Supporting Information

Bistrimethylsilylpropargylic ether: a versatile ambident synthon to access substituted allenynes ethers and α-substituted bispropargylic alcohols

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Table of Contents:

General Methods S2

Experimental procedures and Characterization data for: S2-S10

3-((trimethylsilyloxy)-1,5-bistrimethylsilylpenta-1,4-diyne 3a S2
3-((triethylsilyloxy)-1,5-bistrimethylsilylpenta-1,4-diyne 3b S2
(3-((tert-butyldimethylsilyloxy)penta-1,4-diyne-1,5-diyl)bistrimethylsilane 3c S3
2-((3-trimethylsilyl-1-trimethylsilylethynylprop-2-ynyloxy) tetrahydropropyran 3e S3
1,3-dimethoxy-5-((3-trimethylsilyl-1-trimethylsilylethynylprop-2-ynyloxy)methyl)benzene 3f S4
2-(1-ethynylprop-2-ynyloxy)tetrahydropropyran 4e S4
1,3-dimethoxy-5-((1-ethynyl-prop-2-ynyloxy)methyl)benzene 4f S5
(3-((tert-butyldiphenylsilyloxy)penta-1,4-diyne-1,5-diyl) trimethylsilane 5d S5
2-(1-ethynylprop-1,2-dienyloxy)tetrahydropropyran 8e S6
1,3-dimethoxy-5-((1-ethynylprop-1,2-dienyloxy)methyl)benzene 8f S6
4-((tert-butyldiphenylsilyloxy)-6-trimethylsilanyl-4-trimethylsilaneylethynyl hex-1-en-5-yne 9b S7
2-((1,3-bistrimethylsilyl-1-trimethylsilylethynylprop-2-ynyloxy) tetrahydropropyran 9c S7
2-((1,1-bistrimethylsilylethynylbut-3-enyloxy)tetrahydropropyran 9d S8
2-((1-methyl-3-trimethylsilyl-1-trimethylsilylethynylprop-2-ynyloxy) tetrahydro-propyran 9e S9
1,3-dimethoxy-5-((1,1,3-dimethoxybenzyloxy-3-trimethylsilanyl-1-trimethylsilanyl ethynyl prop-2-ynyloxy)methyl)benzene 9f S9

\(^1\)H NMR and \(^{13}\)C NMR spectra for compounds: S11-S34
3a-f, 4d-f, 5d, 6d-e, 7d, 8d-f, 9a-f, 10 and 11

References S35
General Methods: All reagents are commercial grade and were used as received. All reactions were performed under inert atmosphere using anhydrous solvents which were dried and distilled before being used. Thin-layer chromatograms (TLC) and flash chromatography separations were respectively performed on precoated silica gel 60 F 254 plates and on silica gel 60 (230-400 mesh). $^1$H NMR spectra were recorded at 400 MHz, shifts are relative to internal TMS. $^{13}$C NMR spectra were obtained at 100 MHz. ESITOF mass spectra. High resolution mass spectra were performed on a Maldi-tof (matrix: dihydroxybenzoic acid). IR spectra were recorded on NaCl plates as thin film.

General procedure for the preparation of bistrimethylsilyl propargylic ethers (3a-3c): To a stirred solution of bistrimethylsilyl propargylic alcohol $^1$ (0.44 mmol) in CH$_2$Cl$_2$ (7 mL) was added the corresponding silyl chloride (0.48 mmol) and DMAP (0.48 mmol) and the solution was stirred at room temperature until completion. The mixture was concentrated, diluted with Et$_2$O and washed with brine. The organic layer was separated, dried over magnesium sulfate and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel to yield the corresponding ether.

3-(trimethylsilanyloxy)-1,5-bistrimethylsilanylpen ta-1,4-diyne (3a): From 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol $^2$ (100 mg, 0.44 mmol) and trimethylsilyl chloride (0.17 mL, 0.48 mmol), crude 3a (104 mg, 80%) was obtained following the general procedure. Purification by flash chromatography (Pentane) afforded 3a (104 mg, 80%) as a colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 5.17 (s, 1H), 0.23 (s, 9H), 0.19 (s, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 102.5, 88.8, 53.3, 0.45, -0.48; IR (neat, cm$^{-1}$) 2962, 2178, 1251, 1058, 845; MS (TOF) m/z (M+Na$^+$) = 319.

3-(triethylsilanyloxy)-1,5-bistrimethylsilanylpen ta-1,4-diyne (3b): From alcohol 2 (100 mg, 0.44 mmol) and triethylsilyl chloride (80 µL, 0.48 mmol), ether 3b (118 mg, 82%) was prepared
following the general procedure. Purification by flash chromatography (Pentane/Et₂O: 98/2) afforded 3b (118 mg, 82%) as a colourless oil. ¹H NMR (CDCl₃) δ 5.18 (s, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.71 (q, J = 8.0 Hz, 6H), 0.18 (s, 18H); ¹³C NMR (CDCl₃) δ 102.6, 88.4, 6.6, 53.4, 6.6, 4.8, -0.5; IR (neat, cm⁻¹) 2959, 2180, 1288, 1251, 1083, 844; MS (TOF) m/z (M+Na⁺) = 361.

(3-(tert-butyldimethylsilyloxy)penta-1,4-diyn-1,5-diyl)bistrimethylsilane (3c): From alcohol 2 (100 mg, 0.44 mmol) and tert-butyldimethylsilyl chloride (72 mg, 0.48 mmol) 3c was obtained following the general procedure. Purification by flash chromatography (Pentane/Et₂O: 98/2) afforded 3c (136 mg, 92%) as a colorless oil. ¹H NMR (CDCl₃) δ 5.19 (s, 1H), 0.93 (s, 9H), 0.20 (s, 24H); ¹³C NMR (CDCl₃) δ 102.7, 88.6, 53.8, 25.6, 18.1, -0.5, -4.4; IR (neat, cm⁻¹) 2960, 2180, 1252, 1082, 843; MS (TOF) m/z (M+Na⁺) = 361.

2-(3-trimethylsilanyl-1-trimethylsilanylethynylprop-2-ynyloxy)tetrahydropyran (3e): To a stirred solution of alcohol 2 (100 mg, 0.44 mmol) in CH₂Cl₂ (8 mL) at room temperature was added triphenylphosphine hydrobromide (4 mg, 0.01 mmol) and dihydropyran (44 µL, 0.48 mmol). The resulting reaction was stirred until completion of the reaction. The mixture was concentrated, diluted with Et₂O and filtered through celite. The solution was concentrated under vacuum. Purification by flash chromatography (Pentane/Et₂O: 95/5) afforded 3e as a white solid (104 mg, 75%). ¹H NMR (CDCl₃) δ 5.17 (s, 1H), 4.97 (t, J = 6.4 Hz, 1H), 3.90-3.85 (m, 1H), 3.55-3.53 (m, 1H), 1.90-1.56 (m, 6H), 0.19 (s, 18H); ¹³C NMR (CDCl₃) δ 100.1, 99.7, 95.3, 90.2, 89.4, 61.9, 55.4, 29.9, 25.3, 18.6, -
0.4; IR (neat, cm\(^{-1}\)) 2962, 2182, 1456, 1378, 1311, 1253, 1017, 852; mp: 47°C; MS (TOF) \(m/z\) (M+Na\(^+\)) = 331; HRMS calcd for C\(_{16}\)H\(_{28}\)O\(_2\)Si\(_2\)Na [M+Na\(^+\)] = 331.1526, found 331.1532.

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1,3-dimethoxy-5-(3-trimethylsilyl-1-trimethylsilanylethynylprop-2-ynyloxy)methyl)benzene (3f): To a stirred solution of alcohol 2 (100 mg, 0.44 mmol) in THF (5 mL) at 0°C was added EtMgBr (0.6 mL, 1M in THF, 0.6 mmol), HMPA (0.3 mL) and 3,5-dimethoxybenzyl bromide (122 mg, 0.53 mmol) in solution in THF (1 mL). The mixture was refluxed for 1.5 h and diluted with Et\(_2\)O and washed with saturated ammonium chloride. The organic layer was separated, washed with H\(_2\)O and brine, and then was dried over magnesium sulfate and was concentrated under vacuum. The crude was purified by flash chromatography (Pentane/Et\(_2\)O: 98/2) to afford ether 3f as a brown oil (67 mg, 40%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 6.54 (d, \(J = 2.2\) Hz, 2H), 6.40 (s, 1H), 4.99 (s, 1H), 4.65 (s, 2H), 3.80 (s, 6H), 0.21 (s, 18H); \(^1\)C NMR (CDCl\(_3\)) \(\delta\) 160.8, 139.3, 105.9, 100.1, 99.5, 90.7, 69.0, 58.5, 55.3, -0.4; IR (neat, cm\(^{-1}\)) 2958, 2169, 1599, 1155, 844; MS (TOF) \(m/z\) (M+H\(^+\)) = 375.

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2-(1-ethynylprop-2-ynyloxy)tetrahydropyran (4e): To a stirred solution of ether 3e (77 mg, 0.25 mmol) in MeOH (6 mL) was added K\(_2\)CO\(_3\) (35 mg, 0.25 mmol). The reaction mixture was stirred at room temperature for 1 h and then was quenched with saturated ammonium chloride (10 mL) and extracted with Et\(_2\)O (3 x 10 mL). The organic layer was separated, washed with H\(_2\)O, brine and was dried over anhydrous MgSO\(_4\), filtered and concentrated under vacuum. The crude residue was purified by silica gel flash chromatography (Pentane/Et\(_2\)O: 99/1) to yield 4e (29 mg, 70%) as a
colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 5.20 (dd, $J$ = 2.4, 2.4 Hz, 1H), 4.99 (t, $J$ = 2.8 Hz, 1H), 3.89-3.84 (m, 1H), 3.59-3.54 (m, 1H), 2.56 (d, $J$ = 2.4 Hz, 1H), 2.53 (d, $J$ = 2.4 Hz, 1H), 1.90-1.63 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 95.4, 78.9, 78.4, 73.5, 72.9, 61.9, 54.1, 29.8, 25.1, 18.5; IR (neat, cm$^{-1}$) 3286, 2946, 2121, 1442, 1119, 1018; MS (TOF) m/z (M+K$^+$) = 187.

1,3-dimethoxy-5-(1-ethynyl-prop-2-ynyloxymethyl)benzene (4f): To a stirred solution of ether 3f (94 mg, 0.25 mmol) in MeOH (6 mL) was added K$_2$CO$_3$ (35 mg, 0.25 mmol). The reaction mixture was stirred at room temperature for 1 h and then was quenched with saturated ammonium chloride (10 mL) and extracted with Et$_2$O (3 x 10 mL). The organic layer was separated, washed with H$_2$O, brine and was dried over anhydrous MgSO$_4$, filtered and concentrated under vacuum. The crude residue was purified by silica gel flash chromatography (Pentane/Et$_2$O: 98/2) to afford 4f (37 mg, 65%) as a colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 6.55 (d, $J$ = 2.0 Hz, 2H), 6.41 (t, $J$ = 2.4 Hz, 1H), 5.03 (t, $J$ = 2.4 Hz, 1H), 4.67 (s, 2H), 3.80 (s, 6H), 2.60 (d, $J$ = 2.4 Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 160.8, 138.9, 105.8, 100.1, 78.3, 73.9, 69.2, 57.3, 55.3; IR (neat, cm$^{-1}$) 3284, 2918, 2119, 1598, 1461, 1153, 1054, 665; MS (TOF) m/z (M+Na$^+$) = 253.

(3-(tert-butyldiphenylsilanyloxy)penta-1,4-diyne-1,5-diyl)trimethylsilane (5d): To a stirred solution of ether 4d (250 mg, 0.78 mmol) in THF (25 mL) at $-78^\circ$C was added dropwise n-BuLi (0.5 mL, 1.6 M in hexane, 0.78 mmol). After 10 min of stirring, a solution of TMSCl (0.1 mL, 0.78 mmol) in THF (15 mL) was added. The mixture was warmed to RT for 2.5 h, quenched with saturated ammonium chloride, and extracted with Et$_2$O. The organic layer was separated, washed
with H₂O, brine and then was dried over magnesium sulfate, and was concentrated under vacuum. Purification of the crude by flash chromatography (Pentane/CH₂Cl₂: 9/1) afforded 5d (183 mg, 43%) as a colorless oil, as well as 3d (11%) and starting product 4d (24%). 5d: ¹H NMR (CDCl₃) δ 7.78-7.74 (m, 4H), 7.45-7.27 (m, 6H), 5.07 (d, J = 2.4 Hz, 1H), 2.49 (d, J = 2.4 Hz, 1H), 1.09 (s, 9H), 0.13 (s, 9H); ¹³C NMR (CDCl₃) δ 135.8, 132.6, 129.8, 127.5, 101.9, 89.3, 81.1, 71.9, 54.1, 26.6, 19.2, -0.5; IR (neat, cm⁻¹) 3290, 3072, 2933, 111, 845, 701; MS (TOF) m/z (M+Na⁺) = 413.

2-(1-ethynylpropa-1,2-dienyloxy)tetrahydropyran (8e): To a stirred solution of 3e (200 mg, 0.64 mmol) in THF (12 mL) was added Bu₄NF (0.64 mL, 1M in THF, 0.64 mmol). The resulting brown solution was stirred at room temperature for 10 min. The reaction was quenched with saturated ammonium chloride and extracted with Et₂O. The organic layer was separated, washed with H₂O, brine and then dried over magnesium sulfate and concentrated under vacuum. The crude was purified by flash chromatography on silica gel (Pentane/Et₂O: 99/1) to afford 8e (61 mg, 58%) as an unstable yellow oil. ¹H NMR (CDCl₃) δ 5.60 (dd, J = 1.2, 11.4 Hz, 1H), 5.53 (dd, J = 1.2, 11.4 Hz, 1H), 5.11 (t, J = 2.8 Hz, 1H), 3.91-3.82 (m, 1H), 3.60-3.56 (m, 1H), 3.35 (s, 1H), 1.90-1.43 (m, 6H); ¹³C NMR (CDCl₃) δ 206.8, 113.9, 96.1, 89.7, 83.4, 75.2, 65.7, 29.6, 25.4, 18.3; IR (neat, cm⁻¹) 3271, 2945, 2109, 1942, 1441, 1035; MS (TOF) m/z (M+Na⁺) = 187.

1,3-dimethoxy-5-(1-ethynylpropa-1,2-dienyloxymethyl)benzene (8f): To a stirred solution of 3f (200 mg, 0.53 mmol) in THF (6 mL) was added t-BuOK (65 mg, 0.53 mmol). The resulting brown solution was stirred at room temperature for 10 min. The reaction was quenched with saturated ammonium chloride and extracted with Et₂O. The organic layer was separated, washed with H₂O,
brine and dried over magnesium sulfate, filtered and concentrated under vacuum. The crude was purified by flash chromatography (Pentane/CH$_2$Cl$_2$: 98/2) to afford 8f as a yellow oil (72 mg, 59%).

$^1$H NMR (CDCl$_3$) $\delta$ 6.52 (d, $J = 2.0$ Hz, 2H), 6.40 (t, $J = 2.4$ Hz, 1H), 5.65 (d, $J = 0.8$ Hz, 2H), 4.59 (s, 2H), 3.80 (s, 6H), 3.35 (s, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 205.5, 160.8, 138.8, 117.5, 105.5, 99.9, 92.2, 83.3, 75.4, 70.6, 55.3; IR (neat, cm$^{-1}$) 3269, 2937, 2117, 1723, 1599, 1462, 1205, 1155, 1066, 687; MS (TOF) m/z (M+Na$^+$) = 253.

4-(tert-butyldiphenylsilanloyloxy)-6-trimethylsilanyl-4-trimethylsilanylethynylhex-1-en-5-yne (9b): To a stirred solution of 3d (100 mg, 0.22 mmol) in THF (5 mL) at -78°C was added dropwise $n$-BuLi (0.22 mL, 1.6 M in hexane, 0.22 mmol) and a solution of allyliodide (20 µL, 0.24 mmol) in THF (1 mL). After stirring for 10 min at -78°C, the reaction was quenched with saturated ammonium chloride, warmed to RT and extracted with Et$_2$O. The organic layer was separated, washed with H$_2$O, brine and dried over magnesium sulfate, filtered and concentrated under vacuum. The crude was purified by flash chromatography with pentane to afford 9b (49 mg, 45%) as yellow oil.

$^1$H NMR (CDCl$_3$) $\delta$ 7.77 (d, $J = 7.1$ Hz, 4H), 7.42-7.31 (m, 6H), 6.05-5.96 (m, 1H), 5.20-5.15 (m, 2H), 2.72 (d, $J = 7.2$ Hz, 2H), 1.04 (s, 9H), -0.03 (s, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 136.4, 134.3, 132.7, 129.1, 126.9, 118.7, 104.9, 88.9, 65.2, 50.6, 26.8, 19.3, -0.6; IR (neat, cm$^{-1}$) 3074, 3050, 2960, 2174, 1428, 1250, 110, 843, 700; MS (TOF) m/z (M+Na$^+$) = 525; HRMS calcd for C$_{30}$H$_{42}$OSi$_3$Na [M+Na$^+$] = 525.2441, found 525.2439.

2-(1,3-bistrimethylsilanyl-1-trimethylsilanylethynylprop-2-ynyloxy)tetrahydropyran (9c): To a stirred solution of 3e (60 mg, 0.19 mmol) in THF (5 mL) at -78°C was added dropwise $n$-BuLi (0.12
mL, 1.6 M in hexane, 0.19 mmol) and then a solution of TMSCl (25 µL, 0.19 mmol) in THF (1 mL). After stirring for 10 min at -78°C, the reaction was quenched with saturated ammonium chloride, warmed to RT and extracted with Et₂O. The organic layer was separated, washed with H₂O, brine and dried over magnesium sulfate, filtered and concentrated under vacuum. The crude was purified by flash chromatography (Pentane/Et₂O: 99/1) to afford 9c as a yellow oil (58 mg, 79%). ¹H NMR (CDCl₃) δ 5.3 (s, 1H), 4.02-3.96 (m, 1H), 3.54-3.51 (m, 1H), 1.89-1.54 (m, 6H), 0.20 (s, 9H), 0.16 (s, 18H); ¹³C NMR (CDCl₃) δ 103.9, 103.1, 95.4, 93.7, 90.5, 62.6, 61.4, 30.7, 25.6, 18.7, -0.1, -4.8; IR (neat, cm⁻¹) 2959, 2152, 1249, 844, 758; MS (TOF) m/z (M+Na⁺) = 403.

2-(1,1-bistrimethylsilanylethynylbut-3-enyloxy)tetrahydropyran (9d): To a stirred solution of 3e (200 mg, 0.64 mmol) in THF (5 mL) at -78°C was added dropwise n-BuLi (0.4 mL, 1.6 M in hexane, 0.64 mmol) and then a solution of allyliodide (60 µL, 0.64 mmol) in THF (1 mL). After stirring for 10 min at -78°C, the reaction was quenched with saturated ammonium chloride, warmed to RT and extracted with Et₂O. The organic layer was separated, washed with H₂O, brine and dried over magnesium sulfate, filtered and concentrated under vacuum. The crude was purified by flash chromatography with pentane to afford 9d as a yellow oil (177 mg, 81%). ¹H NMR (CDCl₃) δ 5.99-5.89 (m, 1H), 5.29 (t, J = 3.2 Hz, 1H), 5.18-5.14 (m, 2H), 4.04-3.98 (m, 1H), 3.54-3.48 (m, 1H), 2.68 (d, J = 8.0 Hz, 2H), 1.86-1.56 (m, 6H), 0.17 (s, 18H); ¹³C NMR (CDCl₃) δ 132.3, 118.6, 103.8, 102.2, 95.7, 90.5, 88.6, 68.2, 62.4, 48.3, 30.9, 25.4, 19.3, -0.2; IR (neat, cm⁻¹) 2958, 2173, 1251, 844, 760; MS (TOF) m/z (M+Na⁺) = 371; HRMS calcd for C₁₉H₃₂O₂Na [M+Na⁺] = 371.1839, found 371.1822.
2-(1-methyl-3-trimethylsilanyl-1-trimethylsilanylethynyl-prop-2-ynyloxy)tetrahydro-pyran (9e): To a stirred solution of 3e (100 mg, 0.32 mmol) in THF (5 mL) at -78°C was added dropwise n-BuLi (0.2 mL, 1.6 M in hexane, 0.32 mmol) and then a solution of methyl iodide (20 µL, 0.32 mmol) in THF (1 mL). After stirring for 10 min at -78°C, the reaction was quenched with saturated ammonium chloride, warmed to RT and extracted with Et₂O. The organic layer was separated, washed with H₂O, brine and then dried over magnesium sulfate and concentrated under vacuum. The crude was purified by flash chromatography with pentane to afford 9e as a yellow oil (55 mg, 60%).

¹H NMR (CDCl₃) δ 5.23 (t, J = 2.8 Hz, 1H), 4.03-3.98 (m, 1H), 3.54-3.50 (m, 1H), 1.86-1.54 (m, 12H), 0.18 (s, 18H); ¹³C NMR (CDCl₃) δ 104.8, 103.8, 96.1, 88.6, 87.4, 65.1, 62.8, 31.9, 31.2, 25.3, 19.6, -0.2; IR (neat, cm⁻¹) 2958, 2175, 1442, 1365, 1251, 844, 760; MS (TOF) m/z (M+Na⁺) = 345; HRMS calcd for C₁₇H₃₀O₂Si₂Na [M+Na⁺] = 345.1682, found 345.1682.

1,3-dimethoxy-5-(1,1,3-dimethoxybenzyloxy-3-trimethylsilanyl-1-trimethylsilanyl ethynyl prop-2-ynyloxy)methyl)benzene (9f): To a stirred solution of 3f (150 mg, 0.67 mmol) in THF (5 mL) at -78°C was added dropwise n-BuLi (0.6 mL, 1.6 M in hexane, 0.98 mmol, HMPA (0.05 mL) and a solution of 3,5-dimethoxybenzyl bromide (271 mg, 1.7 mmol) in THF (1 mL). The reaction was warmed to RT for 2 h and was quenched with saturated ammonium chloride and diluted with Et₂O. The organic layer was separated, washed with H₂O, brine and then dried over magnesium sulfate, and was concentrated under vacuum. The crude was purified by flash chromatography (Pentane/ Et₂O: 98/2) to afford 9f as a brown oil (140 mg, 40%). ¹H NMR (CDCl₃) δ 6.58 (s, 2H),
6.51 (s, 2H), 6.38 (s, 2H), 4.71 (s, 2H), 3.77 (s, 12H); 3.21 (s, 2H), 0.17 (s, 18H); $^{13}$C NMR (CDCl$_3$) δ 160.6, 159.9, 140.9, 137.4, 109.5, 105.4, 102.6, 99.6, 99.1, 90.9, 70.5, 67.7, 55.2, 55.1, 49.0, -0.3; IR (neat, cm$^{-1}$) 2960, 2164, 1598, 1468, 1202, 1161, 1051, 832; MS (TOF) m/z (M+Na$^+$) = 547.
References