

Synthesis of highly substituted dihydro-2-oxopyrroles using Fe₃O₄@nano-cellulose-OPO₃H as a novel bio-based magnetic nanocatalyst

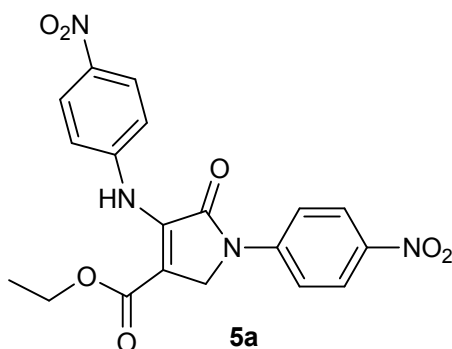
Naeimeh Salehi, Bi Bi Fatemeh Mirjalili*

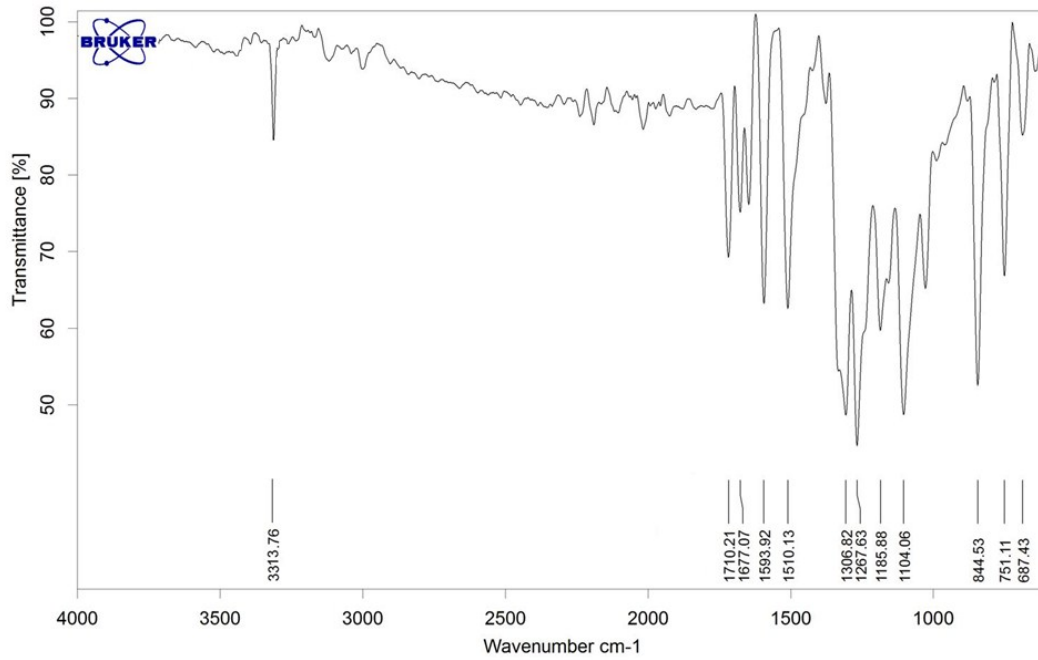
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Characterization Data for Compounds

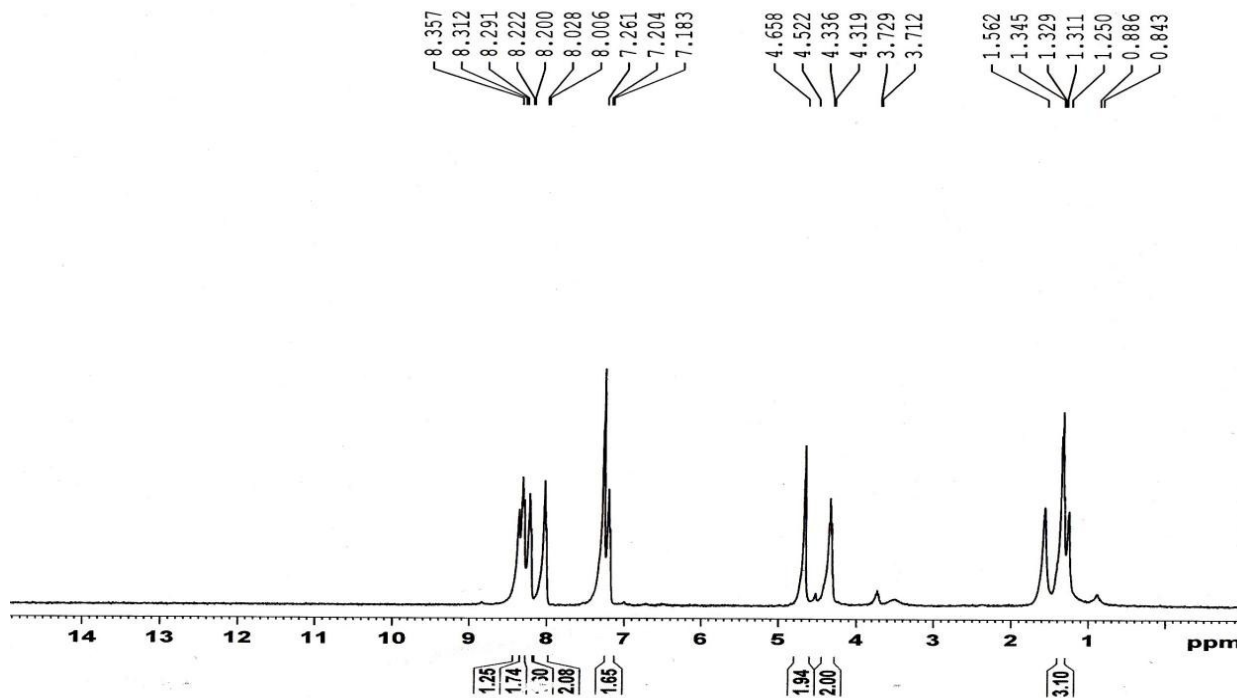
Ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (5a) (Table 2, entry 1)

Yellow solid. M.p. 206-208 °C. FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3313, 1710, 1677, 1593, 1510, 1306, 1267, 1185, 1104, 844.; ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.35 (s, 1H, NH), 8.30 (d 2H, ³J= 8.4 Hz, Ar-H), 8.21 (d, 2H, ³J= 8.8 Hz, Ar-H), 8.01 (d, 2H, ³J= 8.8 Hz, Ar-H), 7.19 (d, 2H, ³J= 8.4 Hz, Ar-H), 4.65 (s, 2H, NCH₂), 4.32 (s, 2H, OCH₂CH₃), 1.32 (t, 3H, OCH₂CH₃).; ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 165.1, 162.5, 146.8, 144.1, 143.7, 141.9, 139.3, 125.0 (2C), 124.1 (2C), 119.6 (2C), 118.5 (2C), 111.9, 60.8, 48.8, 14.2.; MS (*m/z*): 412.1 (M⁺), 339.2, 219.1, 190.1, 174.1, 163.1, 150.1, 129.1, 117.1, 103.0, 92, 76 (100%), 65, 51.1.29; Anal. Calcd for C₁₈H₁₄N₄O₇, C, 54.28; H, 3.54; N, 14.07; O, 28.12; found: C, 55.11; H, 3.14; N, 13.64.

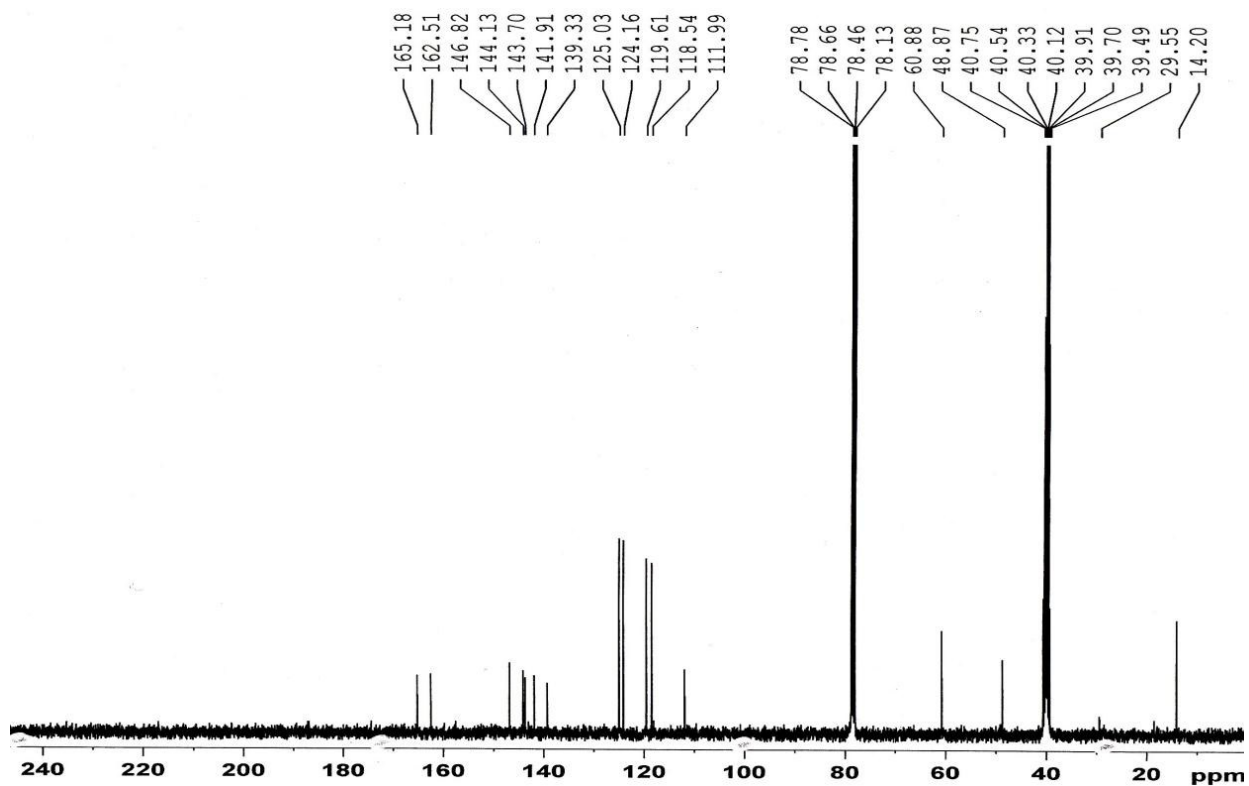




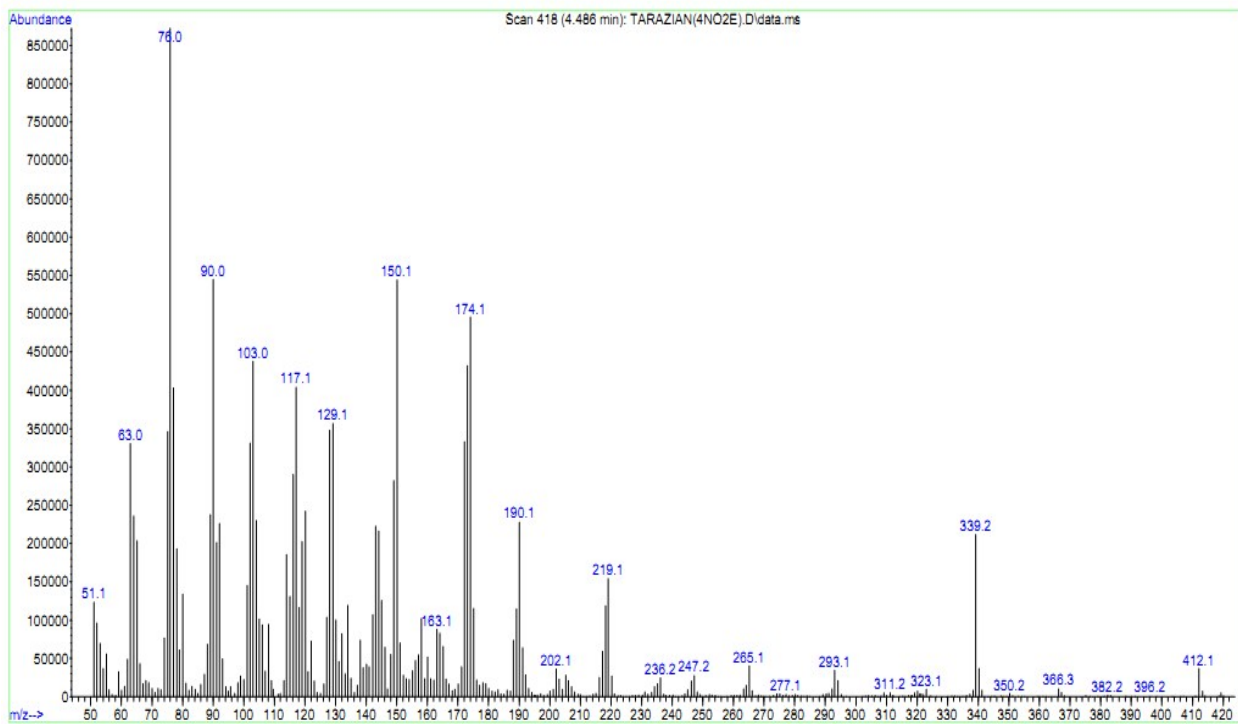
The FT-IR spectrum of product (5a)



The ¹H NMR(400MHz)spectrum of product (5a)



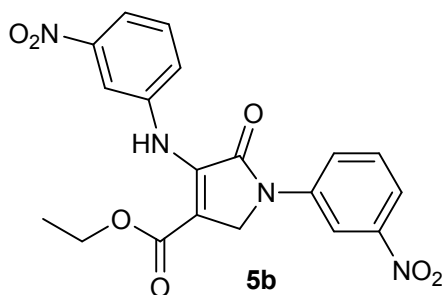
The ^{13}C NMR(100MHz)spectrum of product (5a)

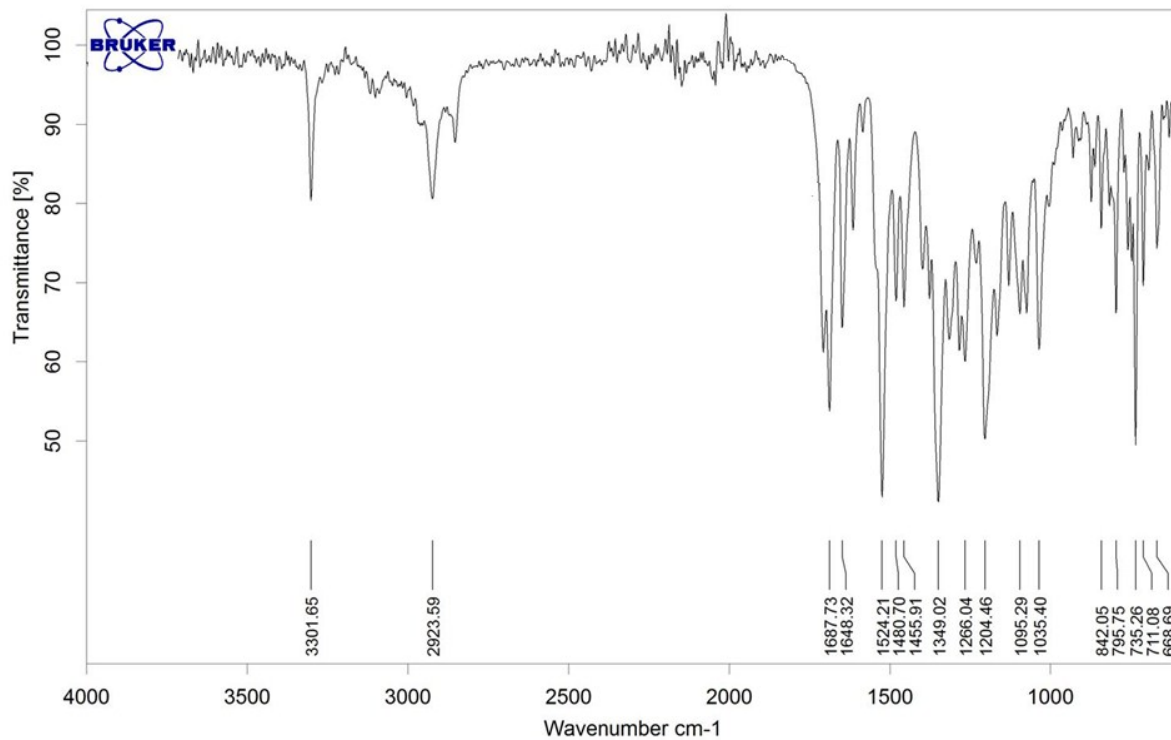


The MS spectrum of product (**5a**)

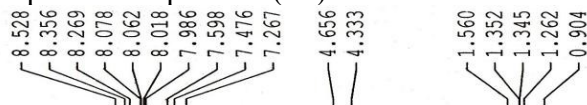
Ethyl-1-(3-nitrophenyl)-4-((3-nitrophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (**5b**)
(Table 2, entry 2)

white solid. M.p. 191-192 °C. FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3301, 2923, 1701, 1687, 1648, 1524, 1480, 1455, 1349, 1204, 1035, 735.; ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.52 (s, 1H, NH), 8.35 (br, s, 1H, Ar-H), 8.26 (s, 1H, Ar-H), 8.06 (d, 1H, ³J= 6.4 Hz, Ar-H), 7.99 (br, s, 2H, Ar-H), 7.59 (br, s, 1H, Ar-H), 7.47 (br, s, 2H, Ar-H), 4.65 (s, 2H, NCH₂), 4.33 (s, 2H, OCH₂CH₃), 1.34 (s, 3H, OCH₂CH₃).; ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 165.4, 162.8, 148.5, 148.0, 142.3, 139.9, 139.3, 131.0, 129.5 (2C), 126.9 (2C), 125.3 (2C), 119.5 (2C), 117.1, 114.8, 113.8, 109.7, 60.6, 49.1, 14.3.; MS (*m/z*): 412.3 (M⁺), 339.1, 219.2, 190.1, 174.1, 163.1, 150.1 (100%), 139.1, 128.1, 116.1, 103.1, 92, 76, 65, 51; Anal. Calcd for C₁₉H₁₆N₄O₇ C, 55.34; H, 3.91; N, 13.59; found C, 54.99; H, 4.21; N, 13.64.

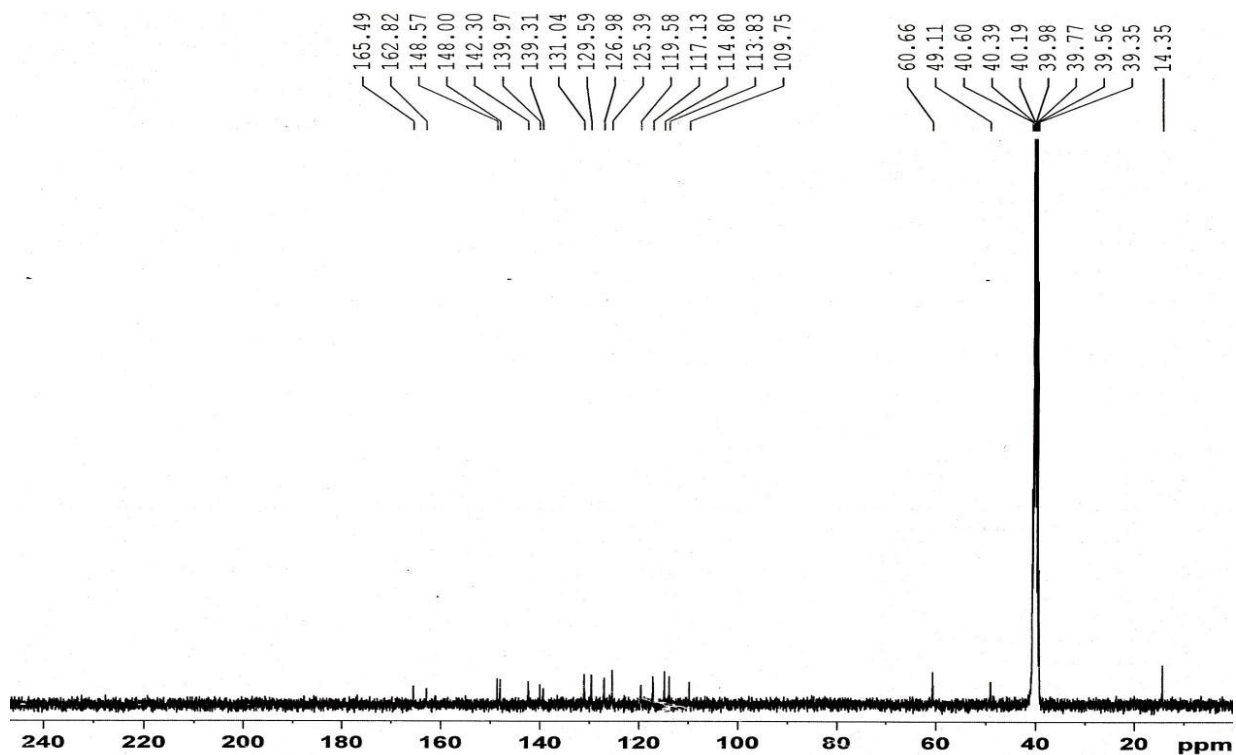




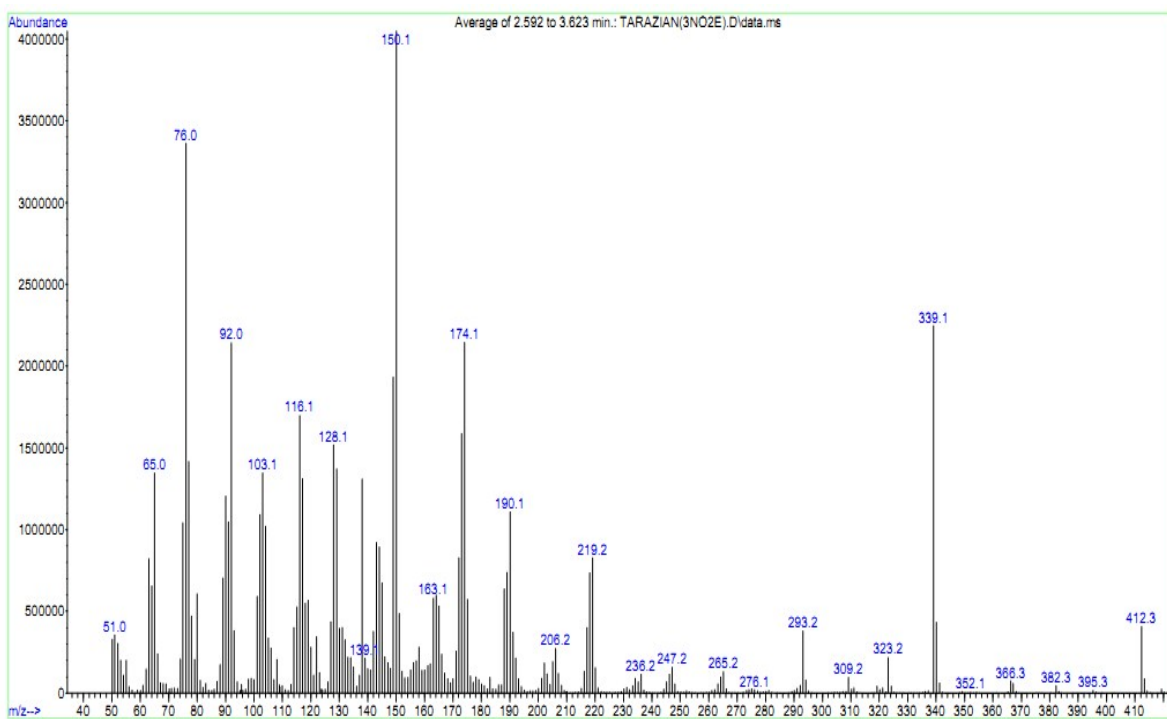
The FT-IR spectrum of product (5b)



The ¹H NMR(400MHz)spectrum of product (5b)



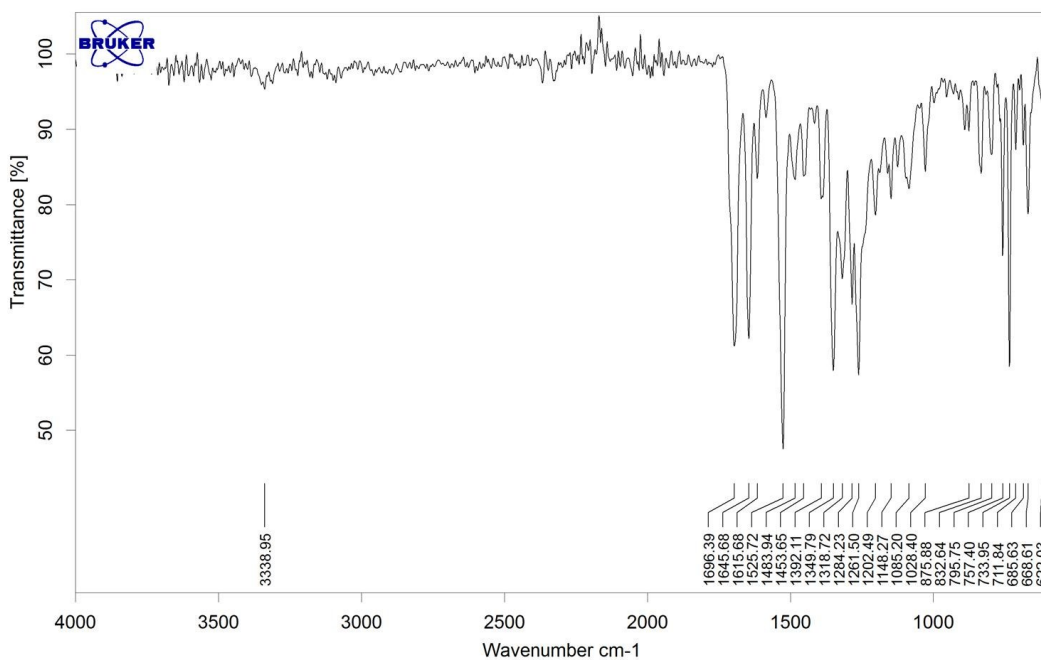
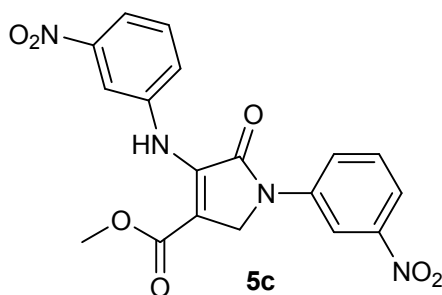
The ^{13}C NMR(100MHz)spectrumof product (**5b**)



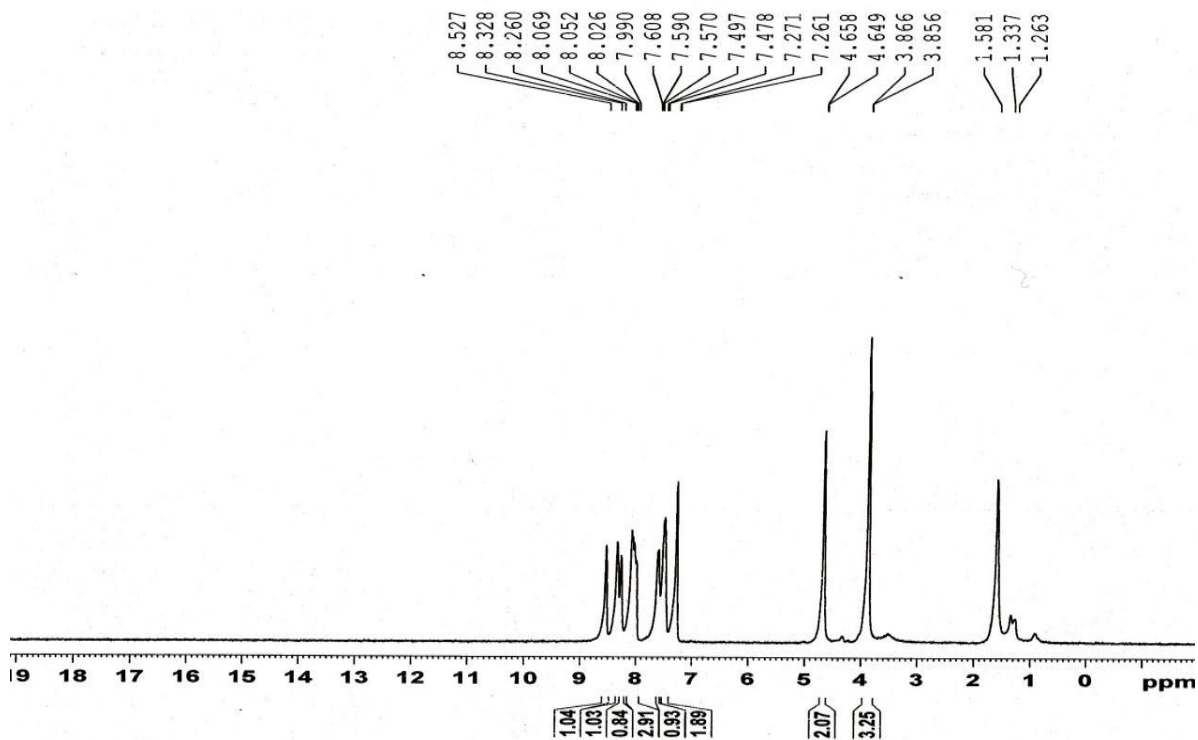
MSpectrumof product (**5b**)

Methyl-(3-nitrophenyl)-4-((3-nitrophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate
(5c) (Table 2, entry 3)

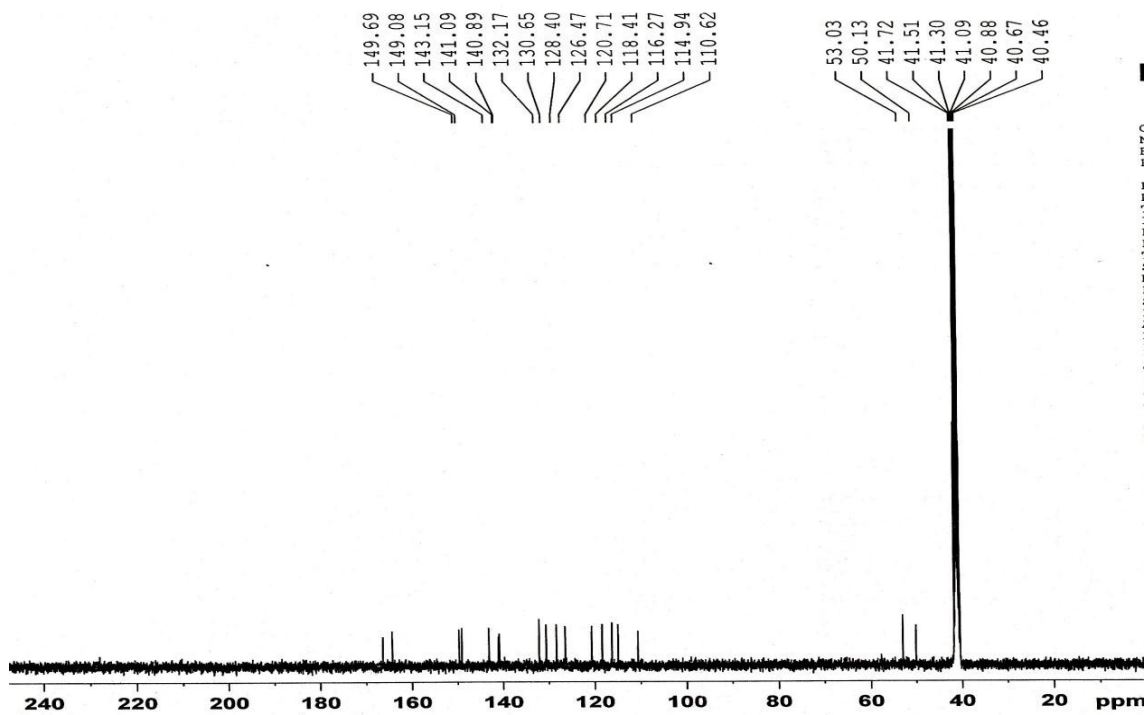
white solid. M.p. 204-206 °C. FT-IR (KBr)/ $\bar{\nu}(\text{cm}^{-1})$: 3338, 1696, 1645, 1615, 1625, 1483, 1349, 1318, 1284, 733. ^1H NMR (CDCl_3 , 400 MHz)/ δ ppm: 8.52 (br, s, 1H, NH), 8.32 (br, s, 1H, Ar-H), 8.26 (br, s, 1H, Ar-H), 8.03 (br, s, 3H, Ar-H), 7.59 (d, 1H, $^3J=7.2$ Hz, Ar-H), 7.48 (d, 2H, $^3J=7.6$ Hz, Ar-H), 4.65 (s, 2H, NCH_2), 3.85 (s, 3H, OCH_3).; ^{13}C NMR (CDCl_3 , 100 MHz)/ δ ppm: 165.2, 162.5, 149.6, 149.0, 143.1, 141.0, 140.8, 132.1, 130.6, 128.4, 126.4, 120.7, 118.4, 116.2, 114.9, 110.6, 53.0, 50.1.; MS (m/z): 398.3 (M^+), 339.3, 218.2, 190.2, 174.1, 164.1, 150.1, 138.1, 128.1, 116.1, 103.1, 92, 76 (100%), 65, 51; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_7$ C, 54.28; H, 3.54; N, 14.07; found C, 53.88; H, 3.74; N, 14.27.



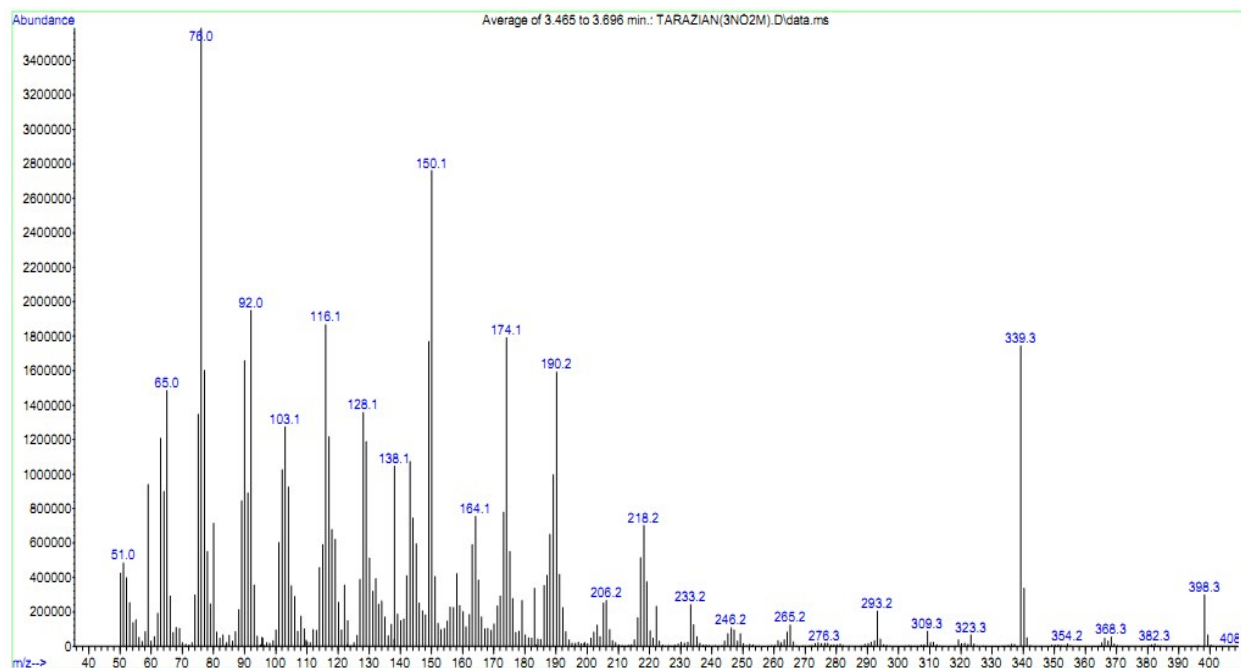
The FT-IR spectrum of product (5c)



The ¹H NMR (400 MHz) spectrum of product (5c)



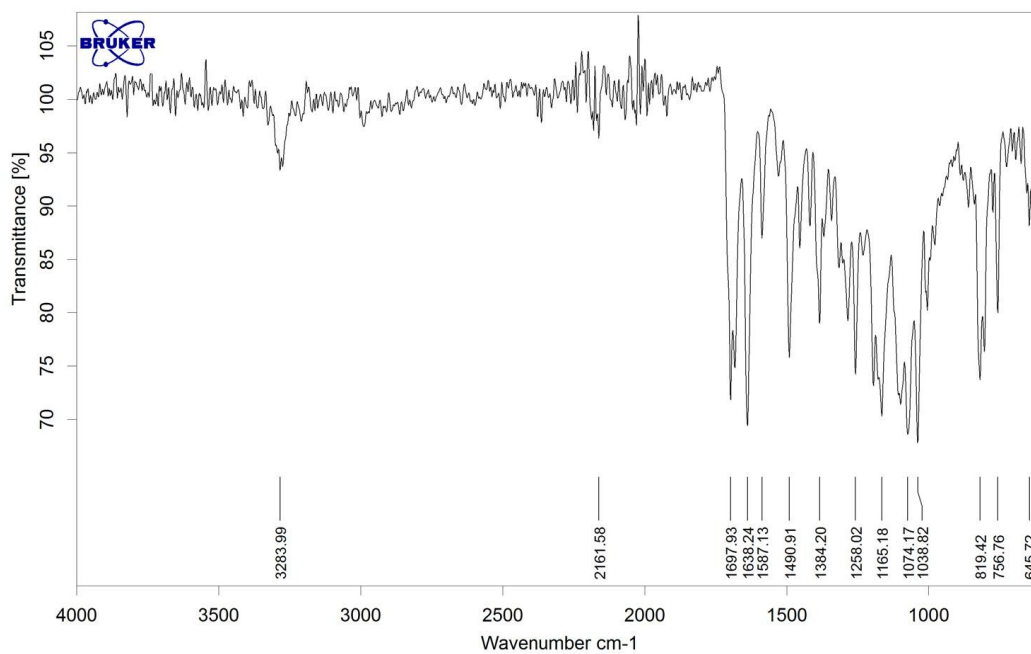
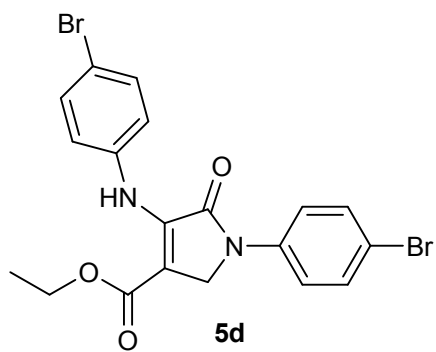
The ¹³C NMR (100 MHz) spectrum of product (5c)



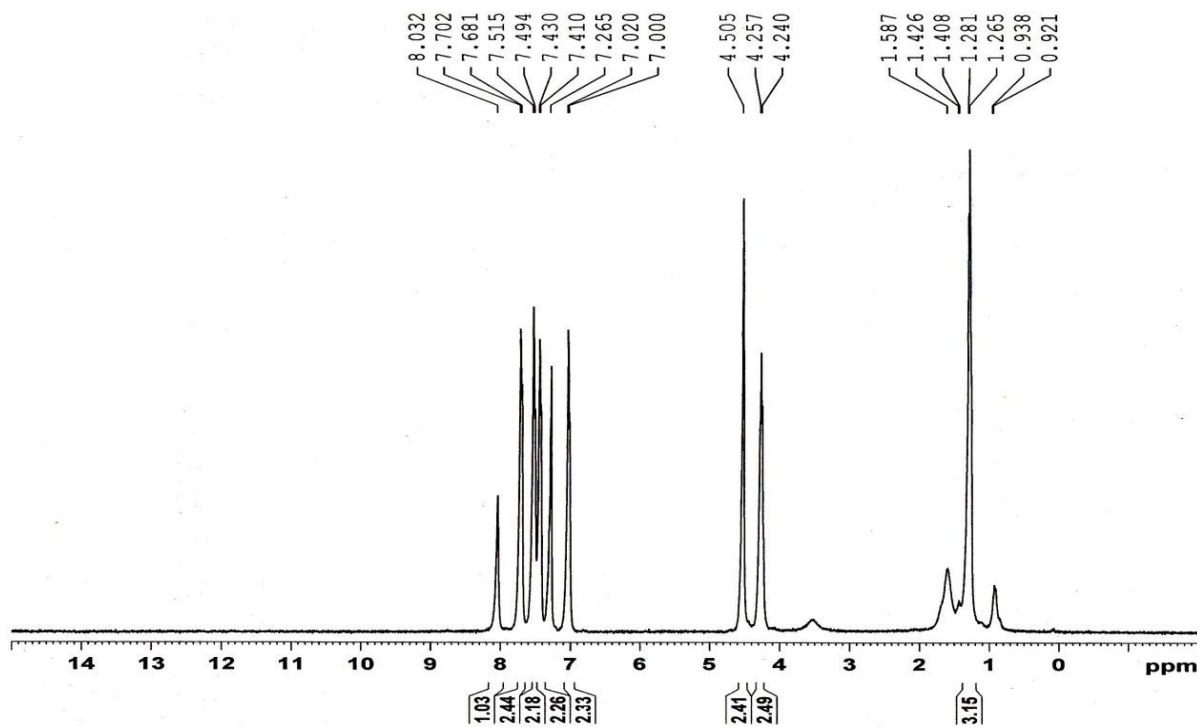
The MS spectrum of product (**5c**)

Ethyl-(4-bromophenyl)-4-((4-bromophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (**5d**)
(Table 2, entry 4)

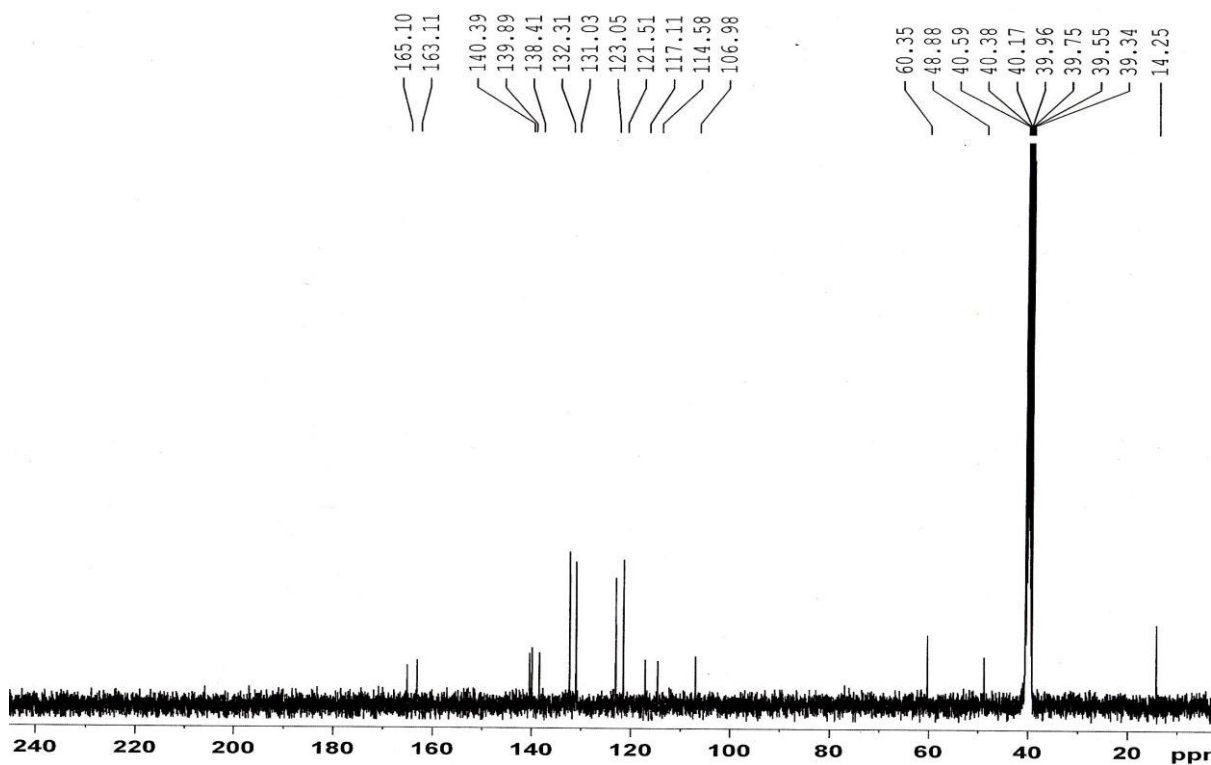
White solid. M.p. 165-166 °C (lit: 164-165 °C [22]). FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3283, 1697, 1638, 1587, 1490, 1384, 1258, 1165, 819.; ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.03 (br, s, 1H, NH), 7.69 (d, 2H, ³J= 8.4 Hz, Ar-H), 7.50 (d, 2H, ³J= 8.4 Hz, Ar-H), 7.42 (d, 2H, ³J= 8.0 Hz, Ar-H), 7.01 (d, 2H, ³J= 8.0 Hz, Ar-H), 4.50 (s, 2H, NCH₂), 4.24 (s, 2H, OCH₂CH₃), 1.27 (s, 3H, OCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 165.1, 163.1, 140.3, 139.8, 138.4, 132.3 (2C), 131.0 (2C), 123.0 (2C), 121.5 (2C), 117.1, 114.5, 106.9, 60.3, 48.8, 14.2.



The FT-IR spectrum of product (**5d**)



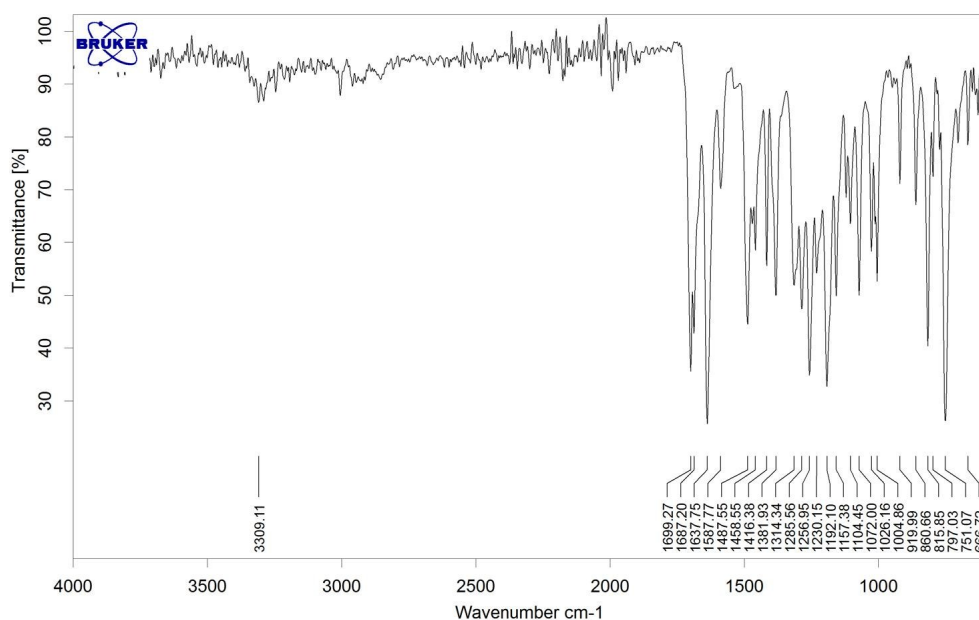
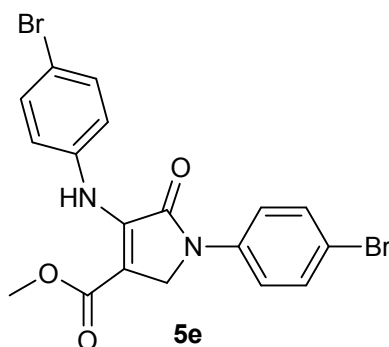
The ^1H NMR(400MHz)spectrum of product (5d)



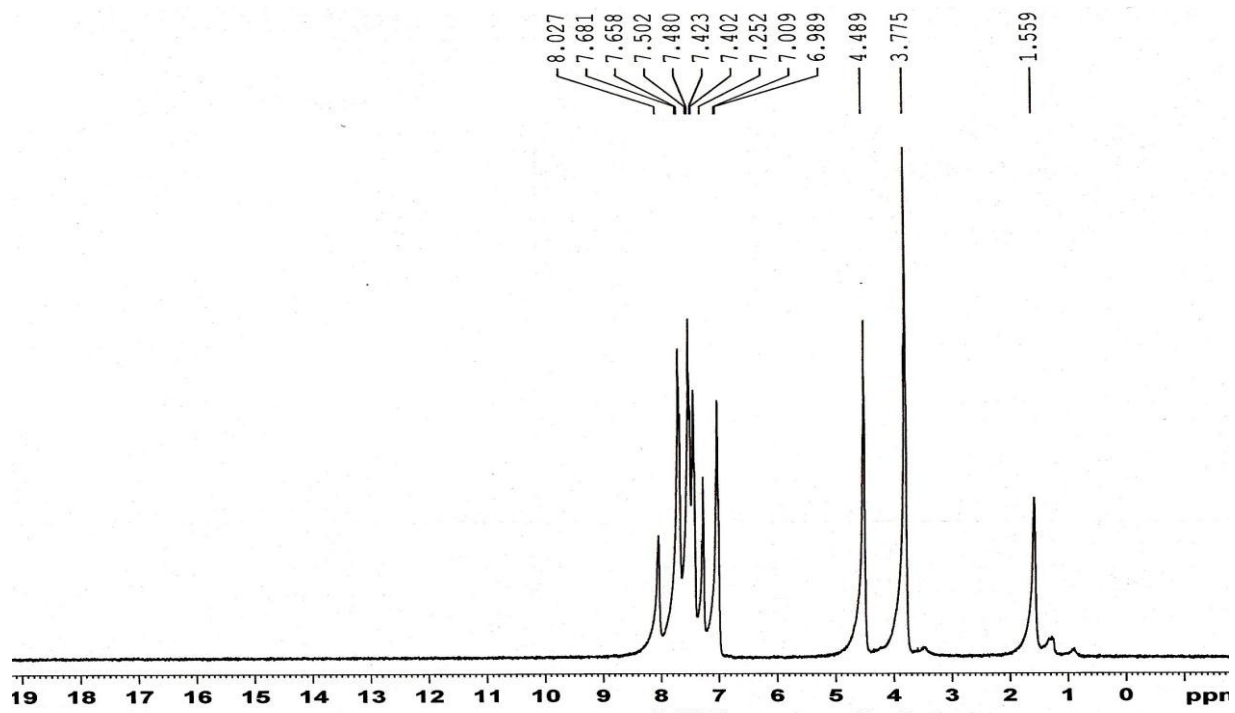
The ^{13}C NMR(100MHz)spectrum of product (5d)

Methyl-(4-bromophenyl)-4-((4-bromophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate(5e)
(Table 2, entry 5)

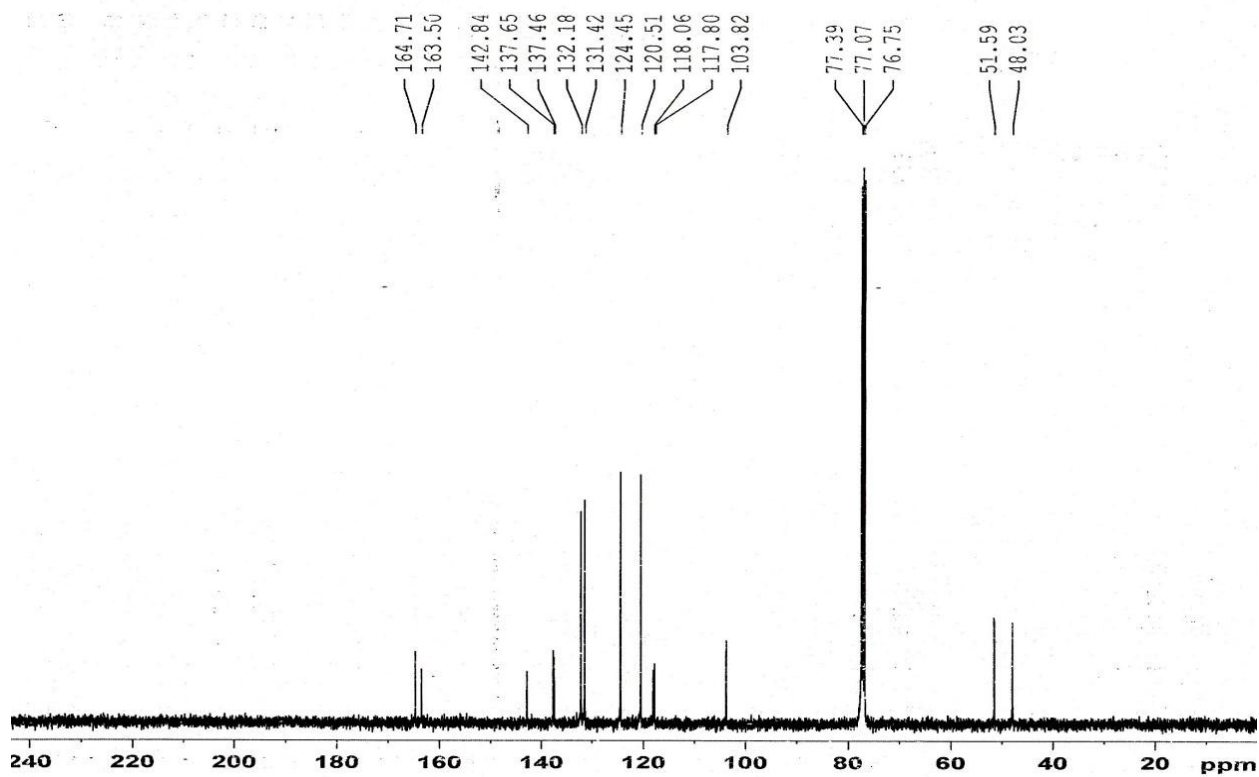
White solid.M.p. 181-182 °C (lit: 181-182 °C [22]). FT-IR (KBr)/ $\bar{\nu}(\text{cm}^{-1})$: 3309, 1699, 1687, 1637, 1587, 1487, 1381, 1192, 815. ^1H NMR (CDCl_3 , 400 MHz)/ δ ppm: 8.02 (br, s, 1H, NH), 7.66 (d, 2H, $^3J=9.2$ Hz, Ar-H), 7.49 (d, 3H, $^3J=8.8$ Hz, Ar-H), 7.41 (d, 1H, $^3J=8.4$ Hz, Ar-H), 6.99 (d, 2H, $^3J=8.0$ Hz, Ar-H), 4.48 (s, 2H, NCH_2), 3.77 (s, 3H, OCH_3). ^{13}C NMR (CDCl_3 , 100 MHz)/ δ ppm: 164.7, 163.5, 142.8, 137.6, 137.4, 132.1 (2C), 131.4 (2C), 124.4 (2C), 120.5 (2C), 118.0, 117.8, 103.8, 51.5, 48.03.



The FT-IR spectrum of product (5e)



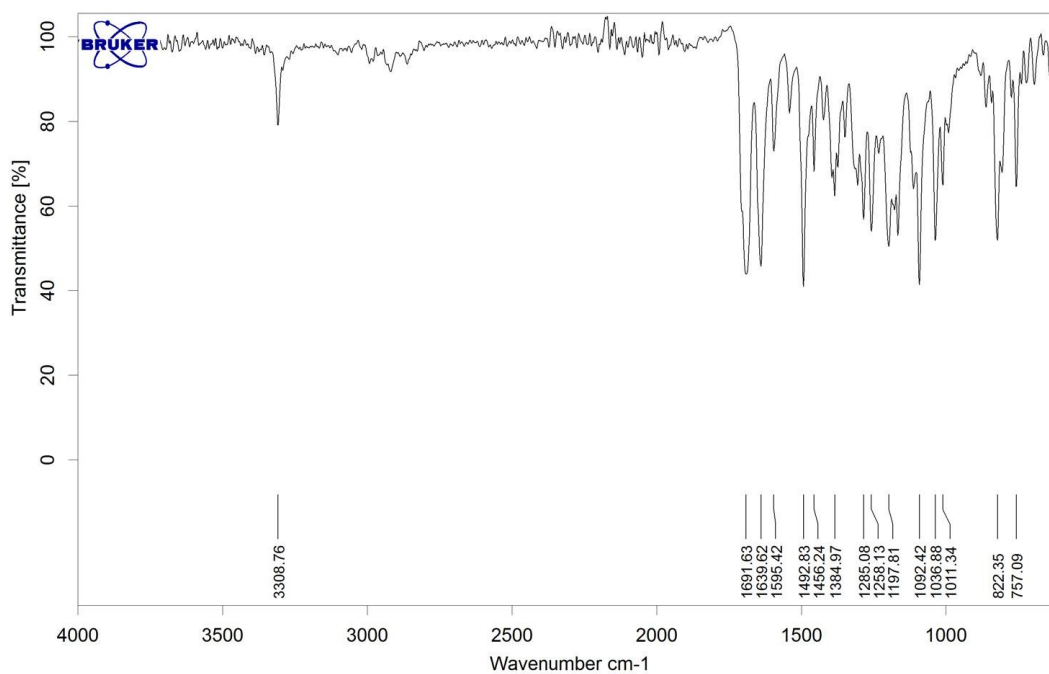
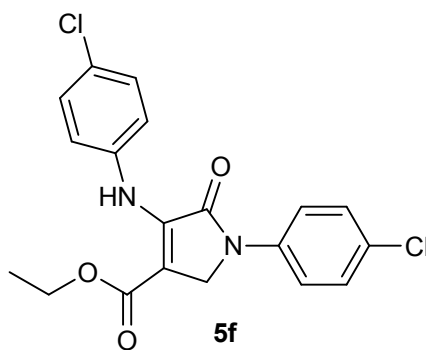
The ^1H NMR(400MHz)spectrum of product (5e)



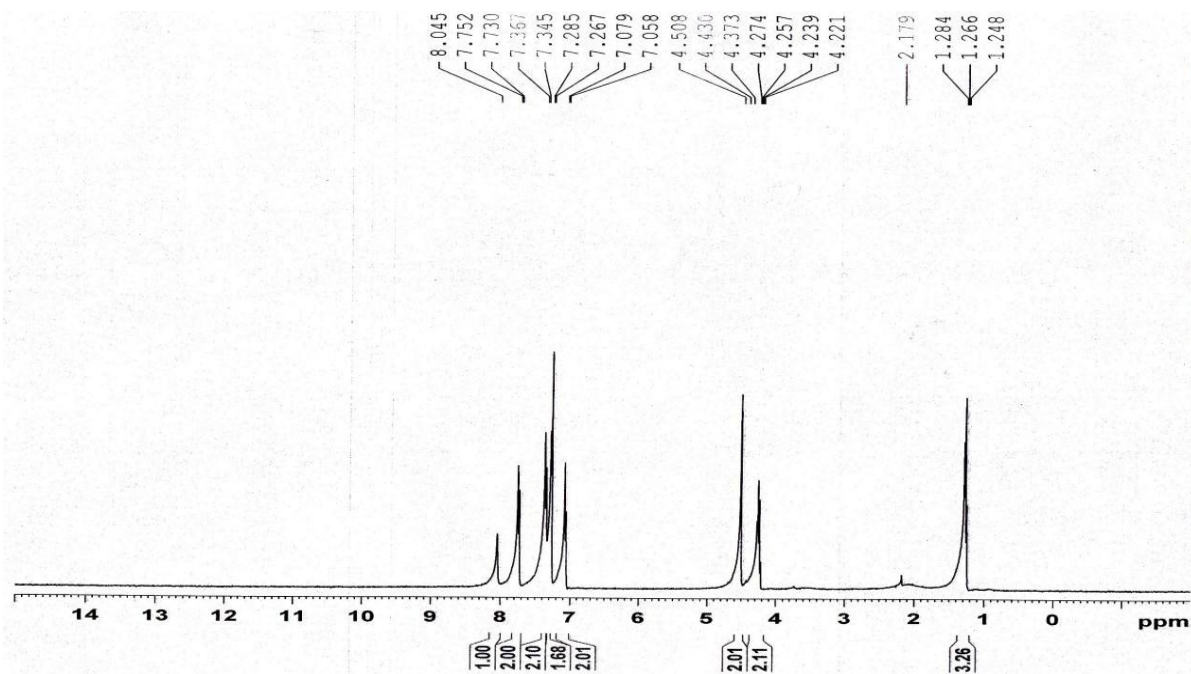
The ^{13}C NMR(100MHz)spectrum of product (5e)

Ethyl-1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate(5f)
(Table 2, entry 6)

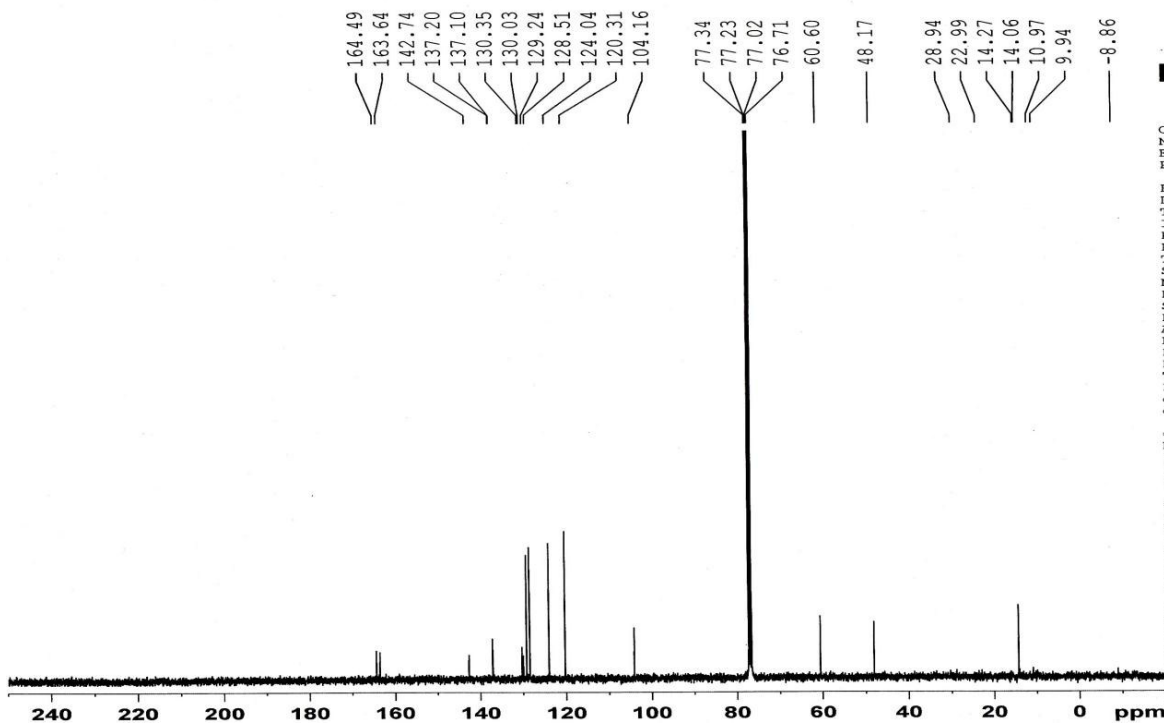
Whitesolid.M.p.165-167 °C (lit: 168-170 °C [26]). FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3308, 1691, 1639, 1595, 1492, 1456, 1384, 1197, 822. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.04 (s, 1H, NH), 7.74 (d, 2H, ³J= 8.8 Hz, Ar-H), 7.35 (d, 2H, ³J= 7.6 Hz, ³J= 8.8 Hz, Ar-H), 7.27 (d, 2H, ³J= 7.6 Hz, Ar-H), 7.06 (d, 2H, ³J= 8.4 Hz, Ar-H), 4.50 (s, 2H, NCH₂), 4.24 (q, 3H, ³J= 7.2 Hz, OCH₂CH₃), 1.26 (t, 3H, ³J= 7.2 Hz, OCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 164.4, 163.6, 142.7, 137.2, 137.1, 130.3, 130.0, 129.2 (2C), 128.5 (2C), 124.0 (2C), 120.3 (2C), 104.1, 60.6, 48.1, 14.0.



The FT-IR spectrum of product (5f)



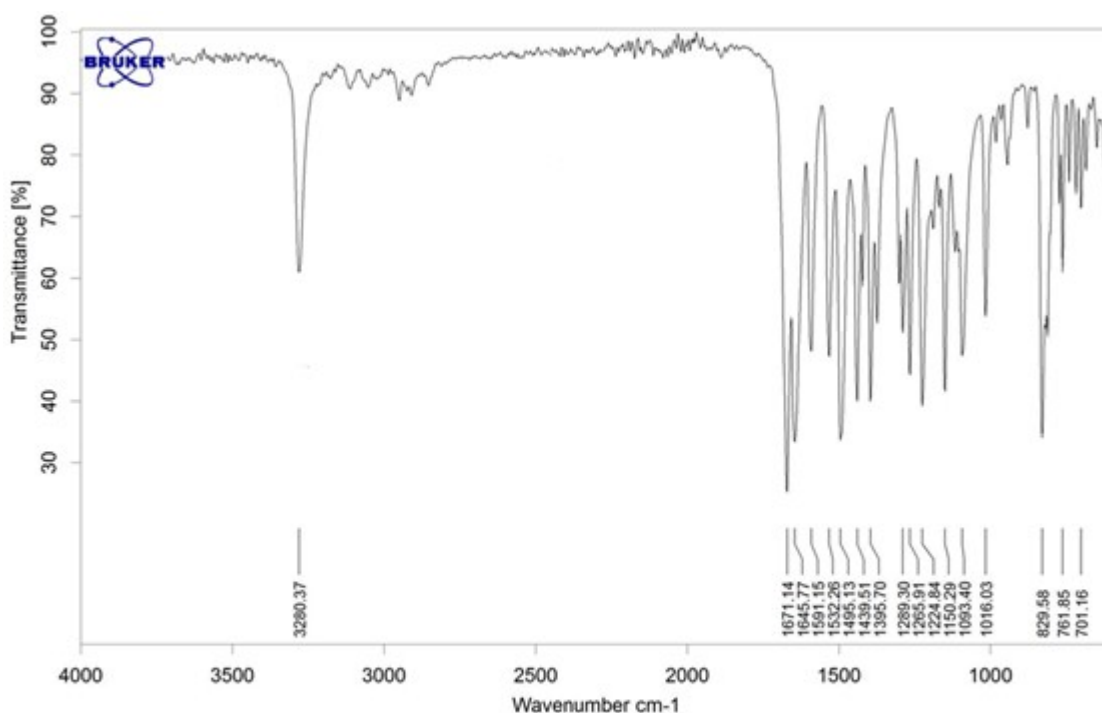
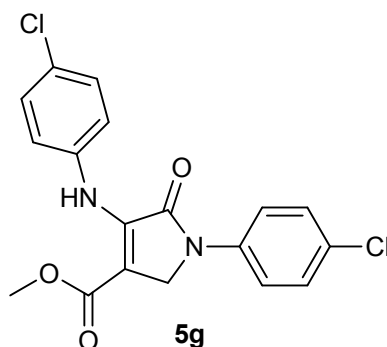
The ^1H NMR(400MHz)spectrum of product (**5f**)



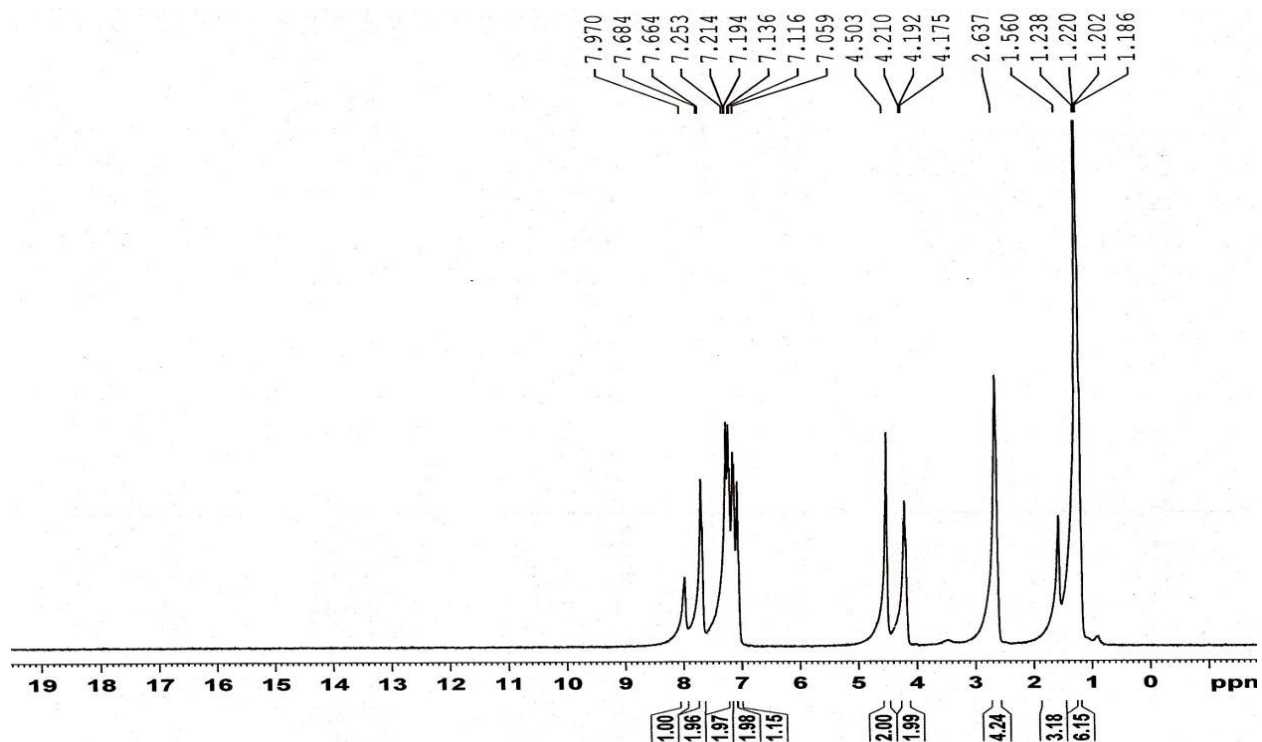
^{13}C NMR(100MHz)spectrum of product (**5f**)

Methyl-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (**5g**) (Table 2, entry 7)

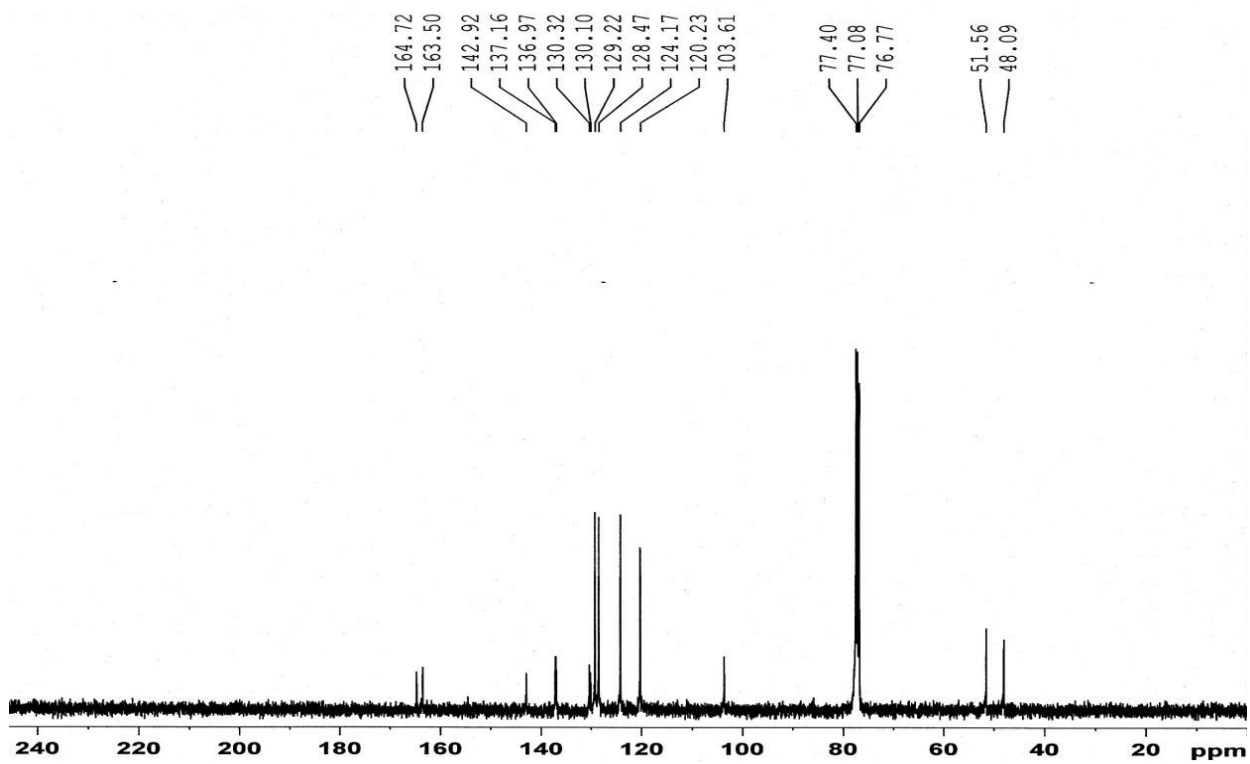
Cream solid. M.p. 173-174 °C (lit: 175-176 °C [25]). FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3280, 1671, 1645, 1591, 1532, 1495, 1439, 1395, 1289, 1224, 1150, 1093, 829. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.05 (br, s, 1H, NH), 7.73 (d, 2H, 3J= 6.4 Hz, Ar-H), 7.35 (s, 3H, Ar-H), 7.27 (d, 1H, 3J= 7.6 Hz, Ar-H), 7.07 (s, 2H, Ar-H), 4.50 (s, 2H, NCH₂), 3.78 (s, 3H, OCH₃). ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 164.7, 163.5, 142.9, 137.1, 136.9, 130.3, 130.1, 129.2 (2C), 128.4 (2C), 124.1 (2C), 120.2 (2C), 103.6, 51.5, 48.0.



The FT-IR spectrum of product (**5g**)



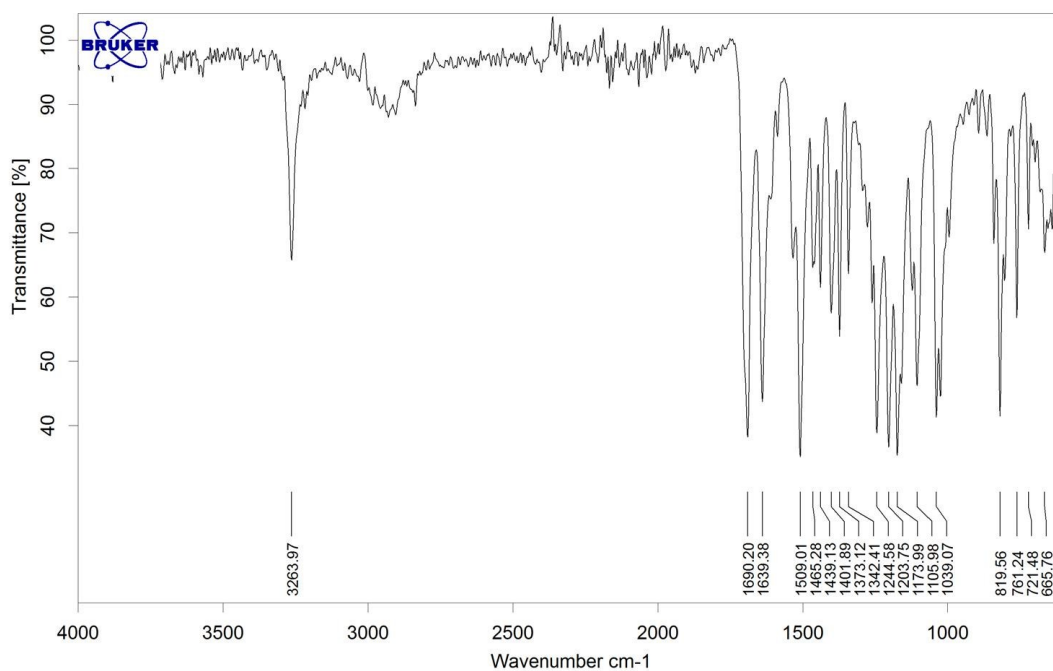
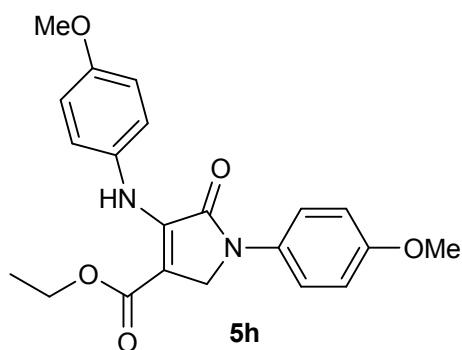
The ^1H NMR(400MHz)spectrum of product (5g)



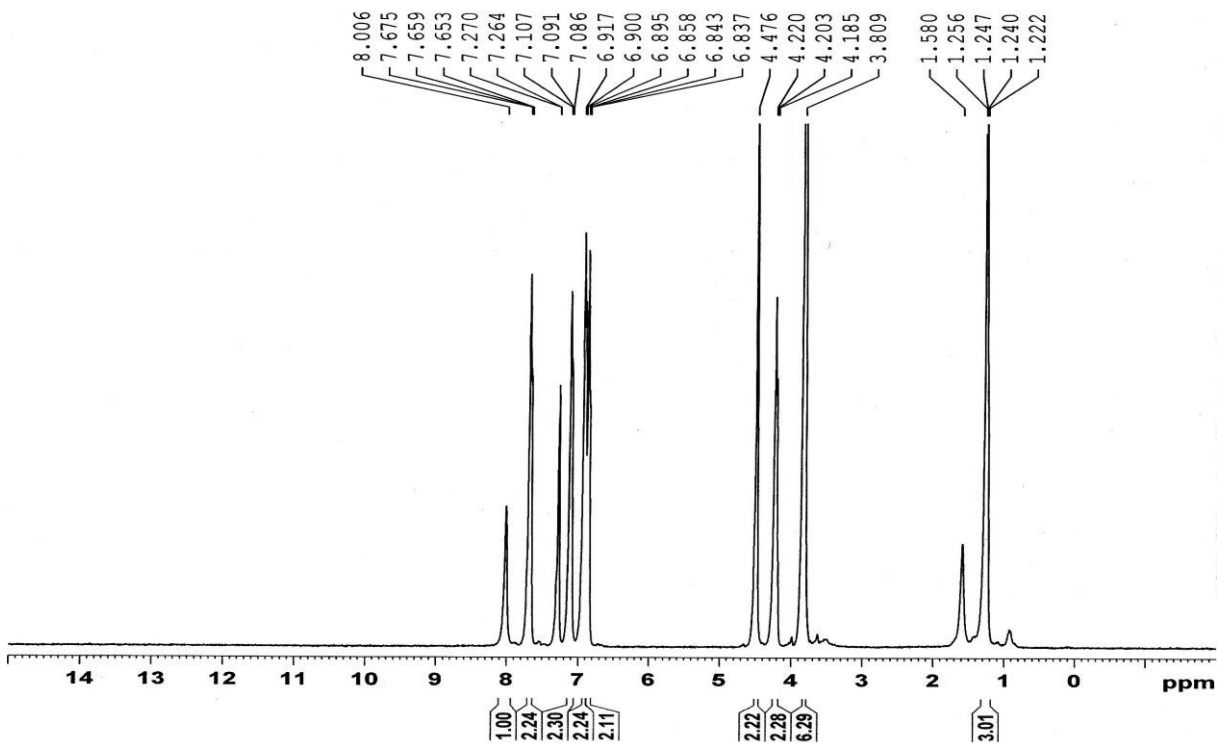
The ^{13}C NMR(100MHz)spectrum of product (5g)

Ethyl-4-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate
(**5h**) (Table 2, entry 8)

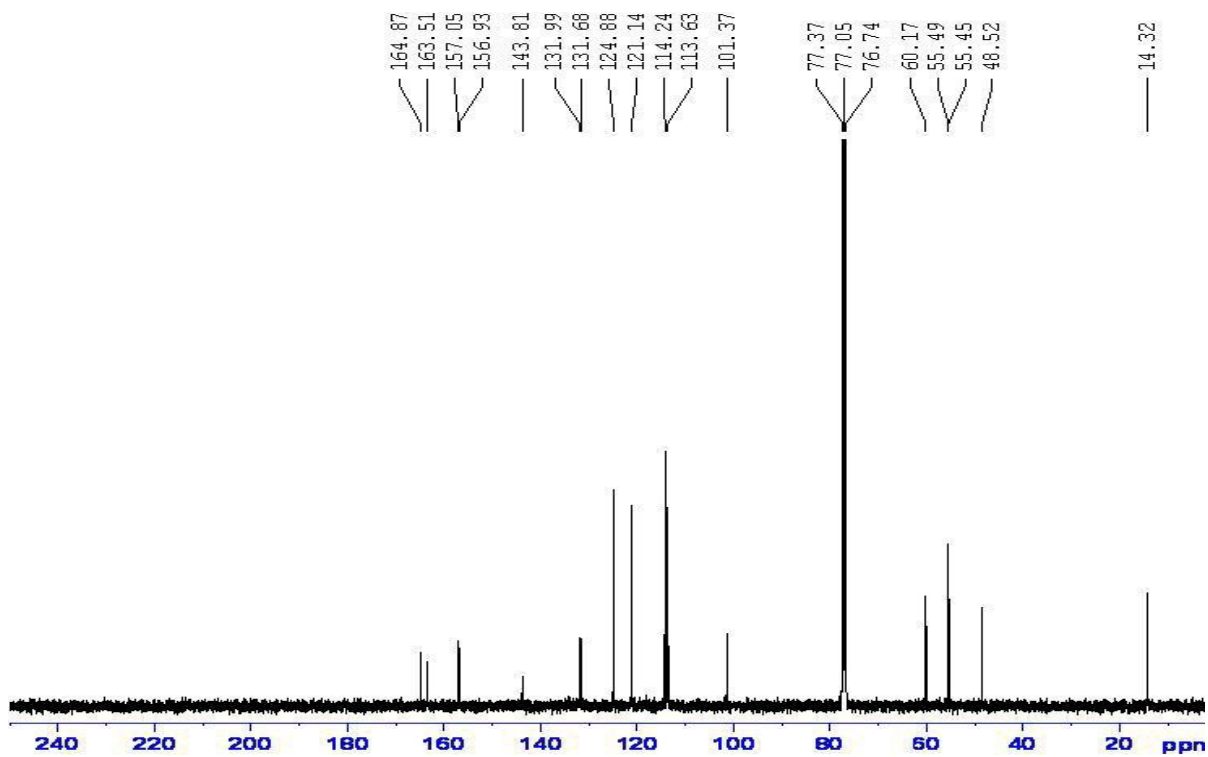
White solid. M.p. 152-154 °C (lit: 152-154 °C [25]). FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3263, 1690, 1639, 1509, 1465, 1439, 1373, 1244, 1173, 1105, 1039, 819. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.00 (br, s, 1H, NH), 7.65 (br, s, 2H, Ar-H), 7.09 (br, s, 2H, Ar-H), 6.90 (br, s, 2H, Ar-H), 6.84 (br, s, 2H, Ar-H), 4.47 (s, 2H, NCH₂), 4.20 (s, 2H, OCH₂CH₃), 3.80 (s, 6H, Ar-OMe), 1.24 (s, 3H, OCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 164.8, 163.5, 157.0, 156.9, 131.9, 131.6, 124.8 (2C), 121.1 (2C), 114.2 (2C), 113.6 (2C), 101.3, 60.1, 55.4, 55.4, 48.5, 14.3.



The FT-IR spectrum of product (**5h**)



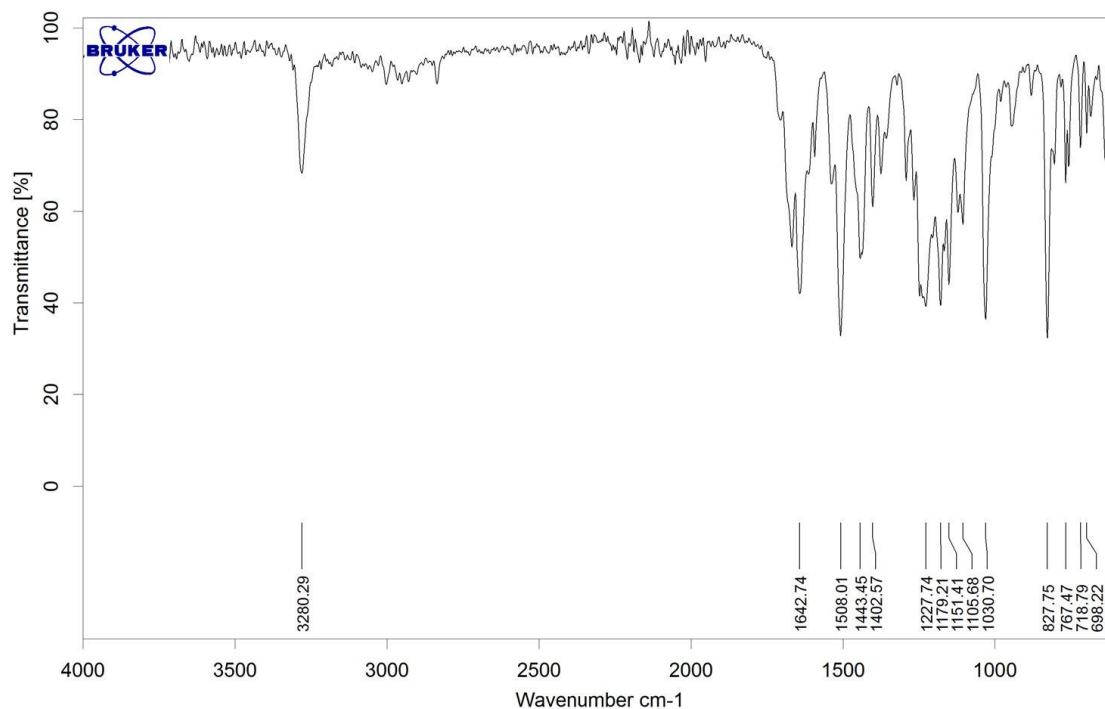
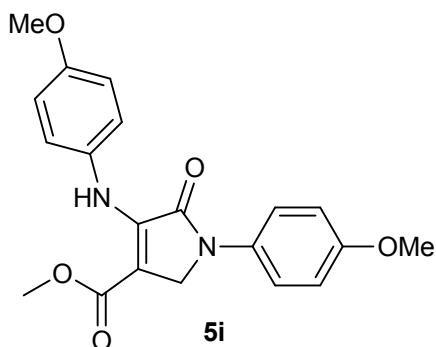
The ¹H NMR(400MHz)spectrum of product (5h)



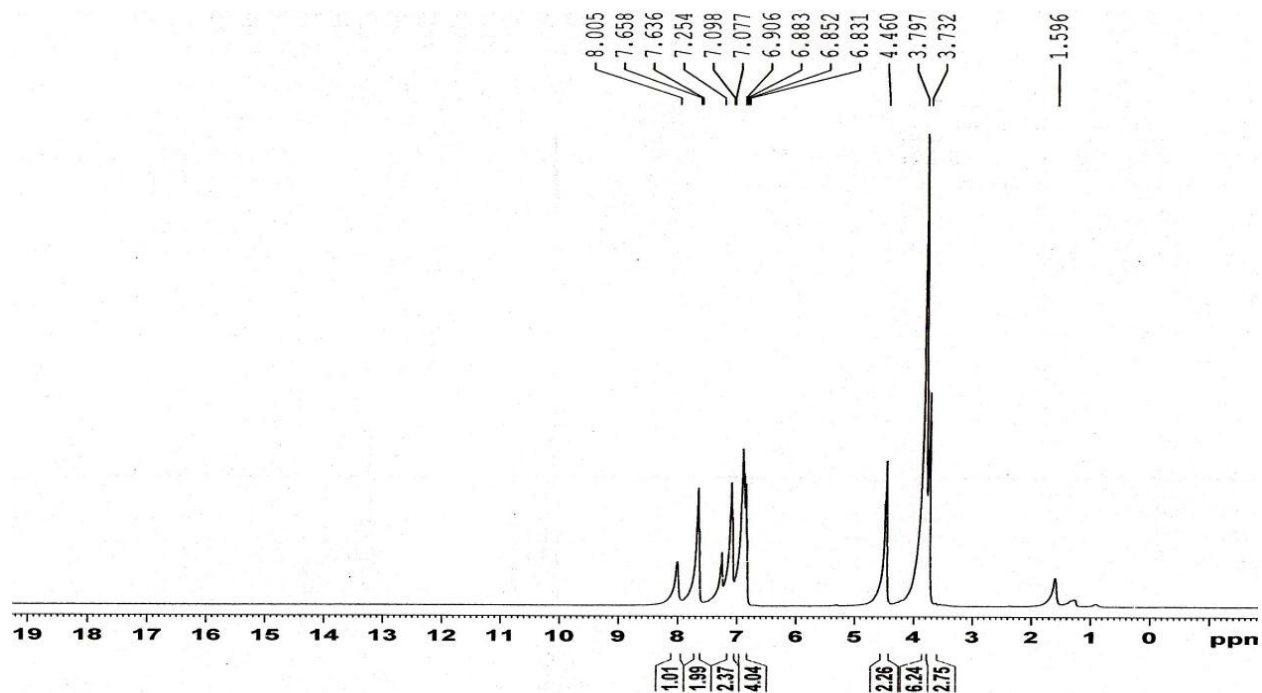
The ¹³C NMR(100MHz)spectrum of product (5h)

Methyl-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate(5i) (Table 2, entry 9)

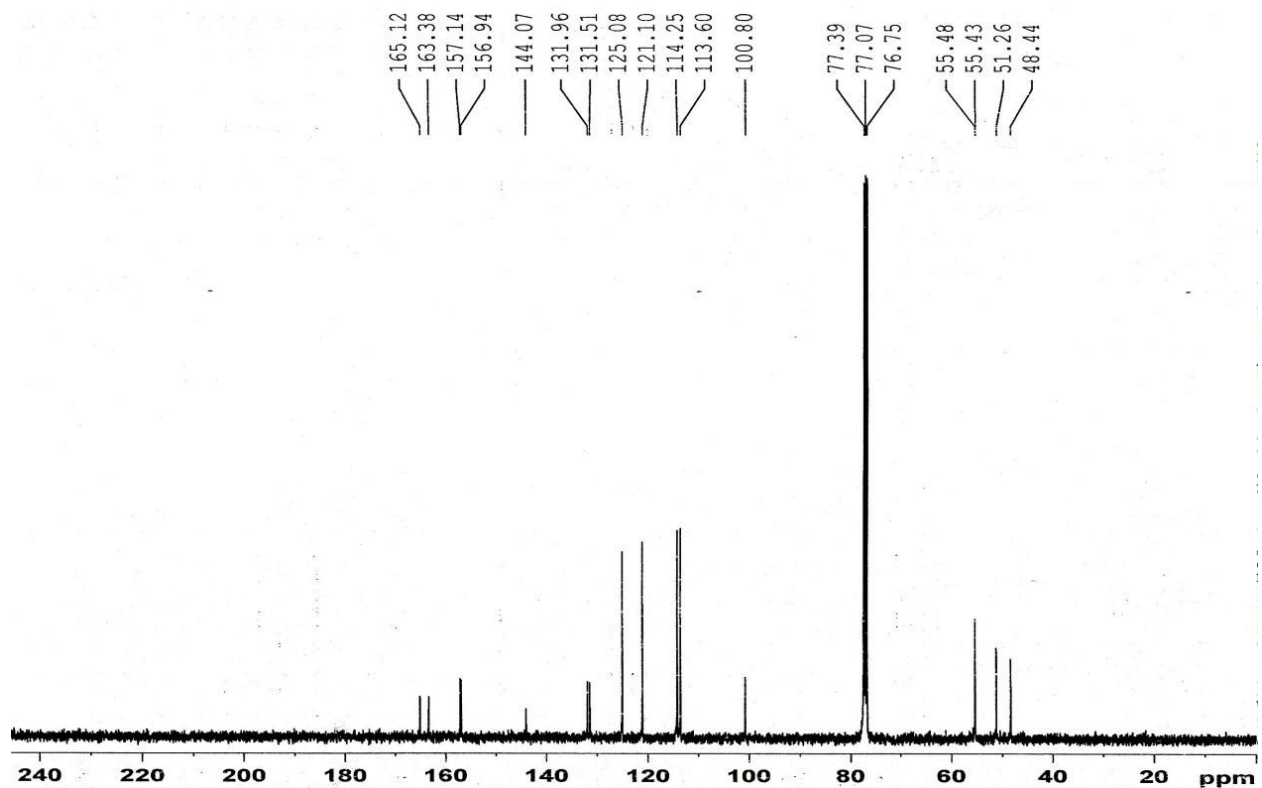
White solid. M.p. 160-162 °C. FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3280, 1642, 1508, 1509, 1443, 1402, 1270, 1179, 1151, 1030. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.00 (br, s, 1H, NH), 7.64 (d, 2H, ³J= 8.8 Hz, Ar-H), 7.08 (d, 2H, ³J= 8.4 Hz, Ar-H), 6.89 (d, 2H, ³J= 8.4 Hz, Ar-H), 6.84 (d, 2H, ³J= 8.4 Hz, Ar-H), 4.46 (br, s, 2H, NCH₂), 3.79 (s, 6H, ArOCH₃), 3.73 (s, 3H, OCH₃).; ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 165.1, 163.3, 157.1, 156.9, 144.0, 131.9, 131.5, 125.0 (2C), 121.1 (2C), 114.2 (2C), 113.6 (2C), 100.8, 55.5, 55.4, 51.2, 48.4.



The FT-IR spectrum of product (5i)



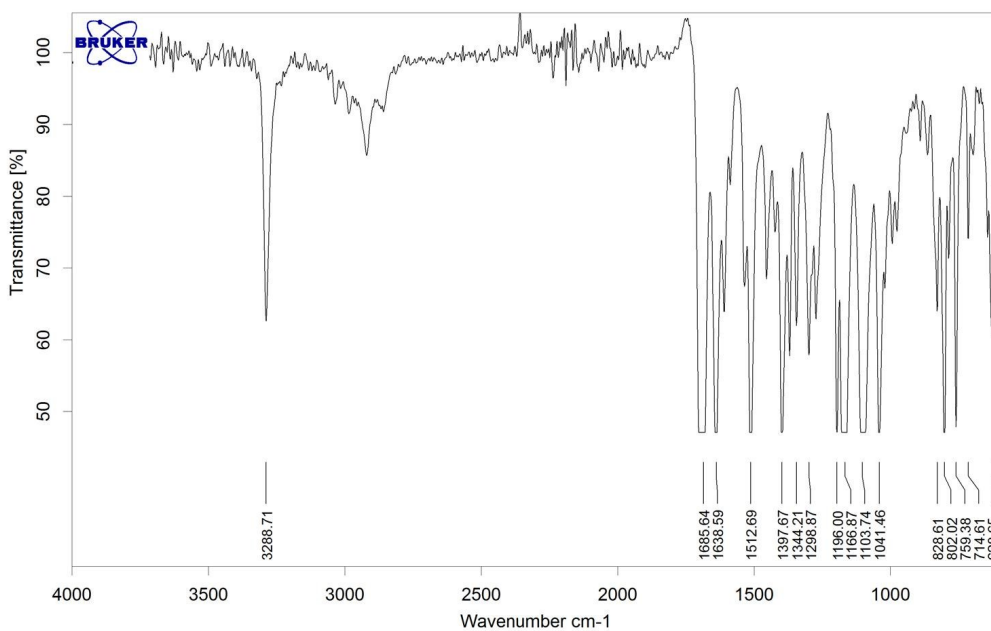
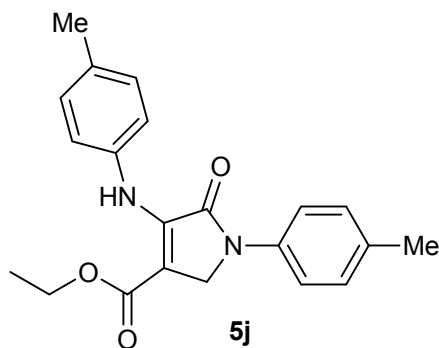
The ^1H NMR(400MHz)spectrum of product (5i)



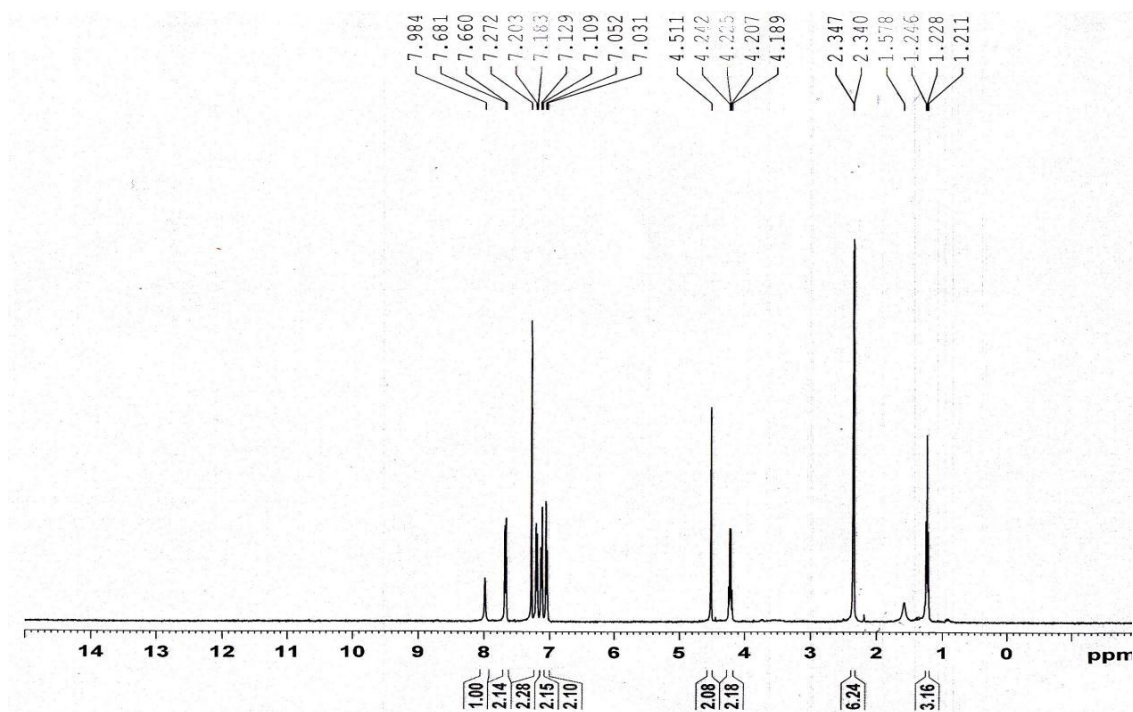
The ^{13}C NMR(100MHz)spectrum of product (5i)

Ethyl 5-oxo-1-(p-tolyl)-4-(p-tolylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate(5j) (Table 2, entry 10)

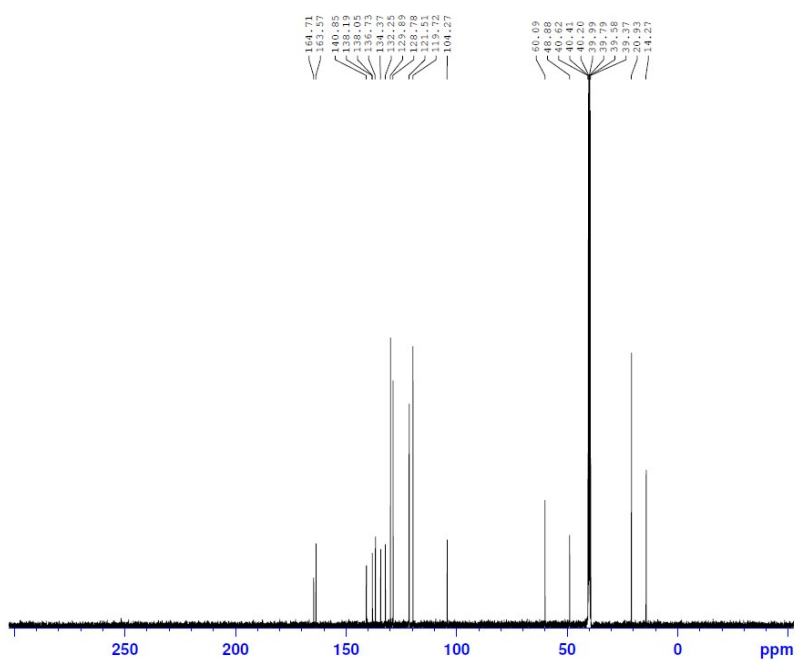
Cream solid. M.p. 128 °C (lit: 131-132 °C [23]). FT-IR (KBr)/ $\bar{\nu}(\text{cm}^{-1})$: 3288, 1685, 1638, 1512, 1397, 1344, 1298, 1196, 1041. ^1H NMR (CDCl_3 , 400 MHz)/ δ ppm: 7.98 (br, s, 2H, NH), 7.67 (d, 2H, $^3J=8.4$ Hz, Ar-H), 7.19 (d, 2H, $^3J=8.0$ Hz, Ar-H), 7.11 (d, 2H, $^3J=8.0$ Hz, Ar-H), 7.04 (d, 2H, $^3J=8.4$ Hz, Ar-H), 4.51 (s, 2H, NCH_2), 4.21 (q, 2H, $^3J=7.2$ Hz, OCH_2), 2.34 (d, 6H, $^3J=2.8$ Hz, Ar-Me), 1.22 (t, 3H, $^3J=7.2$ Hz, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz)/ δ ppm: 164, 163, 140, 138 (2C), 136, 134, 132, 129, 128, 121, 119, 104, 60, 48, 20, 14.



The FT-IR spectrum of product (5j)

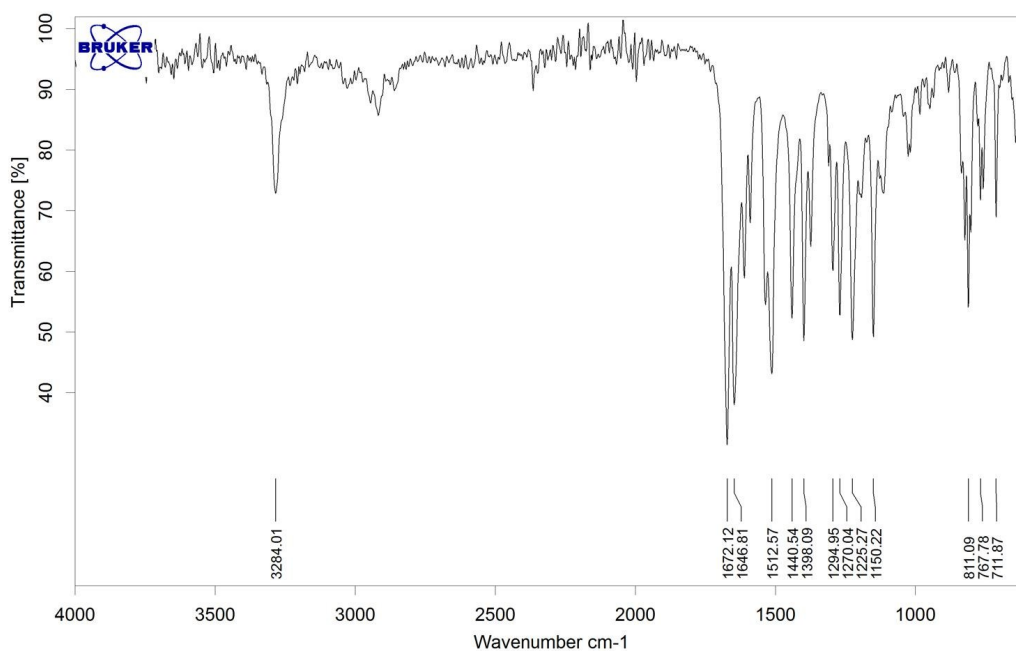
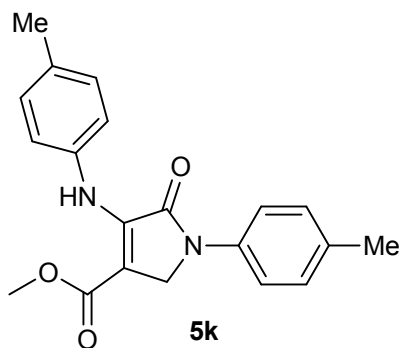


The ¹H NMR(400MHz)spectrum of product (5j)

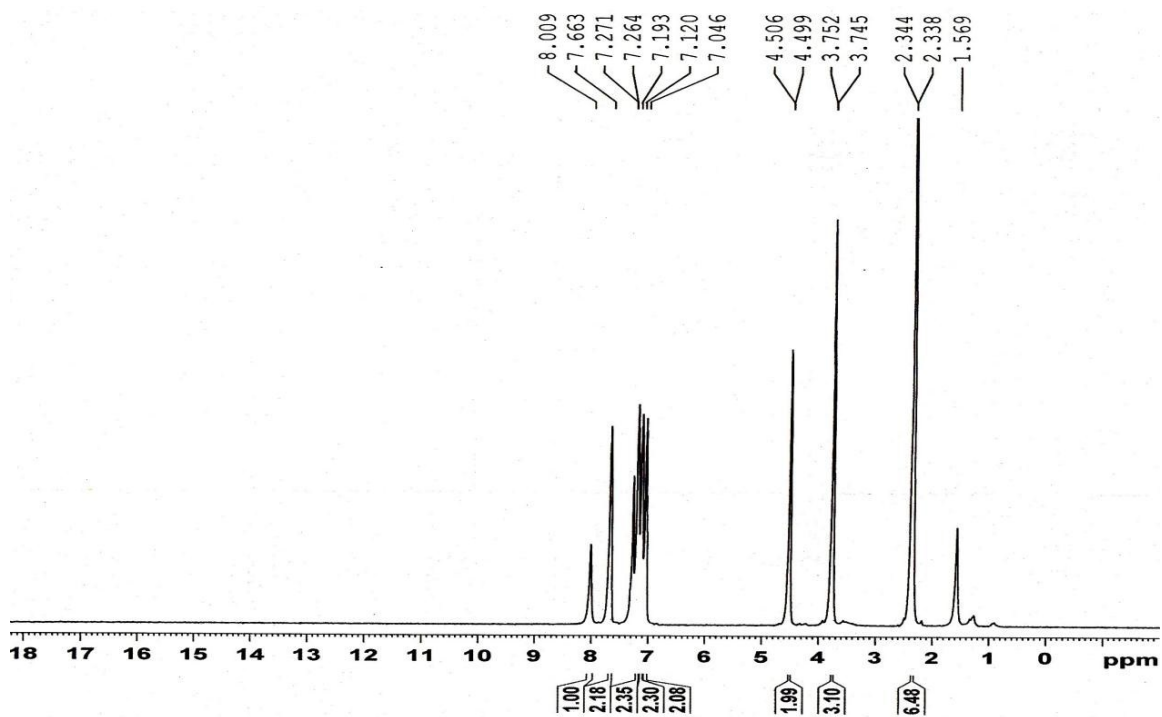


The ¹³C NMR(100MHz)spectrum of product (5j)

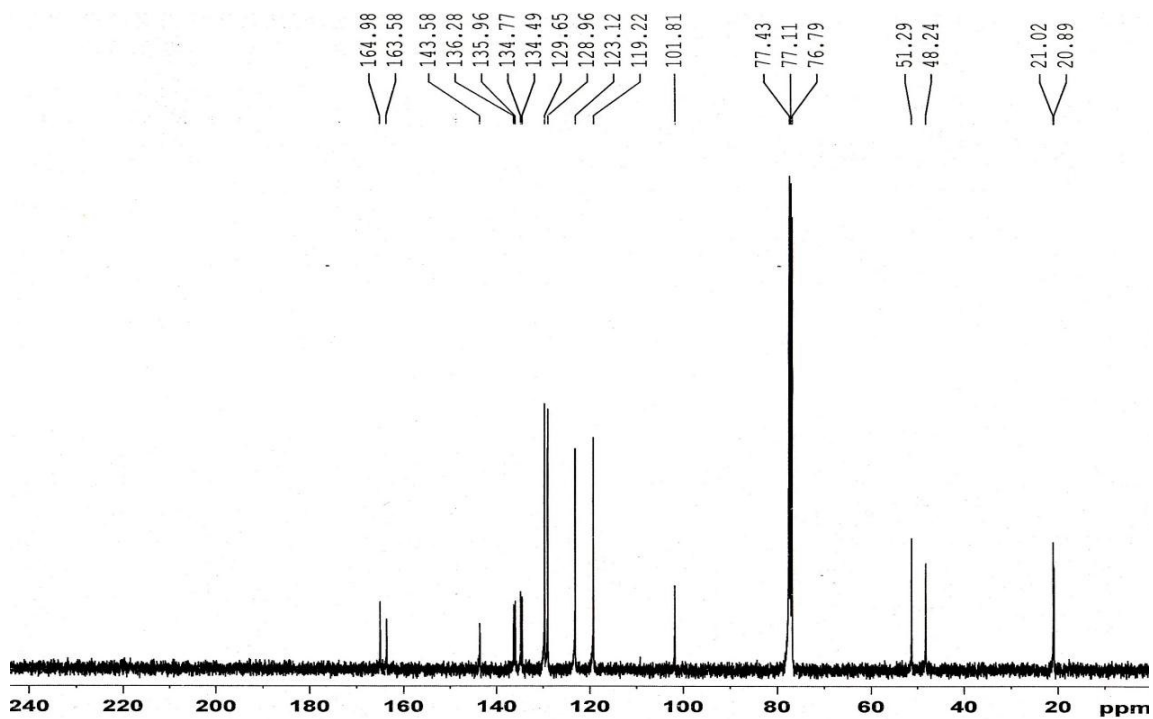
Methyl 5-oxo-1-(p-tolyl)-4-(p-tolylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate (5k) (Table 2, entry 11)
Pale yellow solid. M.p. 175-176 °C (lit: 175-176 °C [22]). FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3284, 1672, 1646, 1512, 1440, 1398, 1225, 1151. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.00 (br, s, 1H, NH), 7.66 (br, s, 2H, Ar-H), 7.19 (br, s, 2H, Ar-H), 7.12 (br, s, 2H, Ar-H), 7.04 (br, s, 2H, Ar-H), 4.50 (s, 2H, NCH₂), 3.75 (s, 3H, OCH₃), 2.34 (s, 6H, Ar-Me). ¹³C NMR (CDCl₃, 100 MHz)/ δ ppm: 164.9, 163.5, 143.5, 136.2, 135.9, 134.7, 134.4, 129.6 (2C), 128.9 (2C), 123.1 (2C), 119.2 (2C), 101.8, 51.2, 48.2, 21.0, 20.8.



The FT-IR spectrum of product (**5k**)



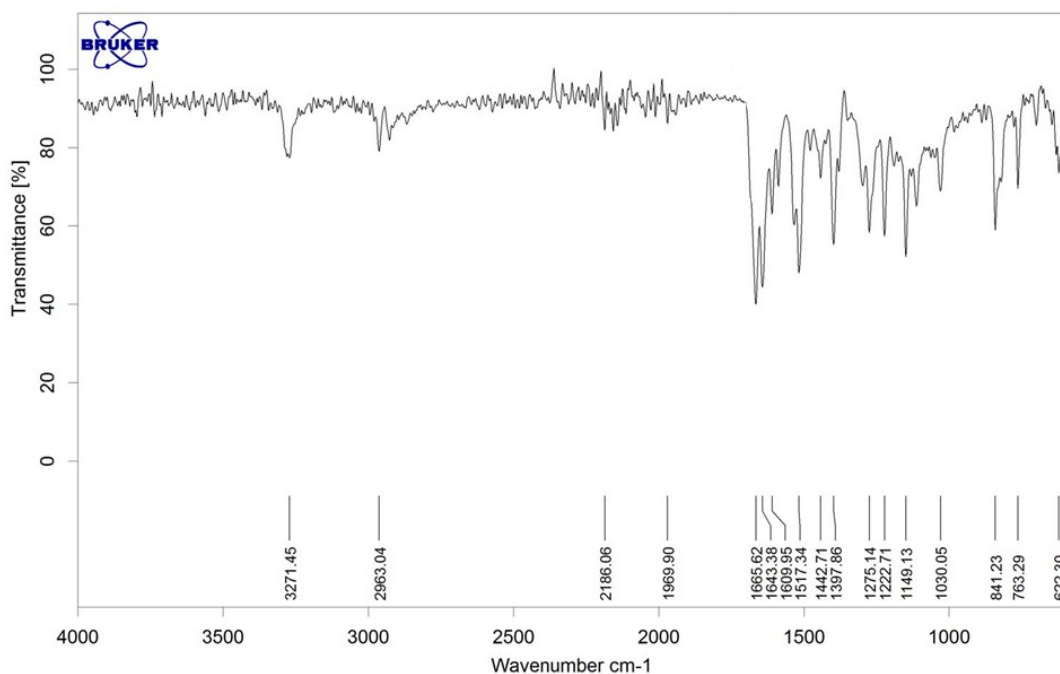
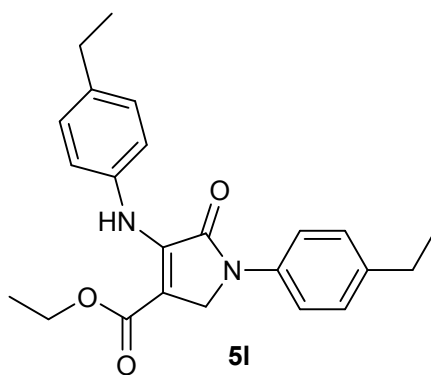
The ¹H NMR(400MHz)spectrum of product (**5k**)



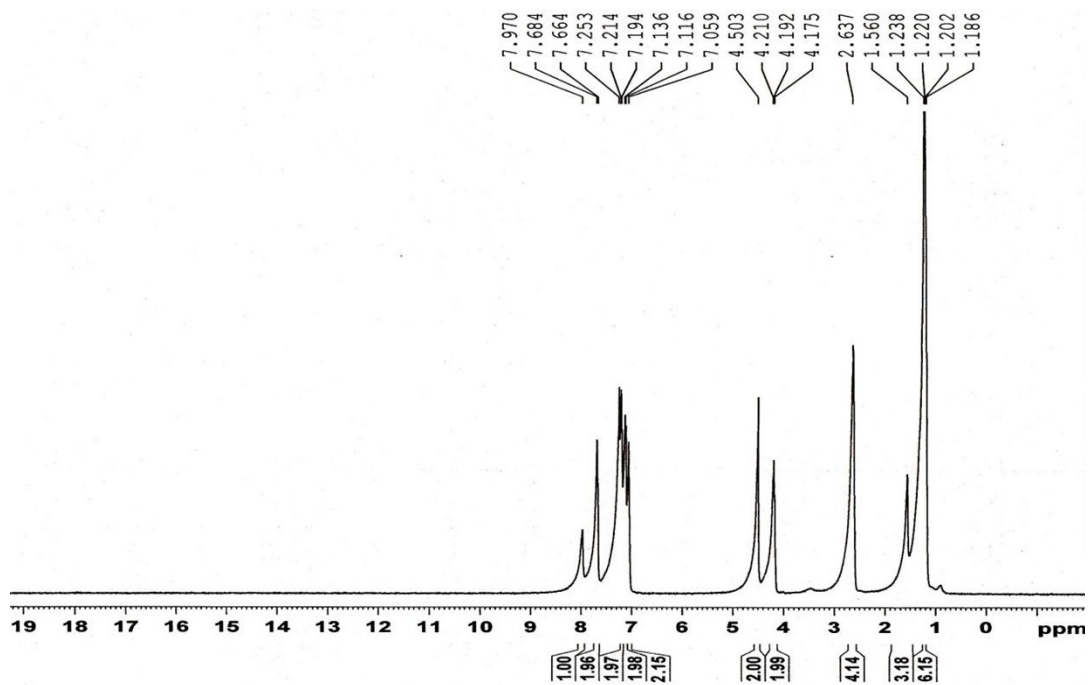
The ¹³C NMR(100MHz)spectrum of product (**5k**)

Ethyl-1-(4-ethylphenyl)-4-((4-ethylphenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (5l) (Table 2, entry 12)

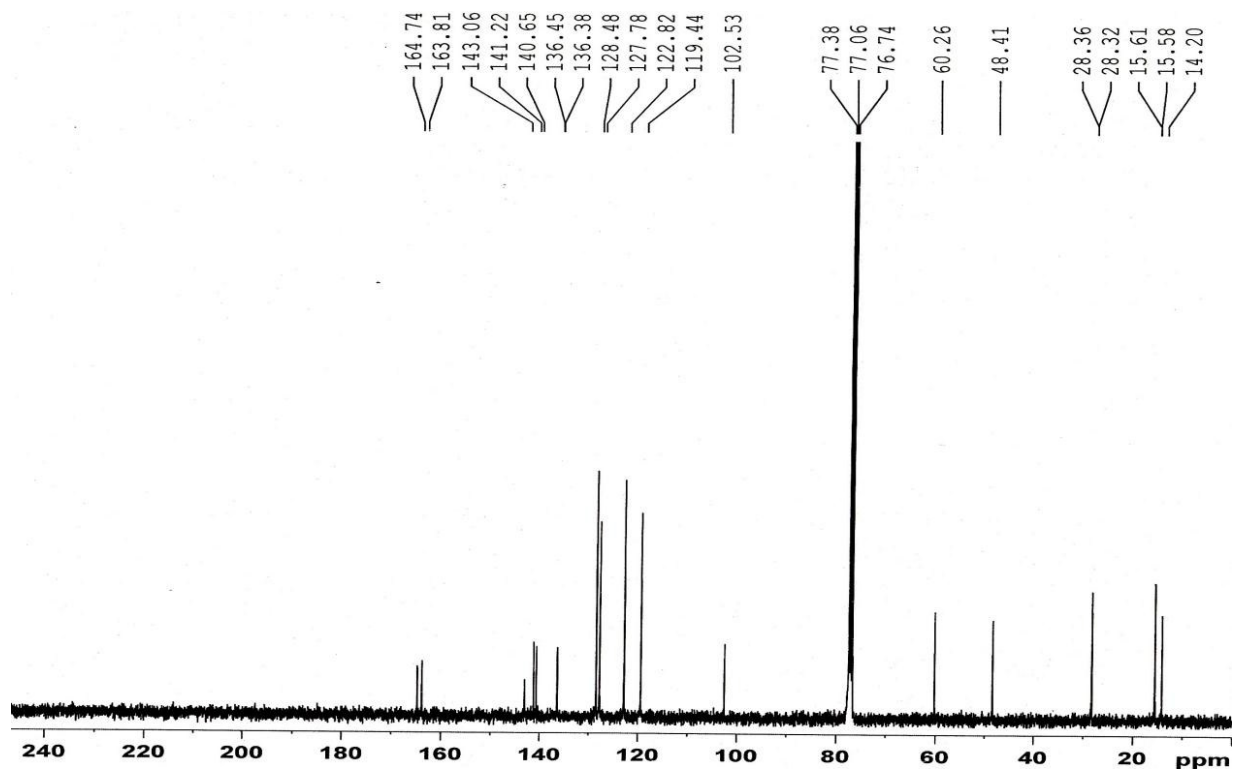
Cream solid. M.p. 98-100 °C. FT-IR (KBr) $\bar{\nu}(\text{cm}^{-1})$: 3271, 2963, 1665, 1643, 1609, 1517, 1442, 1397, 1222, 1149, 1030. ^1H NMR (CDCl_3 , 400 MHz) δ ppm: 7.97 (br, s, 2H, NH), 7.67 (d, 2H, $^3J = 8.0$ Hz, Ar-H), 7.19 (d, 2H, $^3J = 8.0$ Hz, Ar-H), 7.12 (d, 2H, $^3J = 8.0$ Hz, Ar-H), 7.05 (br, s, 2H, Ar-H), 4.50 (s, 2H, NCH_2), 4.19 (br, s, 2H, OCH_2), 2.63 (br, s, 4H, Ar- CH_2CH_3), 1.56 (br, s, 3H, OCH_2CH_3), 1.21 (br, s, 6H, Ar- CH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz) δ ppm: 164.7, 163.8, 143.1, 141.2, 140.6, 136.4, 136.3, 128.4 (2C), 127.7 (2C), 122.8 (2C), 119.4 (2C), 102.5, 60.2, 48.4, 28.3, 28.3, 15.6, 15.5, 14.2. MS (m/z): 378.5 (M^+), 332.4, 317.4, 305.3 (100%), 277.4, 261.3, 230.3, 219.3, 202.2, 173.2, 157.2, 142.1, 132.1, 118.2, 105.1, 91.1, 77.1, 65.0, 55.1; Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_3$. C, 72.99; H, 6.92; N, 7.40.; Found. C, 72.68; H, 7.12; N, 7.51.



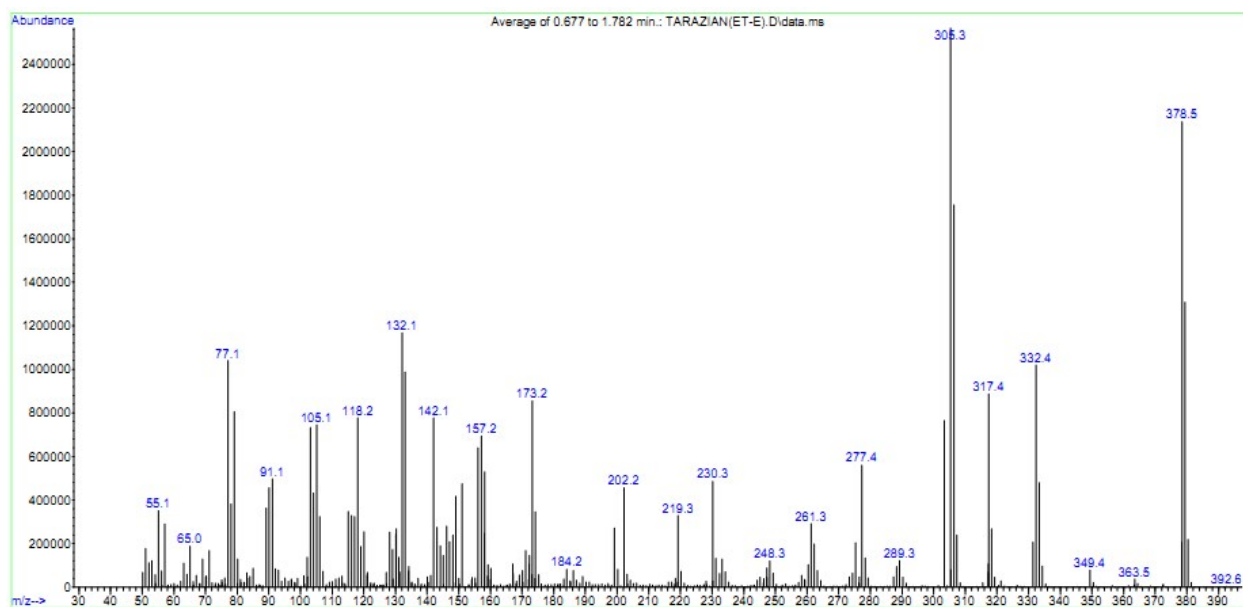
The FT-IR spectrum of product (**5I**)



The ^1H NMR(400MHz)spectrum of product (5I)



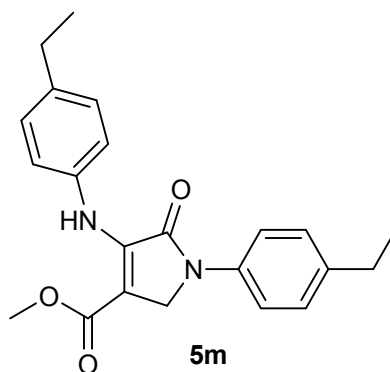
The ^{13}C NMR(100MHz)spectrum of product (5I)

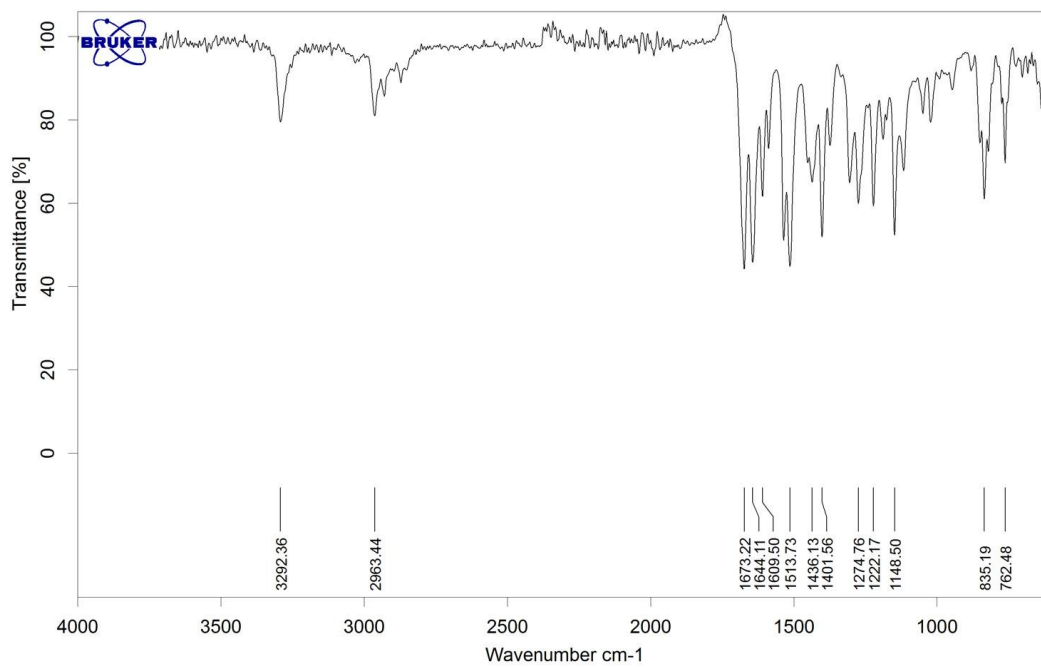


The MS spectrum of product **(5I)**

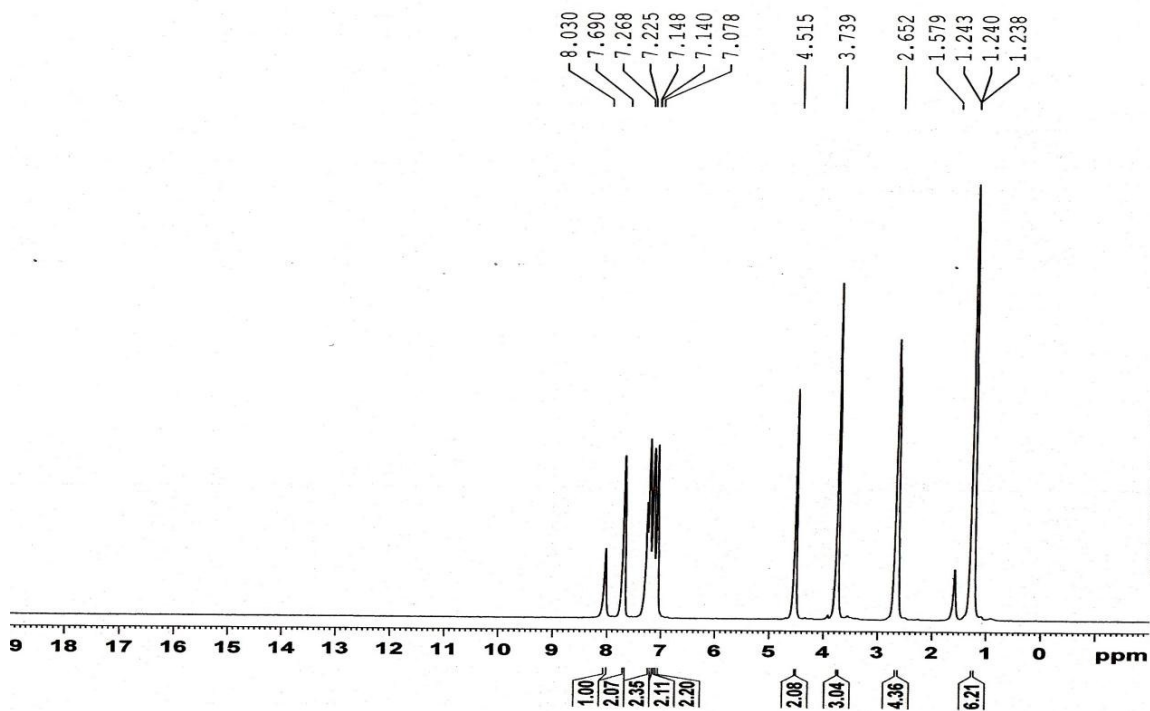
Methyl-(4-ethylphenyl)-4-((4-ethylphenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (**5m**)
(Table 2, entry 13)

Cream solid. M.p. 125-126 °C. FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3292, 2963, 1673, 1644, 1609, 1513, 1436, 1401, 1274, 1222, 1148. ¹H NMR (CDCl₃, 400 MHz)/ δ ppm: 8.03 (br, s, 1H, NH), 7.69 (br, s, 2H, Ar-H), 7.22 (br, s, 2H, Ar-H), 7.14 (br, s, 2H, Ar-H), 7.07 (br, s, 2H, Ar-H), 4.51 (s, 2H, NCH₂), 3.73 (s, 3H, OCH₃), 2.65 (s, 4H, Ar-CH₂CH₃), 1.24 (t, 3J = 5.2 Hz, 6H, Ar-CH₂CH₃).





The FT-IR spectrum of product (5m)



The ¹H NMR (400 MHz) spectrum of product (5m)

