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Synthesis of novel 1,2,3-triazole based silatranes via "click silylation"

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ABSTRACT

A single step reaction for the synthesis of novel 1,2,3-triazole based silatranes (TBS)-scaffolds (**2a**–**2o**) using polyfunctionalised organotriethoxysilanes (**1a**–**1l**) as precursors is described. The synthesized silatranes are the first compounds of this type and hydrolytically more stable than their open chain analogues. The structures of **2a**–**2o** were characterized by IR, NMR (^{1}H and ^{13}C) and mass spectroscopy studies.

Introduction

"Click chemistry" has been honoured as a library of versatile spring loaded reactions that offer covalent assembly of smaller fragments to complex molecules [1–4]. Initiated by the incredible invention of Cu(I) catalysed azide-alkyne cycloaddition reaction (CuAAC), the dummy of 1,2,3-triazole moiety has emerged as a powerful heterocycle in modern chemical and pharmaceutical research [5]. Since innovation, the applications into various research fields have been wholesaled due to its reliability, specificity and biocompatibility [6].

Click reaction is one of the best choices for the design of sophisticated biomaterials requiring high levels of precision and control [7]. One of the key intermediate for the synthesis of such hybrid materials is substituted organotrialkoxysilane [8–14]. We have recently reported "click silylation" to en-cap the precursor triethoxysilanes with wide range of functional groups [15]. Therefore, permutation of click with organosilicon chemistry has resulted into a powerful strategy for the preparation of functional hybrid materials. In order to establish the utility of 1,2,3-triazole based triethoxysilane (TBTES)-linkers, they were used as precursors for the synthesis of various silatranes, that can find numerous applications in biomaterials, catalysis and sol–gel chemistry [16–18].

We herein report an interesting application of the click reaction to organosilicon chemistry with the aim to assemble a small series of well defined 1,2,3-triazole based silatrane (TBS)-scaffolds, that offers a number of imperative advantages. Primarily, this is a general method which could be readily extended to an extensive range of materials, including proteins, micelles, dye molecules and hybrid biomaterials [19–22]. Secondly, unlike triethoxysilanes, assembled TBS-scaffolds are hydrolytically more stable [23,24]. On the tertiary part, the ability of the all nitrogen atoms of 1,2,3-triazole and oxygen atoms of silatrane ring to act as a hydrogen bond acceptor even makes it more attractive in supramolecular chemistry. Therefore, TBS-scaffolds would give boost to ongoing research in the field of "click" and "organosilicon chemistry".

Materials and methods

General reaction procedure for the click silylation

To a 50.0 ml two-necked round bottom flask with alkyne function (2 mmol), azide function (2 mmol/alkyne function), $[CuBr(PPh_3)_3]$ (0.01 mmol/alkyne function), triethylamine (2.0 ml), and THF (2.0 ml) under nitrogen atmosphere and then the mixture was stirred at 60 °C for 5 h. The reaction mixture was allowed to cool, and the solvents were removed under vacuum followed by addition of hexane. The mixture was filtered and washed with 2 × 5.0 ml of hexane. The concentration of the filtrate under reduced pressure afforded the title compound in good to excellent yield.

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General procedure for the synthesis of silatranes

To the stirred solution of trisalkoxyamine (2 mmol) in toluene (50.0 ml), catalytic amount of potassium hydroxide was added, in apparatus fitted with dean stark assembly. After stirring it for 10 min, substituted triethoxysilane (2 mmol/trisalkoxyamine) was added dropwise within 2 min. The reaction mixture was then refluxed at 110 °C for 5 h. Then, the reaction mixture was allowed to cool and toluene was removed by vacuum evaporation and on slow addition of hexane (5.0 ml), white solid precipitated out. The contents were further stirred for 4 h at room temperature. The solid was filtered and washed twice with diethylether (2 × 5.0 ml) and dried under vacuum.

2a: M.pt.: 137 °C. Yield: 78%. IR (neat, cm^{-1}): 2920, 2870, 1682, 1589, 1454, 1438, 1392, 1212, 1160, 1087, 1020, 939, 847, 775, 712, 702, 655, 584, 531. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 10.41 (s, 1H), 7.76–6.97 (m, 5H), 5.25 (s, 2H), 4.28 (t, J = 6 Hz, 2H), 3.68 (t, J = 3 Hz, 6H), 2.74 (t, J = 3 Hz, 6H), 1.97–1.88 (m, 2H), 0.37–0.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 189.9, 160.8, 142.8, 136.0, 128.5, 122.8, 121.2, 113.2, 62.7, 57.5, 53.4, 50.9, 26.2, 13.0. MS (*m*/*z*, assignment): 459 (20.7), 458 (26.6), 457 (100), 441 (73.1), 419 (27.4), 297 (21.7), 215 (5.5), 192 (6.8), 174 (24.1), 172 (9.5), 150 (5.0). HRMS (ES^+) calcd for $C_{19}H_{26}N_4O_5Si$ $[M + K]^+$ 457.1309, found 457.1317.

2b: M.pt.: 127 °C. Yield: 78%. IR (neat, cm^{-1}): 2973, 2926, 2884, 1690, 1599, 1507, 1438, 1390, 1251, 1159, 1099, 1072, 955, 759, 605, 541. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 9.79 (s, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.56 (s, 1H), 7.03 (d, J = 8.6 Hz, 2H), 5.20 (s, 2H), 4.25 (t, J = 7.4 Hz, 2H), 3.65 (t, J = 5.8 Hz, 6H), 2.71 (t, J = 5.8 Hz, 6H), 1.94–1.83 (m, 2H), 0.30–0.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 195.6, 160.8, 142.8, 130.6, 122.5, 114.7, 62.7, 57.6, 53.3, 51.3, 26.2, 12.9. MS (*m*/*z*, assignment): 459 (20.7), 458 (26.6), 457 (100), 441 (73.1), 419 (27.4), 297 (21.7), 215 (5.5), 192 (6.8), 174 (24.1), 172 (9.5), 150 (5.0). HRMS (ES^+) calcd for $C_{19}H_{26}N_4O_5Si$ $[M + K]^+$ 457.1309, found 457.1315.

2c: M.pt.: 127 °C. Yield: 78%. IR (neat, cm^{-1}): 2975, 2925, 2883, 1660, 1596, 1488, 1454, 1366, 1299, 1172, 1152, 1119, 1072, 954, 770, 759, 617, 566, 530. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.67–7.60 (m, 1H), 7.60 (s, 1H), 7.42–6.95 (m, 3H), 5.23 (s, 2H), 4.28 (t, J = 7.4 Hz, 2H), 3.69 (t, J = 5.8 Hz, 6H), 2.74 (t, J = 5.8 Hz, 6H), 2.51 (s, 3H), 1.98–1.88 (m, 2H), 0.39–0.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 189.8, 183.0, 142.5, 133.2, 129.8, 120.5, 102.8, 65.4, 62.1, 56.9, 52.8, 50.3, 25.7, 12.6. MS (*m*/*z*, assignment): 472 (20.4), 471 (100), 455 (82.3), 433 (97.2), 391 (7.8), 279 (9.2), 215 (6.1), 174 (14.9), 150 (15.0), 132 (4.0). HRMS (ES^+) calcd for $C_{20}H_{28}N_4O_5Si$ $[M + K]^+$ 471.1466, found 471.1454.

2d: M.pt.: 96 °C. Yield: 73%. IR (neat, cm^{-1}): 2985, 2925, 2883, 1658, 1566, 1488, 1454, 1366, 1299, 1172, 1152, 1119, 1072, 954, 770, 627, 571, 535. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.83 (d, J = 8.6 Hz, 2H), 7.55 (s, 1H), 6.94 (dd, J = 8.6 Hz, 2H), 5.18 (s, 2H), 4.24 (t, J = 7.4 Hz, 2H), 3.65 (t, J = 5.7 Hz, 6H), 2.71 (t, J = 5.7 Hz, 6H), 2.46 (s, 3H), 1.91–1.86 (m, 2H), 0.32–0.26 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 189.8, 183.1, 142.6, 131.9, 130.5, 122.6, 115.3, 73.3, 62.6, 57.7, 53.4, 51.3, 26.2, 12.9. MS (*m*/*z*, assignment): 472 (20.4), 471 (100), 455 (82.3), 433 (97.2), 391 (7.8), 279 (9.2), 215 (6.1), 174 (14.9), 150 (15.0), 132 (4.0). HRMS (ES^+) calcd for $C_{20}H_{28}N_4O_5Si$ $[M + K]^+$ 471.1466, found 471.1458.

2e: M.pt.: 144 °C. Yield: 78%. IR (neat, cm^{-1}): 3132, 2945, 2868, 2823, 1656, 1597, 1535, 1435, 1350, 1218, 1034, 886, 763, 695. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.43 (s, 1H), 4.23 (t, J = 7.7 Hz, 2H), 3.69 (t, J = 5.8 Hz, 6H), 3.52 (s, 2H), 2.74 (t, J = 5.8 Hz, 6H), 2.20 (s, 6H), 1.97–1.86 (m, 2H), 0.33–0.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 144.6, 122.1, 56.7, 54.1, 52.1, 50.1, 45.9, 24.0, 13.2. MS (*m*/*z*, assignment): 381 (2.4), 380 (13.0), 364 (18.3), 343 (21.0), 342 (100), 206 (10.0), 174 (37.6), 172 (67.0). HRMS (ES^+) calcd for $C_{14}H_{27}N_5O_3Si$ $[M + H]^+$ 342.1961, found 342.1977.

2f: M.pt.: 137 °C. Yield: 76%. IR (neat, cm^{-1}): 3132, 2971, 2927, 2884, 1551, 1438, 1389, 1294, 1214, 1165, 1099, 1072, 954, 876, 780. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.30 (s, 1H), 4.27 (t, J = 6 Hz, 2H), 3.76 (t, J = 5.8 Hz, 6H), 2.81 (t, J = 5.8 Hz, 6H), 2.66 (t, J = 7.4 Hz, 2H), 2.0–1.92 (m, 2H), 1.72–1.63 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.47–0.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 147.7, 120.6, 57.6, 53.3, 51.0, 27.8, 26.4, 22.3, 13.9, 13.3. MS (*m*/*z*, assignment): 365 (15.9), 349 (34.3), 328 (41.2), 327 (100), 285 (18.5), 233 (16.5), 206 (22.7), 174 (27.9), 172 (25.4), 150 (11.7), 132 (6.5). HRMS (ES^+) calcd for $C_{14}H_{26}N_4O_3Si$ $[M + H]^+$ 327.1882, found 327.1870.

2g: M.pt.: 97 °C. Yield: 77%. IR (neat, cm^{-1}): 3370, 2930, 2874, 1735, 1577, 1485, 1414, 1271, 1183, 1120, 1096, 1034, 1010, 820, 797, 775, 671, 620, 577. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.52 (d, J = 16.8 Hz, 1H), 5.12 (s, 2H), 4.25 (t, J = 8.1 Hz, 2H), 3.69 (t, J = 5.8 Hz, 6H), 2.75 (t, J = 5.8 Hz, 6H), 2.0 (s, 3H), 1.97–1.89 (m, 2H), 0.38–0.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 196.1, 195.4, 126.7, 126.1, 123.7, 61.0, 57.6, 53.4, 51.1, 26.2, 13.1. MS (*m*/*z*, assignment): 396 (14.8), 395 (100), 379 (43.6), 357 (18.7), 353 (10.0), 315 (22.6), 297 (7.3), 273 (7.0), 216 (3.7), 206 (11.0), 192 (12.0), 174 (27.7). HRMS (ES^+) calcd for $C_{14}H_{24}N_4O_5Si$ $[M + K]^+$ 395.1153, found 395.1142.

2h: M.pt.: 127 °C. Yield: 76%. IR (neat, cm^{-1}): 2973, 2929, 2887, 1724, 1634, 1439, 1407, 1295, 1267, 1180, 1045, 957, 809, 782. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.58 (s, 1H), 6.37 (d, J = 17.2 Hz, 1H), 6.16-5.92 (m, 1H), 5.78 (d, J = 10.5 Hz, 1H), 5.24 (s, 2H), 4.29 (t, J = 7.1 Hz, 2H), 3.74 (t, J = 6.9 Hz, 6H), 2.80 (t, J = 6.9 Hz, 6H), 2.02–1.79 (m, 2H), 0.67–0.39 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 165.3, 142.3, 130.8, 128.1, 123.6, 58.2, 57.5, 52.1, 24.0, 18.1, 7.3.

2i: M.pt.: 204–205 °C. Yield: 73%. IR (neat, cm^{-1}): 2973, 2926, 2884, 1690, 1599, 1507, 1438, 1390, 1251, 1159, 1099, 1072, 955, 759, 605, 541. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 10.58 (s, 1H), 7.15–7.27 (m, 4H), 7.58 (s, 1H), 5.18 (s, 2H), 4.29 (t, 2H, J = 6.5 Hz), 3.65–3.73 (m, 3H), 2.13–2.46 (m, 6H), 1.78 (m, 2H), 1.02–1.19 (m, 9H), 0.32 (m, 2H). MS (*m*/*z*, assignment): 501 (21.9), 499 (17.2), 216 (8.8), 193 (9.1), 192 (100), 174 (56.7), 156 (16.9). HRMS (ES^+) calcd for $C_{22}H_{32}N_4O_5Si$ $[M + K]^+$ 499.1779, found 499.1785.

2j: M.pt.: 98 °C. Yield: 77%. IR (neat, cm^{-1}): 3133, 2944, 2866, 2824, 1655, 1535, 1435, 1350, 1218, 1034, 886, 767, 694. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.48 (s, 1H), 4.49 (s, 2H), 4.02 (t, J = 6.9 Hz, 6H), 3.40 (d, J = 6.5 Hz, 2H), 2.86 (s, 3H), 2.63–2.54 (m, 4H), 2.34–2.03 (m, 15H), 1.38–1.11 (m, 2H), 0.60–0.40 (m, 2H). MS (*m*/*z*, assignment): 440 (28.4), 422 (26.6), 385 (13.8), 384 (68.0), 285 (21.6), 247 (40.6), 230 (62.5), 214 (99.6), 192 (100), 174 (89.7), 156 (21.6). HRMS (ES^+) calcd for $C_{17}H_{33}N_5O_3Si$ $[M + H]^+$ 384.2430, found 384.2440.

2k: M.pt.: 106 °C. Yield: 77%. IR (neat, cm^{-1}): 3134, 2970, 2927, 2884, 1551, 1438, 1389, 1294, 1214, 1165, 1099, 1072, 954, 876, 780. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.72–7.33 (s, 1H), 4.44–4.15 (m, 1H), 3.82 (s, 2H), 3.20 (d, J = 6.5 Hz, 1H), 2.66 (s, 1H), 2.59–2.21 (m, 4H), 2.14–1.83 (m, 2H), 1.68 (d, J = 6.1 Hz, 2H), 1.18–0.91 (m, 9H), 0.66–0.24 (m, 2H). MS (*m*/*z*, assignment): 425 (13.7), 407 (100), 368 (65.5), 319 (11.9), 216 (3.9), 206 (7.7), 192 (8.4), 174 (27.7), 156 (26.4). HRMS (ES^+) calcd for $C_{17}H_{32}N_4O_3Si$ $[M + K]^+$ 407.1880, found 407.1899.

2l: M.pt.: 71 °C. Yield: 70%. IR (neat, cm^{-1}): 2926, 1599, 1437, 1346, 1214, 1178, 1080, 964, 757, 675. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.26 (dd, J = 45.8, 42.1 Hz, 1H), 3.69 (s, 5H), 2.35 (ddd, J = 30.8, 23.6, 10.7 Hz, 6H), 2.11 (d, J = 9.9 Hz, 1H), 1.21–0.83 (m, 10H).MS (*m*/*z*, assignment): 395 (41.8), 230 (6.2), 216 (14.7), 192 (100), 174 (99.8), 156 (20.7), 116 (8.2), 98 (16.3). HRMS (ES^+) calcd for $C_{15}H_{28}N_4O_4Si$ $[M + K]^+$ 395.1516, found 395.1510.

2m: M.pt.: 120 °C. Yield: 82%. IR (neat, cm^{-1}): 2928, 2873, 1718, 1570, 1450, 1397, 1091, 908, 770, 712, 612, 570, 540. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.77–7.81 (m, 2H), 7.61–7.65 (m, 2H), 7.58 (s, 1H), 4.90 (s, 2H), 4.23 (t, 2H, J = 6.5 Hz), 3.62–3.83 (m, 3H),