

Supporting Information

I₂-DMSO-mediated [4+2] cyclization of methyl ketone with 2-aminobenzimidazole to construct 2,4-disubstituted benzo [4,5]imidazo[1,2-*a*] pyrimidines

*Qian Guo^{a‡}, Mengyi Guo^{b‡}, Luoteng Cheng^a, Yifan Song^a, Wanqian Ma^a, Yibo Song^a, Suzhen Li^a,
Xiaoqiong Deng^a, Xinxin Jia^a, Jianyong Yuan^{a*}*

^aDepartment of Medicinal Chemistry, College of Pharmacy, Chongqing Medical University, Chongqing 400016, China.

^bDepartment of Pharmacy, Rongchang District Maternal and Child Health Care Center of Chongqing, Chongqing 402460, China.

*Email: 102542@cqmu.edu.cn

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1. General

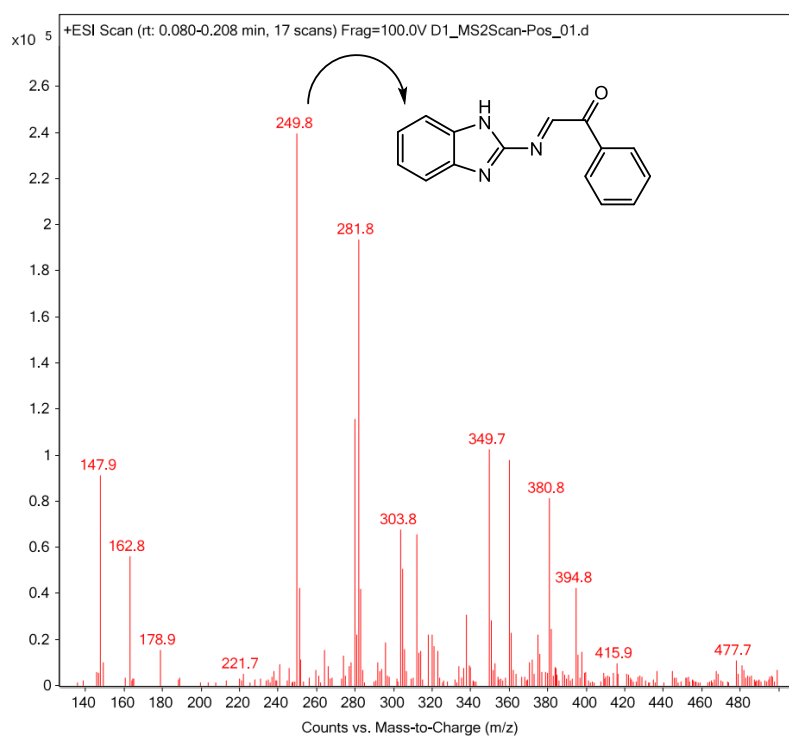
All substrates and reagents are commercially available and can be used without purification. Thin-layer chromatography(TLC) monitors reactions. Separation and purification were carried out using silica gel (200-300 mesh) column chromatography. All ^1H NMR (600 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) and ^{19}F NMR (565 MHz) spectra were recorded on a Bruker Avance-III spectrometer. In CDCl_3 and $\text{DMSO}-d_6$ solutions, all chemical shifts are expressed as δ -values (ppm), with δ -values relative to the TMS ($\delta = 0$) as an internal standard, and coupling constants (J) are reported in hertz (Hz). The following abbreviations have been used to explain multiplicity: s = singlet, d = doublet, t = triplet, dd = doublet, m = multiple, br (broad) or a combination of them. UV-visible and fluorescence spectra were recorded on a Shimadzu UV2600 and an Edinburgh fs5. Recording of high-resolution mass spectra on an Agilent 6230B LC-TOF-MS. Melting points were measured using an x-4 micro melting point meter without calibration.

2. General procedure for the Synthesis of Products 3 and 4 (3a as an Example).

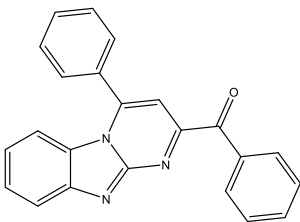
Acetophenone **1a** (2.4 mmol, 2.0 equiv), I_2 (1.2 mmol, 1.0 equiv) and DMSO (4 ml) were added to a 50 ml round bottom flask. The reaction mixture was reacted in air at $100\text{ }^\circ\text{C}$ for 30 min. The reaction was monitored by TLC analysis. After the completion of the previous step, the reaction was continued by adding t-BuOK (2.4 mmol, 2.0 equiv), 2-aminobenzimidazole **2a** (1.2 mmol, 1.0 equiv), and PhCl (8 ml) to the reaction mixture, and the reaction was continued for 2 hours at 100°C . After completion of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate ($3 \times 50\text{ mL}$). The organic layers were separated and combined, dried with anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1) to afford the product **3a** (309 mg, 74% yield).

3. The Detection of Intermediate by MS

MS spectra of intermediate A:

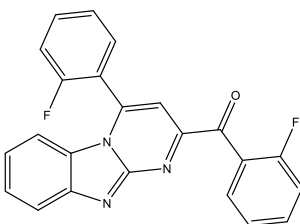


4. Characterization data for compounds



phenyl(4-phenylbenzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3a):

Yield 74%; 309 mg; yellow solid; column chromatography, silica gel (PE:EA, 15:1); mp 218.7–232.7 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.42 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.04 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.71 – 7.62 (m, 5H), 7.57 – 7.48 (m, 4H), 7.13 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 6.82 (dt, *J* = 8.6, 0.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 191.2, 157.4, 150.5, 150.1, 145.9, 135.0, 133.6, 132.1, 131.6 (2C), 131.4, 129.5 (2C), 128.4 (2C), 128.3 (2C), 127.3, 126.7, 122.5, 120.8, 115.1, 107.2. HRMS(ESI) for C₂₃H₁₆N₃O [M+H]⁺ calcd. 350.1288, found 350.1289.

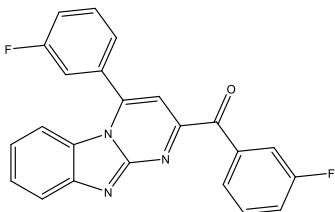


(2-fluorophenyl)(4-(2-fluorophenyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3b):

Yield 70%; 323 mg; yellow solid; column chromatography, silica gel (PE:EA, 5:1); mp 219.4–221.1 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.16 (m, 2H), 7.98 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.74 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.60 – 7.55 (m, 2H), 7.49 – 7.45 (m, 3H), 7.42 (m, 1H), 7.35 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 187.9, 164.7 (d, ¹*J*_{C-F} = 205.4 Hz), 163.0 (d, ¹*J*_{C-F} = 197.8 Hz), 160.5, 153.0, 147.4, 146.6, 140.7 (d, ³*J*_{C-F} = 10.6 Hz), 136.2 (d, ³*J*_{C-F} = 9.1 Hz), 135.6, 133.7, 129.1, 128.5, 128.1 (d, ³*J*_{C-F} = 4.5 Hz), 128.0 (d, ³*J*_{C-F} = 4.5 Hz), 127.3 (d, ³*J*_{C-F} = 10.6 Hz), 125.7 (d, ³*J*_{C-F} = 7.6 Hz), 125.1, 122.7, 120.0 (d, ²*J*_{C-F} = 22.6 Hz), 119.5 (d, ²*J*_{C-F} = 22.6 Hz), 117.1, 110.4 (d, ³*J*_{C-F} = 9.1 Hz). ¹⁹F NMR (565 MHz, DMSO-*d*₆) δ -110.92,

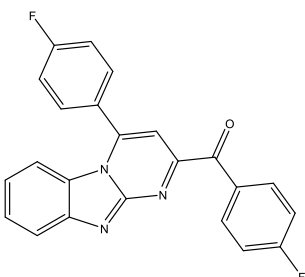
-110.93, -110.94, -110.95, -110.96, -114.45, -114.46, -114.48, -114.49, -114.50.

HRMS(ESI) for C₂₃H₁₄N₃OF₂ [M+H]⁺ calcd. 386.1099, found 386.1105.



(3-fluorophenyl)(4-(3-fluorophenyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3c):

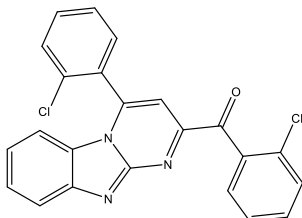
Yield 66%; 305 mg; yellow solid; column chromatography, silica gel (PE:EA, 12:1); mp 234.4-236.1 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.30 – 8.26 (m, 1H), 8.10 (ddd, *J* = 9.5, 2.6, 1.5 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.56 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.54 (s, 1H), 7.53 – 7.50 (m, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.31 (m, 2H), 7.19 (ddd, *J* = 8.4, 7.1, 1.1 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 189.6, 163.0 (d, ¹*J*_{C-F} = 252.2 Hz), 162.5 (d, ¹*J*_{C-F} = 247.6 Hz), 156.6, 149.8, 148.9, 146.2, 136.9 (d, ³*J*_{C-F} = 7.6 Hz), 133.7 (d, ³*J*_{C-F} = 9.1 Hz), 131.6 (d, ³*J*_{C-F} = 7.6 Hz), 130.0 (d, ³*J*_{C-F} = 7.6 Hz), 127.6 (d, ⁴*J*_{C-F} = 4.5 Hz), 127.1, 127.0, 124.1 (d, ⁴*J*_{C-F} = 3.0 Hz), 123.0, 121.1, 120.7 (d, ²*J*_{C-F} = 22.6 Hz), 118.6 (d, ²*J*_{C-F} = 21.1 Hz), 118.0 (d, ²*J*_{C-F} = 22.6 Hz), 115.7 (d, ²*J*_{C-F} = 22.6 Hz), 114.8, 107.0. ¹⁹F NMR (565 MHz, CDCl₃) δ -109.31, -109.32, -109.34, -109.35, -111.87, -111.88, -111.88. HRMS(ESI) for C₂₃H₁₄N₃OF₂ [M+H]⁺ calcd. 386.1099, found 386.1099.



(4-fluorophenyl)(4-(4-fluorophenyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3d):

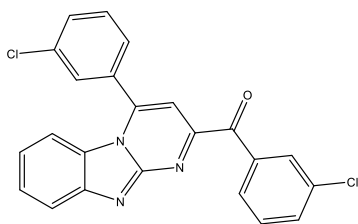
Yield 73%; 337 mg; yellow solid; column chromatography, silica gel (PE:EA, 15:1); mp 240.6-242.3 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.31 – 8.27 (m, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.92-7.88 (m, 2H), 7.61-7.58 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51-7.46 (m, 2H), 7.43 (s, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 190.7, 165.9 (d, ¹*J*_{C-F} = 253.7 Hz), 164.1 (d, ¹*J*_{C-F} = 249.2 Hz), 157.9, 150.4,

150.2, 145.8, 134.5 (2C) (d, $^3J_{C-F}=9.1$ Hz), 132.0 (d, $^4J_{C-F}=3.0$ Hz), 131.6 (2C) (d, $^3J_{C-F}=7.6$ Hz), 128.9 (d, $^4J_{C-F}=4.5$ Hz), 127.6, 126.9, 122.6, 120.5, 117.1 (2C) (d, $^2J_{C-F}=22.6$ Hz), 116.2 (2C) (d, $^2J_{C-F}=22.6$ Hz), 115.3, 107.3. ^{19}F NMR (565 MHz, DMSO- d_6) δ -104.31, -104.32, -104.32, -104.33, -104.34, -108.73, -108.74, -108.75, -108.75, -108.76, -108.77, -108.78. HRMS(ESI) for $\text{C}_{23}\text{H}_{14}\text{N}_3\text{OF}_2$ $[\text{M}+\text{H}]^+$ calcd. 386.1099, found 386.1099.



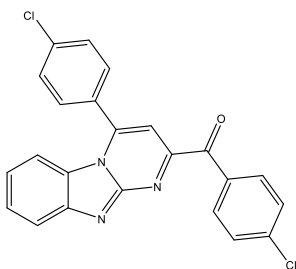
(2-chlorophenyl)(4-(2-chlorophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3e):

Yield 71%; 355 mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 207.4-212.8 °C. ^1H NMR (600 MHz, DMSO- d_6) δ 7.96 (d, $J = 8.3$ Hz, 1H), 7.91 – 7.88 (m, 2H), 7.88 – 7.85 (m, 1H), 7.80 – 7.78 (m, 1H), 7.76 (td, $J = 7.4, 1.4$ Hz, 1H), 7.71 (s, 1H), 7.71 – 7.68 (m, 2H), 7.61 – 7.57 (m, 2H), 7.26 (ddd, $J = 8.4, 7.1, 1.1$ Hz, 1H), 6.47 (d, $J = 8.6$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 193.8, 156.1, 149.8, 148.1, 146.0, 137.1, 133.8, 133.1, 132.6, 131.7, 131.4, 131.0(9), 131.0(6), 130.6, 130.3, 129.1, 127.6, 127.4, 127.3, 123.8, 120.7, 114.2, 106.0. HRMS(ESI) for $\text{C}_{23}\text{H}_{14}\text{N}_3\text{OCl}_2$ $[\text{M}+\text{H}]^+$ calcd. 418.0508, found 418.0510.



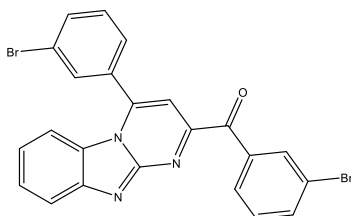
(3-chlorophenyl)(4-(3-chlorophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3f):

Yield 71%; 355 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 222.2-224.7 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, $J = 7.6$ Hz, 1H), 8.31 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 1H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.62 – 7.56 (m, 4H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 189.5, 157.3, 149.2, 149.1, 136.4, 135.9, 134.7, 133.7, 133.3, 131.8, 131.0, 130.9, 130.1, 129.7 (2C), 128.5, 127.4, 126.9, 126.5, 123.3, 120.6, 114.9, 107.7. HRMS(ESI) for $\text{C}_{23}\text{H}_{14}\text{N}_3\text{OCl}_2$ $[\text{M}+\text{H}]^+$ calcd. 418.0508, found 418.0507.



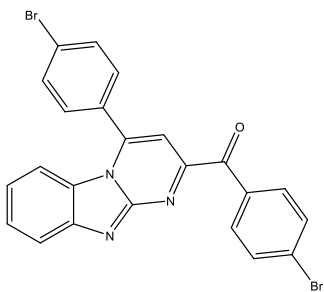
(4-chlorophenyl)(4-(4-chlorophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3g):

Yield 75%; 375 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 228.4–233.0 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.31 (t, *J* = 1.8 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 8.01 – 7.95 (m, 3H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 (s, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 191.0, 157.6, 150.2, 145.9, 139.4, 136.6, 134.1, 133.2, 131.2, 131.0, 130.0, 129.2, 127.5, 127.0, 122.8, 120.5, 115.3, 107.2, 100.0. HRMS(ESI) for C₂₃H₁₄N₃OCl₂ [M+H]⁺ calcd. 418.0508, found 418.0510.



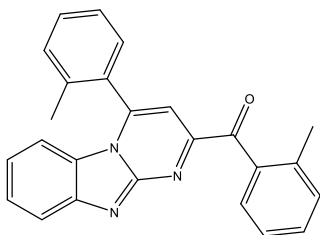
(3-bromophenyl)(4-(3-bromophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3h):

Yield 74%; 448 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 226.8–228.2 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.31 (t, *J* = 1.8 Hz, 1H), 8.17 – 8.14 (m, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 8.02 – 7.96 (m, 3H), 7.86 – 7.82 (m, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.50 (s, 1H), 7.25 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 6.69 (dt, *J* = 8.6, 1.0 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 190.9, 157.3, 150.1, 149.6, 145.9, 137.5, 136.8, 134.6, 134.5, 133.8, 132.1, 131.6, 131.3, 130.1, 128.0, 127.5, 127.0, 122.8, 122.1, 120.6, 115.1, 107.2. HRMS(ESI) for C₂₃H₁₄N₃OBr₂ [M+H]⁺ calcd. 505.9498, found 505.9502.



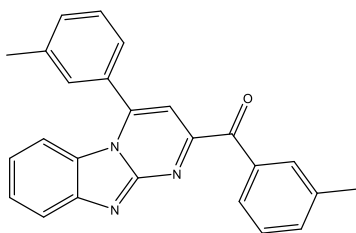
(4-bromophenyl)(4-(4-bromophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3i):

Yield 76%; 461 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 200.2-242.0 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.15 – 8.10 (m, 2H), 8.00 – 7.93 (m, 3H), 7.90 – 7.85 (m, 2H), 7.81 – 7.77 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.45 (s, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 191.3, 157.5, 150.2, 150.1, 145.9, 134.4, 133.3, 133.0, 132.1, 131.5, 131.1, 128.6, 127.5, 127.0, 125.4, 122.8, 120.5, 115.3, 107.1. HRMS(ESI) for C₂₃H₁₄N₃OBr₂ [M+H]⁺ calcd. 505.9498, found 505.9503.



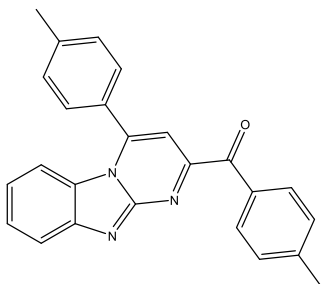
o-tolyl(4-(o-tolyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3j):

Yield 63%; 285 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 188.7-189.0 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.64 – 7.59 (m, 2H), 7.58 – 7.52 (m, 3H), 7.51 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.17 (ddd, *J* = 8.4, 7.1, 1.1 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 2.43 (s, 3H), 2.08 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 195.9, 158.0, 150.5, 150.2, 145.9, 138.3, 136.6, 136.4, 132.1, 132.0, 131.8, 131.6, 131.5, 131.3, 129.3, 127.5, 127.5, 127.0, 125.7, 123.1, 120.5, 114.3, 106.3, 20.7, 19.1. HRMS(ESI) for C₂₅H₂₀N₃O [M+H]⁺ calcd. 378.1601, found 378.1602.



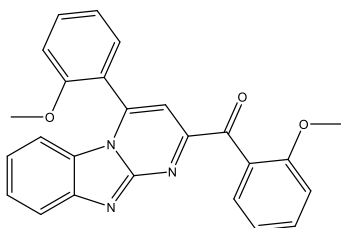
m-tolyl(4-(m-tolyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3k):

Yield 65%; 294 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 191.2-193.8 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.98 – 7.92 (m, 3H), 7.64 – 7.57 (m, 5H), 7.57 – 7.50 (m, 2H), 7.38 (s, 1H), 7.19 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 2.44 (m, 6H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 192.5, 158.5, 151.3, 150.3, 145.8, 139.5, 138.4, 135.4, 135.0, 132.4, 132.3, 131.5, 129.7, 129.1, 128.9, 128.7, 127.6, 126.8, 125.8, 122.4, 120.4, 115.3, 106.9, 21.5, 21.4. HRMS(ESI) for C₂₅H₂₀N₃O [M+H]⁺ calcd. 378.1601, found 378.1607.



p-tolyl(4-(p-tolyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3l):

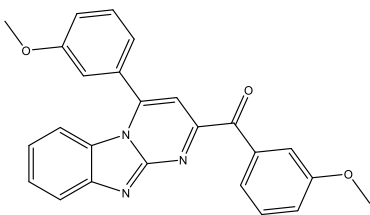
Yield 73%; 330 mg; yellow solid; column chromatography, silica gel (PE:EA, 12:1); mp 196.0-196.8 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.10-8.08 (m, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.70-7.68 (m, 2H), 7.55-7.53 (m, 3H), 7.45-7.43 (m, 2H), 7.35 (s, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 2.53-2.51 (m, 3H), 2.46-2.44 (m, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 190.7, 157.5, 150.3, 149.3, 144.7, 144.0, 140.6, 131.7, 130.4 (2C), 129.3 (2C), 128.5 (3C), 127.7 (2C), 126.5, 125.7, 121.2, 119.3, 114.3, 106.0, 20.8, 20.6. HRMS(ESI) for C₂₅H₂₀N₃O [M+H]⁺ calcd. 378.1601, found 378.1597.



(2-methoxyphenyl)(4-(2-methoxyphenyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-yl)methanone (3m):

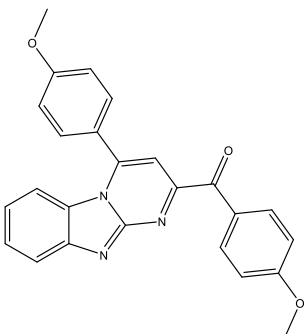
Yield 63%; 309 mg; yellow solid; column chromatography, silica gel (PE:EA, 5:1); mp 171.6-172.3 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.53 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.47 (s, 1H), 7.17 (d, *J* = 8.8 Hz, 3H), 7.01 (d, *J* = 8.9 Hz, 3H), 3.98 (s, 3H), 3.92 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 189.4, 164.2, 161.9, 158.3, 150.6, 150.3, 145.7, 134.2 (2C), 129.8 (2C),

128.0, 127.4, 126.6, 124.3, 122.2, 120.7, 115.2, 114.8 (2C), 113.7 (2C), 107.6, 55.6(0), 55.5(7). HRMS(ESI) for $C_{25}H_{20}N_3O_3$ $[M+H]^+$ calcd. 410.1499, found 410.1503.



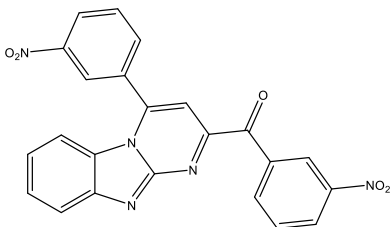
(3-methoxyphenyl)(4-(3-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3n):

Yield 72%; 353 mg; yellow solid; column chromatography, silica gel (PE:EA, 8:1); mp 173.5–176.6 °C. 1H NMR (600 MHz, $DMSO-d_6$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.74 (ddd, J = 7.6, 1.6, 1.0 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.55 (t, J = 7.9 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 7.21 (ddd, J = 8.4, 7.1, 1.2 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 3.85 (m, 6H). ^{13}C NMR (151 MHz, $DMSO-d_6$) δ 192.1, 160.2, 159.6, 158.2, 151.0, 150.2, 145.8, 136.6, 133.6, 131.2, 130.2, 127.5, 126.9, 124.0, 122.5, 120.8, 120.4, 120.3, 117.6, 115.9, 115.4, 114.1, 106.9, 55.9(9), 55.9(5). HRMS(ESI) for $C_{25}H_{20}N_3O_3$ $[M+H]^+$ calcd. 410.1499, found 410.1502.



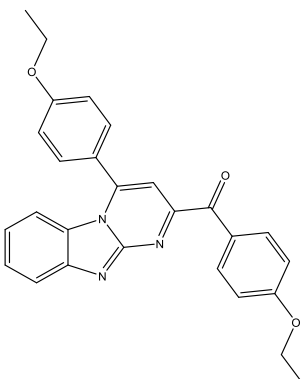
(4-methoxyphenyl)(4-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3o):

Yield 73%; 358 mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 178.1–194.2 °C. 1H NMR (600 MHz, $DMSO-d_6$) δ 8.23 – 8.18 (m, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.53 (t, J = 7.1 Hz, 1H), 7.31 (s, 1H), 7.28 – 7.25 (m, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.85 (d, J = 8.4 Hz, 1H), 3.93–3.91 (m, 6H). ^{13}C NMR (151 MHz, $DMSO-d_6$) δ 190.5, 164.4, 161.8, 158.9, 151.3, 150.5, 145.8, 133.9, 130.5, 127.9, 127.7, 126.7, 124.5, 122.2, 120.3, 115.4, 115.2, 114.4, 107.3, 56.2, 56.0. HRMS(ESI) for $C_{25}H_{20}N_3O_3$ $[M+H]^+$ calcd. 410.1499, found 410.1498.



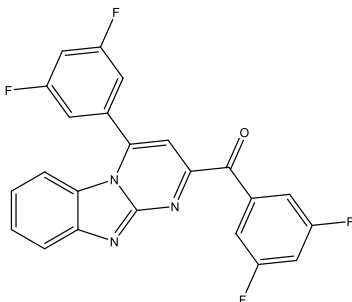
(3-nitrophenyl)(4-(3-nitrophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3p):

Yield 72%; 379 mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 327.7-328.2 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.97 (t, *J* = 2.0 Hz, 1H), 8.75 (t, *J* = 2.0 Hz, 1H), 8.65 – 8.58 (m, 3H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.05 (t, *J* = 8.0 Hz, 1H), 8.01 – 7.94 (m, 2H), 7.64 (s, 1H), 7.60 – 7.56 (m, 1H), 7.22 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 190.2, 156.6, 150.0, 149.0, 148.6, 148.1, 146.0, 137.3, 136.7, 135.6, 133.6, 131.7, 130.8, 128.3, 127.5, 127.1, 126.5, 125.9, 124.4, 123.1, 120.6, 115.4, 107.5. HRMS(ESI) for C₂₃H₁₄N₅O₅ [M+H]⁺ calcd. 440.0990, found 440.0994.



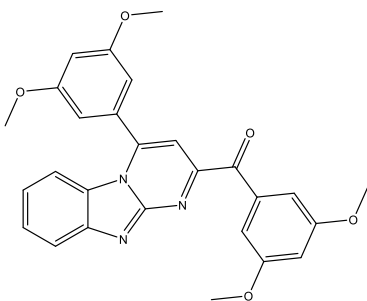
(4-ethoxyphenyl)(4-(4-ethoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3q):

Yield 76%; 399 mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 188.8-192.6 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.21 – 8.17 (m, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.23 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 1H), 4.24 – 4.14 (m, 4H), 1.43-1.38 (m, 6H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 190.5, 163.7, 161.1, 159.0, 151.4, 150.5, 145.7, 133.9, 130.5, 127.8, 127.7, 126.7, 124.4, 122.2, 120.3, 115.6, 115.4, 114.8, 107.2, 64.3, 64.0, 15.1, 15.0. HRMS(ESI) for C₂₇H₂₄N₃O₃ [M+H]⁺ calcd. 438.1811, found 438.1812.



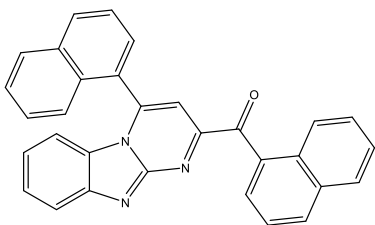
(3,5-difluorophenyl)(4-(3,5-difluorophenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3r):

Yield 66%; 333 mg; yellow solid; column chromatography, silica gel (PE:EA, 20:1); mp 253.9-256.2 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 5.7 Hz, 2H), 7.74 (td, *J* = 9.2, 2.4 Hz, 2H), 7.64 (d, *J* = 5.6 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 189.5, 163.2 (2C) (dd, ¹*J*_{C-F} = 247.6 Hz), 162.5 (2C) (dd, ¹*J*_{C-F} = 247.6 Hz), 156.7, 149.9, 148.6, 146.0, 138.4 (t, ³*J*_{C-F} = 16.6 Hz), 135.1 (t, ³*J*_{C-F} = 21.1 Hz), 127.3, 127.2, 123.2, 120.6, 115.2, 114.5 (2C) (dd, ²*J*_{C-F} = 27.2 Hz), 113.0 (2C) (dd, ²*J*_{C-F} = 27.2 Hz), 109.6 (t, ²*J*_{C-F} = 52.8 Hz), 107.5 (t, ²*J*_{C-F} = 49.8 Hz), 107.0. ¹⁹F NMR (565 MHz, DMSO-*d*₆) δ -106.99, -107.01, -107.02, -108.52, -108.53, -108.55. HRMS(ESI) for C₂₃H₁₂N₃OF₄ [M+H]⁺ calcd. 422.0911, found 422.0910.



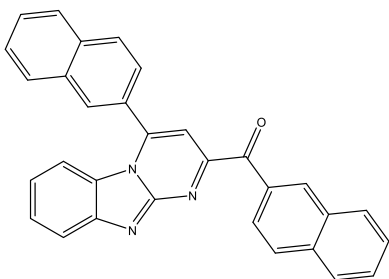
(3,5-dimethoxyphenyl)(4-(3,5-dimethoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3s):

Yield 68%; 383 mg; yellow solid; column chromatography, silica gel (PE:EA, 5:1); mp 220.5-231.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 3H), 7.24 – 7.18 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.78 (t, *J* = 2.2 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 3H), 3.88 (s, 6H), 3.86 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 191.2, 161.6 (2C), 160.6 (2C), 157.6, 150.3, 150.0, 146.0, 136.6, 133.6, 127.2, 126.7, 122.5, 120.8, 115.3, 109.2 (2C), 106.8, 106.5, 106.0 (2C), 103.3, 55.8, 55.7. HRMS(ESI) for C₂₇H₂₄N₃O₅ [M+H]⁺ calcd. 470.1711, found 470.1707.



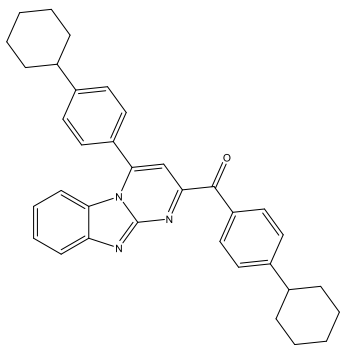
naphthalen-1-yl(4-(naphthalen-1-yl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3t):

Yield 73%; 393 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 233.8-237.5 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 8.4 Hz, 1H), 8.26 – 8.19 (m, 2H), 8.09 (m, 2H), 7.97 (m, 2H), 7.85 (s, 1H), 7.77 – 7.74 (m, 2H), 7.64 – 7.53 (m, 4H), 7.45 – 7.38 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.10 (d, *J* = 8.6 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 194.1, 158.0, 150.1, 149.3, 145.9, 134.0, 133.5, 133.2, 132.5, 132.3, 131.7, 131.5, 130.3, 129.5, 129.0, 128.7, 128.2, 127.9, 127.3(7), 127.3(6), 127.2, 126.7, 126.4, 125.6, 125.5, 124.3, 124.2, 122.8, 120.6, 114.9, 107.8. HRMS(ESI) for C₃₁H₂₀N₃O [M+H]⁺ calcd. 450.1601, found 450.1607.



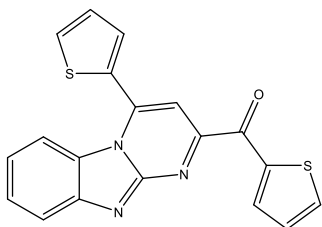
naphthalen-2-yl(4-(naphthalen-2-yl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3u):

Yield 78%; 420 mg; yellow solid; column chromatography, silica gel (PE:EA, 12:1); mp 269.5-271.9 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.15 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.10 – 8.03 (m, 3H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.61 (m, 5H), 7.59 – 7.51 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 191.0, 135.9, 134.8, 134.3, 133.1, 132.4, 132.3, 130.4, 129.3(9), 129.3(2), 129.0, 128.8 (2C), 128.6, 128.3 (2C), 128.2 (2C), 127.7 (2C), 127.6, 127.4, 126.9 (2C), 126.7, 126.1, 124.6 (2C), 122.6, 120.7, 115.3. HRMS(ESI) for C₃₁H₂₀N₃O [M+H]⁺ calcd. 450.1601, found 450.1602.



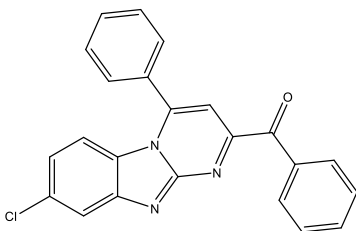
(4-cyclohexylphenyl)(4-(4-cyclohexylphenyl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3v):

Yield 73%; 449 mg; yellow solid; column chromatography, silica gel (PE:EA, 12:1); mp 212.0-216.8 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.36-8.32 (m, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.59-7.56 (m, 2H), 7.53 (t, *J* = 8.3 Hz, 1H), 7.51-7.49 (m, 3H), 7.37-7.35 (m, 2H), 7.14 (t, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.65 – 2.58 (m, 1H), 2.04-2.02 (m, 2H), 1.97 – 1.85 (m, 6H), 1.83-1.77 (m, 3H), 1.57 (d, *J* = 9.6 Hz, 1H), 1.53 – 1.41 (m, 6H), 1.37 – 1.25 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 190.9, 157.9, 154.5, 151.9, 150.8, 150.2, 132.8, 131.9, 129.4, 128.2, 127.9, 127.4, 126.9, 126.6, 122.2, 120.7, 115.2, 107.4, 44.9, 44.6, 34.4, 34.1, 26.7(9), 26.7(5), 26.1. HRMS(ESI) for C₃₅H₃₆N₃O [M+H]⁺ calcd. 514.2853, found 514.2854.



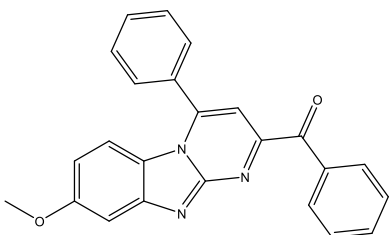
thiophen-2-yl(4-(thiophen-2-yl)benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)methanone (3w):

Yield 65%; 282 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 211.1-222.8 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.49 (dd, *J* = 3.9, 1.2 Hz, 1H), 8.27 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.76 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.46 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.40 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.29 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 6.91 (dt, *J* = 8.6, 1.0 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 182.1, 156.3, 150.2, 146.0, 144.9, 139.3, 139.1, 138.3, 131.5(3), 131.4(8), 131.4(0), 129.1, 128.9, 127.6, 127.2, 122.9, 120.6, 115.3, 107.9. HRMS(ESI) for C₁₉H₁₂N₃OS₂ [M+H]⁺ calcd. 362.0416, found 362.0415.



(8-chloro-4-phenylbenzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)(phenyl)methanone (4a):

Yield 65%; 299 mg; yellow solid; column chromatography, silica gel (PE:EA, 10:1); mp 235.3-239.8 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.40 (d, *J* = 7.5 Hz, 2H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 2H), 7.67 – 7.64 (m, 3H), 7.57 (s, 1H), 7.57 – 7.51 (m, 2H), 7.10 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 190.9, 158.3, 150.6, 134.8, 133.8, 132.8, 131.7, 131.6 (2C), 129.7 (2C), 128.5 (2C), 128.2 (2C), 125.8, 123.3, 120.0, 116.0, 108.0, 100.0. HRMS(ESI) for C₂₃H₁₅N₃OCl [M+H]⁺ calcd. 384.0898, found 384.0893.



(8-methoxy-4-phenylbenzo[4,5]imidazo[1,2-*a*]pyrimidin-2-yl)(phenyl)methanone (4b):

Yield 67%; 305mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 197.9-216.9 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.43 – 8.38 (m, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.67 (m, 5H), 7.57 (s, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 2.5 Hz, 1H), 6.78 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.70 (d, *J* = 9.3 Hz, 1H), 3.92 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 191.2, 159.3, 156.4, 149.6, 135.2, 133.6, 132.0, 131.6 (2C), 131.4, 129.6 (2C), 128.4 (2C), 128.2 (2C), 121.7, 115.8, 114.2, 107.4, 100.6, 55.7. HRMS(ESI) for C₂₄H₁₈N₃O₂ [M+H]⁺ calcd. 380.1394, found 380.1392.

5. X-ray Crystallography Data

X-ray Crystallography Data of **3a**:

The ethyl acetate solution subjected to column chromatography was slowly evaporated to give a single crystal of compound **3a**. The single-crystals of compound **3a**, was measured on a Bruker D8 Quest diffractometer (CCDC No. 2403249).

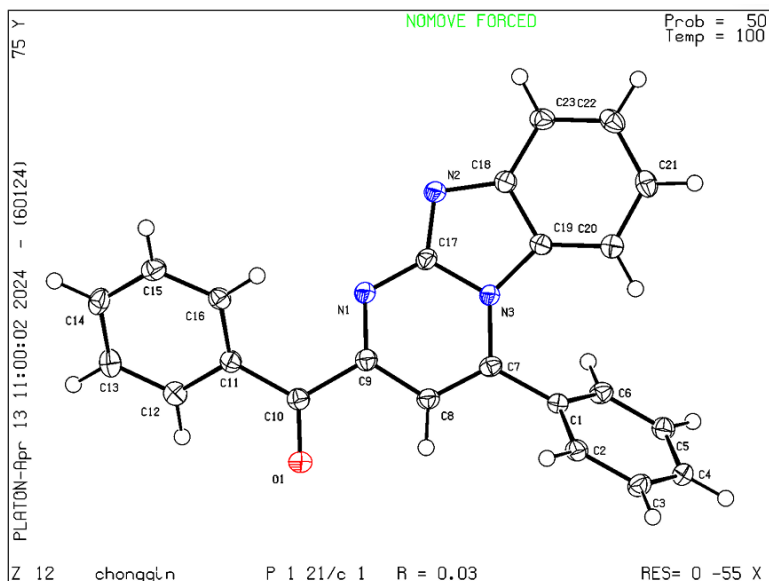


Figure S1. Molecular structure of 3a with 50% probability ellipsoids

Bond precision: C-C = 0.0016 Å Wavelength=1.54184

Cell: a=7.6699(1) b=17.9820(2) c=12.1583(1)
alpha=90 beta=93.293(1) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	1674.11(3)	1674.11(3)
Space group	P 21/c	P 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C23 H15 N3 O	C23 H15 N3 O
Sum formula	C23 H15 N3 O	C23 H15 N3 O
Mr	349.38	349.38
Dx, g cm ⁻³	1.386	1.386
Z	4	4
Mu (mm ⁻¹)	0.693	0.693
F000	728.0	728.0
F000'	730.09	
h, k, lmax	9, 22, 15	9, 22, 15
Nref	3361	3264
Tmin, Tmax	0.898, 0.920	0.901, 1.000
Tmin'	0.895	

Correction method= # Reported T Limits: Tmin=0.901 Tmax=1.000
AbsCorr = MULTI-SCAN

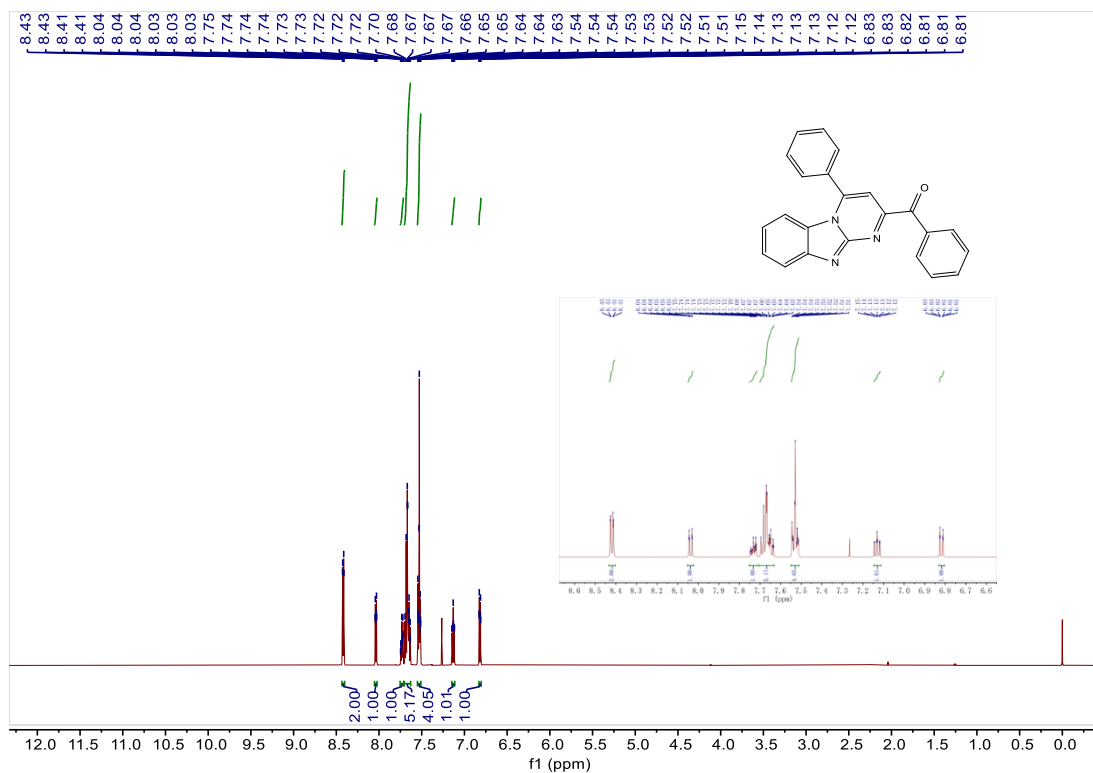
Data completeness= 0.971 Theta(max)= 73.178

R(reflections)= 0.0336(3049) wR2(reflections)=
0.0832(3264)

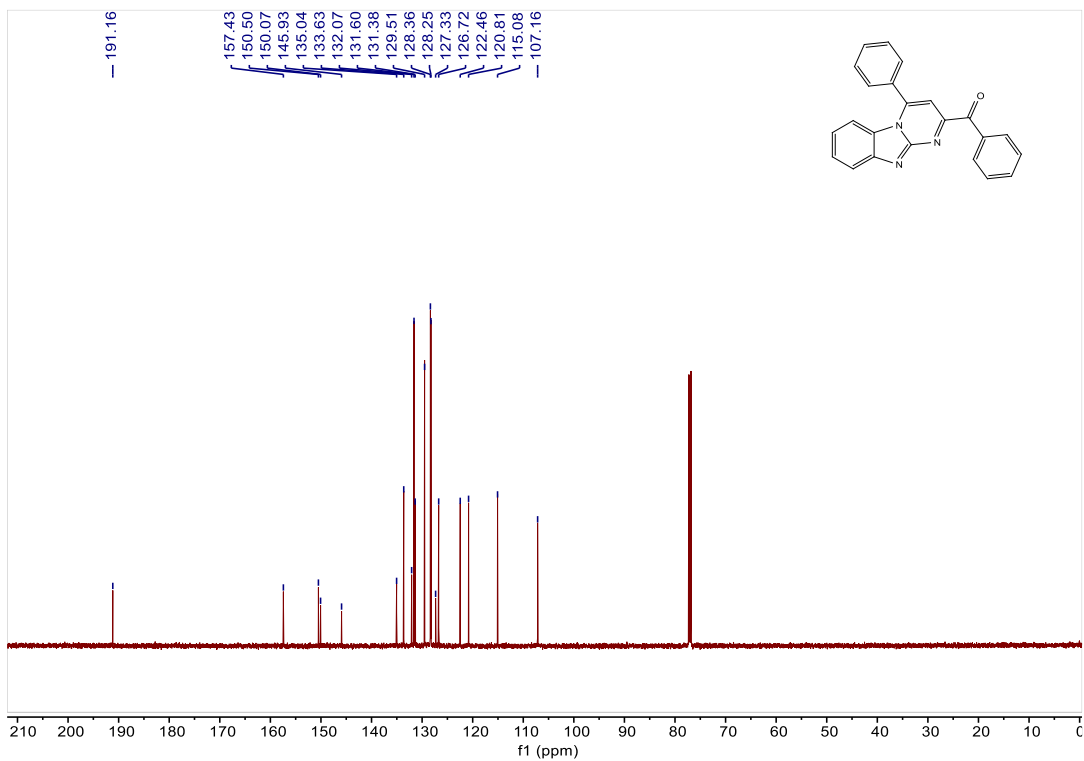
S = 1.043 Npar= 245

6. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and ^{19}F NMR spectra of compounds

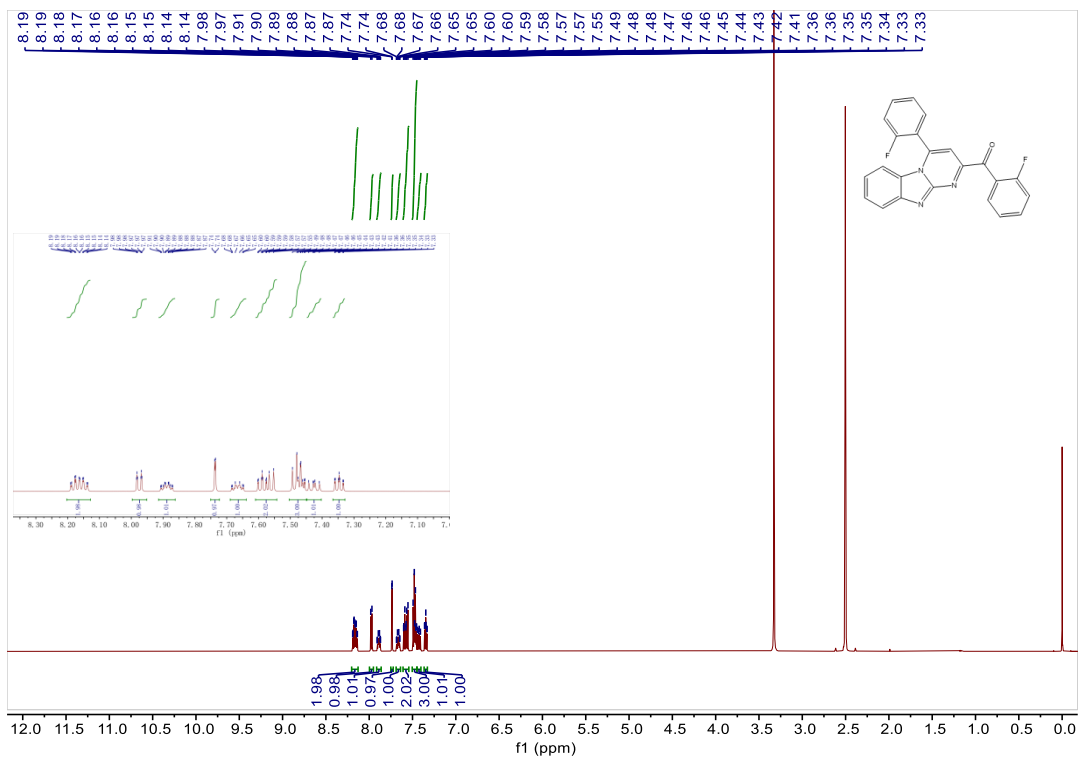
^1H NMR of Compound 3a (600MHz, CDCl_3)



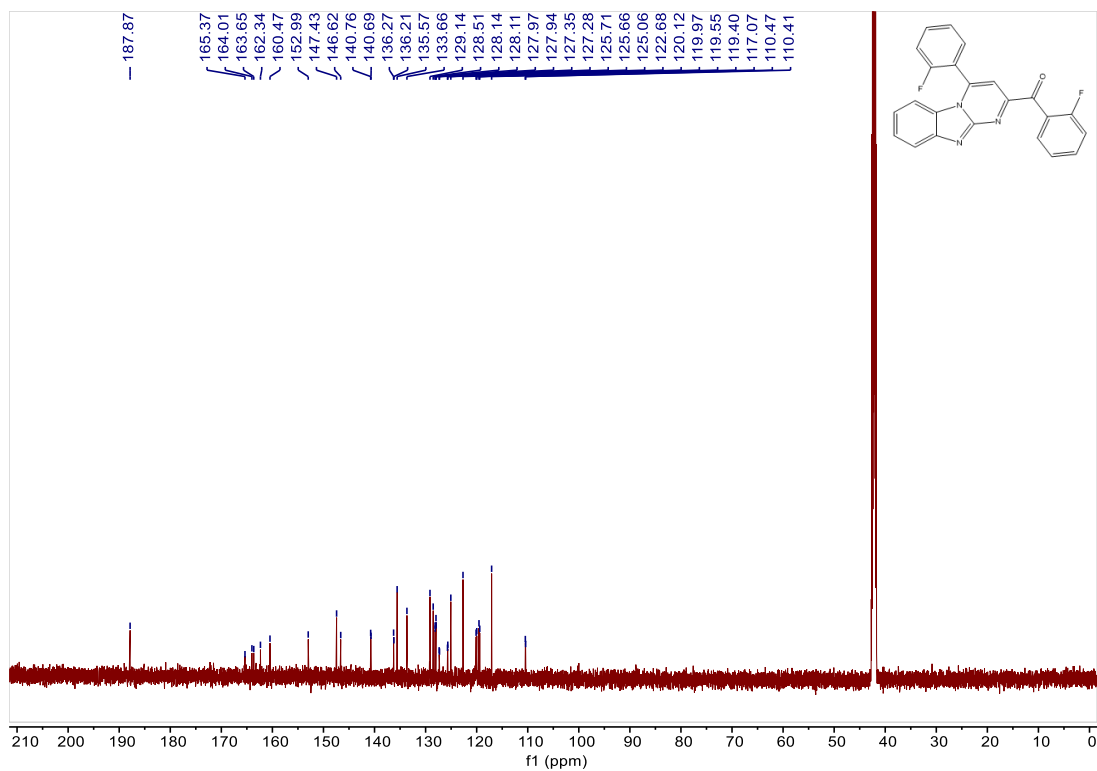
^{13}C NMR of Compound 3a (151MHz, CDCl_3)



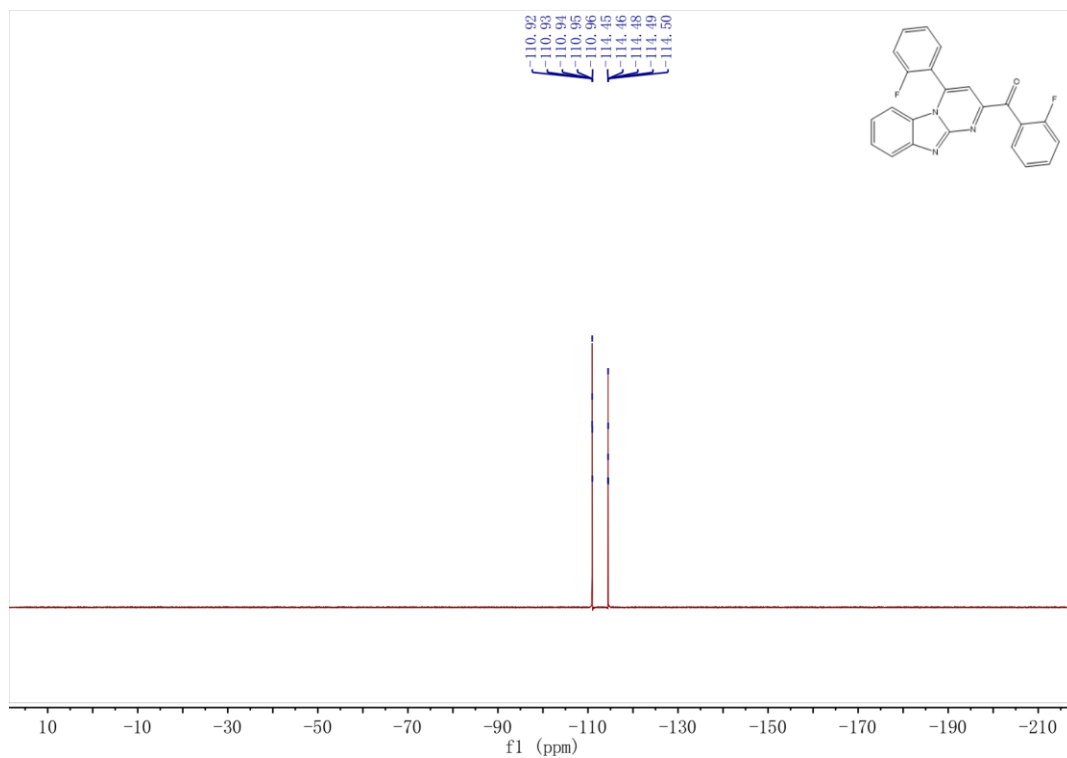
¹H NMR of Compound 3b (600MHz, DMSO-*d*₆)



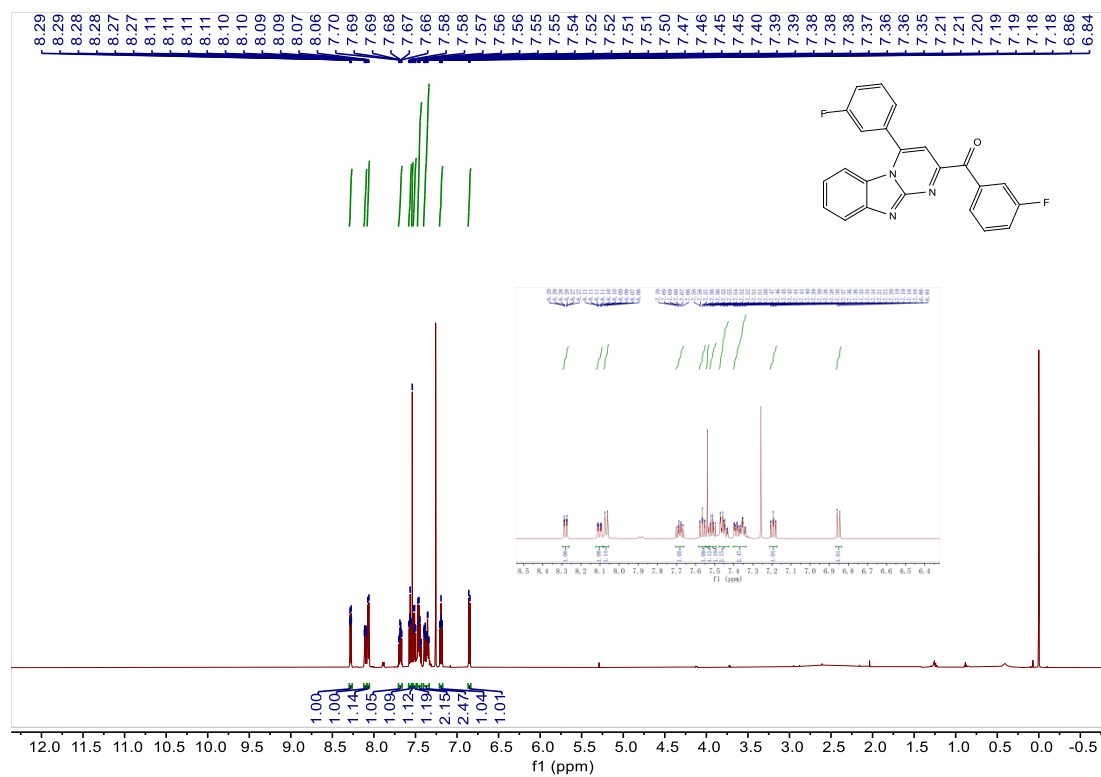
¹³C NMR of Compound 3b (151MHz, DMSO-*d*₆)



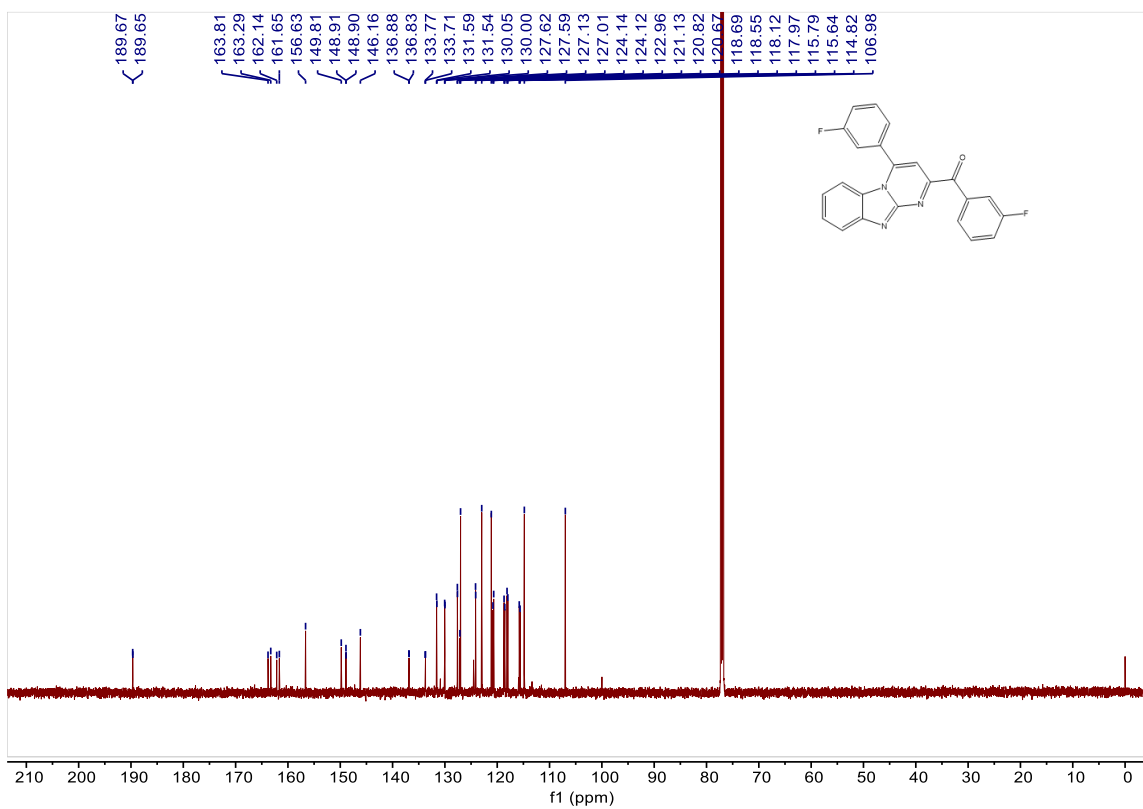
¹⁹F NMR of Compound 3b (565 MHz, DMSO-*d*₆)



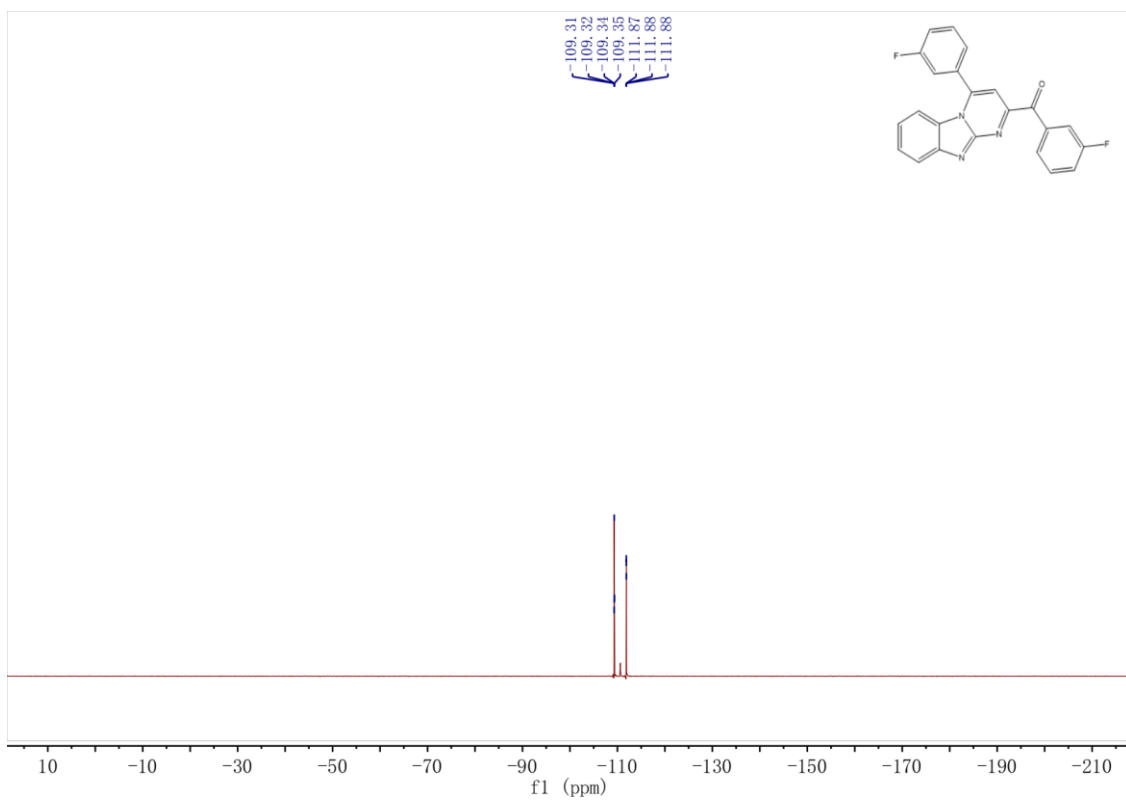
¹H NMR of Compound 3c (600MHz,CDCl₃)



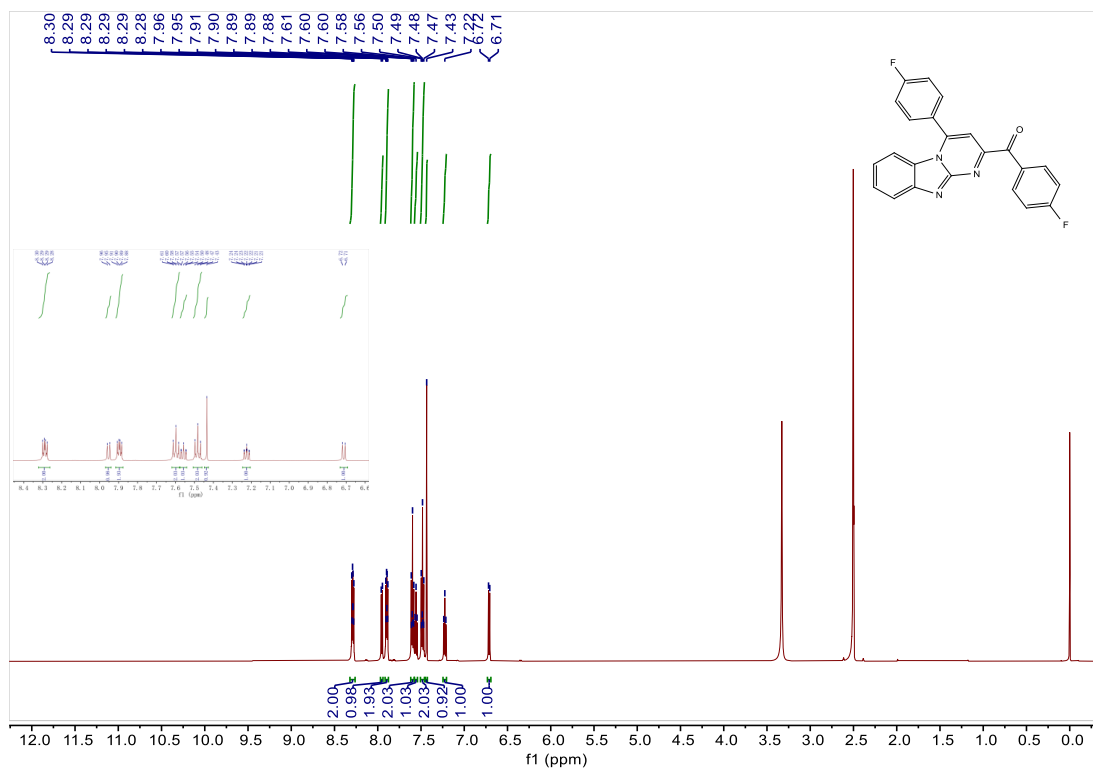
¹³C NMR of Compound 3c (151MHz,CDCl₃)



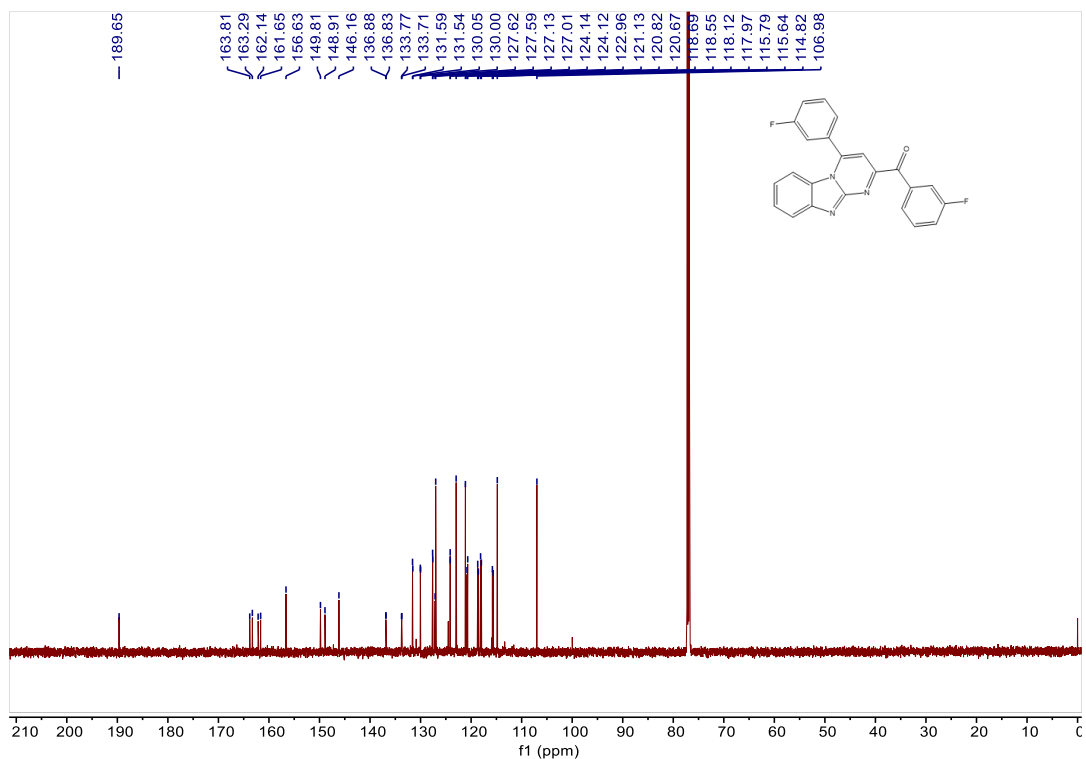
¹⁹F NMR of Compound 3c (565MHz,CDCl₃)



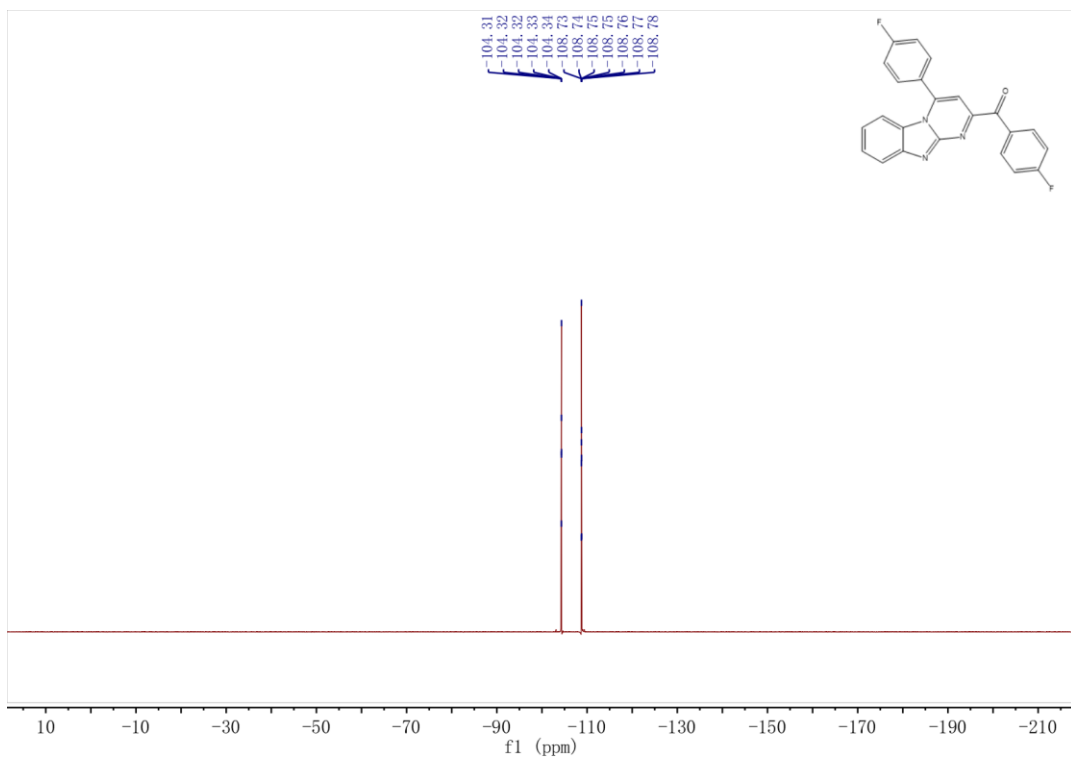
¹H NMR of Compound 3d (600MHz,DMSO-*d*₆)



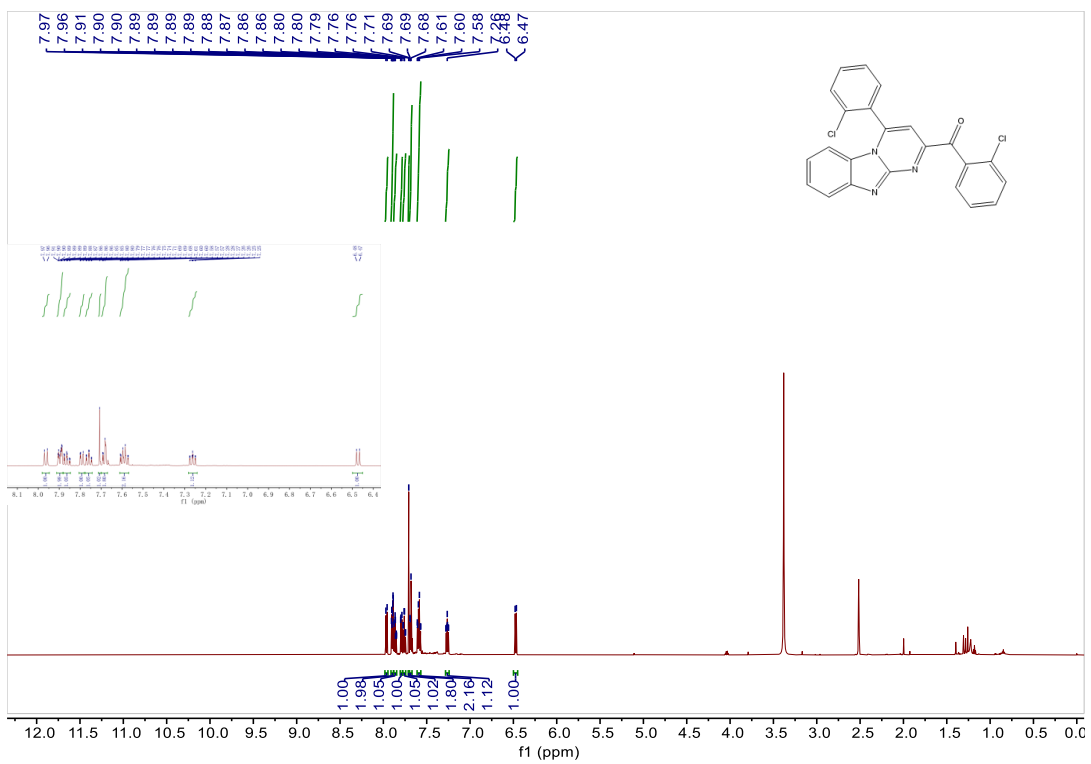
¹³C NMR of Compound 3d (151MHz,DMSO-*d*₆)



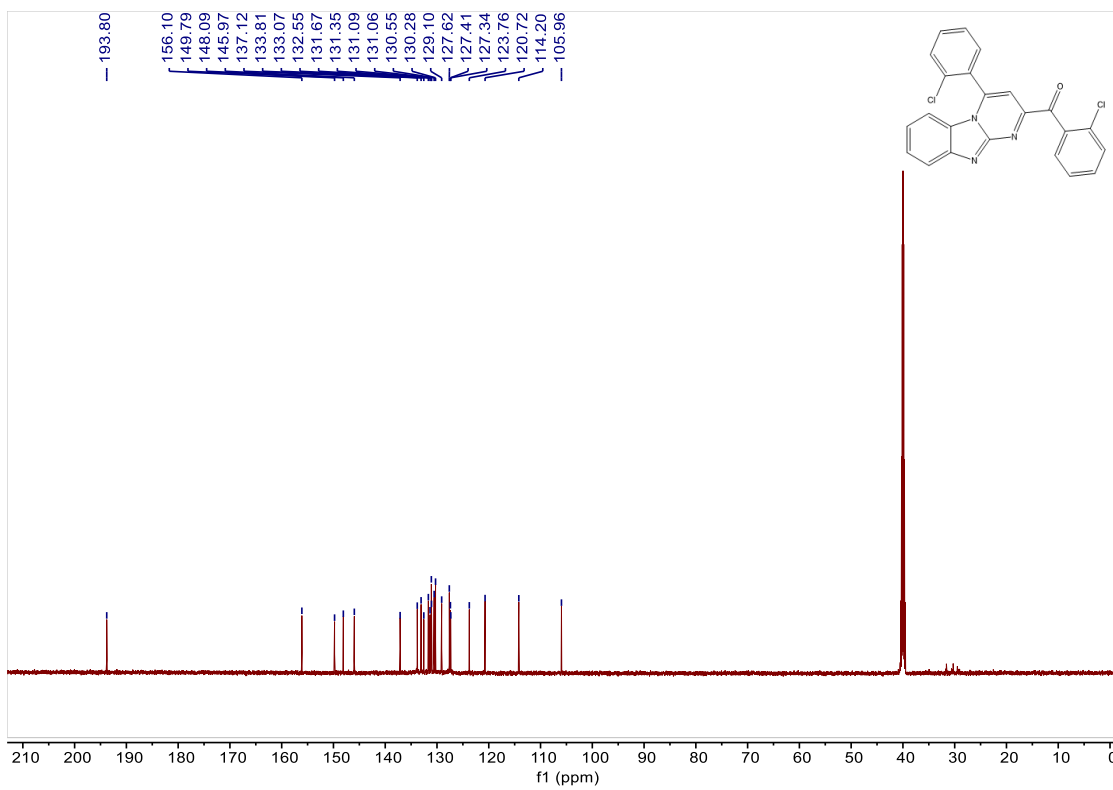
^{19}F NMR of Compound 3d (565MHz,DMSO- d_6)



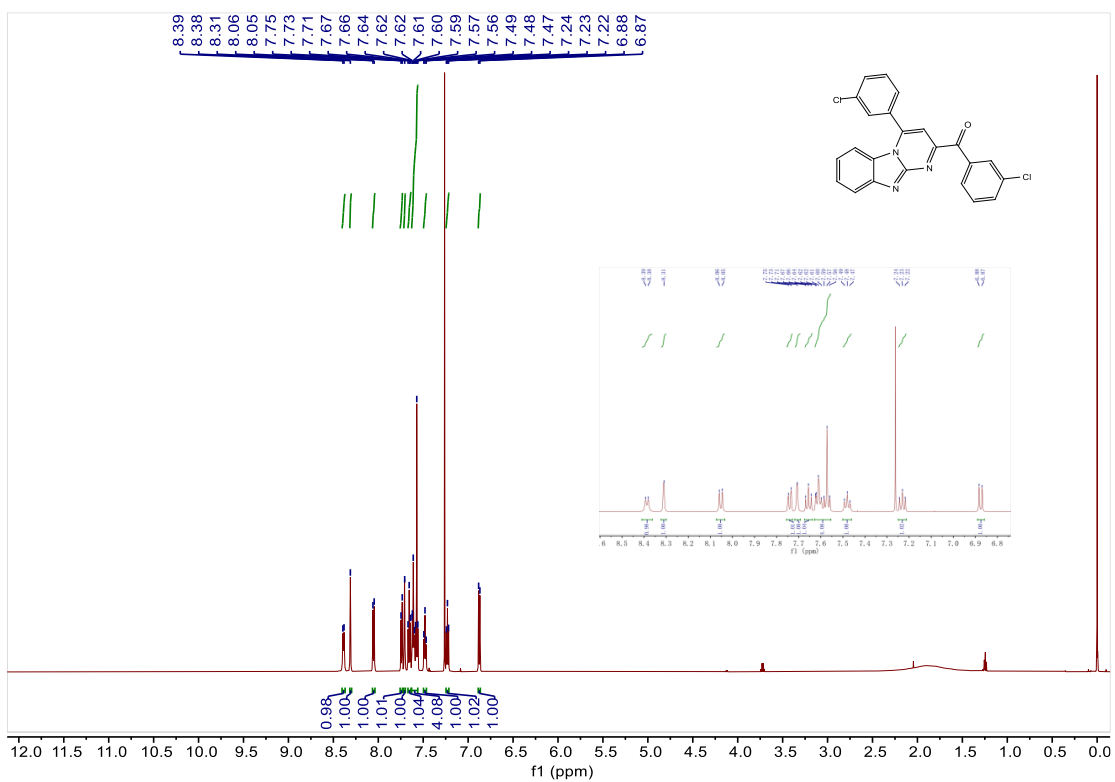
^1H NMR of Compound 3e (600MHz,DMSO- d_6)



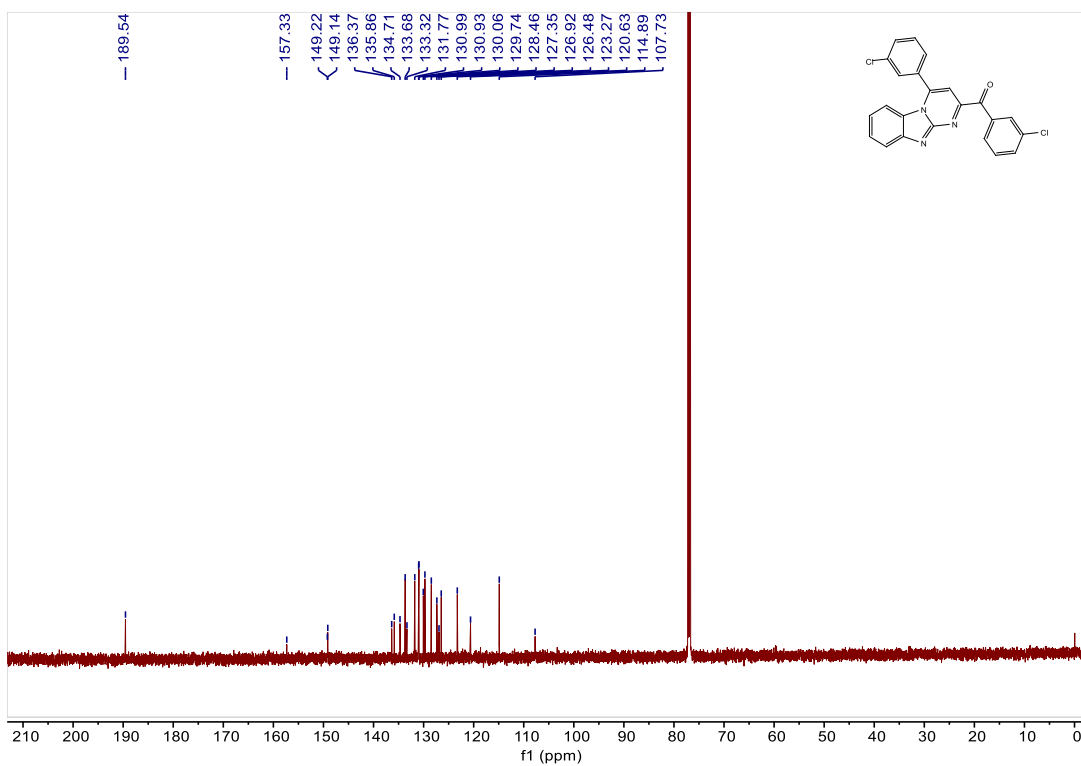
¹³C NMR of Compound 3e (151MHz,DMSO-*d*₆)



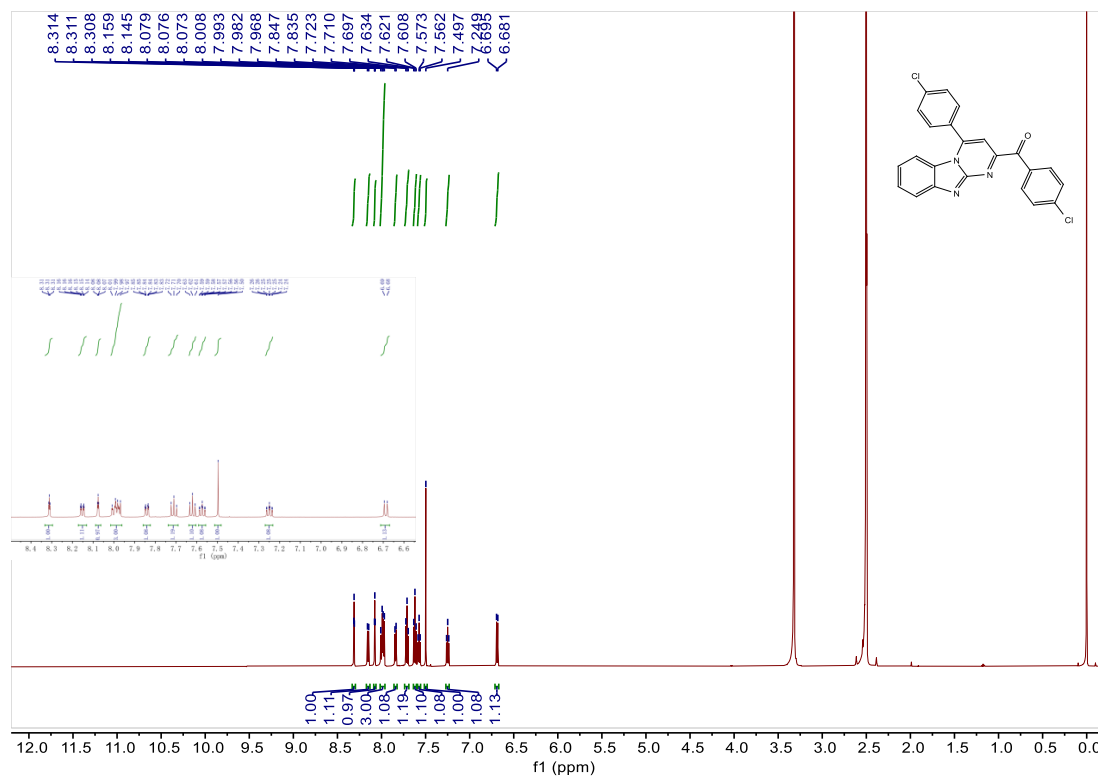
¹H NMR of Compound 3f (600MHz,CDCl₃)



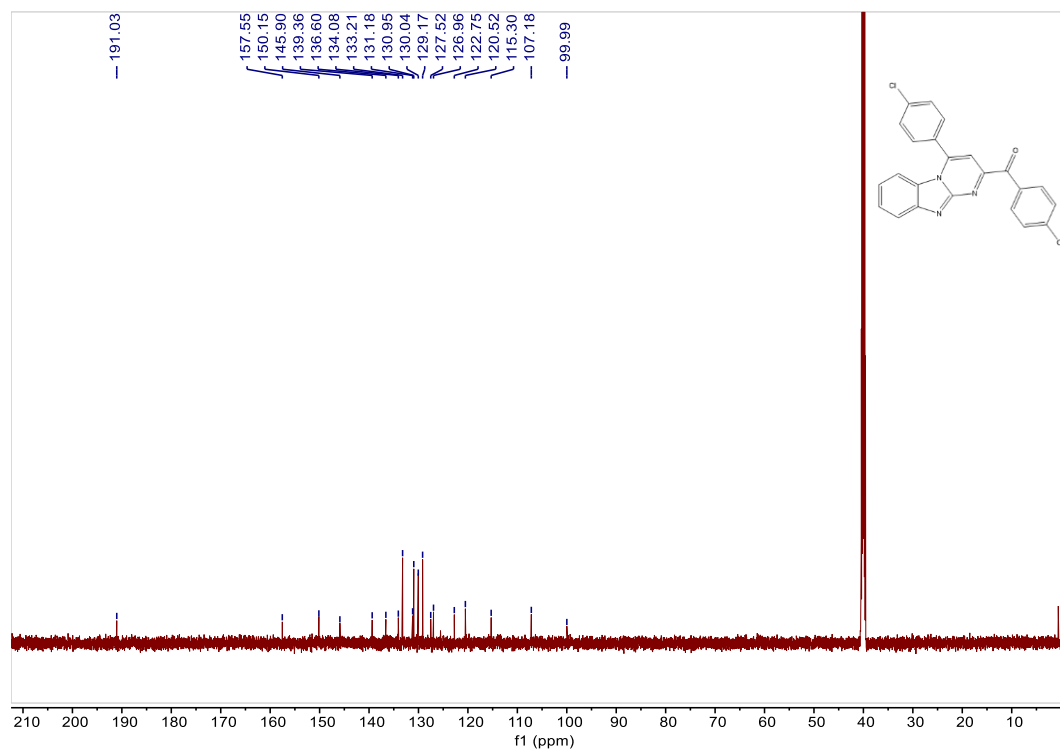
¹³C NMR of Compound 3f (151MHz, CDCl₃)



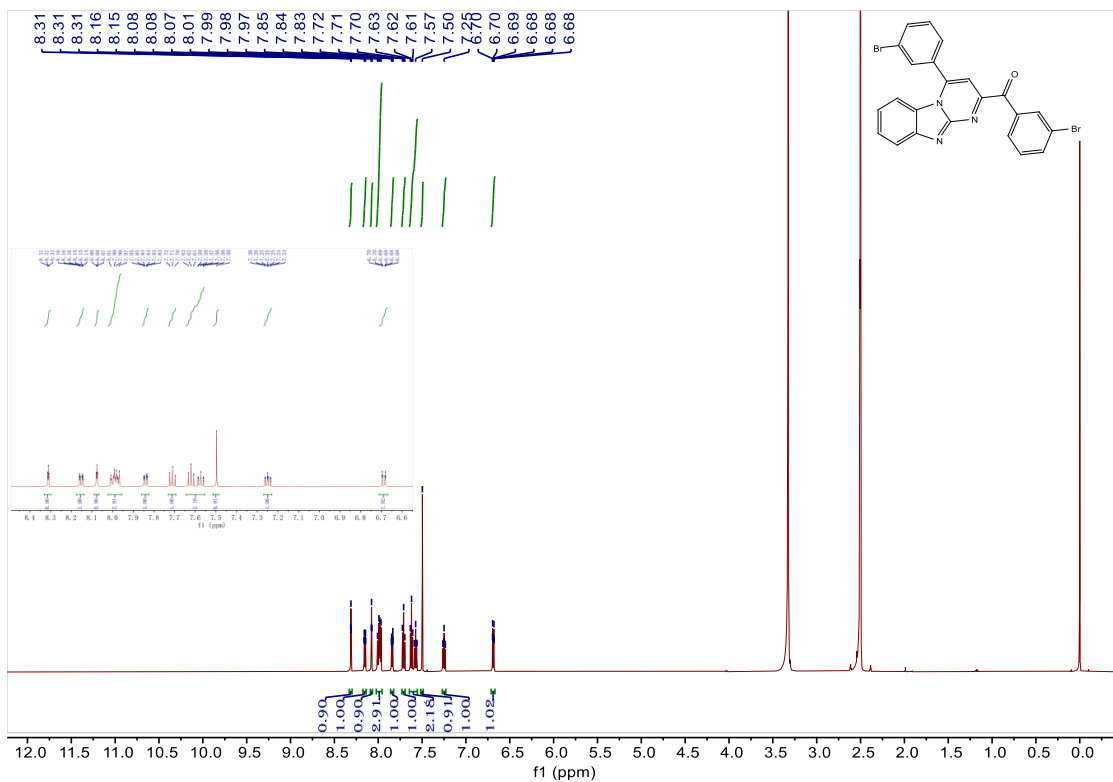
¹H NMR of Compound 3g (600MHz,DMSO-*d*₆)



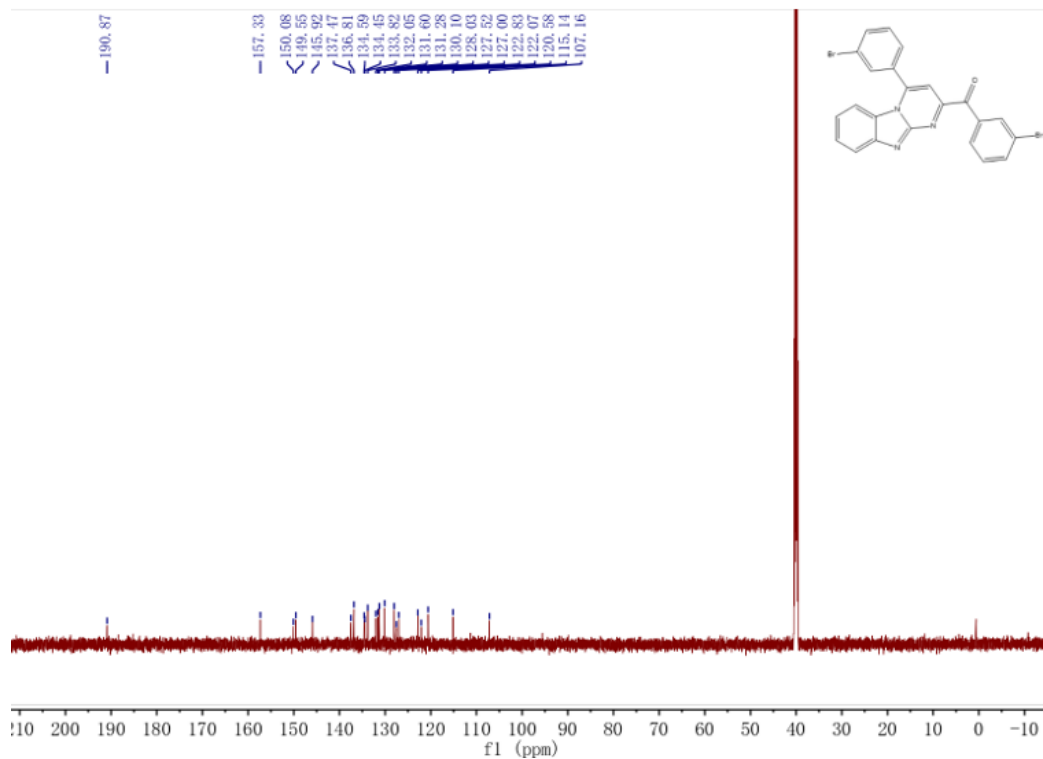
¹³C NMR of Compound 3g (151MHz,DMSO-*d*₆)



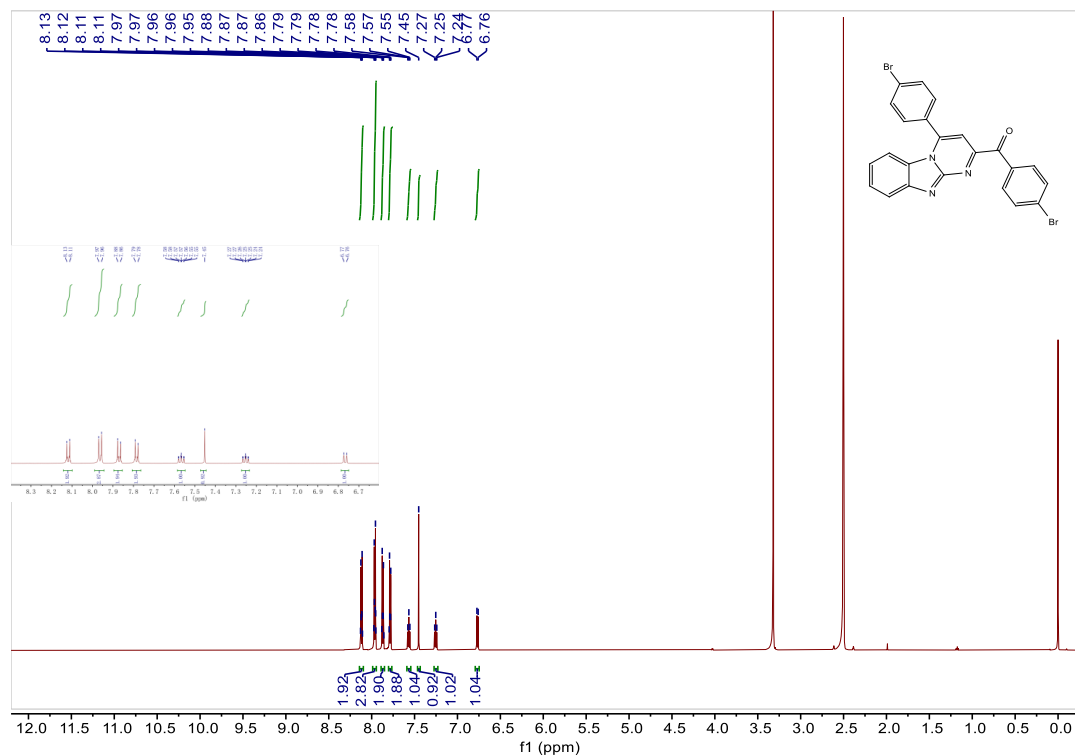
¹H NMR of Compound 3h (600MHz,DMSO-*d*₆)



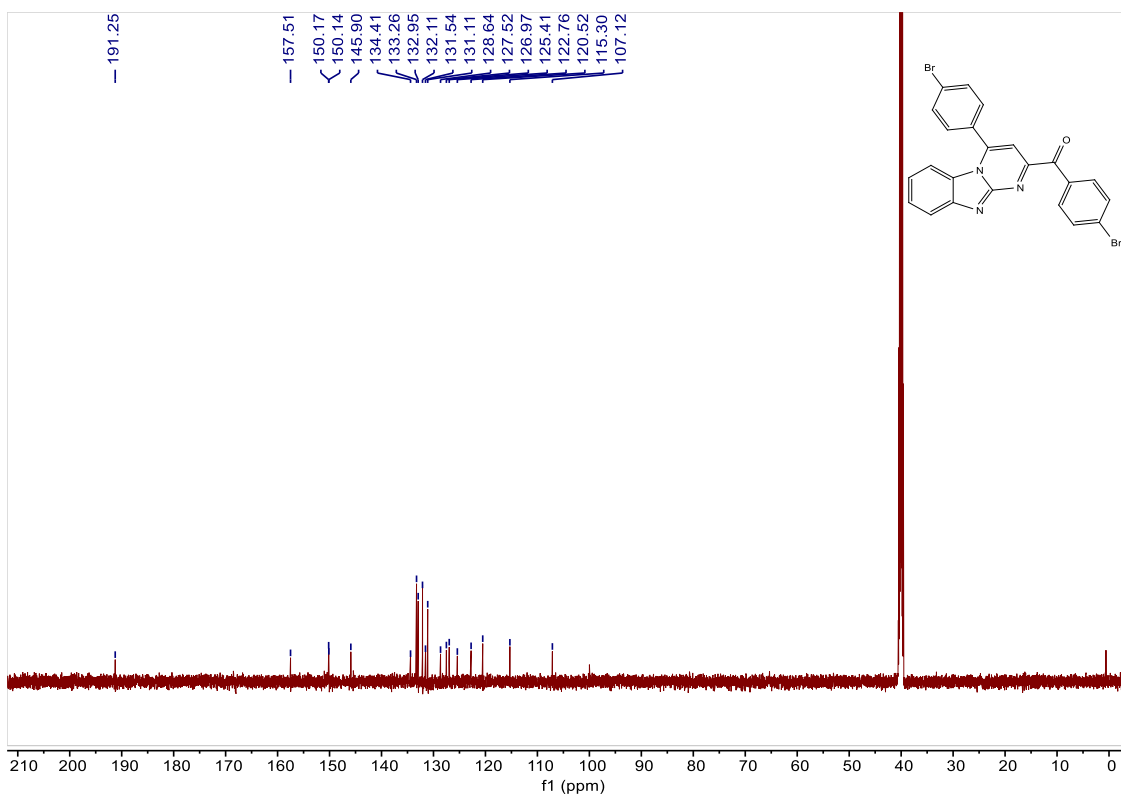
¹³C NMR of Compound 3h (151MHz,DMSO-*d*₆)



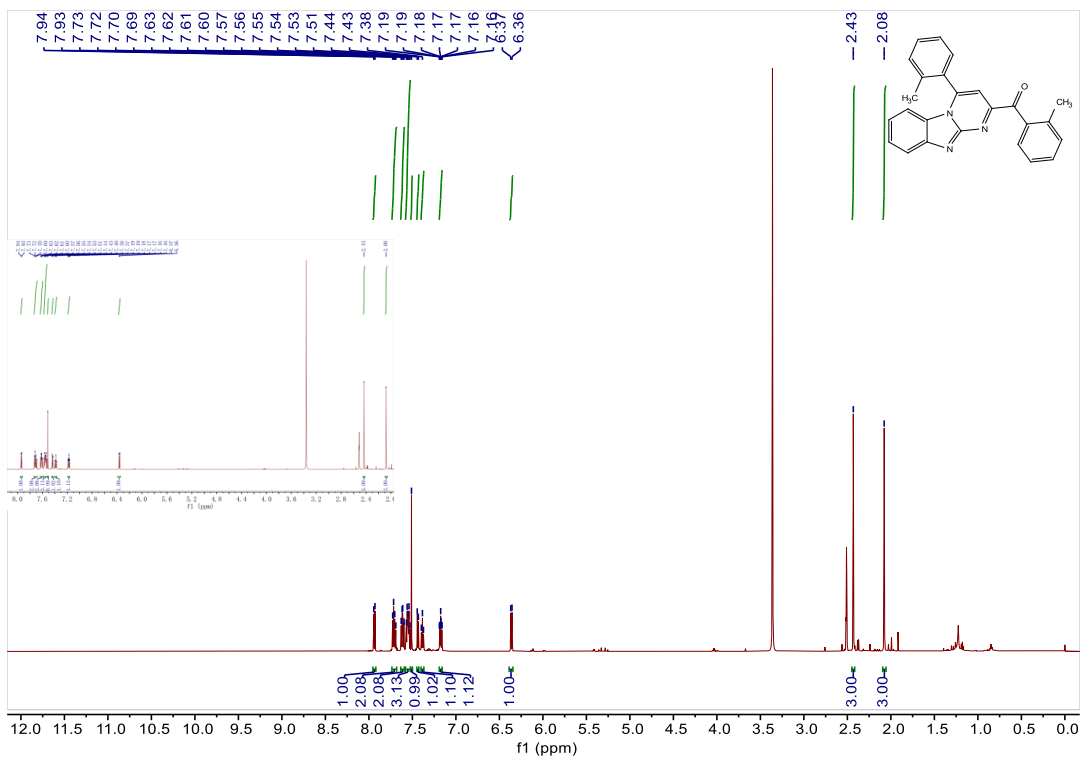
¹H NMR of Compound 3i (600MHz, DMSO-*d*₆)



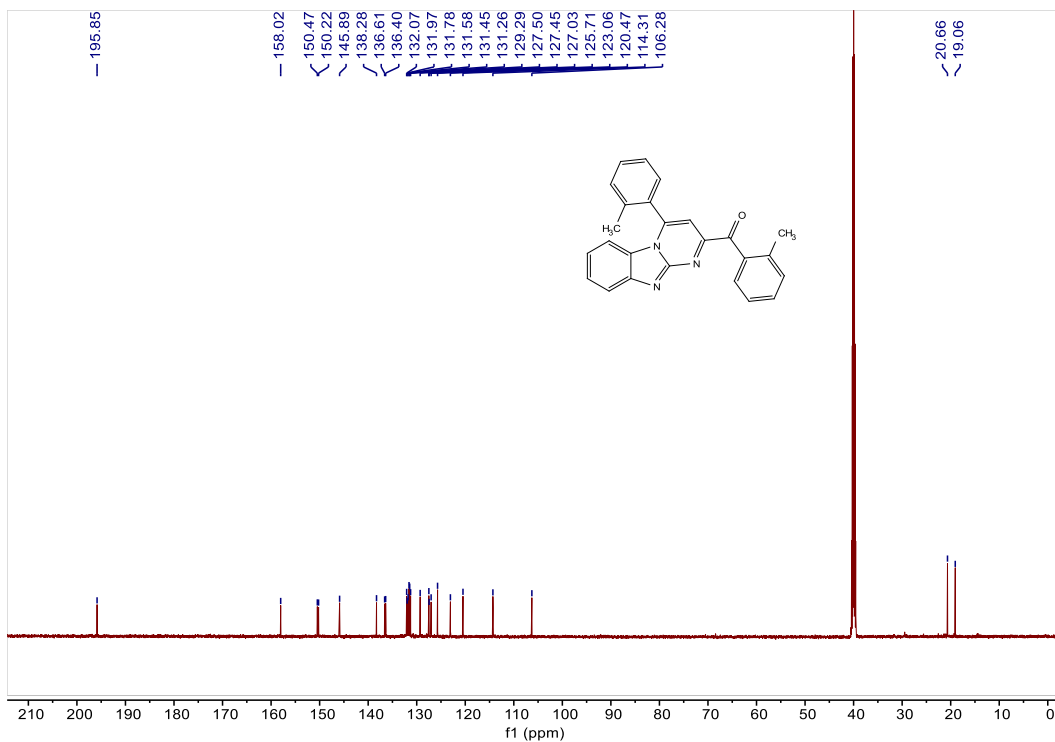
¹³C NMR of Compound 3i (151MHz, DMSO-*d*₆)



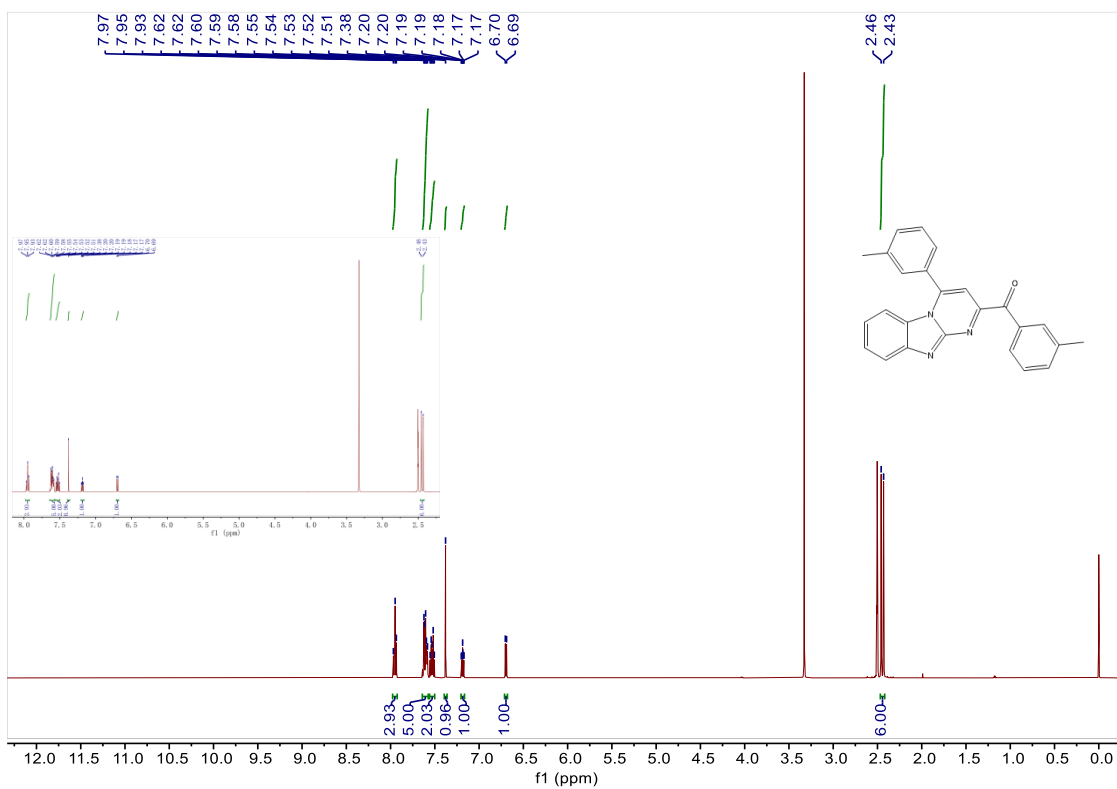
¹H NMR of Compound 3j (600MHz,DMSO-*d*₆)



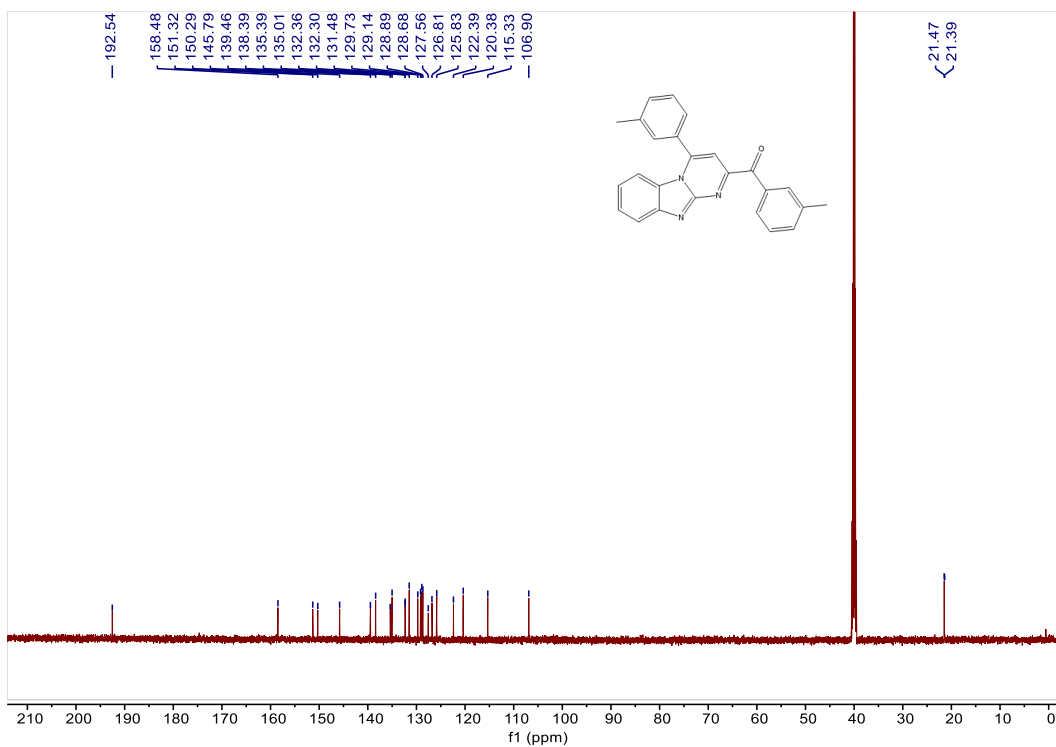
¹³C NMR of Compound 3j (151MHz,DMSO-*d*₆)



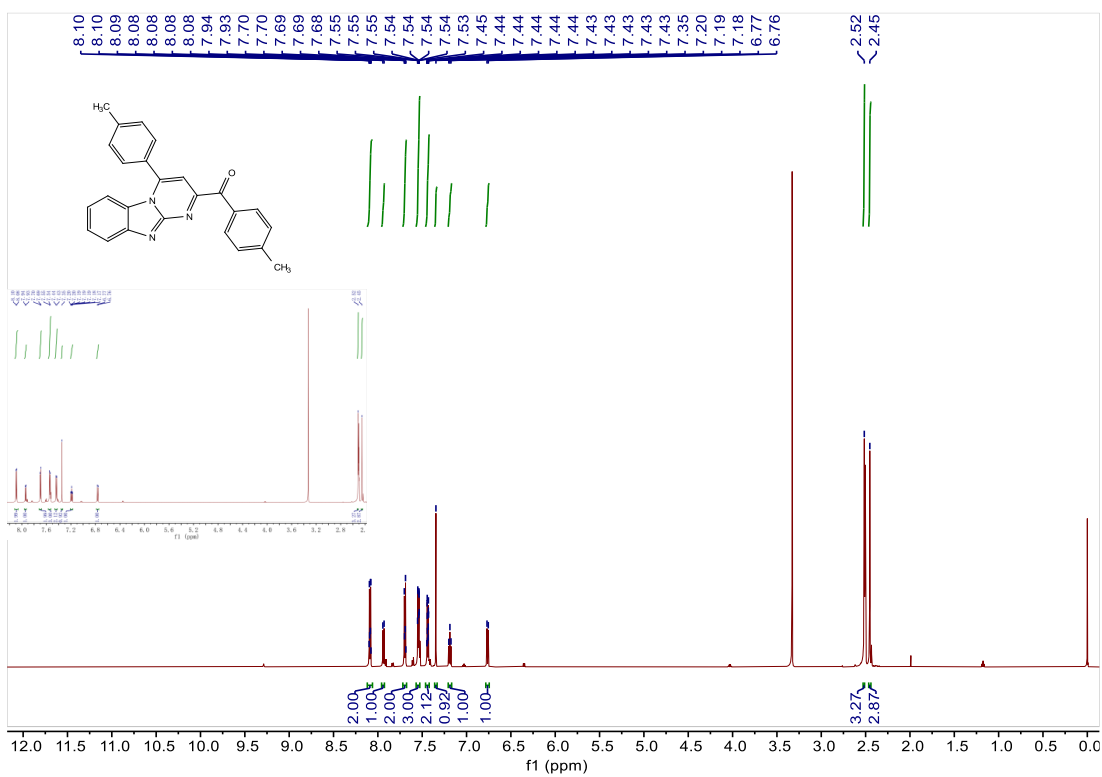
¹H NMR of Compound 3k (600MHz,DMSO-*d*₆)



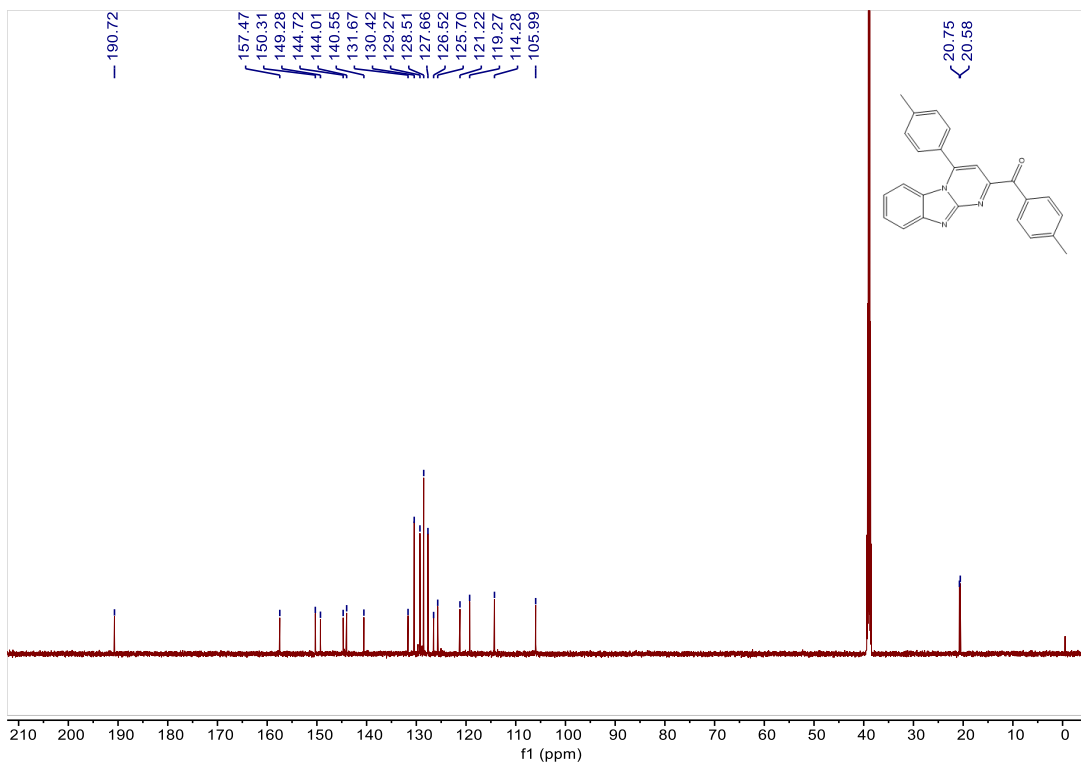
¹³C NMR of Compound 3k (151MHz,DMSO-*d*₆)



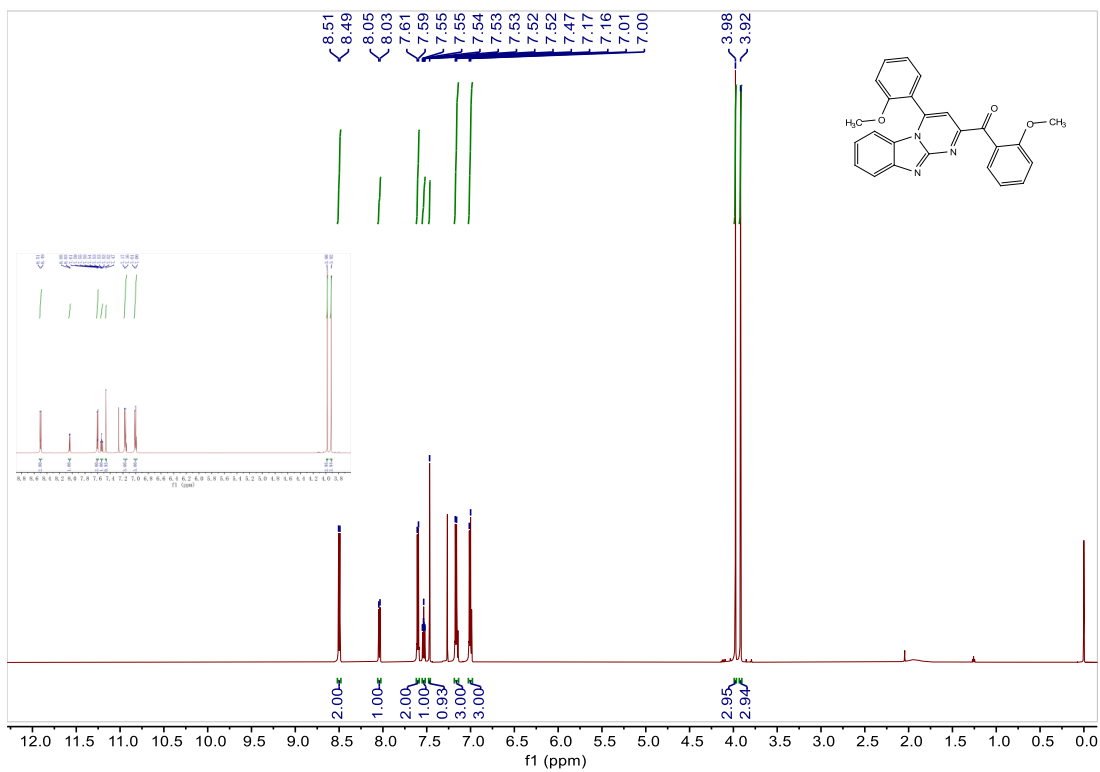
¹H NMR of Compound 3I (600MHz,DMSO-*d*₆)



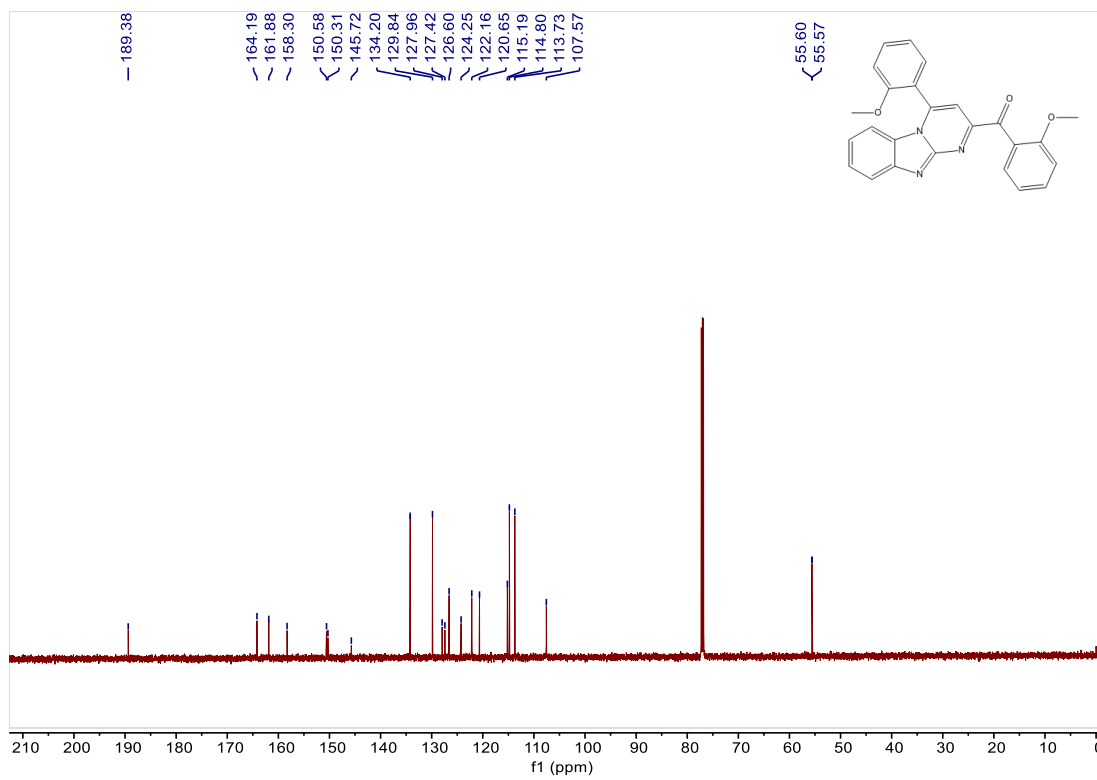
¹³C NMR of Compound 3I (151MHz,DMSO-*d*₆)



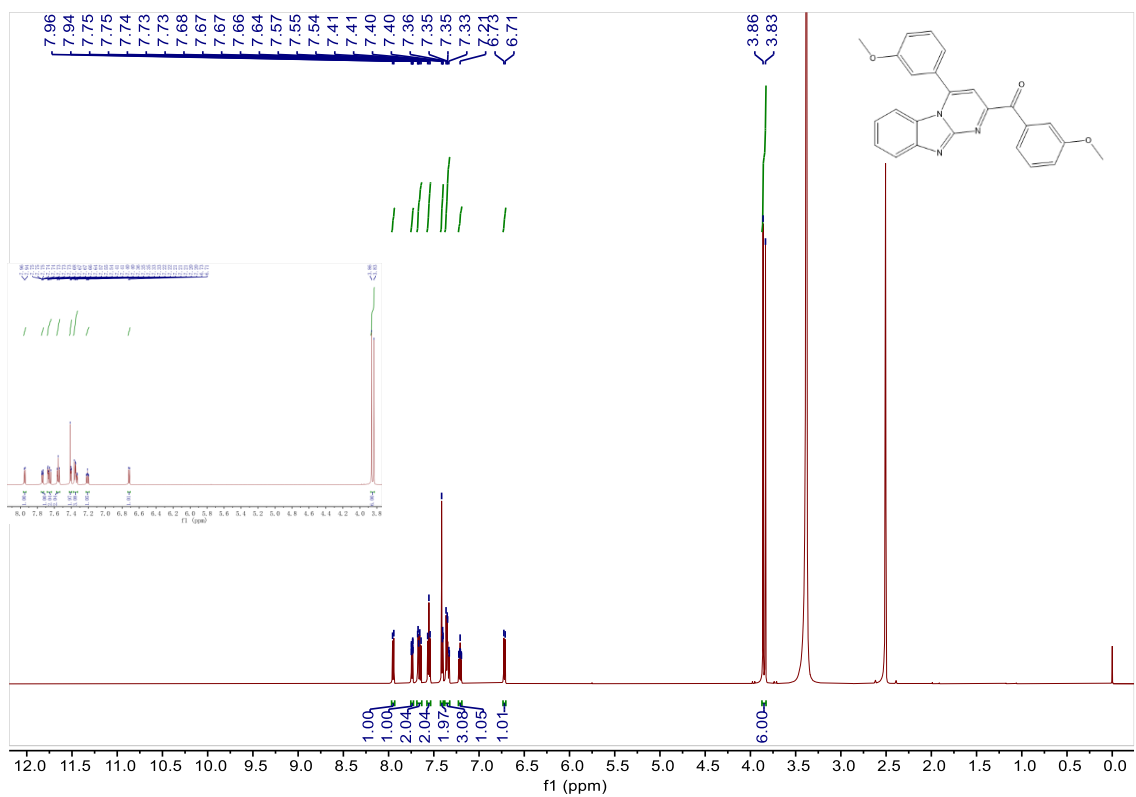
¹H NMR of Compound 3m (600MHz,CDCl₃)



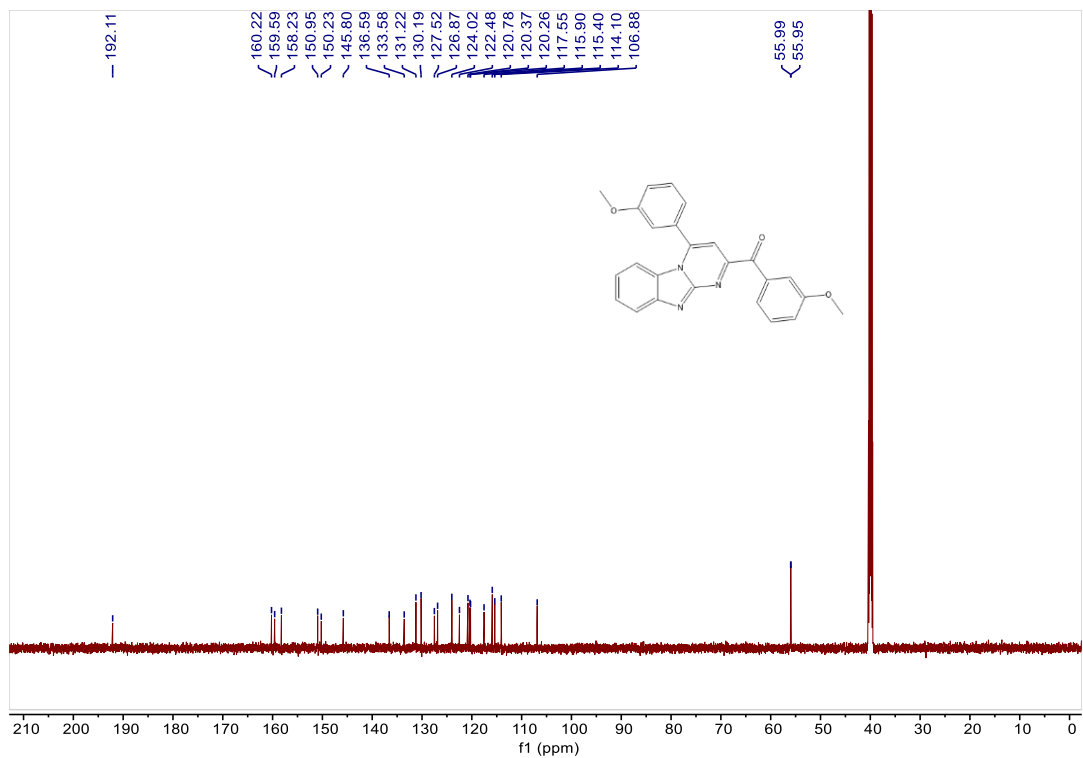
^{13}C NMR of Compound 3m (151MHz, CDCl_3)



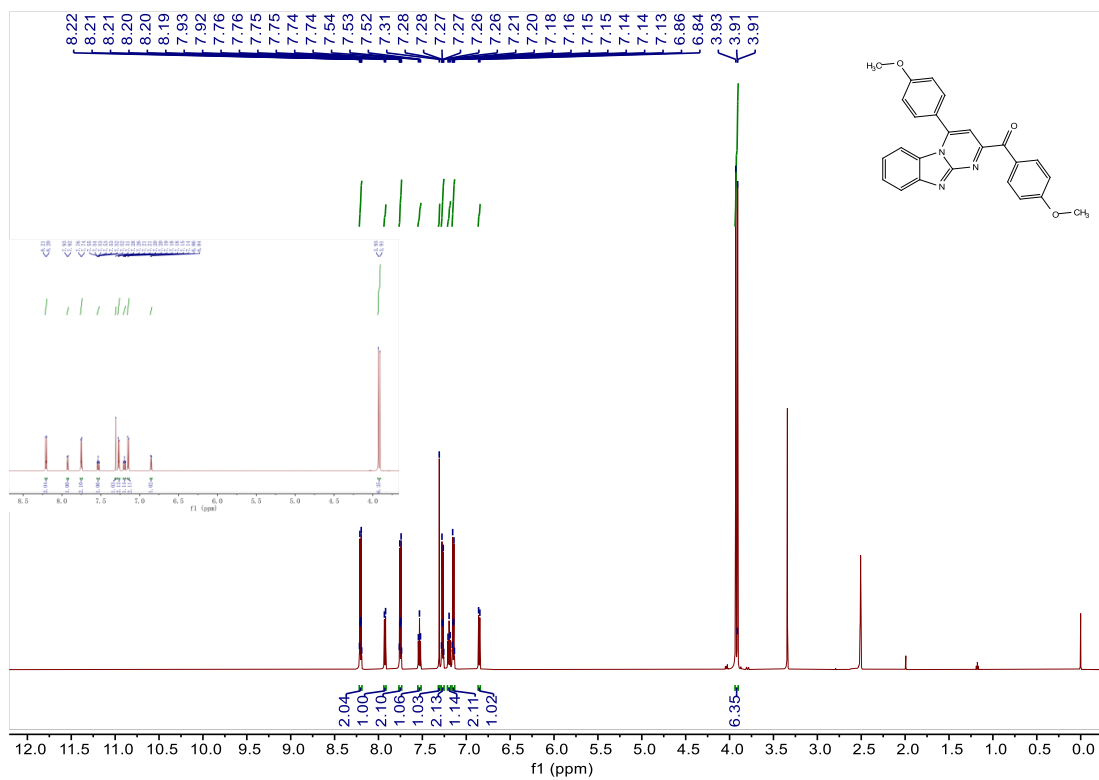
^1H NMR of Compound 3n (600MHz, $\text{DMSO}-d_6$)



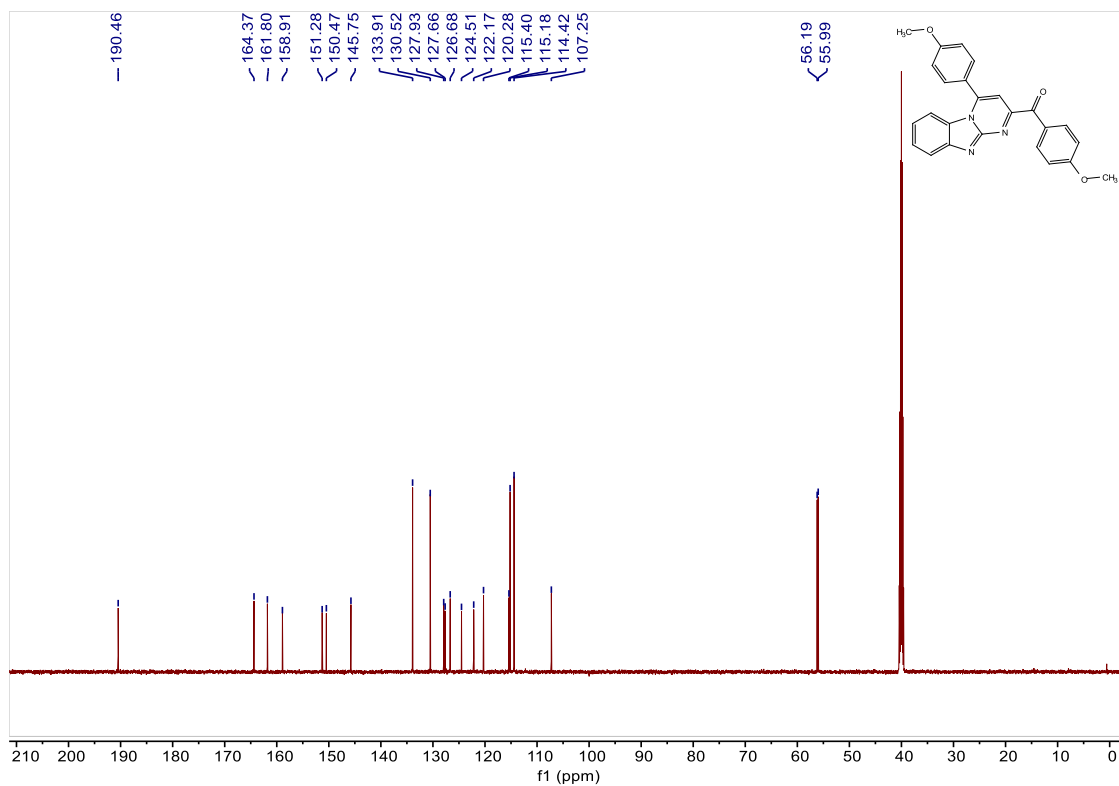
¹³C NMR of Compound 3n (151MHz, DMSO-*d*₆)



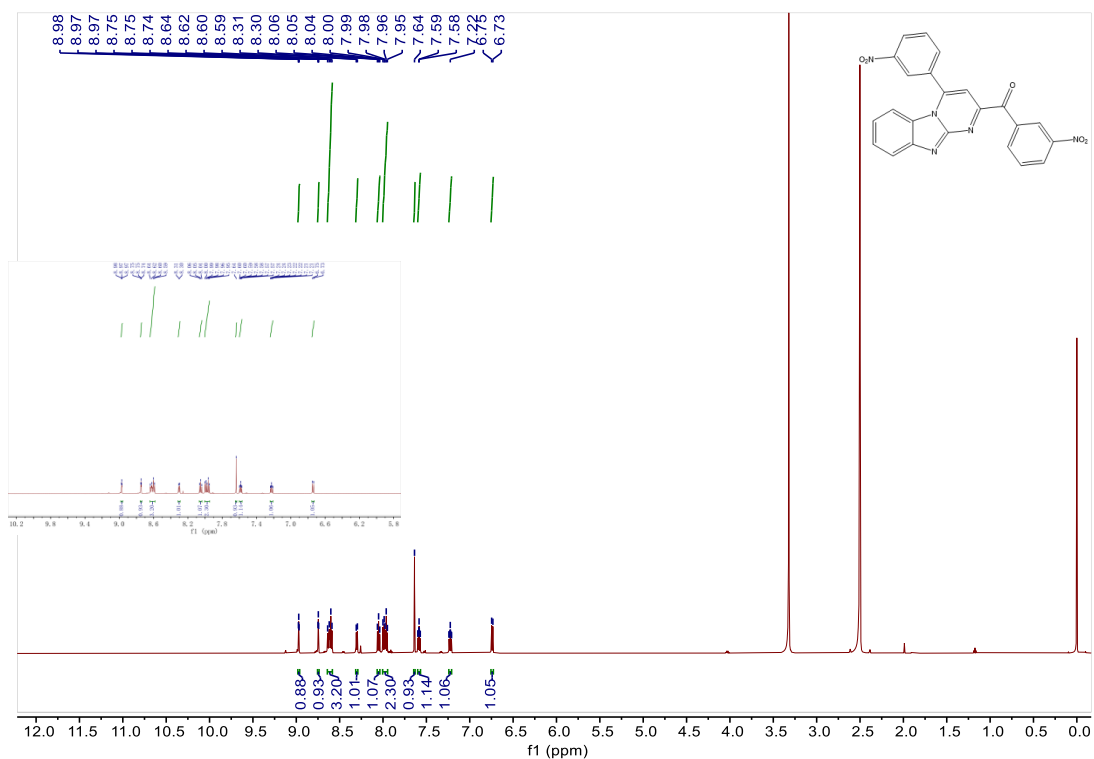
¹H NMR of Compound 3o (600MHz, DMSO-*d*₆)



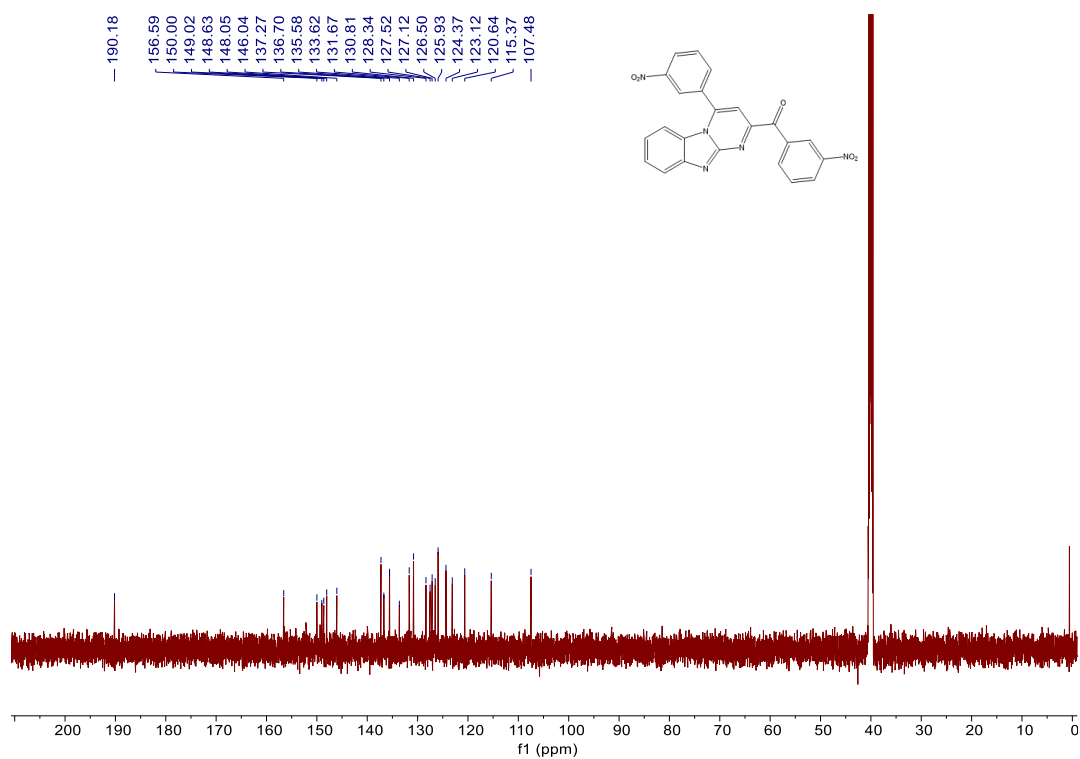
¹³C NMR of Compound 3o (151 MHz, DMSO-*d*₆)



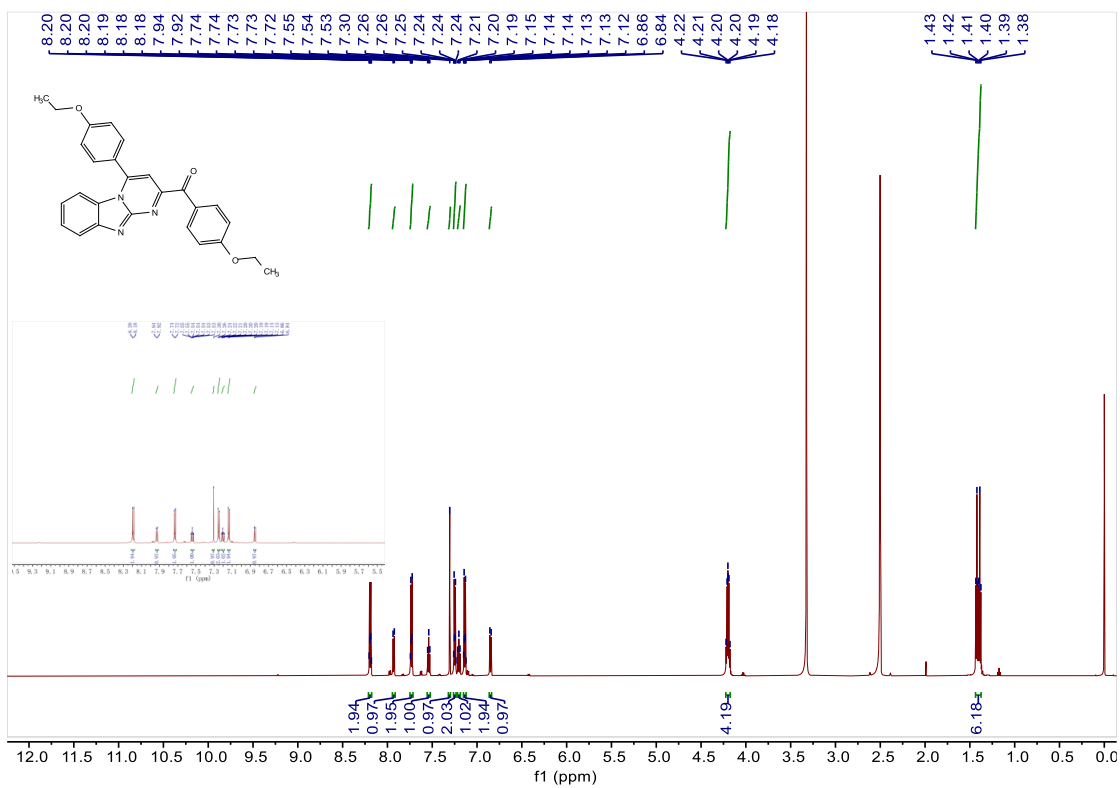
¹H NMR of Compound 3p (600MHz,DMSO-*d*₆)



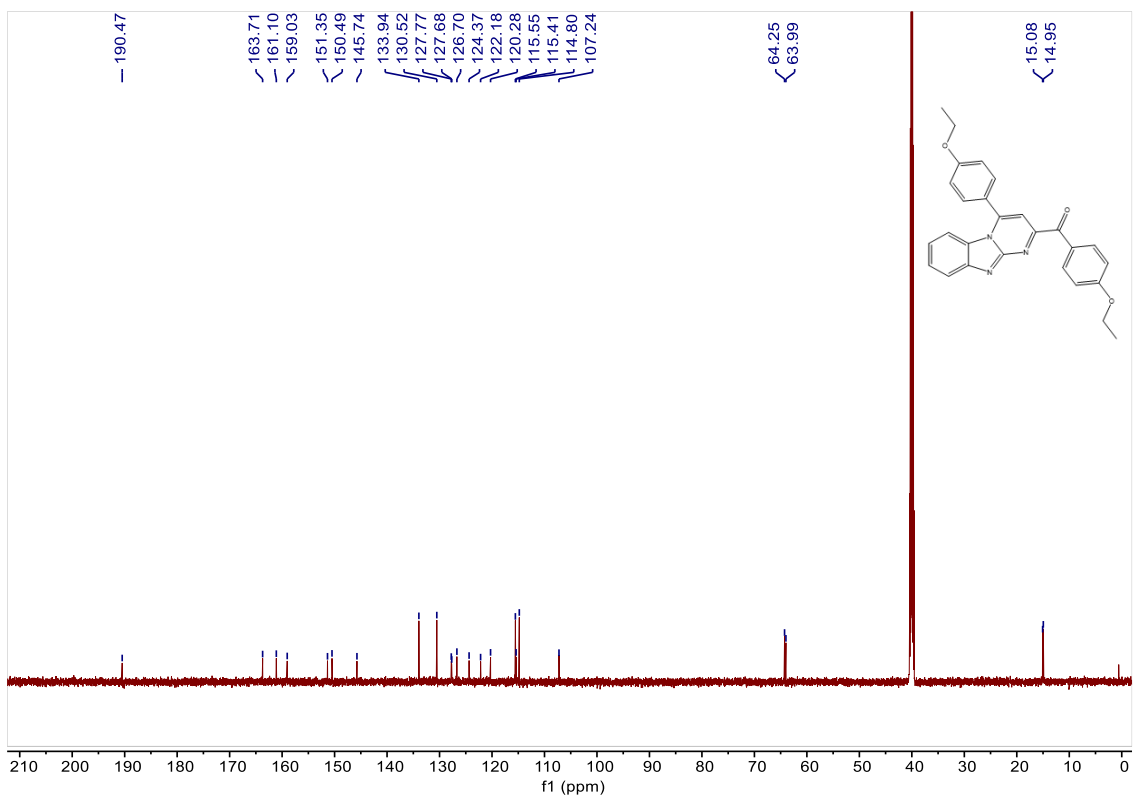
¹³C NMR of Compound 3p (151MHz,DMSO-*d*₆)



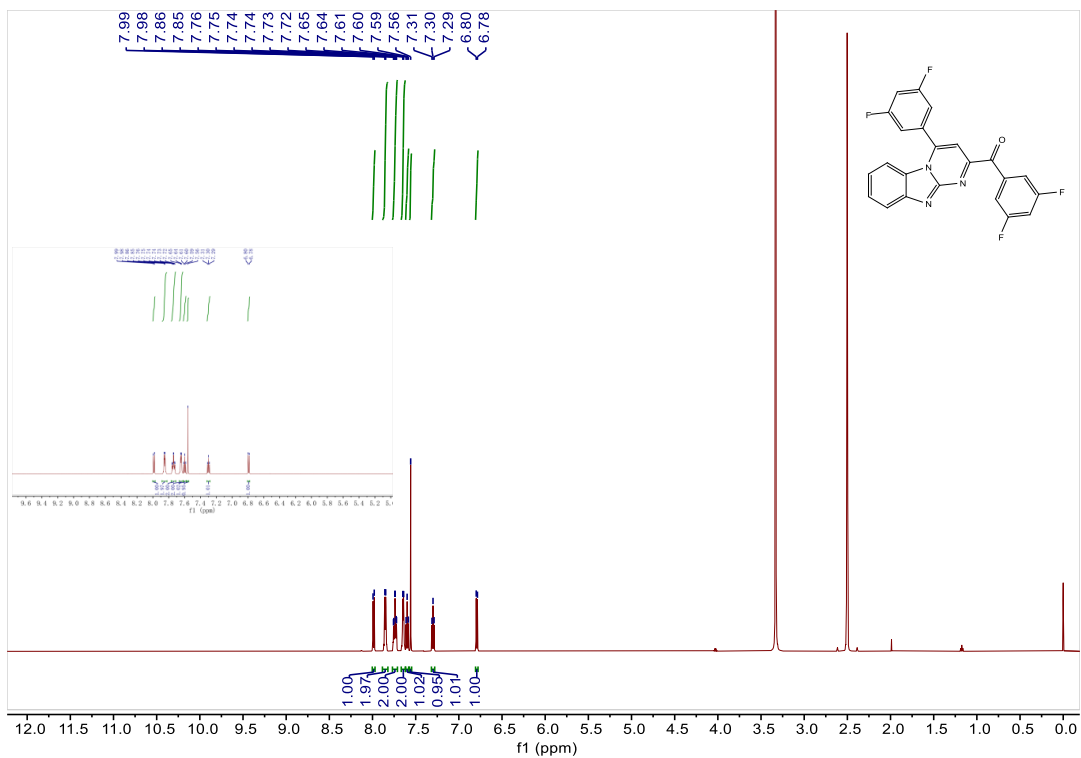
¹H NMR of Compound 3q (600MHz,DMSO-*d*₆)



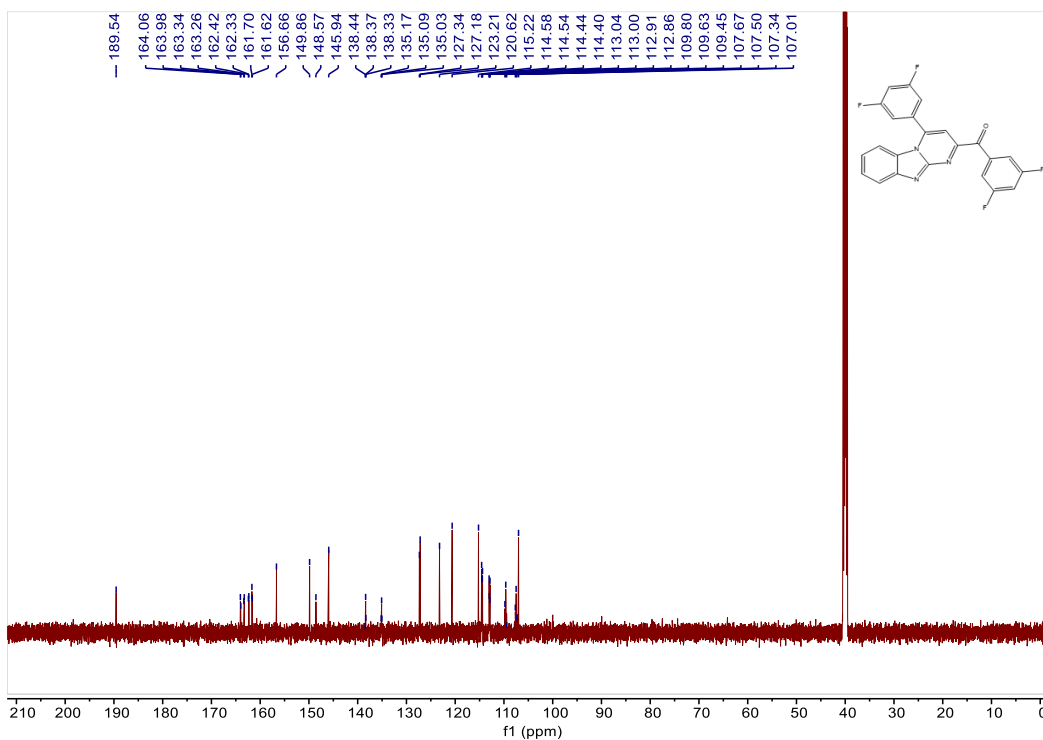
¹³C NMR of Compound 3q (151MHz,DMSO-*d*₆)



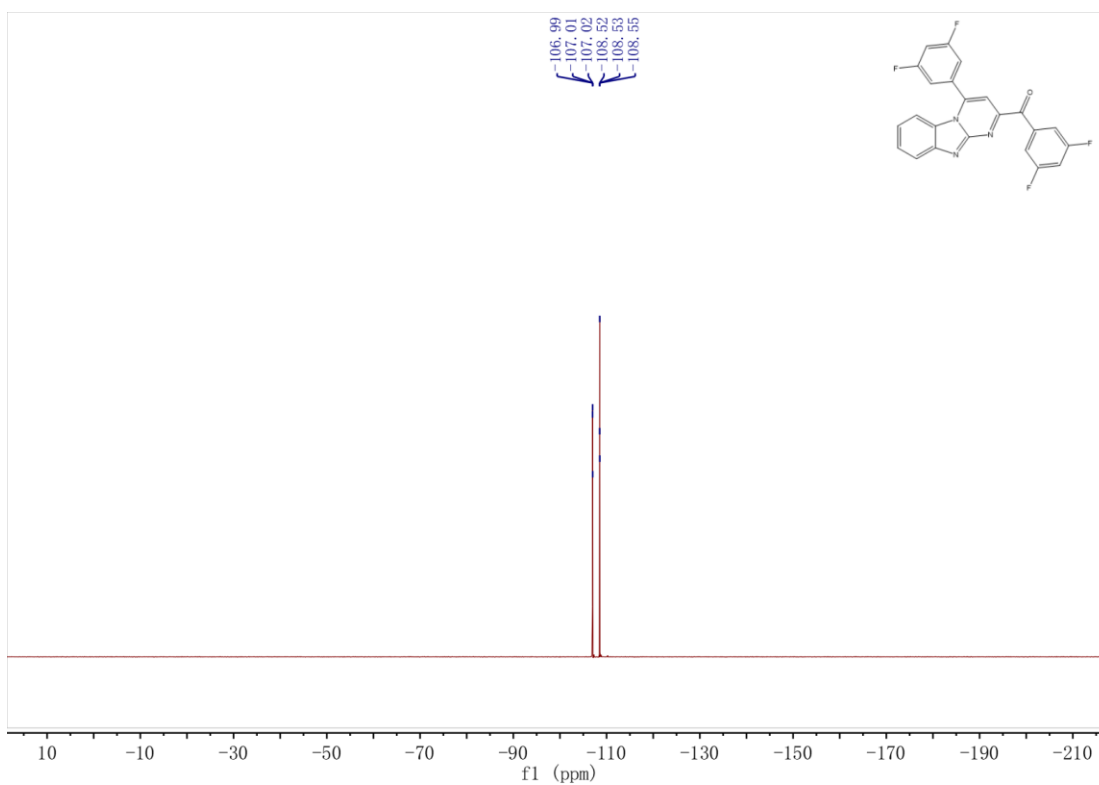
¹H NMR of Compound 3r (600MHz, DMSO-*d*₆)

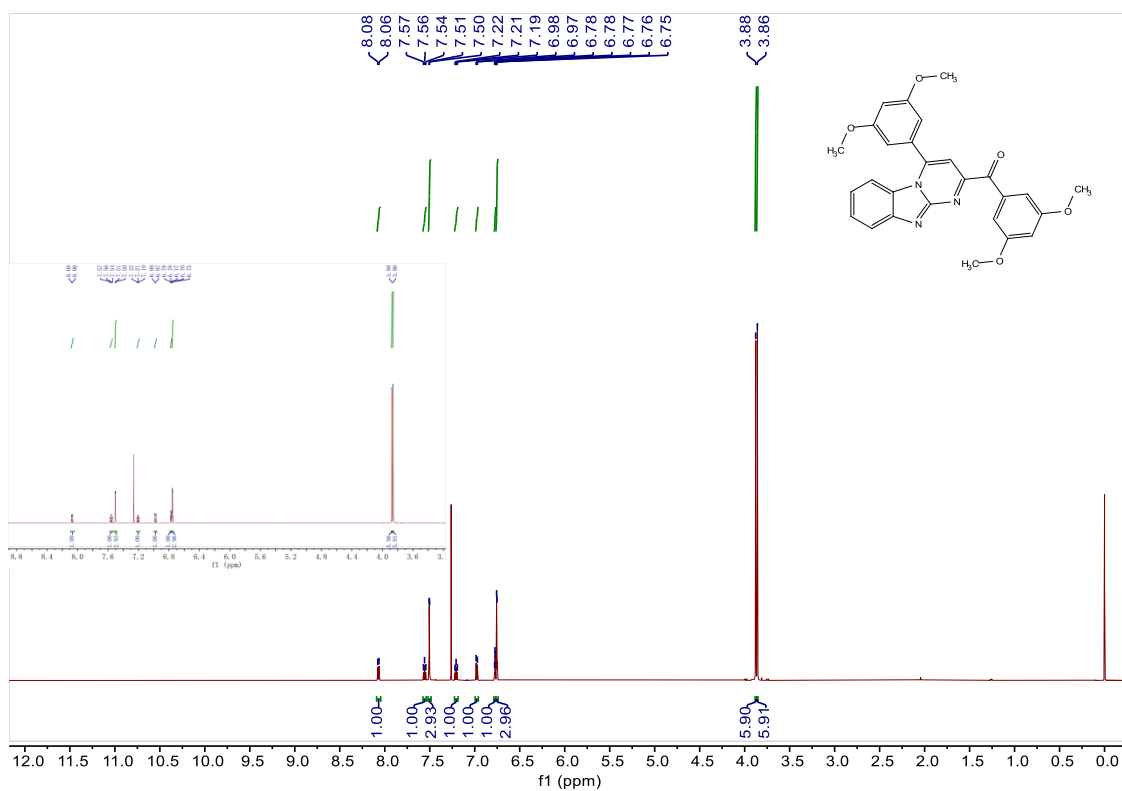


¹³C NMR of Compound 3r (151MHz, DMSO-*d*₆)

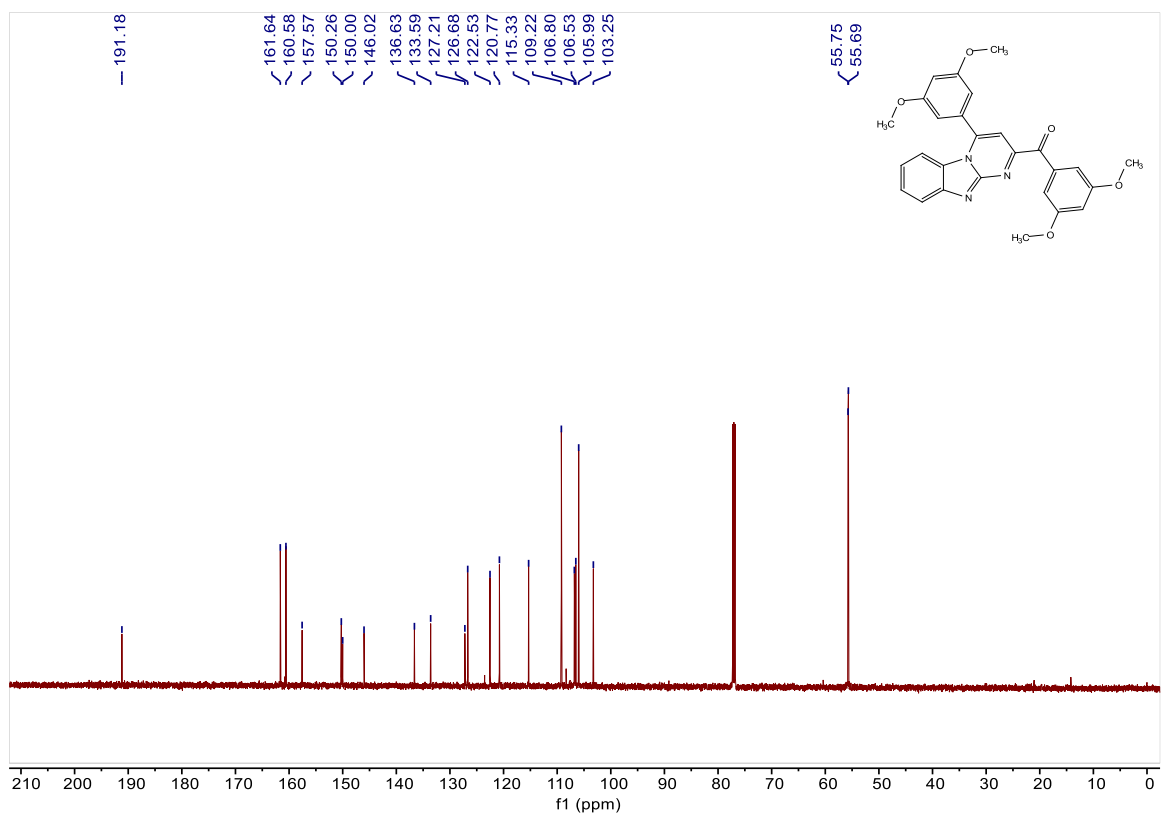


¹⁹F NMR of Compound 3r (565MHz,DMSO-*d*₆)

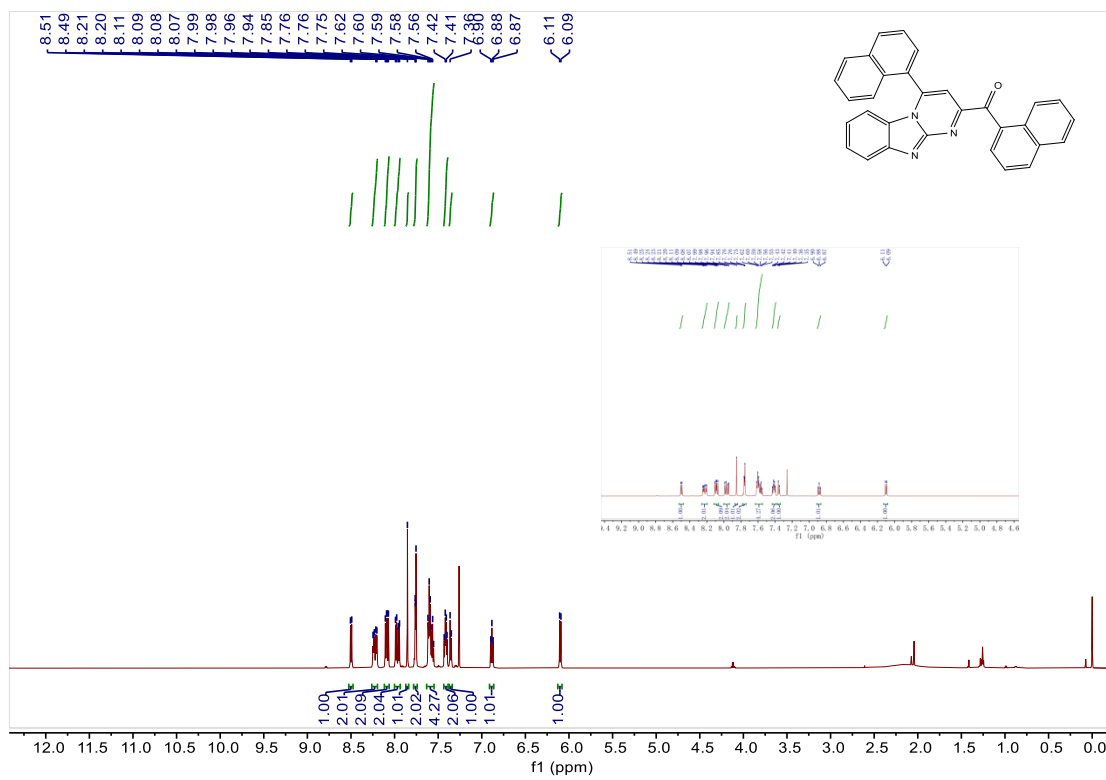




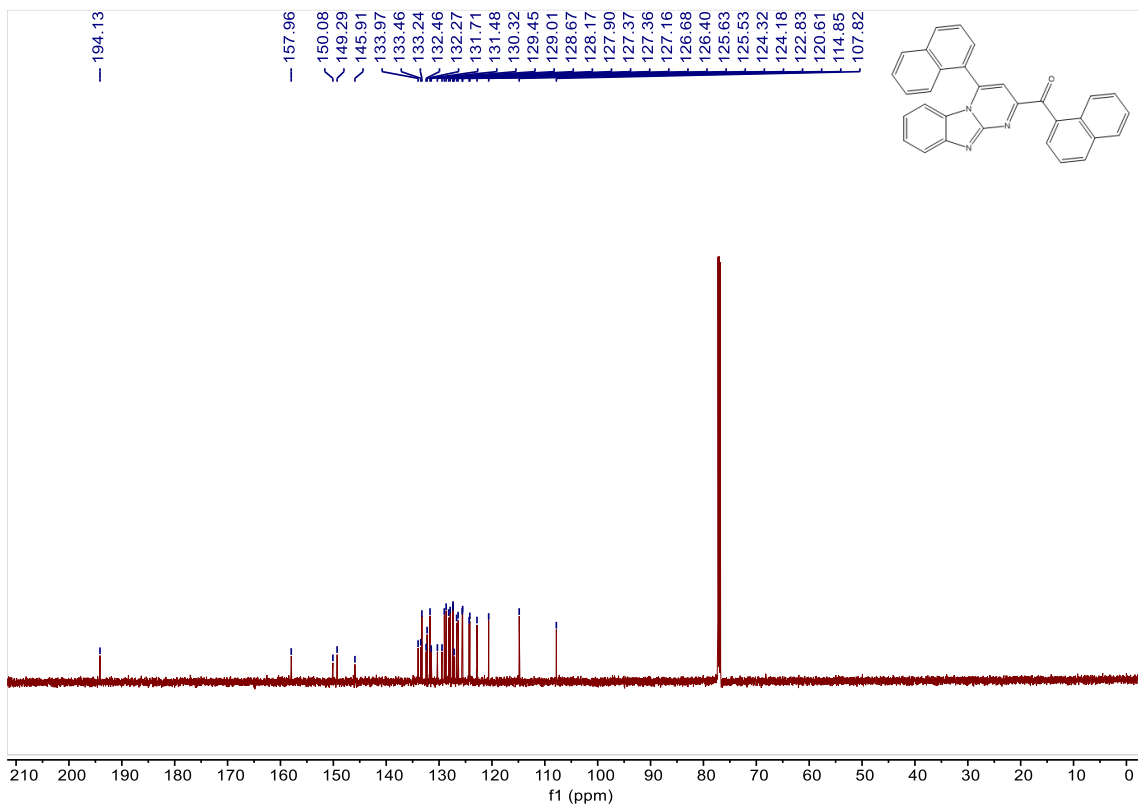
¹³C NMR of Compound 3s (151 MHz, CDCl₃)



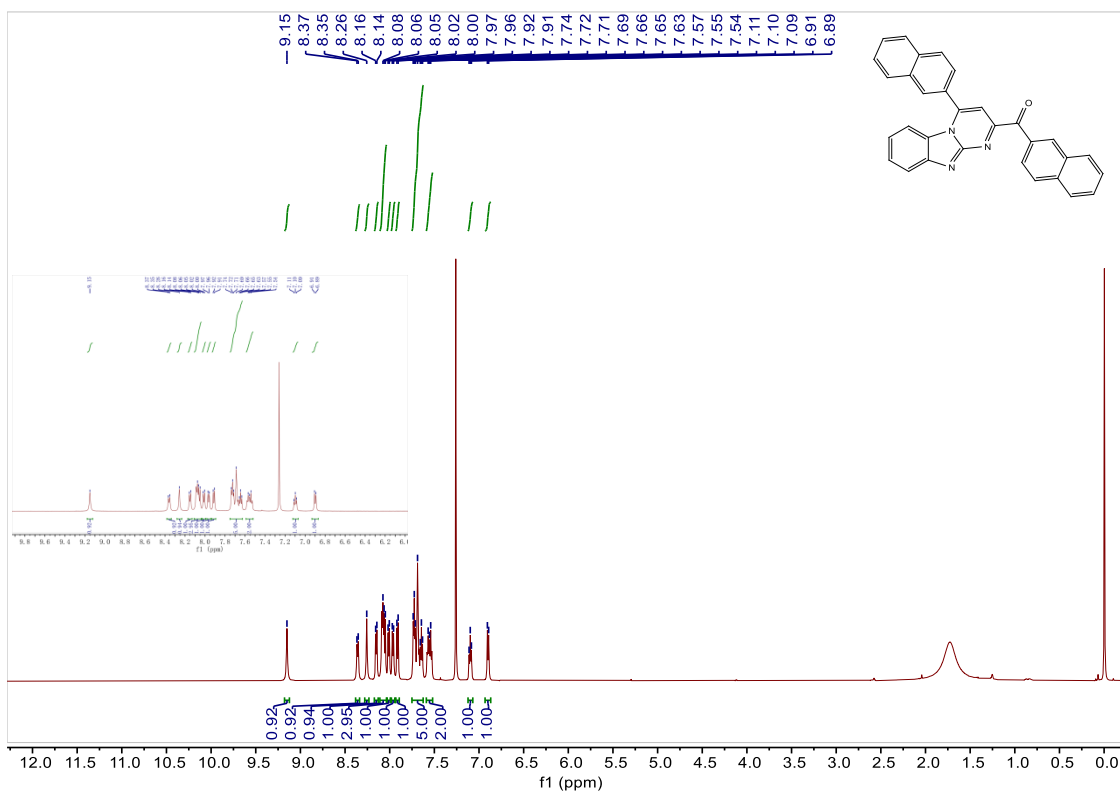
¹H NMR of Compound 3t (600MHz,CDCl₃)



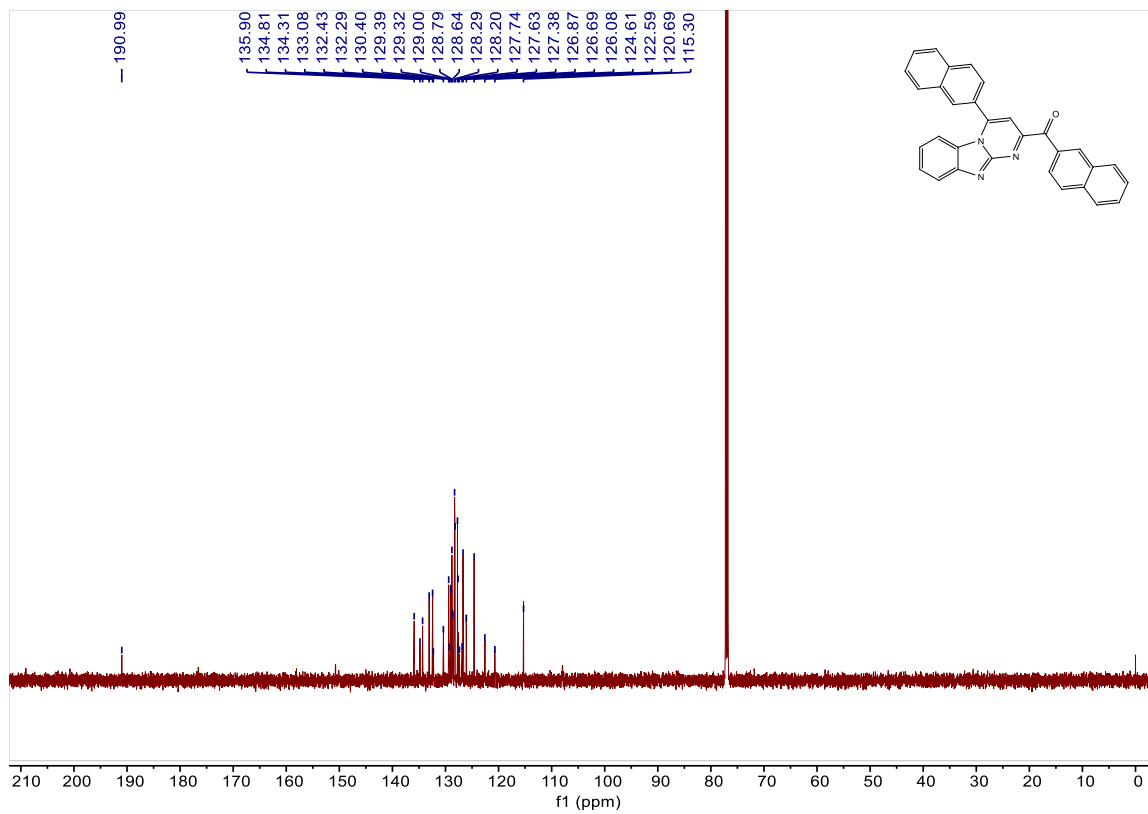
¹³C NMR of Compound 3t (151MHz,CDCl₃)



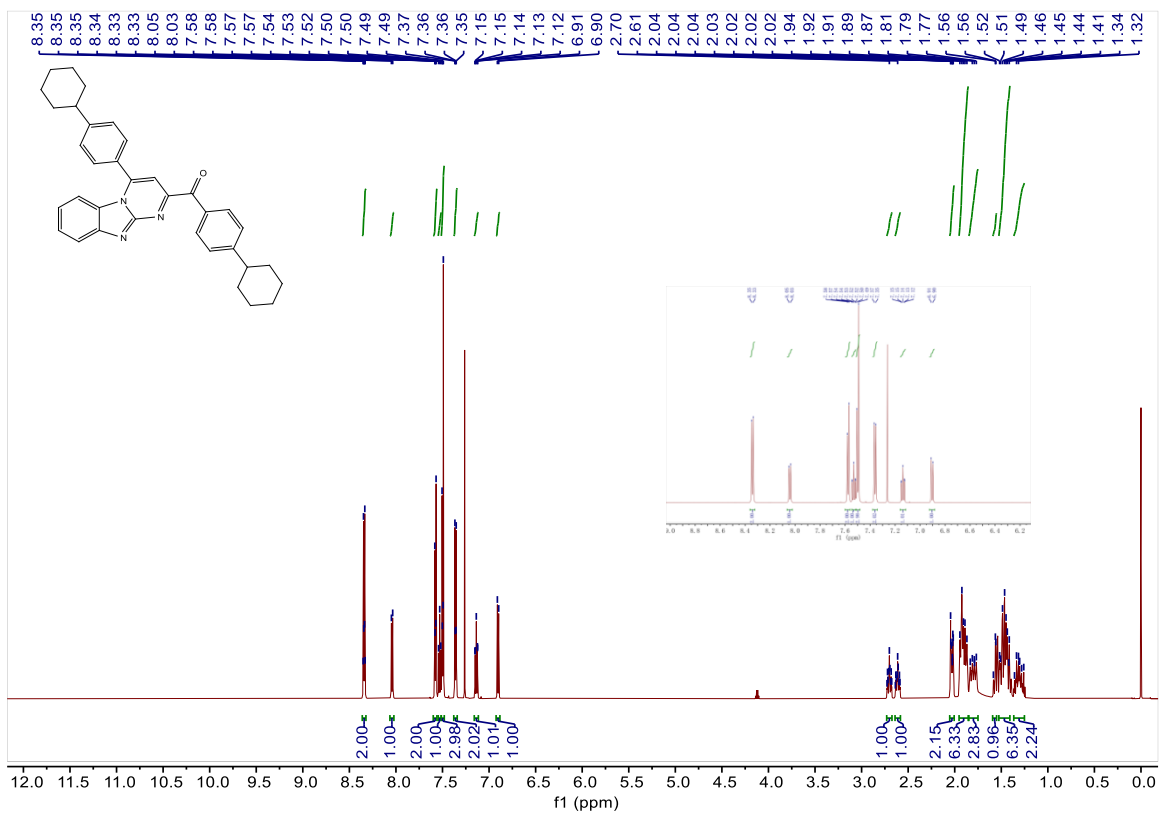
¹H NMR of Compound 3u (600 MHz, CDCl₃)



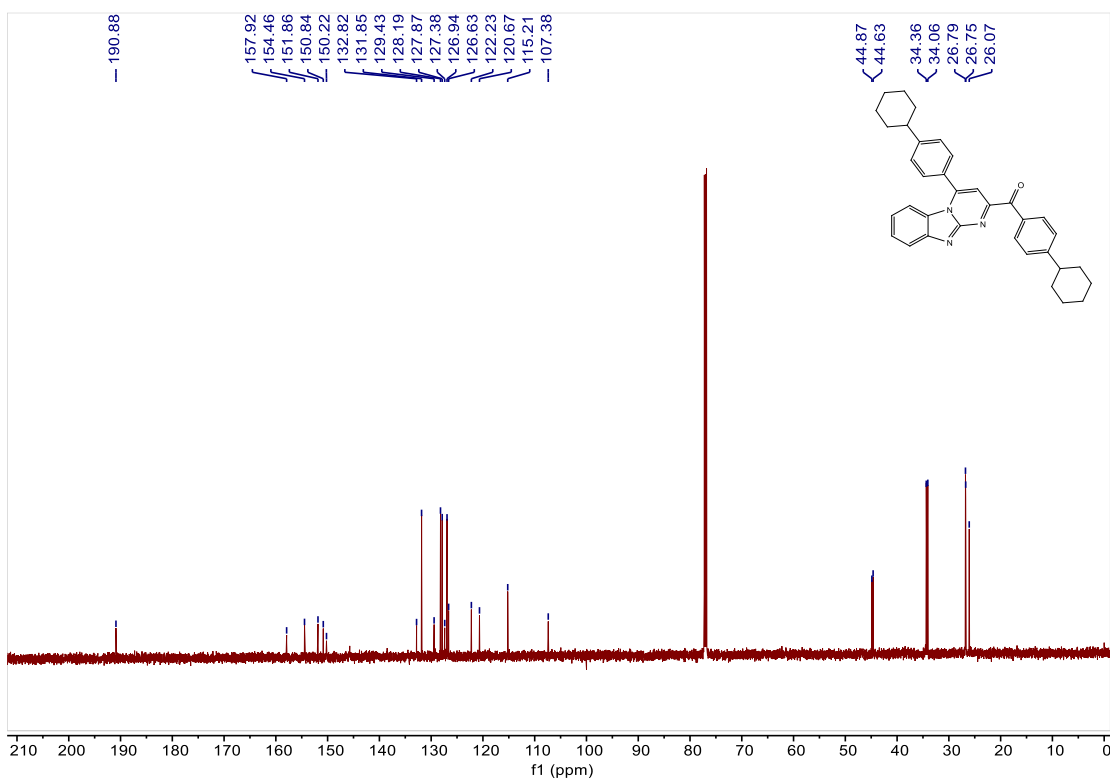
^{13}C NMR of Compound 3u (151MHz, CDCl_3)



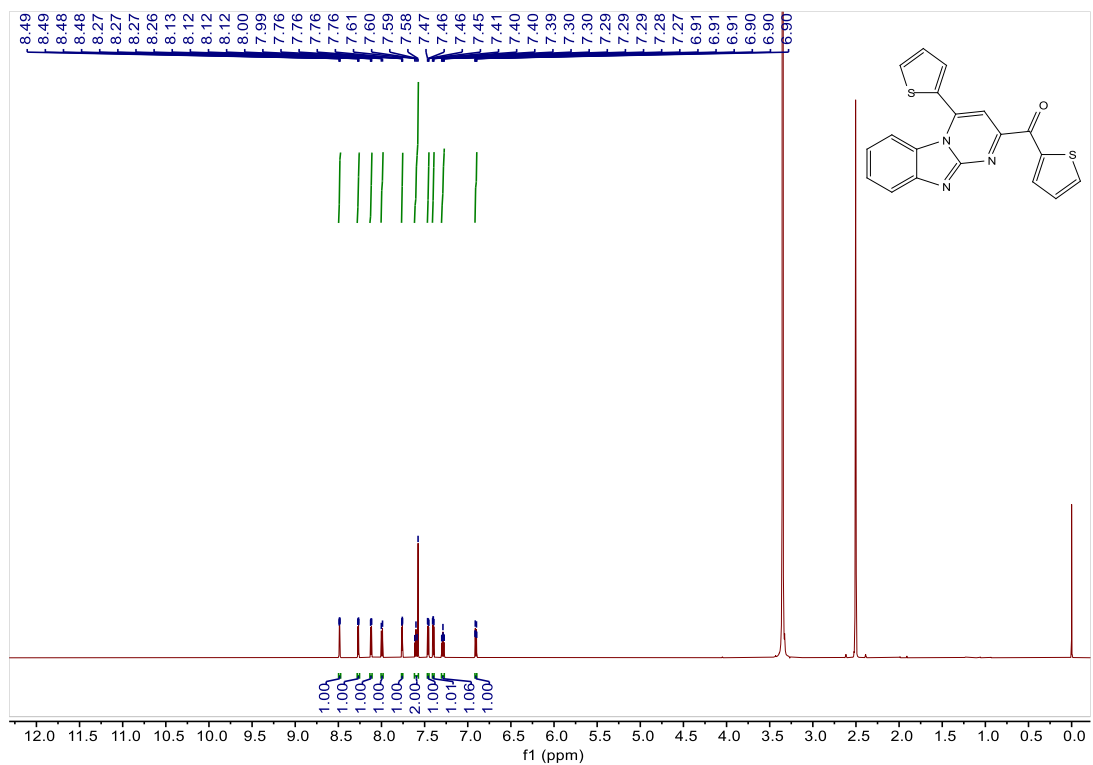
^1H NMR of Compound 3v (600MHz, CDCl_3)



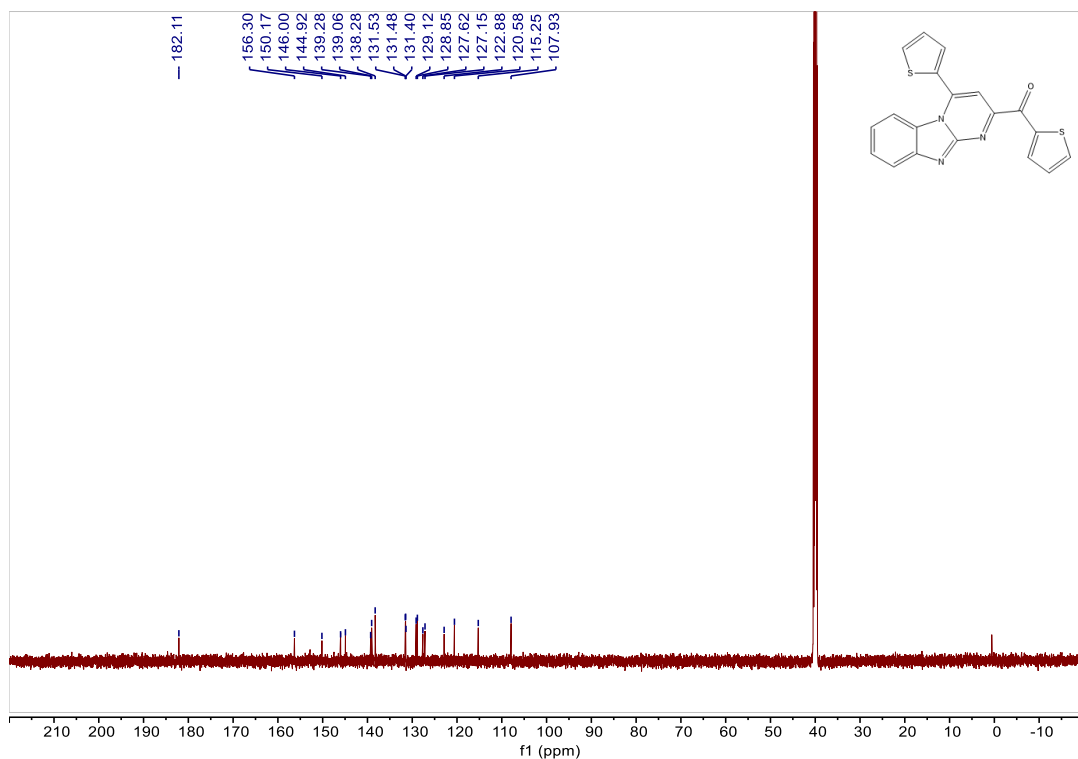
¹³C NMR of Compound 3v (151MHz,CDCl₃)



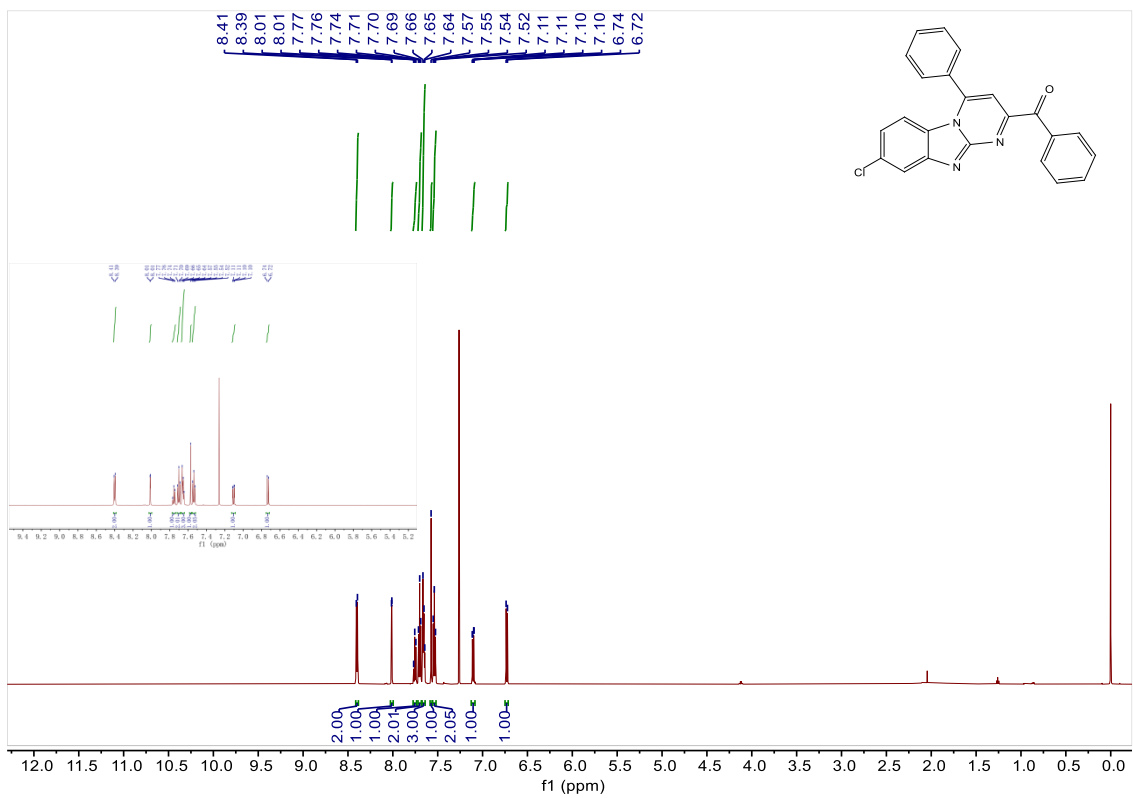
¹H NMR of Compound 3w (600MHz,DMSO-*d*₆)



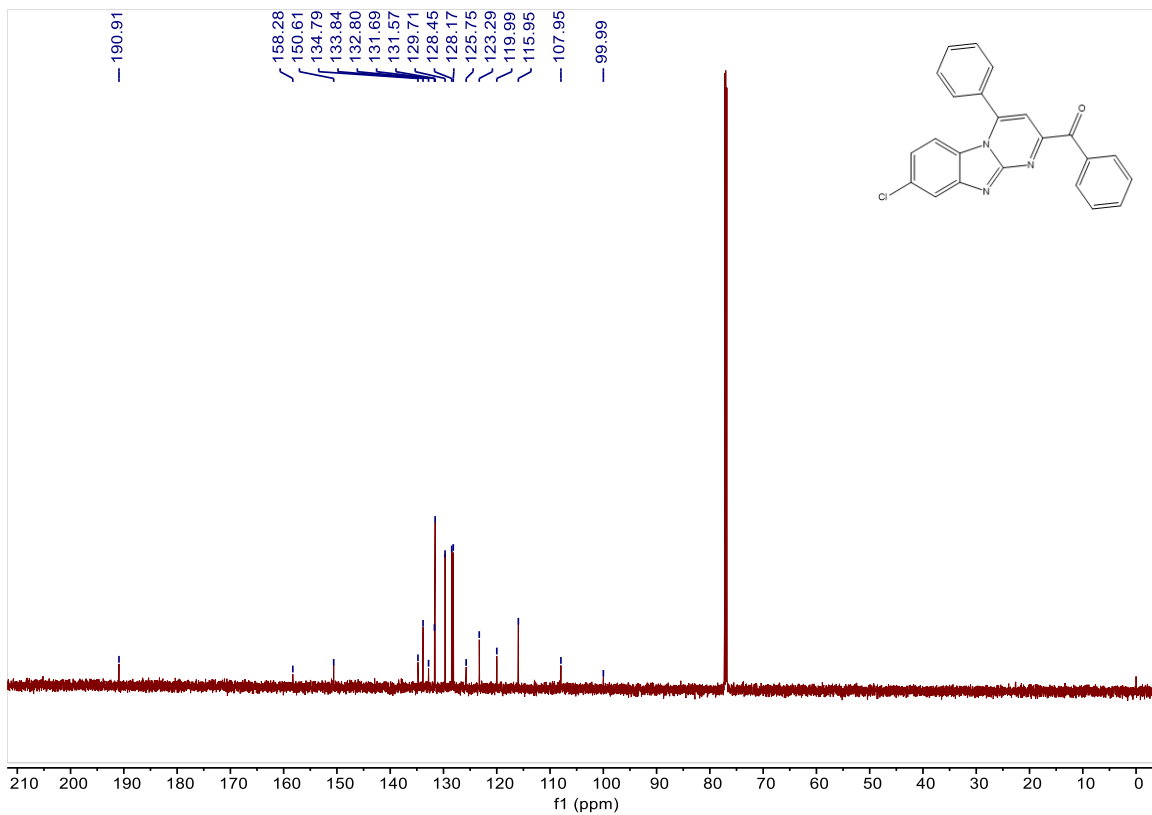
¹³C NMR of Compound 3w (151MHz,DMSO-*d*₆)



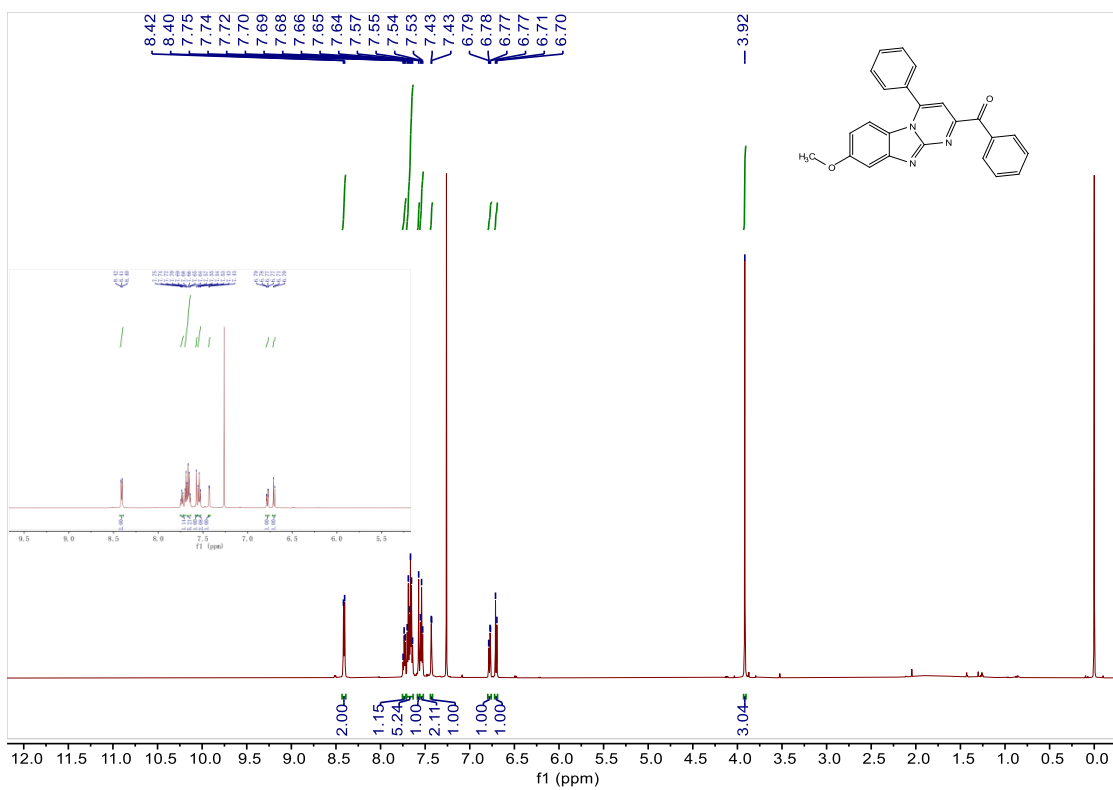
¹H NMR of Compound 4a (600MHz,CDCl₃)



¹³C NMR of Compound 4a (151MHz,CDCl₃)



¹H NMR of Compound 4b (600MHz,CDCl₃)



^{13}C NMR of Compound 4b (151MHz, CDCl_3)

