further, reaction mixture was stirred for 3 h. At the conclusion of the reaction (TLC monitoring), reaction mixture was brought to room temperature. Saturated aq. solution of NH_4Cl was added and reaction mixture was extracted with EtOAc. The combined organic layer was washed with 4N HCl (2 X 100 mL), saturated aq. $NaHCO_3$ (100 mL), water (2 X 200 mL) and brine (200 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed on a rotavapour. The crude product was chromatographed on a silica gel column and elution of the column with petroleum ether/EtOAc mixture to afford the compound **8** (267 mg, 68% yield).

Data for compound **8** $\mathbf{R_f}$ = 0.3 in (10% EtOAc/ petroleum ether mixture):colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (t, *J* = 2 Hz, 6H, 3.91-3.93 (m, 4H), 4.12-4.14 (m, 4H), 4.60 (q, *J* = 2 Hz, 4H), 6.53-6.57 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.62, 67.64, 70.06, 74.15, 83.89, 102.17, 102.30, 107.49, 107.63, 129.99, 159.21, 160.07; HRMS (Q- TOF) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{26}O_5Na$ 417.1677 found 417.1673; IR (neat): υ_{max}: 740, 1265, 1422, 1597, , 2987, 3056 cm^{-1}.

General procedure for Glaser–Eglinton coupling reaction

To a suspension of cupric acetate monohydrate (1 mmol) in MeCN (20 mL), pyridine (0.5 mL) was added and reaction mixture was heated to 60 °C and then a solution of the bis-propargyl ether **6** or (**16**) (0.5 mmol) in MeCN (20 mL) was added. The color of the solution changed from deep blue to green. The reaction mixture was stirred for 2 h and then cooled to room temperature, and water was added (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 50 mL). The combined organic layer was washed with 4N HCl (2 X 100 mL), saturated aq. $NaHCO_3$ (100 mL), water (2 X 200 mL) and brine (200 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed on a rotavapour. The crude product was chromatographed on a silica gel column and elution of the column with petroleum ether/EtOAc mixture to afford the compound **4** or **17** as colorless solids.

Following the general procedure, 1 mmol (366 mg) of bis-propargyl **6** was subjected for Glaser–Eglinton coupling reaction to generate compound **4** (342 mg, 94% yield). Compound **4** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **4** $\mathbf{R_f}$ = 0.3 in (10% EtOAc/ petroleum ether mixture):colorless solid: **mp** 135 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89-3.91 (m, 4H), 4.15-4.17 (m, 4H), 4.72 (s, 4H), 6.49-6.54 (m, 4H), 6.76 (t, *J* = 2.3 Hz, 2H), 7.18 (t, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.48, 67.33, 69.55, 71.63,

74.82, 102.05, 105.96, 110.66, 130.09, 158.71, 160.04; HRMS (Q- TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{20}O_5Na$ 387.1203 found 387.1203; IR (KBr): υ_{max}: 741, 1265, 1422, 1596, 2305, 2987, 3055 cm^{-1}.

Following the general procedure, 1 mmol (366 mg) of bis-propargyl **16** was subjected for Glaser–Eglinton coupling reaction to generate compound **17** (296 mg, 81% yield). Compound **17** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **17** $\mathbf{R_f}$ = 0.3 in (10% EtOAc/ petroleum ether mixture): colorless solid: **mp** 142 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 4.00 (t, *J* = 5.5 Hz, 4H), 4.20 (t, *J* = 5.5 Hz, 4H), 4.72 (s, 4H), 6.90-7.01 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.19, 68.83, 70.09, 71.02, 75.64, 115.49, 119.95, 121.95, 124.56, 148.05, 151.20; HRMS (Q- TOF) *m/z*: $[M+K]^+$ calcd for $C_{22}H_{20}O_5K$ 403.0942 found 403.0942; IR (KBr): υ_{max}: 739, 1265, 1455, 1601, 2923, 3054 cm^{-1}.

General procedure for hydrogenation

The conjugated alkyne **4** (or **17**) was dissolved in EtOAc and degassesd with nitrogen for 15 min. Then, 10% Pd/C was added to the reaction mixture, and the mixture was stirred at room temperature under a hydrogen atmosphere (1 atm) for 12 h. At the conclusion of the reaction (TLC monitoring), the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography to deliver hydrogenated product **7** (or **18**).

Following the general procedure of catalytic hydrogenation, 1 mmol (364 mg) of compound **4** was subjected hydrogenation reaction to generate compound **7** (342 mg, 92% yield). Compound **7** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **7** $\mathbf{R_f}$ = 0.4 in (10% EtOAc/ petroleum ether mixture): colorless solid: **mp** 102 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 1.56-1.58 (m, 4H), 1.78 (t, *J* = 5.8 Hz, 4H), 3.90 (t, *J* = 4.5 Hz, 4H), 3.98 (t, *J* = 4.5 Hz, 4H), 4.13 (t, *J* = 4.5 Hz, 4H), 6.46-6.54 (m, 6H), 7.14 (t, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.03, 28.10, 67.65, 67.89, 70.22, 102.87, 106.93, 107.14, 129.96, 160.22, 160.52; HRMS (Q-TOF) *m/z*: $[M+K]^+$ calcd for $C_{22}H_{28}O_5K$ 411.1568 found 411.1564; IR (KBr): υ_{max}: 741, 1265, 1422, 1597, 2987, 3055 cm^{-1}.

Following the general procedure, 1 mmol (364 mg) of compound **17** was subjected hydrogenation reaction to generate compound **18** (334 mg, 90% yield). Compound **18** has been obtained by elution of the column with 10% EtOAc/petroleum ether.

Data for compound **18** $\mathbf{R_f}$ = 0.4 in (10% EtOAc/ petroleum ether mixture): colorless solid: **mp** 112 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 1.60-1.62 (m, 4H), 1.83 (t, *J* = 5.8 Hz, 4H), 4.02-4.05 (m, 8H), 4.17 (t, *J* = 4.7 Hz, 4H), 6.90 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.45, 29.68, 69.69, 69.84, 70.64, 114.95, 115.44, 121.58, 121.88, 149.41, 149.63; HRMS (Q- TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{28}O_5Na$ 395.1829 found 395.1829; IR (KBr): υ_{max}: 707, 741, 1266, 1421, 2987, 3054 cm^{-1}.

Alternative procedure to synthesis compound 7 and 18

To a stirred solution of bisphenol (**5**/**12**) (1 mmol) in MeCN (15 mL) was added K_2CO_3 (5 mmol) and the resultant suspension was stirred for 30 min. Then, 1,6-dibromohexane (3 mmol) was added dropwise over a period of 10 min. Further, the crude reaction mixture was stirred for 12 h at reflux. At the conclusion of the reaction (TLC monitoring), the crude mixture was filtered through celite pad (washed with CH_2Cl_2) and concentrated under reduced pressure. The crude product was purified by column chromatography. Cyclophane products (**7** and **18**) data obtained by this procedure was compared with data obtained by hydrogenation process.

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REFERENCES

1. H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, 1969, **91**, 3505.
2. M. Sheehan and D. J. Cram, *J. Am. Chem. Soc.*, 1969, **91**, 3544.
3. J. P. Sauvage and J. M. Lehn, *Bull. Soc. Chim.*, 1970, 50.
4. D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1971, **4**, 204.
5. J. Cheney and J. M. Lehn, *J. Chem. Soc., Chem. Comm.*, 1972, 487.
6. C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1021.
7. C. J. Pedersen, *J. Inclu. Phenom.*, 1988, **6**, 337.
8. P. Guerriero, S. Tamburini, and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17.
9. O. Hayashida, *J. Syn. Org. Chem. Jpn.*, 2006, **64**, 1041.
10. A. R. Bogdan, S. V. Jerome, K. N. Houk, and K. James, *J. Am. Chem. Soc.*, 2012, **134**, 2127.
11. R. Zimmer, M. Taszarek, L. Schefzig, and H. U. Reissig, *Synlett*, 2008, 2046.
12. G. Yapar and C. Erk, *J. Incl. Phenom. Macro.*, 2002, **43**, 299.
13. E. S. Hirst and R. Jasti, *J. Org. Chem.*, 2012, **77**, 10473.
14. M. Shibahara, M. Watanabe, K. Aso, and T. Shinmyozu, *Synthesis*, 2008, 3749.
15. F. Diederich and P. J. Stang, Templated Organic Synthesis, Wiley-VCH Verlag GmbH, 2007.
16. P. Wipf and M. Furegati, *Org. Lett.*, 2006, **8**, 1901.
17. H. Okamoto, K. Satake, H. Ishida, and M. Kimura, *J. Am. Chem. Soc.*, 2006, **128**, 16508.

18. H. Hopf and R. Gleiter, Modern Cyclophane Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2005.
19. C. M. Wei, K. F. Mo, and T. L. Chan, *J. Org. Chem.*, 2003, **68**, 2948.
20. S. Kotha, G. T. Waghule, and M. E. Shirbhate, *Eur. J. Org. Chem.*, 2014, 984.
21. E. Weber and F. Vogtle, *Justus Liebigs Ann. Chem.*, 1976, 891.
22. S. Kotha and M. E. Shirbhate, *Synlett*, 2012, 2183.
23. S. Kotha, A. S. Chavan, and M. Shaikh, *J. Org. Chem.*, 2012, **77**, 482.
24. S. Kotha and K. Mandal, *Eur. J. Org. Chem.*, 2006, 5387.
25. S. Kotha, K. Mandal, K. K. Arora, and R. Pedireddi, *Adv. Synth. Catal.*, 2005, **347**, 1215.
26. S. Kotha and S. Halder, *ARKIVOC,* 2005, **iii**, 56.
27. S. Kotha, S. Halder, L. Damodharan, and V. Pattabhi, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1113.
28. S. Kotha and G. T. Waghule, *J. Org. Chem.*, 2012, **77**, 6314.
29. S. Kotha, M. Meshram, and A. Tiwari, *Chem. Soc. Rev.*, 2009, **38**, 2065.
30. Z. Wang, Comprehensive Organic Name Reactions and Reagents, John Wiley & Sons, Inc., 2009, p. 959.
31. K. Jyothish and W. Zhang, *Angew. Chem. Int. Ed.*, 2011, **50**, 8478.
32. G. Valot, C. S. Regens, D. P. O'Malley, E. Godineau, H. Takikawa, and A. Furstner, *Angew. Chem. Int. Ed.*, 2013, **52**, 9534.
33. A. Fürstner, *Chem. Commun.*, 2011, **47**, 6505.
34. B. Mao, M. Fananas-Mastral, M. Lutz, and B. L. Feringa, *Chem. Eur J.*, 2013, **19**, 760.
35. C. Deraedt, M. d'Halluin, and D. Astruc, *Eur. J. Inorg. Chem.*, 2013, 4881.
36. J. W. Li and D. Lee, *Eur. J. Org. Chem.*, 2011, 4269.
37. D. Castagnolo, L. Botta, and M. Botta, *J. Org. Chem.*, 2009, **74**, 3172.
38. S. Beer, K. Brandhorst, J. Grunenberg, C. G. Hrib, P. G. Jones, and M. Tamm, *Org. Lett.*, 2008, **10**, 981.
39. W. Sim, J. Y. Lee, J. S. Kim, J.-G. Kim, and I.-H. Suh, *Acta Crystallogr. Sect. C*, 2001, **57**, 293.
40. S. Kotha, R. Ali, and A. Tiwari, *Synlett*, 2013, **24**, 1921.
41. S. Kotha and P. Khedkar, *Chem. Rev.*, 2012, **112**, 1650.
42. S. Kotha and A. S. Chavan, *J. Org. Chem.*, 2010, **75**, 4319.
43. S. Kotha, D. Kashinath, and P. Khedkar, *Synthesis*, 2007, 3357.
44. S. Kotha, P. Khedkar, and A. K. Ghosh, *Eur. J. Org. Chem.*, 2005, 3581.
45. M. Srinivasan, S. Sankararaman, H. Hopf, I. Dix, and P. G. Jones, *J. Org. Chem.*, 2001, **66**, 4299.