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# Click Approaches to Functional Water-Sensitive Organotriethoxysilanes

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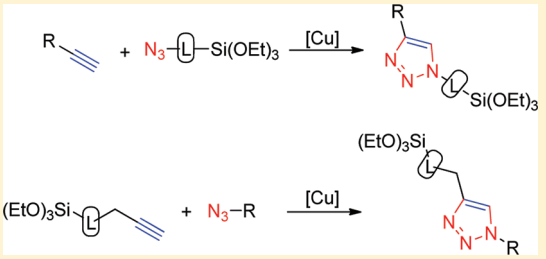
Supporting Information

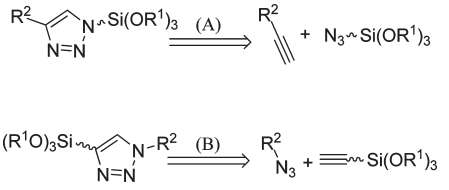
**ABSTRACT:** The derivatization of functional organic fragments with triethoxysilyl groups to afford hydrolyzable organosilanes with targeted properties using the copper-catalyzed alkyne azide cycloaddition reaction under strictly anhydrous conditions is described according to two approaches, starting from five silylated substrates. This high yield, fast, and selective method is applicable to a wide range of substrates and is expected to lead to important achievements in the field of functional hybrid silica.




## INTRODUCTION

Functional organosilicas are promising materials for applications in diverse fields such as optics,[1−3] coatings,[4] separation,[5] drug delivery,[6] or supported catalysis.[7−9] Organotrialkoxysilanes are key intermediates for the synthesis of such hybrid materials. These can be formed either directly from molecular precursors using the sol−gel process or by postfunctionalizing a preformed material (grafting). Since organotrialkoxysilanes are moisture sensitive, it is preferable to functionalize the organic fragment with a trialkoxysilyl group in the late steps of the synthesis. For this reason, it is desirable to use reactions affording the compounds with easy purification steps that can be performed under anhydrous conditions and avoid any chromatographic separation. Therefore, elaborated functional organotriethoxysilanes are often prepared by hydrosilylation or rhodium-catalyzed silylation of aromatic halides using triethoxysilane, by formation of tertiary amines from 3-aminopropyltriethoxysilane (APTES) or 3-chloropropyltriethoxysilane (ClPTES), or by formation of urea and carbamate linkers using 3-isocyanatopropyltriethoxysilane (ICPTES). Alternatively, the addition of organometallic reagents to tetrachlorosilane followed by alcoholysis has already been described, but it usually leads to complicated mixtures from which the compound can only be extracted by distillation or by crystallization. Despite the variety of the already existing synthetic methods and reagents, some substrates are still challenging, as the triethoxysilyl moiety is incompatible with various chemical functions (such as alcohols[10] and acids[11]), as some 1,6-diene groups usually yield cyclic byproducts using radical or organometallic chemistry, and as the use of hydrosilanes can also lead to a partial reduction of the double bonds. The rapid development of the copper-catalyzed alkyne azide cycloaddition reaction (CuAAC) in bio-organic, polymer, and materials chemistry[12] prompted us to envisage its use to link an organic function bearing a triple bond with an alkyltriethoxysilane moiety using this click reaction.[13] Applying microwave activation, a very fast and selective method was developed that yields organotriethoxysilanes in high yield and purity with only simple

**Scheme 1. Two Retrosynthetic Approaches to Organotrialkoxysilanes Using the Click Reaction**




**Scheme 2. Silylated Substrates Containing Functionalities That Can Undergo Click Reactions**

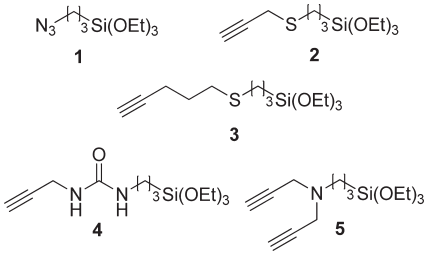



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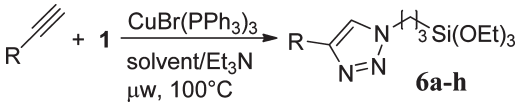
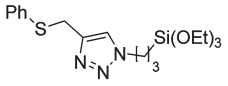
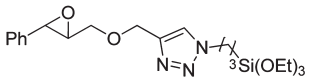
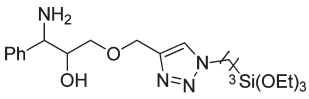
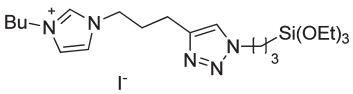
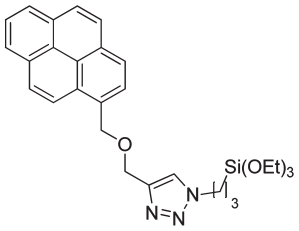
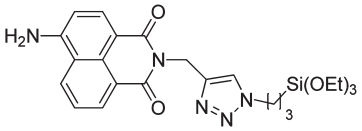
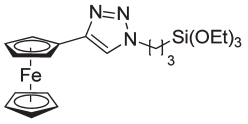
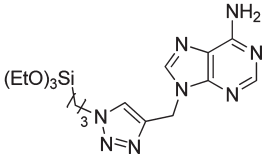
**Table 1. Reaction of AzPTES 1 with Functional Alkynes**[a]



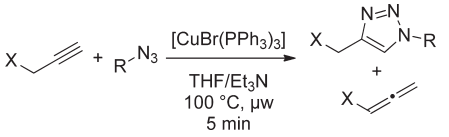

**6a-h**

| | Product | | Yield (%) |
|---|---|---|---|
| 1[b] |  | **6a** | 95 |
| 2 |  | **6b** | 95 |
| 3 |  | **6c** | 90 |
| 4[c] |  | **6d** | 91 |
| 5 |  | **6e** | 95 |
| 6[d] |  | **6f** | 68 |
| 7[e] |  | **6g** | 94 |
| 8 |  | **6h** | 96 |

[a] Reaction conditions: alkyne (2 mmol), azide (2 mmol), $CuBr(PPh_3)_3$ (0.01 mmol), $THF/Et_3N$ 1:1 (1 mL), microwave, 100 °C, 5 min. [b] 0.02 mmol of $CuBr(PPh_3)_3$, reaction time: 10 min. [c] 0,05 mmol of $CuBr(PPh_3)_3$, reaction time: 1 h. [d] DMF was used instead of THF, reaction time: 10 min. [e] Reaction time: 10 min.

extraction and filtration workup procedures. With this method, the triethoxysilyl groups could be incorporated into challenging substrates, allowing the formation of new types of organotriethoxysilanes. A similar synthesis was very recently used for preparing sol−gel precursors bearing fluorescent functional groups.[14] In this paper, we will describe the scope of this first method (retrosynthesis (A), Scheme 1), and develop the complementary retrosynthetic approach (B). In particular, we will focus on triethoxysilyl substrates (Scheme 2) containing functionalities (azide or terminal alkyne) that can undergo click reactions to give new organosilanes, precursors of hybrid silicas that can be used for several interesting applications such as optics, biomaterials, and catalysis.

**Scheme 3**




**Scheme 4**

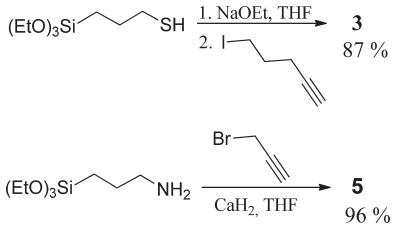
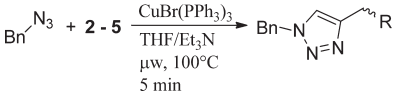



**Table 2. Evaluation of the Alkyne-Based Precursors for the Click Reaction**[a]




| | substrate | catalyst loading (%) | conversion (%) |
|---|---|---|---|
| 1 | **2** | 0.5 | 60 |
| 2 | **3** | 0.5 | 0 |
| 3 | **3** | 2 | 50 |
| 4 | **3** | 2.5 | 100 |
| 5 | **4** | 0.5 | 100 |
| 6 | **5** | 0.5 | 100 |

[a] Alkyne (2 mmol), azide (2 mmol), $CuBr(PPh_3)_3$, $THF/Et_3N$ 1:1 (1 mL), microwave, 100 °C, 5 min.

## RESULTS AND DISCUSSION

Considering the first retrosynthesis, which implies the reaction of 3-azidopropyltriethoxysilane **1** (AzPTES)[15,16] with organic alkynes, our preliminary report[13] described an efficient transformation that can be carried out in 5 min under microwave conditions. This method was proven to be compatible with several functionalities, such as amine (from primary to tertiary), N-heterocycle, alcohol, diol, ether, and ester. As seen in Table 1, the scope can be extended to other functional groups showing the versatility of the method. In all cases, full conversion was obtained (as determined by $^1H$ NMR). Indeed, a thioether derivative that is known to poison catalysts can be incorporated, although slightly more catalyst amount and reaction time was necessary (entry 1). The epoxide functionality can also be preserved thanks to the anhydrous conditions (entry 2).[17] The obtained phenylglycidol ether may subsequently be functionalized to afford chiral catalysts such as bis(oxazolines),[18,19] phosphinite


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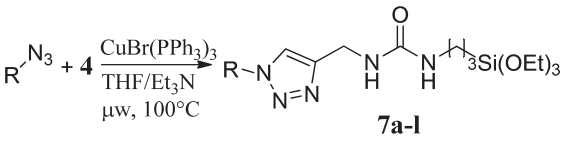
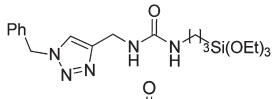
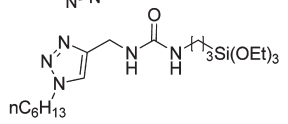
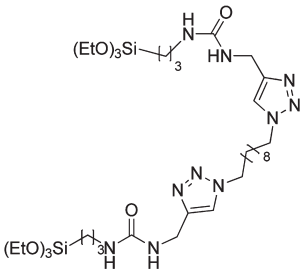
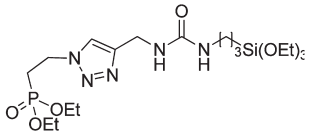
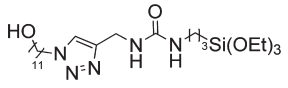
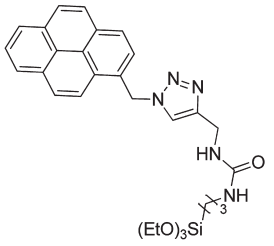
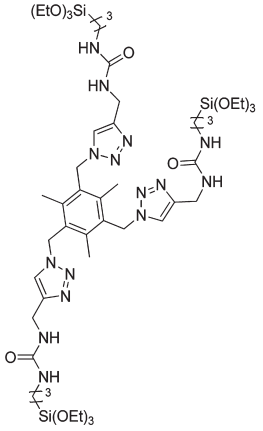
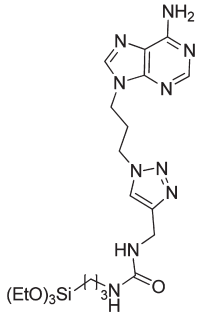
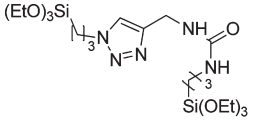
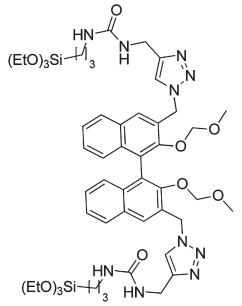
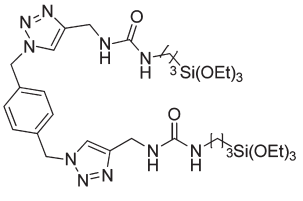
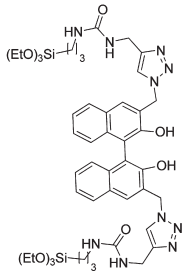
**Table 3. Reaction of 4 with azides** [a]




| | Product | | Yield (%) | | Product | | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 |  | **7a** | 94 | | | | |
| 2 |  | **7b** | 93 | 9 |  | **7i** | 91 |
| 3 |  | **7c** | 94 | | | | |
| 4 |  | **7d** | 96 | | | | |
| 5 |  | **7e** | 83 | 10 |  | **7j** | 96 |
| 6 [b] |  | **7f** | 93 | | | | |
| 7 |  | **7g** | 96 | 11 [b] |  | **7k** | 93 |
| 8 |  | **7h** | 90 | | | | |
| | | | | 12 [b] |  | **7l** | 89 |

[a] Reaction conditions: alkyne (2 mmol), azide (2 mmol), $CuBr(PPh_3)_3$ (0.01 mmol), $THF/Et_3N$ 1: 1 (1 mL), microwave, 100 °C, 5 min. [b] Reaction time: 10 min


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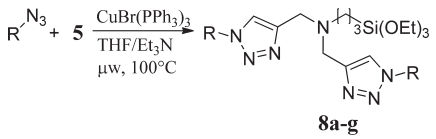
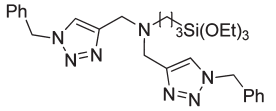
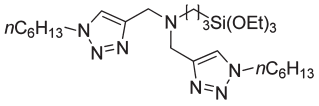
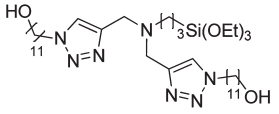
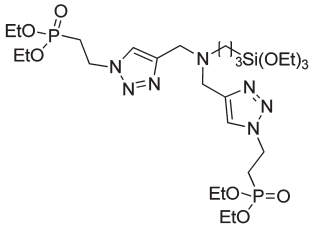
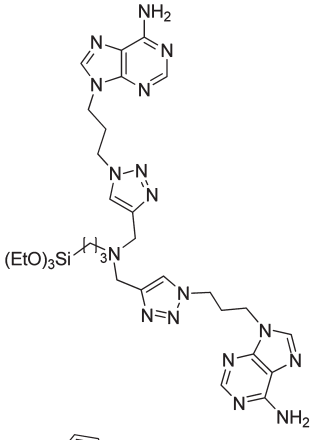
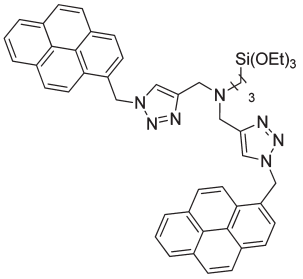
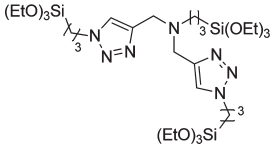
**Table 4. Reaction of 5 with Azides**[a]




**8a-g**

| | Product | | Yield (%) |
|---|---|---|---|
| 1 |  | **8a** | 94 |
| 2 |  | **8b** | 91 |
| 3 |  | **8c** | 84 |
| 4 |  | **8d** | 91 |
| 5[b] |  | **8e** | 90 |
| 6 |  | **8f** | 92 |
| 7 |  | **8g** | 88 |

[a] Reaction conditions: alkyne (2 mmol), azide (2 mmol), $CuBr(PPh_3)_3$ (0.01 mmol), $THF/Et_3N$ 1:1 (1 mL), microwave, 100 °C, 5 min. [b] Reaction time: 20 min.

thioethers,[20] or $\beta$-amino alcohols.[21] Notably, the click alkylsilylation can be performed on a preformed amino alcohol derivative[19] (entry 3). Imidazolium salts are also very important in catalysis, as they can form NHC complexes or act as organocatalysts. Therefore, we first performed this click functionalization on propargyl(methyl)imidazolium iodide. However, under the standard reaction conditions, a 1:1 mixture of the expected organosilane and allene resulting from the isomerization of the propargyl group, was observed (Scheme 3). To circumvent this issue, a pent-4-ynyl group was used (entry 4). Although the reaction was slow, full conversion could be attained. However, because of the high loading of catalyst used, the product was contaminated with triphenylphosphine oxide (ca. 15%).[13] We then focused our efforts on the synthesis of silylated dyes that are useful for a wide range of applications (in sensing, labeling...).[22] Pyrene and aminonaphthalimide[23] derivatives could be easily functionalized (entries 5 and 6). Because of the low solubility of the starting compound, the latter reaction was performed with full conversion in anhydrous DMF, without any important change in the reaction conditions. Furthermore, the electroactive ferrocene derivative could be selectively functionalized (entry 7). This silylation method also allows an alternative approach to adenine-based sol–gel precursors (entry 8) for the synthesis of bio-inspired materials.[24]

Following this first retrosynthetic approach, we considered further developing the click approach to sol–gel precursors with the triethoxysilyl group linked to the terminal triple bond. Indeed, it is sometimes easier to incorporate an azide group rather than an alkyne function on a functional organic fragment. The design and preparation of four silylated terminal alkynes were thus proposed through various linkers (Schemes 2 and 4).

Thioether derivatives **2** (Scheme 2) and **3** were obtained by alkylation of 3-triethoxysilylpropylthiolate with propargyl bromide[25] or 5-iodopent-1-yne, respectively (Scheme 4). The previously reported silylated substrate with a ureido linker, **4** (Scheme 2), was also used.[26] Moreover, (3-di(prop-2-yn-1-yl)aminopropyl)triethoxysilane **5** with two alkynyl functions located in close proximity was synthesized by reaction of APTES with propargyl bromide in the presence of a base. These four precursors were then evaluated as potential candidates for the click-alkylsilylation reaction with benzyl azide under the standard conditions (Table 2). With **2**, the conversion observed was only 60% (entry 1), probably due to a deactivation of the catalyst by the thioether function (as seen in Table 1 entry 1). Furthermore, besides the expected coupling product, the isomerized allene (ca. 10%) was also observed (Scheme 3). A blank reaction performed with neither catalyst nor azide evidenced the partial formation of the allene with 11% conversion. To prevent this side reaction, a longer chain was used: a 2.5% catalyst loading was necessary to fully convert compound **3** under the same conditions (entries 2–4). Much better results were achieved with compounds **4** and **5** that lead to complete transformations under the standard conditions (entries 5 and 6).

The urea functional group is capable of forming hydrogen bonding, and therefore, its presence in the precursor molecule can induce a nanostructuring of the material that is obtained upon a sol–gel hydrolysis/condensation process from organotrialkoxysilane precursors.[27−29] For that reason, we studied the use of **4** to produce organotrialkoxysilanes containing the urea group. Reaction of **4** with different azides has been selected as

promising tool in this screening with the aim to produce organotrialkoxysilanes possessing either one or more urea groups or having both urea and the other functional group in the molecule. The results are reported in Table 3.

The production of monosilylated sol−gel precursors was first examined: the benzyl and hexyl adducts could be obtained in excellent yields (Table 3, entries 1 and 2); functional groups such as diethylphosphonate or hydroxyl are compatible with this reaction (entries 3 and 4). In addition, pyrene and adenine derivatives **7e** and **7f** could also be easily obtained (entries 5 and 6). These results demonstrate that both retrosynthetic approaches (Scheme 1) can be employed to produce these important families of functional sol−gel precursors (**6e** and **7e**; **6h** and **7f**).[22] Moreover, polysilylated precursors, which can yield self-organized bridged silsesquioxanes by sol−gel reactions,[27−29] can also be formed. The dissymmetrical bridged organosilane **7g** was obtained by reaction of **1** with **4** (entry 7), whereas symmetrical compounds can be synthesized from polyazides (entries 8−10). Similarly, BINOL-derived bridged organosilanes (MOM-protected or unprotected) were obtained (entries 11 and 12) with foreseen uses in supported asymmetric catalysis.[30,31]

As the H-bonding urea groups may interfere in the catalytic or optical properties of the materials derived from **4**, we investigated the reactivity of **5**, which lacks a self-assembling group, in the click-alkylsilylation reaction (Table 4). As above, the reactions proceed with full conversion and excellent yield under the standard conditions despite the increased steric hindrance (Table 4). In this case, the reaction with polyazides would lead to mixed oligomers, precluding the production of bridged systems.[32]

## CONCLUSION

In conclusion, the CuAAC-alkylsilylation reaction appears as an efficient, flexible, and wide-scope methodology for the synthesis of organotrialkoxysilanes with targeted functionalities. In addition to our previous report,[13] we have reported here several new clickable alkyne−containing trialkoxysilanes for the complementary retrosynthesis. These tools open new perspectives in the field of functional organosilicas for a wide range of applications. In addition, they may be extended to the design of new functional silicone polymers. The set of clickable trialkoxysilane sol−gel precursors that is herein described will also allow obtaining new functionalizable organosilicas[15,16,33] (e.g., as nanoparticles[25] and thin films) for the development of supported catalysts,[34] sensors,[22] and nanomachines for drug delivery.[35]

## EXPERIMENTAL SECTION

**Caution.** Azide compounds are potentially explosive. Great care and protection are needed for heating of these compounds.

**General Methods.** All of the manipulations were carried out using Schlenk techniques under a dry atmosphere of nitrogen. Microwave reactions were carried out in sealed tubes using a microwave reactor equipped with an infrared temperature sensor. NMR spectra were recorded in dry $CDCl_3$ at 298 K. $^1H$ and $^{13}C$ chemical shifts are reported in ppm relative to $Me_4Si$, and $^{31}P$ chemical shifts are reported in ppm relative to $H_3PO_4$. Organosilanes **1**,[15,16] **2**,[25] **4**,[26] phenylglycidol propargyl ether,[19] 1-amino-1-phenyl-3-(prop-2-yn-1-yloxy)propan-2-ol,[19] (2*S*,4*R*)-dibenzyl 4-(prop-2-yn-1-yloxy)pyrrolidine-1,2-dicarboxylate,[36] 1-butyl-3-(4-pentynyl)imidazolium iodide,[37] 1-(propargyloxymethyl)pyrene,[38] *N*-(propargyl)-4-amino-1,8-naphthalimide,[23] 9-propargyladenine,[39] (2-azidoethyl) diethyl phosphonate,[40] 1-(azidomethyl)pyrene[41] 9-(3-chloropropyl)adenine,[42] hexyl azide,[43] 1,4-bis(azidomethyl)benzene,[43] 1,8-diazidodecane,[43] and 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene[44] were prepared according to published procedures.

**(3-(Pent-4-yn-1-ylthio)propyl)triethoxysilane (3).** To a solution of sodium hydride (95 wt %, 445 mg, 20.0 mmol) in dry THF (100 mL) at −40 °C was added dry ethanol (920 mg, 20.0 mmol). After 20 min, 3-mercaptopropyltriethoxysilane (4.76 g, 20 mmol) was added. The reaction mixture was brought to rt, stirred for 2 h, and was then added dropwise to a solution of 5-iodopent-1-yne (3.86 g, 20.0 mmol) in dry THF (50 mL). The mixture was left overnight at room temperature. The solvent was distilled off and the residue extracted with dry pentane (3 × 15 mL). Concentration of the pentane fractions yielded pure compound **3** as a yellowish oil (5.29 g, 17.4 mmol). Yield: 87%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 3.80 (q, $J$ = 7.0 Hz, 6H), 2.60 (t, $J$ = 7.2 Hz, 2H), 2.52 (t, $J$ = 7.4 Hz, 2H), 2.30 (dt, $J$ = 2.6 and 6.7 Hz, 2H), 1.95 (t, $J$ = 2.6 Hz, 1H), 1.84−1.64 (m, 4H), 1.21 (t, $J$ = 7.0 Hz, 9H), 0.76−0.69 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 83.6, 68.6, 58.4, 35.0, 30.7, 28.3, 18.3, 17.5, 9.9. HRMS (ESI$^+$): calcd for $C_{14}H_{28}O_3SiSNa$ 327.1426, found 327.1426.

**(3-Di(prop-2-yn-1-yl)aminopropyl)triethoxysilane (5).** To a solution of 3-aminopropyltriethoxysilane (6.64 g, 30.0 mmol) in dry THF (100 mL) were added calcium hydride (6.30 g, 150 mmol) and propargyl bromide (80 wt % in toluene, 7.85 g, 66.0 mmol) successively. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvents, extraction of the reaction mixture with pentane and evaporation, compound **5** was obtained as a yellowish viscous oil (8.57 g, 28.8 mmol). Yield: 96%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 3.80 (q, $J$ = 7.0 Hz, 6H), 3.43 (d, $J$ = 2.5 Hz, 4H), 2.50 (t, $J$ = 7.5 Hz, 2H), 2.20 (t, $J$ = 2.5 Hz, 2H), 1.62−1.52 (m, 2H), 1.21 (t, $J$ = 7.0 Hz, 9H), 0.65−0.58 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 77.8, 71.8, 57.3, 54.8, 41.0, 19.8, 17.3, 6.8. HRMS (ESI$^+$): calcd for $C_{15}H_{28}NO_3Si$ 298.1838, found 298.1831.

**General Procedure for the Click Reaction.** A microwave tube was filled under nitrogen with alkyne (2 mmol), azide (2 mmol/alkyne function), [$CuBr(PPh_3)_3$] (0.01 mmol/alkyne function), dry triethylamine (0.5 mL), and dry THF (0.5 mL) and then sealed. After 5 min under microwave irradiation at 100 °C (maximum power =200 W), the reaction mixture was allowed to cool, and then the solvents were removed under vacuum. After addition of dry pentane, the mixture was filtered, and then the filtrate was concentrated to afford the title compound.

**6a.** Yield: 95%. $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ = 7.44−7.07 (m, 6H), 4.27 (t, $J$ = 7.5 Hz 2H), 4.23 (s, 2H), 3.77 (q, $J$ = 7.0 Hz, 6H), 2.02−1.88 (m, 2H), 1.20 (t, $J$ = 7.0 Hz, 9H), 0.60−0.49 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 144.7, 135.6, 129.5, 129.0, 126.4, 122.1, 58.5, 52.4, 28.9, 24.2, 18.3, 7.3. HRMS (ESI$^+$): calcd for $C_{18}H_{30}N_3O_3SSi$ 396.1777, found 396.1776.

**6b.** Yield: 95%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 7.57 (s, 1H), 7.35−7.14 (m, 5H), 4.73−4.70 (m, 2H), 4.32 (t, $J$ = 7.2 Hz, 2H), 3.89 (dd, $J$ = 11.5 and 3.0 Hz, 1H), 3.79 (q, $J$ = 7.0 Hz, 6H), 3.78−3.75 (m, 1H), 3.64 (dd, $J$ = 11.5 and 5.4 Hz, 1H), 3.22−3.18 (m, 1H), 2.05−1.95 (m, 2H), 1.19 (t, $J$ = 7.0 Hz, 9H), 0.61−0.55 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 144.5, 136.8, 128.5, 128.2, 125.7, 122.6, 70.1, 64.8, 60.9, 58.5, 55.8, 52.4, 24.2, 18.3, 7.5. HRMS (ESI$^+$): calcd for $C_{21}H_{34}N_3O_5Si$ 436.2268, found 436.2252.

**6c.** Yield: 90%. $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ = 7.49 (s, 1H), 7.40−7.20 (m, 5H), 4.61 (s, 2H), 4.33 (t, $J$ = 7.2 Hz, 2H), 3.81 (q, $J$ = 7.0 Hz, 6H), 3.51 (br, 2H), 2.09−1.92 (m, 2H), 1.21 (t, $J$ = 7.0 Hz, 9H), 0.65−0.55 (m, 2H). (4H missing). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 144.3, 131.8, 128.1, 122.5, 64.3, 58.2, 52.2, 23.9, 18.0, 7.3. (3C missing). HRMS (ESI$^+$): calcd for $C_{21}H_{37}N_4O_5Si$ 453.2533, found 453.2540.

**6d.** Yield: 91%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 10.18 (s, 1H), 7.65 (d, $J$ = 1.5 Hz, 1H), 7.63 (s, 1H), 7.62 (d, $J$ = 1.5 Hz, 1H), 4.46 (t, $J$ = 7.0 Hz, 2H), 4.36−4.28 (m, 4H), 3.79 (q, $J$ = 7.0 Hz, 6H), 2.78 (t, $J$ = 7.0 Hz, 2H), 2.40−2.33 (m, 2H), 2.03−1.95 (m, 2H), 1.45−1.31 (m, 4H), 1.19 (t, $J$ = 7.0 Hz, 9H), 0.95 (t, $J$ = 7.4 Hz, 3H), 0.61−0.55 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 145.3, 123.0, 122.3, 121.9, 58.6, 52.6, 50.1, 49.1, 32.2, 30.0, 24.3, 21.9, 19.6, 18.4, 13.5, 7.6. HRMS (ESI$^+$): calcd for $C_{21}H_{40}N_5O_3Si$ 438.2900, found 438.2881.

**6e.** Yield: 95%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.31 (d, $J$ = 9.2 Hz, 1H), 8.19−8.06 (m, 4H), 8.05−7.94 (m, 4H), 7.50 (s, 1H), 5.28 (s, 2H), 4.80 (s, 2H), 4.30 (t, $J$ = 7.2 Hz, 2H), 3.80 (q, $J$ = 7.0 Hz, 6H), 2.05−1.95 (m, 2H), 1.20 (t, $J$ = 7.0 Hz, 9H), 0.63−0.56 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 145.1, 131.4, 131.2, 131.0, 130.8, 129.4, 127.8, 127.5, 127.4, 127.2, 125.9, 125.2 (2C), 124.9, 124.7, 124.5, 123.4, 122.6, 71.0, 63.8, 58.5, 52.4, 24.2, 18.3, 7.5. HRMS (ESI$^+$): calcd for $C_{29}H_{36}N_3O_4Si$ 518.2475, found 518.2453.

**6f.** Yield: 68%. $^1$H NMR (250 MHz, DMSO) $\delta$ = 8.63 (d, $J$ = 8.2 Hz, 1H), 8.43 (d, $J$ = 7.1 Hz, 1H), 8.19 (d, $J$ = 8.4 Hz, 1H), 7.94 (s, 1H), 7.66 (t, $J$ = 7.8 Hz, 1H), 7.49 (s, 2H), 6.84 (d, $J$ = 8.4 Hz, 1H), 5.25 (s, 2H), 4.24 (t, $J$ = 6.9 Hz, 2H), 3.66 (q, $J$ = 7.0 Hz, 6H), 1.86−1.70 (m, 2H), 1.07 (t, $J$ = 7.0 Hz, 9H), 0.48−0.37 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 164.5, 163.7, 151.1, 144.1, 134.0, 131.2, 129.6, 128.3, 124.2, 123.3, 122.1, 119.7, 109.9, 108.9, 58.6, 52.6, 34.9, 24.3, 18.3, 7.6. HRMS (ESI$^+$): calcd for $C_{24}H_{32}N_5O_5Si$ 498.2173, found 498.2166.

**6g.** Yield: 94%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.45 (s, 1H), 4.67 (t, $J$ = 1.5 Hz 2H), 4.31 (t, $J$ = 7.1 Hz, 2H), 4.24 (t, $J$ = 1.5 Hz, 2H), 4.03 (s, 5H), 3.78 (q, $J$ = 7.0 Hz, 6H), 2.04−1.96 (m, 2H), 1.19 (t, $J$ = 7.0 Hz, 9H), 0.61−0.54 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 146.4, 118.9, 75.7, 69.5, 68.6, 66.6, 58.6, 52.3, 24.2, 18.3, 7.4. HRMS (ESI$^+$): calcd for $C_{21}H_{32}N_3O_3FeSi$ 458.1562, found 458.1552.

**6h.** Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.37 (s, 1H), 7.99 (s, 1H), 7.65 (s, 1H), 5.73 (br, 2H), 5.48 (s, 2H), 4.31 (t, $J$ = 7.2 Hz, 2H), 3.78 (q, $J$ = 7.0 Hz, 6H), 2.03−1.93 (m, 2H), 1.19 (t, $J$ = 7.0 Hz, 9H), 0.59−0.53 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 155.6, 153.2, 150.0, 142.3, 123.0, 58.7, 52.7, 38.8, 24.3, 18.4, 7.6. (2C missing). HRMS (ESI$^+$): calcd for $C_{17}H_{29}N_8O_3Si$ 421.2132, found 421.2132.

**7a.** Yield: 94%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49 (s, 1H), 7.38−7.30 (m, 3H), 7.27−7.19 (m, 2H), 5.84 (t, $J$ = 5.7 Hz, 1H), 5.45 (s, 2H), 5.18 (t, $J$ = 5.3 Hz, 1H), 4.38 (d, $J$ = 5.9 Hz, 2H), 3.78 (q, $J$ = 7.0 Hz, 6H), 3.17−3.10 (m, 2H), 1.62−1.53 (m, 2H), 1.18 (t, $J$ = 7.0 Hz, 9H), 0.64−0.57 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.4, 146.8, 134.5, 129.2, 128.8, 128.2, 122.3, 58.5, 54.2, 43.0, 35.5, 23.6, 18.3, 7.7. HRMS (ESI$^+$): calcd for $C_{20}H_{34}N_5O_4Si$ 436.2380, found 436.2397.

**7b.** Yield: 93%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.55 (s, 1H), 5.98 (br, 1H), 5.29 (br, 1H), 4.39 (d, $J$ = 5.3 Hz, 2H), 4.27 (t, $J$ = 7.3 Hz, 2H), 3.77 (q, $J$ = 7.0 Hz, 6H), 3.18−3.09 (m, 2H), 1.90−1.79 (m, 2H), 1.63−1.50 (m, 2H), 1.34−1.22 (m, 6H), 1.18 (t, $J$ = 7.0 Hz, 9H), 0.85 (t, $J$ = 6.5 Hz, 3H), 0.64−0.55 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.7, 58.3, 50.3, 42.9, 35.3, 31.1, 30.1, 26.1, 23.7, 22.4, 18.3, 13.9, 7.6 (2C missing).

**7c.** Yield: 94%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.62 (s, 1H), 5.84 (br, 1H), 5.28 (br, 1H), 4.59−4.46 (m, 2H), 4.37 (d, $J$ = 4.9 Hz, 2H), 4.12−3.99 (m, 4H), 3.76 (q, $J$ = 7.0 Hz, 6H), 3.16−3.06 (m, 2H), 2.45−2.29 (m, 2H), 1.61−1.48 (m, 2H), 1.27 (t, $J$ = 7.1 Hz, 6H), 1.16 (t, $J$ = 7.0 Hz, 9H), 0.62−0.53 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.5, 146.6, 122.8, 62.2 (d, $J$ = 6.5 Hz), 58.4, 44.5, 42.9, 35.5, 27.2 (d, $J$ = 141 Hz), 23.7, 18.3, 16.4 (d, $J$ = 6 Hz), 7.7. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 25.5. HRMS (ESI$^+$): calcd for $C_{19}H_{41}N_5O_7SiP$ 510.2513, found 510.2511.

**7d.** Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.52 (s, 1H), 6.30 (br, 1H), 5.56 (br, 1H), 4.30 (d, $J$ = 5.5 Hz, 2H), 4.19 (t, $J$ = 7.2 Hz, 2H), 3.69 (q, $J$ = 7.0 Hz, 6H), 3.51 (t, $J$ = 6.7 Hz, 2H), 3.13 (br, 1H), 3.09−3.02 (m, 2H), 1.82−1.73 (m, 2H), 1.57−1.35 (m, 4H), 1.30−1.13 (m, 14H), 1.10 (t, $J$ = 7.0 Hz, 9H), 0.55−0.49 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.6, 146.3, 122.2, 62.4, 58.2, 50.2, 42.8, 35.1, 32.6, 30.0, 29.4, 29.3, 29.23, 29.18, 28.8, 26.3, 25.7, 23.5, 18.2, 7.5. HRMS (ESI$^+$): calcd for $C_{24}H_{50}N_5O_5Si$ 516.3581, found 516.3558.

**7e.** Yield: 83%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.22−7.94 (m, 8H), 7.85 (d, $J$ = 7.8 Hz, 1H), 7.34 (s, 1H), 6.08 (s, 2H), 5.65 (t, $J$ = 5.6 Hz, 1H), 5.08 (t, $J$ = 5.4 Hz, 1H), 4.30 (d, $J$ = 5.8 Hz, 2H), 3.75 (q, $J$ = 7.0 Hz, 6H), 3.11−3.04 (m, 2H), 1.58−1.49 (m, 2H), 1.16 (t, $J$ = 7.0 Hz, 9H), 0.60−0.54 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.2, 132.1, 131.2, 130.5, 129.2, 129.0, 128.3, 127.7, 127.2, 126.8, 126.4, 125.9, 125.8, 125.1, 125.0, 124.5, 121.9, 58.4, 52.4, 43.0, 35.6, 23.6, 18.4, 7.7 (1C missing). HRMS (ESI$^+$): calcd for $C_{30}H_{38}N_5O_4Si$ 560.2693, found 560.2693.

**7f.** Yield: 93%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.33 (br, 1H), 7.86 (br, 1H), 7.62 (s, 1H), 6.05 (br, 2H), 5.54 (br, 1H), 5.09 (br, 1H), 4.41 (d, $J$ = 5.6 Hz, 2H), 4.34 (t, $J$ = 6.4 Hz, 2H), 4.24 (t, $J$ = 6.3 Hz, 2H), 3.79 (q, $J$ = 7.0 Hz, 6H), 3.18−3.11 (m, 2H), 2.57−2.48 (m, 2H), 1.64−1.54 (m, 2H), 1.19 (t, $J$ = 7.0 Hz, 9H), 0.64−0.58 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.4, 155.8, 153.2 132.1, 122.5, 58.6, 47.2, 43.1, 41.1, 35.8, 30.2, 23.7, 18.4, 7.8 (2C missing). HRMS (ESI$^+$): calcd for $C_{21}H_{37}N_{10}O_4Si$ 521.2769, found 521.2769.

**7g.** Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.55 (s, 1H), 6.01 (br, 1H), 5.32 (br, 1H), 4.38 (d, $J$ = 5.7 Hz, 2H), 4.27 (t, $J$ = 7.3 Hz, 2H), 3.76 (q, $J$ = 7.0 Hz, 6H), 3.75 (q, $J$ = 7.0 Hz, 6H), 3.16−3.09 (m, 2H), 2.01−1.91 (m, 2H), 1.60−1.51 (m, 2H), 1.17 (t, $J$ = 7.0 Hz, 9H), 1.16 (t, $J$ = 7.0 Hz, 9H), 0.62−0.53 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.5, 146.3, 122.4, 58.6, 58.4, 52.6, 43.0, 35.4, 24.2, 23.7, 18.3 (2 C), 7.7, 7.6. HRMS (ESI$^+$): calcd for $C_{22}H_{48}N_5O_7Si_2$ 550.3092, found 550.3083.

**7h.** Yield: 90%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.45 (s, 2H), 7.23 (s, 4H), 5.55−5.35 (m, 6H), 4.99 (br, 2H), 4.37 (d, $J$ = 5.6 Hz, 4H), 3.79 (q, $J$ = 7.0 Hz, 12H), 3.17−3.06 (m, 4H), 1.63−1.50 (m, 4H), 1.20 (t, $J$ = 7.0 Hz, 18H), 0.64−0.56 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.4, 135.4, 128.9, 58.6, 53.7, 43.1, 35.7, 23.7, 18.4, 7.7 (2C missing).

**7i.** Yield: 91%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.56 (s, 2H), 6.18 (br, 2H), 5.46 (br, 2H), 4.37 (d, $J$ = 4.9 Hz, 4H), 4.25 (t, $J$ = 7.0 Hz, 4H), 3.75 (q, $J$ = 7.0 Hz, 12H), 3.15−3.08 (m, 4H), 1.86−1.78 (m, 4H), 1.60−1.50 (m, 4H), 1.29−1.09 (m, 30H), 0.61−0.55 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.7, 146.4, 122.3, 58.4, 50.4, 43.0, 35.4, 30.1, 28.9, 28.6, 26.3, 23.7, 18.3, 7.7.

**7j.** Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.11 (s, 3H), 6.06 (br, 3H), 5.60−5.54 (m, 9H), 4.30 (d, $J$ = 5.6 Hz, 6H), 3.76 (q, $J$ = 7.0 Hz, 18H), 3.09−3.00 (m, 6H), 2.30 (s, 9H), 1.56−1.46 (m, 6H), 1.16 (t, $J$ = 7.0 Hz, 27H), 0.58−0.52 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.7, 147.0, 139.6, 130.8, 121.1, 58.4, 48.9, 43.0, 35.7, 23.7, 18.4, 16.6, 7.7.

**7k.** Yield: 93%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.83−7.76 (m, 4H), 7.74 (s, 2H), 7.39 (t, $J$ = 7.5 Hz, 2H), 7.26 (t, $J$ = 7.6 Hz, 2H), 7.15 (d, $J$ = 8.5 Hz, 2H), 6.22 (br, 2H), 5.87 (d, $J$ = 14.8 Hz, 2H), 5.70 (d, $J$ = 14.8 Hz, 2H), 5.55 (br, 2H), 4.40 (dd, $J$ = 15.3 and 5.7 Hz, 2H), 4.37 (dd, $J$ = 15.3 and 5.7 Hz, 2H), 4.28 (d, $J$ = 5.8 Hz, 2H), 4.23 (d, $J$ = 5.8 Hz, 2H), 3.75 (q, $J$ = 7.0 Hz, 12H), 3.19−3.02 (m, 4H), 2.92 (s, 6H), 1.61−1.51 (m, 4H), 1.15 (t, $J$ = 7.0 Hz, 18H), 0.62−0.56 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 158.6, 152.4, 146.9, 134.1, 130.6, 130.4, 128.7, 128.4, 127.6, 125.8, 125.7, 125.1, 122.6, 99.5, 58.4, 57.0, 50.4, 43.0, 35.6, 23.7, 18.3, 7.7.

**7l.** Yield: 89%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.73−7.35 (m, 8H), 7.28−7.09 (m, 5H), 6.98 (d, $J$ = 8.2 Hz, 2H), 5.84 (br, 2H), 5.40 (br, 6H), 4.01 (br, 4H), 3.68 (q, $J$ = 7.0 Hz, 12H), 2.88 (br, 4H), 1.40 (br, 4H), 1.09 (t, $J$ = 7.0 Hz, 18H), 0.49−0.43 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ = 158.7, 152.7, 146.1, 134.5, 132.1, 128.6, 128.2, 127.3, 124.9, 124.8, 123.8, 122.8, 114.9, 58.5, 45.8, 42.9, 23.7, 18.4, 10.4, 7.8. HRMS (ESI$^+$): calcd for $C_{48}H_{69}N_{10}O_{10}Si_2$ 1001.4737, found 1001.4682.

**8a.** Yield: 94%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.48 (s, 2H), 7.38−7.27 (m, 6H), 7.25−7.19 (m, 4H), 5.48 (s, 4H), 3.76 (q, $J$ = 7.0 Hz, 6H), 3.68 (br, 4H), 2.46−2.41 (m, 2H), 1.66−1.56 (m, 2H), 1.17 (t, $J$ = 7.0 Hz, 9H), 0.57−0.51 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 145.1, 134.9, 129.1, 128.5, 128.0, 123.0, 58.3, 56.5, 54.1, 47.7, 20.6, 18.3, 7.8. HRMS (ESI$^+$): calcd for $C_{29}H_{42}N_7O_3Si$ 564.3118, found 564.3109.

**8b.** Yield: 91%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.57 (s, 2H), 4.31 (t, $J$ = 7.3 Hz, 4H), 3.79 (q, $J$ = 7.0 Hz, 6H), 3.71 (s, 4H), 2.51−2.43 (m, 2H), 1.95−1.81 (m, 4H), 1.74−1.60 (m, 2H), 1.33−1.28 (m, 12H), 1.20 (t, $J$ = 7.0 Hz, 9H), 0.85 (t, $J$ = 6.7 Hz, 6H), 0.64−0.55 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 144.4, 122.9, 58.4, 56.6, 50.3, 47.5, 31.2, 30.3, 26.2, 22.4, 20.6, 18.4, 13.9, 7.9. HRMS (ESI$^+$): calcd for $C_{27}H_{54}N_7O_3Si$ 552.4057, found 552.4063.

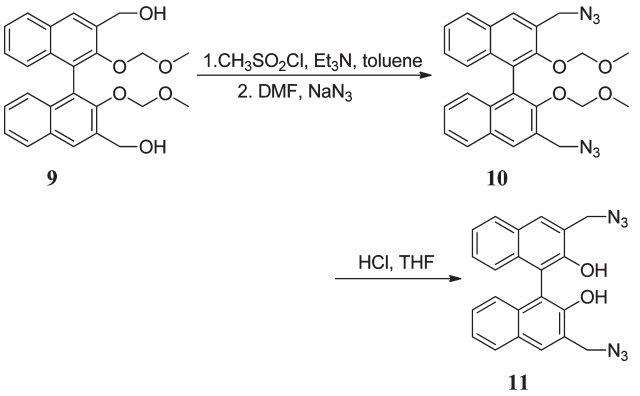
**8c.** Yield: 84%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.59 (s, 2H), 4.30 (t, $J$ = 7.2 Hz, 4H), 3.78 (q, $J$ = 7.0 Hz, 6H), 3.70 (s, 4H), 3.60 (t, $J$ = 6.6 Hz, 4H), 2.50−2.42 (m, 2H), 2.12−1.78 (m, 6H), 1.76−1.38 (m, 6H), 1.35−1.16 (m, 37H), 0.63−0.54 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 143.9, 122.9, 62.1, 58.1, 56.2, 50.0, 47.2, 32.5, 30.0, 29.24, 29.16, 29.1, 29.0, 28.7, 26.2, 25.6, 20.3, 18.1, 7.5. HRMS (ESI$^+$): calcd for $C_{37}H_{74}N_7O_5Si$ 724.5521, found 724.5520.

**8d.** Yield: 91%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.63 (s, 2H), 4.63−4.51 (m, 4H), 4.15−4.00 (m, 8H), 3.77 (q, $J$ = 7.0 Hz, 6H), 3.68 (s, 4H), 2.50−2.30 (m, 6H), 1.71−1.56 (m, 2H), 1.29 (t, $J$ = 7.1 Hz, 12H), 1.18 (t, $J$ = 7.0 Hz, 9H), 0.61−0.52 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 144.5, 123.2, 61.9 (d, $J$ = 6.5 Hz), 58.1, 56.3, 47.4, 44.2, 27.0 (d, $J$ = 141 Hz), 20.4, 18.1, 16.2 (d, $J$ = 6 Hz), 7.6. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 25.58. HRMS (ESI$^+$): calcd for $C_{27}H_{56}N_7O_9SiP_2$ 712.3384, found 712.3374.

**8e.** Yield: 90% (Containing 0.5 eq of $Et_3N$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.34 (s, 2H), 7.97 (s, 2H), 7.75 (s, 2H), 6.64 (br, 4H), 4.36 (t, $J$ = 6.1 Hz, 4H), 4.24 (t, $J$ = 6.2 Hz, 4H), 3.78 (q, $J$ = 7.0 Hz, 6H), 3.72 (s, 4H), 2.56−2.45 (m, 8H), 1.73−1.64 (m, 2H), 1.18 (t, $J$ = 7.0 Hz, 9H), 1.00 (t, $J$ = 7.2, 4H), 0.65−0.57 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 156.1, 153.2, 150.2, 145.1, 128.5, 123.8, 119.9, 58.5, 57.1, 47.6, 46.9, 46.4, 40.9, 30.4, 20.8, 18.4, 11.8, 8.0. HRMS (ESI$^+$): calcd for $C_{31}H_{48}N_{17}O_3Si$ 734.3895, found 734.3868.

**8f.** Yield: 92%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.20−7.95 (m, 16H), 7.75 (d, $J$ = 7.8 Hz, 2H), 7.22 (s, 2H), 6.05 (s, 4H), 3.65 (q, $J$ = 7.0 Hz, 6H), 3.57 (s, 4H), 2.34 (t, $J$ = 4 Hz, 2H), 1.52−1.42 (m, 2H), 1.08 (t, $J$ = 7.0 Hz, 9H), 0.44−0.37 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 145.2, 132.0, 131.2, 130.6, 129.1, 128.9, 128.2, 127.4, 127.3, 127.1, 126.4, 125.9, 125.8, 125.0, 124.9, 124.5, 122.9, 122.0, 58.2, 56.5, 52.3, 47.8, 20.3, 18.3, 7.7. HRMS (ESI$^+$): calcd for $C_{49}H_{50}N_7O_3Si$ 812.3744, found 812.3714.

**8g.** Yield: 88%. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ = 7.56 (s, 2H), 4.29 (t, $J$ = 7.2 Hz, 4H), 3.82−3.65 (m, 22H), 2.48−2.38 (m, 2H), 2.04−1.89 (m, 4H), 1.64 (br, 2H), 1.19−1.11 (m, 27H), 0.59−0.51 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 144.3, 123.1, 58.5, 58.4, 56.6, 52.5, 47.5, 24.3, 20.7, 18.4, 18.3, 7.9, 7.6. HRMS (ESI$^+$): calcd for $C_{33}H_{70}N_7O_9Si_3$ 792.4543, found 792.4557.




**9** **10** **11**

**3,3′-Bis(azidomethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (10).** To a solution of **9**[45] (3.17 g, 7.29 mmol) in toluene (100 mL) were added methanesulfonyl chloride (4.58 g, 40.1 mmol) and triethylamine (5.57 g, 55.0 mmol) at 0 °C. The solution was stirred overnight at rt. DMF (75 mL) and sodium azide (2.08 g, 32 mmol) were added, and the mixture was stirred for 6 h at 60 °C. The solvents were evaporated, and the residue was dissolved in $CH_2Cl_2$ and extracted with water and brine. The organic fraction was dried over $MgSO_4$ and then concentrated. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$, 1% MeOH). The pure product **10** (2.82 g, 5.82 mmol) was obtained as a yellow liquid. Yield: 80%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.02 (s, 2H), 7.92 (d, $J$ = 8.0 Hz, 2H), 7.48−7.42 (m, 2H), 7.32−7.28 (m, 2H), 7.18 (d, $J$ = 7.9 Hz, 2H), 4.79 (d, $J$ = 14.0 Hz, 2H), 4.68 (d, $J$ = 14.0 Hz, 2H), 4.53 (d, $J$ = 5.9 Hz, 2H), 4.48 (d, $J$ = 5.9 Hz, 2H), 3.01 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 152.6, 134.1, 130.7, 130.0, 129.4, 128.3, 127.3, 126.1, 125.7, 125.5, 99.6, 57.0, 51.0.

**3,3′-Bis(azidomethyl)-1,1′-binaphthalene-2,2′-diol (11).** The protected binol **10** (1.05 g, 2.17 mmol) was dissolved in THF (20 mL), and concentrated HCl (12 M, 8.8 mL) was added dropwise at 0 °C. After being stirred for 5 h at rt, the solution was extracted with EtOAc and washed with water, saturated $NaHCO_3$, and brine. After drying over $Na_2SO_4$ and concentration, the residue was purified by chromatography column on silica gel ($CH_2Cl_2$, 5% MeOH). Pure diol **11** was obtained as a yellow oil (0.73 g, 1.84 mmol). Yield: 89%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.00 (s, 2H), 7.92 (d, $J$ = 8.0 Hz, 2H), 7.44−7.39 (m, 2H), 7.35−7.31 (m, 2H), 7.12 (d, $J$ = 7.9 Hz, 2H), 4.67 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 151.1, 133.3, 131.2, 129.3, 128.7, 128.1, 124.8, 124.6, 124.2, 111.3, 50.8.

## ■ ASSOCIATED CONTENT

**Supporting Information.** $^1$H and $^{13}$C NMR spectra of **3**, **5**, **6a**−**h**, **7a**−**l**, **8a**−**g**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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