An Efficient New Method for the Synthesis of Polysubstituted Pyrroles[1]

Biswanath Das,* Gandolla Chinna Reddy, Penagaluri Balasubramanyam, Boyapati Veeranjaneyulu

Organic Chemistry Division-1, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Fax +91(40)27193198; E-mail: biswanathdas@yahoo.com

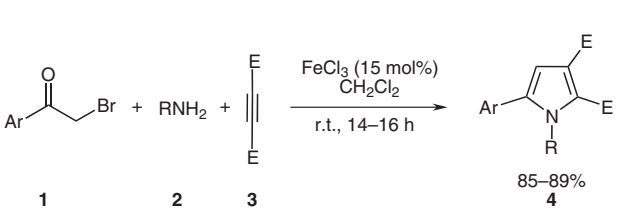
Received 1 February 2010; revised 26 February 2010

Abstract: The three-component reactions of phenacyl bromide or its derivatives, amine, and dialkyl acetylenedicarboxylate in the presence of iron(III) chloride as a catalyst at room temperature afforded polysubstituted pyrroles in high yields.

Key words: polysubstituted pyrroles, three-component reaction, iron(III) chloride

Pyrroles are among the most important heterocyclic compounds as they are structural elements of various bioactive natural products[2] and pharmaceutical agents.[3] They are also valuable intermediates in organic synthesis.[2a,4] Various pyrrole derivatives are widely used as organic conducting materials.[5] Consequently, a wide range of procedures have been devised for the synthesis of pyrroles.[6] However, many of the methods are associated with various drawbacks such as harsh reaction conditions, tedious experimental procedures, unsatisfactory yields, and long reaction times. Moreover, the number of methods for the synthesis of polysubstituted pyrroles is relatively limited. Herein we report an efficient, new method for the synthesis of polysubstituted pyrroles.

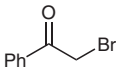
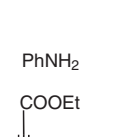
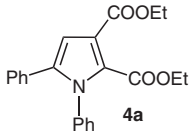
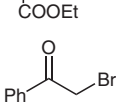
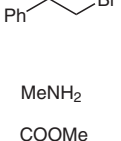
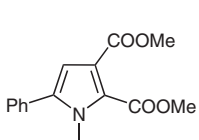
In continuation of our work[7] on the development of useful synthetic methodologies, we have observed that the treatment of phenacyl bromide, or its derivatives, with amine and dialkyl acetylenedicarboxylate in the presence of a catalytic amount of iron(III) chloride produced the corresponding 1,2,3,5-substituted pyrroles at room temperature (Scheme 1).



Scheme 1

Initially phenacyl bromide was treated with aniline and diethyl acetylenedicarboxylate using various catalysts (Table 1). Considering reaction time and yield of the prepared pyrrole **4a**, iron(III) chloride was the most effective catalyst. A similar result was also obtained in the synthesis of **4n** when phenacyl bromide was treated with methylamine and dimethyl acetylenedicarboxylate. Thus, iron(III) chloride was considered to be the catalyst of choice for the subsequent preparation of a series of pyrroles **4a–o** from phenacyl bromide or its derivatives, amine, and dialkyl acetylenedicarboxylate (Table 2). The reaction was complete within 14–16 hours and the products **4a–o** were formed in high yields (84–89%). Both aromatic and aliphatic amines underwent the conversion equally well. The derivatives of phenacyl bromide containing electron-withdrawing groups also afforded the products smoothly. Dimethyl as well as diethyl acetylenedicarboxylate was used to prepare the pyrrole derivatives. The structures of the products were identified by their spectral (IR, ^{1}H and ^{13}C NMR and MS) and analytical data.

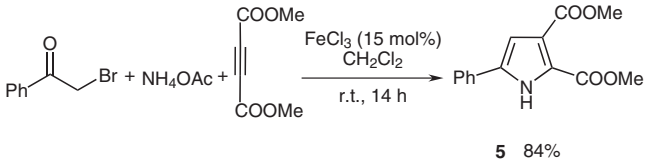
Table 1 Evaluation of Catalytic Activity of Different Catalysts for the Preparation of Polysubstituted Pyrroles **4a**,**n**[a]

Entry	Substrates	Product	Catalyst	Yield[b] (%)
1	 	 **4a**	$FeCl_3$	89
			CuI	63
			$ZnCl_2$	45
			$SnCl_2$	42
			$CeCl_3 \cdot 6\,H_2O$	53
			$ZrCl_4$	78
			I_2	38
			no catalyst	trace
2	 	 **4n**	$FeCl_3$	87
			CuI	63
			$ZnCl_2$	41
			$SnCl_2$	39
			$CeCl_3 \cdot 6\,H_2O$	51
			$ZrCl_4$	75
			I_2	31
			no catalyst	trace

[a] Reaction conditions: phenacyl bromide (1.0 mmol), amine (1.0 mmol), diethyl or dimethyl acetylenedicarboxylate (1.0 mmol), catalyst (15 mol%), r.t.
[b] Yield of pure isolated product after column chromatography.

Treatment of phenacyl bromide with ammonium acetate and dimethyl acetylenedicarboxylate under these reaction conditions gave the trisubstituted pyrrole **5** (Scheme 2).

SYNTHESIS 2010, No. 10, pp 1625–1628
Advanced online publication: 15.03.2010
DOI: 10.1055/s-0029-1218703; Art ID: Z02110SS



Scheme 2

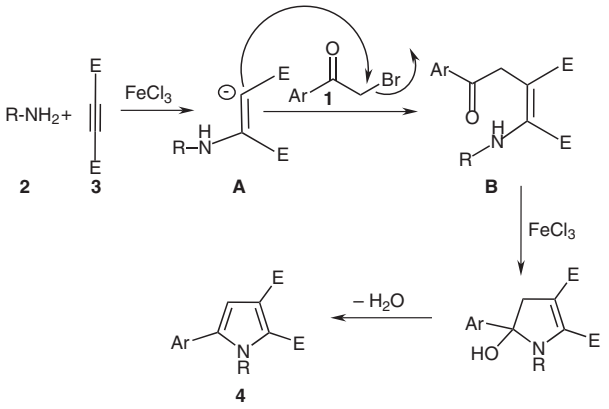
Table 2 Synthesis of Polysubstituted Pyrroles **4a–o** Using Iron(III) Chloride[a]

Entry	Product	Ar	R	E	Time (h)	Yield[b] (%)
1	**4a**	Ph	Ph	CO_2Et	14	89
2	**4b**	Ph	Ph	CO_2Me	14	89
3	**4c**	4-BrC_6H_4	Ph	CO_2Et	15	86
4	**4d**	4-BrC_6H_4	Ph	CO_2Me	15	86
5	**4e**	4-$O_2NC_6H_4$	Ph	CO_2Et	15	85
6	**4f**	4-$O_2NC_6H_4$	Ph	CO_2Me	16	85
7	**4g**	Ph	4-FC_6H_4	CO_2Me	15	84
8	**4h**	4-$O_2NC_6H_4$	4-FC_6H_4	CO_2Et	16	84
9	**4i**	Ph	4-MeC_6H_4	CO_2Me	14	87
10	**4j**	Ph	4-MeC_6H_4	CO_2Et	14	86
11	**4k**	4-$O_2NC_6H_4$	4-MeC_6H_4	CO_2Me	16	84
12	**4l**	4-$O_2NC_6H_4$	4-MeC_6H_4	CO_2Et	16	85
13	**4m**	Ph	Bn	CO_2Me	14	88
14	**4n**	Ph	Me	CO_2Me	14	87
15	**4o**	Ph	Et	CO_2Et	15	87

[a] Reaction conditions: phenacyl bromide **1** (1.0 mmol), amine **2** (1.0 mmol), dialkyl acetylenedicarboxylate **3** (1.0 mmol), $FeCl_3$ (15 mol%), r.t.
[b] Yields of pure isolated products after column chromatography.

The possible mechanism of this conversion involves initial reaction of the amine **2** with dialkyl acetylenedicarboxylate **3** in the presence of the catalyst to form the anion **A**[8] which then attacks phenacyl bromide **1** to produce the intermediate **B**. Subsequent cyclization of **B** followed by dehydration afforded the polysubstituted pyrrole **4** (Scheme 3). When the reaction was carried out separately with aniline and dimethyl acetylenedicarboxylate using iron(III) chloride, only the alkene corresponding to the anion **A** (with *E*-configuration) was obtained.

In conclusion, we have demonstrated a new efficient method for an easy access to 1,2,3,5-tetrasubstituted pyrroles by treatment of phenacyl bromide or its derivatives, amine, and dialkyl acetylenedicarboxylate using iron(III) chloride as a catalyst. The mild reaction conditions, application of an easily available and less expensive catalyst,



Scheme 3

operational simplicity, and impressive yields are the advantages of the method.

The spectra were recorded with the following instruments: IR: Perkin-Elmer RX FT-IR spectrophotometer; NMR: Varian Gemini 300 MHz (^1H) and 75 MHz (^{13}C) spectrometer and ESI-MS: VG-Autospec micromass (70eV) instrument. Column chromatography was performed over silica gel (BDH, 100–200 mesh) and TLC with silica gel F_{254} (Merck) plates.

Dialkyl 5-Aryl-1*H*-pyrrole-2,3-dicarboxylates 4a–o; General Procedure

To a stirred soln of phenacyl bromide or its derivatives **1** (1 mmol) and amine **2** (1 mmol) in CH_2Cl_2 (6 mL) was added $FeCl_3$ (15 mol%). After 5 min, dialkyl acetylenedicarboxylate **3** (1 mmol) was added dropwise. The mixture was stirred at r.t. for 14–16 h (TLC monitoring). After completion, the solvent was evaporated; the residue was washed with cold H_2O (2 × 5 mL) and subsequently extracted with EtOAc (2 × 10 mL). The extract was dried (anhyd Na_2SO_4) and concentrated under vacuum. The residue was subjected to column chromatography (silica gel, 3–8% EtOAc–hexane) to give pure pyrrole derivative.

Diethyl 1,5-Diphenyl-1*H*-pyrrole-2,3-dicarboxylate (4a)

IR (KBr): 1720, 1598, 1502, 1413, 1240 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.20 (m, 10 H), 6.93 (s, 1 H), 4.28 (q, *J* = 7.0 Hz, 2 H), 4.16 (q, *J* = 7.0 Hz, 2 H), 1.24 (t, *J* = 7.0 Hz, 3 H), 1.12 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.4, 160.1, 140.0, 133.1, 128.8, 128.2, 127.9, 127.1, 126.4, 125.9, 124.4, 123.2, 122.2, 61.5, 61.0, 14.0, 13.9.

MS (ESI): *m*/*z* = 364 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.73; H, 5.79; N, 3.86. Found: C, 72.85; H, 5.72; N, 3.82.

Dimethyl 1,5-Diphenyl-1*H*-pyrrole-2,3-dicarboxylate (4b)

IR (KBr): 1727, 1498, 1447, 1255 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.21 (m, 10 H), 6.98 (s, 1 H), 3.81 (s, 3 H), 3.70 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.1, 160.8, 139.6, 133.3, 128.8, 128.2, 127.9, 127.0, 126.1, 126.0, 125.1, 123.2, 52.4, 52.0.

MS (ESI): *m*/*z* = 336 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.64; H, 5.08; N, 4.18. Found: C, 71.58; H, 5.12; N, 4.22.

Diethyl 5-(4-Bromophenyl)-1-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4c)
IR (KBr): 1719, 1452, 1403 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.38 (m, 6 H), 7.40–7.25 (m, 3 H), 6.91 (s, 1 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 4.12 (q, *J* = 7.0 Hz, 2 H), 1.22 (t, *J* = 7.0 Hz, 3 H), 1.11 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.1, 160.2, 139.2, 132.1, 131.8, 131.0, 129.2, 129.0, 128.2, 126.1, 125.6, 121.0, 61.2, 61.0, 13.9, 13.2.

MS (ESI): *m*/*z* = 444, 442 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{20}BrNO_4$: C, 60.00; H, 4.55; N, 3.18. Found: C, 60.21; H, 4.62; N, 3.12.

Dimethyl 5-(4-Bromophenyl)-1-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4d)
IR (KBr): 1716, 1450, 1412 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.41 (m, 5 H), 7.38–7.21 (m, 4 H), 6.92 (s, 1 H), 3.81 (s, 3 H), 3.69 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.6, 160.4, 140.0, 139.2, 132.3, 131.1, 130.8, 129.1, 129.0, 128.5, 128.2, 126.0, 125.2, 124.2, 123.5, 120.9, 120.2, 52.2, 52.0.

MS (ESI): *m*/*z* = 414, 416 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}BrNO_4$: C, 57.97; H, 3.86; N, 3.38. Found: C, 57.91; H, 3.82; N, 3.41.

Diethyl 5-(4-Nitrophenyl)-1-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4e)
IR (KBr): 1716, 1601, 1519, 1343 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.0 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.51–7.42 (m, 3 H), 7.40–7.32 (m, 2 H), 7.06 (s, 1 H), 4.32 (q, *J* = 7.0 Hz, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 1.28 (t, *J* = 7.0 Hz, 3 H), 1.11 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.0, 160.1, 157.2, 140.1, 138.7, 129.1, 129.0, 128.2, 126.3, 123.5, 122.8, 122.6, 121.0, 61.2, 61.0, 13.1, 13.0.

MS (ESI): *m*/*z* = 409 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.71; H, 4.90; N, 6.86. Found: C, 64.78; H, 4.86; N, 6.82.

Dimethyl 5-(4-Nitrophenyl)-1-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4f)
IR (KBr): 1712, 1600, 1511, 1443 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.51–7.41 (m, 3 H), 7.39–7.32 (m, 2 H), 7.02 (s, 1 H), 3.82 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.2, 160.1, 146.5, 139.9, 138.2, 129.0, 128.9, 128.2, 126.1, 126.0, 125.2, 123.8, 122.0, 120.5, 52.1, 52.0.

MS (ESI): *m*/*z* = 381 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}N_2O_6$: C, 63.17; H, 4.21; N, 7.37. Found: C, 63.23; H, 4.26; N, 7.31.

Dimethyl 1-(4-Fluorophenyl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4g)
IR (KBr): 1714, 1451, 1415 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.29 (m, 7 H), 7.12 (t, *J* = 7.0 Hz, 2 H), 6.98 (s, 1 H), 3.83 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.0, 161.1, 146.9, 141.0, 138.3, 132.5, 129.2, 129.0, 127.8, 127.2, 126.7, 125.5, 121.2, 115.2, 115.0, 52.2, 51.7.

MS (ESI): *m*/*z* = 354 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}FNO_4$: C, 67.99; H, 4.53; N, 3.97. Found: C, 67.89; H, 4.56; N, 3.91.

Diethyl 1-(4-Fluorophenyl)-5-(4-nitrophenyl)-1*H*-pyrrole-2,3-dicarboxylate (4h)
IR (KBr): 1721, 1600, 1515 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.0 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.39–7.31 (m, 2 H), 7.12 (t, *J* = 8.0 Hz, 2 H), 7.00 (s, 1 H), 4.30 (q, *J* = 7.0 Hz, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 1.20 (t, *J* = 7.0 Hz, 3 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.1, 164.9, 147.0, 140.1, 135.8, 130.9, 129.1, 129.0, 128.9, 125.1, 123.5, 122.2, 121.1, 115.6, 115.0, 61.2, 60.8, 13.0, 12.9.

MS (ESI): *m*/*z* = 449 $[M + Na]^+$.

Anal. Calcd for $C_{22}H_{19}FN_2O_6$: C, 61.97; H, 4.46; N, 6.57. Found: C, 61.88; H, 4.52; N, 6.61.

Dimethyl 5-Phenyl-1-(4-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4i)
IR (KBr): 1720, 1659, 1451, 1415 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.31 (m, 3 H), 7.30–7.20 (m, 4 H), 7.19–7.02 (m, 2 H), 6.95 (s, 1 H), 3.81 (s, 3 H), 3.70 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.1, 161.1, 138.7, 136.3, 133.3, 131.2, 129.2, 128.6, 128.4, 128.2, 128.0, 127.2, 125.6, 51.8, 51.2, 22.0.

MS (ESI): *m*/*z* = 350 $[M + H]^+$.

Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.21; H, 5.44; N, 4.01. Found: C, 72.28; H, 5.40; N, 4.07.

Diethyl 5-Phenyl-1-(4-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4j)
IR (KBr): 1720, 1601, 1519, 1460 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 2 H), 7.30–7.21 (m, 5 H), 6.94 (s, 1 H), 4.30 (q, *J* = 7.0 Hz, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 2.41 (s, 3 H), 1.31 (t, *J* = 7.0 Hz, 3 H), 1.18 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.7, 160.1, 138.9, 137.1, 133.8, 131.1, 129.8, 128.5, 127.8, 127.0, 126.1, 126.0, 61.2, 61.0, 21.0, 13.6, 13.5.

MS (ESI): *m*/*z* = 378 $[M + H]^+$.

Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.21; H, 6.10; N, 3.71. Found: C, 73.29; H, 6.15; N, 3.78.

Dimethyl 5-(4-Nitrophenyl)-1-(4-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4k)
IR (KBr): 1731, 1556, 1492 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.39–7.03 (m, 4 H), 7.01 (s, 1 H), 3.82 (s, 3 H), 3.60 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.1, 160.2, 146.4, 139.0, 130.1, 129.9, 128.3, 128.1, 127.1, 125.7, 125.1, 123.2, 123.1, 52.1, 52.0, 22.2.

MS (ESI): *m*/*z* = 395 $[M + H]^+$.

Anal. Calcd for $C_{21}H_{18}N_2O_6$: C, 63.96; H, 4.57; N, 7.11. Found: C, 63.87; H, 4.52; N, 7.14.

Diethyl 5-(4-Nitrophenyl)-1-(4-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4l)
IR (KBr): 1718, 1607, 1519, 1432 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.29–7.09 (m, 4 H), 7.02 (s, 1 H), 4.31 (q, *J* = 7.0 Hz, 2 H), 4.14 (q, *J* = 7.0 Hz, 2 H), 2.41 (s, 3 H), 1.32 (t, *J* = 7.0 Hz, 3 H), 1.14 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.7, 160.0, 147.1, 139.0, 130.0, 129.9, 128.1, 128.0, 127.6, 126.2, 126.0, 123.3, 123.1, 61.5, 61.2, 22.5, 13.5, 13.2.

MS (ESI): *m*/*z* = 423 $[M + H]^+$.

Anal. Calcd for $C_{23}H_{22}N_2O_6$: C, 65.40; H, 5.21; N, 6.64. Found: C, 65.32; H, 5.27; N, 6.59.

Dimethyl 1-Benzyl-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4m)
IR (KBr): 1711, 1449, 1404 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.12 (m, 10 H), 6.92 (s, 1 H), 5.51 (s, 2 H), 3.81 (s, 3 H), 3.73 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.2, 160.8, 137.1, 133.2, 129.0, 128.9, 128.2, 127.2, 127.1, 127.0, 125.7, 124.5, 122.2, 121.1, 52.5, 52.4, 51.7.

MS (ESI): *m*/*z* = 350 $[M + H]^+$.

Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.21; H, 5.44; N, 4.01. Found: C, 72.28; H, 5.52; N, 4.08.

Dimethyl 1-Methyl-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4n)
IR (KBr): 1710, 1596, 1447 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 5 H), 6.81 (s, 1 H), 3.90 (s, 3 H), 3.78 (s, 3 H), 3.72 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.1, 160.4, 133.9, 133.2, 128.5, 126.9, 126.5, 125.8, 123.2, 121.1, 51.6, 51.0, 29.1.

MS (ESI): *m*/*z* = 274 $[M + H]^+$.

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.50; N, 5.13. Found: C, 65.86; H, 5.54; N, 5.07.

Diethyl 1-Ethyl-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (4o)
IR (KBr): 1721, 1607, 1462 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.12 (m, 5 H), 6.87 (s, 1 H), 4.40–4.11 (m, 6 H), 1.42 (t, *J* = 7.0 Hz, 3 H), 1.31 (t, *J* = 7.0 Hz, 3 H), 1.22 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.2, 159.8, 133.5, 128.0, 127.2, 126.4, 123.2, 122.0, 120.1, 61.0, 60.3, 44.5, 17.0, 13.7.

MS (ESI): *m*/*z* = 316 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.57; H, 6.67; N, 4.44. Found: C, 68.69; H, 6.61; N, 4.40.

Dimethyl 5-Phenyl-1*H*-pyrrole-2,3-dicarboxylate (5)
IR (KBr): 1720, 1450, 1408 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.32 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 6.82 (d, *J* = 2.0 Hz, 1 H), 3.92 (s, 3 H), 3.84 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.5, 161.0, 135.2, 130.5, 128.6, 128.1, 126.5, 123.6, 122.3, 110.8, 51.2, 50.5.

MS (ESI): *m*/*z* = 260 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.87; H, 5.02; N, 5.41. Found: C, 64.81; H, 5.08; N, 5.45.

Acknowledgment

The authors thank CSIR and UGC, New Delhi for financial assistance.

References

(1) Part 283 in the series 'Studies on Novel Synthetic Methodologies'.
(2) (a) Finar, I. L. *Organic Chemistry: Stereochemistry and Chemistry of Natural Products*, 5th ed., Vol. 2; Longman: London, **1975**, 885–913. (b) O'Hagan, D. *Nat. Prod. Rep.* **2000**, *17*, 435. (c) Walsh, C. T.; Garneau-Tsodikova, S.; Howard-Jones, A. R. *Nat. Prod. Rep.* **2006**, *23*, 517.
(3) (a) Huffman, J. W. *Curr. Med. Chem.* **1999**, *6*, 705. (b) Kidwai, M.; Venkataramanan, R.; Mohan, R.; Sapra, P. *Curr. Med. Chem.* **2002**, *9*, 1209. (c) La Regina, G.; Silvestri, R.; Artico, M.; Lavechia, A.; Novellino, E.; Befani, O.; Turini, P.; Agostinelli, E. *J. Med. Chem.* **2007**, *50*, 922.
(4) (a) Boger, D. L.; Boyce, C. W.; Labrilli, M. A.; Sehon, C. A.; Jin, Q. *J. Am. Chem. Soc.* **1999**, *121*, 54. (b) Abid, M.; Landge, S. M.; Torok, B. *Org. Prep. Proced. Int.* **2006**, *38*, 495.
(5) (a) Facchetti, A.; Abboto, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Pagani, G. A.; Marks, T. J. *Chem. Mater.* **2003**, *15*, 1064. (b) Pu, S.; Liu, G.; Shen, L.; Xu, J. *Org. Lett.* **2007**, *9*, 2139.
(6) Some recent examples: (a) Larionov, O. V.; de Meijere, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 5664. (b) Minetto, G.; Raveglia, L. F.; Sega, A.; Taddei, M. *Eur. J. Org. Chem.* **2005**, *24*, 5277. (c) Shiner, C. M.; Laner, T. D. *Tetrahedron* **2005**, *61*, 11628. (d) Hwang, S. J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 16158. (e) Abid, M.; Teixeira, L.; Torok, B. *Org. Lett.* **2008**, *10*, 933. (f) La, Y. D.; Arndtsen, B. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 5430.
(7) (a) Das, B.; Balasubramanyam, P.; Krishnaiah, M.; Veeranjaneyulu, B.; Reddy, G. C. *J. Org. Chem.* **2009**, *74*, 4393. (b) Das, B.; Damodar, K.; Bhunia, N. *J. Org. Chem.* **2009**, *74*, 5607. (c) Das, B.; Satyalakshmi, G.; Suneel, K.; Damodar, K. *J. Org. Chem.* **2009**, *74*, 8400. (d) Das, B.; Balasubramanyam, P.; Veeranjaneyulu, B.; Reddy, G. C. *J. Org. Chem.* **2009**, *74*, 9505.
(8) Zhu, Q.; Jiang, H.; Li, J.; Zhang, M.; Wang, X.; Qi, C. *Tetrahedron* **2009**, *65*, 4604.