CHAPTER-Ⅰ

SECTION-B

One-pot synthesis of pyrazines from Ethylenediamine and 1, 2-diketone or its analogues under neat reaction condition

Ⅰ.B. Present Investigation

Ⅰ.B.1. Background of the present investigation

Heterocyclic compounds are omnipresent in nature [1]. Among different N-heterocyclic compounds, pyrazine and its congeners have broad spectrum of biological activities[2] such as anticancer, antituberculosis [3], antimicobacterial activity, antimalarial, antiHIV and cytotoxicity [4]. In addition, these heterocycles are widely applied to other industrial fields, for example,in the preparation of perfumes, pharmaceuticals, agricultural chemicals [5]. It also plays an important role in making flavor ingredient in food and pheromones in various insect [6].It is a versatile synthetic intermediates [7]. Owing to vast and outstanding applications, several synthetic strategies have been developed for their synthesis over the years [8]. Among several methods developed, pyrazines are formed by catalytic dehydrogenation of the vapour of ethanolamine.The catalysts used were copper oxide, zinc oxide, copper, sodium carbonate[9]. Condensation of α-amino ketone[10], Pd-catalysed cross coupling reaction also produced pyrazine derivatives [11]. Further, pyrazine compounds were prepared by the reaction of diamine with diol in vapour phase, catalysed by granular alumina [12]. Catalytic system such as copper-zinc-chromium [13], zinc-phosphoric acid-manganese [14], copper-chromium [15] and silver [16] were also used for the preparation of 2-methyl pyrazine from propyleneglycol and ethylenediamine. Pyrazines were synthesized from the condensation of epoxides and diamines using copper-chromium catalyst [17]. Piperazines gets dehydrogenated in the presence of palladium catalyst

to produce pyrazines in high yield[18]. A-hydroxy ketones and 1, 2-diamine also produce pyrazines via MnO_2 catalyzed tandem oxidation reaction under refluxing conditions, but the yields were not so encouraging [19], moreover this reaction requires an excess amount of MnO_2 catalyst that detracts from the commercial point of view and green condition [20]. Direct condensation of 1, 2-diketones with 1, 2-diamine has so far been the better procedure of pyrazine synthesis through dihydropyrazine [21]. Although, there are several methods of pyrazine synthesis in literature, most of them are regarded as ineffective because of poor yield, long reaction time, tedious work-up process and drastic reaction condition [22]. Although, a few of them are apparently successful, but a convenient and milder laboratory procedures for dehydrogenation were unsuccessful and most of the methods are limited by long reaction time, use and generation of hazardous substances and heavy metals as the catalyst [23].Therefore development of efficient, mild and environmental friendly method for pyrazine synthesis has been a long cherished goal for organic chemists.

Recently, environmentally-friendly reaction processes have been extensively studied from the view point of green chemistry. Solid acid catalyst under heterogeneous condition [24] plays an important role in organic synthesis. Generaly solid acid catalysts are clay and silica based[25] .But these type of reaction requires an appreciable amount of solvent in work-up process [26]. The concept of neat reaction is consistent with the dream of green chemistry in true sence. Neat reaction is a solvent-free methodology where a mixture of reactants are grinded in absence of any solvent.The easy work-up and devoid of any solvent makes it justified from the stand point of green chemistry.

The primary demands of green synthesis include minimization of steps which involves one-pot tandem reactions as well as catalytic processes under metal-free conditions [27]. Since there is no

method developed for the one-pot and metal-free tandem synthesis of pyrazines from ethylenediamine with 1,2-dicarbonyl compounds or analogues, we were interested to develop an alternative solvent and metal-free greener process for the synthesis of pyrazines directly from ethylenediamine with 1,2-dicarbonyl compounds or with analogues at room temperature.In recent days , solvent-free synthesis have attracted the attention of chemists because they are environmentally benign processes. In continuation of our interest in the development of solvent-free synthesis [28], herein we report a new synthetic strategy for the preparation of pyrazine derivatives from ethylenediamine with 1, 2-diketone or with analogues under neat reaction condition.

In connection with our present interest , we explored the synthesis of pyrazines through the metal-free, solvent-free tandem condensation in one-pot protocol.

Ⅰ.B.2. Result and discussion

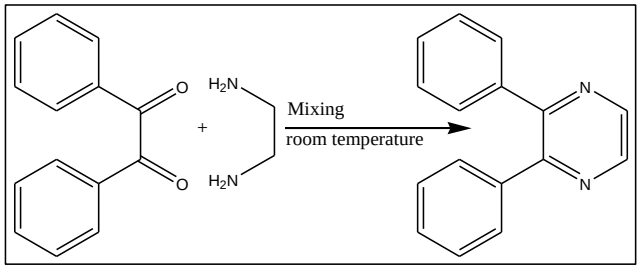
We report herein our findings that finally established a practical and clean procedure for the synthesis of pyrazines derivatives directly from ethylenediamine with 1, 2-diketone or with analogues via one-pot condensation reaction under metal-free condition at room temperature.There was no other by-product detected by analysis of the crude product,the conversion was high and the isolation of the desired pyrazine was achieved in excellent yield.A large variation of functional groups attached with the aromatic ring of 1, 2-diketones was observed with excellent conversions to pyrazines derivatives.

Our studies began with the reaction of ethylenediamine and benzil under neat reaction condition.We set-up the reaction by adding the reacting components i.e mixture of ethylenediamine (1mmol) and benzil (1mmol) mixture into a glass plate and stirred with a glass rod at room temperature and left for 10 hrs. The reaction mixture was then extracted with ethylacetate and washed several times by water and the extract was filtered through anhydrous Na_2SO_4. Finally 56% 2, 3-diphenyl pyrazine (**entry 2, Table.B. 1**) along with unreacted benzil were separated by column chromatography over

silica-gel (60-120 mesh) where pet-ether and ethylacetate mixture was eluent. Thereafter we used mortar for grinding the reaction mixture for a few minutes and transferred the mixture into a 50 ml round-bottom glass bottle and it was kept under magnetic stirrer for better result. We raised the reaction temperature upto 100∘C (**Table.1.B.1. entry 1**) and found no product. We used mono ketone (acetophenone) with ethylenediamine but the reaction was unsuccessful.

Encouraged by the model reaction with benzil and ethylenediamine on neat reaction condition, several experiments regarding time and proportion optimization were carried out for the newly developed general protocol for the synthesis of pyrazine derivatives (Table.1.B.1 and Table.1.B.2). Finally we could optimize the reaction condition as benzil (1mmol) and ethylenediamine (2mmol) mixture was kept on magnetic stirrer for 6 hrs and got 2, 3-diphenyl pyrazine (77%) as a sole product (**entry 3, Table.1.B.1**).

In order to show the general applicability, we attempted the recent procedure to a number of chemically diversified ketone and ethylenediamine to synthesize pyrazine derivative (**Table. Ⅰ.B.3**) and obtained the identical result in each case.In the present investigation, it is found that no additional steps required to aromatize the dihydropyrazine derivatives as reported in the early methods which are the main advantage of this procedure (**scheme. Ⅰ.B.1**).



Scheme. Ⅰ.B.1. One- pot condensation of ethylenediamine with 1, 2-diketone or with analogues resulting pyrazines.

Table. Ⅰ.B.1.Optimization of time(h) for one-pot condensation of ethylenediamine (1mmol) with benzil (1mmol).

Entry	Temp (^{0}C)	Time (h)	Conversion(%)[a]
1	100	12	Nil
2	RT	10	56
3	**RT**	**6**	**77**[b]
4	RT	8	42
5	RT	1	38
6	RT	2	34
7	RT	0.5	25

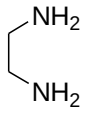
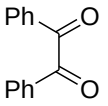
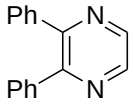
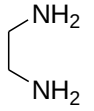
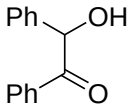
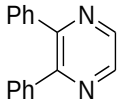
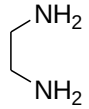
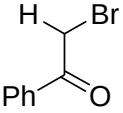
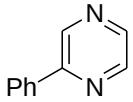
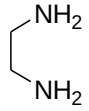
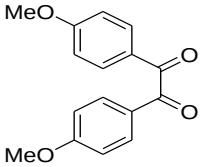
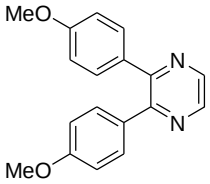
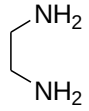
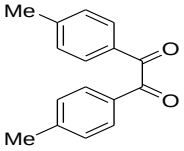
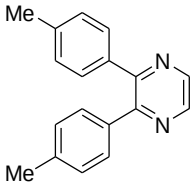
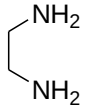
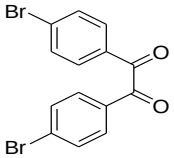
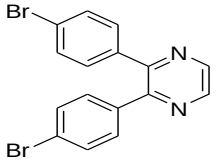
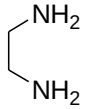
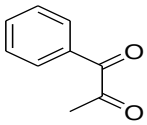
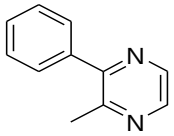
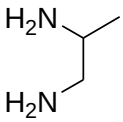
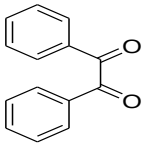
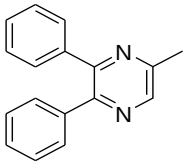
[a]Isolated yield.; [b]Optimized reaction condition.

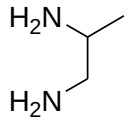
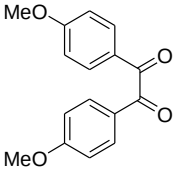
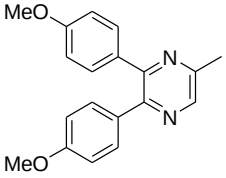
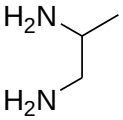
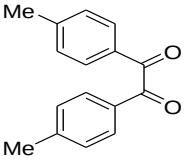
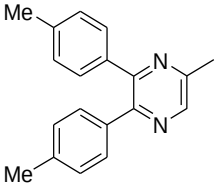
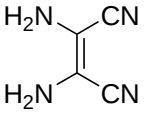
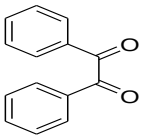
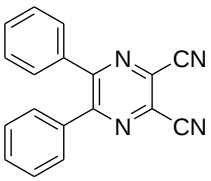
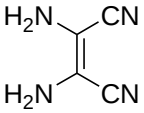
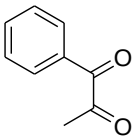
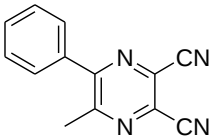
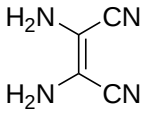
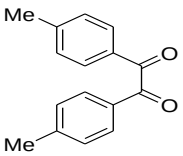
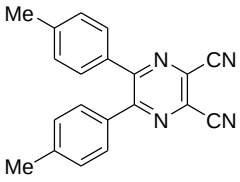
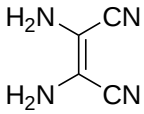
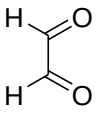
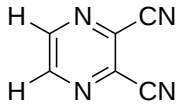
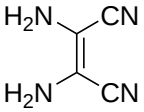
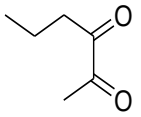
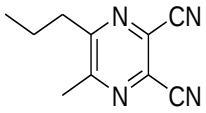
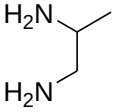
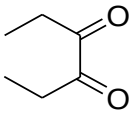
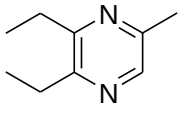
Table. Ⅰ.B.2. Optimization of proportion of ethylenediamine (mmol) with benzil (mmol)

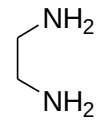
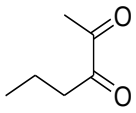
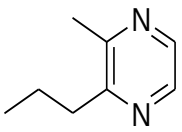
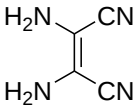
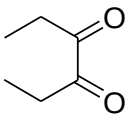
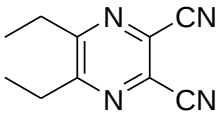
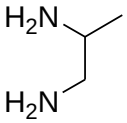
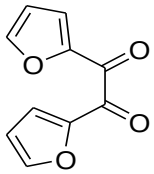
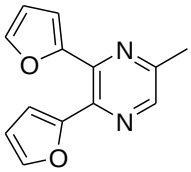
Entry	Ethylenediamine (mmol)	Benzil(mmol)	Conversion(%)[a]
1	1	1	52
2	1	0.5	54
3	**2**	**1**	**77**[b]
4	1.5	1	72
5	0.5	1	51
6	2.5	1	68

[a]Isolated yield; [b]Optimized condition

Table. Ⅰ.B.3. Condensation of ethylenediamine with 1, 2-dicarbonyl compounds or with α-hydroxy ketones or with α-bromo ketone at room temperature

Entry no	Ethylenediamine	1,2-dicarbonyl compound/ analogues	Time(h)	Product	Yield(%)
1			6		77
2			6		75
3			6		68
4			10		76
5			8		81
6			7		80
7			6.5		75
8			5		73

9			5.5		73
10			6		85
11			5		85
12			7		86
13			6		75
14			6.5		82
15			5.5		75
16			7		73

17			8		76
18			7		72
19			5.5		81

Note:% Yield refers to the isolated yield of all compounds.

With the optimized condition (as in Table. Ⅰ.B.1, entry 3), we examined its practical application with a variety of 1, 2-diketone derivatives or with analogues. The result are presented in Table. Ⅰ.B. 2. It can be seen that different keto compounds undergo one-pot condensation with ethylenediamine and gave rise to the formation of corresponding pyrazines in excellent yields.

Ⅰ.B.3. Experimental

Ⅰ.B.3.1. Reaction procedure and purification

1 mmol of recrystallised benzil and 2 mmol of ethylenediamine were added to a mortar. The mixture was grinded for a few minutes and transferred to a 50 ml round bottom flask and was kept stirring with a magnetic spinning bar for 6 hrs. The reaction checked by TLC (ethylacetate and pet-ether). The product was extracted by ethylacetate, washed by water and filtered through anhydrous Na_2SO_4. Product was purified by column chromatography using silica-gel (60-120 mesh). Petroleum ether-

Ethylacetate (PE-EA) mixture were used as eluent. All the products were characterized by IR, ^{1}H NMR and ^{13}C NMR.

Ⅰ.B.3.2. Spectroscopic measurement

UV spectra were recorded in JASCO V-530 UV/VIS Spectrophotometer, IR was recorded in Perkin-Elmer FT-IR Spectrophotometer; NMR was recorded in Bruker Advance 300 MHz FT-NMR instrument using TMS as the internal standard. NMR spectra were recorded in $CDCl_3$. The chemicals used were purchased from Merck, Thomas-Baker and were used as received. No further purification was done.

Ⅰ.B.4. CONCLUSION

In conclusion, we have explored a solvent and metal catalyst free, one-pot facile synthesis of pyrazine derivatives from ethylenediamine (2mmol) and 1, 2-diketone or with α-bromo and α-hydroxy ketone (1mmol) under neat reaction condition at room temperature. Advantages of this protocol are, avoiding harmful organic solvent which causes environmental pollution, excellent yield and easy work-up process**.** the present work demonstrates the synthesis of bio-active scaffold pyrazine derivatives directly from ethylenediamine and 1,2-diketone or with its analogues via one-pot condensation reactions under neat reaction condition at room temperature.The conditions are straightforward, mild, eco-friendly and no other side-products are obtained.Green process of preparation of pyrazines from ethylenediamine and keto-compounds is developed that could override existing metal-catalyzed reaction conditions

Ⅰ.B.5. Characterization data

Ⅰ.B.5.1. 2, 3-diphenyl pyrazine

Mp.117-121^{0}C ^{13}C NMR ($CDCl_3$, 75MHz): δ 128.2, 128.7, 129.6, 138.5, 142.1 and 152.8

^{1}H NMR ($CDCl_3$, 300MHz): δ 6.38-6.44 (m, 5H, five aromatic hydrogen); 6.55-6.58 (m, 5H, five aromatic hydrogen); 7.72 (s, 2H, 2 aromatic hydrogen of the heterocyclic moiety).

Ⅰ.B.5.2. 2, 3-bis (4-methoxy phenyl) pyrazine

Mp.111-113^{0}C, ^{13}C NMR ($CDCl_3$, 75MHz): δ 55.2, 113.7, 130. 9, 131.2, 141.4, 152.1 and 159.9.

^{1}H NMR ($CDCl_3$, 300MHz): δ 3.77 (s, 6H, 2-OCH3); 6.75-6.85 (m, 4H, four aromatic hydrogen); 7.26-7.43 (m, 4H, four aromatic hydrogen); 8.45 (s, 2H, two aromatic hydrogen of the heterocyclic moiety).

Ⅰ.B.5.3. 2, 3-di p-tolyl pyrazine

^{13}C NMR ($CDCl_3$, 75MHz): δ 21.3, 129.0, 129.4, 135.8,138.5, 141.7 and 152.6.

^{1}H NMR ($CDCl_3$, 300MHz): δ 2.31 (s, 6H, 2-CH3);7.04-7.12 (m, 3H, aromatic hydrogen); 7.22-7.46 (m, 5H, five aromatic hydrogen); 8.51 (s, 2H, two aromatic hydrogen of the heterocyclic moiety).

Ⅰ.B.5.4. 2-methyl-3-phenyl pyrazine

^{13}C NMR ($CDCl_3$, 75MHz): δ 23.1, 128.4, 128.7, 128.9, 138.5, 141.5, 142.1, 151.8 and 154.0

^{1}H NMR ($CDCl_3$, 300MHz): δ 2.54 (s, 3H, -CH_3); 7.46-7.59 (m, 5H, five aromatic hydrogen); 8.44 (d, 2H, J=2.4Hz).

Ⅰ.B.5.5. 2, 3-diphenyl-5-methyl pyrazine

Mp.84-86^{0}C ^{13}C NMR ($CDCl_3$, 75MHz): δ 20.5, 127.4, 127.6, 128.7, 128.8, 137.8, 141.0, 148.8, 150.3, 150.7. ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.86 (s, 3H, -CH_3); 6.63 (d, 10H, J-5.1Hz, ten aromatic hydrogen); 7.68 (s, 1H, one aromatic hydrogen of the heterocyclic moiety).

Ⅰ.B.5.6. 2, 3-bis (4-methoxy phenyl)-5-methyl pyrazine

^{13}C NMR ($CDCl_3$, 75MHz): δ 21.2, 53.4, 55.2, 130.8, 130.9,131.2, 131.4, 141.1, 149.0, 150.5, 150. 9, 159.8, 159.6 ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.62 (s, 3H, -CH_3); 3.80 (s, 6H, 2-OCH3); 6.82 (dd, 4H, J=1.8 Hz, four aromatic hydrogen); 7.38 (dd, 4H, J=1.8 Hz, four aromatic hydrogen); 8.39 (s, 1H, one aromatic hydrogen of the heterocyclic moiety).

Ⅰ.B.5.7. 5, 6-diphenyl pyrazine-2, 3-dicarbonitrile

Mp.252-254^{0}C ^{13}C NMR ($CDCl_3$, 75MHz): δ 112.4, 128.2, 129.1, 130.5, 134.5, 154.5, 198.0

^{1}H NMR ($CDCl_3$, 300MHz): δ 7.16-7.30 (m, 5H, five aromatic hydrogen); 7.45 (t, 2H, J=7.3 Hz, two aromatic hydrogen); 7.57 (t, 1H, J=7.3 Hz, aromatic hydrogen); 7.78 (d, 2H, J=7.2 Hz, aromatic hydrogen).

Ⅰ.B.5.8. 5, 6-dip-tolylpyrazine-2, 3-dicarbonitrile

^{13}C NMR ($CDCl_3$, 75MHz): δ 21.6, 126.8, 128.6,129.3, 130.0, 139.2, 144.0, 144.3, 193.3. ^{1}H NMR ($CDCl_3$, 300MHz):δ 2.32 (m, 6H, 2 -CH_3); 6.99 (m, 4H, aromatic protons); 7.43 (m, 1H, aromatic proton); 7.94, (m, 3H, aromatic protons).

Ⅰ.B.5.9. 5-methyl-6-propiopyrazine-2, 3-dicarbonitrile

^{13}C NMR ($CDCl_3$, 75MHz): δ 13.8, 20.4, 22.3, 36.9, 113.3, 113.4, 129.9, 130.4,157.7, 161.2

^{1}H NMR ($CDCl_3$, 300MHz): δ 1.06 (t, 3H, J=7.2Hz); 1.78-1.88 (m, 2H); 2.75 (s, 2H, -CH_3); 2.94 (t, 2H, J=7.5 Hz).

Ⅰ.B.5.10. 2, 3-diethyl 5-methyl pyrazine

Bp. 80^{0}C ^{13}C NMR ($CDCl_3$, 75MHz): 13.1, 13.4, 21.0 , 27.0, 27.69, 116.2, 140.8, 149.9, 152.9, 155.2 ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.25-1.31(m,3H,-CH_3); 2.53, 2.78-2.86(m, 2H); 7.3, 8.2 .

Ⅰ.B.5.11. 2-methyl-3-propylpyrazine

^{13}C NMR ($CDCl_3$, 75MHz): δ 14.0, 21.5, 21.7, 36.9, 141.1, 141.4, 152.3, 156.0.

^{1}H NMR ($CDCl_3$, 300MHz): δ 0.96-1.04 (m, 3H, -CH3); 1.70-1.82 (m, 2H,); 2.57 (s, 3H, -CH3); 2.79 (t, 2H, J=7.5Hz).

Ⅰ.B.5.12. 2, 3 di-(furan-2-yl)-5-methyl pyrazine

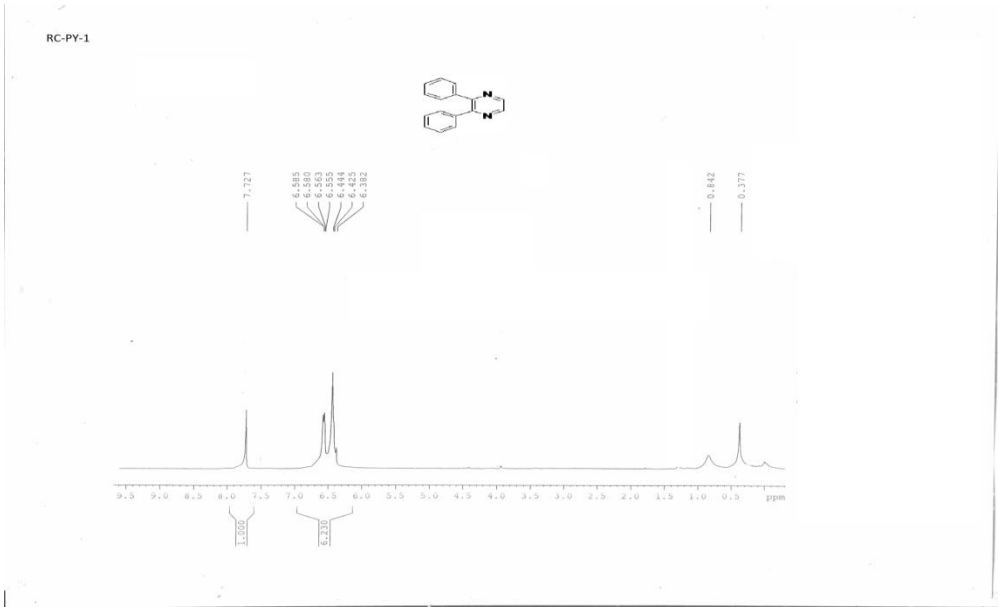
^{13}C NMR ($CDCl_3$, 75MHz): δ 21.3, 112.1, 112.7, 139.2, 140.8, 141.7, 143.4, 143.7, 150.5, 150.6, 151.2. ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.59 (s, 3H, -CH3); 6.56 (m, 4H, aromatic protons); 7.52 (m, 2H, aromatic protons), 8.37 (s, 1H, aromatic proton).

Ⅰ.B.5.13. 1, 4-pyrazine derivative of friedelin

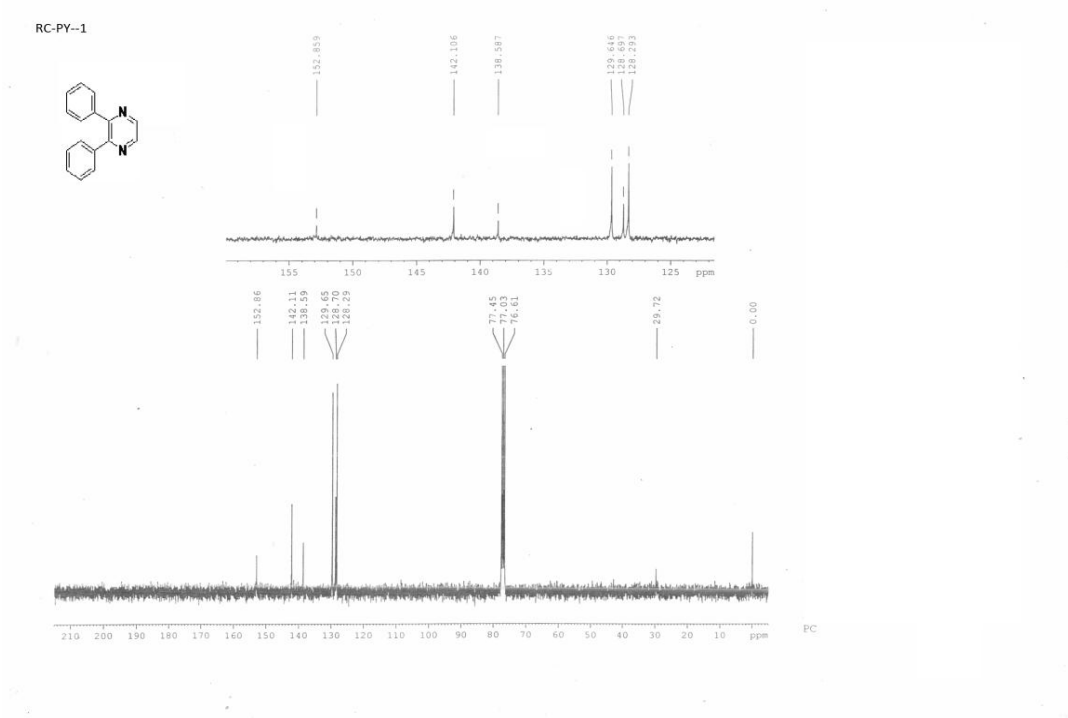
^{13}C NMR($CDCl_3$, 75MHz): δ 150.8, 150.9, 141.4, 142.3

^{1}H NMR ($CDCl_3$, 300MHz): δ 0.82-1.22(7s, 21H, 7t CH_3), 0.99(d, J=6.5 Hz), 8.40 and 8.27 (d, 2H, J=3Hz).

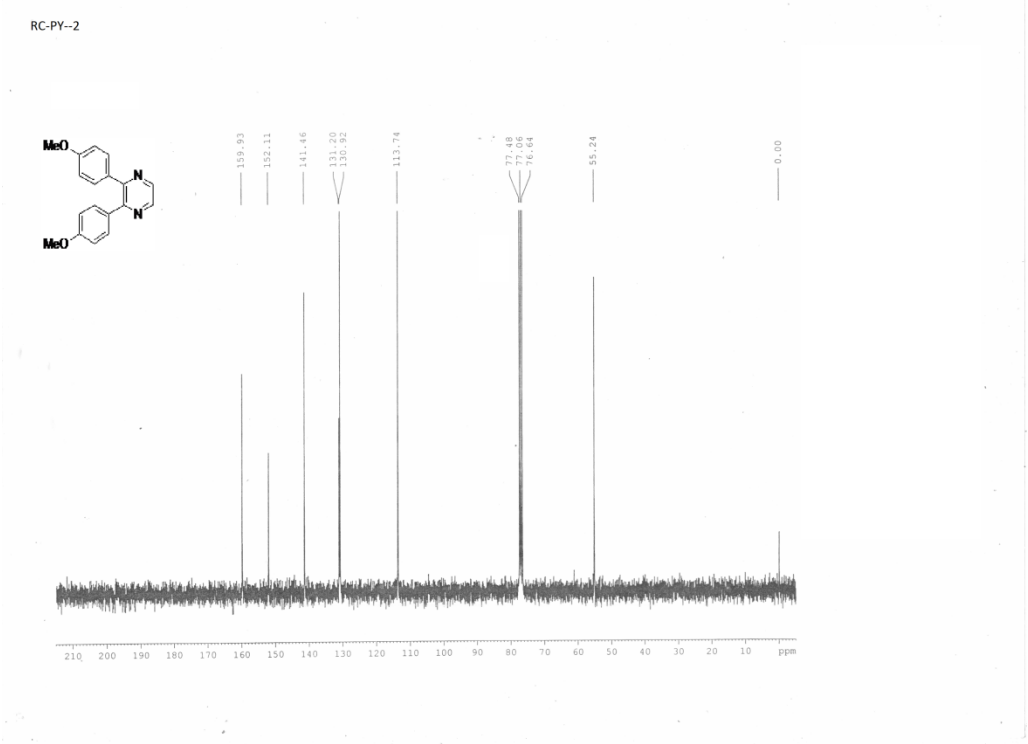
Ⅰ.B.6. Supporting Spectra.



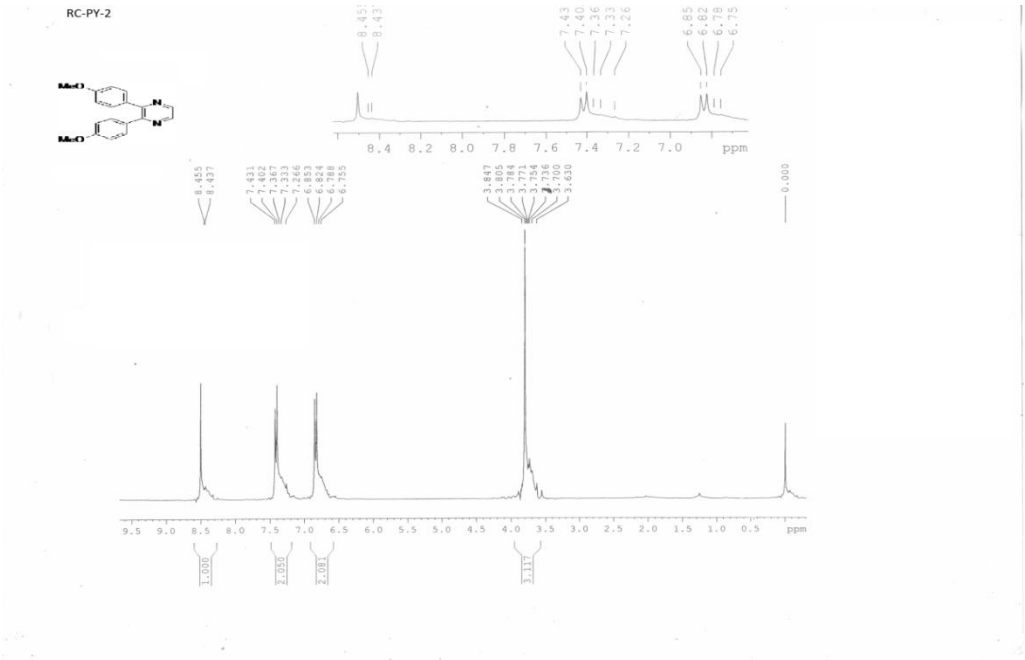
Ⅰ.B.6.1. ^{1}H NMR spectra of 2, 3-diphenyl pyrazine



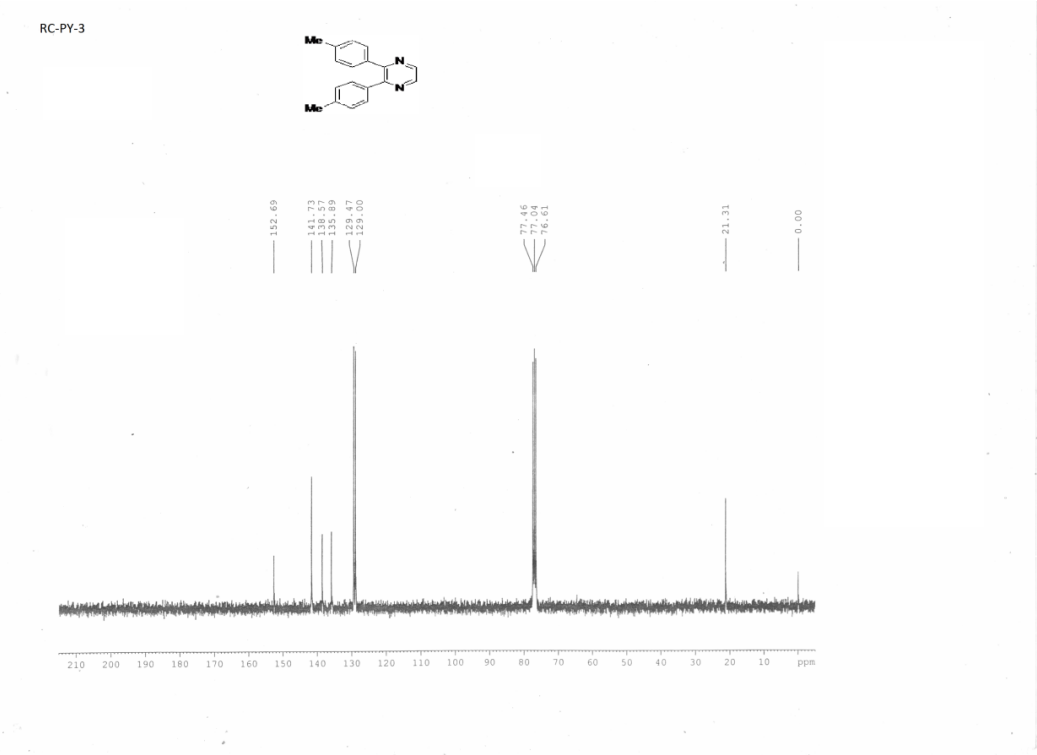
Ⅰ.B.6.2. ^{13}C NMR spectra of 2, 3-diphenyl pyrazine



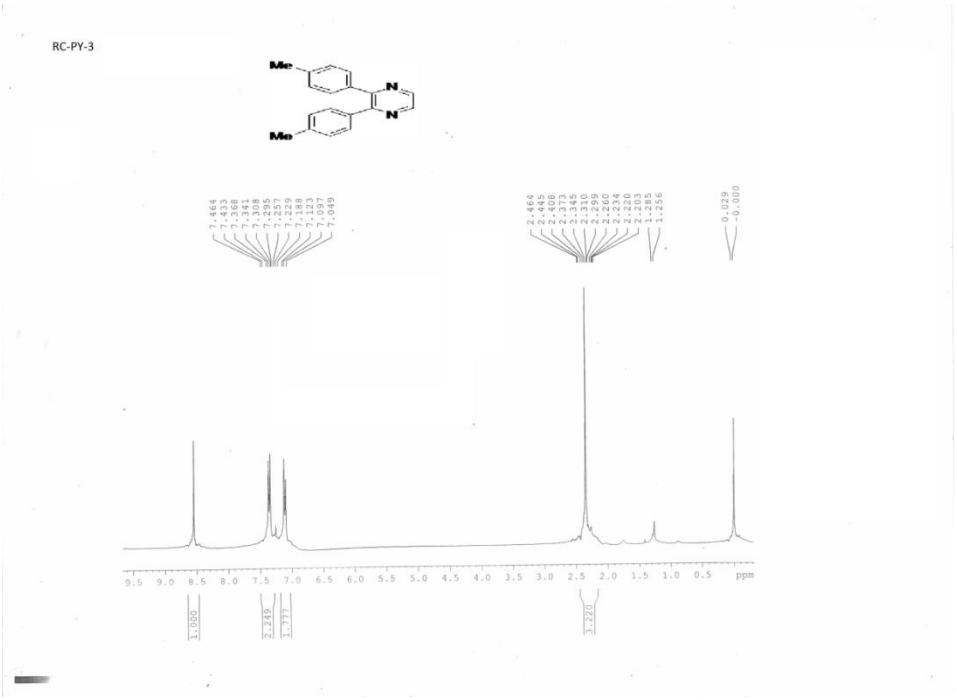
Ⅰ. B.6.3. ^{13}C NMR spetra of 2, 3-bis (4-methoxy phenyl) pyrazine



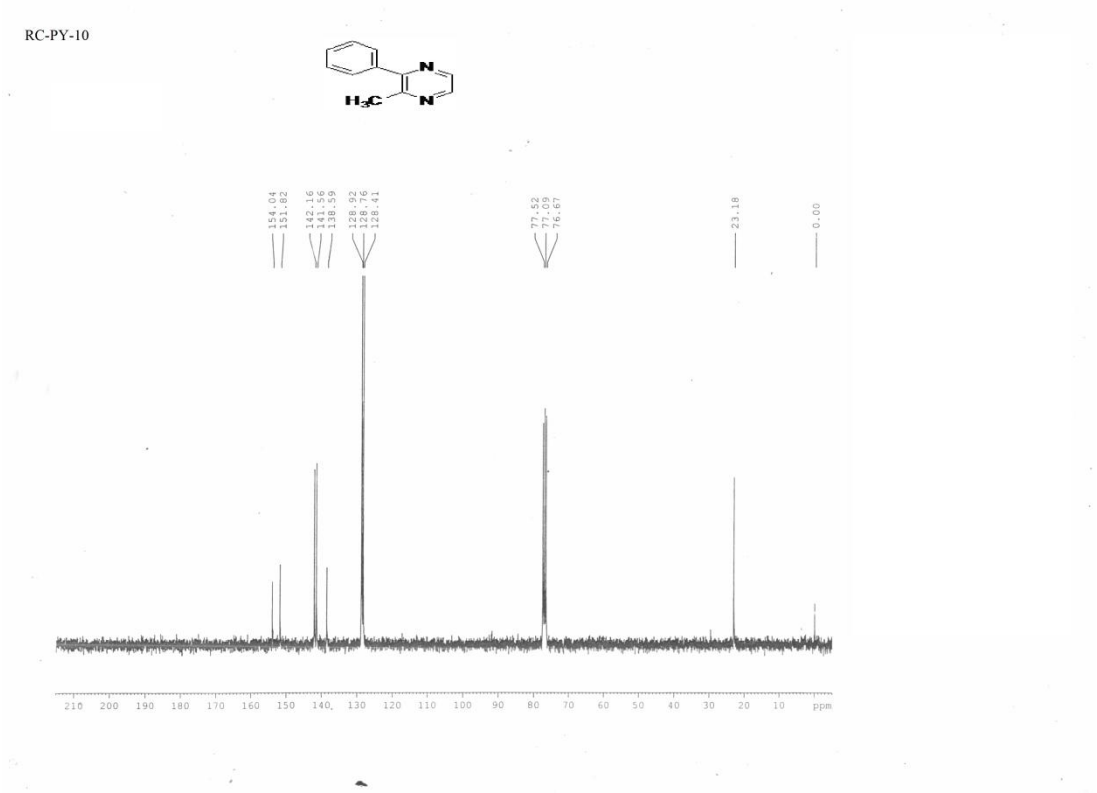
Ⅰ.B.6.4. ^{1}H NMR spectra of 2, 3-bis (4-methoxy phenyl) pyrazine



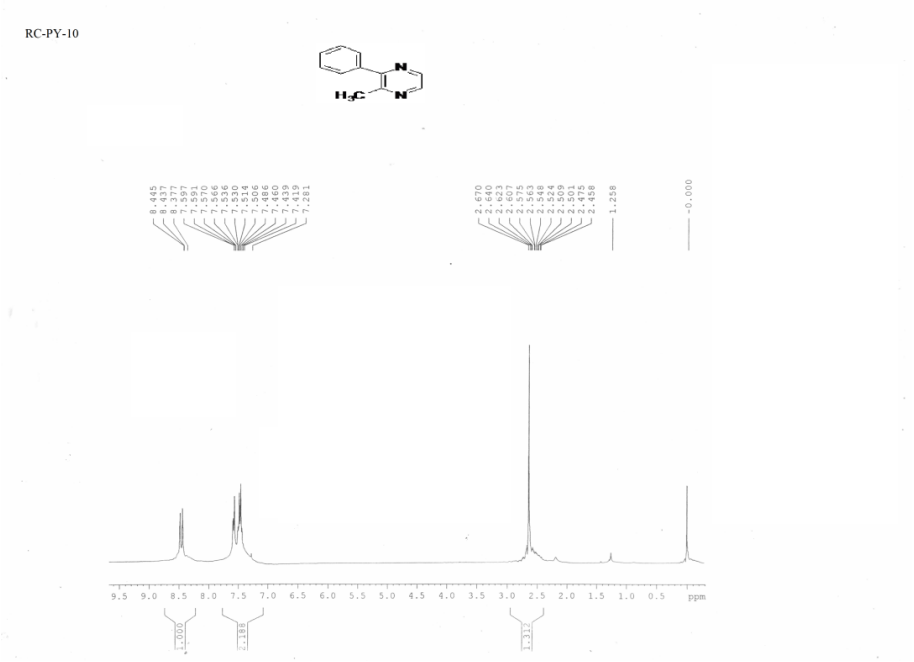
I .B.6.5. ^{13}C NMR spectra of 2, 3-di p-tolyl pyrazine



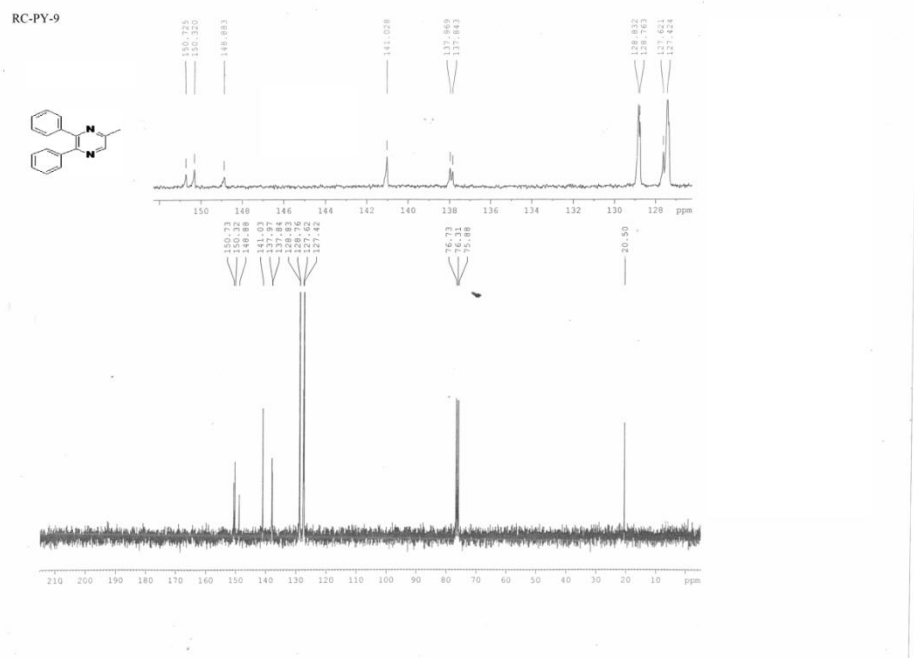
I .B.6.6. ^{1} H NMR spectra of 2, 3-di p-tolyl pyrazine



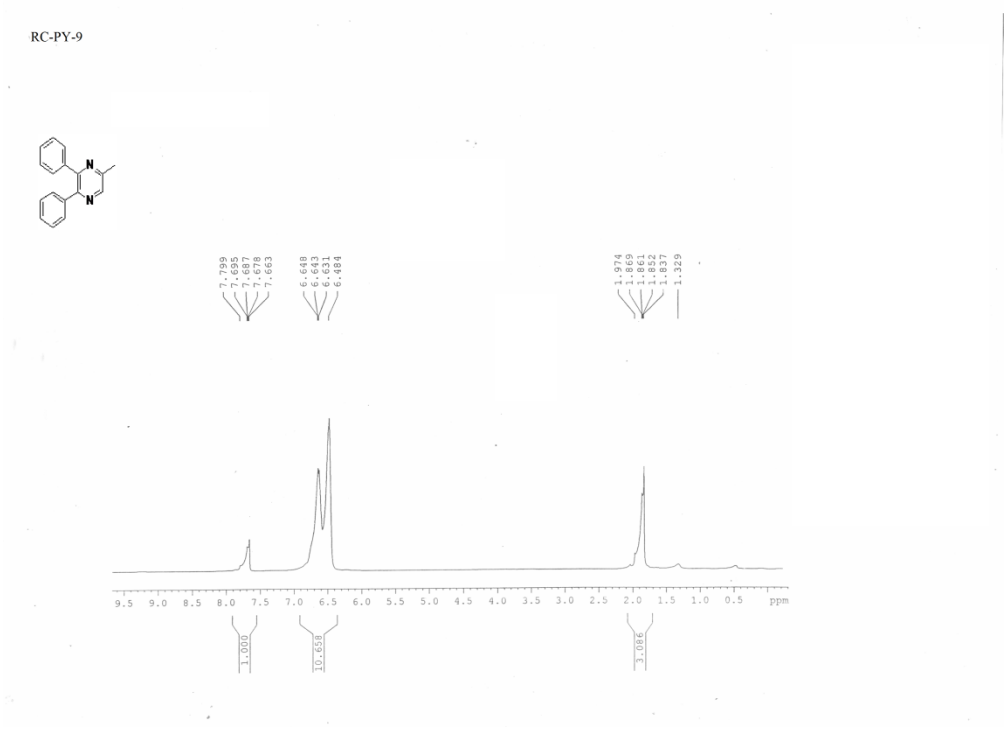
I .B.6.7. ^{13}C NMR spectra of 2-methyl-3-phenyl pyrazine



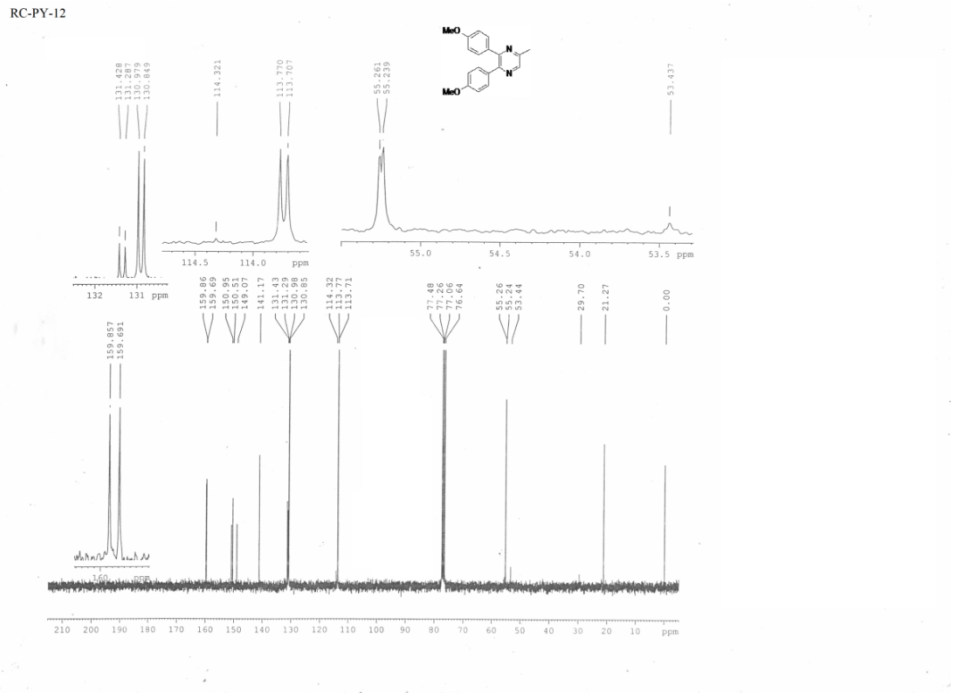
I .B.6.8. ^{1}H NMR spectra of 2-methyl-3-phenyl pyrazine



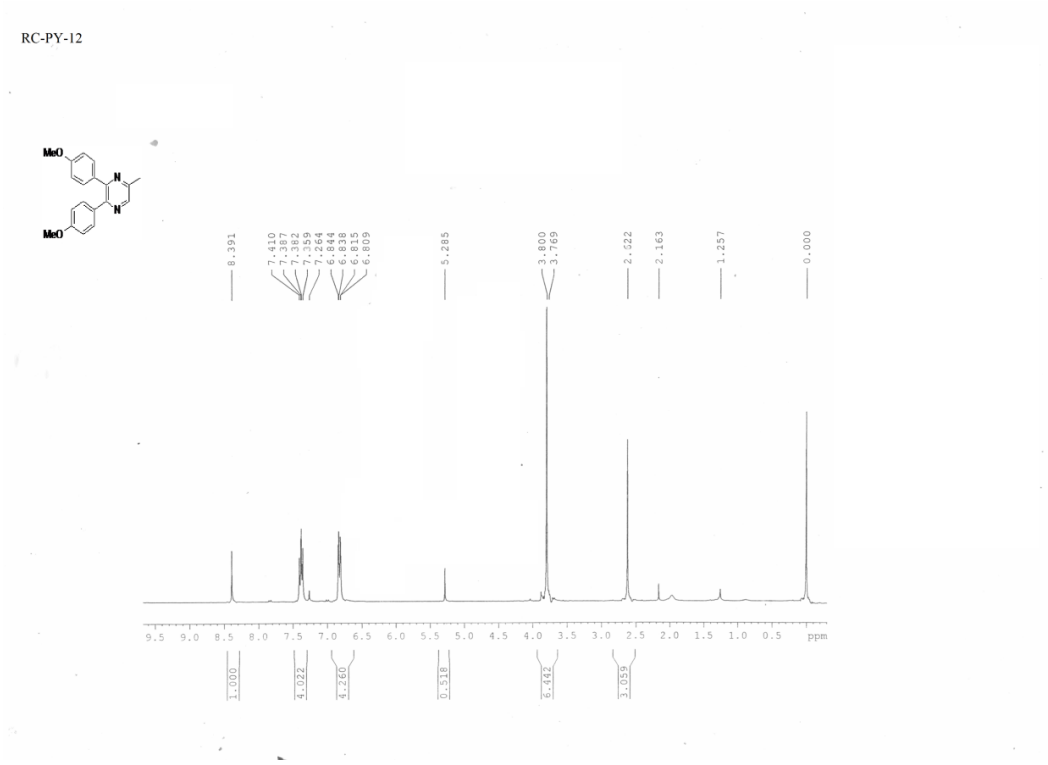
I .B.6.9. ^{13}C NMR spectra of 2, 3-diphenyl-5-methyl pyrazine



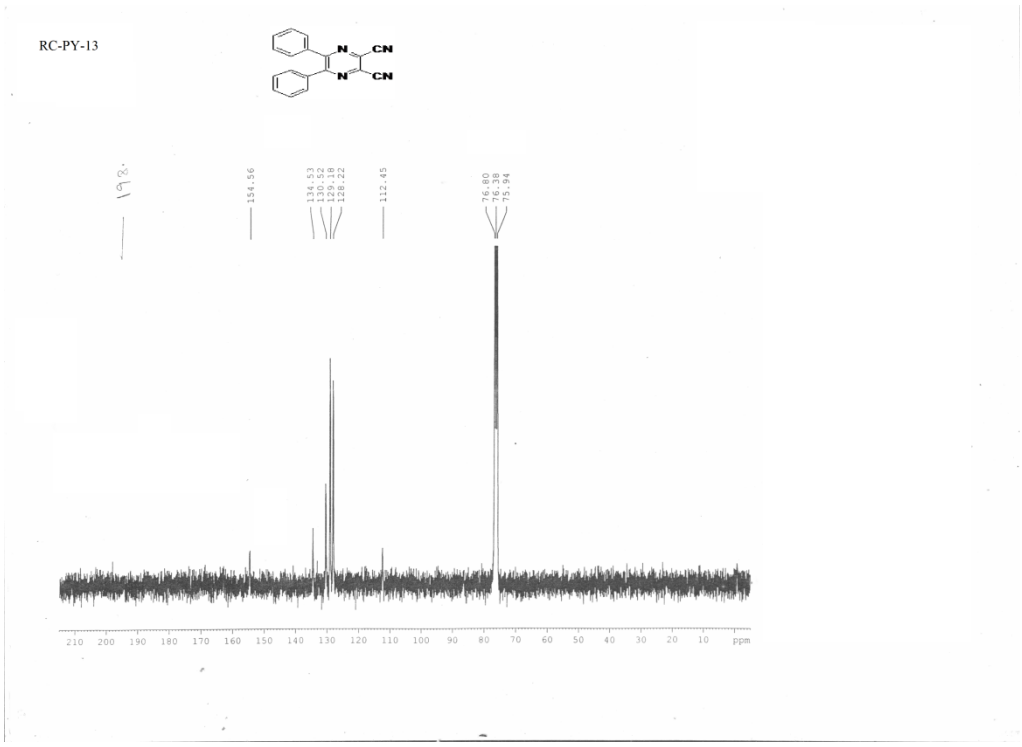
I .B.6.10. ^{1}H NMR spectra of 2, 3-diphenyl-5-methyl pyrazine



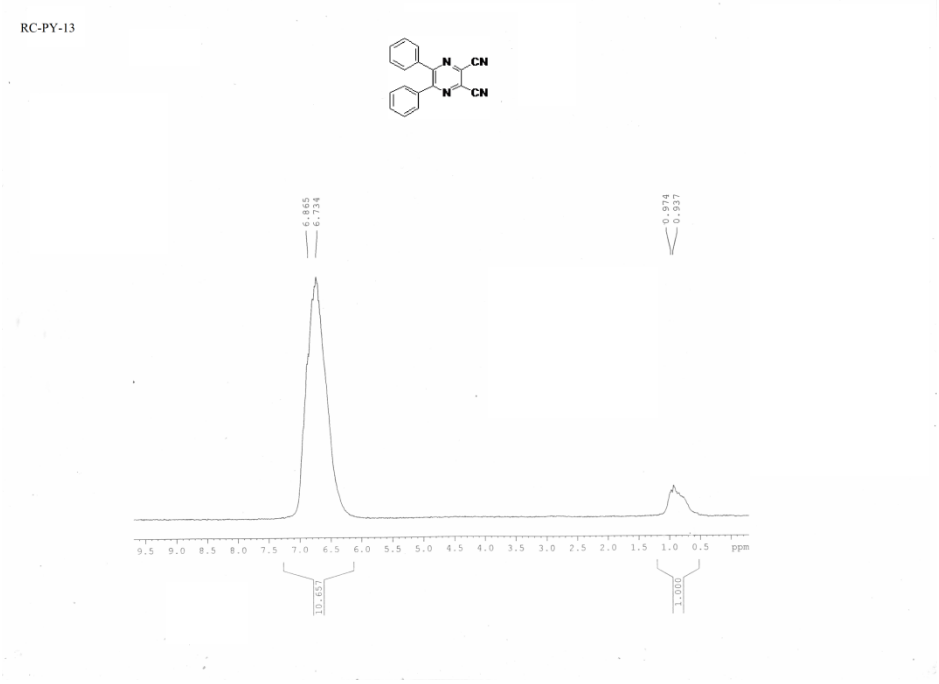
I .B.6.11. **^{13}**C NMR spectra of 2, 3-bis (4-methoxy phenyl)-5-methyl pyrazine



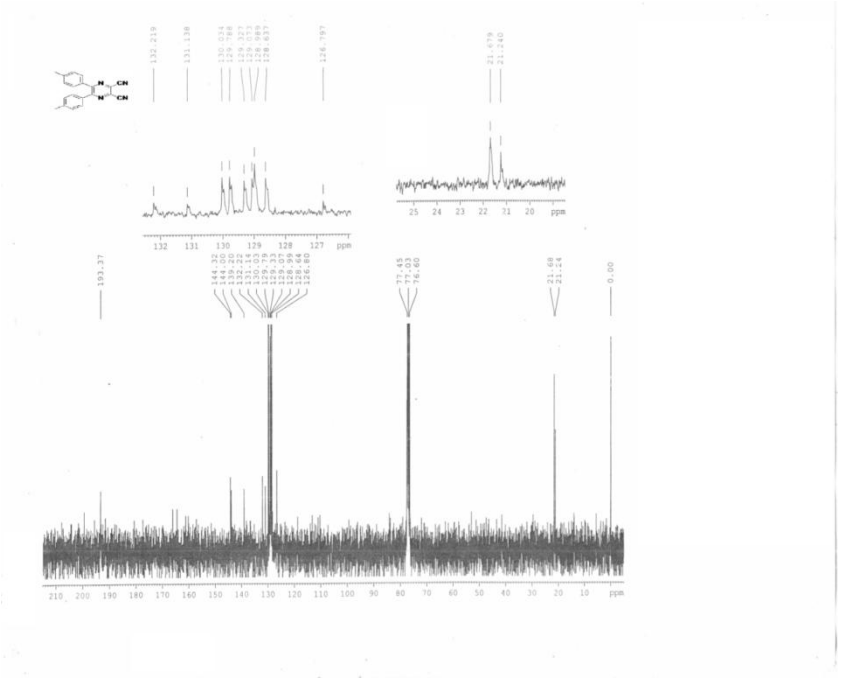
I .B.6.12. ^{1}H NMR spectra of 2, 3-bis (4-methoxy phenyl)-5-methyl pyrazine



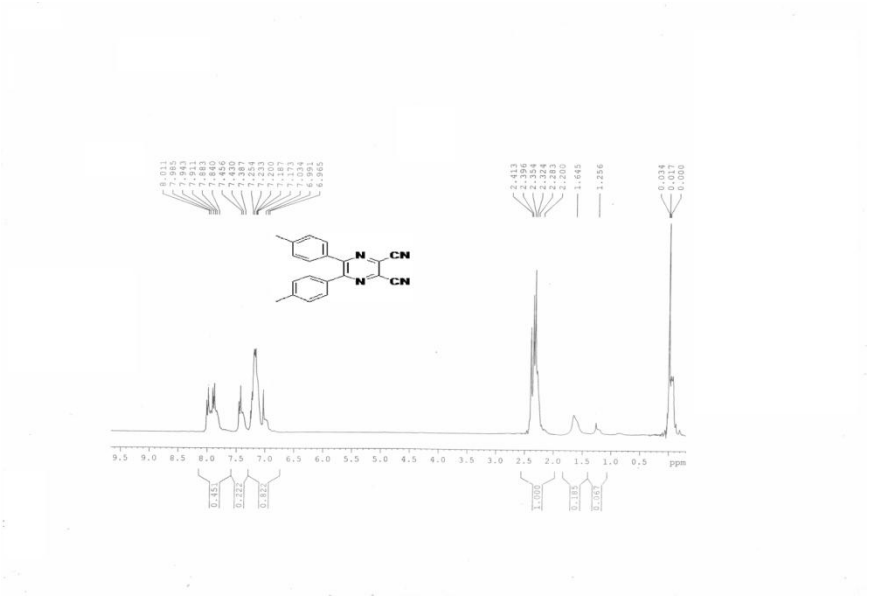
I .B.6.13. [13] C NMR spectra of 5, 6-diphenyl pyrazine-2, 3-dicarbonitrile



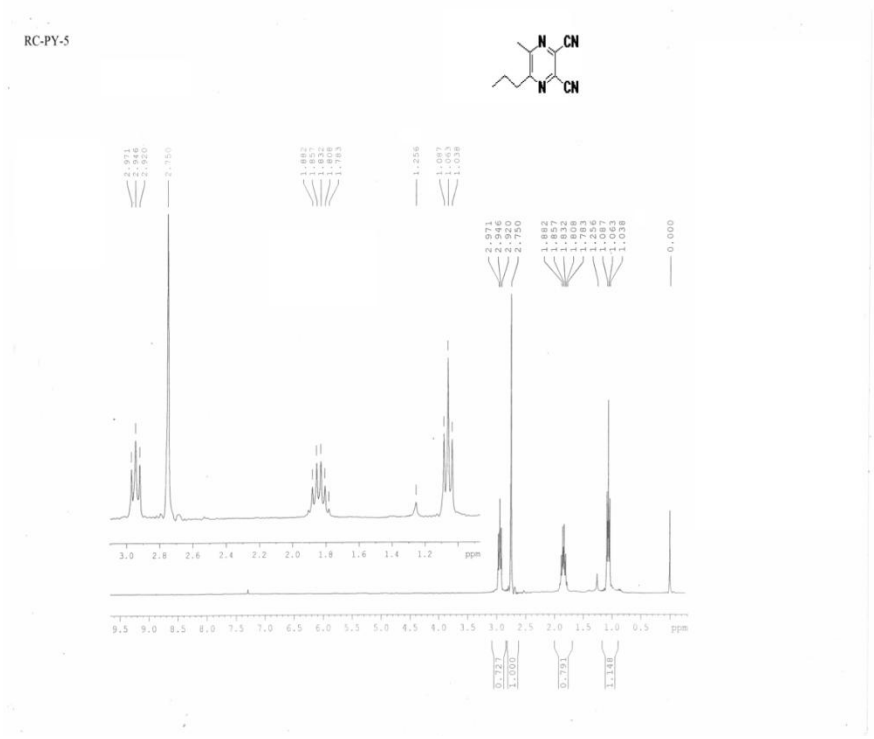
I .B.6.14. [1]H NMR spectra of 5, 6-diphenyl pyrazine-2, 3-dicarbonitrile



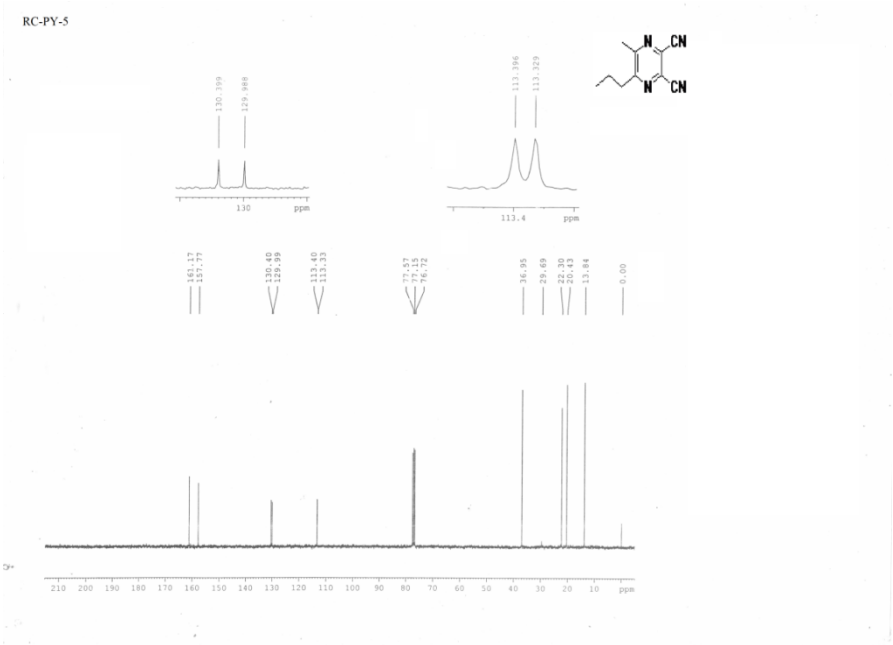
I .B.6.15. ^{13}C NMR spectra of 5, 6-dip-tolylpyrazine-2, 3-dicarbonitrile



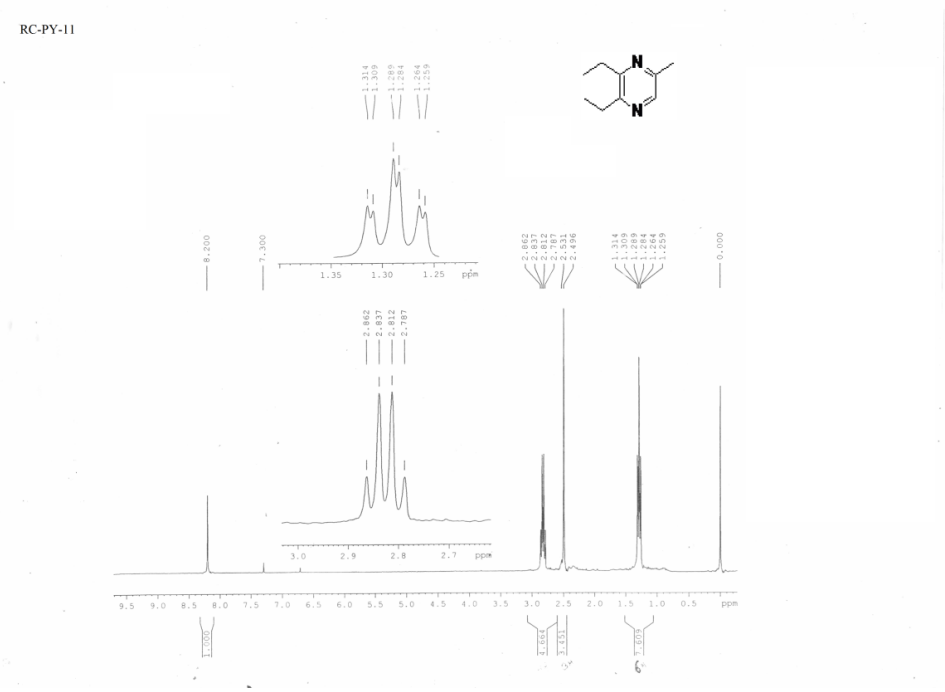
I .B.6.16. ^{1}H NMR spectra of 5, 6-dip-tolylpyrazine-2, 3-dicarbonitrile



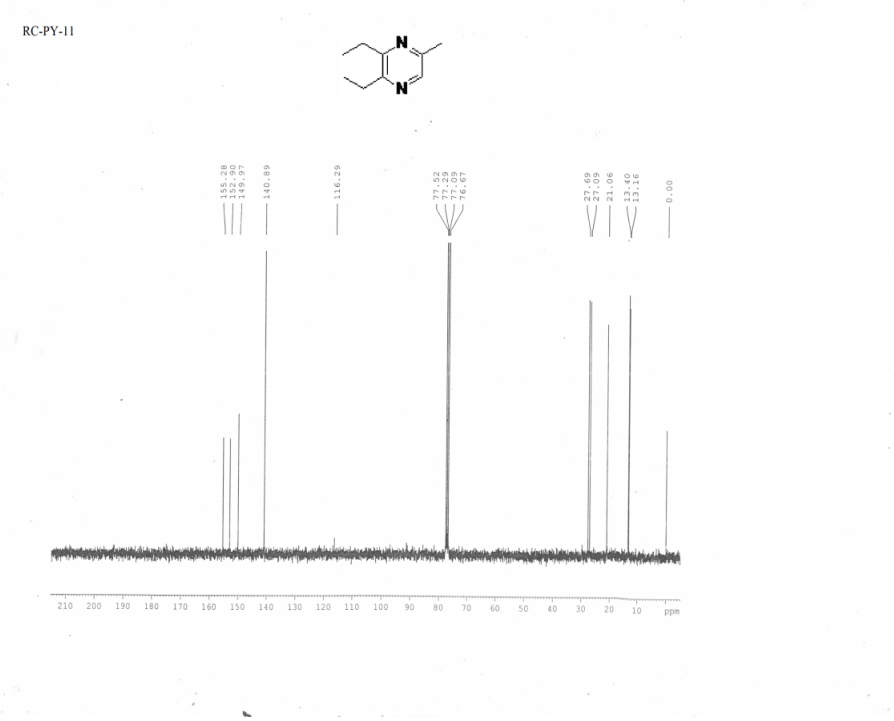
Ⅰ.B.6.17. ^{1}H NMR spectra of 5-methyl-6-propiopyrazine-2, 3-dicarbonitrile



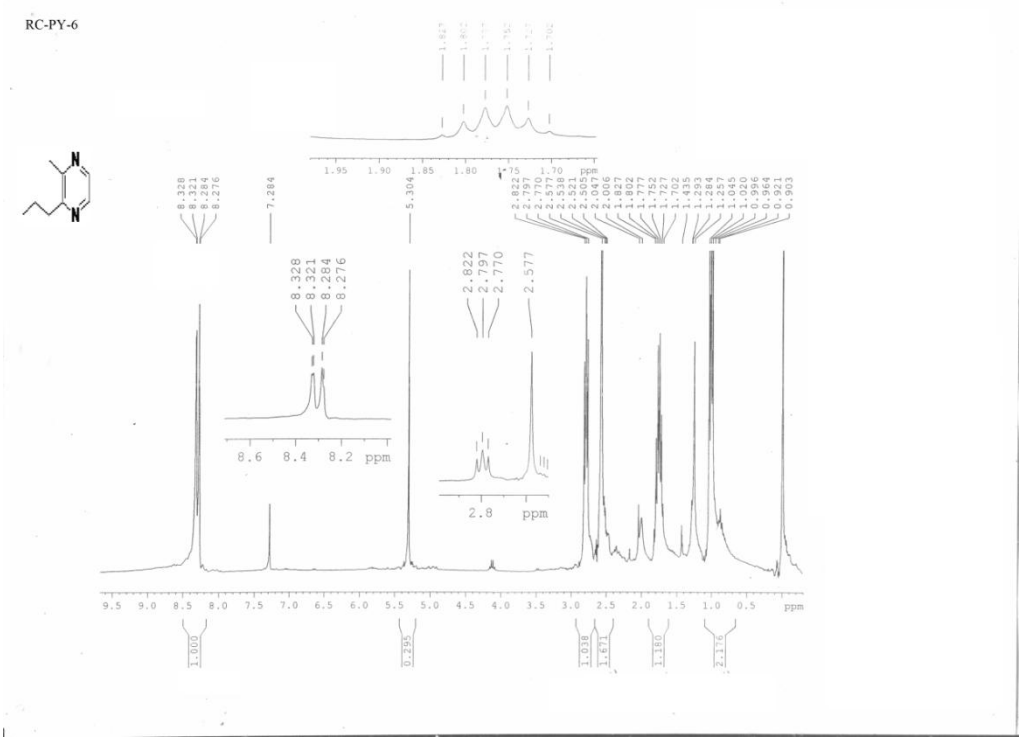
Ⅰ.B.6.18. ^{13}C NMR spectra of 5-methyl-6-propiopyrazine-2, 3-dicarbonitrile



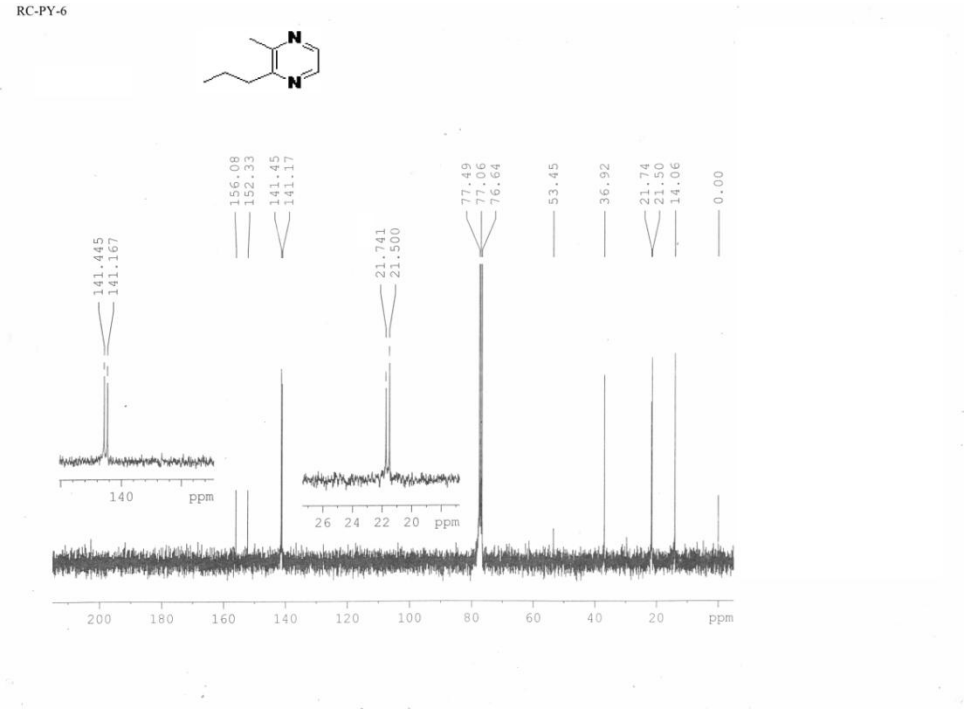
I .B.6.19. ^{1}H NMR spectra of 2, 3-diethyl- 5-methyl pyrazine



I .B.6.20. ^{13}C NMR spectra of 2, 3-diethyl- 5-methyl pyrazine

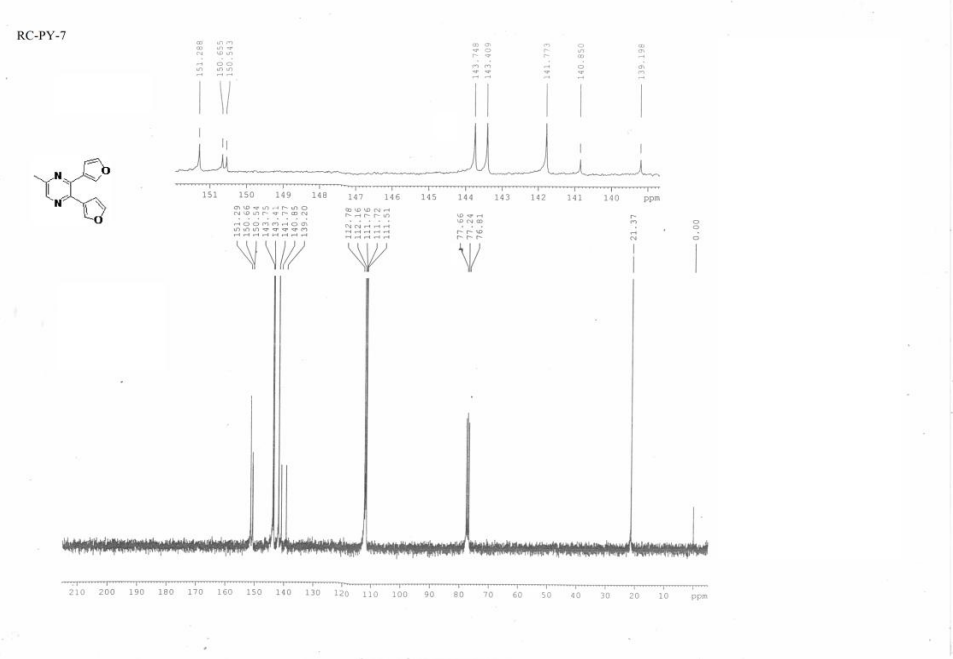


Ⅰ.B.6.21. [1] H NMR spectra of 2-methyl-3-propylpyrazine



Ⅰ.B.6.22. [13]C NMR spectra of 2-methyl-3-propylpyrazine

Ⅰ.B.6.23. ^{1}H NMR spectra of 2, 3 di-(furan-2-yl)-5-methyl pyrazine



Ⅰ.B.6.24. ^{13}C NMR spectra of 2, 3 di-(furan-2-yl)-5-methyl pyrazine

Ⅰ.B.7. References

[1]. (a) Brahmachari, G. Green Synthetic Approaches for Biologically Relevant Heterocycles; Elsevier: Oxford**, 2014**. (b) Alvarez-Builla, J.; Vaquero, J. J.; Barluenga, J. Modern Heterocyclic Chemistry; John Wiley & Sons: Germany, **2011**.

[2]. Wheeler G P,;Bowden B J,Temple C,; Adamson D J.*Can Res*, **1983,** 43, 3567

[3].Fulda, S; Jeremias, I.;Pietsch,T.; Debatin, K.M. *Int. J.Cancer* ,**1999**,82,435

[4]. Milan, U; J, S; Miroslav, K,; Iva, T,; Marian, H. *J. Nat. Prod.* **2007,** *70,* 526

[5]. Archana, T,; Rajesh, M. Int. J. Sci. Res. **2012,** 5, 1

[6]. Wheeler, J.W.; Avery, J.; Olubajo, O.; Shamim, M.T.;Storm, C.B. *Tetrahedron*, **1982**, 38, 1939

[7]. Richa, G,;Vijay, L,; Kamaldeep, P. *Org.Biomol.Chem*,**2015**,13,3525

[8]. (a) Darabi, H. R.; Mohandessi, S.; Aghapoor, K.; Mohsenzadeh, F.A. *Catal. Commun*.**2007**, 8, 389 (b) Mohsenzadeh, F.; Aghapoor, K.; Darabi, H. R. *J. Braz. Chem. Soc***. 2007,** 18, 279–283; (c) Ghosh, P.; Chakraborty, P. *J. Chem. Pharm. Res***. 2010**,2, 154

[9].Aston, J.G,;.Peterson, T.E,;.Holowchak, J. *J.Am.Chem.soc*,**1934**, 56,153

[10]. Nicole S. Y. L,; Sunggak, K,; Cheol-Min, P.*Org.Lett*.**2015**,17, 395

[11]. Hasrat, A,; van Lier, J.E .*Tetrahedron Lett*, **2012,** 53**,**4824

[12].Okada J. Japan Patent 49, 25, 947, 1974.

[13]. Korea Research Institute of Chemical Technology.Japan Patent 05, 52829, **1993.**

[14]. Toti Electro-Chemical Co. Japan Patent 55, 50024,1980.

[15]. Koei Chemical Co. Japan Patent 53, 43512, 1978

[16]. Koei Chemical Co. Japan Patent 09, 48763,1997.

[17]. Koei Chemical Co. Japan Patent 49, 101391, 1974.

[18]. BASF, A.-G. Japan Patent 05, 35140, 1993

[19]. Raw, S.A.; Wilfred C.D.; Taylor, J.K. *Chem.Commun***. 2003**, 39, 2286

[20]. Liyan, F,;Wen, C,; Changtao, Q.*Tetrahedron Lett*, **2013,** 54**,** 231

[21]. Pradhan, B.P.; Ghosh, P. *Indian. J. Chem*. **1993**, 32B, 590.

[22]. Katritzky, A.R. *Advances in Heterocyclic Chemistry*, Academic Press: Cambridge, **2010**.

[23]. Masuda, H.; Tka, M.; Akiyama, T.; Shibamoto, T. *J. Agric. Food Chem.***1980**, 28, 244

[24]. Nasrollahzadeh, M,;.Habibi, D,;Shahkarami, Z,;.Bayat, Y. *Tetrahedron*, **2009**,65,10715

[25]. Habibi, D,; Nasrollahzadeh, M. *Syn.Commun*, **2010**, 40, 3159

[26]. Dittmer, D. C. No-solvent organic synthesis. *Chem. Ind.***1997,** 779,1

[27]. (a) Allais, C.; Grassot, J.-M.; Rodriguez, J.; Constantieux, T. *Chem. Rev***. 2014**, 114,10829

[28]. (a) Nandi, G. C.; Samai, S.; Kumar, R.; Singh, M. S. *Tetrahedron*, **2009**, 65, 7129. (b) Samai, S.; Nandi, G. C.; Kumar, R.; Singh, M. S. *Tetrahedron Lett*. **2009**, 50, 7096