

Supporting information for
An Electrochemical Off-On Method for Pyrimidin-
2(1H)-ones Synthesis via Three-component
Cyclization

Yanyan Kong, Yabo Li, Mengmeng Huang, Jung Keun Kim* and Yangjie Wu*

College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P.R. China.

Experimental details and spectroscopic data

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1. General Information

All reagents were used in analytical grades and were obtained from commercial sources without further purification unless otherwise noted. Some diketones were purchased from commercial suppliers or prepared according to reported procedures (**1i**, **1k-1n**, **1q-1r**).¹ Electrolysis was conducted using a DC power supply (MWSTEK DP3005B) in constant current mode. The anode electrode is platinum plate electrode (10 mm × 10 mm × 0.2 mm) and cathode electrode is graphite rod ($\Phi = 6$ mm). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. Flash chromatography columns were packed with 200-300 mesh silica gel and silica gel was purchased from Qing Dao Hai Yang Chemical Industry. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl₃. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz relative to tetramethylsilane as internal standard ($\delta = 0$ ppm). For the ¹⁹F spectra, α -trifluorotoluene served as external standard ($\delta = -63.9$ ppm). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). The Cyclic voltammetry (CV) was recorded in CH₃CN by CHI650A.

2. Experimental Procedure

General procedure for the electrochemical one-pot synthesis of pyrimidin-2(1H)-ones

Compounds **1** (0.3 mmol), **2** (0.75 mmol) and **3** (0.6 mmol) were heated at 105 °C under air for 9 h. Then EtOH (5 mL) and TBAPF₆ (0.5 mmol) were added into the reaction mixture. The resulting solution was electrolyzed with a C|Pt electrode under a constant current (5 mA) in an undivided cell at 25 °C for 10 hours. After electrolysis, the product was purified by column chromatography on silica gel (elute: dichloromethane/EtOH 80/1-40/1, v/v) to give the desired product.

3. Cyclic Voltammetry Experiments

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M TBAPF₆ in CH₃CN) at different scan rates (40, 50, 60, 80, 100, 120, 150, 200, 220, 250, and 280 mV/s).

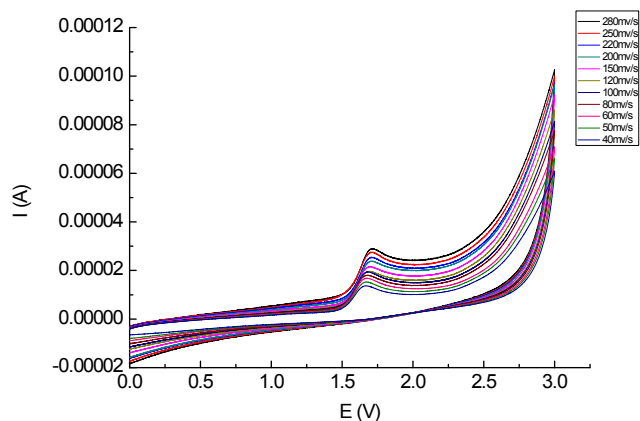


Figure S1. Cyclic voltammograms of 1.0 mM **5a** at different scan rates. Curves are obtained at 40, 50, 60, 80, 100, 120, 150, 200, 220, 250, and 280 mV/s, respectively.

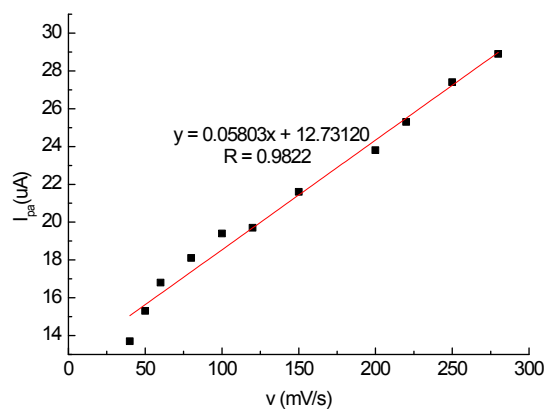


Figure S2. The plot of peak current vs. scan rate

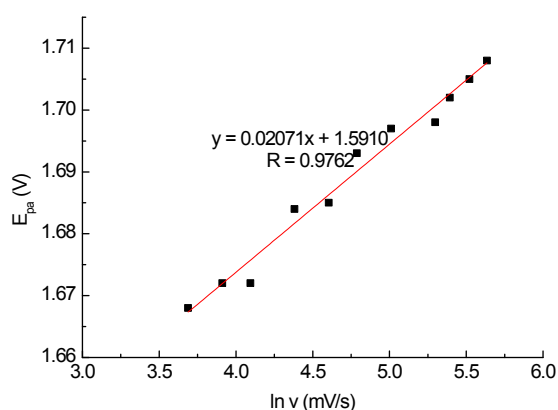


Figure S3. The relationship between E_{pa} and $\ln v$.

The peak current increased linearly with the scan rate in the range of 40-400 mV/s and the equation could be expressed as follows: $y = 0.05803x + 12.7320$, $R = 0.9822$. It could be seen that the oxidation of compound **5a** was an adsorption-controlled process. For an adsorption-controlled and irreversible electrode process, according to Laviron method,² E_{pa} is defined by

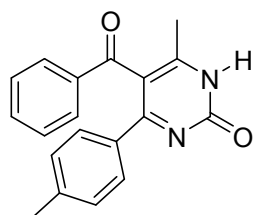
the following equation:

$$E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln v$$

where α is transfer coefficient, k^0 is standard rate constant of the reaction, n is electron transfer number involved in the rate-determining step, v is scan rate, and E^0 is formal potential. Other symbols have their usual meanings. Thus, the value of αn can be easily calculated from the slope of E_{pa} - $\ln v$. In this system, the slope is 0.02071. Generally, transfer coefficient α was assumed as 0.5,³ so the value of the number of electron (n) was calculated to be 2.

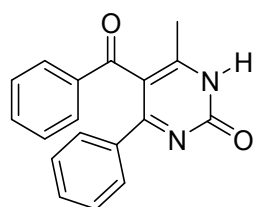
4. Characterization Data

5-benzoyl-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4a):



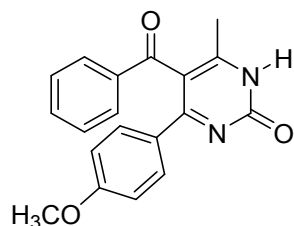
Yellow solid (65.7 mg, 72%). mp. 109.8-112.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.91 (bs, 1H), 7.70-7.64 (m, 2H), 7.49-7.42 (m, 3H), 7.35-7.28 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.7, 158.8, 141.7, 137.2, 133.8, 129.3, 129.3, 129.0, 128.7, 116.9, 21.4. HRMS (ESI) calcd. for C₁₉H₁₇N₂O₂ (M+H)⁺: 305.1285, found: 305.1284.

5-benzoyl-6-methyl-4-phenylpyrimidin-2(1H)-one (4b):



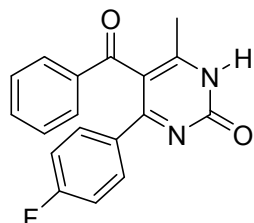
White solid (59.2 mg, 68%). mp. 180.1-183.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.91 (bs, 1H), 7.68-7.61 (m, 2H), 7.58-7.52 (m, 2H), 7.47-7.39 (m, 1H), 7.33-7.28 (m, 2H), 7.26-7.18 (m, 3H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.4, 158.8, 137.2, 133.8, 131.1, 129.3, 128.9, 128.7, 128.5, 117.1. HRMS (ESI) calcd. for C₁₈H₁₅N₂O₂ (M+H)⁺: 291.1128, found: 291.1127.

5-benzoyl-4-(4-methoxyphenyl)-6-methylpyrimidin-2(1H)-one (4c):



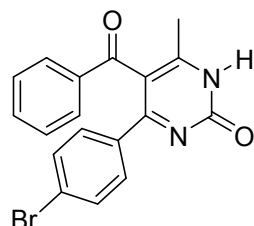
White solid (70.2mg, 73%). mp. 168.9-171.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.86 (bs, 1H), 7.72-7.64 (m, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.48-7.42 (m, 1H), 7.35-7.28 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.9, 162.0, 158.8, 137.2, 133.8, 131.0, 129.3, 128.7, 116.6, 113.9, 55.3. HRMS (ESI) calcd. for C₁₉H₁₇N₂O₃ (M+H)⁺: 321.1234, found: 321.1234.

5-benzoyl-4-(4-fluorophenyl)-6-methylpyrimidin-2(1H)-one (4d):



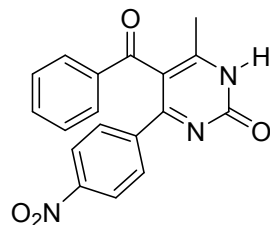
White solid (52.7 mg, 57%). mp. 110.2-113.7 °C. ¹H NMR (400 MHz, CDCl₃): δ 14.00 (bs, 1H), 7.68-7.63 (m, 2H), 7.61-7.55 (m, 2H), 7.50-7.44 (m, 1H), 7.36-7.30 (m, 2H), 6.91 (t, *J* = 8.6 Hz, 2H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.3, 164.3 (d, *J* = 253.1 Hz), 158.7, 137.1, 134.0, 131.3 (d, *J* = 8.8 Hz), 129.3, 128.8, 117.0, 115.7 (d, *J* = 22.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -108.1. HRMS (ESI) calcd. for C₁₈H₁₄FN₂O₂ (M+H)⁺: 309.1034, found: 309.1035.

5-benzoyl-4-(4-bromophenyl)-6-methylpyrimidin-2(1H)-one (4e):



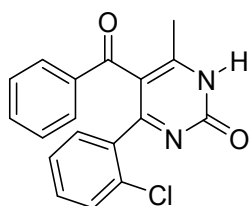
Yellow solid (56.5mg, 51%). mp. 174.2-176.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.98 (bs, 1H), 7.70-7.63 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46-7.40 (m, 2H), 7.39-7.31 (m, 4H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 158.7, 137.0, 134.2, 131.7, 130.5, 129.3, 128.9, 126.1, 117.0. HRMS (ESI) calcd. for C₁₈H₁₄BrN₂O₂ (M+H)⁺: 369.0233, found: 370.0265.

5-benzoyl-6-methyl-4-(4-nitrophenyl)pyrimidin-2(1H)-one (4f):



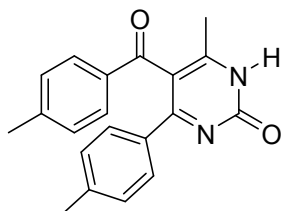
Yellow solid (12.1 mg, 12%). mp. 117.4-119.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.81 (bs, 1H), 8.11-8.05 (m, 2H), 7.75-7.70 (m, 2H), 7.70-7.64 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.39-7.34 (m, 2H), 2.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 158.5, 149.0, 136.9, 134.5, 129.9, 129.3, 129.1, 123.5, 117.3. HRMS (ESI) calcd. for C₁₈H₁₄N₃O₄ (M+H)⁺: 336.0979, found: 336.0979.

5-benzoyl-4-(2-chlorophenyl)-6-methylpyrimidin-2(1H)-one (4g):



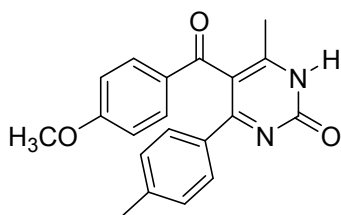
Yellow solid (37.0 mg, 38%). mp. 138.4-140.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.67-7.60 (m, 2H), 7.47-7.40 (m, 1H), 7.35-7.28 (m, 2H), 7.24-7.17 (m, 1H), 7.16-7.05 (m, 3H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.2, 158.0, 137.4, 133.7, 131.8, 131.2, 130.4, 129.9, 129.1, 128.5, 126.5, 118.4. HRMS (ESI) calcd. for C₁₈H₁₄ClN₂O₂ (M+H)⁺: 325.0738, found: 325.0740.

6-methyl-5-(4-methylbenzoyl)-4-(p-tolyl)pyrimidin-2(1H)-one (4i):



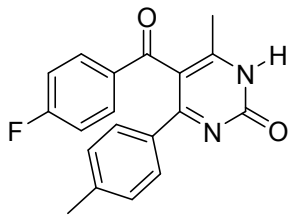
White solid (40.1 mg, 42%). mp. 173.4-176.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.85 (bs, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.3, 158.9, 145.0, 141.7, 134.8, 129.6, 129.5, 129.3, 129.0, 117.1, 21.8, 21.4. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₂ (M+H)⁺: 319.1441, found: 319.1445.

5-(4-methoxybenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4j):



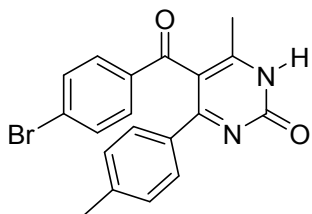
Yellow solid (32.1 mg, 32%). mp. 114.6-117.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.86 (bs, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.28-7.25 (m, 1H), 7.22-7.18 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.03-6.98 (m, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.1, 164.1, 158.8, 141.7, 131.9, 130.3, 129.3, 128.9, 117.2, 114.0, 63.8, 55.5, 21.4. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₃ (M+H)⁺: 335.1390, found: 335.1391.

5-(4-fluorobenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4k):



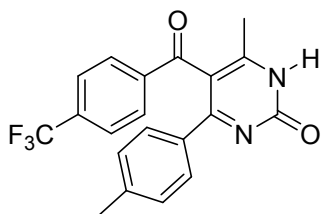
Yellow solid (71.6 mg, 74%). mp. 168.5-170.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.81 (bs, 1H), 7.68 (dt, *J*₁ = 5.4 Hz, *J*₂ = 8.8 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.00-6.93 (m, 2H), 2.46 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.0, 165.9 (d, *J* = 256.8 Hz), 158.7, 114.94, 133.7 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 9.5 Hz), 129.3, 128.9, 116.5, 115.9 (d, *J* = 22.0 Hz), 21.4. ¹⁹F NMR (376 MHz, CDCl₃): δ -103.2. HRMS (ESI) calcd. for C₁₉H₁₆FN₂O₂ (M+H)⁺: 323.1190, found: 323.1192.

5-(4-bromobenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4l):



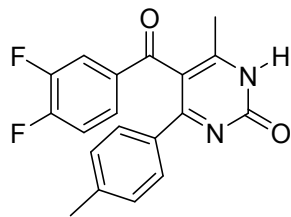
White solid (63.2 mg, 55%). mp. 204.6-207.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.81 (bs, 1H), 7.54-7.48 (m, 2H), 7.47-7.40 (m, 4H), 7.05 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 158.7, 142.1, 136.0, 132.0, 130.7, 129.4, 129.1, 128.9, 116.3, 21.4. HRMS (ESI) calcd. for C₁₉H₁₆BrN₂O₂ (M+H)⁺: 383.0390, found: 383.0389.

6-methyl-4-(p-tolyl)-5-(4-(trifluoromethyl)benzoyl)pyrimidin-2(1H)-one (4m):



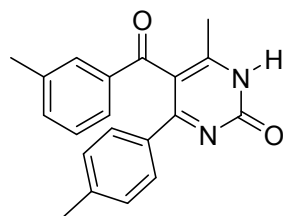
Yellow solid (52.5 mg, 47%). mp. 181.5-184.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.86 (bs, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 2.50 (s, 3H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 158.6, 142.2, 140.0, 134.6 (q, *J* = 33.0 Hz), 129.5, 129.0, 125.6 (q, *J* = 3.7 Hz), 128.3 (d, *J* = 272.9 Hz), 127.4, 116.2, 21.3. ¹⁹F NMR (376 MHz, CDCl₃): δ -63.3. HRMS (ESI) calcd. for C₂₀H₁₆F₃N₂O₂ (M+H)⁺: 373.1158, found: 373.1160.

5-(3,4-difluorobenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4n):



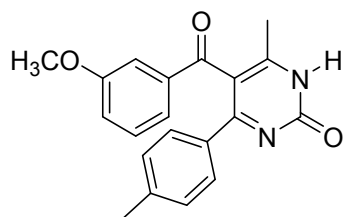
White solid (48.0 mg, 47%). mp. 182.4-184.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.87 (bs, 1H), 7.57-7.49 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.37-7.31 (m, 1H), 7.10-6.99 (m, 3H), 2.48 (s, 3H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.1, 158.6, 153.8 (dd, *J*₁ = 13.2 Hz, *J*₂ = 259.0 Hz), 150.3 (dd, *J*₁ = 13.2 Hz, *J*₂ = 251.6 Hz), 142.2, 134.4, 129.5, 128.9, 126.5 (q, *J* = 2.9 Hz), 118.2 (d, *J* = 18.3 Hz), 117.5 (d, *J* = 18.3 Hz), 115.9, 21.4. ¹⁹F NMR (376 MHz, CDCl₃): δ -127.8 (d, *J* = 17.7 Hz), -135.2 (d, *J* = 21.8 Hz). HRMS (ESI) calcd. for C₁₉H₁₅F₂N₂O₂ (M+H)⁺: 341.1096, found: 341.1098.

6-methyl-5-(3-methylbenzoyl)-4-(p-tolyl)pyrimidin-2(1H)-one (4o):



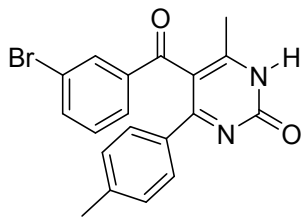
White solid (52.5 mg, 55%). mp. 71.6-73.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.92 (bs, 1H), 7.52-7.42 (m, 4H), 7.30-7.25 (m, 1H), 7.24-7.17 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.8, 158.9, 141.7, 138.6, 137.2, 134.7, 129.8, 129.2, 128.9, 128.6, 126.7, 117.1, 21.4, 21.2. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₂ (M+H)⁺: 319.1441, found: 319.1442.

5-(3-methoxybenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4p):



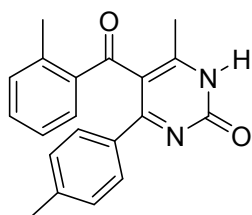
Yellow solid (45.1 mg, 45%). mp. 102.4-103.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.83 (bs, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.28-7.25 (m, 1H), 7.22-7.17 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.02-6.98 (m, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.4, 159.8, 158.8, 141.7, 138.6, 129.7, 129.3, 129.0, 122.4, 120.6, 117.0, 112.9, 55.5, 21.4. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₃ (M+H)⁺: 335.1390, found: 335.1392.

5-(3-bromobenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4q):



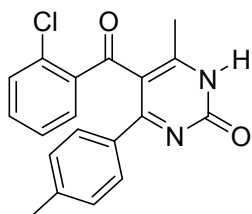
Yellow solid (57.5 mg, 50%). mp. 102.5-103.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.87 (bs, 1H), 7.79-7.75 (m, 1H), 7.56-7.50 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.19-7.12 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.1, 158.7, 142.0, 139.0, 136.4, 132.1, 130.2, 129.4, 128.9, 127.8, 122.9, 116.2, 21.4. HRMS (ESI) calcd. for C₁₉H₁₆BrN₂O₂ (M+H)⁺: 383.0390, found: 383.0388.

6-methyl-5-(2-methylbenzoyl)-4-(p-tolyl)pyrimidin-2(1H)-one (4r):



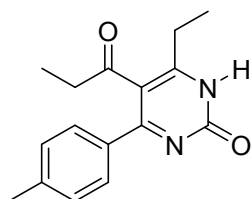
White solid (54.4 mg, 57%). mp. 192.4-195.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.81 (bs, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.28-7.21 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.06-6.98 (m, 3H), 2.55-2.45 (m, 6H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 196.0, 158.9, 141.4, 139.9, 137.2, 132.4, 132.1, 130.6, 129.0, 128.6, 125.6, 118.5, 21.4, 21.3. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₂ (M+H)⁺: 319.1441, found: 319.1443.

5-(2-chlorobenzoyl)-6-methyl-4-(p-tolyl)pyrimidin-2(1H)-one (4s):



White solid (65.0 mg, 64%). mp. 110.3-113.7 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.71 (bs, 1H), 7.36-7.28 (m, 3H), 7.21-7.11 (m, 2H), 7.09-7.03 (m, 1H), 7.03-6.97 (d, *J* = 8.0 Hz, 2H), 2.62 (s, 3H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 192.9, 158.1, 141.6, 137.4, 132.7, 132.6, 131.5, 130.7, 129.1, 128.8, 126.5, 118.0, 21.3. HRMS (ESI) calcd. for C₁₉H₁₆ClN₂O₂ (M+H)⁺: 339.0895, found: 339.0894.

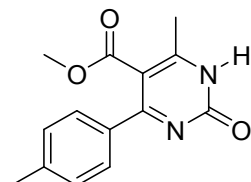
6-ethyl-5-propionyl-4-(p-tolyl)pyrimidin-2(1H)-one (4t):



Yellow solid (26.8 mg, 33%). mp. 125.7-128.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.57 (bs,

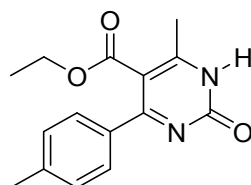
1H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.30-7.23 (m, 2H), 2.73 (q, $J = 7.6$ Hz, 2H), 2.41 (s, 3H), 2.16 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.5$ Hz, 3H), 0.90 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 205.0, 158.7, 142.2, 129.7, 128.8, 118.7, 38.2, 21.5, 8.5. HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 271.1441, found: 271.1443.

Methyl 6-methyl-2-oxo-4-(p-tolyl)-1,2-dihydropyrimidine-5-carboxylate (4v)⁴:



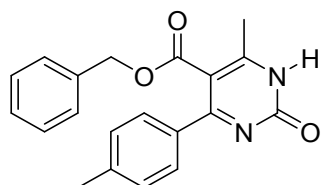
Yellow solid (51.1 mg, 66%). mp. 149.6-152.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 13.66 (bs, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 3.62 (s, 3H), 2.59 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 158.4, 141.6, 129.2, 128.1, 111.0, 52.4, 21.5. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 259.1077, found: 259.1079.

Ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2-dihydropyrimidine-5-carboxylate (4w)^{5,6}:



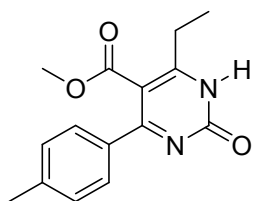
Yellow solid (44.9 mg, 55%). mp. 125.4-128.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 13.73 (bs, 1H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.10 (q, $J = 7.1$ Hz, 2H), 2.59 (s, 3H), 2.40 (s, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.4, 158.4, 141.5, 129.1, 128.2, 111.4, 61.6, 21.5, 13.6. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 273.1234, found: 273.1233.

Benzyl 6-methyl-2-oxo-4-(p-tolyl)-1,2-dihydropyrimidine-5-carboxylate (4x):



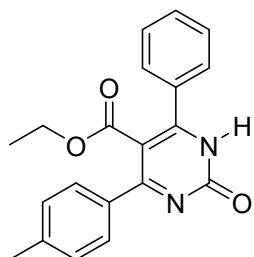
White solid (76.2 mg, 76%). mp. 70.1-73.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 13.70 (bs, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.31-7.20 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.96-6.90 (m, 2H), 5.04 (s, 2H), 2.57 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.2, 157.3, 141.6, 134.3, 129.3, 128.5, 128.4, 128.4, 127.9, 110.8, 67.6, 21.4. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 335.1390, found: 335.1392.

Methyl 6-ethyl-2-oxo-4-(p-tolyl)-1,2-dihydropyrimidine-5-carboxylate (4y):



Yellow solid (28.6 mg, 35%). mp. 141.3-144.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.58 (bs, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.38 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 158.6, 141.6, 129.3, 128.1, 110.6, 52.4, 21.5, 13.4. HRMS (ESI) calcd. for C₁₅H₁₇N₂O₃ (M+H)⁺: 273.1234, found: 273.1235.

Ethyl 2-oxo-6-phenyl-4-(p-tolyl)-1,2-dihydropyrimidine-5-carboxylate (4z)⁶:



Yellow solid (34.1 mg, 34%). mp, 98.3-100.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 13.15 (bs, 1H), 7.64-7.58 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.50-7.41 (m, 3H), 7.30-7.24 (m, 2H), 3.93 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.5, 157.9, 141.8, 131.0, 129.5, 128.6, 128.1, 128.0, 111.8, 61.8, 21.5, 13.4. ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.53 (bs, 1H), 7.59-7.40 (m, 7H), 7.32-7.28 (m, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 166.9, 141.0, 130.9, 129.5, 128.9, 128.4, 128.2, 61.6, 21.4, 13.6. HRMS (ESI) calcd. for C₂₀H₁₉N₂O₃ (M+H)⁺: 335.1390, found: 335.1391.

References:

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- [2] E. Laviron, *J. Electroanal. Chem. Interfacial.*, 1974, **52**, 355.
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5. ^1H , ^{13}C and ^{19}F NMR Spectra

14840-K240-1-H.ESP
14840-K240-1-H.ESP

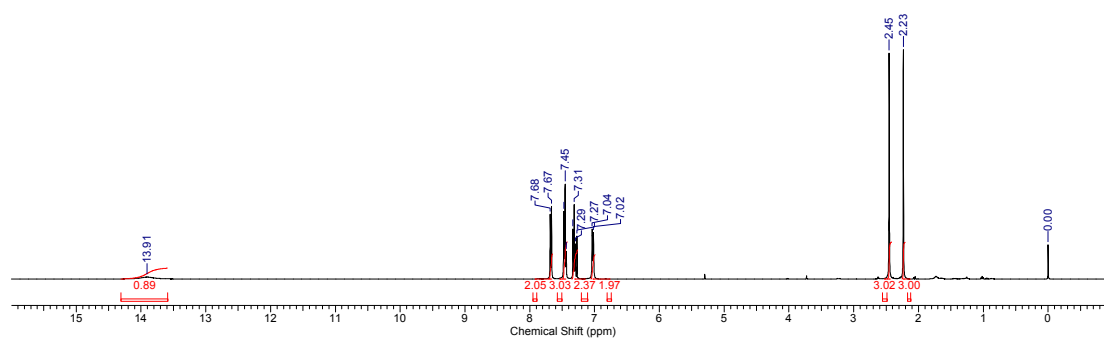
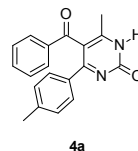
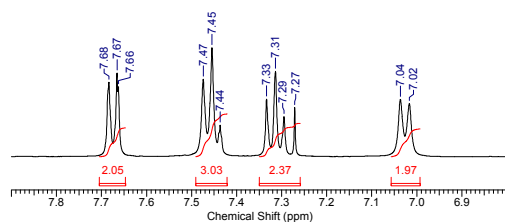


Figure S4. ^1H NMR spectrum of compound 4a

8621-K133-C.ESP

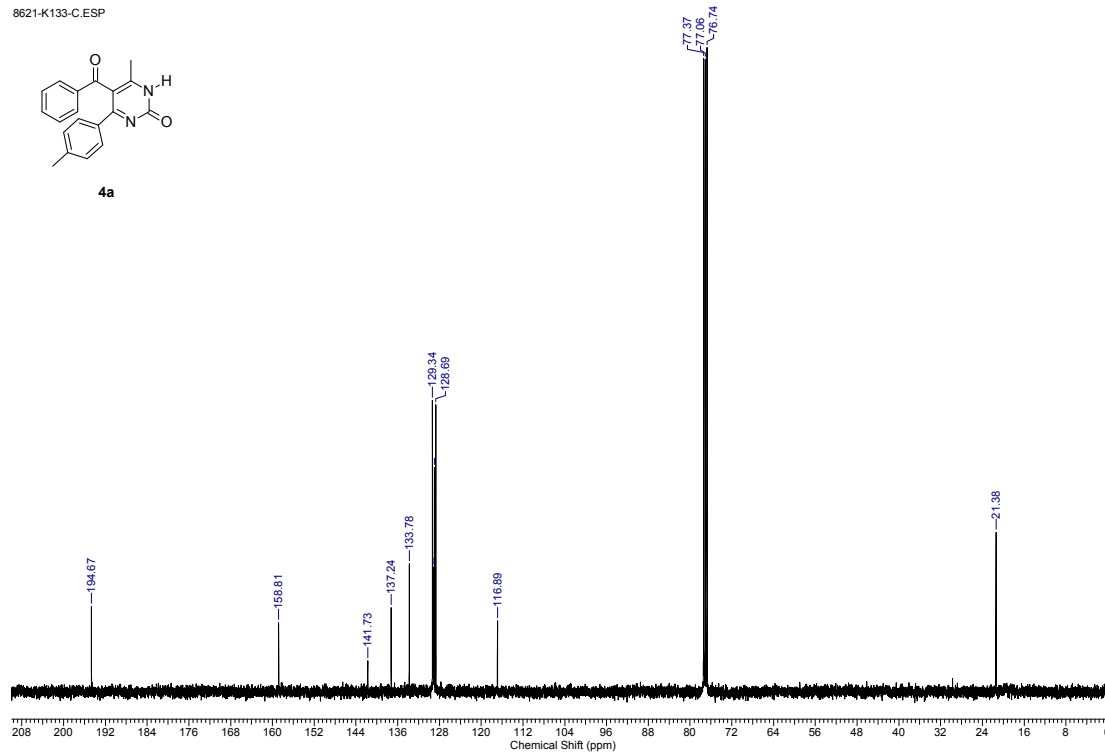


Figure S5. ^{13}C NMR spectrum of compound 4a

9840-K175-4-H.ESP
9840-K175-4-H.ESP

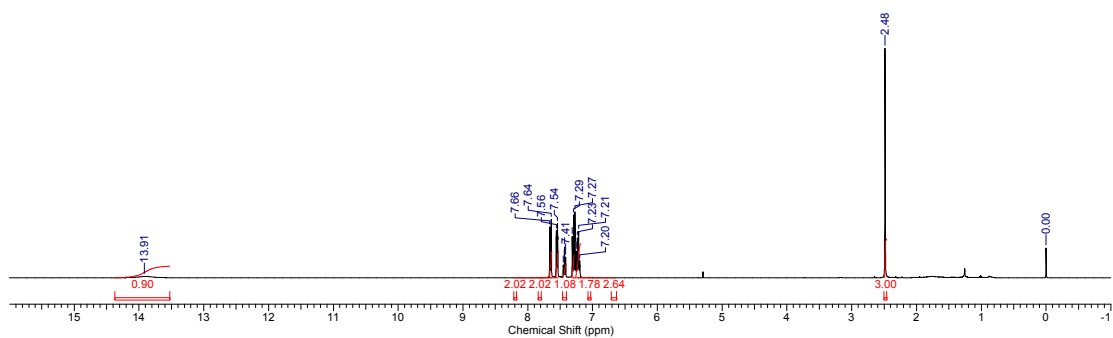
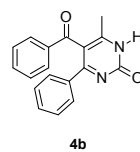
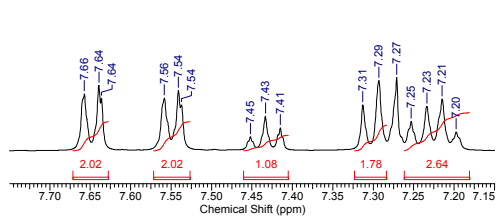


Figure S6. ¹H NMR spectrum of compound 4b

9841-K175-4-C.ESP

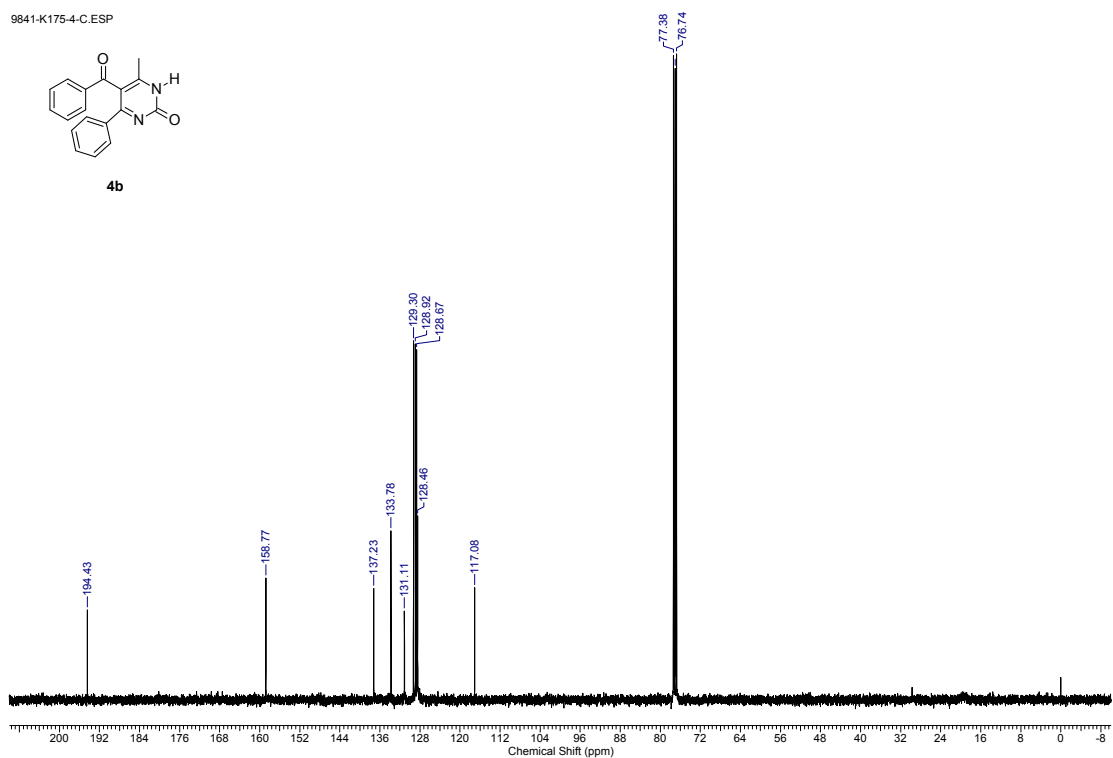
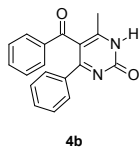


Figure S7. ¹³C NMR spectrum of compound 4b

10490-K176-H.ESP
10490-K176-H.ESP

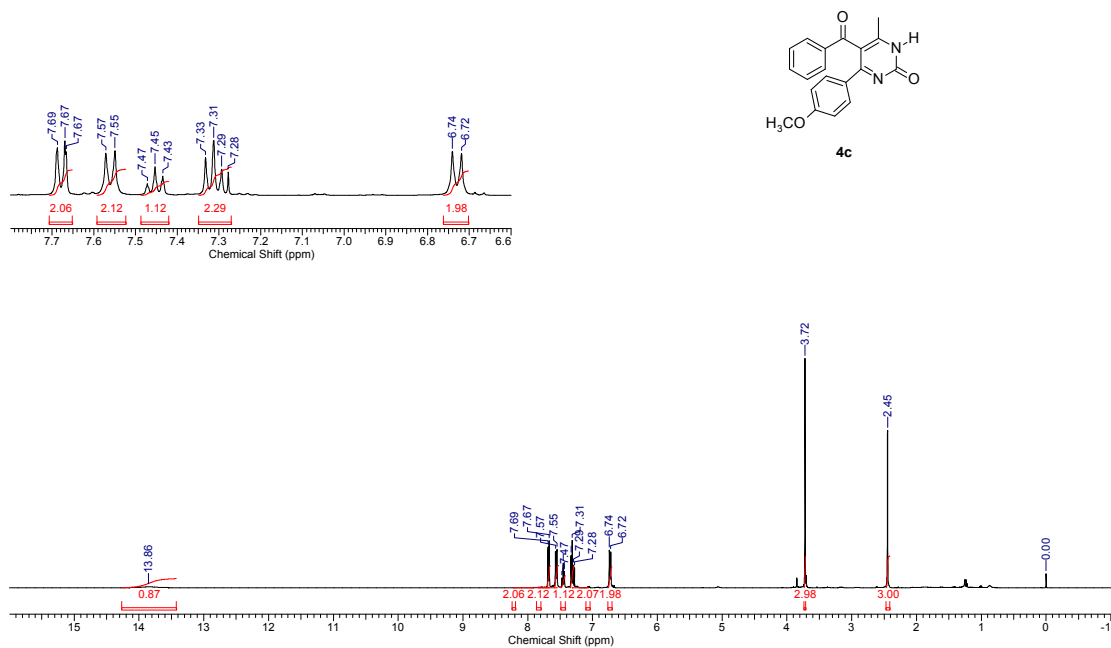


Figure S8. ¹H NMR spectrum of compound 4c

10491-K176-C.ESP

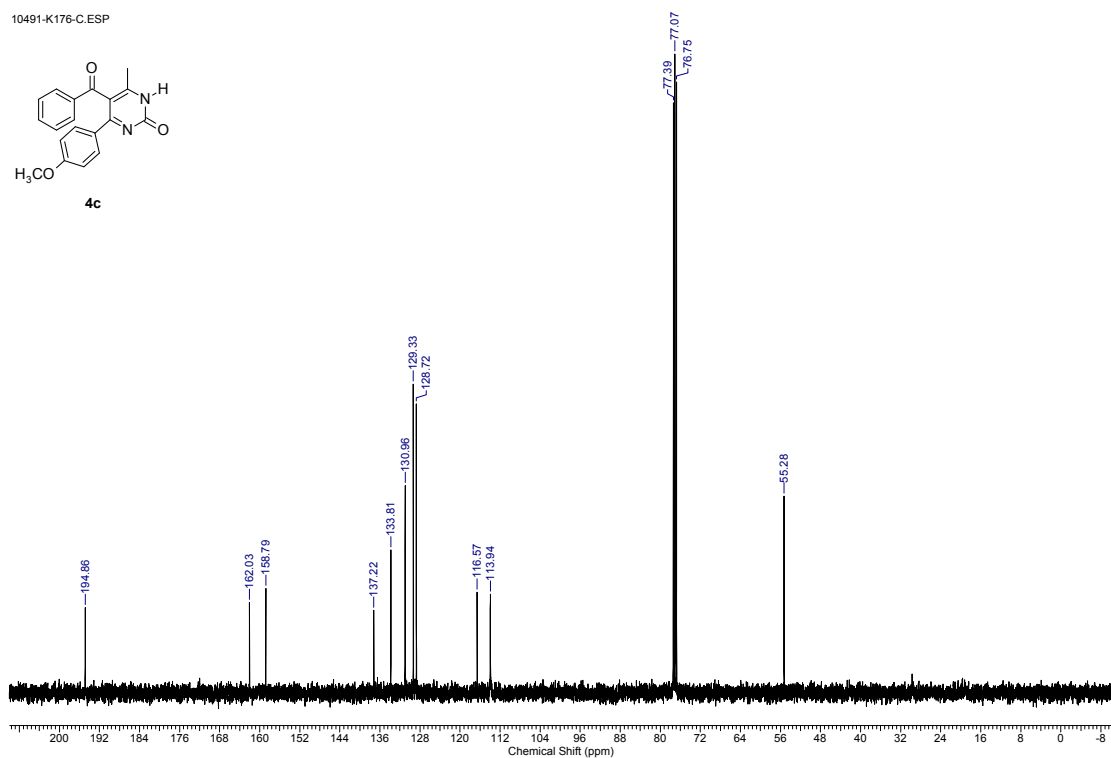


Figure S9. ¹³C NMR spectrum of compound 4c

10543-K182-H.ESP
10543-K182-H.ESP

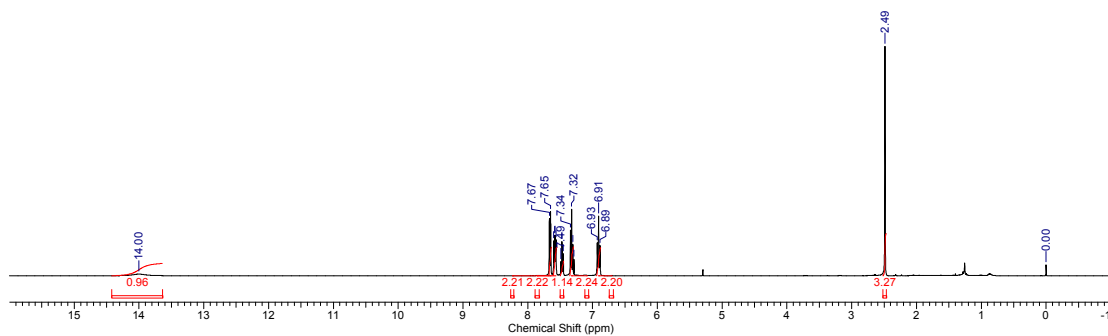
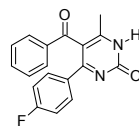
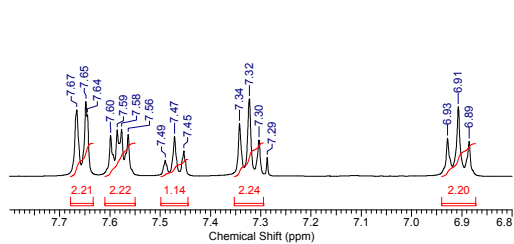


Figure S10. ¹H NMR spectrum of compound 4d

10541-K182-C.ESP

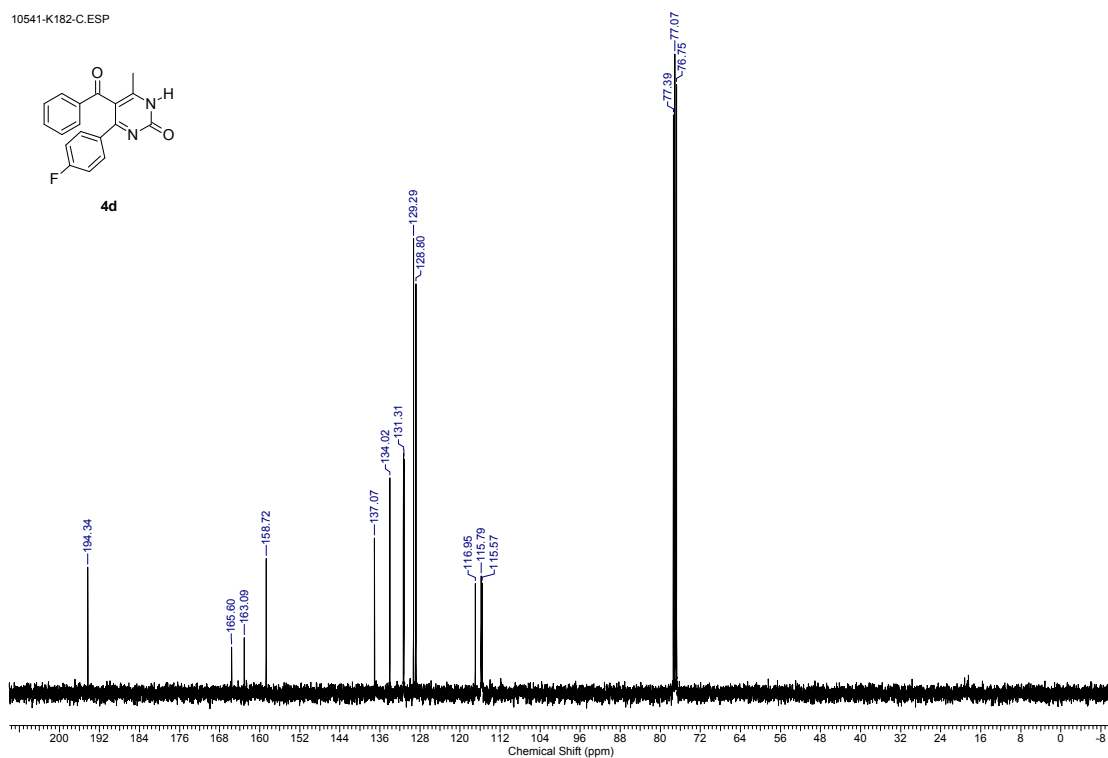
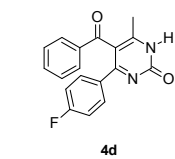


Figure S11. ¹³C NMR spectrum of compound 4d

10542-K182-F.ESP

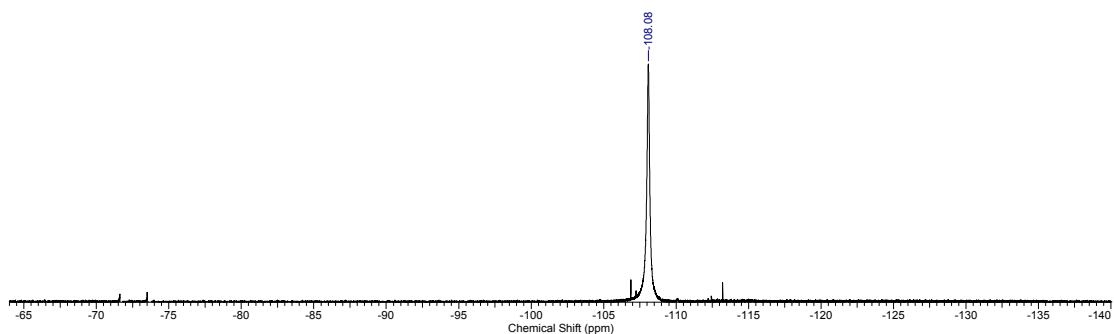
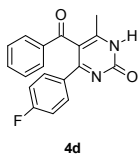


Figure S12. ^{19}F NMR spectrum of compound 4d

10550-K183-3-H.ESP
10550-K183-3-H.ESP

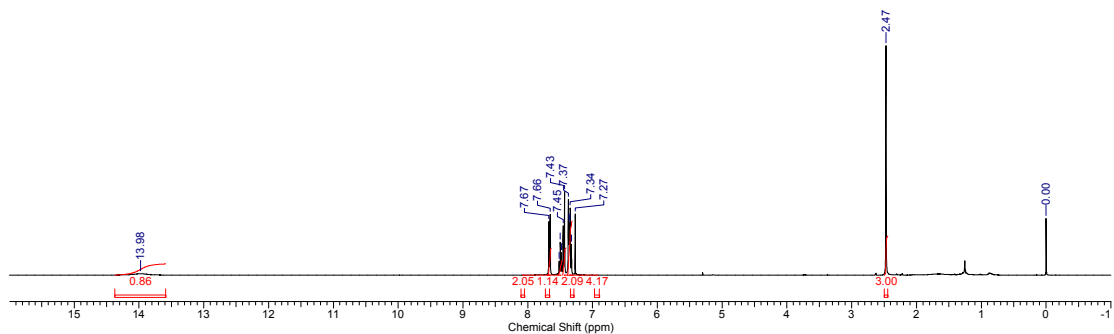
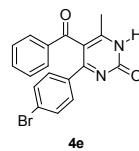
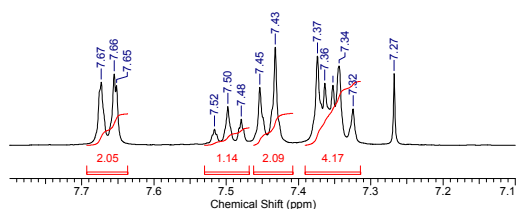


Figure S13. ^1H NMR spectrum of compound 4e

10551-K183-3-C.ESP

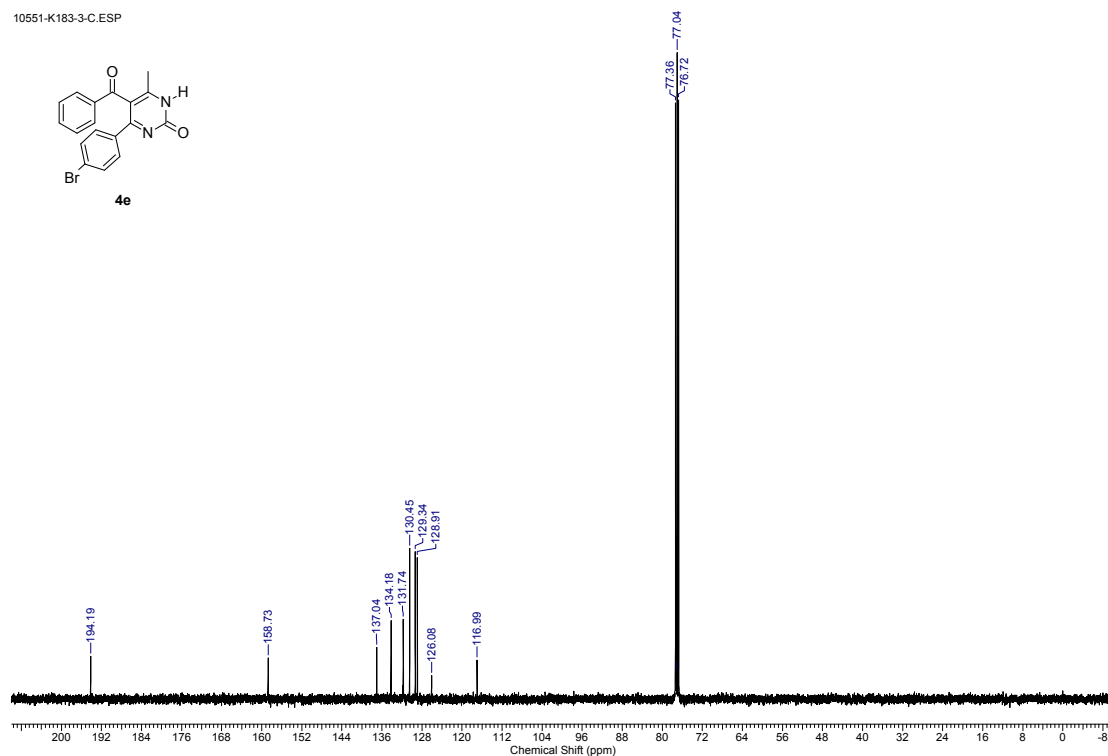


Figure S14. ¹³C NMR spectrum of compound **4e**

1940-K241-6-H.ESP
1940-K241-6-H.ESP

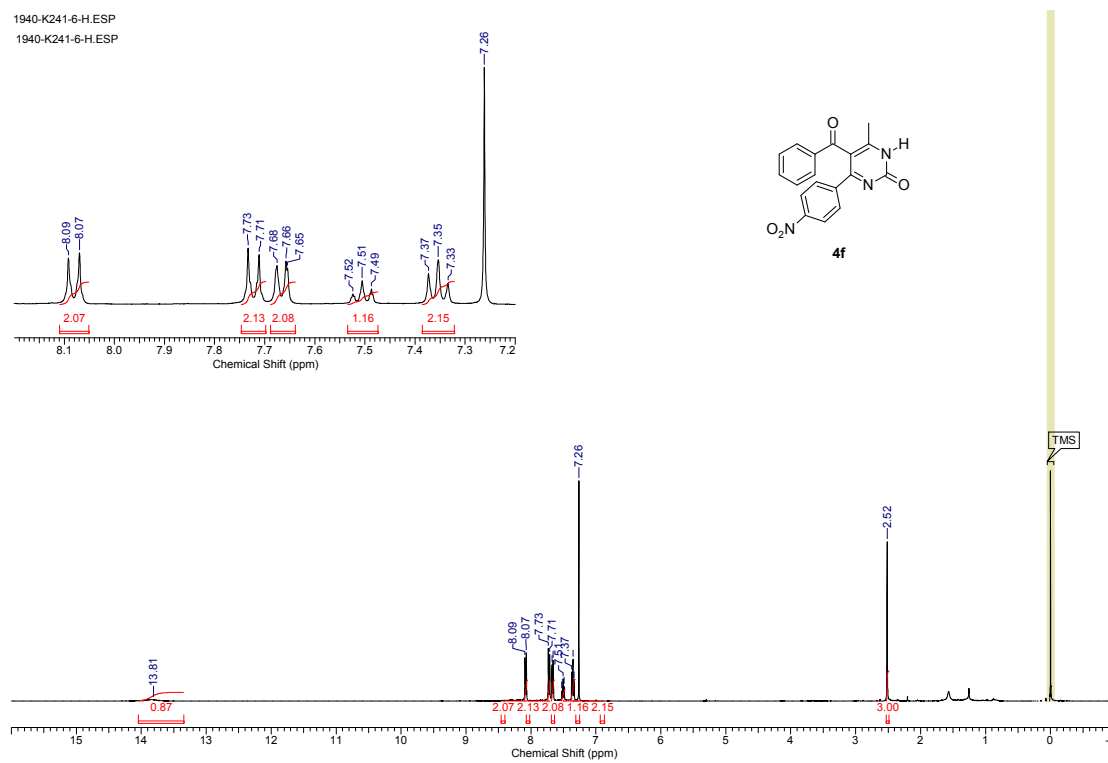


Figure S15. ¹H NMR spectrum of compound **4f**

1511-K241-2-C.ESP

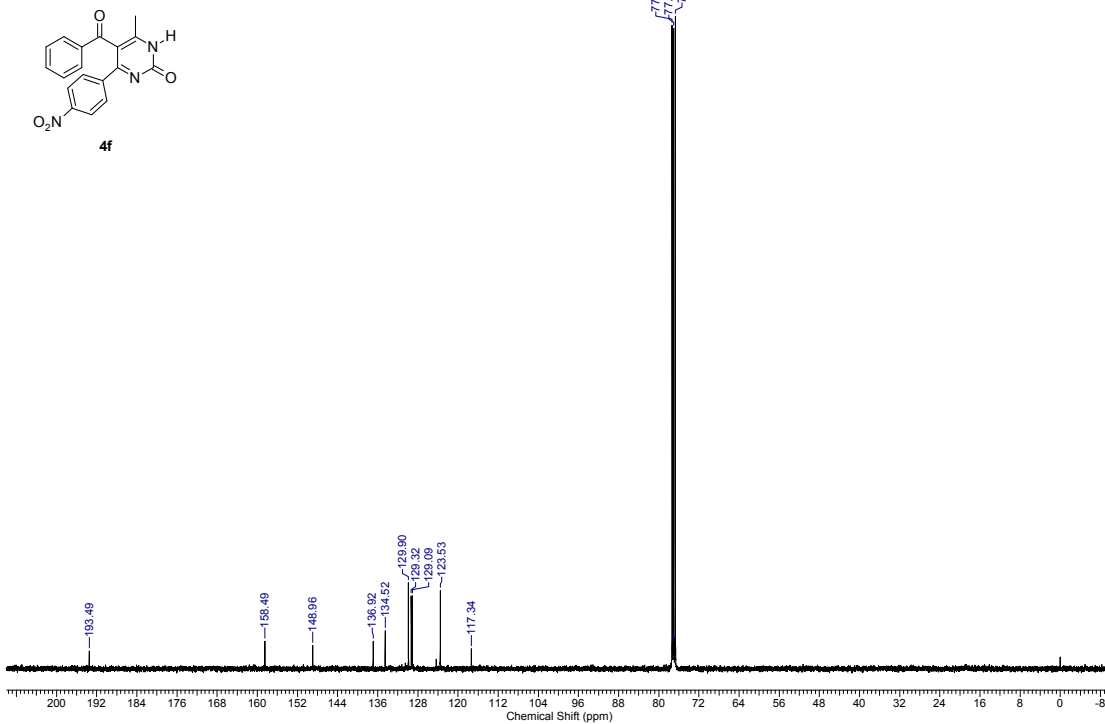


Figure S16. ¹³C NMR spectrum of compound 4f

1620-K242-1-H.ESP

1620-K242-1-H.ESP

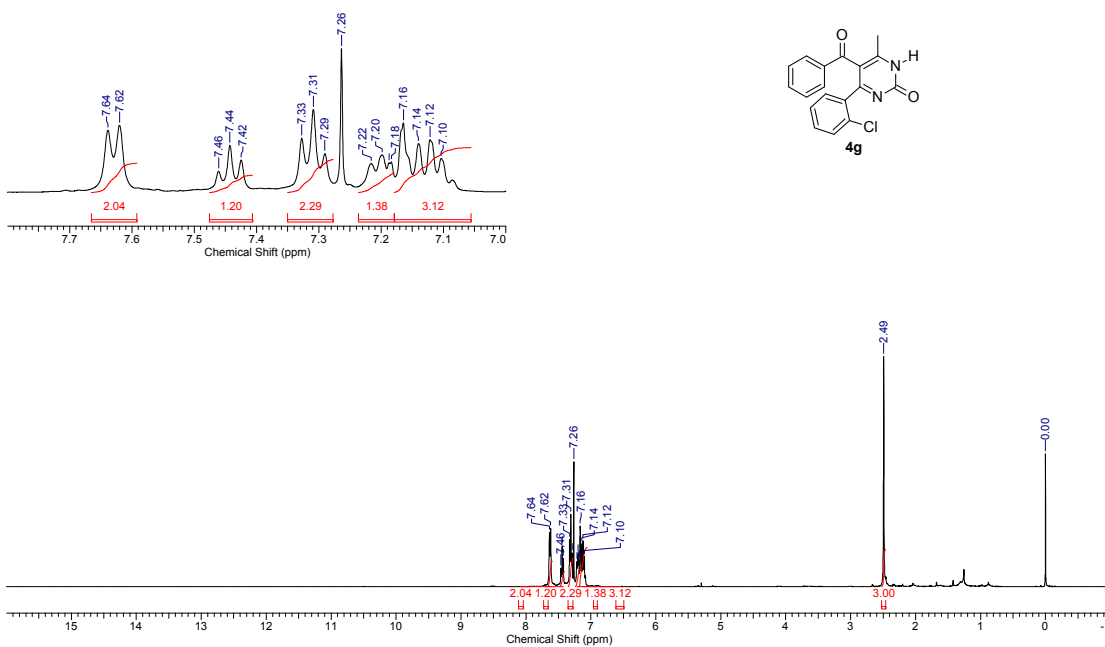


Figure S17. ¹H NMR spectrum of compound 4g

1621-K242-1-C.ESP

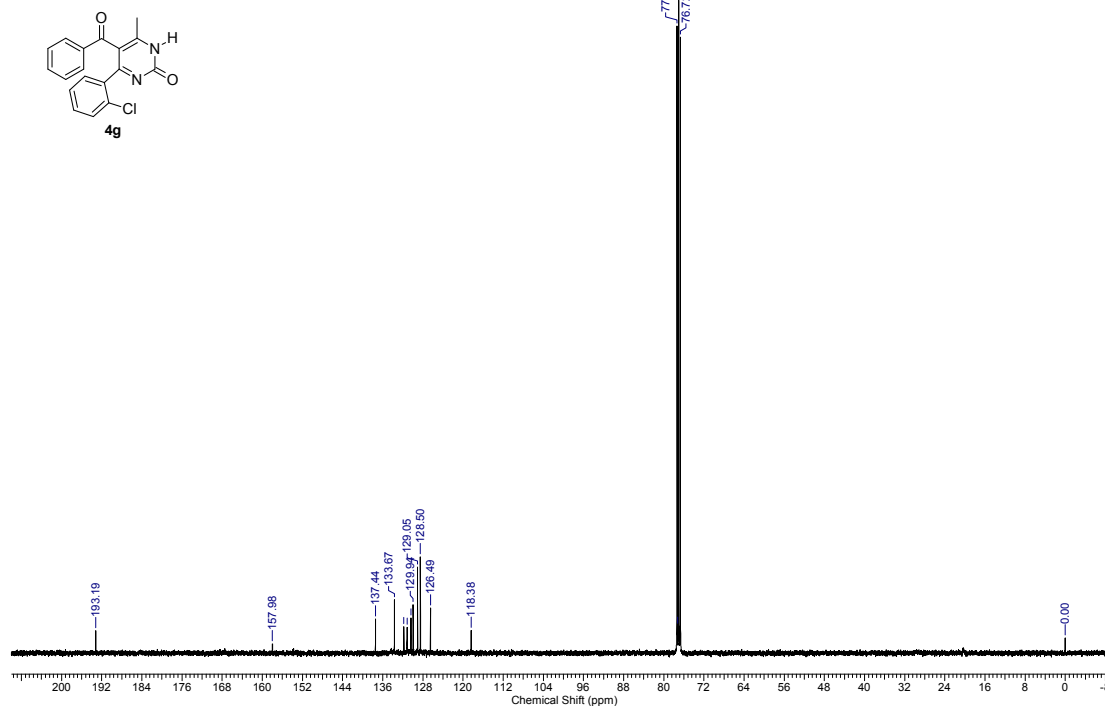


Figure S18. ¹³C NMR spectrum of compound **4g**

14270-K203-6-H.ESP

14270-K203-6-H.ESP

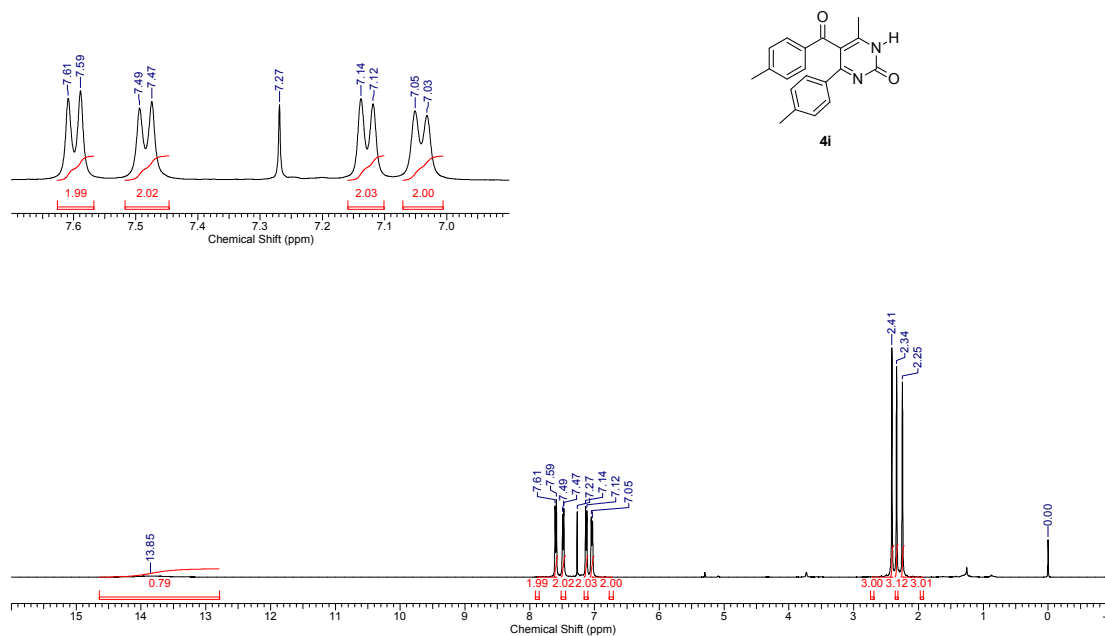


Figure S19. ¹H NMR spectrum of compound **4i**

14271-K203-6-C.ESP

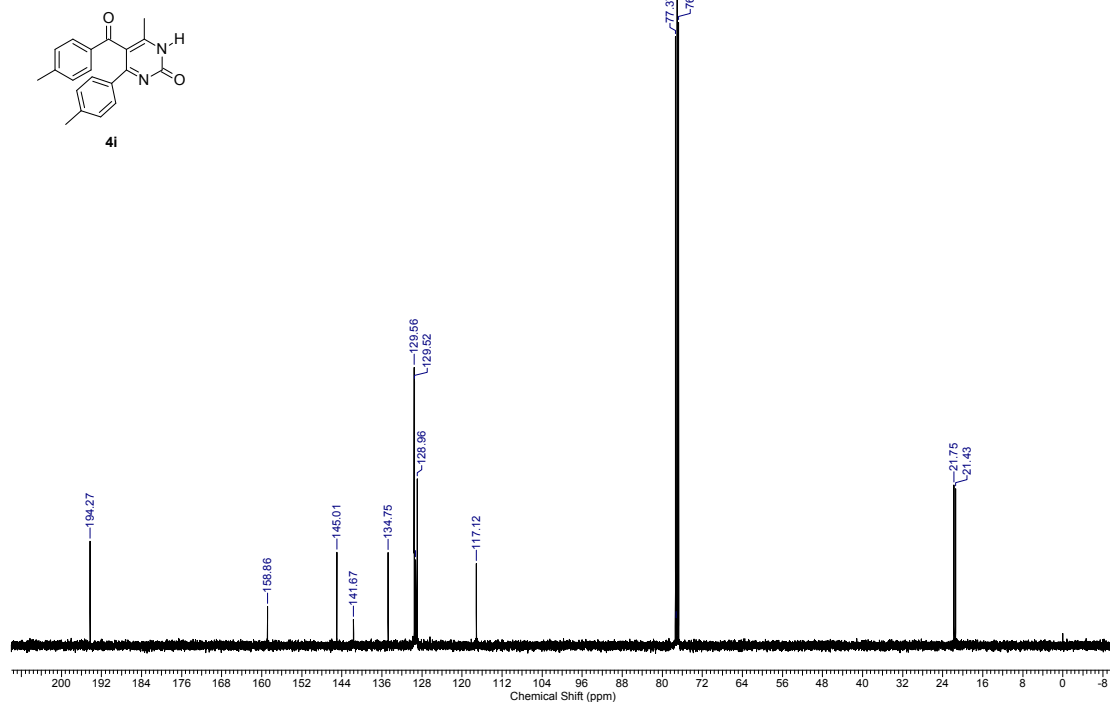


Figure S20. ¹³C NMR spectrum of compound **4i**

350-K205-8-H.ESP
350-K205-8-H.ESP

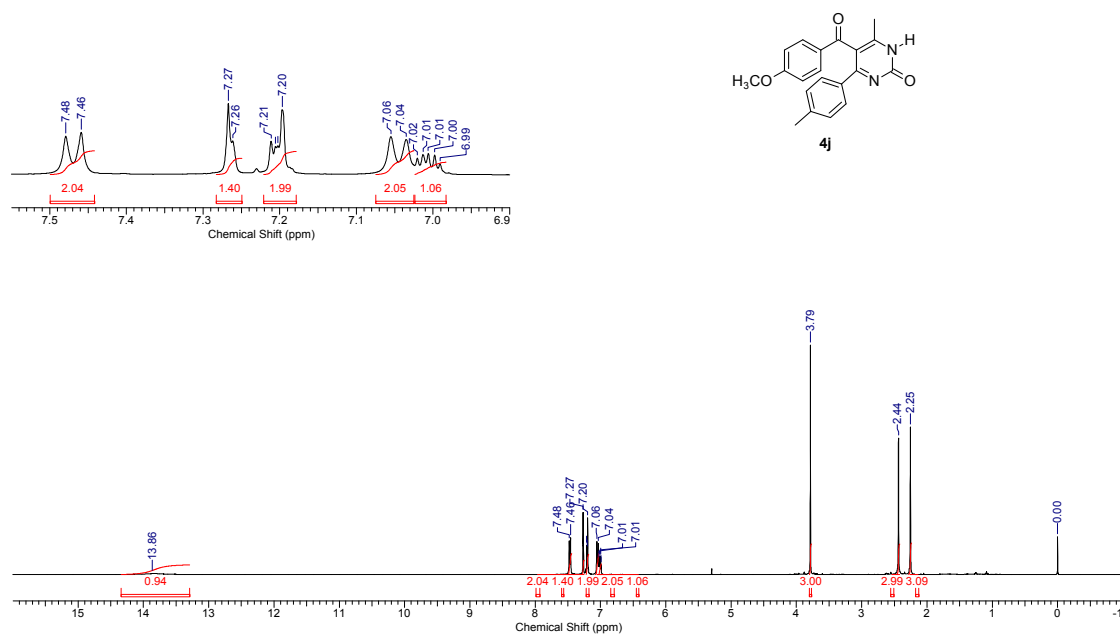


Figure S21. ¹H NMR spectrum of compound **4j**

211-K205-8-C.ESP

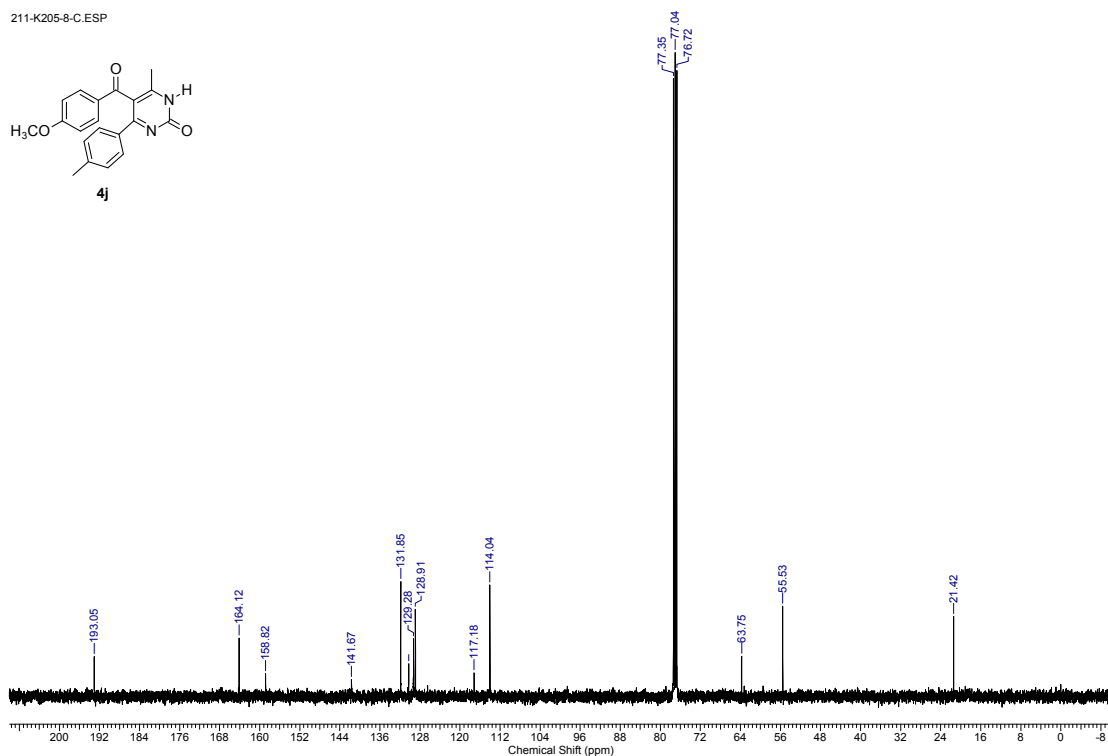
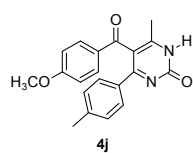


Figure S22. ¹³C NMR spectrum of compound 4j

14280-K206-4-1-H.ESP

14280-K206-4-1-H.ESP

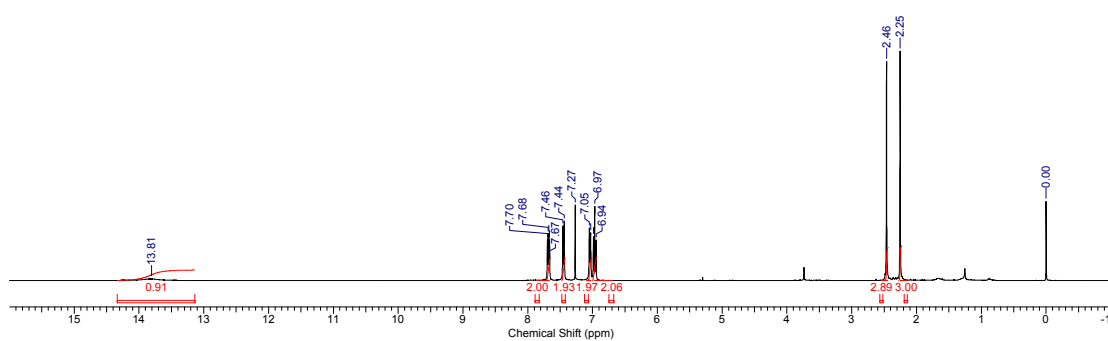
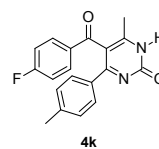
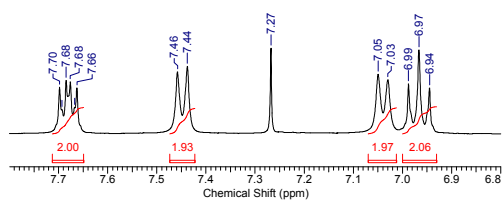


Figure S23. ¹H NMR spectrum of compound 4k

14281-K206-4-1-C.ESP

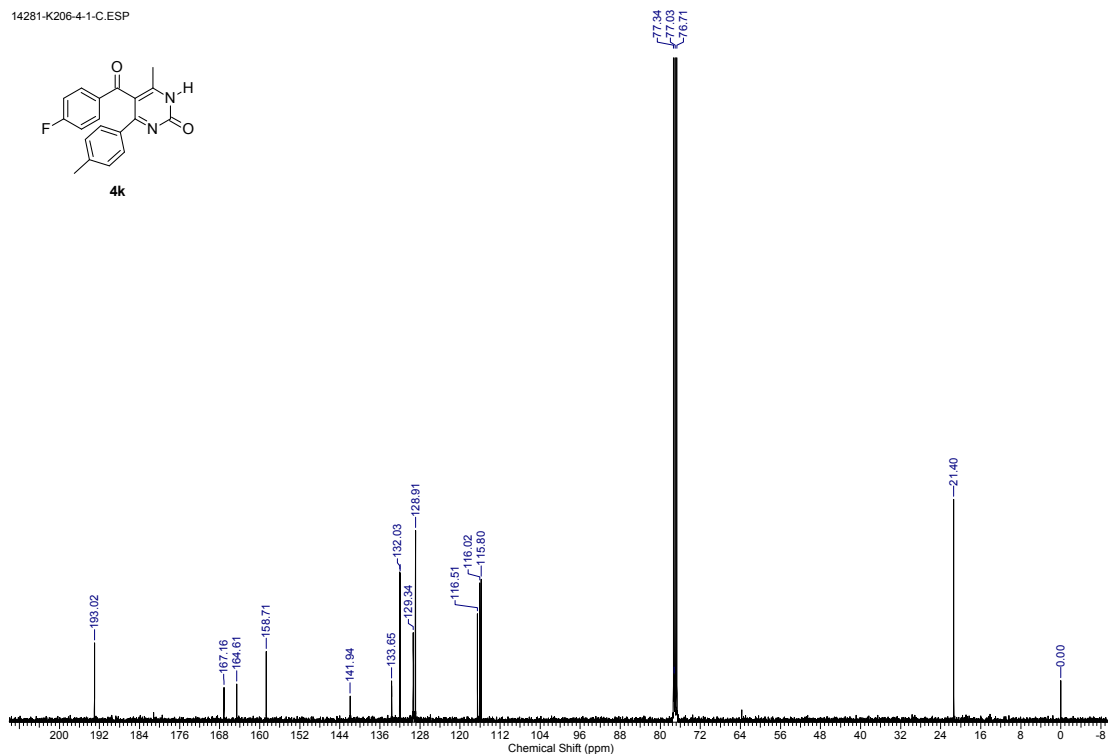
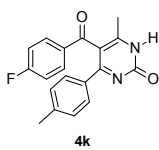


Figure S24. ¹³C NMR spectrum of compound **4k**

14790-K206-4-1-F.ESP

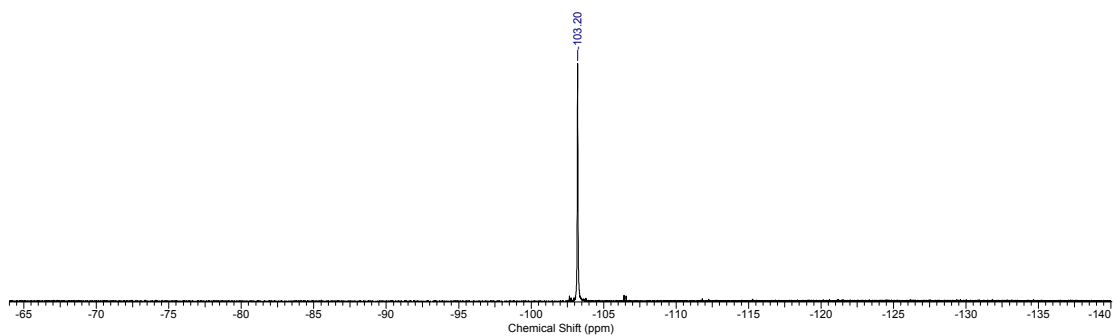
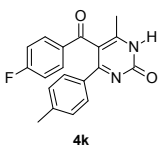


Figure S25. ¹⁹F NMR spectrum of compound **4k**

370-K207-9-H.ESP
370-K207-9-H.ESP

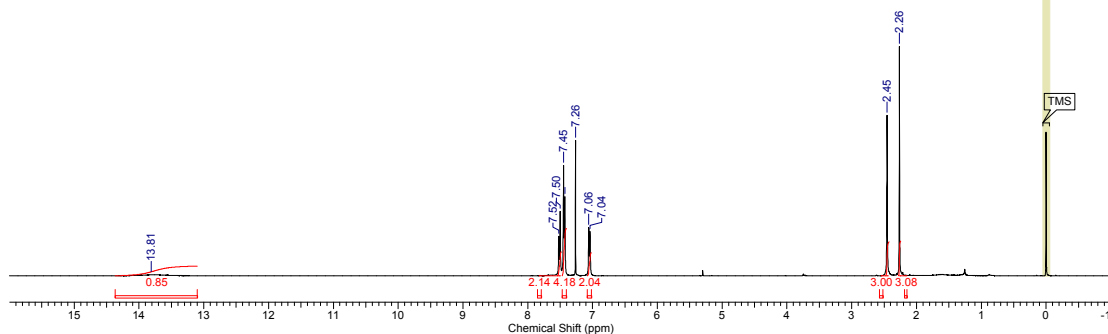
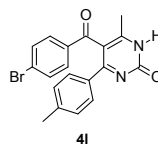
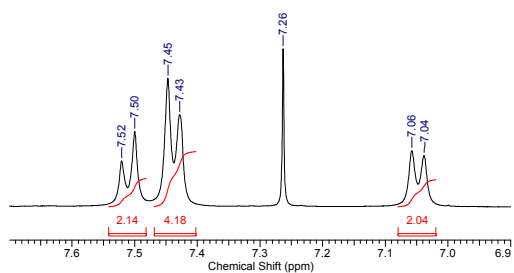


Figure S26. ¹H NMR spectrum of compound 4i

321-K207-7-C.ESP

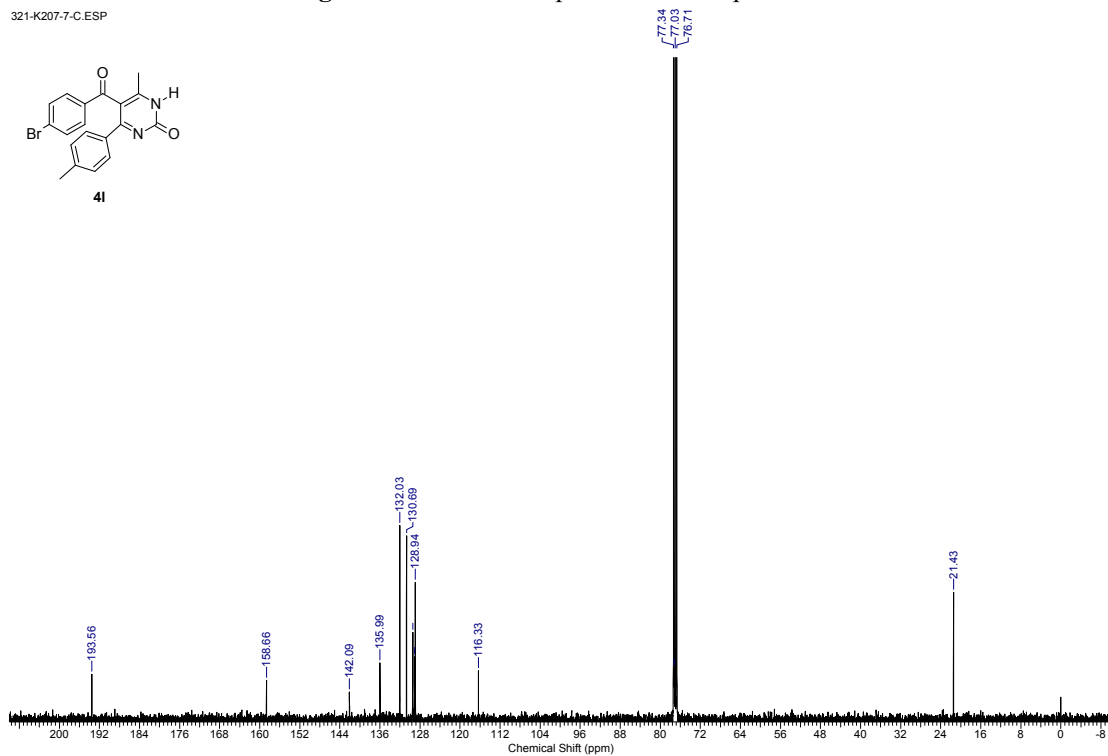
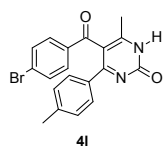


Figure S27. ¹³C NMR spectrum of compound 4i

330-K220-5-H.ESP
330-K220-5-H.ESP

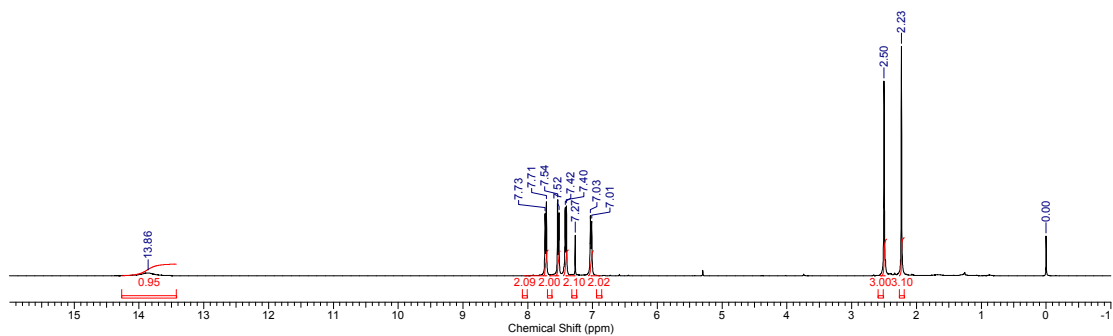
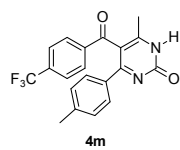
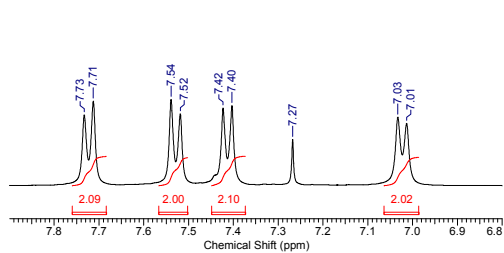


Figure S28. ¹H NMR spectrum of compound 4m

550-K220-5-C.ESP

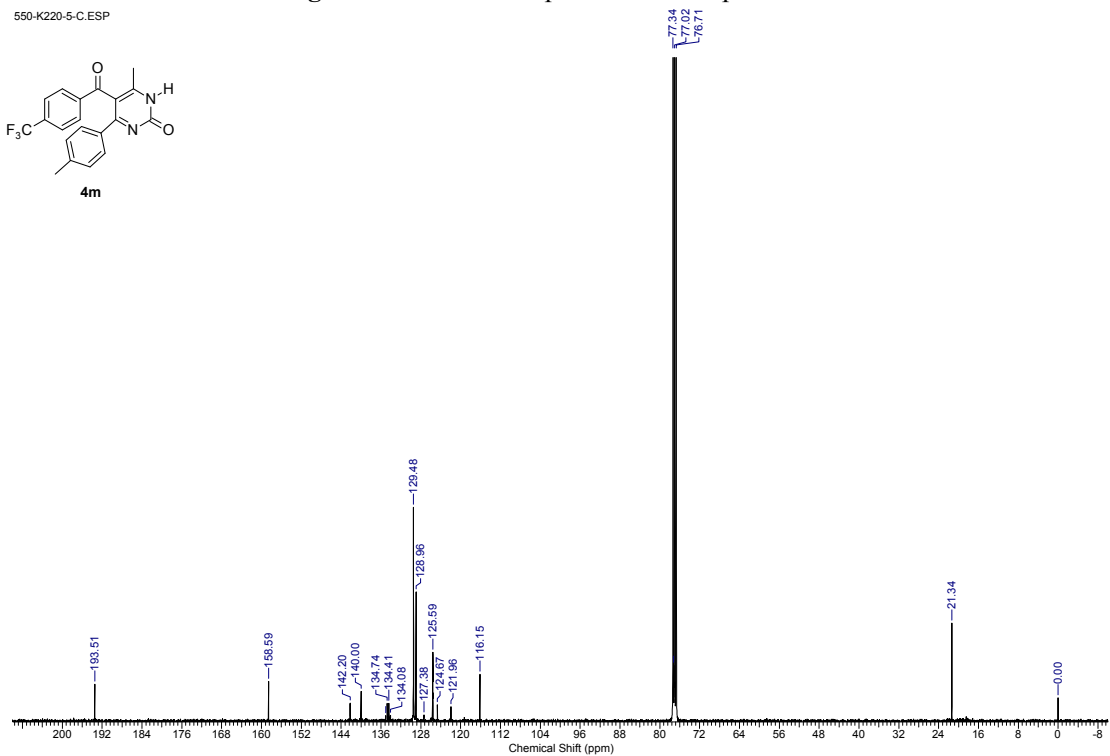
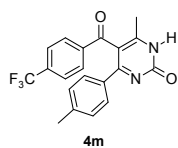


Figure S29. ¹³C NMR spectrum of compound 4m

331-K220-5-F.ESP

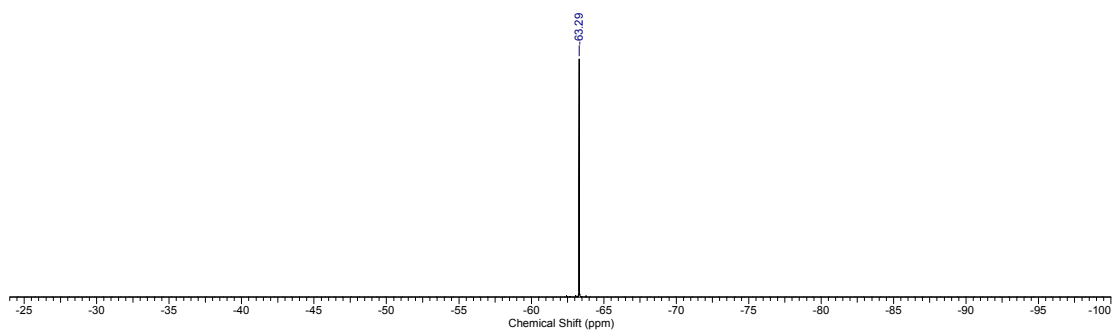
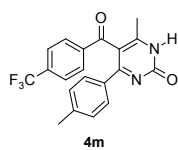


Figure S30. ¹⁹F NMR spectrum of compound 4m

13130-K219-2-H.ESP

13130-K219-2-H.ESP

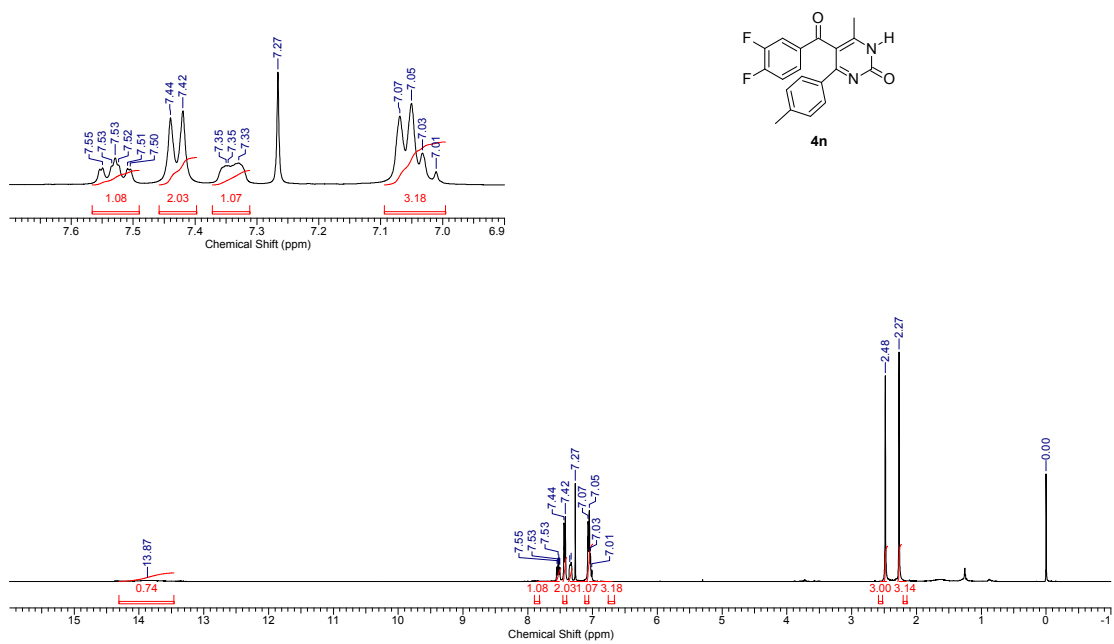


Figure S31. ¹H NMR spectrum of compound 4n

3380-K219-2-C.ESP

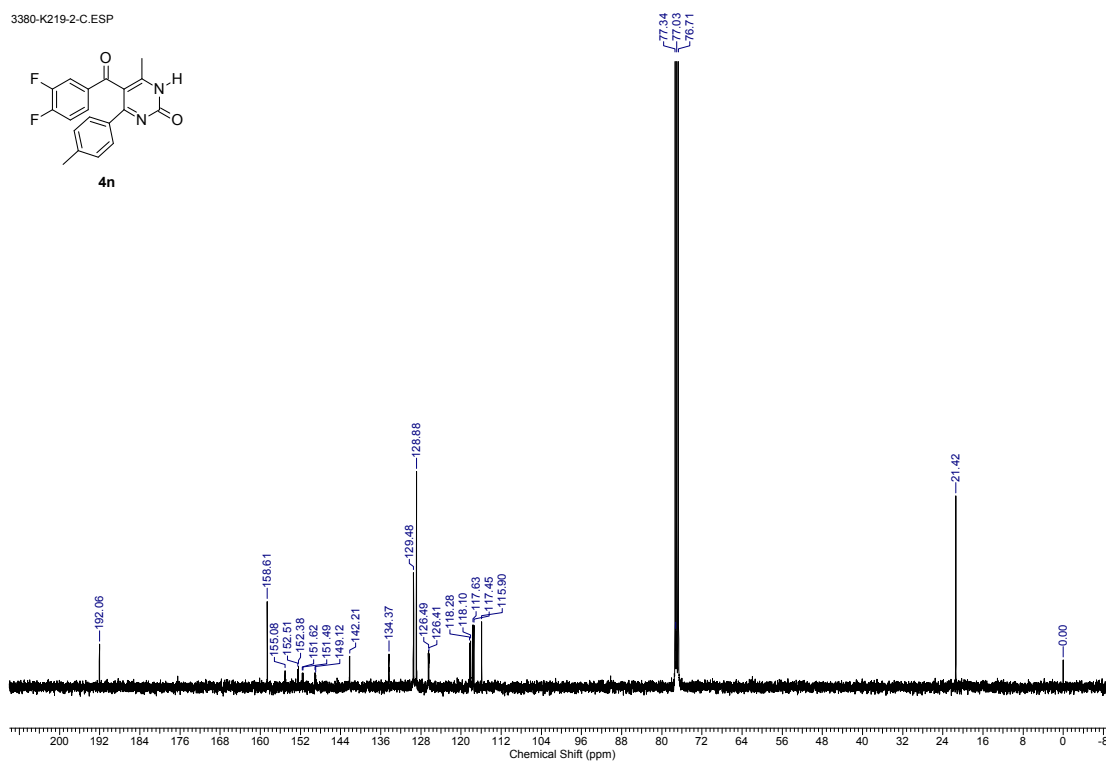


Figure S32. ^{13}C NMR spectrum of compound **4n**

14780-K219-2-F.ESP

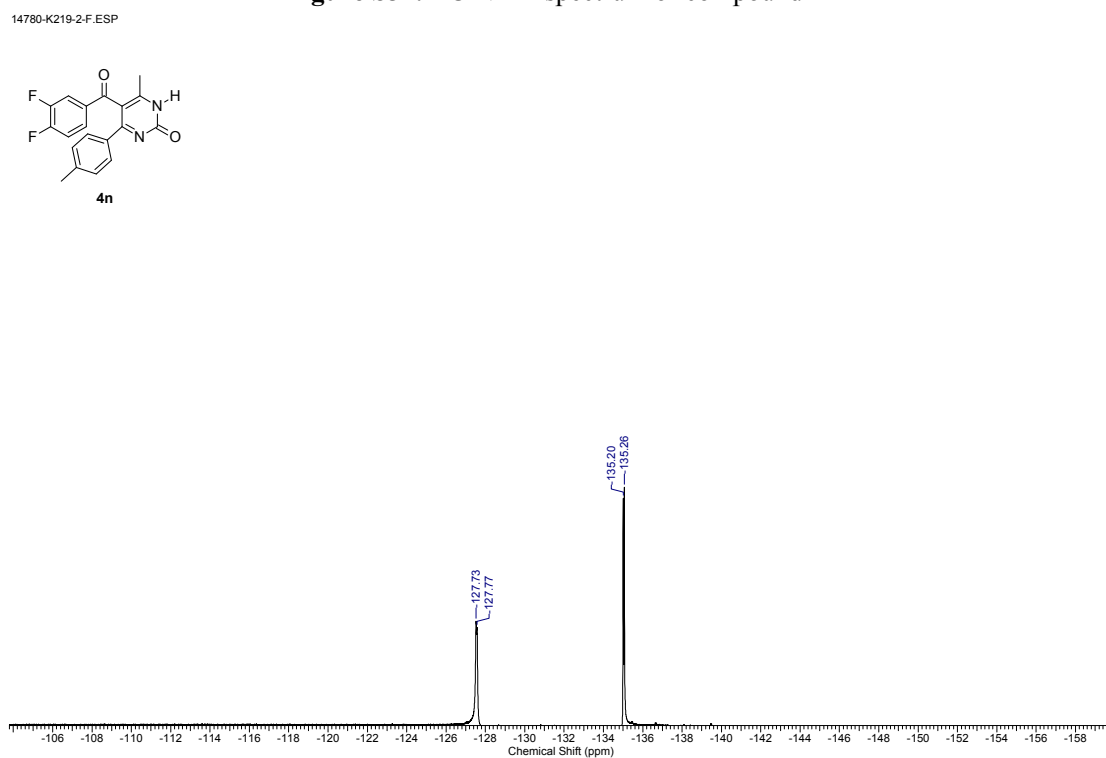


Figure S33. ^{19}F NMR spectrum of compound **4n**

14690-K218-4-H.ESP
14690-K218-4-H.ESP

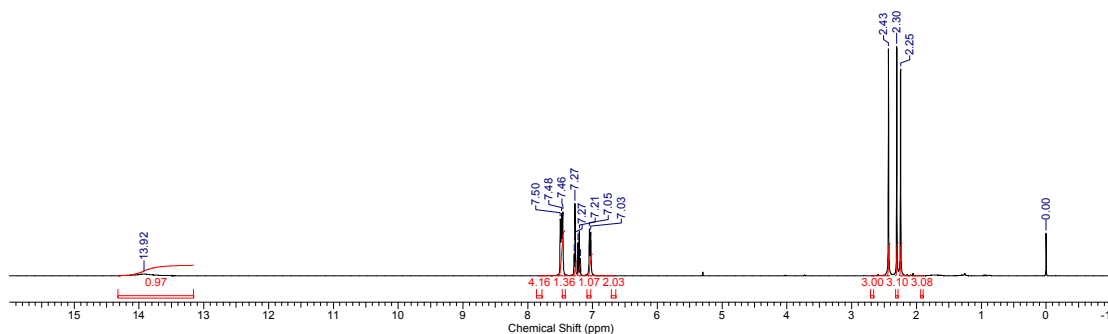
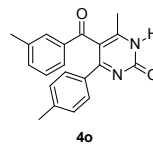
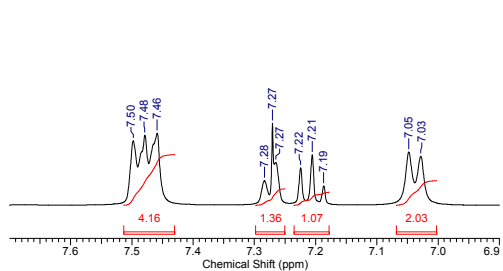


Figure S34. ^1H NMR spectrum of compound **4o**

14691-K218-4-C.ESP

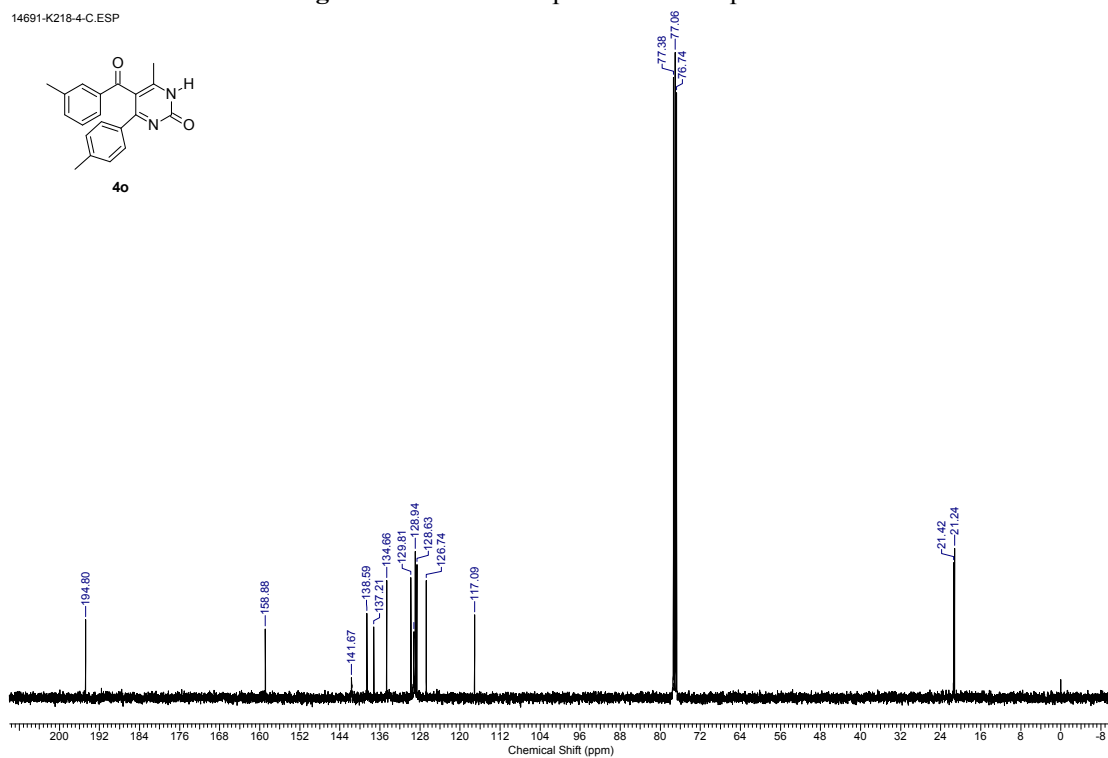
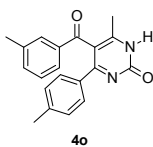


Figure S35. ^{13}C NMR spectrum of compound **4o**

560-K209-2-H.ESP
560-K209-2-H.ESP

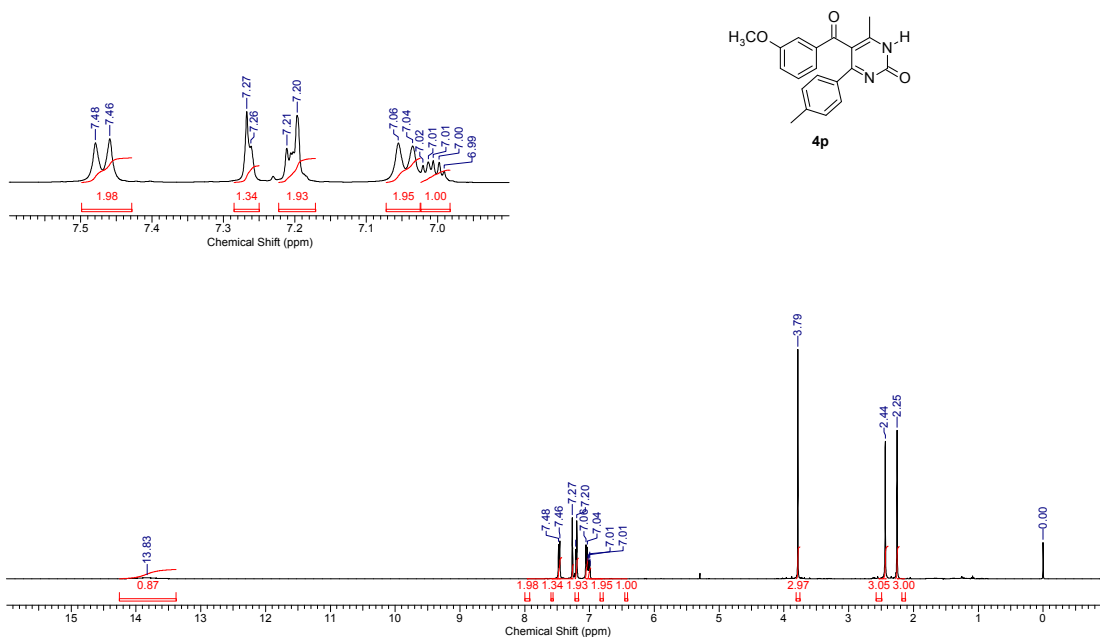


Figure S36. ¹H NMR spectrum of compound 4p

561-K209-2-C.ESP

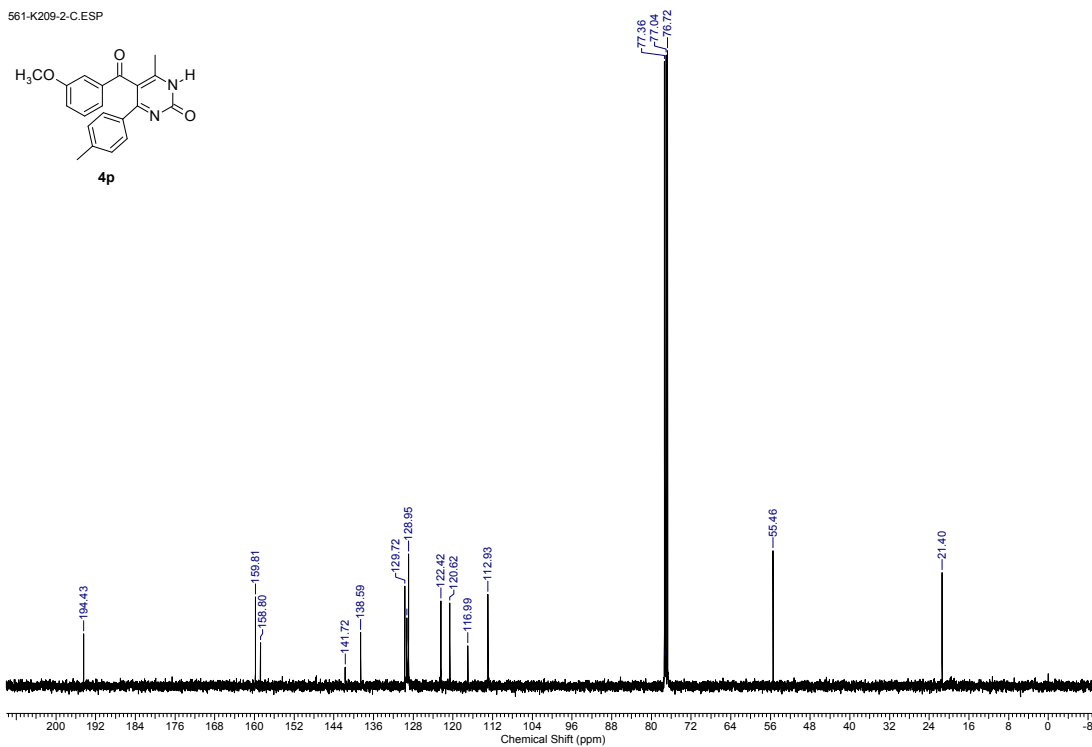


Figure S37. ¹³C NMR spectrum of compound 4p

14700-K221-4-H.ESP
14700-K221-4-H.ESP

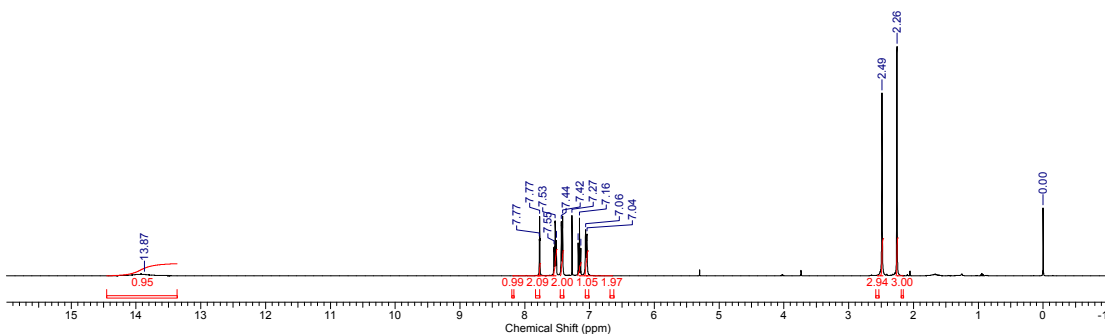
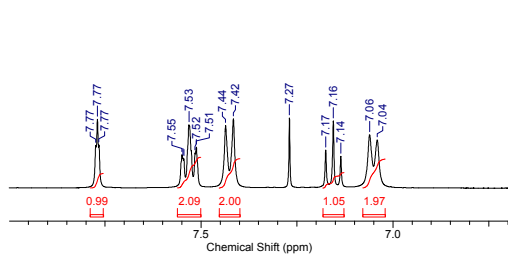


Figure S38. ¹H NMR spectrum of compound 4q

14701-K221-3-C.ESP

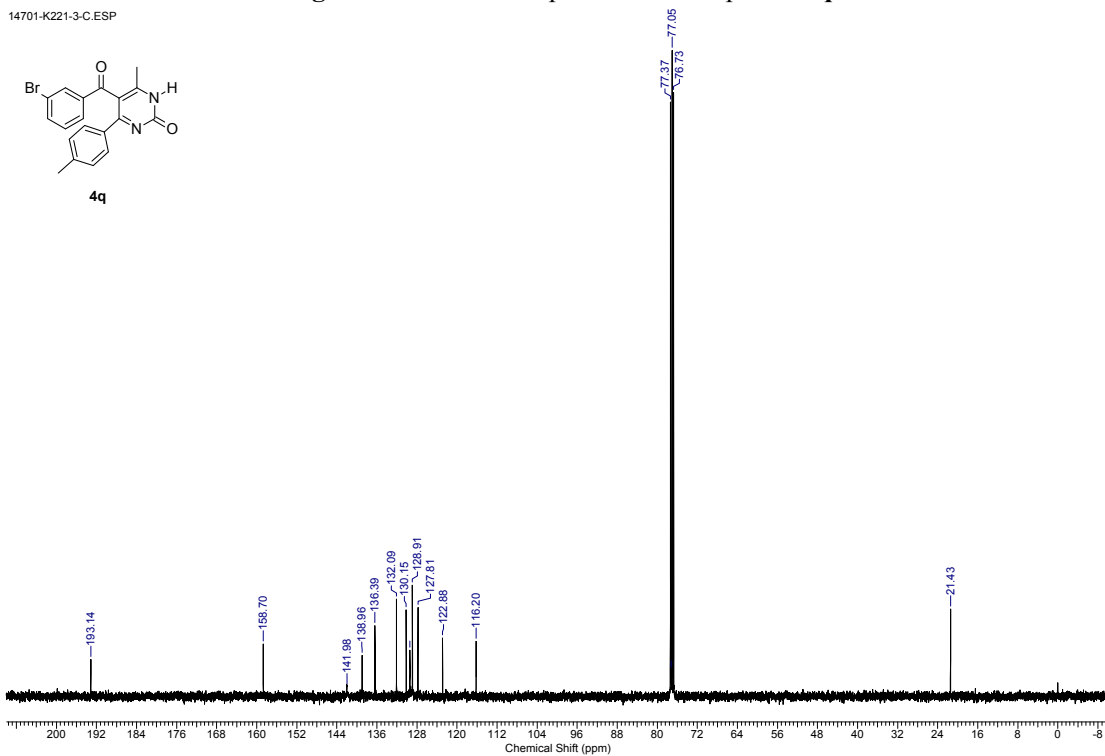
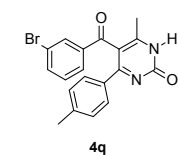


Figure S39. ¹³C NMR spectrum of compound 4q

790-K208-2-H.ESP
790-K208-2-H.ESP

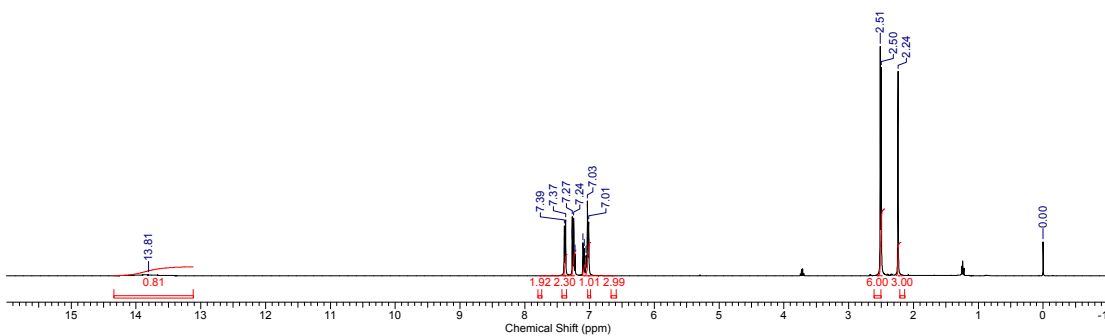
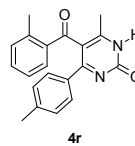
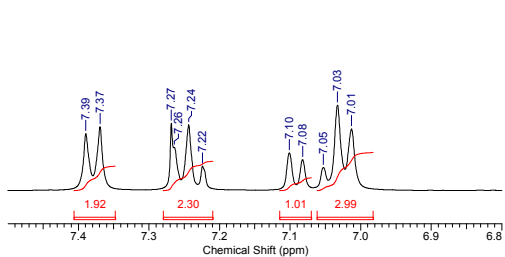


Figure S40. ^1H NMR spectrum of compound **4r**

501-K208-2-C.ESP

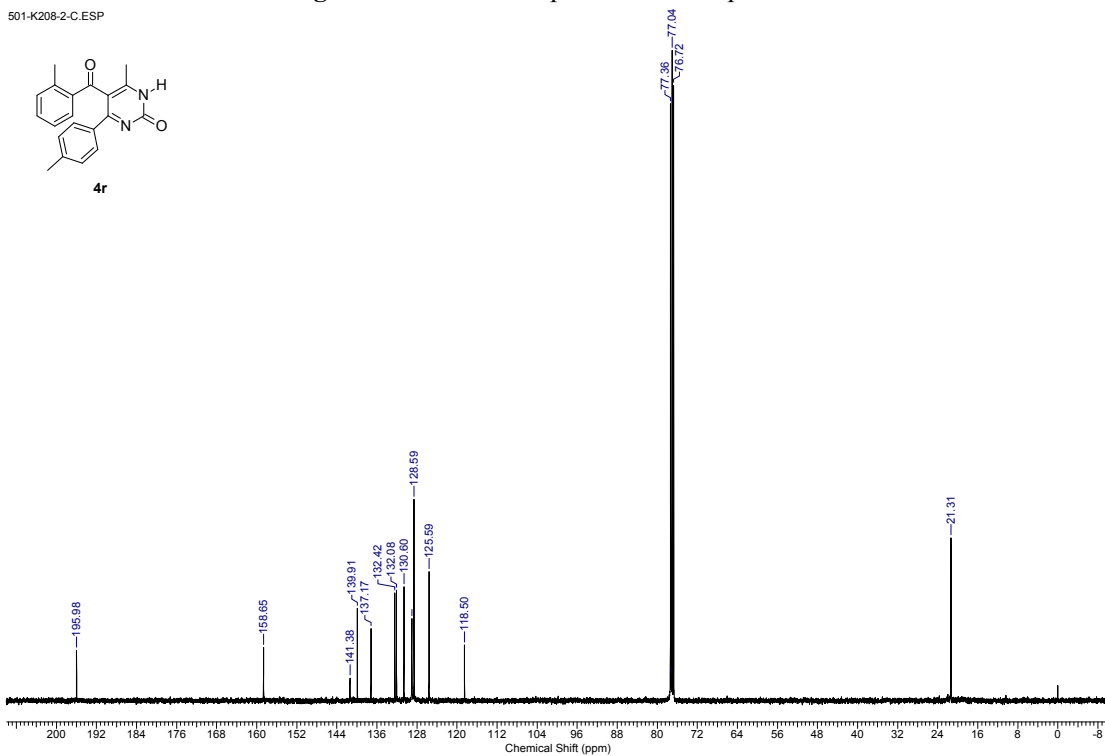
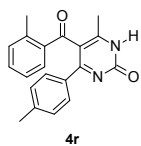


Figure S41. ^{13}C NMR spectrum of compound **4r**

800-K217-2-H.ESP
800-K217-2-H.ESP

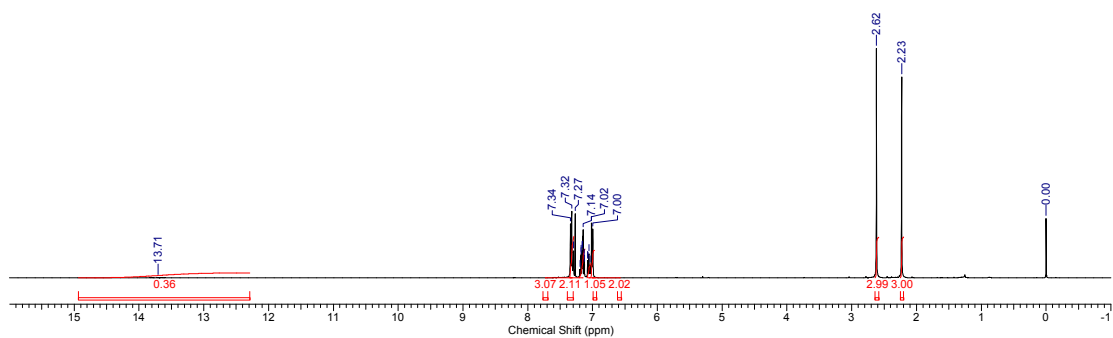
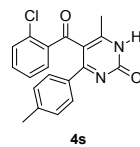
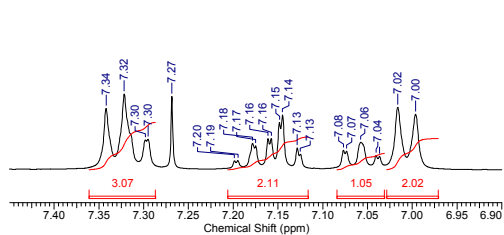


Figure S42. ¹H NMR spectrum of compound 4s

512-K217-2-C.ESP

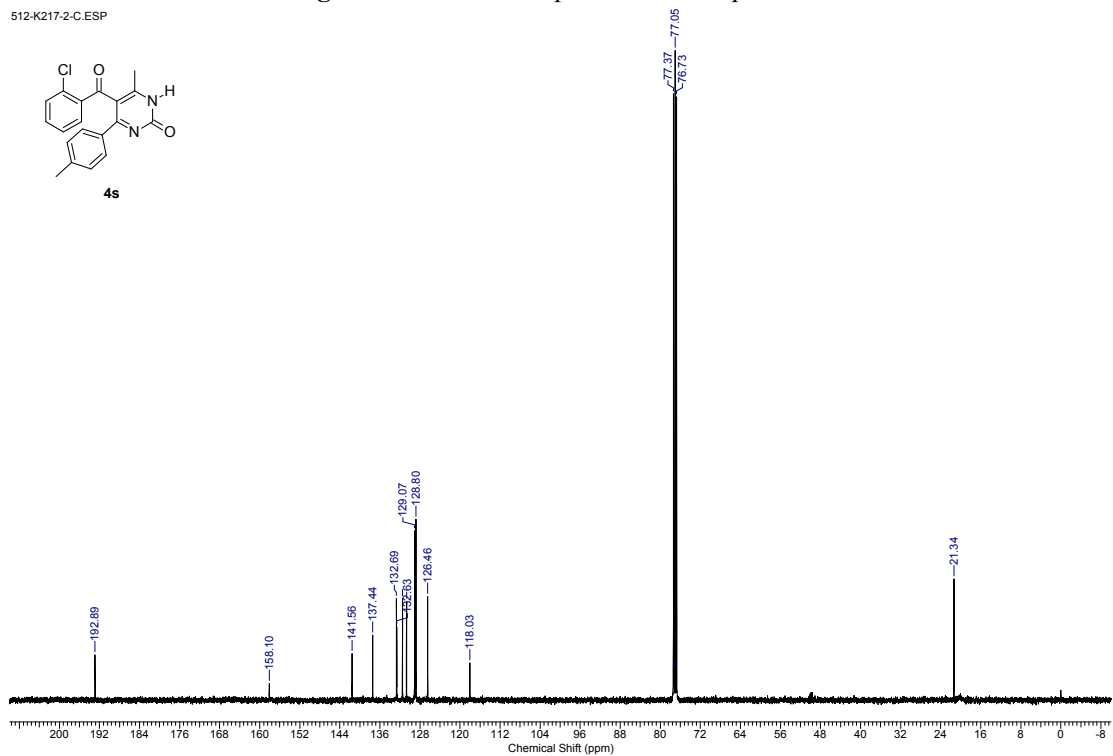
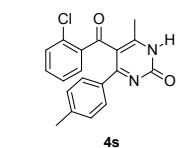


Figure S43. ¹³C NMR spectrum of compound 4s

820-K226-2-H.ESP
820-K226-2-H.ESP

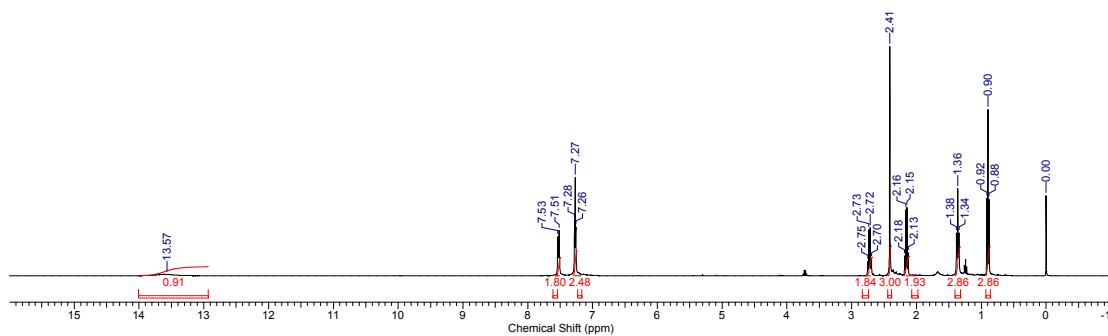
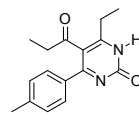
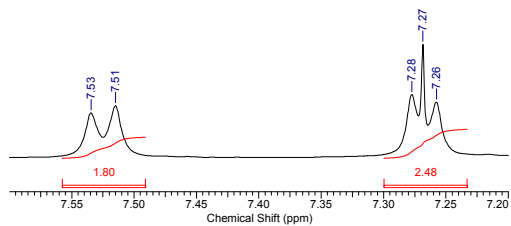


Figure S44. ¹H NMR spectrum of compound 4t

681-K226-2-C.ESP

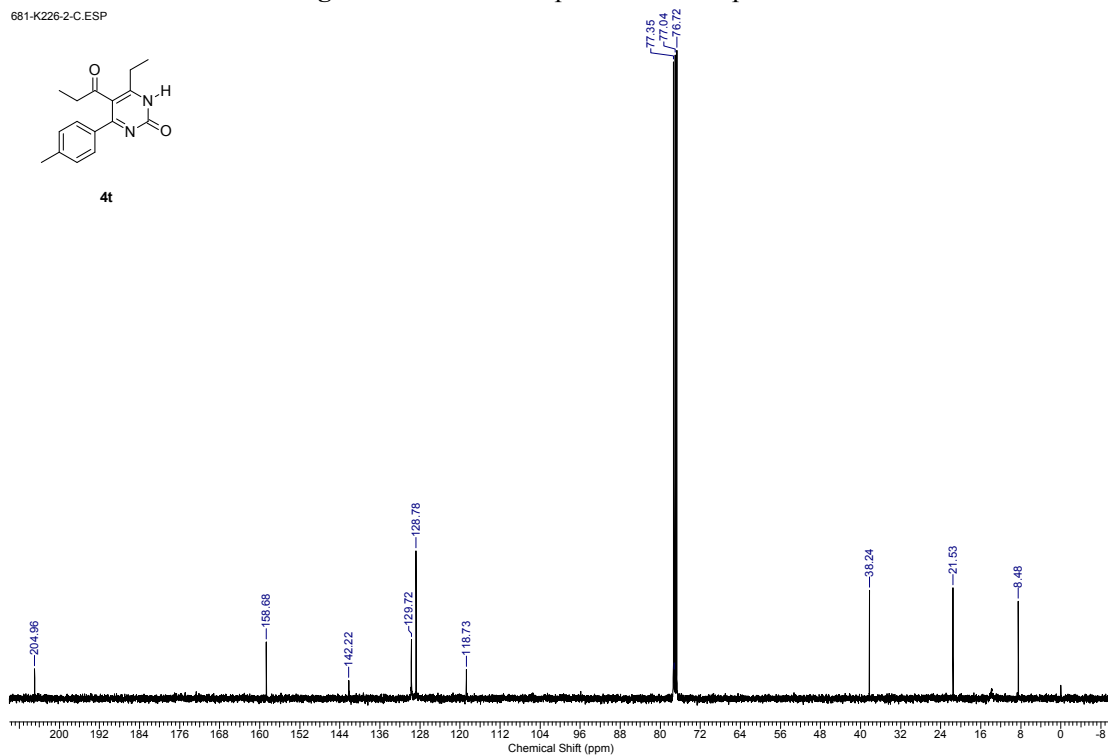
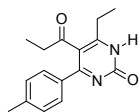


Figure S45. ¹³C NMR spectrum of compound 4t

14180-K232-3-H.ESP
14180-K232-3-H.ESP

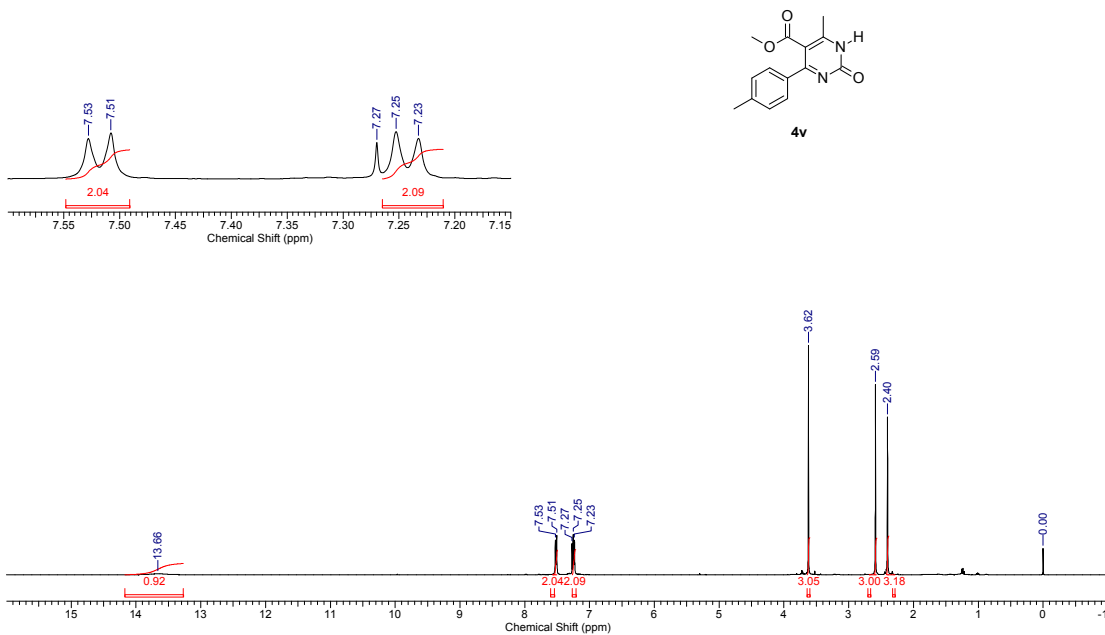


Figure S46. ¹H NMR spectrum of compound 4v

14300-K232-3-C.ESP

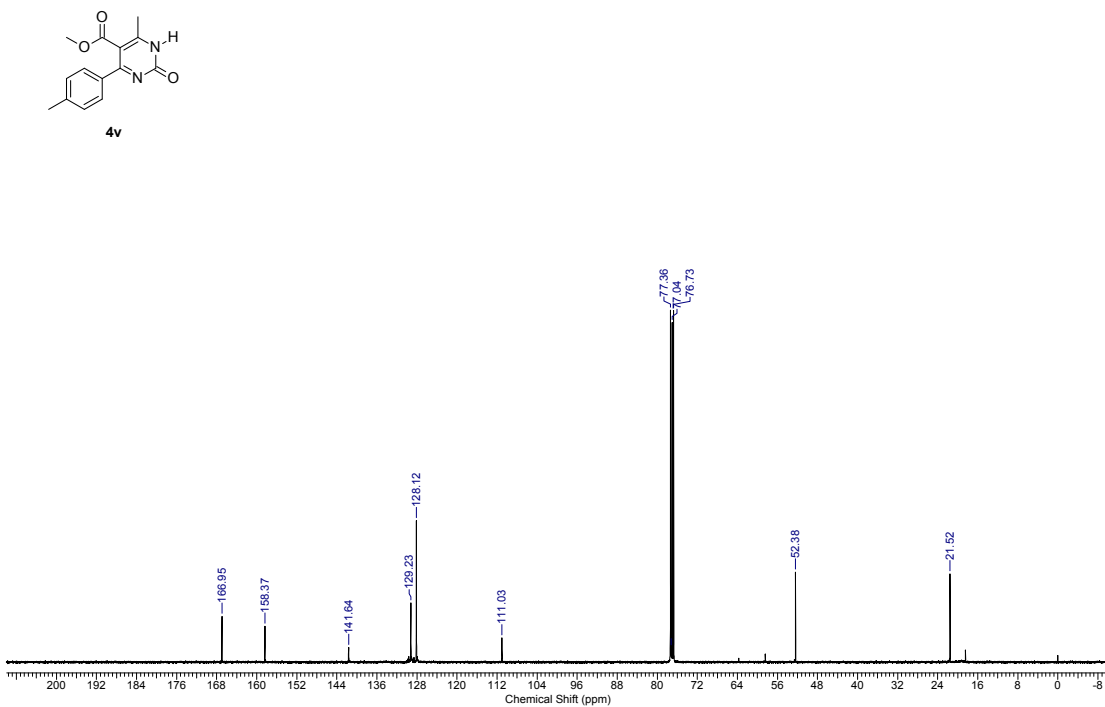
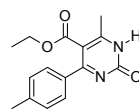
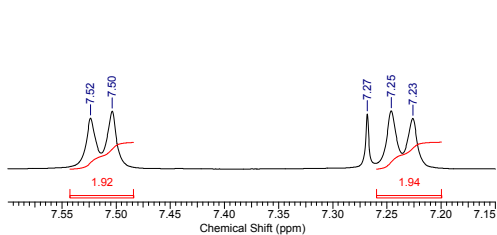


Figure S47. ¹³C NMR spectrum of compound 4v

810-K222-2-H.ESP
810-K222-2-H.ESP



4w

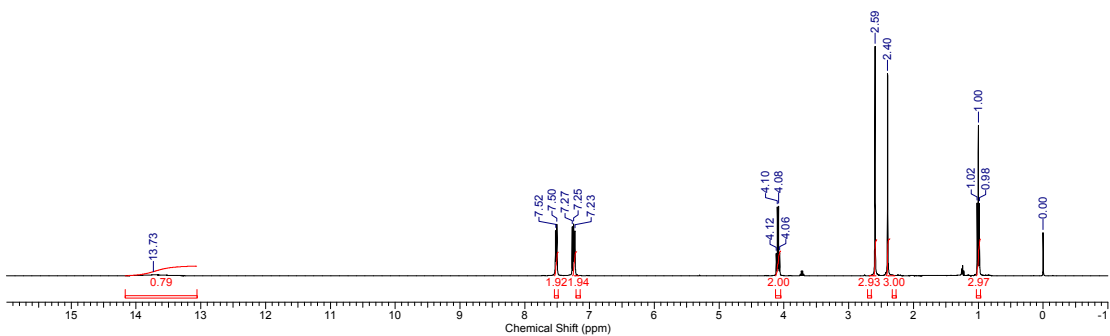
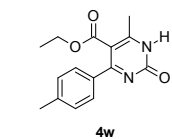


Figure S48. ¹H NMR spectrum of compound 4w

661-K222-2-C.ESP



4w

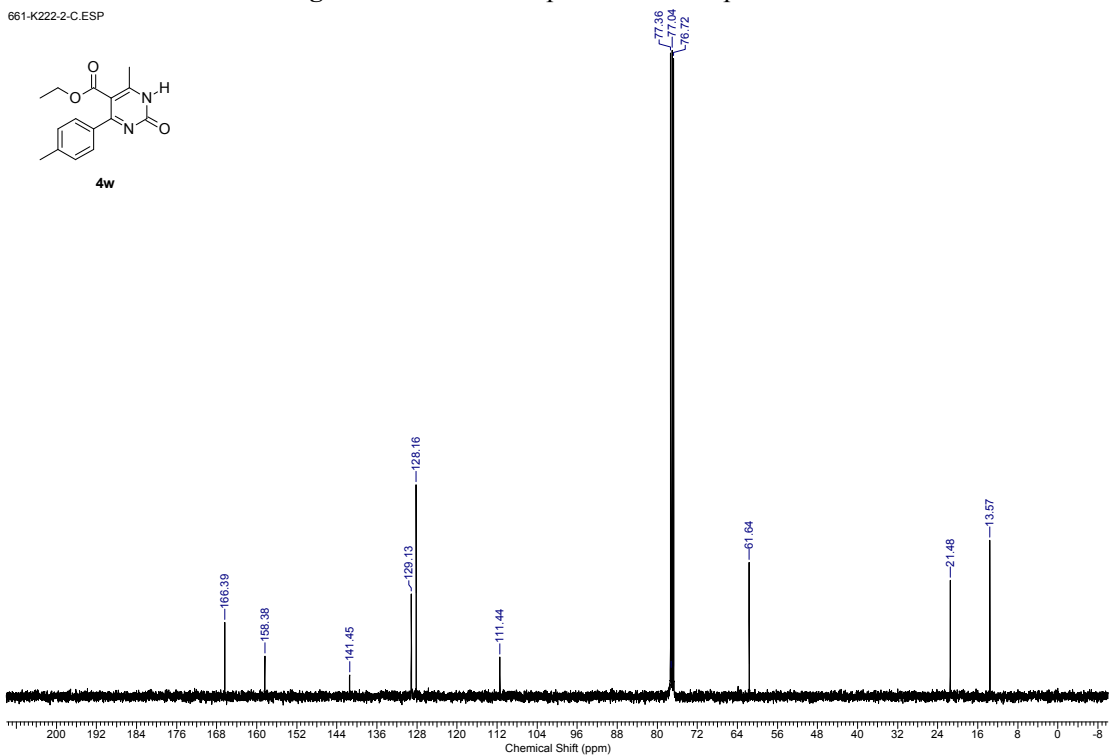
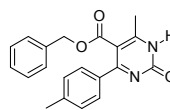
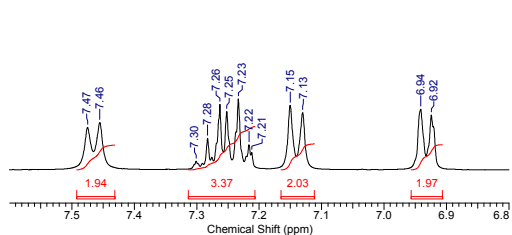


Figure S49. ¹³C NMR spectrum of compound 4w

840-K223-2-H.ESP
840-K223-2-H.ESP



4x

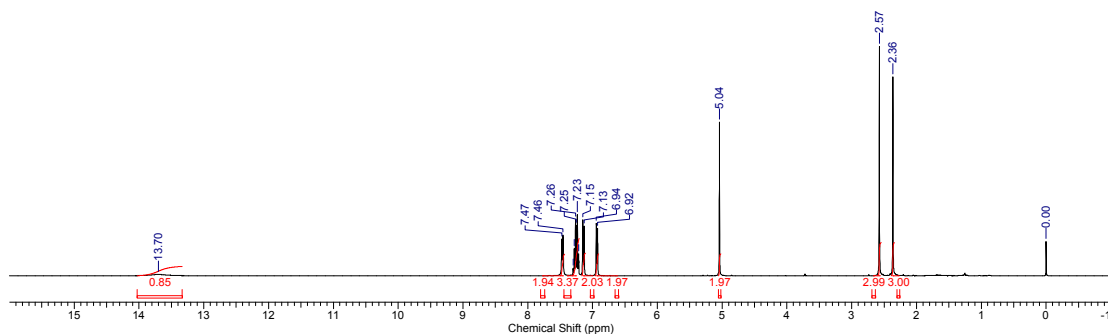
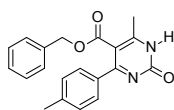


Figure S50. ¹H NMR spectrum of compound 4x

842-K223-2-C.ESP



4x

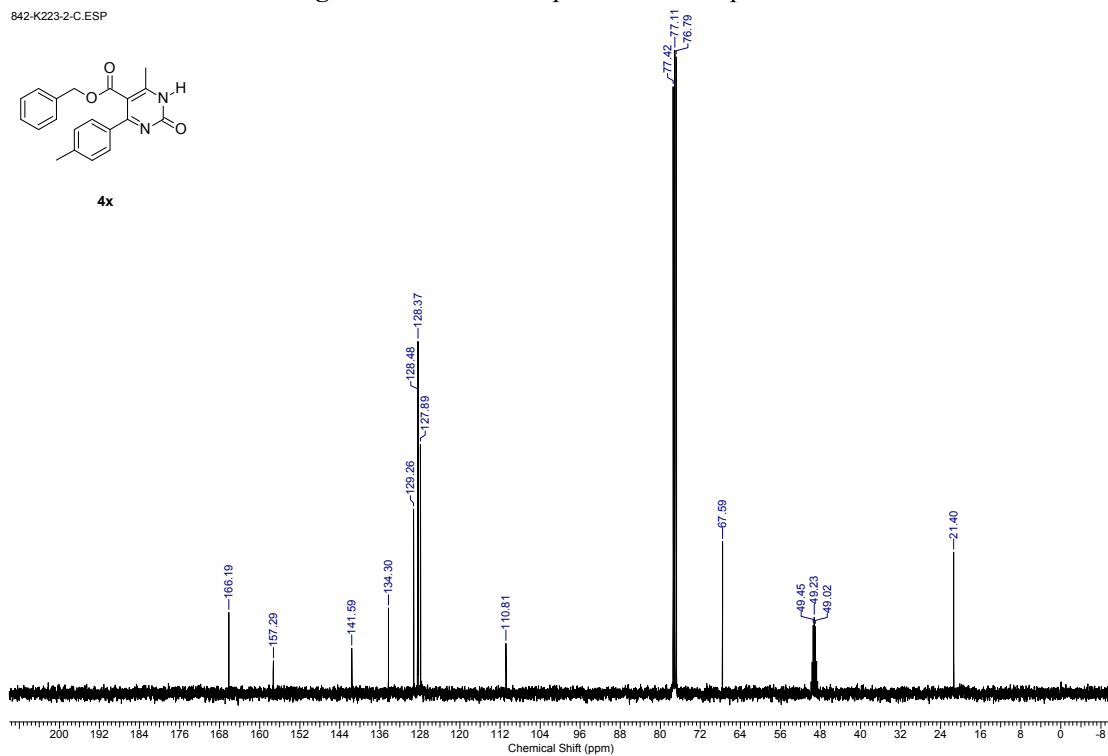


Figure S51. ¹³C NMR spectrum of compound 4x

860-K230-2-H.ESP
860-K230-2-H.ESP

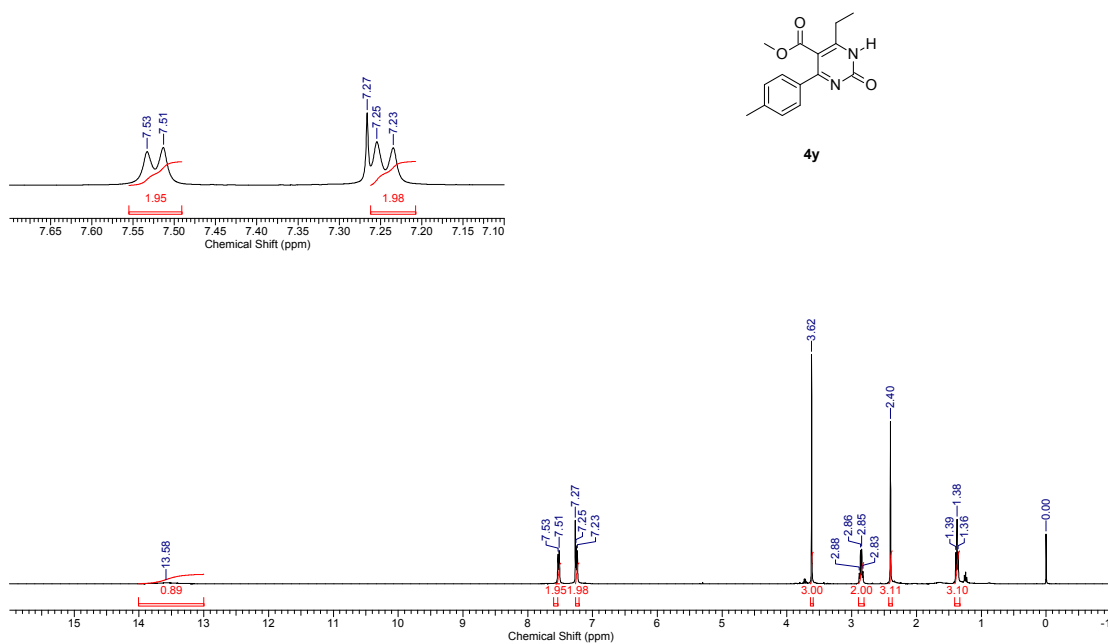


Figure S52. ¹H NMR spectrum of compound 4y

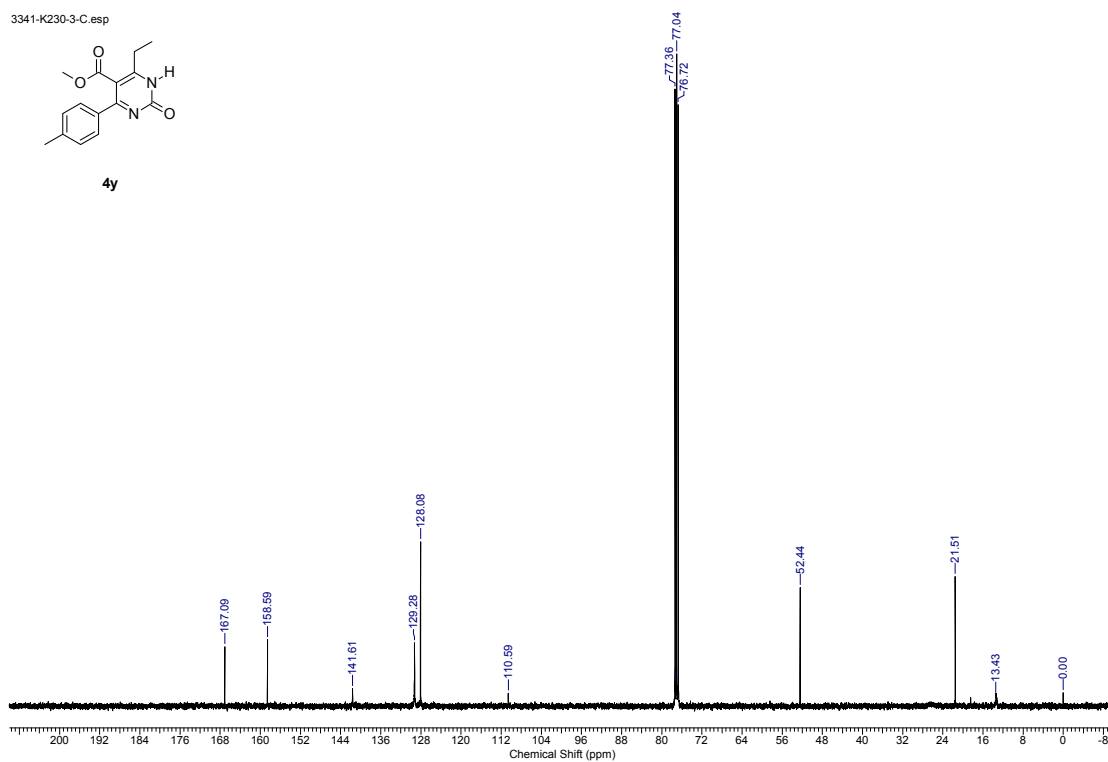


Figure S53. ¹³C NMR spectrum of compound 4y

850-K229-2-H.ESP
850-K229-2-H.ESP

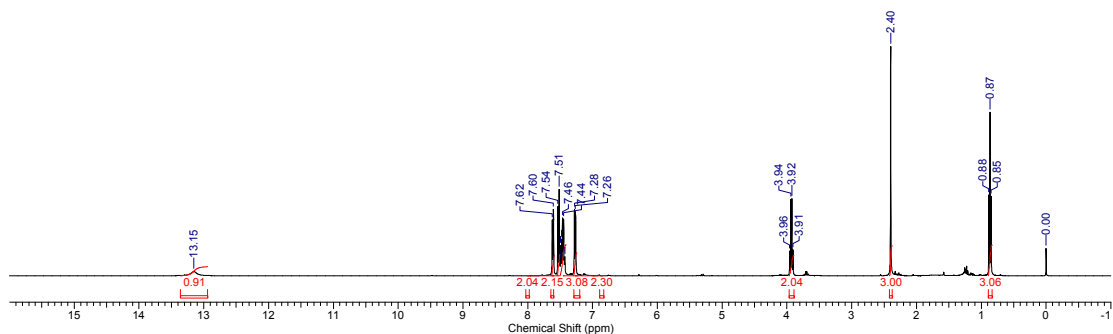
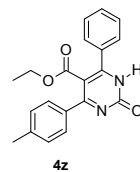
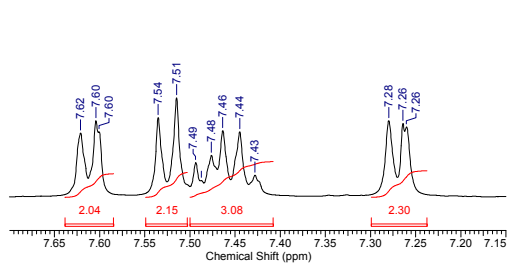


Figure S54. ¹H NMR spectrum of compound **4z** in CDCl₃

3331-K229-3-C.esp

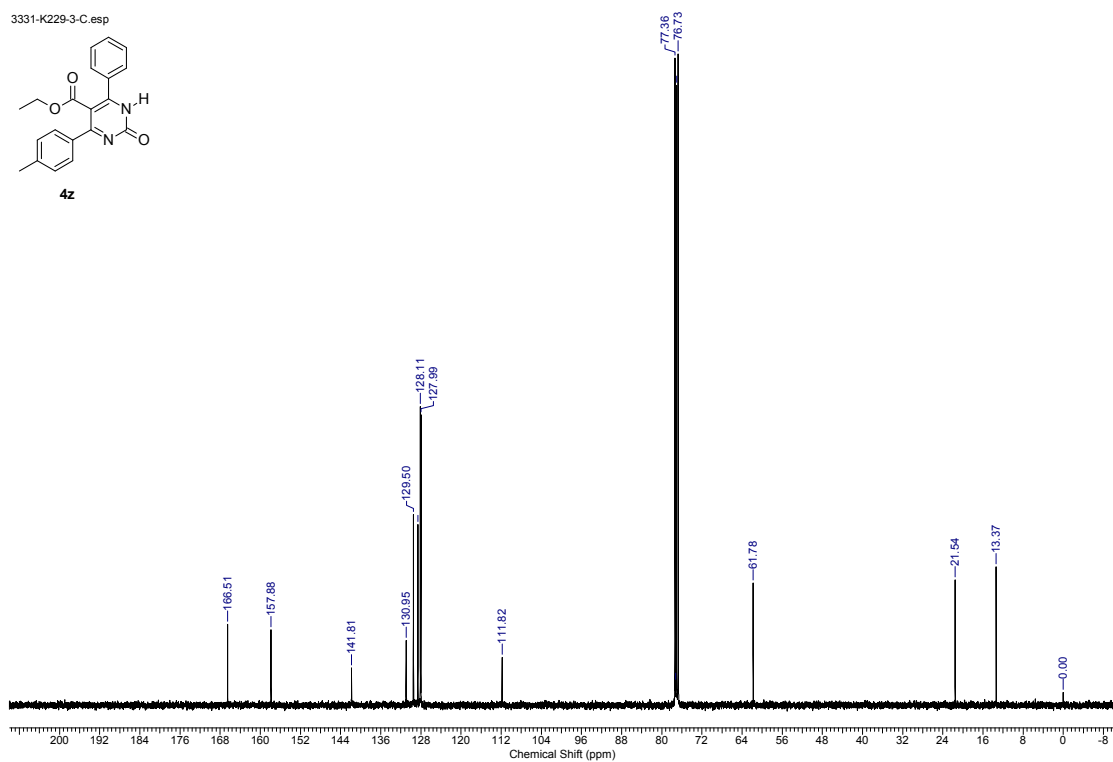
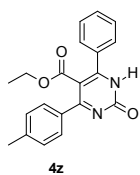


Figure S55. ¹³C NMR spectrum of compound **4z** in CDCl₃

6260-K229-H.ESP

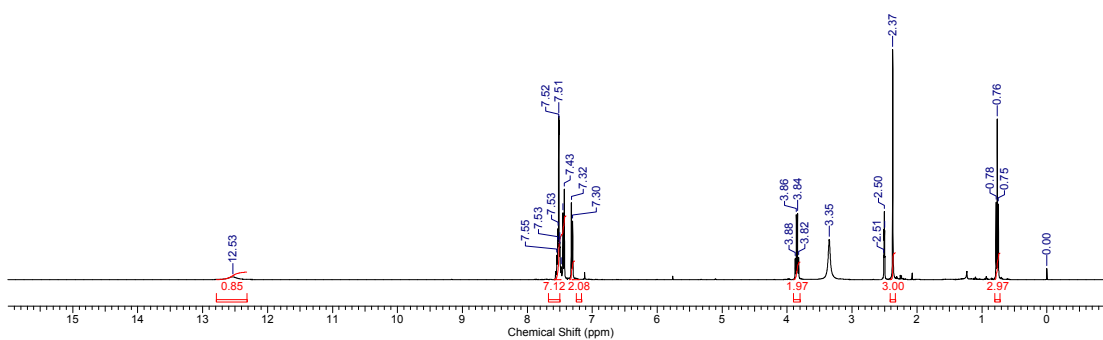
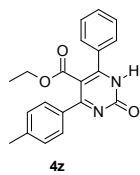


Figure S56. ¹H NMR spectrum of compound **4z** in DMSO-*d*₆

6320-K229-C.esp

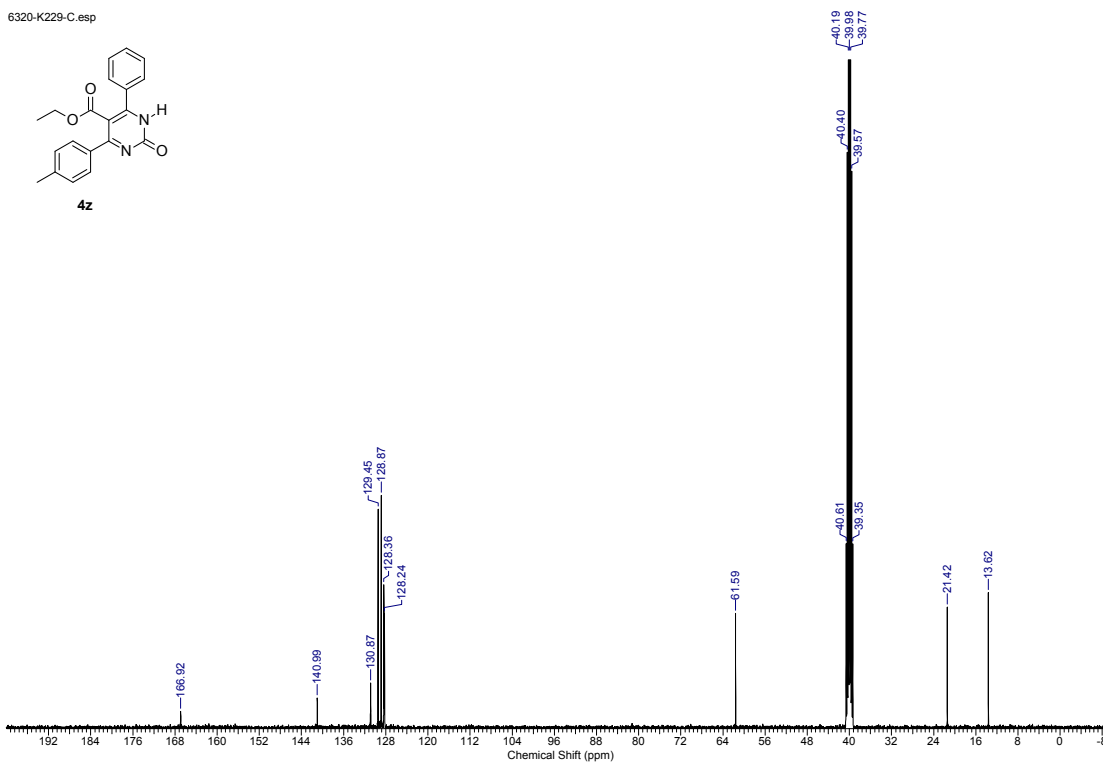
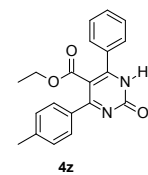


Figure S57. ¹³C NMR spectrum of compound **4z** in DMSO-*d*₆

6. Determination of Structure of 4a

The structure of **4a** was determined by the X-ray diffraction. Recrystallized from dichloromethane/n-hexane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1907956.

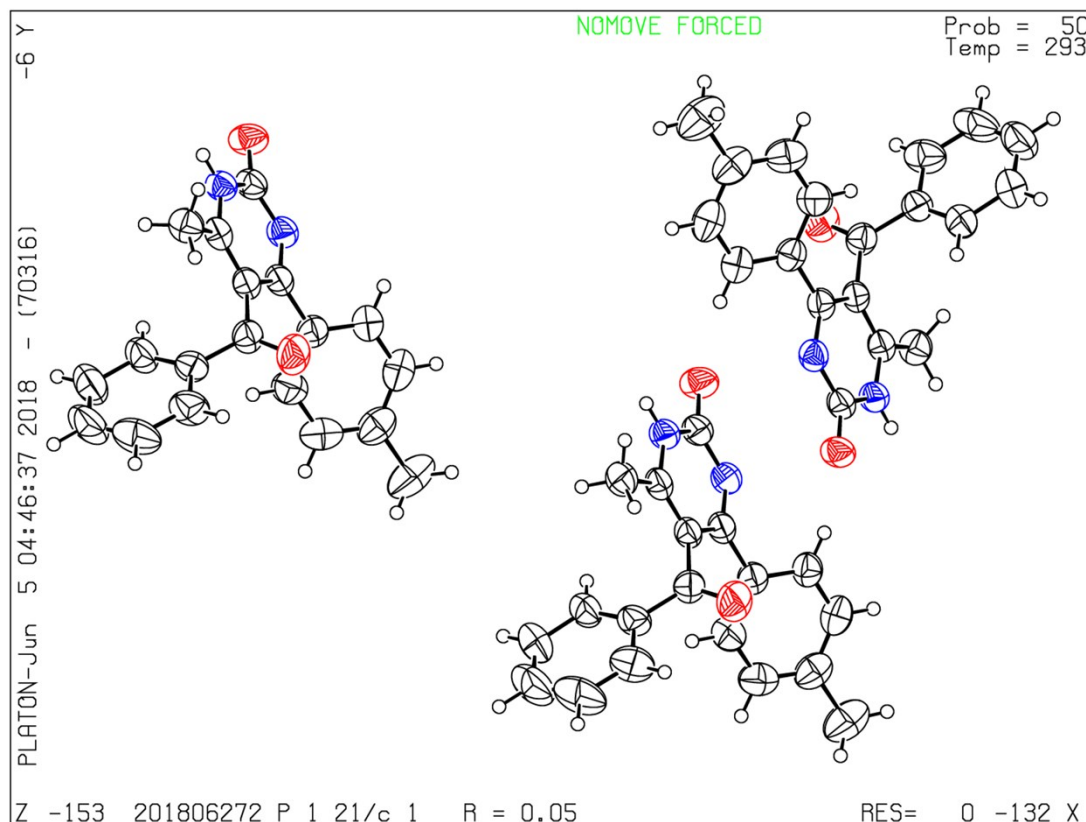


Table 1 Crystal data and structure refinement for 201806272.

Identification code	201806272
Empirical formula	C ₁₉ H ₁₆ N ₂ O ₂
Formula weight	304.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	17.9538(2)
b/Å	13.0669(2)
c/Å	21.0038(3)
α/°	90
β/°	96.8682(13)
γ/°	90
Volume/Å ³	4892.17(12)
Z	12

$\rho_{\text{calc}}/\text{cm}^3$	1.240
μ/mm^{-1}	0.656
F(000)	1920.0
Crystal size/ mm^3	$0.17 \times 0.14 \times 0.1$
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/	7.984 to 141.69
Index ranges	$-21 \leq h \leq 17, -15 \leq k \leq 14, -22 \leq l \leq 25$
Reflections collected	22248
Independent reflections	9225 [$R_{\text{int}} = 0.0229, R_{\text{sigma}} = 0.0268$]
Data/restraints/parameters	9225/0/628
Goodness-of-fit on F^2	1.033
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0511, wR_2 = 0.1457$
Final R indexes [all data]	$R_1 = 0.0729, wR_2 = 0.1660$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.19/-0.17