Triazole-oligomers by 1,3-dipolar cycloaddition

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Abstract
A variety of triazole-oligomers have been prepared under microwave and conventional conditions from novel alkynes and azides.

Keywords: 1,3-Dipolar cycloaddition, microwaves, alkynes, azides, triazoles

Introduction

Triazole-oligomers prepared by 1,3-dipolar cycloadditions of azides to alkynes[1] are new binder cure systems in the initial stage of development for high-energy explosive and propellant formulations.[2] Structural features such as the length of chains between the triazole cross-links significantly impact the mechanical properties of the rubber matrices produced by the triazole-cured polymers. Previous reports on the synthesis of oligomers with 1,2,3-triazole subunits include 1,3-dipolar cycloadditions of dialkynes and diazides,[3a,b] dialkynes and monoazides,[3c] diazides and monoalkynes,[3d] or tris-alkynes and diazides.[3e]

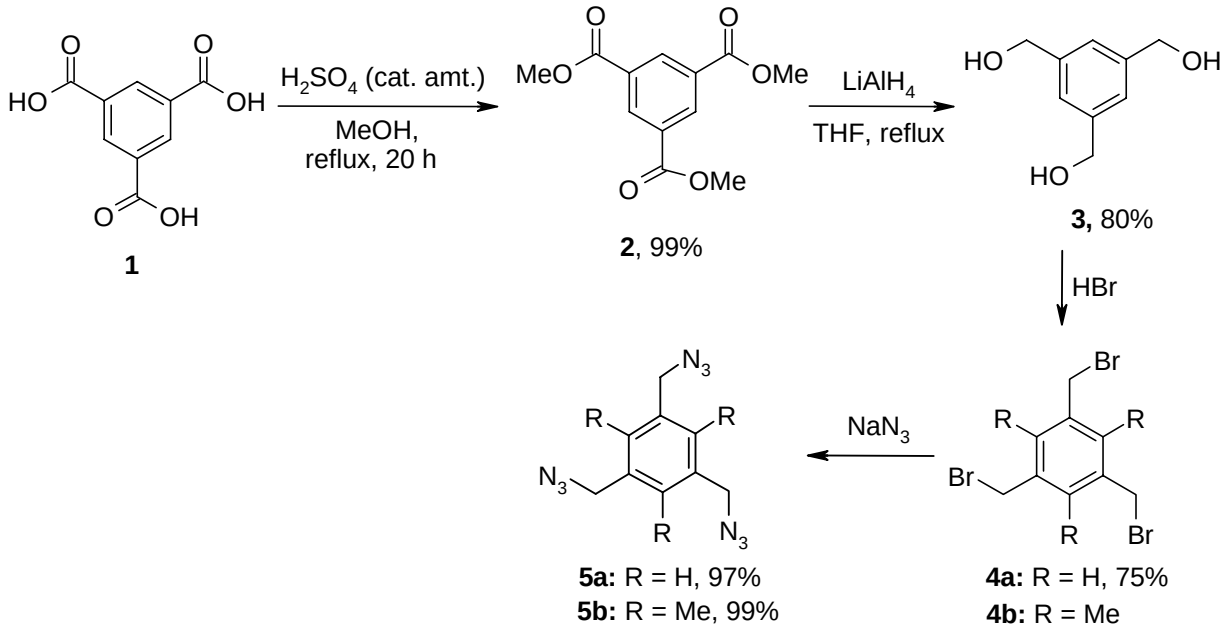
The kinetics of 1,3-dipolar cycloaddition can be controlled by selecting the appropriate functionalities on the alkyne and the azide; reactions are faster with electron-withdrawing substituents on the alkyne while their presence on the azide has the opposite effect.[1e] Previously utilized activating substituents on the alkyne mainly include alkoxycarbonyl,[4] carboxyl, acyl, cyano, aryl, haloalkyl, trimethylsilyl, phenylsulfonyl or phosphonate.[5]

We have studied 1,3-dipolar cycloadditions between a variety of organic azides and alkynes to develop strategies for low-temperature (~ 50 ^{o}C) synthesis of oligo-triazoles as binder

linkages for new high-energy explosive and propellant ingredients possessing the best combination of strength, energy and insensitivity. The azides studied in the present work include mono-, bi-, tri-, tetra- and hexa- azides. Alkynes used in this study include ethyl propiolate, di-propiolates from polyethylene glycols, amido- substituted di-alkynes and trimethylsilyl substituted acetylene core. The 1,3-dipolar cycloadditions between these azides and alkynes were performed under thermal conditions or microwave irradiation.

Results and Discussion

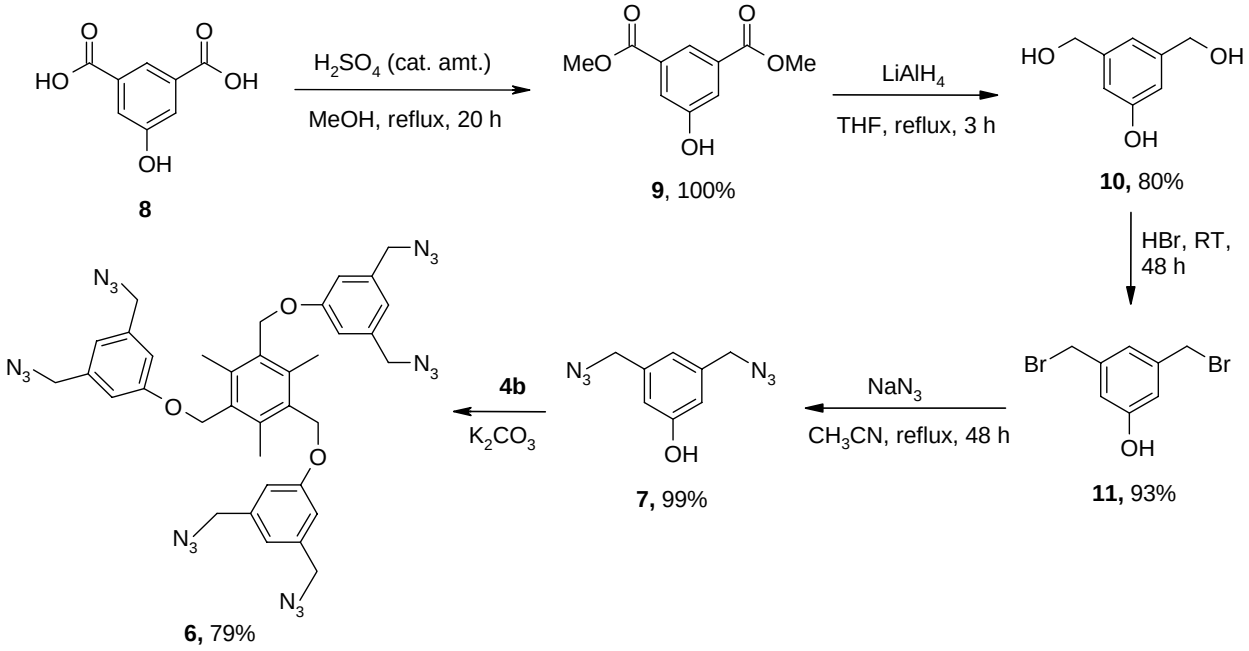
Preparation of tri- and hexa-azide cores. Treatment of 1,3,5-benzenetricarboxylic acid (**1**) with a catalytic amount of H_2SO_4 in refluxing methanol gave trimethyl 1,3,5-benzenetricarboxylate (**2**) in 99% yield. Reduction of **2** with $LiAlH_4$ gave 1,3,5-tris(hydroxymethyl)benzene (**3**) in 80% yield.[6] Further treatment of **3** with HBr gave the tri-bromide **4a** in 75% yield. The desired tri-azide core **5a** was obtained in 97% yield by the reaction of **4a** with NaN_3. Similar reaction of the commercially available tri-bromide **4b** with NaN_3 gave the tri-azide core **5b** in 99% yield (Scheme 1).



Scheme 1

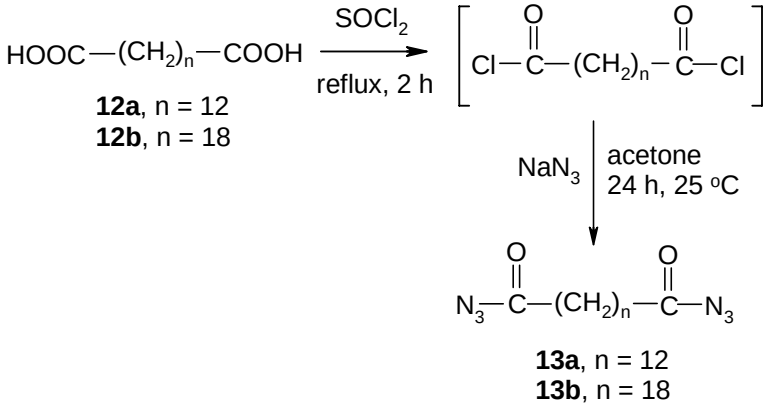
The hexa-azide core **6** was prepared by the reaction of **4b** and 3,5-bis(azidomethyl)phenol **7**, which was synthesized in four steps from commercially available 5-hydroxyisophthalic acid (**8**). Thus, methyl ester derivative **9** was obtained quantitatively by refluxing **8** in methanol in the presence of a catalytic amount of H_2SO_4.[6] Treatment of **9** with $LiAlH_4$ provided 3,5-

bishydroxymethylphenol (**10**) in 80% yield. Subsequent hydroxyl to bromine conversion using HBr gave the bis-bromo derivative **11** in 93% yield; **11** was completely converted into 3,5-bis(azidomethyl)phenol (**7**) using NaN_3. The reaction of tribromide **4b** (1 equiv) and bis-azide **7** (3 equiv) in the presence of K_2CO_3 furnished the desired hexa-azide core **6** in 79% yield (Scheme 2).



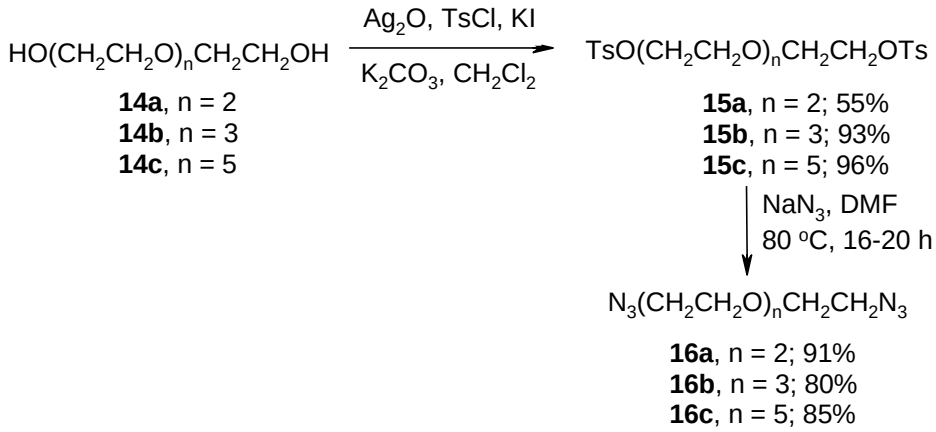
Scheme 2

Preparation of di-carboxyl azides. Reaction of dicarboxylic acid **12a,b** with thionyl chloride and subsequent treatment of the acid chloride intermediate with sodium azide gave the dicarboxyl azides **13a,b** following the literature method (Scheme 3).[7] However, products **13a,b** showed spontaneous decomposition when stored at room temperature; successful dipolar cycloaddition reactions could not be carried out.



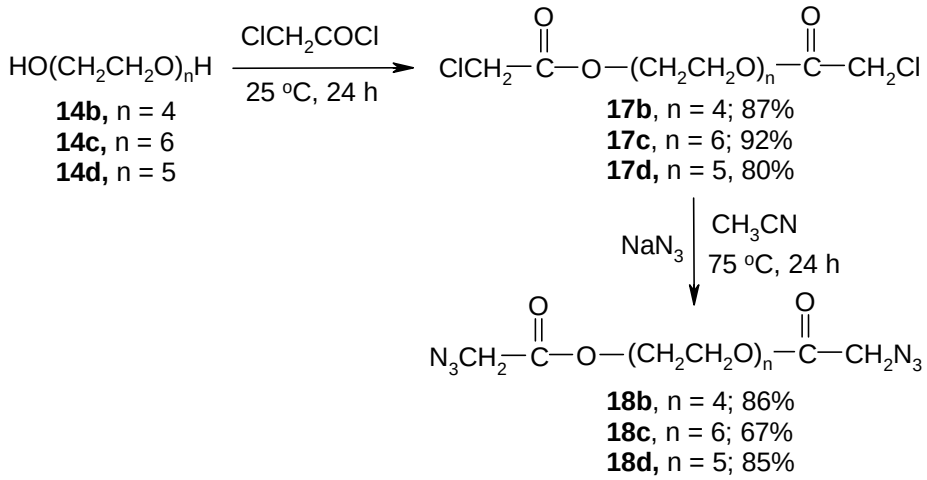
Scheme 3

Preparation of oligoethyleneoxide di-azides. Reaction of oligoethylene glycol **14a** with TsCl in the presence of Ag_2O, KI and K_2CO_3 gave the corresponding tosylate **15a** in 55% yield which was converted to the di-azide **16a** using NaN_3 in 91% yield.[8] Similarly, starting from the oligoethyleneoxide glycol **14b** and **14c,** we prepared the tosylate **15b** and **15c** in 93 and 96% yield respectively which on reaction with NaN_3 gave the corresponding oligoethyleneoxide di-azide **16b** and **16c** in 80 and 85% yield (Scheme 4).



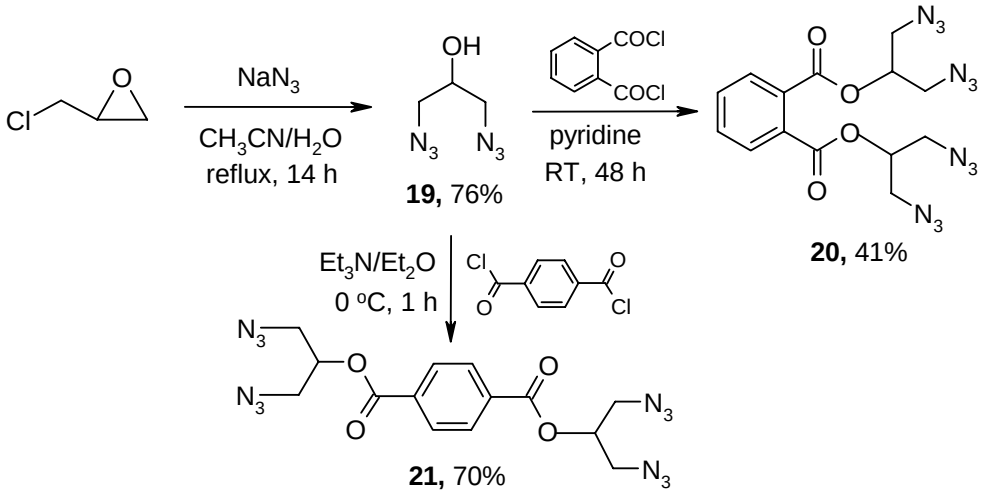
Scheme 4

Preparation of oligoethyleneoxide di-carboxylmethyl azide. The reaction of oligoethylene glycol **14c** with chloroacetyl chloride[9] gave the corresponding di-carboxylmethyl chloride **17c** in 92% yield. Further reaction of **17c** with sodium azide gave the desired di-carboxylmethyl azide **18c** in 67% yield. Similarly, from oligoethylene glycols **14b** and **14d,** di-carboxylmethyl azides **18b** and **18d** were prepared via chlorides **17b** and **17d**, respectively (Scheme 5).



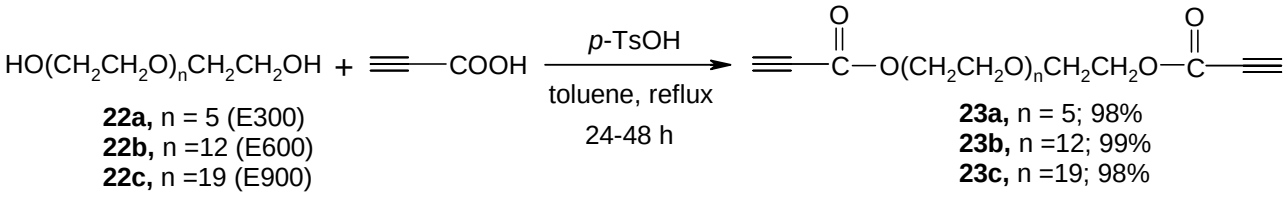
Scheme 5

Preparation of ortho- and para-substituted diazidopropanol derivatives. 1,3-Diazido-2-propanol (**19**) was obtained in 76% yield by the reaction of epichlorohydrin and NaN_3 in refluxing CH_3CN/H_2O and was characterized by ^1H and ^{13}C NMR spectroscopy. Reaction of **19** with phthaloyl dichloride in pyridine gave the corresponding ortho-substituted diazidopropanol derivative **20** in 41% yield. Similar reaction of **19** with terephthaloyl dichloride gave the para-substituted diazidopropanol derivative **21** in 70% yield (Scheme 6).



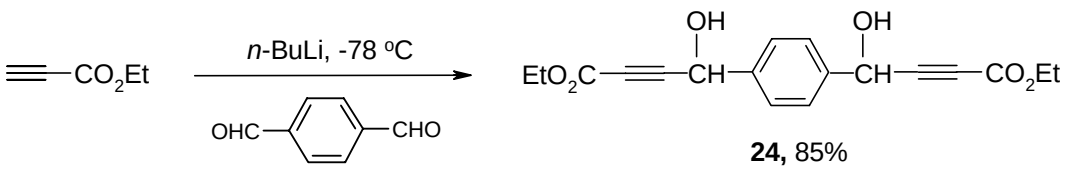
Scheme 6

Preparation of long-chain di-alkynes. The polyethylene glycol (E300) **22a** was reacted with propiolic acid in the presence of a catalytic amount of *p*-TsOH in refluxing toluene to give the di-alkyne **23a** in 98% yield.[10] Similar reactions of polyethylene glycols (E600) **22b** and (E900) **22c** with propiolic acid gave the corresponding di-alkynes **23b** and **23c** in 99 and 98% yields, respectively (Scheme 7). E300, E600 and E900 are mixtures of polyethylene glycols, and their structures are most probable representatives based on average molecular weight.



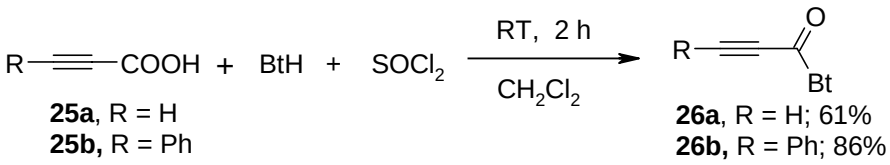
Scheme 7

Preparation of hydroxyl substituted di-acetylene. Lithiation of ethyl propiolate with *n*-BuLi at –78 °C and reaction of the carbanion with terephthalaldehyde gave the hydroxyl substituted di-alkyne **24** in 85% yield (Scheme 8).



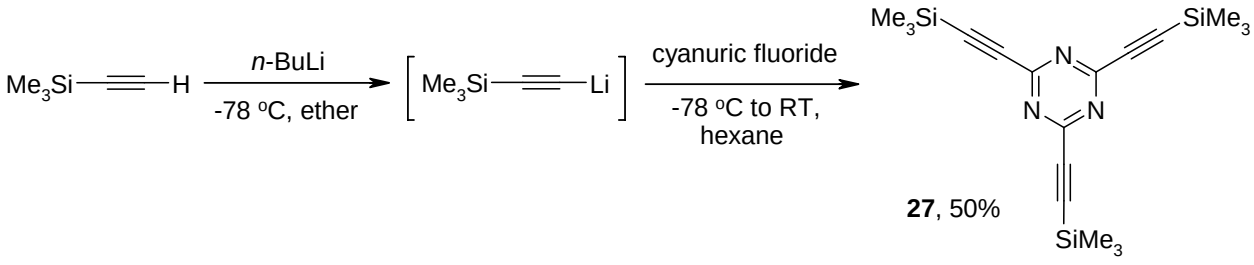
Scheme 8

Preparation of benzotriazolylcarbonyl acetylenes. Reactions of propiolic acid **25a** or phenylpropiolic acid **25b** with benzotriazole and thionyl chloride according to a recently developed procedure[11] gave the corresponding benzotriazolylcarbonyl acetylenes **26a** and **26b** in 61% and 86% yields, respectively (Scheme 9).



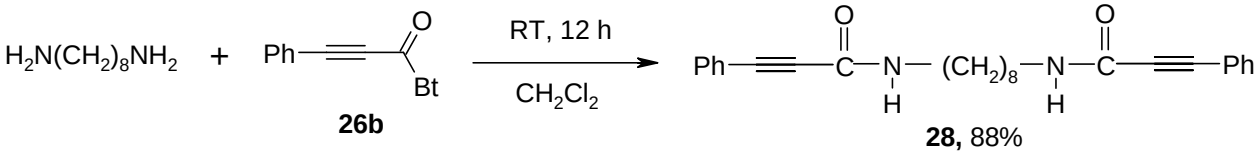
Scheme 9

Preparation of activated acetylene core. Trimethylsilyl- and triazene-substituted activated alkynes should undergo 1,3-dipolar cycloadditions with azides at low temperatures. We prepared the tris-alkyne **27** from trimethylsilyl acetylene and cyanuric fluoride according to a literature procedure.[12] Thus, treatment of trimethylsilyl acetylene (3 equiv) with *n*-BuLi (3 equiv) at –78 °C in diethyl ether and subsequent reaction with cyanuric fluoride (1 equiv) in hexane gave the desired alkyne **27** in 50% yield (Scheme 10).



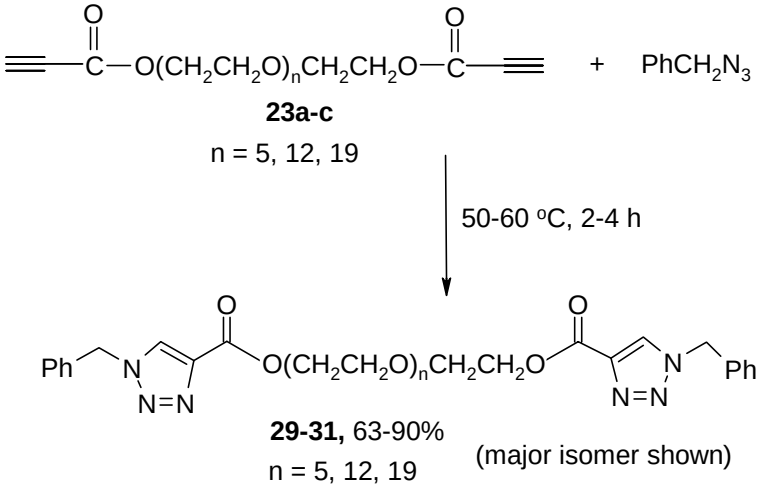
Scheme 10

Preparation of amido-substituted di-alkyne. Reaction of *N*-acylbenzotriazole derivative **26b** with 1,8-diaminooctane gave the desired amido-substituted di-alkyne **28** in 88% yield as a white solid (Scheme 11).



Scheme 11

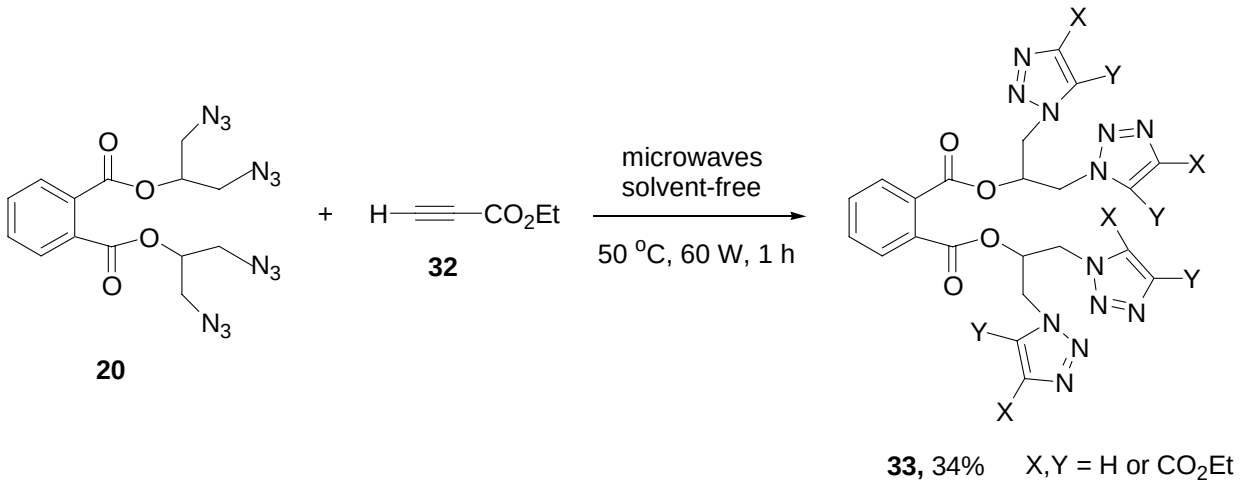
Bistriazoles from long chain di-alkynes and benzyl azide. The mixture of di-alkyne **23a** (1 equiv) and benzyl azide (2.5 equiv) was irradiated under microwaves at 120 W power and at 55 ^{o}C reaction temperature under solvent-free conditions for 1 h. The ^{1}H NMR spectrum of the crude reaction mixture showed signals corresponding to the triazole proton at 8.01 and 8.17 ppm and those from benzylic protons on the N atom of the triazole ring at 5.58 and 5.91 ppm. Further irradiation of the same reaction mixture at 120 W and 85 ^{o}C for 1 h resulted in complete reaction as indicated by disappearance of the acetylenic proton signal at 2.95-2.98 ppm. We also tried the above reaction under thermal conditions. Thus, 1 equiv of diacetylene **23a** was mixed with 2.5 equiv of benzyl azide without any solvent and the resulting mixture was stirred for 2 h at 50-60 ^{o}C (oil bath temperature). The ^{1}H NMR spectrum of the reaction mixture indicated complete reaction, since the signals from acetylene **23a** had disappeared to be replaced by the signals from triazole protons (8.01 and 8.17 ppm). The bistriazole **29** was formed in quantitative yield as a mixture of regioisomers in 1:3 ratio. Similar reaction of dialkynes **23b** and **23c** with benzyl azide gave the corresponding bis-triazoles **30** and **31** (Scheme 12).



Scheme 12

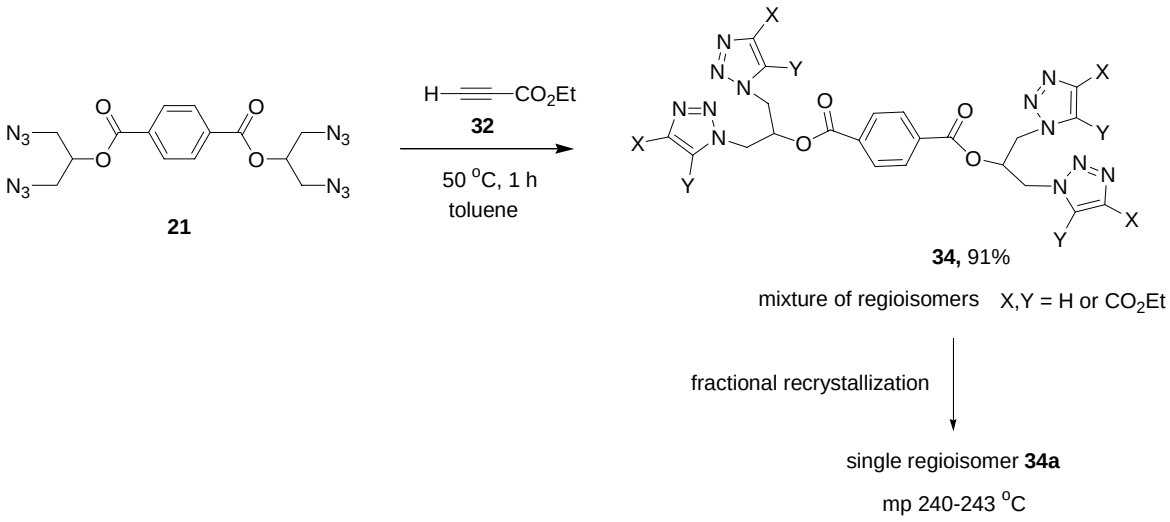
Triazoles from ortho- and para-substituted diazidopropanol derivatives. Reaction of ortho-substituted diazidopropanol derivative **20** with ethyl propiolate (**32**) under solvent-free microwave irradiation at 50 ^{o}C and 60 W for 1 h gave a viscous material. TLC showed the presence of small amounts of starting materials. After repeated purification by column

chromatography on silica-gel, the desired triazole **33** was obtained in 34% yield with 80% purity as indicated by ^{1}H NMR (Scheme 13).



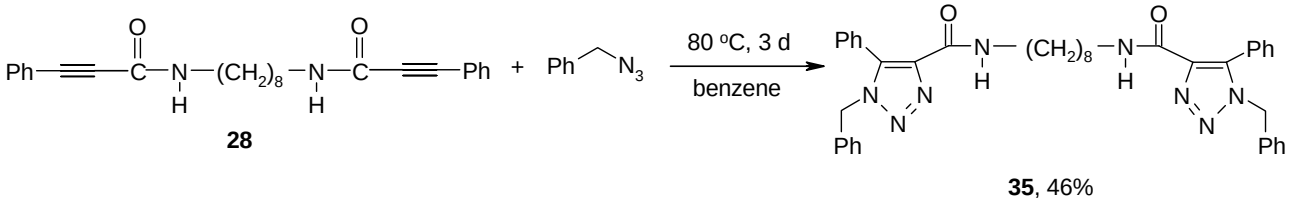
Scheme 13

Reaction of para-substituted diazidopropanol derivative **21** with ethyl propiolate (**32**) in toluene at 50 °C resulted in the formation of triazole **34** as a semi-solid that was recrystallised to give a white powder containing a mixture of six isomers (as indicated by TLC) in 91% yield. After fractional recrystallization of this mixture, we isolated a single regioisomer **34a** in 46% yield (Scheme 14).



Scheme 14

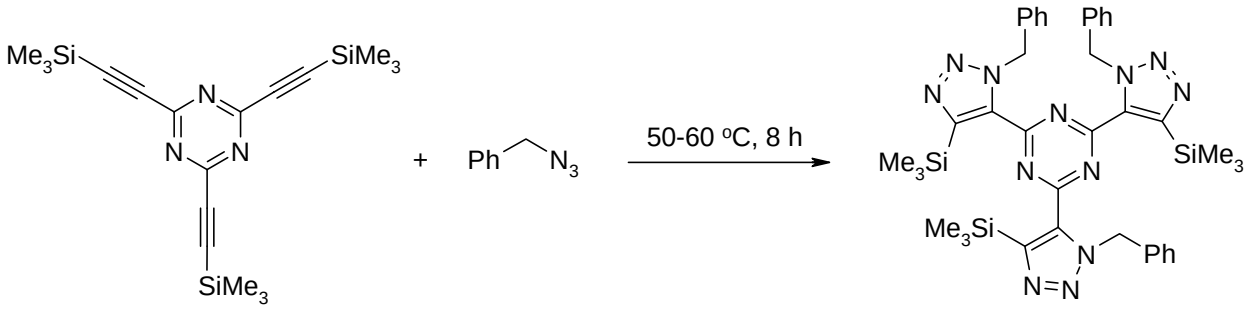
Preparation of triazoles from amido-substituted dialkyne. Reaction of amido-substituted dialkyne **28** with benzyl azide in refluxing benzene for 3 days gave bis-triazole **35** as the major isomer in 46% yield (Scheme 15).



28 **35**, 46%

Scheme 15

Triazole from activated acetylene core. We prepared tris-triazole **36** by the reaction of activated acetylene core **27** and benzyl azide at 50-60 °C for 8 h. The crude material from the 1,3-dipolar cycloaddition reaction contained a mixture of regioisomeric triazoles, the major isomer **36** was separated in 45 % yield by recrystallization (Scheme 16).



27 **36,** 45%

Scheme 16

The structure of **36** was unambiguously established by single crystal X-ray crystallography (Figure 1), which confirmed the overall structure and the regiochemistry of the cycloaddition. In the solid state the molecule exists in a relatively compact conformation. The planes of the triazole rings are twisted relative to the plane of the central triazine ring at angles between 24.3 and 48.3 °, with two of the benzyl substituents above the plane of the central ring and the other on the opposite side.

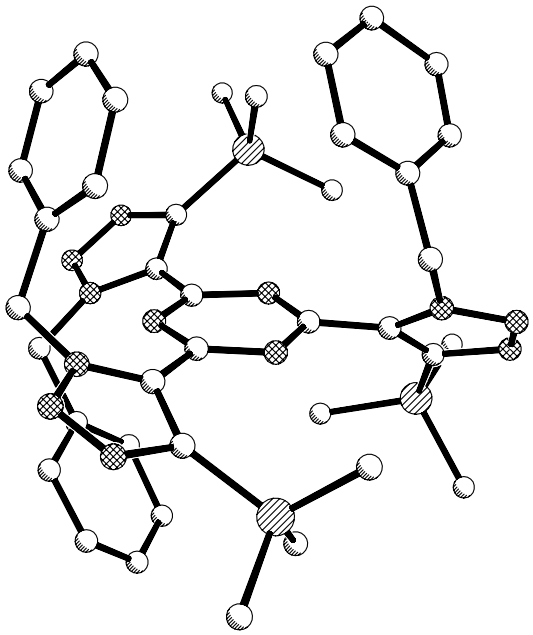


Figure 1. Perspective view of the X-ray crystal structure of **36**. Hydrogen atoms have been omitted for clarity.

1,3-Dipolar cycloaddition reactions can be carried out employing other azides and alkynes substituted with carboxyl, acyl, cyano, arly, haloalkyl, phenylsulfonyl or phosphonate groups.

Conclusions

Various azides and alkyne compounds were prepared and their 1,3-dipolar cycloaddition reactions studied under microwave and conventional conditions. The main aim of the study was to complete the triazole formation at the lowest possible temperature. It has been found that the cycloaddition reactions of azides with alkynes substituted with electron-withdrawing groups are fast and take place at low temperatures (~ 50 ^{o}C), under microwave or conventional conditions.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with tetramethylsilane (TMS) as an internal standard. Solvents were distilled by standard methods. Reagents obtained commercially were used without further purification.

1,3,5-Tris(bromomethyl)benzene (4a). To a solution of 1,3,5-tris(hydroxymethyl)benzene **3** (1.68 g, 10 mmol) in acetic acid (10 mL), HBr 30% in acetic acid (13.5 g, 50 mmol) was added. The mixture was stirred at room temperature for 48 h and extracted with ether (3 × 60 mL). The combined ether extracts were washed with water, 5% Na_2CO_3 and brine and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent gave **4a** (75%) as a brownish powder; mp 93–94 °C (lit.[13] mp 94–95 °C); ^{1}H NMR ($CDCl_3$) δ 4.45 (s, 6H), 7.35 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 32.2, 129.5, 139.0.

General procedure for triazides (5). A mixture of tris-bromomethyl compound **4** (1 mmol) and sodium azide (0.39 g, 6 mmol) in DMF (10 mL) was stirred at 60 °C for 24 h. The reaction mixture was poured into water, and extracted with ether (3 × 30 mL). The combined organic extracts were washed with water and brine and dried over anhydrous $MgSO_4$. After filtration and evaporation of solvent, the corresponding tris-azidomethyl compounds **5a, b** were obtained.

1,3,5-Tris(azidomethyl)benzene (5a). (97%)[14a] Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 6H), 7.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 54.3, 127.5, 137.0. Anal. Calcd for $C_9H_9N_9$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.85; H, 3.79; N, 51.43.

1,3,5-Tris(azidomethyl)-2,4,6-trimethyl-benzene (5b). (99%) White needles (from hexane); mp 64–65 °C, previously reported[14b] without mp; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 9H), 4.49 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 16.4, 48.9, 130.8, 138.1. Anal. Calcd for $C_{12}H_{15}N_9$: C, 50.52; H, 5.30; N, 44.18. Found: C, 50.86; H, 5.26; N, 43.95.

1,3,5-Tris{[3,5-bis(azidomethyl)phenoxy]methyl}-2,4,6-trimethylbenzene (6). A mixture of 3,5-bis(azidomethyl)phenol **7** (0.27g, 1.32 mmol) and 1,3,5-trisbromomethyl-2,4,6-trimethyl-benzene **4b** (0.176 g, 0.44 mmol) in DMF (5 mL) was stirred with K_2CO_3 (0.182 g, 1.32 mmol) for 2 days. The reaction mixture was poured into water and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts was washed with water and brine and dried over anhydrous $MgSO_4$. Filtration and evaporation of solvents followed by recrystallization (from hexane/chloroform), gave **6** (0.26 g, 79%) as white microcrystals, mp 129–131 °C, previously reported[14b] without mp; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 9H), 4.37 (s, 12H), 5.14 (s, 6H), 6.90 (s, 3H), 6.95 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 16.0, 54.5, 65.1, 114.0, 120.1, 131.5, 137.7, 139.5, 159.8. Anal. Calcd for $C_{36}H_{36}N_{18}O_3$: C, 56.24; H, 4.72; N, 32.79 Found: C, 56.06; H, 4.65; N, 31.95.

3,5-Bis(azidomethyl)phenol (7). 3,5-Bis(bromomethyl)phenol **11** (0.28 g, 1 mmol) and sodium azide (0.26 g, 4 mmol) in acetonitrile (10 mL) were stirred at 70 °C for 48 h. The mixture was extracted with ethyl acetate, the organic extracts was washed with water, and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent gave **7** (99%) as an oil; ^{1}H NMR ($CDCl_3$) δ 4.30 (s, 4H), 5.03 (br s, 1H), 6.77 (s, 2H), 6.83 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 54.2, 114.9, 119.9, 137.8, 156.3. Anal. Calcd for $C_8H_8N_6O$: C, 47.06; H, 3.95; N, 41.16 Found: C, 47.39; H, 3.93; N, 40.93. Previously reported[14b] without characterization.

Dimethyl 5-hydroxyisophthalate (9). (100%) Colorless needles (from hexane/ethyl acetate); mp 160–162 °C (lit.[15] mp 165 °C); ^{1}H NMR (DMSO-d_6) δ 3.85 (s, 6H), 7.53–7.55 (m, 2H), 7.92 (s, 1H), 10.32 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 52.4, 120.2, 120.3, 131.4, 157.9, 165.4.

3,5-Bis(hydroxymethyl)phenol (10). A solution of dimethyl 5-hydroxyisophthalate **9** (3.0 g, 14.3 mmol) in dry THF (15 mL) was added slowly to a stirred suspension of $LiAlH_4$ (1.0 g, 26.3 mmol) in THF (50 mL). The reaction was stirred under reflux for 3 h before being left to cool. The mixture was acidified by the addition of 10% H_2SO_4 (20 mL), and THF was removed under vacuum. The resulting solution was extracted with ethyl acetate and the combined extract was dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent gave **10** (80%) as a white solid; mp 73–74 °C (lit.[6] mp 73–74 °C); ^{1}H NMR (DMSO-d_6) δ 4.40 (s, 4H), 4.70 (br s, 1H), 6.60 (s, 2H), 6.68 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 63.1, 111.8, 115.2, 143.9, 157.3.

3,5-Bis(bromomethyl)phenol (11). To a solution of 3,5-bis(hydroxymethyl)phenol **10** (0.26 g, 1.68 mmol) in acetic acid (2 mL), hydrobromic acid 30% in acetic acid (2.0 mL, 7 mmol) was added, and stirred for 48 h. The reaction mixture was diluted with water (10 mL) and stirred for 10 min. It was extracted with ether (3 × 30 mL), the combined ether extract was washed with water (2 × 15 mL), saturated $NaHCO_3$ (2 × 15 mL) and brine (10 mL) and dried over anhydrous $MgSO_4$. After filtration and evaporation of solvent followed by recrystallization (from diethyl ether/hexanes), **11** (0.44 g, 93%) was obtained as colorless needles, mp 82–84 °C, previously reported[16] without mp; ^{1}H NMR ($CDCl_3$) δ 4.41 (s, 4H), 4.85 (br s, 1H), 6.81 (s, 2H), 6.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 32.5, 116.1, 122.1, 139.9, 155.7. Anal. Calcd for $C_8H_8Br_2O$: C, 34.32; H, 2.88. Found: C, 34.41; H, 2.68.

General method for the preparation of ditosylates (15). A mixture of glycol **14** (10 mmol), *p*-toluenesulfonyl chloride (4.19 g, 22 mmol), Ag_2O (6.95 g, 30 mmol), KI (0.66 g, 4 mmol) and K_2CO_3 (3.0 g, 22 mmol) in CH_2Cl_2 (100 mL) was heated under reflux with stirring for 24–48 h. It was cooled to room temperature and the solid was filtered and washed with CH_2Cl_2. The solvent was removed under vacuum to afford the corresponding ditosylates **15a**–**c**.

2-[2-(2-{[(4-Methylphenyl)sulfonyl]oxy}ethoxy)ethoxy]ethyl 4-methylbenzenesulfonate (15a). (55%) Colorless plates (from hexane/CH_2Cl_2); mp 79–80 °C (lit.[17] mp 80–81 °C); ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 6H), 3.53 (s, 4H), 3.64–3.67 (m, 4H), 4.12–4.15 (m, 4H), 7.34 (d, J = 8.4 Hz, 4H), 7.79 (d, J = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 21.9, 68.9, 69.4, 70.9, 128.2, 130.1, 133.1, 145.1.

2-{2-[2-(2-{[(4-Methylphenyl)sulfonyl]oxy}ethoxy)ethoxy]ethoxy}ethyl 4-methylbenzene sulfonate (15b).[17] (93%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 6H), 3.56–3.60 (m, 8H), 3.66–3.69 (m, 4H), 4.14–4.17 (m, 4H), 7.34 (d, J = 7.8 Hz, 4H), 7.79 (d, J = 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 21.8, 68.9, 69.4, 70.7, 70.9, 128.2, 130.0, 133.2, 145.0. Anal. Calcd for $C_{22}H_{30}O_9S_2$: C, 52.57; H, 6.02. Found: C, 52.64; H, 6.18.

17-{[(4-Methylphenyl)sulfonyl]oxy}-3,6,9,12,15-pentaoxaheptadec-1-yl 4-methylbenzenesulfonate (15c).[18] (96%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 6H), 3.58–3.62 (m, 16H), 3.67–3.70 (m, 4H), 4.14–4.17 (m, 4H), 7.34 (d, J = 8.1 Hz, 4H), 7.80 (d, J = 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 21.8, 68.8, 69.4, 70.6, 70.7, 70.7, 70.8, 128.1, 130.0, 133.1, 145.0.

General method for the preparation of diazides (16). A mixture of ditosylate **15** (2 mmol) and NaN_3 (0.52 g, 8 mmol) in DMF (5 mL) was heated at 80–90 °C with stirring for 16–20 h. After cooling to room temperature water (5 mL) was added. The resultant solution was extracted with

ethyl acetate (3 × 20 mL) and the combined extract washed with water (10 mL) and brine (20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated under vacuum to afford the corresponding diazide **16a–c.**

1-Azido-2-[2-(2-azidoethoxy)ethoxy]ethane (16a).[19a] (91%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.38–3.41 (m, 4H), 3.68–3.71 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 50.8, 70.2, 70.8.

1-Azido-2-{2-[2-(2-azidoethoxy)ethoxy]ethoxy}ethane (16b).[19b] (80%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.38–3.41 (m, 4H), 3.67–3.70 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 50.9 (2C), 70.2 (2C), 70.9 (4C).

1,17-Diazido-3,6,9,12,15-pentaoxaheptadecane (16c). (85%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.38–3.41 (m, 4H), 3.67–3.70 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 50.8, 70.2, 70.7, 70.8, 70.8, 70.8. Anal. Calcd for $C_{12}H_{24}N_6O_5$: C, 43.37; H, 7.28; N, 25.29 Found: C, 43.75; H, 7.45; N, 24.96. Previously reported[20] without characterization.

General method for the preparation of di-chloroacetates (17). Chloroacetyl chloride (7.08 mmol) was added very slowly to a solution of glycol **14** (3.54 mmol) and triethylamine (1.0 mL, 7.08 mmol) in dichloromethane (30 mL) at 0 ^{o}C in an ice bath. This mixture was then stirred at room temperature for 2 h before quenching with water (50 mL). The organic layer was separated, washed with aqueous $NaHCO_3$ 5% (2 × 50 mL), brine (30 mL) and water (30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to give the corresponding di-chloroacetate **17b**–**d**.

14-Chloro-13-oxo-3,6,9,12-tetraoxatetradec-1-yl 2-chloroacetate (17b).[21] (87%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 8H), 3.72–3.75 (m, 4H), 4.11 (s, 4H), 4.38–4.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 40.8, 65.1, 68.7, 70.5, 70.6, 167.3. Anal. Calcd for $C_{12}H_{20}Cl_2O_7$: C, 41.51; H, 5.81. Found: C, 41.40; H, 5.84.

20-Chloro-19-oxo-3,6,9,12,15,18-hexaoxaicos-1-yl 2-chloracetate (17c). (92%). Yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 16H), 3.72–3.75 (m, 4H), 4.12 (s, 4H), 4.33–4.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 40.9, 65.2, 68.7, 70.5, 70.6, 167.3. Anal. Calcd for $C_{16}H_{28}Cl_2O_9$: C, 44.15; H, 6.48. Found: C, 43.99; H, 6.50.

17-Chloro-16-oxo-3,6,9,12,15-pentaoxaheptadec-1-yl 2-chloroacetate (17d). (80%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 12H), 3.72–3.75 (m, 4H), 4.11 (s, 4H), 4.33–4.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 40.9, 65.2, 68.8, 70.6, 70.7, 167.4. Anal. Calcd for $C_{14}H_{24}Cl_2O_8$: C, 42.98; H, 6.18. Found: C, 42.80; H, 6.50.

14-Azido-13-oxo-3,6,9,12-tetraoxatetradec-1-yl 2-azidoacetate (18b). (86%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 8H), 3.72–3.75 (m, 4H), 3.92 (s, 4H), 4.35–4.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 50.2, 64.7, 68.7, 70.5, 168.3. Anal. Calcd for $C_{12}H_{20}N_6O_7$: C, 40.00; H, 5.59; N, 23.32. Found: C, 40.34; H, 5.63; N, 23.49.

20-Azido-19-oxo-3,6,9,12,15,18-hexaoxaicos-1-yl 2-azidoacetate (18c). (67%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.64 (s, 16H), 3.73–3.75 (m, 4H), 3.93 (s, 4H), 4.34–4.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 50.2, 64.7, 68.7, 70.5, 70.6, 168.4. Anal. Calcd for $C_{16}H_{28}N_6O_9$: C, 42.85; H, 6.29; N, 18.74. Found: C, 43.24; H, 6.40; N, 18.86.

17-Azido-16-oxo-3,6,9,12,15-pentaoxaheptadec-1-yl 2-azidoacetate (18d). (85%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 12H), 3.72–3.75 (m, 4H), 3.92 (s, 4H), 4.34–4.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 50.0, 64.5, 68.6, 70.3, 70.4, 168.2. HRMS calcd for $C_{14}H_{25}N_6O_8$ $[M + H]^+$ 405.1728, found: 405.1733.

1,3-Diazido-2-propanol (19).[22] To a mixture of epichlorohydrin (2.36 g., 25.6 mmol) in acetonitrile (30 mL) and water (15 mL) was added sodium azide (4 g, 61.5 mmol) and the resulting mixtire was heated under reflux overnight. The reaction mixture was then concentrated under vacuum to remove acetonitrile and the remaining aqueous suspension was extracted with methylene chloride (2 × 15 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under vacuum to obtain **19** (2.79 g, 76%) as a light yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.64 (br s, 1H), 3.36–3.46 (m, 4H), 3.90–3.97 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 54.1, 69.7.

Bis[2-azido-1-(azidomethyl)ethyl] phthalate (20).[23] To an ice cooled solution of **19** (2.4g, 16.9 mmol) in pyridine (20 mL) was added phthaloyl dichloride (2 g, 9.85 mmol) and the resulting mixture was stirred at room temperature for 48 h. The reaction mixture was concentrated on a rotary evaporator to remove most of the pyridine and the residue was dissolved in methylene chloride (100 mL) and washed successively with HCl (100 mL, 5%), saturated $NaHCO_3$ solution (100 mL), dried over anhydrous Na_2SO_4, filtered and the filtrate concentrated in vacuum to afford almost pure diester. Further purification was done by chromatography over silica gel by eluting with 20% ethyl acetate in hexane, to give **20** (2.0 g, 41%) as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.60–3.72 (m, 8H), 5.31 (quintet, J = 5.0 Hz, 2H), 7.60–7.63 (m, 2H), 7.78–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 50.6, 72.0, 128.9, 131.0, 131.8, 166.2. Anal. Calcd for $C_{14}H_{14}N_{12}O_4$: C, 40.58; H, 3.41; N, 40.56. Found: C, 40.80; H, 3.37; N, 40.58.

Bis[2-azido-1-(azidomethyl)ethyl] terephthalate (21). A solution of **19** (3.3 mmol) and Et_3N (0.45 g) in freshly distilled ether was treated dropwise with a solution of terephthaloyl dichloride (0.31 g 1.9 mmol) in freshly distilled ether (10 mL) at 0 °C for 1 h. The solvent was evaporated under reduced pressure, and residue was recrystallized from ethyl acetate to give **21** (0.55 g, 70%) as white crystals; mp 93–95°C; ^{1}H NMR (DMSO-d_6) δ 3.66–3.82 (m, 8H), 5.41–5.46 (m, 2H), 8.20 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 50.7, 72.4, 129.8, 133.3, 164.2. HRMS calcd for $C_{14}H_{14}N_{12}O_4Na$ $[M + Na]^+$ 437.1153, found: 437.1152.

General method for the preparation of dipropiolate (23). A solution of polyethylene glycol, (E 300–900) (16 mmol), propiolic acid (2.25 g, 32 mmol) and *p*-toluenesulfonic acid (0.15 g, 0.8 mmol) in toluene (100 mL) was heated under reflux in a Dean stark apparatus for 24–48 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in chloroform, washed with $NaHCO_3$ (2 × 20 mL), water (30 mL) and brine (20 mL). The chloroform layer was dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent gave the corresponding dipropiolate **23a**–**c**.

19-Oxo-3,6,9,12,15,18-hexaoxa-20-henicosyn-1-yl propiolate (23a). (mixture, see structure in Scheme 7) (98%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.95–2.98 (m, 2H), 3.66 (br s, 16H), 3.72–3.76

(m, Hz, 4H), 4.33–4.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 65.3, 68.6, 70.6, 70.7, 70.8, 74.6, 75.5, 152.8. Anal. Calcd for $C_{18}H_{26}O_9$: C, 55.95; H, 6.80. Found: C, 55.86; H, 6.96.

40-Oxo-3,6,9,12,15,18,21,24,27,30,33,36,39-tridecaoxa-41-dotetracontyn-1-yl propiolate (23b). (mixture, see structure in Scheme 7) (99%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 2H), 3.65–3.66 (m, 44H), 3.72–3.76 (m, 4H), 4.33–4.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 65.3, 68.7, 70.4, 70.6, 70.7, 70.8, 72.7, 74.6, 75.6, 152.8. Anal. Calcd for $C_{32}H_{54}O_{16}$: C, 55.32; H, 7.83. Found: C, 54.99; H, 8.24.

61-Oxo-3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51,54,57,60-eicosaoxa-62-trihexacontyn-1-yl propiolate (23c). (mixture, see structure in Scheme 7) (98%) Yellow semisolid; ^{1}H NMR ($CDCl_3$) δ 3.02 (br s, 2H), 3.64–3.66 (m, 72H), 3.72–3.76 (m, 4H), 4.33–4.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 65.3, 68.6, 70.6, 70.7, 70.8, 74.6, 75.6, 77.4, 152.8. Anal. Calcd for $C_{46}H_{82}O_{23}$: C, 55.08; H, 8.24. Found: C, 54.63; H, 8.50.

Ethyl 4-[4-(4-ethoxy-1-hydroxy-4-oxo-2-butynyl)phenyl]-4-hydroxy-2-butynoate (24). To a solution of ethyl propiolate (2.5 mL, 24 mmol) in THF (100 mL) cooled to –78 °C under nitrogen atmosphere was added *n*-BuLi (15.2 mL, 1.6 M in hexane, 24 mmol) dropwise with stirring. After 45 min., a solution of terephthaldicarboxaldehyde (1.07 g, 8 mmol) in THF (40 mL) was added dropwise. The reaction mixture was stirred for 8 h at -78 °C, then quenched with acetic acid (4 mL). The reaction mixture was allowed to warm to room temperature, water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent gave a residue which was purified by column chromatography (silica gel) with hexane/ethyl acetate (7:3) to afford **24** (2.25 g, 85%) as a yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, *J* = 7.1 Hz, 6H), 3.63 (br s, 2H), 4.24 (q, *J* = 7.1 Hz, 4H), 5.54 (s, 2H), 7.47 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 62.7, 63.9, 78.1, 86.3, 127.3, 139.4, 153.7. Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49. Found: C, 65.05; H, 5.59.

1-(1H-1,2,3-benzotriazol-1-yl)-2-propyn-1-one (26a). (61%) Pale yellow needles (from ethyl acetate/hexane); mp 98 °C (lit.[11] mp 99–100 °C) ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 74.8, 84.1, 114.3, 120.7, 127.2, 130.9, 131.1, 146.5, 149.5.

1-(1*H*-1,2,3-benzotriazol-1-yl)-3-phenyl-2-propyn-1-one (26b). (86%) White needles (from ethyl acetate/hexane); mp 123–124 °C (lit.[11] mp 124–125 °C) ^{1}H NMR ($CDCl_3$) δ 7.44–7.49 (m, 2H), 7.53–7.58 (m, 2H), 7.68–7.73 (m, 1H), 7.79–7.82 (m, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 81.2, 96.0, 114.3, 119.0, 120.4, 126.6, 128.7, 130.6, 130.9, 131.7, 133.6, 146.3, 150.4.

2,4,6-Tris[2-(trimethylsilyl)ethynyl]-1,3,5-triazine (27). Ethynyl(trimethyl)silane (6 mL, 40 mmol) was dissolved in diethyl ether (20 mL) and cooled to –78 °C. Then *n*-BuLi (1.6 M in hexane, 25 mL, 40 mmol) was added dropwise with stirring. After 2 h, all the solvents were removed under vacuum at -10 °C. To the residue, hexane (70 mL) was added at -78 °C. A solution of cyanuric fluoride (1.35 g, 10 mmol) in hexane (10 mL) was added dropwise with stirring. After 24 h, the reaction was allowed to reach to room temperature and stirred for a

further 24 h. The reaction mixture was added to water. The organic layer was separated and the aqueous layer was extracted with hexane (3 × 70 mL). The combined organic layer was dried over anhydrous Na_2SO_4. It was filtered and the solvent was evaporated under vacuum to obtain **27** (1.85 g, 50%) as brown microcrystals; mp 155–157 °C (lit.[12] mp 160 °C); ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 27H); ^{13}C NMR ($CDCl_3$) δ -0.8, 100.0, 102.2, 159.7.

3-Phenyl-*N*-{8-[(3-phenyl-2-propynoyl)amino]octyl}-2-propynamide (28). A solution of 1-(1*H*-1,2,3-benzotriazol-1-yl)-3-phenyl-2-propyn-1-one **26b** (1.24 g, 4.7 mmol) and 1,8-diaminooctane (0.36 g, 2.5 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 12 h. Solvent was removed under reduced pressure and the residue was washed with ether and recrystallized from ethyl acetate to give **28** (0.83 g, 88%) as white crystals; mp 137–138 °C; ^{1}H NMR ($CDCl_3$) δ 1.34–1.41 (m, 8H), 1.55–1.60 (m, 4H), 3.35 (q, *J* = 6.9 Hz, 4H), 5.96 (br s, 2H), 7.32–7.44 (m, 6H), 7.51–7.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.7, 29.0, 29.2, 39.9, 83.1, 84.5, 120.3, 128.5, 130.0, 132.5, 154.0. Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.48; H, 7.13; N, 7.09.

General method for the preparation of bistriazoles (29–31). A mixture of dipropiolate **23** (1 mmol) and benzyl azide (0.33 g, 2.5 mmol) was heated at 50–60 °C for 2–4 h. The reaction mixture was cooled and washed several times with hexane to obtain the corresponding bistriazole compound **(29–31).**

19-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-19-oxo-3,6,9,12,15,18-hexaoxanonadec-1-yl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (29). (mixture of regioisomers in 1:3 ratio, 63%) Colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.59–3.64 (m, 20.8H), 3.74–3.81 (m, 5.2H), 4.41–4.49 (m, 5.2H), 5.58 (s, 4 H), 5.91 (s, 1.2 H), 7.28–7.32 (m, 7.8H), 7.38–7.40 (m, 5.2H), 8.01 (s, 2H), 8.17 (s, 0.6 H); ^{13}C NMR ($CDCl_3$) δ 53.6, 54.6, 64.3, 64.8, 68.8, 69.1, 70.7, 70.7, 70.8, 127.7, 128.2, 128.4, 128.6, 128.9, 129.3, 129.5, 133.9, 135.1, 138.6, 140.3, 158.4, 160.7. Anal. Calcd for $C_{32}H_{40}N_6O_9$: C, 58.89; H, 6.18; N, 12.88. Found: C, 58.75; H, 6.15; N, 13.17.

40-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-40-oxo-3,6,9,12,15,18,21,24,27,30,33,36,39-tridecaoxatetracont-1-yl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (30). (mixture of regioisomers in 1:4 ratio, 90%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.62–3.66 (m, 55H), 3.74–3.82 (m, 5H), 4.42–4.50 (m, 5H), 5.58 (s, 4H), 5.92 (s, 1H), 7.28–7.32 (m, 7.5H), 7.39–7.40 (m, 5H), 8.01 (s, 2H), 8.17 (s, 0.5H); ^{13}C NMR ($CDCl_3$) δ 54.6, 64.3, 69.1, 70.7, 127.7, 128.2, 128.4, 128.9, 129.3, 129.5, 133.9, 140.4, 160.7. Anal. Calcd for $C_{46}H_{68}N_6O_{16}$: C, 57.49; H, 7.13; N, 8.74. Found: C, 57.33; H, 7.53; N, 7.96.

61-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-61-oxo-3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51,54,57,60-eicosaoxahenhexacont-1-yl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (31). (mixture of regioisomers in 1:4 ratio, 79%) Yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.62–3.64 (m, 90H), 3.74–3.82 (m, 5H), 4.42–4.50 (m, 5H), 5.58 (s, 4H), 5.92 (s, 1H), 7.28–7.32 (m, 7.5H), 7.39–7.40 (m, 5H), 8.01 (s, 2H), 8.17 (s, 0.5H); ^{13}C NMR ($CDCl_3$) δ 54.6, 64.3, 68.8, 69.1, 70.7, 127.7, 128.2, 128.4, 128.9, 129.3, 129.5, 133.9, 140.3, 160.7. Anal. Calcd for $C_{60}H_{96}N_6O_{23}$: C, 56.77; H, 7.62; N, 6.62. Found: C, 56.44; H, 7.79; N, 6.35.

Bis{2-[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]-1-{[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]methyl}ethyl}phthalate (33). A mixture of **20** (0.41 g, 1 mmol) and ethyl propiolate **32** (0.43 g, 4.4 mmol) was heated at 50 °C, 60 W for 1 h under microwave irradiation. The mixture was evaporated under reduced pressure to remove ethyl propiolate. The crude product obtained (0.69 g, in 85%), was purified by column chromatography to give bis{2-[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]-1-{[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]methyl}ethyl}phthalate **33** as the major isomer (0.28 g, 34%) as white microcrystals, mp 97–101 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (t, *J* = 6.9 Hz, 12H), 4.39 (q, *J* = 6.9 Hz, 8H), 4.81 (dd, *J* = 14.7, 6.0 Hz, 4H), 4.96 (dd, *J* = 14.7, 4.8 Hz, 4H), 5.92–5.97 (m, 2H), 7.56 (br s, 4H), 8.45 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.2, 50.0, 61.4, 70.8, 129.1, 129.5, 130.2, 132.3, 140.5, 160.5, 165.8. Anal. Calcd for $C_{34}H_{38}N_{12}O_{12}$: C, 50.62; H, 4.75; N, 20.83. Found: C, 50.60; H, 4.73; N, 20.49.

Bis{2-[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]-1-{[4-(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-yl]methyl}ethyl}terephthalate (34a). A mixture of **21** (0.41 g, 1 mmol) and ethyl propiolate **32** (0.43 g, 4.4 mmol) in toluene was heated at 50 °C for 1 h. Ethyl propiolate was removed under vacuum to afford a semi-solid (0.74 g, 91%) that was recrystallised from ethanol to give a white powder containing a mixture of six isomers (as indicated by TLC). After fractional recrystallization of this mixture, a major regioisomer **34a** (0.37 g, 46%) was obtained as white microcrystals (from ethanol), mp 240–243 °C; ^{1}H NMR (DMSO-d_6) δ 1.22–1.29 (m, 12H), 4.27 (q, *J* = 7.2 Hz, 8H), 4.81–4.88 (m, 4H), 5.01–5.06 (m, 4H), 5.89–5.93 (m, 2H), 7.91 (s, 4H), 8.84 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 14.1, 50.2, 60.5, 71.0, 129.5, 130.2, 132.9, 138.9, 160.1, 163.5. Anal. Calcd for $C_{34}H_{38}N_{12}O_{12}$: C, 50.62; H, 4.75; N, 20.83. Found: C, 50.88; H, 4.73; N, 20.43.

1-Benzyl-*N*-(8-{[(1-benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)carbonyl]amino}propyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxamide (35). A mixture of 3-phenyl-*N*-{8-[(3-phenyl-2-propynoyl)amino]octyl}-2-propynamide **28** (0.60 g, 1.5 mmol) and benzyl azide (0.44 g, 3.3 mmol) in benzene (10 mL) was heated at 80–120 °C for 72 h. The solvent was evaporated under reduced pressure, and the residue recrystallized from ethanol to give a mixture of isomers (0.85 g, 85%). The major regioisomer **35** was obtained (0.46 g, 46%) as white microcrystals, mp 165–170 °C; ^{1}H NMR (DMSO-d_6) δ 1.21–1.26 (m, 8H), 1.40–1.45 (m, 4H), 3.19–3.26 (m, 4H), 5.67 (s, 4H), 6.95–6.97(m, 1H), 7.28–7.50 (m, 17H). 7.74–7.76 (m, 3H), 8.93 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 26.4, 28.4, 28.6, 52.1, 126.5, 127.9, 128.1, 128.2, 128.3, 128.6, 128.7, 128.9, 129.9, 135.3, 143.5, 159.3. Anal. Calcd for $C_{40}H_{42}N_8O_2$: C, 72.05; H, 6.35; N, 16.80. Found: C, 71.99; H, 6.20; N, 16.42.

2,4,6-Tris[1-benzyl-4-(trimethylsilyl)-1*H*-1,2,3-triazol-5-yl]-1,3,5-triazine (36). A mixture of **27** (0.37 g, 1 mmol) and benzyl azide (0.7 g, 5 mmol) was heated at 50–60 °C for 8 h. The reaction mixture was washed with hexane several times and the residue was recrystallized from hexane-ethyl acetate mixture to obtain **36** (45%) as light pink microcrystals, mp 236 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 27H), 5.72 (s, 6H), 6.76 (d, *J* = 7.5 Hz, 6H), 7.09 (t, *J* = 7.3 Hz, 6H), 7.18 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ -0.6, 53.2, 127.2, 128.7, 129.2, 135.2, 137.8, 151.8, 166.6. Anal. Calcd for $C_{39}H_{48}N_{12}Si_3$: C, 60.90; H, 6.29; N, 21.85. Found: C, 61.12; H, 6.37; N, 22.11.

X-Ray Crystallography. Data were collected with a Bruker ApexII CCD area detector, using graphite monochromatized MoKα radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz and polarization effects and for absorption.[24] The structure was solved by direct methods using SHELXS[25] and refined on F^2, using all data, by full-matrix least-squares procedures using SHELXTL.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons. Complete crystallographic data, as a CIF file, have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 276346). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 36. $C_{39}H_{48}N_{12}Si_3$, MW 769.16, monoclinic, Cc, colorless prism, 0.30 x 0.21 x 0.19 mm, a = 11.3918(3), b = 20.5533(5), c = 18.2086(5) Å, β = 98.092(1) °, V = 4220.9(2) Å ^{3}, Z = 4, T = -180°C, F(000) = 1632, μ (MoKα) = 0.156 mm^{-1}, D_{calcd} = 1.210 $g.cm^{-3}$, $2\theta_{max}$ 55° (CCD area detector, 100% completeness), $wR(F^2)$ = 0.0728 (all 9698 data), R = 0.0287 (9327 data with $I > 2\sigma I$).

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