2024. Volume 8, Number 1 ***Pages 67-76***

UOT: 547.141:547.539
https://doi.org/10.30546/2521-6317.2024.301

METHANOLYSIS OF DICHLORODIAZADIENES SYNTHESIZED BASED ON 4-METHYLBENZALDEHYDE

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ARTICLE INFO

Article history:

Received:2024-09-27

Received in revised form:2024-09-27

Accepted:2024-10-24

Available online

Keywords:

dichlorodiazadienes, methanolysis reaction, arylhydrazones of α-keto acid esters

ABSTRACT

We carried out methanolysis of dichlorodiazadienes synthesized on the basis of 4-methylbenzaldehyde and as a result of the reaction it was determined that both isomers E/Z of methyl(Z)-2-(2-phenylhydrazineylidene)-2-(p-tolyl) acetate derivatives were obtained. The structures of the obtained compounds were confirmed by NMR and X-ray method. Compared to the E isomer, in the Z isomer, the hydrogen atom of the imine group formed an intramolecular hydrogen bond with the carbonyl group of the ester, which was reflected in the molecular structure. Taking this into account, we proposed two possible mechanisms of the reaction. Based on nucleophilic addition and nucleophilic substitution reactions, we have shown that E/Z isomers have S-cisoid, S-transoid configurations, which is clearly visible in molecular structures. Thus, we proposed a new convenient method for the synthesis of aryl hydrazones of α-keto acid esters from the solvolysis reaction of dichlorodiazadienes in alcohol. Based on the fact that the arylhydrazones of α-keto acid esters obtained as a result of the reaction have many antimicrobial, bactericidal and fungicidal properties, it is worth noting that they are important compounds from the point of view of organic synthesis and pharmacological chemistry.

1. Introduction

We know from the literature that various synthesis methods of α-keto acid esters have been carried out, and transition metal complexes were used as catalysts in these reactions [1-6], which shows how complex and economically expensive the synthesis method is. In general, one of the main problems that arise in conducting this type of syntheses is the occurrence of decarboxylation as a result of the reaction, that is, in other words, decarboxylation occurs after hydrolysis of the ester [7].

An example of the reactions carried out with the direct introduction of α-keto acid ester to the substrate [8] is the reaction in the presence of a platinum catalyst, in which the introduction of the α-keto acid ester group into the molecule occurs as a result of the direct acylation reaction with ethylchloroxoacetate by the method of C-H bond activation [9-13]. Since metalorganic reagents, such as the Grignard reagent, are used in other synthesis methods, as a result of the high reactivity of the latter, conducting the reaction at a very low temperature shows that this method is one of its shortcomings.

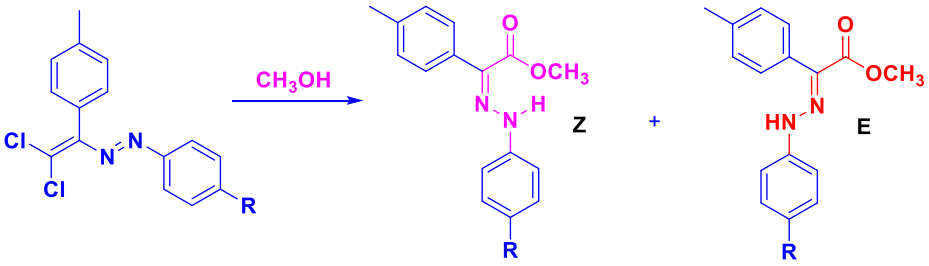
During the acylation according to the Friedel-Crafts reaction [14-16], the use of an excess amount of Lewis acid causes many problems in the purification of the reaction mixture, and the selectivity is also not fully observed. In general, α-keto acid esters are included in the composition of many biological and medical organic molecules, and are also used as starting reagents in the synthesis of many important organic compounds (α-hydroxy acids, α-amino acids). In addition, α-keto acid esters are used as important compounds in other areas of organic synthesis, for example, in the synthesis of heterocycles.

Namely, for the reasons mentioned above, the introduction of α-keto acid ester functional group into compounds is of great importance from the point of view of organic synthesis. Taking these into account, the solvolysis reaction of dichlorodiazadienes [17-25] synthesized by us in previous studies was carried out and arylhydrazones of α-keto acid esters [26] were obtained. As a result of these reactions, both isomers of esters were obtained, but the mechanism was not investigated.

Taking into account that arylhydrazones have antimicrobial, bactericidal and fungicidal properties [27] and at the same time have a pharmochor methyl group [28], our research was continued in the direction of methanolysis of dichlorodiazadienes based on 4-methylbenzaldehyde.

2. Results and Discussion

The methanolysis reactions of dienes synthesized on the basis of 4-CH_3-benzaldehyde were studied in order to investigate the mechanism by which both isomers can be obtained simultaneously during the methanolysis reactions of dichlorodiazadienes (Scheme 1).



Scheme 1. Methanolysis reaction of dichlorodiazadienes.

The synthesized E/Z isomers were separated from the reaction mixture and the structures of the compounds were confirmed by NMR and X-ray methods. Below are NMR spectra of the E and Z isomers of compound 8 as an example.

It is clear from the 1H NMR spectrum that the signals of the Z isomer of compound 8 shift to a weaker area due to the H bond formed by the hydrogen atom of the imine group with the carbonyl group of the ester in the NMR spectrum. However, in the E isomer of that compound, a stronger field was observed than the Z isomer.

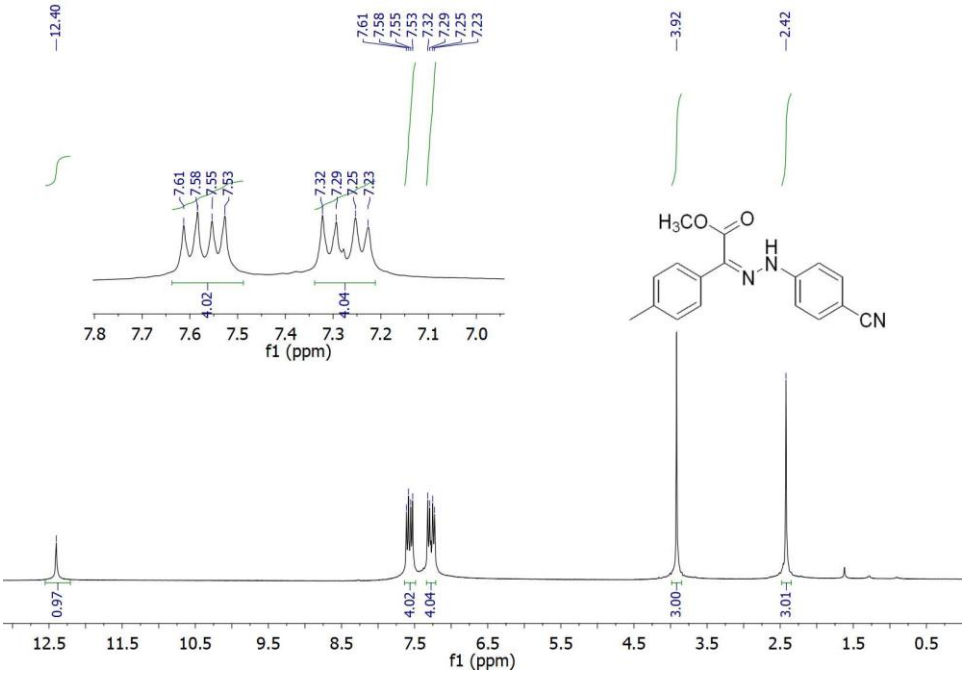


Figure 1. [1]H NMR spectrum of compound 8a

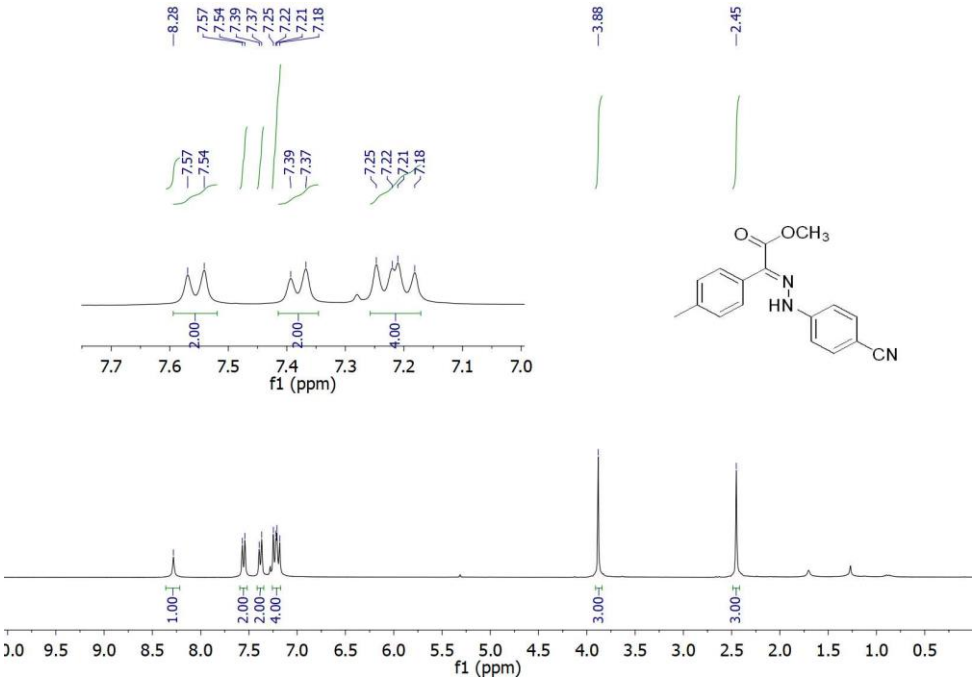
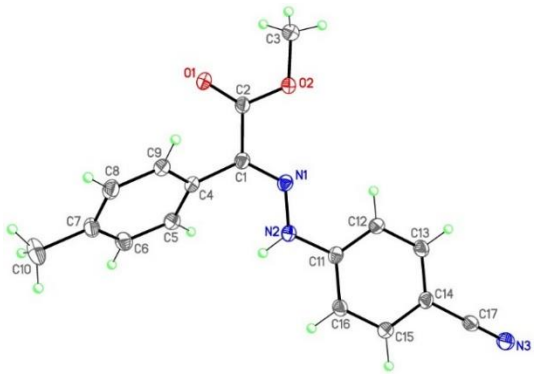
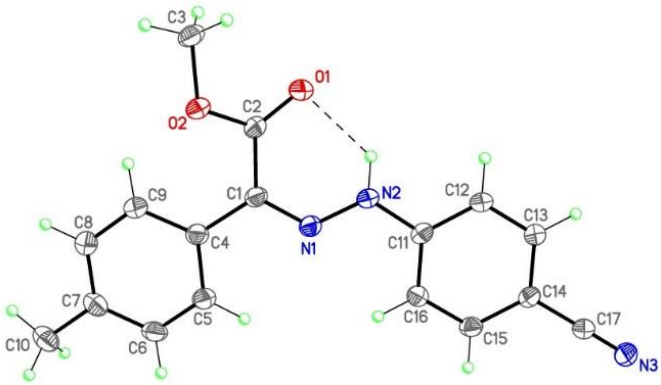


Figure 2. [13]C NMR spectrum of compound 8b

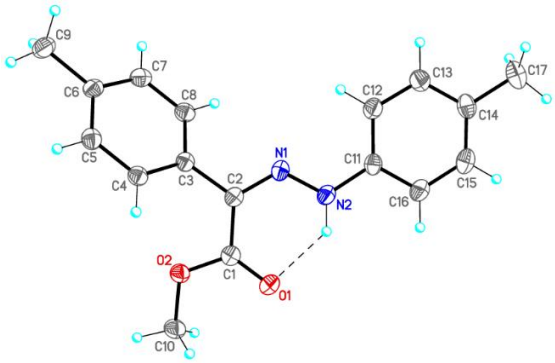
The molecular structure of some methyl (Z)-2-(2-phenylhydrazineylidene)-2-(p-tolyl)acetate derivatives was determined again by X-ray method, and the presence of hydrogen bonds is clearly seen from the molecular structure (Figure 3).



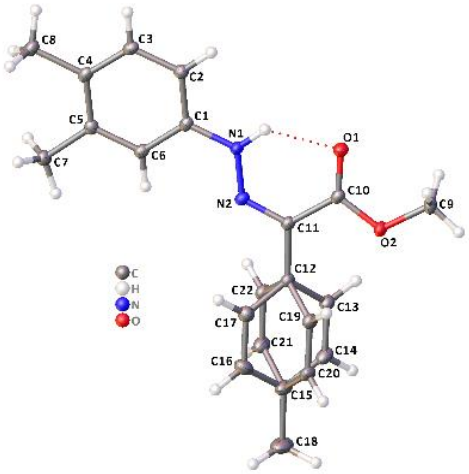
8a



8b



2a

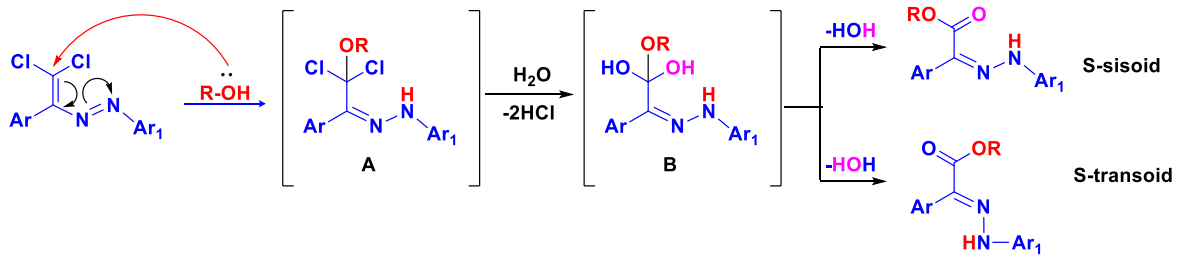


9a

Considering that both isomers are obtained simultaneously during the reaction, two possible reaction mechanisms have been proposed.

1**) Nucleophilic addition reaction to heterodiene**.

As we know, the nucleophilic addition reaction to heterodienes first follows the 1,4-addition reaction. In our reaction, intermediate compound A is probably formed during the 1,4-addition of alcohol. It should be noted that the presence of 2 chlorine atoms in sp^3 hybridized carbon in A and its hydrolysis reaction will lead to obtaining C of carbonyl group B. Thus, one of the methods of obtaining aldehydes is based on the hydrolysis reaction of heminal dichlorinated carbon. Then it is assumed that the hydrolysis of A leads to intermediate B first. Then, depending on which of the heminal hydroxyl groups, which OH group participates in the separation of water, E/Z isomers will be obtained at the same time (Scheme 2).

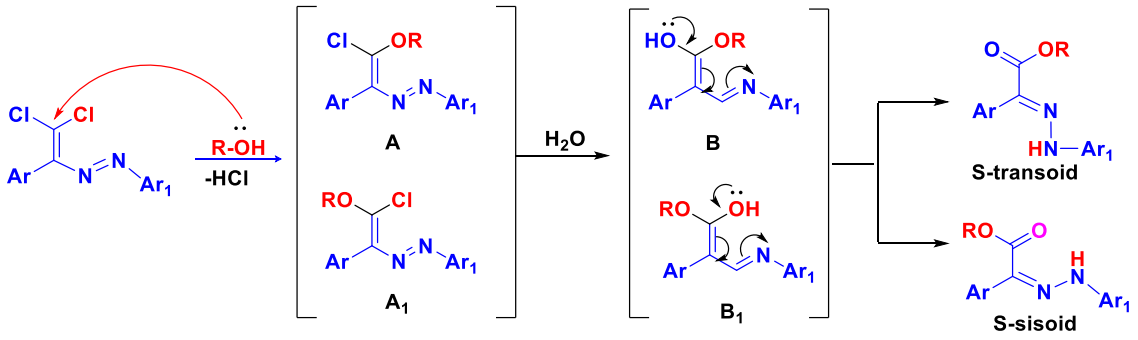


Scheme 2. The first probable mechanism of the reaction.

When we considered the molecular structures of the synthesized esters, we came across an interesting fact. Thus, it was determined that the 1,3-diene system (O=C-C=N-) in the Z-isomers has an S-cisoid configuration, while in the E-isomers have an S-transoid configuration (Figure 3)

1) The second direction is the nucleophilic substitution reaction of the chlorine atom and its hydrolysis:

In the proposed mechanisms for these reactions, taking into account the successive nucleophilic substitution of chlorine atoms, intermediate compound A will be obtained from the substitution of chlorine atom first in this reaction. Then, the hydrolysis of the second chlorine atom leads to the transition to the enol form B, and then to the more stable keto form.



Scheme 3. The second possible mechanism of the reaction.

Thus, both proposed mechanisms involved the production of E/Z-isomers.

Conclusion

Thus, on the basis of a very simple synthesis reaction, the synthesis of methyl (Z)-2-(2-phenylhydrazineylidene)-2-(p-tolyl)acetate derivatives, which is considered an important compound from the point of view of organic synthesis and pharmacological chemistry, was achieved. The synthesis of aryl hydrazones of α-keto acid esters from the solvolysis reaction of dichlorodiazadienes can be considered a new convenient method, and this reaction has created opportunities for the synthesis of compounds with many antimicrobial, bactericidal and fungicidal properties.

Experimental Part

NMR ^{1}H and ^{13}C spectra were also recorded in $CDCl_3$ and DMSO on Bruker Avance 300 (operating frequency 300 MHz spectrometer. SiMe4 was used as an internal standard. UB-254 was performed on NTX Silufol plate, and acidified KMnO4 solution was used for clear visibility of the formed spots and UV lamp rays were used. Column chromatography was performed on silica gel from Merck (63-200).

10 mg of 1,1-dichlorodiazadiene is taken and stirred in 30 ml of ethanol solution for 2 hours using a magnetic stirrer at the boiling temperature of alcohol. After the specified time, the solution is ejected by the rotor. The reaction products are separated by column chromatography. The eluents used for this are dimethyl chloride and n-hexane (1:1), dimethyl chloride and ethanol. The main reaction product fractions separated by thin-layer chromatography are collected and re-evaporated in the rotor and the yield is calculated.

1. **methyl (Z)-2-(2-phenylhydrazineylidene)-2-(p-tolyl)acetate (1a)** yellow solid , (39%), mp 72 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.41 (s, 3H), 3.72 (s, 3H), 7.25 (t, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 7.5, 2H), 7.57 – 7.47 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 8.19 (d, *J* = 7.5 Hz, 1H), 12.33 (s, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 54.4, 110.52, 112.5, 127.7, 130.1, 130.4, 131.8, 136.1, 143.4, 146.8, 151.9, 162.9,

   methyl (E)-2-(2-phenylhydrazineylidene)-2-(p-tolyl)acetate (1b) yellow solid , (28%), mp 114 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.38 (s, 3H), 2.68 (s, 3H), 7.15 (t, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 7.5, 2H), 7.52 – 7.45 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 8.21 (d, *J* = 7.5 Hz, 1H), 8.53 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 50.8, 110.52, 115.7, 127.3, 128.4, 130.8, 135.7, 142.2, 145.7, 150.7, 163.7.

2. **methyl (Z)-2-(p-tolyl)-2-(2-(p-tolyl)hydrazineylidene)acetate (2a)** yellow solid (41%), mp 80 ºC. ^{1}H NMR (300 MHz, Chloroform-d) δ 2.38 (s 3H), 2.36 (s, 3H), 3.89 (s, 3H), 7.27 – 7.05 (m, 6H), 7.56 (d, *J* = 8.1 Hz, 2H), 12.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 21.2, 51.7, 113.8, 125.0, 126.6, 127.5, 129.6, 130.6, 131.8, 136.1, 140.5,164.3.

   methyl (E)-2-(p-tolyl)-2-(2-(p-tolyl)hydrazineylidene)acetate (2b yellow solid, (22%), mp 102 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.31 (s, 3H), 2.45 (s, 3H), 3.82 (s, 3H), 7.13 – 7.04 (m, 4H), 7.30 (d, *J* = 9.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 8.20 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 31.7, 52.8, 115.1, 123.5, 126.4, 127.4, 130.4, 133.5, 133.9, 139.5, 150.9,163.9.

3. **methyl (Z)-2-(p-tolyl)-2-(2-(m-tolyl)hydrazineylidene)acetate (3a)** yellow solid, (39%), mp 64 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.33 (s, 3H), 2.75 (s, 3H), 3.96 (s, 3H), 7.31 – 7.16 (m, 6H), 7.63 (d, *J* = 8.1 Hz, 2H), 11.87 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.7, 34.7, 50.8, 111.7, 121.3, 127.6, 128.8, 130.7, 136.7, 137.8, 141.5, 151.5, 164.7.

4. **methyl (E)-2-(p-tolyl)-2-(2-(m-tolyl)hydrazineylidene)acetate (3b)** yellow solid (20%), mp 123^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.30 (s, 3H), 3.68 (s, 3H), 3.83 (s, 3H), 7.30 – 7.18 (m, 6H), 7.61 (d, *J* = 8.1 Hz, 2H), 9.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 33.9, 50.5, 110.7, 121.3, 125.6, 128.8, 132.6, 135.9, 139.5, 140.5, 153.5, 163.7.

   methyl(Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-(p-tolyl)acetate (4a) yellow solid, (30%), mp 84 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.21 (s, 3H), 3.83 (s, 3H), 3.90 (s, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.4 H, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 12.48 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ31.4, 34.6, 51.6, 112.7, 117.4, 124.9, 128.3, 126.8, 133.8, 136.1, 150.4, 155.5, 162.4.

   methyl(E)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-(p-tolyl)acetate (4b) yellow solid, (21%), mp 126 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.18 (s, 3H), 3.82 (s, 3H), 3.89 (s, 3H), 6.90 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 8.79 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.4, 31.2, 51.4, 114.6, 115.3, 124.7, 128.5, 128.6, 137.7, 153.4, 155.7, 157.6, 162.8.

5. **methyl (Z)-2-(2-(4-chlorophenyl)hydrazineylidene)-2-(p-tolyl)acetate (5a))** yellow solid, (30%), mp 89 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.76 (s, 3H), 3.86 (s, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 8.51 (d, *J* = 8.2 Hz, 2H), 12.24 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 51.6, 112.7, 118.4, 122.6, 123.6, 125.5, 137.2, 138.5, 153.4, 154.5, 165.4.

   methyl (E)-2-(2-(4-chlorophenyl)hydrazineylidene)-2-(p-tolyl)acetate (5b) yellow solid, (23%), mp 119 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.35 (s, 3H), 3.86 (s, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 8.48 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.8, 54.6, 117.7, 123.4, 126.6, 128.6, 134.5, 140.2, 142.8, 154.9, 152.7,162.4.

6. **methyl (Z)-2-(2-(4-bromophenyl)hydrazineylidene)-2-(p-tolyl)acetate (6a)** yellow solid, (35%), mp 66 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.76 (s, 3H), 3.86 (s, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 8.51 (d, *J* = 8.2 Hz, 2H), 12.24 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 51.6, 112.7, 118.4, 122.6, 123.6, 125.5, 137.2, 138.5, 153.4, 154.5, 165.4.

   methyl (E)-2-(2-(4-bromophenyl)hydrazineylidene)-2-(p-tolyl)acetate (6b) yellow solid, (30%), mp 100 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.45 (s, 3H), 3.83 (s, 3H), 6.84 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 8.72 (d, *J* = 8.2 Hz, 2H), 8.48 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.6, 50.6, 110.8, 115.4, 120.3, 121.7, 124.3, 133.7, 139.9, 155.4, 157.9, 166.5.

7. **methyl (Z)-2-(2-(4-nitrophenyl)hydrazineylidene)-2-(p-tolyl)acetate (7a)** yellow solid, (35%), mp 73 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.24 (s, 3H), 3.78 (s, 3H), 7.42 (m, 2H), 7.57 – 7.47 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 2 H), 8.19 (d, *J* = 7.5 Hz, 2 H), 12.89 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 50.6, 110.52, 115.15, 126.40, 127.37, 133.48, 133.98, 135.51, 145.84, 145.58, 157.8, 159.8,

   methyl (E)-2-(2-(4-nitrophenyl)hydrazineylidene)-2-(p-tolyl)acetate (7b) yellow solid, (30%), mp 108 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.69 (s, 3H), 3.65 (s, 3H), 7.37 (m, 2H), 7.55 – 7.46 (m, 2H), 7.69 (d, *J* = 7.5 Hz, 2 H), 8.34 (d, *J* = 7.5 Hz, 2 H), 9.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 51.6, 110.2, 115.1, 124.4, 127.6, 133.4, 133.8, 135.5, 144.4, 145.6, 157.9, 159.4.

8. **methyl (Z)-2-(2-(4-cyanophenyl)hydrazineylidene)-2-(p-tolyl)acetate (8a)** yellow solid, (35%), mp 73 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.41 (s, 3H), 3.91 (s, 3H), 7.23-7.19 (m, 4H), 7.55-7.47 (m, 4H), 12.42 (s, 1H). 128.6, ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 52.6, 104.1, 114.1, 119.3, 128.8, 132.7, 133.1, 138.4, 146.6, 163.7, 169.6.

   methyl (E)-2-(2-(4-cyanophenyl)hydrazineylidene)-2-(p-tolyl)acetate (8b) yellow solid, (35%), mp 73 ^{0}C, ^{1}H NMR (300 MHz, Chloroform-d) δ 2.43 (s, 3H), 3.89 (s, 3H), 7.38-7.30 (m, 4H), 7.50-7.46 (m, 4 H), 8.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 50.4, 101.6, 113.3, 119.93, 127.1, 128.6, 129.7, 130.1, 137.8, 145.4, 163.5, 168.4.

9. **methyl(Z)-2-(2-(3,4-dimethylphenyl)hydrazineylidene)-2-(p-tolyl)acetate (9a)** yellow solid (40%), mp 100 ^{o}C. ^{1}H NMR (300 MHz, Chloroform-d) δ 2.31 (s, 3H), 2.35 (s, 3H), 2.47 (s, 3H), 3.93 (s, 3H), 7.18 – 7.09 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 12.46 (s, 1H),

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 20.1, 21.3, 51.6, 111.4, 116.5, 125.8, 129.7, 130.5, 131.5, 134.8, 137.4, 138.7, 142.3, 162.3.

methyl(E)-2-(2-(3,4-dimethylphenyl)hydrazineylidene)-2-(p-tolyl)acetate(9b) yellow solid (32%), mp 82 °C. ^{1}H NMR (300 MHz, Chloroform-d) δ 2.26 (s, 3H), 2.30 (s, 3H), 2.42 (s, 3H), 3.89 (s, 3H), 7.08 (dd, *J* = 20.2, 8.8 Hz, 3H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 8.12 (s, 1H), 12.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 20.1, 21.3, 51.6, 111.7, 115.5, 126.8, 128.6, 130.3, 130.7, 133.8, 137.4, 137.7, 141.2, 164.3.

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