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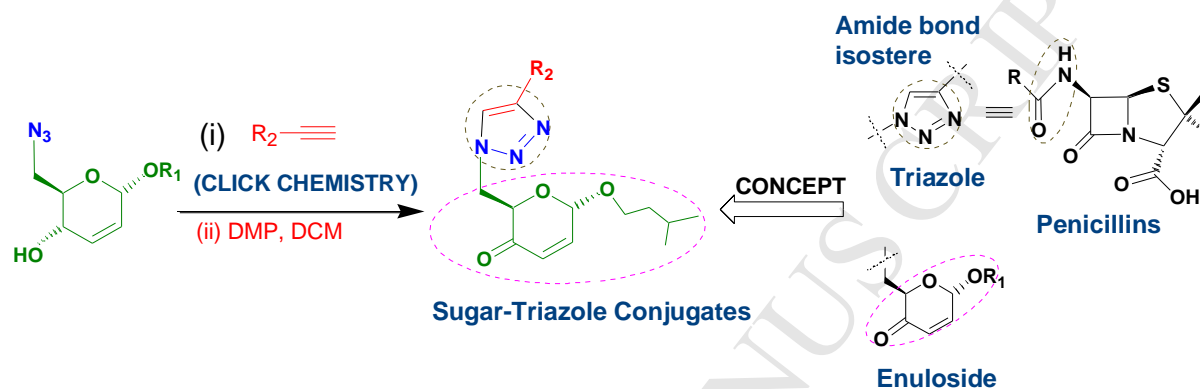
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Graphical Abstract

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Schematic depiction of design and synthesis of novel 6-triazolyl 2,3,6-trideoxy sugars as promising new broad-spectrum antimicrobial agents using click chemistry in key step.

Research Highlights

- Modeled 2,3,6-trideoxy sugar-triazoles as broad-spectrum antibacterial/antifungals
- Novelty of chemistry is in simple reactions leading to desired products
- Some compounds showed antibacterial/antifungal profile comparable to standard drugs
- Compounds' antibacterial activity may be mediated via penicillin binding protein-2
- Compounds showed no toxicity to mammalian cell line L929

Synthesis of 2,3,6-trideoxy sugar triazole hybrids as potential new broad spectrum antimicrobial agents

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ABSTRACT: Here, we describe a molecular hybridization inspired design and synthesis of novel 6-triazolyl 2,3,6-trideoxy sugars as promising new broad-spectrum antimicrobial agents using click chemistry in key step. These compounds showed MIC between 0.39-50 µg/mL against different native and resistant bacteria and fungi with no toxicity. Among them, compound **29** was the most active molecule with MIC 0.78 µg/mL against *Staphylococcus aureus* and *Klebsiella pneumoniae* and 3.12 µg/mL against methicillin- and vancomycin-resistant *S. aureus*. Compound **26** was the most potent anti-fungal candidate with MIC 0.39 µg/mL against *T. mentagrophytes*. Compound **46** was found to be promising with broad-spectrum activity against both bacterial and fungal strains. The bioinformatic studies involving bacteria's protein co-crystals prompted penicillin binding protein-2 as the most likely target of these compounds.

Keywords 2,3,6-Trideoxy Sugars, 1,2,3-Triazole, Molecular Hybridization, Click Chemistry, Antimicrobial Agents, Penicillin binding protein.

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1. Introduction

The discovery of antibiotics revolutionized the treatment of surgical and non-surgical infections [1]. Their overwhelming benefits carried away almost everyone to believe that the infectious diseases would soon be a thing of the past [2]. However the accumulation of drug resistant bacterial strains and slow pace of new antibiotics development turned the situation from one of exhilarating optimism to growing pessimism with a warning of impending return to pre-antibiotic era [2]. The falling numbers of FDA approved antibiotics since 1980 substantiate this scenario [3]. The situation is dim as limited new leads are added to give diversity to the search of potential drugs [4]. Out of the twenty antibiotics approved since 2000, only three - linezolid, daptomycin and retapamulin - originated from new scaffolds [1]. The picture is more grim in case of drugs of Gram-negative bacteria. Adding to the woes, now they are posing more threat than Gram-positive bacteria [5]. Furthermore, recently bedaquiline, a novel diarylquinoline based analogue, is approved by the FDA for multidrug resistant tuberculosis [6].

Fungal infections are another serious health concern. They are mounting pressure on health-care system over the past two decades. The ever increasing immuno-compromised patients and emergence of drug resistance fungal strains has led to this scenario. The existing antifungal drugs e.g., amphotericin-B, flucytosine, azoles etc suffer from severe side effects and/ or resistance [7]. Thus, the situation is warranting discovery of alternative drugs involving new molecules with broad-spectrum activity [8]. Natural products with some desirable activity, pathogens' metabolites and/or their critical functional components often serve as good starting point for exploring new prototypes as drug leads. Nevertheless, merging or joining two or more such skeletons, also referred to as molecular hybridization, offer scope for scaffold hopping and open avenues for discovering novel drug molecules [9-12].

The cell walls of bacteria and fungi respectively carry large proportion of peptidoglycan and glucosamine moieties which share similarity in their sugar units. During the past two decades different sugar like scaffolds which include hex-2-enopyranosid-4-ulose [13-15], 4,6-*O*-butylidene- β -D-glucopyraosyl-3-phthalimido-4-styryl-azetidin-2-one [16] and 9-chloro-8-hydroxy-8,9-deoxyspyrone [17] have been recognized as privileged structure in antibacterial and antifungal drug discovery.

We recently synthesized 2,3-dideoxy hex-2-enopyranosid-4-uloses which showed very mild antibacterial and antifungal activity in *in vitro* screening [18,19]. Furthermore, in medicinal chemistry heterocycles have drawn considerable attention at all times. Here, 1,2,3-triazoles have attracted us due to their facile synthesis through click chemistry [20] and wide biological profiles which include antibacterial and antifungal activities [21-23]. It also mimics the amide features of penicillin antibiotics [24].

Glycoconjugates having a carbohydrate and triazoles moieties are involved in important biological functions, including those on the cell surface, such as the recognition of host compounds, immunological responses, inflammation, cell-cell recognition, bacterial and viral infection, cell communication, metastasis, and many important functions inside cells [25]. Also, many recent reports suggested that different triazole carbohydrate conjugates are endowed with antimicrobial activity [26-30]. In this gamut, we conceptualized the hybridization of our previously reported 2,3-dideoxy hex-2-enopyranosid-4-uloses and 1,2,3-triazole derivatives to result in a new lead to serve as probable broad-spectrum agent with antibacterial and antifungal properties. The synthesis was implemented by choosing the C-6 position of the 2,3,6-trideoxy hex-2-enopyranosid-4-ulose for integration with the 1,2,3-triazole moiety to result in 2,3,6-trideoxy sugar-triazole conjugates [31,32].

2. Chemistry

The synthesis of the target molecules are envisaged as shown in **scheme 1**. The intermediates 2,3-dideoxy hex-2-enopyranosid-4-uloses **1a-c** were synthesized from D-glucal as reported in our earlier work [18]. Tosylation of the hydroxy group at C-6 led to the 6-*O*-tosyl derivative **2a-c**. Luche reduction of **2a-c** furnished their 4-hydroxy derivatives **3a-c** which were then treated with NaN₃ in DMF at 120°C to obtain 6-azido-4-*O*-hydroxy 2,3,6-trideoxy hex-2-enopyranosides **4a-c** in near quantitative yield. The 6-azido derivatives were now reacted with different terminal alkynes using click chemistry to afford 6-triazolo derivatives **5-23**. Oxidation of the 4-hydroxy group of the 6-triazolo derivatives furnished the target sugar triazole conjugates (Table 1).

Insert Scheme 1

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Insert Table 1

3. Biological Evaluation

The synthesized sugar triazole conjugates **10**, **24-42**, **46**, **50**, **51** and **53** were evaluated for *in vitro* antibacterial activity (MIC; the minimum concentration of drug/compound that produced 90% of growth inhibition) by Muller-Hinton broth dilution method against Gram-positive bacteria *Staphylococcus aureus* (Sa) (ATCC 25923) and Gram-negative bacteria

Klebsiella pneumoniae (Kp) (ATCC 27736), *Escherichia coli* (Ec) (ATCC 9637), and *Pseudomonas aeruginosa* (Pa) (ATCC BAA-427). They showed activity in the range of 0.78-50 µg/mL against the mentioned bacterial strains.

4. Result and Discussion

4.1. Antimycobacterial activity

Among the compounds, **29**, **38** and **53** showed MIC 0.78 µg/mL against Sa which make them sixteen-folds more active than standard drugs ampicillin and vancomycin (Table 1). For Kp the MIC of compounds **29** and **46** is 0.78 µg/mL. It makes them as sixteen-, eight- and two-folds more active than ampicillin (also vancomycin), methicillin and gentamycin, respectively (Table 1).

In these analogues structure-activity relationships (SARs) revealed that the antibacterial activity against Sa and Kp improved by increasing the number of carbons in the alkyl chain at C-4 position of triazole ring (compounds **27** to **29**, 3.12 µg/mL to 0.78 µg/mL; Table 1).

In comparison to compound **29**, compound **30** showed eight- and sixty-four-folds less activity against Sa and Kp, respectively, and suggested the unfavorable nature of n-butyl substituent at anomeric position for the activity. Compound **29** with a high CLogP value (4.164) showed better activity indicating that lipophilicity as an important parameter for antibacterial activity, though exceptions exist. Probably, lipophilicity may facilitate the compound's penetration into bacteria's cell wall to result in its rupture and release of cytoplasmic constituents thus leading to its death [4, 33, 34].

The aromatic substituted triazoles **36-41** showed moderate to high activities. Among them compound **38** having a 4-fluorophenyl substituent was found to be most active at MIC 0.78 µg/mL against Sa which may be attributed to the high electro-negativity of fluorine atom. It may modify the electronic nature of the molecule, and thereby influence its absorption,

distribution and metabolism [23]. The compounds' low activity against Gram-negative bacteria may be due to the additional outer membrane of the organism.

Adamantane derivatives have been reported to show antibacterial and antifungal activities [35,36]. Its cage like structure improves the hydrophobicity of a variety of bioactive molecules [37]. In view of this, we synthesized adamantyl moiety containing compound **46**, using **scheme 2A**, which showed activity 1.56µg/mL and 0.78µg/mL against Sa and Kp, respectively. We also probed the role of C-4 keto group towards antibacterial activity of these compounds. Reduction of this group in the most active compound **29** yielded corresponding 4-hydroxy derivative **10**, which was found to be inactive against Gram-positive and Gram-negative bacteria.

The role of triazole ring in the antibacterial activity was explored with the synthesis of two bis-triazolyl compounds **50** and **51** following the **scheme 2B**. They showed activity only against Sa with MIC 25µg/mL and 50µg/mL.

The affect of substituent position of triazole ring on antibacterial activity was scrutinized with 1,5-disubstituted triazole analogue of compound **29** (Compound **53**) synthesized following **scheme 2C** by using ruthenium (II) catalyzed cycloaddition reaction [38]. It showed activity of 0.78µg/mL and 50µg/mL against Sa and Kp, respectively. This suggests that while the position of the substituent on the triazole ring has no effect on the activity of Gram-positive bacteria, it does have a role in case of Gram-negative bacteria.

Insert Scheme 2A, 2B and 2C

All the synthesized compounds were evaluated in vitro against methicillin-resistant *S. aureus* (MRSA) and Vancomycin-resistant *S. aureus* (VRSA) strains. Of there, compounds **29**, **38** and **46** showed MIC 3.12µg/mL against MRSA and VRSA.

4.2. Antifungal activity

The synthesized compounds were also evaluated against fungal strains *Candida albicans* (Ca), *Aspergillus fumigatus* (Af), *Cryptococcus neoformans* (Cn), *Sporothrix schenckii* (Ss) and *Trichophyton mentagrophytes* (Tm) and the results were summarized in Table 2. For Ca, these compounds' MICs values have spread from 6.25µg/mL to 50µg/mL. Among these, compounds **30** and **38** showed highest activity (6.25µg/mL) which was four-folds more active than standard drug miconazole. The MICs of these compounds against Af were between 1.56-50µg/mL. Here, compound **46** showed the best activity (1.56µg/mL). It was five- and eight-folds more active than clotrimazole and miconazole, respectively. In Cn, compound **34** was found to be the most active with an MIC value of 12.5µg/mL. It is equipotent to miconazole. Compound **26** showed highest activity against Ss (3.12µg/mL) and Tm (0.39µg/mL). Its activity against Tm is two- and forty-folds more than miconazole and flucanazole, respectively. Compounds **38** and **46** also showed promising activity (1.56µg/mL) against Tm. The SARs of these compounds revealed that the antifungal activity was enhanced by the introduction of halogen or adamantyl group at C-4 position of the triazole ring.

Insert Table 2

4.3. Molecular modelling

The plausible binding modes and mechanism of action of the synthesized compounds in the bacterial cells were explored using bioinformatics tools and compounds' structural/functional similarities with different ligands of bacteria's protein co-crystals. From these studies, it appeared that penicillin binding protein-2 (PBP-2) as the most likely target of these compounds. Thus in SYBYL X 1.3, PBP-2 of *S. aureus* (PDB code: 4DKI) were used for docking experiments to investigate the binding interactions of these compounds with the protein. In these experiments, the new compounds occupied the binding space of the protein in a way comparable to that of ceftobiprole (ligand in 4DKI) and ampicillin [39].

Furthermore, the docking scores of the new compounds were found to be almost parallel to the reported activities. To maintain brevity, the details of mode of interactions of compound **29** were discussed in comparison to ampicillin. In binding with PBP-2 protein, ampicillin showed interactions with Ser-403, Ser-462, Thr-600 and Tyr-446. Of these former three are directed to its acyl side chain and the fourth one was directed to the carbonyl oxygen of its β -lactam (Figure 1).

Insert Figure 1

In compound **29**, the ethereal and pyran oxygens have mimicked parts of acyl side chain and β -lactam moieties of ampicillin. They showed interaction with Ser-403, Ser-462 and Tyr-446. Apart from these, N2 and N3 of triazole moiety satisfied part of acyl side chain of ampicillin by interacting with Thr-600 (Figure 1). PBP-2 is also common to *K. pneumonia*, *E. coli* and *P. aeruginosa* and with respect to *S. aureus* they showed an identity of 67%, 32% and 27 %, respectively. The activity profiles of the compounds between *S. aureus* and *K. pneumonia* is in agreement with the high identity of their PBP-2 enzymes. In case of *E. coli* and *P. aeruginosa*, the compounds' low order of activity may be due to the altered binding pocket environment along with other reasons. Thus the foregoing offers a rationale for the activities. Among the synthesized compounds, several have shown potent antifungal activity. The structure similarity between standard drugs and the synthesized compounds suggested that triazole moiety may be the key component for antifungal activity. These types of compounds may inhibit the fungal cytochrome P450 enzyme 14 α -demethylase [40]. In brief, 2,3,6-trideoxy sugar-triazole conjugates reported here showed very good *in vitro* antibacterial and antifungal activities (Table 1) as compared to that of 2,3-dideoxy hex-2-enopyranosid-4-ulose alone [18, 19]. This clearly showed the advantage of coupling of 2,3-dideoxy hex-2-enopyranosid-4-uloses with 1,2,3-triazoles, thus justifying the designed compounds [18, 19].

4.4. Toxicity study

Detailed toxicology of the compounds (**24**, **26**, **27**, **28**, **29**, **32**, **35**, **36**, **38**, **46** and **53**) showing low MIC ($\leq 3.12 \mu\text{g/mL}$) against the bacterial or fungal strains were done on mammalian cell L929. The morphological anomalies in the cells were examined under phase contrast microscope. In control, the cells were fairly transparent and attached to wall of the tissue culture plate (Figure 2a). The compounds at MIC dose did not exhibit any toxicity to L929 cells and showed normal morphology (Figure 2b). However, when the cells exposed to $50 \mu\text{g/mL}$ of the compound for 24 hours, they lost normal morphology (Figure 2c). The MTT assay revealed that the viability of the cells was inversely proportional to the concentration of the compounds (Figure 2d).

Insert Figure 2

5. Conclusion

In conclusion, we designed and synthesized a series of novel 6-triazolyl 2,3,6-trideoxy sugar-triazole conjugates using the concept of molecular hybridization. These compounds showed moderate to excellent in vitro activities against different Gram-positive, Gram-negative as well as resistant bacterial strains and fungi with MIC values between 0.39 - $50 \mu\text{g/mL}$. Compound **29** was found to be the most active with MIC $0.78 \mu\text{g/mL}$ against Gram-positive (*S. aureus*) and Gram-negative (*K. pneumoniae*) bacteria and $3.12 \mu\text{g/mL}$ against methicillin- and vancomycin-resistant *S. aureus*. Compounds **38**, **46** and **53** were the other promising antibacterial molecules from this series. Compounds **26**, **38** and **46** showed high activity (MIC, 0.39 - $1.56 \mu\text{g/mL}$) against *T. mentagrophytes* and high to threshold activity (MIC, 3.25 - $50 \mu\text{g/mL}$) against *S. schenckii*. Of these, compound **46** was found to be the most promising one due to its broad spectrum activity against both bacterial and fungal strains. Exploration of bacterial cell enzymes with bioinformatics tools and compounds' structural/functional similarities with different ligands of bacteria's protein co-crystals led to suggest penicillin

binding protein-2 as the most likely target of these compounds. All high active compounds ($MIC \leq 3.12 \mu\text{g/mL}$) did not show any toxicity to mammalian cell L929. Further optimization of high active compounds would be taken up soon.

6. Experimental Section

6.1. Chemistry

General Remarks: The chemicals used in synthesis were purchased from Sigma-Aldrich Co and Spectrochem (India). The organic solvents used in synthesis were dried by standard methods. All the reactions were monitored by thin layer chromatography over basic alumina coated TLC plates and the spots were visualized with the help of CeSO_4 or 10% $\text{H}_2\text{SO}_4/\text{EtOH}$ on hot plate. The pure compound was isolated by column chromatography using silica gel of mesh size 60-120, 100-200 and 230-400. All the products were characterized by ^1H , ^{13}C , DEPT pulse sequence, two-dimensional homonuclear COSY (Correlation Spectroscopy), Heteronuclear Single Quantum Correlation (HSQC), Heteronuclear Multiple Bond Correlation (HMBC), IR, MS (ESI), HRMS (ESI) and HRMS (DART). All NMR spectra were recorded on Bruker Avance DPX 200FT, Bruker DRX 300 Spectrometers at 200, 300 MHz (^1H) and 50, 75, MHz (^{13}C). The chemical shifts (δ) are given in ppm, related to tetramethylsilane (TMS) as an internal standard. For ^{13}C -NMR reference CDCl_3 appeared at 77.10 ppm unless otherwise stated. Electron spray ionization Mass Spectra (ESIMS) were obtained on Micromass quadro II spectrometer. HRMS were recorded on JEOL, JMS T100LC Accu TOF. IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu Spectrophotometers either as KBr disc or neat and value are expressed in cm^{-1} . Optical rotations were determined on an Autopol III polarimeter (Rudolph Research) and using a 1 dm cell in chloroform as solvent at 25 °C unless otherwise stated; concentrations mentioned are in g/100 mL.

6.2. General procedure for the preparation of compounds 2a-2c

To a solution of the enone **1a** (1500 mg, 7.01 mmol) in dry DCM (25 mL) was added dry pyridine (8 mL) and the temperature of the reaction mixture was kept at $-30\text{ }^{\circ}\text{C}$ followed by drop wise addition of *p*-toluenesulphonyl chloride (2268 mg, 11.9 mmol) dissolved in dry dichloromethane (DCM) (10 mL) for 1 hour. After the addition was complete, the reaction mixture was stirred at the same temperature for an additional 1 hour and finally kept in a refrigerator at $5\text{ }^{\circ}\text{C}$ for overnight. On completion of reaction (TLC), the reaction mixture was poured into ice cold water (excess) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (4x5mL). The combined organic layers were washed successively with water and brine, dried over sodium sulphate and evaporated *in vacuo* using co-distillation with toluene to remove pyridine. The crude product so obtained was purified by column chromatography to give the pure compound **2a** as viscous oil; yield (75%); $R_f = 0.45$ (hexane-ethyl acetate, 10:3); eluent for column chromatography (hexane-ethyl acetate, 50:3); $[\alpha]_D^{31} = -31.44$ (c 0.20, CHCl_3); IR (neat, cm^{-1}): 3025, 1699, 1599, 1364, 1179; ^1H NMR ($\text{CDCl}_3 + \text{CCl}_4$, 300 MHz): δ 7.75 (d, 2H, H-2" and H-6", $J = 8.1$ Hz), 7.32 (d, 2H, H-3" and H-5", $J = 8.0$ Hz), 6.82 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.4$ Hz), 6.02 (d, 1H, H-3, $J = 10.3$ Hz), 5.16 (d, 1H, H-1, $J = 3.3$ Hz), 4.59 (dd, 1H, H-5, $J = 5.8$ Hz & $J = 2.0$ Hz), 4.44 (dd, 1H, H-6a, $J = 10.8$ Hz & $J = 2.1$ Hz), 4.25 (dd, 1H, H-6b, $J = 10.8$ Hz & $J = 6.1$ Hz), 3.86-3.78 (m, 1H, H-1'a), 3.58-3.50 (m, 1H, H-1'b), 2.44 (s, 3H, CH_3 of OTs), 1.72-1.61 (m, 1H, H-3'), 1.54-1.41 (m, 2H, H-2'), 0.91 (s, 3H, CH_3 of *i*-amyl), 0.89 (s, 3H, CH_3 of *i*-amyl); ^{13}C NMR ($\text{CDCl}_3 + \text{CCl}_4$, 50 MHz): δ 191.9 (C-4), 144.6 (ArqC), 144.3 (C-2), 133.1 (ArqC), 129.8 (C-3" and C-5"), 128.2 (C-2" and C-6"), 127.2 (C-3), 93.1 (C-1), 72.3 (C-5), 68.1 (C-1'), 68.0 (C-6), 38.4 (C-2'), 25.0 (C-3'), 22.8 and 22.5 (2 CH_3 of *i*-amyl) 21.7 (CH_3 of OTs); MS (ESI): m/z 368; found 386 $[\text{M} + \text{NH}_4]^+$, 391 $[\text{M} + \text{Na}]^+$; HRMS (ESI): Calc for $\text{C}_{18}\text{H}_{24}\text{O}_6\text{S}$ $[\text{M}]^+$ 368.1294, found 368.1302.

Compounds **2b** and **2c** were prepared using the same procedure as described above for **2a**. However they were not isolated by column chromatography and crude product was used as such for the next step.

6.3. General procedure for the preparation of compounds 4a-4c

To a stirred solution of **2a** (1934 mg, 5.25 mmol) in ethanol were added $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1174.49 mg, 3.15 mmol) and NaBH_4 (116.66 mg, 3.15 mmol) at 0 °C and the reaction mixture was stirred continuously for 40 minutes keeping the temperature of the reaction mixture below 10 °C. After completion of the reaction (TLC control), excess NaBH_4 was neutralized with acetone and the solvent was concentrated (rotary evaporator) to obtain the crude product **3a**. To the dried crude product **3a** dissolved dimethyl formamide (DMF) was added NaN_3 (847.6 mg, 13.04 mmol) and the reaction mixture was refluxed at 90-100 °C for 3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with DCM (5x8mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated under reduced pressure to yield the crude product. It was then purified by column chromatography to give the pure compound **4a** as viscous oil; yield (64%); $R_f = 0.57$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 50:3); $[\alpha]_D^{31} = -35.27$ (c 0.40, CHCl_3); IR (neat, cm^{-1}): 3396, 3021, 2102, 1461, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 5.92 (d, 1H, H-3, $J = 15.3$ Hz), 5.77 (dd, 1H, H-2, $J = 15.3$ Hz & $J = 6.9$ Hz), 4.98 (s, 1H, H-1), 4.12 - 4.04 (m, 1H, H-4), 3.92 - 3.76 (m, 1H, H-5), 3.92 - 3.76 (m, 2H, H-5 & H-6a), 3.60 - 3.42 (m, 3H, H-6a & H-6b), 1.76-1.59 (m, 1H, H-3'), 1.56-1.45 (m, 2H, H-2'), 0.93 (s, 3H, CH_3 of *i*-amyl), 0.90 (s, 3H, CH_3 of *i*-amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 132.6 (C-3), 127.1 (C-2), 94.2 (C-1), 71.4 (C-5), 67.4 (C-1'), 65.1 (C-4), 52.0 (C-6), 38.5 (C-2'), 25.1 (C-3'), 22.7 & 22.4 (2 CH_3 of *i*-amyl); MS (ESI): m/z 241; found

259 $[M+NH_4]^+$, 242 $[M+H]^+$; HRMS (ESI): Calc for $C_6H_8NO_2 [M-C_5H_{11}O + N_2]^+$ 126.0555 ; found 126.0544.

Compounds **4b** and **4c** were prepared using the same procedure as described above for **4a**. However they were not isolated by column chromatography and crude product was used as such for the next step.

6.4. General procedure for the preparation of compounds 6-9, 11-12, 14-23

6.4.1. Compound 6

To a vigorously stirred solution of azide **4b** (250 mg, 1.111 mmol) in *tert*-butyl alcohol was added the 5 chloropentyne (0.173 mL, 1.66 mmol). The reaction was initiated by the addition of a solution of $CuSO_4 \cdot 5H_2O$ (49.38 mg, 0.22 mmol) and sodium ascorbate (87.16 mg, 0.44 mmol) in distilled water. The coloured suspension formed and the reaction mixture was stirred at room temperature till the disappearance of the starting material on TLC. After the completion of reaction, ice-cold distilled water was added to the reaction mixture and the aqueous layer was extracted 3-4 times with $CHCl_3$. The combined organic extracts were dried *in vacuo* and purified using column chromatography to afford pure triazolyl 2,3,6 trideoxy hex-2-enopyranoside **6**; yield (78%); R_f = 0.47 (hexane-ethyl acetate, 3:2) ; eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -5.44$ (c 0.08, $CHCl_3$); IR (neat, cm^{-1}): 3855, 3353, 2928, 2361, 1651, 1219, 768; 1H NMR ($CDCl_3$, 300 MHz): δ 7.50 (s, 1H, H-5"), 5.93 (d, 1H, H-3, $J = 9.9$ Hz), 5.71 (d, 1H, H-2, $J = 9.7$ Hz), 4.90 (s, 1H, H-1), 4.72 (d, 1H, H-6a, $J = 14.3$ Hz), 4.56 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 6.7$ Hz), 3.97 (d, 1H, H-4, $J = 6.9$ Hz), 3.85 (d, 1H, H-5, $J = 9.1$ Hz), 3.57 (t, 2H, H-1', $J = 6.0$ Hz), 3.15 (t, 2H, H-3"', $J = 7.0$ Hz), 2.88 (t, 2H, H-1"', $J = 7.0$ Hz), 2.16 (t, 2H, H-2"', $J = 6.7$ Hz), 1.77-1.68 (m, 1H, H-2'), 0.83-0.78 (m, 6H, $2CH_3$ of *i* butyl); ^{13}C NMR ($CDCl_3$, 75MHz): δ 146.3 (C-4"), 133.1 (C-3), 126.4 (C-2), 123.1 (C-5"), 94.6 (C-1), 75.5 (C-1'), 70.7 (C-5), 64.5 (C-4), 51.3 (C-6), 44.2 (C-3'''), 32.0 (C-1'''), 28.4 (C-2'), 22.7 (C-2'''), 19.3 & 19.4 ($2CH_3$ of *i* butyl). MS (ESI): m/z

329; found 330 $[M+H]^+$; HRMS (ESI): Calc for $C_{15}H_{25}ClN_3O_3$ $[M+H]^+$; 330.1584 ; found 330.1618.

Compounds **7**, **8**, **9**, **11**, **12**, **14**, **15**, **16**, **17**, **18**, **19**, **21**, **22**, **23** were prepared following the procedure as described above for compound **6**. While compounds **8**, **9**, **12**, **14**, **15**, **16**, **17**, **18**, **19**, **21**, **22**, **23** were synthesized from precursor 6-azido hex-2-enopyranoside **4a**, compound **7** and **11** were synthesized from precursor **4c**.

6.4.2. Compound 7

This compound was obtained as a viscous oil; yield (86%); R_f = 0.47 (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31}$ = -43.75 (c 0.032, $CHCl_3$); IR (neat, cm^{-1}): 3759, 2364, 1655, 1576, 1218; 1H NMR ($CDCl_3$, 300 MHz): δ 7.50 (s, 1H, H-5''), 5.93 (d, 1H, H-3, J = 10.1 Hz), 5.69 (d, 1H, H-2, J = 10.0 Hz), 4.90 (s, 1H, H-1), 4.72 (dd, 1H, H-6a, J = 14.3 Hz & J = 2.1Hz), 4.57 (dd, 1H, H-6b, J = 14.3 Hz and J = 6.6 Hz), 3.98 (dd, 1H, H-4, J = 6.8 Hz & J = 8.9 Hz), 3.85 (d, 1H, H-5, J = 8.6 Hz), 3.56 (t, 2H, H-3''', J = 6.3Hz), 3.44-3.31 (m, 2H, H-1'), 2.87 (t, 2H, H-1''', J = 7.2 Hz), 2.14 (dd, 2H, H-2''', J = 20.3 Hz & J = 6.5 Hz), 1.46-1.40 (m, 2H, H-3'), 1.28-1.25 (m, 2H, H-2'), 0.86 (t, 3H, H-4', J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75MHz): δ 146.3 (C-4''), 133.2 (C-3), 126.4 (C-2), 123.0 (C-5''), 94.5 (C-1), 70.7 (C-5), 68.6 (C-4), 64.5 (C-1'), 51.3 (C-6), 44.2 (C-3'''), 32.0 (C-2'), 31.7 (C-1'''), 22.7 (C-2'''), 19.4 (C-3'), 13.9 (C-4'). MS (ESI): m/z 329; found 330 $[M+H]^+$; HRMS (ESI): Calc for $C_{15}H_{25}ClN_3O_4$ $[M+H]^+$; 330.1584 ; found 330.1586.

6.4.3. Compound 8

This compound was obtained as a viscous oil; yield (73%); R_f = 0.55 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31}$ = -3.08 (c 0.14, $CHCl_3$); IR (neat, cm^{-1}): 3779, 3346, 2924, 2364, 1461, 1050; 1H NMR ($CDCl_3$, 300 MHz) : δ 7.43 (s, 1H, H-5''), 5.93 (d, 1H, H-3, J = 10.2 Hz), 5.72-5.67 (m, 1H, H-2), 4.91 (s, 1H, H-1), 4.71- 4.55 (m, 2H, H-6), 4.00-3.94 (m, 1H, H-4), 3.83 (d, 1H, H-5, J = 9.0 Hz), 3.52-3.46 (m,

1H, H-1'a), 3.40-3.35 (m, 1H, H-1'b), 2.69 (t, 2H, H-1''', $J = 7.5$ Hz), 1.82 (s, 1H, H-3'), 1.68-1.57 (m, 2H, H-2'), 1.41-1.34 (m, 6H, H-2''', H-3''' & H-4'''), 0.91-0.82 (m, 9H, 2CH₃ of *i*amyl & 1CH₃ of H-5'''); ¹³C NMR (CDCl₃, 75MHz): δ 148.5 (C-4''), 133.1 (C-3), 126.5 (C-2), 122.4 (C-5''), 94.6 (C-1), 70.8 (C-5), 67.2 (C-1'), 64.6 (C-4), 51.2 (C-6), 38.5 (C-2'), 31.6 (C-1'''), 29.8 (C-2'''), 29.3 (C-3'''), 25.7 (C-4'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*amyl), 14.2 (CH₃ of C-5'''). MS (ESI): m/z 337; found 338[M+H]⁺ HRMS (DART): Calc for C₁₈H₃₂N₃O₃[M+H]⁺; 338.2443; found 338.2457.

6.4.4. Compound 9

This compound was obtained as a viscous oil ; yield (78%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -3.91$ (c 0.10, CHCl₃); IR (neat, cm⁻¹): 3411, 3019, 2928, 2364, 1589, 1217, 767; ¹H NMR (CDCl₃, 300 MHz): δ 7.43 (s, 1H, H-5''), 5.93 (d, 1H, H-3, $J = 10.2$ Hz), 5.69 (d, 1H, H-2, $J = 10.1$ Hz), 4.91 (s, 1H, H-1), 4.71-4.53 (m, 2H, H-6), 3.98 (t, 1H, H-4, $J = 9.0$ Hz), 3.84 (d, 1H, H-5, $J = 8.9$ Hz), 3.53-3.32 (m, 2H, H-1') , 2.69 (t, 2H, H-1''', $J = 7.3$ Hz), 1.64-1.57 (m, 3H, H-3' & H-2'), 1.40-1.30 (m, 8H, H-2'''-H-5'''), 0.87- 0.82 (m, 9H, 2CH₃ of *i*amyl & 1CH₃ of H-6'''); ¹³C NMR (CDCl₃, 75MHz): δ 148.4 (C-4''), 133.1 (C-3), 126.4 (C-2), 122.4 (C-5''), 94.5 (C-1), 70.8 (C-5), 67.2 (C-1'), 64.56 (C-4), 51.2 (C-6), 38.4 (C-2'), 31.64 (C-1'''), 29.8 (C-2'''), 29.5 (C-3'''), 29.0 (C-4'''), 25.7 (C-5'''), 25.1 (C-3'), 22.6 and 22.5 (2CH₃ of *i*amyl), 14.1 (CH₃ of C-6'''); MS (ESI): m/z 351; found 352 [M+H]⁺; HRMS (DART): Calc for C₁₉H₃₄N₃O₃ [M+H]⁺; 352.2600 ; found 352.2613.

6.4.5. Compound 11

This compound was obtained as a viscous oil ; yield (66%); $R_f = 0.47$ (hexane-ethyl acetate, 3:2) ; eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = +18.22$ (c 0.06, CHCl₃); IR (neat, cm⁻¹): 3908, 3762, 3455, 2927, 2365, 1631, 1220, 1041, 770; ¹H NMR (CDCl₃, 300 MHz): δ 7.42 (s, 1H, H-5''), 5.93 (d, 1H, H-3, $J = 10.2$ Hz), 5.69 (d, 1H,

H-2, $J = 10.1$ Hz), 4.90 (s, 1H, H-1), 4.70 (d, 1H, H-4, $J = 12.4$ Hz), 4.56 (dd, 1H, H-6a, $J = 14.43$ Hz and $J = 6.72$ Hz), 3.98 (t, 1H, H-6b, $J = 7.2$ Hz), 3.86 (s, 1H, H-5), 3.47-3.33 (m, 2H, H-1'), 2.68 (t, 2H, H-1'', $J = 7.53$ Hz), 1.66-1.61 (m, 4H, H-2' & H-3'), 1.49-1.40 (m, 12H, H-2'''-H-7'''), 0.88-0.84 (m, 6H, H-4' & H-8'''); ^{13}C NMR (CDCl_3 , 75 MHz): δ 148.5 (C-4''), 133.1 (C-3), 126.5 (C-2), 122.4 (C-5''), 94.5 (C-1), 70.8 (C-5), 68.5 (C-1'), 64.6 (C-4), 51.2 (C-1'), 31.9 (C-1'''), 31.8 (C-2'), 29.6 (C-6'''), 29.5 (C-4'''), 29.4 (C-5'''), 29.3 (C-3'''), 25.8 (C-2'''), 25.7 (C-7'''), 19.4 (C-3'), 14.2 (C-4'), 13.9 (C-8'''). MS (ESI): m/z 365; found 366 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{20}\text{H}_{36}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 366.2757; found 366.2742.

6.4.6. Compound 12

This compound was obtained as a viscous oil; yield (83%); $R_f = 0.57$ (chloroform-methanol 24:1); eluent for column chromatography (chloroform-methanol 10:0.1); $[\alpha]_D^{31} = -21.13$ (c 0.08, CHCl_3); IR (neat, cm^{-1}): 3749, 3427, 2930, 2363, 1640, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 7.47 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.1$ Hz), 5.68 (d, 1H, H-2, $J = 10.2$ Hz), 4.91 (s, 1H, H-1), 4.71-4.56 (m, 2H, H-6), 4.00-3.95 (m, 1H, H-4), 3.83 (d, 1H, H-5, $J = 9.2$ Hz), 3.66 (t, 2H, H-1', $J = 6.3$ Hz), 3.54-3.46 (m, 1H, H-4'''a), 3.40-3.33 (m, 1H, H-4'''b), 2.73 (t, 2H, H-1'', $J = 7.2$ Hz), 1.78-1.71 (m, 2H, H-2'''), 1.67-1.56 (m, 2H, H-3'''), 1.40-1.34 (m, 3H, H-3' & H-2'), 0.86-0.82 (m, 6H, 2 CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 147.9 (C-4''), 133.2 (C-3), 126.3 (C-2), 122.6 (C-5''), 94.5 (C-1), 70.7 (C-5), 67.2 (C-1'), 64.3 (C-4), 62.3 (C-4'''), 51.2 (C-6), 38.4 (C-1'''), 32.1 (C-3'''), 25.6 (C-2'), 25.2 (C-2'''), 25.0 (C-3'), 22.6 & 22.4 (2 CH_3 of i -amyl). MS (ESI): m/z 339; found 340 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{17}\text{H}_{30}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 340.2236; found 340.2219.

6.4.7. Compound 14

This compound was obtained as a viscous oil; yield (89%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 15:7); $[\alpha]_D^{31} = +13.71$ (c 0.04, CHCl_3); IR (neat, cm^{-1}): 3752, 3423, 2925, 2363, 1722, 1463, 1287, 1161, 1045; ^1H

NMR (CDCl₃, 300 MHz): δ 7.45 (s, 1H, H-5''), 5.92 (d, 1H, H-3, J = 10.1 Hz), 5.70-5.66 (m, 1H, H-2), 4.90 (s, 1H, H-1), 4.69 (dd, 1H, H-6a, J = 14.4 Hz & J = 2.4 Hz), 4.58 (dd, 1H, H-6b, J = 14.4 Hz & J = 6.7 Hz), 4.05 (t, 2H, H-4 & H-5, J = 6.12 Hz), 3.96 (t, 1H, H-4'''a, J = 2.43 Hz), 3.84 (d, 1H, H-4'''a, J = 8.97 Hz), 3.52-3.44 (m, 1H, H-1'a), 3.35 (dd, 1H, H-1'b, J = 6.7 Hz & J = 2.6 Hz), 2.72 (t, 2H, H-1''', J = 6.75 Hz), 1.71 (d, 4H, H-2''' & H-3'''), 1.64-1.53 (m, 1H, H-3'), 1.39-1.32 (m, 2H, H-2'), 1.23 (s, 9H, OCOC(CH₃)₃), 0.85-0.80 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75 MHz): δ 178.7 (C-5'''), 147.6 (C-4''), 133.2 (C-3), 126.3 (C-2), 122.6 (C-5''), 94.5 (C-1), 70.7 (C-5), 67.1 (C-1'), 64.4 (C-4'''), 64.1 (C-4), 51.2 (C-6), 38.4 (C-2'), 29.7 (C of Piv), 28.3 (C-1'''), 27.2 (3CH₃ of Piv), 25.9 (C-2'''), 25.2 (C-3'''), 25.0 (C-3'), 22.7 & 22.4 (2CH₃ of *i*-amyl). MS (ESI): m/z 423; found 424 [M+H]⁺; HRMS (ESI): Calc for C₂₂H₃₈N₃O₅ [M+H]⁺; 424.2811; found 424.2797.

6.4.8. Compound 15

This compound was obtained as a viscous oil; yield (86%); R_f = 0.53 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31}$ = -20.68 (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3419, 3021, 2930, 2366, 1706, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 7.61 (s, 1H, H-5''), 5.92 (d, 1H, H-3, J = 10.0 Hz), 5.71 (d, 1H, H-2, J = 10.1 Hz), 4.92 (s, 1H, H-1), 4.72 (dd, 1H, H-6a, J = 14.4 Hz & J = 6.3 Hz), 4.61 (dd, 1H, H-6b, J = 14.4 Hz & J = 6.3 Hz), 3.99 (t, 1H, H-4, J = 6.5 Hz), 3.83 (d, 1H, H-5, J = 8.9 Hz), 3.64 (t, 2H, H-2''', J = 6.8 Hz), 3.55-3.47 (m, 1H, H-1'a), 3.38 (m, 1H, H-1'b, J = 13.5 Hz & J = 6.7 Hz), 3.29 (t, 2H, H-1''', J = 6.8 Hz), 1.68-1.55 (m, 1H, H-3'), 1.41-1.32 (m, 2H, H-2'), 0.87-0.82 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75 MHz): δ 144.8 (C-4'''), 132.9 (C-3), 126.6 (C-2), 123.6 (C-5''), 94.5 (C-1), 70.7 (C-4), 67.3 (C-1'), 64.6 (C-5), 51.4 (C-6), 38.4 (C-2'), 29.8 (C-2'''), 29.5 (C-1'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*-amyl). MS (ESI): m/z 373; found 374 [M+H]⁺; HRMS (ESI): Calc for C₁₅H₂₅BrN₃O₃ [M+H]⁺; 374.1079; found 374.1061.

6.4.9. Compound 16

This compound was obtained as a viscous oil; yield (64%); $R_f = 0.53$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -4.38$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3916, 3774, 3373, 2956, 2370, 1598, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.41 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.2$ Hz), 5.61 (d, 1H, H-2, $J = 10.1$ Hz), 4.85 (s, 1H, H-1), 4.77 (d, 1H, H-6a, $J = 13.7$ Hz), 4.39 (t, 1H, H-4, $J = 7.1$ Hz), 3.96 (d, 2H, H-6b & H-5, $J = 13.7$ Hz), 3.37-3.20 (m, 2H, H-1'), 1.59-1.46 (m, 1H, H-3'), 1.31-1.27 (m, 11H, 2H of H-2' & 9H of $\text{C}(\text{CH}_3)_3$), 0.81-0.76 (2 CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 157.3 (C-4''), 133.5 (C-3), 125.9 (C-2), 120.3 (C-5''), 94.3 (C-1), 70.1 (C-5), 66.8 (C-4), 64.5 (C-1'), 51.4 (C-6), 38.3 (C-2'), 30.3 (qC or C-1'''), 29.6 ($\text{C}(\text{CH}_3)_3$), 24.9 (C-3'), 22.6 & 22.4 (2 CH_3 of i -amyl). MS (ESI): m/z 323; found 324 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{17}\text{H}_{30}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 324.2250; found 324.2287.

6.4.10. Compound 17

This compound was obtained as a viscous oil; yield (86%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31} = -29.17$ (c 0.15, CHCl_3); IR (neat, cm^{-1}): 3419, 3020, 1758, 1630, 1216; ^1H NMR (CDCl_3 , 300 MHz): δ 7.94 (s, 1H, H-5''), 7.82 (d, 2H, H-2''' & H-6''', $J = 7.1$ Hz), 7.43-7.29 (m, 3H, H-3''', H-4''' & H-5'''), 5.94 (d, 1H, H-3, $J = 10.2$ Hz), 5.71 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 6.4$ Hz), 4.93 (s, 1H, H-1), 4.81-4.76 (m, 1H, H-6a), 4.69 (dd, 1H, H-6b, $J = 14.2$ Hz & $J = 2.1$ Hz), 4.04 (dd, 1H, H-4, $J = 6.4$ Hz & $J = 2.4$ Hz), 3.91 (d, 1H, H-5, $J = 9.2$ Hz), 3.53-3.47 (m, 1H, H-1'a), 3.41-3.36 (m, 1H, H-1'b), 1.58-1.45 (m, 1H, H-3'), 1.41-1.31 (m, 2H, H-2'), 0.78 (d, 3H, CH_3 of i -amyl, $J = 1.8$ Hz), 0.76 (d, 3H, CH_3 of i -amyl, $J = 1.8$ Hz); ^{13}C NMR (CDCl_3 , 50 MHz): δ 147.8 (qC), 133.0 (C-2), 130.5 (qC), 128.8 (C-3''' & C-5'''), 128.2 (C-4'''), 126.5 (C-3), 125.7 (C-2''' & C-6'''), 121.4 (C-4'''), 94.5 (C-1), 70.7 (C-5), 67.4 (C-1'), 64.6 (C-4), 51.4 (C-6), 38.3 (C-2'), 25.0 (C-3), 22.6 & 22.3 (2 CH_3 of i -amyl); MS (ESI): m/z 343; found 344 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_3$ $[\text{M}]^+$ 343.1896; found 343.1928.

6.4.11. Compound 18

This compound was obtained as a viscous oil; yield (89%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7); $[\alpha]_D^{31} = -25.02$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3752, 3417, 2928, 2367, 1637, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 8.59 (s, 1H, H-3'''), 8.38 (s, 1H, H-5'''), 8.19 (d, 1H, H-6''', $J = 7.7\text{ Hz}$), 7.80 (t, 1H, H-5''', $J = 6.5\text{ Hz}$), 7.28-7.25 (m, 1H, H-4'''), 5.95 (d, 1H, H-3, $J = 10.0\text{ Hz}$), 5.72 (d, 1H, H-2, $J = 10.2\text{ Hz}$), 4.95 (s, 1H, H-1), 4.81 (dd, 2H, H-4 & H-6a, $J = 12.2\text{ Hz}$ & $J = 21.2\text{ Hz}$), 4.11 (d, 1H, H-6b, $J = 20.1\text{ Hz}$), 3.95 (d, 1H, H-5, $J = 8.5\text{ Hz}$), 3.52 – 3.35 (m, 2H, H-1'), 1.58-1.49 (m, 1H, H-3'), 1.39-1.32 (m, 2H, H-2'), 0.89-0.75 (m, 6H, 2CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 150.3 (C-1'''), 149.4 (C-3'''), 148.3 (C-4'''), 137.1 (C-5'''), 133.0 (C-3), 126.7 (C-2), 124.0 (C-6'''), 123.0 (C-4'''), 120.4 (C-5'''), 94.6 (C-1), 70.7 (C-4), 67.5 (C-1'), 64.6 (C-5), 51.5 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.6 & 22.4 (2CH_3 of i -amyl). MS (ESI): m/z 344; found 345 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$; 345.1926; found 345.1907.

6.4.12. Compound 19

This compound was obtained as a viscous oil; yield (69%); $R_f = 0.57$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:7); $[\alpha]_D^{31} = -73.02$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3746, 3420, 2365, 1642, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.91 (s, 1H, H-5'''), 7.78 (dd, 2H, H-3''' & H-2''', $J = 8.61\text{ Hz}$ & $J = 5.4\text{ Hz}$), 7.09 (t, 2H, H-3''' & H-5''', $J = 8.6\text{ Hz}$), 5.94 (d, 1H, H-3, $J = 10.2\text{ Hz}$), 5.70 (d, 1H, H-2, $J = 10.2\text{ Hz}$), 4.93 (s, 1H, H-1), 4.80 (dd, 1H, H-6a, $J = 14.3\text{ Hz}$ & $J = 2.0\text{ Hz}$), 4.66 (dd, 1H, H-6b, $J = 14.3\text{ Hz}$ & $J = 6.5\text{ Hz}$), 4.05 (t, 1H, H-4, $J = 6.9\text{ Hz}$), 3.93 (d, 1H, H-5, $J = 9.1\text{ Hz}$), 3.49-3.32 (m, 3H, H-1' & H-3'), 1.56-1.47 (m, 1H, H-2a'), 1.38-1.25 (m, 2H, H-2b'), 0.87-0.74 (m, 6H, 2CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 164.4 (C-4'''), 161.1 (C-4'''), 146.9 (C-3), 133.1 (C-2), 127.6 (C-6'''), 127.5 (C-2'''), 126.5 (C-3'''), 121.2 (C-5'''), 116.02 (C-4'''), 115.7 (C-5'''), 94.6 (C-1), 70.8 (C-

5), 67.4 (C-4), 64.6 (C-1'), 51.5 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.6 & 22.3 (2CH₃ of *i*amyl). MS (ESI): *m/z* 361; found 362 [M+H]⁺; HRMS (ESI): Calc for C₁₉H₂₅FN₃O₃ [M+H]⁺; 362.1880; found 362.1870.

6.4.13. Compound 21

This compound was obtained as a viscous oil; yield (70%); *R_f* = 0.56 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7); [α]_D³¹ = -100.67 (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3298, 2926, 2369, 1657, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.39 (s, 1H, H-5''), 5.92 (dd, 1H, H-3, *J* = 10.1 Hz), 5.67 (d, 1H, H-3, *J* = 10.1 Hz), 4.89 (s, 1H, H-1), 4.68 (d, 1H, H-4, *J* = 12.45 Hz), 4.52 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 6.6 Hz), 3.94 (d, 1H, H-6b, *J* = 6.6 Hz), 3.86 (d, 1H, H-5, *J* = 9.09 Hz), 3.47-3.33 (m, 2H, H-1'), 1.91 (s, 1H, H-1'''), 1.59 (t, 1H, H-3', *J* = 6.63 Hz), 1.34 (t, 4H, H-2', H-2'''a & H-3'''a *J* = 6.81 Hz), 0.93-0.80 (m, 8H, H-2'''a, H-3'''b, & 2CH₃ of *i*amyl). ¹³C NMR (CDCl₃, 75 MHz): δ 150.1 (C-4''), 133.3 (C-3), 126.2 (C-2), 121.5 (C-5''), 94.5 (C-1), 70.8 (C-5), 67.2 (C-4), 64.4 (C-1'), 51.2 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.7 & 22.4 (2CH₃ of *i*amyl), 7.77 (C-1'''), 6.66 (C-2''' & C-3'''). MS (ESI): *m/z* 307; found 308 [M+H]⁺; HRMS (ESI): Calc for C₁₆H₂₆N₃O₃ [M+H]⁺; 308.1974; found 308.1962.

6.4.14. Compound 22

This compound was obtained as a viscous oil; yield (58%); *R_f* = 0.53 (chloroform: methanol 49:1); eluent for column chromatography (chloroform: methanol, 10:0.1); [α]_D³¹ = -7.93 (c 0.04, CHCl₃); IR (neat, cm⁻¹): 3769, 3379, 2928, 2362, 1710, 1398, 1030; ¹H NMR (CDCl₃, 300 MHz): δ 7.81 (dd, 2H, H-6''' & H-9'', *J* = 5.49 Hz & *J* = 3.06 Hz), 7.69 (dd, 2H, H-7''' & H-8'', *J* = 5.37 Hz & *J* = 3.03 Hz), 7.57 (s, 1H, H-5''), 5.91 (d, 1H, H-3, *J* = 10.2 Hz), 5.69-5.65 (m, 1H, H-2), 4.90 (s, 1H, H-1), 4.70-4.60 (m, 2H, H-4 & H-6a), 3.95 (d, 1H, H-6b, *J* = 6.06 Hz), 3.83 (d, 1H, H-5, *J* = 8.97 Hz), 3.72 (t, 2H, H-3''', *J* = 6.9 Hz), 3.52-3.46 (m, 1H, H-1'a), 3.38-3.33 (m, 1H, H-1'b), 2.62 (t, 2H, H-1'', *J* = 7.32 Hz), 2.14-2.02 (m, 2H, H-2'''),

1.62-1.53 (m, 1H, H-3'), 1.37-1.31 (m, 2H, H-2'), 0.82-0.78 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 168.5 (C-5''' & C-10'''), 134.0 (2×*q*C), 133.2 (C-7''' & C-8'''), 132.1 (C-4'''), 126.3 (C-6''', C-9''' & C-2), 123.3 (C-5'' & C-3), 94.5 (C-1), 70.8 (C-5), 51.23 (C-4), 38.4 (C-1' & C-6), 37.4 (C-3'''), 28.2 (C-2' & C-1'''), 25.0 (C-3'), 23.0 (C-2'''), 22.7 & 22.4 (2CH₃ of *i*-amyl). MS (ESI): *m/z* 454; found 455 [M+H]⁺; HRMS (ESI): Calc for C₂₄H₃₁N₄O₅ [M+H]⁺; 455.2294; found 455.2292.

6.4.15. Compound 23

This compound was obtained as a viscous oil; yield (72%); *R_f* = 0.53 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:2); [α]_D³¹ = -20.20 (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3962, 3768, 3322, 2930, 2365, 1568, 1035; ¹H NMR (CDCl₃, 300 MHz): δ 7.71 (d, 2H, H-4'' & H-5'', *J* = 10.65 Hz), 5.93 (d, 1H, H-3, *J* = 10.1 Hz), 5.69 (d, 1H, H-2, *J* = 10.1 Hz), 4.90 (s, 1H, H-1), 4.79 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 2.3 Hz), 4.65 (dd, 1H, H-6b, *J* = 14.2 Hz & *J* = 6.5 Hz), 4.00 (t, 1H, H-4, *J* = 6.87 Hz), 3.85 (d, 1H, H-5, *J* = 8.91 Hz), 3.49-3.30 (m, 2H, H-1'), 1.66-1.53 (m, 1H, H-3'), 1.38-1.31 (m, 2H, H-2'), 0.85-0.81 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 133.7 (C-3), 133.1 (C-5'''), 126.5 (C-2), 125.2 (C-4'''), 94.5 (C-1), 70.7 (C-4), 67.3 (C-5), 64.6 (C-6), 51.2 (C-1'), 38.4 (C-2'), 25.1 (C-3'), 22.7 & 22.5 (2 CH₃ of *i*-amyl). MS (ESI): *m/z* 267; found 268 [M+H]⁺; HRMS (DART): Calc for C₁₃H₂₂N₃O₃ [M+H]⁺; 268.1661; found 268.1643.

6.5. General procedure for the preparation of compounds 25-28, 30-31, 14-23

6.5.1. Compound 25

To a solution of **6** (285 mg, 0.8662 mmol) in dry DCM (20 mL) was added Dess-Martin periodinane (DMP) reagent (556 mg, 1.299 mmol) at -5 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4 hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic

layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **25**; yield (63%); $R_f = 0.52$ (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 17:3); $[\alpha]_D^{31} = -24.82$ (c 0.04, CHCl_3); IR (neat, cm^{-1}): 3754, 2925, 2368, 2102, 1721, 1219; ^1H NMR (CDCl_3 , 300 MHz): δ 7.51 (d, 1H, H-2, $J = 5.89$ Hz), 7.41 (s, 1H, H-5"), 6.26 (d, 1H, H-3, $J = 6.09$ Hz), 4.67-4.49 (m, 3H, H-6 & H-5), 3.58-3.46 (m, 5H, H-1, H-3''' & H-1'), 2.87 (t, 2H, H-1'', $J = 7.1$ Hz), 2.15 (dd, 2H, H-2'', $J = 13.4$ Hz & $J = 6.6$ Hz), 2.02-1.92 (m, 1H, H-2'), 0.97-0.84 (m, 6H, 2 CH_3 of *i*-butyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 192.9 (C-4), 172.2 (C-4''), 168.1 (C-3), 141.1 (C-2), 132.6 (C-5''), 94.3 (C-1), 88.03 (C-1'), 62.6 (C-6), 53.5 (C-3'''), 41.2 (C-1'''), 39.1 (C-2'''), 38.2 (C-5), 28.7 (C-2'), 19.3 & 19.4 (2 CH_3 of *i*-butyl). MS (ESI): m/z 327; found 328 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{15}\text{H}_{23}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 328.1428; found 328.1410.

Compounds **26**, **27**, **28**, **30**, **31**, **33**, **34**, **35**, **36**, **37**, **38**, **40**, **41**, **42** were prepared using the same procedure as for compound **25**.

6.5.2. Compound 26

This compound was obtained as a viscous oil; yield (63.7%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31} = -174.25$ (c 0.012, CHCl_3); IR (neat, cm^{-1}): 3751, 2925, 3406, 2362, 1697, 1219; ^1H NMR (CDCl_3 , 300 MHz): 7.43 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 3.4$ Hz), 6.10 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.3$ Hz), 5.02 (dd, 1H, H-6a, $J = 14.4$ Hz and $J = 3.0$ Hz), 4.81 (dd, 1H, H-5, $J = 7.6$ Hz and $J = 3.0$ Hz), 4.53 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 7.6$ Hz), 3.56-3.43 (m, 2H, H-1'), 2.87 (t, 2H, H-3''', $J = 7.2$ Hz), 2.16 (t, 2H, H-1'', $J = 6.6$ Hz), 1.49-1.40 (m, 2H, H-2'''), 1.31-1.16 (m, 4H, H-2' & H-3'), 0.85 (t, 3H, H-4', $J = 7.3$ Hz); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 146.3 (C-4''), 144.5 (C-3), 127.1 (C-2), 122.6 (C-5''), 93.2

(C-1), 72.8 (C-5), 69.6 (C-6), 49.5 (C-1'), 44.1 (C-3'''), 32.0 (C-2'), 29.7 (C-1'''), 22.7 (C-2'''), 19.3 (C-3'), 13.8 (C-4'). MS (ESI): m/z 327; found 328 $[M+H]^+$; HRMS (ESI): Calc for $C_{15}H_{23}ClN_3O_4$ $[M+H]^+$; 328.1428; found 328.1421.

6.5.3. Compound 27

This compound was obtained as a viscous oil; yield (57%); R_f = 0.5 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = -127.56$ (c 0.13, $CHCl_3$); IR (neat, cm^{-1}): 3380, 2932, 2365, 1699, 1218; 1H NMR ($CDCl_3$, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, J = 10.3 Hz & J = 3.5 Hz), 6.09 (d, 1H, H-3, J = 10.3 Hz), 5.19 (d, 1H, H-1, J = 3.4 Hz), 5.02 (dd, 1H, H-6a, J = 14.5 Hz & J = 3.0 Hz), 4.80 (dd, 1H, H-5, J = 7.8 Hz and J = 3.0 Hz), 4.51 (dd, 1H, H-6b, J = 14.5 Hz & J = 7.8 Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1''', J = 7.6 Hz), 1.69-1.59 (m, 3H, H-3' and H-2'), 1.41-1.27 (m, 6H, H-2'', H-3''' & H-4'''), 0.88-0.81 (m, 9H, 1 CH_3 of H-5''' & 2 CH_3 of i -amyl); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.5 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.2 (C-1'), 49.4 (C-6), 38.2 (C-2'), 31.5 (C-1'''), 29.3 (C-2'''), 25.7 (C-3'''), 25.0 (C-3'), 22.6 (C-4'''), 22.5 & 22.4 (2 CH_3 of i -amyl), 14.1 (CH_3 of C-5'''); MS (ESI): m/z 335; found 336 $[M+H]^+$; HRMS (DART): Calc for $C_{18}H_{30}N_3O_3$ $[M+H]^+$; 336.2287; found 336.2275.

6.5.4. Compound 28

This compound was obtained as a viscous oil; yield (61%); R_f = 0.52 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); $[\alpha]_D^{31} = -136.6794$ (c 0.12, $CHCl_3$); IR (neat, cm^{-1}): 3772, 3455, 2925, 1685, 1463, 1031; 1H NMR ($CDCl_3$, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, J = 10.3 Hz & J = 3.5 Hz), 6.09 (d, 1H, H-3, J = 10.3 Hz), 5.19 (d, 1H, H-1, J = 3.4 Hz), 5.02 (dd, 1H, H-6a, J = 14.4 Hz and J = 3.0 Hz), 4.80 (dd, 1H, H-5, J = 7.8 Hz & J = 3.0 Hz), 4.51 (dd, 1H, H-6b, J = 14.5 Hz & J = 7.8 Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1''', J = 7.6 Hz), 1.65-1.57 (m, 3H, H-3' & H-2'), 1.41-

1.30 (m, 8H, H-2'''-H-5'''), 0.89-0.80 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-6'''); ¹³C NMR (CDCl₃, 75MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.5 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 73.0 (C-5), 68.2 (C-1'), 49.5 (C-6), 38.23 (C-2'), 31.7 (C-1'''), 29.8 (C-2'''), 29.6 (C-3'''), 29.0 (C-4'''), 25.7 (C-5'''), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*-amyl), 14.1 (CH₃ Of C-6'''). MS (ESI): m/z 349; found 350 [M+H]⁺; HRMS (DART): Calc for C₁₉H₃₂N₃O₃ [M+H]⁺, 350.2443; found 350.2424.

6.5.5. Compound 30

This compound was obtained as a viscous oil; yield (56%); R_f = 0.47 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); [α]_D³¹ = -15.67 (c 0.04, CHCl₃); IR (neat, cm⁻¹): 3755, 3693, 3374, 2928, 2363, 1660, 1591, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, *J* = 10.1 Hz & *J* = 3.1 Hz), 6.10 (d, 1H, H-3, *J* = 10.2 Hz), 5.19 (d, 1H, H-1, *J* = 2.9 Hz), 5.03 (dd, 2H, H-6, *J* = 14.4 Hz & *J* = 2.3 Hz), 4.81 (dd, 1H, H-5, *J* = 7.6 Hz & *J* = 2.6 Hz), 4.50 (dd, 2H, H-1', *J* = 14.3 Hz & *J* = 8.0 Hz), 3.52-3.43 (m, 2H, H-1'''), 2.69 (t, 2H, H-2', *J* = 7.5 Hz), 1.62 (d, 2H, *J* = 6.8 Hz), 1.49-1.42 (m, 12H, H-2'''-H-7'''), 0.87-0.85 (m, 6H, 2CH₃ of H-8''' & H-4''); ¹³C NMR (CDCl₃, 75MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.4 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 69.6 (C-1'), 49.4 (C-6), 31.9 (C-2'), 31.6 (C-1'''), 29.6 (C-2'''), 29.4 (C-3'''), 29.32 (C-4'''), 29.3 (C-5'''), 25.7 (C-6'''), 22.7 (C-7'''), 19.3 (C-3'), 14.2 (C-4'), 13.8 (C-8'''). MS (ESI): m/z 363; found 364 [M+H]⁺; HRMS (ESI): Calc for C₂₀H₃₄N₃O₄ [M+H]⁺; 364.2600; found 364.2602.

6.5.6. Compound 31

This compound was obtained as a viscous oil; yield (63 %); R_f = 0.47 (hexane-ethyl acetate 1:1); eluent for column chromatography (hexane-ethyl acetate, 16:9); [α]_D³¹ = +4.95 (c 0.27, CHCl₃); IR (neat, cm⁻¹): 3754, 3432, 2923, 2372, 1646, 1464, 1220; ¹H NMR (CDCl₃, 300 MHz): δ 9.74 (s, 1H, H-1'''), 7.40 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5

Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.5$ Hz), 5.00 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 3.1$ Hz), 4.79 (dd, 1H, H-5, $J = 7.5$ Hz & $J = 3.1$ Hz), 4.54 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 7.5$ Hz), 3.62-3.42 (m, 2H, H-1'), 2.73 (t, 2H, H-1'', $J = 7.5$ Hz), 2.51 (t, 2H, H-3'', $J = 7.2$ Hz), 2.03-1.95 (m, 2H, H-2''), 1.62-1.53 (m, 1H, H-3'), 1.40-1.33 (m, 2H, H-2'), 0.84-0.78 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 202.0 (C-1'''), 193.1 (C-4), 147.0 (C-4''), 144.5 (C-2), 127.1 (C-3), 122.4 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 43.1 (C-3'''), 38.2 (C-2'), 24.9 (C-2''), 24.8 (C-3'), 22.6 (C-2'''), 22.3 & 21.9 (2CH₃ of *i*-amyl); MS (ESI): m/z 335; found 336 [M+H]⁺; HRMS (DART): Calc for C₁₇H₂₆N₃O₄[M+H]⁺; 336.1923; found 336.1904.

6.5.7. Compound 33

This compound was obtained as a viscous oil; yield (59 %); $R_f = 0.53$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = -33.35$ (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3750, 3422, 2364, 1642, 1218; ¹H NMR (CDCl₃, 300 MHz): δ 7.37 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 3.2$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.03$ Hz), 5.01 (dd, 1H, H-6a $J = 14.3$ Hz & $J = 2.7$ Hz), 4.80 (dd, 1H, H-6b, $J = 7.44$ Hz, $J = 2.79$ Hz), 4.53 (dd, 1H, H-5, $J = 14.4$ Hz, & $J = 7.4$ Hz), 4.07 (d, 2H, H-4'', $J = 5.9$ Hz), 3.61-3.42 (m, 2H, H-1'), 2.72 (d, 2H, H-1'', $J = 6.8$ Hz), 1.70-1.53 (m, 4H, H-2'', H-3'''), 1.40 (m, 1H, H-3'), 1.24-1.18 (m, 11H, H-2' & 9H OCOC(CH₃)₃), 0.89-0.88 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 193.2 (C-4), 178.7 (C-5'''), 147.7 (C-4''), 144.5 (C-2), 127.1 (C-3), 122.2 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 64.1 (C-4'''), 49.5 (C-6), 38.2 (C-2'), 29.7 (C of OCOC(CH₃)₃), 28.3 (C-1'''), 27.3 (CH₃ of OCOC(CH₃)₃), 25.98 (C-2'''), 25.3 (C-3'''), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): m/z 421; found 422 [M+H]⁺; HRMS (ESI): Calc for C₂₂H₃₆N₃O₅ [M+H]⁺; 422.2655; found 422.2639.

6.5.8. Compound 34

This compound was obtained as a viscous oil ; yield (74%); $R_f = 0.53$ (hexane-ethyl acetate 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 17:3) ; $[\alpha]_D^{31} = -0.34$ (c 0.17, CHCl_3); IR (neat, cm^{-1}): 3880, 3751, 3444, 2364, 1655, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.56 (s, 1H, H-5''), 6.87 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.11 (d, 1H, H-3, $J = 10.2$ Hz), 5.21 (d, 1H, H-1, $J = 3.4$ Hz), 5.06 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.94$ Hz), 4.82 (dd, 1H, H-5, $J = 7.7$ Hz & $J = 3.1$ Hz), 4.59-4.50 (m, 1H, H-6b), 3.64 (t, 2H, H-2''', $J = 6.7$ Hz), 3.51- 3.43 (m, 1H, H-1'a), 3.29 (t, 3H, H-1'''& H-1'b, $J = 6.75$ Hz), 1.65-1.54 (m, 1H, H-3'), 1.42-1.36 (m, 2H, H-2'), 0.86-0.80 (m, 6H, 2CH_3 of i -amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 144.8 (C-4''), 144.5 (C-2), 127.1 (C-3), 123.3 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.3 (C-1'), 49.6 (C-6), 38.2 (C-2'), 31.7 (C-2'''), 29.2 (C-1'''), 25.0 (C-3'), 22.6 & 22.3 (2CH_3 of i -amyl). MS (ESI): m/z 371; found 372 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{15}\text{H}_{23}\text{BrN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 372.0922 ; found 372.0932.

6.5.9. Compound 35

This compound was obtained as a viscous oil; yield (86%); $R_f = 0.52$ (hexane-ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 9:1); $[\alpha]_D^{31} = +5.84$ (c 0.10, CHCl_3); IR (neat, cm^{-1}): 3420, 2926, 2365, 1700, 1217; ^1H NMR (CDCl_3 , 300 MHz): δ 7.34 (s, 1H, H-5''), 6.84 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.45$ Hz), 6.07 (d, 1H, H-3, $J = 10.3$ Hz), 5.18 (d, 1H, H-1, $J = 3.3$ Hz), 5.04 (dd, 1H, H-6a, $J = 14.5$ Hz & $J = 2.9$ Hz), 4.78 (dd, 1H, H-5, $J = 8.8$ Hz & $J = 2.82$ Hz), 4.42 (dd, 1H, H-6b, $J = 14.5$ Hz & $J = 8.3$ Hz), 3.51-3.39 (m, 2H, H-1'), 1.58-1.51 (m, 1H, H-3'), 1.33-1.25 (m, 11H, H-2', & $\text{C}(\text{CH}_3)_3$), 0.88-0.78 (m, 6H, 2CH_3 of i -amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 157.6 (C-4''), 144.4 (C-2), 127.1 (C-3), 120.2 (C-5''), 96.5 (C-1), 72.9 (C-5), 68.0 (C-1'), 49.3 (C-6), 38.2 (C-2'), 30.4 ($\text{C}(\text{CH}_3)_3$), 29.3 ($\text{C}(\text{CH}_3)_3$) 24.9 (C-3'), 22.6 & 22.3 (2CH_3 of i -amyl). MS (ESI): m/z 321; found 322 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{17}\text{H}_{28}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 322.2131 ; found 322.2122.

6.5.10. Compound 36

This compound was obtained as a Glassy solid; yield (81%); $R_f = 0.43$ (hexane/ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 89:11); $[\alpha]_D = -147.80$ (c 0.24, CHCl_3); IR (neat, cm^{-1}): 3423, 3020, 1633, 1426, 1216; ^1H NMR (CDCl_3 , 300 MHz): δ 7.86 (s, 1H, H-5''), 7.83-7.80 (m, 2H, H-2''' & H-6'''), 7.43-7.32 (m, 3H, H-3''', H-4''' & H-5'''), 6.86 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 5.21 (d, 1H, H-1, $J = 3.4$ Hz), 5.10 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 3.1$ Hz), 4.87 (dd, 1H, H-5, $J = 7.6$ Hz & $J = 3.1$ Hz), 4.63 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 7.6$ Hz), 3.63-3.55 (m, 1H, H-1'a), 3.51-3.36 (m, 1H, H-1'b), 1.58-1.45 (m, 1H, H-3'), 1.41-1.31 (m, 2H, H-2'), 0.78(d, 3H, CH_3 of i -amyl, $J = 1.8$ Hz), 0.76 (d, 3H, CH_3 of i -amyl, $J = 1.8$ Hz); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 147.8 ($q\text{C}$), 144.5 (C-2), 130.6 ($q\text{C}$), 128.8 (C-3''' & C-5'''), 128.2 (C-4'''), 127.1 (C-3), 125.8 (C-2''' & C-6'''), 121.0 (C-4'''), 93.3 (C-1), 72.8 (C-5), 68.4 (C-1'), 49.6 (C-6), 38.2 (C-2'), 25.0 (C-3), 22.5 & 22.3 (2 CH_3 of i -amyl); MS (ESI): m/z 341; found 342 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_3$ $[\text{M}]^+$ 341.1739; found 341.1741.

6.5.11. Compound 37

This compound was obtained as a viscous oil; yield (89%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7) ; $[\alpha]_D^{31} = -25.02$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3752, 3417, 2928, 2367, 1637, 1218 ; ^1H NMR (CDCl_3 , 300 MHz): δ 8.56 (d, 1H, H-3''', $J = 4.2$ Hz), 8.25 (s, 1H, H-5''), 8.16 (d, 1H, H-6''', $J = 7.9$ Hz), 7.75 (t, 1H, H-5''', $J = 7.56$ Hz), 7.22-7.18 (m, 1H, H-4'''), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.4$ Hz), 6.11 (d, 1H, H-3, $J = 10.3$ Hz), 5.20 (d, 1H, H-1, $J = 3.3$ Hz), 5.12 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.9$ Hz), 4.86 (dd, 1H, H-5, $J = 7.8$ Hz & $J = 2.8$ Hz), 4.63 (dd, 1H, H-6b, $J = 14.34$ Hz & $J = 7.92$ Hz), 3.60-3.41 (m, 2H, H-1'), 1.56-1.44 (m, 1H, H-3'), 1.37-1.33 (m, 2H, H-2'), 0.75-0.72 (m, 6H, 2 CH_3 of i -amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 192.9 (C-4), 150.4 (C-1'''), 149.4 (C-3'''), 148.4 (C-5'''), 144.5 (C-2), 136.9 (C-3), 127.2 (C-6'''), 123.6 (C-4'''), 122.9 (C-4'''), 120.3 (C-5'''), 93.3 (C-1), 72.7 (C-5), 68.5 (C-6), 49.8 (C-1'), 38.2 (C-2'),

25.0 (C-3'), 22.5 & 22.3 (2CH₃ of *i*amyl). MS (ESI): *m/z* 342; found 343 [M+H]⁺; HRMS (DART): Calc for C₁₈H₂₃N₄O₃ [M+H]⁺; 343.1770 ; found 343.1780.

6.5.12. Compound 38

This compound was obtained as a viscous oil; yield (66%); *R_f* = 0.57 (hexane-ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 9:1); [α]_D³¹ = -94.93(c 0.08, CHCl₃); IR (neat, cm⁻¹): 3733, 3437, 2955, 1695, 1367, 1222 ; ¹H NMR (CDCl₃, 300 MHz): δ 7.79 (dd, 3H, H-5'', H-3''' & H-2''', *J* = 9.27 Hz & *J* = 6.21 Hz), 7.10 (t, 2H, H-5''' & H-6''', *J* = 8.64 Hz), 6.87 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.4 Hz), 6.12 (d, 1H, H-3, *J* = 10.3 Hz), 5.22 (d, 1H, H-1, *J* = 3.27 Hz), 5.09 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 3.1 Hz), 4.87 (dd, 1H, H-5, *J* = 7.4 Hz & *J* = 3.1 Hz), 4.63 (dd, 1H, H-6b, *J* = 14.3 Hz & *J* = 7.4 Hz), 3.63-3.44 (m, 2H, H-1'), 1.60-1.53 (m, 1H, H-3'), 1.41-1.34 (m, 2H, H-2'), 0.87-0.76 (m, 6H, 2CH₃ of *i*amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 193.1 (C-4), 147.0 (C-4'''), 144.6 (C-4''), 127.6 (C-2), 127.5 (C-3), 127.2 (C-6''' & C-2'''), 120.8 (C-5''), 116.0 (C-1'''), 115.7 (C-5''' & C-3'''), 93.4 (C-1), 72.8 (C-5), 68.4 (C-1'), 49.7 (C-6'), 38.2 (C-2'), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*amyl). MS (ESI): *m/z* 359; found 360 [M+H]⁺; HRMS (ESI): Calc for C₁₉H₂₃FN₃O₃ [M+H]⁺ ; 360.1723 ; found 360.1710.

6.5.13. Compound 40

This compound was obtained as a viscous oil; yield (75%); *R_f* = 0.47 (hexane-ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 4:1); [α]_D³¹ = -122.58 (c 0.014, CHCl₃); IR (neat, cm⁻¹): 3752, 2957, 2361, 1697, 1219 ; ¹H NMR (CDCl₃, 300 MHz): δ 7.31 (s, 1H, H-5''), 6.84 (dd, 1H, H-2, *J* = 10.3 Hz and *J* = 3.5 Hz), 6.09 (d, 1H, H-3, *J* = 10.3 Hz), 5.19 (d, 1H, H-1, *J* = 3.3 Hz), 4.99 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 2.9 Hz), 4.77 (dd, 1H, H-5, *J* = 7.68 Hz and *J* = 2.97 Hz), 4.51-4.46 (m, 1H, H-6b), 3.60-3.42 (m, 2H, H-1'), 1.96-1.87 (m, 1H, H-1'''), 1.63-1.52 (m, 1H, H-3'), 1.38 (dd, 2H, H-2', *J* = 13.47 Hz & *J* = 6.75 Hz), 0.94-0.79 (m, 10H, 6H of *i*amyl & 4H of H-2''' & H-3'''); ¹³C NMR

(CDCl₃, 75 MHz): δ 193.1 (C-4), 150.3 (C-4''), 144.4 (C-2), 127.1 (C-3), 121.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.3 (C-1'), 38.2 (C-6), 34.0 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2CH₃ of *i*-amyl), 7.7 (C-1'''), 6.7 (C-2''' & C-3'''). MS (ESI): m/z 305; found 306 [M+H]⁺; HRMS (ESI): Calc for C₁₆H₂₄N₃O₃ [M+H]⁺; 306.1818; found 306.1806.

6.5.14. Compound 41

This compound was obtained as a viscous oil; yield (59%); R_f = 0.53 (chloroform-methanol, 97:3); eluent for column chromatography (chloroform-methanol, 99:1); $[\alpha]_D^{31}$ = -18.30 (c 0.15, CHCl₃); IR (neat, cm⁻¹): 3458, 2358, 1696, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 7.82 (dd, 2H, H-8''' & H-7'', J = 5.4 Hz & J = 3.1 Hz), 7.70 (dd, 2H, H-9''' & H-6'', J = 5.37 Hz & J = 3.09 Hz), 7.50 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, J = 10.3 Hz & J = 3.48 Hz), 6.09 (d, 1H, H-3, J = 10.3 Hz), 5.20 (d, 1H, H-1, J = 3.39 Hz), 4.99 (dd, 1H, H-6a, J = 14.4 Hz & J = 3.0 Hz), 4.80 (dd, 1H, H-5, J = 7.71 Hz & J = 3.06 Hz), 4.53 (d, 1H, H-6b, J = 14.4 Hz & J = 7.7 Hz), 3.72 (t, 2H, H-1', J = 6.93 Hz), 3.60-3.35 (m, 2H, H-3'), 2.75 (t, 2H, H-2'', J = 7.5 Hz), 2.09-2.0 (m, 2H, H-1'''), 1.61-1.50 (m, 1H, H-3'), 1.39-1.33 (m, 2H, H-2'), 0.82-0.76 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75 MHz): δ 193.1 (C-4), 168.4 (C-5''' & C-10'''), 146.8 (C-2), 144.5 (C-3), 134.0 (2 \times qC), 132.1 (C-7''' & C-8'''), 127.1 (C-4''), 123.3 (C-6''' & C-9'''), 122.5 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 38.2 (C-3'''), 37.3 (C-2'), 28.3 (C-1'''), 25.0 (C-3'), 23.1 (C-2'''), 22.6 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): m/z 452; found 453 [M+H]⁺; HRMS (ESI): Calc for C₂₄H₂₉N₄O₅ [M+H]⁺; 453.2138; found 453.2314.

6.5.15. Compound 42

This compound was obtained as a viscous oil; yield (62%); R_f = 0.46 (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 21:4); $[\alpha]_D^{31}$ = -54.69 (c 0.017, CHCl₃); IR (neat, cm⁻¹): 3957, 3453, 2926, 2366, 1697, 1225, 1101; ¹H NMR (CDCl₃, 300 MHz): δ 7.66 (d, 2H, H-5'' & H-4'', J = 4.11 Hz), 6.85 (dd, 1H, H-2, J = 10.3 Hz and J = 3.5 Hz), 6.09 (d, 1H, H-2, J = 10.3 Hz), 5.18 (d, 1H, H-1, J = 3.33 Hz), 5.08 (dd, 1H, H-6a, J

= 14.4 Hz & $J = 2.91$ Hz), 4.81 (dd, 1H, H-5, $J = 7.71$ Hz & $J = 2.97$ Hz), 4.59 (dd, 1H, H-6b, $J = 14.37$ Hz & $J = 7.74$ Hz), 3.55-3.42 (m, 2H, H-1'), 0.91-0.80 (m, 9H, 2CH₃ of ⁱamyl); ¹³C NMR (CDCl₃, 75 MHz): δ 193.0 (C-4), 144.5 (C-5''), 133.8 (C-4''), 127.1 (C-2), 124.9 (C-3), 93.2 (C-1), 72.8 (C-5), 68.3 (C-6), 49.4 (C-1'), 38.1 (C-2'), 25.0 (C-3'), 22.5 & 22.4 (2CH₃ of ⁱamyl). MS (ESI): m/z 265; found 266 [M+H]⁺; HRMS (ESI): Calc for C₁₃H₂₀N₃O₃ [M+H]⁺; 266.1505; found 266.1495.

6.6. General method for one pot two step procedure for the preparation of compounds 24, 29, 32 and 39.

6.6.1. Compound 24

To a vigorously stirred solution of azide **4a** (200 mg, 0.829 mmol) in *tert*-butyl alcohol was added the 5-chloropentyne (0.104 mL, 0.994 mmol). The reaction was initiated by the addition of a solution of CuSO₄·5H₂O (41.19 mg, 0.165 mmol) and sodium ascorbate (65.57 mg, 0.331 mmol) in distilled water. The colored suspension formed was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were evaporated *in vacuo* to afford the crude product mixture of **5** which was dissolved in dry DCM followed by the addition of Dess-Martin periodinane (392 mg, 0.918 mmol) at 0 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4 hours). The reaction was quenched by addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **24** as a white solid in 64 % over 2 steps. Mp 61°C - 64°C; $R_f = 0.44$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 22:3); $[\alpha]_D^{31} = -42.14$ (c 0.20,

CHCl₃); IR (neat, cm⁻¹): 3021, 1701, 1216; ¹H NMR (CDCl₃, 300 MHz): δ 7.43 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5 Hz), 6.11 (d, 1H, H-3, *J* = 10.3 Hz), 5.20 (d, 1H, H-1, *J* = 3.2 Hz), 5.03 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 3.0 Hz), 4.81 (dd, 1H, H-5, *J* = 7.6 Hz & *J* = 3.0 Hz), 4.54 (dd, 1H, H-6b, *J* = 14.4 Hz & *J* = 7.6 Hz), 3.62-3.43 (m, 4H, H-3'', H-1'a & H-1'b), 2.87 (t, 2H, H-1''', *J* = 7.3 Hz), 2.20-2.11 (m, 2H, H-2'') 1.60 (pent., 1H, H-3', *J* = 6.7 Hz), 1.43-1.36 (m, 2H, H-2'), 0.85 (d, 3H, CH₃ of ⁱamyl, *J* = 6.7 Hz), 0.82 (d, 3H, CH₃ of ⁱamyl, *J* = 6.6 Hz); ¹³C NMR (CDCl₃, 50MHz): δ 193.0 (C-4), 146.3 (*q*C), 144.4 (C-2), 127.1 (C-3), 122.5 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 44.1 (C-3''), 38.2 (C-2'), 31.9 (C-2'''), 24.9 (C-3'), 22.7 (C-1'''), 22.6 & 22.3 (2 CH₃ of ⁱamyl); MS (ESI): *m/z* 341; found 342 [M+H]⁺. HRMS (DART): Calc for C₁₆H₂₅ClN₃O₃ [M+H]⁺ 342.1584; found 342.1600.

6-triazolyl 2,3,6 trideoxy hex-2- enopyranosid-4-uloses **29**, **32** and **39** were likewise prepared from **4a** via intermediates **10**, **13** and **20** respectively using the same two step procedure as described above for compound **24**.

6.6.2. Compound 29

This compound was obtained as a viscous oil ; yield (63% in 2 steps); *R_f* = 0.57 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 4:1); [*α*]_D³¹ = -18.30 (c 0.13, CHCl₃); IR (neat, cm⁻¹): 3749, 3458, 2358, 1696, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5 Hz), 6.10 (d, 1H, H-3, *J* = 10.3 Hz), 5.19 (d, 1H, H-1, *J* = 3.3 Hz), 5.03 (dd, 1H, H-6a, *J* = 14.5 Hz & *J* = 3.0 Hz), 4.80 (dd, 1H, H-5, *J* = 7.7 Hz & *J* = 3.0 Hz), 4.51 (dd, 1H, H-6b, *J*=14.5Hz & *J*=7.7 Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1''', *J* = 7.5 Hz), 1.64-1.57 (m, 3H, H-2' & H-3'), 1.33-1.25 (m, 12H, H-2'''-H-7'''), 0.91-0.80 (m, 9H, 2CH₃ of ⁱamyl and 1CH₃ of H-8'''); ¹³C NMR (CDCl₃,75MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.4 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.2 (C-1'), 49.4 (C-6), 38.2 (C-2'), 31.9 (C-1'''), 29.7 (C-2'''), 29.6 (C-3'''),

29.4 (C-4'''), 29.3 (C-5''' & C-6'''), 25.7 (C-7'''), 25.0 (C-3'), 22.7 & 22.5 (2CH₃ of *i*amyl), 14.2 (C-8'''); MS (ESI): *m/z* 377; found 378 [M+H]⁺; HRMS (DART): Calc for C₂₁H₃₆N₃O₃ [M+H]⁺; 378.2756; found 378.2758.

6.6.3. Compound 32

This compound was obtained as a viscous oil; yield (48% in 2 steps); *R_f* = 0.51 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 17:3); [α]_D³¹ = -153.09 (*c* 0.02, CHCl₃); IR (neat, cm⁻¹): 3904, 3778, 3388, 3020, 1701, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 10.13 (s, 1H, H-1'''), 8.22 (s, 1H, H-5''), 6.88 (dd, 1H, H-2, *J* = 10.3 Hz and *J* = 3.4 Hz), 6.12 (d, 1H, H-3, *J* = 10.3 Hz), 5.21 (d, 1H, H-1, *J* = 3.2 Hz), 5.11 (dd, 1H, H-6a, *J* = 14.3 Hz & *J* = 3.0 Hz), 4.85 (dd, 1H, H-5, *J* = 7.5 Hz & *J* = 3.03 Hz), 4.67 (dd, 1H, H-6b, *J* = 14.3 Hz, & *J* = 7.56 Hz), 3.58-3.44 (m, 2H, H-1'), 1.63-1.54 (m, 1H, H-3'), 1.41-1.34 (m, 2H, H-2'), 0.84-0.79 (m, 6H, 2CH₃ of *i*amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 192.5 (C-4), 185.1 (C-1'''), 147.9 (C-4''), 144.6 (C-2), 127.1 (C-3), 126.7 (C-5''), 93.4 (C-1), 72.3 (C-5), 68.5 (C-6), 49.9 (C-6), 38.2 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2CH₃ of *i*amyl). MS (ESI): *m/z* 293; found 294 [M+H]⁺; HRMS (DART): Calc for C₁₄H₂₀N₃O₄ [M+H]⁺; 294.1453; found 294.1474.

6.6.4. Compound 39

This compound was obtained as a glassy solid; Yield (57 % in 2 steps); *R_f* = 0.50 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); [α]_D = -26.42 (*c* 0.21, CHCl₃); IR (neat, cm⁻¹): 3020, 1699, 1520, 1216. ¹H NMR (CDCl₃, 300 MHz): δ 7.36 (s, 1H, H-5''), 6.88 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 6.8 Hz), 6.11 (d, 1H, H-3, *J* = 10.3 Hz), 5.20 (d, 1H, H-1, *J* = 3.5 Hz), 5.05 (dd, 1H, H-6a, *J* = 14.5 Hz & *J* = 3.0 Hz), 4.80 (dd, 1H, H-5, *J* = 7.9 Hz & *J* = 3.0 Hz), 4.49 (dd, 1H, H-6b, *J* = 14.5 Hz & *J* = 7.9 Hz), 3.59-3.42 (m, 2H, H-1'a & H-1'b), 3.23-3.15 (m, 1H, H-1'''), 2.10-2.04 (m, 2H, H-2'''a & H-5'''a), 1.75-1.55 (m, 7H, H-2'''b, H-3''', H-4''', H-5'''b and H-3') 1.42-1.32 (m, 2H, H-2'), 0.86

(d, 3H, CH₃ of *i*-amyl, *J* = 6.6 Hz), 0.82(d, 3H, CH₃ of *i*-amyl, *J* = 6.6 Hz); ¹³C NMR (CDCl₃, 75MHz): δ 193.1 (C-4), 152.7 (*q*C), 144.4 (C-2), 127.1 (C-3), 121.0 (C-5"), 93.2 (C-1), 72.9 (C-5), 68.1 (C-1'), 49.4 (C-6), 38.2 (C-2'), 36.7 (C-1'''), 33.3 (C-2'''), 33.2 (C-5'''), 25.1 (C-3''' & C-4'''), 24.9 (C-3'), 22.6 & 22.3 (2 CH₃ of *i*-amyl); MS (ESI): *m/z* 333; found 334 [M+H]⁺; HRMS (DART): Calc for C₁₈H₂₈N₃O₃ [M+H]⁺ 334.2130; found 334.2119.

6.7. General procedure for the preparation of compounds 45 and 46

6.7.1. Compound 45

To a solution of adamantane methanol **43** (997.56 mg, 6 mmol) in 15 mL of anhydrous THF was added NaH (100.80 mg, 4.2 mmol) at 0 °C. After hydrogen was entirely emitted the catalytic amount of tetrabutylammonium iodide (TBAI) and propargyl bromide (1.3 mL, 14.4 mmol) was added, respectively. The mixture was then warmed to room temperature and stirred for an additional 24 hours. The reaction was quenched by ice cold water and then left for stirring for about 15 min. After the completion of reaction it was extracted with ethyl acetate. The combined organic extracts were dried, evaporated and purified by column chromatography to obtain compound **44** (101.53 mg, 0.4978 mmol, 8%) [41]. To a vigorously stirred solution of isoamyl 6-azido-2,3,6-trideoxy-hex-2-enopyranoside **4a** (80mg, 0.3319 mmol) in *tert*-butyl alcohol compound **44** (101.53 mg, 0.4978 mmol) was added. The reaction was initiated by the addition of a solution of CuSO₄·5H₂O (16.52 mg, 0.066 mmol) and sodium ascorbate (26.15 mg, 0.132 mmol) in distilled water. The coloured suspension formed was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were dried evaporated and passed through column to afford pure compound **45** as a viscous oil; yield (80%); *R_f* = 0.57 (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 20:7); [α]_D³¹ = -1.68 (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3763, 3626, 3403, 2915, 2360, 1582, 1219; ¹H NMR

(CDCl₃, 300 MHz): δ 7.67 (s, 1H, H-5''), 5.92 (d, 1H, H-3, J = 9.7 Hz), 5.71 (d, 1H, H-2, J = 10.3 Hz), 4.92 (s, 1H, H-1), 4.74-4.60 (m, 4H, H-4, H-5 & H-6), 3.98 (d, 1H, H-1'''a), 3.84 (s, 1H, H-1'''b), 3.52 (dd, 1H, H-1'a, J = 16.3 Hz & J = 7.1 Hz), 3.41-3.30 (m, 1H, H-5), 3.06 (s, 1H, H-2a'''), 1.94 (s, 4H, 3 \times CH_{Ad} & H-2b'''), 1.68-1.52 (m, 12H, 6 \times CH_{2Ad}), 1.41-1.25 (m, 3H, H-2' & H-3'), 0.87-0.83 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75MHz): δ 142.6 (C-4''), 132.8 (C-3), 126.7 (C-2), 124.0 (C-5''), 94.6 (C-1), 81.6 (C-2'''), 70.7 (C-5), 67.3 (C-1'), 65.2 (C-4), 64.7 (C-1'''), 51.3 (C-6), 39.8 (3CH_{2Ad}), 38.4 (C-2'), 37.3 (3CH_{2Ad}), 29.8 (C_{Ad}) 28.3 (3CH_{Ad}) 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*-amyl). MS (ESI): m/z 445; found 446 [M+H]⁺; HRMS (ESI): Calc for C₂₅H₄₀N₃O₄ [M+H]⁺; 446.3019; found 446.3006.

6.7.2. Compound 46

Compound **45** (121 mg, 0.270 mmol) was dissolved in dry DCM (20 mL) and the temperature of the reaction mixture was lowered to 0 °C. DMP (173.34 mg, 0.406 mmol) was added to the reaction mixture. Subsequently the reaction mixture was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **46** as a viscous oil; yield (54 %); R_f = 0.48 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31}$ = -30.95 (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3772, 3398, 2927, 2364, 1724, 1593, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.60 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, J = 10.3 Hz & J = 3.5 Hz), 6.10 (d, 1H, H-3, J = 10.3 Hz), 5.20 (d, 1H, H-1, J = 3.4 Hz), 5.06 (dd, 1H, H-6a, J = 14.4 Hz & J = 3.0 Hz), 4.83 (dd, 1H, H-5, J = 7.71 Hz & J = 3.0 Hz), 4.58 (d, 3H, H-6b & H-1''', J = 4.32 Hz),

3.62-3.54 (m, 2H, H-1'), 3.05 (s, 2H, H-2'''), 1.94 (s, 4H, 3×CH_{Ad} & 1H of CH_{2Ad}) 1.68-1.55 (m, 12H, 1H of CH_{2bAd} & 5×CH_{2Ad} & H-3'), 1.44-1.32 (m, 2H, H-2'), 0.85-0.80 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 193.0 (C-4), 146.1 (C-4''), 144.5 (C-2), 127.1 (C-3), 123.6 (C-5''), 93.3 (C-1), 81.6 (C-2'''), 72.8 (C-5), 68.2 (C-1'), 65.2 (C-1'''), 49.6 (C-6), 39.7 (3CH_{2Ad}), 38.2 (C-2'), 37.3 (3CH_{2Ad}), 28.3 (C_{Ad} & 3CH_{Ad}), 25.01 (C-3'), 22.6 & 22.4 (2CH₃ of *i*-amyl). MS (ESI): m/z 443; found 444 [M+H]⁺; HRMS (DART): Calc for C₂₅H₃₈N₃O₄ [M+H]⁺; 444.2862; found 444.2845.

6.7. General procedure for the preparation of bis triazolyl compounds 48, 50 and 51

6.7.1. Compound 48

To a solution of compound **15** (250 mg, 0.6702 mmol) in DMF was added NaN₃ (174.25 mg, 2.6808 mmol) and the reaction mixture was allowed to stirred under reflux (90 °C-100 °C) for 3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with dichloromethane (5×8 mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated to yield crude product of compound **47** which was used for the next step as such without further purification. To a vigorously stirred solution of azide **47** (108 mg, 0.3214 mmol) in *tert*-butyl alcohol, cyclopropyl acetylene (0.0407 mL, 0.4821 mmol) was added. The reaction was initiated by the addition of a solution of CuSO₄·5H₂O (16.03 mg, 0.064 mmol) and sodium ascorbate (25.35 mg, 0.128 mmol) in distilled water. The colored suspension was formed and the reaction mixture was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were dried, evaporated and passed through a column to afford pure compound **48**. This compound was obtained as a viscous oil; yield (62 %); R_f = 0.53 (CHCl₃-methanol, 1:10); eluent for column chromatography (CHCl₃-methanol, 10:0.1); [α]_D³¹ = -47.91 (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3745, 2923, 2360, 1602, 1219; ¹H NMR

(CDCl₃, 300 MHz): δ 7.36 (s, 1H, H-5''), 7.14 (s, 1H, H-7'''), 5.91(d, 1H, H-3, J = 10.0 Hz), 5.69 (d, 1H, H-2, J = 10.5 Hz), 4.91 (s, 1H, H-1), 4.64 (t, 4H, H-6 & H-2''', J = 7.44 Hz), 3.96 (t, 1H, H-5, J = 4.71 Hz), 3.75 (d, 1H, H-4, J = 8.94 Hz), 3.51 (dd, 1H, H-1'a, J = 16.38 Hz & J = 7.44 Hz), 3.42-3.29 (m, 3H, H-1'b & H-1'''), 1.90-1.81 (m, 1H, H-8'''), 1.68-1.56 (m, 1H, H-3'), 1.41-1.32 (m, 4H, H-2', H-9'''a, H-10'''a), 0.92-0.78 (m, 8H, 2CH₃ of *i*-amyl & 2H of H-9'''b & 10'''b); ¹³C NMR (CDCl₃, 75 MHz): δ 150.2 (C-6'''), 143.2 (C-4''), 133.0 (C-3), 126.5 (C-2), 123.9 (C-5''), 120.4 (C-7'''), 94.6 (C-1), 70.5 (C-5), 67.3 (C-1'), 64.3 (C-4), 51.3 (C-2'''), 49.3 (C-6), 38.4 (C-2'), 29.8 (C-1'''), 25.1 (C-3'), 22.7 & 22.4 (2CH₃ of *i*-amyl), 7.80 (C-8'''), 6.68 (C-9''' & C-10'''). MS (ESI): m/z 402; found 425 [M+Na]⁺; HRMS (ESI): Calc for C₂₀H₃₁N₆O₃ [M+H]⁺; 403.2458; found 403.2448.

6.7.2. Compound 50

To a solution of the compounds **48** (80 mg, 0.199 mmol) in dry chloroform (CHCl₃) taken in a round bottom flask fitted with a guard tube was added activated MnO₂ (342.28 mg, 3.98 mmol) in 2-3 instalments at intervals of 8-9 h and the reaction mixture was allowed to stir at room temperature for the requisite time (20-30 hours). After completion (TLC), the reaction mixture was filtered over a bed of celite. The celite bed was washed with CHCl₃ a number of times. The filtrate and washings were then concentrated *in vacuo* to obtain the crude product. The crude product was chromatographed to yield the pure compound **50** as a viscous oil; yield (49%); R_f = 0.51 (chloroform-methanol, 1:10); eluent for column chromatography (chloroform-methanol, 10:0.2); $[\alpha]_D^{31}$ = +1.48 (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3957, 3745, 2923, 2360, 1602, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.30 (s, 1H, H-5''), 7.14 (s, 1H, H-7'''), 6.86 (d, 1H, H-2, J = 10.3 Hz & J = 3.5 Hz), 6.09 (d, 1H, H-3, J = 10.3 Hz), 5.19 (d, 1H, H-1, J = 3.42 Hz), 4.79 (dd, 1H, H-6a, J = 7.08 Hz & J = 3.1 Hz), 4.60 (dd, 1H, H-5, J = 10.2 Hz & J = 6.9 Hz), 4.55 (t, 3H, H-6b, H-2'''), 3.60-3.46 (m, 2H, H-1'), 3.30 (t, 2H, H-1'', J = 6.90 Hz), 1.91-1.86 (m, 1H, H-8'''), 1.65-1.56 (m, 1H, H-3'), 1.43-1.34 (m, 4H, H-2',

H-9'''a& H-10'''a), 0.95-0.79 (m, 8H, 6H of *i*-amyl & 2H of H-9'''b & H-10'''b); ¹³C NMR (CDCl₃,75MHz): δ 193.0 (C-4), 151.1 (C-6'''), 144.5 (C-4''), 143.3 (C-2), 127.1 (C-3), 123.5 (C-5''), 120.3 (C-7'''), 93.3 (C-1), 72.7 (C-5), 68.3 (C-1'), 49.6 (C-2'''), 49.3 (C-6), 38.2 (C-1'''), 29.8 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2CH₃ of *i*-amyl), 7.80 (C-8'''), 6.72 (C-9''' & C-10'''). MS (ESI): m/z 400; found 401 [M+H]⁺; HRMS (ESI): Calc for C₂₀H₂₉ N₆O₃ [M+H]⁺ ; 401.2301 ; found 401.2305.

6.7.3. Compound 51

To a solution of compound **15** (250 mg, 0.6702 mmol) in DMF was added NaN₃ (174.25 mg, 2.6808 mmol) and the reaction mixture was allowed to stirred under reflux (90 °C-100 °C) for 3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with dichloromethane (5x8 mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated to yield crude product of compound **47** which was used for the next step as such without further purification. To a vigorously stirred solution of azide **47** (110 mg, 0.327 mmol) in *tert*-butyl alcohol, Phenyl acetylene (0.053 mL, 0.4905 mmol) was added. The reaction was initiated by the addition of a solution of CuSO₄.5H₂O (16.22 mg, 0.0654 mmol) and sodium ascorbate (25.91 mg, 0.131 mmol) in distilled water. The colored suspension was formed and the reaction mixture was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were evaporated *in vacuo* to afford the crude product mixture of **49** , which was dissolved in dry chloroform (CHCl₃), followed by the addition of activated MnO₂ (392.16 mg, 4.56 mmol) in 2-3 instalments at intervals of 8-9 h and the reaction mixture was allowed to stir at room temperature (RT) for the requisite time (20-30 hours). After completion (TLC), the reaction mixture was filtered over a bed of celite. The celite bed was washed with CHCl₃ a number of times. The filtrate and washings were then concentrated

in vacuo to obtain the crude product. The crude product was chromatographed to yield the pure compound **51** as a viscous oil; yield (50% in 2 steps); $R_f = 0.55$ (chloroform-methanol, 10:1); eluent for column chromatography (chloroform-methanol, 49:1); $[\alpha]_D^{31} = -7.91$ (c 0.02, CHCl_3); IR (neat, cm^{-1}): 3872, 3745, 2923, 2360, 1602, 1219; ^1H NMR (CDCl_3 , 300 MHz): δ 7.77 (d, 2H, H-8''' & H-13''', $J = 7.29$ Hz), 7.64 (s, 1H, H-5''), 7.41 (t, 2H, H-10''' & H-12''', $J = 7.14$ Hz), 7.32 (t, 2H, H-7''' & H-11'''), 6.72 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 5.99 (d, 1H, H-3, $J = 10.3$ Hz), 5.1 (d, 1H, H-1, $J = 3.24$ Hz), 4.89 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 3.2$ Hz), 4.80-4.74 (m, 3H, H-6b, H-5, & H-2'''a), 4.60 (dd, 1H, H-2'''b, $J = 6.7$ Hz & $J = 14.0$ Hz), 3.60-3.52 (m, 1H, H-1'''a), 3.39 (t, 3H, H-1'''b, H-1', $J = 6.7$ Hz), 1.61-1.50 (m, 1H, H-3'), 1.42-1.37 (m, 2H, H-2'), 0.87-0.79 (m, 6H, 2 CH_3 of *i*-amyl); ^{13}C NMR (CDCl_3 , 75 MHz): δ 193.0 (C-4), 151.1 (C-6'''), 144.5 (C-4''), 143.3 (C-2), 130.9 (C-3), 128.9 (C-10''' & C-12'''), 125.7 (C-9''' & C-13'''), 125.7 (C-8'''), 120.4 (C-5'''), 120.3 (C-7'''), 114.1 (C-11'''), 93.2 (C-1), 73.7 (C-5), 68.2 (C-1'), 58.4 (C-2'''), 49.4 (C-6), 38.2 (C-2'), 29.7 (C-1'''), 25.0 (C-3'), 22.7 & 22.6 (2 CH_3 of *i*-amyl).). MS (ESI): m/z 436; found 437 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{23}\text{H}_{29}\text{N}_6\text{O}_3$ $[\text{M}+\text{H}]^+$; 437.2301 ; found 437.2305.

6.8. General procedure for the preparation of 1,5 triazolyl compounds **52** and **53**

6.8.1. Compound **52**

To a stirred solution of azide **4a** (150 mg, 0.622 mmol) in dry toluene was added decyne (0.107 mL, 0.9336 mmol). The reaction was initiated by the addition of a catalyst $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (4.956 mg, 0.00622 mmol) and it continued for 3 h at 80 °C. The combined organic extracts were dried, evaporated & passed through a column to afford pure compound **52** as a viscous oil; yield (81%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -2.71$ (c 0.08, CHCl_3); IR (neat, cm^{-1}): 3775, 3399, 2925, 2358, 1634, 1459, 1244, 1030; ^1H NMR (CDCl_3 , 300 MHz): δ 7.44 (s, 1H, H-5''), 5.94 (d, 1H, H-3, $J = 10.2$ Hz), 5.67 (d, 1H, H-2, $J = 10.2$ Hz), 4.85 (s, 1H, H-1), 4.58

(t, 2H, H-4 & H-6a, $J = 3.39$ Hz), 3.98 (dd, 2H, H-6b & H-5, $J = 12.0$ Hz & $J = 5.3$ Hz), 3.42-3.30 (m, 2H, H-1'), 2.71 (t, 2H, H-1'', $J = 7.4$ Hz), 1.69-1.53 (m, 1H, H-3'), 1.39-1.25 (m, 14H, H-2'''-H-7''' & H-2'), 0.88-0.83 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-8'''); ¹³C NMR (CDCl₃, 75 MHz): δ 146.4 (C-5''), 132.3 (C-4''), 131.9 (C-3), 126.3 (C-2), 94.5 (C-1), 71.3 (C-5), 67.1 (C-1'), 65.0 (C-4), 48.6 (C-6), 38.4 (C-2'), 32.0 (C-1'''), 31.9 (C-2'''), 29.8 (C-3'''), 29.5 (C-4'''), 29.4 (C-5'''), 29.3 (C-6'''), 28.2 (C-7'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*-amyl), 14.2 (C-8'''). MS (ESI): m/z 379; found 380 [M+H]⁺; HRMS (DART): Calc for C₂₁H₃₈N₃O₃ [M+H]⁺; 380.2903; found 380.2913.

6.8.2. Compound 53

To a solution of **52** (217 mg, 0.5725 mmol) in dry DCM (20 mL) was added Dess-Martin periodinane (DMP) reagent (367 mg, 0.858 mmol) at -5 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4 hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **53** as a viscous oil; yield (61%); $R_f = 0.57$ (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 10:1); $[\alpha]_D^{31} = +24.52$ (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3951, 3396, 1636, 1220; ¹H NMR (CDCl₃, 300 MHz): δ 7.40 (s, 1H, H-5''), 6.83 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.4$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.12 (d, 1H, H-1, $J = 3.3$ Hz), 4.97-4.91 (m, 2H, H-5 & H-6a), 4.34 (dd, 1H, H-6b, $J = 15.0$ Hz & $J = 9.7$ Hz), 3.34 (dd, 2H, H-1', $J = 12.3$ Hz & $J = 6.8$ Hz), 2.63 (dd, 2H, H-1'', $J = 12.8$ Hz & $J = 7.7$ Hz), 1.66-1.57 (m, 2H, H-2'), 1.55-1.51 (m, 1H, H-3'), 1.33-1.22 (m, 12H, H-2'''-H-7'''), 0.85-0.75 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-8'''). ¹³C NMR

(CDCl₃, 75 MHz): δ 193.3 (C-4), 144.3 (C-2), 138.6 (C-5"), 131.8 (C-4"), 127.1 (C-3), 93.1 (C-1), 73.1 (C-5), 68.1 (C-6), 46.9 (C-1'), 38.1 (C-2'), 31.8 (C-1'''), 29.7 (C-2'''), 29.3 (C-3'''), 29.2 (C-4'''), 29.2 (C-5'''), 28.1 (C-6'''), 25.0 (C-3'), 22.7 (C-7'''), 22.5 & 22.4 (2CH₃ of *i*-amyl), 14.1 (C-8'''). MS (ESI): *m/z* 377; found 378 [M+H]⁺; HRMS (ESI): Calc for C₂₁H₃₆N₃O₃ [M+H]⁺; 378.2757; found 378.2755.

6.9. Biological Assay

6.9.1. In vitro antibacterial and antifungal activity assay

All the prepared 2,3,6-trideoxy sugar-triazole conjugates were evaluated for their *in vitro* antibacterial activity against *S. aureus* (ATCC 25923), *E. coli* (ATCC 9637), *P. aeruginosa* (ATCC BAA-427), *K. pneumoniae* (ATCC 27736) and antifungal activity against *C. albicans* (Ca), *A. fumigatus* (Af), *C. neoformans* (Cn), *S. schenckii* (Ss), and *T. mentagrophytes* (Tm). In this process, the minimum inhibitory concentration of compounds was tested according to the standard microbroth dilution technique as per guidelines of National Committee for Clinical Laboratory Standards.[42,43] Briefly, testing was performed in flat-bottomed 96-well tissue culture plates (CELLSTAR* Greiner bio-one GmbH, Germany) in RPMI 1640 medium buffered with MOPS (3-[N-morpholino] propanesulfonic acid) (Sigma–Aldrich Chemical Co., St. Louis, MO, USA) for fungal strains and in Muller Hinton broth (Titan Biotech Ltd, India) for bacterial strains. The concentration range of test compounds was 50–0.36 and 32–0.0018 μ g/mL for standard compounds. Initial inocula of fungal and bacterial strains were maintained at 1–5 $\times 10^3$ cells/mL. These plates were incubated in a moist chamber at 35 °C, and an absorbance at 492 nm was recorded on a Versa Max microplate reader (Molecular devices, Sunnyvale, USA) after 24 hours for bacterial strains, 48 hours for *C. albicans* (Ca) and 72 hours for *A. fumigatus* (Af), *C. neoformans* (Cn), *S. schenckii* (Ss) and 96 hours for *T. mentagrophytes* (Tm). The MICs were determined as

90% inhibition of growth with respect to the growth control as observed using SOFT-max Pro 4.3 Software (Molecular Devices, Sunnyvale, USA).

6.9.2. Cytotoxicity assay

The cytotoxicity of compounds **24**, **26**, **27**, **28**, **29**, **32**, **35**, **36**, **38**, **46** and **53** against mammalian cells, mouse fibroblast cell line L929 was tested as follows. Stock solutions (1 mg/mL) of the test compounds were prepared in DMSO. The cell line L929 was grown in DMEM medium supplemented with 10% FBS and 1 × antimycotic and antibacterial solution (sigma USA) at 37 °C in humidified atmosphere having 5% CO₂. One hundred ml (1×10³ cells in DMEM) of the confluent fibroblast stock suspension (1×10⁵ cells/ml) was dispensed in 96-well tissue culture plate. The original medium from the wells was replaced with 100 mL serum free DMEM when the cells reached 90% confluency after 5 hours of incubation in a CO₂ incubator. Various concentrations of the test compounds (25, 12.5, 6.25, 3.12, 1.56, 0.78, 0.39, 0.19, 0.09 mg/ml) were added to the growing cells and incubated for 24 hours. Response of L929 cells to the test compounds was determined spectrophotometrically at 570 and 630 nm. The difference between absorbance at 570 and 630 nm was used as an index of the cell viability.[44]

(A570 - A630) sample

----- × 100

(A570 - A630) control

The morphology of the cells was observed using Giemsa stain under Phase contrast microscope. After fixation of the cells in the wells of 96-well tissue culture plate, Geimsa stain was added to each well and incubated for 30 min at 37 °C. The excess stain was removed by thorough washing with PBS and the culture plates were air dried and observed under a phase contrast microscope.

7.0. Bioinformatics and Modeling studies

The structures of the compounds were compared for their similarity with the ligands of well known antibacterial targets. This has led to the identification of hydrolase and penicillin binding proteins (PBPs) as potential enzyme classes for the new compounds. The exploration has included pdb 3D4F, 3RKJ, 1BLH, 2YZ3 and 1KO3 for hydrolase and pdb 4DKI, 3VSL, 3HUN, 3MZE and 3PBR for penicillin binding proteins. Trial docking studies with these enzymes suggested that PBP-2 as most appropriate target of these compounds. Also similar to reference compounds, the synthesized compounds showed interaction with conserved serine residues of PBP.[45] Following this Basic Local Alignment Search Tool (BLAST: <http://blast.ncbi.nlm.nih.gov/Blast.cgi>) were used to find out the similarity of PBP-2 between different strains of bacteria. The molecular docking study was carried out in SYBYLX 1.3.[46] For docking experiment, the penicillin binding protein 2 of *Staphylococcus aureus* (PDB: 4DKI) was prepared by adding hydrogen atoms, fixing side chain amides and applying Gastregial-Huckle charges. Followed by this, energy of the protein was minimized by the Powell method using Tripos force field with a distance dependent dielectric constant of 1.0 and non-bonding interaction cut-off of 8.0Å and iterations up to 1000 (convergence criteria 0.001 kcal/mol.Å). Using automated based option procedures, the binding pocket was generated in the Protomol module of SYBYLX 1.3. The energy minimized standard inhibitors and synthesized compounds were docked using Surflex-Dock-Geom X docking mode into the pockets of selected target. The best docking poses of the compounds were selected based on the crash and polar and total scores. The best docked conformation was used for site directed residue interaction analysis and visualization in Pymol and SYBYLX 1.3.

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Supplementary data:

Experimental procedures, spectroscopic data of synthesized compounds, biological assay and bioinformatics & modeling studies, ^1H , ^{13}C NMR and HRMS spectra

References

- [1] M.S. Butler, M.A. Cooper, J. Antibiot. 64 (2011) 413-425.
- [2] P.C. Appelbaum, J. Antimicrob. Chemother. 67 (2012) 2062-2068.
- [3] B. Spelberg, R. Guidos, D. Gilbert, J. Bradley, H.W. Boucher, W.M. Scheld, J.G. Bartlett, J. Jr. Edwards, Clin. Infect. Dis. 46 (2008) 155-164.
- [4] L.L. Silver, Clin. Microbiol. Rev. 24 (2011) 71-109.
- [5] T.R. Walsh, M.A. Toleman, J. Antimicrobial. Chemother. 67 (2012) 1-3.
- [6] Bedaquiline Medline Plus Drug Information: <http://www.nlm.nih.gov/medlineplus/druginfo/meds/a613022.html> (accessed on 08-09-2013).
- [7] N. Tani, M. Rahnasto-Rilla, C. Wittekindt, K.A. Salminen, A. Ritvanen, R. Ollakka, J. Koskiranta, H. Raunio, R.O. Juvonen, Eur. J. Med. Chem. 47 (2012) 270-277.
- [8] Y. Niu, S. Padhee, H. Wu, G. Bai, Q. Qiao, Y. Hu, L. Harrington, W.N. Burda, L.N. Shaw, C. Cao, J. Cai. J. Med. Chem. 55 (2012) 4003-4009.
- [9] C. Viegas-Junior, A. Danuello, V. da Silva Bolzani, E.J. Barreiro, C.A. Fraga, Curr. Med. Chem. 14 (2007) 1829-1852.

- [10] Z. Qiao, Q. Wang, F. Zhang, Z. Wang, T. Bowling, B. Nare, R.T. Jacobs, J. Zhang, D. Ding, Y. Liu, H. Zhou, *J. Med. Chem.* 55 (2012) 3553-3557.
- [11] R. Dosselli, M. Gobbo, E. Bolognini, S. Campestrini, E. Reddi, *ACS Med. Chem. Lett.* 1 (2010) 35-38.
- [12] S.N. Patpi, L. Pulipati, P. Yogeewari, D. Sriram, N. Jain, B. Sridhar, R. Murthy, A. Devi, T.S.V. Kalivendhi, and S. Kantevari, *J. Med. Chem.* 55 (2012) 3911-3922.
- [13] M.P. Georgiadis, E.A. Couladouros, A.K. Delitheos, *J. Pharm. Sci.* 81 (1992) 1126-1131.
- [14] E.A. Couladouros, A.T. Strongilos, *Angew. Chem. Int. Ed. Engl.* 41 (2002) 3677-3680.
- [15] M. Saquib, M.K. Gupta, R.Sagar, Y.S. Prabhakar, A.K. Shaw, R. Kumar, P.R. Maulik, A.N. Gaikwad, S. Sinha, A.K. Srivastava, V. Chaturvedi, R. Srivastava, B.S. Srivastava, *J. Med. Chem.* 50 (2007) 2942-2950.
- [16] S. Nagarajan, P. Arjun, N. Raaman, A. Shah, M.E. Sobhia, T.M. Das, *Tetrahedron*, 68 (2012) 3037-3045.
- [17] M. Namikoshi, R. Negishi, H. Nagai, A. Dmitrenok and H. Kobayashi, *J. Antibiot.* 56 (2003) 755-761.
- [18] M. Saquib, I. Husain, S. Sharma, G. Yadav, V.K. Singh, S.K. Sharma, P. Shah, M.I. Siddiqi, B. Kumar, J. Lal, G. K. Jain, B.S. Srivastava, R. Srivastava, A.K. Shaw, *Eur. J. Med.* 46 (2011) 2217-2223.
- [19] The most active anti-tubercular compound (S007-724, MIC, 0.78µg/mL) reported in ref.18 showed very mild activity against bacterial and fungal strains used in the current study (*S. aureus*, MIC 12.5µg/mL; *K. pneumoniae*, MIC 50µg/mL; *E. Coli*, MIC >50µg/mL; *P. aeruginosa*, MIC >50µg/mL; *C. albicans*, MIC 50µg/mL; *C. neoformans*, MIC 50µg/mL; *S.*

schenckii, MIC 12.5µg/mL; *T. mentagrophytes*, MIC 0.78µg/mL; *A. fumigatus*, MIC >50µg/mL).

- [20] M. Meldel, C.W. Tornøe. *Chem. Rev.* 108 (2008) 2952-3015.
- [21] R. Dhondikubeer, S. Bera, G.G. Zhanel, and F. Schweizer, *J. Antibiot.* 65 (2012) 495-498.
- [22] S. Bera, G.G. Zhanel, F. Schweizer, *Bioorg Med. Chem. Lett.* 20 (2010) 3031-3035.
- [23] X-L. Wang, K. Wan, C-H. Zhou, *Eur. J. Med. Chem.* 45 (2010) 4631-4639.
- [24] V. D. Bock, D. Speijer, H. Hiemstra, and J.H. Van Maarseveen, *Org. Biomol. Chem.* 5 (2007) 971-975.
- [25] V.K. Tiwari, R.C. Mishra, A. Sharma, R.P. Tripathi, *Mini Rev Med Chem.* 12 (2012) 1497-1519
- [26] D.C. Crick, S. Mahapatra, P.J. Brennan, *Glycobiology*, 11 (2001) 107-118.
- [27] B. Cao, J.M. White, S.J. Williams, *Beilstein J. Org. Chem.* 7 (2011) 369-377.
- [28] D.T.G. Gonzaga, D.R. da Rocha, F.C. da Silva, V. F. Ferreira, *Curr. Topics Med. Chem.* 13 (2013) 2850-2865.
- [29] B.L. Wilkinson, H. Long, E. Sim, A.J. Fairbanks, *Bioorg. Med. Chem. Lett.* 18 (2008) 6265-6267.
- [30] B.K. Singh, A.K. Yadav, B. Kumar, A. Gaikwad, S.K. Sinha, V. Chaturvedi, R.P. Tripathi, *Carbohydr. Res.* 343 (2008) 1153-1162.
- [31] T. Amaya, D. Takahashi, H. Tanaka, T. Takahashi, *Angew. Chem. Int. Ed.* 42 (2003) 1833-1836 and references cited therein.
- [32] M.B. Yunker, S.Y-K. Hicks, B. Fraser-Reid, *Can. J. Chem.* 54 (1976) 2411-2416.
- [33] E.J. Lien, C. Hansch, *J. Med Chem.* 11 (1968) 430-431.
- [34] I. Kubo, H. Muroi, M. Himejima, A. Kubo. *Bioorg. Med. Chem. Lett.* 3 (1993) 1305-1308.

- [35] O. Andrzej, K. Beata, G. Orzeszko, B.J. Starosciak, *Farmaco* 11. 55 (2000) 619–623.
- [36] B. Orzeszko, A.E. Laudy, B.J. Starosciak, A. Orzeszko, Z. Kazimierczuk, *Acta. Polo. Pharm.* 61 (2004) 455-460.
- [37] L. Wanka, K. Iqbal and P.R. Schreiner, *Chem. Rev.* 113 (2013) 3516-3604.
- [38] Li. Zhang, X. Chen, P. Xue, H.Y. Sun, 2005. *J. Am. Chem. Soc.* 127 (2005) 15998-15999.
- [39] A.L. Lovering, M.C. Gretes, S.S. Safadi, F. Danel, L. de Castro, M.G.P. Page, N.C.J. Strynadka, *J. Biol. Chem.* 287 (2012) 32096-32102.
- [40] Q-Y. Sun, J-M. Xu, Y-B. Cao, W-N. Zhang, Q-Y. Wu, D-Z. Zhang, J. Zhang, H-Q Zhao, Y-Y. Jiang, *Eur. J. Med. Chem.* 42 (2007) 1226-1233.
- [41] Robinson, A.; Messbah, J.; Smith, T and Foroozech, M.; *J. Undergrad. Chem. Res.* 1 (2002) 157–159.
- [42] P. A.Villanova, *Approved standard*, 5th ed.; National Committee for Clinical Laboratory Standards.: 2000, pp M7-A5.
- [43] N. Yamamotoa, J. Fujita, T. Shintazo, F. Higa, M. Tateyamaa, M. Tohyamaa, I. Nakasone, N. Yamaned, *Int. J. Antimicrob. Agents.* 27 (2006) 171–173.
- [44] H. Liu, J. Chenb, J. Jiang, J. P. Giesy, H. Yua, X. Wang, *Environ. Toxicol Pharmacol.* 26 (2008) 309–314.
- [45] M. P. van der Linden, L. de Haan, O. Dideberg, W. Keck, *Biochem J.* 303 (1994) 357-62.
- [46] SYBYL-X 1.3, Tripos International, St Louis, Missouri, USA.


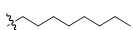
Figure legends

Figure 1. Binding Poses of ampicillin (grey) and compound **29** (green) in ball-and-stick mode in the active site of PBP-2 (4DKI). The residues (Ser-403, Thr 444, Tyr-446, Ser-462, Thr-600, Ala 642 and Asn 464) surrounding the pocket are shown in stick mode. The dashed yellow lines represent selected H-bond interactions between the residues and the ligand/compound. In order to signify the binding pocket, it is shown in surface view mode with cavity depth.

Figure 2. (A) Normal growth of mammalian cell L929. (B) Morphological changes in mammalian cells L929 at MIC of compounds ($\text{MIC} \leq 3.12 \mu\text{g/mL}$). (C) Morphological changes in mammalian cells L929 at $50 \mu\text{g/mL}$ of compounds. (D) Viability (determined by MTT assay) of mammalian cells L929 exposed to compounds **24, 26, 27, 28, 29, 32, 35, 36, 38, 46** and **53**.

Table 1. Sugar-triazole conjugates, their CLogP values and antibacterial activities.

Comp	R ₂	CLog P ^a	Sa (MR				
			Sa ^b	and VR) ^b	Kp ^b	Ec ^b	Pa ^b
10		4.658	>50	>50	>50	>50	>50
24		1.232	1.56	6.25	3.12	50	50
25		0.703	12.5	>50	50	>50	>50
26		0.833	12.5	>50	>50	>50	>50
27		2.577	3.12	6.25	3.12	>50	>50
28		3.106	3.12	6.25	1.56	>50	>50
29		4.164	0.78	3.12	0.78	>50	>50
30		3.765	6.25	>50	>50	>50	>50
31		0.601	>50	>50	50	>50	>50
32		0.124	50	>50	50	50	50
33		2.244	12.5	>50	12.5	50	50
34		0.843	12.5	>50	50	>50	>50
35		1.788	1.56	12.5	>50	>50	>50
36		2.290	6.25	12.5	3.12	50	50
37		1.175	6.25	12.5	6.25	>50	>50
38		2.470	0.78	3.12	>50	>50	>50
39		2.023	50	>50	50	50	50
40		0.905	6.25	>50	>50	>50	>50
41		1.810	6.25	25	>50	>50	>50
42	H	0.192	25	>50	>50	50	>50

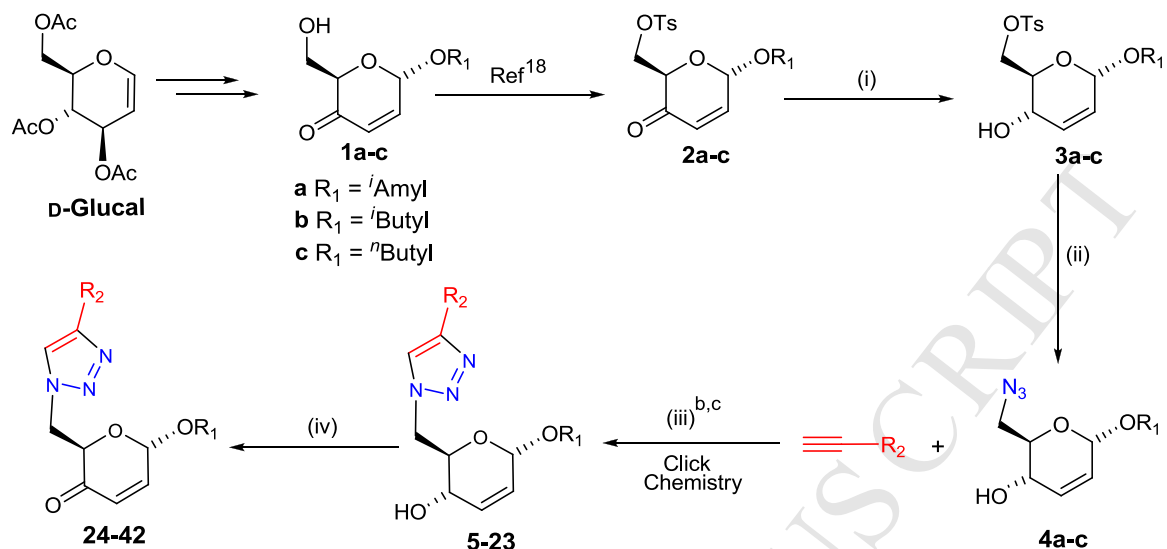
46		4.168	1.56	3.12	0.78	50	50
50		0.1002	25	>50	>50	>50	>50
51		1.485	50	>50	>50	>50	>50
53 ^c		4.164	0.78	12.5	50	>50	>50
	Ciprofloxacin		0.09	0.38	0.01	0.01	0.09
	Gentamycin		0.39	1.56	1.56	1.56	0.39
	Ampicillin		12.5	0.78	12.5	50	>50
	Vancomycin		12.5	-	12.5	12.5	>50
	Methicillin		0.04	-	6.25	50	>50

^aCLogP calculated by Chemdraw Ultra 10.0 software. ^b*Staphylococcus aureus* (Sa), methicillin- and vancomycin-resistant (MR and VR) Sa, *Klebsiella pneumoniae* (Kp), *Escherichia Coli* (Ec), *Pseudomonas aeruginosa* (Pa); Antibacterial activity as MIC in µg/mL. ^cCompound **53** is 1,5- disubstituted analogue of compound **29**.

Table 2. Sugar-triazole conjugates and their antifungal activities.

Comp	Ca ^a	Af ^a	Cn ^a	Ss ^a	Tm ^a
10	>50	>50	25	>50	50
24	25	50	50	12.5	50
25	50	>50	>50	50	>50
26	25	>50	50	3.12	0.39
27	>50	>50	>50	12.5	3.12
28	>50	>50	>50	25	12.5
29	>50	>50	>50	50	3.12
30	6.25	>50	25	25	6.25
31	>50	>50	>50	12.5	25
32	>50	25	50	25	3.12
33	>50	25	50	12.5	25
34	12.5	50	12.5	25	6.25
35	25	>50	25	12.5	>50
36	12.5	50	25	12.5	50
37	>50	>50	>50	25	12.5
38	6.25	50	50	6.25	1.56
39	25	50	50	50	50
40	12.5	>50	25	12.5	6.25
41	25	>50	50	50	25
42	50	>50	50	>50	>50
46	>50	1.56	50	50	1.56
50	50	>50	50	>50	>50
51	50	>50	50	50	50
53	50	>50	25	6.25	25
Clotrimazole	0.25	8	0.25	4	2
Flucanazole	1.00	>32	2.00	4	16
5-Fluorocytosine	0.25	>32	0.13	>32	>32
Miconazole	25	12.5	12.5	3.12	0.78

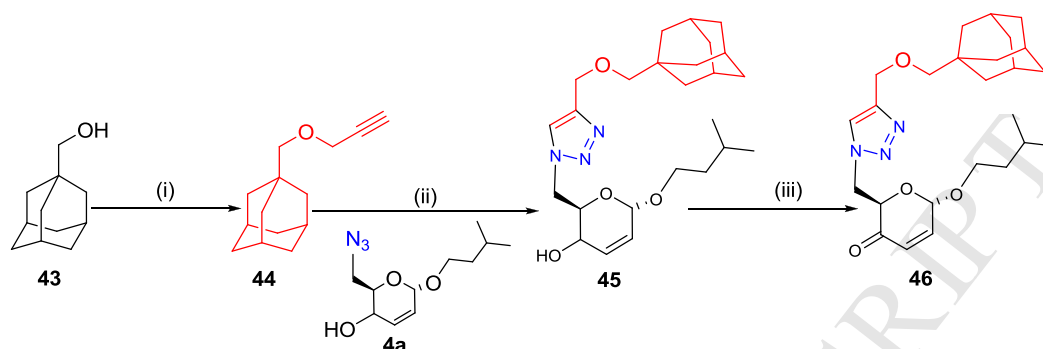
^aCandida albicans (Ca); Cryptococcus neoformans (Cn); Sporothrix schenckii (Ss); Trichophyton mentagrophytes (Tm); Aspergillus fumigatus (Af); Antifungal activity as MIC in µg/mL.

Scheme 1. General synthetic strategy^a

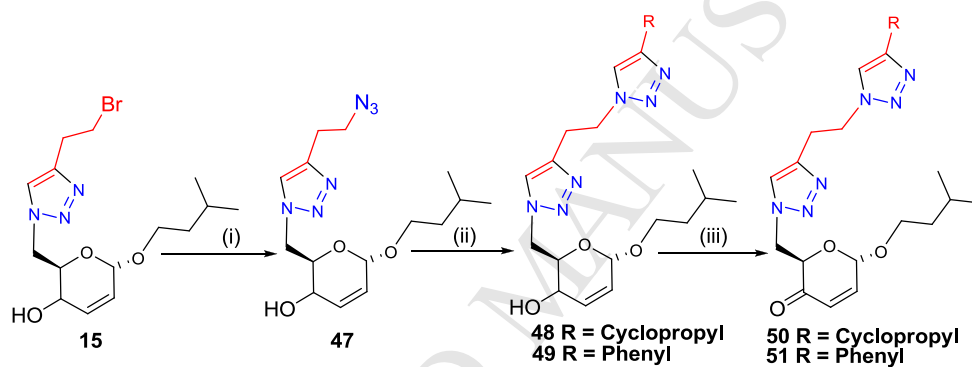
^a**Reagents and Conditions:** (i) NaBH_4 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, EtOH , 1 hour, $0 \rightarrow 10^\circ\text{C}$ (ii) NaN_3 , DMF , 2-5 h, $80-120^\circ\text{C}$, yield:~ 60% (iii) Sodium ascorbate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $t\text{BuOH}:\text{H}_2\text{O}$, yield:~75% (^bFor compound **22** and **23** $\text{MeOH}:\text{H}_2\text{O}$ was used as solvent. ^cIn case of preparation of compound **23** K_2CO_3 was also used along with other reagents) (iv) DMP , DCM , 3-6 hours, $-5-10^\circ\text{C}$, yield: ~50%; for compound **6**, **25** $R_1 = i\text{Butyl}$ and **7**, **11**, **26**, **30** $R_1 = n\text{Butyl}$.

Scheme 2. Synthesis of adamantyl (A), bis triazole (B) and 1,5-disubstituted triazole (C) containing sugar-triazole conjugates^a

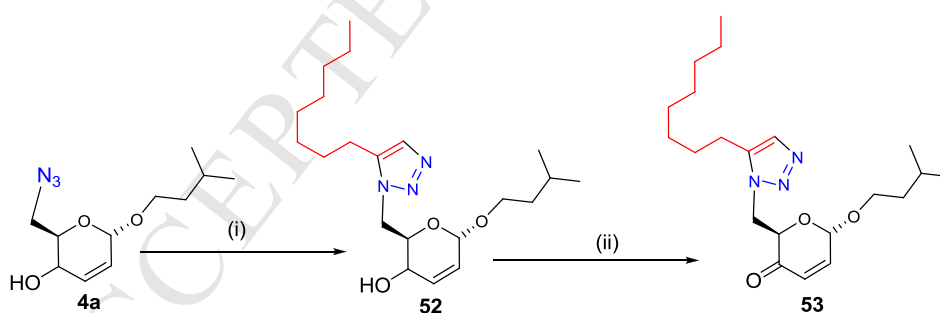
A



B



C



^a**Reagents and Conditions:** **A** (i) NaH, THF, TBAI, $\text{Br-CH}_2\text{-C}\equiv\text{C-CH}_3$, 24-48 hours (ii) $\text{C}_6\text{H}_7\text{NaO}_6$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, tBuOH: H_2O , yield: 80% (iii) DMP, DCM, 3-6 hours, 0-20 °C, yield: 54% ; **B** (i) NaN_3 , DMF, 2-5h, 80 °C-120 °C, yield: ~ 49% (ii) $\text{C}_6\text{H}_7\text{NaO}_6$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, tBuOH: H_2O , yield: ~60% (iii) DMP, DCM, 3-6 hours, 0-20 °C, yield: ~ 50% ; **C** (i) $\text{Cp}^*\text{RuCl (PPh}_3)_2$, toluene, 3 hours, 80 °C, yield: 81% (iii) DMP, DCM, 3-6 hours, 0-20 °C, yield: 61%.

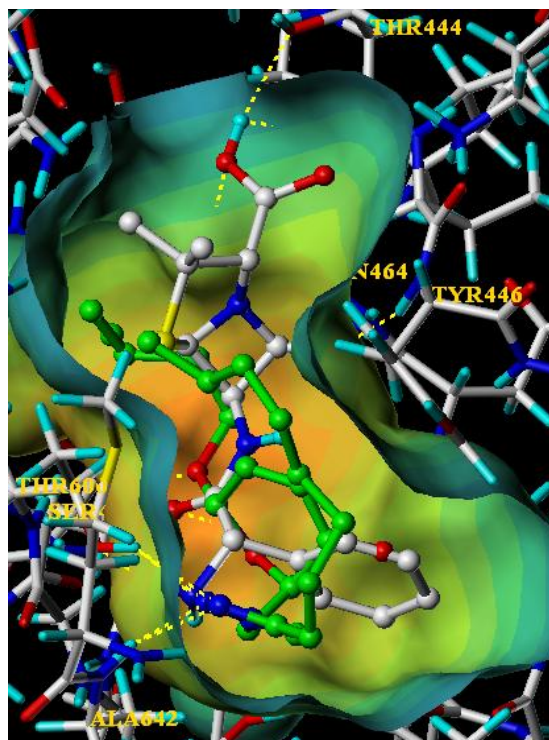


Figure 1. Binding Poses of ampicillin (grey) and compound **29** (green) in ball-and-stick mode in the active site of PBP-2 (4DKI). The residues (Ser-403, Thr 444, Tyr-446, Ser-462, Thr-600, Ala 642 and Asn 464) surrounding the pocket are shown in stick mode. The dashed yellow lines represent selected H-bond interactions between the residues and the ligand/compound. In order to signify the binding pocket, it is shown in surface view mode with cavity depth.

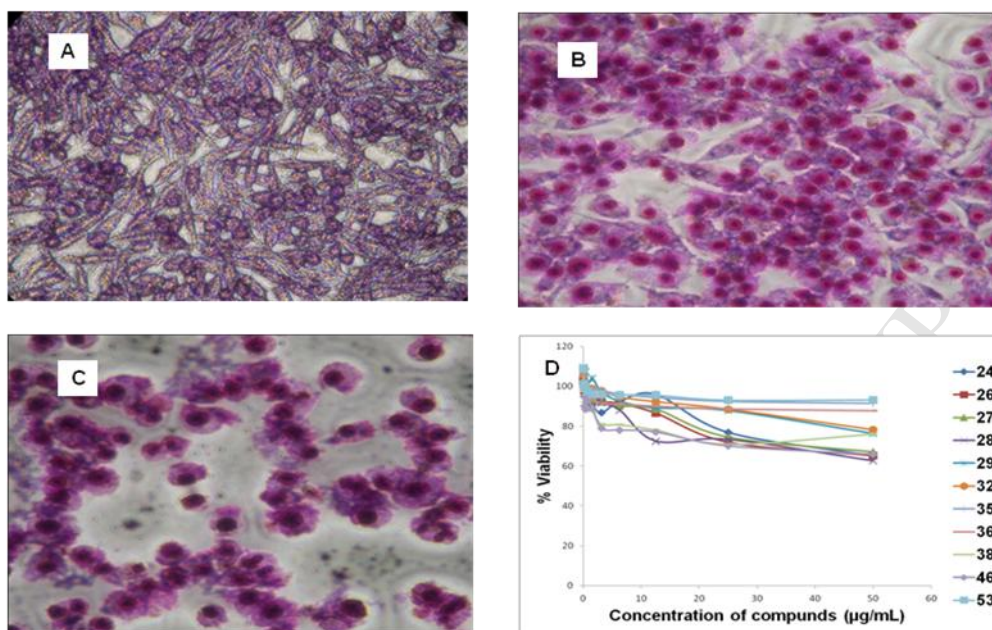
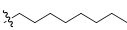









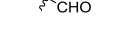
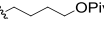

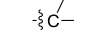




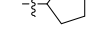



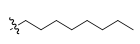


Figure 2. (A) Normal growth of mammalian cell L929. (B) Morphological changes in mammalian cells L929 at MIC of compounds ($\text{MIC} \leq 3.12 \mu\text{g/mL}$). (C) Morphological changes in mammalian cells L929 at $50 \mu\text{g/mL}$ of compounds. (D) Viability (determined by MTT assay) of mammalian cells L929 exposed to compounds **24, 26, 27, 28, 29, 32, 35, 36, 38, 46** and **53**.

Table 1. Sugar-triazole conjugates, their CLogP values and antibacterial activities.

Comp	R ₂	CLog P ^a	Sa (MR				
			Sa ^b	and VR) ^b	Kp ^b	Ec ^b	Pa ^b
10		4.658	>50	>50	>50	>50	>50
24		1.232	1.56	6.25	3.12	50	50
25		0.703	12.5	>50	50	>50	>50
26		0.833	12.5	>50	>50	>50	>50
27		2.577	3.12	6.25	3.12	>50	>50
28		3.106	3.12	6.25	1.56	>50	>50
29		4.164	0.78	3.12	0.78	>50	>50
30		3.765	6.25	>50	>50	>50	>50
31		0.601	>50	>50	50	>50	>50
32		0.124	50	>50	50	50	50
33		2.244	12.5	>50	12.5	50	50
34		0.843	12.5	>50	50	>50	>50
35		1.788	1.56	12.5	>50	>50	>50
36		2.290	6.25	12.5	3.12	50	50
37		1.175	6.25	12.5	6.25	>50	>50
38		2.470	0.78	3.12	>50	>50	>50
39		2.023	50	>50	50	50	50
40		0.905	6.25	>50	>50	>50	>50
41		1.810	6.25	25	>50	>50	>50

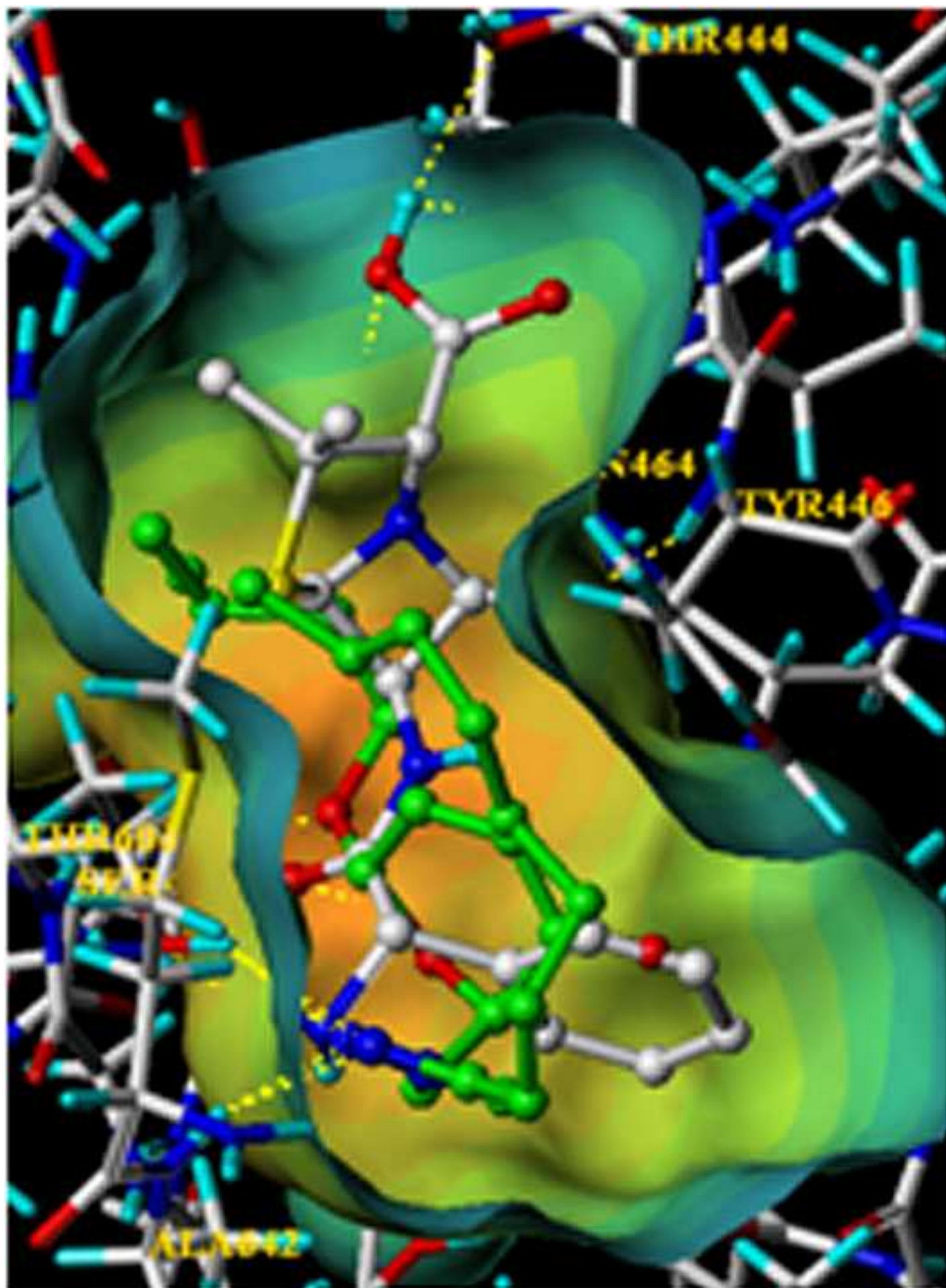
42	H	0.192	25	>50	>50	50	>50
46		4.168	1.56	3.12	0.78	50	50
50		0.1002	25	>50	>50	>50	>50
51		1.485	50	>50	>50	>50	>50
53 ^c		4.164	0.78	12.5	50	>50	>50
	Ciprofloxacin		0.09	0.38	0.01	0.01	0.09
	Gentamycin		0.39	1.56	1.56	1.56	0.39
	Ampicillin		12.5	0.78	12.5	50	>50
	Vancomycin		12.5	-	12.5	12.5	>50
	Methicillin		0.04	-	6.25	50	>50

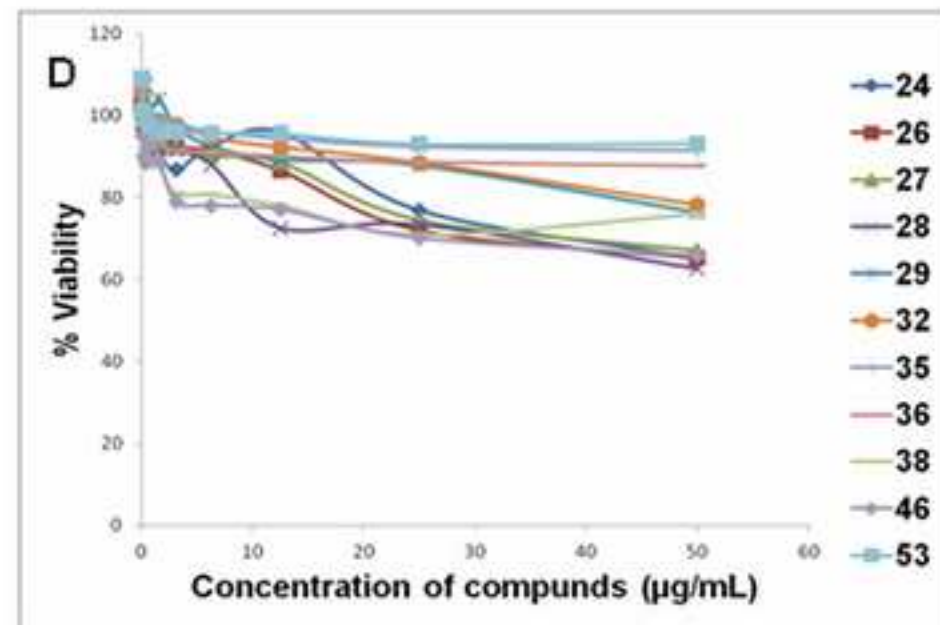
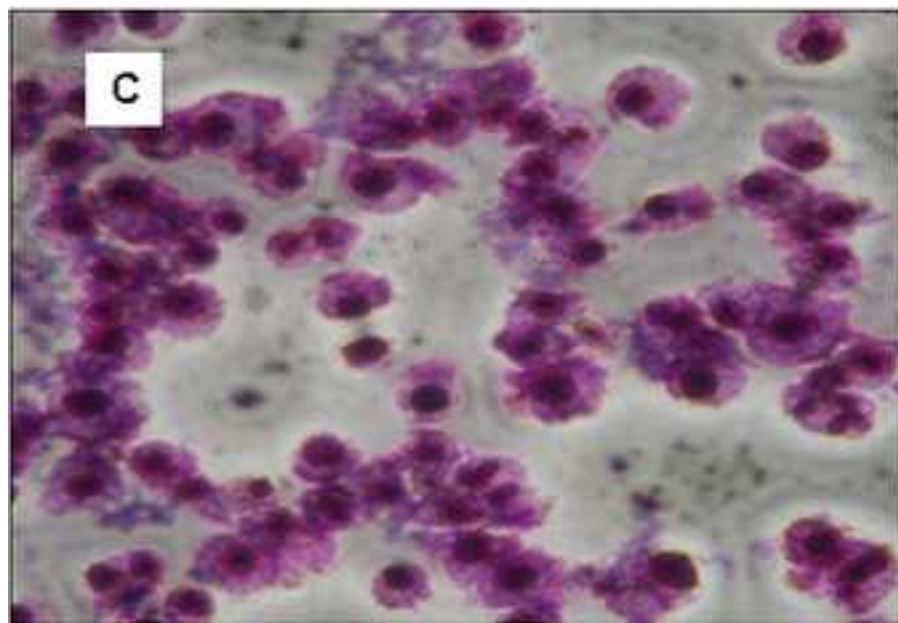
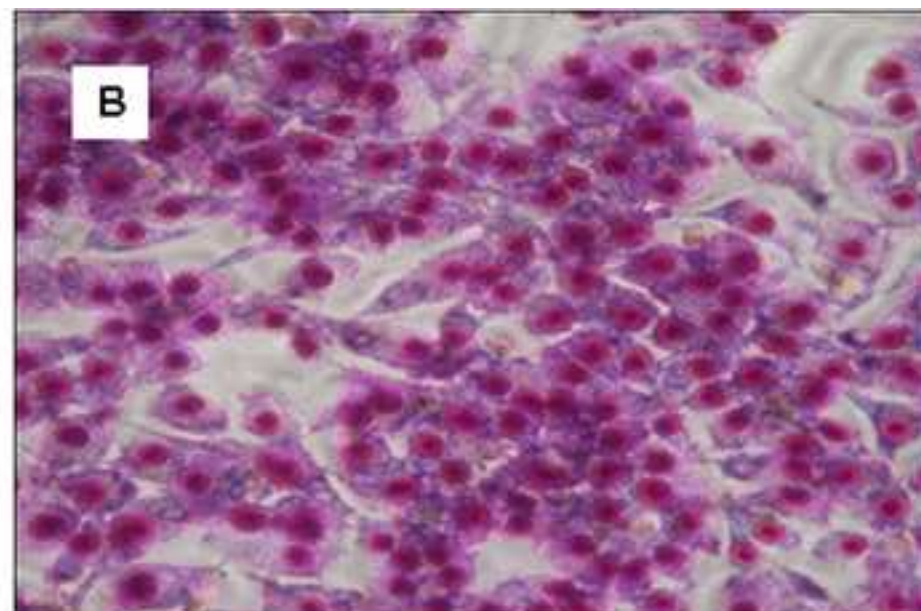
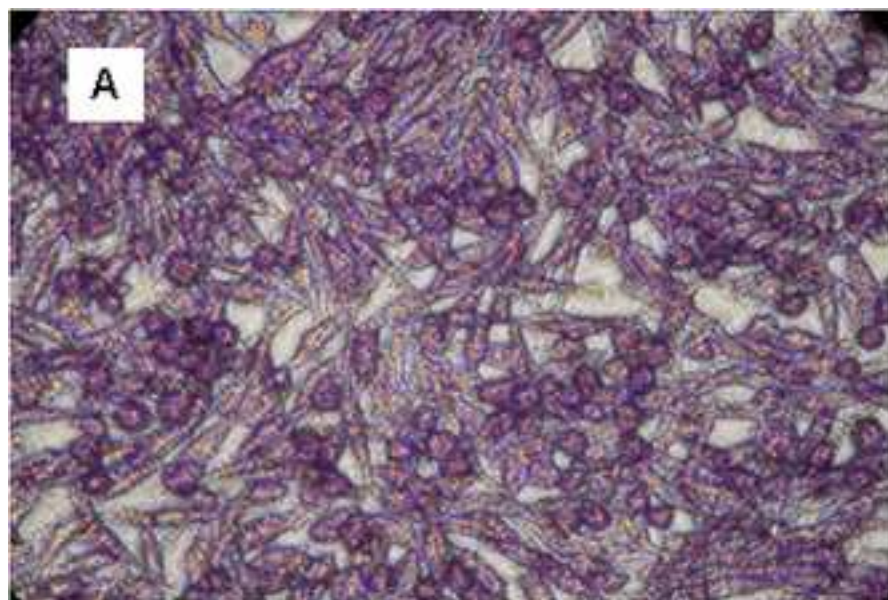
^aCLogP calculated by Chemdraw Ultra 10.0 software. ^b*Staphylococcus aureus* (Sa), methicillin- and vancomycin-resistant (MR and VR) Sa, *Klebsiella pneumoniae* (Kp), *Escherichia Coli* (Ec), *Pseudomonas aeruginosa* (Pa); Antibacterial activity as MIC in $\mu\text{g/mL}$. ^cCompound **53** is 1,5- disubstituted analogue of compound **29**.

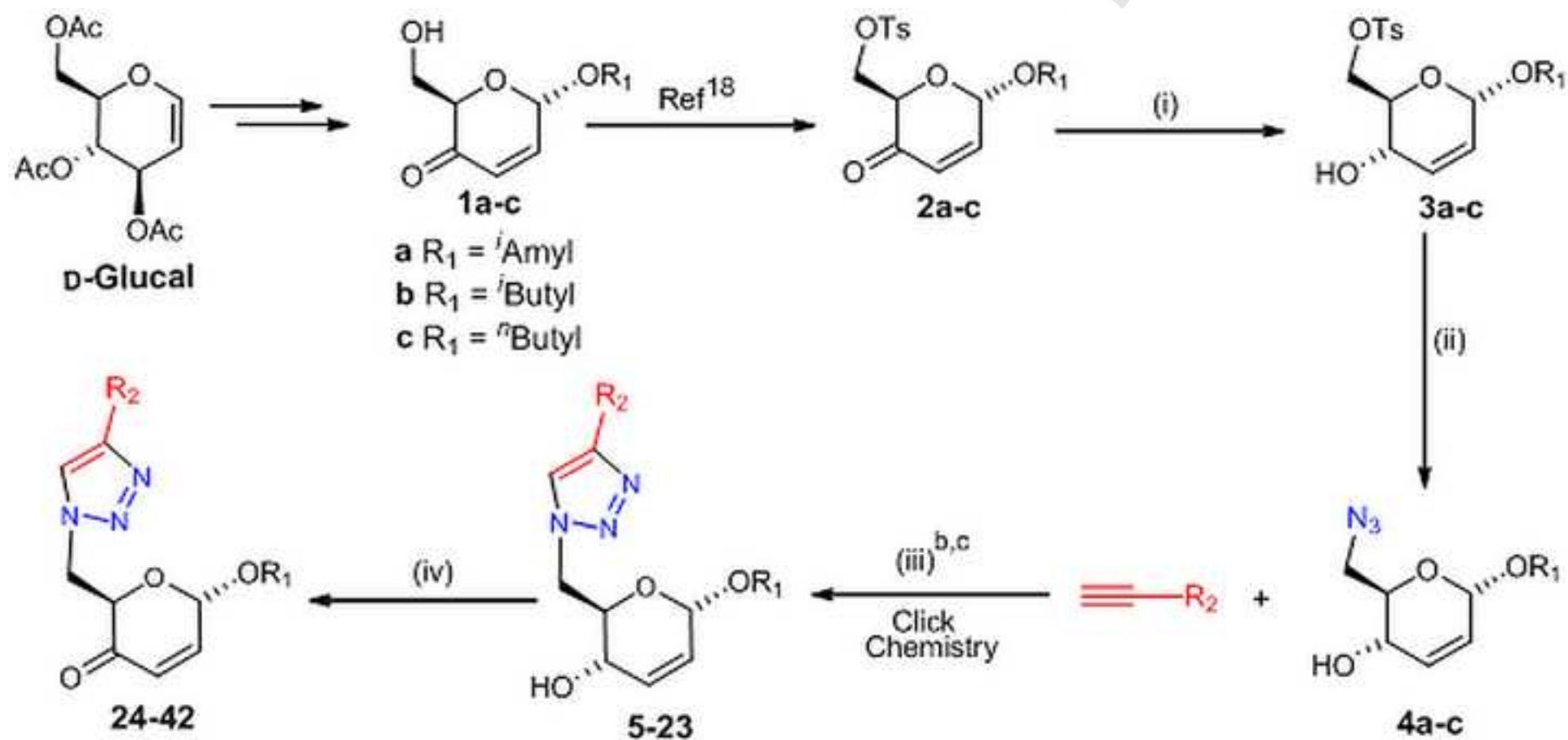
Table 2. Sugar-triazole conjugates and their antifungal activities.

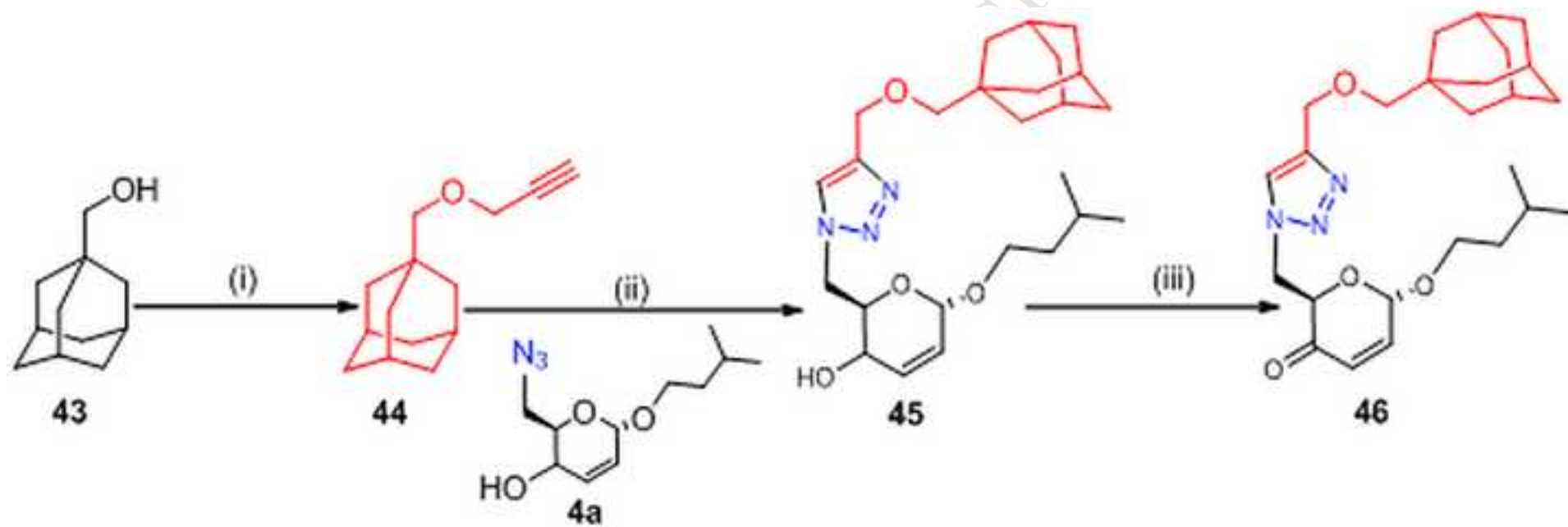
Comp	Ca ^a	Af ^a	Cn ^a	Ss ^a	Tm ^a
10	>50	>50	25	>50	50
24	25	50	50	12.5	50
25	50	>50	>50	50	>50
26	25	>50	50	3.12	0.39
27	>50	>50	>50	12.5	3.12
28	>50	>50	>50	25	12.5
29	>50	>50	>50	50	3.12
30	6.25	>50	25	25	6.25
31	>50	>50	>50	12.5	25
32	>50	25	50	25	3.12
33	>50	25	50	12.5	25
34	12.5	50	12.5	25	6.25
35	25	>50	25	12.5	>50
36	12.5	50	25	12.5	50
37	>50	>50	>50	25	12.5
38	6.25	50	50	6.25	1.56
39	25	50	50	50	50
40	12.5	>50	25	12.5	6.25
41	25	>50	50	50	25
42	50	>50	50	>50	>50
46	>50	1.56	50	50	1.56
50	50	>50	50	>50	>50
51	50	>50	50	50	50
53	50	>50	25	6.25	25
Clotrimazole	0.25	8	0.25	4	2
Flucanazole	1.00	>32	2.00	4	16
5-Fluorocytosine	0.25	>32	0.13	>32	>32
Miconazole	25	12.5	12.5	3.12	0.78

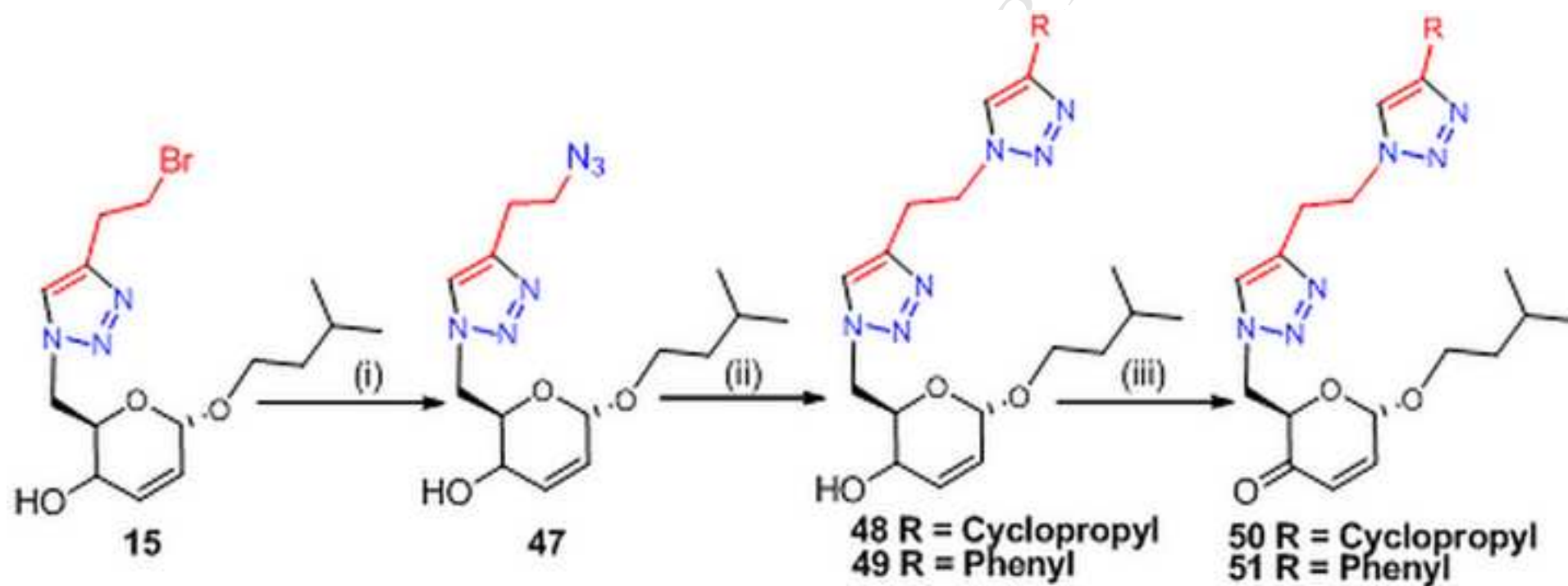
^aCandida albicans (Ca); Cryptococcus neoformans (Cn); Sporothrix schenckii (Ss); Trichophyton mentagrophytes (Tm); Aspergillus fumigatus (Af); Antifungal activity as MIC in µg/mL.

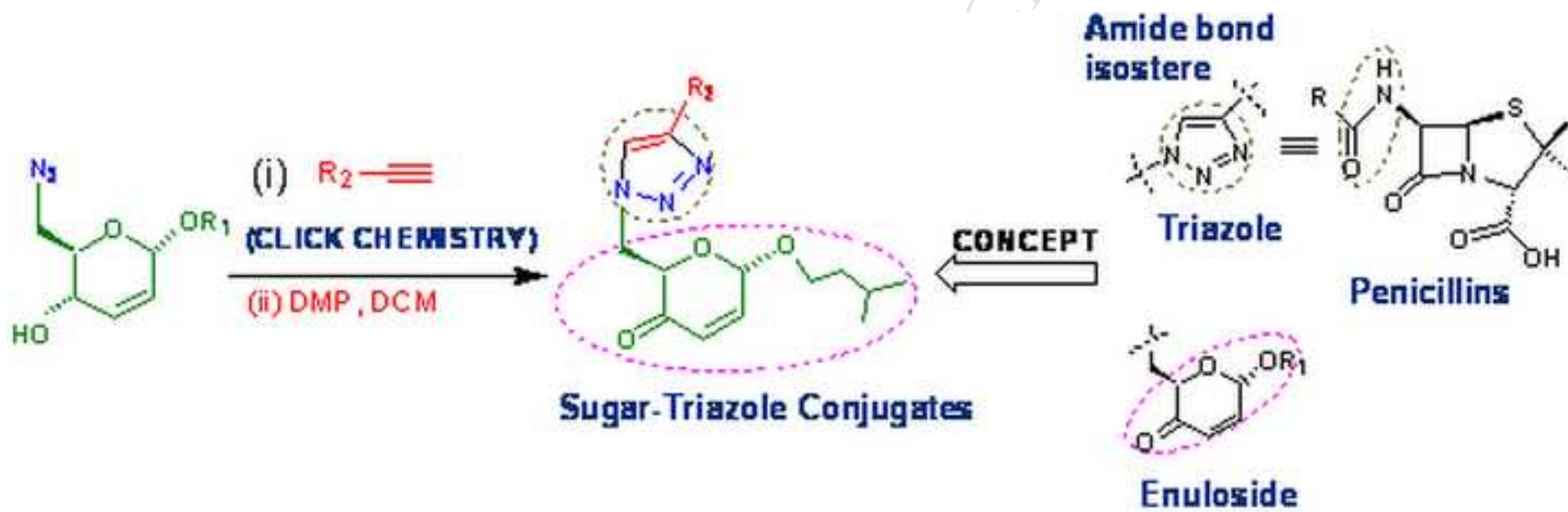












Supplementary data

Synthesis of 2,3,6-trideoxy sugar triazole hybrids as potential new broad spectrum antimicrobial agents

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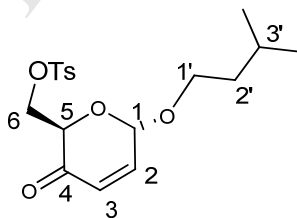
Title Page	S1
Experimental section - Chemistry	S2
General remarks	S2
Spectral data of all new compounds	S3 - S33
Assay for <i>invitro</i> antibacterial, antifungal activity and cytotoxicity	S33 - S35
Bioinformatics and modeling studies	S35 - S36
¹ H NMR and ¹³ C NMR Spectra	S37 - S121

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Experimental Section- Chemistry

General Remarks: The chemicals used in synthesis were purchased from Sigma-Aldrich Co and Spectrochem (India). The organic solvents used in synthesis were dried by standard methods. All the reactions were monitored by thin layer chromatography over basic alumina coated TLC plates and the spots were visualized with the help of CeSO_4 or 10% $\text{H}_2\text{SO}_4/\text{EtOH}$ on hot plate. The pure compound was isolated by column chromatography using silica gel of mesh size 60-120, 100-200 and 230-400. All the products were characterized by ^1H , ^{13}C , DEPT pulse sequence, two-dimensional homonuclear COSY (Correlation Spectroscopy), Heteronuclear Single Quantum Correlation (HSQC), Heteronuclear Multiple Bond Correlation (HMBC), IR, MS (ESI), HRMS (ESI) and HRMS (DART). All NMR spectra were recorded on Bruker Avance DPX 200FT, Bruker DRX 300 Spectrometers at 200, 300 MHz (^1H) and 50, 75, MHz (^{13}C). The chemical shifts (δ) are given in ppm, related to tetramethylsilane (TMS) as an internal standard. For ^{13}C -NMR reference CDCl_3 appeared at 77.10 ppm unless otherwise stated. Electron spray ionization Mass Spectra (ESIMS) were obtained on Micromass quadro II spectrometer. HRMS were recorded on JEOL, JMS T100LC Accu TOF. IR spectra were recorded on Perkin-Elmer 881 and FTIR-8210 PC Shimadzu Spectrophotometers either as KBr disc or neat and value are expressed in cm^{-1} . Optical rotations were determined on an Autopol III polarimeter (Rudolph Research) and using a 1 dm cell in chloroform as solvent at 25 °C unless otherwise stated; concentrations mentioned are in g/100 mL.

Compound 2a

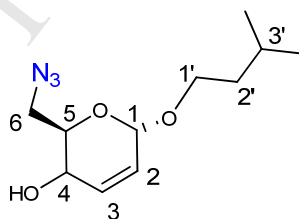


To a solution of the enone **1a** (1500 mg, 7.01 mmol) in dry DCM (25 mL) was added dry pyridine (8 mL) and the temperature of the reaction mixture was kept at -30 °C followed by drop wise addition of *p*-toluenesulphonyl chloride (2268 mg, 11.9 mmol) dissolved in dry dichloromethane (DCM) (10 mL) for 1 hour. After the addition was complete, the reaction mixture was stirred at the same temperature for an additional 1 hour and finally kept in a refrigerator at 5 °C for overnight. On completion of reaction (TLC), the reaction mixture was poured into ice cold water (excess) and the organic layer was separated. The aqueous layer

was extracted with dichloromethane (4x5mL). The combined organic layers were washed successively with water and brine, dried over sodium sulphate and evaporated *in vacuo* using co-distillation with toluene to remove pyridine. The crude product so obtained was purified by column chromatography to give the pure compound **2a** as viscous oil; yield (75%); R_f = 0.45 (hexane-ethyl acetate, 10:3); eluent for column chromatography (hexane-ethyl acetate, 50:3); $[\alpha]_D^{31} = -31.44$ (c 0.20, CHCl_3); IR (neat, cm^{-1}): 3025, 1699, 1599, 1364, 1179; ^1H NMR ($\text{CDCl}_3 + \text{CCl}_4$, 300 MHz): δ 7.75 (d, 2H, H-2" and H-6", $J = 8.1$ Hz), 7.32 (d, 2H, H-3" and H-5", $J = 8.0$ Hz), 6.82 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.4$ Hz), 6.02 (d, 1H, H-3, $J = 10.3$ Hz), 5.16 (d, 1H, H-1, $J = 3.3$ Hz), 4.59 (dd, 1H, H-5, $J = 5.8$ Hz & $J = 2.0$ Hz), 4.44 (dd, 1H, H-6a, $J = 10.8$ Hz & $J = 2.1$ Hz), 4.25 (dd, 1H, H-6b, $J = 10.8$ Hz & $J = 6.1$ Hz), 3.86-3.78 (m, 1H, H-1'a), 3.58-3.50 (m, 1H, H-1'b), 2.44 (s, 3H, CH_3 of OTs), 1.72-1.61 (m, 1H, H-3'), 1.54-1.41 (m, 2H, H-2'), 0.91 (s, 3H, CH_3 of *i*-amyl), 0.89 (s, 3H, CH_3 of *i*-amyl); ^{13}C NMR ($\text{CDCl}_3 + \text{CCl}_4$, 50 MHz): δ 191.9 (C-4), 144.6 (ArqC), 144.3 (C-2), 133.1 (ArqC), 129.8 (C-3" and C-5"), 128.2 (C-2" and C-6"), 127.2 (C-3), 93.1 (C-1), 72.3 (C-5), 68.1 (C-1'), 68.0 (C-6), 38.4 (C-2'), 25.0 (C-3'), 22.8 and 22.5 (2 CH_3 of *i*-amyl) 21.7 (CH_3 of OTs); MS (ESI): m/z 368; found 386 $[\text{M} + \text{NH}_4]^+$, 391 $[\text{M} + \text{Na}]^+$; HRMS (ESI): Calc for $\text{C}_{18}\text{H}_{24}\text{O}_6\text{S}$ $[\text{M}]^+$ 368.1294, found 368.1302.

Compounds **2b** and **2c** were prepared using the same procedure as described above for **2a**. However they were not isolated by column chromatography and crude product was used as such for the next step.

Compound 4a

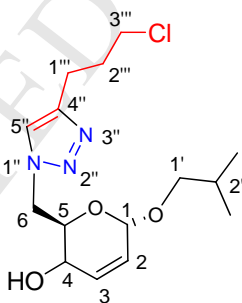


To a stirred solution of **2a** (1934 mg, 5.25 mmol) in ethanol were added $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1174.49 mg, 3.15 mmol) and NaBH_4 (116.66 mg, 3.15 mmol) at 0 °C and the reaction mixture was stirred continuously for 40 minutes keeping the temperature of the reaction mixture below 10 °C. After completion of the reaction (TLC control), excess NaBH_4 was neutralized with acetone and the solvent was concentrated (rotary evaporator) to obtain the crude product **3a**. To the dried crude product **3a** dissolved dimethyl formamide (DMF) was added NaN_3 (847.6 mg, 13.04 mmol) and the reaction mixture was refluxed at 90-100 °C for

3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with DCM (5x8mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated under reduced pressure to yield the crude product. It was then purified by column chromatography to give the pure compound **4a** as viscous oil; yield (64%); $R_f = 0.57$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 50:3); $[\alpha]_D^{31} = -35.27$ (c 0.40, CHCl_3); IR (neat, cm^{-1}): 3396, 3021, 2102, 1461, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 5.92 (d, 1H, H-3, $J = 15.3$ Hz), 5.77 (dd, 1H, H-2, $J = 15.3$ Hz & $J = 6.9$ Hz), 4.98 (s, 1H, H-1), 4.12 - 4.04 (m, 1H, H-4), 3.92 - 3.76 (m, 1H, H-5), 3.92 - 3.76 (m, 2H, H-5 & H-6a), 3.60 - 3.42 (m, 3H, H-6a & H-6b), 1.76-1.59 (m, 1H, H-3'), 1.56-1.45 (m, 2H, H-2'), 0.93 (s, 3H, CH_3 of i -amyl), 0.90 (s, 3H, CH_3 of i -amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 132.6 (C-3), 127.1 (C-2), 94.2 (C-1), 71.4 (C-5), 67.4 (C-1'), 65.1 (C-4), 52.0 (C-6), 38.5 (C-2'), 25.1 (C-3'), 22.7 & 22.4 (2 CH_3 of i -amyl); MS (ESI): m/z 241; found 259 $[\text{M}+\text{NH}_4]^+$, 242 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_6\text{H}_8\text{NO}_2$ $[\text{M}-\text{C}_5\text{H}_{11}\text{O} + \text{N}_2]^+$ 126.0555; found 126.0544.

Compounds **4b** and **4c** were prepared using the same procedure as described above for **4a**. However they were not isolated by column chromatography and crude product was used as such for the next step.

Compound 6

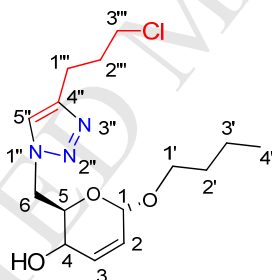


To a vigorously stirred solution of azide **4b** (250 mg, 1.111 mmol) in *tert*-butyl alcohol was added the 5 chloropentyne (0.173 mL, 1.66 mmol). The reaction was initiated by the addition of a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (49.38 mg, 0.22 mmol) and sodium ascorbate (87.16 mg, 0.44 mmol) in distilled water. The coloured suspension formed and the reaction mixture was stirred at room temperature till the disappearance of the starting material on TLC. After the completion of reaction, ice-cold distilled water was added to the reaction mixture and the aqueous layer was extracted 3-4 times with CHCl_3 . The combined organic extracts were dried *in vacuo* and purified using column chromatography to afford pure triazolyl 2,3,6 trideoxy hex-2-enopyranoside **6**; yield (78%); $R_f = 0.47$ (hexane-ethyl acetate, 3:2); eluent for column

chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -5.44$ (c 0.08, CHCl_3); IR (neat, cm^{-1}): 3855, 3353, 2928, 2361, 1651, 1219, 768; ^1H NMR (CDCl_3 , 300 MHz): δ 7.50 (s, 1H, H-5"), 5.93 (d, 1H, H-3, $J = 9.9$ Hz), 5.71 (d, 1H, H-2, $J = 9.7$ Hz), 4.90 (s, 1H, H-1), 4.72 (d, 1H, H-6a, $J = 14.3$ Hz), 4.56 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 6.7$ Hz), 3.97 (d, 1H, H-4, $J = 6.9$ Hz), 3.85 (d, 1H, H-5, $J = 9.1$ Hz), 3.57 (t, 2H, H-1', $J = 6.0$ Hz), 3.15 (t, 2H, H-3"', $J = 7.0$ Hz), 2.88 (t, 2H, H-1"', $J = 7.0$ Hz), 2.16 (t, 2H, H-2"', $J = 6.7$ Hz), 1.77-1.68 (m, 1H, H-2'), 0.83-0.78 (m, 6H, 2CH_3 of *i* butyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 146.3 (C-4"), 133.1 (C-3), 126.4 (C-2), 123.1 (C-5"), 94.6 (C-1), 75.5 (C-1'), 70.7 (C-5), 64.5 (C-4), 51.3 (C-6), 44.2 (C-3'''), 32.0 (C-1'''), 28.4 (C-2'), 22.7 (C-2''), 19.3 & 19.4 (2CH_3 of *i* butyl). MS (ESI): m/z 329; found 330 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{15}\text{H}_{25}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 330.1584; found 330.1618.

Compounds **7**, **8**, **9**, **11**, **12**, **14**, **15**, **16**, **17**, **18**, **19**, **21**, **22**, **23** were prepared following the procedure as described above for compound **6**. While compounds **8**, **9**, **12**, **14**, **15**, **16**, **17**, **18**, **19**, **21**, **22**, **23** were synthesized from precursor 6-azido hex-2-enopyranoside **4a**, compound **7** and **11** were synthesized from precursor **4c**.

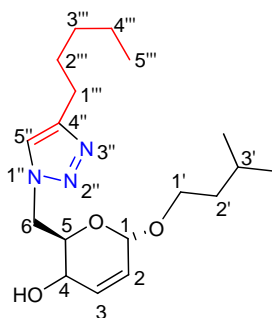
Compound 7



This compound was obtained as a viscous oil; yield (86%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31} = -43.75$ (c 0.032, CHCl_3); IR (neat, cm^{-1}): 3759, 2364, 1655, 1576, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 7.50 (s, 1H, H-5"), 5.93 (d, 1H, H-3, $J = 10.1$ Hz), 5.69 (d, 1H, H-2, $J = 10.0$ Hz), 4.90 (s, 1H, H-1), 4.72 (dd, 1H, H-6a, $J = 14.3$ Hz & $J = 2.1$ Hz), 4.57 (dd, 1H, H-6b, $J = 14.3$ Hz and $J = 6.6$ Hz), 3.98 (dd, 1H, H-4, $J = 6.8$ Hz & $J = 8.9$ Hz), 3.85 (d, 1H, H-5, $J = 8.6$ Hz), 3.56 (t, 2H, H-3"', $J = 6.3$ Hz), 3.44-3.31 (m, 2H, H-1'), 2.87 (t, 2H, H-1"', $J = 7.2$ Hz), 2.14 (dd, 2H, H-2"', $J = 20.3$ Hz & $J = 6.5$ Hz), 1.46-1.40 (m, 2H, H-3'), 1.28-1.25 (m, 2H, H-2'), 0.86 (t, 3H, H-4', $J = 7.3$ Hz); ^{13}C NMR (CDCl_3 , 75MHz): δ 146.3 (C-4"), 133.2 (C-3), 126.4 (C-2), 123.0 (C-5"), 94.5 (C-1), 70.7 (C-5), 68.6 (C-4), 64.5 (C-1'), 51.3 (C-6), 44.2 (C-3'''), 32.0 (C-2'),

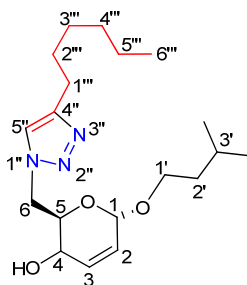
31.7 (C-1'''), 22.7 (C-2'''), 19.4 (C-3'), 13.9 (C-4'). MS (ESI): m/z 329; found 330 $[M+H]^+$; HRMS (ESI): Calc for $C_{15}H_{25}ClN_3O_4$ $[M+H]^+$; 330.1584; found 330.1586.

Compound 8



This compound was obtained as a viscous oil; yield (73%); R_f = 0.55 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31}$ = -3.08 (c 0.14, $CHCl_3$); IR (neat, cm^{-1}): 3779, 3346, 2924, 2364, 1461, 1050; 1H NMR ($CDCl_3$, 300 MHz): δ 7.43 (s, 1H, H-5''), 5.93 (d, 1H, H-3, J = 10.2 Hz), 5.72-5.67 (m, 1H, H-2), 4.91 (s, 1H, H-1), 4.71- 4.55 (m, 2H, H-6), 4.00-3.94 (m, 1H, H-4), 3.83 (d, 1H, H-5, J = 9.0 Hz), 3.52-3.46 (m, 1H, H-1'a), 3.40-3.35 (m, 1H, H-1'b), 2.69 (t, 2H, H-1''', J = 7.5 Hz), 1.82 (s, 1H, H-3'), 1.68-1.57 (m, 2H, H-2'), 1.41-1.34 (m, 6H, H-2''', H-3''' & H-4'''), 0.91-0.82 (m, 9H, 2CH₃ of i amyl & 1CH₃ of H-5''); ^{13}C NMR ($CDCl_3$, 75MHz): δ 148.5 (C-4''), 133.1 (C-3), 126.5 (C-2), 122.4 (C-5''), 94.6 (C-1), 70.8 (C-5), 67.2 (C-1'), 64.6 (C-4), 51.2 (C-6), 38.5 (C-2'), 31.6 (C-1'''), 29.8 (C-2'''), 29.3 (C-3'''), 25.7 (C-4'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of i amyl), 14.2 (CH₃ of C-5''). MS (ESI): m/z 337; found 338 $[M+H]^+$ HRMS (DART): Calc for $C_{18}H_{32}N_3O_3$ $[M+H]^+$; 338.2443; found 338.2457.

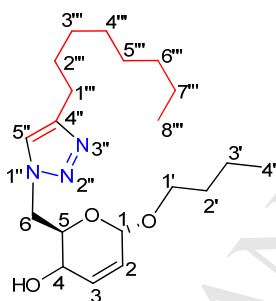
Compound 9



This compound was obtained as a viscous oil; yield (78%); R_f = 0.51 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31}$ = -3.91 (c 0.10, $CHCl_3$); IR (neat, cm^{-1}): 3411, 3019, 2928, 2364, 1589, 1217, 767; 1H NMR ($CDCl_3$, 300 MHz): δ 7.43 (s, 1H, H-5''), 5.93 (d, 1H, H-3, J = 10.2 Hz), 5.69 (d, 1H, H-2, J = 10.1 Hz),

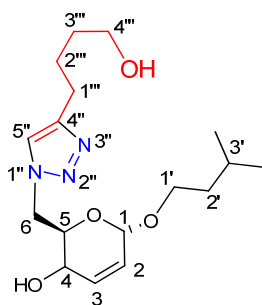
4.91 (s, 1H, H-1), 4.71-4.53 (m, 2H, H-6), 3.98 (t, 1H, H-4, $J = 9.0$ Hz), 3.84 (d, 1H, H-5, $J = 8.9$ Hz), 3.53-3.32 (m, 2H, H-1'), 2.69 (t, 2H, H-1'', $J = 7.3$ Hz), 1.64-1.57 (m, 3H, H-3' & H-2'), 1.40-1.30 (m, 8H, H-2'''-H-5'''), 0.87-0.82 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-6'''); ¹³C NMR (CDCl₃, 75MHz): δ 148.4 (C-4''), 133.1 (C-3), 126.4 (C-2), 122.4 (C-5''), 94.5 (C-1), 70.8 (C-5), 67.2 (C-1'), 64.56 (C-4), 51.2 (C-6), 38.4 (C-2'), 31.64 (C-1'''), 29.8 (C-2'''), 29.5 (C-3'''), 29.0 (C-4'''), 25.7 (C-5'''), 25.1 (C-3'), 22.6 and 22.5 (2CH₃ of *i*-amyl), 14.1 (CH₃ of C-6''); MS (ESI): m/z 351; found 352 [M+H]⁺; HRMS (DART): Calc for C₁₉H₃₄N₃O₃ [M+H]⁺; 352.2600; found 352.2613.

Compound 11



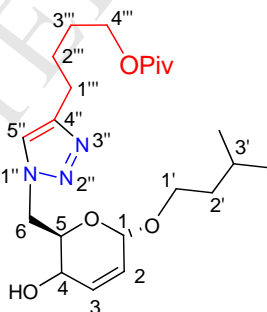
This compound was obtained as a viscous oil; yield (66%); $R_f = 0.47$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = +18.22$ (c 0.06, CHCl₃); IR (neat, cm⁻¹): 3908, 3762, 3455, 2927, 2365, 1631, 1220, 1041, 770; ¹H NMR (CDCl₃, 300 MHz): δ 7.42 (s, 1H, H-5''), 5.93 (d, 1H, H-3, $J = 10.2$ Hz), 5.69 (d, 1H, H-2, $J = 10.1$ Hz), 4.90 (s, 1H, H-1), 4.70 (d, 1H, H-4, $J = 12.4$ Hz), 4.56 (dd, 1H, H-6a, $J = 14.43$ Hz and $J = 6.72$ Hz), 3.98 (t, 1H, H-6b, $J = 7.2$ Hz), 3.86 (s, 1H, H-5), 3.47-3.33 (m, 2H, H-1'), 2.68 (t, 2H, H-1'', $J = 7.53$ Hz), 1.66-1.61 (m, 4H, H-2' & H-3'), 1.49-1.40 (m, 12H, H-2'''-H-7'''), 0.88-0.84 (m, 6H, H-4' & H-8'''); ¹³C NMR (CDCl₃, 75MHz): δ 148.5 (C-4''), 133.1 (C-3), 126.5 (C-2), 122.4 (C-5''), 94.5 (C-1), 70.8 (C-5), 68.5 (C-1'), 64.6 (C-4), 51.2 (C-1'), 31.9 (C-1'''), 31.8 (C-2'), 29.6 (C-6''), 29.5 (C-4'''), 29.4 (C-5'''), 29.3 (C-3'''), 25.8 (C-2'''), 25.7 (C-7'''), 19.4 (C-3'), 14.2 (C-4'), 13.9 (C-8'''). MS (ESI): m/z 365; found 366 [M+H]⁺; HRMS (ESI): Calc for C₂₀H₃₆N₃O₃ [M+H]⁺; 366.2757; found 366.2742.

Compound 12



This compound was obtained as a viscous oil ; yield (83%); $R_f = 0.57$ (chloroform-methanol 24:1); eluent for column chromatography (chloroform-methanol 10:0.1); $[\alpha]_D^{31} = -21.13$ (c 0.08, CHCl_3); IR (neat, cm^{-1}): 3749, 3427, 2930, 2363, 1640, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 7.47 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.1$ Hz), 5.68 (d, 1H, H-2, $J = 10.2$ Hz), 4.91 (s, 1H, H-1), 4.71-4.56 (m, 2H, H-6), 4.00-3.95 (m, 1H, H-4), 3.83 (d, 1H, H-5, $J = 9.2$ Hz), 3.66 (t, 2H, H-1', $J = 6.3$ Hz), 3.54-3.46 (m, 1H, H-4''a), 3.40-3.33 (m, 1H, H-4''b), 2.73 (t, 2H, H-1'', $J = 7.2$ Hz), 1.78-1.71 (m, 2H, H-2''), 1.67-1.56 (m, 2H, H-3''), 1.40-1.34 (m, 3H, H-3' & H-2'), 0.86-0.82 (m, 6H, 2 CH_3 of *i*-amyl). ^{13}C NMR (CDCl_3 , 75MHz): δ 147.9 (C-4''), 133.2 (C-3), 126.3 (C-2), 122.6 (C-5''), 94.5 (C-1), 70.7 (C-5), 67.2 (C-1'), 64.3 (C-4), 62.3 (C-4''), 51.2 (C-6), 38.4 (C-1''), 32.1 (C-3''), 25.6 (C-2'), 25.2 (C-2''), 25.0 (C-3'), 22.6 & 22.4 (2 CH_3 of *i*-amyl). MS (ESI): m/z 339; found 340 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{17}\text{H}_{30}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 340.2236 ; found 340.2219.

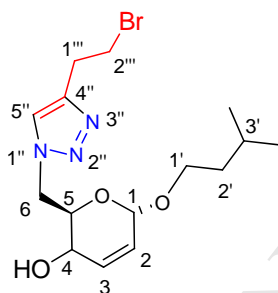
Compound 14



This compound was obtained as a viscous oil; yield (89%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 15:7); $[\alpha]_D^{31} = +13.71$ (c 0.04, CHCl_3); IR (neat, cm^{-1}): 3752, 3423, 2925, 2363, 1722, 1463, 1287, 1161, 1045; ^1H NMR (CDCl_3 , 300 MHz): δ 7.45 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.1$ Hz), 5.70-5.66 (m, 1H, H-2), 4.90 (s, 1H, H-1), 4.69 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.4$ Hz), 4.58 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 6.7$ Hz), 4.05 (t, 2H, H-4 & H-5, $J = 6.12$ Hz), 3.96 (t, 1H, H-4''a, $J = 2.43$ Hz), 3.84 (d, 1H, H-4''a, $J = 8.97$ Hz), 3.52-3.44 (m, 1H, H-1'a), 3.35 (dd, 1H, H-1'b, J

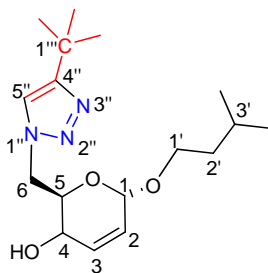
= 6.7 Hz & $J = 2.6$ Hz), 2.72 (t, 2H, H-1''', $J = 6.75$ Hz), 1.71 (d, 4H, H-2''' & H-3'''), 1.64-1.53 (m, 1H, H-3'), 1.39-1.32 (m, 2H, H-2'), 1.23 (s, 9H, OCOC(CH₃)₃), 0.85-0.80 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 178.7 (C-5'''), 147.6 (C-4'''), 133.2 (C-3), 126.3 (C-2), 122.6 (C-5''), 94.5 (C-1), 70.7 (C-5), 67.1 (C-1'), 64.4 (C-4'''), 64.1 (C-4), 51.2 (C-6), 38.4 (C-2'), 29.7 (C of Piv), 28.3 (C-1'''), 27.2 (3CH₃ of Piv), 25.9 (C-2'''), 25.2 (C-3'''), 25.0 (C-3'), 22.7 & 22.4 (2CH₃ of *i*-amyl). MS (ESI): m/z 423; found 424 [M+H]⁺; HRMS (ESI): Calc for C₂₂H₃₈N₃O₅ [M+H]⁺; 424.2811; found 424.2797.

Compound 15



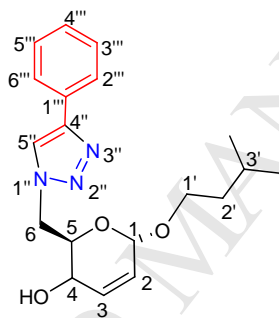
This compound was obtained as a viscous oil; yield (86%); $R_f = 0.53$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = -20.68$ (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3419, 3021, 2930, 2366, 1706, 1217; ¹H NMR (CDCl₃, 300 MHz): δ 7.61 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.0$ Hz), 5.71 (d, 1H, H-2, $J = 10.1$ Hz), 4.92 (s, 1H, H-1), 4.72 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 6.3$ Hz), 4.61 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 6.3$ Hz), 3.99 (t, 1H, H-4, $J = 6.5$ Hz), 3.83 (d, 1H, H-5, $J = 8.9$ Hz), 3.64 (t, 2H, H-2''', $J = 6.8$ Hz), 3.55-3.47 (m, 1H, H-1'a), 3.38 (m, 1H, H-1'b, $J = 13.5$ Hz & $J = 6.7$ Hz), 3.29 (t, 2H, H-1''', $J = 6.8$ Hz), 1.68-1.55 (m, 1H, H-3'), 1.41-1.32 (m, 2H, H-2'), 0.87-0.82 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 144.8 (C-4'''), 132.9 (C-3), 126.6 (C-2), 123.6 (C-5''), 94.5 (C-1), 70.7 (C-4), 67.3 (C-1'), 64.6 (C-5), 51.4 (C-6), 38.4 (C-2'), 29.8 (C-2'''), 29.5 (C-1'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*-amyl). MS (ESI): m/z 373; found 374 [M+H]⁺; HRMS (ESI): Calc for C₁₅H₂₅BrN₃O₃ [M+H]⁺; 374.1079; found 374.1061.

Compound 16



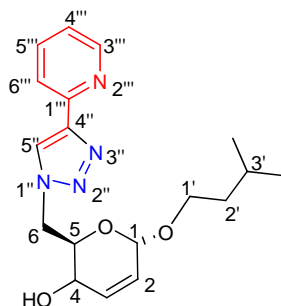
This compound was obtained as a viscous oil; yield (64%); $R_f = 0.53$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -4.38$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3916, 3774, 3373, 2956, 2370, 1598, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.41 (s, 1H, H-5''), 5.92 (d, 1H, H-3, $J = 10.2$ Hz), 5.61 (d, 1H, H-2, $J = 10.1$ Hz), 4.85 (s, 1H, H-1), 4.77 (d, 1H, H-6a, $J = 13.7$ Hz), 4.39 (t, 1H, H-4, $J = 7.1$ Hz), 3.96 (d, 2H, H-6b & H-5, $J = 13.7$ Hz), 3.37-3.20 (m, 2H, H-1'), 1.59-1.46 (m, 1H, H-3'), 1.31-1.27 (m, 11H, 2H of H-2' & 9H of $\text{C}(\text{CH}_3)_3$), 0.81-0.76 (2CH₃ of i -amyl). ^{13}C NMR (CDCl_3 , 75MHz): δ 157.3 (C-4''), 133.5 (C-3), 125.9 (C-2), 120.3 (C-5''), 94.3 (C-1), 70.1 (C-5), 66.8 (C-4), 64.5 (C-1'), 51.4 (C-6), 38.3 (C-2'), 30.3 (qC or C-1'''), 29.6 ($\text{C}(\text{CH}_3)_3$), 24.9 (C-3'), 22.6 & 22.4 (2CH₃ of i -amyl). MS (ESI): m/z 323; found 324 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{17}\text{H}_{30}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 324.2250; found 324.2287.

Compound 17



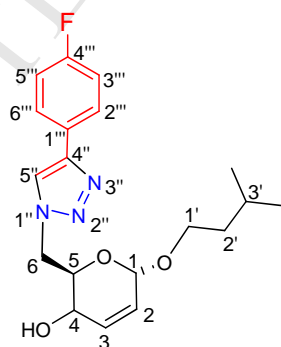
This compound was obtained as a viscous oil; yield (86%); $R_f = 0.47$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31} = -29.17$ (c 0.15, CHCl_3); IR (neat, cm^{-1}): 3419, 3020, 1758, 1630, 1216; ^1H NMR (CDCl_3 , 300 MHz): δ 7.94 (s, 1H, H-5''), 7.82 (d, 2H, H-2''' & H-6''', $J = 7.1$ Hz), 7.43-7.29 (m, 3H, H-3''', H-4''' & H-5'''), 5.94 (d, 1H, H-3, $J = 10.2$ Hz), 5.71 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 6.4$ Hz), 4.93 (s, 1H, H-1), 4.81-4.76 (m, 1H, H-6a), 4.69 (dd, 1H, H-6b, $J = 14.2$ Hz & $J = 2.1$ Hz), 4.04 (dd, 1H, H-4, $J = 6.4$ Hz & $J = 2.4$ Hz), 3.91 (d, 1H, H-5, $J = 9.2$ Hz), 3.53-3.47 (m, 1H, H-1'a), 3.41-3.36 (m, 1H, H-1'b), 1.58-1.45 (m, 1H, H-3'), 1.41-1.31 (m, 2H, H-2'), 0.78 (d, 3H, CH₃ of i -amyl, $J = 1.8$ Hz), 0.76 (d, 3H, CH₃ of i -amyl, $J = 1.8$ Hz); ^{13}C NMR (CDCl_3 , 50MHz): δ 147.8 (qC), 133.0 (C-2), 130.5 (qC), 128.8 (C-3''' & C-5'''), 128.2 (C-4'''), 126.5 (C-3), 125.7 (C-2''' & C-6'''), 121.4 (C-4'''), 94.5 (C-1), 70.7 (C-5), 67.4 (C-1'), 64.6 (C-4), 51.4 (C-6), 38.3 (C-2'), 25.0 (C-3), 22.6 & 22.3 (2 CH₃ of i -amyl); MS (ESI): m/z 343; found 344 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_3$ $[\text{M}]^+$ 343.1896; found 343.1928.

Compound 18



This compound was obtained as a viscous oil; yield (89%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7); $[\alpha]_D^{31} = -25.02$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3752, 3417, 2928, 2367, 1637, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 8.59 (s, 1H, H-3'''), 8.38 (s, 1H, H-5'''), 8.19 (d, 1H, H-6''', $J = 7.7\text{Hz}$), 7.80 (t, 1H, H-5''', $J = 6.5\text{Hz}$), 7.28-7.25 (m, 1H, H-4'''), 5.95 (d, 1H, H-3, $J = 10.0\text{ Hz}$), 5.72 (d, 1H, H-2, $J = 10.2\text{ Hz}$), 4.95 (s, 1H, H-1), 4.81 (dd, 2H, H-4 & H-6a, $J = 12.2\text{Hz}$ & $J = 21.2\text{ Hz}$), 4.11 (d, 1H, H-6b, $J = 20.1\text{ Hz}$), 3.95 (d, 1H, H-5, $J = 8.5\text{ Hz}$), 3.52 – 3.35 (m, 2H, H-1'), 1.58-1.49 (m, 1H, H-3'), 1.39-1.32 (m, 2H, H-2'), 0.89-0.75 (m, 6H, 2 CH_3 of *i*-amyl). ^{13}C NMR (CDCl_3 , 75MHz): δ 150.3 (C-1'''), 149.4 (C-3'''), 148.3 (C-4''), 137.1 (C-5'''), 133.0 (C-3), 126.7 (C-2), 124.0 (C-6'''), 123.0 (C-4'''), 120.4 (C-5''), 94.6 (C-1), 70.7 (C-4), 67.5 (C-1'), 64.6 (C-5), 51.5 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.6 & 22.4 (2 CH_3 of *i*-amyl). MS (ESI): m/z 344; found 345 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$; 345.1926; found 345.1907.

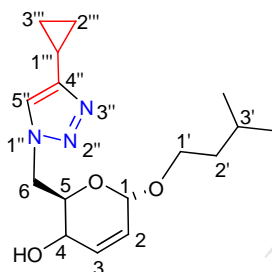
Compound 19



This compound was obtained as a viscous oil; yield (69%); $R_f = 0.57$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:7); $[\alpha]_D^{31} = -73.02$ (c 0.06, CHCl_3); IR (neat, cm^{-1}): 3746, 3420, 2365, 1642, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.91 (s, 1H, H-5'''), 7.78 (dd, 2H, H-3''' & H-2''', $J = 8.61\text{ Hz}$ & $J = 5.4\text{ Hz}$), 7.09 (t, 2H, H-3''' & H-5''', $J = 8.6\text{ Hz}$), 5.94 (d, 1H, H-3, $J = 10.2\text{ Hz}$), 5.70 (d, 1H, H-2, $J = 10.2\text{ Hz}$), 4.93 (s, 1H, H-1), 4.80 (dd, 1H, H-6a, $J = 14.3\text{ Hz}$ & $J = 2.0\text{ Hz}$), 4.66 (dd, 1H, H-6b, $J = 14.3\text{ Hz}$ & $J = 6.5$

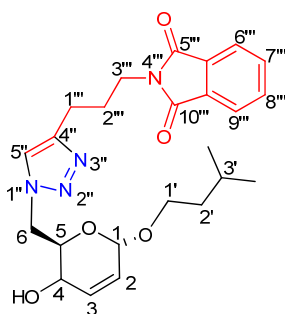
Hz), 4.05 (t, 1H, H-4, $J = 6.9$ Hz), 3.93 (d, 1H, H-5, $J = 9.1$ Hz), 3.49-3.32 (m, 3H, H-1' & H-3'), 1.56-1.47 (m, 1H, H-2a'), 1.38-1.25 (m, 2H, H-2b'), 0.87-0.74 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 164.4 (C-4'''), 161.1 (C-4''), 146.9 (C-3), 133.1 (C-2), 127.6 (C-6'''), 127.5 (C-2'''), 126.5 (C-3'''), 121.2 (C-5''), 116.02 (C-4'''), 115.7 (C-5'''), 94.6 (C-1), 70.8 (C-5), 67.4 (C-4), 64.6 (C-1'), 51.5 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.6 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): m/z 361; found 362 [M+H]⁺; HRMS (ESI): Calc for C₁₉H₂₅FN₃O₃ [M+H]⁺; 362.1880; found 362.1870.

Compound 21



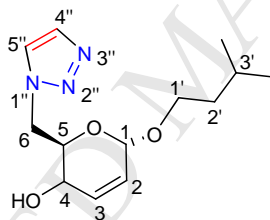
This compound was obtained as a viscous oil; yield (70%); $R_f = 0.56$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7); $[\alpha]_D^{31} = -100.67$ (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3298, 2926, 2369, 1657, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.39 (s, 1H, H-5''), 5.92 (dd, 1H, H-3, $J = 10.1$ Hz), 5.67 (d, 1H, H-3, $J = 10.1$ Hz), 4.89 (s, 1H, H-1), 4.68 (d, 1H, H-4, $J = 12.45$ Hz), 4.52 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 6.6$ Hz), 3.94 (d, 1H, H-6b, $J = 6.6$ Hz), 3.86 (d, 1H, H-5, $J = 9.09$ Hz), 3.47-3.33 (m, 2H, H-1'), 1.91 (s, 1H, H-1'''), 1.59 (t, 1H, H-3', $J = 6.63$ Hz), 1.34 (t, 4H, H-2', H-2'''a & H-3'''a $J = 6.81$ Hz), 0.93-0.80 (m, 8H, H-2'''a, H-3'''b, & 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 150.1 (C-4''), 133.3 (C-3), 126.2 (C-2), 121.5 (C-5''), 94.5 (C-1), 70.8 (C-5), 67.2 (C-4), 64.4 (C-1'), 51.2 (C-6), 38.4 (C-2'), 25.1 (C-3'), 22.7 & 22.4 (2CH₃ of *i*-amyl), 7.77 (C-1'''), 6.66 (C-2''' & C-3'''). MS (ESI): m/z 307; found 308 [M+H]⁺; HRMS (ESI): Calc for C₁₆H₂₆N₃O₃ [M+H]⁺; 308.1974; found 308.1962.

Compound 22



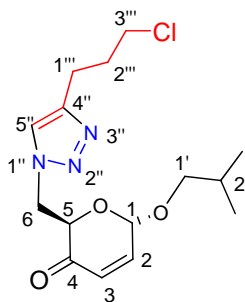
This compound was obtained as a viscous oil; yield (58%); $R_f = 0.53$ (chloroform: methanol 49:1) ; eluent for column chromatography (chloroform:methanol, 10:0.1); $[\alpha]_D^{31} = -7.93$ (c 0.04, CHCl_3); IR (neat, cm^{-1}): 3769, 3379, 2928, 2362, 1710, 1398, 1030; ^1H NMR (CDCl_3 , 300 MHz): δ 7.81 (dd, 2H, H-6'' & H-9'', $J = 5.49$ Hz & $J = 3.06$ Hz), 7.69 (dd, 2H, H-7'' & H-8'', $J = 5.37$ Hz & $J = 3.03$ Hz), 7.57 (s, 1H, H-5''), 5.91 (d, 1H, H-3, $J = 10.2$ Hz), 5.69-5.65 (m, 1H, H-2), 4.90 (s, 1H, H-1), 4.70-4.60 (m, 2H, H-4 & H-6a), 3.95 (d, 1H, H-6b, $J = 6.06$ Hz), 3.83 (d, 1H, H-5, $J = 8.97$ Hz), 3.72 (t, 2H, H-3'', $J = 6.9$ Hz), 3.52-3.46 (m, 1H, H-1'a), 3.38-3.33 (m, 1H, H-1'b), 2.62 (t, 2H, H-1'', $J = 7.32$ Hz), 2.14-2.02 (m, 2H, H-2''), 1.62-1.53 (m, 1H, H-3'), 1.37-1.31 (m, 2H, H-2'), 0.82-0.78 (m, 6H, 2CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 168.5 (C-5'' & C-10''), 134.0 ($2 \times q\text{C}$), 133.2 (C-7'' & C-8''), 132.1 (C-4''), 126.3 (C-6'', C-9'' & C-2), 123.3 (C-5' & C-3), 94.5 (C-1), 70.8 (C-5), 51.23 (C-4), 38.4 (C-1' & C-6), 37.4 (C-3''), 28.2 (C-2' & C-1''), 25.0 (C-3'), 23.0 (C-2''), 22.7 & 22.4 (2CH_3 of i -amyl). MS (ESI): m/z 454; found 455 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{24}\text{H}_{31}\text{N}_4\text{O}_5$ $[\text{M}+\text{H}]^+$; 455.2294; found 455.2292.

Compound 23



This compound was obtained as a viscous oil ; yield (72%); $R_f = 0.53$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 3:2); $[\alpha]_D^{31} = -20.20$ (c 0.02, CHCl_3); IR (neat, cm^{-1}): 3962, 3768, 3322, 2930, 2365, 1568, 1035; ^1H NMR (CDCl_3 , 300 MHz): δ 7.71 (d, 2H, H-4'' & H-5'', $J = 10.65$ Hz), 5.93 (d, 1H, H-3, $J = 10.1$ Hz), 5.69 (d, 1H, H-2, $J = 10.1$ Hz), 4.90 (s, 1H, H-1), 4.79 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.3$ Hz), 4.65 (dd, 1H, H-6b, $J = 14.2$ Hz & $J = 6.5$ Hz), 4.00 (t, 1H, H-4, $J = 6.87$ Hz), 3.85 (d, 1H, H-5, $J = 8.91$ Hz), 3.49-3.30 (m, 2H, H-1'), 1.66-1.53 (m, 1H, H-3'), 1.38-1.31 (m, 2H, H-2'), 0.85-0.81 (m, 6H, 2CH_3 of i -amyl). ^{13}C NMR (CDCl_3 , 75 MHz): δ 133.7 (C-3), 133.1 (C-5''), 126.5 (C-2), 125.2 (C-4''), 94.5 (C-1), 70.7 (C-4), 67.3 (C-5), 64.6 (C-6), 51.2 (C-1'), 38.4 (C-2'), 25.1 (C-3'), 22.7 & 22.5 (2CH_3 of i -amyl). MS (ESI): m/z 267; found 268 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{13}\text{H}_{22}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 268.1661 ; found 268.1643.

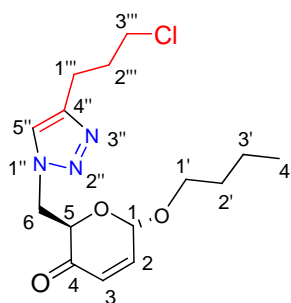
Compound 25



To a solution of **6** (285 mg, 0.8662 mmol) in dry DCM (20 mL) was added Dess-Martin periodinane (DMP) reagent (556 mg, 1.299 mmol) at -5 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **25**; yield (63%); $R_f = 0.52$ (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 17:3); $[\alpha]_D^{31} = -24.82$ (c 0.04, CHCl₃); IR (neat, cm⁻¹): 3754, 2925, 2368, 2102, 1721, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.51 (d, 1H, H-2, $J = 5.89$ Hz), 7.41 (s, 1H, H-5''), 6.26 (d, 1H, H-3, $J = 6.09$ Hz), 4.67-4.49 (m, 3H, H-6 & H-5), 3.58-3.46 (m, 5H, H-1, H-3''' & H-1'), 2.87 (t, 2H, H-1'', $J = 7.1$ Hz), 2.15 (dd, 2H, H-2'', $J = 13.4$ Hz & $J = 6.6$ Hz), 2.02-1.92 (m, 1H, H-2'), 0.97-0.84 (m, 6H, 2CH₃ of *i*butyl); ¹³C NMR (CDCl₃, 75MHz): δ 192.9 (C-4), 172.2 (C-4''), 168.1 (C-3), 141.1 (C-2), 132.6 (C-5''), 94.3 (C-1), 88.03 (C-1'), 62.6 (C-6), 53.5 (C-3'''), 41.2 (C-1'''), 39.1 (C-2'''), 38.2 (C-5), 28.7 (C-2'), 19.3 & 19.4 (2CH₃ of *i*butyl). MS (ESI): m/z 327; found 328 [M+H]⁺; HRMS (ESI): Calc for C₁₅H₂₃ClN₃O₃ [M+H]⁺; 328.1428; found 328.1410.

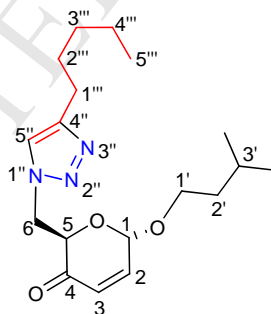
Compounds **26**, **27**, **28**, **30**, **31**, **33**, **34**, **35**, **36**, **37**, **38**, **40**, **41**, **42** were prepared using the same procedure as for compound **25**.

Compound 26



This compound was obtained as a viscous oil ; yield (63.7%); R_f = 0.47 (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 3:1); $[\alpha]_D^{31} = -174.25$ (c 0.012, CHCl_3); IR (neat, cm^{-1}): 3751, 2925, 3406, 2362, 1697, 1219 ; ^1H NMR (CDCl_3 , 300 MHz): 7.43 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 3.4$ Hz), 6.10 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.3$ Hz), 5.02 (dd, 1H, H-6a, $J = 14.4$ Hz and $J = 3.0$ Hz), 4.81 (dd, 1H, H-5, $J = 7.6$ Hz and $J = 3.0$ Hz), 4.53 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 7.6$ Hz), 3.56-3.43 (m, 2H, H-1'), 2.87 (t, 2H, H-3''', $J = 7.2$ Hz), 2.16 (t, 2H, H-1''', $J = 6.6$ Hz), 1.49-1.40 (m, 2H, H-2'''), 1.31-1.16 (m, 4H, H-2' & H-3'), 0.85 (t, 3H, H-4', $J = 7.3$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 193.1 (C-4), 146.3 (C-4''), 144.5 (C-3), 127.1 (C-2), 122.6 (C-5''), 93.2 (C-1), 72.8 (C-5), 69.6 (C-6), 49.5 (C-1'), 44.1 (C-3'''), 32.0 (C-2'), 29.7 (C-1'''), 22.7 (C-2'''), 19.3 (C-3'), 13.8 (C-4'). MS (ESI): m/z 327; found 328 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{15}\text{H}_{23}\text{ClN}_3\text{O}_4$ $[\text{M}+\text{H}]^+$; 328.1428 ; found 328.1421.

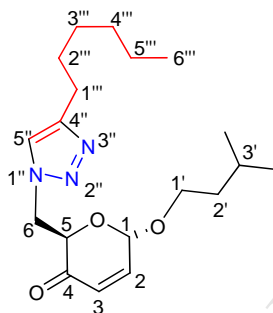
Compound 27



This compound was obtained as a viscous oil; yield (57%); R_f = 0.5 (hexane-ethyl acetate, 1:1) ; eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = -127.56$ (c 0.13, CHCl_3); IR (neat, cm^{-1}): 3380, 2932, 2365, 1699, 1218; ^1H NMR (CDCl_3 , 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.4$ Hz), 5.02 (dd, 1H, H-6a, $J = 14.5$ Hz & $J = 3.0$ Hz), 4.80 (dd, 1H, H-5, $J = 7.8$ Hz and $J = 3.0$ Hz), 4.51 (dd, 1H, H-6b, $J = 14.5$ Hz & $J = 7.8$ Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1''', $J = 7.6$ Hz), 1.69-1.59 (m, 3H, H-3' and H-2'), 1.41-1.27 (m,

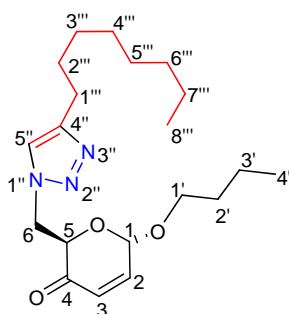
6H, H-2''', H-3''' & H-4'''), 0.88-0.81(m, 9H, 1CH₃ of H-5''' & 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75MHz): δ 193.2 (C-4), 148.5 (C-4'''), 144.5 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.2 (C-1'), 49.4 (C-6), 38.2 (C-2'), 31.5 (C-1'''), 29.3 (C-2'''), 25.7 (C-3'''), 25.0 (C-3'), 22.6 (C-4'''), 22.5 & 22.4 (2CH₃ of *i*-amyl), 14.1 (CH₃ of C-5'''); MS (ESI): *m/z* 335; found 336 [M+H]⁺; HRMS (DART): Calc for C₁₈H₃₀N₃O₃ [M+H]⁺; 336.2287; found 336.2275.

Compound 28



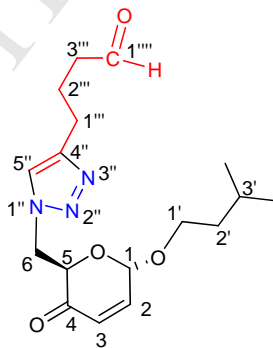
This compound was obtained as a viscous oil; yield (61%); *R_f* = 0.52 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); [α]_D³¹ = -136.6794 (c 0.12, CHCl₃); IR (neat, cm⁻¹): 3772, 3455, 2925, 1685, 1463, 1031; ¹H NMR (CDCl₃, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5 Hz), 6.09 (d, 1H, H-3, *J* = 10.3 Hz), 5.19 (d, 1H, H-1, *J* = 3.4 Hz), 5.02 (dd, 1H, H-6a, *J* = 14.4 Hz and *J* = 3.0 Hz), 4.80 (dd, 1H, H-5, *J* = 7.8 Hz & *J* = 3.0 Hz), 4.51 (dd, 1H, H-6b, *J* = 14.5 Hz & *J* = 7.8 Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1'', *J* = 7.6 Hz), 1.65- 1.57 (m, 3H, H-3' & H-2'), 1.41- 1.30 (m, 8H, H-2'''-H-5'''), 0.89-0.80 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-6'''); ¹³C NMR (CDCl₃, 75MHz): δ 193.2 (C-4), 148.5 (C-4'''), 144.5 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 73.0 (C-5), 68.2 (C-1'), 49.5 (C-6), 38.23 (C-2'), 31.7 (C-1'''), 29.8 (C-2'''), 29.6 (C-3'''), 29.0 (C-4'''), 25.7 (C-5'''), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*-amyl), 14.1 (CH₃ Of C-6'''). MS (ESI): *m/z* 349; found 350 [M+H]⁺; HRMS (DART): Calc for C₁₉H₃₂N₃O₃ [M+H]⁺, 350.2443; found 350.2424.

Compound 30



This compound was obtained as a viscous oil; yield (56%); $R_f = 0.47$ (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); $[\alpha]_D^{31} = -15.67$ (c 0.04, CHCl_3); IR (neat, cm^{-1}): 3755, 3693, 3374, 2928, 2363, 1660, 1591, 1217; ^1H NMR (CDCl_3 , 300 MHz): δ 7.35 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, $J = 10.1$ Hz & $J = 3.1$ Hz), 6.10 (d, 1H, H-3, $J = 10.2$ Hz), 5.19 (d, 1H, H-1, $J = 2.9$ Hz), 5.03 (dd, 2H, H-6, $J = 14.4$ Hz & $J = 2.3$ Hz), 4.81 (dd, 1H, H-5, $J = 7.6$ Hz & $J = 2.6$ Hz), 4.50 (dd, 2H, H-1', $J = 14.3$ Hz & $J = 8.0$ Hz), 3.52-3.43 (m, 2H, H-1''), 2.69 (t, 2H, H-2', $J = 7.5$ Hz), 1.62 (d, 2H, $J = 6.8$ Hz), 1.49-1.42 (m, 12H, H-2'''-H-7'''), 0.87-0.85 (m, 6H, 2 CH_3 of H-8''' & H-4'); ^{13}C NMR (CDCl_3 , 75 MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.4 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 69.6 (C-1'), 49.4 (C-6), 31.9 (C-2'), 31.6 (C-1'''), 29.6 (C-2'''), 29.4 (C-3'''), 29.32 (C-4'''), 29.3 (C-5'''), 25.7 (C-6'''), 22.7 (C-7'''), 19.3 (C-3'), 14.2 (C-4'), 13.8 (C-8'''). MS (ESI): m/z 363; found 364 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{20}\text{H}_{34}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$; 364.2600; found 364.2602.

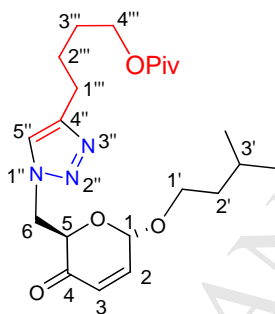
Compound 31



This compound was obtained as a viscous oil; yield (63 %); $R_f = 0.47$ (hexane-ethyl acetate 1:1); eluent for column chromatography (hexane-ethyl acetate, 16:9); $[\alpha]_D^{31} = +4.95$ (c 0.27, CHCl_3); IR (neat, cm^{-1}): 3754, 3432, 2923, 2372, 1646, 1464, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 9.74 (s, 1H, H-1'''), 7.40 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.5$ Hz), 5.00 (dd, 1H, H-6a, $J =$

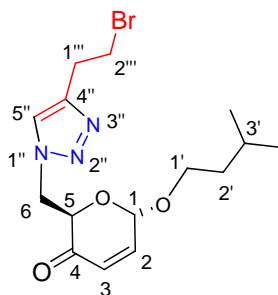
14.4 Hz & $J = 3.1$ Hz), 4.79 (dd, 1H, H-5, $J = 7.5$ Hz & $J = 3.1$ Hz), 4.54 (dd, 1H, H-6b, $J = 14.4$ Hz & $J = 7.5$ Hz), 3.62-3.42 (m, 2H, H-1'), 2.73 (t, 2H, H-1'', $J = 7.5$ Hz), 2.51 (t, 2H, H-3'', $J = 7.2$ Hz), 2.03-1.95 (m, 2H, H-2''), 1.62-1.53 (m, 1H, H-3'), 1.40-1.33 (m, 2H, H-2'), 0.84-0.78 (m, 6H, 2CH₃ of *i*amyl); ¹³C NMR (CDCl₃, 75MHz): δ 202.0 (C-1'''), 193.1 (C-4), 147.0 (C-4''), 144.5 (C-2), 127.1 (C-3), 122.4 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 43.1 (C-3'''), 38.2 (C-2'), 24.9 (C-2''), 24.8 (C-3'), 22.6 (C-2'''), 22.3 & 21.9 (2CH₃ of *i*amyl); MS (ESI): m/z 335; found 336 [M+H]⁺; HRMS (DART): Calc for C₁₇H₂₆N₃O₄[M+H]⁺; 336.1923; found 336.1904.

Compound 33



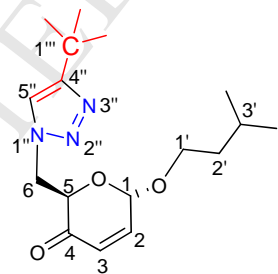
This compound was obtained as a viscous oil; yield (59 %); $R_f = 0.53$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 7:3); $[\alpha]_D^{31} = -33.35$ (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3750, 3422, 2364, 1642, 1218; ¹H NMR (CDCl₃, 300 MHz): δ 7.37 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.2$ Hz & $J = 3.2$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.03$ Hz), 5.01 (dd, 1H, H-6a $J = 14.3$ Hz & $J = 2.7$ Hz), 4.80 (dd, 1H, H-6b, $J = 7.44$ Hz, $J = 2.79$ Hz), 4.53 (dd, 1H, H-5, $J = 14.4$ Hz, & $J = 7.4$ Hz), 4.07 (d, 2H, H-4'', $J = 5.9$ Hz), 3.61-3.42 (m, 2H, H-1'), 2.72 (d, 2H, H-1'', $J = 6.8$ Hz), 1.70-1.53 (m, 4H, H-2'', H-3''), 1.40 (m, 1H, H-3'), 1.24-1.18 (m, 11H, H-2' & 9H OCOC(CH₃)₃), 0.89-0.88 (m, 6H, 2CH₃ of *i*amyl); ¹³C NMR (CDCl₃, 75MHz): δ 193.2 (C-4), 178.7 (C-5''), 147.7 (C-4''), 144.5 (C-2), 127.1 (C-3), 122.2 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 64.1 (C-4''), 49.5 (C-6), 38.2 (C-2'), 29.7 (C of OCOC(CH₃)₃), 28.3 (C-1''), 27.3 (CH₃ of OCOC(CH₃)₃), 25.98 (C-2''), 25.3 (C-3''), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*amyl). MS (ESI): m/z 421; found 422 [M+H]⁺; HRMS (ESI): Calc for C₂₂H₃₆N₃O₅ [M+H]⁺; 422.2655; found 422.2639.

Compound 34



This compound was obtained as a viscous oil ; yield (74%); $R_f = 0.53$ (hexane-ethyl acetate 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 17:3) ; $[\alpha]_D^{31} = -0.34$ (c 0.17, CHCl_3); IR (neat, cm^{-1}): 3880, 3751, 3444, 2364, 1655, 1220; ^1H NMR (CDCl_3 , 300 MHz): δ 7.56 (s, 1H, H-5''), 6.87 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.11 (d, 1H, H-3, $J = 10.2$ Hz), 5.21 (d, 1H, H-1, $J = 3.4$ Hz), 5.06 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.94$ Hz), 4.82 (dd, 1H, H-5, $J = 7.7$ Hz & $J = 3.1$ Hz), 4.59-4.50 (m, 1H, H-6b), 3.64 (t, 2H, H-2'', $J = 6.7$ Hz), 3.51- 3.43 (m, 1H, H-1'a), 3.29 (t, 3H, H-1''' & H-1'b, $J = 6.75$ Hz), 1.65-1.54 (m, 1H, H-3'), 1.42-1.36 (m, 2H, H-2'), 0.86-0.80 (m, 6H, 2 CH_3 of *i*-amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 144.8 (C-4''), 144.5 (C-2), 127.1 (C-3), 123.3 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.3 (C-1'), 49.6 (C-6), 38.2 (C-2'), 31.7 (C-2'''), 29.2 (C-1'''), 25.0 (C-3'), 22.6 & 22.3 (2 CH_3 of *i*-amyl). MS (ESI): m/z 371; found 372 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{15}\text{H}_{23}\text{BrN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 372.0922 ; found 372.0932.

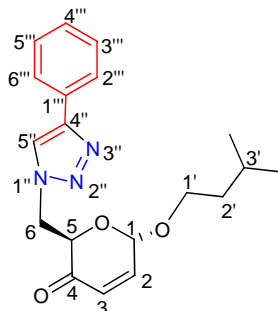
Compound 35



This compound was obtained as a viscous oil; yield (86%); $R_f = 0.52$ (hexane-ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 9:1); $[\alpha]_D^{31} = +5.84$ (c 0.10, CHCl_3); IR (neat, cm^{-1}): 3420, 2926, 2365, 1700, 1217; ^1H NMR (CDCl_3 , 300 MHz): δ 7.34 (s, 1H, H-5''), 6.84 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.45$ Hz), 6.07 (d, 1H, H-3, $J = 10.3$ Hz), 5.18 (d, 1H, H-1, $J = 3.3$ Hz), 5.04 (dd, 1H, H-6a, $J = 14.5$ Hz & $J = 2.9$ Hz), 4.78 (dd, 1H, H-5, $J = 8.8$ Hz & $J = 2.82$ Hz), 4.42 (dd, 1H, H-6b, $J = 14.5$ Hz & $J = 8.3$ Hz), 3.51-3.39 (m, 2H, H-1'), 1.58-1.51 (m, 1H, H-3'), 1.33-1.25 (m, 11H, H-2', & C(CH_3)₃), 0.88-0.78 (m, 6H, 2 CH_3 of *i*-amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.1 (C-4), 157.6 (C-4''), 144.4 (C-2),

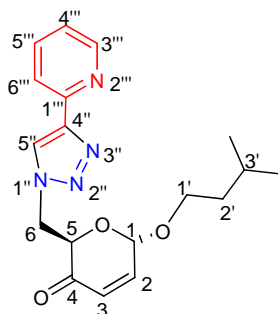
127.1 (C-3), 120.2 (C-5''), 96.5 (C-1), 72.9 (C-5), 68.0 (C-1'), 49.3 (C-6), 38.2 (C-2'), 30.4 (C(CH₃)₃), 29.3 (C(CH₃)₃) 24.9 (C-3'), 22.6 & 22.3 (2CH₃ of *i*amyl). MS (ESI): *m/z* 321; found 322 [M+H]⁺; HRMS (ESI): Calc for C₁₇H₂₈N₃O₃ [M+H]⁺; 322.2131; found 322.2122.

Compound 36



This compound was obtained as a Glassy solid; yield (81%); *R_f* = 0.43 (hexane/ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 89:11); [*α*]_D = -147.80 (c 0.24, CHCl₃); IR (neat, cm⁻¹): 3423, 3020, 1633, 1426, 1216; ¹H NMR (CDCl₃, 300 MHz): δ 7.86 (s, 1H, H-5''), 7.83-7.80 (m, 2H, H-2''' & H-6'''), 7.43-7.32 (m, 3H, H-3''', H-4''' & H-5'''), 6.86 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5 Hz), 5.21 (d, 1H, H-1, *J* = 3.4 Hz), 5.10 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 3.1 Hz), 4.87 (dd, 1H, H-5, *J* = 7.6 Hz & *J* = 3.1 Hz), 4.63 (dd, 1H, H-6b, *J* = 14.4 Hz & *J* = 7.6 Hz), 3.63-3.55 (m, 1H, H-1'a), 3.51-3.36 (m, 1H, H-1'b), 1.58-1.45 (m, 1H, H-3'), 1.41-1.31 (m, 2H, H-2'), 0.78 (d, 3H, CH₃ of *i*amyl, *J* = 1.8 Hz), 0.76 (d, 3H, CH₃ of *i*amyl, *J* = 1.8 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 193.1 (C-4), 147.8 (*q*C), 144.5 (C-2), 130.6 (*q*C), 128.8 (C-3''' & C-5'''), 128.2 (C-4'''), 127.1 (C-3), 125.8 (C-2''' & C-6'''), 121.0 (C-4'''), 93.3 (C-1), 72.8 (C-5), 68.4 (C-1'), 49.6 (C-6), 38.2 (C-2'), 25.0 (C-3), 22.5 & 22.3 (2 CH₃ of *i*amyl); MS (ESI): *m/z* 341; found 342 [M+H]⁺; HRMS (ESI): Calc for C₁₉H₂₃N₃O₃ [M]⁺ 341.1739; found 341.1741.

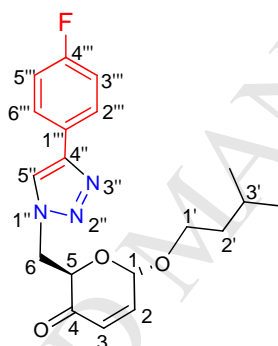
Compound 37



This compound was obtained as a viscous oil; yield (89%); *R_f* = 0.51 (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 13:7); [*α*]_D³¹ = -25.02 (c 0.06,

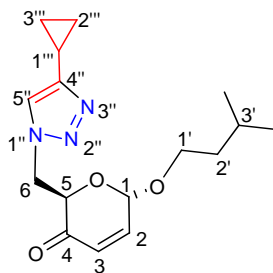
CHCl₃); IR (neat, cm⁻¹): 3752, 3417, 2928, 2367, 1637, 1218 ; ¹H NMR (CDCl₃, 300 MHz): δ 8.56 (d, 1H, H-3''', *J* = 4.2 Hz), 8.25 (s, 1H, H-5''), 8.16 (d, 1H, H-6''', *J* = 7.9 Hz), 7.75 (t, 1H, H-5''', *J* = 7.56 Hz), 7.22-7.18 (m, 1H, H-4'''), 6.85 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.4 Hz), 6.11 (d, 1H, H-3, *J* = 10.3 Hz), 5.20 (d, 1H, H-1, *J* = 3.3 Hz), 5.12 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 2.9 Hz), 4.86 (dd, 1H, H-5, *J* = 7.8 Hz & *J* = 2.8 Hz), 4.63 (dd, 1H, H-6b, *J* = 14.34 Hz & *J* = 7.92 Hz), 3.60-3.41 (m, 2H, H-1'), 1.56-1.44 (m, 1H, H-3'), 1.37-1.33 (m, 2H, H-2'), 0.75-0.72 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 192.9 (C-4), 150.4 (C-1'''), 149.4 (C-3'''), 148.4 (C-5'''), 144.5 (C-2), 136.9 (C-3), 127.2 (C-6'''), 123.6 (C-4'''), 122.9 (C-4'''), 120.3 (C-5''), 93.3 (C-1), 72.7 (C-5), 68.5 (C-6), 49.8 (C-1'), 38.2 (C-2'), 25.0 (C-3'), 22.5 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): *m/z* 342; found 343 [M+H]⁺; HRMS (DART): Calc for C₁₈H₂₃N₄O₃ [M+H]⁺; 343.1770 ; found 343.1780.

Compound 38



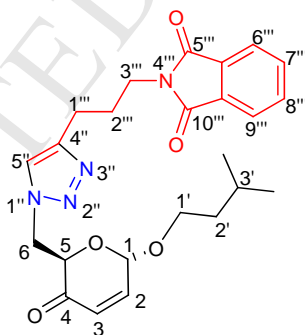
This compound was obtained as a viscous oil; yield (66%); *R_f* = 0.57 (hexane-ethyl acetate, 7:3) ; eluent for column chromatography (hexane-ethyl acetate, 9:1); [*α*]_D³¹ = -94.93(c 0.08, CHCl₃); IR (neat, cm⁻¹): 3733, 3437, 2955, 1695, 1367, 1222 ; ¹H NMR (CDCl₃, 300 MHz): δ 7.79 (dd, 3H, H-5'', H-3''' & H-2''', *J* = 9.27 Hz & *J* = 6.21 Hz), 7.10 (t, 2H, H-5''' & H-6''', *J* = 8.64 Hz), 6.87 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.4 Hz), 6.12 (d, 1H, H-3, *J* = 10.3 Hz), 5.22 (d, 1H, H-1, *J* = 3.27 Hz), 5.09 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 3.1 Hz), 4.87 (dd, 1H, H-5, *J* = 7.4 Hz & *J* = 3.1 Hz), 4.63 (dd, 1H, H-6b, *J* = 14.3 Hz & *J* = 7.4 Hz), 3.63-3.44 (m, 2H, H-1'), 1.60-1.53 (m, 1H, H-3'), 1.41-1.34 (m, 2H, H-2'), 0.87-0.76 (m, 6H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75 MHz): δ 193.1 (C-4), 147.0 (C-4'''), 144.6 (C-4''), 127.6 (C-2), 127.5 (C-3), 127.2 (C-6''' & C-2'''), 120.8 (C-5''), 116.0 (C-1'''), 115.7 (C-5''' & C-3'''), 93.4 (C-1), 72.8 (C-5), 68.4 (C-1'), 49.7 (C-6'), 38.2 (C-2'), 25.0 (C-3'), 22.6 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): *m/z* 359; found 360 [M+H]⁺; HRMS (ESI): Calc for C₁₉H₂₃FN₃O₃ [M+H]⁺ ; 360.1723 ; found 360.1710.

Compound 40



This compound was obtained as a viscous oil; yield (75%); $R_f = 0.47$ (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -122.58$ (c 0.014, CHCl_3); IR (neat, cm^{-1}): 3752, 2957, 2361, 1697, 1219; ^1H NMR (CDCl_3 , 300 MHz): δ 7.31 (s, 1H, H-5''), 6.84 (dd, 1H, H-2, $J = 10.3$ Hz and $J = 3.5$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.3$ Hz), 4.99 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.9$ Hz), 4.77 (dd, 1H, H-5, $J = 7.68$ Hz and $J = 2.97$ Hz), 4.51-4.46 (m, 1H, H-6b), 3.60-3.42 (m, 2H, H-1'), 1.96-1.87 (m, 1H, H-1''), 1.63-1.52 (m, 1H, H-3'), 1.38 (dd, 2H, H-2', $J = 13.47$ Hz & $J = 6.75$ Hz), 0.94-0.79 (m, 10H, 6H of *i*-amyl & 4H of H-2''' & H-3'''); ^{13}C NMR (CDCl_3 , 75 MHz): δ 193.1 (C-4), 150.3 (C-4''), 144.4 (C-2), 127.1 (C-3), 121.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.3 (C-1'), 38.2 (C-6), 34.0 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2 CH_3 of *i*-amyl), 7.7 (C-1'''), 6.7 (C-2''' & C-3'''). MS (ESI): m/z 305; found 306 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{16}\text{H}_{24}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$; 306.1818; found 306.1806.

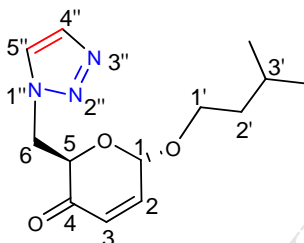
Compound 41



This compound was obtained as a viscous oil; yield (59%); $R_f = 0.53$ (chloroform-methanol, 97:3); eluent for column chromatography (chloroform-methanol, 99:1); $[\alpha]_D^{31} = -18.30$ (c 0.15, CHCl_3); IR (neat, cm^{-1}): 3458, 2358, 1696, 1217; ^1H NMR (CDCl_3 , 300 MHz): δ 7.82 (dd, 2H, H-8''' & H-7'', $J = 5.4$ Hz & $J = 3.1$ Hz), 7.70 (dd, 2H, H-9''' & H-6'', $J = 5.37$ Hz & $J = 3.09$ Hz), 7.50 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.48$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.20 (d, 1H, H-1, $J = 3.39$ Hz), 4.99 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 3.0$ Hz), 4.80 (dd, 1H, H-5, $J = 7.71$ Hz & $J = 3.06$ Hz), 4.53 (d, 1H, H-6b, $J = 14.4$ Hz & $J = 7.7$ Hz),

3.72 (t, 2H, H-1', $J = 6.93$ Hz), 3.60-3.35 (m, 2H, H-3'), 2.75 (t, 2H, H-2'', $J = 7.5$ Hz), 2.09-2.0 (m, 2H, H-1'''), 1.61-1.50 (m, 1H, H-3'), 1.39-1.33 (m, 2H, H-2'), 0.82-0.76 (m, 6H, 2CH₃ of *i*-amyl). ¹³C NMR (CDCl₃, 75MHz): δ 193.1 (C-4), 168.4 (C-5''' & C-10'''), 146.8 (C-2), 144.5 (C-3), 134.0 (2 \times qC), 132.1 (C-7''' & C-8'''), 127.1 (C-4''), 123.3 (C-6''' & C-9'''), 122.5 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 38.2 (C-3'''), 37.3 (C-2'), 28.3 (C-1'''), 25.0 (C-3'), 23.1 (C-2''), 22.6 & 22.3 (2CH₃ of *i*-amyl). MS (ESI): m/z 452; found 453 [M+H]⁺; HRMS (ESI): Calc for C₂₄H₂₉N₄O₅ [M+H]⁺; 453.2138; found 453.2314.

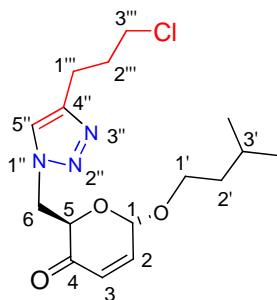
Compound 42



This compound was obtained as a viscous oil; yield (62%); $R_f = 0.46$ (hexane-ethyl acetate, 3:2); eluent for column chromatography (hexane-ethyl acetate, 21:4); $[\alpha]_D^{31} = -54.69$ (c 0.017, CHCl₃); IR (neat, cm⁻¹): 3957, 3453, 2926, 2366, 1697, 1225, 1101; ¹H NMR (CDCl₃, 300 MHz): δ 7.66 (d, 2H, H-5'' & H-4'', $J = 4.11$ Hz), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz and $J = 3.5$ Hz), 6.09 (d, 1H, H-2, $J = 10.3$ Hz), 5.18 (d, 1H, H-1, $J = 3.33$ Hz), 5.08 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 2.91$ Hz), 4.81 (dd, 1H, H-5, $J = 7.71$ Hz & $J = 2.97$ Hz), 4.59 (dd, 1H, H-6b, $J = 14.37$ Hz & $J = 7.74$ Hz), 3.55-3.42 (m, 2H, H-1'), 0.91-0.80 (m, 9H, 2CH₃ of *i*-amyl); ¹³C NMR (CDCl₃, 75MHz): δ 193.0 (C-4), 144.5 (C-5''), 133.8 (C-4''), 127.1 (C-2), 124.9 (C-3), 93.2 (C-1), 72.8 (C-5), 68.3 (C-6), 49.4 (C-1'), 38.1 (C-2'), 25.0 (C-3'), 22.5 & 22.4 (2CH₃ of *i*-amyl). MS (ESI): m/z 265; found 266 [M+H]⁺; HRMS (ESI): Calc for C₁₃H₂₀N₃O₃ [M+H]⁺; 266.1505; found 266.1495.

One pot two step procedure for the synthesis of compound **24**, **29**, **32** and **39**.

Compound 24

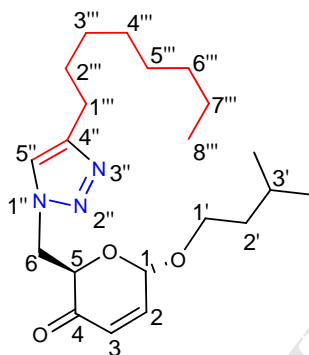


To a vigorously stirred solution of azide **4a** (200 mg, 0.829 mmol) in *tert*-butyl alcohol was added the 5-chloropentyne (0.104 mL, 0.994 mmol). The reaction was initiated by the addition of a solution of CuSO₄·5H₂O (41.19 mg, 0.165 mmol) and sodium ascorbate (65.57 mg, 0.331 mmol) in distilled water. The colored suspension formed was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were evaporated *in vacuo* to afford the crude product mixture of **5** which was dissolved in dry DCM followed by the addition of Dess-Martin periodinane (392 mg, 0.918 mmol) at 0 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4 hours). The reaction was quenched by addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **24** as a white solid in 64 % over 2 steps. Mp 61°C - 64°C ; R_f = 0.44 (hexane-ethyl acetate, 3:2) ; eluent for column chromatography (hexane-ethyl acetate, 22:3); [α]_D³¹ = -42.14 (*c* 0.20, CHCl₃); IR (neat, cm⁻¹): 3021, 1701, 1216; ¹H NMR (CDCl₃, 300 MHz): δ 7.43 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, *J* = 10.3 Hz & *J* = 3.5 Hz), 6.11 (d, 1H, H-3, *J* = 10.3 Hz), 5.20 (d, 1H, H-1, *J* = 3.2 Hz), 5.03 (dd, 1H, H-6a, *J* = 14.4 Hz & *J* = 3.0 Hz), 4.81 (dd, 1H, H-5, *J* = 7.6 Hz & *J* = 3.0 Hz), 4.54 (dd, 1H, H-6b, *J* = 14.4 Hz & *J* = 7.6 Hz), 3.62-3.43 (m, 4H, H-3''', H-1'a & H-1'b), 2.87 (t, 2H, H-1''', *J* = 7.3 Hz), 2.20-2.11 (m, 2H, H-2''') 1.60 (pent., 1H, H-3', *J* = 6.7 Hz), 1.43-1.36 (m, 2H, H-2'), 0.85 (d, 3H, CH₃ of *i*-amyl, *J* = 6.7 Hz), 0.82 (d, 3H, CH₃ of *i*-amyl, *J* = 6.6 Hz); ¹³C NMR (CDCl₃, 50MHz): δ 193.0 (C-4), 146.3 (*q*C), 144.4 (C-2), 127.1 (C-3), 122.5 (C-5''), 93.2 (C-1), 72.8 (C-5), 68.2 (C-1'), 49.5 (C-6), 44.1 (C-3'''), 38.2 (C-2'), 31.9 (C-2'''), 24.9 (C-3'), 22.7 (C-1'''), 22.6 & 22.3 (2 CH₃ of *i*-amyl); MS (ESI):

m/z 341; found 342 $[M+H]^+$. HRMS (DART): Calc for $C_{16}H_{25}ClN_3O_3$ $[M+H]^+$ 342.1584; found 342.1600.

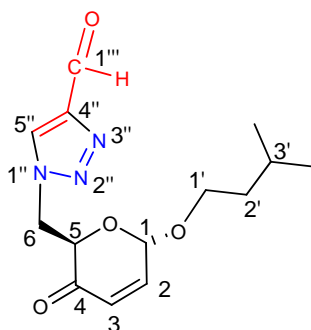
6-triazolyl 2,3,6 trideoxy hex-2- enopyranosid-4-uloses **29**, **32** and **39** were likewise prepared from **4a** via intermediates **10**, **13** and **20** respectively using the same two step procedure as described above for compound **24**.

Compound 29



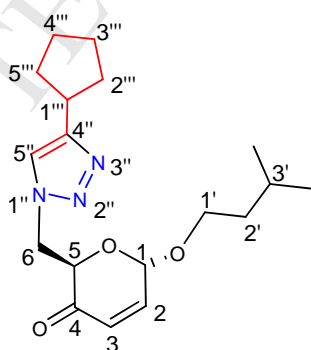
This compound was obtained as a viscous oil ; yield (63% in 2 steps); R_f = 0.57 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -18.30$ (c 0.13, $CHCl_3$); IR (neat, cm^{-1}): 3749, 3458, 2358, 1696, 1217; 1H NMR ($CDCl_3$, 300 MHz): δ 7.35 (s, 1H, H-5''), 6.85 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.10 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.3$ Hz), 5.03 (dd, 1H, H-6a, $J = 14.5$ Hz & $J = 3.0$ Hz), 4.80 (dd, 1H, H-5, $J = 7.7$ Hz & $J = 3.0$ Hz), 4.51 (dd, 1H, H-6b, $J = 14.5$ Hz & $J = 7.7$ Hz), 3.58-3.44 (m, 2H, H-1'), 2.68 (t, 2H, H-1''', $J = 7.5$ Hz), 1.64-1.57 (m, 3H, H-2' & H-3'), 1.33-1.25 (m, 12H, H-2'''-H-7'''), 0.91-0.80 (m, 9H, 2 CH_3 of i -amyl and 1 CH_3 of H-8'''); ^{13}C NMR ($CDCl_3$, 75MHz): δ 193.2 (C-4), 148.5 (C-4''), 144.4 (C-2), 127.2 (C-3), 122.0 (C-5''), 93.2 (C-1), 72.9 (C-5), 68.2 (C-1'), 49.4 (C-6), 38.2 (C-2'), 31.9 (C-1'''), 29.7 (C-2'''), 29.6 (C-3'''), 29.4 (C-4'''), 29.3 (C-5''' & C-6'''), 25.7 (C-7'''), 25.0 (C-3'), 22.7 & 22.5 (2 CH_3 of i -amyl), 14.2 (C-8'''); MS (ESI): m/z 377; found 378 $[M+H]^+$; HRMS (DART): Calc for $C_{21}H_{36}N_3O_3$ $[M+H]^+$; 378.2756 ; found 378.2758.

Compound 32



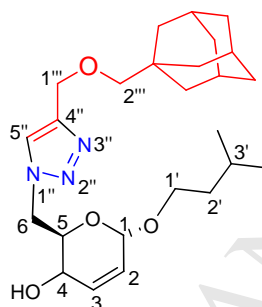
This compound was obtained as a viscous oil; yield (48% in 2 steps); R_f = 0.51 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 17:3); $[\alpha]_D^{31} = -153.09$ (c 0.02, CHCl_3); IR (neat, cm^{-1}): 3904, 3778, 3388, 3020, 1701, 1217; ^1H NMR (CDCl_3 , 300 MHz): δ 10.13 (s, 1H, H-1'''), 8.22 (s, 1H, H-5''), 6.88 (dd, 1H, H-2, J = 10.3 Hz and J = 3.4 Hz), 6.12 (d, 1H, H-3, J = 10.3 Hz), 5.21 (d, 1H, H-1, J = 3.2 Hz), 5.11 (dd, 1H, H-6a, J = 14.3 Hz & J = 3.0 Hz), 4.85 (dd, 1H, H-5, J = 7.5 Hz & J = 3.03 Hz), 4.67 (dd, 1H, H-6b, J = 14.3 Hz, & J = 7.56 Hz), 3.58-3.44 (m, 2H, H-1'), 1.63-1.54 (m, 1H, H-3'), 1.41-1.34 (m, 2H, H-2'), 0.84-0.79 (m, 6H, 2 CH_3 of i -amyl); ^{13}C NMR (CDCl_3 , 75 MHz): δ 192.5 (C-4), 185.1 (C-1'''), 147.9 (C-4''), 144.6 (C-2), 127.1 (C-3), 126.7 (C-5''), 93.4 (C-1), 72.3 (C-5), 68.5 (C-6), 49.9 (C-6), 38.2 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2 CH_3 of i -amyl). MS (ESI): m/z 293; found 294 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$; 294.1453; found 294.1474.

Compound 39



This compound was obtained as a glassy solid; Yield (57 % in 2 steps); R_f = 0.50 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 9:1); $[\alpha]_D = -26.42$ (c 0.21, CHCl_3); IR (neat, cm^{-1}): 3020, 1699, 1520, 1216. ^1H NMR (CDCl_3 , 300 MHz): δ 7.36 (s, 1H, H-5''), 6.88 (dd, 1H, H-2, J = 10.3 Hz & J = 6.8 Hz), 6.11 (d, 1H, H-3, J = 10.3 Hz), 5.20 (d, 1H, H-1, J = 3.5 Hz), 5.05 (dd, 1H, H-6a, J = 14.5 Hz & J = 3.0 Hz), 4.80 (dd, 1H, H-5, J = 7.9 Hz & J = 3.0 Hz), 4.49 (dd, 1H, H-6b, J = 14.5 Hz & J = 7.9 Hz),

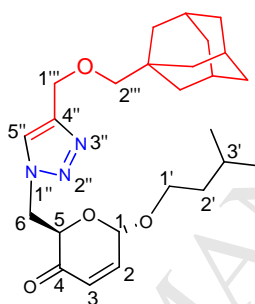
Compound 45



S-27

(CDCl₃, 300 MHz): δ 7.67 (s, 1H, H-5''), 5.92 (d, 1H, H-3, J = 9.7 Hz), 5.71 (d, 1H, H-2, J = 10.3 Hz), 4.92 (s, 1H, H-1), 4.74-4.60 (m, 4H, H-4, H-5 & H-6), 3.98 (d, 1H, H-1'''a), 3.84 (s, 1H, H-1'''b), 3.52 (dd, 1H, H-1'a, J = 16.3 Hz & J = 7.1 Hz), 3.41-3.30 (m, 1H, H-5), 3.06 (s, 1H, H-2a''), 1.94 (s, 4H, 3 \times CH_{Ad} & H-2b''), 1.68-1.52 (m, 12H, 6 \times CH_{2Ad}), 1.41-1.25 (m, 3H, H-2' & H-3'), 0.87-0.83 (m, 6H, 2CH₃ of *i*amyl); ¹³C NMR (CDCl₃, 75MHz): δ 142.6 (C-4''), 132.8 (C-3), 126.7 (C-2), 124.0 (C-5''), 94.6 (C-1), 81.6 (C-2'''), 70.7 (C-5), 67.3 (C-1'), 65.2 (C-4), 64.7 (C-1'''), 51.3 (C-6), 39.8 (3CH_{2Ad}), 38.4 (C-2'), 37.3 (3CH_{2Ad}), 29.8 (C_{Ad}) 28.3 (3CH_{Ad}) 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*amyl). MS (ESI): m/z 445; found 446 [M+H]⁺; HRMS (ESI): Calc for C₂₅H₄₀N₃O₄ [M+H]⁺; 446.3019; found 446.3006.

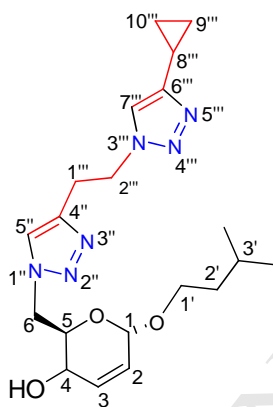
Compound 46



Compound **45** (121 mg, 0.270 mmol) was dissolved in dry DCM (20 mL) and the temperature of the reaction mixture was lowered to 0 °C. DMP (173.34 mg, 0.406 mmol) was added to the reaction mixture. Subsequently the reaction mixture was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **46** as a viscous oil; yield (54 %); R_f = 0.48 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -30.95$ (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3772, 3398, 2927, 2364, 1724, 1593, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.60 (s, 1H, H-5''), 6.86 (dd, 1H, H-2, J = 10.3 Hz & J = 3.5 Hz), 6.10 (d, 1H, H-3, J = 10.3 Hz), 5.20 (d, 1H, H-1, J = 3.4 Hz), 5.06 (dd, 1H, H-6a, J = 14.4 Hz & J = 3.0 Hz), 4.83 (dd, 1H, H-5, J = 7.71 Hz & J = 3.0 Hz), 4.58 (d, 3H, H-6b & H-1''', J = 4.32 Hz), 3.62-3.54 (m, 2H, H-1'), 3.05 (s, 2H, H-2'''), 1.94 (s, 4H, 3 \times CH_{Ad} & 1H of CH_{2Ad}) 1.68-1.55 (m, 12H, 1H of CH_{2bAd} & 5 \times CH_{2Ad} & H-3'), 1.44-1.32 (m, 2H, H-2'), 0.85-0.80 (m, 6H, 2CH₃

of *i*-amyl); ^{13}C NMR (CDCl_3 , 75MHz): δ 193.0 (C-4), 146.1 (C-4''), 144.5 (C-2), 127.1 (C-3), 123.6 (C-5''), 93.3 (C-1), 81.6 (C-2'''), 72.8 (C-5), 68.2 (C-1'), 65.2 (C-1'''), 49.6 (C-6), 39.7 ($3\text{CH}_2\text{Ad}$), 38.2 (C-2'), 37.3 ($3\text{CH}_2\text{Ad}$), 28.3 (C_{Ad} & 3CH_{Ad}), 25.01 (C-3'), 22.6 & 22.4 (2CH_3 of *i*-amyl). MS (ESI): m/z 443; found 444 $[\text{M}+\text{H}]^+$; HRMS (DART): Calc for $\text{C}_{25}\text{H}_{38}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$; 444.2862; found 444.2845.

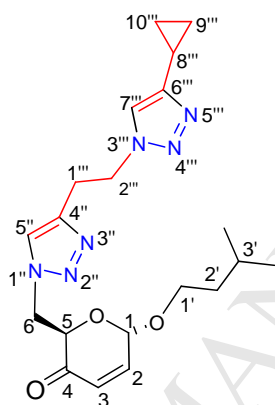
Compound 48



To a solution of compound **15** (250 mg, 0.6702 mmol) in DMF was added NaN_3 (174.25 mg, 2.6808 mmol) and the reaction mixture was allowed to stirred under reflux ($90\text{ }^\circ\text{C}$ - $100\text{ }^\circ\text{C}$) for 3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with dichloromethane (5x8 mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated to yield crude product of compound **47** which was used for the next step as such without further purification. To a vigorously stirred solution of azide **47** (108 mg, 0.3214 mmol) in *tert*-butyl alcohol, cyclopropyl acetylene (0.0407 mL, 0.4821 mmol) was added. The reaction was initiated by the addition of a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (16.03 mg, 0.064 mmol) and sodium ascorbate (25.35 mg, 0.128 mmol) in distilled water. The colored suspension was formed and the reaction mixture was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl_3 . The combined organic extracts were dried, evaporated and passed through a column to afford pure compound **48**. This compound was obtained as a viscous oil; yield (62 %); R_f = 0.53 (CHCl_3 -methanol, 1:10); eluent for column chromatography (CHCl_3 -methanol, 10:0.1); $[\alpha]_D^{31} = -47.91$ (c 0.02, CHCl_3); IR (neat, cm^{-1}): 3745, 2923, 2360, 1602, 1219; ^1H NMR (CDCl_3 , 300 MHz): δ 7.36 (s, 1H, H-5''), 7.14 (s, 1H, H-7'''), 5.91(d, 1H, H-3, J = 10.0 Hz), 5.69 (d, 1H, H-2, J = 10.5 Hz), 4.91 (s, 1H, H-1), 4.64 (t, 4H, H-6 & H-2''', J = 7.44Hz), 3.96 (t, 1H, H-5, J = 4.71 Hz), 3.75 (d, 1H, H-4, J = 8.94 Hz), 3.51 (dd, 1H, H-1'a, J = 16.38 Hz &

$J = 7.44$ Hz), 3.42-3.29 (m, 3H, H-1'b & H-1'''), 1.90-1.81 (m, 1H, H-8'''), 1.68-1.56 (m, 1H, H-3'), 1.41-1.32 (m, 4H, H-2', H-9'''a, H-10'''a), 0.92-0.78 (m, 8H, 2CH₃ of *i*-amyl & 2H of H-9'''b & 10'''b); ¹³C NMR (CDCl₃, 75MHz): δ 150.2 (C-6'''), 143.2 (C-4''), 133.0 (C-3), 126.5 (C-2), 123.9 (C-5''), 120.4 (C-7'''), 94.6 (C-1), 70.5 (C-5), 67.3 (C-1'), 64.3 (C-4), 51.3 (C-2'''), 49.3 (C-6), 38.4 (C-2'), 29.8 (C-1'''), 25.1 (C-3'), 22.7 & 22.4 (2CH₃ of *i*-amyl), 7.80 (C-8'''), 6.68 (C-9''' & C-10'''). MS (ESI): m/z 402; found 425 [M+Na]⁺; HRMS (ESI): Calc for C₂₀H₃₁N₆O₃ [M+H]⁺; 403.2458; found 403.2448.

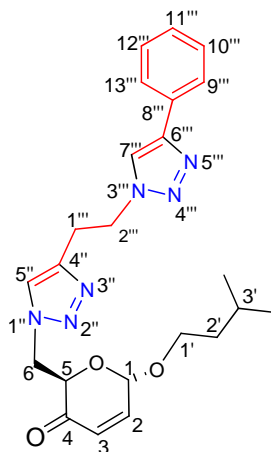
Compound 50



To a solution of the compounds **48** (80 mg, 0.199 mmol) in dry chloroform (CHCl₃) taken in a round bottom flask fitted with a guard tube was added activated MnO₂ (342.28 mg, 3.98 mmol) in 2-3 instalments at intervals of 8-9 h and the reaction mixture was allowed to stir at room temperature for the requisite time (20-30 hours). After completion (TLC), the reaction mixture was filtered over a bed of celite. The celite bed was washed with CHCl₃ a number of times. The filtrate and washings were then concentrated *in vacuo* to obtain the crude product. The crude product was chromatographed to yield the pure compound **50** as a viscous oil; yield (49%); $R_f = 0.51$ (chloroform-methanol, 1:10); eluent for column chromatography (chloroform-methanol, 10:0.2); $[\alpha]_D^{31} = +1.48$ (c 0.02, CHCl₃); IR (neat, cm⁻¹): 3957, 3745, 2923, 2360, 1602, 1219; ¹H NMR (CDCl₃, 300 MHz): δ 7.30 (s, 1H, H-5''), 7.14 (s, 1H, H-7'''), 6.86 (d, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 6.09 (d, 1H, H-3, $J = 10.3$ Hz), 5.19 (d, 1H, H-1, $J = 3.42$ Hz), 4.79 (dd, 1H, H-6a, $J = 7.08$ Hz & $J = 3.1$ Hz), 4.60 (dd, 1H, H-5, $J = 10.2$ Hz & $J = 6.9$ Hz), 4.55 (t, 3H, H-6b, H-2'''), 3.60-3.46 (m, 2H, H-1'), 3.30 (t, 2H, H-1'', $J = 6.90$ Hz), 1.91-1.86 (m, 1H, H-8'''), 1.65-1.56 (m, 1H, H-3'), 1.43-1.34 (m, 4H, H-2', H-9'''a & H-10'''a), 0.95-0.79 (m, 8H, 6H of *i*-amyl & 2H of H-9'''b & H-10'''b); ¹³C NMR (CDCl₃, 75MHz): δ 193.0 (C-4), 151.1 (C-6'''), 144.5 (C-4''), 143.3 (C-2), 127.1 (C-3), 123.5 (C-5''), 120.3 (C-7'''), 93.3 (C-1), 72.7 (C-5), 68.3 (C-1'), 49.6 (C-2'''), 49.3 (C-6), 38.2 (C-

1'''), 29.8 (C-2'), 25.0 (C-3'), 22.6 & 22.4 (2CH₃ of *i*-amyl), 7.80 (C-8'''), 6.72 (C-9''' & C-10'''). MS (ESI): m/z 400; found 401 [M+H]⁺; HRMS (ESI): Calc for C₂₀H₂₉ N₆O₃ [M+H]⁺ ; 401.2301 ; found 401.2305.

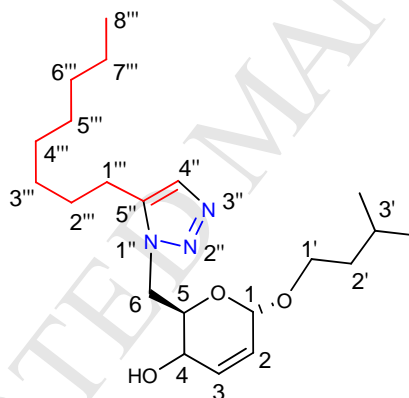
Compound 51



To a solution of compound **15** (250 mg, 0.6702 mmol) in DMF was added NaN₃ (174.25 mg, 2.6808 mmol) and the reaction mixture was allowed to stirred under reflux (90 °C-100 °C) for 3 hours. The cooled reaction mixture was poured into excess of ice-cold water and extracted with dichloromethane (5x8 mL). The combined organic layers were washed with brine, dried over sodium sulphate and evaporated to yield crude product of compound **47** which was used for the next step as such without further purification. To a vigorously stirred solution of azide **47** (110 mg, 0.327 mmol) in *tert*-butyl alcohol, Phenyl acetylene (0.053 mL, 0.4905 mmol) was added. The reaction was initiated by the addition of a solution of CuSO₄.5H₂O (16.22 mg, 0.0654 mmol) and sodium ascorbate (25.91 mg, 0.131 mmol) in distilled water. The colored suspension was formed and the reaction mixture was stirred at the room temperature till the formation of triazole. After the completion of reaction ice-cold distilled water was added and the aqueous layer was extracted 3-4 times with CHCl₃. The combined organic extracts were evaporated *in vacuo* to afford the crude product mixture of **49**, which was dissolved in dry chloroform (CHCl₃), followed by the addition of activated MnO₂ (392.16 mg, 4.56 mmol) in 2-3 instalments at intervals of 8-9 h and the reaction mixture was allowed to stir at room temperature (RT) for the requisite time (20-30 hours). After completion (TLC), the reaction mixture was filtered over a bed of celite. The celite bed was washed with CHCl₃ a number of times. The filtrate and washings were then concentrated *in vacuo* to obtain the crude product. The crude product was chromatographed to yield the pure compound **51** as a viscous oil; yield (50% in 2 steps); R_f = 0.55 (chloroform-methanol,

10:1); eluent for column chromatography (chloroform-methanol, 49:1); $[\alpha]_D^{31} = -7.91$ (c 0.02, CHCl_3); IR (neat, cm^{-1}): 3872, 3745, 2923, 2360, 1602, 1219; ^1H NMR (CDCl_3 , 300 MHz): δ 7.77 (d, 2H, H-8''' & H-13''', $J = 7.29$ Hz), 7.64 (s, 1H, H-5''), 7.41 (t, 2H, H-10''' & H-12''', $J = 7.14$ Hz), 7.32 (t, 2H, H-7''' & H-11'''), 6.72 (dd, 1H, H-2, $J = 10.3$ Hz & $J = 3.5$ Hz), 5.99 (d, 1H, H-3, $J = 10.3$ Hz), 5.1 (d, 1H, H-1, $J = 3.24$ Hz), 4.89 (dd, 1H, H-6a, $J = 14.4$ Hz & $J = 3.2$ Hz), 4.80-4.74 (m, 3H, H-6b, H-5, & H-2'''a), 4.60 (dd, 1H, H-2'''b, $J = 6.7$ Hz & $J = 14.0$ Hz), 3.60-3.52 (m, 1H, H-1'''a), 3.39 (t, 3H, H-1'''b, H-1', $J = 6.7$ Hz), 1.61-1.50 (m, 1H, H-3'), 1.42-1.37 (m, 2H, H-2'), 0.87-0.79 (m, 6H, 2 CH_3 of *i*-amyl); ^{13}C NMR (CDCl_3 , 75 MHz): δ 193.0 (C-4), 151.1 (C-6'''), 144.5 (C-4''), 143.3 (C-2), 130.9 (C-3), 128.9 (C-10''' & C-12'''), 125.7 (C-9''' & C-13'''), 125.7 (C-8'''), 120.4 (C-5''), 120.3 (C-7'''), 114.1 (C-11'''), 93.2 (C-1), 73.7 (C-5), 68.2 (C-1'), 58.4 (C-2'''), 49.4 (C-6), 38.2 (C-2'), 29.7 (C-1'''), 25.0 (C-3'), 22.7 & 22.6 (2 CH_3 of *i*-amyl). MS (ESI): m/z 436; found 437 $[\text{M}+\text{H}]^+$; HRMS (ESI): Calc for $\text{C}_{23}\text{H}_{29}\text{N}_6\text{O}_3$ $[\text{M}+\text{H}]^+$; 437.2301; found 437.2305.

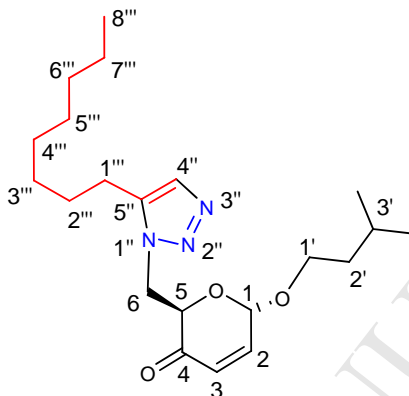
Compound 52



To a stirred solution of azide **4a** (150 mg, 0.622 mmol) in dry toluene was added decyne (0.107 mL, 0.9336 mmol). The reaction was initiated by the addition of a catalyst $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (4.956 mg, 0.00622 mmol) and it continued for 3 h at 80 °C. The combined organic extracts were dried, evaporated & passed through a column to afford pure compound **52** as a viscous oil; yield (81%); $R_f = 0.51$ (hexane-ethyl acetate, 1:1); eluent for column chromatography (hexane-ethyl acetate, 4:1); $[\alpha]_D^{31} = -2.71$ (c 0.08, CHCl_3); IR (neat, cm^{-1}): 3775, 3399, 2925, 2358, 1634, 1459, 1244, 1030; ^1H NMR (CDCl_3 , 300 MHz): δ 7.44 (s, 1H, H-5''), 5.94 (d, 1H, H-3, $J = 10.2$ Hz), 5.67 (d, 1H, H-2, $J = 10.2$ Hz), 4.85 (s, 1H, H-1), 4.58 (t, 2H, H-4 & H-6a, $J = 3.39$ Hz), 3.98 (dd, 2H, H-6b & H-5, $J = 12.0$ Hz & $J = 5.3$ Hz), 3.42-3.30 (m, 2H, H-1'), 2.71 (t, 2H, H-1''', $J = 7.4$ Hz), 1.69-1.53 (m, 1H, H-3'), 1.39-1.25 (m, 14H, H-2'''-H-7''' & H-2'), 0.88-0.83 (m, 9H, 2 CH_3 of *i*-amyl & 1 CH_3 of H-8'''); ^{13}C NMR

(CDCl₃, 75MHz): δ 146.4 (C-5''), 132.3 (C-4''), 131.9 (C-3), 126.3 (C-2), 94.5 (C-1), 71.3 (C-5), 67.1 (C-1'), 65.0 (C-4), 48.6 (C-6), 38.4 (C-2'), 32.0 (C-1'''), 31.9 (C-2'''), 29.8 (C-3'''), 29.5 (C-4'''), 29.4 (C-5'''), 29.3 (C-6'''), 28.2 (C-7'''), 25.1 (C-3'), 22.7 & 22.5 (2CH₃ of *i*-amyl), 14.2 (C-8'''). MS (ESI): m/z 379; found 380 [M+H]⁺; HRMS (DART): Calc for C₂₁H₃₈N₃O₃ [M+H]⁺; 380.2903; found 380.2913.

Compound 53



To a solution of **52** (217 mg, 0.5725 mmol) in dry DCM (20 mL) was added Dess-Martin periodinane (DMP) reagent (367 mg, 0.858 mmol) at -5 °C. Subsequently the reaction was allowed to warm to 5 °C and stirred till all the starting material was converted into the oxidised product (4hours). The reaction was quenched by the addition of saturated aqueous solution of NaHCO₃ maintaining the temperature of the reaction mixture at 5 °C. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate and evaporated *in vacuo* to obtain the crude product. The crude product was chromatographed over silica gel to yield the pure 6-triazolyl-2,3,6-trideoxy hex-2-enopyranosid-4-ulose **53** as a viscous oil; yield (61%); R_f = 0.57 (hexane-ethyl acetate, 7:3); eluent for column chromatography (hexane-ethyl acetate, 10:1); $[\alpha]_D^{31}$ = +24.52 (c 0.03, CHCl₃); IR (neat, cm⁻¹): 3951, 3396, 1636, 1220; ¹H NMR (CDCl₃, 300 MHz): δ 7.40 (s, 1H, H-5''), 6.83 (dd, 1H, H-2, J = 10.3 Hz & J = 3.4 Hz), 6.09 (d, 1H, H-3, J = 10.3 Hz), 5.12 (d, 1H, H-1, J = 3.3 Hz), 4.97-4.91 (m, 2H, H-5 & H-6a), 4.34 (dd, 1H, H-6b, J = 15.0 Hz & J = 9.7 Hz), 3.34 (dd, 2H, 2.63, H-1', J = 12.3 Hz & J = 6.8 Hz), 2.63 (dd, 2H, H-1''', J = 12.8 Hz & J = 7.7 Hz) 1.66-1.57 (m, 2H, H-2'), 1.55-1.51 (m, 1H, H-3'), 1.33-1.22 (m, 12H, H-2'''-H-7'''), 0.85-0.75 (m, 9H, 2CH₃ of *i*-amyl & 1CH₃ of H-8'''). ¹³C NMR (CDCl₃, 75MHz): δ 193.3 (C-4), 144.3 (C-2), 138.6 (C-5''), 131.8 (C-4''), 127.1 (C-3), 93.1 (C-1), 73.1 (C-5), 68.1 (C-6), 46.9 (C-1'), 38.1 (C-2'), 31.8 (C-1'''), 29.7 (C-2'''), 29.3 (C-3'''), 29.2 (C-4'''), 29.2 (C-5'''), 28.1 (C-6'''), 25.0 (C-3'), 22.7 (C-7'''), 22.5 & 22.4 (2CH₃ of *i*-amyl),

14.1 (C-8^{'''}). MS (ESI): m/z 377; found 378 [M+H]⁺; HRMS (ESI): Calc for C₂₁H₃₆ N₃O₃ [M+H]⁺; 378.2757; found 378.2755.

Experimental Section- Biology

Assay for *invitro* antibacterial, antifungal activity and cytotoxicity

All the prepared 2,3,6-trideoxy sugar-triazole conjugates were evaluated for their *in vitro* antibacterial activity against *S. aureus* (ATCC 25923), *E. coli* (ATCC 9637), *P. aeruginosa* (ATCC BAA-427), *K. pneumoniae* (ATCC 27736) and antifungal activity against *C. albicans* (Ca), *A. fumigatus* (Af), *C. neoformans* (Cn), *S. schenckii* (Ss), and *T. mentagrophytes* (Tm). In this process, the minimum inhibitory concentration of compounds was tested according to the standard microbroth dilution technique as per guidelines of National Committee for Clinical Laboratory Standards.^{36,37} Briefly, testing was performed in flat-bottomed 96-well tissue culture plates (CELLSTAR* Greiner bio-one GmbH, Germany) in RPMI 1640 medium buffered with MOPS (3-[N-morpholino] propanesulfonic acid) (Sigma–Aldrich Chemical Co., St. Louis, MO, USA) for fungal strains and in Muller Hinton broth (Titan Biotech Ltd, India) for bacterial strains. The concentration range of test compounds was 50–0.36 and 32–0.0018 µg/mL for standard compounds. Initial inocula of fungal and bacterial strains were maintained at 1–5×10³ cells/mL. These plates were incubated in a moist chamber at 35 °C, and an absorbance at 492 nm was recorded on a Versa Max microplate reader (Molecular devices, Sunnyvale, USA) after 24 hours for bacterial strains, 48 hours for *C. albicans* (Ca) and 72 hours for *A. fumigatus* (Af), *C. neoformans* (Cn), *S. schenckii* (Ss) and 96 hours for *T. mentagrophytes* (Tm). The MICs were determined as 90% inhibition of growth with respect to the growth control as observed using SOFT-max Pro 4.3 Software (Molecular Devices, Sunnyvale, USA).

The cytotoxicity of compounds **24**, **26**, **27**, **28**, **29**, **32**, **35**, **36**, **38**, **46** and **53** against mammalian cells, mouse fibroblast cell line L929 was tested as follows. Stock solutions (1 mg/mL) of the test compounds were prepared in DMSO. The cell line L929 was grown in DMEM medium supplemented with 10% FBS and 1 × antimycotic and antibacterial solution (sigma USA) at 37 °C in humidified atmosphere having 5% CO₂. One hundred ml (1×10³ cells in DMEM) of the confluent fibroblast stock suspension (1×10⁵ cells/ml) was dispensed in 96-well tissue culture plate. The original medium from the wells was replaced with 100 µL serum free DMEM when the cells reached 90% confluency after 5 hours of incubation in a CO₂ incubator. Various concentrations of the test compounds (25, 12.5, 6.25, 3.12, 1.56,

0.78, 0.39, 0.19, 0.09 mg/ml) were added to the growing cells and incubated for 24 hours. Response of L929 cells to the test compounds was determined spectrophotometrically at 570 and 630 nm. The difference between absorbance at 570 and 630 nm was used as an index of the cell viability.³⁸

(A570 - A630) sample

----- × 100

(A570 - A630) control

The morphology of the cells was observed using Giemsa stain under Phase contrast microscope. After fixation of the cells in the wells of 96-well tissue culture plate, Geimsa stain was added to each well and incubated for 30 min at 37 °C. The excess stain was removed by thorough washing with PBS and the culture plates were air dried and observed under a phase contrast microscope.

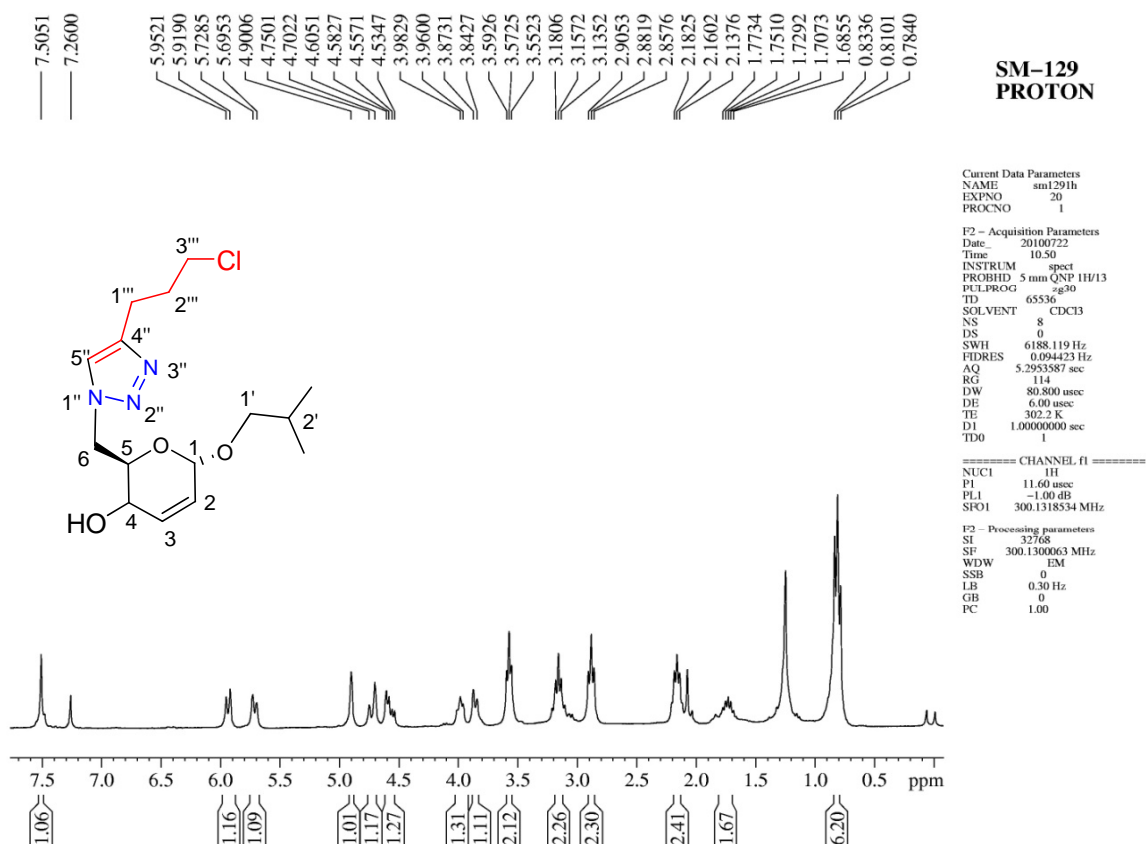
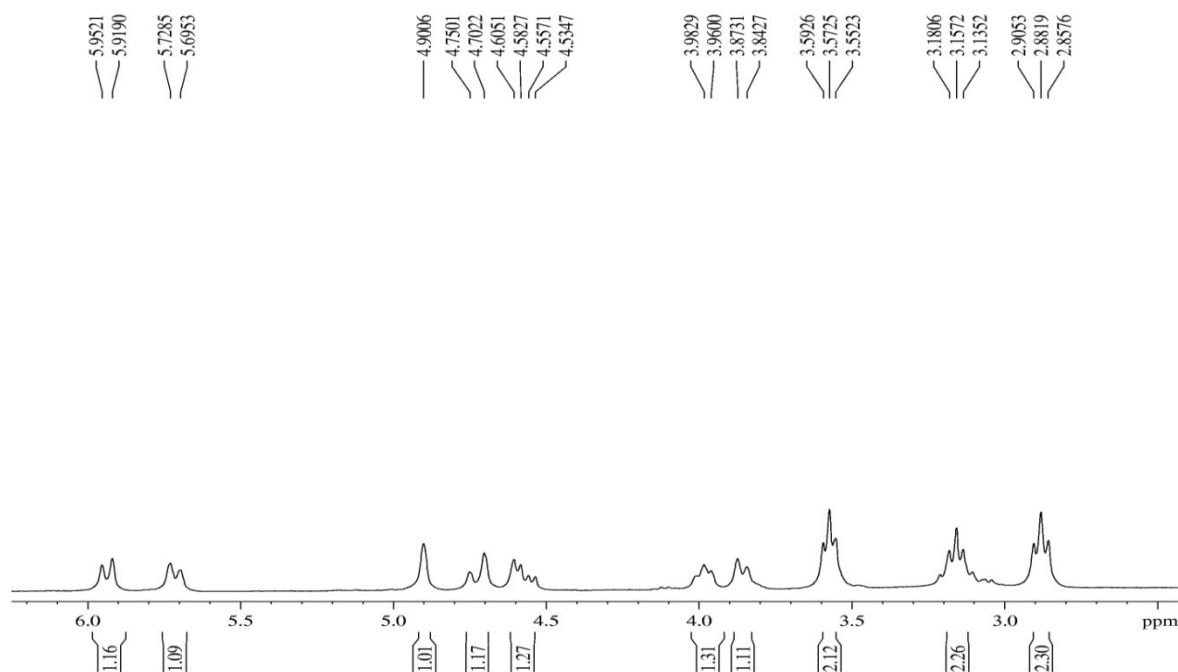
Experimental Section-Bioinformatics and Modeling studies

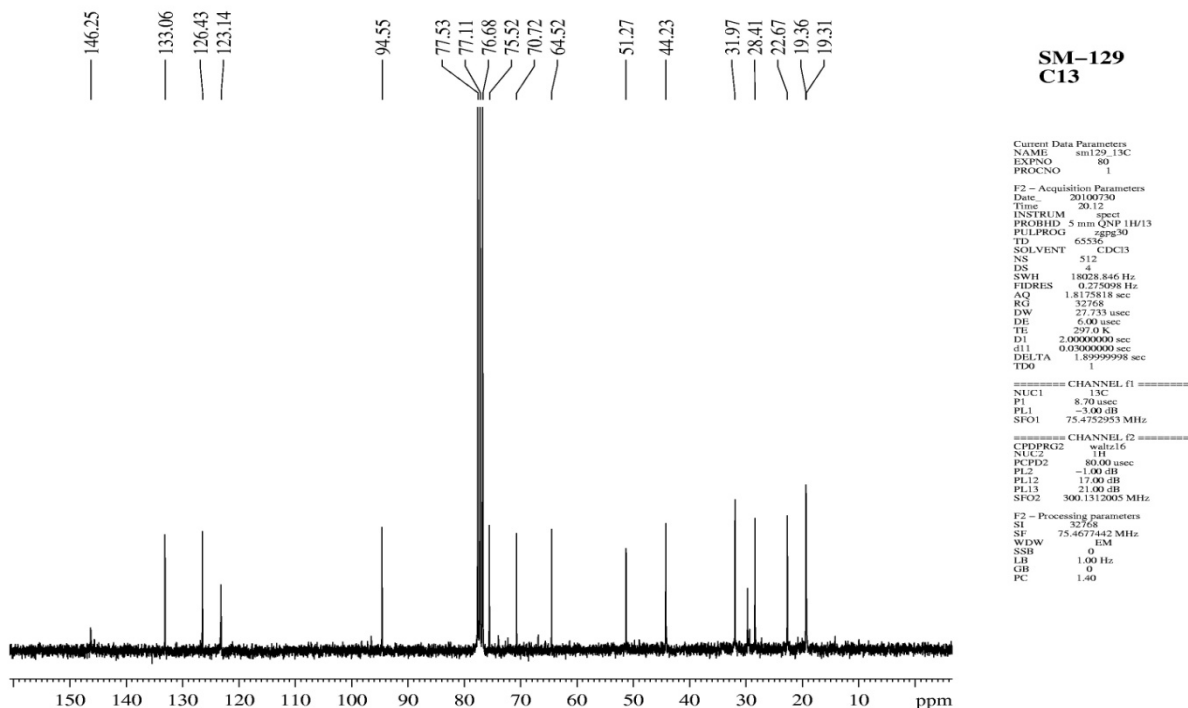
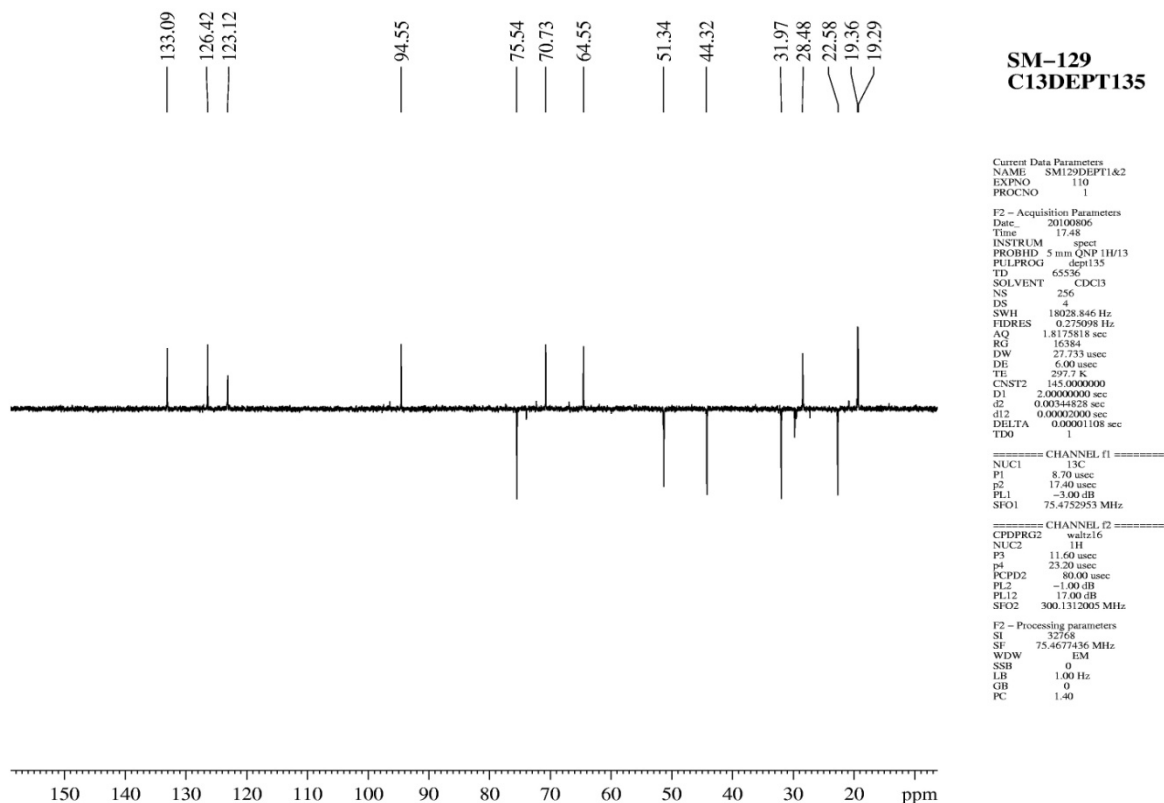
The structures of the compounds were compared for their similarity with the ligands of well known antibacterial targets. This has led to the identification of hydrolase and penicillin binding proteins (PBPs) as potential enzyme classes for the new compounds. The exploration has included pdb 3D4F, 3RKJ, 1BLH, 2YZ3 and 1KO3 for hydrolase and pdb 4DKI, 3VSL, 3HUN, 3MZE and 3PBR for penicillin binding proteins. Trial docking studies with these enzymes suggested that PBP-2 as most appropriate target of these compounds. Also similar to reference compounds, the synthesized compounds showed interaction with conserved serine residues of PBP.³⁹ Following this Basic Local Alignment Search Tool (BLAST: <http://blast.ncbi.nlm.nih.gov/Blast.cgi>) were used to find out the similarity of PBP-2 between different strains of bacteria. The molecular docking study was carried out in SYBYLX 1.3.⁴⁰ For docking experiment, the penicillin binding protein 2 of *Staphylococcus aureus* (PDB: 4DKI) was prepared by adding hydrogen atoms, fixing side chain amides and applying Gastregial-Huckle charges. Followed by this, energy of the protein was minimized by the Powell method using Tripos force field with a distance dependent dielectric constant of 1.0 and non-bonding interaction cut-off of 8.0Å and iterations up to 1000 (convergence criteria 0.001 kcal/mol.Å). Using automated based option procedures, the binding pocket was generated in the Protomol module of SYBYLX 1.3. The energy minimized standard inhibitors and synthesized compounds were docked using Surflex-Dock-Geom X docking mode into the pockets of selected target. The best docking poses of the compounds were

selected based on the crash and polar and total scores. The best docked conformation was used for site directed residue interaction analysis and visualization in Pymol and SYBYLX 1.3.

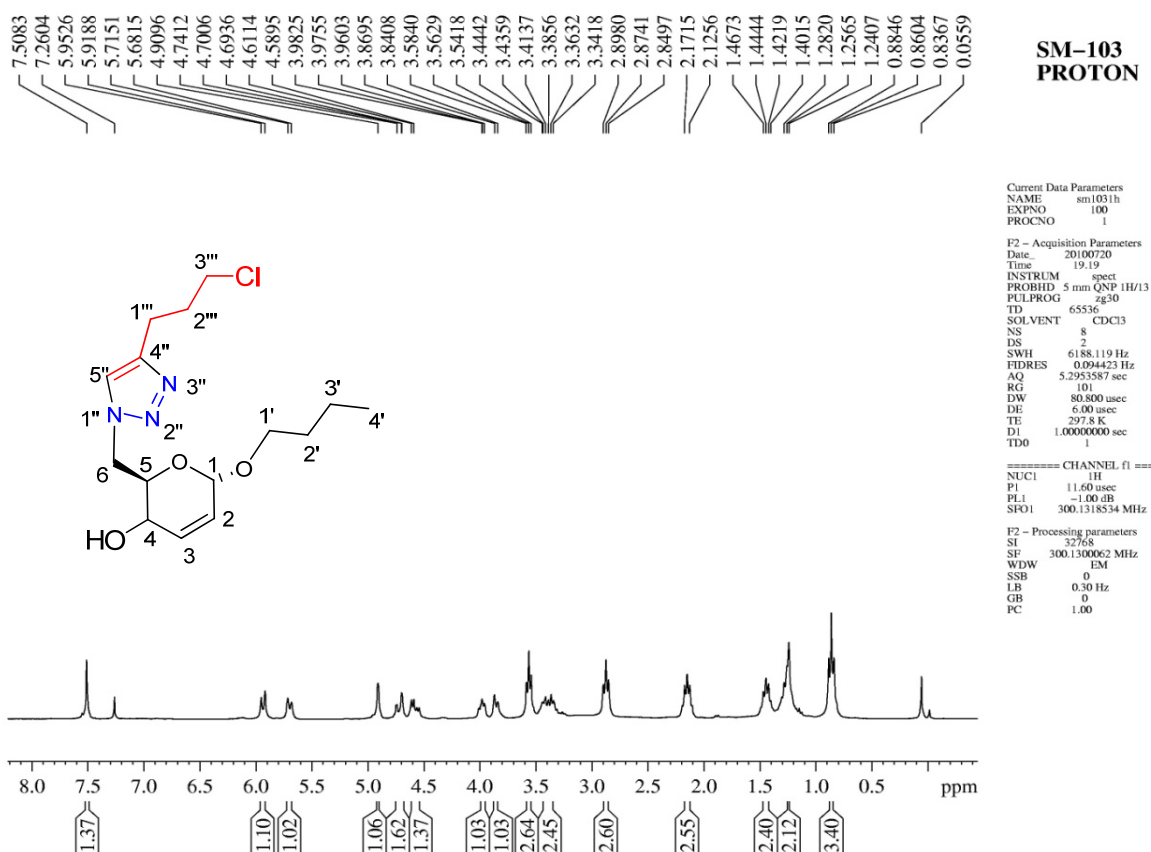
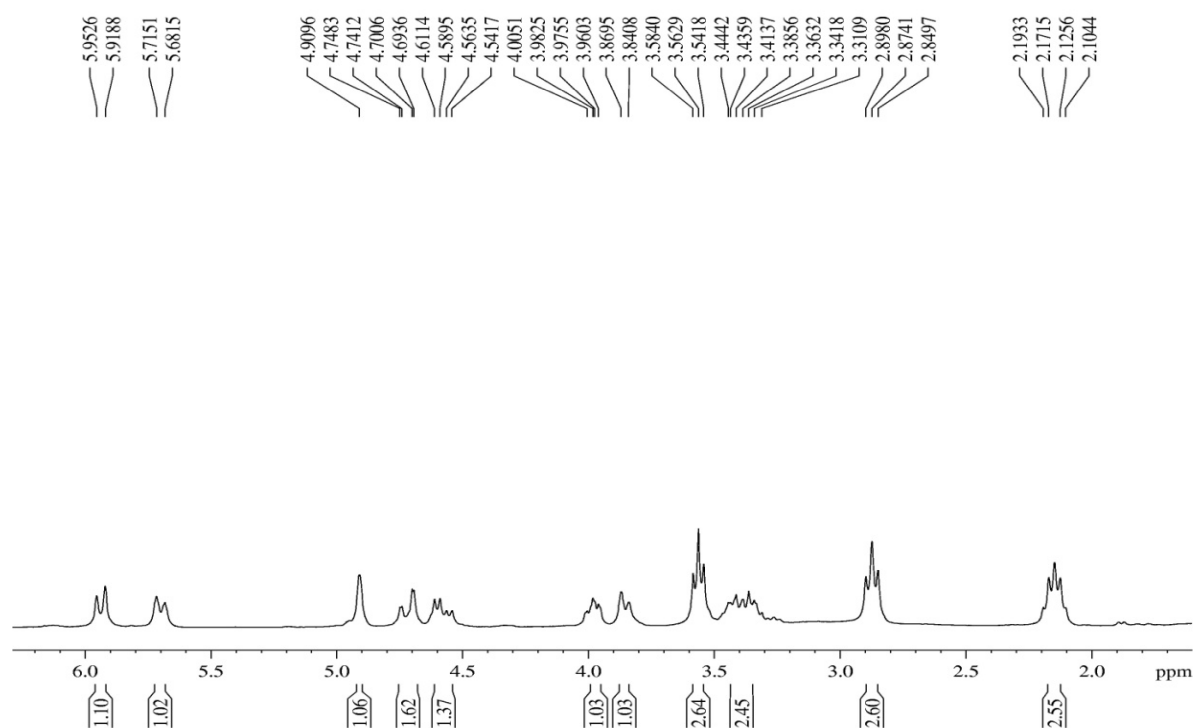
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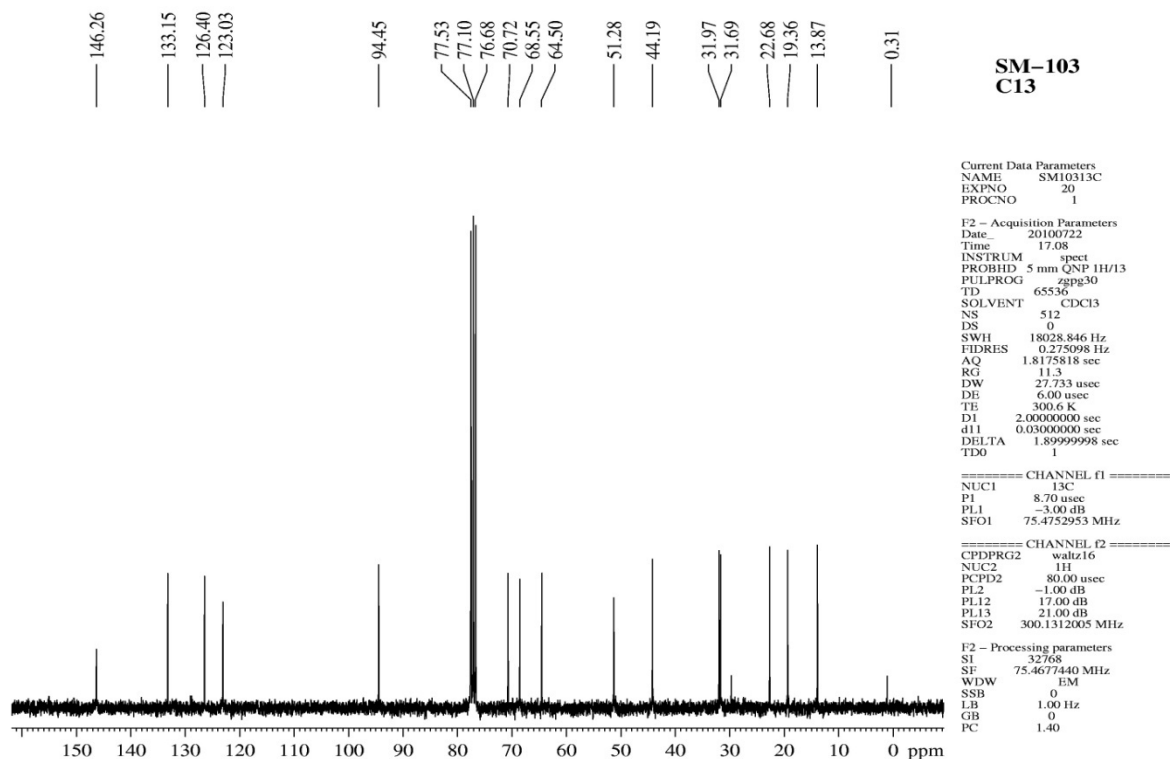
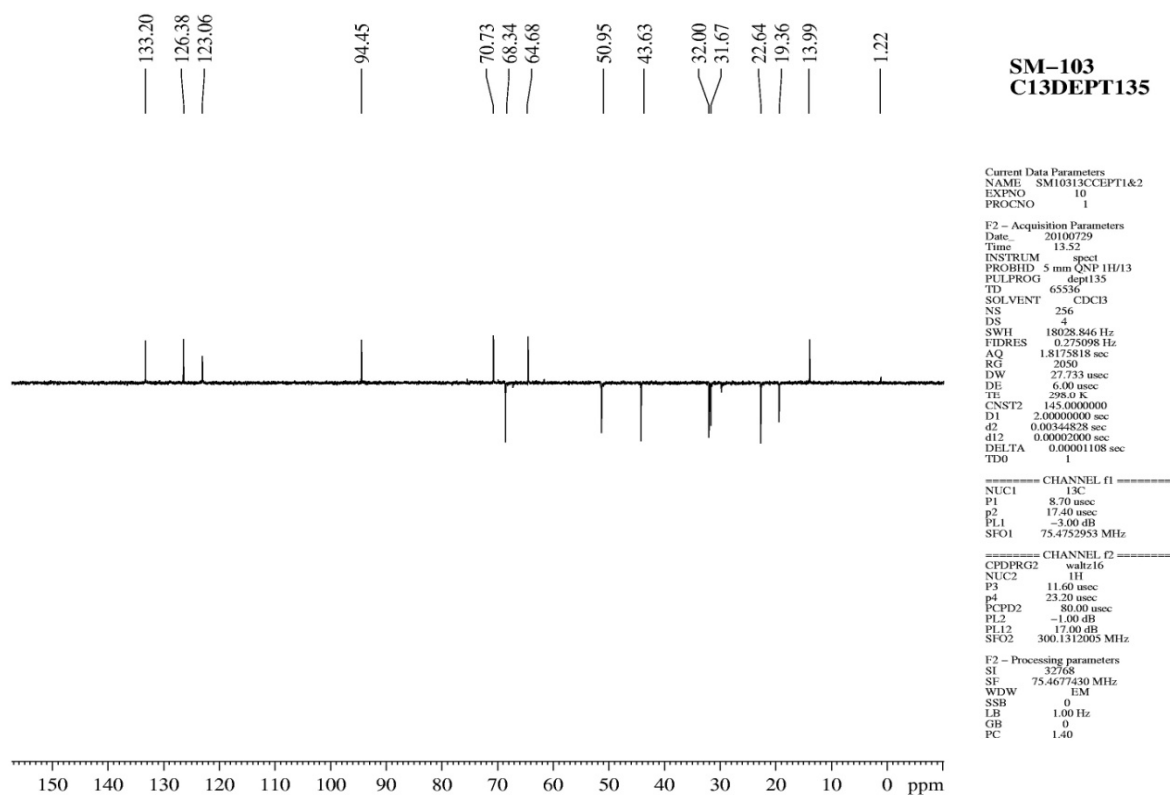
- (35) Robinson, J.; Messbah, T.; Smith, and Foroozech, M.; *J. Undergrad. Chem. Res.* **2002**, *1*, 157–159.
- (36) Villanova, P. A. Methods for dilution antimicrobial susceptibility tests for bacteria that grow aerobically. Approved standard, 5th ed.; National Committee for Clinical Laboratory Standards.: 2000, pp M7-A5.
- (37) Yamamotoa, N.; Fujita, J.; Shintazo, T.; Higa, F.; Tateyamaa, M.; Tohyamaa, M.; Nakasone, I.; Yamaned, N. *Int. J. Antimicrob. Agents.* **2006**, *27*, 171–173.
- (38) Liu, H.; Chenb, J.; Jiang, J.; Giesy, J. P.; Yua, H.; Wang, X. *Environ. Toxicol Pharmacol.* **2008**, *26*, 309–314.
- (39) van der Linden, M. P.; de Haan, L.; Dideberg, O.; Keck, W. Site-directed mutagenesis of proposed active-site residues of penicillin-binding protein 5 from *Escherichia coli*. *Biochem J.* **1994**, *303*, 357-62.
- (40) SYBYL-X 1.3, Tripos International, St Louis, Missouri, USA.

¹H NMR Spectrum of Compound **6** and its expansion

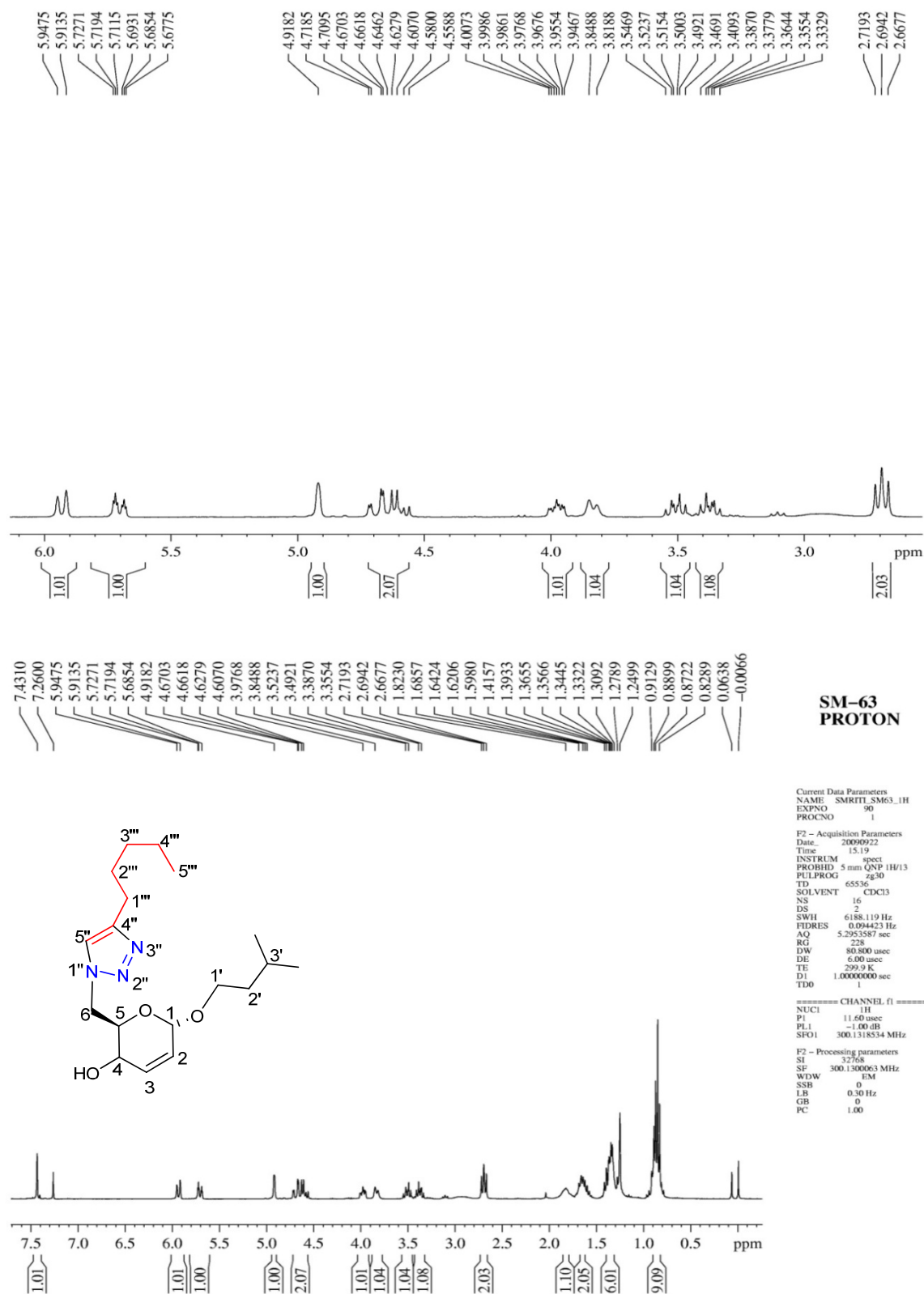


^{13}C NMR Spectrum and its DEPT 135 of compound **6**

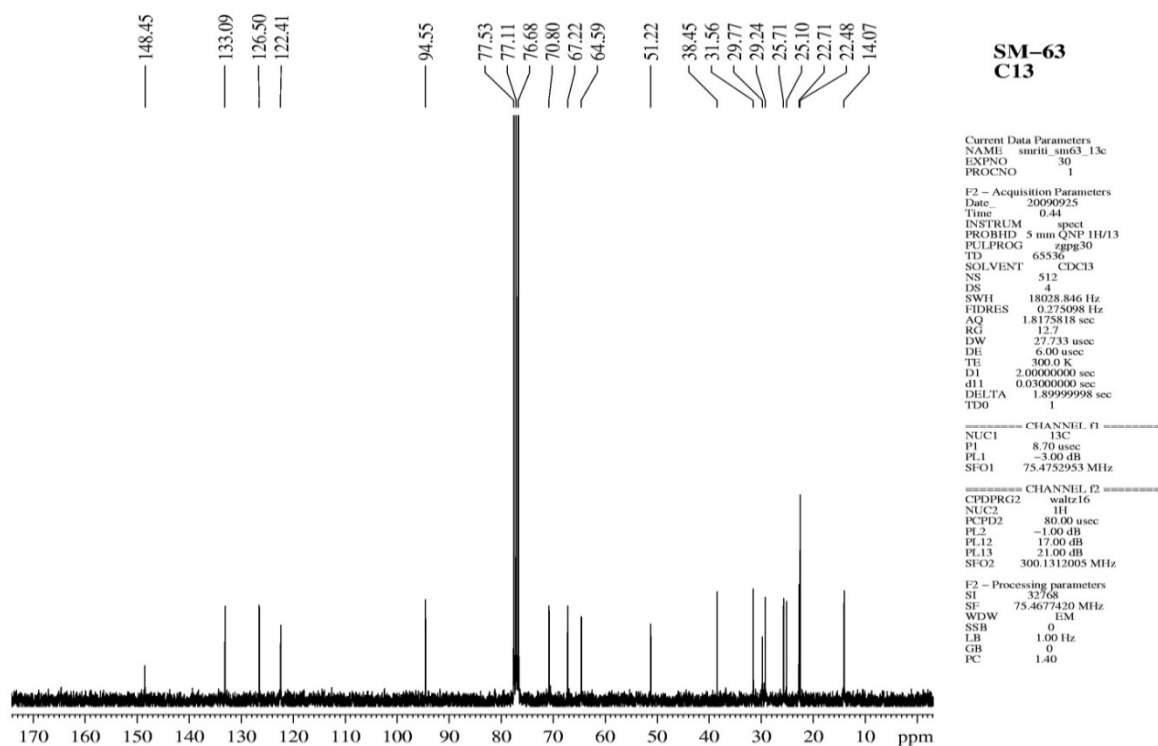
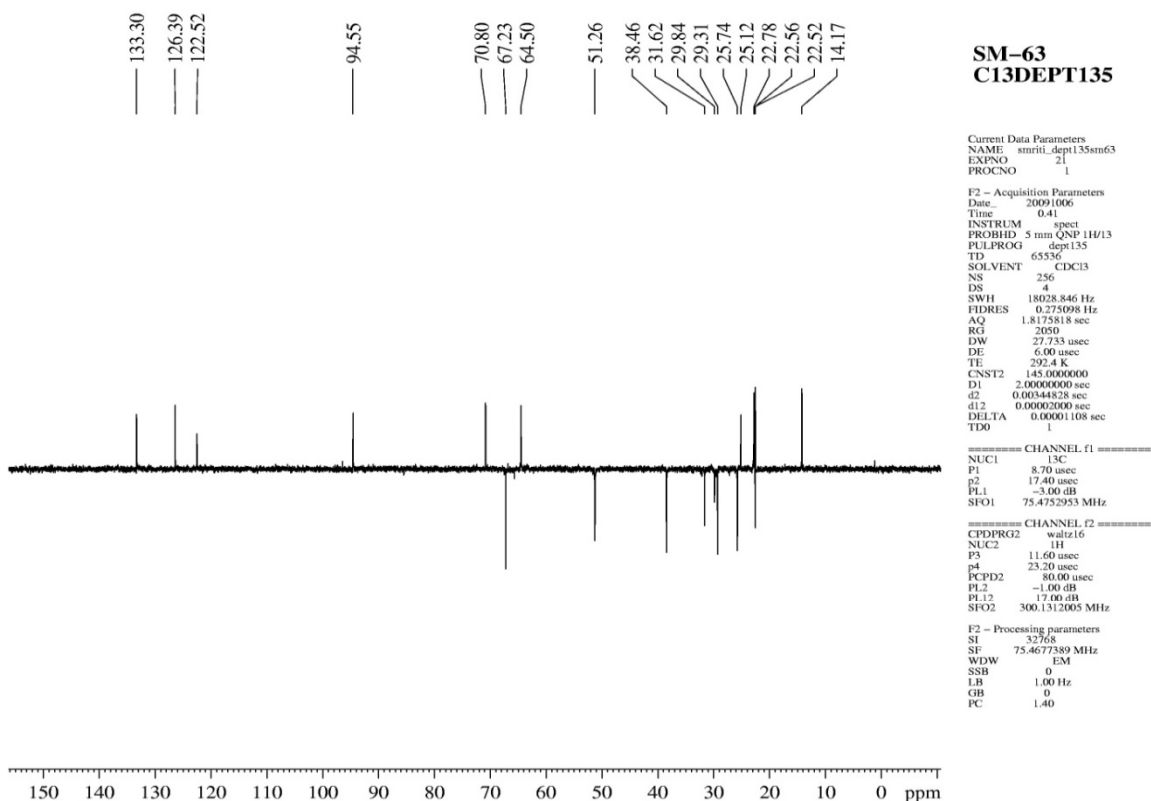
¹H NMR Spectrum of compound **7** and its expansion



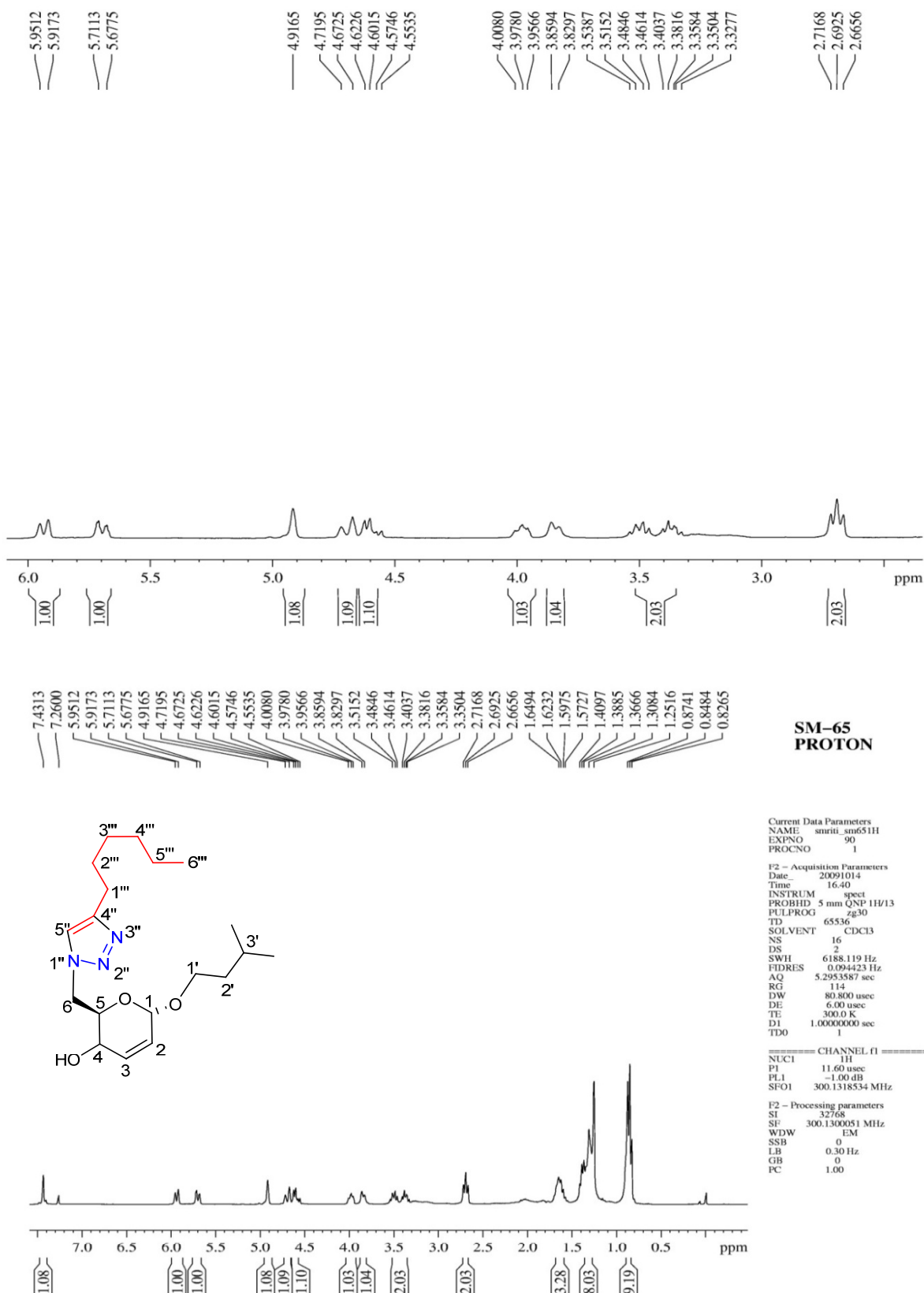
^{13}C NMR Spectrum and its Dept 135 of compound **7**

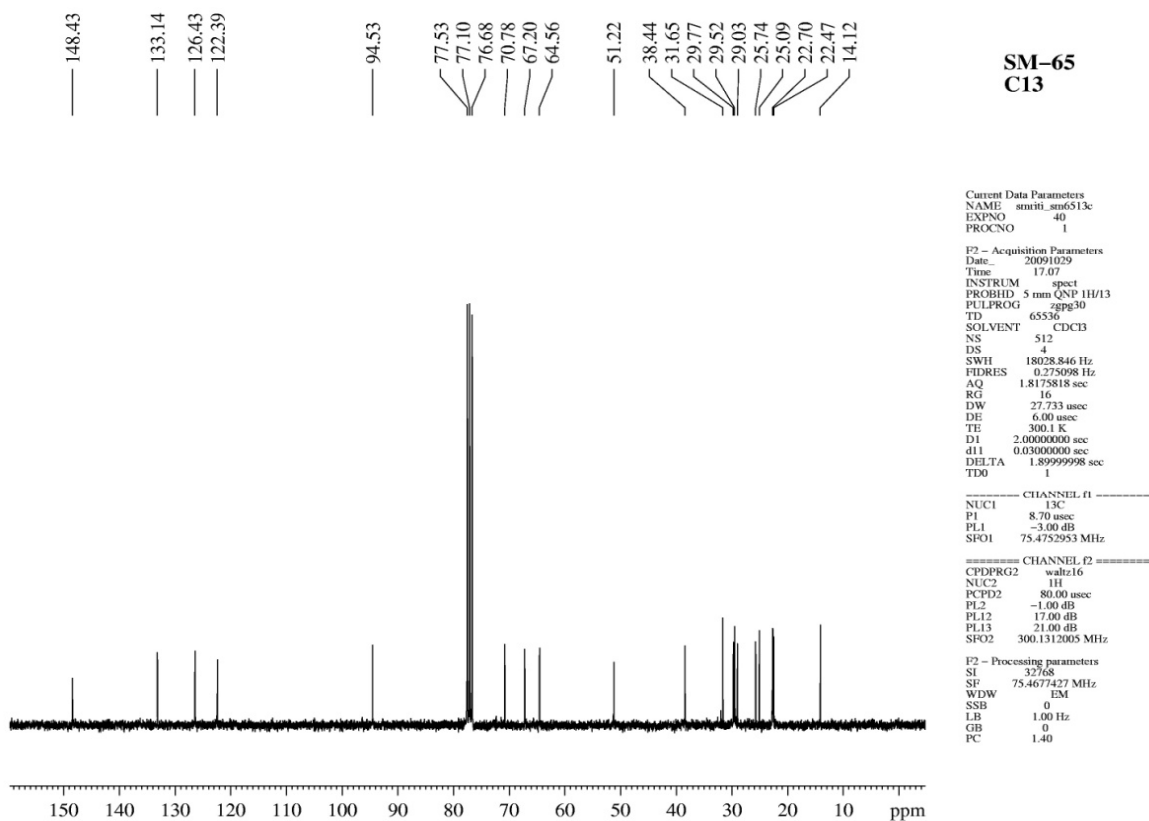
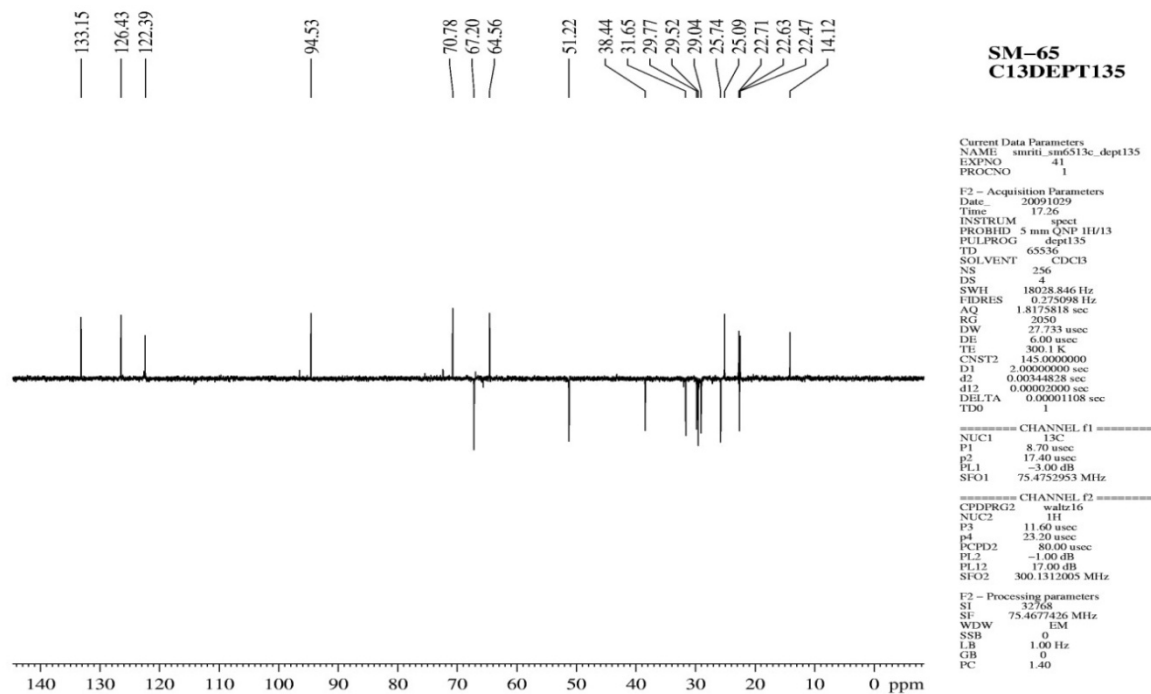


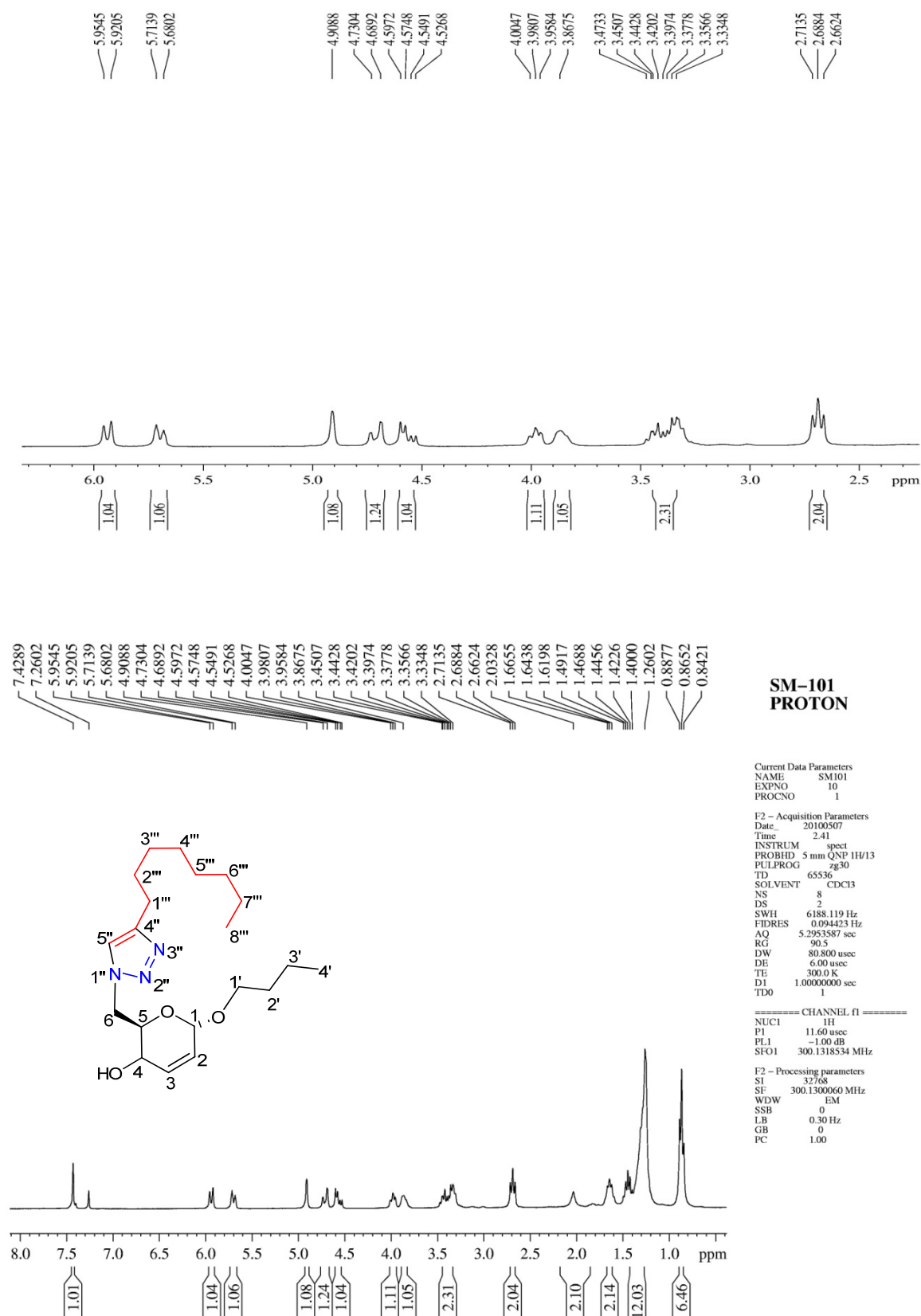
¹H NMR Spectrum of compound **8** and its expansion



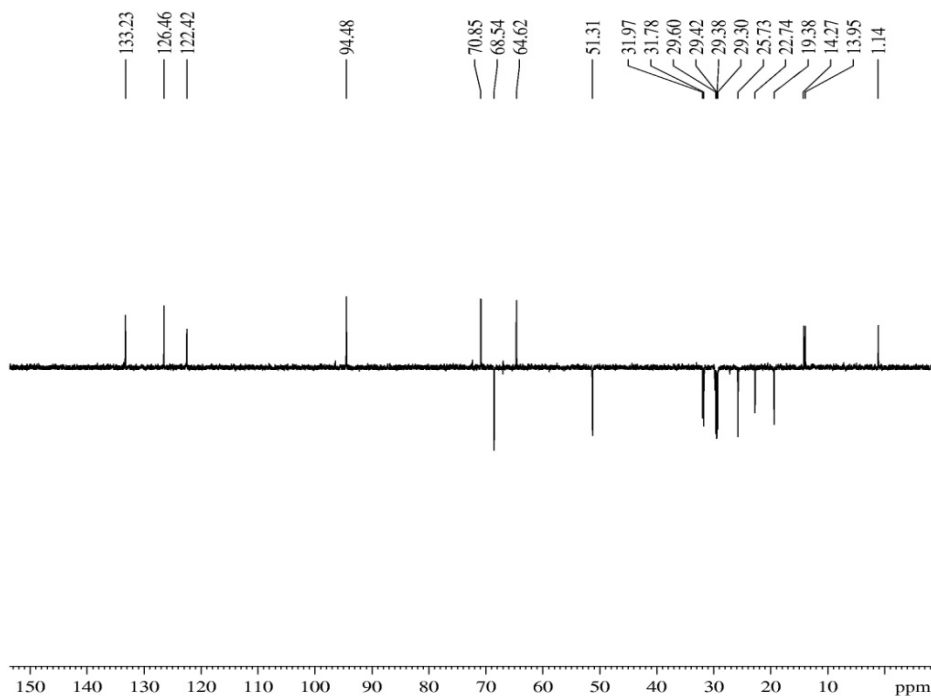
¹³C NMR Spectrum and its DEPT 135 of compound 8

¹H NMR Spectrum of compound **9** and its expansion

 ^{13}C NMR Spectrum and its DEPT 135 of compound **9**



¹H NMR Spectrum of compound **11** and its expansion



SM-101
C13DEPT135

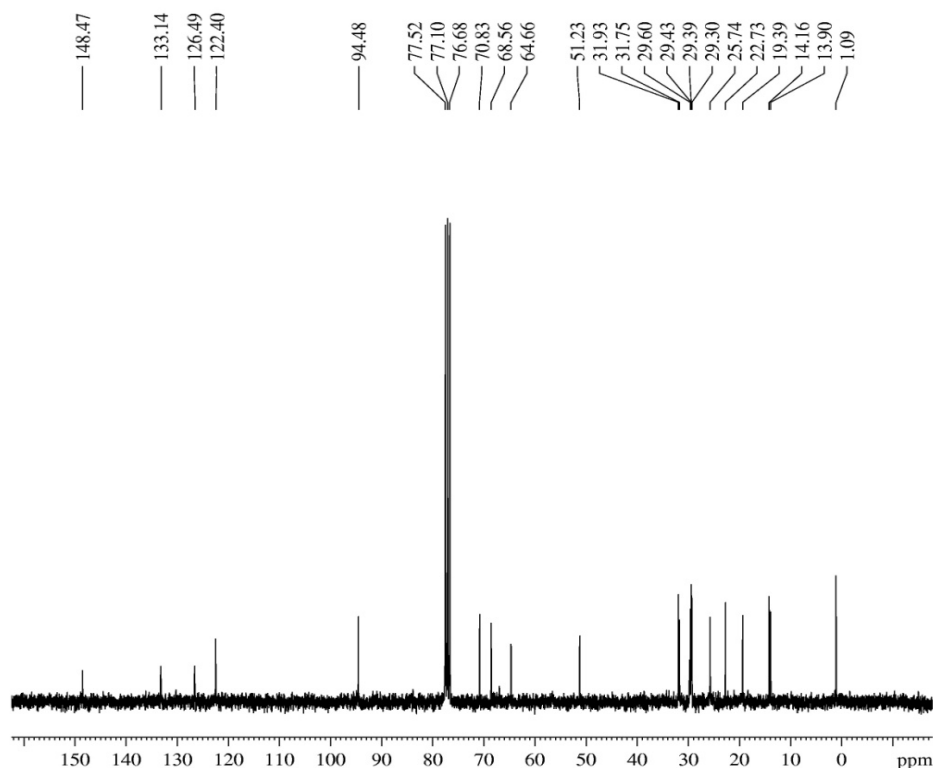
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F2 - Processing parameters
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SM-101
C13

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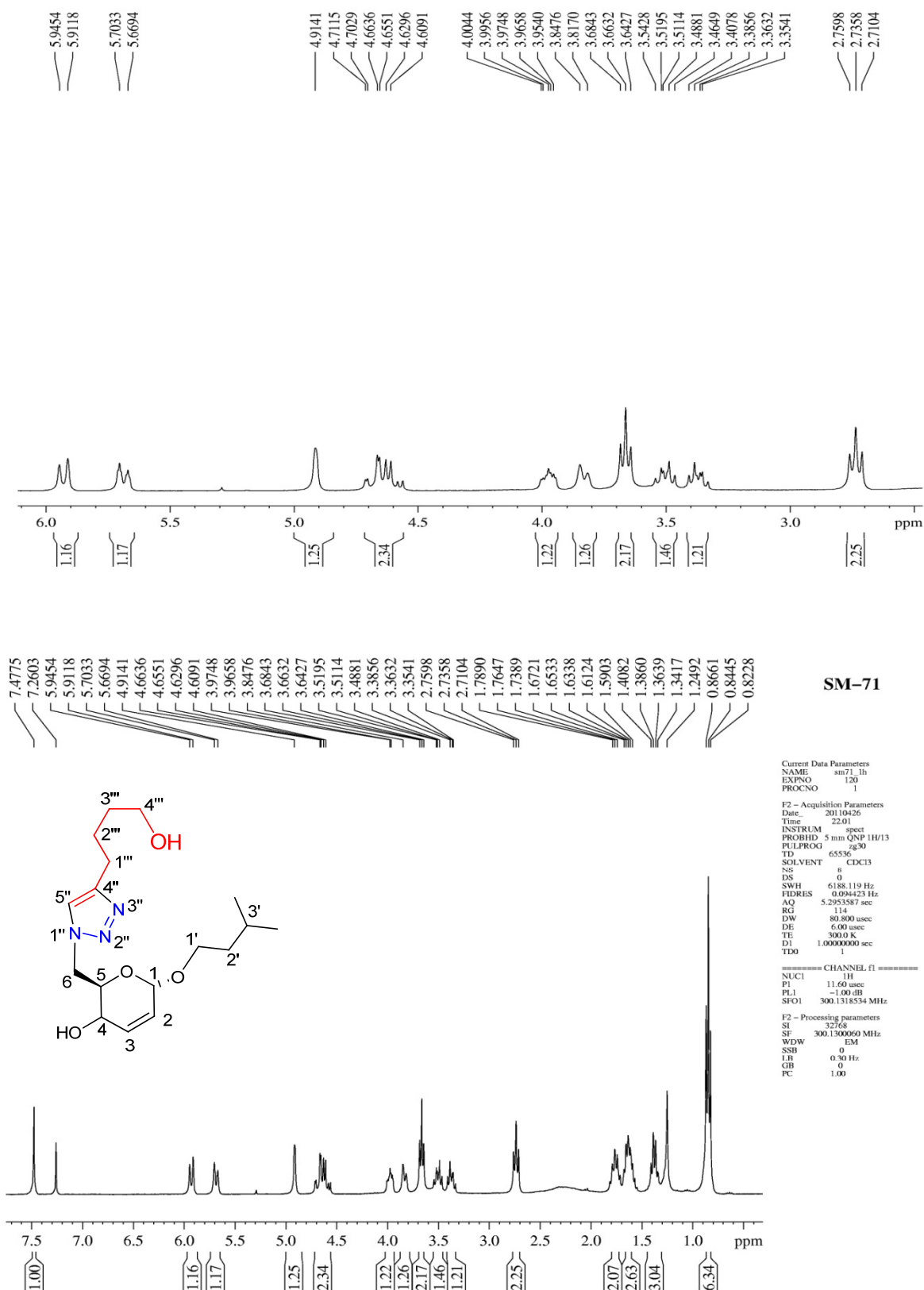
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===== CHANNEL f1 =====
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SFO1 75.4752953 MHz

===== CHANNEL f2 =====
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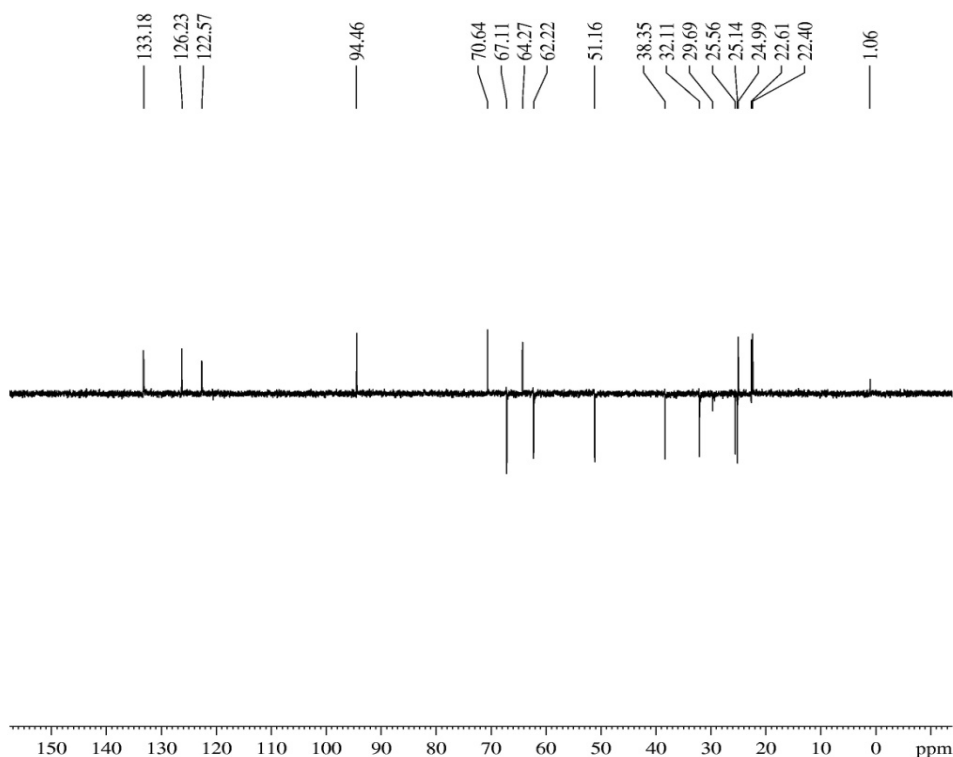
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^{13}C NMR and its Dept 135 Spectrum of compound 11



SM-71

¹H NMR Spectrum of compound **12** and its expansion



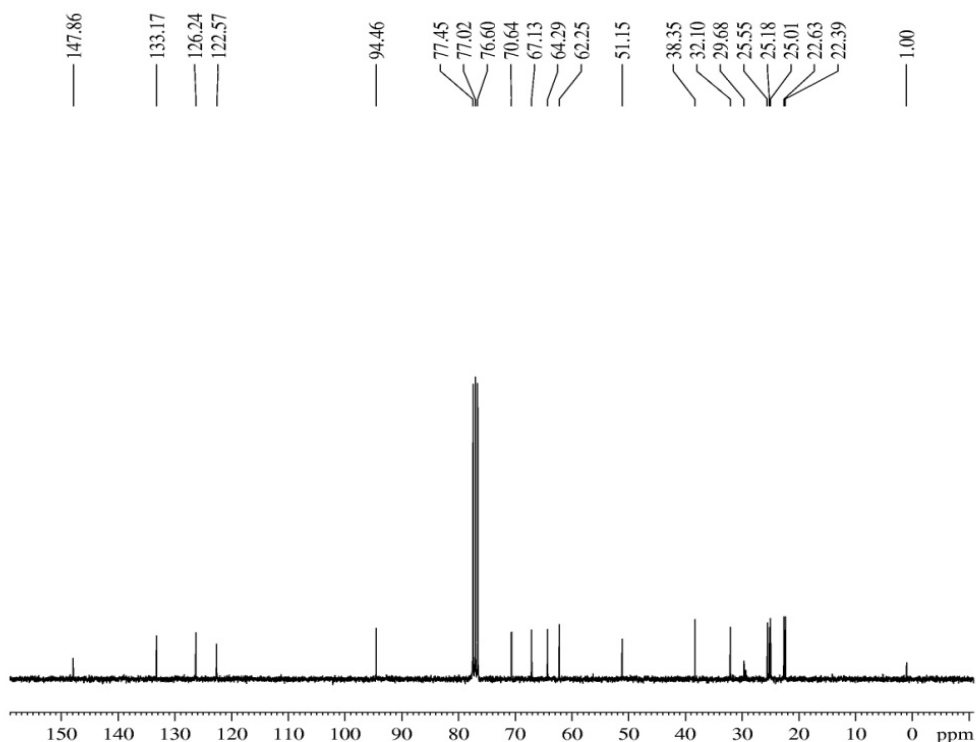
SM-71

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===== CHANNEL f2 =====
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SM-71

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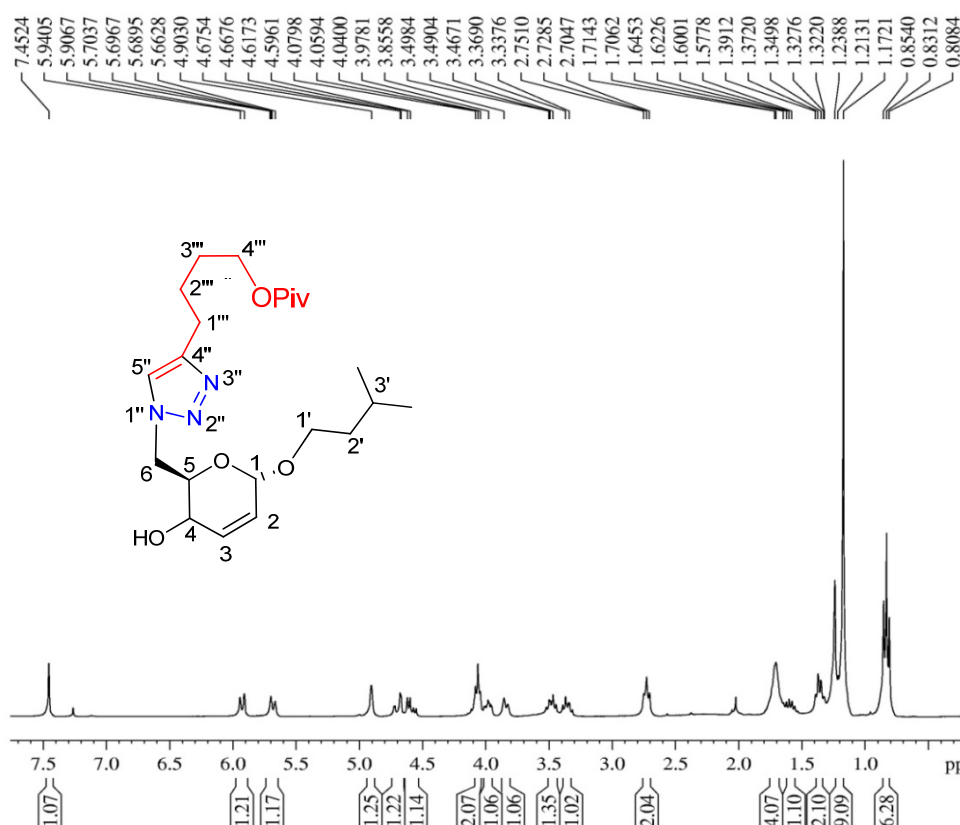
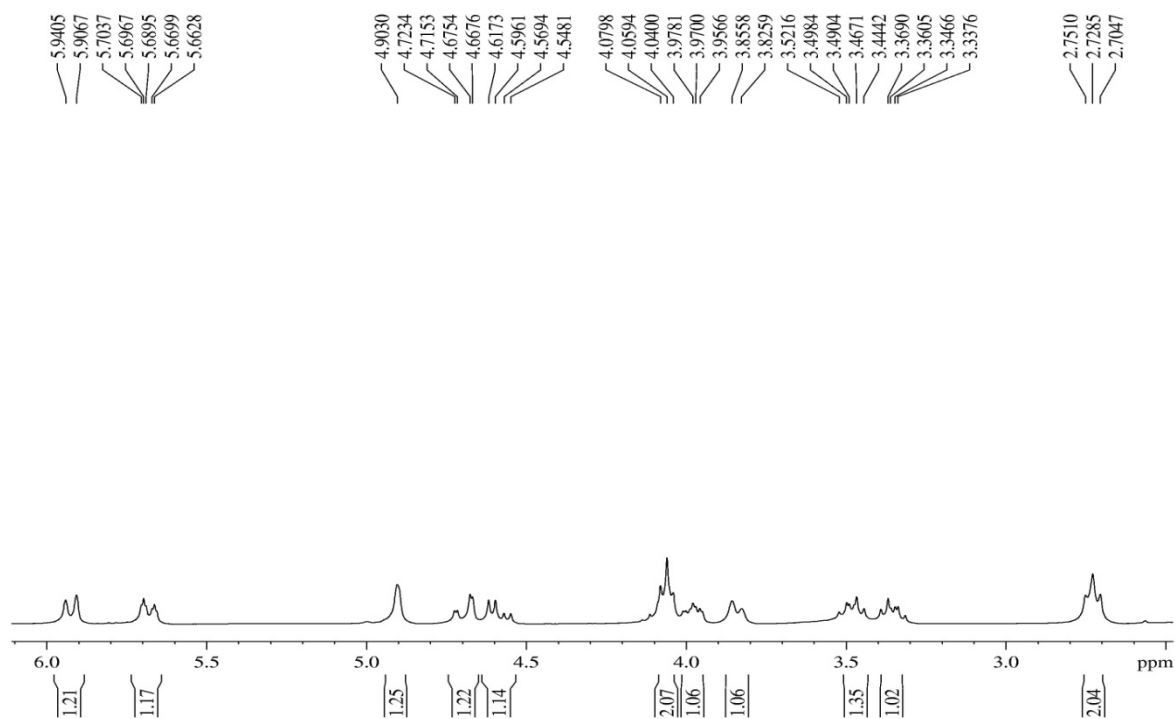
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¹³C NMR Spectrum and its DEPT 135 of compound **12**



SM-75 PROTON

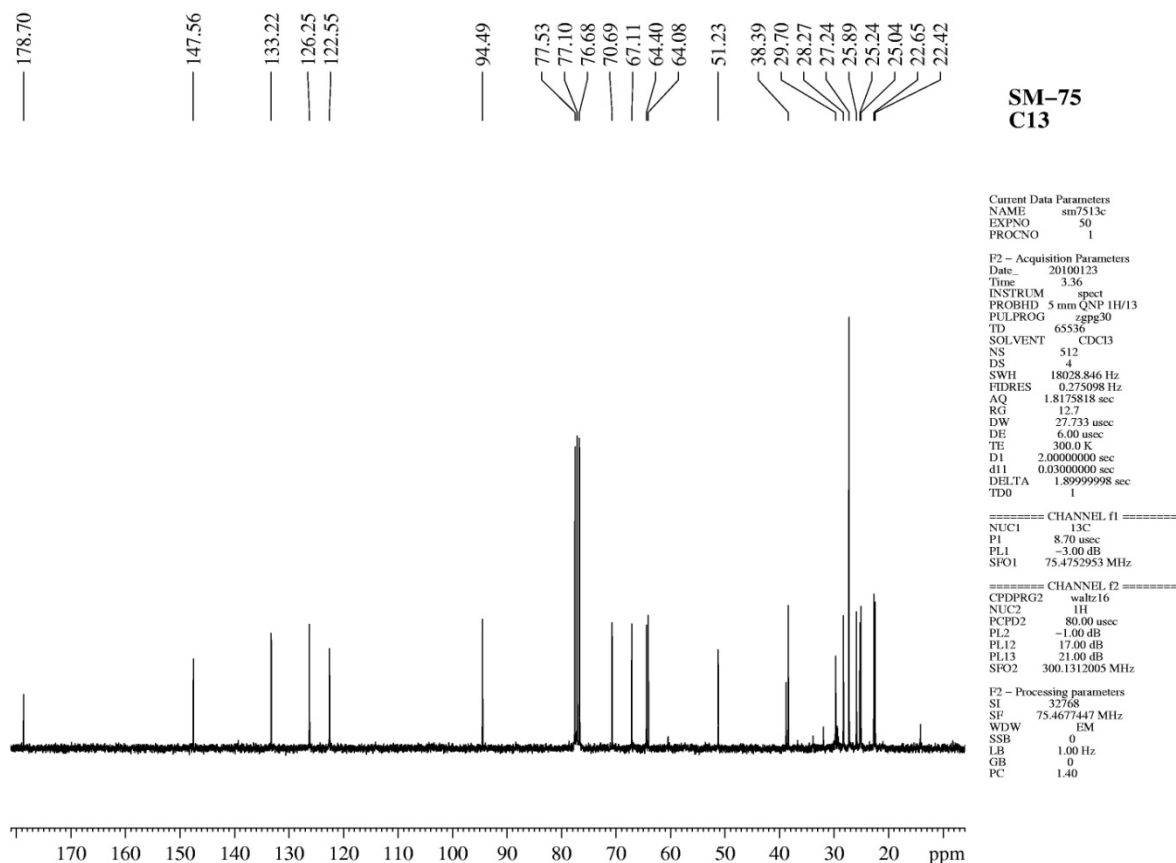
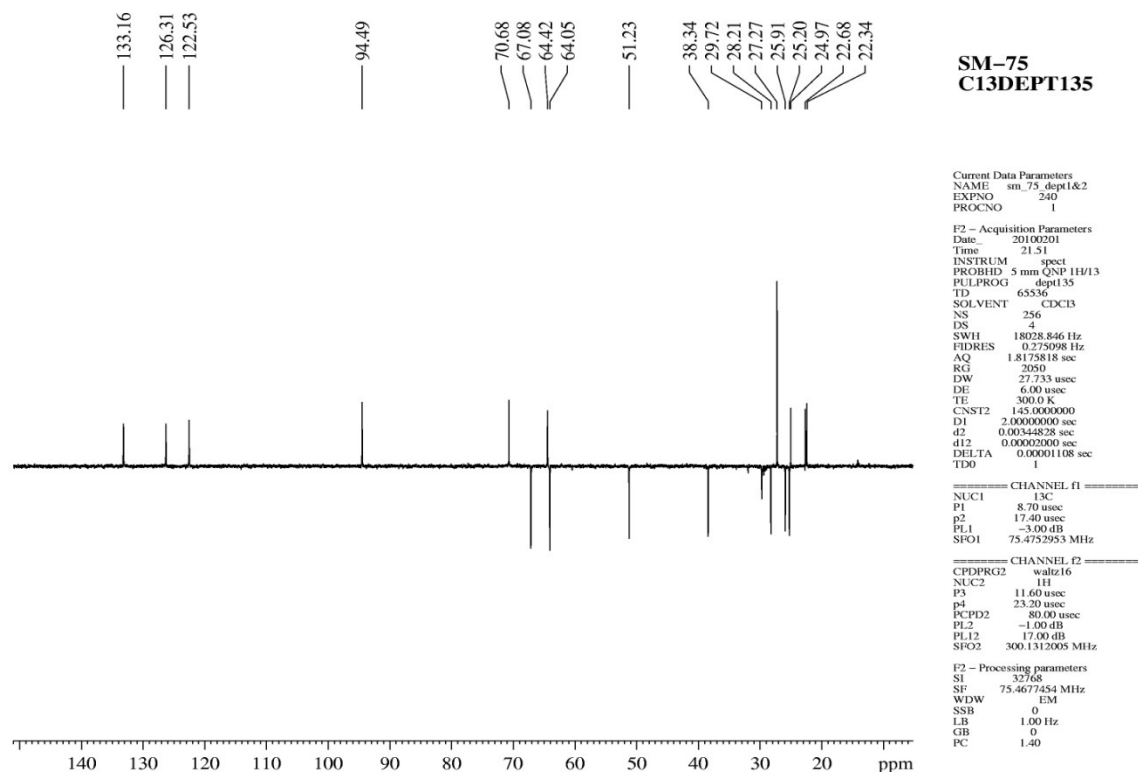
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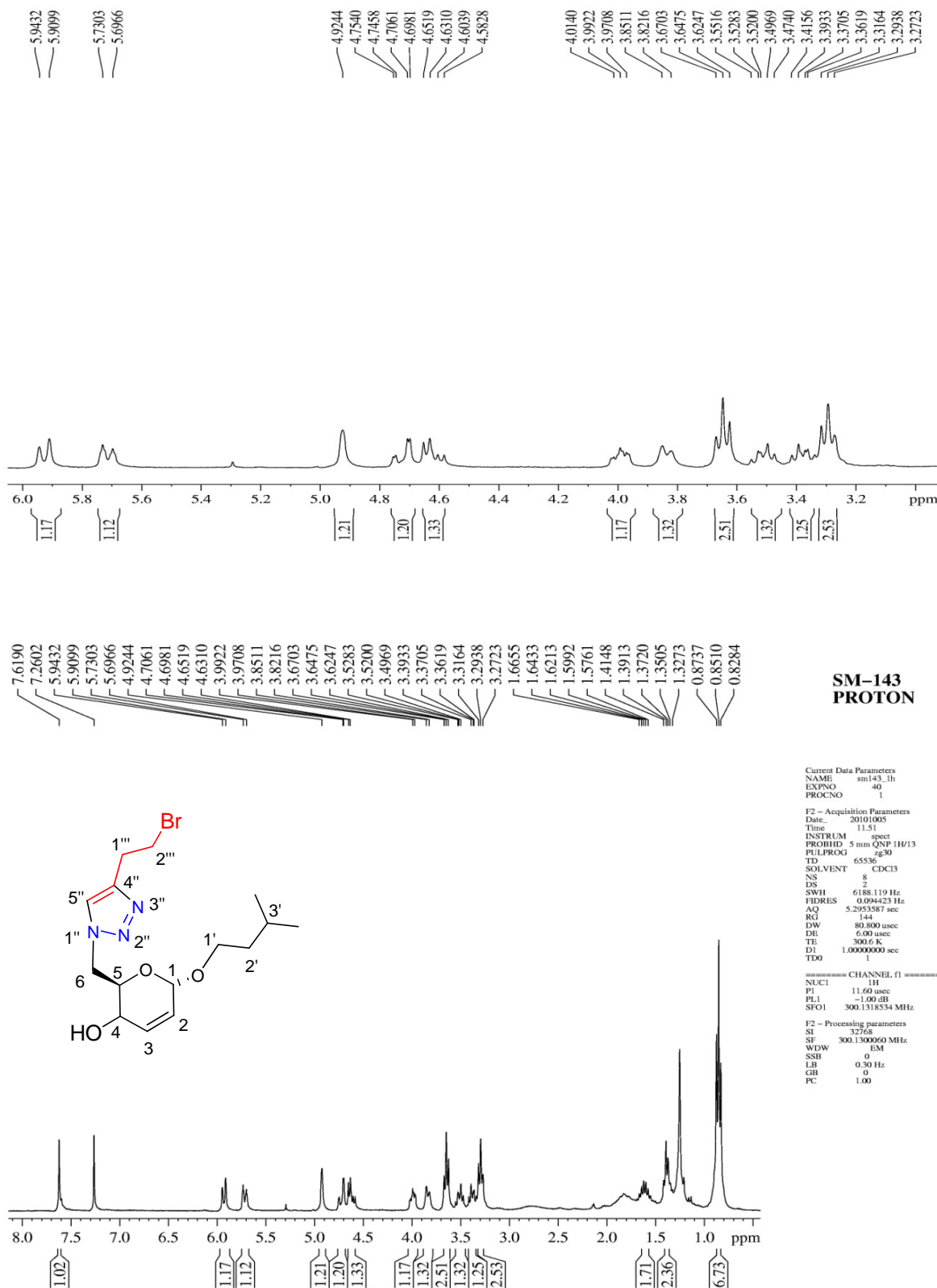
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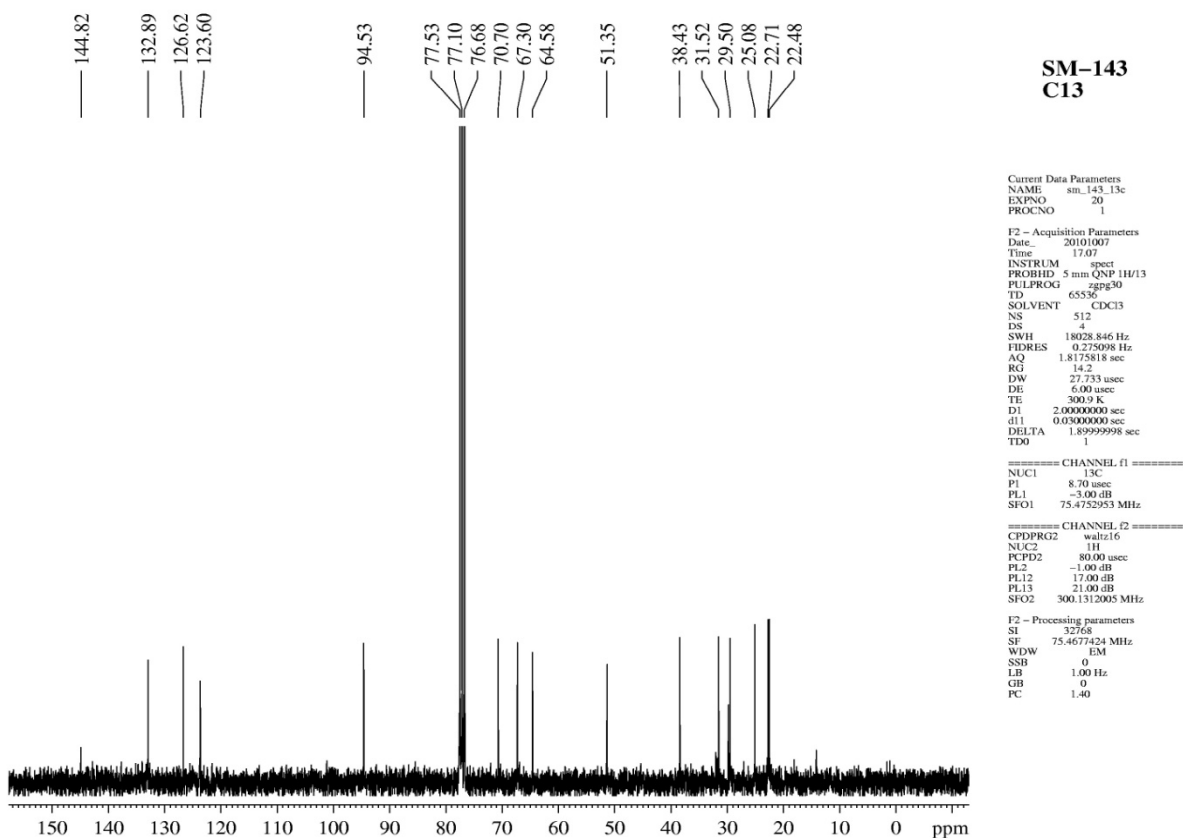
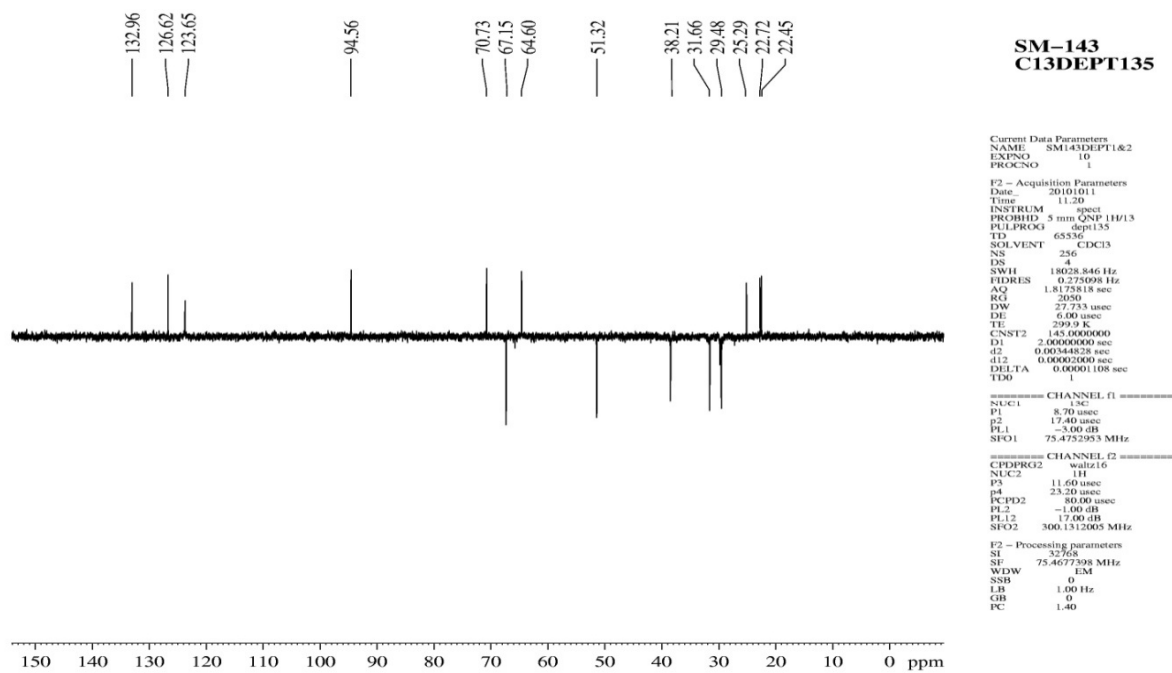
¹H NMR Spectrum of compound **14** and its expansion



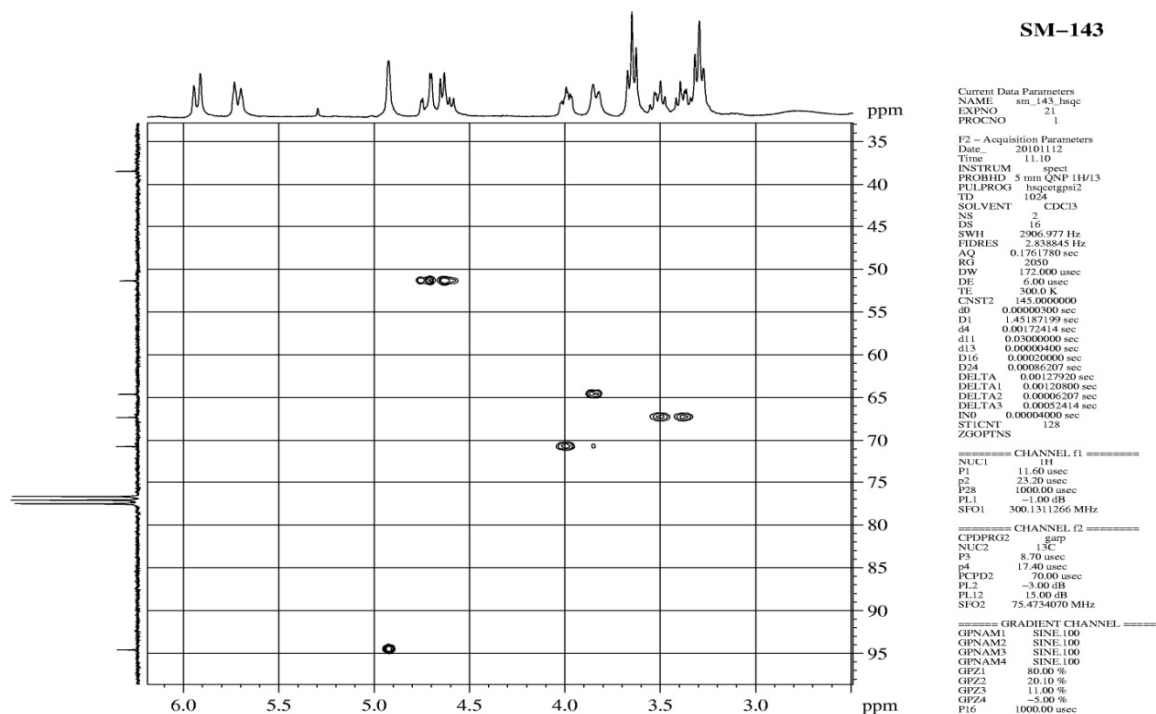
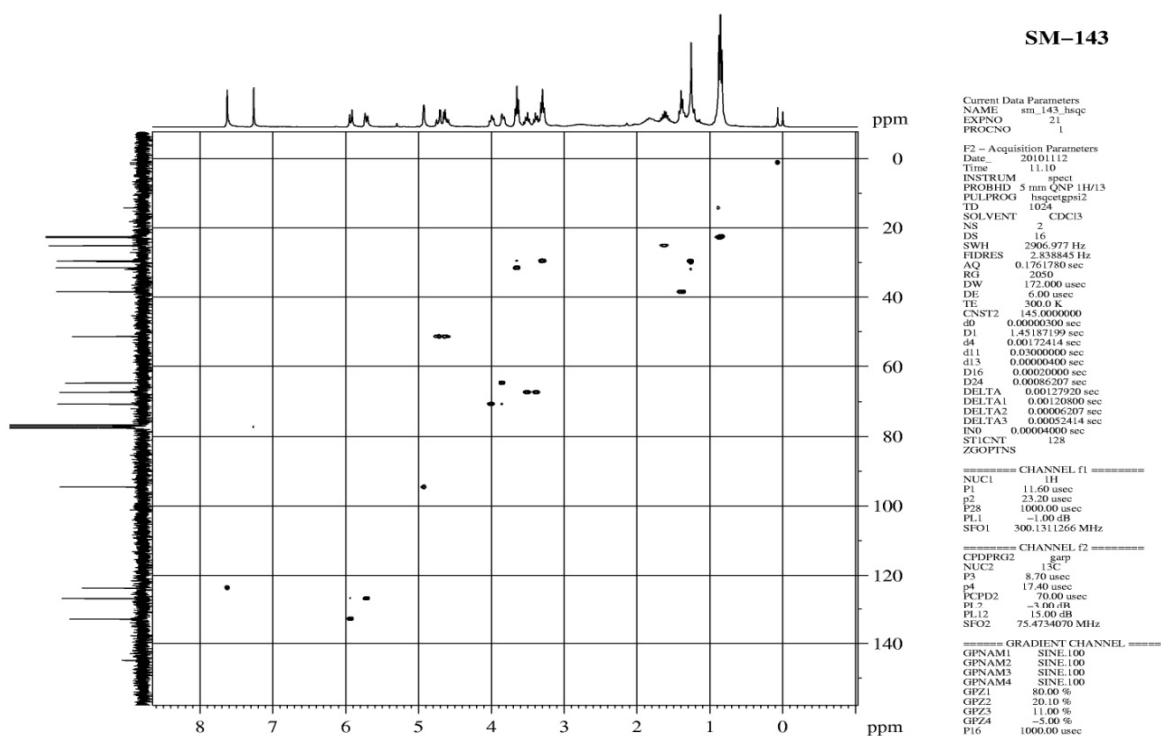
^{13}C NMR and its DEPT 135 spectrum of compound **14**



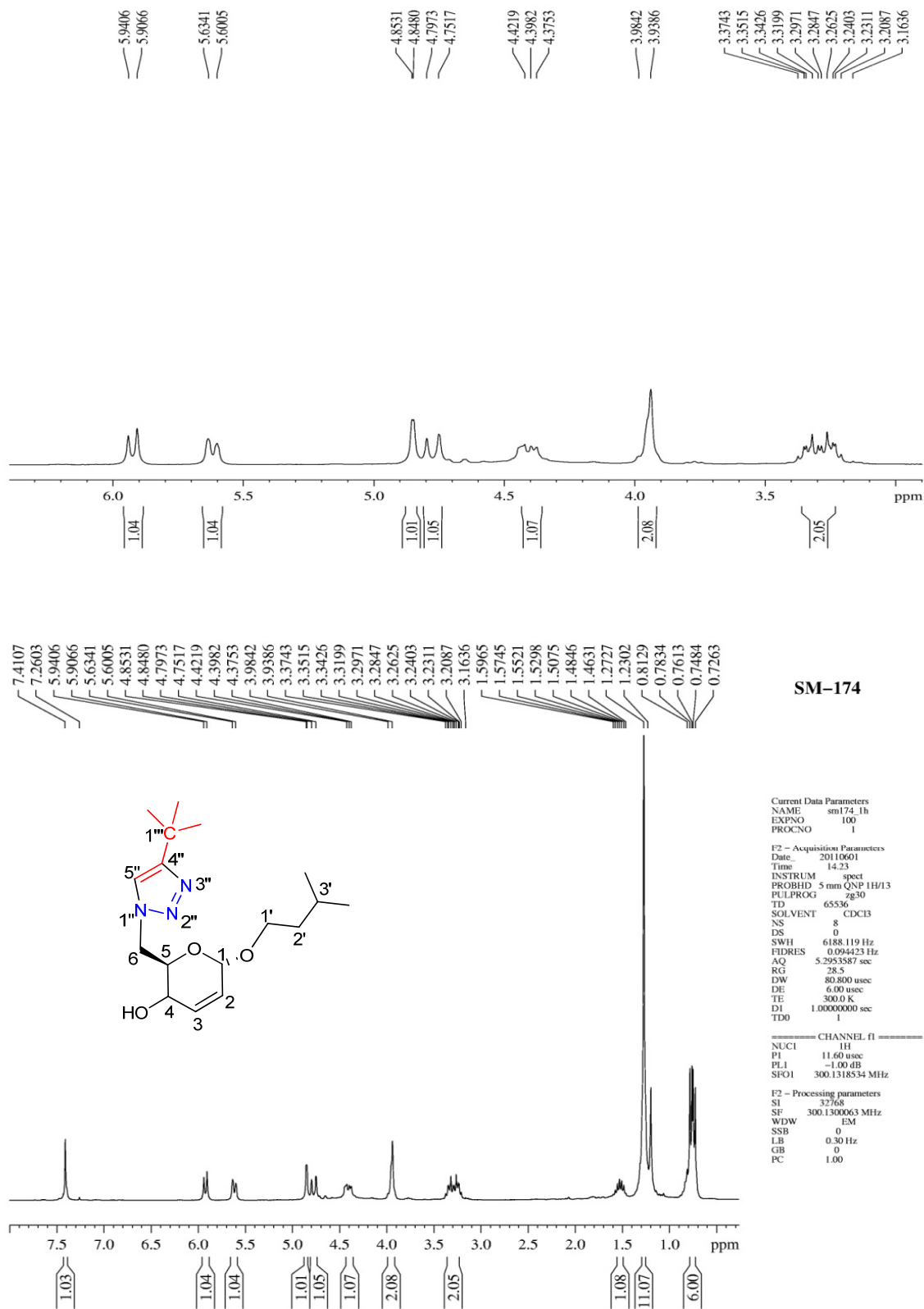
¹H NMR Spectrum of compound **15** and its expansion



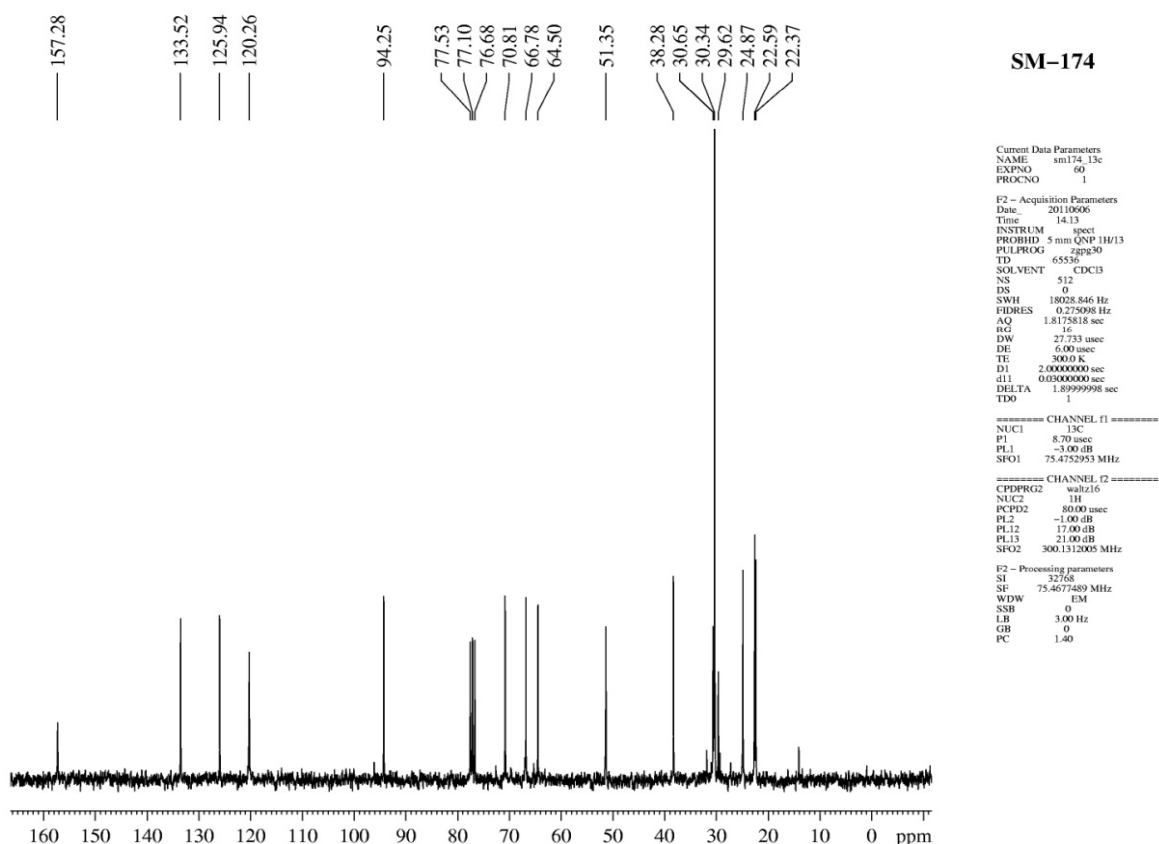
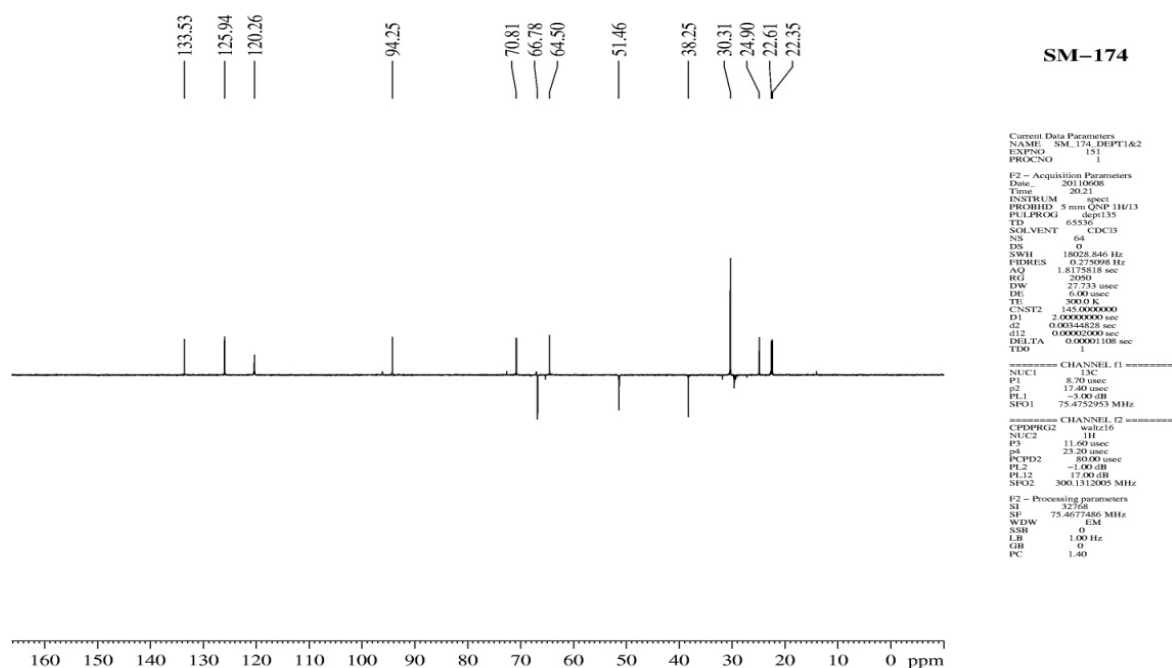
^{13}C NMR and its DEPT 135 spectrum of compound **15**



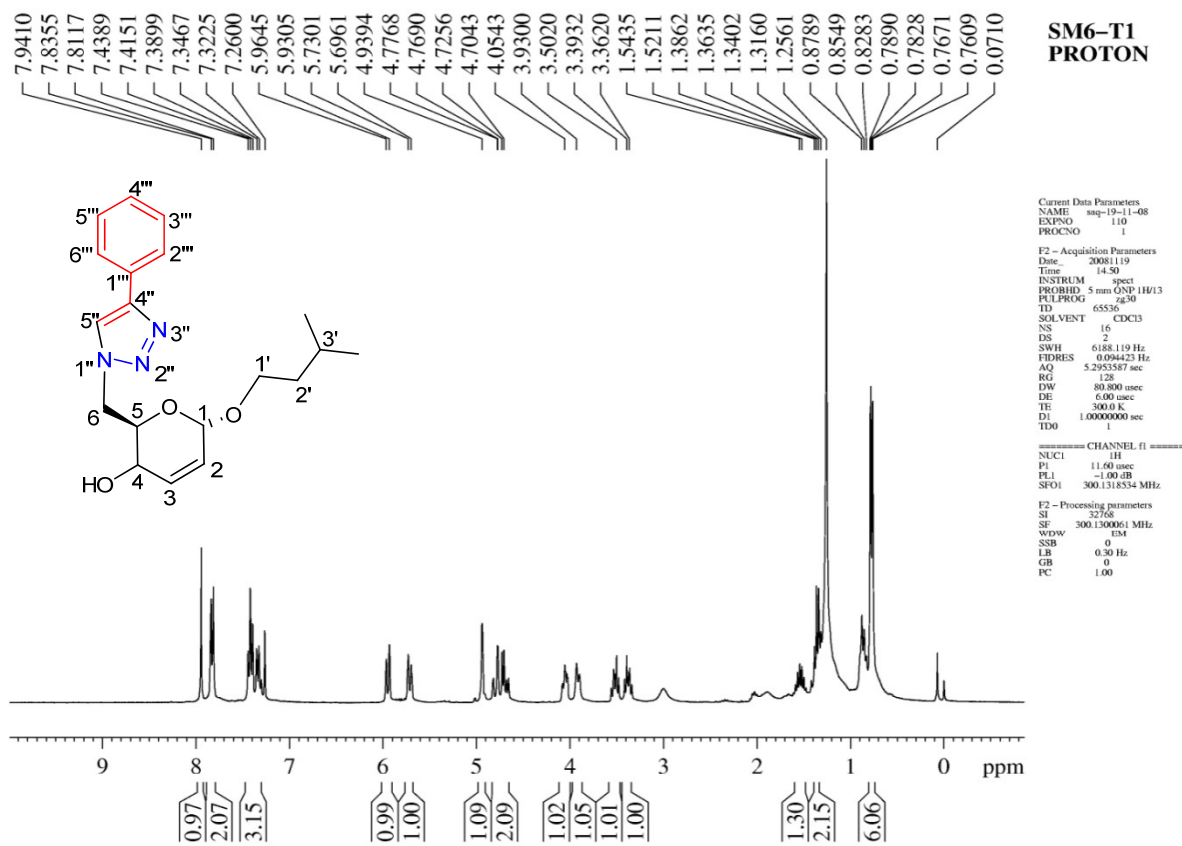
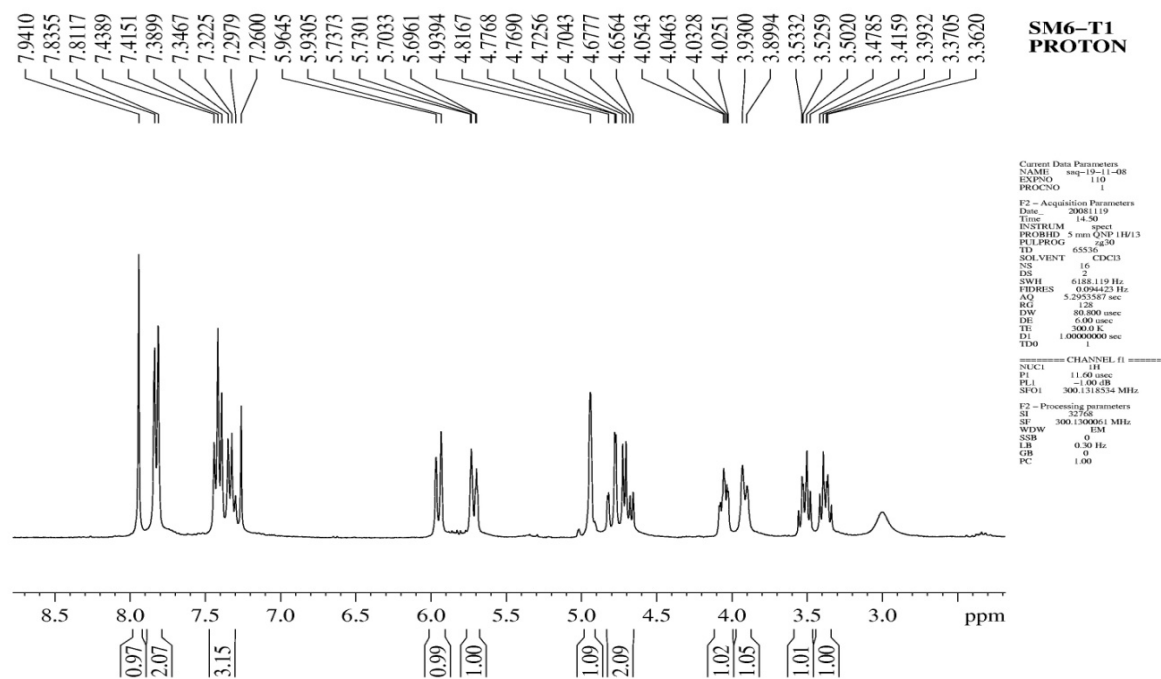
HSQC Spectrum and its expansion of compound 15

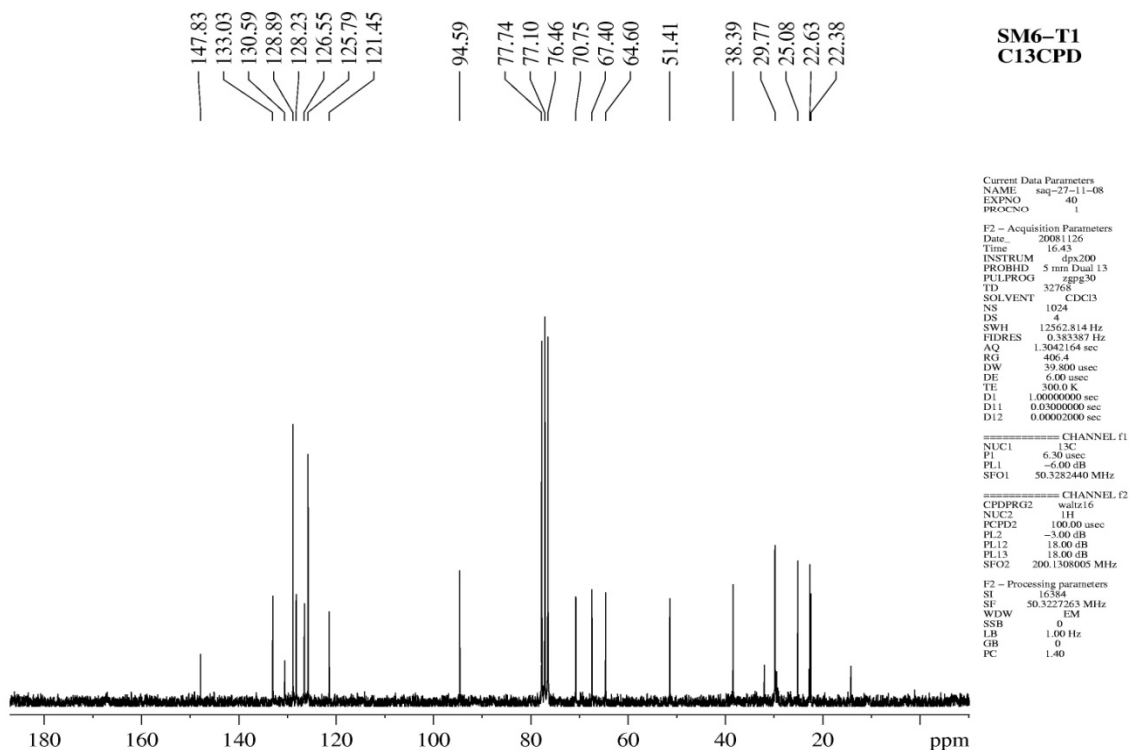
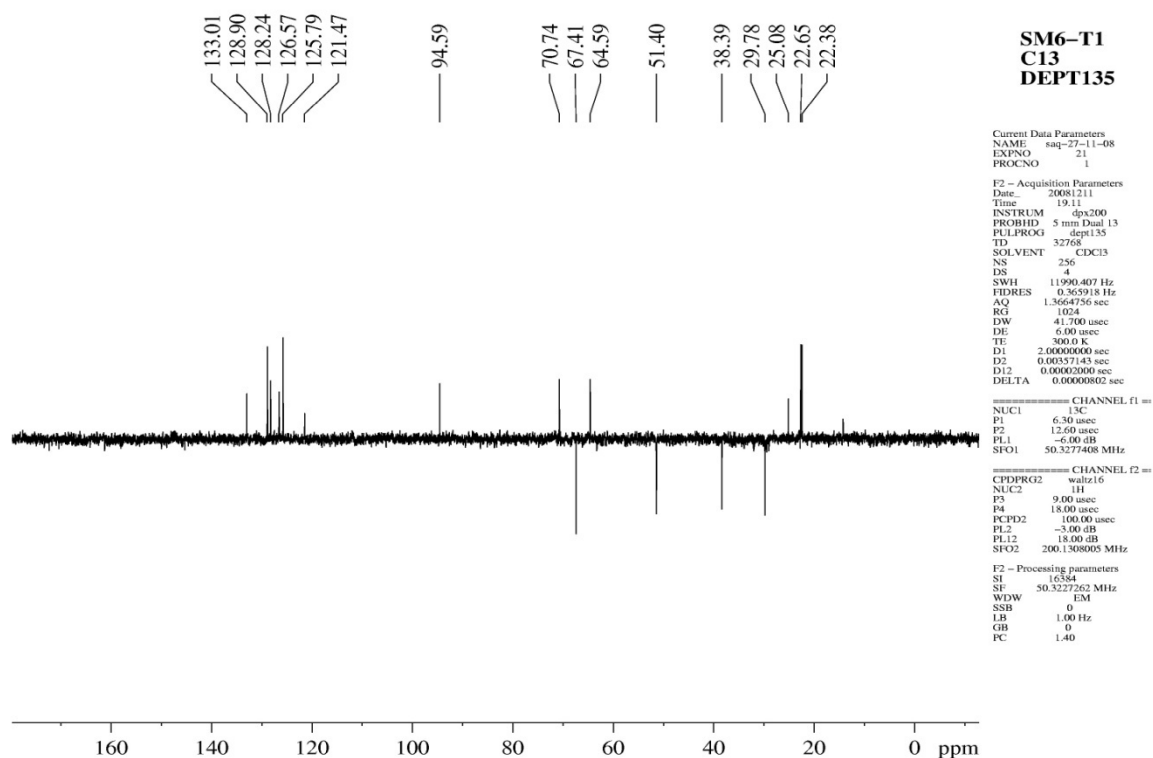


¹H NMR Spectrum of compound **16** and its expansion

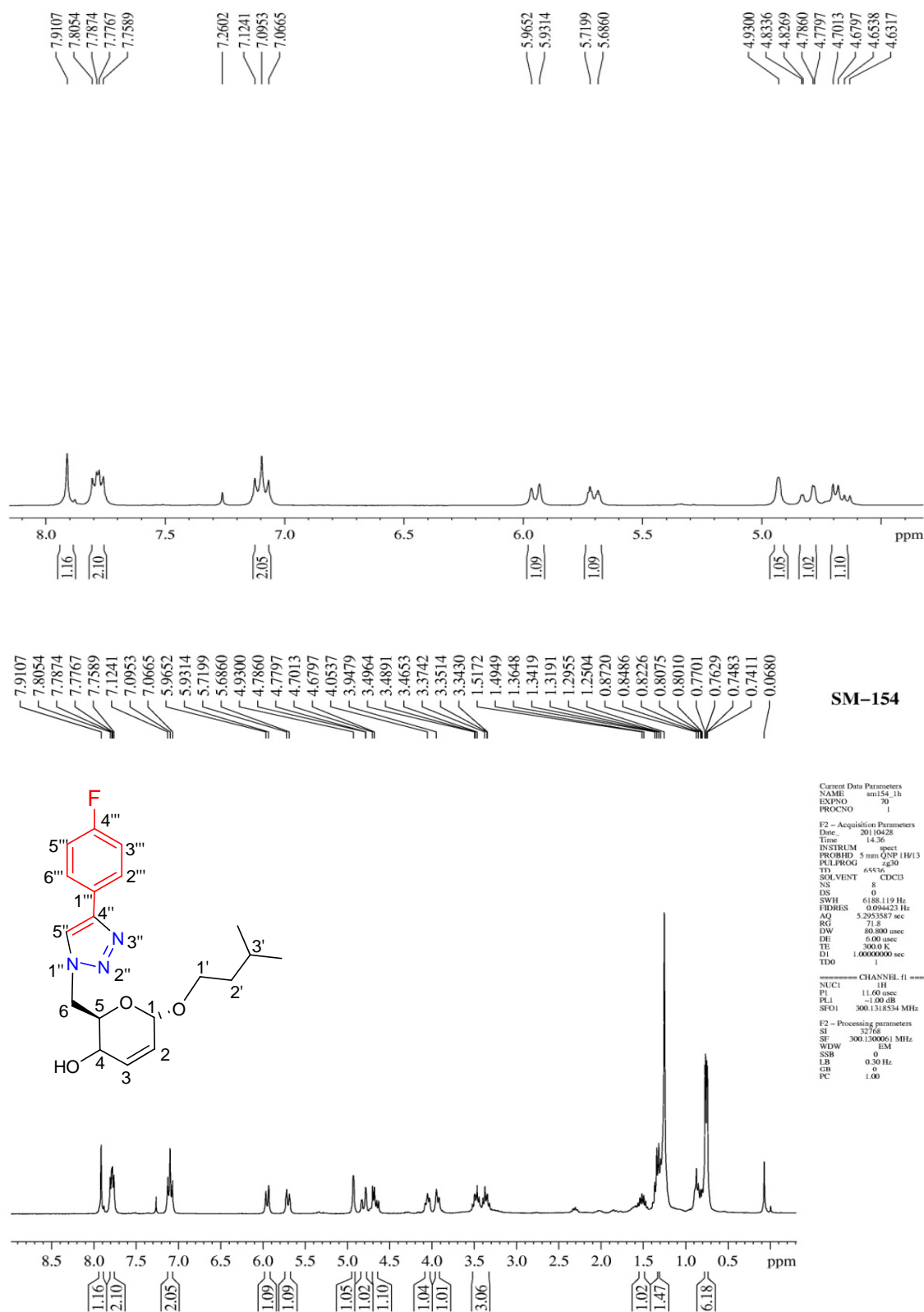


^{13}C NMR and its DEPT 135 spectrum of compound **16**

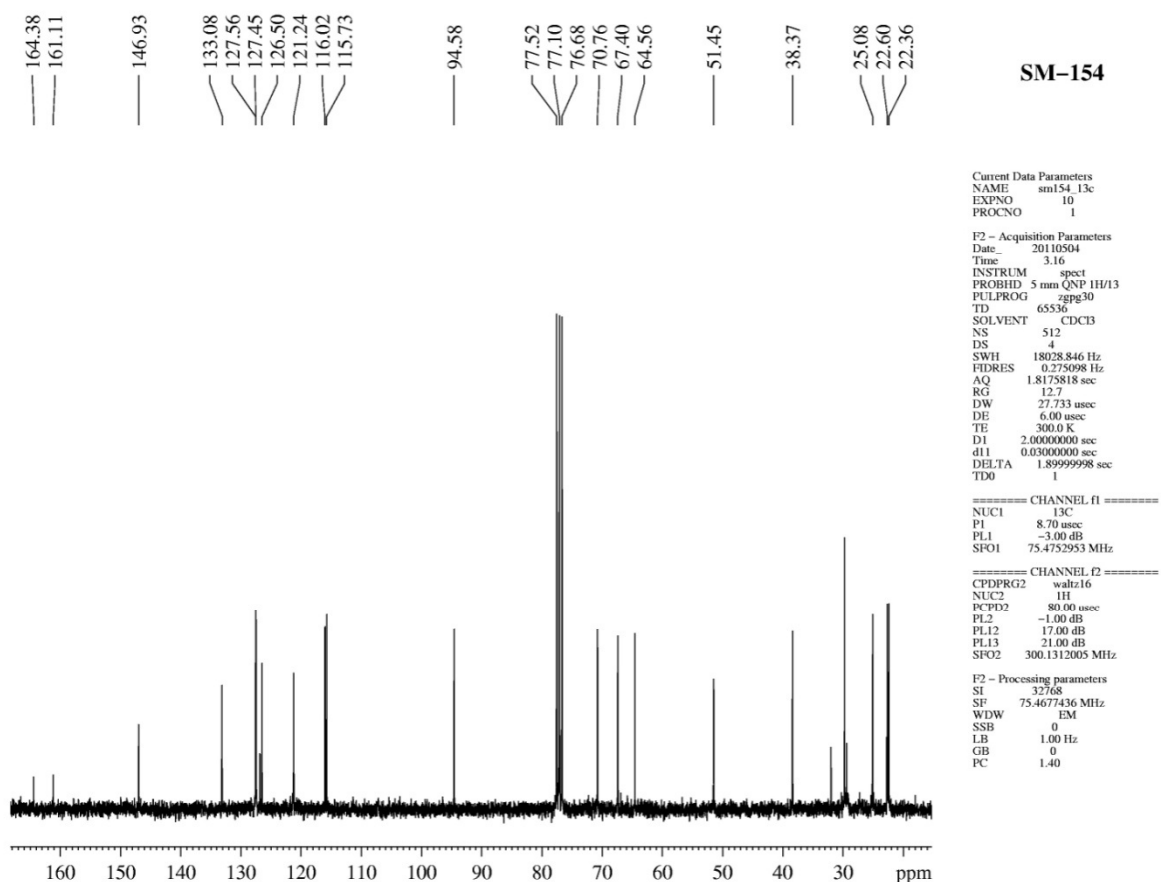
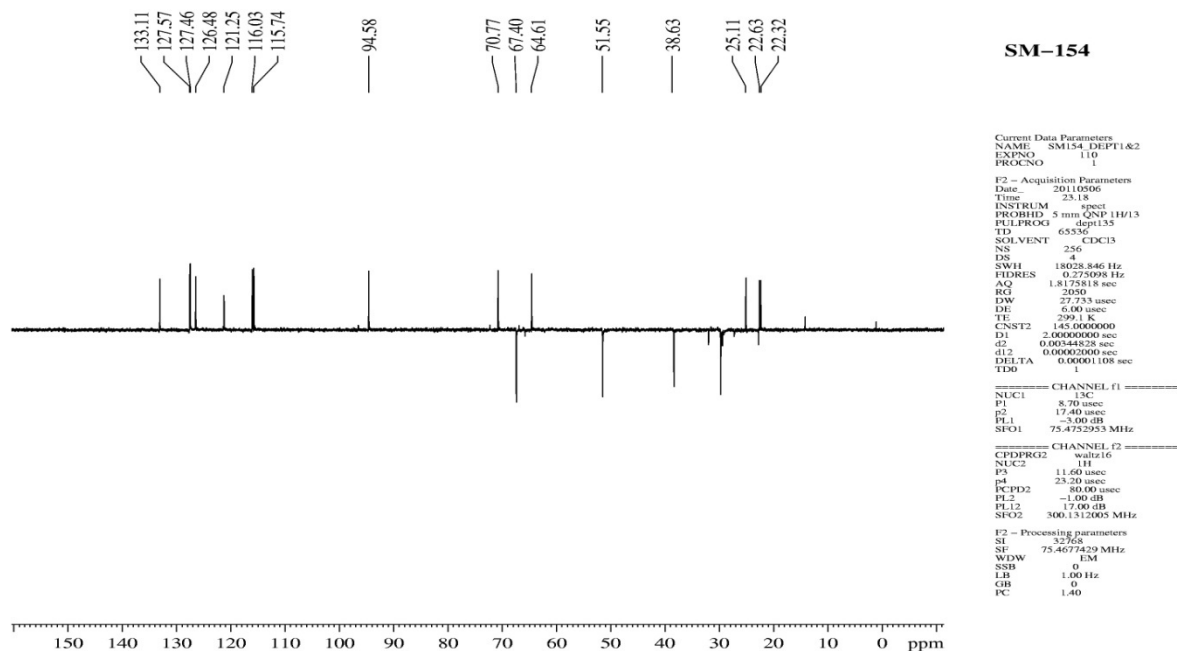
¹H NMR Spectrum of compound **17** and its expansion



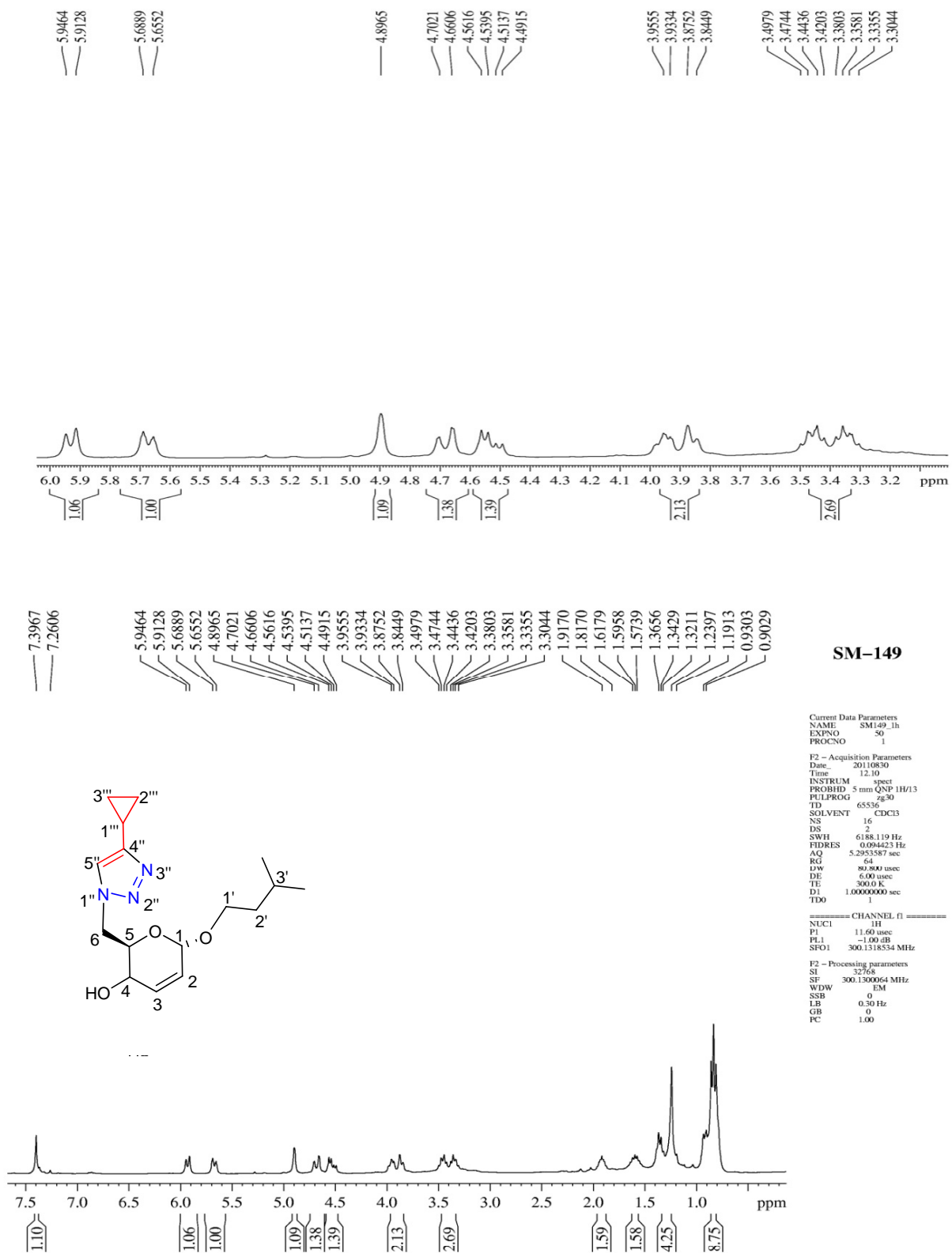
^{13}C NMR and its DEPT 135 spectrum of compound **17**



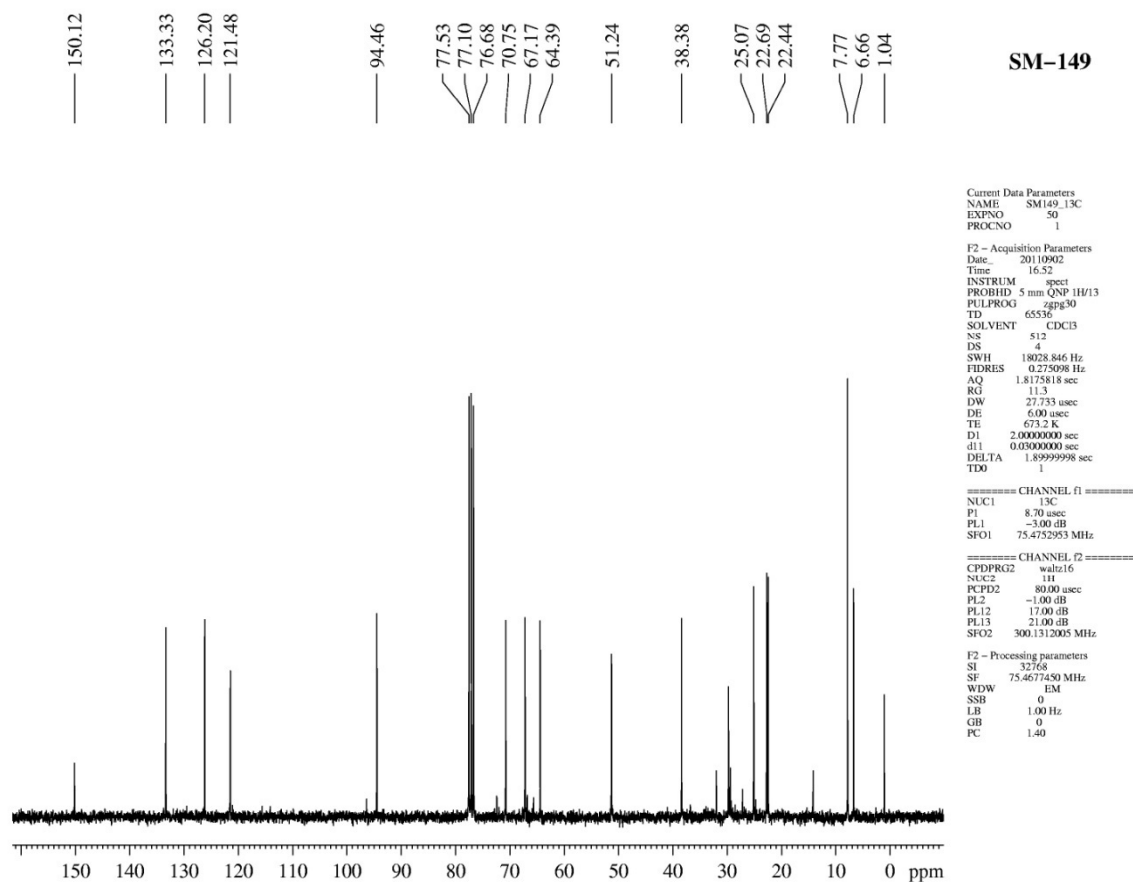
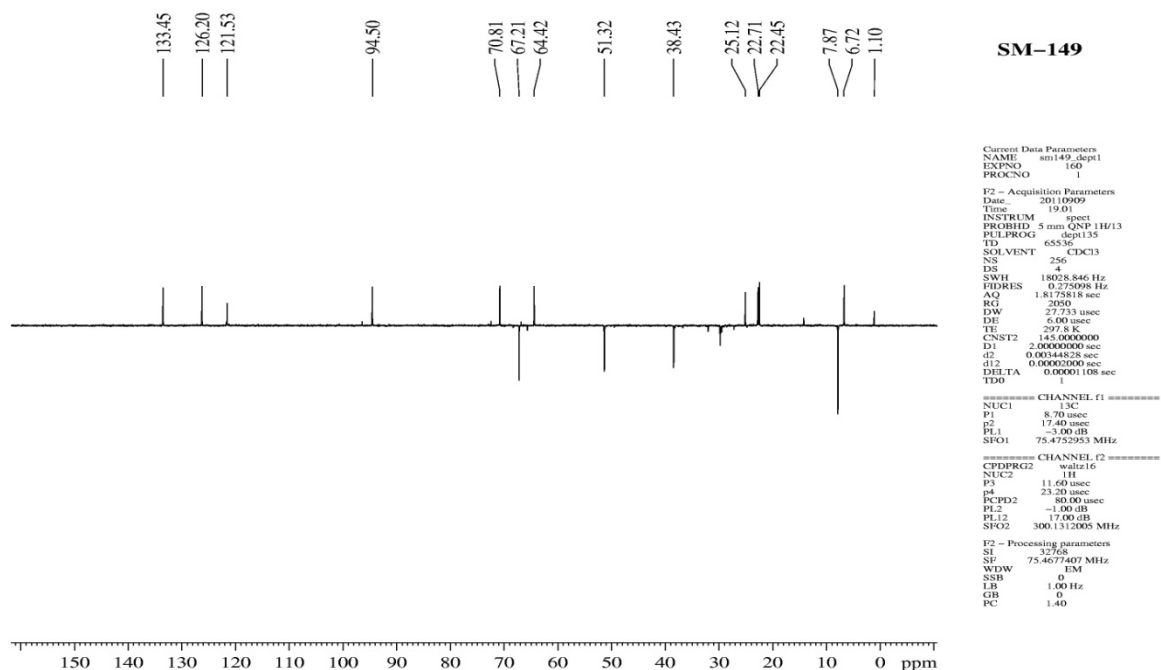
¹H NMR Spectrum of compound **19** and its expansion

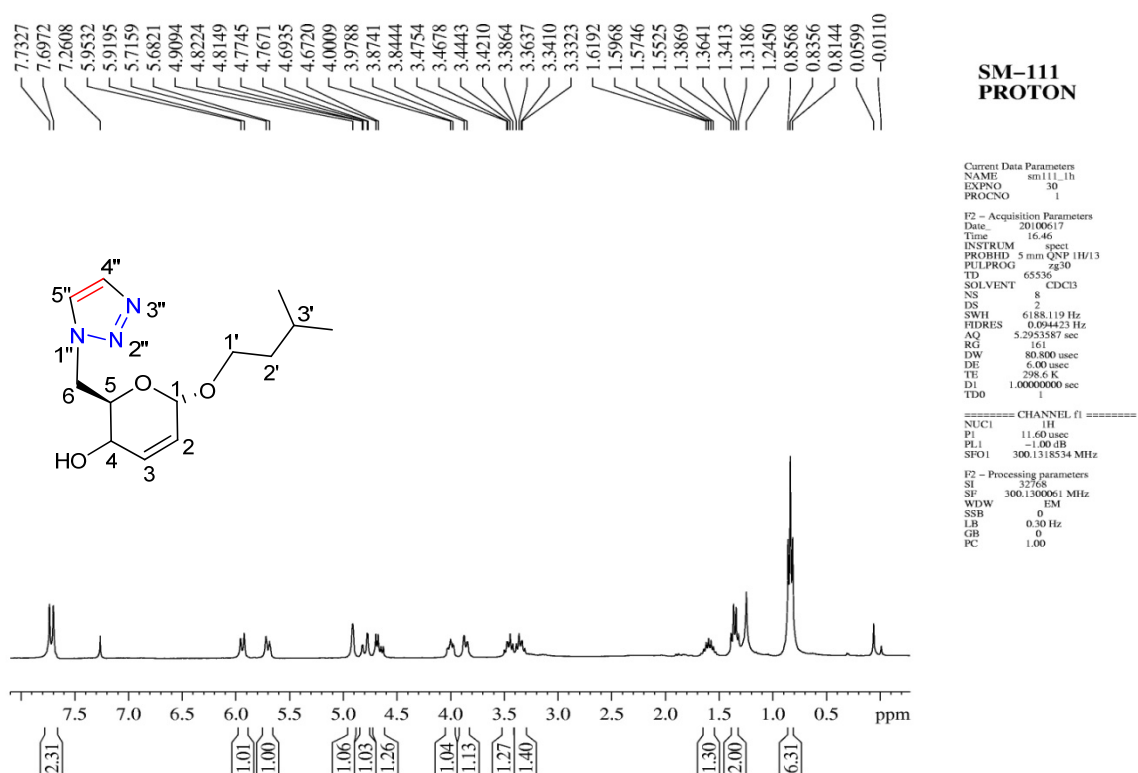
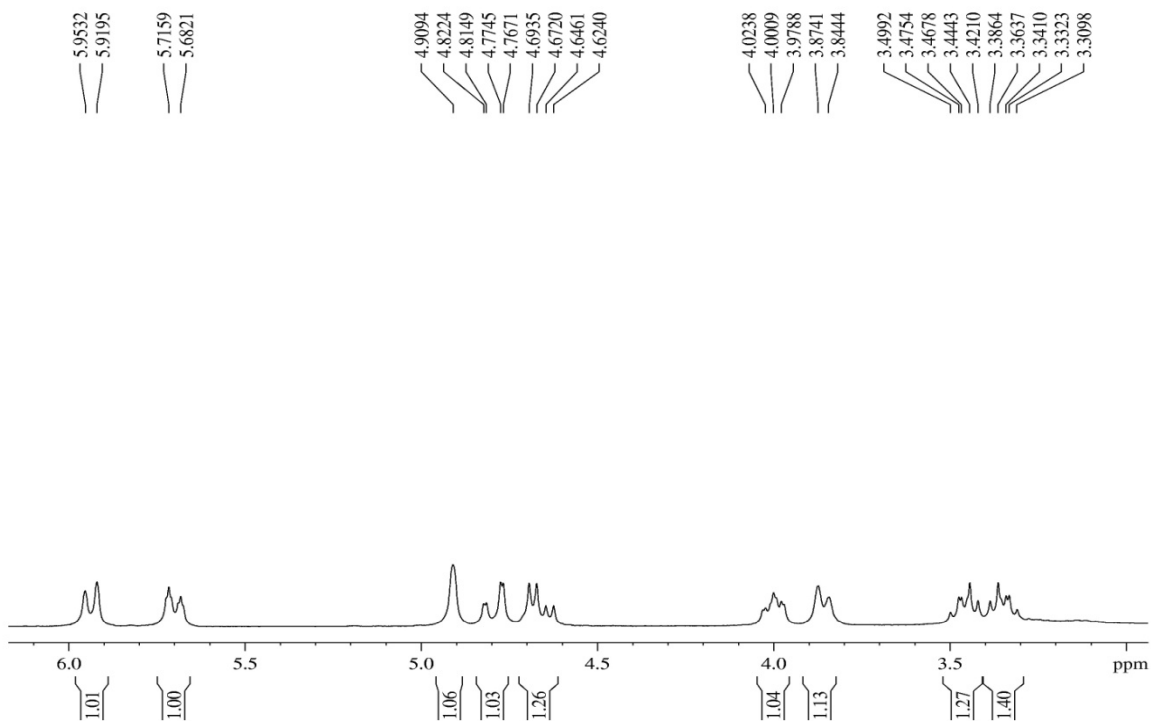


^{13}C NMR and its DEPT 135 spectrum of compound **19**

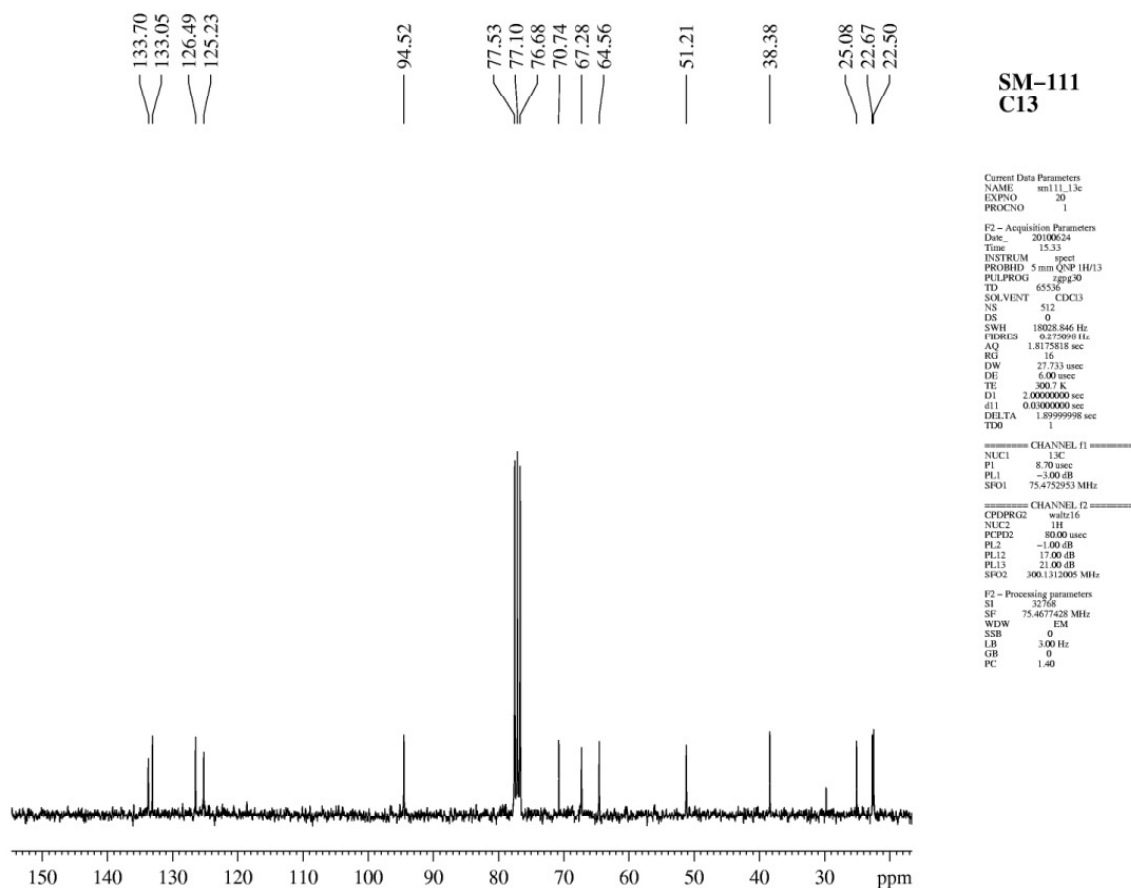


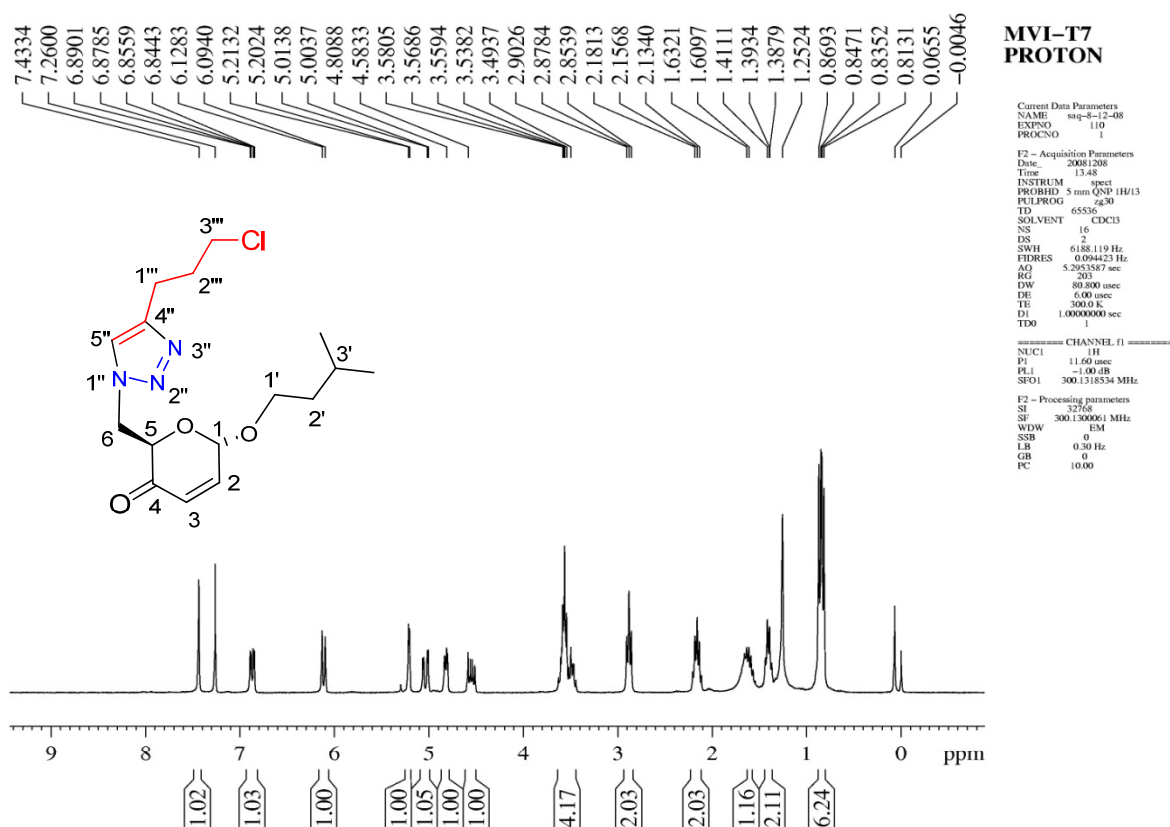
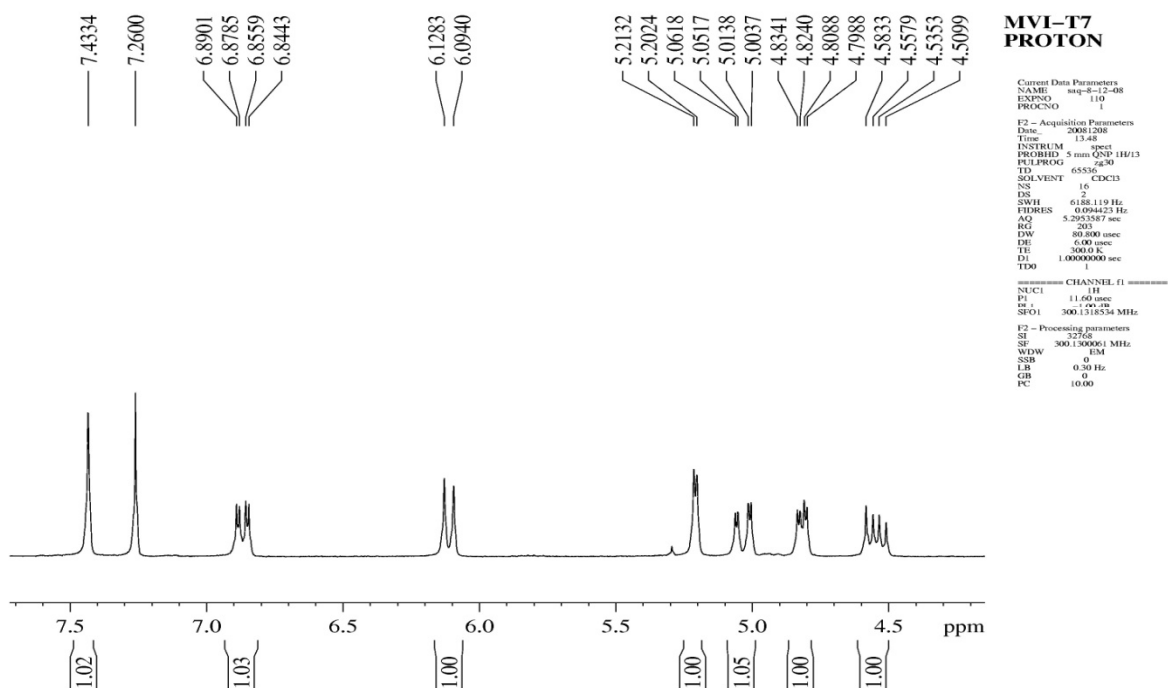
¹H NMR Spectrum of compound **21** and its expansion



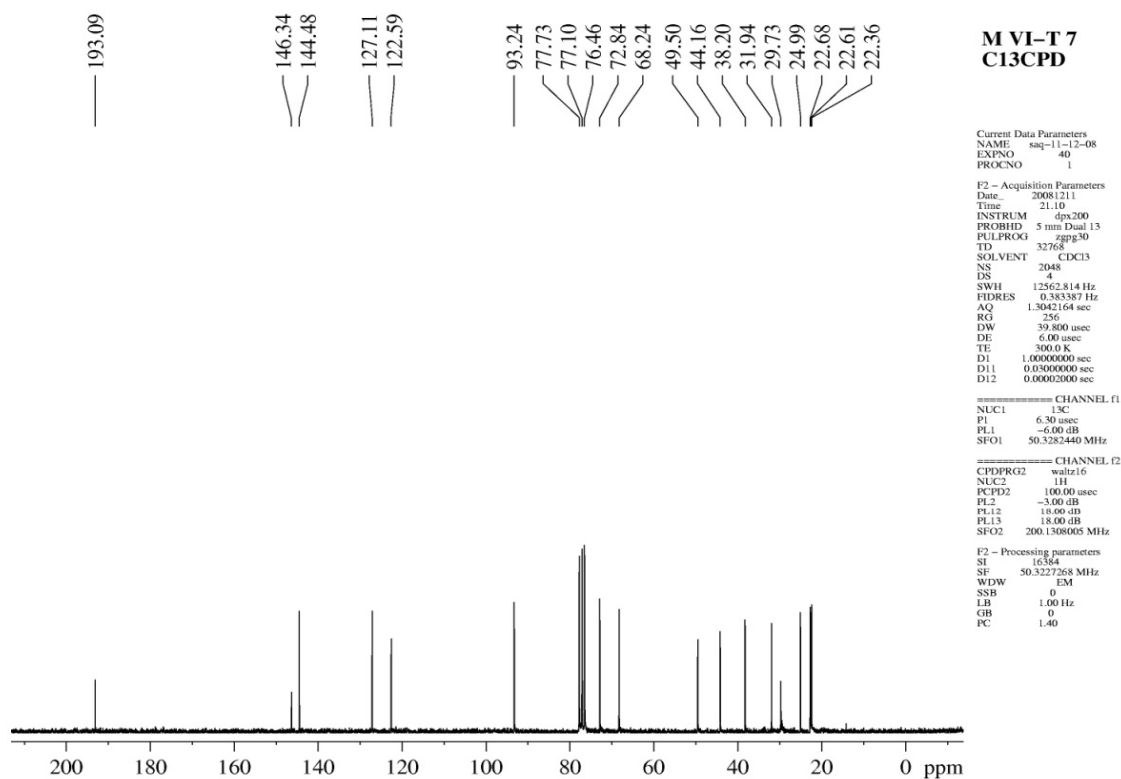
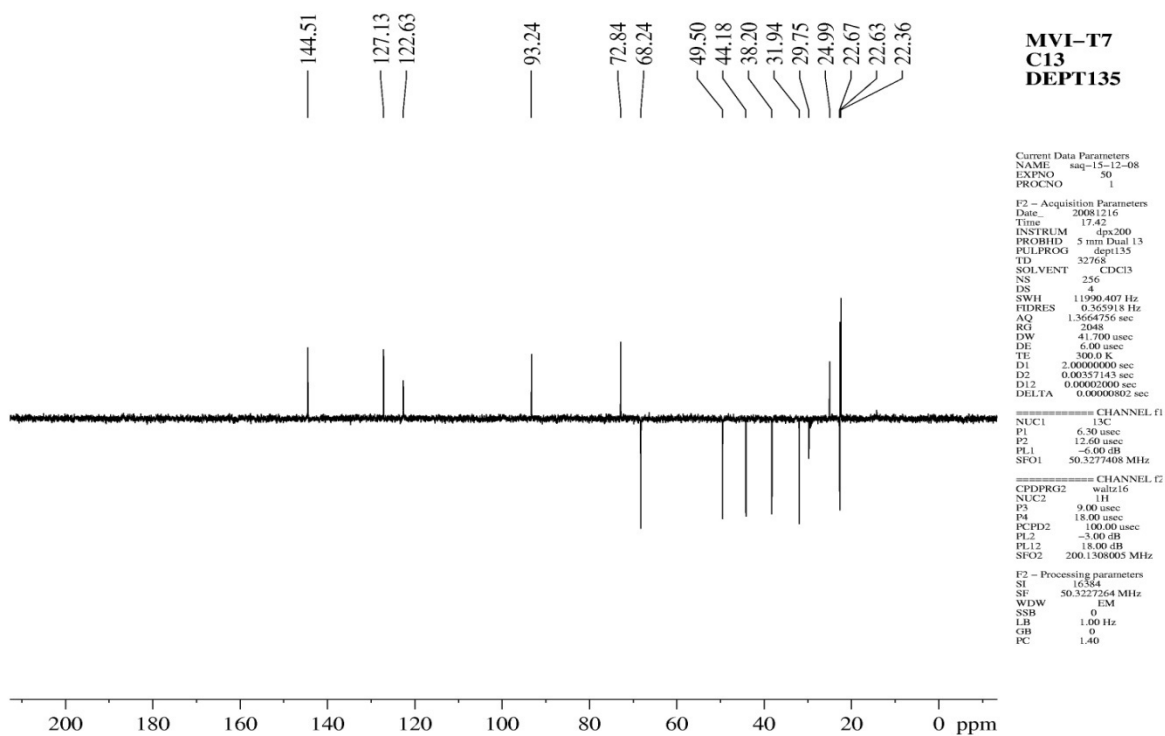


¹H NMR Spectrum of compound **23** and its expansion

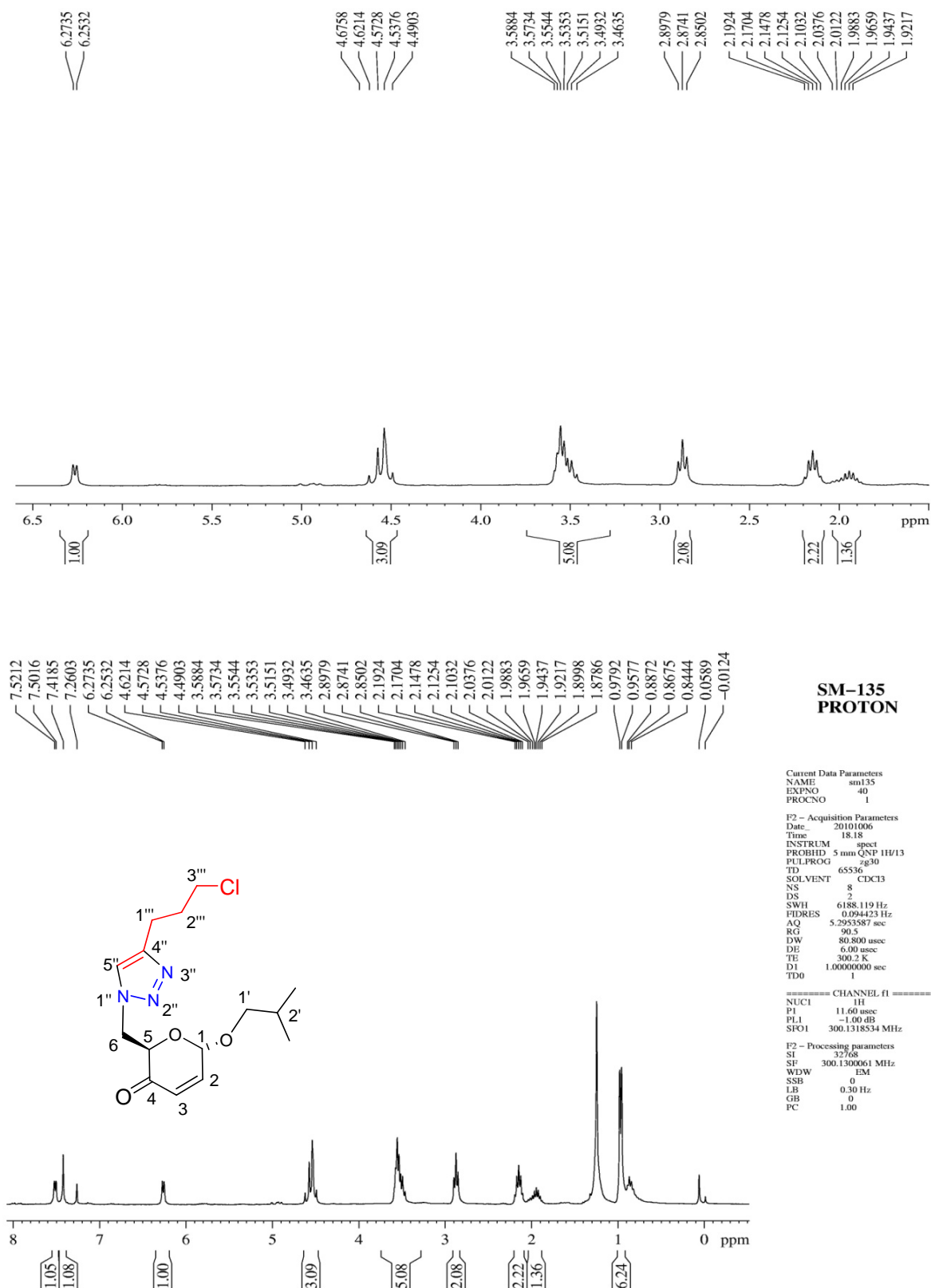
 ^{13}C NMR Spectrum of compound **23**

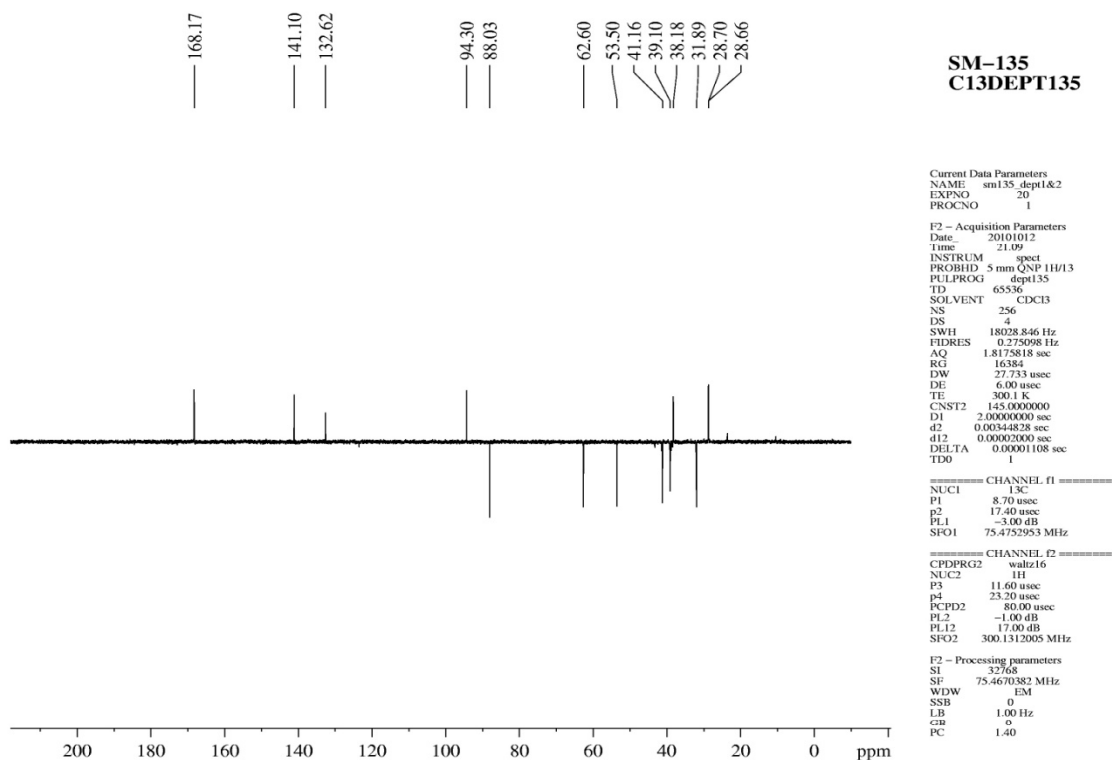


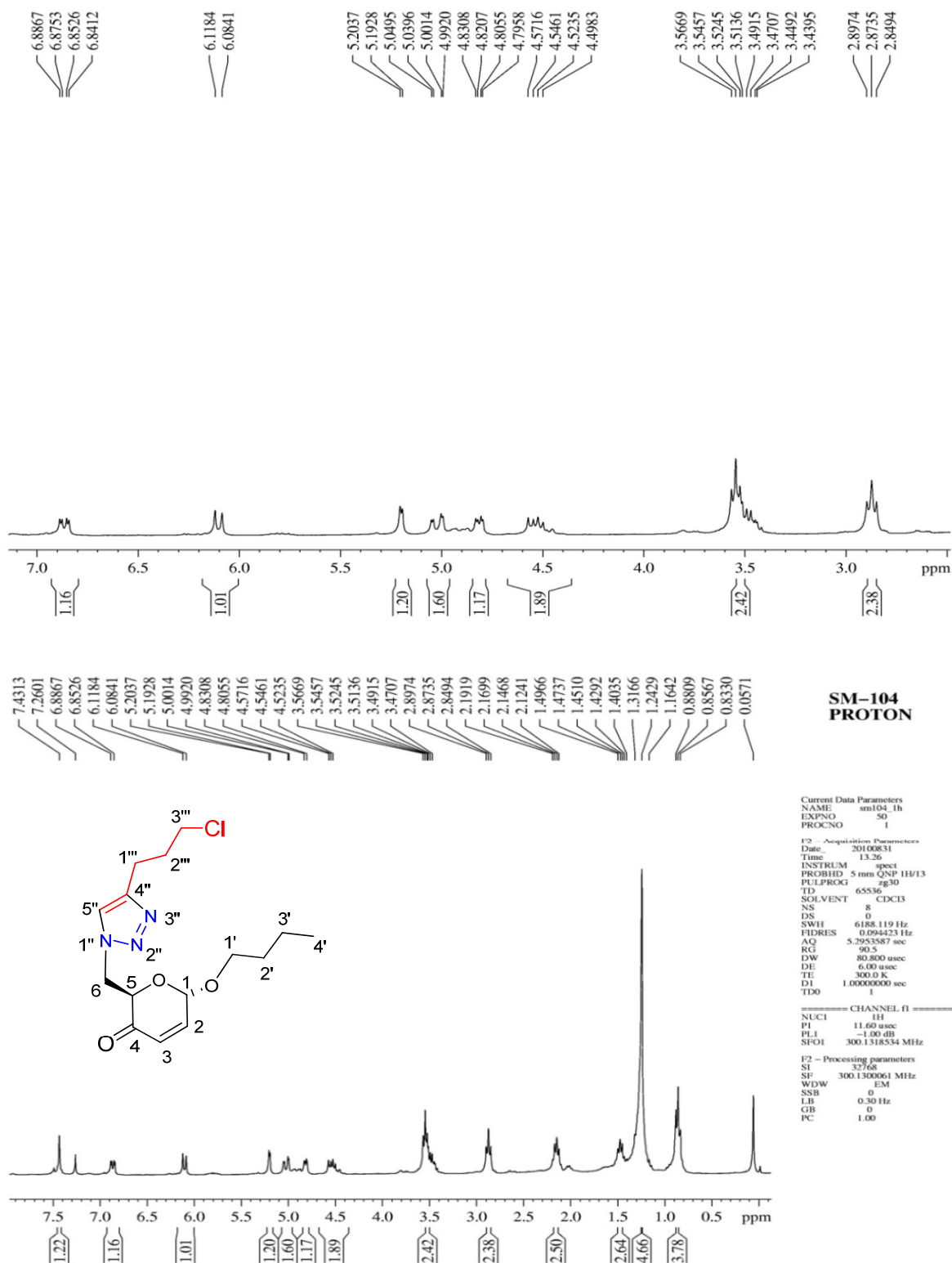
¹H NMR Spectrum of compound **24** and its expansion



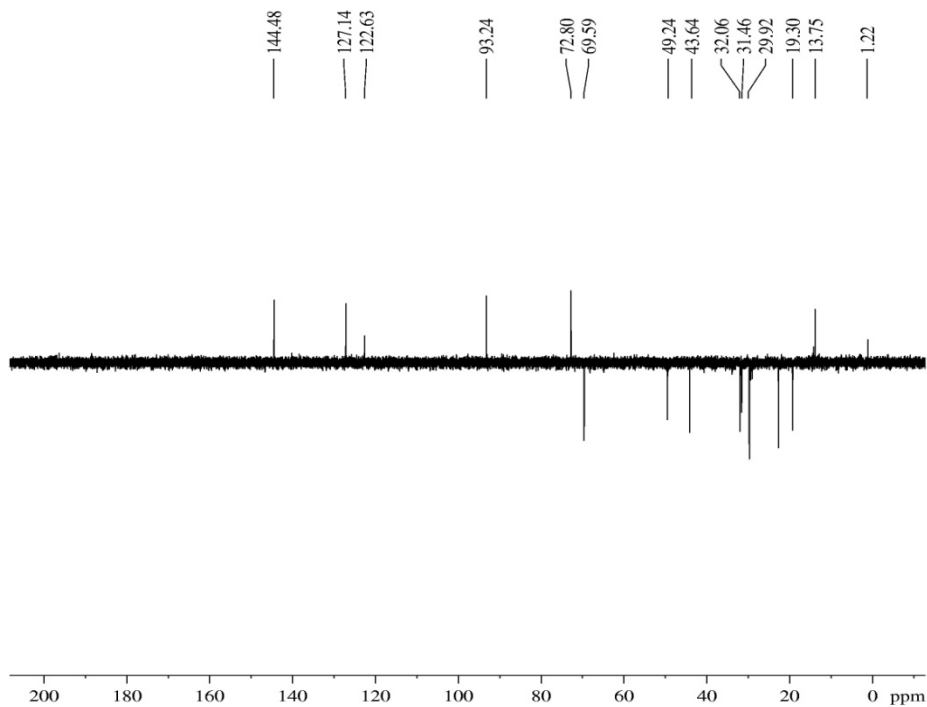
¹³C NMR and its Dept 135 Spectrum of compound **24**

¹H NMR Spectrum of compound **25** and its expansion

DEPT 135 spectrum of compound **25**

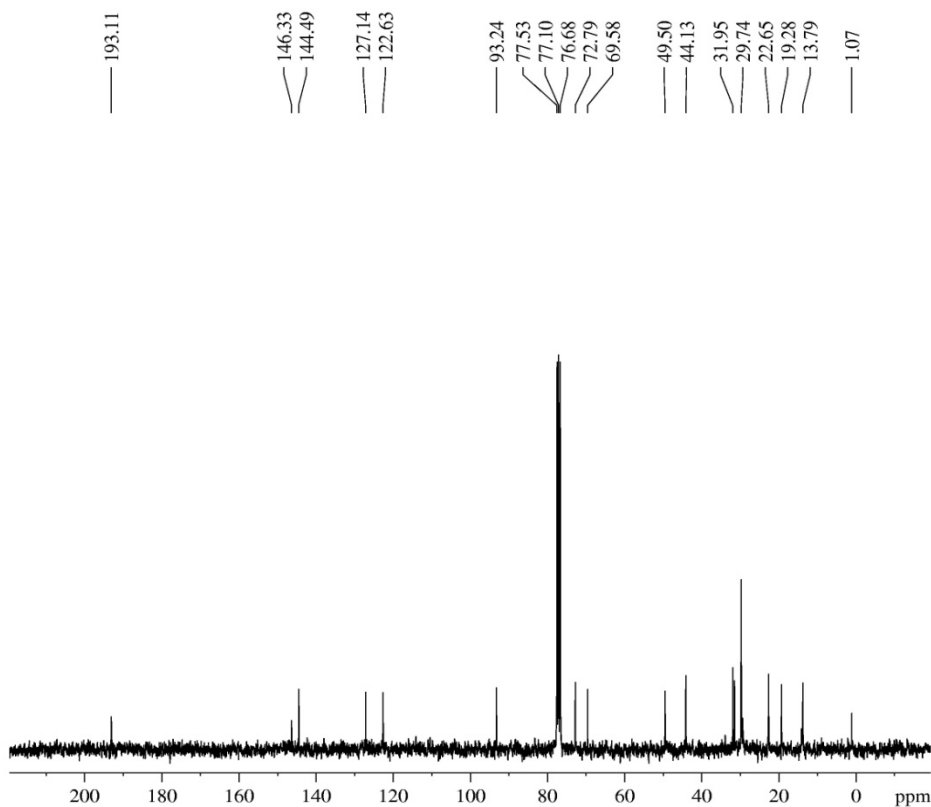


¹H NMR Spectrum of compound **26** and its expansion



SM-104

Current Data Parameters
NAME sm104_dept1&2
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101022
Time 16:24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG dept135
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 27.733 usec
DE 6.00 usec
TE 300.6 K
CNST2 1.45000000
D1 2.00000000 sec
d2 0.00044828 sec
d12 0.00002000 sec
DELTA 0.00001108 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
p2 17.40 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P3 11.60 usec
p4 23.20 usec
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677434 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40



SM-104
C13

Current Data Parameters
NAME sm104_13c
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100903
Time 11:30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 16
DW 27.733 usec
DE 6.00 usec
TE 300.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677438 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

^{13}C NMR Spectrum and its DEPT 135 of compound **26**

Qualitative Compound Report

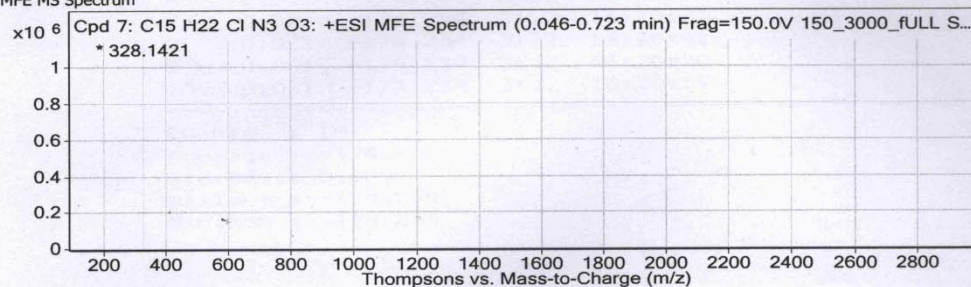
Data File	150_3000_FULL SCAN_ISOCRATIC GENERALSM-104_260A.d	Sample Name	SM-104
Sample Type	Sample	Position	Vial 74
Instrument Name	Instrument 1	User Name	
Acq Method	150_3000_FULL SCAN_ISOCRATIC GENERAL. P.M	Acquired Time	2/14/2011 12:10:41 PM
IRM Calibration Status	Success	DA Method	PAAN_MFE.m
Comment			

Compound Table

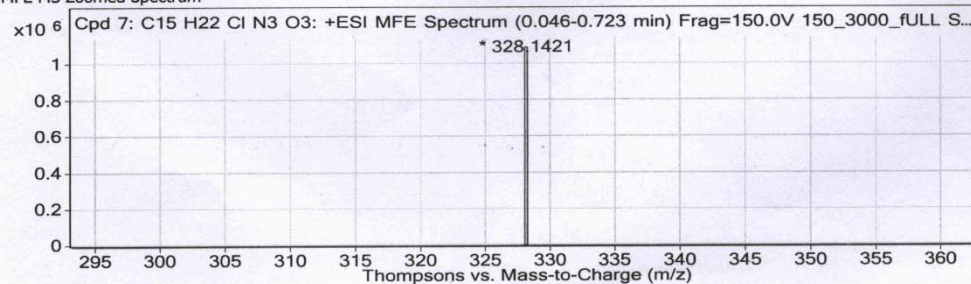
Compound Label	RT	Mass	MFG Formula	MFG Diff (ppm)
Cpd 7: C15 H22 Cl N3 O3	0.239	327.1348	C15 H22 Cl N3 O3	0.43

Compound Label	RT	Algorithm	Mass
Cpd 7: C15 H22 Cl N3 O3	0.239	Find by Molecular Feature	327.1348

MFE MS Spectrum



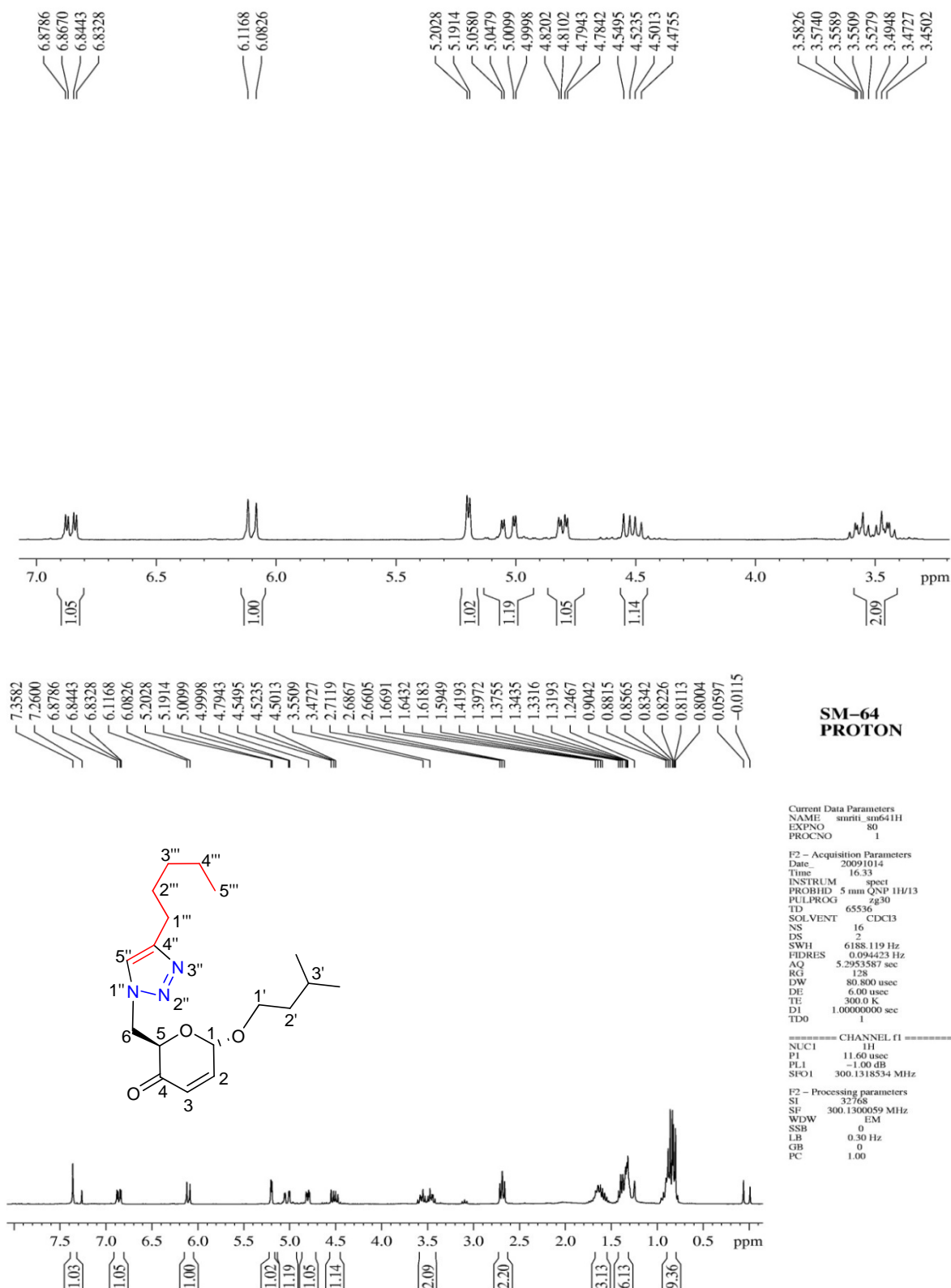
MFE MS Zoomed Spectrum



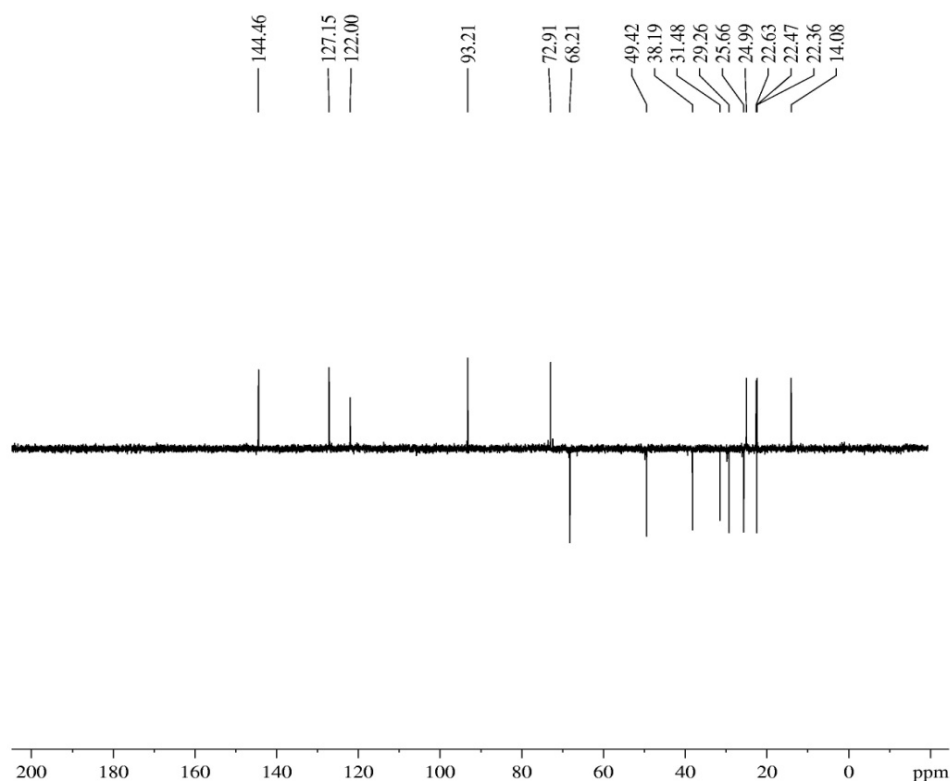
MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
328.1421	1	1084944	C15 H23 Cl N3 O3	(M+H)+

--- End Of Report ---



¹H NMR Spectrum of compound **27** and its expansion



**SM-64
C13DEPT135**

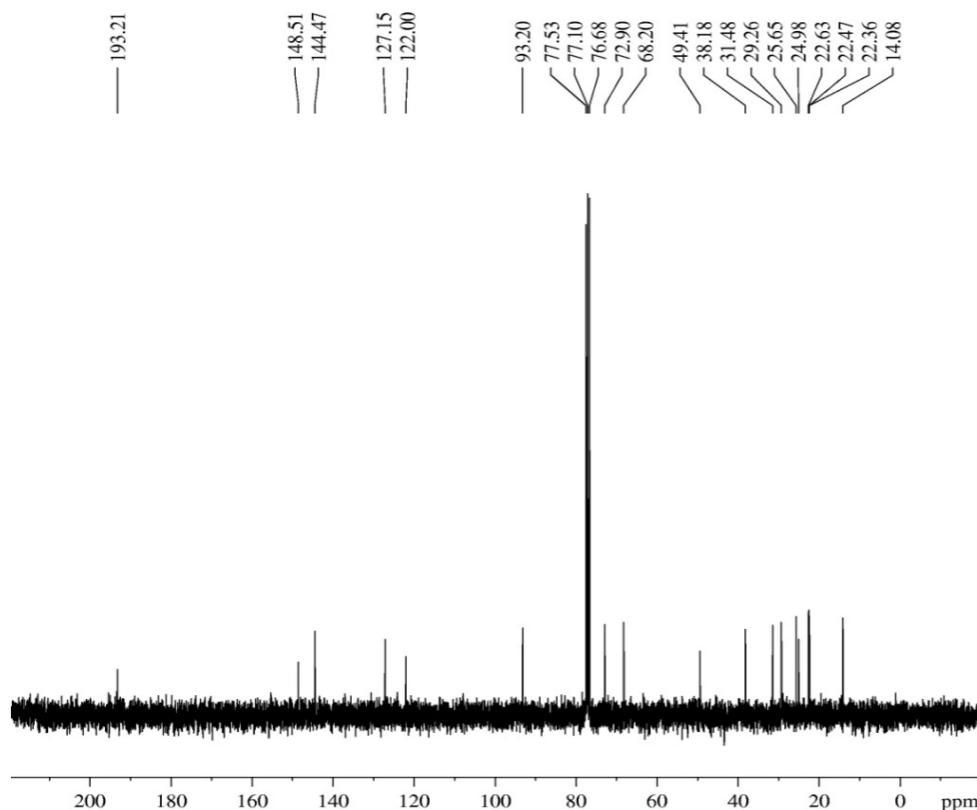
Current Data Parameters
NAME smrti_sm64dept135
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091026
Time 16.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG dept135
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 27.733 usec
DE 6.00 usec
TE 295.3 K
CNST2 145.000000
D1 2.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001108 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 dB
PL1 -3.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P3 11.60 usec
PL3 23.20 dB
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677444 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



**SM-64
C13**

Current Data Parameters
NAME smrti_sm6413c
EXPNO 20
PROCNO 1

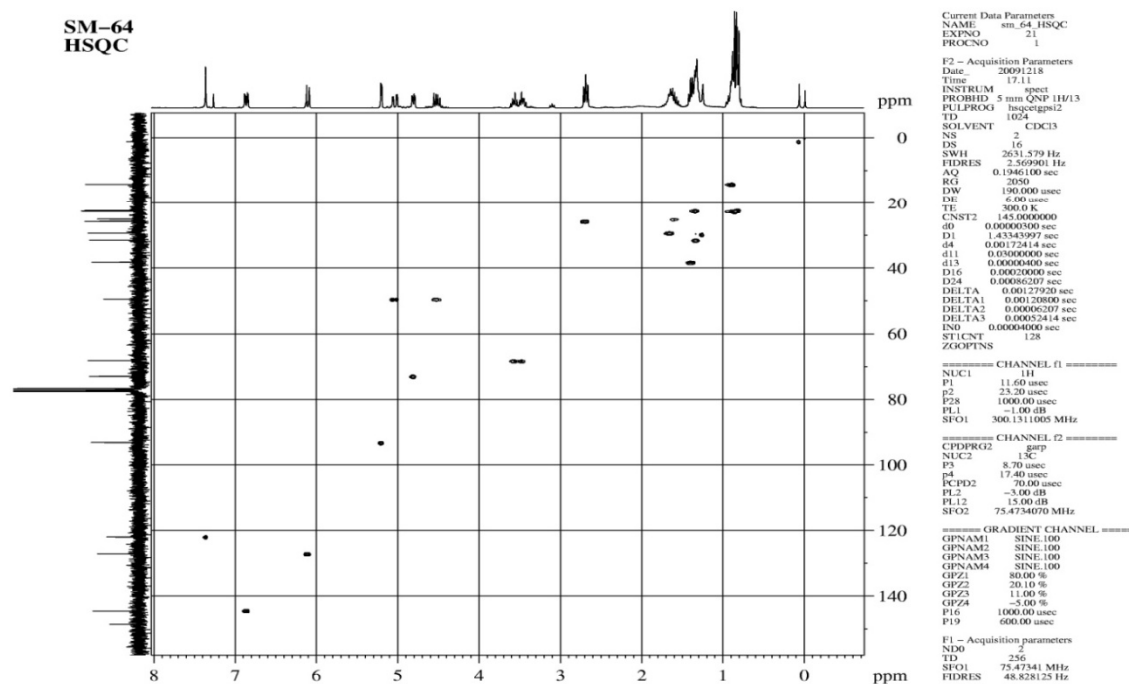
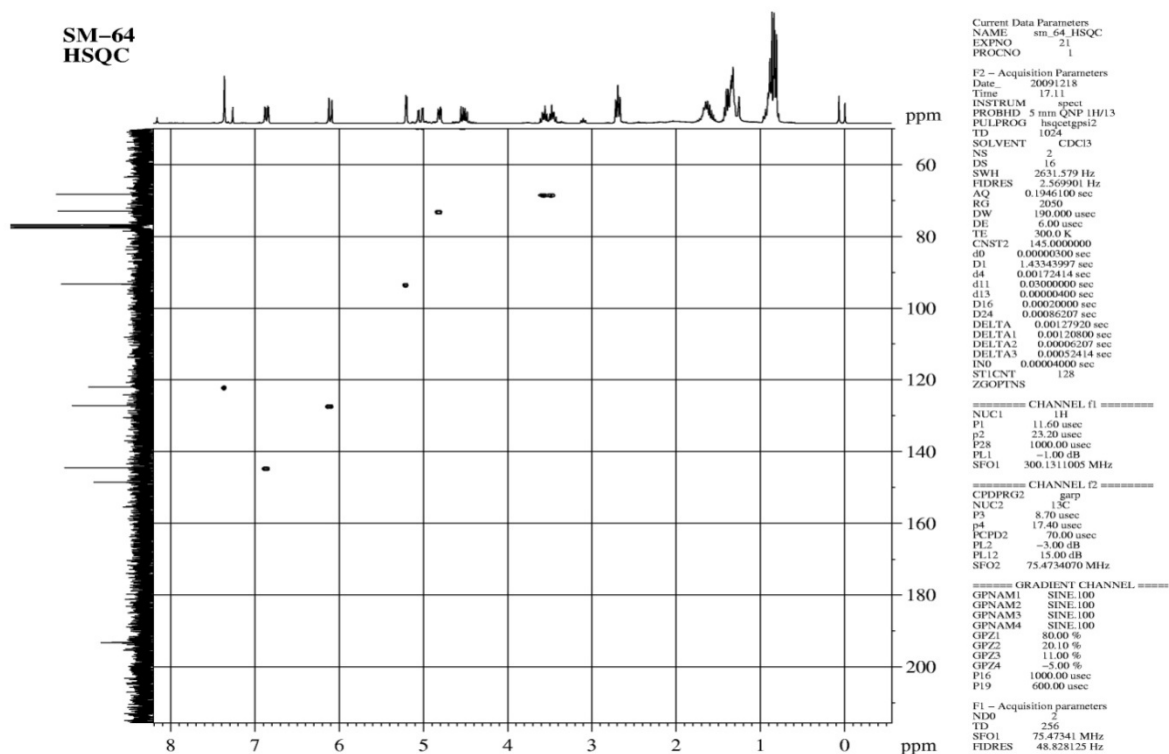
F2 - Acquisition Parameters
Date_ 20091026
Time 15.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 11.3
DW 27.733 usec
DE 6.00 usec
TE 293.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

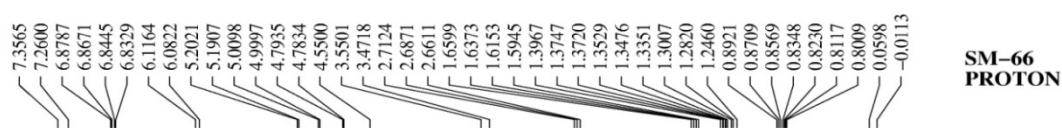
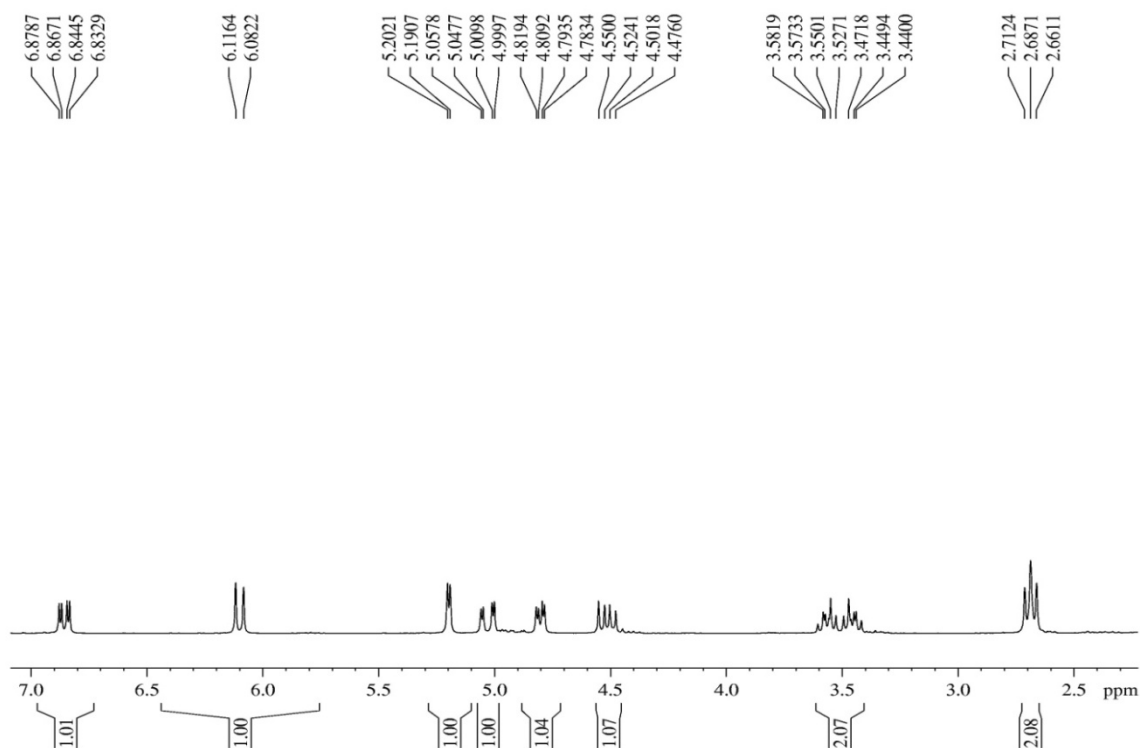
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677448 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum and its DEPT 135 of compound **27**



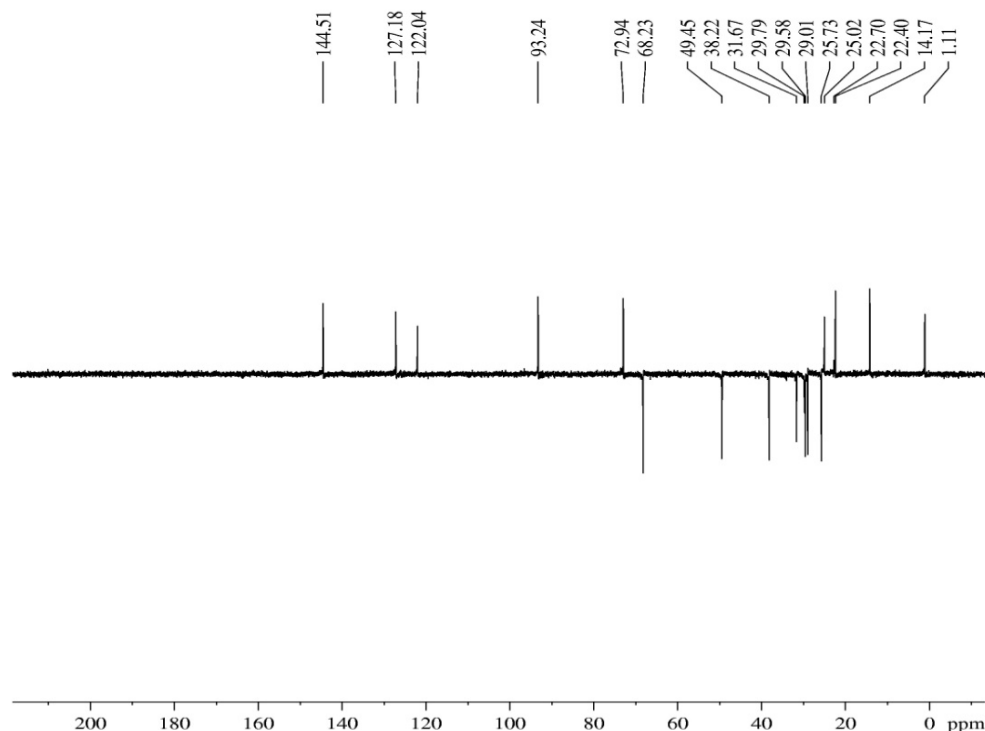
HSQC Spectrum and its expansion of compound **27**



**SM-66
PROTON**

Current Data Parameters
 NAME: sm66_1h
 EXPNO: 20
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20091117
 Time: 19:38
 INSTRUM: spect
 PROBHID: 5 mm QNP 1H/13
 PULPROG: zg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 16
 DS: 2
 SWH: 6188.119 Hz
 FIDRES: 0.094423 Hz
 AQ: 5.2953587 sec
 RG: 114
 DW: 80.800 usec
 DE: 6.00 usec
 TE: 300.0 K
 D1: 1.00000000 sec
 TDO: 1
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 11.60 usec
 PL1: -1.00 dB
 SFO1: 300.1318534 MHz
 F2 - Processing parameters
 SI: 32768
 SF: 300.1300661 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00

¹H NMR Spectrum of compound **28** and its expansion



**SM-66
C13DEPT135**

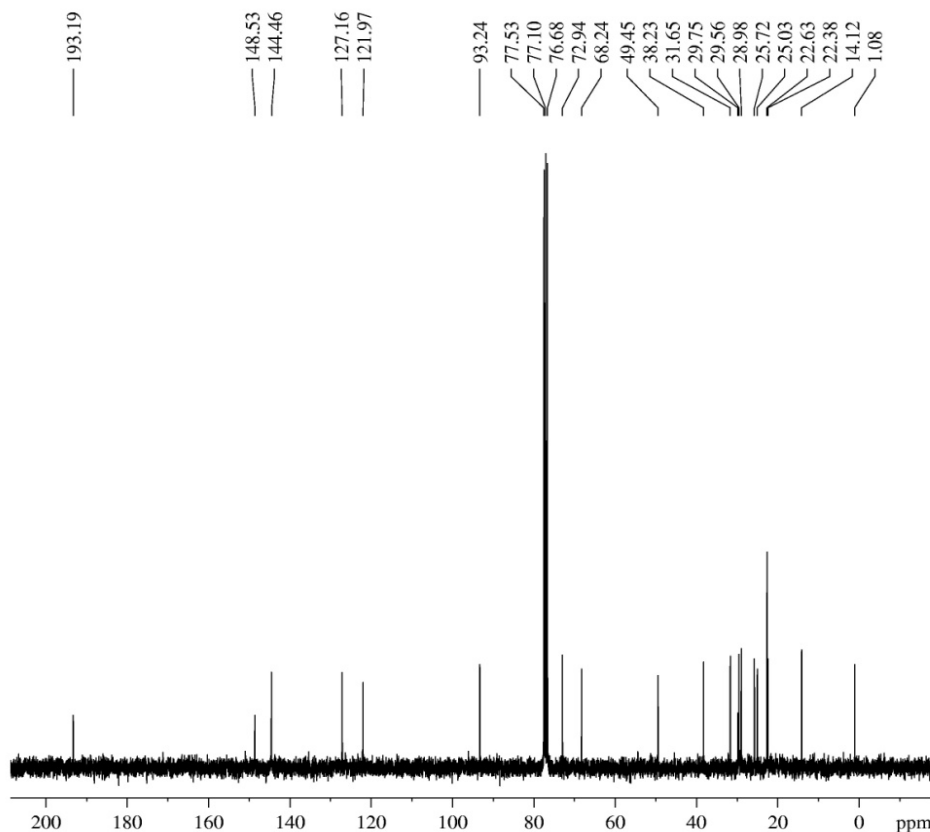
Current Data Parameters
NAME SM66_DEPT1&2
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100209
Time 10.12
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG dept135
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 27.733 usec
DE 6.00 usec
TE 295.8 K
CNST2 145.0000000
d1 2.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001108 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 dB
PL1 -3.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P3 11.60 usec
p4 23.20 usec
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677414 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



**SM-66
C13**

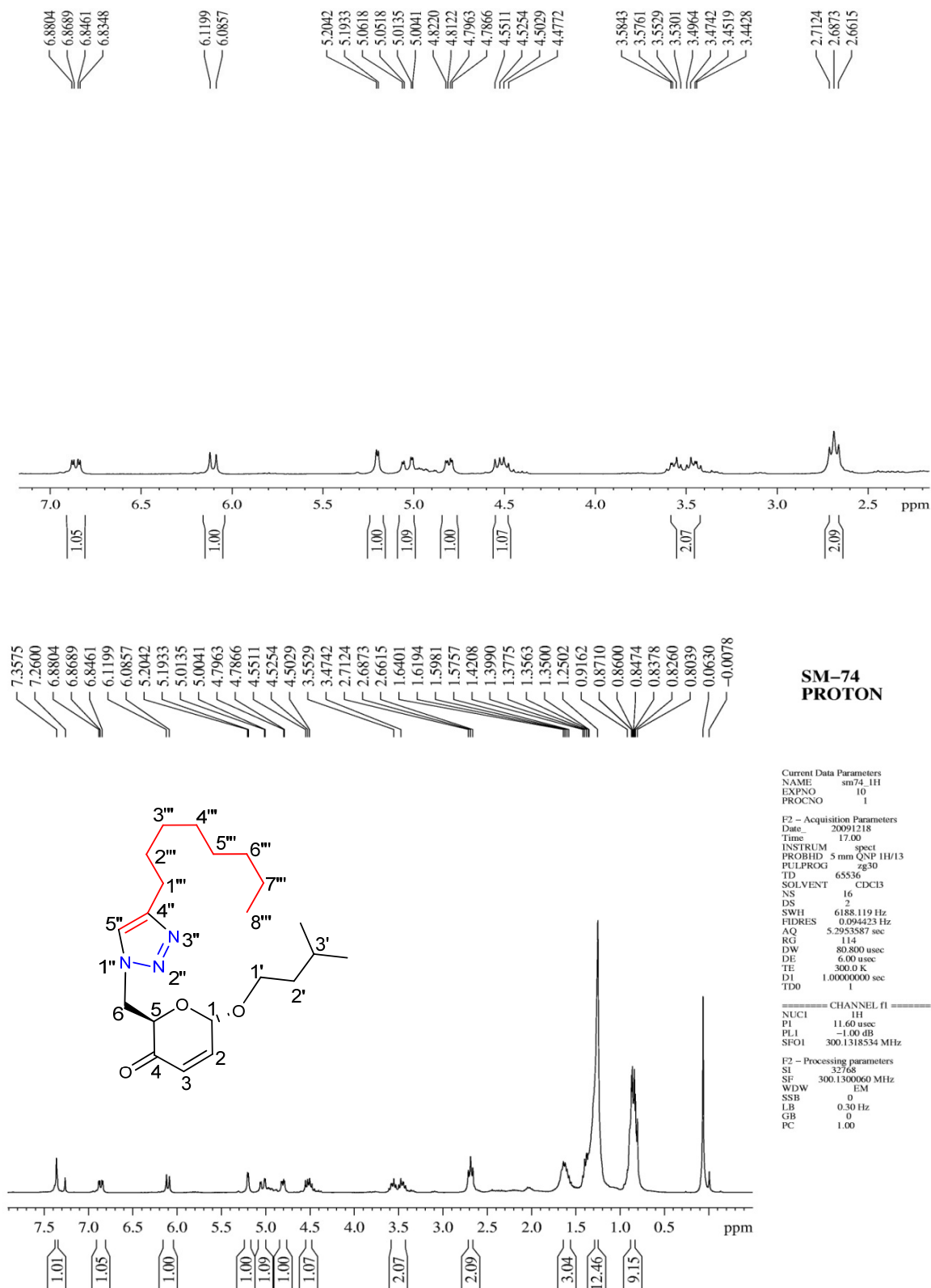
Current Data Parameters
NAME sm_66_13c
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091119
Time 15.43
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 12.7
DW 27.733 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

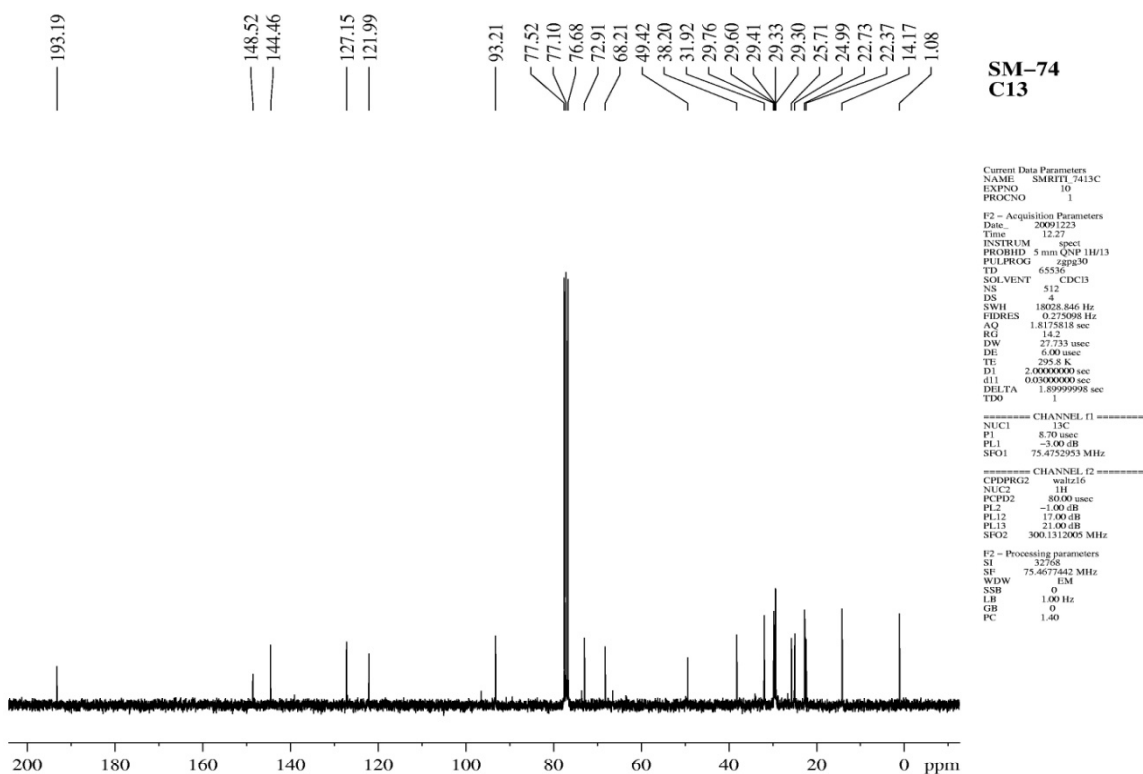
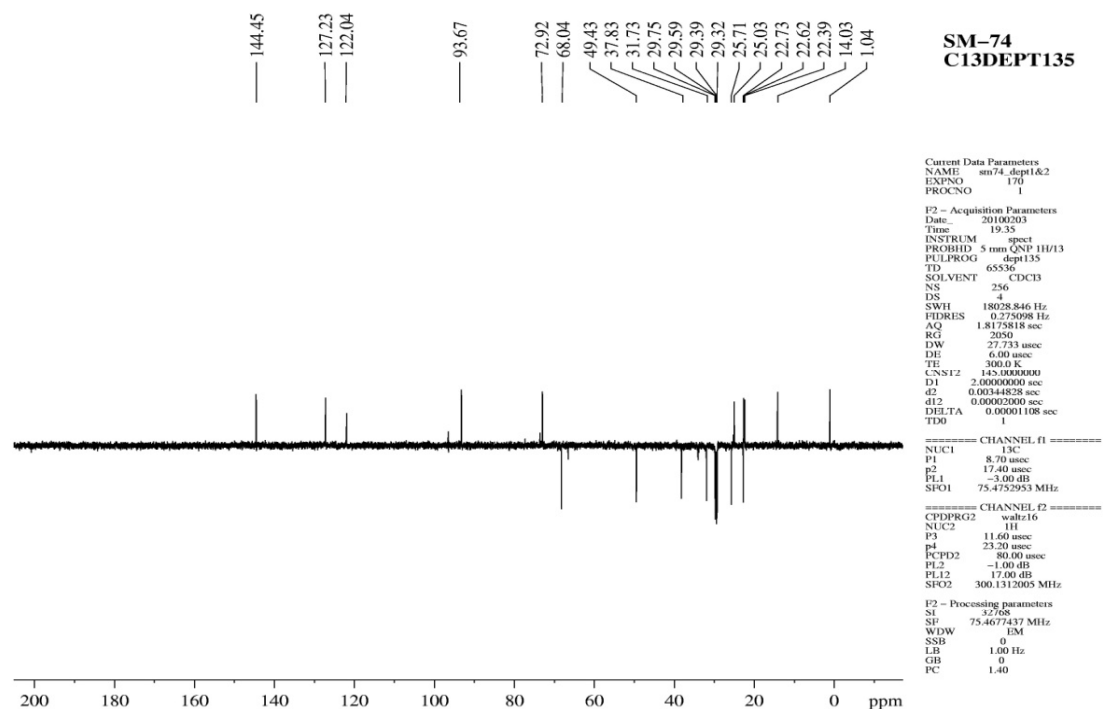
===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 dB
PL1 -3.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz

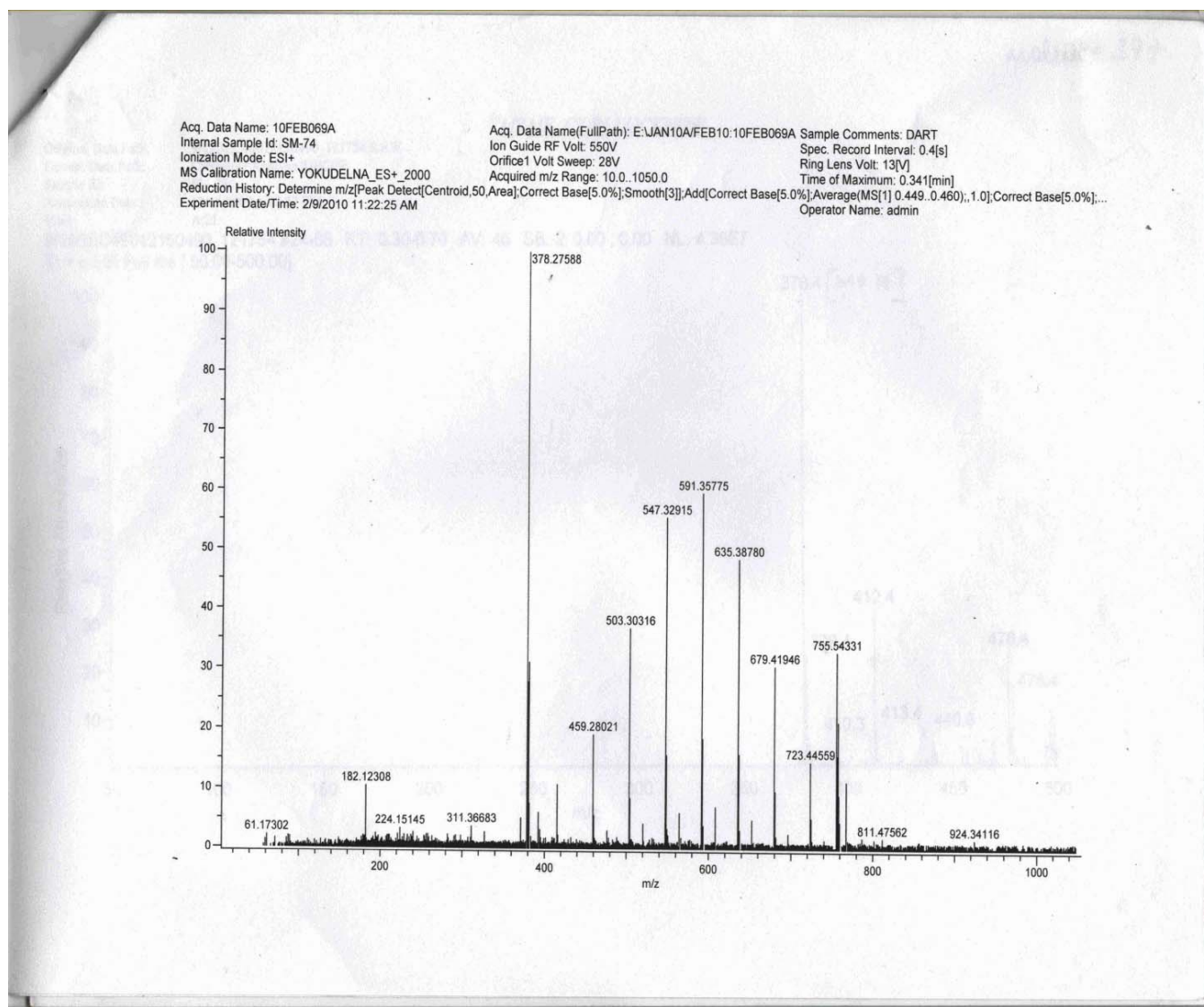
F2 - Processing parameters
SI 32768
SF 75.4677424 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

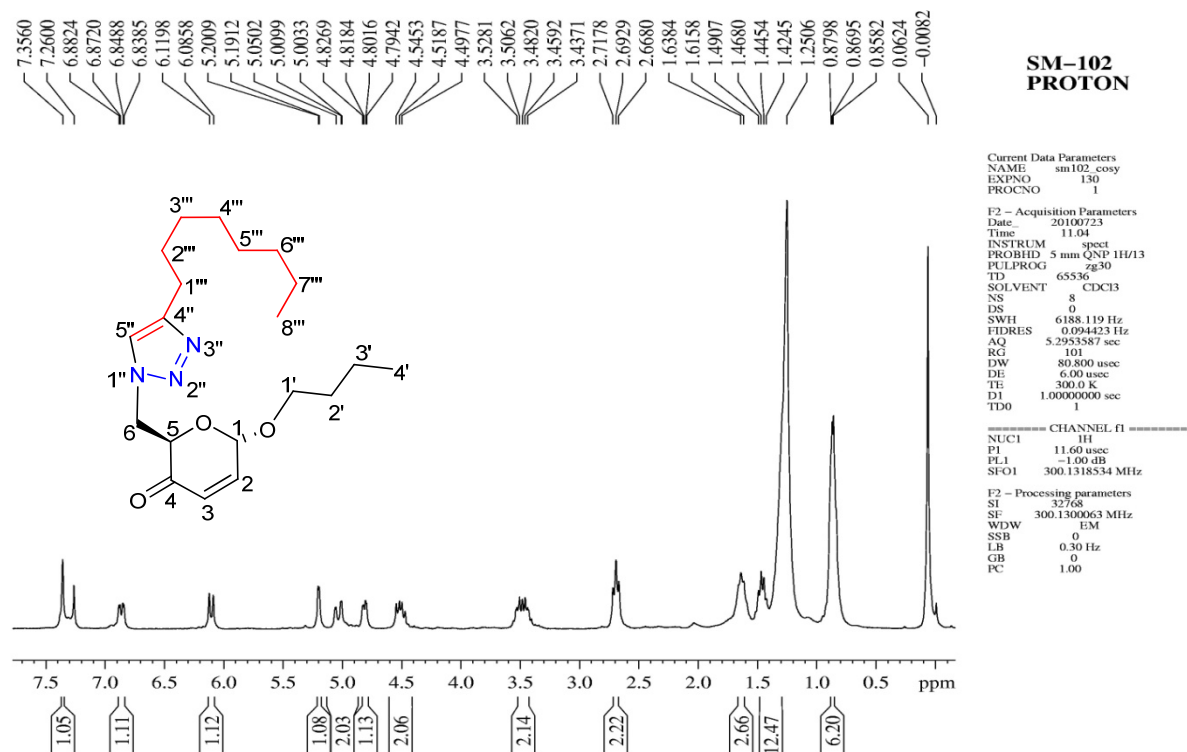
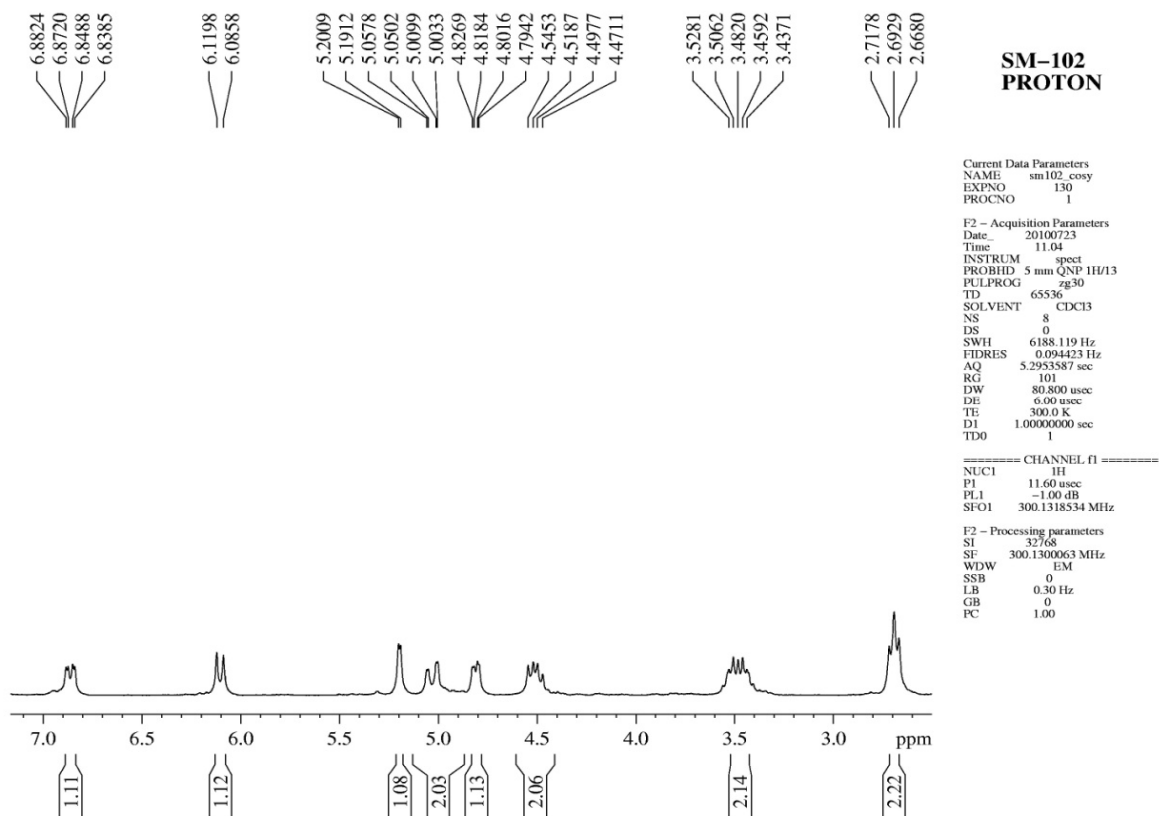


¹H NMR Spectrum of compound **29** and its expansion

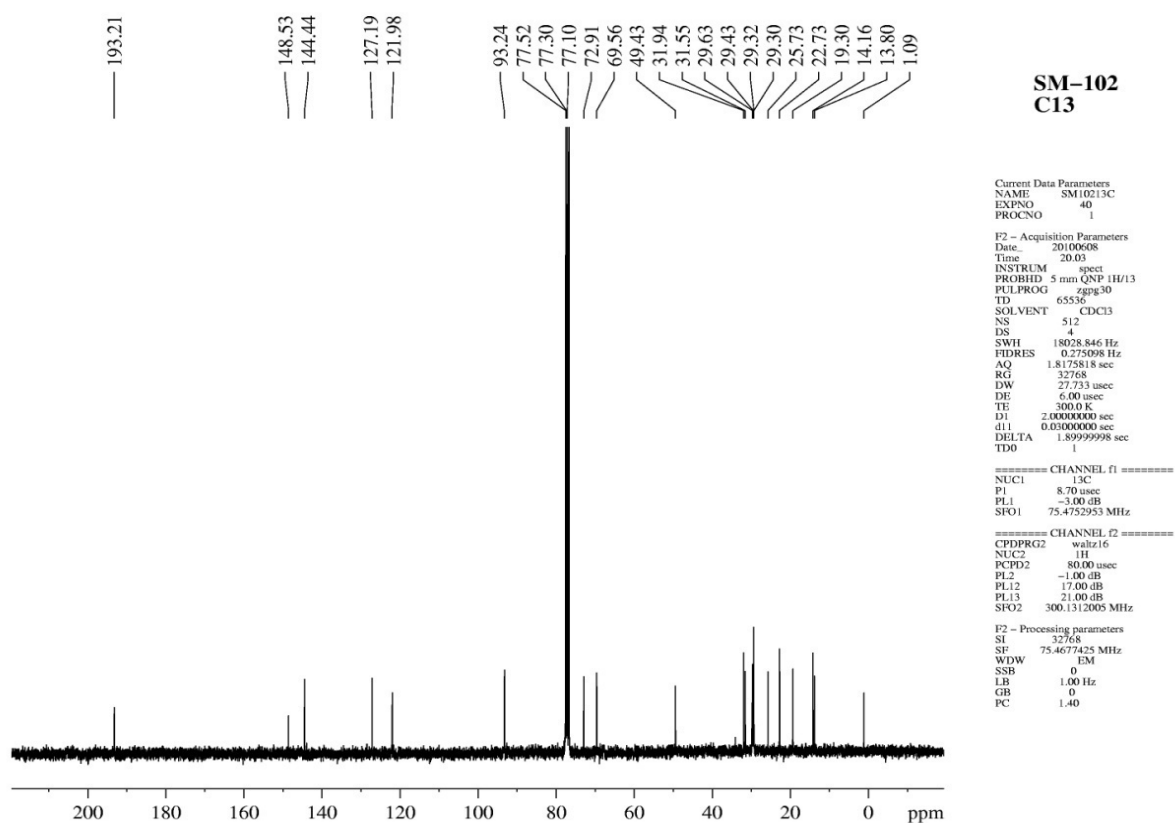


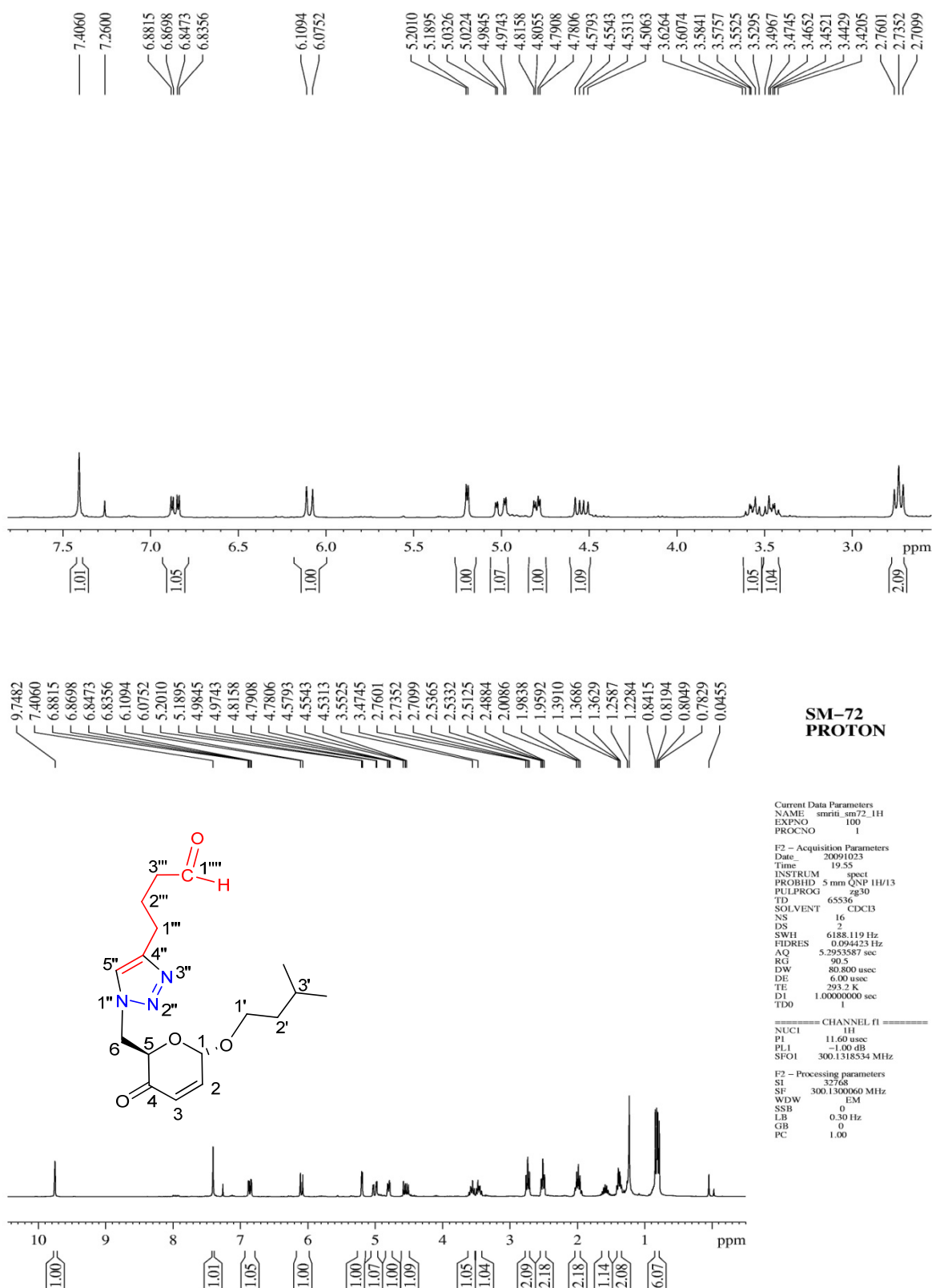
^{13}C NMR Spectrum and its Dept 135 of compound **29**

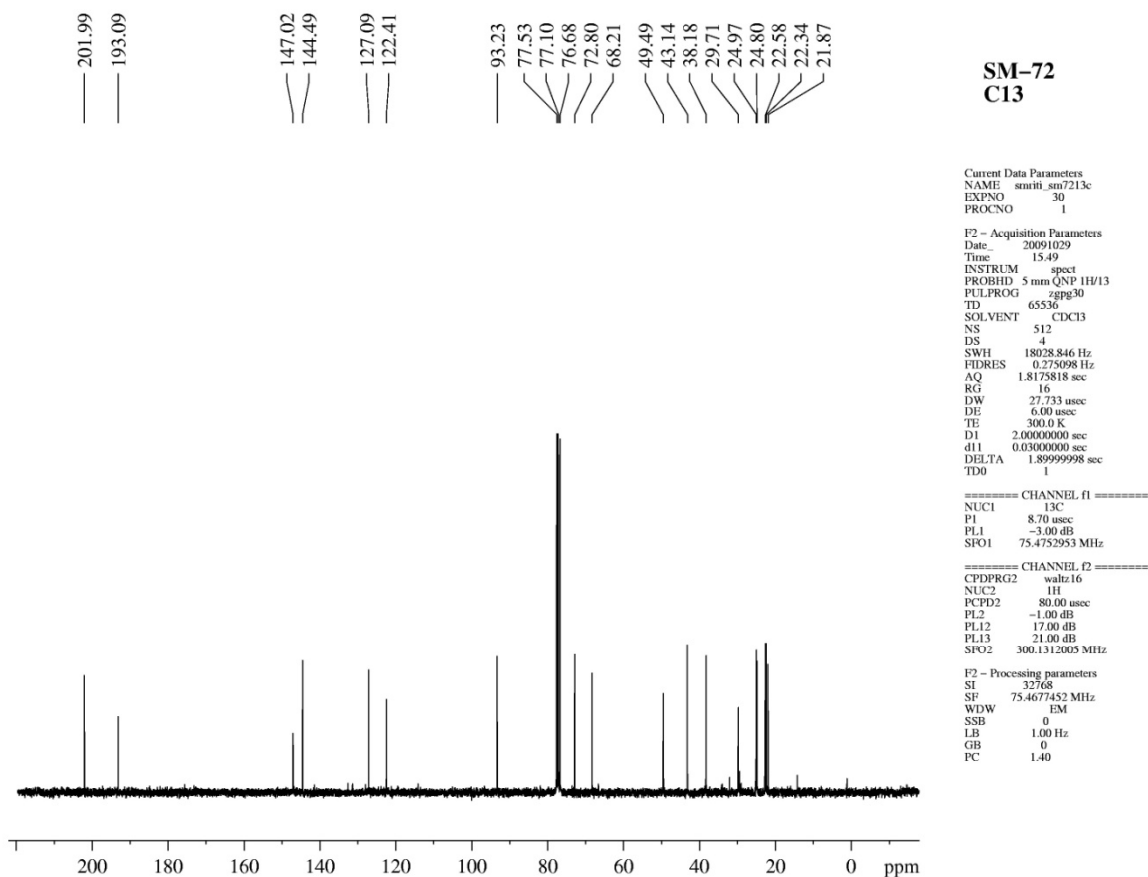
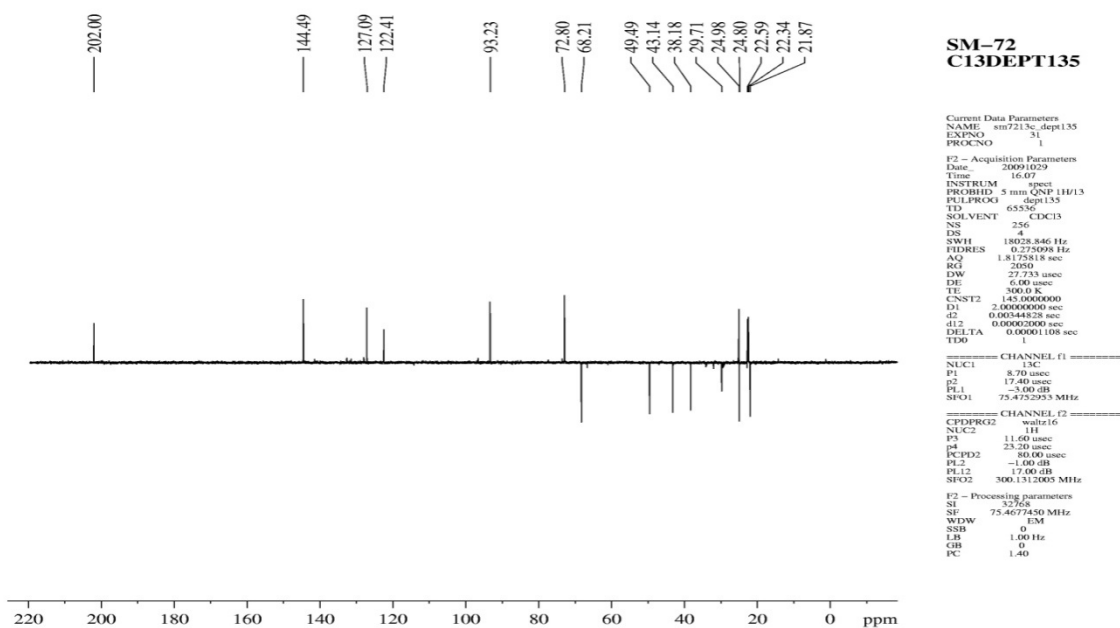
HRMS Spectrum of compound **29**



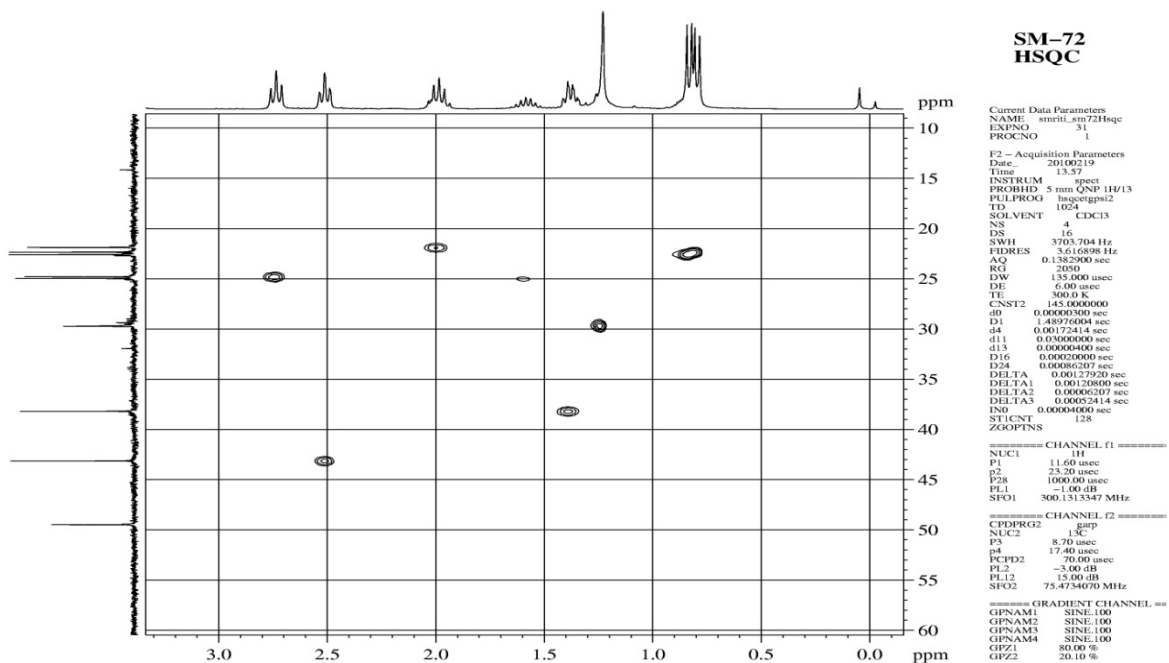
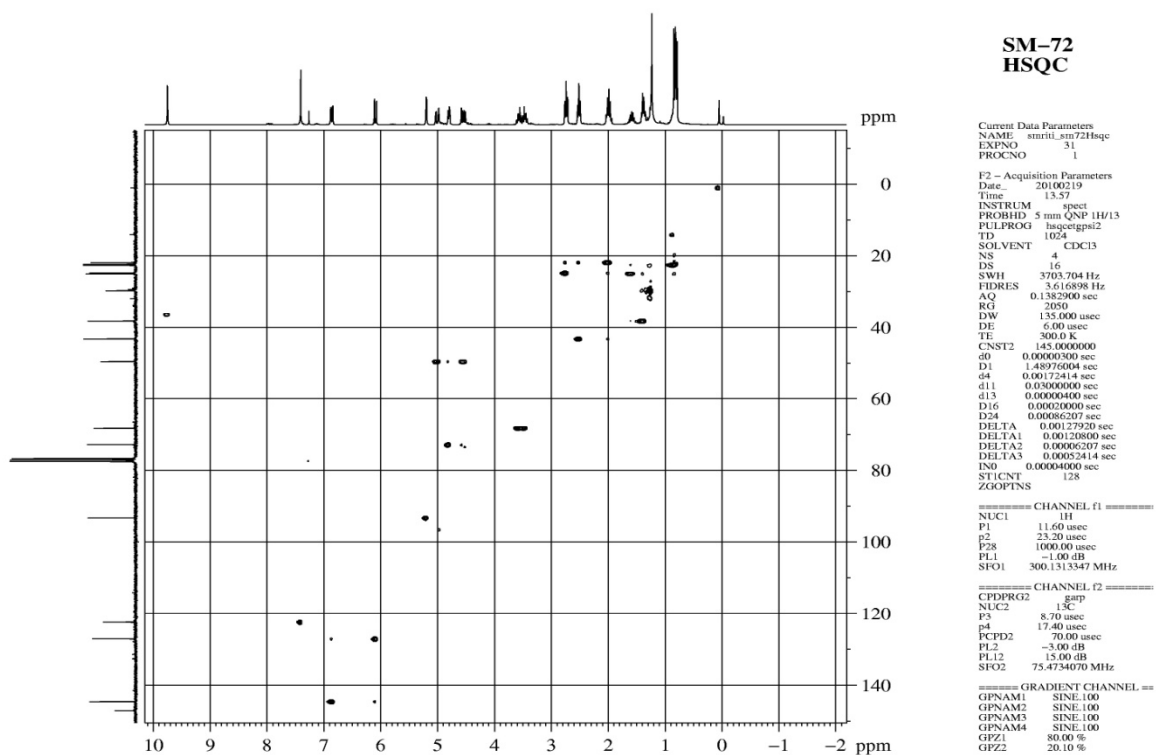
^1H NMR Spectrum of compound **30** and its expansion

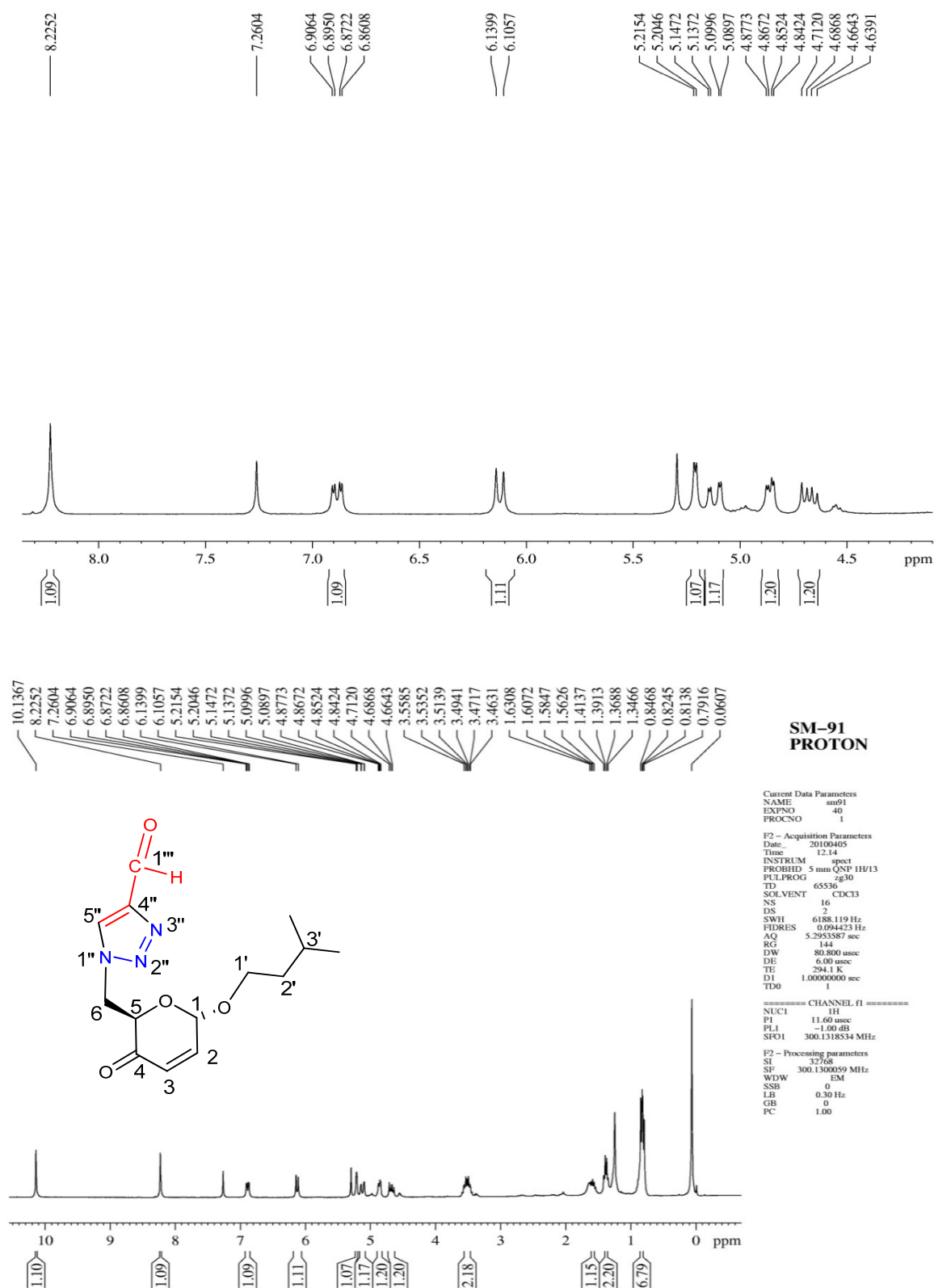
 ^{13}C NMR Spectrum of compound **30**

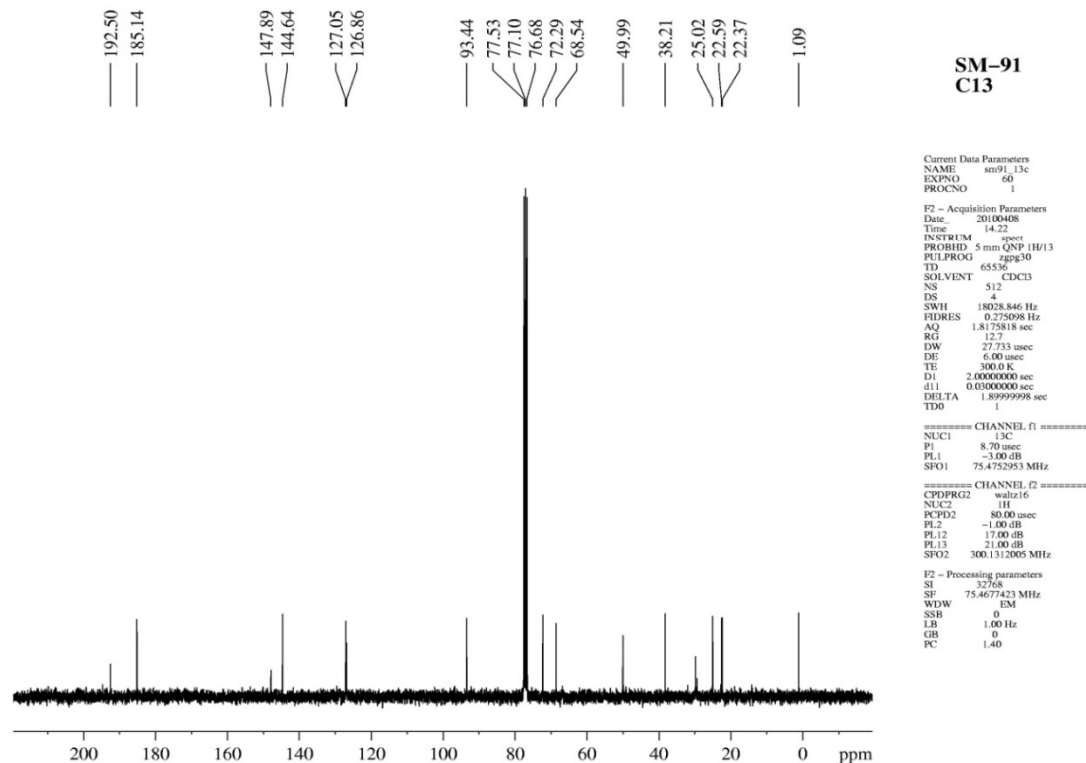
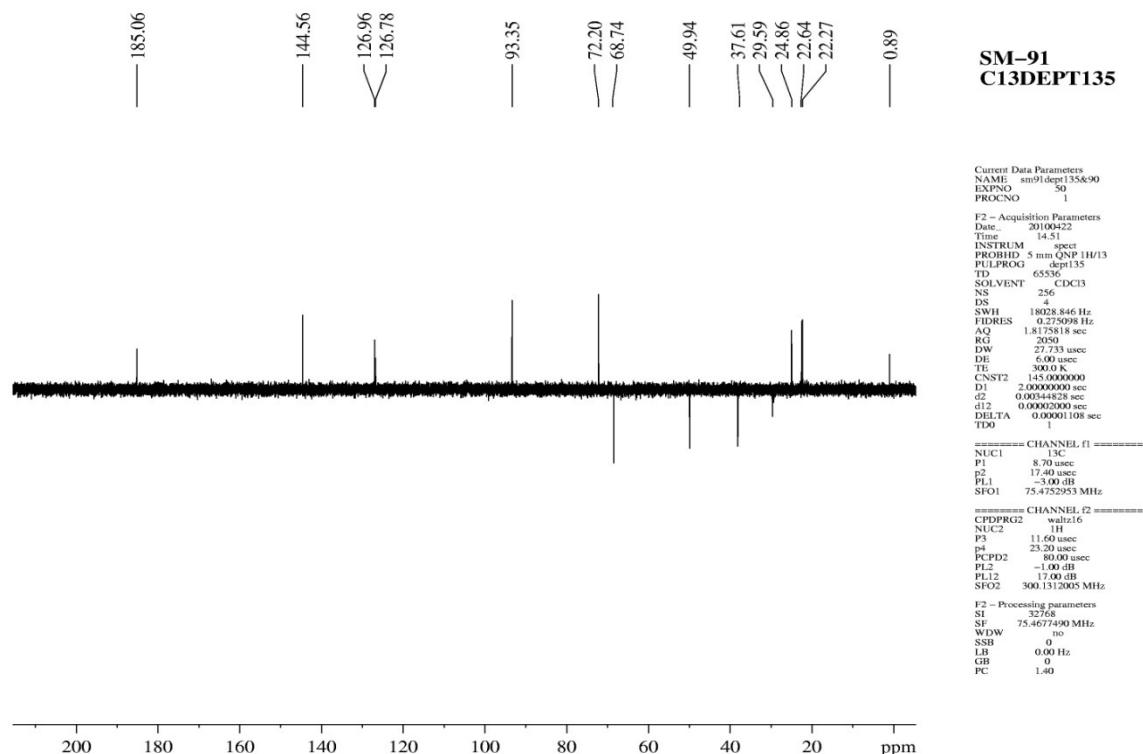
¹H NMR Spectrum of compound **31** and its expansion



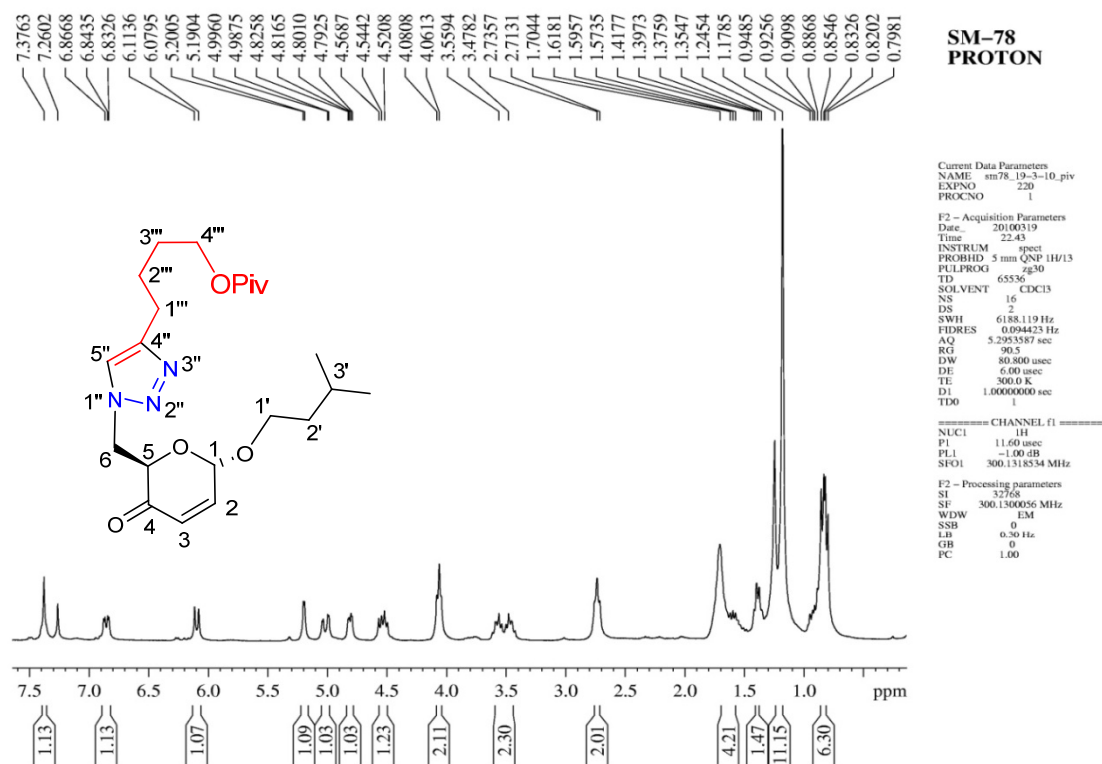
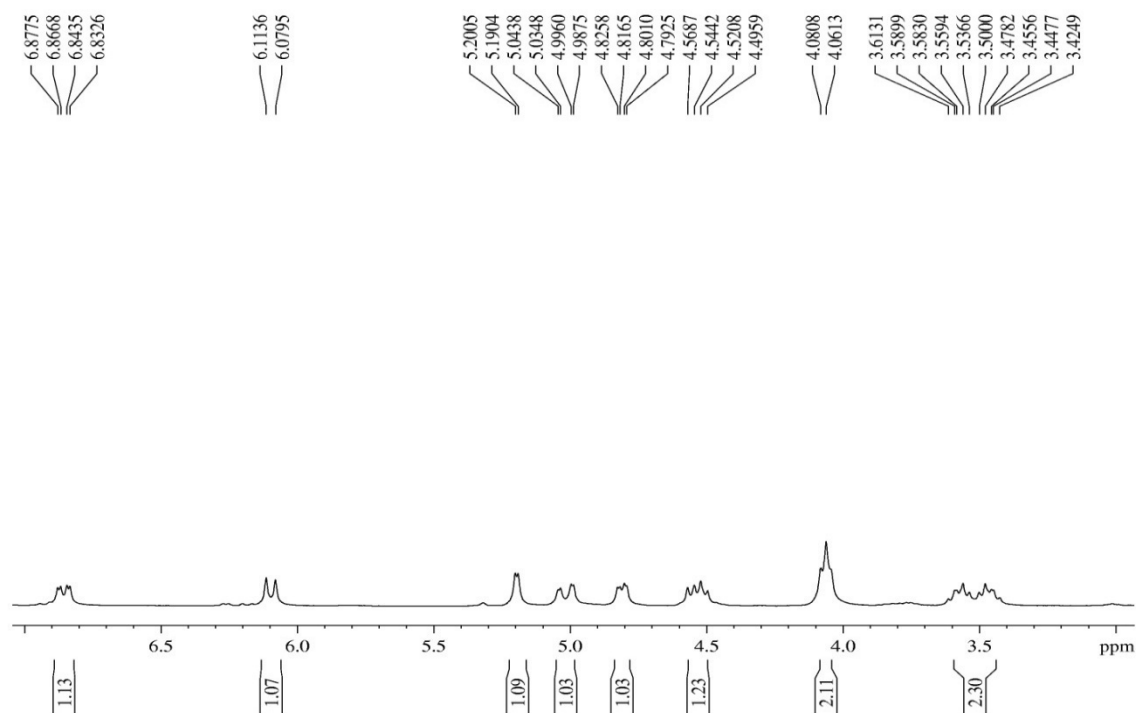
^{13}C NMR and its DEPT 135 spectra of compound **31**

HSQC Spectrum and its expansion of compound **31**

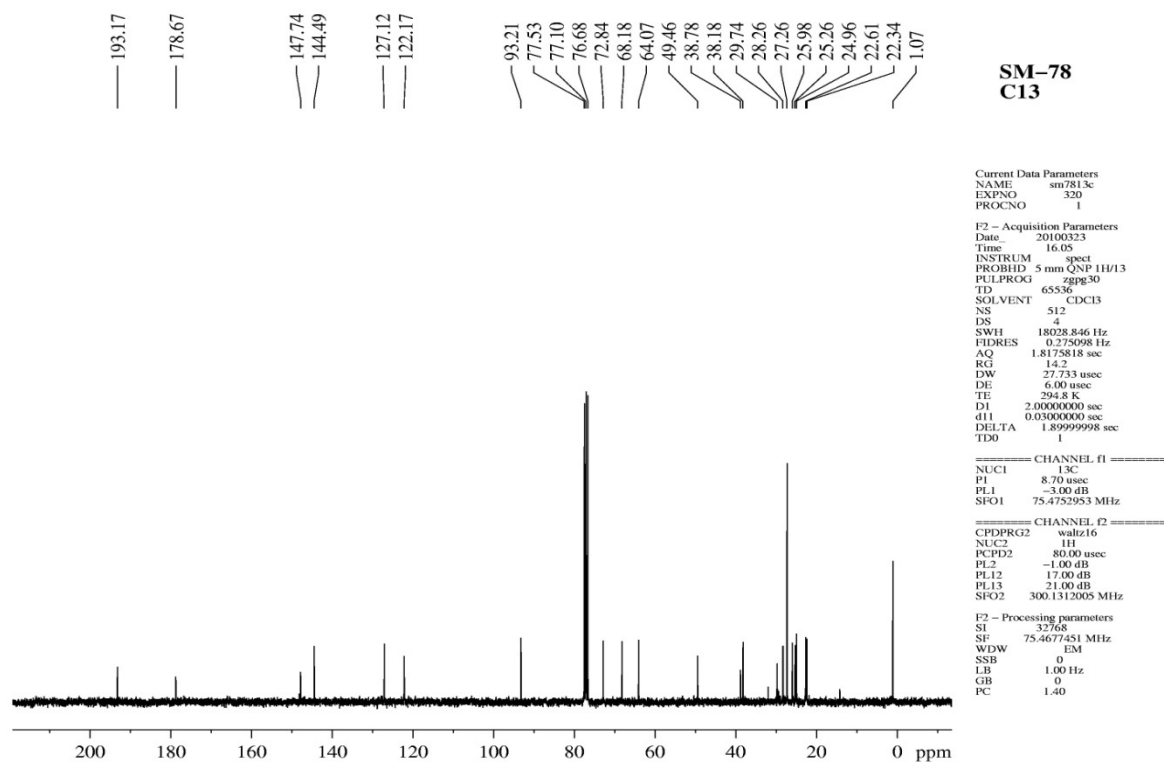
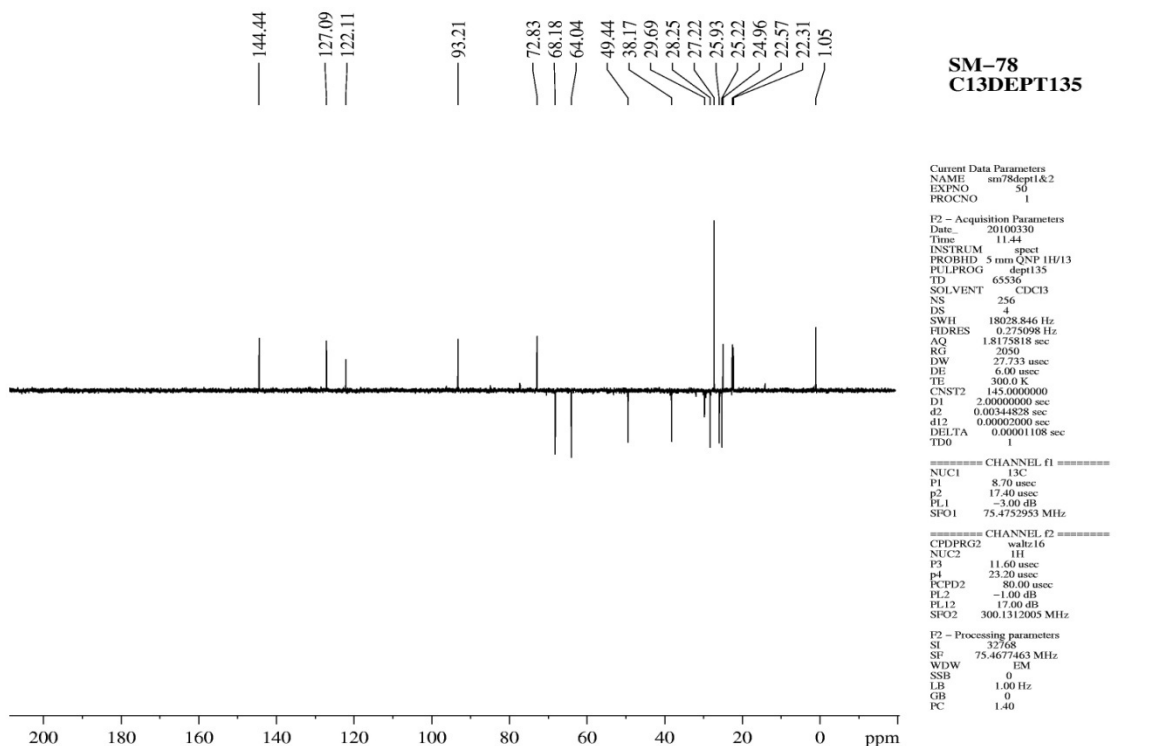
¹H NMR Spectrum of compound **32** and its expansion



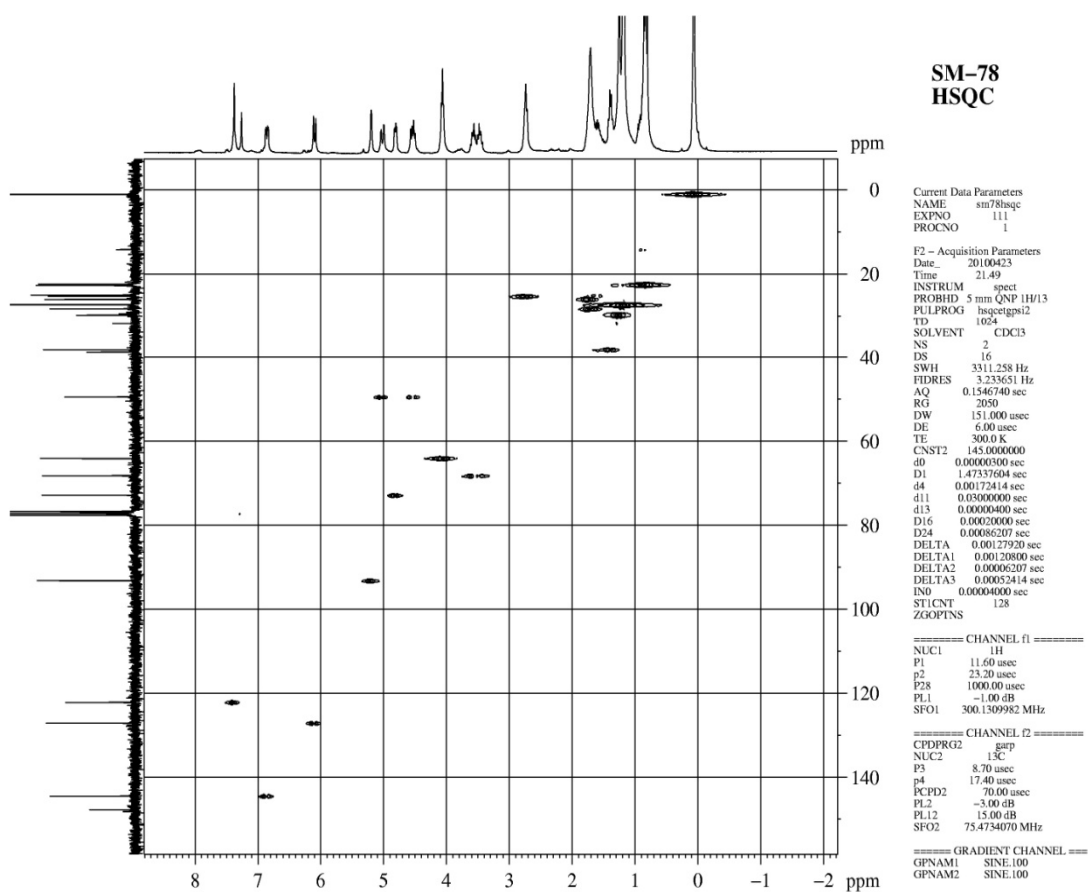
^{13}C NMR Spectrum and its DEPT 135 of compound **32**

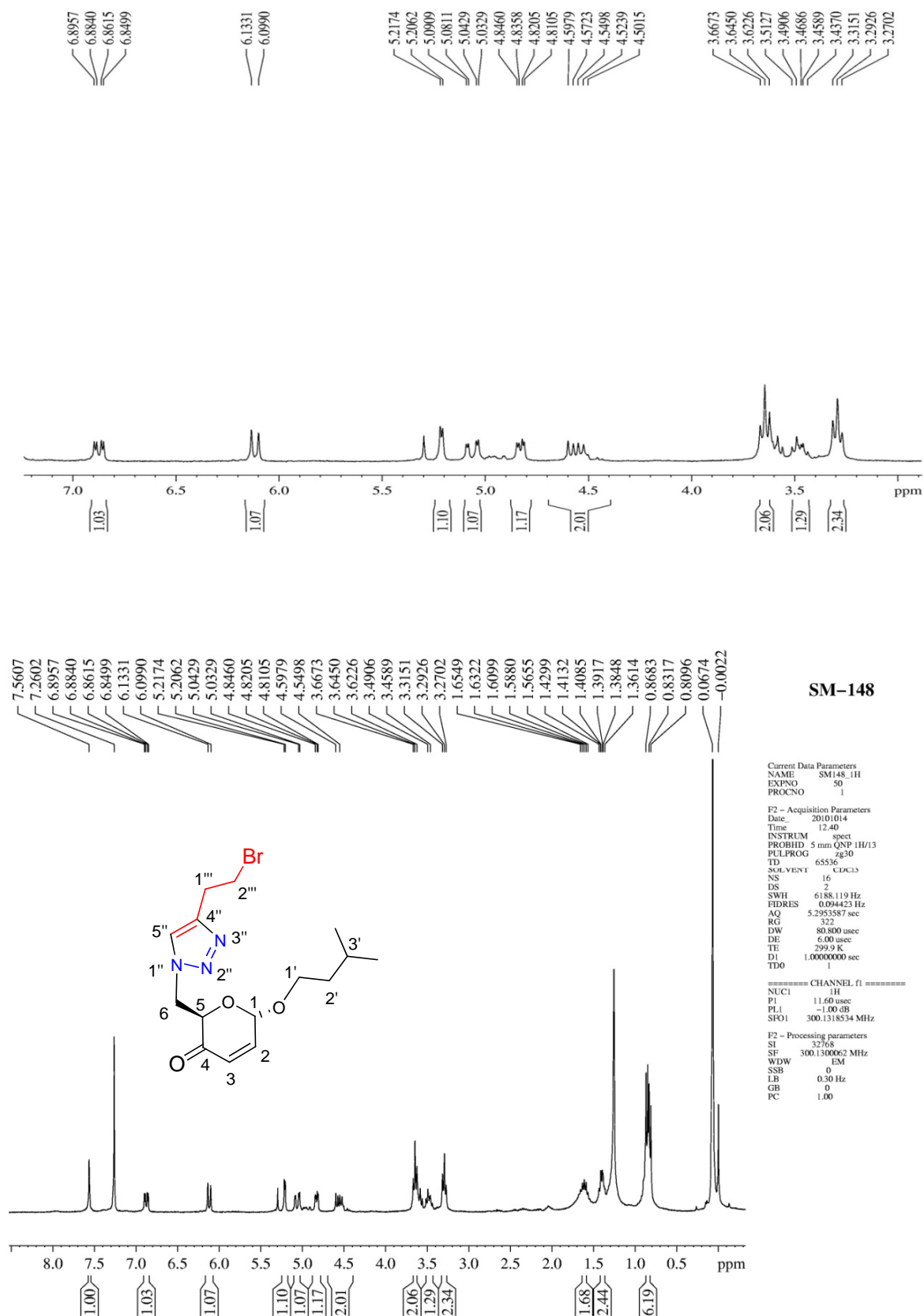


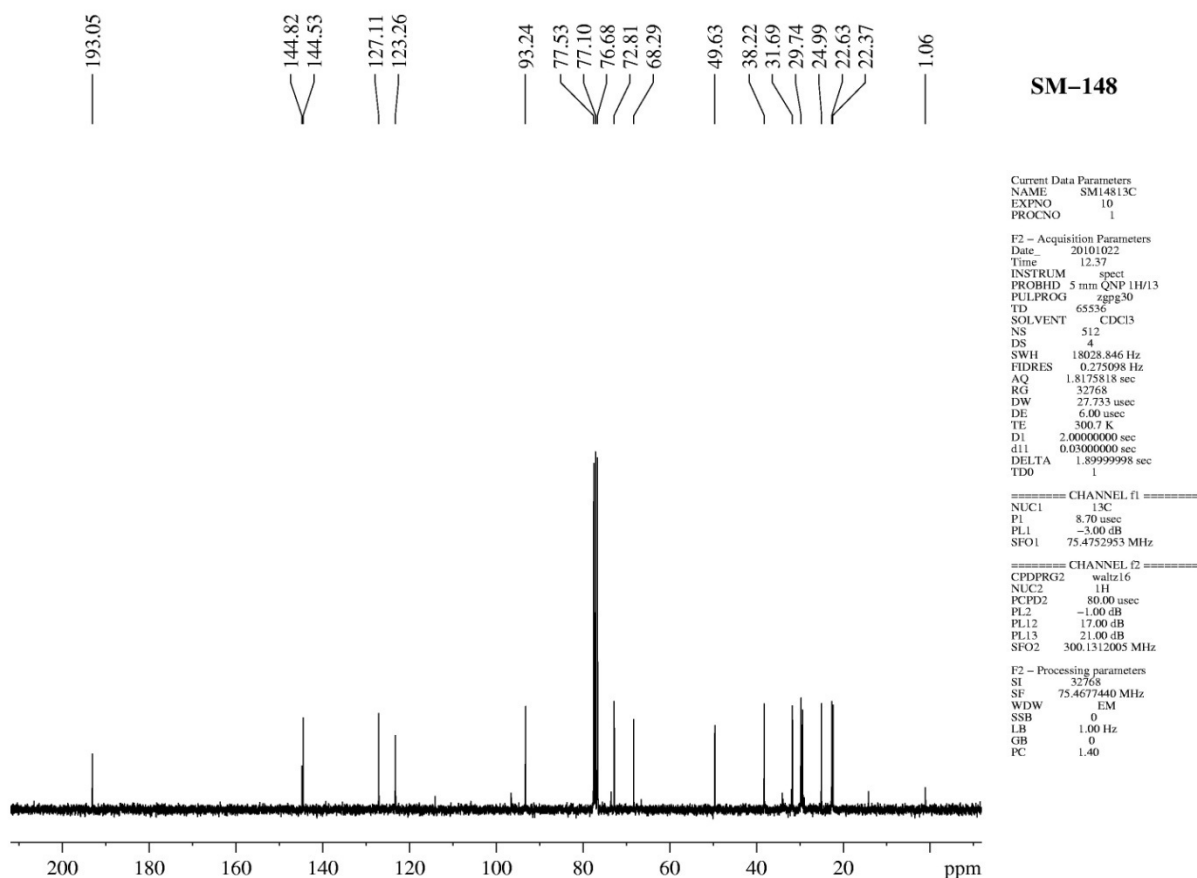
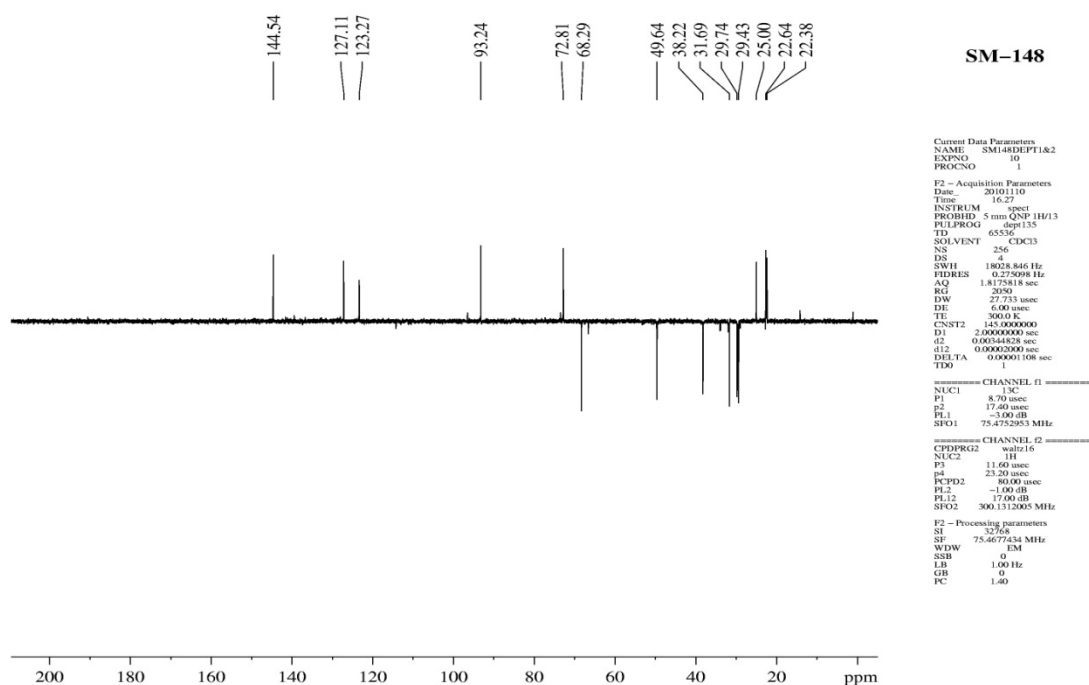
¹H NMR Spectrum of compound **33** and its expansion



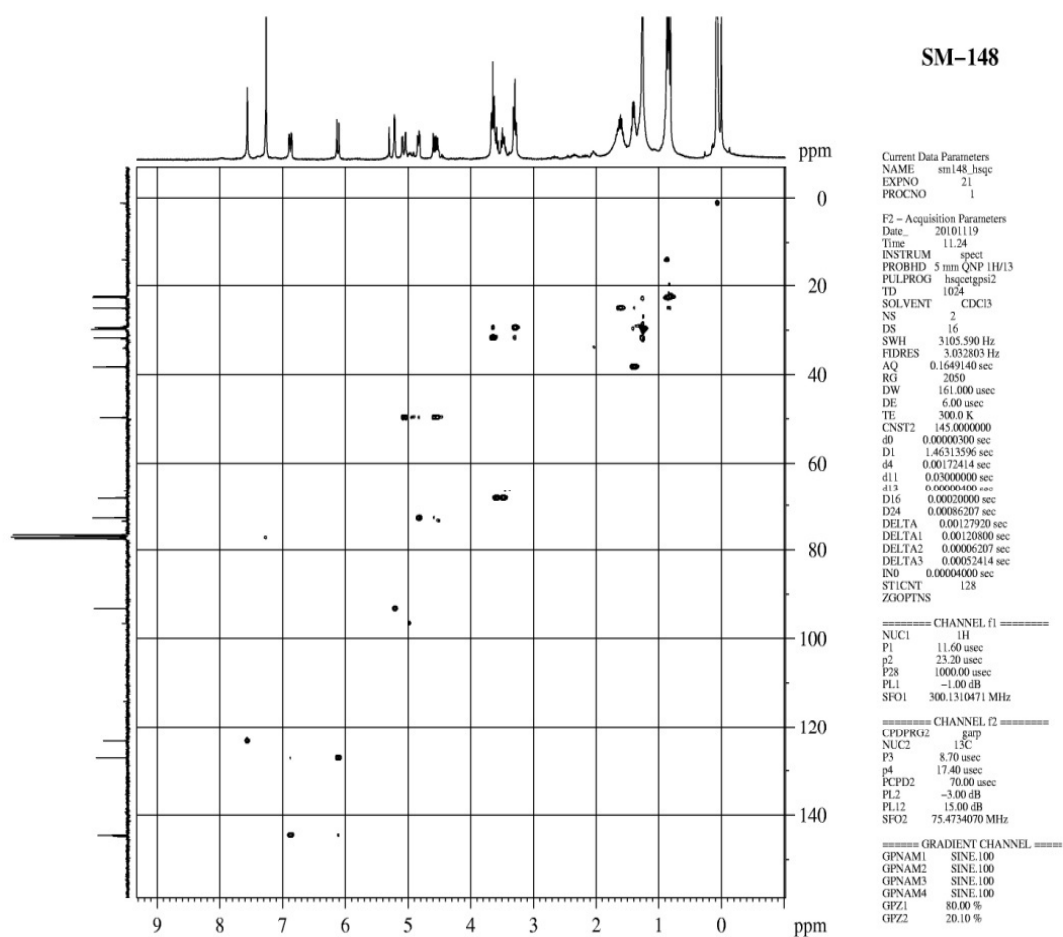
^{13}C NMR Spectrum and its DEPT 135 of compound **33**

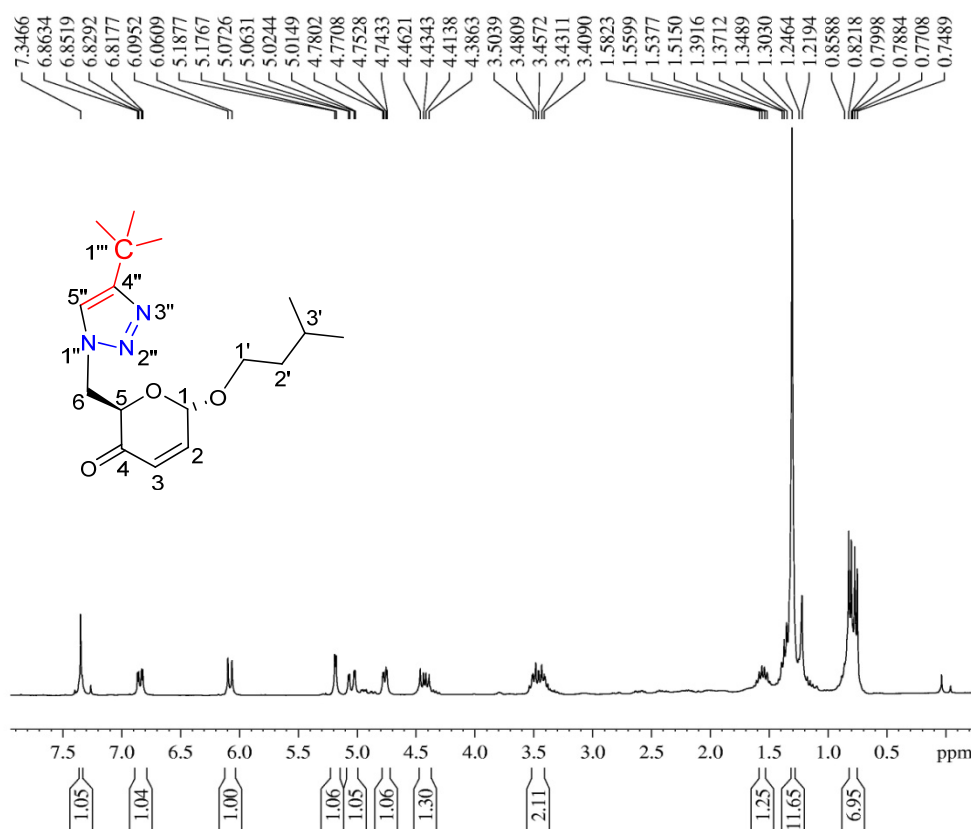
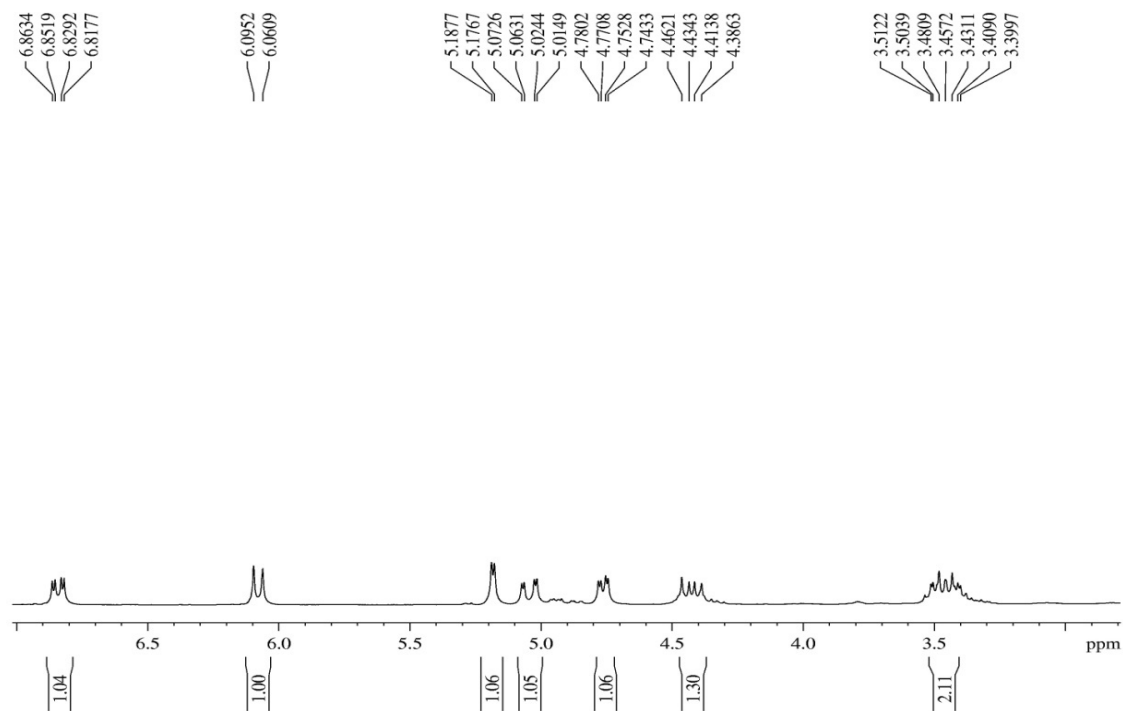
HSQC Spectrum of compound **33**

¹H NMR Spectrum of compound **34** and its expansion



^{13}C NMR Spectrum and its Dept 135 of compound **34**

HSQC Spectrum of compound **34**



SM-176

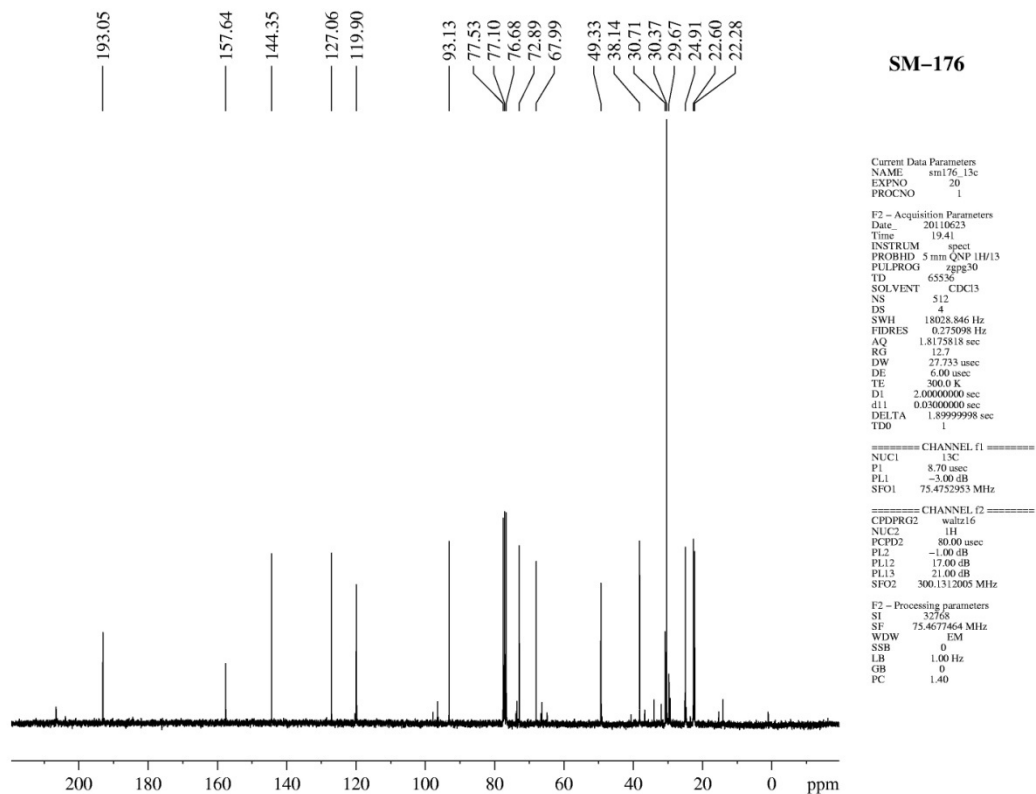
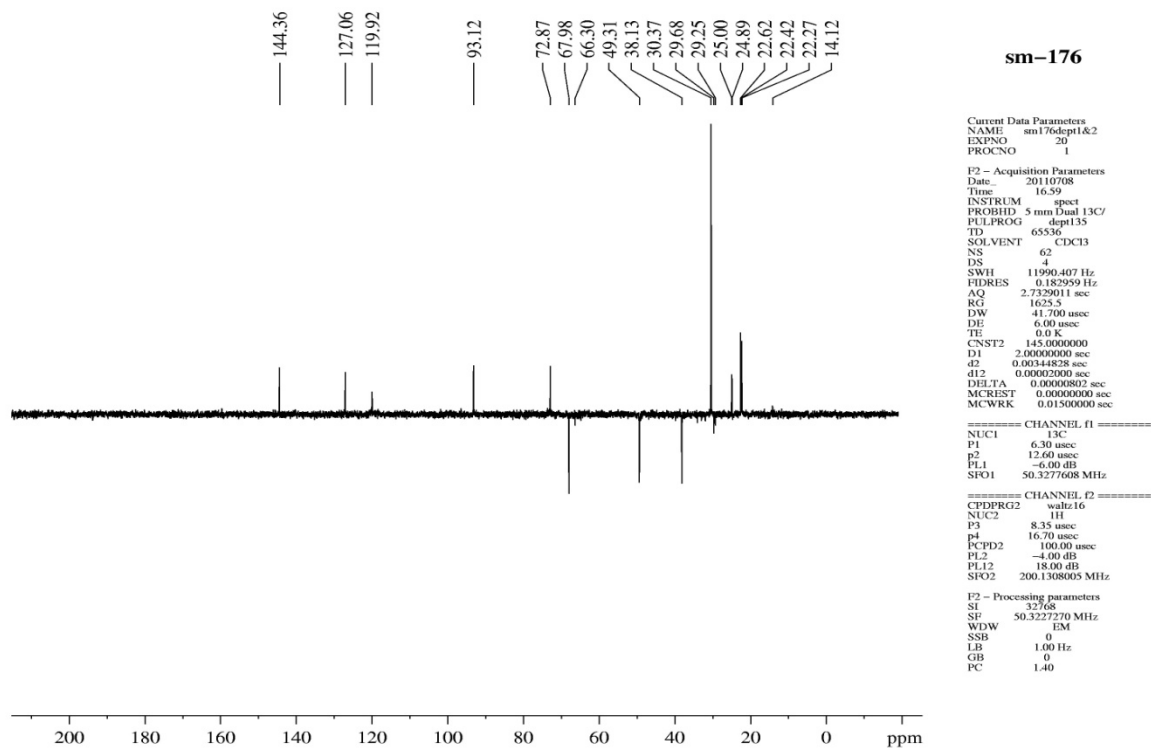
Current Data Parameters
NAME: sm176_1h
EXPNO: 60
PROCNO: 1

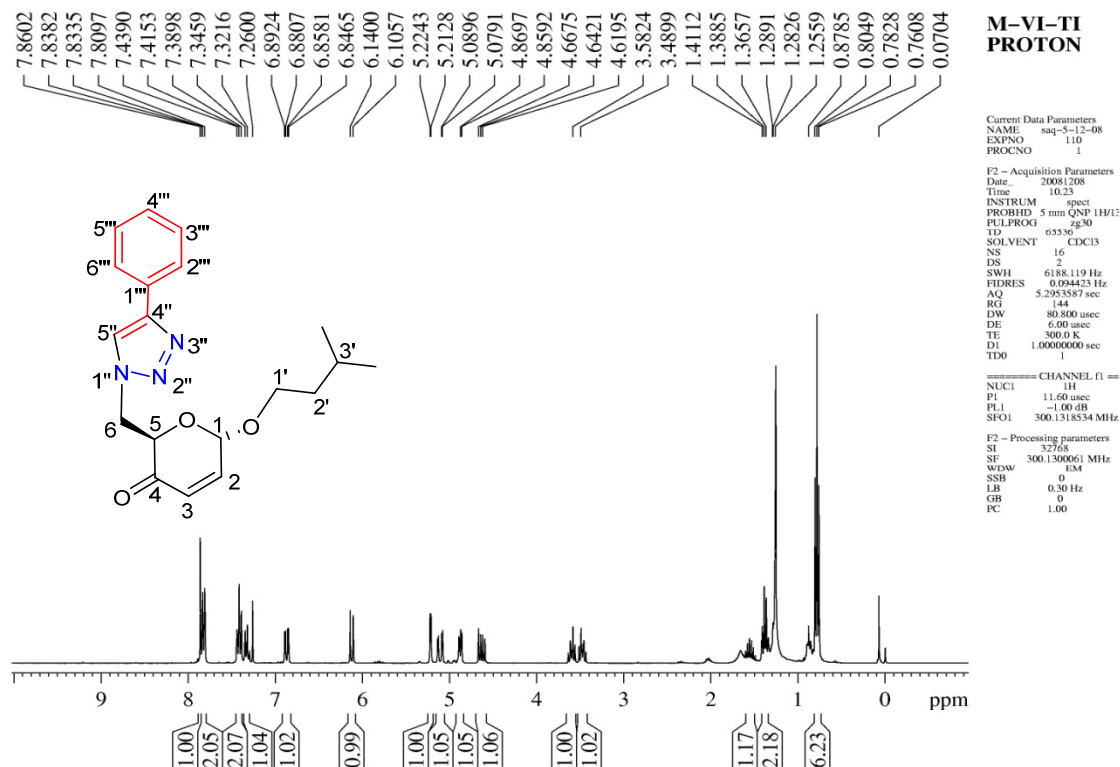
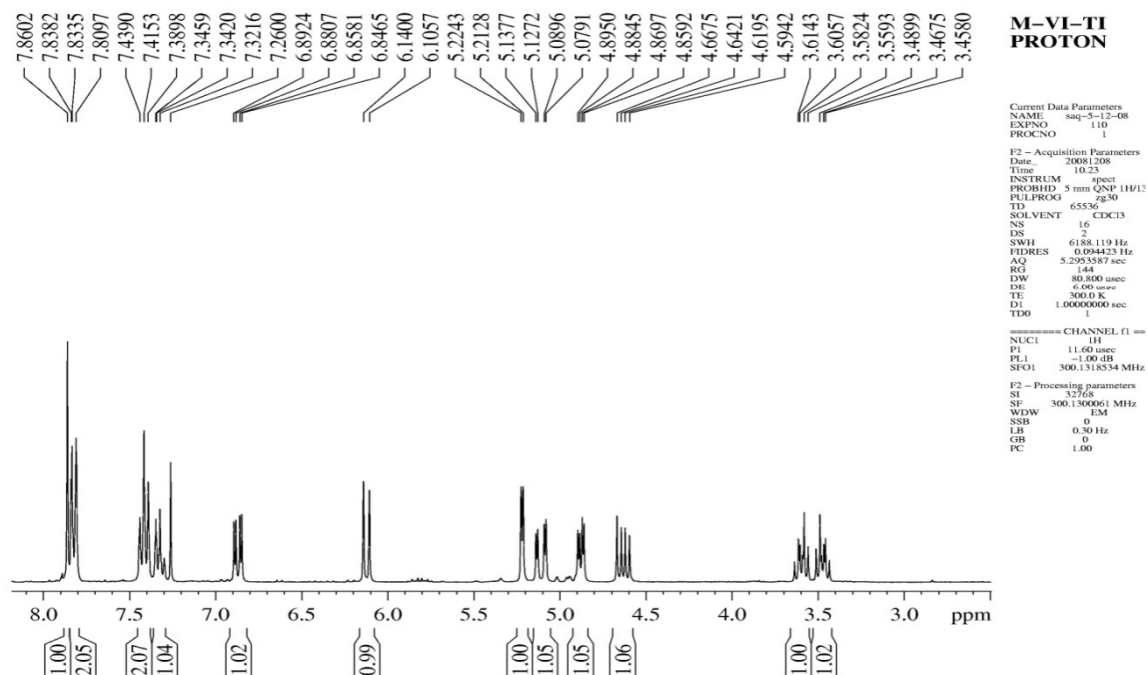
F2 - Acquisition Parameters
Date_: 20110621
Time: 11:31
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zg30
TD: 65536
SOLVENT: CDCl3
DS: 8
SWH: 6188.119 Hz
FIDRES: 0.094425 Hz
AQ: 3.2933587 sec
RG: 57
DW: 80.890 usec
DE: 6.00 usec
TE: 298.6 K
D1: 1.0000000 sec
TDO: 1

===== CHANNEL f1 =====
NUC1: 1H
P1: 11.60 usec
PL1: -1.00 dB
SFO1: 300.1318534 MHz

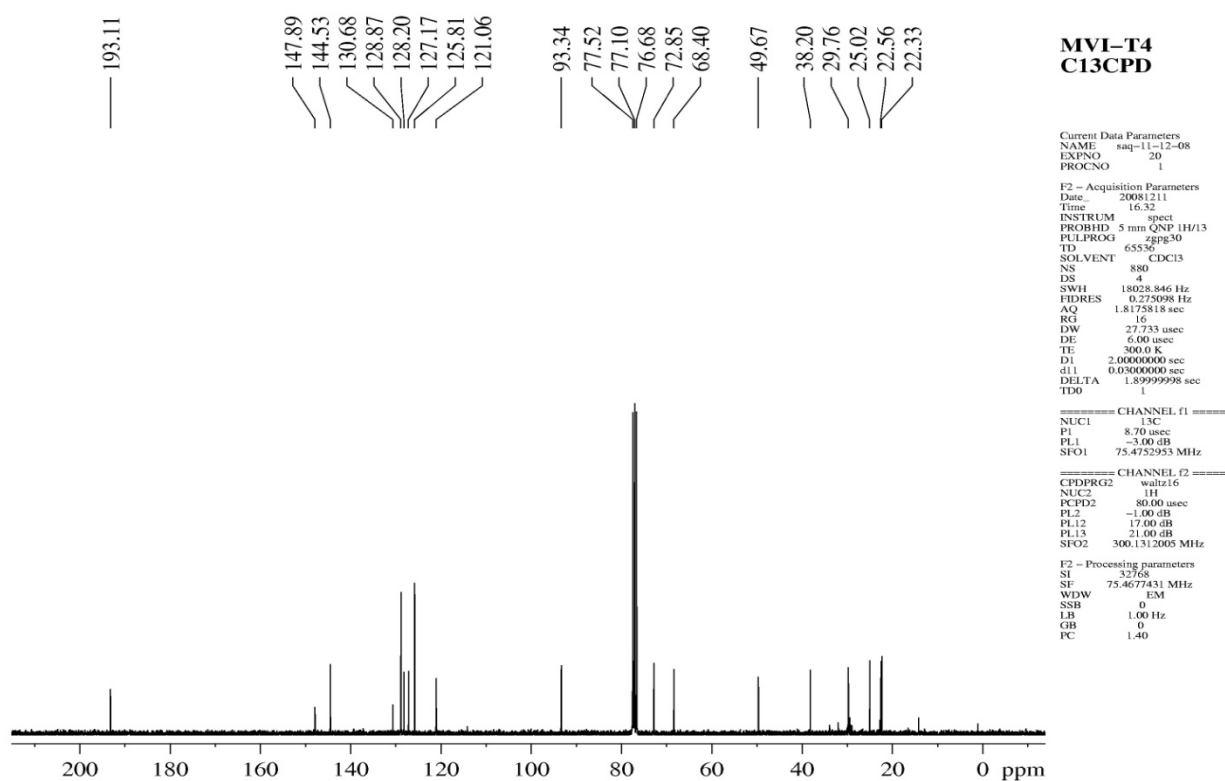
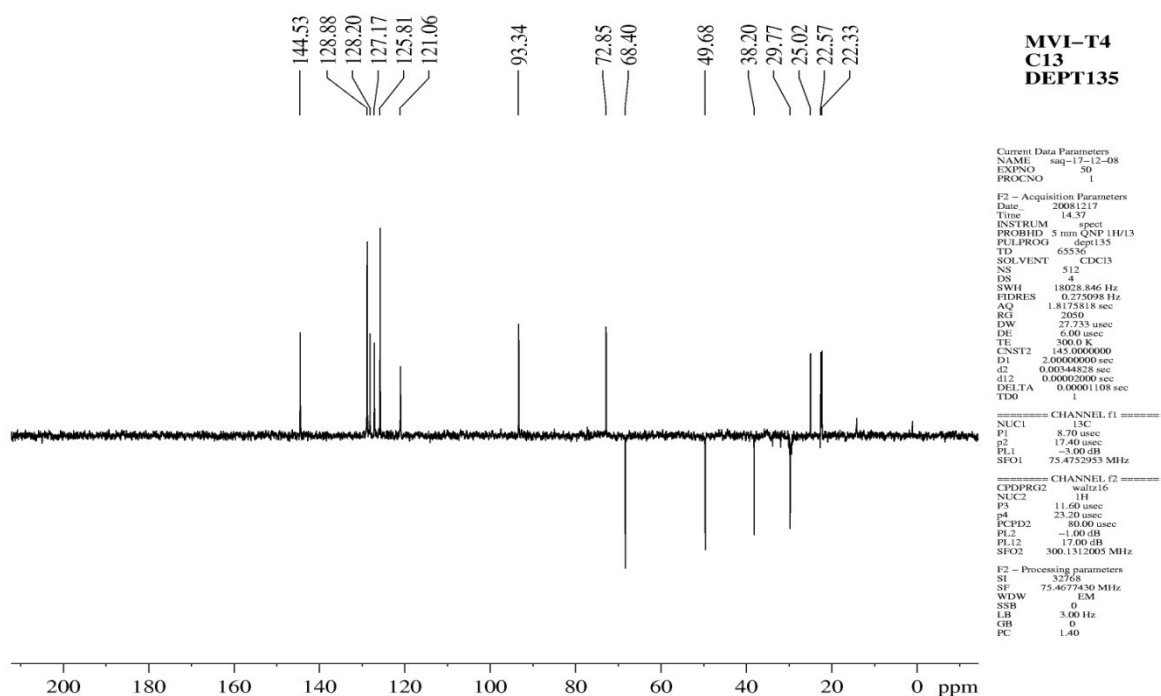
F2 - Processing parameters
SI: 32768
SF: 300.1300063 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

^1H NMR Spectrum of compound **35** and its expansion

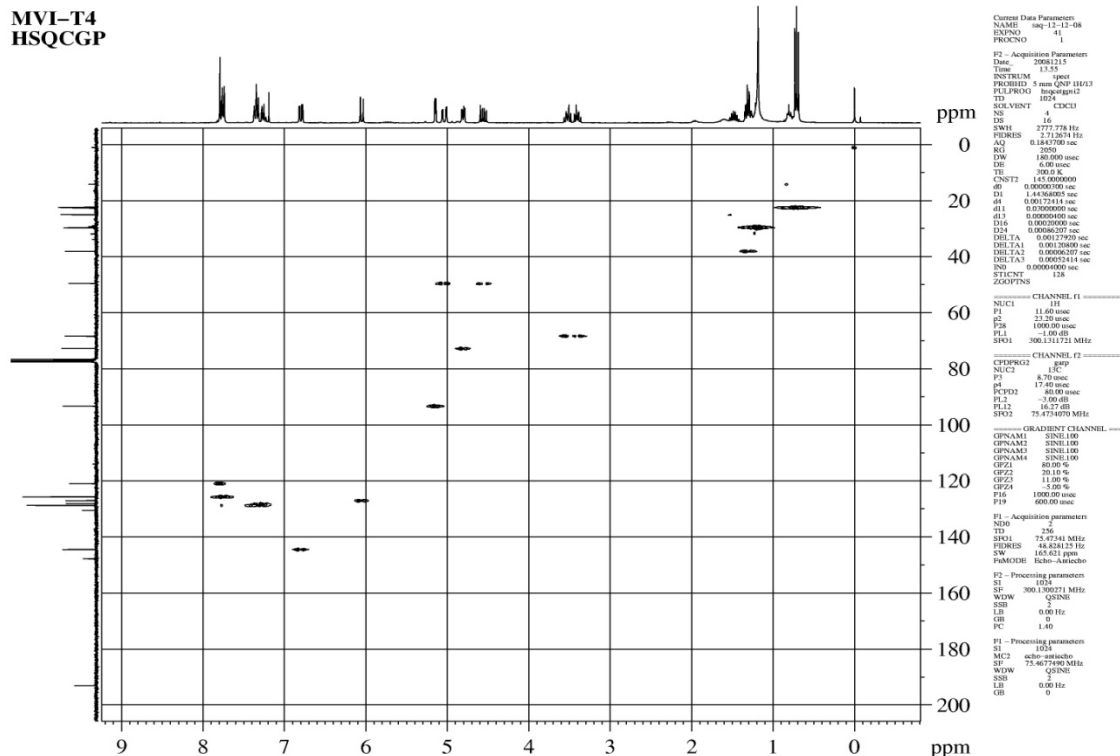
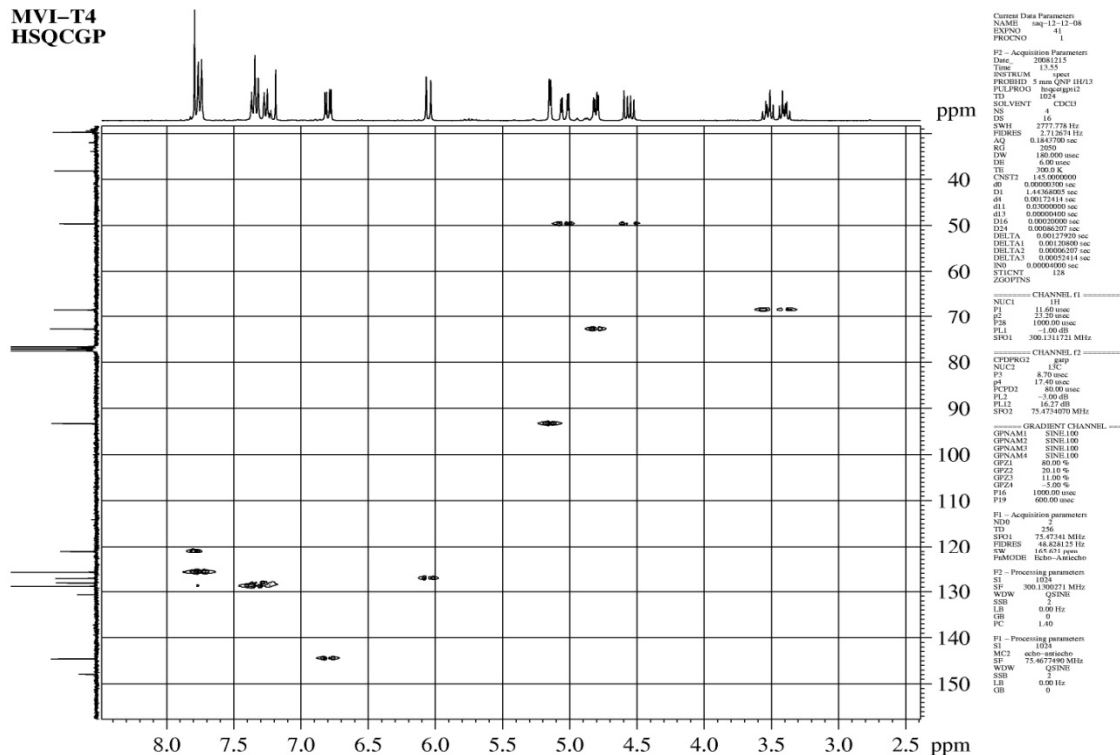


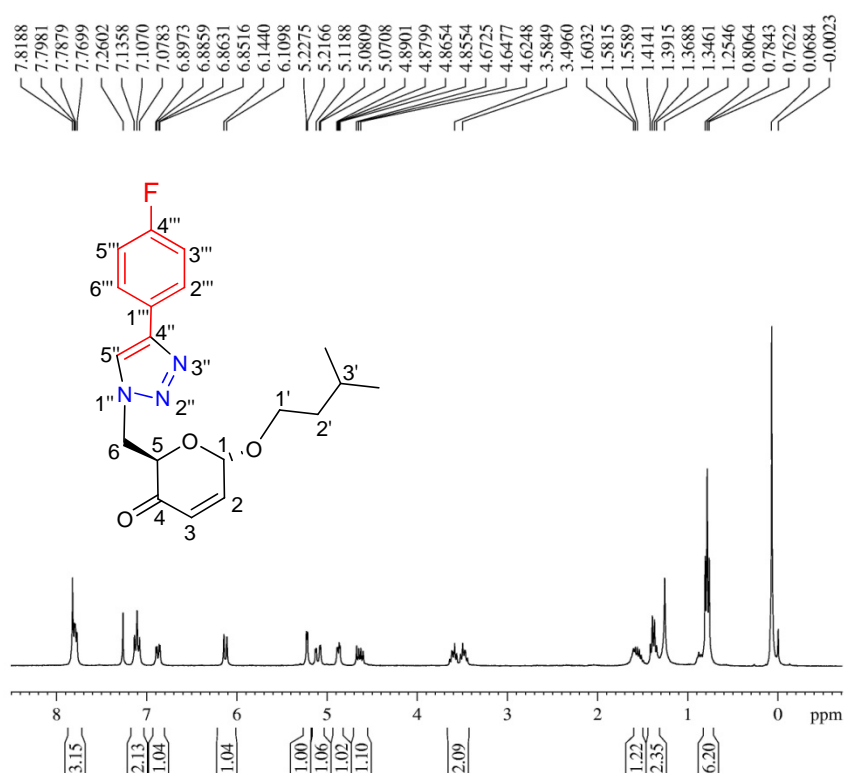
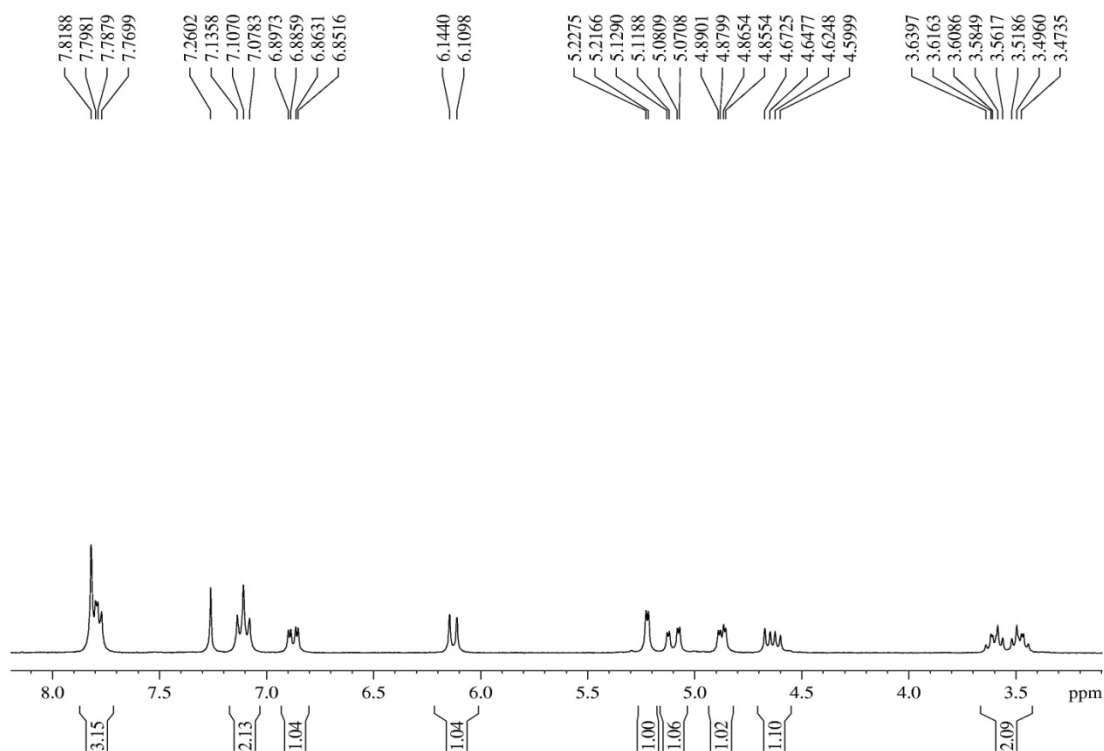


¹H Spectrum of compound **36** and its expansion



^{13}C NMR Spectrum and its DEPT 135 of compound **36**

HSQC Spectrum and its expansion of compound **36**



SM-155

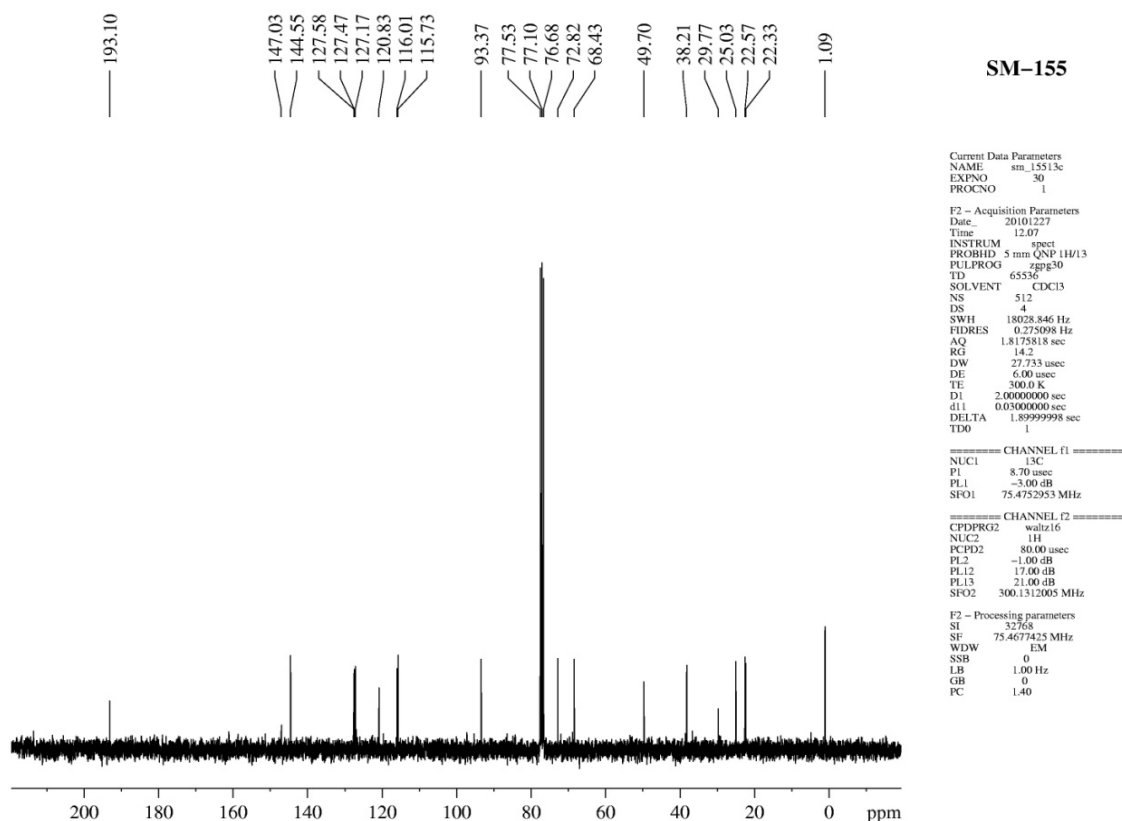
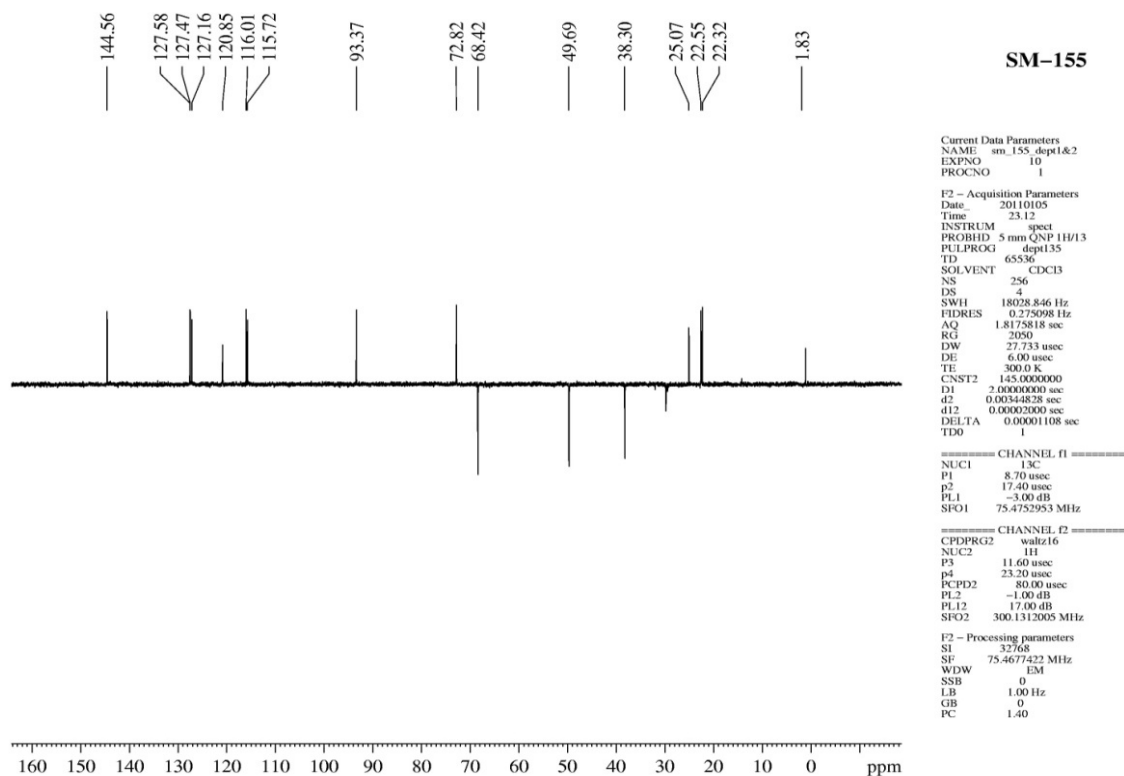
Current Data Parameters
NAME sm155
EXPNO 60
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101216
Time 12.27
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.295587 sec
RG 256
DW 80.800 usec
DE 6.00 usec
TE 300.3 K
D1 1.00000000 sec
TD0 1

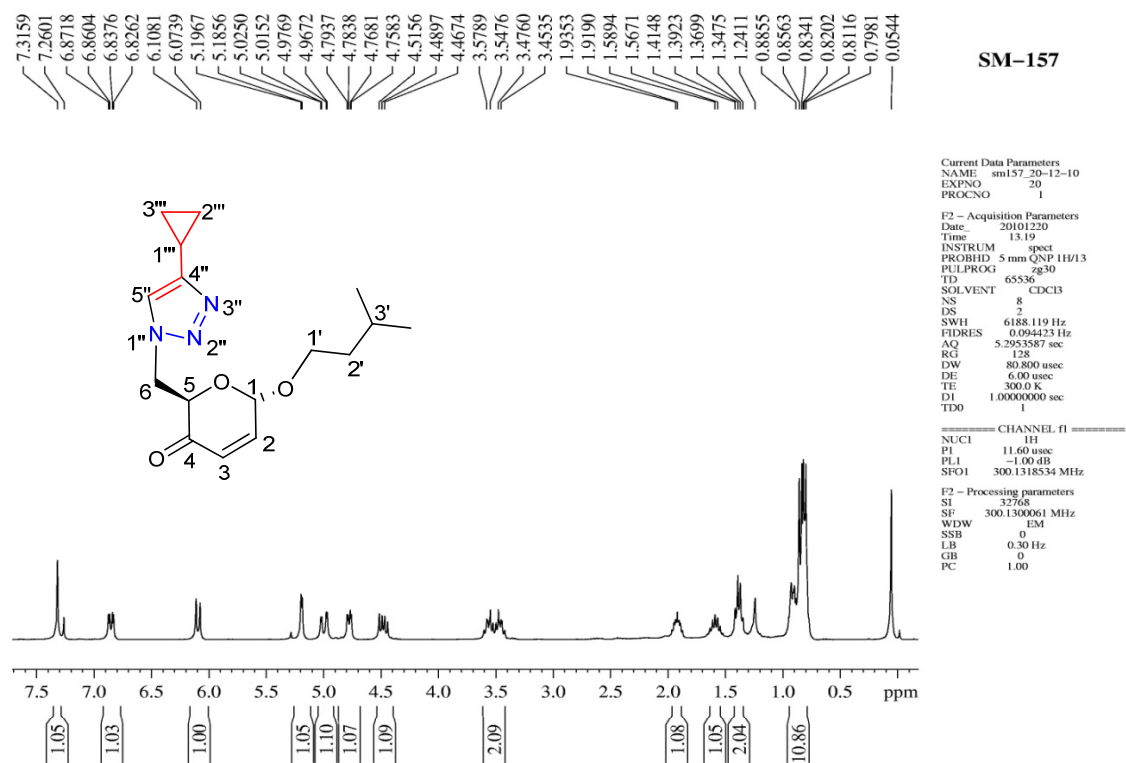
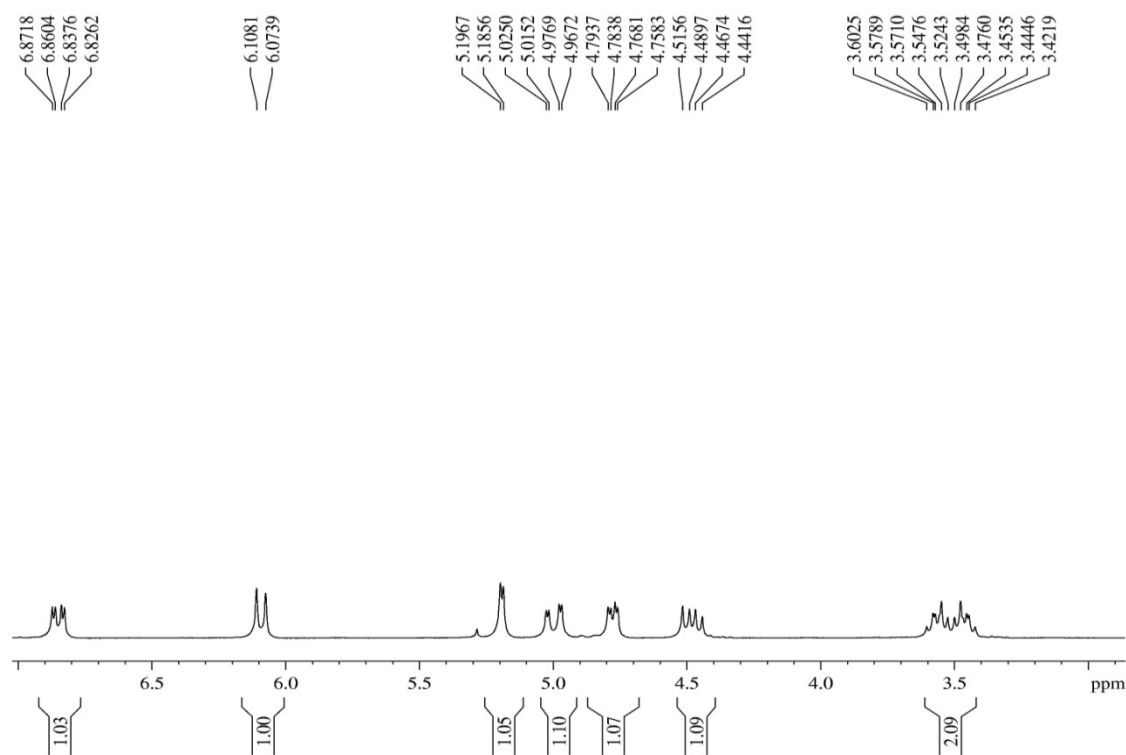
===== CHANNEL f1 =====
NUC1 13C
P1 11.60 usec
PL1 -1.00 dB
SFO1 300.131834 MHz

F2 - Processing parameters
SI 32768
SF 300.130063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

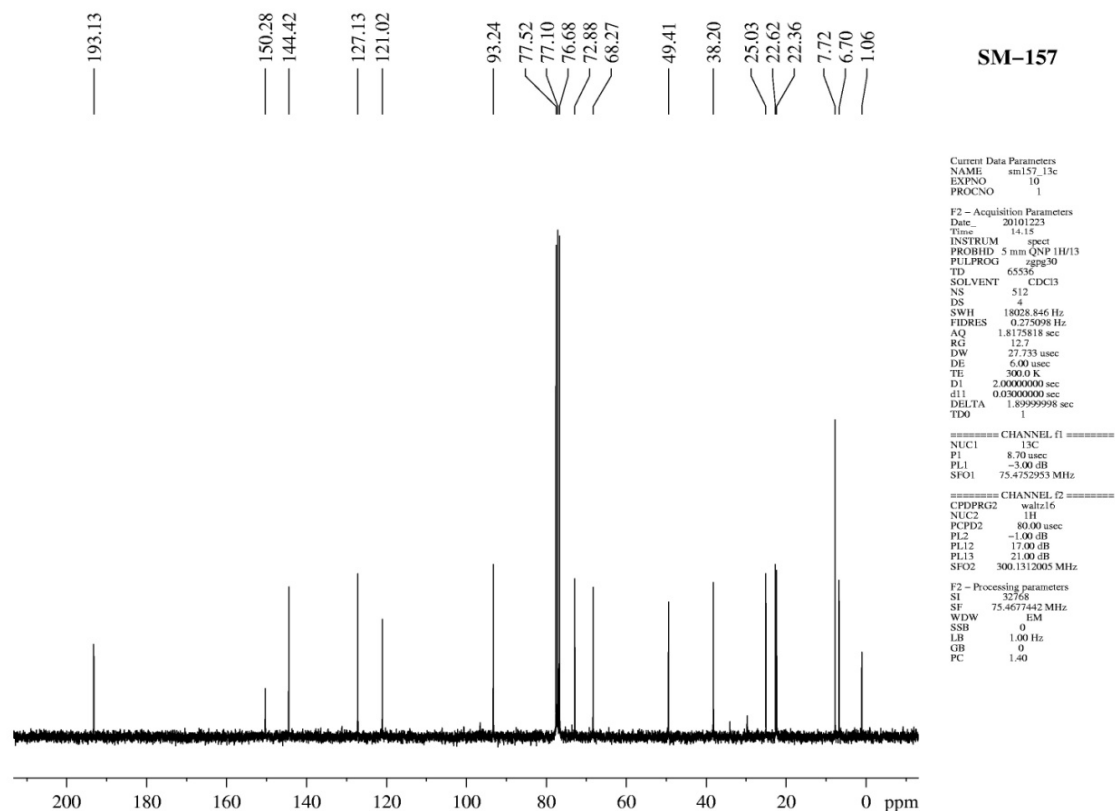
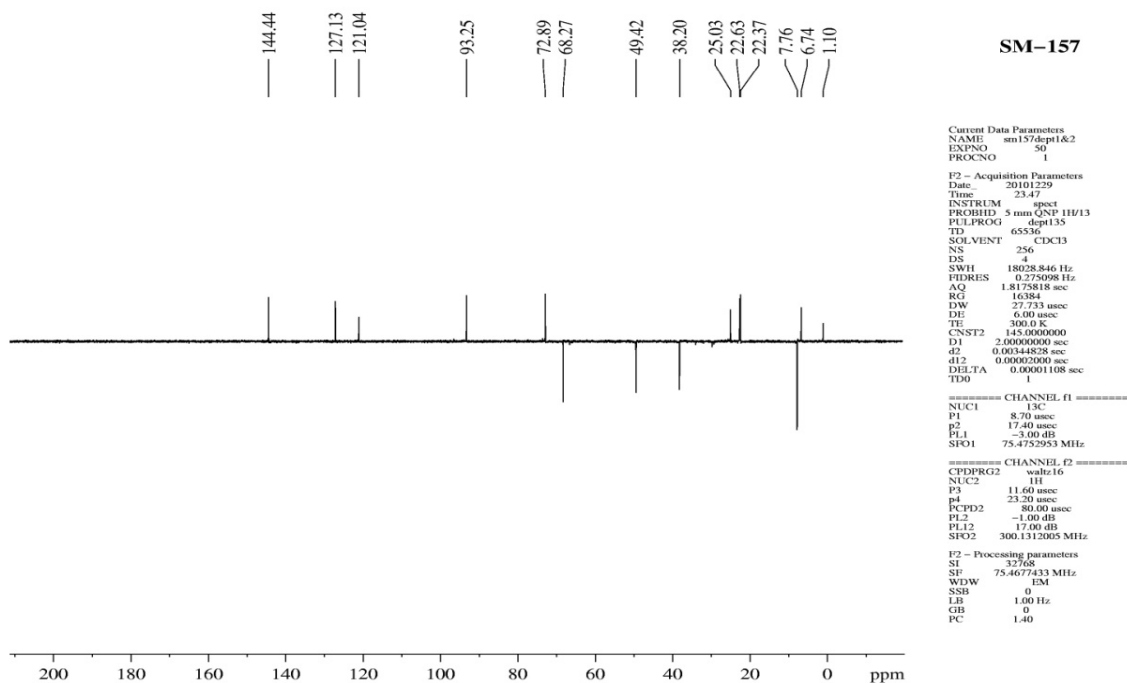
¹H NMR Spectrum of compound **38** and its expansion



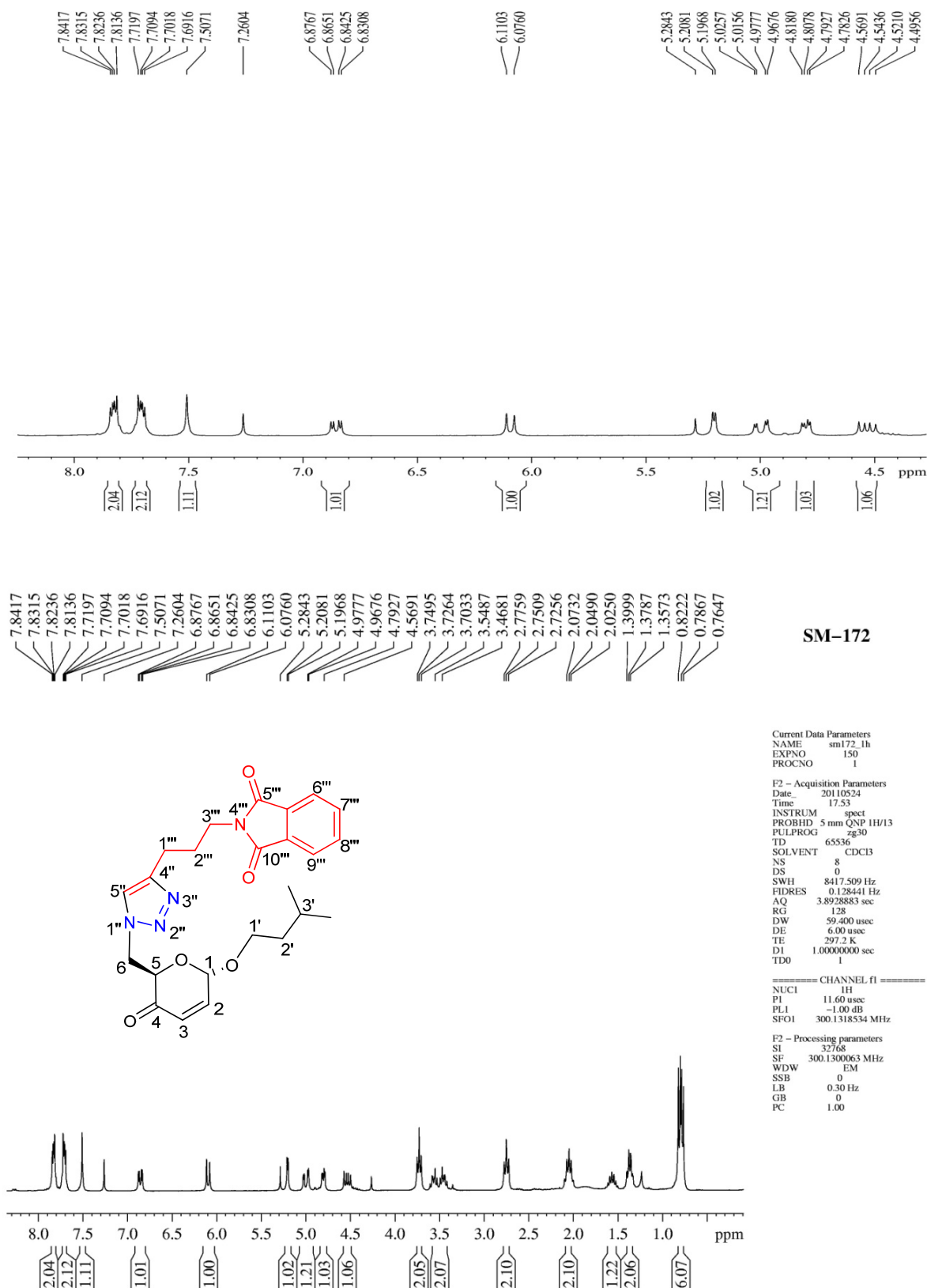
^{13}C NMR Spectrum and its DEPT 135 of compound **38**



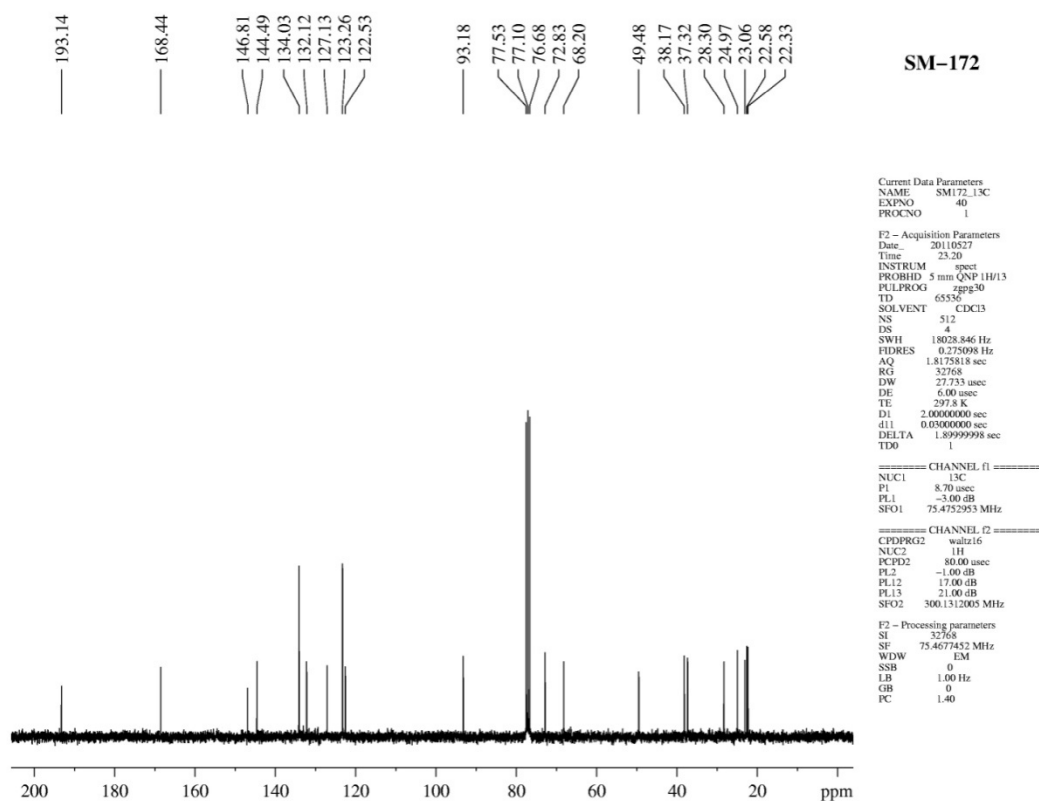
¹H NMR Spectrum of compound **40** and its expansion



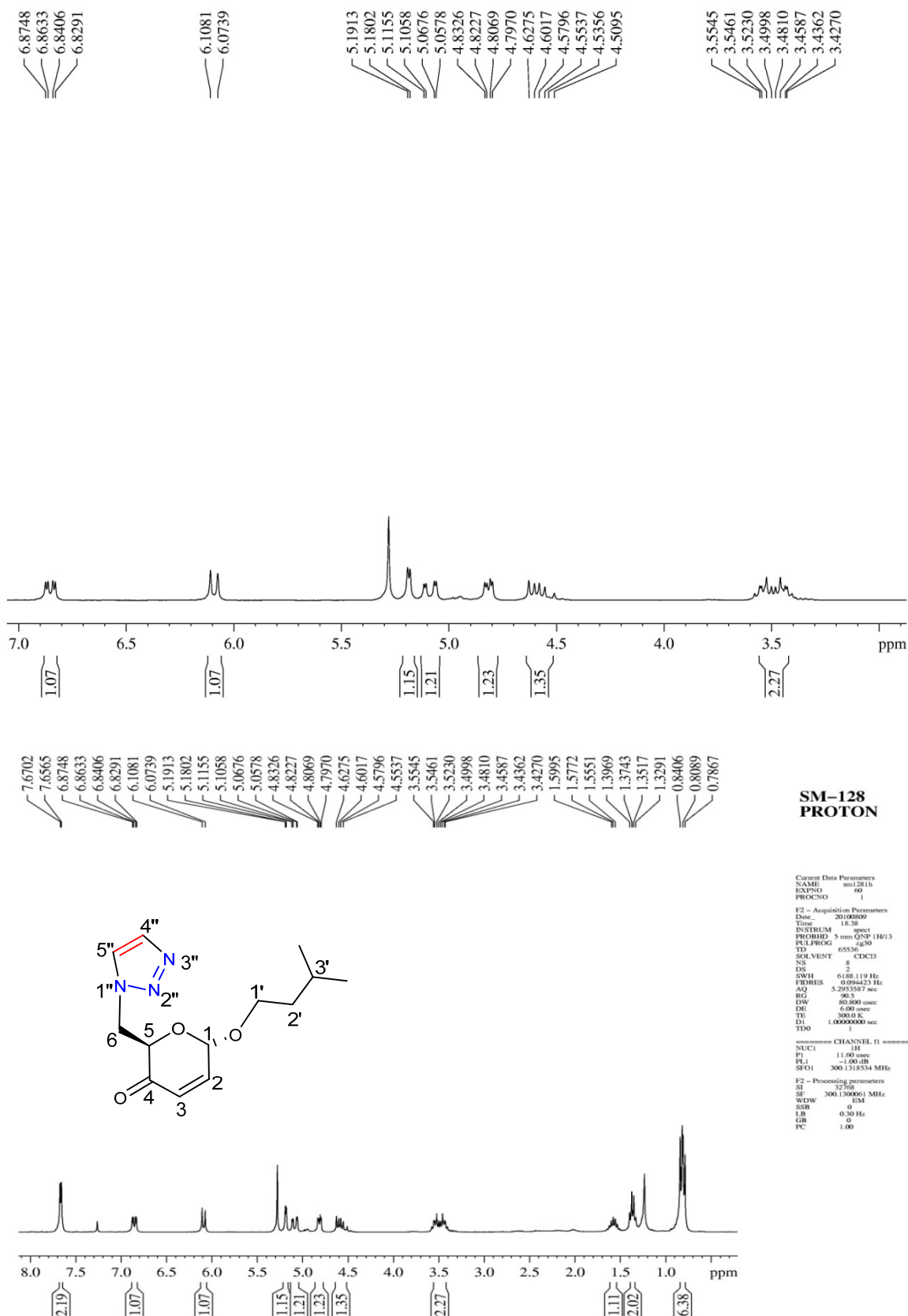
^{13}C NMR Spectrum and its DEPT 135 of compound **40**



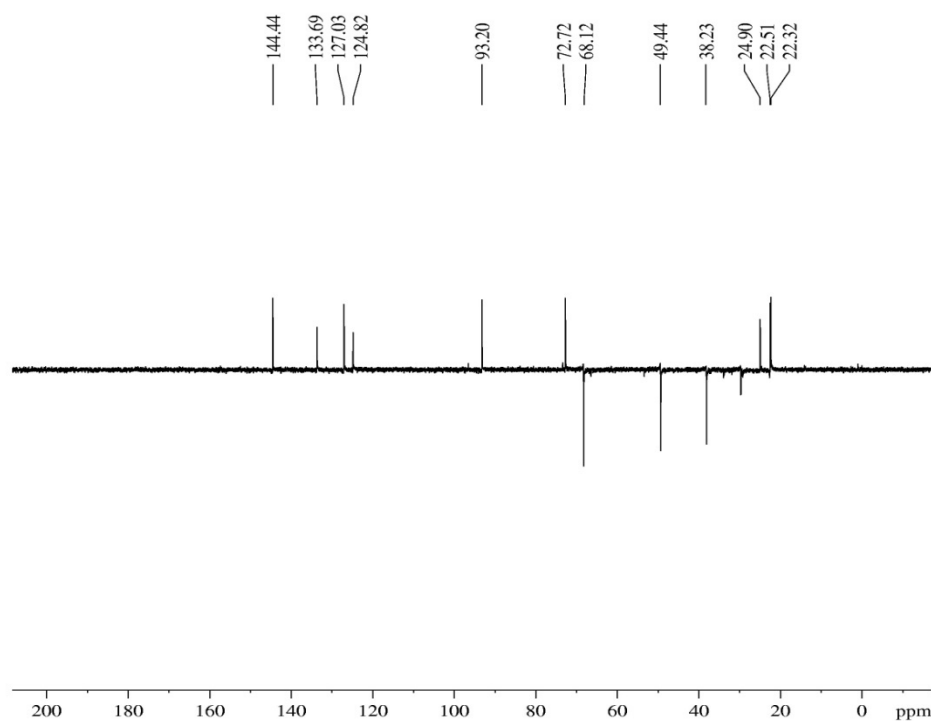
¹H NMR Spectrum of compound **41** and its expansion



^{13}C NMR Spectrum of compound **41**



¹H NMR Spectrum of compound **42** and its expansion



**SM-128
C13DEPT135**

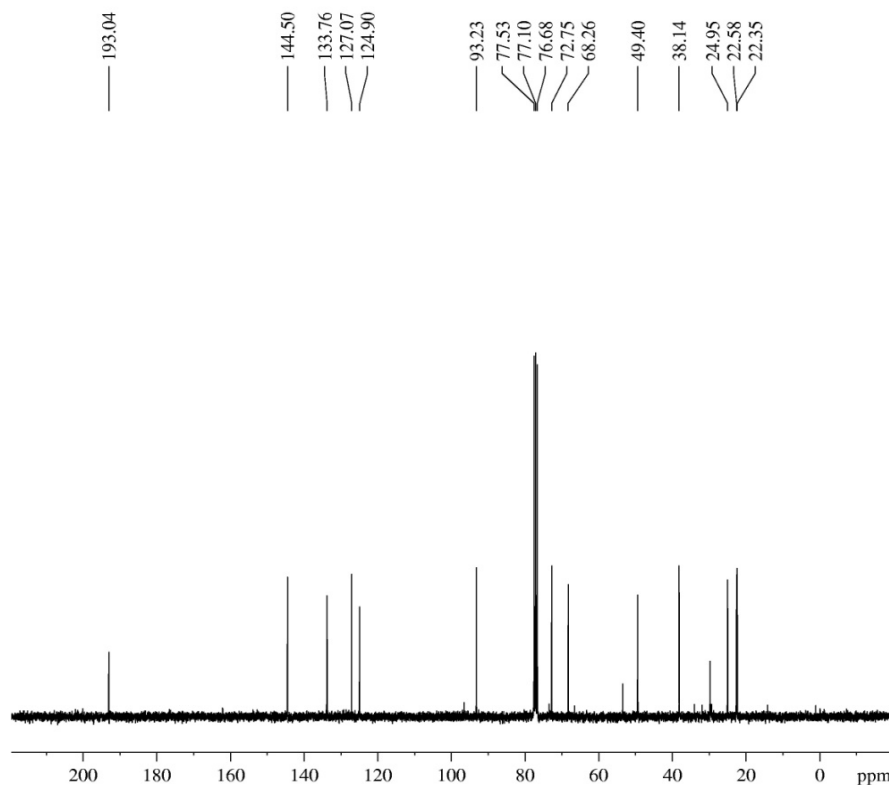
Current Data Parameters
NAME SM128DEPT1&2
EXPNO 41
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100817
Time 11.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 256
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 27.733 usec
DE 6.00 usec
TE 300.0 K
CNS2 145.000000
D1 2.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001108 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 dB
PL1 -3.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P3 11.60 usec
p4 23.20 usec
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



**SM-128
C13**

Current Data Parameters
NAME SM128_13C
EXPNO 10
PROCNO 1

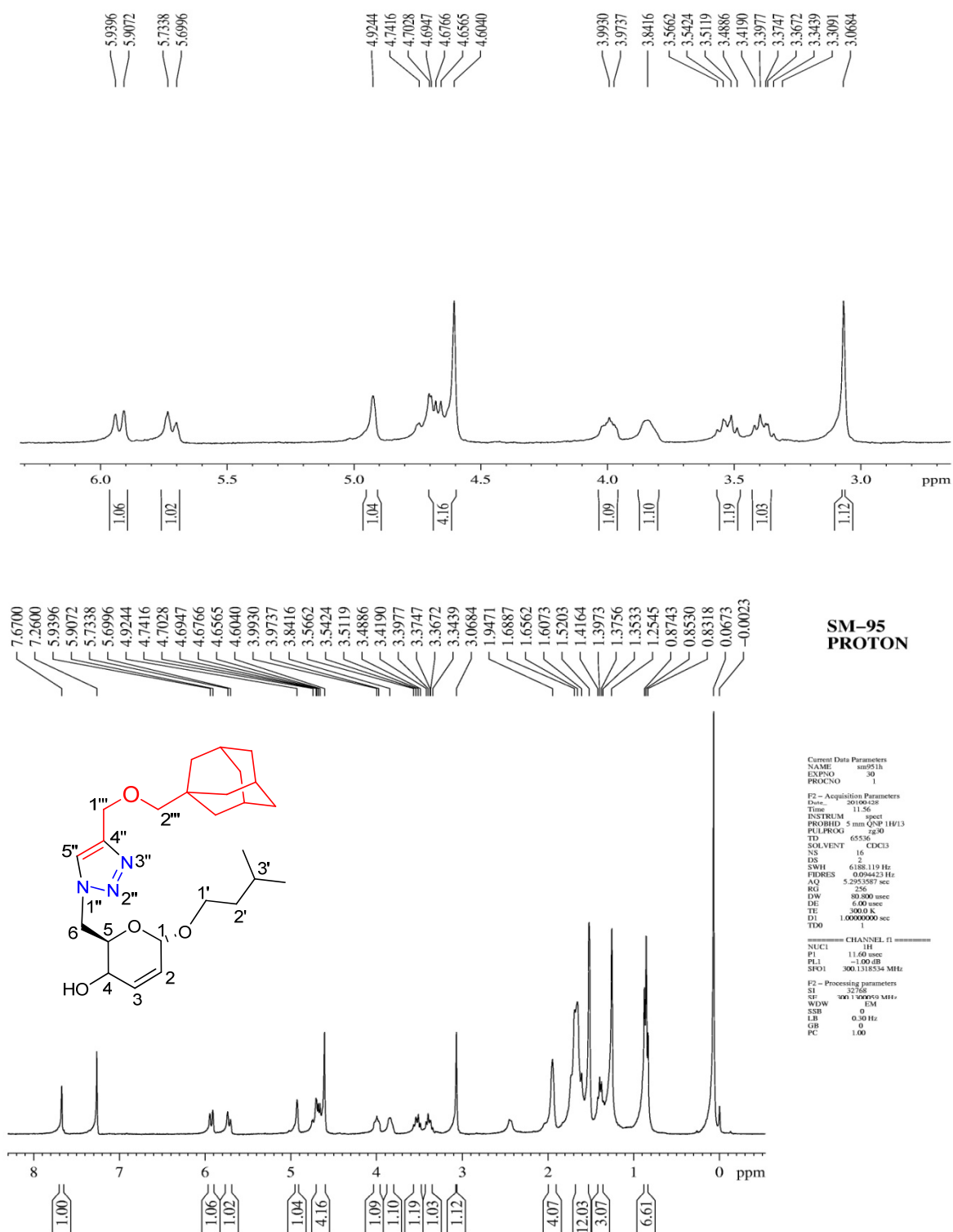
F2 - Acquisition Parameters
Date_ 20100812
Time 10.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 12.7
DW 27.733 usec
DE 6.00 usec
TE 297.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

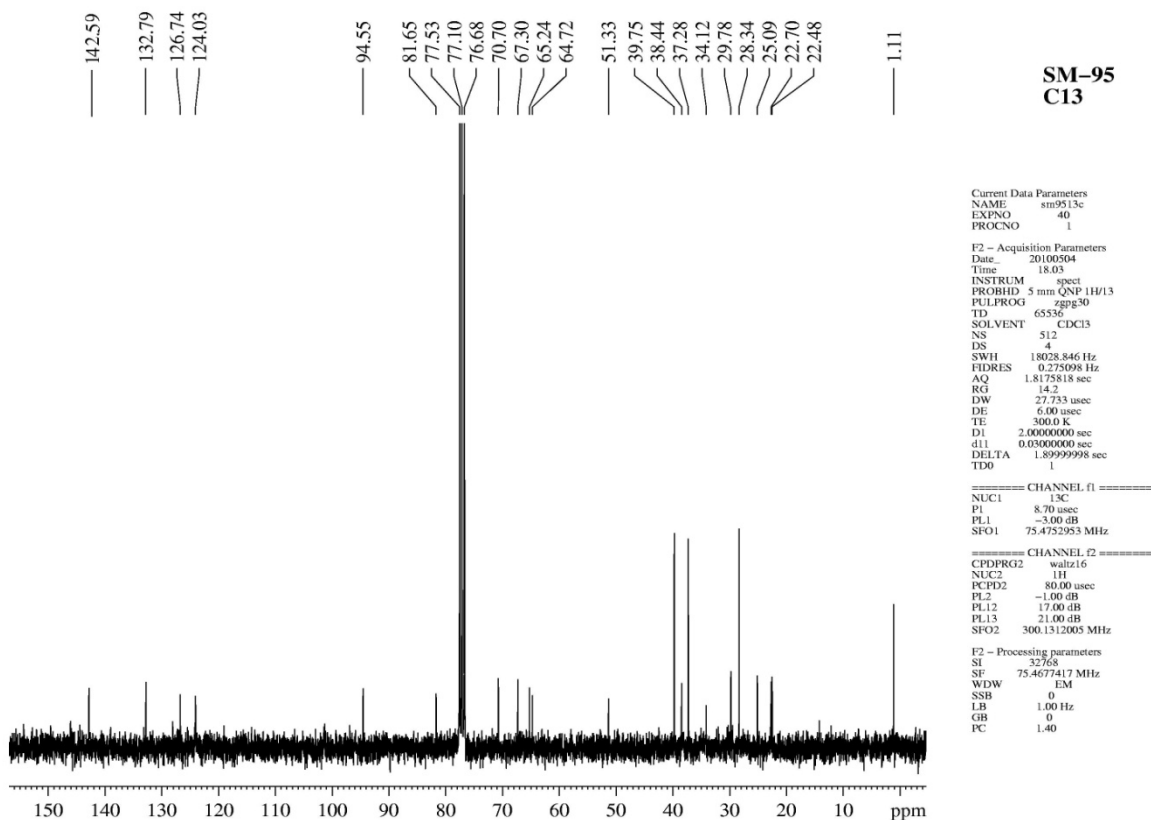
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz

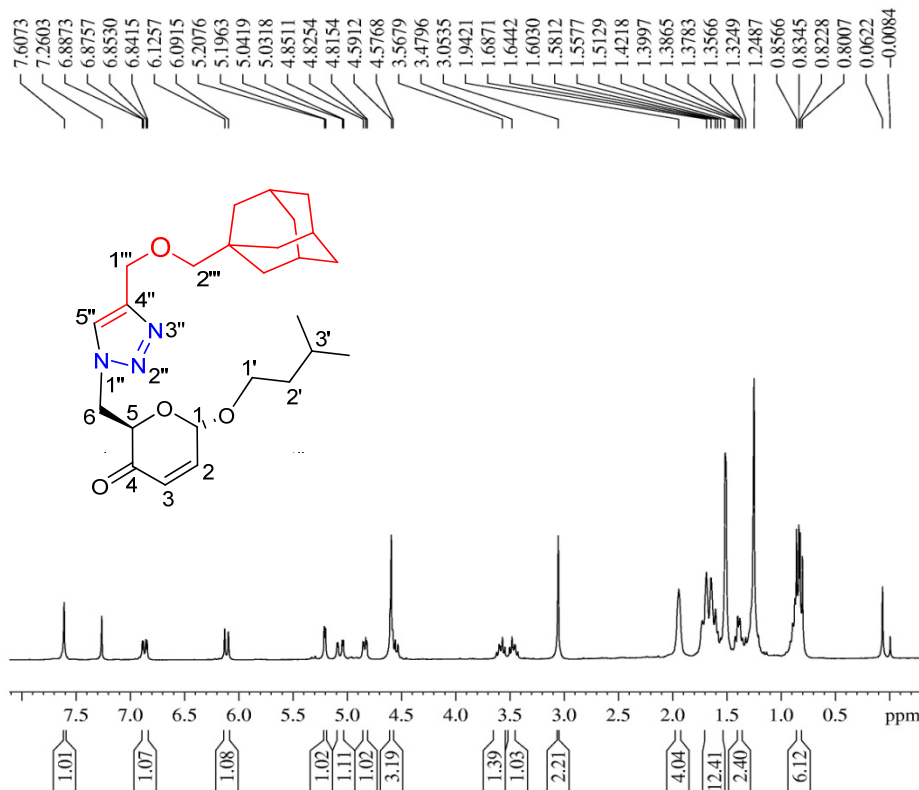
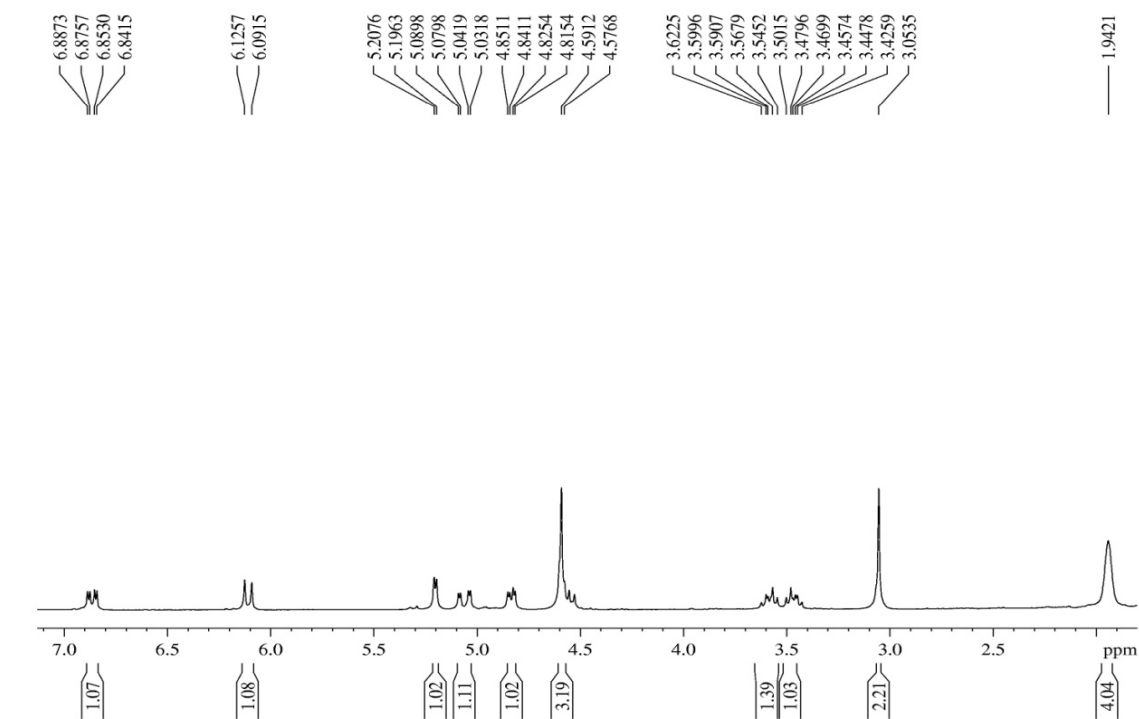
F2 - Processing parameters
SI 32768
SF 75.4677460 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹³C NMR Spectrum and its DEPT 135 of compound **42**



^1H NMR Spectrum of compound **45** and its expansion

 ^{13}C NMR Spectrum of compound **45**



SM-96

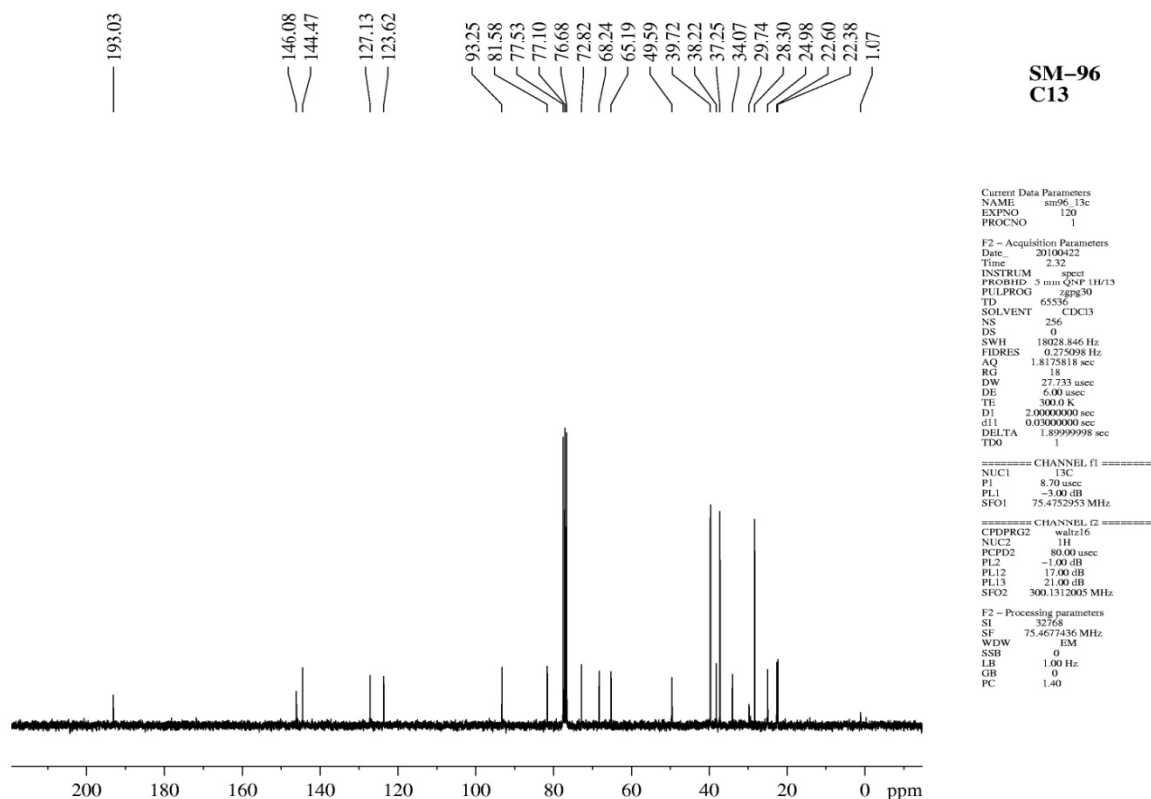
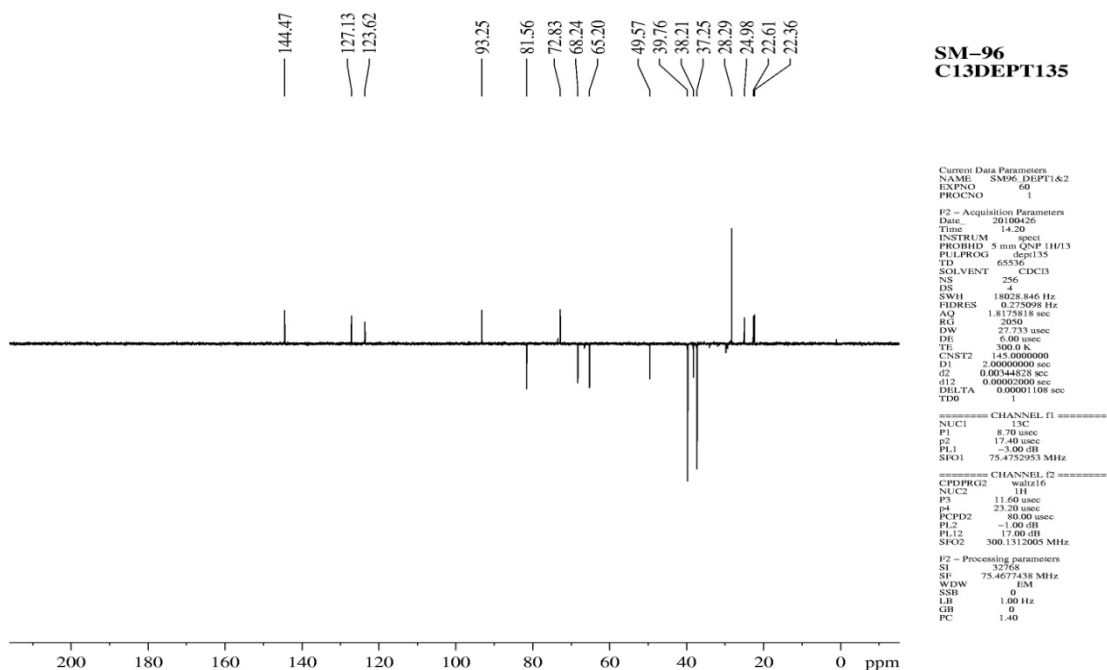
Current Data Parameters
NAME SM96.1H_15-10-10
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101015
Time 18.32
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 101
DW 80.800 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1

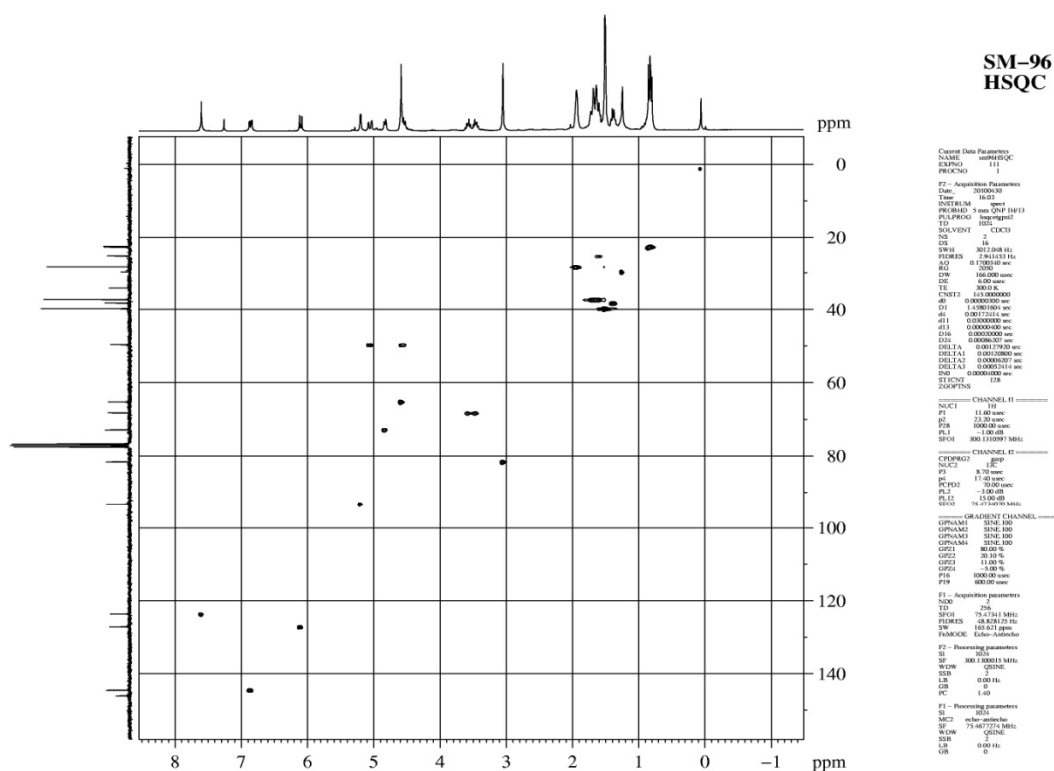
===== CHANNEL f1 =====
NUC1 1H
P1 11.60 usec
PL1 -1.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

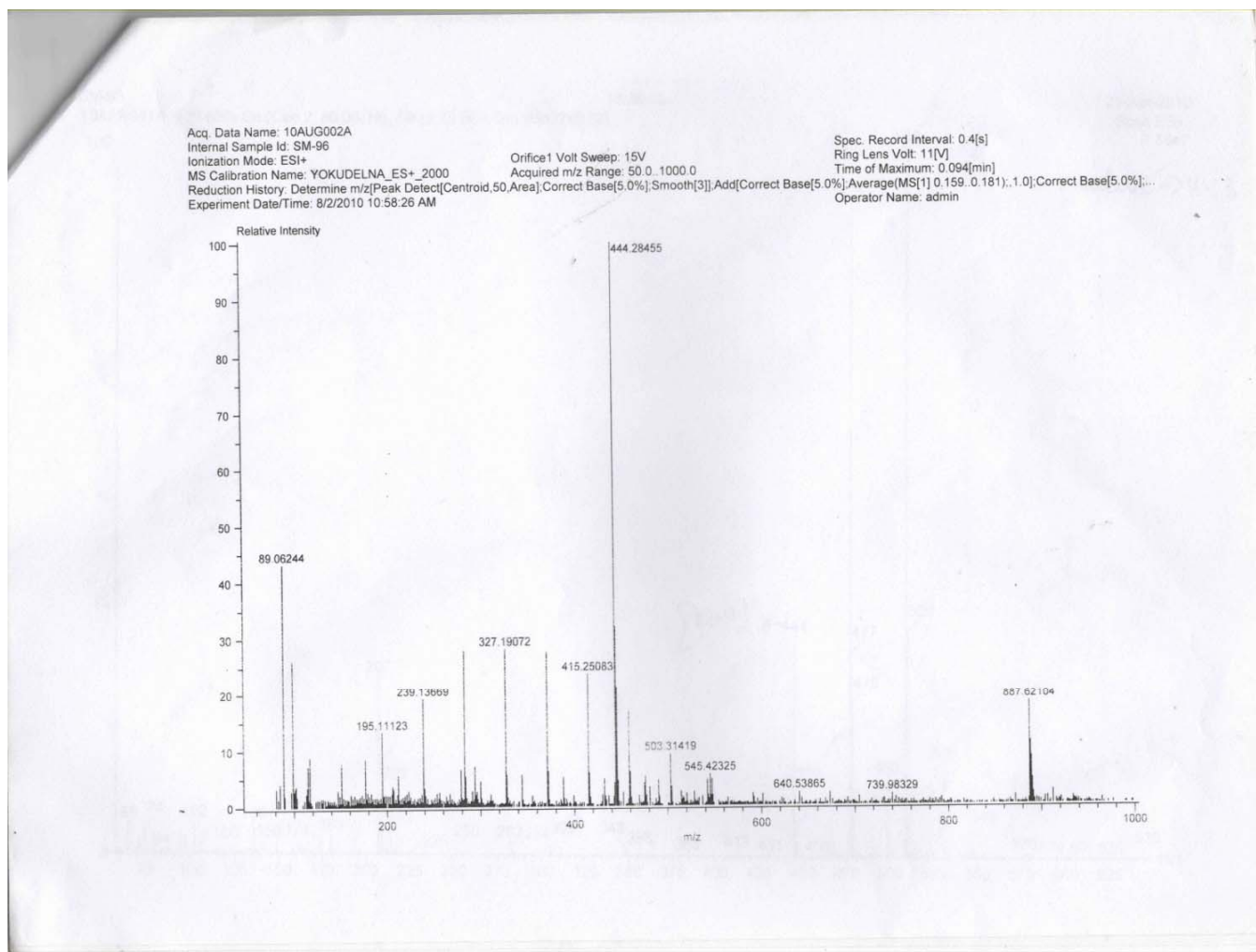
¹H NMR Spectrum of compound **46** and its expansion

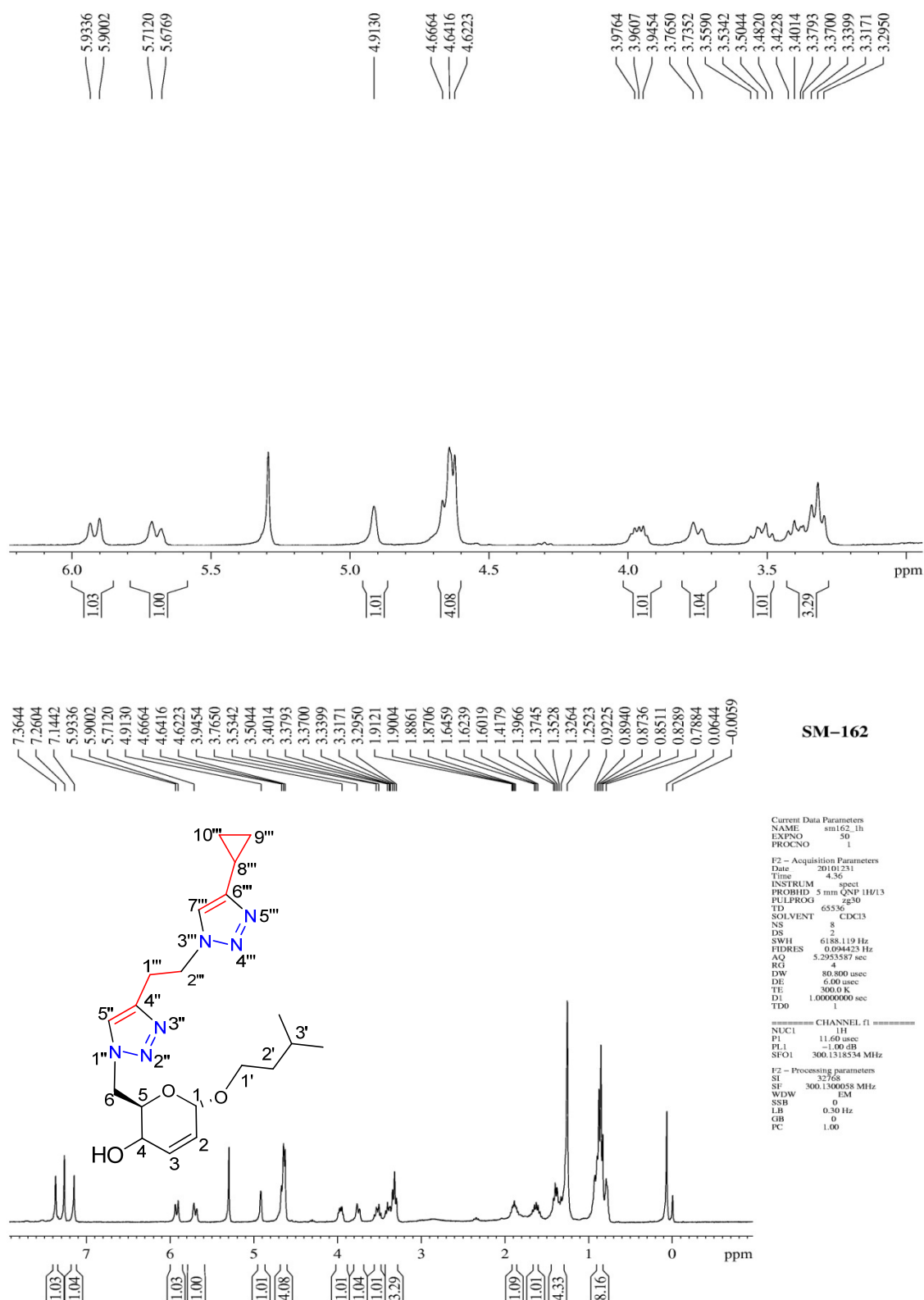


^{13}C NMR Spectrum and its DEPT 135 of compound **46**

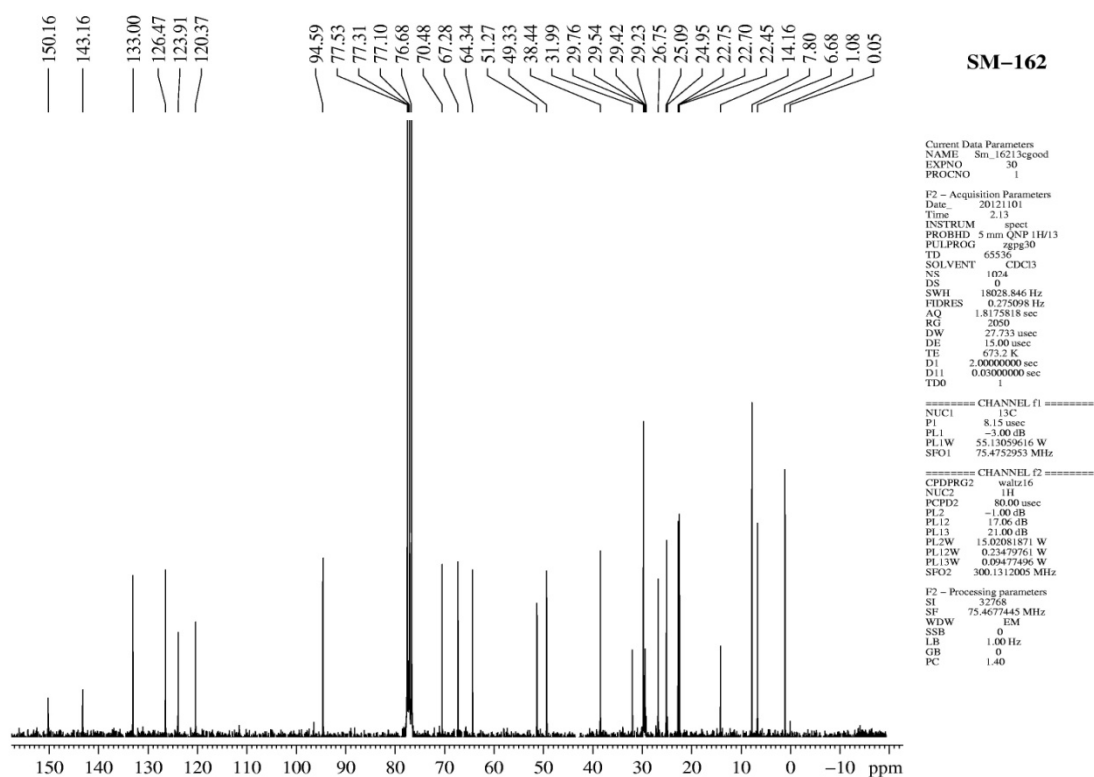
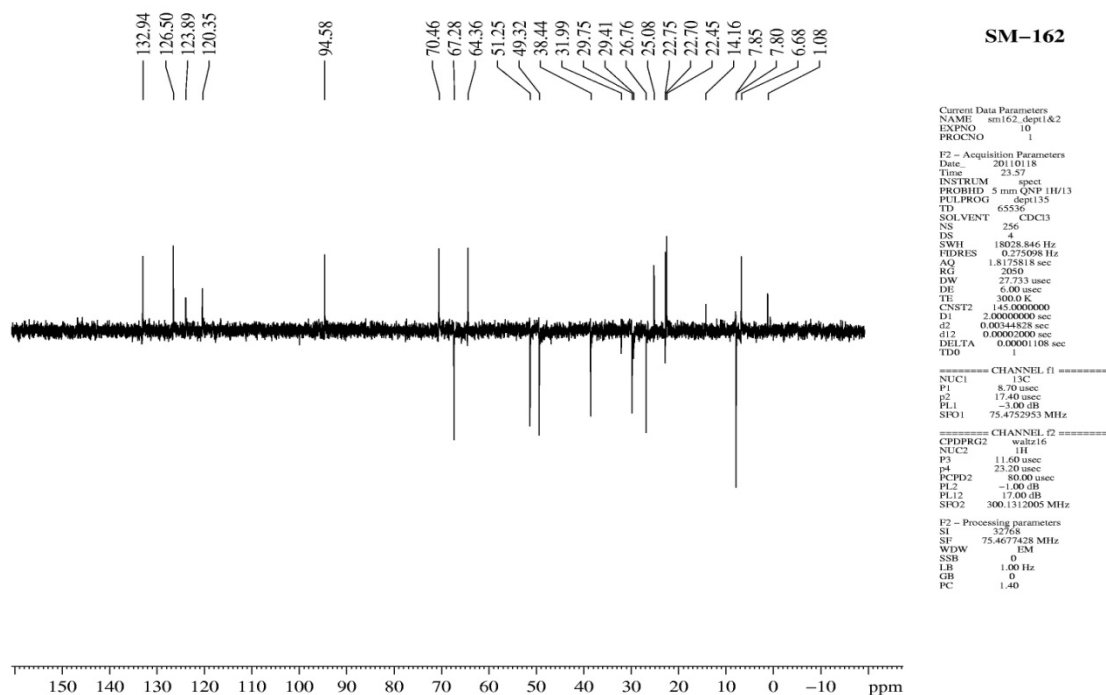


S-109

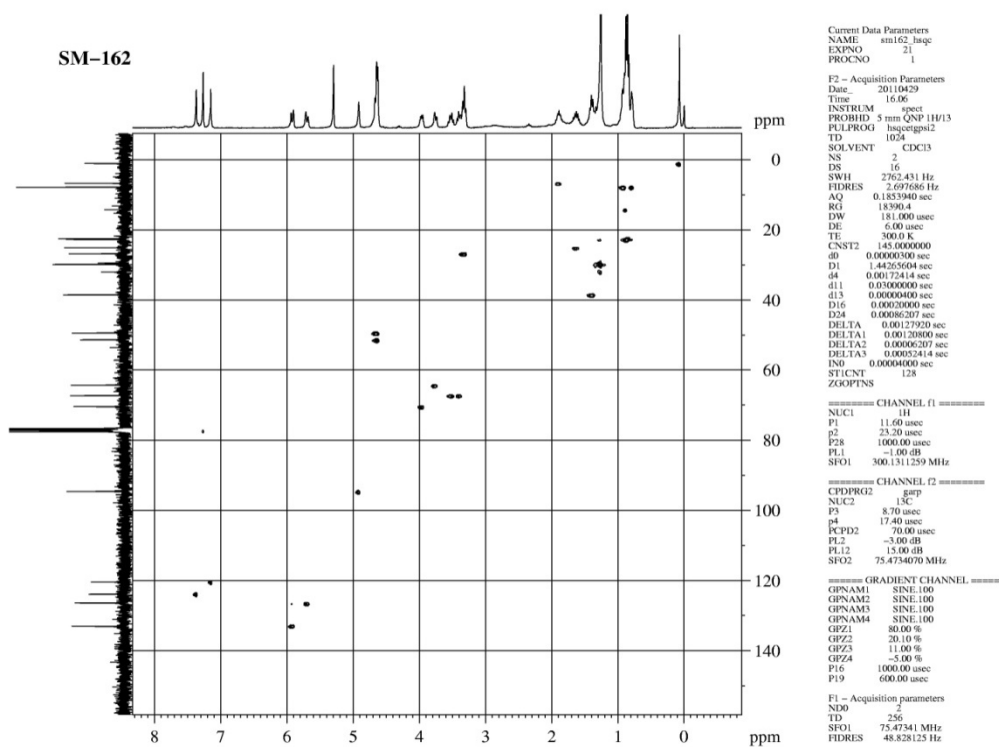
HRMS Spectrum of compound **46**



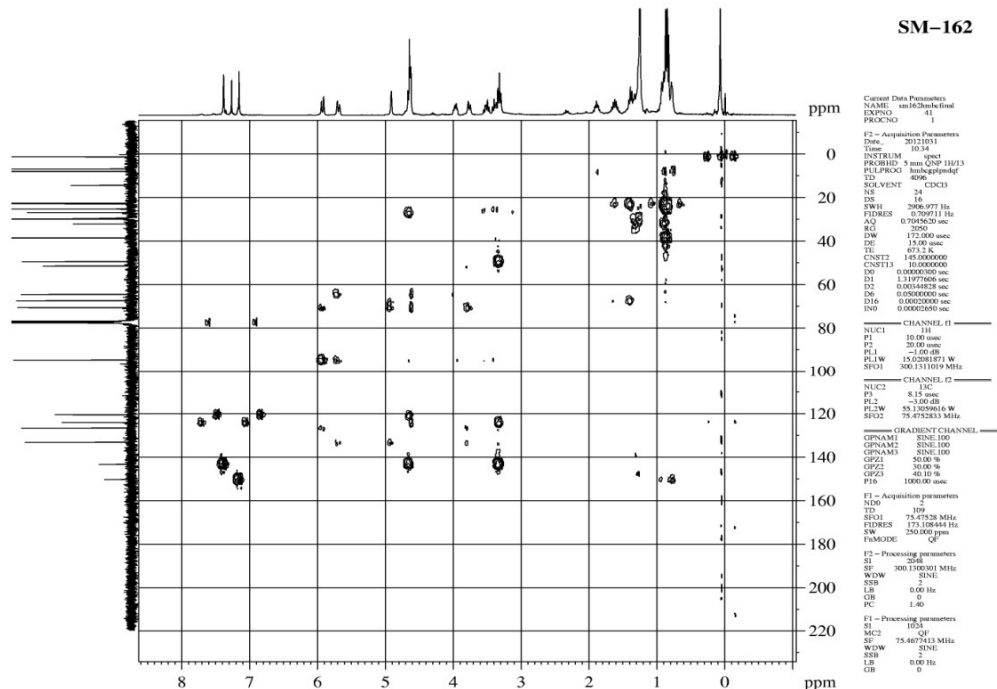
¹H NMR Spectrum of compound **48** and its expansion



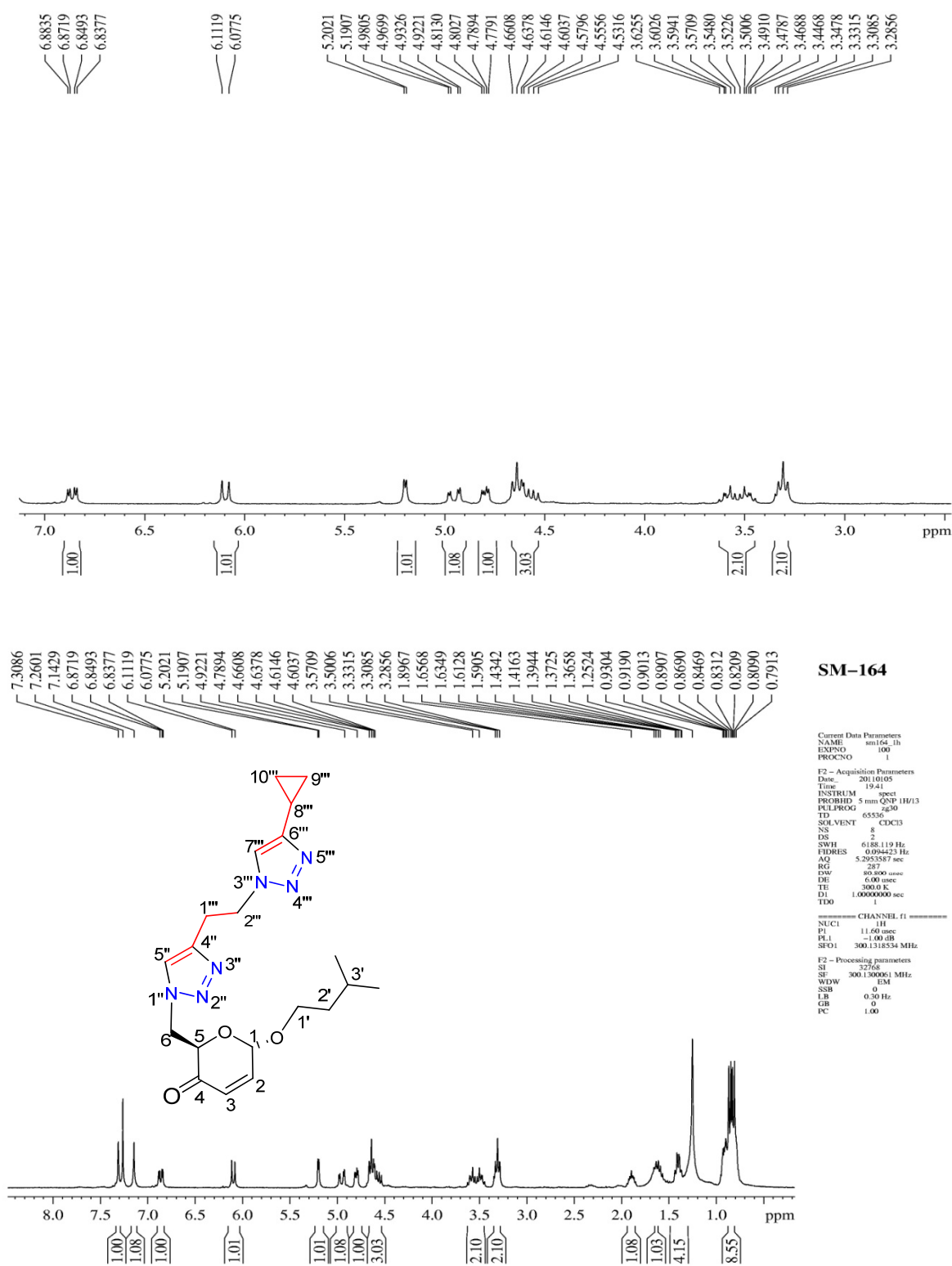
^{13}C NMR Spectrum and its DEPT 135 of compound **48**



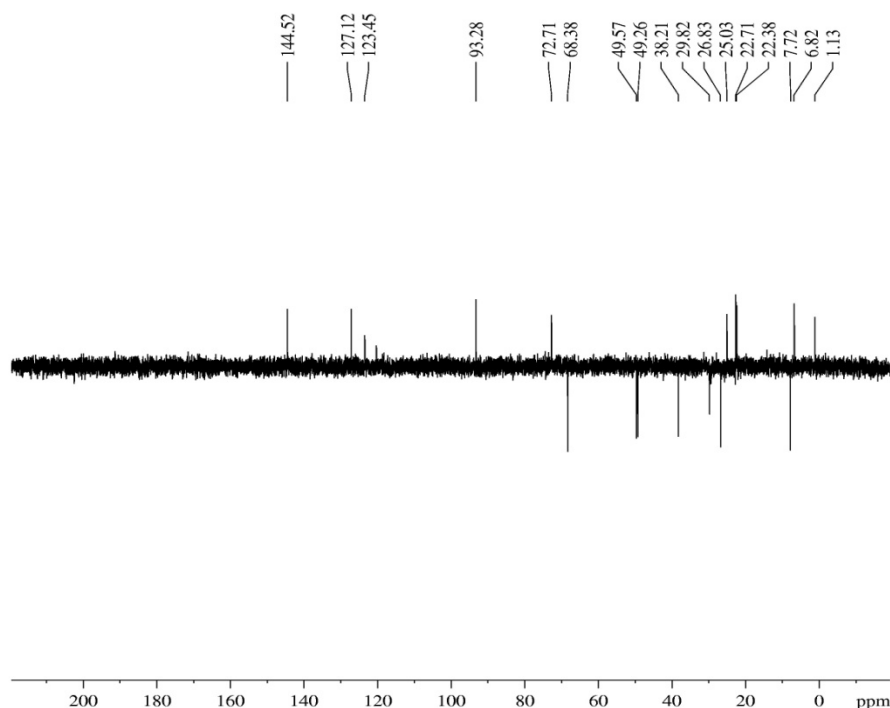
HSQC Spectrum of compound 48



HMBC Spectrum of compound 48



¹H NMR Spectrum of compound **50** and its expansion



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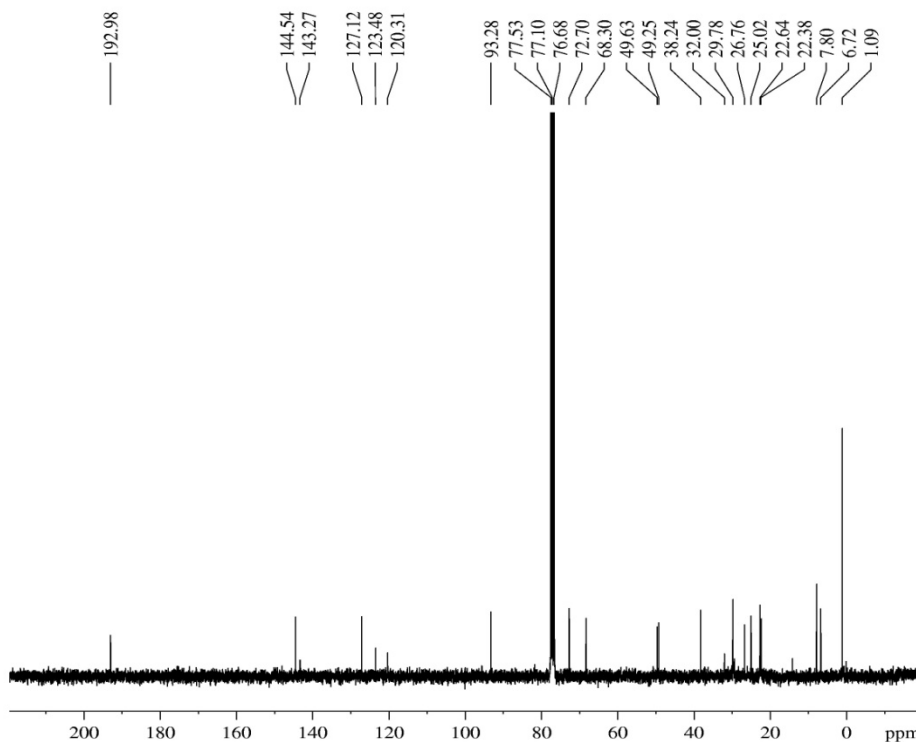
Current Data Parameters
NAME SM164 DEPT1&2
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110409
Time 5.47
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 16384
DW 27.733 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.000000
D1 2.0000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001108 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 11.60 usec
PL2 23.20 usec
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677420 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



SM-164

Current Data Parameters
NAME SM16418AUG
EXPNO 20
PROCNO 1

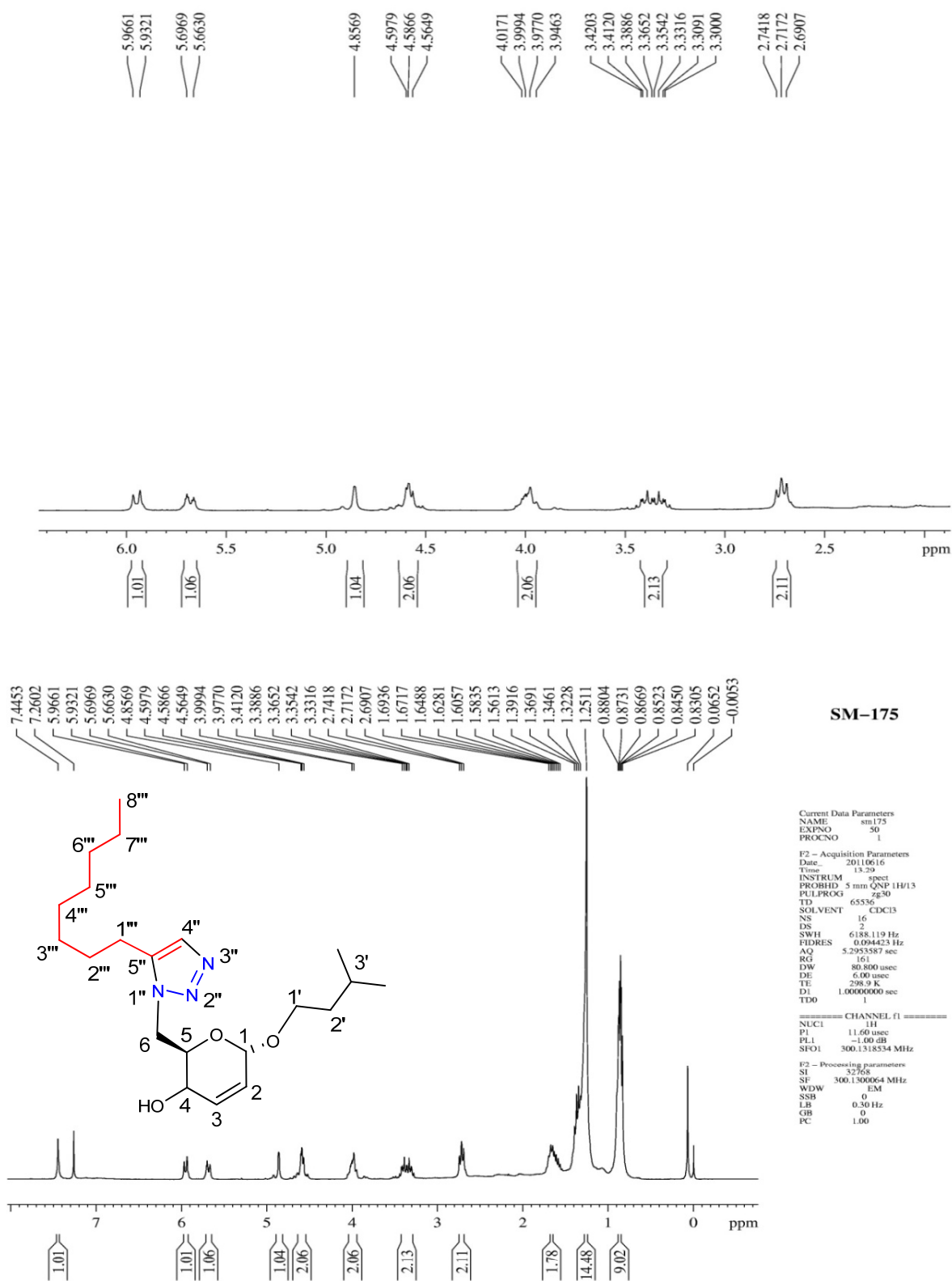
F2 - Acquisition Parameters
Date_ 20110818
Time 20.15
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 0
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 16384
DW 27.733 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.70 usec
PL1 17.40 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

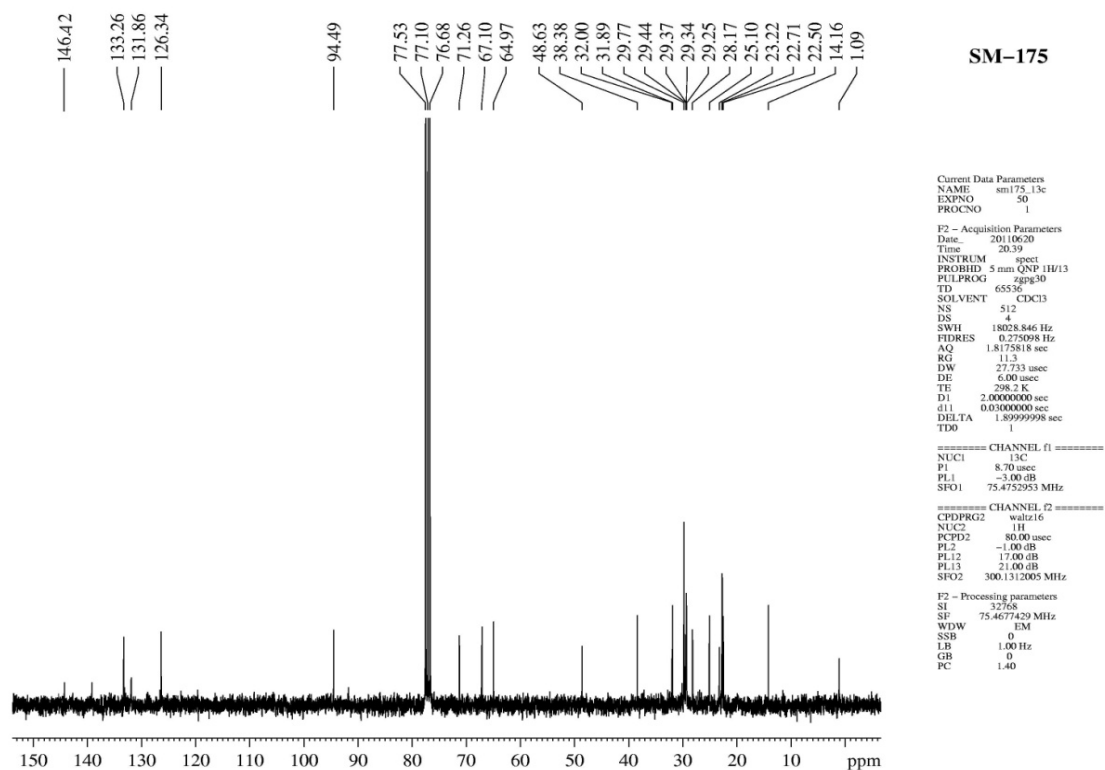
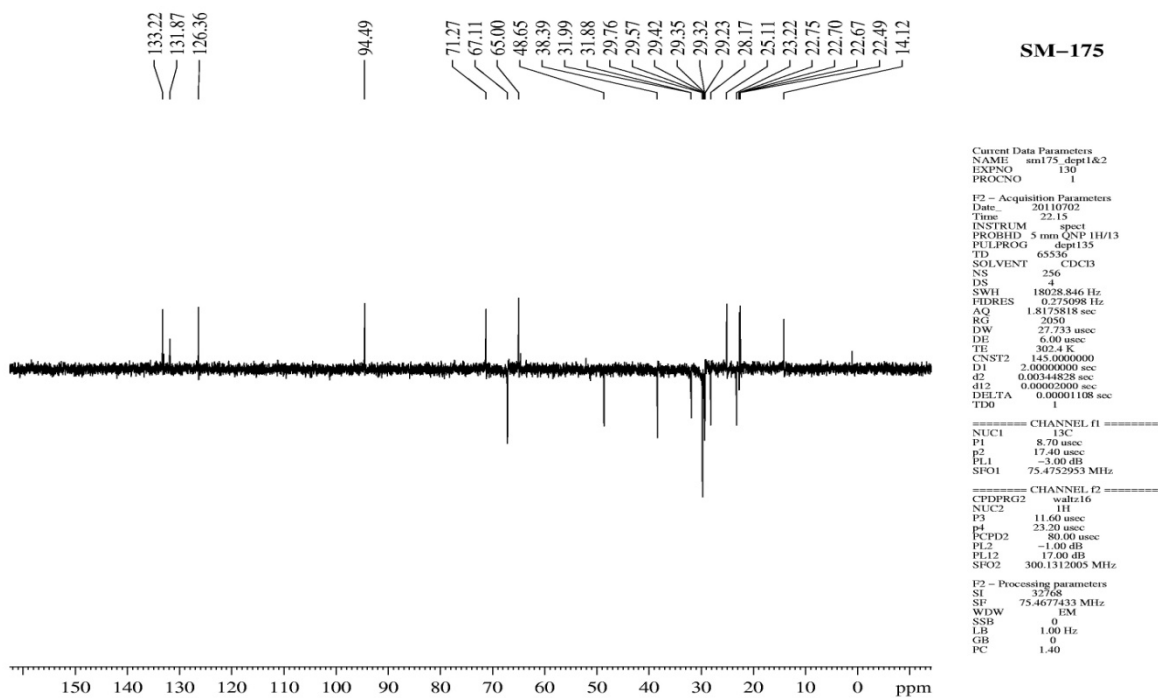
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 11.60 usec
PL2 23.20 usec
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677423 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

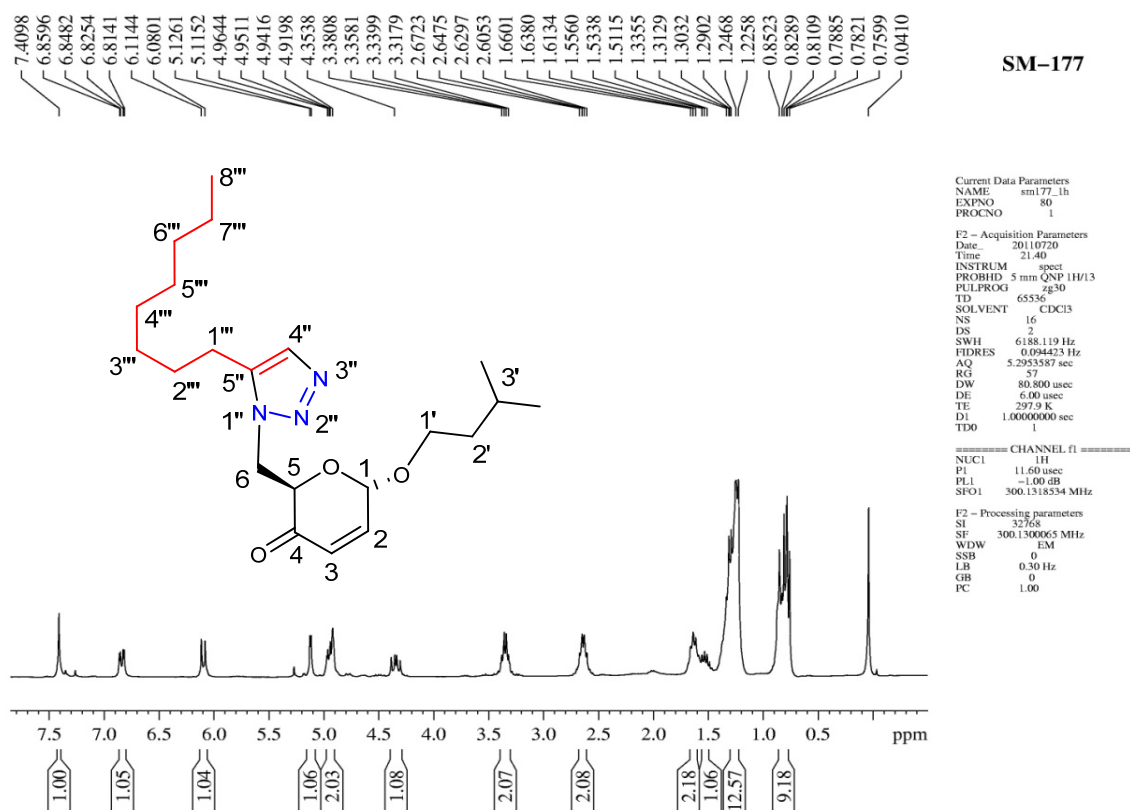
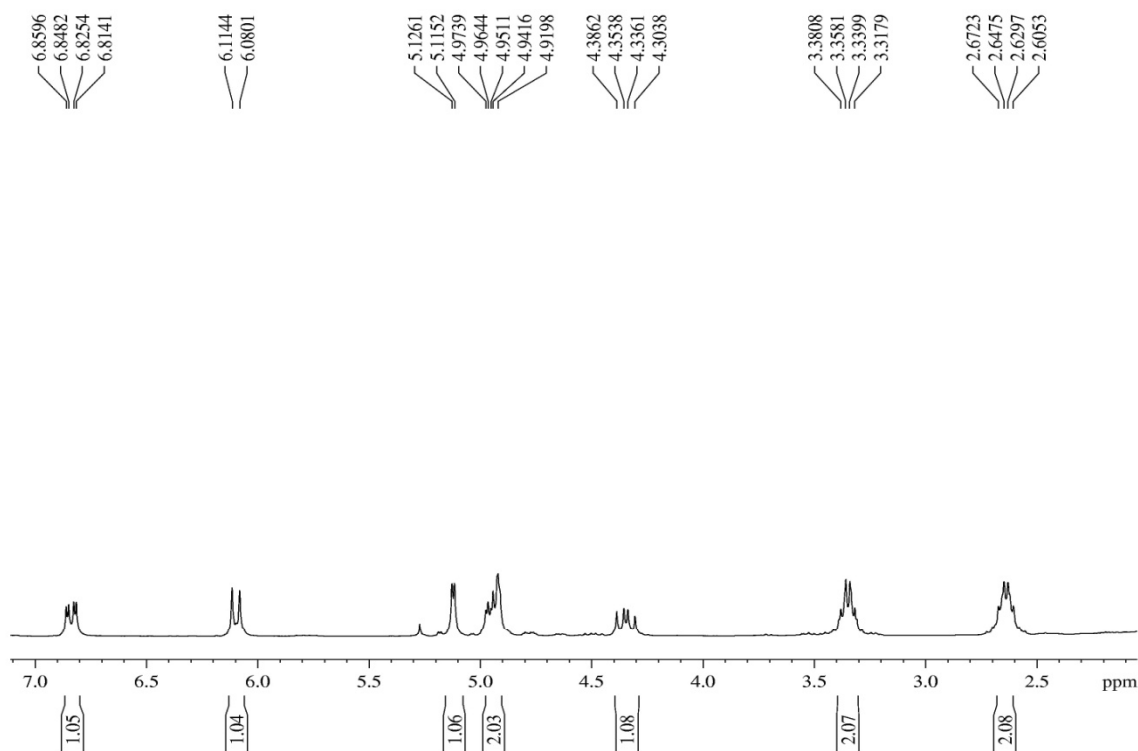
^{13}C NMR Spectrum and its DEPT 135 of compound **50**

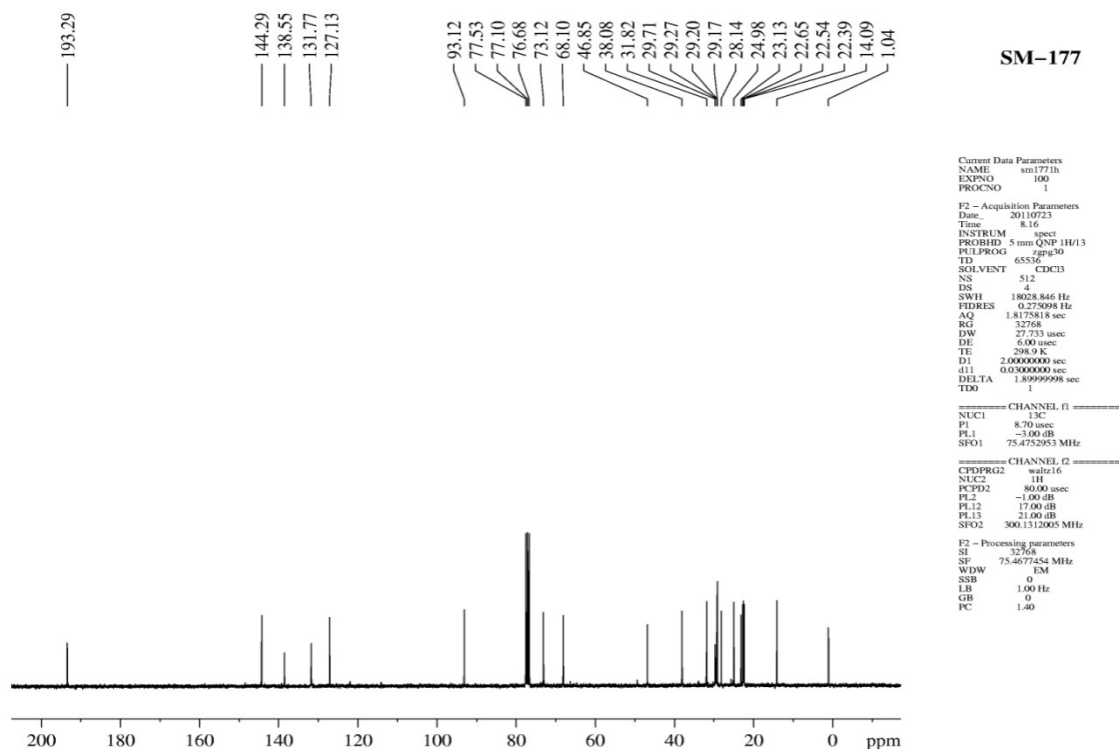
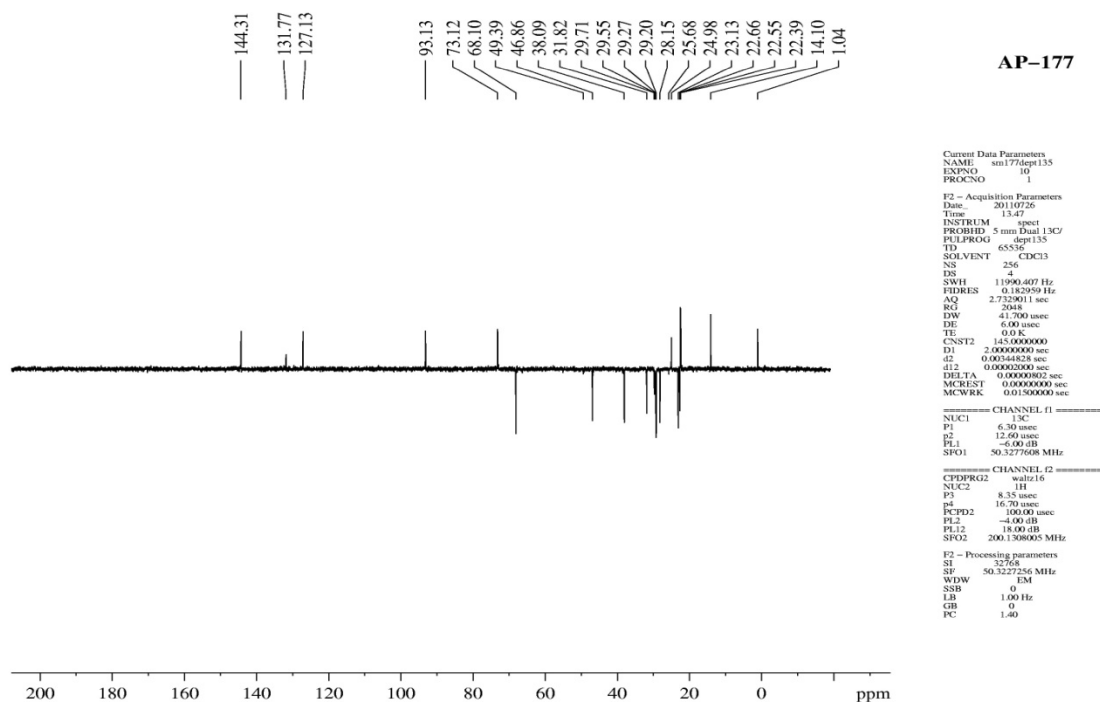


¹H NMR Spectrum of compound **52** and its expansion

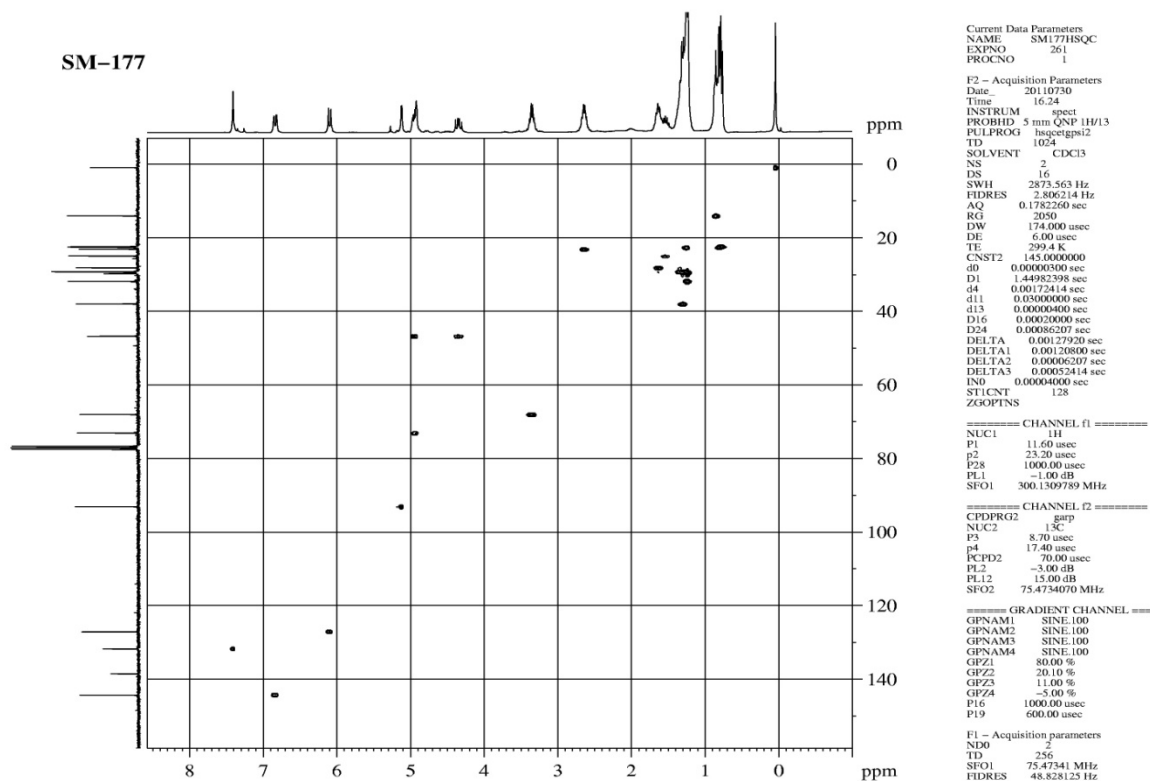
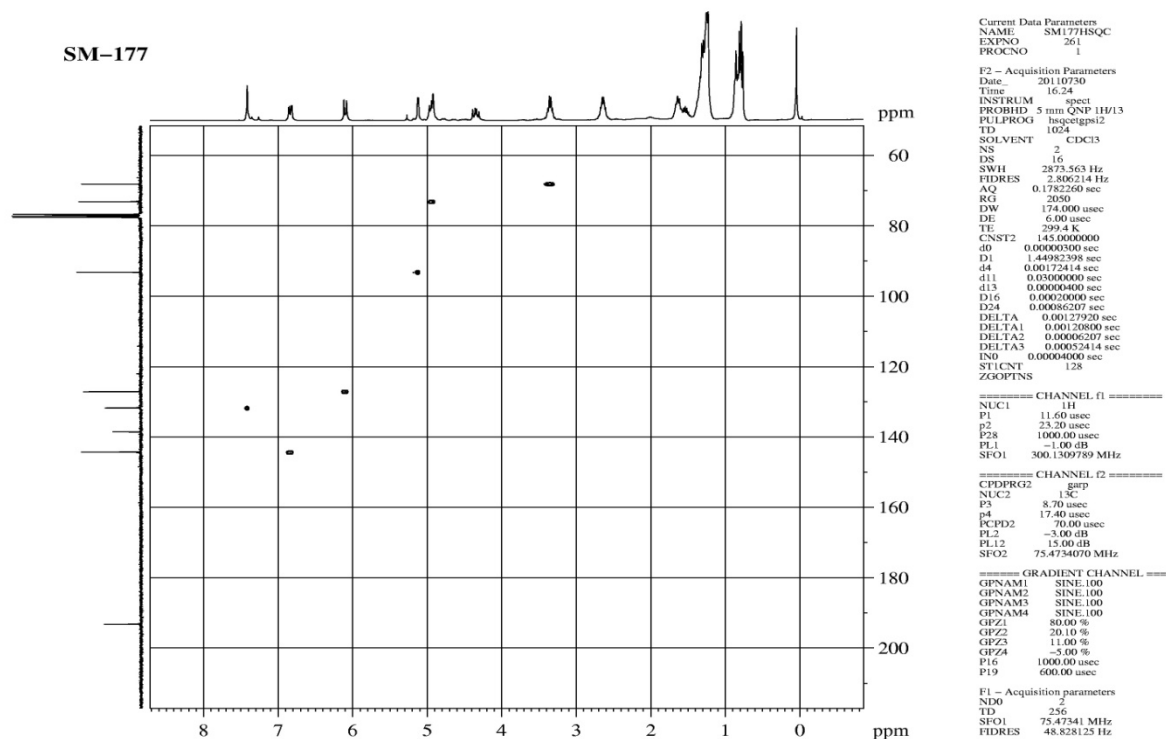


^{13}C NMR Spectrum and its DEPT 135 of compound **52**

¹H NMR Spectrum of compound **53** and its expansion



^{13}C NMR Spectrum and its DEPT 135 of compound **53**

HSQC Spectrum and its expansion of compound **53**

Qualitative Compound Report

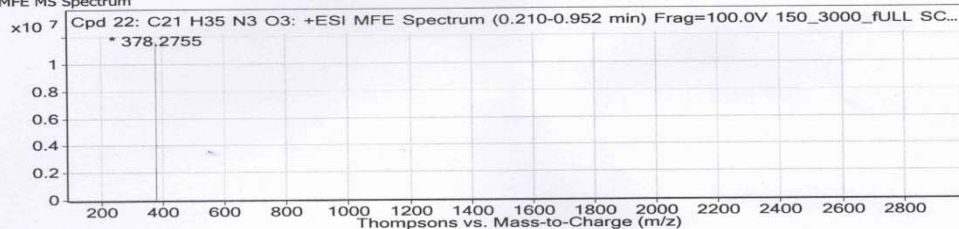
Data File 150_3000_FULL
 SCAN_ISOCRATIC
 GENERALSM-177_368A.d
Sample Name SM-177
Sample Type Sample
Instrument Name Instrument 1
Acq Method 150_3000_FULL
 SCAN_ISOCRATIC
 GENERAL. P.M
Position Vial 24
User Name
Acquired Time 8/10/2011 11:13:36 AM
IRM Calibration Status Success
DA Method 100-1500_AJUGA_APR.m
Comment

Compound Table

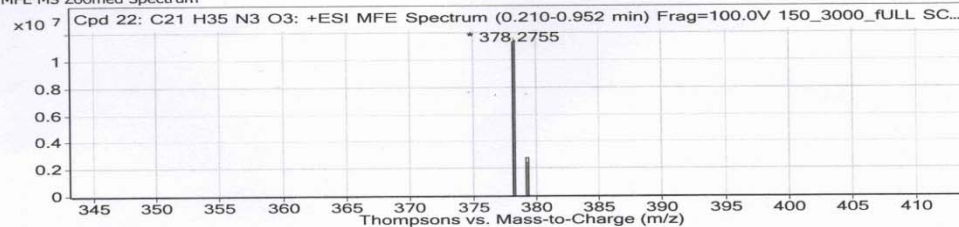
Compound Label	RT	Mass	MFG Formula	MFG Diff (ppm)
Cpd 22: C21 H35 N3 O3	0.462	377.2682	C21 H35 N3 O3	-0.96

Compound Label	RT	Algorithm	Mass
Cpd 22: C21 H35 N3 O3	0.462	Find by Molecular Feature	377.2682

MFE MS Spectrum



MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
378.2755	1	11636184	C21 H36 N3 O3	(M+H)+
379.2787	1	2455614	C21 H36 N3 O3	(M+H)+

HRMS Spectrum of compound **53**