Research Article

One-Pot Solvent-Free Three-Component Synthesis of Conjugated Enaminones Containing Three Alkyl Carboxylate Groups

N. Zohreh,¹ A. Alizadeh,² and M. Babaki²

¹ Department of Chemistry, Faculty of Science, University of Qom, P.O. Box 37185-359, Qom 3716146611, Iran

² Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran 1411713116, Iran

Correspondence should be addressed to N. Zohreh; nasrin.zohreh@gmail.com or A. Alizadeh; aalizadeh@modares.ac.ir

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An effective, one-pot, multicomponent, and solvent-free reaction for synthesis of conjugated enaminones containing three alkyl carboxylate groups is described. The reaction of primary amine, alkyl acetoacetate, and dialkyl acetylenedicarboxylate obtained the title compound in good yields in a short time.

1. Introduction

The multicomponent coupling reactions are emerging as a useful source for synthesizing small drug-like molecules with several levels of structural diversity [1]. They are also welcome in the context of economic and practical considerations. Moreover, multicomponent coupling strategies offer significant advantages over conventional linear-type syntheses [2].

β -Functionalized enaminone derivatives are valuable precursors in organic synthesis, as they combine nucleophilicity of the enamine and electrophilicity of the enone functions [3, 4]. They are useful synthones for the synthesis of various pharmaceuticals [5, 6] and bioactive heterocycles [7, 8]. In particular, they have been utilized for the preparation of different important antibacterial, anticonvulsant, anti-inflammatory, and antitumour agents [9, 10]. They are important intermediates for the synthesis of several amino acids, aminols, peptides, and alkaloids [11–15]. In addition, open-chain enaminones (the characteristic group is part of a chain) may be potential prodrugs since they could release biologically active primary amines [16].

Regarding their wide range of activity and importance, a variety of synthetic methods for enaminones [17–23] has been developed. Surprisingly, no efficient solvent-free procedure currently exists for the synthesis of conjugated enaminones via a one-pot reaction.

2. Results and Discussion

Our research group investigated the synthesis of series of heterocycles based on the use of enaminones [24–28]. Recently, we reported the synthesis of hydrazine-substituted enaminones [29] using diisopropyl diazodicarboxylate as an electron-deficient compound in a four-component reaction (Scheme 1).

In continuation, we decided to employ dialkyl acetylene dicarboxylate **3** as an electron-deficient compound in reaction with enaminones derived in situ from the solvent-free reaction of primary amines **1** and alkyl acetoacetate **2** for synthesis of conjugated enaminones **4**. Our strategy is outlined in Scheme 2. The reaction proceeds under solvent-free condition at ambient temperature and in a very short time to produce conjugated enaminone 1,3-pentadiene-1,2,3-tricarboxylate derivatives in 80–90% yields.

To investigate the reaction scope and limitations, different types of primary amines, alkyl acetoacetates, and dialkyl acetylenedicarboxylates were used in the above reaction under the same condition. It was found that the reaction is general toward all of these components (Table 1). However, compound **4** could be produced as two *E* and *Z* isomers, but in the mentioned condition; we recovered it as a single isomer in all examples (Figure 1).

SCHEME 1

SCHEME 2

The structures of compounds **4a–i** were deduced from their elemental analysis, IR, and ^1H and ^{13}C NMR spectra that clearly indicated the formation of 1,3-pentadiene-1,2,3-tricarboxylate derivatives. The mass spectrum of **4a** displayed a molecular ion peak at m/z 299, which was consistent with the 1:1:1 adduct of *n*-propyl amine, methyl acetoacetate, and dimethyl acetylenedicarboxylate. The most important absorption band in IR spectrum is due to the NH stretching frequency of amide moiety that is appeared at 3420 cm^{-1} . Absorption bands at 1714 , 1690 , and 1645 cm^{-1} are due to the three $\text{C}=\text{O}$ of ester groups. In the ^1H NMR spectrum of **4a**, characteristic singlet signals at $\delta_{\text{H}} = 3.59$, 3.71 , and 3.78 ppm revealed that both of the methyl acetoacetate and dimethyl acetylenedicarboxylate are present in the product. The spectrum exhibited also three sharp singlet signals recognized as arising from $\text{C}=\text{CMe}$ ($\delta_{\text{H}} = 1.87\text{ ppm}$), $\text{C}=\text{CH}$ ($\delta_{\text{H}} = 6.78\text{ ppm}$), and NH ($\delta_{\text{H}} = 9.63\text{ ppm}$) groups. The *n*-propyl moiety gave rise to characteristic signals in the aliphatic region of the spectrum. The ^1H decoupled ^{13}C NMR spectrum of **4a** showed 14 distinct resonances compatible with the proposed product. The signals at 165.76 , 168.85 , and 168.87 ppm are due to the three CO_2Me . The ^1H and ^{13}C NMR spectra of compounds **4b–i** were similar to those of **4a**, except for the R , R' , and R'' which exhibited characteristic signals with appropriate chemical shifts for the specific substitution patterns. Unfortunately, based on these spectroscopic data, we were not able to identify which isomer *E* or *Z* is produce (Figure 1).

Although we have not established the mechanism of this reaction in an experimental manner, a possible explanation is proposed in Scheme 3. It is conceivable that initial event is the formation of enaminone **5** under solvent-free condition [30]. Subsequently, compound **5** reacts with dialkyl acetylenedicarboxylate to produce intermediate **6**. Finally, tautomerization converts imine **6** to the product **4** (Scheme 3).

3. Experimental

All the chemicals used in the synthesis were of laboratory grade. Elemental analyses for C, H, and N were performed using a *Herpes* CHN-O-Rapid analyzer. Mass spectra were recorded on a *FINNIGAN-MAT* 8430 mass spectrometer operating at an ionization potential of 20 eV . ^1H - and ^{13}C -NMR spectra were measured (CDCl_3 solution) with a *Bruker* DRX-500 AVANCE spectrometer at 500.1 and 125.7 MHz , respectively. IR spectra were recorded on a *Shimadzu* IR-460 spectrometer.

4. Typical Procedure for Preparation of Compound 4 (e.g. 4a)

To a magnetically stirred 5 mL flat bottom flask containing 0.06 gr of *n*-propyl amine (1 mmol), 0.12 gr methyl acetoacetate (1 mmol) was added. After 10 min , 0.14 gr dimethyl acetylenedicarboxylate (1 mmol) was added. The reaction mixture was allowed to stir 15 min . The product was separated by silica gel (Merck 230–240 mesh) column chromatography using *n*-hexane–EtOAc ($5:1$) mixture as eluent.

4.1. Trimethyl 4-(Propylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4a. Pale yellow oil, yield 0.24 g (80%); IR (KBr): 3420 (NH), 1714 , 1690 and 1645 ($\text{C}=\text{O}$), 1233 and 1133 ($\text{C}-\text{O}$); ^1H -NMR (500.13 MHz , CDCl_3): ^1H NMR (500.13 MHz , CDCl_3): 1.02 (3H , t, $^3J_{\text{HH}} = 7.5\text{ Hz}$, $\text{NCH}_2\text{CH}_2\text{Me}$), 1.67 (2H , sextet, $^3J_{\text{HH}} = 7.2\text{ Hz}$, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.87 (3H , s, $\text{C}=\text{CMe}$), 3.24 – 3.27 (2H , m, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 3.59 (3H , s, OMe), 3.71 (3H , s, OMe), 3.78 (3H , s, OMe), 6.78 (1H , s, $\text{C}=\text{CH}$), 9.63 (1H , s, NH); ^{13}C NMR (125.7 MHz , CDCl_3): $\delta_{\text{C}} = 11.41$ ($\text{NCH}_2\text{CH}_2\text{Me}$), 16.41 ($\text{C}=\text{CMe}$), 23.32 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 45.28 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 50.44 (OMe), 51.55 (OMe), 52.59 (OMe), 88.32 ($\text{C}=\text{CMe}$), 126.61 ($\text{C}=\text{CH}$), 143.14 ($\text{C}=\text{CH}$),

162.44 (C=CMe), 165.76 (CO₂Me), 168.85 (CO₂Me), 168.87 (CO₂Me); EI-MS: m/z (%) = 299 (10) [M^+], 294 (19), 293 (25), 278 (20), 265 (8), 238 (13), 236 (40), 222 (7), 206 (22), 195 (26), 168 (15), 154 (61), 141 (100), 127 (45), 115 (33), 111 (16), 97 (15), 77 (43), 57 (42), 43 (95), 41 (47); Anal. Calc. for C₁₄H₂₁NO₆ (299.32): C 56.18, H 7.07, N 4.68; found: C 56.21, H 7.09, N 4.60.

4.2. 1,2-Diethyl 3-Methyl 4-(Propylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4b. Pale yellow oil, yield 0.27 g (85%); IR (KBr) ($\nu_{\max}$, cm⁻¹): 3495 (NH), 1712, 1677 and 1647 (C=O), 1237 and 1158 (C-O); ¹H NMR (500.13 MHz, CDCl₃): δ_H = 0.97 (3H, t, ³ J_{HH} = 7.3 Hz, NCH₂CH₂Me), 1.21 (3H, t, ³ J_{HH} = 6.9 Hz, OCH₂Me), 1.25 (3H, t, ³ J_{HH} = 7.0 Hz, OCH₂Me), 1.62 (2H, sextet, ³ J_{HH} = 7.1 Hz, NCH₂CH₂Me), 1.83 (3H, s, C=CMe), 3.18–3.22 (2H, m, NCH₂CH₂Me), 3.54 (3H, s, OMe), 4.08–4.14 (2H, m, OCH₂Me), 4.15–4.24 (2H, m, OCH₂Me), 6.71 (1H, s, C=CH), 9.57 (1H, s, NH); ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 11.32 (NCH₂CH₂Me), 14.05 (OCH₂Me), 14.10 (OCH₂Me), 16.32 (C=CMe), 23.26 (NCH₂CH₂CH₃), 45.17 (NCH₂CH₂CH₃), 50.25 (OMe), 60.26 (OCH₂Me), 61.29 (OCH₂Me), 88.45 (C=CMe), 126.97 (C=CH), 142.93 (C=CH), 162.18 (C=CMe), 165.40 (CO₂Et), 168.19 (CO₂Et), 168.81 (CO₂Me); MS (EI, 70 eV): m/z (%) = 326 (23) [M^+], 313 (12), 298 (29), 240 (6), 236 (19), 231 (3), 217 (4), 208 (17), 198 (2), 175 (2), 151 (20), 129 (31), 113 (16), 121 (10), 105 (10), 70 (15), 62 (18), 43 (100), 41 (19); Anal. Calc. for C₁₆H₂₅NO₆ (327.37): C 58.70, H 7.70, N 4.28; found: C 58.78, H 7.73, N 4.30.

4.3. 3-Ethyl 1,2-Dimethyl 4-(Propylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4c. Pale yellow oil, yield 0.26 g (84%); IR (KBr) ($\nu_{\max}$, cm⁻¹): 3425 (NH), 1714, 1686 and 1643 (C=O), 1229 and 1159 (C-O); ¹H NMR (500.13 MHz, CDCl₃): δ_H = 1.03 (3H, t, ³ J_{HH} = 7.5 Hz, NCH₂CH₂Me), 1.16 (3H, t, ³ J_{HH} = 7.2, OCH₂Me), 1.66–1.69 (2H, m, NCH₂CH₂CH₃), 1.89 (3H, s, C=CMe), 3.25–3.27 (2H, m, NCH₂CH₂CH₃), 3.71 (3H, s, OMe), 3.78 (3H, s, OMe), 3.99–4.14 (2H, m, OCH₂Me), 6.73 (1H, s, C=CH), 9.68 (1H, s, NH); ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 11.40 (NCH₂CH₂Me), 14.34 (OCH₂Me), 16.42 (C=CMe), 23.29 (NCH₂CH₂CH₃), 45.27 (NCH₂CH₂CH₃), 51.48 (OMe), 52.47 (OMe), 58.82 (OCH₂Me), 88.66 (C=CMe), 125.87 (C=CH), 143.46 (C=CH), 162.55 (C=CMe), 165.79 (CO₂Et), 168.46 (CO₂Me), 169.07 (CO₂Me); MS (EI, 70 eV): m/z (%) = 313 (13) [M^+], 298 (4), 282 (45), 268 (5), 252 (6), 250 (35), 238 (20), 222 (33), 206 (33), 194 (36), 180 (12), 164 (16), 152 (12), 138 (11), 125 (10), 108 (8), 82 (7), 59 (29), 43 (100); Anal. Calc. for C₁₅H₂₃NO₆ (313.35): C 57.50, H 7.40, N 4.47%; found: C 57.54, H 7.44, N 4.46%.

4.4. Triethyl 4-(Propylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4d. Pale yellow oil, yield 0.29 g (85%); IR (KBr) ($\nu_{\max}$, cm⁻¹): 3485 (NH), 1712, 1687 and 1643 (C=O), 1231 and 1158 (C-O); ¹H NMR (500.13 MHz, CDCl₃): δ_H = 1.02 (3H, t, ³ J_{HH} = 7.3 Hz, NCH₂CH₂Me), 1.17 (3H, t, ³ J_{HH} =

TABLE 1: The reaction of primary amine, alkyl acetoacetate, and dialkyl acetylenedicarboxylate.

Product 4	R	R'	R''	Yield % 4
a	<i>n</i> -Pr	Me	Me	80
b	<i>n</i> -Pr	Me	Et	85
c	<i>n</i> -Pr	Et	Me	84
d	<i>n</i> -Pr	Et	Et	85
e	<i>i</i> -Pr	Me	Me	86
f	<i>i</i> -Pr	Me	Et	90
g	<i>i</i> -Pr	Et	Me	87
h	Allyl	Me	Me	94
i	Allyl	Et	Me	90

6.9 Hz, OCH₂Me), 1.26 (3H, t, ³ J_{HH} = 7.0 Hz, OCH₂Me), 1.30 (3H, t, ³ J_{HH} = 7.0 Hz, OCH₂Me), 1.62–1.69 (2H, m, NCH₂CH₂Me), 1.87 (3H, s, C=CMe), 3.18–3.30 (2H, m, NCH₂CH₂Me), 4.01–4.06 (2H, m, OCH₂Me), 4.08–4.16 (2H, m, OCH₂Me), 4.16–4.24 (2H, m, OCH₂Me), 6.73 (1H, s, C=CH), 9.64 (1H, s, NH); ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 11.39 (NCH₂CH₂Me), 13.87 (OCH₂Me), 14.15 (OCH₂Me), 14.33 (OCH₂Me), 16.40 (C=CMe), 23.31 (NCH₂CH₂CH₃), 45.22 (NCH₂CH₂CH₃), 58.80 (OCH₂Me), 60.27 (OCH₂Me), 61.33 (OCH₂Me), 88.82 (C=CMe), 126.57 (C=CH), 143.27 (C=CH), 162.19 (C=CMe), 165.53 (CO₂Et), 168.45 (CO₂Et), 168.52 (CO₂Et); MS (EI, 70 eV): m/z (%) = 339 (1) [M^+], 326 (16), 298 (14), 240 (55), 236 (76), 231 (3), 217 (4), 203 (17), 188 (2), 175 (2), 161 (20), 149 (31), 129 (4), 113 (16), 104 (10), 85 (10), 71 (15), 62 (18), 43 (100), 41 (19); Anal. Calc. for C₁₇H₂₇NO₆ (341.40): C 59.81, H 7.97, N 4.10%; found: C 59.85, H 7.99, N 4.11%.

4.5. Trimethyl 4-(Isopropylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4e. Pale yellow oil, yield 0.26 g (86%); IR (KBr) ($\nu_{\max}$, cm⁻¹): 3425 (NH), 1715, 1688 and 1645 (C=O), 1243 and 1180 (C-O); ¹H NMR (500.13 MHz, CDCl₃): δ_H = 1.22 (6H, d, ³ J_{HH} = 6.0 Hz, NCHMe₂), 1.84 (3H, s, C=CMe), 3.51 (3H, s, OMe), 3.64 (3H, s, OMe), 3.71 (3H, s, OMe), 3.71–3.72 (1H, m, NCHMe₂), 6.70 (1H, s, C=CH), 9.56 (1H, d, ³ J_{HH} = 7.9 Hz, NH); ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 16.07 (C=CMe), 23.77 (NCHMe₂), 24.06 (NCHMe₂), 44.89 (NCHMe₂), 50.31 (OMe), 51.48 (OMe), 52.50 (OMe), 88.14 (C=CMe), 126.66 (C=CH), 143.03 (C=CH), 161.31 (C=CMe), 162.55 (CO₂Me), 165.66 (CO₂Me), 168.73 (CO₂Me); MS (EI, 70 eV): m/z (%) = 299 (4) [M^+], 267 (5), 240 (7), 236 (5), 221 (5), 208 (6), 193 (6), 179 (6), 156 (11), 149 (20), 127 (5), 122 (5), 105 (10), 96 (10), 70 (13), 58 (25), 43 (100), 41 (28); Anal. Calc. for C₁₄H₂₁NO₆ (299.32): C 56.18, H 7.07, N 4.68%; found: C 56.24, H 7.12, N 4.66%.

4.6. 1,2-Diethyl 3-Methyl 4-(Isopropylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4f. Pale yellow oil, yield 0.29 g (90%); IR (KBr) ($\nu_{\max}$, cm⁻¹): 3385 (NH), 1712, 1690 and 1647 (C=O), 1240 and 1172 (C-O); ¹H NMR (500.13 MHz, CDCl₃): δ_H = 1.23 (3H, t, ³ J_{HH} = 7.1 Hz, OCH₂Me), 1.25

FIGURE 1

SCHEME 3

(6H, d, $^3J_{\text{HH}} = 6.2$ Hz, NCHMe_2), 1.27 (3H, t, $^3J_{\text{HH}} = 7.7$ Hz, OCH_2Me), 1.88 (3H, s, $\text{C}=\text{CMe}$), 3.56 (3H, s, OMe), 3.72–3.77 (1H, m, NCHMe_2), 4.10–4.17 (2H, m, OCH_2Me), 4.18–4.26 (2H, m, OCH_2Me), 6.74 (1H, s, $\text{C}=\text{CH}$), 9.55 (1H, d, $^3J_{\text{HH}} = 8.1$ Hz, NH); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta_{\text{C}} = 14.16$ ($2\text{OCH}_2\text{Me}$), 16.10 ($\text{C}=\text{CMe}$), 23.87 (NCHMe_2), 24.11 (NCHMe_2), 44.89 (NCHMe_2), 50.29 (OMe), 60.33 (OCH_2Me), 61.35 (OCH_2Me), 88.37 ($\text{C}=\text{CMe}$), 127.30 ($\text{C}=\text{CH}$), 142.85 ($\text{C}=\text{CH}$), 161.09 ($\text{C}=\text{CMe}$), 165.49 (CO_2Me), 168.24 (CO_2Me), 168.82 (CO_2Me); MS (EI, 70 eV): m/z (%) = 326 (35) [M^+], 313 (17), 298 (7), 267 (16), 240 (2), 236 (4), 221 (9), 207 (16), 194 (21), 179 (23), 156 (22), 149 (25), 129 (6), 121 (4), 105 (18), 96 (20), 70 (13), 58 (2), 43 (100), 41 (43); Anal. Calc. for $\text{C}_{16}\text{H}_{25}\text{NO}_6$ (327.37): C 58.70, H 7.70, N 4.28%; found: C 58.74, H 7.73, N 4.26%.

4.7. 3-Ethyl 1,2-Dimethyl 4-(Isopropylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4g. Pale yellow oil, yield 0.27 g (87%); IR (KBr) (ν_{max} , cm^{-1}): 3295 (NH), 1712, 1657 and 1430 ($\text{C}=\text{O}$), 1230 ($\text{C}-\text{O}$); ^1H NMR (500.13 MHz, CDCl_3): $\delta_{\text{H}} = 1.13$ (3H, t, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2Me), 1.23 (6H, d, $^3J_{\text{HH}} = 6.0$ Hz, NCHMe_2), 1.87 (3H, s, $\text{C}=\text{CMe}$), 3.66 (3H, s, OMe), 3.73 (3H, s, OMe), 3.75–3.76 (1H, m, NCHMe_2), 3.91–3.93 (1H, m, OCH_2Me), 4.04–4.06 (1H, m, OCH_2Me), 6.68 (1H, s, $\text{C}=\text{CH}$), 9.58 (1H, d, $^3J_{\text{HH}} = 7.4$ Hz, NH); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta_{\text{C}} = 14.33$ (OCH_2Me), 16.13 ($\text{C}=\text{CMe}$), 23.77 (NCHMe_2), 24.11 (NCHMe_2), 44.90 (NCHMe_2), 51.46 (OMe), 52.42 (OMe), 58.73 (OCH_2Me), 88.52 ($\text{C}=\text{CMe}$), 125.94 ($\text{C}=\text{CH}$), 143.40 ($\text{C}=\text{CH}$), 161.45 ($\text{C}=\text{CMe}$), 165.74 (CO_2Et), 168.36 (CO_2Me),

169.02 (CO_2Me); MS (EI, 70 eV): m/z (%) = 313 (15) [M^+], 298 (4), 267 (10), 240 (3), 236 (10), 220 (6), 209 (6), 194 (6), 179 (15), 156 (10), 149 (25), 129 (6), 121 (25), 105 (10), 96 (20), 70 (13), 58 (12), 43 (100), 41 (45); Anal. Calc. for $\text{C}_{15}\text{H}_{23}\text{NO}_6$ (313.35): C 57.50, H 7.40, N 4.47%; found: C 57.52, H 7.44, N 4.46%.

4.8. Trimethyl 4-(Allylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4h. Pale yellow oil, yield 0.28 g (94%); IR (KBr) (ν_{max} , cm^{-1}): 3420 (NH), 1715, 1690 and 1643 ($\text{C}=\text{O}$), 1237 and 1164 ($\text{C}-\text{O}$); ^1H NMR (500.13 MHz, CDCl_3): $\delta_{\text{H}} = 1.86$ (3H, s, $\text{C}=\text{CMe}$), 3.60 (3H, s, OMe), 3.71 (3H, s, OMe), 3.78 (3H, s, OMe), 3.89–3.90 (2H, m, $\text{NCH}_2\text{CHCH}_2$), 5.21 (1H, d of d, $^3J_{\text{HH}} = 10.0$ Hz, $^2J_{\text{HH}} = 2.2$ Hz, $\text{NCH}_2\text{CHCH}_2$), 5.30 (1H, d of d, $^3J_{\text{HH}} = 15.1$ Hz, $^2J_{\text{HH}} = 2.2$ Hz, $\text{NCH}_2\text{CHCH}_2$), 5.81–5.94 (1H, m, $\text{NCH}_2\text{CHCH}_2$), 6.81 (1H, s, $\text{C}=\text{CH}$), 9.68 (1H, s, NH); ^{13}C NMR (125.7 MHz, CDCl_3): $\delta_{\text{C}} = 16.02$ ($\text{C}=\text{CMe}$), 45.55 ($\text{NCH}_2\text{CHCH}_2$), 50.49 (OMe), 51.55 (OMe), 52.58 (OMe), 89.12 ($\text{C}=\text{CMe}$), 116.30 ($\text{NCH}_2\text{CHCH}_2$), 127.16 ($\text{C}=\text{CH}$), 134.11 ($\text{NCH}_2\text{CHCH}_2$), 142.75 ($\text{C}=\text{CH}$), 162.12 ($\text{C}=\text{CMe}$), 165.66 (CO_2Me), 168.58 (CO_2Me), 168.80 (CO_2Me); MS (EI, 70 eV): m/z (%) = 297 (1) [M^+], 298 (2), 279 (3), 245 (40), 236 (63), 219 (14), 206 (7), 188 (17), 174 (16), 160 (26), 150 (30), 127 (6), 112 (8), 103 (19), 85 (10), 71 (5), 62 (8), 43 (100), 41 (39); Anal. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}_6$ (297.30): C 56.56, H 6.44, N 4.71%; found: C 56.57, H 6.46, N 4.75%.

4.9. 3-Ethyl 1,2-Dimethyl 4-(Allylamino)-1,3-pentadiene-1,2,3-tricarboxylate 4i. Pale yellow oil, yield 0.28 g (90%); IR

(KBr) ($\nu_{\max}$, cm^{-1}): 3430 (NH), 1716, 1695 and 1644 (C=O), 1228 and 1158 (C–O); ^1H NMR (500.13 MHz, CDCl_3): δ_{H} = 1.15 (3H, t, $^3J_{\text{HH}}$ = 6.8 Hz, OCH_2Me), 1.84 (3H, s, C=CMe), 3.68 (3H, s, OMe), 3.75 (3H, s, OMe), 3.89–3.91 (2H, m, OCH_2Me), 4.06–4.13 (1H, m, $\text{NCH}_2\text{CHCH}_2$), 4.15–4.18 (1H, m, $\text{NCH}_2\text{CHCH}_2$), 5.18 (1H, d of d, $^3J_{\text{HH}}$ = 9.5 Hz, $^2J_{\text{HH}}$ = 2.0 Hz, $\text{NCH}_2\text{CHCH}_2$), 5.28 (1H, d of d, $^3J_{\text{HH}}$ = 14.9 Hz, $^2J_{\text{HH}}$ = 2.0 Hz, $\text{NCH}_2\text{CHCH}_2$), 5.85–5.89 (1H, m, $\text{NCH}_2\text{CHCH}_2$), 6.74 (1H, s, C=CH), 9.69 (1H, s, NH); ^{13}C NMR (125.7 MHz, CDCl_3): δ_{C} = 14.29 (OCH_2Me), 16.57 (C=CMe), 45.54 ($\text{NCH}_2\text{CHCH}_2$), 51.49 (OMe), 52.46 (OMe), 58.89 (OCH_2Me), 89.4 (C=CMe), 116.26 ($\text{NCH}_2\text{CHCH}_2$), 126.46 (C=CH), 134.13 ($\text{NCH}_2\text{CHCH}_2$), 143.05 (C=CH), 162.23 (C=CMe), 165.68 (CO_2Et), 168.34 (CO_2Me), 168.78 (CO_2Me); MS (EI, 70 eV): m/z (%) = 310 (5) [M^+], 298 (9), 285 (22), 277 (5), 243 (5), 232 (5), 217 (4), 206 (17), 188 (14), 175 (7), 161 (20), 149 (32), 129 (6), 113 (19), 103 (12), 85 (10), 70 (15), 62 (18), 43 (100), 41 (90); Anal. Calc. for $\text{C}_{15}\text{H}_{21}\text{NO}_6$ (311.33): C 57.87, H 6.80, N 4.50%; found: C 57.90, H 6.87, N 4.53%.

5. Conclusion

In summary, we have developed an efficient method for the synthesis of conjugated enaminones. The advantages of our work are as follows. (1) The reaction is performed under neutral condition that no acid/base or metal catalyst is required. (2) The reaction is in green chemistry category because of its solvent-free condition. (3) Three carboxylate functional groups are on the product, which is capable to convert to other functional groups. (4) Short reaction time and high yield of all derivatives are considerable. (5) The simplicity of the present procedure makes it an interesting alternative to the complex multistep approaches.

Conflict of Interests

The authors report no conflict of interests. The authors alone are responsible for the content and writing of the paper.

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