# An Efficient Synthesis of 1-*H*-Pyrazole-4-Carboxylic Acid Esters With Vilsmeier Reagent Under Neat Conditions



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Received July 22, 2003

A convenient, solvent-free Vilsmeier reagent is experimented under neat condition (both thermal and microwave conditions). An efficient method for the synthesis of various substituted 1*H*-pyrazole-4-carboxylic acid esters is reported.

*J. Heterocyclic Chem.*, **41**, 405 (2004).

## Introduction.

Aldehyde synthesis employing a formylating agent derived from a formamide, most commonly DMF and $POCl_3$ has come to be known as 'the Vilsmeier aldehyde synthesis' or 'the Vilsmeier-Haack formylation' [1,2]. It is a versatile method both in the introduction of a formyl group [3] and in the synthesis of various cyclised products [4] by the addition of chloromethyleneiminium salt. Solvents used [5] in Vilsmeier reaction include $CHCl_3$, $CH_2Cl_2$, benzene, toluene, *o*-dichlorobenzene, dioxane and THF. In case of liquid amides like DMF, dimethyl acetamide, *N*-methyl pyrrolidone, an excess of the amide is employed to act as solvent. Excess $POCl_3$ is also employed as solvent in cases where the amide taken is in quantitative amounts. Recently solvent-free solid supported Vilsmeier reaction using microwaves has been reported [6,7]. However, it is observed that the Vilsmeier reaction under neat condition has not been attempted so far.

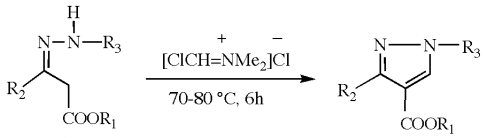
In continuation of our work on the synthesis of pyrazoles [7] through the application of Vilsmeier reagent on solid support we herein report a novel solvent-free application of Vilsmeier reagent under neat conditions. Though solid supported Vilsmeier reactions are novel, the recyclability and disposability of the solid support in these reactions are questionable. Aforementioned novel neat reaction method overcomes these difficulties in using the solid support.

## Results and Discussion.

Kira *et al* have reported the synthesis of 1*H*-pyrazoles from hydrazones [8a], and semicarbazones [8b] of acetophenone upon treatment with $POCl_3$ and DMF. Herein we report the reaction of hydrazones of β-keto esters with six equivalents of the chloromethylenedimethylammonium chloride under neat conditions to target pyrazoles in excellent yield (Scheme 1). Also we have made a comparison between the above-mentioned neat method and the reaction of hydrazones of β-keto esters with DMF and $POCl_3$.

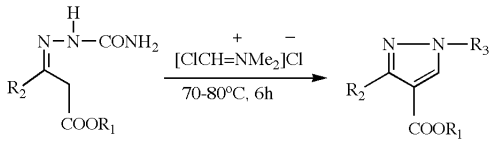
When semicarbazones of β-keto esters were reacted with Vilsmeier reagent, 1*H*-pyrazole-4-carboxylates unsubstituted at 1-position were obtained (Scheme 2).

Scheme 1




Where $R_1 = CH_3$, $C_2H_5$, $CH_2C_6H_5$, $C(CH_3)_3$
$R_2 = CH_3$, n-$C_3H_7$, $C_6H_5$, *p*-$ClC_6H_4$, *o*-$FC_6H_4$, $ClCH_2$
$R_3 = C_6H_3(NO_2)_2$

Scheme 2



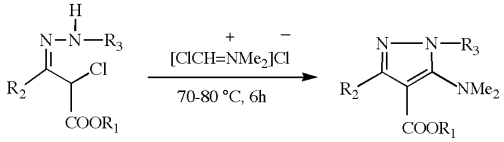

Where $R_1 = CH_3$, $C_2H_5$, $R_2 = CH_3$, n-$C_3H_7$, $R_3 = H$

The acidity of the active methylene protons in the hydrazones or semicarbazones of β-keto esters eases the cyclization and thereby facilitating the formation of pyrazoles after adding to the Vilsmeier reagent.

In order to study the effect of an electronegative chlorine atom on the acidity of the active methylene proton and to substitute the 5-position of the pyrazole moiety, the hydrazone of ethyl 2-chloroacetoacetate was subjected to similar reaction conditions. 5-Substituted 1*H*-pyrazole was obtained after cyclisation followed by the loss of one HCl molecule (Scheme 3).

Various substituted 1*H*-pyrazole-4-carboxylic acid esters have been prepared and characterized (Table 1).

Scheme 3




Where $R_1 = C_2H_5$, $R_2 = CH_3$, $R_3$ = 2,4-dinitrophenyl

Table 1

Synthesis of 1*H*-Pyrazole-4-carboxylic Acid Esters: Comparison Between Conventional Heating and Microwave-assisted Methods Under Neat Condition

| Entry | $R_1$ | $R_2$ | $R_3$ | Mp (°C) [b] | Conventional heating method | | | Microwave-assisted method | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Time (hrs) | Yield [a] % [c] | % [d] | Time (min) | Yield [a] % |
| **2a** | $CH_3$ | $CH_3$ | $C_6H_3(NO_2)_2$ | 114 | 6 | 84 | 78 | 5 | 86 |
| **2b** | $C_2H_5$ | $CH_3$ | $C_6H_3(NO_2)_2$ | 122 | 6 | 82 | 80 | 5 | 85 |
| **2c** | $CH_2C_6H_5$ | $CH_3$ | $C_6H_3(NO_2)_2$ | 140 | 6 | 88 | 84 | 5 | 88 |
| **2d** | $C(CH_3)_3$ | $CH_3$ | $C_6H_3(NO_2)_2$ | 125 | 6 | 85 | 81 | 5 | 87 |
| **2e** | $C_2H_5$ | $ClCH_2$ | $C_6H_3(NO_2)_2$ | 96 | 6 | 88 | 84 | 5 | 87 |
| **2f** | $CH_3$ | *n*-$C_3H_7$ | $C_6H_3(NO_2)_2$ | 133 | 6 | 84 | 79 | 5 | 86 |
| **2g** | $C_2H_5$ | $C_6H_5$ | $C_6H_3(NO_2)_2$ | 138 | 6 | 85 | 83 | 5 | 86 |
| **2h** | $C_2H_5$ | *p*-Cl $C_6H_4$ | $C_6H_3(NO_2)_2$ | 169 | 6 | 90 | 88 | 5 | 92 |
| **2i** | $C_2H_5$ | *o*-F $C_6H_4$ | $C_6H_3(NO_2)_2$ | 128 | 6 | 85 | 84 | 5 | 87 |
| **2j** | $C_2H_5$ | $CH_3$ | H | 80 | 6 | 86 | 81 | 5 | 89 |
| **2k** | $CH_3$ | n-$C_3H_7$ | H | 97 | 6 | 82 | 75 | 5 | 84 |
| **4l** | $C_2H_5$ | $CH_3$ | $C_6H_3(NO_2)_2$ | 107 | 6 | 87 | 78 | 5 | 88 |

[a] Isolated yields after column chromatography; [b] All the products were characterised by $^1H$ and $^{13}C$ NMR, Mass spectral and elemental analysis data; [c] Yield obtained in the neat method; [d] Yield obtained in the method with solvent (DMF).

Substrate to reagent ratio needs to be 1:6 for obtaining maximum yield. For attaining homogeneity of the reaction mixture, the reagent dissolved in $CH_2Cl_2$ was added to the substrate at 0-5 °C. After 15 min vacuum was applied to this mixture to remove the solvent. Then the reaction vessel is maintained at 50 °C in an oil bath and again connected to vacuum for 20 min to remove traces of DMF present in reagent itself. After drying the reaction mixture the content was maintained at 70-80 °C for about 6h.

The effect of microwave on the reaction yield was also studied by the application of microwave on the reaction mixture after drying the solvent (Table 1). There was no appreciable increase in the yield using microwaves, but there was a considerable reduction in the reaction time. The neat method is not only convenient for the synthesis of 1*H*-pyrazole-4-carboxylates but also the yields obtained through the neat are better in comparison with the usual solution phase method (Table 1).

## Conclusion.

In summary a convenient, solvent-free Vilsmeier reagent under neat condition is reported (both in thermal and microwave conditions) to synthesis various substituted 1*H*-pyrazole-4-carboxylates in comparatively better yields. Proven antibacterial activity [9] of 1*H*-pyrazole-4-carboxylic acids and carboxylates prompted us to synthesize the title compounds through this novel methodology.

## EXPERIMENTAL

The microwave reactions were carried out in a domestic microwave oven. A BPL microwave cooking system, Model BMO-700T, manufactured by BPL-SANYO Utilities and Appliances Ltd.; Bangalore, India was used in the present studies. The overall dimensions of the domestic oven are 525(W) x 419 (D) x 281 (H) mm with a chamber of 350 (W) x 370 (D) x 208 (H) mm. The microwave frequency is 50 Hz and the oven capacity is 26 liters. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany) using 15 % ethyl acetate:petroleum ether solvent system. IR spectra (KBr pellet) were obtained on a Perkin Elmer Spectrum RX I FT-IR. $^1H$ NMR spectra were obtained on a JEOL instrument at 500 MHz or on a Brucker instrument at 300 MHz in $CDCl_3$ and $^{13}C$ NMR spectra were recorded at 125 MHz or at 75 MHz in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded using JEOL DX-303 in EI ionization mode at 70 eV. Commercially available chloromethylenedimethylammonium chloride (Aldrich) was used as such for the synthesis of title compound.

### General Procedure for the Synthesis of 1*H*-Pyrazole-4-carboxylic Acid Esters Under Neat Condition.

To chloromethylenedimethylammonium chloride (6 mmol, Aldrich) dissolved in 10 mL of dichloromethane, substrate (1 mmol) was added at 0 °C. The mixture was stirred for 15 min. Then $CH_2Cl_2$ was removed by applying vacuum at room temperature. Afterwards the residue was heated to 50 °C and again evaporated. This mixture was then kept in an oil bath at 70-80 °C for 6 h or irradiated in microwave for 5 min with a pulse rate of 20 sec. and 40% of power. Then the content was added to cold saturated NaOAc and stirred. Finally the product was extracted with $CHCl_3$ and separated through column chromatography with ethyl acetate: hexane 15:85. All the products were characterized by $^1H$ and $^{13}C$ NMR, Mass spectral and elemental analysis data.

### Methyl 1-(2,4-Dinitrophenyl)-3-methyl-1*H*-pyrazole-4-carboxylate (Entry **2a**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 114 °C; $^1H$ NMR (300 MHz,

$CDCl_3$): δ 8.73 (d, *J* = 2.4 Hz, 1H), 8.55 (dd, *J* = 2.4 Hz, *J* = 8.7 Hz, 1H), 8.21 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H), 2.52 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 162, 154, 146, 143, 137, 134, 128, 126, 121, 115, 52, 13; IR (KBr): $cm^{-1}$ 3090, 1725, 1690, 1546, 1353, 1267; MS: (*m/z*) 306 ($M^+$).

*Anal.* Calcd. for $C_{12}H_{10}N_4O_6$: C, 47.06; H, 3.27; N, 18.30. Found: C, 47.45; H, 3.36; N, 18.51.

Ethyl 1-(2,4-Dinitrophenyl)-3-methyl-1*H*-pyrazole-4-carboxylate (Entry **2b**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 122 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, *J* = 2.4 Hz, 1H), 8.50 (dd, *J* = 2.4 Hz, *J* = 8.7 Hz, 1H), 8.20 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 163, 155, 147, 144, 137, 135, 128, 126, 122, 117, 61, 15, 14; IR (KBr): $cm^{-1}$ 3074, 1722, 1693, 1550, 1349, 1276; MS: (*m/z*) 320 ($M^+$).

*Anal.* Calcd. for $C_{13}H_{12}N_4O_6$: C, 48.75; H, 3.75; N, 17.50. Found: C, 48.82; H, 3.81; N, 17.46.

Benzyl 1-(2,4-Dinitrophenyl)-3-methyl-1*H*-pyrazole-4-carboxylate (Entry **2c**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 140 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ 8.70-8.70 (d, *J*=2.9 Hz, 1H), 8.49-8.52 (d, *J*=2.9, 8.6 Hz, 1H), 8.25 (s, 1H, pyrazole -CH), 7.78-7.80 (d, *J*=8.6 Hz, 1H), 7.33-7.42 (m, 5H), 5.30 (s, 2H), 2.50 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 162, 155, 146, 143, 137, 136, 134, 129, 129, 128, 128, 126, 121, 116, 67, 14; IR (KBr): $cm^{-1}$ 3363, 3088, 2947, 2891, 1691, 1608, 1547, 1510, 1352, 1278, 1121, 745; MS: (*m/z*) 382 ($M^+$).

*Anal.* Calcd. for $C_{18}H_{14}N_4O_6$: C, 56.55; H, 3.69; N, 14.65. Found: C, 56.42; H, 3.76; N, 14.51.

*t*-Butyl 1(2,4-Dinitrophenyl)-3-methyl-1*H*-pyrazole-4-carboxylate (Entry **2d**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 125 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 8.83-8.83 (d, *J*=2.3 Hz, 1H), 8.59-8.61 (dd, *J*=2.3, 9.2 Hz, 1H), 8.21 (s, 1H, pyrazole -CH), 8.15-8.17 (d, *J*=9.2 Hz, 1H), 3.79 (s, 9H, *t*-Butyl), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 163, 153, 146, 143, 136, 135, 128, 127, 121, 115, 51, 30, 13; IR (KBr): $cm^{-1}$ 3100, 3091, 2984, 2900, 1715, 1608, 1548, 1349, 1264, 1106, 836, 780, 739; MS: (*m/z*) 348 ($M^+$).

*Anal.* Calcd. for $C_{15}H_{16}N_4O_6$: C, 51.73; H, 4.63; N, 16.09. Found: C, 51.72; H, 4.70; N, 16.18.

Ethyl 1(2,4-Dinitrophenyl)-3-chloromethyl-1*H*-pyrazole-4-carboxylate (Entry **2e**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 96 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 8.75-8.76 (d, *J*=2.3 Hz, 1H), 8.55-8.58 (dd, *J*=2.3, 8.6 Hz, 1H), 8.29 (s, 1H, pyrazole -CH), 7.87-7.89 (d, *J*=8.6 Hz, 1H), 4.83 (s, 2H, chloromethyl), 4.34-4.38 (q, *J*=6.9, 7.5 Hz, 2H), 1.37-1.39 (t, *J*=6.9, 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 162, 153, 147, 144, 137, 135, 128, 127, 121, 116, 61, 37, 14; IR (KBr): $cm^{-1}$ 3100, 3091, 2984, 2900, 1715, 1608, 1548, 1349, 1264, 1106, 836, 780, 739; MS: (*m/z*) 355 ($M^+$).

*Anal.* Calcd. for $C_{13}H_{11}ClN_4O_6$: C, 44.02; H, 3.13; N, 15.80. Found: C, 44.15; H, 3.18; N, 15.69.

Methyl 1(2,4-Dinitrophenyl)-3-propyl-1*H*-pyrazole-4-carboxylate (Entry **2f**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 133 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ: 8.70-8.70 (d, *J*=2.3 Hz, 1H), 8.51-8.53 (d, *J*=2.3, 8.6 Hz, 1H), 8.23 (s, 1H, pyrazole -CH), 7.80-7.82 (d, *J*=8.6 Hz, 1H), 3.85 (s, 3H), 2.86-2.89 (d, *J*=7.5 Hz, 2H), 1.67-1.74 (sextet, *J*=7.5 Hz, 2H), 0.95-0.98 (t, *J*=7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 163, 159, 146, 144, 137, 134, 128, 126, 121, 116, 52, 29, 22, 14; IR (KBr): $cm^{-1}$ 3326, 3106, 1716, 1699, 1620, 1535, 1340, 1280, 742; MS: (*m/z*) 334 ($M^+$).

*Anal.* Calcd. for $C_{14}H_{14}N_4O_6$: C, 50.29; H, 4.22; N, 16.77. Found: C, 50.35; H, 4.29; N, 16.68.

Ethyl 1-(2,4-Dinitrophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (Entry **2g**).

This compound was obtained as orange crystals (15% ethyl acetate:petroleum ether); mp. 138 °C; $^1$H NMR (200 MHz, $CDCl_3$, ppm): δ 8.72-8.73 (d, *J*=2.2 Hz, 1H), 8.46-8.52 (dd, *J*=2.2, 8.9 Hz, 1H), 8.37 (s, 1H, pyrazole -CH), 7.79 -7.84 (d, *J*=8.9 Hz, 1H), 7.72-7.77 (m, 2H), 7.40-7.44 (m, 3H), 4.26-4.37 (q, *J*=7.0, 7.2 Hz, 2H), 1.29-1.36 (t, *J*=7.0, 7.2 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$, ppm): δ 162, 156, 146, 144, 137, 135, 131, 129, 128, 127, 126, 121, 116, 61, 14; IR (KBr): $cm^{-1}$ 3137, 3098, 2911, 1728, 1606, 1537, 1448, 1280, 832; MS: (*m/z*) 382 ($M^+$).

*Anal.* Calcd. for $C_{18}H_{14}N_4O_6$: C, 56.53; H, 3.69; N, 14.66. Found: C, 56.47; H, 3.66; N, 14.59.

Ethyl 1-(2,4-Dinitrophenyl)-3(4-chlorophenyl)-1*H*-pyrazole-4-carboxylate (Entry **2h**).

This compound was obtained as yellow crystals (15% ethyl acetate:petroleum ether); mp. 169 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 8.77-8.77 (d, *J*=2.3 Hz, 1H), 8.55-8.57 (d, *J*=2.3, 8.9 Hz, 1H), 8.39 (s, 1H,pyrazole -CH), 7.88 -7. 90 (d, *J*=8.9 Hz, 1H), 7.74 -7.76 (d, *J*=8.0 Hz, 2H, p-chlorophenyl), 7.39 -7.41 (d, *J*=8.0 Hz, 2H, p-chlorophenyl), 4.30-4.34 (q, *J*=6.9, 7.4 Hz, 2H), 1.32-1.35 (t, *J*=6.9, 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 162, 155, 146, 144, 137, 136, 135, 131, 129, 128, 128, 126, 121, 116, 61, 14; IR (KBr): $cm^{-1}$ 3136, 3091, 2926, 1691, 1603, 1536, 1349, 1285, 848, 774, 741; MS: (*m/z*) 417 ($M^+$).

*Anal.* Calcd. for $C_{18}H_{13}ClN_4O_6$: C, 51.87; H, 3.14; N, 13.44. Found: C, 51.72; H, 3.10; N, 13.51.

Ethyl 1-(2,4-Dinitrophenyl)-3(2-fluorophenyl)-1*H*-pyrazole-4-carboxylate (Entry **2i**).

This compound was obtained as yellow crystals (15% ethyl acetate:petroleum ether); mp. 128 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 8.74-8.74 (d, *J*=2.3 Hz, 1H), 8.51-8.54 (dd, *J*=2.3, 9.2 Hz, 1H), 8.40 (s, 1H,pyrazole -CH), 7.86-7.88 (d, *J*=9.2 Hz, 1H), 7.45-7.48 (t, *J*=7.45 Hz, 1H, *o*-fluorophenyl), 7.39-7.43 (m, 1H, *o*-fluorophenyl), 7.18-7.22 (t, *J*=7.45 Hz, 1H, *o*-fluorophenyl), 7.10-7.13 (m, 1H, *o*-fluorophenyl), 4.21-4.26 (q, *J*=6.85, 7.45 Hz, 2H), 1.20-1.22 (t, *J*=6.85, 7.45 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 162, 160, 151, 146, 144, 137, 134, 131, 131, 128, 126, 124, 121, 118, 116, 115, 61, 14; IR (KBr): $cm^{-1}$ 3143, 3090, 2992, 2775, 1721, 1608, 1548, 1350, 1294, 1132, 837, 767, 741; MS: (*m/z*) 400 ($M^+$).

*Anal.* Calcd. for $C_{18}H_{13}FN_4O_6$: C, 54.01; H, 3.27; N, 14.00. Found: C, 53.89; H, 3.29; N, 13.88.

Ethyl 3-Methyl-1*H*-pyrazole-4-carboxylate (Entry **2j**).

This compound was obtained as yellow solid (15% ethyl acetate:petroleum ether); mp. 80 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 8.89 (bs, 1H, pyrazole -NH), 7.95 (s, 1H, pyrazole -CH), 4.25-4.35 (q, *J*=6.9, 7.4 Hz, 2H), 2.57 (s, 3H), 1.35-1.37 (t, *J*=6.9, 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 164, 146, 141, 111, 60, 14, 12; MS: (*m/z*) 154 ($M^+$).

*Anal.* Calcd. for $C_7H_{10}N_2O_2$: C, 54.54; H, 6.54; N, 18.17. Found: C, 54.47; H, 6.62; N, 18.05.

Methyl 3-Propyl-1*H*-pyrazole-4-carboxylate (Entry **2k**)**.**

This compound was obtained as yellow solid (15% ethyl acetate:petroleum ether); mp. 97 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ 9.8 (bs, 1H), 8.01 (s, 1H,pyrazole -CH), 3.6 (s, 3H), 2.87-2.88 (d, *J*= 7.5 Hz, 2H), 2.07-2.09 (m, 2H), 1.24-1.26 (t, *J*= 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 163, 148, 135, 128, 62, 38, 30, 14; MS: (*m/z*) 168 ($M^+$).

*Anal.* Calcd. for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.25; H, 7.29; N, 16.78.

Ethyl 1-(2,4-Dinitrophenyl)-3-methyl-5(*N,N*-dimethyl)-1*H*-pyrazole-4-carboxylate (Entry **4l**).

This compound was obtained as pale yellow crystals (15% ethyl acetate:petroleum ether); mp. 107 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ 8.78-8.78 (d, *J* = 2.9 Hz, 1H), 8.53-8.55 (dd, *J* = 2.9 Hz, *J* = 8.6 Hz, 1H), 7.85-7.87 (d, *J* = 8.6 Hz, 1H), 4.31-4.35 (q, *J* = 6.9, 7.5 Hz, 2H), 2.59 (s, 6H), 2,45 (s, 3H), 1.37-1.40 (t, *J* = 6.9, 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163, 155, 154, 146, 144, 136, 129, 128, 121, 107, 60, 41, 15, 15; IR (KBr): $cm^{-1}$ 3098, 2931, 1703, 1609, 1540, 1347, 1262, 1101, 834; MS: (*m/z*) 363 ($M^+$).

*Anal.* Calcd. for $C_{15}H_{17}N_5O_6$: C, 49.59; H, 4.72; N, 19.28. Found: C, 49.72; H, 4.81; N, 19.26.

Acknowledgement.

Authors R. S. and G. S. are thankful to CSIR, New Delhi for the award of Fellowship.

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