兰州大学

硕士学位论文

含葡萄糖及苯并氮杂卓骨架的1，2，4-三唑、1，3，4-噁二唑、1，3，4-噻二唑杂环衍生物的合成及抗菌活性

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中文摘要

第--部分 含糖骨架的三唑，噁二唑，噻二唑杂环衍生物的合成研究进展

本部分对含有三唑、噁二唑、噻二唑杂环的 N-和 C-糖苷以及其它--些含糖化合物的合成的研究进展进行了综述。

第二部分 含 1,2,4-三唑、1,3,4-噁二唑、1,3,4-噻二唑糖苷衍生物的合成及抗菌活性

通过 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑中巯基对溴代乙酰葡萄糖中溴原子的亲核取代反应，制得 57 个新的 S-及 N-糖苷，其中含三唑环的只生成 S-糖苷产物，并经过水解脱去乙酰保护基，得到水溶性的产物。新化合物通过 NMR、FAB-MS、元素分析确定结构并讨论了其波谱性质，初步评价了它们的抗菌活性。

第三部分 3-杂环基硫取代-1,3,4,5-四氢-2-氧代苯并氮杂卓衍生物的合成

以芳酰肼为原料，合成了一系列 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑，并通过硫原子对 3-溴-2-氧代-苯并氮杂卓 3-位上的亲核取代反应将杂环化合物引入了苯并氮杂卓的结构当中，合成了 32 个新的苯并氮杂卓杂环衍生物，为了提高其在有机溶剂中的溶解性，在苯并氮杂卓的 1-N 位引入乙酸乙酯和乙酸叔丁酯基取代基，合成了其它 36 个新衍生物。所有化合物经质谱，核磁共振及元素分析确证了结构。

ABSTRACT

The dissertation is composed of three parts and 147 new compounds have been synthesized and characterized.

PART I. The Research Process on Synthesis of Triazole, Oxadiazole and Thiadiazole Derivates with Sugar Moiety

The synthesis of triazole, oxadiazole and thiadiazole N- and C- glycosides and other derivatives substituted by sugar moiety were summarized in this part.

PART II. Synthesis and Antibacterial Activity of Thio-glucopyranoside Derivatives Bearing 1,2,4-triazole, 1,3,4-oxadiazole or 1,3,4-thiadiazole

S- and N-glycoside of 5-aryl-1,2,4-triazole-3-thiones, 5-aryl-1,3,4-oxadiazole-2-thiones, and 5-aryl-1,3,4-thiadiazole-2-thiones were synthesized by their stereoselective coupling reaction with bromo sugar in presence of potassium hydroxide, followed by deprotection using sodium methoxide in methanol. All products were characterized by ^{1}H NMR, ^{13}C NMR, MS spectra and elemental analysis. Result from primary antibacterial activity test indicated that some of the compounds were effective against *Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Streptococcus, Candida albicans.*

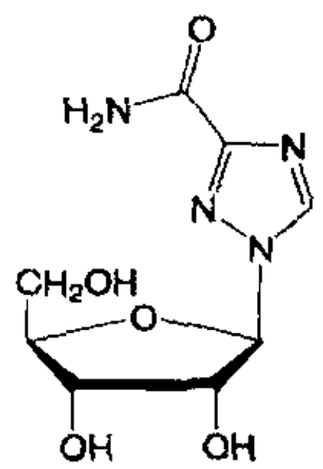
PART III. Synthesis and Antibacterial Activity of 3-Thio-benzazepine Derivatives Bearing 1,2,4-triazole, 1,3,4-oxadiazole or 1,3,4-thiadiazole

The three types of heterocyclyl thio compounds were synthesized from hydrazides through different ways. By the nucleophilic substitution of S to Br, we synthesized 33 derivatives of tetrahydro-2-oxo-1*H*-benazepine and other 36 derivatives which have an ester substituent on the 1-*N* position of benazepine in order to gain a strengthened dissolving ability in organic solvents. The structures of these compounds were determined by MS, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis. The antibacterial activities were also evaluated.

第一部分 含糖骨架的三唑，噁二唑，噻二唑杂环衍生物的合成研究进展

一、引言

抗病毒药物利巴伟林，又名病毒唑（Ribavirin, 1-β-D-呋喃核糖基-1,2,4-三唑-3-酰胺）首先由 Witkoski 小组于 1972 年合成并报道[1]，它对 DNA 和 RNA 病毒都具有高效、广谱的抗病毒活性[2,3]。早在 1986 年，FDA 就已经批准用 Ribavirin 作为治疗 respiratory syncytial virus(RSV)感染的药物。



Ribavirin

此药为广谱抗病毒核苷类药物，可抑制单磷酸次黄嘌呤核苷（IMB）脱氢酶，从而抑制 IMB 转变为鸟苷酸，阻碍病毒核酸的合成，而达抗病毒作用。对多种病毒，如呼吸道合胞病毒、流感病毒、单纯疱疹病毒等有抑制作用。对流感(由流感病毒 A 和 B 引起)、腺病毒肺炎、甲型肝炎、疱疹、麻疹流行性出血热及病毒性脑炎等有防治作用。治疗丙型肝炎的标准疗法是联用 Ribavirin 加干扰素，而 SARS 的治疗也是以抗病毒药物 Ribavirin 及类固醇为主，并且 Ribavirin 被证实具有很强的抗 HIV 活性，是治疗艾滋病的药物之一。

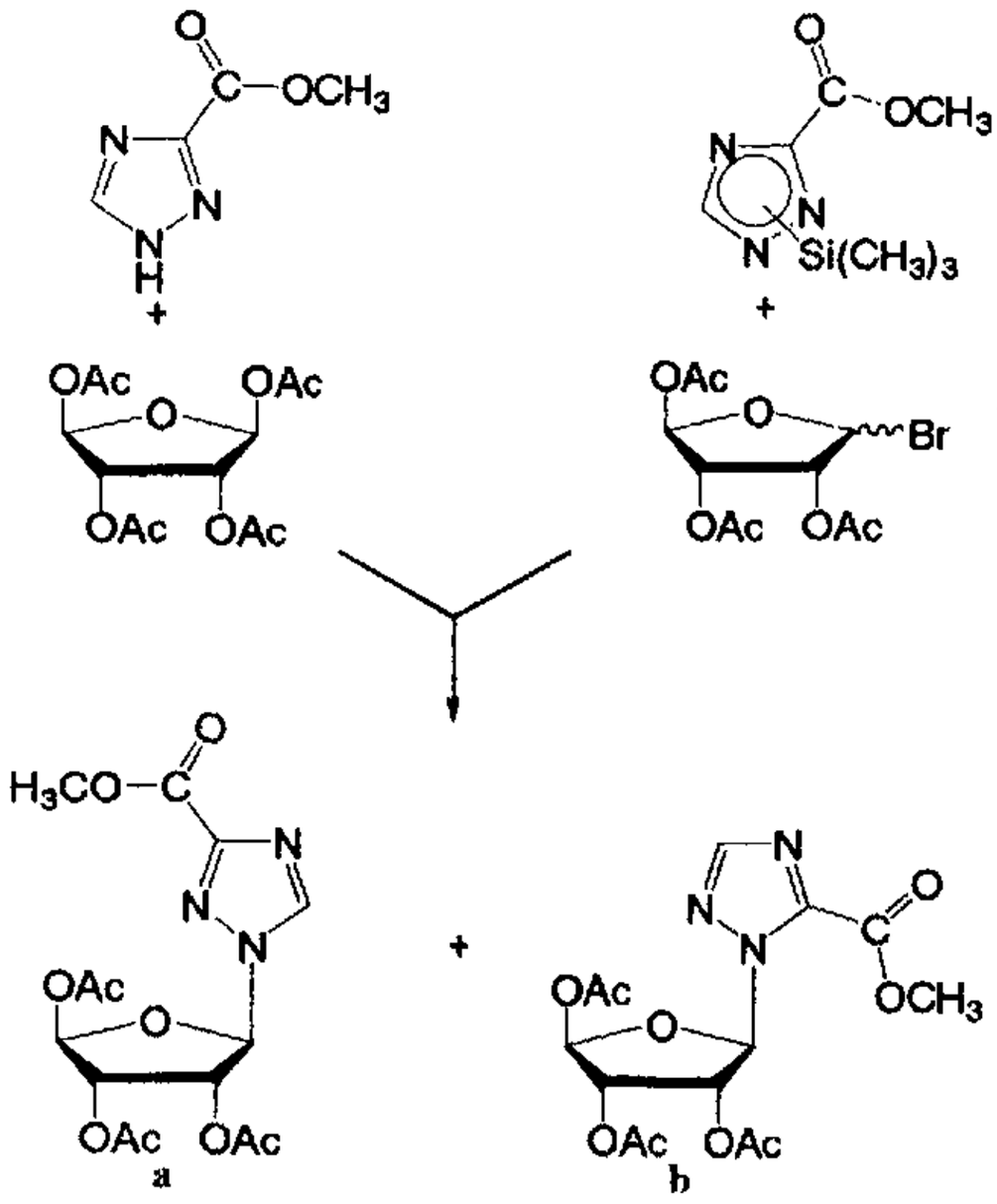
单晶 X-ray 研究表明[4,5]，Ribavirin 中酰胺基上的羰基氧原子和氨基氮原子和次黄嘌呤及鸟嘌呤中 O-6 和 N-1 原子在空间上很相似。因此其作用相信与抑制病毒复制有关。

鉴于 Ribavirin 的广泛作用以及抗病毒药物种类缺乏的现状，许多科学家对杂环接糖类化合物的合成产生了浓厚兴趣，现对糖接三唑，噁二唑，噻二唑杂环衍生物合成的研究进展综述如下。

二、三唑类化合物的合成

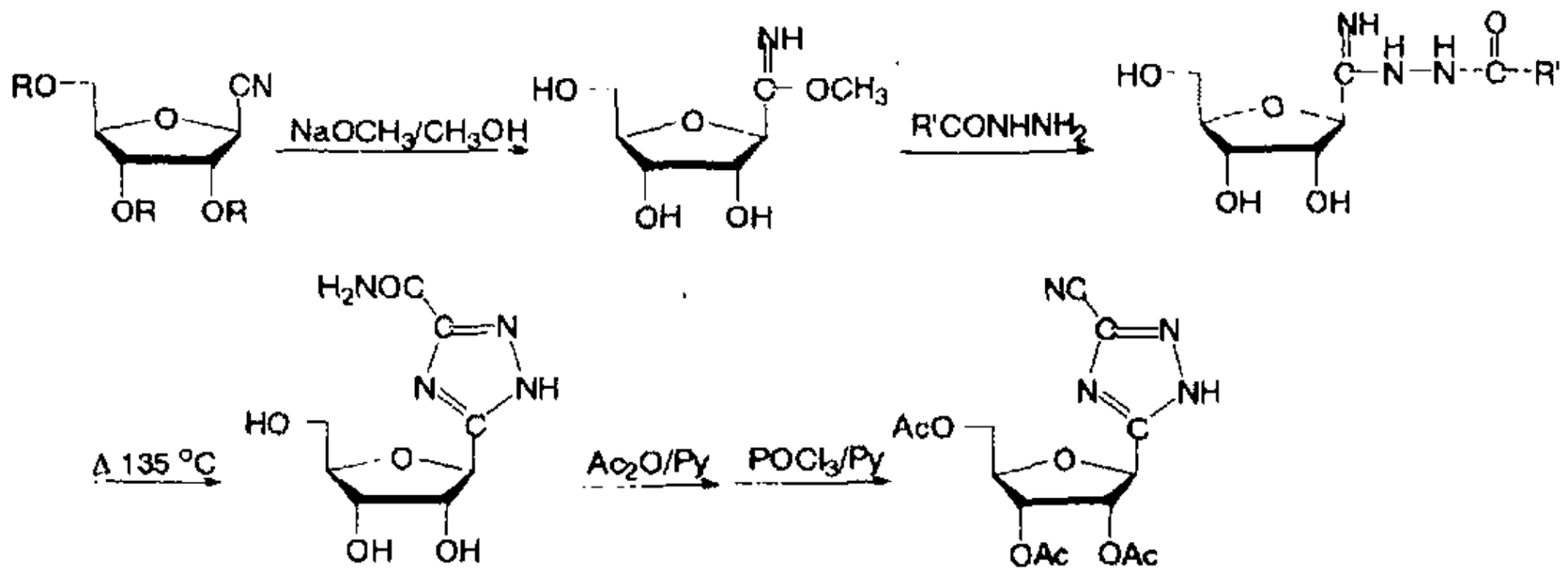
1. 1,2,4-三唑

Witkoski于1972年分别用两种方法合成了1-β-D-核糖基-1,2,4-三唑[1]。一种方法是将乙酰核糖和三唑混合后在油浴上加热至160-165 °C融化，加入二对硝基苯基磷酸酯，在减压下保持温度15-20分钟重结晶后即以78%的产率得到产物a。另一种方法是将三甲基硅基保护的三唑与溴代核糖在乙腈溶液中室温反应，得到a (46%)与b (51%)的混合物。1988年Sanghvi用第一种方法合成了其它一些带氰基和卤素等取代基的化合物，并测定了对嘌呤核苷磷酸化酶（PNPase）的阻拒活性[6]。



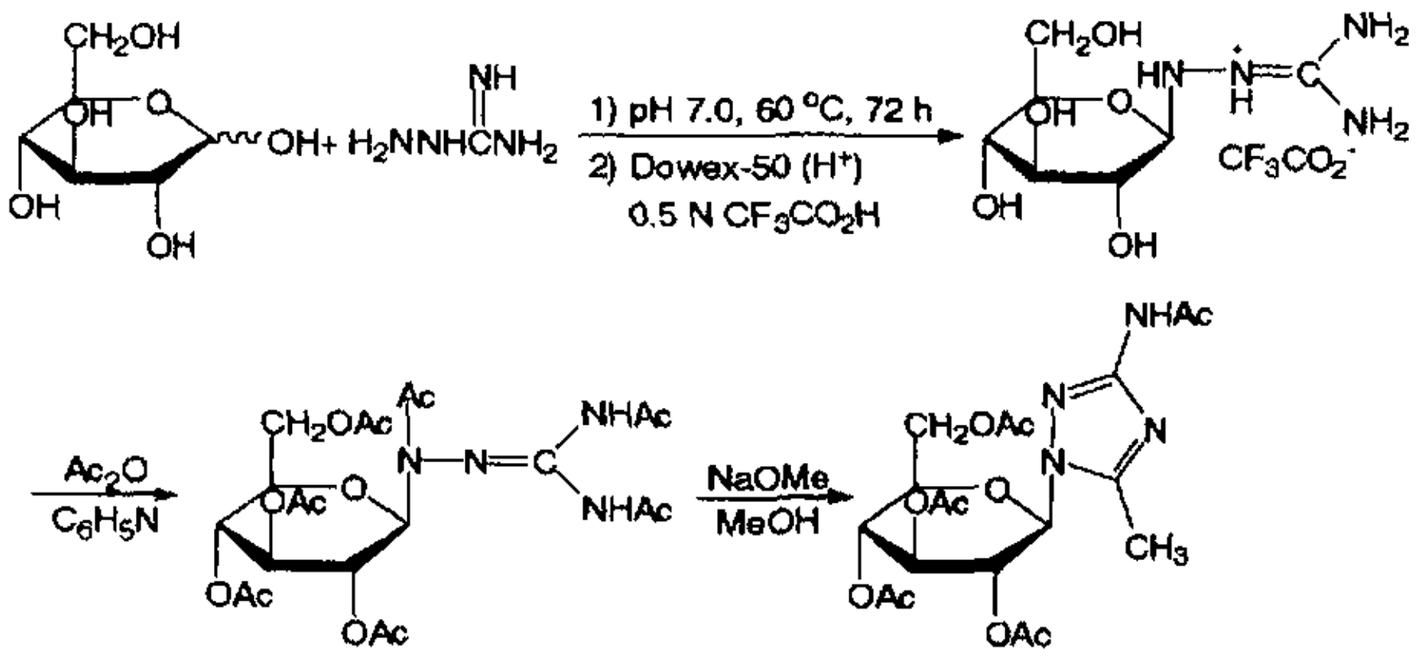
Scheme 1-1

之后Wigfield于1977年发表了Ribavirin的C-核苷类似物的合成[7]。他的方法是将bofuranosyl-1-carboximidic acid methyl ester与草酰胺酰肼反应后再加热至135 °C脱水关环得到产物。



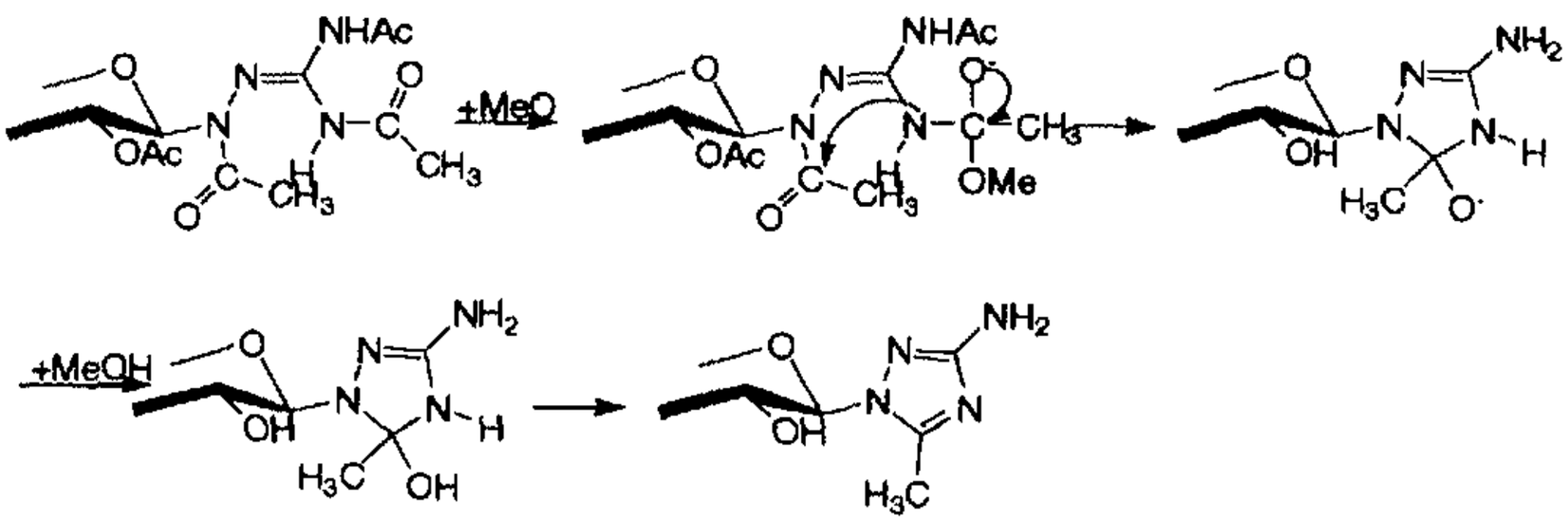
Scheme 1-2

1997 年 Gyorgydeak 用 D-葡糖与氨基胍反应得到的糖基氨基胍，乙酰化后在温和的条件下关环得到 3-氨基-N^1-吡喃葡糖基-5-甲基-1*H*-1,2,4-三唑[8,9]。



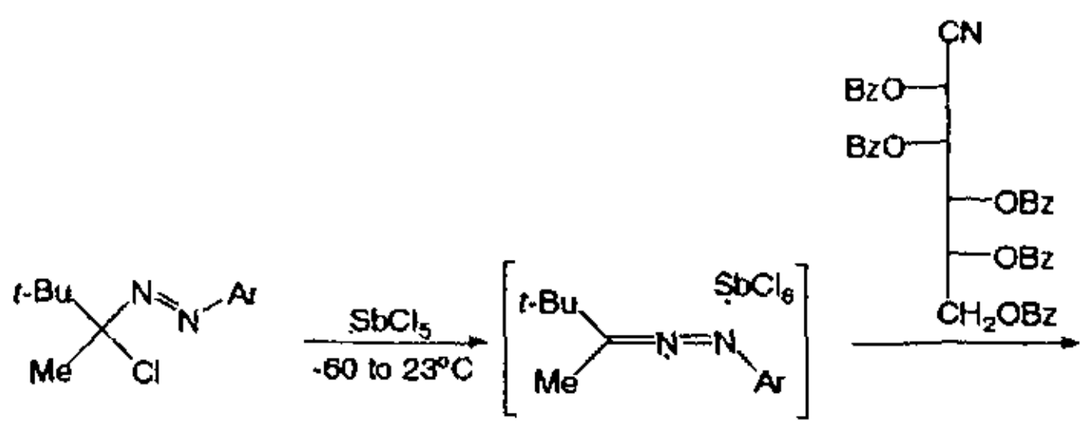
Scheme 1-3

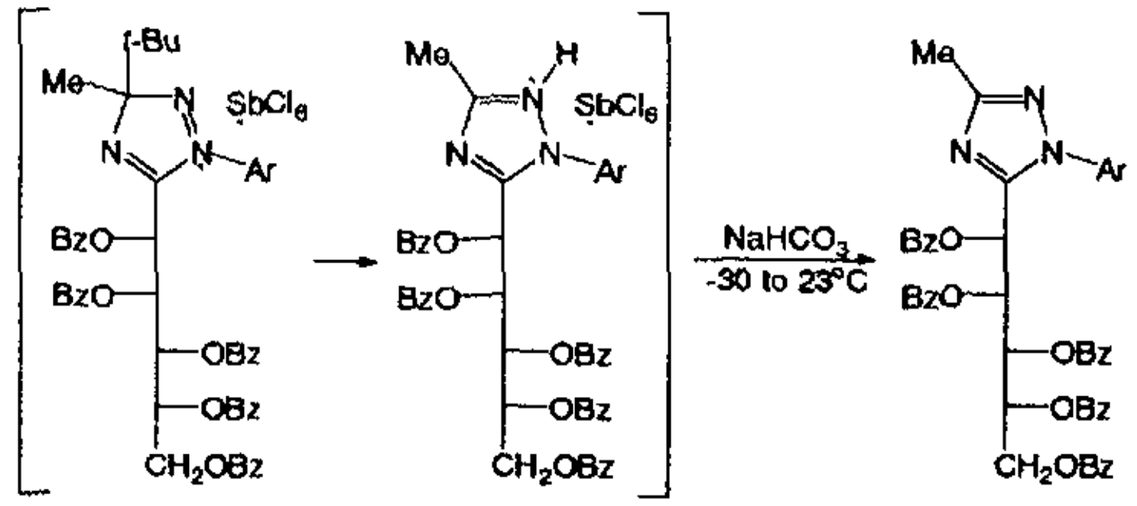
Yu 解释了其合环机理如下[10]，应该是由氮进攻羰基合环后再脱水得到 1,2,4-三唑：



Scheme 1-4

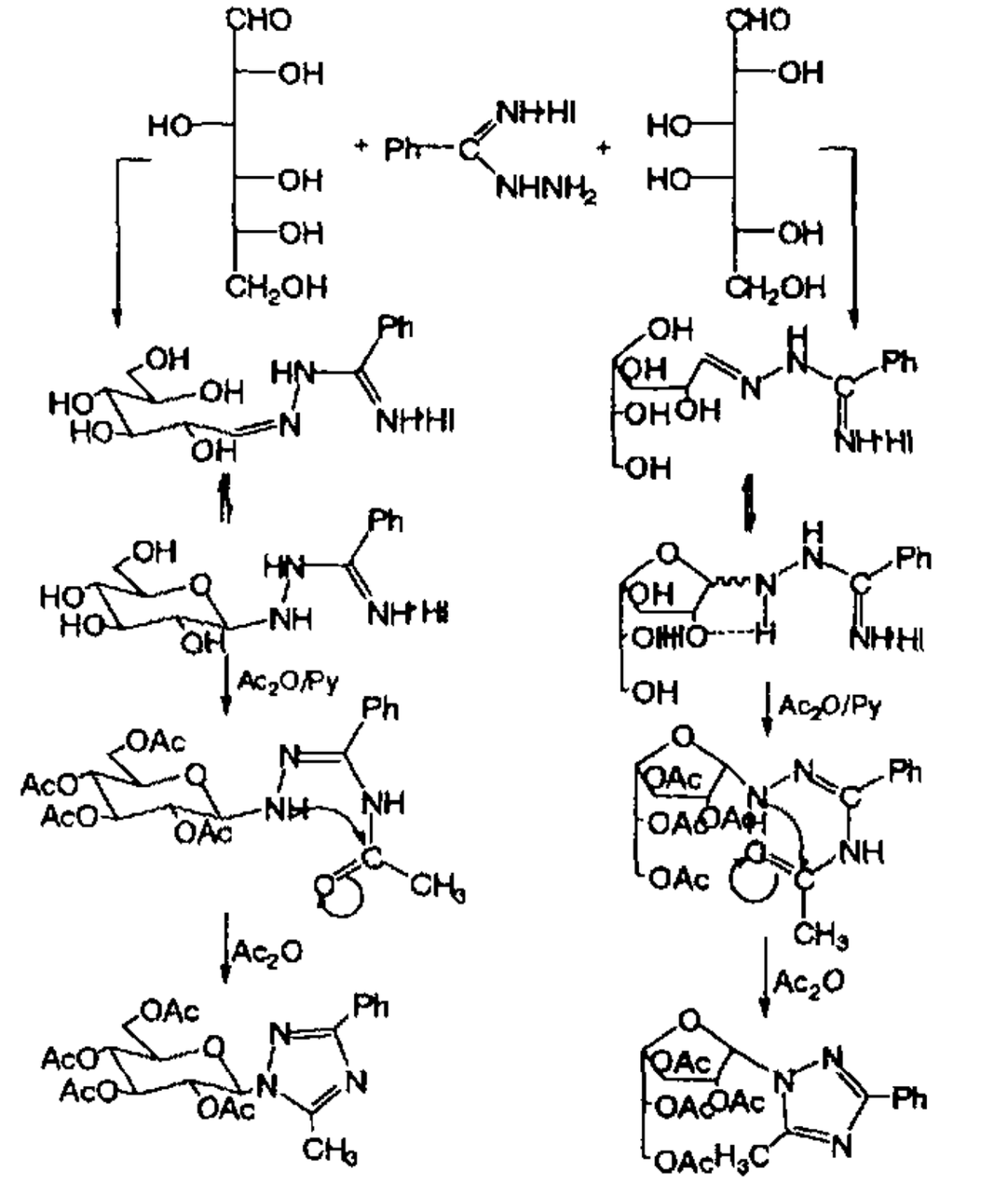
Al-Masoudi 等人用 1-氮杂-2-氮翁丙二烯盐和苯甲酰基保护的糖基氰进行环加成，生成的中间体重排得到质子化的 1,2,4-三唑，之后再水解生成非环状的 1,2,4-三唑 C-核苷[11-13]。





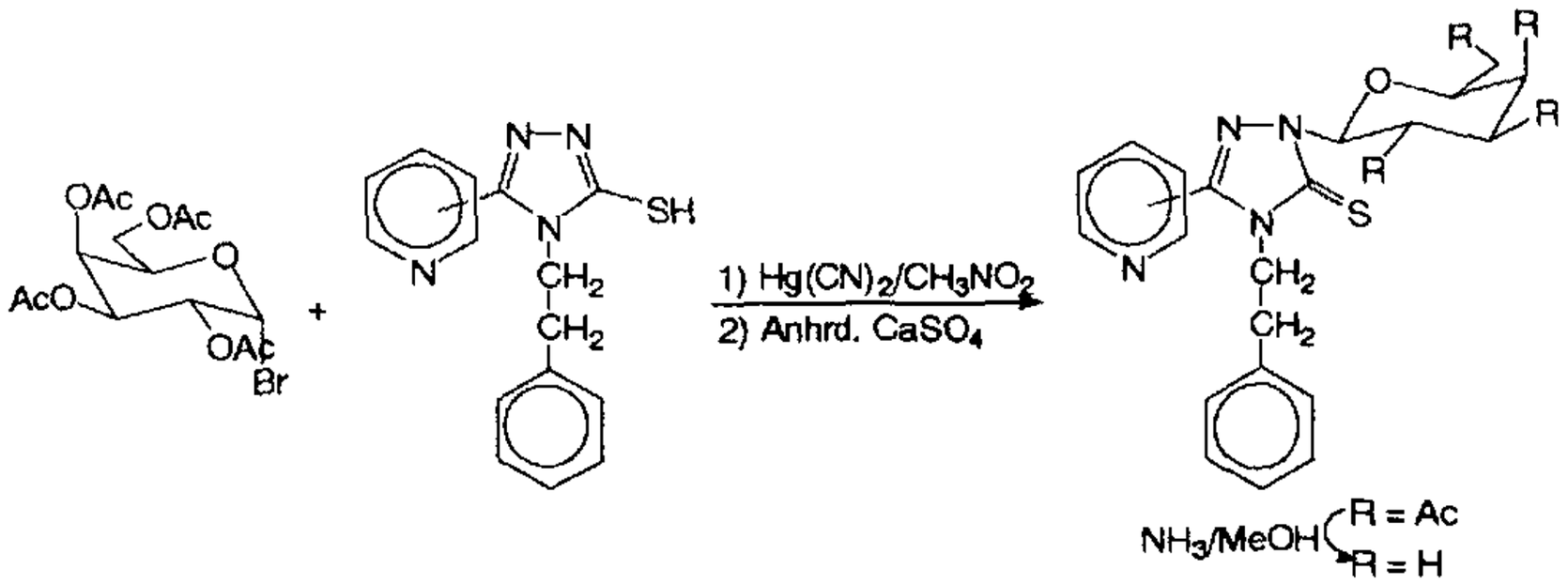
Scheme 1-5

苯甲酰胺腙的氢碘酸盐与 D-葡糖和 D-半乳糖反应后再乙酰化，既可分别得到 1-(2,3,4,6-四-*O*-乙酰基-β-D-吡喃葡糖基)-和 1-(2,3,5,6-四-*O*-乙酰基-α-D-呋喃半乳糖基)-5-甲基-3-苯基-1*H*-1,2,4-三唑[14]。



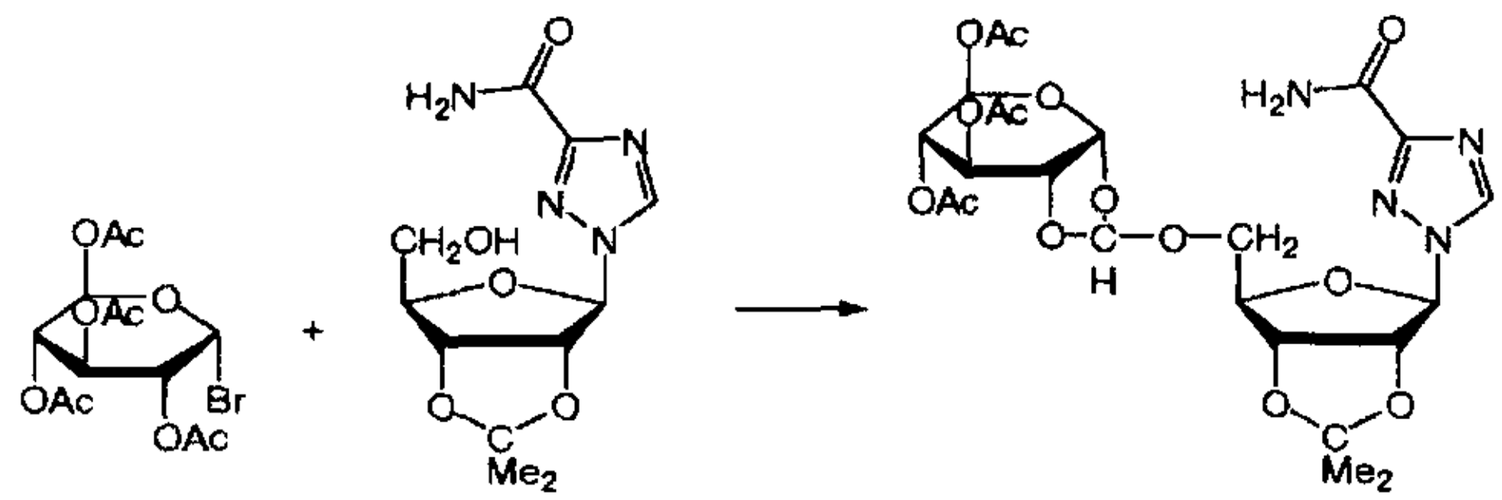
Scheme 1-6

Zamani 等人用卤代糖和 4,5-二取代-1,2,4-三唑-3-硫酮在氧化汞的存在下发生偶联反应，制得一系列 N-糖苷[15]。



Scheme 1-7

以及合成 Ribavirin 多糖的类似物的例子[16]：

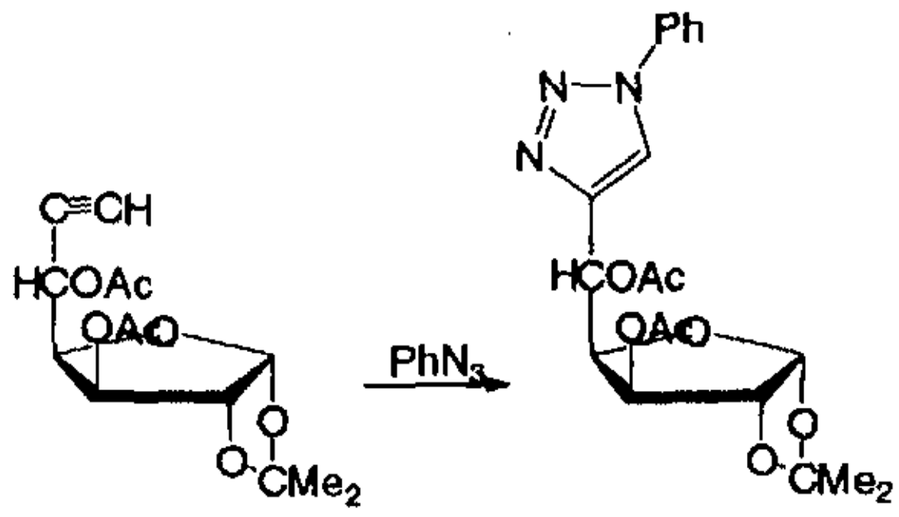


Scheme 1-8

2. 1,2,3-三唑

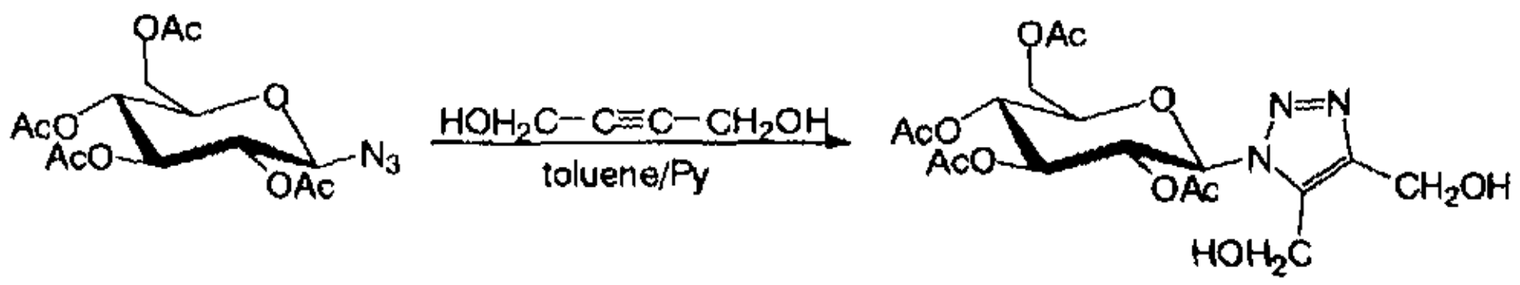
2.1 接 1,2,3-三唑的糖苷

乙炔糖与苯基叠氮共同加热生成 4-糖基-1,2,3-三唑，同时也混有少量 5-取代产物[17,18]。



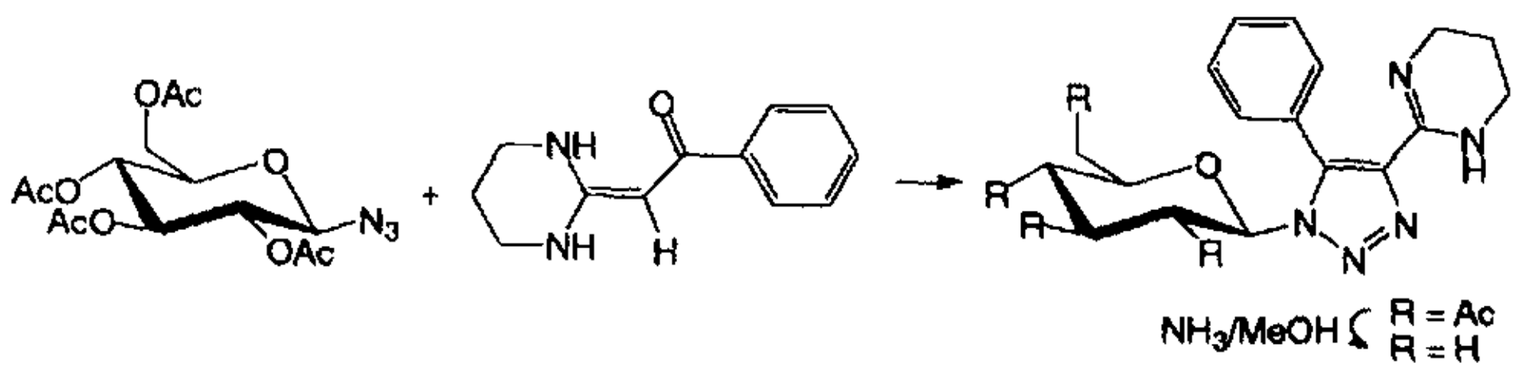
Scheme 1-9

相应的另一种合成方法就是用糖基叠氮与取代炔烃反应[19,20]。



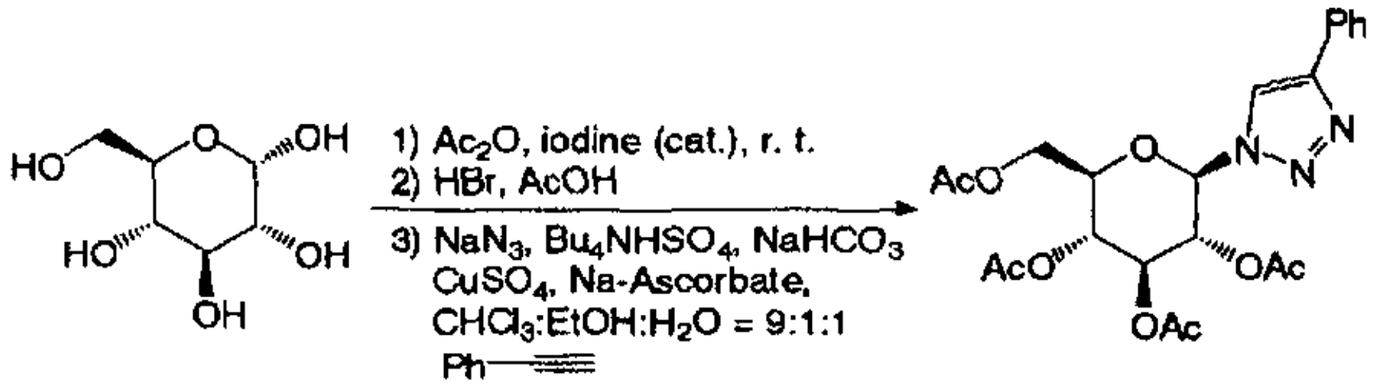
Scheme 1-10

Chen 等人用苯甲酰基取代的乙烯酮缩胺和葡糖基叠氮反应，合成了一系列1-葡糖基-4-杂环基-5-苯基-1,2,3-三唑，并初步发现它们具有抗肿瘤和抗菌的活性[21]。



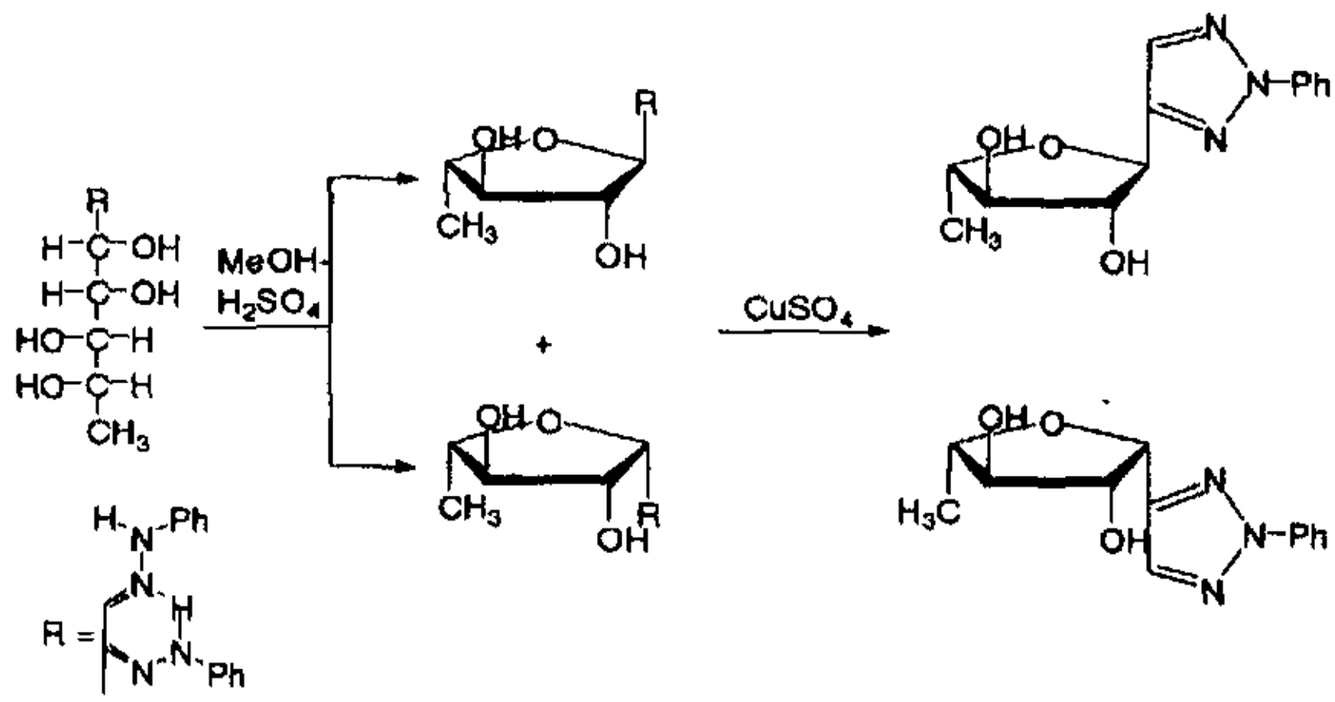
Scheme 1-11

2005年Chittaboina等人报道了糖接1,2,3-三唑的高效一锅合成方法[22]。其中关键步骤是Cu(I)催化的1,3-偶极环加成。它提供了一个通过未保护或全乙酰化的糖合成N-糖苷的便利方法。



Scheme 1-12

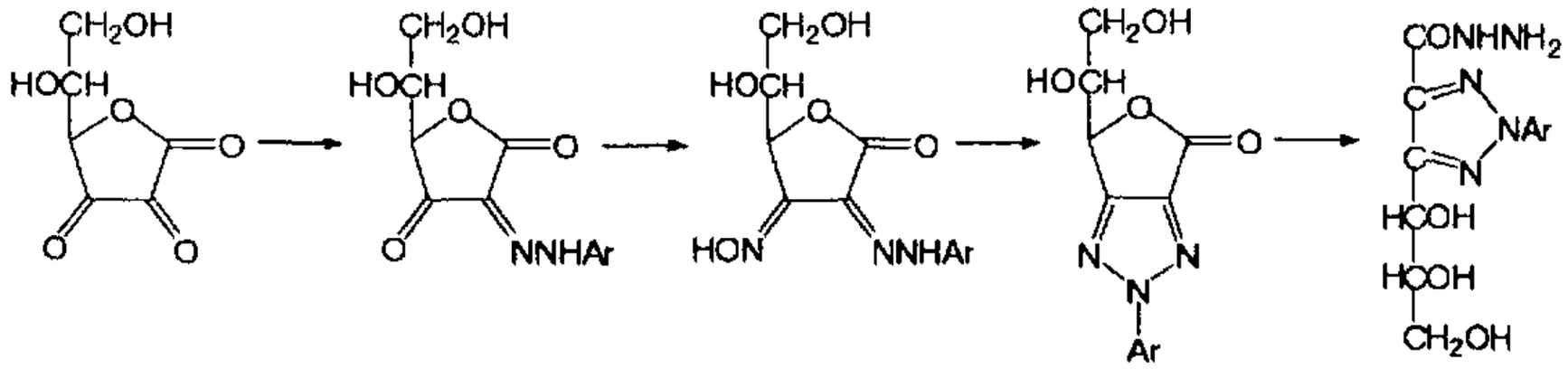
Sallam 报道了用糖脎与硫酸铜在乙醇中回流得到 1,2,3-三唑的 C-糖苷[23, 24]。



Scheme 1-13

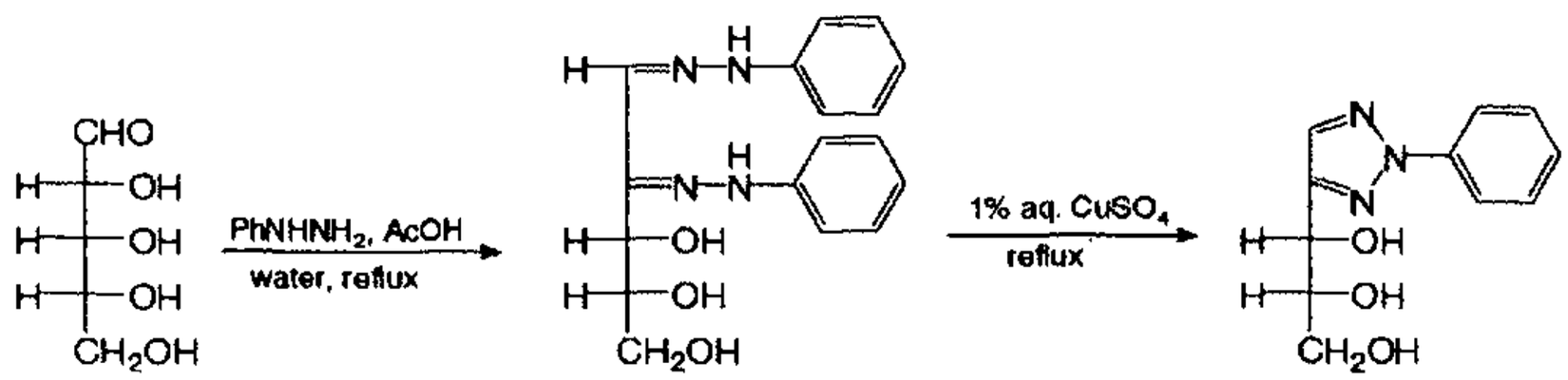
2.2 在糖环或链上直接构筑1,2,3-三唑

EL Sekily 等人用酮与芳基肼反应得腙，另一羰基与羟胺反应得肟，此化合物在醋酐中加热即得到带 1,2,3-三唑的内酯，之后再用水合肼处理得到 2-芳基-4-(D-赤-丙三醇-1-基)-1,2,3-三唑-5-乙酰肼[25-29]。



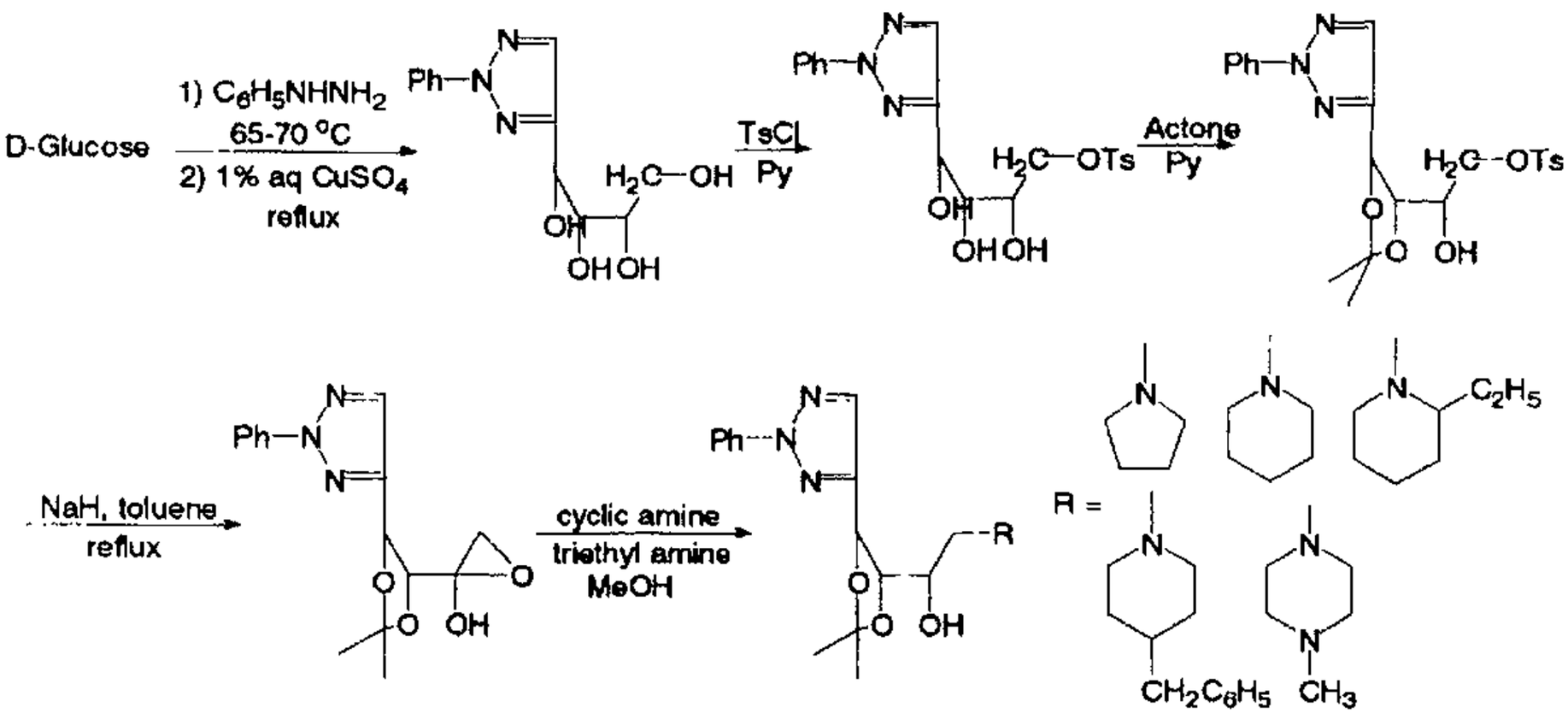
Scheme 1-14

Hann等人从相应的糖出发与苯肼反应转变为腙再于1%硫酸铜水溶液中合环，以两步43-54%的总产率制得三唑基糖[30-34]。



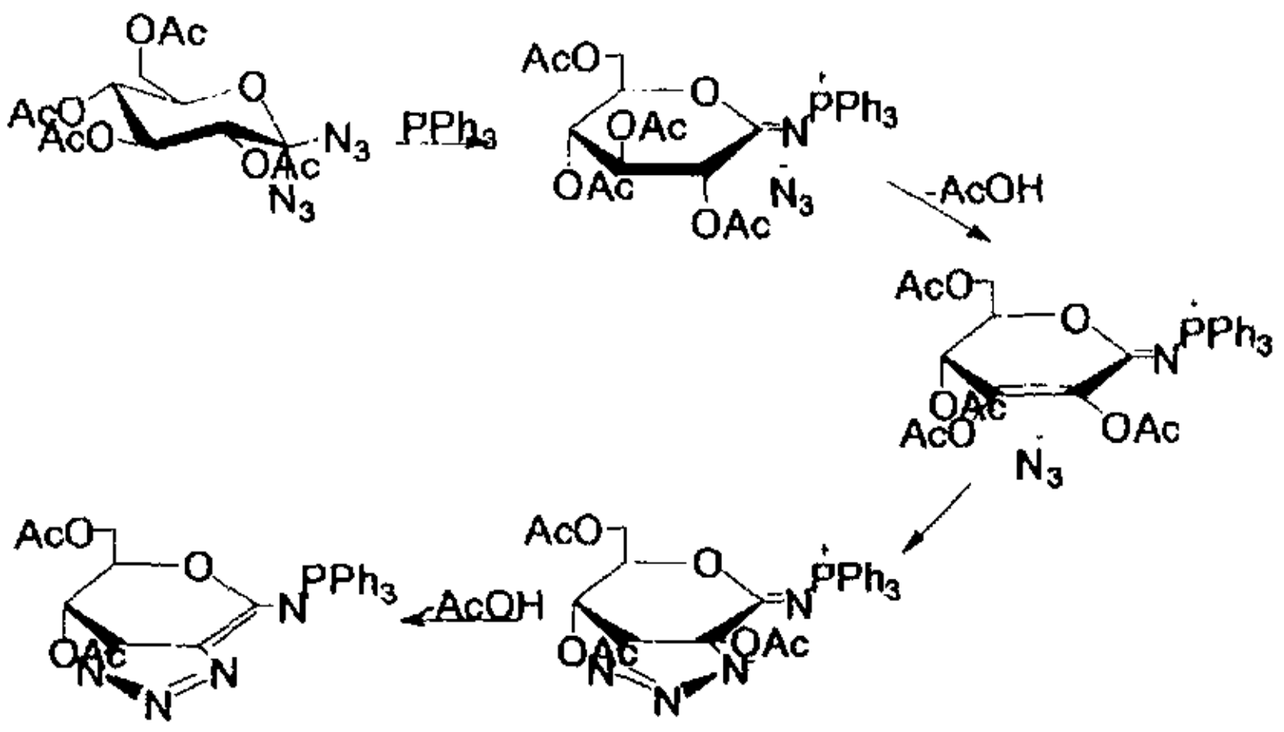
Scheme 1-15

Tyagi 等人用同上的方法从 D-葡糖开始以五步 15%的总产率合成了环氧化合物，以 70-85%的产率用相应的环胺使环氧开环合成了五个带有非天然碱基的非环状核苷，并检测了它们的抗病毒和抗 HIV 活性[35]。



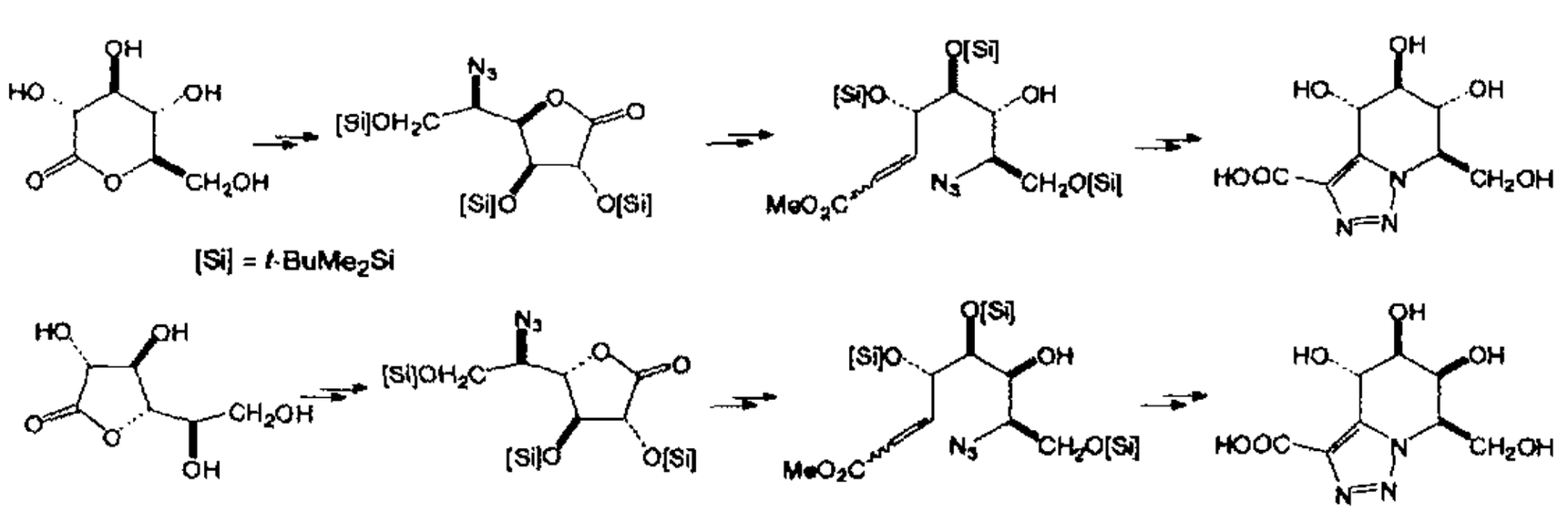
Scheme 1-16

Kovacs 等人用 1,1-二叠氮基葡糖与三苯基磷在干燥乙醚中室温反应 24 小时即可以 86%的产率得到 6,7-脱氢吡喃并[3,4-*d*]υ-三唑[36,37]。



Scheme 1-17

最后一类反应是通过叠氮基对不饱和酯的分子内[1,3]-二偶极环加成得到与三唑相关的 D-葡糖和 D-半乳糖[38-42]。

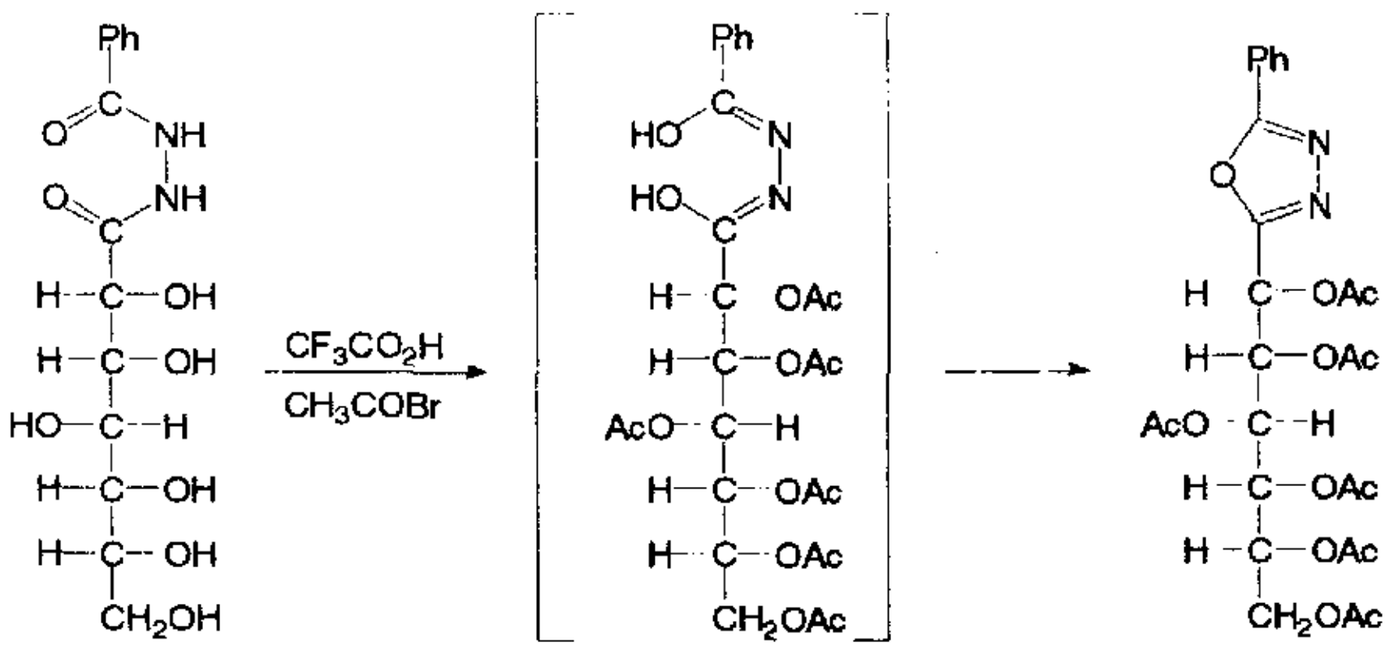


Scheme 1-18

三、噁二唑类化合物的合成

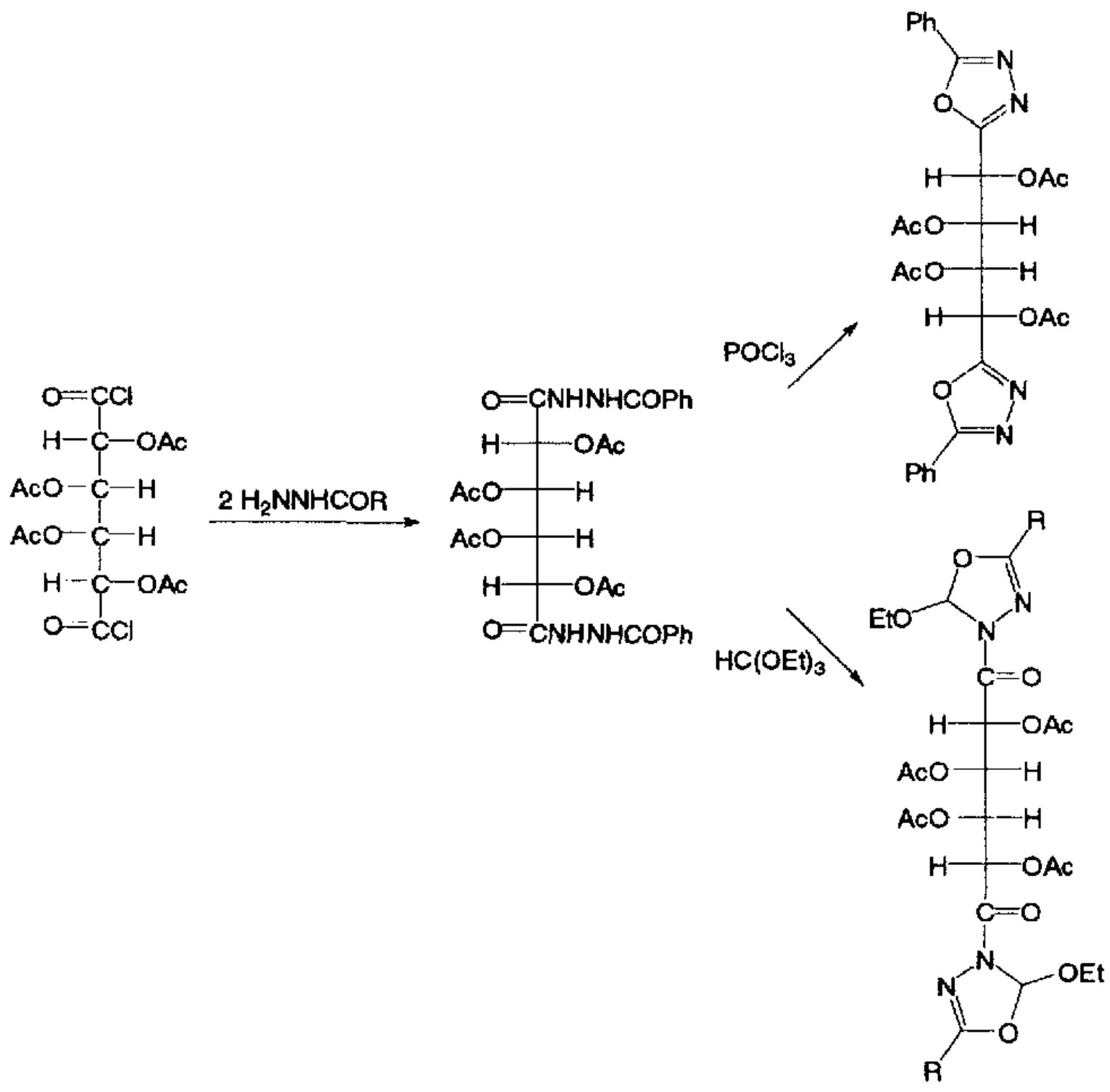
1. 1,3,4-噁二唑

Sallam 报道了将苯甲酰肼连庚糖用三氟乙酸和乙酰基溴乙酰化并环化制得噁二唑 C-糖苷[43]。



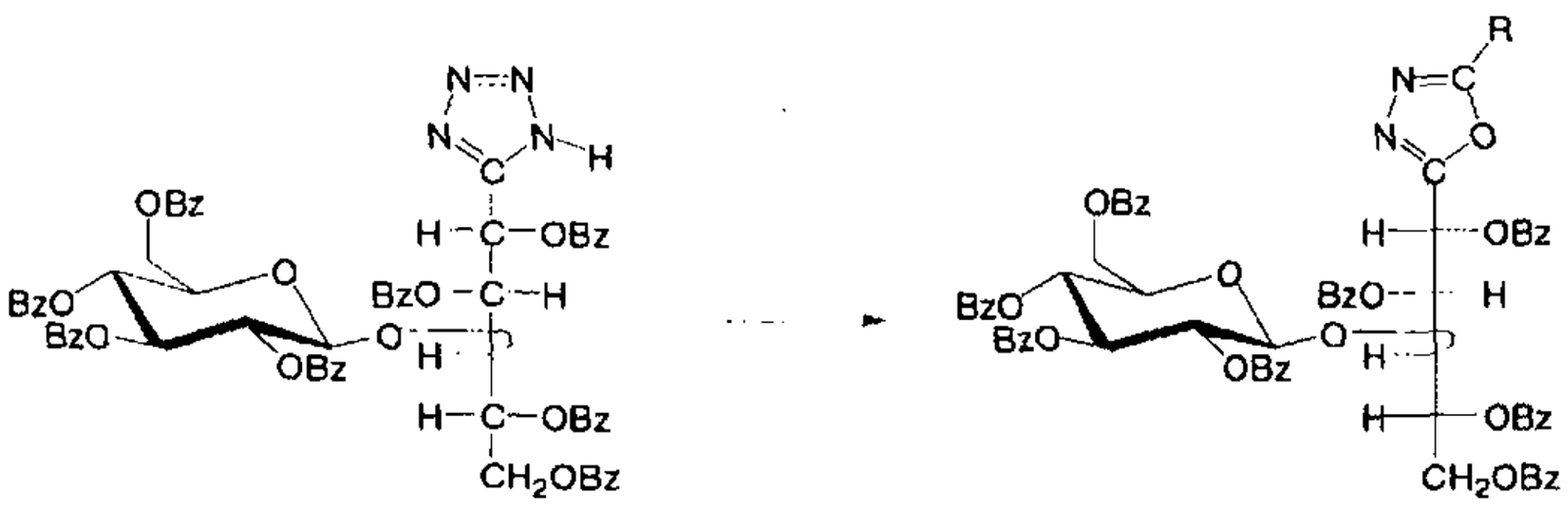
Scheme 1-19

Shaban 等人连续报道了双噁二唑糖苷的合成方法。在三氯氧磷中脱水关环可以同上得到 C-糖苷，但在原甲酸三乙酯存在下关环则得到连 N 的 1,3,4-噁二唑产物[44-47]。



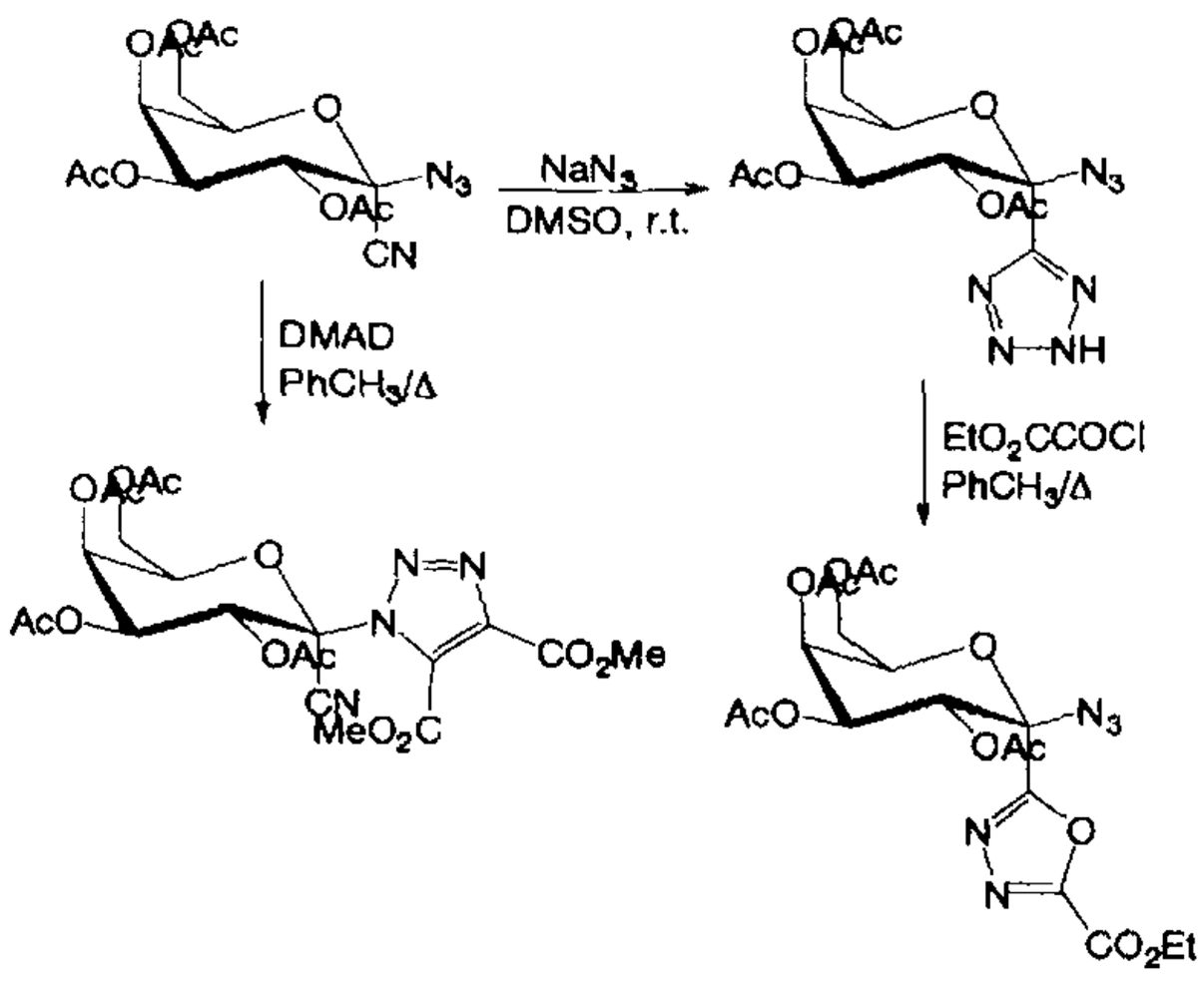
Scheme 1-20

Alho 等人用乙酸酐或苯甲酰氯处理四唑得到 1,3,4-噁二唑产物[48]。



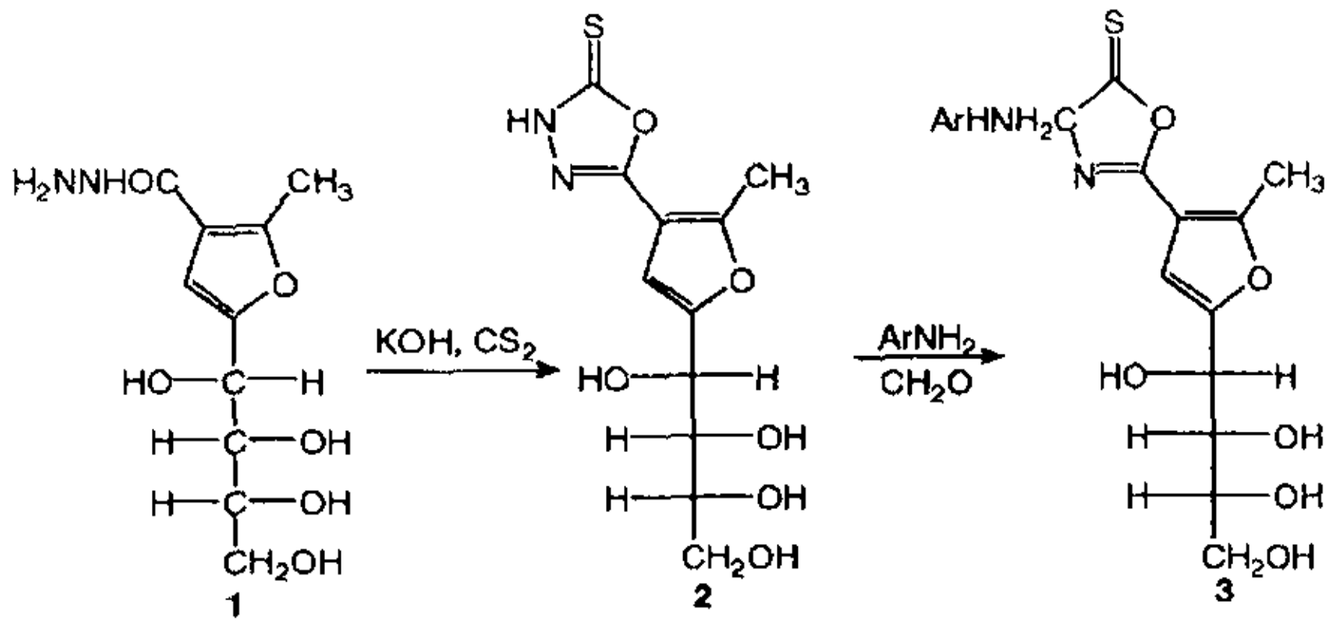
Scheme 1-21

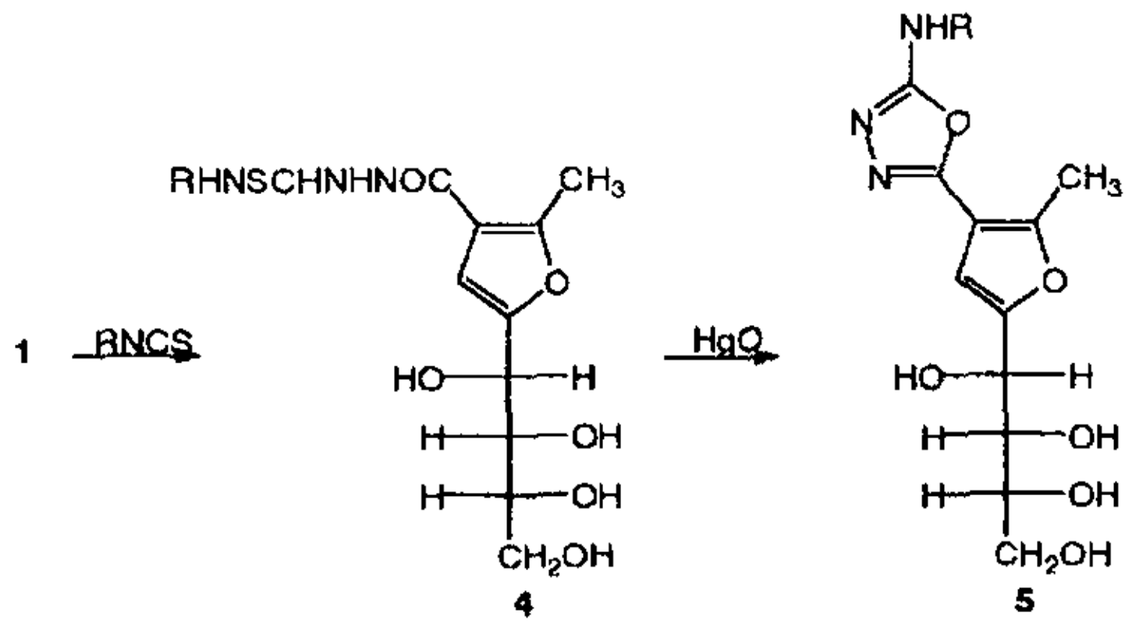
Somsak 等报道了用叠氮基氰基糖分别用 DMAD 处理得三唑接糖和用叠氮化钠、酰氯处理得噁二唑接糖的产物[49]。



Scheme 1-22

Hassan 等人用酰肼和二硫化碳合成糖接呋喃接噁二唑的产物[50]。

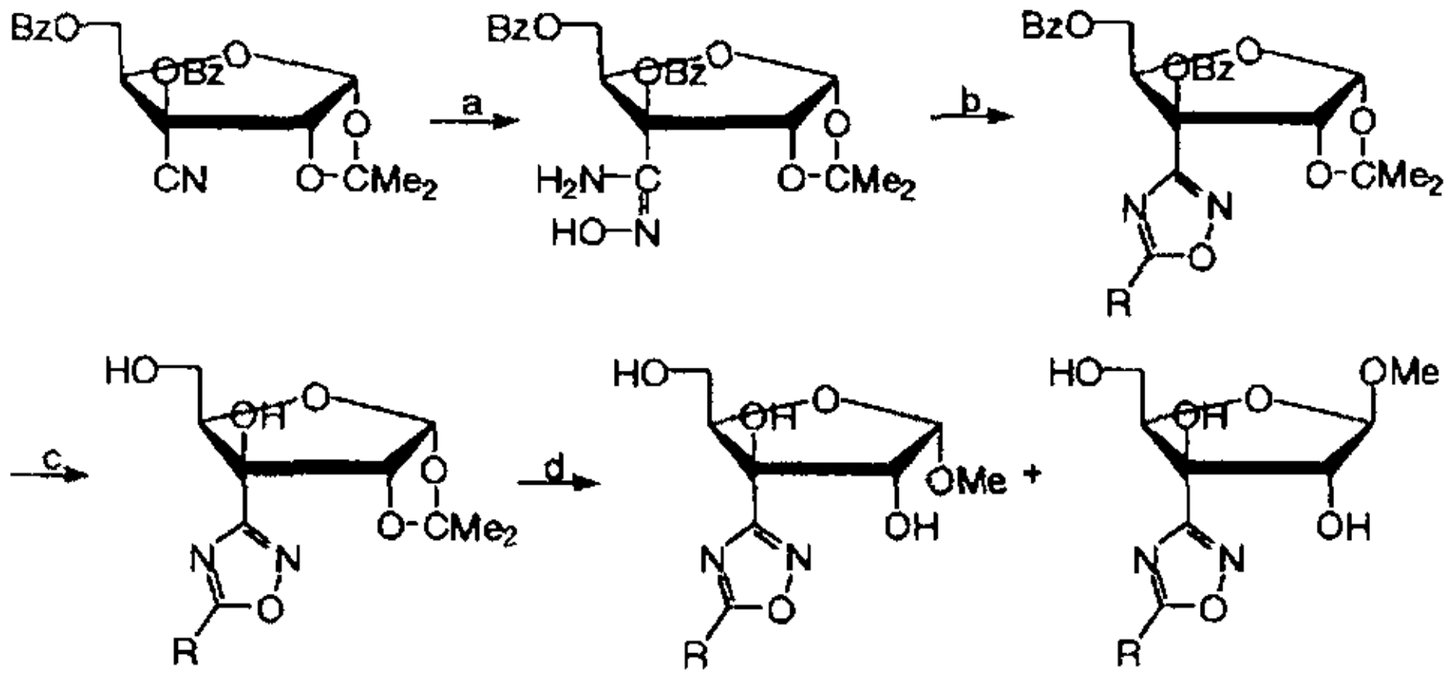




Scheme 1-23

2. 1,2,4-噁二唑

由糖基羟腈合成糖-3-基-1,2,4-噁二唑，再分别在甲醇钠和酸性条件下脱去苯甲酰基和丙叉基保护[51,52]，得最终产物。



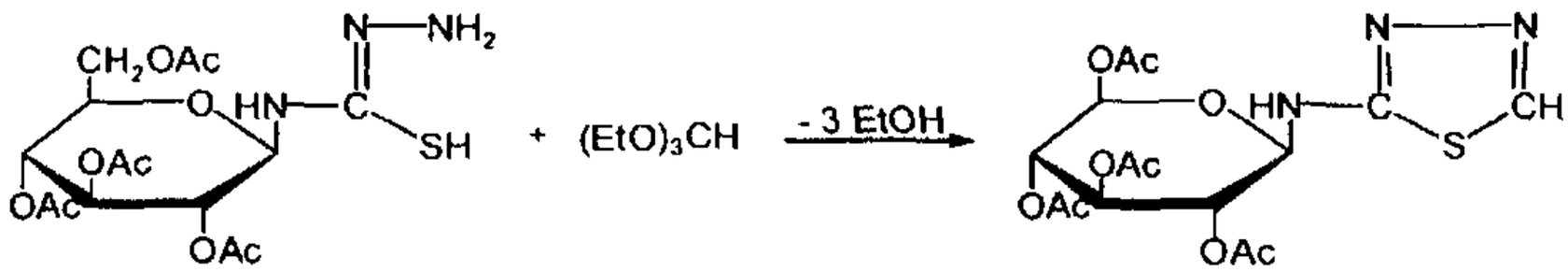
a. NH_2OHCH_2OH, b. Ac_2O, $(C_2H_5CO)_2O$, or benzoyl chloride,

c. MeOH, NaOMe, d. 1% anhydrous HCl-MeOH.

Scheme 1-24

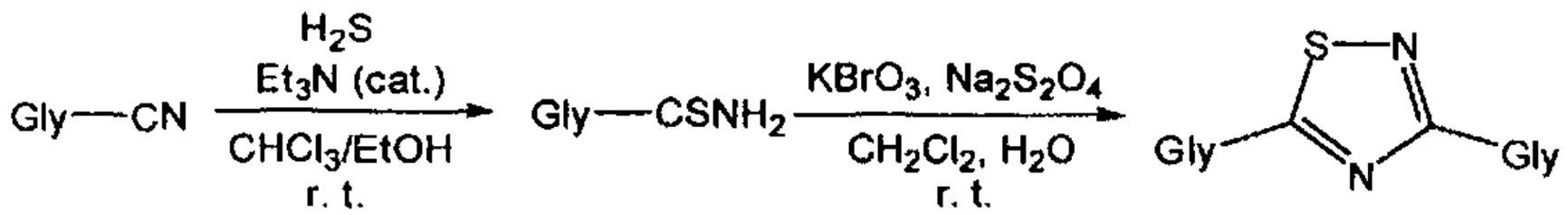
四、噻二唑类化合物的合成

糖基氨基硫脲和原甲酸三甲酯反应生成葡糖基氨基噻二唑[53]。



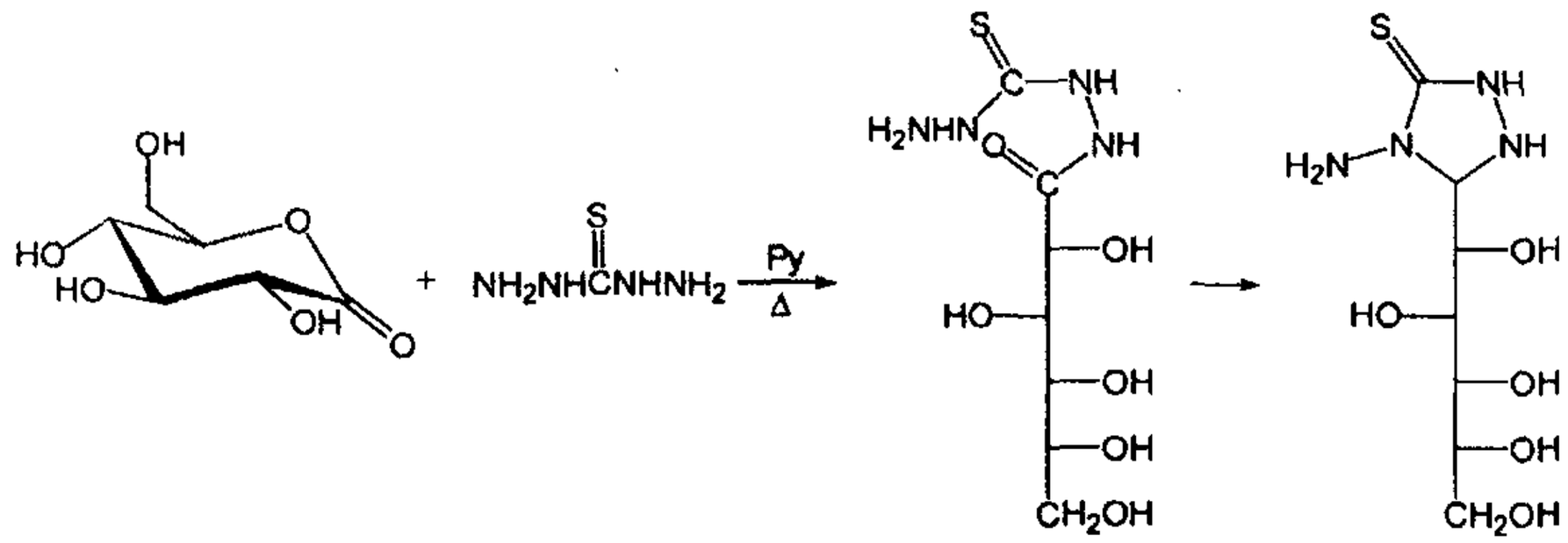
Scheme 1-25

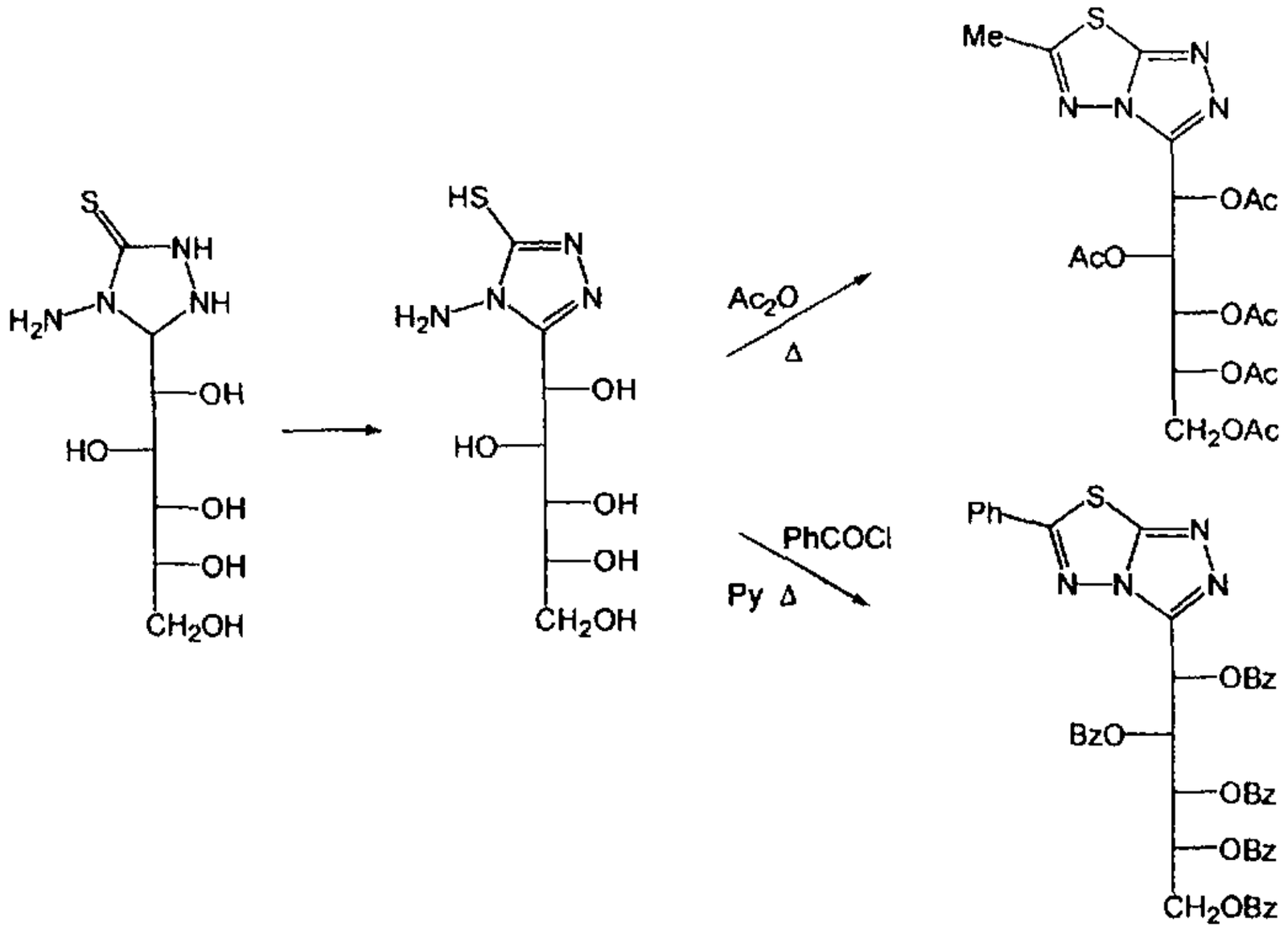
乙酰基取代的 D-葡糖、D-半乳糖、D-木糖的 C-苷由相应的糖基氰和硫化氢在三乙胺存在下反应，生成的硫代甲酰胺再在二氯甲烷和水的两相溶液中与溴酸钾和硫代硫酸钠反应，得到 3,5-β-D-二吡喃糖基-1,2,4-噻二唑[54]。



Scheme 1-26

Awad 等人用羰基与氨基硫脲通过脱水合环得到氨基巯基三唑，其再与乙酸酐或苯甲酰氯反应生成糖基三唑并噻二唑[55]。





Scheme 1-27

展望：

综上所述，糖接杂环化合物的合成在抗病毒药物的合成及筛选中具有极其重要的地位。近年来，有关糖苷衍生物的合成和应用开发的论文及专利逐年增加，可以预想，随着对这方面工作的深入研究，可能筛选出更多更好的抗病毒类药物，使得人们得以减少病痛，甚至治愈现在还无法攻克的顽症。

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第二部分 含 1,2,4-三唑、1,3,4-噁二唑、1,3,4-噻二唑糖苷衍生物的合成及抗菌活性

摘要

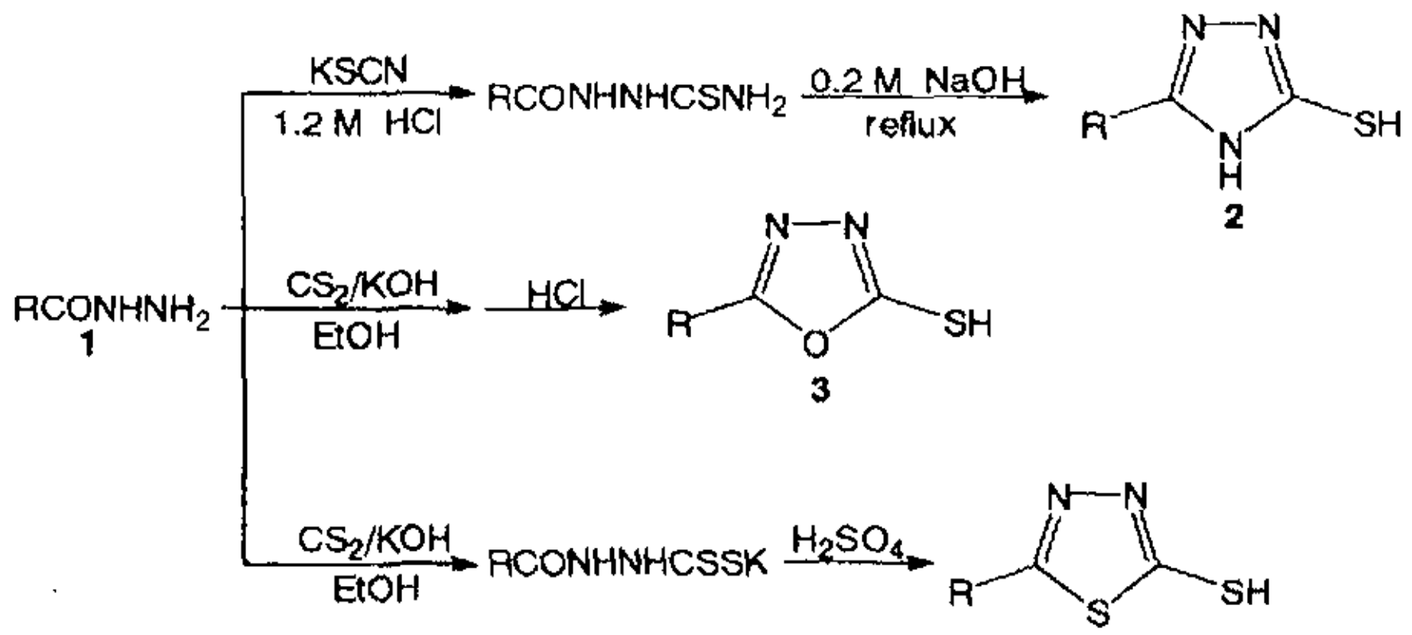
通过 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑中巯基对溴代乙酰葡糖中溴原子的亲核取代反应，制得 58 个新的 5-芳基-3-*N*-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑-2-硫酮及 5-芳基-3-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,2,4-三唑或 5-芳基-2-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑，其中含三唑环的只生成 S-糖苷产物，反应高立体选择性的得到全是β构型的产物。经过水解脱去乙酰基得到水溶性的产物。新化合物经 NMR、FAB-MS、元素分析确定结构，并初步评价了它们的抗菌活性。

1-β-D-呋喃核糖基-1,2,4-三唑-3-酰胺(Ribavirin)是被 FDA 批准的广谱抗病毒核苷类药物，能阻碍病毒核酸的合成，而达到抗病毒作用。为了得到更多和更高活性的化合物，许多科学家致力于 Ribavirin 的 C-、N-核苷的环状及非环状类似物的合成。众所周知，杂环化合物如：1,2,4-三唑 [1-4]、1,3,4-噁二唑 [5-8]、1,3,4-噻二唑 [9-12] 具有广谱的生物活性和多种用途。基于以上考虑，本文选择了将 1,2,4-三唑、1,3,4-噁二唑、1,3,4-噻二唑结构与糖相连，经多步反应制得目标化合物 **5**，本文将主要报道其合成及抗菌实验结果。

结果与讨论

1 合成

1.1 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑。



Scheme 2-1

将取代苯甲酰肼于盐酸中与硫氰酸钾反应生成芳酰胺基硫脲，再于碱性条件下合环得到 3-巯基-5-芳基-1,2,4-三唑(**2**)；将取代苯甲酰肼、KOH 和 CS_2 在乙醇中回流，反应放出 H_2S 并生成 2-巯基-5-芳基-1,3,4-噁二唑(**3**)；将取代苯甲酰肼、KOH 和 CS_2 在乙醇中室温反应生成芳酰肼基二硫代甲酸钾，再将其进一步在浓硫酸内关环得到 2-巯基-5-芳基-1,3,4-噻二唑(**4**)。

1.2 溴代乙酰葡糖的合成

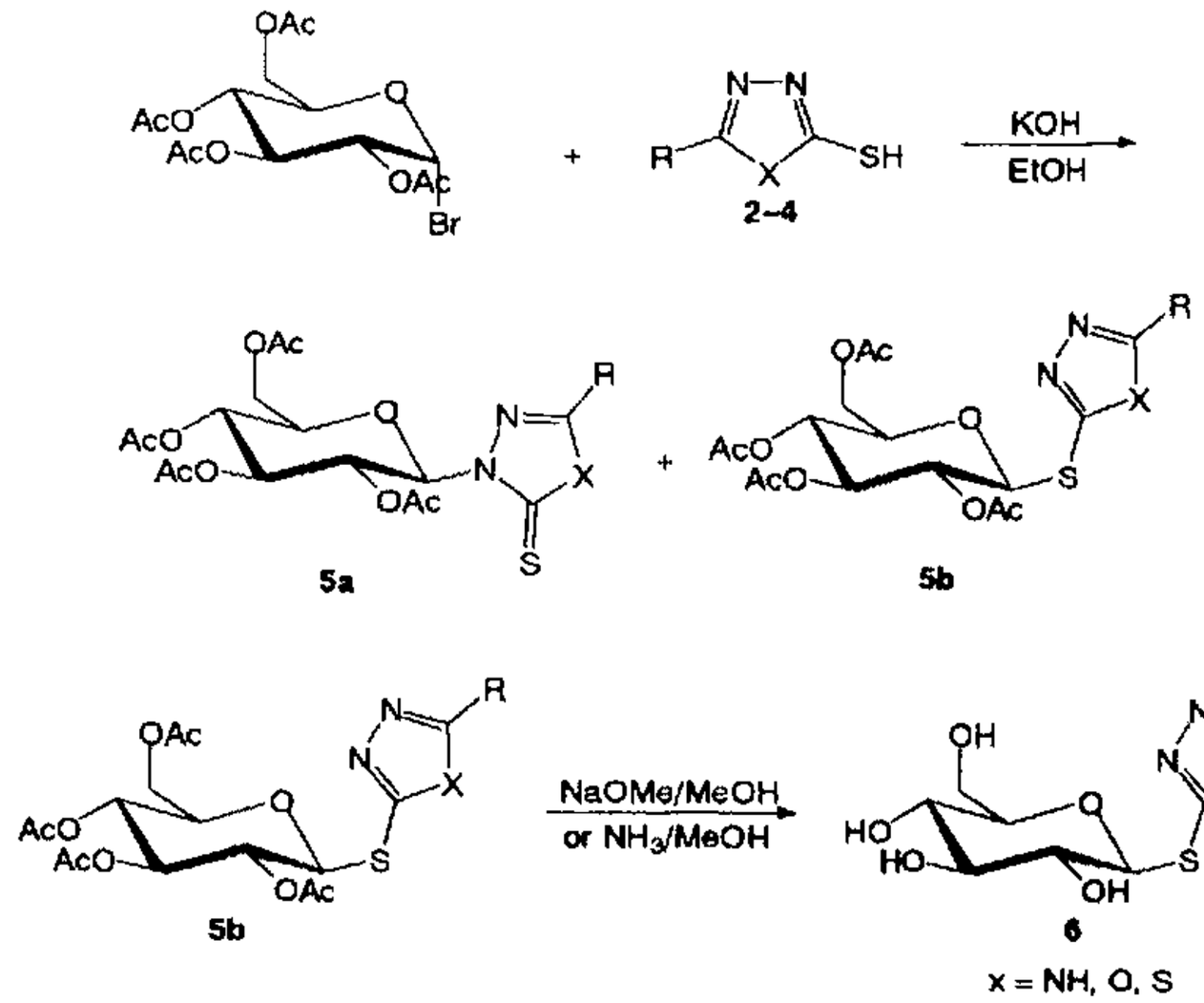
将 D-葡萄糖的羟基用乙酰基保护后再与溴化氢-乙酸溶液反应，得到 1-位溴代的产物。

1.3 5-芳基-3-*N*-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑-2-硫酮及 5-芳基-3-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,2,4-三唑或 5-芳基-2-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑衍生物的合成

将 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑和溴代乙酰葡糖在 KOH 存在下室温反应，生成白色沉淀。反应高立体选择性得到全是β构型的产物。其中在 3-巯基-5-芳基-1,2,4-三唑的反应中，产物只有 **5b** 一种；而在 2-巯基-5-芳基-1,3,4-噁二唑和 2-巯基-5-芳基-1,3,4-噻二唑的反应中，有 **5a** 和 **5b** 两个产物，其中 **5b** 是主要产物。

其中接 1,2,4-三唑的 12 个新化合物用甲醇钠-甲醇溶液脱保护得水溶性产物 **6-1~6-12**。在水解接噁二唑和噻二唑的化合物时，甲醇钠碱性太强，得到的是硫醚键断裂的产物。改用饱合氨气的甲醇溶液后反应可以顺利进行，最后得到的脱保护产物不溶于水（其结构经 ^{1}H NMR, ^{13}C NMR 和 H,H-COSY 鉴定），原因尚不

清楚。



Scheme 2-2

2 抗菌活性

用杯盘培养法测定了化合物 **5** 和 **6** 在质量浓度为 200 μg/mL 时对链球菌、大肠杆菌、金黄色葡萄球菌、枯草杆菌和白色念珠球菌的抑菌活性。结果表明部分化合物有一定的抑菌作用，其中 **5-26** 和 **5-27** 对金黄色葡萄球菌、枯草杆菌和白色念珠球菌有较好的抑制作用，其活性接近在相同浓度下作为对比的氯霉素。

Table 1. 化合物 **5** 和 **6** 的结构及抑菌活性

化合物	X	R	金黄色葡萄球菌	大肠杆菌	链球菌	枯草杆菌	白色念珠球菌
5b-1	NH	Ph	+	+	-	+	++
5b-2	NH	*o*-Me-Ph	+	+	-	+	++
5b-3	NH	*p*-Me-Ph	+	++	++	+	-
5b-5	NH	*p*-Cl-Ph	-	-	-	-	+
5b-6	NH	*m*-Cl-Ph	+	+	+	++	-
5b-7	NH	*o*-Br-Ph	+	-	-	+	+
5b-8	NH	*p*-Br-Ph	-	+	+	+	-
5b-9	NH	*o*-OH-Ph	+	+	+	+	-
5b-10	NH	*o*-OMe-Ph	-	-	-	-	-
5b-11	NH	*p*-OMe-Ph	++	+	+	++	-
5a-12	O	Me	-	-	-	-	-
5b-12	O	Me	+	-	+	-	-
5b-13	O	Ph	+++	+	+	-	+
5a-14	O	Py	+	-	-	-	+
5b-14	O	Py	++	-	++	-	-
5a-16	O	*p*-Me-Ph	+	-	+	+	-

Entry	X	R	金黄色葡萄球菌	大肠杆菌	链球菌	枯草杆菌	白色念珠球菌
5b-16	O	*p*-Me-Ph	-	-	-	++	-
5a-17	O	*o*-Cl-Ph	-	-	-	++	-
5b-17	O	*o*-Cl-Ph	-	-	-	-	-
5a-18	O	*p*-Cl-Ph	-	-	+	-	-
5b-18	O	*p*-Cl-Ph	-	-	-	-	-
5a-19	O	*m*-Cl-Ph	+++	-	+	-	-
5b-19	O	*m*-Cl-Ph	+++	-	+	-	-
5a-20	O	*o*-Br-Ph	++	+	+	-	++
5b-20	O	*o*-Br-Ph	+++	+	+	-	+++
5a-21	O	*p*-Br-Ph	-	-	-	+	-
5b-21	O	*p*-Br-Ph	-	-	-	-	-
5b-22	O	*o*-OH-Ph	+	++	-	+	+++
5a-23	O	*p*-OH-Ph	+	-	+	+	-
5b-23	O	*p*-OH-Ph	+	-	-	-	-
5a-24	O	*o*-OMe-Ph	+	-	+++	-	+++
5b-24	O	*o*-OMe-Ph	-	-	+++	++	+++
5a-25	O	*p*-OMe-Ph	+	+	+	+++	+
5b-25	O	*p*-OMe-Ph	+	++	++	++	+
5a-26	S	Me	-	-	+++	+++	+++
5b-26	S	Me	-	-	+++	+++	+++
5a-27	S	Ph	-	+	+++	++	+++
5b-27	S	Ph	-	-	-	+	-
5b-28	S	*o*-Me-Ph	+	-	+	-	+
5a-29	S	*p*-Me-Ph	+	++	-	-	+
5b-29	S	*p*-Me-Ph	-	-	-	-	-
5a-30	S	*o*-Cl-Ph	-	+	+	-	-
5b-30	S	*o*-Cl-Ph	-	+	+	-	-
5a-31	S	*p*-Cl-Ph	+	-	-	-	-
5b-31	S	*p*-Cl-Ph	+	-	+++	++	-
5a-32	S	*o*-Br-Ph	-	-	-	+	-
5b-32	S	*o*-Br-Ph	+	-	-	+	-
5a-33	S	*p*-Br-Ph	+	-	-	+	-
5b-33	S	*p*-Br-Ph	-	-	-	-	-
5b-34	S	*o*-OH-Ph	++	++	-	-	++
5a-35	S	*p*-OH-Ph	-	-	-	-	-
5b-35	S	*p*-OH-Ph	+	-	-	+	-
5b-36	S	*o*-OMe-Ph	-	-	-	-	-
5a-37	S	*p*-OMe-Ph	+	-	+++	-	++
5b-37	S	*p*-OMe-Ph	+++	++	+++	+++	-
6-1	NH	Ph	-	-	-	+	-
6-2	NH	*o*-Me-Ph	+	-	+	-	-
6-3	NH	*p*-Me-Ph	+	+	-	-	-
6-4	NH	*o*-Cl-Ph	-	-	+	-	-
6-5	NH	*p*-Cl-Ph	+	-	+	++	++
6-6	NH	*m*-Cl-Ph	++	-	-	+	+
6-7	NH	*o*-Br-Ph	-	+	+	-	-
6-8	NH	*p*-Br-Ph	+	-	-	-	-
6-9	NH	*o*-OH-Ph	+	+	+	-	-
6-10	NH	*p*-OH-Ph	+	+	+	+	-
6-11	NH	*o*-OMe-Ph	-	-	-	-	-
6-12	NH	*p*-OMe-Ph	-	-	-	-	-

Zone diameter of growth inhibition: <10 mm (-), 10-13 mm (+) and 14-17 mm (++). Diameter of the cup = 8 mm.

3 晶体结构

3.1 5-取代苯基-3-*N*-(2,3,4,6-四-*O*-乙酰基-β-D-吡喃葡糖基)-1,3,4-噁二唑-2-硫酮(**5a-19**)与 5-取代苯基-2-(2,3,4,6-四-*O*-乙酰基-β-D-吡喃葡糖基巯基)-1,3,4-噁二唑(**5b-19**)、(**5b-13**)和(**5b-25**)

化合物 **5a-19** ($C_{22}H_{23}ClN_2O_{10}S$)、**5b-19** ($C_{22}H_{23}ClN_2O_{10}S$)、**5b-13** ($C_{22}H_{24}N_2O_{10}S$)和 **5b-25** ($C_{23}H_{26}N_2O_{11}S$)的单晶从石油醚-乙酸乙酯溶液中得到，晶体结构由 X-ray 衍射证实。

a 类化合物 **5a-19** 中糖环直接连于平面的杂环的氮原子上。糖环是一个基本的 $^4C_1$ 椅式构型，所有的取代基都处于平伏键位置。杂环在实验误差范围内是平面结构，环内的 N(1)-C(15)和 N(2)-C(16)的键长分别为 1.343(9)和 1.288(9) Å，这表明它们分别是单键和双键，环内键角相对于 120° 的较大偏差在五元环中非常普遍[13]。糖环和杂环直接相连，噁二唑基团相对于糖环的位置可由以下扭转角表示： O(1)-C(5)-N(1)-N(2) = 42.8 (8)°, O(1)-C(5)-N(1)-C(15) = 125.8 (8)°, C(4)-C(5)-N(1)-C(15) = 115.6 (8)°, C(4)-C(5)-N(1)-N(2) = -70.4 (8)°。晶体结构还证明了此化合物是β构型。

b 类化合物以 **5b-13** 为例：它是由一个糖环和一个平面的杂环通过硫原子相连。糖环是一个基本的椅式构型，所有的取代基都处于平伏键位置，糖环上的 C(1)，C(2)，C(4)和 C(5)原子构成一个平面。晶体结构也证明了此化合物是β构型，C(1)-S-C(15)的键角为 102.9°(1)。杂环在实验误差范围内是平面结构，环内的 N(1)-C(15)和 N(2)-C(16)的键长分别为 1.287(3)和 1.297(3) Å，这表明它们都是双键，环内键角相对于 120° 的较大偏差在五元环中非常普遍[13]。

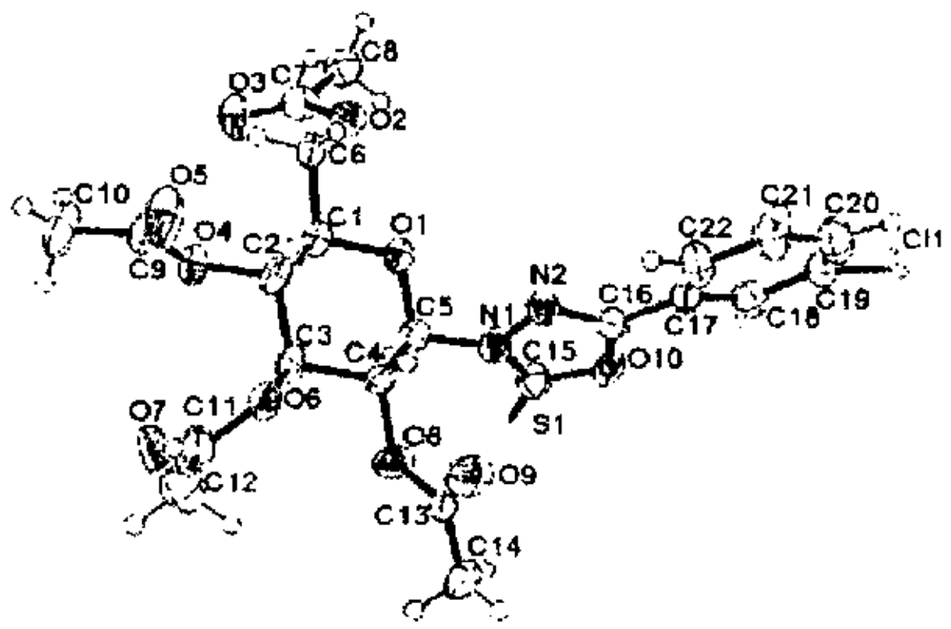


Fig. 1. View of compound **5a-19** with the atom-numbering scheme.

Crystal data

$C_{22}H_{23}ClN_2O_{10}S$
M_r =542.94
Monoclinic
$P2_1$
a = 5.847 (7) Å
b = 13.51 (2) Å
c = 16.05 (2) Å
β = 93.87 (2)°
V = 1265.6 (2) Å ^{3}
Z = 2
D_x = 1.425 Mg/m^3
Mo $K\alpha$ radiation
λ = 0.7107 Å
θ = 3.0-27.5°
μ(MoKa) = 2.91 cm^{-1}
Chip
T = 173 K
0.20 x 0.15 x 0.02 mm^3
Colorless
F_{000} = 564.00

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan
9060 measured reflections
5226 independent reflections
5213 observed reflections
[$F^2>2.0\sigma(F^2)$]
$R_{int.}$= 0.045
θ_{max} = 27.47°
h = -5→7
k = -17→17
l = -17→20
intensity variation: none

Refinement

Refinement on F
R= 0.0945
wR = 0.1279
5213 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2 (F_o) + 0.00063 |F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.0016
$\Delta\rho_{max}$ = 0.59 e Å $^{-3}$
$\Delta\rho_{min}$ = -0.62 e Å $^{-3}$
Atomic scattering factors from *International Tables for Crystallography* [1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 2. Bond Lengths(Å) and Bond Angles(°)

Cl(1)-C(19)	1.722(8)	S(1)-C(15)	1.648(8)
O(1)-C(1)	1.444(8)	O(1)-C(5)	1.426(9)
O(2)-C(6)	1.464(8)	O(2)-C(7)	1.366(8)
O(3)-C(7)	1.189(9)	O(4)-C(2)	1.453(8)
O(4)-C(9)	1.356(9)	O(5)-C(9)	1.202(9)
O(6)-C(3)	1.441(8)	O(6)-C(11)	1.349(9)
O(7)-C(11)	1.173(10)	O(8)-C(4)	1.440(8)
O(8)-C(13)	1.367(8)	O(9)-C(13)	1.192(9)
O(10)-C(15)	1.370(8)	O(10)-C(16)	1.388(9)
N(1)-N(2)	1.401(8)	N(1)-C(5)	1.440(8)
N(1)-C(15)	1.343(9)	N(2)-C(16)	1.288(9)
C(1)-C(2)	1.51(1)	C(1)-C(6)	1.51(1)
C(2)-C(3)	1.51(1)	C(3)-C(4)	1.535(9)
C(4)-C(5)	1.511(9)	C(7)-C(8)	1.51(1)
C(9)-C(10)	1.49(1)	C(11)-C(12)	1.49(1)
C(13)-C(14)	1.48(1)	C(16)-C(17)	1.439(10)
C(17)-C(18)	1.42(1)	C(17)-C(22)	1.38(1)
C(18)-C(19)	1.38(1)	C(19)-C(20)	1.39(1)
C(20)-C(21)	1.38(1)	C(21)-C(22)	1.36(1)
C(1)-O(1)-C(5)	111.9(5)	C(6)-O(2)-C(7)	114.5(6)

C(2)-O(4)-C(9)	117.8(6)	C(3)-O(6)-C(11)	118.6(5)
C(4)-O(8)-C(13)	117.7(5)	C(15)-O(10)-C(16)	105.3(5)
N(2)-N(1)-C(5)	119.9(5)	N(2)-N(1)-C(15)	112.5(6)
C(5)-N(1)-C(15)	127.4(6)	N(1)-N(2)-C(16)	102.4(6)
O(1)-C(1)-C(2)	110.0(5)	O(1)-C(1)-C(6)	105.3(6)
C(2)-C(1)-C(6)	109.5(6)	O(4)-C(2)-C(1)	105.0(5)
O(4)-C(2)-C(3)	107.2(6)	C(1)-C(2)-C(3)	111.6(6)
O(6)-C(3)-C(2)	112.0(6)	O(6)-C(3)-C(4)	105.0(5)
C(2)-C(3)-C(4)	109.8(6)	O(8)-C(4)-C(3)	109.4(5)
O(8)-C(4)-C(5)	106.8(6)	C(3)-C(4)-C(5)	110.5(5)
O(1)-C(5)-N(1)	106.7(6)	O(1)-C(5)-C(4)	109.4(6)
N(1)-C(5)-C(4)	110.1(5)	O(2)-C(6)-C(1)	110.1(5)
O(2)-C(7)-O(3)	123.4(7)	O(2)-C(7)-C(8)	109.1(7)
O(3)-C(7)-C(8)	127.6(7)	O(4)-C(9)-O(5)	123.9(7)
O(4)-C(9)-C(10)	109.0(7)	O(5)-C(9)-C(10)	126.7(7)
O(6)-C(11)-O(7)	123.9(8)	O(6)-C(11)-C(12)	110.1(7)
O(7)-C(11)-C(12)	125.9(8)	O(8)-C(13)-O(9)	122.5(7)
O(8)-C(13)C(14)	109.5(6)	O(9)-C(13)-C(14)	127.9(7)
S(1)-C(15)-O(10)	123.7(5)	S(1)-C(15)-N(1)	130.7(6)
O(10)-C(15)-N(1)	105.6(6)	O(10)-C(16)-N(2)	114.2(6)
O(10)-C(16)-C(17)	118.2(6)	N(2)-C(16)-C(17)	127.5(7)
C(16)-C(17)-C(18)	120.2(7)	C(16)-C(17)-C(22)	121.3(7)
C(18)-C(17)-C(22)	118.4(7)	C(17)-C(18)-C(19)	118.8(7)
Cl(1)-C(19)-C(18)	118.4(7)	Cl(1)-C(19)-C(20)	120.0(6)
C(18)-C(19)-C(20)	121.6(7)	C(19)-C(20)-C(21)	118.7(7)
C(20)-C(21)-C(22)	120.7(8)	C(17)-C(22)-C(21)	121.6(8)

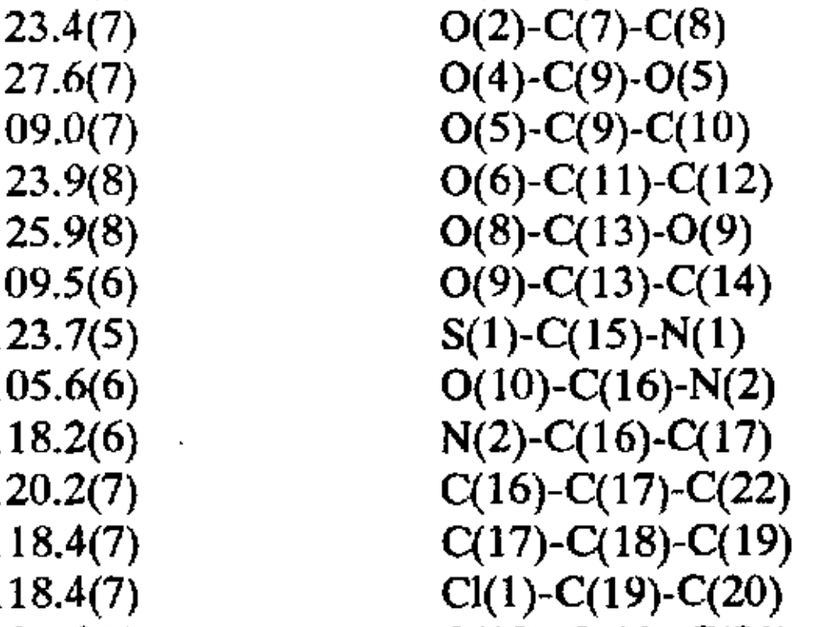


Fig. 2. View of compound **5b-19** with the atom-numbering scheme.

Crystal data

$C_{22}H_{23}ClN_2O_{10}S$	D_x = 1.413 Mg/m^3
M_r = 542.94	Mo $K\alpha$ radiation
Monoclinic	λ = 0.7107 Å
$P2_1$	θ = 3.3-27.5°
a = 5.549 (3) Å	μ(MoKa) = 2.88 cm^{-1}
b = Å	Needle
c = 17.216 (10) Å	T = 173 K
β = 94.230 (6)°	0.05 x 0.05 x 0.02 mm
V = 1275.9 (1) Å^3	Colorless
Z = 2	F_{000} = 564.00

Data collection
Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan
10051 measured reflections
5397 independent reflections
5266 observed reflections
$[F^2>2.0\sigma(F^2)]$

$R_{int.}$= 0.025
θ_{max} 27.46°
h = -5→7
k = -16→17
l = -22→22
intensity variation: none

Refinement
Refinement on F
R = 0.0447
wR = 0.0567
5266 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = -0.29e Å^{-3}
Atomic scattering factors from
International Tables for Crystallography
[1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 3. Bond Lengths(Å) and Bond Angles(°)

Cl(1)-C(19)	1.740(3)	S(1)-C(5)	1.819(3)
S(1)-C(15)	1.735(3)	O(1)-C(1)	1.439(3)
O(1)-C(5)	1.422(3)	O(2)-C(6)	1.442(4)
O(2)-C(7)	1.351(4)	O(3)-C(7)	1.205(4)
O(4)-C(2)	1.444(3)	O(4)-C(9)	1.354(4)
O(5)-C(9)	1.207(4)	O(6)-C(3)	1.443(3)
O(6)-C(11)	1.355(3)	O(7)-C(11)	1.194(3)
O(8)-C(4)	1.438(3)	O(8)-C(13)	1.344(3)
O(9)-C(13)	1.197(4)	O(10)-C(15)	1.371(3)
O(10)-C(16)	1.364(3)	N(1)-N(2)	1.416(4)
N(1)-C(15)	1.274(4)	N(2)-C(16)	1.295(4)
C(1)-C(2)	1.534(4)	C(1)-C(6)	1.510(4)
C(2)-C(3)	1.518(4)	C(3)-C(4)	1.520(4)
C(4)-C(5)	1.529(4)	C(7)-C(8)	1.490(5)
C(9)-C(10)	1.487(4)	C(11)-C(12)	1.487(4)
C(13)-C(14)	1.495(4)	C(16)-C(17)	1.456(4)
C(17)-C(18)	1.389(4)	C(17)-C(22)	1.393(4)
C(18)-C(19)	1.381(5)	C(19)-C(20)	1.372(5)
C(20)-C(21)	1.385(6)	C(21)-C(22)	1.391(5)
C(5)-S(1)-C(15)	98.9(1)	C(1)-O(1)-C(5)	111.5(2)
C(6)-O(2)-C(7)	116.2(2)	C(2)-O(4)-C(9)	117.7(2)
C(3)-O(6)-C(11)	118.5(2)	C(4)-O(8)-C(13)	117.6(2)
C(15)-O(10)-C(16)	102.1(2)	N(2)-N(1)-C(15)	106.5(2)
N(1)-N(2)-C(16)	105.6(3)	O(1)-C(1)-C(2)	107.9(2)
O(1)-C(1)-C(6)	106.7(2)	C(2)-C(1)-C(6)	111.5(2)
O(4)-C(2)-C(1)	109.8(2)	O(4)-C(2)-C(3)	105.8(2)
C(1)-C(2)-C(3)	111.5(2)	O(6)-C(3)-C(2)	108.5(2)
O(6)-C(3)-C(4)	106.0(2)	C(2)-C(3)-C(4)	112.2(2)
O(8)-C(4)-C(3)	106.3(2)	O(8)-C(4)-C(5)	109.5(2)
C(3)-C(4)-C(5)	109.3(2)	S(1)-C(5)-O(1)	107.0(2)
S(1)-C(5)-C(4)	107.9(2)	O(1)-C(5)-C(4)	109.0(2)
O(2)-C(6)-C(1)	107.4(2)	O(2)-C(7)-O(3)	122.5(3)
O(2)-C(7)-C(8)	111.0(3)	O(3)-C(7)-C(8)	126.6(3)

O(4)-C(9)-O(5)	123.0(3)	O(4)-C(9)-C(10)	110.6(2)
O(5)-C(9)-C(10)	126.4(3)	O(6)-C(11)-O(7)	123.5(3)
O(6)-C(11)-C(12)	110.7(2)	O(7)-C(11)-C(12)	125.8(2)
O(8)-C(13)-O(9)	123.9(3)	O(8)-C(13)-C(14)	110.2(2)
O(9)-C(13)-C(14)	125.9(3)	S(1)-C(15)-O(10)	120.5(2)
S(1)-C(15)-N(1)	126.6(2)	O(10)-C(15)-N(1)	113.0(3)
O(10)-C(16)-N(2)	112.7(3)	O(10)-C(16)-C(17)	119.3(3)
N(2)-C(16)-C(17)	127.9(3)	C(16)-C(17)-C(18)	119.5(3)
C(16)-C(17)-C(22)	120.4(3)	C(18)-C(17)-C(22)	120.1(3)
C(17)-C(18)-C(19)	119.0(3)	Cl(1)-C(19)-C(18)	118.8(3)
Cl(1)-C(19)-C(20)	119.8(3)	C(18)-C(19)-C(20)	121.4(3)
C(19)-C(20)-C(21)	120.1(3)	C(20)-C(21)-C(22)	119.4(4)
C(17)-C(22)-C(21)	120.1(3)		

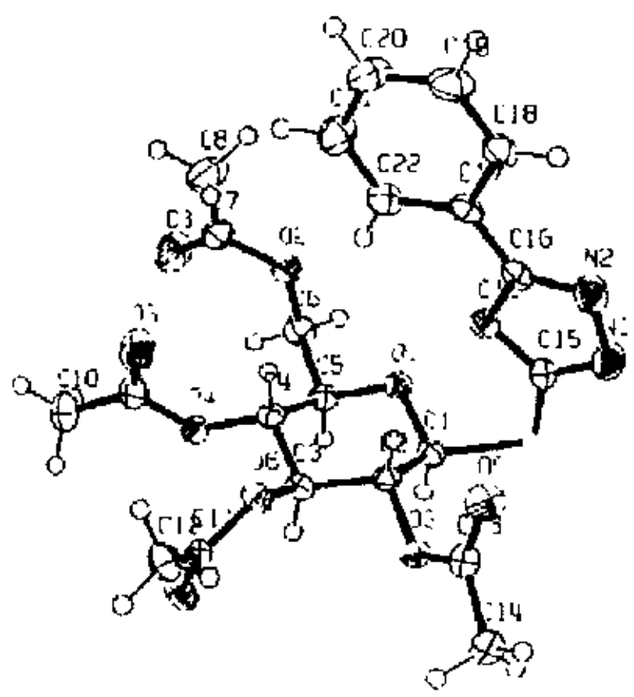


Fig. 3. View of compound **5b-13** with the atom-numbering scheme.

Crystal data

$C_{22}H_{24}N_2O_{10}S$	D_x = 1.398 Mg/m^3
M_r =508.50	Mo $K\alpha$ radiation
Monoclinic	λ = 0.7107 Å
$P12_11$	θ = 3.1-27.5°
a = 11.50 (2) Å	μ = 0.192 mm^{-1}
b = 7.35 (1) Å	Plate
c = 14.30 (2) Å	T = 173 K
β = 92.42 (2)°	0.35 x 0.2 x 0.15 mm^3
V = 1208 (2) Å^3	Colorless
Z = 2	

Data collection

Rigaku/MSC Mercury CCD diffractometer	$R_{int.}$= 0.021
ω scans	θ_{max} = 27.44°
Absorption correction: multi-scan	h = -14→14
9357 measured reflections	k = -7→9
2953 independent reflections	l = -18→12
4441 observed reflections	intensity variation: none
[F^2>2.0\σ(F^2)]	

Refinement
Refinement on F
R= 0.0355
wR = 0.0458
4971 reflections
315 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.0032$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = -0.18 e Å^{-3}
Atomic scattering factors from
International Tables for Crystallography
[1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 4. Bond Lengths(Å) and Bond Angles(°)

S-C(1)	1.805(3)	N(1)-C(15)	1.287(3)
S-C(15)	1.745(3)	N(2)-C(16)	1.297(3)
O(1)-C(1)	1.425(2)	C(1)-C(2)	1.528(3)
O(1)-C(5)	1.433(3)	C(2)-C(3)	1.521(3)
O(2)-C(6)	1.443(3)	C(3)-C(4)	1.533(3)
O(2)-C(7)	1.354(3)	C(4)-C(5)	1.522(3)
O(3)-C(7)	1.209(3)	C(5)-C(6)	1.512(3)
O(4)-C(4)	1.446(3)	C(7)-C(8)	1.485(4)
O(4)-C(9)	1.359(3)	C(9)-C(10)	1.491(4)
O(5)-C(9)	1.199(3)	C(11)-C(12)	1.490(3)
O(6)-C(3)	1.443(2)	C(13)-C(14)	1.495(3)
O(6)-C(11)	1.358(2)	C(16)-C(17)	1.453(3)
O(7)-C(11)	1.203(3)	C(17)-C(18)	1.398(3)
O(8)-C(2)	1.441(2)	C(17)-C(22)	1.391(3)
O(8)-C(13)	1.377(3)	C(18)-C(19)	1.376(4)
O(9)-C(13)	1.193(3)	C(19)-C(20)	1.379(4)
O(10)-C(15)	1.364(3)	C(20)-C(21)	1.387(4)
O(10)-C(16)	1.374(3)	C(21)-C(22)	1.385(3)
N(1)-N(2)	1.413(3)		

C(1)-S-C(15)	102.9(1)	O(2)-C(7)-C(8)	111.2(2)
C(1)-O(1)-C(5)	111.4(1)	O(3)-C(7)-C(8)	125.9(2)
C(6)-O(2)-C(7)	117.1(2)	O(4)-C(9)-O(5)	123.0(2)
C(4)-O(4)-C(9)	118.5(2)	O(4)-C(9)-C(10)	110.2(2)
C(3)-O(6)-C(11)	118.4(2)	O(5)-C(9)-C(10)	126.8(2)
C(2)-O(8)-C(13)	117.7(1)	O(6)-C(11)-O(7)	123.2(2)
C(15)-O(10)-C(16)	102.1(2)	O(6)-C(11)-C(12)	110.0(2)
N(2)-N(1)-C(15)	105.7(2)	O(7)-C(11)-C(12)	126.7(2)
N(1)-N(2)-C(16)	106.4(2)	O(8)-C(13)-O(9)	122.9(2)
S-C(1)-O(1)	109.2(1)	O(8)-C(13)-C(14)	110.5(2)
S-C(1)-C(2)	115.5(1)	O(9)-C(13)-C(14)	126.6(2)
O(1)-C(1)-C(2)	110.1(2)	S-C(15)-O(10)	120.4(2)
O(8)-C(2)-C(1)	109.9(2)	S-C(15)-N(1)	125.9(2)
O(8)-C(2)-C(3)	107.2(1)	O(10)-C(15)-N(1)	113.5(2)
C(1)-C(2)-C(3)	110.1(2)	O(10)-C(16)-N(2)	112.2(2)
O(6)-C(3)-C(2)	105.7(2)	O(10)-C(16)-C(17)	118.4(2)
O(6)-C(3)-C(4)	109.9(2)	N(2)-C(16)-C(17)	129.4(2)
C(2)-C(3)-C(4)	110.4(1)	C(16)-C(17)-C(18)	118.9(2)
O(4)-C(4)-C(3)	109.5(1)	C(16)-C(17)-C(22)	121.1(2)
O(4)-C(4)-C(5)	107.4(1)	C(18)-C(17)-C(22)	119.9(2)
C(3)-C(4)-C(5)	110.7(2)	C(17)-C(18)-C(19)	119.7(2)
O(1)-C(5)-C(4)	107.8(2)	C(18)-C(19)-C(20)	120.6(2)
O(1)-C(5)-C(6)	108.7(2)	C(19)-C(20)-C(21)	120.0(2)
C(4)-C(5)-C(6)	113.0(2)	C(20)-C(21)-C(22)	120.2(2)
O(2)-C(6)-C(5)	109.2(2)	C(17)-C(22)-C(21)	119.6(2)
O(2)-C(7)-O(3)	122.9(2)		

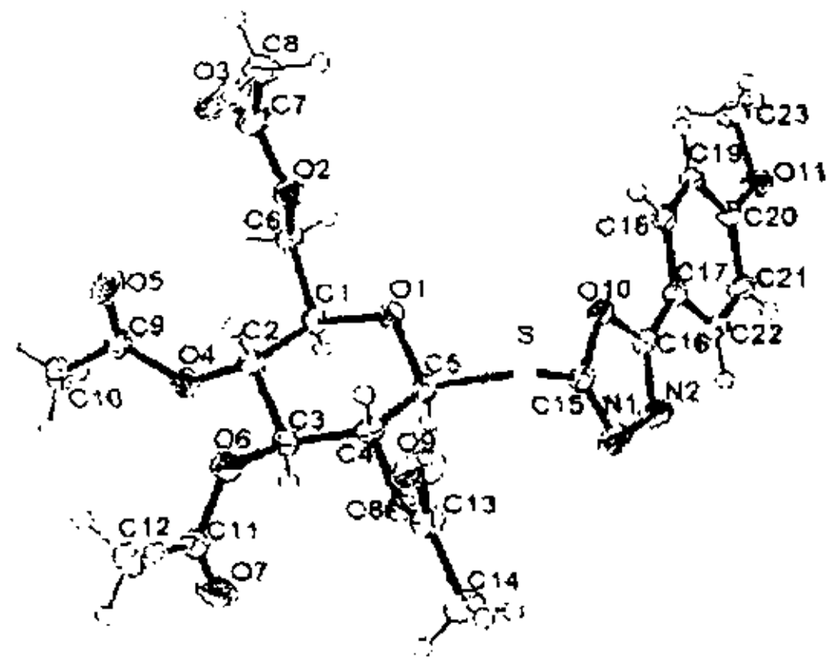


Fig. 4. View of compound **5b-25** with the atom-numbering scheme.

Crystal data

$C_{23}H_{26}N_2O_{11}S$
M_r =538.53
Monoclinic
$P2_1$
a = 11.316 (5) Å
b = 7.160 (3) Å
c = 16.093 (7) Å
β = 108.938 (5)°
V = 1233.3 (9) Å^3
Z = 2

D_x = 1.450 Mg/m^3
Mo $K\alpha$ radiation
λ = 0.7107 Å
θ = 3.8-27.5°
μ(MoKa) = 1.96 cm^{-1}
Block
T = 173 K
0.20 x 0.10 x 0.05 mm^3
Colorless
F_{000} = 564.00

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan
9451 measured reflections
5391 independent reflections
5352 observed reflections
[$F^2>2.0\sigma(F^2)$]

$R_{int.}$ = 0.014
θ_{max} = 27.48°
h = -10→14
k = -9→9
l = -20→20
intensity variation: none

Refinement

Refinement on F
R= 0.0348
wR = 0.0477
5352 reflections
334 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.11
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = -0.29 e Å^{-3}
Atomic scattering factors from
International Tables for Crystallography
[1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 5. Bond Lengths(Å) and Bond Angles(°)

S-C(5)	1.817(2)	S-C(15)	1.739(2)
O(1)-C(1)	1.436(2)	O(1)-C(5)	1.411(2)
O(2)-C(6)	1.444(2)	O(2)-C(7)	1.342(2)
O(3)-C(7)	1.191(3)	O(4)-C(2)	1.441(2)
O(4)-C(9)	1.359(2)	O(5)-C(9)	1.198(2)
O(6)-C(3)	1.442(2)	O(6)-C(11)	1.357(2)
O(7)-C(11)	1.194(3)	O(8)-C(4)	1.429(2)
O(8)-C(13)	1.361(2)	O(9)-C(13)	1.201(2)
O(10-C(15)	1.376(2)	O(10)-C(16)	1.361(2)
O(11)-C(20)	1.362(2)	O(11)-C(23)	1.423(2)
N(1)-N(2)	1.400(2)	N(1)-C(15)	1.284(2)
N(2)-C(16)	1.294(2)	C(1)-C(2)	1.533(2)
C(1)-C(6)	1.507(2)	C(2)-C(3)	1.516(2)
C(3)-C(4)	1.524(2)	C(4)-C(5)	1.531(2)
C(7)-C(8)	1.496(3)	C(9)-C(10)	1.489(3)
C(11)-C(12)	1.496(3)	C(13)-C(14)	1.488(3)
C(16)-C(17)	1.459(3)	C(17)-C(18)	1.390(3)
C(17)-C(22)	1.399(3)	C(18)-C(19)	1.392(3)
C(19)-C(20)	1.384(3)	C(20)-C(21)	1.400(2)
C(21)-C(22)	1.378(3)		
C(5)-S-C(15)	101.03(8)	C(1)-O(1)-C(5)	113.9(1)
C(6)-O(2)-C(7)	116.0(1)	C(2)-O(4)-C(9)	118.3(1)
C(3)-O(6)-C(11)	119.0(1)	C(4)-O(8)-C(13)	117.4(1)
C(15)-O(10)- C(16)	102.2(1)	C(20)-O(11)-C(23)	117.7(1)
N(2)-N(1)-C(15)	106.2(2)	N(1)-N(2)-C(16)	106.7(2)
O(1)-C(1)-C(2)	110.8(1)	O(1)-C(1)-C(6)	106.4(1)
C(2)-C(1)-C(6)	111.9(1)	O(4)-C(2)-C(1)	108.7(1)
O(4)-C(2)-C(3)	106.8(1)	C(1)-C(2)-C(3)	112.9(1)
O(6)-C(3)-C(2)	106.0(1)	O(6)-C(3)-C(4)	108.1(1)
C(2)-C(3)-C(4)	110.5(1)	O(8)-C(4)-C(3)	108.2(1)
O(8)-C(4)-C(5)	110.3(1)	C(3)-C(4)-C(5)	108.9(1)
S-C(5)-C(1)	107.3(1)	S-C(5)-C(4)	108.3(1)
O(1)-C(5)-C(4)	108.5(1)	O(2)-C(6)-C(1)	107.5(1)
O(2)-C(7)-O(3)	122.8(2)	O(2)-C(7)-C(8)	112.8(2)
O(3)-C(7)-C(8)	124.5(2)	O(4)-C(9)-O(5)	123.0(2)
O(4)-C(9)-C(10)	110.4(2)	O(5)-C(9)-C(10)	126.6(2)
O(6)-C(11)-O(7)	124.0(2)	O(6)-C(11)-C(12)	109.7(2)
O(7)-C(11)-C(12)	126.3(2)	O(8)-C(13)-O(9)	123.7(2)
O(8)-C(13)-C(14)	110.0(2)	O(9)-C(13)-C(14)	126.3(2)
S-C(15)-O(10)	120.3(1)	S-C(15)-N(1)	126.9(1)
O(10)-C(15)-N(1)	112.6(2)	O(10)-C(16)-N(2)	112.3(2)
O(10)-C(16)-C(17)	121.1(1)	N(2)-C(16)-C(17)	126.6(2)
C(16)-C(17)-C(18)	122.7(2)	C(16)-C(17)-C(22)	118.1(2)
C(18)-C(17)-C(22)	119.3(2)	C(17)-C(18)-C(19)	120.6(2)
C(18)-C(19)-C(20)	119.8(2)	O(11)-C(20)-C(19)	125.4(2)
O(11)-C(20)-C(21)	114.8(2)	C(19)-C(20)-C(21)	119.9(2)
C(20)-C(21)-C(22)	120.2(2)	C(17)-C(22)-C(21)	120.2(2)

3.2 5-取代苯基-2-(2,3,4,6-四-*O*-乙酰基-β-D-吡喃葡糖基巯基)-1,3,4-噻二唑(**5b-27**)、(**5b-31**)和(**5b-37**)

化合物 **5b-27** ($C_{22}H_{24}N_2O_9S_2$)、**5b-31** ($C_{22}H_{23}ClN_2O_9S_2$)和 **5b-37**

($C_{23}H_{26}N_2O_{10}S_2$)的单晶从石油醚-乙酸乙酯(v/v 4:1)溶液中得到，晶体结构由 X-ray 衍射证实。以化合物 **5b-27** 为例：

糖环是一个基本的 $^4C_1$ 椅式构型，所有的取代基都处于平伏键位置。糖基上 C-C 和 C-O 键的平均键长分别为 1.519(2)和 1.422(2) Å，这和以前在吡喃糖中观测到的结果非常相近[14]。环内的两个 C-O 键几乎是相同的(1.432 (2), 1.422 (2) Å)。环外的 C(1)-C(6)键是 *gauche-trans* 结构，O(2)-C(6)-C(1)-O(1)和 O(2)-C(6)-C(1)-C(2)的扭转角分别为-59.7(2)和 60.9(2)°。

杂环在实验误差范围内是平面结构，环内的 N(1)-C(15)和 N(2)-C(16)的键长分别为 1.299(2)和 1.306(2) Å，这表明它们都是双键，N(1)-N(2) (1.375(2) Å)较 1,3,4-噻二唑啉中的 N-N 单键(1.393(4) Å)稍短。环内键角相对于 120°的较大的偏差在五元环中非常普遍[13]。

糖环和杂环通过硫原子相连。噻二唑基团相对于糖环的位置可由以下扭转角表示： N(1)-C(15)-S(1)-C(5) = -106.9 (2)°, S(2)-C(15)-S(1)-C(5) = 78.2 (1)°, C(15)-S(1)-C(5)-O(1) = -67.1 (1)°, C(15)-S(1)-C(5)-C(4) = 176.3 (1)°. 晶体结构还证明了此化合物是β构型。

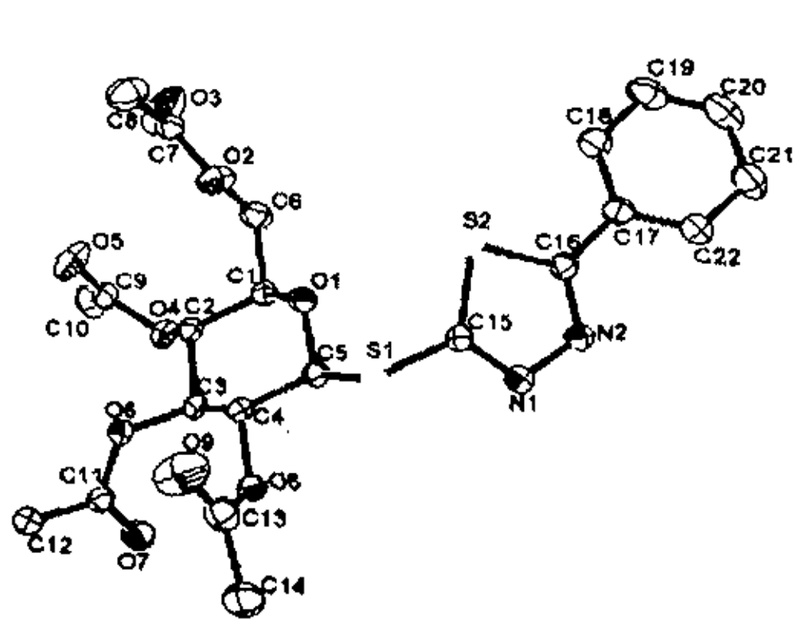


Fig. 5. View of compound **5b-27** with the atom-numbering scheme.

Crystal data

$C_{22}H24N_2O_9S_2$
M_r = 524.56
Orthorhombic
P 21 21 21
a = 8.010(2) Å
b = 10.526(2) Å
c = 28.685(6) Å
β = 90°
V = 2418.7(9) Å^3
Z = 4
D_x = 1.440 Mg/m^3^
Mo $K\alpha$ radiation
λ = 0.7107 Å
θ = 3.2-27.5°
μ(MoKa) = 2.75 cm^{-1}
T = 173 K
Block
0.35 * 0.25 * 0.20 mm
Colorless
F000 = 1096

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan
19569 measured reflections
3142 independent reflections
5151 observed reflections
$[F^2>2.0\sigma(F^2)]$

$R_{int} = 0.037$
$\theta_{max} = 27.48^{\circ}$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 13$
$l = -37 \rightarrow 37$
intensity variation: none

Refinement

Refinement on F
$R = 0.0334$
$wR = 0.0463$
5499 reflections
317 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.0011$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Atomic scattering factors from
International Tables for Crystallography
[1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 6. Bond Lengths(Å) and Bond Angles(°)

S(1)-C(5)	1.807(2)	N(1)-C(15)	1.299(2)
S(1)-C(15)	1.753(2)	N(2)-C(16)	1.306(2)
S(2)-C(15)	1.715(2)	C(1)-C(2)	1.533(2)
S(2)-C(16)	1.715(2)	C(1)-C(6)	1.510(2)
O(1)-C(1)	1.432(2)	C(2)-C(3)	1.522(2)
O(1)-C(5)	1.422(2)	C(3)-C(4)	1.519(2)
O(2)-C(6)	1.439(2)	C(4)-C(5)	1.521(2)
O(2)-C(7)	1.347(2)	C(7)-C(8)	1.492(3)
O(3)-C(7)	1.189(3)	C(9)-C(10)	1.486(3)
O(4)-C(2)	1.441(2)	C(11)-C(12)	1.487(3)
O(4)-C(9)	1.361(2)	C(13)-C(14)	1.488(3)
O(5)-C(9)	1.188(3)	C(16)-C(17)	1.463(2)
O(6)-C(3)	1.436(2)	C(17)-C(18)	1.393(3)
O(6)-C(11)	1.357(2)	C(17)-C(22)	1.398(3)
O(7)-C(11)	1.206(2)	C(18)-C(19)	1.385(3)
O(8)-C(4)	1.433(2)	C(19)-C(20)	1.371(3)
O(8)-C(13)	1.363(2)	C(20)-C(21)	1.392(3)
O(9)-C(13)	1.193(3)	C(21)-C(22)	1.383(3)
N(1)-N(2)	1.375(2)		
C(5)-S(1)-C(15)	100.61(8)	O(2)-C(7)-C(8)	110.8(2)
C(15)-S(2)-C(16)	87.54(8)	O(3)-C(7)-C(8)	125.2(2)
C(1)-O(1)-C(5)	112.0(1)	O(4)-C(9)-O(5)	122.8(2)
C(6)-O(2)-C(7)	118.0(2)	O(4)-C(9)-C(10)	111.6(2)
C(2)-O(4)-C(9)	117.5(1)	O(5)-C(9)-C(10)	125.6(2)
C(3)-O(6)-C(11)	118.8(1)	O(6)-C(11)-O(7)	123.4(2)
C(4)-O(8)-C(13)	117.4(1)	O(6)-C(11)-C(12)	110.3(1)
N(2)-N(1)-C(15)	112.0(2)	O(7)-C(11)-C(12)	126.3(2)
N(1)-N(2)-C(16)	113.0(2)	O(8)-C(13)-O(9)	122.8(2)

O(1)-C(1)-C(2)	110.0(1)	O(8)-C(13)-C(14)	110.7(2)
O(1)-C(1)-C(6)	106.6(1)	O(9)-C(13)-C(14)	126.5(2)
C(2)-C(1)-C(6)	112.3(1)	S(1)-C(15)-S(2)	123.5(1)
O(4)-C(2)-C(1)	107.6(1)	S(1)-C(15)-N(1)	122.2(1)
O(4)-C(2)-C(3)	108.1(1)	S(2)-C(15)-N(1)	114.2(1)
C(1)-C(2)-C(3)	112.0(1)	S(2)-C(16)-N(2)	113.3(1)
O(6)-C(3)-C(2)	107.9(1)	S(2)-C(16)-C(17)	124.5(1)
O(6)-C(3)-C(4)	107.1(1)	N(2)-C(16)-C(17)	122.2(2)
C(2)-C(3)-C(4)	109.9(1)	C(16)-C(17)-C(18)	121.4(2)
O(8)-C(4)-C(3)	109.0(1)	C(16)-C(17)-C(22)	119.4(2)
O(8)-C(4)-C(5)	110.1(1)	C(18)-C(17)-C(22)	119.2(2)
C(3)-C(4)-C(5)	109.6(1)	C(17)-C(18)-C(19)	120.1(2)
S(1)-C(5)-O(1)	108.8(1)	C(18)-C(19)-C(20)	120.4(2)
S(1)-C(5)-C(4)	107.7(1)	C(19)-C(20)-C(21)	120.2(2)
O(1)-C(5)-C(4)	107.7(1)	C(20)-C(21)-C(22)	119.9(2)
O(2)-C(6)-C(1)	107.8(1)	C(17)-C(22)-C(21)	120.1(2)
O(2)-C(7)-O(3)	123.9(2)		

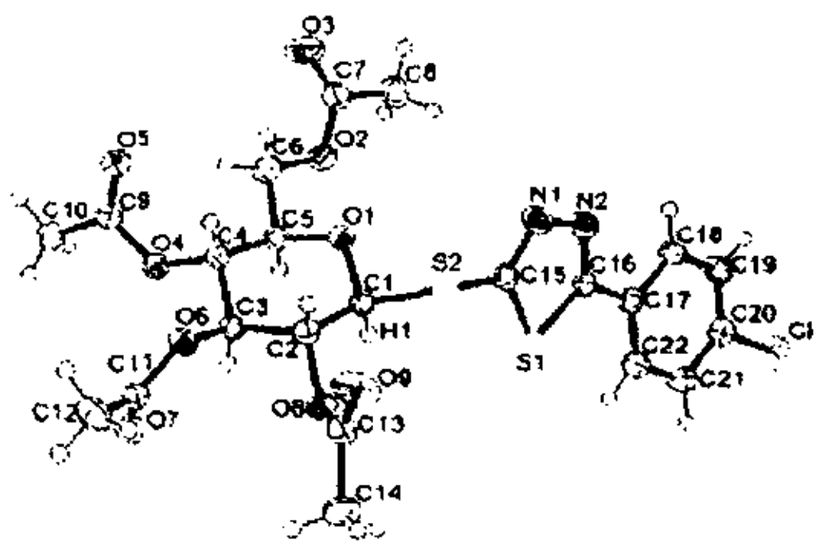


Fig. 6. View of compound **5b-31** with the atom-numbering scheme.

Crystal data

$C_{22}H_{23}ClN_2O_9S_2$	D_x = 1.486 Mg/m^3
M_r =559.00	Mo $K\alpha$ radiation
Orthorhombic	λ = 0.7107 Å
$P2_12_12_1$	θ = 3.2-27.5°
a = 5.573 (1) Å	μ(MoKa) = 3.74 cm^{-1}
b = 13.973 (3) Å	Needle
c = 32.094 (7) Å	T = 173 K
β = 90 °	0.10 x 0.10 x 0.05 mm^3
V = 2499.1 (9) Å^3	Colorless
Z = 4	F000 = 1160

Data collection

Rigaku/MSC Mercury CCD diffractometer	$R_{int.}$= 0.038
ω scans	θ_{max} = 27.48°.

Absorption correction: multi-scan
20438 measured reflections
5734 independent reflections
5678 observed reflections
$[F^2>2.0\sigma(F^2)]$

$h = -7 \rightarrow 7$
$k = -16 \rightarrow 18$
$l = -34 \rightarrow 41$
intensity variation: none

Refinement
Refinement on *F*
$R = 0.0398$
$wR = 0.05398$
5678 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.0032$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* [1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C, N, O, S) and 6.1.1.2 (H)]

Table 7. Bond Lengths(Å) and Bond Angles(°)

Cl-C(20)	1.738(3)	S(1)-C(15)	1.725(3)
S(1)-C(16)	1.725(3)	S(2)-C(1)	1.811(3)
S(2)-C(15)	1.753(3)	O(1)-C(1)	1.420(3)
O(1)-C(5)	1.431(3)	O(2)-C(6)	1.438(3)
O(2)-C(7)	1.337(4)	O(3)-C(7)	1.199(4)
O(4)-C(4)	1.440(3)	O(4)-C(9)	1.353(3)
O(5)-C(9)	1.202(3)	O(6)-C(3)	1.449(3)
O(6)-C(11)	1.351(3)	O(7)-C(11)	1.198(3)
O(8)-C(2)	1.436(3)	O(8)-C(13)	1.359(3)
O(9)-C(13)	1.197(4)	N(1)-N(2)	1.379(3)
N(1)-C(15)	1.298(4)	N(2)-C(16)	1.302(4)
C(1)-C(2)	1.523(3)	C(2)-C(3)	1.523(4)
C(3)-C(4)	1.508(4)	C(4)-C(5)	1.536(3)
C(5)-C(6)	1.507(4)	C(7)-C(8)	1.496(4)
C(9)-C(10)	1.482(4)	C(11)-C(12)	1.496(4)
C(13)-C(14)	1.491(4)	C(16)-C(17)	1.475(4)
C(17)-C(18)	1.393(4)	C(17)-C(22)	1.390(4)
C(18)-C(19)	1.385(4)	C(19)-C(20)	1.378(4)
C(20)-C(21)	1.378(4)	C(21)-C(22)	1.380(4)
C(15)-S(1)-C(16)	86.9(1)	C(1)-S(2)-C(15)	101.9(1)
C(1)-O(1)-C(5)	113.2(2)	C(6)-O(2)-C(7)	116.4(2)
C(4)-O(4)-C(9)	118.4(2)	C(3)-O(6)-C(11)	118.2(2)
C(2)-O(8)-C(13)	118.2(2)	N(2)-N(1)-C(15)	112.3(2)
N(1)-N(2)-C(16)	112.6(2)	S(2)-C(1)-O(1)	107.0(2)
S(2)-C(1)-C(2)	106.5(2)	O(1)-C(1)-C(2)	110.2(2)
O(8)-C(2)-C(1)	109.6(2)	O(8)-C(2)-C(3)	105.8(2)
C(1)-C(2)-C(3)	111.2(2)	O(6)-C(3)-C(2)	104.5(2)
O(6)-C(3)-C(4)	109.5(2)	C(2)-C(3)-C(4)	112.5(2)
O(4)-C(4)-C(3)	106.1(2)	O(4)-C(4)-C(5)	109.9(2)
C(3)-C(4)-C(5)	109.6(2)	O(1)-C(5)-C(4)	108.9(2)
O(1)-C(5)-C(6)	106.0(2)	C(4)-C(5)-C(6)	111.1(2)
O(2)-C(6)-C(5)	107.6(2)	O(2)-C(7)-O(3)	122.9(3)
O(2)-C(7)-C(8)	111.1(3)	O(3)-C(7)-C(8)	126.0(3)
O(4)-C(9)-O(5)	123.6(3)	O(4)-C(9)-C(10)	110.9(2)
O(5)-C(9)-C(10)	125.5(3)	O(6)-C(11)-O(7)	123.7(2)
O(6)-C(11)-C(12)	110.5(2)	O(7)-C(11)-C(12)	125.8(3)
O(8)-C(13)-O(9)	123.6(3)	O(8)-C(13)-C(14)	109.6(2)
O(9)-C(13)-C(14)	126.8(2)	S(1)-C(15)-S(2)	123.0(2)
S(1)-C(15)-N(1)	114.2(2)	S(2)-C(15)-N(1)	122.3(2)
S(1)-C(16)-N(2)	113.9(2)	S(1)-C(16)-C(17)	122.8(2)

N(2)-C(16)-C(17)	123.1(2)	C(16)-C(17)-C(18)	119.8(2)
C(16)-C(17)-C(22)	120.7(2)	C(18)-C(17)-C(22)	119.5(2)
C(17)-C(18)-C(19)	120.2(3)	C(18)-C(19)-C(20)	119.2(3)
Cl-C(20)-C(19)	120.1(2)	Cl-C(20)-C(21)	118.6(2)
C(19)-C(20)-C(21)	121.3(2)	C(20)-C(21)-C(22)	119.5(3)
C(17)-C(22)-C(21)	120.2(3)		

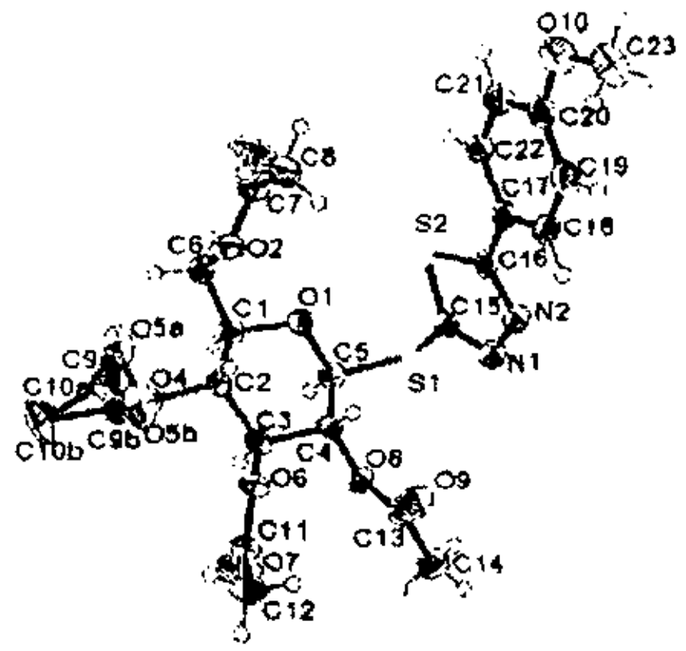


Fig. 7. View of compound **5h-37** with the atom-numbering scheme.

Crystal data

$C_{23}H_{26}N_2O_{10}S_2$	D_x = 1.393 Mg/m^3
M_r =554.59	Mo $K\alpha$ radiation
Monoclinic	λ = 0.7107 Å
$P2_1$	θ = 3.4-27.5°
a = 5.751 (2) Å	μ(MoKa) = 2.58 cm^{-1}
b = 22.691 (7) Å	Block
c = 10.147 (3) Å	T = 173 K
β = 93.263 (6)°	0.30 x 0.15 x 0.05 mm^3
V = 1322.0 (7) Å^3	Colorless
Z = 2	F000 = 580

Data collection

Rigaku/MSC Mercury CCD diffractometer	$R_{int.}$= 0.017
ω scans	θ_{max} = 27.48°
Absorption correction: multi-scan	h = -7→5
10440 measured reflections	k = -28→28
5880 independent reflections	l = -13→13
5865 observed reflections	intensity variation: none
[F^2>2.0\σ(F^2)]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 1.7815
R= 0.0393	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
wR = 0.0503	$\Delta\rho_{min}$ = -0.28 e Å^{-3}
5865 reflections	Atomic scattering factors from
361 parameters	*International Tables for Crystallography*
H-atom parameters constrained	[1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1(C,
$w = 1/[\sigma^2(F_o) + 0.00063\|F_o\|^2]$	N, O, S) and 6.1.1.2 (H)]

Table 8. Bond Lengths(Å) and Bond Angles(°)

S(1)-C(5)	1.811(2)	S(1)-C(15)	1.752(3)
S(2)-C(15)	1.732(2)	S(2)-C(16)	1.722(2)
O(1)-C(1)	1.438(3)	O(1)-C(5)	1.420(3)
O(2)-C(6)	1.441(3)	O(2)-C(7)	1.338(3)
O(3)-C(7)	1.203(3)	O(4)-C(2)	1.439(3)
O(4)-C(9a)	1.344(7)	O(4)-C(9b)	1.352(8)
O(5a)-O(5b)	1.368(6)	O(5a)-C(9a)	1.193(7)
O(5a)-C(9b)	1.391(8)	O(5b)-C(9a)	1.594(7)
O(5b)-C(9b)	1.208(8)	O(6)-C(3)	1.444(3)
O(6)-C(11)	1.357(3)	O(7)-C(11)	1.193(3)
O(8)-C(4)	1.432(3)	O(8)-C(13)	1.354(3)
O(9)-C(13)	1.198(3)	O(10)-C(20)	1.363(3)
O(10)-C(23)	1.424(4)	N(1)-N(2)	1.380(3)
N(1)-C(15)	1.295(3)	N(2)-C(16)	1.309(3)
C(1)-C(2)	1.527(3)	C(1)-C(6)	1.513(3)
C(2)-C(3)	1.518(3)	C(3)-C(4)	1.522(3)
C(4)-C(5)	1.526(3)	C(7)-C(8)	1.493(4)
C(9a)-C(9b)	0.586(7)	C(9a)-C(10a)	1.42(1)
C(9a)-C(10b)	1.54(2)	C(9b)-C(10a)	1.55(1)
C(9b)-C(10b)	1.59(1)	C(10a)-C(10b)	0.23(4)
C(11)-C(12)	1.489(3)	C(13)-C(14)	1.499(4)
C(16)-C(17)	1.464(3)	C(17)-C(18)	1.392(3)
C(17)-C(22)	1.400(3)	C(18)-C(19)	1.382(4)
C(19)-C(20)	1.386(4)	C(20)-C(21)	1.393(4)
C(21)-C(22)	1.373(4)		
C(5)-S(1)-C(15)	100.8(1)	C(15)-S(2)-C(16)	87.4(1)
C(1)-O(1)-C(5)	112.5(2)	C(6)-O(2)-C(7)	118.0(2)
C(2)-O(4)-C(9a)	121.3(3)	C(2)-O(4)-C(9b)	116.1(3)
C(9a)-O(4)-C(9b)	25.1(3)	O(5b)-O(5a)-C(9a)	76.6(4)
O(5b)-O(5a)-C(9b)	51.9(4)	C(9a)-O(5a)-C(9b)	24.7(3)
O(5a)-O(5b)-C(9a)	46.7(3)	O(5a)-O(5b)-C(9b)	65.0(4)
C(9a)-O(5b)-C(9b)	18.3(4)	C(3)-O(6)-C(11)	117.5(2)
C(4)-O (8)-C(13)	117.6(2)	C(20)-O(10)-C(23)	117.8(2)
N(2)-N(1)-C(15)	112.2(2)	N(1)-N(2)-C(16)	113.2(2)
O(1)-C(1)-C(2)	110.0(2)	O(1)-C(1)-C(6)	106.4(2)
C(2)-C(1)-C(6)	113.3(2)	O(4)-C(2)-C(1)	107.3(2)
O(4)-C(2)-C(3)	106.8(2)	C(1)-C(2)-C(3)	111.6(2)
O(6)-C(3)-C(2)	106.5(2)	O(6)-C(3)-C(4)	108.9(2)
C(2)-C(3)-C(4)	111.1(2)	O(8)-C(4)-C(3)	108.7(2)
O(8)-C(4)-C(5)	107.0(2)	C(3)-C(4)-C(5)	108.3(2)
S(1)-C(5)-O(1)	109.4(1)	S(1)-C(5)-C(4)	113.6(2)
O(1)-C(5)-C(4)	109.0(2)	O(2)-C(6)-C(1)	109.5(2)
O(2)-C(7)-O(3)	122.4(3)	O(2)-C(7)-C(8)	111.9(2)
O(3)-C(7)-C(8)	125.7(2)	O(4)-C(9a)-O(5a)	120.7(6)
O(4)-C(9a)-O(5b)	100.4(4)	O(4)-C(9a)-C(9b)	78(1)
O(4)-C(9a)-C(10a)	111.8(7)	O(4)-C(9a)-C(10b)	114.4(8)
O(5a)-C(9a)-O(5b)	56.6(4)	O(5a)-C(9a)-C(9b)	96(1)
O(5a)-C(9a)-C(10a)	127.4(8)	O(5a)-C(9a)-C(10b)	123.9(9)
O(5b)-C(9a)-C(9b)	40(1)	O(5b)-C(9a)-C(10a)	112.9(9)
O(5b)-C(9a)-C(10b)	105.1(8)	C(9b)-C(9a)-C(10a)	90(1)
C(9b)-C(9a)-C(10b)	84(1)	C(10a)-C(9a)-C(10b)	7(1)
O(4)-C(9b)-O(5a)	107.1(5)	O(4)-C(9b)-O(5b)	124.0(6)
O(4)-C(9b)-C(9a)	76(1)	O(4)-C(9b)-C(10a)	104.3(8)
O(4)-C(9b)-C(10b)	110.8(8)	O(5a)-C(9b)-O(5b)	63.0(4)

O(5a)-C(9b)-C(9a)	58(1)	O(5a)-C(9b)-C(10a)	106.1(6)
O(5a)-C(9b)-C(10b)	108.1(8)	O(5b)-C(9b)-C(9a)	121(1)
O(5b)-C(9b)-C(10a)	131.7(9)	O(5b)-C(9b)-C(10b)	124.9(9)
C(9a)-C(9b)-C(10a)	67(1)	C(9a)-C(9b)-C(10b)	74(1)
C(10a)-C(9b)-C(10b)	8(1)	C(9a)-C(10a)-C(9b)	22.3(4)
C(9a)-C(10a)-C(10b)	115(7)	C(9b)-C(10a)-C(10b)	96(6)
C(9a)-C(10b)-C(9b)	21.5(3)	C(9a)-C(10b)-C(10a)	56(6)
C(9b)-C(10b)-C(10a)	74(6)	O(6)-C(11)-O(7)	123.4(2)
O(6)-C(11)-C(12)	110.4(2)	O(7)-C(11)-C(12)	126.2(2)
O(8)-C(13)-O(9)	123.9(2)	O(8)-C(13)-C(14)	109.7(2)
O(9)-C(13)-C(14)	126.3(2)	S(1)-C(15)-S(2)	123.1(1)
S(1)-C(15)-N(1)	122.7(2)	S(2)-C(15)-N(1)	114.0(2)
S(2)-C(16)-N(2)	113.1(2)	S(2)-C(16)-C(17)	123.6(2)
N(2)-C(16)-C(17)	123.2(2)	C(16)-C(17)-C(18)	120.9(2)
C(16)-C(17)-C(22)	120.6(2)	C(18)-C(17)-C(22)	118.5(2)
C(17)-C(18)-C(19)	121.0(2)	C(18)-C(19)-C(20)	120.1(2)
O(10)-C(20)-C(19)	124.8(2)	O(10)-C(20)-C(21)	115.8(2)
C(19)-C(20)-C(21)	119.4(2)	C(20)-C(21)-C(22)	120.5(2)
C(17)-C(22)-C(21)	120.6(2)		

4 物理性质与波谱学性质

核磁共振谱：以 $CDCl_3$ 或 DMSO-d_6 为溶剂，对所合成的化合物的核磁共振氢谱进行了测定。化合物 **5** 的乙酰基都在 1.96-2.14 ppm 范围内出四个单峰。糖环上的七个氢原子中 H-1 处在最低场，$J_{H1,H2}$ = 9.0-9.9 Hz，说明化合物都是β构型；H-3、H-2、H-4 出在 5-6 ppm 的范围内，其中 **5a** 的三个氢位置分得较开而 **5b** 的有部分重叠；再较低场有两个 H-6，它们由于相互的耦合和与 H-5 的耦合都呈 dd 峰；最低场为 H-5，它由于受 H-4 和两个 H-6 耦合而呈 ddd 峰。而化合物 **6** 的氢谱中糖环氢除去 H-1 出在最低场外其他氢的峰都比较集中，在 3-4 ppm 范围内。碳谱中，**5a** 和 **5b** 的主要区别在于 **5a** 中 C=S 较明显的处于最低场的约 190 ppm 的位置。

质谱：化合物 **5** 的 FAB 质谱均出 M+1、M+Li 和 M+Na 的峰。

化合物 **5** 和 **6** 的产率、熔点、旋光、^{1}H NMR、^{13}C NMR、质谱及元素分析数据如下：

5-Phenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-1**).

Yield: 49%. Mp 149-151 °C. $[\alpha]_D$ –43 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 3 H, CH_3C=O), 1.97 (s, 3 H, CH_3C=O), 1.98 (s, 3 H, CH_3C=O) 2.00 (s, 3 H, CH_3C=O), 3.76-3.82 (m, 1 H, Glc-H-5), 4.14-4.16 (m, 2 H, Glc-H-6), 5.04-5.14 (m, 2 H, Glc-H-2, H-4), 5.23-5.29 (m, 2 H, Glc-H-1, H-3), 7.36-7.39 (m, 3 H, ArH), 7.94-7.98 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.39, 61.75, 67.96, 69.89, 73.52, 75.95, 83.27, 126.30,

128.15, 128.71, 130.07, 169.33, 169.53, 169.99, 170.90. FABMS *m/z* 508 (M+1), 514 (M+Li), 530 (M+Na). Anal. Calcd. for $C_{22}H_{25}N_3O_9S$: C, 52.06; H, 4.97; N, 8.28. Found: C, 52.21; H, 4.94; N, 8.16.

5-o-Methylphenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole **(5b-2)**.

Yield: 53.%. Mp 100-102 °C. $[\alpha]_D$ –31 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H, CH_3C=O), 1.99 (s, 3 H, CH_3C=O), 2.00 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.53 (s, 3 H, $ArCH_3$), 3.78-3.82 (m, 1 H, Glc-H-5), 4.17-4.21 (m, 2 H, Glc-H-6), 5.06-5.19 (m, 2 H, Glc-H-2, H-4), 5.24-5.32 (m, 2 H, Glc-H-1, H-3), 7.19-7.30 (m, 3 H, ArH), 7.65-7.67 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 21.03, 29.56, 61.84, 68.03, 69.84, 73.66, 76.04, 83.27, 125.95, 129.03, 129.86, 131.28, 137.05, 169.39, 169.51, 170.08, 170.83. FABMS *m/z* 522 (M+1), 528 (M+Li), 544 (M+Na). Anal. Calcd. for $C_{23}H_{27}N_3O_9S$: C, 52.97; H, 5.22; N, 8.06. Found: C, 53.04; H, 5.61; N, 8.21.

5-p-Methylphenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole **(5b-3)**.

Yield: 33%. Mp 150-152 °C. $[\alpha]_D$ –46 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H, CH_3C=O), 1.99 (s, 3 H, CH_3C=O), 2.00 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.35 (s, 3 H, $ArCH_3$), 3.78-3.81 (m, 1 H, Glc-H-5), 4.15-4.18 (m, 2 H, Glc-H-6), 5.06-5.15 (m, 2 H, Glc-H-2, H-4), 5.24-5.27 (m, 2 H, Glc-H-1, H-3), 7.20 (d, 2 H, J = 8.1 Hz, ArH), 7.85 (d, 2 H, J = 8.1 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.43, 21.29, 61.78, 68.01, 69.93, 73.58, 75.98, 83.37, 129.46, 136.30, 140.39, 169.36, 169.57, 170.05, 170.92. FABMS *m/z* 522 (M+1), 528 (M+Li), 544 (M+Na). Anal. Calcd. for $C_{23}H_{27}N_3O_9S$: C, 52.97; H, 5.22; N, 8.06. Found: C, 52.70; H, 5.21; N, 8.09.

5-o-Chlorophenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole **(5b-4)**.

Yield: 34%. Mp 133-135 °C. $[\alpha]_D$ –19 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 3.79-3.85 (m, 1 H, Glc-H-5), 4.18-4.23 (m, 2 H, Glc-H-6), 5.14-5.23 (m, 2 H, Glc-H-2, H-4), 5.31 (t, 1 H, $J_{H2,H3}$ = 9.3 Hz, Glc-H-3), 5.38 (d, 1 H, $J_{H1,H2}$ = 10.5 Hz, Glc-H-1), 7.38-7.41 (m, 2 H, ArH), 7.47-7.49 (m, 1 H, ArH), 8.14-8.18 (m, 1 H, ArH). ^{13}C NMR

($CDCl_3$): δ 20.51, 61.45, 67.61, 69.58, 73.44, 76.47, 83.18, 122.47, 127.16, 130.97, 131.26, 132.94, 161.36, 164.69, 169.31, 169.42, 169.94, 170.55. FABMS *m/z* 542 (M+1), 548 (M+Li), 564 (M+Na). Anal. Calcd. for $C_{22}H_{24}ClN_3O_9S$: C, 48.76; H, 4.46; N, 7.75. Found: C, 48.44; H, 4.57; N, 7.78.

5-p-Chlorophenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-5**).

Yield: 53%. Mp 86-88 °C. $[\alpha]_D$ –55 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.99 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 3.80 (ddd, $J_{H4,H5}$ = 9.9 Hz, Glc-H-5), 4.17 (dd, $J_{H5,H6'}$ = 4.5 Hz, Glc-H-6'), 4.24 (dd, 1 H, $J_{H5,H6}$ = 2.4 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 5.05-5.16 (m, 3 H, Glc-H-2, H-3, H-4), 5.24-5.30 (m, 1 H, Glc-H-1), 7.37 (d, 2 H, *J* = 8.4 Hz, ArH), 7.95 (d, 2 H, *J* = 8.4 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.46, 20.66, 61.78, 67.96, 69.95, 73.40, 76.21, 83.12, 127.68, 128.96, 135.84, 169.38, 169.57, 170.03, 171.05. FABMS *m/z* 542 (M+1), 548 (M+Li), 564 (M+Na). Anal. Calcd. for $C_{22}H_{24}ClN_3O_9S$: C, 48.76; H, 4.46; N, 7.75. Found: C, 48.59; H, 4.39; N, 7.71.

5-m-Chlorophenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-5**).

Yield: 31%. Mp 138-140 °C. $[\alpha]_D$ –54 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 2.13(s, 3 H, $CH_3C=O$), 3.82 (ddd, $J_{H4,H5}$ = 9.9 Hz, Glc-H-5), 4.16 (dd, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 4.34 (dd, 1 H, $J_{H5,H6}$ = 2.4 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 5.04-5.14 (m, 3 H, Glc-H-2, H-3, H-4), 5.25-5.32 (m, 1 H, Glc-H-1), 7.35-7.39 (m, 2 H, ArH), 7.92-7.99 (m, 1 H, ArH), 8.07 (s, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.75, 61.78, 67.93, 69.93, 73.28, 76.30, 82.94, 124.42, 126.48, 129.74, 129.98, 131.38, 134.71, 169.38, 169.57, 170.02, 171.16. FABMS *m/z* 542 (M+1), 548 (M+Li), 564 (M+Na). Anal. Calcd. for $C_{22}H_{24}ClN_3O_9S$: C, 48.76; H, 4.46; N, 7.75.Found: C, 48.94; H, 4.47; N, 7.73.

5-o-Bromophenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-7**).

Yield: 71%. Mp 132-134 °C. $[\alpha]_D$ –18 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.99 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 3.82

(ddd, $J_{H4,H5}$ = 9.9 Hz, Glc-H-5), 4.14 (dd, $J_{H5,H6'}$ = 2.4 Hz, Glc-H-6'), 4.22 (dd, 1 H, $J_{H5,H6}$ = 5.1 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 5.11 (d, 1 H, $J_{H2,H3}$ = 9.9 Hz,Glc-H-2), 5.17 (t, 1 H, $J_{H4,H5}$ = 9.9 Hz,Glc-H-4), 5.29 (d, 1 H, $J_{H3,H4}$ = 9.6 Hz,Glc-H-3), 5.36 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz,Glc-H-1), 7.28 (t, 1 H, J = 7.8 Hz, ArH), 7.40 (t, 1 H, J = 7.8 Hz, ArH), 7.65 (d, 1 H, J = 7.8 Hz, ArH), 7.98 (d, 1 H, J = 7.8 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 61.87, 68.06, 69.87, 73.69, 76.08, 83.37, 120.75, 127.74, 131.35, 131.86, 133.89, 169.34, 169.45, 170.06, 170.76. FABMS *m/z* 586 (M+1), 592 (M+Li), 608 (M+Na). Anal. Calcd. for $C_{22}H_{24}BrN_3O_9S$: C, 45.06; H, 4.13; N, 7.17. Found: C, 44.97; H, 4.16; N, 7.40.

5-p-Bromophenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-8**).

Yield: 55%. Mp 159-161 °C. $[\alpha]_D$ –48 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.07 (s, 3 H, CH_3C=O), 2.10 (s, 3 H, CH_3C=O), 3.80 (ddd, $J_{H4,H5}$ = 9.9 Hz, Glc-H-5), 4.17 (dd, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 4.30 (dd, 1 H, $J_{H5,H6}$ = 2.4 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 5.06-5.14(m, 3 H, Glc-H-2, H-3, H-4), 5.25-5.28 (m, 1 H, Glc-H-1), 7.55 (d, 2 H, J = 8.1 Hz, ArH), 7.92 (d, 2 H, J = 8.4 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.75, 61.77, 67.93, 69.92, 73.32, 76.25, 83.00, 127.92, 131.92, 169.39, 169.60, 170.06, 171.16. FABMS *m/z* 586 (M+1), 592 (M+Li), 608 (M+Na). Anal. Calcd. for $C_{22}H_{24}BrN_3O_9S$: C, 45.06; H, 4.13; N, 7.17. Found: C, 45.10; H, 3.94; N, 7.08.

5-o-Hydroxyphenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-9**).

Yield: 50%. Mp 178-180 °C. $[\alpha]_D$ –49 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.04 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 3.82-3.85 (m, 1 H, Glc-H-5), 4.20-4.23 (m, 2 H, Glc-H-6), 5.07-5.17 (m, 3 H, Glc-H-2, H-3, H-4), 5.27-5.30 (m, 1 H, Glc-H-1), 6.91 (t, 1 H, J = 7.5 Hz, ArH), 7.01 (d, 1 H, J = 7.5 Hz, ArH), 7.31 (t, 1 H, J = 7.8 Hz, ArH), 7.82 (d, 1 H, J = 7.8 Hz, ArH), 10.71 (s, 1 H, Ar-OH). ^{13}C NMR ($CDCl_3$): δ 20.45, 20.54, 61.81, 67.92, 69.80, 73.54, 76.22, 83.11, 117.53, 119.63, 125.95, 132.15, 156.65, 169.44, 169.70, 170.11, 177.22. FABMS *m/z* 524 (M+1), 530 (M+Li), 546 (M+Na). Anal. Calcd. for $C_{22}H_{25}N_3O_{10}S$: C, 50.47; H,

4.81; N, 8.03. Found: C, 50.40; H, 4.96; N, 8.09.

5-o-Methoxyphenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-10**).

Yield: 34%. Mp 157-158 °C. $[\alpha]_D$ –31 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.98 (s, 3 H, $CH_3C=O$), 2.00 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 3.83 (ddd, $J_{H4,H5}$ = 9.9 Hz, Glc-H-5), 4.04 (s, 3 H, Ar-OCH_3), 4.10 (dd, $J_{H5,H6'}$ = 1.8 Hz, Glc-H-6'), 4.25 (dd, 1 H, $J_{H5,H6}$ = 4.5 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 5.12-5.52 (m, 3 H, Glc-H-2, H-3, H-4), 5.50 (d, 1 H, $J_{H1,H2}$ = 10.5 Hz,Glc-H-1), 7.05 (d, 1 H, J = 8.1 Hz, ArH), 7.11 (t, 1 H, J = 7.8 Hz, ArH), 7.44 (t, 1 H, J = 7.8 Hz, ArH), 8.28 (d, 1 H, J = 7.5 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.57, 56.00, 61.87, 68.07, 69.84, 73.93, 75.96, 83.67, 111.18, 114.66, 121.52, 129.52, 131.90, 153.82, 156.71, 156.87, 169.38, 169.45, 170.15, 170.67. FABMS *m/z* 538 (M+1), 544 (M+Li), 560 (M+Na). Anal. Calcd. for $C_{23}H_{27}N_3O_{10}S$: C, 51.39; H, 5.06; N, 7.82. Found: C, 51.24; H, 4.99; N, 7.91.

5-p-Methoxyphenyl-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,2,4-triazole (**5b-11**).

Yield: 70%. Mp 172-174 °C. $[\alpha]_D$ –23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.09 (s, 3 H, $CH_3C=O$), 3.72-3.79 (m, 1 H, Glc-H-5), 3.83 (s, 3 H, $ArOCH_3$), 4.15-4.25 (m, 2 H, Glc-H-6), 5.07-5.19 (m, 2 H, Glc-H-2, H-4), 5.25-5.31 (m, 2 H, Glc-H-1, H-3), 6.94 (d, 2 H, J = 8.1 Hz, ArH), 7.93 (d, 2 H, J = 8.1 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 20.53, 20.68, 55.30, 61.78, 68.00, 69.92, 73.55, 76.07, 83.29, 114.17, 127.92, 161.10, 169.41, 169.62, 170.09, 171.02. FABMS *m/z* 538 (M+1), 544 (M+Li), 560 (M+Na). Anal. Calcd. for $C_{23}H_{27}N_3O_{10}S$: C, 51.39; H, 5.06; N, 7.82. Found: C, 51.11; H, 5.00; N, 7.76.

5-Methyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-12**)

Mp 144-145 °C. $[\alpha]_D$ +34 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.92 (s, 3 H, $CH_3C=O$), 1.98 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 3.37 (s, 3 H, CH_3), 3.92 (ddd, J = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.10 (dd, J = 1.8, 12.9 Hz, 1 H, Glc-H-6), 4.25 (dd, J = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.15 (t, J = 9.6 Hz, 1 H, Glc-H-4), 5.34 (t, J = 9.3 Hz, 1 H, Glc-H-2), 5.44 (t, J = 9.3 Hz, 1 H, Glc-H-3), 5.82 (d, J = 9.0 Hz,

1 H, Glc-H-1). ^{13}C NMR ($CDCl_3$): δ 11.46, 20.42, 20.59, 61.46, 67.46, 69.25, 72.97, 74.59, 82.68, 159.62, 169.88, 170.41, 178.33. FABMS *m/z* 447 (M+1), 453 (M+Li), 469 (M+Na). Anal. Calcd. for $C_{17}H_{22}N_2O_{10}S$: C, 45.74; H, 4.97; N, 6.27. Found: C, 45.69; H, 5.14; N, 6.36.

5-13 Yield: 60.2%. **a**:**b** = 1:10

5-Phenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione **(5a-13)**

Mp 223-225 °C. $[\alpha]_D$ -23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.94 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.09 (s, 3 H, $CH_3C=O$), 3.99 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, *J* = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.25 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.41 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.66 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.95 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.47~7.57 (m, 2 H, ArH), 7.92~7.95 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.54, 20.69, 61.49, 67.49, 69.19, 73.17, 74.65, 82.95, 121.88, 126.77, 129.16, 132.77, 159.58, 168.92, 169.34, 170.05, 170.58, 177.91. FABMS *m/z* 509 (M+1), 515 (M+Li), 531 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S$: C, 51.96; H, 4.76; N, 5.51. Found: C, 51.80; H, 4.63; N, 5.36.

5-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole **(5b-13)**

Mp 129-130 °C. $[\alpha]_D$ -23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.00 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 3.88 (ddd, *J* = 1.8, 4.5, 9.9 Hz, 1 H, Glc-H-5), 4.12 (dd, *J* = 1.8, 12.6 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* = 4.5, 12.6 Hz, 1 H, Glc-H-6), 5.12~5.32 (m, 3 H, Glc-H-4, H-2, H-3), 5.51 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.47~7.54 (m, 3 H, ArH), 7.99~8.01 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 61.52, 67.69, 69.74, 73.74, 76.47, 83.37, 123.23, 124.82, 126.74, 129.09, 132.99, 160.58, 166.48, 169.31, 169.92, 170.54. FABMS *m/z* 509 (M+1), 515 (M+Li), 531 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S$: C, 51.96; H, 4.76; N, 5.51. Found: C, 51.76; H, 4.52; N, 5.37.

5-14 Yield: 48.5%. **a**:**b** = 1:4

5-Piridyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione **(5a-14)**

$[\alpha]_D$ -21 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.92 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 3.98 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.25 (t, *J* = 9.3 Hz, 1 H, Glc-H-4), 5.41 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.66 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.95 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.76 (d, *J* = 6.3 Hz, 2 H, ArH), 8.80 (d, *J* = 6.3 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.43, 20.59, 61.42, 67.45, 69.25, 72.94, 74.70, 83.01, 119.77, 129.09, 159.92, 157.42, 168.89, 169.25, 169.88, 170.38, 177.62. FABMS *m/z* 510 (M+1), 516 (M+Li), 532 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S$: C, 49.51; H, 4.55; N, 8.25. Found: C, 49.35; H, 4.47; N, 8.38.

5-Piridyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole (**5b-14**)

Mp 147-149 °C. $[\alpha]_D$ -22 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 3.89 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.12 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.12~5.35 (m, 3 H, Glc-H-4, H-2, H-3), 5.55 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.84 (d, *J* = 5.1 Hz, 2 H, ArH), 8.80 (d, *J* = 5.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.78, 20.90, 61.70, 67.87, 69.83, 73.64, 83.45, 120.31, 130.54, 151.20, 162.59, 164.82, 169.60, 170.19, 170.77. FABMS *m/z* 510 (M+1), 516 (M+Li), 532 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S$: C, 49.51; H, 4.55; N, 8.25. Found: C, 49.26; H, 4.32; N, 8.31.

5-15 Yield: 50.0%. **a**:**b** = 1:8

5-o-Methylphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-15**)

Mp 177-179 °C. $[\alpha]_D$ -28 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.91 (s, 3 H, $CH_3C=O$), 2.00 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.60 (s, 3 H, $Ar\text{-}CH_3$), 3.99 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, *J* = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.22 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.40 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.67 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.94 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.24~7.30 (m, 2 H, ArH), 7.38~7.43 (m, 1 H, ArH), 7.83~7.85 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.37, 20.51, 21.96, 61.39, 67.46, 68.94, 73.15, 74.47, 82.75, 120.58, 126.13, 128.51, 131.77, 132.09, 138.86, 168.70, 169.25, 169.85, 170.35,

177.33. FABMS *m/z* 523 (M+1), 529 (M+Li), 545 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S$: C, 52.87; H, 5.02; N, 5.36. Found: C, 52.80; H, 4.83; N, 5.17.

5-o-Methylphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazol e (**5b-15**)

Mp 139-141 °C. $[\alpha]_D$ -23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.98~2.06 (m, 12 H, $3CH_3C=O$), 2.65 (s, 3 H, Ar-CH_3), 3.86 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.10 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.26 (dd, 1 H, *J* = 4.8, 12.3 Hz, Glc-H-6), 5.10~5.31 (m, 3 H, Glc-H-4, H-2, H-3), 5.50 (d, 1 H, *J* = 9.9 Hz, Glc-H-1), 7. 31~7.40 (m, 3 H, ArH), 7.82~7.84 (m, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.42, 21.93, 61.46, 67.64, 69.64, 73.43, 76.39, 83.18, 122.21, 126.15, 128.70, 131.40, 131.70, 138.25, 160.14, 166.58, 169.24, 169.31, 169.83, 170.41. FABMS *m/z* 510 (M+1), 516 (M+Li), 532 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S$: C, 52.87; H, 5.02; N, 5.36. Found: C, 52.55; H, 4.76; N, 5.28.

5-16 Yield: 45.1%. **a**:**b** = 1:5

5-p-Methylphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-16**)

Mp 210-212 °C. $[\alpha]_D$ -31 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 2.41 (s, 3 H, Ar-CH_3), 3.98 (ddd, *J* = 1.8, 5.1, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 1.8, 12.6 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 5.6, 12.3 Hz, 1 H, Glc-H-6), 5.23 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.41 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.66 (t, *J* = 9.9 Hz, 1 H, Glc-H-3), 5.95 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.28 (d, *J* = 8.1 Hz, 2 H, ArH), 7.81 (d, *J* = 8.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.50, 20.65, 21.67, 61.54, 67.57, 69.20, 73.23, 74.67, 82.95, 119.10, 126.73,129.83,143.56, 159.77, 168.84, 169.30, 170.00, 170.50,177.89. FABMS *m/z* 523 (M+1), 529 (M+Li), 545 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S$: C, 52.87; H, 5.02; N, 5.36. Found: C, 52.71; H, 4.85; N, 5.52.

5-p-Methylphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazol e (**5b-16**)

Mp 149-150 °C. $[\alpha]_D$ -21 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.99 (s, 3 H, $CH_3C=O$), 2.00 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.39 (s, 3 H,

Ar-CH_3), 3.86 (ddd, J = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.10 (dd, J = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.26 (dd, J = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.10~5.33 (m, 3 H, Glc-H-4, H-2, H-3), 5.48 (d, J = 10.8 Hz, 1 H, Glc-H-1), 7.28 (d, J = 8.1 Hz, 2 H, ArH), 7.86 (d, J = 8.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 21.55, 61.49, 67.69, 69.74, 73.44, 76.39, 85.35,120.44,126.67129.74, 142.56, 160.11, 166.60, 169.25, 169.33, 169.85, 170.44. FABMS *m/z* 523 (M+1), 529 (M+Li), 545 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S$: C, 52.87; H, 5.02; N, 5.36. Found: C, 52.65; H, 4.89; N, 5.26.

5-17 Yield: 61.8%. **a**:**b** = 1:6

5-o-Chlorophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-17**)

Mp 181-183 °C. $[\alpha]_D$ -9 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 3 H, CH_3C=O), 1.99 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.04 (s, 3 H, CH_3C=O), 3.98 (ddd, J = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, J = 1.8, 12.6 Hz, 1 H, Glc-H-6), 4.27 (dd, 1 H, J = 4.8, 12.6 Hz, Glc-H-6), 5.21 (t, J = 9.6 Hz, 1 H, Glc-H-4), 5.39 (t, J = 9.9 Hz, 1 H, Glc-H-2), 5.63 (t, J = 9.6 Hz, 1 H, Glc-H-3), 5.92 (d, J = 9.3 Hz, 1 H, Glc-H-1), 7.34~7.52 (m, 3 H, ArH), 7.84 (m, J = 8.1 Hz 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.42, 20.56, 61.39, 67.45, 16.12, 73.12, 74.57, 82.92, 120.96, 127.02, 130.53, 131.41, 133.11, 133.41, 157.47, 168.70, 169.22, 169.91, 170.40, 177.46. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16. Found: C, 48.95; H, 4.32; N, 5.54.

5-o-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole (**5b-17**)

Mp 158-160 °C. $[\alpha]_D$ -25 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H, CH_3C=O), 1.99 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.04 (s, 3 H, CH_3C=O), 3.84~3.88 (m, 1 H, Glc-H-5), 4.10 (d, J = 12.3 Hz, 1 H, Glc-H-6), 4.25 (dd, 1 H, J = 4.5, 12.9 Hz, Glc-H-6), 5.10~5.33 (m, 3 H, Glc-H-4, H-2, H-3), 5.50 (d, J = 9.9 Hz, 1 H, Glc-H-1), 7.35~7.53 (m, 3 H, ArH), 7.92 (m, J = 9.0 Hz 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.42, 61.45, 67.63, 69.61, 73.41, 76.42, 83.15, 122.46, 127.10, 130.93, 131.22, 132.59, 132.90, 161.29, 164.64, 169.24, 169.33, 169.85, 170.44. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16.

Found: C, 48.79; H, 4.57; N, 5.39.

5-18 Yield: 49.5%. **a**:**b** = 1:5

5-p-Chlorophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-18**)

Mp 228-229 °C. $[\alpha]_D$ -35 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 3.98 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, *J* = 1.8, 12.6 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 4.8, 12.6 Hz, 1 H, Glc-H-6), 5.23 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.40 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.61 (t, *J* = 9.3 Hz, 1 H,Glc-H-3), 5.93 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.48 (d, *J* = 9.0 Hz, 2 H, ArH), 7.87 (d, *J* = 9.0 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.50, 20.65,29.62, 61.52, 67.54, 69.25, 73.12, 74.71, 83.01, 120.39, 128.01, 129.60, 139.18, 158.71, 168.90, 169.31, 169.97, 170.49, 177.75. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal.Calcd for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16. Found: C, 48.71; H, 4.65; N, 5.52.

5-p-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazol e (**5b-18**)

Mp 139-141 °C. $[\alpha]_D$ -18 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.00~2.05 (m, 12 H, 3 $CH_3C=O$) 3.87 (ddd, *J* = 2.4, 4.5, 9.9 Hz, 1 H, Glc-H-5), 4.10 (dd, *J* = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.25 (dd, *J* = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.10~5.31 (m, 3 H, Glc-H-4, H-2, H-3), 5.50 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.46 (d, *J* = 8.7 Hz, 2 H, ArH), 7.92 (d, *J* = 8.7 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.43, 29.56, 61.46, 67.66, 69.69, 73.41, 76.44, 83.27, 121.68, 127.97, 129.46, 138.22, 160.83, 165.59, 169.24, 169.33, 169.83, 170.41. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16. Found: C, 48.52; H, 4.59; N, 5.41.

5-19 Yield: 37.7%. **a**:**b** = 1:4

5-m-Chlorophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole -2-thione (**5a-19**)

Mp 209-212 °C. $[\alpha]_D$ -27 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 3.98 (ddd, *J* = 2.1, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* =

4.8, 12.6 Hz, 1 H, Glc-H-6), 5.22 (t, J = 9.9 Hz, 1 H, Glc-H-4), 5.40 (t, J = 9.3 Hz, 1 H, Glc-H-2), 5.61 (t, J = 9.3 Hz, 1 H,Glc-H-3), 5.93 (d, J = 9.3 Hz, 1 H, Glc-H-1), 7.43 (t, J = 7.8 Hz, 1 H, ArH), 7.52 (d, J = 7.8 Hz, 1 H, ArH), 7.80 (d, J = 7.5 Hz, 1 H, ArH), 7.91 (s, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 20.62, 61.48, 67.49, 69.26, 73.03, 74.67, 82.97, 123.51, 124.76, 126.67, 130.48, 132.76, 135.37, 158.25, 168.90, 169.27, 169.94, 170.46, 177.68. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16. Found: C, 48.71; H, 4.65; N, 5.52.

5-m-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole (**5b-19**)

Mp 119-121 °C. $[\alpha]_D$ -20 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.07 (s, 3 H, CH_3C=O), 3.88 (ddd, J = 2.1, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.12 (dd, J = 2.1, 12.3 Hz, 1 H, Glc-H-6), 4.27 (dd, J = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.12~5.35 (m, 3 H, Glc-H-4, H-2, H-3), 5.53 (d, J = 9.9 Hz, 1 H, Glc-H-1), 7.42~7.53 (m, 2 H, ArH), 7.90 (d, J = 7.5 Hz, 1 H, ArH), 7.99 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 20.51, 29.64, 61.52, 67.71, 69.72, 73.49, 83.35, 124.84, 126.73, 130.50, 132.04, 135.29, 161.22, 165.32, 169.42, 169.94, 170.54. FABMS *m/z* 543 (M+1), 549 (M+Li), 565 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_{10}S$: C, 48.67; H, 4.27; N, 5.16. Found: C, 49.01; H, 4.18; N, 5.15.

5-20 Yield: 50.0%. **a**:**b** = 1:20

5-o-Bromophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-20**)

Mp 177-179 °C. $[\alpha]_D$ -28 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 2.07 (s, 3 H, CH_3C=O), 3.98 (ddd, J = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, J = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.29 (dd, J = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.24 (t, J = 9.9 Hz, 1 H, Glc-H-4), 5.40 (t, J = 9.3 Hz, 1 H, Glc-H-2), 5.66 (t, J = 9.3 Hz, 1 H, Glc-H-3), 5.94 (d, J = 9.3 Hz, 1 H, Glc-H-1), 7.37~7.47 (m, 2 H, ArH), 7.74 (d, J = 7.5 Hz, 1 H, ArH), 7.84 (d, J = 7.8 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.53, 20.69, 61.45, 67.45, 69.23, 73.23, 74.68, 83.00, 121.68, 123.00, 127.63, 131.09, 133.25, 134.93, 158.16, 168.87, 169.33, 170.08, 170.57, 177.63. FABMS *m/z* 587 (M+1), 593 (M+Li), 609 (M+Na). Anal. Calcd. for

$C_{22}H_{23}BrN_2O_{10}S$: C, 44.98; H, 3.95; N, 4.77. Found: C, 45.21; H, 4.17; N, 4.56.

5-o-Bromophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole **(5b-20)**

Mp 149-151 °C. $[\alpha]_D$ -25 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.15 (s, 3 H, $CH_3C=O$), 3.88 (ddd, *J* = 2.1, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.11 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.27 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.12~5.34 (m, 3 H, Glc-H-4, H-2, H-3), 5.52 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.35~7.47 (m, 2 H, ArH), 7.73 (d, *J* = 7.5 Hz, 1 H, ArH), 7.87 (s, *J* = 7.8 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 61.45, 67.61, 69.58, 73.44, 76.45, 83.18, 121.40, 124.55, 127.66, 131.45, 132.73, 134.59, 161.41, 165.21, 169.33, 169.44, 169.65, 170.55. FABMS *m/z* 587 (M+1), 593 (M+Li), 609 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_{10}S$: C, 44.98; H, 3.95; N, 4.77. Found: C, 44.93; H, 4.22; N, 4.98.

5-21 Yield: 54.3%. **a**:**b** = 1:7

5-p-Bromophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazole-2-thione (**5a-21**)

Mp 222-224 °C. $[\alpha]_D$ -37 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 3.98 (ddd, *J* = 2.1, 5.1, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 5.1, 12.6 Hz, 1 H, Glc-H-6), 5.22 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.40 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.61 (t, *J* = 9.0 Hz, 1 H,Glc-H-3), 5.92 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.63 (d, *J* = 11.1 Hz, 2 H, ArH), 7.78 (d, *J* = 11.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.46, 20.62, 61.49, 67.51, 69.22, 73.09, 74.67, 82.98, 120.81, 127.64, 128.07, 132.53, 158.75, 168.87, 169.28, 169.94, 170.46, 177.71. FABMS *m/z* 587 (M+1), 593 (M+Li), 609 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_{10}S$: C, 44.98; H, 3.95; N, 4.77. Found: C, 45.25; H, 4.20; N, 5.09.

5-p-Bromophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole **(5b-21)**

Mp 151-153 °C. $[\alpha]_D$ -17 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.02~2.06 (m, 12 H, 3 $CH_3C=O$) 3.88 (ddd, *J* = 2.1, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.11 (dd, *J* = 2.1, 12.9 Hz, 1 H, Glc-H-6), 4.25 (dd, *J* = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.12~5.35 (m, 3 H, Glc-H-4, H-2,

H-3), 5.51 (d, J = 9.9 Hz, 1 H, Glc-H-1), 7.64 (d, J = 8.4 Hz, 2 H, ArH), 7.87 (d, J = 8.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 29.64, 61.49, 67.67, 73.46, 83.30, 122.12, 126.74, 128.13, 132.48, 160.95, 165.74, 165.74, 169.31, 169.92, 170.50. FABMS *m/z* 587 (M+1), 593 (M+Li), 609 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_{10}S$: C, 44.98; H, 3.95; N, 4.77. Found: C, 45.34; H, 4.15; N, 4.99.

5-22 Yield: 60.6%. **a**:**b** = 0

5-o-Hydroxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole (**5b-22**)

Mp 147-149 °C. $[\alpha]_D$ -29 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3 H, CH_3C=O), 2.00 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 3.87 (ddd, J = 2.4, 4.5, 9.9 Hz, 1 H, Glc-H-5), 4.11 (dd, J = 2.4, 12.6 Hz, 1 H, Glc-H-6), 4.26 (dd, J = 4.5, 12.6 Hz, 1 H, Glc-H-6), 5.10~5.34 (m, 3 H, Glc-H-4, H-2, H-3), 5.47 (d, J = 9.9 Hz, 1 H, Glc-H-1), 6.97(t, J = 8.1 Hz, 1 H, ArH), 7.08 (d, J = 8.1 Hz, 1 H, ArH), 7.42 (t, J = 8.4 Hz, 1 H, ArH), 7.67 (d, J = 8.1 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 61.51, 67.67, 69.69, 73.38, 83.26, 107.53, 117.57, 120.03, 126.47, 133.96, 157.27, 159.93, 165.85, 169.25, 169.34, 169.86, 170.43. FABMS *m/z* 525 (M+1), 531 (M+Li), 647 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{11}S$: C, 50.38; H, 4.61; N, 5.34. Found: C, 50.63; H, 4.20; N, 4.98.

5-23 Yield: 37.3%. **a**:**b** = 0

5-p-Hydroxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiazole (**5b-23**)

Mp 108-110 °C. $[\alpha]_D$ -16 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.07 (s, 3 H, CH_3C=O), 3.89 (ddd, J = 2.4, 4.8, 9.3 Hz, 1 H, Glc-H-5), 4.12 (d, J = 12.6 Hz, 1 H, Glc-H-6), 4.26 (dd, J = 4.5, 12.6 Hz, 1 H, Glc-H-6), 5.11~5.34 (m, 3 H, Glc-H-4, H-2, H-3), 5.45 (d, J = 9.9 Hz, 1 H, Glc-H-1), 6.99 (d, J = 8.4 Hz, 2 H, ArH), 7.86 (d, J = 8.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 61.61, 67.74, 69.80, 73.51, 76.37, 83.24, 114.73, 116.37, 128.90, 159.87, 160.23, 166.80, 169.50, 169.59, 170.09, 170.87. FABMS *m/z* 525 (M+1), 531 (M+Li), 647 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{11}S$: C, 50.38; H, 4.61; N, 5.34. Found: C, 50.51; H, 4.55; N, 5.17.

5-24 Yield: 62.0%. **a**:**b** = 1:5

5-o-Methoxlphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazol e-2-thione (**5a-24**)

Mp 205-207 °C. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 2.07 (s, 3 H, CH_3C=O), 3.94~4.01 (m, 4 H, Ar-OCH_3, Glc-H-5), 4.16 (d, *J* = 12.3 Hz, 1 H, Glc-H-6), 4.30 (d, *J* = 12.3 Hz, 1 H, Glc-H-6), 5.24 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.40 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.71 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.92 (d, *J* = 9.6 Hz, 1 H, Glc-H-1), 7.00~7.06 (m, 2 H, ArH), 7.51 (t, *J* = 7.8 Hz, 1 H, ArH), 7.79 (d, *J* = 7.8 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.82, 20.96, 56.10, 61.79, 67.80, 69.27, 73.62, 74.89, 83.24, 111.12, 112.13, 120.89, 130.26, 134.34, 158.58, 169.05, 169.64, 170.38, 170.86, 178.01. FABMS *m/z* 539 (M+1), 545 (M+Li), 561 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{11}S$: C, 51.30; H, 4.87; N, 5.20. Found: C, 51.11; H, 4.73; N, 5.07.

5-o-Methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiaz ole (**5b-24**)

Mp 125-126 °C. $[\alpha]_D$ -16 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 3.86 (ddd, *J* = 2.4, 4.5, 9.9 Hz, 1 H, Glc-H-5), 3.95 (s, 3 H, Ar-OCH_3), 4.10 (dd, *J* = 2.4, 12.6 Hz, 1 H, Glc-H-6), 4.27 (dd, 1 H, *J* = 4.5, 12.3 Hz, Glc-H-6), 5.12~5.31 (m, 3 H, Glc-H-4, H-2, H-3), 5.50 (d, 1 H, *J* = 9.9 Hz, Glc-H-1), 7.03~7.08 (m, 2 H, ArH), 7.50 (t, *J* = 8.7 Hz, 1 H, ArH), 7.87 (d, *J* = 7.8 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.81, 56.20, 61.73, 67.90, 69.99, 73.80, 76.66,83.50, 112.16, 112.59, 121.00, 130.55, 133.62, 158.03, 160.53, 165.51, 169.61, 169.73, 170.24, 170.86. FABMS *m/z* 539 (M+1), 545 (M+Li), 561 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{11}S$: C, 51.30; H, 4.87; N, 5.20. Found: C, 50.96; H, 4.72; N, 5.15.

5-25 Yield: 62.6%. **a**:**b** = 1:5

5-p-Methoxyphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-oxadiazol e-2-thione (**5a-25**)

Mp 207-210 °C. ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 3 H, CH_3C=O), 2.00 (s, 3 H, CH_3C=O), 2.04 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 3.84 (s, 3 H, Ar-OCH_3), 3.97 (dd, *J* =

3.0, 9.9 Hz, 1 H, Glc-H-5), 4.14 (d, *J* = 12.3 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.22 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.39 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.63 (t, *J* = 9.6 Hz, 1 H, Glc-H-3), 5.92 (d, *J* = 9.6 Hz, 1 H, Glc-H-1), 6.95 (d, *J* = 8.4 Hz, 2 H, ArH), 7.84 (d, *J* = 8.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.50, 20.60, 55.45, 61.52, 67.55, 69.16, 73.20, 74.59, 82.89, 114.17, 114.55, 128.62, 159.59, 163.07, 168.81, 169.96, 170.47, 177.77. FABMS *m/z* 539 (M+1), 545 (M+Li), 561 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{11}S$: C, 51.30; H, 4.87; N, 5.20. Found: C, 51.11; H, 4.65; N, 5.03.

5-p-Methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-oxadiaz ole (**5b-25**)

Mp 214-215 °C. $[\alpha]_D$ -57 ° (c 1.1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 3 H, CH_3C=O), 1.97 (s, 3 H, CH_3C=O), 1.98 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 3.82~3.86 (m, 4 H, Ar-OCH_3, Glc-H-5), 4.08 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.21 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.07~5.28 (m, 3 H, Glc-H-4, H-2, H-3), 5.44 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 6.95 (d, *J* = 9.9 Hz, 2 H, ArH), 7.88 (d, *J* = 9.9 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.37, 55.30, 61.46, 67.66, 69.72, 73.40, 76.30, 83.30, 114.43, 115.60, 128.44, 159.59, 162.40, 166.35, 169.18, 169.25, 169.77, 170.35. FABMS *m/z* 539 (M+1), 545 (M+Li), 561 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{11}S$: C, 51.30; H, 4.87; N, 5.20. Found: C, 51.53; H, 5.14; N, 5.08.

5-26 Yield: 46.8%. a:b = **1:3**

5-Methyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-26**)

Mp 182-184 °C. $[\alpha]_D$ +52 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 3 H, CH_3C=O), 1.97 (s, 3 H, CH_3C=O), 2.00 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.43 (s, 3 H, CH_3), 3.93 (ddd, *J* = 1.8, 5.1, 9.9 Hz, 1 H, Glc-H-5), 4.09 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.26 (dd, *J* = 5.1, 12.3 Hz, 1 H, Glc-H-6), 5.17 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.36 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.55 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 6.25 (d, *J* = 8.7 Hz, 1 H, Glc-H-1). ^{13}C NMR ($CDCl_3$): δ 16.21, 20.40, 20.57, 61.49, 67.61, 70.15, 73.23,74.56, 82.02, 155.82, 168.80, 169.24, 169.88, 170.41, 189.90. FABMS *m/z* 463 (M+1), 469 (M+Li), 485 (M+Na). Anal. Calcd. for $C_{17}H_{22}N_2O_9S_2$: C, 44.15; H, 4.79; N,

6.06. Found: C, 45.51; H, 5.10; N, 6.17.

5-Methyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-26**)

Mp 139-141 °C. $[\alpha]_D$ -22 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.92 (s, 3 H, $CH_3C=O$), 1.93 (s, 3 H, $CH_3C=O$), 1.96 (s, 3 H, $CH_3C=O$), 1.99 (s, 3 H, $CH_3C=O$), 2.69 (s, 3 H, CH_3), 3.78 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.08 (dd, *J* = 2.4, 12.3 Hz, 1 H, Glc-H-6), 4.21 (dd, *J* = 4.8, 12.3 Hz, 1 H, Glc-H-6), 5.02~5.09 (m, 2 H, Glc-H-4, H-2), 5.18~5.28 (m, 2 H, Glc-H-3, H-1). ^{13}C NMR ($CDCl_3$): δ 15.49, 20.33, 20.51, 61.49, 67.67, 69.43, 73.34, 76.02, 83.49, 159.99, 167.09, 169.13, 169.71, 170.23. FABMS *m/z* 463 (M+1), 469 (M+Li), 485 (M+Na). Anal. Calcd. for $C_{17}H_{22}N_2O_9S_2$: C, 44.15; H, 4.79; N, 6.06. Found: C, 45.29; H, 5.00; N, 6.25.

5-27 Yield: 61.9%. **a**:**b** =1:5

5-Phenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-27**)

Mp 220-221 °C. $[\alpha]_D$ -10 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 4.00 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 2.4, 12.6 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 4.8, 12.6 Hz, 1 H, Glc-H-6), 5.27 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.43 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.84 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 6.31 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.43~7.51 (m, 3 H, ArH), 7.67~7.71 (m, 3 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.65, 61.55, 67.77, 69.95, 73.57, 74.67, 82.45, 126.81, 128.32, 129.26, 131.87, 157.18, 168.87, 169.36, 170.02, 170.54, 189.07 FABMS *m/z* 525 (M+1), 531 (M+Li), 547 (M+Na). Anal .Calcd. for $C_{22}H_{24}N_2O_9S_2$: C, 50.37; H, 4.61; N, 5.34. Found: C, 50.77; H, 4.63; N, 5.39.

5-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-27**)

Mp 150-153 °C. $[\alpha]_D$ -17 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 3.86 (ddd, *J* = 2.0, 4.8, 9.6 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 2.0, 12.8 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 4.8, 12.8 Hz, 1 H, Glc-H-6), 5.13~5.20 (m, 2 H, Glc-H-4, H-2), 5.31 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.44 (d, *J* = 10.4 Hz, 1 H, Glc-H-1), 7.26~7.51 (m, 3 H, ArH), 7.91 (dd, *J* = 2.0, 7.6 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.54, 20.68, 61.69, 67.86, 69.69, 73.60,

76.34, 83.78, 127.83, 129.28, 129.60, 131.45, 159.94, 169.36, 169.99, 170.50. FABMS *m/z* FABMS *m/z* 525 (M+1), 531 (M+Li), 547 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_9S_2$: C, 50.37; H, 4.61; N, 5.34. Found: C, 50.55; H, 4.79; N, 5.58.

5-28 Yield: 52.9%. **a**:**b** =1:3

5-o-Methylphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-28**)

$[\alpha]_D$ -28 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.94 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.56 (s, 3 H, Ar-CH_3), 4.00 (ddd, *J* = 2.1, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, *J* = 2.1, 12.9 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.24 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.43 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.69 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 6.40 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.25~7.32 (m, 2 H, ArH), 7.36~7.46 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 20.53, 20.65, 21.64, 61.55, 67.71, 70.22, 73.51, 74.68, 82.30, 126.45, 127.22, 129.75, 131.19, 131.99, 137.57, 157.62, 168.92, 169.41, 170.03, 170.54, 189.22. FABMS *m/z* 539 (M+1), 545 (M+Li), 551 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_9S_2$: C, 51.29; H, 4.87; N, 5.20. Found: C, 51.65; H, 4.83; N, 5.46.

5-o-Methylphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-28**)

Mp 94-97 °C. $[\alpha]_D$ -5 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.96 (s, 3 H, $CH_3C=O$), 1.98 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.51 (s, 3 H, $ArCH_3$), 3.84 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.11 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.24 (dd, 1 H, *J* = 4.8, 12.3 Hz, Glc-H-6), 5.07~5.16 (m, 2 H, Glc-H-4, H-2,), 5.26 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.43 (d, *J* = 10.5 Hz, 1 H, Glc-H-1), 7.20~7.35 (m, 3 H, ArH), 7.55 (d, *J* = 7.5 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.73, 20.87, 21.69, 61.88, 68.05, 69.83, 73.76, 76.46, 83.79, 126.54, 128.77, 130.86, 131.91, 137.42, 160.82, 169.57, 169.80, 170.12, 170.65. FABMS *m/z* 539 (M+1), 545 (M+Li), 551 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_9S_2$: C, 51.29; H, 4.87; N, 5.20. Found: C, 51.44; H, 4.59; N, 5.48.

5-29 Yield: 60.3%. **a**:**b** =1:4

5-p-Methylphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-29**)

Mp 236-237 °C. $[\alpha]_D$ -20 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.91 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 2.40 (s, 3 H, Ar-CH_3), 3.99 (ddd, *J* = 2.1, 5.4, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 2.1, 12.6 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 5.4, 12.6 Hz, 1 H, Glc-H-6), 5.26 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.42 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.82 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 6.30 (d, *J* = 9.6 Hz, 1 H, Glc-H-1), 7.25 (d, *J* = 7.1 Hz, 2 H, ArH), 7.57 (d, *J* = 7.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.53, 20.68, 21.55, 61.58, 67.81, 69.96, 73.64, 74.70, 82.48, 125.66, 126.76, 129.95, 142.60, 157.36, 168.87, 169.39, 170.57, 189.05. FABMS *m/z* 539 (M+1), 545 (M+Li), 551 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_9S_2$: C, 51.29; H, 4.87; N, 5.20. Found: C, 51.41; H, 4.87; N, 5.13.

5-p-Methylphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-29**)

Mp 164-166 °C. $[\alpha]_D$ -27 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.97 (s, 3 H, $CH_3C=O$), 1.99 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.35 (s, 3 H, Ar-CH_3), 3.83 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.11 (dd, *J* = 2.4, 12.9 Hz, 1 H, Glc-H-6), 4.24 (dd, *J* = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.07~5.16 (m, 2 H, Glc-H-4, H-2), 5.27 (t, *J* = 9.9 Hz, 1 H, Glc-H-3), 5.35 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.22 (d, *J* = 8.1 Hz, 2 H, ArH), 7.74 (d, *J* = 8.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.73, 20.88, 21.69, 61.93, 68.08, 69.90, 73.76, 76.48, 83.98, 127.09, 127.93, 130.14, 142.20, 159.55, 169.57, 170.15, 170.67, 170.88. Anal. Calcd. for $C_{23}H_{26}N_2O_9S_2$: C, 51.29; H, 4.87; N, 5.20. Found: C, 51.25; H, 4.77; N, 5.26.

5-30 Yield: 63.0%. **a**:**b** =1:5

5-o-Chlorophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-30**)

Mp 193-195 °C. $[\alpha]_D$ +5 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.93 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 3.99~4.04 (m, 1 H, Glc-H-5), 4.15 (d, *J* = 12.3 Hz, 1 H, Glc-H-6), 4.31 (dd, 1 H, *J* = 5.1, 12.3 Hz, Glc-H-6), 5.25 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.43 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.81 (t, *J* = 9.6 Hz, 1 H, Glc-H-3), 6.36 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.38~7.47 (m, 3 H, ArH), 8.05 (d, 1 H, ArH), 7.83~7.85 (m, *J* = 8.7 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.53,

20.68, 61.52, 67.69, 69.98, 73.44, 74.71, 82.21, 127.29, 127.60, 130.38, 130.64, 132.38, 154.00, 168.99, 169.38, 169.99, 170.54, 189.58. FABMS *m/z* 559 (M+1), 565 (M+Li), 581 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_9S_2$: C, 47.27; H, 4.15; N, 5.01. Found: C, 47.61; H, 4.08; N, 4.89.

5-o-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-30**)

Mp 150-152 °C. $[\alpha]_D$ -27 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.00 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 3.87(ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.29 (dd, 1 H, *J* = 4.8, 12.3 Hz, Glc-H-6), 5.11~5.20 (m, 2 H, Glc-H-4, H-2), 5.29 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 5.44 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.40~7.52 (m, 3 H, ArH), 8.27 (d, *J* = 8.7 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.50, 20.65, 61.57, 67.72, 69.60, 73.51, 76.24, 83.72, 127.47, 128.45, 130.51, 130.83, 131.87, 132.38, 165.61, 169.34, 169.92, 170.50. FABMS *m/z* 559 (M+1), 565 (M+Li), 581 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_9S_2$: C, 47.27; H, 4.15; N, 5.01. Found: C, 47.52; H, 4.11; N, 4.97.

5-31 Yield: 30.2%. **a:b** =1:3

5-p-Chlorophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-31**)

Mp 241-242 °C. $[\alpha]_D$ -28 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.91 (s, 3 H, $CH_3C=O$), 2.02 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 3.99 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 5.1, 12.6 Hz, 1 H, Glc-H-6), 5.25 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.41 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.79 (t, *J* = 9.3 Hz, 1 H,Glc-H-3), 6.29 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.43 (d, *J* = 8.1 Hz, 2 H, ArH), 7.62 (d, *J* = 9.0 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.48, 20.63, 29.58, 61.52, 67.75, 69.93, 73.47, 74.68, 82.43, 126.82, 127.98, 129.58, 138.09, 155.84, 168.87, 169.34, 169.97, 170.49, 188.85. FABMS *m/z* 559 (M+1), 565 (M+Li), 581 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_9S_2$: C, 47.27; H, 4.15; N, 5.01. Found: C, 47.55; H, 4.14; N, 4.83.

5-p-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-31**)

Mp 146-148 °C. $[\alpha]_D$ -29 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 3.86 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 2.4, 12.6 Hz, 1 H, Glc-H-6), 4.29 (dd, *J* = 4.5, 12.6 Hz, 1 H, Glc-H-6), 5.12~5.20 (m, 2 H, Glc-H-4, H-2), 5.30 (t, *J* = 9.6 Hz, 1 H, Glc-H-3), 5.42 (d, *J* = 9.9 Hz, 1 H, Glc-H-1), 7.45 (d, *J* = 8.4 Hz, 2 H, ArH), 7.84 (d, *J* = 8.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.53, 20.69, 61.61, 67.75, 69.55, 73.49, 76.30, 83.62, 128.03, 128.93, 129.57, 137.57, 160.25, 169.41, 169.97, 170.49. FABMS *m/z* 559 (M+1), 565 (M+Li), 581 (M+Na). Anal. Calcd. for $C_{22}H_{23}ClN_2O_9S_2$: C, 47.27; H, 4.15; N, 5.01. Found: C, 47.44; H, 4.05; N, 4.87.

5-32 Yield: 57.0%. **a**:**b** =1:4

5-o-Bromophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-32**)

Mp 190-192 °C. $[\alpha]_D$ +23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.94 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 4.02 (ddd, *J* = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.16 (dd, *J* = 1.8, 12.6 Hz, 1 H, Glc-H-6), 4.31 (dd, *J* = 4.8, 12.6 Hz, 1 H, Glc-H-6), 5.25 (t, *J* = 9.9 Hz, 1 H, Glc-H-4), 5.43 (t, *J* = 9.6 Hz, 1 H, Glc-H-2), 5.79 (t, *J* = 9.3 Hz, 1 H, Glc-H-3), 6.37 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 7.34 (t, *J* = 8.1 Hz, 1 H, ArH), 7.46 (t, *J* = 8.4 Hz, 1 H, ArH), 7.65 (d, *J* = 8.4 Hz, 1 H, ArH), 7.96 (d, *J* = 8.1 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.54, 20.71, 61.55, 67.71, 70.07, 73.44, 74.76, 82.28, 121.77, 128.10, 129.34, 131.25, 132.50, 134.09, 155.47, 169.02, 169.41, 170.16, 170.58, 189.57. FABMS *m/z* 603 (M+1), 609 (M+Li), 625 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_9S_2$: C, 43.79; H, 3.84; N, 4.64. Found: C, 44.10; H, 3.62; N, 4.65.

5-o-Bromophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-32**)

Mp 151-153 °C. $[\alpha]_D$ -23 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.99 (s, 3 H, $CH_3C=O$), 2.01 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 3.85~3.88 (m, 1 H, Glc-H-5), 4.13 (d, 12.3 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.11~5.19 (m, 2 H, Glc-H-4, H-2), 5.29 (t, *J* = 9.6 Hz, 1 H, Glc-H-3), 5.45 (d, *J* = 10.8 Hz, 1 H, Glc-H-1), 7.33 (t, *J* = 7.5 Hz, 1 H, ArH), 7.43 (t, *J* = 7.5 Hz, 1 H, ArH),

7.69 (d, J = 7.5 Hz, 1 H, ArH), 8.10 (d, J = 7.5 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.46, 20.65, 61.52, 67.69, 69.57, 73.46, 76.19, 83.64, 122.24, 127.87, 130.44, 131.60, 131.95, 133.92, 161.74, 166.98, 169.31, 169.88, 170.46. FABMS *m/z* 603 (M+1), 609 (M+Li), 625 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_9S_2$: C, 43.79; H, 3.84; N, 4.64. Found: C, 44.10; H, 3.54; N, 4.68.

5-33 Yield: 57.4%. **a**:**b** =1:3

5-p-Bromophenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazole-2-thione (**5a-33**)

Mp 229-231 °C. $[\alpha]_D$ -24 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 3.99 (ddd, J = 2.1, 5.1, 9.9 Hz, 1 H, Glc-H-5), 4.15 (dd, J = 2.1, 12.3 Hz, 1 H, Glc-H-6), 4.31 (dd, J = 4.8, 12.6 Hz, 1 H, Glc-H-6), 5.25 (t, J = 9.9 Hz, 1 H, Glc-H-4), 5.41 (t, J = 9.6 Hz, 1 H, Glc-H-2), 5.79 (t, J = 9.3 Hz, 1 H,Glc-H-3), 6.29 (d, J = 9.3 Hz, 1 H, Glc-H-1), 7.54 (d, J = 8.4 Hz, 2 H, ArH), 7.60 (d, J = 8.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.65, 61.54, 67.75, 69.93, 73.49, 74.71, 82.46, 126.50, 127.26, 128.12, 132.54, 155.94, 168.87, 169.34, 169.97, 170.49, 188.82. FABMS *m/z* 603 (M+1), 609 (M+Li), 625 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_9S_2$: C, 43.79; H, 3.84; N, 4.64. Found: C, 44.05; H, 3.77; N, 4.85.

5-p-Bromophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-33**)

Mp 143-145 °C. $[\alpha]_D$ -27 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.02 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 3.82~3.87 (m, 1 H, Glc-H-5), 4.14 (dd, J = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.27 (dd, J = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.09~5.31 (m, 3 H, Glc-H-4, H-2, H-3), 5.39 (d, J = 9.9 Hz, 1 H, Glc-H-1), 7.58 (d, J = 9.0 Hz, 2 H, ArH), 7.74 (d, J = 9.0 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.43, 20.59, 61.58, 67.75, 69.55, 73.43, 76.25, 83.58, 125.83, 128.07, 128.42, 129.03, 132.44, 160.20, 169.25, 169.83, 170.34. FABMS *m/z* 603 (M+1), 609 (M+Li), 625 (M+Na). Anal. Calcd. for $C_{22}H_{23}BrN_2O_9S_2$: C, 43.79; H, 3.84; N, 4.64. Found: C, 44.66; H, 3.85; N, 4.72.

5-34 Yield: 62.8%. **a**:**b** = 0

5-o-Hydroxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiaz ole (**5b-34**)

Mp 179-181 °C. $[\alpha]_D$ -29 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.09 (s, 3 H, $CH_3C=O$), 3.89 (ddd, *J* = 1.8, 4.5, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.30 (dd, *J* = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.11~5.20 (m, 2 H, Glc-H-4, H-2), 5.27~5.38 (m, 2 H, Glc-H-3, H-1), 6.94(t, *J* = 7.5 Hz, 1 H, ArH), 7.09 (d, *J* = 7.5 Hz, 1 H, ArH), 7.35~7.43 (m, 2 H, ArH), 11.09 (s, 1 H, Ar-OH). ^{13}C NMR ($CDCl_3$): δ 20.53, 20.69, 61.65, 67.72, 69.55, 73.40, 76.39, 83.53, 113.60, 118.17, 120.04, 129.52, 133.12, 157.00, 158.71, 169.33, 169.94, 170.46, 171.89. FABMS *m/z* 541 (M+1), 547 (M+Li), 563 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S_2$: C, 48.88; H, 4.48; N, 5.18. Found: C, 48.79; H, 4.53; N, 4.91.

5-35 Yield: 12.7%. **a**:**b** =1:4

5-p-Hydroxyphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazol e-2-thione (**5a-35**)

Mp 228-230 °C. $[\alpha]_D$ -36 ° (c 1.2, Acetone). ^1H NMR ($CDCl_3$): δ 1.94 (s, 3 H, $CH_3C=O$), 2.04 (s, 3 H, $CH_3C=O$), 2.07 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 3.98~4.03 (m, 1 H, Glc-H-5), 4.17 (dd, *J* = 2.1, 12.9 Hz, 1 H, Glc-H-6), 4.33 (dd, *J* = 4.8, 12.9 Hz, 1 H, Glc-H-6), 5.27 (t, *J* = 9.6 Hz, 1 H, Glc-H-4), 5.43 (t, *J* = 9.3 Hz, 1 H, Glc-H-2), 5.83 (t, *J* = 9.3 Hz, 1 H,Glc-H-3), 6.31 (d, *J* = 9.3 Hz, 1 H, Glc-H-1), 6.89 (d, *J* = 8.4 Hz, 2 H, ArH), 7.57 (d, *J* = 8.4 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.69, 61.72, 67.81, 69.64, 73.55, 76.22, 83.69, 116.47, 121.34, 129.63, 158.83, 159.73, 169.54, 170.09, 170.78, 171.13. FABMS *m/z* 541 (M+1), 547 (M+Li), 563 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S_2$: C, 48.88; H, 4.48; N, 5.18. Found: C, 48.62; H, 4.59; N, 5.07.

5-p-Hydroxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiaz ole (**5b-35**)

Mp 182-185 °C. $[\alpha]_D$ -34 ° (c 1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.05 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 3.87 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.17 (dd, *J* = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.28 (dd, *J* =

4.8, 12.3 Hz, 1 H, Glc-H-6), 5.15~5.34 (m, 4 H, Glc- H-4, H-2, H-3, H-1), 6.99 (d, J = 8.1 Hz, 2 H, ArH), 7.76 (d, J = 8.1 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.51, 20.69, 61.72, 67.81, 69.64, 73.55, 76.22, 83.69, 116.47, 121.34, 129.63, 158.83, 159.73, 169.54, 170.09, 170.78, 171.13. FABMS *m/z* 541 (M+1), 547 (M+Li), 563 (M+Na). Anal. Calcd. for $C_{22}H_{24}N_2O_{10}S_2$: C, 48.88; H, 4.48; N, 5.18. Found: C, 48.73; H, 4.66; N, 5.12.

5-36 Yield 50.0%. **a**:**b** =1:7

5-o-Methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiaz ole (**5b-36**)

Mp 142-145 °C. $[\alpha]_D$ -13 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3 H, CH_3C=O), 2.01 (s, 3 H, CH_3C=O), 2.06 (s, 3 H, CH_3C=O), 2.13 (s, 3 H, CH_3C=O), 3.81~3.86 (m, 1 H, Glc-H-5), 3.98 (s, 3 H, Ar-OCH_3), 4.12 (d, J = 12.3 Hz, 1 H, Glc-H-6), 4.28 (dd, 1 H, J = 4.8, 12.3 Hz, Glc-H-6), 5.10~5.18 (m, 2 H, Glc-H-4, H-2), 5.28 (t, J = 9.3 Hz, 1 H, Glc-H-3), 5.43 (d, J = 9.9 Hz, 1 H, Glc-H-1), 7.00~7.11 (m, 2 H, ArH), 7.45 (t, J = 8.7 Hz, 1 H, ArH), 8.42 (d, J = 8.7 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.45, 20.53, 55.66, 61.61, 67.89, 69.78, 73.60, 76.08, 83.90, 111.25, 111.69, 125.30, 128.22, 132.35, 155.70, 160.57, 164.08, 169.27, 169.33, 169.88, 170.44. FABMS *m/z* 555 (M+1), 561 (M+Li), 577 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S_2$: C, 49.81; H, 4.73; N, 5.05. Found: C, 49.54; H, 4.70; N, 5.15.

5-37 Yield: 67.9%. **a**:**b** =1:4

5-p-Methoxyphenyl-3-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,3,4-thiadiazol e-2-thione (**5a-37**)

Mp 210-213 °C. $[\alpha]_D$ -23 ° (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.93 (s, 3 H, CH_3C=O), 2.03 (s, 3 H, CH_3C=O), 2.05 (s, 3 H, CH_3C=O), 2.08 (s, 3 H, CH_3C=O), 3.85 (s, 3 H, Ar-OCH_3), 3.99 (ddd, J = 1.8, 4.8, 9.9 Hz, 1 H, Glc-H-5), 4.14 (dd, J = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.31 (dd, J = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.26 (t, J = 9.9 Hz, 1 H, Glc-H-4), 5.41 (t, J = 9.3 Hz, 1 H, Glc-H-2), 5.82 (t, J = 9.3 Hz, 1 H, Glc-H-3), 6.29 (d, J = 9.6 Hz, 1 H, Glc-H-1), 6.94 (d, J = 8.7 Hz, 2 H, ArH), 7.61 (d, J = 8.7 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.54, 20.68, 55.49, 61.60, 67.81, 69.96, 73.63, 74.67, 82.46, 114.66, 120.97, 128.50, 162.51, 168.90, 169.41, 170.08, 170.60, 188.90. FABMS *m/z* 555

(M+1), 561 (M+Li), 577 (M+Na). Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S_2$: C, 49.81; H, 4.73; N, 5.05. Found: C, 49.75; H, 4.46; N, 4.88.

5-p-Methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylthio)-1,3,4-thiadiazole (**5b-37**)

Mp 170-172 °C. $[\alpha]_D$ -11 ° (c 1.1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, $CH_3C=O$), 2.03 (s, 3 H, $CH_3C=O$), 2.06 (s, 3 H, $CH_3C=O$), 2.08 (s, 3 H, $CH_3C=O$), 3.82~4.13 (m, 4 H, Ar-OCH_3, Glc-H-5), 4.15 (dd, J = 1.8, 12.3 Hz, 1 H, Glc-H-6), 4.21 (dd, J = 4.5, 12.3 Hz, 1 H, Glc-H-6), 5.12~5.21 (m, 2 H, Glc-H-4, H-2), 5.27~5.43 (m, 2 H, Glc-H-3, H-1), 6.98 (d, J = 8.7 Hz, 2 H, ArH), 7.85 (d, J = 8.7 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 20.54, 20.69, 55.46, 61.71, 67.87, 69.72, 73.61, 76.30,83.87, 114.63, 122.27, 129.42, 158.74, 162.17, 169.36, 169.99, 170.52. Anal. Calcd. for $C_{23}H_{26}N_2O_{10}S_2$: C, 49.81; H, 4.73; N, 5.05. Found: C, 49.99; H, 4.83; N, 4.60.

5-Phenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-1**).

$[\alpha]_D$ +27 ° (c 1, MeOH). ^1H NMR (D_2O): δ 3.29-3.36 (m, 3 H, Glc-H-2, H-3, H-5), 3.49 (t, 1 H, $J_{H4,H5}$ = 8.7 Hz, Glc-H-4), 3.61 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.78 (dd, 1 H, $J_{H5,H6}$ = 1.8 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.77 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.31-7.43 (m, 3 H, ArH), 7.88 (d, 2 H, J = 7.8 Hz, ArH). ^{13}C NMR (D_2O): δ 49.00, 60.95, 69.54, 72.35, 77.37, 80.14, 86.85, 125.82, 129.06, 131.47, 153.72, 164.22.

5-o-Methylphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-2**).

$[\alpha]_D$ –5 ° (c 0.5, MeOH). ^1H NMR (D_2O): δ 2.33 (s, 1 H, $ArCH_3$), 3.30-3.41 (m, 3 H, Glc-H-2, H-3, H-5), 3.52 (t, 1 H, $J_{H4,H5}$ = 9.0 Hz, Glc-H-4), 3.65 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.83 (dd, 1 H, $J_{H5,H6}$ = 1.5 Hz, $J_{H6,H6'}$ = 12.6 Hz, Glc-H-6), 4.81 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.13-7.21 (m, 3 H, ArH), 7.48 (d, 1 H, J = 6.9 Hz, ArH). ^{13}C NMR (D_2O): δ 22.46, 63.55, 72.12, 74.87, 79.86, 82.73, 89.34, 128.45, 131.47, 132.12, 133.27, 134.77, 139.82, 155.42, 167.38.

5-p-Methylphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-3**).

$[\alpha]_D$ -90 ° (c 1, MeOH). ^1H NMR (D_2O): δ 2.17 (s, 1 H, $ArCH_3$), 3.24-3.35 (m, 3 H, Glc-H-2, H-3, H-5), 3.44 (t, 1 H, $J_{H4,H5}$ = 8.4 Hz, Glc-H-4), 3.57 (dd, 1 H, $J_{H5,H6'}$ = 8.1 Hz, Glc-H-6'), 3.75 (d, 1 H, $J_{H6,H6'}$ = 12.0 Hz, Glc-H-6), 4.72 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.14 (d, 2 H, J = 8.1 Hz, ArH), 7.71 (d, 2 H, J = 8.1 Hz, ArH). ^{13}C NMR

(D_2O): δ 20.44, 60.95, 69.58, 72.14, 77.47, 80.14, 86.95, 125.74, 128.55, 129.56, 139.16, 153.55, 164.22.

5-o-Chlorophenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-4**).

$[\alpha]_D$ +8 ° (c 1, MeOH). ^1H NMR (D_2O): δ 3.26-3.35 (m, 3 H, Glc-H-2, H-3, H-5), 3.47 (t, 1 H, $J_{H4,H5}$ = 9.0 Hz, Glc-H-4), 3.59 (dd, 1 H, $J_{H5,H6'}$ = 5.4 Hz, Glc-H-6'), 3.77 (dd, 1 H, $J_{H5,H6}$ = 1.8 Hz, $J_{H6,H6'}$ = 12.6 Hz, Glc-H-6), 4.75 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.29-7.32 (m, 2 H, ArH), 7.44-7.61 (m, 2 H, ArH). ^{13}C NMR (D_2O): δ 32.31, 60.88, 69.74, 72.20, 77.28, 80.11, 86.69, 127.06, 130.08, 131.16, 153.05, 162.59.

5-p-Chlorophenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-5**).

$[\alpha]_D$ +7 ° (c 1, MeOH). ^1H NMR (D_2O): δ 3.31-3.44 (m, 3 H, Glc-H-2, H-3, H-5), 3.53 (t, 1 H, $J_{H4,H5}$ = 9.0 Hz, Glc-H-4), 3.67 (dd, 1 H, $J_{H5,H6'}$ = 2.4 Hz, Glc-H-6'), 3.84 (d, 1 H, $J_{H6,H6'}$ = 12.6 Hz, Glc-H-6), 4.83 (d, 1 H, $J_{H1,H2}$ = 9.0 Hz, Glc-H-1), 7.49 (d, 2 H, J = 8.1 Hz, ArH), 7.88 (d, 2 H, J = 8.1 Hz, ArH). ^{13}C NMR (D_2O): δ 60.94, 69.53, 72.31, 77.33, 80.11, 86.88, 127.06, 128.83, 129.96, 133.71, 153.62, 163.23.

5-m-Chlorophenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-6**).

$[\alpha]_D$ +3 ° (c 1, MeOH). ^1H NMR (D_2O): δ 3.27-3.41 (m, 3 H, Glc-H-2, H-3, H-5), 3.49 (t, 1 H, $J_{H4,H5}$ = 8.1 Hz, Glc-H-4), 3.61 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.79 (dd, 1 H, $J_{H5,H6}$ = 1.2 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.75 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.18-7.27 (m, 2 H, ArH), 7.67 (d, 1 H, J = 7.5 Hz, ArH), 7.73 (s, 1 H, ArH). ^{13}C NMR (D_2O): δ 30.27, 60.84, 69.38, 72.15, 77.10, 80.02, 86.67, 123.91, 125.41, 128.42, 130.34, 133.03, 134.08, 153.65, 162.80.

5-o-Bromophenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-7**).

$[\alpha]_D$ +8 ° (c 0.5, MeOH). ^1H NMR (D_2O): δ 3.25-3.39 (m, 3 H, Glc-H-2, H-3, H-5), 3.45 (t, 1 H, $J_{H4,H5}$ = 8.1 Hz, Glc-H-4), 3.60 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.77 (dd, 1 H, $J_{H5,H6}$ = 1.8 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.76 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.26 (t, 1 H, J = 7.5 Hz, ArH), 7.34-7.44 (m, 2 H, ArH), 7.65 (d, 1 H, J = 7.5 Hz, ArH). ^{13}C NMR (D_2O): δ 60.95, 69.62, 72.37, 77.57, 80.24, 86.85, 122.19, 127.58, 130.49, 131.03, 133.13, 133.62, 153.07, 163.87.

5-p-Bromophenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-8**).

$[\alpha]_D$ +3 ° (c 1, MeOH). ^{1}H NMR (D_2O): δ 3.27-3.42 (m, 3 H, Glc-H-2, H-3, H-5), 3.49 (t, 1 H, $J_{H4,H5}$ = 9.0 Hz, Glc-H-4), 3.62 (dd, 1 H, $J_{H5,H6'}$ = 5.4 Hz, Glc-H-6'), 3.79 (dd, 1 H, $J_{H5,H6}$ = 1.8 Hz, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.77 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.46 (d, 2 H, J = 8.4 Hz, ArH), 7.67 (d, 2 H, J = 8.4 Hz, ArH). ^{13}C NMR (D_2O): δ 60.88, 69.42, 72.22, 77.19,80.05, 86.75, 122.10, 127.36, 130.35, 131.85, 153.75, 163.38.

5-o-Hydroxyphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-9**).

$[\alpha]_D$ –10 ° (c 0.6, MeOH). ^{1}H NMR (D_2O): δ 3.15-3.30 (m, 3 H, Glc-H-2, H-3, H-5), 3.36 (t, 1 H, $J_{H4,H5}$ = 8.4 Hz, Glc-H-4), 3.51 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.67 (d, 1 H, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.84 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 6.63-6.72 (m, 2 H, ArH), 7.08 (t, 1 H, J = 7.5 Hz, ArH), 7.52 (d, 1 H, J = 7.5 Hz, ArH). ^{13}C NMR (D_2O): δ 60.83, 69.36, 72.09, 77.21, 80.14, 86.47, 117.55, 118.28, 127.62, 130.60, 152.94, 159.69, 162.80.

5-p-Hydroxyphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-10**).

$[\alpha]_D$ +14 ° (c 1, MeOH). ^{1}H NMR (D_2O): δ 3.27-3.43 (m, 3 H, Glc-H-2, H-3, H-5), 3.50 (t, 1 H, $J_{H4,H5}$ = 8.7 Hz, Glc-H-4), 3.63 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.79 (d, 1 H, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 4.78 (d, 1 H, $J_{H1,H2}$ = 8.7 Hz, Glc-H-1), 6.70 (d, 2 H, J = 8.1 Hz, ArH), 7.67 (d, 2 H, J = 8.1 Hz, ArH). ^{13}C NMR (D_2O): δ 63.44, 71.97, 74.73, 79.69, 82.59, 89.19, 120.97, 121.20, 130.26, 155.72, 167.20, 168.42.

5-o-Methoxyphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-11**).

$[\alpha]_D$ +9 ° (c 0.5, MeOH). ^{1}H NMR (D_2O): δ 3.25-3.37 (m, 3 H, Glc-H-2, H-3, H-5), 3.47 (t, 1 H, $J_{H4,H5}$ = 8.7 Hz, Glc-H-4), 3.61 (dd, 1 H, $J_{H5,H6'}$ = 5.1 Hz, Glc-H-6'), 3.78 (d, 1 H, $J_{H6,H6'}$ = 12.3 Hz, Glc-H-6), 3.76 (s, 3 H, $ArOCH_3$), 4.76 (d, 1 H, $J_{H1,H2}$ = 9.9 Hz, Glc-H-1), 7.02 (t, 1 H, J = 7.5 Hz, ArH), 7.10 (d, 1 H, J = 8.7 Hz, ArH), 7.39 (t, 1 H, J = 8.7 Hz, ArH), 7.82 (d, 1 H, J = 7.8 Hz, ArH).^{13}C NMR (D_2O): δ 56.08, 62.60, 71.12, 73.77, 79.24, 82.06, 87.89, 112.62, 121.22, 121.69, 131.10, 131.79, 154.26, 158.58, 159.10.

5-p-Methoxyphenyl-3-(β-D-glucopyranosylthio)-1,2,4-triazole (**6-12**).

$[\alpha]_D$ –37 ° (c 1, MeOH). ^{1}H NMR (D_2O): δ 3.24-3.35 (m, 3 H, Glc-H-2, H-3, H-5), 3.44 (t, 1 H, $J_{H4.H5}$ = 8.7 Hz, Glc-H-4), 3.56 (m, 1 H, Glc-H-6'), 3.60 (s, 1 H, $ArOCH_3$), 3.74 (d, 1 H, $J_{H6.H6'}$ = 12.3 Hz, Glc-H-6), 4.70 (d, 1 H, $J_{H1,H2}$ = 9.6 Hz, Glc-H-1), 6.82 (d, 2 H,

J = 8.1 Hz, ArH), 7.71 (d, 2 H, J = 8.4 Hz, ArH). ^{13}C NMR (D_2O): δ 55.30, 60.83, 69.39, 72.19, 77.16, 80.00, 86.73, 114.22, 124.51, 127.19, 153.22, 159.11, 163.93.

5-Phenyl-2-(β-D-glucopyranosylthio)-1,3,4-oxazole (**6-13**).

^{1}H NMR (DMSO-d_6): δ 3.16-3.18 (m, 1 H), 3.31-3.35 (m, 3 H), 3.43 (dd, J = 6.0, 11.7 Hz, 1 H), 3.63 (dd, J = 5.4, 11.7 Hz, 1 H), 4.58 (t, J = 5.7 Hz, 1 H), 5.09 (d, J = 5.1 Hz, 1 H), 5.17 (d, J = 8.7 Hz, 1 H), 5.27 (d, J = 3.6 Hz, 1 H), 5.70 (d, J = 5.4 Hz, 1 H), 7.58~7.60 (m, 3 H), 7.98~8.01 (m, 2 H). ^{13}C NMR δ 60.86, 69.65, 72.91, 77.97, 81.97, 86.11, 123.20, 126.65, 129.56, 132.22, 161.89, 165.58.

5-o-Methylphenyl-2-(β-D-glucopyranosylthio)-1,3,4-oxazole (**6-14**).

^{1}H NMR (D_2O): δ 2.18 (s, 3 H), 3.45-3.56 (m, 4 H), 3.67 (d, J =12.1 Hz, 1 H), 3.81 (d, J = 12.1 Hz, 1 H), 5.12 (d, J = 9.3 Hz, 1 H), 6.97~7.30 (m, 2 H), 7.15 (t, J = 7.8 Hz, 1 H), 7.38 (d, J = 7.8 Hz, 1 H). ^{13}C NMR δ 21.24, 60.65, 69.03, 72.06, 77.15, 80.53, 85.40, 120.97, 136.20, 128.58, 131.64, 137.86, 161.63, 166.60.

5-p-Methylphenyl-2-(β-D-glucopyranosylthio)-1,3,4-oxazole (**6-15**).

^{1}H NMR (DMSO-d_6): δ 2.38 (s, 3 H), 3.13-3.19 (m, 1 H), 3.21-3.30 (m, 3 H), 3.42 (dd, J = 6.0, 11.7 Hz, 1 H), 3.62 (dd, J = 5.4, 11.7 Hz, 1 H), 4.56 (t, J = 5.4 Hz, 1 H), 5.08 (d, J = 5.1 Hz, 1 H), 5.16 (d, J = 9.3 Hz, 1 H), 5.68 (d, J = 5.7 Hz, 1 H), 7.38 (d, J = 8.1 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H). ^{13}C NMR δ 21.83, 61.39, 70.19, 73.47, 78.52, 82.50, 86.67, 121.01, 127.16, 130.66, 142.93, 162.06, 166.22.

5-o-Hydroxrphenyl-2-(β-D-glucopyranosylthio)-1,3,4-oxazole (**6-16**).

^{1}H NMR (D_2O): δ 3.30-3.47 (m, 3 H), 3.70 (dd, J = 5.1, 12.6 Hz, 1 H), 3.74 (dd, J = 1.8, 12.3 Hz, 1 H), 5.07 (d, J = 9.6 Hz, 1 H), 6.79~6.84 (m, 2 H), 7.26 (t, J = 7.8 Hz, 1 H), 7.47 (d, J = 8.1 Hz, 1 H). ^{13}C NMR δ 60.65, 69.07, 72.05, 77.13, 80.58, 85.43, 108.19, 117.04, 120.36, 128.10, 134.17, 155.62, 161.11, 165.43.

5-o-Methoxyphenyl-2-(β-D-glucopyranosylthio)-1,3,4-oxazole (**6-17**).

^{1}H NMR (D_2O): δ 3.46-3.57 (m, 4 H), 3.57 (dd, J = 5.1, 12.6 Hz, 1 H), 3.77 (s, 3 H), 3.85 (d, J = 12.3 Hz, 1 H), 5.14 (d, J = 9.3 Hz, 1 H), 6.85~6.95 (m, 2 H), 7.35~7.47 (m, 2 H). ^{13}C NMR δ 55.67, 60.68, 69.10, 72.08, 77.15, 80.60, 85.40, 110.13, 112.25, 120.83, 129.42, 134.26, 157.29, 161.17, 164.88.

5-o-Methylphenyl-2-(β-D-glucopyranosylthio)-1,3,4-thiazole (**6-18**).

^{1}H NMR (D_2O): δ 3.45~3.60 (m, 4 H), 3.79 (dd, *J* = 4.8, 12.3 Hz, 1 H), 3.86~3.90 (m, 1 H), 4.74~4.79 (m, 1 H), 6.66 (d, *J* = 8.7 Hz, 1 H), 6.83 (t, *J* = 7.5 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR δ 60.69, 69.19, 71.96, 77.16, 80.26, 86.09, 114.22, 117.73, 121.00, 125.93, 133.36, 159.92, 166.90, 168.93.

5-p-Bromophenyl-2-(β-D-glucopyranosylthio)-1,3,4-thiazole (**6-19**).

^{1}H NMR (DMSO-d_6): δ 3.19~3.22 (m, 3 H), 3.31~3.33 (m, 1 H), 3.47~3.55 (m, 1 H), 3.75 (dd, *J* = 5.1, 11.7 Hz, 1 H), 4.65 (t, *J* = 5.4 Hz, 1 H), 4.93 (d, *J* = 9.9 Hz, 1 H), 5.12 (d, *J* = 4.5 Hz, 1 H), 5.26 (s, 1 H), 5.69 (d, *J* = 5.4 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR δ 60.86, 69.61, 72.72, 77.90, 81.83, 86.17, 124.88, 128.74, 129.36, 132.63, 163.66, 168.07.

5-o-Hydroxyphenyl-2-(β-D-glucopyranosylthio)-1,3,4-thiazole (**6-20**).

^{1}H NMR (D_2O): δ 3.36~3.53 (m, 4 H), 3.60 (dd, *J* = 4.8, 12.3 Hz, 1 H), 3.76 (d, *J* = 12.3 Hz, 1 H), 4.71 (d, *J* = 9.3 Hz, 1 H), 6.46 (t, *J* = 8.7 Hz, 1 H), 6.65 (d, *J* = 9.0 Hz, 1 H), 7.11 (t, *J* = 8.4 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR δ 60.69, 69.19, 71.76, 77.16, 80.26, 86.09, 114.22, 117.73, 121.00, 125.93, 133.36, 159.92, 166.90, 168.93.

5-p-Hydroxyphenyl-2-(β-D-glucopyranosylthio)-1,3,4-thiazole (**6-21**).

^{1}H NMR (D_2O): δ 3.40~3.56 (m, 4 H), 3.76 (dd, *J* = 5.1, 12.6 Hz, 1 H), 3.93 (dd, *J* = 1.8, 12.6 Hz, 1 H), 4.91 (d, *J* = 9.9 Hz, 1 H), 6.71 (d, *J* = 8.7 Hz, 2 H), 7.54 (d, *J* = 8.7 Hz, 2 H). ^{13}C NMR δ 60.69, 69.22, 72.09, 77.12, 80.34, 86.04, 116.28, 118.56, 129.61, 160.45, 167.06, 172.76.

5-o-Methoxyphenyl-2-(β-D-glucopyranosylthio)-1,3,4-thiazole (**6-22**).

^{1}H NMR (D_2O): δ 3.45~3.60 (m, 4 H), 3.79 (dd, *J* = 4.8, 12.3 Hz, 1 H), 3.86~3.90 (m, 1 H), 4.74~4.79 (m, 1 H), 6.66 (d, *J* = 8.7 Hz, 1 H), 6.83 (t, *J* = 7.5 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR δ 55.72, 60.19, 68.47, 71.28, 77.59, 80.07, 86.63, 112.05, 114.86, 117.88., 121.45, 130.56, 156.21, 162.79, 163.56.

实验部分

仪器与试剂

Bruker FT-AC 200 MHz / Varian Mercury 300 MHz 型核磁共振仪（TMS 为内

标）；Elementar Vario 型元素分析仪；VGZAB-HS(FAB)型质谱仪；X4 型显微熔点仪（未校正）。溴化氢-乙酸溶液为进口试剂（AVOCADO），其余药品均为市售品；溶剂为分析纯，经干燥、重蒸等处理。

1. 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑衍生物的合成

a. 3-巯基-5-芳基-1,2,4-三唑的制备 [15]

将 0.01 mol 芳酰肼溶于 25 ml 1.2 M 的盐酸中，然后把 0.02 mol 的硫氰酸钾固体分批加入，于油浴上回流 5~6 小时，产生大量白色固体，冷却后过滤，用大量水洗得芳酰基氨基硫脲，晾干后可直接用于下一步反应。

取上步制得的芳酰基氨基硫脲 0.08 mol 溶于 25 ml 10% NaOH 水溶液中，于油浴中回流 6～7 小时后，过滤，冷却，用稀盐酸酸化滤液到 pH = 2~3，得大量白色固体。水洗，干燥，乙醇重结晶，得 3-芳基-5-巯基-1,2,4-三唑。熔点与文献值 [15] 相吻合。

b. 2-巯基-5-芳基-1,3,4-噁二唑的制备 [16]

将取代苯甲酰肼 80 mmol，KOH 0.12 mmol 溶于适量的 95%乙醇后再缓慢滴加 0.12 mol CS_2，搅拌回流至无 H_2S 气体放出（约 48 小时）。反应终止后，蒸出多余乙醇，倒入 500 ml 冷水中，用稀盐酸酸化至 pH ＝ 2~3，产生大量白色沉淀，抽滤，水洗，晾干，用无水乙醇重结晶，得白色针状晶体。熔点与文献值吻合 [16]。

c. 2-巯基-5-芳基-1,3,4-噻二唑的制备 [17]

取 0.05 mol 的芳酰肼，加入到溶有 0.075 mol 氢氧化钾的 250 ml 绝对无水乙醇中，待溶液完全澄清后，滴加 0.075 mol 的二硫化碳，室温搅拌反应 24 小时，然后加入 50 ml 无水乙醚，继续反应 2 小时，抽滤，用无水乙醚洗去过量的二硫化碳，干燥，得黄色或浅黄色固体。此固体为芳酰肼基二硫代甲酸钾，无需进一步纯化，可直接进行下一步反应。

取上步所制得的芳酰肼基二硫代甲酸钾 0.02 mol，于研钵中仔细研碎。将此研细的钾盐分批缓慢的加入到冰盐浴冷却的浓硫酸中（每克钾盐约需 5 ml 浓硫酸），同时不断搅拌，并控制体系温度不超过 6℃。待钾盐完全加入后，继续搅拌 3~5 分钟。将硫酸溶液倾入 300 克碎冰中（每克钾盐约需 50 克碎冰）。搅拌，

析出大量白色固体，抽滤，水洗，乙醇重结晶，得 2-芳基-5-巯基-1-3-4-噻二唑。熔点与文献值[17]吻合。

2. 溴代乙酰葡糖的合成[18]。

将 6.6 g D-葡萄糖和 28 ml 乙酸酐加入 100ml 圆底烧瓶中，再向其中滴入三滴浓硫酸，反应立即开始。摇晃烧瓶，体系内随着反应的进行温度急剧增加，当温度升至接近沸点时将反应瓶置入冷水浴中，约 10-15 min 后葡糖基本反应完并溶解。将烧瓶置于沸水裕上加热 2 h，减压蒸出剩余的乙酸酐和反应生成的乙酸，剩余物倒入冰水中得到白色固体全乙酰化葡萄糖。

将乙酰化葡萄糖和 4.1 M 的 HBr-乙酸溶液以每毫摩尔 3 mL 的比例加入圆底烧瓶中室温搅拌，直到所有固体完全溶解(30-60 min)。所得溶液倒入冰水中，用 $CHCl_3$ 萃取生成的沉淀，有机层用饱和 $NaHCO_3$ 水溶液洗至中性后再用水洗。有机层用 $MgSO_4$ 干燥后蒸干，所得油状物用石油醚:乙醚=1:1 溶液固化，得到粉末状溴代乙酰葡萄糖，产率为 93-97%。

3．5-芳基-3-*N*-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑-2-硫酮及 5-芳基-3-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,2,4-三唑或 5-芳基-2-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑衍生物的合成

称取 1 mmol KOH 溶于约 10 ml 乙醇中，再加入 1 mmol 3-巯基-5-芳基-1,2,4-三唑(或 2-巯基-5-芳基-1,3,4-噁二唑，2-巯基-5-芳基-1,3,4-噻二唑)，室温搅拌 0.5 h（如果有钾盐沉淀生成则加少量水使其溶解）。加入 1 mmol 溴代乙酰葡萄糖，室温搅拌，体系中逐渐生成大量白色沉淀，反应 12 h 后体系中沉淀不再增多且点板再无变化，停止搅拌，抽滤得白色固体。其中在 3-巯基-5-芳基-1,2,4-三唑的反应中，产物只有 **5b** 一种；而在 2-巯基-5-芳基-1,3,4-噁二唑和 2-芳基-5-巯基-1,3,4-噻二唑的反应中，有 **5a** 和 **5b** 两个产物。拌样后用 PE:EA=6:1~1:1 柱层析，分别得到 N-和 S-糖苷的产物，其中 **5b** 即 S-糖苷是主要产物。

4．5-芳基-3-*β*-*D*-吡喃葡糖基-1,2,4-三唑或 5-芳基-2-*β*-*D*-吡喃葡糖基-1,3,4-噁二唑/1,3,4-噻二唑衍生物的合成

其中 5-芳基-3-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,2,4-三唑(0.2 mmol)加入到 NaOMe (0.5 M)-MeOH (3 ml) 中室温搅拌，TLC 跟踪至化合物 **5** 反应完全，

5-芳基-2-(2,3,4,6-四-*O*-乙酰基-*β*-*D*-吡喃葡糖基)-1,3,4-噁二唑/1,3,4-噻二唑(0.2 mmol)加入到饱和氨气的甲醇溶液中，室温搅拌，TLC跟踪至化合物**5**反应完全。反应体系浓缩后过层析得水溶性的脱保护产物**6**。

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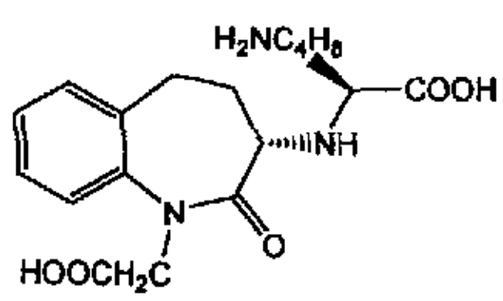
第三部分　3-杂环基硫取代-1, 3, 4, 5-四氢-2-氧代苯并氮杂卓衍生物的合成

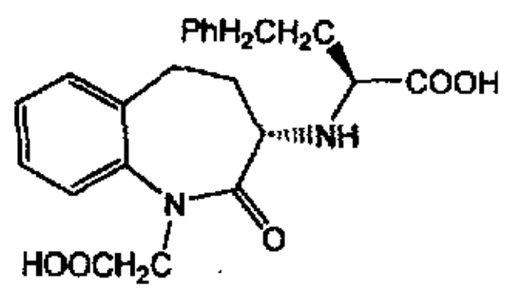
摘 要

本文以芳酰肼为原料，合成了一系列含 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑，并通过硫原子对 3-溴-2-氧代-苯并氮杂卓 3-位上的亲核取代反应将杂环化合物引入了苯并氮杂卓的结构当中，合成了 32 个新的苯并氮杂卓杂环衍生物。为提高其在有机溶剂中的溶解性，在苯并氮杂卓的 1-N 位引入乙酸乙酯和乙酸叔丁酯基取代基，合成了 36 个新衍生物。所有化合物经质谱，核磁共振氢谱及元素分析确证了结构。

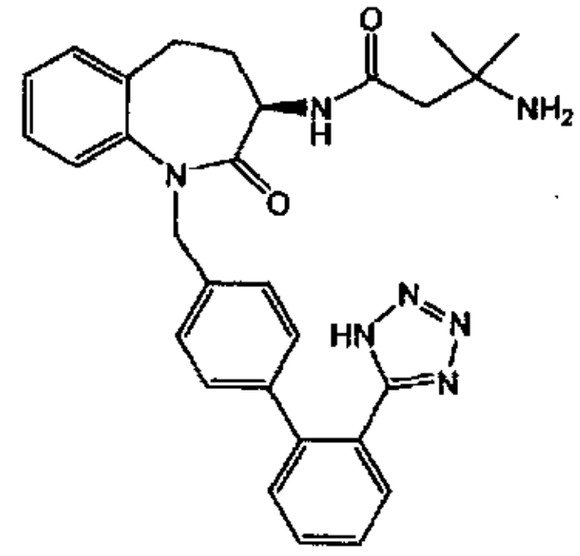
苯并氮杂卓衍生物具有高效的生物活性和药理活性 [1-3]。如，美国开发的两个抗高血压药物 *Libenzapril* 和 *Benazeprilat*，这两个药物均为血管紧张素转化酶抑制剂，是当今比较流行的抗高血压药物之一。而这两个化合物都含有 2-氧代苯并氮杂卓的基本骨架。另外，在生长激素促分泌素 L-692,429 和 L-739,943 中也含有该骨架 [4]。所以，有机化学家、药物化学家对它的合成与研究产生了浓厚的兴趣。对其进行结构修饰是当今有机化学研究的热点之一，现在的工作主要集中在 2-氧代苯并氮杂卓 1-位的氮原子和 3-位的碳原子上 [6-11]。



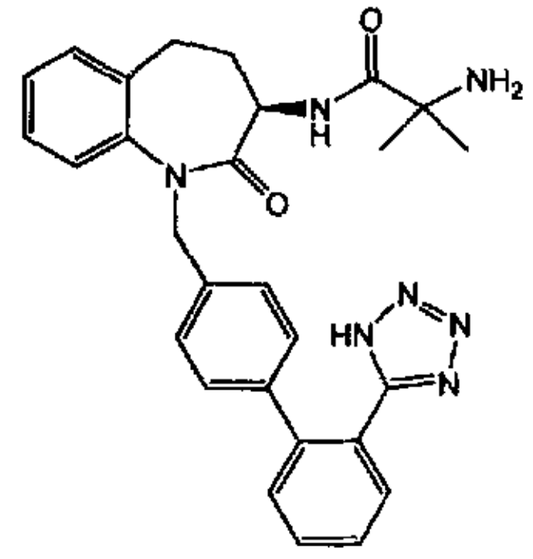
Libenzapril



Bennazeprilat



L-692,429



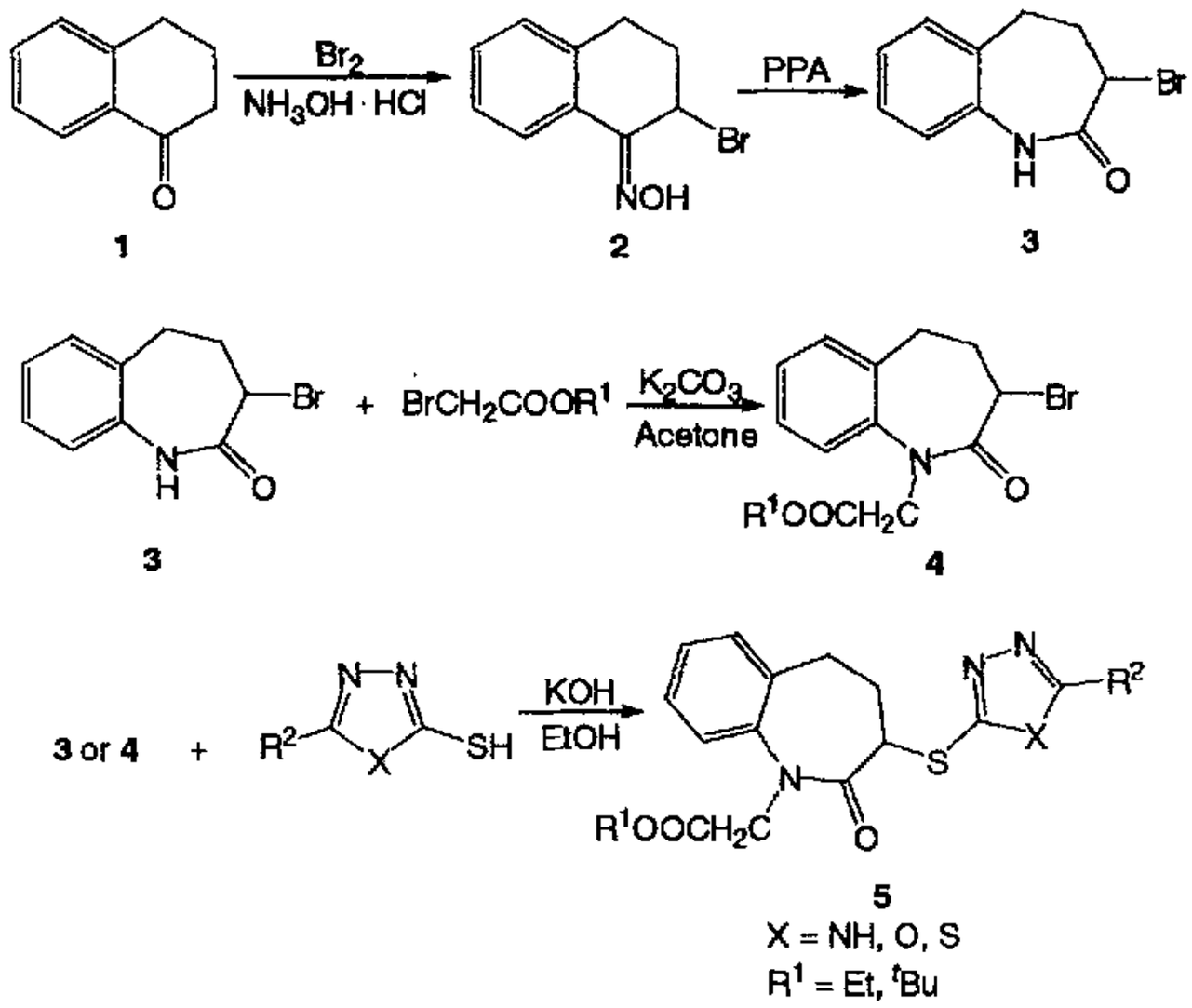
L-739,943

众所周知，杂环化合物如：1,2,4-三唑、1,3,4-噁二唑、1,3,4-噻二唑具有广谱的生物活性和多种用途 [12~14]。Pathak 和 Sharm 提出，1,2,4-三唑取代的硫醚化合物比其前体的硫醇化合物具有更高的抗菌活性。目前，杂环化合物的合成越来越趋向于将多个具有生物活性的分子在同一个分子当中聚集，实现其活性叠加来合成具有较强生物活性的衍生物。为此，我们合成了一系列 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑，通过硫原子对 3-溴-2-氧代苯并氮杂卓 3 位上的亲核取代反应，将杂环化合物引入到苯并氮杂卓结构中，合成了一系列苯并氮杂卓杂环衍生物，以期寻找活性更高的化合物。

结果与讨论

1 合成

从 . -四氢萘酮出发,经溴化及贝克曼重排制得 3-溴-2-氧代苯并氮杂卓。以芳酰肼为原料合成了一系列 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑，通过硫原子对 3-溴-2-氧代苯并氮杂卓 3 位上的亲核取代反应，将杂环化合物引入到苯并氮杂卓的结构中，合成了 33 个新的苯并氮杂卓杂环衍生物。为了提高其在有机溶剂中的溶解性，而在苯并氮杂卓的 1-N 位引入乙酸乙和乙酸叔丁酯基取代基，合成了其它 36 个新衍生物，以期寻找活性更高的化合物。合成路线如下：



Scheme 3-1

2 物理性质与波谱学性质

Comp.	R^1	R^2	X	Mp (°C)	M^+ (m/z)	Yield (%)
5-1	H	Me	O	161-163	275	94.1
5-2	H	Ph	O	201-203	337	95.7
5-3	H	Py	O	218-220	338	93.3
5-4	H	*m*-Me-Ph	O	183-185	351	90.7
5-5	H	*p*-Me-Ph	O	228-230	351	93.2
5-6	H	*o*-Cl-Ph	O	180-182	371	90.2
5-7	H	*m*-Cl-Ph	O	196-198	371	86.4
5-8	H	*p*-Cl-Ph	O	221-224	371	95.6
5-9	H	*o*-Br-Ph	O	149-150	415	92.0
5-10	H	*p*-Br-Ph	O	241-243	415	93.5
5-11	H	*p*-OH-Ph	O	242-243	353	95.1
5-12	H	*o*-MeO-Ph	O	199-201	367	68.2
5-13	Et	Ph	O	153-155	423	78.8
5-14	Et	Py	O	136-138	424	68.1
5-15	^{t}Bu	Me	O	158-160	389	66.8
5-16	^{t}Bu	Py	O	123-126	452	78.5
5-17	^{t}Bu	*o*-Cl-Ph	O	136-138	485	69.4
5-18	^{t}Bu	*m*-Cl -Ph	O	138-141	485	68.1
5-19	^{t}Bu	*o*-Br-Ph	O	134-136	529	62.8
5-20	^{t}Bu	*o*-OH-Ph	O	137-139	467	75.0
5-21	^{t}Bu	*p*-OH-Ph	O	118-120	467	60.2
5-22	^{t}Bu	*o*-MeO-Ph	O	174-175	481	68.8
5-23	^{t}Bu	*p*-MeO-Ph	O	141-144	481	52.2
5-24	H	Ph	NH	212-214	336	83.6
5-25	H	Py	NH	136-139	337	65.3
5-26	H	*m*-Me-Ph	NH	240-242	350	86.8
5-27	H	*p*-Me-Ph	NH	226-230	350	70.5
5-28	H	*m*-Cl-Ph	NH	248-250	370	66.9
5-29	H	*p*-Cl-Ph	NH	212-213	370	89.1
5-30	H	*o*-OH-Ph	NH	225-227	352	86.5
5-31	H	*p*-OH-Ph	NH	290-291	352	89.7
5-32	H	*o*-MeO-Ph	NH	248-250	366	83.5
5-33	H	*p*-MeO-Ph	NH	231-232	366	85.4
5-34	Et	Ph	NH	158-160	422	55.1
5-35	Et	Py	NH	136-138	423	86.2
5-36	Et	*m*-Me-Ph	NH	155-157	436	82.0
5-37	Et	*p*-Me-Ph	NH	181-183	436	63.8
5-38	Et	*o*-OH-Ph	NH	227-229	438	77.8
5-39	Et	*p*-OH-Ph	NH	212-214	438	54.5
5-40	Et	*o*-MeO-Ph	NH	205-207	452	83.4
5-41	Et	*p*-MeO-Ph	NH	154-156	452	89.8
5-42	^{t}Bu	Ph	NH	196-198	450	62.7
5-43	^{t}Bu	Py	NH	208-210	451	80.3
5-44	^{t}Bu	*p*-Me-Ph	NH	200-201	464	56.4
5-45	^{t}Bu	*m*-Cl-Ph	NH	205-207	484	80.0
5-46	^{t}Bu	*p*-Cl-Ph	NH	206-208	484	60.5
5-47	^{t}Bu	*o*-MeO-Ph	NH	155-157	480	84.7
5-48	H	Me	S	155-156	291	61.7
5-49	H	Ph	S	205-208	353	99.0
5-50	H	*m*-Me-Ph	S	227-229	367	67.9
5-51	H	*p*-Me-Ph	S	215-217	367	85.1
5-52	H	*m*-Cl-Ph	S	197-199	387	82.9
5-53	H	*p*-Cl-Ph	S	239-241	387	63.8

Comp.	R^1	R^2	X	Mp (°C)	M^+ (m/z)	Yield (%)
5-54	H	*p*-Br-Ph	S	248-250	431	82.5
5-55	H	*p*-OH-Ph	S	200-202	369	68.3
5-56	H	*o*-MeO-Ph	S	246-247	383	69.5
5-57	H	*p*-MeO-Ph	S	213-215	383	79.4
5-58	Et	Me	S	86-88	377	89.3
5-59	Et	Ph	S	248-250	439	72.7
5-60	Et	*m*-Me-Ph	S	157-159	453	64.5
5-61	Et	*p*-Me-Ph	S	163-164	453	70.2
5-62	Et	*o*-MeO-Ph	S	220-222	469	94.5
5-63	^{t}Bu	Me	S	168-170	405	69.0
5-64	^{t}Bu	*m*-Me-Ph	S	157-159	481	77.3
5-65	^{t}Bu	*m*-Cl-Ph	S	155-156	501	41.5
5-66	^{t}Bu	*p*-Cl-Ph	S	184-186	501	60.3
5-67	^{t}Bu	*p*-Br-Ph	S	186-188	545	67.2
5-68	^{t}Bu	*o*-MeO-Ph	S	177-178	497	65.0

氢谱：以 $CDCl_3$ 或 DMSO-d_6 为溶剂，对所合成的化合物的核磁共振氢谱进行了测定。苯并氮杂卓1-位N上的氢在7.99~9.88 ppm出现一个单峰，该峰受杂环基的影响较大，化学位移不太固定；当1-位N上带上乙酸乙酯取代基后在1.2左右出现三重峰，在4.2左右出现四重峰，在4.5和4.7左右分别出现两个二重峰；当1-位N上带上乙酸叔丁酯取代基后在1.4左右出现很高的单峰，在4.3和4.6左右分别出现两个二重峰。苯环上的质子出现在6.88~8.12 ppm，随苯环的个数出现一到两组多重峰。当有对位取代苯时，可以看见明显的偶合。所有化合物在4.5~4.7 ppm左右都有一组dd峰，这是氮杂卓3-位C上的质子吸收。原因是受到邻位（4-位）C上两个质子的偶合。该两质子磁不等价，其差别类似于a-H和e-H。在氢谱上对应于2.50 ppm左右和2.80 ppm左右的两组多重峰。此外，在3.0 ppm附近有两个质子也呈现多重峰，这是氮杂卓 5-位 C 上的两个质子吸收。详细的化学位移见后。

质谱：所有化合物的分子离子峰相对丰度都很小，大约1%左右，可能是因为在硫醚键容易断裂，形成 *m/z*=159 的基峰。

5-1 ^{1}H NMR (DMSO-d_6) δ: 2.28-2.39 (m, 1H), 2.41 (s, 3H), 2.73-2.88 (m, 3H), 4.373 (dd, J=6.9, 11.7 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 7.12-7.17 (m, 1H), 7.24-7.32 (m, 2H), 10.20 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 11.18, 29.83, 37.34, 50.18, 122.91, 126.34, 128.32, 130.52, 133.65, 138.20, 162.77, 165.55, 169.76. Anal. Calcd. for $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.76; N, 15.26. Found: C, 56.92; H, 4.62; N, 15.43.

5-2 ^{1}H NMR ($CDCl_3$) δ: 2.41-2.61 (m,1H), 2.72-2.83 (m, 1H), 2.97-3.15 (m, 2H), 4.96 (dd, J = 7.5, 11.4 Hz, 1H), 7.09 (d, J = 6.9 Hz, 1H), 7.16-7.21 (m, 1H), 7.25-7.30 (m, 2H), 7.43-7.53 (m, 3H), 7.94 (dd, J = 1.6, 7.8 Hz, 2H), 8.52 (s,1H). ^{13}C NMR ($CDCl_3$) δ: 29.78, 36.69, 49.22, 122.52, 123.40, 126.59, 126.70, 128.04, 128.96, 130.04, 131.61, 133.20, 136.36, 163.24, 165.57, 170.75. Anal. Calcd. for $C_{18}H_{15}N_3O_2S$: C, 64.08; H, 4.48; N, 12.45. Found: C, 64.36; H, 4.50; N, 12.16.

5-3 ^{1}H NMR (DMSO-d_6) δ: 2.39-2.47 (m,1H), 2.80-2.92 (m, 3H), 4.57 (dd, J = 7.2, 11.7 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.30-7.38 (m, 2H), 8.81 (d, J = 6.3 Hz, 2H), 8.81 (d, J = 6.3 Hz, 2H), 10.32(s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.29, 35.35, 48.53, 118.49, 120.97, 124.48, 126.39, 128.44, 128.93, 131.51, 136.15, 149.39, 162.11, 163.51, 168.08. Anal. Calcd. for $C_{17}H_{14}N_4O_2S$: C, 60.34; H, 4.17; N, 16.56. Found: C, 60.48; H, 3.98; N, 16.23.

5-4 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.33 (s, 3H), 2.38-2.41 (m, 1H), 2.69-2.73 (m, 1H), 2.80-2.96 (m, 2H), 4.49-4.54 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.03-7.10 (m, 1H), 7.17-7.32 (m, 4H), 7.61-7.63 (m, 2H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 20.83, 29.34, 36.43, 49.31, 121.98, 122.82, 123.23, 125.47, 126.48, 127.38, 128.63, 129.44, 132.13, 132.57, 138.43, 162.75, 165.01, 169.29. Anal. Calcd. for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.48; N, 11.96. Found: C, 65.00; H, 4.59; N, 12.15.

5-5 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.32 (s, 3H), 2.35-2.39 (m, 1H), 2.66-2.72 (m, 1H), 2.84-2.96 (m, 2H), 4.51 (dd, J = 7.2, 11.4 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.01-7.03 (m, 1H), 7.16-7.22 (m, 4H), 7.71 (d, J = 8.4 Hz, 2H), 9.95 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 20.31, 28.55, 35.65, 48.49, 119.37 121.17, 124.67, 125.20, 126.59, 128.59, 131.77, 136.36, 140.95, 161.70, 164.23, 168.58. Anal. Calcd. for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.48; N, 11.96. Found: C, 65.12; H, 4.54; N, 12.23.

5-6 ^{1}H NMR ($CDCl_3$) δ: 2.47-2.52 (m, 1H), 2.76-2.80 (m, 1H), 2.99-3.10 (m, 2H), 4.68 (dd, J = 4.8, 11.7 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.15-7.50 (m, 6H), 7.88 (d, J = 7.2 Hz, 1H), 8.69 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 29.76, 36.78, 49.28, 122.53, 126.64, 126.97, 128.01, 129.95, 130.76, 131.16, 132.25, 132.86, 133.15, 136.44, 163.88, 170.70. Anal. Calcd. for $C_{18}H_{14}ClN_3O_2S$: C, 58.14; H, 3.79; N, 11.30. Found: C, 57.93; H, 3.84; N, 11.17.

5-7 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.32-2.40 (m, 1H), 2.73-2.77 (m, 1H), 2.80-2.98 (m, 2H), 4.51 (dd, J = 6.3, 11.1 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 7.06-7.13 (m, 1H), 7.20-7.26 (m, 2H), 7.44-7.53 (m, 2H), 7.77-7.80 (m, 2H), 10.16 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 27.75, 34.84, 47.98, 120.53, 122.97, 123.17, 123.95, 124.16, 125.90, 128.01, 129.22, 129.84, 131.12, 132.68, 135.84, 161.90, 162.05, 167.47. Anal. Calcd. for $C_{18}H_{14}ClN_3O_2S$: C, 58.14; H, 3.79; N, 11.30. Found: C, 58.08; H, 3.99; N, 11.16.

5-8 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.34-2.41 (m, 1H), 2.70-2.74 (m, 1H), 2.81-2.95 (m, 2H), 4.51 (dd, J = 6.6, 11.4 Hz, 1H), 7.02 (d, J=7.8 Hz, 1H), 7.04-7.11 (m, 1H), 7.17-7.22 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 10.09 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.08, 35.18, 48.21, 120.35, 120.78, 124.23, 126.16, 126.32, 127.84, 128.24, 131.34, 135.76, 136.01, 161.94, 162.77, 167.89. Anal. Calcd. for $C_{18}H_{14}ClN_3O_2S$: C, 58.14; H, 3.79; N, 11.30. Found: C, 58.14; H, 3.62; N, 10.94.

5-9 ^{1}H NMR ($CDCl_3$) δ: 2.44-2.55 (m, 1H), 2.74-2.82 (m, 1H), 2.94-3.14 (m, 2H), 4.68 (dd, J = 7.5, 11.7 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.15-7.69 (m, 5H), 7.82 (d, J = 1.8 Hz, 1H), 7.84 (d, J = 1.8 Hz, 1H), 8.73 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 29.76, 36.89, 49.34, 121.26, 122.55, 124.64, 126.65, 127.51, 128.01, 129.95, 131.20, 132.35, 133.15, 134.48, 136.42, 163.88, 164.32, 170.70. Anal. Calcd. for $C_{18}H_{14}BrN_3O_2S$: C, 51.93; H, 3.39; N, 10.09. Found: C, 52.17; H, 3.64; N, 9.87.

5-10 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.34-2.41 (m, 1H), 2.72-2.78 (m, 1H), 2.81-2.94 (m, 2H), 4.50 (dd, J = 6.9 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.08-7.12 (m, 1H), 7.20-7.25 (m, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 10.15 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 27.81, 34.95, 48.03, 120.55, 123.98, 125.93, 126.30, 128.04, 130.62, 131.16, 135.86, 161.70, 162.61, 167.53. Anal. Calcd. for $C_{18}H_{14}BrN_3O_2S$ C, 51.93; H, 3.39; N, 10.09. Found: C, 52.12; H, 3.32; N, 9.87.

5-11 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.31-2.41 (m, 1H), 2.72-2.92 (m, 3H), 4.46 (dd, J = 6.9, 11.7 Hz, 1H), 6.86 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 8.1 Hz, 1H), 7.08-7.11 (m, 1H), 7.13-7.26 (m, 2H), 7.67 (d, J = 9.0 Hz, 2H), 10.01 (s, 1H), 10.15 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 27.64, 34.87, 47.79, 112.03, 114.29, 120.42, 123.81, 125.80, 126.39, 127.93, 131.11, 135.80, 159.07, 159.94, 163.44, 167.47. Anal. Calcd. for

$C_{18}H_{15}N_3O_3S$: C, 61.18; H, 4.28; N, 11.89. Found: C, 61.02; H, 3.91; N, 12.16.

5-12 ^{1}H NMR ($CDCl_3$) δ: 2.41-2.56 (m, 1H), 2.70-2.81 (m, 1H), 2.70-2.81 (m, 1H), 2.96-3.12 (m, 2H), 3.88 (s, 3H), 4.68 (dd, *J* = 7.2, 11.4 Hz, 1H), 6.99-7.09 (m, 3H), 7.15-7.20 (m, 1H), 7.24-7.29 (m, 2H), 7.46 (td, *J* = 1.2, 7.8 Hz, 1H), 7.81 (dd, *J* = 1.2, 7.5 Hz, 1H), 8.46 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 29.81, 36.84, 49.21, 55.81, 111.79, 112.52, 120.61, 122.52, 126.64, 127.98, 130.00, 132.97, 133.28, 136.41, 157.62, 162.80, 164.31, 170.83. Anal. Calcd. for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44. Found: C, 62.36; H, 4.79; N, 11.35.

5-13 ^{1}H NMR ($CDCl_3$) δ: 1.23 (t, *J* = 7.2Hz, 3H), 2.43-2.53 (m, 1H), 2.71-2.75 (m, 1H), 2.90-2.98 (m, 1H), 3.45-3.54 (m, 1H), 4.10-4.21 (m, 2H), 4.37 (d, *J* = 17.1 Hz, 1H), 4.66 (dd, *J* = 8.1, 11.4 Hz, 1H), 4.77 (d, *J* = 17.1 Hz, 1H),7.18-7.34 (m, 4H), 7.40-7.46 (m, 3H), 7.90-7.93 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.96, 29.18, 36.80, 49.40, 50.50, 61.37, 122.56, 123.40, 126.50, 127.45, 128.10, 128.87, 129.84, 131.49, 134.93, 140.66, 163.30, 165.45, 168.32, 169.39. Anal. Calcd. for $C_{22}H_{21}N_3O_4S$: C, 62.40; H, 5.00; N, 9.92. Found: C, 62.54; H, 4.98; N, 10.16.

5-14 ^{1}H NMR ($CDCl_3$) δ: 1.19-1.24 (m, 3H), 2.41-2.52 (m, 1H), 2.68-2.75 (m, 1H), 2.85-2.99 (m, 1H), 3.44-3.51 (m, 1H), 4.09-4.20 (m, 2H), 4.37 (d, *J* = 17.4 Hz, 1H), 4.63-4.70 (m, 1H), 4.73 (d, *J* = 17.4 Hz, 1H), 7.17-7.33 (m, 4H), 7.76 (dd, *J* = 1.8, 6.0 Hz, 2H), 8.73 (dd, *J* = 1.8, 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.95, 29.13, 36.61, 49.54, 50.55, 61.42, 119.85, 122.58, 127.52, 128.18, 129.84, 130.39, 134.79, 140.60, 150.69, 163.59, 164.98, 168.28, 169.13. Anal. Calcd. for $C_{21}H_{20}N_4O_4S$: C, 59.42; H, 4.75; N, 13.20. Found: C, 59.54; H, 4.70; N, 13.06.

5-15 ^{1}H NMR ($CDCl_3$) δ: 1.14 (s, 9H), 2.42 (s, 3H), 2.63-2.71 (m, 1H), 2.83-2.91 (m, 1H), 3.43-3.46 (m, 1H), 4.24 (d, *J* = 16.8 Hz, 1H), 4.50-4.57 (m, 1H), 4.64 (d, *J* = 16.8 Hz, 1H), 7.13-7.32 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 10.833, 27.882, 29.317, 36.888, 49.31, 51.30, 82.11, 122.38, 127.25, 128.03, 129.80, 134.86, 140.85, 163.16, 164.38, 167.28, 169.22. Anal. Calcd. for $C_{19}H_{23}N_3O_4S$: C, 58.59; H, 5.96; N, 10.79. Found: C, 58.54; H, 5.79; N, 10.65.

5-16 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.44-2.55 (m, 1H), 2.70-2.76 (m, 1H), 2.90-2.99 (m,1H), 3.50-3.53 (m, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.68 (d, J=17.1 Hz, 1H),

4.65-4.71 (m, 1H), 7.17-7.35 (m, 4H), 7.78-7.80 (d, J = 6.6 Hz, 2H), 8.75-8.77 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 27.94, 29.33, 36.67, 49.71, 51.39, 82.28, 119.95, 122.50, 127.45, 128.19, 129.89, 130.50, 134.83, 140.85, 150.78, 163.64, 165.13, 167.30, 169.05. Anal. Calcd. for $C_{23}H_{24}N_4O_4S$: C, 61.05; H, 5.35; N, 12.38. Found: C, 61.11; H, 5.24; N, 12.16.

5-17 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.45-2.55 (m, 1H), 2.71-2.75 (m, 1H), 2.92-2.98 (m, 1H), 3.47-3.54 (m, 1H), 4.25 (d, J = 16.8 Hz, 1H), 4.62-4.67 (m, 1H), 4.71 (d, J = 16.8 Hz, 1H), 7.16-7.50 (m, 7H), 7.86-7.89 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.93, 29.35, 36.90, 49.57, 51.30, 82.21, 122.47, 122.61, 126.99, 127.37, 129.84, 130.71, 131.17, 132.22, 132.82, 134.93, 140.85, 163.71, 164.05, 167.31, 169.19. Anal. Calcd. for $C_{24}H_{24}ClN_3O_4S$: C, 59.31; H, 4.98; N, 8.65. Found: C, 59.40; H, 4.79; N, 8.53.

5-18 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.44-2.54 (m, 1H), 2.69-2.76 (m, 1H), 2.87-3.00 (m, 1H), 3.46-3.58 (m, 1H), 4.27 (d, J = 17.1 Hz, 1H), 4.63-4.73 (m, 2H), 7.17-7.47 (m, 6H), 7.83 (dd, J = 1.2, 7.8 Hz, 1H), 7.90 (d, J = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.94, 29.35, 36.74, 49.59, 51.37, 82.25, 122.49, 124.65, 125.05, 126.52, 127.42, 128.16, 129.89, 130.35, 131.60, 134.89, 135.06, 140.86, 164.00, 164.31, 167.33, 169.19. Anal. Calcd. for $C_{24}H_{24}ClN_3O_4S$: C, 59.31; H, 4.98; N, 8.65. Found: C, 59.48; H, 4.93; N, 8.37.

5-19 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.46-2.56 (m, 1H), 2.69-2.75 (m, 1H), 2.87-3.01 (m, 1H), 3.47-3.58 (m, 1H), 4.26 (d, J = 17.1 Hz, 1H), 4.63-4.68 (m, 1H), 4.71 (d, J = 17.1 Hz, 1H), 7.16-7.43 (m, 6H), 7.68 (d, J = 7.5Hz, 1H), 7.37 (d, J = 7.8Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.93, 29.35, 37.06, 49.68, 51.28, 82.24, 121.26, 122.50, 124.64, 127.39, 127.52, 128.10, 129.84, 131.19, 132.35, 134.51, 134.96, 140.85, 164.08, 164.25, 167.31, 169.19. Anal. Calcd. for $C_{24}H_{24}BrN_3O_4S$: C, 54.34; H, 4.56; N, 7.92. Found: C, 54.54; H, 4.62; N, 8.15.

5-20 ^{1}H NMR ($CDCl_3$) δ: 1.48 (s, 9H), 2.46-2.57 (m, 1H), 2.71-2.77 (m, 1H), 2.88-3.02 (m, 1H), 3.47-3.59 (m, 1H), 4.30 (d, J = 16.8 Hz, 1H), 4.62-4.72 (m, 2H), 6.96 (td, J = 1.2, 7.5 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 7.21-7.42 (m, 5H), 7.64 (dd, J = 1.8, 7.5 Hz, 1H), 9.77 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.93, 29.32, 36.80, 49.69, 51.39, 82.28, 107.74, 117.33, 119.89, 122.47, 126.43, 127.48, 128.19, 129.87, 133.52, 134.82, 140.82,

157.01, 162.86, 164.87, 167.28, 169.02. Anal. Calcd. for $C_{24}H_{25}N_3O_5S$: C, 61.65; H, 5.39; N, 8.99. Found: C, 61.88; H, 5.24; N, 9.04.

5-21 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.42-2.52 (m, 1H), 2.70-2.88 (m, 2H), 3.46-3.53 (m, 1H), 4.28 (d, J = 17.1 Hz, 1H), 4.62 (dd, J = 7.5, 12.3 Hz, 1H), 4.71 (d, J = 17.1 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 7.17-7.35 (m, 4H), 7.65 (d, J = 8.7 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 18.25, 27.93, 29.30, 36.38, 48.93, 51.65, 58.39, 82.48, 114.44, 116.04, 122.65, 127.57, 128.26, 128.47, 129.80, 134.83, 140.71, 160.19, 162.20, 165.80, 167.41, 169.79. Anal. Calcd. for $C_{24}H_{25}N_3O_5S$: C, 61.65; H, 5.39; N, 8.99. Found: C, 61.45; H, 5.43; N, 9.17.

5-22 ^{1}H NMR ($CDCl_3$) δ: 1.40 (s, 9H), 2.44-2.54 (m, 1H), 2.67-2.74 (m, 1H), 2.88-3.01 (m, 1H), 3.46-3.53 (m, 1H), 3.87 (s, 1H), 4.25 (d, J = 17.1 Hz, 1H), 4.62-4.69 (m, 1H), 4.71 (d, J = 17.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 7.15-7.34 (m, 4H), 7.45 (t, J = 7.8 Hz, 1H), 7. 79 (d, J = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.91, 29.36, 36.95, 49.50, 51.25, 55.80, 82.16, 111.77, 112.55, 120.56, 122.42, 127.28, 128.03, 129.81, 130.06, 132.90, 135.00, 140.88, 157.61, 162.96, 164.19, 167.36, 169.39. Anal. Calcd. for $C_{25}H_{27}N_3O_5S$: C, 62.35; H, 5.65; N, 8.73. Found: C, 62.27; H, 5.58; N, 8.91.

5-23 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.43-2.53 (m, 1H), 2.68-2.74 (m, 1H), 2.87-3.00 (m, 1H), 3.45-3.59 (m, 1H), 3.84 (s, 3H), 4.25 (d, J = 17.1 Hz, 1H), 4.63 (dd, J = 7.5, 11.7 Hz, 1H), 4.70 (d, J = 17.1 Hz, 1H), 6.95 (d, J = 9.0 Hz, 1H), 7.16-7.34 (m, 4H), 7. 86 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.93, 29.36, 36.87, 49.51, 51.31, 55.37, 82.19, 114.35, 115.97, 122.44, 127.32, 128.09, 129.86, 134.96, 140.88, 162.14, 162.63, 165.47, 167.36, 169.34. Anal. Calcd. for $C_{25}H_{27}N_3O_5S$: C, 62.35; H, 5.65; N, 8.73. Found: C, 62.14; H, 5.70; N, 8.78.

5-24 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.32-2.42 (m, 1H), 2.70-2.82 (m, 2H), 2.91-3.04 (m, 1H), 4.50 (dd, J = 7.8, 11.7 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.23-7.28 (m, 2H), 7.40-7.42 (m, 3H), 7.88-7.92 (m, 2H), 9.89 (s, 1H), 14.06 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.52, 35.73, 47.53, 120.78, 124.10, 124.68, 126.16, 127.34, 128.26, 131.99, 136.65, 169.59. Anal. Calcd. for $C_{18}H_{16}N_4OS$: C, 64.26; H, 4.79; N, 16.65. Found: C, 64.56; H, 4.55; N, 16.58.

5-25 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.35-2.45 (m, 1H), 2.73-2.79 (m, 2H), 2.94-3.04 (m, 1H), 4.51-4.57 (m, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.25-7.30 (m, 2H), 7.84 (d, J = 6.9 Hz, 1H), 8.64 (d, J = 6.9 Hz, 1H), 9.85 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.84, 36.05, 47.89, 119.08, 121.14, 124.59, 126.59, 128.62, 132.22, 136.76, 149.09, 169.73. Anal. Calcd. for $C_{17}H_{15}N_5OS$: C, 60.52; H, 4.48; N, 20.76. Found: C, 60.71; H, 4.39; N, 20.96.

5-26 ^{1}H NMR ($CDCl_3$) δ: 2.39 (s, 3H), 2.43-2.51 (m, 1H), 2.75-2.81 (m, 1H), 2.90-3.10 (m, 2H), 4.83 (dd, J = 7.8, 11.7 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.16-7.35 (m, 5H), 7.62 (d, J = 7.2 Hz, 1H), 7.66 (s, 1H), 7.77 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 21.29, 29.93, 36.43, 49.63, 122.47, 124.88, 126.71, 128.06, 128.19, 129.03, 130.10, 131.89, 133.41, 136.39, 139.02, 163.21, 170.67. Anal. Calcd. for $C_{19}H_{18}N_4OS$: C, 65.12; H, 5.18; N, 15.99. Found: C, 65.07; H, 5.09; N, 16.14.

5-27 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.35-2.40 (m, 1H), 2.37 (s, 3H), 2.72-2.75 (m, 2H), 2.94-3.04 (m, 1H), 4.49 (dd, J = 7.8, 11.7 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.23-7.27 (m, 4H), 7.77 (d, J = 7.8 Hz, 2H), 9.85 (s, 1H), 14.06 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 19.95, 28.58, 37.77, 46.47, 120.76, 122.90, 124.06, 124.70, 126.15, 128.10, 132.09, 136.74, 138.74, 154.13, 169.82. Anal. Calcd. for $C_{19}H_{18}N_4OS$: C, 65.12; H, 5.18; N, 15.99. Found: C, 65.34; H, 4.98; N, 15.86.

5-28 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.32-2.43 (m, 1H), 2.72-2.78 (m, 2H), 2.93-3.02 (m, 1H), 4.51 (dd, J = 6.0, 11.7 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.23-7.29 (m, 2H), 7.36-7.38 (m, 2H), 7.80-7.94 (m, 1H), 7.99 (s, 1H), 9.87 (s, 1H), 14.15 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.66, 35.73, 120.94, 122.99, 124.30, 124.81, 126.36, 128.41, 128.93, 132.07, 133.00, 136.72, 169.62. Anal. Calcd. for $C_{18}H_{15}ClN_4OS$: : C, 58.30; H, 4.08; N, 15.11. Found: C, 58.43; H, 4.29; N, 15.00.

5-29 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.23-2.33 (m, 1H), 2.64-2.67 (m, 2H), 2.83-2.90 (m, 1H), 4.01 (d, J = 7.8, 11.7 Hz, 1H), 6.99 (d, J = 5.7 Hz, 1H), 7.06 (d, J = 5.7 Hz, 1H), 7.15-7.19 (m, 1H), 7.32 (d, J = 9.6 Hz, 2H), 7.81 (d, J = 9.6 Hz, 2H), 9.84 (s, 1H), 14.17 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.37, 35.59, 46.44, 120.67, 124.00, 126.06, 127.34, 128.16, 131.83, 136.51, 169.39. Anal. Calcd. for $C_{18}H_{15}ClN_4OS$: C, 58.30; H, 4.08; N, 15.11. Found: C, 58.38; H, 4.32; N, 15.08.

5-30 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.32-2.48 (m, 1H), 2.57-2.82 (m, 2H), 2.94-3.09 (m, 1H), 4.50 (dd, J = 7.0, 12.0 Hz, 1H), 6.87-7.00 (m, 2H), 7.12-7.17 (m, 2H), 7.19-7.33 (m, 2H), 7.82 (s, 1H), 9.78 (s, 1H), 11.03 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.62, 35.26, 46.40, 109.57, 115.92, 118.07, 121.08, 124.30, 124.96, 126.36, 128.32, 130.58, 132.04, 136.68, 152.95, 155.10, 169.66. Anal. Calcd. for $C_{18}H_{16}N_4O_2S$: C, 61.35; H, 4.58; N, 15.90. Found: C, 61.23; H, 4.57; N, 16.11.

5-31 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.31-2.41 (m, 1H), 2.72-2.75 (m, 2H), 2.94-3.04 (m, 1H), 4.47 (dd, J = 6.0, 11.7 Hz, 1H), 6.84 (d, J = 7.8 Hz, 2H), 7.06-7.15 (m, 2H), 7.23-7.27 (m, 2H), 7.71 (d, J = 7.8 Hz, 2H), 9.60 (s, 1H), 9.83 (s, 1H), 13.84 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.62, 35.82, 46.46, 114.41, 116.76, 120.79, 124.07, 126.16, 126.41, 128.24, 132.13, 136.76, 158.06, 169.88. Anal. Calcd. for $C_{18}H_{16}N_4O_2S$: C, 61.35; H, 4.58; N, 15.90. Found: C, 61.43; H, 4.40; N, 15.65.

5-32 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.46-2.35 (m, 1H), 2.72-2.91 (m, 3H), 3.93 (s, 3H), 4.44 (dd, J = 6.9, 11.7 Hz, 1H), 7.02-7.17 (m, 4H), 7.25-7.31 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 10.02 (s, 1H), 13.61 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 29.56, 36.85, 47.45, 55.37, 111.58, 115.02, 120.66, 122.05, 125.27, 127.44, 128.88, 129.62, 131.56, 133.32, 138.10, 152.23, 156.46, 170.38. Anal. Calcd. for $C_{19}H_{18}N_4O_2S$: C, 62.28; H, 4.95; N, 15.29. Found: C, 62.25; H, 4.73; N, 15.08.

5-33 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.23-2.33 (m, 1H), 2.60-2.72 (m, 2H), 2.85-2.90 (m, 1H), 3.74 (s, 3H), 4.40 (dd, J = 5.7, 11.7 Hz, 1H), 6.85 (d, J = 9.9 Hz, 2H), 6.99-7.06 (m, 2H), 7.13-7.19 (m, 2H), 7.74 (d, J = 9.9 Hz, 2H), 9.73 (s, 1H), 13.86 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 28.66, 35.82, 46.53, 53.95, 112.87, 118.33, 120.84, 124.12, 126.42, 128.29, 132.18, 136.80, 154.00, 157.56, 159.61, 169.95. Anal. Calcd. for $C_{19}H_{18}N_4O_2S$: C, 62.28; H, 4.95; N, 15.29. Found: C, 62.49; H, 4.77; N, 15.04.

5-34 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 1.21-1.25 (m, 3H), 2.32-2.42 (m, 1H), 2.70-2.72 (m, 2H), 3.40-3.42 (m, 1H), 4.10-4.22 (m, 2H), 4.46 (d, J = 17.4 Hz, 1H), 4.48-4.55 (m, 1H), 4.67 (d, J = 17.4 Hz, 1H), 7.21-7.33 (m, 3H), 7.36-7.45 (m, 3H), 7.88-7.90 (m, 2H), 14.07 (s, 1H).^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 12.68, 27.81, 35.79, 46.61, 49.02, 59.66,

121.29, 124.61, 125.63, 126.55, 127.29, 128.12, 138.81, 139.86, 167.21, 168.76. Anal. Calcd. for $C_{22}H_{22}N_4O_3S$: C, 62.54; H, 5.25; N, 13.26. Found: C, 62.69; H, 5.13; N, 13.51.

5-35 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 1.51 (t, J = 6.9 Hz, 3H), 2.24-2.35 (m, 1H), 2.46-2.49 (m, 2H), 3.32-3.37 (m, 1H), 4.01-4.11 (m, 2H), 4.41 (d, J = 17.1 Hz, 1H), 4.39-4.48 (m, 1H), 4.58 (d, J = 17.1 Hz, 1H), 7.15-7.33 (m, 4H), 7.72 (d, J = 5.7 Hz, 2H), 8.53 (d, J = 6.0 Hz, 2H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 13.82, 28.84, 36.76, 50.21, 60.79, 119.75, 122.51, 126.88, 127.79, 129.30, 134.78, 140.90, 149.94, 168.35, 169.54. Anal. Calcd. for $C_{21}H_{21}N_5O_3S$: C, 59.56; H, 5.00; N, 16.54. Found: C, 59.54; H, 4.74; N, 16.25.

5-36 ^{1}H NMR ($CDCl_3$) δ: 1.23 (t, J=7.8 Hz, 3H), 2.23-2.31 (m, 1H), 2.34 (s, 3H), 2.56-2.58 (m, 1H), 2.64-2.68 (m, 1H), 3.34-3.36 (m, 1H), 4.14-4.27 (m, 3H), 4.42 (d, J = 17.7 Hz, 1H), 4.70 (d, J = 17.7 Hz, 1H), 7.12-7.30 (m, 6H), 7.84 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.02, 21.27, 29.38, 36.54, 48.44, 50.98, 61.68, 122.50, 123.33, 126.99, 124.45, 128.13, 128.48, 129.69, 130.30, 135.17, 138.25, 140.85, 168.63, 171.45. Anal. Calcd. for $C_{23}H_{24}N_4O_3S$: C, 63.28; H, 5.54; N, 12.83. Found: C, 63.36; H, 5.49; N, 12.94.

5-37 ^{1}H NMR ($CDCl_3$) δ: 0.86-0.99 (m, 3H), 2.10-2.24 (m, 4H), 2.63-2.67 (m, 2H), 3.34-3.39 (m, 1H), 4.14-4.16 (m, 2H), 4.28-4.36 (m, 1H), 4.39 (d, J = 17.4 Hz, 1H), 4.72 (d, J = 17.4 Hz, 1H), 7.10-7.26 (m, 6H), 7.84 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.99, 21.32, 29.33, 36.55, 48.41, 50.90, 61.58, 122.47, 126.19, 127.35, 128.06, 129.25, 129.63, 135.17, 139.58, 140.80, 168.60, 171.34. Anal. Calcd. for $C_{23}H_{24}N_4O_3S$: C, 63.28; H, 5.54; N, 12.83. Found: C, 63..22; H, 5.31; N, 13.05.

5-38 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 1.20-1.25 (m, 3H), 2.35-2.38 (m, 1H), 2.65-2.76 (m, 2H), 3.46-3.48 (m, 1H), 4.15 (q, J = 3.9 Hz, 2H), 4.42 (d, J = 17.7 Hz, 1H), 4.45-4.50 (m, 1H), 4.76 (d, J = 17.7 Hz, 1H), 6.87-6.92 (m, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.25-7.35 (m, 5H), 7.80 (d, J = 7.8 Hz, 1H), 10.96 (s, 1H), 14.19 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 12.71, 27.82, 35.00, 45.99, 49.16, 59.71, 109.47, 115.83, 118.01, 121.48, 124.88, 125.74, 126.70, 128.19, 130.05, 133.86, 139.81, 152.81, 155.01, 155.87, 167.24, 168.84. Anal. Calcd. for $C_{22}H_{22}N_4O_4S$: C, 60.26; H, 5.06; N, 12.78.

Found: C, 60.01; H, 5.18; N, 12.90.

5-39 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 1.12-1.17 (m, 3H), 2.23-2.34 (m, 1H), 2.59-2.62 (m, 2H), 3.30-3.43 (m, 1H), 4.04-4.07 (m, 2H), 4.33 (d, J = 17.7 Hz, 1H), 4.36-4.41 (m, 1H), 4.59 (d, J = 17.7 Hz, 1H), 6.74 (d, J = 7.8 Hz, 2H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 12.97, 28.17, 36.19, 46.72, 49.34, 60.04, 114.59, 121.52, 125.92, 126.59, 126.82, 128.44, 134.24, 140.16, 158.11, 167.54, 169.45. Anal. Calcd. for $C_{22}H_{22}N_4O_4S$: C, 60.26; H, 5.06; N, 12.78. Found: C, 60.15; H, 5.08; N, 12.87.

5-40 ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, J = 7.2 Hz, 3H), 2.40-2.50 (m, 1H), 2.67-2.69 (m, 2H), 3.46-3.48 (m, 1H), 4.08 (s, 3H), 4.10-4.19 (m, 2H), 4.35 (d, J = 17.1 Hz, 1H), 4.56 (d, J = 6.6, 11.4 Hz, 1H), 4.77 (d, J = 17.1 Hz, 1H), 6.97-7.06 (m, 2H), 7.16-7.28 (m, 4H), 7.38 (t, J = 8.7 Hz, 1H), 8.12 (d, J = 7.5 Hz, 1H), 11.86 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.01, 29.44, 36.99, 47.83, 50.43, 55.91, 61.29, 111.07, 114.84, 121.31, 122.49, 126.97, 127.81, 129.34, 129.55, 131.52, 133.57, 141.31, 153.39, 156.61, 168.75, 170.79. Anal. Calcd. for $C_{23}H_{24}N_4O_4S$: C, 61.05; H, 5.35; N, 12.38. Found: C, 61.24; H, 5.29; N, 12.22.

5-41 ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, J=7.8 Hz, 3H), 2.24-2.34 (m, 1H), 2.57-2.67 (m, 2H), 3.33-3.37 (m, 1H), 3.81 (s, 3H), 4.12-4.26 (m, 3H), 4.39 (d, J = 15.6 Hz, 1H), 4.71 (d, J = 15.6 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 7.10-7.29 (m, 4H), 7.88 (d, J = 8.7 Hz, 2H), 12.70 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.01, 29.36, 36.58, 48.38, 50.93, 55.23, 61.61, 113.94, 122.50, 127.40, 127.80, 128.10, 129.66, 135.20, 140.85, 160.67, 168.64, 171.37. Anal. Calcd. for $C_{23}H_{24}N_4O_4S$: C, 61.05; H, 5.35; N, 12.38. Found: C, 61.33; H, 5.16; N, 12.45.

5-42 ^{1}H NMR ($CDCl_3$) δ: 1.35 (s, 9H), 2.22-2.33 (m, 1H), 2.55-2.68 (m, 2H), 3.32-3.34 (m, 1H), 4.16-4.21 (m, 1H), 4.33 (d, J = 15.6 Hz, 1H), 4.62 (d, J = 15.6 Hz, 1H), 7.11-7.34 (m, 4H), 7.38-7.39 (m, 3H), 7.99-8.01 (m, 2H), 12.73 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.94, 29.49, 36.54, 48.46, 51.77, 82.53, 122.35, 126.29, 127.31, 128.10, 128.53, 129.43, 129.63, 135.11, 141.00, 167.56, 171.28. Anal. Calcd. for $C_{24}H_{26}N_4O_3S$: C, 63.98; H, 5.82; N, 12.44. Found: C, 63.99; H, 5.87; N, 12.21.

5-43 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 1.41 (s, 9H), 2.34-2.44 (m, 1H), 2.70-2.74 (m, 2H), 3.39-3.42 (m, 1H), 4.36 (d, J = 17.4 Hz, 1H), 4.49-4.53 (m, 1H), 4.59 (d, J = 17.4

Hz, 1H), 7.23-7.40 (m, 4H), 7.81 (d, J = 6.0 Hz, 2H), 8.63 (d, J = 6.0 Hz, 2H), 14.29 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 26.46, 27.85, 35.64, 49.77, 80.24, 118.62, 121.13, 125.61, 126.61, 128.12, 133.64, 139.89, 148.77, 166.15, 168.25. Anal. Calcd. for $C_{23}H_{25}N_5O_3S$: C, 61.18; H, 5.58; N, 15.51. Found: C, 61.32; H, 5.43; N, 15.25.

5-44 ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 2.26-2.28 (m, 1H), 2.35 (s, 3H), 2.55-2.68 (m, 2H), 3.33-3.36 (m, 1H), 4.18-4.25 (m, 1H), 4.32 (d, J = 17.1 Hz, 1H), 4.64 (d, J = 17.1 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 7.19-7.31 (m, 4H), 7.90 (d, J = 7.5 Hz, 2H), 12.76 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 21.35, 27.91, 29.47, 36.54, 48.43, 51.69, 82.43, 122.33, 126.21, 127.25, 128.04, 129.25, 129.60, 135.14, 139.50, 141.00, 167.57, 171.24. Anal. Calcd. for $C_{25}H_{28}N_4O_3S$: C, 64.63; H, 6.07; N, 12.06. Found: C, 64.47; H, 6.10; N, 12.34.

5-45 ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 2.26-2.29 (m, 1H), 2.54-2.70 (m, 2H), 3.31-3.35 (m, 1H), 4.17-4.22 (m, 1H), 4.36 (d, J = 17.4 Hz, 1H), 4.63 (d, J = 17.4 Hz, 1H), 7.13-7.32 (m, 6H), 7.87-7.90 (m, 1H), 8.03 (s, 1H), 12.74 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 29.47, 36.34, 48.73, 51.38, 82.68, 122.33, 124.27, 126.45, 127.42, 128.22, 129.25, 129.66, 129.80, 134.48, 135.01, 141.15, 167.82, 171.56. Anal. Calcd. for $C_{24}H_{25}ClN_4O_3S$: C, 59.43; H, 5.20; N, 11.55. Found: C, 59.45; H, 5.47; N, 11.62.

5-46 ^{1}H NMR ($CDCl_3$) δ: 1.44 (s, 9H), 2.19-2.29 (m, 1H), 2.50-2.58 (m, 1H), 2.66-2.70 (m, 1H), 3.29-3.31 (m, 1H), 4.07-4.13 (m, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.19-7.32 (m, 3H), 7.37 (d, J = 7.8 Hz, 2H), 7.97 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 27.99, 29.52, 36.48, 48.40, 51.92, 82.72, 122.35, 127.61, 128.24, 128.76, 129.71, 135.02, 135.23, 140.99, 167.60, 171.44. Anal. Calcd. for $C_{24}H_{25}ClN_4O_3S$: C, 59.43; H, 5.20; N, 11.55. Found: C, 59.51; H, 5.16; N, 11.78.

5-47 ^{1}H NMR ($CDCl_3$) δ: 1.38 (s, 9H), 2.40-2.50 (m, 1H), 2.62-2.69 (m, 2H), 3.48-3.56 (m, 1H), 3.98 (s, 3H), 4.23 (d, J = 17.4 Hz, 1H), 4.74 (d, J = 17.4 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H), 7.13-7.29 (m, 4H), 7.38 (t, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 11.81 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.90, 29.58, 36.96, 47.91, 51.13, 55.91, 81.90, 111.07, 114.85, 121.34, 122.29, 126.79, 127.75, 129.35, 129.51, 131.51, 135.57, 141.47, 153.39, 156.61, 159.07, 167.71, 170.60. . Anal. Calcd. for $C_{25}H_{28}N_4O_4S$: C, 62.48; H, 5.87; N, 11.66. Found: C, 62,27; H, 5.93; N, 11.72.

5-48 ^{1}H NMR ($CDCl_3$) δ: 2.34-2.44 (m, 1H), 2.63 (s, 3H), 2.69-2.75 (m, 1H), 2.83-2.94 (m, 1H), 2.97-3.08 (m, 1H), 4.70 (dd, J = 7.8, 11.7 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 7.12-7.26 (m, 3H), 8.75 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 15.43, 29.79, 36.45, 49.60, 122.42, 126.33, 127.86, 129.81, 133.19 , 136.57, 163.54, 165.41, 171.10. Anal. Calcd. for $C_{13}H_{13}N_3OS_2$: C, 53.58; H, 4.50; N, 14.42. Found: C, 53.54; H, 4.63; N, 14.68.

5-49 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.34-2.43 (m, 1H), 2.76-2.98 (m, 3H), 4.66 (dd, J = 7.2, 11.1 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.14-7.18 (m, 1H), 7.26-7.31 (m, 2H), 7.49-7.50 (m, 3H), 7.18-7.84 (m, 2H), 10.15 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 29.39, 36.30, 49.96, 122.07, 125.40, 127.23, 129.07, 129.55, 130.97, 132.78, 137.52, 163.42, 167.89, 169.28. Anal. Calcd. for $C_{18}H_{15}N_3OS_2$: C, 61.16; H, 4.28; N, 11.89. Found: C, 61.11; H, 4.30; N, 12.04.

5-50 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.35-2.45 (m, 4H), 2.96-3.00 (m, 2H), 3.20-3.23 (m, 1H), 4.52 (dd, J = 7.1, 12.0 Hz, 1H), 7.06-7.15 (m, 2H), 7.22-7.27 (m, 4H), 7.70-7.73 (m, 2H), 9.74 (s, 1H).^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 20.95, 29.60, 36.78, 47.60, 121.81, 122.80, 125.14, 126.48, 127.18, 128.36, 129.27, 130.56, 133.10, 137.65, 155.21, 158.79, 171.03. Anal. Calcd. for $C_{19}H_{17}N_3OS_2$: C, 62.10; H, 4.66; N, 11.43. Found: C, 62.25; H, 4.79; N, 11.31.

5-51 ^{1}H NMR (DMSO-d_6) δ: 2.31-2.39 (m, 4H), 2.74-2.90 (m, 3H), 4.66 (dd, J = 6.9, 11.7 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.16-7.21 (m, 1H), 7.30-7.34 (m, 4H), 7.75 (d, J = 7.8 Hz, 1H), 10.21 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 21.10, 29.37, 36.36, 50.21, 122.31, 125.67, 126.59, 127.78, 130.10, 133.13, 137.81, 141.56, 163.20, 168.32, 169.34. Anal. Calcd. for $C_{19}H_{17}N_3OS_2$: C, 62.10; H, 4.66; N, 11.43. Found: C, 62.32; H, 4.72; N, 11.25.

5-52 ^{1}H NMR (DMSO-d_6) δ: 2.32-2.41 (m, 1H), 2.78-2.91 (m, 3H), 4.62 (dd, J = 7.2, 11.7 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.16-7.21 (m, 1H), 7.30-7.36 (m, 2H), 7.53-7.63 (m, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.94 (s, 1H), 10.22 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 29.37, 36.29, 50.25, 122.33, 125.69, 126.39, 126.82, 127.78, 129.93, 131.14, 131.46, 133.12, 134.16, 137.79, 164.65, 166.70, 169.28. Anal. Calcd. for $C_{18}H_{14}ClN_3OS_2$: C, 55.73; H, 3.64; N, 10.83. Found: C, 55.99; H, 3.90; N, 10.71.

5-53 ^{1}H NMR (DMSO-d_6+$CDCl_3$) δ: 2.37-2.47 (m, 1H), 2.77-2.81 (m, 1H), 2.85-3.07

(m, 2H), 4.71 (dd, J = 7.2, 11.7 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.13-7.18 (m, 1H), 7.24-7.29 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 10.04 (s, 1H). ^{13}C NMR (DMSO-d_6+$CDCl_3$) δ: 29.41, 36.28, 49.91, 121.96, 125.39, 127.34, 127.79, 128.44, 129.02, 129.40, 132.61, 136.32, 137.24, 163.78, 166.69, 169.47. Anal. Calcd. for $C_{18}H_{14}ClN_3OS_2$: C, 55.73; H, 3.64; N, 10.83. Found: C, 55.89; H, 3.67; N, 10.69.

5-54 ^{1}H NMR (DMSO-d_6) δ: 2.34-2.40 (m, 1H), 2.78-3.09 (m, 3H), 4.60-4.65 (m, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.16-7.21 (m, 1H), 7.30-7.36 (m, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 10.21 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 29.37, 36.32, 50.27, 122.31, 124.89, 125.69, 127.78, 128.43, 129.38, 129.93, 132.54, 133.12, 137.77, 164.27, 167.17, 169.29. Anal. Calcd. for $C_{18}H_{14}BrN_3OS_2$: C, 50.00; H, 3.26; N, 9.72. Found: C, 49.85; H, 3.30; N, 9.94.

5-55 ^{1}H NMR (DMSO-d_6) δ: 2.31-2.35 (m, 1H), 2.70-2.86 (m, 3H), 4.54 (dd, J = 6.6, 11.7 Hz, 1H), 6.86 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 7.5 Hz, 1H), 7.12-7.17 (m, 1H), 7.25-7.31 (m, 2H), 7.67 (d, J = 8.4 Hz, 2H), 10.17 (s, 1H), 10.22 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 29.42, 36.44, 50.21, 116.31, 120.31, 122.34, 125.72, 127.81, 129.43, 133.20, 137.85, 160.52, 162.00, 168.52, 169.45. Anal. Calcd. for $C_{18}H_{15}N_3O_2S_2$ C, 58.52; H, 4.09; N, 11.37. Found: C, 58.70; H, 4.10; N, 11.19.

5-56 ^{1}H NMR (DMSO-d_6) δ: 2.26-2.36 (m, 1H), 2.71-2.87 (m, 3H), 3.95 (s, 3H), 4.57 (dd, J = 6.9, 11.7 Hz, 1H), 7.04-7.18 (m, 3H), 7.23-7.33 (m, 3H), 7.73 (t, J = 8.1 Hz, 1H), 8.17 (d, J = 8.1Hz, 1H), 10.17 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 29.40, 36.41, 50.03, 56.28, 112.56, 117.95, 121.37, 122.30, 125.69, 127.29, 127.81, 129.98, 132.80, 133.21, 137.88, 155.50, 161.71, 164.18, 169.78. Anal. Calcd. for $C_{19}H_{17}N_3O_2S_2$: C, 59.51; H, 4.47; N, 10.96. Found: C, 59.38; H, 4.26; N, 10.83.

5-57 ^{1}H NMR (DMSO-d_6) δ: 2.27-2.36 (m, 1H), 2.70-2.86 (m, 3H), 3.79 (s, 3H), 4.55 (dd, J = 6.9, 11.7 Hz, 1H), 7.02-7.06 (m, 3H), 7.12-7.17 (m, 1H), 7.26-7.32 (m, 2H), 7.77 (dd, J = 8.7 Hz, 2H), 10.18 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 29.40, 36.40, 50.21, 55.60, 114.96, 121.81, 122.33, 125.71, 127.79, 129.24, 129.96, 133.17, 137.84, 161.72, 162.55, 168.09, 169.40. Anal. Calcd. for $C_{19}H_{17}N_3O_2S_2$: : C, 59.51; H, 4.47; N, 10.96. Found: C, 59.54; H, 4.59; N, 10.76.

5-58 ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, J = 6.9 Hz, 3H), 2.02-2.44 (m, 1H), 2.63 (s, 3H),

2.66-2.71 (m, 1H), 2.78-2.85 (m, 1H), 3.41-3.48 (m, 1H), 4.05-4.19 (m, 2H), 4.31 (d, *J* = 17.1 Hz, 1H), 4.68 (dd, *J* = 6.9, 11.7 Hz, 1H), 4.75 (d, *J* = 17.1 Hz, 1H), 7.15-7.31 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 13.96, 15.43, 29.21, 36.48, 49.66, 50.52, 61.32, 122.58, 127.28, 128.03, 129.75, 135.02, 140.73, 163.71, 165.28, 168.44, 169.70. Anal. Calcd. for $C_{17}H_{19}N_3O_3S_2$: C, 54.09; H, 5.07; N, 11.13. Found: C, 54.40; H, 4.95; N, 11.41.

5-59 ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, *J* = 6.9 Hz, 3H), 2.42-2.53 (m, 1H), 2.70-2.76 (m, 1H), 2.84-2.98 (m, 1H), 3.47-3.58 (m, 1H), 4.12-4.23 (m, 2H), 4.37 (d, *J* = 17.7 Hz, 1H), 4.78-4.86 (m, 2H), 7.12-7.41 (m, 4H), 7.43-7.48 (m, 3H), 7.82-7.84 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.99, 29.27, 36.63, 49.83, 50.59, 61.39, 122.62, 127.37, 127.54, 128.07, 129.06, 129.61, 130.96, 135.03, 140.74, 163.58, 168.47, 169.71. Anal. Calcd. for $C_{22}H_{21}N_3O_3S_2$: C, 60.11; H, 4,82; N, 9.56. Found: C, 60.02; H, 4.83; N, 9.47.

5-60 ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, *J* = 6.9 Hz, 3H), 2.39 (s, 3H), 2.42-2.53 (m, 1H), 2.70-2.76 (m, 1H), 2.83-2.97 (m, 1H), 3.47-3.58 (m, 1H), 4.10-4.26 (m, 2H), 4.37 (d, *J* = 17.7 Hz, 1H), 4.79-4.85 (m, 2H), 7.16-7.35 (m, 6H), 7.62 (d, *J* = 6.9 Hz, 1H), 7.67 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.02, 21.22, 29.31, 36.62, 49.83, 50.60, 61.41, 122.65, 124.80, 127.38, 128.10, 128.98, 129.53, 129.85, 131.79, 135.07, 138.94, 140.78, 163.40, 168.51, 168.88, 169.77. Anal. Calcd. for $C_{23}H_{23}N_3O_3S_2$: C, 60.90; H, 5.11; N, 9.26. Found: C, 60.72; H, 5.05; N, 9.48.

5-61 ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, *J* = 6.9 Hz, 3H), 2.38 (s, 3H), 2.42-2.52 (m, 1H), 2.69-2.76 (m, 1H), 2.84-2.95 (m, 1H), 3.47-3.58 (m, 1H), 4.12-4.23 (m, 2H), 4.37 (d, *J* = 17.1 Hz, 1H), 4.78-4.85 (m, 2H), 7.20-7.35 (m, 6H), 7.72 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.01, 17.98, 21.41, 29.30, 36.66, 49.82, 50.59, 61.40, 122.62, 126.93, 127.37, 127.48, 128.07, 129.75, 129.84, 135.06, 140.77, 141.44, 163.04, 168.51, 168.80, 169.77. Anal. Calcd. for $C_{23}H_{23}N_3O_3S_2$: C, 60.90; H, 5.11; N, 9.26. Found: C, 60.83; H, 4.81; N, 9.55.

5-62 ^{1}H NMR ($CDCl_3$) δ: 1.24 (t, *J* = 6.9 Hz, 3H), 2.42-2.53 (m, 1H), 2.68-2.75 (m, 1H), 2.85-2.96 (m, 1H), 3.47-3.53 (m, 1H), 3.96 (s, 3H), 4.12-4.23 (m, 2H), 4.36 (d, *J* = 17.1 Hz, 1H), 4.78-4.88 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.19-7.34 (m, 4H), 7.43 (t, *J* = 8.7 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.02, 29.35, 36.92, 49.65, 50.59, 55.60, 61.37, 111.19, 118.73, 121.13, 122.61, 127.31,

127.98, 129.86, 131.95, 135.14, 140.80, 155.49, 162.35, 164.25, 168.54, 169.99. Anal. Calcd. for $C_{23}H_{23}N_3O_4S_2$: C, 58.83; H, 4.94; N, 8.95. Found: C, 58.96; H, 4.91; N, 8.77.

5-63 ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 2.37-2.48 (m, 1H), 2.67 (s, 3H), 2.69-2.88 (m, 2H), 3.44-3.51 (m, 1H), 4.24 (d, J = 17.1 Hz, 1H), 4.67-4.74 (m, 2H), 7.16-7.34 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 15.47, 27.90, 29.39, 36.52, 49.83, 51.34, 82.07, 122.46, 127.16, 128.01, 129.74, 135.03, 140.99, 163.83, 165.30, 167.45, 169.54. Anal. Calcd. for $C_{19}H_{23}N_3O_3S_2$: C, 56.26; H, 5.72; N, 10.36. Found: C, 56.13; H, 5.95; N, 10.08.

5-64 ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 2.39 (s, 3H), 2.42-2.53 (m, 1H), 2.69-2.75 (m, 1H), 2.83-2.96 (m, 1H), 3.46-3.57 (m, 1H), 4.27 (d, J = 16.8 Hz, 1H), 4.73 (d, J = 16.8 Hz, 1H), 4.77-4.83 (m, 1H), 7.18-7.34 (m, 6H), 7.61 (d, J = 7.5 Hz, 1H), 7.66 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 21.24, 27.93, 29.45, 36.64, 49.97, 51.39, 82.10, 122.50, 124.81, 127.22, 128.04, 128.10,128.97, 129.58, 129.80, 131.78, 135.05, 138.94, 141.00, 163.47, 167.48, 168.86, 169.56. Anal. Calcd. for $C_{25}H_{27}N_3O_3S_2$: C, 62.34; H, 5.65; N, 8.72. Found: C, 62.44; H, 5.90; N, 8.57.

5-65 ^{1}H NMR ($CDCl_3$) δ: 1.43 (s, 9H), 2.42-2.52 (m, 1H), 2.72-2.76 (m, 1H), 2.86-2.90 (m, 1H), 3.51-3.53 (m, 1H), 4.29 (d, J = 17.1 Hz, 1H), 4.71 (d, J = 17.1 Hz, 1H), 4.76-4.83 (m, 1H), 7.19-7.44 (m, 6H), 7.69 (d, J = 6.9 Hz, 1H), 7.85 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.91, 29.41, 36.54, 50.06, 51.42, 82.13, 122.50, 125.71, 127.26, 127.37, 128.07, 129.78, 130.36, 130.88, 131.26, 134.96, 135.09, 140.95, 164.45, 167.02, 167.44, 169.39. Anal. Calcd. for $C_{24}H_{24}ClN_3O_3S_2$: C, 57.42; H, 4.82; N, 8.37. Found: C, 52.40; H, 4.75; N, 8.22.

5-66 ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 2.42-2.53 (m, 1H), 2.69-2.75 (m, 1H), 2.71-2.76 (m, 1H), 3.49-3.54 (m, 1H), 4.27 (d, J = 17.1 Hz, 1H), 4.71 (d, J = 17.1 Hz, 1H), 4.76-4.83 (m, 1H), 7.18-7.35 (m, 4H), 7.61 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.93, 29.44, 36.61, 50.06, 51.42, 82.14, 122.50, 127.26, 128.08, 128.73, 128.97, 129.38, 129.80, 135.00, 137.03, 140.97, 164.11, 167.45, 169.44. Anal. Calcd. for $C_{24}H_{24}ClN_3O_3S_2$: C, C, 57.42; H, 4.82; N, 8.37. Found: C, 57.63; H, 4.98; N, 8.29.

5-67 ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 2.42-2.52 (m, 1H), 2.71-2.76 (m, 1H), 2.82-2.93 (m, 1H), 3.46-3.53 (m, 1H), 4.28 (d, J = 17.1 Hz, 1H), 4.71 (d, J = 17.1 Hz, 1H),

4.76-4.83 (m, 1H), 7.18-7.35 (m, 4H), 7.57 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.90, 29.39, 36.57, 50.03, 51.39, 82.10, 122.49, 125.37, 127.23, 128.06, 128.58, 128.88, 129.77, 132.30, 134.96, 140.94, 164.14, 167.42, 169.39. Anal. Calcd. for $C_{24}H_{24}BrN_3O_3S_2$: C, 52.75; H, 4.43; N, 7.69. Found: C, 52.68; H, 4.59; N, 7.90.

5-68 ^{1}H NMR ($CDCl_3$) δ: 1.40 (s, 9H), 2.42-2.52 (m, 1H), 2.66-2.73 (m, 1H), 2.87-2.95 (m, 1H), 3.46-3.53 (m, 1H), 3.95 (s, 3H), 4.23 (d, J = 17.1 Hz, 1H), 4.73 (d, J = 17.1 Hz, 1H), 4.78-4.85 (m, 1H), 6.98-7.08 (m, 2H), 7.16-7.32 (m, 4H), 7.42 (t, J = 7.2 Hz, 1H), 8.34 (t, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.91, 29.49, 36.64, 49.77, 51.34, 55.60, 82.04, 111.21, 118.81, 121.14, 122.46, 127.14, 127.95, 128.00, 129.80, 131.93, 135.14, 141.02, 155.52, 162.34, 164.32, 167.50, 169.80. Anal. Calcd. for $C_{25}H_{27}N_3O_4S_2$: C, 60.34; H, 5.47; N, 8.44. Found: C, 60.28; H, 5.29; N, 8.71.

3 抗菌活性

用杯盘培养法测定了化合物 **5** 在质量浓度为 200 . g/mL 时对链球菌、大肠杆菌、金黄色葡萄球菌、枯草杆菌和白色念珠球菌的抑菌活性。结果表明大部分化合物无明显的抑菌作用，其中只有 **5-45**、**5-63** 和 **5-64** 对链球菌有较好的抑制作用，其活性接近在相同浓度下作为对比的氯霉素。

化合物	金黄色葡萄球菌	大肠杆菌	链球菌	枯草杆菌	白色念珠球菌
5-1	+	-	+	-	-
5-2	-	-	-	-	-
5-3	-	+	-	+	-
5-4	-	+	-	+	-
5-5	-	-	-	-	-
5-6	-	+	+	+	-
5-7	+	+	+	+	+
5-8	+	+	++	+	-
5-9	+	+	+	+	+
5-10	+	+	+	+	++
5-11	+	-	+	-	+
5-12	-	-	-	+	+
5-13	-	-	-	+	+
5-14	-	-	+	-	+
5-15	-	-	+	-	-
5-16	-	-	-	-	-
5-17	-	-	-	-	-
5-18	-	-	-	-	-

化合物	金黄色葡萄球菌	大肠杆菌	链球菌	枯草杆菌	白色念珠球菌
5-19	-	+	-	-	-
5-20	-	+	-	-	-
5-21	-	-	-	+	-
5-22	+	-	-	+	-
5-23	+	-	-	-	-
5-24	++	-	-	-	++
5-25	++	+	-	-	+
5-26	+	+	-	++	-
5-27	+	+	-	+	-
5-28	-	-	-	-	-
5-29	-	-	-	+	-
5-30	+	-	-	-	-
5-31	++	-	-	+	-
5-32	+	-	-	+	-
5-33	-	+	-	-	-
5-34	-	+	+	-	+
5-35	-	+	-	-	-
5-36	-	+	-	-	-
5-37	+	+	-	-	-
5-38	-	+	-	-	-
5-39	-	+	-	-	-
5-40	-	+	-	-	-
5-41	+	+	++	+	-
5-42	+	+	+	+	-
5-43	+	+	+	+	-
5-44	+	+	++	++	-
5-45	+	+	+++	++	-
5-46	-	-	+	+	+
5-47	+	+	+	+	+
5-48	+	+	+	+	+
5-49	+	+	+	+	-
5-50	+	+	+	+	++
5-51	++	++	++	-	++
5-52	++	+	+	-	-
5-53	+++	-	+	+	-
5-54	++	-	+	+	-
5-55	+	+	+	+	-
5-56	++	-	+	++	-
5-57	-	+	+	++	-
5-58	+	++	+	++	+
5-59	++	+	++	++	+
5-60	-	-	-	+	-
5-61	++	-	++	+	-
5-62	-	+	+++	+	-
5-63	+	+	+++	+	++
5-64	-	-	+	+	+
5-65	-	-	+	+	-
5-66	-	-	+	+	-
5-67	-	+	-	+	-
5-68	-	+	-	-	-

实验部分

仪器与试剂

元素分析用德国 Elementar Vario El 仪测定，^{1}H MNR 用 Bruker 公司的 FT-AC 200 M 核磁共振仪测定，质谱用 HP-5988 型质谱仪测定，熔点在 kofler 熔点仪上测定，温度计未校正。所用试剂均为国产市售分析纯。

原料的制备与化合物的合成

1. 3-溴-1,3,4,5-四氢-2-氧代苯并氮杂卓的制备[15]

在氮气氛下，. -1,3,4,5-四氢萘酮（**1**）80 g（0.55 mol）溶解在 660 ml 甲醇中，室温搅拌，一小时内向其中缓慢滴加 87.6 g（0.55 mol）的 Br_2。所得黄色溶液先加入 99 g（1.42mol）盐酸羟胺，然后再加入 90 ml 水使其分解，所得黄色悬浮液在室温下搅拌 3 天，然后再加入 400 ml 水继续搅拌 3 天，把混合物冷却至 5 °C，过滤，水洗，真空下 40 °C 干燥，得黄色固体（**2**）112 g，产率 85%。

在氮气氛下将化合物（**2**）72 g (0.3 mol)分批加入到 360 g 80 °C 的 PPA 中，混合物在 80 °C 搅拌 18 小时，然后加入 700 ml 水稀释，所得产物的悬浮液过滤，水洗，再用 5% $NaHCO_3$ 溶液洗，乙醇重结晶得浅灰色片状晶体 64 g，产率 88%，熔点 164-166 °C（文献值[9]：163-165 °C）。

2. 3-巯基-5-芳基-1,2,4-三唑、2-巯基-5-芳基-1,3,4-噁二唑、2-巯基-5-芳基-1,3,4-噻二唑衍生物的合成见第二部分。

3. 3-杂环硫基-1,3,4,5-四氢-2-氧代苯并氮杂卓衍生物的合成

a. 合成通法（以 2-苯基-5-巯基-1,3,4-噁二唑为例）：

取 2-苯基-5-巯基-1,3,4-噁二唑 0.89 g (5 mmol)，加入到溶有 0.28 g (5 mmol) KOH 的 20 ml 无水乙醇溶液中，搅拌回流数分钟，待溶液完全澄清后，将 1.2 g (5 mmol)的 3-溴-1,3,4,5-四氢-2-氧代苯并氮杂卓(**3**)溶于 20 ml 无水乙醇并将其滴入上述反应瓶中。搅拌回流 2 小时，溶液中析出白色固的 KBr 固体。待反应完全后，趁热滤去不溶的 KBr 固体，滤液冷却至室温析出大量白色固体。抽滤，滤液浓缩还可得一部分产品。

b. 少数化合物在 KOH-乙醇溶液中溶解性不好，可用 DMF 作溶剂。方法如下（以 2-(4-氯苯基)-5-巯基-1,3,4-噁二唑为例）：

取 2-(4-氯苯基)-5-巯基-1,3,4-噁二唑 1.063 克(5 mmol)溶于 10 ml DMF 中，将 0.28 g (5 mmol) KOH 溶解在 10 ml 水中，并加入到上述 DMF 溶液中，搅拌回流数分钟。称取 3-溴-1,3,4,5-四氢-2-氧代苯并氮杂卓(**3**) 1.2 g (5 mmol)溶解在 10 ml DMF 中，加入到上述溶液中，搅拌回流 4 小时。反应完毕后，减压蒸除部分 DMF，将剩余物倒入 200 ml 水中，析出大量白色固体，抽滤，水洗，干燥，用 DMF 和水重结晶。

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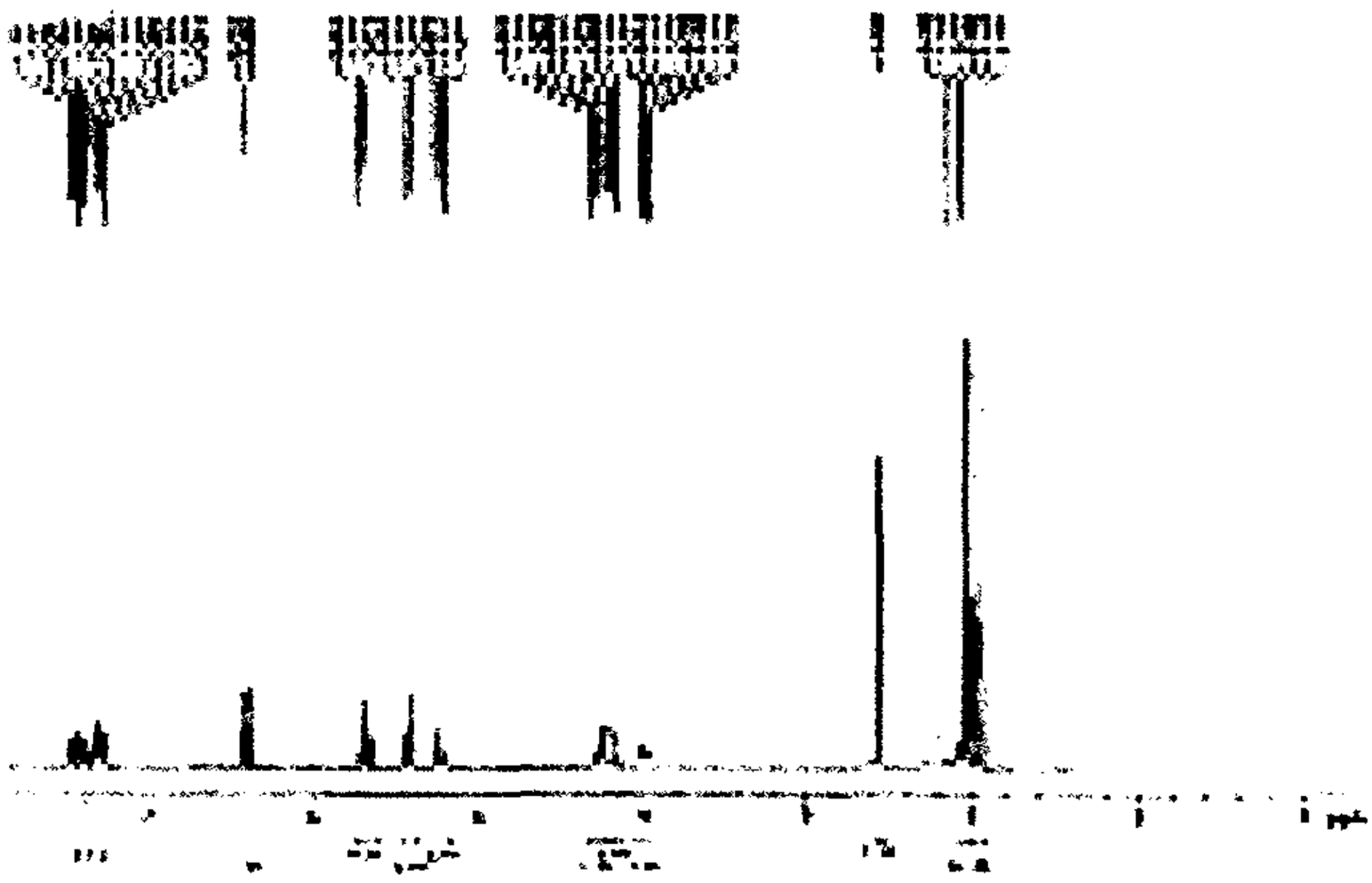
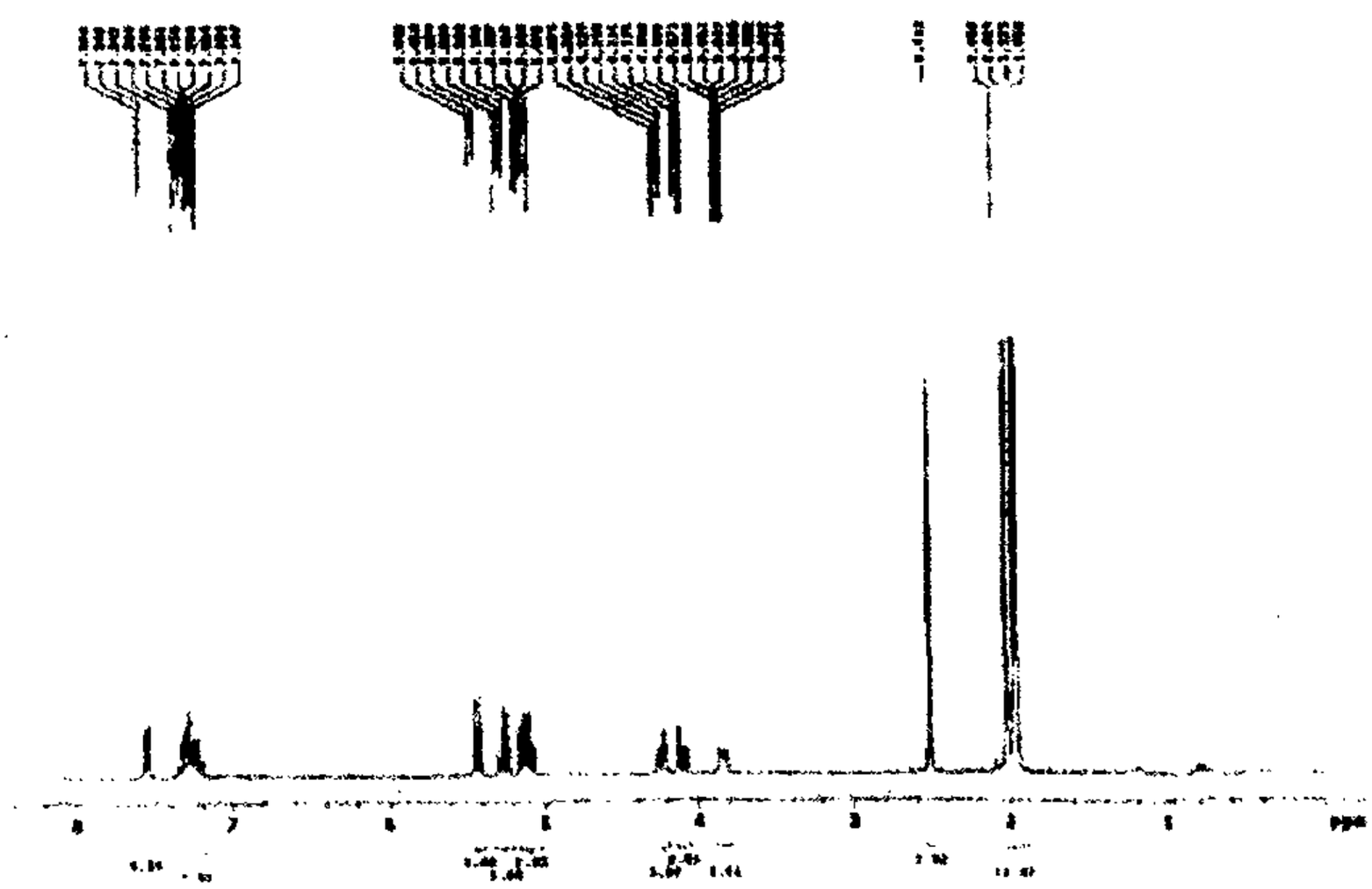
附录

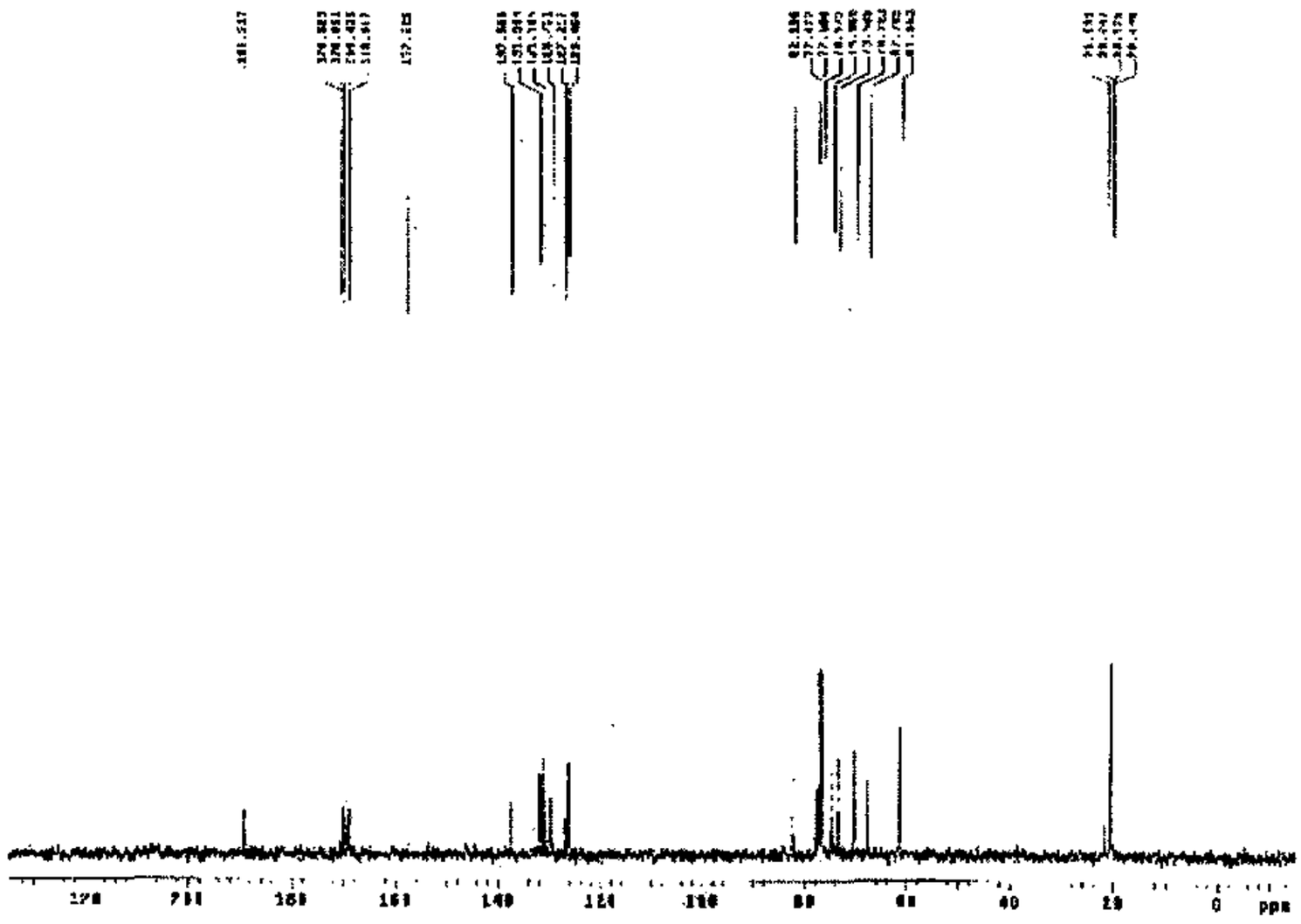
第二部分化合物 **5a-28** 的 ^{1}H NMR



第二部分化合物 **5b-28** 的 ^{1}H NMR



第二部分化合物 **5a-28** 的 ^{13}C NMR



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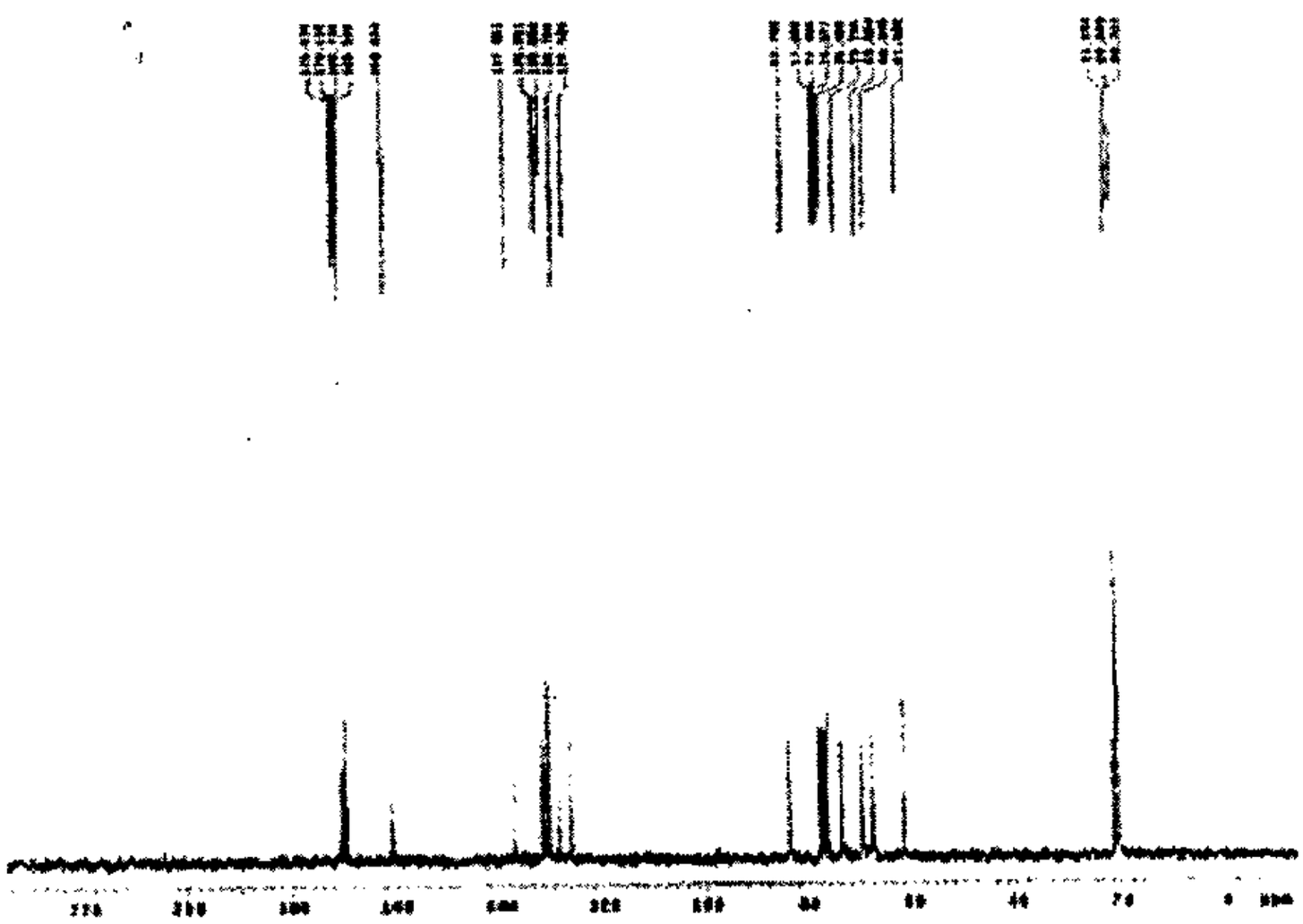
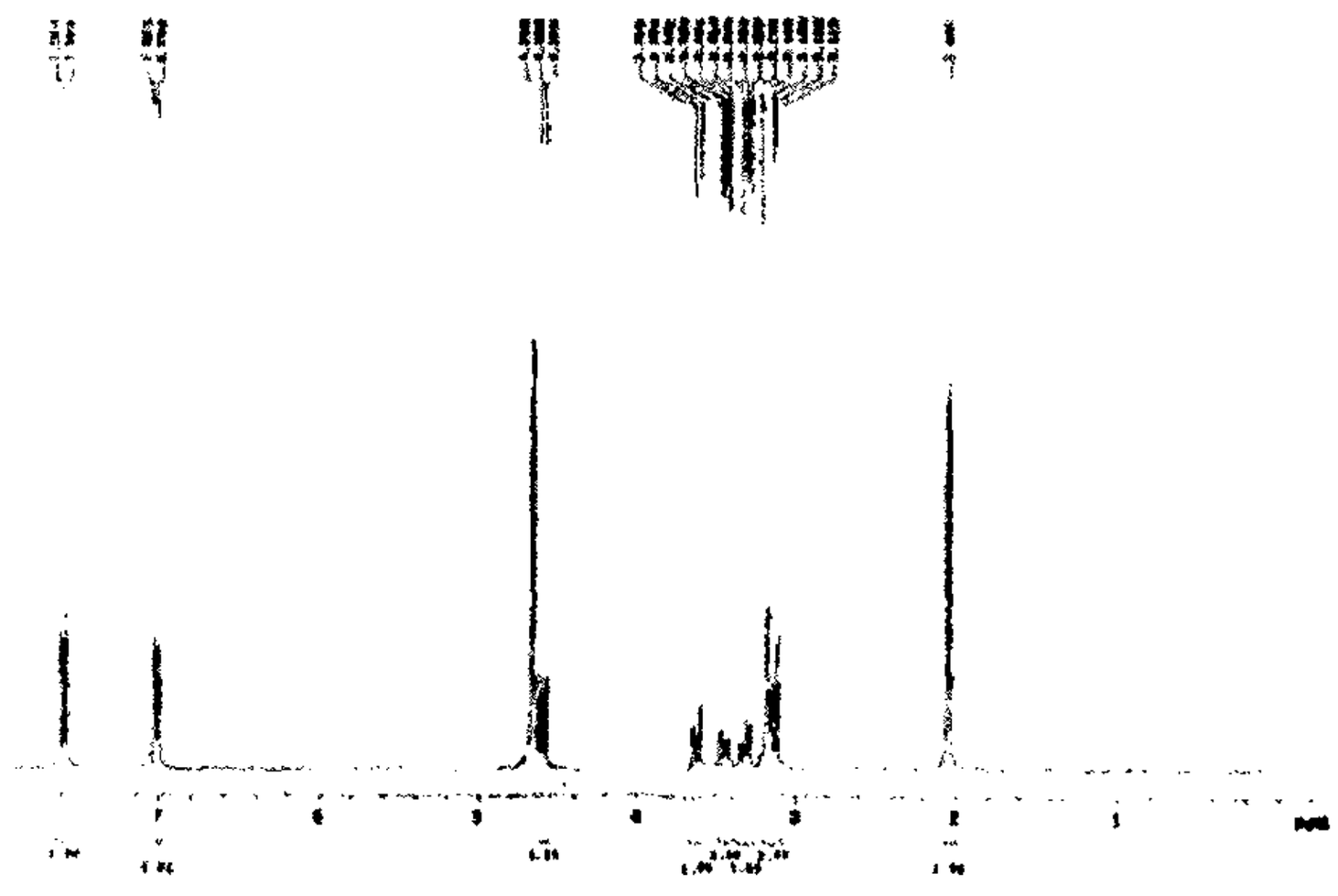
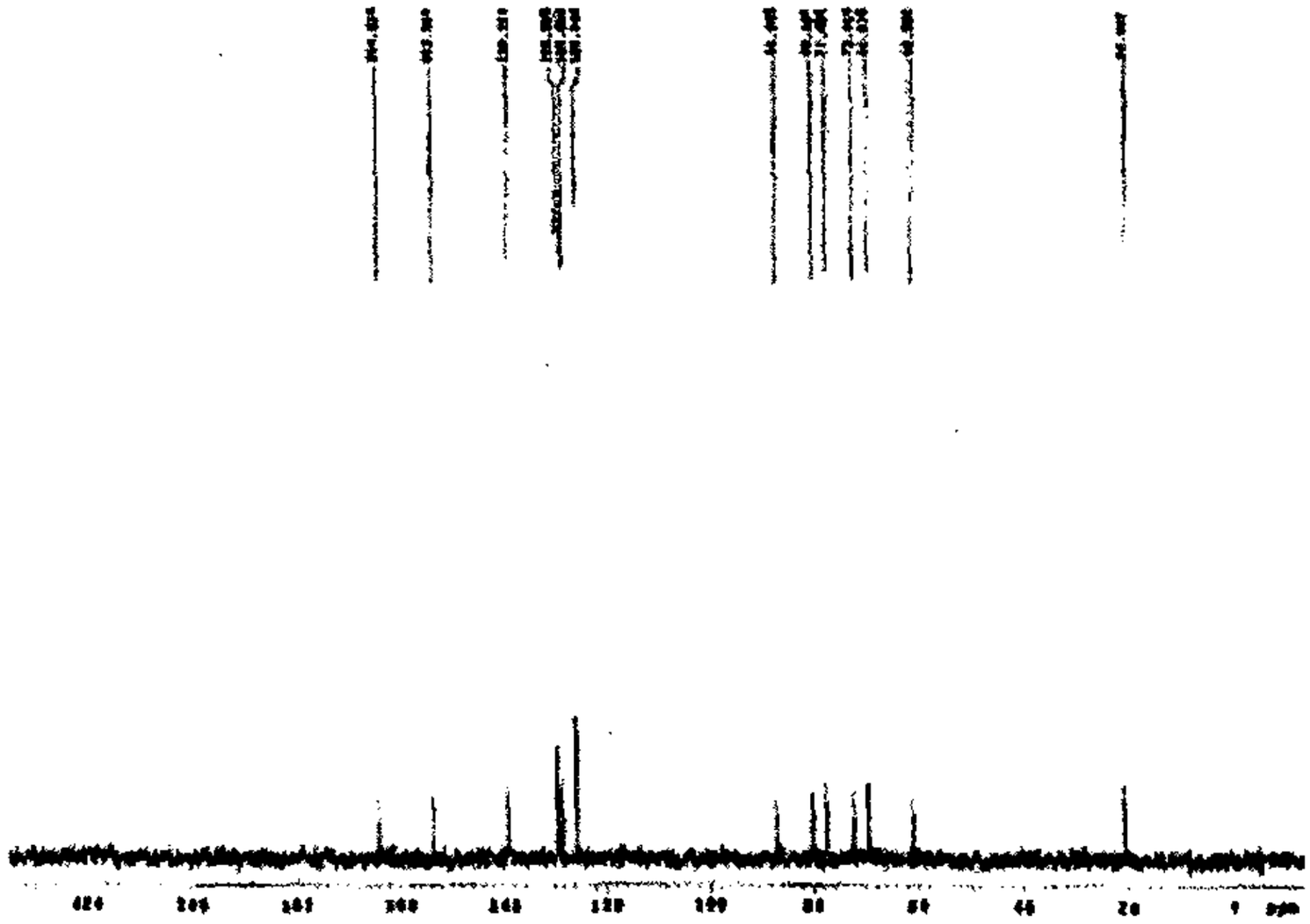


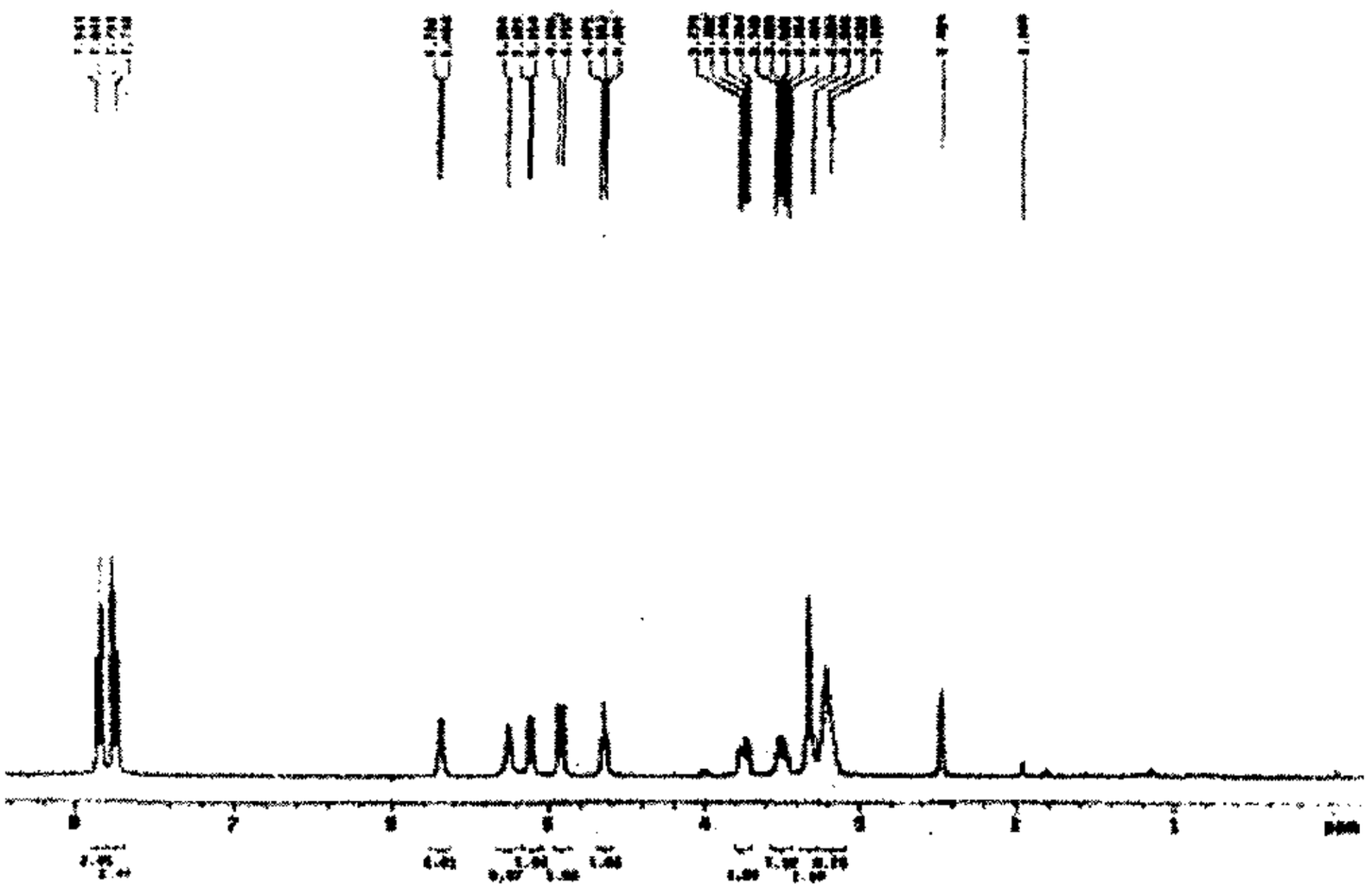
第二部分化合物 6-3 的 ^{1}H NMR



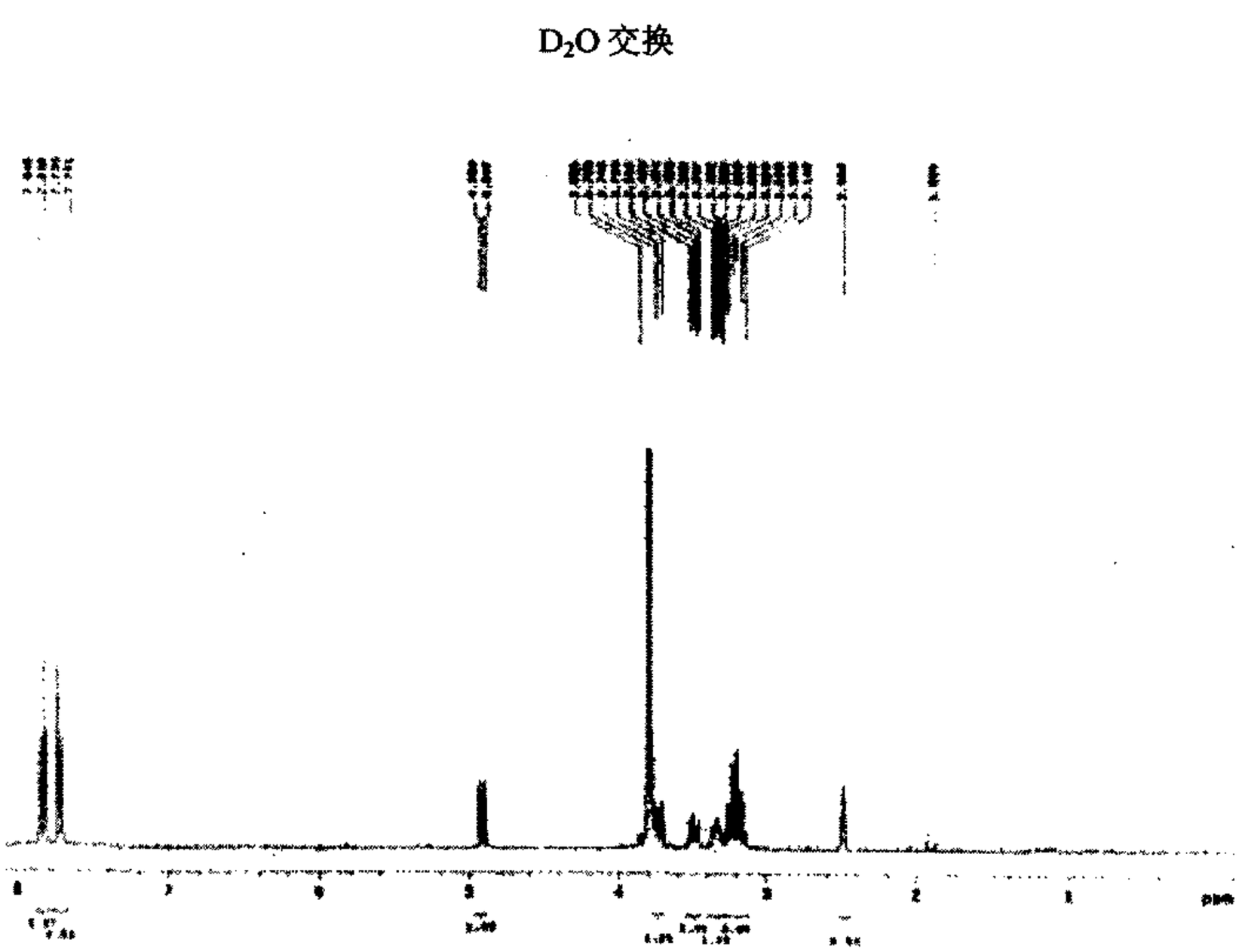
第二部分化合物 6-3 的 ^{13}C NMR



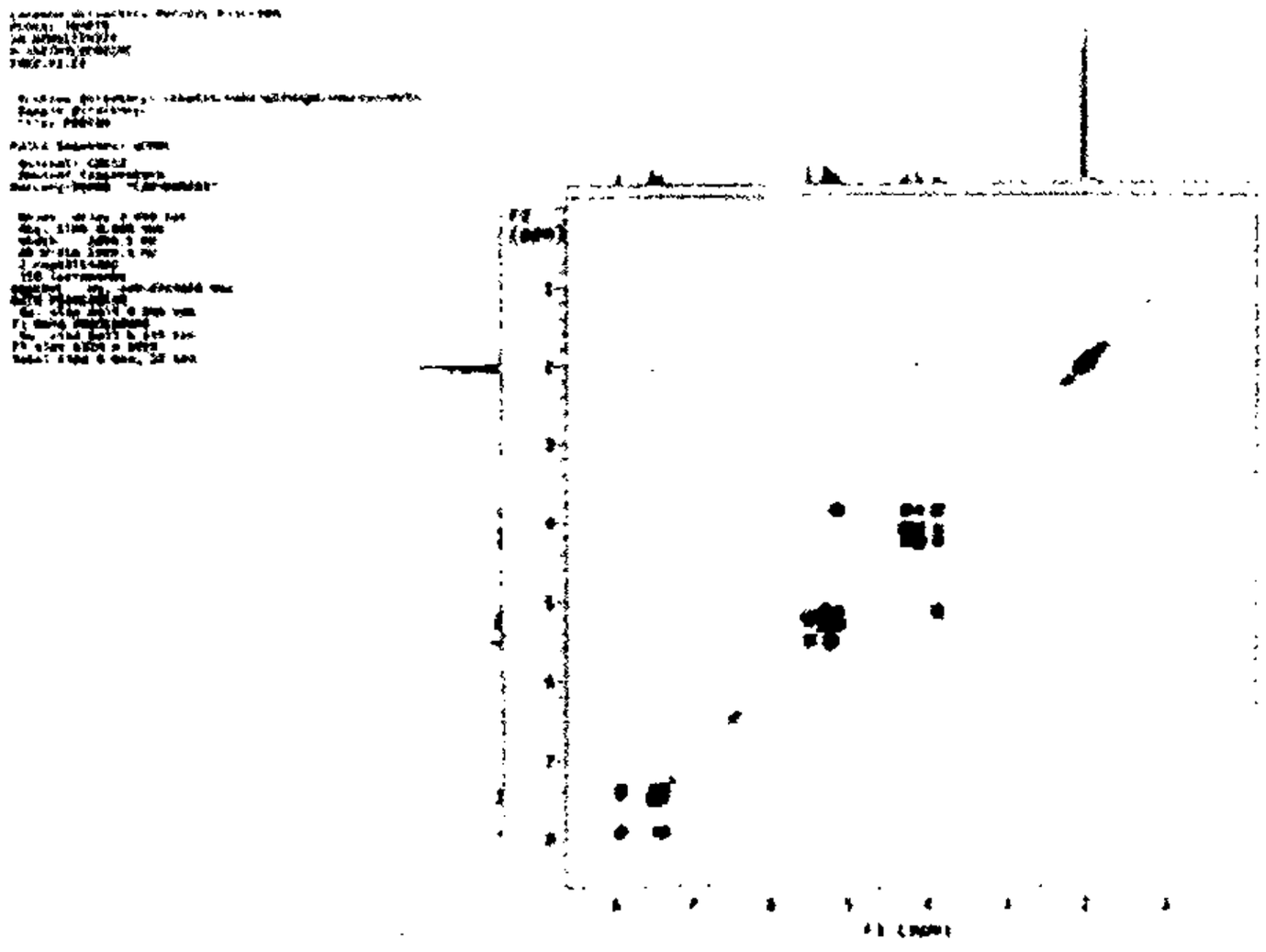
第二部分化合物 **6-19** 的 ^{1}H NMR



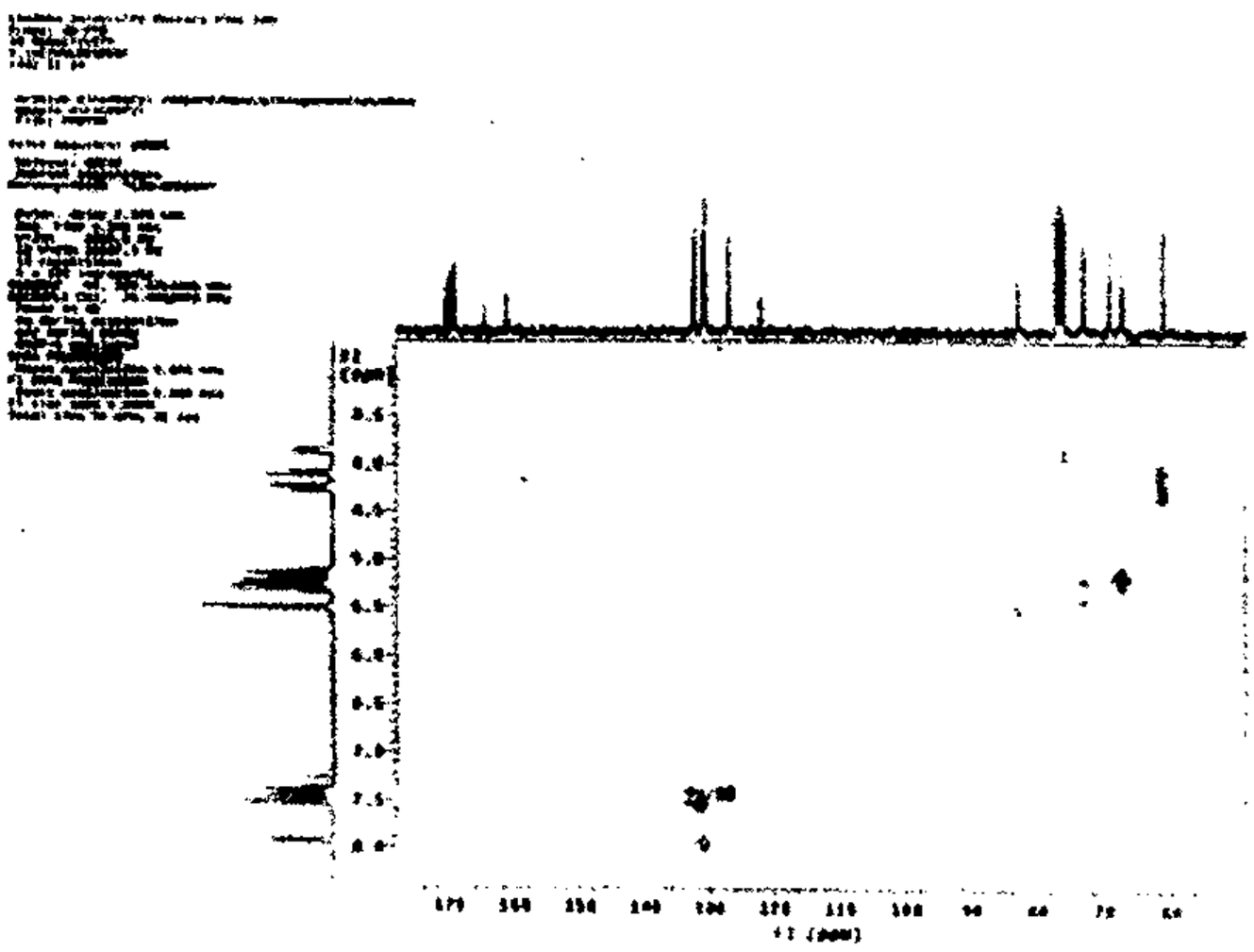
D_2O 交换



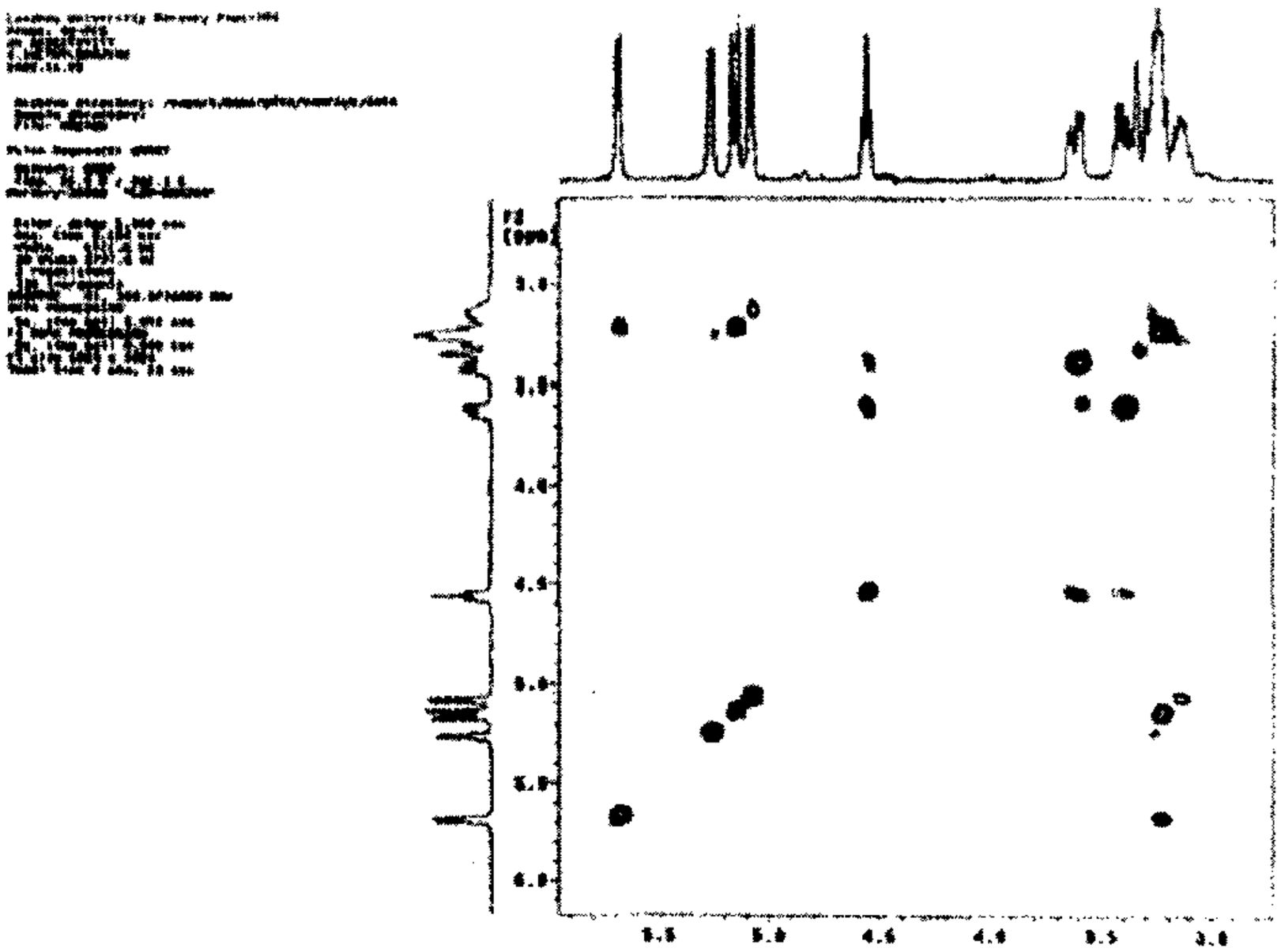
第二部分化合物 **5b-17** 的 H-H COSY



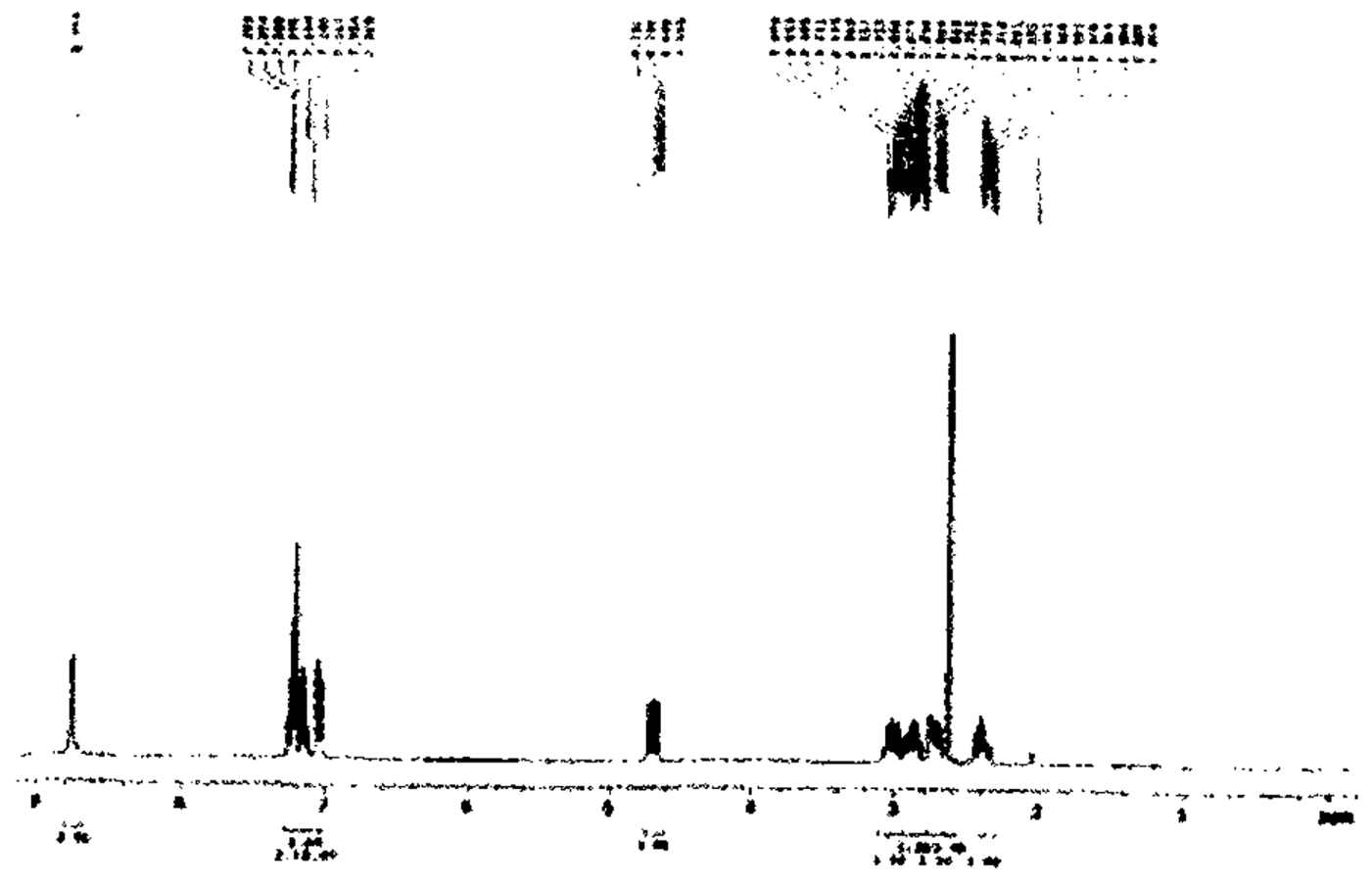
第二部分化合物 **5b-17** 的 HMBC



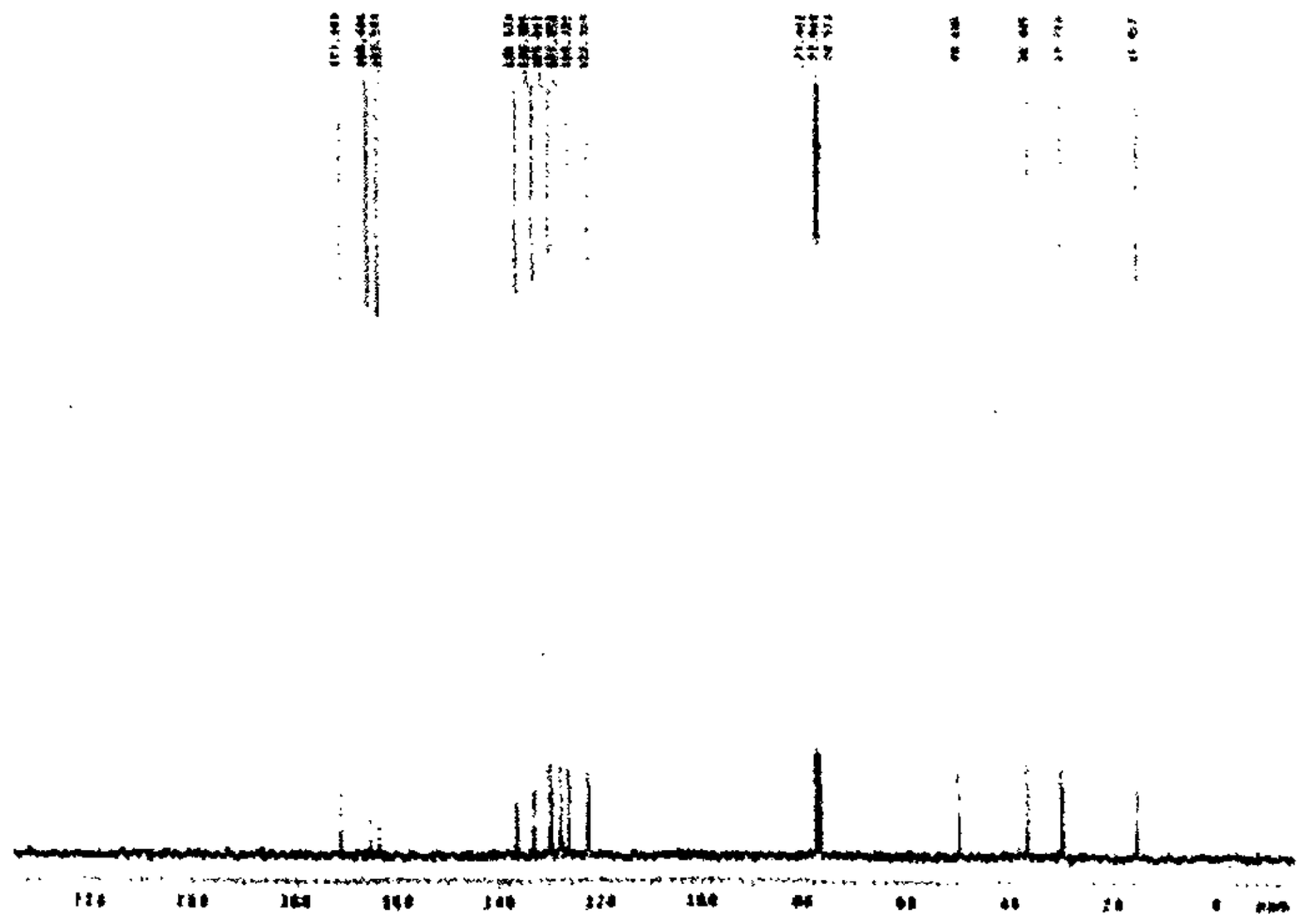
第二部分化合物 **6-15** 的 H-H COSY



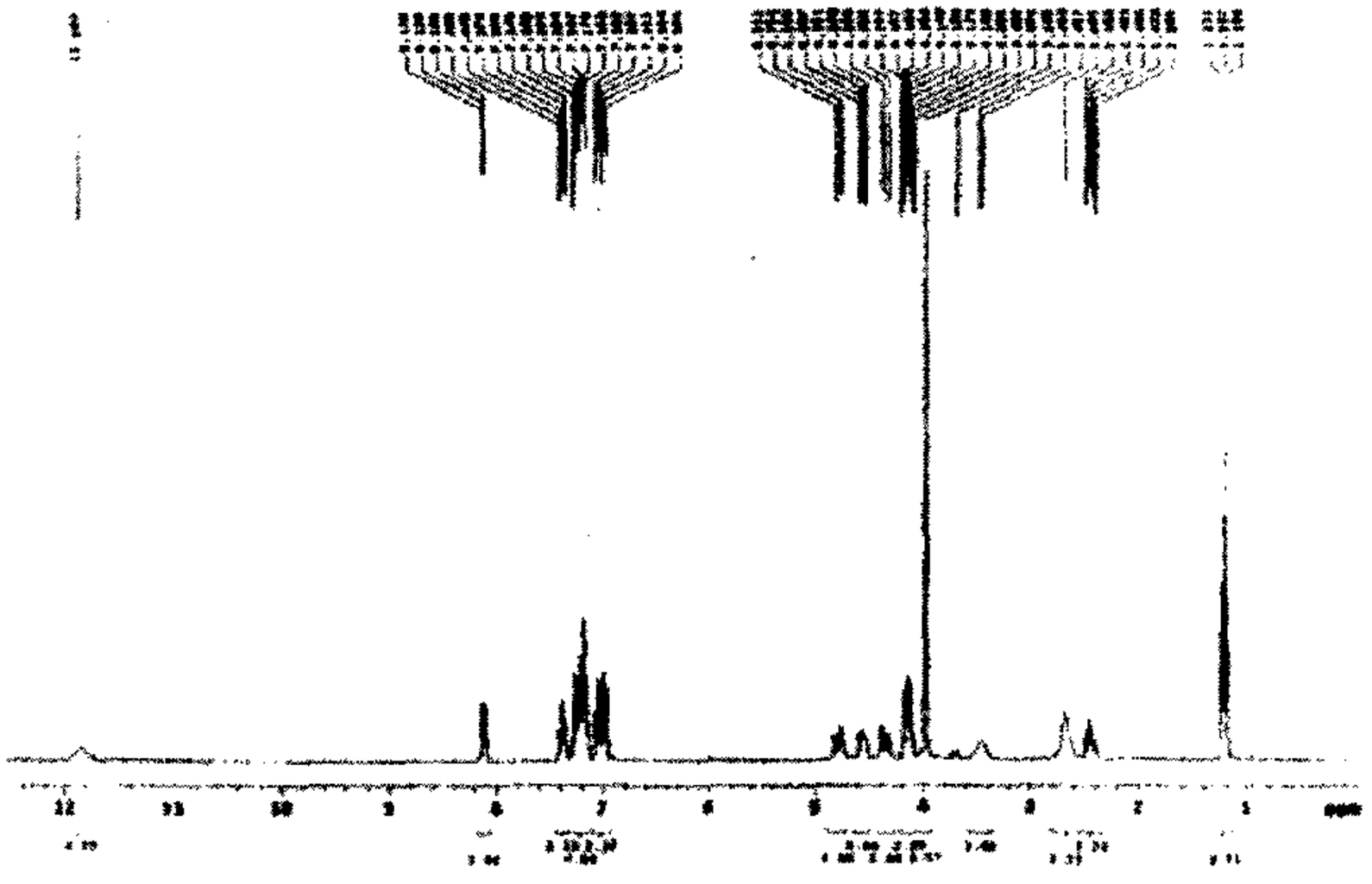
第三部分化合物 **5-48** 的 ^{1}H NMR



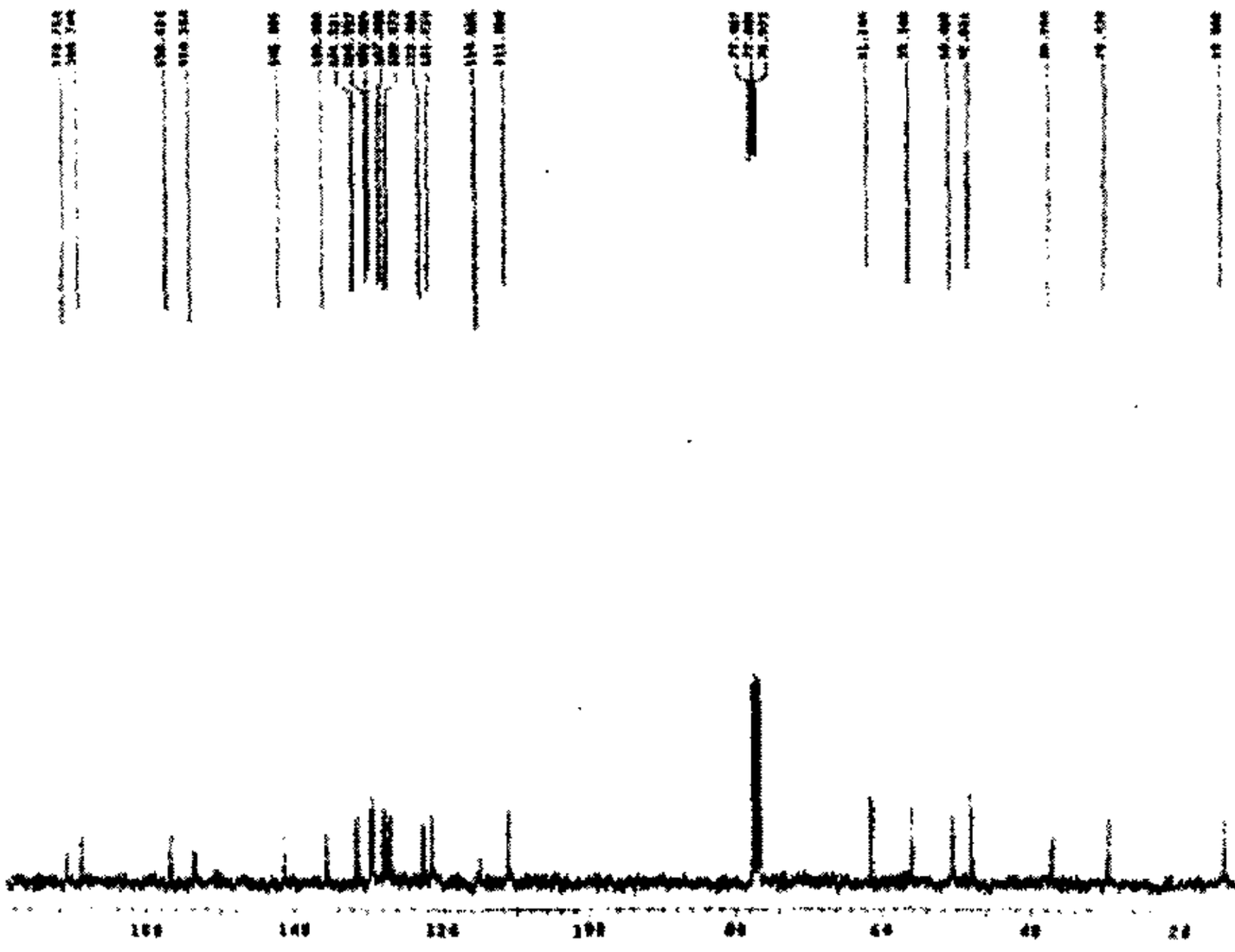
第三部分化合物 **5-48** 的 ^{13}C NMR



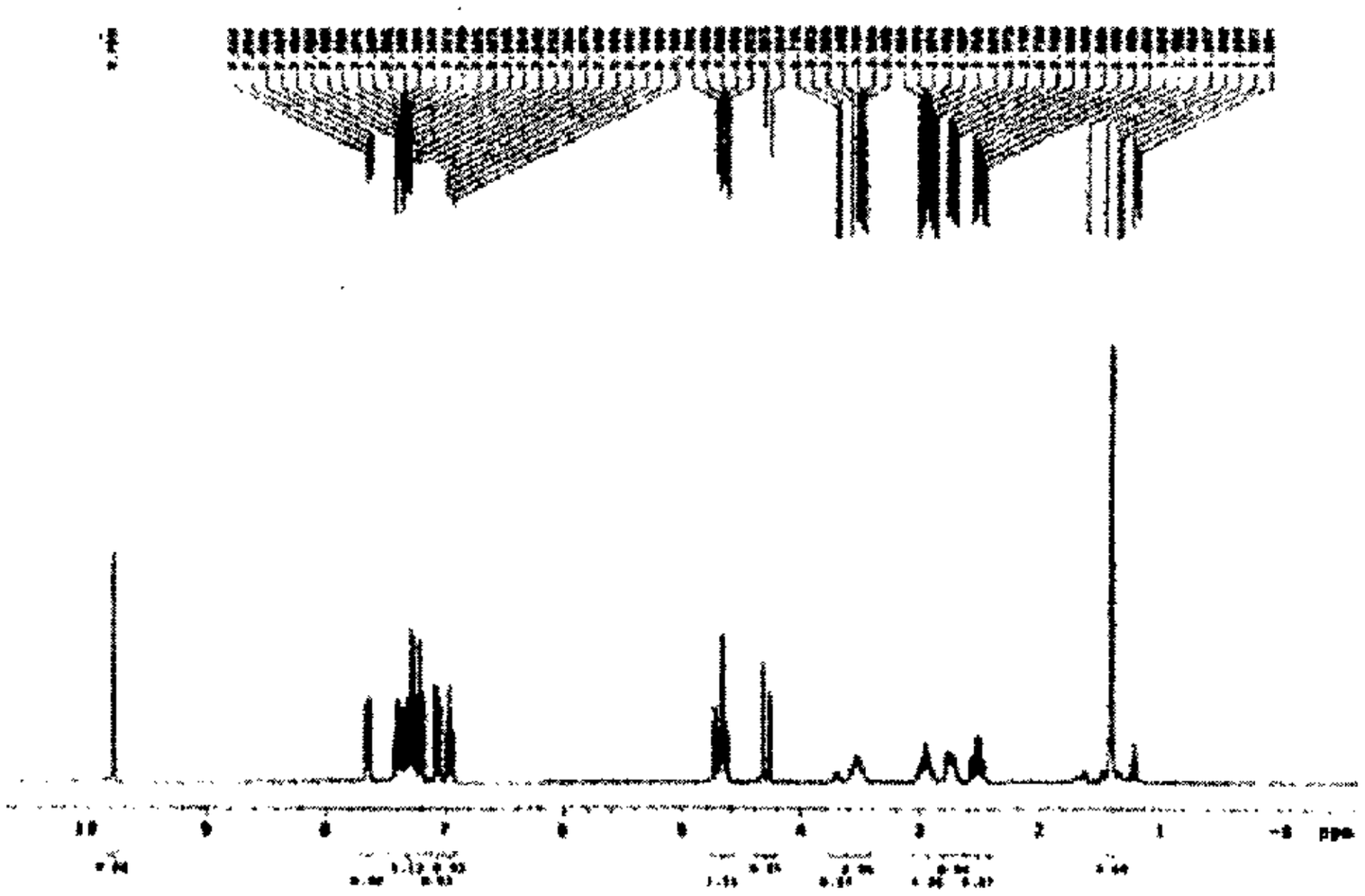
第三部分化合物 **5-40** 的 ^{1}H NMR



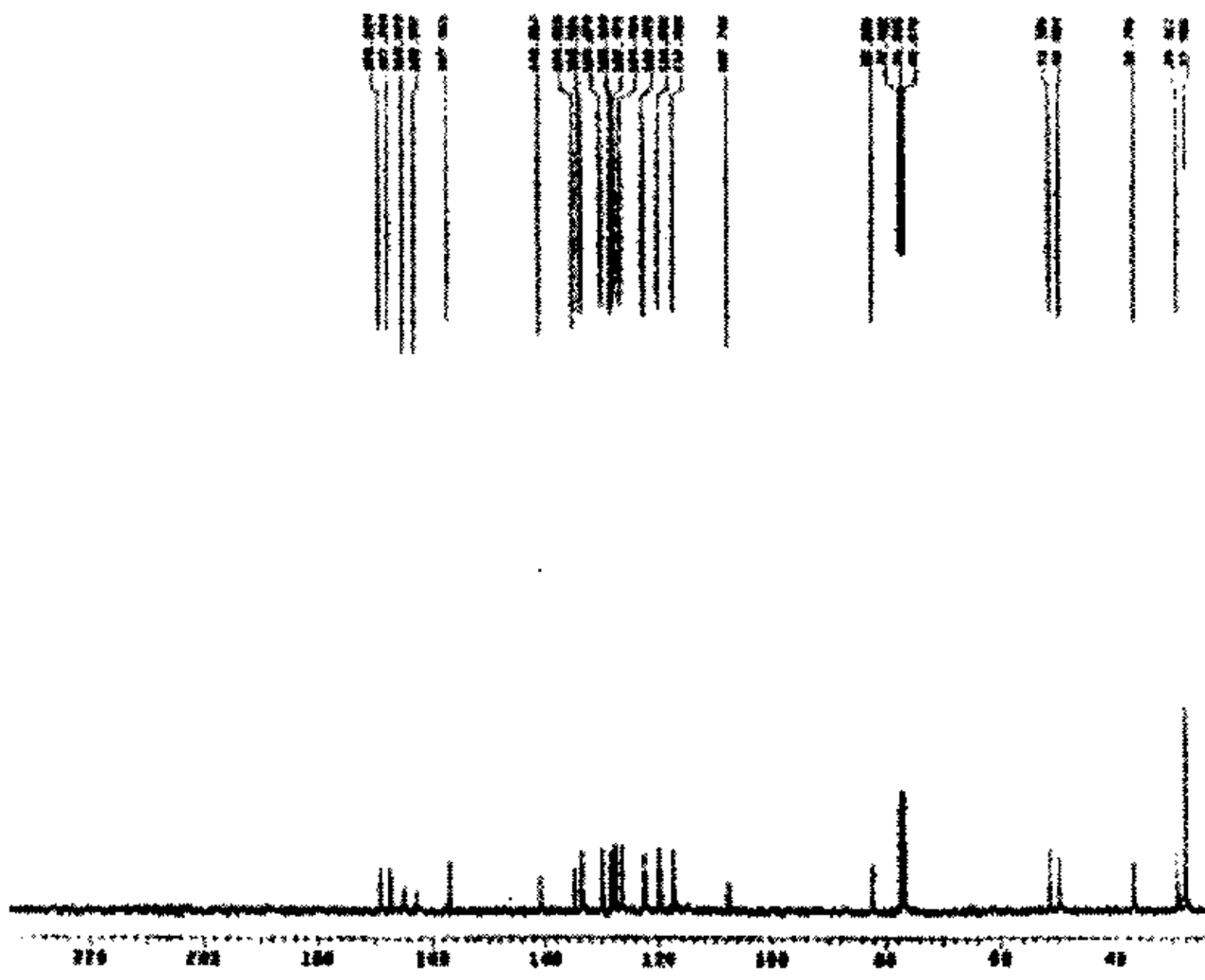
第三部分化合物 **5-40** 的 ^{13}C NMR



第三部分化合物 **5-20** 的 ^{1}H NMR



第三部分化合物 **5-20** 的 ^{13}C NMR



硕士期间发表论文

1. **Zao-Zao Qiu**, Chao-Feng Dai, Shu-Jun Chao, Peng-Fei Xu and Zi-Yi Zhang. A New Route to Synthesis of 3,6-Diaryl-1,2,4-triazolo[3,4-*b*]1,3,4-oxadiazoles. *J. Chin. Chem. Soc.*, **2004**, *51*, 1343-1346.

2. **Z. Z. Qiu** and P. F. Xu. 5-Phenyl-1,3,4-dioxazol-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-glucopyranoside. *Acta Cryst.* **2004**, *E(60)*, o1365-o1366.

3. **Z. Z. Qiu** and P. F. Xu 2,3,4,6-Tetra-O-Acetyl-5'-Phenyl-1',3',4'-Thiadiazole-2'-yl-1-Thio-β-D-Glucopyranoside. *Acta Cryst. C.* **2005**, *In Print*.

4. Shu-Jun Chao, Xin-Ping Hui, Shuo Li, **Zao-Zao Qiu**, Peng-Fei Xu, Zi-Yi Zhang, Qin Wang. Synthesis and Antibacterial Activities of Novel Biphenyltetrazole Derivatives Bearing 1,3,4-Oxadiazole.

5. **Zao-Zao Qiu**, Chao-Feng Dai, Shu-Jun Chao, Xin-Ping Hui and Peng-Fei Xu. A New Route to Synthesis of 3,6-Diaryl-1,2,4-triazolo[3,4-*b*]1,3,4-oxadiazoles. *Chin. J. Org. Chem.* **2004**, *24(Suppl)*, 174.

6. 邱早早，晁淑军，惠新平，许鹏飞，郑荣梁. 3-杂环基硫取代-1, 3, 4, 5-四氢-2-氧代-苯并氮杂卓衍生物的合成。*有机化学* 2004，*24(增刊)*, 175。

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邱早早

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