This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Graphical Abstract

Synthetic approach towards ‘Click’ modified chalcone based organotriethoxysilanes; UV–Vis study

Gurjaspreet Singh,* Jandeep Singh, Satinderpal Singh Mangat, Aanchal Arora

Department of Chemistry and Centre of Advanced Studies, Panjab University, Chandigarh, 160014, India.

*Corresponding Author

Email: gipsingh@pu.ac.in, Phone: +91-0172-2534428
Synthetic approach towards ‘Click’ modified chalcone based organotriethoxysilanes;

UV–Vis study

Abstract

The efficient linkage of conjugate chalcone to n-propyltriethoxysilanes (nPTES) via 1,2,3-triazole is being reported, in good yield which involves Claisen–Schmidt condensation followed by Copper (I) catalyzed azide–alkyne cycloaddition (CuAAC) reaction as synthetic intermediary routes. Two different approaches followed for syntheses, restrict us to follow single pathway exclusively as an efficient route for organotriethoxysilanes (OTES) preparation. The performance of click reaction under thermal reaction conditions has also been optimized using [CuBr(PPh$_3$)$_3$] catalyst. The photoelectronic spectroscopy study in UV–Vis region show significant absorption maxima in range of 300–325 nm. Moreover, the solvatochromic aspects showing the effect of change in solvent polarity on absorption maxima is being investigated for the first time on functionalised OTES.

Keywords: CuAAC, chalcone, click silylation, γ-propyltriethoxysilane, solvatochromism
Introduction

The modification in organic segment of hybrid silica precursors have manifolded their utility in the field of drug discovery, catalysis, surface coating of materials, polymer formation, ion detecting fluorescent probes, HPLC packing, and in nano chemistry. The synthetic approach leading to generation of polyfunctional triethoxysilanes (PfTES) acting as precursor to these materials follow different pathways such as cross-coupling reaction, hydrosilylation, and transmetalation reaction. These reaction methodologies require the use of expensive metals, show limited functional group tolerance and result in moderate to good yield. The major shortcoming in these conventional methodologies is the purification of ‘hydrolytically unstable’ PfTES and control of regioselectivity.

To override these limitations, a new technique was pioneered in 2001 by Sharpless and Meldal, and exploited by Cattoen et al., to fine tune nearly all functional groups hooked to azide linked nPTES using Cu(I), thereby expanding the scope and utility of this methodology. This technique follows CuAAC reaction of azide–alkyne fragments to 1,2,3-triazole with efficient conversion of above 80% and 100% control over regioselectivity. Numerous catalytic systems have been reported for click reaction but the use of [CuBr(PPh3)3]/THF–TEA system has been promising as efficient catalytic scheme for the synthesis of functionalised OTES. Further, 1,2,3-triazolyl heterocycle proves to be an important pharmacore associated with immense medicinal importance as antimycobacterial activity, antituberculosis, antiinflammatory, antiangiogenic, antiviral, anticancerous as histone deacetylase inhibitor and anti–HIV activity.

The combination of smaller fragments to assemble as larger unit with enhanced pharmacological activity forms an important aspect of synthetic biochemistry and is acquiring constant attention with increasing benefits in medicinal chemistry. The
applicability of combinatorial approach has led to generation of substituted chalcone based moieties that act as primary precursor to flavonoids and isoflavonoids, that are abundantly distributed in edible plants and are associated to be essential cancer chemo–preventive food components.\textsuperscript{39–41} A chalcone unit comprises of two aromatic rings connected by a three carbon chain as α,β unsaturated carbonyl group (Figure 1). They are considered as pharmacologically relevant entities known to exert pathogenic activity\textsuperscript{41} along with antitumorigenic,\textsuperscript{43} antiinflammatory,\textsuperscript{44} antiangiogenic,\textsuperscript{45} antioxidant,\textsuperscript{46} antituberculosis,\textsuperscript{47} antimalarial,\textsuperscript{48} and anti–HIV properties.\textsuperscript{49} With this perspective to synthesize material with merged activity of both functionalities, the integration of pharmacore chalcone moiety onto medicinally vibrant 1,2,3–triazole was carried out.

![Chemical structure of chalcone unit](image)

**Figure 1**: Chemical structure of chalcone unit consisting of two aromatic rings linked by three-carbon chain forming α–β unsaturated carbonyl moiety

**Experimental**

**General material and methods**: All the syntheses were carried out under dry nitrogen atmosphere using vacuum glass line. The organic solvents used were dried and purified according to the standard procedure and stored under dry nitrogen atmosphere. Bromotris(triphenylphosphine)copper(I) (Aldrich), γ-chloropropyltriethoxysilane (CPTES) (Aldrich), propargyl bromide (80% wt. solution in toluene) (Aldrich), sodium azide (SDFCL), potassium carbonate (THOMAS BAKER), N,N-dimethylformamide (SDFCL), were used as supplied. Acetophenone (SDFCL), 2-hydroxyacetophenone (SDFCL), 3-
hydroxyacetophenone (SDFCL), 4-hydroxyacetophenone (SDFCL), salicylaldehyde (Aldrich), 3-hydroxybenzaldehyde (SDFCL), 4-hydroxybenzaldehyde (SDFCL), p-methoxyacetophenone (HIMEDIA), 2,4-dimethoxyacetophenone (HIMEDIA) were used as supplied for synthesis of terminal alkynes 3a–3i and 5a–5i. γ-azidopropyltriethoxysilane (AzPTES) was synthesized according to procedure known in literature.20

**Synthesis of compounds 2a(i–iii) and 2b(i–iii)**

To a uniformly stirred solution of 1a/1b (2g, 16.40 mmol, 1 equiv) in 15 ml of DMF cooled in ice bath to –5 °C K2CO3 (6.76 g, 47.2 mmol, 3 equiv) was added. To this stirring mixture, propargyl bromide (2.15 g, 1.61 ml, 18.06 mmol, 1.1 equiv) was slowly injected dropwise within 5 min. After complete addition of reactants, the temperature of reaction mixture was slowly raised to 30 °C in 1 h and stirred at this temperature for 14 h. The reaction mixture was quenched by addition of ice cold water and filtered the solid product (in case of 2a(i, iii); 2b(i–iii)). In case of low melting solid 2a(ii), ethyl acetate was used for extraction. The combined organic layers were dried over anhydrous MgSO4 and vacuum evaporation of solvent resulted into the formation of desired compound. The solid alkynes were recrystallized by dissolving in minimum amount of absolute ethanol.

**Synthesis of compounds 3a–3i/5a–5i**

The compounds 2a/2b (1 equiv) and 1c(a–c) (1 equiv) were independently dissolved in minimum amounts of absolute ethanol till clear solution. In another round bottom flask, KOH (0.02 g, 0.36 mmol) was dissolved in ethanol and slowly added solution of 2a/2b and 1c(a–c) respectively. The reaction was stirred for 4 h and monitored the end point using TLC (hexane:ethyl acetate (8:2)). The aldol condensation mixture of 2a and 1c(a–c) yielded compounds 3a–3i while mixture of 2a and 2b yielded compounds 5a–5i. On completion, the reaction was quenched by ice cold water, extracted with methylene chloride and washed
twice with brine solution. The combined organic phases were dried over anhydrous MgSO$_4$ and vacuum evaporation of solvent afforded the desired product.

**Synthesis of compounds 4a–4i/6a–6i**

In a 25 ml two neck round bottom flask, alkyne 3a–3i/5a–5i were dissolved in 1:1 solution of THF:TEA (3 ml) till uniform solution followed by catalyst loading (0.02 mmol for 3a–3i and 0.04 mmol for 5a–5i). The slow and dropwise addition of AzPTES (1 equiv for 3a–3i and 2 equiv for 5a–5i) under carried out inert atmosphere. The temperature of reaction mixture was raised slowly to 65 °C and stirred vigorously for 3 h. After completion of reaction, the assembly was cooled to room temperature, filtered the mixture containing used Cu(I) catalyst and vacuum evaporation of solvents resulted into desired nPTES 4a–4i/6a–6i.

**Spectroscopic data for compounds 4a–4i**

1-phenyl-3-(2-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl) methoxy)phenyl)prop-2-en-1-one (4a): Yield: 91%, Empirical formula: C$_{27}$H$_{35}$N$_3$O$_5$Si; Anal. Calcd: C, 63.6; H, 6.9; N, 8.2; Found: C, 63.4; H, 6.8; N, 8.0; IR (neat, cm$^{-1}$): 2965, 2929, 2876, 1659, 1597, 1574, 1485, 1448, 1332, 1258, 1213, 1162, 1073, 1015, 907, 792, 726, 691, 646. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ = 8.00 (d, $^3$$J$ = 15.8 Hz, 1H), 7.87 (d, $^3$$J$ = 7.5 Hz, 1H), 7.55 (d, $^3$$J$ = 6.3 Hz, 3H), 7.44 (d, $^3$$J$ = 7.4 Hz, 2H), 7.38 (d, $^3$$J$ = 7.7 Hz, 2H), 7.01 (d, $^3$$J$ = 8.3 Hz, 1H), 6.92 (d, $^3$$J$ = 8.1 Hz, 2H), 5.21 (s, 2H), 4.25 (t, $^3$$J$ = 7.2 Hz, 2H), 3.69 (q, $^3$$J$ = 7.0 Hz, 6H), 2.04 – 1.90 (m, 2H), 1.10 (t, $^3$$J$ = 7.0 Hz, 9H), 0.57 – 0.41 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 189.8, 156.4, 142.5, 139.1, 137.3, 131.6, 130.7, 128.6, 127.5, 123.2, 122.0, 120.3, 111.7, 57.4, 55.1, 51.5, 23.3, 17.3, 6.4.

1-phenyl-3-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4b): Yield: 89%, Empirical formula: C$_{27}$H$_{35}$N$_3$O$_5$Si; Anal. Calcd: C, 63.6; H,
6.9; N, 8.2; Found: C, 63.3; H, 6.7; N, 8.3; IR (neat, cm⁻¹): 2972, 2925, 2884, 1663, 1596, 1578, 1485, 1447, 1315, 1289, 1235, 1073, 1161, 1034, 1016, 955, 770, 688, 566. ¹H NMR (400 MHz, CDCl₃) δ = 8.08 – 7.86 (m, 2H), 7.77 (d, ³J = 15.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.36 – 7.31 (m, 1H), 7.27 (dd, ³J = 11.4, 5.3 Hz, 2H), 7.10 – 6.98 (m, 2H), 5.26 (s, 2H), 4.37 (t, ³J = 7.2 Hz, 2H), 3.81 (q, ³J = 7.0 Hz, 6H), 2.20 – 1.90 (m, 2H), 1.21 (t, ³J = 7.0 Hz, 9H), 0.68 – 0.53 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.3, 157.6, 156.8, 143.4, 137.0, 135.3, 131.8, 129.0, 127.5, 121.4, 120.7, 115.9, 113.5, 113.3, 66.9, 61.1, 57.5, 54.8, 51.5, 24.5, 23.1, 17.2, 6.4.

1-phenyl-3-(4-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4c): Yield: 90%, Empirical formula: C₂₇H₃₅N₃O₅Si; Anal. Calcd: C, 63.6; H, 6.9; N, 8.2; Found: C, 63.4; H, 7.0; N, 8.1; IR (neat, cm⁻¹): 2972, 2933, 2885, 1659, 1595, 1572, 1507, 1447, 1422, 1389, 1335, 1291, 1213, 1172, 1072, 1015, 956, 827, 778, 691, 657, 513. ¹H NMR (400 MHz, CDCl₃) δ = 7.92 (d, ³J = 7.3 Hz, 1H), 7.69 (d, ³J = 15.6 Hz, 1H), 7.51 (dd, ³J = 8.7, 4.1 Hz, 2H), 7.40 (t, ³J = 7.5 Hz, 1H), 7.35 (d, ³J = 7.8 Hz, 2H), 7.32 (d, ³J = 3.5 Hz, 1H), 7.17 (dd, ³J = 10.1, 6.0 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.96 – 6.89 (m, 2H), 5.16 (s, 2H), 4.31 – 4.25 (m, 2H), 3.72 (d, ³J = 7.4 Hz, 6H), 2.00 – 1.90 (m, 2H), 1.14 (d, ³J = 7.0 Hz, 9H), 0.56 – 0.42 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.5, 158.5, 143.4, 137.4, 131.6, 129.1, 127.4, 126.8, 124.1, 121.8, 119.2, 114.3, 113.7, 61.1, 57.5, 54.8, 52.8, 23.2, 17.3, 6.4. MS (ES⁺) Calcd for [M+Na]⁺ 532.2; Found 532.3.

1-(4-methoxyphenyl)-3-(2-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4d): Yield: 88%, Empirical formula: C₂₈H₇₃N₃O₆Si; Anal. Calcd: C, 62.3; H, 6.9; N, 7.8; Found: C, 62.2; H, 6.8; N, 8.0; IR (neat, cm⁻¹): 2973, 2933, 2888, 1654, 1597, 1573, 1509, 1455, 1308, 1256, 1216, 1165, 1103, 1074, 1019, 907, 753, 725, 646, 614, 587, 541.¹H NMR (400 MHz, CDCl₃) δ = 8.05 – 7.97 (m, 2H), 7.91 (d, ³J
= 8.8 Hz, 2H), 7.65 – 7.53 (m, 3H), 7.28 (t, $^3J = 7.2$ Hz, 1H), 7.03 (d, $^3J = 8.3$ Hz, 1H), 6.94 (d, $^3J = 7.6$ Hz, 1H), 6.88 (d, $^3J = 8.8$ Hz, 2H), 5.24 (s, 2H), 4.28 (t, $^3J = 7.2$ Hz, 2H), 3.79 (s, 3H), 3.71 (q, $^3J = 6.9$ Hz, 6H), 2.01 – 1.90 (m, 2H), 1.12 (t, $^3J = 7.0$ Hz, 9H), 0.63 – 0.39 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 188.1, 162.3, 142.6, 138.3, 131.1, 130.5, 129.8, 127.4, 125.1, 123.3, 121.9, 121.6, 120.3, 112.6, 111.7, 61.5, 57.5, 54.4, 51.6, 23.2, 17.3, 6.4.

1-(4-methoxyphenyl)-3-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4e): Yield: 90%, Empirical formula: C$_{28}$H$_{37}$N$_3$O$_6$Si; Anal. Calcd: C, 62.3; H, 6.9; N, 7.8; Found: C, 62.1; H, 6.7; N, 7.7; IR (neat, cm$^{-1}$): 2975, 2938, 2889, 1659, 1500, 1484, 1389, 1251, 1168, 1075, 906, 831, 785, 724, 646, 616, 541. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.97 (d, $^3J = 8.8$ Hz, 2H), 7.68 (d, $^3J = 15.6$ Hz, 1H), 7.58 (s, 1H), 7.46 (d, $^3J = 15.6$ Hz, 1H), 7.26 (t, $^3J = 7.9$ Hz, 1H), 7.19 (dd, $^3J = 10.5$, 4.9 Hz, 2H), 6.97 (dd, $^3J = 8.1$, 2.1 Hz, 2H), 6.91 (d, $^3J = 8.8$ Hz, 2H), 5.19 (s, 2H), 4.30 (t, $^3J = 7.2$ Hz, 2H), 3.81 (s, 3H), 3.73 (q, $^3J = 7.0$ Hz, 6H), 2.01 – 1.90 (m, 2H), 1.14 (t, $^3J = 7.0$ Hz, 9H), 0.62 – 0.44 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 187.6, 162.5, 157.6, 142.7, 135.6, 131.1, 129.9, 127.5, 121.8, 121.3, 120.7, 115.7, 113.3, 112.9, 57.5, 54.5, 51.5, 17.3, 6.4.

1-(4-methoxyphenyl)-3-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4f): Yield: 87%, Empirical formula: C$_{28}$H$_{37}$N$_3$O$_6$Si; Anal. Calcd: C, 62.3; H, 6.9; N, 7.8; Found: C, 62.4; H, 6.7; N, 7.5; IR (neat, cm$^{-1}$): 2973, 2933, 2884, 1656, 1600, 1507, 1422, 1390, 1257, 1216, 1165, 1074, 958, 905, 787, 725, 646. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.98 (d, $^3J = 8.8$ Hz, 2H), 7.75 (m, 2H), 7.63 (d, $^3J = 4.4$ Hz, 1H), 7.54 (d, $^3J = 8.6$ Hz, 1H), 7.42 (d, $^3J = 9.6$ Hz, 1H), 7.37 (s, 1H), 7.06 (d, $^3J = 8.6$ Hz, 1H), 6.98 (d, $^3J = 8.6$ Hz, 1H), 6.92 (d, $^3J = 8.8$ Hz, 1H), 5.22 (d, $^3J = 14.5$ Hz, 2H), 4.33 (t, $^3J = 7.1$ Hz, 2H), 3.82 (s, 3H), 3.76 (q, $^3J = 7.0$ Hz, 6H), 2.09 – 1.91 (m, 2H), 1.17 (t, $^3J = 7.0$ Hz, 9H), 0.61 – 0.50 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 187.6, 162.3, 142.4, 131.1,
HRMS (ES\textsuperscript{+}) Calcd for [M+Na]\textsuperscript{+} 562.2245; Found 762.2288.

1-(2,4-dimethoxyphenyl)-3-(2-((1-(3-(triethoxysilyl)propyl)1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4g): Yield: 88%, Empirical formula: C\textsubscript{29}H\textsubscript{39}N\textsubscript{3}O\textsubscript{7}Si; Anal. Calcd: C, 61.1; H, 6.9; N, 7.4; Found: C, 60.9; H, 6.7; N, 7.5; IR (neat, cm\textsuperscript{-1}): 2970, 2925, 2880, 2839, 1687, 1597, 1577, 1507, 1422, 1310, 1248, 1212, 1108, 1073, 1018, 827, 759, 643. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.84 – 7.64 (m, 3H), 7.64 – 7.53 (m, 1H), 7.53 – 7.44 (m, 2H), 7.43 – 7.15 (m, 1H), 7.07 – 6.99 (m, 1H), 6.96 – 6.89 (m, 2H), 6.55 – 6.34 (m, 2H), 5.22 (s, 2H), 4.30 (td, \textit{j} = 7.2, 3.1 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.86 – 3.76 (m, 3H), 3.76 (q, \textit{j} = 7.0 Hz, 6H), 2.08 – 1.87 (m, 2H), 1.12 (t, \textit{j} = 7.0 Hz, 9H), 0.60 – 0.42 (m, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 190.8, 163.2, 143.0, 141.8, 132.8, 131.9, 130.6, 130.3, 130.0, 122.9, 115.1, 105.1, 98.7, 62.2, 58.6, 52.6, 24.2, 18.3, 7.5.

1-(2,4-dimethoxyphenyl)-3-(3-((1-(3-(triethoxysilyl)propyl)1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4h): Yield: 89%, Empirical formula: C\textsubscript{29}H\textsubscript{39}N\textsubscript{3}O\textsubscript{7}Si; Anal. Calcd: C, 61.1; H, 6.9; N, 7.4; Found: C, 61.0; H, 6.8; N, 7.2; IR (neat, cm\textsuperscript{-1}): 2970, 2924, 2886, 1689, 1658, 1597, 1576, 1508, 1462, 1438, 1421, 1358, 1254, 1210, 1106, 1159, 1072, 1022, 826, 799, 721, 695, 644, 568, 541. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.65 (d, \textit{j} = 8.4 Hz, 1H), 7.55 (d, \textit{j} = 13.8 Hz, 2H), 7.46 (d, \textit{j} = 7.8 Hz, 2H), 7.31 (d, \textit{j} = 15.7 Hz, 2H), 6.92 (d, \textit{j} = 8.0 Hz, 2H), 6.47 (d, \textit{j} = 8.3 Hz, 2H), 6.41 (s, 1H), 5.16 (s, 2H), 4.27 (t, \textit{j} = 7.2 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.72 (dd, \textit{j} = 13.4, 6.6 Hz, 6H), 2.02 – 1.90 (m, 2H), 1.13 (t, \textit{j} = 6.7 Hz, 9H), 0.61 – 0.43 (m, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 189.5, 163.0, 159.3, 158.8, 142.5, 140.8, 131.7, 131.1, 128.9, 127.6, 124.3, 121.9, 121.4, 114.1, 104.2, 61.1, 57.5, 54.7, 54.5, 51.5, 23.2, 17.3, 6.4.
1-(2,4-dimethoxyphenyl)-3-(4-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (4i): Yield: 87%, Empirical formula: C_{29}H_{39}N_{3}O_{7}Si; Anal. Calcd: C, 61.1; H, 6.9; N, 7.4; Found: C, 61.3; H, 6.8; N, 7.2; IR (neat, cm\(^{-1}\)): 2962, 2922, 2884, 1658, 1601, 1509, 1443, 1417, 1257, 1166, 1074, 1010, 864, 786, 695, 541. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.96\) (d, \(^3\)J = 16.0 Hz, 1H), 7.66 (d, \(^3\)J = 8.6 Hz, 1H), 7.55 (dd, \(^3\)J = 10.0, 2.1 Hz, 2H), 7.46 (d, \(^3\)J = 15.9 Hz, 1H), 7.42 – 7.28 (m, 1H), 7.24 (dd, \(^3\)J = 12.0, 5.1 Hz, 1H), 7.17 (dd, \(^3\)J = 13.9, 8.1 Hz, 1H), 7.01 (d, \(^3\)J = 8.3 Hz, 1H), 6.91 (t, \(^3\)J = 7.6 Hz, 1H), 6.47 (dd, \(^3\)J = 8.6, 2.2 Hz, 1H), 6.40 (d, \(^4\)J = 2.2 Hz, 1H), 5.23 (s, 2H), 4.26 (t, \(^3\)J = 7.2 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.72 (q, \(^3\)J = 7.0 Hz, 6H), 2.04 – 1.92 (m, 2H), 1.12 (t, \(^3\)J = 7.0 Hz, 9H), 0.60 – 0.43 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 189.8, 163.1, 159.4, 156.2, 142.9, 136.1, 131.8, 130.3, 127.5, 126.7, 123.8, 121.7, 121.4, 120.3, 111.9, 104.2, 97.6, 61.9, 57.5, 54.7, 54.5, 51.6, 23.2, 17.3, 6.4. HRMS (ES\(^{+}\)) Calcd for [M+Na]\(^+\) 592.2455; Found 592.2365.

Spectroscopic data for compounds 6a–6i

1,3-bis(2-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6a): Yield: 90%, Empirical formula: C_{39}H_{58}N_{6}O_{9}Si\(_2\); Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.5; H, 7.1; N, 10.2; IR (neat, cm\(^{-1}\)): 3072, 3024, 2921, 2891, 1652, 1597, 1482, 1448, 1371, 1327, 1287, 1216, 1162, 1105, 1050, 1015, 925, 872, 834, 820, 748, 676, 633, 584. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.00\) (d, \(^3\)J = 7.3 Hz, 2H), 7.67 (s, 2H), 7.60 (d, \(^3\)J = 8.6 Hz, 2H), 7.48 (d, \(^3\)J = 7.1 Hz, 2H), 7.44 (s, 2H), 7.03 (d, \(^1\)J = 8.6 Hz, 2H), 5.25 (s, 4H), 4.37 (t, \(^3\)J = 7.2 Hz, 4H), 3.81 (dd, \(^3\)J = 14.4, 7.4 Hz, 12H), 2.08 – 1.96 (m, 4H), 1.21 (t, \(^3\)J = 7.0 Hz, 18H), 0.65 – 0.53 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 189.5, 159.3, 143.5, 137.4, 131.6, 130.9, 129.2, 127.5, 127.1, 127.1, 126.5 (m), 126.5, 119.1, 114.2, 61.1, 57.5, 52.7, 51.5, 23.2, 21.6, 17.3, 6.5.
1-(2-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)-3-(3-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6b):
Yield: 90%, Empirical formula: C39H58N6O9Si2; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.6; H, 7.0; N, 10.5; IR (neat, cm⁻¹): 2972, 2929, 2885, 1660, 1598, 1484, 1448, 1389, 1286, 1236, 1162, 1071, 954, 783, 757, 696, 542. ¹H NMR (400 MHz, CDCl₃) δ = 7.58 (dd, 3J = 13.8, 7.4 Hz, 2H), 7.48 (d, 3J = 15.9 Hz, 1H), 7.39 (dd, 3J = 19.2, 11.6 Hz, 2H), 7.32 – 7.13 (m, 2H), 7.05 (dd, 3J = 12.8, 8.3 Hz, 2H), 7.01 – 6.87 (m, 2H), 6.81 (s, 1H), 5.24 (s, 2H), 5.14 (s, 2H), 4.28 (t, 3J = 7.1 Hz, 2H), 4.04 (t, 3J = 7.1 Hz, 2H), 3.71 (td, 3J = 13.8, 6.9 Hz, 12H), 1.94 (dd, 3J = 15.4, 7.6 Hz, 2H), 1.88 – 1.67 (m, 2H), 1.28 – 0.94 (m, 18H), 0.56 – 0.47 (m, 2H), 0.46 – 0.32 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 191.3, 157.7, 155.9, 141.2, 135.5, 132.2, 131.2, 130.8, 129.6, 129.0, 128.5, 127.5, 126.7, 121.9, 120.7, 115.9, 113.2, 112.1, 61.9, 61.1, 51.4, 23.1, 17.3, 6.4.

1-(2-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)-3-(4-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6c):
Yield: 89%, Empirical formula: C39H58N6O9Si2; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.5; H, 7.1; N, 10.2; IR (neat, cm⁻¹): 2972, 2929, 2885, 1654, 1597, 1508, 1482, 1449, 1422, 1389, 1330, 1292, 1239, 1172, 1071, 1026, 954, 858, 752, 542. ¹H NMR (400 MHz, CDCl₃) δ = 7.68 – 7.59 (m, 2H), 7.58 – 7.50 (m, 2H), 7.46 (d, 3J = 7.5 Hz, 3H), 7.29 (t, 3J = 7.9 Hz, 1H), 7.13 (d, 3J = 8.3 Hz, 1H), 7.05 (t, 3J = 7.5 Hz, 1H), 6.98 (t, 3J = 8.3 Hz, 2H), 5.30 (s, 2H), 5.23 (s, 2H), 4.36 (t, 3J = 6.7 Hz, 2H), 4.17 (t, 3J = 7.2 Hz, 2H), 3.87 – 3.69 (m, 12H), 2.08 – 1.97 (m, 2H), 1.93 – 1.83 (m, 2H), 1.20 (dt, 3J = 10.1, 3.5 Hz, 18H), 0.63 – 0.55 (m, 2H), 0.54 – 0.42 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 192.6, 160.1, 156.7, 143.6, 143.3, 142.1, 132.8, 130.4, 130.0, 129.8, 128.1, 125.4, 122.8, 121.4, 115.2, 113.1, 67.9, 63.0, 62.1, 58.5, 52.5, 24.1, 18.2, 11.3, 7.4. MS (ES⁺) Calcd for [M+Na]⁺ 833.4; Found 833.5.
3-(2-((1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-ylmethoxy)phenyl)-1-(3-(1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-ylmethoxy)phenyl)prop-2-en-1-one (6d):
Yield: 87%, Empirical formula: C$_{39}$H$_{58}$N$_6$O$_9$Si$_2$; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.5; H, 7.0; N, 10.1; IR (neat, cm$^{-1}$): 2973, 2926, 2884, 1660, 1594, 1577, 1485, 1438, 1389, 1328, 1273, 1240, 1164, 1099, 1071, 1007, 954, 867, 782, 750, 721, 696, 679, 593, 541. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.68$ (d, $^3$J = 15.7 Hz, 1H), 7.60 (d, $^3$J = 4.3 Hz, 2H), 7.55 (d, $^3$J = 7.2 Hz, 1H), 7.45 (s, 1H), 7.40 – 7.31 (m, 2H), 7.23 (t, $^3$J = 7.1 Hz, 1H), 2.04 – 1.83 (m, 4H), 1.22 – 1.05 (m, 18H), 0.59 – 0.43 (m, 4H).

13C NMR (101 MHz, CDCl$_3$) $\delta = 188.9, 157.6, 156.9, 143.6, 142.5, 138.5, 135.3, 131.0, 128.9, 128.7, 128.4, 127.4, 121.3, 120.8, 120.5, 118.9, 116.0, 113.1, 61.1, 57.5, 51.5, 23.2, 17.3, 6.4.

1,3-bis(3-(1-(3-(triethoxysilyl)propyl)-1H,2,3-triazol-4-ylmethoxy)phenyl)prop-2-en-1-one (6e): Yield: 83%, Empirical formula: C$_{39}$H$_{58}$N$_6$O$_9$Si$_2$; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.5; H, 7.1; N, 10.2; IR (neat, cm$^{-1}$): 3019, 2977, 2881, 1651, 1593, 1521, 1484, 1390, 1325, 1214, 1161, 1075, 1033, 1015, 742, 669, 665, 627, 542. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.05$ (d, $^3$J = 15.8 Hz, 1H), 7.60 (s, 1H), 7.57 (s, 2H), 7.54 – 7.45 (m, 2H), 7.39 (dd, $^3$J = 8.5, 1.9 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.13 (dd, $^3$J = 8.1, 2.3 Hz, 1H), 7.05 (d, $^3$J = 8.3 Hz, 1H), 6.95 (t, $^3$J = 7.5 Hz, 1H), 5.26 (s, 2H), 5.19 (s, 2H), 4.29 (q, $^3$J = 7.1 Hz, 4H), 3.81 – 3.64 (m, 12H), 2.02 – 1.88 (m, 4H), 1.13 (dd, $^3$J = 13.6, 6.9 Hz, 18H), 0.53 (dd, $^3$J = 16.5, 8.5 Hz, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 189.3, 157.5, 156.5, 139.2, 138.8, 131.2, 130.4, 128.7, 128.3, 127.5, 123.2, 121.8, 120.5, 118.6, 113.1, 111.8, 61.6, 61.2, 57.5, 51.6, 23.2, 17.3, 6.4.
1-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)-3-(4-(1-(3-)
(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one  (6f):
Yield: 84%, Empirical formula: C$_{39}$H$_{58}$N$_6$O$_9$Si$_2$; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found:
C, 57.9; H, 7.0; N, 10.1; IR (neat, cm$^{-1}$): 2972, 2935, 2885, 1660, 1572, 1508, 1484, 1438,
1389, 1289, 1242, 1172, 1071, 1010, 954, 783, 722, 696, 542. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
= 7.62 – 7.55 (m, 3H), 7.54 (d, $^3$J = 8.5 Hz, 2H), 7.51 – 7.26 (m, 3H), 7.16 (dd, $^3$J = 14.0, 6.4
Hz, 2H), 6.96 (d, $^3$J = 8.6 Hz, 2H), 5.20 (d, $^3$J = 8.4 Hz, 4H), 4.30 (t, $^3$J = 7.2 Hz, 4H), 3.73
(q, $^3$J = 7.0 Hz, 12H), 2.03 – 1.88 (m, 4H), 1.14 (t, $^3$J = 7.0 Hz, 18H), 0.63 – 0.39 (m, 4H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 189.0, 159.3, 157.5, 143.6, 142.5, 138.9, 131.1, 129.3,
128.7, 127.5, 127.1, 121.9, 120.4, 119.0, 118.4, 114.2, 113.2, 61.2, 57.5, 51.5, 23.2, 17.3, 6.5.

3-(2-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)-1-(4-((1-(3-
(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one  (6g):
Yield: 89%, M.Pt: 83 °C, Empirical formula: C$_{39}$H$_{58}$N$_6$O$_9$Si$_2$; Anal. Calcd: C, 57.8; H, 7.2; N,
10.4; Found: C, 57.6; H, 6.9; N, 10.2; IR (neat, cm$^{-1}$): 2982, 2884, 1620, 1554, 1457, 1368,
1321, 1218, 1160, 1052, 1025, 1007, 922, 820, 752, 725, 663, 618, 541. $^1$H NMR (400 MHz,
CDCl$_3$) $\delta$ = 8.08 – 7.99 (m, 1H), 7.98 – 7.88 (m, 2H), 7.63 – 7.54 (m, 3H), 7.39 (td, $^3$J = 7.4,
2.9 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.01 – 6.92 (m, 4H), 5.26 (s, 2H), 5.22 (s, 2H), 4.32 – 4.26
(m, 4H), 3.83 – 3.62 (m, 12H), 1.98 – 1.91 (m, 4H), 1.23 – 1.07 (m, 18H), 0.55 – 0.48 (m,
4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 188.0, 161.9, 161.0, 160.8, 157.5, 143.5, 143.3, 139.6,
139.4, 138.3, 132.0, 131.3, 131.1, 130.5, 129.7, 129.4, 128.3, 121.8, 120.3, 114.6, 113.5,
112.9, 111.8, 62.7, 62.3, 61.6, 61.2, 58.6, 57.5, 52.7, 51.6, 24.3, 23.2, 18.4, 17.3, 7.5, 6.4.

3-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)-1-(4-((1-(3-
(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one  (6h):
Yield: 87%, Empirical formula: C$_{39}$H$_{58}$N$_6$O$_9$Si$_2$; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C,
57.5; H, 7.1; N, 10.1; IR (neat, cm\(^{-1}\)): 3019, 2994, 2886, 1521, 1455, 1322, 1217, 1163, 1033, 929, 742, 670, 542. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.94\) (d, \(\text{J} = 8.7\) Hz, 1H), 7.81 (d, \(\text{J} = 8.8\) Hz, 1H), 7.62 (d, \(\text{J} = 15.4\) Hz, 1H), 7.55 (d, \(\text{J} = 16.2\) Hz, 1H), 7.44 (s, 1H), 7.38 (dd, \(\text{J} = 9.1, 6.4\) Hz, 1H), 7.21 (t, \(\text{J} = 6.6\) Hz, 1H), 7.12 (d, \(\text{J} = 7.8\) Hz, 1H), 6.98 (d, \(\text{J} = 8.7\) Hz, 2H), 6.94 – 6.87 (m, 2H), 5.20 (d, \(\text{J} = 12.1\) Hz, 4H), 4.29 (t, \(\text{J} = 7.1\) Hz, 4H), 3.77 – 3.64 (m, 12H), 2.02 – 1.88 (m, 4H), 1.13 (t, \(\text{J} = 7.0\) Hz, 18H), 0.53 – 0.42 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 186.1, 160.7, 157.5, 142.3, 131.0, 130.4, 130.6, 131.0, 129.6, 128.7, 127.3, 120.9, 115.6, 113.4, 112.9, 61.1, 57.3, 51.1, 23.1, 17.3, 6.3.

\(1,3\)-bis(4-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6i): Yield: 89%, Empirical formula: C\(_{39}\)H\(_{58}\)N\(_6\)O\(_9\)Si\(_2\); Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.6; H, 7.1; N, 10.2; IR (neat, cm\(^{-1}\)): 2982, 2884, 1653, 1550, 1456, 1321, 1249, 1051, 1017, 1006, 923, 820, 750, 726,663, 542. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.93\) (d, \(\text{J} = 8.5\) Hz, 1H), 7.93 (d, \(\text{J} = 8.5\) Hz, 1H), 7.83 (d, \(\text{J} = 8.7\) Hz, 1H), 7.74 (d, \(\text{J} = 8.5\) Hz, 1H), 7.61 – 7.54 (m, 1H), 7.50 (d, \(\text{J} = 8.5\) Hz, 1H), 7.40 (d, \(\text{J} = 7.6\) Hz, 1H), 7.35 – 7.19 (m, 1H), 7.21 (s, 1H), 7.04 – 6.92 (m, 1H), 6.97 (ddd, \(\text{J} = 13.1, 11.2, 5.5\) Hz, 2H), 5.37 – 4.97 (m, 2H), 5.34 – 5.02 (m, 2H), 4.29 (t, \(\text{J} = 7.0\) Hz, 2H), 4.29 (t, \(\text{J} = 7.0\) Hz, 2H), 3.72 (q, \(\text{J} = 7.0\) Hz, 6H), 3.72 (q, \(\text{J} = 7.0\) Hz, 6H), 2.08 – 1.66 (m, 2H), 2.01 – 1.91 (m, 2H), 1.14 (t, \(\text{J} = 6.9\) Hz, 9H), 1.14 (t, \(\text{J} = 6.9\) Hz, 9H), 0.54 – 0.45 (m, 2H), 0.59 – 0.38 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 194.6, 188.8, 186.8, 161.9, 160.9, 158.9, 142.5, 130.9, 129.5, 128.9, 127.5, 127.1, 61.2, 57.3, 51.3, 23.1, 17.3, 6.4.

**Result and discussion**

**Synthetic approach**

Synthesis of conjugate chalcone based organotriethoxysilanes (OTES) was efficiently achieved in a three step route. First step involves the synthesis of propynyloxybenzaldehydes
2a(i–iii) and propynloxyacetophenones 2b(i–iii) by reaction of o-, m- and p-isomers of hydroxylbenzaldehyde and hydroxylacetophenone, respectively, with propargyl bromide in presence of K$_2$CO$_3$ as base. The strong base helps in easy proton abstraction from hydroxyl group and enhances the rate of forwarding reaction. Second step follows Claisen–Schmidt condensation reaction of 2a with i) substituted acetophenones 1c(a–c) resulting into chalcone substituted terminal alkynes 3a–3i, and ii) propynloxyacetophenones 2b(i–iii) resulting into chalcone substituted terminal di–alkynes product 5a–5i. The aldol condensation reaction was carried out under strongly basic conditions provided by KOH, using ethanol as solvent. After vigorous stirring for 4 h, the reaction progress was monitored by TLC (hexane:ethyl acetate (8:2)). On completion, the reaction mixture was quenched by acidic (2N HCl) ice cold water (till pH of 4 was attained) and the product was isolated by methylene dichloride in good yield. Third and the final step of mono–OTES 4a–4i and di–OTES 6a–6i synthesis via CuAAC reaction of chalcone based terminal alkynes with AzPTES was proceeded with [CuBr(PPh$_3$)$_3$]/THF–TEA system at 65 °C for 3 h under inert conditions. The final products have 1,2,3–triazole linking chalcone to nPTES were synthesized in good yield (Scheme 1, Table 1).
Scheme 1: Synthesis of conjugate chalcone based nPTES (4a–4i) and (6a–6i)

<table>
<thead>
<tr>
<th>Product ID/Texture</th>
<th>Substrate alkyne</th>
<th>Ar</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a/ Dark red oil</td>
<td></td>
<td></td>
<td>[Chemical Structure]</td>
<td>91</td>
</tr>
</tbody>
</table>
4b/ Chocolate brown oil

4c/ Orange red oil

4d/ Dark brown oil

4e/ Light brown oil

4f/ Light brown oil

4g/ Thick yellow oil
<table>
<thead>
<tr>
<th>Product ID/ Texture</th>
<th>Substrate alkyne (A1)</th>
<th>Substrate alkyne (A2)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4h/ Brown oil</td>
<td>![Image]</td>
<td>![Image]</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>4i/ Dark red oil</td>
<td>![Image]</td>
<td>![Image]</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>6a/ Brown oil</td>
<td>![Image]</td>
<td>![Image]</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>6b/ Dark brown oil</td>
<td>![Image]</td>
<td>![Image]</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>6c/ Dark brown solid</td>
<td>![Image]</td>
<td>![Image]</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>6d/ Brown oil</td>
<td>![Image]</td>
<td>![Image]</td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>
Table 1: Synthesis of mono–nPTES (4a–4i) and di–nPTES (6a–6i) using ‘Click Silylation’ at 65 °C for 3 h

We proceeded in the two possible pathways (Scheme 2) for generation of chalcone based triethoxysilane (4a) to investigate the affect on yield of product formed and rapidity in hydrolysis of chalcone functionalised triethoxysilanes. In experiment, pathway 1 involves
Claisen–Schmidt condensation of propynylbenzaldehyde 2 with differently substituted acetophenones, followed by cycloaddition reaction with AzPTES resulting into OTES with good yield and high purity. In comparison, following pathway 2, the first step involving click reaction efficiently gives OTES with more than 90% yield, but the second step of chalcone formation results into hydrolysis of triethoxysilanes as prominent reaction associated with poor yield. This confirms the incapability of pathway 2 to synthesize nPTES and exclusively follow pathway 1 for the efficient synthesis of nPTES.

**Scheme 2**: Probable pathways followed for synthesis of OTES from a common scaffold

The synthesized OTES ((4a–4i) and (6a–6i)) clearly point outs in $^1$H NMR with two major shifts i) 1.0 unit in triplet of $\text{N}_3\text{CH}_2\text{CH}_2$– after cyclization to heterocycle and ii) 5.0 units in...
the triplet at 2.5 ppm for terminal alkynes ($^3J = 2–3$ Hz) 7.5 ppm. Silanes (6a–6i) exhibit different multiplets arising due to each –CH$_2$ unit of propyl chain arm in nPTES (NMR A and NMR B, Figure 2). NMR A (6a) show unsplit multiplets of two propyl chains while NMR B (6c) marks out the separate identity to each –CH$_2$ unit of the two –N$_3$CH$_2$CH$_2$CH$_2$Si– chains. In case of $^{13}$C NMR, each carbon of nPTES (6a–6i) appeared as separate singlet giving unique identity to each carbon atom and show significant chemical shift. The E (trans) geometry of the chalcone double bond was evident by the large olefinic coupling constant ($J = 14–16$ Hz) between the relevant signals in the $^1$H NMR spectrum.

![NMR A](image1)

![NMR B](image2)

**Figure 2:** NMR A (6a) reveals unsplit multiplets due to two propyl chain arms; NMR B (6c) shows isolated multiplets for each propyl chain arm

Precedingly reported by Cattoen et al.,$^{20}$ hybrid silica precursors were synthesized under microwave conditions in excellent yield. We herein report optimized thermal reaction
conditions (4a, Table 2) for synthesis of chalcone stapled to nPTES via 1,2,3-triazole. The affect of variation in temperature, reaction time along with catalyst loading was keenly examined. On performing reaction at room temperature with 0.01 mmol of catalyst loading, only 20% of product was isolated. With increase in catalyst loading to 0.02 mmol and extending time duration, no significant improvement in product yield was observed. But on raising the temperature of reaction mixture to 65 °C and vigorous stirring for 3 h drastically improved yield from 24% to 91%. Further raising temperature under similar reaction conditions does not alter product yield. Therefore, thermally optimised reaction conditions for OTES 4a–4i and 6a–6i following Click silylation are as per entry 7 in table 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (%)</th>
<th>Reaction conditions</th>
<th>Reaction Duration (h)</th>
<th>(^{a})Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 x 10(^{-5})</td>
<td>rt, st</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>1 x 10(^{-5})</td>
<td>rt, st</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>1 x 10(^{-5})</td>
<td>55 °C, st</td>
<td>3</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>1 x 10(^{-5})</td>
<td>55 °C, st</td>
<td>3</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>1 x 10(^{-5})</td>
<td>65 °C, st</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>1 x 10(^{-5})</td>
<td>65 °C, st</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>1 x 10(^{-5})</td>
<td>65 °C, st</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>1 x 10(^{-5})</td>
<td>65 °C, st</td>
<td>5</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>1 x 10(^{-5})</td>
<td>65 °C, st</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>1 x 10(^{-5})</td>
<td>75 °C, st</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>11</td>
<td>1 x 10(^{-5})</td>
<td>75 °C, st</td>
<td>3</td>
<td>91</td>
</tr>
</tbody>
</table>

\(^{a}\)Determined by \(^{1}\)H NMR analysis of crude sample

**Table 2:** Optimization of reaction conditions under thermal environmental conditions
Solvatochromism

As defined by Hantzschlater, solvatochromism refers to the change in the position, intensity, and shape of absorption bands intensity maxima in UV–Vis spectroscopy with change of solvent polarity.\textsuperscript{50} The major factor governing this phenomenon involves variation in solute–solvent interactions with change in solvent polarity that affects position, shape and intensity of absorption bands.\textsuperscript{51} The preferential solvation taking place in vicinity of solute molecule alters the salvation shell arrangements, thereby shifting maxima of wavelength absorbed. Negative solvatochromism corresponds to hypsochromic shift (blue shift) whereas reverse is referred to positive solvatochromism or bathochromic shift (red shift).\textsuperscript{52} It is for the first time, to the best of our knowledge, that solavotochromic effect is being reported for OTES.

The term ‘solvent polarity’ lacks an exact definition, although numerous attempts have been made so far, but it broadly describes all of the intermolecular interactions of solute with solvent. The important point concerning the so called ‘polarity of a solvent’ is the overall solvation capability, which is the cumulative effect of all the solvent–solute interactions, excluding those such as protonation, oxidation, reduction, complexation, etc., that might lead to a chemical change of the solute.\textsuperscript{53} A number of scales have been established to quantify the influence of solvent on chemical properties. These scales are based on some physicochemical property, which could be an equilibrium constant, reaction rate constant, spectral shift using absorption spectroscopy, etc.\textsuperscript{54} We followed the Dimroth and Reichardt polarity scale to examine the effect of variation in polarity solvents on various PFTES.

The observed solvatochromism depends upon the chemical structure and physical properties of the chromophore and their interaction with the solvent molecules which, in turn determines the strength of the intermolecular solute/solvent interactions in the equilibrium ground state and the Franck-Condon excited state. Typically, a large change in dipole moment upon excitation exhibits strong solvatochromism. In addition, the ability of solute molecules to
donate or to accept hydrogen bonds to or from surrounding solvent molecules in its ground and Franck-Condon excited state determines further the extent and sign of its solvatochromism. The pronounced shift in the position of the absorption bands is due to solvent–induced change in electronic ground state structure from a less dipolar (in less polar solvents) to a more dipolar chromophore (in high polar solvents) with increasing solvent polarity.

Moreover, the ability of solute to form hydrogen bond with solvent molecules in ground state and Franck Condon excited state too determines the extent of solvatochromism exhibited which is a result of π–π* transitions. Typically, solvatochromic compounds can be described by extreme resonance contributing structures. The change in absorption band with solvent arises from variation in contribution of these conjugated π electronic systems.\(^{55}\)

To examine solvatochromic effects on chalcone modified OTES, UV–Vis photoelectronic study was performed using chloroform, acetonitrile and ethanol (with relative polarity of 0.26, 0.46, 0.65 as per Dimroth and Reichardt polarity scale) as solvent media (shown for 4b in Figure 3, for other see supporting information) within the concentration range of 0.1 mM–1 mM. Non–polar solvents proved to be inefficient owing to their incapability to solubilize the compounds; while other polar solvents were ineffective as they have \(\lambda_{\text{max}}\) cut off value above absorption maxima intensity region. The effect on absorption maxima due to different substituents and positional isomers was observed and plotted as shown in Figure 4. With increase in polarity of a solvent, the shift in \(\lambda_{\text{max}}\) value for triethoxysilanes was observed to be both bathochromic and hypsochromic. Beginning with chloroform, the absorption maxima for all nPTES lie in the region between 272–331 nm (4a–4i), with maximum moieties absorbing in the region of 300 and 320 nm. With increase in polarity using acetonitrile, bathochromic shift was observed for 4c, 4d, and 4h. Further increasing polarity using
ethanol, the most polar of three, red and blue shifts were observed for 4a, 4b, 4e, 4f, 4g and 4i, and 4c, 4d and 4h, respectively (Table 3).

**Figure 3:** UV–Vis spectra of compound 4b in different solvents at 25 °C (1 mM)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>4a</th>
<th>4b</th>
<th>4c</th>
<th>4d</th>
<th>4e</th>
<th>4f</th>
<th>4g</th>
<th>4h</th>
<th>4i</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>302</td>
<td>300,250</td>
<td>322</td>
<td>314</td>
<td>318</td>
<td>327</td>
<td>272</td>
<td>331</td>
<td>295</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>293</td>
<td>298,247</td>
<td>333</td>
<td>318</td>
<td>314</td>
<td>324</td>
<td>271</td>
<td>335</td>
<td>294</td>
</tr>
<tr>
<td>Ethanol</td>
<td>295</td>
<td>301,249</td>
<td>327</td>
<td>314</td>
<td>318</td>
<td>328</td>
<td>272</td>
<td>329</td>
<td>296</td>
</tr>
</tbody>
</table>

**Table 3:** The absorption maxima values of 4a–4i (0.1 mM–1 mM) in various solvents at 25 °C
**Figure 4**: Plot depicting the effect of polarity change using CHCl₃, CH₃CN and C₂H₅OH on OTES 4a–4i

Di nPTES 6a–6i exhibit distinct behavior for shift in λ<sub>max</sub> value (shown for 6c in Figure 5 for other see supporting information) as compared to mono nPTES 4a–4i in these solvents. The decrease or increase in solvent polarity using chloroform, acetonitrile and ethanol, the π electron cloud remains conjugated and hence appear significantly in absorption spectra. With increase in polarity of solvent using acetonitrile, the hypsochromic shift was observed for all compounds except 6d, 6h and 6i which exhibit bathochromic shift (Figure 6, Table 4). On further raising polarity of solvent system using ethanol, red shift in absorption maxima was recorded for 6b, 6c, 6f, 6g and 6i while other significantly exhibit hypsochromic shift in wavelength.
Figure 5: UV–Vis spectra of compound 6c in different solvents at 25 °C (0.5 mM)

Table 4: Representation of absorption maxima values of 6a–6i (0.1 mM–1 mM) in various solvents at 25 °C
Solvatochromic study performed on a series of nPTES illustrating the effect of polarity change show best activity for silanes using chloroform and acetonitrile as solvent media in UV–Vis spectra. Moreover, on consideration of different polarity scale which alters the polarity index of solvents used, there will be change in corresponding batho– and hypso–chromic shifts observed. OTES being hydrolytically unstable have limited solubility and solvent tolerance. Its dissolution in protonating solvent like ethanol may cause hindrance towards absorption spectra for some OTES that may actually be active in other aprotic polar solvents. The rapidity in hydrolysis of OTES tends to overcome the solubility in protic solvents at high concentrations but at concentration of $10^{-3}$ M or lower, we can study their photophysical properties.

Conclusions
We have synthesized 1,2,3-triazolyl chalcone linked n–propyltriethoxysilanes (4a–4i and 6a–6i) by an efficient and promising methodology. The optimized thermal reaction conditions for CuAAC, using ‘[CuBr(PPh₃)₃]/THF–TEA’ system, prove their excellence for the product formation at 65 °C in 3 h. The variation in substituent moiety and effect of positional isomerism in nPTES considerably affected the absorption spectral properties as displayed in UV–Vis spectra of final compounds. Solvatochromic study illustrated the dissimilarity in λₓᵧ value arising as a result of increase in dipole moment, which confirmed the different behavior of each o, m and p substituted TES in spectroscopic study. The blue shift in the absorption bands seems to be due to some strong stabilising interactions of solvent for substituted OTES while the red shift in the absorption band can correspond to an increased solvation of the conjugated system. The extent of interaction of different isomers (o-, m- and p-) with solvent system and the degree of solvation determines the band shift observed in UV–Vis spectra.

Acknowledgments

We thank Mr. Avtar Singh for the NMR studies (SAIF, Panjab University, Chandigarh). One of the authors, Jandeep Singh, thank Council of Scientific and Industrial Research (CSIR), India for providing financial support in the form of CSIR–SRF(NET) fellowship.

Notes

The authors declare no competing financial interest.

References


