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PAPER

One-pot synthesis of pillar[*n*]arenes catalyzed by a minimum amount of TfOH and a solution-phase mechanistic study†

Kai Wang,[a] Li-Li Tan,[a] Dai-Xiong Chen,[a] Nan Song,[a] Guan Xi,[a] Sean Xiao-An Zhang,*[a] Chunju Li[b] and Ying-Wei Yang*[a]

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A practical and effective trifluoromethanesulfonic acid (TfOH)-catalyzed cyclooligomerization strategy was developed for the synthesis of functionalized pillar[*n*]arenes and copillar[5]arenes from 1,4-dialkoxybenzenes with paraformaldehyde under mild reaction conditions, and the reaction mechanism of solution-phase catalytic synthesis of pillararenes was investigated by room-temperature X-band ESR spectroscopy, mass spectroscopy, NMR and control experiments, suggesting a free radical process initially and a Friedel–Crafts alkylation process during the consequent coupling and ring-closure stage.

Introduction

Supramolecular macrocyclic hosts,[1] such as crown ethers, cyclophanes, cyclodextrins, cucurbiturils, and calixarenes, have drawn great attention over the past several decades. Extensive and intensive research has been done, showing their diverse properties and potential applications.[2] Pillar[*n*]arenes, as a new family of supramolecular host molecules with tubular-shape and rigid macrocyclic structures, aroused considerable interest and advanced significantly in recent years,[3] in terms of their synthetic strategy, molecular recognition and selective binding towards guest molecules,[4] and their self-assembly properties,[4j,l,5] since the discovery by Ogoshi *et al*. and Cao *et al*.[6]

Some catalytic systems were employed for the synthesis of pillar[*n*]arenes, including (a) condensation of 1,4-dialkoxybenzene and paraformaldehyde with an equivalent amount of $BF_3{\cdot}OEt_2$ under dry conditions,[6a,7] (b) cyclization of 1,4-dialkoxy-2,5-bis(alkoxy-methyl)benzenes using a catalytic amount of *p*-toluenesulfonic acid as a catalyst,[6b,8] and (c) cyclooligomerization of 2,5-dialkoxybenzyl bromides or 2,5-dialkoxybenzyl alcohols with an appropriate Lewis acid as the catalyst in dichloromethane.[9] However, these catalytic systems still, in general, suffer from harsh reaction conditions, low reaction yield, and/or relatively long reaction routes, which definitely have not met the goal required for the rapid development of this emerging field. Moreover, a mechanism for pillar[*n*]arene synthesis has not yet been elucidated clearly with experimental details. So, despite these catalytic systems being available, it is still highly desirable to develop a more simple and effective catalytic system for the preparation of pillararenes starting from easily obtained and cheaper materials, and more importantly rule out their reaction mechanism with direct experimental insights.

For the synthesis of functional organic molecules *via* cross-coupling/cyclization[10] and Friedel–Crafts reaction, sulfonic acids, trifluoromethanesulfonic acid (TfOH) in particular, have emerged to be versatile catalysts for these smart organic reactions.[11] Significantly, we found out that TfOH could be an efficient catalyst for the cyclization of monomers in the synthesis of pillar[*n*]arenes. Herein, we wish to report our successful one-pot catalytic synthesis of pillar[*n*]arenes from the cyclooligomerization of applicable 1,4-dialkoxy-benzenes and paraformaldehyde with a catalytic amount of TfOH as a robust and efficient catalyst in dichloromethane under mild conditions. Meanwhile, various methods were employed to probe the mechanism of solution-phase pillararene synthesis, suggesting a free radical intermediate initially and a Friedel–Crafts alkylation process during the coupling and ring-closure stage.

Results and discussion

At first, the survey of reaction parameters including Brønsted acid catalysts and solvents was performed using the cyclization of 1,4-dimethoxybenzene **1a** with paraformaldehyde as a model reaction, because DMpillar[5]arene **2a** has proved to be a convenient precursor for pillar[5]arene by simply removing the methyl groups.[6a,7] Meanwhile, pillar[5]arene can be amenable for further functionalization.[4d,g,12] Although a few procedures for the synthesis of **2a** are available to date, it is highly desirable to search for a simple, robust and efficient catalyst system. As

[a]*State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, China. E-mail: ywyang@jlu.edu.cn, seanzhang04@yahoo.com*
[b]*Department of Chemistry, Shanghai University, Shanghai, 200444, China*

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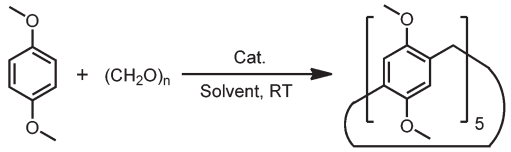
Table 1 Cyclooligomerization of 1,4-dimethoxybenzene **1a** with paraformaldehyde under different reaction conditions[a]

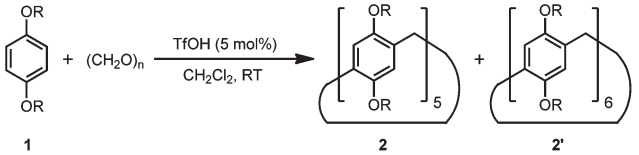


1 a **2 a**

Entry	Cat. (mol%)	Solvent	Time (h)	Yield[b] (%)
1	$TsOH·H_2O$ (15)	CH_2Cl_2	24 (50)[c]	Trace (65)[c]
2	TfOH (15)	CH_2Cl_2	4	66
3	TfOH (5)	CH_2Cl_2	6	66
4	TfOH (1)	CH_2Cl_2	24	15
5	CH_3SO_3H (15)	CH_2Cl_2	24	61
6	98% H_2SO_4 (15)	CH_2Cl_2	24	Trace
7	H_3PO_4 (15)	CH_2Cl_2	24	0
8	CF_3COOH (15)	CH_2Cl_2	24	0
9	HCl (15)	CH_2Cl_2	24	0
10	No catalyst	CH_2Cl_2	24	0
11	TfOH (30)	DCE[d]	16	46
12	TfOH (15)	$CHCl_3$	24	Trace
13	TfOH (15)	Toluene	24	0

[a] Reaction conditions: **1a** (2 mmol), paraformaldehyde (3 mmol), and catalyst (*y* mol%) in solvent (60 mL) at room temperature (25 °C). [b] Isolated yields. [c] Under reflux. [d] DCE = 1,2-dichloroethane.

Table 2 TfOH catalyzed 1,4-dialkoxybenzene-paraformaldehyde cyclooligomerization in dichloromethane[a]



1 **2** **2'**

Monomer	R	Time (h)	Product/yield[b] (%) 2		2′	
1b	Ethyl	8	**2b**	61	**2b′**	—
1c	*n*-Hexyl	12	**2c**	59	**2c′**	—
1d	*n*-Decyl	12	**2d**	61	**2d′**	—
1e	i-Propyl	12	**2e**	34	**2e′**	—
1f	CH_2CH_2Br	12	**2f**	45	**2f′**	—
1g	$CH_2(CH_2)_2CH_2Br$	12	**2g**	56	**2g′**	6
1h	Acetyl	24	—	—	—	—

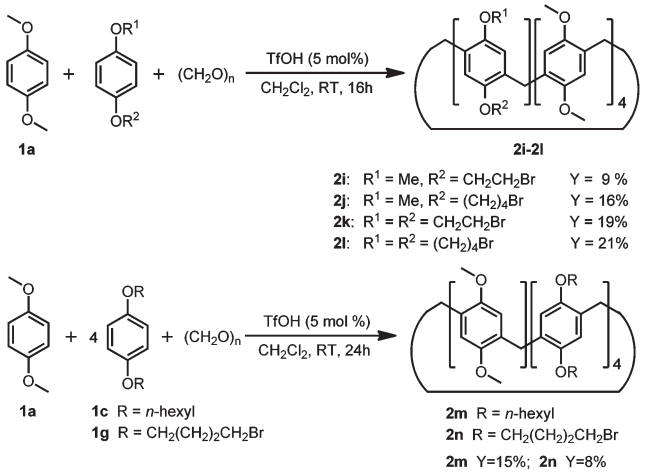
[a] Reagents and conditions: **1** (2 mmol), $(CH_2O)_n$ (3 mmol) and TfOH (5 mol%) in dichloromethane (60 mL) at 25 °C. [b] Isolated yields.

shown in Table 1, in the presence of 15 mol% *p*-toluenesulfonic acid, the cyclization occurred very slowly, and a reaction time of 50 h was required even under reflux (entry 1). With TfOH as the catalyst, this reaction went to completion within a very short period of time even at room temperature and without the need for strict dry conditions, affording DMpillar[5]arene in a relatively good yield (entry 2). Next, we varied the amount of TfOH, and the results showed that a slightly longer reaction time can compensate for the decrease in reaction rate caused by reducing the catalyst amount (entry 3); while the reaction stopped before full conversion when using 1 mol% catalyst, further prolonging of the reaction time did not change the reaction yield (entry 4). In addition, methanesulfonic acid could also result in a high conversion of cyclization with a good yield but would require a longer reaction time (24 h, entry 5). However, when using H_2SO_4 (98%) as a catalyst, only trace amounts of the product could be obtained as detected by mass spectrometry (entry 6). Other Brønsted acids (phosphoric acid, trifluoroacetic acid and hydrochloric acid) showed little or no catalytic effect, similar to the situation without a catalyst (entries 7–10). In contrast, the use of other representative solvents, *i.e.*, 1,2-dichloroethane, chloroform and toluene, resulted in a much slower reaction rate or only trace amounts of DMpillar[5]arene **2a** (entries 11–13). Although methanesulfonic acid showed a highly catalytic effect and was relatively cheaper than TfOH, the range of applicability for the synthesis of functionalized pillar[*n*]arenes was considerably limited when employing methanesulfonic acid as a catalyst. Consequently, TfOH was a practical and highly efficient catalyst for the preparation of pillararenes and their derivatives.

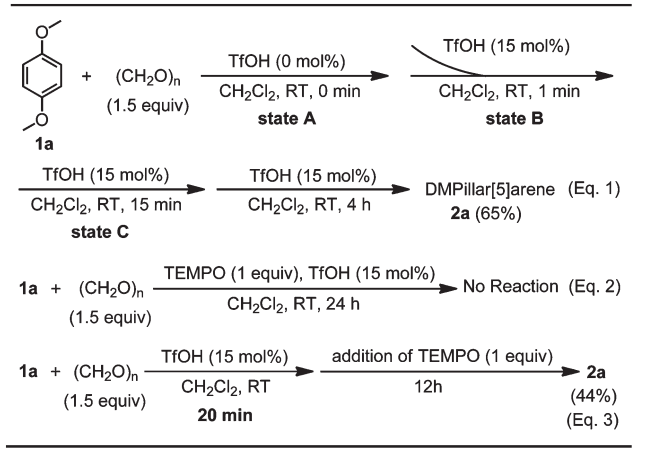
With a reliable protocol in hand, the reaction scope catalyzed by TfOH in dichloromethane was further investigated (Table 2). Under the optimal conditions (Table 1, entry 3), for all the examined substrates, reactions proceeded smoothly and reached completion in a short period of time at room temperature, and the 1,4-disubstituted pillararenes were obtained in good yields. The efficiency of the reaction was confirmed by the successful cyclization of 1,4-dialkoxybenzene (R = ethyl, *n*-hexyl, *n*-decyl, i-propyl) with paraformaldehyde (**2b–2e**). In addition to entirely alkyl chains with R, functional groups including bromine were also well tolerated. Importantly, higher cyclooligomers, *i.e.*, pillar[6]arene derivatives, were also formed under the optimal reaction conditions using a similar approach, and thus both functionalized pillar[5]arenes and pillar[6]arenes were obtained (**2f**, **2g**, **2g′**). Noticeably, the electronic nature of the R group of **1** has a significant impact on the cyclooligomerization, as can be seen from the accelerated reaction rate contributed by electron-donating groups on the alkoxyl substituents of benzene. Unfortunately, the employment of 1,4-phenylene diacetate with an electron-withdrawing group as a benzene substituent completely failed to afford any desired product.

Significantly, copillar[5]arenes **2i–2n** were successfully obtained from the co-oligomerization of different 1,4-dialkoxybenzene monomers using the same catalytic system. A mixture of 5 equiv. of 1,4-dimethoxybenzene **1a**, 1 equiv. of 1,4-dialkoxybenzene and 6 equiv. of paraformaldehyde was catalyzed by a catalytic amount of TfOH in dichloromethane under ambient conditions at room temperature for 16 h, affording the desired copillar[5]arene **2i–2l** in appreciable yields, respectively. Under the optimal reaction conditions, new copillar[5]arenes **2m** and **2n** were synthesized in appreciable isolated yields (Scheme 1).

Overall, we provided a facile synthetic access to functionalized pillar[*n*]arene derivatives with easily obtained starting materials **1** and paraformaldehyde in the presence of a catalytic amount of TfOH in dichloromethane. TfOH appears to act as an activator for pillar[*n*]arene synthesis. To unravel the mechanism of this cyclization reaction, mechanistic investigations were carried out and valuable insights were obtained (Scheme 2). Interestingly,



Scheme 1 Catalytic synthesis of copillar[5]arene **2i–2n** by TfOH.



Scheme 2 Investigation on the reaction mechanism.

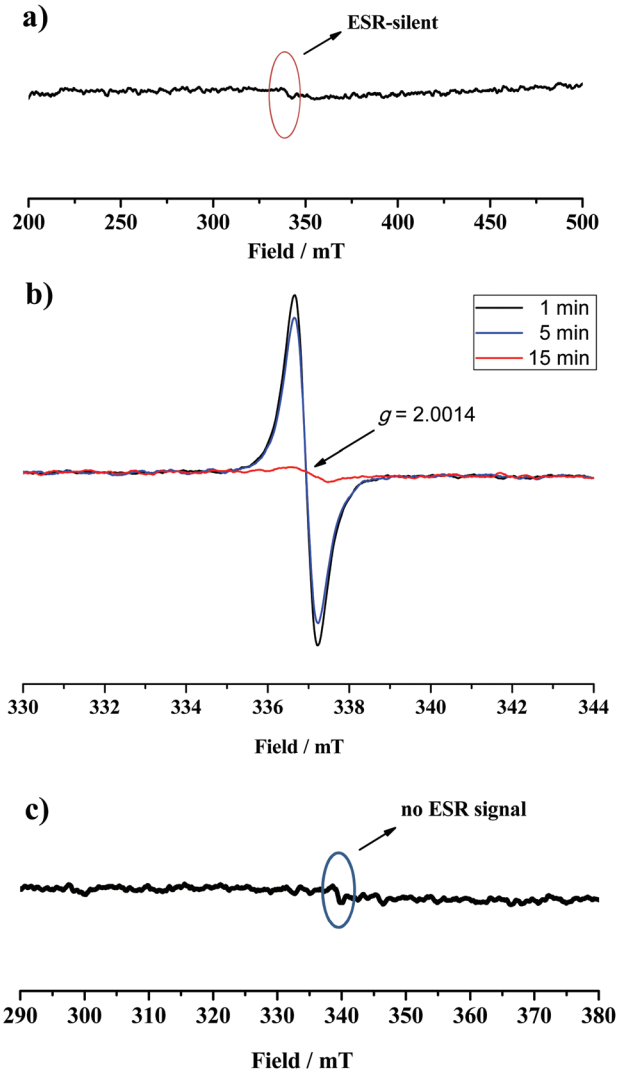


Fig. 1 Analysis of room-temperature X-band ESR spectra: (a) during the reaction without the addition of TfOH, state A (0 min); (b) during the reaction proceeded between states B and C (1–15 min); (c) after the reaction proceeded for 20 min.

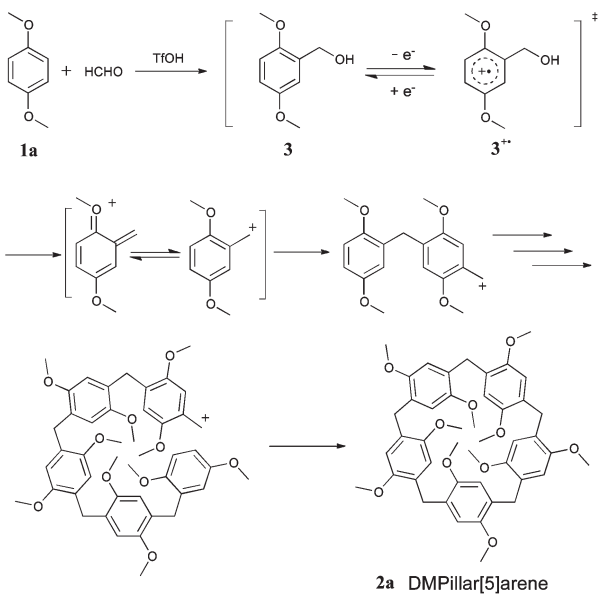
the reaction appeared to proceed *via* a different mechanistic pathway from Cao's system[6b] and simple Friedel–Crafts alkylation.[9b]

First, spectroscopic evidence for solution-phase mechanistic study on the synthesis of pillararenes was provided by room-temperature X-band Electron Spin Resonance (ESR)[13] measurements from state A to state C (Scheme 2, eqn (1)). A mixture of 1,4-dimethoxybenzene **1a** and 1.5 equiv. of paraformaldehyde without the addition of TfOH was ESR-silent, indicating that no localized unpaired electrons were present in this condition (state A and Fig. 1a). However, upon the addition of TfOH for only one minute, the initially ESR-silent reaction system showed a strongly intense ESR signal characteristic of a free radical (state B and Fig. 1b, black line). The appearance of a distinct singlet signal (g = 2.0014 ± 0.0002) indicated that a paramagnetic centre was generated during the reaction activation initially. In comparison, both **1a** with TfOH and paraformaldehyde with TfOH in dichloromethane were ESR-silent. Indeed, electron loss from the 1,4-dialkoxybenzyl alkyl ether may occur when the benzyl alkyl ether was subjected to an oxidant or electrochemical oxidation, which has been proposed by several research groups previously.[14] The loss of a single electron generated an organic aromatic radical cation, which can be detected by ESR spectroscopy.[15] Therefore, this observation demonstrated that the ESR signal can be attributed to the presence of delocalized carbon-centred radical cations according to the hyperfine splitting (single hyperfine line) and g value (g = 2.0014). Meanwhile, the radical cation intermediate could be detected by ESI-HRMS upon addition of one equivalent of TEMPO as a radical capturing agent after the reaction proceeded for one minute and five minutes, respectively (Fig. S30, ESI†). The signal intensity of the ESR-active species in solution decreased as the reaction proceeded. Fifteen minutes later, the free radical signals disappeared and became hard to detect by ESR (state C and Fig. 1b, red line). This observation indicated that the paramagnetic centre disappeared and the aromatic radical cation regained a single electron accordingly. However, only trace amounts of DMpillar[5]arene **2a** were detected at the moment, most ingredients were benzylic cations, dimeric and tetrameric

benzylic cations (Fig. S31, ESI†). The reaction went to completion in 4 hours, affording the desired product **2a** in the end.

Inhibition of the cyclooligomerization by a free radical scavenger (TEMPO) indicated that the reaction proceeded through a radical mechanism initially (Scheme 2, eqn (2)).[16] Moreover, oxygen as the origin of free radicals can be ruled out because the reaction was not affected under a nitrogen atmosphere, showing the same results by ESR. Furthermore, the reaction continued smoothly in spite of the addition of TEMPO after the reaction proceeded for 20 minutes (Fig. 1c), which implied that the reaction underwent a Friedel–Crafts alkylation process instead of a radical route during the later stage (Scheme 2, eqn (3)).

Based on our mechanistic studies described above, a plausible reaction mechanism was proposed which involves a free radical initially and a Friedel–Crafts alkylation process during the later coupling and ring-closure stage (Scheme 3). Benzylic alcohol **3** was first formed by a Friedel–Crafts alkylation from **1a** and paraformaldehyde. Subsequently, **3** was converted to a benzylic cation, in which the generation of a partially aromatic radical cation $\mathbf{3}^{+\bullet}$ was involved under the conditions with TfOH as an oxidant. A short time later, the aromatic radical cation captured an electron and regenerated benzylic alcohol. The benzylic cation underwent further reaction with **3** to give a dimeric benzylic cation under acidic conditions. Because of the orientation effect of the benzylic alcohol group, the benzylic carbon cation was attached at the 4-position of **3**. In the same way, other oligomeric cations can form accordingly. In the end, the pentameric cation formed a ring through cyclization to afford the most stable macrocyclic form, *i.e.*, **2a**. Furthermore, formaldehyde gas was used to replace paraformaldehyde in this reaction, giving the same results, and another stepwise route with 2,5-dimethoxy benzylic alcohol **3** as an isolated intermediate for the catalytic synthesis of DMpillar[5]arenes by TfOH was successful as well. This also suggested that a formaldehyde unit participated in the cyclooligomerization essentially and an intermediate of the radical cation species of benzylic alcohol **3** was formed initially in this reaction, followed by a Friedel–Crafts alkylation process (see Schemes S2 and S3, ESI†).



Scheme 3 A plausible mechanism on the synthesis of pillar[*n*]arene.

Conclusions

In summary, we have demonstrated that TfOH can serve as a robust and efficient catalyst for the cyclooligomerization of 1,4-dialkoxybenzene with paraformaldehyde in dichloromethane at room temperature, resulting in a variety of functionalized pillar[*n*]arenes and copillar[5]arenes. Due to the simplicity and practicality of starting materials and the catalytic system, our findings would be expected to benefit the research field of pillar[*n*]arene-based supramolecular chemistry and nanoscience. More importantly, the reaction was found to go through a free radical route initially and Friedel–Crafts alkylation later on based on our mechanistic study.

Experimental section

General procedure for synthesis of pillar[*n*]arenes (see ESI† for more details)

Representative synthetic procedure of pillar[*n*]arenes:

2g and **2g′**. Paraformaldehyde (0.09 g, 3 mmol) was added to a solution of 1,4-bis(4-bromobutoxy)benzene **1g** (0.76 g, 2 mmol) in dichloromethane (60 mL). Then, TfOH (9.2 μL, 5 mol%) was added to the solution and the mixture was stirred at room temperature (25 °C in our case). When the starting material was consumed completely, as detected by TLC, the mixture was poured into an aqueous NH_4Cl solution (60 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and then the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography with an appropriate eluting solvent (using dichloromethane–petroleum ether from 1 : 1 to 2 : 1) to get pure functionalized pillar[5]arene **2g** and pillar[6]-arene **2g′**. Characterization data for **2g**: white solid, m.p. 84–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.81 (s, 10H), 3.93 (t, J = 5.7 Hz, 20H), 3.75 (s, 10H), 3.44 (t, J = 5.7 Hz, 20H), 2.09–2.01 (m, 20H), 1.97–1.90 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.8, 128.3, 114.9, 67.6, 33.8, 29.8, 29.5, 28.5. MS (MALDI–TOF) calcd for $C_{75}H_{100}O_{10}Br_{10}$, m/z = 1960.628 $[M]^+$, found m/z = 1960.346; characterization data for **2g′**: white solid, m.p. 80–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.67 (s, 12H), 3.83–3.79 (m, 36H), 3.39 (t, J = 6.3 Hz, 24H), 1.98–1.91 (m, 24H), 1.88–1.81 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 150.0, 128.5, 115.1, 67.8, 34.0, 30.0, 29.7, 28.7. MS (MALDI–TOF) calcd for $C_{90}H_{120}O_{12}Br_{12}$, m/z = 2352.754 $[M]^+$, found m/z = 2352.476.

2l. Paraformaldehyde (0.18 g, 6 mmol) was added to a solution of 1,4-dimethoxybenzene **1a** (0.69 g, 5 mmol) and 1,4-bis-(4-bromobutoxy)-benzene **1g** (0.38 g, 1 mmol) in dichloromethane (150 mL). Then, TfOH (27.6 μL, 5 mol%) was added to the solution and the mixture was stirred at room temperature (25 °C in our case) for 16 h. The mixture was poured into the aqueous NH_4Cl solution (150 mL), the organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous

Na_2SO_4, filtered, and then the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography with an appropriate eluting solvent (petroleum ether–dichloromethane–ethyl acetate 100 : 75 : 1) to get the desired copillar[5]arene **2l** as a white solid, m.p. 195–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.81–6.75 (m, 9H), 6.71 (s, 1H), 3.77 (s, 10H), 3.75 (s, 4H), 3.72–3.63 (m, 24H), 3.03 (s, 4H), 1.62 (s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 150.8(6), 150.8(1), 150.7, 150.6, 149.9, 128.5, 128.3, 128.2, 128.1, 114.9, 114.2, 113.9, 113.7, 67.4, 55.9, 55.8, 55.7, 33.3, 29.8, 29.5, 29.2, 28.3. MS (MALDI–TOF) calcd for $C_{51}H_{60}O_{10}Br_2$, m/z = 992.446 $[M]^+$, found m/z = 992.246.

Acknowledgements

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