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Graphical abstract

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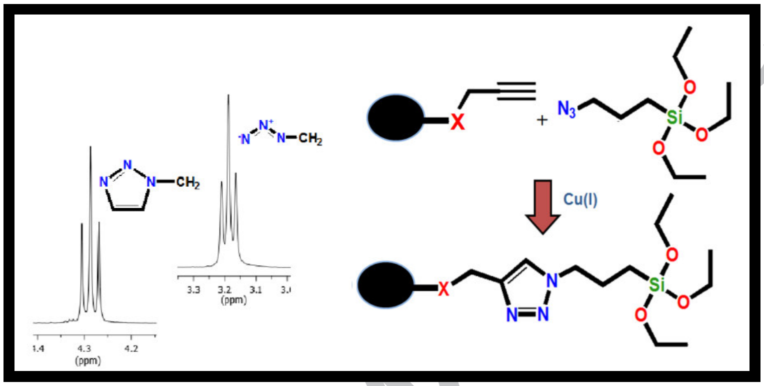

Synthesis of polyfunctional triethoxysilanes by "click silylation"

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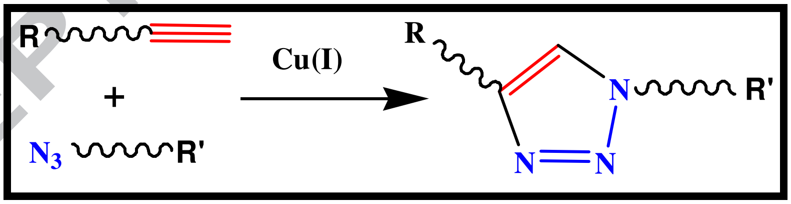
Abstract

The copper-catalyzed “click silylation” has been exploited for the chemical modification of γ-azidopropyltriethoxysilane (AzPTES) with a wide range of terminal alkynes (**1a-1v**) in a one-pot operation. The novel 1,2,3-triazole-triethoxysilane derivatives (**2a-2v**) were synthesized by this procedure and comprehensively characterized by IR spectra, ^{1}H and ^{13}C NMR and HRMS studies.

Keywords:
Triethoxysilane
Click silylation
Functional alkyne
Heterocycle
$[CuBr(PPh_3)_3]$

The extension of functional group versatility in organotriethoxysilanes (OTES) has made it a flexible building block in organic synthesis.[1,2] The OTES are key modules for the synthesis of well designed organic-inorganic hybrid materials[3] having potential applications as biosensors,[4] surface group modifiers[5] and supported catalysts[6]. The syntheses of OTES with enhanced properties require the functionalization of triethoxysilyl moiety with various challenging substrates. This has been achieved either through an organometallic route[7] or by the hydrosilylation[8] of olefins or dienes thus leading to complicated mixtures which considerably affects isolation of products. Thus purification process requires skillful techniques such as distillation or crystallization[9] to avoid hydrolytic decomposition of triethoxysilanes. Therefore, a revolutionary method is required to override these purification steps to conventional total synthesis.

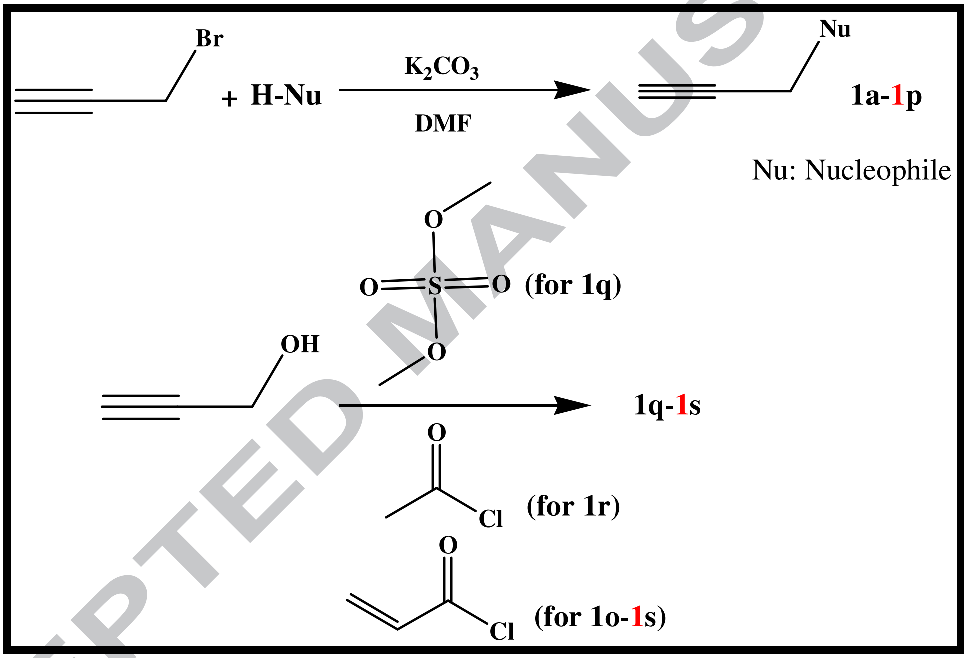
Initiated by Sharpless[10] and co-workers, 'click chemistry' is well known for its flexibility[11] and is a valuable technique that has become a simple solution for long known challenges.[12] The research in this field is booming with the use of copper-catalyzed azide alkyne cycloaddition reaction (CuAAC) (Scheme 1), that allows a safe and selective post functionalization over other synthetic routes. This cross-coupling reaction has come up as an important addition to the usual synthetic methodologies for the synthesis of OTES. The integration of triethoxysilanes with heterocyclic triazole can extend its physical, chemical and mechanical properties, and can provide a robust route for drug discovery,[13] polymer chemistry[14] and sol-gel processes.[15]



Scheme 1: General reaction Scheme for CuAAC

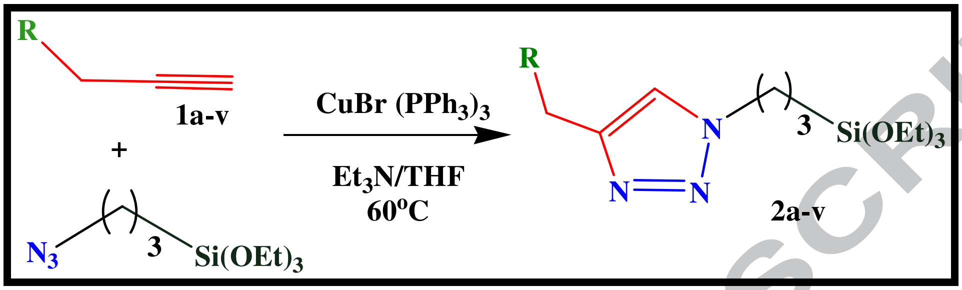
The restricted research on 1,2,3-triazole based OTES is primarily due to their hygroscopic nature. As a part of our ongoing work, we herein report the synthesis of OTES substituted with various terminal polyfunctionalized molecular entities[16] via 1,2,3-triazole linkage, that have made it a flagship reaction of the click chemistry. The quest for the synthesis of polyfunctional OTES under milder reaction conditions has been exploited by the use of Cu(I) and is gaining wide popularity under the term "click-silylation".[17]

Inspired by the pioneering work of Cattoen *et al.*[1,17] on click silylation, the cycloaddition of alkyne functionalities has been carried out with 3-azidopropyltriethoxysilane (AzPTES) to obtain products having importance, well documented in research fields. This methodology is based on [CuBr(PPh$_3$)$_3$]-THF/Et$_3$N system, under strict anhydrous conditions for synthesis of hybrid silica precursors. Terminal alkyne functionalities (Table 1) such as N-heterocycle, aniline, ether, acrylate, acetate, Schiff base, aldehyde and ketone group were synthesized (Scheme 2) following the procedure[18] described in the literature and have been found to be in harmony with click strategy.



Scheme 2: Synthesis of terminal alkynes from propargyl bromide and propargyl alcohol

The CuAAC reaction between these terminal alkynes and AzPTES afforded polyfunctionalized triethoxysilanes (PfTES) in high yield with upto 95% conversion (Scheme 3, Table 2). IR, NMR (^{1}H, ^{13}C) and High Resolution Mass spectroscopic details provide a handful of information for the complete structure elucidation of PfTES. The downfield shift of triplet due to -N$_3$$CH_2$- protons from δ = 3.19 to δ = 4.19-4.31 ppm signifies the C-N bond formation resulting into triazole (Figure 1). The sharing of two free π bonded electrons of terminal alkyne to form a conjugated heterocycle drastically changes chemical shift from δ = 2.0 to δ = 7.12-7.58 ppm. The parallel shifting of the peaks has been observed in ^{13}C NMR spectra as well. FT-IR spectroscopic data (Figure 2) show absorption due to N_3 functionality existing in uncyclized silane at 2096 cm^{-1} whereas upon cyclization this peak disappears. The blank region between 2140-2100 cm^{-1} and the distinctive bands around 1650 cm^{-1} points out to the successful cycloaddition of two molecular entities.



Scheme 3: General reaction Scheme for the synthesis of polyfunctional triethxoysilanes.

To determine the scope of this methodology, AzPTES was derivatized with N-heterocycles such as morpholine, piperidine and phthalimide which have maintained the interest of researchers through decades of historical development of organic synthesis.[19,20,21] So, 1:1 mixture of the N-heterocycle (**1a**-**1c**) and AzPTES was totted up in the beginning to obtain the functionalized compounds (**2a-2c**) with desired moiety. The cycloaddition proceeded smoothly under standard condition at 60 °C for 5 h to give a small series of N-heterocyclic derivatives in excellent yield. Furthermore, the aniline derivatives[22] could be selectively functionalized as this silylation method has proven to be very helpful to explore the triazole substitution in material chemistry. Therefore, compounds (**1d**-**1i**) were chosen as starting material for the synthesis of bulky aniline derivatives (**2d-2i**) in outstanding yield. The use of benzylamine[23] in bacterial degradation encouraged us to link this functionality (**1j**) with sol-gel precursors for the synthesis of bio-inspired materials (**2j**).

Click silylation also proved to be an effective route to immobilize aldehyde and ketone functionality on to silica supports, as it would play important role for protease inhibition[24]. The potent antimalarial activity of precursor compounds (**1k-1n**), on incorporation of aldehyde or ketone side chain in 1,2,3-triazole (**2k-2n**), may lead to an increase in anti-HIV activity. Aromatic Schiff base functionalities are amongst the most popular photochromic compounds.[25] Therefore, newly synthesized acetylenic Schiff bases (**1o**,**1p**) were substituted with OTES by click strategy in 15 h for the synthesis of compounds (**2o,2p**) with motive of further advancement in the field of photochemistry.

To further enlarge the scope, propargyl derivatives having ether[26] (**1q**), acetate[27] (**1r**), N, N-dimethyl[28] (**1s**), alkyl[29] (**1t**) acrylate[30] (**1u**) and cyclic olefin[31] (**1v**) groups were also used in this one pot labelling approach. In all cases, the reactions were carried out for 5 h at 60 °C. The disappearance of azide peak in IR spectra clearly indicated the completion of reaction in this short period. The synthesized silica precursors (**2q**-2**v**) may be useful as secondary organic aerosols.

In the present work, we have synthesized the 1,2,3-triazole based PfTES **(2a-2v)**. The coupling of modified alkyne with AzPTES was achieved by CuAAC with keeping the precursor as wide functional group to make this approach commercially attractive. This methodology to synthesize triethoxysilanes is gaining wide popularity due to hooking of polyfunctionalized groups that can be put to wonderful applications in fields of medicine, optical sensors and material chemistry.

Acknowledgment

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16. **General reaction procedure for the click silylation:**

To a 50 ml two-necked round bottom flask with alkyne function (2 mmol), azide function (2 mmol/alkyne function), $[CuBr(PPh_3)_3]$ (0.01 mmol/alkyne function), triethylamine (2 ml), and THF (2 ml) under nitrogen atmosphere and then the mixture was stirred at 60 °C for 5 h. The reaction mixture was allowed to cool, and the solvents were removed under vacuum followed by addition of hexane. The mixture was filtered and washed with 2 x 5 ml of hexane. The concentration of the filtrate under reduced pressure afforded the title compound in good to excellent yield.

2a. Yield: 95%; IR (Neat, cm^{-1}) 2971, 2926, 2889, 2812, 1453, 1389, 1325, 1285, 1215, 1164, 1114, 1100, 1070, 1003, 954, 913, 865, 784; NMR (400 MHz, $CDCl_3$, 25 °C) $\delta_H = 7.43$ (s, 1H, Tz-H), 4.28 (t, 2H, -NCH_2CH$_2$-, $J = 7.2$ Hz), 3.74 (q, 6H, -OCH_2CH$_3$, $J = 7.0$ Hz), 3.63 (t, 4H, -OCH_2CH$_2$N-, J = 4.6 Hz), 3.59 (s, 2H, -NCH_2-), 2.44 (t, 4H, -NCH_2CH$_2$O-, J = 4.4 Hz), 1.99 - 1.91 (m, 2H, -CCH_2C-), 1.14 (t, 9H, -OCH$_2$$\mathit{CH}_3$, J = 7.5 Hz), 0.53 - 0.51 (m, 2H, -SiCH_2-). δ_C = 143.9, 122.6, 66.8, 58.5, 53.7, 53.4, 52.4, 24.2, 18.2, 7.4. HRMS (ES$^+$) calcd for $C_{16}H_{32}N_4O_4Si$ [M + H]$^+$ 373.2271, found 373.2276.

2b. Yield: 93%; IR (Neat, cm^{-1}) 2962, 1718, 1395, 1258, 1215, 1073, 864, 790; NMR (400 MHz, CDCl$_3$, 25 °C) δ_H = 7.76 (dd, 2H, Ar-H), 7.63 (dd, 2H, Ar-H), 7.54 (s, 1H, Tz-H), 4.91 (s, 2H, -NCH_2-), 4.24 (t, 2H, -N$_3$$\mathit{CH}_2CH_2$-, J = 8.0 Hz), 3.71 (q, 6H, -OCH_2CH$_3$, J = 8.0 Hz), 1.95 - 1.88 (m, 2H, -CCH_2C-), 1.12 (t, 9H, -OCH$_2$$\mathit{CH}_3$, J = 8.0 Hz), 0.52 - 0.48 (m, 2H, -SiCH_2-). δ_C = 166.5, 133.0, 131.9, 122.4, 121.8, 57.4, 51.5, 32.0, 23.1, 17.2, 6.3. HRMS (ES$^+$) calcd for $C_{20}H_{28}N_4O_5Si$ [M + Na]$^+$ 455.1726, found 455.1705.

2c. 2j. Yield: 93%; IR (Neat, cm^{-1}) 2972, 2928, 1082, 1439, 1389, 1295, 1164, 1100, 991, 954, 861, 782; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.41 (s, 1H, Tz-H), 4.26 (t, 2H, -N$_3$$\mathit{CH}_2CH_2$-, J = 7.1 Hz), 3.74 (q, 12H, -OCH_2CH$_3$, J = 7.2 Hz), 3.55 (s, 2H, -NCH_2-), 2.37 (m, 4H, -CCH$_2$$\mathit{CH}_2$N-), 1.99-1.90 (m, 2H, -CCH_2C-), 1.51-1.49 (m, 4H, -CCH_2CN-), 1.38 - 1.36 (m, 2H, -CH_2CH$_2$C-), 1.14 (t, 18H, -OCH$_2$$\mathit{CH}_3$, J = 7.1 Hz), 0.52 - 0.47 (m, 2H, -SiCH_2-). δ_C = 139.1, 125.2, 57.9, 52.5, 52.1,51.9, 23.7, 23.5, 23.2, 22.4, 17.9, 7.1. HRMS (ES$^+$) calcd for $C_{20}H_{28}N_4O_5Si$ [M + 1]$^+$ 371.2478, found 371.2471.

2d. Yield: 94%; IR (Neat, cm^{-1}) 2972, 2885, 1599, 1505, 1389, 1294, 1215, 1164, 1071, 953, 877, 780; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.33 (s, 2H, Tz-H), 7.14 - 7.08 (m, 2H, Ar-H), 6.80 (d, 1H, Ar-H), 6.67 - 6.64 (m, 1H, Ar-H), 6.60 - 6.58 (m, 1H, Ar-H) 4.60 (s, 4H, -NCH_2-), 4.21 (t, 4H, -N$_3$$\mathit{CH}_2CH_2$-, J = 7.2 Hz), 3.72 (q, 12H, -OCH_2CH$_3$, J = 5.9 Hz), 1.94 - 1.88 (m, 4H, -CCH_2C-), 1.13 (t, 18H, -OCH$_2$$\mathit{CH}_3$, J = 7.0 Hz), 0.51 - 0.47 (m, 4H, -SiCH_2-). δ_C = 148.3, 129.1, 117.8, 113.8, 58.4, 52.2, 46.7, 24.2, 18.3, 7.4. HRMS (ES$^+$) calcd for $C_{30}H_{53}N_7O_6Si_2$ [M + Na]$^+$ 686.3493, found 686.3443.

2e. Yield: 93%; IR (Neat, cm^{-1}) 2966, 2926, 2868, 1654, 1599, 1493, 1452, 1373, 1343, 1152, 1107, 1072, 952, 879, 780; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.17 -7.09 (m, 2H, Ar-H, 1H, Tz-H), 6.69 - 6.60 (m, 3H, Ar-H), 4.55 (s, 2H, -NCH_2-), 4.19 (t, 2H, -N$_3$$\mathit{CH}_2CH_2$-, J = 7.1 Hz), 3.68 (q, 6H, -OCH_2CH$_3$, J = 7.2 Hz), 2.92 (s, 3H, -NCH_3-), 1.91 - 1.83 (m, 2H, -CCH_2C-), 1.12 (t, 9H, -OCH$_2$$\mathit{CH}_3$, J = 7.1 Hz), 0.44 - 0.42 (m, 2H, -SiCH_2-). δ_C = 149.0, 145.0, 129.2, 121.4, 117.3, 113.1, 58.3, 52.1, 48.7, 38.3, 24.0, 18.1, 7.2. HRMS (ES$^+$) calcd for $C_{19}H_{32}N_4O_3Si$ [M + H]$^+$ 393.2321, found 393.2302.

2f. Yield: 86%; IR (Neat, cm^{-1}) 2974, 2926, 2887, 1597, 1498, 1438, 1389, 1294, 1215, 1164, 1099, 1072, 954, 747; NMR (300 MHz, $CDCl_3$, 25 °C) δ_H = 7.28 (s, 2H, Tz-H), 7.09 - 6.90 (m, 2H, Ar-H), 6.69-6.79 (m, 2H, Ar-H), 4.52 (s, 4H, -N*CH₂*-), 4.24 (t, 4H, -N₃*CH₂*CH₂-, *J* = 8.2 Hz), 3.75 (q, 12H, -O*CH₂*CH₃, *J* = 7.2 Hz), 1.93 - 1.71 (m, 4H, -C*CH₂*C-), 1.17 (t, 18H, -OCH₂*CH₃*, *J* = 7.1 Hz), 0.50 - 0.29 (m, 4H, -Si*CH₂*-). δ_C = 146.7, 144.6, 129.0, 122.0, 121.9, 115.0, 114.1, 58.3, 52.4, 46.8, 46.0, 24.0, 18.2, 7.3. HRMS (ES$^+$) calcd for $C_{30}H_{52}ClN_7O_6Si_2$ [M + H]$^+$ 698.3284, found 698.3294.

2g. Yield: 91%; IR (Neat, cm^{-1}) 2973, 2927, 2887, 1595, 1490, 1438, 1389, 1294, 1224, 1169, 1098, 1072, 954, 748; NMR (400 MHz, $CDCl_3$, 25 °C) δ_H = 7.35 (s, 1H, Tz-H), 6.76 (dd, 4H, Ar-H, *J* = 11.7, 7.1 Hz), 4.51 (s, 4H, -N*CH₂*-), 4.21 (t, 4H, -N₃*CH₂*CH₂-, *J* = 7.1 Hz), 3.70 (q, 12H, -O*CH2*CH3, *J* = 7.0 Hz), 1.96 - 1.83 (m, 4H, -C*CH₂*C-), 1.11 (t, 18H, -OCH₂*CH₃*, *J* = 7.0 Hz), 0.50 - 0.41 (m, 4H, -Si*CH₂*-). δ_C = 157.0, 154.7, 144.5, 131.7, 128.3, 122.0, 115.5, 115.4, 115.1, 58.2, 52.1, 47.2, 23.9, 18.0, 7.0. HRMS (ES$^+$) calcd for $C_{30}H_{52}FN_7O_6Si_2$ [M + Na]$^+$ 704.3399, found 704.3337.

2h. Yield: 89%; IR (Neat, cm^{-1}) 2975, 2926, 2886, 1500, 1438, 1389, 1293, 1241, 1165, 1101, 1076, 957, 907, 780; NMR (300 MHz, $CDCl_3$, 25 °C) δ_H = 7.29 (s, 2H, Tz-H), 6.83 - 6.72 (m, 2H), 6.66 (d, 2H, *J* = 8.9 Hz), 4.43 (s, 4H, -N*CH₂*-), 4.20 (t, 4H, -N₃*CH₂*CH₂-, *J* = 7.0 Hz), 3.70 (q, 12H, -O*CH₂*CH₃, *J* = 7.1 Hz), 3.60 (s, 3H, -O*CH₃*) 1.89 - 1.96 (m, 4H, -C*CH₂*C-), 1.13 (t, 18H, -OCH₂*CH₃*, *J* = 7.5 Hz), 0.51 - 0.38 (m, 4H, -Si*CH₂*-). δ_C = 132.1, 131.2, 128.6, 123.2, 121.8, 58.4, 53.7, 52.2, 46.9, 24.1, 18.2, 7.3. HRMS (ES$^+$) calcd for $C_{31}H_{55}N_7O_7Si_2$ [M + Na]$^+$ 716.3599, found 716.3560.

2i. Yield: 88%; IR (Neat, cm^{-1}) 2975, 2928, 2887, 1502, 1437, 1388, 1293, 1241, 1165, 1100, 1076, 958, 907, 784; NMR (300 MHz, $CDCl_3$, 25 °C); NMR (300 MHz, $CDCl_3$, 25 °C) δ_H = 7.58 - 7.28 (m, 2H), 6.83 - 6.72 (m, 4H), 4.43 (s, 4H, -N*CH₂*-), 4.20 (t, 4H, -N₃*CH₂*CH₂-, *J* = 7.0 Hz), 3.70 (q, 12H, *J* = 7.2 Hz), 1.89-1.97 (m, 4H, -C*CH₂*C-), 1.13 (t, 18H, -OCH₂*CH₃*, *J* = 7.5 Hz), 0.51 - 0.38 (m, 4H, -Si*CH₂*-). δ_C = 132.4, 128.4, 123.2, 121.2, 120.9, 58.4, 52.2, 46.8, 24.2, 18.4, 7.4. HRMS (ES$^+$) calcd for $C_{31}H_{55}N_7O_7Si_2$ [M + Na]$^+$ 716.3599, found 716.3567.

2j. Yield: 88%; IR (Neat, cm^{-1}) 2973, 2927, 2888, 1438, 1390, 1293, 1257, 1216, 1164, 1073, 957, 748; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.53 (s, 2H, Tz-H), 7.29 - 7.15 (m, 5H, Ar-H), 4.29 (t, 4H, -N$_3$*CH*$_2$CH$_2$-, *J* = 8.2 Hz), 3.72 (q, 12H, -O*CH*$_2$CH$_3$, *J* = 7.2 Hz), 3.55 (m, 6H, -N*CH*$_2$-), 1.99 -1.94 (m, 4H, -C*CH*$_2$C-), 1.15 (t, 18H, -OCH$_2$*CH*$_3$, *J* = 7.1 Hz), 0.54 - 0.49 (m, 4H, -Si*CH*$_2$-). δ_C = 132.1, 131.8, 128.9, 128.2, 126.9, 123.1, 58.2, 52.1, 31.4, 24.1, 22.7, 18.1, 13.9, 7.3. HRMS (ES$^+$) calcd for $C_{31}H_{55}N_7O_6Si_2$ [M + H]$^+$ 678.3830, found 678.3873.

2k. Yield: 94%; IR (Neat, cm^{-1}) 2972, 2926, 2885, 1674, 1598, 1576, 1507, 1419, 1389, 1358, 1305, 1271, 1247, 1099, 1072, 1050, 999, 861, 783; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.64 (dd, 1H, Ar-H), 7.57 (s, 1H, Tz-H), 7.41 - 6.92 (m, 3H, Ar-H), 5.24 (s, 2H, -O*CH*$_2$-), 4.31 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.2 Hz), 3.73 (q, 6H, -O*CH*$_2$CH$_3$, *J* = 7.0 Hz,), 2.49 (s, 3H, -C*CH*$_3$-), 1.99 - 1.91 (m, 2H, -C*CH*$_2$C-), 1.14 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.1 Hz), 0.54 - 0.49 (m, 2H, -Si*CH*$_2$-). δ_C = 199.4, 158.3, 144.1, 133.4, 130.3, 128.7, 122.8, 121.2, 113.0, 62.5, 58.4, 48.0, 31.7, 24.1, 18.0, 13.9, 7.2. HRMS (ES$^+$) calcd for $C_{20}H_{31}N_3O_5Si$ [M + H]$^+$ 444.1930, found 444.1940.

2l. Yield: 93%; IR (Neat, cm^{-1}) 2972, 2926, 2883, 1685, 1597, 1481, 1456, 1389, 1284, 1236, 1213, 1189, 1162, 1099, 1071, 998, 953, 782; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 9.80 (s, 1H, -HC=O), 7.75 (d, 2H, Ar-H), 7.56 (s, 1H, Tz-H), 7.03 (d, 2H, Ar-H), 5.22 (s, 2H, -O*CH*$_2$-), 4.30 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.1 Hz,), 3.72 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 7.0 Hz), 2.01 - 1.91 (m, 2H, -C*CH*$_2$C-), 1.14 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.0 Hz), 0.52 - 0.47 (m, 2H, -Si*CH*$_2$-). δ_C = 190.1, 163.2, 132.0, 130.6, 122.8, 115.2, 62.3, 58.4, 52.4, 24.2, 18.3, 7.4. HRMS (ES$^+$) calcd for $C_{19}H_{29}N_3O_5Si$ [M + Na]$^+$ 430.1774, found 430.1770.

2m. Yield: 95%; IR (Neat, cm^{-1}) 2972, 2927, 2885, 1675, 1597, 1576, 1509, 1421, 1389, 1355, 1305, 1271, 1250, 1099, 1071, 1050, 999, 861, 781; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.82 (d, 2H, Ar-H), 7.58 (s, 1H, Tz-H), 6.94 (d, 2H, Ar-H), 5.18 (s, 2H, -O*CH*$_2$-), 4.30 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 6.9 Hz), 3.74 (q, 6H, -O*CH*$_2$CH$_3$, *J* = 8.8 Hz,), 2.46 (s, 3H, -C*CH*$_3$-), 2.01 - 1.94 (m, 2H, -C*CH*$_2$C-), 1.14 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 8.7 Hz), 0.53 - 0.47 (m, 2H, -Si*CH*$_2$-). δ_C 195.7, 162.1, 132.0, 130.8, 130.5, 128.4, 114.4, 62.0, 58.3, 26.0, 24.1, 18.2, 7.3. HRMS (ES$^+$) calcd for $C_{20}H_{31}N_3O_5Si$ [M + H]$^+$ 444.1930, found 444.1942.

2n. Yield: 94%; IR (Neat, cm^{-1}) 2975, 2923, 2884, 1685, 1597, 1480, 1454, 1389, 1283, 1236, 1213, 1187, 1162, 1099, 1071, 998, 954, 782; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 10.36 (s, 1H, -*HC*=O), 7.73 - 7.69 (m, 2H, Ar-H), 7.46 (s, 1H, Tz-H), 7.12 - 7.10 (m, 1H, Ar-H), 6.97 - 6.93 (m, 1H, Ar-H), 5.25 (s, 2H, -O*CH*$_2$-), 4.31 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.1 Hz), 3.72 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 8.6 Hz), 1.99 - 1.95 (m, 2H, -C*CH*$_2$C-), 1.13 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 8.5 Hz), 0.52 - 0.47 (m, 2H, -Si*CH*$_2$-). δ_C = 188.8, 160.4, 135.6, 128.5, 125.7, 121.0, 112.5, 62.4, 58.2, 52.2, 23.9, 18.1, 7.2. HRMS (ES$^+$) calcd for $C_{19}H_{29}N_3O_5Si$ [M + Na]$^+$ 430.1774, found 430.1768.

2o. Yield: 93%; IR (Neat, cm^{-1}) 2972, 2884, 1674, 1618, 1599, 1481, 1454, 1388, 1363, 1285, 1241, 1207, 1186, 1161, 1100, 1072, 1001, 954, 876, 753; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 8.78 (s, 1H, -*CH*=N), 8.10 - 6.95 (m, 8H, Ar-H), 7.48 (s, 1H, Tz-H), 5.24 (s, 2H, -O*CH*$_2$-), 4.26 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.2 Hz), 3.67 (q, 6H, -O*CH*$_2$CH$_3$, *J* = 7.0 Hz), 1.98 - 1.89 (m, 2H, -C*CH*$_2$C-), 1.12 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.1 Hz), 0.50 - 0.45 (m, 2H, -Si*CH*$_2$-). δ_C = 158.3, 156.3, 152.8, 136.0, 132.7, 129.1, 127.8, 125.7, 122.8, 121.5, 121.0, 113.1, 112.8, 62.6, 58.4, 52.4, 30.7, 24.1, 18.1, 7.3. HRMS (ES$^+$) calcd for $C_{25}H_{34}N_4O_4Si$ [M + H]$^+$ 483.2427, found 483.2237.

2p. Yield: 88%; IR (Neat, cm^{-1}) 2931, 2873, 1682, 1598, 1582, 1558, 1482, 1456, 1431, 1352, 1259, 1210, 1161, 1121, 1094, 1050, 1013, 937, 908, 876, 754; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 9.48 (s, 1H, -*CH*=N), 8.40 - 6.95 (m, 7H, Ar-H), 7.58 (s, 1H,Tz-H), 5.29 (s, 2H, -O*CH*$_2$-), 4.27 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.2 Hz), 3.70 (q, 6H, -O*CH*$_2$CH$_3$, *J* = 7.1 Hz), 1.99 - 1.90 (m, 2H , -C*CH*$_2$C-), 1.12 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.2 Hz), 0.52 - 0.46 (m, 2H, -Si*CH*$_2$-). δ_C = 188.9, 160.5, 158.9, 158.6, 137.7, 135.7, 133.3, 128.8, 128.2, 122.7, 121.3, 113.1, 112.9, 88.9, 62.8, 58.5, 52.5, 24.2, 18.4, 7.5. HRMS (ES$^+$) calcd for $C_{24}H_{33}N_5O_4Si$ [M + H]$^+$ 484.2380, found 484.2361.

2q. Yield: 94%; IR (Neat, cm^{-1}) 2972, 2933, 2885, 1440, 1389, 1260, 1164, 954, 787; NMR (300 MHz, CDCl$_3$, 25 °C) δ_H = 7.48 (s, 1H, Tz-H), 4.51 (s, 2H, -O*CH*$_2$-), 4.29 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.2 Hz,), 3.74 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 7.0 Hz), 3.34 (s, 3H, -O*CH*$_3$), 1.91 - 1.91 (m, 2H, -C*CH*$_2$C-), 1.15 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.0 Hz), 0.55 - 0.51 (m, 2H, -Si*CH*$_2$-) δ_C = 144.9, 122.3, 66.0, 58.5, 58.3, 52.4, 24.2, 18.3, 7.4. HRMS (ES$^+$) calcd for $C_{13}H_{27}N_3O_4Si$ [M + Na]$^+$ 340.1667, found 340.1650.

2r. Yield: 93%. IR (Neat, cm^{-1}) 2974, 2929, 2892, 1741, 1439, 1389, 1366, 1230, 1164, 1073, 956, 784; NMR (300 MHz, $CDCl_3$, 25 °C) δ_H = 7.52 (s, 1H, Tz-H), 5.11 (s, 2H, -O*CH*$_2$-), 4.28 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 5.6 Hz,), 3.73 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 6.9 Hz), 2.0 - 1.93 (m, 2H, -C*CH*$_2$C-), 1.15 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 6.8 Hz), 0.53 - 0.48 (m, 2H, -Si*CH*$_2$-). δ_C = 170.3, 132.0, 128.3, 123.7, 121.1, 58.2, 57.4, 52.1, 23.6, 20.5, 18.1, 7.2. HRMS (ES$^+$) calcd for $C_{14}H_{27}N_3O_5Si$ [M + Na]$^+$ 368.1617, found 368.1614.

2s. Yield: 93%. IR (Neat, cm^{-1}) 2973, 2929, 2887, 1724, 1634, 1439, 1407, 1295, 1267, 1180, 1045, 957, 809, 782; NMR (300 MHz, $CDCl_3$, 25 °C) δ_H = 7.58 (s, 1H, Tz-H), 6.37 (d, 1H, -*H*$_2$*C*=CH-, *J* = 17.1 Hz), 6.11 - 6.02 (m, 1H, -H$_2$C=*CH*-), 5.78 (d, 1H, -*H*$_2$*C*=CH-, *J* = 10.5 Hz), 5.24 (s, 2H, -O*CH*$_2$-), 4.29 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.2 Hz), 3.74 (q, -O*CH*$_2$CH$_3$-, 6H, *J* = 6.9 Hz,), 1.98 - 1.93 (m, 2H, -C*CH*$_2$C-), 1.15 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 6.9 Hz), 0.56 - 0.55 (m, 2H, -Si*CH*$_2$-). δ_C = 165.3, 142.3, 130.8, 128.1, 123.6, 58.2, 57.5, 52.1, 24.0, 18.1, 7.3. HRMS (ES$^+$) calcd for $C_{15}H_{27}N_3O_5Si$ [M + Na]$^+$ 380.1617, found 380.1694.

2t. Yield: 95%. IR (Neat, cm^{-1}) 3132, 2971, 2927, 2884, 1551, 1438, 1389, 1294, 1214, 1165, 1099, 1072, 954, 876, 780; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 7.19 (s, 1H, Tz-H), 4.24 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.1 Hz), 3.72 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 7.0 Hz,), 2.61 (t, *J* = 7.5 Hz, 2H), 2.07-1.78 (m, 2H, -*CH*$_2$C-), 1.6 - 1.59 (m, 2H, -C*CH*$_2$C-), 1.14 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.0 Hz), 0.91 (t, 3H, -C*CH*$_3$ *J* = 7.3 Hz), 0.57 - 0.35 (m, 2H, -Si*CH*$_2$-). δ_C = 132.2, 128.5, 58.3, 52.1, 27.6, 24.2, 22.6, 18.2, 13.7, 7.4. HRMS (ES$^+$) calcd for $C_{14}H_{29}N_3O_3Si$ [M + Na]$^+$ 338.1875, found 338.1828.

2u. Yield: 95%. IR (Neat, cm^{-1}) 3133, 2955, 2823, 1655, 1587, 1534, 1432, 1351, 1218, 1034, 886, 763, 696 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 7.48 (s, 1H, Tz-H), 4.28 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 6.9 Hz), 3.72 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 7.0 Hz), 3.51 (s, 2H, -*CH*$_2$N-), 2.18 (s, 6H, -N*CH*$_3$), 1.99 - 1.81 (m, 2H, -*CH*$_2$C-), 1.12 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.0 Hz), 0.58 - 0.42 (m, 2H, -Si*CH*$_2$-). δ_C = 144.6, 122.1, 58.3, 54.1, 52.1, 45.9, 24.0, 17.1, 7.1. HRMS (ES$^+$) calcd for $C_{14}H_{30}N_4O_3Si$ [M + H]$^+$ 331.2165, found 331.2171.

2v. Yield: 94%. IR (Neat, cm^{-1}) 2975, 2928, 1437, 1390, 1294, 1221 ,1165, 1101, 1075, 957, 907, 782; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 7.33 (s, 1H, Tz-H), 6.50-6.36 (m, 1H, -*CH*=*CH*-), 4.25 (t, 2H, -N$_3$*CH*$_2$CH$_2$-, *J* = 7.1 Hz), 3.74 (q, 6H, -O*CH*$_2$CH$_3$-, *J* = 7.0 Hz), 2.38-2.25 (m, 2H, =C*CH*$_2$-), 2.12 (dd, 2H, -C*CH*$_2$- *J* = 5.9, 2.6 Hz), 2.02-1.84 (m, 2H, -*CH*$_2$C-), 1.73-1.66 (m, 2H, -C*CH*$_2$C-), 1.63 - 1.54 (m, 2H, -C*CH*$_2$C-), 1.14 (t, 9H, -OCH$_2$*CH*$_3$, *J* = 7.0 Hz), 0.61 -

0.46 (m, 2H, -SiCH_2-). δ_C = 148.9, 127.6, 124.2, 118.4, 58.2, 53.3, 26.4, 25.2, 22.5, 22.2, 18.1, 7.2. HRMS (ES^+) calcd for $C_{17}H_{31}N_3O_4Si$ $[M + Na]^+$ 376.2031, found 376.2080.

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Captions of figures and Tables:

Figure 1: Comparison of ^{1}H NMR spectra between cyclized silane and AzPTES.

Figure 2: FT-IR spectra of AzPTES and polyfunctional triethoxysilanes (**2a-2v**).

Table 1: Clickable terminal alkynes (**1a-1v**).

Table 2: Synthesized polyfunctional triethoxysilanes (**2a-2v**).

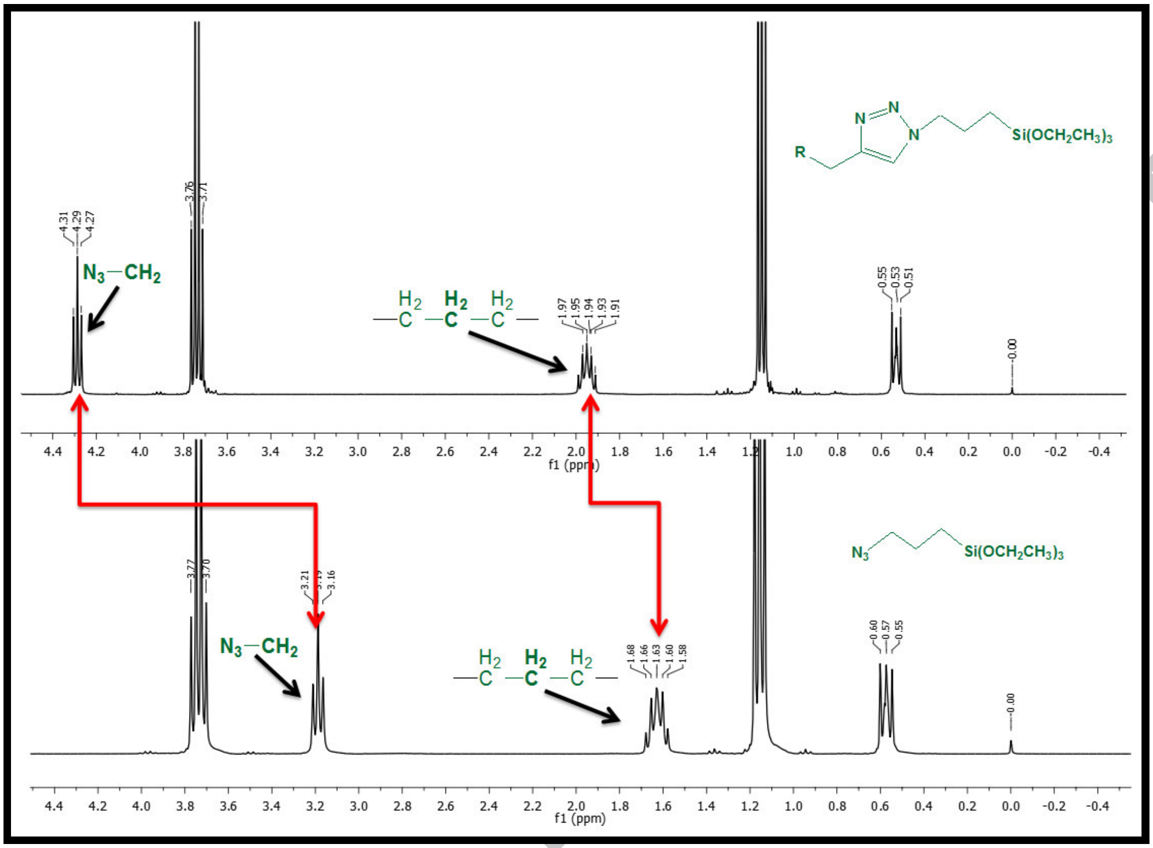


Figure 1: Comparison of ^{1}H NMR spectra between cyclized silane and AzPTES

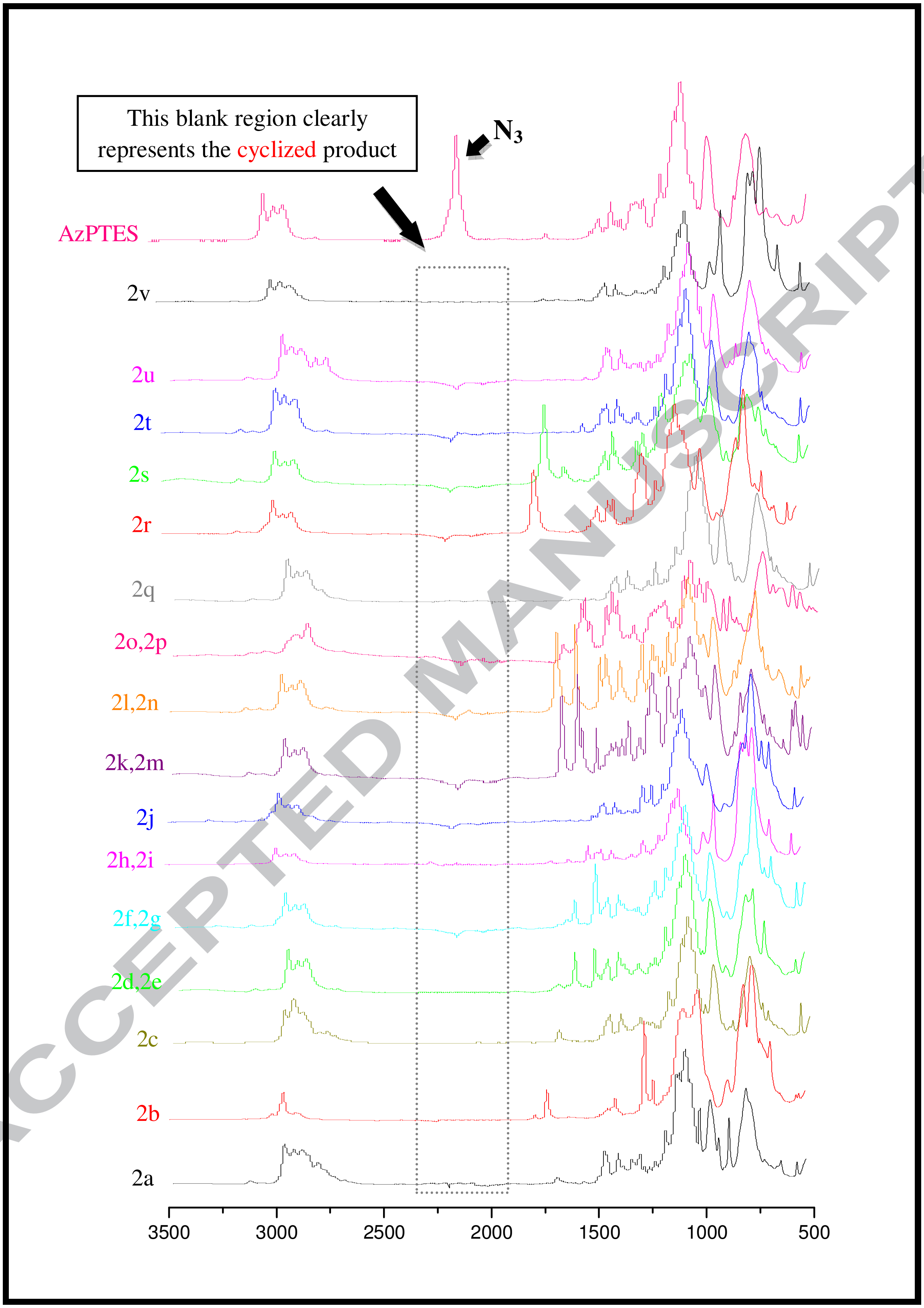


Figure 2: FT-IR spectra of AzPTES and polyfunctional triethoxysilanes (**2a-2v**)

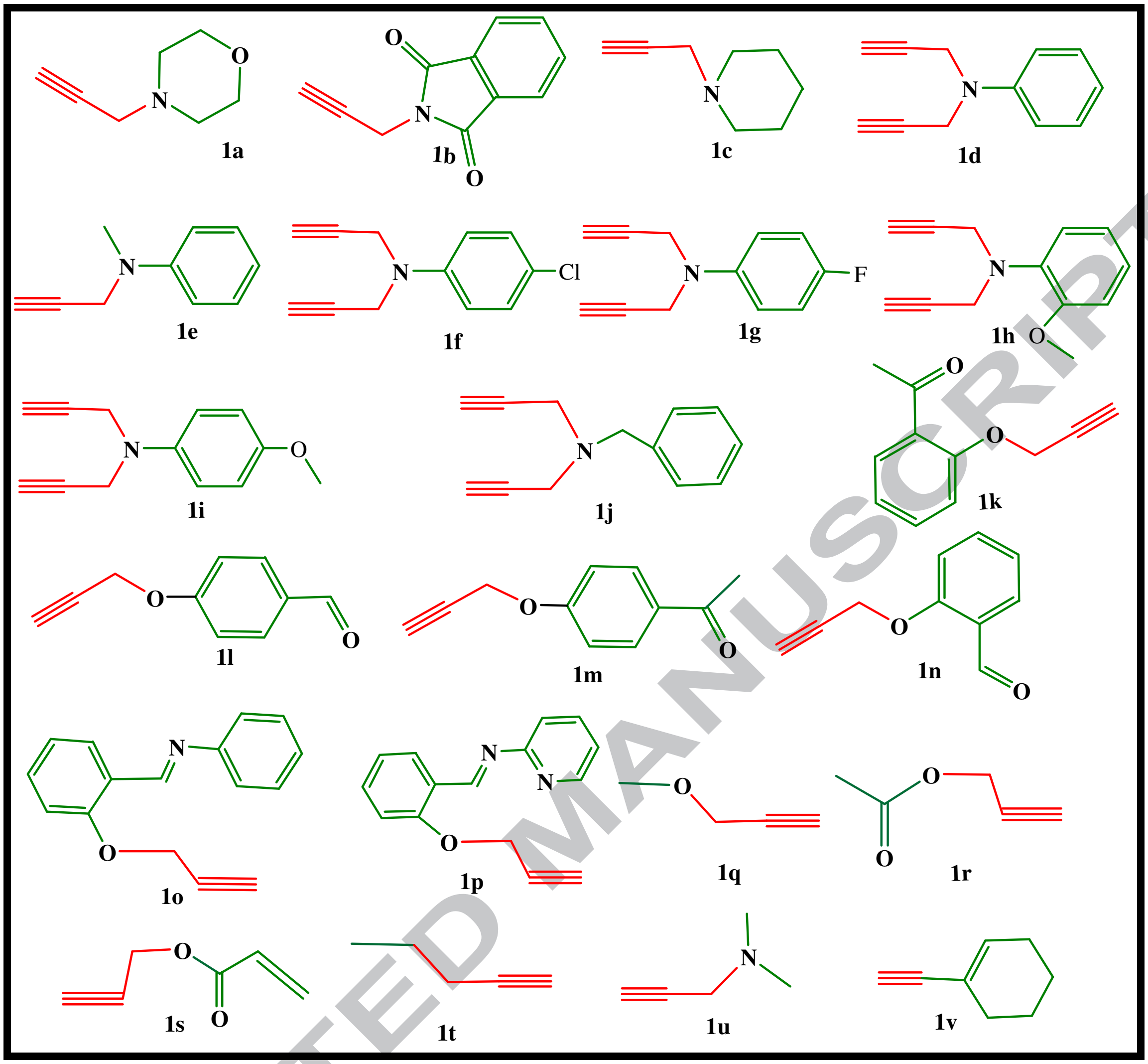
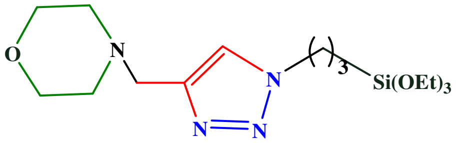
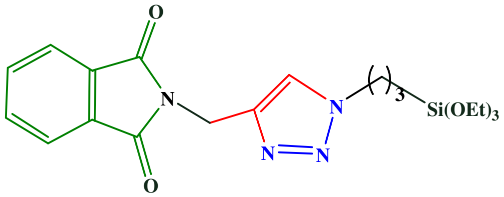
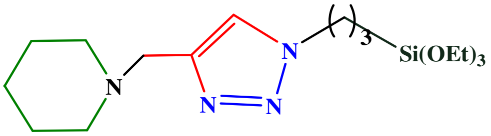
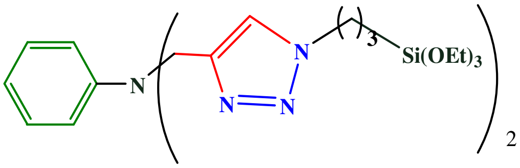
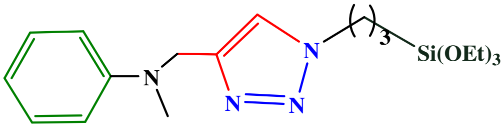
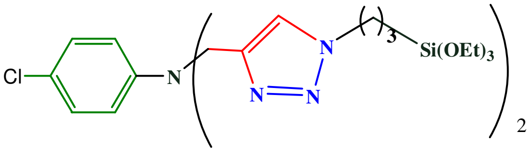
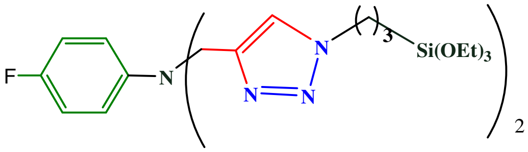
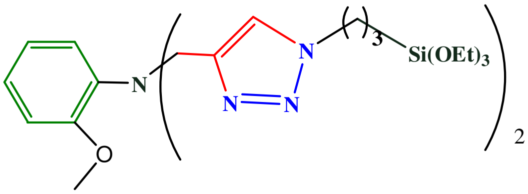
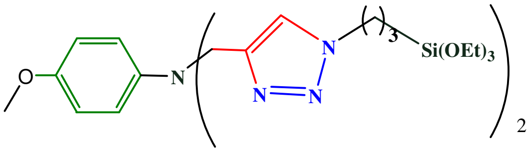
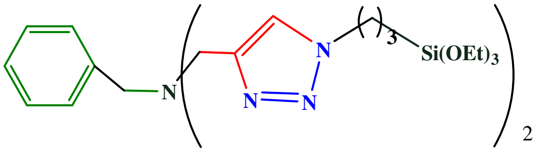
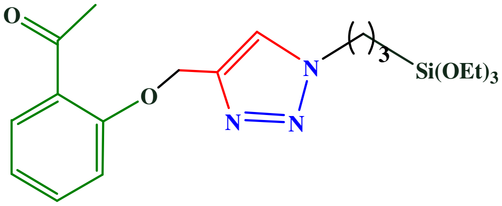
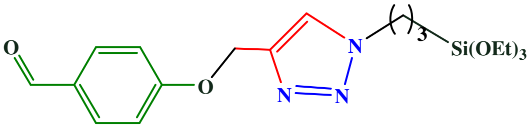
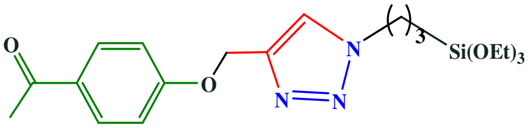
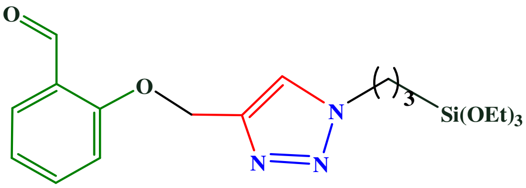
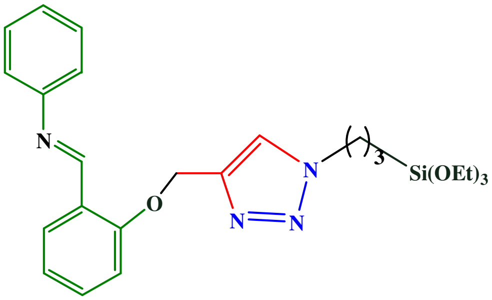


Table 1: Clickable terminal alkynes (**1a-1v**)

Terminal Alkyne	Reaction Time (h)	Product	Compound name	Yield (%)
1a	5		**2a**	**95**
1b	5		**2b**	**93**
1c	20		**2c**	**93**
1d	20		**2d**	**94**
1e	10		**2e**	**93**
1f	10		**2f**	**86**
1g	10		**2g**	**91**
1h	10		**2h**	**89**

1i	10		**2i**	**88**
1j	10		**2j**	**88**
1k	5		**2k**	**94**
1l	5		**2l**	**93**
1m	5		**2m**	**95**
1n	5		**2n**	**94**
1o	15		**2o**	**93**

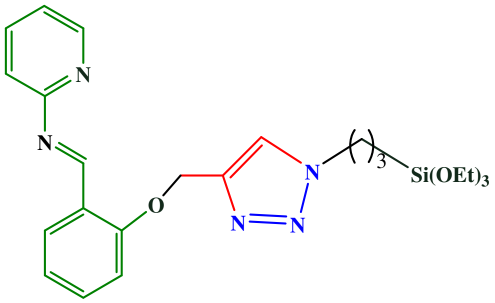
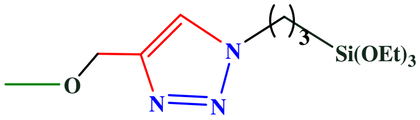
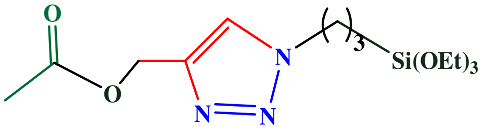
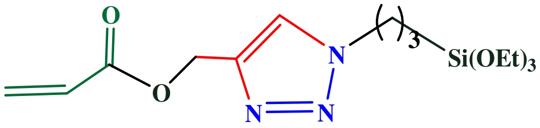
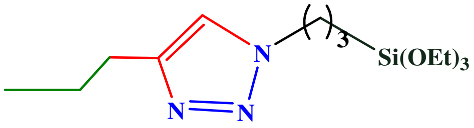
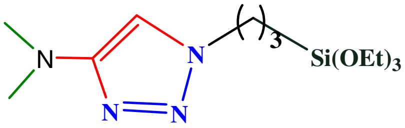
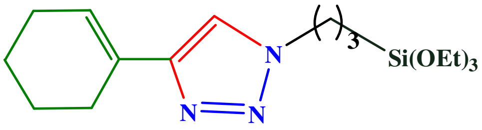
1p	15		**2p**	**88**
1q	5		**2q**	**94**
1r	5		**2r**	**93**
1s	5		**2s**	**93**
1t	5		**2t**	**95**
1u	5		**2u**	**95**
1v	5		**2v**	**94**

Table 2: Synthesized polyfunctional triethoxysilanes (**2a-2v**).