Supporting Information

Recyclable graphite catalyzed four-component synthesis of functionalized pyrroles

K. N. Nandeesh, G. M. Raghavendra, C. N. Revanna, T. A. Jenifer Vijay, K. S. Rangappa and K. Mantelingu**

Department of Studies in Chemistry

Manasagangothri, Mysore, University of Mysore, Mysore-570006, INDIA

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1.The LCMS ^1H NMR, and ^{13}C NMR of 1c-16c.

Method info : A=0.1%HOCH₃;B=ACN Flow: 1.2ml/min,
 Column-ATLANTIS C18 (50X4.6mm-5 μ m,) POSITIVE MODE
 TIME (MIN) 0--4 4--5 5--5.5 5.5-7
 %B 5-95 95 95-5 5

Peak No	RT min	Area	Area %
1	3.22	1200.55	10.95
2	3.90	150.90	10.72
3	4.22	97.93	10.47
4	4.58	49.16	10.23
5	4.88	19548.09	92.88
6	5.12	482.59	12.29
7	5.27	418.92	11.99
8	5.41	98.74	10.47

Method info : A=0.1%HOAc ; B=ACN Flow = 1.2ML/MIN Column=Atlantis d
C18 (75X4.6mm-5µm,SC\742) Positive Mode
Time (min.): 0--4.0 4.0--5.0 5.0--5.5 5.5--7.0
% B : 05-95 95 95-05 05

Peak No	RT min	Area	Area %
1	2.53	13.99	0.16
2	2.59	111.84	1.25
3	2.84	48.10	0.54
4	3.84	33.52	0.26
5	3.90	320.64	3.57
6	4.13	82.66	0.92
7	4.42	58.18	0.65
8	4.50	7813.82	87.11
9	4.68	497.00	5.54

Method info : A-0.1% HCOOH ;B-MEOH Flow: 1.2ml/min
 Column-Atlantis dC18 (50X4.6mm-5 μm)
 TIME (MIN) : 0--4.0 4.0--5.0 5.0--5.5 5.5-7.0
 %B 10-95 95 95-10 10

Peak No	RT min	Area	Area %
1	2.55	132.34	1.19
2	3.33	127.56	1.15
3	3.70	1361.90	13.27
4	4.12	100.17	0.90
5	4.68	73.81	0.67
6	4.96	66.79	0.60
7	5.09	9516.50	85.91
8	5.21	466.59	4.21
9	5.32	102.97	0.93
10	5.84	128.42	1.16

Method info : A-0.1% HCOOH ;B- ACN Flow: 1.2ml/min,
 Column-ATLANTIS C18 (50X4.6mm-5 μm ,) POSITIVE MODE
 TIME (MIN) : 0--4 4--5 5--5.5 5.5-7
 %B 5-95 95 95-5 5

Peak No	RT min	Area	Area %
1	2.09	350.93	2.12
2	2.75	133.49	0.81
3	3.33	557.07	3.37
4	4.02	94.78	0.57
5	4.54	112.71	0.68
6	5.17	55.67	0.34
7	5.31	14187.28	85.89
8	5.49	156.23	0.95
9	5.79	787.92	4.77
10	6.07	82.56	0.50

Method info : A-0.1%HCOOH;B-MEOH Flow: 1.2ml/min,
 Column-X-Terra C8 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--3.5 3.5--5.0 5.0--5.5 5.5-7.0
 %B 30-95 95 95-30 30

Peak No	RT min	Area	Area %
1	2.82	114.04	0.77
2	3.03	155.60	1.05
3	3.24	47.49	0.32
4	3.33	179.94	1.21
5	3.64	124.84	0.84
6	3.79	133.43	0.90
7	4.47	634.02	4.27
8	4.54	12636.29	85.07
9	4.64	353.68	2.38
10	4.78	453.93	3.06
11	5.09	20.67	0.14

Method info : A=0.1%HOAc;B=ACN Flow: 1.2ml/min,
 Column=ATLANTIS C18 (50X4.6mm=Sum, | POSITIVE MODE
 TIME (MIN) : 0--4 4--5 5--5.5 5.5--7
 %B 5-95 95 95-5 5

Peak No	RT min	Area	Area %
1	4.08	95.66	0.69
2	4.87	13203.16	94.63
3	5.12	369.84	2.65
4	5.26	284.35	2.04

Method info : A-0.1% HCOOH; B-MEOH Flow: 1.2ml/min,
 Column-Atlantis dC18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--4.0 4.0--5.0 5.0--5.5 5.5-7.0
 %B 10-95 95 95-10 10

Method info : A=0.1% HCOOH ;B=MEOH Flow: 1.2ml/min,
 Column-X-Terra C8 (50X4.6mm-5 μm ,) POSITIVE MODE
 TIME (MIN) : 0--3.5 3.5--5.0 5.0--5.5 5.5--7.0
 %B 30-95 95 95-30 30

Peak No	RT min	Area	Area %
1	2.89	26.20	0.20
2	2.93	110.91	0.85
3	3.10	221.50	1.69
4	3.37	87.76	0.67
5	3.57	85.11	0.65
6	3.65	108.66	0.83
7	4.02	34.11	0.26
8	4.09	11708.20	89.38
9	4.18	421.16	3.22
10	4.36	295.84	2.26

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nd info : MOBILE PHASE:A-0.1%HCOOH;B-MEOH, Flow: 1.2ml/min,
 COLUMN:Atlantis dc18 (50X4.6mm-5um,) POSITIVE MODE
 TIME (MIN) : 0--4.0 4.0--5.0 5.0--5.5 5.5--7.0
 %B 10-95 95 95-10 10

Peak No	RT min	Area	Area %
1	4.46	146.52	0.67
2	4.74	229.85	1.06
3	4.90	110.54	0.51
4	5.24	20682.47	95.19
5	5.47	558.59	2.57

Method info : A-0.1%HOAc;B-ACN Flow: 1.2ml/min,
 Column-ATLANTIS C18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--4 4--5 5--5.5 5.5-7
 %B 5-95 95 95-5 5

Peak No	RT min	Area	Area %
1	4.23	162.35	1.46
2	4.40	22.28	0.20
3	4.77	193.10	1.74
4	4.89	10542.28	94.78
5	5.08	121.71	1.09
6	5.20	34.11	0.31
7	5.29	47.35	0.43

Method info : A-0.1%HOAc:B-ACN Flow: 1.2ml/min,
 Column-ATLANTIS C18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--4 4--5 5--5.5 5.5--7
 %B 5-95 95 95-5 5

Peak No	RT min	Area	Area %
1	3.30	68.24	0.33
2	4.23	106.78	0.52
3	4.40	138.66	0.68
4	4.56	65.41	0.32
5	4.74	238.64	1.16
6	4.92	98.81	0.48
7	5.14	73.23	0.36
8	5.28	164.00	0.80
9	5.40	18508.23	90.19
10	5.62	1058.75	5.16

Method info : A-0.1% HCOOH; B-MEOH Flow: 1.2ml/min
 Column-Atlantis dC18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) 0--4.0 4.0--5.0 5.0--5.5 5.5-7.0
 %B 10-95 95 95-10 10

Peak No	RT min	Area	Area %
1	4.45	31.36	0.29
2	4.66	41.79	0.30
3	5.19	19.21	0.18
4	5.29	55.31	0.51
5	5.39	270.94	2.49
6	5.47	10396.68	95.73
7	5.65	45.56	0.42

Method info : MOBILE PHASE:A-0.1% HCOOH ;B-MEOH, Flow: 1.2ml/min,
 COLUMN:Atlantis dC18 (50X4.6mm-5 μm ,) POSITIVE MODE
 TIME (MIN) : 0--4.0 4.0--5.0 5.0--5:5 5.5-7.0
 %B 10-95 95 95-10 10

Peak No	RT min	Area	Area %
1	5.46	14511.62	99.41
2	5.90	85.73	0.59

Method info : Zorbax KDB C-18 (4.6*50mm)
 A: 0.1% Formic acid in water
 B: Methanol
 Flow: 1.0mL/min
 Time B1
 0 10
 4 95
 6 95
 6.5 10
 8 10

Peak	RT	Area	Area
no	min		%
1	5.594	(5.735e+003)	99.514
2	5.925	(2.802e+001)	0.486

EXPERIMENTAL SECTION

Materials and methods:

All work relating to analytical thin layer chromatography were performed with E. Merck silica gel 60F₂₅₄ aluminum plates and were visualized with UV light. The following mobile phases were employed for TLC: chloroform, methanol and hexane, and ethyl acetate in different ratios. The instrumental techniques employed for the characterization of the newly synthesized compounds include ¹H and ¹³C NMR and mass spectroscopy. ¹H and ¹³C NMR spectra were recorded on a ((400 and 300 MHz) Fourier transform spectrophotometer in CDCl₃ or DMSO-d₆ solution using tetramethylsilane (TMS) as internal standard. Chemical shifts were recorded in ppm relative to TMS. Mass and purity were recorded on a LC–MSD-Trap-XCT.

Typical procedure

Graphite (20 mol %) was added to a solution of benzo[d][1,3]dioxole-5-carbaldehyde (100 mg, 0.666 mmol), aniline (93.03 mg, 1.10 mmol), ethyl acetoacetate (86 mg, 0.666 mmol) in nitromethane (1.5 ml). The mixture was refluxed at 90-100 °C for 5 h (TLC monitoring). Reaction mixture was cooled to room temperature and filtered the graphite. The filtrate was concentrated under vacuum and the residue was directly purified by column chromatography with ethyl acetate in hexanes as eluent afforded the desired product. The products were further identified by ¹H NMR, ¹³C NMR and LCMS, which were all in good agreement with the assigned structures.

Ethyl-4-(benzo[d][1, 3]dioxol-5-yl)-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (1c).

Brown coloured semi liquid: 0.152 g (65%). IR (KBr): 1739 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 7.15-7.29 (m, 5H, ArH), 6.91 (s, 1H, ArH), 6.78-6.87 (d, 2H, ArH, J =8.0 Hz), 6.62 (s, 1H, ArH), 5.96 (s, 2H, CH_2), 4.18 (q, 2H, OCH_3 , J =7.5 Hz), 2.40 (s, 3H, CH_3), 1.18 (t, 3H, CH_3 , J =7.5 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.6, 163.0, 161.0, 136.5, 134.9, 129.3, 128.0, 122.3, 120.7, 111.7, 110.1, 107.6, 100.8, 59.5, 14.1, 12.6; MS: m/z = 350.20 [$\text{M}^+ + \text{H}$]; Anal calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.02; H, 5.65; N, 3.90.

Ethyl- 4-(4-acetylphenyl)-1-(4-methoxybenzyl)-2-methyl-1H-pyrrole-3-carboxylate (2c).

Brown coloured semi liquid: 0.190 g (73%); IR (KBr): 1718, 1740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, 2H, ArH, J =8.0 Hz), 7.45 (d, 2H, ArH, J =8.4 Hz), 7.30 (d, 1H, ArH, J =8.8 Hz), 6.89-6.89 (d, 2H, ArH, J =8.4 Hz), 6.72 (d, 1H, ArH, J =7.6 Hz), 6.63 (s, 1H, ArH), 5.05 (s, 2H, CH_2), 4.15 (q, 2H, OCH_2 , J =7.2 Hz), 3.87 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 1.13 (t, 3H, CH_3 , J =7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ = 197.9, 165.6, 156.5, 141.2, 134.7, 129.0, 128.3, 127.6, 124.8, 121.0, 120.8, 110.2, 59.4, 55.3, 45.7, 26.5, 14.1, 11.3; MS: m/z = 392.00 [$\text{M}^+ + \text{H}$]; Anal calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.78; H, 6.30; N, 3.78.

Ethyl-4-(4-acetylphenyl)-2-methyl-1-(4-methylbenzyl)-1H-pyrrole-3-carboxylate (3c).

Brown coloured semi liquid: 0.173 g (68%); IR (KBr): 1718, 1737 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, 2H, ArH, J =8.0 Hz), 7.44 (d, 2H, ArH, J =8.4 Hz), 7.14 (d, 2H, ArH, J =7.6 Hz), 6.96 (d, 2H, ArH, J =8.0 Hz), 6.62 (s, 1H, ArH), 5.02 (s, 2H, CH_2), 4.14 (q, 2H, OCH_2 , J =7.2 Hz), 2.57 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.13 (t, 3H, CH_3 , J =7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ = 197.9, 165.5, 141.1, 137.7, 136.7, 136.9, 134.8, 133.3, 129.1, 128.3, 127.6, 126.6, 125.0, 120.8, 110.9, 59.5, 50.4, 26.5, 21.0, 14.1, 11.5; MS: m/z = 376.20 [$\text{M}^+ + \text{H}$]; Anal calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.46; H, 6.90; N, 3.93.

Ethyl-4-(benzo[d][1,3]dioxol-5-yl)-1-(4-ethylphenyl)-2-methyl-1H-pyrrole-3-carboxylate (4c).

Brown coloured semi liquid: 0.182 g (70%); IR (KBr): 1740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.28 (d, 2H, ArH, J =8.4 Hz), 7.20 (d, 2H, ArH, J =8.4 Hz), 6.92 (s, 1H, ArH), 6.86 (d, 1H, ArH, J =8.4 Hz), 6.77 (d, 1H, ArH, J =8.4 Hz), 6.64 (s, 1H, ArH), 5.95 (s, 2H, CH_2), 4.17 (q, 2H, OCH_2 , J =6.8 Hz), 2.69 (q, 2H, CH_2 , J =8.0 Hz), 2.42 (s, 3H, CH_3), 1.23 (t, 3H, CH_3 , J =7.2 Hz), 1.18 (t, 3H, CH_3 , J =7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.7, 146.1, 144.3, 136.5, 129.6, 128.6, 126.1, 122.3, 120.7, 114.4, 110.2, 107.5, 100.6, 59.4, 28.4, 15.3, 14.1, 12.7; MS: m/z = 378.20 [M^+ + H]; Anal calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 72.98; H, 6.40; N, 3.44.

Ethyl-1-(4-tert-butylbenzyl)-2-methyl-4-phenyl-1H-pyrrole-3-carboxylate (5c).

Brown coloured semi liquid: 0.240 g (67%); IR (KBr): 1739 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.32-7.40 (m, 5H, ArH), 7.22 (d, 2H, ArH, J =7.2 Hz), 7.015 (d, 2H, ArH, J =8.0 Hz), 6.57 (s, 1H, ArH), 5.02 (s, 2H, CH_2), 4.12 (q, 2H, OCH_2 , J =6.8 Hz), 2.48 (s, 3H, CH_3), 1.25 (s, 9H, CH_3), 1.23 (t, 3H, CH_3 , J =7.2 Hz), 1.10 (t, 3H, CH_3 , J =7.6 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.8, 150.8, 136.3, 135.9, 133.6, 129.2, 128.8, 127.4, 126.0, 125.7, 120.3, 110.9, 59.3, 50.2, 34.5, 31.2, 14.0, 11.4; MS: m/z = 376.20 [M^+ + H]; Anal calcd for $\text{C}_{25}\text{H}_{29}\text{NO}_2$: C, 79.96; H, 7.78; N, 3.73. Found: C, 79.86; H, 7.98; N, 3.70.

Ethyl-4-(benzo[d][1,3]dioxol-5-yl)-1-(4-fluorophenyl)-2-methyl-1H-pyrrole-3-carboxylate (6c).

Brown coloured semi liquid: 0.173 g (70%); IR (KBr): 1740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.27 (d, 2H, J =8.4 Hz), 7.14 (d, 2H, J =8.4 Hz), 6.91 (s, 1H, ArH), 6.85 (d, 1H, ArH, J =8.0 Hz), 6.77 (d, 1H, ArH, J =7.6 Hz), 6.62 (s, 1H, ArH), 5.95 (s, 2H, CH_2), 4.17 (q, 2H, OCH_2 , J =7.6 Hz), 2.40 (s, 3H, CH_3), 1.17 (t, 3H, CH_3 , J =7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ =

165.6, 163.3, 160.8, 146.2, 136.5, 134.9, 129.3, 128.0, 126.3, 122.3, 120.7, 116.1, 118.8, 110.1, 100.7, 59.4, 29.6, 14.1, 12.1; MS: m/z = 368.20 [$M^+ + H$]; Anal calcd for $C_{21}H_{18}FNO_4$: C, 68.66; H, 4.94; N, 3.81. Found: C, 68.44; H, 4.86; N, 3.92.

Ethyl -4-(4-acetylphenyl)-1-(4-chlorobenzyl)-2-methyl-1H-pyrrole-3-carboxylate (7c).

Brown coloured semi liquid: 0.190 g (70%); IR (KBr): 1720, 1749 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, 2H, J =8.4 Hz), 7.46 (d, 2H, J =8.0 Hz), 7.27 (d, 2H, ArH, J =8.0 Hz), 7.08 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.63 (s, 1H, ArH), 5.05 (s, 2H, CH_2), 4.15 (q, 2H, OCH_2 , J =7.2 Hz), 2.60 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 1.13 (t, 3H, CH_3 , J =7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 165.4, 140.8, 138.5, 136.7, 135.0, 134.9, 130.2, 129.2, 128.1, 127.7, 126.6, 125.4, 124.5, 120.7, 111.3, 59.6, 50.0, 26.5, 14.0, 11.4; MS: m/z = 396.2 [$M^+ + H$]; Anal calcd for $C_{23}H_{22}ClNO_3$: C, 69.78; H, 5.60; N, 3.54. Found: C, 69.95; H, 5.84; N, 3.73.

Ethyl-1-(4-(difluoromethoxy) benzyl)-2-methyl-4-phenyl-1H-pyrrole-3-carboxylate (8c).

Brown coloured semi liquid: 0.244 g (67%); IR (KBr): 1752 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, 2H, J =7.2 Hz), 7.29 (t, 3H, J =7.6 Hz), 7.23 (s, 1H, ArH), 7.05-7.11 (d, 4H, ArH, J =8.8 Hz), 6.56 (s, 1H), 5.04 (s, 2H, CH_2), 4.15 (q, 2H, OCH_2 , J =7.2 Hz), 2.46 (s, 3H, CH_3), 1.10 (t, 3H, CH_3 , J =7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 150.6, 136.1, 135.7, 133.9, 129.5, 127.4, 126.1, 120.1, 118.3, 115.7, 113.1, 111.3, 61.7, 34.3, 14.0, 11.4; MS: m/z = 386.0 [$M^+ + H$]; Anal calcd for $C_{22}H_{21}F_2NO_3$: C, 68.56; H, 5.49; N, 3.63. Found: C, 68.74; H, 5.63; N, 3.44.

Ethyl-2-methyl-4-phenyl-1-(4-(trifluoromethyl) benzyl)-1H-pyrrole-3-carboxylate (9c).

Brown coloured semi liquid: 0.242 g (66%); IR (KBr): 1754 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, 2H, J =8.4 Hz), 7.36 (d, 2H, J =6.8 Hz), 7.22-7.33 (t, 3H, ArH, J =8.0 Hz), 7.16 (d, 2H, ArH, J =8.0 Hz), 6.58 (s, 1H, ArH), 5.13 (s, 2H, CH_2), 4.12 (q, 2H, OCH_2 , J =7.6 Hz), 2.45 (s, 3H, CH_3), 1.10 (t, 3H, CH_3 , J =7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 140.8, 136.1, 135.5,

129.2, 127.50, 126.2, 125.2, 120.2, 111.5, 59.4, 50.0, 13.9, 11.3; MS: $m/z = 388.0$ [$M^+ + H$]; Anal calcd for $C_{22}H_{20}F_3NO_2$: C, 68.21; H, 5.20; N, 3.62. Found: C, 68.42; H, 5.66; N, 3.32.

Ethyl-1-cyclobutyl-4-(3-methoxyphenyl)-2-methyl-1H-pyrrole-3-carboxylate (10c).

Brown coloured semi liquid: 0.138 g (60%); IR (KBr): 1748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 6.78\text{--}7.26$ (m, 4H, ArH) 6.72 (s, 1H, ArH), 4.56 (m, 1H, CH), 4.1 (q, 2H, OCH_2 , $J = 7.2$ Hz), 3.81 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.32 (q, 4H, CH_2 , $J = 7.2$ Hz), 1.83 (m, 2H, CH_2), 1.10 (t, 3H, CH_3 , $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 166.3, 159.3, 138.0, 136.1, 128.8, 125.9, 122.3, 116.6, 115.2, 112.0, 111.1, 59.7, 55.6, 50.8, 31.0, 15.4, 14.5, 11.8$; MS: $m/z = 314.2$ [$M^+ + H$]; Anal calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.89; H, 7.48; N, 4.31.

Ethyl-1-(cyclohexylmethyl)-4-(3-methoxyphenyl)-2-methyl-1H-pyrrole-3-carboxylate (11c).

Brown coloured semi liquid: 0.170 g (65%); IR (KBr): 1743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.19$ (t, 1H, ArH, $J = 8.4$ Hz), 6.94 (d, 1H, ArH, $J = 8.0$ Hz), 6.92 (s, 1H, ArH), 6.77 (d, 1H, ArH, $J = 8.0$ Hz), 6.49 (s, 1H, ArH), 4.12 (q, 2H, OCH_2 , $J = 6.8$ Hz), 3.64 (d, 2H, CH_2 , $J = 6.8$ Hz), 2.50 (s, 3H, CH_3), 1.10 (t, 3H, CH_3 , $J = 6.8$ Hz), 0.91–1.74 (m, 11H, Aliphatic-H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 165.9, 158.9, 137.4, 136.0, 128.3, 125.3, 121.8, 120.5, 114.8, 111.5, 110.3, 59.2, 55.1, 53.1, 39.1, 30.7, 25.6, 14.0, 11.5$; MS: $m/z = 356.4$ [$M^+ + H$]; Anal calcd for $C_{22}H_{29}NO_3$: C, 74.33; H, 8.22; N, 3.94. Found: C, 74.24; H, 8.48; N, 3.83.

Ethyl-1-(cycloheptylmethyl)-4-(3-methoxyphenyl)-2-methyl-1H-pyrrole-3-carboxylate (12c).

Brown coloured semi liquid: 0.182 g (67%); IR (KBr): 1743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.16$ (t, 1H, ArH, $J = 8.0$ Hz), 6.85 (s, 1H, ArH), 6.82 (s, 1H, ArH), 6.78 (d, 1H, ArH, $J = 8.4$ Hz), 6.75 (d, 1H, ArH, $J = 8.4$ Hz), 4.02 (q, 2H, OCH_2 , $J = 7.2$ Hz), 3.73 (s, 3H, OCH_3), 3.69 (d, 2H, CH_2 , $J = 7.6$ Hz), 2.0 (s, 3H, CH_3), 1.13–1.59 (m, 15H, AliphaticH), 1.10 (t, 3H, CH_3 , $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.4, 168.3, 139.5, 136.5, 131.0, 130.4, 129.8, 128.2, 123.2, 122.7, 120.1, 119.1, 114.3, 111.7, 110.6, 62.0, 55.7, 53.7, 32.0, 28.0, 23.1, 18.9, 14.5$; MS:

$m/z = 370.2$ [$M^+ + H$]; Anal calcd for $C_{23}H_{31}NO_3$: C, 74.76; H, 8.46; N, 3.79. Found: C, 74.39; H, 8.68; N, 3.98.

Ethyl -1, 4-bis (4-chlorophenyl)-2-methyl-1H-pyrrole-3-carboxylate (13c).

Yellow coloured solid: 0.236 g (88%); mp 142-145 °C; IR (KBr): 1758 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$ (d, 2H, ArH, $J=8.5$ Hz), 7.32 (d, 2H, ArH, $J=8.5$ Hz), 7.29 (d, 2H, ArH, $J=8.5$ Hz), 7.25 (d, 1H, ArH, $J=8.5$ Hz), 6.65 (s, 1H, ArH), 4.17 (q, 2H, OCH_2 , $J=7.0$ Hz), 2.43 (s, 3H, CH_3), 1.15 (t, 3H, CH_3 , $J=7.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.4$, 137.2, 136.7, 134.1, 133.8, 132.2, 130.5, 129.6, 125.7, 120.7, 111.9, 59.6, 14.1, 12.6.; MS: $m/z = 373.0$ [$M^+ + H$]; Anal calcd for $C_{20}H_{17}Cl_2NO_2$: C, 64.18; H, 4.58; N, 3.74. Found: C, 64.36; H, 4.74; N, 3.63

Diethyl-1-benzyl-4-(4-chlorophenyl)-1H-pyrrole-2, 3-dicarboxylate (14c).

Brown coloured semi liquid: 0.236 g (80%); IR (KBr): 1756 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, 2H, ArH, $J=7.6$ Hz), 7.25-7.33 (m, 5H, ArH), 7.17 (d, 2H, ArH, $J=7.2$ Hz), 6.91 (s, 1H, ArH), 5.51 (s, 2H, CH_2), 4.23 (q, 2H, OCH_2 , $J=8.0$ Hz), 1.25 (t, 3H, CH_3 , $J=6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.4$, 160.2, 136.8, 132.8, 131.9, 128.6, 127.5, 126.8, 125.2, 122.2, 121.6, 60.7, 52.4, 14.0; MS: $m/z = 412.10$ [$M^+ + H$]; Anal calcd for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N, 3.40. Found: C, 69.97; H, 5.62; N, 3.32.

Diethyl-4-(4-chlorophenyl)-1-(3-methoxybenzyl)-1H-pyrrole-2, 3-dicarboxylate (15c).

White solid: 0.270 g (85%); mp 147-150 °C; IR (KBr): 1757 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.66$ (s, 1H, ArH), 7.41 (d, 2H, ArH, $J=7.76$ Hz), 7.36 (s, 2H, ArH, $J=7.7$ Hz), 7.22 (t, 1H, ArH, $J=8.3$ Hz), 6.83 (d, 1H, ArH, $J=8.3$ Hz), 6.76 (s, 1H, ArH), 6.71 (d, 1H, ArH, $J=7.2$ Hz), 5.46 (s, 2H, CH_2), 4.14 (q, 2H, OCH_2 , $J=7.4$ Hz), 3.70 (s, 3H, CH_3), 1.13 (t, 6H, CH_3 , $J=6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.5$, 161.2, 141.1, 132.2, 131.6, 130.2, 128.8, 123.4, 122.6, 120.8, 114.4, 62.7, 15.6; MS: $m/z = 442.10$ [$M^+ + H$]; Anal calcd for $C_{24}H_{24}ClNO_5$: C, 65.23; H, 5.47; N, 3.17. Found: C, 65.45; H, 5.61; N, 3.20.

Diethyl-4-(4-chlorophenyl)-1-(2-fluorobenzyl)-1H-pyrrole-2, 3-dicarboxylate (16c).

Brown coloured semi liquid: 0.254 g (82%); IR (KBr): 1757 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ = 7.57 (s, 1H, ArH), 7.49-7.52 (d, 3H, ArH, J =8.6 Hz), 7.42-7.44 (d, 2H, ArH, J =8.4 Hz), 7.36 (t, 1H, ArH, J =8.08 Hz), 7.18 (d, 1H, ArH, J =8.80 Hz), 6.62 (t, 1H, ArH, J =6.2 Hz), 5.56 (s, 2H, CH_2), 4.19 (q, 2H, OCH_2 , J =7.06 Hz), 4.03 (q, 2H, OCH_2 , J =7.30 Hz), 1.14 (t, 3H, CH_3 , J =7.10 Hz), 1.01 (t, 3H, CH_3 , J =6.30 Hz); ^{13}C NMR (100 MHz, DMSO- d_6): δ = 166.1, 162.8, 160.3, 159.5, 132.2, 131.9, 129.0, 128.9, 127.6, 122.4, 121.3, 117.0, 115.2, 61.0, 49.8, 14.1; MS: m/z = 430.10 [M^+ + H].