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Ministry of Higher Education

And Scientific Research

Thi-Qar University

Collage of Science

Synthesis, characterization and Antioxidant Study of some new Dihydropyrimidine-2-(1H)-ones /thion derivative

A thesis

Submitted to the council of the collage of science/Thi-Qar university , in partial fulfillment of the requirements for the degree of master in Chemistry

By

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B.Sc. Chemistry /2011

Supervised by

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2018 A.D 1439.H

بسم الله الرحمن الرحيم

وأن ليس للإنسان إلا ما سعى

وأن سعيه سوف يرى

النجم (39-40)

صدق الله العلي العظيم

Ministry of Higher Education
& Scientific Research
University of Thi-Qar
College of Science
Unit Of Higher Studies

وزارة التعليم العالي و البحث العلمي
جامعة ذي قـــار ـــ كلية العلـــوم
مكتب معاون العميد للشؤون العلمية
والدراسات العليا

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التاريخ : ١٨ / ٦ / ٢٠١٨

الى / رئاسة قسم الكيمياء

م/ استلال الكتروني

تحية طيبة .....

اشارة طلبكم في تاريخ (2018/6/12) نحيل اليكم تقرير الاستلال قبل المقوم العلمي لرسالة طالبة الماجستير (نور ريسان علي)الموسومة بـــــ:

Synthesis, characterization and biological activity of some new) (compounds of Monastrol(3,4- dihydropyrimidine-2-(1H)-ones /thions)

والذي بلغت نسبته (12%) فقط.

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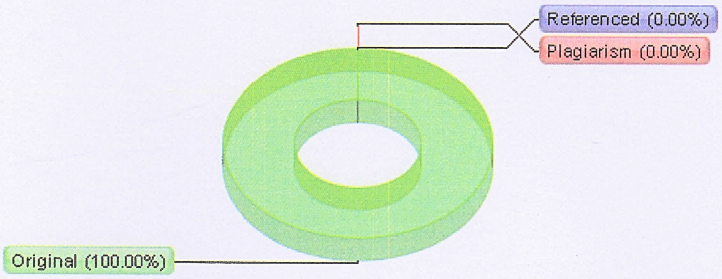
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3.General
Results and Discussion :The physical properties of the synthesis derivatives which included3,4-Dihydropopyrimidine -2(1H)- ones/thioljnes as shown in Tables(3-1)-(3-4) showed that all the projgducts. The structures of the newly synthesized derivatives are assigned on the basis of their FT- IR , 1H- NMR , 13C - NMR, 13C- NMR DEPT and mass spectra.3.1: 3,4-Dihydropyrimidine -2(1H)-ones/thio
nes compound :3,4-Dihydropy
.rimidine -2(1H)-ones/thioones 2(a-j) are Syntheusis by the reacgrtion of a selehfcted aldehkiyde or kethfone and urofea or thiourea with ethylacfsetoacetate in the prepusence of Ferrice chloride and some droops from HCl as acatalyst and ethhjganoal as a solvent . shown in table (3-1) .Scheme(3-1)
The suggestion mechanism
using Thiourea78Scheme(3-2)
The suggestion mechanism using Urea79Scheme (3-
3)Table(3-1):

جامعة زي قار
كلية العلوم

استمارة تعهد الالتزام بأخلاقيات البحث العلمي

وزارة التعليم العالي والبحث العلمي

نتعهد بالتقيد التام بما جاء في مضمون كتاب وزارة التعليم العالي والبحث العلمي/جهاز الاشراف والتقويم المرقم ج ت/425 الصادر بتاريخ 2014/3/24، والمبلغ الينا بكتاب رئاسة جامعة ذي قار/قسم البحث والتطوير المرقم 4704/54/7 والصادر بتاريخ 2014/3/31، عند اعداد الرسالة أو الاطروحة الموسومة:

Synthess, Characterization and biological activity of some new compounds of Monastrol (3,4-dihydropyrimidine-2-(1H)-ones/thions)

وبخلافه نتحمل نحن الموقعون أدناه المسؤولية القانونية حال وجود ما يخالف مضمون الكتاب أعلاه أو ما ينافي أخلاقيات البحث العلمي.

	الاسم	القسم والكلية أو المعهد	التوقيع	التاريخ
1- المشرف الاول:	د. محمود شاكر	كلية الكيمياء/العلوم		١٨/١٠/٢٠١٦
2- المشرف الثاني:				...../...../.....
3- طالب الدراسات:	نور ريان علي	الكيمياء/العلوم		١٨/١٠/٢٠١٦

ملاحظات هامة:

1- تعتبر استمارة التعهد هذه جزء من متطلبات اعتماد مشاريع كلية الدراسات العليا وتوزيع المشرفين على الطلبة.
2- تطبق استمارة التعهد هذه على السادة المشرفين على الرسالة أو الاطروحة وعلى طلبة الماجستير والدكتوراه.
3- السطو العلمي هو سرقة نتاج فكري، وعند الاقتباس ضرورة الاشارة للمصدر، وفي حالات الاقتباس ضرورة إعادة صياغة الفقرة المقتبسة دون الخروج من محدود فكرة الفقرة الاصلية المقتبسة والمشار لمصدرها في متن الرسالة أو الاطروحة.
4- تشمل استمارة التعهد هذه الرسائل والاطاريح التي لم تنجز حتى تاريخ كتاب جهاز الاشراف والتقويم أدناه.
5- اعدت استمارة التعهد هذه استنادا للفقرة-4 من كتاب وزارة التعليم العالي والبحث العلمي/جهاز الاشراف والتقويم المرقم ج ت/425 الصادر بتاريخ 2014/3/24 والمبلغ الينا عن طريق كتاب رئاسة جامعة ذي قار/قسم البحث والتطوير المرقم 4704/54/7 بتاريخ 2014/3/31.

وزارة التعليم العالي والبحث العلمي

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جامعة ذي قار

كلية العلوم

ملاحظـــــــات

وزارة التعليم العالي والبحث العلمي

حول الحد من ظاهرة انتهاك حقوق الملكية الفكرية

تعد السرقة العلمية سرقة فكرية وانتهاك لحقوق الملكية الفكرية للآخرين، لذا يجب أن تتضافر الجهود مع الجهات المعنية لإيجاد الحلول لوضع آلية تضمن الحد من ظهورها في كلياتنا والحد من وجودها وانتشارها، وذلك من خلال ما يلي:

1- على جميع الباحثين وطلاب الدراسات العليا التحلي بأخلاقيات البحث العلمي، وعدم نقل النصوص عن البحوث والاطاريح والتحلي الدائم بالامانة العلمية.
2- على الباحثين وطلاب الدراسات العليا والتدريسيين التحلي بالوعي الكافي بالاضرار الناتجة من اقتباس أو استغلال معلومات عن بحث منشور أو أطروحة دون الاشارة اليها كمصدر.
3- التزام الباحثين وطلاب الدراسات العليا والتدريسيين بثقافة الرصانة العلمية ورفض أي حالة منافية لأخلاقيات البحث العلمي، متجنبين بذلك أي السرقات العلمية والاقتباس العلمي والحد منها.
4- السرقة العلمية عواقبها وخيمة على الباحثين والمؤسسات العلمية على حد سواء، وعليه تم الشروع بوضع ضوابط رادعة تحذر من عواقب السرقة العلمية.
5- تم استخدام برمجيات حديثة للكشف عن حالات الاقتباس الجزئي والكلي من بحوث وأطاريح منشورة سابقا، بحيث تؤشر السرقات العلمية بألوان ومؤشرات واضحة.
6- تم وضع استمارة تعهد يوقع عليها الباحث والمشرف على الأطروحة تتضمن التعهد بعدم الاقتباس والاعتماد عن أي سرقة علمية أو اقتباس فيه تشبه السرقة العلمية، ويتحملان المسؤولية القانونية في حالة وجود سرقة علمية.
7- على الباحثين التمييز بين الاقتباس العلمي السليم والسطو العلمي والسطو العلمي هو سرقة نتاج فكري، بينما الاقتباس العلمي السليم هو نقل الفكرة أو النص مع الاشارة الى المصدر (اسم الكاتب والكتاب أو البحث).
8- الاهتمام بالبحوث المتوافقة مع الاختصاص الدقيق للباحث، حيث تم حصر بحوث الترقيات من الخمس سنوات الأخيرة في مجال الاختصاص التي يسهل الكشف عليها ومتابعتها بواسطة اللجان المختصة، واستخدام برامج عالمية خاصة على الحاسوب تقوم بعملية مسح للنص لتمييز ما يحتويه أو ترتيب مكتبة الكلية والجامعة والجامعات الأخرى للوقوف على احتمالية وجود مطابقة ما لأي بحث مع أي نشاط موجود على الانترنت.
9- يشترط أن لا تتجاوز نسبة الاستلال البحثي المتفق عليه بين الكليات العلمية 15%.
10- أتمتة المكتبات المركزية في الكليات والجامعات العراقية وربطها بالمكتبة الافتراضية، من شأنه توفير مساعدة كبيرة في معرفة [illegible] النشر الداخلي من بحوث ودراسات علمية بالشكل الذي يمكنهم ويساعدهم على كتابة وتقديم البحوث العلمية.
11- سيتم نشر أسماء المخالفين والمتحايلين على الجامعات العراقية والعلمية، لتعكس المؤثرات الادارية والعلمية لردعهم عن هذا السلوك المنافي لأخلاقيات البحث العلمي [illegible] في المستقبل القريب خطوط أي تلك من التعليمي والمؤلفين بهذا الصدد.
12- تم نشر الرسائل والاطاريح الكترونيا من خلال الكشافات السنوية بين الجامعات مع وضع الموافقات الاصولية من قبل الجامعات والباحثين.
13- وضعت آليات لمراقبة ومتابعة المكاتب التي تعمل على بيع الرسائل دون الموافقات الاصولية [illegible] نشرت أكثر عدد من البحوث حفاظا على ديمومة اصدارها دون تناقل.
14- تأسيس أعداد المجلات العلمية الصادرة في الجامعات والأوساط العلمية، وذلك لصدور العديد من المجلات الضعيفة التي نشرت البحوث المقدمة للنشر.
15- تشكيل وتدريب بالعمل لجنة مركزية تتولى متابعة الرسائل والاطاريح والبحوث العلمية والتأكد من عدم سرقتها بأي شكل من الأشكال، تضم هذه اللجنة من بين أعضائها من يجيد اللغة الانجليزية، ومن ثم عرض البحث أو الدراسة التي يحتمل سرقتها على خبراء عراقيين للتأكد والمقارنة ومعرفة الأصل إذا كانت الدراسة مترجمة أو من نتاج الباحث.
16- جمع الأبحاث العلمية التي يتداولها كل مجال علمي على حدة في داخل الكلية والجامعة وعمل أرشيف الكتروني خاص بها، وفي حالة تقدم باحث لأحد موضوعات البحث يتم فحص الأبحاث الموجودة والتعرف اذا كان البحث قد تم تقديمه من قبل أم لا، ويكون هذا الجهد تراكميا ويتم بصورة دورية.
17- استخدام برامج متخصصة على الحاسوب تقوم بعمل مسح للانترنت وعملية مطابقة لأي بحث مع أي نشاط موجود على الانترنت مثلا يوجد برنامج على الانترنت عنوانه (Copy escape) يساعد في اكتشاف المقالات المسروقة وهي خدمة مجانية [illegible] معرفة البحث من السرقة ونشره على الانترنت.
18- يوضح عضو هيئة التدريس للطالب عند قبوله بالمعهد أن المكاتب التي تقوم بتجهيز هذه البحوث لحساب الطالب ويحرص بعض الطلاب على [illegible] مع الطالب نقاط القوة والضعف فيها، حتى يدرك الطالب أن المدرس على علم بما هو موجود وينتج أن معظم هذه البحوث لا ترقى الى المستوى المطلوب، ومن أكثر أسباب اللجوء للسرقة العلمية قصر الوقت وتأجيل انجاز العمل الى أن يحل الموعد النهائي لتسليم البحث أو المسودة للبحث المطلوب.
19- تشكيل فريق عمل لاعداد (وثيقة الاخلاقيات البحث العلمي) من خلال الاطلاع على مجموعة من المواثيق الصادرة عن جامعات أخرى (عراقية عربية أجنبية) للاستفادة مما جاء فيها يتم نشرها وتوزيعها على الباحثين [illegible] والتركيز على المحاور الاساسية والوازع الديني [illegible] وأن تكون الموافقة على الشروع بالبحث وليس بعده.
20- مراعاة أخذ البصمات في عملية التسجيل الرقمي (التقاط الصور وتسجيل صوتي أو مرئي) لاثبات المسؤولية من البحوث، قانون الخدمة الجامعية، قانون انضباط موظفي الدولة، قانون حماية حق المؤلف).
21- وضع آليات لمتابعة ومراقبة أخلاقيات البحث العلمي وتفعيل التشكيلات الخاصة بالسرقات العلمية ومعاقبة المخالفين وفق القوانين المعمول بها في العراق (قانون الخدمة الجامعية، قانون انضباط موظفي الدولة، قانون حماية حق المؤلف).
22- أن الهيئات الاكاديمية المختصة يتكرس أن تقوم بسد هذه الظاهرة بعقوبات صارمة وفصلهم منها نهائيا سواء عبر التوقيف عن العمل أو الدراسة، أو المنع من النشر أو المشاركة في المؤتمرات أو منع مناقشة الرسائل والاطروحات المعنية بهذه الممارسات.
23- دعم قيمة الاجتهاد والحث عليه، كمدخل أساسي يدعم لتحسين القيم المثالية لدى طلاب العلم، وشرح خطورة الغش في الامتحانات والتي يعتبر إعداد البحوث الخاطئة وغيرها جزءا منها.
24- العمل التشاركي بانشاء اجراءات تأديبية تمنع الحد من مزاولة مهنة البحث والتعليم بشكل نهائي أو لفترات محددة أو الحرمان من المشاركة في الندوات والفعاليات في المؤسسات العلمية.
25- شمول السرقات العلمية بقانون التزوير في المحاكم العراقية.
26- السماح لطلبة الدراسات العليا بنشر بحوثهم في المجلات المحكمة بغض النظر عن انتهاء مهلة الصرف [illegible] في حالة الرغبة بذلك ضمن الضوابط.
27- الزام التدريسي بالكتابة باختصاصه الدقيق وليس الملاحقة وراء البحوث من أجل برامج ومسابقة ويمكن أنه تكون البحوث المقدمة للمؤتمرات عنوان واحد والاحالة الى لجنة [illegible].
28- الزام المجلات بطلب تواقيع المشاركين في كل بحث على تعهد يشير الى عائدية ذلك البحث وأنه غير منشور على أن تتأكد المجلة من صحة التواقيع المقدمة لها، والحرص على استخدام الاعتماد المطلوب على [illegible] التأكد من حصول المكتب.
29- تشكيل لجان علمية متخصصة بمعايير السلوك العلمي وأخلاقيات البحث العلمي للنظر في كافة البحوث المقترحة وتقييمها قبل النشر، عند تقديم سرقة الأدبيات من البحوث التي أستند اليها في ترقيته.
30- الدعاية التركيزية العلمية لعضو الهيئة التدريسية بجعله لكل القيمات المالية المترتبة عن ترقيته السابقة غير المستحقة، والتشاور لأي نسبة الاستلال من غيره.
31- تشكيل لجنة الاستلال مركزية تساعد لجان الاستلال العلمية في كل قسم علمي لفحص مدى كفاءة البحوث، ضرورة أن مدققة نسبة لا تؤثر في انجاز البحث وعدم الاستلال في حالة لم تتم الاشارة اليه.
32- زيادة الدرجة المخصصة للاشارة العلمية في تقييم رسائل الماجستير والدكتوراه لتكون مقدمة من منح الدرجة في حال ثبوت السرقة العلمية.
33- التأكيد على ضرورة وجود ملخص للبحث المراد نشره باللغة الانكليزية إذا كان البحث باللغة العربية، وملخص باللغة العربية إذا كان البحث باللغة الانكليزية.
34- التأكيد على المجلات العلمية باحالة التقويم حصرا الى متخصص التخصص في موضوع البحث المطلوب نشره، وكذا بالنسبة لتقويم الاطاريح ورسائل الدراسات العليا.
35- ضرورة أن يلتفت المشرف على الطالب في مطالبة الطالب بالمصادر المستخدمة والاطلاع عليها بين الحين والآخر.
36- ضرورة أن يلتزم المشرف بتزويد لجنة الاستلال المركزية في الكلية بقرص (CD) للرسالة أو الاطروحة الكترونية في القسم المختص ويتم لجنة الاستلال العلمية في الكلية ويتم عرض الرسالة أو الاطروحة على لجان الاستلال بالاشتراك ببرامج متخصصة، ويكون كشف الاستلال قبل ارسال الرسالة أو الاطروحة الى الخبير العلمي (الكشف الأولي) لكشف الاستلال الموجود فيها على غرار الترقيات العلمية وذلك بالاستلال شبه جزئي) لكشف الاستلال الموجود فيها على غرار الترقيات العلمية.
37- ضرورة تحلي المشرف على الطالب على حد سواء بالمعايير والنهي الكافي للالتزام بأخلاقيات البحث العلمي.
38- لا تتم الرسائل العلمية والبحث العلمي بالانتقاد الاحصائي البرنامج الذي يؤكد على أهمية الموضوعات التي يتناولها بالبحث وتطويرها الأفكار الابداعية مع أفكار الباحثين الآخرين.
39- يشمل كتابة الرسائل والاطاريح بتحرير الباحث الخاص به وعدم ادخاله بأساليب الاقتباس غير الشرعي.
40- ضرورة توعية التدريسيين والباحثين بالاسلوب الصحيح للاقتباس ومخاطر الاقتباس غير الشرعي.
41- أن يكون للمكتبة الافتراضية العراقية الاشتراك في مواقع عالمية للبحوث والكتب بحيث تمكن لجان الترقيات من الاطلاع عليها من خلال البحوث المقدمة للترقية للتأكد من صحتها.
42- يجب أن يكون البحث التطبيقي مرفقا بمستمسكات رسمية تثبت العمل التجريبي الذي استند عليها البحث وتكون موثقة بصورة رسمية.
43- ارسال بحوث المجلات العلمية الى محكمين من الاختصاص الدقيق حصرا.
44- السطو العلمي والاقتباس غير السليم يعد اعتداء على ملكية فكرية محمية بموجب قانون حماية حق المؤلف (3 لسنة 1971 بدلالة المادة 49 منه) وهو ما يشكل مخالفة جزائية يعاقب عليها القانون بموجب المادة 476 من قانون العقوبات والتي أستوجب العقاب لمرتكب هذا الفعل الى جانب الغرامة العلمية لاتخاذ العقوبات بحقه.
45- انشاء برامج خاصة لمعرفة أصالة البحوث والكشف عن نسب الاستلال وضمنا البرنامج التدريبي المعد لعمادة الانسان والبيئة من قبل بعض كوادرها من لجان الترقيات ولجان تحرير المجلات.
46- الحد من ظاهرة السرقات العلمية وانها ظاهرة تدام في مجتمع الجامعات الاكاديمي وغيرها من المجتمعات الاكاديمية الرصينة بل يجب تطبيق التشريعات الخاصة بحماية حقوق المفكرين والعلماء وتتضمن تلك عقوبات صارمة منها:

أ. سحب الشهادة.
ب. ابطال الترقيات العلمية.
ج. اعتبار الامر جريمة السرقة لا مضى زمن بعد عليها الاقرار بتأثا بالعقوبة.
د. الاعتبار مكافأة السارق الوظيفية كظرف مشدد بتأتا.

47- ضرورة تدريب الكوادر الاكاديمية ابتداء من مدرسين مساعدين) من قبل الباحثين الذين لديهم الخبرة والامكانية على كتابة البحوث العلمية بالطرق الصحيحة وتنبيههم لعدم اللجوء مطلقا وبوقت مبكر الى الاستلال أو النسخ من رسالة الماجستير أو أطروحة الدكتوراه.
48- نشر تلك البحوث والرسائل والاطاريح من قبل المجلات العلمية بالنسبة للبحوث أو من قبل الكليات بالنسبة للرسائل والاطاريح وأن يكون ذلك النشر عبر المواقع الالكترونية الخاصة بتلك المجلات، أو الكليات لتفادي سرقة كل المتخصصين بها من جانب وليكون لدى الباحث علم مسبق بأن عمله سوف يطلع به الجميع وبالتالي يكون رسالة رادعة لم يفكر بسرقة النتاجات العلمية للآخرين.
49- اختيار موضوع الطالب البحث / الرسالة / الاطروحة خلال السنة التحضيرية وتفعيل السيمنار للطلبة كل ثلاثة أشهر.
50- يتوجب على المشرف أخذ الدور المسند له من خلال متابعة الطلبة المشرف عليهم لمعرفة امكانيتهم على الكتابة وتدريسهم أخلاقيات البحث العلمي وتوجيههم التوجيه الصحيح وصولا الى تشخيص الأخطاء وتصويبها لكتابة الطالب.
51- وضع حد على عاتق الاساتذة الذين يقومون بدور الاشراف مسألة الزامهم بالتقيد بمنع الطالب من التعامل مع المكاتب التي تقوم بمهمة طبع وبيع البحوث والرسائل والاطاريح لطلبة الدراسات العليا، ووضع صيغة من قبل الكليات بعد توجيههم من خلال العمادة.
52- تقديم تقرير كل ثلاثة أشهر عن عملية سير الاشراف من قبل المشرف ولكل طالب على حدة ويكون ملزما لهذا الاستاذ مشرفا على طلبته أيبين من خلاله امكانية الطالب على الكتابة ومستوى استيعابه للموضوع المختار للكتابة فيه ومدى معرفته لأخلاقيات البحث العلمي ليستخلص من هذه التقارير تقريرا نهائيا يقدم الى المقوم العلمي لدى تقييم (الرسالة أو الاطروحة)، وترسل نسخة من كل تقرير دوري الى مكتب معاون العميد للشؤون العلمية والدراسات العليا لاعتماده وارسال نسخة منه الى ملف الطالب في مكتب الدراسات العليا (القسم المعني).

أستماره مراجعة الجانب الاحصائي في الرسائل والاطاريح الجامعية

وزارة التعليم العالي والبحث العلمي

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3- أ.د. بلاغ حسن حمزه	

عنوان الرسالة أو الاطروحة: Synthesis, characterization and biological activity of some new compounds of Monastrol (3,4-dihydropyrimidine-2-(1H)-ones/thions)

أني الطالب: لقمان سيان علي أتعهد بتولي وتنظيم الدراسة الاحصائية بنفسي من دون المساعدة بكتابة الجانب الاحصائي من قبل أساتذة.

التوقيع:

التاريخ:

ملاحظة: أعدت هذه الاستمارة أستنادا الى كتاب وزارة التعليم العالي والبحث العلمي / جهاز الاشراف والتقويم العلمي ذي العدد ج ع/2043 الصادر بتاريخ 2014/11/10 والمبلغ الينا عبر كتاب رئاسة جامعة ذي قار- قسم الشؤون العلمية والدراسات العليا ذي العدد 7/ 54/ 14447 الصادر بتاريخ 2014/11/19.

Certificate

I certify that this thesis 'Synthesis, characterization and Antioxidant Study of some newDihydropyrimidine-2-(1H)-ones /thion derivative' ***is*** prepared by Noor Raisan Ali under my supervision at the Department of Chemistry ,College of Science ,University of Thi-Qar ,Iraq in partial fulfillment of the requirements for Master degree of science in chemistry .

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In view of the available recommendation , I forwad this thesis for debate by the examining committee

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إهداء

مع جناح الذل..
اقدم قطاف جهدي..
الى والديّ..
بعض الوفاء..

نور

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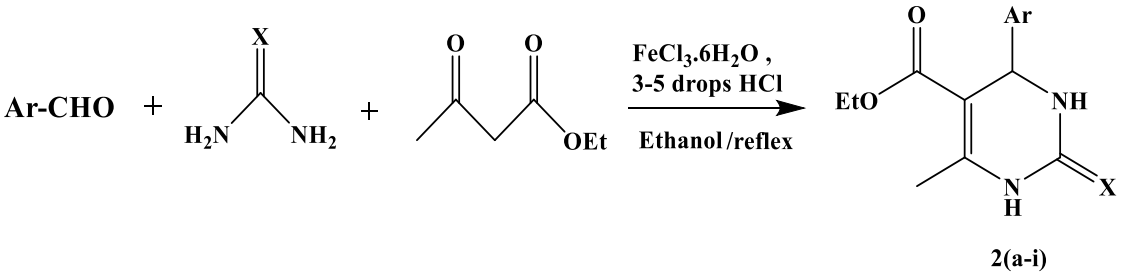
Abbreviation

Abbreviations symbols	Definition
α	Alpha
β	Beta
δ	Chemical shift
Δ	Heat to reflux
^{o}C	Degrees Celsius
^{13}C-NMR	Carbon nuclear Magnetic Resonance
DEPT	Distortionless Enhancement by polarization Transfer
DMSO	Dimethyl Sulfoxide
DPPH	(1,1-diphenyl-2-picrylhydrazyl)
EtOH	Ethanol
h	Hours
^{1}H-NMR	Proton nuclear Magnetic Resonance
m/z	Mass to Charge ratio
m.p	Melting Point
min	Minutes
m	Multiplet
MS	Mass Spectrum
ppm	Part Per Million
Ph	Phenyl
ml	Molar Concentration
μl	Micro Molar

Summary

This study is concerned with the synthesis and characterization some of 3,4-dihydropyrimidine-2-(1H)ones /thione .These compounds 2(a-i) were prepared by reacting ethylacetoacetate and aromatic aldehyde with urea or thiourea in the presence of $FeCl_3.6H_2O$ with 3-5 drops from HCl and ethanol as a solvent at 60-65 ^{O}C .in good yield (55-90%) .

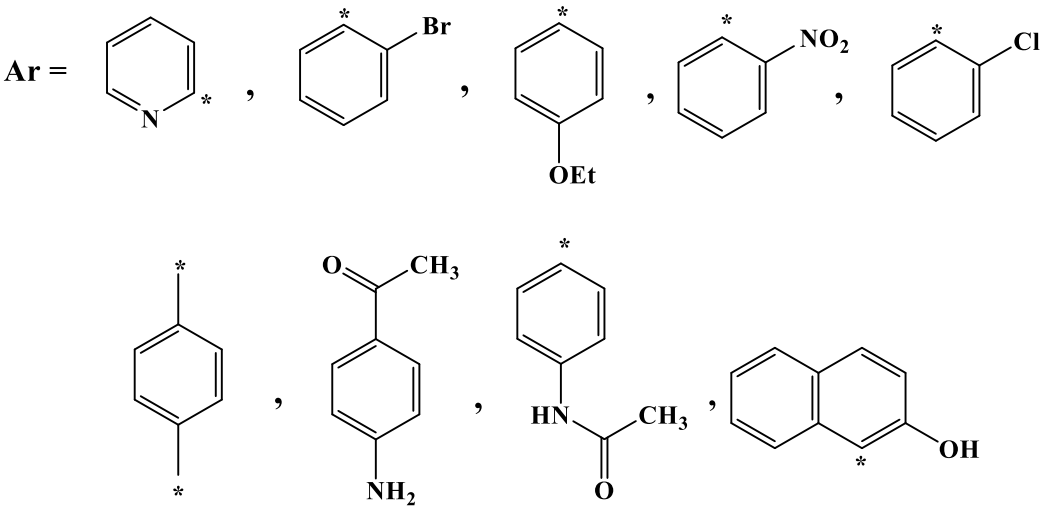
Ganeral Synthesis of 3,4-dihydropyrimidin-2-(1H)ones /thione



2(a-i)

X = O

Ar =



All prepared compounds are characterized by spectral techniques such as FT-IR , ^{1}H-NMR ,^{13}C-NMR and Mass spectra .

Chapter One

Introduction

1.1: Pyrimidine

Diazines which belong to the most important hetrocycles six-membered aromatics with two nitrogen atoms .There are different structures which can be distinguished according to the relative position from the nitrogen atoms: pyridazine (1,2-diazine)[1],pyrazine (1,4-diazine)[2] and pyrimidine (1,3-diazine)[3] , as shown in figure1.

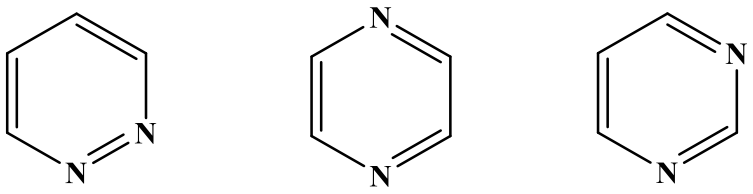
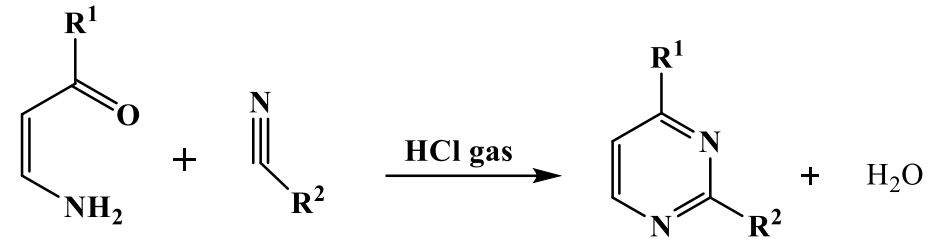


Figure 1

Among them the 1,3-diazine derivatives which are the most studied because the pyrimidine core is found in many natural products[4] . Pyrimidine was an important method for the synthesis of pyrimidine derivatives because its cores with extended π-systems which have interesting fluorescence properties and similar compounds are useful in the development of advanced electronic and photonic material[5] . The ability of protonation, hydrogen bond formation and chelation of the nitrogen atoms of the pyrimidine ring are also of great importance: such derivatives could be therefore used for the formation of supramolecular assemblies and used as sensors[6].We can notice that thymine, cytosine and uracil which have a pyrimidine ring are important as building blocks for the nucleic acids. Moreover numerous pyrimidine derivatives exhibit a large range of biological activities and was used for pharmaceuticals[7] , antibiotics[8]or herbicides applications[9].

1.2: Synthesis of Pyrimidine

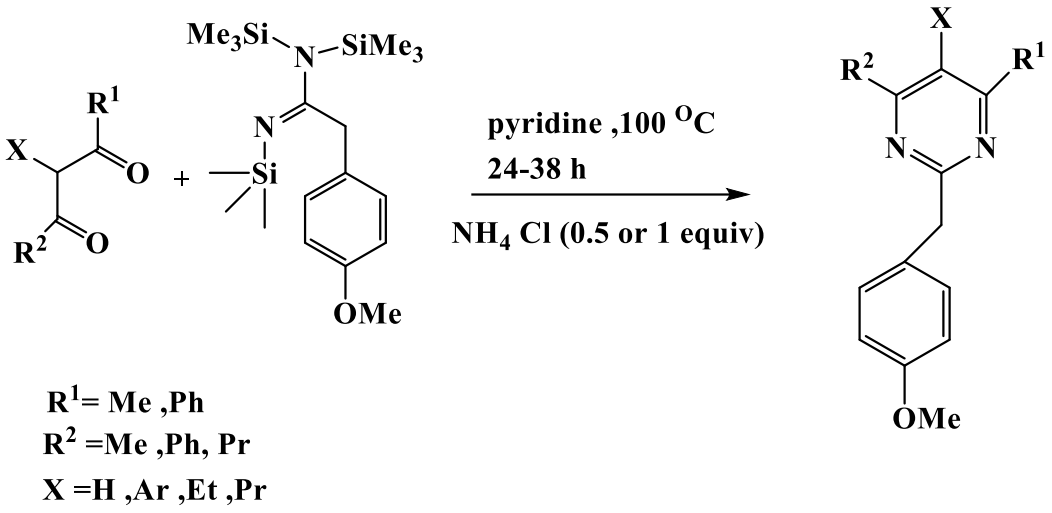
pyrimidine synthesis from the reaction of *ortho* amino carbonyl compounds such as ester, amides , nitriles and ketones with nitriles in the presence of hydrogen chloride . The reaction consists of reacting the two components in the presence of dry hydrogen chloride gas with or without a solvent followed by the usual work up to isolate the pyrimidine formed in the reaction[10] as shown in scheme1.



$R^1 = OC_2H_5$,NHR
R^2=C_6H_5 ,C_4H_4O

Equation 1

Ghosh et al[11] have developed a general method for the synthesis of tri- and tetra-substituted pyrimidines using1,3-dicarbonyl compounds and *N*,*N*, *N*'-tris-(trimethylsilyl) amidines in place of amidines. The yields for tri-substituted pyrimidines is 74-89%, depending on substituents, as shown in scheme2.



R^1= Me ,Ph
R^2 =Me ,Ph, Pr
X =H ,Ar ,Et ,Pr

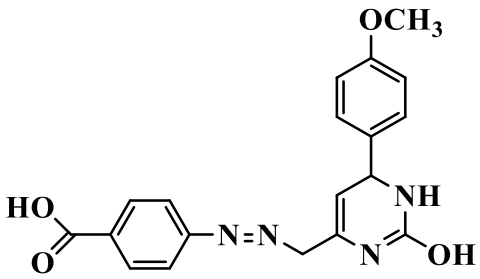
Equation 2

Multicomponent reaction(MCRs) have provided new prospects for advancement in the synthesis of pyrimidine derivatives. MCRs are often one-pot reactions (three or more components) are incorporated into the final product , will high-atom economy ,convergence and efficiency .Generally ,one-pot procedures have many advantages compared to multiple-step syntheses[12-14].MCRs found numerous applications in combinatorial chemistry , target oriented synthesis polymer science[15]. The most important MCRs are the Biginelli dihydropyimidone synthesis (condensation of aldehydes and β- keto carbonyls with urea or thiourea)[16]and Traube-Schwarz(condensation of α,β-unsaturated carbonyl compounds with amino heterocyclic or amidines) reaction have served as powerful tools for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and tricyclic 1,6-dihydropyrimidine derivative under different condition[17-18].

1.3: Biological activity of pyrimidine:

Pyrimidine and derivatives was a part of many pharmaceutically interesting drugs that exhibit a variety of biological activities including anti hypertensive[19], antimicrobialagents[20], anti bacteiral agent[21]. DNA and RNA bases are the most commonly identified bases and due to the component of nucleic acid[4,22].Many pyrimidine derivatives are used for the production of thyroid drugs in the treatment of leukemia[22]. pyrimidine are the building blocks of many natural compounds such as vitamins ,liposacharides ,and antibiotics[23].

Bukhari et al[24] synthesized a new series of chalcone based pyrimidine derivatives and screened for their antihypertensive activity by inhibition of angiotensin converting enzyme (ACE).One of the synthesized compound {4-(2-hydroxy-6-(4-methoxyphenyl)-1,6-dihydropyri midine-4-yl)methyl)diazenyl) benzoic acid} as shown in figure 2.it shows more ACE inhibitor activity with lowest IC_{50} value of 0.201 *mM* when compared with captopril used as standard.



4-(2-hydroxy-6-(4-methoxyphenyl)-1,6-dihydropyrimidin-4-yl) methyl)diazenyl)benzoic acid

Figure 2

Kandeel et al[25] synthesized a novel series of pyrazolo[3,4-d]pyrimidine derivatives .The compound [9-Methyl-2-phenylamino-7-phenyl-7Hpyrazolo [4,3-e] [1, 2, 4] triazolo[1,5-c] pyrimidine screened it vitro anticancer activity against MCF-7 human breast cancer gives exhibition to the highest activity due to an amino group attached to pyrazole and triazole rings and compared to methotrexate as the standard drug ,figure 3.

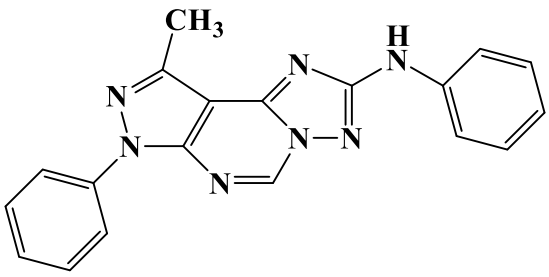
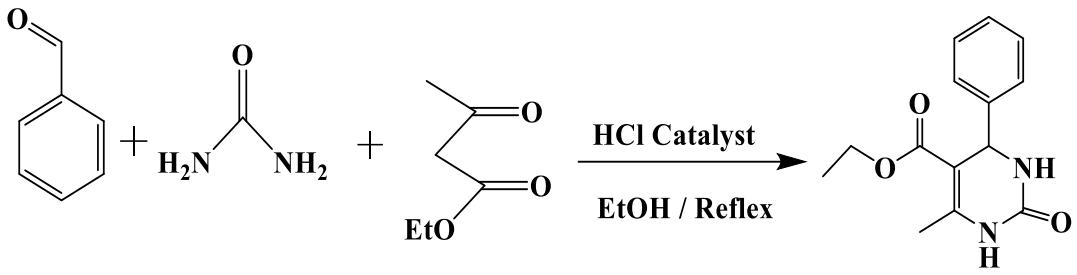


Figure 3

1.4:Dihydropyrimidine :

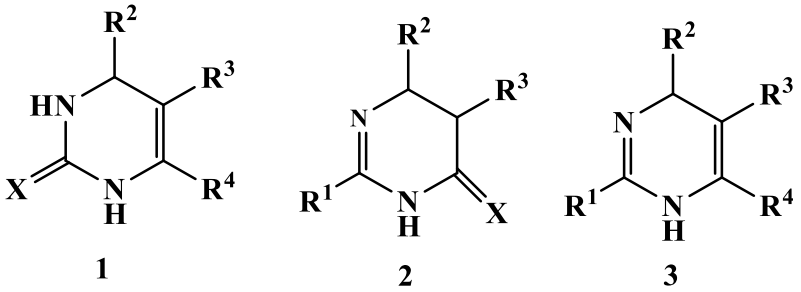
Dihydropyrimidines (DHPMs) and their derivatives was an important class of heterocycles compound that can be synthesized *via* Biginelli reaction. DHPMs was reported for the first time by the Italian chemist Pietro Biginelli over a century ago by a very simple reaction in a one pot ,three component condensation of β-keto esters and aldehydes with urea or thiourea ,under acidic conditions[16,26](Scheme3).A strong acidic catalyst was employed in the original Biginelli reaction, but the yields of product (DHPMs) were low. A Lewis acid is a common catalyst for the Biginelli reaction ,such as $SbCl_3$[27] ,CaF_2[28] and ZnI_2[29] and many ionic liquids have been applied to the Biginelli reaction including [Et_3NSO_3H] HSO_4[30] ,[Hmim]HSO_4[31]andsulfonicacid-funztionalized Bronsted acidic ionic liquids[32].



ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Equation 3

Since Biginelli reported ,many researchers , Kappe[33] , Cho[34] , Atwal[35] and so on, have studied the reactivity physical properties , synthetic mechanism and various analogue syntheses of pyrimidine-2-one 1and 2. A review on dihydropyrimidines 1 was described in 1993 under the title:100 years of the Biginelli synthesis by Kappe[33]. On the other hand , the synthesis of the other types of dihydropyrimidine 3 was first reported in 1899 by Traube and Schwarz[36],followed by only a few researchers , Ruhemann[37] ,Dodson[38] ,Heyes[39] and Silversmith[40] .Dihydropyrimidine 1 and 2 could be regarded as Keto-forms of the general chemical structure of 3[41a]. The reported chemical structures of 3 were initially poorly characterized because of the lack of NMR spectra in those days[41(b,c)],as shown in figure 4.

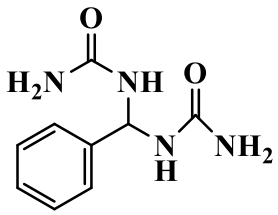


1 **2** **3**

X = O , S
R^1 , R^2 ,R^3 = H ,Aryl ,Alkyl

Figure 4

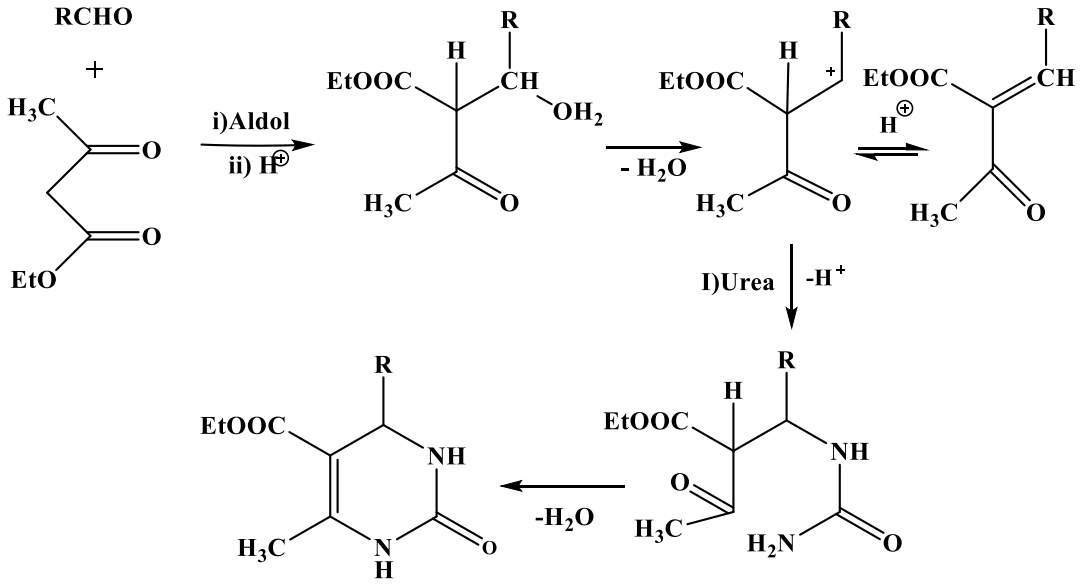
In(1933) Folkers et al[42] is suggested a pathway of Biginelli reaction under acidic conditions they could prove an intermediate 1,1-(phenyl methanediyl) diurea (4) to transform to end product Biginelli compound.



4

Figure 5

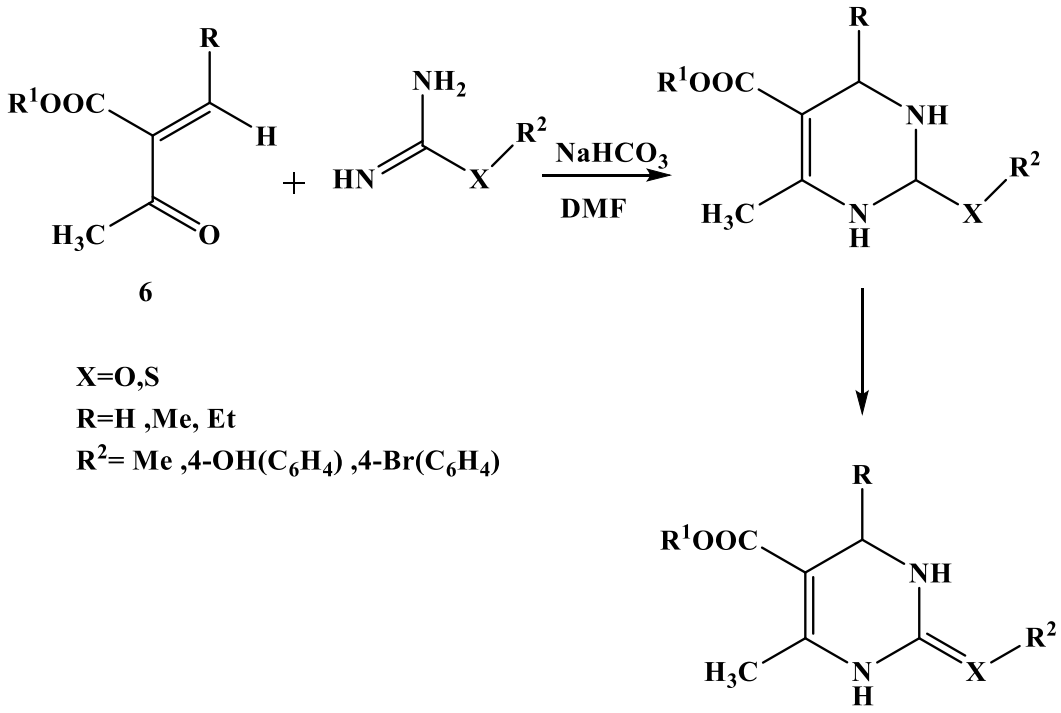
Sweet et al[43]. report that condensation aromatic aldehyde with ester to give carbenium ion in absolute ethanol afforded the corresponding 2,3-Dihydropyrimidine under these scheme 4.



Scheme 4

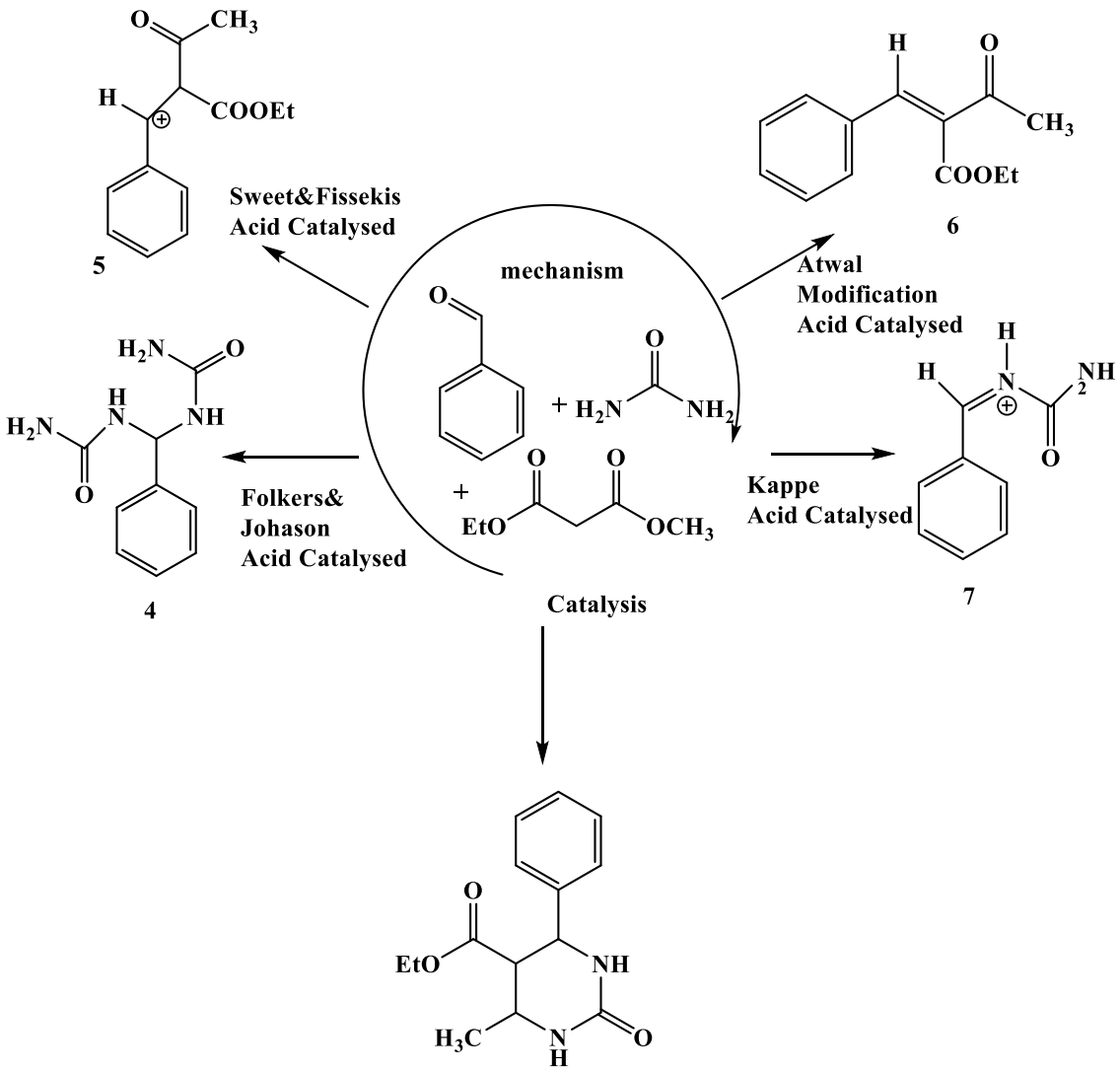
Atwal et al[35(a)] have given a proposal to surmount troubles linked with poor yield of the typical Biginelli compounds mainly in the case of aliphatic aldehydes, aldehydes having a slightly hindered carbonyl function by *ortho*-substituents. This new approach involves two steps,

first step is concerned with separate synthesis of unsaturated carbonyl compound (6) via Knoevenagel condensation and second step is involved in the base catalyzed addition of substituted ureas[40]as shown in scheme5.



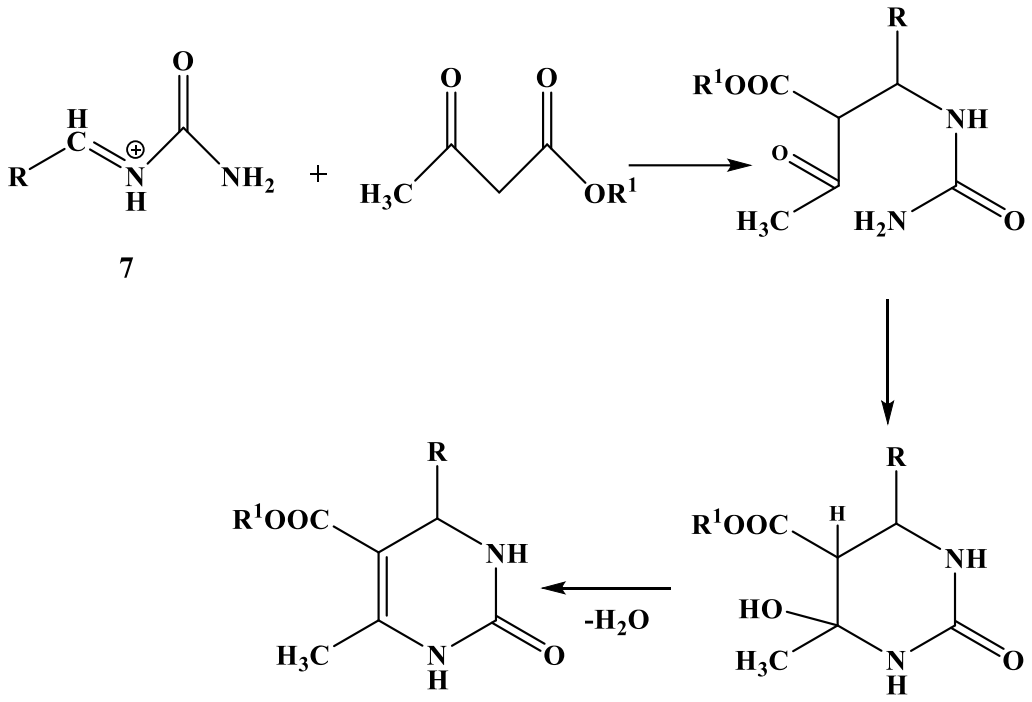
Scheme 5

Some intermediate compounds are proposed by several scientists to interact Biginelli reaction as shown in scheme6. Depicting of all these mechanistic proposals so far advanced were necessary to be presented here because there are very few synthetic studies on mechanism aspect of this reaction prior to or after Kappe's mechanistic proposal. This reaction has attracted the attention of a large number of chemists around the world as far as number of publications are concerned. Clearly these were catalysts efficacy/ cataly development investigations only. It is not out of point to mention here that every research journal was flooded describing these changes i.e. catalysts and every paper made a mention of Kappe's mechanism which was based upon spectroscopic evidence only in next papar.



Scheme 6

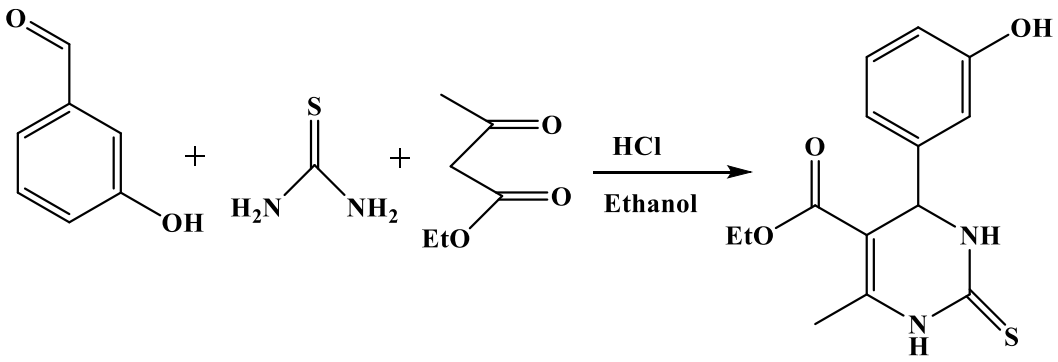
Kappe[33(d)] used spectra techiques like ^{1}HNMR and ^{13}C NMR spectroscopy in multicomponent reaction to the formation of dihydropyrimidine by two step in the first step foramation N-acyliminium ion intermediate (7) by attack nucleophilic of urea on the electron deficient carbon of the aldehyde function under acidic conditions and second steps active methylene compound adds onto this intermediate in a Michael fashion. He found that in this reaction dihydropyridines are always formed in minor quantities.



Scheme 7

1.4.1: Monastrol :

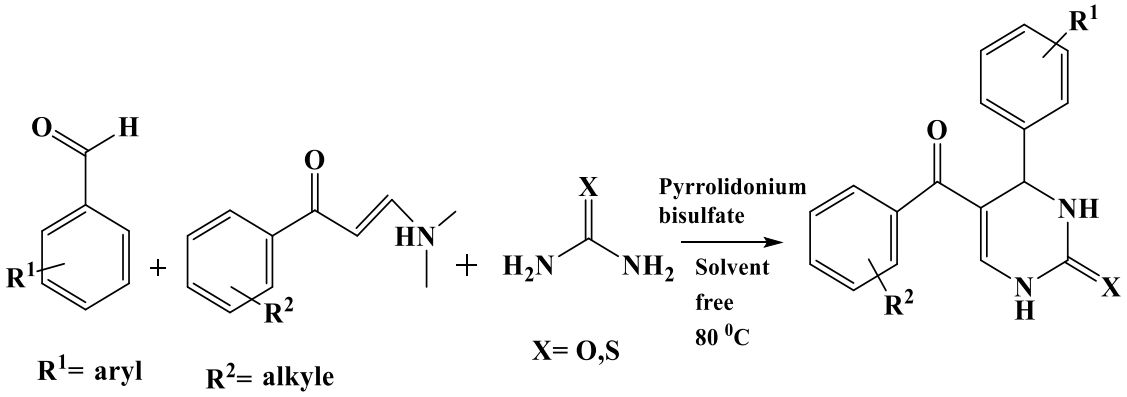
Monastrol is a simple low molecular of 3,4-Dihydropyrimidine-2(1*H*)-thione when condensation 3-Hydroxy benzaldehyde and ethyl acetoacetate with thiourea by Biginelli reaction to give ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbo -xylate][21].Monastrol has been discovered a decade ago to be specifically known about the affect of mitosis via a mechanism consisting of specific and reversible inhibition of the motility of the motor protein, mitotic kinesin reversible inhibition of the motility of the motor protein, mitotic kinesin Eg5[44-46].



ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Equation 8

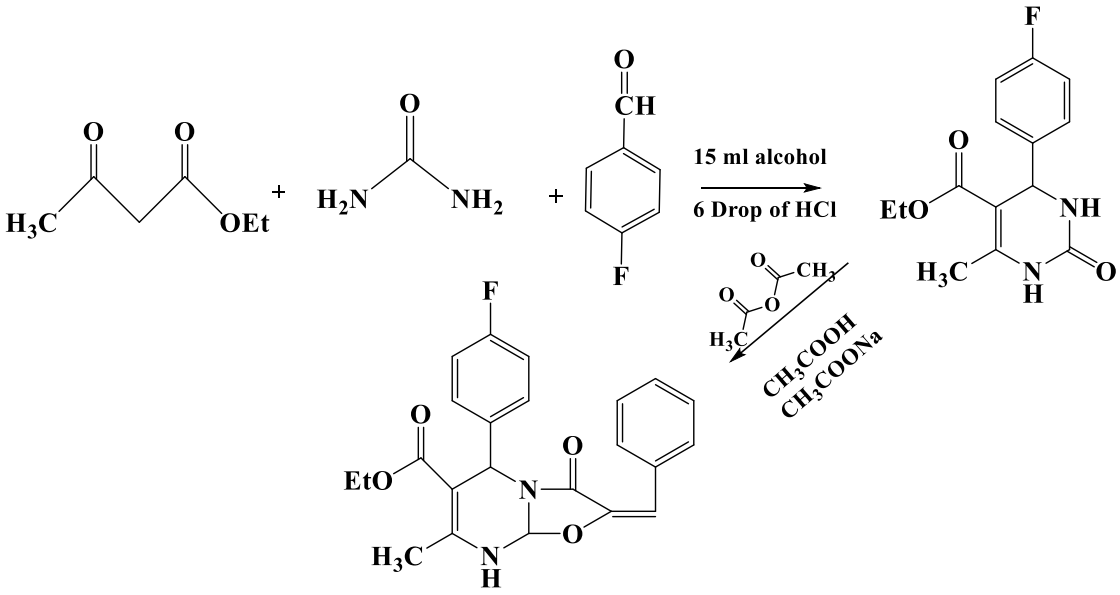
Alinezhad et al[47] synthesized a series of 6-unsubstitued dihydropy - rimidinones in presence of 2-pyrrolidinium bisulphate as an acidic ionic liquid catalyst by using different aromatic aldehyde (both electron-with drawing and electron donating) substituents performed to excellent yield ,short reaction time ,simple procedure and avoidance of the use of organic solvents are some advantages of this mothed.



R[1]= aryl **R[2]= alkyle** **X= O,S**

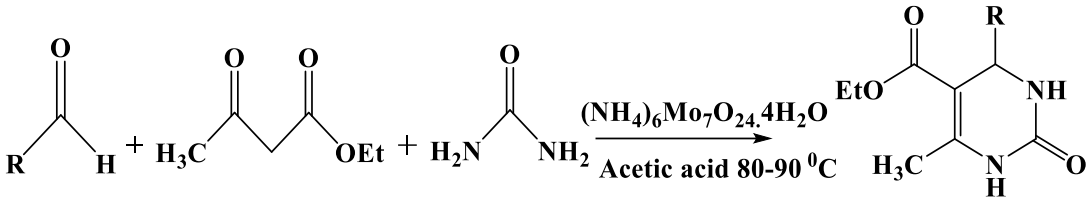
Equation 9

Chadotra and Baldaniya [48] have synthesized and characterizations of Oxazolo Pyrimidine by two step reaction sequence involving in the first preparation of ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate and two step preparation ethyl (Z)-2-benzylidene-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5H-oxazolo[3,2-a]pyrimidine-6-carboxylate in presence Benzylaldehyde, Chloroacetic acid, Sodium acetic ,Acetic anhydride in acetic acid as acatalyst, the yield of this compound was 58% and then studies the biological activity(antibacterial activity ,antifungal activity).



Scheme 10

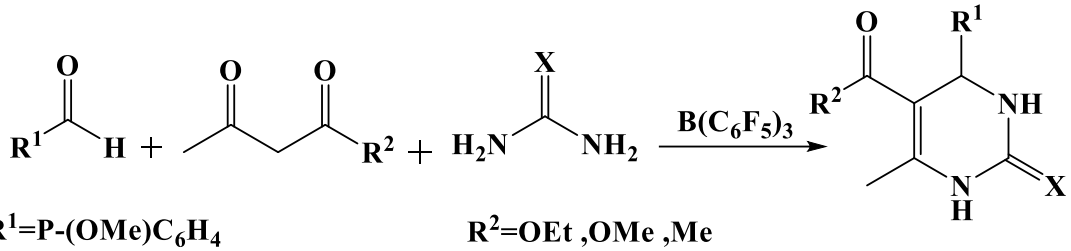
Srikanth et al[49] have synthesized some new 4-substituted-5-ethoxy carbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one derivatives were prepared by using aromatic aldehyde which consists of electron donated and withdrawing groups in presence ammonium molybdate as acatalyst and acetic acid as solvent .



R= p-$(NO_2)C_6H_4$
P-$(OH)C_6H_4$,P$(CH_3)C_6H_4$
P-$(OMe)C_6H_4$, P-(OH),m$(OMe)C_6H_3$

Equation 11

Prajapti et al[50] developed novel synthetic methodologies. They report an efficient and environmentally benign protocol for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones(thiones) using catalytic amount of *tri* (pentafluorophenyl)borane as a convenient and non-conventional Lewis acid. *Tri* (pentafluorophenyl)boraneis gaining importance due to its availability ,less toxicity ,thermal stability and water-tolerant nature .It was observed that the compounds containing both electron-with drawing and donataing substituents on aromatic ring reacted efficiently under the present reaction condition give excellent yield (92-97) and high purity; however, ortho-substituted aromatic aldehydes required longer reaction time to achieve desired products in high yield.

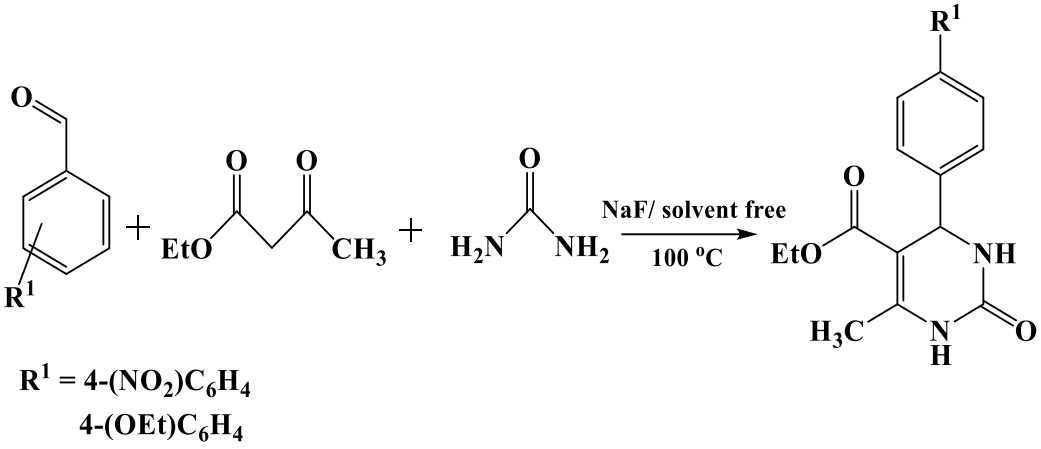


R^1=P-$(OMe)C_6H_4$ R^2=OEt ,OMe ,Me
P-$(CH_3)C_6H_4$,P-$(NO_2)C_6H_4$ X=O ,S

Scheme 12

Farhadi et al[5] reported on the preparation of 2-oxo-1,2,3,4-tetrahydro pyrimidines using the NaF as catalyst. This catalyst afforded the target molecules in good to excellent yield(70-95). They also studied this reaction in different solvents such as EtOH ,CH_3CN ,H_2O and DMSO in

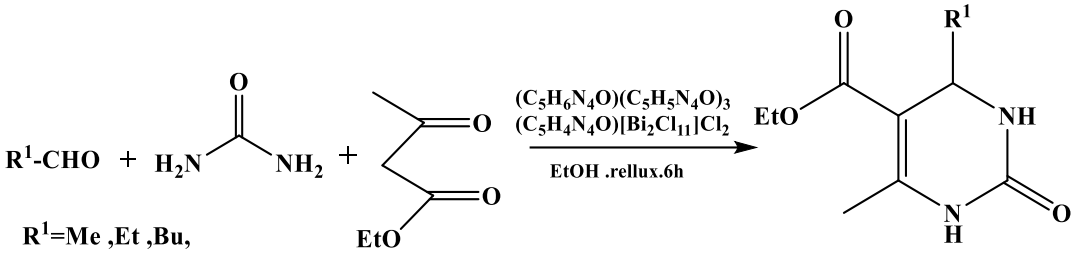
presence NaF as a catalyst reaction was sluggish and lower yields were observed (23-85).



R^1 = 4-$(NO_2)C_6H_4$
4-$(OEt)C_6H_4$

Scheme 13

Zhang et al[51] at first preparted the complex $(C_5H_6N_4O)(C_5H_5N_4O)_3(C_5H_4N_4O)[Bi_2Cl_{11}]Cl_2$ as acatalyst in the reaction of synthesis a series compound of 3,4-dihydropyrimidin-2-(1H)ones/thiones from the condensation of aldehyde, β-dicarbonyl compound and urea/thiourera . The synthesis of this compound were characterized by spectral studies (MS and ^{1}H NMR).

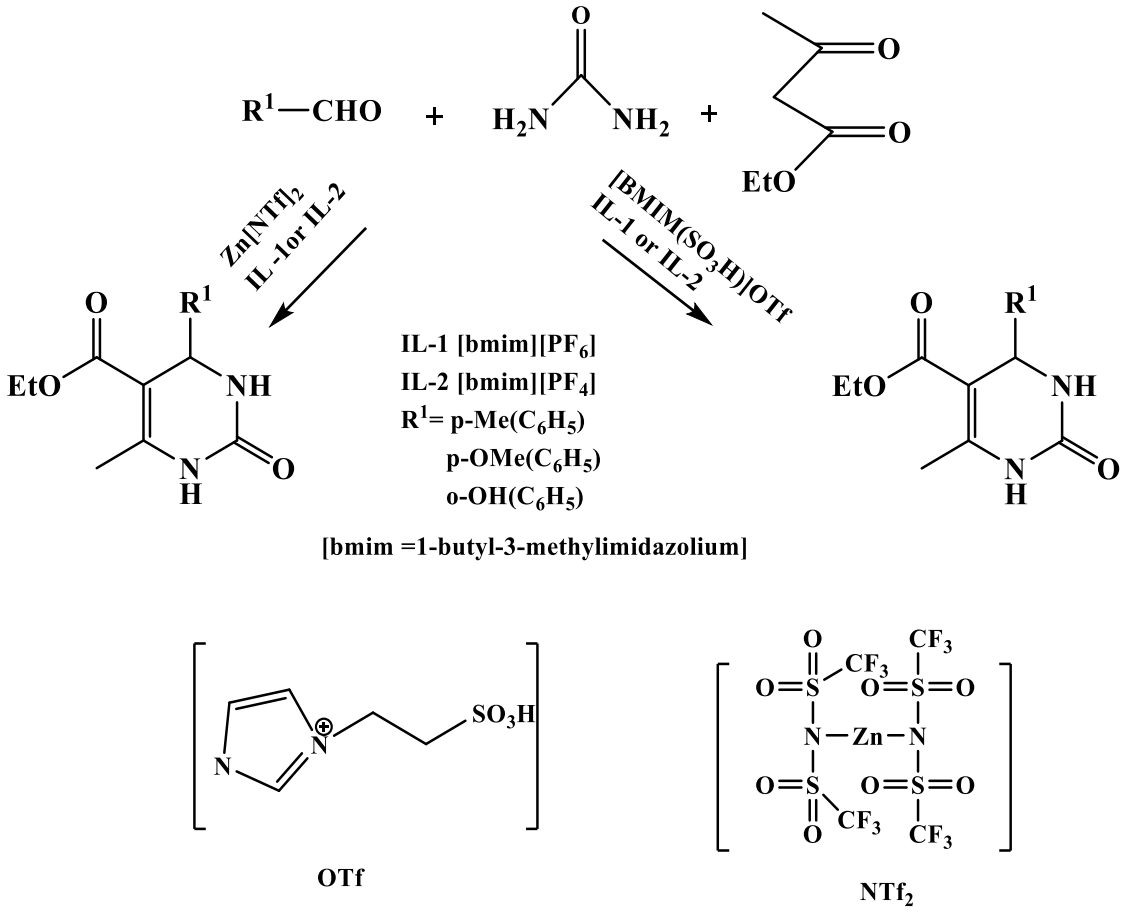


R^1=Me ,Et ,Bu,
2-OH(C_6H_4)
3-$NO_2(C_6H_4)$
4-PH(C_6H_4)

Scheme 14

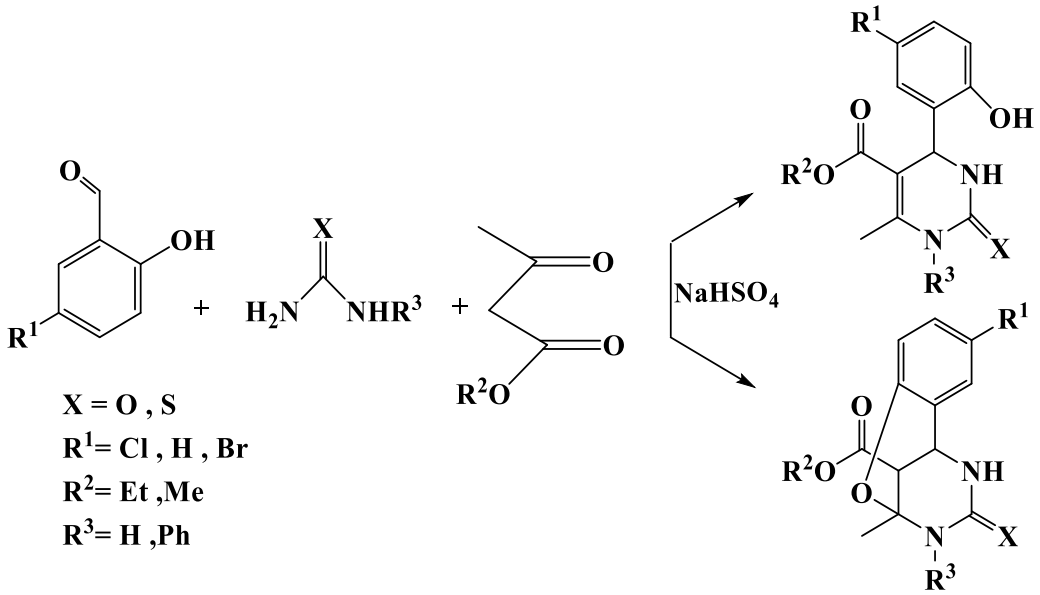
Savanur et al[52] have synthesized dihydropyrimidinones and thiones in their library by simple method via the reaction between aldehyde ,ethyl

acetoacetate with urea or thiourea , imidazolium-ILs was used as asolvent along with catalytic amounts of Bronsted acidic IL [bmim(SO_3H][OTf] or Lewis acid $Zn(NTf_2)_2$,both reaction exhibited good yield (68-92) in presence Bronsted acidic and (76-94) in presence Lewisacid).



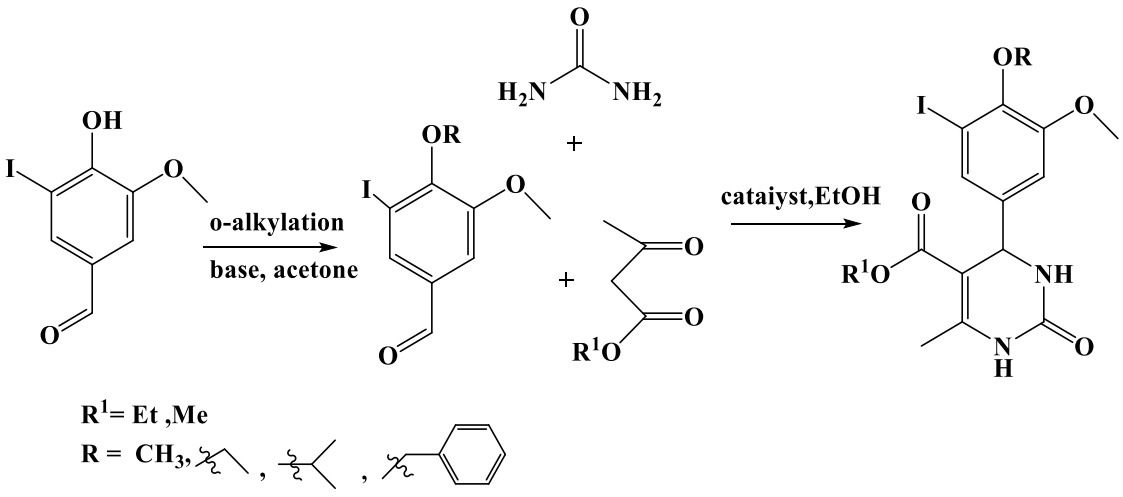
Scheme 15

Cheng et al[53]has synthesized by one pot condensation reaction of three component salicylaldehyde analogues , β- ketoester and urea or thiourea under solvent-free conditions with $NaHSO_4$ as catalyst in high yields. The reactions formed two different products,4-(2-hydroxyphenyl) pyrimidines and9-methy-11-oxo(orthioxo)-8-oxa-10,12-diazatricyclotrideca derivatives.



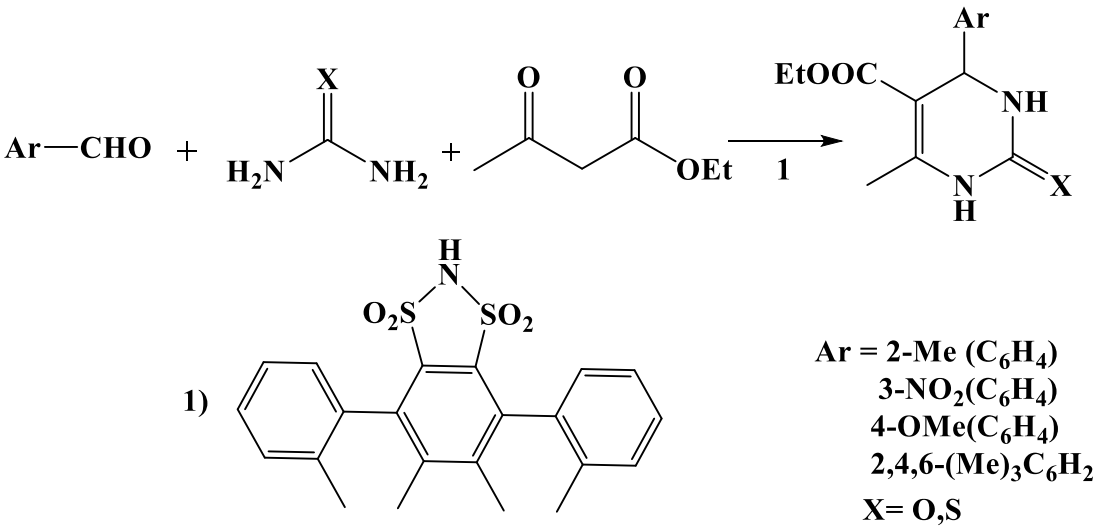
Scheme 16

Muškinja et al[54] synthesized novel 2-oxo-1,2,3,4-tetrahydro pyrimidin -es via reaction vanillin and substituted with β-ketoester and urea. *(*$PhNH_3)_2CuCl_4$ complex is used for the first time as a homogeneous and heterogenous catalyst.



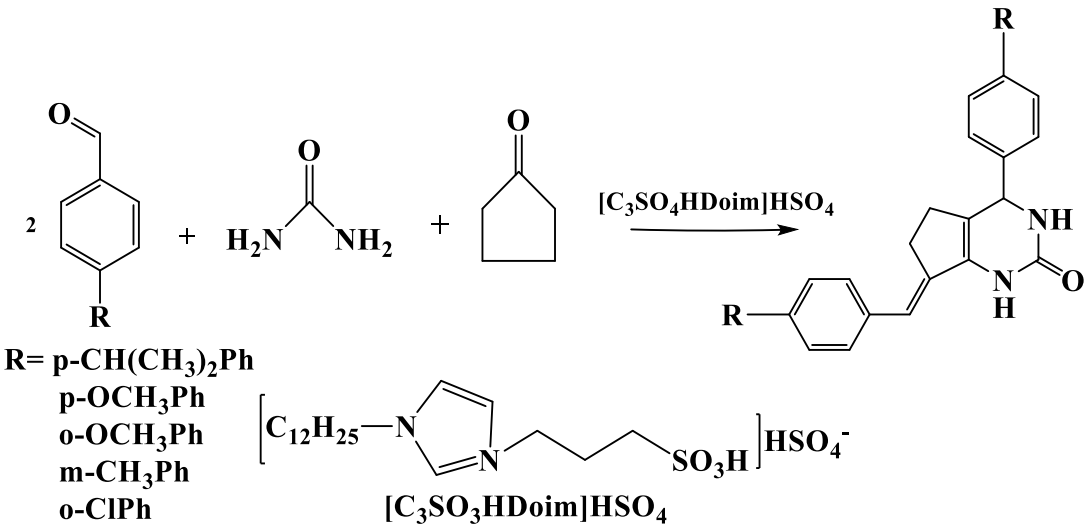
Scheme 17

Barbero et al[55] used a chiral derivative of 1,2-benzene disulfon imide,namely(−)4,5-dimethyl-3,6-bis(o-tolyl)-1,2-benzenedisulfonimide in Biginelli reaction as a Bronsted acid catalyst. The yields of the target dihydropyrimidines was very high (average 91%) and enantiomeric excesses was always excellent (average 97%).



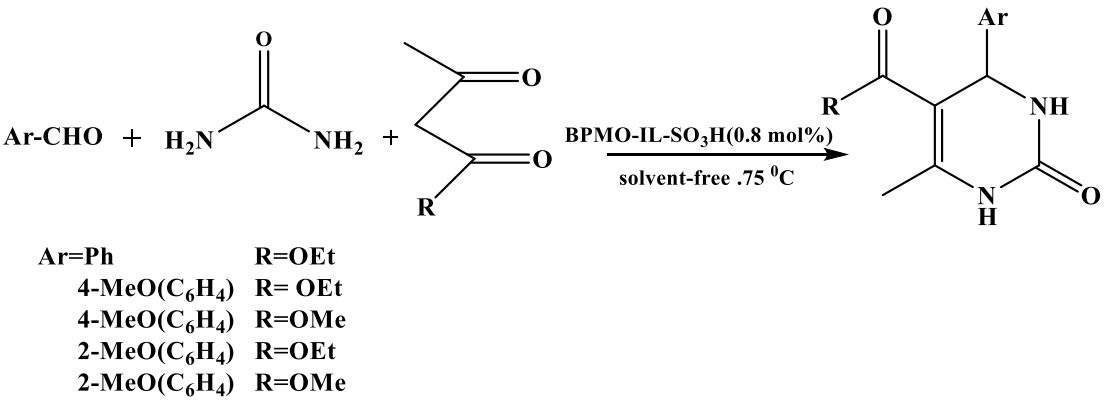
Scheme 18

Zhou et al[56] has synthesized pyrimidinone derivatives by condensation among aromatic aldehydes, urea or thiourea and cyclopentanone. By a novel, eco-friendly functionalized IL [C_3SO_3H Doim]HSO_4 as a catalyst the reaction proceeded efficiently at(80 ^{0}C) to afford the desired products in good yield (up to 96%).



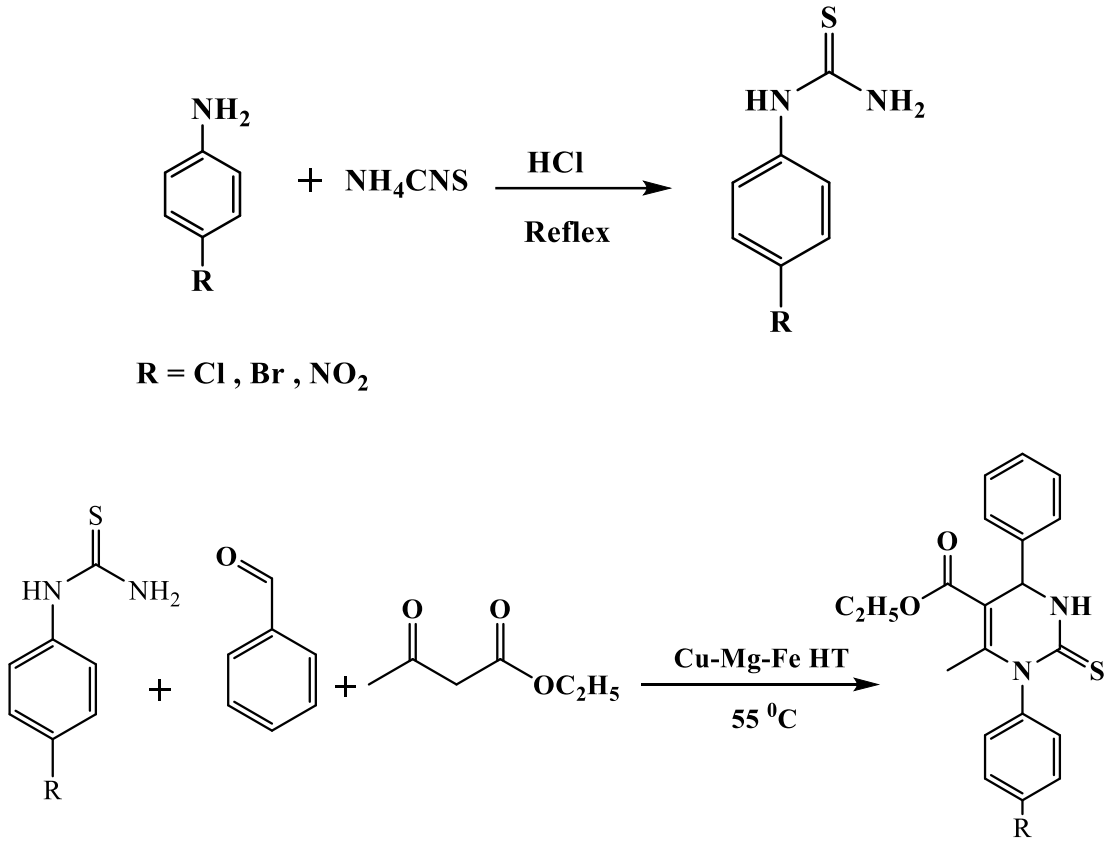
Scheme 19

Elhamifar et al[57] used a novel sulfonic acid and ionic-liquid-containing bifunctional periodic mesoporous organosilica (BPMO– IL–SO_3H) was synthesized, characterized, and its catalytic activity was studied in the Biginelli condensation of a variety of different aldehydes with alkyl acetoacetate and urea under solvent- free conditions. The catalyst exhibited excellent activity and delivered corresponding Biginelli products in high to excellent yield and delivered corresponding Biginelli products in high to excellent yields and selectivities.



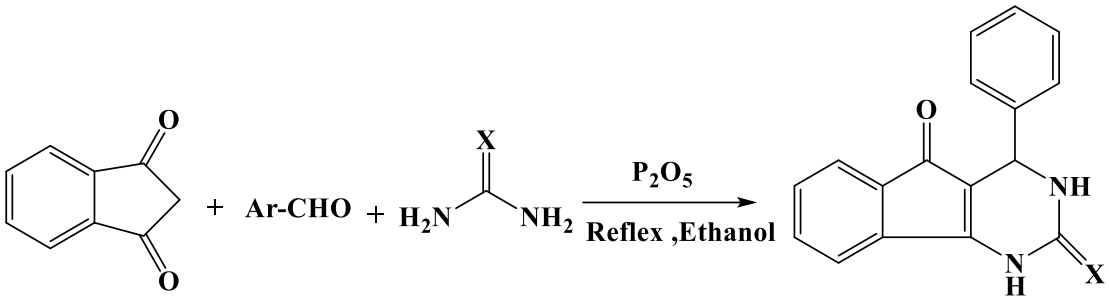
Scheme 20

Dabholkar et al[58] has synthesized 3,4-dihydropyrimidinones/thiones from using substituted aromatic aldehyde, ethyl acetoacetate and urea or thiourea and synthesized 3,4-dihydropyrimidin-2-thiones from *α,β*-unsaturated aldehyde ,1-(*p*-substituted/*o*-substituted phenyl) thiourea with ethyl acetoacetate by using Cu-Mg-Fe hydrotalcite as acatalyst. This reaction furnish good yield of desired products.



Scheme 21

Warekar et al[59] has Synthesized 3, 4-dihydro-1H-indeno [1, 2- d] pyrimidine-2,5-dione by multi-component condensation of 1,3 indanedi - one aromatic aldehydes and urea/thiourea by using Phosphorous Pentoxide as acatalyst .

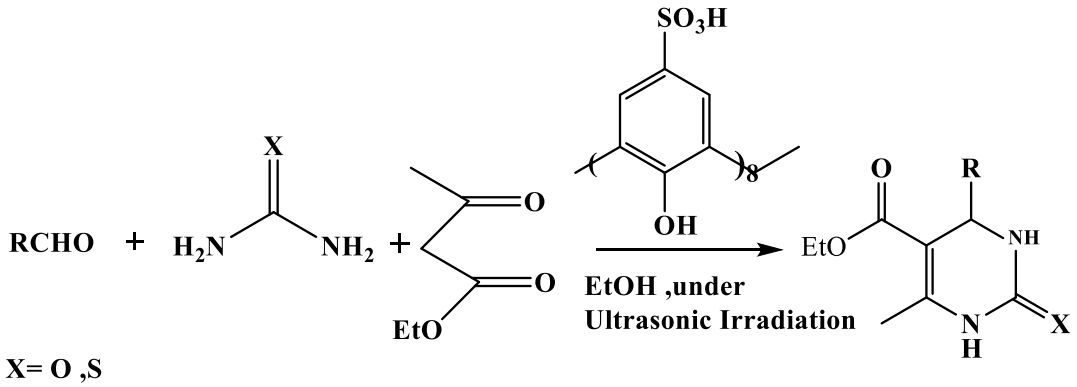


Ar =2-OH (C_6H_4)
4-Cl (C_6H_4)
4-OCH_3(C_6H_4)
C_6H_5
4-OH (C_6H_3)
3-NO_2(C_6H_4)

X = O ,S

Scheme 22

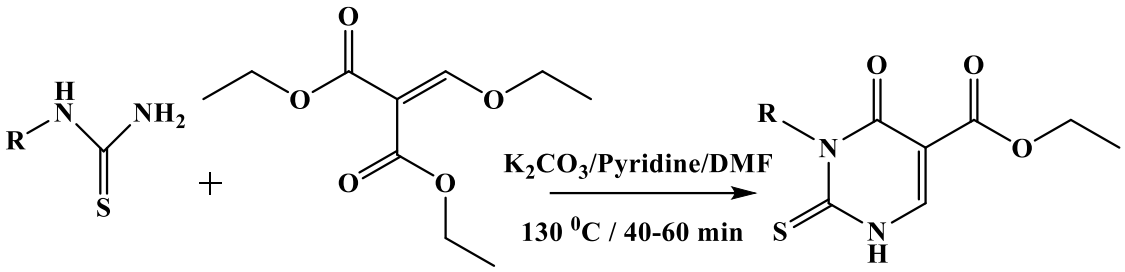
Lin An[60] et al has used Ultrasonic Irradiation to Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones/thiones via reaction of aldehydes with ethyl acetoacetate and urea or thiourea in ethanol by calix[8]arene sulfonic acid as a catalyzed .The yield of this reaction was (46–93%) .



X= O ,S
R= C_6H_5–CH=CH
C_6H_5
4-CH_3O–C_6H_4
C_6H_5–CH=CH

Scheme 23

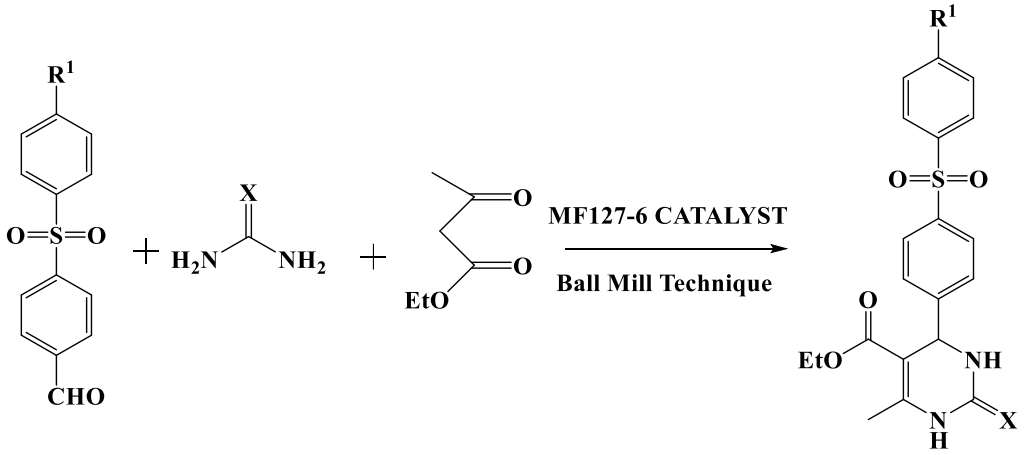
Mundra and Mahesh [61] has Synthesized under microwave irradiation ethyl3-substituted-4-oxo-2-thioxo-1,2,3,4-tetrahydropyrimidine-5carboxylate derivatives by reaction two component N-substituted thiourea with diethyl ethoxymalonate using Pyridine as a catalyzed.



R= $CH_2CH=CH_2$
$n\text{-}C_3H_7$
C_6H_5
$C_6H_5CH_2$

Scheme 24

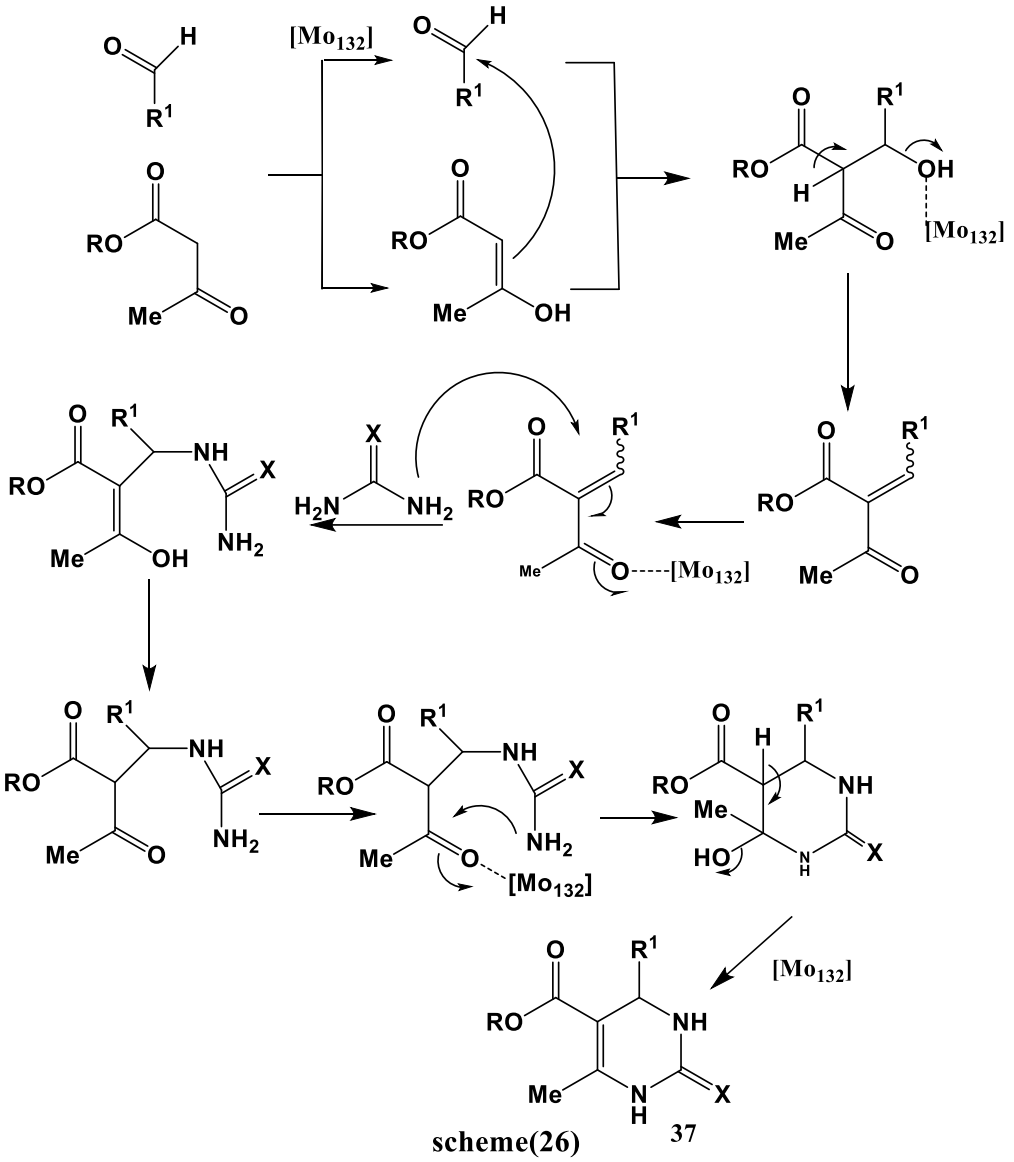
Shahid et al[62]has synthesized some of dihydropyrimidinones (DHPMs) derivatives by three-component β-ketoester derivatives ,aldehyde and urea or thiourea over the alkali-treated H-ZSM-5 zeolite under ball-miling. The yield was(86-96%) at a very short time.



Scheme 25

Nakhaei et al[63]has synthesized 3,4-dihydropyrimidin-2(1*H*)-ones/ thiones via Biginelli reaction in presence of Kelperate type giant nanoporous Isopolyoxo molybdate $(NH_4)_{42}$ $[Mo^{VI}_{72}$ $Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$,presented as $[Mo_{132}]$ as an efficient catalyst under solvent -free conditions. this is new synthetic approach includes short reaction time with high yields(30-93%) and a simple work-up procedure.

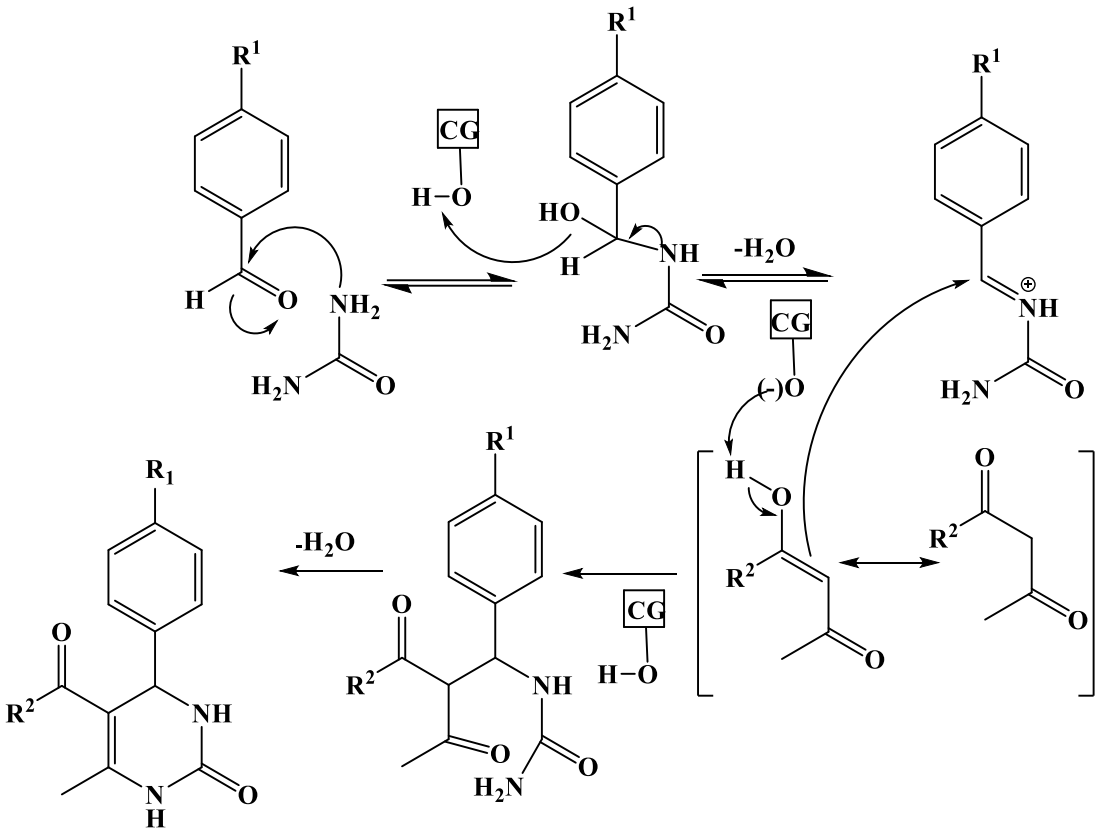
They suggested Plausible mechanism for the {Mo132}-catalyzed formation of DHPMs as shown in scheme 26.



scheme(26)

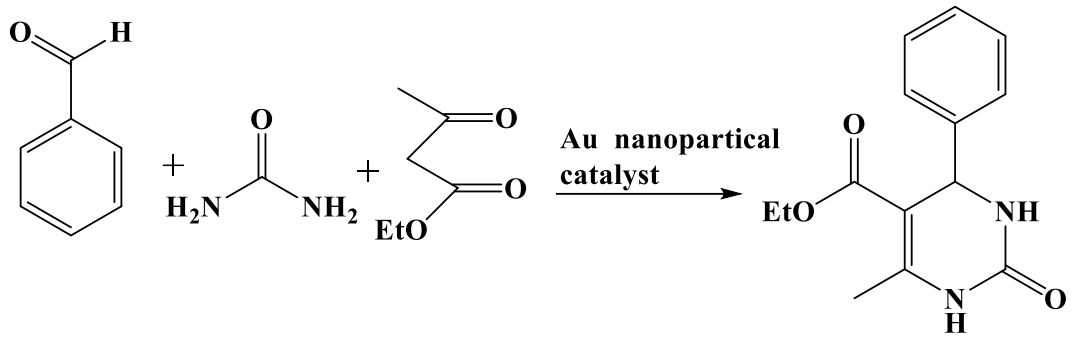
37

Narayanan et al[64] has synthesized 3,4-dihydropyrimidinones in presentclay -graphene oxide nano composite catalysts for the first time in this in Biginelli reaction .This method gives high product yield and short time, and they suggested a mechanism for this reaction ,see scheme(27).



Scheme 27

Thi Nguyen et al[65] have used Gold nanoparticle catalysts and reported the synthesis of a series of shapes of gold nano crystals by simple reduction of $HAuCl_4.3H_2O$ and application them as the catalysts for multicomponent Biginelli reaction Amongst these,unsupported gold nanorods show the best catalytic activity. Its efficiency allows one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones to proceed in high yield under mild conditions.



Scheme 28

Marvaniya et al[66]. synthesized a novel series of 3,4-dihydropyrimidin-2(1H)-one derivatives by Biginelli reaction. The synthesized chemical structures of the compounds were confirmed by mass spectroscopy, UV, IR, and NMR studies. The synthesized derivatives were evaluated for their in vitro antihypertensive and channel blocking activities. Compound 4-(4-chlorophenyl)-N,N-diethyl-6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxamide (figure 6)was found to be most potent calcium channel blocker

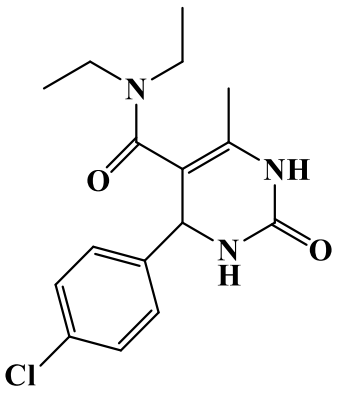
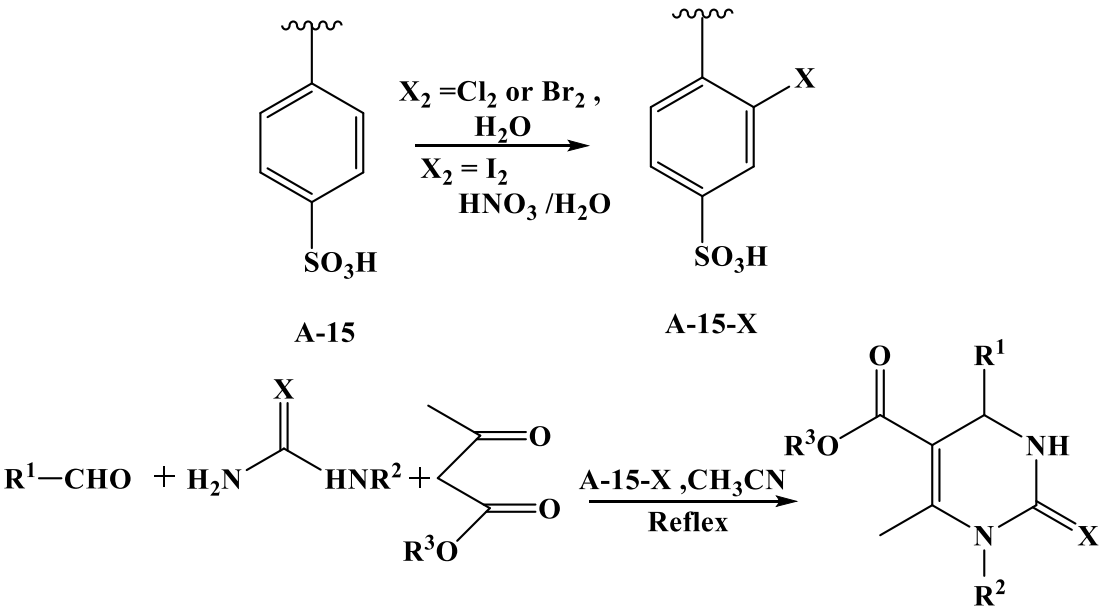


Figure 6

Shen et al[67] has synthesized a series of halogenated macroporous sulfonic resins A-15-Cl, A-15-Br and A-15-I and were synthesized from the precursor Amberlyst 15 by a typical halogenation reaction. They were evaluated for the catalytic activities of the halogenated macroporous sulfonic resins via the Biginelli reaction in detail. These modified resins possessed a larger contact angle of water droplet than the precursor and a significantly improved thermal stability, which contributed to their higher catalytic activity. In particular, the resin A-15-Br containing 31.27% bromine exhibited the best catalytic activity and excellent recyclability.

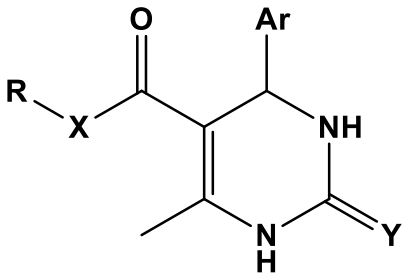


Scheme 29

1.4.3: Biological activity of Dihydropyrimidine :

Dihydropyrimidinone and their derivatives are one of the prime interest class of heterocyclic compounds which has attracted considerable attention of medicinal chemists . DHPMs have been considered a multi-functional cyclic compound against serious diseases that arise from stress or pollution[68]. Monastrol is the first Biginelli compound which has excellent anticancer activity[69].

The antimicrobial activity of thirty six novel dihydropyrimidine derivative was evaluated against common pathogenic bacteria. Significant anti microbal activity (MIC=32, 64 μg/ml) was observed; ***Escherichia coli*** and ***Pseudomonas aeruginosa*** as Gram-negative bacteria and ***Staphylococcus aureus*** as Gram-positive. The highest inhibitory activity was observed against Gram-negative microorganisms[70]



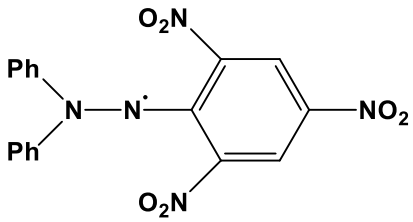
Ar=$_2$-ClC_6H_4 ,4-BrC_6H_4, 4-$CH_3OC_6H_4$
Y=O ,S
X=NH,O
R=4-BrC_6H_4 ,3-BrC_6H_4 ,C_6H_5

Figure 7

1.4.3.1: Antioxidant activity :

Antioxidants are compounds that protect cells against damaging effects of reactive oxygen species which can neutralize free radicals and undo some damage already caused to specific cells. Many medicinal plants are known to possess free radical scavenging molecules, such as phenolic compounds, vitamins, and some other endogenous metabolites, that are rich in antioxidant activity[71]. An antioxidant is a molecule that inhibits the oxidation of other molecules. Oxidation is a chemical reaction involving the loss of electrons or an increase in oxidation state. Oxidation reactions can produce free radicals. In turn, these radicals can start chain reactions , when the chain reaction occurs in a cell, it can cause damage or death to the cell. Antioxidants terminate these chain reactions by removing free radical intermediates, and inhibit other oxidation reactions. Antioxidants are often reducing agents and the most common vitamin E ,ascorbic acid [72].

DPPH is a useful reagent for investigating the free radical-scavenging activities of DHPMs compounds and a substrate to evaluate the antioxid ative activity of antioxidants , the results obtained from antioxidant, screening of the novel compounds are encouraging. Most of the compounds tested showed moderate to good when compared to standerd[73,74].



DPPH= [Di phenyl-1-picry Hydrazyl]

The Aim of The Work

The aim of the present work is :

* Prepare some of 3,4-Dihydropyrimidine -2(1H)-ones/thiones via Bignelli Reaction in one pot , all compounds were confirmed by Spectral techniques such as : IR ,^{1}H-NMR , ^{13}C –NMR , Mass spectra and Dept -135 .

* The activity of some 3,4-Dihydropyrimidine -2(1H)-ones/thione was also evaluated as Antioxidant activity.

Chapter Two

Experimental

2.The Experimental

2.1 .Analytical Techniques

2.1.1 Melting Point Measurement

The uncorrected melting points are expressed in degree (°C). They are Measured in the Department of Chemistry, College of Science, University of Thi-Qar ,Iraq, by used melting point / SMP3.

2.1.2 .FT-IR spectra

Was recorded, using Shimadzu affinity and BURKER FT-IR affinity spectrophotometer as KBr disks in the Department of Chemistry, College of Science , Thi-Qar University, Iraq . Only principal absorption bands of interest are reported and expressed in cm^{-1}.

2.1.3.^{1}H-NMR spectra

^{1}H-NMR spectra recorded, using BRUKER spectrophotometer (400 MHz) in the Department of Chemistry , University of Isfahan , Iran.The chemical shift values are expressed in δ(ppm), using tetramethylsilane (TMS)as internal standard and using d6-DMSO as a solvent.

2.1.4.^{13}C-NMR spectra

^{13}C-NMR spectra are recorded, using BRUKER spectrophotometer(125 MHz) in the Department of Chemistry , University of Isfahan , Iran.The chemical shift values are expressed in δ (ppm), using tetramethylsilane (TMS) as internal standard and using d_6-DMSO as a solvent.

2.1.5 .Mass spectra

Mass spectra are recorded by using Electron impact (EI) at 70eV using HPLC-LCQ Fleet /Thermo Scientific Mass spectrophotometer (ESI) in the Department of Chemistry, Tehran University, Iran.

2.1.6.Thin layer chromatography(TLC)

Thin layer chromatography(TLC) is performed using TLC grade silica gel 'G' (Acme Synthetic Chemicals)[75] . The spots are made visible by exposing plates to iodine vapor , and eluted with n- hexane :ethyl acetate 7:3 mixtures.

2.2. Chemicals Material

Table (2-1) represents the chemicals and their manufacturers:

Table (2-1) Chemicals

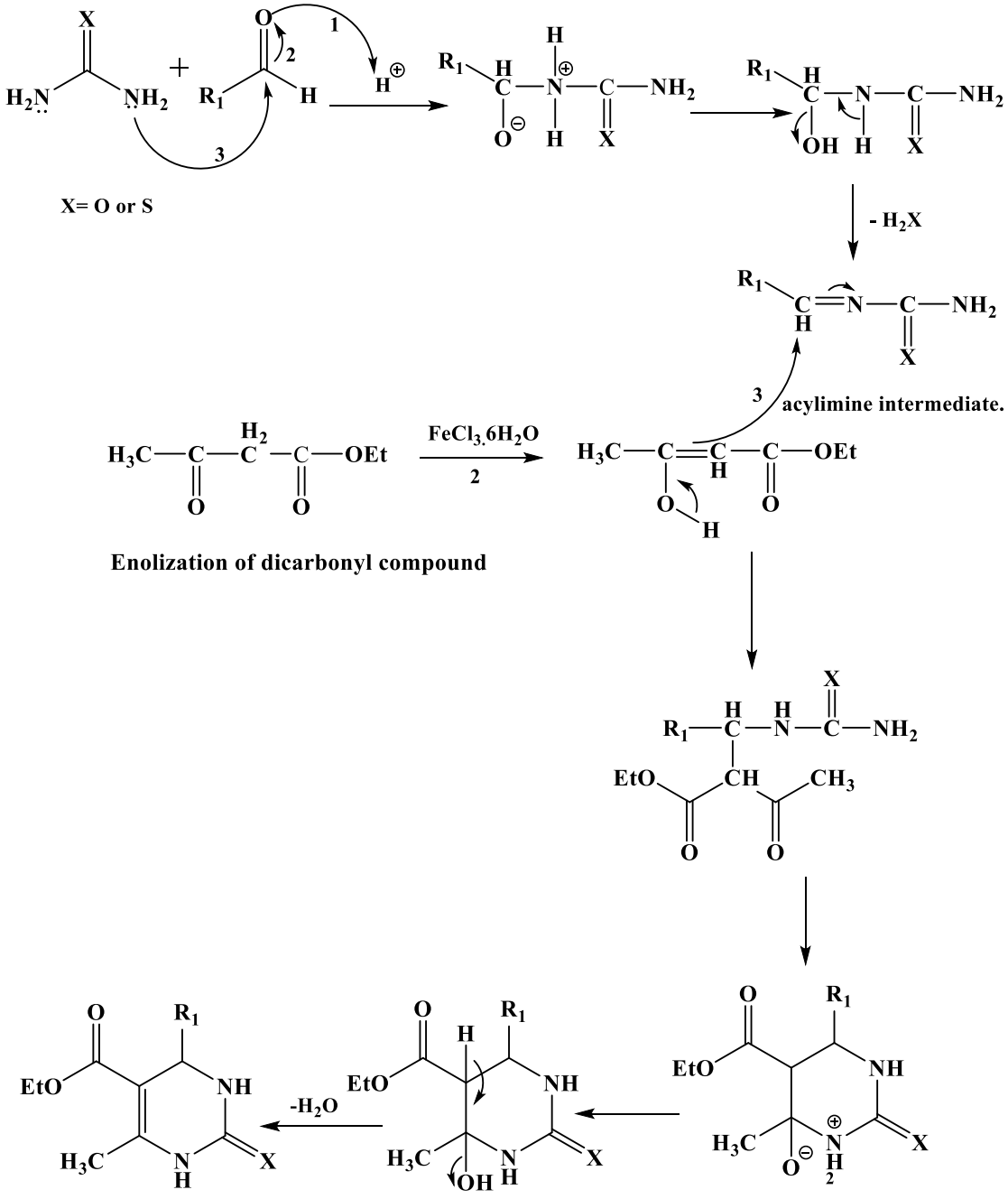
NO.	Material	Purity%	Company
1	*Ethyl acetate*	98	B.D.H
	n-Hexan	99	
	Ethylacetoacetate	99	
2	*TLC plates*		GCC
	Ethanol	99	
3.	*2-Nitrobenzaldehyde*	99	Aldrich
	2-Bromobenzaldehyde	98	
	4-Acetoamidobenzaldehyde	99	
	4-Aminoacetophenone	99	
	2-Hydroxy-1-naphthaldehyde	99	
	1-Naphthaldehyde	99	
	2-Chloroobenzaldehyde	99	
	Iodine		
4	*4-Ethoxybenzaldehde*	99	T.C.I
	Terephthalaldehyde	99	T.C.I
5	*Pyridinecarboxaldehyde*	99	Merck

2.2 :Synthesis of compound

2.2.1 :General Procedures for the synthesis of 3,4-Dihydropyrimidine -2(1H)-ones/thiones[76] 2(a-j) :

In general, the 3,4-dihydropyrimidinosderivatives 2(a-j) are synthesized by mixing of (0.01 or 0.02) mole of aldehyde and(0.01or 0.02) mole ethyl acetoacetate with(0.015 or 0.025) mole urea or thiourea in 25 ml of ethanol using(5mmole%) Ferrice chloride and 3-5 drops of HCl concentration as a catalyst. The reaction mixture is refluxed for(5-30) hrs and the progress of the reaction is monitored by TLC using hexane :ethyl acetate 7:3 as eluent . After the completion of the reaction then was cooled and washed with mixture ice cooled water and ethanol, the separated solid was filtered and dried in vacuum**,** finally recrystallized from ethanol to afford the desired product in pure form..**Table**(2-2)

The suggestion mechanism using thiourea[78] or Urea[79]



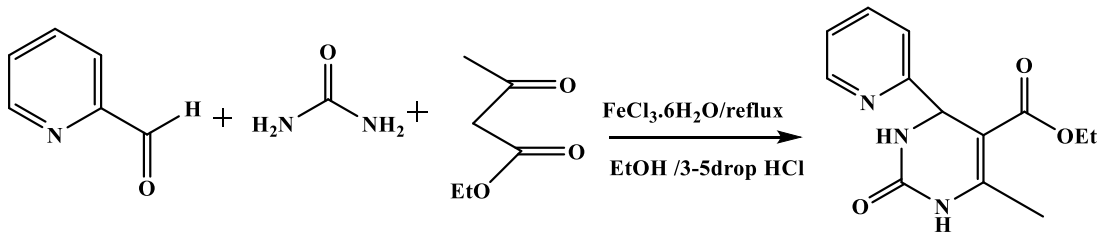
1: Formation of acylimine intermediate.

2: Enolization of dicarbonyl compound.

3: Formation of the dihydropyrimidinone.

2.2.1.1:ethyl-2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2a):

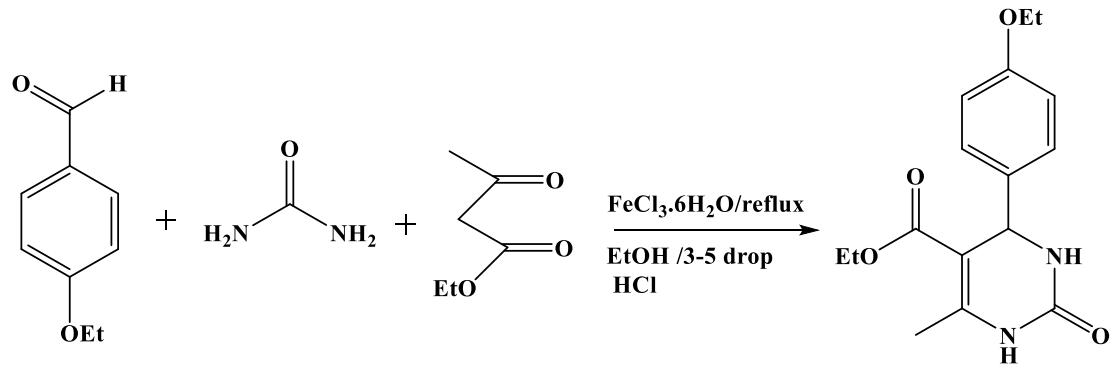
The compound is synthesized by reacting (1.9ml,0.02mol) of 2-Pyridine carboxaldehyde and(2.8ml,0.02mol) of ethyl acetoacetate with (1.5g,0.025) mol urea. Yield =71%,m.p=266-268^{O}C**,**time 8h.



2-Pyridine carboxaldehyde **2a**

2.2.1.2 :ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2b):

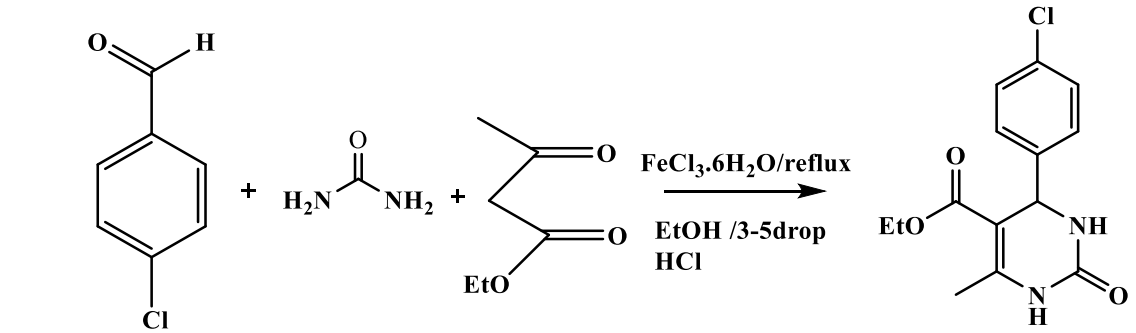
The compound is synthesized by reacting (1.4 ml,0.01mol) of 4-ethoxy benzaldehyde and(1.4 ml ,0.02 mol) of ethyl acetoacetate with (0.9 g ,0.015) urea . Yield =90%,m.p =190-191 ^{O}C, time 10h.



4-ethoxybenzaldehyde **2b**

2.2.1.3 :ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrop yrimidine-5-carboxylate (2c)[48]:

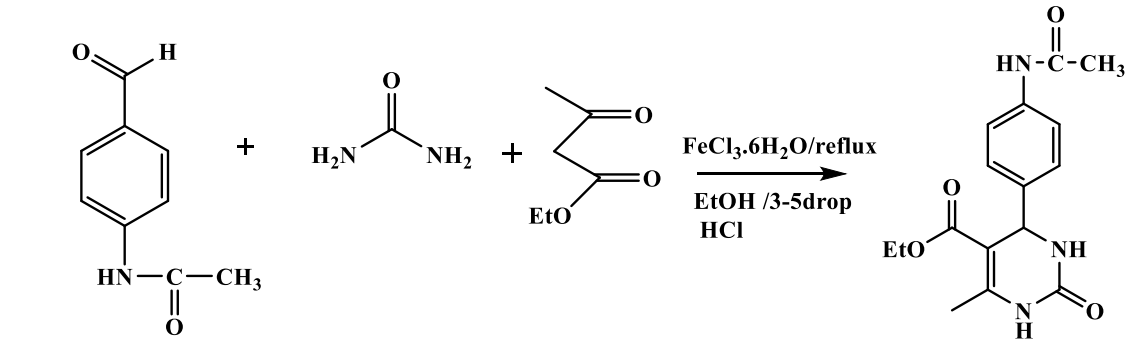
The compound is synthesized by reacting (1.4 ml,0.01mol) of 4-Chloro benzaldehyde and(1.4 ml ,0.02 mol) of ethyl acetoacetate with (0.9 g ,0.015) urea . Yield =88%,m.p =209-213 ^{O}C ,time 5h.



4-chlorobenzaldehyde 2c

2.2.1.4 :ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (2d) :

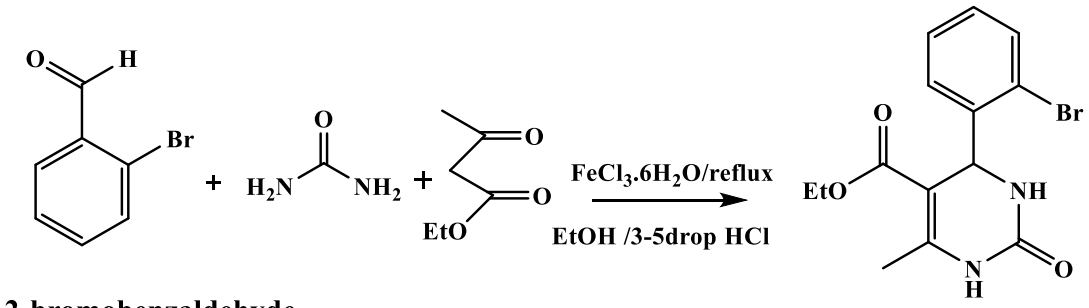
The compound is synthesized by reaction (1.63 g,0.01mol) of N-(4-formyl phenyl)acetamide and (1.4 ml ,0.01 mol) of ethyl acetoacetate with (0.9 g ,0.015) urea . Yield =75%,m.p =233-237 ^{O}C,time 30h .



***N*-(4-formylphenyl)acetamide** **2d**

2.2.1.5 :ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (2e)[65] :

The compound is synthesized by reaction (2.3 ml ,0.02mol) of 2-bromo benzaldehyde and (2.8 ml ,0.02 mol) of ethyl acetoacetate with (1.5 g, 0.025 mol) urea .Yield =86%,m.p =207-208 ^{O}C, time 22h.

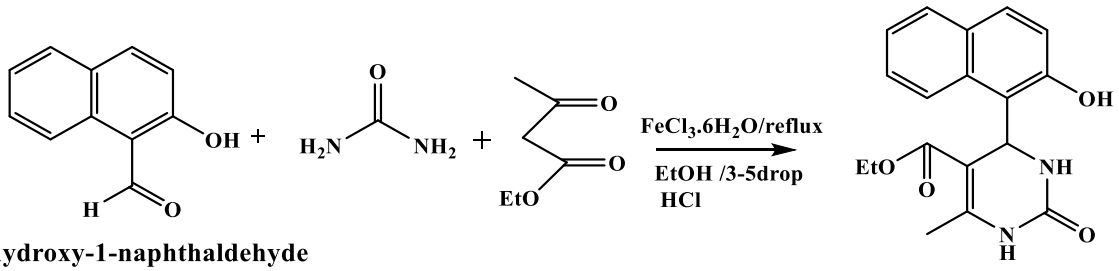


2-bromobenzaldehyde

2e

2.2.1.6:ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2f) :

The compound is synthesized by reacting (1.7 g ,0.01mol)of 2-hydroxy-1-naphthaldehyde and (1.4 ml ,0.01 mol) of ethyl acetoacetate with (0.9 g ,0.015) urea . Yield =89%, m.p = 255-257^{O}C,time 30 h .

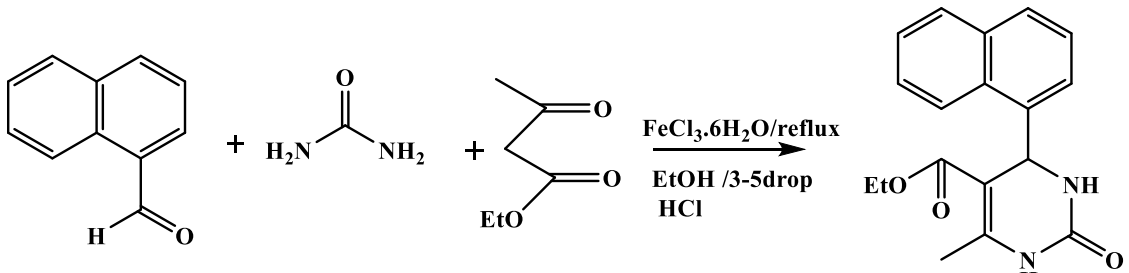


2-hydroxy-1-naphthaldehyde

2f

2.2.1.7:ethyl 6-methyl-4-(naphthalen-1-yl)-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate (2g) :

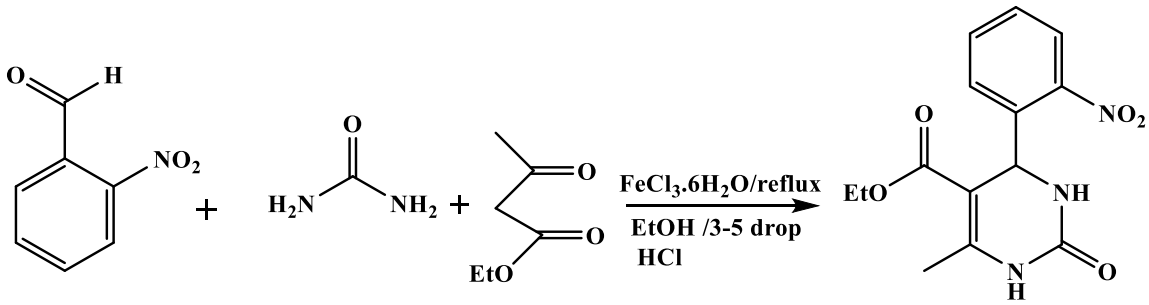
The compound is synthesized by reacting (1.35 ml ,0.01mol) of1-naphth aldehyde and (1.4 ml ,0.01 mol) of ethyl acetoacetate with (0.9 g ,0.015) urea . Yield =80%,m.p =244-246^{O}C,time 24 h.



1-naphthaldehyde **2g**

2.2.1.8:ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate(2h):[48,58]

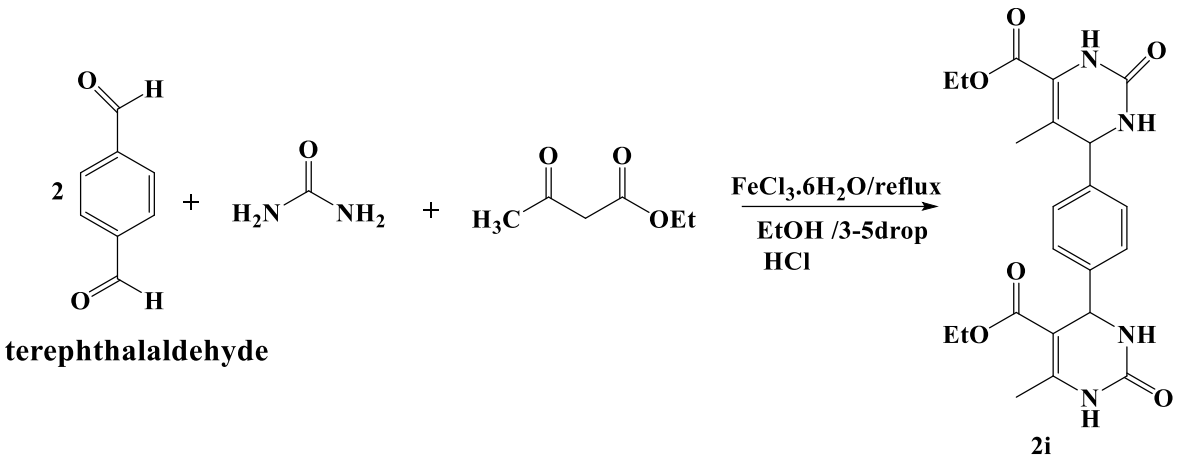
The compound is synthesized by reacting(3.02g ,0.02mol) of 2-nitro benaldehyde and(2.8ml,0.02mol) of ethyl acetoacetate with(1.5g, 0.025mol) urea .Yield =63%, m.p =209-210^{O}C,time 24 h.



2-nitrobenzaldehyde **2h**

2.2.1.9 :diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate)(2i) :

The compound is synthesized by reaction (1.34 g,0.01 mol)of terephthal aldehyde and (2.8ml ,0.02 mol) of ethyl acetoacetate with (1.8g ,0.03) urea . Yield =90% ,m.p =>300 ^{O}C, time 12 h.

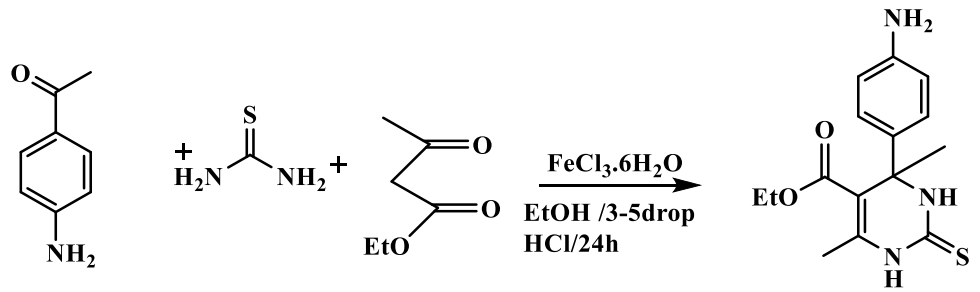


terephthalaldehyde

2i

2.2.1.10:4-(4-aminophenyl)-5-(ethoxymethyl)-4,6-dimethyl-3,4-dihydro pyrimidine-2(1H)-thione(2j):

The compound is synthesized by reacting (2.7g,0.02mol) of 4-aminoaceto phenone and (2.8ml,0.02mol) of ethyl acetoacetate with (1.9 g ,0.025 mol) thiourea .Yield =55%,m.p=250-252 ^{O}C, time 24 h.



1-(4-aminophenyl)ethan-1-one

2j

Table(2-2): Physical properties of 3,4-Dihydropyrimidine -2(1H)-ones/thioes

No.	Comps.	Yield (%)	M.p.(°C)	Colour	Solvent of recrystalization
1	2a	71	266-268	Dark brown	Ethanol
1	2b	90	190-191	White	Ethanol
2	2c	88	209-213	White	Ethanol
3	2d	75	233-237	Yellow	Ethanol
5	2e	86	207-208	Brown	Ethanol
6	2f	89	255-257	Brown	Ethanol
7	2g	80	244-246	Brown	Ethanol
8	2h	63	209-210	Yellow	Ethanol
9	2i	90	>300	White	Ethanol
10	2j	55	250-252	Dark brown	Ethanol

2.2.2:Antioxidant activity

DPPH radical scavenging activity :

The scavenging effect on the DPPH radical was determined according to the methods developed by Gangwar and Kasana (2012). Methanolic solutions of 1,000 ppm concentration of each DHPMs derivative were prepared. Varying amounts(10, 15, 20, and 25μl) of each methanolic solution of DHPMs derivatives were taken in separate test tubes containing 5ml of 0.004% methanolic solution of DPPH. All the test solutions were prepared in triplicate. The mixtures were shaken vigorously and placed in dark for until stable values were obtained . The absorbance of the samples was measured at 517 nm. The percent DPPH radical scavenging activity of each sample and standard was calculated using following equation:

% DPPH radical scavenging activity = $[1 - (A_t / A_o)] \times 100$

where, A_t is the absorbance of the sample, and A_o is the absorbance of the control. Mean values from three independent samples were calculated for each compound and Butylated hydroxyl toluene (BHT) were used as standards[77].

Chapter Three

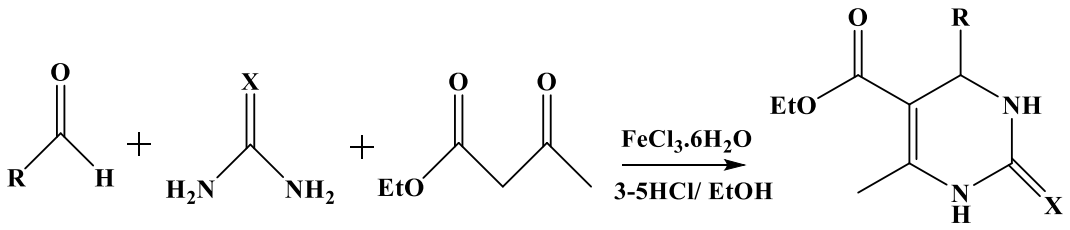
Results & Discussion

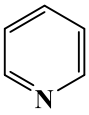
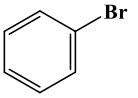
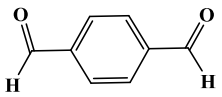
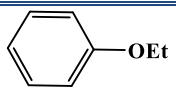
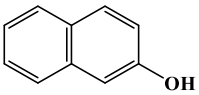
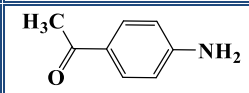
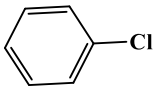
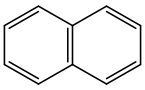
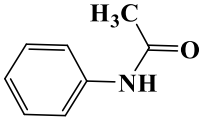
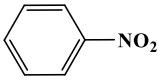
3.General Results and Discussion :

The chemical structures of 3,4-Dihydropyrimidine -2(1H)- ones/ thione as shown in **Table (3-1)** .All the newly synthesized derivatives are assigned on the basis of their FT- IR ,^{1}H- NMR , ^{13}C – NMR, ^{13}C- NMR DEPT and Mass Spectra.

3.1: 3,4-Dihydropyrimidine -2(1H)-ones/thione compound :

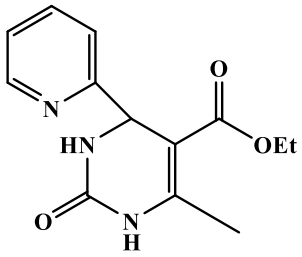
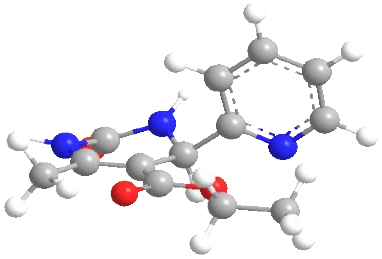
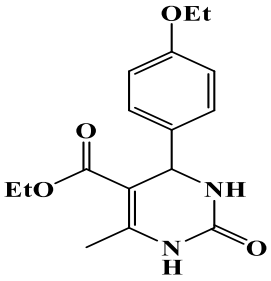
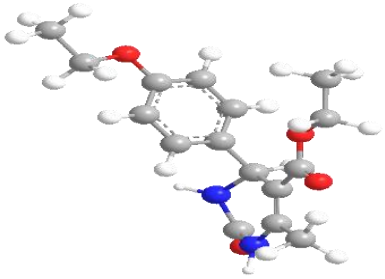
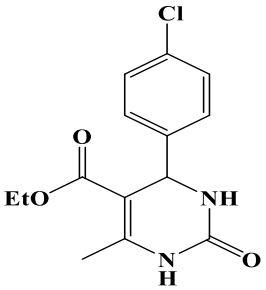
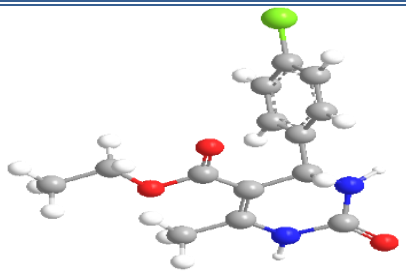
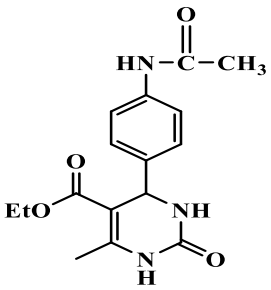
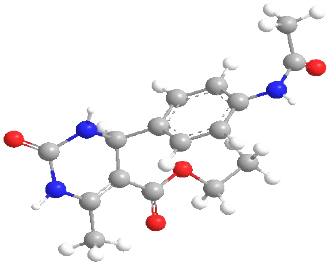
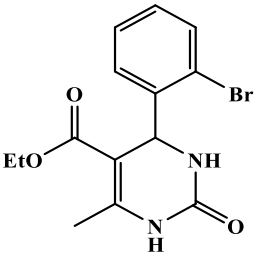
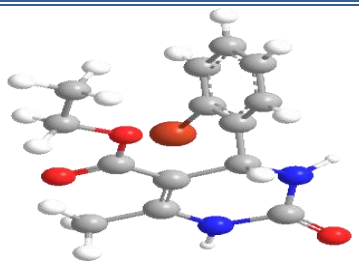
3,4-Dihydropyrimidine-2(1H)-ones/thione**2(a-i)** are Synthesis by the reaction of a selected aldehyde and urea or thiourea with ethyl acetoacetate in the presence of Ferrice chloride and some drops from HCl as a catalyst and ethanoal as a solvent .shown scheme 3-1 .

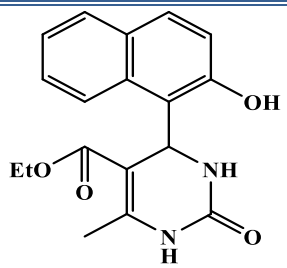
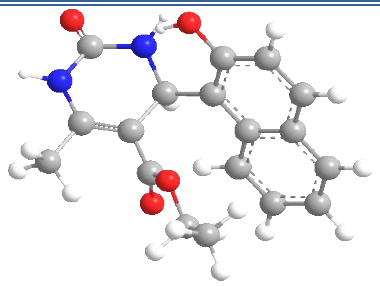
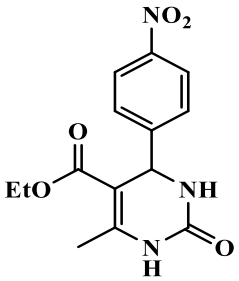
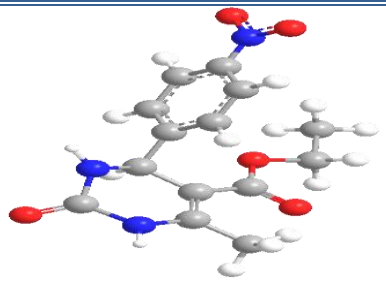
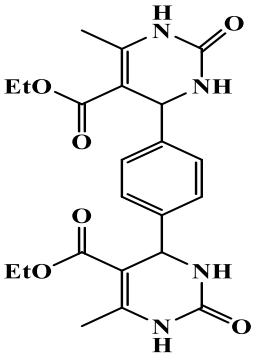
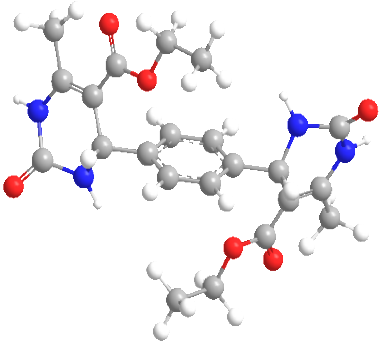
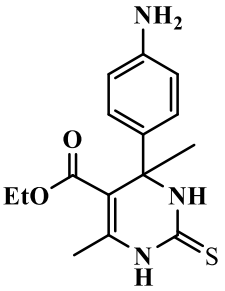
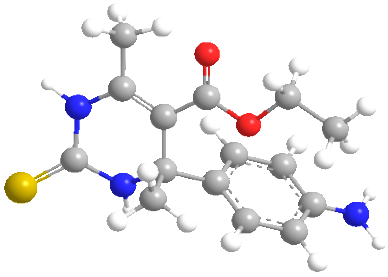


No.	*R*	*X*	*No.*	*R*	*X*	*No*	*R*	*X*
2a		O	**2e**		O	**2i**		O
2b		O	**2f**		O	**2j**		S
2c		O	**2g**		O			
2d		O	**2h**		O			

Scheme 3-1

Table(3-1):*The chemical Structures of the3,4- Dihydropyrimidine- 2(1H)ones/Thione*

Comp.	Molecular formula	Structure formula	Structure three dimension
2a	$C_{13}H_{15}N_3O_3$ **M.Wt**=261		
2b	$C_{16}H_{20}N_2O_4$ **M.Wt** =304		
2c	$C_{14}H_{15}ClN_2O_3$ **M.Wt**=294		
2d	$C_{16}H_{19}N_3O_4$ **M.Wt** =317		
2e	$C_{14}H_{15}N_2BrO_3$ **M.Wt**=339		

2f	$C_{18}H_{18}N_2O_4$ **M.Wt** =326		
2g	$C_{14}H_{15}N_3O_5$ **M.Wt** =305		
2h	$C_{22}H_{26}N_4O_6$ **M.Wt** =442		
2i	$C_{15}H_{19}N_3O_2S$ **M.Wt** =305		

3.2: Infrared (IR) spectra of 3,4-Dihydropyrimidine-2(1H)-ones/ thione

IR spectra of the 3,4-Dihydropyrimidine-2(1H)-ones /thione ,as KBr disc and representative spectra are shown in **table (3-2)**,The IR spectra of 3,4-Dihydropyrimidine-2(1H)-ones /thione 2(a-i) are characterized by the seven bands corresponding to the stretching vibration of the aromatic C-H ,aliphatic C-H , carbonyl group(O-C=O ,HN-C=S,HN-C=O), N-H amide and alkene) which occurs within the ranges at[3062-3194 ,2978-2985,(1658-1728,1180-1273,1627-1666),3194-3441,1442-1582][80,81] respectively.

Table(3-2) :*FT-IR spectra of3,4-Dihydropyrimidine -2(1H)- ones/thione*

Comp.	NH Amide	Aromatic C-H	Aliphatic C-H	C=O Ester	C=OAmide C=S Thio amide	C=C Aromatic
2a	3232*w*	3109*w*	2985*w*	1712*m*	1666 *s*	1481*m*
2b	3235*m*	3114*w*	2980*w*	1713*s*	1648*s*	1466*w*
2c	3237 *w*	3122*w*	2980 *w*	1726 *s*	1650 *s*	1582 *s*
2d	3127*s*, 3194*s*	3072*s*	2982;*m*	1697*s*	1640*s*	1510*s*
2e	3224s, 3348s	3116 *s*	2978 *s*	1712*w*	1635*w*	1458*m*
2f	3340*w*	3062*w*	2985*w*	1728*w*	1627*m*	1465*w*
2g	3371*s*, 3240*m*	3132*s*	2978*s*	1712*s*	1651*s*	1450*s*

Comp.	NH Amide	Aromatic C-H	Aliphatic C-H	C=O Ester	C=OAmide C=S Thioamide	C=C Aromatic
2h	3310*m* 3249*w*	3122*w*	2981*w*	1707*w*	1651*w*	1448*m*
2i	3302*w*	3194*w*	2978*w*	1674*s*	C=S 1180*s*	1445s

w: weak. m: medium. s: strong.

3.3:[1]H-NMR spectral analysis of 3,4-Dihydropyrimidine-2(1H) ones :

[1]H-NMR spectral data of the 3,4-Dihydropyrimidine-2(1H)-ones are included in .**Table (3-3)** and their expanded spectra are shown in Figures **(3-1,3-17)** and all spectra showed two signals at 2.5 ppm and 3.3 attribute to d_6-DMSO and D_2O ,respectivity.

***[1]H-NMR** spectrum of **ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydro pyrimidine -5-carboxylate (2a)**.Shows triplet signal at (1.08 ppm)[81]δ for three protons (t,3H,C_{10}- H) ,singlet signal at (2.23 ppm)[82] δ for three protons (s,3H,C_7- H) and quartet signal at (3.98ppm) δ for two protons(q,2H,C_9-H) ,The (C_4) return for 3,4-Dihydropyrimidine ring it a chiral carbon gives racemic mixture (R,S) configuration (enantiomers) show at (δ 5.22 ppm)[83],as shown in figure 3-1.

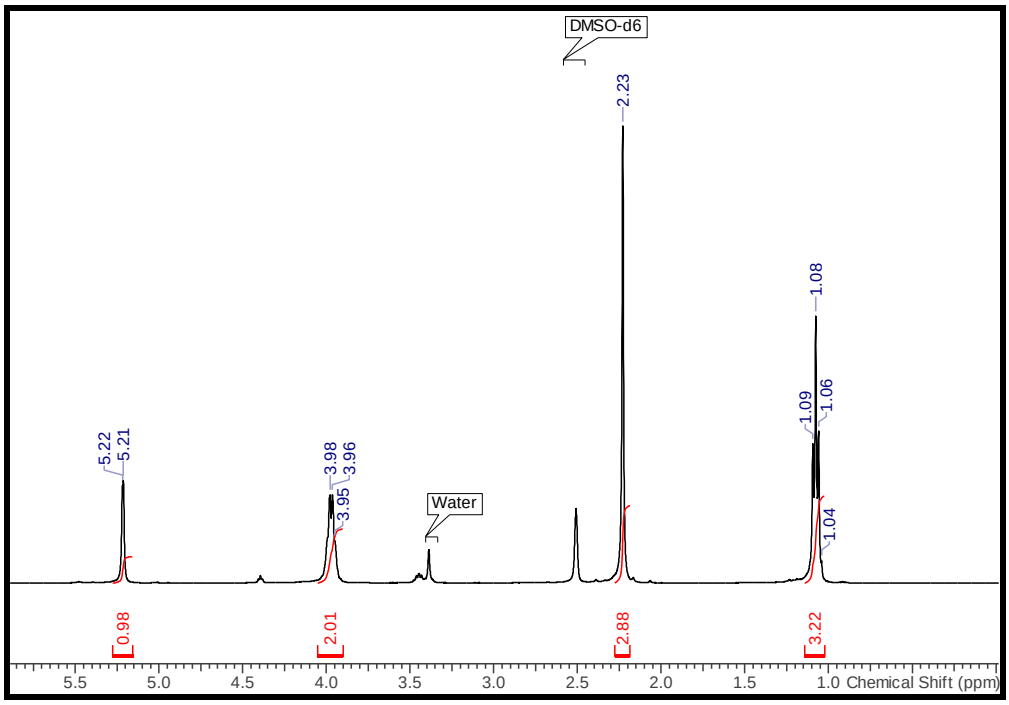


Figure 3-1: ^{1}H-NMR spectrum expanded of **2a.**

The ring of pyridine shows multiplet signal at(7.23–7.76 ppm)[81]δ for four proton ,finally it shows singlet signal at chemical shift (8.52 ppm) δ for N_3- H and singlet signal at (9.18 ppm)[84] δ for second N_1-H, can be seen in figure 3-2.

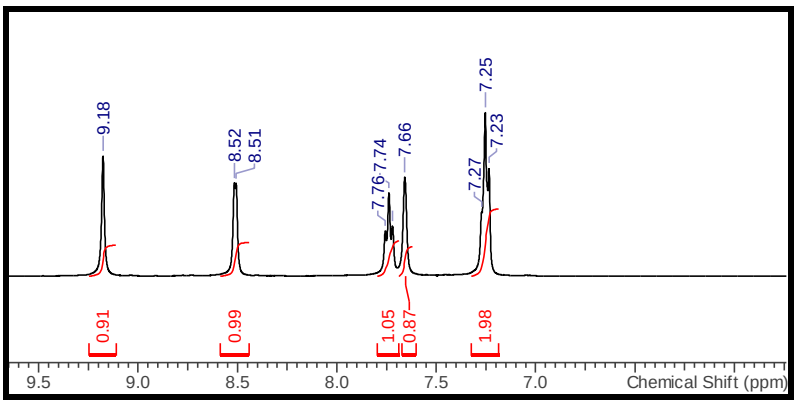
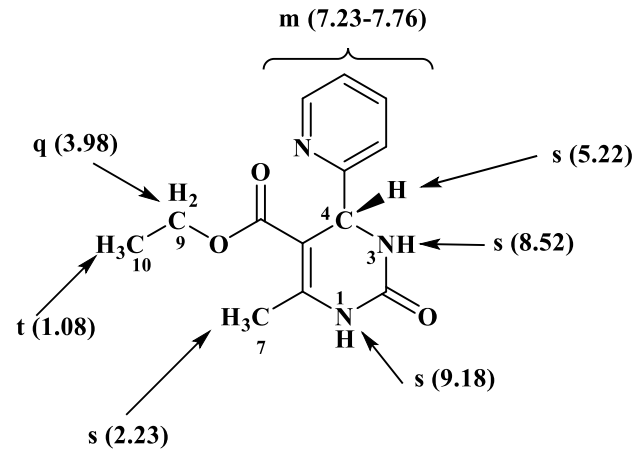
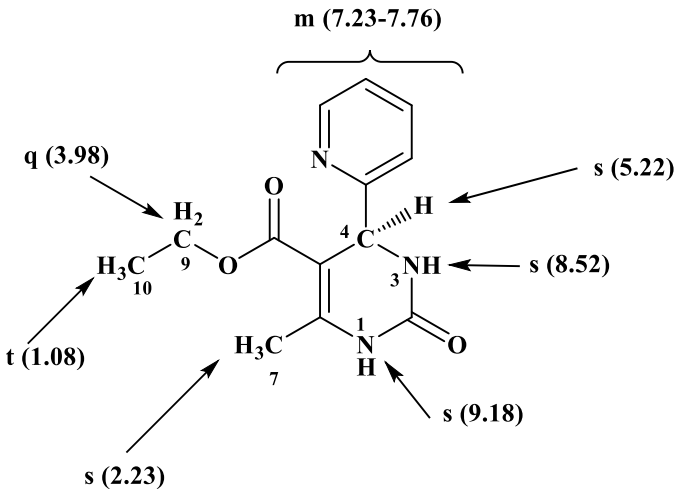


Figure 3-2: ^{1}H-NMR spectrum expanded of **2a.**



R configuration (Major)



S configuration (Minor)

***^{1}H-NMR** spectrum of **ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2b)** shows triplet signal at (1.1ppm)[85] δ for three protons (t,3H,C_{10}- H) and methyl group gives triplet signal at (1.30 ppm)[81] δ, as shown in figure 3-3.

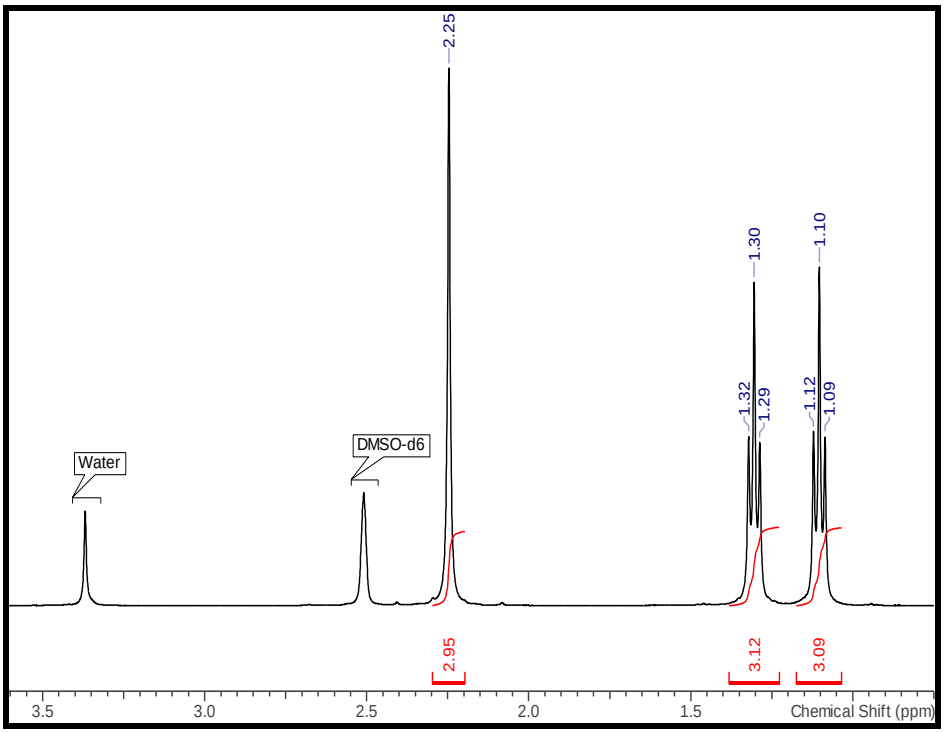


Figure 3-3: ^{1}H-NMR spectrum expanded of **2b.**

[OCH_2] group shows quartet signal at (3.98ppm)[85] δ for four protons. The (C_4) return for 3,4-Dihydropyrimidine ring it a chiral carbon gives racemic mixture (R,S) configuration appeared at (δ 5.09 ppm) δ .Phenyl ring shows doublet of doublet signal return to four proton at (6.85-7.15ppm) δ , finally it show singlet signal at chemical shift (7.7ppm) δ for N_3- H and singlet signal at (9.19 ppm) δ for second N_1-H ,as shown in figure 3-4, 3-5.

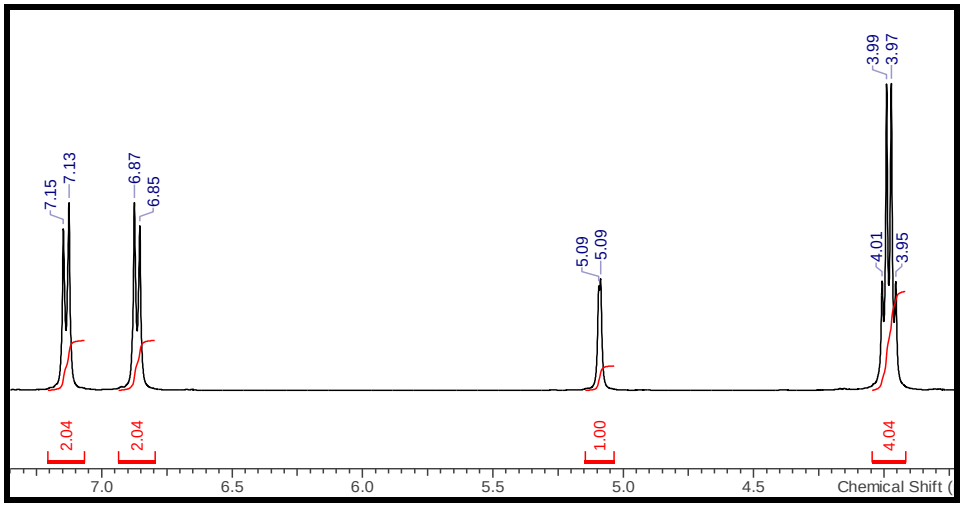


Figure 3-4: ^{1}H-NMR spectrum expanded of **2b.**

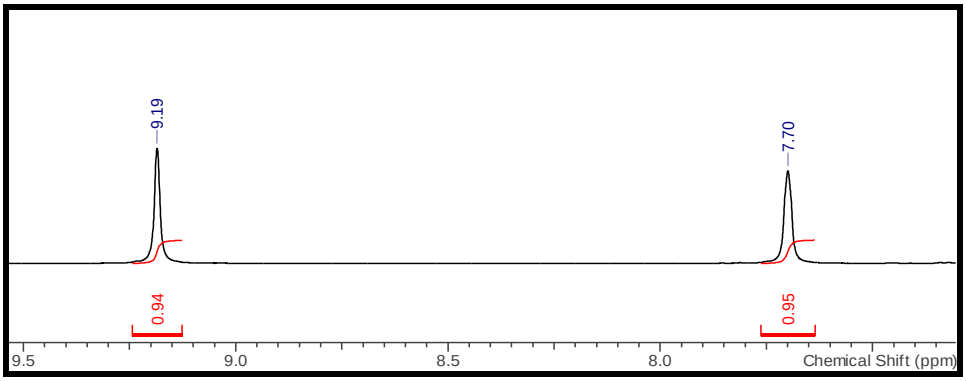


Figure 3-5: ^{1}H-NMR spectrum expanded of **2b.**

***^{1}H-NMR** spectrum of **ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3, 4-tetrahydropyrimidine-5-carboxylate(2c)** shows triplet signal at (1.09 ppm) δ for three protons (t,3H,C_{10}- H) ,singlet signal at (2.26 ppm) δ for three protons (s,3H,C_{7}- H) and quartet signal at (4.01ppm) δ for two protons(q,2H,C_{9}-H).The (C_{4}) return for 3,4-Dihydropyrimidine ring it a chiral carbon gives racemic mixture (R,S) configuration (enantiomers) show at (δ 5.16ppm), as shown in figure 3-6.

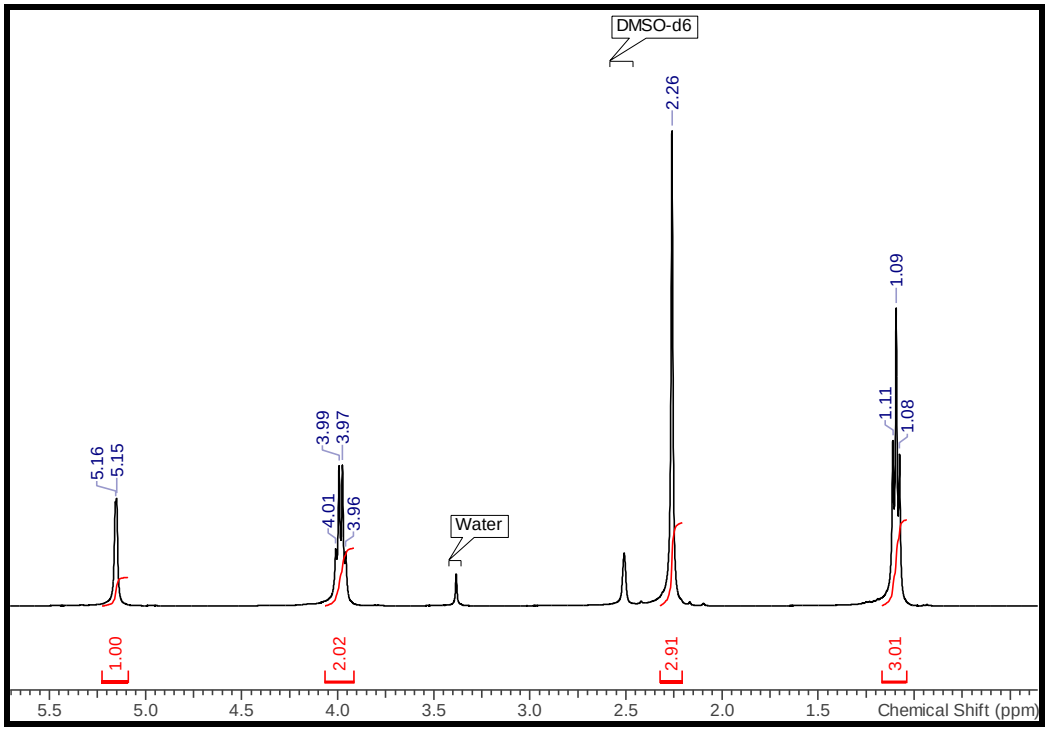


Figure 3-6: ^{1}H-NMR spectrum expanded of **2c.**

Phenyl ring shows doublet ,doublet signal return to four proton at (7.25-7.41ppm) δ ,finally it show singlet signal at chemical shift (7.81ppm) δ for N_3- H and singlet signal at (9.29 ppm) δ for second N_1-H as shown in figure 3-7.

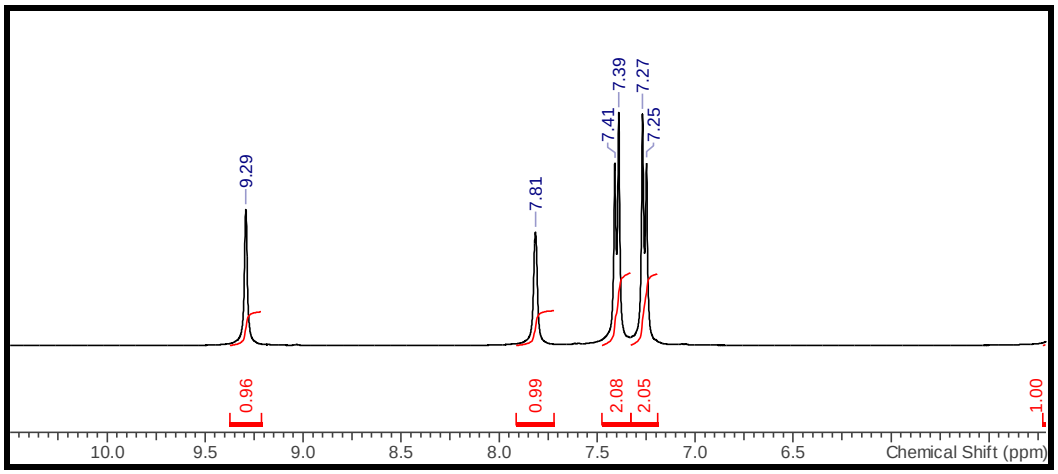


Figure 3-7: ^{1}H-NMR spectrum expanded of **2c.**

***^{1}H-NMR** spectrum of **ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2d).** shows triplet signal at δ (1.1ppm) for three protons (t,3H,C_{10}- H) ,singlet signal at (2.02 ppm) δ for three protons (s,3H,C_7- H) and quartet signal at (3.98ppm) δ for two protons(q,2H,C_9-H) ,in addition a singlet signal at(2.24ppm) δ for three proton of methyl group (s,3H,CH_3-C=O),The3,4-Dihydropyrimidine ring for (C_4) show at (5.09 ppm) δ, as shown in figure 3-8.

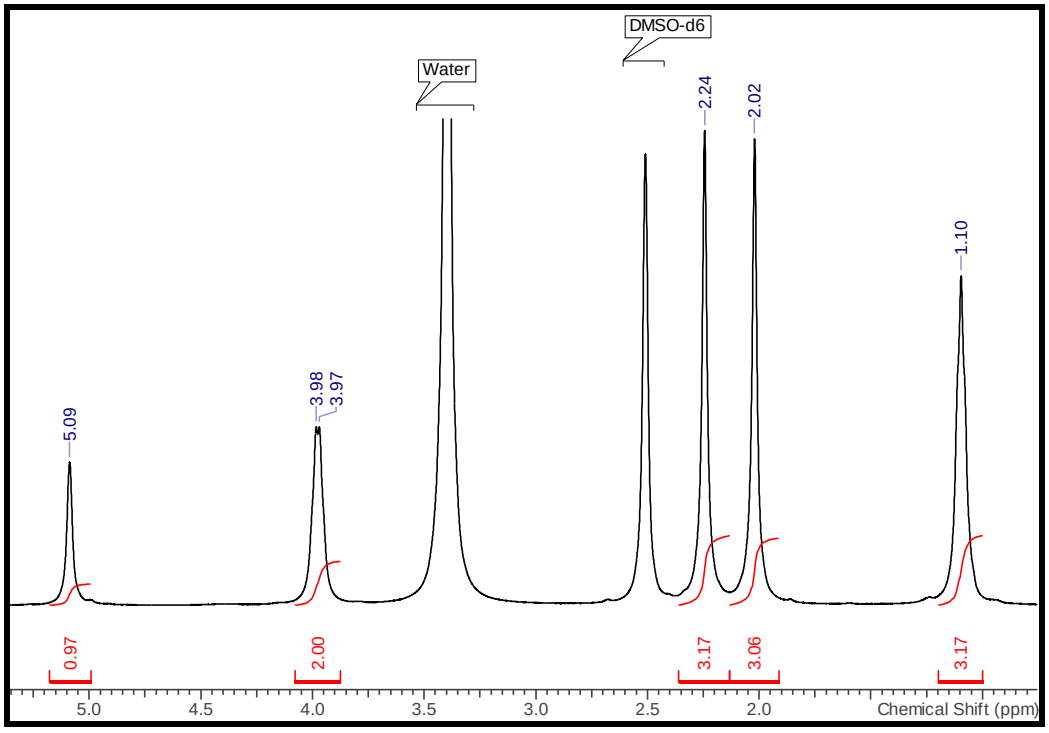


Figure 3-8: ^{1}H-NMR spectrum expanded of **2d.**

Phenyl ring shows doublet , doublet signal return to four proton at (7.14-7.5ppm) δ, and singlet signal at chemical shift (7.71ppm) δ for N_3- H and singlet signal at (9.19 ppm) δ for second N_1-H, finally it shows singlet signal at (9.95 ppm) δ for one proton of amide carbon. See figure 3-9.

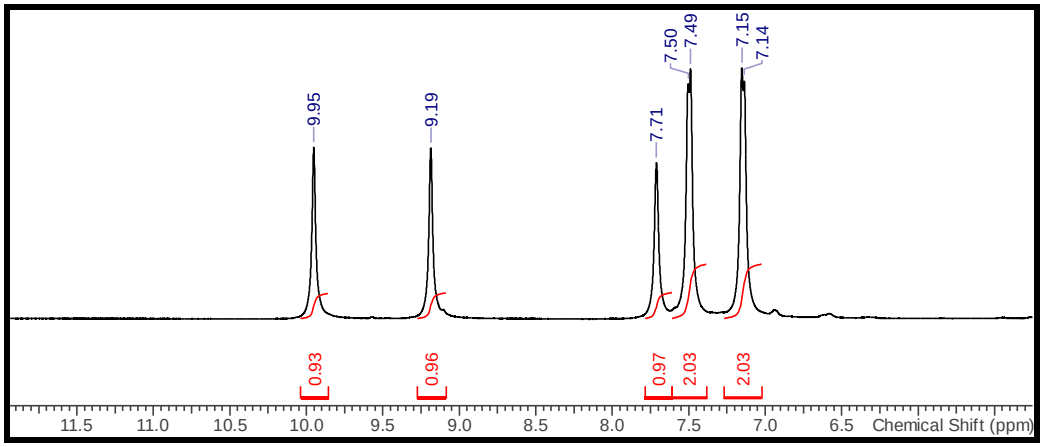


Figure 3-9: ^{1}**H-NMR** spectrum expanded of **2d.**

***^{1}H-NMR** spectrum of **ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3, 4-tetrahydropyrimidine-5-carboxylate(2e)**.Shows triplet signal at (1.0 ppm) δ for three protons (t,3H,C_{10}- H) ,singlet signal at (2.32 ppm) δ for three protons (s,3H,C_7- H) and quartet signal at (3.91ppm) δ for two protons(q,2H,C_9-H) and the (C_4) of 3,4-Dihydropyrimidine ring gives singlet signal at (5.63ppm) δ, as shown in figure 3-10.

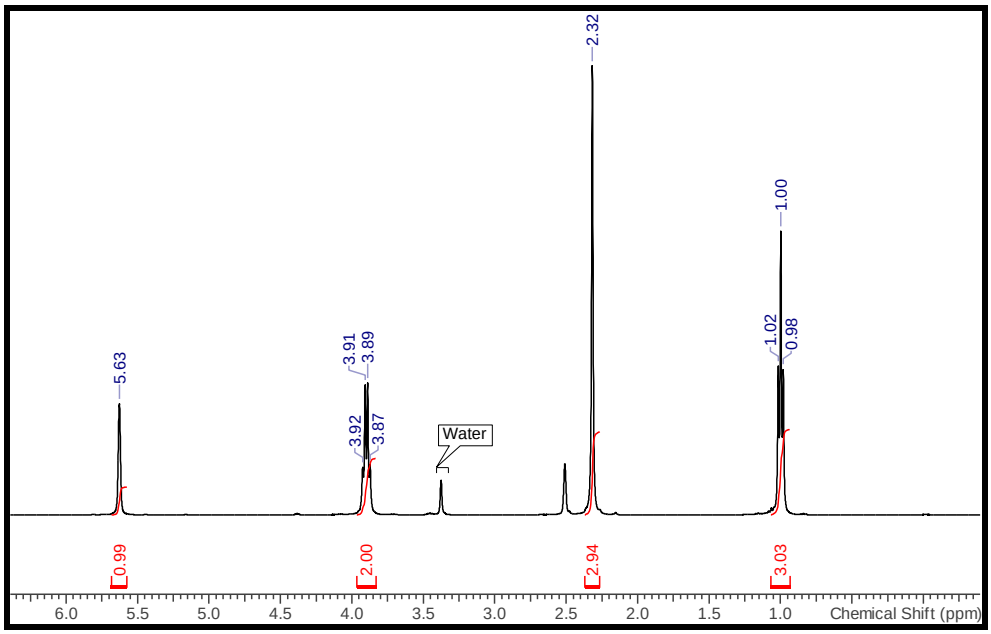


Figure 3-10: ^{1}**H-NMR** spectrum expanded of **2e.**

Phenyl ring shows multiplet signal at (7.17-7.59ppm) δ for four protons ,and singlet signal at (7.74ppm)[86] δ for N_3- H and singlet signal at (9.32ppm) δ for second N_1-H, as shown in figure 3-11.

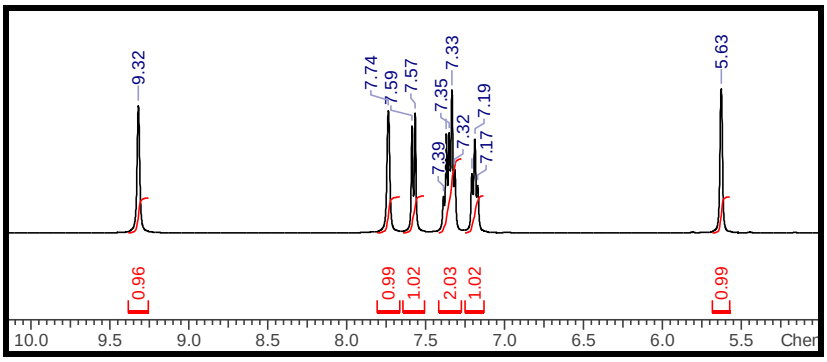


Figure 3-11: ^{1}H-NMR spectrum expanded of **2e.**

***^{1}H-NMR** spectrum of **ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2f).** Shows triplet signal at δ (1.28ppm) for three protons (t,3H,C_{10}- H) ,singlet signal at (1.8 ppm) δ for three protons (s,3H,C_7- H) and quartet signal at (4.21ppm) δ for two protons(q,2H,C_9-H) and the (C_4) of 3,4-Dihydropyrimidine ring gives singlet signal at (5.07ppm) δ, naphthalen-1-yl ring show multiplet signal at (7.04-7.96ppm) δ for sex protons ,also shows singlet signal at (9. 3ppm) δ for N_3- H and singlet signal at (9.7ppm) δ for second N_1-H ,in addition appeared singlet signal at (10.5ppm)[87] δ return to one proton for hydroxyl group ,as shown in figure 3-12 , 3-13.

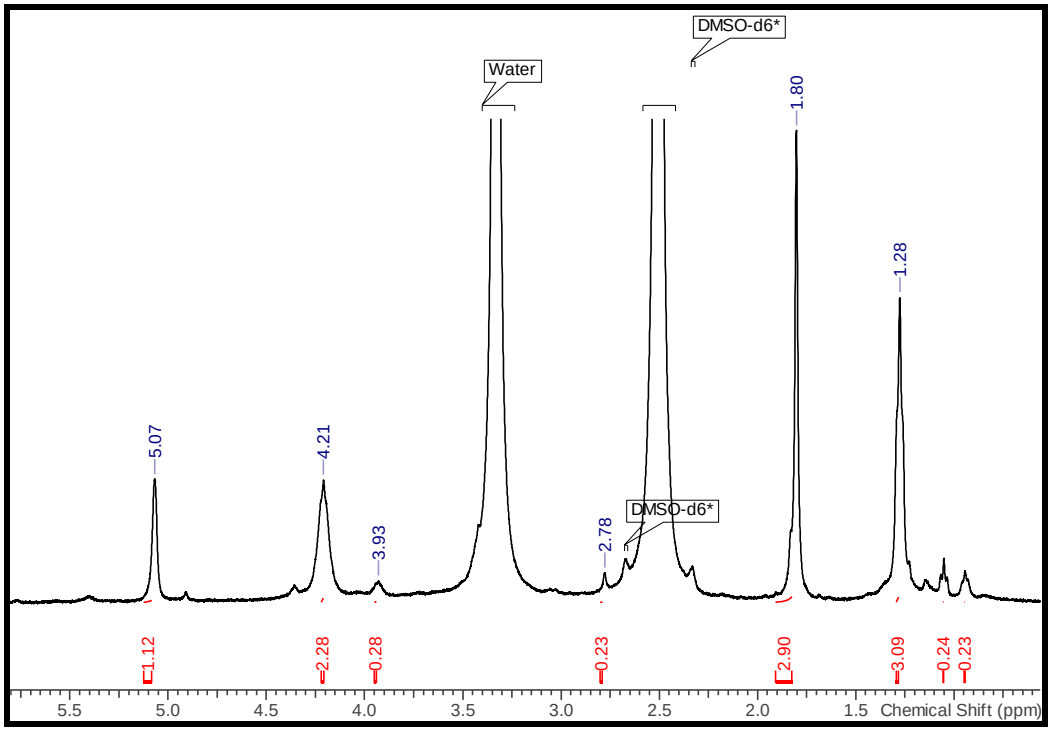


Figure 3-12: ^{1}H-NMR spectrum expanded of **2f.**

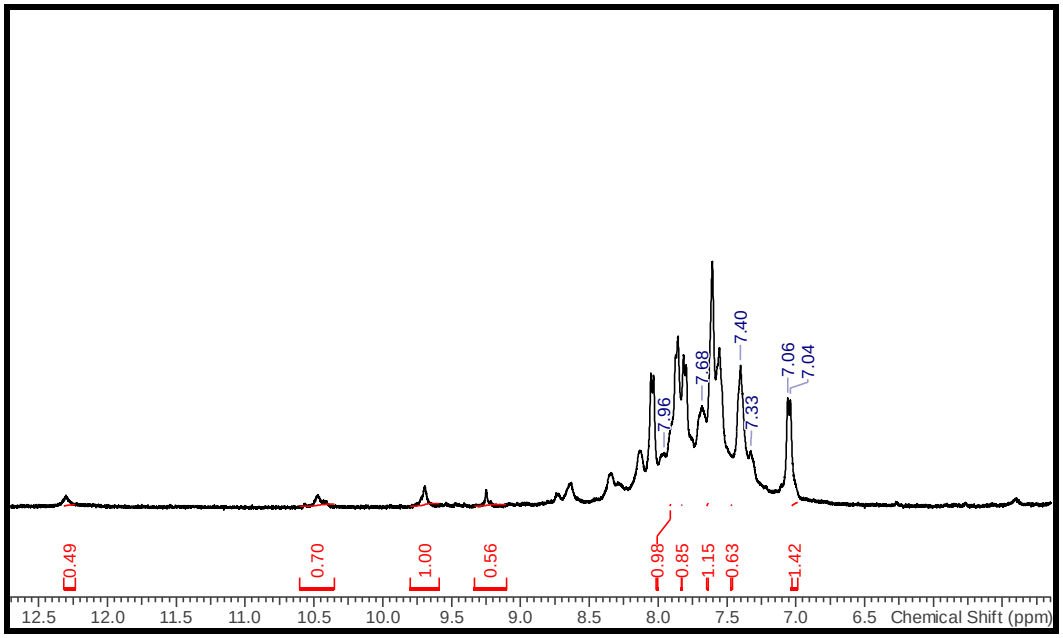


Figure 3-13: ^{1}H-NMR spectrum expanded of **2f.**

***^{1}H-NMR** spectrum of **ethyl 6-methyl-4-(2-nitro phenyl)-2-oxo-1,2,3,4 -tetrahydropyrimidine-5-carboxylate (2g)**. shows triplet signal at δ (0.92ppm) for three protons (t,3H,C_{10}- H) ,singlet signal at (2.29 ppm) δ for three protons (s,3H,C_7- H) and quartet signal at (3.36ppm) δ for two protons(q,2H,C_9-H), the (C_4) of 3,4-Dihydropyrimidine ring gives singlet signal at (5.85ppm) δ, as shown in figure 3-14.

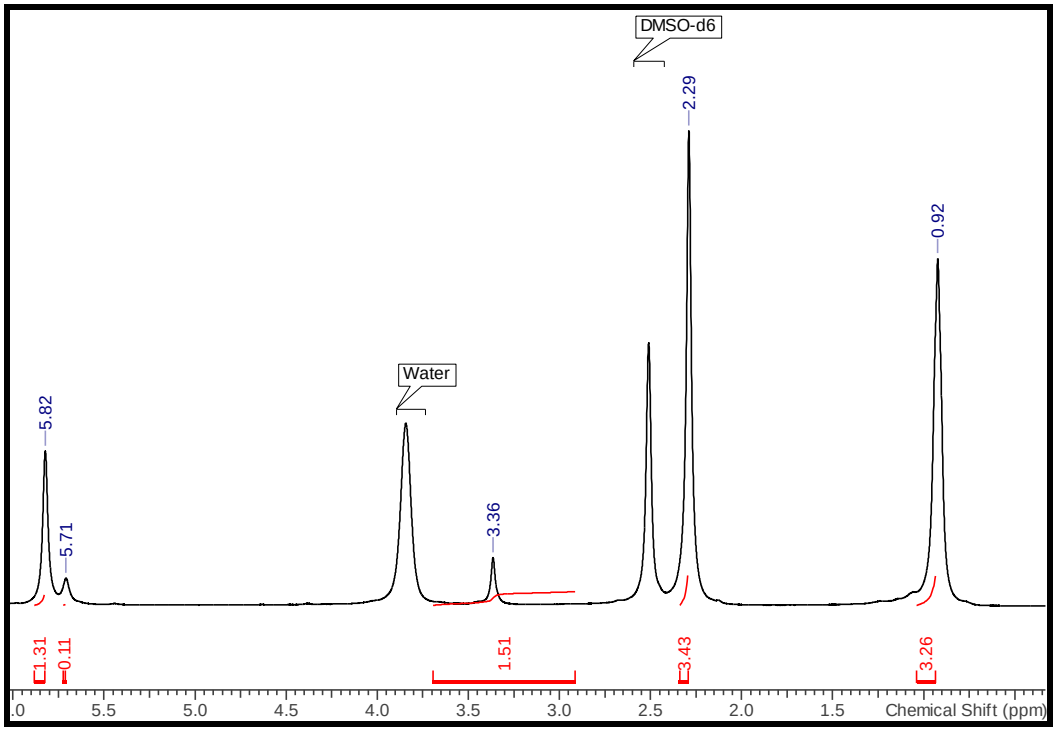


Figure 3-14: ^{1}H-NMR spectrum expanded of **2g.**

Phenyl ring shows doublet , doublet signal return to four proton at (7.52-7.79ppm) δ, and singlet signal at chemical shift (7.9ppm) δ for N_3- H and singlet signal at (9.42 ppm) δ for second N_1-H, as shown in figure 3-15.

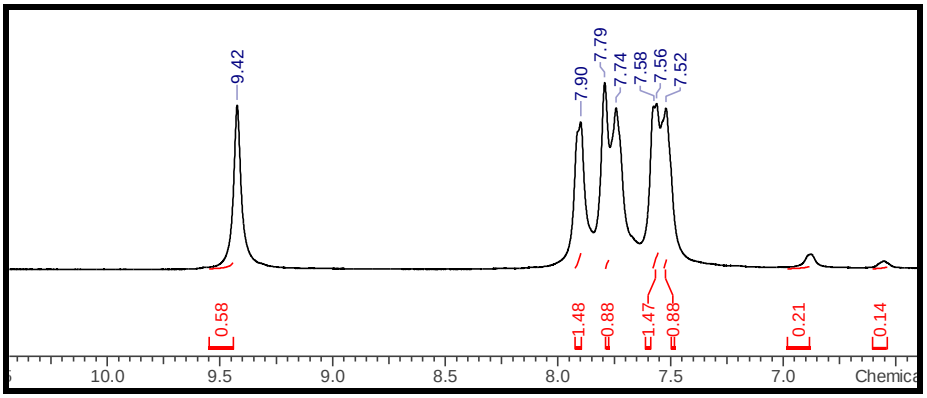


Figure 3-15: ^{1}H-NMR spectrum expanded of **2g.**

***^{1}H-NMR** spectrum of **diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate)(2h)**.shows triplet signal at (1.07ppm) δ for sex equivalent protons (t,6H,C_{10}- H) ,singlet signal at (2.21 ppm) δ for sex equivalent protons (s,6H,C_7- H) and quartet signal at (3.95ppm) δ for four protons(q,4H,C_9-H) and the (C_4) of 3,4-Dihydropyrimidine ring gives singlet signal at (5.08ppm) δ for two equivalent protons (s,2H,C_4-H) , as shown in figure 3-16.

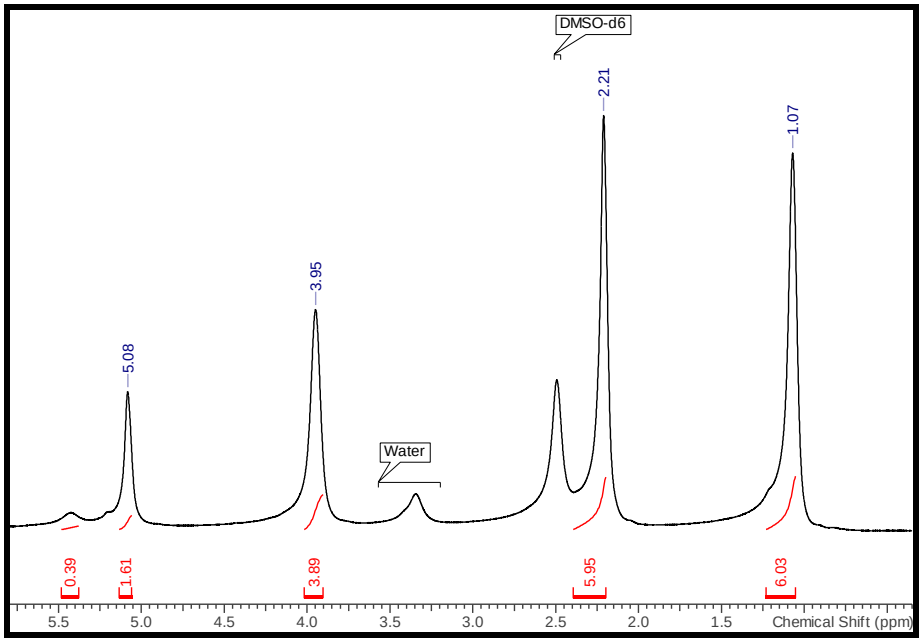


Figure 3-16: ^{1}H-NMR spectrum expanded of **2h.**

Phenyl ring shows doublet , doublet signal return to four proton at (7.15ppm) δ, singlet signal at (7.96ppm) δ for two equivalent protons N_3-H and singlet signal at (9.42 ppm) δ for tow equivalent protons N_1-H, as shown in figure 3-17.

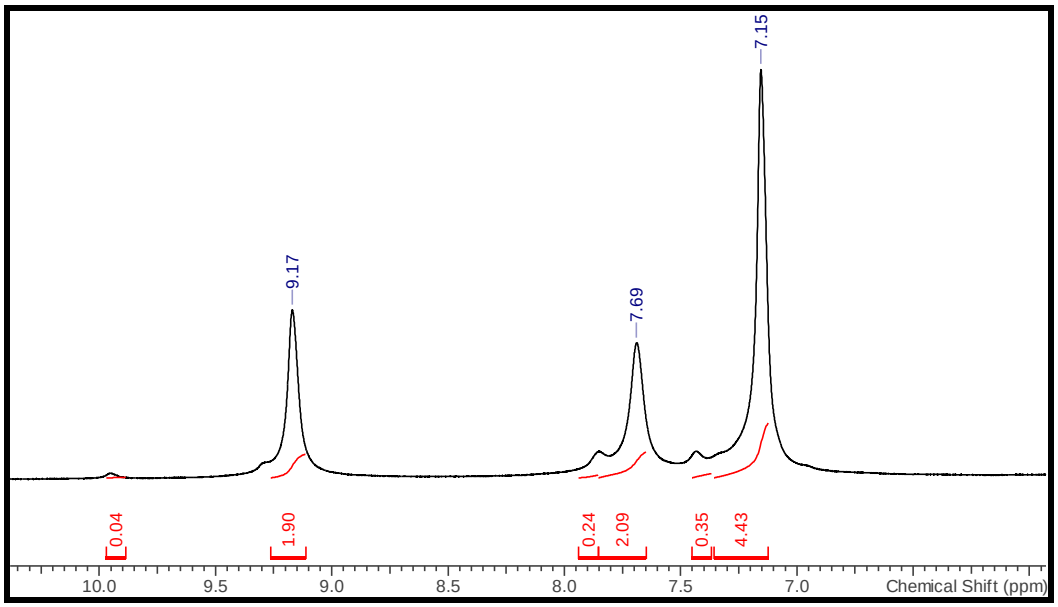


Figure 3-17: ^{1}H-NMR spectrum extension of **2h.**

Tables 3-3: *^{1}H-NMR signals of3,4-Dihydropyrimidine -2(1H)-ones/thione*

Comp	Chemical shift ppm		
	Aliphatic protons	Aromatic protons	Other protons
2a	1.08 (t,3H, -CH_3) 2.23(s,3H.CH_3) 3.98 (q,2H,CH_2 -O)	7.23-7.25 7.27 – 7.66 7.74 -7.76	8.52 (s,1H ,NH) 9.18 (s ,1H ,NH) 5.22 (s,1H,CH)
2b	1.1(s,3H, -CH_3) 1.30 (t,3H, -CH_3) 2.25 (t,3H, -CH_3) 3.99 (q,2H,CH_2 -O) 4.01 (q,2H,CH_2 –O)	6.85 -6.87 7.13 -7..15	7.70 (s,1H ,NH) 9.19(s ,1H ,NH) 5.09(s,1H,CH)
2c	1.09(t,3H, -CH_3) 2.26(s,3H, -CH_3) 3.99(q,2H,CH_2 -O)	7.25 -7.27 7.39 -7.41	7.81 (s,1H ,NH) 9.29 (s,1H ,NH) 5.16 (s,1H ,CH)
2d	1.1 (q,3H, -CH_3) 2.02 (s,3H, -CH_3) 2.24 (s,3H, -CH_3) 3.98 (q,2H,CH_2 -O)	7.14-7.15 7.49-7.50	7.71 (s,1H ,NH) 9.19 (s,1H ,NH) 9.95(s,1H ,NH-C=O) 5.09(s,1H,CH)

2e	1.00 (q,3H, -CH_3) 2.32 (s,3H, -CH_3) 3.91(q,2H,CH_2 -O)	7.17-7.19 7.32-7.33 7.35-7.39 7.57-7.59	7.74 (s,1H ,NH) 9.32 (s,1H ,NH) 5.63(s,1H,CH)
2f	1.28 (s,3H, -CH_3) 1.8 (s,3H, -CH_3) 4.21(s,2H,CH_2 -O)	7.04 -7.06 7.33 -7.40 7.68 -7.96	9.3 (s,1H ,NH) 9.7 (s,1H ,NH) 10.5(s,1H ,OH) 5.07(s,1H,CH)
2g	0.92(s,3H, -CH_3) 2.29(s,3H, -CH_3) 3.36(s,2H,CH_2 -O)	7.52 -7.56 7.58 -7.74 7.79	7.90(s,1H ,NH) 9.42(s,1H ,NH) 5.82(s,1H,CH)
2h	1.07 (s,6H,CH_3) 2.21 (s,6H ,CH_3) 3.95 (s,4H,CH_2 –O)	7.15	7.69 (s,2H ,NH) 9.17(s,2H ,NH) 5.08(s ,1H ,CH)

3.3:^{13}C-NMR spectra :

^{13}C-NMR spectra spectral data of the 3,4-Dihydropyrimidine-2(1H)-ones are included in .**Table (3-4)** and their spectra are shown in Figures**(3-18,3-22)** and all spectra show signal at 38-40 ppm to d_6-DMSO .

***^{13}C-NMR** spectrum of **ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2b)** shows signal at Chemical δ (14.06 ppm for CH_3)[84] , signal at δ (17.65 ppm for CH_3 protons)and signal at δ (53.28,62.89ppm)[83]for CH_2 ,The3,4-Dihydropyr imidine ring for carbon at δ(99.49ppm), also multiplet signal at(113.74-136.87ppm) for phenyl ring as shown in figure (3-18),finally it shows signal at chemical shift δ (157.97ppm)[83] for NH and signal at δ (165.33 ppm) for carbonyl ester.

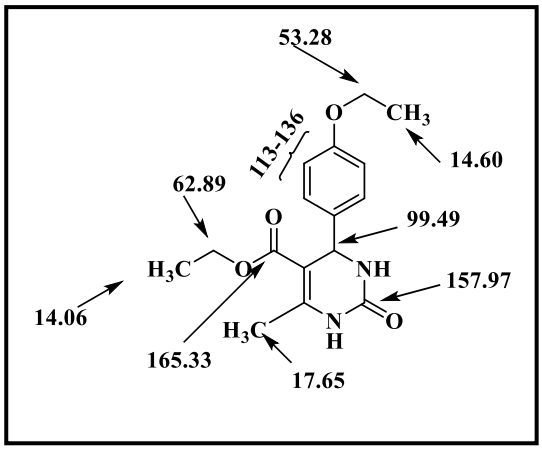


Figure 3-18

***^{13}C-NMR** spectrum of **ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2d).** shows signal at Chemical δ (14.07ppm for CH_3) , signal at δ (17.74ppm for CH_3),in addition to signal at δ (23.90ppm for CH_3)and signal at δ(59.13ppm)for CH_2.The3,4-Dihydropyrimidine ring for carbon at δ(99.24), also multiplet

singlet at (118.93-139.48 ppm)[81]for phenyl ring as shown in figure (3-19),finally it shows signal at chemical shift δ (165.30ppm for C=O-NH)[83] and signal at δ (168.16ppm) for carbonyl ester.

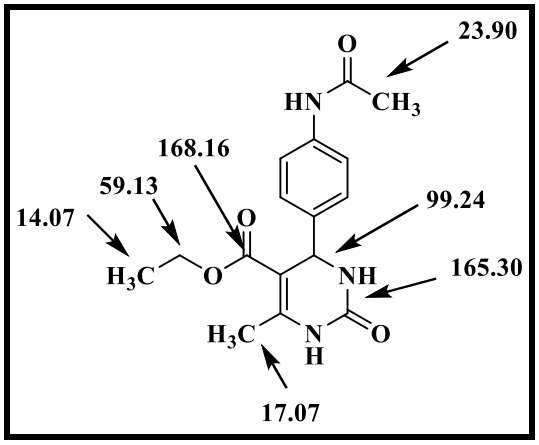


Figure 3-19

***^{13}C-NMR** spectrum of **ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(2e).** shows signal at Chemical δ (13.94ppm for CH_3) , signal at δ (17.62ppm for CH_3 protons), signal at δ(59.03ppm) for CH_2 ,The3,4-Dihydropyrimidine ring for carbon at δ(98.21ppm), also multiplet signal at(122.24-132.36ppm)for phenyl ring as shown in figure (3-20),finally it shows signal at chemical shift δ (151.26ppmfor C=O-NH) and signal at δ (164.91ppm) for carbonyl ester.

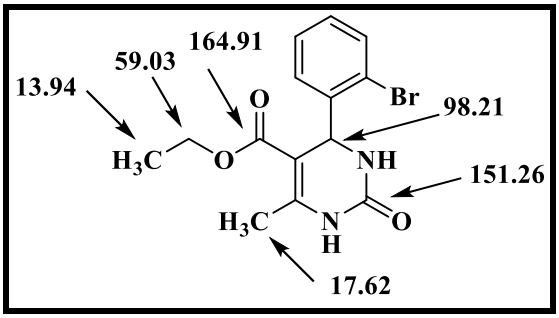


Figure 3-20

***^{13}C-NMR spectrum of ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2f).** Shows signal at Chemical δ (14.17ppm for CH_3) , signal at δ (23.84ppm for CH_3 protons), signal at δ(60.73ppm)for CH_2 ,The3,4-Dihydropyrimidine ring for carbon at δ(83.07ppm), also multiplet signal at(116.67-130.81ppm)for phenyl ring as shown in figure (3-21),finally it shows signal at chemical shift δ(154.45ppm for C=O-NH)[84] and signal at δ (168.48ppm) for carbonyl ester.

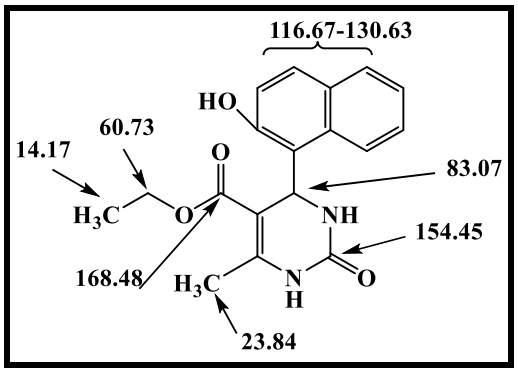


Figure 3-21

***^{13}C-NMR** spectrum of **diethyl 4,4'-(1,4-phenylene) bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate)(2i).** Shows signal at Chemical δ (14.09ppm for CH_3) , signal at δ (17.78ppm for CH_3), signal at δ(59.22ppm)for CH_2 ,The3,4-Dihydropyrimidine ring for carbon at δ(99.14ppm), also multiplet singlet at(126.26-143.90ppm)for phenyl ring as shown in figure (3-22),finally it shows signal at chemical shift δ (152.08ppm for C=O-NH) and signal at δ (165.24ppm) for carbonyl ester.

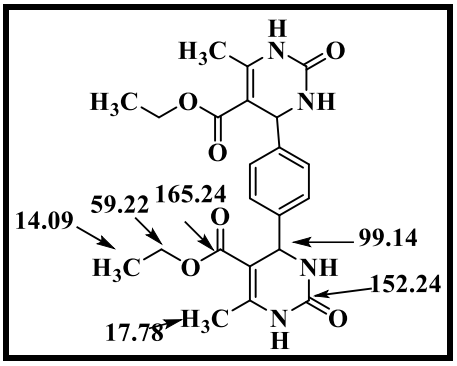


Figure 3-22

Tables 3-4: *^{13}C-NMR spectra of 3,4-Dihydropyrimidine -2(1H)-ones*

Comp.	C_{10}-alphatic ppm	C_7-(CH_3-C=C) ppm	C_8-(CH_2-O) ppm	C_4(CH) ppm	C –Ar ppm	C=O ester ppm
2b	14.06	17.65	62.89	99.49	113 -136	165
2d	14.07	17.74	59.13	99.24	118-139	168
2e	13.94	17.62	59.03	98.21	122-132	164
2f	14.17	23.84	60.73	83.07	116-130	168
2i	14.09	17.78	59.22	99.14	126-143	165

3.4 :^{13}C- NMR DEPT spectral analysis :

^{13}C- NMR DEPT spectrum of **ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,23,4-tetrahydropyrimidine-5-carboxylate (2d)**. show triplet at Chemical shift δ(39.29-40.12)for d_6.DMSO solvent. Also it shows positive signal at Chemical δ (14.07ppm for CH_3) ,positive signal at δ (17.74ppm for CH_3),in addition to positive signal at δ (23.90ppm for CH_3)and negative signal at δ(59.13ppm)for CH_2.

3.5.Mass spectra of analysis of 3,4-Dihydropyrimidine -2(1H)-ones/thione :

*Mass spectra of **ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydro pyrimidine -5-carboxylate (2a)** show the molecular ion peak corresponding to the particular compound = 261 m/z, and the fragmentation of **2a** showed the peaks in {252,244,231,216,205, 183,155, 136,110,96,78,67,51,42} m/z which is attributed to the fragments of`[$C_{13}H_6N_3O_3^+$,$C_{13}H_{14}N_3O_2^+$,$C_{12}H_{12}N_3O_2^+$,$C_{11}H_{10}N_3O_2^+$,$C_{10}H_{11}N_3O_2^+$,$C_8H_{11}N_2O_3^+$,$C_6H_7N_2O_3^+$, $C_6H_5N_2O_2^+$,$C_4H_4N_2O^+$, $C_3H_2N_2O^+$, $C_{5,}H_5N^+$, C_3NH^+] ,respectively. as shown in **scheme 3-2.**

***ethyl4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2b)** show the molecular ion peak corresponding to the particular compound = 304 m/z, and the fragmentation of **2b** showed the peaks in { 289 ,275 ,259 ,247 ,231,183,155,137,122,110,94 } m/z which is attributed to the fragments of [$C_{15}H_{17}N_2O_4^+$,$C_{14}H_{15}N_2O_4^+$,$C_{14}H_{15}N_2O_3^+$,$C_{13}H_{15}N_2O_3^+$,$C_{13}H_{15}N_2O_2^+$,$C_8H_{11}N_2O_3^+$,$C_6H_7N_2O_3^+$,$C_6H_5N_2O_2^+$, $C_5H_2N_2O_2^+$,$C_4H_2N_2O_2^+$,$C_4H_2N_2O^+$] ,respectively. as shown in **scheme 3-3.**

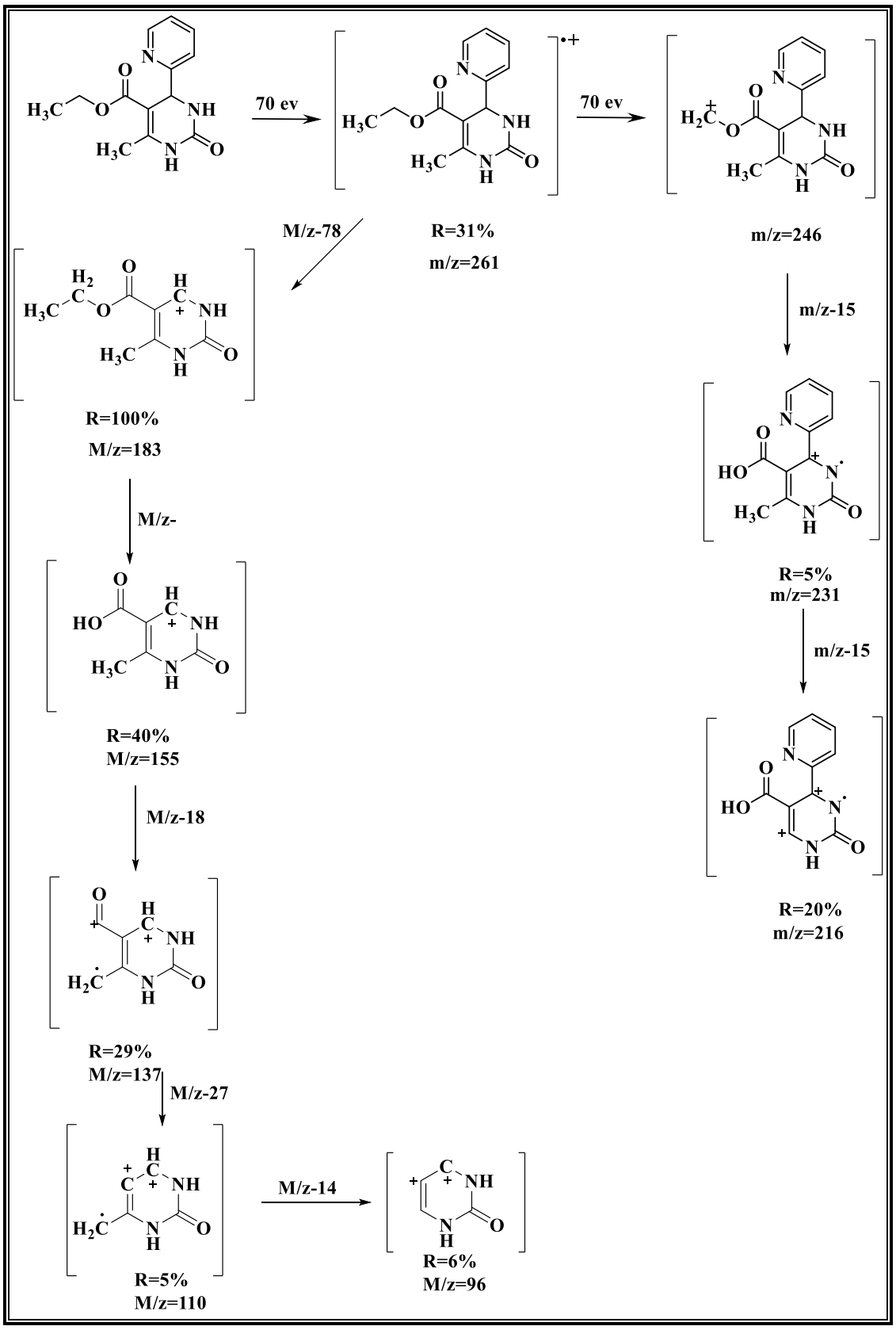
***ethyl4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(2c)** show the molecular ion peak corresponding to the particular compound = 294 m/z, and the fragmentation of **2c** showed the peaks in {279,265 ,249 ,221,183,155,137,110,94 } m/z which is attributed to the fragments of [$C_{13}H_{12}ClN_2O_3^+$, $C_{12}H_{10}ClN_2O_3^+$,$C_{11}H_{10}ClN_2O^+$,$C_8H_{11}N_2O_3^+$,$C_6H_7N_2O_3^+$,$C_6H_5N_2O_2^+$,$C_4H_2N_2O_2^+$,$C_4H_2N_2O^+$], respectively. as shown in **scheme 3-4**.

***ethyl4-(4-acetamidophenyl)-6-methyl-2-oxo-1,23,4-tetrahydro pyrimidine-5-carboxylate (2d)** show the molecular ion peak corresponding to the particular compound = 317 m/z, and the fragmentation of **2d** showed the peaks in {302,288,275,265,244, 231,183,155,137} m/z which is attributed to the fragments of [$C_{15}H_{16}N_3O_4^+$, $C_{14}H_{14}N_3O_4^+$,$C_{13}H_{13}N_3O_4^+$, $C_{13}H_4N_3O_4^+$, $C_{12}H_9N_3O_3^+$, $C_{11}H_8N_3O_3^+$,$C_8H_{11}N_2O_3^+$,$C_6H_7N_2O_3^+$, $C_6H_5N_2O_2^+$] ,respectively. as shown in **Scheme 3-5**.

*Mass spectra of **ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2f)** show the molecular ion peak corresponding to the particular compound = 326 m/z,and the fragmentation of **2f** showed the peaks in { 309 ,297,279,235, 183 ,169,154,,129 ,115 ,89 ,79,57 ,42 } m/z .

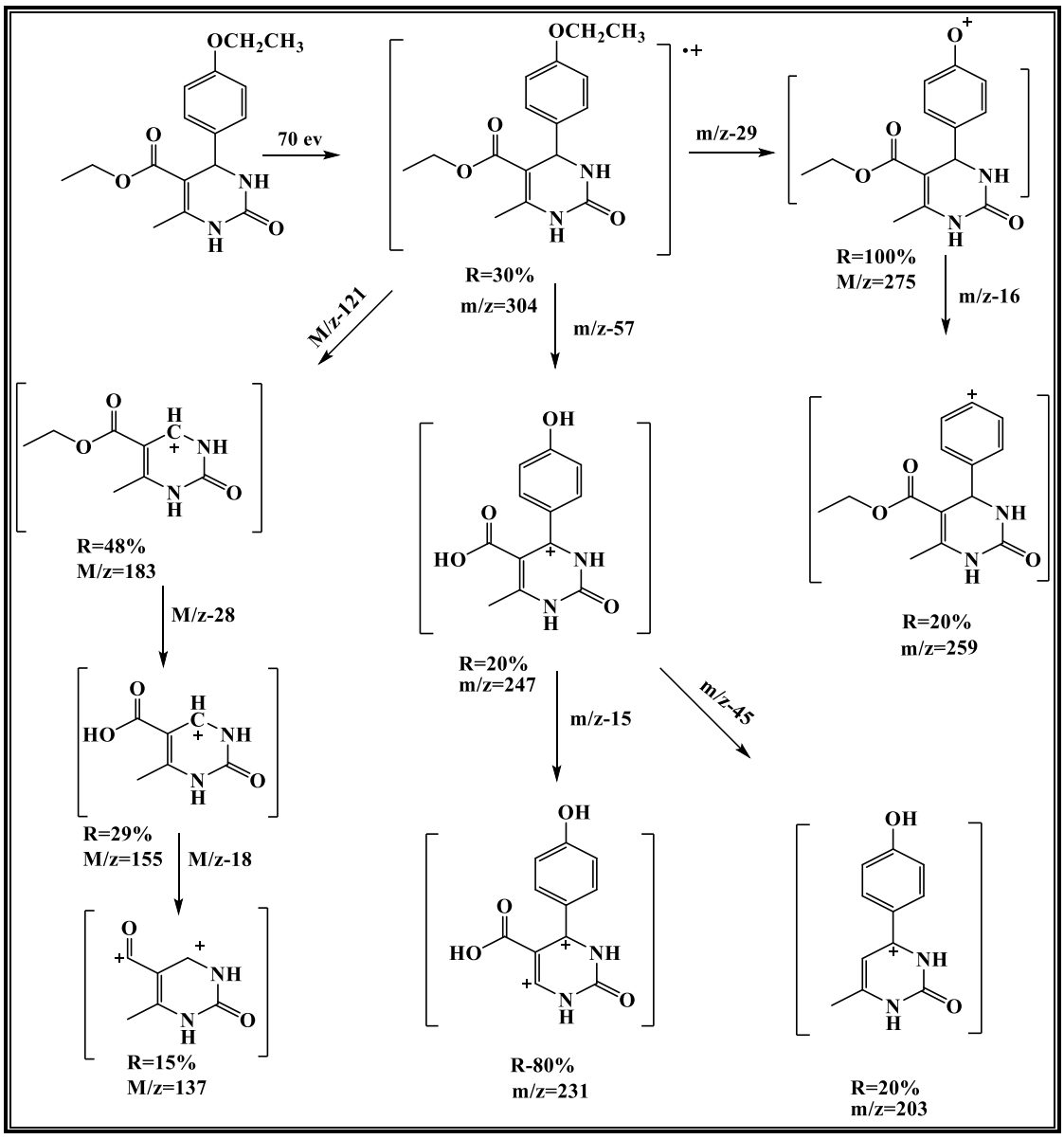
***4-(4-aminophenyl)-5-(ethoxymethyl)-4,6-dim-ethyl-3,4-dihydropy rimidine-2(1H)-thione(2i)**show the molecular ion peak corresponding to the particular compound = 305 m/z, and the fragmentation of **2j**showed the peaks in {290 ,275 ,245 ,217 ,193 ,178 , 92 ,87 ,76 } m/z which is attributed to the fragments of [$C_{14}H_{16}N_3O_2S^+$,$C_{13}H_{13}N_3O_2S^+$, $C_{12}H_{11}N_3OS^+$, $C_{11}H_{11}N_3S^+$, $C_9H_{11}N_3S^+$,$C_8H_8N_3S^+$,$C_6H_6N^+$,$C_2H_3N_2S^+$, $C_6H_4^+$], respectively. as shown in **scheme 3-6.**

Compound (2a) :Molecular formula :$C_{13}H_{15}N_3O_3$,R=35%



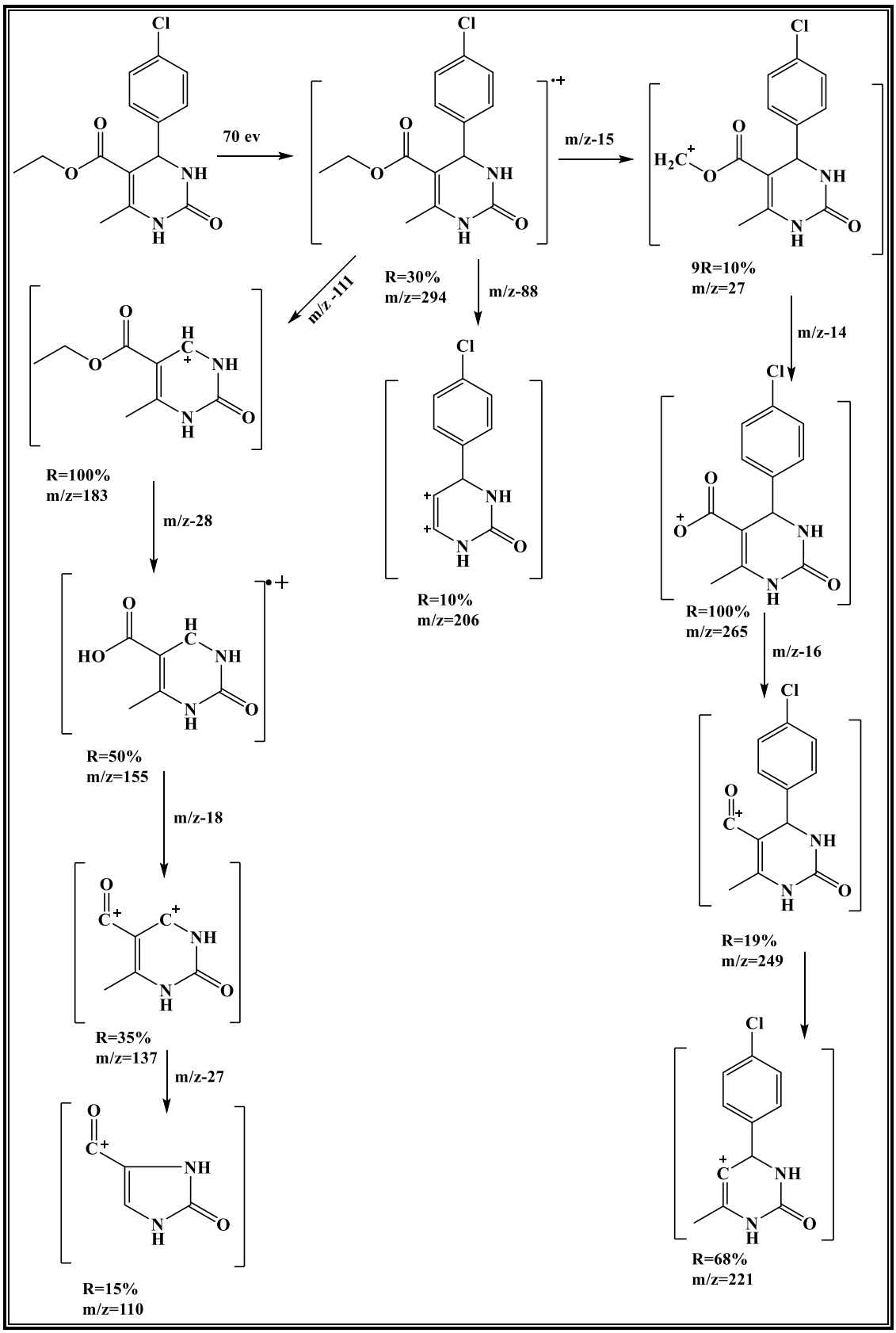
Scheme 3-2

Molecular formula :$C_{16}H_{20}N_2O_4$**(2b)** ,**M.Wt** =304 ,**R**=30%



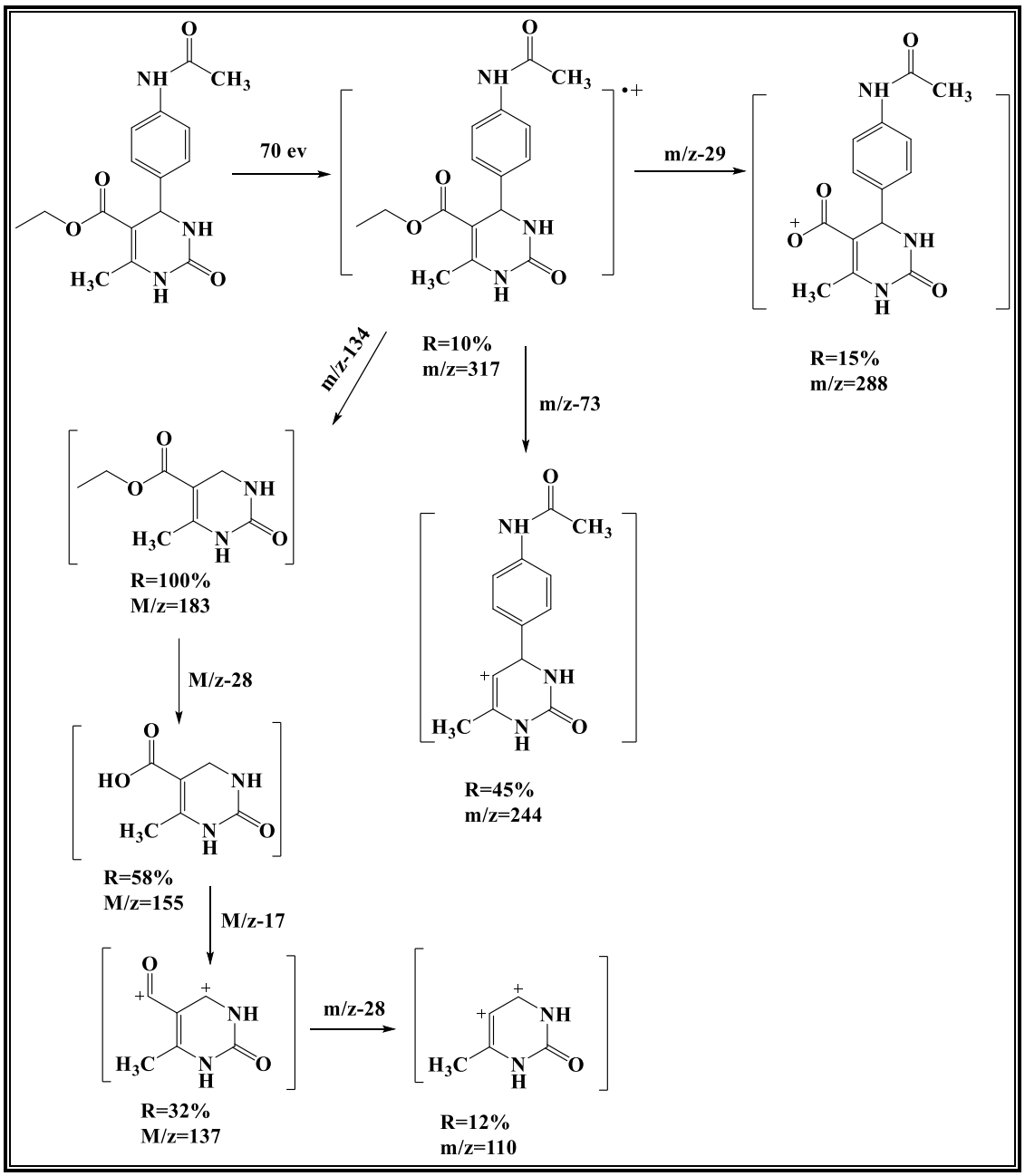
Scheme 3-3

Molecular formula :$C_{14}H_{15}ClN_2O_3$**(2c)** ,**M.Wt** =294 ,**R**=22%



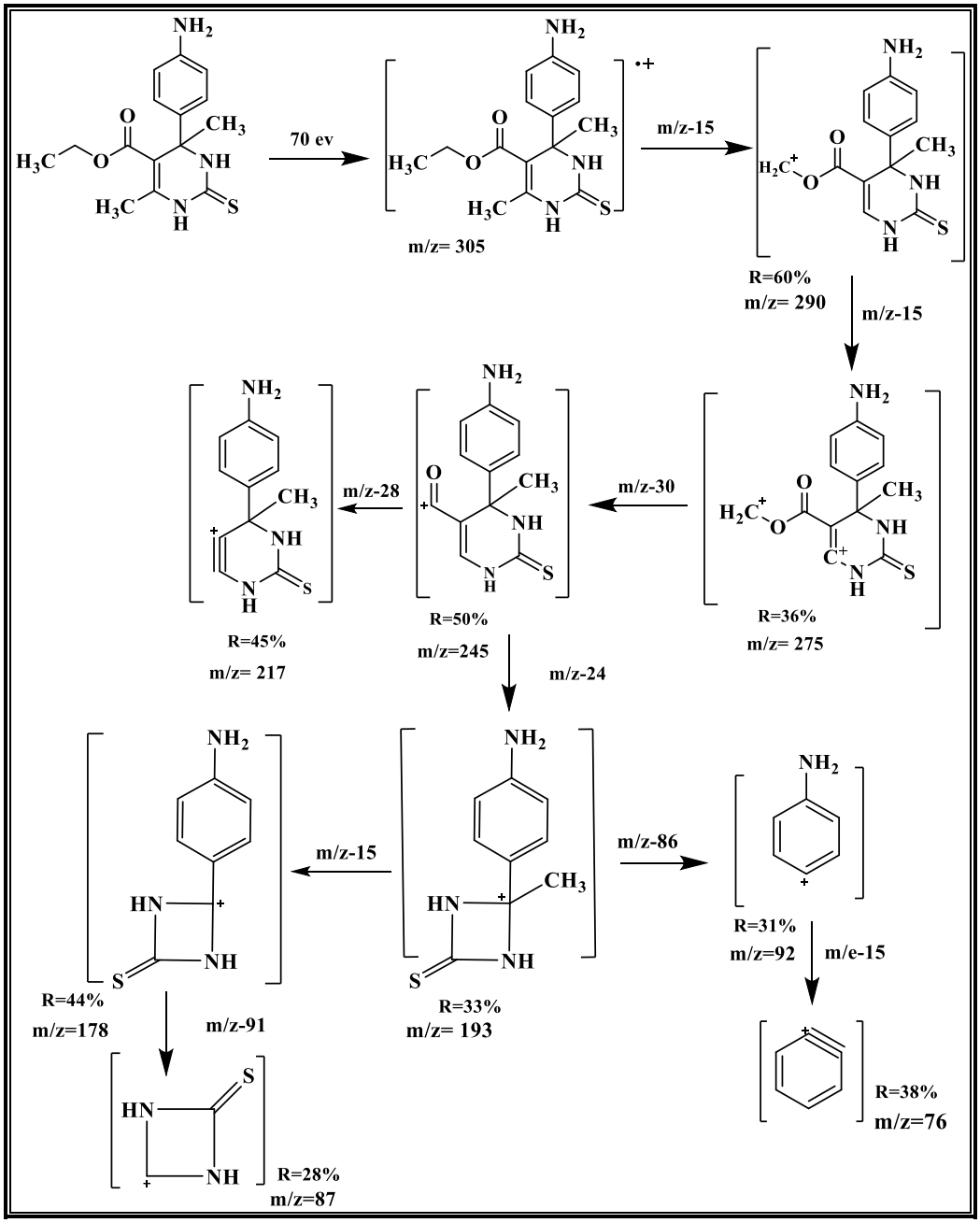
Scheme 3-4

Molecular formula: $C_{16}H_{19}N_3O_4$**(2d)**; M.Wt =317 ,**R**=10%



Scheme 3-5

Molecular formula :$C_{15}H_{19}N_3O_2S$**(2j)** ,**M.Wt** =305 ,**R**=28%



Scheme 3-6

Anti Oxidant:

DPPH radical scavenging activity :

The fresh prepared DPPH solution displays deep purple color with maximum absorption at 517 nm. When Antioxidants exist in average, color density ,Decreases that give less absorption, Antioxidants molecules infuse DPPH free radicals by providing hydrogen atoms or electron scross the free radicals attack on DPPH molecule and convert them yellow-colored[88]diphenylpicrylhydrazine. The results of antioxidant study reveals the different substitution group in dihydropyrimidine ring give different values in oxidation such as **OH**-group in (2-hydroxynaphthalen) **(2f)**give higher antioxidant than naphthalene **(2g)** in pyrimidine ring ,because easy release of H in **(2f)** which is responsible for scavenging action of DPPH and the study of Mondal et al[89] ,also supports our observation, who explained the role of the –OH group in increasing the compound give good activity when we compare with the stander controls BHT .The Bromo substitution at meta position of phenyl ring increases the antioxidant activity **(2e)** compound which have amide carbonyl in compound **(2d)** give higher antioxidant because of its ability to give protons faster than other compounds. The compounds **(2a ,2h)** also give higher antioxidant when we compared with BHT .The result shown in Table**(3-5)**

Table(3-5):*free radical scavenging activity of DHPM derivatives and standard in the antioxidant activity evaluation assays*

vol.µl	DPPH inhibition %.						BHT
	2a	2b	2d	2e	2f	2g	
10	46.59	50.78	69.31	43.03	78.84	48.69	32.52
15	51.8	62.4	70.47	48.16	80.41	53.29	38.87
20	54.97	67.01	72.89	51.98	81.04	59.05	40.67
25	61.67	70.65	74.97	54.93	82.93	63.97	43.26

All this values shown in Figure **25** .

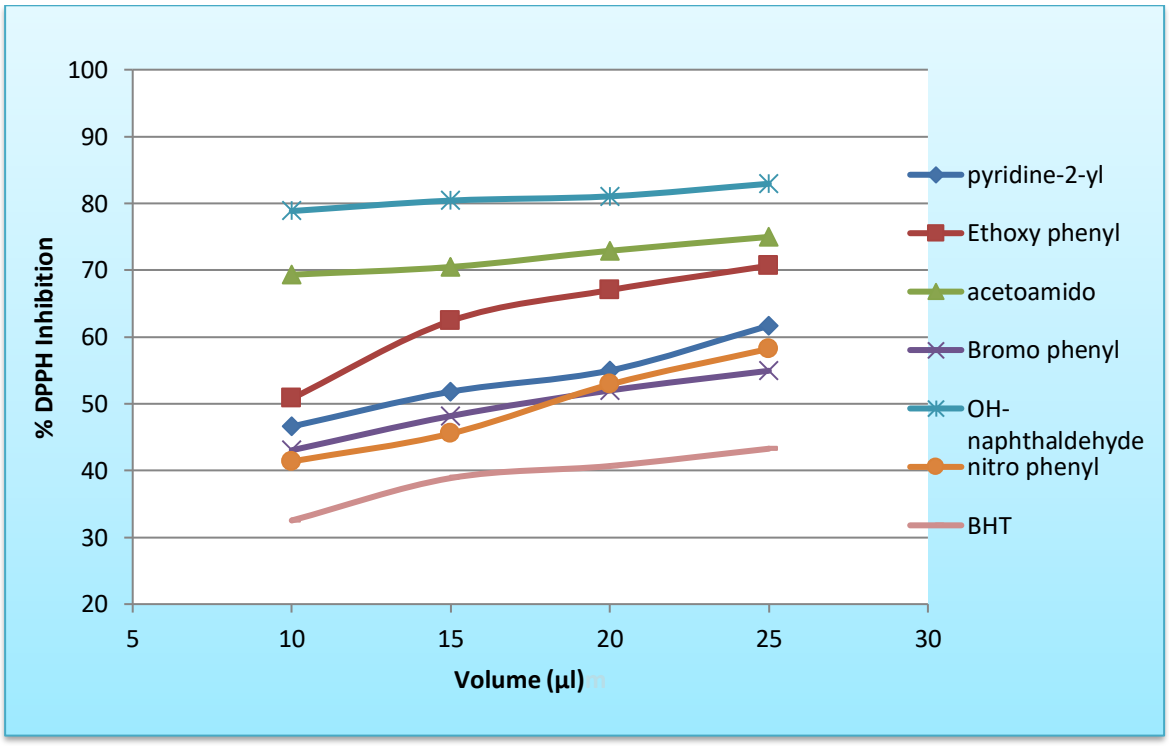


Figure 25

List of Spectra

List of spectra

1-Figure 3-1: FT-IR spectrum of *ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydro pyrimidine -5-carboxylate* ***2a.***

2-Figure3-8: FT-IR spectrum of *ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2b.***

3- Figure3-3: FT-IR spectrum of*ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2c.***

4-Figure3-9: FT-IR spectrum of *ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate****2d****.*

5-Figure3-5: FT-IR spectrum of *ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2e.***

6- Figure3-6: FT-IR spectrum of *ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2f.***

7-Figure3-7 : FT-IR spectrum of *ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2g*** *.*

8-Figure3-8: FT-IR spectrum of *diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate)* ***2h.***

9-Figure3-9: FT-IR spectrum of *4-(4-aminophenyl)-5-(ethoxymethyl)-4,6-dimethyl-3,4-dihydropyrimidine-2(1H)-thione* ***2i.***

10-Figure3-10:The^{1}H-NMR total spectrum of *ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,tetrahydro pyrimidine -5-carboxylate* ***2a.***

11-Figure3-11:The^{1}H-NMR total spectrum of *ethyl 4-(4-ethoxy phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2b.***

12- Figure3-12: ***The^{1}H-NMR total*****spectrum of**ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2c.**

13-Figure3-13:The^{1}H-NMR total spectrum of *ethyl 4-(4-acetamid ophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2d.***

14-Figure3-14:The^{1}H-NMR total spectrum *of ethyl 4-(2-bromophenyl)-6- methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**2e**.*

15-Figure3-15:The^{1}H-NMR total spectrum of *ethyl4-(2-hydroxy naphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f**.*

16-Figure3-16:The^{1}H-NMR total spectrum *of of ethyl 6-methyl-4-(4-nitro phenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2g.***

17-Figure3-17:The^{1}H-NMR total spectrum of *diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carbox ylate) **2h.***

18-Figure3-18:The^{13}C-NMR spectrum of *ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b**.*

19-Figure3-19:The ^{13}C-NMR spectrum of *ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2d**.*

20-Figure3-20:The ^{13}C-NMR spectrum of *ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2e.***

21-Figure3-21:The ^{13}C-NMR spectrum of *ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f.***

22-Figure3-24:The ^{13}C-NMR spectrum of *diethyl 4,4'-(1,4-phenylene) bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate) **2i.***

23-Figure3-23: The ^{13}C-NMR DEPT*spectrum of ethyl 4-(acetamidophenyl)-6-methyl-2-oxo-1,23,4-tetrahydropyrimidine-5-carboxylate**2b**.*

24-Figure3-24: The Mass spectrum of *ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4- tetrahydro pyrimidine -5-carboxylate **2a.***

25-Figure3-25: The Mass spectrum of *ethyl 4-(4-ethoxyphenyl)-6-methyl- 2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b**.*

26- Figure3-26: The Mass spectrum of*ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2c.***

27-Figure 3-27: The Mass spectrum of *ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,23,4-tetrahydropyrimidine-5-carboxylate****2d****.*

28-Figure 3-28: The Mass spectrum of *ethyl4-(2-hydroxynaphthalen-1-yl)- 6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate* ***2f.***

29-Figure3-29: The Masss pectrum of *4-(4-aminophenyl)-5-(ethoxy methyl)-4,6-dimethyl-3,4-dihydropyrimidine-2(1H)-thione* ***2j.***

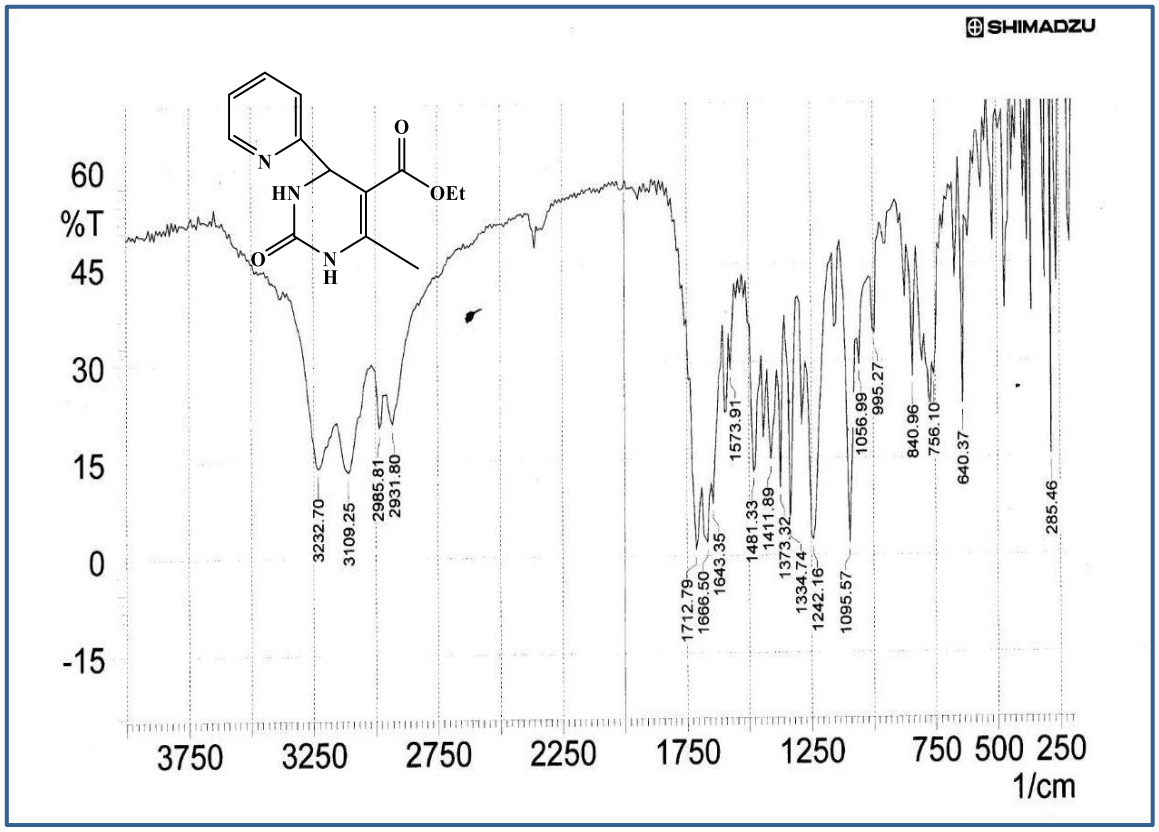


Figure 3-1: FT-IR spectrum of ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydro pyrimidine -5-carboxylate **2a**.

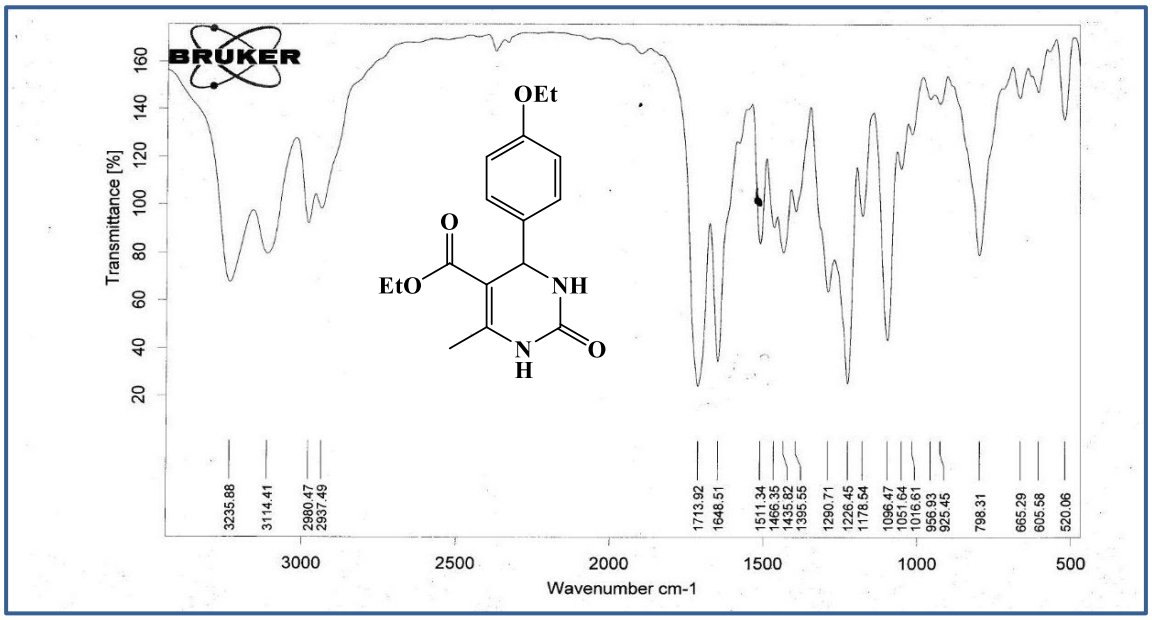


Figure 3-2: FT-IR spectrum of ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b.**

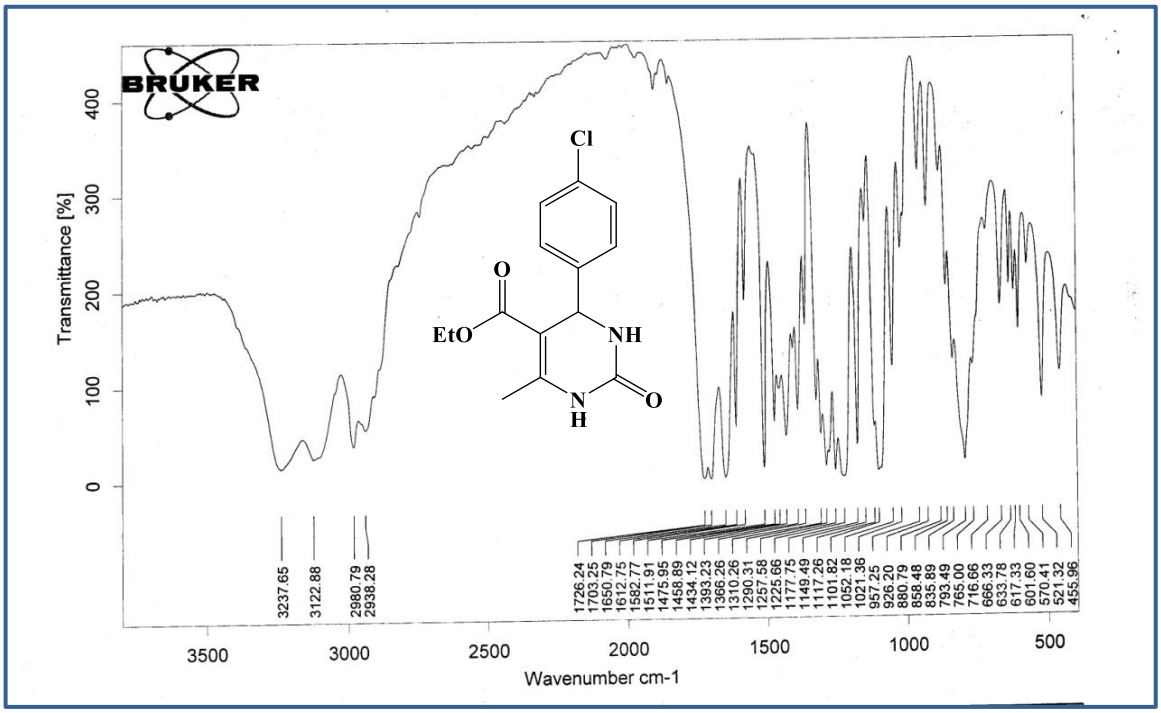


Figure 3-3: FT-IR spectrum of ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2c.**

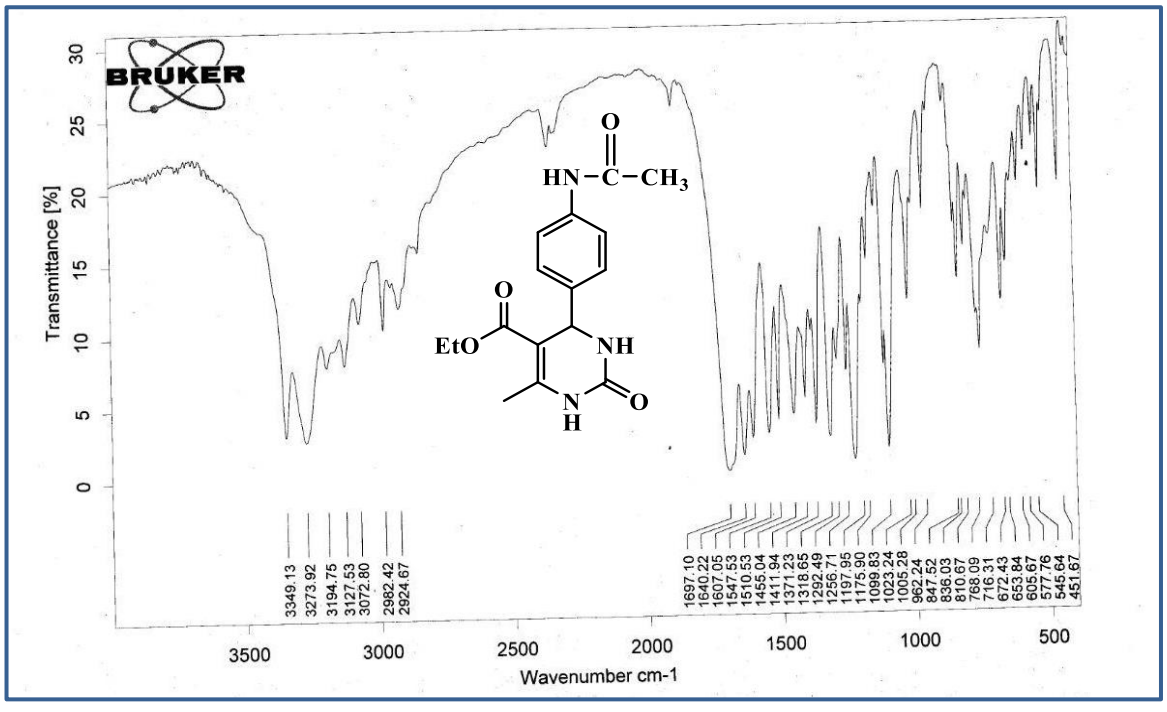


Figure 3-4: FT-IR spectrum of ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2d.**

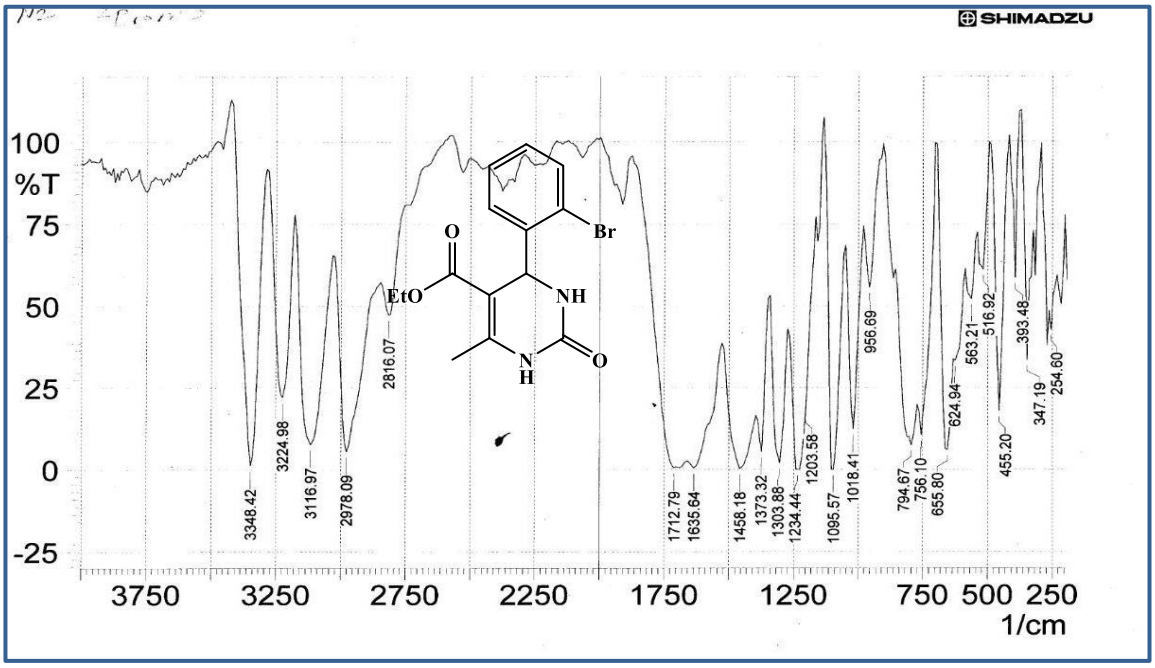


Figure 3-5: FT-IR spectrum of ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2e.**

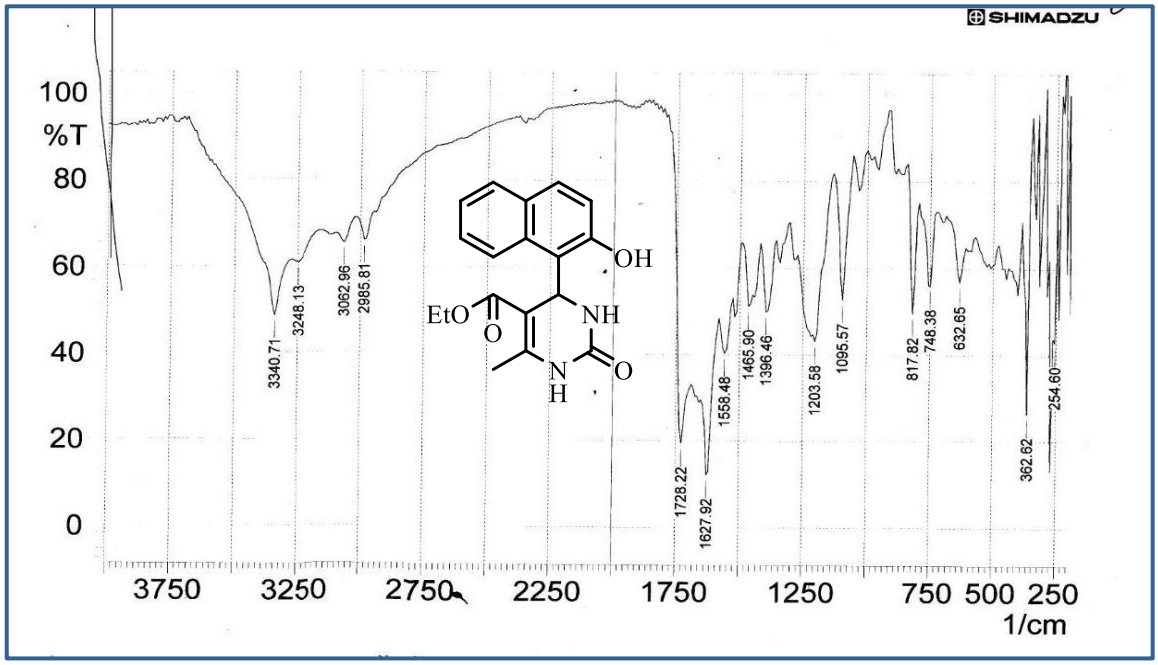


Figure 3-6: FT-IR spectrum of ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f.**

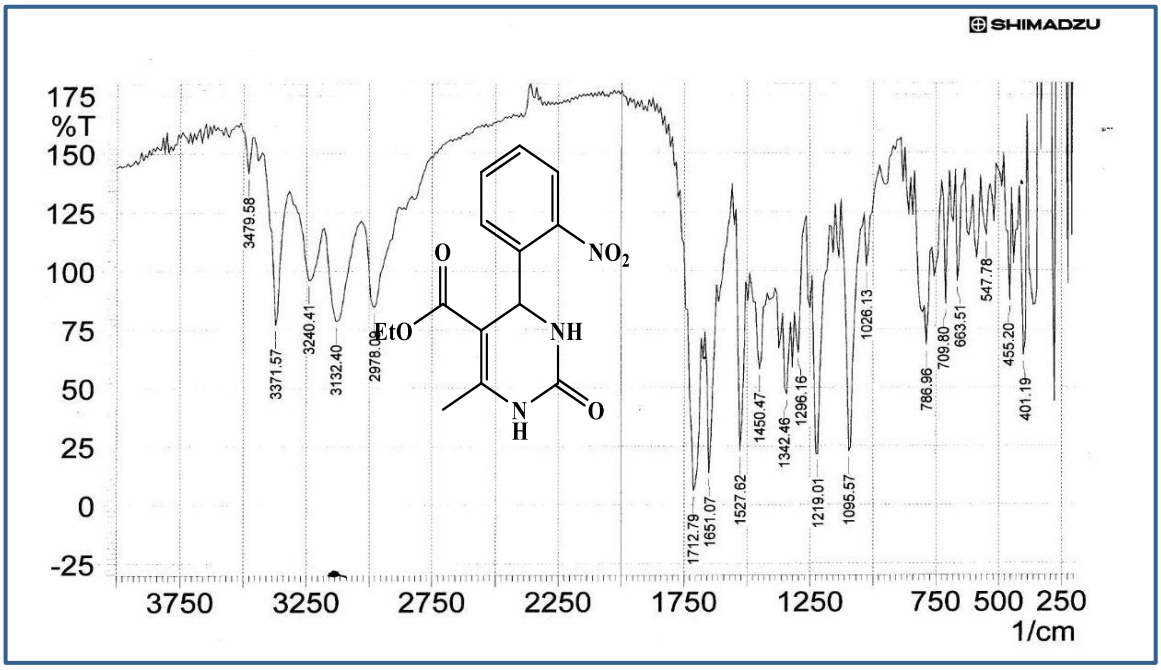


Figure 3-7: FT-IR spectrum of ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetra hydropyrimidine-5-carboxylate **2g**.

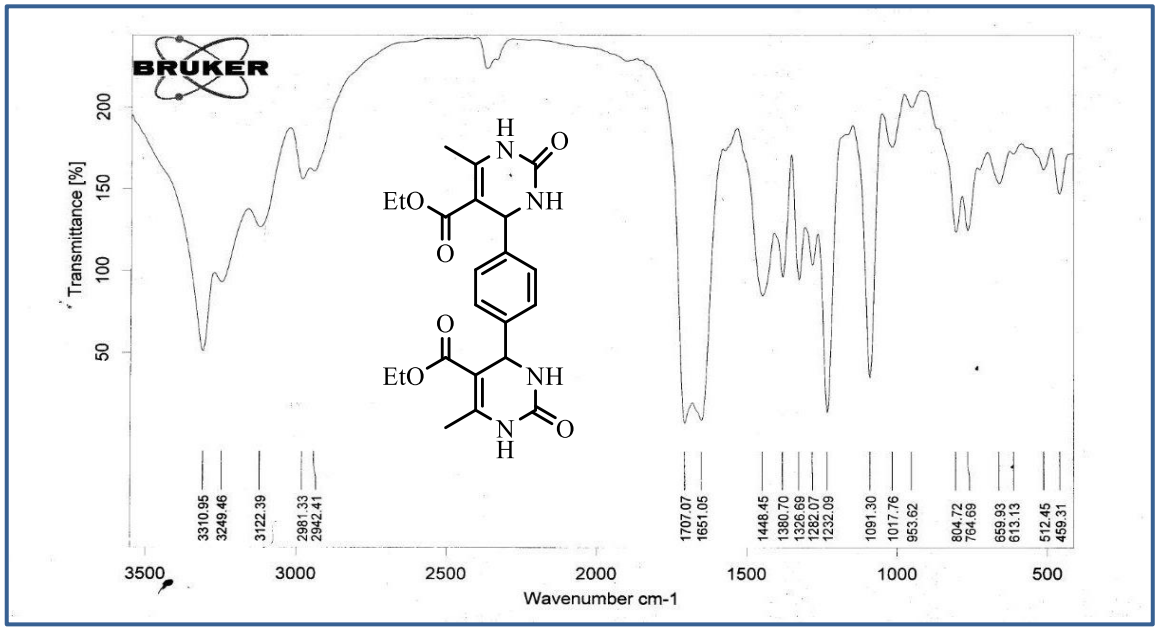


Figure 3-8: FT-IR spectrum of diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate)**2h.**

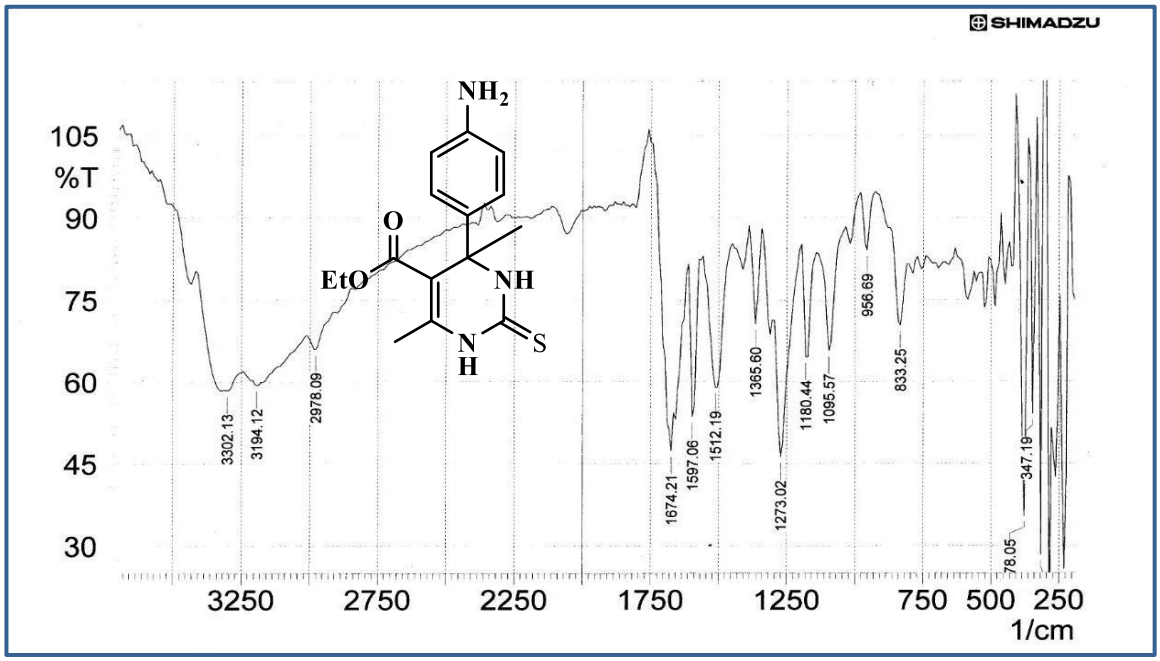


Figure 3-9: FT-IR spectrum of4-(4-aminophenyl)-5-(ethoxymethyl)-4,6-dimethyl-3,4-dihydropyrimidine-2(1H)-thione **2i**.

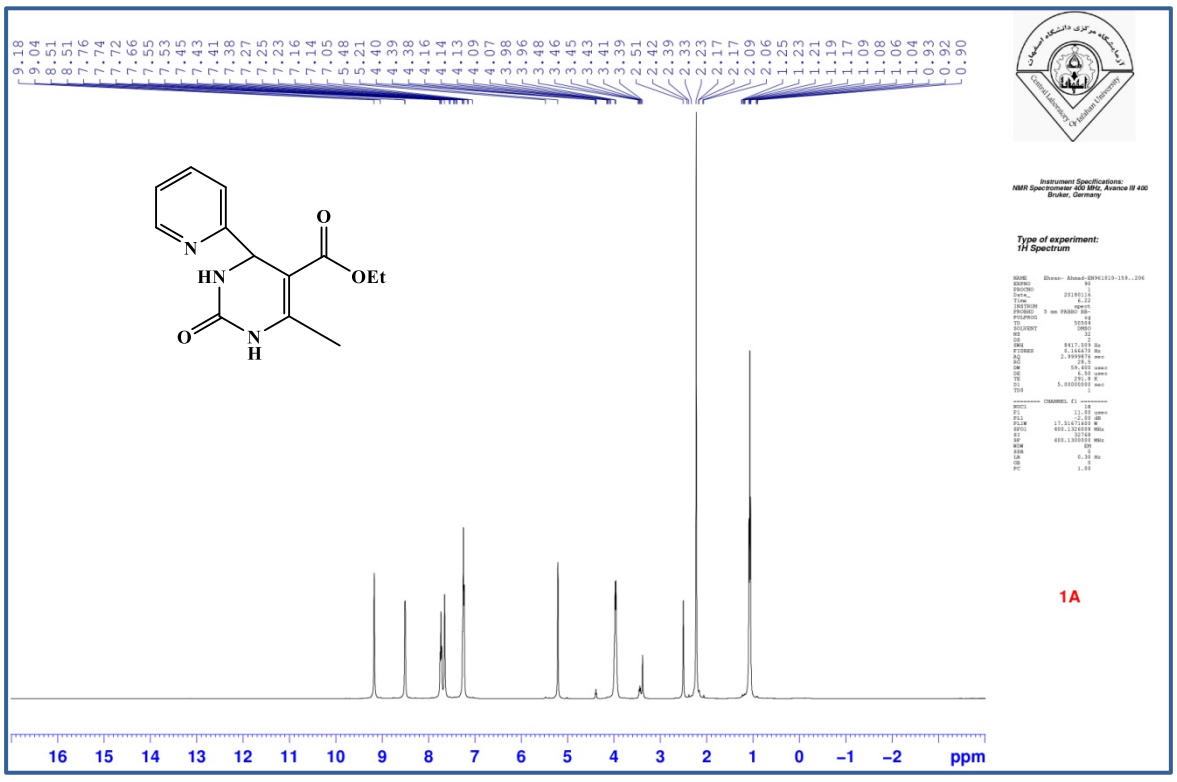


Figure 3-10:The^{1}H-NMR total spectrum of ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4-tetrahydropyrimidine -5-carboxylate **2a.**

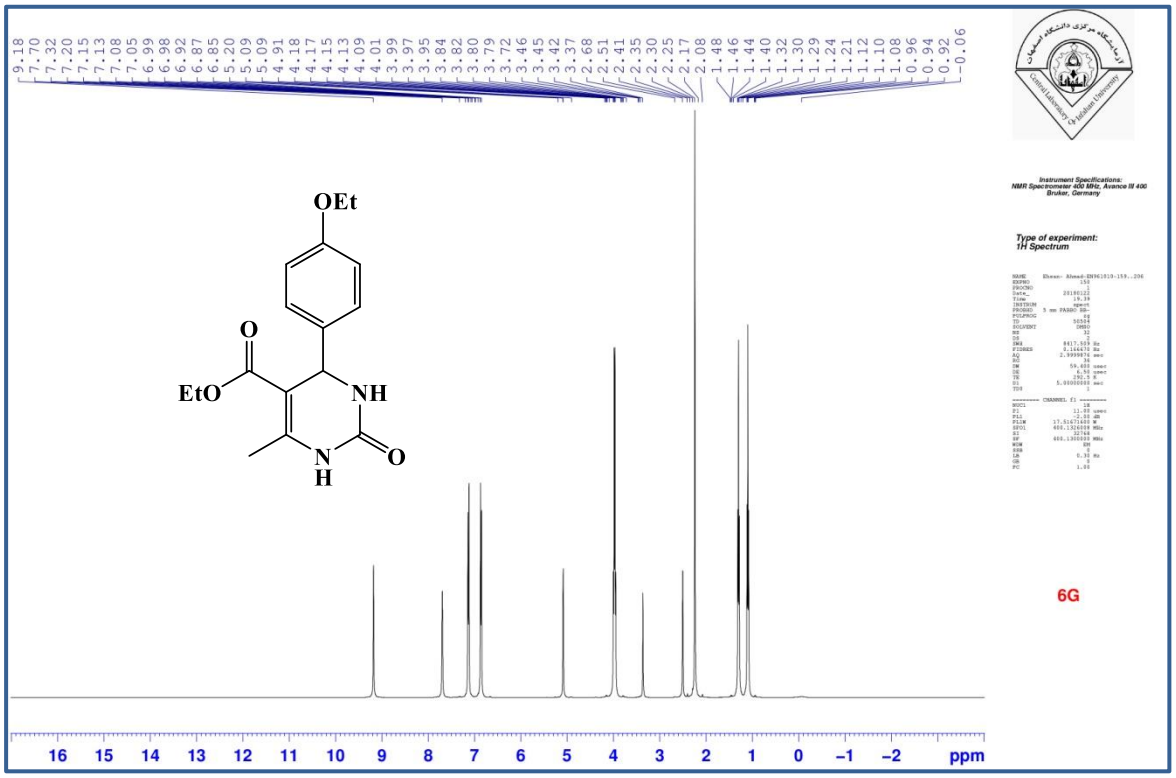


Figure 3-11:The^{1}H-NMR total spectrum of ethyl 4-(4-ethoxy phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b.**

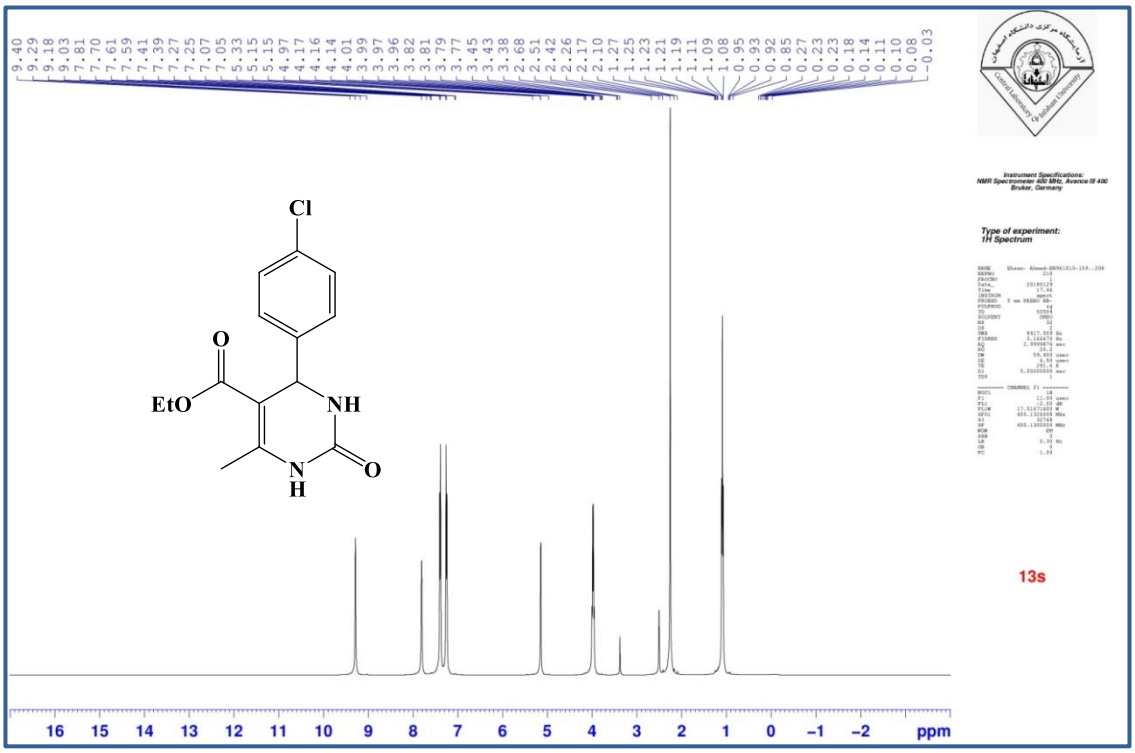


Figure 3-12: The^{1}H-NMR total spectrum of ethyl 4-(4-chloro phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**2c.**

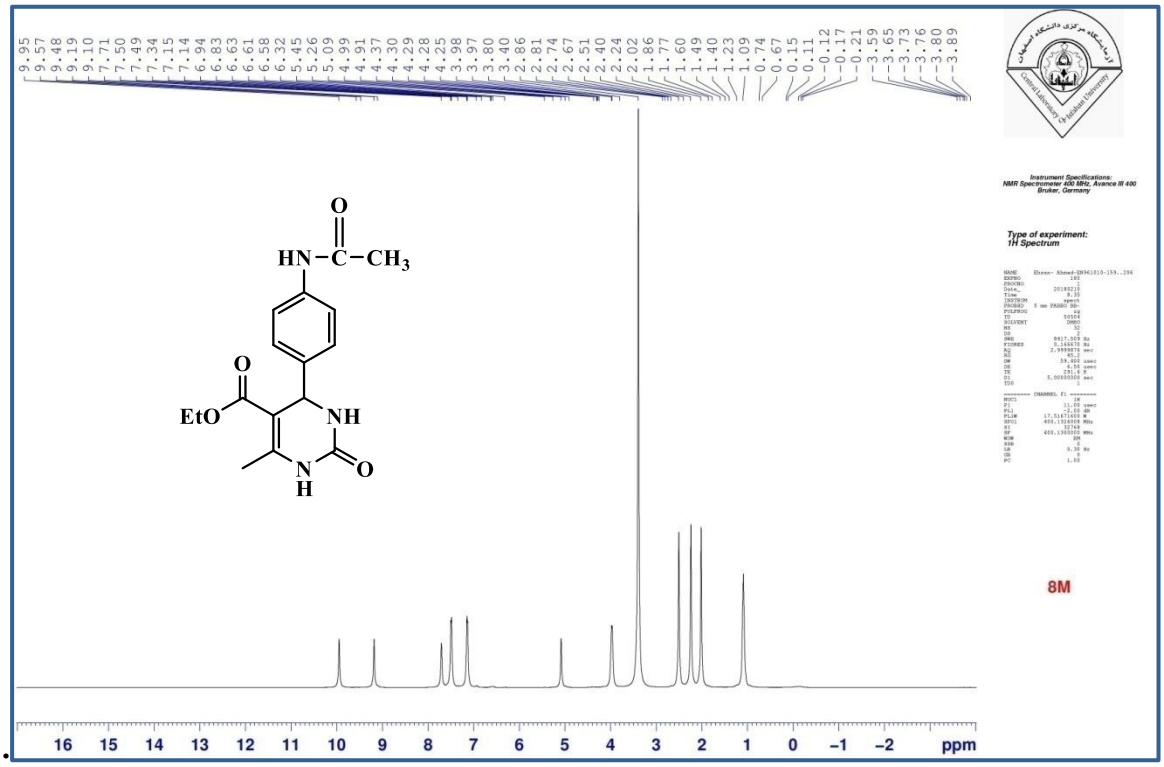


Figure 3-13:The^{1}H-NMR total spectrum of ethyl 4-(4-acetamid ophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2d .**

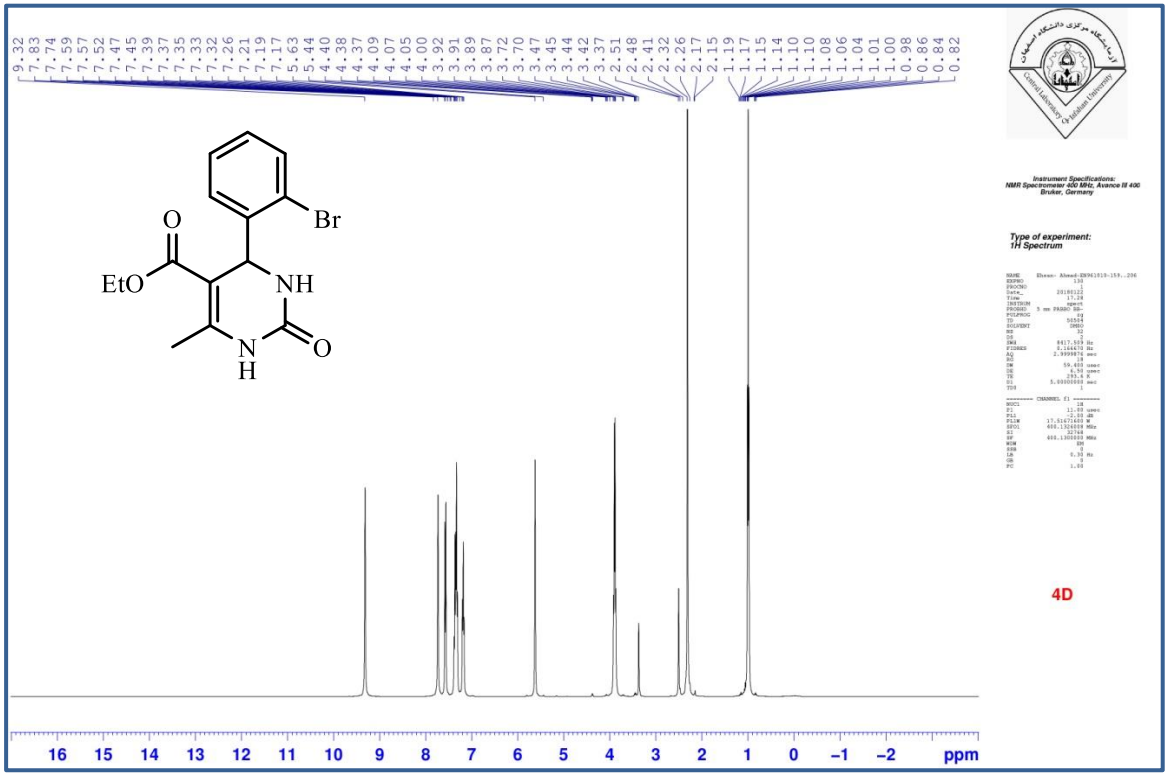


Figure 3-14:The^{1}H-NMR total spectrum of ethyl 4-(2-bromophenyl)-6- methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxyl ate **2e**.

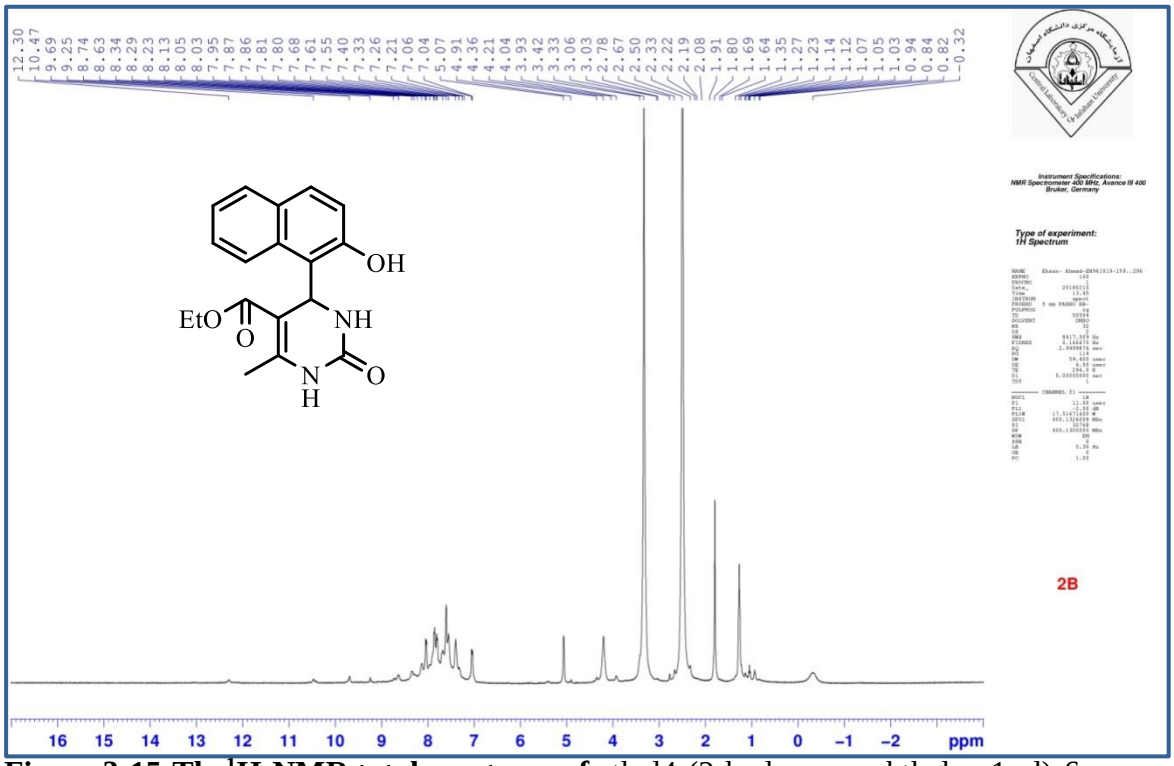


Figure 3-15:The[1]H-NMR total spectrum of ethyl4-(2-hydroxy naphthalen-1-yl)-6-methyl- 2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f**.

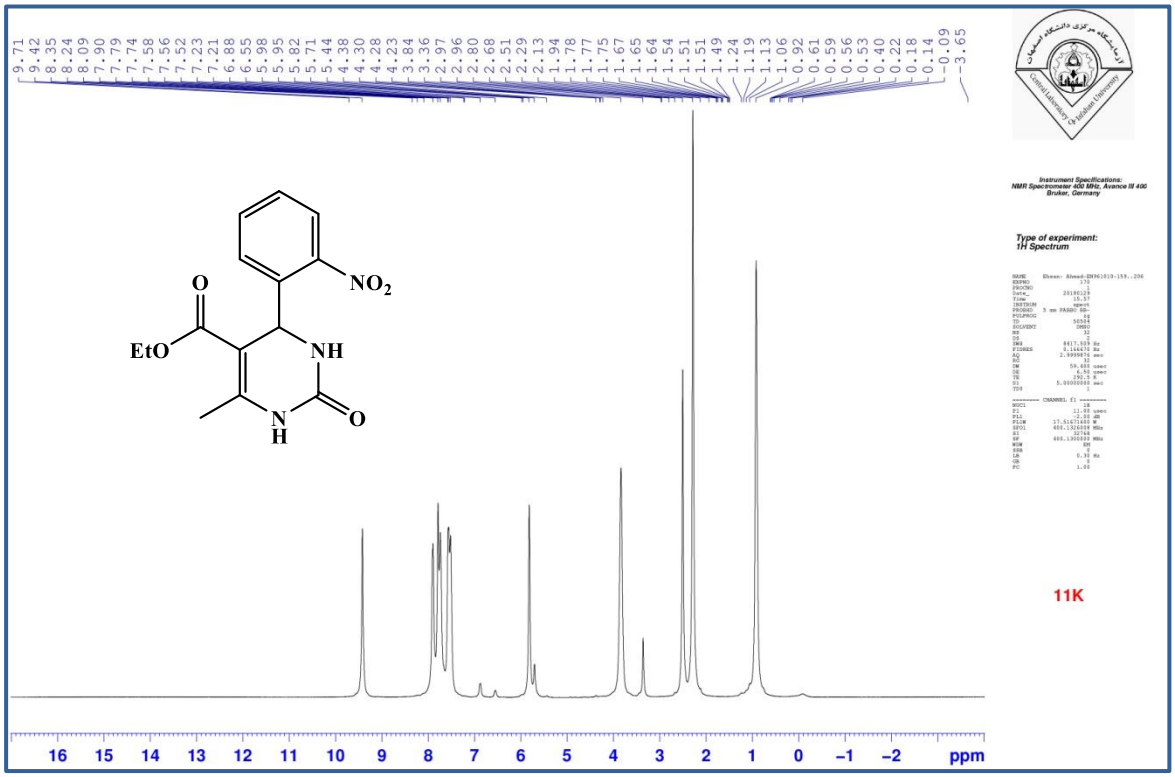


Figure 3-16:The[1]H-NMR total spectrum of of ethyl 6-methyl-4-(4-nitro phenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2g.**

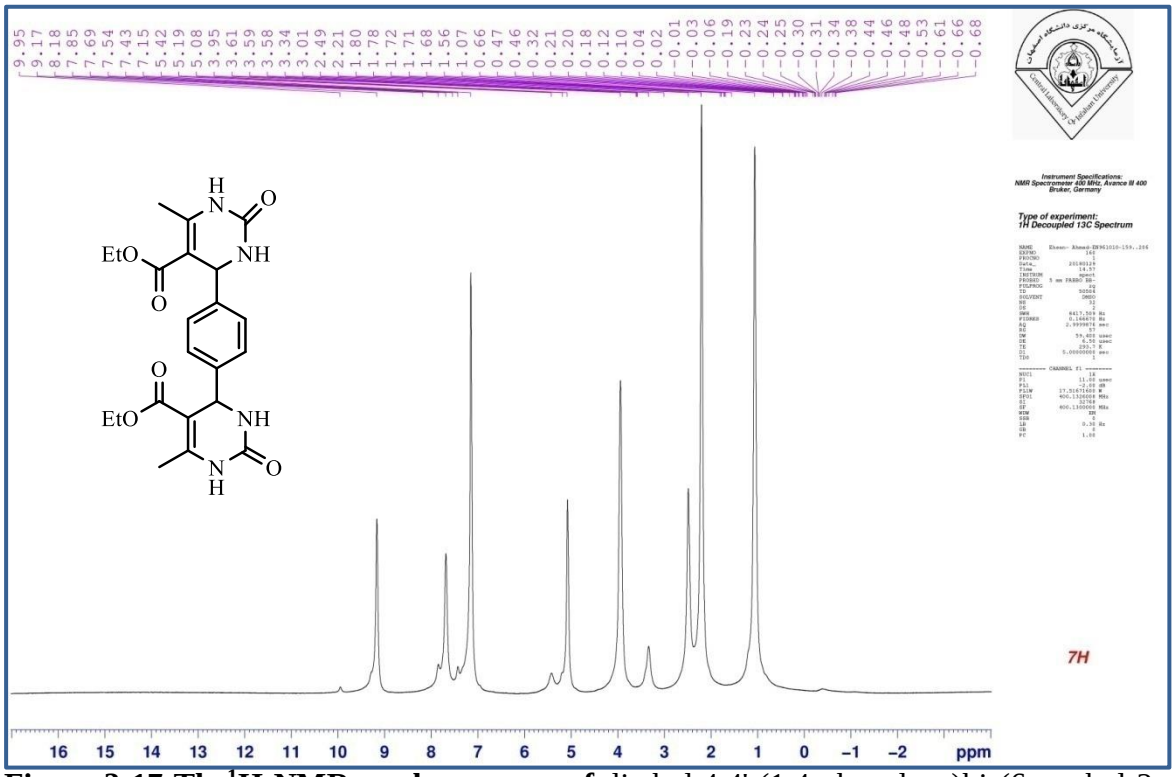


Figure 3-17:The^{1}H-NMR total spectrum of diethyl 4,4'-(1,4-phenylene)bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate) **2h.**

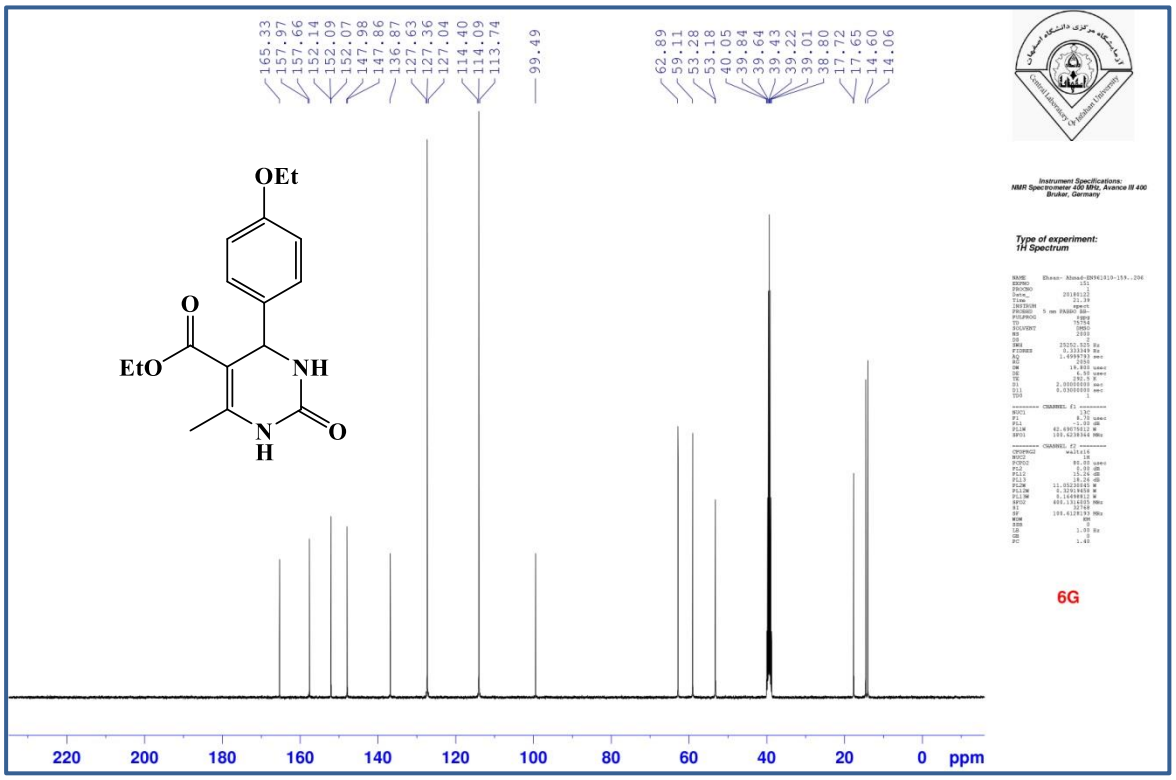


Figure3-18:**The^{13}C-NMR spectrum of** ethyl 4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b**.

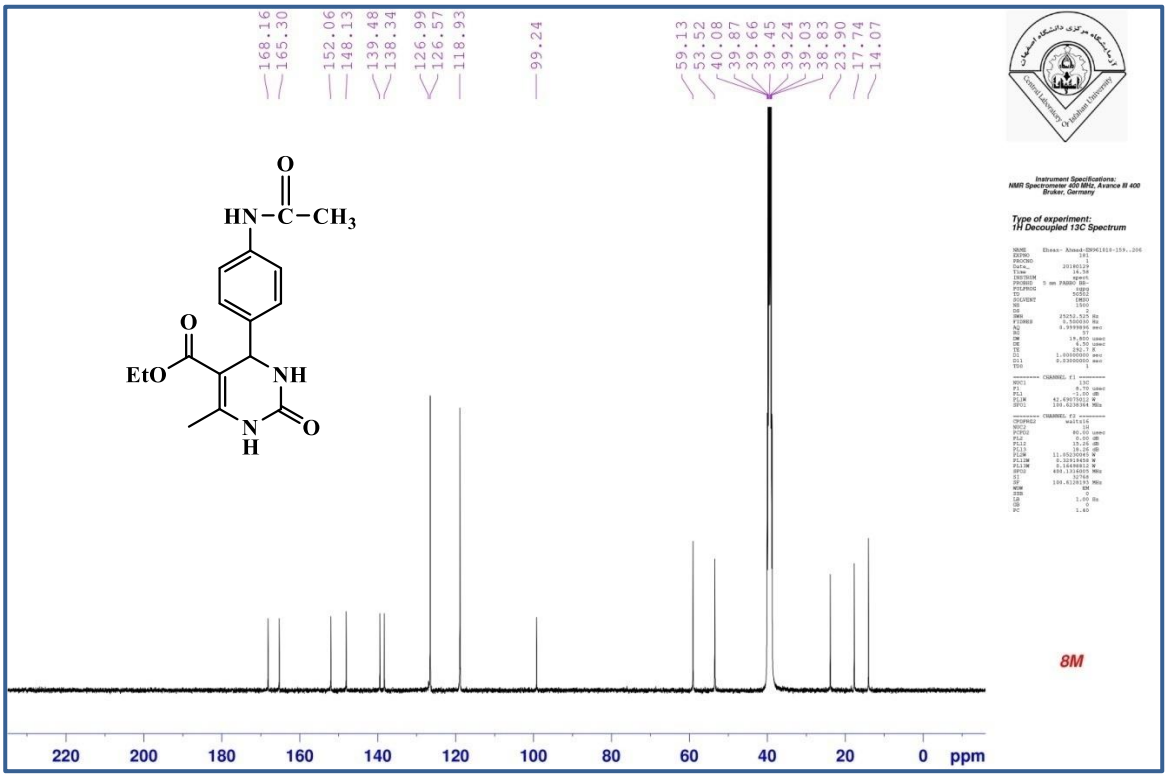


Figure 3-19:The ^{13}C-NMR spectrum of ethyl 4-(4-acetamidophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2d.**

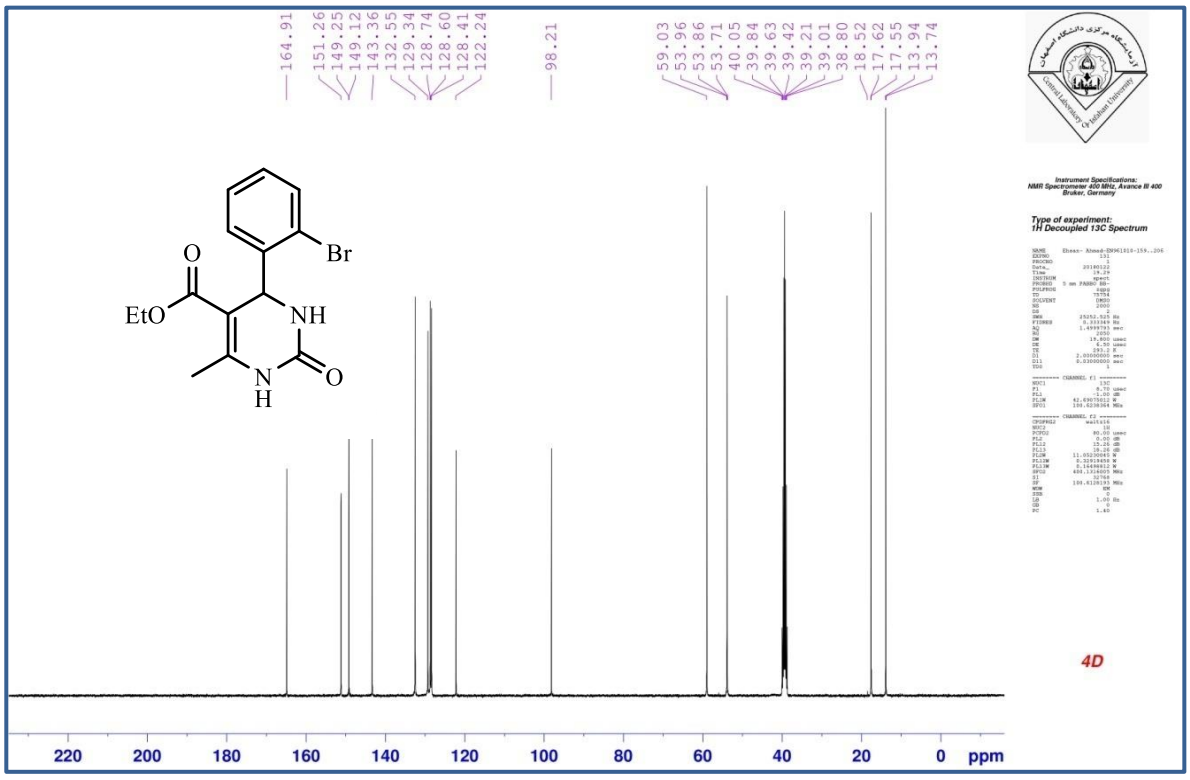


Figure 3-20:The ^{13}C-NMR spectrum of ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2e.**

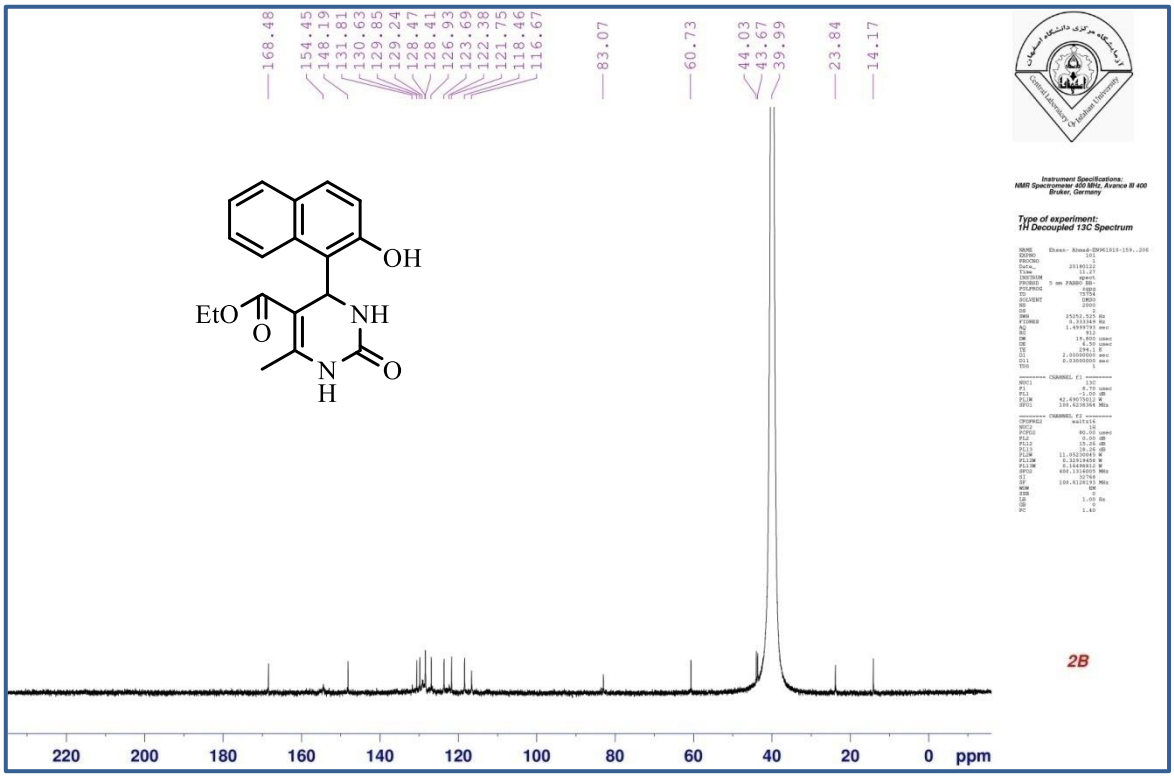


Figure 3-21:The ^{13}C-NMR spectrum of ethyl4-(2-hydroxynaphthalen-1-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f.**

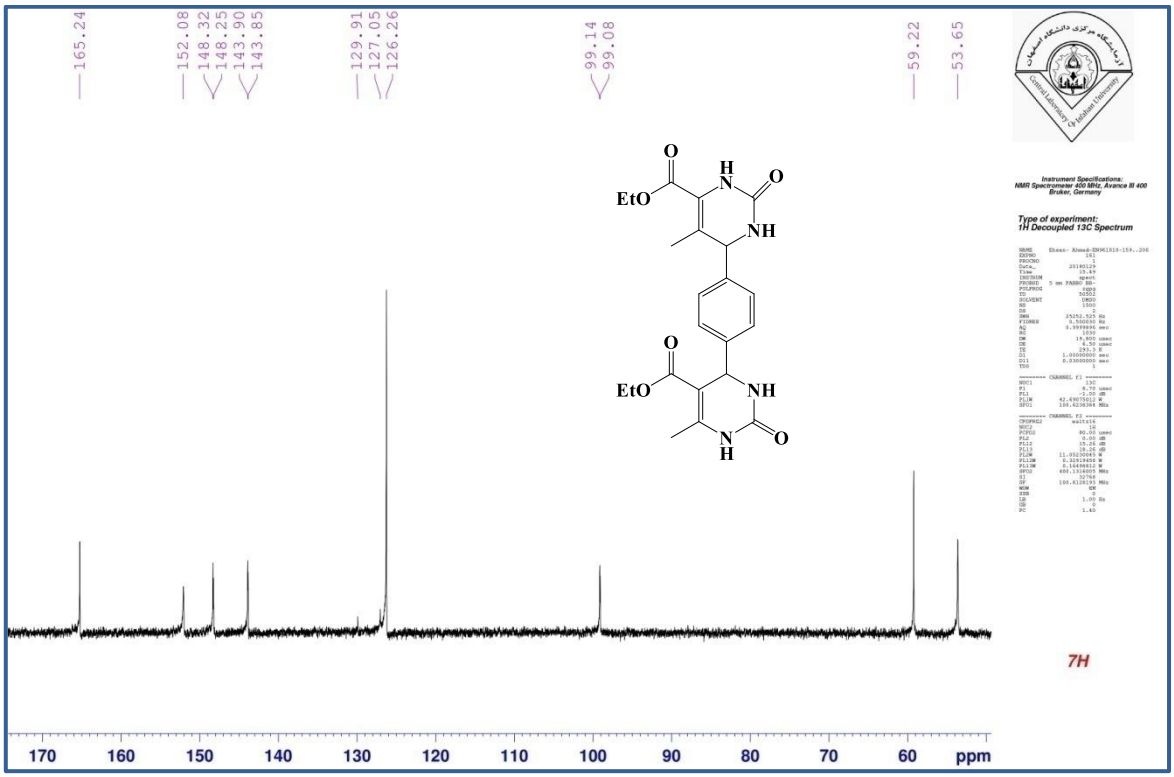


Figure 3-22:The ^{13}C-NMR spectrum of diethyl 4,4'-(1,4-phenylene) bis(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate) **2h.**

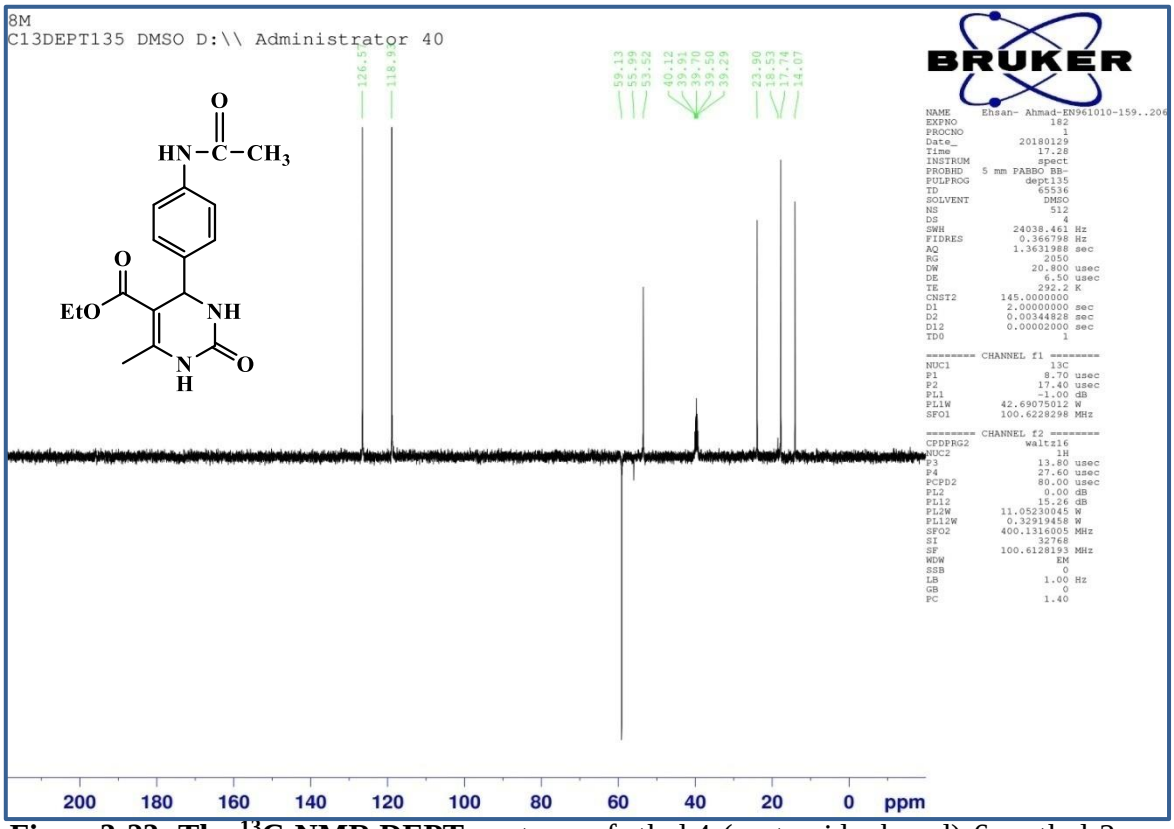


Figure3-23: The ^{13}C-NMR DEPTspectrum of ethyl 4-(acetamidophenyl)-6-methyl-2-oxo-1,23,4-tetrahydropyrimidine-5-carboxylate **2d**.

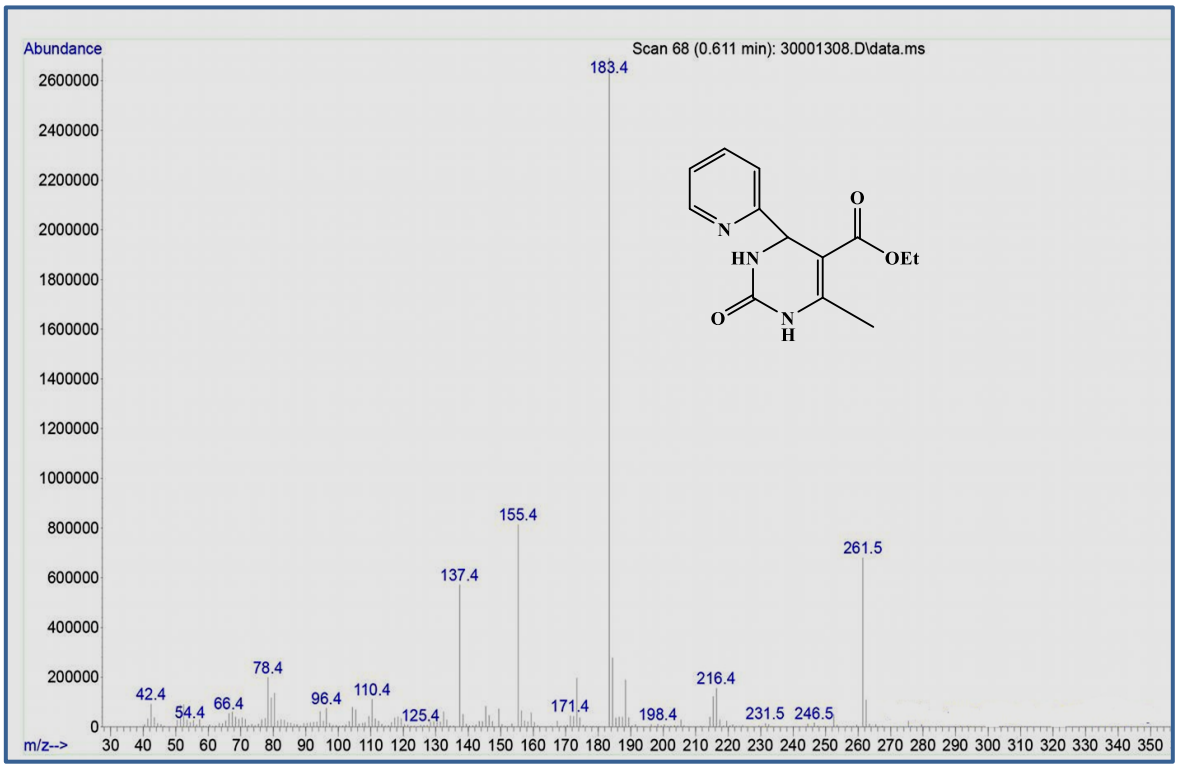


Figure 3-24: The Mass spectrum of ethyl 2-oxo-4-(pyridin-2-yl)-1,2,3,4- tetrahydro pyrimidine -5-carboxylate **2a.**

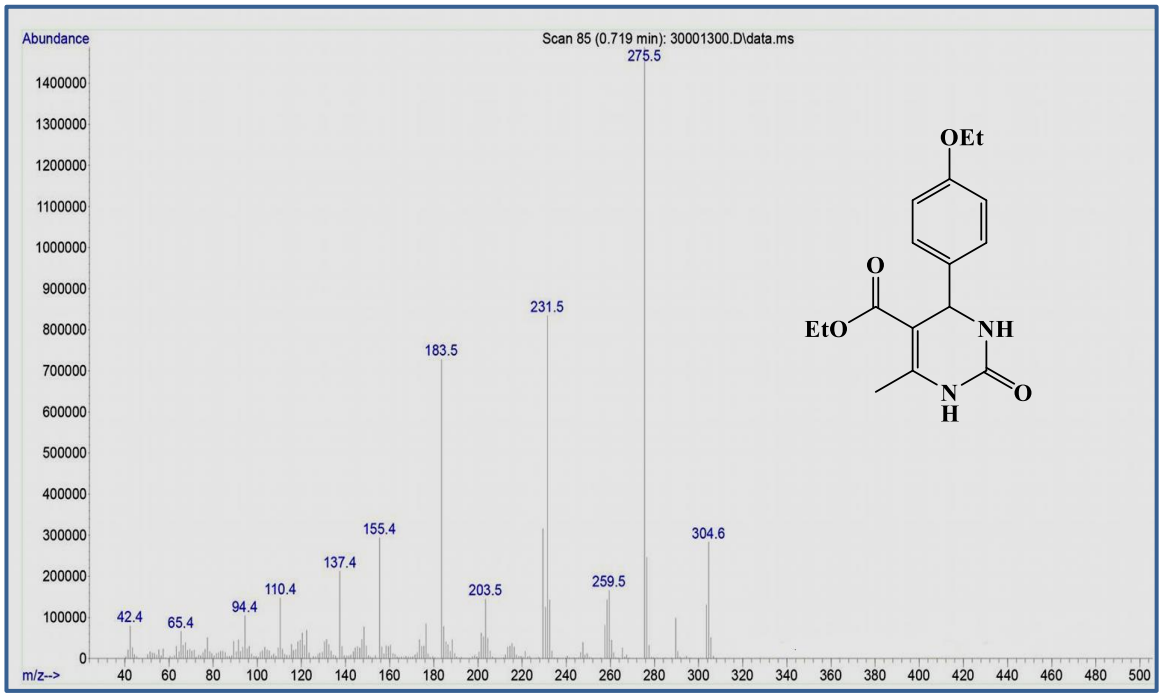


Figure 3-25: The Mass spectrum of ethyl 4-(4-ethoxyphenyl)-6-methyl- 2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2b**.

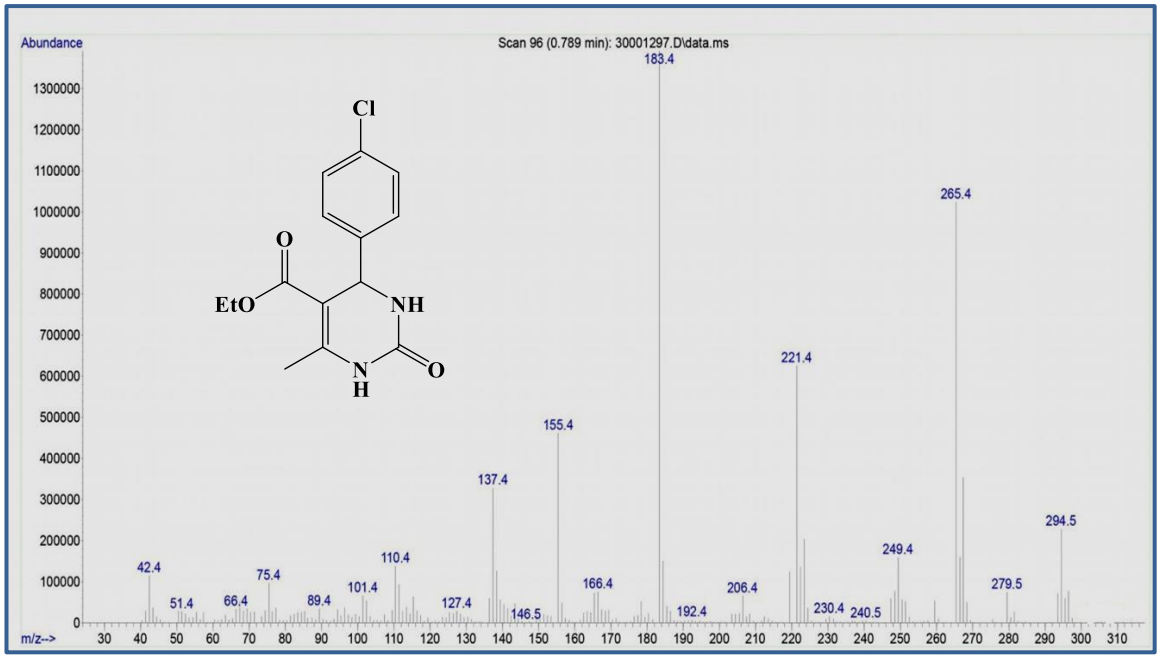


Figure3-26: The Mass spectrum of ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2c.**

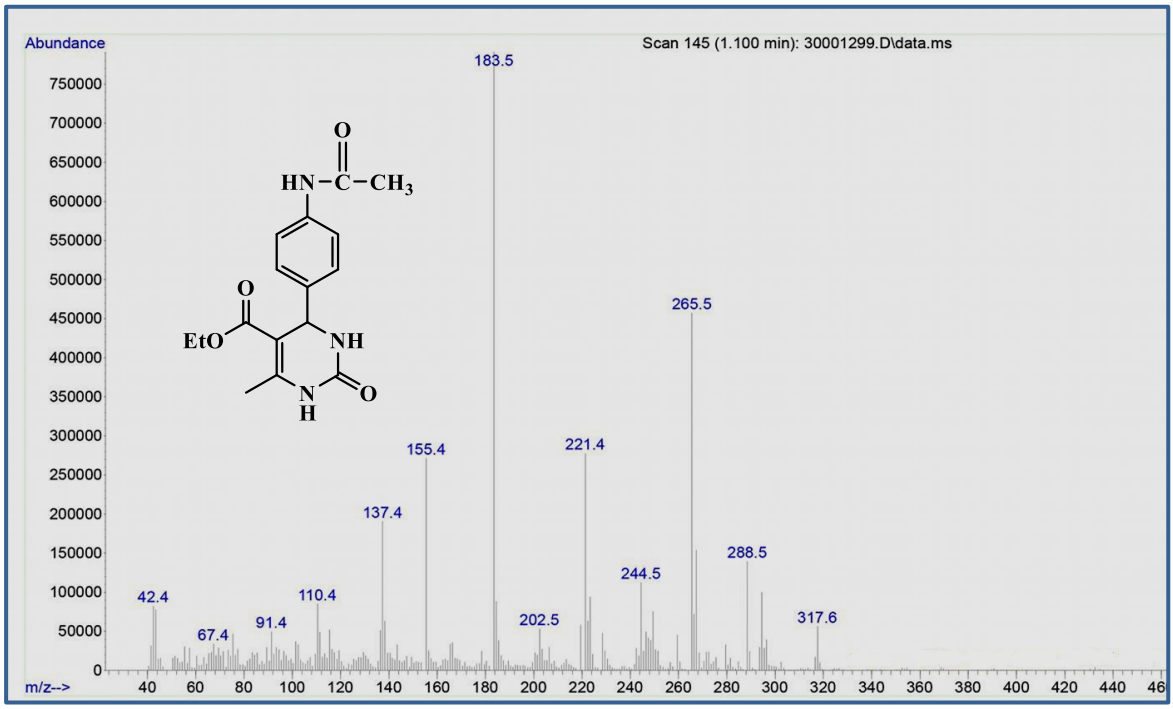


Figure 3-27: The Mass spectrum of ethyl 4-(4-acetamidophenyl)-6- methyl-2-oxo-1,23,4-tetrahydropyrimidine-5-carboxylate **2d**.

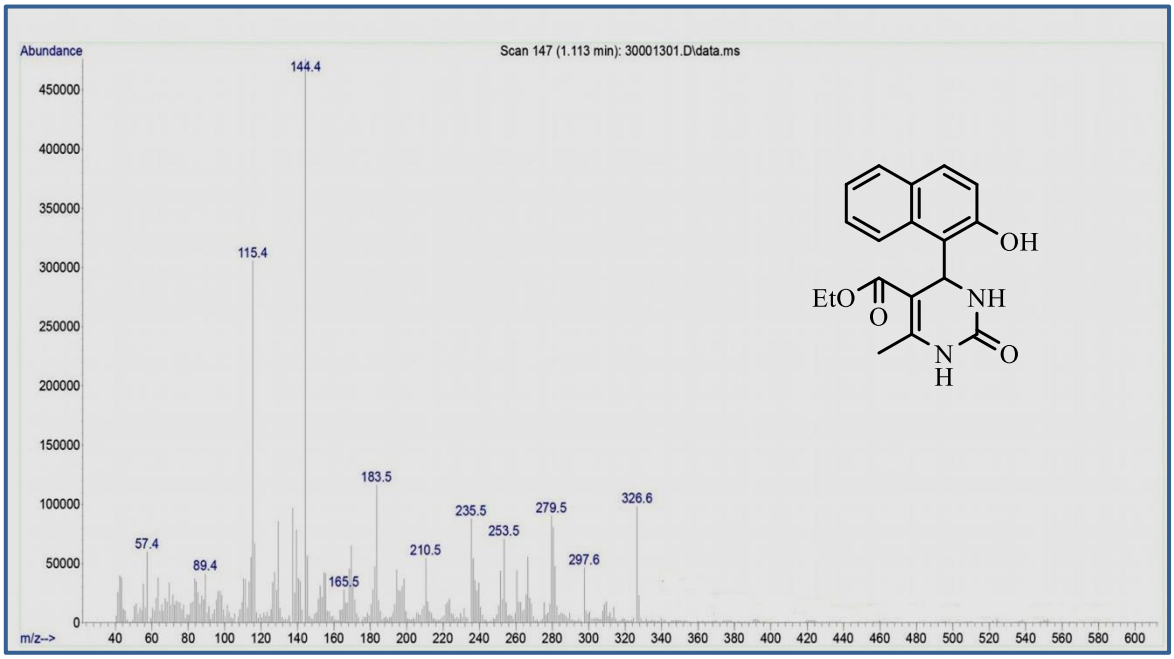


Figure 3-28: The Mass spectrum of ethyl4-(2-hydroxynaphthalen-1-yl)- 6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **2f**.

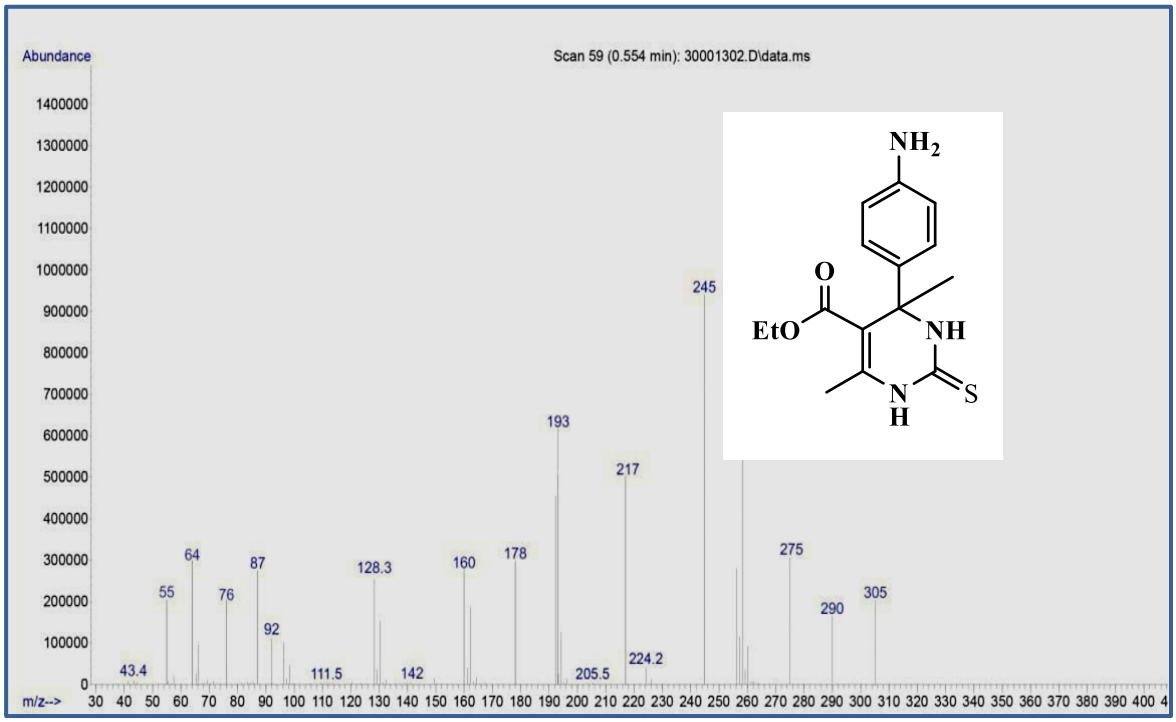


Figure3-29: The Masss pectrum of 4-(4-aminophenyl)-5-(ethoxy methyl) -4,6-dimethyl-3,4-dihydropyrimidine-2(1H)/thione **2i.**

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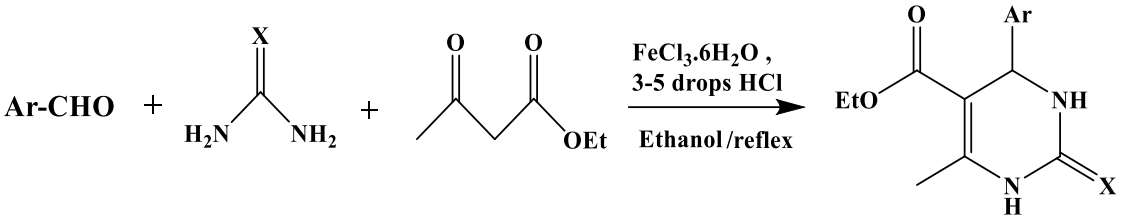
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الخلاصة

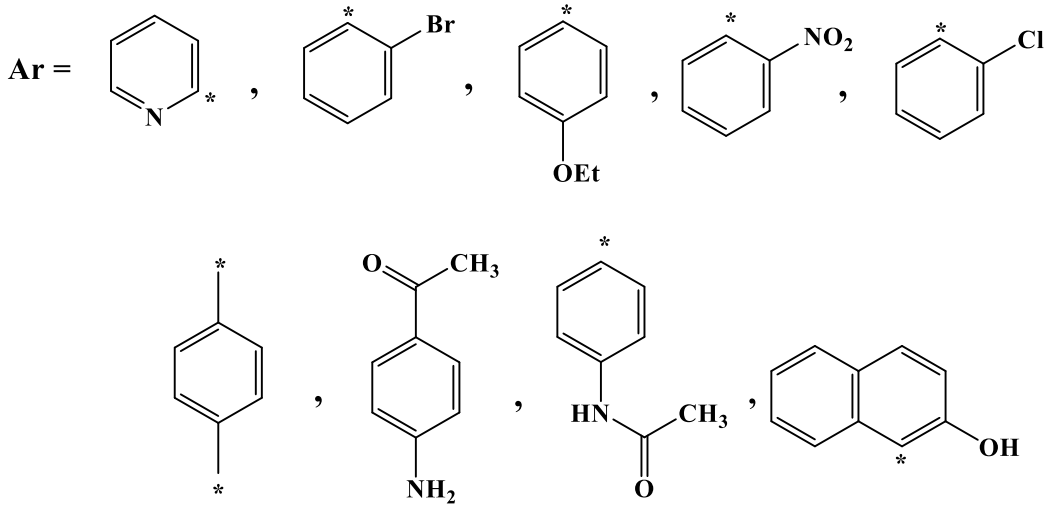
تضمنت الدراسه تخليق وتشخيص بعض مركبات 3و4- داي هايدروبرميدين/ثايون حيث حضرت هذه المركبات من تفاعل ايثل استواستيت ,الالديهايدات الاروماتيه مع اليوريا او الثايويوريا بوجود العامل المساعد كلوريد الحديديك سداسي الماء مع قطرات من حامض الهيدروكلوريك المركز والايثانول كمذيب . بدرجه حراريه (65-60) درجه سليزيه وبحصيله جيده (92%-55).

التفاعل العام لتحضير 3و4- داي هايدروبرميدين/ثايون



X = O

Ar =



شخصت المركبات المحضرة بالاعتماد على : طيف الاشعة تحت الحمراء , طيف الرنين النووي المغناطيسي , طيف كاربون-الرنين النووي المغناطيسي وطيف الكتلة.

جمهوريه العراق

وزاره التعليم العالي والبحث العلمي

جامعه ذي قار

كليه العلوم

قسم الكيمياء الدراسات العليا

تخليق وتشخيص ودراسه مضادات الاكسده لبعض المشتقات الجديده (لداي هايدروبرميدين/ثايون)

رسالة مقدمة الى كليه العلوم- جامعة ذي قار وهي جزء من متطلبات نيل درجة ماجستير علوم في الكيمياء من قبل الطالبة

نور ريسان علي

بكالوريوس علوم الكيمياء /*2011*

اشراف

الاستاذ الدكتور :محمود شاكر مكطوف

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