1355

Synthesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   Special Topic

Exploring Silyl Protecting Groups for the Synthesis of Carbon Nanohoops

Remigiusz B. Kręcijasz[a]

Juraj Malinčík[b,c]

Tomáš Šolomek[*a,c] (iD)

[a] Van't Hoff Institute for Molecular Sciences, University of Amsterdam, PO Box 94157, 1090 GD Amsterdam, Netherlands
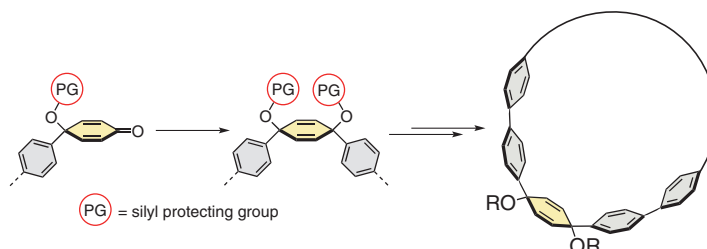t.solomek@uva.nl

[b] Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
tomas.solomek@unibe.ch

[c] Prievidza Chemical Society, M. Hodžu 10/16, 971 01 Prievidza, Slovakia

Novel protection strategy using robust silyl ethers

PG = silyl protecting group

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Abstract The synthesis of topological molecular nanocarbons, such as hoop-like [n]cycloparaphenylenes, requires the use of spatially prearranged, pro-aromatic units to overcome a build-up of large molecular strain in their curved structures. The used cyclohexadienyl units, however, contain tertiary alcohols that need protection to prevent side reactions until the aromatization step that affords the final curved hydrocarbon. Although alkyl and triethylsilyl groups have been successfully applied as protecting groups for this purpose, each suffers from specific drawbacks. Here, we explore the potential of sterically more crowded silyl groups, namely, *tert*-butyldimethylsilyl and triisopropylsilyl, as alternatives to the established protection strategies. We show that *tert*-butyldimethylsilyl can be easily installed and removed under mild conditions, displaying markedly higher resistance towards acids or bases than the triethylsilyl group used to date. Unlike in the case of alkyl groups, *tert*-butyldimethylsilyl also preserves a high stereoselectivity during the nucleophilic additions of ArLi. Furthermore, we demonstrate that both *tert*-butyldimethylsilyl and triethylsilyl groups can be installed on the same substrate, and that the latter be selectively deprotected. Thus, the high stereoselectivity, improved stability, and easy deprotection make *tert*-butyldimethylsilyl an excellent protecting group for the synthesis of carbon nanohoops.

Key words topological molecular nanocarbons, carbon nanohoops, cycloparaphenylenes, protecting groups, silyl ethers, *tert*-butyldimethylsilyl, macrocycles, orthogonality

Protecting groups are an indispensable tool to control the selectivity of chemical transformations in modern natural product synthesis or the synthesis of organic materials. An ideal protecting group needs to match several criteria, such as high-yielding introduction and removal steps, suffi-cient stability and highly specific deprotection conditions to afford orthogonality towards other protecting groups. Particularly useful types of scaffolds bearing tertiary alcohols, which require protection, are **A** and **B** (Figure 1). For example, compounds **1** and **2** (Figure 2), that contain scaffolds **A** and **B**, are important building blocks for the synthesis of topological molecular nanocarbons that involve carbon nanohoops, such as [n]cycloparaphenylenes ([n]CPPs).[1] Carbon nanohoops exhibit unique size-dependent optoelectronic properties[2] and host–guest chemistry,[3] giving rise to applications in bioimaging, optoelectronic materials and supramolecular carbon-rich nanomaterials.[4] Although envisioned decades ago, the first synthesis of these strained molecules was accomplished only in 2008 by Jasti and Bertozzi.[5] Their strategy relies on masking a *p*-phenylene unit as a 1,4-dimethoxycyclohexa-2,5-diene-1,4-diyl moiety. Here, the two tertiary alcohols prearrange the geometry in scaffold **B** with *cis* configuration for an effective macrocyclization. The reductive aromatization of the cyclohexa-2,5-diene unit then provides the necessary driving force to build up the strain in the final step.

(PG) =	-Me	-Si(CH₂CH₃)₃	-SiᵗBu(CH₃)₂
Stereoselectivity	Low	**High**	**High**
Stability	**High**	Low	**High**
Deprotection	No	**Yes**	**Yes**
Aromatization	Harsh	**Mild**	**Mild**

Figure 1 Protection of important structural scaffolds **A** and **B** in the synthesis of carbon nanohoops

1356

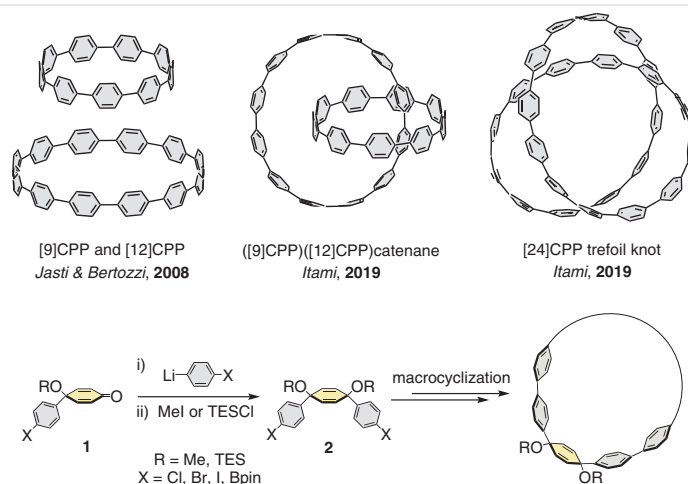**Syn**thesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   **Special Topic**
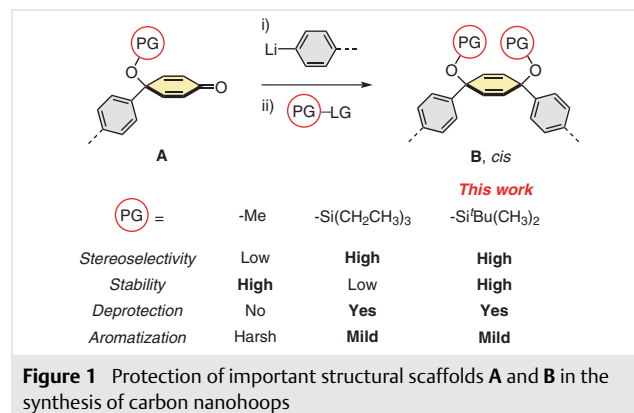
Figure 2 Topological molecular nanocarbons based on cycloparaphenylene nanohoops (top) and their synthesis using scaffolds **A** and **B** (bottom)[1i,5]

The exergonicity of the aromatization, however, requires that the tertiary alcohols be protected throughout the multistep synthesis to avoid side reactions. The electronic nature and the size of the methyl group used originally, however, result in a poor diastereoselectivity of the addition of organolithium reagents, typically ArLi, to ketone scaffold **A**.[5,6] Moreover, their removal during the aromatization often necessitates the use of harsh reagents, such as lithium/sodium naphthalide. Although the diastereoselectivity of the addition was found to be mostly dictated by electrostatics,[7,8] Yamago and co-workers[9,10] proposed the use of bulkier triethylsilyl (TES) as the protecting group for the tertiary alcohols in **A** or **B**. TES improves the stereoselectivity of ArLi addition and the exclusive formation of the *cis*-diastereomer of **B** is typically observed. TES is also relatively straightforward to deprotect with tetra-*n*-butylammonium fluoride (TBAF) before the aromatization of the ensuing 1,4-dihydroxycyclohexa-2,5-diene-1,4-diyl, performed under mild conditions with H_2SnCl_4.[8]

In our own experience, however, the sensitivity of the TES group towards acids compromises the stability of compounds that contain the structural motif **B**. Such compounds are prone to decomposition, either during the purification step after their synthesis or when stored, even at low temperatures, although such negative results are rarely reported in the literature.[1k,4d,11] Because of the individual drawbacks of the methyl and TES groups, we decided to search for an alternative protecting group that would (a) be easy to introduce, (b) would undergo stereoselective addition of ArLi to ketones **A**, (c) would be significantly more stable than TES, and (d) would be easy to remove to allow for a mild aromatization. Such a protecting group could introduce additional orthogonality to the synthesis of topological molecular nanocarbons.

The steric bulk around the silicon determines the stability of a silyl protecting group and permits selective protection/deprotection in the presence of another silyl ether.[12–14] The stability of the TES ethers used in **A** and **B** is relatively low in comparison to other silyl ethers in the presence of both acids and bases. For example, the half-lives of TES-protected *p*-cresol in the presence of 1% hydrochloric acid or 5% sodium hydroxide are <1 minute, while the half-lives of *tert*-butyldimethylsilyl (TBDMS)-protected *p*-cresol are 273 minutes and 3.5 minutes, respectively.[13] In general, the relative stability of different silyl groups to acids increase in the following order: trimethylsilyl (TMS) (1) < TES (64) < TBDMS (20,000) < triisopropylsilyl (TIPS) (700,000) < *tert*-butyldiphenylsilyl (TBDPS) (5,000,000), while to bases the
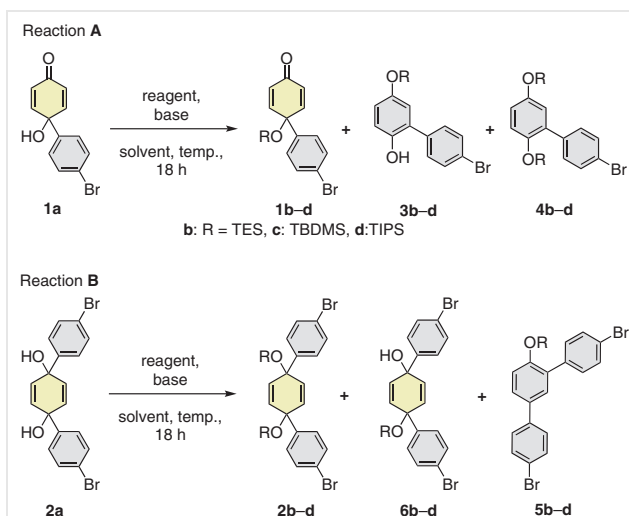
Scheme 1 Introduction of silyl protecting groups to scaffolds **A** and **B** using two model alcohols **1a** and **2a**

1357

Synthesis   R. B. Kręcijasz et al.   Special Topic

order is: TMS (1) < TES (10–100) < TBDMS ~ TBDPS (20,000) < TIPS (100,000).[14] Therefore, protecting groups with additional steric bulk, such as TBDMS or TIPS, represent great candidates as considerably more stable protecting groups. In addition, the extra steric bulk of the silyl ether in **A** is expected to display excellent diastereoselectivity for an ArLi nucleophilic addition to form the motif **B**. Protection of a tertiary alcohol, however, becomes more challenging with increasing steric bulk of the silyl protecting group.[15]

We selected model alcohols **1a** and **2a** (Scheme 1) as proxies for the motifs **A** and **B**, respectively. In fact, these two alcohols are frequently used in the synthesis of carbon nanohoops, including CPPs,[1,5–8,16] and their protection with TES to give **1b** and **2b** can be achieved in 92%[1f] and ≥82%[8] yields, respectively, in a clean transformation.

We first tested the standard silylation of **1a** with *tert*-butyldimethylsilyl chloride (TBDMSCl) and imidazole[17] in CH$_2$Cl$_2$ at room temperature (Table 1, entry 1; see also Table S1, entry 1 in the Supporting Information) and obtained full conversion of **1a**. However, we observed the formation of a complicated mixture of unknown products. We assumed that the steric bulk slows down the nucleophilic substitution of the chloride in TBDMSCl, allowing other reactions to compete. We thus exchanged CH$_2$Cl$_2$ for significantly more polar DMF, which we expected to stabilize the alcoholate

that would be generated from **1a** and imidazole in a very small amount. Such attempts resulted only in a slow conversion of **1a** into an unknown product, even when larger amounts of the reagents and an elevated temperature were used (Table 1, entry 2). Diol **2a** was completely inert under the same reaction conditions (Table 1, entry 5). Similarly, alcohol **1a** turned unreactive when bulkier 2,6-lutidine with a similar basicity was used (Table 1, entry 3). Likely, the observed side reactions are catalyzed by a general base. To accelerate the nucleophilic substitution at silicon, we decided to replace the chloride in TBDMSCl for triflate, which is an excellent nucleofuge. The combination of 2,6-lutidine with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) in CH$_2$Cl$_2$, however, afforded a full conversion of **1a** into **3c** and **4c** (Table S1, entry 4). Product **3c** is most probably formed through a rearrangement involving a 1,2-aryl shift (Scheme 2), while **4c** ensues from the excess TBDMSOTf reacting with **3c**. The observed transformation nicely illustrates the power of aromatization to drive rearrangements of cyclohexadienones.[18] To our satisfaction, we observed the formation of **1c** when the reaction was repeated under the same conditions but in polar DMF, albeit the reaction appeared significantly slower (Table S1, entry 5).

Table 1   Optimization of the Reaction Conditions to Introduce Silyl Ethers to **1a** and **2a**

Entry	Reagent (equiv.)	Base (equiv.)	Solvent	Temp (°C)	Ratio[a]		Yield (%)[b]		
Reaction **A**					**1a:1c:3c:4c**		**1c**	**3c**	**4c**
1	TBDMSCl (2)	imidazole (3)	CH$_2$Cl$_2$	RT[c]	0:0:0:0[d]		–	–	–
2	TBDMSCl (5)	imidazole (6)	DMF	60	<100:0:0:0[d,e]		–	–	–
3	TBDMSCl (5)	2,6-lutidine (6)	DMF	70	n.c.[f]		–	–	–
4	TBDMSOTf (2.5)	2,6-lutidine (4)	DMF	70	0:82:0:18		63 (71)[g]	0	14 (17)[g]
Reaction **B**					**2a:2c:6c:5c**		**2c**	**6c**	**5c**
5	TBDMSCl (5)	imidazole (6)	CH$_2$Cl$_2$	RT[c]	n.c.[f]		–	–	–
	TBDMSCl (5)	imidazole (6)	DMF	70	n.c.[f]		–	–	–
6	TBDMSOTf (5)	2,6-lutidine (6)	DMF	70	0:52:0:48		–	–	–
7	TBDMSOTf (5)	2,6-lutidine (6)	DMF	50	0:98:0:2		70	0	<5[h]
Reaction **A**					**1a:2d:3d:4d**		**1d**	**3d**	**4d**
8	TIPSOTf (5)	2,6-lutidine (6)	DMF	70	–[i]		3	0	34[j]
Reaction **B**					**2a:2d:6d:5d**		**2d**	**6d**	**5d**
9	TIPSOTf (5)	2,6-lutidine (6)	DMF	50	46:0:49:5		0	39	6[k]

[a] Ratio of products determined by ^{1}H NMR in CDCl$_3$ after 18 h.
[b] Yield of the isolated product after 18 h.
[c] RT = room temperature.
[d] Formation of unidentified product(s).
[e] Product ratio determined after 38 h.
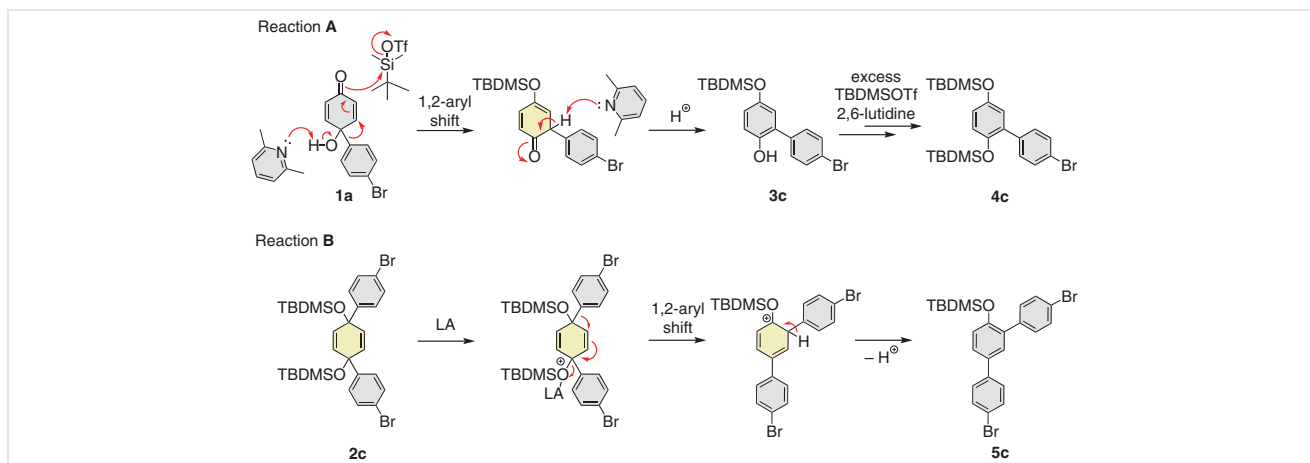[f] n.c. = no conversion.
[g] Performed on 1.00 g (3.77 mmol) scale.
[h] Compound **5c** was isolated along with a minor unidentified product.
[i] Determination of the ratio was not successful due to overlap of the ^{1}H resonances.
[j] Compound **1a** was recovered in 36% yield.
[k] Compound **2a** was recovered in 35% yield.

1358

Synthesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   Special Topic

Scheme 2 Proposed mechanisms for the observed rearrangements of **1a** and **2c**. LA = Lewis acid.
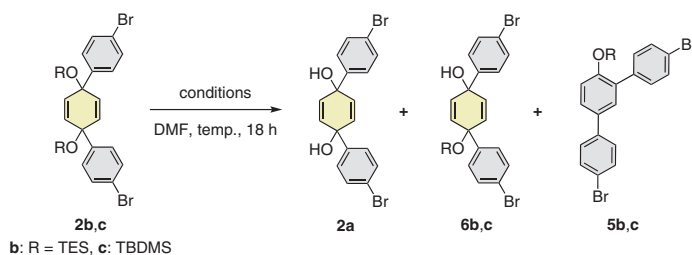
Increasing the amounts of the TBDMSOTf and 2,6-lutidine and increasing the temperature provided a faster reaction, which was, however, accompanied by the formation of **4c** (Table S1, entries 6–10). The optimal temperature was found to be 70 °C because it resulted in a full conversion of **1a** in 18 hours (incomplete at 60 °C) and a lower yield of **4c** compared to the reaction at 80 °C. The reaction at 70 °C afforded **1c** and **4c** in 58% and 8% isolated yields, respectively, after an easy separation by column chromatography. Finally, reducing the amounts of the reagents and the solvent (Table S1, entries 11–17) provided the optimal conditions that allowed us to isolate **1c** in 71% yield on one-gram scale (Table 1, entry 4). We also tested different bases in combination with TBDMSOTf (Table S1, entries 18–23), however, the reaction was slower or no significant improvement of the **1c**:**4c** ratio or the isolated yield of **1c** could be achieved.

We next attempted the protection of diol **2a** with TBDMSOTf (Scheme 1, Reaction **B**). The optimal conditions found for the protection of **1a** led to a full conversion of **2a** (Table 1, entry 6). In addition to the desired product **2c**, however, formation of a significant portion of **5c** was observed. Similar to the formation of **3c**, this rearrangement involves a 1,2-aryl shift aromatizing the cyclohexa-2,5-diene-1,4-diyl unit (Scheme 2). Increasing the amount of TBDMSOTf and 2,6-lutidine improved the relative yield of **2c** (see Table S2, entry 3 in the Supporting Information). In analogy to our experiments with **1a**, we hypothesized that the rate-limiting step in the rearrangement has a higher barrier. We noticed almost exclusive formation of **5c** at 100 °C, while the reaction at 40 °C showed the opposite effect and provided mostly **2c** (Table S2, entries 4 and 5). At room temperature, however, a small amount of the monoprotected compound **6c** was observed (Table S2, entry 6). Finally, the reaction performed at 50 °C with reduced amounts of TBDMSOTf and 2,6-lutidine provided the best result (Table 1, entry 7). Compounds **2c** and **5c** are relatively nonpolar with similar retention factors. Nevertheless, we achieved

their full separation by column chromatography and isolated **2c** in 70% yield. Although the isolated yields upon protection with TBDMS are somewhat lower than those with TES, the optimized protocols provide satisfactory results that improve with the reaction scale and allow for using TBDMS protection in a multistep synthesis of hoop-like molecular nanocarbons.

We were then interested whether the steric bulk on silicon could further be increased. We thus attempted protecting **1a** with TIPSOTf by employing the base and solvent used in the case of TBDMSOTf (Table 1, entry 4). We reached an incomplete conversion after 18 hours and isolated the desired TIPS-protected **1d** in only 3% yield along with the rearranged product **4d** in 34% yield (Table 1, entry 8). A similar unsatisfactory result was obtained when **2a** was reacted with TIPSOTf (Table 1, entry 9). In this case, no formation of doubly protected **2d** was observed. Instead, the reaction afforded the monoprotected product **6d** in 39% isolated yield, together with 6% of the rearranged product **5d**. Although increasing the amounts of TIPSOTf and the base and elevating the temperature allowed us to improve the conversion (see Table S3, entries 3 and 4 in the Supporting Information), heating favored the formation of **5d**, the exclusive product at 100 °C. Clearly, the bulkiness of the TIPS group leads to its relatively difficult introduction to **1a**, and precludes installing two TIPS protecting groups on **2a** due to their proximity in **2d**.

The nearly exclusive formation of **5c** at 100 °C (see Table S2, entry 4 in the Supporting Information) was rather intriguing because we expected the formation of **2c** and **5c** in similar amounts if the protection and the rearrangement were parallel processes. Instead, the result suggests that it is compound **2c** that is transformed into **5c** in a subsequent reaction. We thus conducted a series of experiments to determine the conditions that promote the rearrangement and that may have a detrimental effect on the stability of **2c** (Table 2).

1359

Synthesis   R. B. Kręcijasz et al.   Special Topic

Table 2 Stability of **2b** and **2c** under Different Conditions

2b,c
b: R = TES, **c**: TBDMS

2a   **6b,c**   **5b,c**

Entry	Conditions	Substrate	Result[a]
1	no additive, 100 °C	**2c**	n.c.[b]
2	2,6-lutidine (12 equiv.), 100 °C	**2c**	n.c.
3	TBDMSOTf (10 equiv.), 100 °C	**2c**	**2c:5c** = 0:100[c]
4	TBDMSCl (10 equiv.), 100 °C	**2c**	n.c.
5	TfOH (10 mol%), 100 °C	**2c**	**2c:5c** = 0:100[d]
6	TFA (10 mol%), 35 °C[e]	**2b**	**2b:6b** = 83:17
		2c	n.c.
7	HCl (1 mol%), 35 °C	**2b**	n.c.
		2c	n.c.
8	HCl (10 mol%), 35 °C	**2b**	**2b:2a:6b** = 63:8:29
		2c	n.c.
9	TfOH (10 mol%), 35 °C	**2b**	unknown product(s) and traces of **2a**
		2c	**2c:5c** = 83:17

[a] Ratio of products determined by ^{1}H NMR in CDCl$_3$ after 18 h.
[b] n.c. = no conversion.
[c] Compound **5c** was isolated in 83% yield.
[d] Compound **5c** was isolated in 84% yield.
[e] Temperature required to dissolve **2c** in DMF.

When a DMF solution of **2c** was stirred at 100 °C, with or without addition of 2,6-lutidine, no conversion of **2c** was observed (Table 2, entries 1 and 2). An excess of TBDMSOTf in the absence of base converted **2c** fully into **5c**, which we isolated in 83% yield (Table 2, entry 3). Using an excess of TBDMSCl, a weaker Lewis acid, did not show any sign of rearrangement (Table 2, entry 4). This indicates that TBDMSOTf may act in the rearrangement as a Lewis acid.[11] We suspected that TBDMSOTf may contain traces of triflic acid (TfOH) that could catalyze the rearrangement. Indeed, a catalytic amount (10 mol%) of TfOH led to a clean rearrangement of **2c** at 100 °C to furnish **5c**, which we isolated in 84% yield (Table 2, entry 5). It is worth noting that the second TBDMS group in **5c** was not cleaved during the reaction. The TBDMS group is known to be more resistant to acidic conditions than the TES group,[14] which motivated us to compare their stabilities in **2b** and **2c** in the presence of acids such as TFA, HCl, and TfOH. In a typical experiment, a DMF solution of **2b** or **2c** was stirred with a catalytic amount of the selected acid at 35 °C for 18 hours, and the reaction progress was monitored by ^{1}H NMR spectroscopy

(Table 2, entries 6–9). Compound **2c** was inert to the presence of TFA (pK_a = 0.52 in water[19]), while partial deprotection of one of the TES groups in **2b** was observed. The much stronger acid HCl (pK_a = –5.9[20]) affected neither **2b** nor **2c** when only 1 mol% was used. Increasing the amount of HCl to 10 mol%, however, promoted deprotection of the TES groups, while the TBDMS was inert. No rearrangement was observed in any of these attempts. Both **2b** and **2c** reacted in the presence of 10 mol% of the very strong acid TfOH (pK_a = –14.7[20]). Only a partial conversion of **2c** was reached after 18 hours at 35 °C compared to the full rearrangement into **5c** at 100 °C (Table 2, entries 5 and 9), and no TBDMS deprotection could be detected. On the other hand, compound **2b** was fully transformed into a mixture of unknown products. These results indicate that **2c** is considerably more resistant to acids than **2b**. In our experience, some TES-protected moieties similar to **2b** (see **2** in Figure 2) are surprisingly labile.[11] Their stability is influenced by the solvent and traces of impurities. For example, we even observed a rearrangement analogous to **2c** → **5c** in the presence of Mg^{2+} ions in one specific case.[21] We thus expect that
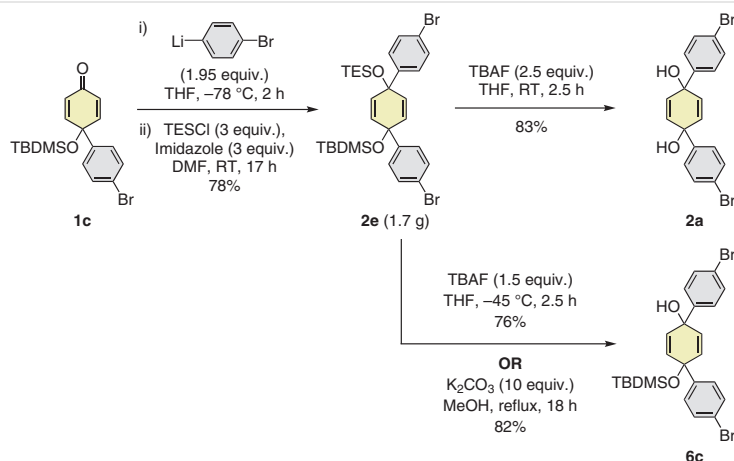
Scheme 3 Synthesis of **2e** and its selective deprotection to **2a** or **6c**

many issues associated with the stability of the building blocks (**1** and **2** in Figure 2) used in the synthesis of hoop-like molecular nanocarbons that rely on the strategy employing triethylsilyl protecting groups (TES) can now be avoided by using TBDMS. Clearly, the 1,2-aryl shift of TBDMS-protected **2c** in DMF requires a very strong Lewis or Brønsted acid and an elevated temperature to proceed on a reasonable timescale (see Scheme 2 for the proposed mechanism). However, we cannot exclude that the formation of **5c** first involves the rapid formation of **6c**, although our results with HCl indicate that this process is likely not particularly facile.

We next aimed to demonstrate that the TBDMS protecting group in **1c** preserves the high stereoselectivity of ArLi addition to the carbonyl group and that both TBDMS and TES groups could be installed on a single 1,4-dihydroxycyclohexa-2,5-diene-1,4-diyl moiety, as in compound **2e** (Scheme 3), with the latter being selectively removed in a subsequent step. The addition was accomplished via the reaction of monolithiated 1,4-dibromobenzene with **1c** at –78 °C, followed by protection of the resulting alcohol with a TES group to provide **2e** (1.7 g, 78% yield). We noticed the formation of a single *cis* diastereomer, which confirms that TBDMS displays the same high stereoselectivity as observed for **1b** bearing a TES group. We fully deprotected both silyl groups with TBAF at room temperature, isolating **2a** in 83% yield. Similarly, both TBDMS groups in **2c** could be cleaved in 73% yield. When the temperature was decreased to –45 °C, we successfully achieved the selective deprotection of TES in **2e** to afford **6c** in 76% yield. Similarly, the selective deprotection of TES could also be accomplished in 82% yield when **2e** was stirred with an excess of K_2CO_3 in refluxing methanol. The selective deprotection of the TES group can thus be easily achieved under mild conditions with two complementary methods. As such, combination of both silyl groups represents an attractive strategy to construct

versatile building blocks that may prove useful beyond the synthesis of macrocycles found in topological molecular nanocarbons.

Finally, we evaluated the effect of the steric bulk of the protecting groups on the 'bite' angle defined by the two phenylenes attached to the central cyclohexadienyl unit in **2**. Building blocks such as **2** are key intermediates in the synthesis of a variety of carbon nanohoops and the size of the bite angle may affect the efficiency of the macrocyclization step. The steric hindrance between two bulky protecting groups, such as TBDMS, could decrease this angle and prevent macrocycle formation if a wider bite angle is required. Therefore, we compared the impact of the size of the protecting group (Me, TMS, TBDMS) in **2** on the bite angle using DFT calculations. We found that the value of the bite angle in **2** (65° ± 5°) is not particularly sensitive to the type of the protecting group (see Table S4 in the Supporting Information). Analysis of the few reported[16b,22] crystal structures of compounds analogous to **2** (see Figures S1–S3 and Table S4) to validate the accuracy of the selected DFT functionals confirmed that our calculations reproduce the bite angles well. In addition, analysis of the crystal structures further revealed that the phenylenes can adopt surprisingly acute bite angles (47°). As a result, it can be expected that **2c** with bulky TBDMS protecting groups can be used in place of **2b** (or Me-protected **2a**) in the synthesis of carbon nanohoops. However, in cases where the TES introduction or removal steps prevent successful synthesis of a carbon nanohoop, the use of TBDMS will likely lead to the same outcome.

In conclusion, we have demonstrated that *tert*-butyldimethylsilyl is a versatile protecting group in the preparation of important building blocks used in the synthesis of topological molecular nanocarbons, such as hoop-like CPPs. We developed the methodology to install and cleave *tert*-butyldimethylsilyl under mild conditions, minimizing un-

1361

Synthesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   **Special Topic**

desired rearrangements driven by aromatization of cyclohexa-2,5-diene-1,4-diyl units. The tested *tert*-butyldimethylsilyl ethers were substantially more stable towards acids and bases than the corresponding triethylsilyl groups frequently used to date. The steric bulk in the *tert*-butyldimethylsilyl group preserves the high stereoselectively of ArLi additions to afford spatially prearranged building blocks used in CPP synthesis. We also explored the conditions that trigger the undesired rearrangements involving 1,2-aryl shifts. In addition, we successfully prepared a compound with both *tert*-butyldimethyl and triethylsilyl ethers, and identified conditions that permit removing the triethylsilyl chemoselectively. We anticipate that the strategies developed in this work will not only find applications in the synthesis of carbon nanohoops, such as CPPs and their derivatives, but also of other macrocycles, e.g., unprecedented macrocyclic drugs that incorporate a biphenyl or a terphenyl moiety.

Unless otherwise stated, all glassware used to perform moisture-sensitive reactions was oven-dried at 120 °C overnight, assembled hot and allowed to cool to room temperature under a stream of argon, or flame-dried under high vacuum and filled with argon. All reactions that require heating were conducted in an oil bath and the indicated temperature corresponds to the temperature of the oil bath. To obtain a temperature of –78 °C or –45 °C, a bath of acetone or acetonitrile, respectively, was cooled with dry ice. All commercially available reagents and solvents were used directly without purification unless stated otherwise. Flash column chromatography was performed using silica gel 60 Å (230–400 mesh particle size) from Supelco®. Thin-layer chromatography (TLC) was performed on silica gel plates F$_{254}$ 60 (aluminum-supported) from Supelco® using UV (254 nm) visualization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz), or a Bruker Avance III HD 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). Chemical shifts (δ) are reported in parts per million (ppm) referenced to the residual solvent peak (^{1}H: 7.26 ppm for CDCl$_3$, 5.32 ppm for CD$_2$Cl$_2$; ^{13}C: 77.16 ppm for CDCl$_3$, 53.84 ppm for CD$_2$Cl$_2$). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). High-resolution mass spectra (HRMS) were recorded on a ThermoScientific LTQ Orbitrap XL mass instrument using nanoelectrospray (NSI-MS) or electron ionization (EI-MS). Elemental analysis was performed in triplicate on a Thermo Scientific Flash 2000 Series instrument using the CHN method with sulfanilamide or cyclohexanone as the reference. Melting points were determined on a Büchi B-545 apparatus and are uncorrected.

4′-Bromo-1-hydroxy-[1,1′-biphenyl]-4(1*H*)-one (1a)

We modified a literature procedure for the synthesis of **1a**.[6] To a solution of 4′-bromo-(1,1′-biphenyl)-4-ol [CAS Reg. No. 29558-77-8] (20.00 g, 80.3 mmol, 1 equiv.) and imidazole [CAS Reg. No. 288-32-4] (8.75 g, 128.0 mmol, 1.6 equiv.) in CH$_2$Cl$_2$ (210 mL) was added chlorotrimethylsilane [CAS Reg. No. 75-77-4] (14.0 mL, 128.0 mmol, 1.6 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 19 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (60 mL) and extracted with CH$_2$Cl$_2$ (3 × 50 mL). The organic layers were combined, washed with saturated aqueous NaHCO$_3$ solution (100 mL) and brine (100 mL),

dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to afford a beige solid that was used in the next step without further purification.

(Diacetoxyiodo)benzene [CAS Reg. No. 3240-34-4] (33.62 g, 104.4 mmol, 1.3 equiv.) was added portionwise to a solution of the above solid in THF (300 mL), distilled H$_2$O (130 mL) and MeCN (75 mL) over 30 min. The reaction mixture was stirred at room temperature for 21.5 h. The solvents were then removed in vacuo to afford an orange solid. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:4 → EtOAc/*n*-pentane = 1:0, then MeOH/EtOAc = 1:19) to afford **1a** as a pale orange solid (17.26 g, 65.1 mmol, 81%). The spectral data match the literature-reported values.[6]

Pale orange solid; R_f = 0.27 (SiO$_2$, EtOAc/*n*-pentane = 3:7); mp 176–177 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.51 (d, *J* = 8.7 Hz, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 10.1 Hz, 2 H), 6.25 (d, *J* = 10.0 Hz, 2 H), 2.39 (s, 1 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 185.44, 150.20, 137.90, 132.20, 127.37, 127.27, 122.74, 70.88.

HRMS (NSI): *m/z* [M – H]$^+$ calcd for C$_{12}$H$_8$O$_2$Br: 262.9713; found: 262.9706.

Anal. Calcd for C$_{12}$H$_9$O$_2$Br: C, 54.37; H, 3.42. Found: C, 54.52; H, 3.46.

4′-Bromo-1-((triethylsilyl)oxy)-[1,1′-biphenyl]-4(1*H*)-one (1b)

According to a literature procedure,[1f] chlorotriethylsilane [CAS Reg. No. 994-30-9] (0.475 mL, 2.83 mmol, 3 equiv.) was added to a solution of **1a** (500.0 mg, 1.89 mmol, 1 equiv.) and imidazole (257.0 mg, 3.77 mmol, 2 equiv.) in DMF (10 mL). The reaction mixture was stirred at 40 °C for 15 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with saturated aqueous NaHCO$_3$ solution (50 mL), H$_2$O (2 × 50 mL) and brine (50 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo to afford an orange oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:99 → EtOAc/*n*-pentane = 3:97) to afford **1b** as a yellow oil (539.8 mg, 1.42 mmol, 75%). The spectral data match the literature-reported values.[1f]

Yellow oil; R_f = 0.30 (SiO$_2$, EtOAc/*n*-pentane = 1:19).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 6.78 (d, *J* = 10.1 Hz, 2 H), 6.22 (d, *J* = 10.0 Hz, 2 H), 0.97 (t, *J* = 7.9 Hz, 9 H), 0.65 (q, *J* = 7.9 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 185.73, 151.62, 139.29, 131.95, 127.35, 126.89, 122.23, 72.96, 7.02, 6.35.

HRMS (NSI): *m/z* [M + H]$^+$ calcd for C$_{18}$H$_{24}$O$_2$BrSi: 379.0723; found: 379.0721.

Anal. Calcd for C$_{18}$H$_{23}$O$_2$BrSi: C, 56.99; H, 6.11. Found: C, 56.89; H, 5.99.

4′-Bromo-1-((*tert*-butyldimethylsilyl)oxy)-[1,1′-biphenyl]-4(1*H*)-one (1c)

To a solution of **1a** (200.0 mg, 0.754 mmol, 1 equiv.) in DMF (10 mL) was added 2,6-lutidine [CAS Reg. No. 108-48-5] (0.351 mL, 3.02 mmol, 4 equiv.), followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate [CAS Reg. No. 69739-34-0] (0.433 mL, 1.89 mmol, 2.5 equiv.). The reaction mixture was stirred at 70 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (10 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford a dark orange oil. The crude product was purified by flash chro-

1362

Synthesis   R. B. Kręcijasz et al.   Special Topic

matography (SiO$_2$, EtOAc/n-pentane = 1:99 → EtOAc/n-pentane = 1:19) to afford **4c** as a white solid (36.8 mg, 0.075 mmol, 10%) and **1c** as a white solid (197.8 mg, 0.521 mmol, 69%).

White solid; R_f = 0.29 (SiO$_2$, EtOAc/n-pentane = 1:19); mp 88–89 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (d, J = 8.6 Hz, 2 H), 7.31 (d, J = 8.6 Hz, 2 H), 6.79 (d, J = 10.0 Hz, 2 H), 6.23 (d, J = 10.1 Hz, 2 H), 0.97 (s, 9 H), 0.12 (s, 6 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 185.66, 151.67, 139.34, 131.96, 127.31, 126.92, 122.23, 73.15, 25.86, 18.54, –2.49.

HRMS (NSI): m/z [M + H]$^+$ calcd for C$_{18}$H$_{24}$O$_2$BrSi: 379.0723; found: 379.0707.

Anal. Calcd for C$_{18}$H$_{23}$O$_2$BrSi: C, 56.99; H, 6.11. Found: C, 57.10; H, 6.18.

4′-Bromo-5-(($tert$-butyldimethylsilyl)oxy)-[1,1′-biphenyl]-2-ol (3c)

To a solution of **1a** (200.0 mg, 0.754 mmol, 1 equiv.) in CH$_2$Cl$_2$ (10 mL) was added 2,6-lutidine (0.263 mL, 2.26 mmol, 3 equiv.), followed by $tert$-butyldimethylsilyl trifluoromethanesulfonate (0.346 mL, 1.51 mmol, 2 equiv.). The reaction mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (10 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The organic layers were combined, washed with brine (50 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo to afford an orange solid. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/n-pentane = 1:19) to afford **4c** as a white solid (194.7 mg, 0.392 mmol, 52%) and **3c** as a pale orange solid (49.3 mg, 0.130 mmol, 17%).

Pale orange solid; R_f = 0.32 (SiO$_2$, EtOAc/n-pentane = 1:9); mp 77–78 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.60 (d, J = 8.4 Hz, 2 H), 7.35 (d, J = 8.4 Hz, 2 H), 6.81 (d, J = 8.5 Hz, 1 H), 6.74 (dd, J = 8.5, 2.9 Hz, 1 H), 6.71 (d, J = 2.9 Hz, 1 H), 4.74 (s, 1 H), 0.99 (s, 9 H), 0.19 (s, 6 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 149.58, 146.71, 136.34, 132.29, 130.89, 127.74, 122.08, 121.35, 120.76, 116.88, 25.85, 18.32, –4.31.

HRMS (NSI): m/z [M + H]$^+$ calcd for C$_{18}$H$_{24}$O$_2$BrSi: 379.0723; found: 379.0721.

Anal. Calcd for C$_{18}$H$_{23}$O$_2$BrSi: C, 56.99; H, 6.11. Found: C, 57.06; H, 6.16.

((4′-Bromo-[1,1′-biphenyl]-2,5-diyl)bis(oxy))bis($tert$-butyldimethylsilane) (4c)

See compound **1c** or **3c** for the synthetic procedure.

White solid; R_f = 0.69 (SiO$_2$, EtOAc/n-pentane = 1:99); mp 78–79 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.49 (d, J = 8.5 Hz, 2 H), 7.36 (d, J = 8.5 Hz, 2 H), 6.76 (d, J = 8.7 Hz, 1 H), 6.75 (d, J = 3.0 Hz, 1 H), 6.69 (dd, J = 8.7, 3.0 Hz, 1 H), 0.98 (s, 9 H), 0.82 (s, 9 H), 0.18 (s, 6 H), –0.09 (s, 6 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 150.01, 146.78, 138.12, 132.70, 131.53, 131.09, 121.82, 121.16, 121.02, 119.91, 25.86, 25.78, 18.32, 18.19, –4.29, –4.43.

HRMS (NSI): m/z [M + H]$^+$ calcd for C$_{24}$H$_{38}$O$_2$BrSi$_2$: 493.1588; found: 493.1584.

Anal. Calcd for C$_{24}$H$_{37}$O$_2$BrSi$_2$: C, 58.40; H, 7.56. Found: C, 58.29; H, 7.59.

4′-Bromo-1-((triisopropylsilyl)oxy)-[1,1′-biphenyl]-4(1H)-one (1d)

To a solution of **1a** (200.0 mg, 0.754 mmol, 1 equiv.) in DMF (10 mL) was added 2,6-lutidine (0.527 mL, 4.52 mmol, 6 equiv.), followed by triisopropylsilyl trifluoromethanesulfonate [CAS Reg. No. 80522-42-5] (1.01 mL, 3.77 mmol, 5 equiv.). The reaction mixture was stirred at 70 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (10 mL), extracted with EtOAc (3 × 10 mL), washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford an orange oil. The crude product was purified by flash chromatography (SiO$_2$, n-pentane → EtOAc/n-pentane = 3:97) to afford **4d** as a pale yellow solid (148.0 mg, 0.256 mmol, 34%), **1a** as a beige solid (72.7 mg, 0.274 mmol, 36%) and an impure material that was further purified by flash chromatography (SiO$_2$, n-pentane → EtOAc/n-pentane = 1:49) to afford **1d** as a yellow oil (8.4 mg, 0.020 mmol, 3%).

Yellow oil; R_f = 0.33 (SiO$_2$, EtOAc/n-pentane = 1:19).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47 (d, J = 8.7 Hz, 2 H), 7.35 (d, J = 8.7 Hz, 2 H), 6.82 (d, J = 10.1 Hz, 2 H), 6.23 (d, J = 10.1 Hz, 2 H), 1.11–1.05 (m, 21 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 185.68, 151.53, 139.46, 131.99, 127.47, 126.88, 122.25, 73.22, 18.36, 13.43.

HRMS (EI): m/z [M]$^+$ calcd for C$_{21}$H$_{29}$O$_2$BrSi: 420.1115; found: 420.1123.

Elemental analysis was not performed due to an insufficient amount of the material.

((4′-Bromo-[1,1′-biphenyl]-2,5-diyl)bis(oxy))bis(triisopropylsilane) (4d)

See compound **1d** for the synthetic procedure.

Pale yellow solid; R_f = 0.57 (SiO$_2$, EtOAc/n-pentane = 1:99); mp 49–50 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.49 (d, J = 8.5 Hz, 2 H), 7.37 (d, J = 8.4 Hz, 2 H), 6.79 (d, J = 2.7 Hz, 1 H), 6.77 (d, J = 8.5 Hz, 1 H), 6.72 (dd, J = 8.5, 2.7 Hz, 1 H), 1.26–1.21 (m, 3 H), 1.11–1.06 (m, 21 H), 0.94 (d, J = 7.2 Hz, 18 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 150.10, 147.18, 138.28, 132.24, 131.48, 131.02, 121.81, 120.92, 120.14, 119.71, 18.08, 17.96, 13.02, 12.76.

HRMS (EI): m/z [M]$^+$ calcd for C$_{30}$H$_{49}$O$_2$BrSi$_2$: 576.2449; found: 576.2467.

Anal. Calcd for C$_{30}$H$_{49}$O$_2$BrSi$_2$: C, 62.36; H, 8.55. Found: C, 62.24; H, 8.65.

4,4″-Dibromo-[1,1′:4′,1″-terphenyl]-1′,4′-diol (2a)

From p-Benzoquinone

We modified a literature procedure for the synthesis of **2a**.[16i] N-Butyllithium [CAS Reg. No. 109-72-8] (2.5 M in hexanes, 14.5 mL, 36.1 mmol, 2.6 equiv.) was added dropwise to a solution of 1,4-dibromobenzene [CAS Reg. No. 106-37-6] (9.18 g, 38.9 mmol, 2.8 equiv.) in THF (92 mL) at –78 °C. The reaction was stirred at this temperature for 30 min, before a solution of p-benzoquinone [CAS Reg. No. 106-51-4] (1.50 g, 13.9 mmol, 1 equiv.) in THF (32 mL) was added via cannula. The resulting reaction mixture was stirred at –78 °C for 1 h and then at room temperature for 15 h. The reaction was quenched with H$_2$O (50 mL), diluted with Et$_2$O (100 mL) and extracted with Et$_2$O (3 × 50 mL). The organic layers were combined, washed with brine (150 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo to afford a dark oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/n-pentane = 1:9 → EtOAc/n-pentane = 1:1) to afford **2a** as a beige solid (2.95 g, 7.0 mmol, 50%). The spectral data match the literature-reported values.[23]

From Compound 2c

1363

Synthesis   R. B. Kręcijasz et al.   Special Topic

Tetrabutylammonium fluoride [CAS Reg. No. 429-41-4] (1 M solution in THF, 0.161 mL, 0.161 mmol, 2.5 equiv.) was added to a solution of **2c** (42.0 mg, 0.065 mmol, 1 equiv.) in THF (1 mL). The reaction mixture was stirred at room temperature for 2.5 h. The reaction was quenched with H_2O (5 mL), extracted with EtOAc (3 × 5 mL) and concentrated in vacuo to afford a yellow oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 3:7 → EtOAc/*n*-pentane = 2:3) to afford **2a** as a white solid (19.8 mg, 0.047 mmol, 73%).

From Compound 2e

Tetrabutylammonium fluoride (1 M solution in THF, 0.384 mL, 0.384 mmol, 2.5 equiv.) was added to a solution of **2e** (100.0 mg, 0.154 mmol, 1 equiv.) in THF (2.5 mL). The reaction mixture was stirred at room temperature for 2.5 h. The reaction was quenched with H_2O (5 mL), extracted with EtOAc (3 × 5 mL) and concentrated in vacuo to afford a colorless oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:9 → EtOAc/*n*-pentane = 1:1) to afford **2a** as a white solid (53.6 mg, 0.127 mmol, 83%).

Beige solid; R_f = 0.34 (SiO$_2$, EtOAc/*n*-pentane = 1:1); mp 141–142 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.48 (d, *J* = 8.6 Hz, 4 H), 7.29 (d, *J* = 8.6 Hz, 4 H), 6.04 (s, 4 H), 2.25 (s, 2 H).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 7.48 (d, *J* = 8.6 Hz, 4 H), 7.31 (d, *J* = 8.6 Hz, 4 H), 6.03 (s, 4 H), 2.34 (s, 2 H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ = 143.46, 132.34, 131.97, 127.81, 121.94, 69.32.

HRMS (NSI): *m/z* [M – H]$^+$ calcd for C$_{18}$H$_{13}$O$_2$Br$_2$: 418.9288; found: 418.9275.

Anal. Calcd for C$_{18}$H$_{14}$O$_2$Br$_2$: C, 51.22; H, 3.34. Found: C, 51.46; H, 3.36.

((4,4″-Dibromo-[1,1′:4′,1″-terphenyl]-1′,4-diyl)bis(oxy))bis(triethylsilane) (2b)

We adapted a literature procedure for the synthesis of **2b**.[1f] Chlorotriethylsilane (2.1 mL, 12.8 mmol, 3 equiv.) was added to a solution of **2a** (1.80 g, 4.3 mmol, 1 equiv.) and imidazole (1.16 g, 17.0 mmol, 4 equiv.) in DMF (16 mL). The reaction mixture was stirred at 40 °C for 12 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (15 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with saturated aqueous NaHCO$_3$ solution (100 mL), H_2O (2 × 100 mL) and brine (100 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo to afford an orange oil. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane → EtOAc/*n*-pentane = 1:19) to afford **2b** as a white solid (2.14 g, 3.3 mmol, 77%). The spectral data match the literature-reported values.[16i]

White solid; R_f = 0.35 (SiO$_2$, *n*-pentane); mp 63–64 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39 (d, *J* = 8.6 Hz, 4 H), 7.18 (d, *J* = 8.7 Hz, 4 H), 5.96 (s, 4 H), 0.93 (t, *J* = 7.9 Hz, 18 H), 0.60 (q, *J* = 7.9 Hz, 12 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 145.11, 131.56, 131.41, 127.76, 121.46, 71.25, 7.15, 6.57.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{30}$H$_{42}$O$_2$Br$_2$Si$_2$: 648.1085; found: 648.1103.

Anal. Calcd for C$_{30}$H$_{42}$O$_2$Br$_2$Si$_2$: C, 55.38; H, 6.51. Found: C, 55.35; H, 6.47.

4,4″-Dibromo-4′-((triethylsilyl)oxy)-[1,1′:4′,1″-terphenyl]-1′(4′H)-ol (6b)

n-Butyllithium (2.5 M in hexanes, 0.221 mL, 0.553 mmol, 1.95 equiv.) was added dropwise to a solution of 1,4-dibromobenzene (134.0 mg, 0.567 mmol, 2 equiv.) in THF (1 mL) at –78 °C. The reaction was

stirred at this temperature for 30 min, before a solution of **1b** (107.6 mg, 0.284 mmol, 1 equiv.) in THF (1 mL) was added via cannula. The resulting reaction mixture was stirred at –78 °C for 2 h. The reaction was quenched with EtOH (1 mL) and after the addition of H_2O (5 mL), the organic phases were extracted with EtOAc (3 × 10 mL). The organic layers were combined and concentrated in vacuo to afford an orange oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:19) to afford **6b** as a colorless oil (93.6 mg, 0.175 mmol, 62%).

Colorless oil; R_f = 0.16 (SiO$_2$, EtOAc/*n*-pentane = 1:19).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.48 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 2 H), 7.22 (d, *J* = 8.6 Hz, 2 H), 5.99 (d, *J* = 10.5 Hz, 2 H), 5.97 (d, *J* = 10.5 Hz, 2 H), 0.99 (t, *J* = 7.9 Hz, 9 H), 0.68 (q, *J* = 7.9 Hz, 6 H).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.49 (d, *J* = 8.6 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H), 6.00 (s, 4 H), 0.99 (t, *J* = 7.9 Hz, 9 H), 0.69 (q, *J* = 8.0 Hz, 6 H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ = 145.29, 143.91, 133.36, 131.95, 131.66, 131.10, 127.97, 127.83, 121.95, 121.45, 71.52, 69.36, 7.20, 6.81.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{24}$H$_{28}$O$_2$Br$_2$Si: 534.0220; found: 534.0232.

Anal. Calcd for C$_{24}$H$_{28}$O$_2$Br$_2$Si: C, 53.74; H, 5.26. Found: C, 53.79; H, 5.26.

((4,4″-Dibromo-[1,1′:4′,1″-terphenyl]-1′,4-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (2c)

To a solution of **2a** (100.0 mg, 0.237 mmol, 1 equiv.) in DMF (4 mL) was added 2,6-lutidine (0.166 mL, 1.42 mmol, 6 equiv.), followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.272 mL, 1.18 mmol, 5 equiv.). The reaction mixture was stirred at 50 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with H_2O (2 × 30 mL) and concentrated in vacuo to afford a white solid. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane) to afford **2c** as a white solid (108.1 mg, 0.166 mmol, 70%).

White solid; R_f = 0.36 (SiO$_2$, *n*-pentane); mp 161–162 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.40 (d, *J* = 8.6 Hz, 4 H), 7.20 (d, *J* = 8.6 Hz, 4 H), 5.96 (s, 4 H), 0.94 (s, 18 H), 0.04 (s, 12 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 145.05, 131.51, 131.44, 127.75, 121.48, 71.34, 26.00, 18.50, –2.17.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{30}$H$_{42}$O$_2$Br$_2$Si$_2$: 648.1085; found: 648.1107.

Anal. Calcd for C$_{30}$H$_{42}$O$_2$Br$_2$Si$_2$: C, 55.38; H, 6.51. Found: C, 55.35; H, 6.47.

tert-Butyl((4,4″-dibromo-[1,1′:3′,1″-terphenyl]-4′-yl)oxy)dimethylsilane (5c)

From compound 2a

To a solution of **2a** (25.0 mg, 0.059 mmol, 1 equiv.) in DMF (1 mL) was added 2,6-lutidine (0.083 mL, 0.710 mmol, 12 equiv.), followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.136 mL, 0.592 mmol, 10 equiv.). The reaction mixture was stirred at 100 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with H_2O (2 × 30 mL) and concentrated in vacuo to afford a brown solid. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane → EtOAc/*n*-pentane = 1:99) to afford **5c** as a white solid (23.3 mg, 0.045 mmol, 76%).

1364

Synthesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   Special Topic

From Compound 2c with TBDMSOTf

tert-Butyldimethylsilyl trifluoromethanesulfonate (0.177 mL, 0.768 mmol, 10 equiv.) was added to a solution of **2c** (50.0 mg, 0.077 mmol, 1 equiv.) in DMF (2 mL). The reaction mixture was stirred at 100 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford a colorless waxy solid. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane) to afford **5c** as a white solid (32.1 mg, 0.064 mmol, 83%).

From Compound 2c with TfOH

Triflic acid [CAS Reg. No. 1493-13-6] (0.08 M in DMF, 0.096 mL, 0.1 equiv.) was added to a solution of **2c** (50.0 mg, 0.077 mmol, 1 equiv.) in DMF (2 mL). The reaction mixture was stirred at 100 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford a white solid. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane → EtOAc/*n*-pentane = 1:19) to afford **5c** as a white solid (32.4 mg, 0.065 mmol, 84%).

White solid; R_f = 0.26 (SiO$_2$, *n*-pentane); mp 101–102 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.54 (d, *J* = 8.6 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.46–7.39 (m, 6 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 0.85 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 152.59, 139.65, 137.93, 133.62, 132.74, 131.99, 131.56, 131.21, 129.30, 128.50, 127.23, 121.28, 121.20, 120.96, 25.73, 18.26, –4.29.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{24}$H$_{26}$OBr$_2$Si: 516.0114; found: 516.0118.

Anal. Calcd for C$_{24}$H$_{26}$OBr$_2$Si: C, 55.61; H, 5.06. Found: C, 55.73; H, 5.26.

4,4″-Dibromo-4′-((*tert*-butyldimethylsilyl)oxy)-[1,1′:4′,1″-terphenyl]-1′(4′*H*)-ol (6c)

With TBAF

Tetrabutylammonium fluoride (1 M solution in THF, 0.231 mL, 0.231 mmol, 1.5 equiv.) was added to a solution of **2e** (100.0 mg, 0.154 mmol, 1 equiv.) in THF (5 mL) at –45 °C. The reaction mixture was stirred at this temperature for 2.5 h. The reaction was quenched with H$_2$O (5 mL), extracted with EtOAc (3 × 5 mL) and concentrated in vacuo to afford a colorless oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:19 → EtOAc/*n*-pentane = 1:9) to afford **6c** as a white solid (62.9 mg, 0.117 mmol, 76%).

With K$_2$CO$_3$

A solution of **2e** (100.0 mg, 0.154 mmol, 1 equiv.) and K$_2$CO$_3$ [CAS Reg. No. 584-08-7] (212.0 mg, 1.54 mmol, 10 equiv.) in MeOH (3 mL) was stirred at 65 °C for 18 h. After cooling to room temperature, the reaction mixture was diluted with H$_2$O (10 mL), extracted with EtOAc (3 × 10 mL) and concentrated in vacuo to afford a colorless oil. The crude product was purified by flash chromatography (SiO$_2$, EtOAc/*n*-pentane = 1:9) to afford **6c** as a white solid (67.7 mg, 0.126 mmol, 82%).

White solid; R_f = 0.15 (SiO$_2$, EtOAc/*n*-pentane = 1:19); mp 63–64 °C.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.49 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 6.00 (d, *J* = 10.1 Hz, 2 H), 5.96 (d, *J* = 10.1 Hz, 2 H), 2.06 (s, 1 H), 0.96 (s, 9 H), 0.17 (s, 6 H).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.49 (d, *J* = 8.6 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 6.01 (d, *J* = 10.5 Hz, 2 H), 5.99 (d, *J* = 10.5 Hz, 2 H), 2.18 (s, 1 H), 0.96 (s, 9 H), 0.18 (s, 6 H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ = 145.30, 143.96, 133.40, 131.96, 131.68, 131.08, 127.97, 127.84, 121.97, 121.46, 71.73, 69.44, 25.99, 18.68, –2.14.

HRMS (EI): *m/z* [M – H$_2$O]$^+$ calcd for C$_{24}$H$_{26}$OBr$_2$Si: 516.0114; found: 516.0127.

Anal. Calcd for C$_{24}$H$_{28}$O$_2$Br$_2$Si: C, 53.74; H, 5.26. Found: C, 53.65; H, 5.24.

((4,4″-Dibromo-[1,1′:3′,1″-terphenyl]-4′-yl)oxy)triisopropylsilane (5d)

See compound **6d** for the procedure. Alternatively, **5d** was obtained in a higher purity and yield according to the procedure below.

To a solution of **2a** (49.8 mg, 0.118 mmol, 1 equiv.) in DMF (2 mL) was added 2,6-lutidine (0.110 mL, 0.944 mmol, 8 equiv.), followed by triisopropylsilyl trifluoromethanesulfonate (0.222 mL, 0.826 mmol, 7 equiv.). The reaction mixture was stirred at 100 °C for 16.5 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford a yellow oil. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane) to afford **5d** as a colorless oil (56.3 mg, 0.100 mmol, 85%).

Colorless oil; R_f = 0.24 (SiO$_2$, *n*-pentane).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.53 (d, *J* = 8.7 Hz, 2 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.46–7.38 (m, 6 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 1.19–1.14 (m, 3 H), 1.00 (d, *J* = 7.3 Hz, 18 H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 153.05, 139.62, 138.05, 133.01, 132.27, 131.96, 131.50, 131.11, 129.32, 128.41, 127.15, 121.18, 121.09, 119.88, 18.00, 13.10.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{27}$H$_{32}$OBr$_2$Si: 558.0584; found: 558.0602.

Anal. Calcd for C$_{27}$H$_{32}$OBr$_2$Si: C, 57.86; H, 5.76. Found: C, 57.82; H, 5.58.

4,4″-Dibromo-4′-((triisopropylsilyl)oxy)-[1,1′:4′,1″-terphenyl]-1′(4′*H*)-ol (6d)

To a solution of **2a** (100.0 mg, 0.237 mmol, 1 equiv.) in DMF (4 mL) was added 2,6-lutidine (0.166 mL, 1.43 mmol, 6 equiv.), followed by triisopropylsilyl trifluoromethanesulfonate (0.318 mL, 1.18 mmol, 5 equiv.). The reaction mixture was stirred at 50 °C for 18 h. The reaction was quenched with saturated aqueous NaHCO$_3$ solution (5 mL), extracted with EtOAc (3 × 10 mL), washed with H$_2$O (2 × 30 mL) and concentrated in vacuo to afford a yellow oil. The crude product was purified by flash chromatography (SiO$_2$, *n*-pentane → EtOAc/*n*-pentane = 1:1) to afford **5d** as a colorless oil (8.1 mg, 0.015 mmol, 6%), **6d** as a colorless oil (53.0 mg, 0.092 mmol, 39%) and **2a** as a white solid (35.0 mg, 0.083 mmol, 35%).

Colorless oil; R_f = 0.53 (SiO$_2$, EtOAc/*n*-pentane = 1:9).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.48 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 2 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 9.4 Hz, 2 H), 6.01 (d, *J* = 10.1 Hz, 2 H), 5.99 (d, *J* = 10.1 Hz, 2 H), 1.19–1.12 (m, 3 H), 1.09 (d, *J* = 5.0 Hz, 18 H).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 7.48 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.28 (d, *J* = 8.7 Hz, 2 H), 6.05 (d, *J* = 10.3 Hz, 2 H), 6.00 (d, *J* = 10.2 Hz, 2 H), 2.14 (s, 1 H), 1.19–1.12 (m, 3 H), 1.09 (d, *J* = 5.2 Hz, 18 H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ = 145.41, 143.73, 133.33, 131.93, 131.65, 131.07, 128.02, 127.95, 121.95, 121.49, 71.68, 69.34, 18.63, 13.78.

HRMS (EI): *m/z* [M – H$_2$O]$^+$ calcd for C$_{27}$H$_{32}$OBr$_2$Si: 558.0584; found: 558.0602.

1365

Synthesis   R. B. Kręcijasz et al.   THIEME OPEN ACCESS   Special Topic

Anal. Calcd for $C_{27}H_{34}O_2Br_2Si$: C, 56.06; H, 5.92. Found: C, 56.06; H, 5.86.

tert-Butyl((4,4″-dibromo-4′-((triethylsilyl)oxy)-[1,1′:4′,1″-terphenyl]-1′(4′*H*)-yl)oxy)dimethylsilane (2e)

n-Butyllithium (2.5 M in hexanes, 2.62 mL, 6.55 mmol, 1.95 equiv.) was added dropwise to a solution of 1,4-dibromobenzene (1.58 g, 6.72 mmol, 2 equiv.) in THF (13 mL) at –78 °C. The reaction was stirred at this temperature for 30 min, before a solution of **1c** (1.27 g, 3.36 mmol, 1 equiv.) in THF (13 mL) was added via cannula. The resulting reaction mixture was stirred at –78 °C for 2 h. The reaction was quenched with MeOH (20 mL) and the solvents were removed in vacuo. To the residue was added H_2O (15 mL) and the organic phases were extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined and concentrated in vacuo to afford an orange oil that was used in the next step without further purification.

Chlorotriethylsilane (1.69 mL, 10.10 mmol, 3 equiv.) was added to a solution of the obtained oily crude product and imidazole (0.686 g, 10.10 mmol, 3 equiv.) in DMF (13 mL). The reaction mixture was stirred at room temperature for 17 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with EtOAc (3 × 20 mL). The organic layers were combined, washed with H_2O (2 × 50 mL), brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a yellow oil. The crude product was purified by flash chromatography (SiO_2, *n*-pentane) to afford **2e** as a white solid (1.71 g, 3.36 mmol, 78%).

White solid; R_f = 0.32 (SiO_2, *n*-pentane); mp 68–69 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.7 Hz, 2 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 7.20 (d, *J* = 8.7 Hz, 2 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 5.98 (d, *J* = 10.2 Hz, 2 H), 5.94 (d, *J* = 10.2 Hz, 2 H), 0.96–0.92 (m, 18 H), 0.62 (q, *J* = 7.9 Hz, 6 H), 0.01 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.11, 145.06, 131.63, 131.45, 131.41, 131.41, 127.82, 127.69, 121.52, 121.41, 71.30, 71.28, 25.96, 18.50, 7.17, 6.57, –2.27.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{30}H_{42}O_2Br_2Si_2$: 648.1085; found: 648.1105.

Anal. Calcd for $C_{30}H_{42}O_2Br_2Si_2$: C, 55.38; H, 6.51. Found: C, 55.57; H, 6.56.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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