Recyclable Triphenyl bismuth（Ⅴ）bisperfluorooctanesulfonate catalysted synthesis of dihydropyrimidinones

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1. General Considerations

All chemicals were purchased from Aldrich. Co. Ltd and used as received unless otherwise indicated. The preparation of catalyst was carried out under a N_2 atmosphere with freshly distilled solvents unless otherwise noted. THF and diethyl ether were distilled from sodium/benzophenone. Dichloromethane was distilled from CaH_2. The NMR spectra were recorded at 25 ^oC on INOVA-400M (USA) calibrated with tetramethylsilane (TMS) as an internal reference.

2. Synthesis of $Ph_3Bi(OSO_2C_8F_{17})_2$

$AgOSO_2C_8F_{17}$ (0.61 g, 1.0 mmol) was added to a solution of $Ph_3Bi(Cl)_2$ (0.26 g, 0.5 mmol) in 10 mL CH_2Cl_2, and the resulting solution was stirred in the dark at room temperature for 3 h. Then the reaction mixture was filtered, and 1.0 mL of dry hexane was added dropwise to the filtrate until the solution appeared turbid. A white crystal was obtained after the solution was kept in a refrigerator overnight. (590 mg, 82%). M.p. 158-160 ^oC; ^1H NMR(400 MHz, $CDCl_3$) δ: 8.14 (d, J = 8.0 Hz, 6H), 7.90 (t, J = 7.4 Hz, 6H), 7.72 (t, J = 7.2 Hz, 3H); ^{19}F NMR(400 MHz, $CDCl_3$) δ: -80.73~-80.80(t, 3F), -112.84(s, 2F), -120.63(s, 2F), -121.63~-121.89(d, 6F), -122.72(s, 2F), -126.12(s, 2F).

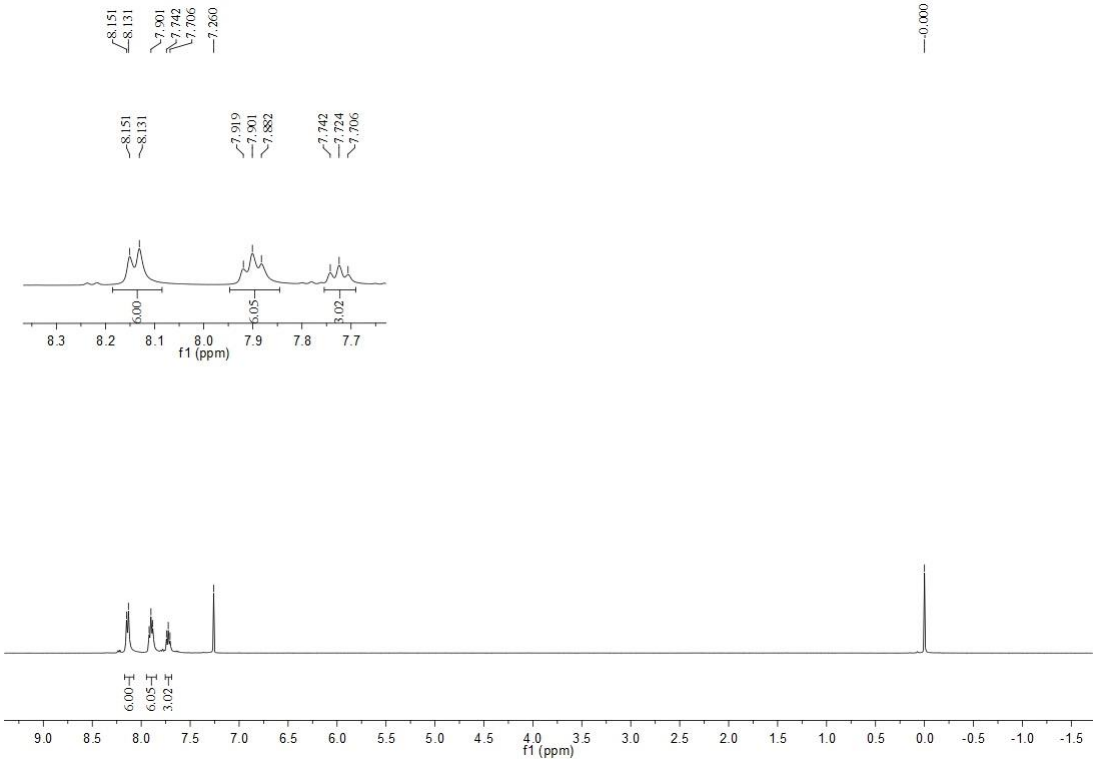


Figure S1. ^1H NMR of $Ph_3Bi(OO_2C_8F_{17})_2$

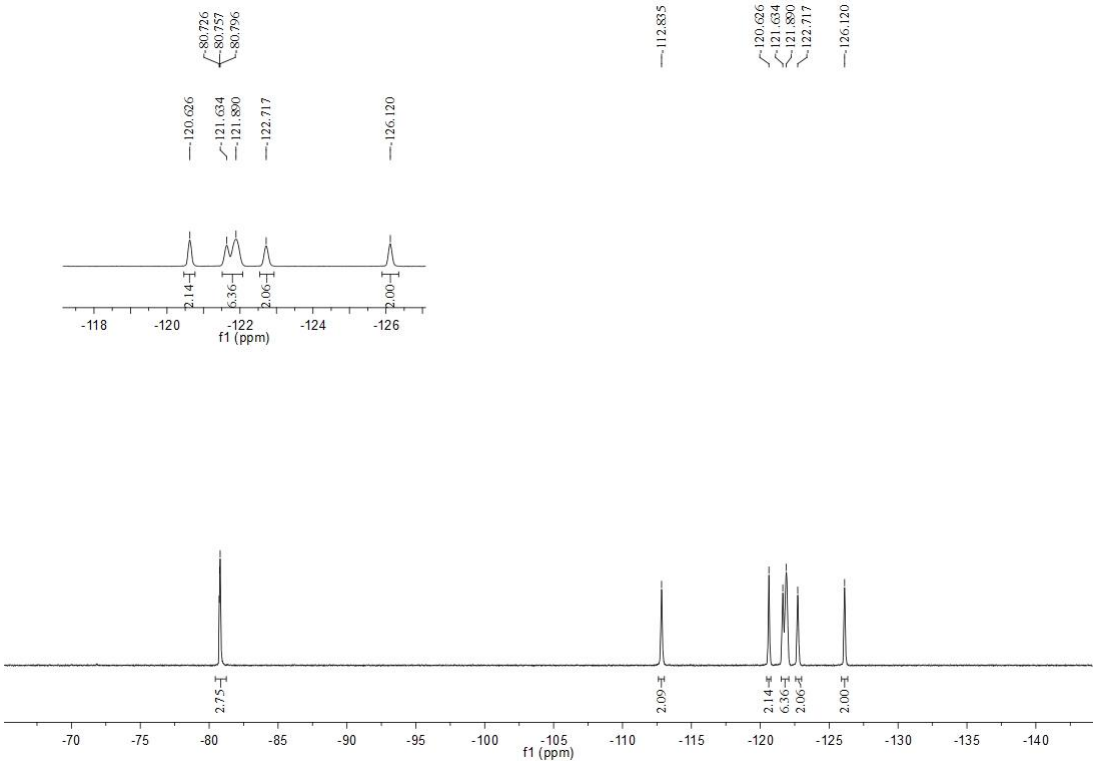


Figure S2. ^{19}F NMR of $Ph_3Bi(OSO_2C_8F_{17})_2$

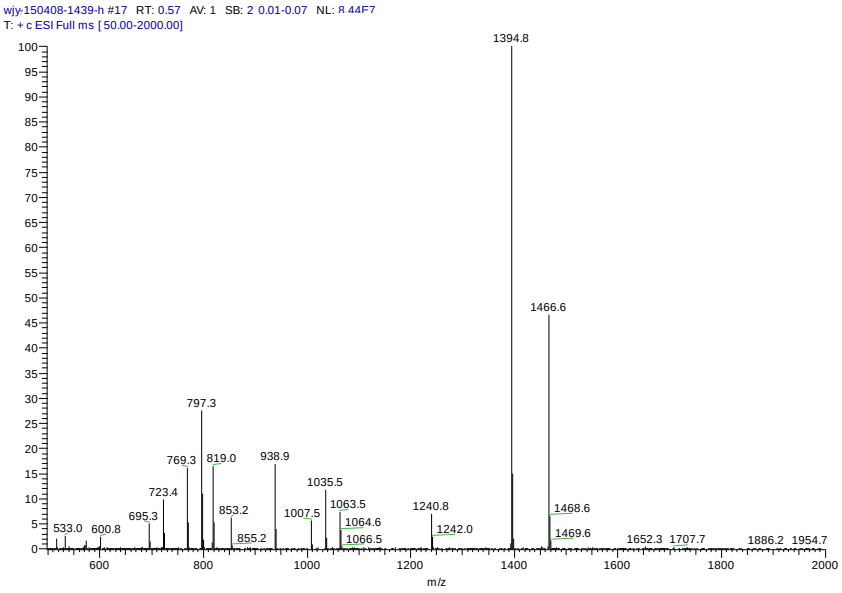
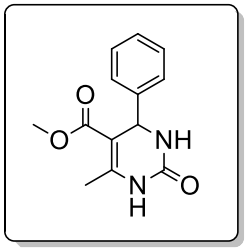


Figure S3. ESI-MS of $Ph_3Bi(OSO_2C_8F_{17})_2$

3. Typical procedure for the preparation of dihydropyrimidinones catalyzed by 1

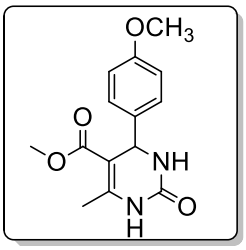
Aldehyde (0.5 mmol), 1,3-dicarbonyl compound (0.5 mmol) were added to a stirred solution of triphenyl bismuth bisperfluorooctanesulfonates (0.025 mmol) and urea (0.6 mmol), and heated at 100 °C. As indicated by TLC, the reaction was stopped at completion. The reaction mixture was diluted with petroleum ether (10 mL), leached and washed to obtain the crude products. An appropriate amount of alcohol (10 mL) was added to the crude products, and the solution was subject to filtration. The filtrate was concentrated under vacuum to collect the catalyst for the next reaction cycle. Finally, the desired products were obtained by flash chromatography using petroleum ether/ethyl acetate (1:1) as eluent.

***5-(Methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one*(5a)[16]**:



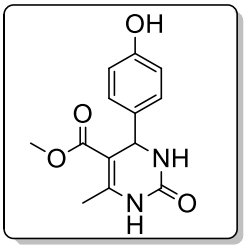
White solid, Mp: 214-216 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.29 (s, 1H), 7.83 (s, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.30-7.27 (m, 3H), 5.20 (d, J = 3.2 Hz, 1H), 3.58 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.31, 152.67, 149.15, 145.14, 128.93, 127.77, 126.64, 99.46, 54.26, 51.26, 18.31.

***5-(Methoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one* (5b)[16]**:



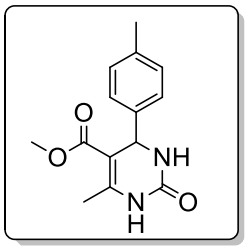
White solid, Mp: 190-192 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.25 (s, 1H), 7.76 (s, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 5.14 (d, J = 3.2 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.33, 158.92, 152.68, 148.82, 137.31, 127.81, 114.22, 99.74, 55.49, 53.66, 51.23, 18.28.

***5-(Methoxycarbonyl)-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one*(5c)[17]**:



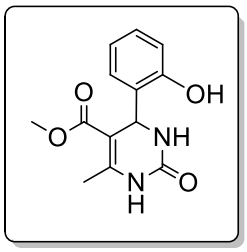
White solid, Mp: 240-242°C; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.36 (s, 1H), 9.17 (s, 1H), 7.66 (s, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 5.05 (d, J = 2.8 Hz, 1H), 3.53 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.38, 157.04, 152.70, 148.58, 135.69, 127.81, 115.51, 99.90, 53.73, 51.20, 18.27.

***5-(Methoxycarbonyl)-4-(4-methylphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one*(5 d)[18]**:



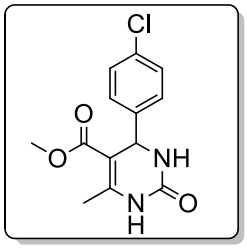
White solid, Mp: 200-201ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.24 (s, 1H), 7.76 (s, 1H), 7.17 (d, *J* = 6.4 Hz, 4H), 5.15 (d, *J* = 3.6 Hz, 1H), 3.56 (s, 3H), 2.29 (d, *J* = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.32, 152.68, 148.94, 142.23, 136.88, 129.42, 126.55, 99.60, 53.96, 51.22, 21.09, 18.27.

***5-(Methoxycarbonyl)-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one*(5e)[17]**:



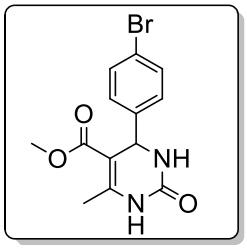
White solid, Mp: 228-230ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.70 (s, 1H), 9.21 (s, 1H), 7.15 (s, 1H), 7.13-7.09 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 5.51 (d, *J* = 3.2 Hz, 1H), 3.53 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.39, 155.14, 152.82, 149.56, 130.01, 128.81, 127.39, 118.90, 115.91, 97.87, 51.18, 49.40, 18.24.

***5-(Methoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one*(5 f)[18]**:



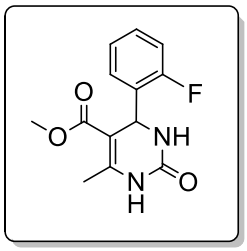
White solid, Mp: 204-206ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.34 (s, 1H), 7.86 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.20 (d, *J* = 3.2 Hz, 1H), 3.58 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.18, 152.47, 149.49, 144.06, 133.23, 128.93, 128.59, 99.05, 53.72, 51.31, 18.33.

***5-(Methoxycarbonyl)-6-methyl-4-(4-bromophenyl)-3,4-dihydropyrimidin-2(1H)-one*(5 g)[17]**:



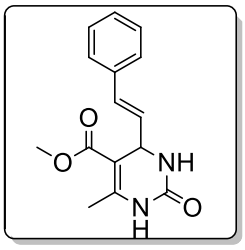
White solid, Mp: 208-209ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.34 (s, 1H), 7.86 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.18 (d, *J* = 3.2 Hz, 1H), 3.58 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.17, 152.45, 149.51, 144.47, 131.85, 128.96, 120.84, 98.98, 53.79, 51.32, 18.33.

***5-(Methoxycarbonyl)-6-methyl-4-(2-fluorophenyl)-3,4-dihydropyrimidin-2(1H)-one*(5 h)[17]**:



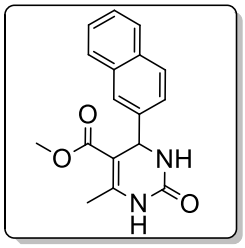
White solid, Mp: 260-263ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.35 (s, 1H), 7.78 (s, 1H), 7.37-7.30 (m, 2H), 7.22-7.18 (m, 2H), 5.49 (d, *J* = 2.8 Hz, 1H), 3.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 165.99, 161.07, 158.62, 152.09, 149.69, 131.95, 131.82, 129.92, 129.83, 129.20, 129.16, 125.05, 125.01, 116.11, 115.89, 97.68, 51.21, 49.06, 18.29.

***5-(Methoxycarbonyl)-6-methyl-4-styryl-3,4-dihydropyrimidin-2(1H)-one*(5i)[17]**:



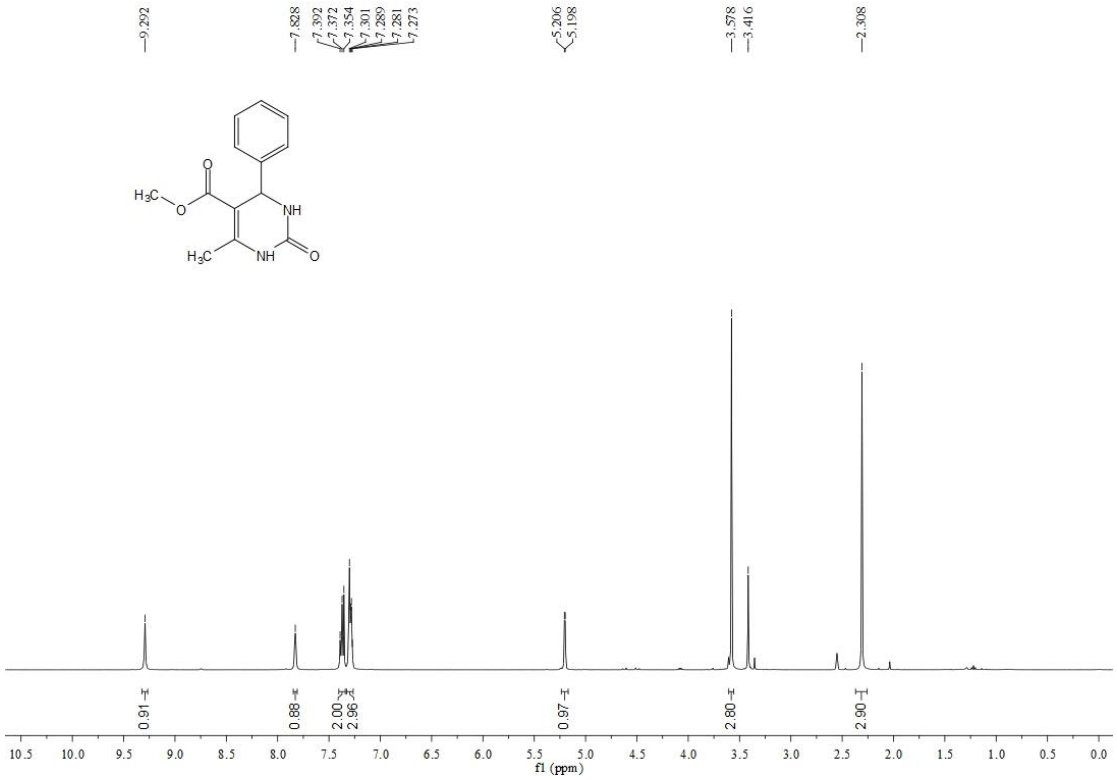
Pale yellow solid, Mp: 229-230ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.24 (s, 1H), 7.63 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.29-6.24 (m, 1H), 4.80-4.78 (m, 1H), 3.69 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.17, 153.10, 149.22, 136.69, 130.48, 129.12, 128.43, 128.06, 126.84, 98.12, 52.14, 51.37, 18.28.

***5-(Methoxycarbonyl)-6-methyl-4-(naphthalen-2-yl)-3,4-dihydropyrimidin-2(1H)-one*(5j)[17]**:

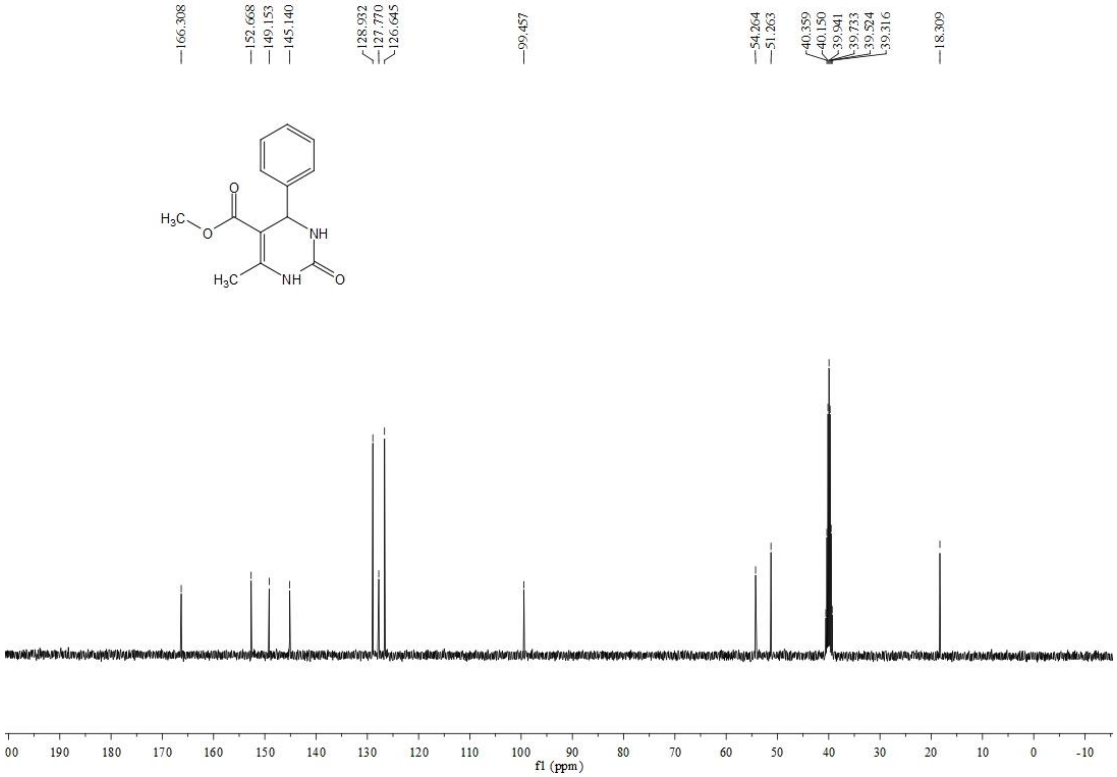


White solid, Mp: 253-256ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.22 (s, 1H), 7.84-7.80 (m, 4H), 7.60 (s, 1H), 7.46-7.42 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 2.8 Hz, 1H), 3.46 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 166.33, 152.54, 149.39, 142.43, 133.19, 132.81, 128.85, 128.36, 127.93, 126.75, 126.40, 125.36, 124.86, 99.20, 54.58, 51.29, 18.40.

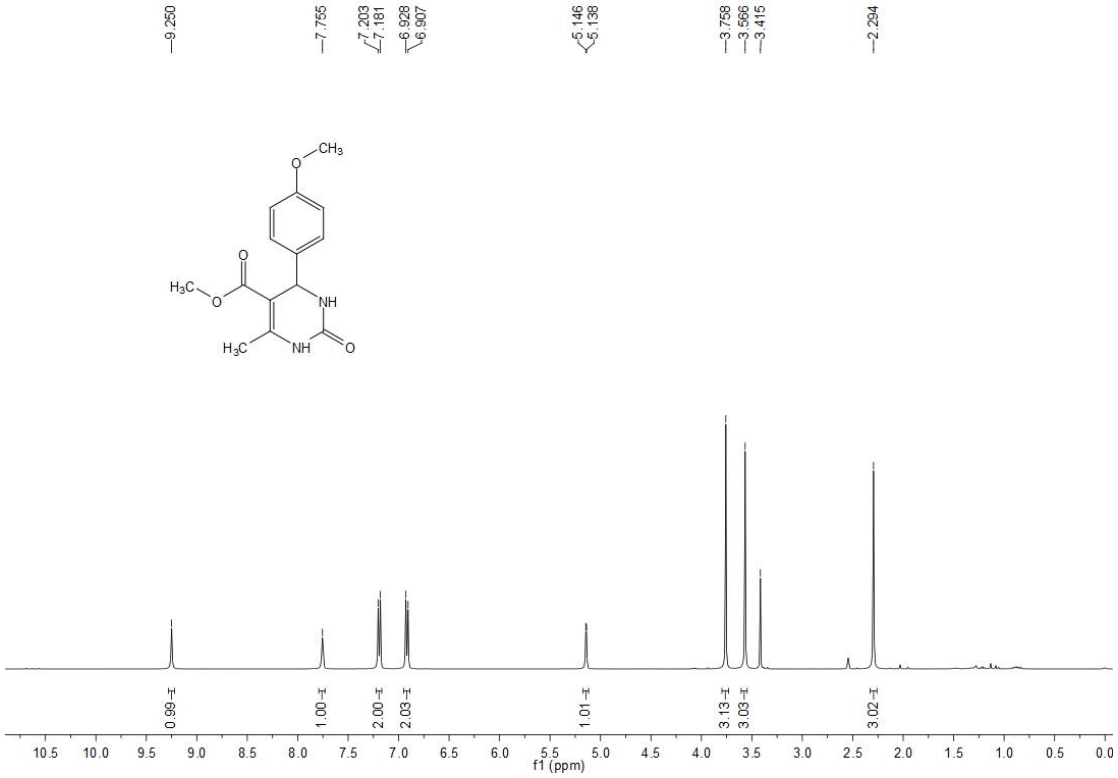
^{1}H NMR of **5a**



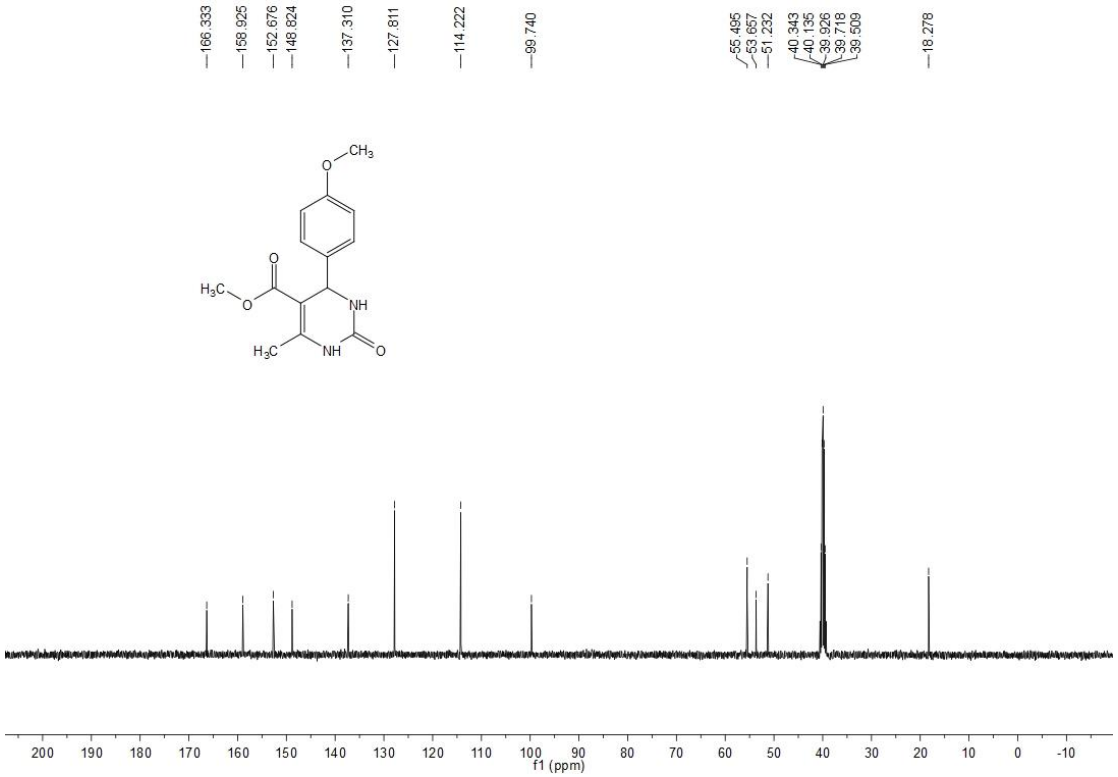
^{13}C NMR of **5a**



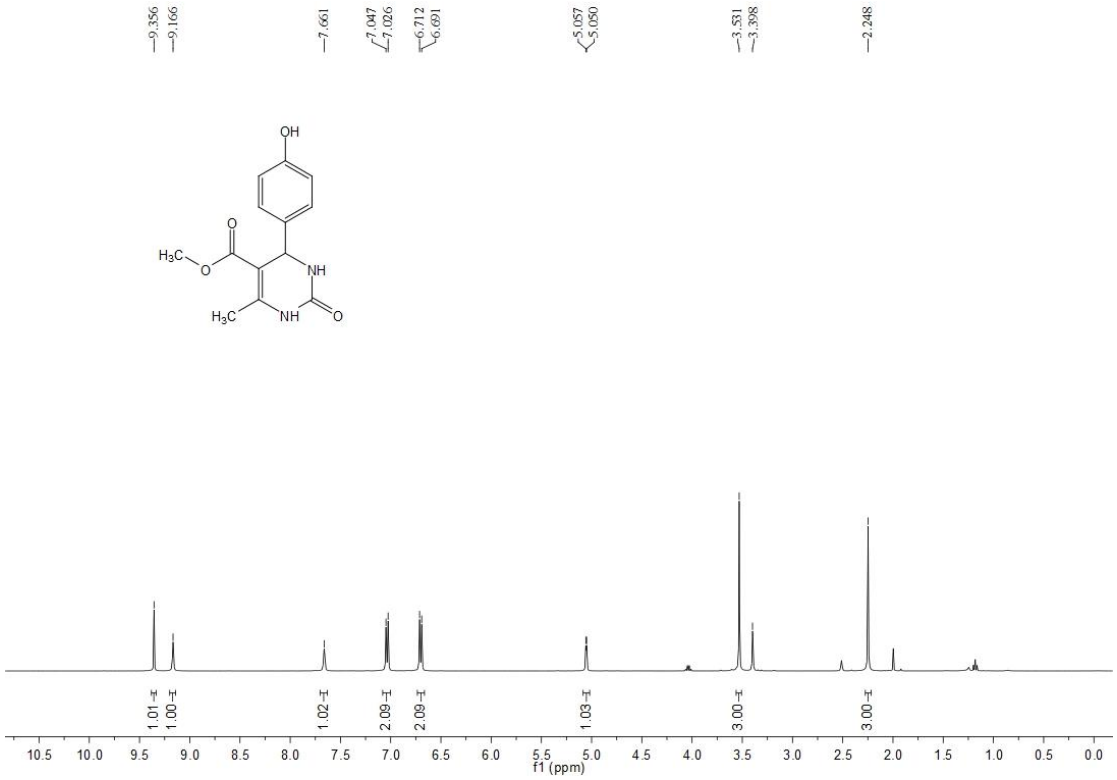
^{1}H NMR of **5b**



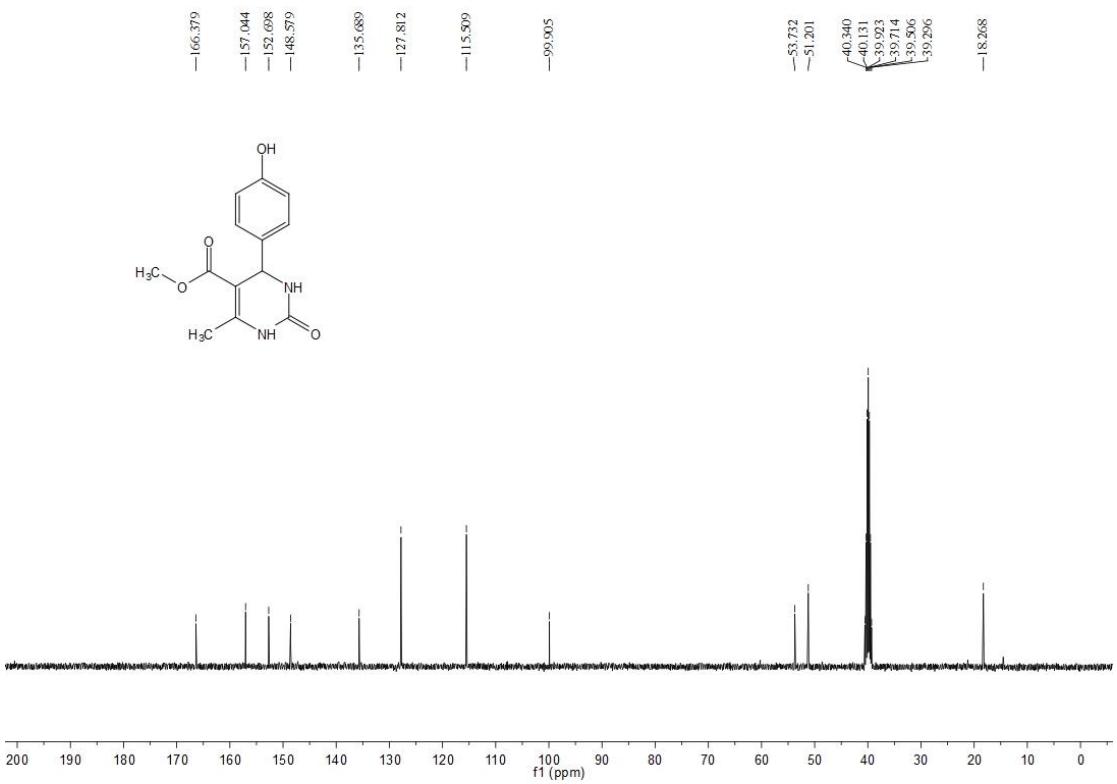
^{13}C NMR of **5b**



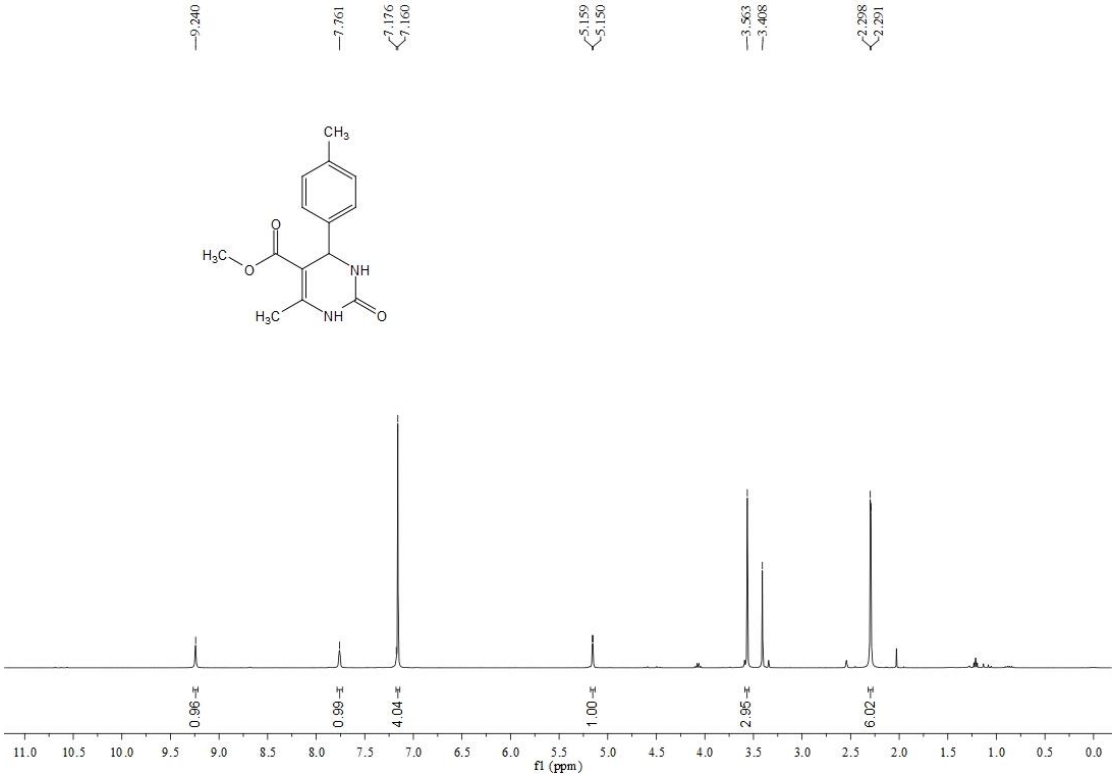
^{1}H NMR of **5c**



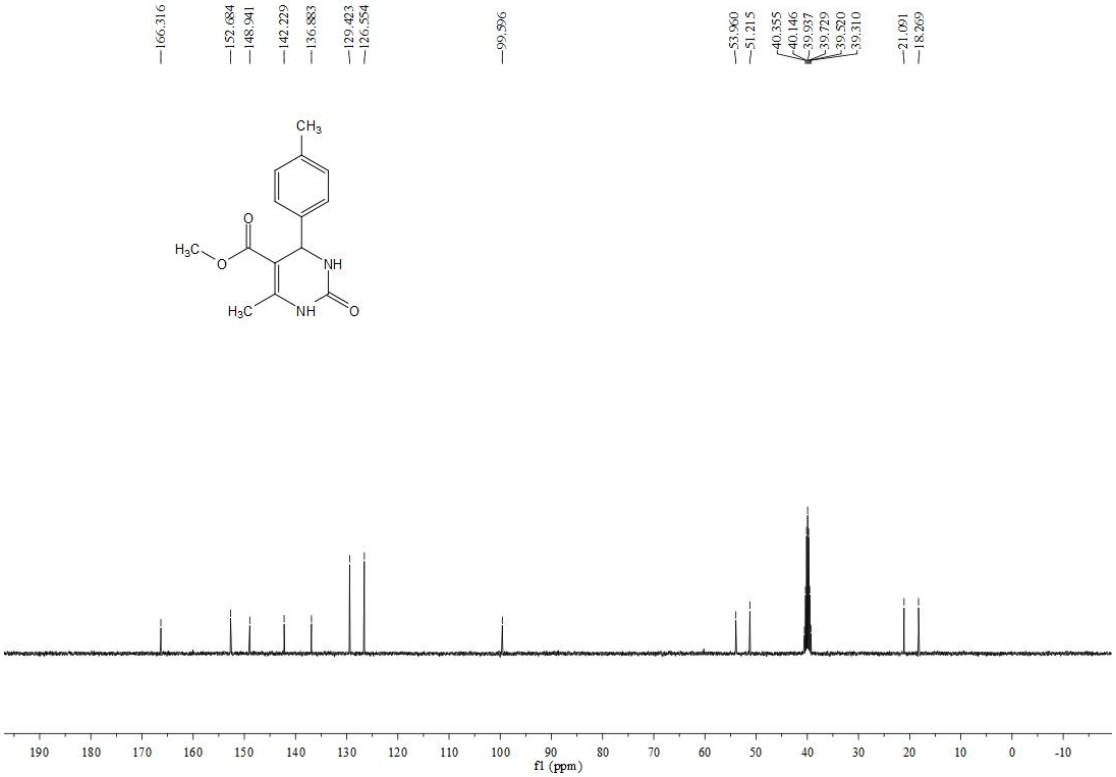
^{13}C NMR of **5c**



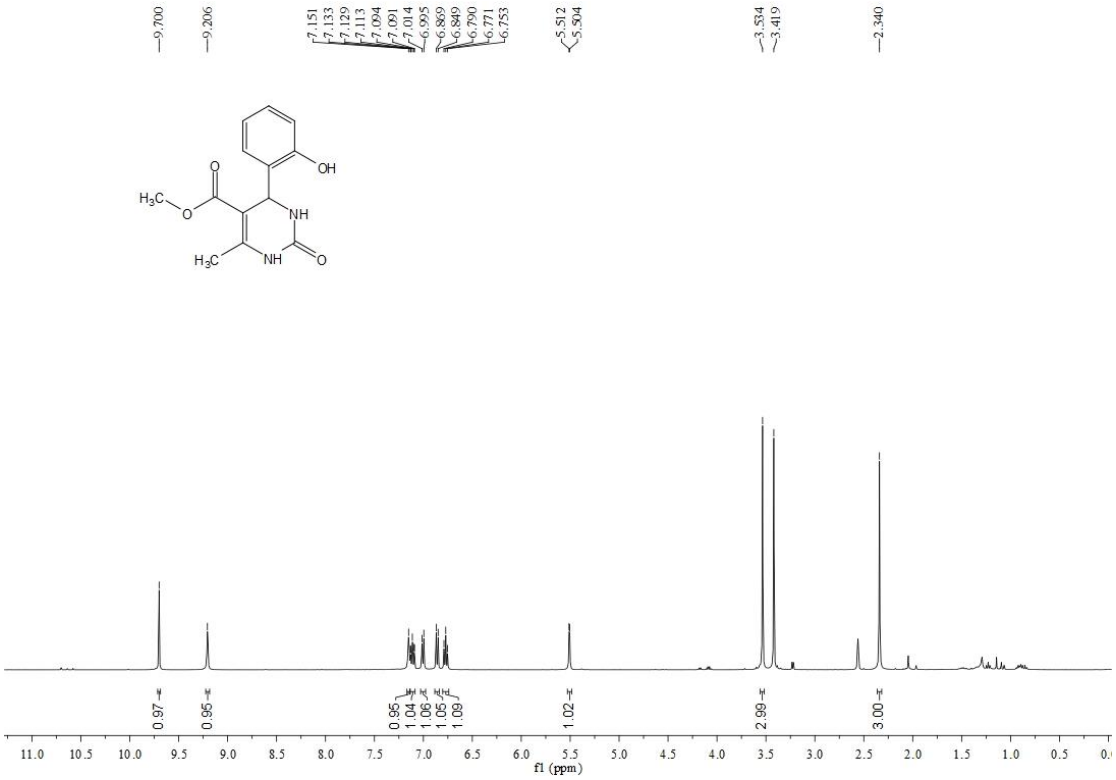
^{1}H NMR of **5d**



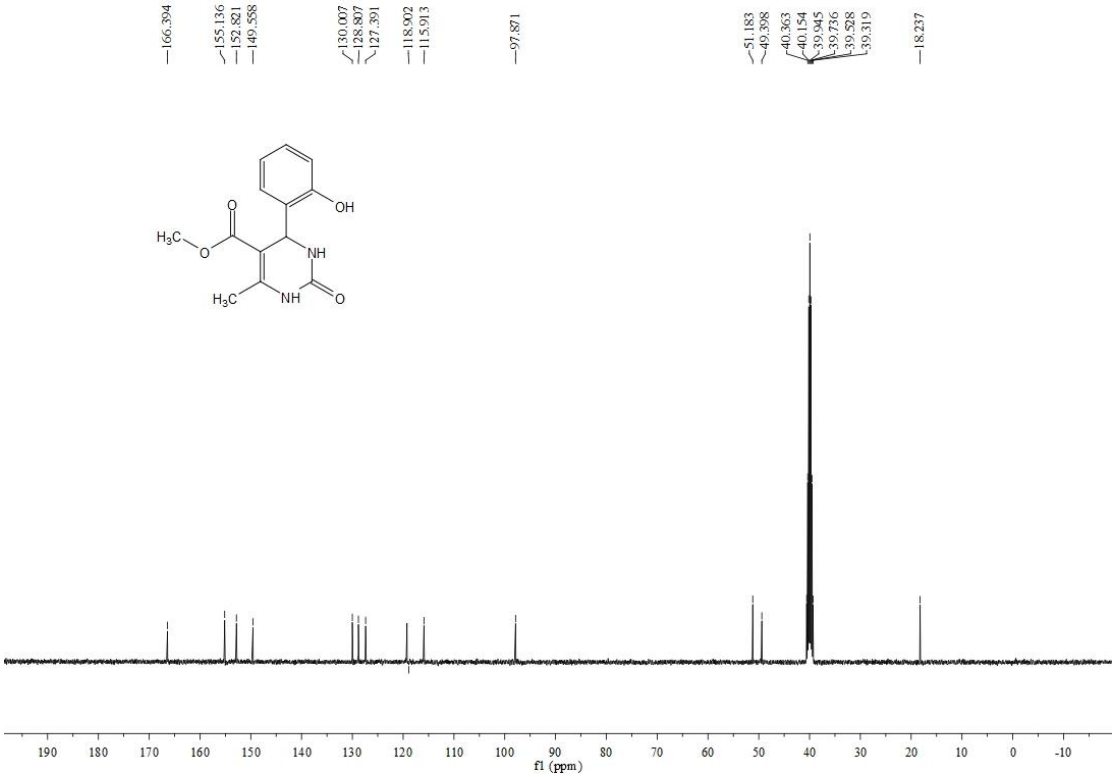
^{13}C NMR of **5d**



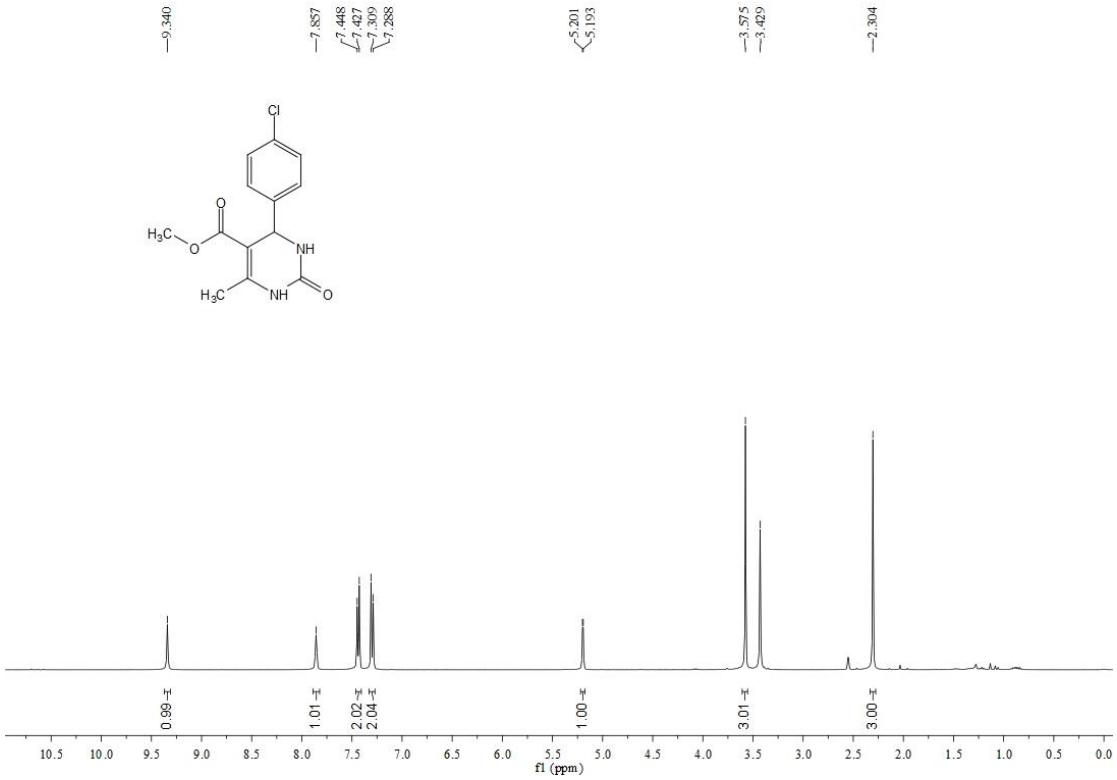
^{1}H NMR of **5e**



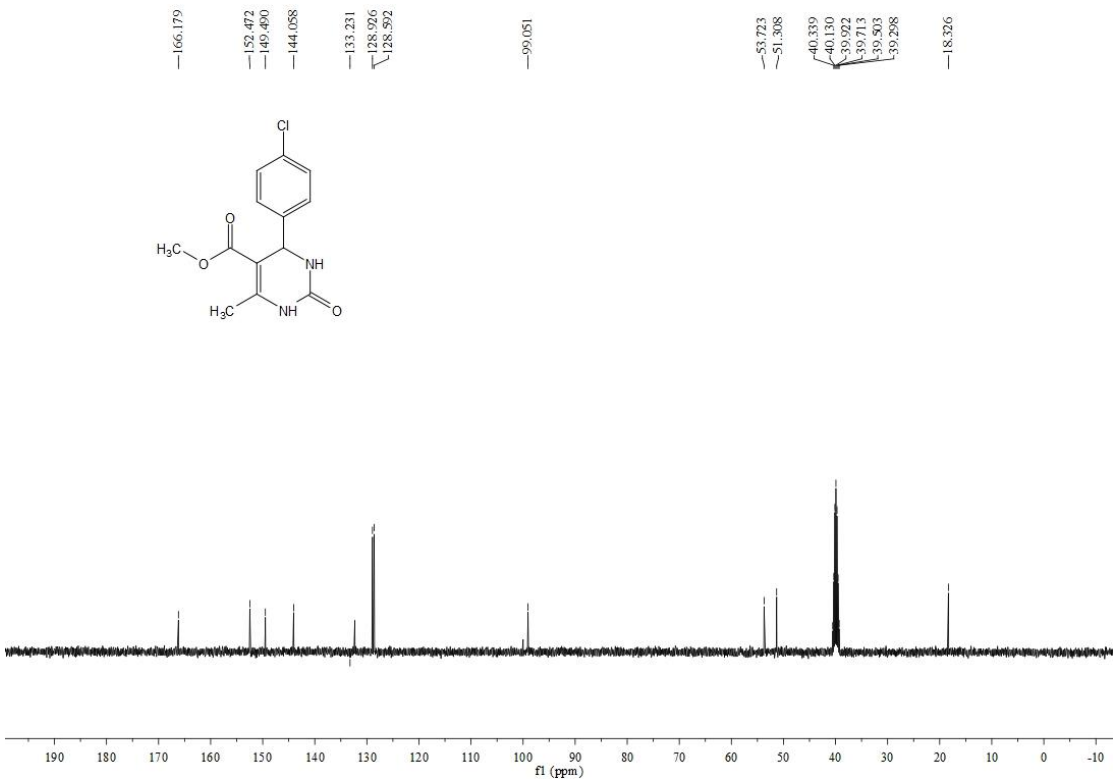
^{13}C NMR of **5e**



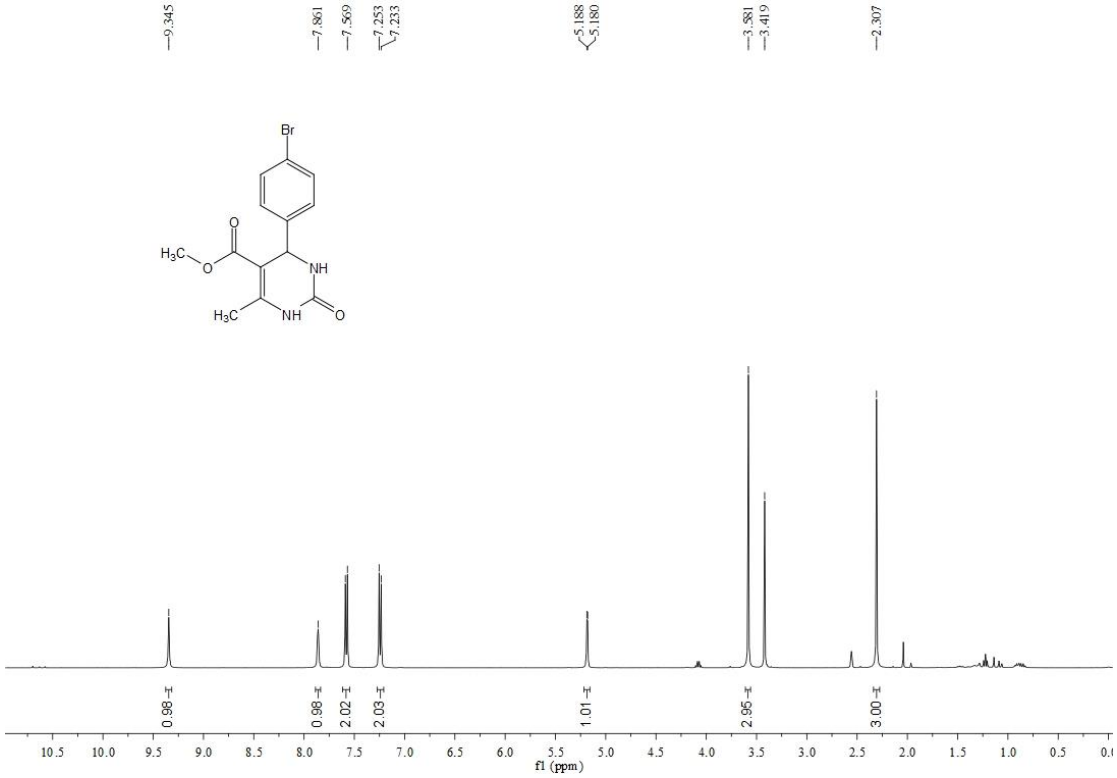
^{1}H NMR of **5f**



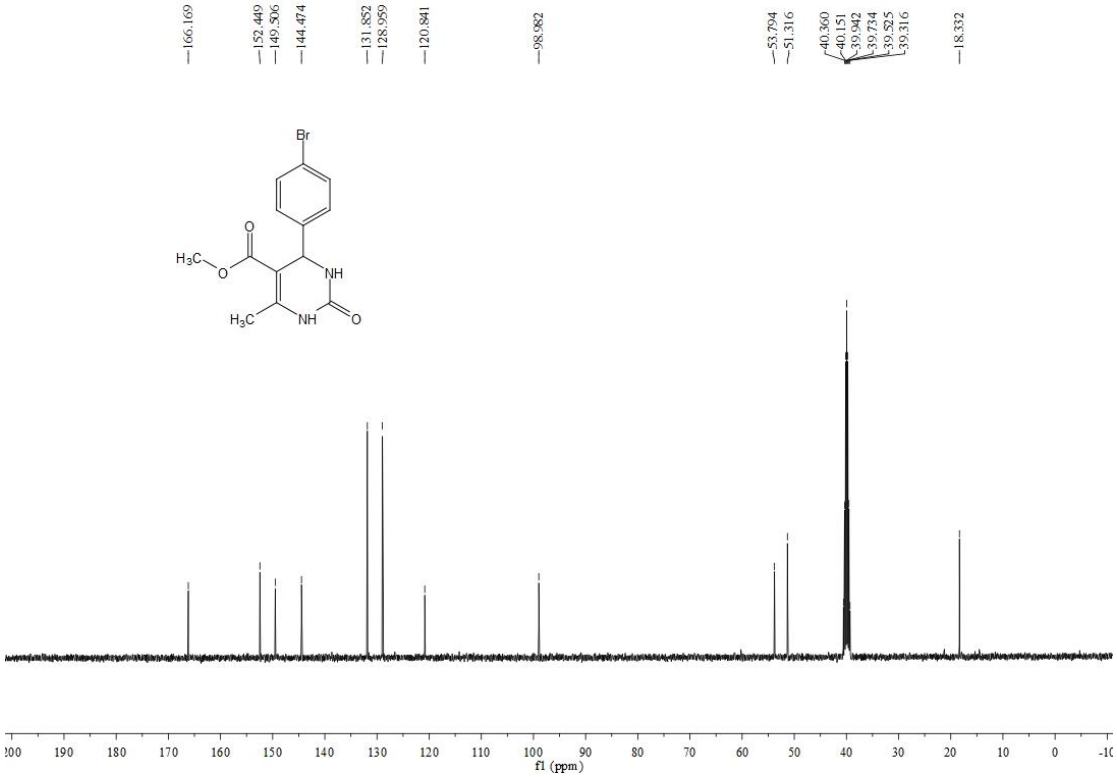
^{13}C NMR of **5f**



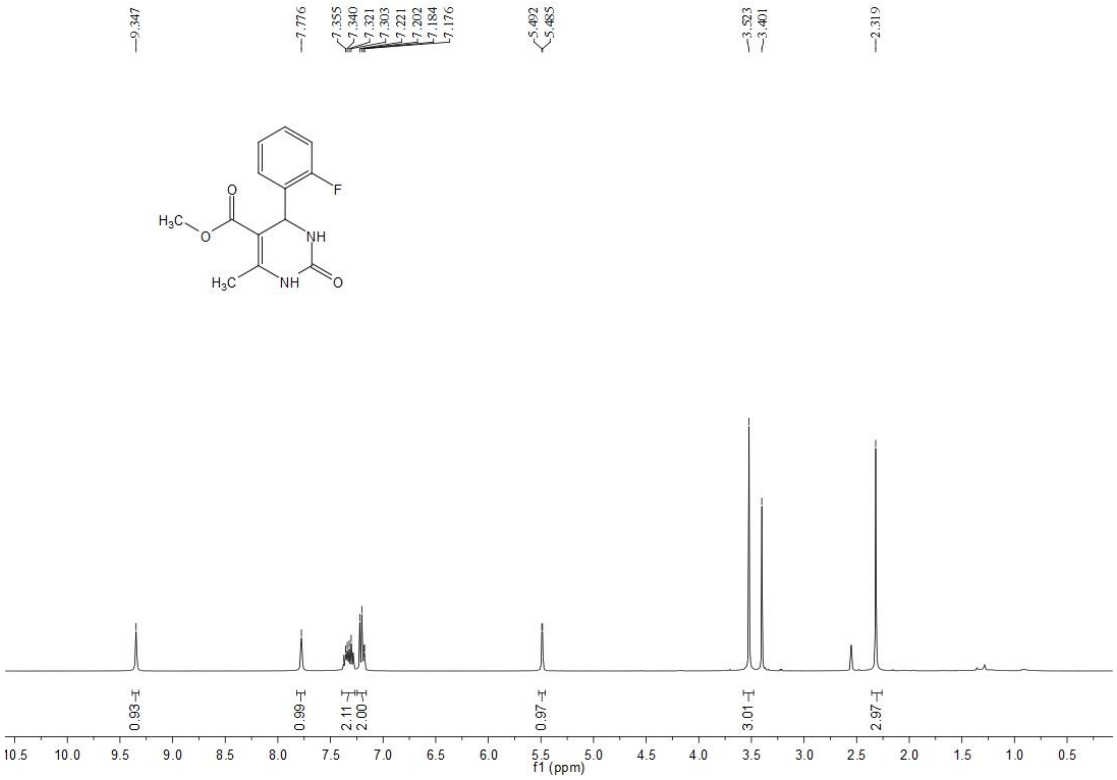
^{1}H NMR of **5g**



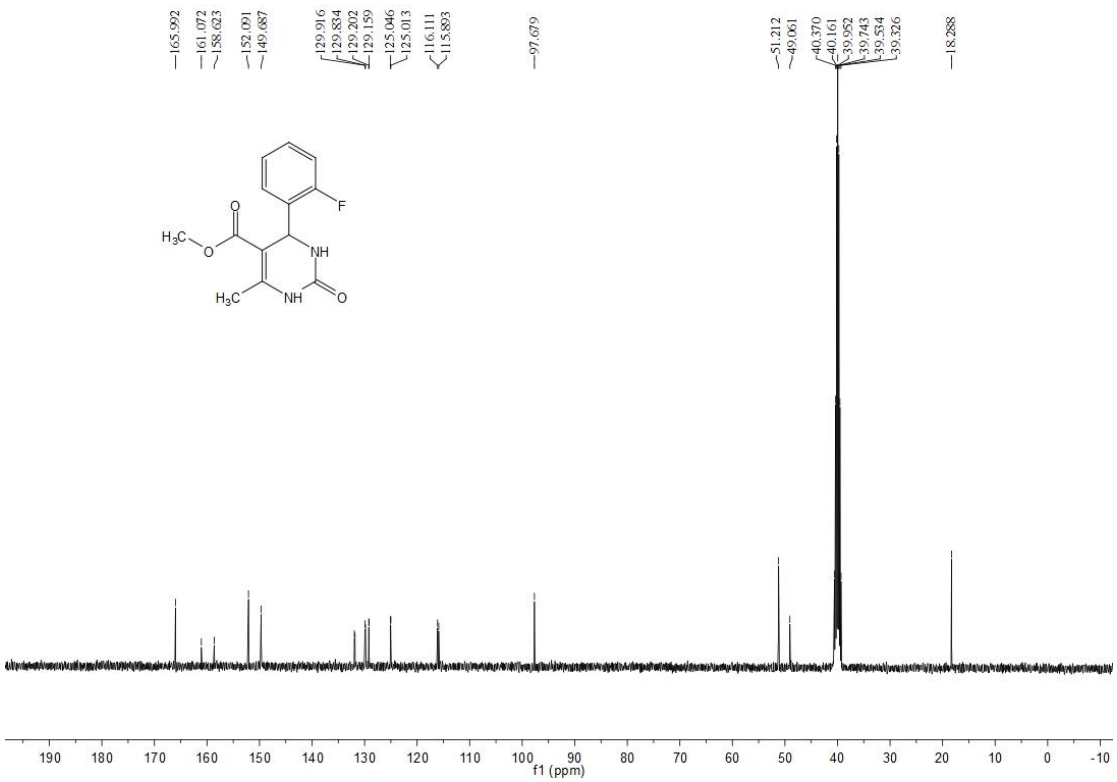
^{13}C NMR of **5g**



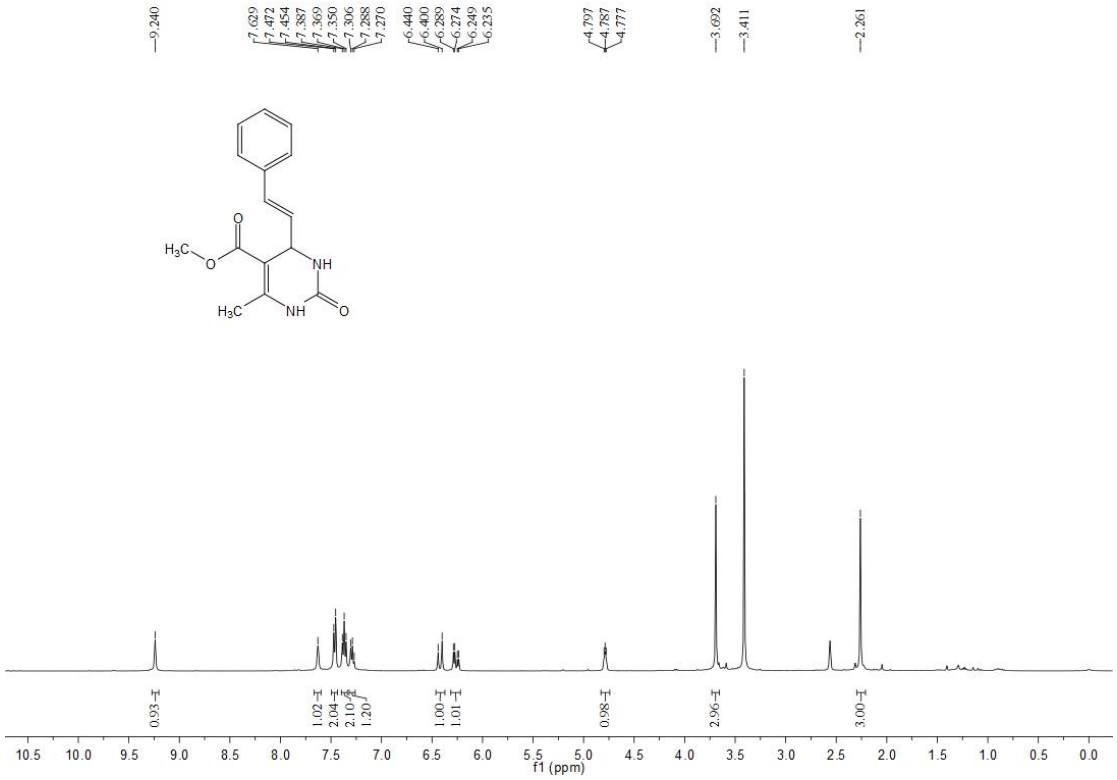
^{1}H NMR of **5h**



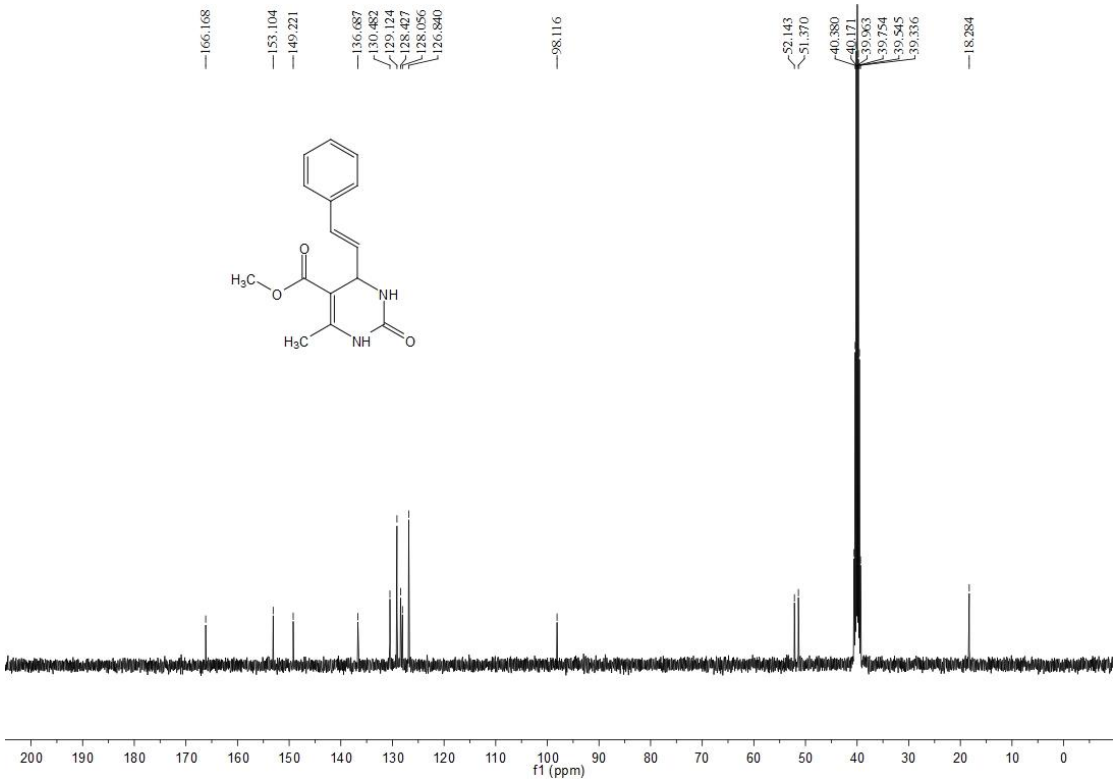
^{13}C NMR of **5h**



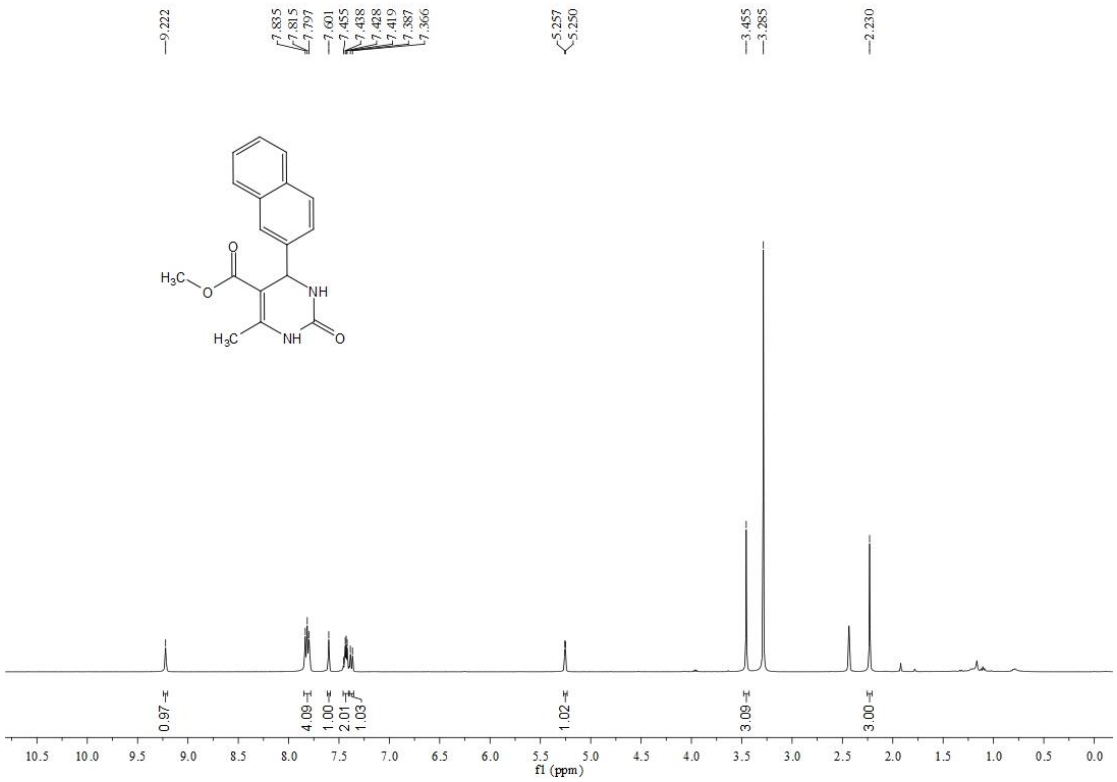
^{1}H NMR of **5i**



^{13}C NMR of **5i**



^{1}H NMR of **5j**



^{13}C NMR of **5j**