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Graphical Abstract

Synthetic approach towards 'Click' modified chalcone based organotriethoxysilanes;

UV-Vis study

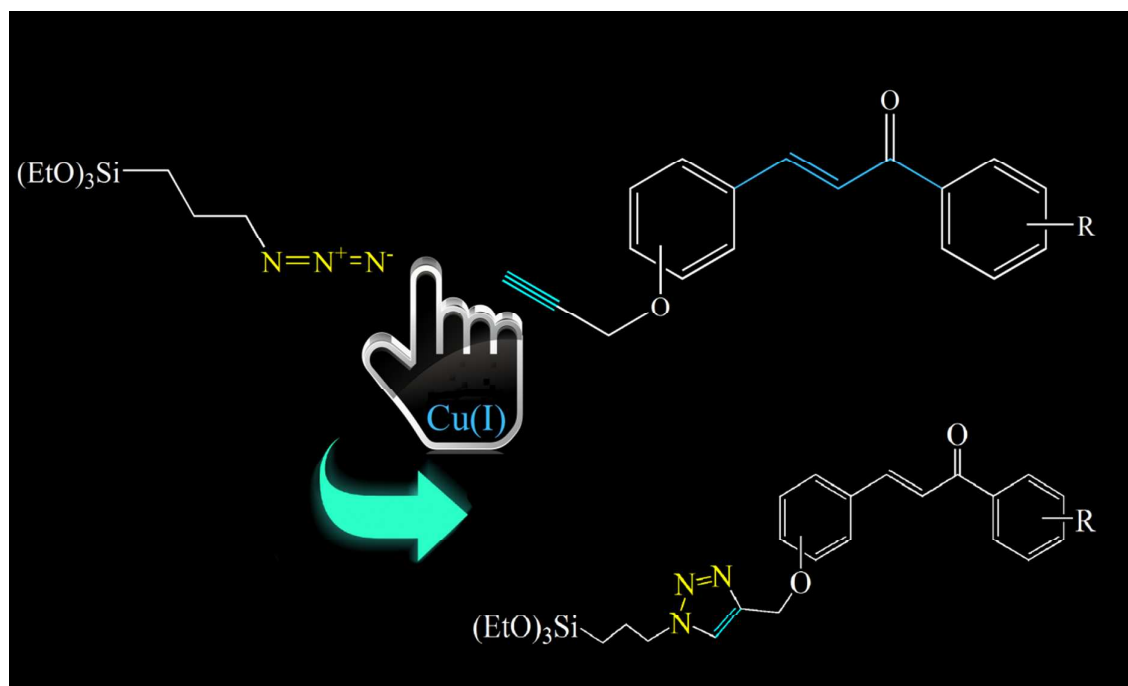
Gurjaspreet Singh,* Jandeep Singh, Satinderpal Singh Mangat, Aanchal Arora

Department of Chemistry and Centre of Advanced Studies, Panjab University, Chandigarh,

160014, India.

*Corresponding Author

Email: gjsingh@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(PPh₃)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,¹ catalysis,² surface coating of materials,^{3,4} polymer formation,⁵ ion detecting fluorescent probes,^{6,7} HPLC packing,⁸ and in nano chemistry.⁹ The synthetic approach leading to generation of polyfunctional triethoxysilanes (PFTES) acting as precursor to these materials follow different pathways such as cross-coupling reaction,¹⁰⁻¹² hydrosilylation,^{13,14} and transmetalation reaction.¹⁵ 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,¹⁶⁻¹⁸ and exploited by Cattoen *et al.*,^{19,20} 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-triazole²¹ with efficient conversion of above 80% and 100% control over regioselectivity.²² 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.²³⁻²⁸ Further, 1,2,3-triazolyl heterocycle proves to be an important pharmacore²⁹ associated with immense medicinal importance as antimycobacterial activity,^{30,31} antituberculosis,³² antiinflammatory,³³ antiangiogenic,³⁴ antiviral,³⁵ anticancerous as histone deacetylase inhibitor^{36,37} and anti-HIV activity.³⁸

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.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 activity⁴¹ along with antitumorigenic,⁴³ antiinflammatory,⁴⁴ antiangiogenic,⁴⁵ antioxidant,⁴⁶ antituberculosis,⁴⁷ antimalarial,⁴⁸ and anti-HIV properties.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.

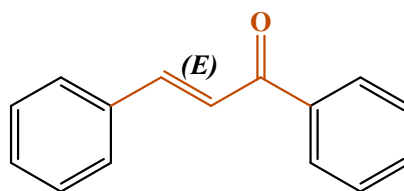


Figure 1: Chemical structure of chalcone unit consisting of two aromatic rings linked by three-carbon chain forming α - β unsaturated carbonyl moiety

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 (CIPTES) (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 $-5\text{ }^{\circ}\text{C}$ K_2CO_3 (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 $30\text{ }^{\circ}\text{C}$ 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 MgSO_4 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: $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\text{Si}$; 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, 1315, 1258, 1213, 1162, 1073, 1015, 907, 792, 726, 691, 646. ^1H NMR (400 MHz, CDCl_3), δ = 8.00 (d, 3J = 15.8 Hz, 1H), 7.87 (d, 3J = 7.5 Hz, 1H), 7.55 (d, 3J = 6.3 Hz, 3H), 7.44 (d, 3J = 7.4 Hz, 2H), 7.38 (d, 3J = 7.7 Hz, 2H), 7.01 (d, 3J = 8.3 Hz, 1H), 6.92 (d, 3J = 8.1 Hz, 2H), 5.21 (s, 2H), 4.25 (t, 3J = 7.2 Hz, 2H), 3.69 (q, 3J = 7.0 Hz, 6H), 2.04 – 1.90 (m, 2H), 1.10 (t, 3J = 7.0 Hz, 9H), 0.57 – 0.41 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ = 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: $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\text{Si}$; 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, CDCl_3) 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), 22.04 – 1.90 (m, 2H), 1.21 (t, 3J = 7.0 Hz, 9H), 0.68 – 0.53 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) 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: $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\text{Si}$; 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, CDCl_3) 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). ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{M}+\text{Na}]^+$ 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: $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_6\text{Si}$; 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, CDCl_3) 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) $\delta = 188.1, 162.3, 142.6, 138.3, 131.1, 130.5, 129.8, 127.4, 125.1, 123.3, 121.9, 121.6, 120.3, 112.6, 111.7, 61.5, 57.5, 54.4, 51.6, 23.2, 17.3, 6.4$.

1-(4-methoxyphenyl)-3-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-

yl)methoxy)phenyl)prop-2-en-1-one (4e): Yield: 90%, Empirical formula: $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_6\text{Si}$;

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, 1600, 1484, 1389, 1251, 1168, 1075, 906, 831, 785, 724, 646, 616, 541. ^1H NMR (400 MHz, CDCl_3) $\delta = 7.97$ (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) $\delta = 187.6, 162.5, 157.6, 142.7, 135.6, 131.1, 129.9, 127.5, 121.8, 121.3, 120.7, 115.7, 113.3, 112.9, 57.5, 54.5, 51.5, 17.3, 6.4$.

1-(4-methoxyphenyl)-3-(4-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-

yl)methoxy)phenyl)prop-2-en-1-one (4f): Yield: 87%, Empirical formula: $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_6\text{Si}$;

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. ^1H NMR (400 MHz, CDCl_3) $\delta = 7.98$ (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) $\delta = 187.6, 162.3, 142.4, 131.1,$

130.3, 129.7, 129.0, 127.7, 127.3, 122.0, 118.8, 114.1, 112.9, 61.1, 57.4, 54.5, 51.5, 23.2, 17.3, 6.4. HRMS (ES⁺) Calcd for [M+Na]⁺ 562.2245; Found 762.2288.

1-(2,4-dimethoxyphenyl)-3-(2-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-

yl)methoxy)phenyl)prop-2-en-1-one (4g): Yield: 88%, Empirical formula: C₂₉H₃₉N₃O₇Si; Anal. Calcd: C, 61.1; H, 6.9; N, 7.4; Found: C, 60.9; H, 6.7; N, 7.5; IR (neat, cm⁻¹): 2970, 2925, 2880, 2839, 1687, 1597, 1577, 1507, 1422, 1310, 1248, 1212, 1108, 1073, 1018, 827, 759, 643. ¹H NMR (400 MHz, CDCl₃) 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, ³J = 7.2, 3.1 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.86 – 3.76 (m, 3H), 3.76 (q, ³J = 7.0 Hz, 6H), 2.08 – 1.87 (m, 2H), 1.12 (t, ³J = 7.0 Hz, 9H), 0.60 – 0.42 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) 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)-1H-1,2,3-triazol-4-

yl)methoxy)phenyl)prop-2-en-1-one (4h): Yield: 89%, Empirical formula: C₂₉H₃₉N₃O₇Si; Anal. Calcd: C, 61.1; H, 6.9; N, 7.4; Found: C, 61.0; H, 6.8; N, 7.2; IR (neat, cm⁻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. ¹H NMR (400 MHz, CDCl₃) δ = 7.65 (d, ³J = 8.4 Hz, 1H), 7.55 (d, ³J = 13.8 Hz, 2H), 7.46 (d, ³J = 7.8 Hz, 2H), 7.31 (d, ³J = 15.7 Hz, 2H), 6.92 (d, ³J = 8.0 Hz, 2H), 6.47 (d, ³J = 8.3 Hz, 2H), 6.41 (s, 1H), 5.16 (s, 2H), 4.27 (t, ³J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.72 (dd, ³J = 13.4, 6.6 Hz, 6H), 2.02 – 1.90 (m, 2H), 1.13 (t, ³J = 6.7 Hz, 9H), 0.61 – 0.43 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) 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: C₂₉H₃₉N₃O₇Si; 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. ¹H NMR (400 MHz, CDCl₃) δ = 7.96 (d, ³J = 16.0 Hz, 1H), 7.66 (d, ³J = 8.6 Hz, 1H), 7.55 (dd, ³J = 10.0, 2.1 Hz, 2H), 7.46 (d, ³J = 15.9 Hz, 1H), 7.42 – 7.28 (m, 1H), 7.24 (dd, ³J = 12.0, 5.1 Hz, 1H), 7.17 (dd, ³J = 13.9, 8.1 Hz, 1H), 7.01 (d, ³J = 8.3 Hz, 1H), 6.91 (t, ³J = 7.6 Hz, 1H), 6.47 (dd, ³J = 8.6, 2.2 Hz, 1H), 6.40 (d, ⁴J = 2.2 Hz, 1H), 5.23 (s, 2H), 4.26 (t, ³J = 7.2 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.72 (q, ³J = 7.0 Hz, 6H), 2.04 – 1.92 (m, 2H), 1.12 (t, ³J = 7.0 Hz, 9H), 0.60 – 0.43 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 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: 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): 3072, 3024, 2921, 2891, 1652, 1597, 1482, 1448, 1371, 1327, 1287, 1216, 1162, 1105, 1050, 1015, 925, 872, 834, 820, 748, 676, 633, 584. ¹H NMR (400 MHz, CDCl₃) δ = 8.00 (d, ³J = 7.3 Hz, 2H), 7.67 (s, 2H), 7.60 (d, ³J = 8.6 Hz, 2H), 7.48 (d, ³J = 7.1 Hz, 2H), 7.44 (s, 2H), 7.03 (d, ³J = 8.6 Hz, 2H), 5.25 (s, 4H), 4.37 (t, ³J = 7.2 Hz, 4H), 3.81 (dd, ³J = 14.4, 7.4 Hz, 12H), 2.08 – 1.96 (m, 4H), 1.21 (t, ³J = 7.0 Hz, 18H), 0.65 – 0.53 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ = 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-1,2,3-triazol-4-yl)methoxy)phenyl)-3-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-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, 57.5, 51.4, 23.1, 17.3, 6.4.

1-(2-((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 (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-1,2,3-triazol-4-yl)methoxy)phenyl)-1-(3-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6d):

Yield: 87%, Empirical formula: C₃₉H₅₈N₆O₉Si₂; 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. ¹H NMR (400 MHz, CDCl₃) δ = 7.68 (d, ³J = 15.7 Hz, 1H), 7.60 (d, ³J = 4.3 Hz, 2H), 7.55 (d, ³J = 7.2 Hz, 1H), 7.45 (s, 1H), 7.40 – 7.31 (m, 2H), 7.23 (dd, ³J = 9.5, 6.4 Hz, 2H), 7.15 (dd, ³J = 15.6, 7.7 Hz, 2H), 6.97 (d, ³J = 8.1 Hz, 1H), 5.26 – 5.04 (m, 4H), 4.29 (t, ³J = 7.1 Hz, 4H), 3.78 – 3.65 (m, 12H), 2.04 – 1.83 (m, 4H), 1.22 – 1.05 (m, 18H), 0.59 – 0.43 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ = 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-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6e):

Yield: 83%, 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): 3019, 2977, 2881, 1651, 1593, 1521, 1484, 1390, 1325, 1214, 1161, 1075, 1033, 1015, 742, 669, 665, 627, 542. ¹H NMR (400 MHz, CDCl₃) δ = 8.05 (d, ³J = 15.8 Hz, 1H), 7.60 (s, 1H), 7.57 (s, 2H), 7.54 – 7.45 (m, 2H), 7.39 (dd, ³J = 8.5, 1.9 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.13 (dd, ³J = 8.1, 2.3 Hz, 1H), 7.05 (d, ³J = 8.3 Hz, 1H), 6.95 (t, ³J = 7.5 Hz, 1H), 5.26 (s, 2H), 5.19 (s, 2H), 4.29 (q, ³J = 7.1 Hz, 4H), 3.81 – 3.64 (m, 12H), 2.02 – 1.88 (m, 4H), 1.13 (dd, ³J = 13.6, 6.9 Hz, 18H), 0.53 (dd, ³J = 16.5, 8.5 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ = 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: C₃₉H₅₈N₆O₉Si₂; 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. ¹H NMR (400 MHz, CDCl₃) δ = 7.62 – 7.55 (m, 3H), 7.54 (d, ³J = 8.5 Hz, 2H), 7.51 – 7.26 (m, 3H), 7.16 (dd, ³J = 14.0, 6.4 Hz, 2H), 6.96 (d, ³J = 8.6 Hz, 2H), 5.20 (d, ³J = 8.4 Hz, 4H), 4.30 (t, ³J = 7.2 Hz, 4H), 3.73 (q, ³J = 7.0 Hz, 12H), 2.03 – 1.88 (m, 4H), 1.14 (t, ³J = 7.0 Hz, 18H), 0.63 – 0.39 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ = 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: C₃₉H₅₈N₆O₉Si₂; 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. ¹H NMR (400 MHz, CDCl₃) δ = 8.08 – 7.99 (m, 1H), 7.98 – 7.88 (m, 2H), 7.63 – 7.54 (m, 3H), 7.39 (td, ³J = 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). ¹³C NMR (101 MHz, CDCl₃) δ = 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: C₃₉H₅₈N₆O₉Si₂; 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. ^1H NMR (400 MHz, CDCl_3) δ = 7.94 (d, 3J = 8.7 Hz, 1H), 7.81 (d, 3J = 8.8 Hz, 1H), 7.62 (d, 3J = 15.4 Hz, 1H), 7.55 (d, 3J = 16.2 Hz, 1H), 7.44 (s, 1H), 7.38 (dd, 3J = 9.1, 6.4 Hz, 1H), 7.21 (t, 3J = 6.6 Hz, 1H), 7.12 (d, 3J = 7.8 Hz, 1H), 6.98 (d, 3J = 8.7 Hz, 2H), 6.94 – 6.87 (m, 2H), 5.20 (d, 3J = 12.1 Hz, 4H), 4.29 (t, 3J = 7.1 Hz, 4H), 3.77 – 3.64 (m, 12H), 2.02 – 1.88 (m, 4H), 1.13 (t, 3J = 7.0 Hz, 18H), 0.53 – 0.42 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ = 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.

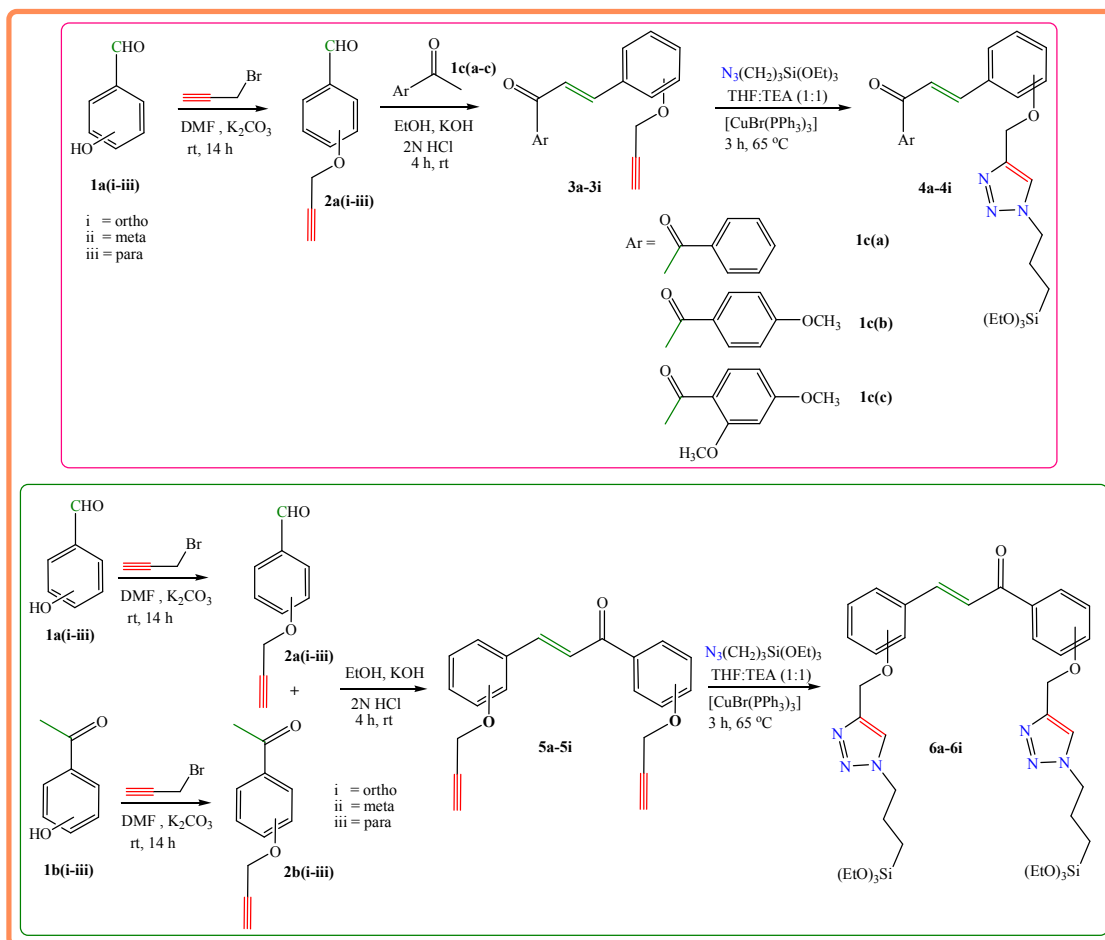
1,3-bis(4-((1-(3-(triethoxysilyl)propyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one (6i): Yield: 89%, Empirical formula: $\text{C}_{39}\text{H}_{58}\text{N}_6\text{O}_9\text{Si}_2$; Anal. Calcd: C, 57.8; H, 7.2; N, 10.4; Found: C, 57.6; H, 7.1; N, 10.2; IR (neat, cm^{-1}): 2982, 2884, 1653, 1550, 1456, 1321, 1249, 1051, 1017, 1006, 923, 820, 750, 726, 663, 542. ^1H NMR (400 MHz, CDCl_3) δ = 7.93 (d, 3J = 8.5 Hz, 1H), 7.93 (d, 3J = 8.5 Hz, 1H), 7.83 (d, 3J = 8.7 Hz, 1H), 7.74 (d, 3J = 8.5 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.50 (d, 3J = 8.5 Hz, 1H), 7.40 (d, 3J = 7.6 Hz, 1H), 7.35 – 7.19 (m, 1H), 7.21 (s, 1H), 7.04 – 6.92 (m, 1H), 6.97 (ddd, 3J = 13.1, 11.2, 5.5 Hz, 2H), 5.37 – 4.97 (m, 2H), 5.34 – 5.02 (m, 2H), 4.29 (t, 3J = 7.0 Hz, 2H), 4.29 (t, 3J = 7.0 Hz, 2H), 3.72 (q, 3J = 7.0 Hz, 6H), 3.72 (q, 3J = 7.0 Hz, 6H), 2.08 – 1.66 (m, 2H), 2.01 – 1.91 (m, 2H), 1.14 (t, 3J = 6.9 Hz, 9H), 1.14 (t, 3J = 6.9 Hz, 9H), 0.54 – 0.45 (m, 2H), 0.59 – 0.38 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ = 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

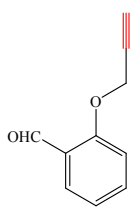
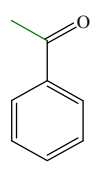
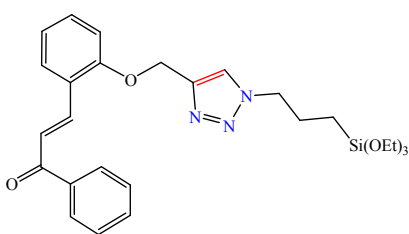
Synthetic approach

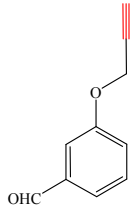
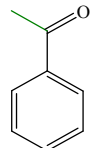
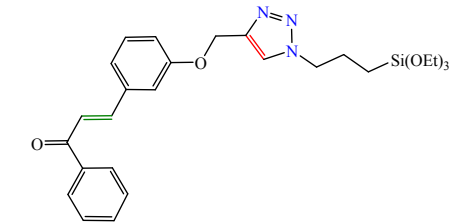
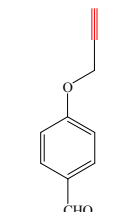
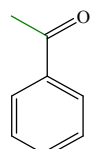
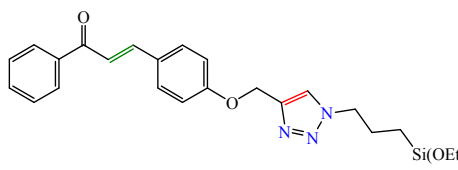
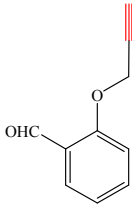
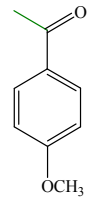
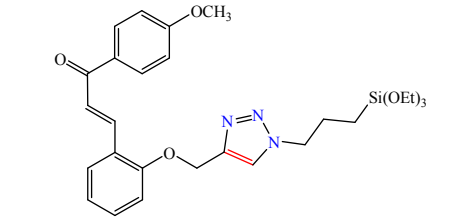
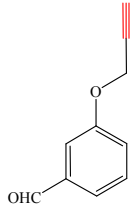
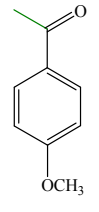
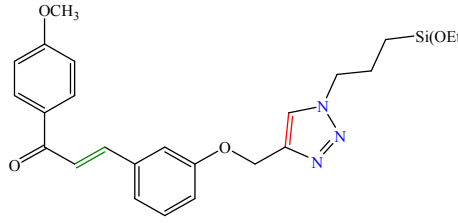
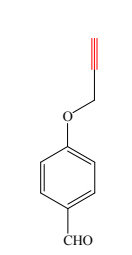
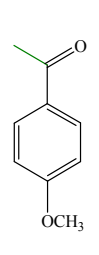
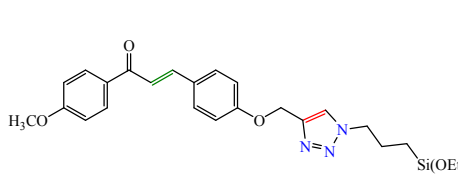
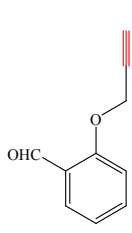
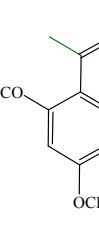
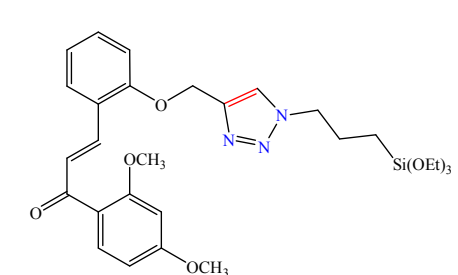
Synthesis of conjugate chalcone based organotriethoxysilanes (OTES) was efficiently achieved in a three step route. First step involves the synthesis of propynyloxybenzaldehydes

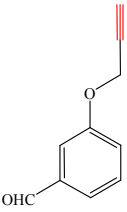
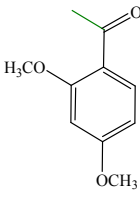
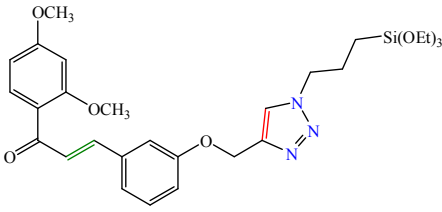
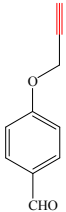
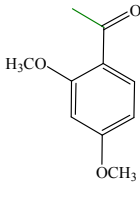
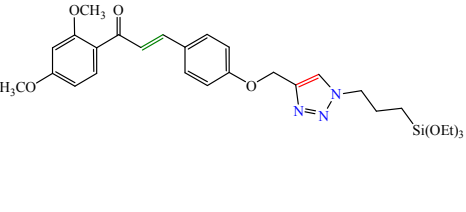
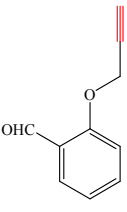
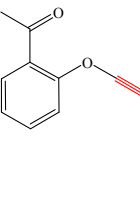
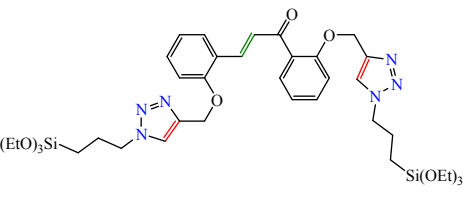
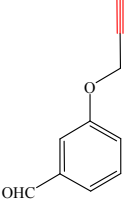
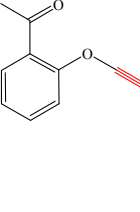
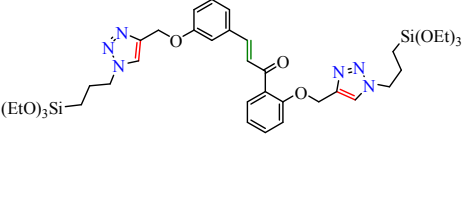
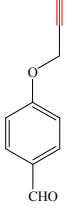
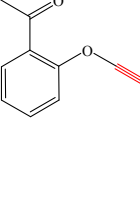
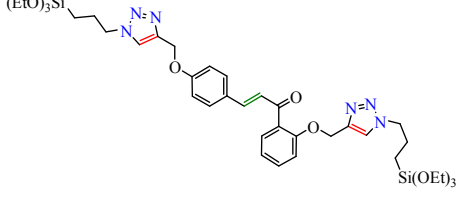
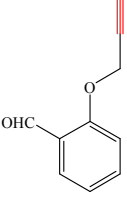
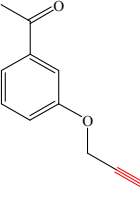
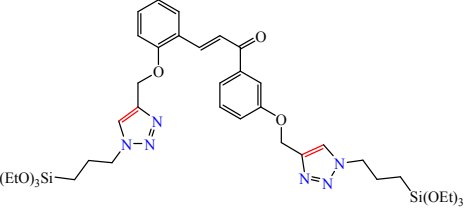
2a(i-iii) and propynyloxyacetophenones **2b(i-iii)** by reaction of o-, m- and p-isomers of hydroxybenzaldehyde and hydroxyacetophenone, respectively, with propargyl bromide in presence of K_2CO_3 as base. The strong base helps in easy proton abstraction from hydroxyl group and enhances the rate of forwarding 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) propynyloxyacetophenones **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**)

Product ID/ Texture	Substrate alkyne	Ar	Product	Yield (%)
4a/ Dark red oil				91

<p>4b/ Chocolate brown oil</p>				89
<p>4c/ Orange red oil</p>				90
<p>4d/ Dark brown oil</p>				88
<p>4e/ Light brown oil</p>				90
<p>4f/ Light brown oil</p>				87
<p>4g/ Thick yellow oil</p>				88

4h/ Brown oil				89
4i/ Dark red oil				87
Product ID/ Texture	Substrate alkyne (A1)	Substrate alkyne (A2)	Product	Yield (%)
6a/ Brown oil				90
6b/ Dark brown oil				90
6c/ Dark brown solid				89
6d/ Brown oil				87

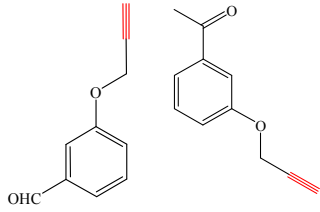
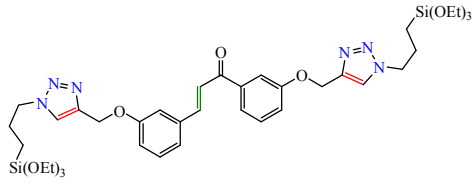
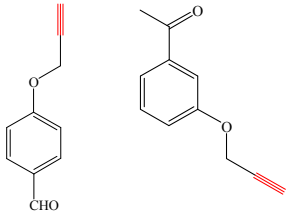
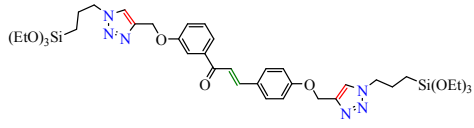
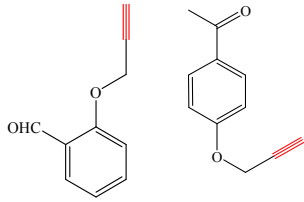
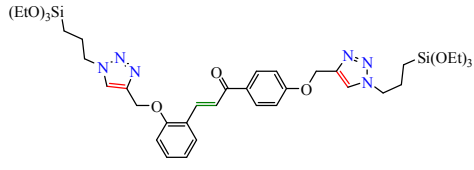
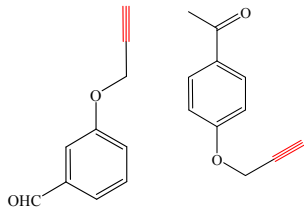
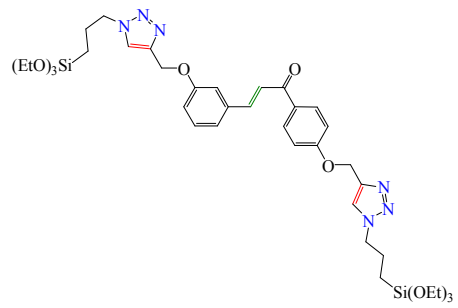
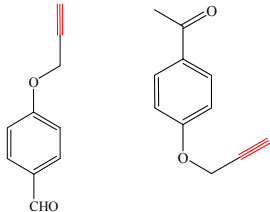
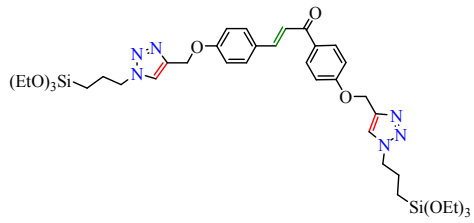
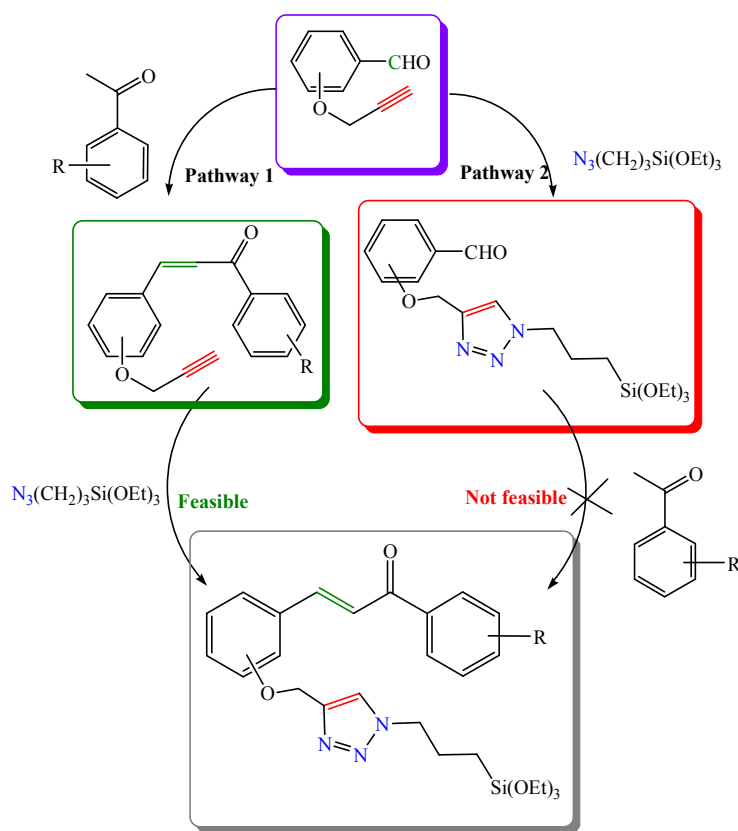
6e/ Dark red oil			83
6f/ Dark brown oil			84
6g/ Dark brown solid			89
6h/ Brown oil			87
6i/ Orange red oil			91

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 out in ^1H 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 ($^4J = 2-3$ 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 $-N_3CH_2CH_2CH_2Si-$ 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 1H NMR spectrum.

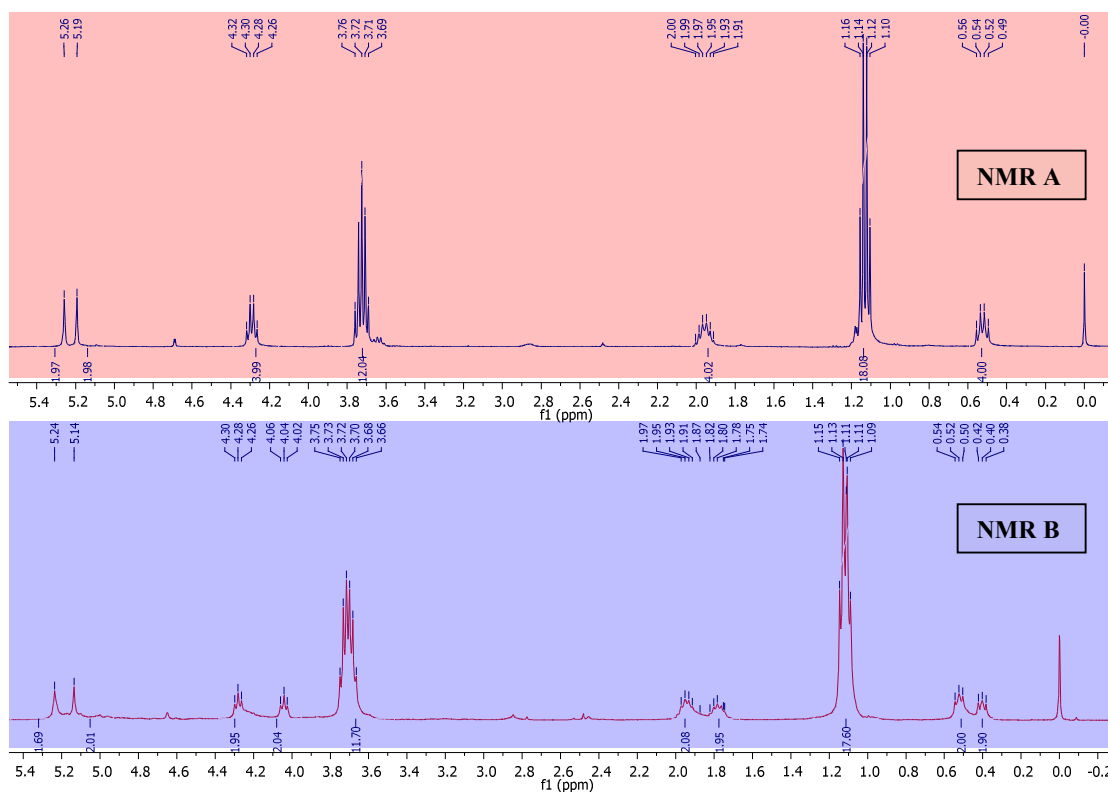


Figure 2: NMR A (**6a**) reveals unsplit multiplets due to two propyl chain arms; NMR B (**6c**) shows isolated multiplets for each propyl chain arm

Previously 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.

Entry	Catalyst (%)	Reaction conditions	Reaction Duration (h)	^a Yield (%)
1	1 x 10 ⁻⁵	rt, st	3	20
2	1 x 10 ⁻⁵	rt, st	3	24
3	1 x 10 ⁻⁵	55 °C, st	3	76
4	1 x 10 ⁻⁵	55 °C, st	3	81
5	1 x 10 ⁻⁵	65 °C, st	1	45
6	1 x 10 ⁻⁵	65 °C, st	3	86
7	1 x 10⁻⁵	65 °C, st	3	91
8	1 x 10 ⁻⁵	65 °C, st	5	91
9	1 x 10 ⁻⁵	65 °C, st	3	91
10	1 x 10 ⁻⁵	75 °C, st	3	85
11	1 x 10 ⁻⁵	75 °C, st	3	91

^aDetermined by ¹H 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.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.⁵¹ The preferential solvation taking place in vicinity of solute molecule alters the solvation 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).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.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.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 λ_{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 λ_{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).

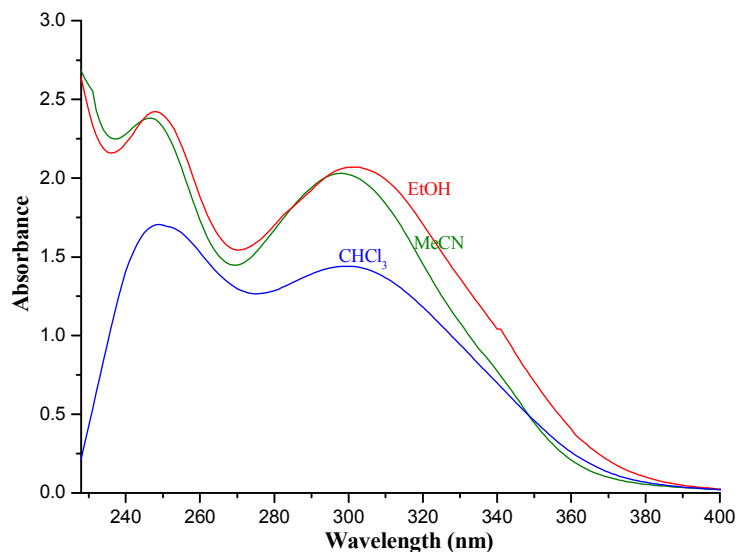


Figure 3: UV–Vis spectra of compound **4b** in different solvents at 25 °C (1 mM)

Sample ID	4a	4b	4c	4d	4e	4f	4g	4h	4i
λ_{\max} (nm)									
Chloroform	302	300,250	322	314	318	327	272	331	295
Acetonitrile	293	298,247	333	318	314	324	271	335	294
Ethanol	295	301,249	327	314	318	328	272	329	296

Table 3: The absorption maxima values of **4a–4i** (0.1 mM–1 mM) in various solvents at 25 °C

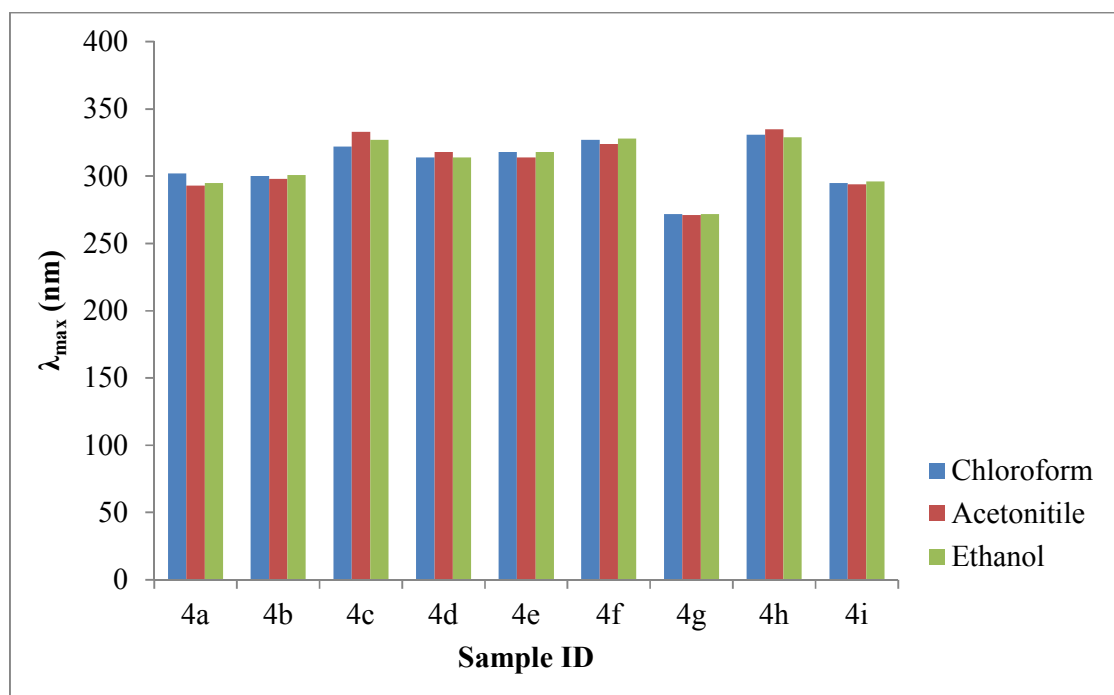


Figure 4: Plot depicting the effect of polarity change using CHCl_3 , CH_3CN and $\text{C}_2\text{H}_5\text{OH}$ on OTES **4a–4i**

Di nPTES **6a–6i** exhibit distinct behavior for shift in λ_{max} 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.

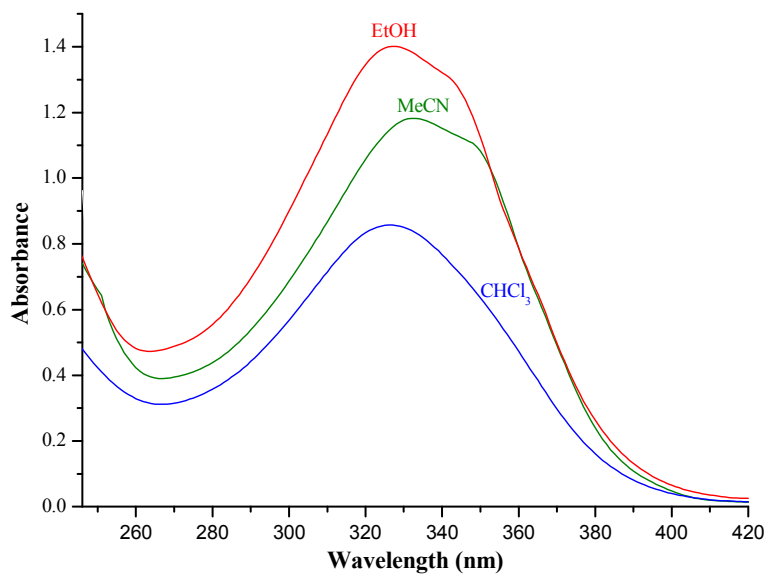


Figure 5: UV–Vis spectra of compound **6c** in different solvents at 25 °C (0.5 mM)

Sample ID	6a	6b	6c	6d	6e	6f	6g	6h	6i
λ_{\max} (nm)									
Chloroform	332,298	301	297	274	265	337	301	263	274
Acetonitrile	328,291	298	293	334	313	324	299	314	328
Ethanol	328	302	299	303	301	335	304	265	330,275

Table 4: Representation of absorption maxima values of **6a–6i** (0.1 mM–1 mM) in various solvents at 25 °C

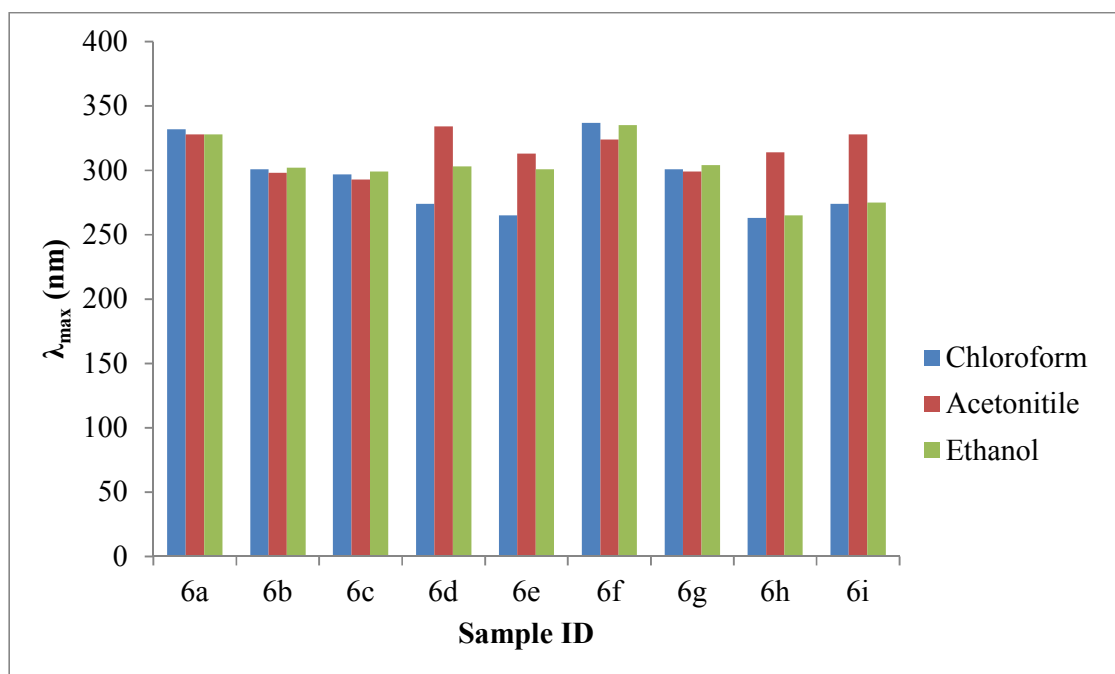


Figure 6: Plot depicting the effect of polarity change using CHCl_3 , CH_3CN and $\text{C}_2\text{H}_5\text{OH}$ on OTES **6a–6i**

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 λ_{\max} 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.

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Notes

The authors declare no competing financial interest.

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