The Gould-Jacob Type of Reaction for the Synthesis of Novel Pyrimidopyrrolopyrimidines : A Comparison of Classical heating *vs* Solvent Free Microwave Irradiation

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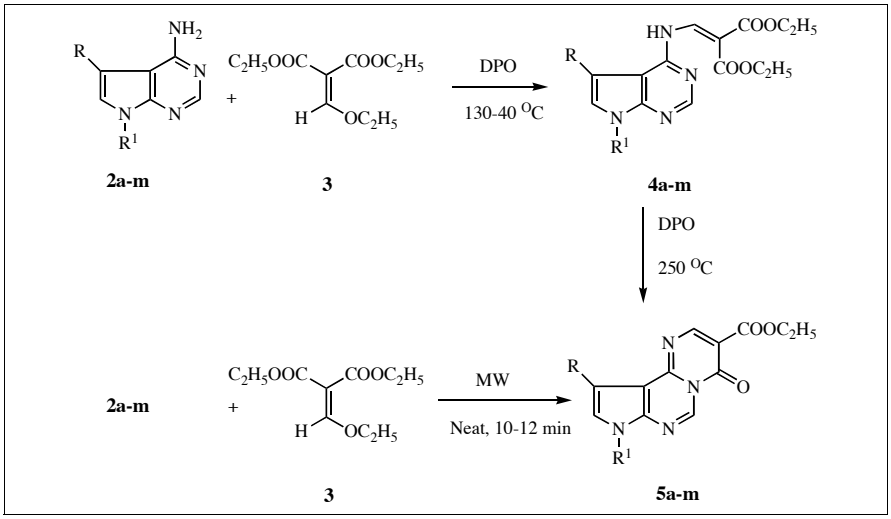
Dedicated to the Memory of Dr. Chaitanya G. Dave



The Gould-Jacob type of reaction for the synthesis of ethyl 4-oxo-8,10-substituted-4,8-dihydropyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylates **5** has been carried out conventionally by the condensation between 4-aminopyrrolo[2,3-*d*]pyrimidines **2** and diethyl ethoxymethylenemalonate **3** *via* acyclic intermediates diethyl *N*-[5,7-substituted-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-*yl*]aminomethylenemalonates **4** and the results obtained were compared with single step microwave irradiation under solvent free conditions for the synthesis of **5**.

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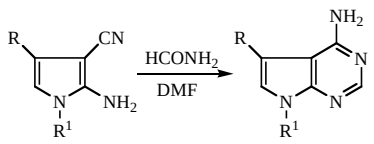
Introduction.

Diethyl ethoxymethylenemalonate (EMME) has been employed frequently in Gould-Jacob reaction for the synthesis of quinoline derivatives [1]. Many heterocyclic systems such as 1,8-naphthyridines, 2*H*-pyrido[1,2-*a*]pyrimidin-4-ones, pyrazolinones, pyrons, xanthyrones, guanidine derivatives, 1,2,4-triazoles, 3-oxo-1,2,6-thiadiazines, 8-oxoimidazo[1,2-*a*]pyrimidines, 3*H*-pyrrolo[1,2-*a*]indol-3-one derivatives and 1*H*-1,4-benzodiazepines have been obtained using EMME as synthon [2]. EMME is widely used in push-pull alkane [3], 1,4-addition elimination [4], 1,4 addition [5], [3+2] cyclo-additions [6], Diels-Alder reactions [8] and extensively reviewed as Michael reagent [7]. Dave *et al* [9,10] reported a novel route for the synthesis of pyrido[3,2-*e*]pyrimido[1,2-*c*]pyrimidines and thieno[3,2-*e*]pyrimido[1,2-*c*]pyrimidines using the same synthon. Microwave accelerated organic synthesis is an effective and an alternative route proposed during the last decade due to drastic reduction in the reaction time, to minimize cumbersome work-up and better yields [11-14]. Organic synthesis under solvent free conditions is of great relevance because of emerging environmental issues [15]. The solvent-free reactions [16-18] under microwave conditions are especially appealing for providing an environmentally benign system. So far no attention has been given towards the synthesis of angular triheterocyclic pyrimidopyrrolopyrimidine using EMME as a synthon. Therefore in continuation of our interest [19] in fused triheterocyclic systems, we report herein Gould-Jacob type of reaction for the synthesis of novel pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidines **5** using conventional as well as microwave methodologies and comparative study of both the methods have been carried out.

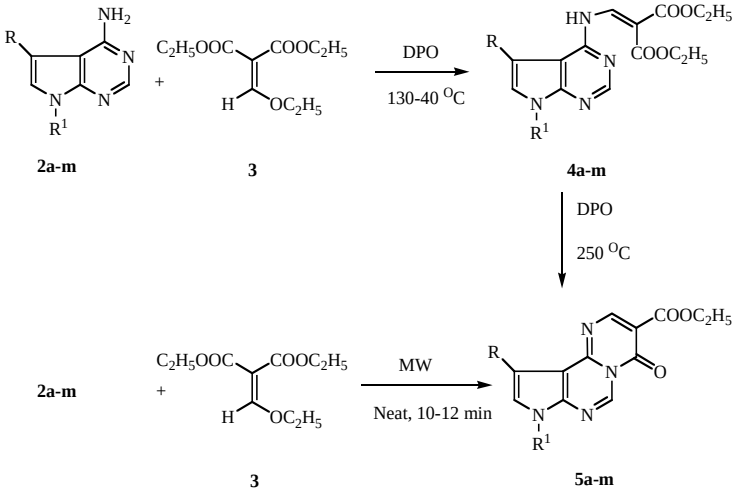
Cyclocondensation of 2-amino-4,5-substituted-1*H*-pyrrole-3-carbonitriles [20-22] **1** with formamide afforded the building blocks 4-amino-5,7-substituted-7*H*-pyrrolo[2,3-*d*]pyrimidine [21,22] **2** required for the synthesis of pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidines **5** (Scheme-1).

Scheme 1



In two step conventional method 4-aminopyrrolo[2,3-*d*]pyrimidines **2** were condensed with EMME **3** at 130-140 °C for 3.5-4.5 hours to obtain diethyl *N*-[5,7-substituted-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-*yl*]aminomethylenemalonates **4**, which on thermal cyclization in boiling diphenyl oxide at 250 °C for 2-3 hours provided ethyl 4-oxo-8,10-substituted-4,8-dihydropyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylates **5** in 50-65 % overall yields from 4-

Scheme 2



Compound **4** ,**5** (**a**-**m**)	R	R^1
a	C_6H_5	C_6H_5
b	C_6H_5	4-$OCH_3C_6H_4$
c	C_6H_5	4-FC_6H_4
d	C_6H_5	4-ClC_6H_4
e	C_6H_5	3-Cl-4-FC_6H_3
f	4-$OCH_3C_6H_4$	C_6H_5
g	4-$OCH_3C_6H_4$	4-$OCH_3C_6H_4$
h	4-$OCH_3C_6H_4$	4-FC_6H_4
i	4-$OCH_3C_6H_4$	3-Cl-4-FC_6H_3
j	4-Cl C_6H_4	C_6H_5
k	4-Cl C_6H_4	4-FC_6H_4
l	4-Cl C_6H_4	4-ClC_6H_4
m	4-Cl C_6H_4	3-Cl-4-FC_6H_3

Table 1

A comparison between conventional and microwave assisted synthesis of pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidines **5**.

Compound No.	Conventional (Method A) Time[c] Hours	Yield[d] %	Microwave[e] (Method B) Time[c] Minutes	Yield[d] %	Melting point °C
5a	5	60	10	68	168-70
5b	5.5	63	12	64	183-85
5c	6	65	11	69	198-200
5d	5	57	12	66	240-42
5e	5.5	62	11.5	69	225-27
5f	6	64	12	75	202-04
5g	5.5	57	10.5	65	186-88
5h	5	55	11	74	193-95
5i	5	60	10	68	245-47
5j	6	61	12	72	248-50
5k	5	65	10.5	76	213-15
5l	5.5	54	10	70	220-22
5m	5	62	12	65	240-42

[c] = overall time on the basis of two steps, [d] = overall yields on the basis of starting compound **2**; [e] = microwave irradiation was carried out in a domestic microwave oven (BPL, BMO 700T).

aminopyrrolo[2,3-*d*]pyrimidines **2** (Method A). On the other hand, single step microwave assisted reaction of **2** with EMME **3** without solvent (Method B) provided identical compound **5** within 10-12 min in 65-75 % overall yields (Scheme 2). Thus microwave assisted synthesis of pyrimidopyrrolopyrimidines **5** has remarkable advantages over the conventional techniques because of easier workup, better yields, rapid and solvent free cleaner reactions. The comparison between conventional and microwave methodologies has been shown in Table 1.

IR (KBr) spectra of **4** exhibited a characteristic band for NH in the region 3280-3260 cm^{-1} along with two sharp absorption around 1720-1668 cm^{-1} due to carbonyl groups of two ester functionalities and the C=C and C=N vibrations were found at 1608-1500 cm^{-1}. The absence of amino vibrations in the region 3500-3400 cm^{-1} and the presence of absorption near 3256-3250 cm^{-1} due to NH suggested the formation of acyclic intermediate **4**. ^1H NMR ($CDCl_3$) of **4** exhibited a doublet at δ 10.78-11.28 integrating for 1H because of the NH proton, a doublet for vinyl proton in the area δ 9.29-9.67 and singlet at δ 8.60-8.78 due to pyrimidine ring proton were found to be present. Twin triplet and quartet in the region δ 1.23-1.42 and δ 4.08-4.31 integrating for 3H and 2H respectively were responsible for two ethyl groups present in malonates **4**. The absence of a band due to NH group in the area 3256-3250 cm^{-1} in IR (KBr) spectra supported the formation of angular pyrimidopyrrolopyrimidines **5**. Absorption at 1744-1724 cm^{-1} appeared due to an ester carbonyl group whereas absorption due to lactone was found to be shifted 20-30 cm^{-1} higher wave number as compared to ketones of acyclic malonates producing a sharp band in the region 1704-1692 cm^{-1}. The presence of triplet at δ 1.36-1.51 (3H) and quartet at δ 4.36-4.46 (2H) in the ^1H NMR (DMSO-d_6) spectra of **5** indicated a single ethyl group, where as pyrimidine protons at C2 and C6 were appeared as singlet at δ 8.81-9.11 and 9.75-9.81 each integrating for one proton. While pyrrole ring proton at C9 was merged in aromatic region δ 6.98-7.71. The mass spectrum of ethyl 8-(3-chloro-4-fluorophenyl)-10-(4-methoxyphenyl)-4-oxo-4,8-dihydro-pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylate **5i** exhibited a characteristic molecular ion peak at m/e 492. The fragment ion (M–$COOC_2H_5$) was obtained at m/e = 419.

In conclusion, we have developed a simple, fast, solvent-free and high yielding method for the synthesis of novel pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidines.

Table 2

Physical and Analytical Data of Compounds **4a-4m**

Compound No.	Reaction time (hours)	Yield %	mp °C Crystallization Solvent	Molecular Formula/ Molecular weight	Analysis % Calcd / Found C	H	N
4a	3	63	120-22 [a]	$C_{26}H_{24}N_4O_4$ 456.49	68.41 68.20	5.30 5.12	12.27 12.49
4b	3.5	68	153-55 [a]	$C_{27}H_{26}N_4O_5$ 486.52	66.65 66.41	5.39 5.25	11.52 11.22
4c	4	60	128-30 [a]	$C_{26}H_{23}FN_4O_4$ 474.48	65.81 65.44	4.89 5.02	11.81 11.77
4d	4.5	65	171-73 [a]	$C_{26}H_{23}ClN_4O_4$ 490.94	63.61 63.38	4.72 4.36	11.41 11.32
4e	5	73	158-60 [a]	$C_{26}H_{22}ClFN_4O_4$ 508.93	61.36 61.30	4.36 4.32	11.01 10.91
4f	5	52	138-40 [a]	$C_{27}H_{26}N_4O_5$ 486.52	66.65 66.53	5.39 5.11	11.52 11.61
4g	4	70	155-57 [a]	$C_{28}H_{28}N_4O_6$ 516.55	65.11 65.43	5.46 5.11	10.85 10.61
4h	4	61	143-45 [a]	$C_{27}H_{25}FN_4O_5$ 504.51	64.28 64.41	4.99 4.62	11.11 10.93
4i	3.5	67	165-67 [a]	$C_{27}H_{24}ClFN_4O_5$ 538.95	60.17 59.96	4.49 4.72	10.40 10.69
4j	3	69	135-37 [a]	$C_{26}H_{23}ClN_4O_4$ 490.94	63.61 63.45	4.72 4.48	11.41 11.36
4k	4	68	163-65 [a]	$C_{26}H_{22}ClFN_4O_4$ 508.93	61.36 61.64	4.36 4.61	11.01 11.30
4l	3	70	202-04 [a]	$C_{26}H_{22}Cl_2N_4O_4$ 525.38	59.44 59.10	4.22 4.47	10.66 10.39
4m	4	75	210-12 [a]	$C_{26}H_{21}Cl_2FN_4O_4$ 543.37	57.47 57.22	3.90 3.62	10.31 10.09

[a] = chloroform$^+$.

Table 2 (continued)

Physical and Analytical Data of Compounds **5a-5m**

Compound No.	Reaction time (hours)	Yield %	mp °C Crystallization Solvent	Molecular Formula/ Molecular weight	Analysis % Calcd / Found C	H	N
5a	5	60	168-70 [b]	$C_{24}H_{18}N_4O_3$ 410.42	70.23 70.42	4.42 4.12	13.65 13.89
5b	5.5	63	183-85 [b]	$C_{25}H_{20}N_4O_4$ 440.45	68.17 68.44	4.58 4.69	12.72 12.49
5c	6	65	198-200 [b]	$C_{24}H_{17}FN_4O_3$ 428.42	67.28 67.53	4.00 3.73	13.08 12.88
5d	5	57	240-42 [b]	$C_{24}H_{17}ClN_4O_3$ 444.87	64.80 64.88	3.85 4.08	12.59 12.31
5e	5.5	62	225-27 [b]	$C_{24}H_{16}ClFN_4O_3$ 462.86	62.28 62.04	3.48 3.39	12.10 11.88
5f	6	64	202-04 [b]	$C_{25}H_{20}N_4O_4$ 440.45	68.17 68.39	4.58 4.22	12.72 12.64
5g	5.5	57	186-88 [b]	$C_{26}H_{22}N_4O_5$ 470.48	66.37 66.62	4.71 4.44	11.91 12.10
5h	5	55	193-95 [b]	$C_{25}H_{19}FN_4O_4$ 458.44	65.50 65.41	4.18 4.33	12.22 12.49
5i	5	60	245-47 [b]	$C_{25}H_{18}ClFN_4O_4$ 492.89	60.92 60.75	3.68 3.89	11.37 11.02
5j	6	61	248-50 [b]	$C_{24}H_{17}ClN_4O_3$ 444.87	64.80 64.63	3.85 3.62	12.59 12.71
5k	5	65	213-15 [b]	$C_{24}H_{16}ClFN_4O_3$ 462.68	62.28 62.48	3.48 3.65	12.10 11.98
5l	5.5	54	220-22 [b]	$C_{24}H_{16}Cl_2N_4O_3$ 479.31	60.14 60.31	3.36 3.11	11.69 11.48
5m	5	62	240-42 [b]	$C_{24}H_{15}Cl_2FN_4O_3$ 497.31	57.96 59.63	3.04 3.39	11.27 10.97

[b] = *N*,*N*-dimethylformamide:ethanol (6:4 v\v).

EXPERIMENTAL

Melting points were determined by electro thermal method in open capillary tube and are uncorrected. The IR spectra were recorded in cm^{-1} for KBr pellets on Buck scientific spectrophotometer. The ^1H NMR spectra were recorded on Varian 400 MHz spectrophotometer in deuteriodimethyl sulfoxide or deuteriochloroform using TMS as internal standard and the chemical shifts are expressed in ppm. MS spectra were recorded on LKB 9000 mass spectrophotometer. Microwave irradiation was carried out in domestic BPL microwave oven, Model BMO 700T (2450 MHz, 700 W). The purity of the compounds was routinely checked by TLC using silica gel G and spots were exposed in iodine vapour.

General Procedure for the synthesis of Ethyl 4-oxo-8,10-substituted-4,8-dihydropyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylates **5a**-**5m**.

Two Step Conventional Method A.

Step 1: Synthesis of Diethyl *N*-[5,7-substituted-7*H*-pyrrolo[2,3-*d*]-pyrimidin-4-*yl*]aminomethylenemalonates **4a**-**4m**.

A mixture of 4-amino-5,7-substituted-7*H*-pyrrolo[2,3-*d*]pyrimidine [21,22] **2** (0.01 mol), EMME **3** (2.16 g 0.01 mol) and diphenyl oxide (5 ml) was heated at 130-140 °C for 3.5 to 4.0 hours, and the alcohol generated from the reaction mixture was allowed to escape. The reaction mixture was then cooled and diluted with *n*-hexane (25 ml). The precipitates thus formed were filtered, washed with cold methanol, dried and crystallized (Table 2).

Step 2: Synthesis of Ethyl 4-oxo-8,10-substituted-4,8-dihydro-pyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylates **5a**-**5m**.

Diethyl *N*-[5,7-substituted-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-*yl*]-aminomethylenemalonate **4** (1.0 g) was dissolved in boiling diphenyl oxide (5 ml) and heated at 250 °C for 1.5-2.0 hours. The excess of solvent distilled *in vacuo* and methanol (15 ml) was added to the cooled reaction mixture, the solid obtained was collected by filtration and crystallized (Table 2).

Microwave Assisted Method B.

Single Step Synthesis of Ethyl 4-oxo-8,10-substituted-4,8-dihydropyrimido[1,2-*c*]pyrrolo[3,2-*e*]pyrimidine-3-carboxylates **5a**-**5m**.

A neat mixture of 4-amino-5,7-substituted-7*H*-pyrrolo[2,3-*d*]-pyrimidine **2** (0.01 mole) and diethyl ethoxymethylenemalonate **3** (2.16 g 0.01 mole) was taken in an open Pyrex tube and subjected to microwave irradiation in a domestic microwave oven (BPL, BMO 700T) at an output of about 700 watts for specified time mentioned in (Table 1). Progress of reaction was monitored through TLC at an interval of 45 seconds. On completion, the reaction mixture was allowed to cool at room temperature and the solid obtained was crystallized from *N*,*N*-dimethylformamide:ethanol (6:4 v/v). The products thus obtained were identical with products formed by method A which were confirmed on the basis of TLC, mp, elemental and spectral analysis. The yields and melting points are given in (Table 1).

Table 3

IR and ^{1}H NMR Spectral Data for Compounds **4a**-**4m**

Compound No.	IR (KBr) cm^{-1}	^{1}H NMR ($CDCl_3$ / TMS) (δ ppm)
4a	3270,1696,1668,1600,1510	1.25-1.36 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 4.09-4.29 (two q, 4H, OCH_2CH_3, J = 7.14 Hz), 7.26-7.87(m, 11H, Ar-H), 8.65 (s, 1H, H at C_2), 9.31-9.34 (d, 1H, =CH, J = 12.24 Hz), 10.80-10.83 (d, 1H, NH, J = 12.2 Hz)
4b	3270,1712,1672,1624,1520	1.26-1.37 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 3.89 (s, 3H, OCH_3), 4.11-4.31 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.22-7.91 (m, 10H, Ar-H), 8.72 (s, 1H, H at C_2), 9.32-9.35 (d, 1H, =CH, J = 12.16 Hz), 10.81-10.84 (d, 1H, NH, J = 12 Hz)
4c	3280,1724,1678,1612,1512	1.24-1.35 (two t, 6H, OCH_2CH_3, J = 7.08 Hz), 4.12-4.32 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.26-7.99 (m, 10H, Ar-H), 8.68 (s, 1H, H at C_2), 9.33-9.36 (d, 1H, =CH, J = 12.12 Hz), 10.83-10.86 (d, 1H, NH, J = 12 Hz)
4d	3270,1716,1668,1616,1512	1.26-1.37 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 4.10-4.30 (two q, 4H, OCH_2CH_3, J = 7.16 Hz), 7.20-7.88 (m, 10H, Ar-H), 8.69 (s, 1H, H at C_2), 9.32-9.35 (d, 1H, =CH, J = 12.16 Hz), 10.82-10.85 (d, 1H, NH, J = 12.08 Hz)
4e	3270,1708,1668,1612,1508	1.23-1.34 (two t, 6H, OCH_2CH_3, J = 7.08 Hz), 4.09-4.29 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.21-7.90 (m, 9H, Ar-H), 8.71(s, 1H, H at C_2), 9.31-9.34 (d, 1H, =CH, J = 12.12 Hz), 10.81-10.84 (d, 1H, NH, J = 12 Hz)
4f	3280,1712,1672,1612,1504	1.26-1.37 (two t, 6H, OCH_2CH_3, J = 7.0 Hz), 3.89 (s, 3H, OCH_3), 4.10-4.30 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.21-7.93 (m, 10H, Ar-H), 8.71 (s, 1H, H at C_2), 9.31-9.34 (d,1H, =CH, J = 12.24 Hz), 10.82-10.85 (d, 1H, NH, J = 12.16 Hz)
4g	3270,1714,1672,1612,1504	1.23-1.34 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 3.91 (s, 6H, OCH_3), 4.09-4.29 (two q, 4H, OCH_2CH_3, J = 7.16 Hz), 7.23-7.89 (m, 9H, Ar-H), 8.68 (s, 1H, H at C_2), 9.32-9.35 (d, 1H, =CH, J = 12.24 Hz), 10.81-10.84 (d, 1H, NH, J = 12.12 Hz)
4h	3280,1716,1668,1616,1516	1.26-1.37 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 3.93 (s, 3H, OCH_3), 4.11-4.31 (two q, 4H, OCH_2CH_3, J = 7.08 Hz), 7.21-7.84 (m, 9H, Ar-H), 8.71 (s, 1H, H at C_2), 9.31-9.34 (d, 1H, =CH, J = 12.08 Hz), 10.82-10.85 (d, 1H, NH, J = 12 Hz)
4i	3260,1700,1670,1618,1524	1.24-1.35 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 3.90 (s, 3H, OCH_3), 4.08-4.28 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.20-7.95 (m, 8H, Ar-H), 8.69(s, 1H, H at C_2), 9.30-9.33 (d, 1H, =CH, J = 12.24 Hz), 10.80-10.83 (d, 1H, NH, J = 12.12 Hz)
4j	3270,1716,1664,1600,1506	1.27-1.38 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 4.10-4.30 (two q, 4H, OCH_2CH_3, J = 7.08 Hz), 7.19-7.81 (m, 10H, Ar-H), 8.67 (s, 1H, H at C_2), 9.31-9.34 (d, 1H, =CH, J = 12.16 Hz), 10.82-10.85 (d, 1H, NH, J = 12.08 Hz)
4k	3260,1718,1668,1610,1512	1.25-1.36 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 4.11-4.31 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.24-7.96 (m, 9H, Ar-H), 8.71 (s, 1H, H at C_2), 9.29-9.32 (d, 1H, =CH, J = 12.20 Hz), 10.80-10.85 (d, 1H, NH, J = 12.08 Hz)
4l	3270,1712,1664,1612,1516	1.24-1.35 (two t, 6H, OCH_2CH_3, J = 7.08 Hz), 4.08-4.28 (two q, 4H, OCH_2CH_3, J = 7.12 Hz), 7.26-7.90 (m, 9H, Ar-H), 8.69 (s, 1H, H at C_2), 9.30-9.33 (d, 1H, =CH, J = 12.24 Hz), 10.79-10.82(d, 1H, NH, J = 12.08 Hz)
4m	3260,1720,1686, 1600,1524	1.23-1.34 (two t, 6H, OCH_2CH_3, J = 7.12 Hz), 4.11-4.31 (two q, 4H, OCH_2CH_3, J = 7.16 Hz), 7.20-7.79 (m, 8H, Ar-H), 8.69 (s, 1H, H at C_2), 9.32-9.35 (d, 1H, =CH, J = 12.20 Hz), 10.81-10.84 (d, 1H, NH, J = 12 Hz)

Table 3 (continued)

IR and ^{1}H NMR Spectral Data for Compounds **5a**-**5m**

Compound No.	IR (KBr) cm^{-1}	^{1}H NMR (DMSO-d_6 / TMS) (δ ppm)
5a	1740,1692,1600,1500	1.39-1.42 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 4.38-4.43 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.06-7.60 (m, 11H, Ar-H), 8.99 (s, 1H, H at C_2), 9.77 (s, 1H, H at C_6)
5b	1740,1702,1592,1520	1.38-1.41 (t, 3H, OCH_2CH_3, J = 7.08 Hz), 3.91 (s, 3H, OCH_3), 4.39-4.44 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.02-7.64 (m, 10H, Ar-H), 9.01 (s, 1H, H at C_2), 9.76 (s, 1H, H at C_6)
5c	1740,1704,1604,1516	1.37-1.40 (t, 3H, OCH_2CH_3, J = 7.16 Hz), 4.38-4.43 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.01-7.65 (m, 10H, Ar-H), 9.01 (s, 1H, H at C_2), 9.75 (s, 1H, H at C_6)
5d	1736,1700,1600,1512	1.39-1.42 (t, 3H, OCH_2CH_3, J = 7.08 Hz), 4.37-4.42 (q, 2H, OCH_2CH_3, J = 7.08 Hz), 7.02-7.69 (m, 10H, Ar-H), 9.03 (s, 1H, H at C_2), 9.76 (s, 1H, H at C_6)
5e	1740,1704,1610,1500	1.36-1.39 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 4.38-4.43 (q, 2H, OCH_2CH_3, J = 7.16 Hz), 7.01-7.67 (m, 9H, Ar-H), 9.01 (s, 1H, H at C_2), 9.78 (s, 1H, H at C_6)
5f	1740,1704,1596,1508	1.37-1.40 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 3.89 (s, 3H, OCH_3), 4.39-4.44(q, 2H, CH_2CH_3, J = 7.12 Hz), 7.01-7.67 (m, 10H, Ar-H), 9.02 (s, 1H, H at C_2), 9.76 (s, 1H, H at C_6)
5g	1740,1692,1604,1510	1.39-1.42 (t, 3H, OCH_2CH_3, J = 7.08 Hz), 3.89(s, 6H, OCH_3), 4.37-4.42 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.01-7.67 (m, 9H, Ar-H), 9.02 (s, 1H, H at C_2), 9.76 (s, 1H, H at C_6)

Table 3 (continued)

Compound No.	IR (KBr) cm^{-1}	^1H NMR (DMSO-d_6 / TMS) (δ ppm)
5h	1736,1700,1616,1512	1.37-1.40 (t, 3H, OCH_2CH_3, J = 7.16 Hz), 3.90 (s, 3H, OCH_3), 4.36-4.41 (q, 2H, OCH_2CH_3, J = 7.16 Hz), 7.07-7.63 (m, 9H, Ar-H), 9.01 (s, 1H, H at C_2), 9.78 (s, 1H, H at C_6)
5i	1740,1692,1604,1520	1.38-1.41 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 3.92 (s, 3H, OCH_3), 4.39-4.44 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 6.99-7.61 (m, 8H, Ar-H), 9.04 (s, 1H, H at C_2), 9.77 (s, 1H, H at C_6)
5j	1736,1696,1600,1508	1.36-1.39 (t, 3H, OCH_2CH_3, J = 7.08 Hz), 4.38-4.43 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.01-7.67 (m, 10H, Ar-H), 9.01(s, 1H, H at C_2), 9.78 (s, 1H, H at C_6)
5k	1740,1696,1608,1504	1.39-1.42 (t, 3H, OCH_2CH_3, J = 7.04 Hz), 4.37-4.42 (q, 2H, OCH_2CH_3, J = 7.08 Hz), 7.05-7.61 (m, 9H, Ar-H), 9.02 (s, 1H, H at C_2), 9.74 (s, 1H, H at C_6)
5l	1744,1700,1610,1512	1.36-1.39 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 4.38-4.43 (q, 2H, OCH_2CH_3, J = 7.12 Hz), 7.03-7.60 (m, 9H, Ar-H), 9.05 (s, 1H, H at C_2), 9.72 (s, 1H, H at C_6)
5m	1736,1696,1604,1508	1.38-1.41 (t, 3H, OCH_2CH_3, J = 7.12 Hz), 4.36-4.41 (q, 2H, OCH_2CH_3, J = 7.16 Hz), 7.03-7.60 (m, 8H, Ar-H), 8.99(s, 1H, H at C_2), 9.74 (s, 1H, H at C_6)

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REFRENCES AND NOTES

[+] Caution: May be irritating to eyes, skin and respiratory tract. Storing: Keep in a tightly closed light-resistant container, stored in a cool, dry, ventilated area. Other Precautions: Do not expose to open flames or hot surface it may result in to toxic fumes of chlorides, carbon monoxide and phosgene in fire.

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