Synthesis of Enaminones and Their Reaction with Dimethyl Acetylene Dicarboxylate

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ABSTRACT: *In present paper a simple procedure for the synthesis of enaminones without catalyst from 1,3-diketones that reacted with primary or secondary amines in ethanol as solvent, as well as the reaction of enaminones with unsaturated esters such as dimethyl acetylene dicarboxylate are reported.*

KEY WORDS: *Enaminones, 1,3-diketones, Dimethyl acetylene dicarboxylate.*

INTRODUCTION

The synthesis and reactivity of enaminones represent an active area of investigation in organic chemistry [1]. Enaminones have been studied extensively for their properties and as precursors of several interesting classes of compounds [2]. The special value of these compounds is due to their use as valuable intermediate for the synthesis of several interesting compounds [7-20]. They can also be used as starting materials for the stereo-selective preparation of γ-aminoalcohols (by reduction) [3]. Despite their wide range of pharmacological activity and synthetic applications, the synthesis of enaminones has received little attention [4].

Several improved procedures have been reported including the reaction of amines and 1, 3-dicarbonyl compounds supported on silica with microwave irradiation, clay K_{10}/ultra-sound or $NaAuCl_4$ [4].

Recently these compounds have been prepared by direct condensation of 1,3-dicarbonyl compounds and primary amines in water as solvent [4].

However, these methods suffer from drawbacks such as long reaction times, unsatisfactory yields, low selectivity or the use of toxic solvents that limit these methods to small-scale synthesis [4]. Enaminones were also prepared under mild, efficeient region and chemoselective method from 1,3-dicarbonyl compounds in water, in good to excellent yields, catalyzed with $Bi(TFA)_3$ [4]. While the acylation of lithium imines with ester is another reported method for its regioselective preparation [2].

The reaction of nucleophiles with actived acetylenes for C-C bond formation is of great significance in organic synthesis. In these processes, zwitterionic species are known to arise form the addition of nucleophiles, such as triphenyl phosphine, pyridine, and a wide range of tertiary amines to activated acetylenes such as dimethyl acetylene dicarboxylate (DMAD) [6]. Then, these inter-mediates can be trapped by suitable substrates, such as dioxide, isocyanate, and carbonyl compounds and this interception can either be a two-component reaction or a

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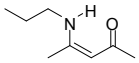
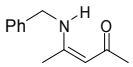
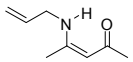
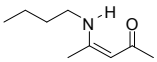
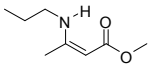
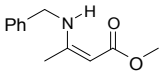
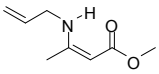
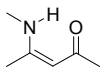
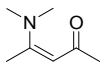
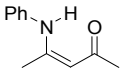
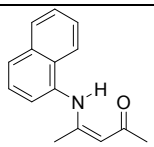
Table 1: Structural of β-diketones and amines and enaminones structures and reaction yields.

Entry	R_1	R_2	R_3	R_4	Product	Yield (%)
1	Me	Me	Propyl	H		97
2	Me	Me	Benzyl	H		85
3	Me	Me	Allyl	H		88
4	Me	Me	Butyl	H		96
5	Me	OMe	Propyl	H		83
6	Me	OMe	Benzyl	H		95
7	Me	OMe	Allyl	H		76
8	Me	Me	Me	H		96
9	Me	Me	Me	Me		93
10	Me	Me	Ph	H		78
11	Me	Me	Naphthalene	H		82

multicomponent reaction. However, to the best of our knowledge, no attempts have been made to trap the zwitterionic intermediates with ketene [5].

Herein, we report a simple and direct procedure for the regioselective preparation of enaminones by reaction of 1,3-dicarbonyl compound with primary or secondary amines in ethanol as solvent.

First, we prepared some enaminones (table 1) with primary and secondary amines with β-diketones and β-ketoesters. After separation and purification of these compounds, each compound was reacted with DMAD in CH_2Cl_2 solvent for preparation of some conjugated derivatives of fumaric acid (table 2). The reaction mechanism pathway for this two step synthesis is shown in scheme 1.

EXPERIMENTAL

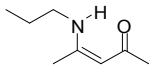
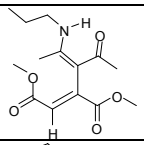
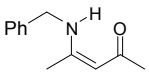
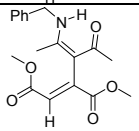
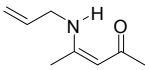
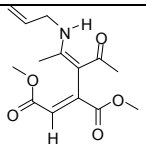
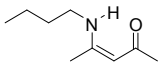
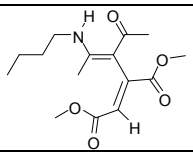
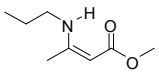
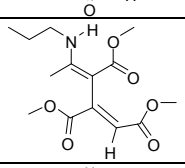
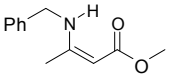
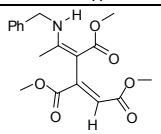
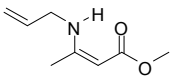
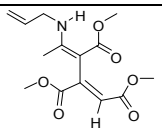
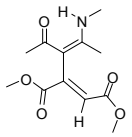
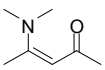
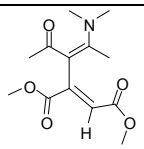
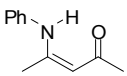
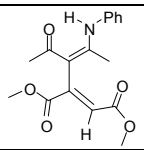
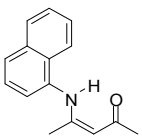
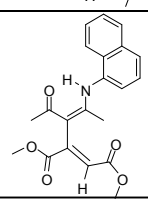
General experimental procedure for preparation of enaminones

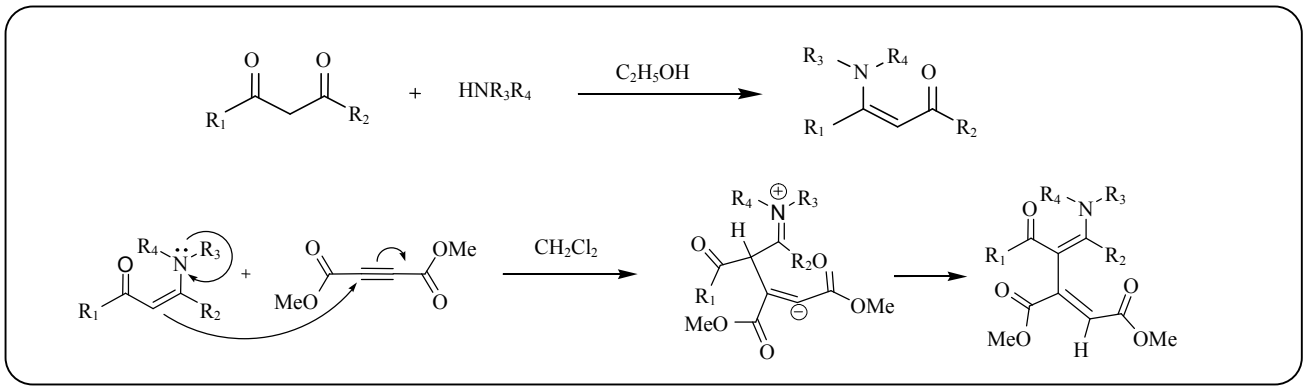
To a solution of 1,3-dicarbonyl compound (20 mmol) and ethanol (5 ml) was added the primary or secondary amines (20 mmol). The reaction mixture was stirred at room temperature for the appropriate time (2-3 days).The solvent was gradually removed by evaporation until solid product was obtained.

General experimental procedure for reaction between enaminones and diethyl acetylene dicarboxylate or ethyl phenyl propyolate

To a solution of enaminones (1 mmol) and CH_2Cl_2 (8 ml) was added dimethyl acetylene dicarboxylate

Table 2: Enaminones and product of reaction enaminones with DMAD and reaction yield.

Entry	Enaminon	Product	Yield (%)
12			88
13			60
14			70
15			50
16			80
17			50
18			60
19			91
20			87
21			62
22			74



Scheme 1.

(1 mmol). The reaction mixture was stirred at below 0 °C tempreture for the appropriate time. The progress of the reaction was followed by TLC. Evaporation of the solvent followed by chromatography on a silica-gel plate or silica-gel column.

CONCLUSIONS

In summery we have shown that enaminones can be prepared without using any catalyst with yields. Then several enaminones (symmetrical and unsymmetrical) were reacted with DMAD to prepare conjugated derivatives of fumaric acid.

4-(propylamino) pent-3-en-2-one

Yellow crystals, yield: 0.85g (97%). IR (KBr) (ν_{max}/cm^{-1}): 3426 (N-H), 1610 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J (Hz): 0.47 (t, 3H, CH_3), 1.07 (m, 2H, CH_2), 1.38 (s, 3H, CH_3), 1.42 (S, 3H, CH_3), 2.63 (m, 2H, CH_2), 4.42 (s, 1H, CH), 10.36 (s, br, 1H, NH). ^{13}C NMR: δ_C(ppm) 11 (Me), 22 (CH_3), 24 (CH_2), 29 (CH_3), 46 (CH_2), 99 (CH), 160 (C), 198 (C). *m/z*: 141.12 (100.0%). Anal. Calcd for $C_8H_{15}NO$ (141.21): C, 68.04; H, 10.71; N, 9.92%.

4-(benzylamino) pent-3-en-2-one

Orang crystals, yield: 0.68g (85%). IR (KBr) (ν_{max}/cm^{-1}): 3326 (N-H), 1710 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J(Hz): 1.64 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 4.12 (s, 2H, CH_2), 4.81 (s, H, CH), 6.92 (m, 5H, Ph), 10.97 (sb, 1H, NH). ^{13}C NMR δ_C(ppm): 22 (Me), 29 (CH_3), 47 (CH_2), 99 (CH), 127 (CH), 128 (CH), 141 (C), 160 (C), 197 (C). *m/z*: 189.12 (100.0%). Anal. Calcd for $C_{12}H_{15}NO$ (189.25): C, 76.16; H, 7.99; N, 7.40%.

4-(allylamino) pent-3-en-2-one

Yellow crystals, yield: 0.74g (88%). IR (KBr) (ν_{max}/cm^{-1}): 3420 (N-H), 1710 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J (Hz): 1.72 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 3.52 (m, 2H, CH_2), 4.72 (s, H, CH), 4.91 (m, 2H, CH_2), 5.72 (m, H, CH), 10.57 (s, br, 1H, NH). ^{13}C NMR δ_C(ppm): 22 (CH_3), 29 (CH_3), 45 (CH_2), 99 (CH), 116 (CH_2), 134 (CH), 160 (C), 160 (C), 197 (C). *m/z:* 139.10 (100.0%). Anal. Calcd for $C_8H_{13}NO$ (139.19): C, 69.03; H, 9.41; N, 10.06%

4-(butylamino) pent-3-en-2-one

Yellow crystals, yield: 0.72g (96%). IR (KBr) (ν_{max}/cm^{-1}): 3324 (N-H), 1669 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J (Hz): 0.28 (t, 3H, CH_3), 0.74 (m, 2H, CH_2), 0.87 (m, 2H, CH_2), 1.72 (s, 3H, CH_3), 2.11 (S, 3H, CH_3), 2.56 (m, 2H, CH_2), 4.26 (s, 1H, CH), 10.21 (s br, 1H, NH). ^{13}C NMR δ_C(ppm): 13 (Me), 20 (CH_2), 22 (CH_3), 29 (CH_3), 33 (CH_2), 43 (CH_2), 99 (CH), 160 (C), 197(C). *m/z:* 155.13 (100.0%). Anal. Calcd for $C_9H_{17}NO$ (155.24): C, 69.63; H, 11.04; N, 9.02%.

Methyl 3-(propylamino) but-2-enoate

Orang crystals, yield: 0.65g (83%). IR (KBr) (ν_{max}/cm^{-1}): 3426 (N-H), 3000 (=C-H), 2948 (C-H), 1620 (C=O), 1074-1120 (C-C). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J (Hz): 0.64 (t, 3H, CH_3), 1.23 (m, 2H, CH_2), 1.53 (s, 3H, CH_3), 2.28 (m, 2H, CH_2), 3.21 (s, 3H, CH_3), 4.06 (s, 1H, CH), 8.24 (s, br, 1H, NH). ^{13}C NMR δ_C(ppm): 11 (CH_3), 23 (CH_3), 24 (CH_2), 46 (CH_2), 52 (CH_3), 85 (CH), 161 (C), 166 (C). *m/z:* 157.11 (100.0%). Anal. Calcd for $C_8H_{15}NO_2$ (157.21): C, 61.12; H, 9.62; N, 8.91%.

Methyl 3-(benzylamino) but-2-enoate

Yellow crystals, yield: 0.87g (95%). IR (KBr) (ν_{max}/cm^{-1}): 3364 (N-H), 3010 (=C-H), 2995 (C-H), 1729 (C=O), 1050-1125 (C-C). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J(Hz): 1.71 (s, 3H, CH_3), 3.62 (s, 3H, OCH_3), 4.21 (s, 2H, CH_2), 4.60 (s, H, CH), 7.42 (m, 5H, Ph), 9.15 (s, br, 1H, NH). ^{13}C NMR δ_C(ppm): 22 (CH_3), 47 (CH_2), 52 (CH_3), 85 (CH), 127 (CH), 128 (CH), 141 (C), 161 (C), 166 (C). *m/z*: 205.11 (100.0%). Anal. Calcd for $C_{12}H_{15}NO_2$ (205.25): C, 70.22; H, 7.37; N, 6.82%.

Methyl 3-(allylamino) but-2-enoate

Brown crystals, yield: 0.65g (76%). IR (KBr) (ν_{max}/cm^{-1}): 3365 (N-H), 3020 (=C-H), 2982 (C-H), 1736 (C=O), 1068-1145 (C-C). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J(Hz): 1.71 (s, 3H, CH_3), 4.15 (s, 3H, OCH_3), 3.52 (m, 2H, CH_2), 4.92 (m, 2H, CH_2), 5.32 (s, H, CH), 5.68 (m, H, CH), 8.54 (s, br, 1H, NH). ^{13}C NMR δ_C(ppm): 22 (CH_3), 45 (CH_2), 52 (CH_3), 85 (CH), 116 (CH_2), 134 (CH), 161 (C), 166 (C). *m/z:* 155.09 (100). Anal. Calcd for $C_8H_{13}NO_2$ (155.19): C, 61.91; H, 8.44; N, 9.03%.

4-(methylamino) pent-3-en-2-one

Brown crystals, yield: (96%). IR (KBr) (ν_{max}/cm^{-1}): 3426(NH), 3000(=CH), 1610(C=O).^{1}HNMR (300MHz, $CDCl_3$) δ_H(ppm), J(Hz): 10.63 (br, 1H, NH), 4.91 (s, 1H, =CH), 2.8 (d, J=6Hz, 3H, N-CH_3), 1.91 (s, 3H, CH_3), 1.84 (s, 3H, CH_3).^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 196.2, 160.5, 94.7, 30, 27.7, 23.8. m/z: 113.08 (100.0%), 114.09 (6.7%).Anal. Calcd for $C_6H_{11}NO$ (113.16): C, 63.68; H, 9.80; N, 12.23.

4-(dimethylamino) pent-3-en-2-one

Orange crystals, yield: (93%). IR (KBr) (ν_{max}/cm^{-1}): 2921(CH), 1543(C=O), 1031(C-N), 775(=CH).^{1}HNMR (300MHz, $CDCl_3$) δ_H(ppm), J(Hz): 5.03 (s, 1H, =CH), 2.97 (s, 6H, N(CH_3)$_2$) 2.51 (s, 3H, CH_3), 2.07 (s, 3H, CH_3). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 196.2, 163.1, 95.7, 39.3(2CH_3), 27.5, 21.9. m/z: 127.10 (100.0%), 128.10 (8.0%). Anal. Calcd for $C_7H_{13}NO$ (127.18): C, 66.10; H, 10.30; N, 11.01.

4-(phenylamino) pent-3-en-2-one

Milky crystals, yield: (78%). IR (KBr) (ν_{max}/cm^{-1}): 3450(NH), 3050(=CH), 1595(C=O), 1437(CH_3).^{1}HNMR (300MHz, $CDCl_3$) δ_H(ppm), J(Hz): 12.44 (br, 1H, NH), 7.05-7.32 (m, 5H, Ph), 5.15 (s, 1H, =CH), 2.05 (s, 3H, CH_3), 1.95 (s, 3H, CH_3). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 196.3, 159.5, 138.8, 129.5(2CH), 129.4(2CH), 122.5, 97.7, 27.5, 19.9. m/z: 175.10 (100.0%), 176.10 (12.3%). Anal. Calcd for $C_{11}H_{13}NO$ (175.23): C, 75.40; H, 7.48; N, 7.99.

4-(Naphthalen-1-ylamino)-Pent-3-en-2-one

Glass crystals, yield: (82%). IR (KBr) (ν_{max}/cm^{-1}): 3476 (NH), 3064(=CH), 2916(CH), 1598(C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J (Hz): 1.83(s, 3H, CH_3), 2.13(s, 3H, CH_3), 5.27(s, 1H, =CH), 7.21(m, 7H, =CH), 12.71(s, 1H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 21.7, 29.2(CH_3), 97.8, 97.9, 109.6, 119.1, 121.2, 125.1, 126.2, 126.6, 128.5(CH), 124.7, 140.8, 159.7, 197.7(C). m/z: 225.12(100%), 226.12(16.4%). Anal. Calcd for $C_{15}H_{15}NO$ (225.29): C, 79.97; H, 6.71; N, 6.22; O, 7.10.

Dimethyl 2-(4-oxo-2-(propylamino) pent-2-en-3-yl) fumarate

Brown crystals, yield: 0.78g (88%). IR (KBr) (ν_{max}/cm^{-1}): 3345 (N-H), 1736 (C=Oester), 1646 (C=C), 1625 (C=O). ^{1}HNMR(300MHz,$CDCl_3$) δ_H(ppm), J(Hz): 0.87 (t, H, CH_3), 0.91 (t, 3H, CH_3), 1.42 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.92 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.71 (m, 2H, CH_2), 3.32 (m, 2H, CH_2), 3.72 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.42 (s, H, CH), 10.93 (s, br, H, NH). ^{13}CNMR (75MHz,$CDCl_3$) δ_C(ppm): 11 (CH_3), 16 (CH_3), 24 (CH_2), 27 (CH_3), 46 (CH_2), 52 (CH_3), 53 (CH_3), 115 (C), 125 (CH), 142 (C), 164 (C), 165 (C), 166 (C), 198 (C). *m/z*: 283.14 (100.0%). Anal. Calcd for $C_{14}H_{21}NO_5$ (283.32): C, 59.35; H, 7.47; N, 4.94%.

Dimethyl 2-(2-(benzylamino)-4-oxopent-2-en-3-yl) fumarate

Brown crystals , yield: 0.55 g (60 %). IR (KBr) (ν_{max}/cm^{-1}): 3320 (N-H), 1735 (C=O), 1632 (C=C), 1658 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H(ppm), J(Hz): 1.87 (s, H, CH_3), 2.08 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 4.52 (s, 2H, CH_2), 5.35 (s, H, CH), 7.31 (m, 5H, Ph), 11.35 (s, br, 1H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 16 (CH_3), 27 (CH_3), 48 (CH_2), 52 (CH_3), 53 (CH_3), 115 (C), 125 (CH), 126 (2CH), 127 (2CH), 129 (2CH), 141 (C), 143 (C), 165 (2C), 167 (C), 197 (C). m/z: 331.14 (100.0%), 332.15 (19.9%). Anal.

Calcd for $C_{18}H_{21}NO_5$ (331.36): C, 65.24; H, 6.39; N, 4.23; O, 24.14%.

Dimethyl 2-(2-(allylamino)-4-oxopent-2-en-3-yl) fumarate

Orange crystals, yield: 0.65g (70%). IR (KBr) (ν_{max}/cm^{-1}): 3335 (N-H), 1735 (C=O), 1560 (C=C), 1699 (C=O), 1275 (C-N). ^{1}HNMR(300MHz,$CDCl_3$) δ_H(ppm), J(Hz): 1.71 (s, H, CH_3), 2.10 (s, 3H, CH_3), 2.36 (m, 2H, CH_2), 3.81 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 5.11 (s, H, CH), 5.91 (m, H, CH), 5.32 (m, H, CH_2), 11.21 (s, br, H, NH). ^{13}CNMR (75MHz,$CDCl_3$) δ_C(ppm): 16 (CH_3), 27 (CH_3), 46 (CH_2), 52 (CH_3), 53 (CH_3), 115 (C), 117 (CH_2), 125 (CH), 135 (CH), 144 (C), 165 (C), 166 (C), 168 (C), 198 (C). *m/z*: 281.13 (100.0%). Anal. Calcd for $C_{14}H_{19}NO_5$ (281.3): C, 59.78; H, 6.81; N, 4.98%.

Dimethyl 2-(2-(butylamino)-4-oxopent-2-en-3-yl) fumarate

Brown crystals, yield: 0.54g (50%). IR (KBr) (ν_{max}/cm^{-1}): 3425 (N-H), 1735 (C=Oester), 1560 (C=C), 1699 (C=O). ^{1}HNMR(300MHz,$CDCl_3$) δ_H(ppm), J(Hz): 0.71 (t, H, CH_3), 1.36 (m, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.91 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.25 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.11 (s, H, CH), 10.85 (s, br, H, NH). ^{13}CNMR (75MHz,$CDCl_3$) δ_C(ppm): 14 (CH_3), 16 (CH_3), 22 (CH_2), 29 (CH_3), 35 (CH_2), 46 (CH_2), 52 (CH_3), 54 (CH_3), 116 (C), 127 (CH), 143 (C), 164 (C), 166 (C), 167 (C), 198 (C). *m/z*: 297.16 (100.0%). Anal. Calcd for $C_{15}H_{23}NO_5$ (297.35): C, 60.59; H, 7.80; N, 4.71%.

Trimethyl 4-(propylamino) penta-1,3-diene-1,2,3-tricarboxylate

Yellow crystals, yield: 0.62g (80%). IR (KBr) (ν_{max}/cm^{-1}): 3320 (N-H), 1736 (C=O), 1646 (C=C), 1675 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H (ppm), J(Hz): 0.91 (t, H, CH_3), 1.52 (m, 2H, CH_2), 1.81 (s, 3H, CH_3), 3.15 (m, 2H, CH_2), 3.61 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 4.12 (s, 3H, OCH_3), 5.56(s, H, CH), 9.56 (s, br, H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 11 (CH_3), 16 (CH_3), 24 (CH_2), 46 (CH_2), 52 (CH_3), 53 ($2CH_3$), 82 (C), 125 (CH), 142 (C), 164 (C), 165 (C), 165 (2C), 167 (C). *m/z*: 299.14 (100.0%). Anal. Calcd for $C_{14}H_{21}NO_6$ (299.32): C, 56.18; H, 7.07; N, 4.68%.

Trimethyl 4-(benzylamino) penta-1, 3-diene-1, 2, 3-tricarboxylate

Yellow crystals, yield: 0.53g (50%). IR (KBr) (ν_{max}/cm^{-1}): 3320 (N-H), 1735 (C=O), 1635 (C=C), 1645 (C=O). ^{1}HNMR (300MHz, $CDCl_3$) δ_H(ppm), J(Hz): 1.82 (s, 3H, CH_3), 3.9 (s, 2H, CH_2), 4.61 (s, 3H, OCH_3), 4.35 (s, 3H, OCH_3), 4.42 (s, 3H, OCH_3), 5.26 (s, H, CH), 7.31 (m, 5H, Ph), 10.65 (s, br , H). ^{13}CNMR(75MHz,$CDCl_3$) δ_C(ppm): 17 (CH_3), 48 (CH_2), 52 (CH_3), 53 ($2CH_3$), 83 (C), 125 (CH), 126 (CH), 127 (2CH), 129 (2CH), 142 (2C), 164 (C), 165 (2C), 167 (C). *m/z*: 347.14 (100.0%). Anal. Calcd for $C_{18}H_{21}NO_6$ (347.36): C, 62.24; H, 6.09; N, 4.03%.

Trimethyl 4-(allylamino) penta-1, 3-diene-1, 2, 3-tricarboxylate

Brown crystals, yield: 0.65g (60%). IR (KBr) (ν_{max}/cm^{-1}): 3420 (N-H), 2998 (CH), 1745, 1669 (C=O), 1635 (C=C), 1235 (C-N). ^{1}HNMR(300MHz,$CDCl_3$) δ_H(ppm), J(Hz): 1.72 (s, 3H, CH_3), 3.9 (s, 3H, OCH_3), 3.61 (m, 2H), 3.73 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.60 (s, H), 5.42 (m, 2H), 6.11 (s, 1H), 9.85 (s, br , 1H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 17 (CH_3), 46 (CH_2), 52 (CH_3), 54 ($2CH_3$), 83 (C), 117 (CH2), 126 (CH), 133 (CH), 144 (C), 163 (C), 166 (2C), 168 (C). *m/z:* 297.12 (100.0%). Anal. Calcd for $C_{14}H_{19}NO_6$ (297.3): C, 56.56; H, 6.44; N, 4.71%.

Dimethyl 2-(2-(methylamino)-4-oxopent-2-en-3-yl) fumarate

Yellow oil, yield: (91%). IR (KBr) (ν_{max}/cm^{-1}) : 3444, 1719 , 1603 , 784 .

^{1}HNMR (300 MHz , $CDCl_3$) δ_H(ppm), J(Hz): 1.79 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.9 (d, 3H, NCH_3), 3.69 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.98 (s, 1H, =C–H), 11.89(br, 1H, NH). ^{13}CNMR (75 MHz, $CDCl_3$) δ_C(ppm): 16.59 (CH_3), 17.02 (CH_3), 30.31 (NCH_3), 52.31(OCH_3), 52.75(OCH_3), 130.98 (= C– H), 127.44, 143.84, 147.58 (C), 165 .78, 168 .55, 195 (C = O). m/z: 255.11 (100.0%), 256.11 (13.5%). Anal. Calcd for $C_{12}H_{17}NO_5$ (255.27): C, 56.46; H, 6.71; N, 5.49; O, 31.34%.

Dimethyl 2-(2-(dimethylamino)-4-oxopent-2-en-3-yl) fumarate

Yellow oil, yield: (87%). IR (KBr) (ν_{max}/cm^{-1}): 2951 – 2787, 1728. ^{1}HNMR (300 M Hz, $CDCl_3$) δ_H(ppm),

J(Hz): 2.33, 2.71 (s, 3H, CH_3), 2.97 (s, 6H, $(N(CH_3)_2)$, 3.85, 3.88(s, 3H, OCH_3), 7.08 (s, 1H, = C– H). ^{13}CNMR (75 MHz, $CDCl_3$) δ_C(ppm): 21.80, 30.06 (CH_3) , 45.41($N(CH_3)_2$), 52.81, 52.93(OCH_3), 124.99, 140.47, 152.41 (C), 129.42 (=C–H), 167, 170.09, 195 (C = O). m/z: 269.13 (100.0%), 270.13 (14.5%). Anal. Calcd for $C_{13}H_{19}NO_5$ (269.29): C, 57.98; H, 7.11; N, 5.20; O, 29.71%.

Dimethyl 2-(4-oxo-2-(phenylamino) pent-2-en-3-yl) fumarate

Yellow oil, yield: (62%). IR (KBr) (ν_{max}/cm^{-1}): 3468, 1731, 1646, 1593. ^{1}HNMR (300MHz , $CDCl_3$) δ_H(ppm), J(Hz): 2.03 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.03 (s, 1H, = C – H), 7.05– 7.36 (m, 5H, ph) , 13.53 (s, 1H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 18.46, 29.10 52.48, 52.90, 105.20, (CH_3), 131.65, 138.46, 147.65, 161.62, 165.72, 194.95(C), 126.03, 126.80, 127.79, 129.61(CH). m/z: 317.13 (100.0%), 318.13 (18.8%). Anal. Calcd for $C_{17}H_{19}NO_5$ (317.34): C, 64.34; H, 6.03; N, 4.41; O, 25.21%.

Dimethyl 2-(2-(naphthalen-1-ylamino)-4-oxopent-2-en-3-yl) fumarate

Yellow oil, yield: (74%). IR (KBr) (ν_{max}/cm^{-1}): 3438, 1728, 1597, 1509.^{1}HNMR (300 MHz , $CDCl_3$) δ_H(ppm), J(Hz): 1.95 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.10 (s, 1H, = C– H), 7.07 – 7.94 (m, 7H, =C –H), 13.82 (s, 1H, NH). ^{13}CNMR (75MHz, $CDCl_3$) δ_C(ppm): 18.33, 29.04, 52.4, 52.85 (CH_3), 122.55, 124.23, 125.62, 125.62, 127.03, 127.45, 127.79, 127.87, 128.67 (CH), 123.79, 126.89, 130.26, 134.61, 134.66, 146.88, 163, 165.68 (C). m/z: 367.14 (100.0%), 368.15 (23.1%). Anal. Calcd for (367.40): C, 68.65; H, 5.76; N, 3.81; O, 21.77%.

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