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Electronic Supplementary Information (ESI)

UiO-66-SO_3H metal-organic framework as a green catalyst for facile synthesis of dihydro-2-oxypyrrole derivatives

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S1. ***Characterization data fordimethyl 2-((4-chlorophenyl)amino)maleate.***

Pale yellow solid,mp:decomposed at 305°C. ^{1}H NMR (DMSO-d_6, 300 MHz):δ_H(ppm)9.77 (br, s, 1H, NH), 8.13 (d, 2H, ^{3}J = 8.7 Hz, Ar–H), 7.05 (d, 2H, ^{3}J = 8.7 Hz, Ar–H), 5.75 (s, 1H, =CH), 3.74 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3).

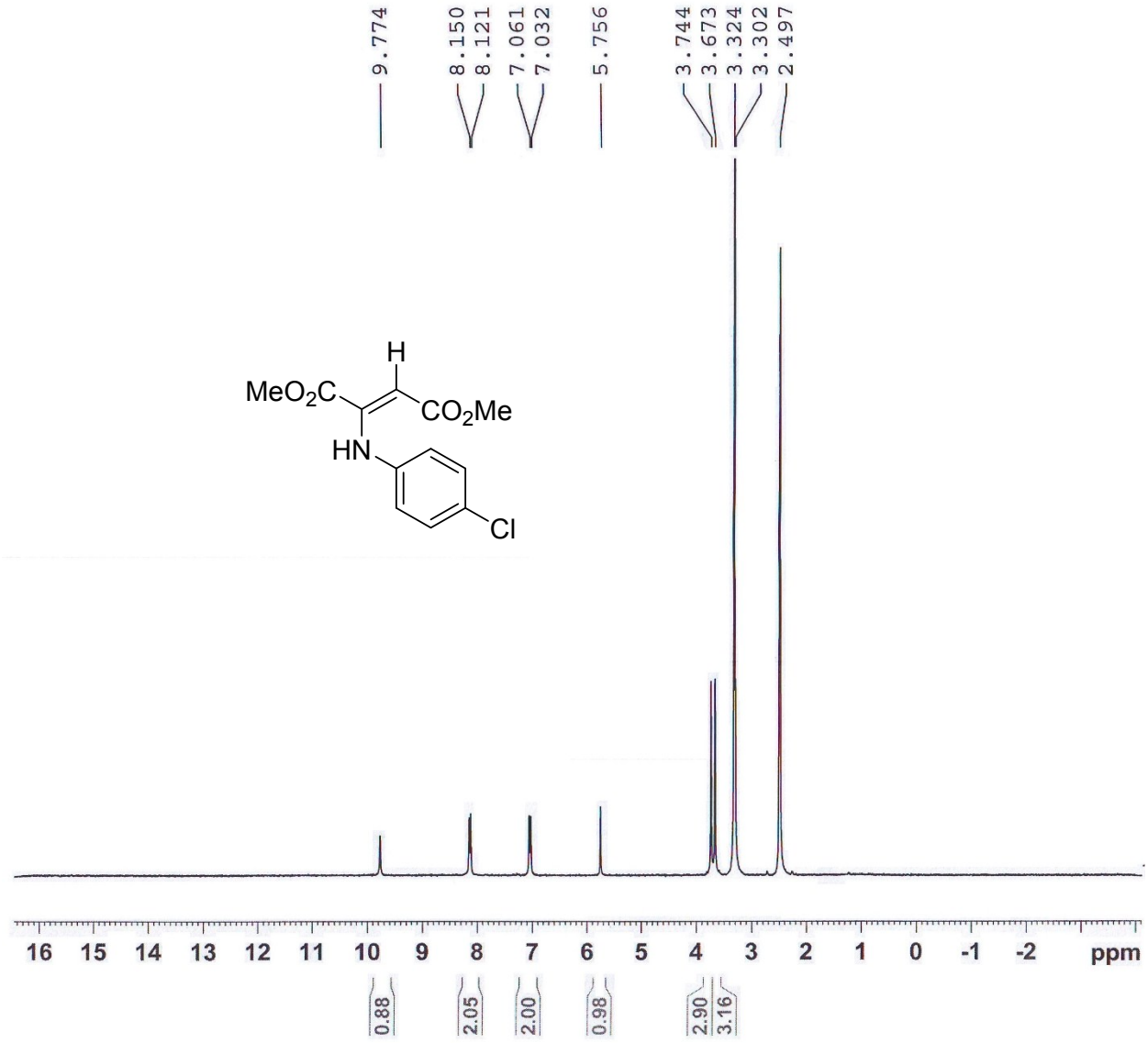
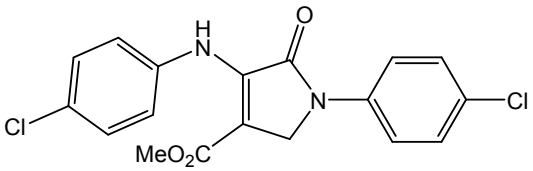


Fig. S1 The ^{1}H NMR (300MHz) spectrum of dimethyl 2-((4-chlorophenyl)amino)maleate

S2. ***Characterizationdatafor methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate*** **1a** ***(Table 3, Entry 1):***



Cream solid,mp: 174-175 °C (lit.: 175-176 °C [3]). FT-IR (KBr):$\bar{\upsilon}$(cm^{-1}) 3275, 1693, 1634, 1594, 1546, 1493, 1454, 1362, 1263, 1137, 826, 756.^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm)7.97 (br, s, 1H, NH), 7.66 (d, 2H, ^3J= 9.25 Hz, Ar–H), 7.28 (d, 2H, ^3J= 8 Hz, Ar–H), 7.21 (d, 2H, ^3J=8.26 Hz, Ar–H), 7.00 (d, 2H, ^3J= 8.6 Hz,Ar–H), 4.43 (s, 2H, NCH_2), 3.71 (s, 3H, OCH_3).

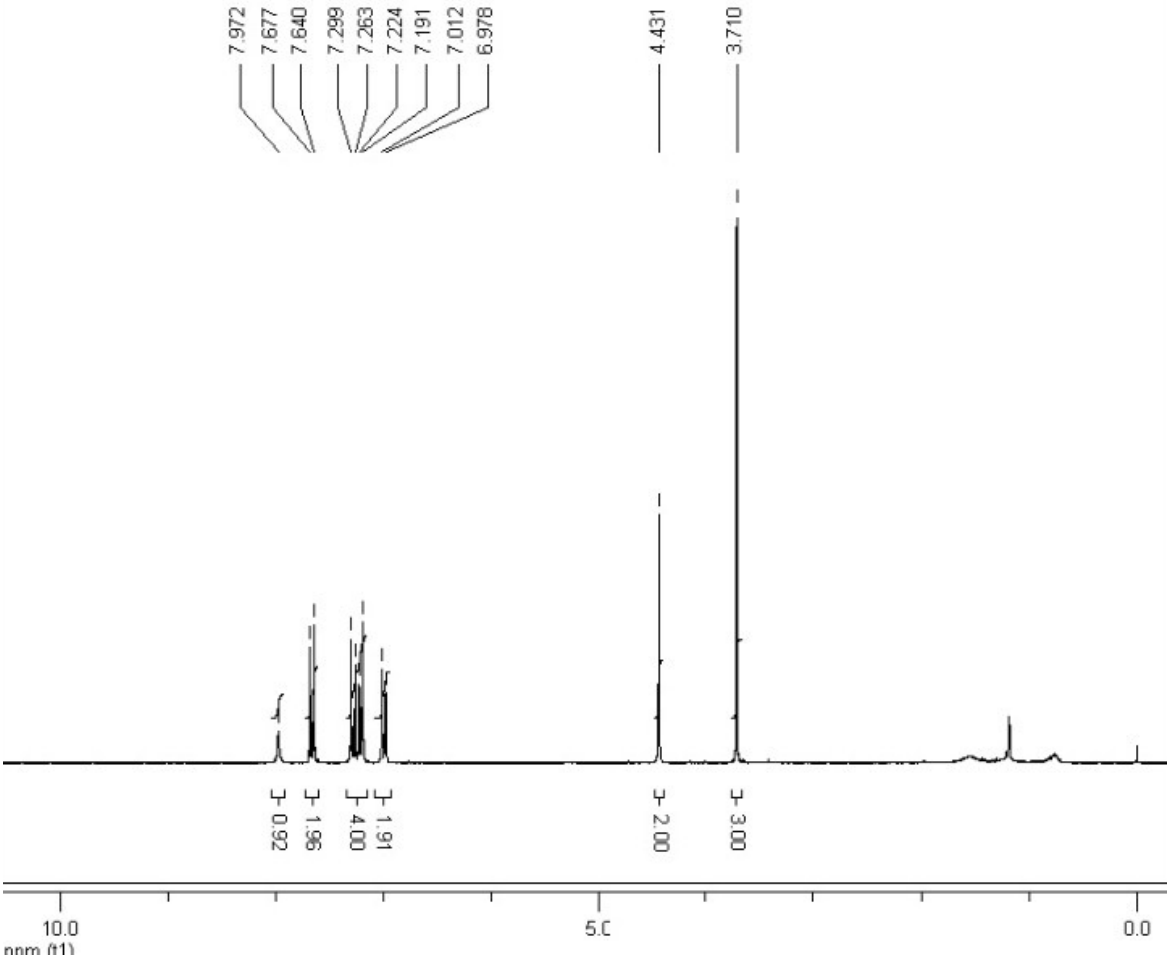
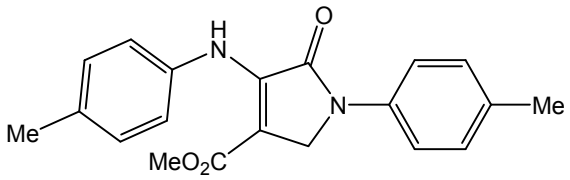


Fig. S2 The ^{1}H NMR(250MHz)spectrum of product (**1a**)

S3. ***Characterization dataformethyl 5-oxo-1-(p-tolyl)-4-(p-tolylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate* <u>2a</u> *(Table 3, Entry 2):***



Pale yellow solid,mp: 176-177 °C (lit.: 175-176 °C [3]). FT-IR (KBr):ῡ (cm^{-1}) 3282, 1685,1657, 1544, 1439, 1360, 1300, 1132. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm)7.93 (br, s, 1H, NH), 7.68 (d, 2H, ^3J= 8.76 Hz, Ar–H), 7.19 (s, 2H, Ar–H), 7.11 (d, 2H, ^3J= 8.76 Hz, Ar–H), 7.00 (d, 2H, ^3J= 12.76 Hz, Ar–H), 4.43 (s, 2H, NCH_2), 3.67 (s, 3H, OCH_3),2.26 (s, 6H, Ar-Me).

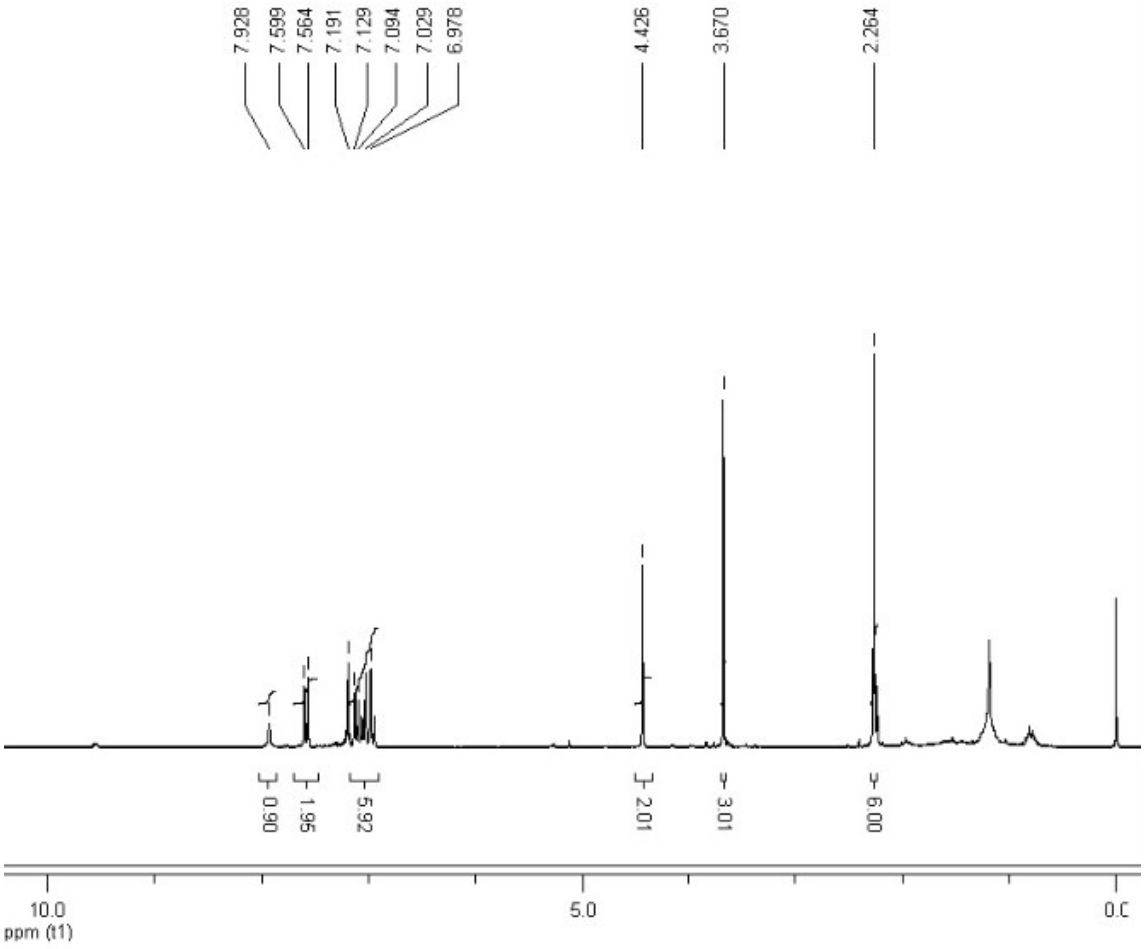
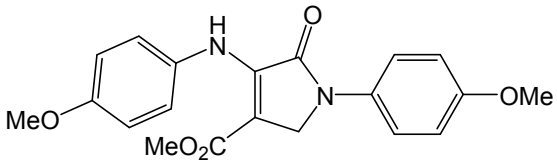


Fig. S3 The ^{1}H NMR(250MHz)spectrum of product (**2a**)

S4. ***Characterization dataformethyl 1-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate*** **3a** ***(Table 3, Entry 3):***



White solid,mp:161-162 °C (lit.: 160-162 °C [3]). FT-IR (KBr):ῡ (cm^{-1}) 3282, 1685, 1657, 1543, 1513, 1402, 1300, 1034. ^{1}H NMR ($CDCl_3$, 300 MHz):δ_H(ppm) 8.01 (br, s, 1H, NH), 7.67 (d, 2H, ^3J= 8 Hz, Ar–H), 7.11 (d, 2H, ^3J=8.7 Hz, Ar–H), 6.93-6.84 (m, 4H, Ar–H), 4.48 (s, 2H, NCH_2), 3.82 (s, 6H, OCH_3), 3.75 (s, 3H, OCH_3).

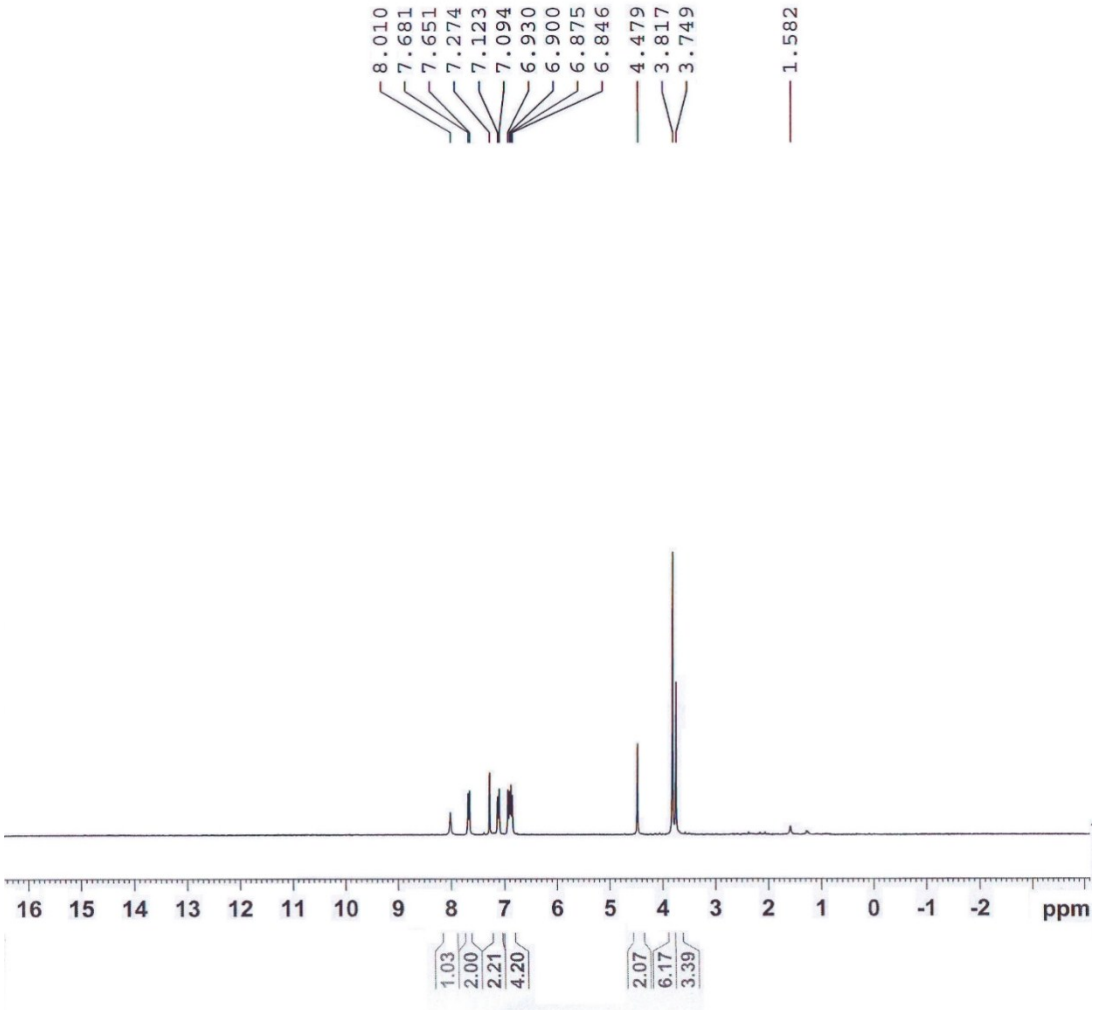
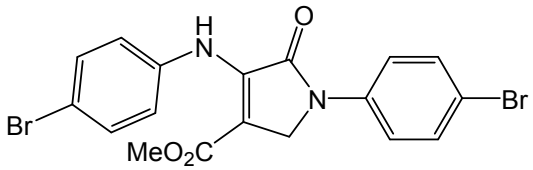


Fig. S4 The ^{1}H NMR(300MHz)spectrum of product (**3a**)

S5. ***Characterization dataformethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate*** **4a** ***(Table 3, Entry 4):***



White solid,mp: 180-182 °C (lit.: 181-182 °C [3]). FT-IR (KBr):ῡ (cm^{-1})3274, 1691, 1651, 1533, 1353, 1217, 813. ^{1}H NMR ($CDCl_3$, 300 MHz):δ_H(ppm) 8.05 (br, s, 1H, NH), 7.74 (d, 2H, ^3J= 8.7 Hz, Ar–H), 7.34-7.27 (m, 4H, Ar–H), 7.07 (d, 2H, ^3J=8.4 Hz, Ar–H), 4.51 (s, 2H, NCH_2), 3.79 (s, 3H, OCH_3).

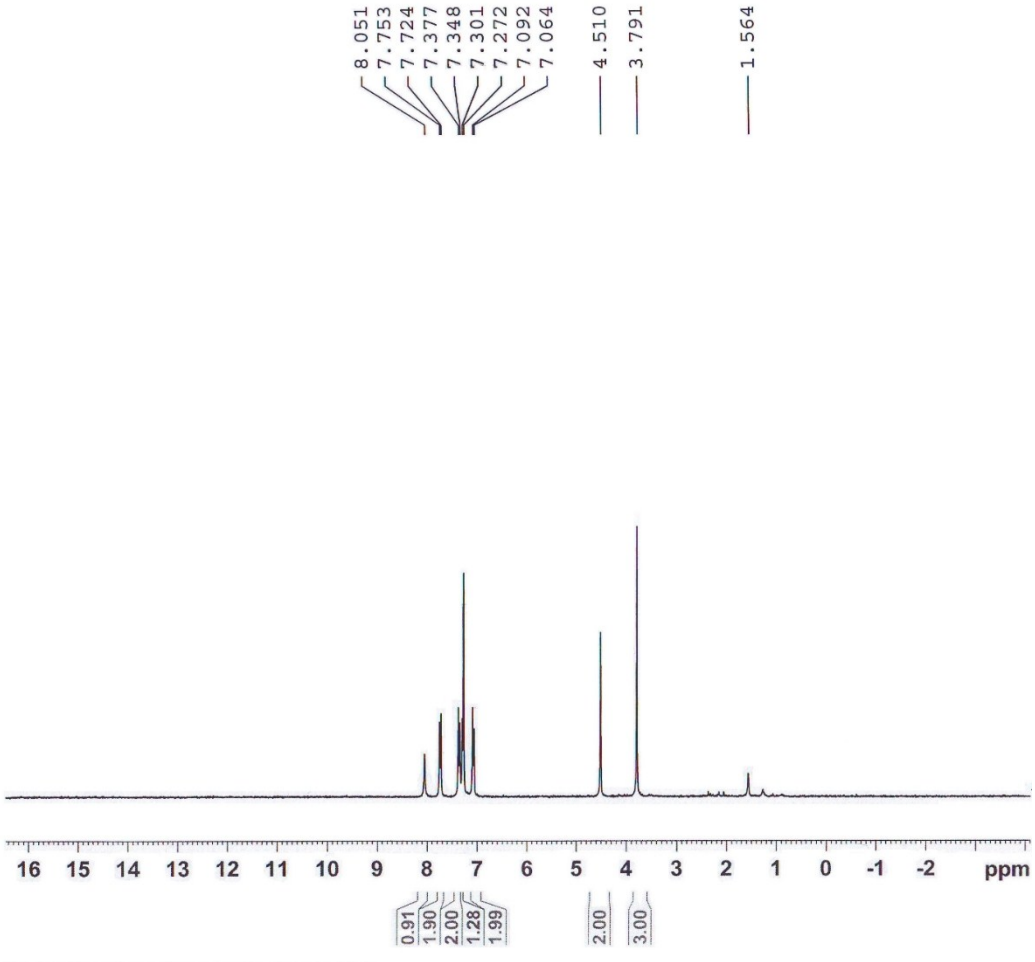
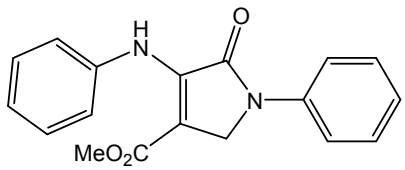


Fig. S5 The ^{1}H NMR(300MHz)spectrum of product (**4a**)

S6. ***Characterization dataformethyl 5-oxo-1-phenyl-4-(phenylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate*** **5a** ***(Table 3, Entry 5):***



Yellow solid, mp: 160-161 °C (lit.: 160-162 °C [3]). FT-IR (KBr):ῡ (cm^{-1}) 3285, 1684, 1648, 1510, 1444, 1437, 1267, 1242, 841. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm)7.94 (br, s, 1H, NH), 7.73-7.69 (m, 2H, Ar–H), 7.36-7.05 (m, 8H, Ar–H), 4.47 (s, 2H, NCH_2), 3.67 (s, 3H, OCH_3).

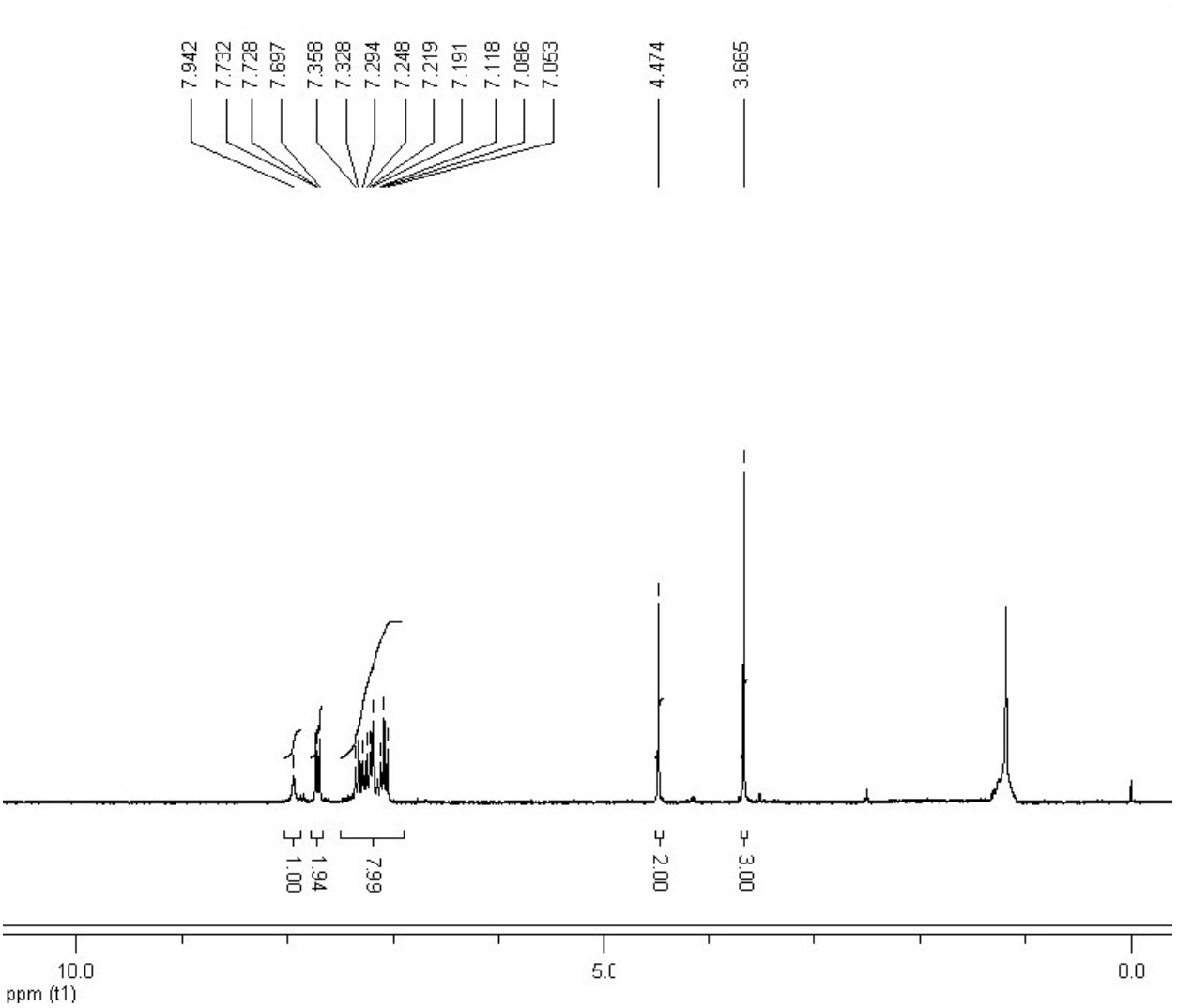
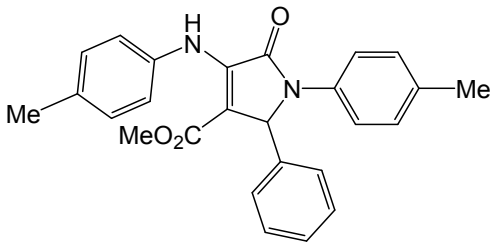


Fig. S6 The ^{1}H NMR(250MHz)spectrum of product (**5a**)

S7. ***Characterization dataformethyl 5-oxo-2-phenyl-1-(p-tolyl)-4-(p-tolylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate*** **6a** ***(Table 3, Entry 6):***



White solid,mp: 167-168 °C. FT-IR (KBr):ῡ (cm^{-1}) 3274, 1691, 1651, 1533, 1514, 1391, 1353, 1217, 811. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm) 8.06 (br, s, 1H, NH), 7.23-7.02 (m, 13H, Ar–H), 5.69 (s, 1H, NCH), 3.47 (s, 3H, OCH_3), 2.26 (s, 3H, Ar-Me), 2.15 (s, 3H, Ar-Me). ^{13}C NMR ($CDCl_3$,100 MHz):δ_C(ppm) 168.14, 166.90, 137.05, 136.15, 135.91, 135.43, 134.63, 133.96, 129.38, 129.02, 128.41, 128.02, 127.58, 123.21, 123.17, 122.72, 63.13, 51.05, 20.99, 20.89. MS (*m/z*): 412.5(M^+), 379.5, 353.5 (100%), 278.4, 194.4, 158.3, 142.3, 121.3, and 91.3. Elemental anal. Calcd (%) for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.72; H, 5.85; N, 6.79.

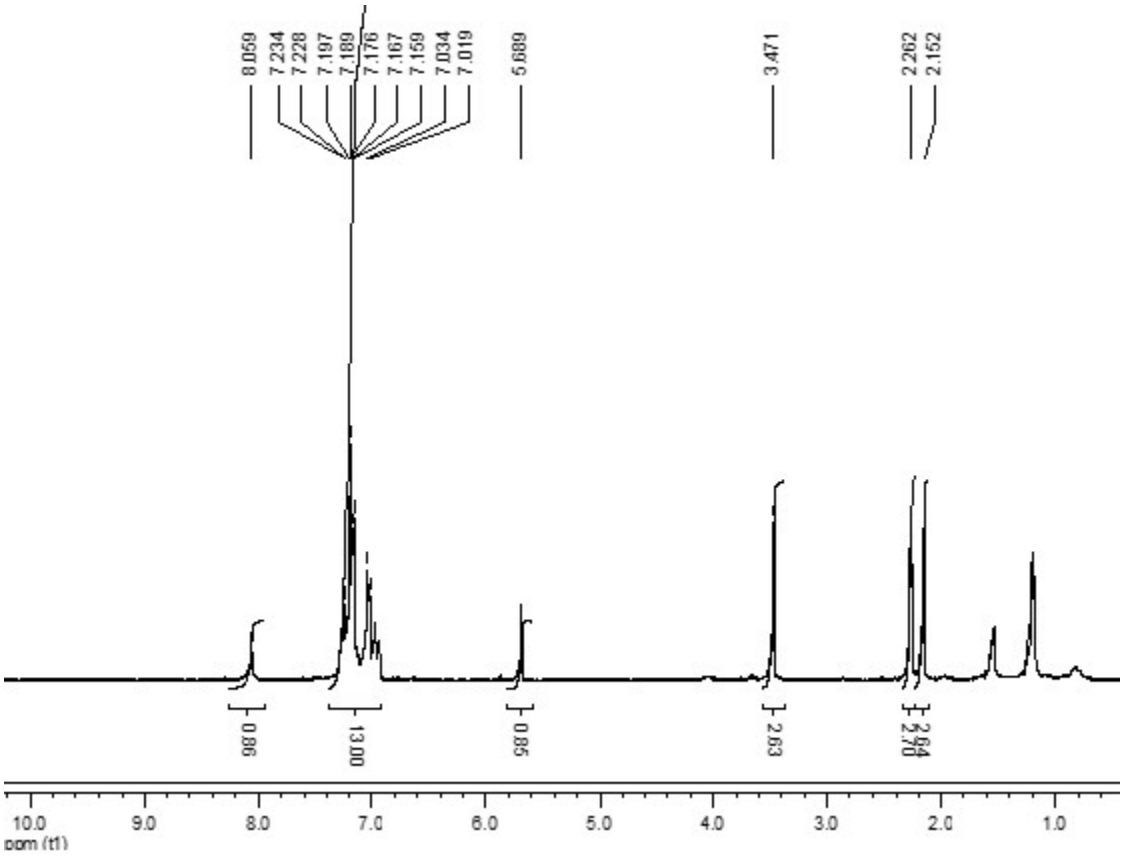


Fig. S7 The ^{1}H NMR(250MHz)spectrum of product (**6a**)

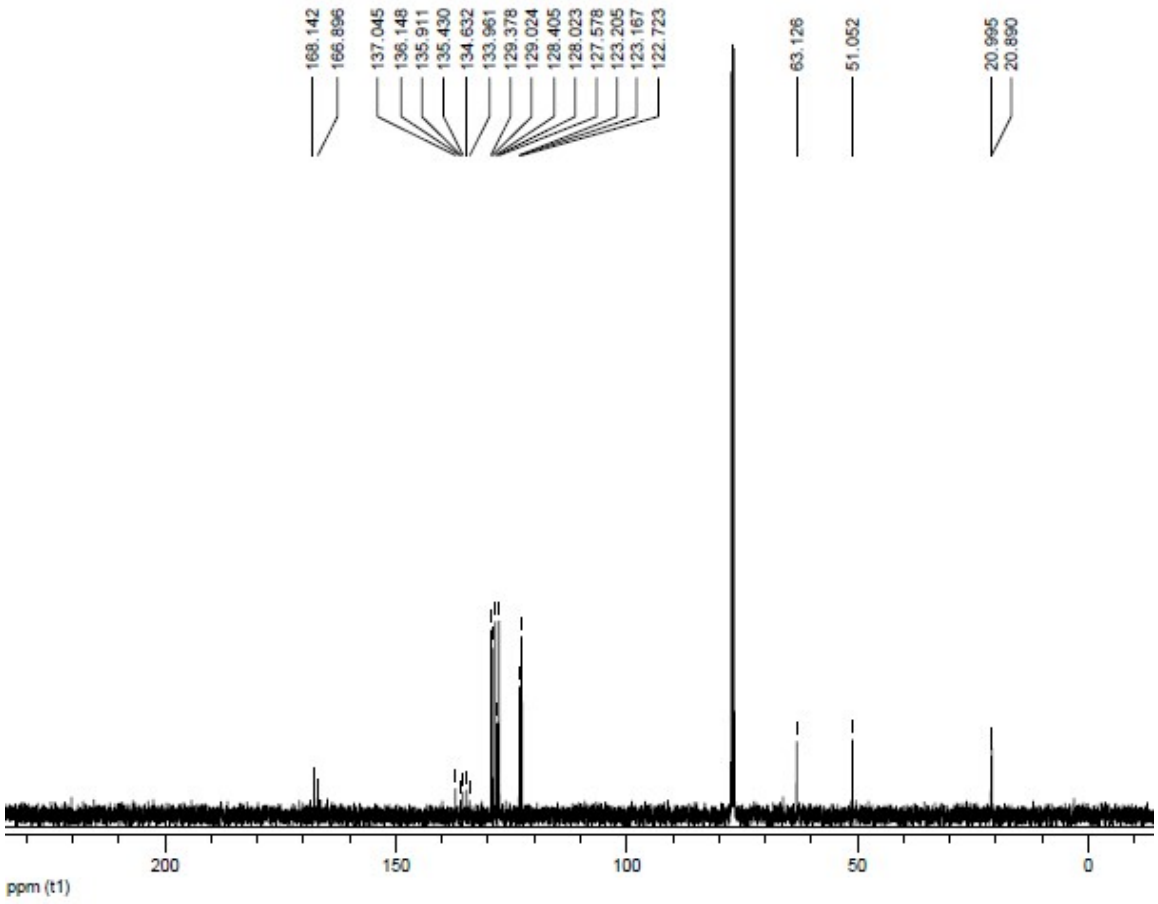


Fig. S8 The ^{13}C NMR (100MHz) spectrumof product (**6a**)

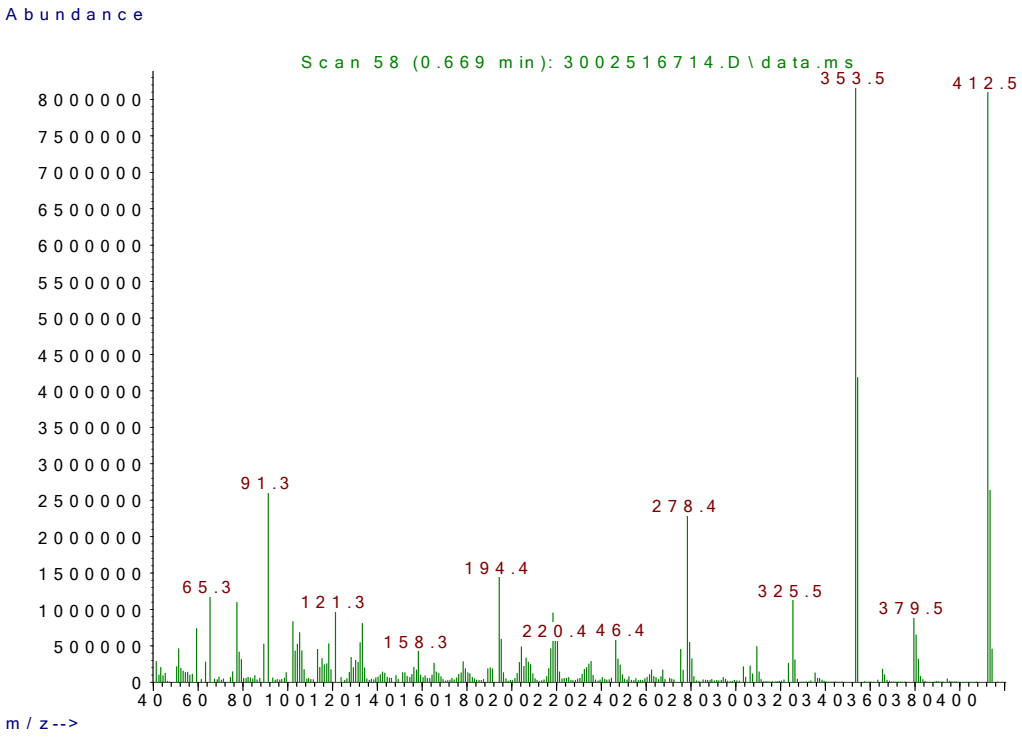
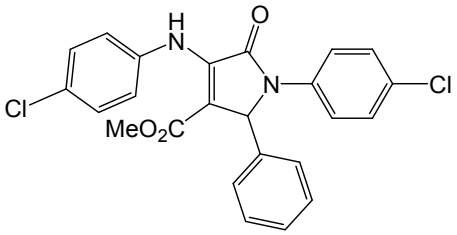


Fig. S9 The MS spectrum of product (**6a**)

S8. ***Characterization dataformethyl1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-5-oxo-2-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate* <u>7a</u> *(Table 3, Entry 7):***



Yellow solid,mp: 176-177 °C (lit.: 175-177 °C [3]). FT-IR (KBr):ῡ (cm^{-1}) 3289, 1676, 1649, 1537, 1516, 1441, 1399, 1294, 1150, 1224, 1150, 811. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm) 8.13 (br, s, 1H, NH), 7.36-7.06 (m, 13H, Ar–H), 5.69 (s, 1H, NCH), 3.51 (s, 3H, OCH_3).

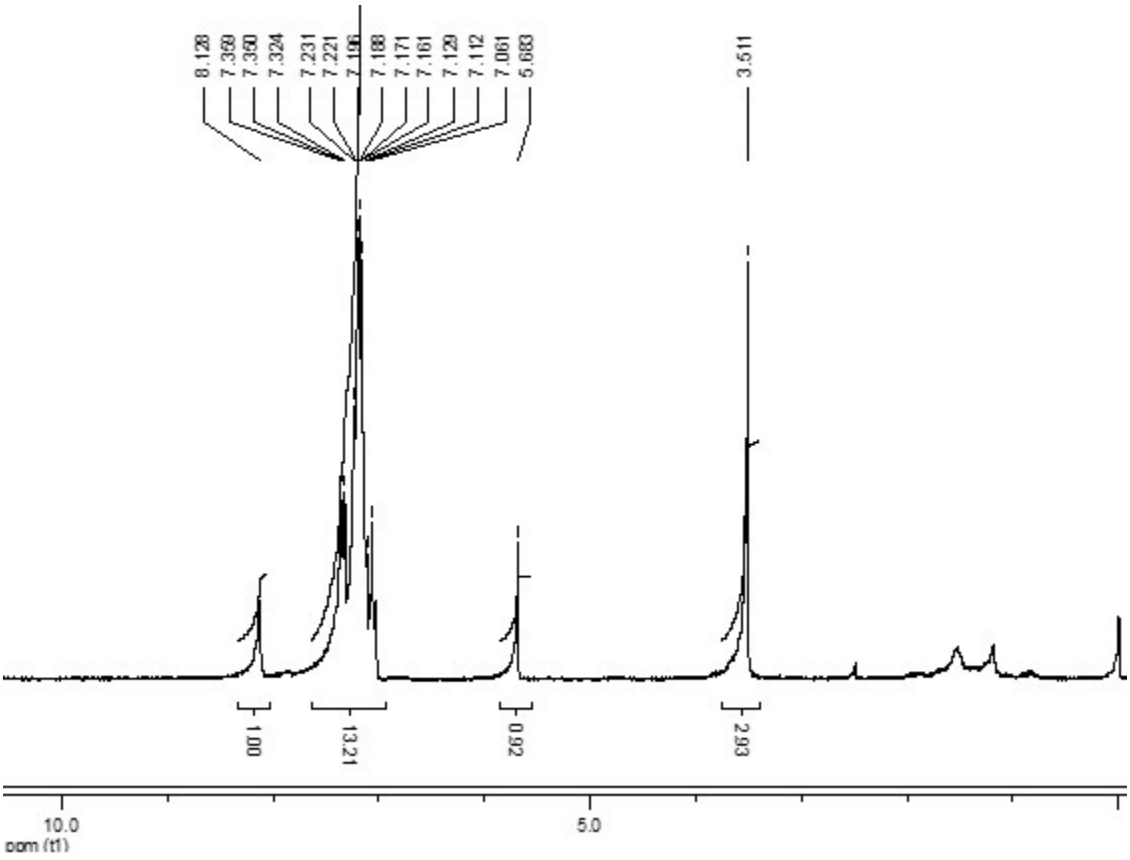
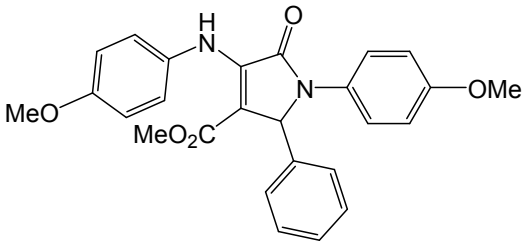


Fig. S10 The ^{1}H NMR(250MHz)spectrum of product (**7a**)

S9. ***Characterization dataformethyl 1-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate*** **8a** ***(Table 3, Entry 8):***



White solid,mp: 167-168 °C. FT-IR (KBr):ῡ (cm^{-1}) 3282, 1686, 1667, 1544, 1514, 1495, 1439, 1395, 1242, 1232, 1034, 1093, 834. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm) 8.08 (br, s, 1H, NH), 7.23-7.06 (m, 9H, Ar–H), 6.78 (d, 2H, ^3J =7.6 Hz, Ar–H), 6.68 (d, 2H, ^3J=7.6 Hz, Ar–H), 5.62 (s, 1H, NCH), 3.73 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3).MS (*m/z*): 444.2 (M^+), 385.1, 339.1, 294.1, 235.1, 188.1(100%), 160.0, 132.0, and77.1.Elemental anal. Calcd (%) for $C_{26}H_{24}N_2O_5$: C, 70.26; H, 5.44; N, 6.30. Found: C, 70.25; H, 5.45; N, 6.31.

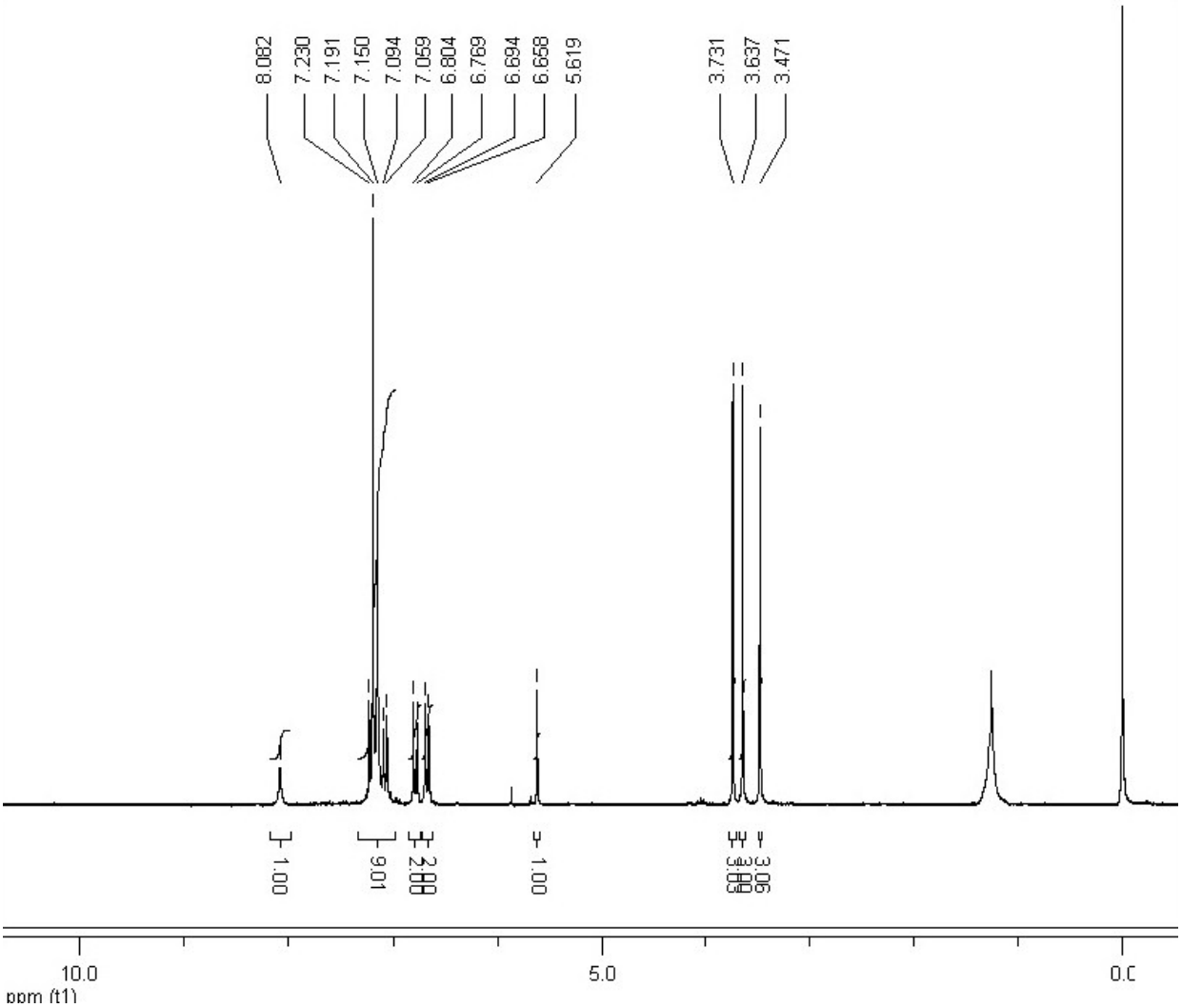


Fig. S11 The ^{1}H NMR(250MHz)spectrum of product (**8a**)

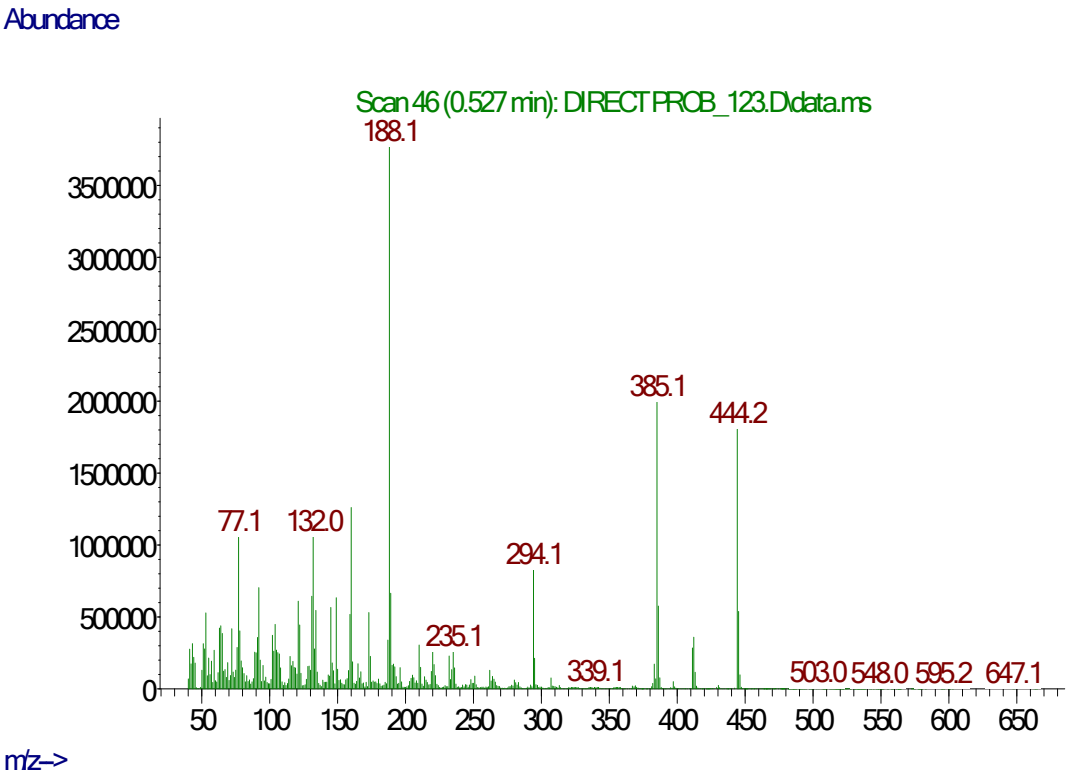
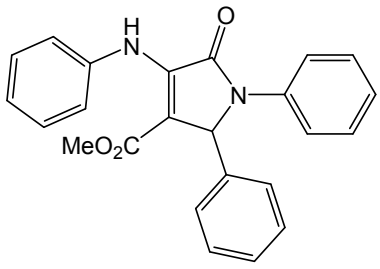


Fig. S12 The MS spectrum of product (**8a**)

S10. ***Characterization dataformethyl 5-oxo-1,2-diphenyl-4-(phenylamino)-2,5-dihydro-1H-pyrrole-3-carboxylate*** **9a** ***(Table 3, Entry 9):***



Cream solid,mp:155-156 °C. FT-IR (KBr):ῡ (cm^{-1}) 3282, 1685, 1657, 1543, 1513, 1402, 1300, 1242,1034, 834. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm) 8.08 (br, s, 1H, NH), 7.41-7.10 (m, 15H, Ar–H), 5.75 (s, 1H, NCH), 3.47 (s, 3H, OCH_3).^{13}C NMR ($CDCl_3$, 100 MHz):δ_C(ppm) 164.69, 164.00, 138.56, 136.76, 128.83, 128.56, 128.47, 127.56, 126.15 125.43, 124.84, 124.60. 122.96, 122.76, 109.31, 63.17, 51.13.MS (*m/z*): 384.5 (M^+),325.5 (100%), 297.4, 264.4, 232.3, 204.4, 180.4, 144.3, 102.3, and 77.3. Elemental anal. Calcd (%) for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.98; H, 5.24; N, 7.29.

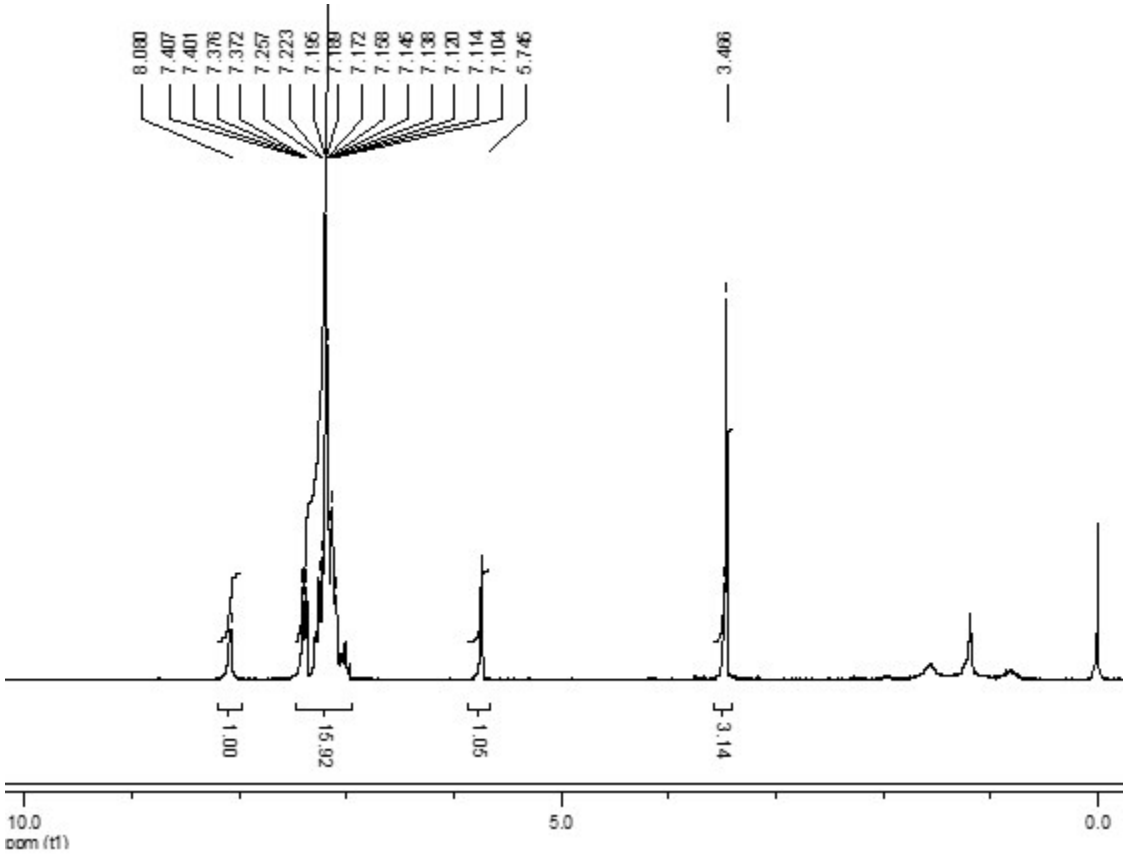


Fig. S13 The ^{1}H NMR(250MHz)spectrum of product (**9a**)

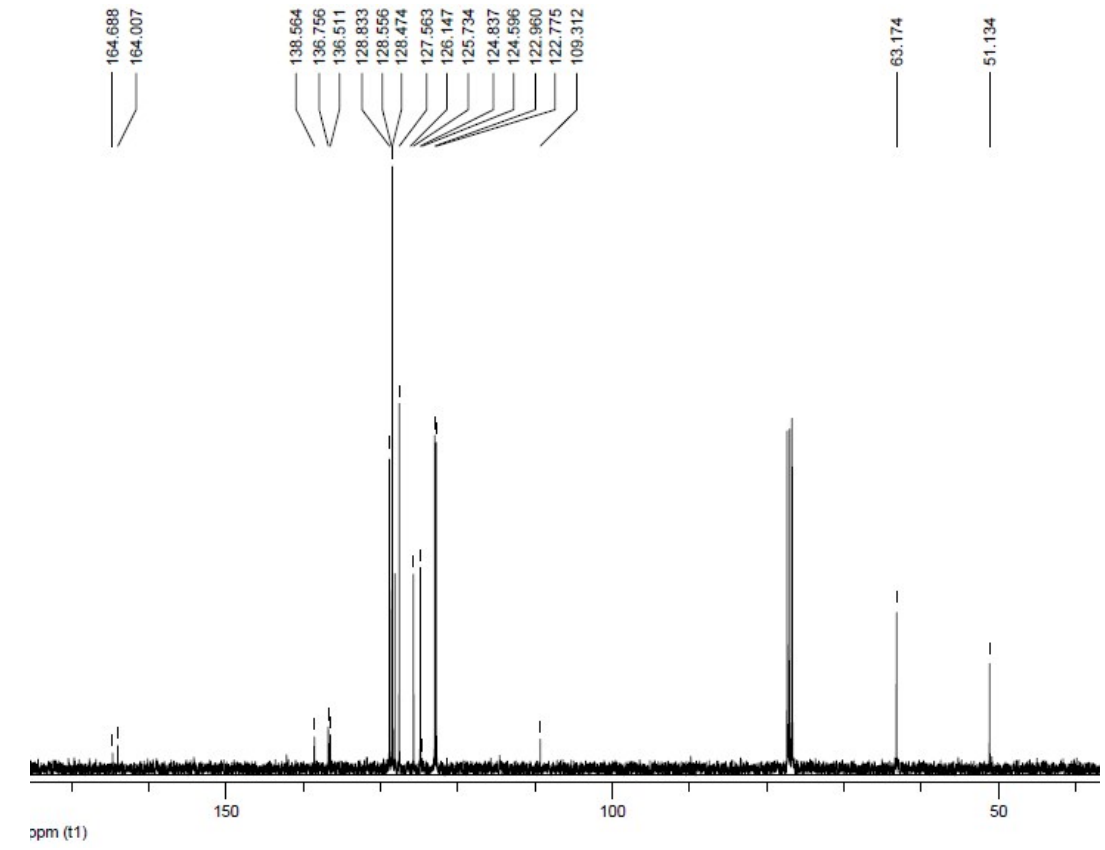


Fig. S14 The ^{13}C NMR (100MHz) spectrumof product (**9a**)

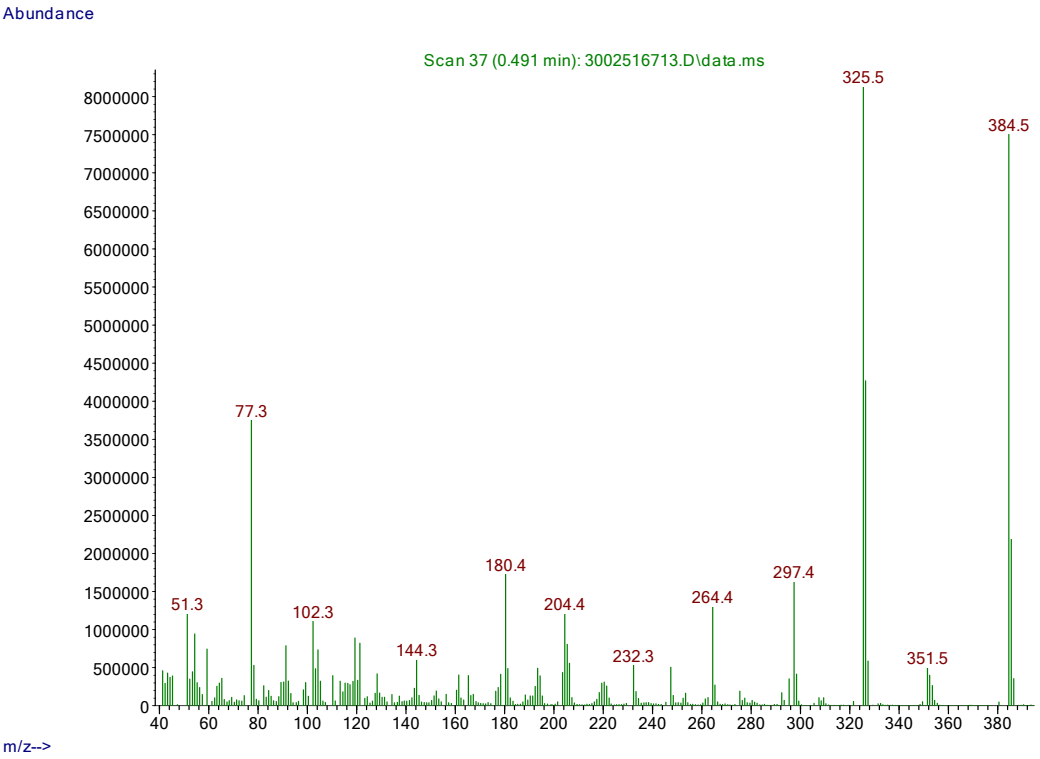
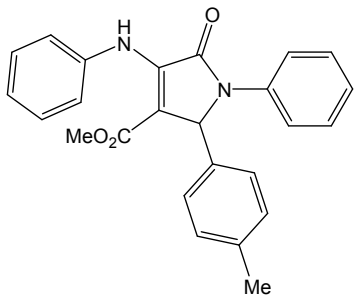


Fig. S15 The MSspectrumof product (**9a**)

S11. *Characterization dataforMethyl 5-oxo-1-phenyl-4-(phenylamino)-2-(p-tolyl)-2,5-dihydro-1H-pyrrole-3-carboxylate* <u>10a</u> *(Table 3, Entry 10):*



White solid,mp:163-164 °C. FT-IR (KBr):ῡ (cm^{-1}) 3283, 1674, 1648, 1554, 1538, 1440, 1373, 1266, 1150, 1094, 831. ^{1}H NMR ($CDCl_3$, 250 MHz):δ_H(ppm) 8.04 (br, s, 1H, NH), 7.41-6.98 (m, 14H, Ar–H), 5.71 (s, 1H, NCH), 3.47 (s, 3H, OCH_3), 2.18(s, 3H, Ar-Me). ^{13}C NMR ($CDCl_3$, 100 MHz):δ_C(ppm) 164.69, 164.05, 141.94, 138.66, 137.81, 136.51, 133.60, 129.22, 128.81, 128.46, 127.41, 125.65, 124.75, 122.86, 122.75, 109.53, 62.05, 51.13, 21.16. Elemental anal. Calcd (%) for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.35; H, 5.58; N, 7.01.

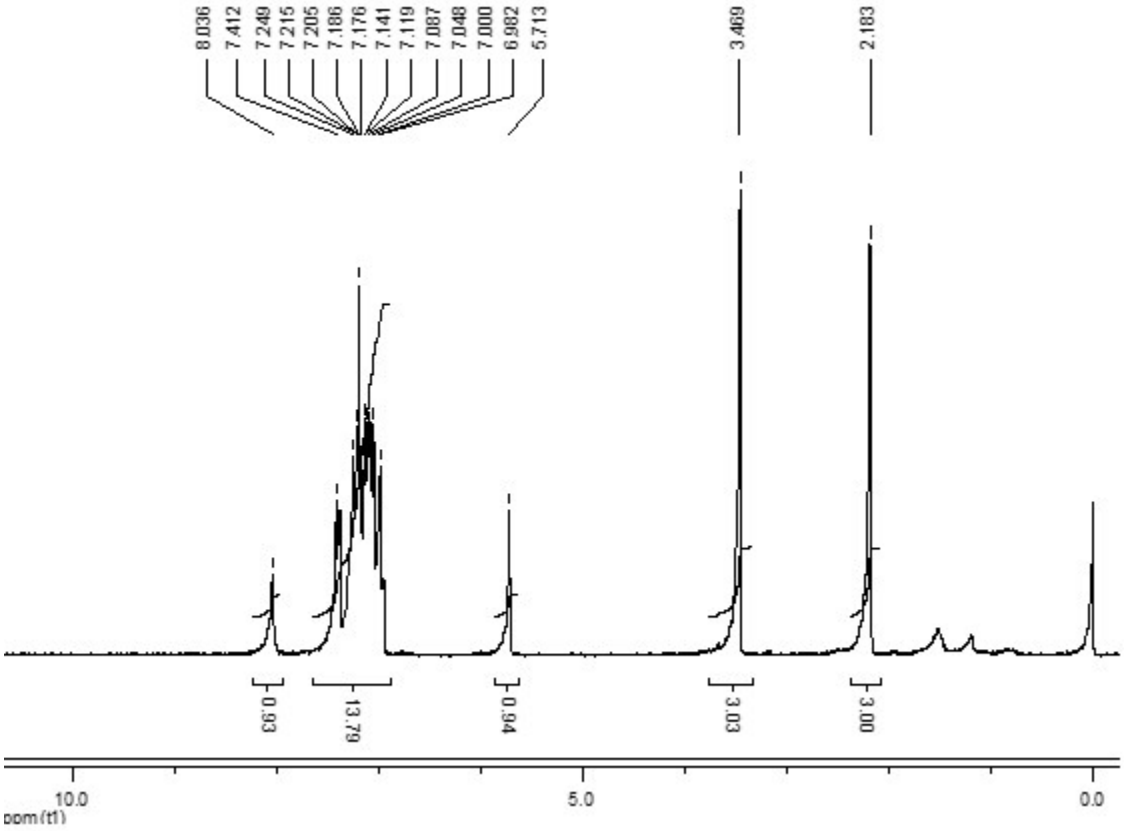


Fig. S16 The ^{1}H NMR(250MHz)spectrum of product (**10a**)

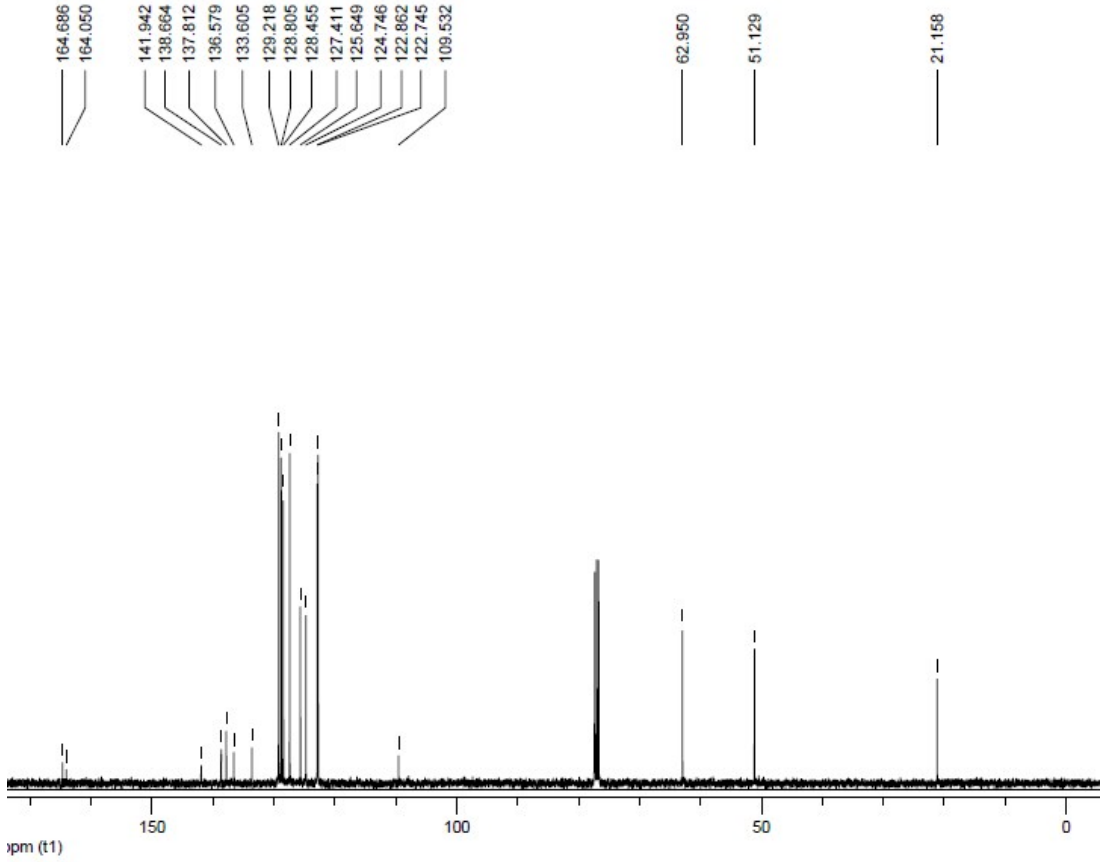


Fig. S17 The ^{13}C NMR (100MHz) spectrumof product (**10a**)