#### **Electronic Supplementary Information**

# Three-way competition in a topochemical reaction: Permutative azide-alkyne cycloaddition reactions leading to a vast library of products in the crystal

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#### 1. Materials and methods

All the required chemicals and solvents were purchased from commercial suppliers. Chemicals were used without further purification and the solvents were used after distillation. Reactions were monitored by thin layer chromatography using pre-coated silica gel plates (60 F254). Thin layer chromatograms were visualized under UV light and by heating the plates dipped in the cerium molybdate solution. Column chromatography was carried out using silica gel (230-400 mesh). <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135 spectra were recorded on a 500 MHz NMR spectrometer. Proton chemical shifts ( $\delta$ ) are relative to tetramethylsilane (TMS,  $\delta$  = 0.0) as internal standard and expressed in parts per million. Spin multiplicities of the protons were reported as s (singlet), d (doublet), t (triplet), (q) quartet, dd (doublet of doublet) and m (multiplet). Coupling constants (J) are given in Hertz. Protons and carbons were assigned using 2D NMR spectra COSY, HMQC and HMBC. IR spectra were recorded using IR Prestige-21 (Shimadzu) spectrometer. Melting points were determined using Stuart, SMP-30 melting point apparatus and were uncorrected. Specific rotations were recorded on a Rudolph Autopol III automatic polarimeter. Elemental analyses were done on Elementar, vario MICRO cube elemental analyzer. DSC analyses were done at a heating rate of 5 °C/min using DSC Q20 differential scanning calorimeter. Powder X-ray diffraction spectra were recorded using X'pertPRO (PANalytics) X-ray diffractometer. The PXRD experiments were done using slow and continuous scan rate mode using Cu as the anode material ( $K\alpha 1 = 1.540598$ Å). X-ray intensity data measurements of freshly grown crystals were carried out at 298K on a Bruker-KAPPA APEX II CCD diffractometer with graphite-monochromatized (MoK = 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with scan width of 0.3° at different settings of  $\phi$  (0°, 90° and 180°) keeping the sample to detector distance fixed at 40 mm. The X-ray data collection was monitored by SMART program (Bruker, 2003).<sup>1</sup> All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2003). SHELXS-13 and SHELXT were used for structure solution and full matrix least-squares refinement on F2.<sup>2</sup> All the hydrogen atoms were placed in geometrically idealized position and refined in the riding model approximation with C-H = 0.95 Å, and with  $U_{iso}$  (H) set to 1.2 $U_{eq}$  (C). Molecular diagrams were generated using ORTEP-3.<sup>3</sup> Since the source used was Molybdenum, the flack parameter values are in the range 0.4-0.5. Since all the compounds were made from known optically active starting materials and no condition was used that could alter the stereochemistry of all the chiral centres, we are sure about the reported absolute configuration. The cavities in the crystal were developed using Mercury (version 3.9) with a probe radius of 1.1 Å. The dihedral angle scans were performed using B3LYP/6-31++G(d,p)<sup>4</sup> level of theory of Gaussian09<sup>5</sup> package. The overlapping of different conformers was done using Chemcraft (version 1.8). MALDI-TOF mass spectra of samples were recorded using either 2,5-dihydroxybenzoic acid or Paraformaldehyde as the matrix using Bruker Daltonics flex Analysis mass spectrometer. Solid state <sup>13</sup>C NMR experiment (CP/MAS) was recorded on a 400 MHz Delta\_2 NMR spectrometer.

#### 2. Synthesis of compound 1

The ribofuranoside derivative **9** was synthesized from D-Xylose (**5**) by modifying the reported procedures.<sup>6</sup> Compound **1** was synthesized from **9** in two steps.



Scheme S1 Synthesis of compound 1.

#### A) Synthesis of compound 6

To a suspension of D-xylose **5** (10.0 g, 66.61 mmol) in anhydrous DMF (50 mL), camphorsulfonic acid (1.54 g, 6.66 mmol) and 2,2-dimethoxypropane (32.64 mL, 266.43 mmol) were added and heated at 70 °C. After completion of the starting material (1 h), the reaction mass was quenched with triethylamine. The solvent was evaporated in a rotary evaporator and the obtained crude reaction mass was dissolved in EtOAc and washed successively with sat. NaHCO<sub>3</sub>, water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in a rotary evaporator. The residue obtained was purified by column chromatography (8:2, petroleum ether/EtOAc) to afford **6** (10.05 g, 65%). <sup>1</sup>H NMR of the compound was found to be indistinguishable with the reported data.<sup>7</sup>

#### B) Synthesis of compound 7

To a solution of diketal **6** (10.0 g, 43.42 mmol) in MeOH (50 mL),  $H_2SO_4$ -silica<sup>8</sup> (0.2 g) was added. The reaction mixture was stirred at room temperature and after 3h TLC showed complete conversion of the starting material. Then, the acid catalyst was neutralized with Et<sub>3</sub>N (2 mL) and stirred for 15 min. The reaction mass was filtered and the solvent was evaporated under reduced pressure. The crude mass thus obtained was purified by column chromatography (1:1, petroleum ether/EtOAc) to afford **7** (7.35 g, 89%). <sup>1</sup>H NMR of the compound was found to be indistinguishable with the reported data.<sup>9</sup>

#### C) Synthesis of compound 8

To a solution of diol **7** (7.0 g, 36.80 mmol) in anhydrous pyridine (40 mL), tosyl chloride (7.73 g, 40.48 mmol) was added at 0 °C. After 2 h TLC showed complete conversion of the starting material. Then, the pyridine was evaporated under reduced pressure and the crude reaction mass obtained was diluted in EtOAc and washed successively with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in a rotary evaporator. The residue obtained was purified by column chromatography (3:2, petroleum ether/EtOAc) to afford **8** (10.01 g, 79%) as a white solid. <sup>1</sup>H NMR of the compound was found to be indistinguishable with the reported data.<sup>7</sup>

#### D) Synthesis of compound 9

Compound **8** (10.0 g, 29.03 mmol) was dissolved in dry DMSO (30 mL) and to this solution, mixture of DMSO (60 mL) and Ac<sub>2</sub>O (40 mL) (3:2) was added drop-wise using dropping funnel and stirred at room temperature. When the starting material was consumed completely, the reaction mixture

was added to a cold saturated NaHCO<sub>3</sub> solution. Then, the compound was extracted with EtOAC and the organic layer was washed with water and brine successively. The solvent was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue thus obtained was dissolved in a mixture of EtOH (50 mL) and H<sub>2</sub>O (50 mL) and NaBH<sub>4</sub> (1.21 g, 31.94 mmol) was added portion-wise. When TLC showed complete consumption of the starting material, solvent was partially evaporated. The reaction mixture was diluted with EtOAc and washed successively with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude mass thus obtained was purified through column chromatography (3:2, petroleum ether/EtOAc) to afford the ribofuranoside derivative **9** (7.05 g, 70%) as a white solid. <sup>1</sup>H NMR of the compound was found to be indistinguishable with the reported data.<sup>6</sup>

#### E) Synthesis of compound 10

To a solution of compound **9** (7.0 g, 20.32 mmol) in anhydrous DMF (40 mL), NaN<sub>3</sub> (1.58 g, 24.39 mmol) was added under nitrogen and heated at 80 °C. After 4 h TLC showed complete conversion of the starting material. Then, DMF was evaporated in a rotary evaporator. The residue was diluted with EtOAc and washed successively with water and brine. The crude mass thus obtained was purified through column chromatography (7:3, petroleum ether/EtOAc) to afford azide **10** (3.98 g, 91%) as a white solid. <sup>1</sup>H NMR of the compound was found to be indistinguishable with the reported data.<sup>10</sup>

#### F) Synthesis of the compound 1

To a solution of **10** (3.95 g, 18.35 mmol) in anhydrous DMF (20 mL), NaH (1.12 g, 46.79 mmol) and propargyl bromide (2.36 mL, 31.19 mmol) were added at 0 °C and stirred for 30 min. After complete conversion of the starting material, reaction mass was quenched with ice cold water. Then, DMF was evaporated, the residue was diluted with EtOAc and the organic layer was washed with water and brine respectively and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the EtOAc was evaporated under reduced pressure and the crude mass obtained was purified by column chromatography (8:2, petroleum ether/EtOAc) to afford **1** (4.37 g, 94%) as a white solid: m.p. = 79-80 °C;  $[\alpha]_D^{25.0}$  = 190 (c 0.1, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr, cm<sup>-1</sup>) 3252, 2991, 2950, 2906, 2128, 2107, 1025; <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>)  $\delta$  5.69 (d, *J* = 3.65 Hz, 1H, H-1), 4.69 (t, *J* = 3.95 Hz, H-2), 4.17 (d ABq, *J* = 2.45 Hz, 15.90 Hz, 47.60 Hz, 2H), 3.93-3.97 (m, 1H, H-4), 3.84 (dd, *J* = 4.27 Hz, 8.92 Hz, 1H, H-3), 3.51 (dd, *J* = 2.45 Hz, 13.60 Hz, 1H, H-5A), 3.20 (dd, *J* = 5.00 Hz, 13.60 Hz, 1H, H-5B), 2.89 (t, *J* = 2.32 Hz, 1H), 1.34 (s, 3H, CH<sub>3</sub>), 1.18 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>)  $\delta$  113.4, 105.4 (C-1), 80.1, 78.6 (C-3), 78.3 (C-4), 77.8 (C-2), 76.6, 57.7 (CH<sub>2</sub>-), 51.8 (C-5), 27.0, 26.8. Elemental analysis calcd. for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.82; H, 5.88; N, 16.90.

#### 3. Crystallization of compound 1

Compound **1** (500 mg) was crystallized from a mixture of DCM and n-hexane (1:1 v/v). Colourless hexagonal crystals were resulted from the solution on slow evaporation of the solvent. Using X-ray diffractometer, the crystal structure of **1** was solved.

#### 4. Crystal data of compound 1

CCDC No. 1574972. Molecular formula =  $C_{11}H_{15}N_3O_4$ , Formula weight = 253.26, colorless blocks, 0.25 x 0.20 x 0.20 mm<sup>3</sup>, Orthorhombic, space group P2(1)2(1)2(1), a = 7.2124(6), b = 10.5820(5), c = 17.2167(9) Å, V = 1314.01(14) Å<sup>3</sup>, Z = 4, T = 296(2) K, 20max = 50.00°, D<sub>calc</sub> (g cm<sup>-3</sup>) = 1.280, F(000) = 536,  $\mu$  (mm<sup>-1</sup>) = 0.099, 2566 reflections measured, 2161 unique reflections (R<sub>int</sub> = 0.0226), multi-scan absorption correction, T<sub>min</sub> = 0.9756, T<sub>max</sub> = 0.9804, number of parameters = 165, number of restraints = 0, GoF = 1.031, R1 = 0.0423, wR<sub>2</sub> = 0.0928, R indices based on 2566 reflections with I >2s(I),  $\Delta\rho_{max} = 0.117$ ,  $\Delta\rho_{min} = -0.125$  (eÅ<sup>-3</sup>), absolute structure Flack = -0.1(6).

#### 5. Interpretation of regiochemistry of triazolyl signals formed in the TAAC reaction

The highly heterogeneous mixture of products obtained in TAAC reaction of **1** (crude) was analyzed using NMR spectroscopic techniques. The **1**,5-disubstituted triazolyl proton (structure A) will have spatial interaction with **O**-*CH*<sub>2</sub> protons in the NOESY spectrum. The **1**,5-disubstituted triazolyl proton (structure B) will have spatial interaction with both **O**-*CH*<sub>2</sub> and *CH*<sub>2</sub>-**N** protons in the NOESY spectrum. Hence, the proton peaks at 7-69-7.79 ppm and 8.02 to 8.08 ppm were assigned as **1**,5-disubstituted and **1**,4-disubstituted triazolyl protons. For complete characterization of TAAC product see the spectral data.



Fig. S1 NOESY spectrum of TAAC product mixture.

#### 6. NMR spectra of mixture of triazole linked linear oligomers having linker homogeneity



**Fig. S2** NMR spectra of mixtures of triazole linked oligomers reported previously having a single triazole isomer.<sup>11-14</sup> A) Adapted from ref 11. Copyright 2017 Wiley-VCH. B) Adapted from ref 12. Copyright 2017 Wiley-VCH. C) Adapted from ref 13. Copyright 2017 Wiley-VCH.D) Adapted from ref 14. Copyright 2017 American Chemical Society.

#### 7. Chromatographic separation of 2

The products obtained after the TAAC reaction were dissolved in dichloromethane and purified through column chromatography (2:3, petroleum ether/EtOAc). Compound **2** was obtained in pure form and was crystallized from a solution of DCM/n-hexane (2:1).

m.p. = 181-182 °C; IR (KBr, cm<sup>-1</sup>) 3120, 2987, 1375, 1220, 1109, 1026 ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (s, 1H), 5.77 (d, *J* = 3.45 Hz, 1H, H-1), 5.27 (dd, *J* = 3.25 Hz, 13.45 Hz 1H, H-5b), 5.09 (d, *J* = 14.65 Hz, 1H, -OCH<sub>2</sub>CCH), 4.74 (t, *J* = 3.80 Hz, 1H, H-2), 4.48 (d, *J* = 14.60 Hz, 1H, -OCH<sub>2</sub>CCH), 4.15 (dd, *J* = 10.80 Hz, 13.40 Hz, 1H, H-5a), 3.94 (m, 1H, H-4), 3.64 (dd, *J* = 4.25 Hz, 8.80 Hz, 1H, H-3), 1.47 (s, 3H, CH<sub>3</sub>), 1.29 (s, 3H, CH<sub>3</sub>) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  134.4, 133.1, 113.1, 102.4 (C-1), 86.8 (C-3), 77.5 (C-2), 71.1 (C-4), 62.0, 50.7 (C-5), 25.3, 25.1. Elemental analysis calcd. for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>: C, 52.17; H, 5.97; N, 16.59. Found: C, 53.06; H, 5.71; N, 16.96.

#### 8. Crystal data of compound 2

CCDC No. 1574973. Molecular formula =  $C_{11}H_{15}N_3O_4$ , Formula weight = 253.26, colorless blocks, 0.25 x 0.15 x 0.15 mm<sup>3</sup>, Monoclinic, space group P2(1), a = 10.9281(2), b = 9.8404(3), c = 11.7942(3) Å, V = 1257.36(6) Å<sup>3</sup>, Z = 4, T = 296(2) K,  $2\theta_{max} = 50.00^\circ$ ,  $D_{calc}$  (g cm<sup>-3</sup>) = 1.338, F(000) = 536,  $\mu$  (mm<sup>-1</sup>) = 0.103, 3885 reflections measured, 3283 unique reflections (R<sub>int</sub> = 0.0649), multi-scan absorption correction,  $T_{min}$  = 0.9796,  $T_{max}$  = 0.9846, number of parameters = 329, number of restraints = 1, GoF = 0.985, R1 = 0.0406, wR<sub>2</sub> = 0.0802, R indices based on 3283 reflections with I >2s(I),  $\Delta\rho_{max}$  = 0.097,  $\Delta\rho_{min}$  = -0.138 (eÅ<sup>-3</sup>), absolute structure Flack = -0.5(10).



Fig. S3. ORTEP diagram of intramolecular cycloadduct 2 at 30% probability.

#### 9. DFT calculations

To calculate the energy required for conformational change, we have performed the dihedral scans for C4-C5-N1-N2 (rotation of CH<sub>2</sub>-N bond about 100 degrees) and C3-O3-C9-C10 (rotation of O-CH<sub>2</sub> bond about 60 degrees) of **1** using Density Functional Theory (DFT). Energies of the conformers were calculated for every 10° rotation. B3LYP function was used with 6-31++G(d,p) as basis set. Of various conformers obtained, conformers with distance less than 5Å and angle less than 50° between azide and alkyne groups were considered as having orientation similar to conformer **B** and their energies were obtained. The energies of such conformers were found to be higher by only 4.2 to 6.5 kcal/mol relative to the starting conformer **A**. This suggests that mild activation is sufficient for the attainment of conformers as in **B**.



Fig. S4 Formation of conformer B from conformer A by rotation of CH<sub>2</sub>-N and O-CH<sub>2</sub> bonds.



**Fig. S5** Gaussian scan grid obtained for the C4-C5-N1-N2 and C3-O3-C9-C10 dihedral scans showing 77 conformers of **1**. The energies of the conformers in required orientation (circled) are given in brackets in kcal/mol.

С	1.07953800	-1.04370900	-0.79226000
Н	0.96454300	-1.53356900	-1.76304900
С	0.87669700	0.46140500	-0.76269300
Н	0.93743400	0.92837700	-1.75430300
С	-0.46918600	0.62079100	-0.08618400
Н	-1.27104100	0.52016300	-0.83134400
С	-0.50408100	-0.57918200	0.84004900
Н	0.08460500	-0.34892100	1.74092300
С	-1.86731400	-1.04260500	1.27576600
н	-1.76994700	-1.91483400	1.93290800
Н	-2.34406600	-0.23787000	1.84144600
С	3.00277800	0.00379300	0.03250600
С	4.02412700	0.42115900	-1.02682700
Н	4.81064800	-0.33432600	-1.10963000
Н	4.47825200	1.37924200	-0.75738400
Н	3.54255500	0.52339100	-2.00386300
С	3.60473800	-0.12000400	1.42380800
Н	4.40884000	-0.86096400	1.41862300
н	2.83731400	-0.43547200	2.13425100
Н	4.01309800	0.84276100	1.74391800

С	-1.10708000	2.91445500	-0.08207100
Н	-0.62775200	2.96111000	-1.07064500
Н	-0.81079300	3.80921200	0.47399200
С	-2.56627100	2.89591100	-0.26252600
С	-3.76613400	2.87958500	-0.41513600
Н	-4.82450700	2.85539000	-0.54528700
Ν	-2.77063000	-1.33954800	0.14150800
Ν	-2.76342000	-2.50445900	-0.27160100
Ν	-2.87525400	-3.54022300	-0.73845100
0	2.40656200	-1.24869700	-0.35238000
0	1.91679500	0.93425900	0.08597000
0	-0.62408300	1.80934300	0.66466300
0	0.12436100	-1.61161300	0.07207800

С	0.88534000	-0.99045300	-0.82703100
Н	0.65021600	-1.35388400	-1.83098200
С	0.66631000	0.49094800	-0.57214400
Н	0.58599600	1.08761300	-1.48941700
С	-0.58225200	0.51866700	0.28498300
Н	-1.46216300	0.49656400	-0.36525500
С	-0.47907800	-0.79209800	1.04026600
Н	0.21368600	-0.66898300	1.88607000
С	-1.76687600	-1.35076900	1.58063100
Н	-1.56004200	-2.31646500	2.06098800
Н	-2.15156200	-0.67681700	2.34916300
С	2.88408100	-0.00070100	-0.11921500
С	3.75618200	0.58022000	-1.23339800
Н	4.53560600	-0.13462300	-1.51196300
Н	4.22811800	1.50868200	-0.89867900
Н	3.15259700	0.79330200	-2.12057200
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Н	4.46676000	-0.99574000	0.95488200
Н	2.99244600	-0.71350700	1.90906100
Н	4.09290800	0.63883200	1.54934000
С	-1.24769900	2.77098000	0.67445400
Н	-0.45424600	3.48877500	0.41625300
Н	-1.79151600	3.22570300	1.51284600
С	-2.18140400	2.64338300	-0.44745600
С	-2.96607000	2.61393600	-1.36800800
Н	-3.66129600	2.57176900	-2.17612600
Ν	-2.88256600	-1.52213500	0.62729700
Ν	-2.66044500	-1.95543500	-0.50765800
Ν	-2.64882300	-2.33675400	-1.58513900
0	2.26062800	-1.21066200	-0.58846600
0	1.80218800	0.88205900	0.19275100
0	-0.65559500	1.59419700	1.20038200
0	0.05951300	-1.69554900	0.06898100

#### Atomic co-ordinates for the conformer 3

C 0.89949200 -0.98509200 -0.83249700

Н	0.66671800	-1.34388400	-1.83863800
С	0.65541300	0.49003100	-0.56430200
Н	0.56139500	1.09324100	-1.47592600
С	-0.59044300	0.48858500	0.29720100
Н	-1.47048600	0.46046800	-0.35216200
С	-0.46166300	-0.82649100	1.04097100
Н	0.23051800	-0.69779800	1.88624600
С	-1.73757300	-1.41223200	1.58087300
Н	-1.50909100	-2.37059900	2.06522400
Н	-2.13653800	-0.74490400	2.34875600
С	2.88297300	0.03384500	-0.12374500
С	3.73886600	0.64000100	-1.23699900
Н	4.52967200	-0.05812900	-1.52573100
Н	4.19571200	1.57391800	-0.89658600
Н	3.12711700	0.84968500	-2.11937900
С	3.66992500	-0.24808600	1.14692900
Н	4.48800200	-0.94186900	0.93477900
Н	3.01349500	-0.69338700	1.89795400
Н	4.08833500	0.68097700	1.54435800
С	-1.29391400	2.72549800	0.70801800
Н	-0.51410400	3.45926400	0.45327300
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Н	-3.71276500	2.50042000	-2.13635500
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0	-0.67943400	1.55490000	1.22194500
0	0.08929000	-1.71211700	0.06025000

С	0.90750300	-0.97852100	-0.84027600
Н	0.67583600	-1.33015300	-1.84917900
С	0.64848400	0.49136200	-0.55770800
Н	0.54596600	1.10232300	-1.46319900
С	-0.59534400	0.46867700	0.30642200
Н	-1.47514700	0.44080800	-0.34284900
С	-0.45103000	-0.85187900	1.03752400
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С	-1.71947200	-1.45610400	1.57464200
Н	-1.47622500	-2.39975500	2.07886300
Н	-2.13819400	-0.78360500	2.32854000
С	2.88165900	0.05478100	-0.12662300
С	3.72744100	0.68096600	-1.23649300
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#### 10. Solid state <sup>13</sup>C NMR of 1 (Cross Polarization Magic Angle Spinning experiment)

Comparison of solid state <sup>13</sup>C NMR of **1** taken at 25 °C and 45 °C displayed broadening of peaks at high temperature (plotted at same intensity scale). Slight chemical shift (0.1 ppm) was observed in the  $CH_2$  carbon peaks linked to azide and alkyne suggesting the motion in solid state.



Fig. S6 Solid state <sup>13</sup>C NMR of 1 at 25 °C and 45 °C.

#### 11. Topochemical azide-alkyne cycloaddition of 1

Crystals of **1** (300 mg) were taken in a test tube and kept in a pre-heated oil bath at 45  $^{\circ}$ C and continued heating at the same temperature for 18 days. The progress of the reaction was monitored by withdrawing a small quantity of sample and by recording its <sup>1</sup>H NMR, FT-IR, DSC and PXRD at regular time intervals.

#### 12. Kinetics of the topochemical azide-alkyne cycloaddition reaction of 1

Crystals of **1** were taken in a test-tube and heated in a pre-heated oil bath at a constant temperature of 45 °C. 2-3 mg of the sample was withdrawn at different time intervals and <sup>1</sup>H NMR was recorded in DMSO-*d*<sub>6</sub>. Gradual decrease in the intensity of peaks corresponding to **1** and simultaneous formation of new peaks was observed with increase in time. The <sup>1</sup>H NMR was recorded until no considerable change in the ratio of product and starting material (**1**) peaks was observed. The alkyne proton signal at  $\delta$  3.54 and the triazolyl proton signals from  $\delta$  8.02-8.08 and  $\delta$  7.69-7.79 were integrated and the relative integration was used to calculate the percentage of conversion at each stage by the following equation.

% of conversion =  $\frac{(\text{Area of peaks in the region } \delta \ 8.02 - 8.08 + \text{Area of peaks in the region } \delta \ 7.69 - 7.79) \ X \ 100}{(\text{Area of peaks in the region } \delta \ 8.02 - 8.08 + \text{Area of peaks in the region } \delta \ 7.69 - 7.79 + \text{Area of peak at } \delta \ 3.54)}$ 



**Fig. S7** A) TAAC reaction of **1** at 45 °C monitored by 1H NMR taken at different time intervals. B) Sigmoidal kinetics of TAAC reaction.



#### 13. Time dependent FT-IR and DSC of TAAC reaction

**Fig. S8** A) Time-dependent FT-IR of TAAC reaction of **1** showing gradual decrease in the intensities of azide and alkyne peaks. B) Time-dependent DSC of **1** showing depression in melting point from 78.5 °C to 59 °C and gradual reduction in the intensity of exothermic peak.

A) The solid state AAC reaction was monitored by time-dependent FT-IR spectroscopy by withdrawing small amount of sample during the progress of reaction. FT-IR spectrum of **1** displayed sharp peaks at 3252, 2128 and 2107 cm<sup>-1</sup> corresponding to alkyne C-H, C=C and azide N=N=N stretching frequencies respectively. When the crystals were heated at 45 °C, the intensities of these signals in FT-IR reduced with time as anticipated. Even when the reaction was complete, the sample showed these signals in low intensity indicating the formation of linear oligomers.

B) DSC profile of the crystals of **1** from 25 °C to 250 °C at a heating rate of 5 °C/min showed a sharp endothermic transition centered at 78.5 °C due to the melting of **1** and a broad exothermic peak from 95 °C to 160 °C due to the uncontrolled Huisgen reaction in the melt. DSC profiles of samples of **1** kept at 45 °C for different durations were recorded at the same heating rate as before. With the increase in the duration of preheating (at 45 °C) time, the melting point shifted from 78.5 °C to 59 °C. Also, with time the intensity of exothermic peak due to uncontrolled reaction reduced gradually and after 18 days no exothermic transition was observed. These observations suggest that with the progress of time, the amount of reacting motifs left for uncontrolled reaction diminished. This is due to their time dependent consumption in their topochemical reaction.

#### 14. Solution state azide-alkyne cycloaddition of 1

Compound **1** (300 mg, 1.18 mmol) was dissolved in toluene (10 mL) and heated at 120 °C. After 3 h, TLC showed complete consumption of the starting material. The toluene was evaporated under reduced pressure to afford compound **2** (282 mg, 94%) as the sole product. Compound **1** dissolved in toluene reacts to give compound **2** even

at room temperature within 3-4 days. This is due to the flexibility of both  $CH_2-N_3$  group and O-CH<sub>2</sub>CCH groups, which can rotate and adopt a conformation suitable for intramolecular reaction in an isotropic medium (solution).



Fig. S9 FT-IR spectrum of the crude reaction mass obtained by solution-state AAC showing the absence of azide signal.

#### 15. Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) of 1

To a solution of **1** (250 mg, 0.98 mmol) in anhydrous THF (50 mL), CuI (188 mg, 0.98 mmol) and DIPEA (3.44 mL, 19.74 mmol) were added and stirred at room temperature for overnight. TLC showed complete consumption of the starting material. Then the reaction mixture was passed through celite and the solvent was evaporated under reduced pressure. The residue obtained was purified through column chromatography (acetone/DCM, 3:7 v/v) to afford cyclic dimer (**3**, 185 mg, 74%) and cyclic trimer (**4**, 30 mg, 12%) as white solids. These compounds decomposed before melting when tried to find melting point.



Fig. S10 <sup>1</sup>H NMR spectrum of the crude reaction mixture obtained by CuAAC of 1.



**Fig. S11** A) MALDI spectrum of the crude reaction mass obtained by CuAAC of **1** showing the presence of cyclic dimer to cyclic tetramer. B) FTIR of the crude reaction mixture obtained by CuAAC of **1** showing the absence of azide signal.

**Cyclic dimer (3)**:  $[\alpha]_D^{25} = 104.5$  (c 0.2, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr, cm<sup>-1</sup>) 3128, 2987, 1643,1381, 1219, 1103, 1028; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.88 (s, 1H), 5.81 (d, *J* = 3.6 Hz, 1H, H-1), 4.85 (t, *J* = 3.7 Hz, 1H, H-2), 4.7 (dd, *J* = 3.1 Hz, 13.9 Hz, 1H, H-5A), 4.63 (d, *J* = 11.2 Hz, 1H, -OCH<sub>2</sub>), 4.5 (dd, *J* = 8.1 Hz, 14 Hz, 1H, H-5B), 4.4 (d, *J* = 11.2 Hz, 1H, -OCH<sub>2</sub>), 4.1 (m, 1H, H-4), 3.7 (dd, *J* = 4.1 Hz, 8.7 Hz, 1H, H-3), 1.46 (s, 3H, CH<sub>3</sub>), 1.32 (s, 3H, CH<sub>3</sub>). 13 C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  143.1, 126.1, 112.7, 104.1 (C-1), 81.1 (C-3), 77.1 (C-2), 75.7 (C-4), 62.4, 50.7 (C-5), 27.0, 26.9.

**Cyclic trimer (4)**:  $[\alpha]_D^{25} = 130 (c \ 0.1, CH_2Cl_2)$ ; IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) 2929, 1460, 1379, 1220, 1099, 1037; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (s, 1H), 5.59 (d, *J* = 3.25 Hz, 1H, H-1), 4.87 (d, *J* = 13.20 Hz, 1H, -OCH<sub>2</sub>), 4.62 (dd, *J* = 2.20 Hz, 14.95 Hz, 1H, H-5A), 4.57-4.50 (m, 2H, H-5B & -OCH<sub>2</sub>), 4.32 (t, *J* = 3.35, 2H, H-2 & H-4), 3.20 (dd, *J* = 4.05 Hz, 8.95 Hz, 1H, H-3), 1.53 (s, 3H, CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.7, 124.2, 112.4, 103.0 (C-1), 76.1 (C-2 or C-4), 75.3 (C-3), 75.0 (C-2 or C-4), 62.2, 48.0 (C-5), 25.8, 25.5.

We observed that the copper (I) catalyzed click reaction carried out at higher concentration (100 mM) also resulted in the formation of cyclic oligomers.



Fig. S12 FTIR of the crude reaction mixture obtained by CuAAC of 1 (100 mM) showing the absence of azide signal.

MALDI-TOF of compounds 3 and 4



Fig. S13 MALDI spectra of A) cyclic dimer (3) and B) cyclic trimer (4).

#### 16. Crystallization of compound 3

Compound **1** (100 mg) was crystallized from a mixture of DCM and n-hexane (3:1 v/v). Colourless rectangular like crystals were resulted from the solution on slow evaporation of the solvent. Using X-ray diffractometer, the crystal structure of **3** was solved.



Fig. S14 ORTEP diagram of cyclic dimer 3 at 30% probability.

#### 17. Crystal data of compound 3

CCDC No. 1574974. Molecular formula =  $C_{22}H_{30.63}N_6O_{8.32}$ , Formula weight = 512.20, colorless rectangular crystals, 0.25 x 0.15 x 0.15 mm<sup>3</sup>, Orthorhombic, space group P2(1)2(1)2(1), a = 5.4430(2), b = 21.1577(6), c = 21.2367(6) Å, V = 2445.65(13) Å<sup>3</sup>, Z = 4, T = 296(2) K, 2 $\theta_{max}$  = 50.00°,  $D_{calc}$  (g cm<sup>-3</sup>) = 1.391, F(000) = 1085,  $\mu$  (mm<sup>-1</sup>) = 0.108, 4302 reflections measured, 3646 unique reflections (R<sub>int</sub> = 0.0706), multi-scan absorption correction, T<sub>min</sub> = 0.9738, T<sub>max</sub> = 0.9842, number of parameters = 329, number of restraints = 1, GoF = 1.056, R1 = 0.0370, wR<sub>2</sub> = 0.0900, R indices based on 4302 reflections with I >2s(I),  $\Delta\rho_{max}$  = 0.178,  $\Delta\rho_{min}$  = -0.164 (eÅ<sup>-3</sup>), absolute structure Flack = -0.4(5).

#### 18. Comparison of DSC of compound 2 and sample obtained after TAAC reaction

It is interesting to note that DSC profile of the fully reacted (compound **1** heated at  $45^{\circ}$ C for 18 days) sample did not show the melting endotherm for the compound **2** (m.p. 188 °C) even though it is the major product (16%) of the reaction. The complex heterogeneity formed in a crystal-like environment (rigid and restricted molecular motion) due to tripartite competition in TAAC reactionin would not permit nucleation and growth of the product phase. This is the reason why the DSC profile of fully reacted sample did not show any melting endotherm for the otherwise crystalline intramolecular adduct **2**.



Fig. S15 DSC of sample obtained after TAAC reaction of 1 and intramolecular cycloadduct 2.

#### 19. Spectral data



### <sup>1</sup>H NMR of **10** (zoom)



### <sup>1</sup>H NMR of **1**



1.09

1:03

1.05







<sup>1</sup>H NMR of **2** 



<sup>1</sup>H NMR of 2 (zoom)





DEPT-135 of **2** 



## <sup>13</sup>C NMR of **2**







<sup>1</sup>H NMR of **3** 







































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