Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Electrochemically facilitated oxidative C−H amination enables access to fluorescent N9-fused tricyclic xanthines

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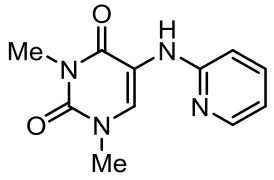
1. General Information

All the electrochemical oxidations were performed in an undivided cell equipped with two platinum electrodes (10 × 15 × 2 mm^3) unless otherwise noted. All commercial reagents were purchased from TCI, Sigma-Aldrich, laajoo and Adamas-beta of the highest purity grade and used without further purification. The conversion of starting materials was monitored by thin layer chromatography using silica gel plates, and components were visualized by observation under UV light (254 and 365 nm).

^{1}H NMR spectra was recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane (TMS), and were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), dt (doublets of triplet), and m (multiplet). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using an Agilent Q-TOF 6540 mass spectrometer. Fluorescence spectra were obtained with fluorescence spectrophotometer. The fluorescence lifetimes were measured at the room temperature by using the Edinburgh instruments FLS980-STM. The response of the instrument was measured with 30% silica suspension solution using nanosecond flash lamp as pulse light source. Unless otherwise noted, all other compounds have been reported in the literature or are commercially available.

2 Preparation of substrate

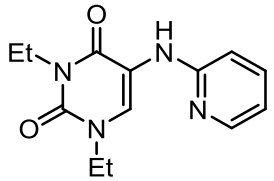
All the starting substrates were prepared according to a protocol reported in the literature (J. Maes, T. R. M. Rauws and B. U. W. Maes, *Chem. Eur. J.*, 2013, **19**, 9137–9141.).



1a

1,3-Dimethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1a)

White solid. **M. p.**: 191.9 – 192.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.76 (s, 1 H), 8.20 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.51 – 7.45 (m, 1 H), 7.01 (s, 1 H), 6.76 – 6.72 (m, 1 H), 6.71 – 6.68 (m, 1 H), 3.47 (s, 3 H), 3.45 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.7, 154.8, 149.7, 147.2, 137.1, 125.1, 116.6, 114.8, 111.4, 37.3, 28.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{11}H_{13}N_4O_2$ $[M+H]^+$ 233.1033, found 233.1041.

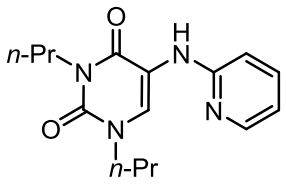


1b

1,3-Diethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1b)

White solid. **M. p.**: 151.6 – 152.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.73 (s, 1 H), 8.19 (d, *J* = 4.2 Hz, 1 H), 7.53 – 7.39 (m, 1 H), 7.03 (s, 1 H), 6.76 – 6.59 (m, 2 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 3.87 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.3, 154.9, 148.8, 147.3, 137.1, 124.1, 116.9, 114.7, 111.3, 45.0, 37.1, 14.2, 12.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{17}N_4O_2$

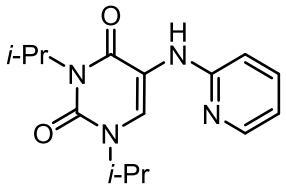
$[M+H]^+$ 261.1356, found 261.1361.



1c

1,3-Dipropyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1c)

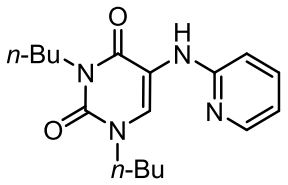
White solid. **M. p.**: 119.7 – 120.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.70 (s, 1 H), 8.16 (dd, *J* = 5.4, 1.8 Hz, 1 H), 7.48 – 7.35 (m, 1 H), 7.06 (s, 1 H), 6.73 – 6.62 (m, 2 H), 4.04 – 3.88 (m, 2 H), 3.81 – 3.68 (m, 2 H), 1.81 – 1.70 (m, 2 H), 1.69 – 1.57 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.9, 149.2, 147.2, 137.0, 124.6, 116.6, 114.6, 111.3, 51.4, 43.5, 22.2, 20.9, 11.3, 11.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{21}N_4O_2$ $[M+H]^+$ 289.1659, found 289.1656.



1d

1,3-Diisopropyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1d)

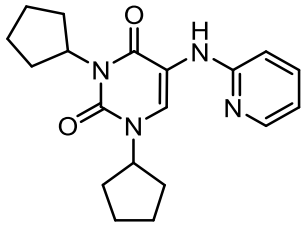
White solid. **M. p.**: 116.7– 118.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.83 (s, 1 H), 8.18 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.44 (m, 1 H), 7.05 (s, 1 H), 6.73 – 6.55 (m, 2 H), 5.36 – 5.20 (m, 1 H), 5.02 – 4.88 (m, 1 H), 1.50 (d, *J* = 7.2 Hz, 6 H), 1.36 (d, *J* = 6.8 Hz, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.4, 155.0, 149.0, 147.3, 137.0, 120.4, 116.9, 114.5, 111.2, 47.9, 46.8, 21.3, 19.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{21}N_4O_2$ $[M+H]^+$ 289.1659, found 289.1666.



1e

1,3-Dibutyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1e)

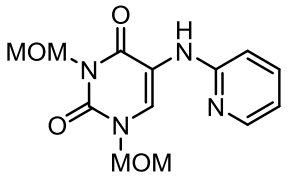
White solid. **M. p.**: 130.0 – 131.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.71 (s, 1 H), 8.18 (d, *J* = 4.0 Hz, 1 H), 7.55 – 7.40 (m, 1 H), 7.04 (s, 1 H), 6.72 – 6.62 (m, 2 H), 4.01 (t, *J* = 7.6 Hz, 2 H), 3.79 (t, *J* = 7.2 Hz, 2 H), 1.83 – 1.66 (m, 2 H), 1.65 – 1.54 (m, 2 H), 1.46 – 1.24 (m, 4 H), 1.03 – 0.84 (m, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.5, 154.9, 149.2, 147.3, 137.0, 124.6, 116.6, 114.6, 111.3, 49.7, 41.8, 31.0, 29.7, 20.2, 19.8, 13.8, 13.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{25}N_4O_2$ $[M+H]^+$ 317.1972, found 317.1978.



1f

1,3-Dicyclopentyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1f)

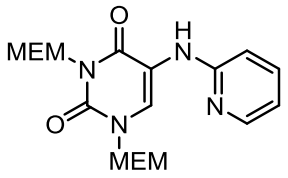
White solid. **M. p.**: 134.4 – 136.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.86 (s, 1 H), 8.17 (dd, *J* = 4.8, 0.8 Hz, 1 H), 7.51 – 7.36 (m, 1 H), 7.04 (s, 1 H), 6.77 – 6.54 (m, 2 H), 5.54 – 5.26 (m, 1 H), 5.15 – 5.00 (m, 1 H), 2.20 – 2.05 (m, 4 H), 2.04 – 1.93 (m, 2 H), 1.92 – 1.80 (m, 4 H), 1.79 – 1.65 (m, 4 H), 1.64 – 1.55 (m, 2 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.4, 155.0, 149.4, 147.3, 137.0, 121.4, 116.9, 114.5, 111.2, 57.4, 54.2, 31.5, 28.3, 26.0, 24.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{19}H_{25}N_4O_2$ $[M+H]^+$ 341.1972, found 341.1979.



1g

1,3-Bis(methoxymethyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1g)

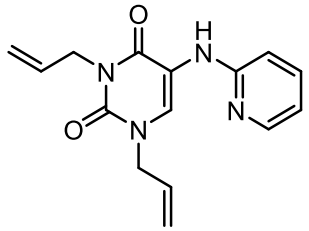
White solid. **M. p.**: 176.7 – 178.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.90 (s, 1 H), 8.21 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.52 – 7.45 (m, 1 H), 6.99 (s, 1 H), 6.77 – 6.72 (m, 1 H), 6.71 – 6.66 (m, 1 H), 5.49 (s, 2 H), 5.23 (s, 2 H), 3.47 (s, 3 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.8, 154.6, 150.0, 147.4, 137.2, 123.4, 117.3, 115.1, 111.3, 79.4, 72.8, 58.0, 57.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{17}N_4O_4$ $[M+H]^+$ 293.1244, found 293.1242.



1h

1,3-Bis((2-methoxyethoxy)methyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1h)

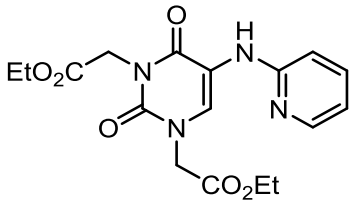
White solid. **M. p.**: 118.7 – 119.0 °C. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ 10.8 (s, 1 H), 10.16 (d, *J* = 3.6 Hz, 1 H), 9.52 – 9.37 (m, 1 H), 8.98 (s, 1 H), 8.72 – 8.64 (m, 2 H), 7.42 (s, 2 H), 7.20 (s, 2 H), 5.75 – 5.61 (m, 4 H), 5.49 – 5.44 (m, 2 H), 5.44 – 5.39 (m, 2 H), 5.26 (s, 3 H), 5.25 (s, 3 H). **^{13}C NMR (100 MHz, CD_2Cl_2):** δ 162.7, 156.7, 151.8, 149.2, 139.1, 125.7, 119.1, 116.8, 113.2, 80.5, 73.7, 73.6, 73.5, 71.7, 70.7, 60.6, 60.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{25}N_4O_6$ $[M+H]^+$ 381.1769, found 381.1756.



1i

1,3-Diallyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1i)

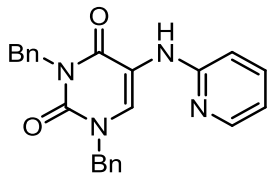
White solid. **M. p.**: 110.1 – 110.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.73 (s, 1 H), 8.20 – 8.10 (m, 1 H), 7.43 (t, *J* = 6.7 Hz, 1 H), 7.13 – 7.03 (s, 1 H), 6.72 – 6.65 (d, *J* = 8.4 Hz, 2 H), 6.03 – 5.79 (m, 2 H), 5.36 – 5.15 (m, 4 H), 4.63 (d, *J* = 4.2 Hz, 2 H), 4.42 (d, *J* = 3.8 Hz, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.2, 154.8, 148.9, 147.3, 137.1, 132.0, 131.6, 124.2, 118.8, 117.9, 116.9, 114.8, 111.4, 51.5, 44.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{17}N_4O_2$ $[M+H]^+$ 285.1346, found 285.1349.



1j

Dimethyl 2,2'-(2,4-dioxo-5-(pyridin-2-ylamino)pyrimidine-1,3(2H,4H)-diyl)diacetatee (1j)

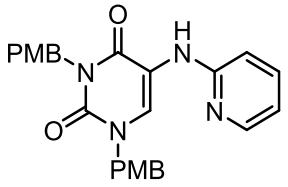
White solid. **M. p.**: 153.3 – 154.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.77 (s, 1 H), 8.22 – 8.07 (m, 1 H), 7.53 – 7.38 (m, 1 H), 7.03 (s, 1 H), 6.79 – 6.61 (m, 2 H), 4.71 (s, 2 H), 4.50 (s, 2 H), 4.32 – 4.11 (m, 4 H), 1.31 – 1.21 (m, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.6, 167.5, 160.2, 154.6, 149.1, 147.1, 137.2, 124.8, 117.0, 114.9, 111.4, 62.0, 61.7, 50.7, 42.7, 14.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{21}N_4O_6$ $[M+H]^+$ 377.1456, found 377.1462.



1k

1,3-Dibenzyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1k)

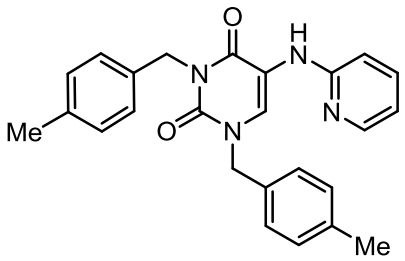
White solid. **M. p.**: 174.1 – 174.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.84 (s, 1 H), 8.13 (d, *J* = 3.6 Hz, 1 H), 7.51 – 7.46 (m, 2 H), 7.45 – 7.41 (m, 1 H), 7.38 – 7.22 (m, 8 H), 7.00 (s, 1 H), 6.69 (dd, *J* = 6.8, 5.4 Hz, 1 H), 6.62 (d, *J* = 8.4 Hz, 1 H), 5.23 (s, 2 H), 5.00 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.7, 149.6, 147.3, 137.1, 136.7, 136.0, 129.0, 128.9, 128.5, 128.2, 128.1, 127.7, 124.5, 117.0, 114.8, 111.3, 53.0, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{21}N_4O_2$ $[M+H]^+$ 385.1659, found 385.1658.



1l

1,3-Bis(4-methoxybenzyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1l)

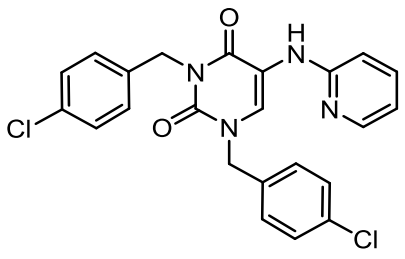
White solid. **M. p.**: 174.8 – 175.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.81 (s, 1 H), 8.14 (d, *J* = 3.6 Hz, 1 H), 7.60 – 7.40 (m, 3 H), 7.38 – 7.30 (m, 2 H), 6.97 (s, 1 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 6.75 – 6.66 (m, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 5.17 (s, 2 H), 4.93 (s, 2 H), 3.78 (d, *J* = 6.0 Hz, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.5, 159.5, 159.1, 154.7, 149.5, 147.3, 137.1, 130.6, 129.7, 129.0, 128.1, 124.4, 116.9, 114.7, 114.3, 113.8, 111.2, 55.3, 55.3, 52.4, 44.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{25}N_4O_4$ $[M+H]^+$ 445.1870, found 445.1864.



1m

1,3-Bis(4-methylbenzyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1m)

White solid. **M. p.**: 197.6– 198.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.81 (s, 1 H), 8.12 (d, *J* = 3.0 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.38 (d, *J* = 7.2 Hz, 2 H), 7.26 (d, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* = 7.2 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 6.97 (s, 1 H), 6.67 (t, *J* = 5.4 Hz, 1 H), 6.60 (d, *J* = 8.4 Hz, 1 H), 5.18 (s, 2 H), 4.94 (s, 2 H), 2.32 (s, 3 H), 2.30 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.7, 149.6, 147.3, 138.0, 137.4, 137.1, 133.8, 133.0, 129.6, 129.2, 129.0, 128.1, 124.5, 117.0, 114.7, 111.2, 52.7, 45.0, 21.2. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{25}N_4O_2$ $[M+H]^+$ 413.1972, found 413.1961.

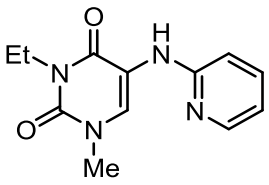


1n

1,3-Bis(4-chlorobenzyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1n)

White solid. **M. p.**: 214.6 – 215.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.83 (s, 1 H), 8.15 (dd, *J* = 5.4, 1.2 Hz, 1 H), 7.49 – 7.45 (m, 1 H), 7.44 – 7.40 (m, 2 H), 7.36 – 7.32 (m, 2 H), 7.31 – 7.29 (m, 2 H), 7.28 – 7.27 (m, 1 H), 7.26 – 7.25 (m, 1 H), 6.95 (s, 1 H), 6.74 – 6.70 (m, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 5.17 (s, 2 H), 4.95 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.4, 154.6, 149.4, 147.3, 137.2, 135.0, 134.6, 134.2, 133.7,

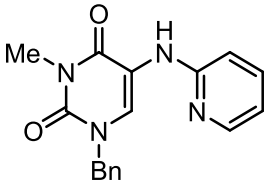
130.5, 129.4, 129.2, 128.7, 124.1, 117.2, 115.0, 111.3, 52.4, 44.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{19}Cl_2N_4O_2$ $[M+H]^+$ 453.0880, found 453.0874.



1o

3-Ethyl-1-methyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1H,3H)-dione (1o)

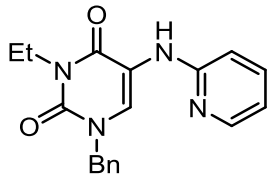
White solid. **M. p.**: 170.1 – 172.9 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.68 (s, 1 H), 8.15 (d, *J* = 4.2 Hz, 1 H), 7.47 – 7.37 (m, 1 H), 7.04 (s, 1 H), 6.70 – 6.64 (m, 2 H), 4.06 (q, *J* = 7.2 Hz, 2 H), 3.40 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.3, 154.8, 149.3, 147.2, 137.1, 125.2, 116.7, 114.7, 111.4, 37.2, 37.1, 12.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{15}N_4O_2$ $[M+H]^+$ 247.1190, found 247.1189.



1p

1-Benzyl-3-methyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1p)

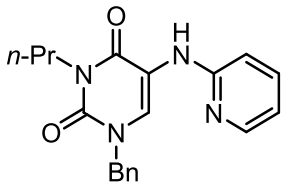
White solid. **M. p.**: 186.3 – 187.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.86 (s, 1 H), 8.14 (dd, *J* = 4.8, 1.8 Hz, 1 H), 7.47 – 7.41 (m, 1 H), 7.39 – 7.33 (m, 4 H), 7.32 – 7.27 (m, 1 H), 7.03 (s, 1 H), 6.71 – 6.62 (m, 2 H), 4.99 (s, 2 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 154.8, 149.6, 147.3, 137.1, 136.0, 128.9, 128.2 , 128.1, 124.3, 116.9, 114.8, 111.3, 52.9, 28.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{17}N_4O_2$ $[M+H]^+$ 309.1346, found 309.1348.



1q

1-Benzyl-3-ethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1H,3H)-dione (1q)

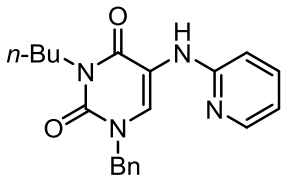
White solid. **M. p.**: 180.6 – 183.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.82 (s, 1 H), 8.14 (dd, *J* = 5.4, 1.2 Hz, 1 H), 7.46 – 7.41 (m, 1 H), 7.39 – 7.34 (m, 4 H), 7.33 – 7.29 (m, 1 H), 7.03 (s, 1 H), 6.68 (ddd, *J* = 7.2, 5.4, 1.2Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 4.99 (s, 2 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 1.262 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.3, 154.8, 149.3, 147.3, 137.1, 136.1, 128.9, 128.2, 128.1, 124.3, 117.0, 114.7, 111.3, 52.8, 37.3, 12.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{19}N_4O_2$ $[M+H]^+$ 323.1503, found 323.1506.



1r

1-Benzyl-3-propyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1r)

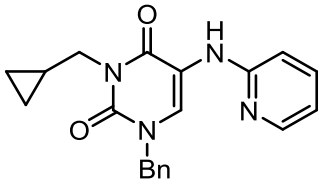
White solid. **M. p.**: 158.6 – 159.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.83 (s, 1 H), 8.14 (dd, *J* = 4.2, 1.2 Hz, 1 H), 7.47 – 7.42 (m, 1 H), 7.40 – 7.33 (m, 4 H), 7.32 – 7.28 (m, 1 H), 7.02 (s, 1 H), 6.69 (ddd, *J* = 7.2, 5.4, 0.6 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 4.99 (s, 2 H), 4.04 – 3.98 (m, 2 H), 1.75 – 1.65 (m, 2 H), 0.96 (t, *J* = 8.4 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.8, 149.5, 147.3, 137.1, 136.1, 128.9, 128.1, 128.0, 124.3, 116.9, 114.7, 111.3, 52.9, 43.7, 21.0, 11.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{19}H_{21}N_4O_2$ $[M+H]^+$ 337.1659, found 337.1661.



1s

1-Benzyl-3-butyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1s)

White solid. **M. p.**: 142.9 – 143.1 °C. **^{1}H NMR (600 MHz, CDCl$_3$):** δ 8.83 (s, 1 H), 8.14 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.46-7.41 (m, 1 H), 7.39 – 7.33 (m, 4 H), 7.32 – 7.28 (m, 1 H), 7.03 (s, 1 H), 6.69 (ddd, *J* = 7.2, 4.8, 0.6 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 4.99 (s, 2 H), 4.11 – 3.98 (m, 2 H), 1.74 – 1.58 (m, 2 H), 1.46 – 1.28 (m, 2 H), 0.95 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR (150 MHz, CDCl$_3$):** δ 160.4, 154.8, 147.3, 137.1, 136.1, 128.9, 128.1, 128.0, 124.3, 116.9, 114.7, 111.3, 52.9, 42.0, 29.8, 20.2, 13.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{20}H_{23}N_4O_2$ $[M+H]^+$ 351.1816, found 351.1819.

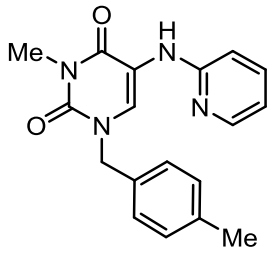


1t

1-Benzyl-3-(cyclopropylmethyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1t)

White solid. **M. p.**: 156.0 – 156.4 °C. **^{1}H NMR (600 MHz, CDCl$_3$):** δ 8.83 (s, 1 H), 8.19 – 8.09 (m, 1 H), 7.45 – 7.40 (m, 1 H), 7.39 – 7.31 (m, 4 H), 7.32 – 7.26 (m, 1 H), 7.07 (s, 1 H), 6.73 – 6.59 (m, 2 H), 4.99 (s, 2 H), 3.94 (d, *J* = 7.2 Hz, 2 H), 1.35 – 1.25 (m, 1 H), 0.55 – 0.34 (m, 4 H). **^{13}C NMR (150 MHz, CDCl$_3$):** δ 160.7, 154.8, 149.7, 147.3, 137.0, 136.2, 128.9, 128.1, 128.1, 124.4, 117.0, 114.7, 111.3, 52.9, 46.5, 9.9, 3.9.

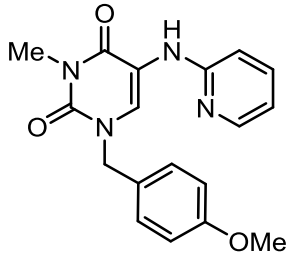
HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{21}N_4O_2$ $[M+H]^+$ 349.1659, found 349.1661.



1u

3-Methyl-1-(4-methylbenzyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1u)

White solid. **M. p.**: 195.4 – 196.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.86 (s, 1 H), 8.23 – 8.10 (m, 1 H), 7.46 – 7.43 (m, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 7.00 (s, 1 H), 6.74 – 6.69 (m, 1 H), 6.66 (d, *J* = 8.4 Hz, 1 H), 4.96 (s, 2 H), 3.45 (s, 3 H), 2.33 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.7, 154.8, 149.6, 147.3, 138.0, 137.07, 133.0, 129.6, 128.2, 124.3, 116.8, 114.7, 111.3, 52.7, 28.6, 21.2. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{19}N_4O_2$ $[M+H]^+$ 323.1503, found 323.1500.

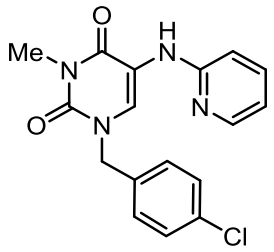


1v

1-(4-Methoxybenzyl)-3-methyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1v)

White solid. **M. p.**: 193.7 – 194.4 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.85 (s, 1 H), 8.25 – 8.12 (m, 1 H), 7.52 – 7.40 (m, 1 H), 7.37 – 7.30 (m, 2 H), 6.98 (s, 1 H), 6.93 – 6.85 (m, 2 H), 6.76 – 6.68 (m, 1 H), 6.66 (d, *J* = 8.4 Hz, 1 H), 4.94 (s, 2 H), 3.79 (s, 3

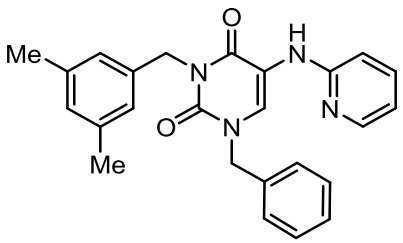
H), 3.45 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 159.6, 154.8, 149.6, 147.2, 137.1, 129.7, 128.1, 124.2, 116.7, 114.7, 114.3, 111.3, 55.3, 52.5, 28.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{19}N_4O_3$ $[M+H]^+$ 339.1452, found 339.1456.



1w

1-(4-Chlorobenzyl)-3-methyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1w)

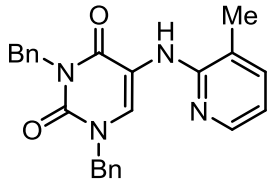
White solid. **M. p.**: 200.1 – 201.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.85 (s, 1 H), 8.16 (d, *J* = 4.0 Hz, 1 H), 7.53 – 7.42 (m, 1 H), 7.32 (s, 4 H), 7.01 (s, 1 H), 6.75 – 6.70 (m, 1 H), 6.68 (d, *J* = 8.4 Hz, 1 H), 4.96 (s, 2 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 154.7, 149.6, 147.3, 137.2, 134.5, 134.2, 129.5, 129.1, 123.8, 117.0, 114.9, 111.4, 52.4, 28.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{16}ClN_4O_2$ $[M+H]^+$ 343.0956, found 343.0939.



1x

1-Benzyl-3-(3,5-dimethylbenzyl)-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1x)

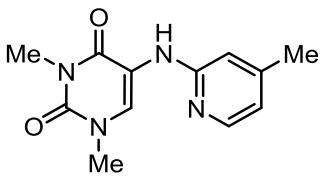
White solid. **M. p.**: 204.4—206.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.85 (s, 1 H), 8.14 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.48 – 7.43 (m, 1 H), 7.41 – 7.35 (m, 4 H), 7.35 – 7.30 (m, 1 H), 7.07 (s, 2 H), 7.01 (s, 1 H), 6.90 (s, 1 H), 6.73 – 6.67 (m, 1 H), 6.65 – 6.62 (m, 1 H), 5.18 (s, 2 H), 5.02 (s, 2 H), 2.29 (s, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.7, 149.6, 147.3, 138.0, 137.1, 136.5, 136.0, 129.4, 128.9, 128.2, 128.0, 126.3, 124.5, 117.0, 114.8, 111.3, 53.0, 45.2, 21.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{25}N_4O_2$ $[M+H]^+$ 413.1972, found 413.1979.



1y

1,3-Dibenzyl-5-((3-methylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1y)

White solid. **M. p.**: 150.1 – 150.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.96 (s, 1 H), 8.05 (d, *J* = 4.4 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 2 H), 7.45 – 7.25 (m, 9 H), 7.01 (s, 1 H), 6.67 (dd, *J* = 7.1, 5.1 Hz, 1 H), 5.28 (s, 2 H), 5.03 (s, 2 H), 2.25 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.7, 153.2, 149.6, 144.9, 137.3, 136.7, 136.1, 129.0, 128.9, 128.5, 128.2, 128.1, 127.7, 124.6, 118.6, 117.1, 114.9, 53.0, 45.3, 16.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{23}N_4O_2$ $[M+H]^+$ 399.1816, found 399.1819.

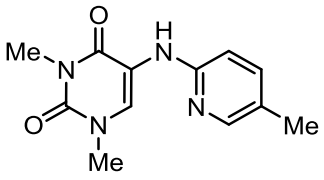


1z

1,3-Dimethyl-5-((4-methylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1z)

White solid. **M. p.**: 219.8 – 220.8 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.74 (s, 1 H),

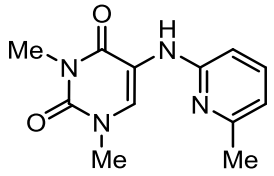
8.06 (d, J = 5.2 Hz, 1 H), 6.91 (s, 1 H), 6.59 – 6.56 (m, 1 H), 6.52 (s, 1 H), 3.47 (s, 3 H), 3.44 (s, 3 H), 2.27 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.8, 155.0, 149.7, 148.3, 146.9, 125.0, 116.7, 116.5, 111.4, 37.3, 28.5, 21.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{15}N_4O_2$ $[M+H]^+$ 247.1190, found 247.1198.



1aa

1,3-Dimethyl-5-((5-methylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1aa)

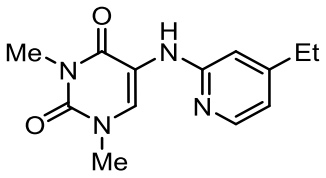
Pale yellow solid. **M. p.**: 185.9 – 187.0 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.70 (s, 1 H), 8.02 (s, 1 H), 7.33 (d, J = 8.3 Hz, 1 H), 6.88 (s, 1 H), 6.63 (d, J = 8.4 Hz, 1 H), 3.46 (d, J = 14.1 Hz, 6 H), 2.23 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.8, 152.9, 149.7, 146.7, 138.3, 124.5, 123.8, 116.9, 111.0, 37.3, 28.5, 17.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{15}N_4O_2$ $[M+H]^+$ 247.1190, found 247.1193.



1ab

1,3-Dimethyl-5-((6-methylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ab)

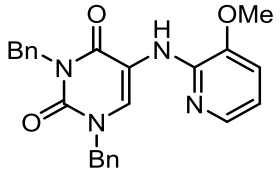
White solid. **M. p.**: 183.9 – 184.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** 8.82 – 8.73 (m, 1 H), 7.35 – 7.31 (m, 1 H), 6.96 (s, 1 H), 6.58 – 6.51 (m, 1 H), 6.47 (d, J = 8.1 Hz, 1 H), 3.47 – 3.34 (m, 6 H), 2.45 – 2.37 (m, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.7, 156.1, 154.3, 149.6, 137.4, 124.9, 116.8, 113.7, 108.1, 37.4, 28.5, 24.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{15}N_4O_2$ $[M+H]^+$ 247.1190, found 247.1197.



1ac

5-((4-Ethylpyridin-2-yl)amino)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (1ac)

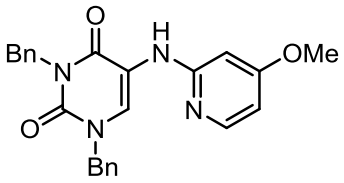
White solid. **M. p.**: 126.1 – 126.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.70 (s, 1 H), 8.04 (d, *J* = 5.3 Hz, 1 H), 6.95 (s, 1 H), 6.55 (d, *J* = 5.3 Hz, 1 H), 6.50 (s, 1 H), 3.41 (d, *J* = 7.1 Hz, 6 H), 2.52 (q, *J* = 7.6 Hz, 2 H), 1.18 (t, *J* = 7.6 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.7, 155.1, 154.2, 149.7, 146.9, 124.9, 116.8, 115.3, 110.2, 37.2, 28.5, 28.1, 14.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{17}N_4O_2$ $[M+H]^+$ 261.1346, found 261.1351.



1ad

1,3-Dibenzyl-5-((3-methoxypyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ad)

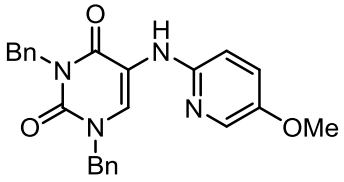
White solid. **M. p.**: 171.2 – 172.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.91 (s, 1 H), 7.71 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.62 (s, 1 H), 7.49 (d, *J* = 7.3 Hz, 2 H), 7.39 – 7.33 (m, 4 H), 7.32 – 7.27 (m, 3 H), 7.27 – 7.20 (m, 1 H), 6.89 (dd, *J* = 7.8, 1.1 Hz, 1 H), 6.65 (dd, *J* = 7.8, 5.1 Hz, 1 H), 5.23 (s, 2 H), 5.00 (s, 2 H), 3.84 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 149.7, 145.9, 143.0, 137.8, 136.8, 136.1, 129.0, 128.9, 128.5, 128.1, 128.0, 127.7, 124.2, 117.0, 114.2, 114.2, 55.4, 53.0, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{23}N_4O_3$ $[M+H]^+$ 415.1765, found 415.1760.



1ae

1,3-Dibenzyl-5-((4-methoxypyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ae)

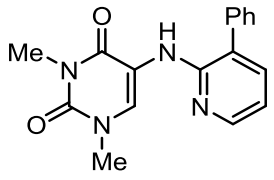
White solid. **M. p.**: 130.1 – 132.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.79 (s, 1 H), 7.94 (d, *J* = 5.9 Hz, 1 H), 7.47 (d, *J* = 7.1 Hz, 2 H), 7.35 (d, *J* = 4.4 Hz, 4 H), 7.32 – 7.27 (m, 3 H), 7.27 – 7.23 (m, 1 H), 6.91 (s, 1 H), 6.32 (dd, *J* = 5.9, 2.2 Hz, 1 H), 6.08 (d, *J* = 2.1 Hz, 1 H), 5.22 (s, 2 H), 4.98 (s, 2 H), 3.76 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 166.6, 160.5, 156.4, 149.6, 148.4, 136.7, 136.0, 128.9, 128.9, 128.5, 128.2, 128.0, 127.7, 124.8, 117.2, 104.3, 94.3, 55.0, 53.0, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{23}N_4O_3$ $[M+H]^+$ 415.1765, found 415.1761.



1af

1,3-Dibenzyl-5-((5-methoxypyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1af)

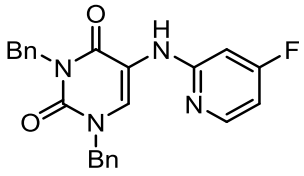
Pale yellow solid. **M. p.**: 167.0 – 168.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.72 (s, 1 H), 7.82 (s, 1 H), 7.47 (d, *J* = 7.3 Hz, 2 H), 7.41 – 7.18 (m, 8 H), 7.12 (d, *J* = 7.1 Hz, 1 H), 6.86 (s, 1 H), 6.60 (d, *J* = 8.9 Hz, 1 H), 5.23 (s, 2 H), 4.99 (s, 2 H), 3.79 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 149.7, 149.6, 149.2, 136.7, 136.1, 131.9, 128.9, 128.9, 128.5, 128.1, 128.0 , 127.7 , 125.6, 122.9, 117.5, 111.9, 56.2, 52.9, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{23}N_4O_3$ $[M+H]^+$ 415.1765, found 415.1769.



1ag

1,3-Dimethyl-5-((3-phenylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ag)

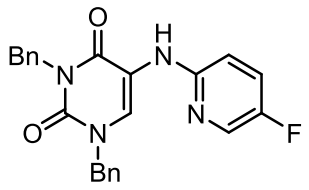
White solid. **M. p.**: 178.3 – 178.6°C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.76 (s, 1 H), 8.17 (dd, *J* = 5.0, 1.8 Hz, 1 H), 7.55 – 7.46 (m, 2 H), 7.45 – 7.35 (m, 5 H), 6.78 (dd, *J* = 7.3, 5.1 Hz, 1 H), 3.41 (s, 3 H), 3.33 (s, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.7, 151.9, 149.6, 146.3, 137.4, 136.7, 129.5, 128.8, 128.5, 125.1, 124.5, 116.5, 114.9, 37.3, 28.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{17}N_4O_2$ $[M+H]^+$ 309.1351, found 309.1351.



1ah

1,3-Dibenzyl-5-((4-fluoropyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ah)

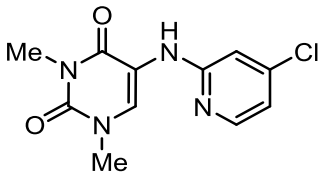
White solid. **M. p.**: 193.3 – 194.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.76 (s, 1 H), 8.16 – 7.99 (m, 1 H), 7.47 (d, *J* = 7.5 Hz, 2 H), 7.39 – 7.33 (m, 4 H), 7.31 (q, *J* = 7.3 Hz, 3 H), 7.28 – 7.21 (m, 1 H), 7.03 (s, 1 H), 6.48 (t, *J* = 6.8 Hz, 1 H), 6.32 (d, *J* = 10.4 Hz, 1 H), 5.22 (s, 2 H), 5.00 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 169.3 (d, $^{1}J_{C\text{-}F}$ = 256.5 Hz), 160.4, 156.7 (d, $^{3}J_{C\text{-}F}$ = 10.5 Hz), 149.8 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 149.6, 136.6, 135.9, 129.0, 128.9, 128.5, 128.3, 128.1, 127.8, 125.4, 116.7, 104.1 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 97.4 (d, $^{2}J_{C\text{-}F}$ = 19.5 Hz), 53.0, 45.3. **^{19}F NMR (565 MHz, $CDCl_3$):** δ 102.77. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}FN_4O_2$ $[M+H]^+$ 403.1565, found 403.1563.



1ai

1,3-Dibenzyl-5-((5-fluoropyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ai)

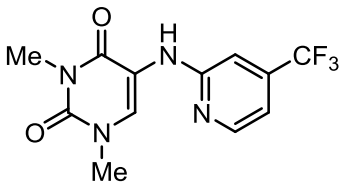
White solid. **M. p.**: 191.8 – 195.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.69 (s, 1 H), 7.97 (s, 1 H), 7.47 (d, *J* = 7.2 Hz, 2 H), 7.42 – 7.13 (m, 9 H), 7.02 (s, 1 H), 6.60 (dd, *J* = 8.7, 2.7 Hz, 1 H), 5.23 (s, 2 H), 4.99 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.5, 154.0 (d, $^{1}J_{C\text{-}F}$ = 245.0 Hz), 151.1, 149.6, 136.6, 135.9, 133.7 (d, $^{2}J_{C\text{-}F}$ = 25.5 Hz), 129.0, 128.9, 128.5, 128.2, 128.1, 127.7, 125.5 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 123.8, 117.0, 111.9 (d, $^{3}J_{C\text{-}F}$ = 4.5 Hz), 52.9, 45.3. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -140.12. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}FN_4O_2$ $[M+H]^+$ 403.1565, found 403.1557.



1aj

5-((4-Chloropyridin-2-yl)amino)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (1aj)

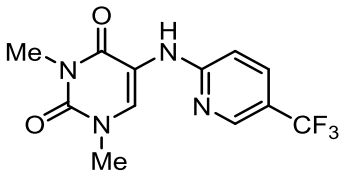
White solid. **M. p.**: 240.0 – 240.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.69 (s, 1 H), 8.09 (d, *J* = 5.5 Hz, 1 H), 7.06 (s, 1 H), 6.79 – 6.70 (m, 2 H), 3.47 (s, 3 H), 3.45 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 155.5, 149.7, 148.3, 144.3, 126.1, 116.1, 115.5, 110.9, 37.4, 28.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{11}H_{12}ClN_4O_2$ $[M+H]^+$ 267.0643, found 267.0642



1ak

1,3-Dimethyl-5-((4-(trifluoromethyl)pyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ak)

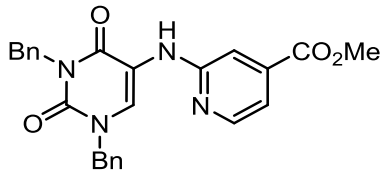
White solid. **M. p.**: 176.0 – 176.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.74 (s, 1 H), 8.32 (d, *J* = 5.3 Hz, 1 H), 7.49 (s, 1 H), 7.02 (s, 1 H), 6.88 (dd, *J* = 5.4, 1.4 Hz, 1 H), 3.47 (s, 3 H), 3.43 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 155.1, 149.7, 148.6, 139.4 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 126.5, 122.8 (q, $^{1}J_{C\text{-}F}$ = 271.5 Hz), 109.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 107.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 116.1, 37.4, 28.6. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -65.20. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{12}F_3N_4O_2$ $[M+H]^+$ 301.0907, found 301.0910.



1al

1,3-Dimethyl-5-((5-(trifluoromethyl)pyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1al)

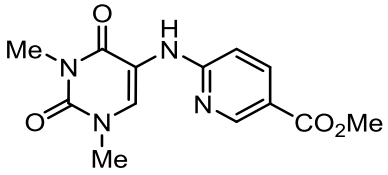
White solid. **M. p.**: 230.0 – 236.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.76 (s, 1 H), 8.47 (s, 1 H), 7.67 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.30 (s, 1 H), 6.76 (d, *J* = 8.8 Hz, 1 H), 3.49 (s, 3 H), 3.45 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.6, 156.5, 149.7, 145.3 (q, $^{3}J_{C\text{-}F}$ = 4.5 Hz), 134.0 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 126.8, 124.2 (q, $^{1}J_{C\text{-}F}$ = 268.5 Hz), 117.5 (q, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 115.7, 111.0, 37.5, 28.6. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -61.56. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{12}F_3N_4O_2$ $[M+H]^+$ 301.0907, found 301.0909



1am

Methyl 2-((1,3-dibenzyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)amino)isonicotinate (1am)

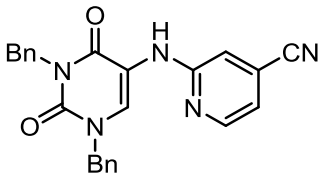
Pale yellow solid. **M. p.**: 160.1 – 160.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.79 (s, 1 H), 8.24 (d, *J* = 5.2 Hz, 1 H), 7.48 (d, *J* = 7.2 Hz, 2 H), 7.40 – 7.20 (m, 10 H), 7.16 (s, 1 H), 5.24 (s, 2 H), 5.01 (s, 2 H), 3.92 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 165.6, 160.3, 155.1, 149.56 , 148.2, 138.6, 136.6 , 135.8, 129.0, 128.9, 128.6, 128.3, 128.1, 127.8, 125.1, 116.7, 113.5, 111.4, 53.0, 52.7, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_4O_4$ $[M+H]^+$ 443.1714, found 443.1722



1an

Methyl 6-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)amino)nicotinate (1an)

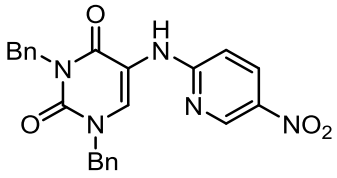
Pale yellow solid. **M. p.**: 249.6 – 250.8 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.86 (d, *J* = 1.8 Hz, 1 H), 8.81 (s, 1 H), 8.04 (dd, *J* = 8.7, 2.1 Hz, 1 H), 7.32 (s, 1 H), 6.70 (d, *J* = 8.7 Hz, 1 H), 3.89 (s, 3 H), 3.49 (s, 3 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 166.0, 160.6, 157.0, 150.6, 149.7, 137.8, 127.0, 117.2, 115.7, 110.6, 51.9, 37.5, 28.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{15}N_4O_4$ $[M+H]^+$ 291.1088, found 291.1088.



1ao

2-((1,3-Dibenzyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)amino)isonicotinonitrile (1ao)

Pale yellow solid. **M. p.**: 156.5 – 160.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.69 (s, 1 H), 8.21 (d, *J* = 5.2 Hz, 1 H), 7.45 (d, *J* = 6.8 Hz, 2 H), 7.41 – 7.15 (m, 9 H), 6.85 (s, 1 H), 6.82 (dd, *J* = 5.2, 1.0 Hz, 1 H), 5.21 (s, 2 H), 4.99 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.2, 154.7, 149.6, 148.7, 136.4, 135.7, 129.0, 128.9, 128.5, 128.4, 128.1, 127.8, 126.1, 121.1, 116.6, 116.1, 115.0, 113.8, 53.0, 45.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{20}N_5O_2$ $[M+H]^+$ 410.1607, found 410.1607.

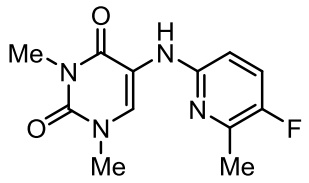


1ap

1,3-Dibenzyl-5-((4-nitropyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ap)

White solid. **M. p.**: 200.8－201.9 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 9.03 (d, *J* = 2.4 Hz, 1 H), 8.84 (s, 1 H), 8.19 (dd, *J* = 9.2, 2.5 Hz, 1 H), 7.63 (s, 1 H), 7.50 – 7.44 (m, 2 H), 7.43 – 7.34 (m, 5 H), 7.33 – 7.30 (m, 2 H), 7.29 – 7.25 (m, 1 H), 6.67 (d, *J* = 9.0 Hz, 1 H), 5.23 (s, 2 H), 5.03 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.1, 157.3, 149.5, 145.7, 137.1, 136.2, 135.4, 132.3, 129.1, 128.9, 128.6, 128.2, 127.9, 127.4, 115.4, 110.7,

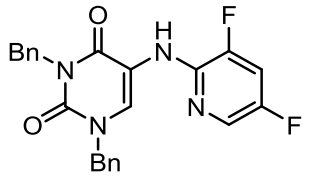
53.1, 45.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}N_5O_4$ $[M+H]^+$ 430.1510, found 430.1501.



1aq

5-((5-Fluoro-6-methylpyridin-2-yl)amino)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (1aq)

White solid. **M. p.**: 228.5 – 229.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.69 (s, 1 H), 7.19 (t, *J* = 8.7 Hz, 1 H), 6.93 (s, 1 H), 6.51 (dd, *J* = 8.8, 2.7 Hz, 1 H), 3.46 (s, 3 H), 3.44 (s, 3 H), 2.43 (d, *J* = 3.0 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.8, 152.0 (d, $^1J_{C-F}$ = 243.0 Hz), 150.3 (d, $^4J_{C-F}$ = 1.5 Hz), 149.7, 142.5 (d, $^2J_{C-F}$ = 18.0 Hz), 125.1 (d, $^2J_{C-F}$ = 21.0 Hz), 124.2, 116.9, 109.5 (d, $^3J_{C-F}$ = 4.5 Hz), 37.4, 28.5, 17.8. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -138.02. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{14}FN_4O_2$ $[M+H]^+$ 265.1095, found 265.1093.

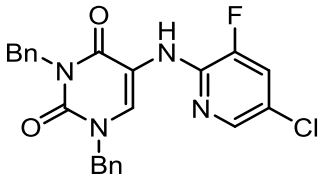


1ar

1,3-Dibenzyl-5-((3,5-difluoropyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ar)

White solid. **M. p.**: 136.4 – 145.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (s, 1 H), 7.83 (d, *J* = 2.4 Hz, 1 H), 7.49 (d, *J* = 7.0 Hz, 2 H), 7.41 – 7.18 (m, 9 H), 7.13 (ddd, *J* = 10.2, 7.7, 2.4 Hz, 1 H), 5.23 (s, 2 H), 5.00 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ

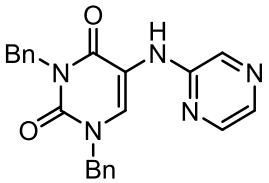
160.1, 152.5 (d, $^{1}J_{C\text{-}F}$ = 252.0, 3.0 Hz), 149.7, 146.1 (d, $^{1}J_{C\text{-}F}$ = 262.0, 6.0 Hz), 141.2 (d, $^{3}J_{C\text{-}F}$ = 9.0, 2.0 Hz), 136.5, 135.8, 129.0, 128.6 (d, $^{2}J_{C\text{-}F}$ = 24.0, 6.0 Hz), 128.5, 12.8.3, 128.1, 127.8, 124.2, 116.3, 111.1 (d, $^{2}J_{C\text{-}F}$ = 25.0, 19.0 Hz), 52.9, 45.4. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -133.41, -136.94. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{19}F_2N_4O_2$ $[M+H]^+$ 421.1471, found 421.1466.



1as

1,3-Dibenzyl-5-((5-chloro-3-fluoropyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1as)

White solid. **M. p.**: 170.1 – 171.8 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.67 (s, 1 H), 7.88 (d, *J* = 1.9 Hz, 1 H), 7.49 (d, *J* = 7.3 Hz, 2 H), 7.41 – 7.28 (m, 8 H), 7.28 – 7.23 (m, 2 H), 5.22 (s, 2 H), 5.00 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.1, 149.6, 147.2, 145.5, 143.0 (d, $^{2}J_{C\text{-}F}$ = 10.5 Hz), 140.6 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 136.5, 135.7, 129.0, 128.5, 128.4, 128.1, 127.8, 125.0, 121.6 (d, $^{1}J_{C\text{-}F}$ = 18.0 Hz), 120.6, 115.9, 52.9, 45.4. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -135.00. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{19}ClFN_4O_2$ $[M+H]^+$ 437.1175, found 437.1162.

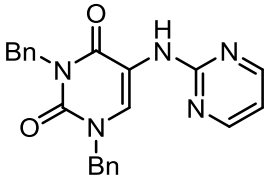


1at

1,3-Dibenzyl-5-(pyrazin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1at)

White solid. **M. p.**: 203.0 – 206.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.69 (s, 1 H),

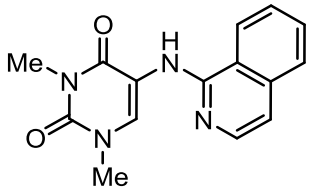
8.13 (s, 1 H), 8.01 (s, 1 H), 7.92 (s, 1 H), 7.47 (d, *J* = 7.2 Hz, 2 H), 7.40 – 7.17 (m, 9 H), 5.23 (s, 2 H), 5.00 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.2, 151.1, 149.6, 140.8, 136.4, 135.7, 135.3, 134.4, 129.0, 129.0, 128.5, 128.3, 128.0, 127.8, 125.3, 116.1, 53.0, 45.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{20}N_5O_2$ $[M+H]^+$ 386.1612, found 386.1612.



1au

1,3-Dibenzyl-5-(pyrimidin-2-ylamino)pyrimidine-2,4(1H,3H)-dione (1au)

White solid. **M. p.**: 112.5 – 118.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.59 (s, 1 H), 8.35 (d, *J* = 4.8 Hz, 2 H), 7.65 (s, 1 H), 7.49 (d, *J* = 7.2 Hz, 2 H), 7.39 – 7.33 (m, 4 H), 7.33 – 7.27 (m, 3 H), 7.27 – 7.20 (m, 1 H), 6.66 (t, *J* = 4.8 Hz, 1 H), 5.23 (s, 2 H), 4.99 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 159.9, 159.3, 157.8, 149.7, 136.6, 135.9, 129.0, 129.0, 128.5, 128.3, 128.0, 127.7, 125.9, 116.0, 112.6, 52.9, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{20}N_5O_2$ $[M+H]^+$ 386.1612, found 386.1613.

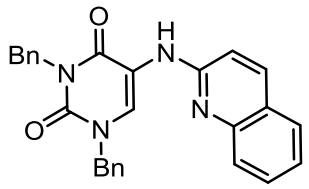


1av

1,3-Dibenzyl-5-(isoquinolin-1-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1av)

Pale yellow solid. **M. p.**: 171.2 – 172.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.89 (s, 1 H), 8.00 – 7.97 (m, 1 H), 7.94 (s, 1 H), 7.89 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 7.2 Hz, 1 H), 7.02 (d, *J* = 4.8 Hz, 1 H), 3.40 (s, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** 160.8, 151.1, 149.6, 140.3, 136.8, 130.0, 127.3,

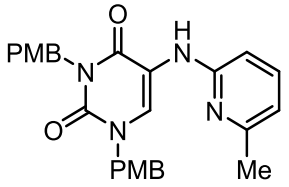
126.7, 126.2, 121.2, 118.7, 116.0, 113.0, 37.3, 28.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_4O_2$ $[M+H]^+$ 283.1190, found 283.1199



1aw

1,3-Dibenzyl-5-(quinolin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione (1aw)

White solid. **M. p.**: 201.1 – 202.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 9.31 (s, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.60 (d, *J* = 7.8 Hz, 1 H), 7.57 (d, *J* = 4.2 Hz, 2 H), 7.50 (d, *J* = 7.8 Hz, 2 H), 7.46 (d, *J* = 7.8 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.38 – 7.26 (m, 5 H), 7.22 (s, 1 H), 6.75 (d, *J* = 9.0 Hz, 1 H), 5.26 (s, 2 H), 5.05 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 160.4, 152.8, 149.7, 147.0, 137.2, 136.6, 135.8, 129.7, 129.1, 128.9, 128.6, 128.5, 128.5, 127.8, 127.5, 126.7, 125.4, 123.8, 123.5, 116.7, 113.5, 52.8, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{23}N_4O_2$ $[M+H]^+$ 435.1816, found 435.1814

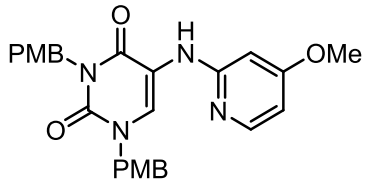


1ax

1,3-Bis(4-methoxybenzyl)-5-((6-methylpyridin-2-yl)amino)pyrimidine-2,4(1*H*,3*H*)-dione (1ax)

Pale yellow solid. **M. p.**: 167.5 – 168.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.84 (s, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.41 – 7.27 (m, 3 H), 6.97 – 6.87 (m, 3 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 7.6 Hz, 1 H), 6.41 (d, *J* = 8.4 Hz, 1 H), 5.17 (s, 2 H), 4.93 (s, 2

H), 3.79 (s, 3 H), 3.78 (s, 3 H), 2.34 (s, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.4, 159.7, 159.1, 156.1, 154.1, 149.6, 137.5, 130.6, 130.2, 129.0, 127.9, 123.8, 117.1, 114.4, 113.8, 113.7, 108.0, 55.3, 55.3, 52.0, 44.7, 24.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{26}H_{27}N_4O_4$ $[M+H]^+$ 459.2027, found 459.2020



1ay

1,3-Bis(4-methoxybenzyl)-5-((4-methoxypyridin-2-yl)amino)pyrimidine-2,4(1H,3H)-dione (1ay)

White solid. **M. p.**: 138.8 – 140.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.77 (s, 1 H), 7.96 (d, *J* = 6.0 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 6.95 – 6.74 (m, 5 H), 6.33 (dd, *J* = 6.0, 2.0 Hz, 1 H), 6.08 (d, *J* = 2.8 Hz, 1 H), 5.16 (s, 2 H), 4.92 (s, 2 H), 3.79 (s, 3 H), 3.77 (s, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.6, 160.5, 159.5, 159.1, 156.4, 149.5, 148.4, 130.6, 129.6, 129.0, 128.1, 124.6, 117.1, 114.3, 113.8, 104.2, 94.2, 55.3, 55.3, 55.0, 52.4, 44.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{26}H_{27}N_4O_5$ $[M+H]^+$ 475.1976, found 475.1974.

3. Graphical Supporting Information for Electrochemical Cycloamination

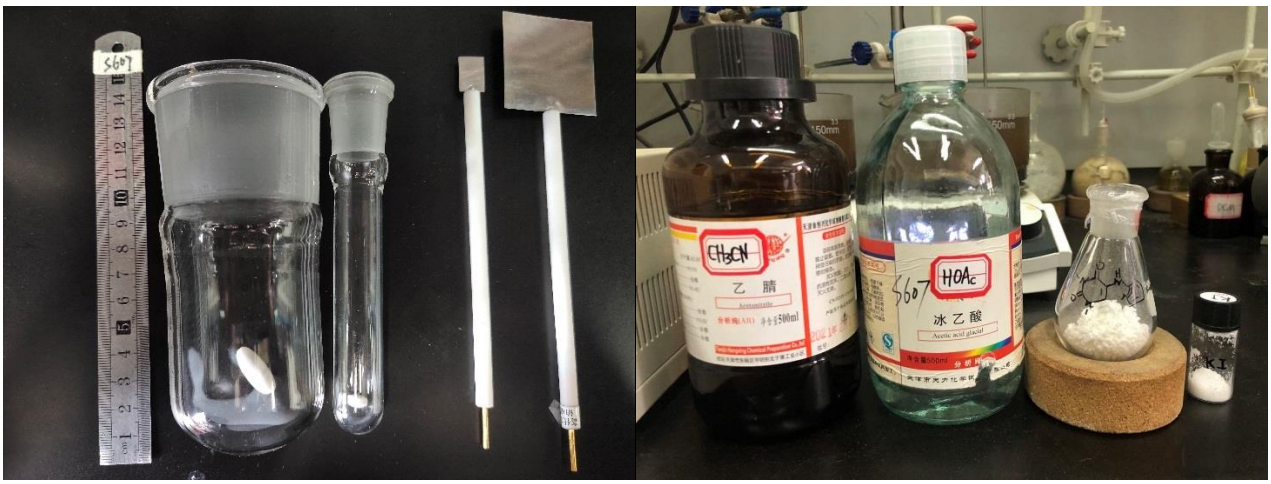


Figure S1. (*Left*): General equipment for electrolysis. **(*Right*):** All reagents for this reaction.

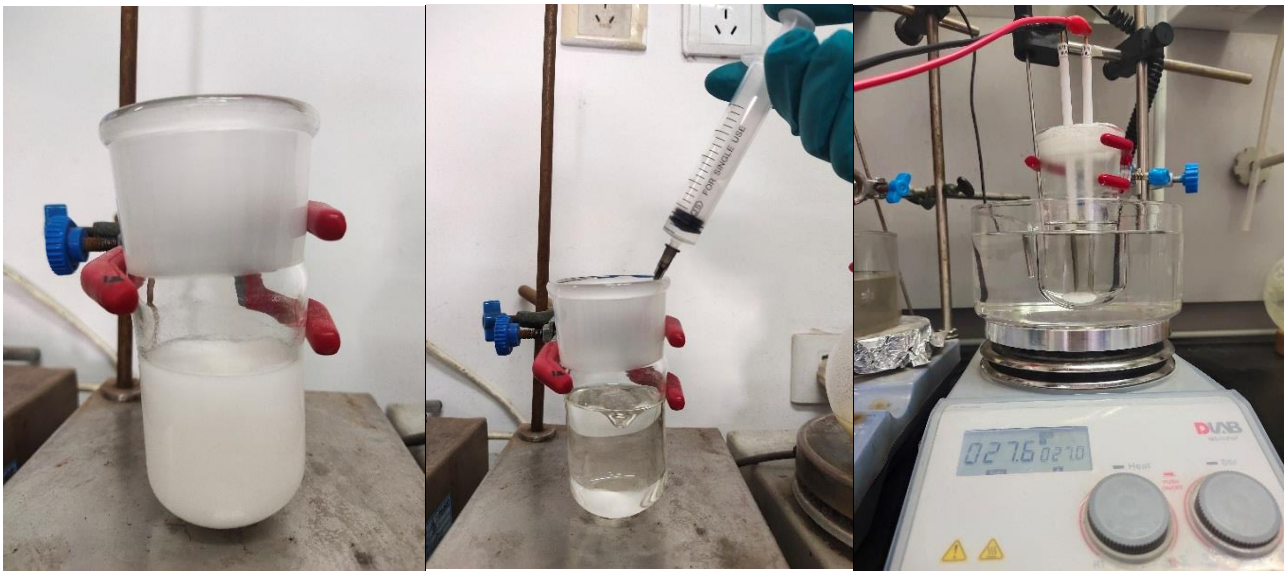


Figure S2. (*Left*): After adding CH_3CN (mL) to the electrolytic cell. **(*Center*):** After adding HOAc (mL) to the electrolytic cell. **(*Right*):** The mixture was placed in an oil bath preheated to 27 °C.

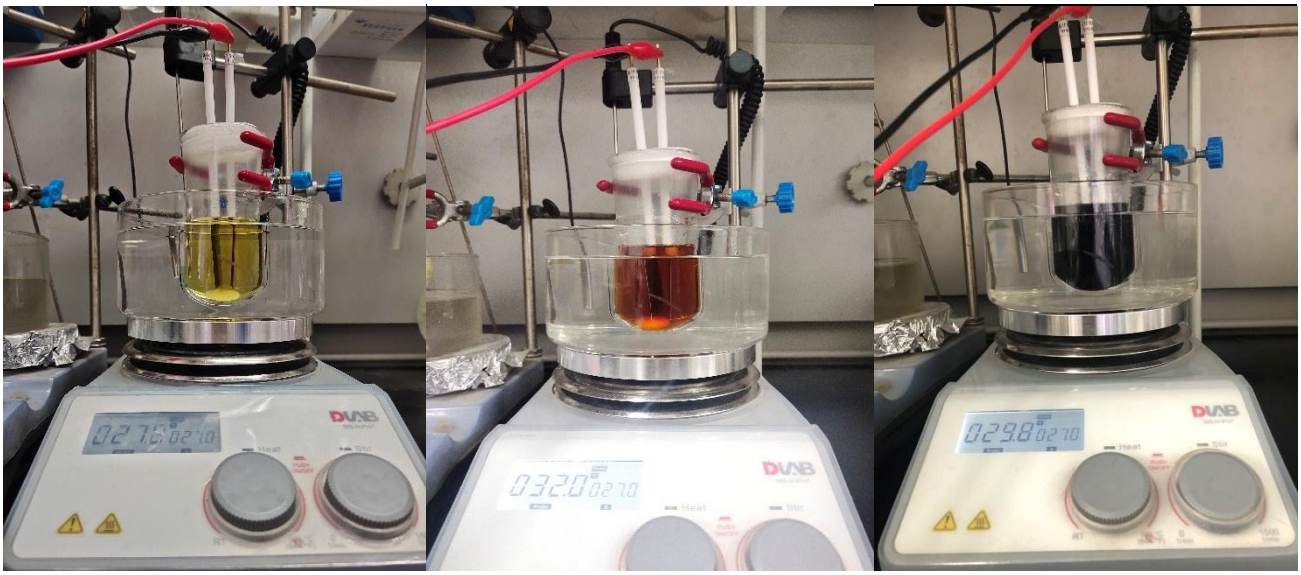


Figure S3. (*Left and Center*): The reaction mixture was subjected to constant current electrolysis (I = 50 mA). **(*Right*):** The reaction mixture after 21 h of electrolysis.

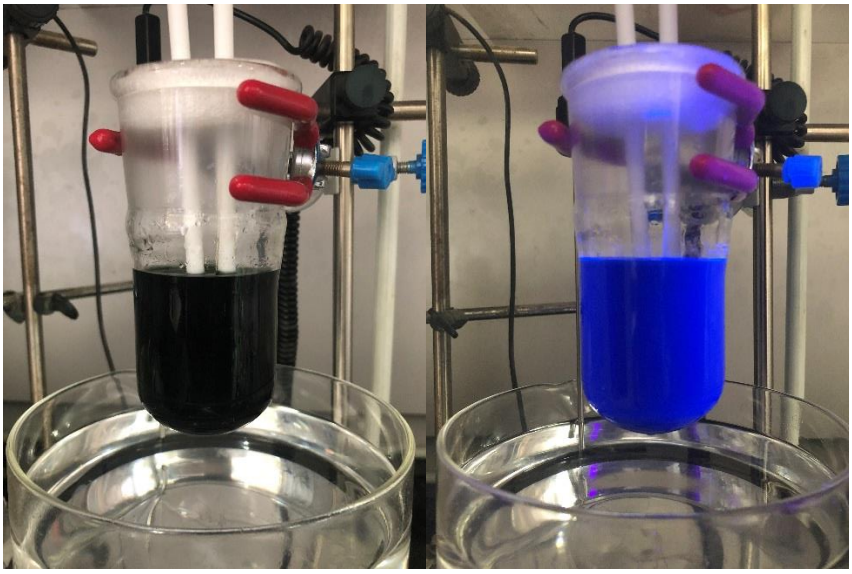
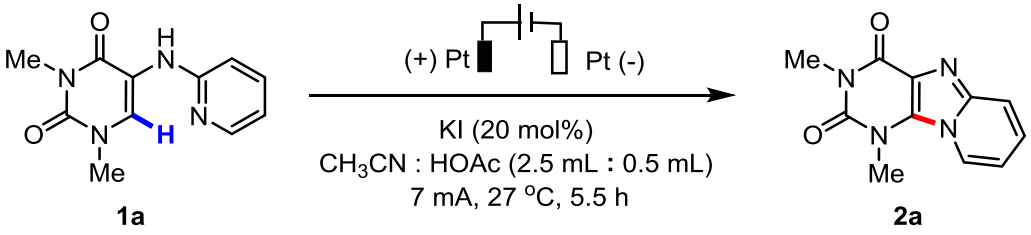


Figure S4. (*Left*): The mixture was removed from the oil bath. **(Right):** The mixture was under 365 nm ultraviolet irradiation

4. Optimization of the Reaction Conditions[a]



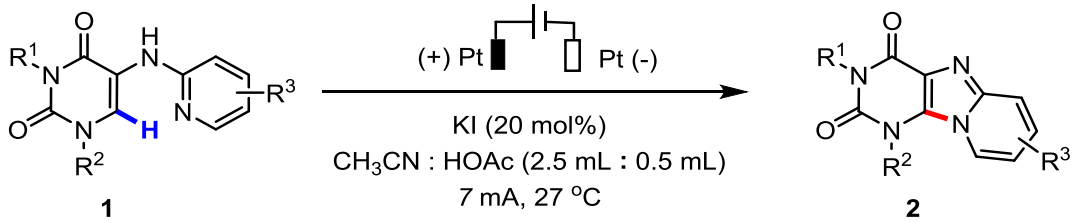
Entry	variation from standard conditions above	Yield (%)[b]
1	MeOH (3 mL)	95
2	EtOH (3 mL)	20
3	DMF (3 mL)	23
4	DMF : H_2O (2.8 mL :0.2 mL)	82
5	CH_3CN (3 mL)	13
6	CH_3CN : H_2O (2.5 mL :0.5 mL)	85
6	CH_3CN : HOAc (2.5 mL :0.5 mL)	99(96)[c]
7	20 mol% LiCl	16
8	20 mol% KBr	31
9	20 mol% HI	65
10	20 mol% NaI	89
11	20 mol% $^{n}Bu_4NI$	90
12	20 mol% DMMI[d]	88
13	10 mol% KI	67
14	15 mol% KI	69
15	No KI, $^{n}Bu_4NPF_6$ (0.2 mmol) as the electrolyte	trace
16	No KI, $LiClO_4$ (0.2 mmol) as the electrolyte	trace

17	3 mA, 24 h	15
18	5 mA, 8 h	44
19	9 mA, 4.8 h	90
20	10 mA, 3.5 h	72
21	11 mA, 3.5 h	43
22	graphite felt(+)/Pt(-)	92
23	graphite rod(+)/Pt(-)	62
24	Pt(+)/Ni form(-)	trace
25	Pt(+)/Fe sheet(-)	40
26	In the dark	91
27	No electric current	nr[e]

[a]Standard conditions: substrate **1a** (0.2 mmol), KI (20 mol%) in CH_3CN/HOAc (3 mL, v/v = 5/1), two platinum electrodes (each 15 × 10 × 2 mm^3), undivided cell, 27 °C, 7 mA (j_{anode} = 2.33 mA cm^{-2}), 5.5 h. [b]Yield determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. [c]Isolated yield in parentheses. [d]DMMI = 1,3-dimethylimidazolium iodide. [e]nr: no reaction.

5. General procedure for Electrochemical C−H Amination

5.1 General Procedure:

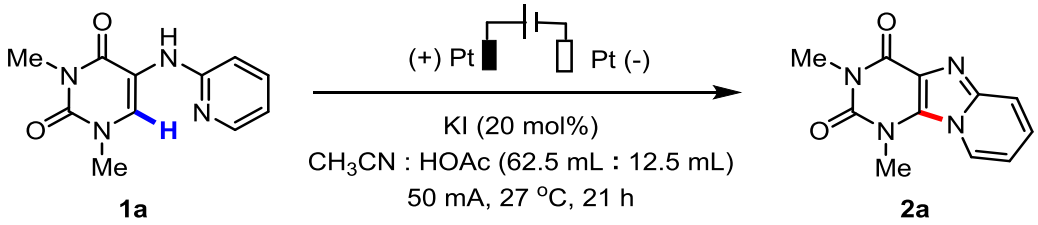


1 2

The electrocatalysis was carried out in an undivided cell equipped with two platinum electrodes (1.0 × 1.5 cm^2). The substrates **1** (0.2 mmol) and KI (6.7 mg, 0.04 mmol, 20 mol%) were dissolved in the mixture solvent CH_3CN/HOAc (2.5/0.5 mL). The electrolysis was carried out at 27 °C (oil bath temperature) using a constant current of 7.0 mA until complete consumption of the substrate (monitored by TLC or ^1H NMR analysis). After the reaction, the solvent was removed under reduced pressure. The resulting residue was chromatographed through silica gel eluting with hexane/AcOEt or CH_2Cl_2/MeOH to afford the corresponding product.

To obtain a satisfactory yield, a higher reaction temperature 50 °C or 60 °C was required in the cases of **1g, 1w, 1x, 1ao, 1ap, and 1ar.**

5.2 General Procedure for a Gram-Scale Experiment

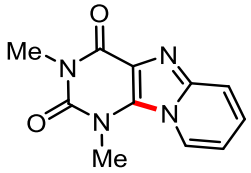


1a **2a**

The gram scale reaction was conducted in a 100 mL beaker-type cell equipped with two platinum electrodes (4.0 × 4.0 cm^2). The substrates **1** (1.16 g, 5.0 mmol) and KI (116 mg, 1.0 mmol, 0.2 equiv) were dissolved in the mixture solvent CH_3CN/HOAc (62.5/12.5 mL). The electrolysis was carried out at 27 °C (oil bath temperature) using a constant current of 50 mA for 21 hours (7.8 F mol^{-1}). After the reaction, the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of $Na_2S_2O_3$ and the product was then extracted with DCM (3 × 60 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was chromatographed

through silica gel eluting with CH_2Cl_2/MeOH to afford the corresponding product **3a** as white solid with 85% yield (980 mg).

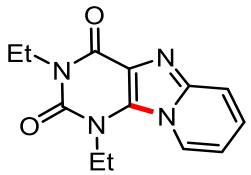
6. Characterization Data for Electrolysis Products



2a

1,3-Dimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2a)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1a** (46.4 mg, 0.02 mmol) at 27 °C for 5.5 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2a** (44.2 mg, 96%) as a white solid. **M. p.:** 285.5 – 285.7 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.46 (d, *J* = 7.2 Hz, 1 H), 7.57 (d, *J* = 9.6 Hz, 1 H), 7.25-7.13 (m, 1 H), 6.96 – 6.65 (m, 1 H), 4.00 (s, 3 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.5, 152.4, 144.5, 133.2, 126.7, 125.1, 121.4, 121.3, 115.0, 33.3, 30.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{11}H_{11}N_4O_2$ $[M+H]^+$ 231.0877, found 231.0879.

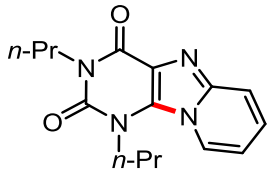


2b

1,3-Diethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2b)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1b** (52.1 mg, 0.2 mmol) at 27 °C for 6.6 h. Purification by column

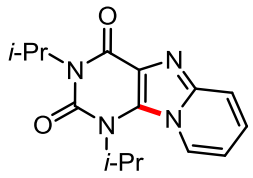
chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2b** (46.5 mg, 90%) as a white solid. **M. p.:** 231.1 – 232.6 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.24 (d, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 9.6 Hz, 1 H), 7.30 – 7.14 (m, 1 H), 6.94 – 6.81 (m, 1 H), 4.45 (q, *J* = 7.2 Hz, 2 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 1.49 (t, *J* = 7.2 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.2, 151.8, 144.5, 132.7, 126.5, 125.0, 121.7, 121.5, 115.3, 40.8, 38.5, 16.3, 14.2. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{15}N_4O_2$ $[M+H]^+$ 259.1190, found 259.1190.



2c

1,3-Dipropylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2c)

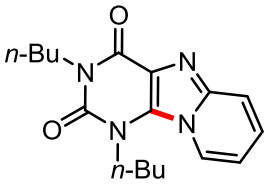
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1c** (57.7 mg, 0.2 mmol) at 27 °C for 7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2c** (49.8 mg, 87%) as a white solid. **M. p.:**164.7 – 165.1 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.15 (d, *J* = 7.2 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.26 – 7.14 (m, 1 H), 6.94 – 6.78 (m, 1 H), 4.42 – 4.35 (m, 2 H), 4.10 – 3.97 (m, 2 H), 1.90 – 1.81 (m, 2 H), 1.74 – 1.65 (m, 2 H), 1.06 (t, *J* = 7.8 Hz, 3 H), 0.96 (t, *J* = 7.8 Hz, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.4, 152.2, 144.5, 132.7, 126.5, 125.0, 121.7, 121.5, 115.4, 46.8, 44.9, 24.6, 22.4, 12.4, 11.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{19}N_4O_2$ $[M+H]^+$ 287.1503, found 287.1504.



2d

1,3-Diisopropylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2d)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1d** (57.7 mg, 0.2 mmol) at 27 °C for 2.6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2d** (56.7 mg, 99%) as a yellow solid. **M. p.:** 164.8 – 165.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 7.2 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.22 – 7.09 (m, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 5.39 – 5.23 (m, 1 H), 4.76 – 4.61 (m, 1 H), 1.72 (d, *J* = 7.2 Hz, 6 H), 1.49 (d, *J* = 6.6 Hz, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.9, 150.5, 143.2, 131.6, 125.1, 123.8, 121.1, 120.5, 113.9, 52.2, 46.0, 20.7, 19.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{19}N_4O_2$ $[M+H]^+$ 287.1503, found 287.1505.

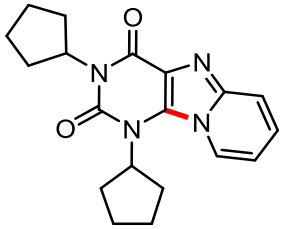


2e

1,3-Dibutylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2e)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1e** (63.3 mg, 0.2 mmol) at 27 °C for 7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2e** (62.3 mg, 99%) as a white solid. **M. p.:** 91.6 – 92.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 7.2 Hz, 1 H), 7.64 (d, *J* = 9.6 Hz, 1 H), 7.22 – 7.12 (m, 1 H), 6.94 – 6.79 (m, 1 H), 4.45 – 4.32 (m, 2

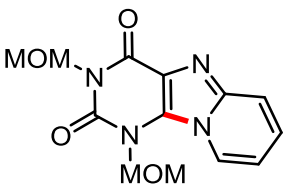
H), 4.16 – 4.03 (m, 2 H), 1.90 – 1.77 (m, 2 H), 1.72 – 1.61 (m, 2 H), 1.57 – 1.45 (m, 2 H), 1.45 – 1.32 (m, 2 H), 1.02 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 158.0, 150.9, 143.2, 131.0, 125.2, 123.3, 120.6, 120.6, 114.2, 44.1, 42.1, 32.1, 29.9, 20.2, 19.8, 13.8, 13.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{23}N_4O_2$ $[M+H]^+$ 315.1816, found 315.1817.



2f

1,3-Dicyclopentylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2f)

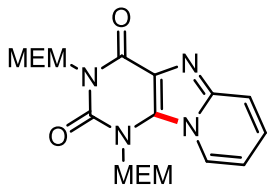
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1f** (68.1 mg, 0.2 mmol) at 27 °C for 4.2 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2f** (54.1 mg, 80%) as a white solid. **M. p.:** 213.4 – 215.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 (d, *J* = 7.2 Hz, 1 H), 7.60 (d, *J* = 9.2 Hz, 1 H), 7.23 – 7.05 (m, 1 H), 6.84 (t, *J* = 6.8 Hz, 1 H), 5.56 – 5.35 (m, 1 H), 4.91 – 4.68 (m, 1 H), 2.55 – 2.27 (m, 2 H), 2.26 – 1.90 (m, 8 H), 1.89 – 1.76 (m, 2 H), 1.76 – 1.47 (m, 4 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.0, 150.2, 143.1, 132.0, 125.0, 123.7, 121.0, 120.5, 113.8, 60.2, 53.7, 30.2, 28.2, 25.7, 25.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{19}H_{23}N_4O_2$ $[M+H]^+$ 339.1816, found 339.1817.



2g

1,3-Bis(methoxymethyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2g)

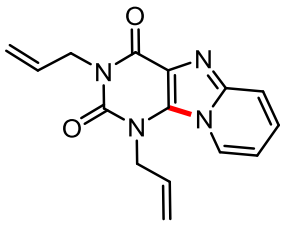
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1g** (58.5 mg, 0.2 mmol) at 50 °C for 6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2g** (57.5 mg, 99%) as a white solid. **M. p.:** 170.1 – 170.8 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.53 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 9.0 Hz, 1 H), 7.24 – 7.15 (m, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 5.73 (s, 2 H), 5.52 (s, 2 H), 3.59 (s, 3 H), 3.46 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.1, 151.7, 143.9, 131.2, 126.1, 125.2, 120.1, 119.8, 114.2, 75.1, 72.8, 57.9, 57.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{15}N_4O_4$ $[M+H]^+$ 291.1088, found 291.1085.



2h

1,3-Bis((2-methoxyethoxy)methyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2h)

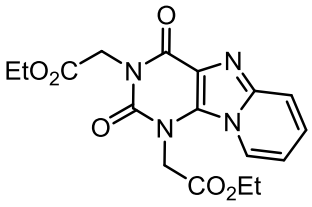
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1h** (76.1 mg, 0.2 mmol) at 27 °C for 3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 50/1) yielded **2h** (53.4 mg, 70%) as a yellow solid. **M. p.:** 72.8 – 73.4 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.61 (d, *J* = 7.2 Hz, 1 H), 7.62 (d, *J* = 9.6 Hz, 1 H), 7.24 – 7.18 (m, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 5.80 (s, 2 H), 5.63 (s, 2 H), 3.98 – 3.91 (m, 2 H), 3.86 – 3.80 (m, 2 H), 3.60 – 3.54 (m, 2 H), 3.54 – 3.48 (m, 2 H), 3.32 (s, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.2, 151.7, 143.9, 131.2, 126.1, 125.3, 120.2, 119.8, 114.1, 73.9, 71.9, 71.7, 71.2, 69.8, 68.9, 59.0, 59.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{23}N_4O_6$ $[M+H]^+$ 379.1612, found 379.1619.



2i

1,3-Diallylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2i)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1i** (56.9 mg, 0.2 mmol) at 27 °C for 5.7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2i** (40.7 mg, 72%) as a white solid. **M. p.:** 139.4 – 142.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 7.2 Hz, 1 H), 7.61 (d, *J* = 9.6 Hz, 1 H), 7.24 – 7.13 (m, 1 H), 6.83 (t, *J* = 7.8 Hz, 1 H), 6.23 – 6.10 (m, 1 H), 6.03 – 5.89 (m, 1 H), 5.37 (d, *J* = 10.8 Hz, 1 H), 5.29 (d, *J* = 16.8 Hz, 1 H), 5.26 – 5.15 (m, 2 H), 5.07 (s, 2 H), 4.74 (d, *J* = 6 Hz, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.7, 150.6, 143.3, 131.8, 131.8, 131.2, 125.6, 124.0, 120.2, 120.2, 118.0, 117.7, 113.9, 46.3, 44.2. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_4O_2$ $[M+H]^+$ 283.1190, found 183.1194.

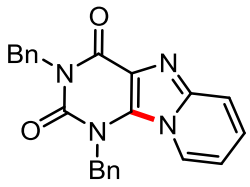


2j

Diethyl 2,2'-(2,4-dioxopyrido[1,2-*e*]purine-1,3(2*H*,4*H*)-diyl)diacetate (2j)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1j** (75.3 mg, 0.2 mmol) at 27 °C for 4.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2j** (67.4 mg, 90%) as a white

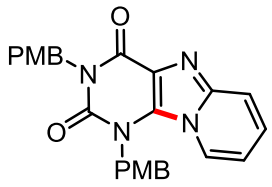
solid. **M. p.:** 88.2 – 89.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 9.2 Hz, 1 H), 7.21 – 7.10 (m, 1 H), 6.88 – 6.69 (m, 1 H), 5.19 (s, 2 H), 4.80 (s, 2 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 1.27 – 1.19 (m, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.7, 167.5, 157.4, 150.8, 143.4, 131.0, 125.7, 122.9, 120.3, 120.2, 114.4, 62.8, 61.6, 45.8, 43.0, 14.1, 14.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{19}N_4O_6$ $[M+H]^+$ 375.1299, found 375.1305.



2k

1,3-Dibenzylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2k)

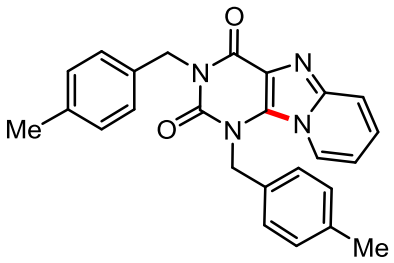
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1k** (77.0 mg, 0.2 mmol) at 50 °C for 5.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2k** (73.4 mg, 96%) as a white solid. **M. p.:** 168.1 – 169.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 7.2 Hz,, 1 H), 7.59 (d, *J* = 9.0 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 2 H), 7.37 (t, *J* = 7.8 Hz, 2 H), 7.34 – 7.28 (m, 3 H), 7.26 – 7.17 (m, 3 H), 7.12 – 7.03 (m, 1 H), 6.59 (t, *J* = 7.2 Hz, 1 H), 5.64 (s, 2 H), 5.36 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.1, 151.4, 143.5, 136.9, 135.2, 131.3, 129.6, 129.1, 128.4, 128.3, 127.7, 125.5, 125.2, 123.7, 120.5, 120.2, 113.9, 48.0, 45.4. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{19}N_4O_2$ $[M+H]^+$ 383.1503, found 383.1493.



2l

1,3-Bis(4-methoxybenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2l)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1l** (88.9 mg, 0.2 mmol) at 27 °C for 2.8 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2l** (69.9 mg, 79%) as a white solid. **M. p.:** 216.2 – 216.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.97 (d, *J* = 7.2 Hz, 1 H), 7.58 (d, *J* = 9.0 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 7.10 – 7.05 (m, 1 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 6.61 (t, *J* = 7.2 Hz, 1 H), 5.56 (s, 2 H), 5.29 (s, 2 H), 3.78 (d, *J* = 2.4 Hz, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 159.5, 159.1, 158.2, 151.4, 143.4, 131.3, 130.8, 129.3, 127.0, 126.6, 125.4, 123.8, 120.6, 120.2, 115.0, 113.9, 113.7, 55.3, 55.2, 47.6, 44.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_4O_4$ $[M+H]^+$ 443.1714, found 443.1714.

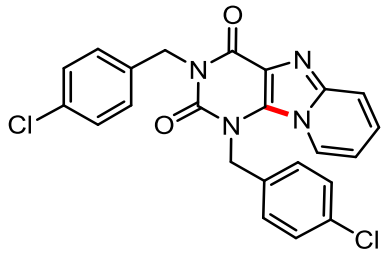


2m

1,3-Bis(4-methylbenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2m)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1m** (82.5 mg, 0.2 mmol) at 40 °C for 4.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2m** (52.5 mg, 64%) as a

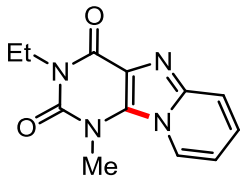
white solid. **M. p.:** 255.3 – 256.7 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 7.96 (d, *J* = 7.2 Hz, 1 H), 7.51 (d, *J* = 9.0 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.13 – 7.04 (m, 5 H), 6.64 – 6.55 (m, 1 H), 5.57 (s, 2 H), 5.24 (s, 2 H), 2.30 (d, *J* = 7.2 Hz, 6 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.5, 152.6, 144.7, 139.4, 138.6, 135.6, 133.7, 132.9, 131.3, 130.3, 129.8, 126.8, 126.5, 125.4, 121.7, 121.1, 115.0, 49.0, 46.3, 22.1, 22.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_4O_2$ $[M+H]^+$ 411.1816, found 411.1795.



2n

1,3-Bis(4-chlorobenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2n)

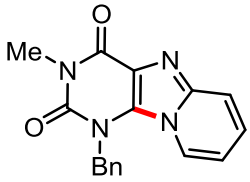
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1n** (90.7 mg, 0.2 mmol) at 40 °C for 6.7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 50/1) yielded **2n** (36.1 mg, 40%) as a white solid. **M. p.:** 220.6 – 222.8 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 7.2 Hz, 1 H), 7.54 (d, *J* = 9.0 Hz, 1 H), 7.46 (d, *J* = 9.0 Hz, 2 H), 7.37 – 7.30 (m, 2 H), 7.25 – 7.20 (m, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 7.11 – 7.04 (m, 1 H), 6.67 – 6.57 (m, 1 H), 5.59 (s, 2 H), 5.25 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.9, 151.2, 143.5, 135.3, 134.3, 133.6, 133.6, 131.1, 130.7, 129.8, 128.6, 126.7, 125.7, 123.4, 120.4, 120.2, 114.2, 47.6, 44.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{17}Cl_2N_4O_2$ $[M+H]^+$ 451.0723, found 451.0725.



2o

3-Ethyl-1-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2o)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1o** (49.3 mg, 0.2 mmol) at 27 °C for 5 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2o** (42.5 mg, 87%) as a white solid. **M. p.:** 240.1 – 240.7 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.46 (d, *J* = 7.2 Hz, 1 H), 7.58 (d, *J* = 9.0 Hz, 1 H), 7.22 – 7.10 (m, 1 H), 6.84 (t, *J* = 6.6 Hz, 1 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 4.04 (s, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.8, 150.8, 143.2, 131.6, 125.4, 123.5, 120.3, 120.2, 113.9, 37.5, 32.0, 13.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{13}N_4O_2$ $[M+H]^+$ 245.1033, found 245.1024.

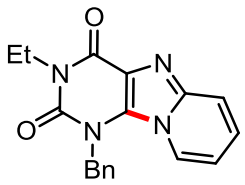


2p

1-Benzyl-3-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2p)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1p** (61.7 mg, 0.2 mmol) at 27°C for 5.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2p** (57.6 mg, 94%) as a white solid. **M. p.:** 254.4 – 255.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$) :** δ 7.93 (d, *J* = 7.2 Hz, 1 H), 7.51 (d, *J* = 9.6 Hz, 1 H), 7.39 – 7.33 (m, 2 H), 7.32 – 7.27 (m, 1 H), 7.24 – 7.20 (m, 2 H), 7.10 – 7.04 (m, 1 H), 6.64 – 6.56 (m, 1 H), 5.66 (s, 2 H), 3.50 (s, 3 H). **^{13}C NMR**

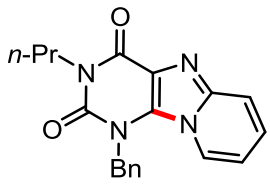
(150 MHz, $CDCl_3$): δ 158.3, 151.5, 143.3, 135.3, 131.2, 129.6, 128.3, 125.5, 125.3, 123.8, 120.3, 120.0, 113.9, 48.0, 29.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{15}N_4O_2$ $[M+H]^+$ 307.1190, found 307.1193.



2q

1-Benzyl-3-ethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2q)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1q** (64.5 mg, 0.2 mmol) at 40 °C for 4.2 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2q** (57.7 mg, 90%) as a yellow solid. **M. p.:** 214.8 – 215.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 7.6 Hz, 1 H), 7.57 (d, *J* = 9.6 Hz, 1 H), 7.43 – 7.36 (m, 2 H), 7.35 – 7.28 (m, 1 H), 7.23 (d, *J* = 7.2 Hz, 2 H), 7.14 – 7.02 (m, 1 H), 6.68 – 6.54 (m, 1 H), 5.67 (s, 2 H), 4.23 (q, *J* = 6.8 Hz, 2 H), 1.32 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.9, 151.1, 143.3, 135.4, 131.3, 129.6, 128.3, 125.4, 125.3, 123.7, 120.6, 120.2, 113.8, 47.9, 37.7, 13.2. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{17}N_4O_2$ $[M+H]^+$ 321.1346, found 321.1342.

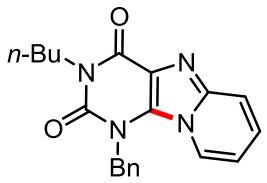


2r

1-Benzyl-3-propylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2r)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1r** (67.3 mg, 0.2 mmol) at 40 °C for 8.3 h. Purification by column

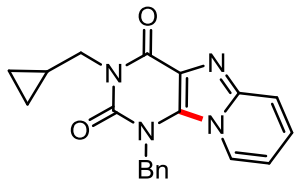
chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2r** (63.5 mg, 95%) as a white solid. **M. p.:** 179.5 – 180.0 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.97 (d, *J* = 7.2 Hz, 1 H), 7.60 – 7.50 (m, 1 H), 7.45 – 7.20 (m, 5 H), 7.17 – 7.02 (m, 1 H), 6.62 (t, *J* = 7.2 Hz, 1 H), 5.68 (s, 2 H), 4.21 – 3.96 (m, 2 H), 1.85 – 1.64 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.0, 151.3, 143.3, 135.4, 131.2, 129.6, 128.3, 125.5, 125.3, 123.8, 120.4, 120.0, 113.8, 47.9, 43.9, 21.1, 11.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{19}H_{19}N_4O_2$ $[M+H]^+$ 335.1503, found 335.1505.



2s

1-Benzyl-3-butylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2s)

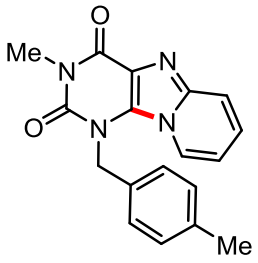
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1s** (70.0 mg, 0.2 mmol) at 27 °C for 4.2 h. Purification by column chromatography on silica gel (hexane/EtOAc: 50/1) yielded **2s** (66.2 mg, 95%) as a white solid. **M. p.:** 142.8 – 145.1 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 7.96 (d, *J* = 7.8 Hz, 1 H), 7.56 (d, *J* = 9.0 Hz, 1 H), 7.44 – 7.36 (m, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.25 (d, *J* = 7.2 Hz, 2 H), 7.16 – 7.08 (m, 1 H), 6.67 – 6.58 (m, 1 H), 5.65 (s, 2 H), 4.17 – 4.07 (m, 2 H), 1.77 – 1.61 (m, 2 H), 1.48 – 1.34 (m, 2 H), 0.97 (t, *J* = 7.8 Hz, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.4, 152.6, 144.6, 137.0, 132.8, 130.8, 129.4, 126.8, 126.6, 125.2, 121.7, 121.2, 115.0, 49.1, 43.5, 31.2, 21.6, 14.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{20}H_{21}N_4O_2$ $[M+H]^+$ 345.1659, found 345.1662.



2t

1-Benzyl-3-(cyclopropylmethyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2t)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1t** (69.7 mg, 0.2 mmol) at 27 °C for 3.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2t** (67.9 mg, 98%) as a white solid. **M. p.:** 190.6 – 195.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.97 (d, *J* = 7.2 Hz, 1 H), 7.58 (d, *J* = 9.2 Hz, 1 H), 7.46 – 7.19 (m, 5 H), 7.15 – 7.04 (m, 1 H), 6.62 (t, *J* = 6.8 Hz, 1 H), 5.69 (s, 2 H), 4.07 (d, *J* = 7.2 Hz, 2 H), 1.45 – 1.31 (m, 1 H), 0.62 – 0.36 (m, 4 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.3, 151.6, 143.3, 135.4, 131.3, 129.6, 128.3, 125.5, 125.3, 123.8, 120.5, 120.1, 113.9, 47.9, 46.7, 10.1, 3.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{20}H_{19}N_4O_2$ $[M+H]^+$ 347.1503, found 347.1449.

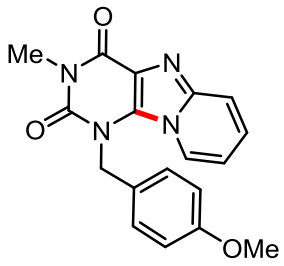


2u

3-Methyl-1-(4-methylbenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2u)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1u** (64.5 mg, 0.2 mmol) at 40 °C for 5 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2u** (55.1 mg, 86%) as a white solid. **M. p.:** 273.6 – 274.1 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 7.98 (d, *J* = 7.2 Hz, 1

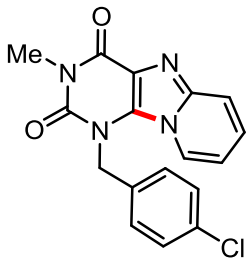
H), 7.53 (d, *J* = 9.0 Hz, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.17 – 7.07 (m, 3 H), 6.63 (t, *J* = 7.2 Hz, 1 H), 5.61 (s, 2 H), 3.49 (s, 3 H), 2.32 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 158.3, 151.5, 143.3, 138.1, 132.5, 131.5, 130.0, 125.5, 125.3, 124.1, 120.3, 119.9, 113.7, 47.7, 28.7, 20.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{17}N_4O_2$ $[M+H]^+$ 321.1346, found 321.1342.



2v

1-(4-Methoxybenzyl)-3-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2v)

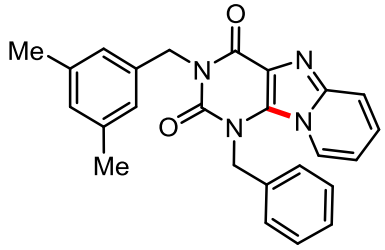
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1v** (67.7 mg, 0.2 mmol) at 27 °C for 3.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2v** (49.1 mg, 73%) as a white solid. **M. p.:** 220.1 – 223.0 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.2 Hz, 1 H), 7.58 (d, *J* = 9.6 Hz, 1 H), 7.16 (d, *J* = 9.0 Hz, 2 H), 7.13 – 7.07 (m, 1 H), 6.92 – 6.87 (m, 2 H), 6.68 – 6.61 (m, 1 H), 5.60 (s, 2 H), 3.78 (s, 3 H), 3.55 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 159.5, 158.3, 151.5, 143.4, 131.3, 127.0, 126.6, 125.5, 123.9, 120.4, 120.2, 115.0, 113.9, 55.4, 47.6, 29.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{17}N_4O_3$ $[M+H]^+$ 337.1295, found 337.1295.



2w

1-(4-Chlorobenzyl)-3-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2w)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1w** (68.6 mg, 0.2 mmol) at 60 °C for 4.8 h. Purification by column chromatography on silica gel (hexane/EtOAc: 1/1) yielded **2w** (57.3 mg, 84%) as a white solid. **M. p.:** 286.2 – 287.1 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 7.91 (d, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 9.6 Hz, 1 H), 7.41 – 7.35 (m, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 7.19 – 7.11 (m, 1 H), 6.73 – 6.64 (m, 1 H), 5.62 (s, 2 H), 3.50 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 158.2, 151.5, 143.4, 134.2, 134.0, 131.2, 129.6, 126.9, 125.6, 123.6, 120.3, 120.0, 114.0, 47.4, 28.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{14}N_4O_2$ $[M+H]^+$ 341.0800, found 341.0808.

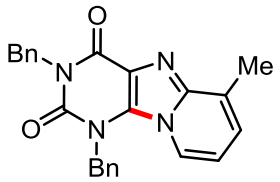


2x

1-Benzyl-3-(3,5-dimethylbenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2x)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1x** (82.5 mg, 0.2 mmol) at 60 °C for 12 h. Purification by column chromatography on silica gel (hexane/EtOAc: 1/1) yielded **2x** (42.7 mg, 52%) as a white

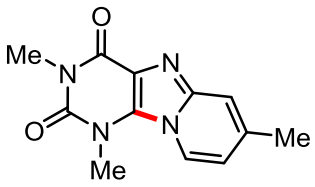
solid. **M. p.:** 204.6—206.3 °C. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ 7.94 (d, *J* = 7.2 Hz, 1 H), 7.56 (d, *J* = 9.2 Hz, 1 H), 7.40 – 7.33 (m, 2 H), 7.33 – 7.27 (m, 1 H), 7.24 – 7.18 (m, 2 H), 7.13 (s, 2 H), 7.06 (ddd, *J* = 9.4, 6.6, 0.8 Hz, 1 H), 6.88 (s, 1 H), 6.62 – 6.53 (m, 1 H), 5.64 (s, 2 H), 5.28 (s, 2 H), 2.26 (s, 6 H). **^{13}C NMR (100 MHz, CD_2Cl_2):** δ 158.2, 151.3, 143.4, 137.9, 136.8, 135.2, 131.3, 129.6, 129.3, 128.3, 126.6, 125.5, 125.3, 123.7, 120.5, 120.1, 113.9, 47.9, 45.3, 21.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_4O_2$ $[M+H]^+$ 411.1816, found 411.1808.



2y

1,3-Dibenzyl-6-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2y)

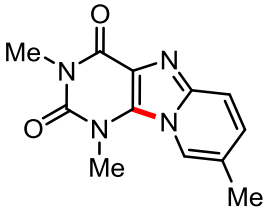
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1y** (79.7 mg, 0.2 mmol) at 27 °C for 4 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2y** (57.9 mg, 73%) as a white solid. **M. p.:** 216.2 – 216.5 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.2 Hz, 1 H), 7.62 – 7.49 (m, 2 H), 7.38 – 7.32 (m, 2 H), 7.31 – 7.26 (m, 3 H), 7.25 – 7.21 (m, 1 H), 7.21 – 7.16 (m, 2 H), 6.87 (d, *J* = 6.6 Hz, 1 H), 6.50 (t, *J* = 7.2 Hz, 1 H), 5.62 (s, 2 H), 5.34 (s, 2 H), 2.58 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.3, 151.4, 144.2, 137.0, 135.2, 131.7, 130.3, 129.5, 129.2, 128.4, 128.2, 127.6, 125.3, 123.9, 121.5, 120.1, 114.0, 47.9, 45.3, 17.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{21}N_4O_2$ $[M+H]^+$ 397.1659, found 397.1659.



2z

1,3,7-trimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2z)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1z** (49.3 mg, 0.2 mmol) at 27 °C for 5.1 h. Purification by column chromatography on silica gel (hexane/EtOAc: 1/1) yielded **2z** (38.6 mg, 79%) as a white solid. **M. p.:** 278.6 – 279.5 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.33 (d, *J* = 7.2 Hz, 1 H), 7.31 – 7.27 (m, 1 H), 6.68 (dd, *J* = 7.2, 1.2 Hz, 1 H), 3.97 (s, 3 H), 3.42 (s, 3 H), 2.37 (d, *J* = 1.2 Hz, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.6, 152.4, 145.1, 138.1, 133.1, 124.2, 121.0, 119.0, 117.9, 33.2, 29.9, 22.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{13}N_4O_2$ $[M+H]^+$ 245.1033, found 245.1032.

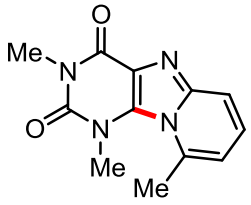


2aa

1,3,8-trimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2aa)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1aa** (49.3 mg, 0.2 mmol) at 40 °C for 24 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2aa** (43.5 mg, 89%) as a white solid. **M. p.:** 306.5 – 307.2 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.22 (s, 1 H), 7.50 (d, *J* = 9.6 Hz, 1 H), 7.07 (d, *J* = 9.6 Hz, 1 H), 4.00 (s, 3 H), 3.44 (s, 3 H), 2.33 (s,

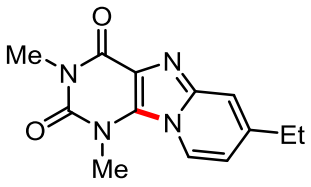
3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.6, 152.5, 143.9, 132.9, 130.4, 125.0, 122.1, 121.2, 120.5, 33.4, 29.9, 19.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{13}N_4O_2$ $[M+H]^+$ 245.1033, found 245.1042.



2ab

1,3,9-Trimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ab)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ab** (49.3 mg, 0.2 mmol) at 27 °C for 5.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ab** (46.4 mg, 95%) as a white solid. **M. p.:** 243.2 – 244.1 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ 7.41 (d, *J* = 9.2 Hz, 1 H), 7.26 – 7.16 (m, 1 H), 6.78 (d, *J* = 6.8 Hz, 1 H), 3.58 (s, 3 H), 3.27 (s, 3 H), 2.82 (s, 3 H). **^{13}C NMR (100 MHz, DMSO-d_6):** δ 158.9, 154.0, 145.0, 137.0, 134.6, 127.0, 121.8, 116.8, 115.4, 42.2, 28.6, 21.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{13}N_4O_2$ $[M+H]^+$ 245.1033, found 245.1021.

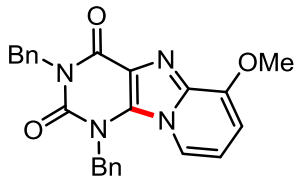


2ac

7-Ethyl-1,3-dimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ac)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ac** (52.1 mg, 0.2 mmol) at 27 °C for 6.6 h. Purification by column

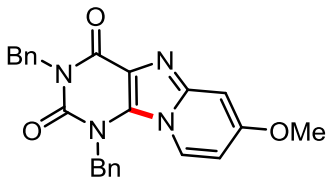
chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ac** (43.9 mg, 85%) as a white solid. **M. p.:** 268.6 – 267.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.35 (d, *J* = 7.8 Hz, 1 H), 7.23 (s, 1 H), 6.70 (dd, *J* = 7.8, 1.2 Hz, 1 H), 4.01 (s, 3 H), 3.44 (s, 3 H), 2.67 (q, *J* = 7.8 Hz, 2 H), 1.28 (t, *J* = 7.8 Hz, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.1, 151.0, 143.8, 142.7, 131.4, 123.0, 119.6, 116.1, 115.8, 32.0, 28.9, 28.2, 13.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{15}N_4O_2$ $[M+H]^+$ 259.1190, found 259.1190.



2ad

1,3-Dibenzyl-6-methoxypyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ad)

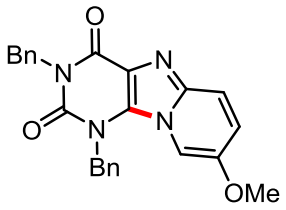
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ad** (82.9 mg, 0.2 mmol) at 27 °C for 7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ad** (66.0 mg, 80%) as a white solid. **M. p.:** 250.6 – 251.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 7.2 Hz, 2 H), 7.45 (d, *J* = 6.6 Hz, 1 H), 7.38 – 7.23 (m, 6 H), 7.16 (d, *J* = 7.2 Hz, 2 H), 6.33 (t, *J* = 7.2 Hz, 1 H), 5.91 (d, *J* = 7.8 Hz, 1 H), 5.60 (s, 2 H), 5.29 (s, 2 H), 3.86 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.6, 151.3, 149.7, 138.3, 137.0, 135.3, 131.9, 129.7, 129.5, 128.3, 128.1, 127.8, 125.2, 119.5, 116.4, 114.0, 100.7, 56.0, 47.8, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{21}N_4O_3$ $[M+H]^+$ 413.1608, found 413.1608.



2ae

1,3-Dibenzyl-7-methoxypyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ae)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ae** (82.9 mg, 0.2 mmol) at 27 °C for 5 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ae** (58.6 mg, 71%) as a white solid. **M. p.:** 217.8 – 218.1 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.31 – 7.26 (m, 3 H), 7.23 (t, *J* = 7.2 Hz, 1 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 6.69 (s, 1 H), 6.31 (dd, *J* = 7.8, 1.8 Hz, 1 H), 5.60 (s, 2 H), 5.32 (s, 2 H), 3.80 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.0, 157.8, 151.3, 145.3, 137.0, 135.1, 131.3, 129.6, 129.0, 128.4, 128.3, 127.6, 125.2, 124.1, 120.1, 110.2, 95.3, 55.7, 47.9, 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{21}N_4O_3$ $[M+H]^+$ 413.1608, found 413.1591.

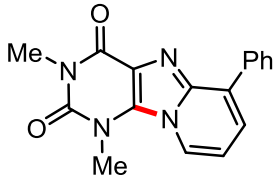


2af

1,3-Dibenzyl-8-methoxypyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2af)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1af** (82.9 mg, 0.2 mmol) at 50 °C for 6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2af** (61.0 mg, 74%) as a white solid. **M. p.:** 210.2 – 211.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 7.2 Hz, 2 H), 7.44 – 7.36 (m, 3 H), 7.35 – 7.26 (m, 4 H), 7.26 – 7.20 (m, 3 H), 6.85 (dd, *J* = 9.6, 1.8 Hz, 2 H), 5.65 (s, 2 H), 5.34 (s, 2 H), 3.36 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.1, 151.6, 149.7, 141.1, 137.0, 135.8, 132.0, 129.7, 129.1, 128.4, 128.4, 127.6,

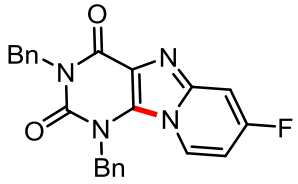
125.1, 122.4, 120.7, 119.9, 104.6, 55.8, 48.1 45.3. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{21}N_4O_3$ $[M+H]^+$ 413.1608, found 413.1607.



2ag

1,3-Dimethyl-6-phenylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ag)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ag** (61.7 mg, 0.2 mmol) at 27 °C for 5 h. Purification by column chromatography on silica gel (hexane/EtOAc: 1/1) yielded **2ag** (33.7 mg, 55%) as a white solid. **M. p.:** 307.5 – 309.1 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.52 – 8.44 (m, 1 H), 7.99 – 7.92 (m, 2 H), 7.57 – 7.41 (m, 3 H), 7.32 (dd, *J* = 6.6, 0.6 Hz, 1 H), 6.95 (t, *J* = 7.2 Hz, 1 H), 4.03 (s, 3 H), 3.46 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.6, 152.5, 143.7, 136.9, 133.9, 133.6, 130.3, 130.1, 129.8, 125.1, 124.0, 121.4, 115.2, 33.4, 30.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{15}N_4O_2$ $[M+H]^+$ 307.1190, found 307.1184.

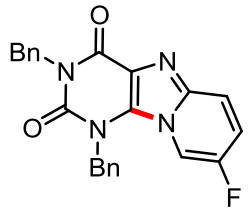


2ah

1,3-Dibenzyl-7-fluoropyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ah)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ah** (80.5 mg, 0.2 mmol) at 27 °C for 4.6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ah** (68.9 mg, 86%) as a white solid. **M. p.:** 179.6 – 180.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 7.6,

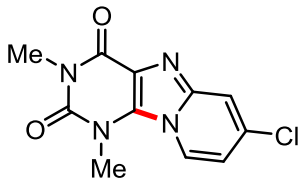
5.2 Hz, 1 H), 7.57 – 7.50 (m, 2 H), 7.41 – 7.22 (m, 6 H), 7.21 – 7.14 (m, 3 H), 6.55 – 6.47 (m, 1 H), 5.62 (s, 2 H), 5.34 (s, 2 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8 (d, $^{1}J_{C\text{-}F}$ = 256.0 Hz), 157.8, 151.2, 143.7 (d, $^{3}J_{C\text{-}F}$ = 14.0 Hz), 136.8, 134.9, 131.6, 129.7, 129.1, 128.5, 128.4, 127.7, 125.4 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 125.1, 121.2, 107.4 (d, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 103.0 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 48.0, 45.4. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -109.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}FN_4O_2$ $[M+H]^+$ 401.1408, found 401.1418.



2ai

1,3-Dibenzyl-8-fluoropyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ai)

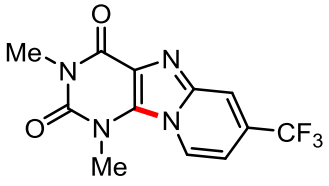
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ai** (80.5 mg, 0.2 mmol) at 27 °C for 3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ai** (52.9 mg, 66%) as a yellow solid. **M. p.:** 139.1 – 140.9 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.90 (s, *J* = 4.2 Hz, 1 H), 7.61 – 7.50 (m, 3 H), 7.42 – 7.36 (m, 2 H), 7.34 – 7.27 (m, 3 H), 7.26 – 7.16 (m, 3 H), 7.08 – 6.98 (m, 1 H), 5.61 (s, 2 H), 5.34 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.9, 153.5 (d, $^{1}J_{C\text{-}F}$ = 240.0 Hz), 151.2, 141.2, 136.8, 135.0, 132.3 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 129.7, 129.1, 128.5, 128.4, 127.7, 125.2, 121.7, 120.8 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 118.7 (d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 110.6 (d, $^{2}J_{C\text{-}F}$ = 45.0 Hz), 47.7, 45.4. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -136.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}FN_4O_2$ $[M+H]^+$ 401.1408, found 401.1410.



2aj

7-Chloro-1,3-dimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2aj)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1aj** (53.3mg, 0.2 mmol) at 27 °C for 6.7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2aj** (42.4 mg, 80%) as a white solid. **M. p.:** 311.6 – 313.2 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.39 (d, *J* = 7.8 Hz, 1 H), 7.60 (d, *J* = 1.2 Hz, 1 H), 6.84 (dd, *J* = 7.8, 1.8 Hz, 1 H), 3.98 (s, 3 H), 3.44 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.3, 152.1, 144.1, 133.5, 133.2, 125.5, 121.9, 119.9, 116.8, 33.2, 30.0. **HRMS** (ESI-TOF) m/z Calcd for $C_{11}H_{10}ClN_4O_2$ $[M+H]^+$ 265.0487, found 265.0481.

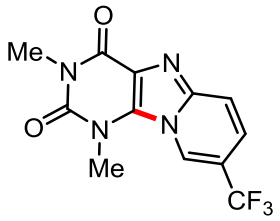


2ak

1,3-Dimethyl-7-(trifluoromethyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ak)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ak** (60.0 mg, 0.2 mmol) at 27 °C for 9 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ak** (51.9 mg, 87%) as a white solid. **M. p.:** 239.8 – 240.9 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.59 (d, *J* = 7.2 Hz, 1 H), 7.92 (s, 1 H), 7.00 (dd, *J* = 7.2, 1.8 Hz, 1 H), 4.02 (s, 3 H), 3.46 (s, 3 H). **^{13}C**

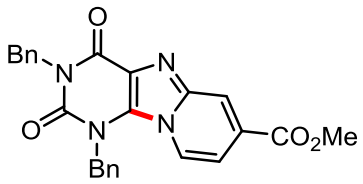
NMR (150 MHz, CD_2Cl_2): δ 157.8, 150.9, 141.1, 132.5, 126.6 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 125.0, 122.7 (q, $^1J_{C\text{-}F}$ = 270.0 Hz) , 122.0, 118.6 (q, $^3J_{C\text{-}F}$ = 4.5 Hz), 109.3 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 31.9, 28.7. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -64.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{10}FN_4O_2$ $[M+H]^+$ 299.0740, found 299.0738.



2al

1,3-Dimethyl-8-(trifluoromethyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2al)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1al** (60.0 mg, 0.2 mmol) at 27 °C for 11 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2al** (55.5 mg, 93%) as a white solid. **M. p.:** 216.0 – 216.9 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.80 (s, 1 H), 7.72 (d, *J* = 9.6 Hz, 1 H), 7.32 (dd, *J* = 9.6, 0.6 Hz, 1 H), 4.03 (s, 3 H), 3.46 (s, 3 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 159.1, 152.2, 143.7, 134.2, 124.7 (q, $^3J_{C\text{-}F}$ = 6.0 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 122.6, 122.3 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 119.3 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 33.2, 30.1. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -63.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{10}F_3N_4O_2$ $[M+H]^+$ 299.0750, found 299.0747.

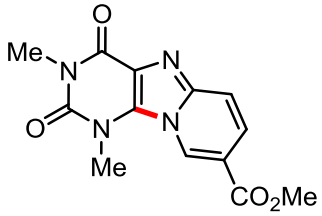


2am

Methyl 1,3-dibenzyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[1,2-*e*]purine-7-carboxyl-

ate (2am)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1am** (88.5 mg, 0.2 mmol) at 27 °C for 3.6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2am** (71.4 mg, 81%) as a light green solid. **M. p.:** 238.0 – 239.0 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.27 (s, 1 H), 7.96 (d, *J* = 7.8 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.34 – 7.27 (m, 3 H), 7.27 – 7.23 (m, 1 H), 7.20 (d, *J* = 7.2 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 5.66 (s, 2 H), 5.36 (s, 2 H), 3.92 (s, 1 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 164.6, 157.8, 151.2, 142.4, 136.7, 134.9, 131.9, 129.7, 129.2, 128.5, 128.5, 127.8, 127.0, 125.2, 123.4, 123.0, 122.5, 112.9, 52.8, 48.0, 45.5. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{21}N_4O_4$ $[M+H]^+$ 441.1557, found 441.1557.

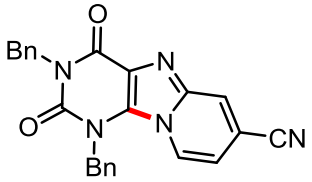


2an

Methyl 1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[1,2-*e*]purine-8-carboxyl-ate (2an)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1an** (58.1 mg, 0.24 mmol) at 27 °C for 4 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2an** (38.1 mg, 66%) as a white solid. **M. p.:** 265.1 – 265.7 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 9.20 (s, 1 H), 7.70 – 7.67 (m, 1 H), 7.57 (d, *J* = 9.6Hz, 1 H), 4.06 (s, 3 H), 3.96 (s, 3 H) 3.46 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 164.4, 157.9, 150.9, 143.1, 132.7, 128.4, 124.6, 120.9,

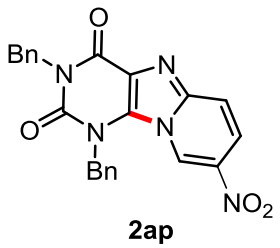
119.3, 118.0, 52.7, 31.9, 28.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{13}N_4O_4[M+H]^+$ 289.0931, found 289.0922.



2ao

1,3-Dibenzyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[1,2-*e*]purine-7-carbonitrile (2ao)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ao** (81.9 mg, 0.2 mmol) at 50 °C for 24 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ao** (63.6 mg, 78%) as a white solid. **M. p.:** 231.5 – 232.3 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 7.8 Hz, 1 H), 7.96 (s, 1 H), 7.52 (d, *J* = 7.2 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.31 – 7.22 (m, 3 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 6.67 (dd, *J* = 7.8, 1.8 Hz, 1 H), 5.64 (s, 2 H), 5.33 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.5, 151.0, 140.9, 136.4, 134.6, 132.31, 129.9, 129.1, 128.7, 128.5, 127.9, 126.8, 125.1, 124.8, 122.8, 116.4, 113.4, 108.6, 48.0, 45.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{18}N_5O_2$ $[M+H]^+$ 408.1455, found 408.1450.

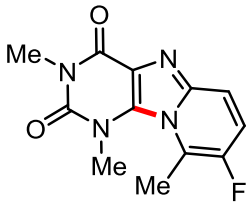


2ap

1,3-Dibenzyl-7-nitropyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ap)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ap** (85.9 mg, 0.2 mmol) at 60 °C for 9 h. Purification by column

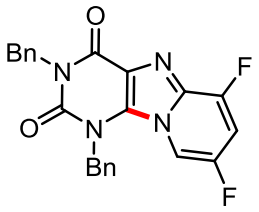
chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2ao** (45.3 mg, 53%) as a yellow solid. **M. p.:** 203.8 – 205.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.25 (d, J = 2.0 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.67 – 7.49 (m, 3H), 7.45 – 7.37 (m, 2H), 7.35 – 7.22 (m, 6H), 5.73 (s, 2H), 5.5 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.5, 151.2, 142.4, 138.0, 136.5, 134.3, 133.2, 123.0, 129.2, 128.9, 128.5, 127.9, 125.6, 125.5, 122.8, 119.7, 119.3, 48.0, 45.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}N_5O_4$ $[M+H]^+$ 428.1353, found 428.1361.



2aq

8-Fluoro-1,3,9-trimethylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2aq)

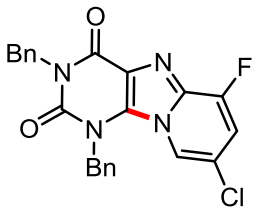
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1aq** (52.9 mg, 0.2 mmol) at 27 °C for 3.6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2aq** (49.8 mg, 95%) as a white solid. **M. p.:** 272.4 – 273.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.42 (m, 1 H), 7.20 – 7.10 (m, 1 H), 3.63 (s, 3 H), 3.40 (s, 3 H), 2.76 (d, J = 4.4 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.2, 155.4, 154.1 (d, $^1J_{C\text{-}F}$ = 234.0 Hz), 144.5, 136.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 124.9, 123.8 (d, $^2J_{C\text{-}F}$ = 37.0 Hz), 120.4 (d, $^2J_{C\text{-}F}$ = 29.0 Hz), 120.1 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 120.1, 42.7, 30.1, 16.1 (d, $^3J_{C\text{-}F}$ = 3.0 Hz). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -134.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{12}FN_4O_2$ $[M+H]^+$ 263.0939, found 263.0944.



2ar

1,3-Dibenzyl-8-chloro-6-fluoropyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ar)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ar** (84.1 mg, 0.2 mmol) at 50 °C for 6.7 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ar** (77.8 mg, 93%) as a white solid. **M. p.:** 210.2 – 211.3 °C. **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.83 – 7.79 (m, 1 H), 7.57 – 7.52 (m, 2 H), 7.42 – 7.37 (m, 2 H), 7.36 – 7.32 (m, 1 H), 7.32 – 7.27 (m, 2 H), 7.27 – 7.24 (m, 1 H), 7.23 – 7.18 (m, 2 H), 6.85 – 6.78 (m, 1 H), 5.61 (s, 2 H), 5.34 (s, 2 H). **^{13}C NMR (150 MHz, CDCl$_3$):** δ 157.5, 152.9 (dd, $^1J_{C\text{-}F}$ = 76.5, 10.5 Hz), 151.2 (dd, $^1J_{C\text{-}F}$ = 94.5, 10.5 Hz), 151.1, 136.6, 134.8, 134.4 (d, $^2J_{C\text{-}F}$ = 30.0 Hz), 133.5, 129.8, 129.2, 128.6, 128.5, 127.8, 125.2, 121.6, 107.5 (dd, $^3J_{C\text{-}F}$ = 45.0, 6.0 Hz), 102.5 (dd, $^4J_{C\text{-}F}$ = 31.5, 19.5 Hz), 47.7, 45.6. **^{19}F NMR (565 MHz, CDCl$_3$):** δ -120.8 (d, *J* = 5.7 Hz), -134.3 (d, *J* = 5.7 Hz). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{17}F_2N_4O_2$ $[M+H]^+$ 419.1314, found 419.1307.

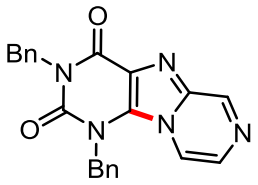


2as

1,3-Dibenzyl-8-chloro-6-fluoropyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2as)

Following the general procedure, the electrochemical C–H amination reaction was

carried out with **1as** (87.4 mg, 0.2 mmol) at 27 °C for 4.6 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2as** (56.5 mg, 65%) as a white solid. **M. p.:** 112.8 – 113.6 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.90 (s, 1 H), 7.54 (d, *J* = 6.0 Hz, 2 H), 7.42 – 7.38 (m, 2 H), 7.36 – 7.32 (m, 1 H), 7.31 – 7.28 (m, 2 H), 7.27 – 7.23 (m, 1 H), 7.23-7.18 (m, 2 H), 6.83 – 6.78 (m, 1 H), 5.62 (s , 2 H), 5.34 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.5, 151.3 (d, $^1J_{C\text{-}F}$ = 262.5 Hz), 151.2, 136.6, 134.8, 134.8 (d, $^2J_{C\text{-}F}$ = 30.0 Hz), 132.5, 129.8, 129.2, 128.7, 128.5, 127.8, 125.3, 121.2, 121.1 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 118.4 (d, $^4J_{C\text{-}F}$ = 6.0 Hz), 110.3 (d, $^2J_{C\text{-}F}$ = 19.5 Hz), 47.9, 45.6. **^{19}F NMR (565 MHz, $CDCl_3$):** δ -123.1. **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{17}ClFN_4O_2$ $[M+H]^+$ 435.1019, found 435.1013.

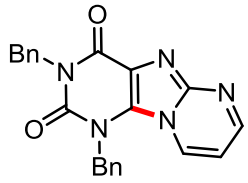


2at

1,3-Dibenzylpyrazino[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2at)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1at** (77.1 mg, 0.2 mmol) at 27 °C for 3.8 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2at** (56.7 mg, 74%) as a white solid. **M. p.:** 122.5 – 123.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.11 (s, 1 H), 7.82 (d, *J* = 4.4 Hz, 1 H), 7.64 (d, *J* = 5.2 Hz, 1 H), 7.57 (d, *J* = 7.2 Hz, 2 H), 7.45 – 7.28 (m, 6 H), 7.25 – 7.20 (m, 2 H), 5.67 (s, 2 H), 5.38 (s, 2 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.8, 151.1, 147.6, 137.6, 136.5, 134.6, 131.4, 129.8, 129.1, 128.6, 128.5, 127.9, 125.2, 121.8, 116.2, 47.8, 45.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{18}N_5O_2$ $[M+H]^+$

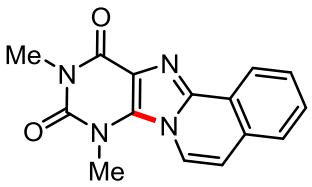
384.1455, found 384.1447.



2au

1,3-Dibenzylpyrimido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2au)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1au** (77.0 mg, 0.2 mmol) at 27 °C for 3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2au** (28.4 mg, 37%) as a yellow solid. **M. p.:** 221.2 – 221.4 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.38 – 8.29 (m, 1 H), 8.22 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.56 (d, *J* = 7.2 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.35 – 7.29 (m, 3 H), 7.28 – 7.23 (m, 1 H), 7.19 (d, *J* = 7.4 Hz, 2 H), 6.60 (q, *J* = 3.6 Hz, 1 H), 5.65 (s, 2 H), 5.34 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 157.8, 151.9, 151.1, 144.6, 136.7, 134.8, 131.9, 129.9, 129.8, 129.3, 128.5, 128.5, 127.8, 125.1, 120.5, 109.7, 47.8, 45.6. **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{18}N_5O_2$ $[M+H]^+$ 384.1455, found 384.1461.

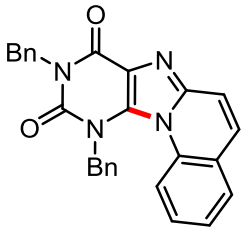


2av

8,10-Dibenzylpurino[8,9-*a*]isoquinoline-9,11(8*H*,10*H*)-dione (2av)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1av** (56.5 mg, 0.2 mmol) at 27 °C for 7.3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2av** (51.0 mg, 91%) as a

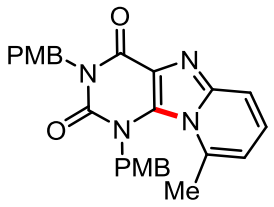
yellow solid. **M. p.**: 310.9 – 311.8 °C. **^{1}H NMR (600 MHz, CD_2Cl_2):** δ 8.66 (d, *J* = 7.8 Hz, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H), 7.76 – 7.57 (m, 3 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 4.00 (s, 3 H), 3.45 (s, 3 H). **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 159.3, 152.5, 142.8, 135.3, 130.9, 130.5, 130.2, 128.4, 125.6, 125.2, 122.0, 119.7, 116.2, 33.4, 29.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{15}H_{13}N_4O_2$ $[M+H]^+$ 281.1033, found 281.1027.



2aw

9,11-Dibenzylpurino[9,8-*a*]quinoline-8,10(9*H*,11*H*)-dione (2aw)

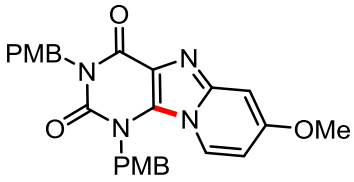
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1aw** (86.9 mg, 0.2 mmol) at 27 °C for 24 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2aw** (64.0 mg, 74%) as a yellow solid. **M. p.:** 238.4 – 240.2 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 8.4 Hz, 1 H), 7.82 (dd, *J* = 7.8, 0.6 Hz, 1 H), 7.64 – 7.58 (m, 1 H), 7.57 – 7.51 (m, 2 H), 7.47 (d, *J* = 9.6 Hz, 1 H), 7.31 – 7.25 (m, 2 H), 7.24 – 7.18 (m, 3 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 2 H), 6.72 (d, *J* = 7.4 Hz, 2 H), 5.37 (s, 2 H), 5.21 (s, 2 H). **^{13}C NMR (150 MHz, $CDCl_3$):**δ 158.1, 153.8, 143.2, 136.7, 135.8, 134.3, 132.9, 129.2, 128.8, 128.7, 128.5, 128.3, 128.1, 127.9, 127.4, 126.4, 125.1, 122.4, 118.3, 118.0, 54.3, 44.8. **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{21}N_4O_2$ $[M+H]^+$ 433.1659, found 433.1659.



2ax

1,3-Bis(4-methoxybenzyl)-9-methylpyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ax)

Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ax** (91.7 mg, 0.2 mmol) at 27 °C for 3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ax** (41.1 mg, 45%) as a white solid. **M. p.:** 295.2 – 296.1 °C**. ^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.51 (d, *J* = 9.0 Hz, 1 H), 7.21 – 7.13 (m, 3 H), 6.76 – 6.69 (m, 4 H), 6.67 (d, *J* = 6.6 Hz, 1 H), 6.63 – 6.54 (m, 2 H), 5.14 (s, 2 H), 5.05 (s, 2 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 2.90 (s, 3 H). **^{13}C NMR (150 MHz, CDCl$_3$):** δ 159.6, 158.8, 158.5, 154.0, 145.7, 135.4, 133.0, 130.1, 129.5, 129.0, 126.6, 125.9, 123.7, 117.7, 115.8, 114.0, 113.5, 57.5, 55.2, 55.1, 44.0, 19.9. **HRMS** (ESI-TOF) m/z Calcd for $C_{26}H_{25}N_4O_4$ $[M+H]^+$ 457.1870, found 457.1865.



2ay

7-Methoxy-1,3-bis(4-methoxybenzyl)pyrido[1,2-*e*]purine-2,4(1*H*,3*H*)-dione (2ay)

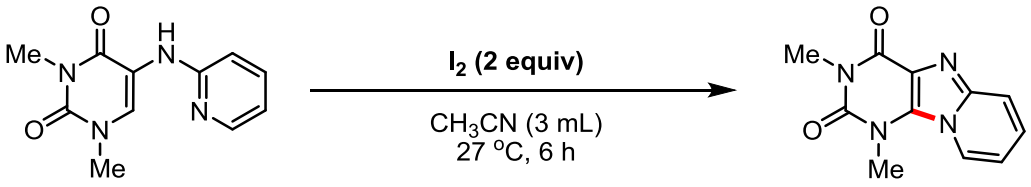
Following the general procedure, the electrochemical C–H amination reaction was carried out with **1ay** (94.9 mg, 0.2 mmol) at 27 °C for 3 h. Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2ay** (60.5 mg, 64%) as a white solid. **M. p.:** 218.2 – 218.6 °C**. ^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.78 (d, *J* = 7.8

Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.72 (s, 1 H), 6.34 (d, *J* = 7.8 Hz, 1 H), 5.52 (s, 2 H), 5.26 (s, 2 H), 3.81 (s, 3 H), 3.77 (d, *J* = 1.8 Hz, 6 H). **^{13}C NMR (150 MHz, $CDCl_3$):** δ 159.5, 159.1, 158.0, 157.8, 151.3, 145.3, 131.3, 130.8, 129.4, 126.9, 126.5, 124.2, 120.2, 115.0, 113.7, 110.2, 95.4, 55.7, 55.3, 55.2, 47.4, 44.7. **HRMS** (ESI-TOF) m/z Calcd for $C_{26}H_{25}N_4O_5$ $[M+H]^+$ 473.1819, found 473.1816.

7 Preliminary mechanistic studies

7.1 Control experiments for the investigation of active iodine-containing species

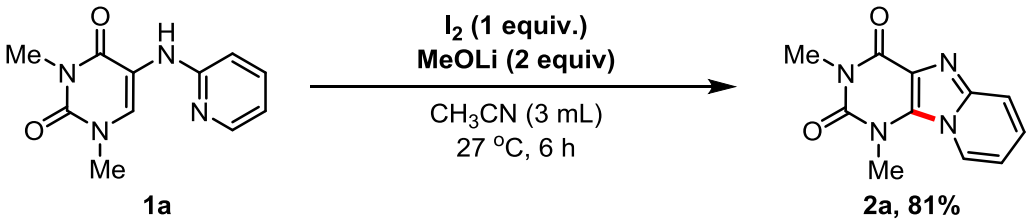
(1) The reaction of **1a** with stoichiometric amount of I_2 under the standard conditions without current.



1a **2a, 38%**

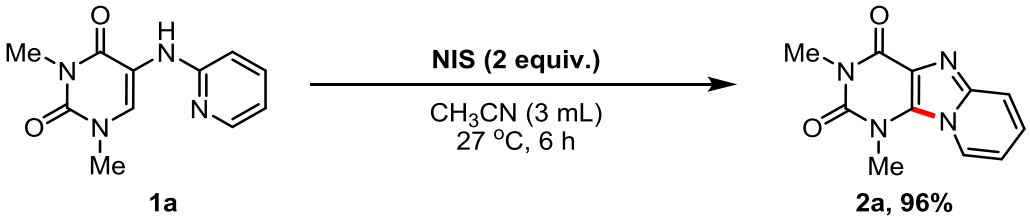
A 25 mL round-bottomed flask was charged with 1,3-dimethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione **1a** (0.20 mmol), I_2 (0.4 mmol), and CH_3CN (3 mL). The reaction vessel was allowed to stir at 27 °C for 6 h. After the reaction, the solution was concentrated in vacuum and the resulting residue was purified by column chromatography (hexane/EtOAc: 2/1) to afford the compound **2a** as a white solid (17.5 mg, 38% yield).

(2) The reaction of **1a** with stoichiometric amount of I_2 in the presence of MeOLi under the standard conditions without current.



A 25 mL round-bottomed flask was charged with 1,3-dimethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione **1a** (0.20 mmol), I_2 (0.2 mmol), MeOLi (0.4 mmol), and CH_3CN (3 mL). The reaction vessel was allowed to stir at 27 °C for 6 h. After the reaction, the solution was concentrated in vacuum and the resulting residue was purified by column chromatography (hexane/EtOAc: 2/1) to afford the compound **2a** as a white solid (37.3 mg, 81% yield).

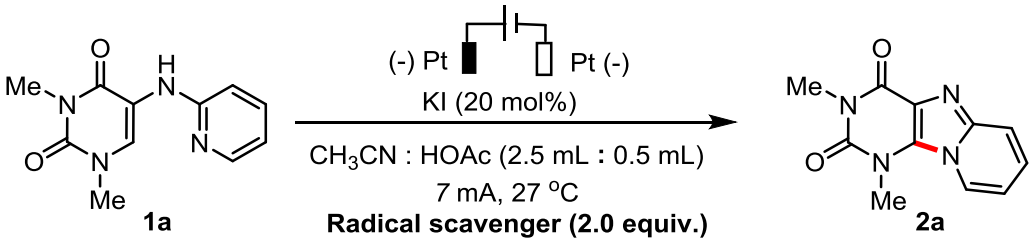
(3) The reaction of **1a** with stoichiometric amount of NIS under the standard conditions without current.



A 25 mL round-bottomed flask was charged with 1,3-dimethyl-5-(pyridin-2-ylamino)pyrimidine-2,4(1*H*,3*H*)-dione **1a** (0.20 mmol), NIS (0.2 mmol), and CH_3CN (3 mL). The reaction vessel was allowed to stir at 27 °C for 6 h. After the reaction, the solution was concentrated in vacuum and the resulting residue was purified by column chromatography (hexane/EtOAc: 2/1) to afford the compound **2a** as a white solid (44.2 mg, 96% yield).

Based on these studies, an in situ generated molecular iodine and hyperiodide intermediate (I^+) may be the active species for this reaction.

7.2 Radical scavenger addition experiments



Radical scavenger	none	TEMPO	BHT	DPE
Yield of **2a** [%]	97	77	15	56

Three parallel radical scavenger addition experiments were conducted under standard conditions using **1a** (46.4 mg, 0.2 mmol) as substrates with 2 equiv TEMPO (46.4 mg, 0.4 mmol), BHT (46.4 mg, 0.4 mmol), and 1,1-diphenylethylene (46.4 mg, 0.4 mmol) respectively. The electrochemical C-H amination was not completely inhibited but led to a significant decrease in the yield of **2a**, suggesting a possible radical pathway in this system.

8 Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI660E potentiostat at room temperature in MeCN. $LiClO_4$ (0.1 M) was used as the supporting electrolyte, and a Pt electrode (area = 0.03 cm^2) was used as the working electrode. The auxiliary electrode was a Pt sheet. All potentials are referenced against the Ag/AgCl redox couple.

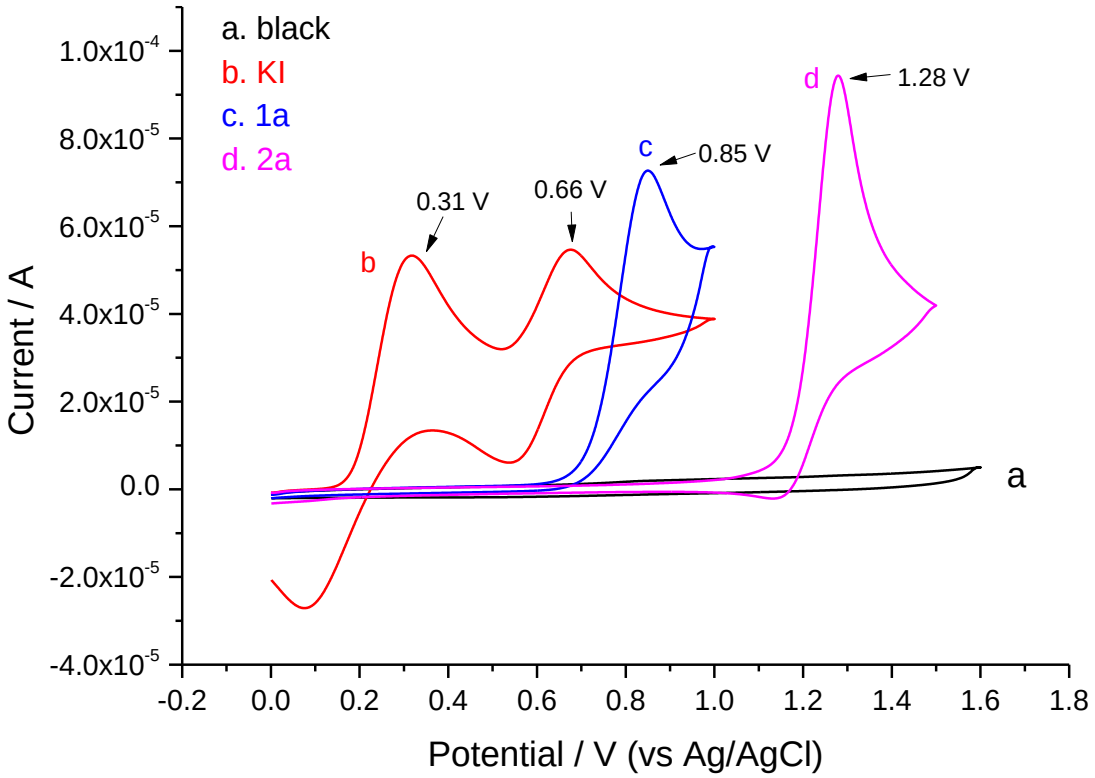


Figure S5. Cyclic voltammograms recorded on a Pt disk working electrode (area = 0.03 cm^2). The scan rate was 100 mV/s. (a) MeCN containing 0.1 M $LiClO_4$; (b) MeCN containing 0.1 M $LiClO_4$ after addition of 5 mM **KI**; (c) MeCN containing 0.1 M $LiClO_4$, after addition of 5 mM **1a**; (d) MeCN containing 0.1 M $LiClO_4$, after addition of 5 mM **2a**.

9 Photophysical properties

Fluorescence experimental procedure:

Weigh compound **2a** of 23 mg (0.1 mmol), add 1 mL DCM into EP tube to dissolve, then transfer to 100 ml volumetric bottle, continue to dilute with CH_2Cl_2 to scale, shake well, and set aside. Take 1mL of the above solution, transfer it to a 100 mL volumetric bottle and dilute it to the scale, then mix it into 10^{-5} mol/L standard reserve solution for fluorescence test. Turn on the power, turn on the

fluorophotometer and the computer, preheat the instrument, initialize the instrument, and measure the fluorescence intensity according to the excitation and emission fluorescence spectrometry. Determine the fluorescence intensity of compound **2a** in different solvents, replace CH_2Cl_2 with other solvents and repeat the above experimental steps.

Initially we investigated the effects of solvents on the fluorescence emission and intensity by using **2a** as a model substrate. It was found that the the maximum fluorescence intensity was obtained in CH_2Cl_2 as depicted in Figure S6. After intensive optimization studies of the solvent, we found that CH_2Cl_2 was the suitable solvent for the photophysical analysis.

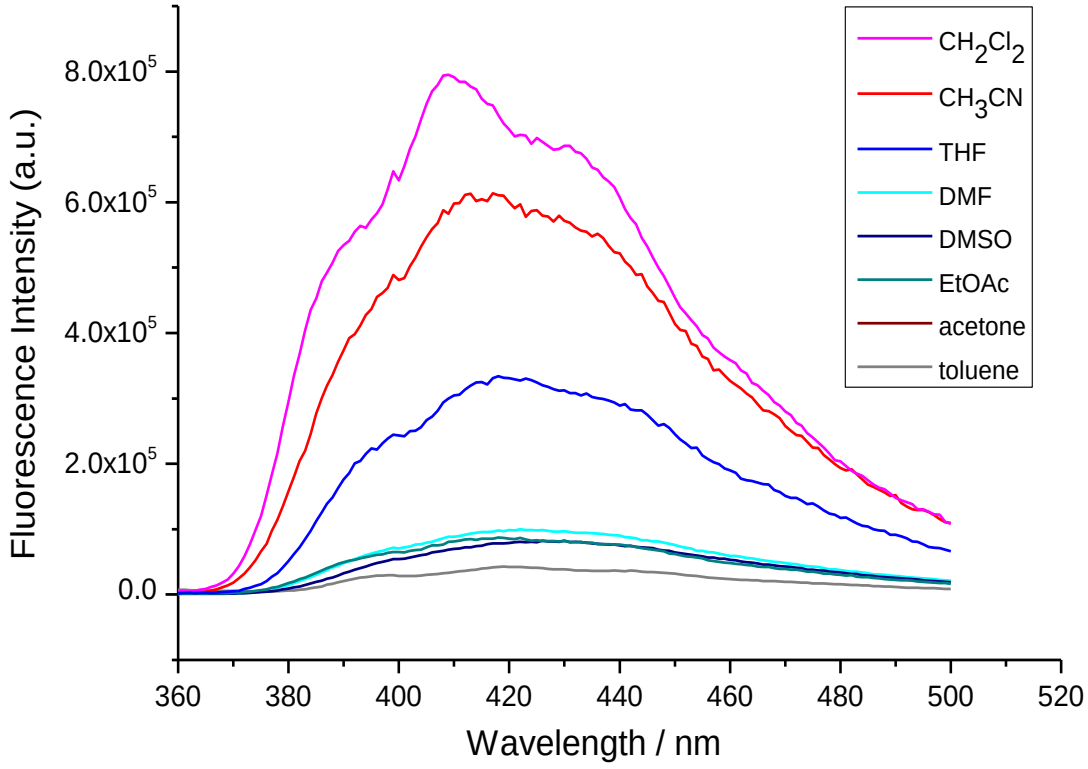


Figure S6. Fluorescence spectra of **2a** in different solvents (1×10^{-5} M).

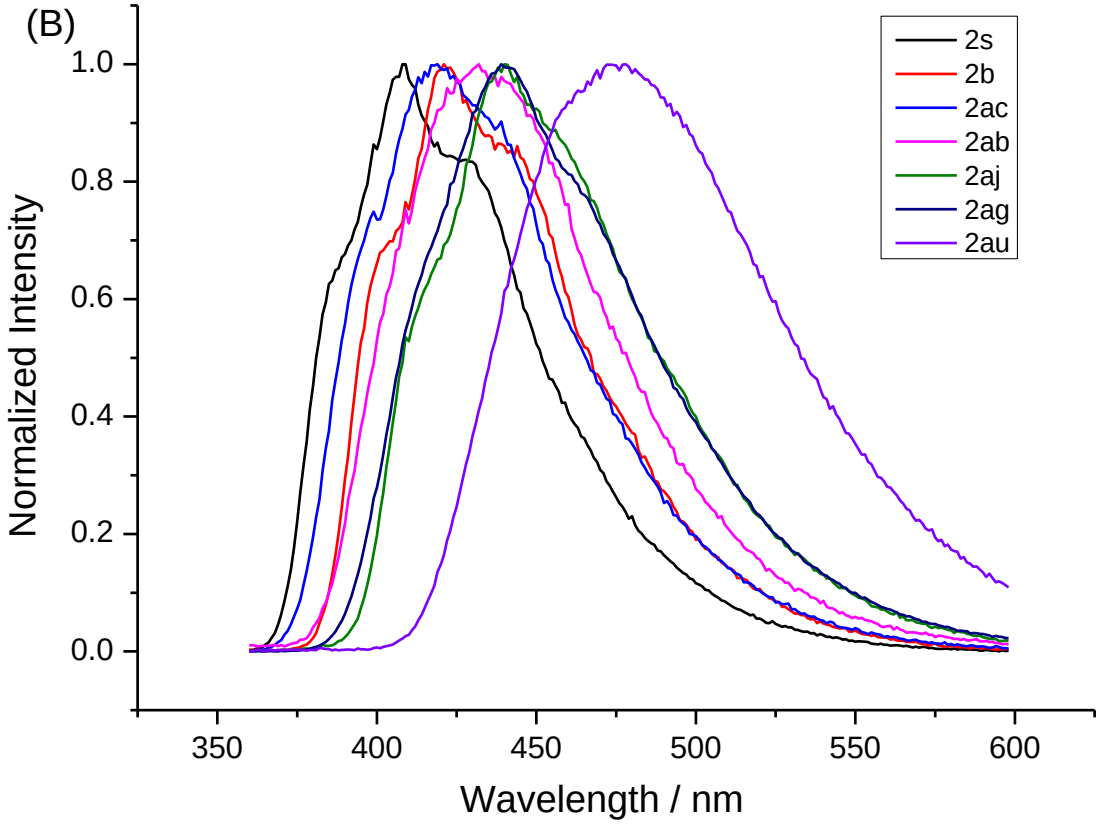
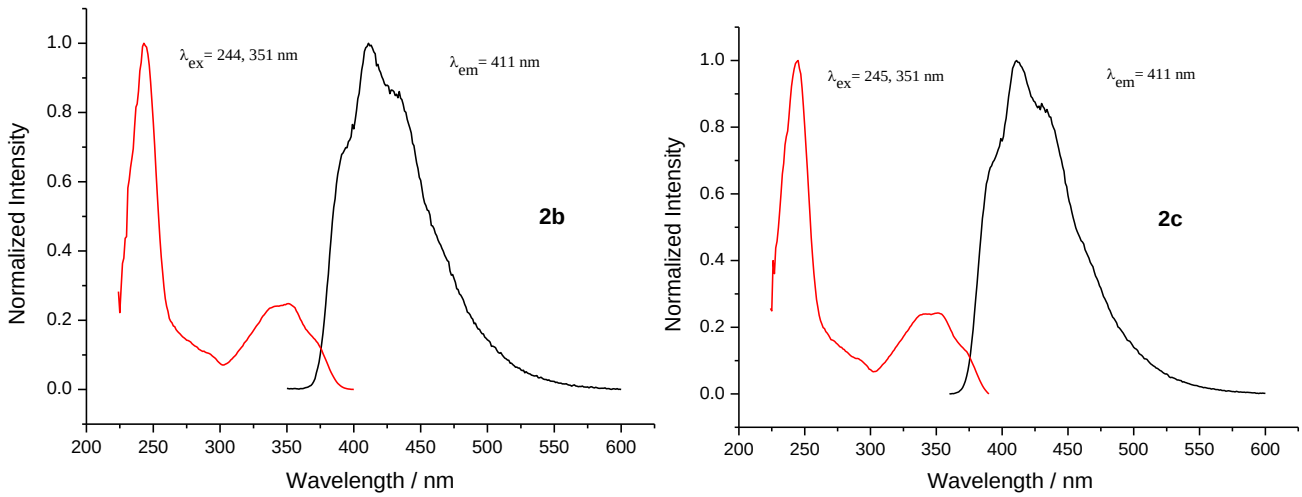
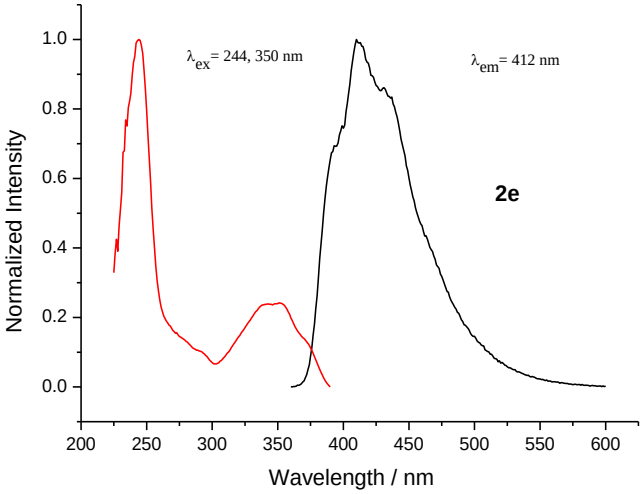
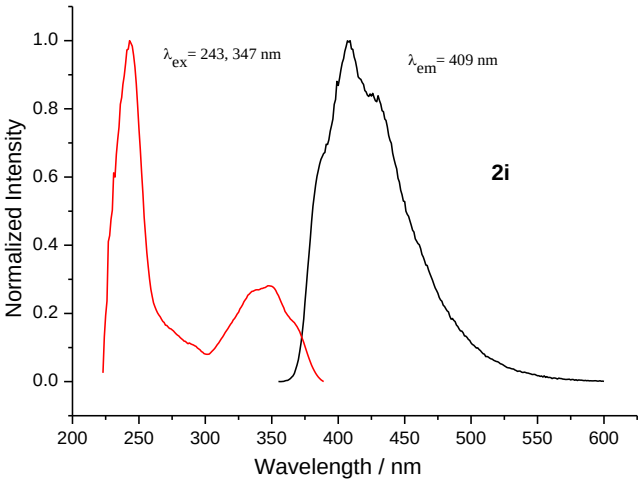
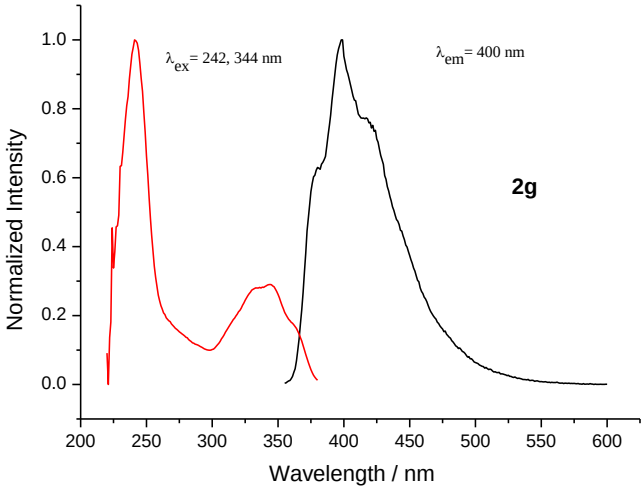


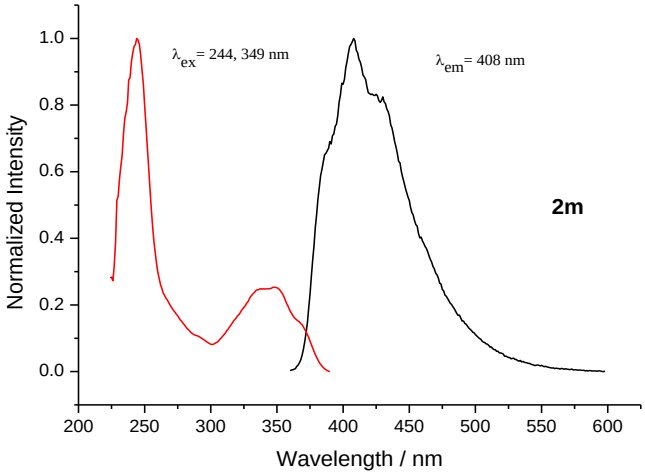
Figure S7. Emission spectra of selected tricyclic xanthines in CH_2Cl_2 at RT (1.0 $\times$ 10^{-5} M), the maximum intensity was normalized to 1 for each.

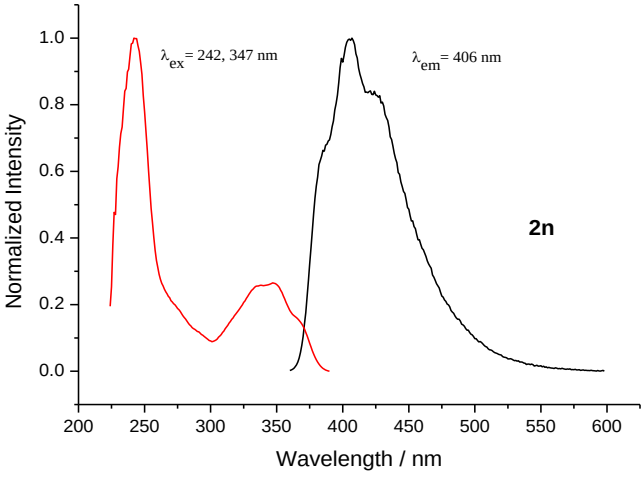



λex= 244, 350 nm
λem= 412 nm
2e
Normalized Intensity
Wavelength / nm


λex= 243, 347 nm
λem= 409 nm
2i
Normalized Intensity
Wavelength / nm


λex= 242, 344 nm
λem= 400 nm
2g
Normalized Intensity
Wavelength / nm


λex= 244, 349 nm
λem= 408 nm
2m
Normalized Intensity
Wavelength / nm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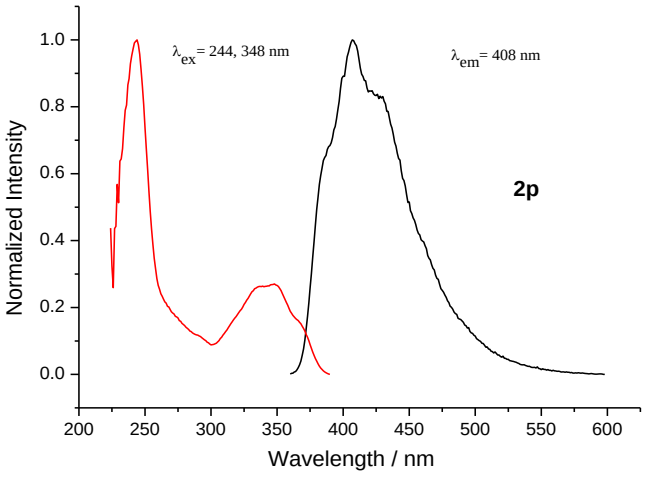
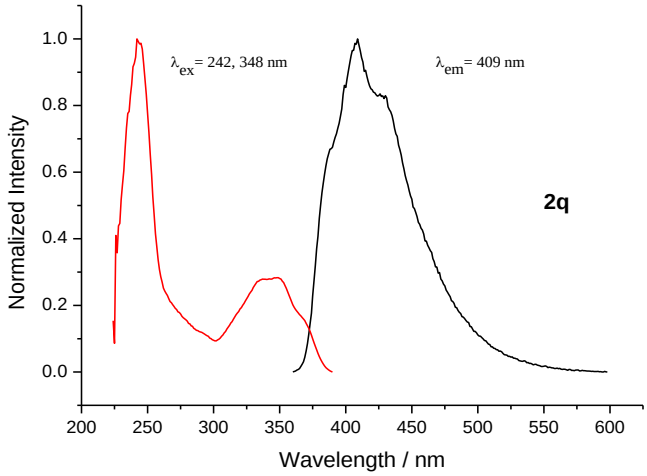
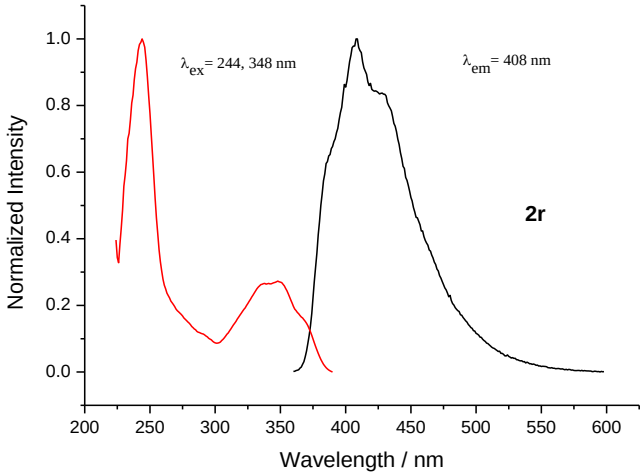
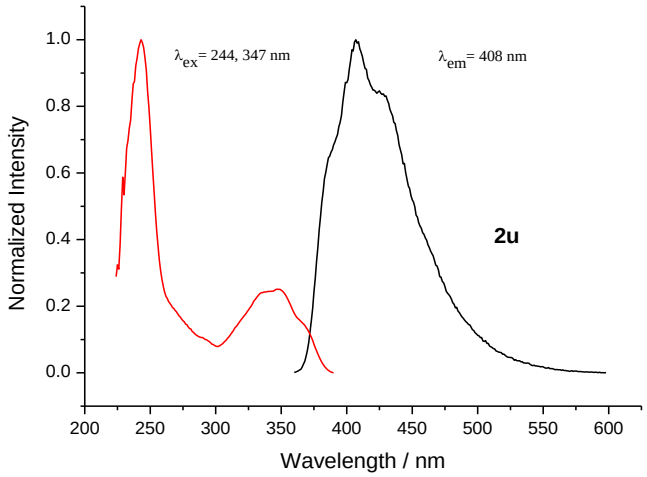
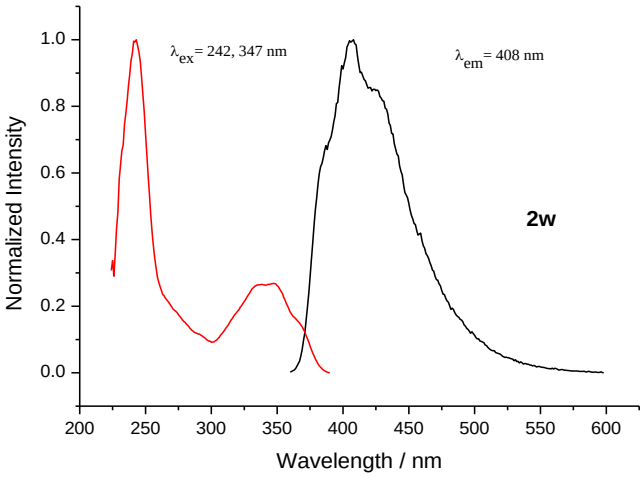
λem= 406 nm
2n
Normalized Intensity
Wavelength / nm

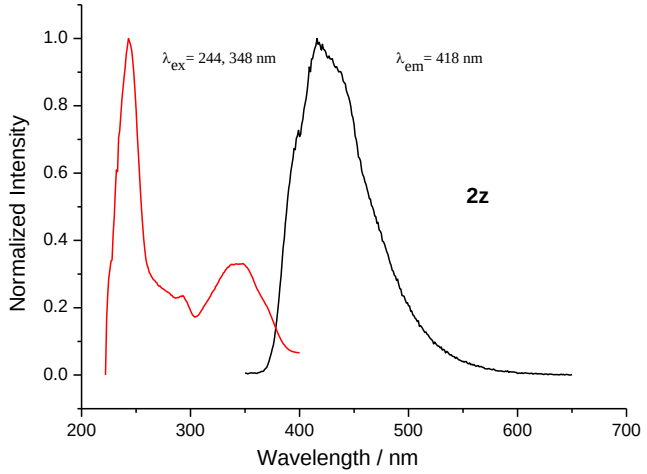

λex= 244, 348 nm
λem= 408 nm
2p
Normalized Intensity
Wavelength / nm

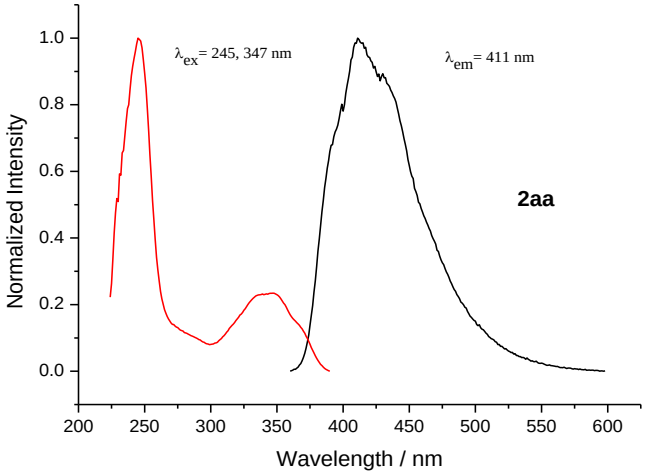

λex= 242, 348 nm
λem= 409 nm
2q
Normalized Intensity
Wavelength / nm

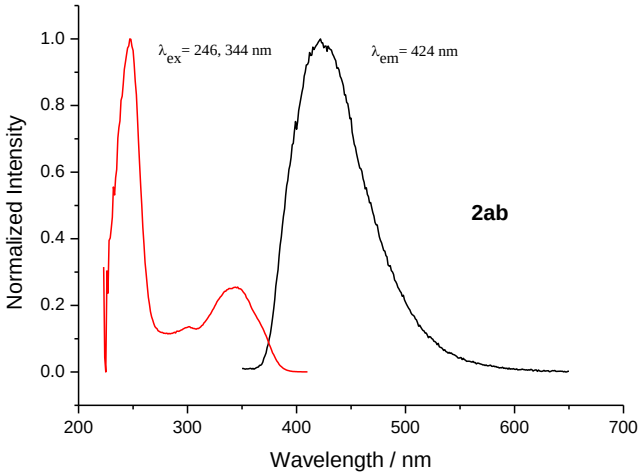

λex= 244, 348 nm
λem= 408 nm
2r
Normalized Intensity
Wavelength / nm

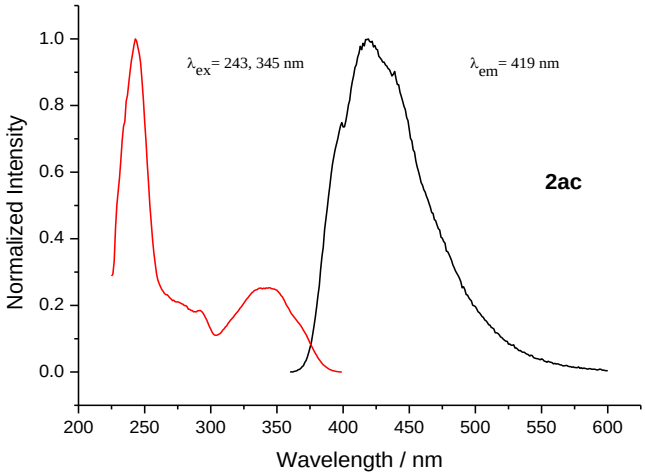

λex= 244, 347 nm
λem= 408 nm
2u
Normalized Intensity
Wavelength / nm

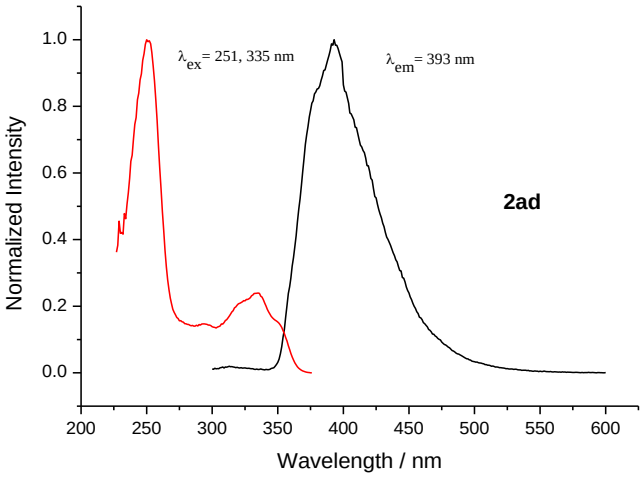

λex= 242, 347 nm
λem= 408 nm
2w
Normalized Intensity
Wavelength / nm

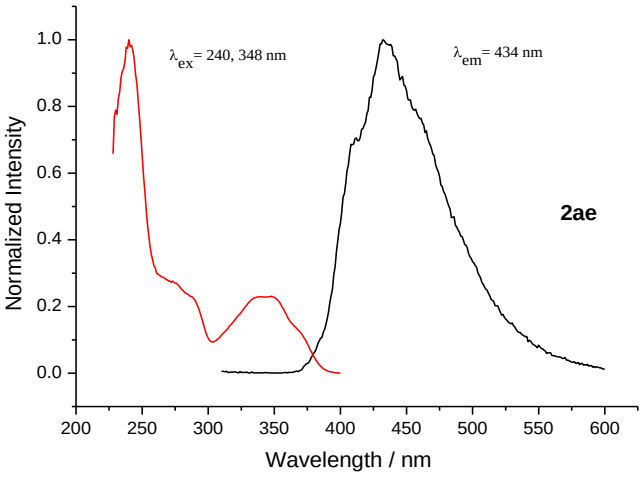

λex= 244, 348 nm
λem= 418 nm
2z
Normalized Intensity
Wavelength / nm

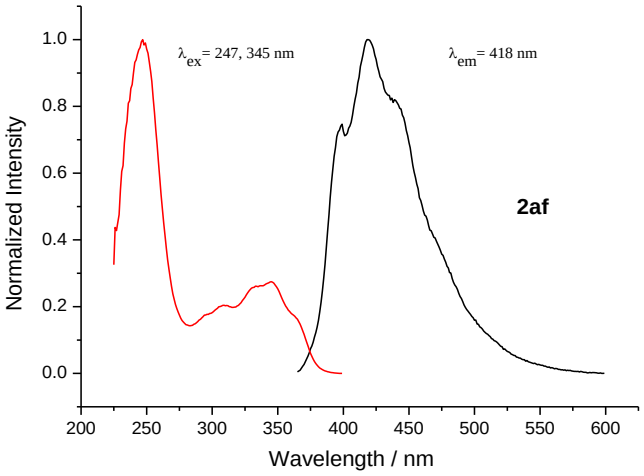

λex= 245, 347 nm
λem= 411 nm
2aa
Normalized Intensity
Wavelength / nm

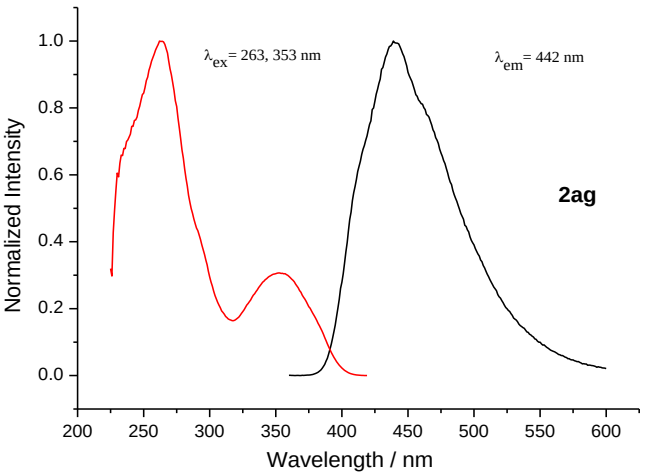

λex= 246, 344 nm
λem= 424 nm
2ab
Normalized Intensity
Wavelength / nm

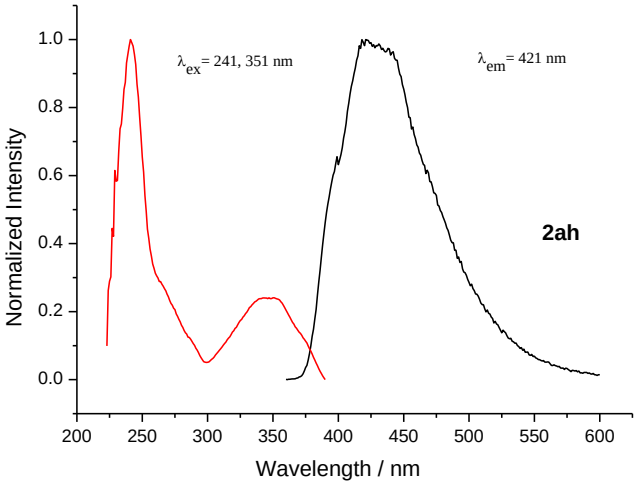

λex= 243, 345 nm
λem= 419 nm
2ac
Normalized Intensity
Wavelength / nm

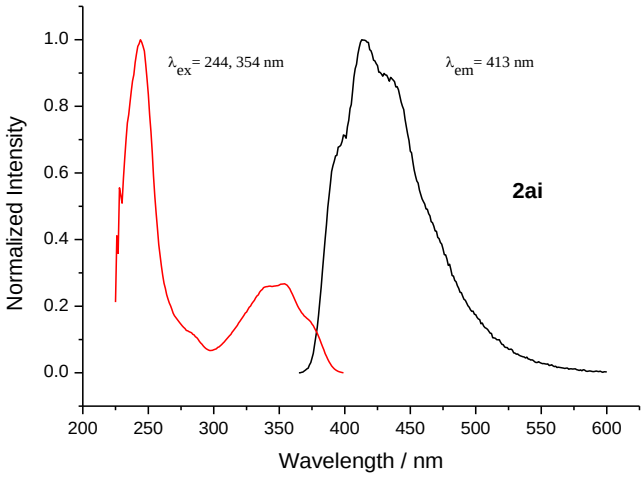

λex= 251, 335 nm
λem= 393 nm
2ad
Normalized Intensity
Wavelength / nm


λex= 240, 348 nm
λem= 434 nm
2ae
Normalized Intensity
Wavelength / nm


λex= 247, 345 nm
λem= 418 nm
2af
Normalized Intensity
Wavelength / nm


λex= 263, 353 nm
λem= 442 nm
2ag
Normalized Intensity
Wavelength / nm


λex= 241, 351 nm
λem= 421 nm
2ah
Normalized Intensity
Wavelength / nm


λex= 244, 354 nm
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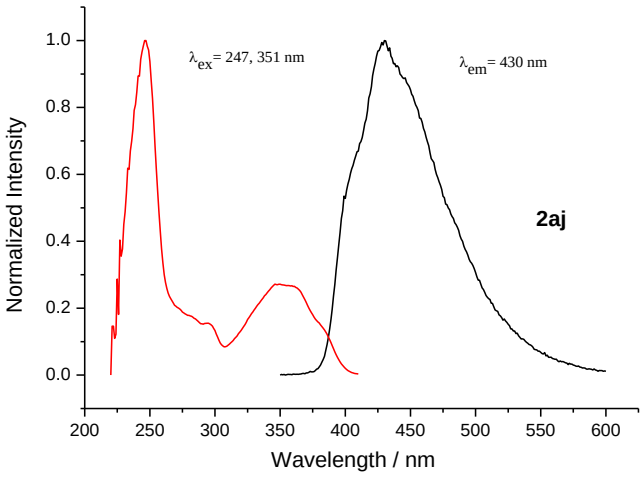
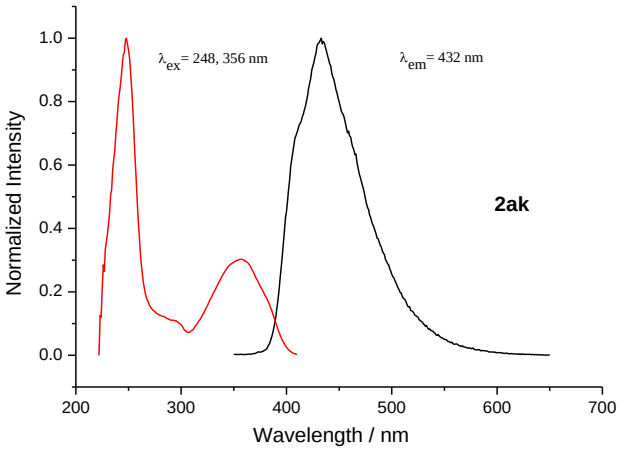
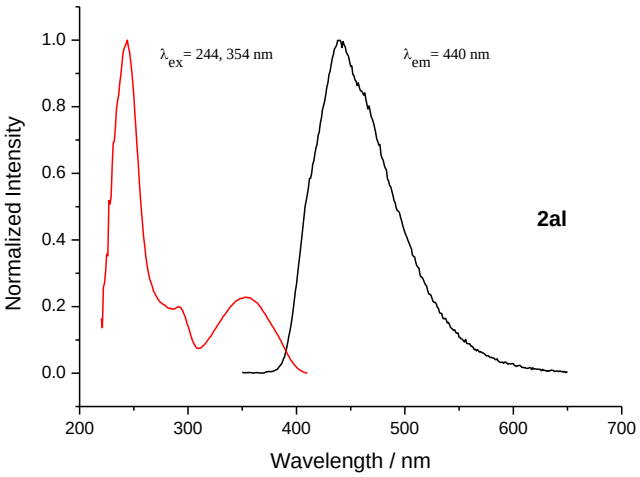
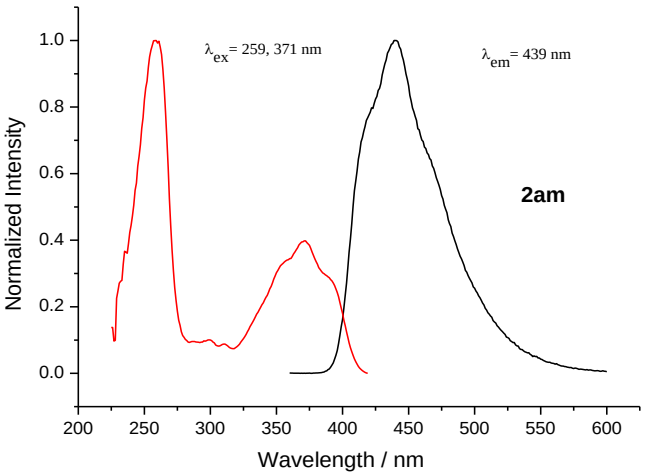
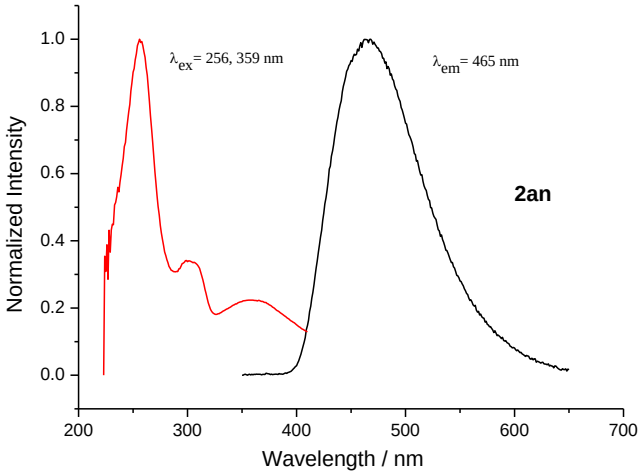
2ai
Normalized Intensity
Wavelength / nm

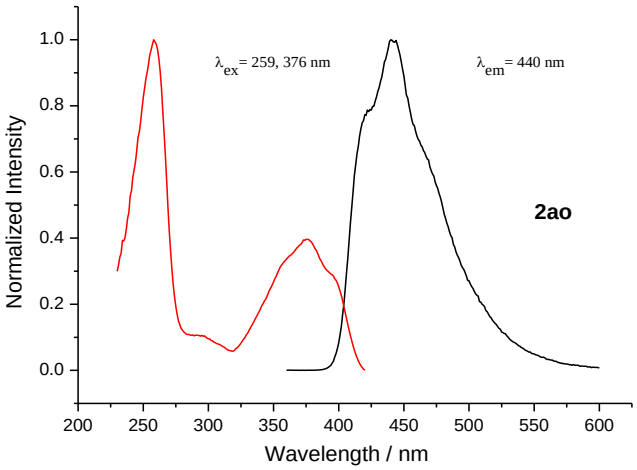

λex= 247, 351 nm
λem= 430 nm
2aj
Normalized Intensity
Wavelength / nm

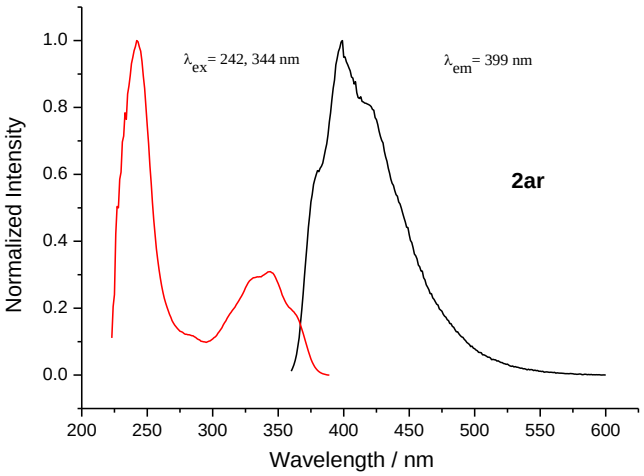

λex= 248, 356 nm
λem= 432 nm
2ak
Normalized Intensity
Wavelength / nm

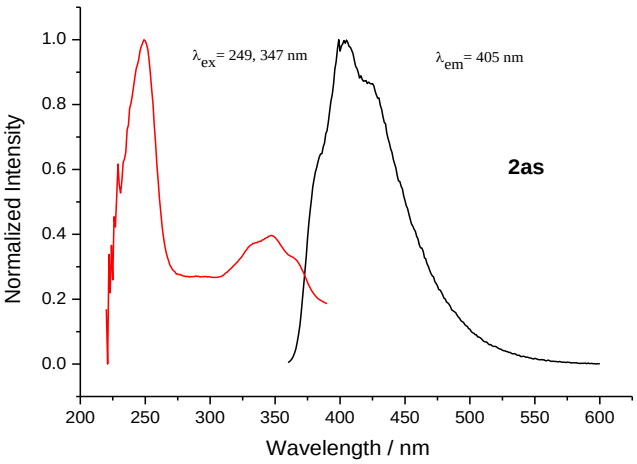

λex= 244, 354 nm
λem= 440 nm
2al
Normalized Intensity
Wavelength / nm

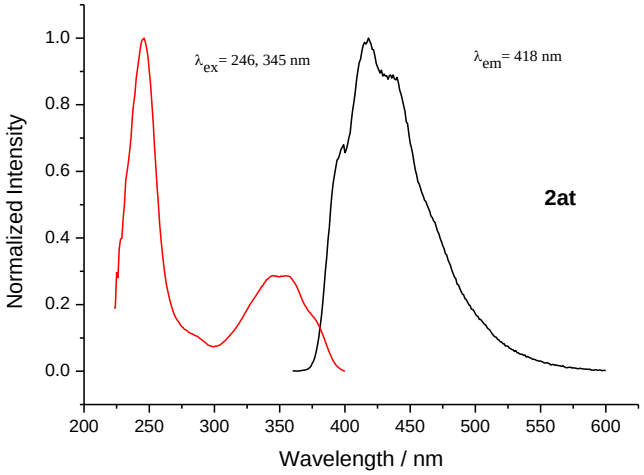

λex= 259, 371 nm
λem= 439 nm
2am
Normalized Intensity
Wavelength / nm

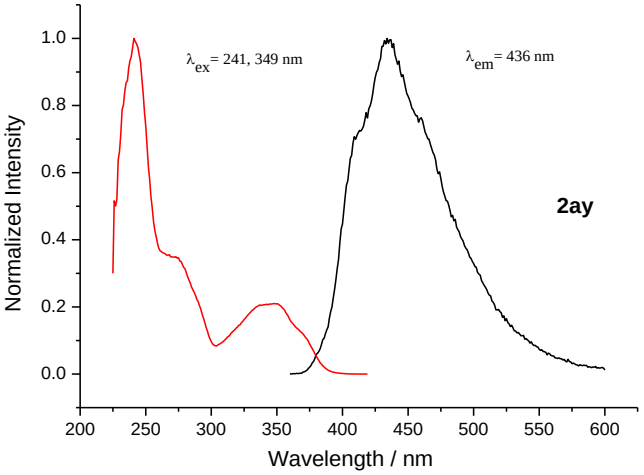

λex= 256, 359 nm
λem= 465 nm
2an
Normalized Intensity
Wavelength / nm

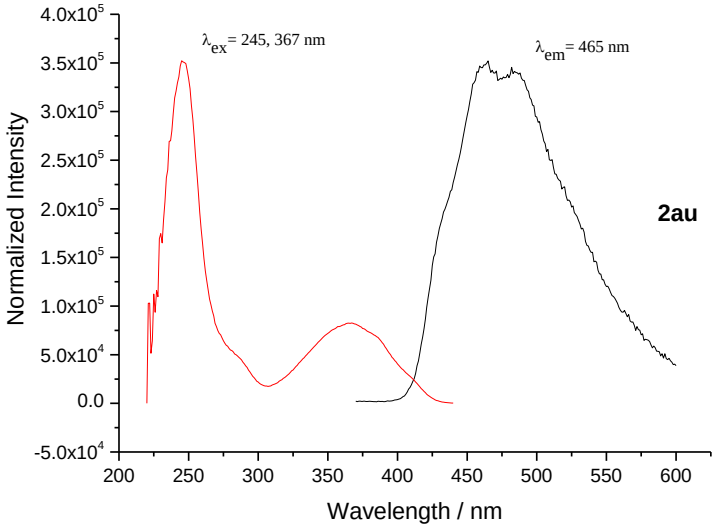

λex= 259, 376 nm
λem= 440 nm
2ao
Normalized Intensity
Wavelength / nm


λex= 242, 344 nm
λem= 399 nm
2ar
Normalized Intensity
Wavelength / nm


λex= 249, 347 nm
λem= 405 nm
2as
Normalized Intensity
Wavelength / nm


λex= 246, 345 nm
λem= 418 nm
2at
Normalized Intensity
Wavelength / nm


λex= 241, 349 nm
λem= 436 nm
2ay
Normalized Intensity
Wavelength / nm



9.2 Spectral properties of selected tricyclic xanthines in CH_2Cl_2 at RT (10^{-5} M)

After a preliminary screen, we focused our investigation of fluorescence properties on a selected group of tricyclic xanthines **2**. The results are summarized below.

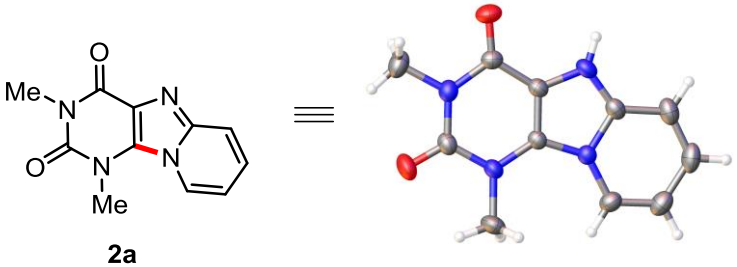
Compd	λ_{ex} (nm)	λ_{em} (nm)b	Stokes shift (nm)	Φf (%)[c]	τ_f (ns)[d]
2an	256, 359	465	209	34.6	20.4
2au	245, 367	465	178	39.7	13.0
2ag	263, 353	442	179	63.9	13.3
2ao	259, 376	440	181	67.1	7.2
2al	244, 354	440	196	44.7	14.7
2am	259, 371	439	180	57.6	6.3
2ay	241, 349	436	195	60.0	7.8
2ae	247, 351	430	183	30.0	10.9

[a] Excitation-emission fluorescence spectra were measured in CH_2Cl_2 at a

concentration of 1.0 × 10^{-5} M; [b] Excited at the longest maximun absorption band in CH_2Cl_2, [c] Absolute fluorescence quantum yields in CH_2Cl_2 (1.0 × 10^{-5} M) determined with an integrating sphere system. [d] Fluorescent lifetime.

10 X-ray Crystallographic Data

Compound 2a (CCDC 2073617)

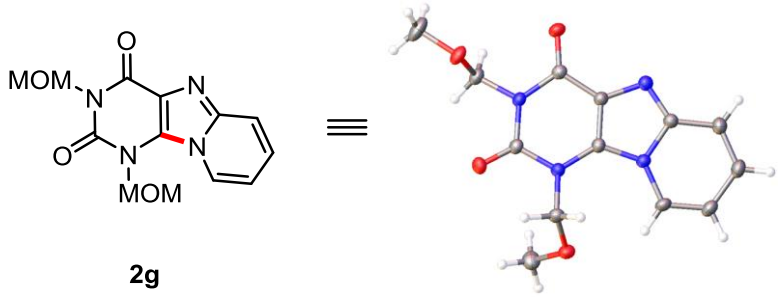


2a

Empirical formula	$C_{11}H_{12}N_4O_3$
Formula weight	248.25
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.5203(4)
b/Å	8.7465(4)
c/Å	9.6550(5)
α/°	70.463(5)
β/°	84.892(4)
γ/°	69.150(5)
Volume/$Å^3$	558.99(5)
Z	2
$\rho_{calc}g/cm^3$	1.475
μ/mm^{-1}	0.931
F(000)	260.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.726 to 143.238
Index ranges	$-9 \le h \le 9$, $-6 \le k \le 10$, $-10 \le l \le 11$
Reflections collected	4630
Independent reflections	2137 [R_{int} = 0.0217, R_{sigma} = 0.0280]
Data/restraints/parameters	2137/0/169
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.1049

Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1081
Largest diff. peak/hole / e Å^{-3}	0.20/-0.16

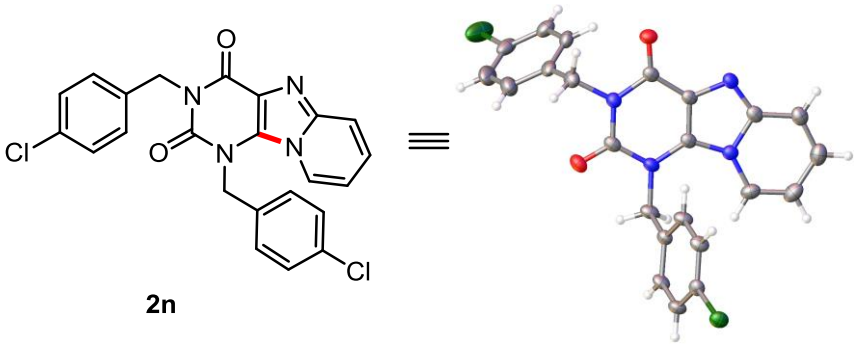
Compound 2g (CCDC 2073615)



2g

Empirical formula	$C_{13}H_{14}N_4O_4$
Formula weight	290.28
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7843(4)
b/Å	13.7263(4)
c/Å	7.4329(2)
α/°	90
β/°	92.219(3)
γ/°	90
Volume/Å^3	1303.35(7)
Z	4
ρ_{calc}g/cm^3	1.479
μ/mm^{-1}	0.947
F(000)	608.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.92 to 133.182
Index ranges	-15 ≤ h ≤ 14, -12 ≤ k ≤ 16, -6 ≤ l ≤ 8
Reflections collected	4494
Independent reflections	2292 [R_{int} = 0.0317, R_{sigma} = 0.0427]
Data/restraints/parameters	2292/0/200
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0510, wR_2 = 0.1112
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24

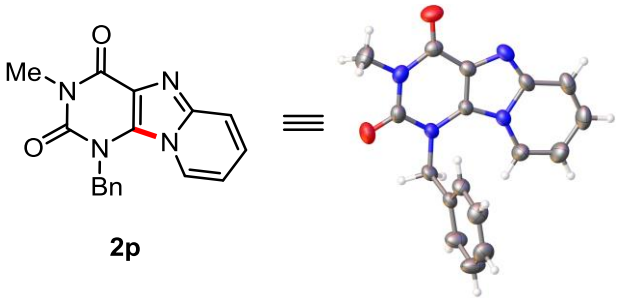
Compound 2n (CCDC 2073618)



2n

Empirical formula	$C_{23}H_{16}Cl_2N_4O_2$
Formula weight	451.30
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.8857(6)
b/Å	10.0289(7)
c/Å	11.4665(6)
α/°	97.757(5)
β/°	95.026(5)
γ/°	97.668(6)
Volume/Å^3	997.60(11)
Z	2
ρ_{calc}g/cm^3	1.502
μ/mm^{-1}	0.356
F(000)	464.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.144 to 49.992
Index ranges	-9 ≤ h ≤ 10, -11 ≤ k ≤ 11, -13 ≤ l ≤ 11
Reflections collected	6910
Independent reflections	3512 [R_{int} = 0.0249, R_{sigma} = 0.0421]
Data/restraints/parameters	3512/0/280
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.0976
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.1046
Largest diff. peak/hole / e Å^{-3}	0.40/-0.50

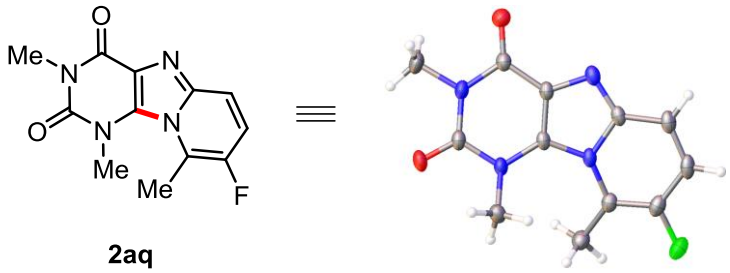
Compound 2p (CCDC 2073630)



2p

Empirical formula	$C_{17}H_{14}N_4O_2$
Formula weight	306.32
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.2162(2)
b/Å	9.41800(10)
c/Å	30.1780(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2903.61(8)
Z	8
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	0.782
F(000)	1280.0
Crystal size/mm^3	0.14 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.458 to 142.598
Index ranges	$-12 \le h \le 12$, $-11 \le k \le 9$, $-37 \le l \le 37$
Reflections collected	6750
Independent reflections	2761 [R_{int} = 0.0278, R_{sigma} = 0.0312]
Data/restraints/parameters	2761/0/209
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0646, wR_2 = 0.1718
Final R indexes [all data]	R_1 = 0.0727, wR_2 = 0.1785
Largest diff. peak/hole / e Å^{-3}	0.31/-0.33

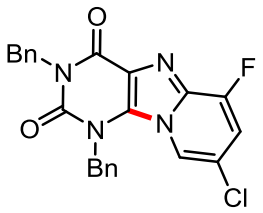
Compound 2aq (CCDC 2073616)



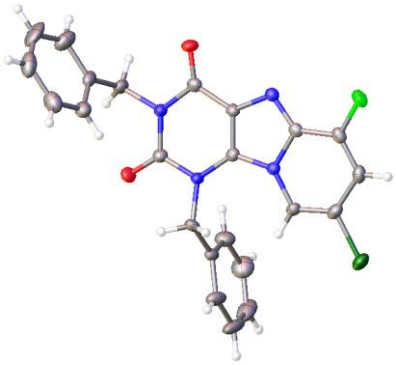
2aq

Empirical formula	$C_{12}H_{11}FN_4O_2$
Formula weight	262.25
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5108(7)
b/Å	6.6696(5)
c/Å	20.015(2)
α/°	90
β/°	101.966(9)
γ/°	90
Volume/Å^3	1111.44(17)
Z	4
ρ_{calc}g/cm^3	1.567
μ/mm^{-1}	1.038
F(000)	544.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.032 to 133.194
Index ranges	$-8 \le h \le 10$, $-7 \le k \le 4$, $-23 \le l \le 19$
Reflections collected	3422
Independent reflections	1952 [R_{int} = 0.0463, R_{sigma} = 0.0444]
Data/restraints/parameters	1952/0/175
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0682, wR_2 = 0.1770
Final R indexes [all data]	R_1 = 0.0715, wR_2 = 0.1835
Largest diff. peak/hole / e Å^{-3}	0.42/-0.60

Compound 2as (CCDC 2073613)

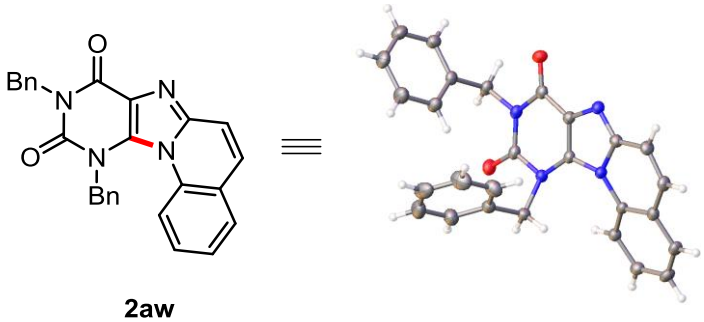


2as



Empirical formula	$C_{24}H_{18}Cl_3FN_4O_2$
Formula weight	519.77
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3994(5)
b/Å	12.1363(6)
c/Å	17.1162(6)
α/°	102.133(3)
β/°	91.902(3)
γ/°	98.107(4)
Volume/Å^3	2287.10(17)
Z	4
ρ_{calc}g/cm^3	1.510
μ/mm^{-1}	0.440
F(000)	1064.0
Crystal size/mm^3	0.14 × 0.11 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.23 to 49.998
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	16376
Independent reflections	8068 [R_{int} = 0.0275, R_{sigma} = 0.0474]
Data/restraints/parameters	8068/0/613
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0620, wR_2 = 0.1083
Largest diff. peak/hole / e Å^{-3}	0.56/-0.53

Compound 2aw (CCDC 2073614)

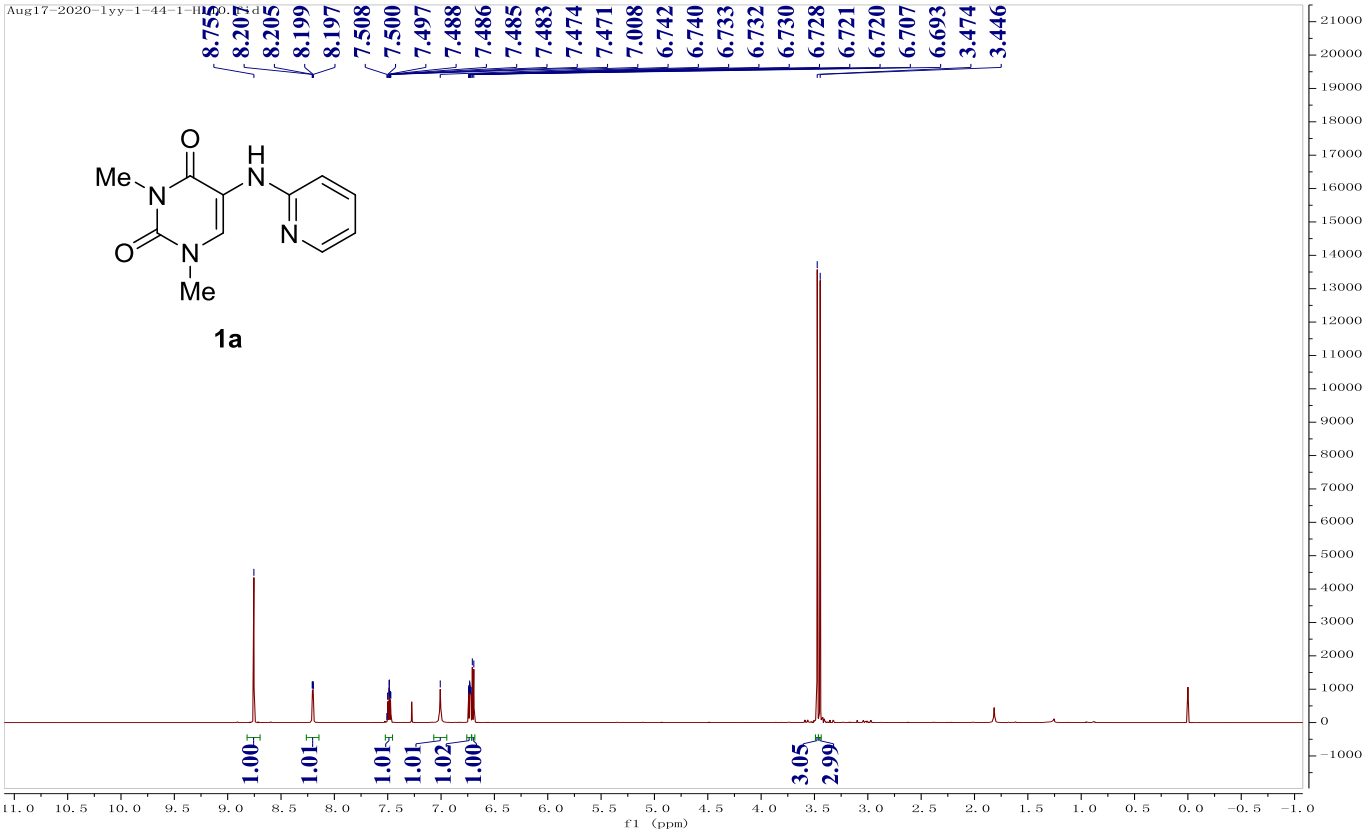


2aw

Empirical formula	$C_{27}H_{20}N_4O_2$
Formula weight	432.47
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0682(7)
b/Å	10.7628(10)
c/Å	11.0063(10)
α/°	82.013(8)
β/°	80.721(7)
γ/°	85.528(7)
Volume/Å^3	1048.17(16)
Z	2
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	0.714
F(000)	452.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.208 to 148.33
Index ranges	-11 ≤ h ≤ 8, -13 ≤ k ≤ 13, -12 ≤ l ≤ 13
Reflections collected	6996
Independent reflections	4095 [R_{int} = 0.0303, R_{sigma} = 0.0456]
Data/restraints/parameters	4095/0/298
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1152
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1256
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29

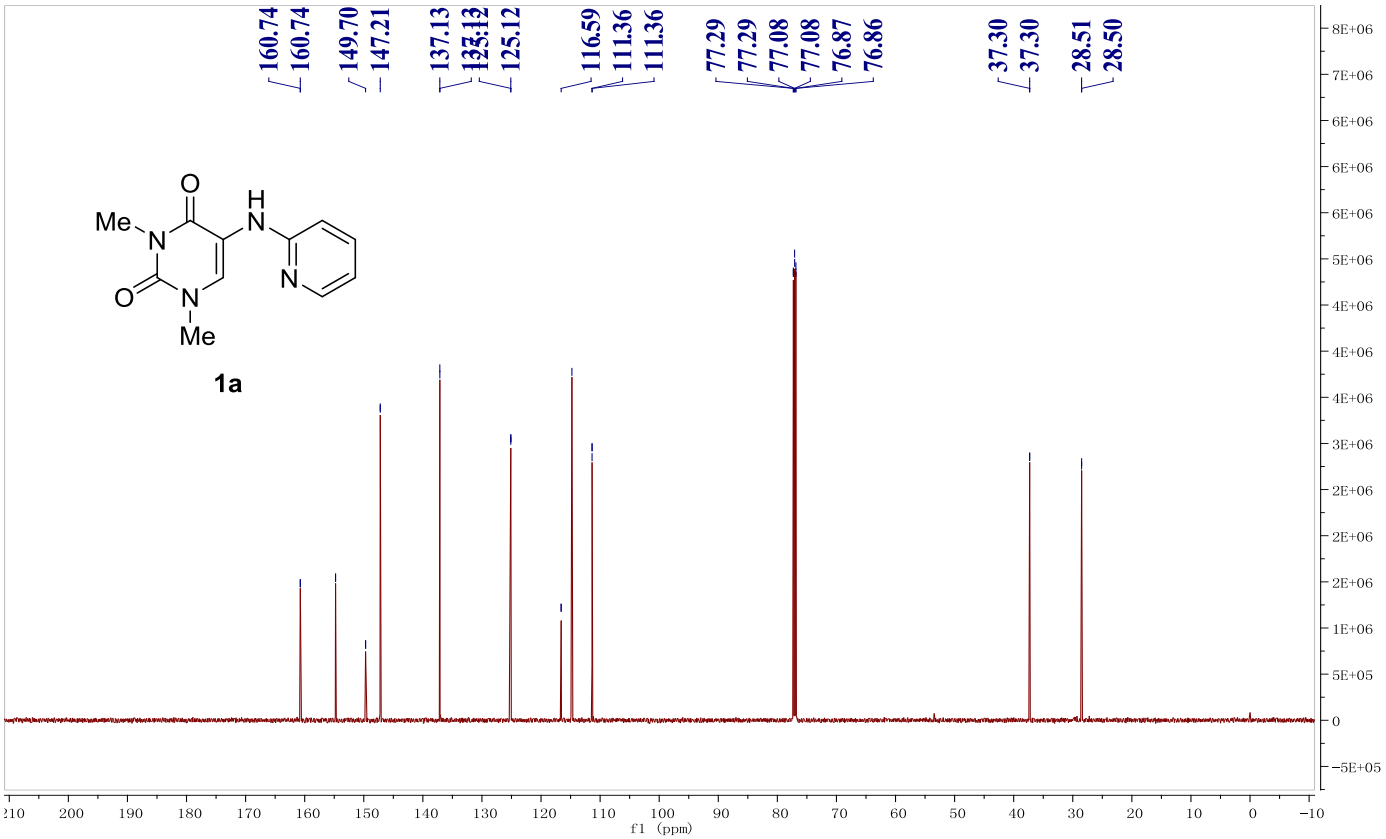
11 NMR Spectra

^{1}H NMR Spectrum of 1a at 25 °C ($CDCl_3$, 600 MHz)



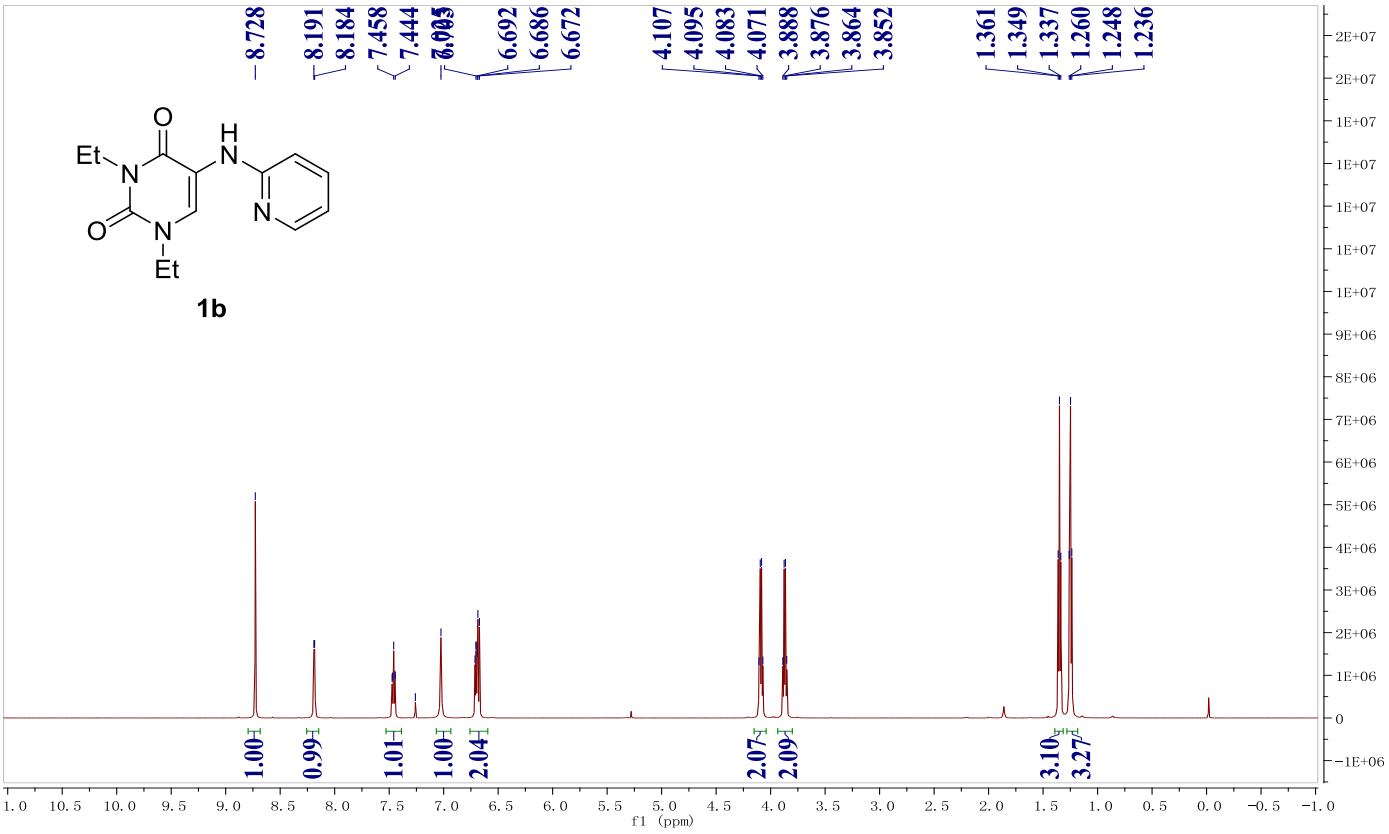
1a

^{13}C NMR Spectrum of 1a at 25 °C ($CDCl_3$, 150 MHz)

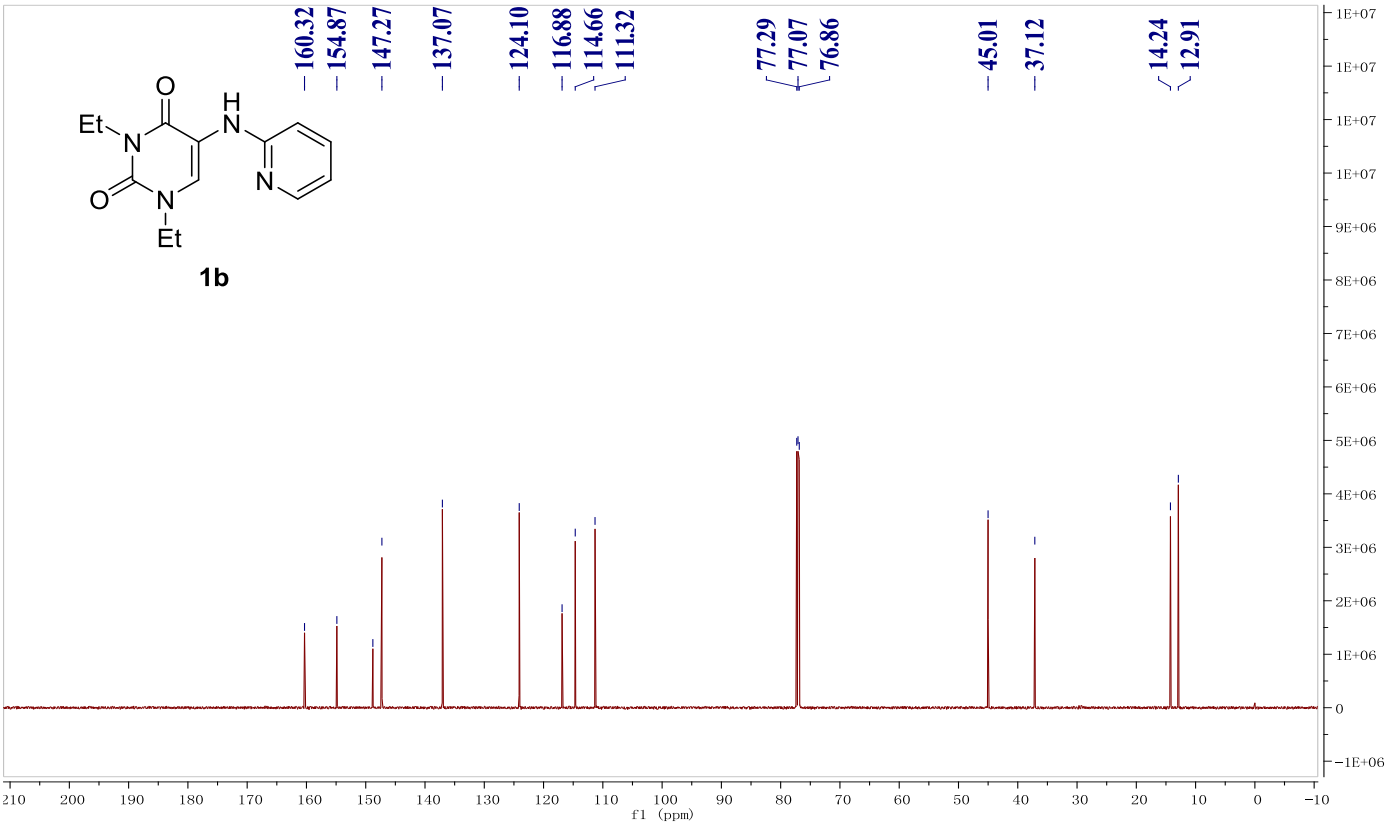


1a

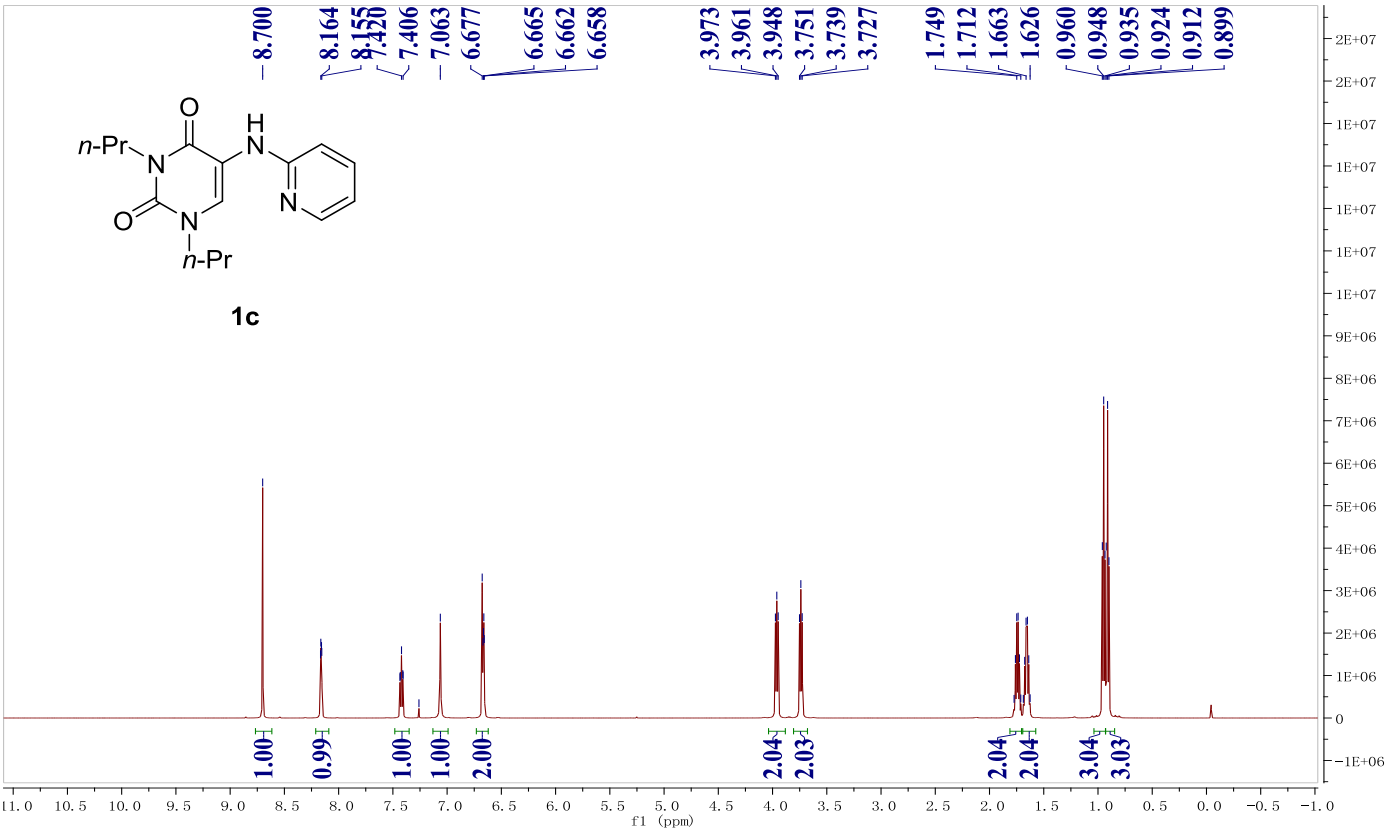
^{1}H NMR Spectrum of 1b at 25 °C ($CDCl_3$, 600 MHz)



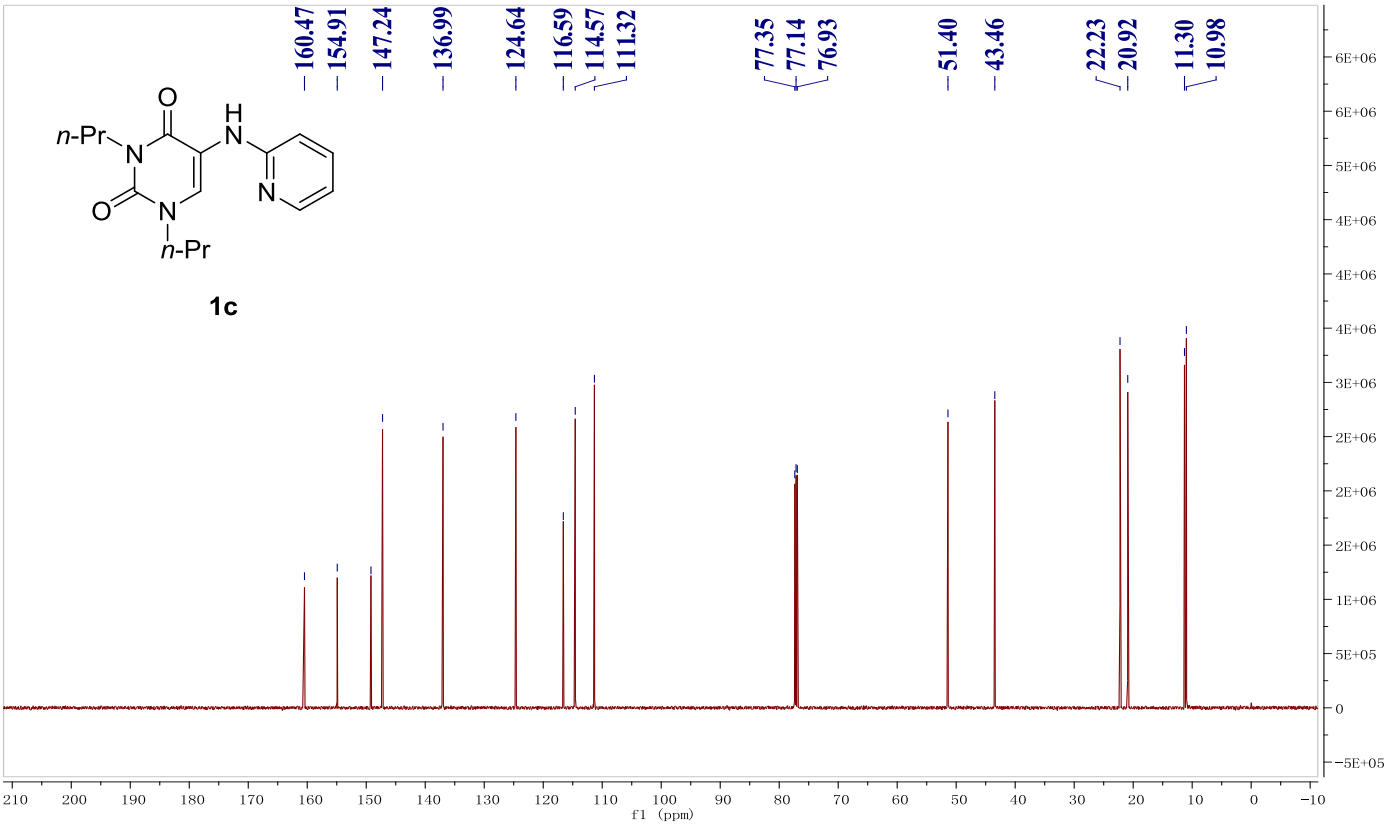
^{13}C NMR Spectrum of 1b at 25 °C ($CDCl_3$, 150 MHz)



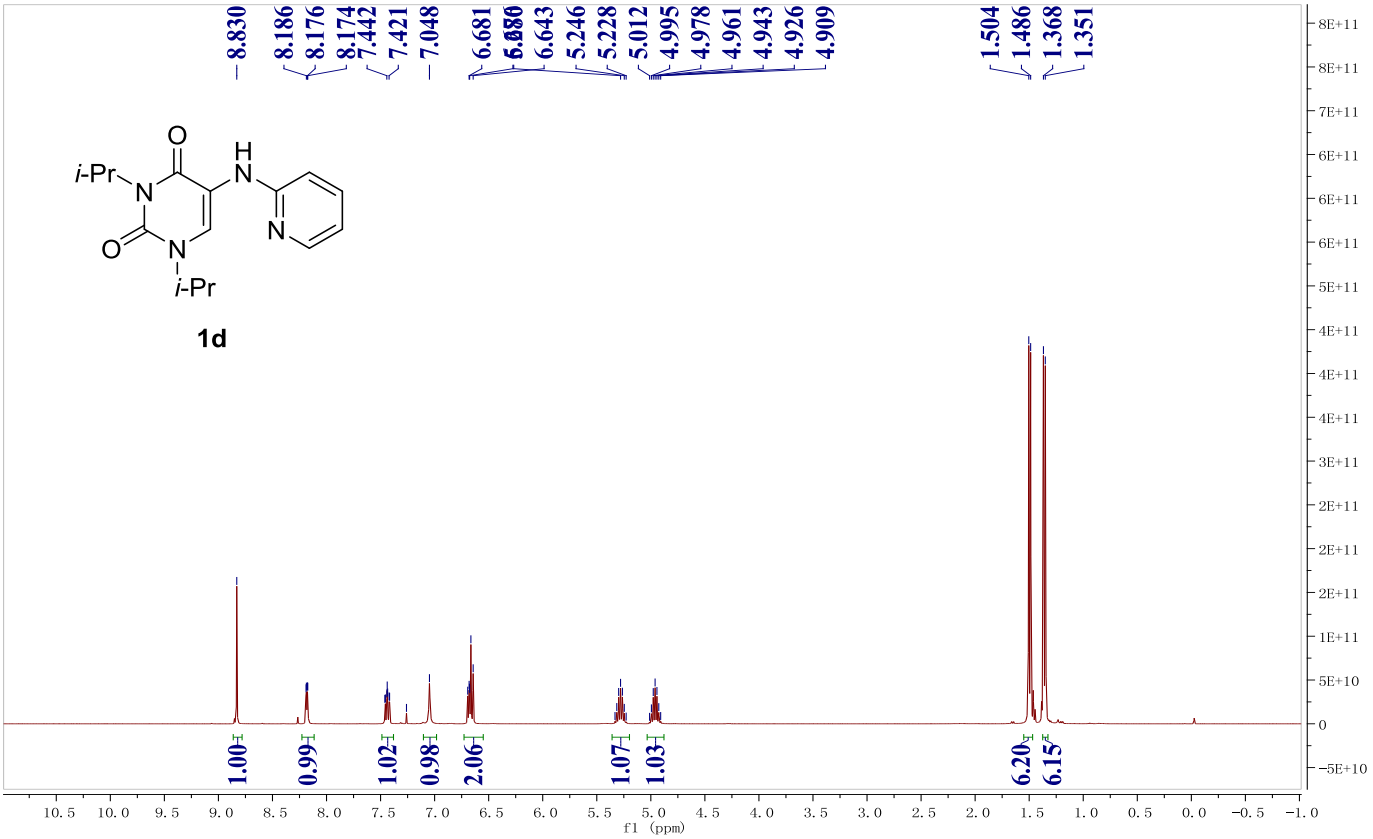
^{1}H NMR Spectrum of 1c at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 1c at 25 °C ($CDCl_3$, 150 MHz)

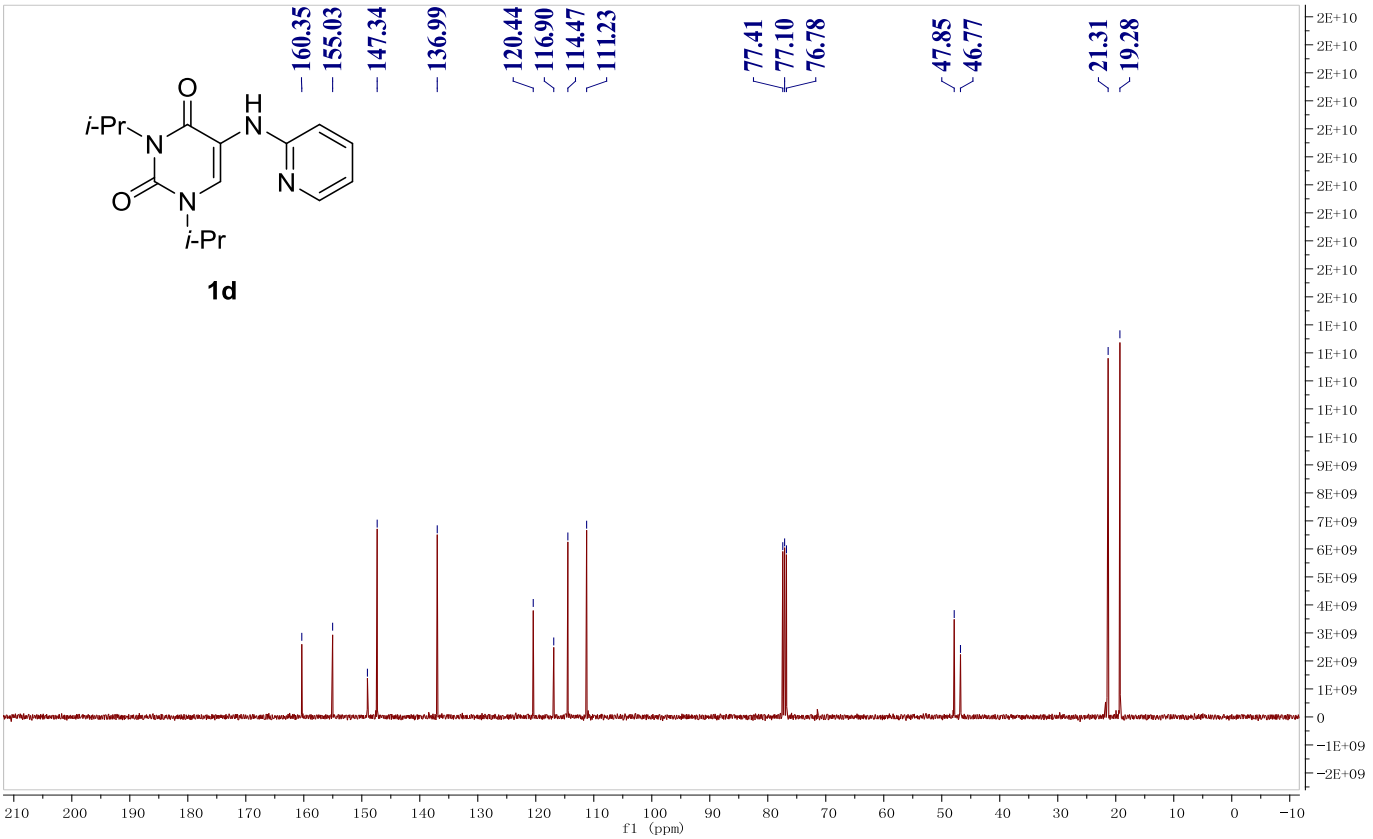


^{1}H NMR Spectrum of 1d at 25 °C ($CDCl_3$, 400 MHz)



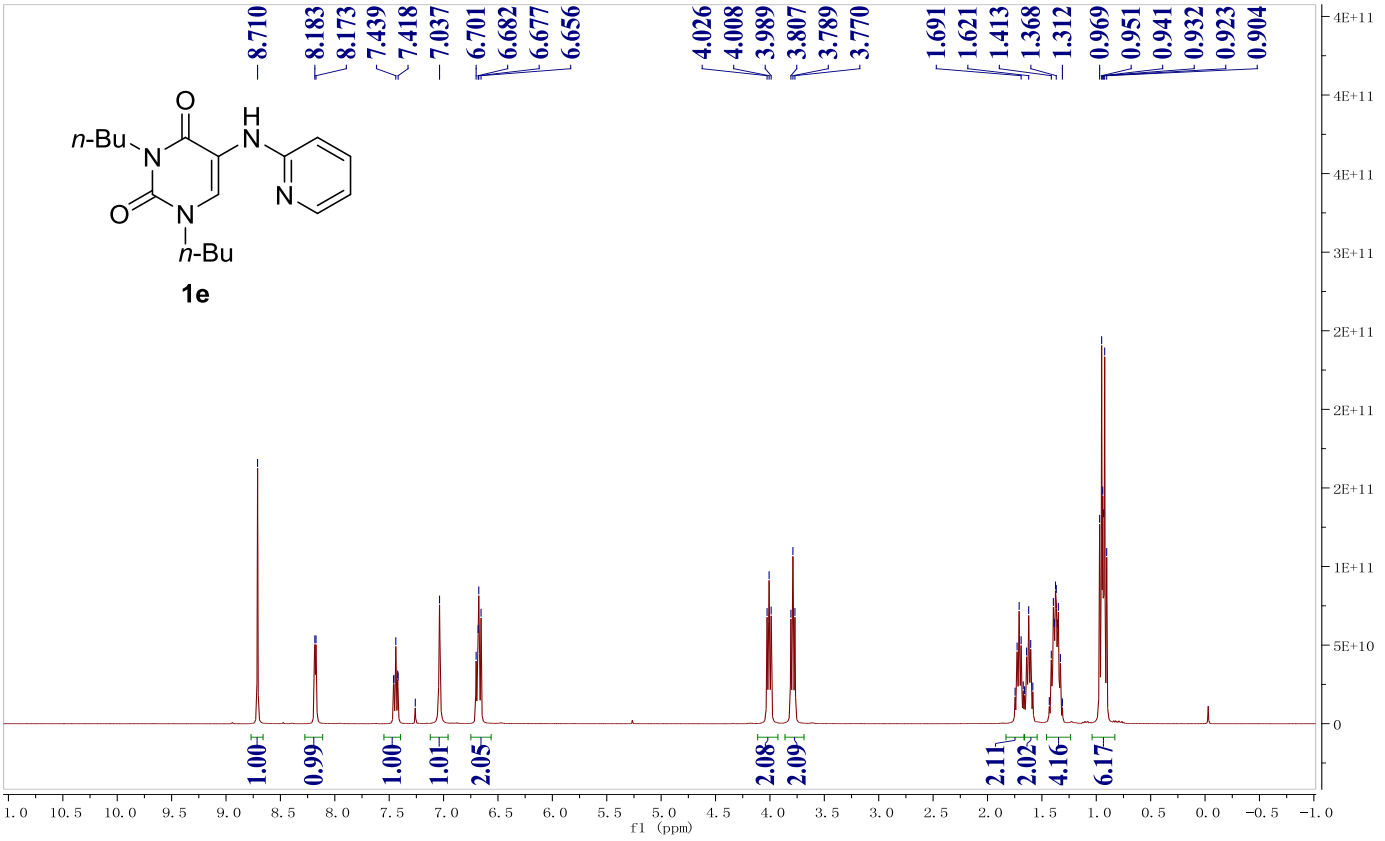
1d

^{13}C NMR Spectrum of 1d at 25 °C ($CDCl_3$, 100 MHz)

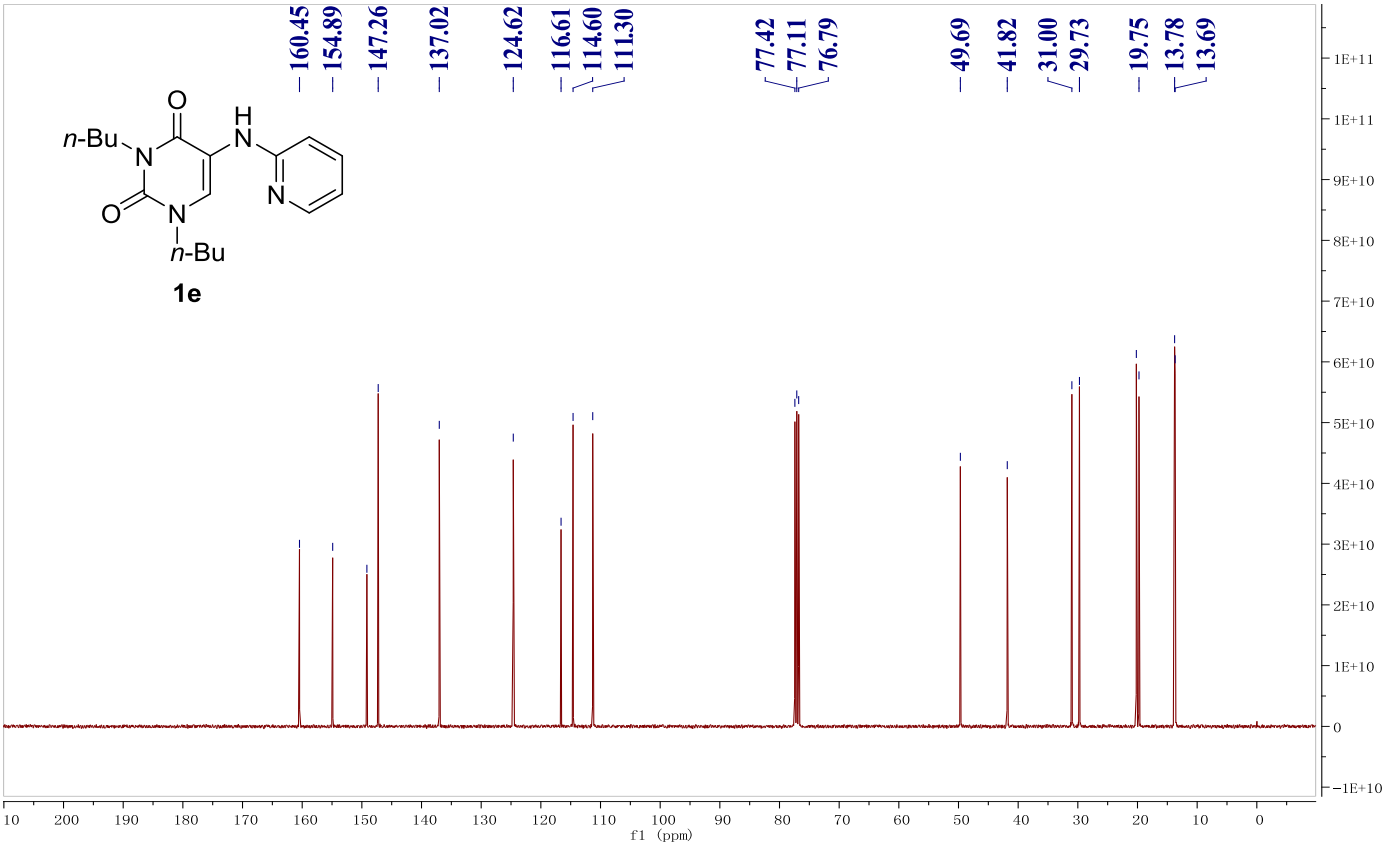


1d

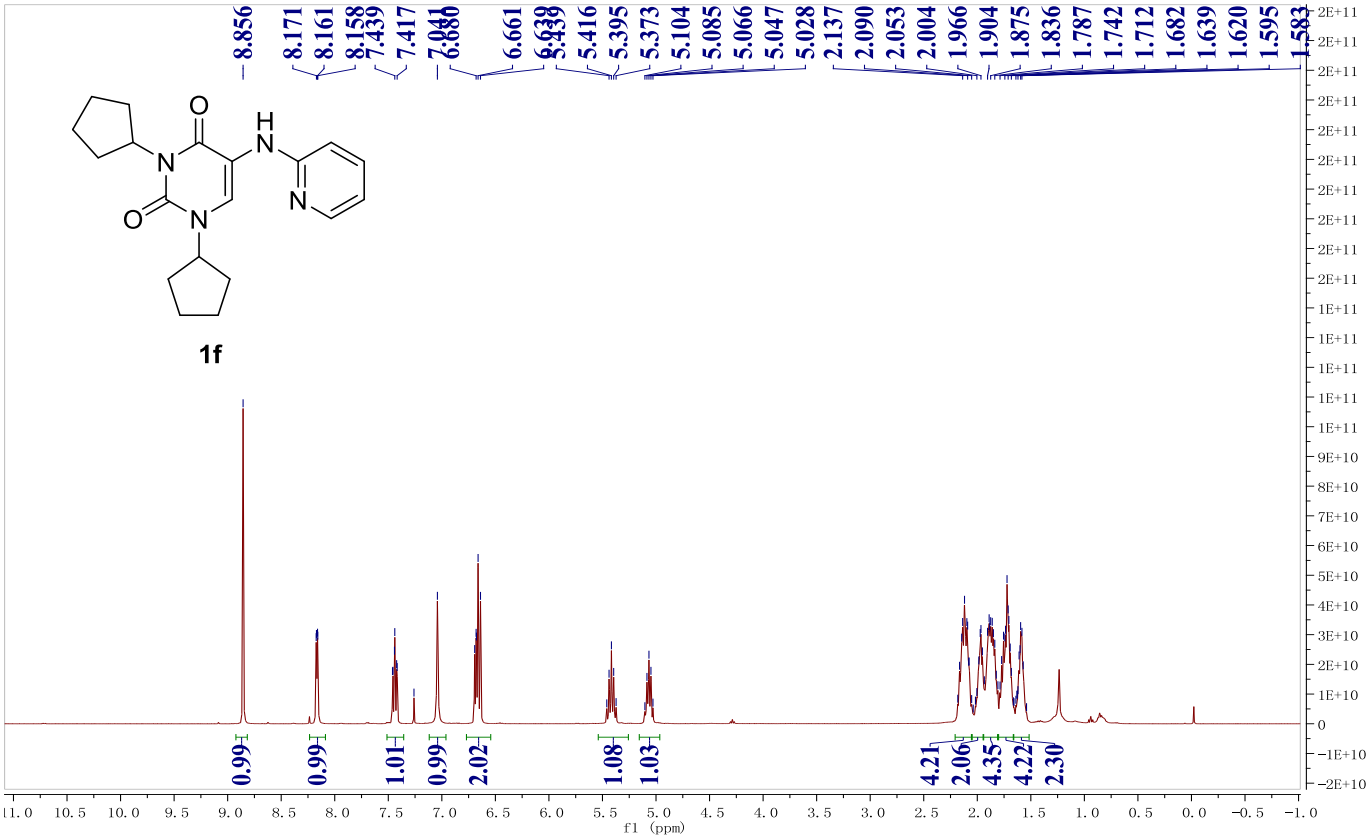
^{1}H NMR Spectrum of 1e at 25 °C ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of 1e at 25 °C ($CDCl_3$, 100 MHz)

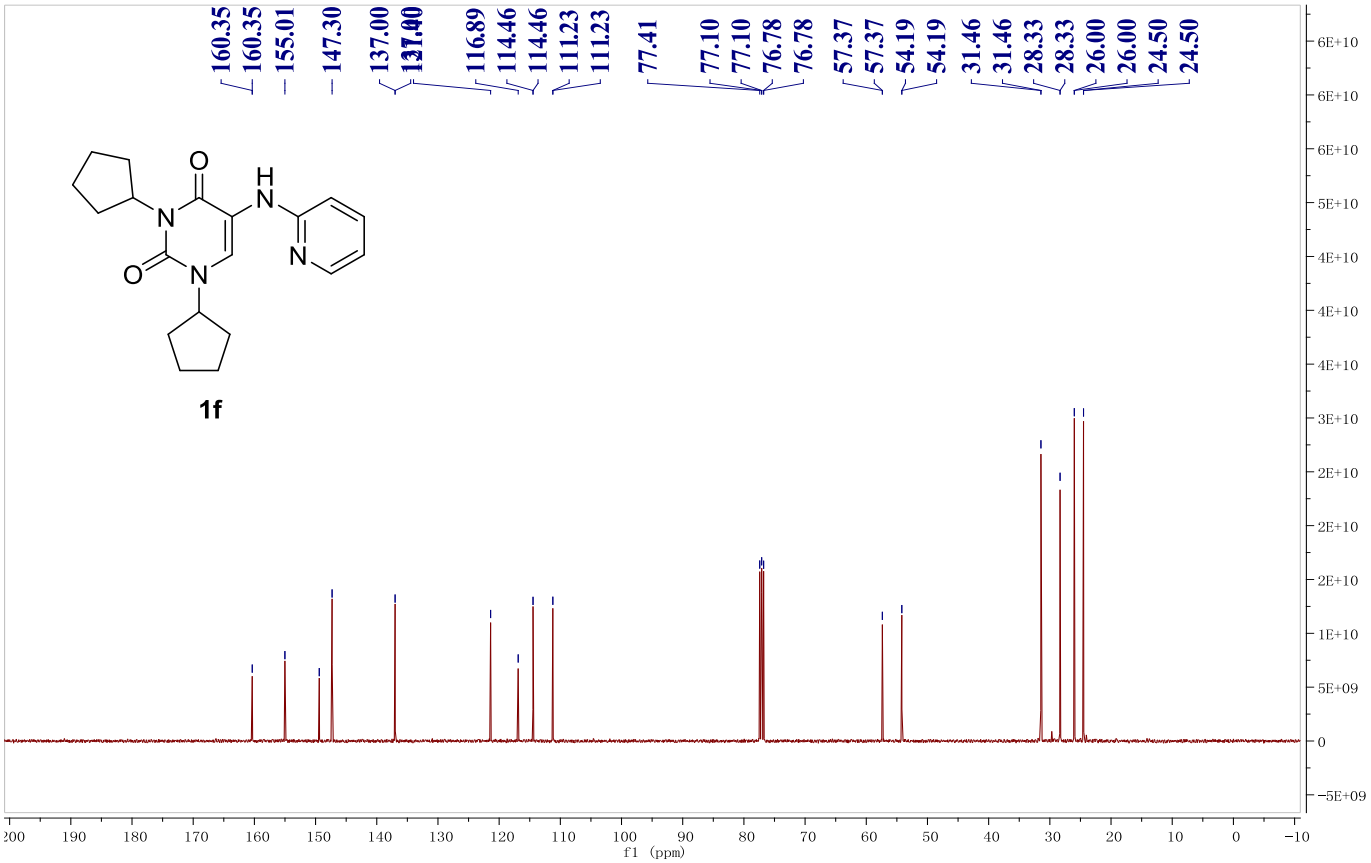


^{1}H NMR Spectrum of 1f at 25 °C ($CDCl_3$, 400 MHz)



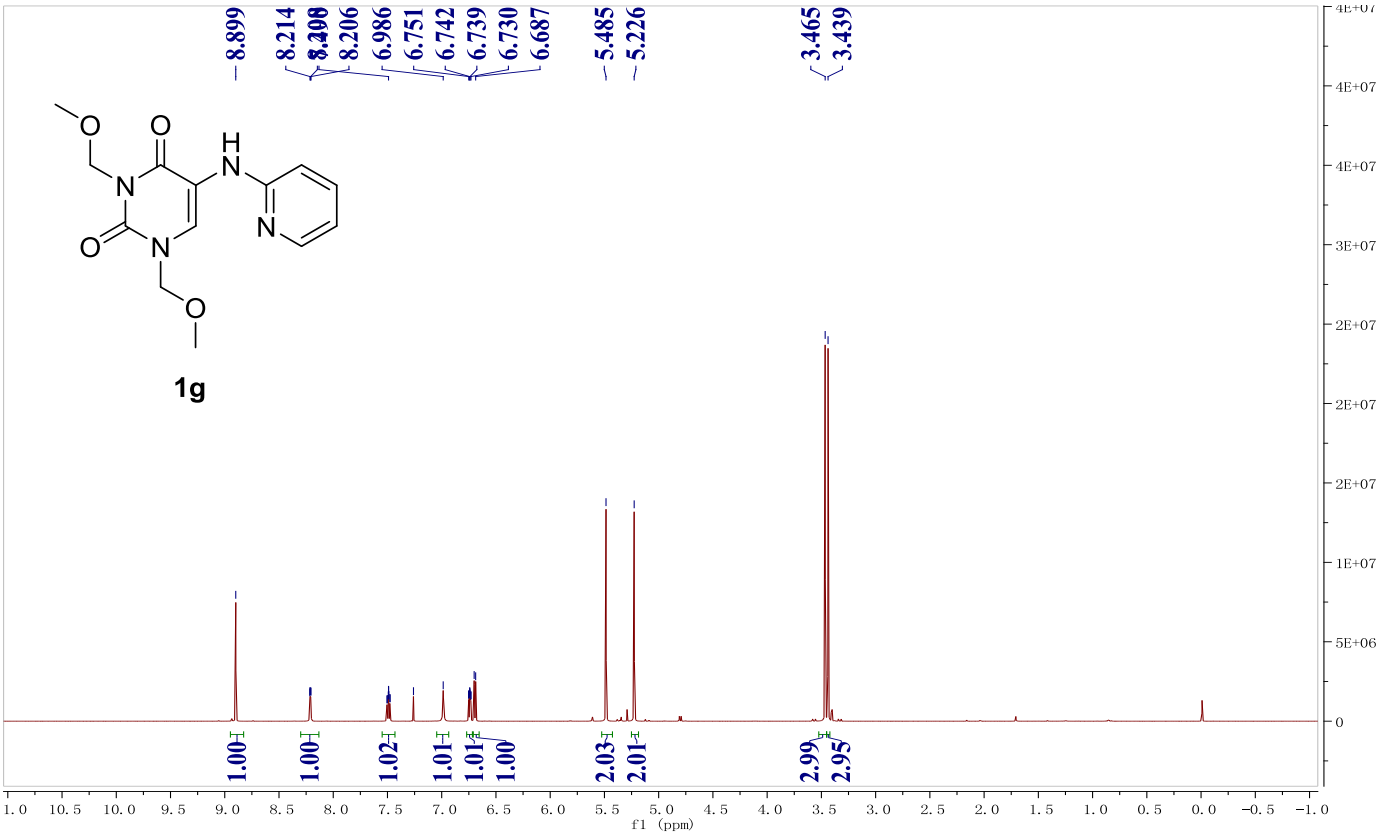
1f

^{13}C NMR Spectrum of 1f at 25 °C ($CDCl_3$, 100 MHz)



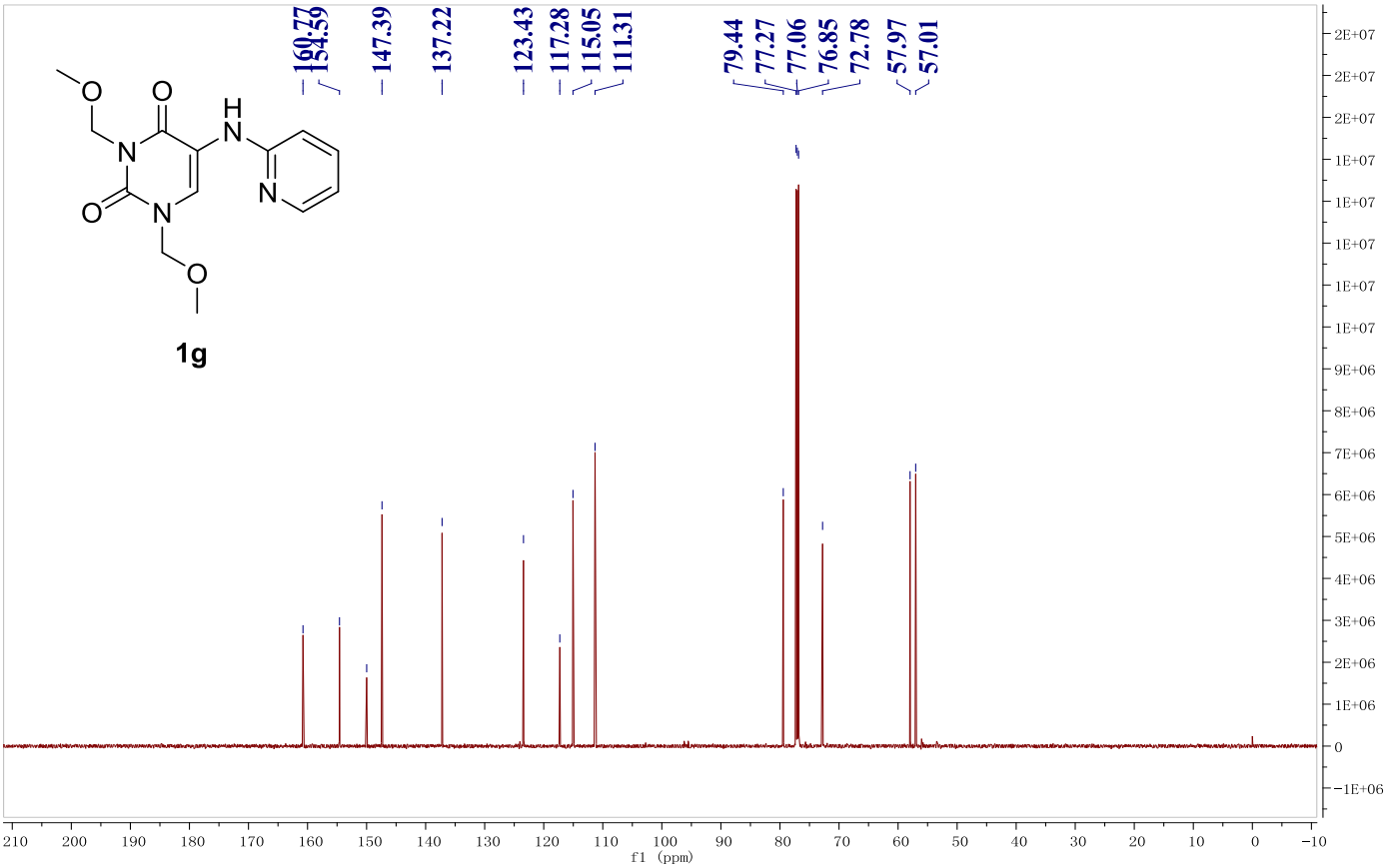
1f

^{1}H NMR Spectrum of 1g at 25 °C ($CDCl_3$, 600 MHz)



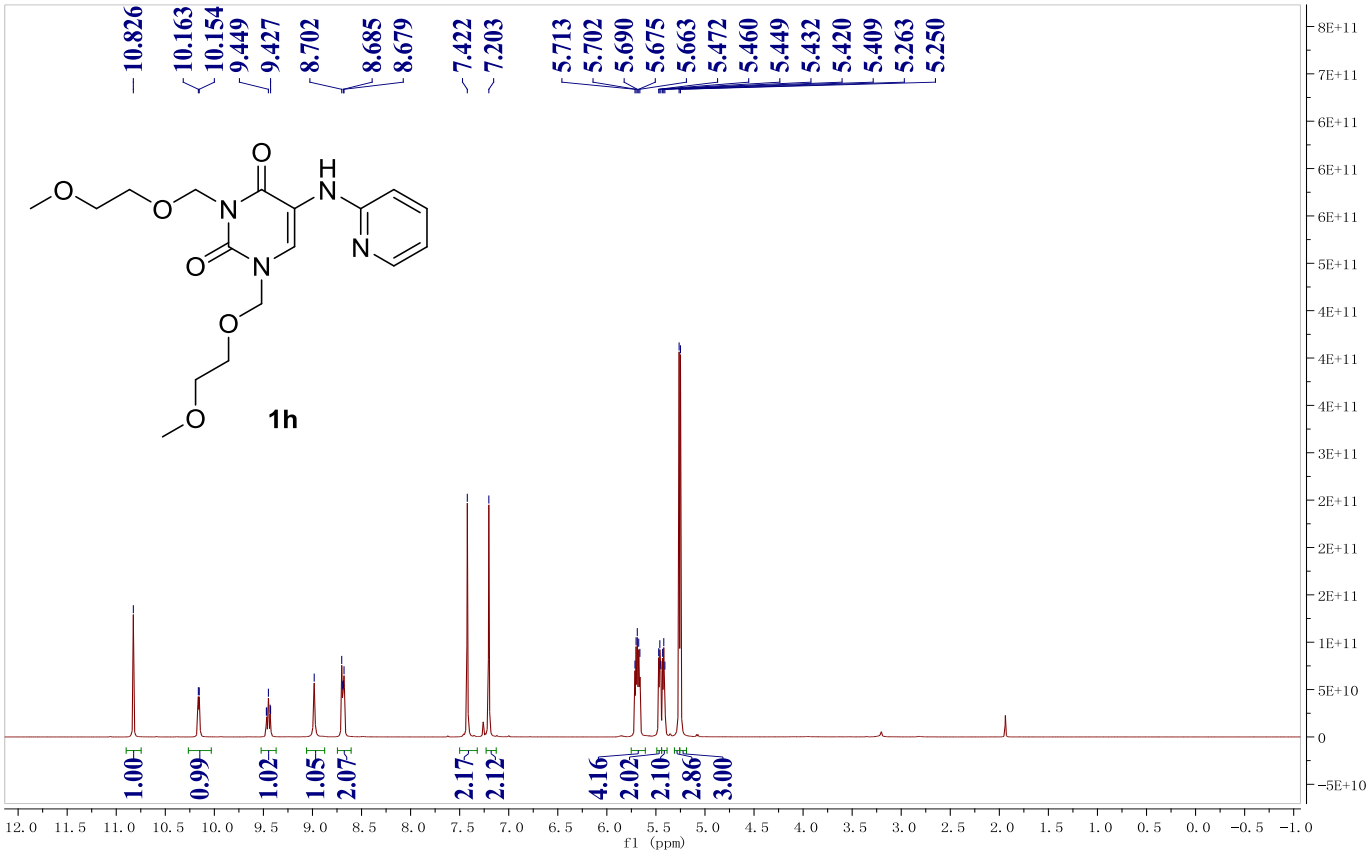
1g

^{13}C NMR Spectrum of 1g at 25 °C ($CDCl_3$, 150 MHz)

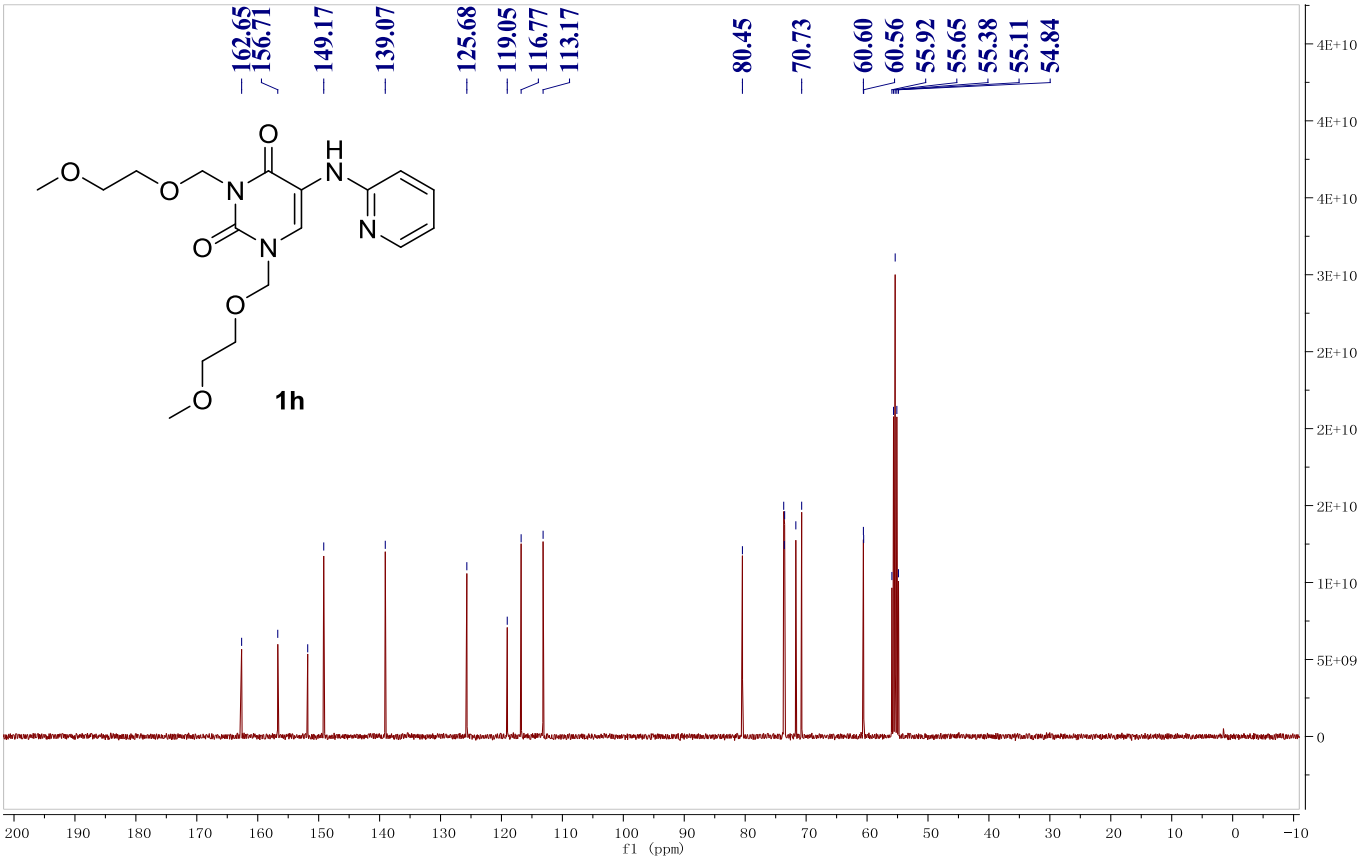


1g

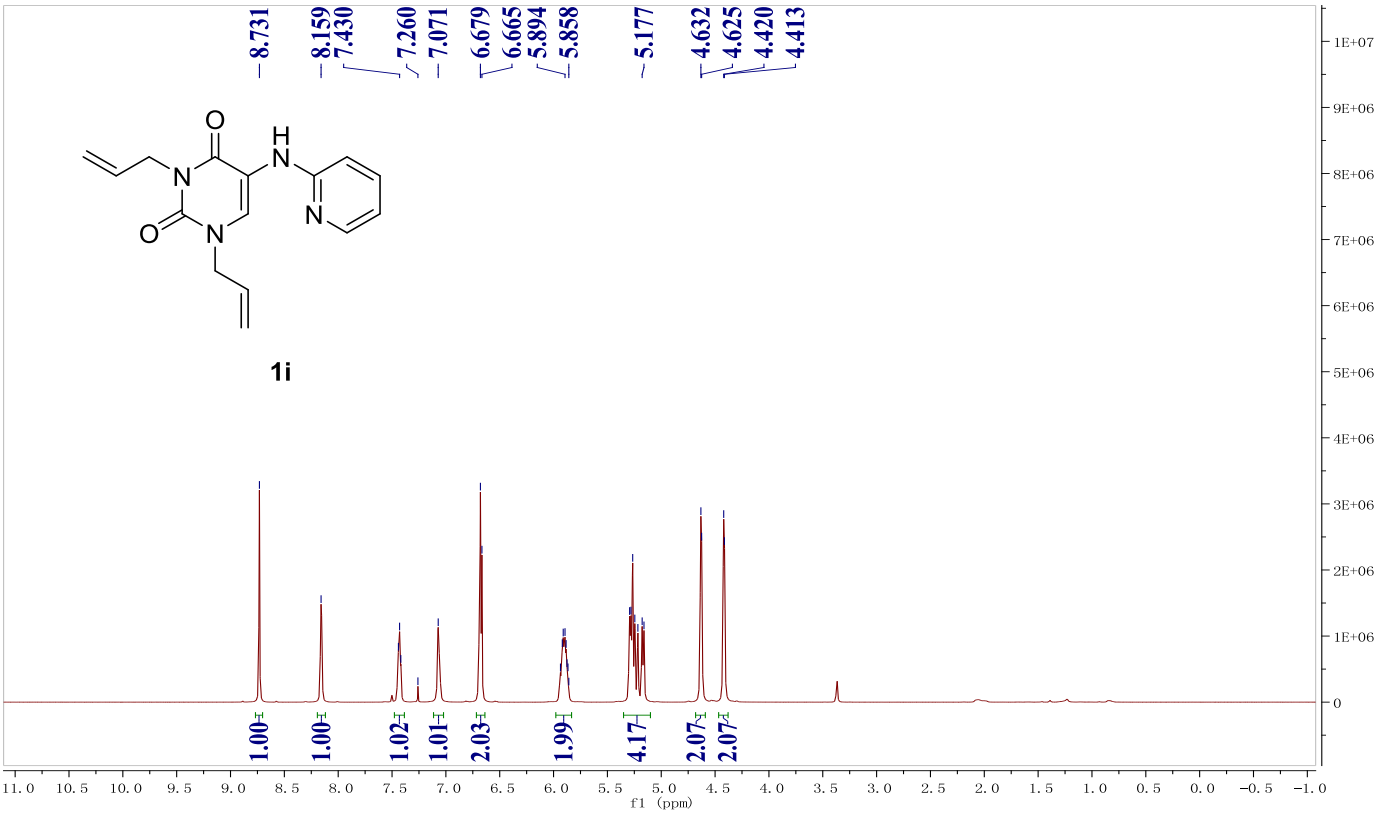
^{1}H NMR Spectrum of 1h at 25 °C (CD_2Cl_2, 400 MHz)



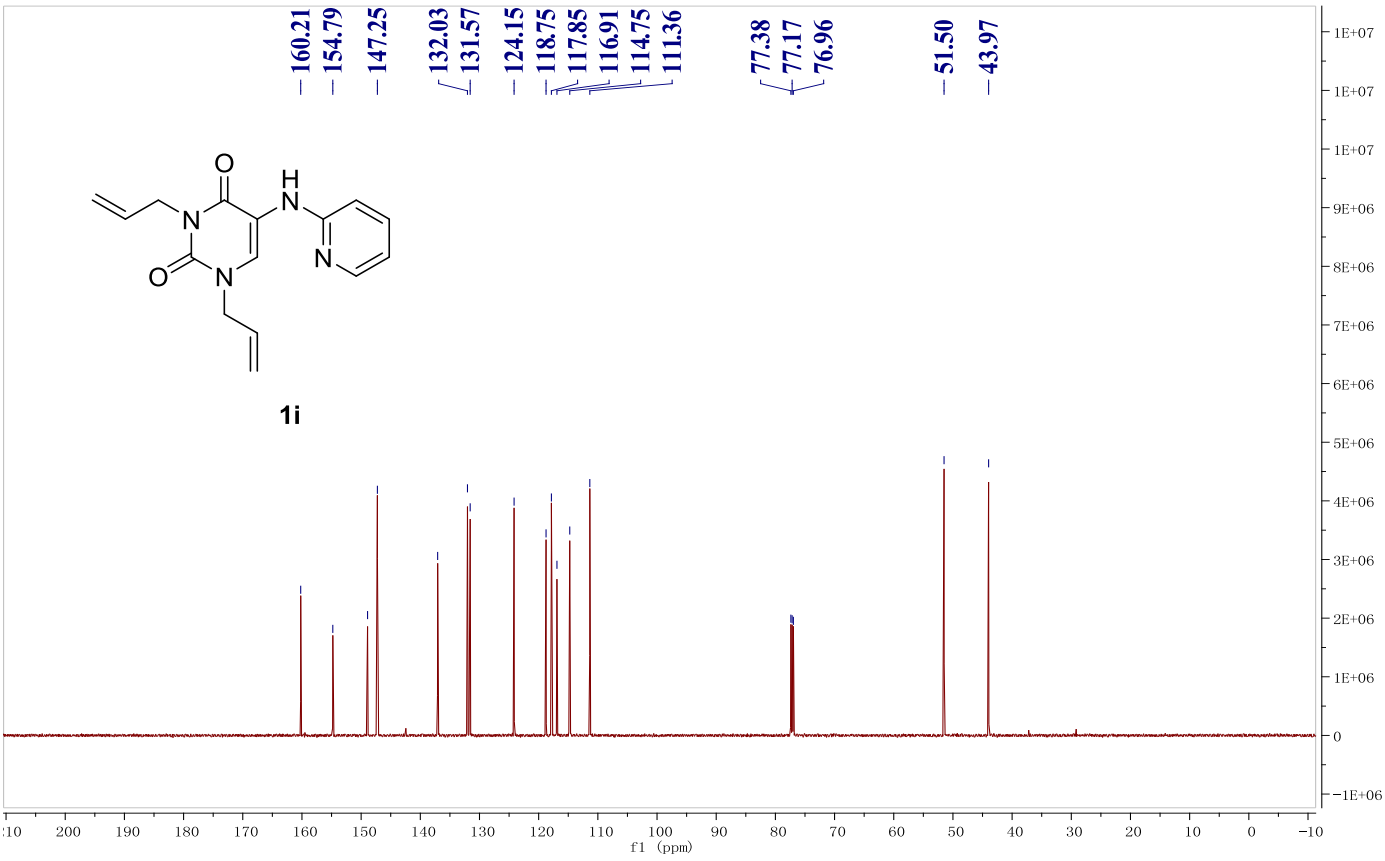
^{13}C NMR Spectrum of 1h at 25 °C (CD_2Cl_2, 100 MHz)



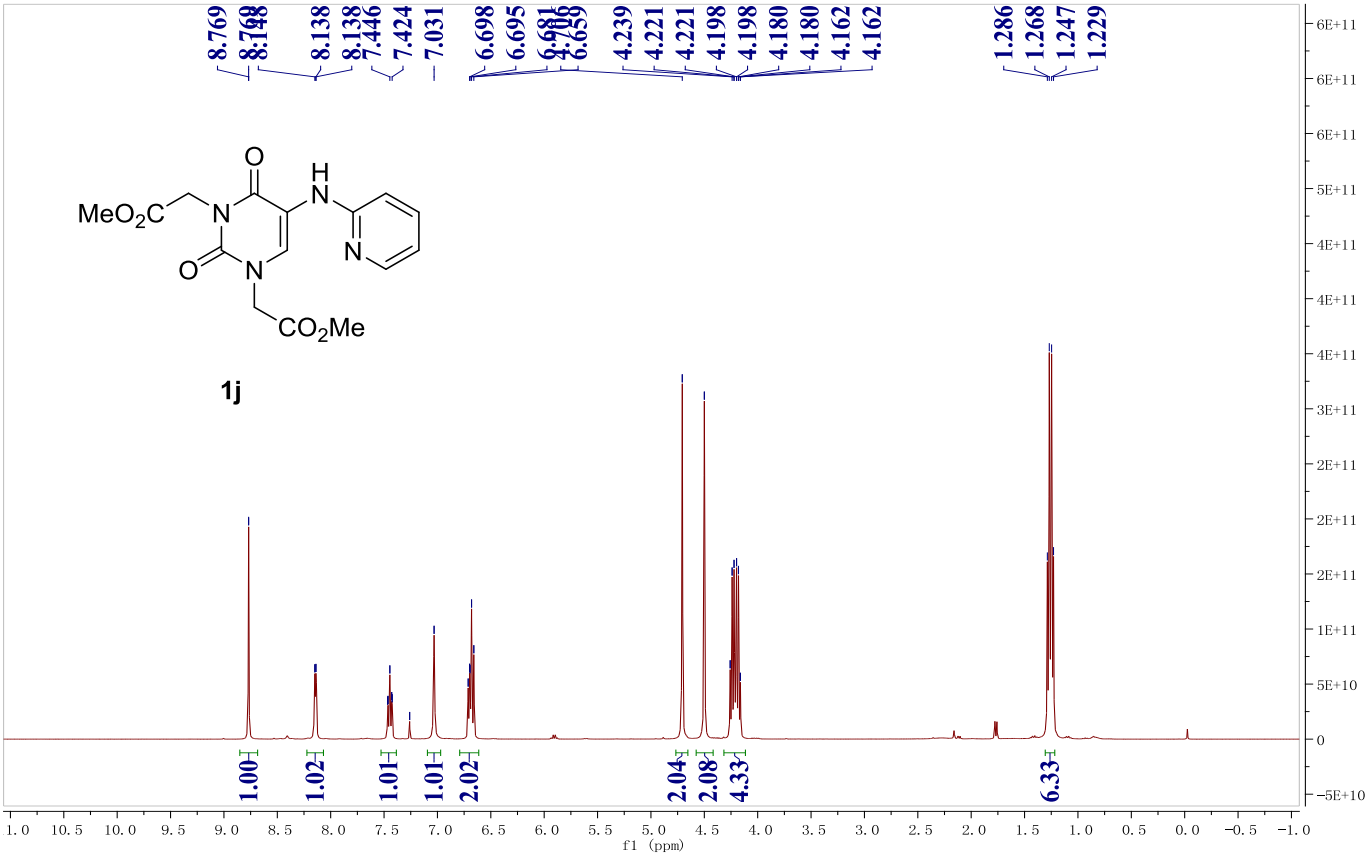
^{1}H NMR Spectrum of 1i at 25 °C ($CDCl_3$, 600 MHz)



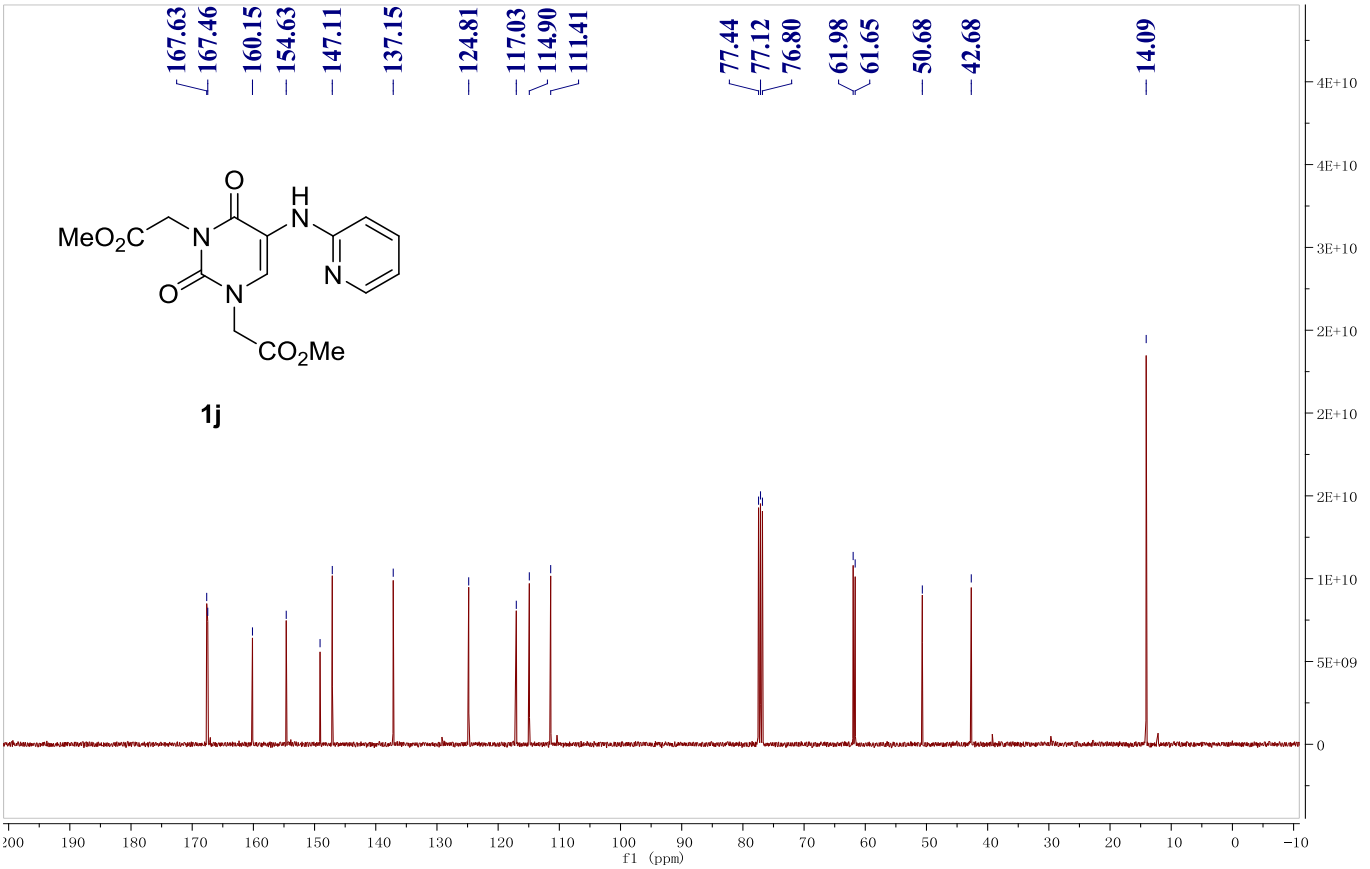
^{13}C NMR Spectrum of 1i at 25 °C ($CDCl_3$, 150 MHz)



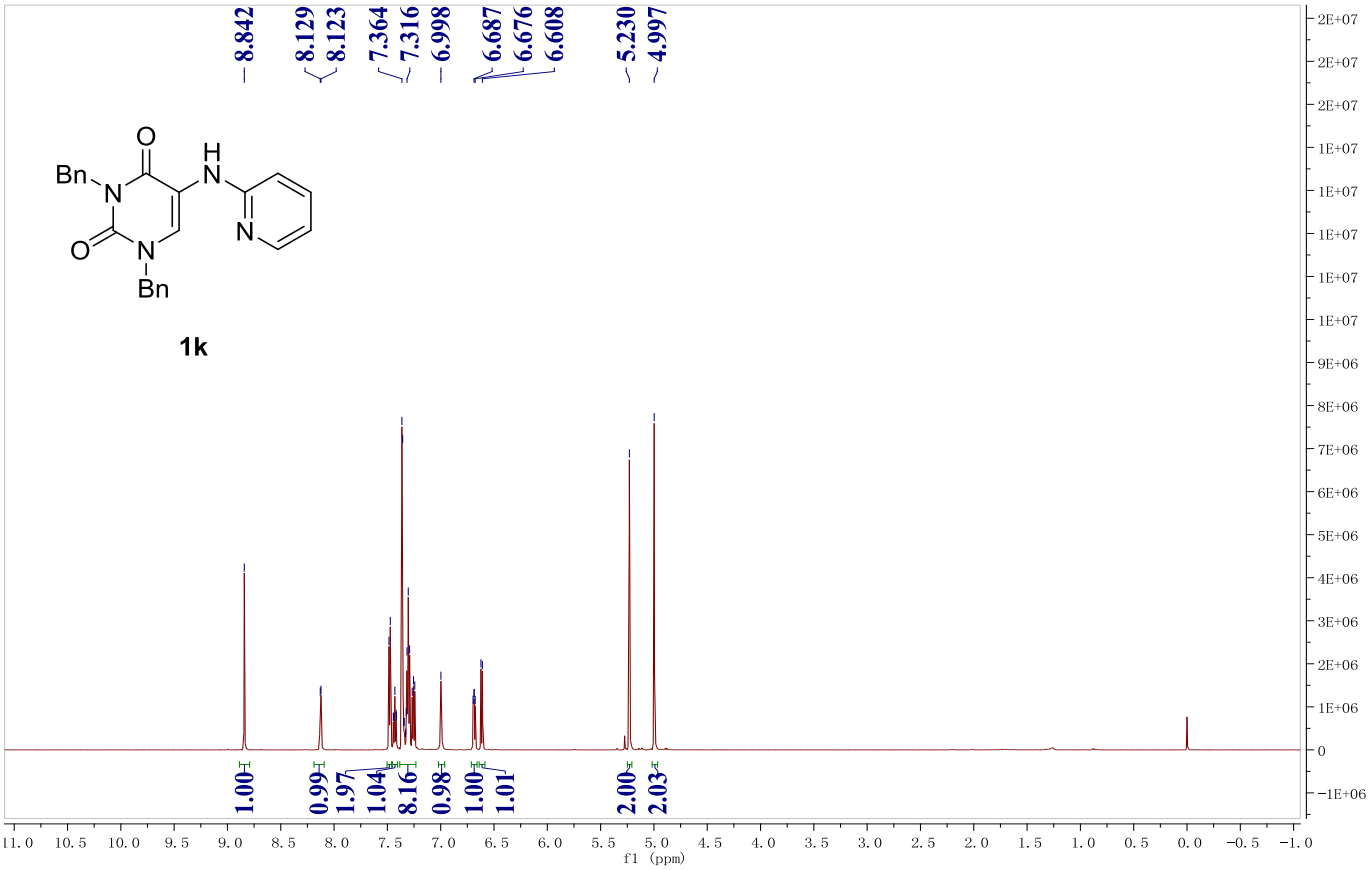
^{1}H NMR Spectrum of 1j at 25 °C ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of 1j at 25 °C ($CDCl_3$, 100 MHz)

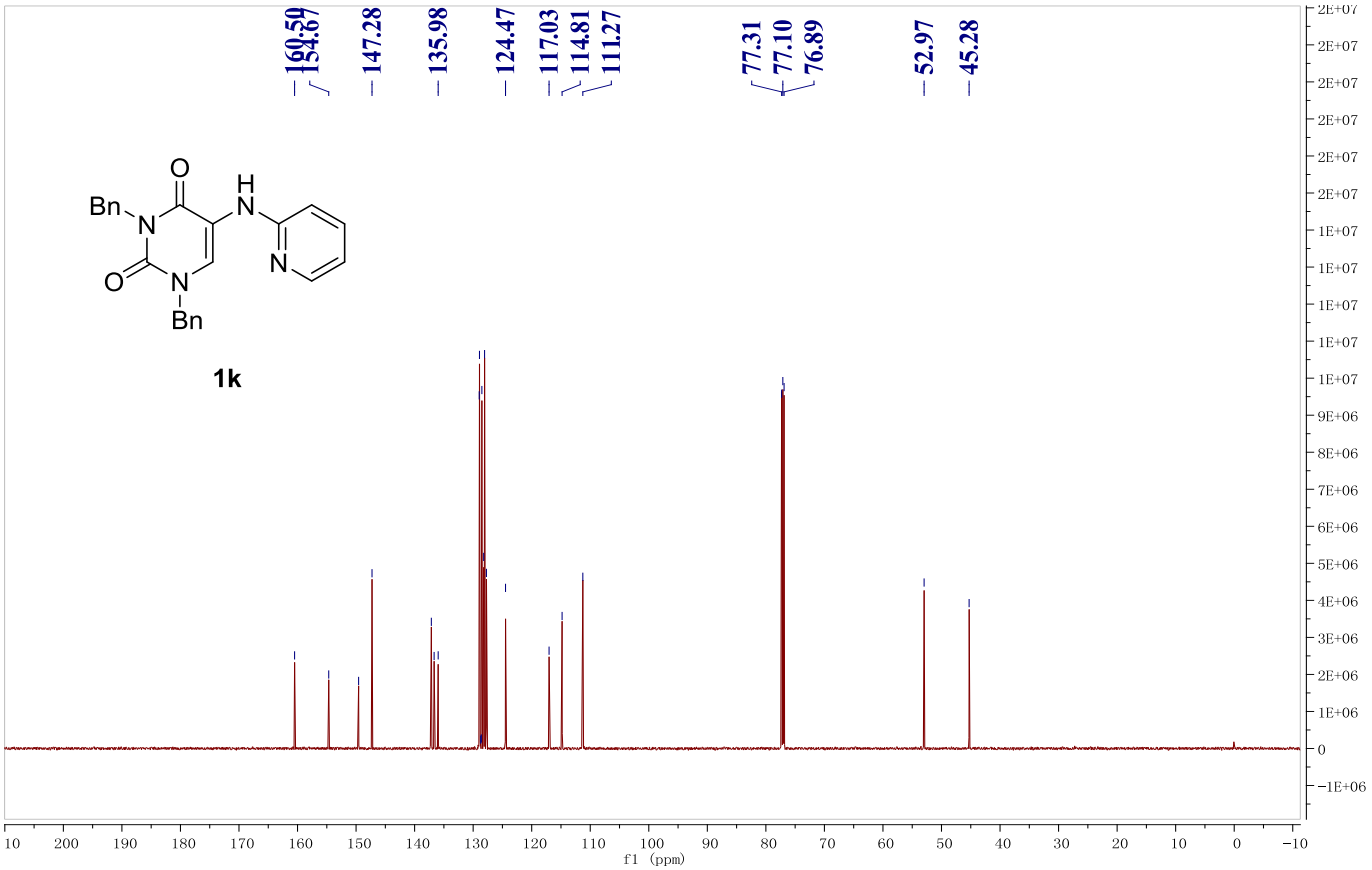


^{1}H NMR Spectrum of 1k at 25 °C ($CDCl_3$, 600 MHz)



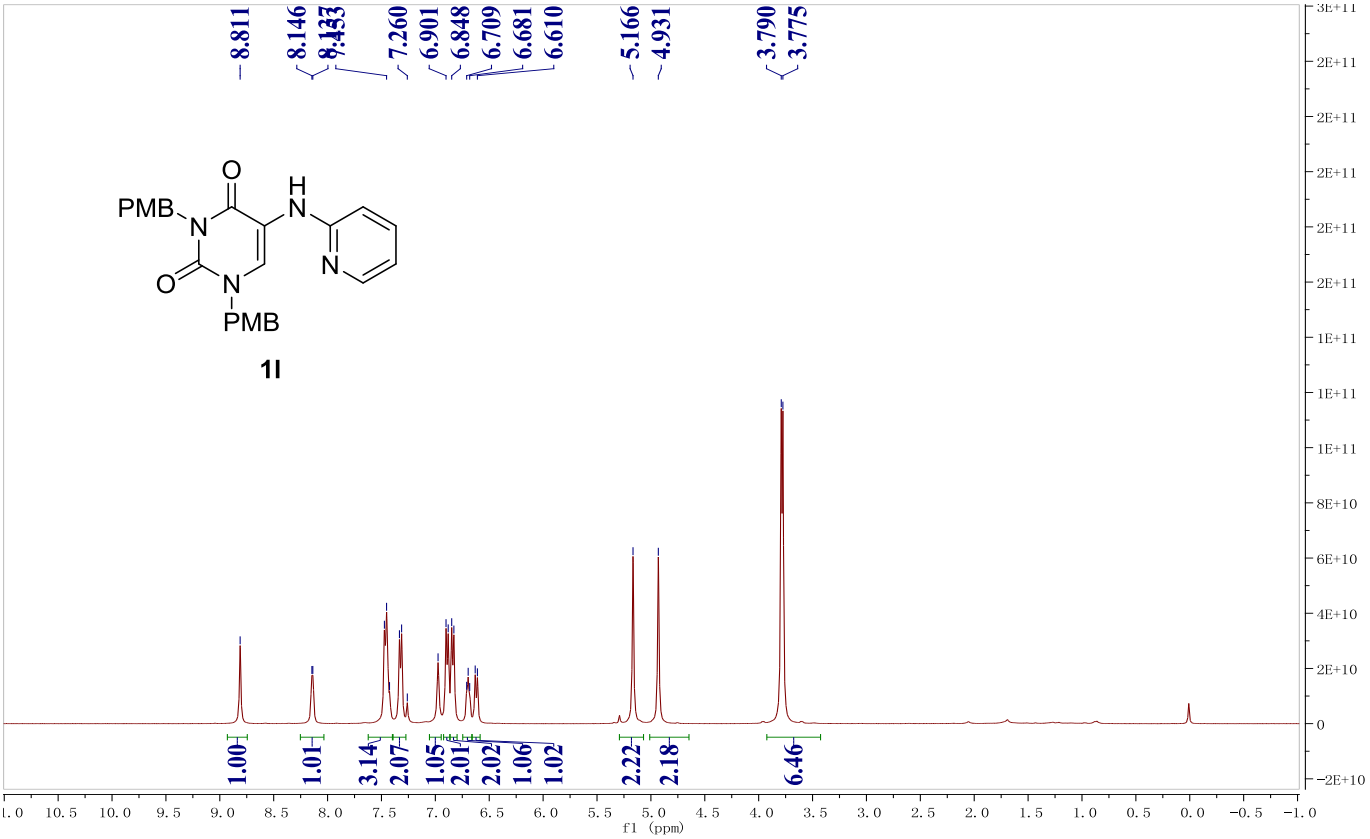
1k

^{13}C NMR Spectrum of 1k at 25 °C ($CDCl_3$, 150 MHz)

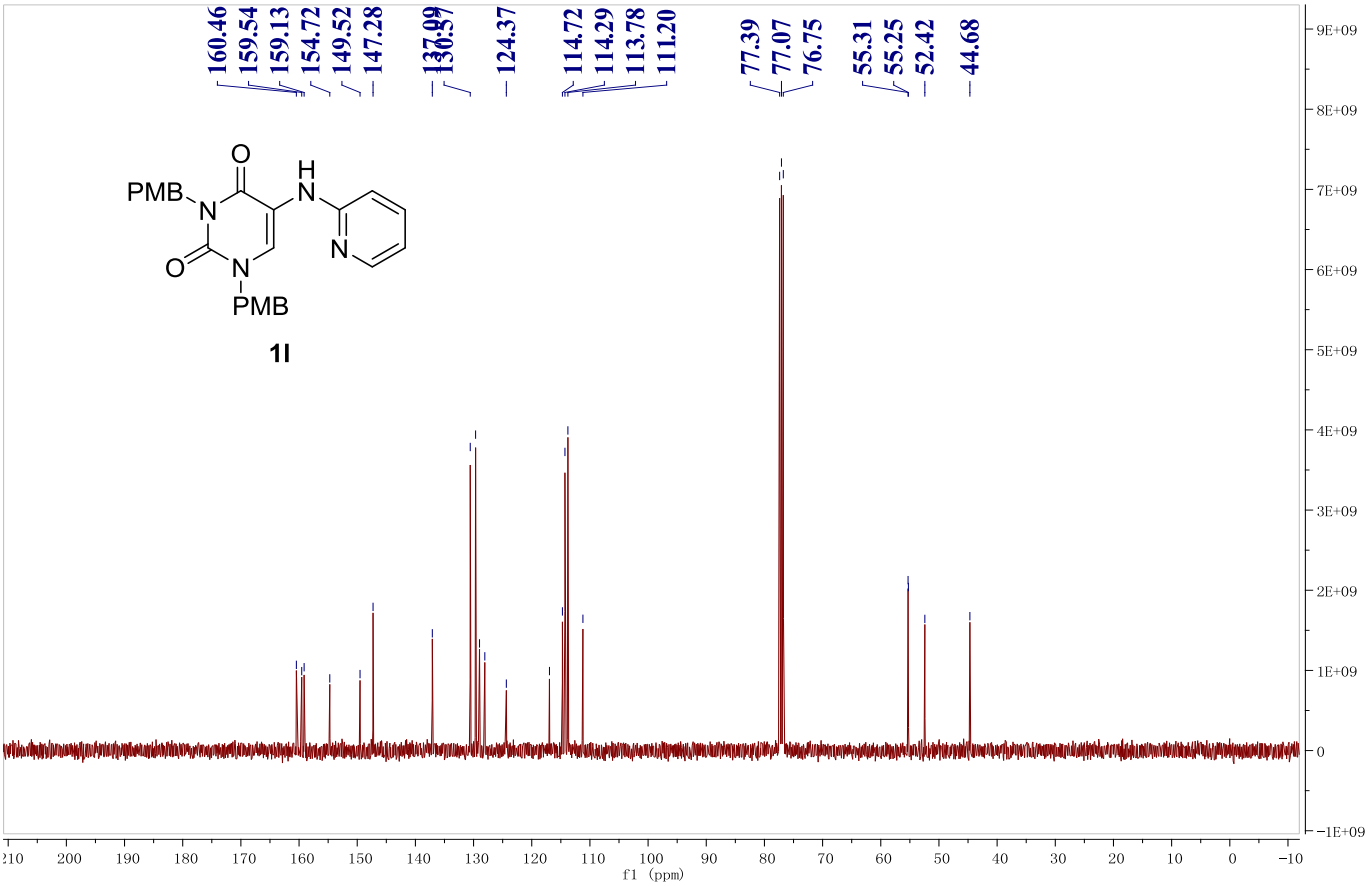


1k

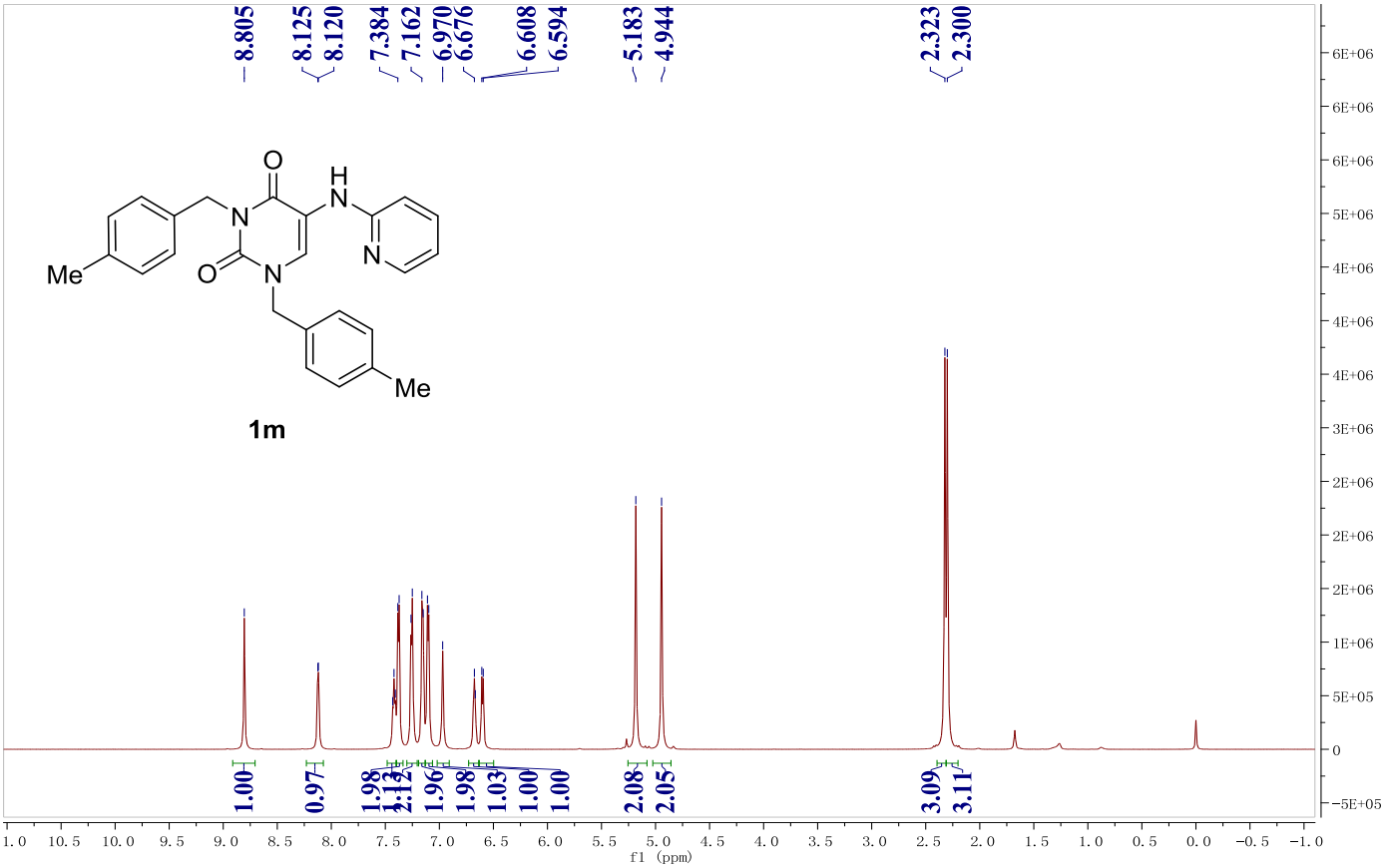
^{1}H NMR Spectrum of 1l at 25 °C ($CDCl_3$, 400 MHz)



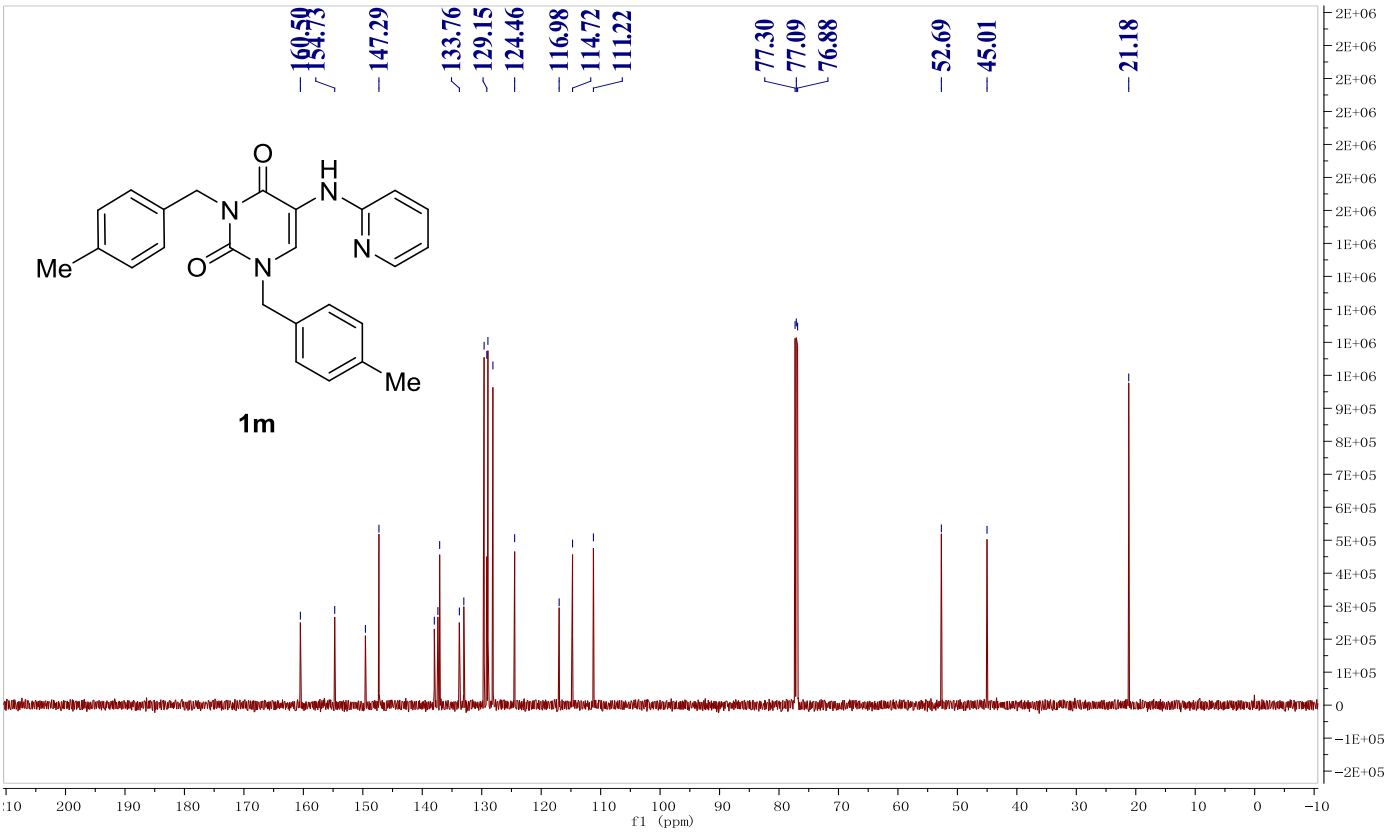
^{13}C NMR Spectrum of 1l at 25 °C ($CDCl_3$, 100 MHz)



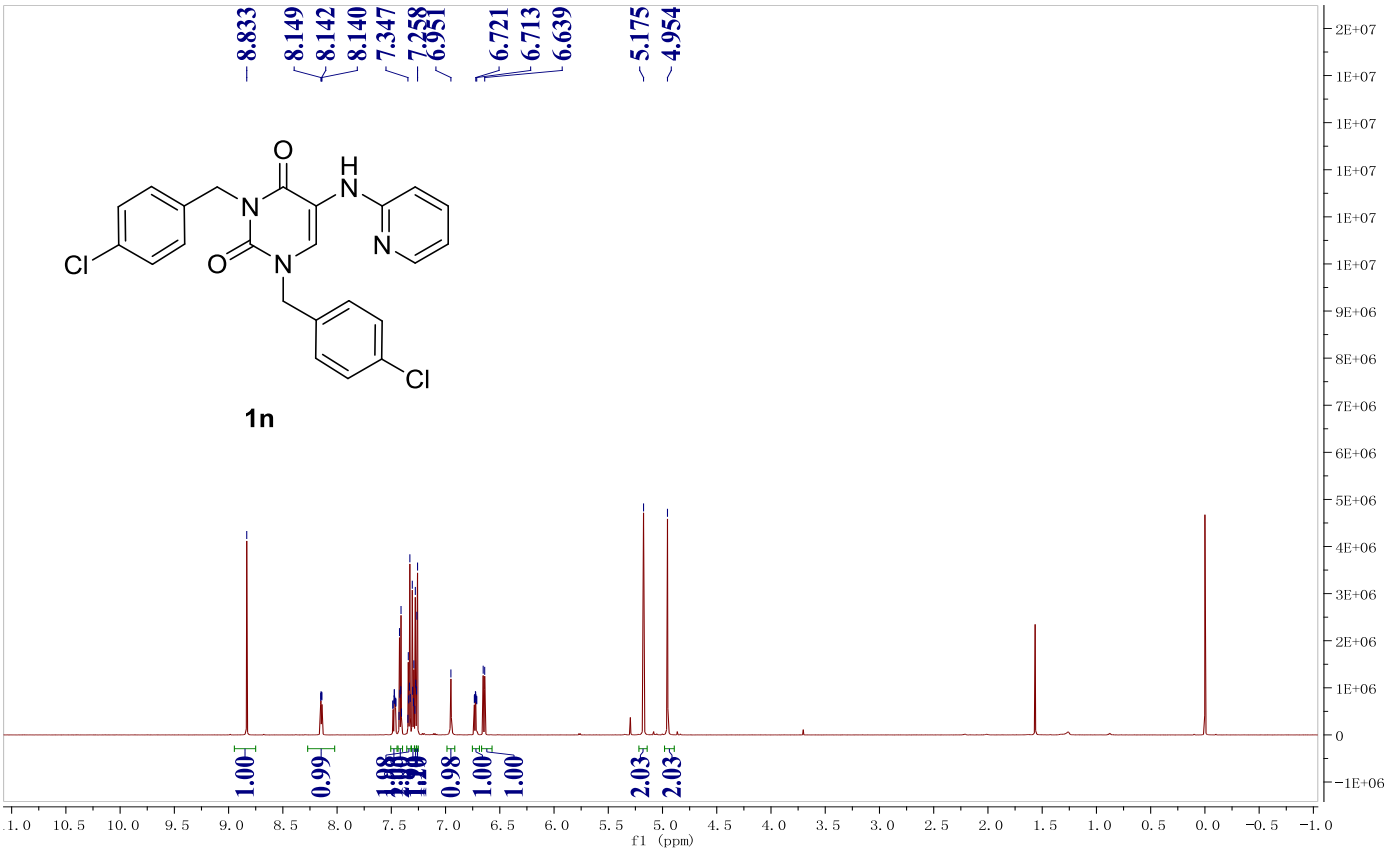
^{1}H NMR Spectrum of 1m at 25 °C ($CDCl_3$, 600 MHz)



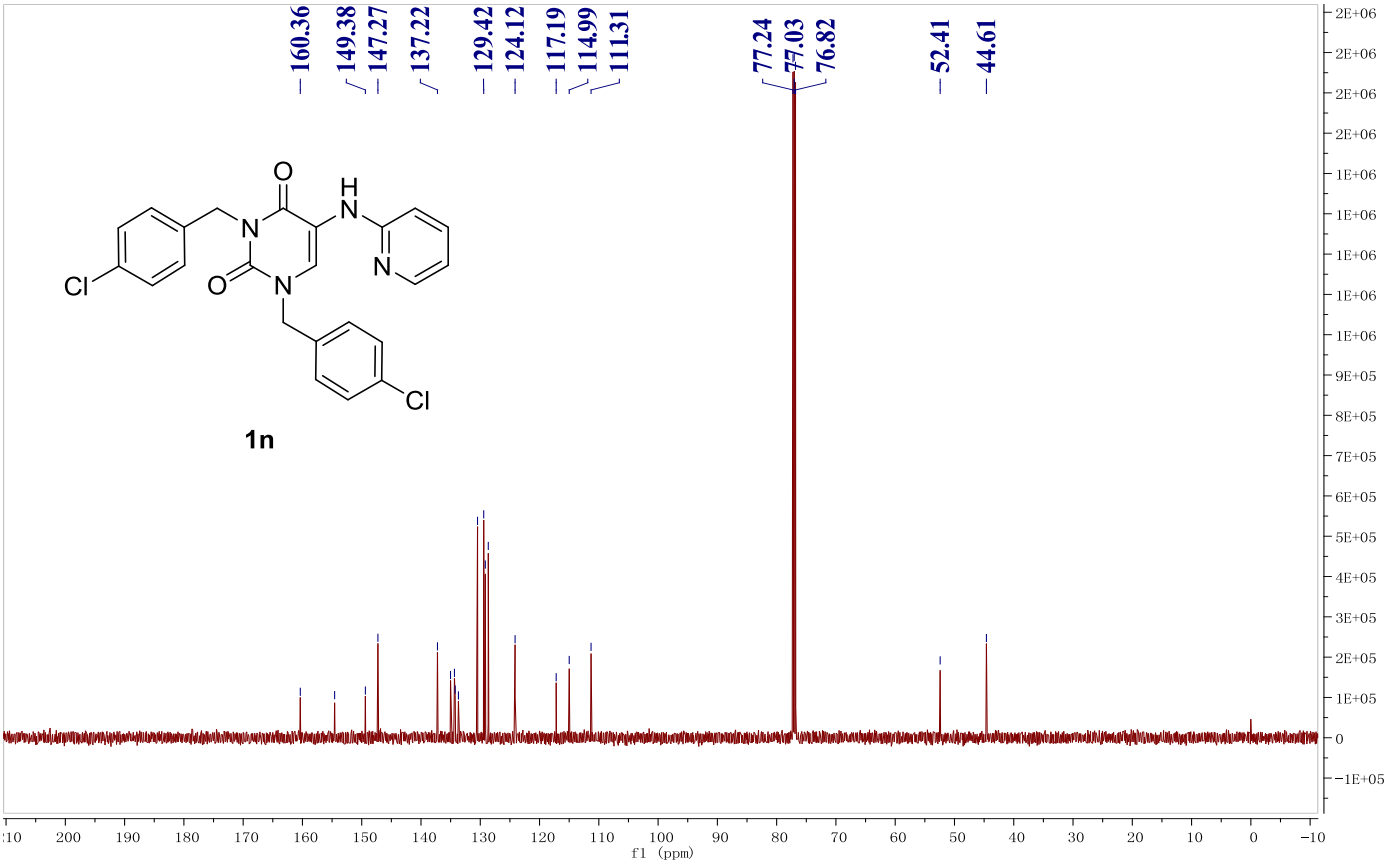
^{13}C NMR Spectrum of 1m at 25 °C ($CDCl_3$, 150 MHz)



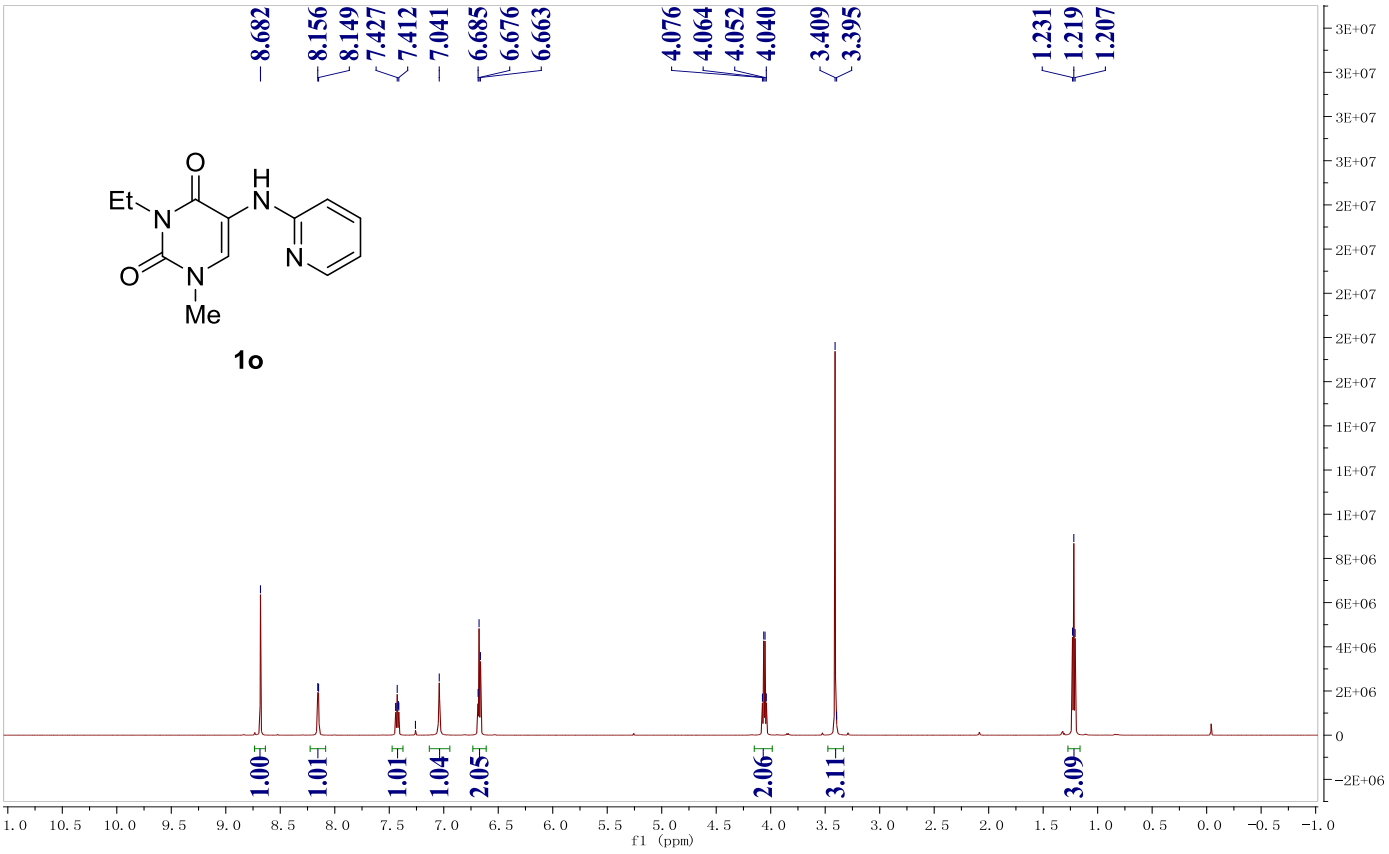
^{1}H NMR Spectrum of 1n at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 1n at 25 °C ($CDCl_3$, 150 MHz)

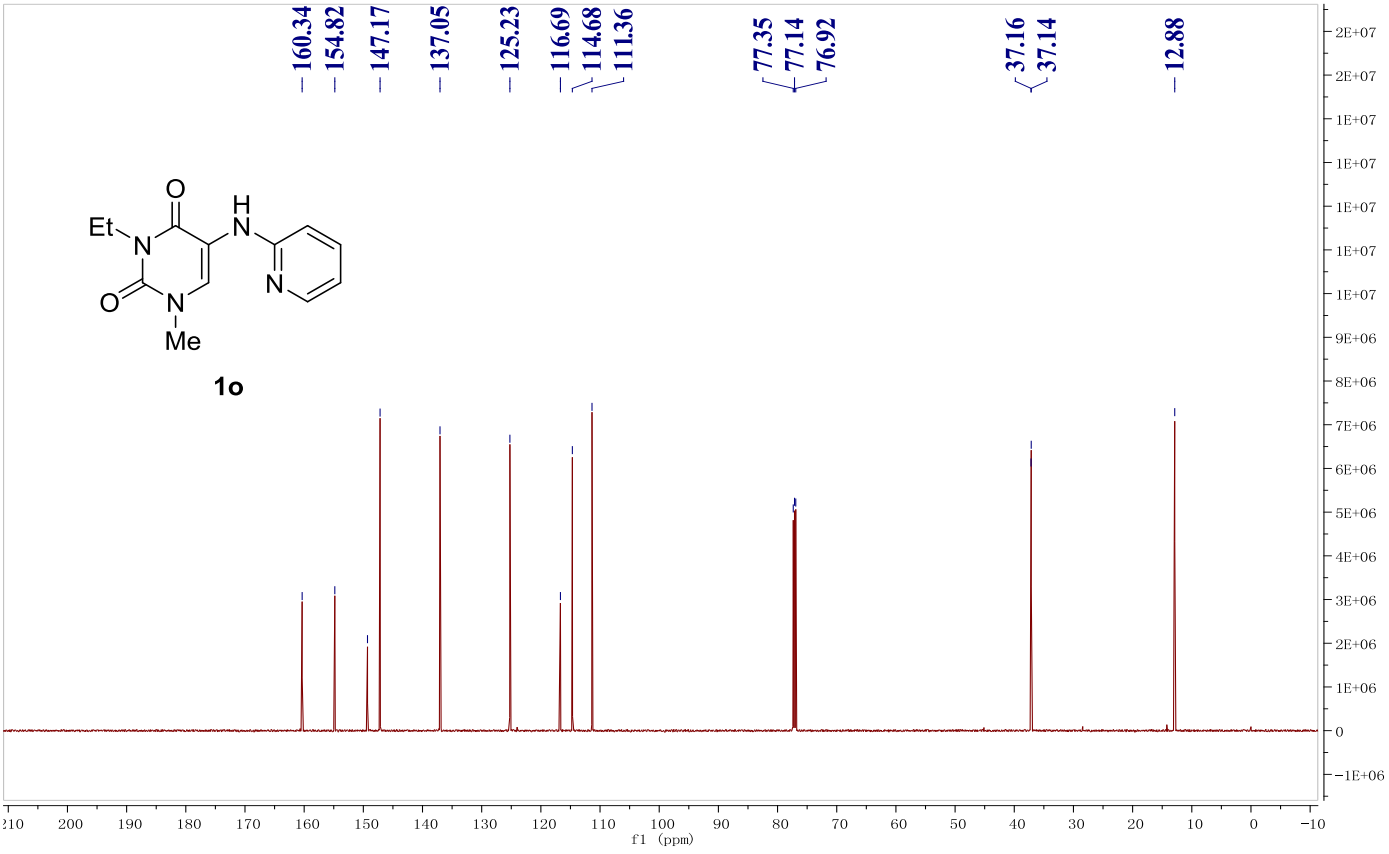


^{1}H NMR Spectrum of 1o at 25 °C ($CDCl_3$, 600 MHz)



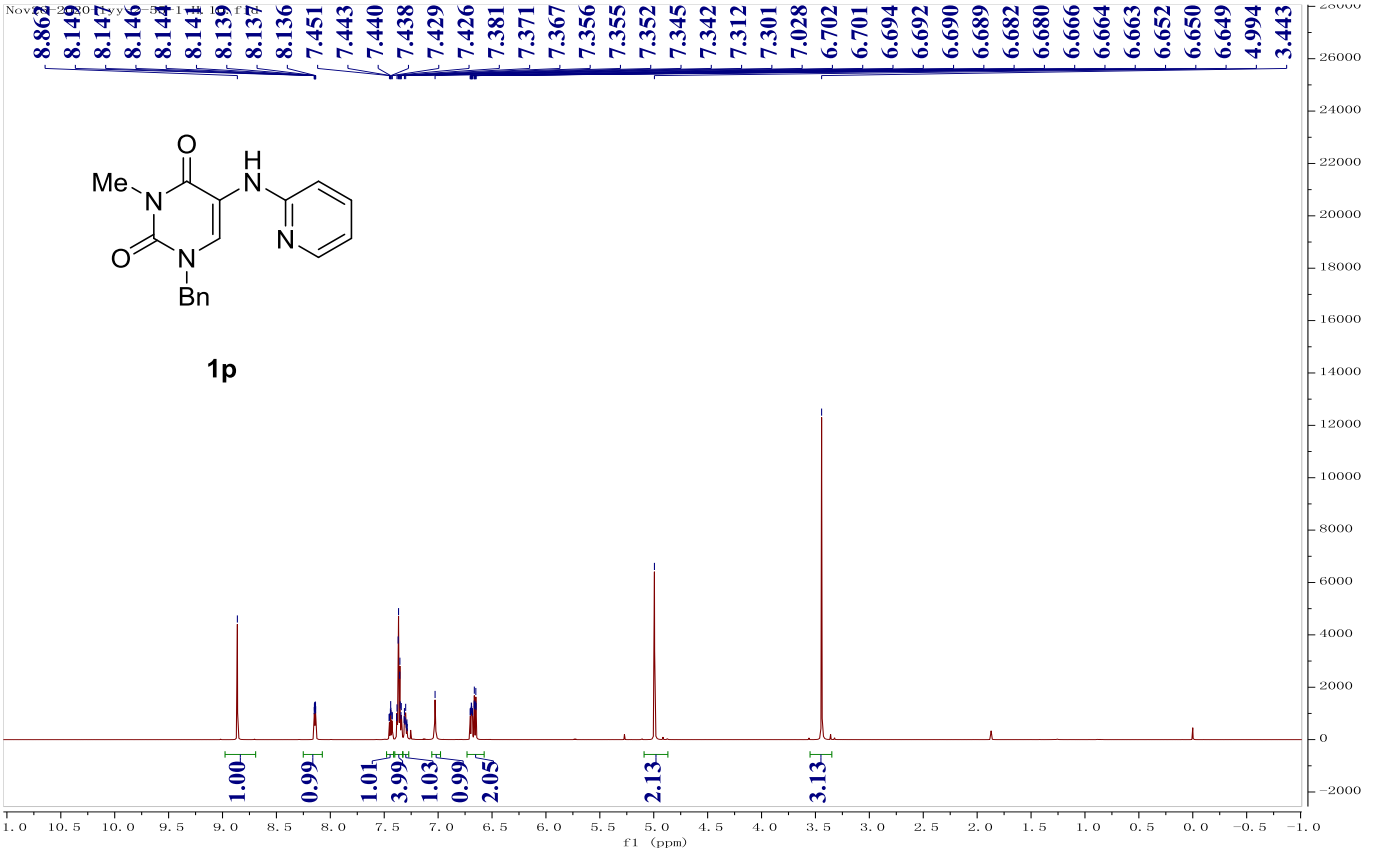
1o

^{13}C NMR Spectrum of 1o at 25 °C ($CDCl_3$, 150 MHz)

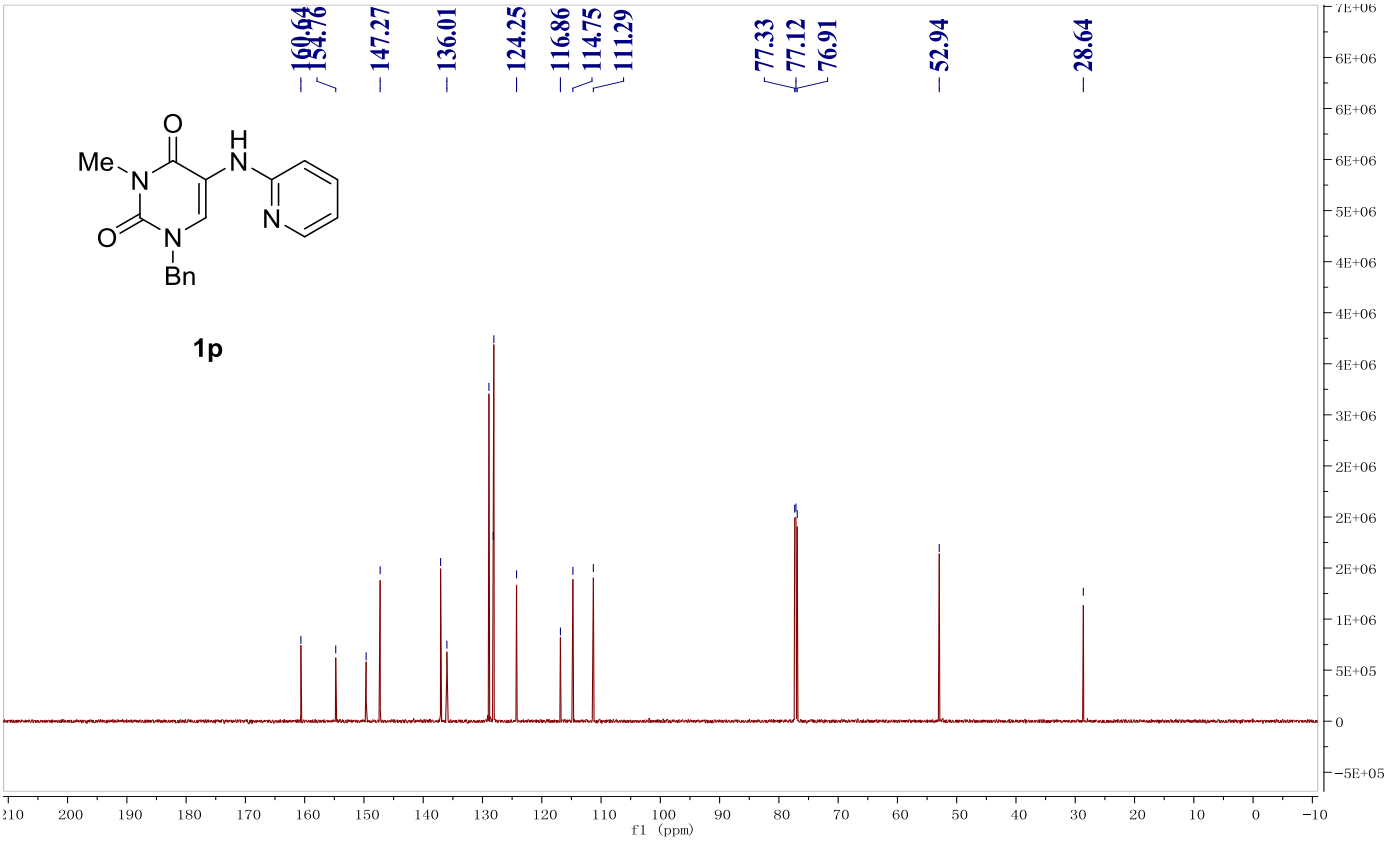


1o

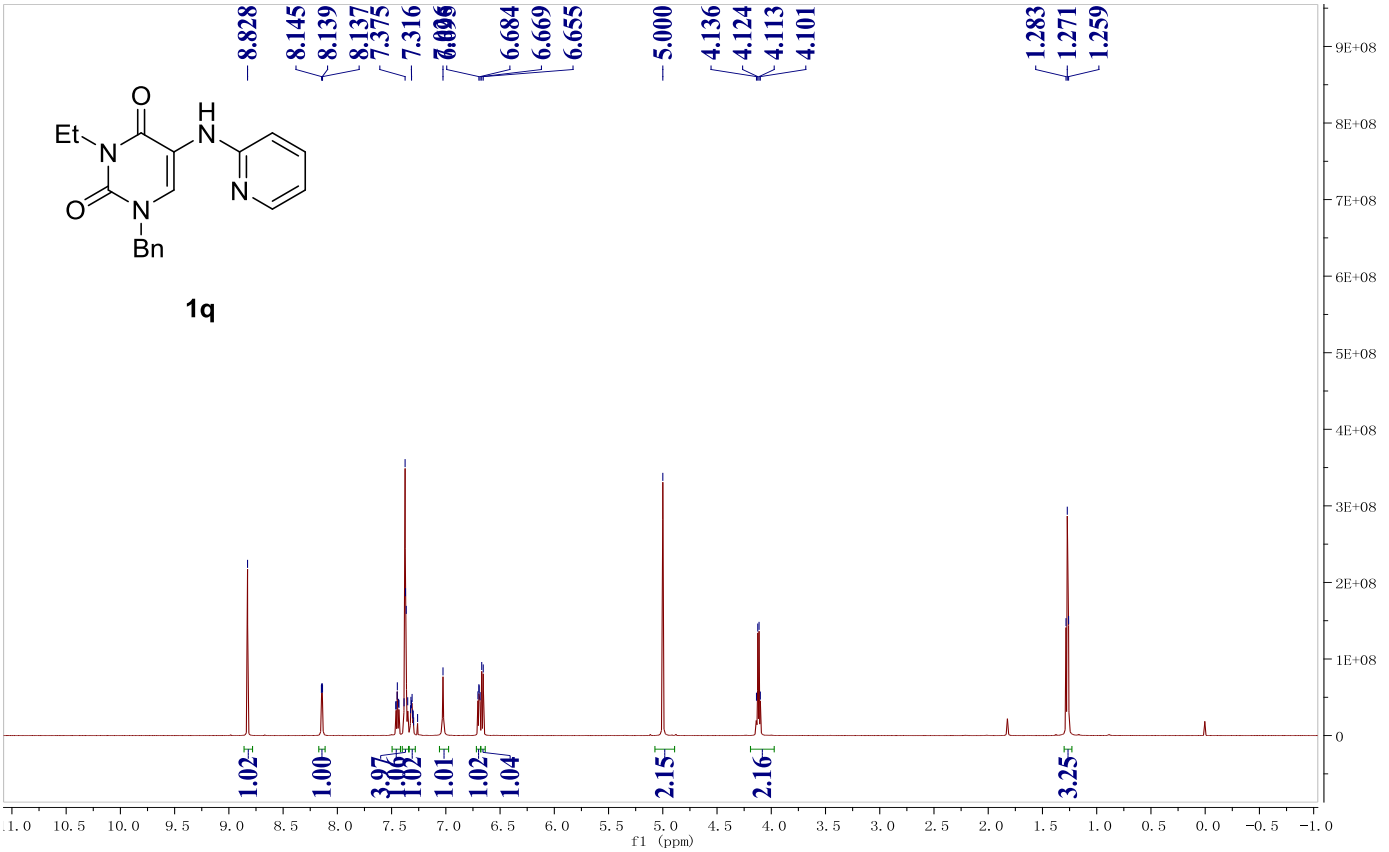
^{1}H NMR Spectrum of 1p at 25 °C ($CDCl_3$, 600 MHz)



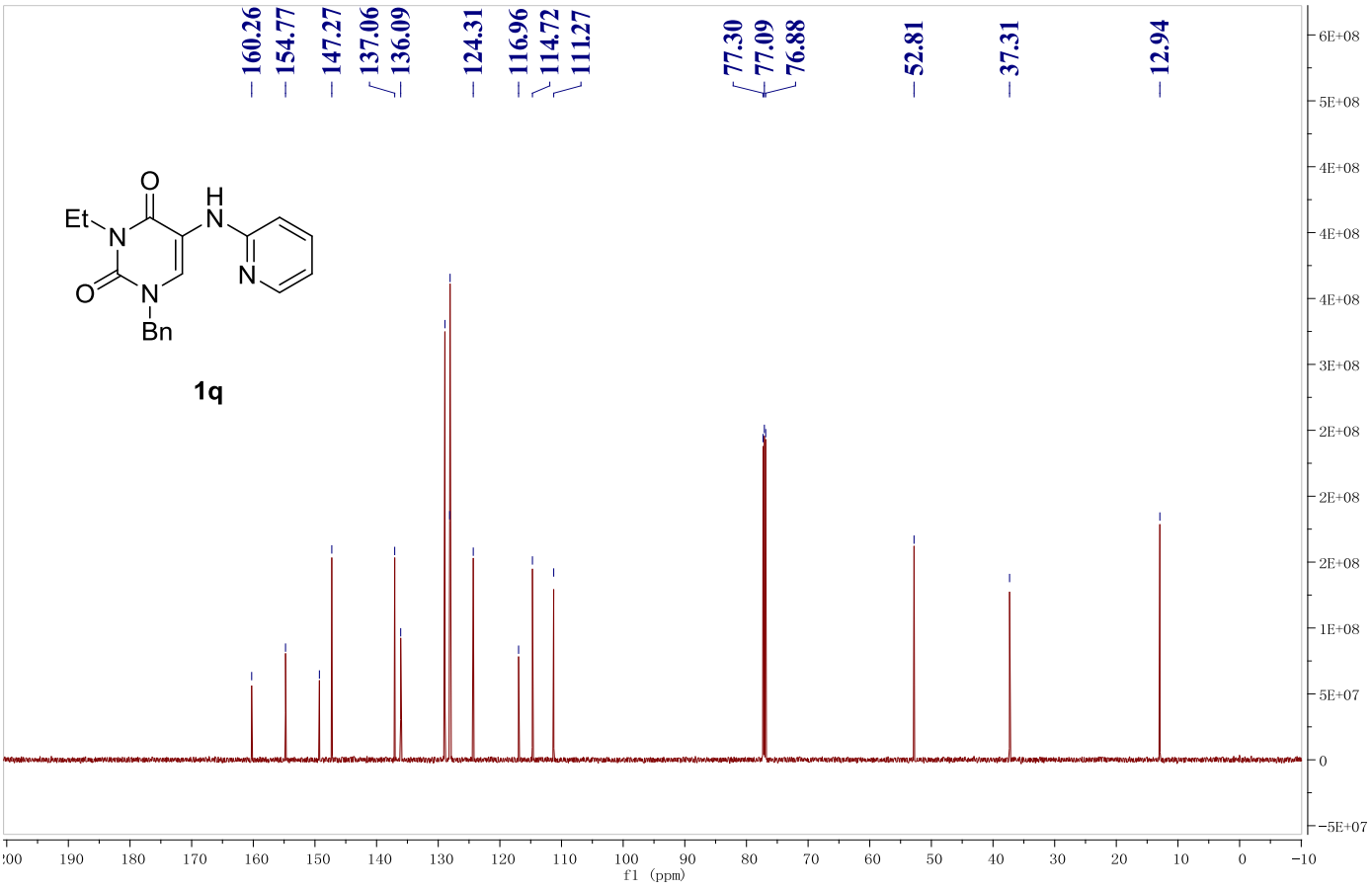
^{13}C NMR Spectrum of 1p at 25 °C ($CDCl_3$, 150 MHz)



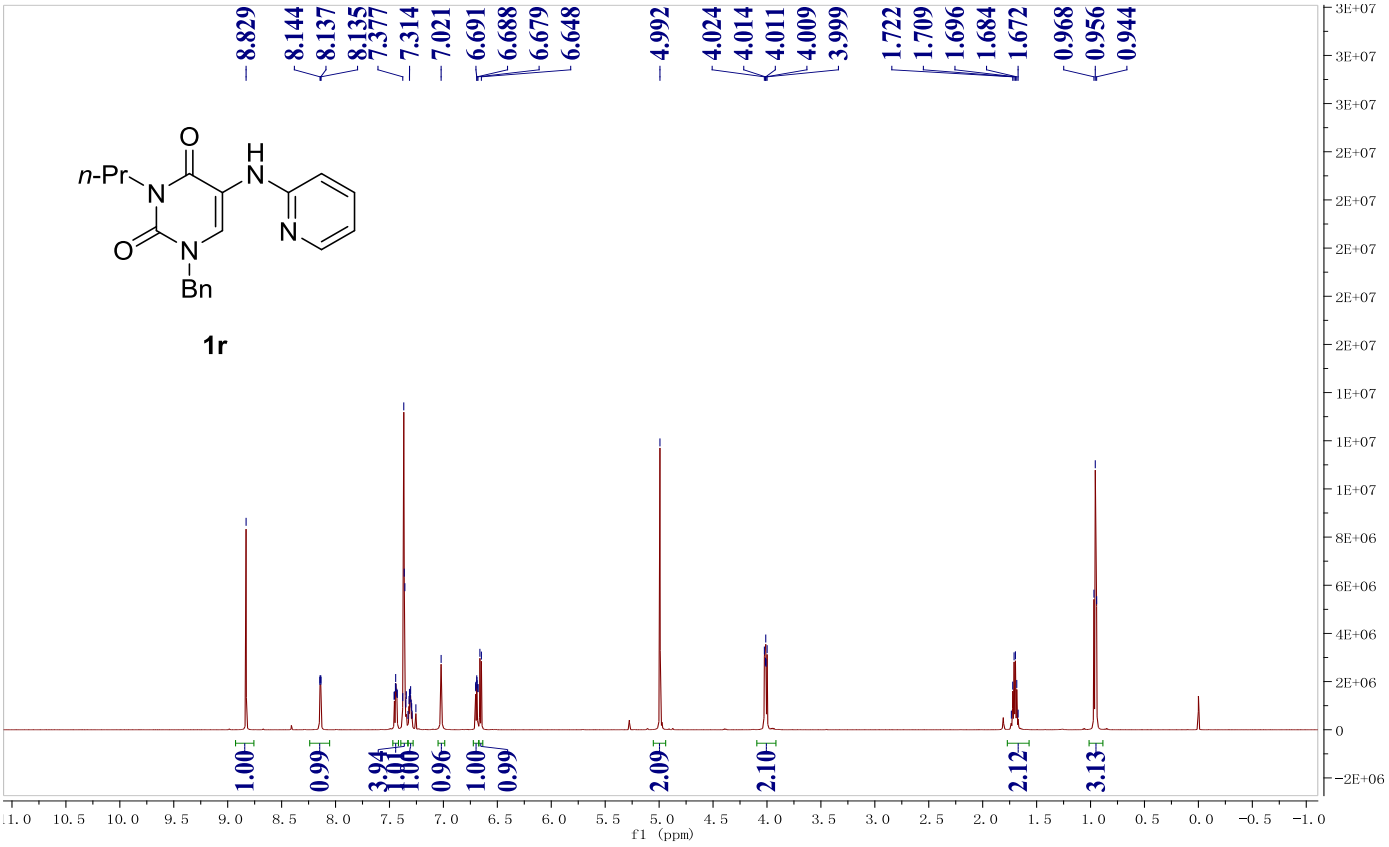
^{1}H NMR Spectrum of 3a at 25 °C ($CDCl_3$, 600 MHz)



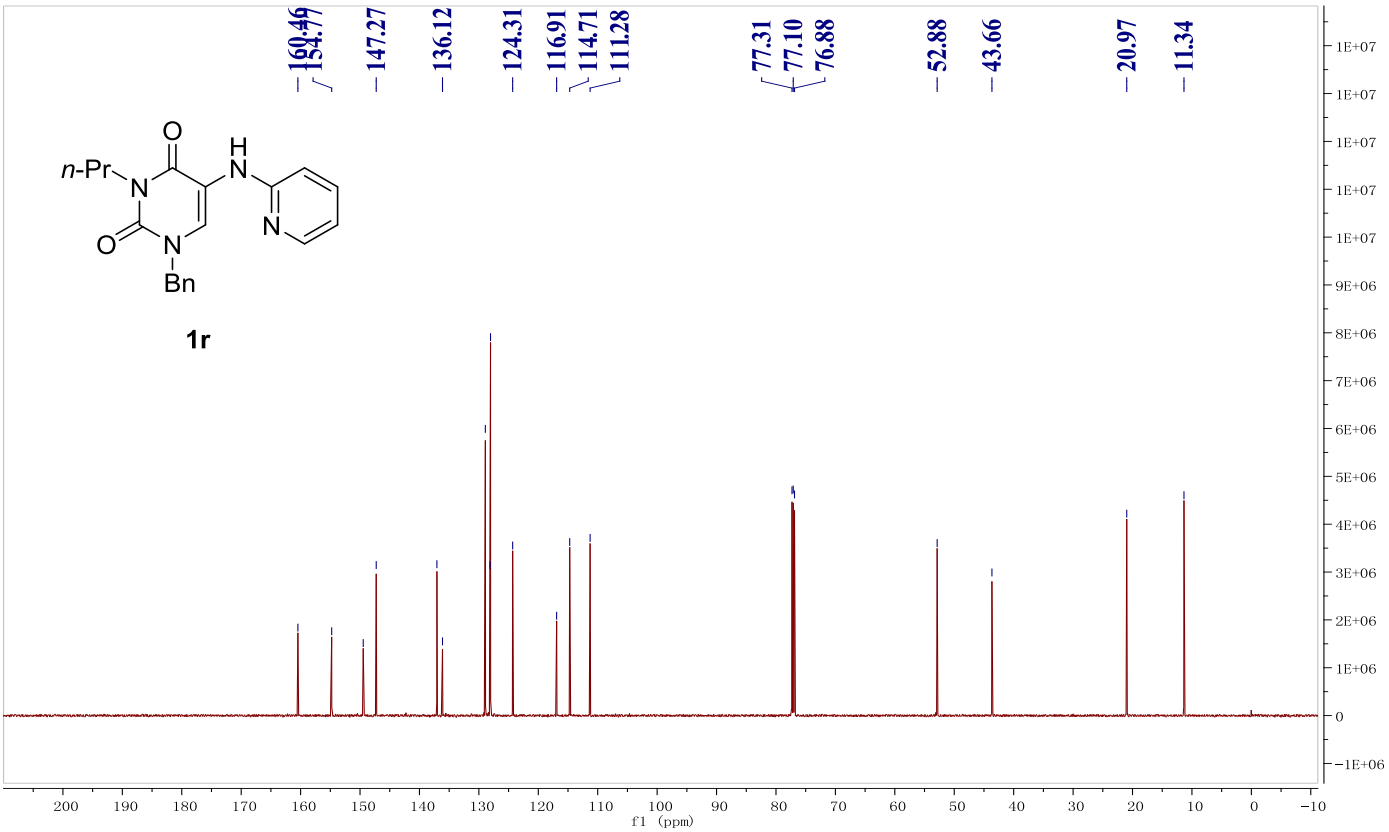
^{13}C NMR Spectrum of 1q at 25 °C ($CDCl_3$, 150 MHz)



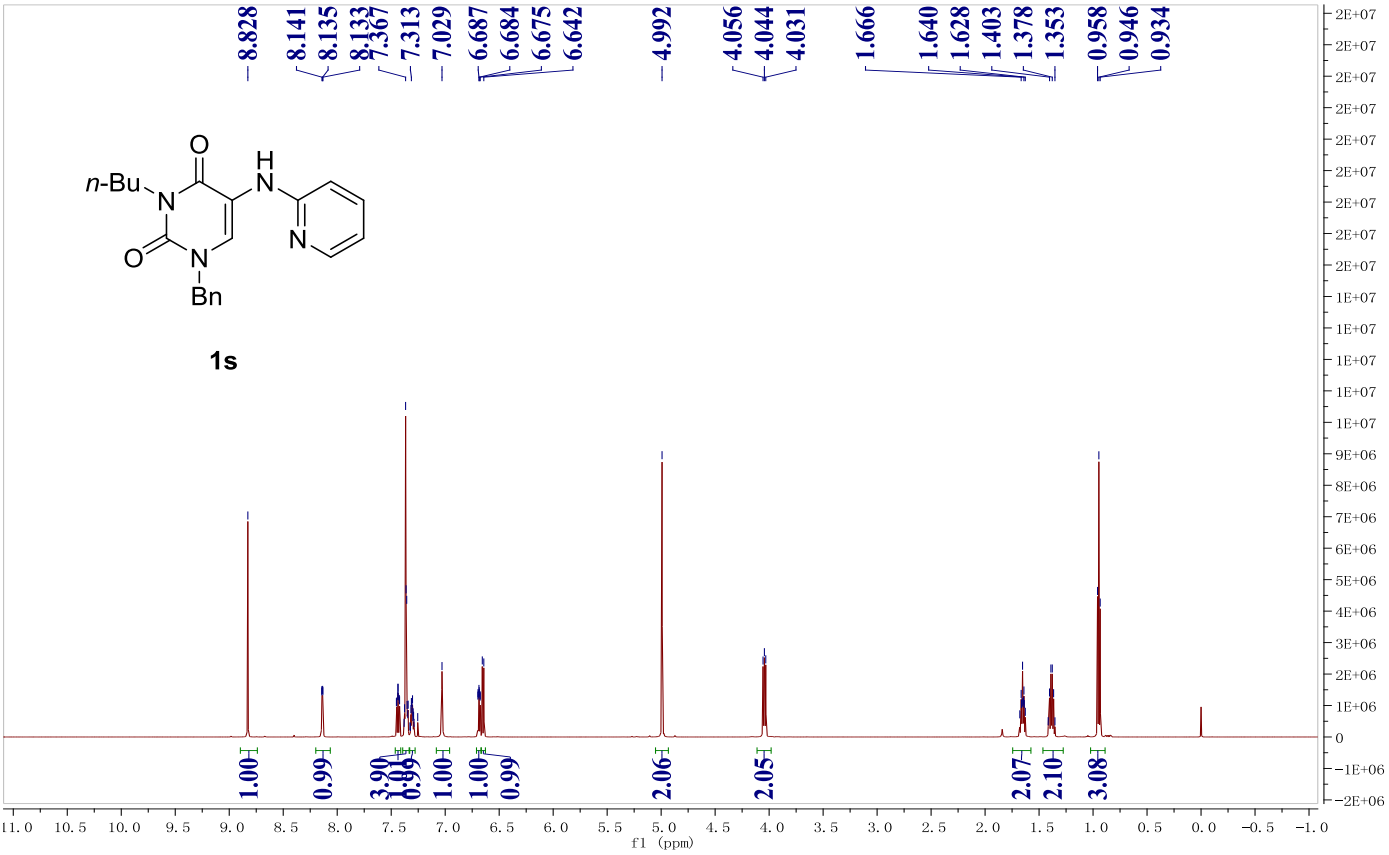
^{1}H NMR Spectrum of 1r at 25 °C ($CDCl_3$, 600 MHz)



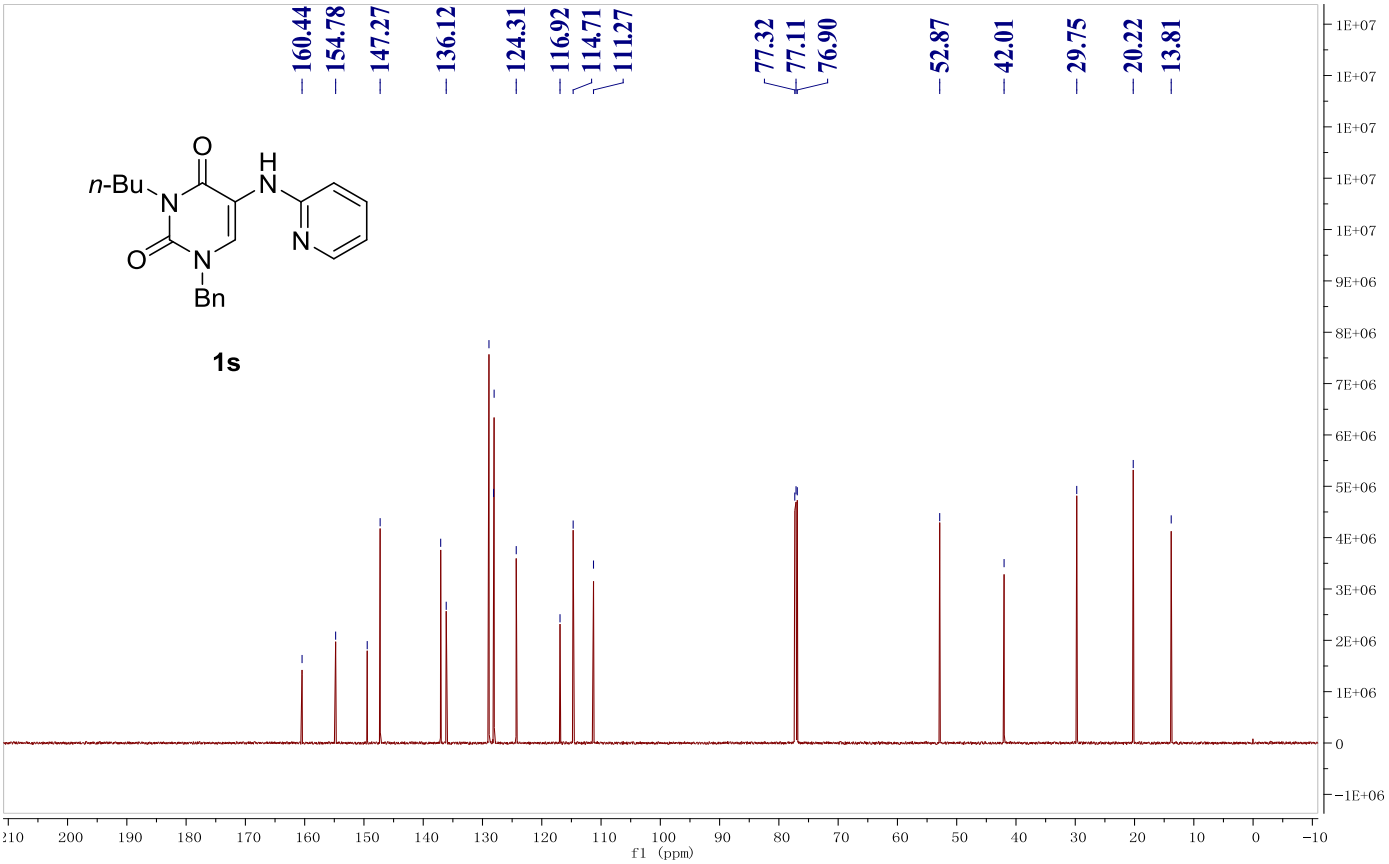
^{13}C NMR Spectrum of 1r at 25 °C ($CDCl_3$, 150 MHz)



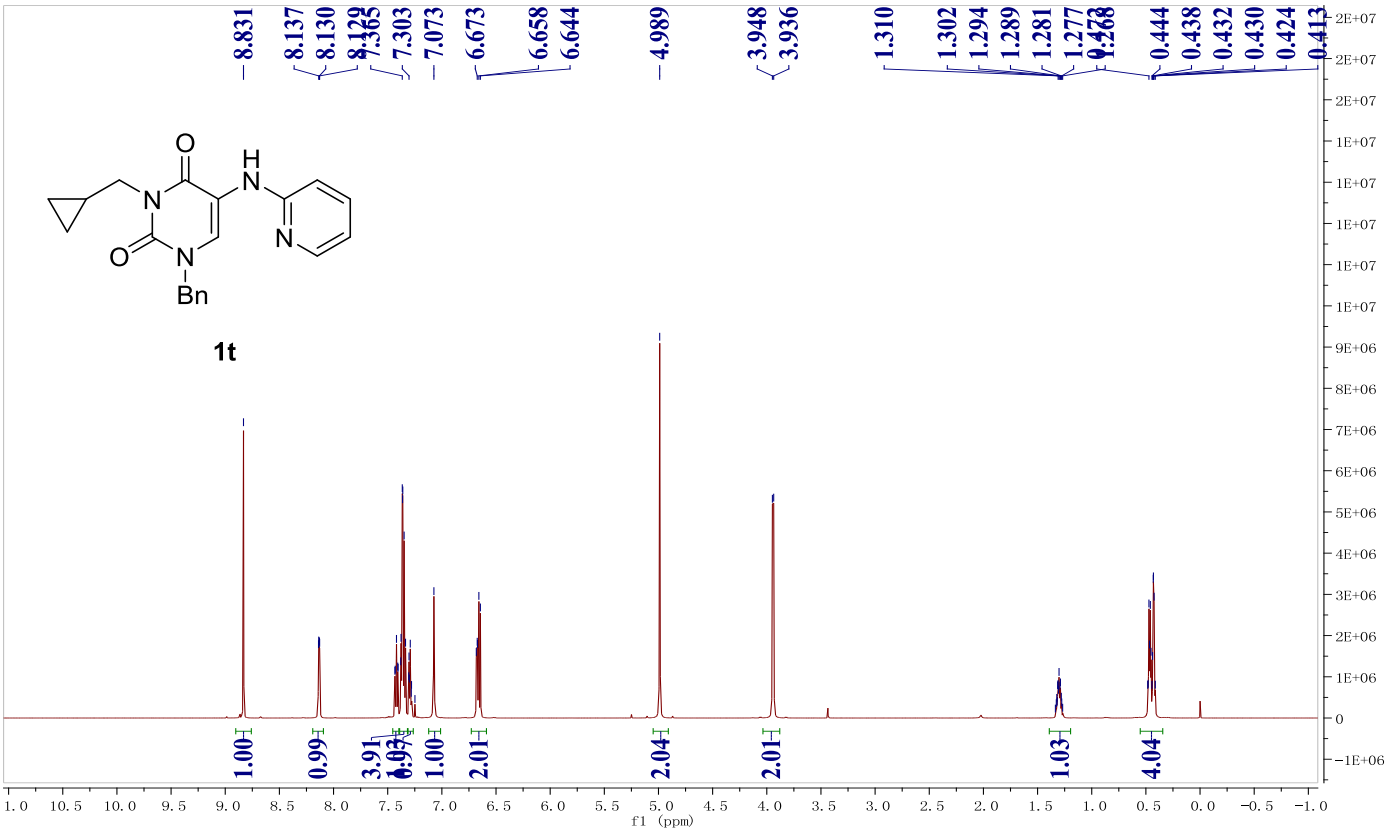
^{1}H NMR Spectrum of 1s at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 1s at 25 °C ($CDCl_3$, 150 MHz)

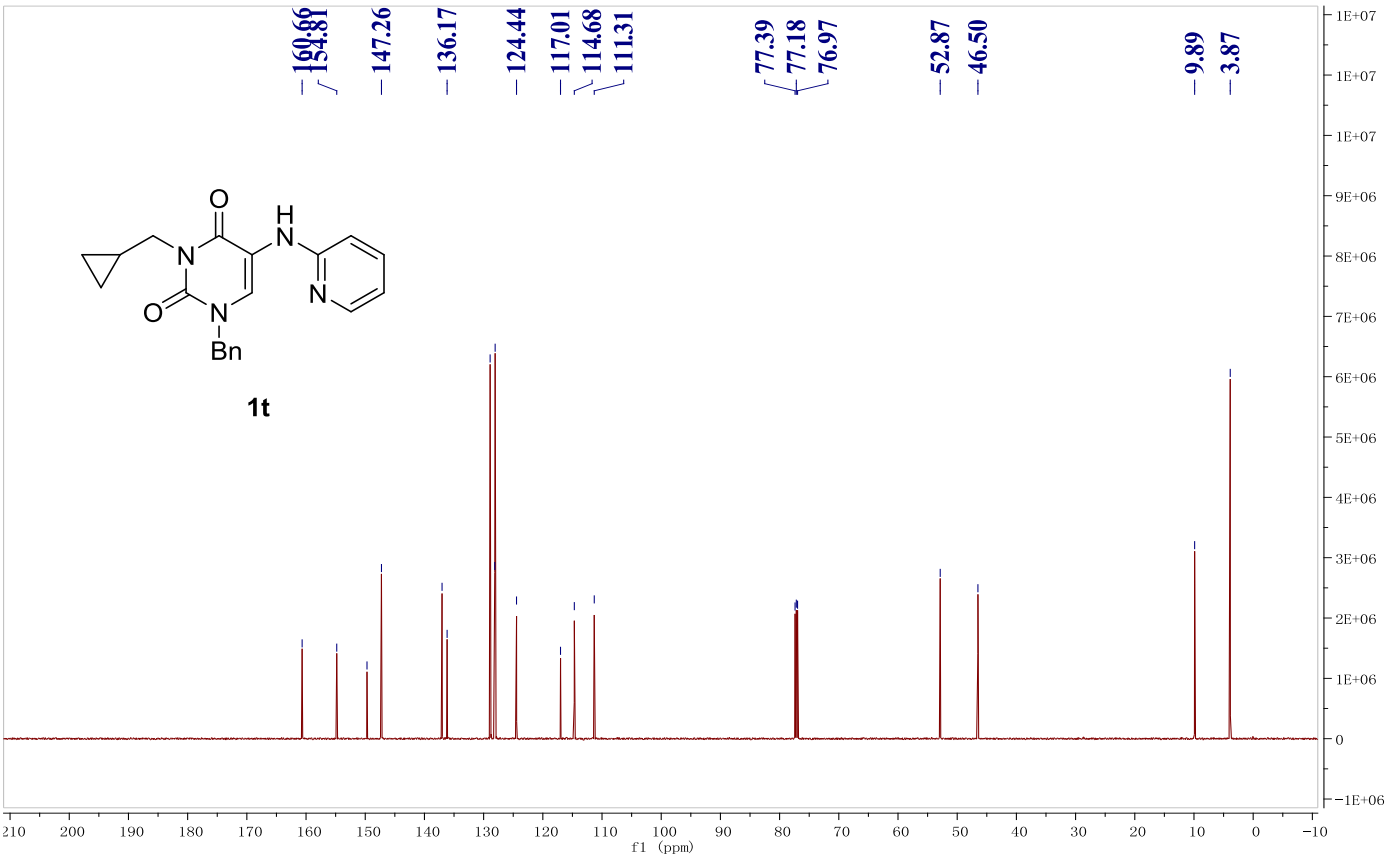


^{1}H NMR Spectrum of 1t at 25 °C ($CDCl_3$, 600 MHz)



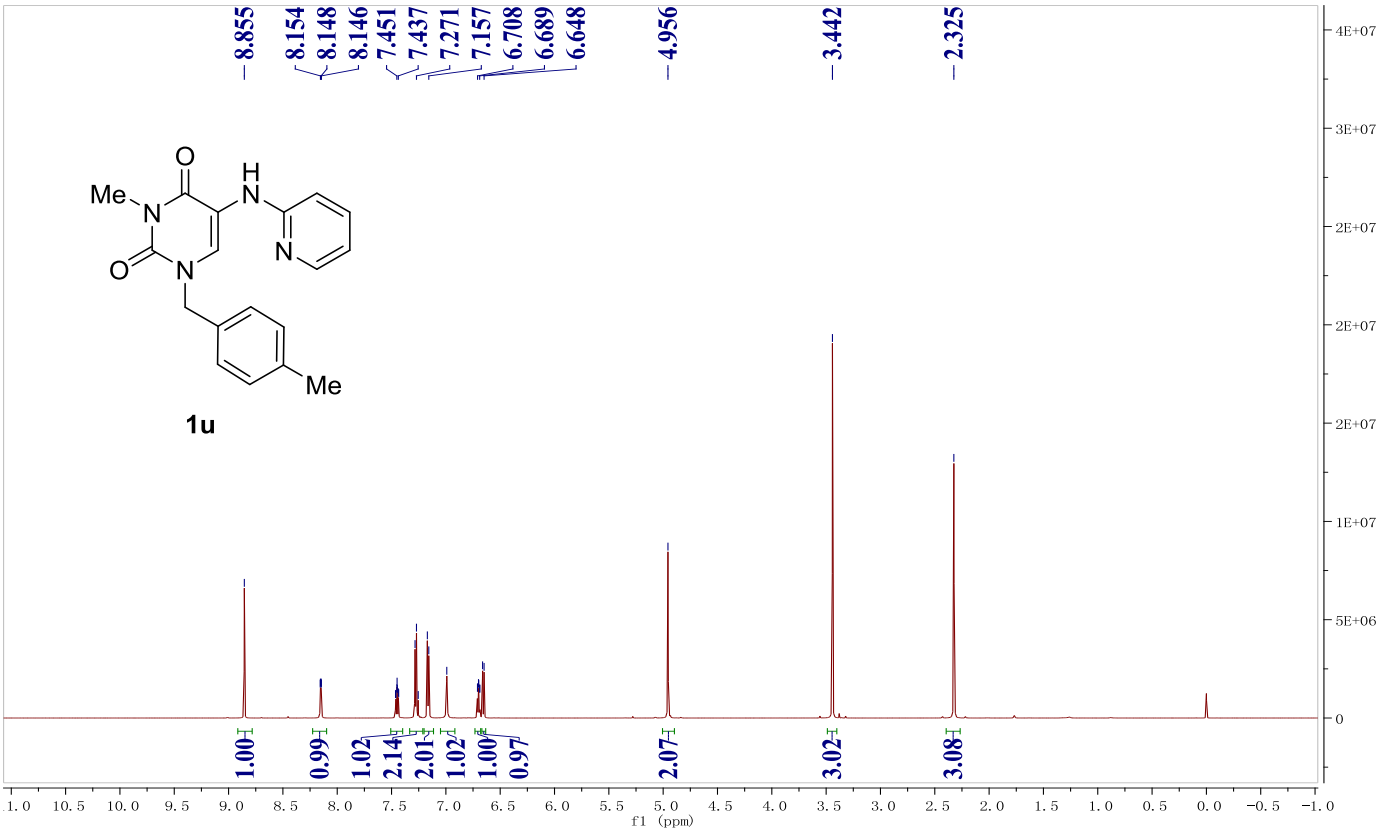
1t

^{13}C NMR Spectrum of 1t at 25 °C ($CDCl_3$, 150 MHz)

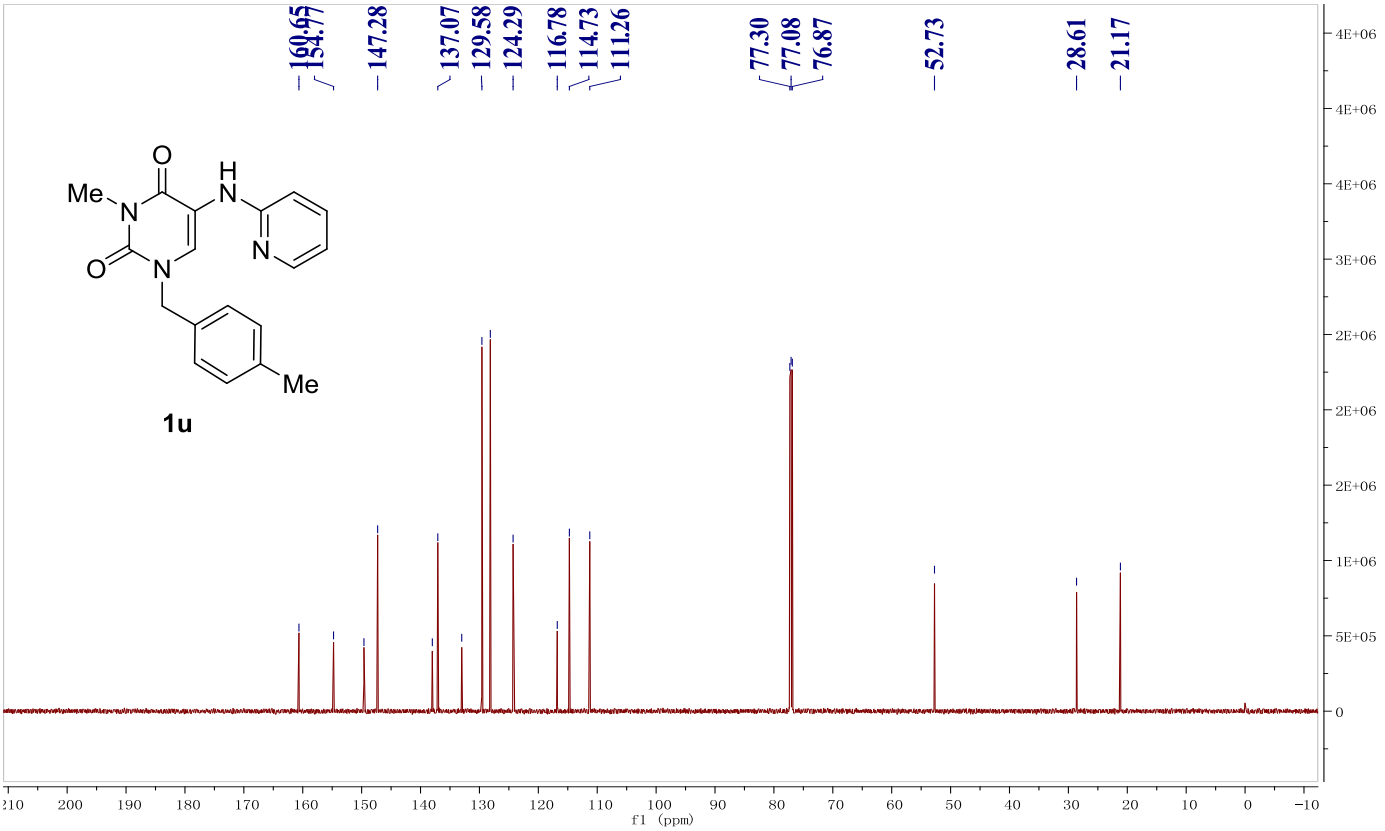


1t

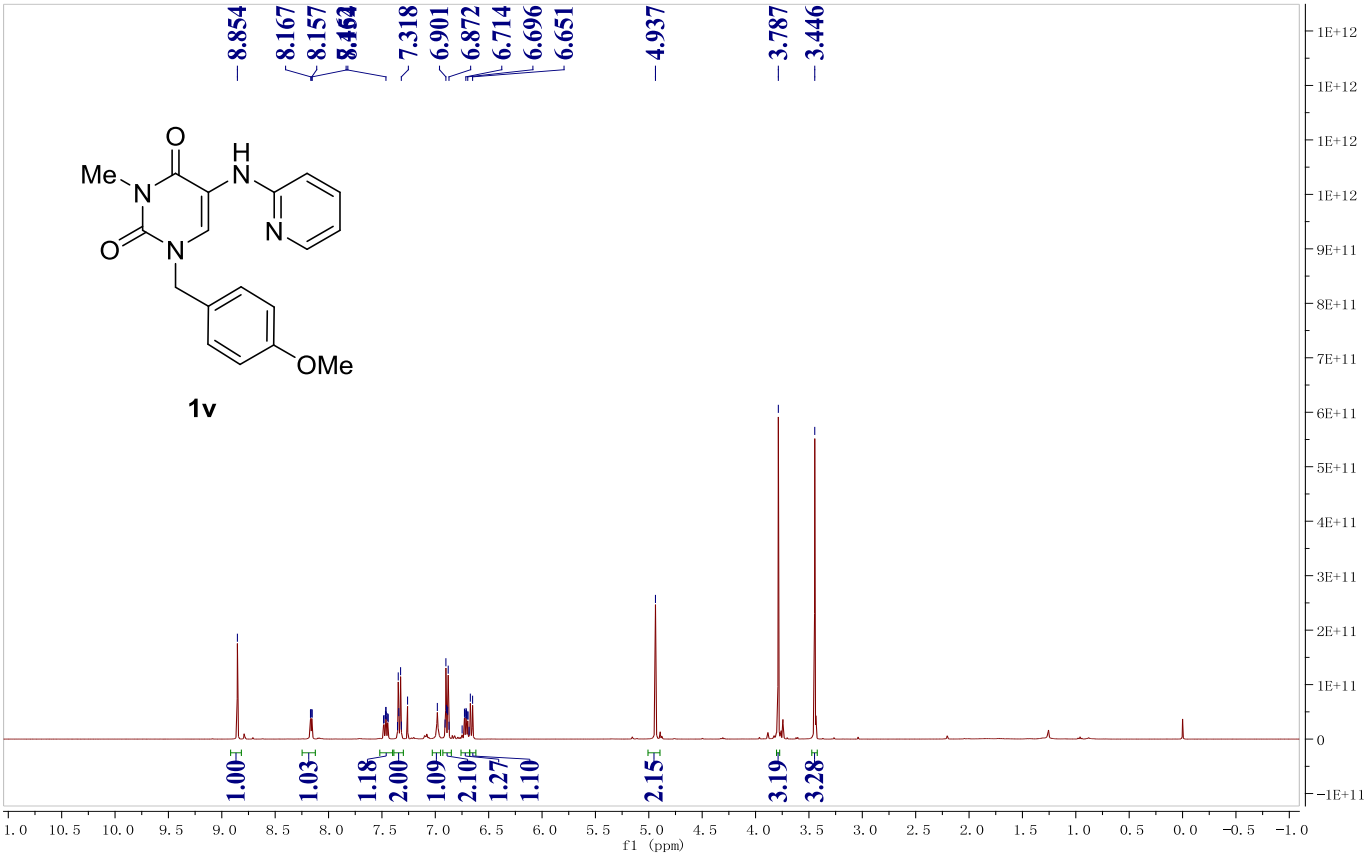
^{1}H NMR Spectrum of 1u at 25 °C ($CDCl_3$, 600 MHz)



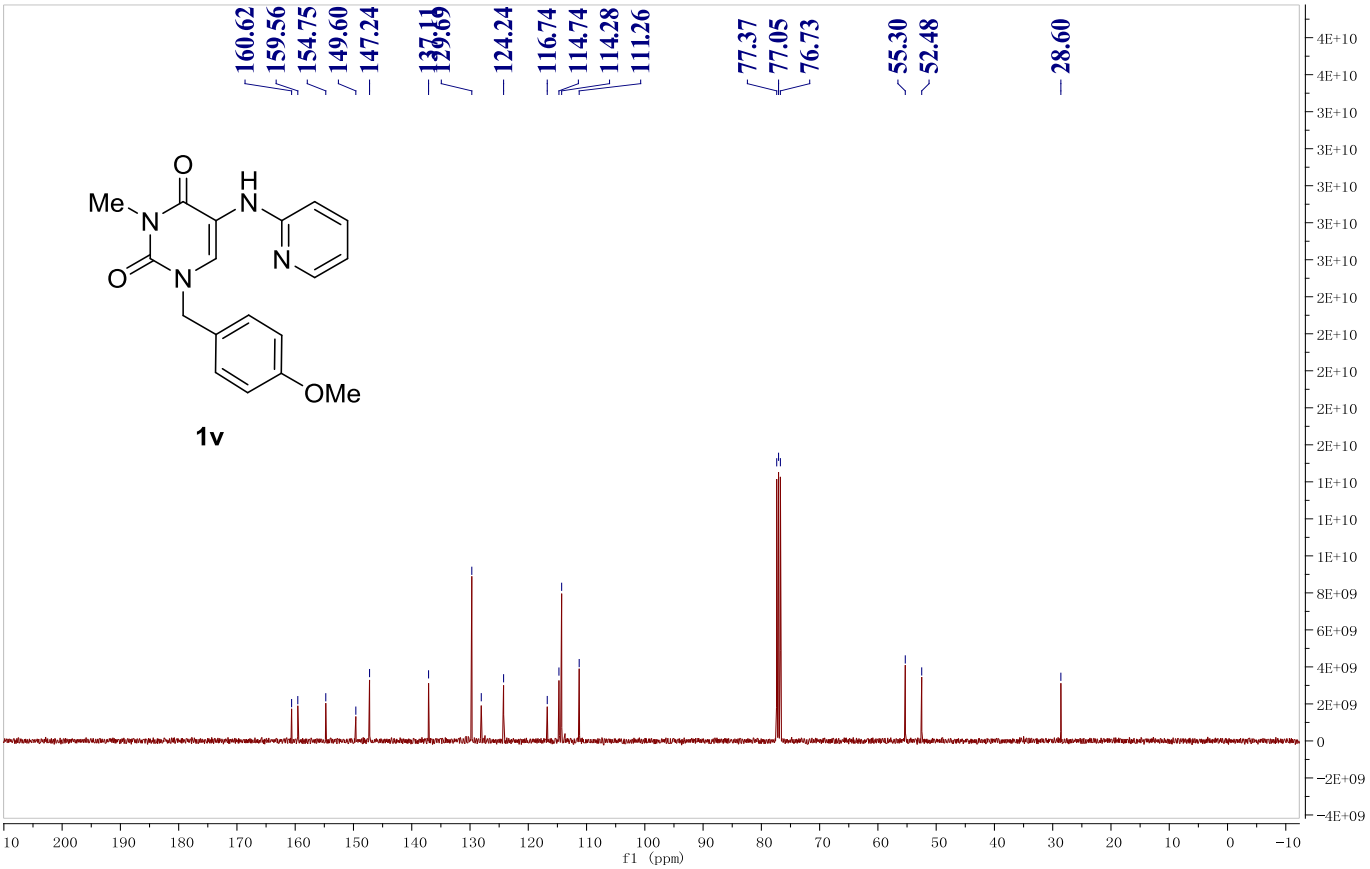
^{13}C NMR Spectrum of 1u at 25 °C ($CDCl_3$, 150 MHz)



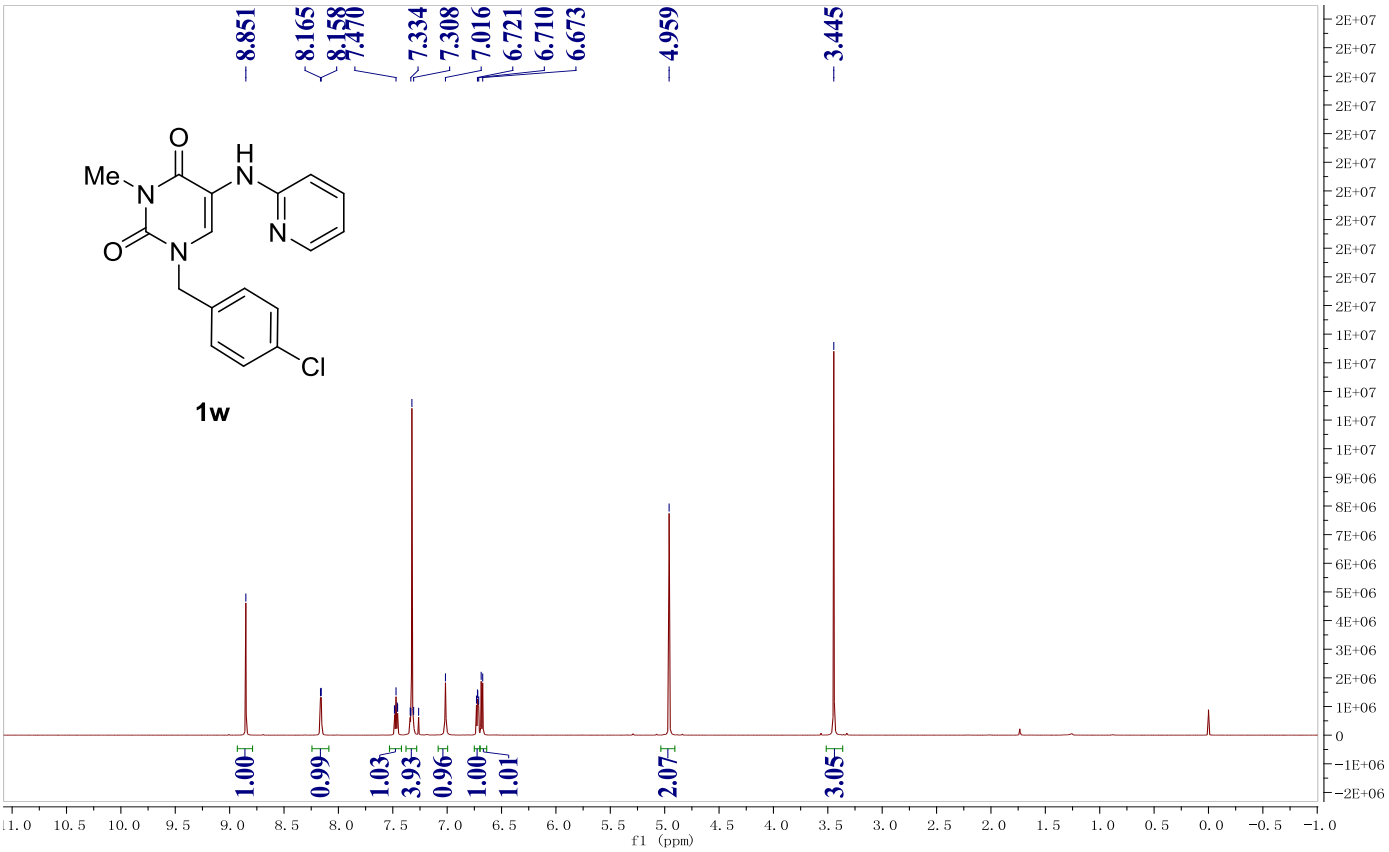
^{1}H NMR Spectrum of 1v at 25 °C ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of 1v at 25 °C ($CDCl_3$, 100 MHz)

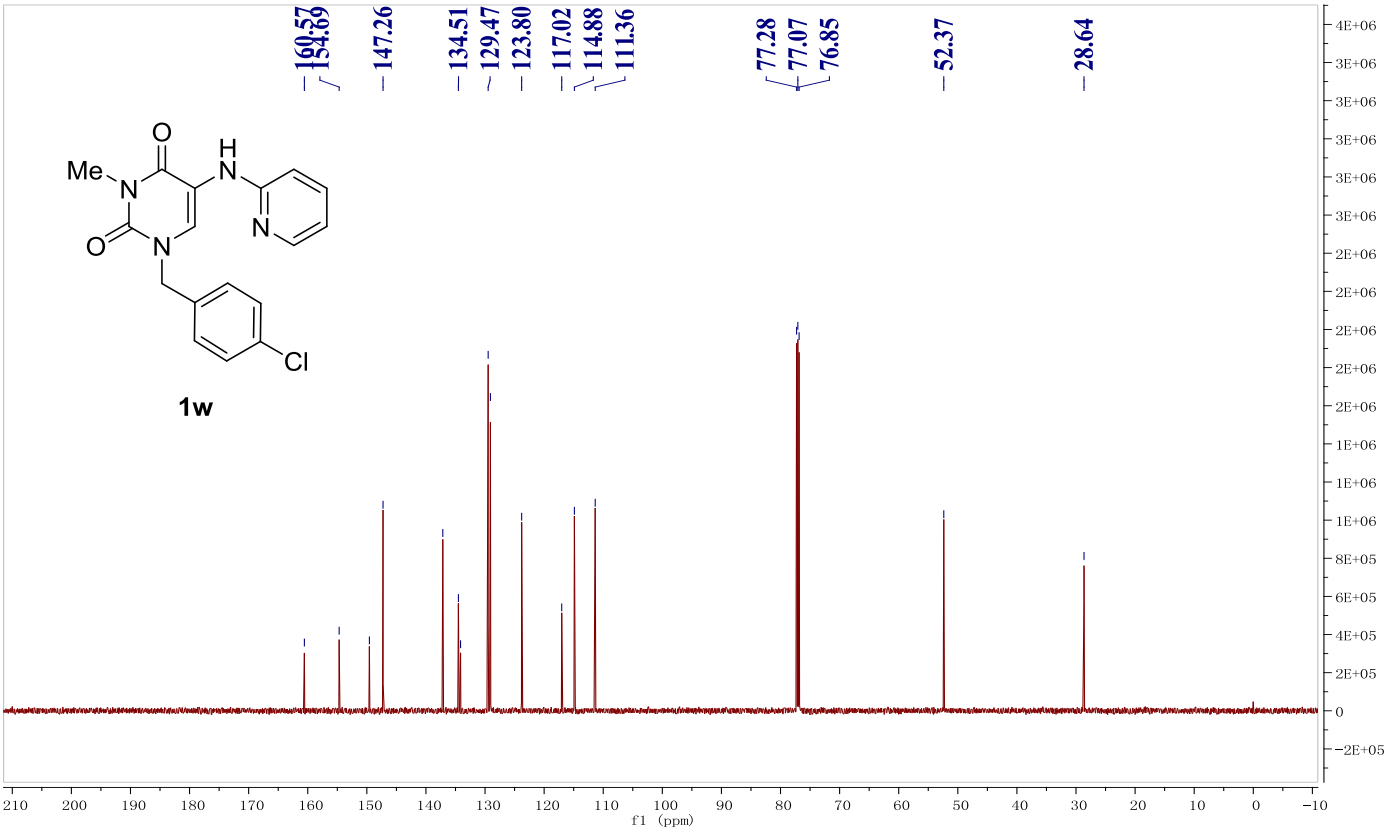


^{1}H NMR Spectrum of 1w at 25 °C ($CDCl_3$, 600 MHz)



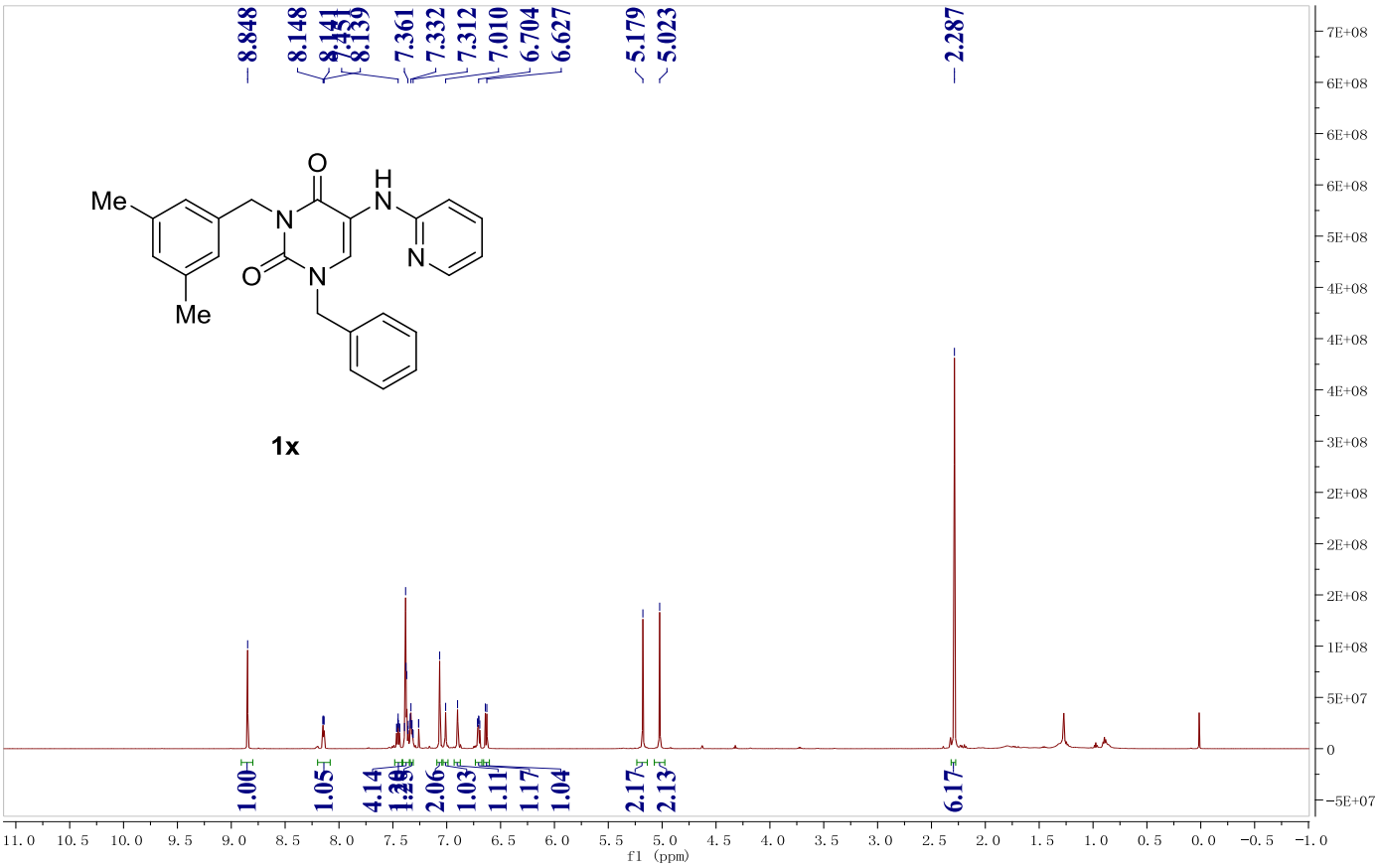
1w

^{13}C NMR Spectrum of 1w at 25 °C ($CDCl_3$, 150 MHz)

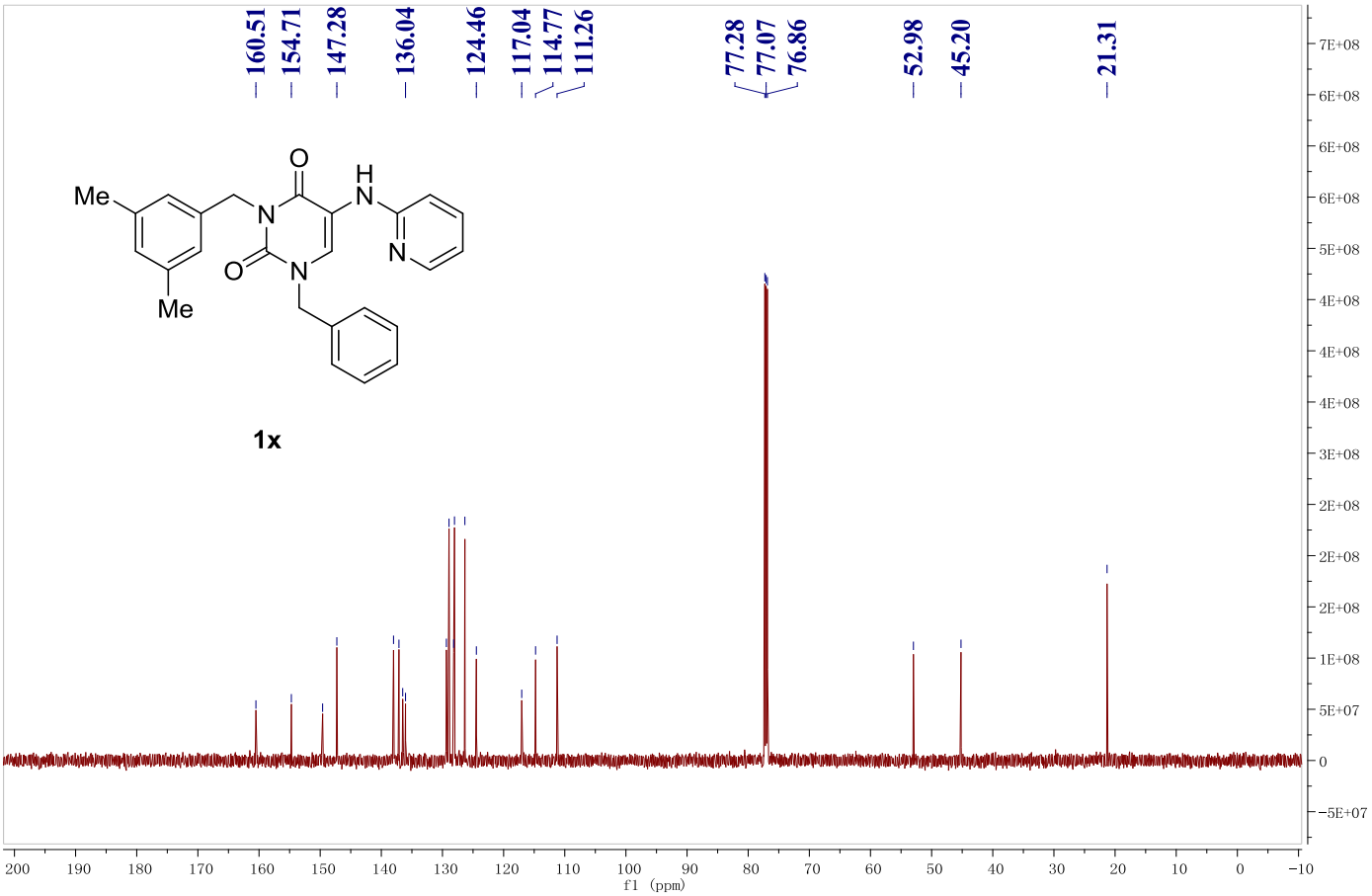


1w

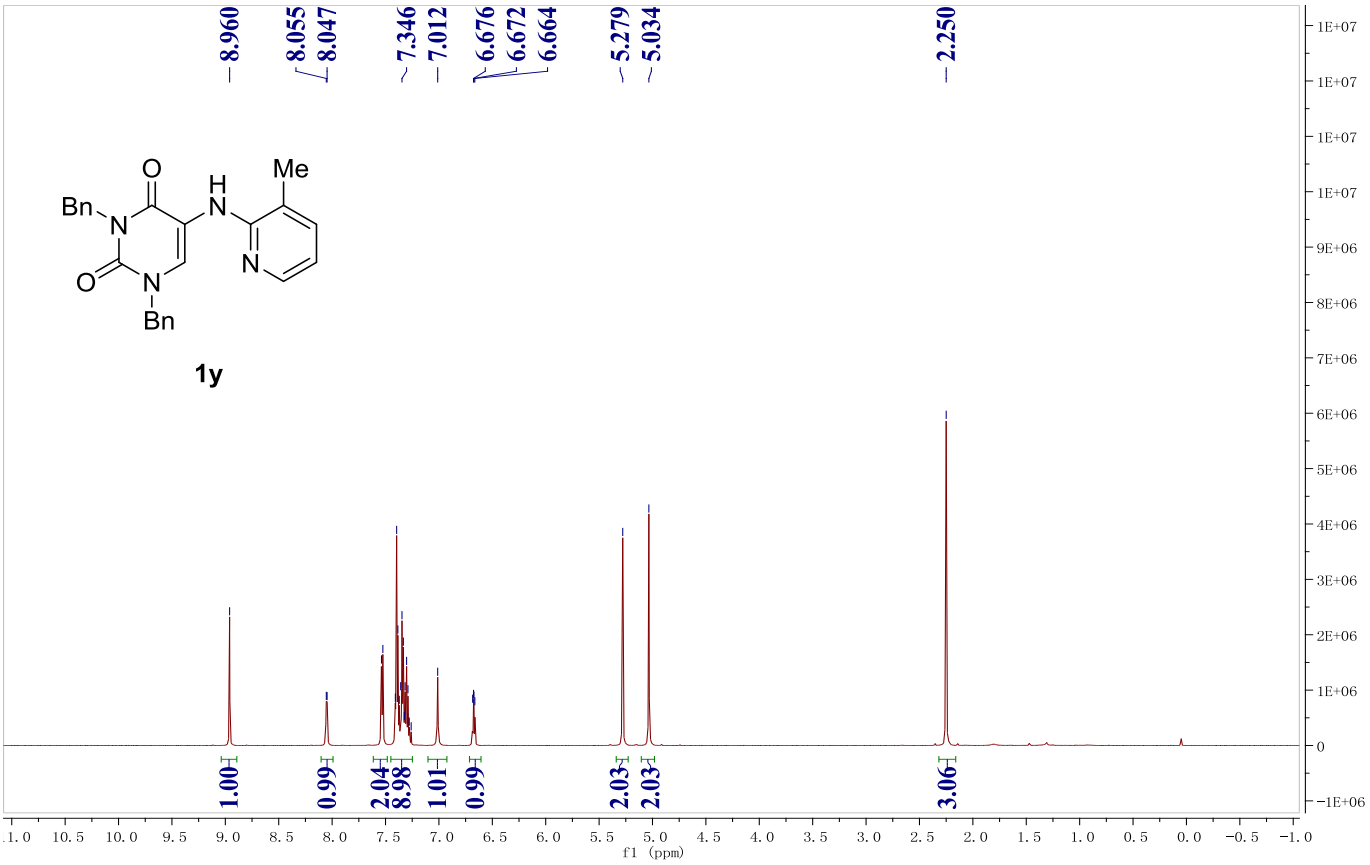
^{1}H NMR Spectrum of 1x at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 1x at 25 °C ($CDCl_3$, 150 MHz)

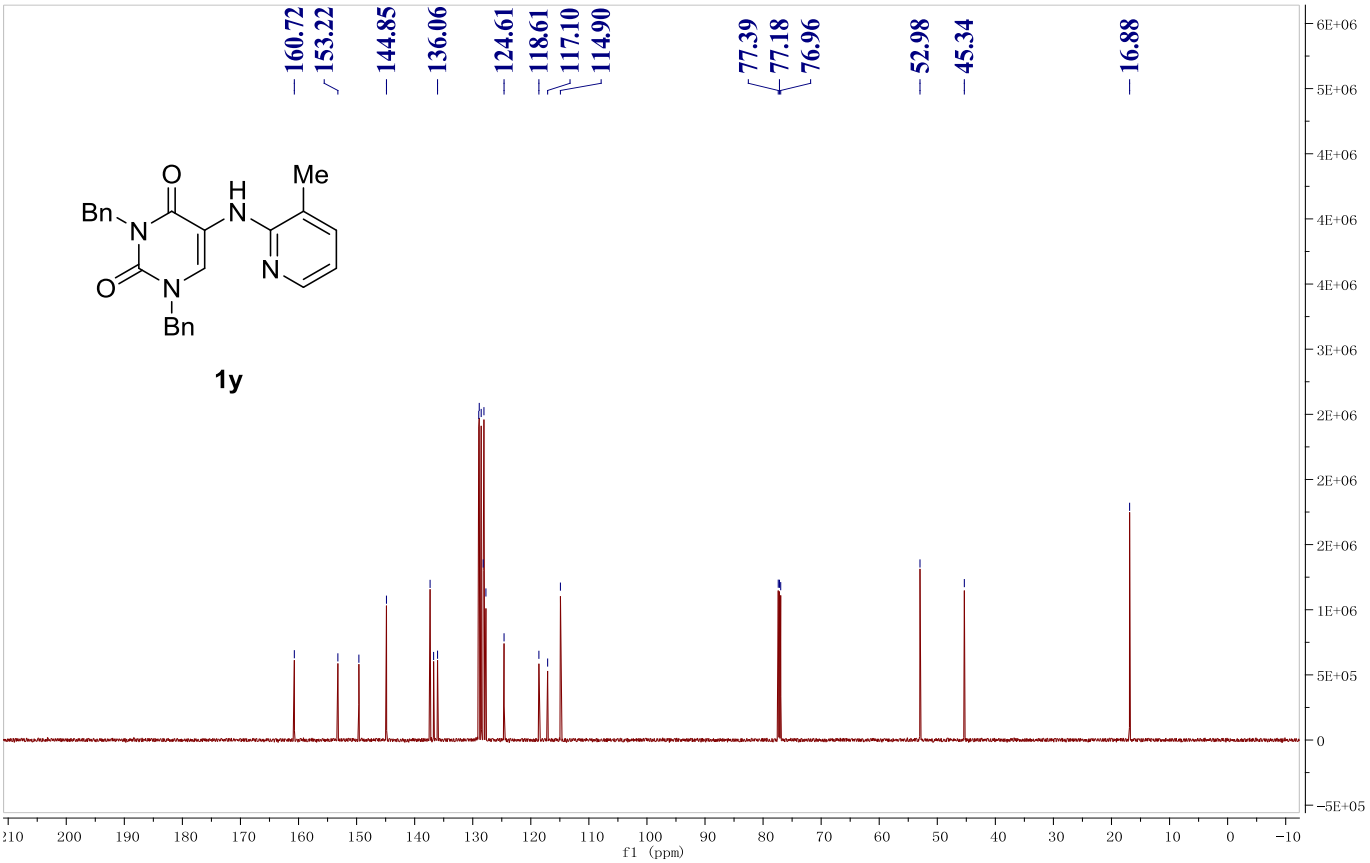


^{1}H NMR Spectrum of 1y at 25 °C ($CDCl_3$, 600 MHz)



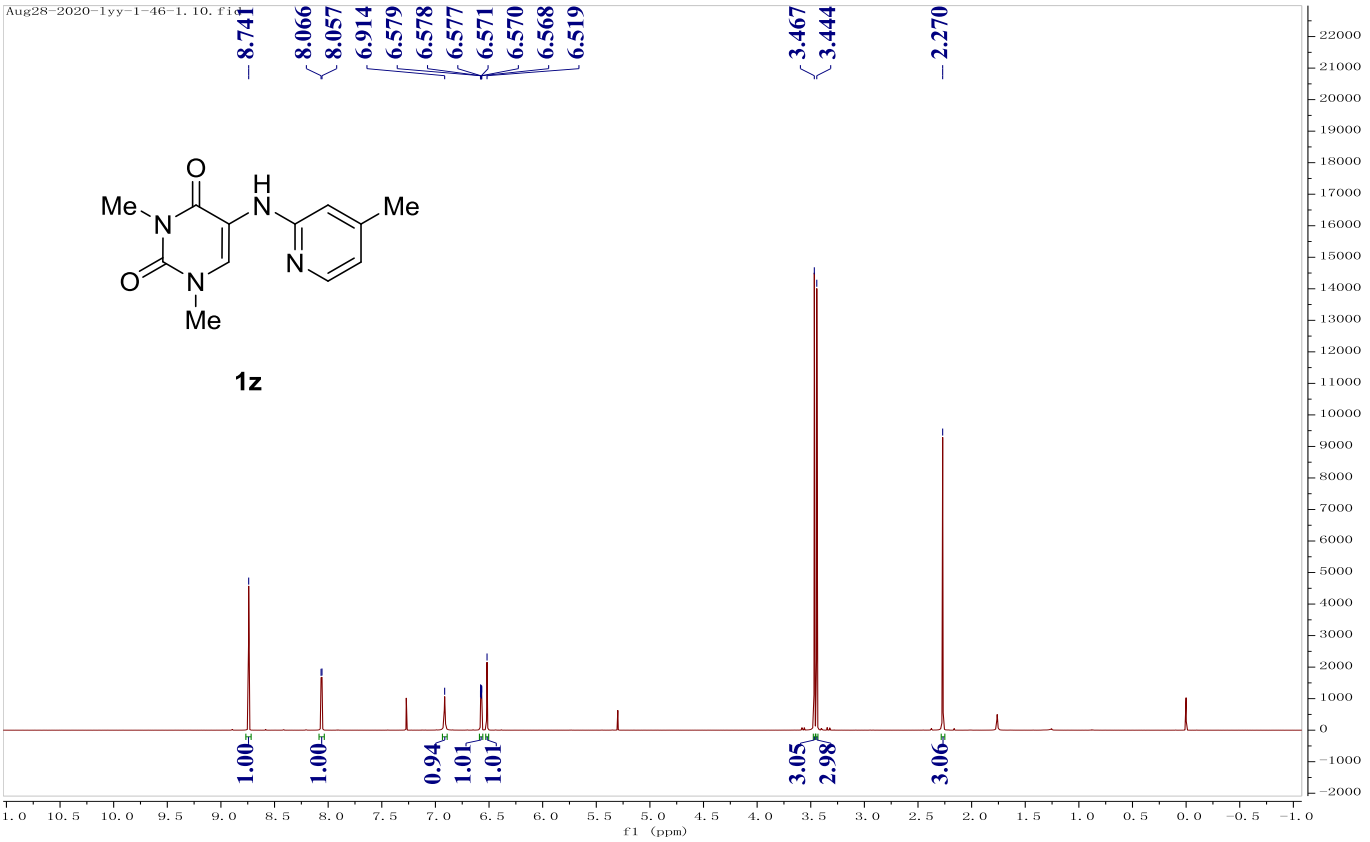
1y

^{13}C NMR Spectrum of 1y at 25 °C ($CDCl_3$, 150 MHz)



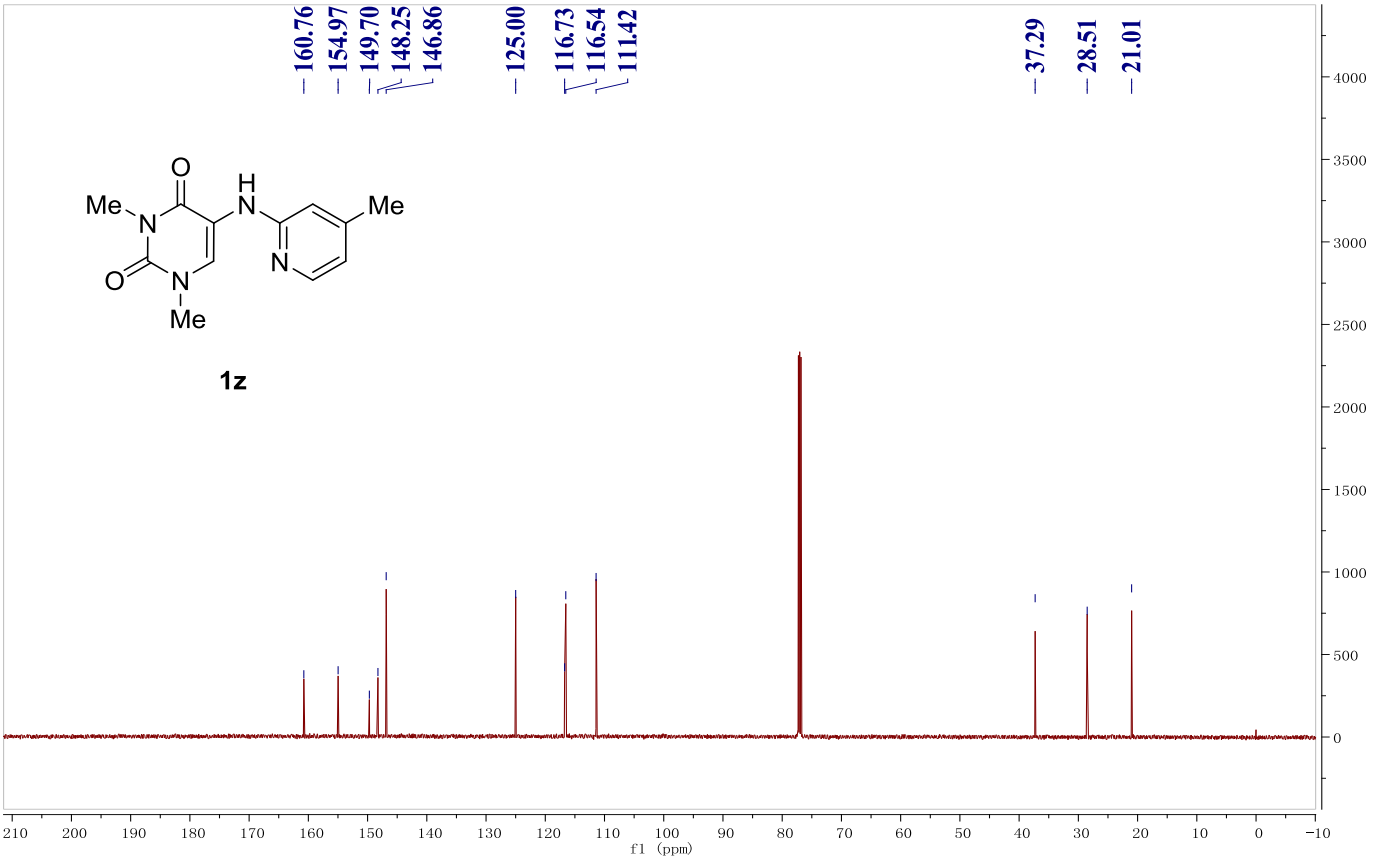
1y

^{1}H NMR Spectrum of 1z at 25 °C ($CDCl_3$, 600 MHz)



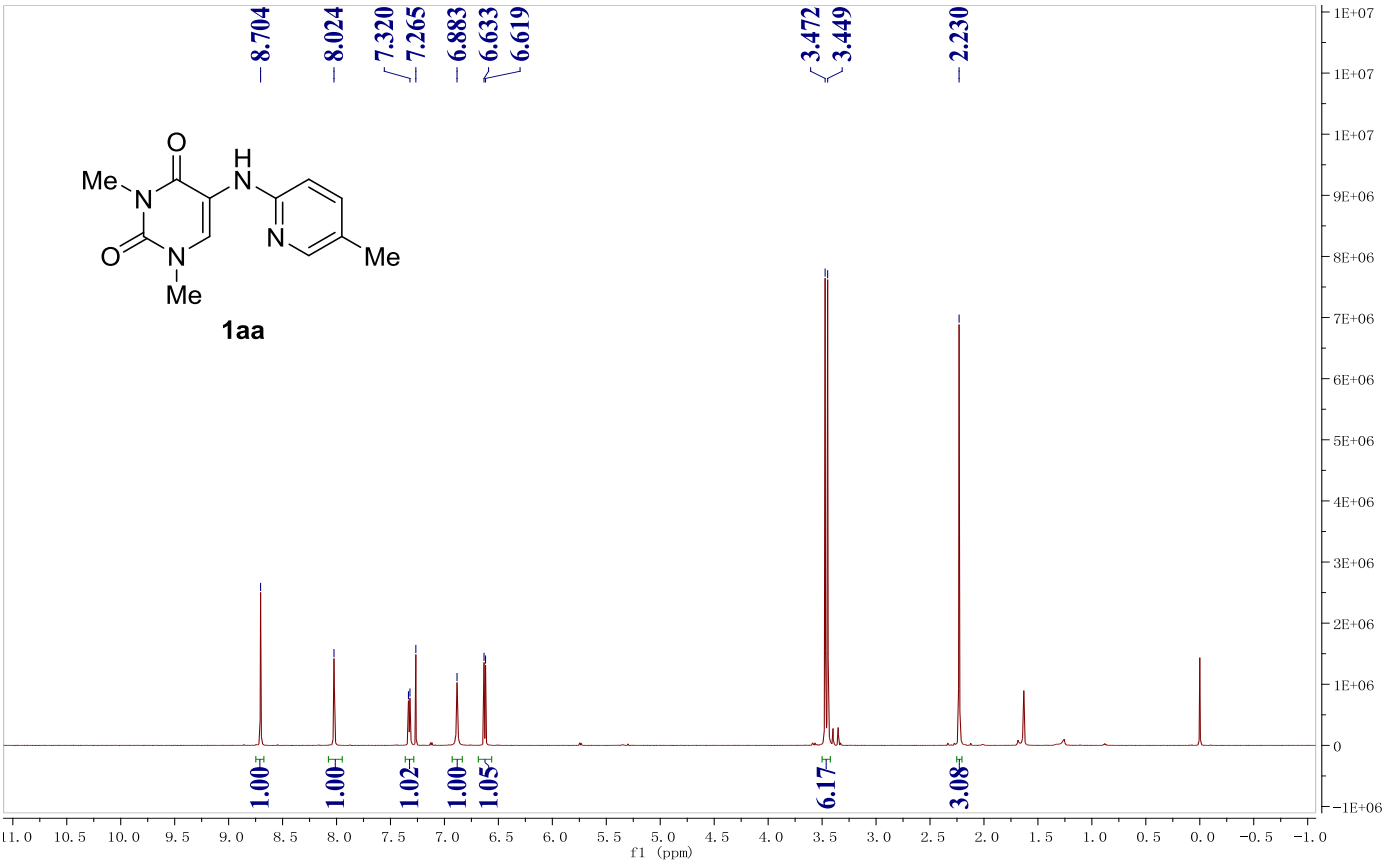
1z

^{13}C NMR Spectrum of 1z at 25 °C ($CDCl_3$, 150 MHz)



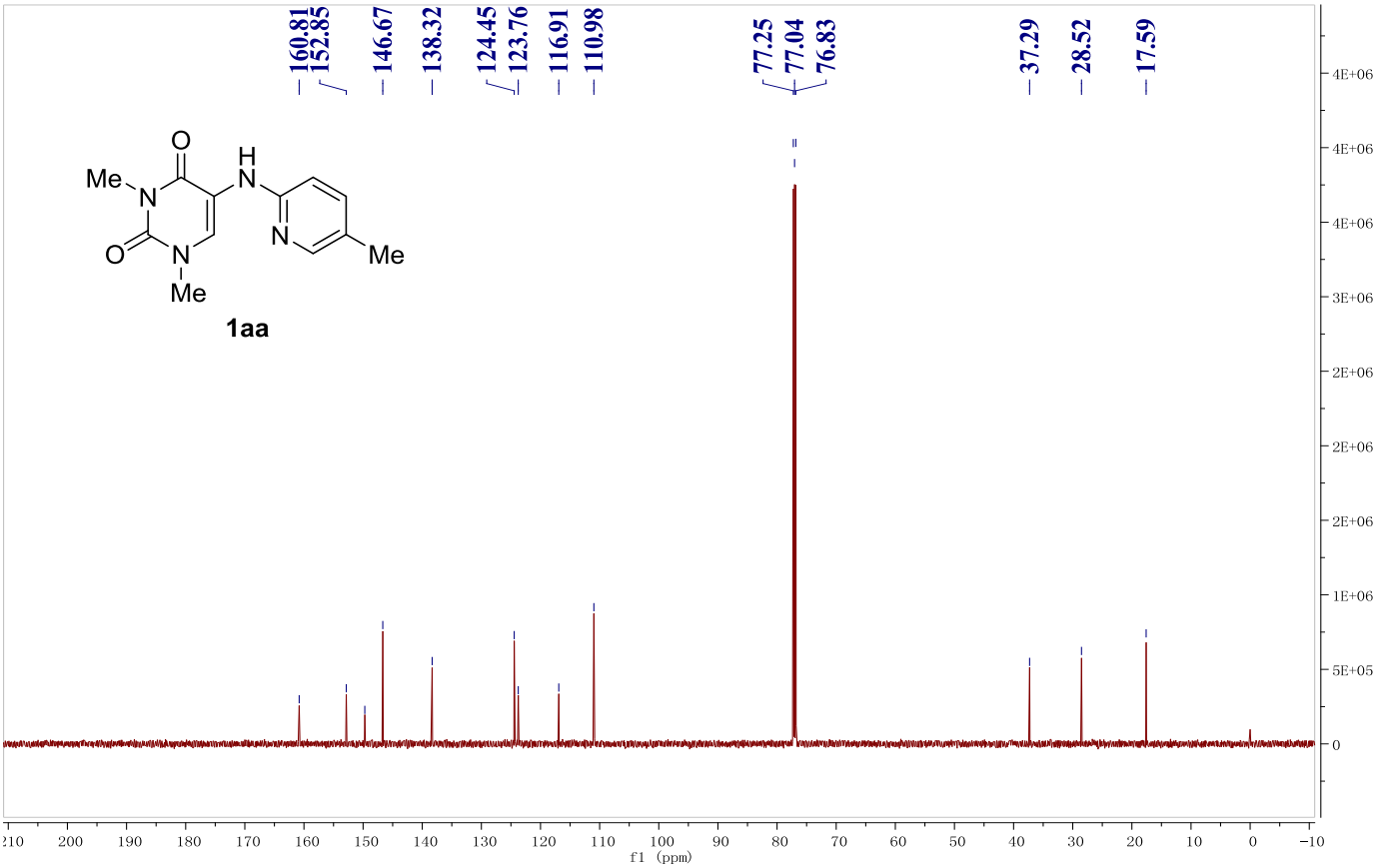
1z

^{1}H NMR Spectrum of 1aa at 25 °C ($CDCl_3$, 600 MHz)



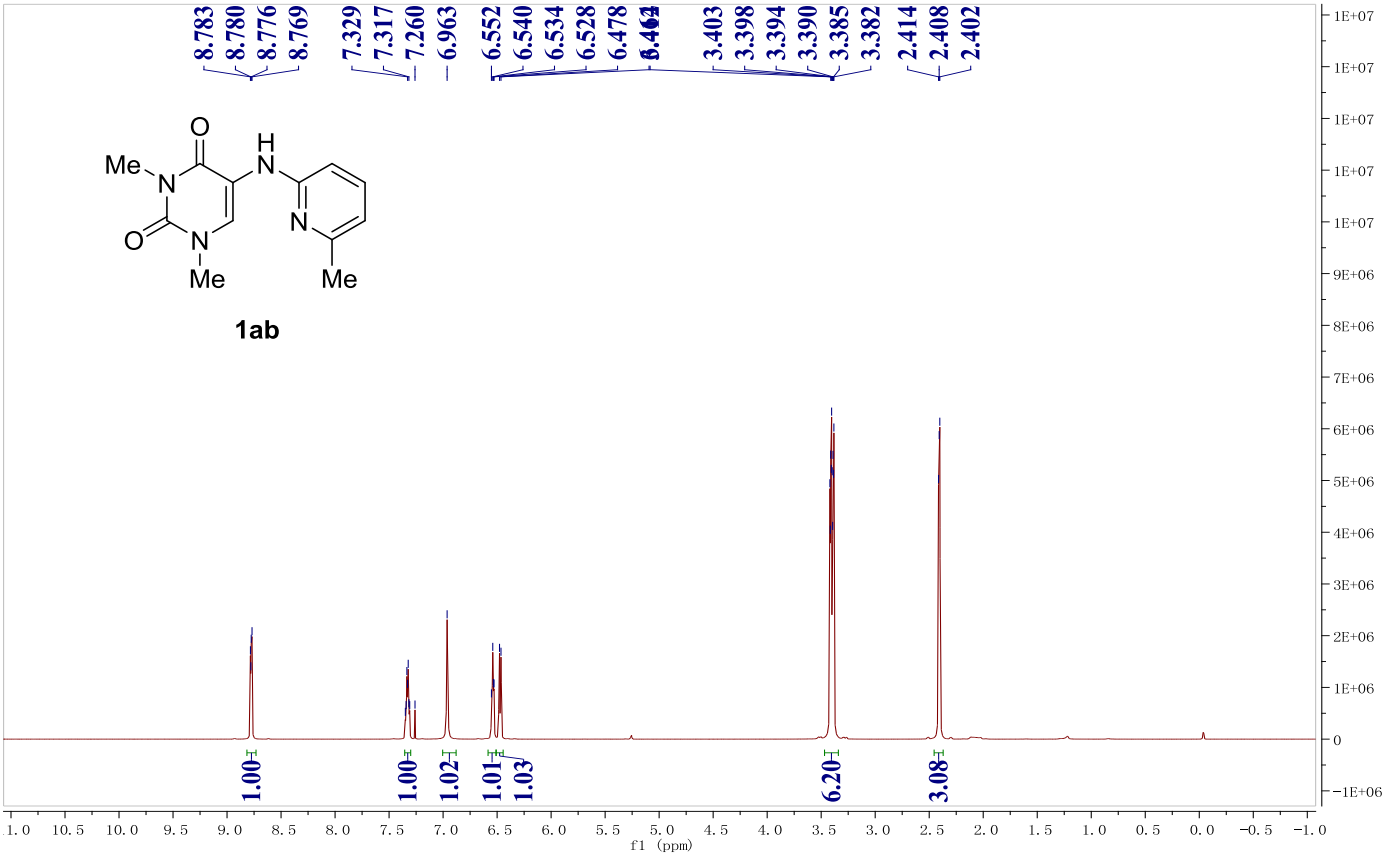
1aa

^{13}C NMR Spectrum of 1aa at 25 °C ($CDCl_3$, 150 MHz)

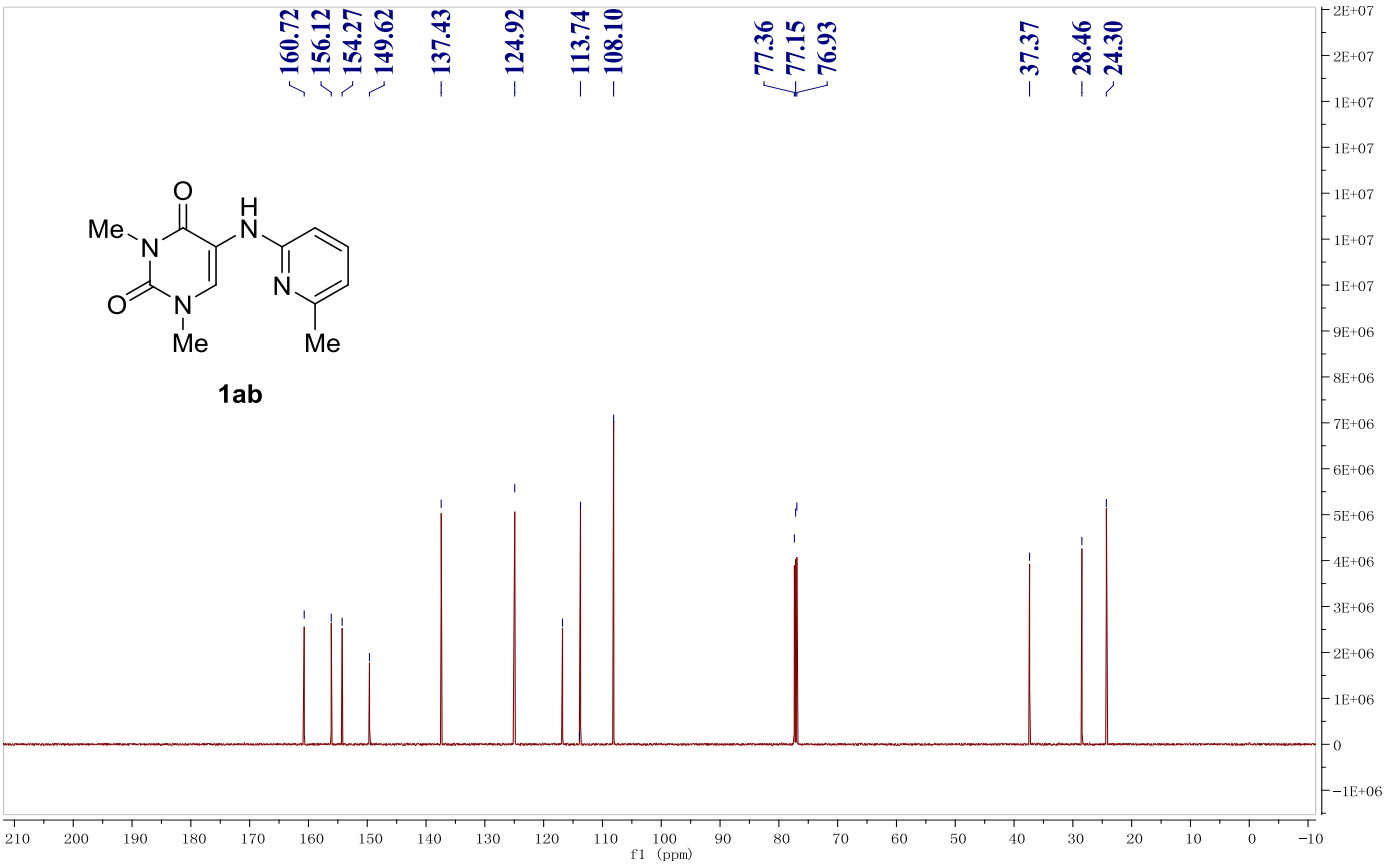


1aa

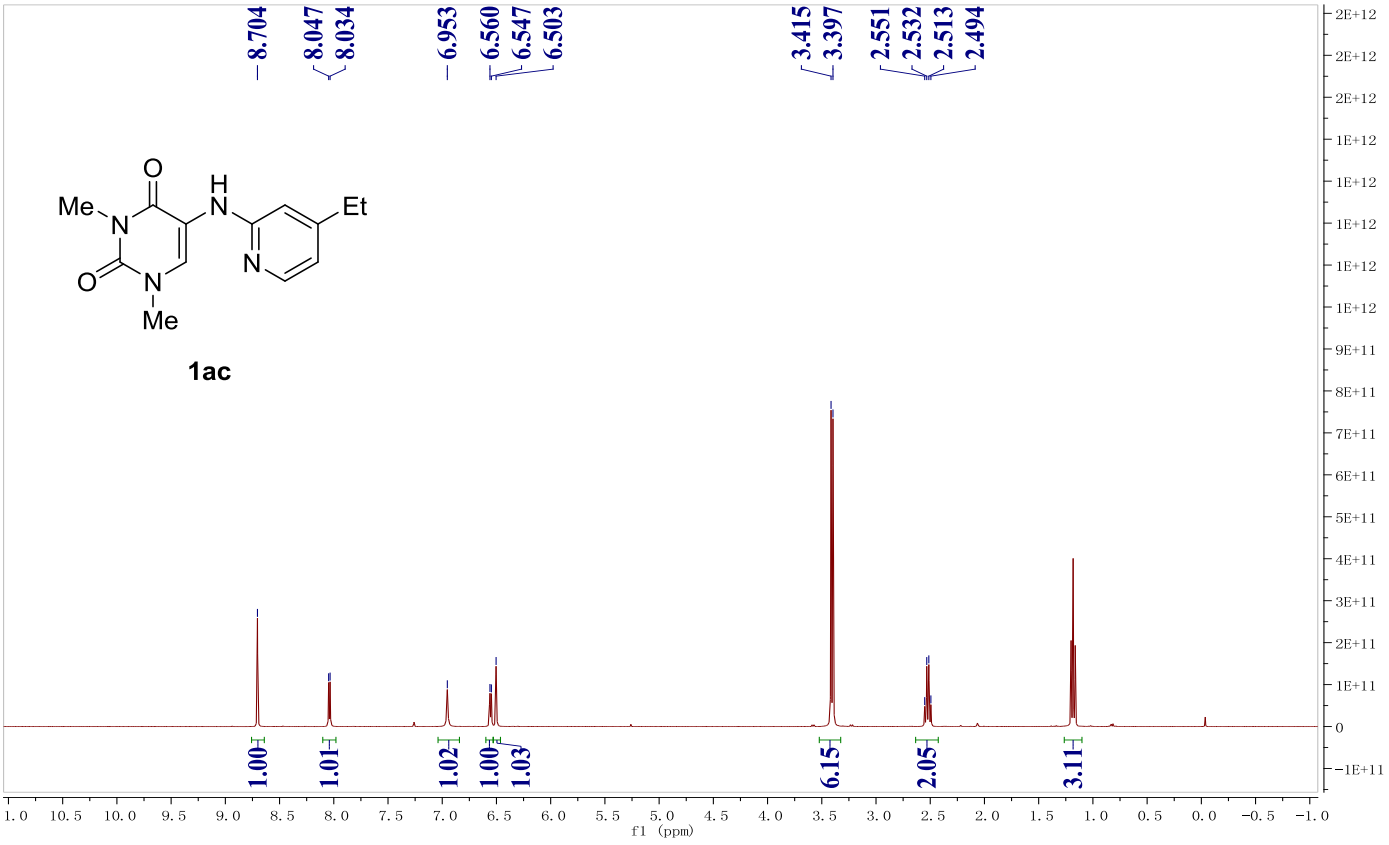
^{1}H NMR Spectrum of 1ab at 25 °C ($CDCl_3$, 600 MHz)



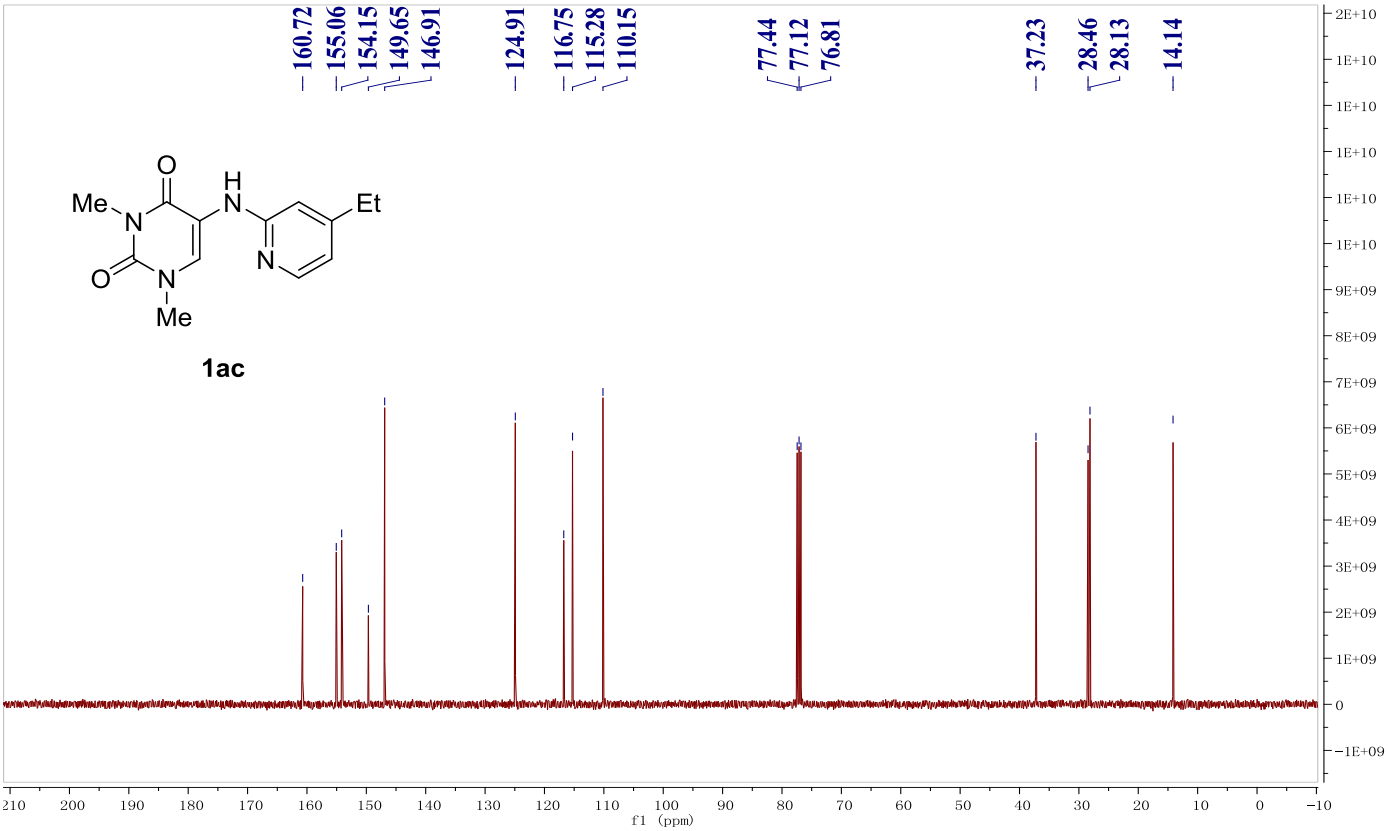
^{13}C NMR Spectrum of 1ab at 25 °C ($CDCl_3$, 150 MHz)



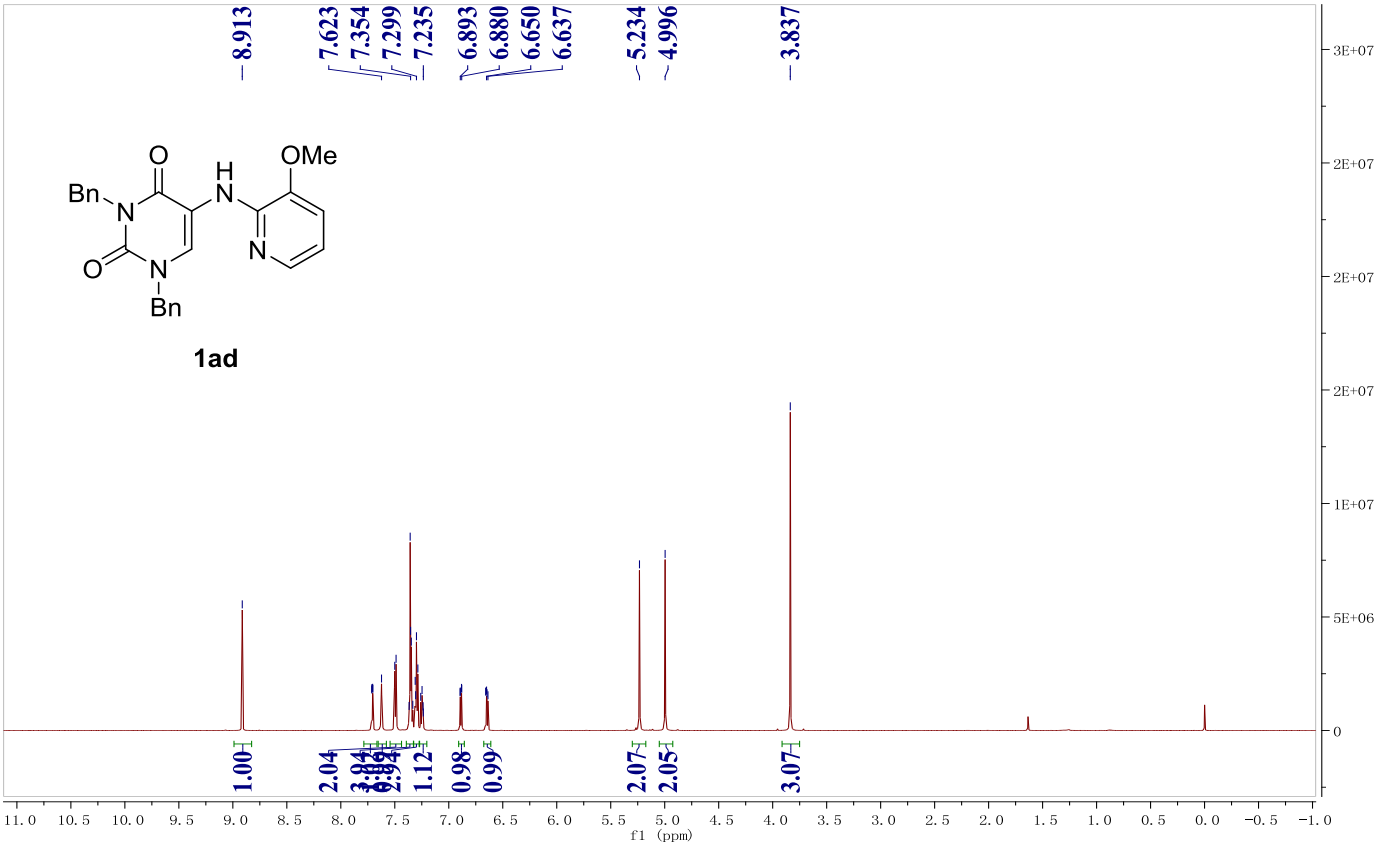
^{1}H NMR Spectrum of 1ac at 25 °C ($CDCl_3$, 400 MHz)

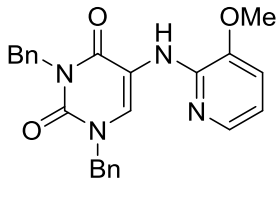


^{13}C NMR Spectrum of 1ac at 25 °C ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of 1ad at 25 °C ($CDCl_3$, 600 MHz)



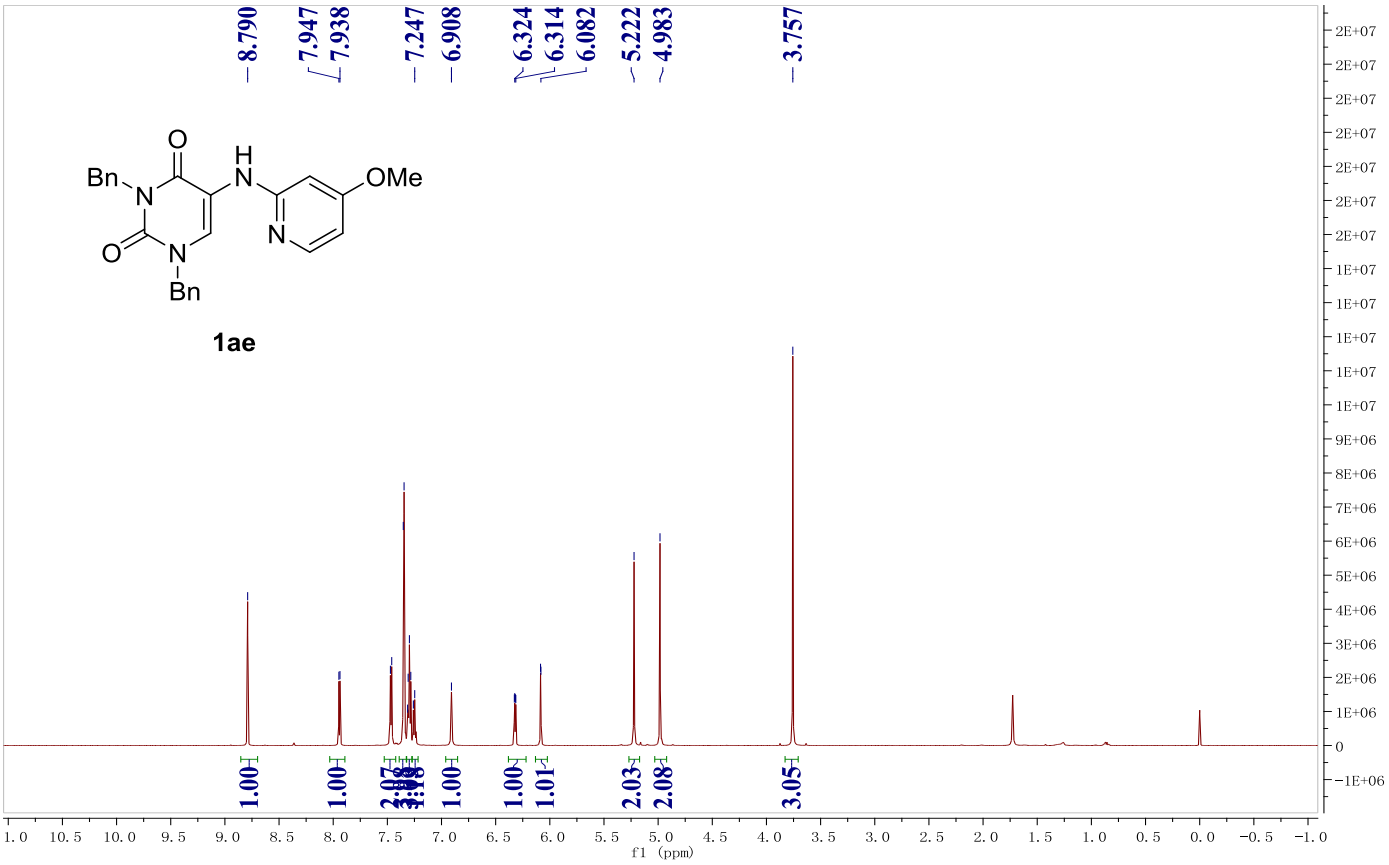


1ad

^{13}C NMR Spectrum of 1ad at 25 °C ($CDCl_3$, 150 MHz)

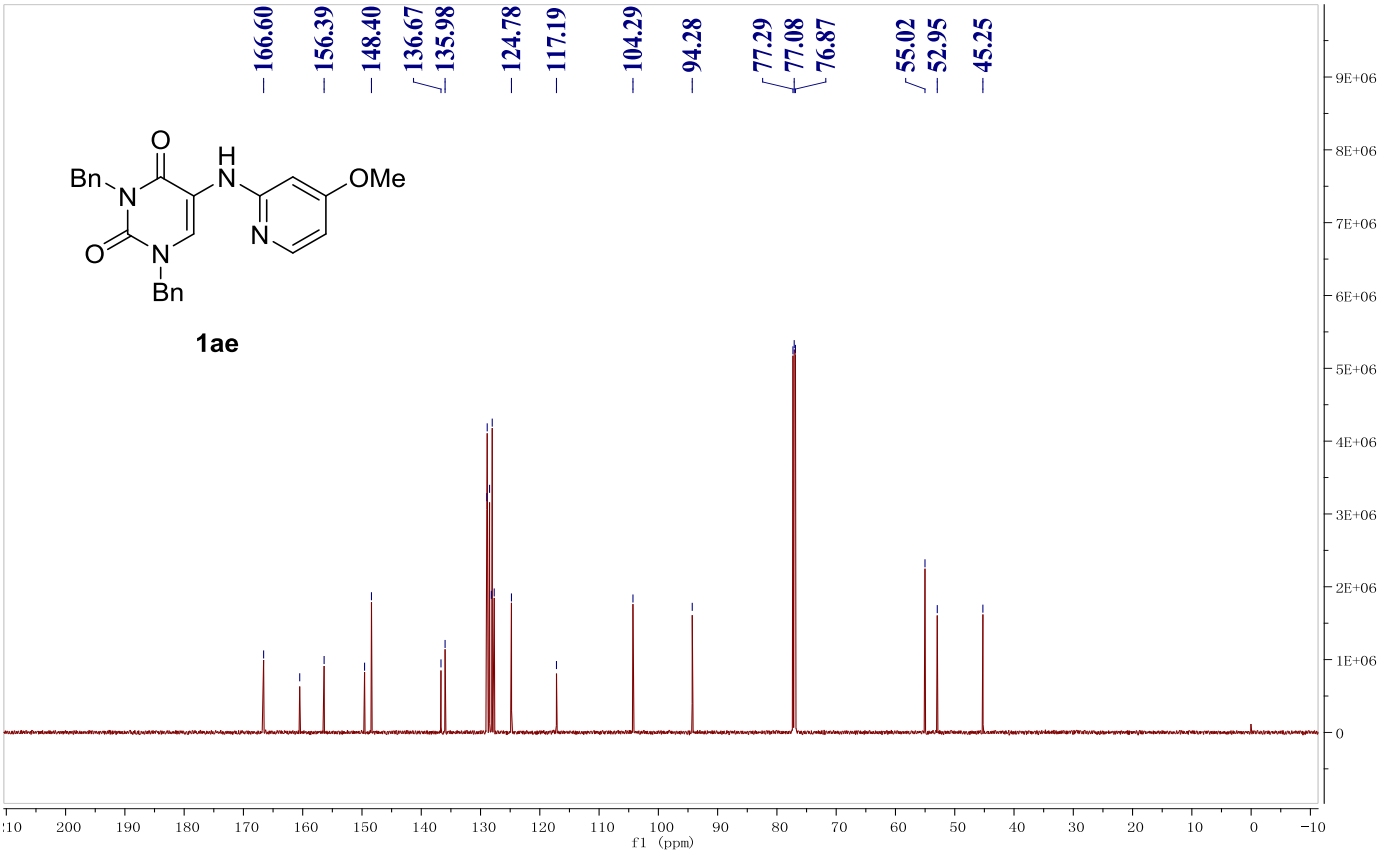
1ad

^{1}H NMR Spectrum of 1ae at 25 °C ($CDCl_3$, 600 MHz)



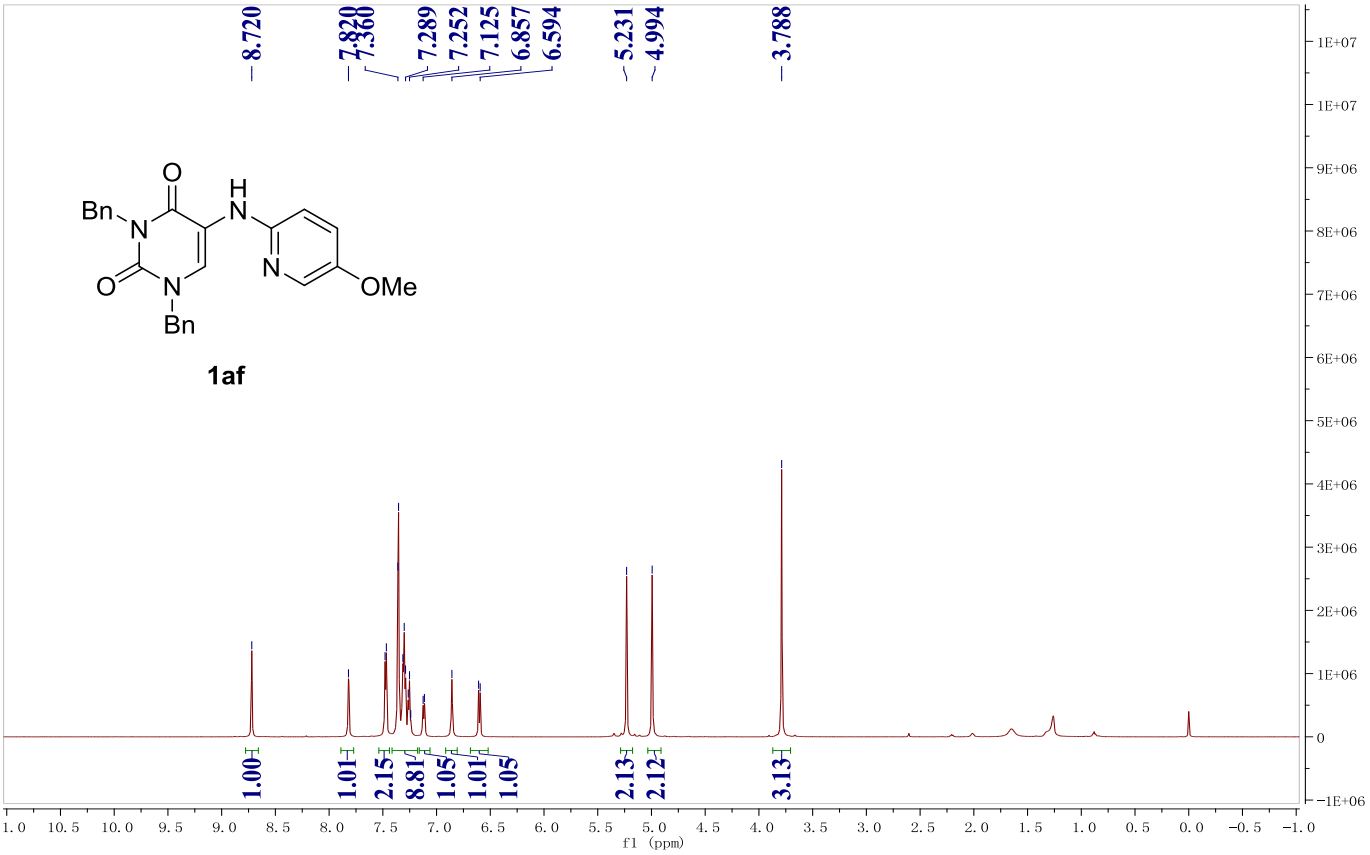
1ae

^{13}C NMR Spectrum of 1ae at 25 °C ($CDCl_3$, 150 MHz)

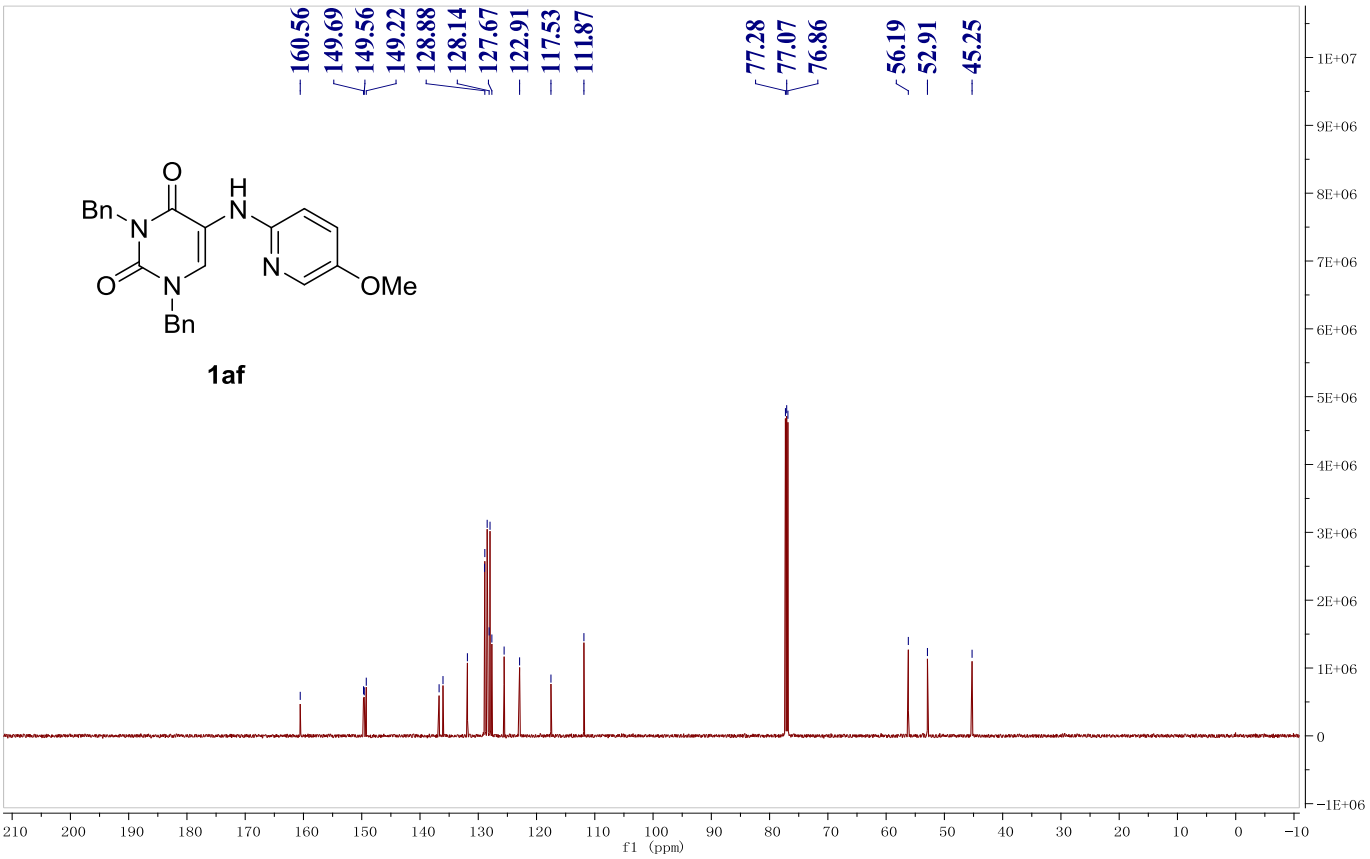


1ae

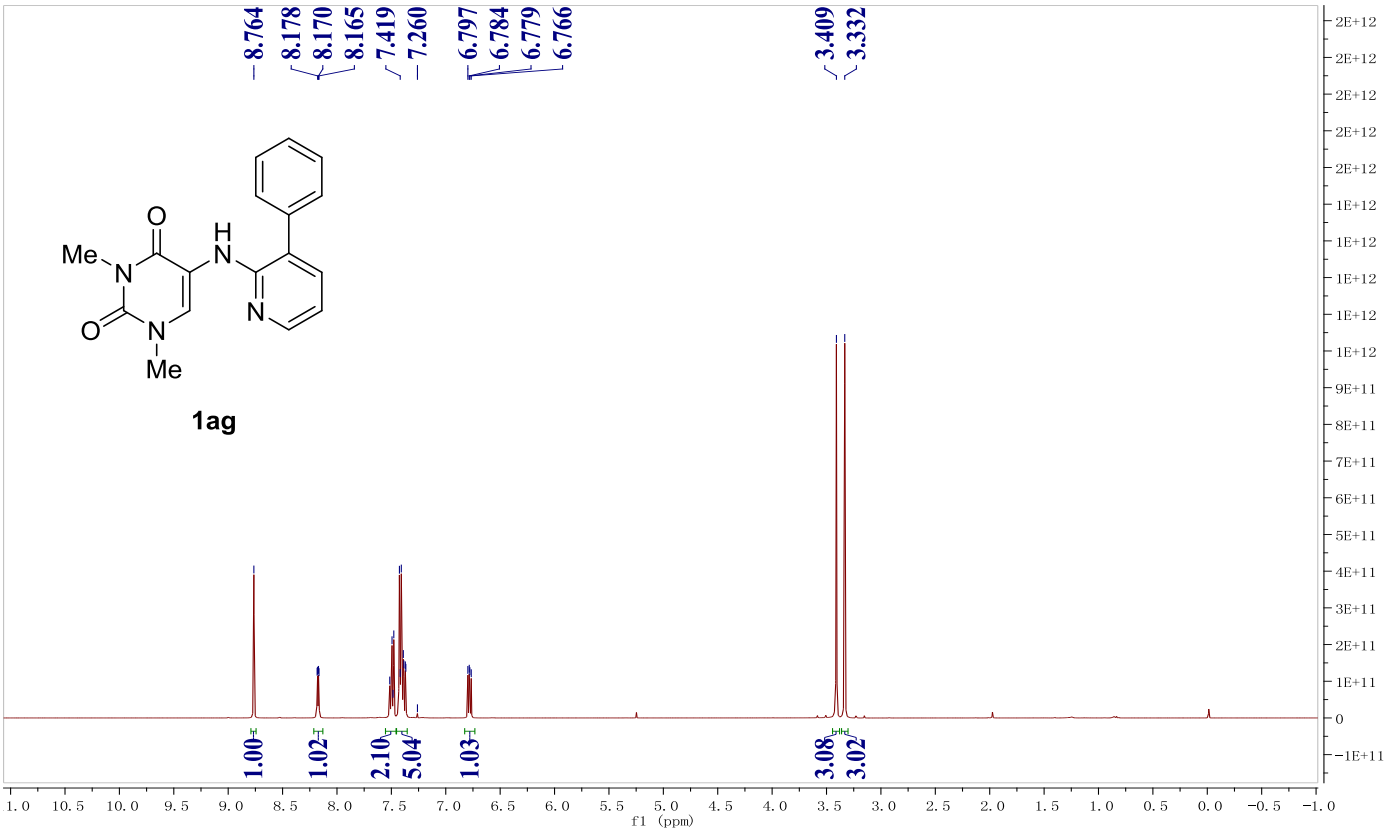
^{1}H NMR Spectrum of 1af at 25 °C ($CDCl_3$, 600 MHz)



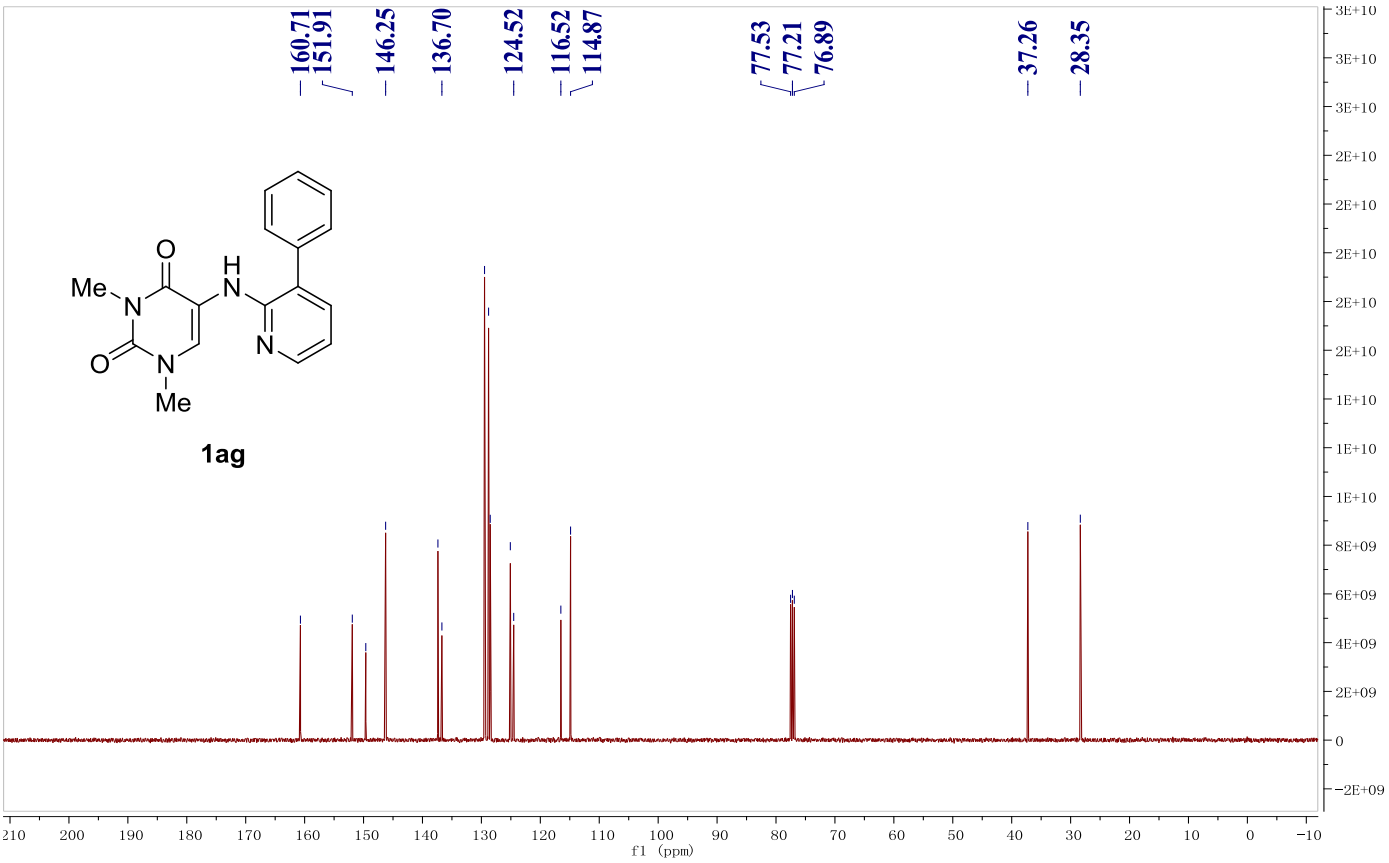
^{13}C NMR Spectrum of 1af at 25 °C ($CDCl_3$, 150 MHz)



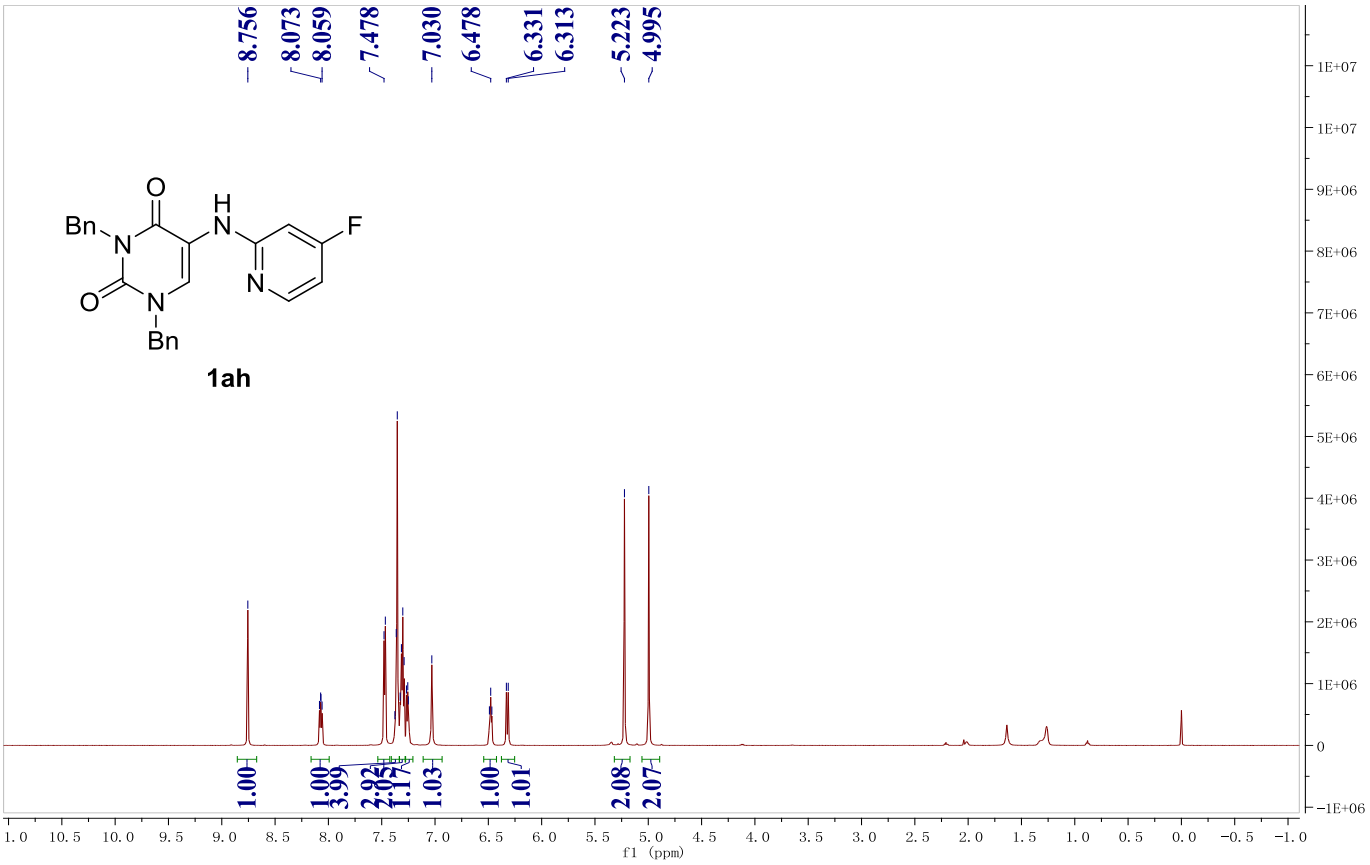
^{1}H NMR Spectrum of 1ag at 25 °C ($CDCl_3$, 400 MHz)



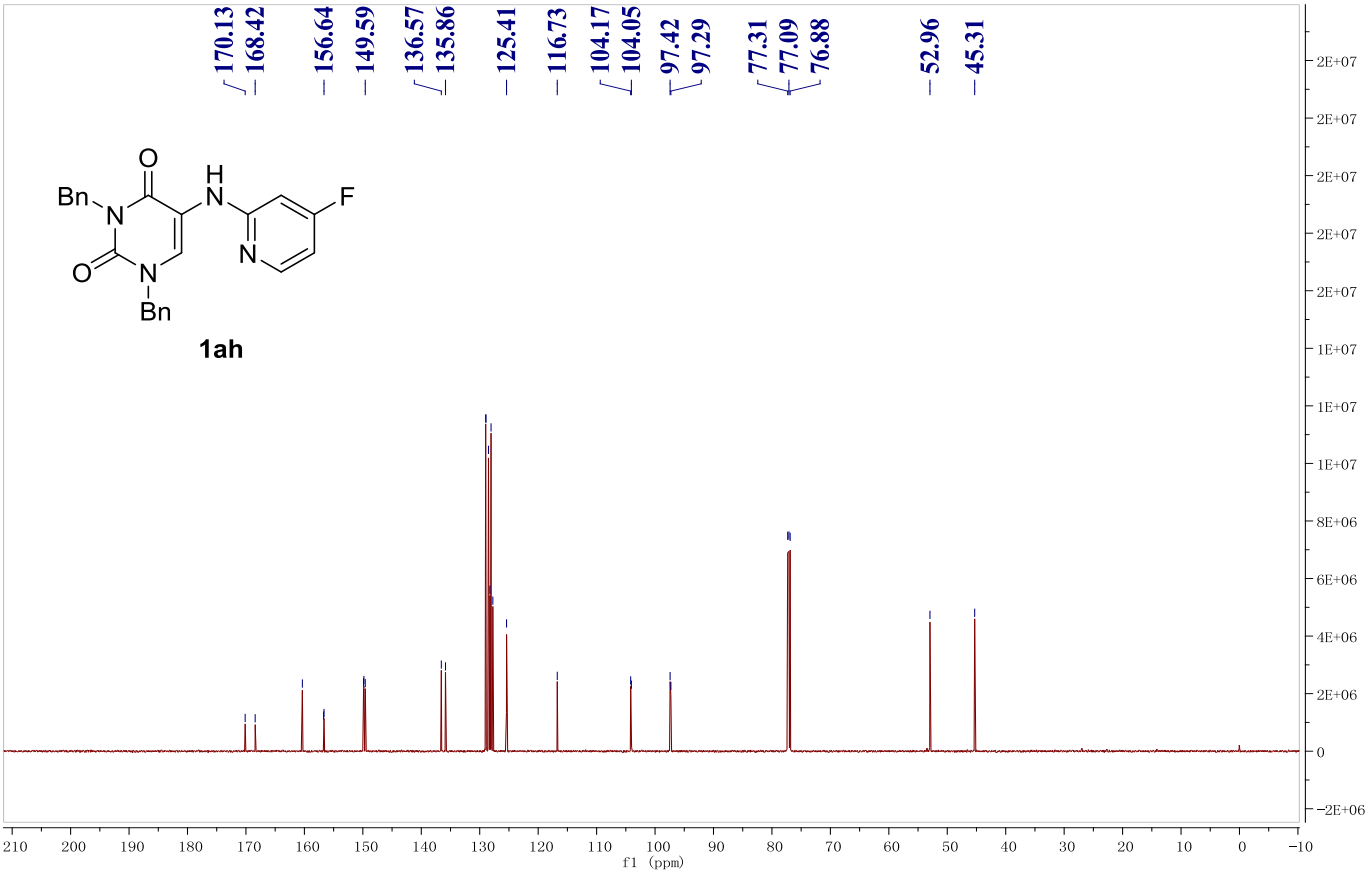
^{13}C NMR Spectrum of 1ag at 25 °C ($CDCl_3$, 100 MHz)



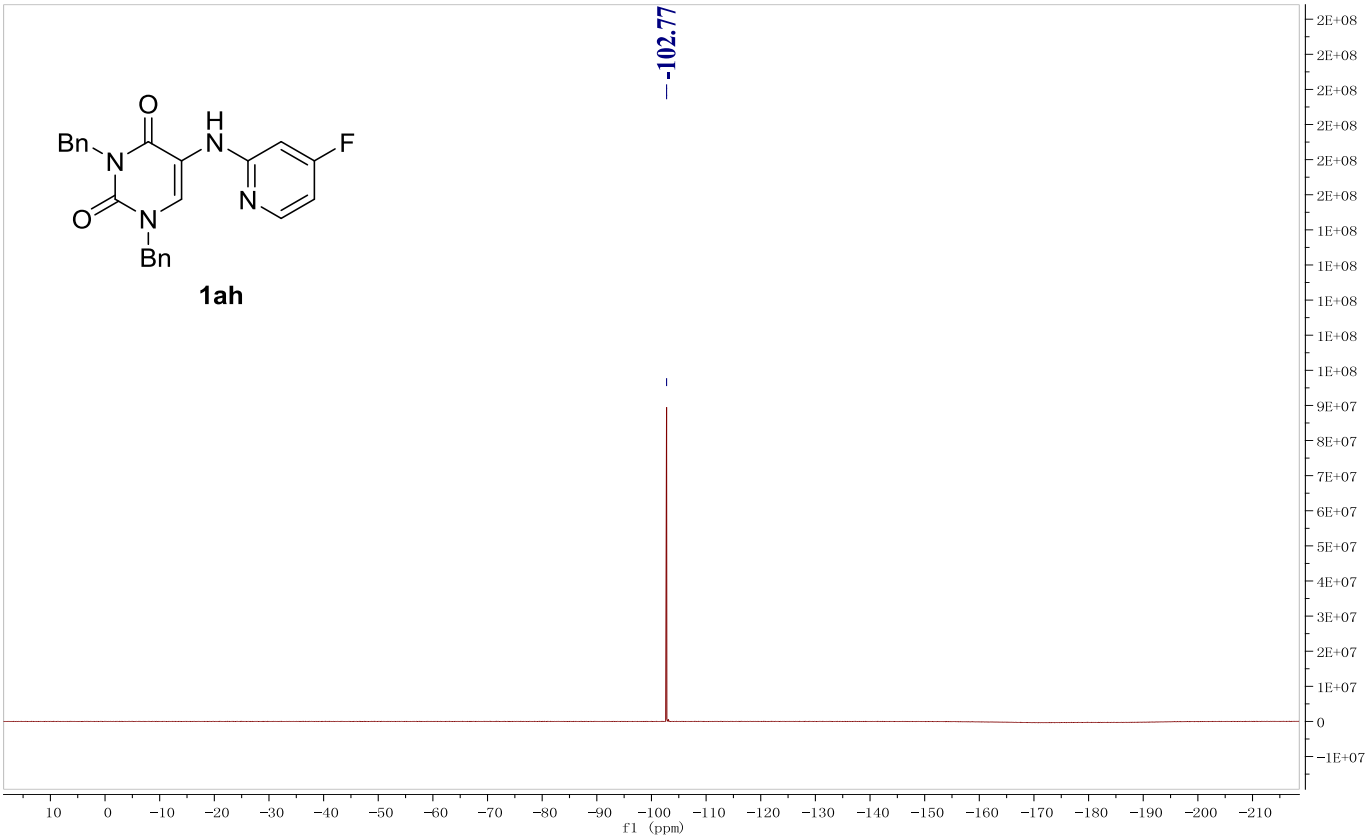
^{1}H NMR Spectrum of 1ah at 25 °C ($CDCl_3$, 600 MHz)



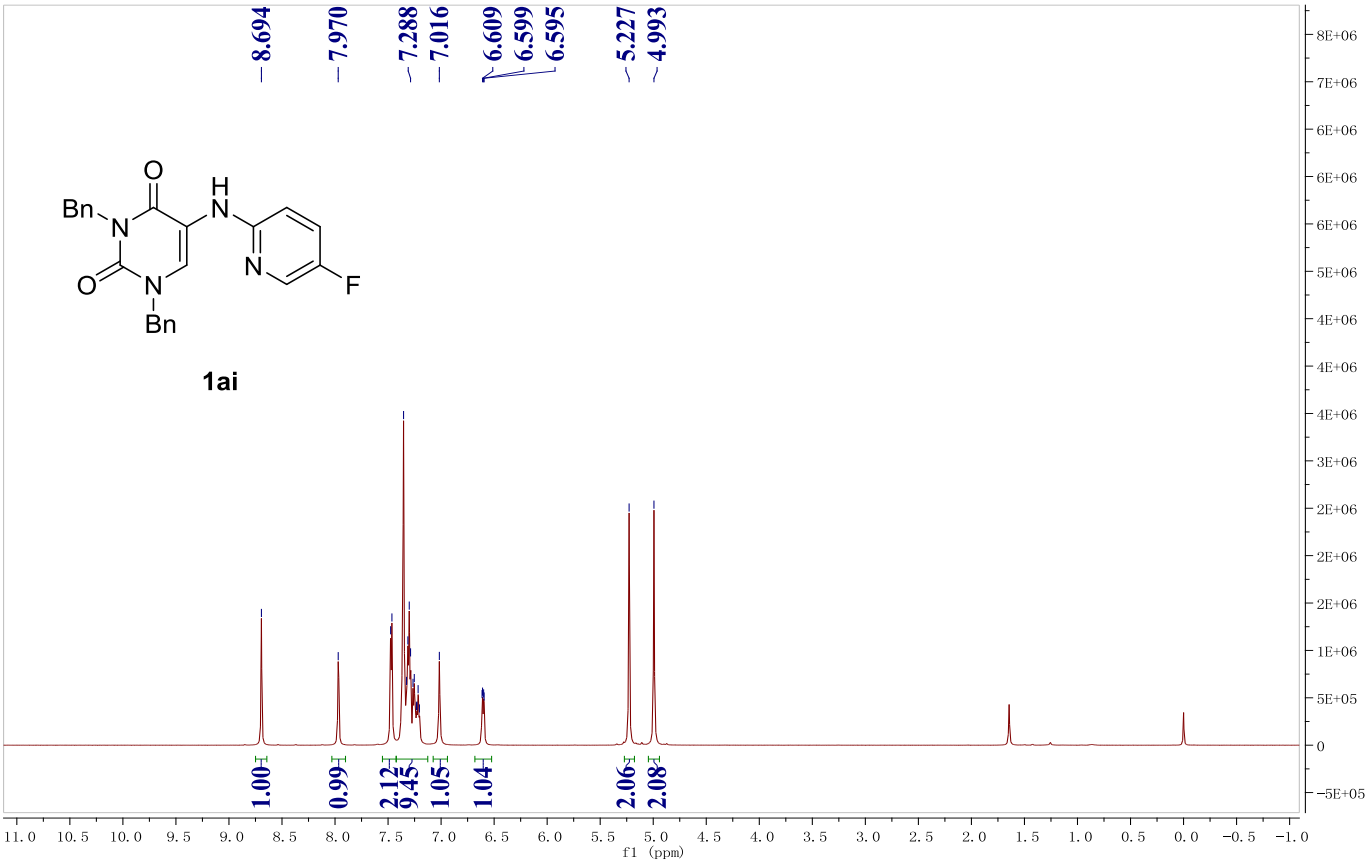
^{13}C NMR Spectrum of 1ah at 25 °C ($CDCl_3$, 150 MHz)



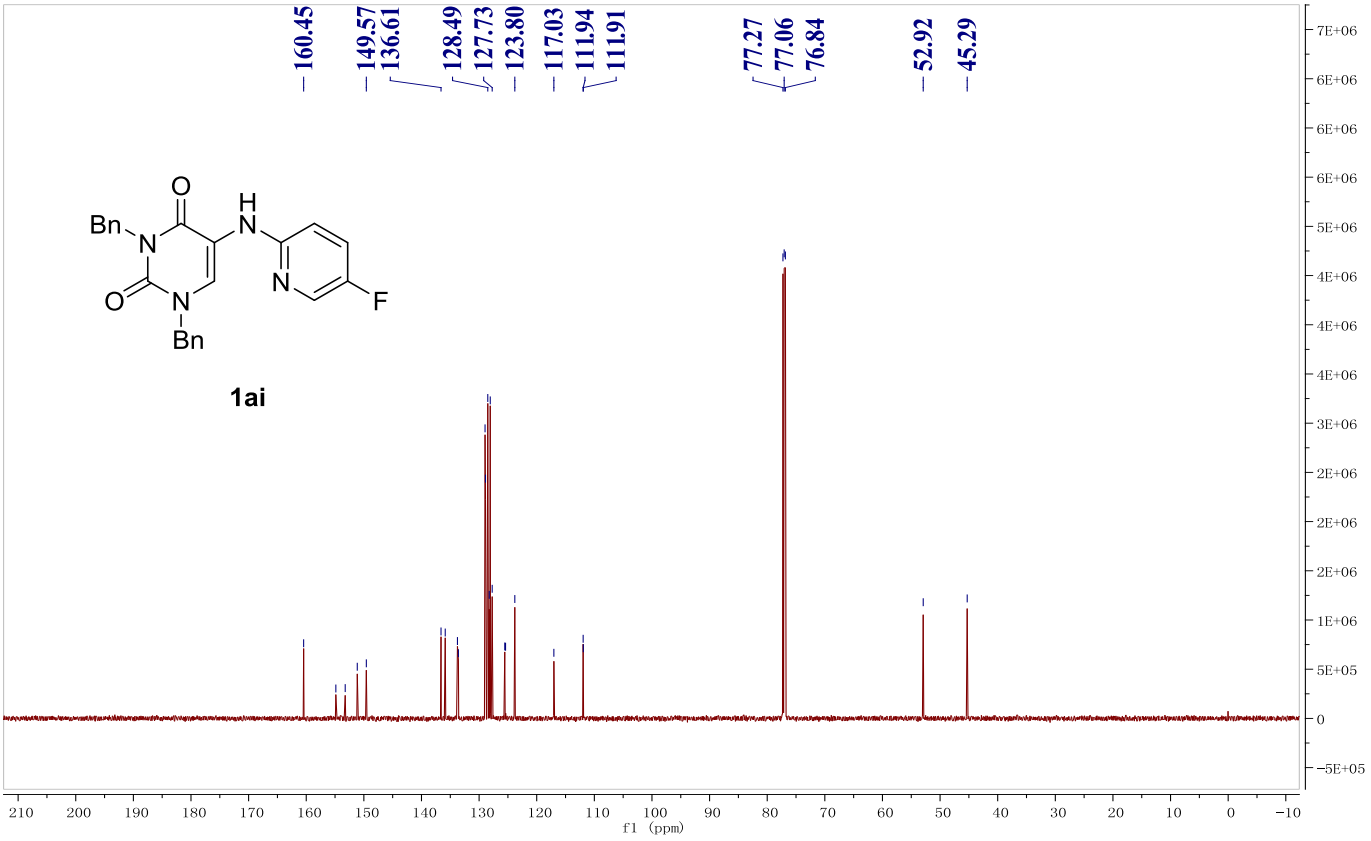
^{19}F NMR Spectrum of 1ah at 25 °C ($CDCl_3$, 565 MHz)



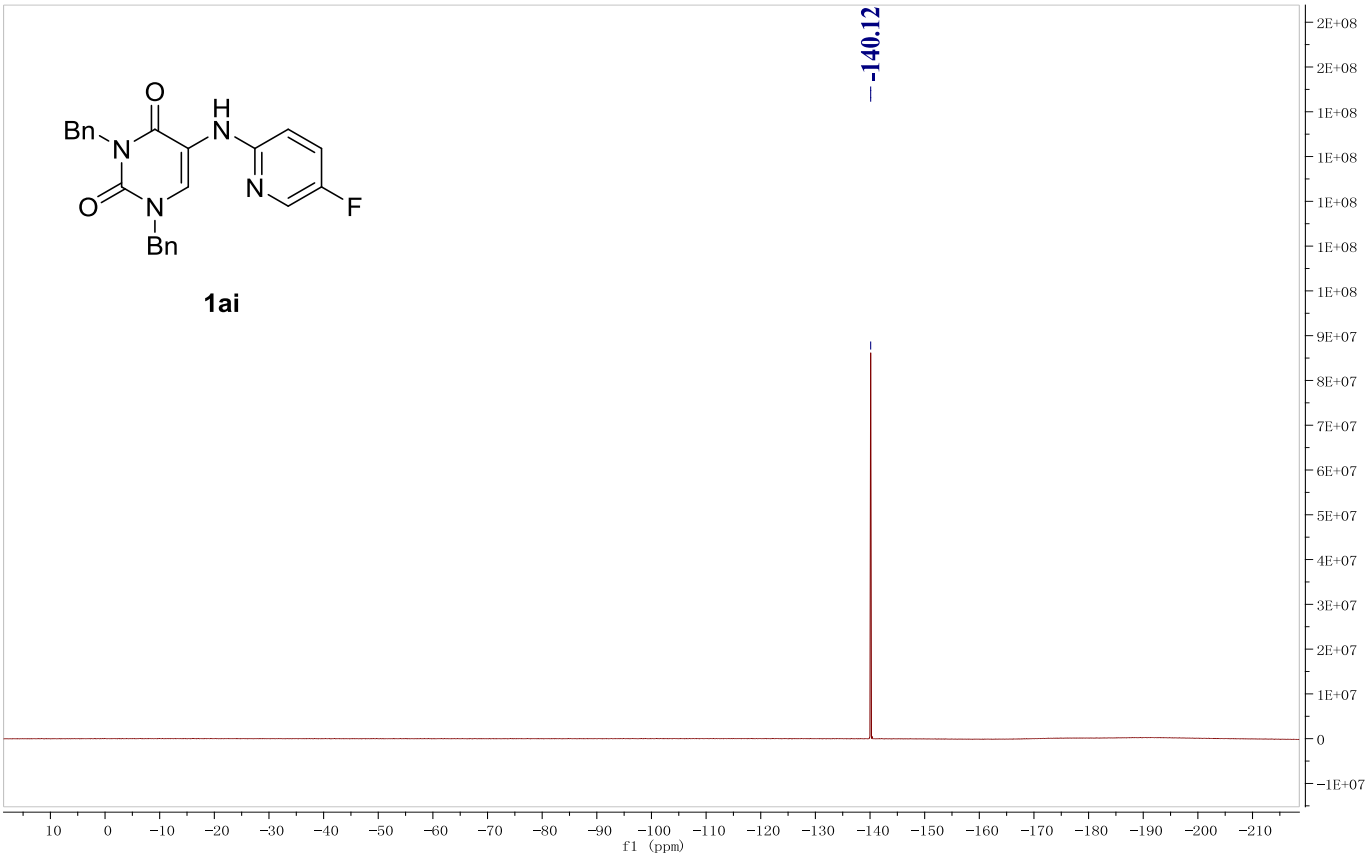
^{1}H NMR Spectrum of 1ai at 25 °C ($CDCl_3$, 600 MHz)



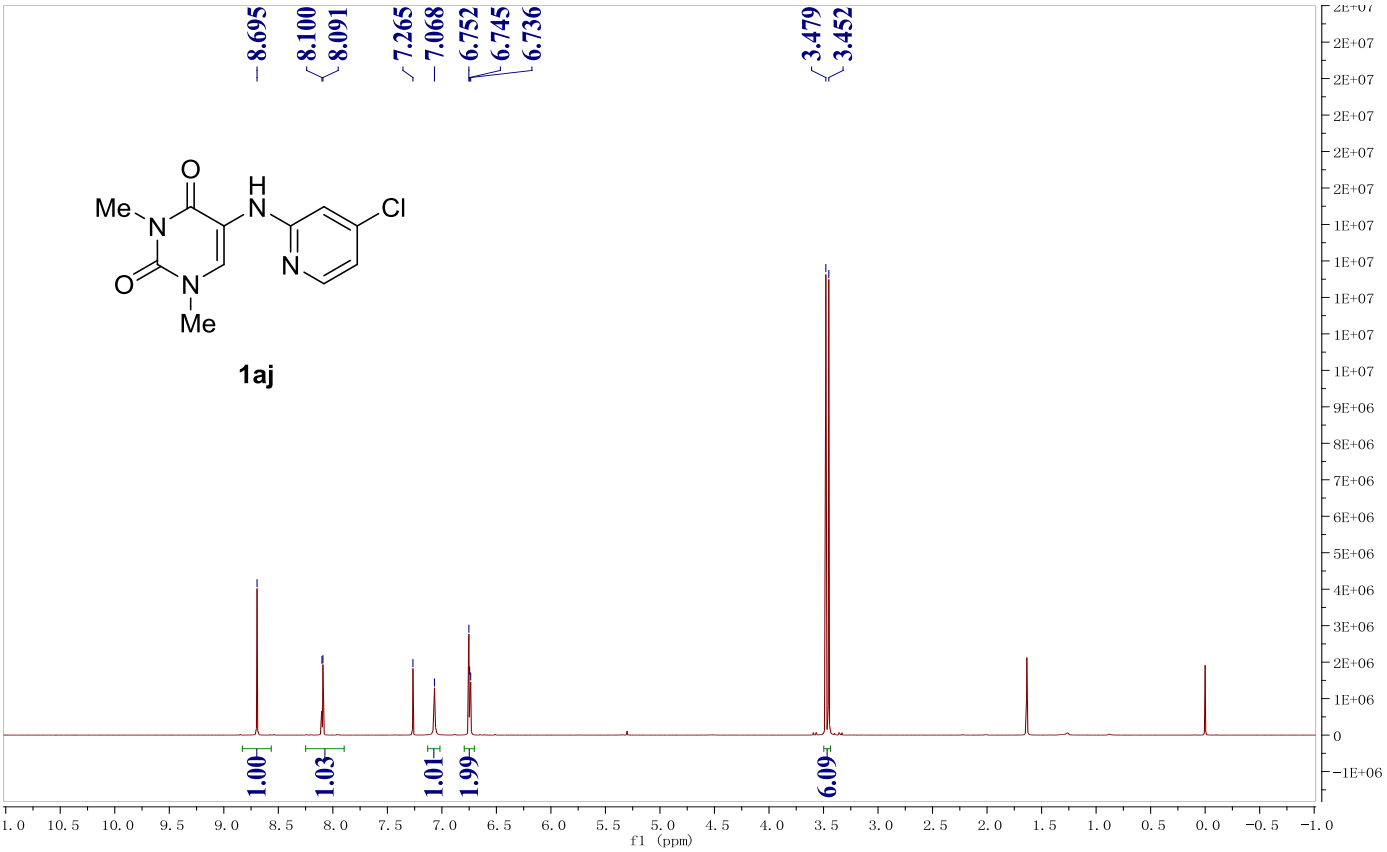
^{13}C NMR Spectrum of 1ai at 25 °C ($CDCl_3$, 150 MHz)



^{19}F NMR Spectrum of 1ai at 25 °C ($CDCl_3$, 565 MHz)

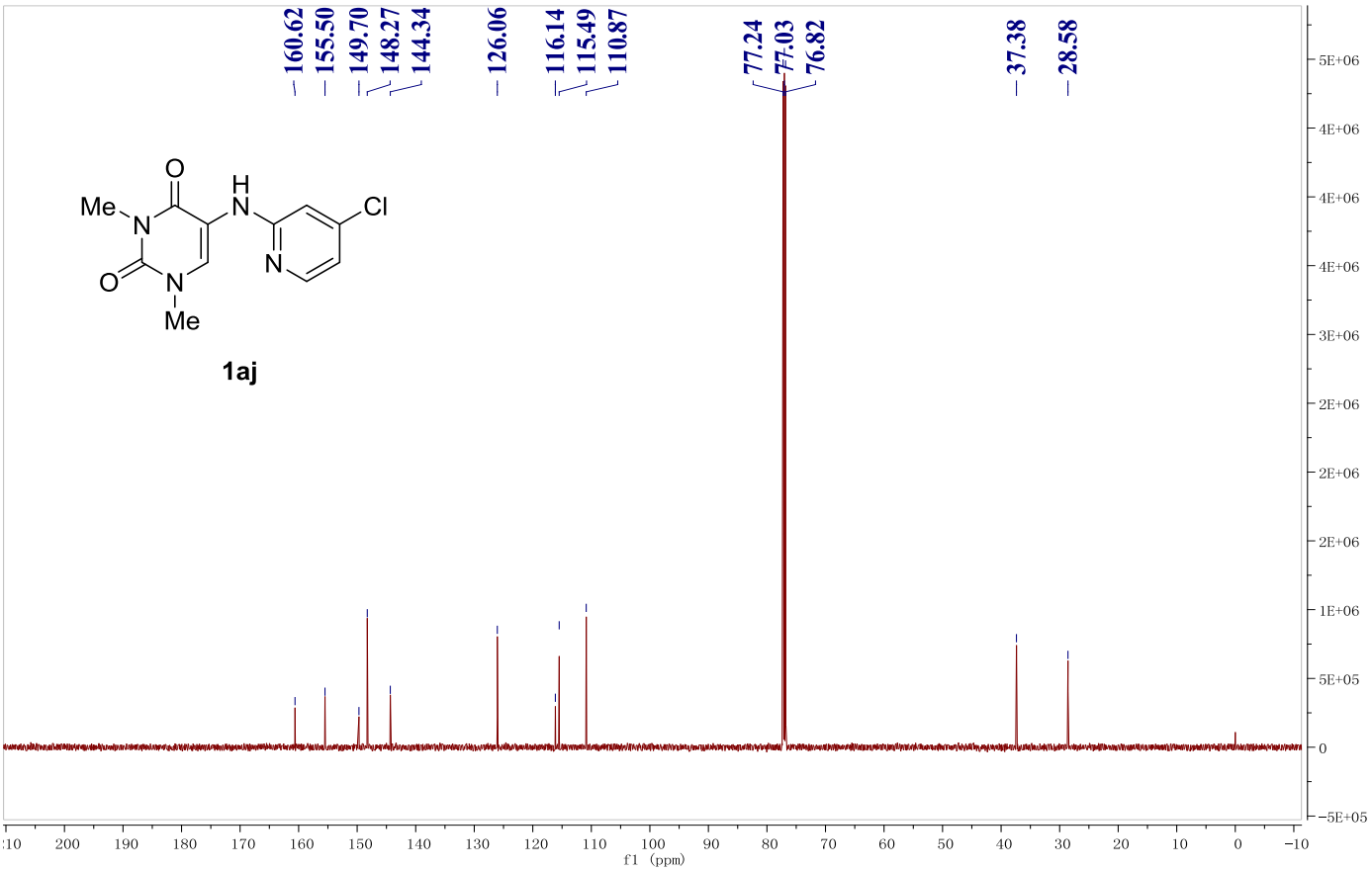


^{1}H NMR Spectrum of 1aj at 25 °C ($CDCl_3$, 600 MHz)



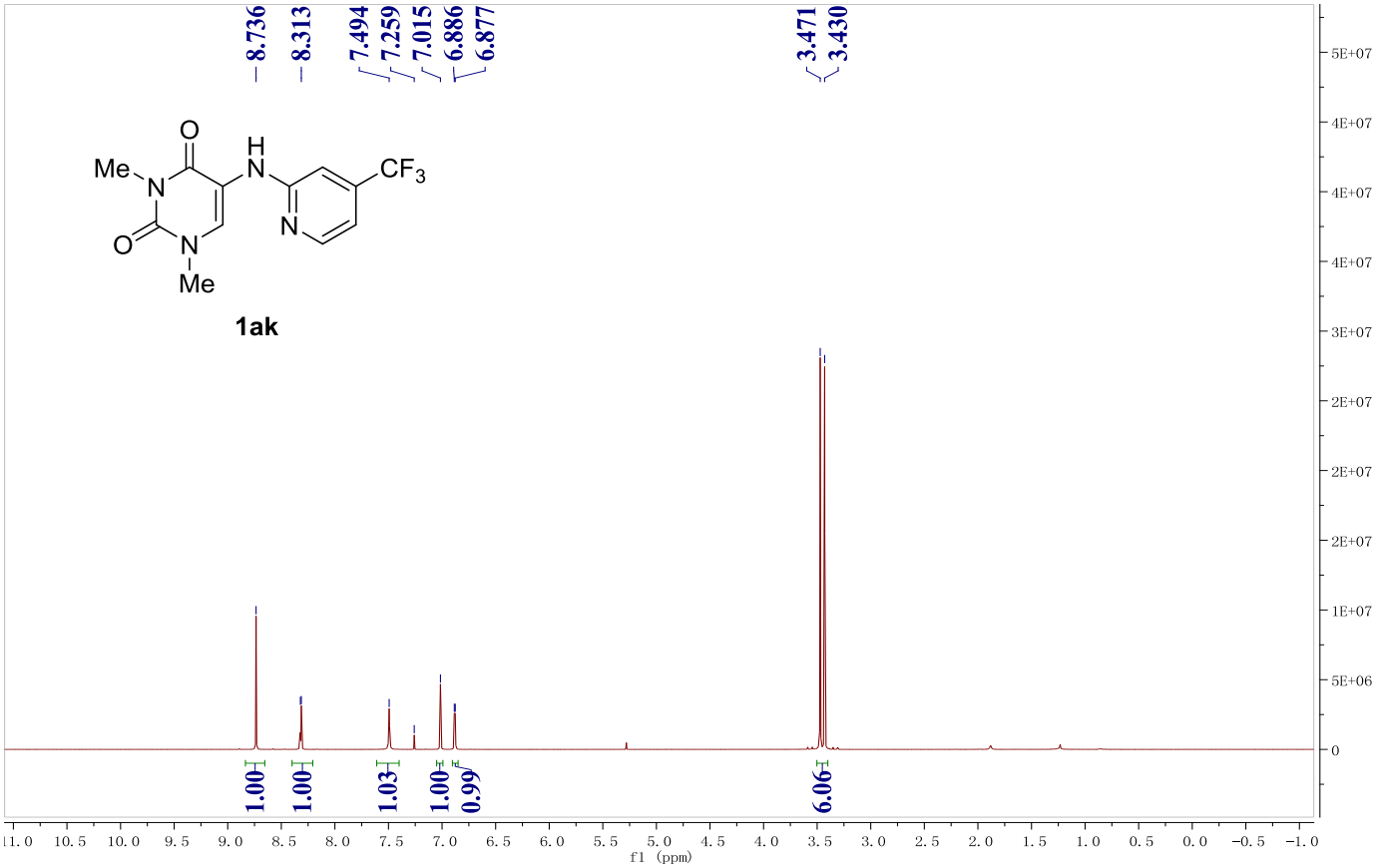
1aj

^{13}C NMR Spectrum of 1aj at 25 °C ($CDCl_3$, 150 MHz)

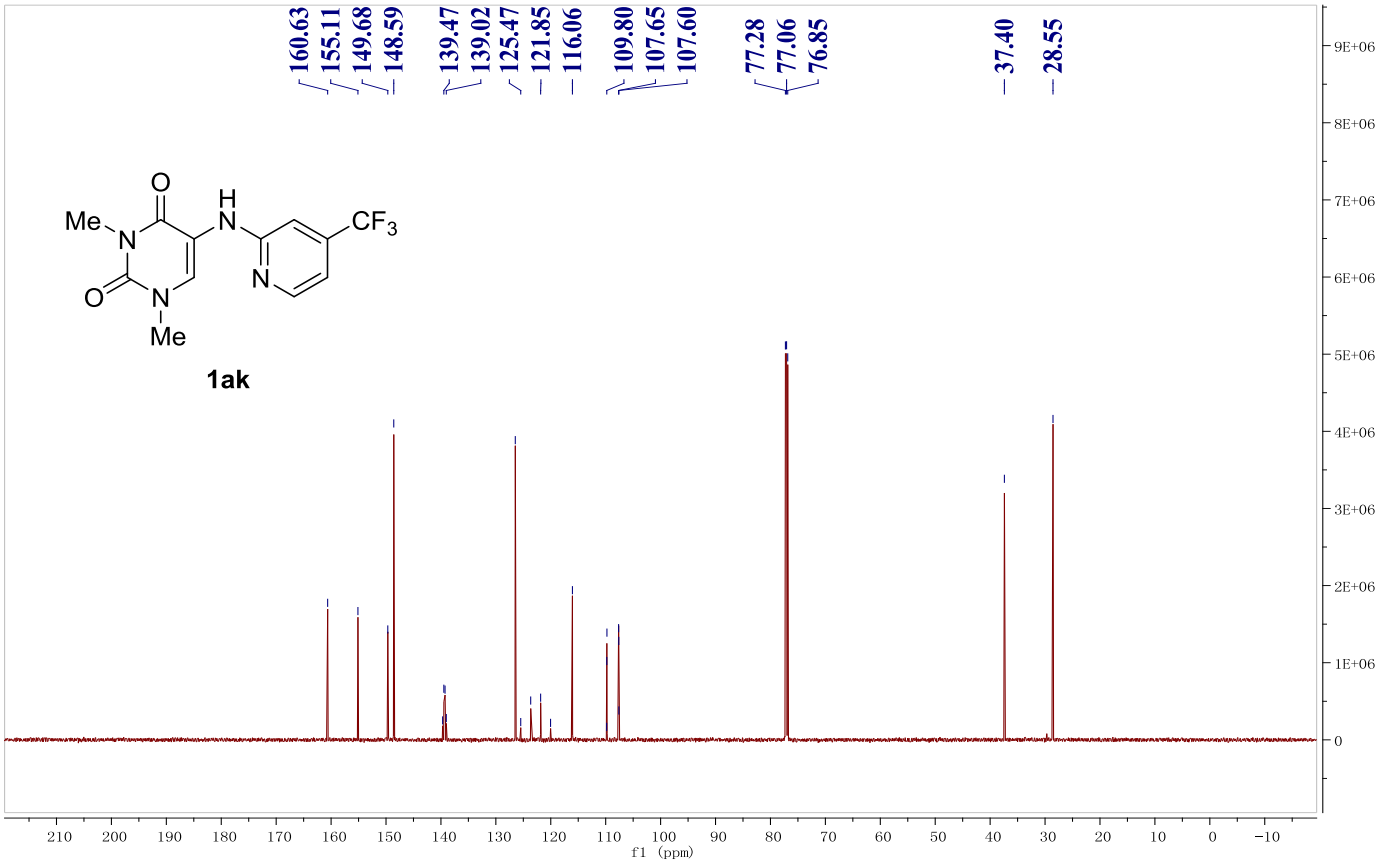


1aj

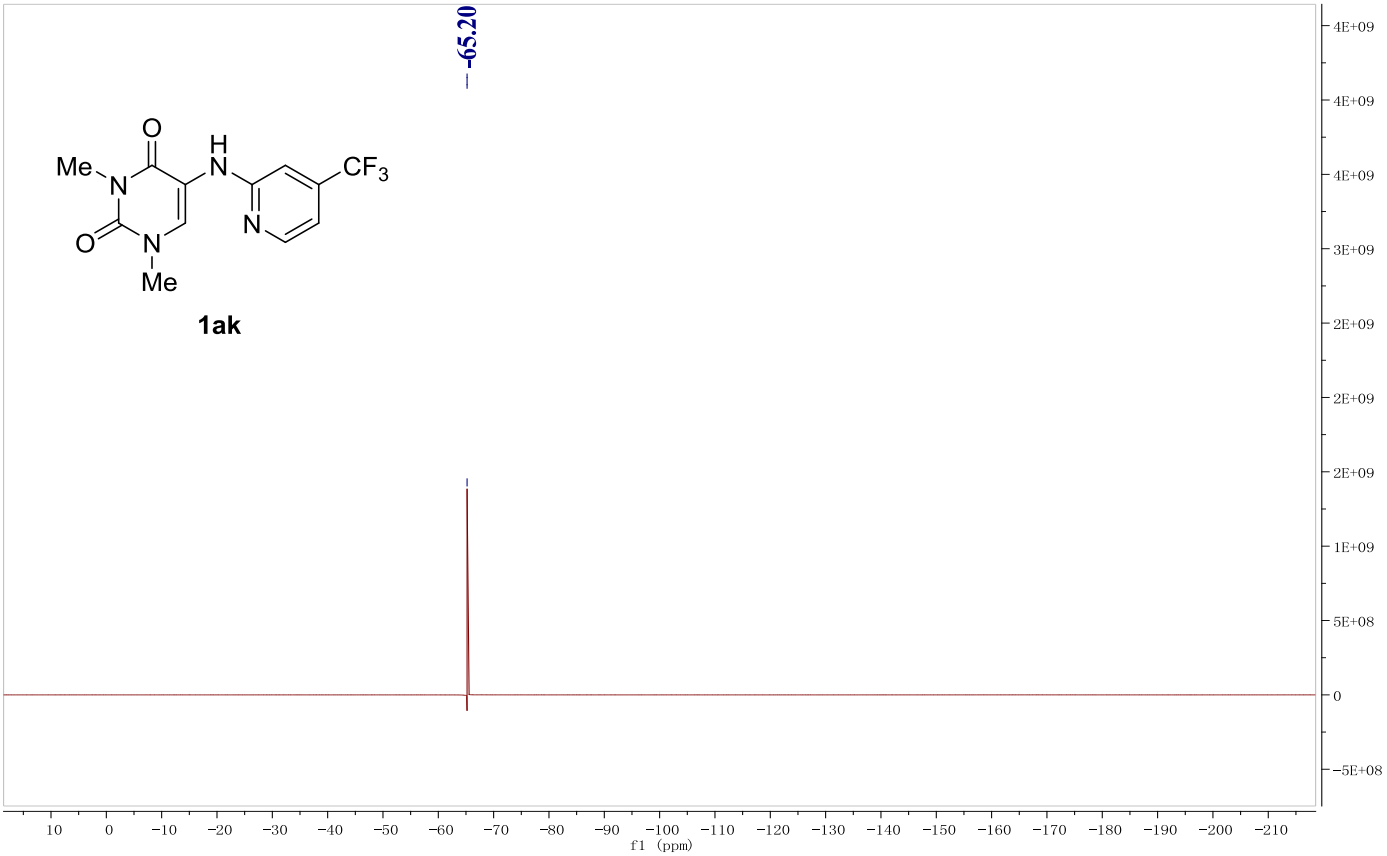
^{1}H NMR Spectrum of 1ak at 25 °C ($CDCl_3$, 600 MHz)



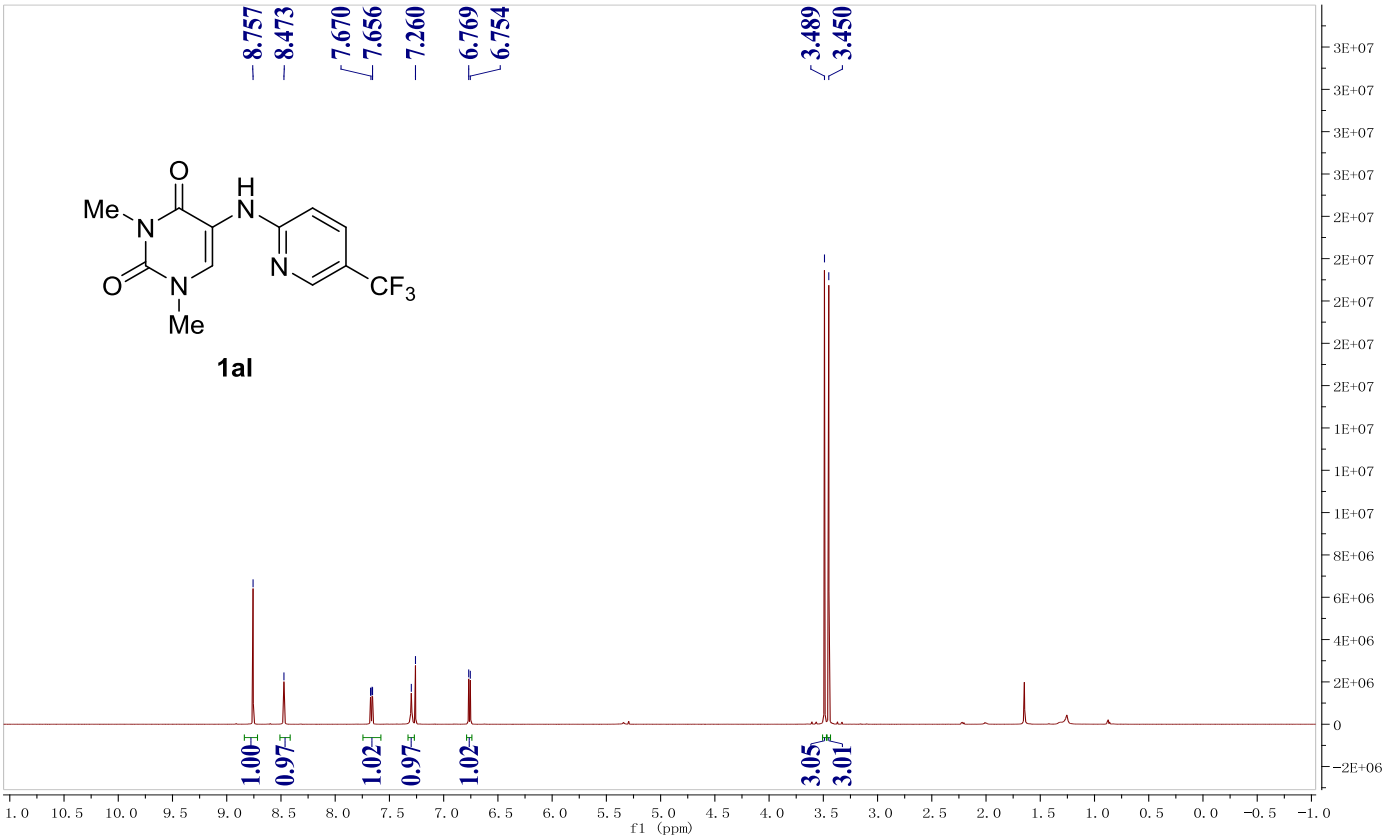
^{13}C NMR Spectrum of 1ak at 25 °C ($CDCl_3$, 150 MHz)



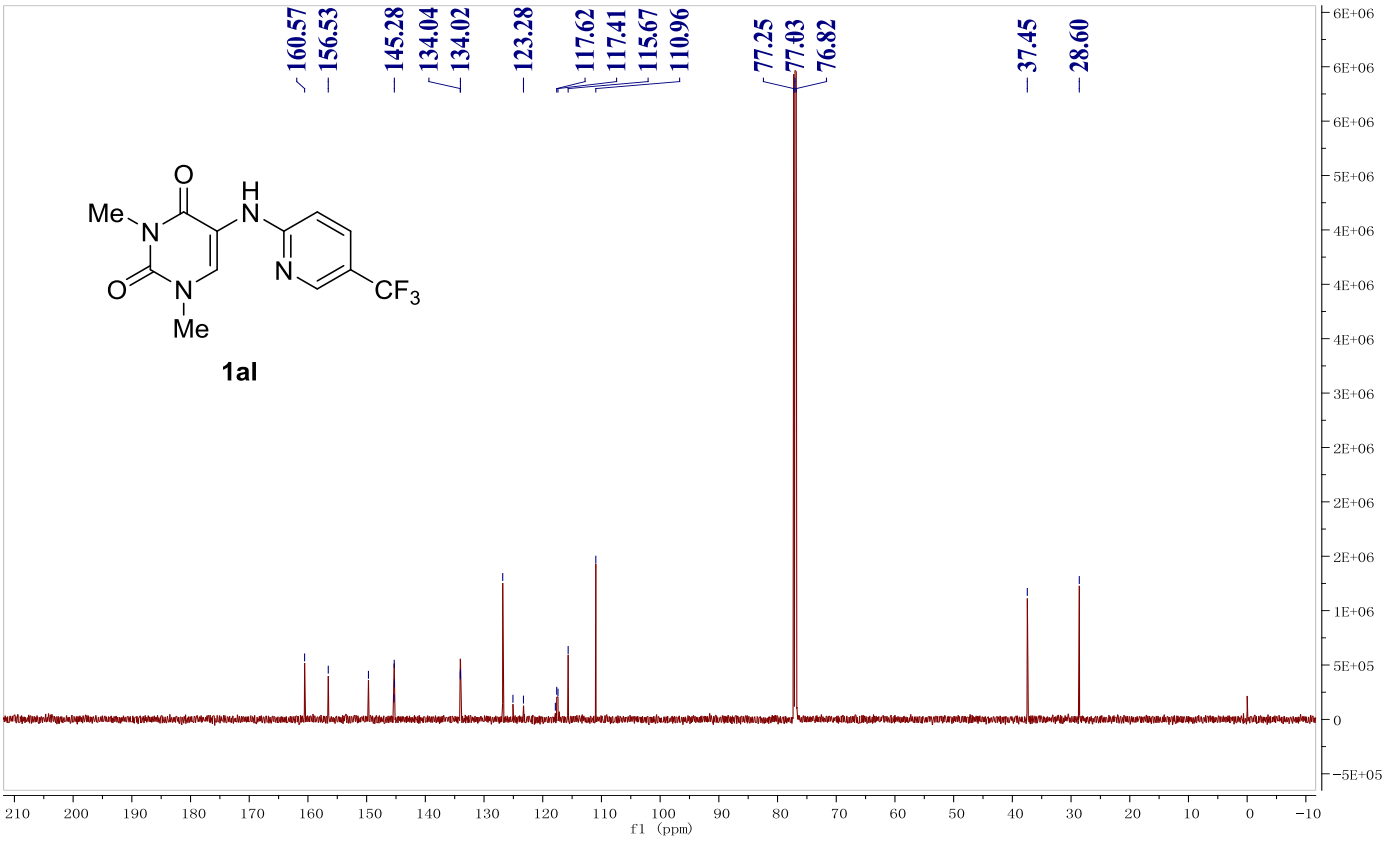
^{19}F NMR Spectrum of 1ak at 25 °C ($CDCl_3$, 565 MHz)



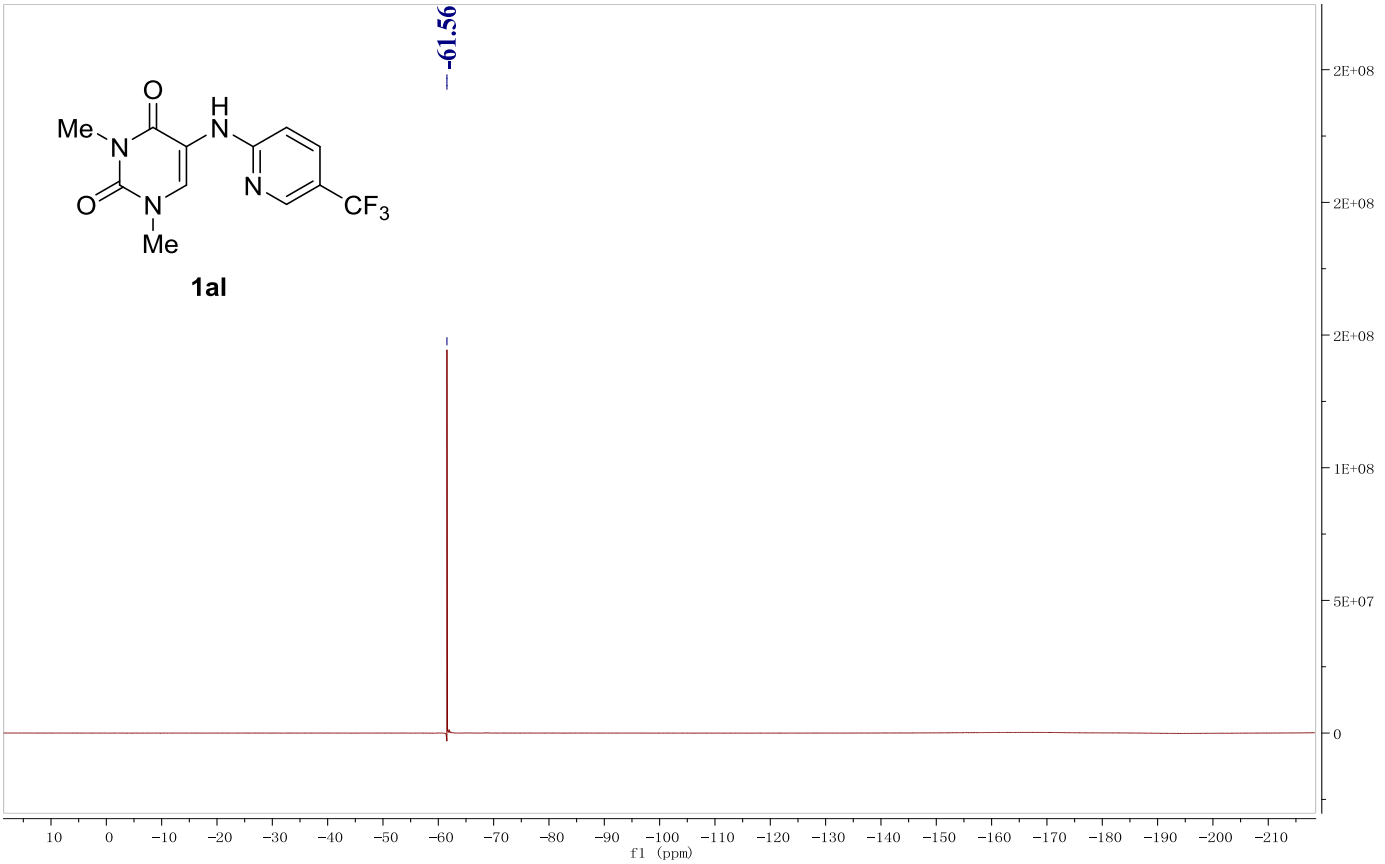
^{1}H NMR Spectrum of 1al at 25 °C ($CDCl_3$, 600 MHz)



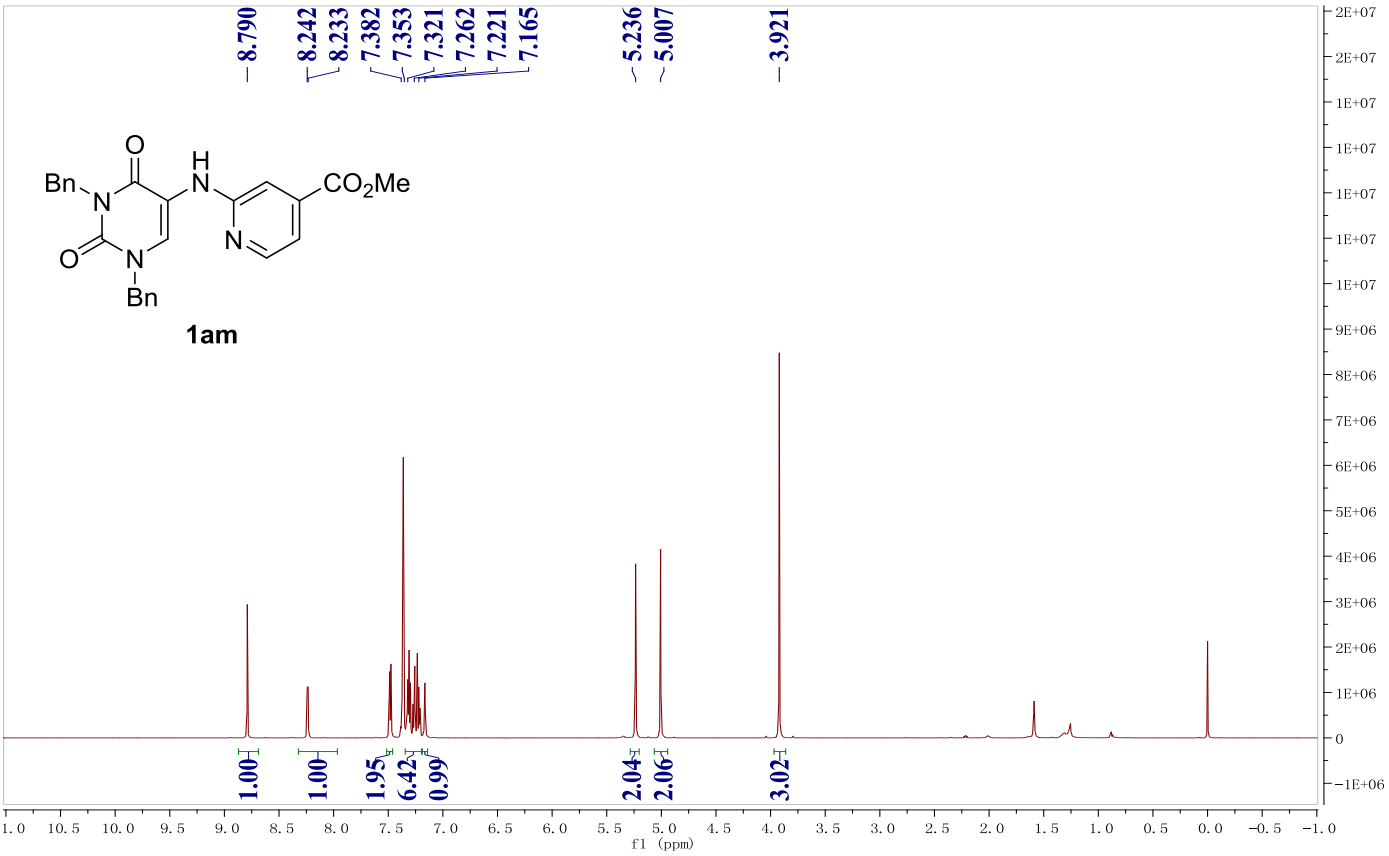
^{13}C NMR Spectrum of 1al at 25 °C ($CDCl_3$, 150 MHz)



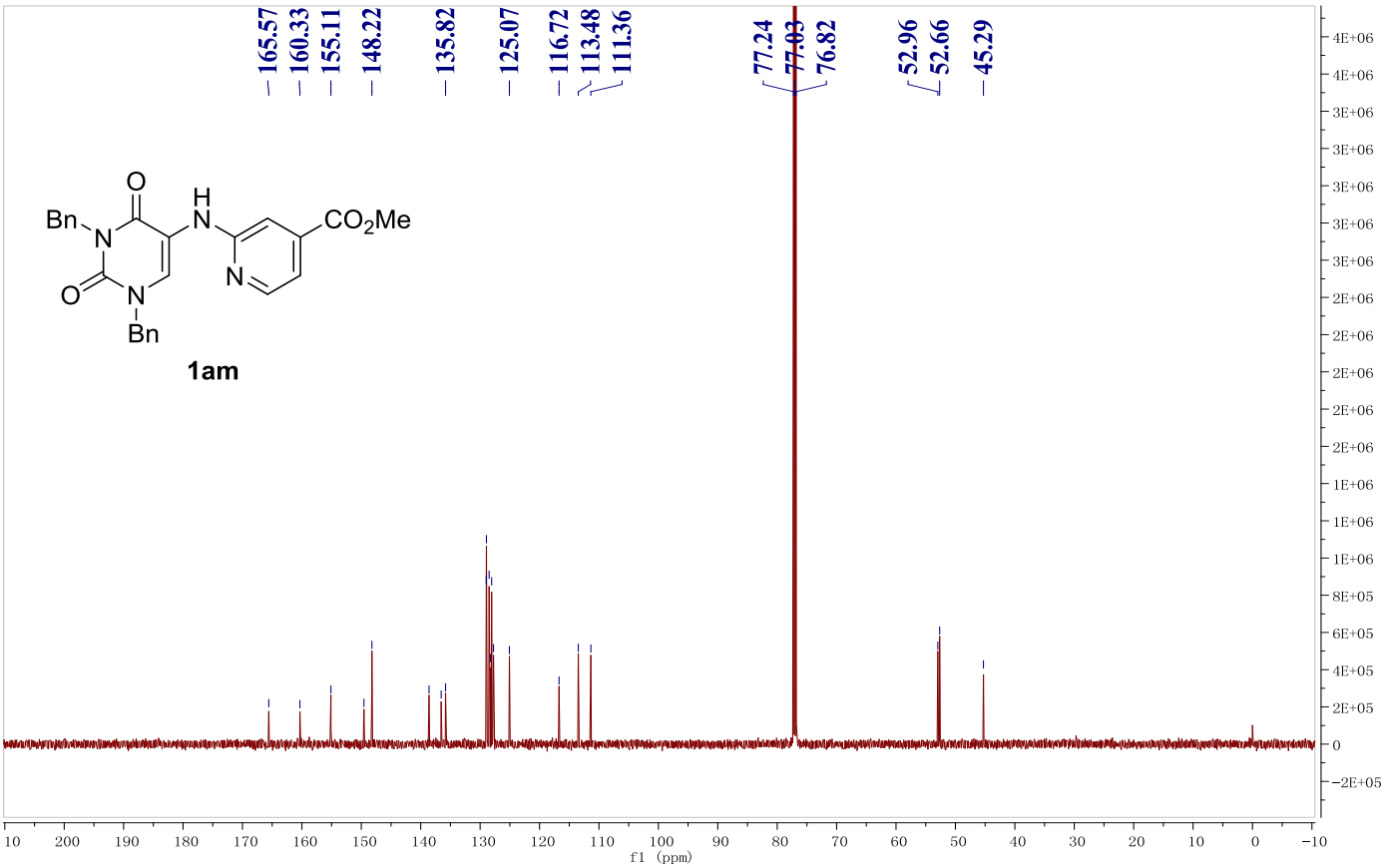
^{19}F NMR Spectrum of 1al at 25 °C ($CDCl_3$, 565 MHz)



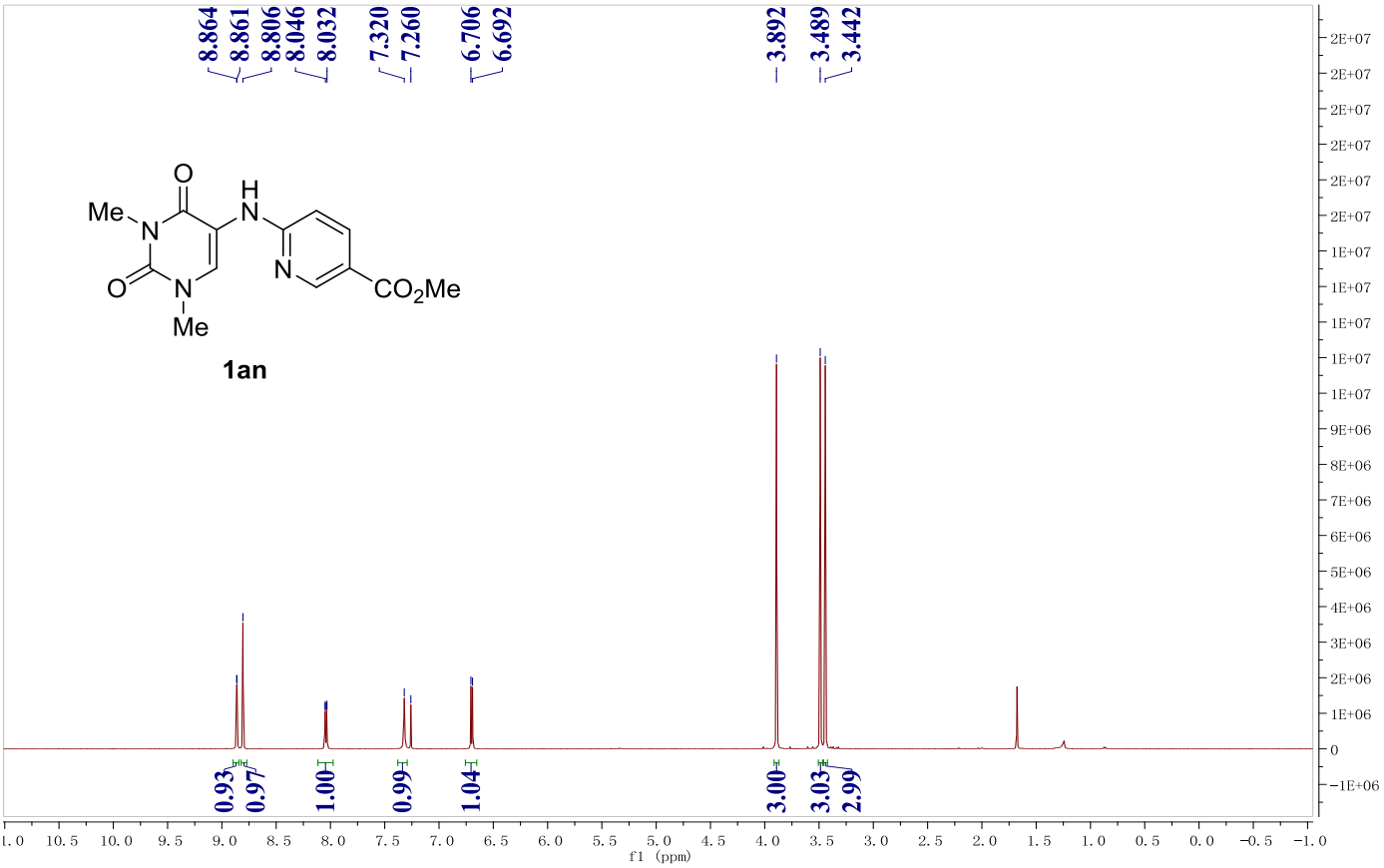
^{1}H NMR Spectrum of 1am at 25 °C ($CDCl_3$, 600 MHz)



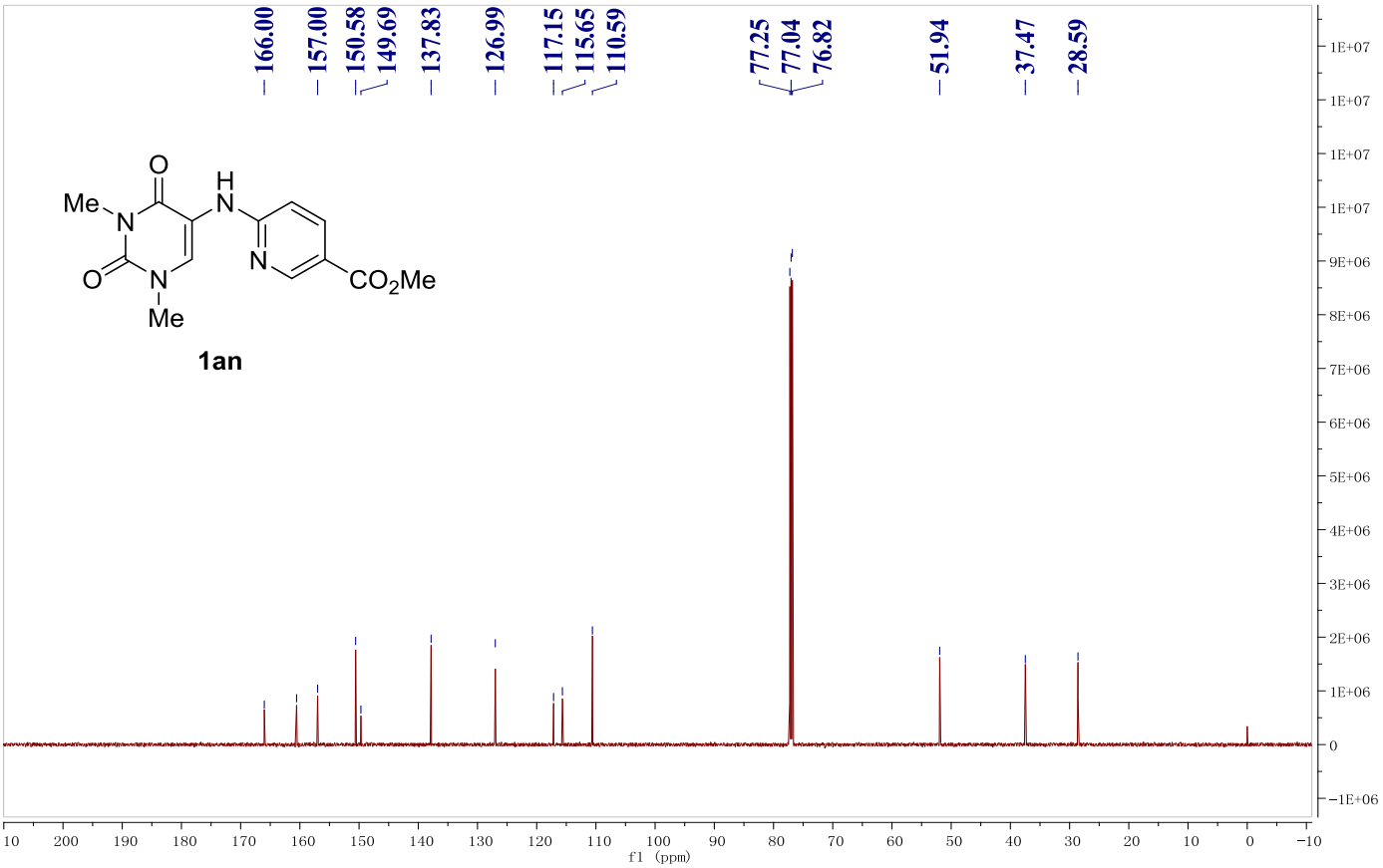
^{13}C NMR Spectrum of 1am at 25 °C ($CDCl_3$, 150 MHz)



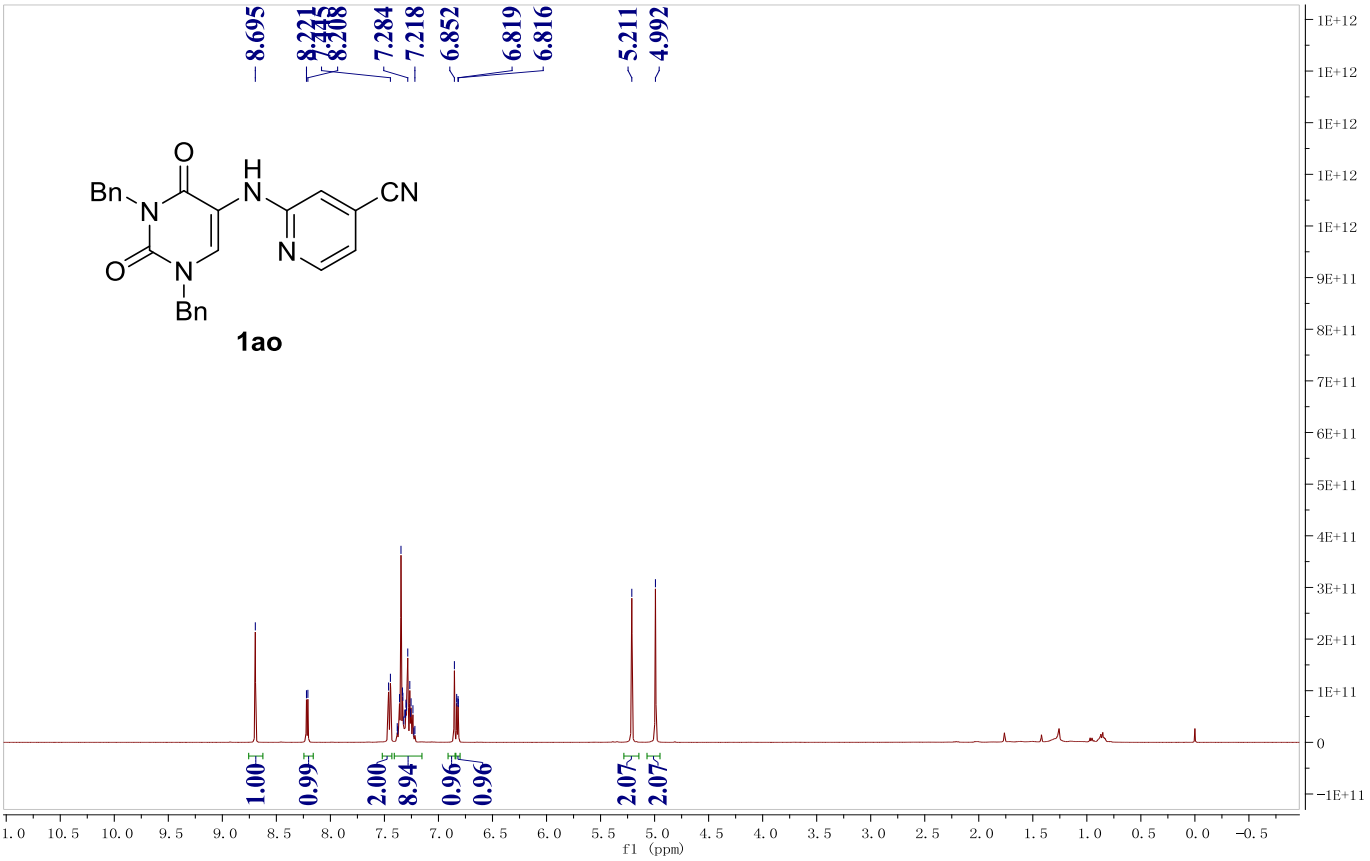
^{1}H NMR Spectrum of 1an at 25 °C ($CDCl_3$, 600 MHz)



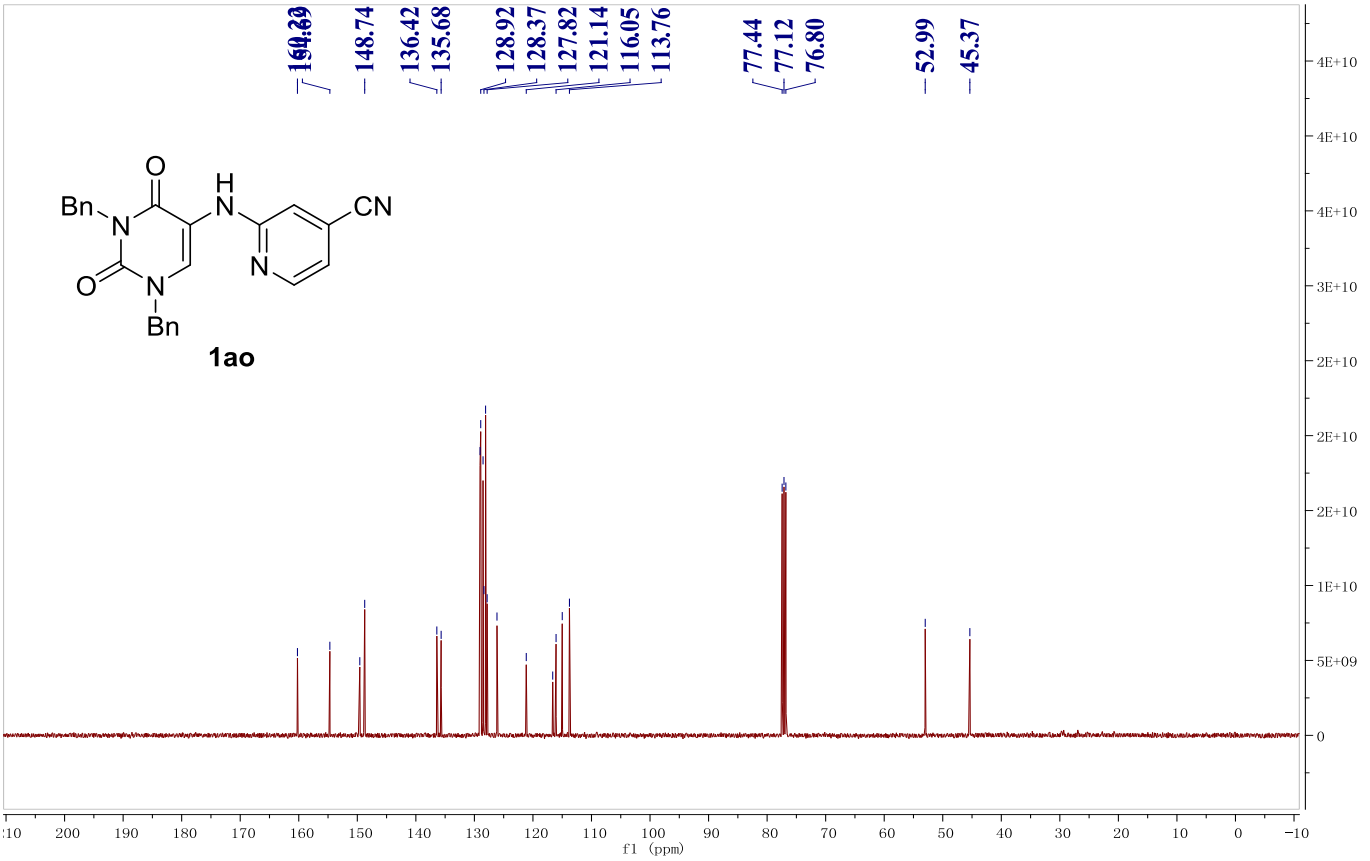
^{13}C NMR Spectrum of 1an at 25 °C ($CDCl_3$, 150 MHz)



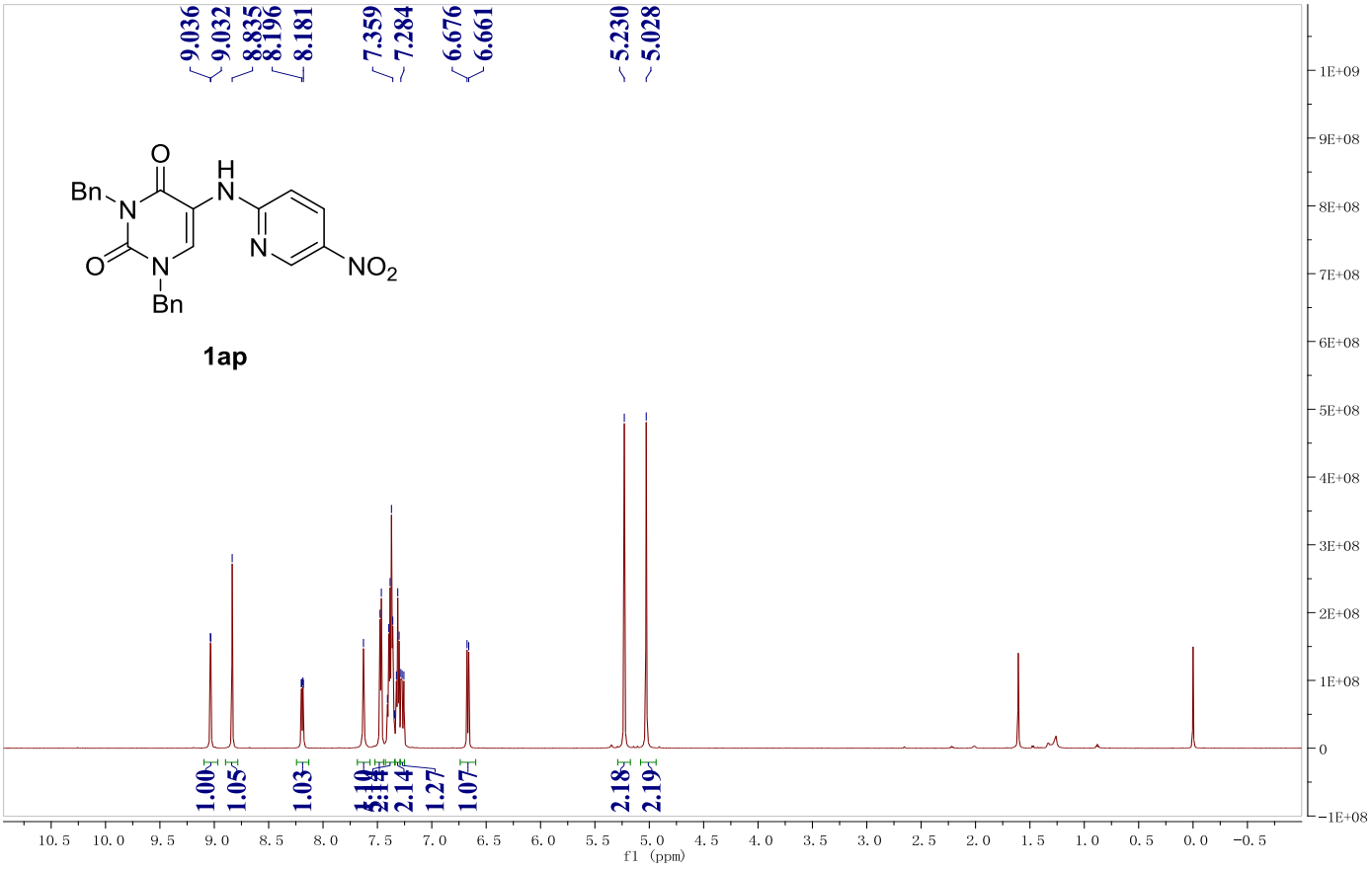
^{1}H NMR Spectrum of 1ao at 25 °C ($CDCl_3$, 400 MHz)



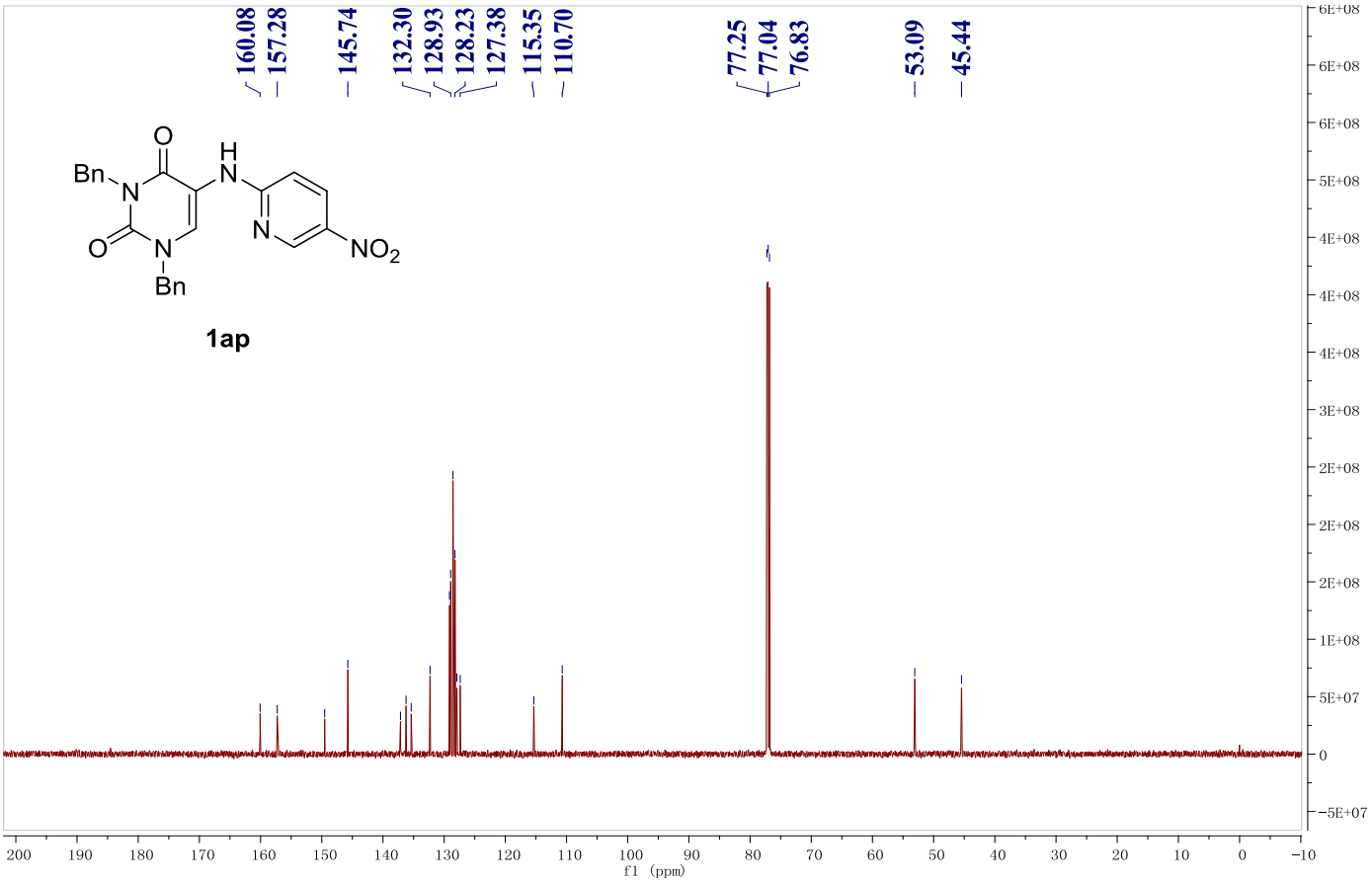
^{13}C NMR Spectrum of 1ao at 25 °C ($CDCl_3$, 100 MHz)



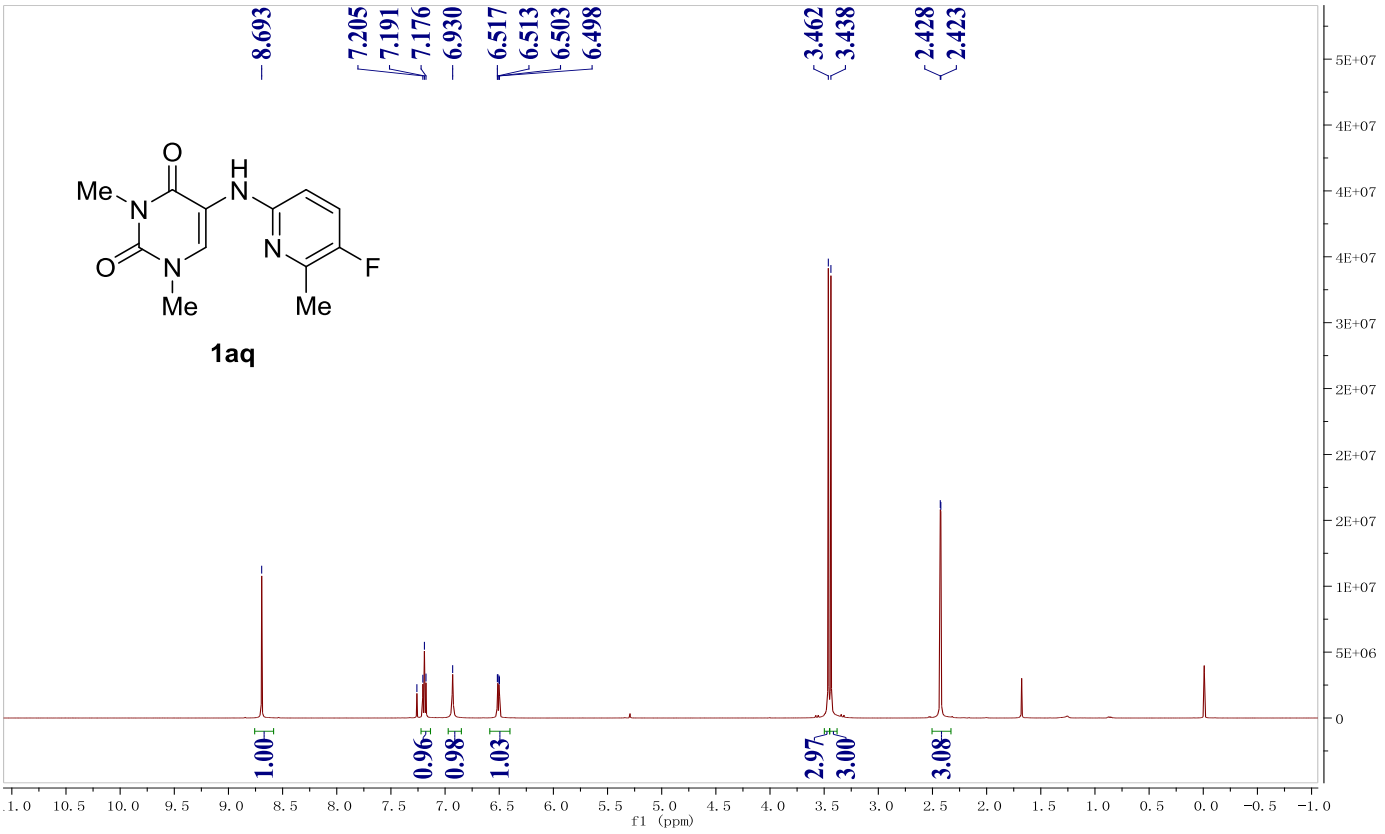
^{1}H NMR Spectrum of 1ap at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 1ap at 25 °C ($CDCl_3$, 150 MHz)

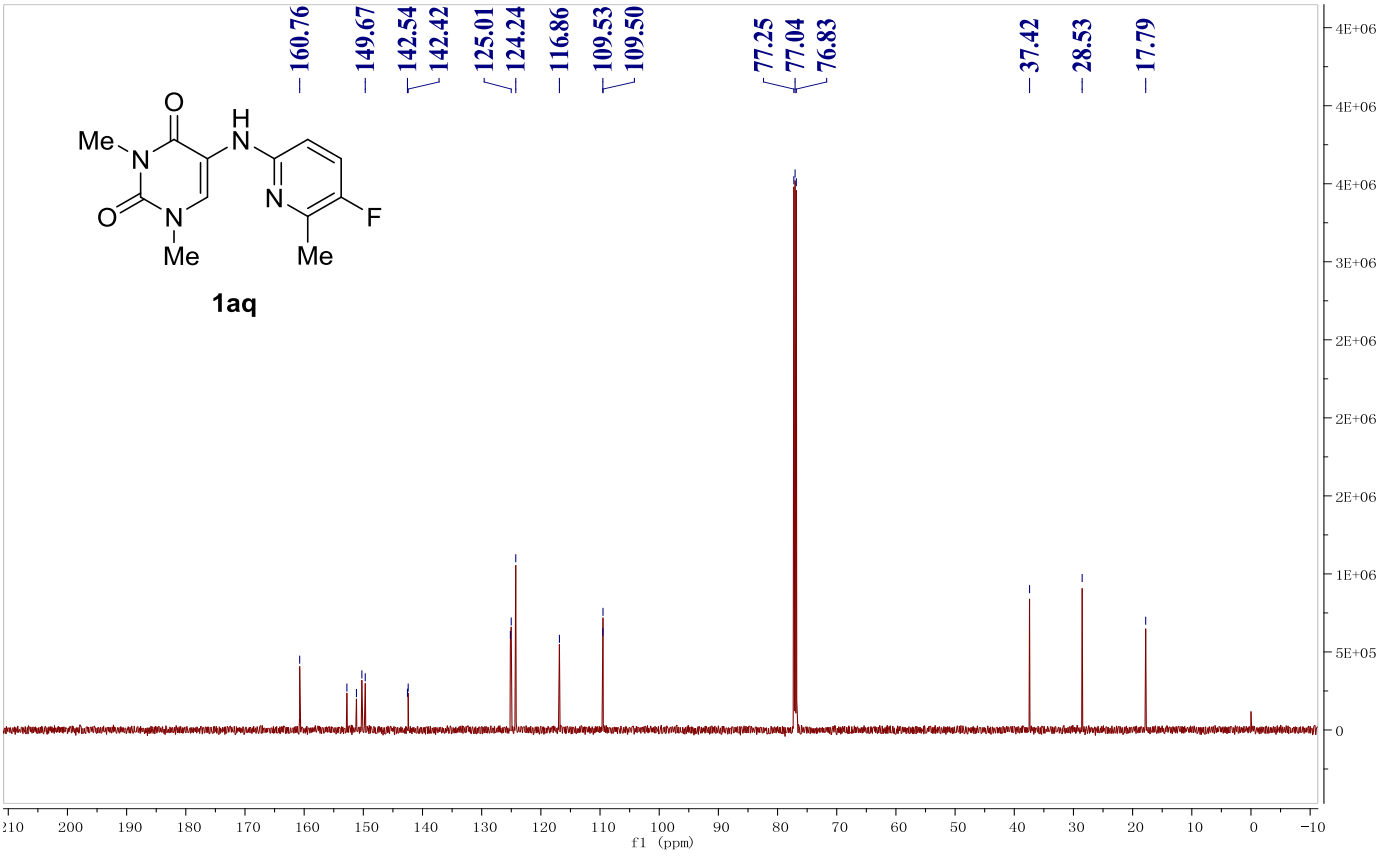


^{1}H NMR Spectrum of 1aq at 25 °C ($CDCl_3$, 600 MHz)



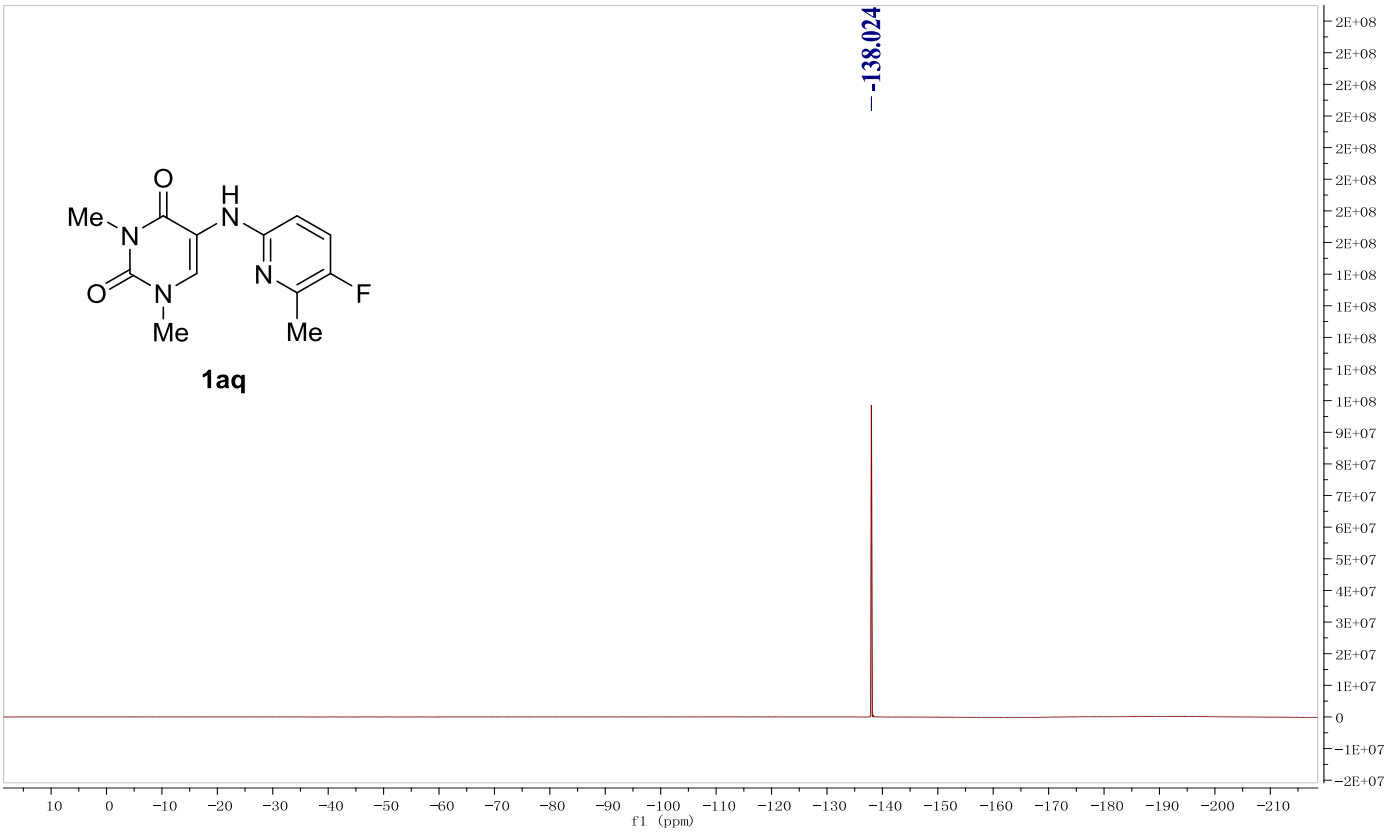
1aq

^{13}C NMR Spectrum of 1aq at 25 °C ($CDCl_3$, 150 MHz)

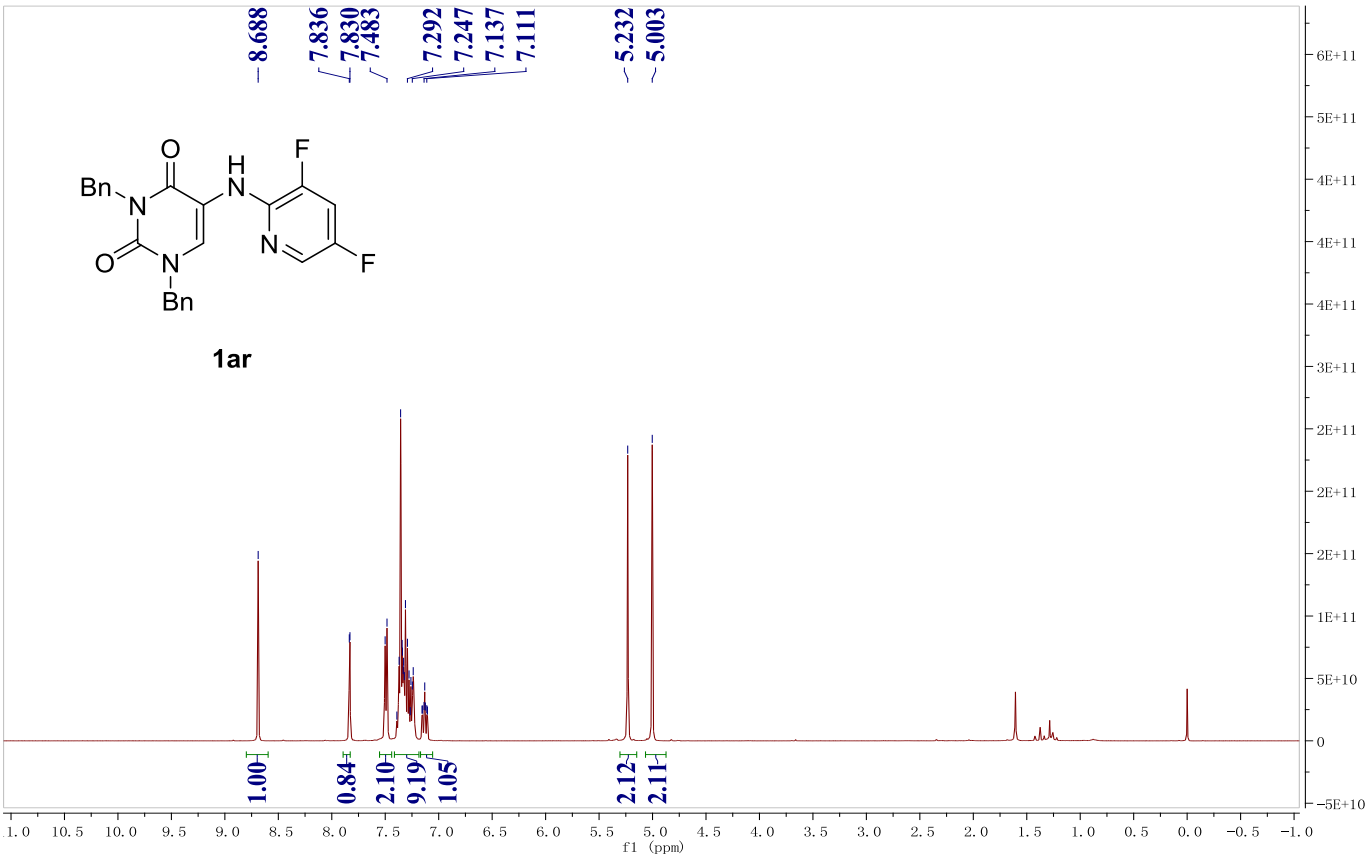


1aq

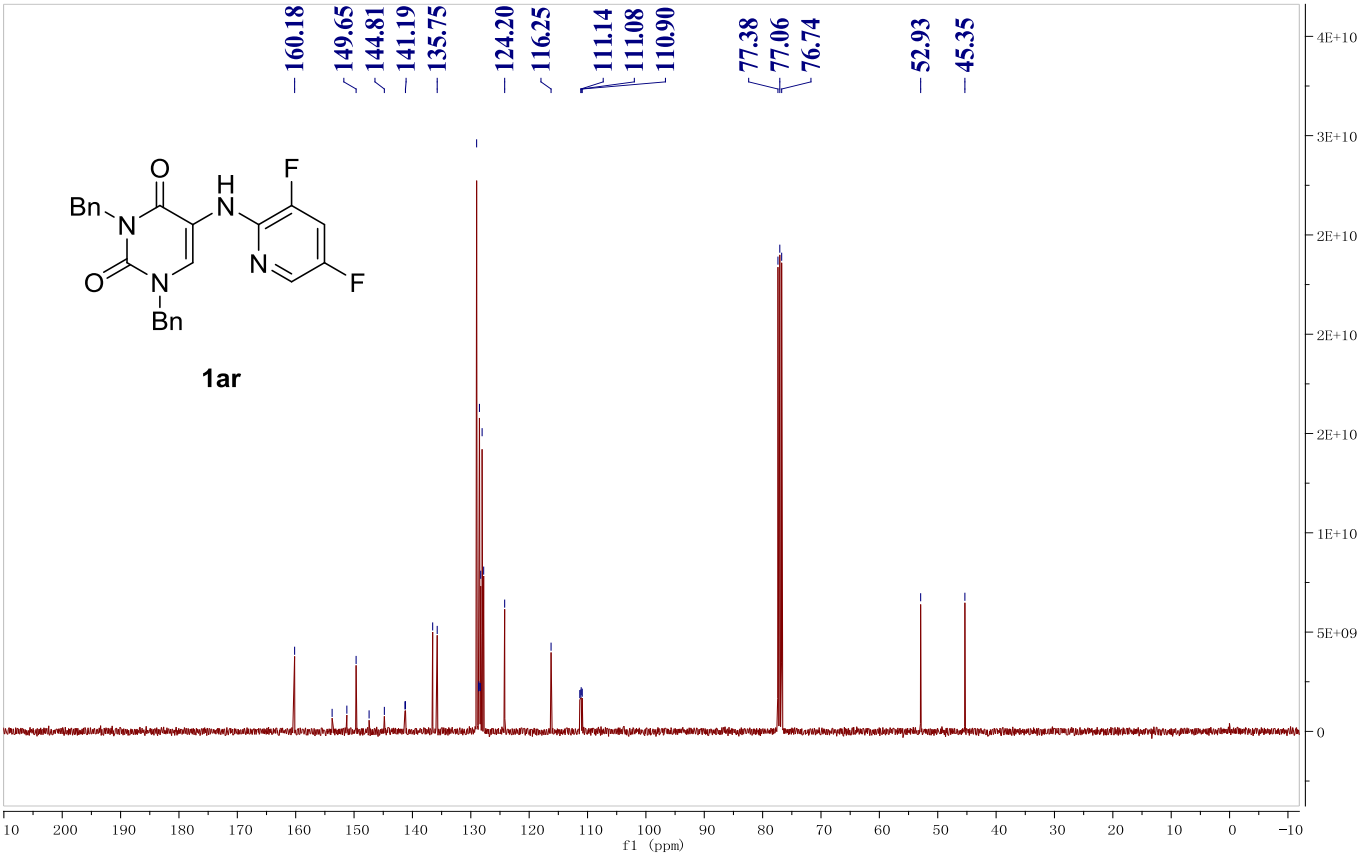
^{19}F NMR Spectrum of 1aq at 25 °C ($CDCl_3$, 565 MHz)



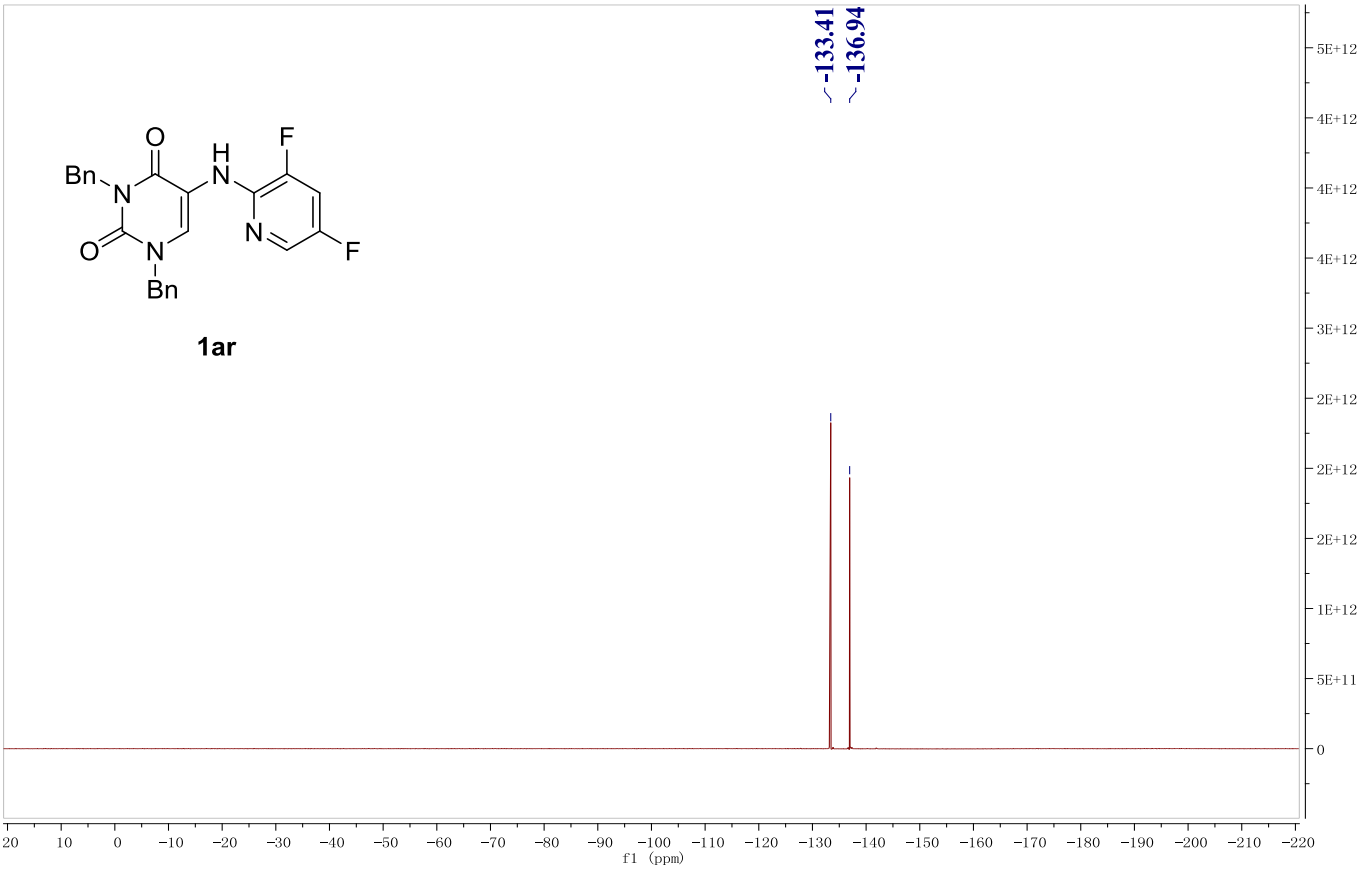
^{1}H NMR Spectrum of 1ar at 25 °C ($CDCl_3$, 400 MHz)



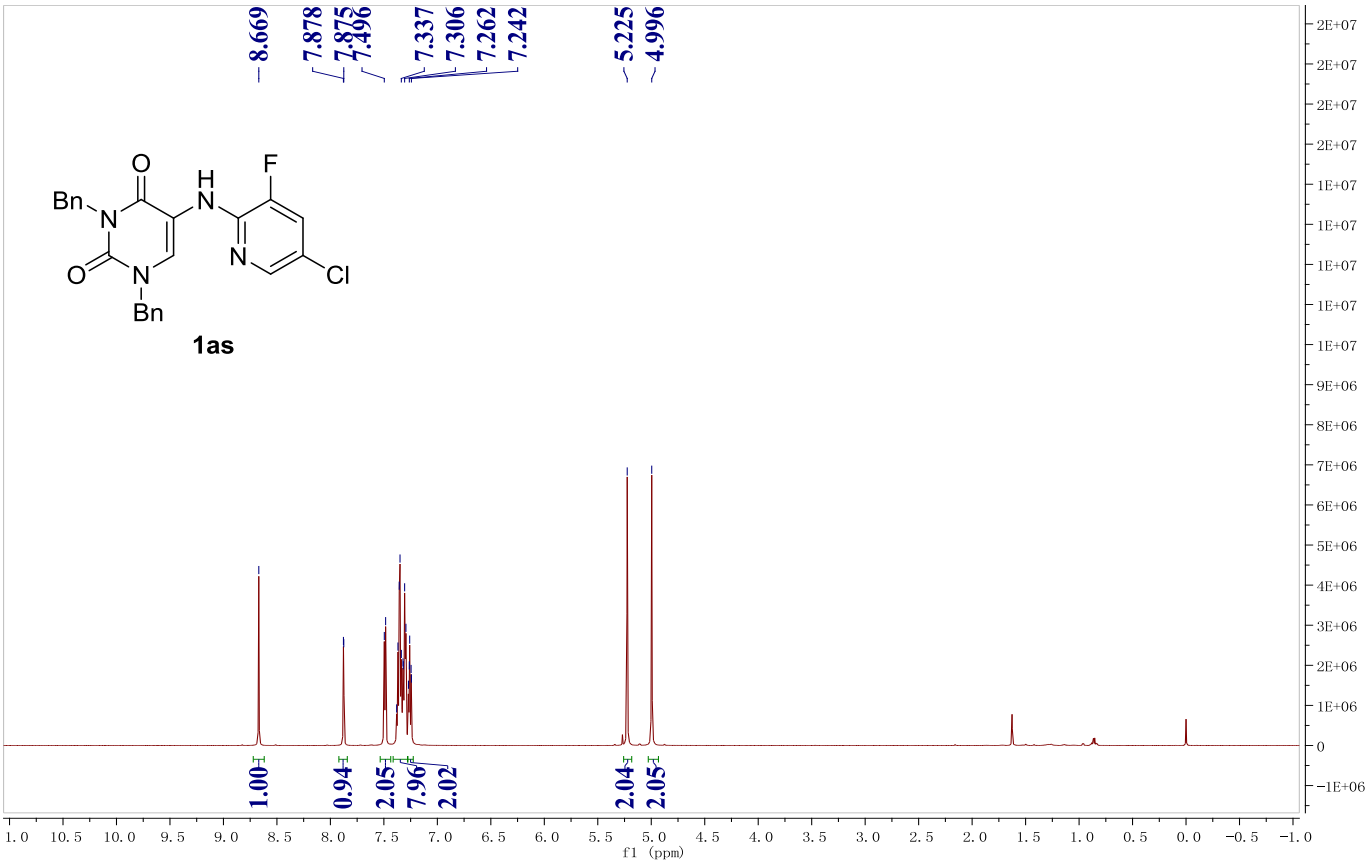
^{13}C NMR Spectrum of 1ar at 25 °C ($CDCl_3$, 100 MHz)



^{19}F NMR Spectrum of 1ar at 25 °C ($CDCl_3$, 376 MHz)

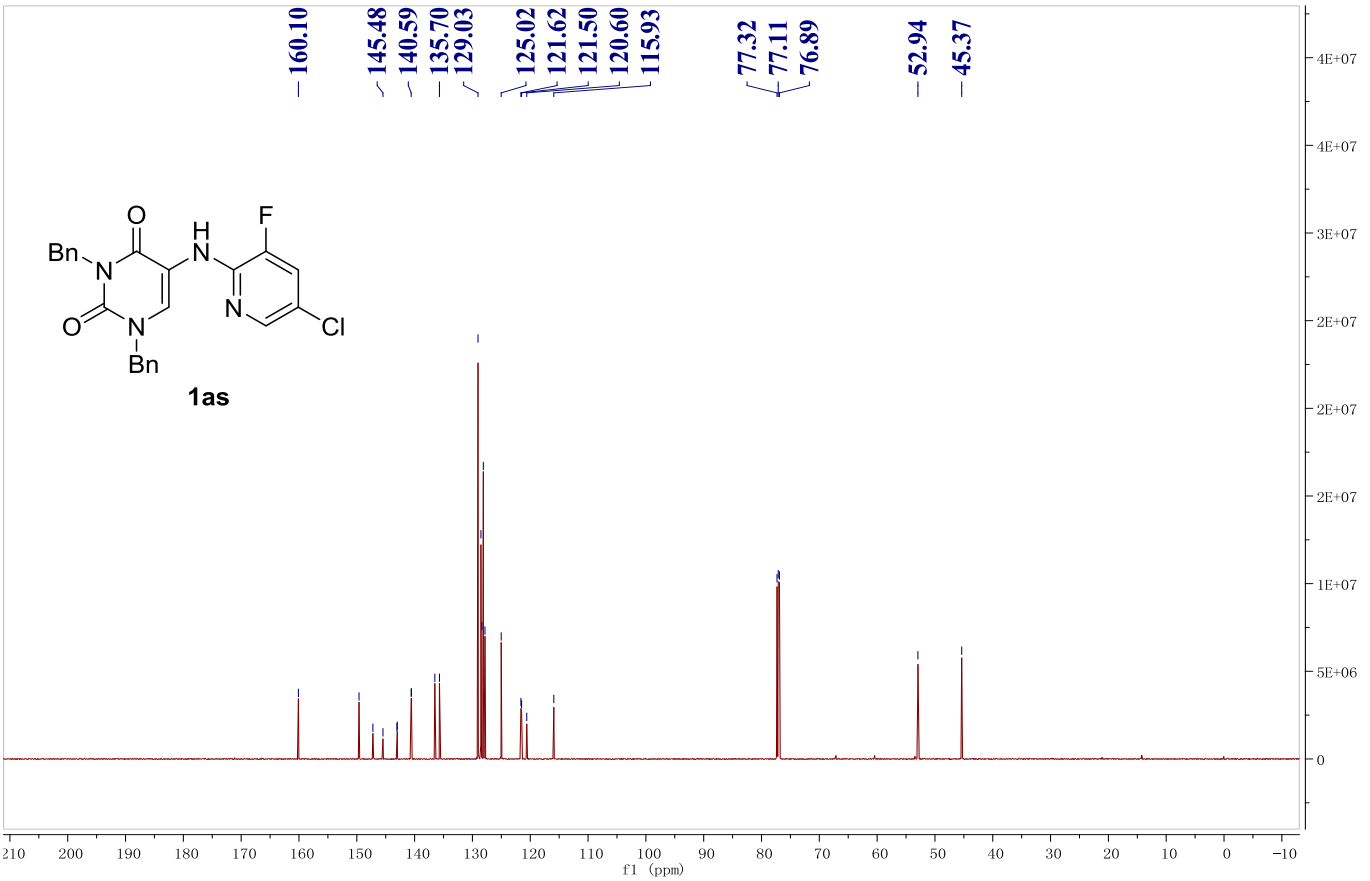


^{1}H NMR Spectrum of 1as at 25 °C ($CDCl_3$, 600 MHz)



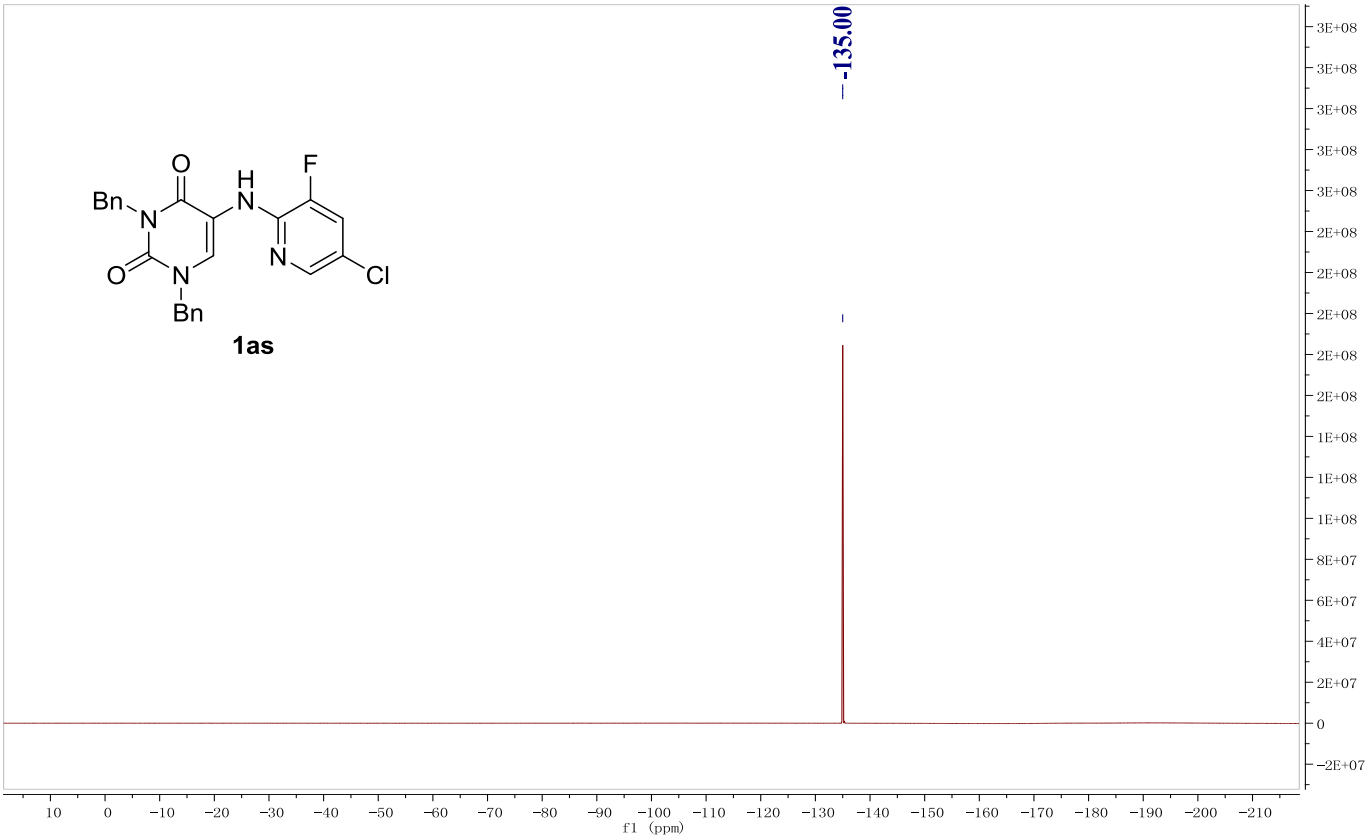
1as

^{13}C NMR Spectrum of 1as at 25 °C ($CDCl_3$, 150 MHz)

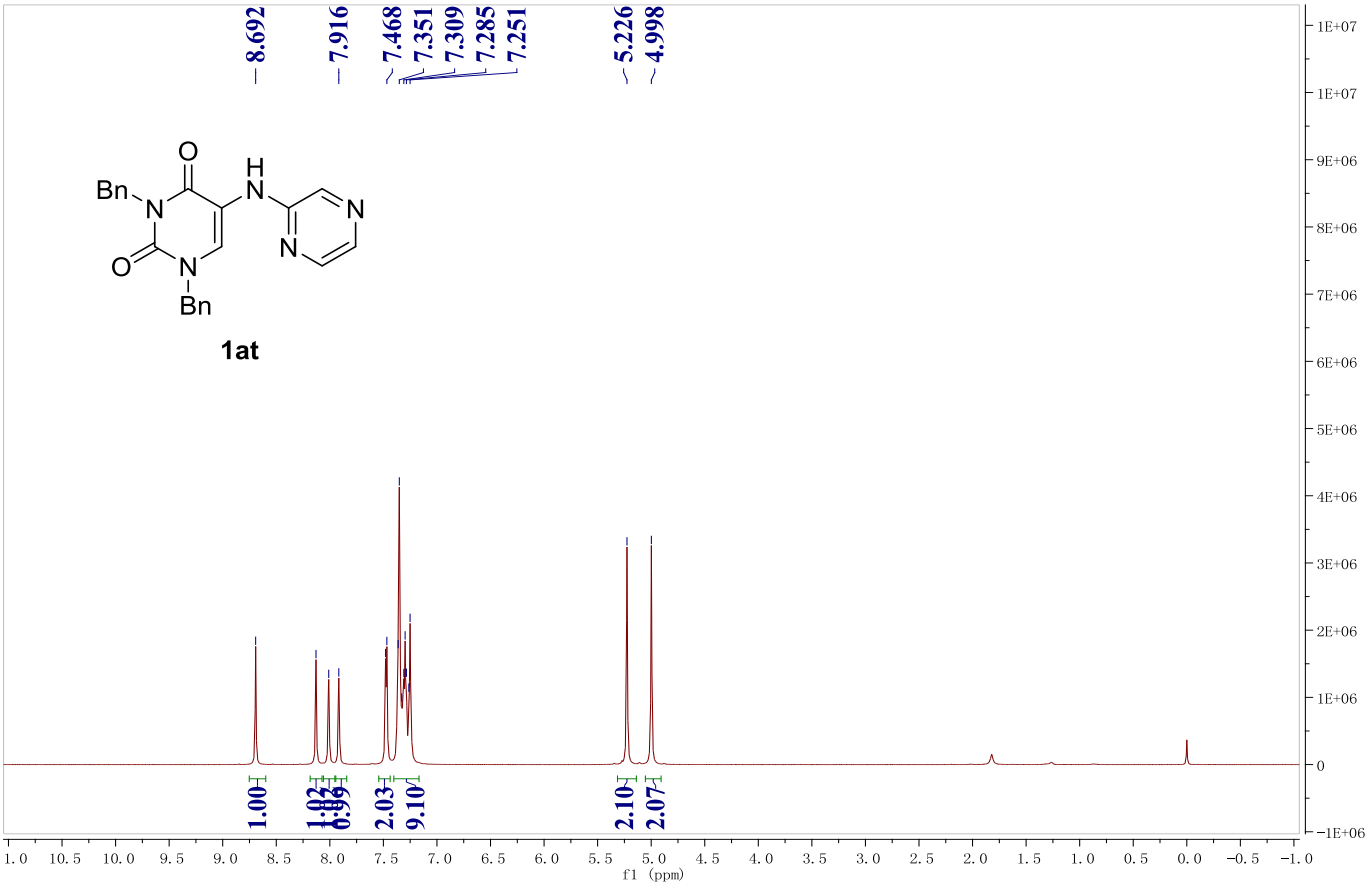


1as

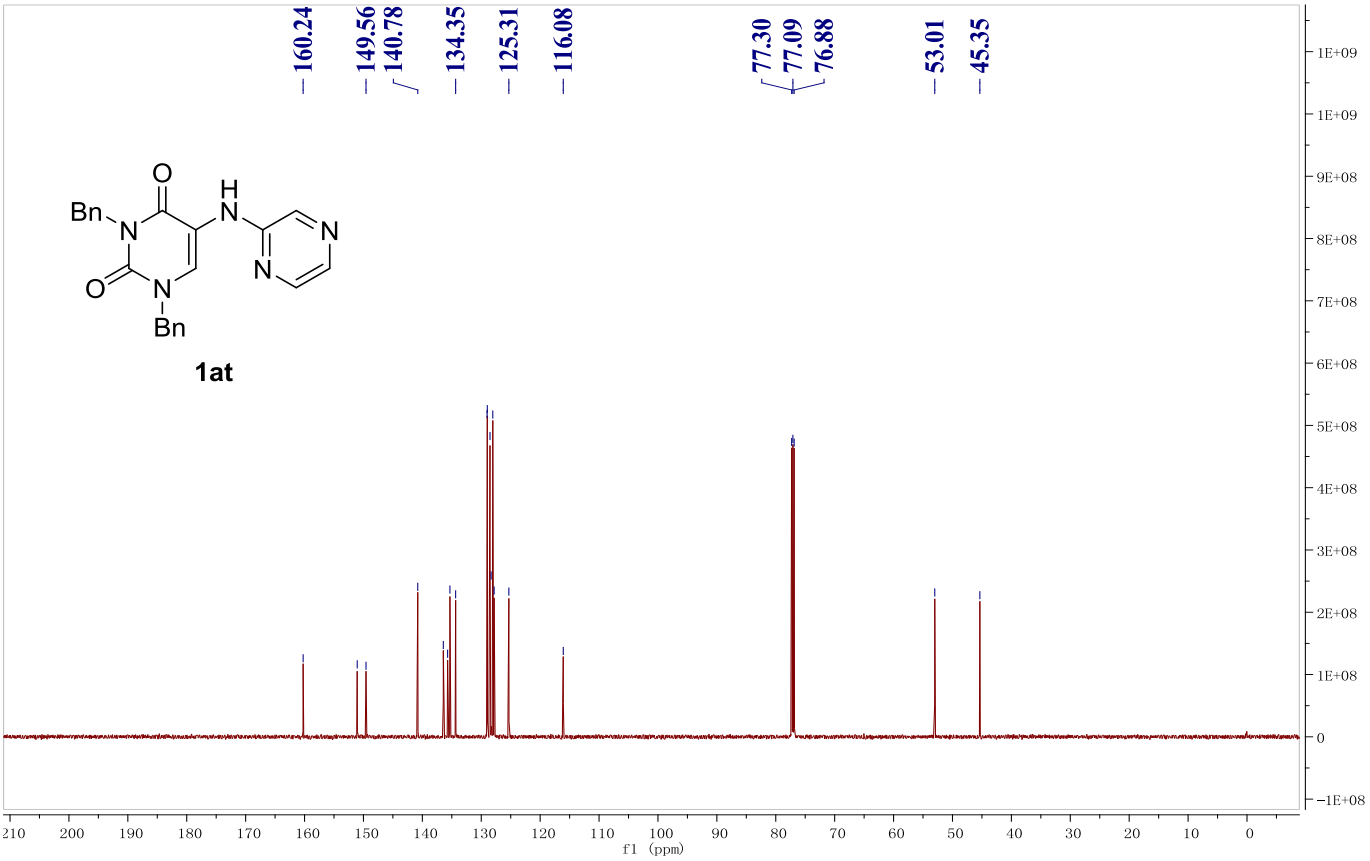
^{19}F NMR Spectrum of 1as at 25 °C ($CDCl_3$, 565 MHz)



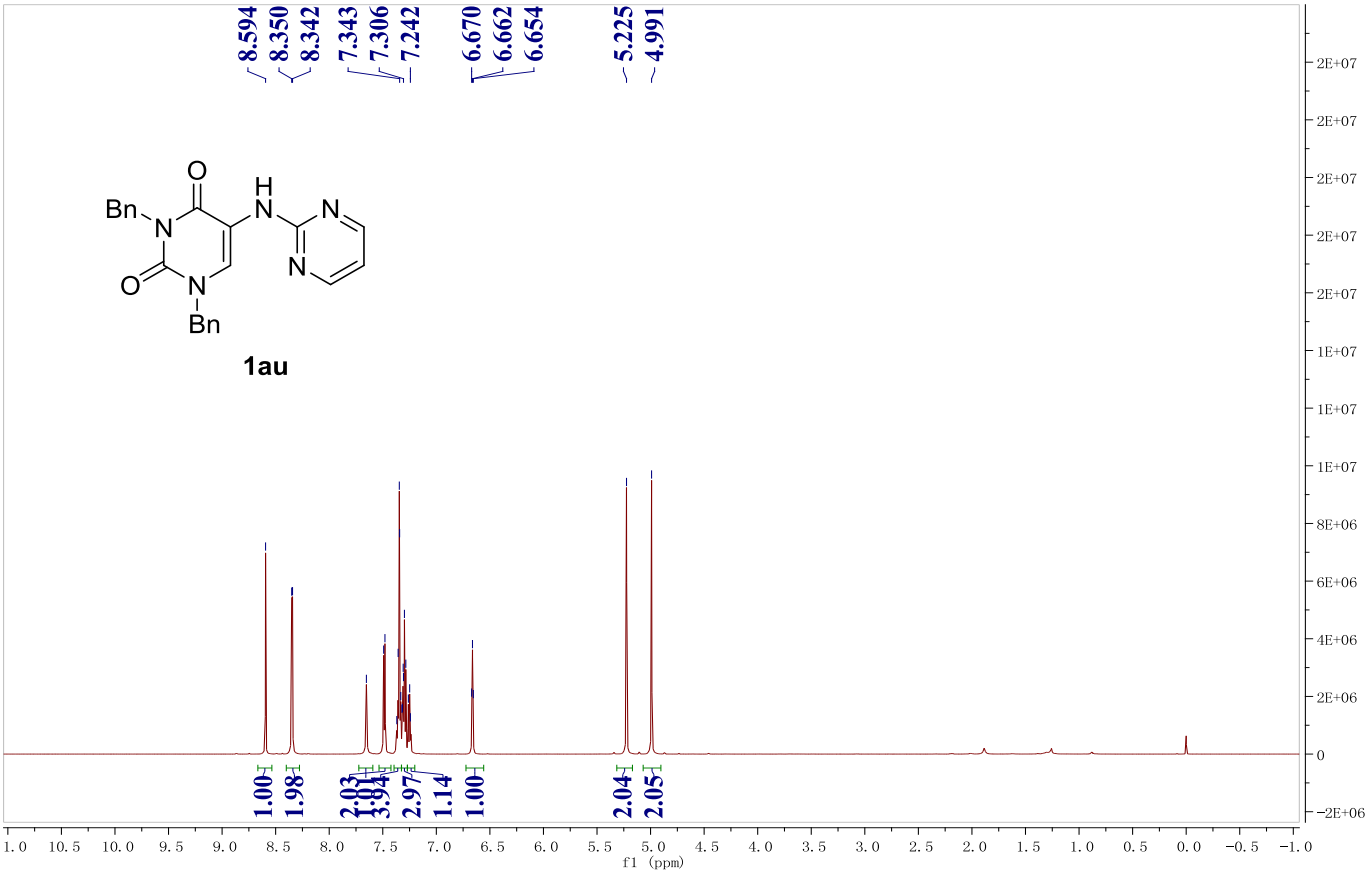
^{1}H NMR Spectrum of 1at at 25 °C ($CDCl_3$, 600 MHz)



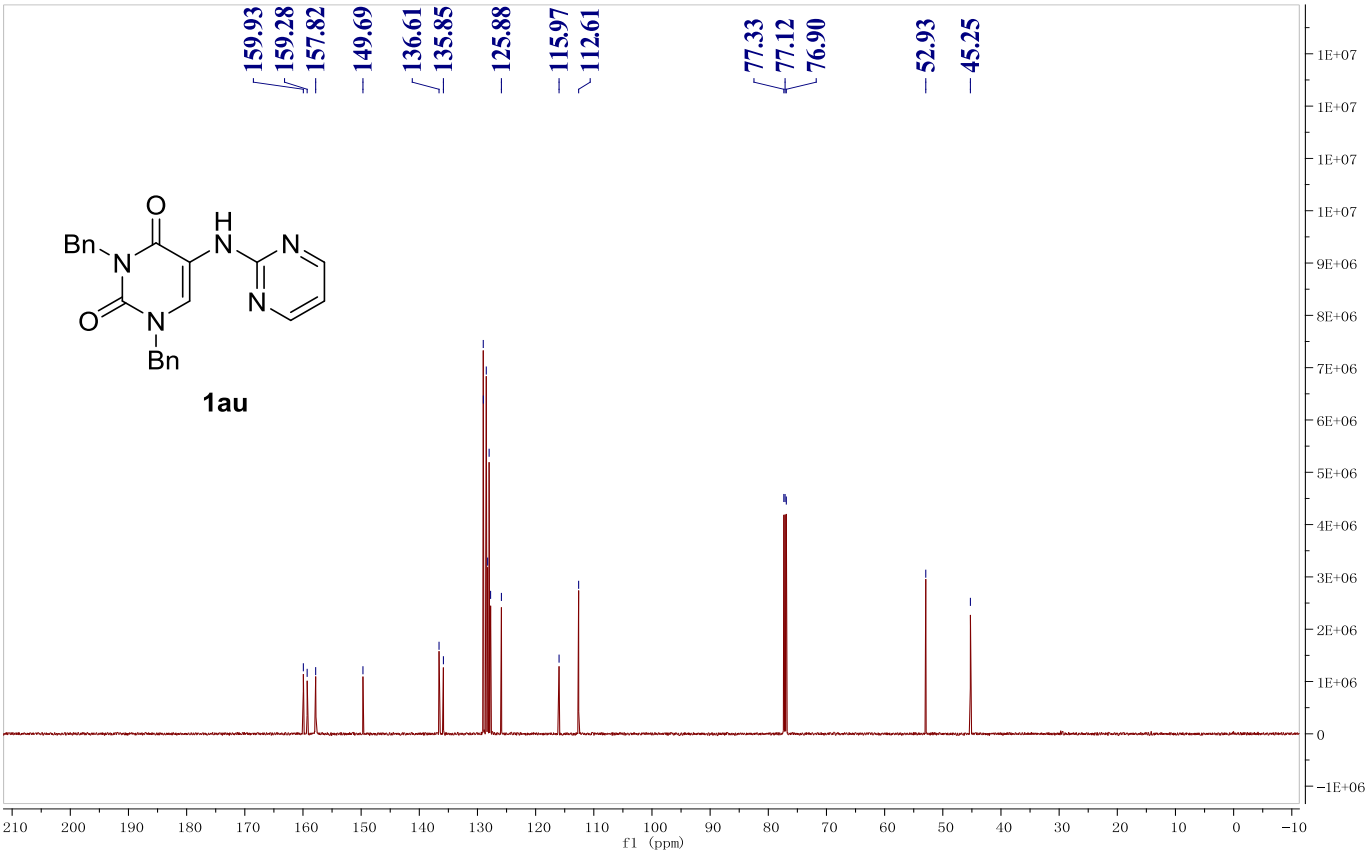
^{13}C NMR Spectrum of 1at at 25 °C ($CDCl_3$, 150 MHz)



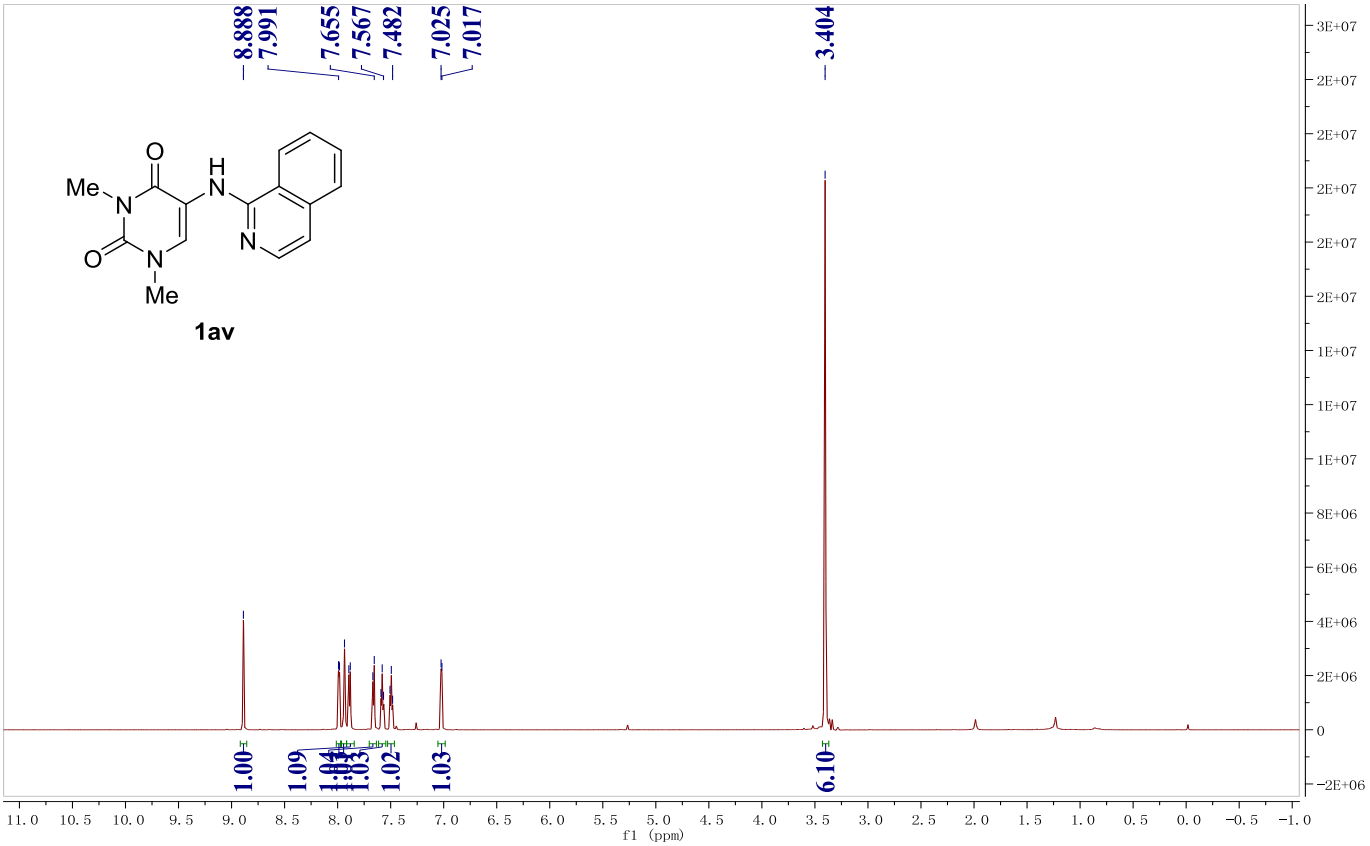
^{1}H NMR Spectrum of 1au at 25 °C ($CDCl_3$, 600 MHz)



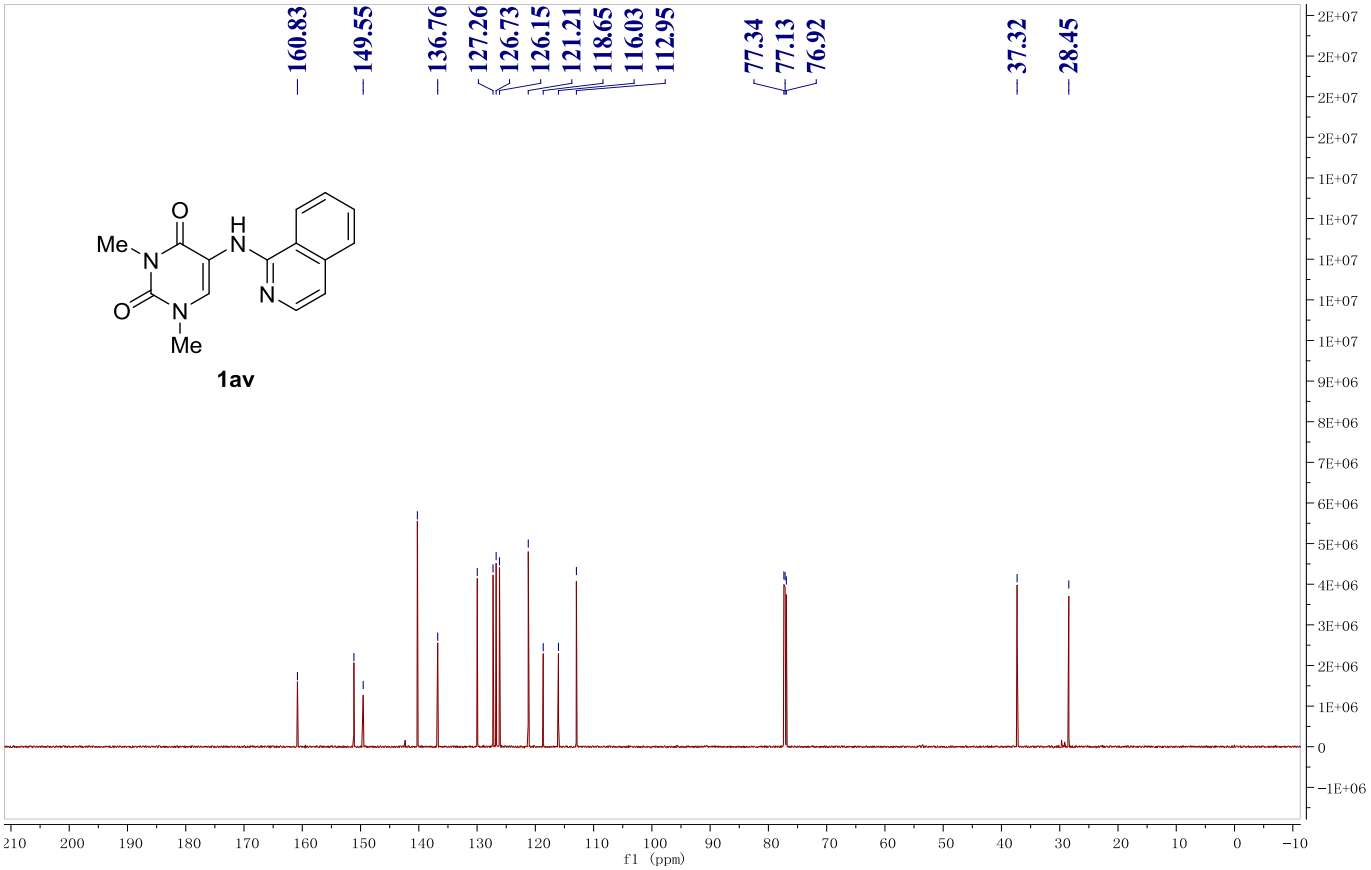
^{13}C NMR Spectrum of 1au at 25 °C ($CDCl_3$, 150 MHz)



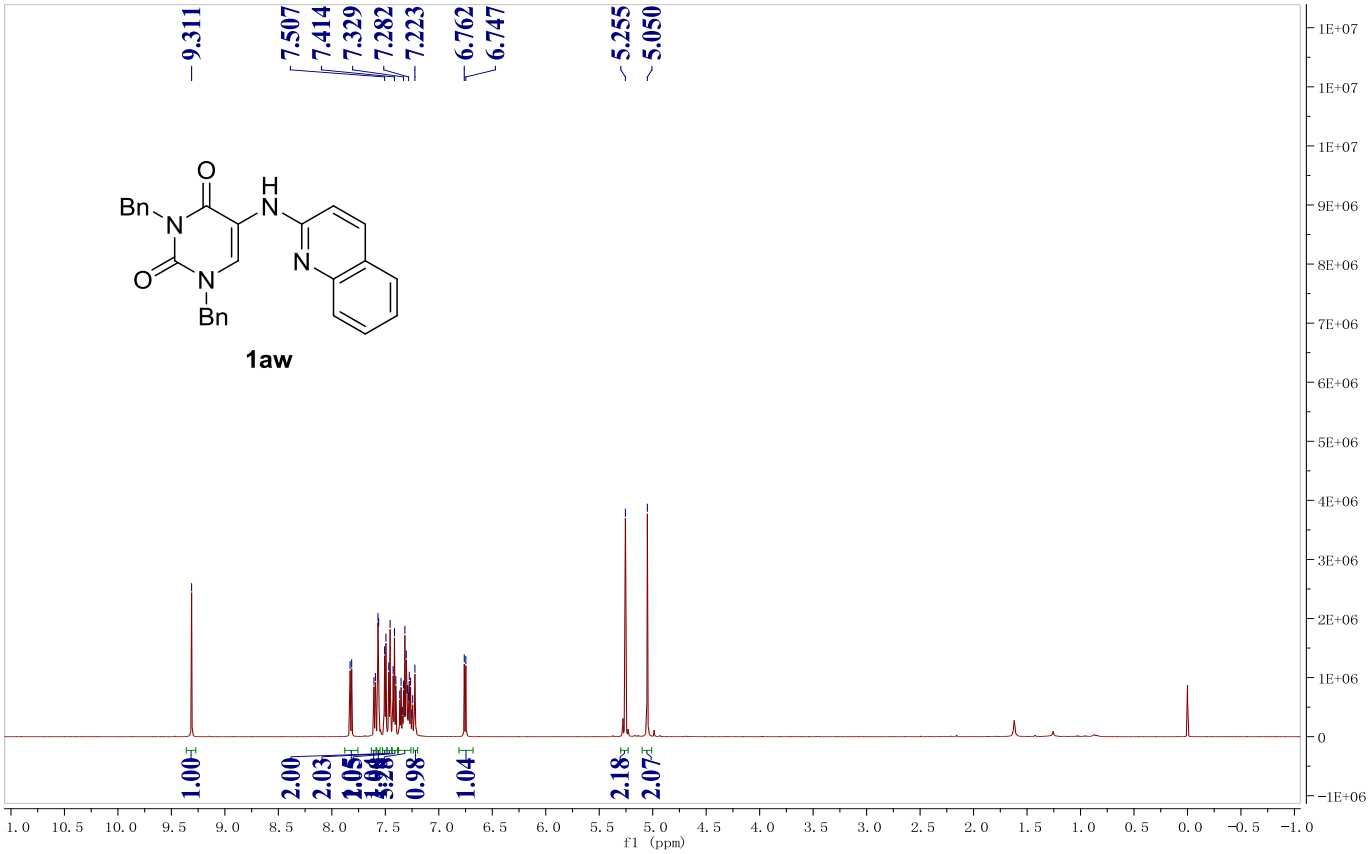
^{1}H NMR Spectrum of 1av at 25 °C ($CDCl_3$, 600 MHz)



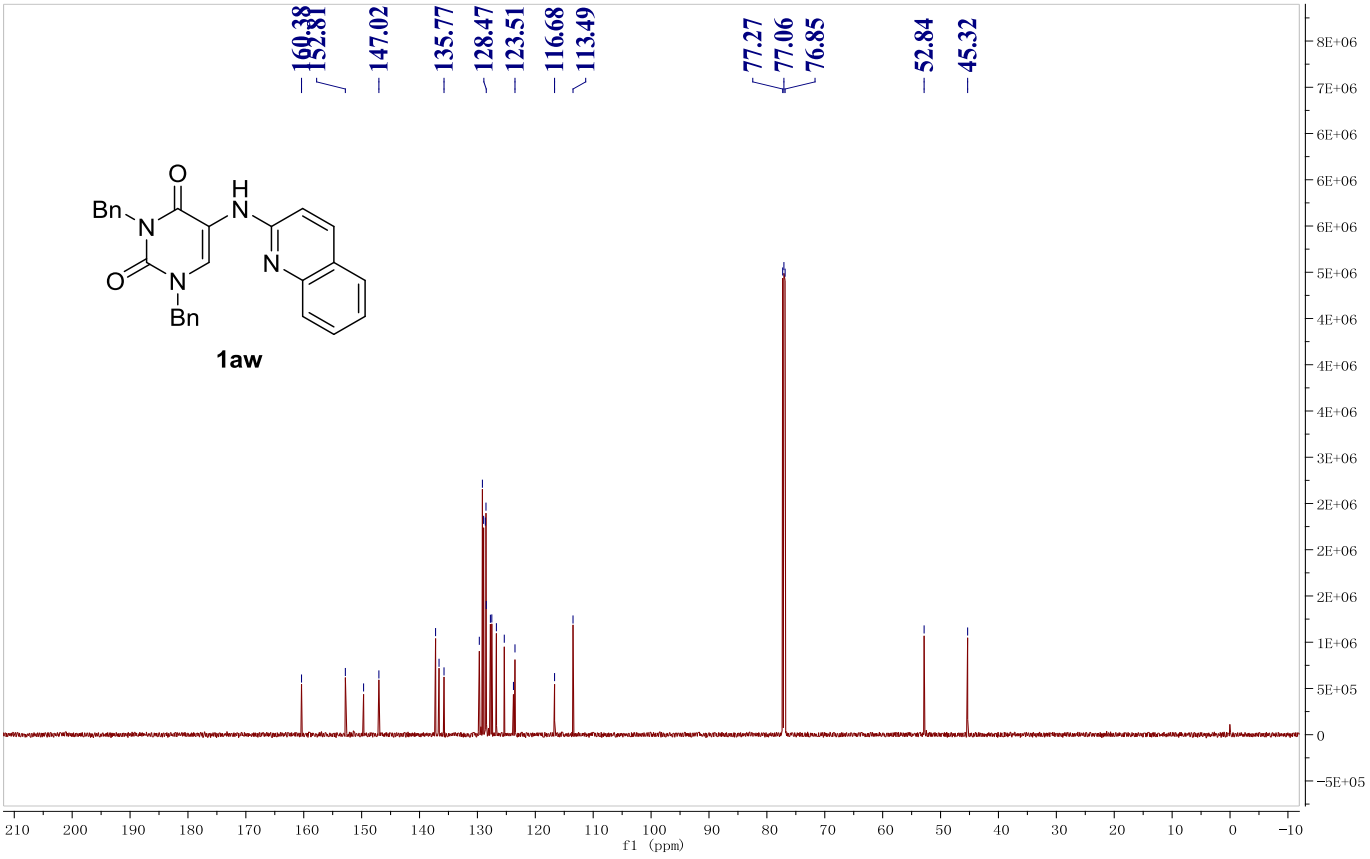
^{13}C NMR Spectrum of 1av at 25 °C ($CDCl_3$, 150 MHz)



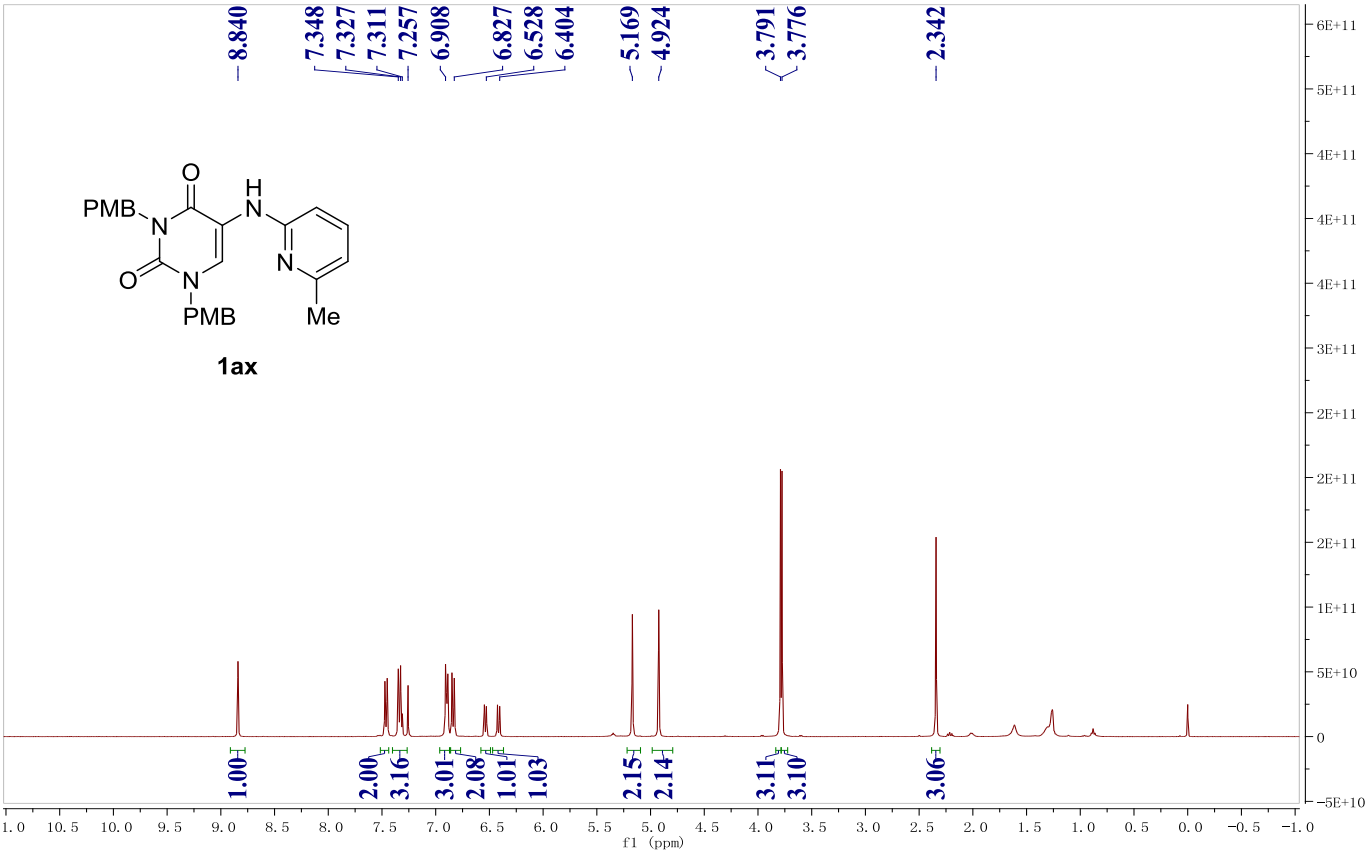
^{1}H NMR Spectrum of 1aw at 25 °C ($CDCl_3$, 600 MHz)



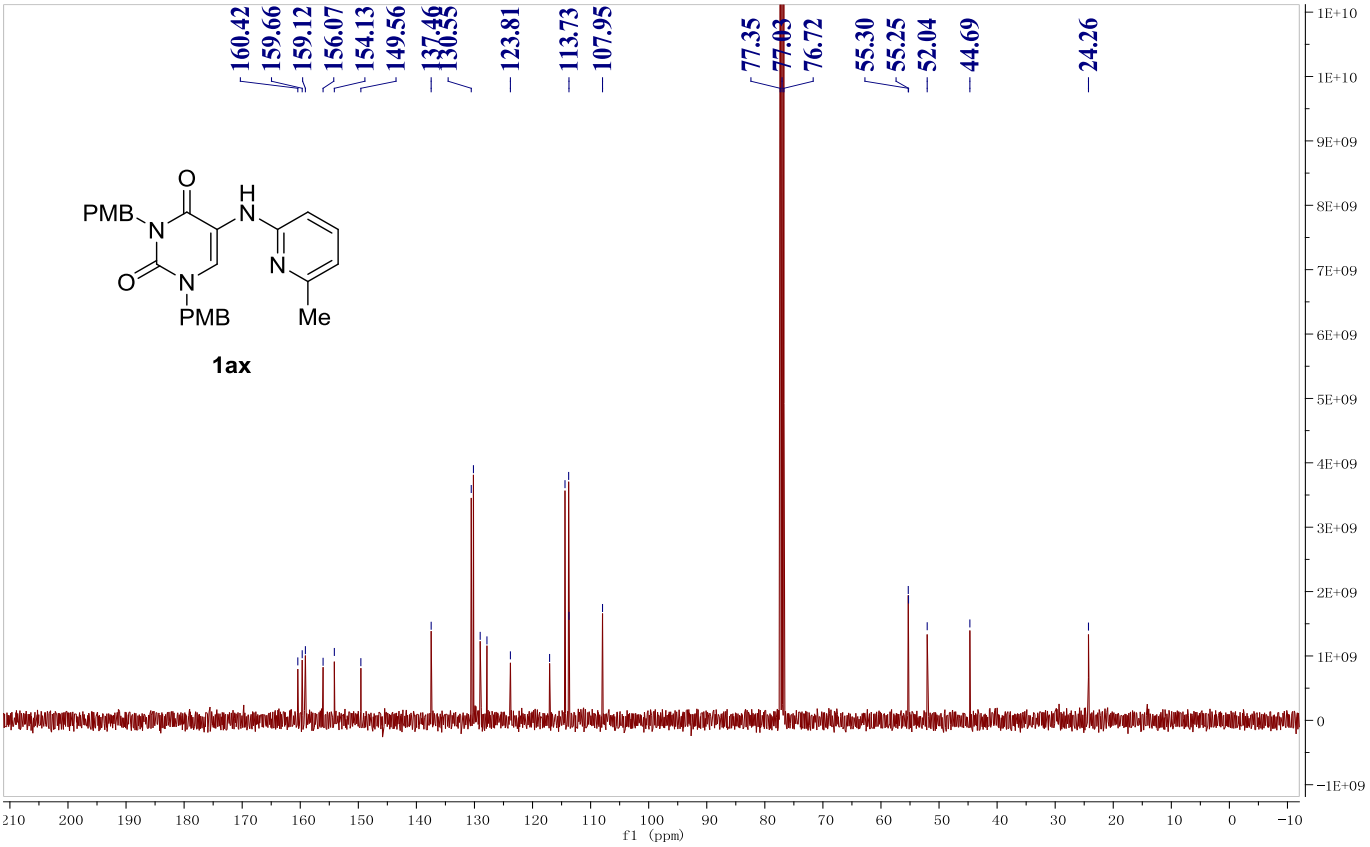
^{13}C NMR Spectrum of 1aw at 25 °C ($CDCl_3$, 150 MHz)



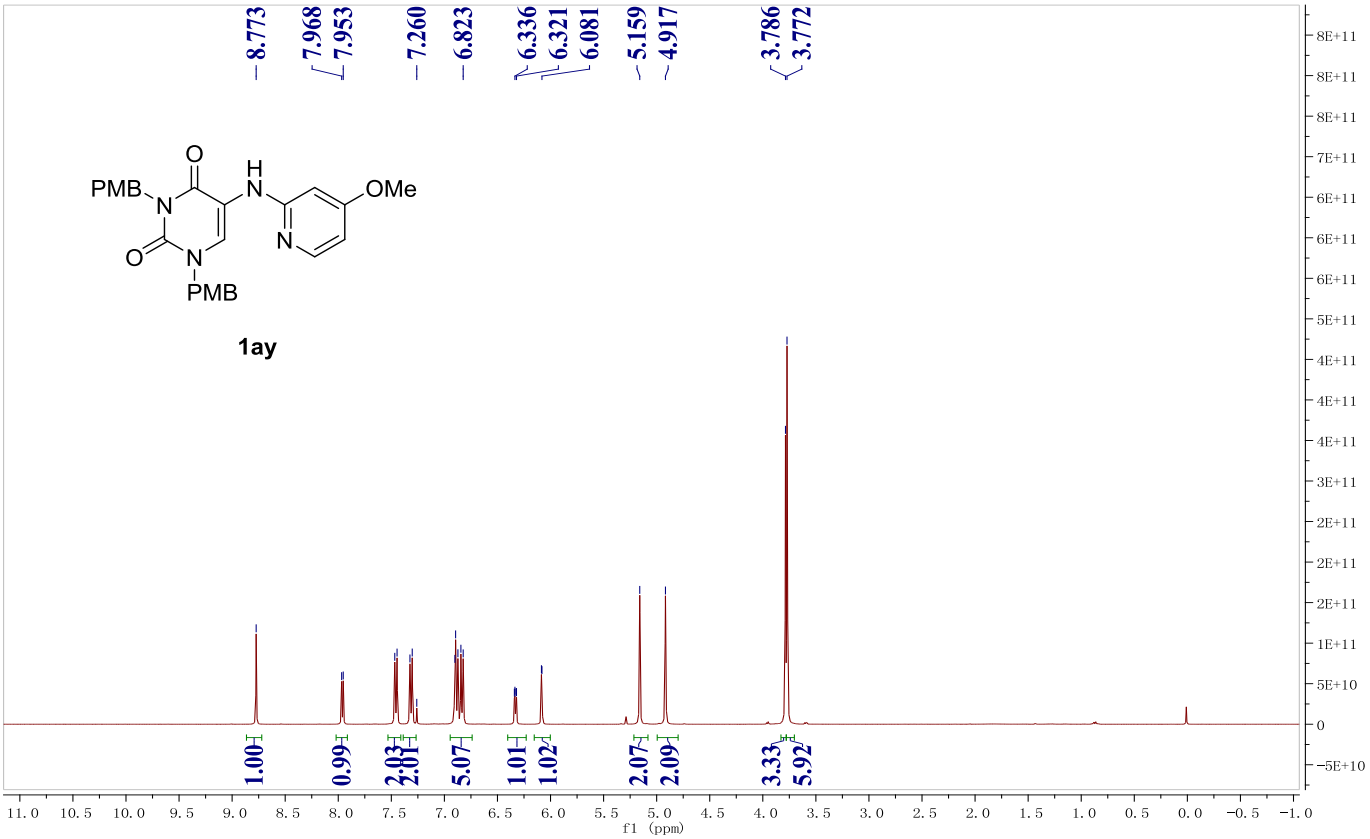
^{1}H NMR Spectrum of 1ax at 25 °C ($CDCl_3$, 400 MHz)



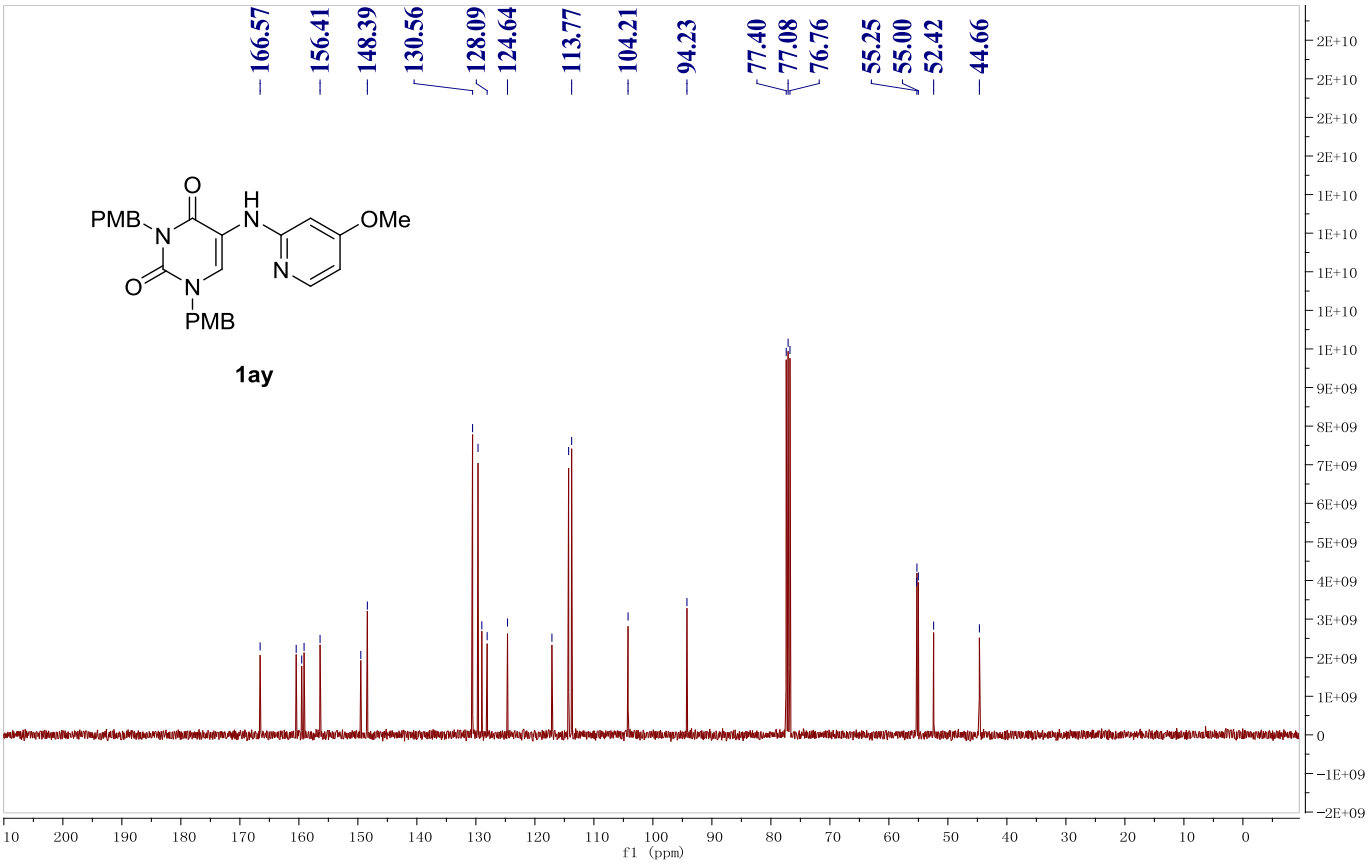
^{13}C NMR Spectrum of 1ax at 25 °C ($CDCl_3$, 100 MHz)



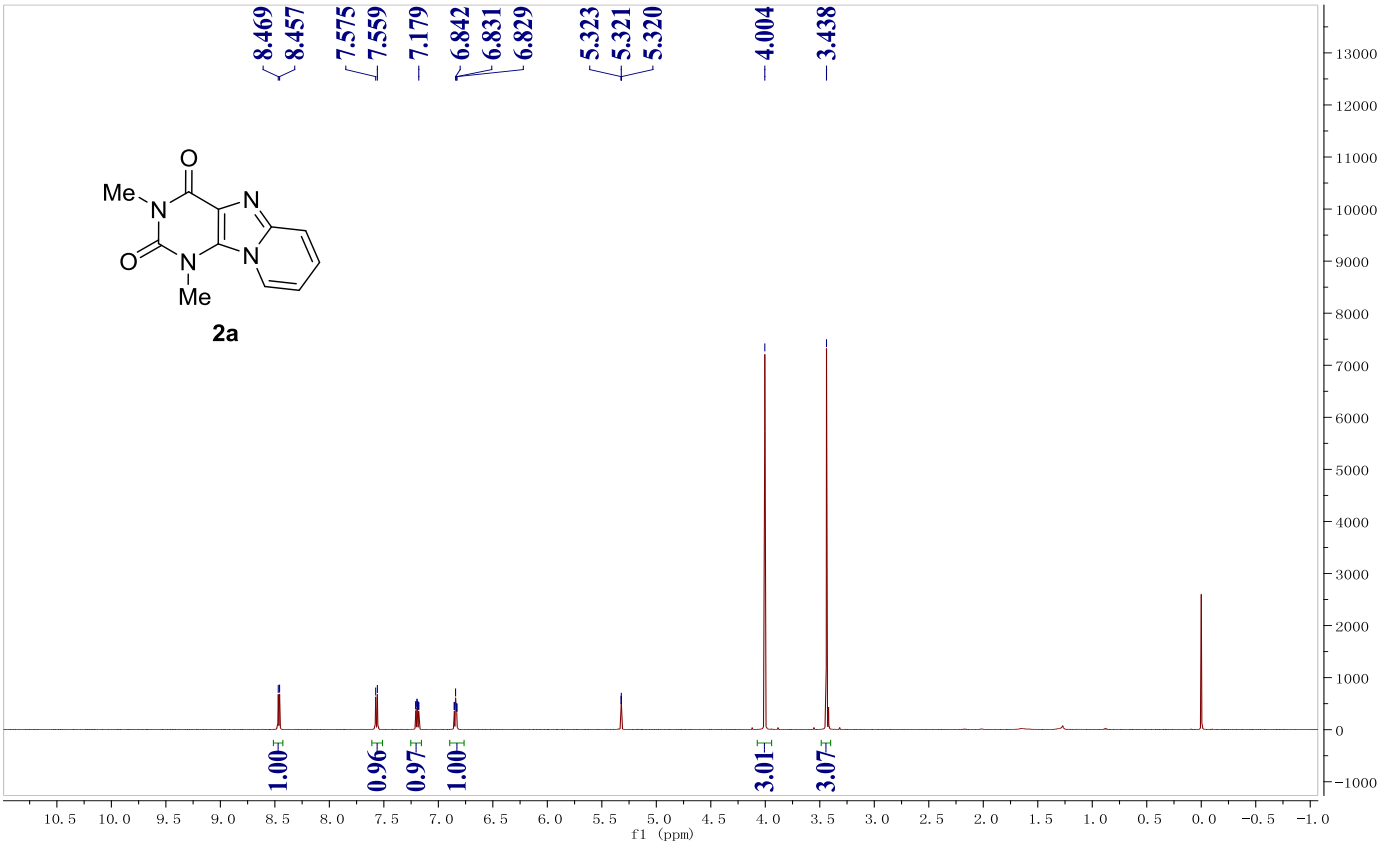
^{1}H NMR Spectrum of 1ay at 25 °C ($CDCl_3$, 400 MHz)



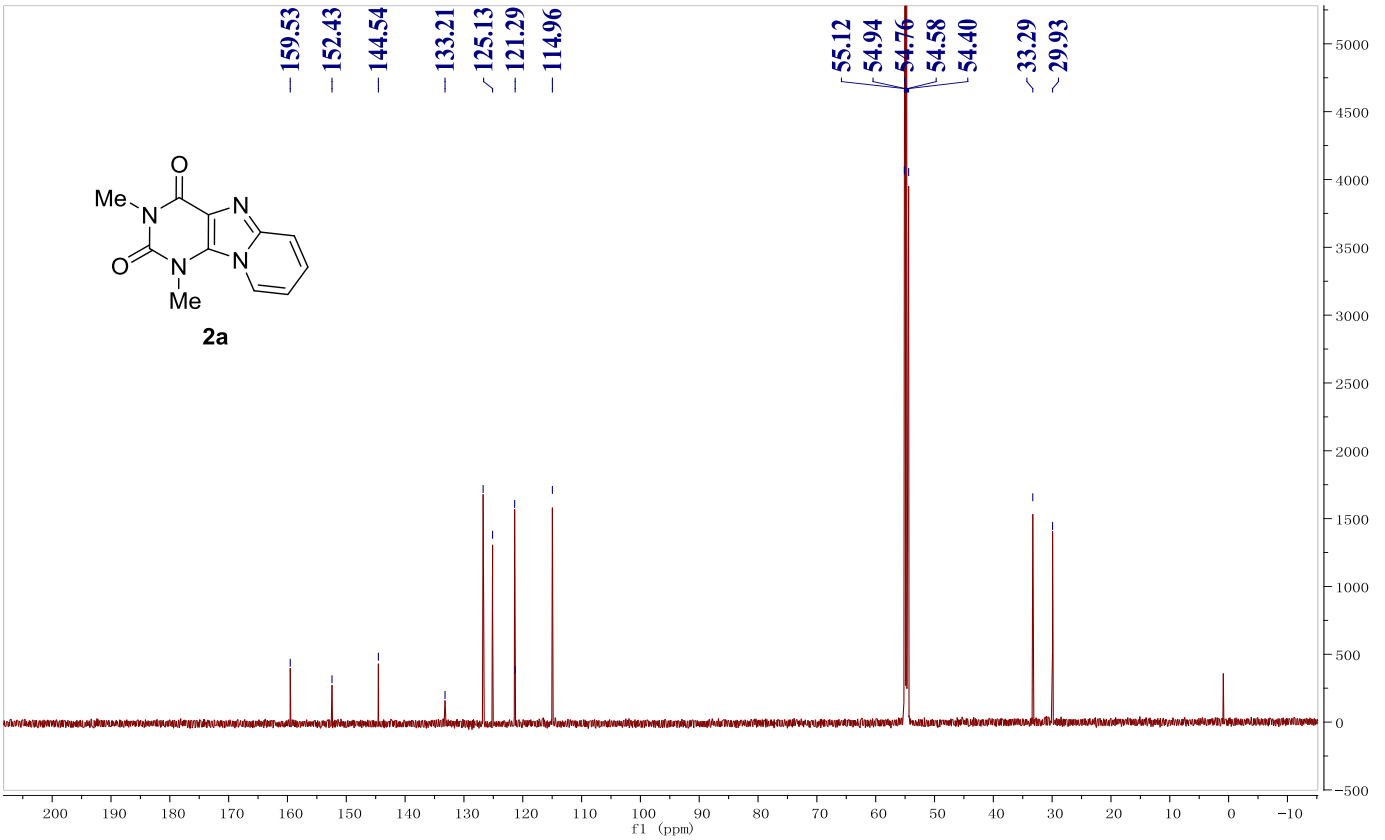
^{13}C NMR Spectrum of 1ay at 25 °C ($CDCl_3$, 100 MHz)



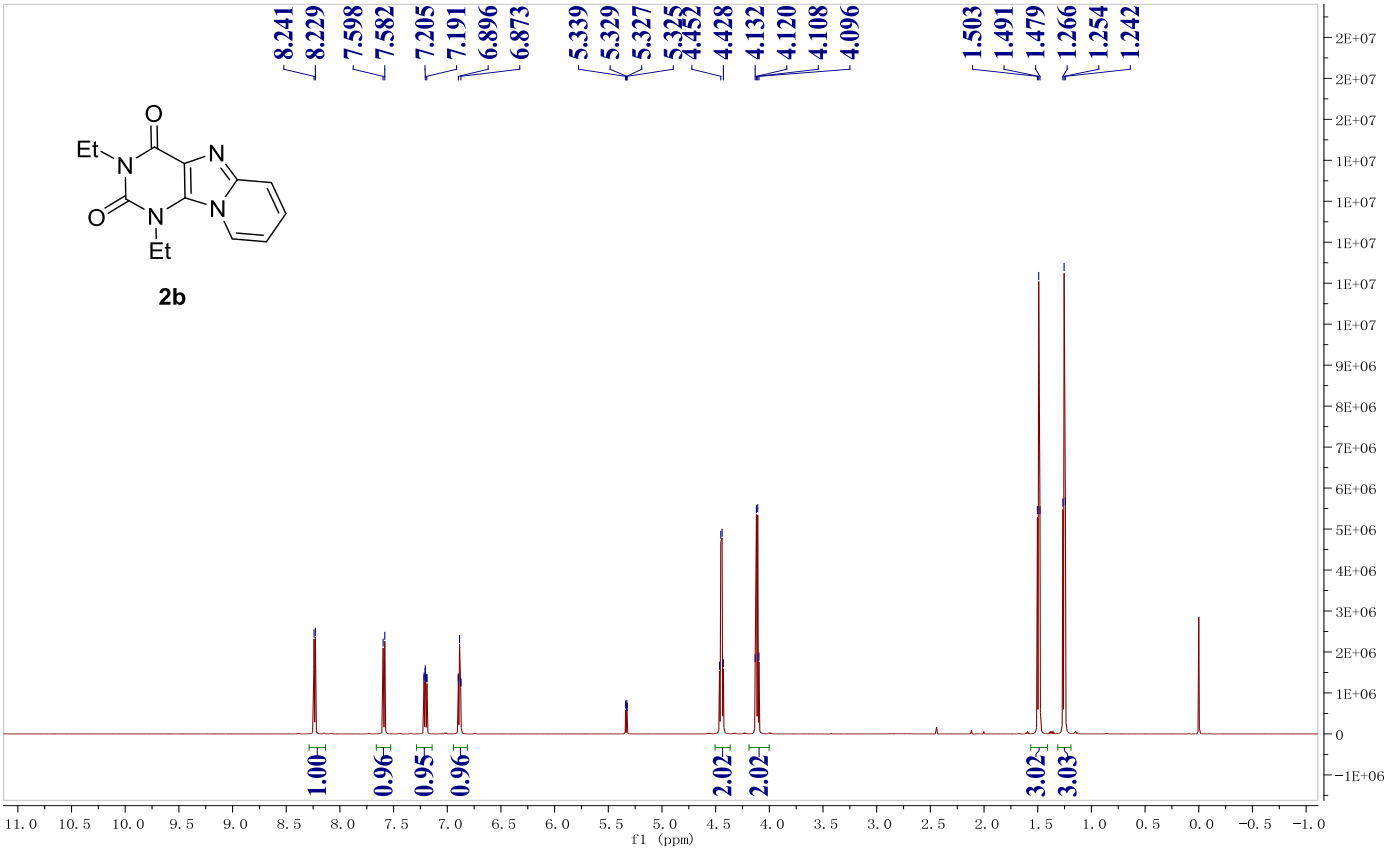
^{1}H NMR Spectrum of 2a at 25 °C (CD_2Cl_2, 600 MHz)



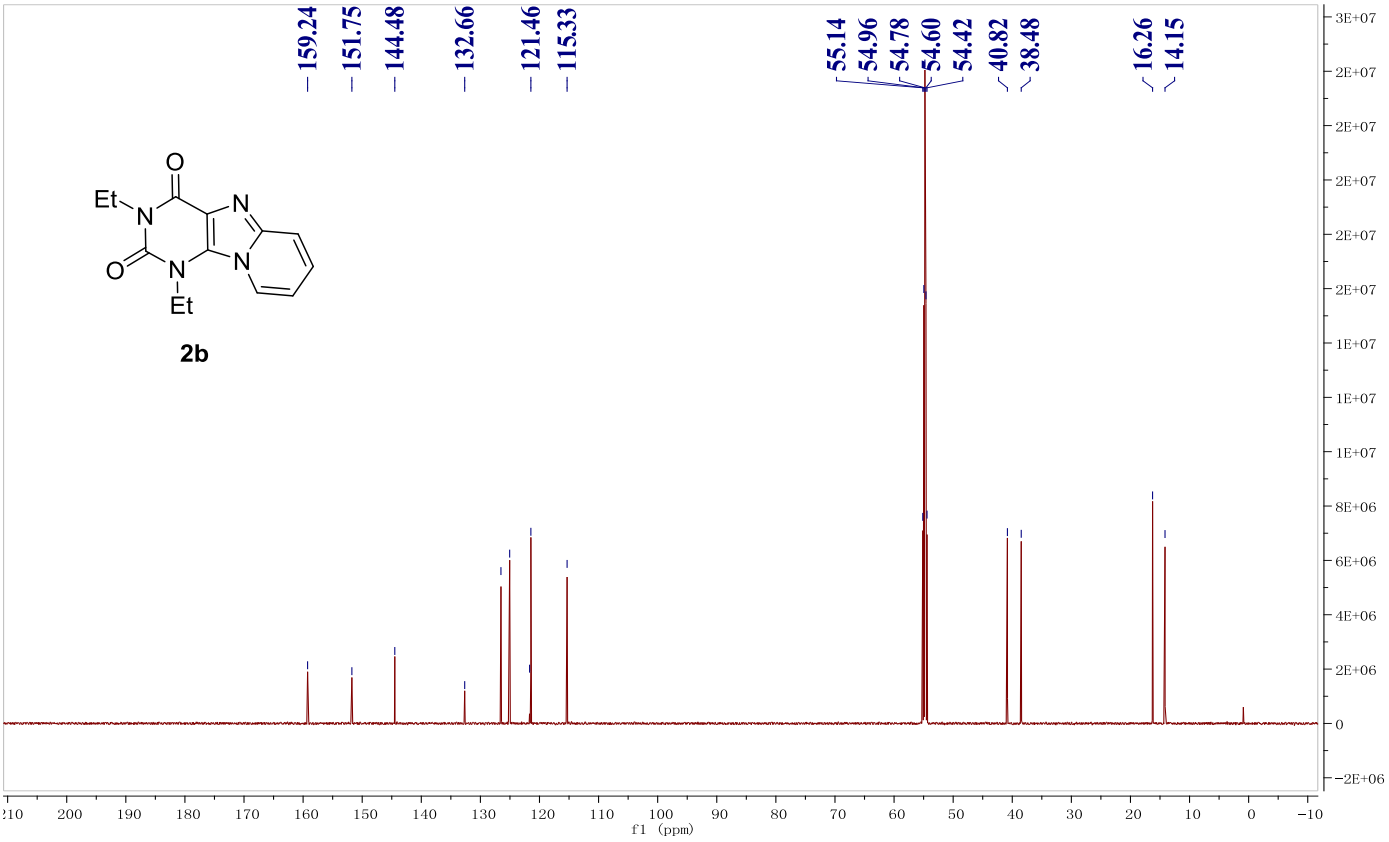
^{13}C NMR Spectrum of 2a at 25 °C (CD_2Cl_2, 150 MHz)



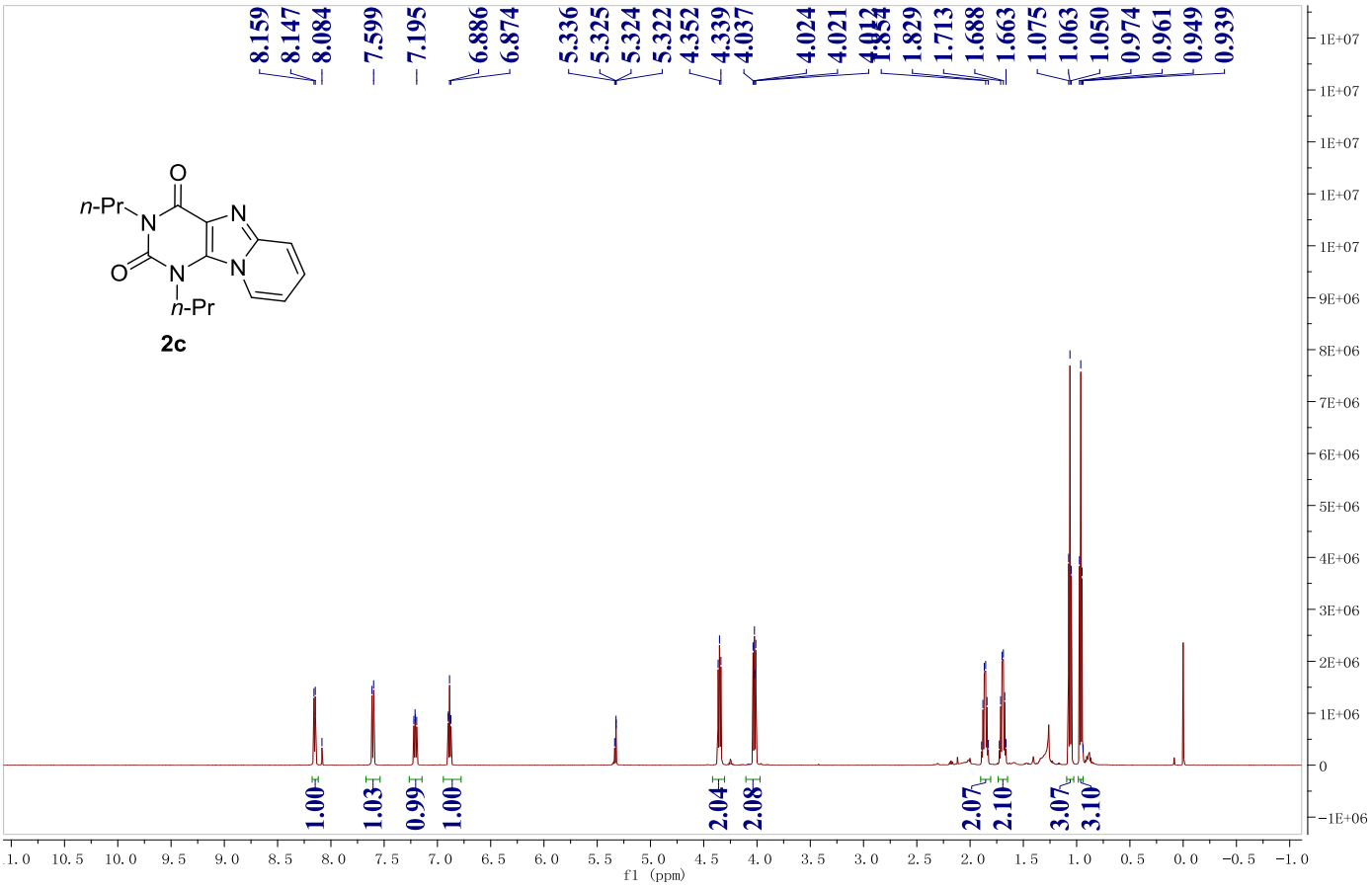
^{1}H NMR Spectrum of 2b at 25 °C ($CD2Cl_2$, 600 MHz)



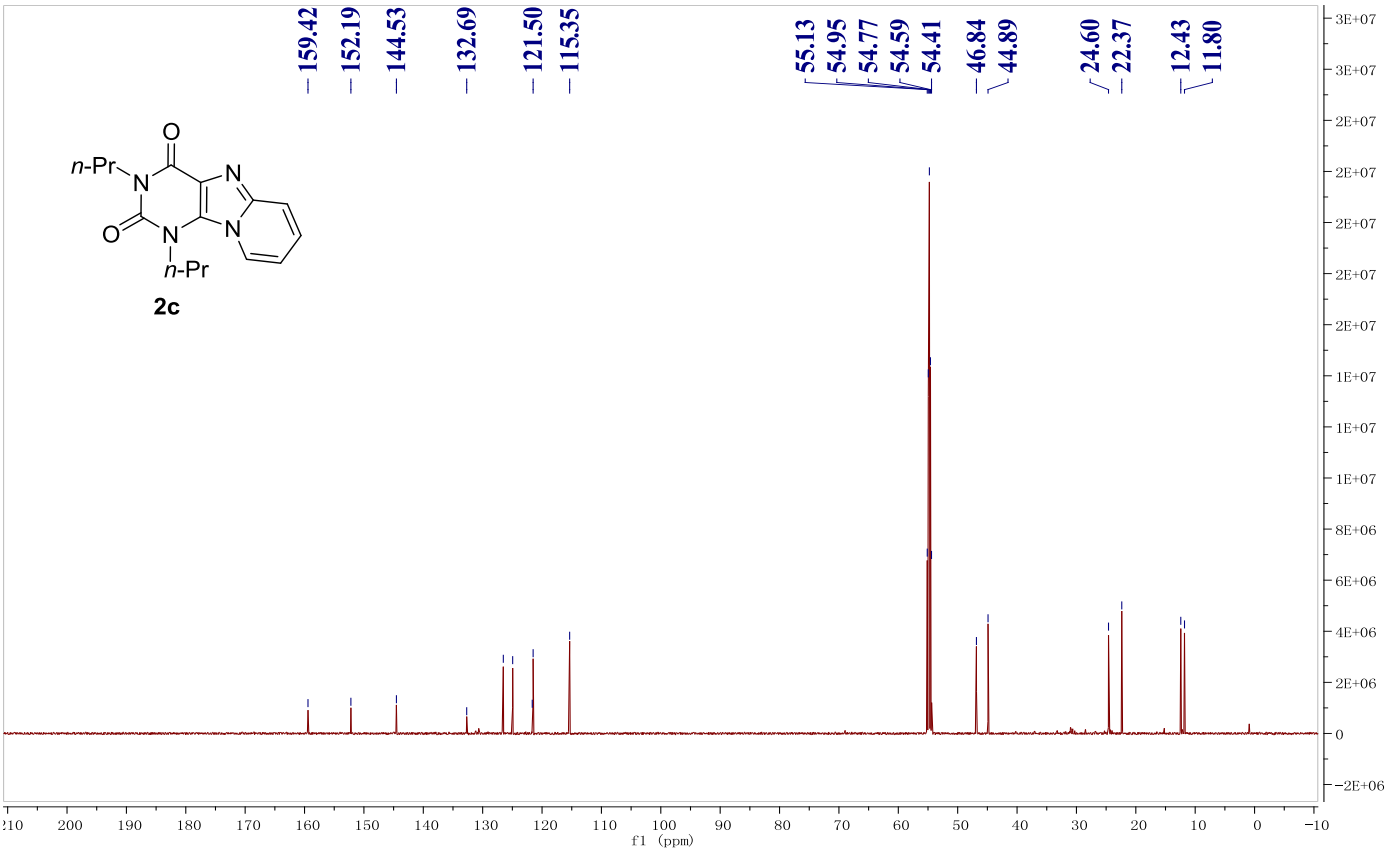
^{13}C NMR Spectrum of 2b at 25 °C ($CDCl_3$, 150 MHz)



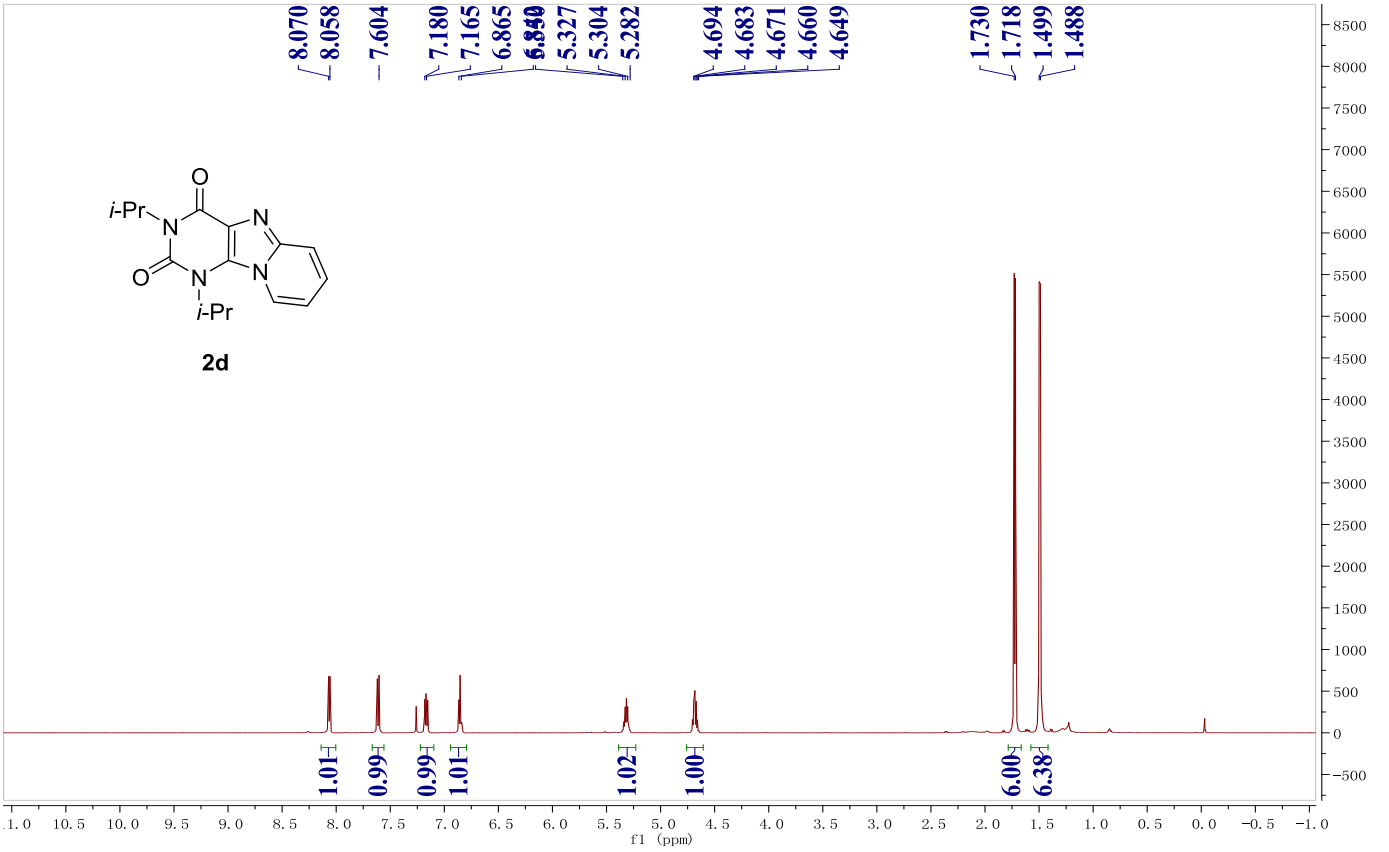
^{1}H NMR Spectrum of 2c at 25 °C ($CDCl_3$, 600 MHz)



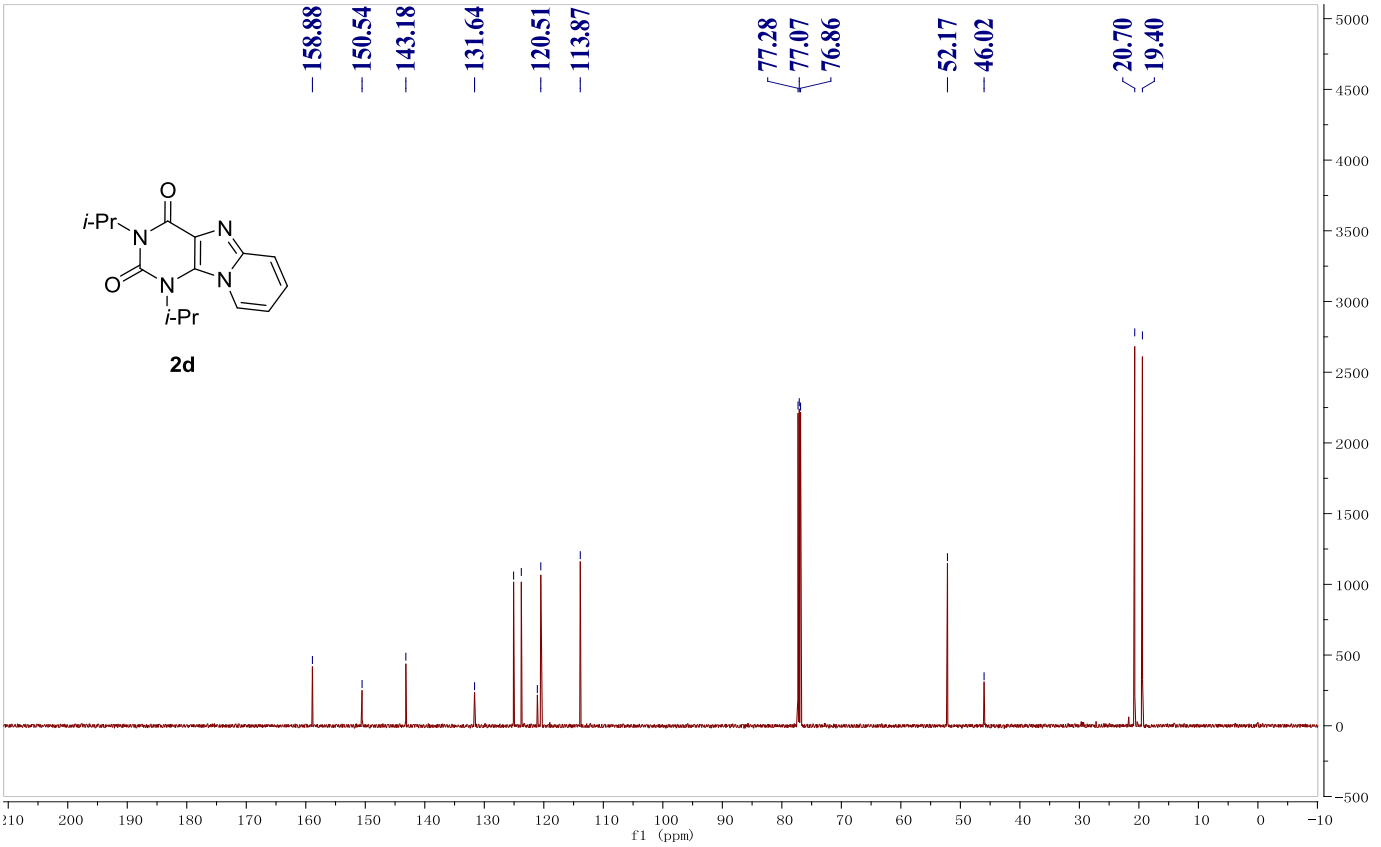
^{13}C NMR Spectrum of 2c at 25 °C ($CDCl_3$, 150 MHz)



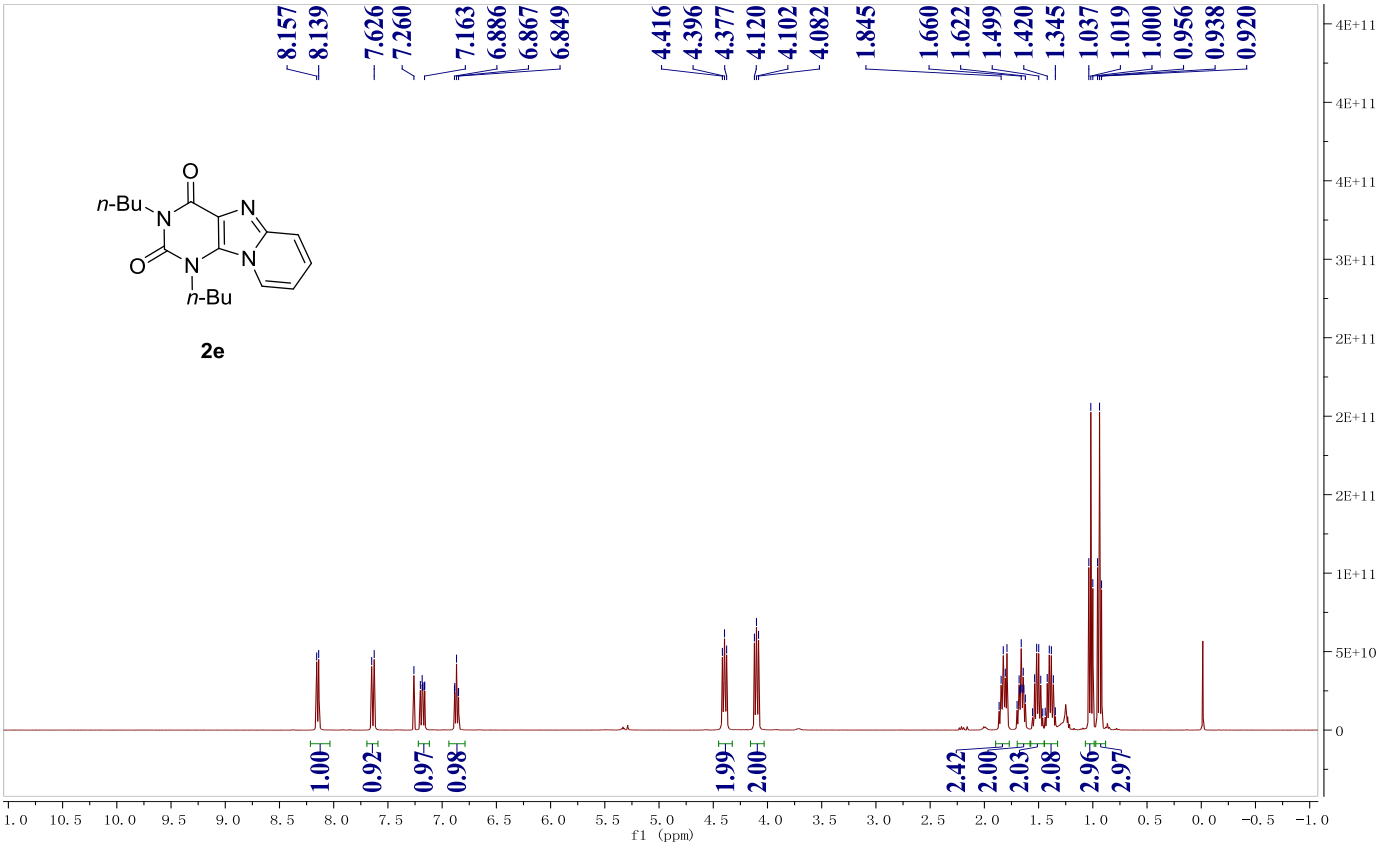
^{1}H NMR Spectrum of 2d at 25 °C ($CDCl_3$, 600 MHz)



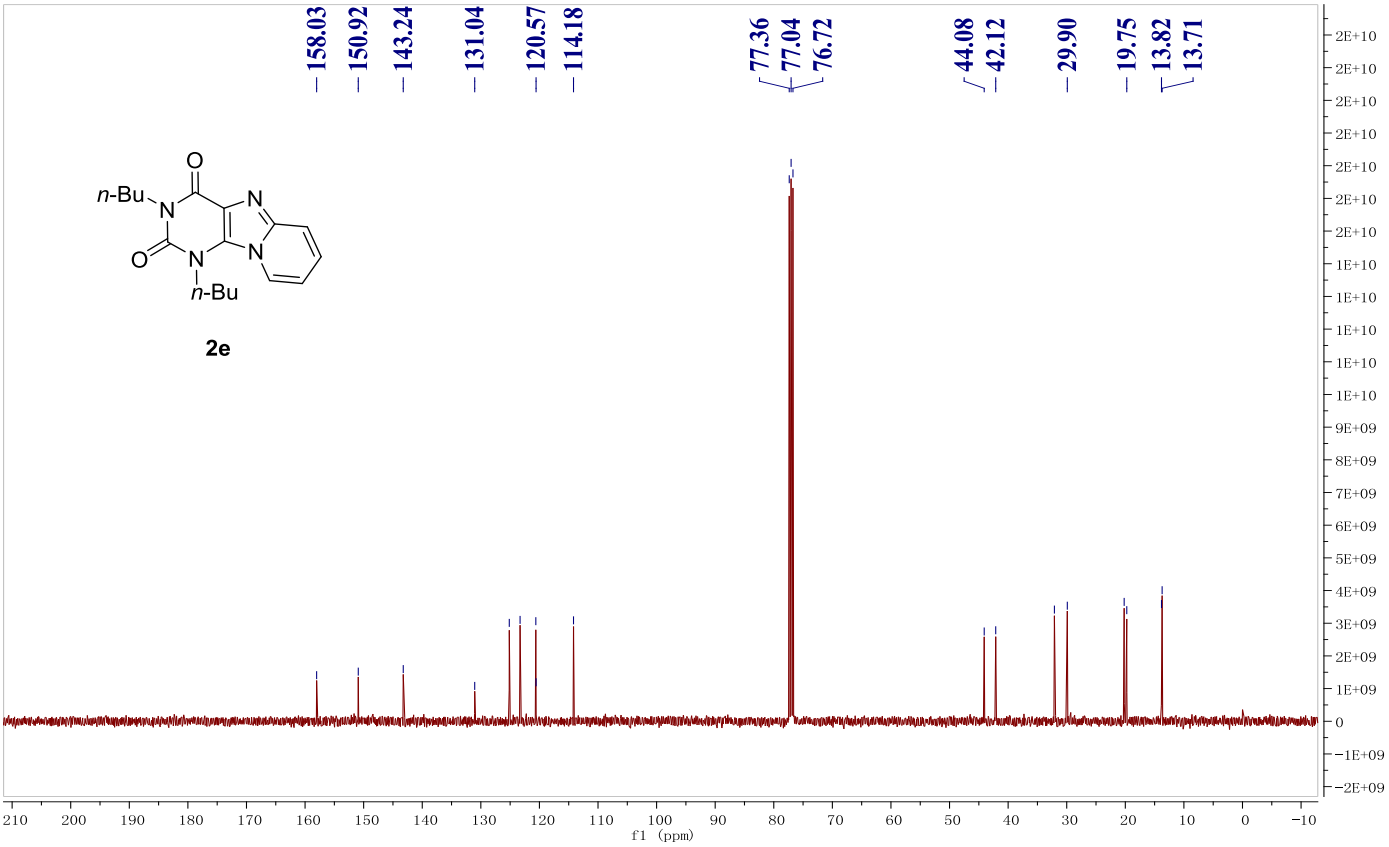
^{13}C NMR Spectrum of 2d at 25 °C ($CDCl_3$, 150 MHz)



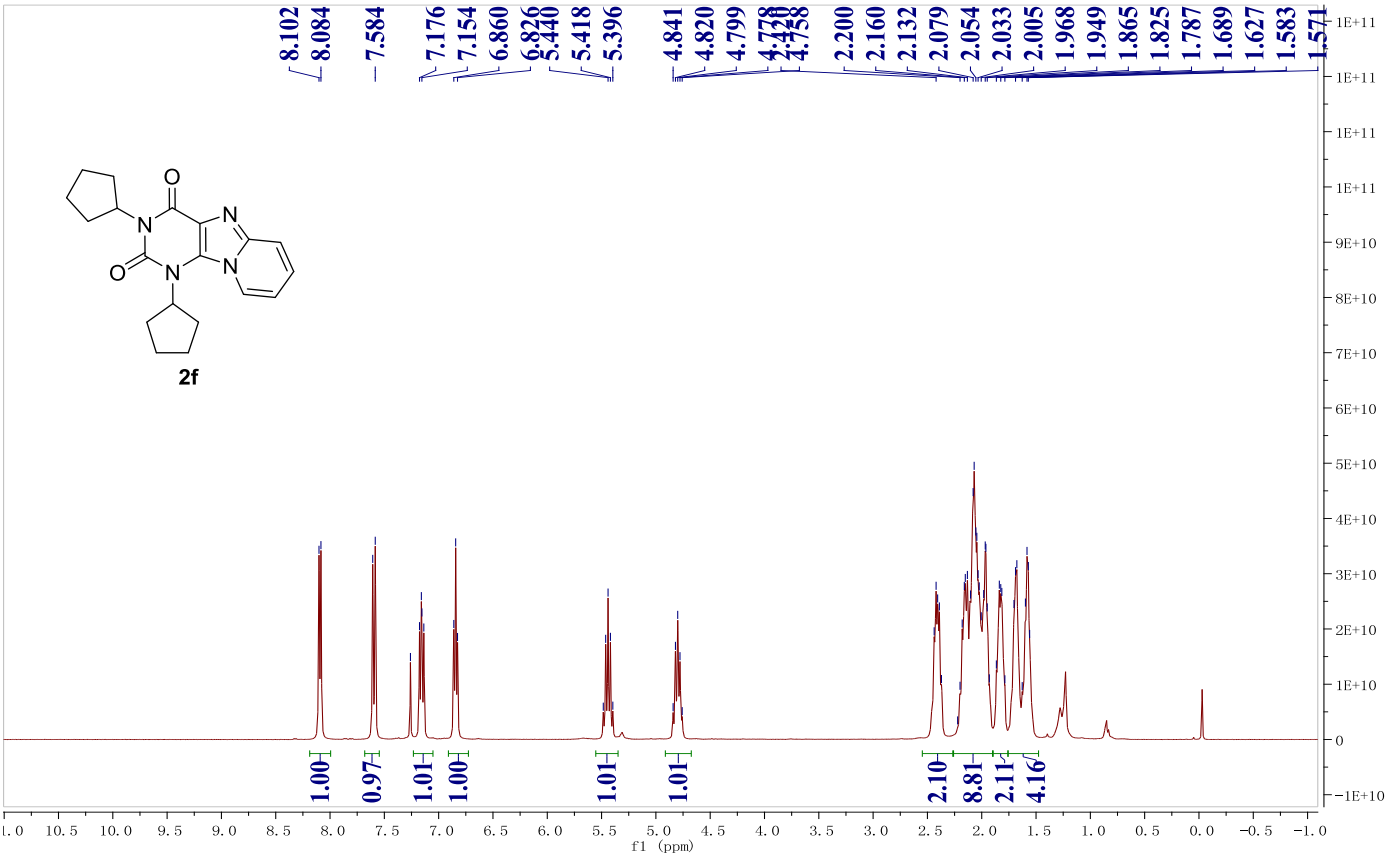
^{1}H NMR Spectrum of 2e at 25 °C ($CDCl_3$, 400 MHz)



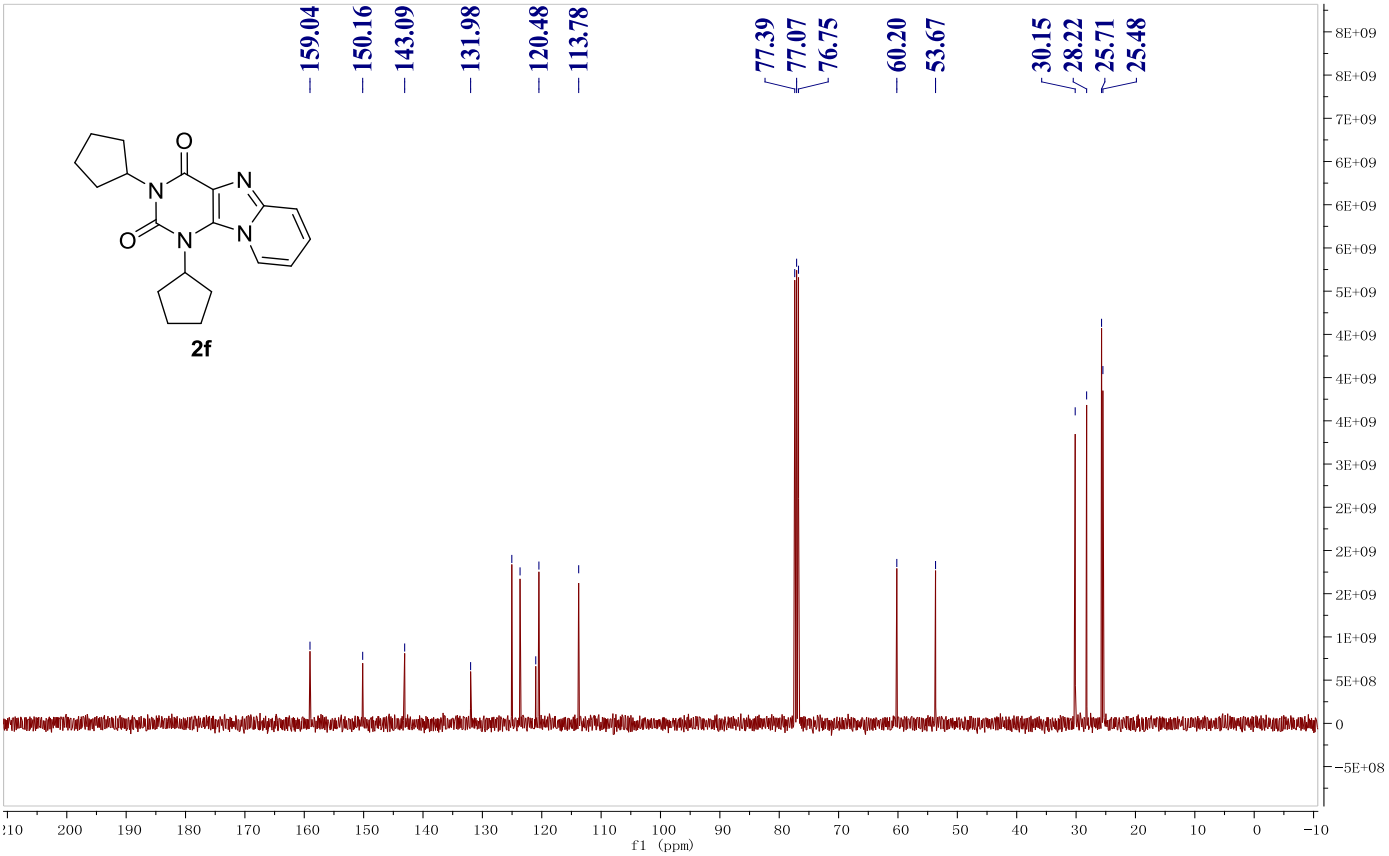
^{13}C NMR Spectrum of 2e at 25 °C ($CDCl_3$, 100 MHz)



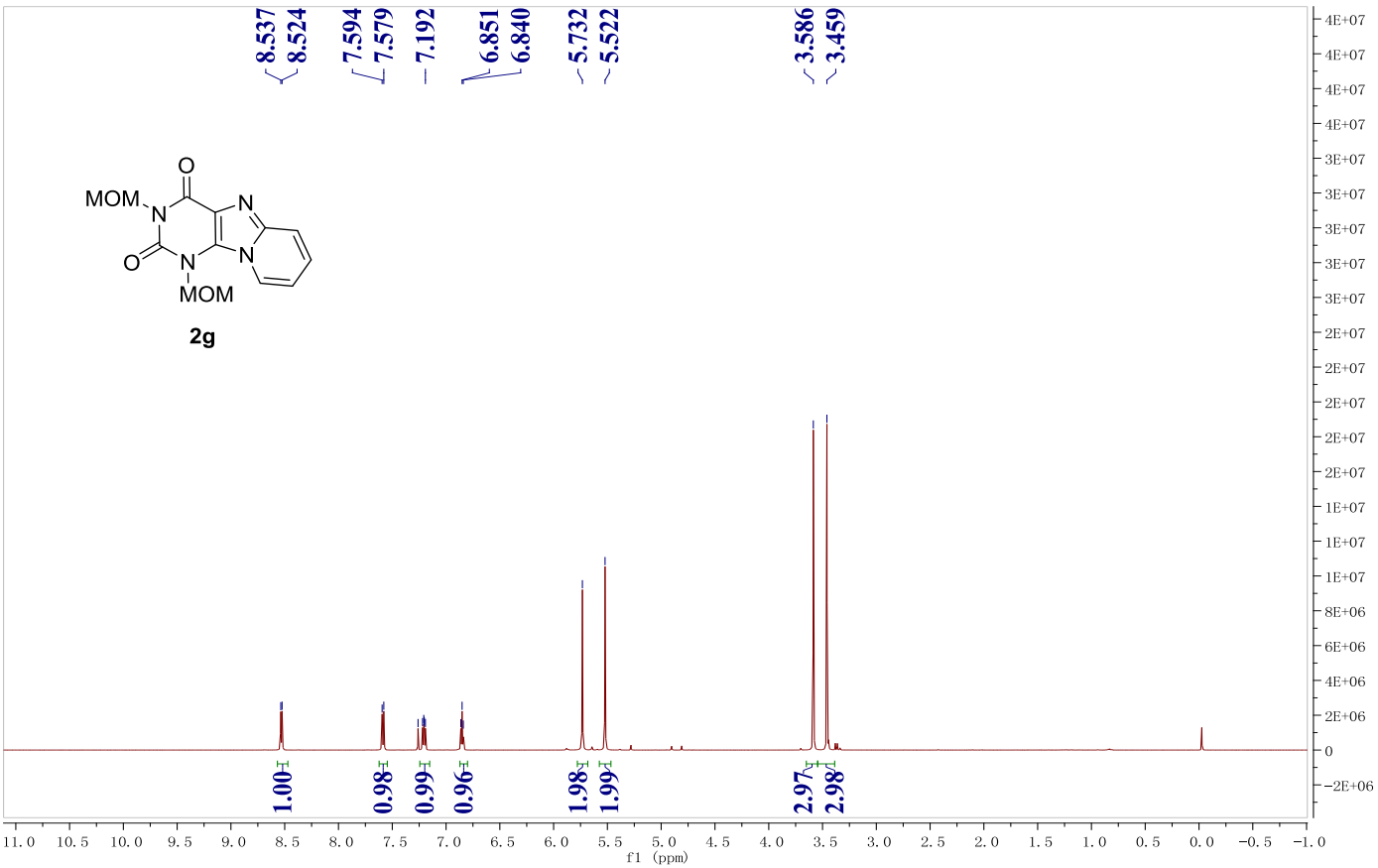
^{1}H NMR Spectrum of 2f at 25 °C ($CDCl_3$, 400 MHz)



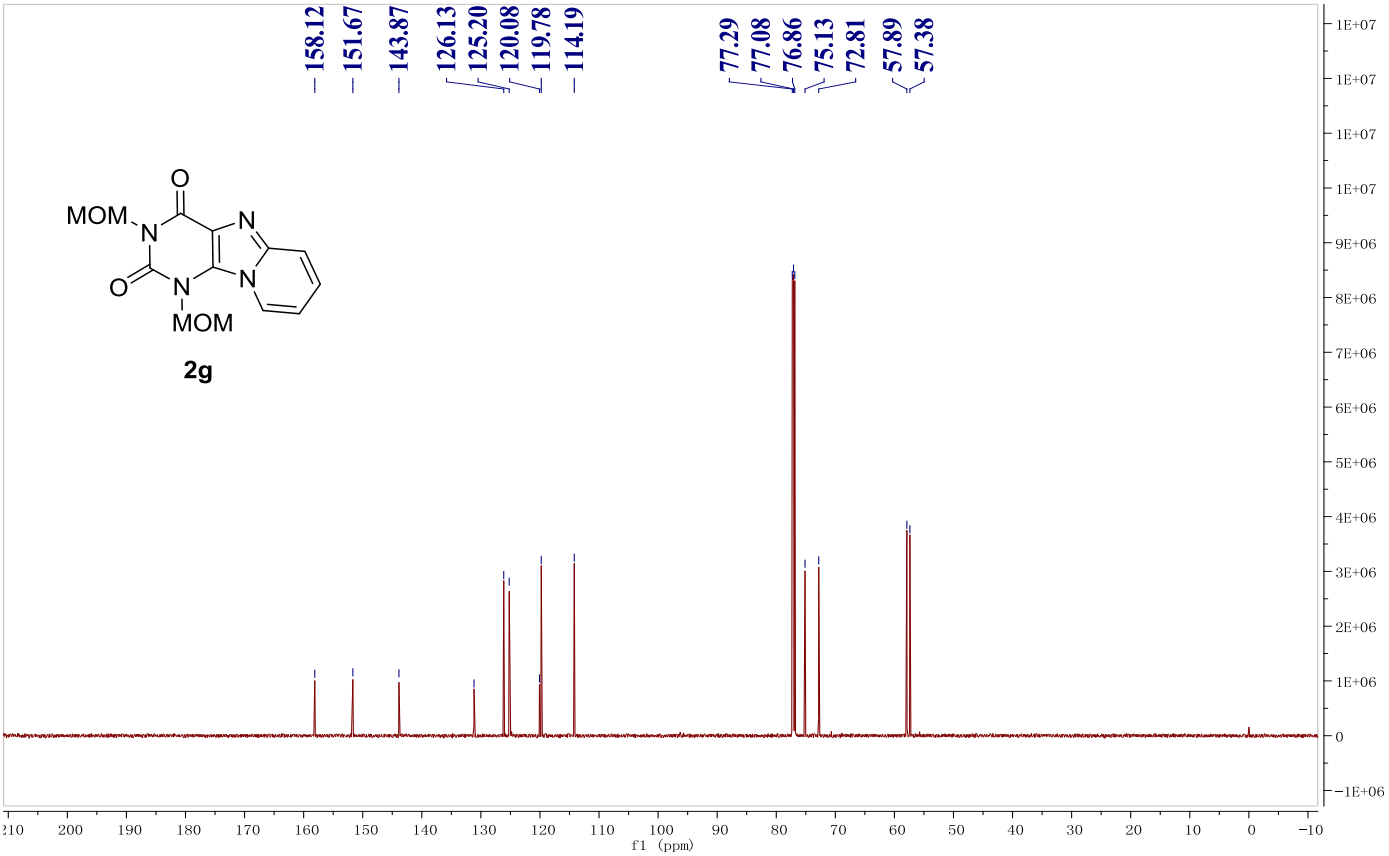
^{13}C NMR Spectrum of 2f at 25 °C ($CDCl_3$, 100 MHz)



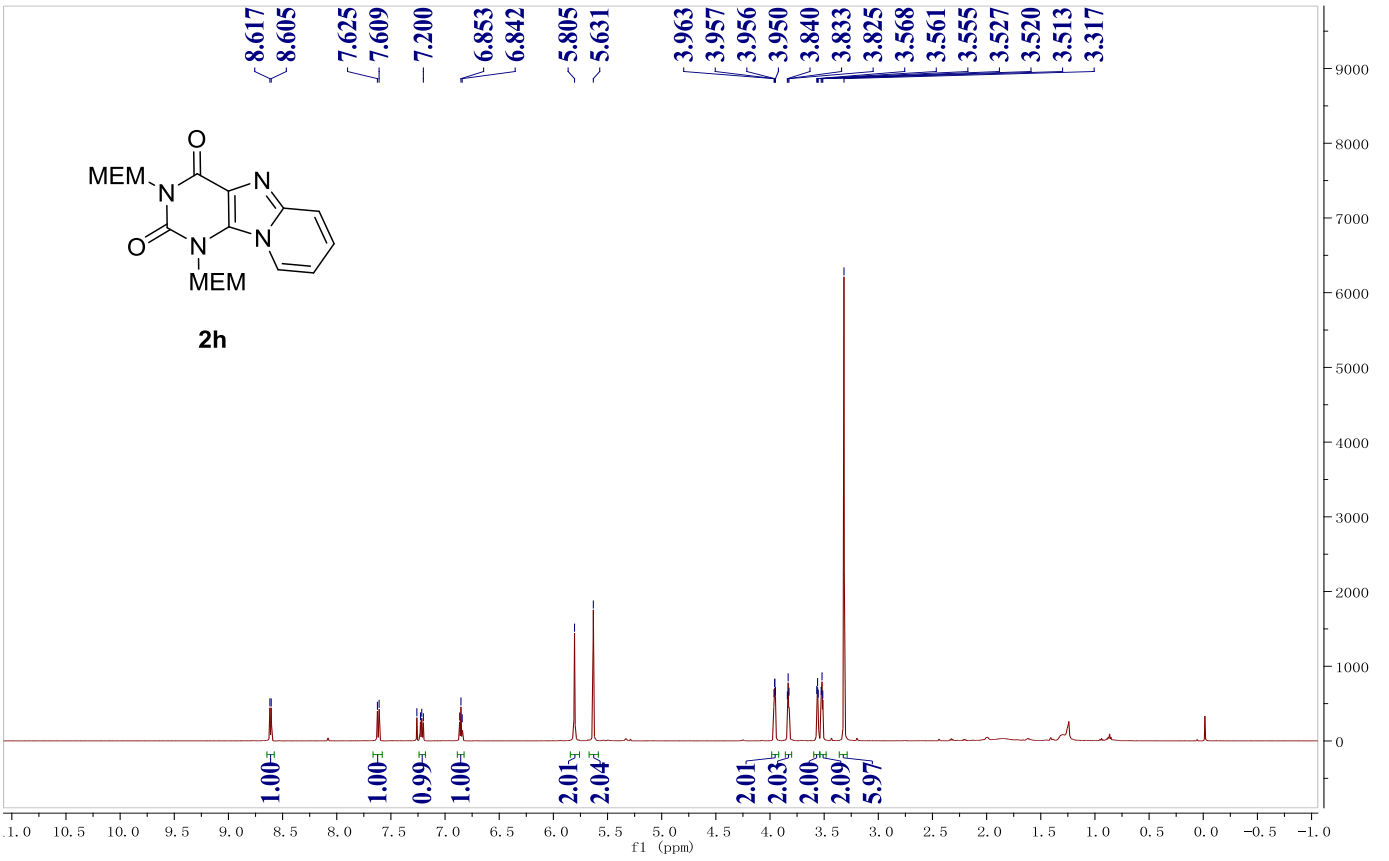
^{1}H NMR Spectrum of 2g at 25 °C ($CDCl_3$, 600 MHz)



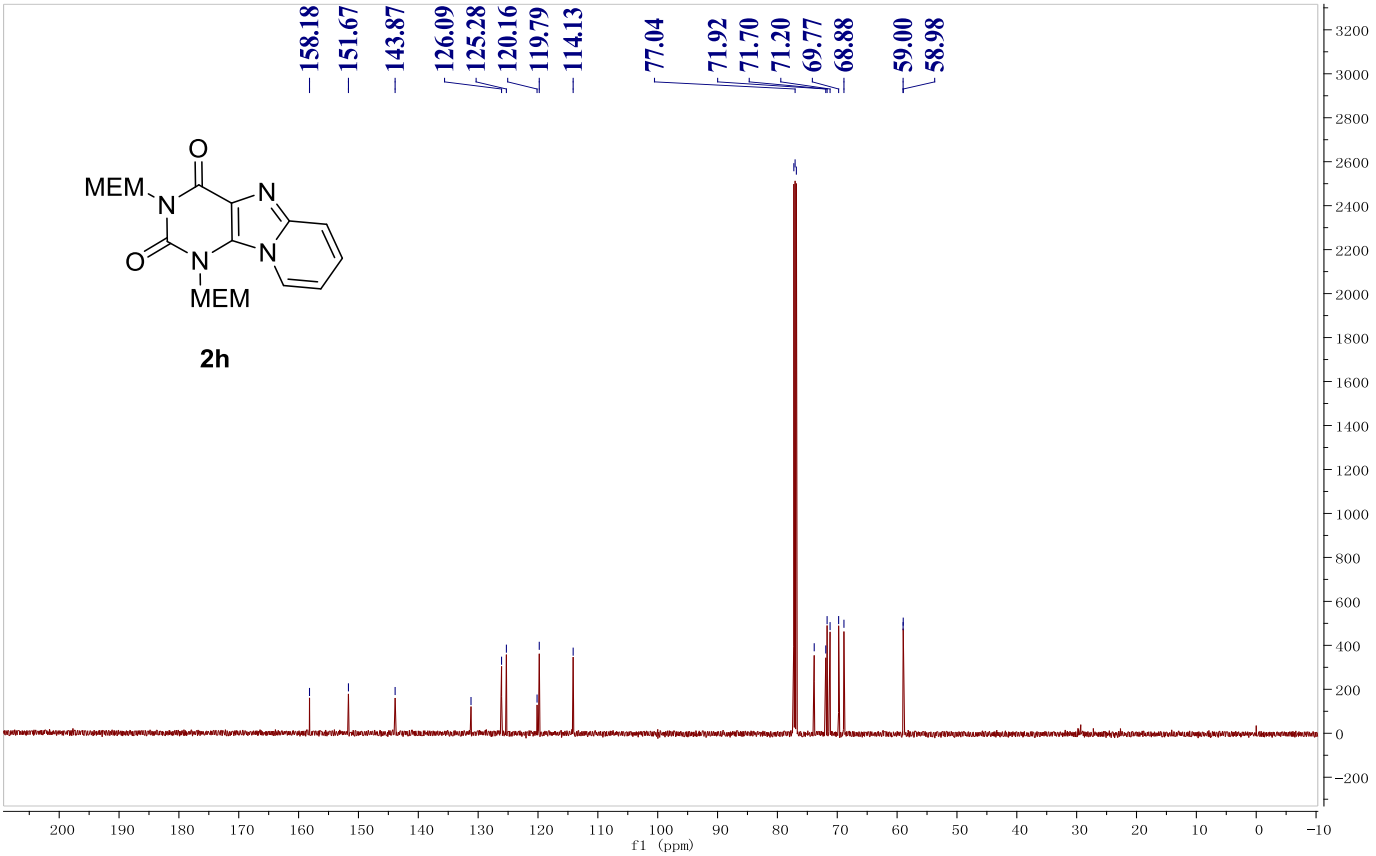
^{13}C NMR Spectrum of 2g at 25 °C ($CDCl_3$, 150 MHz)



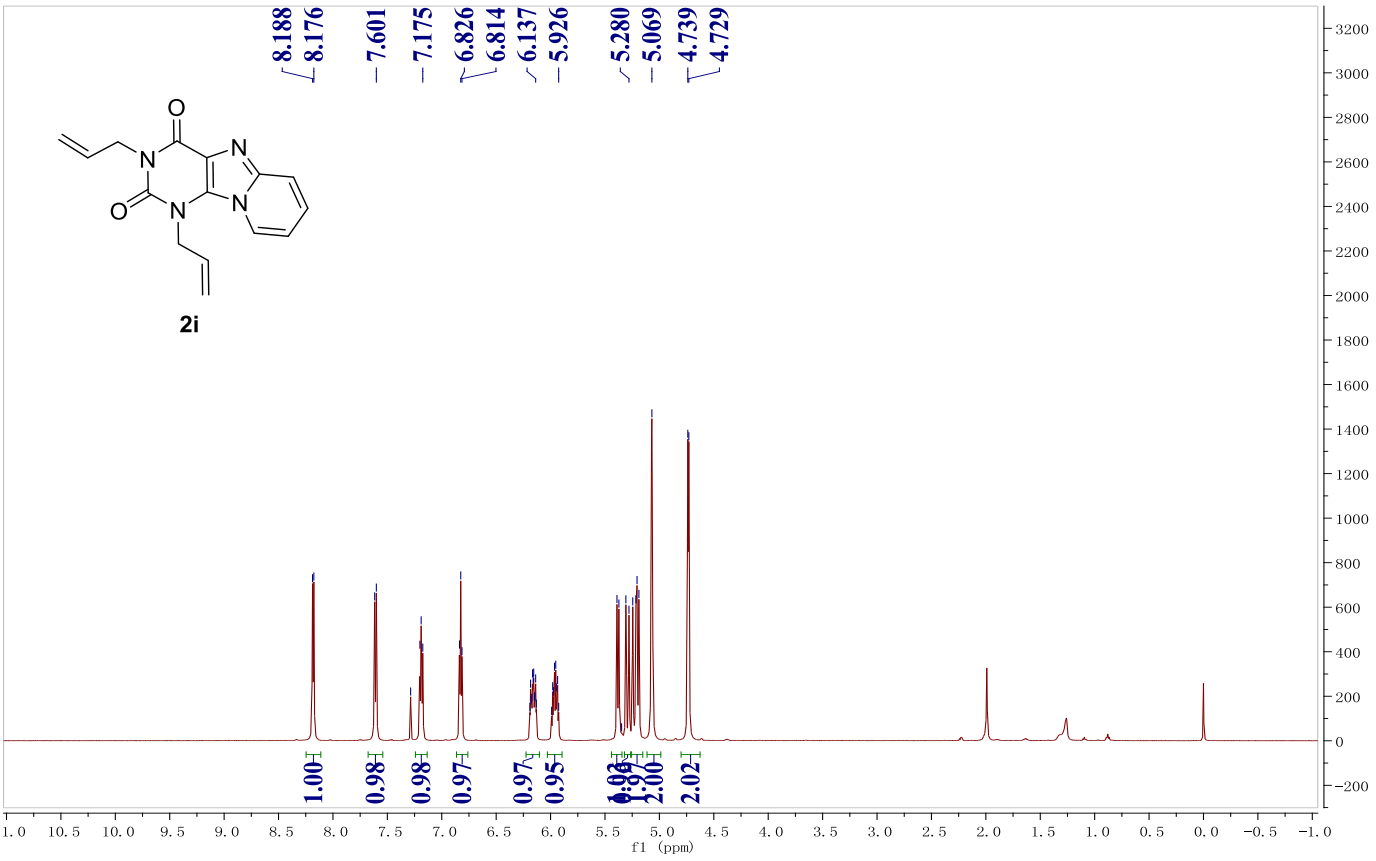
^{1}H NMR Spectrum of 2h at 25 °C ($CDCl_3$, 600 MHz)



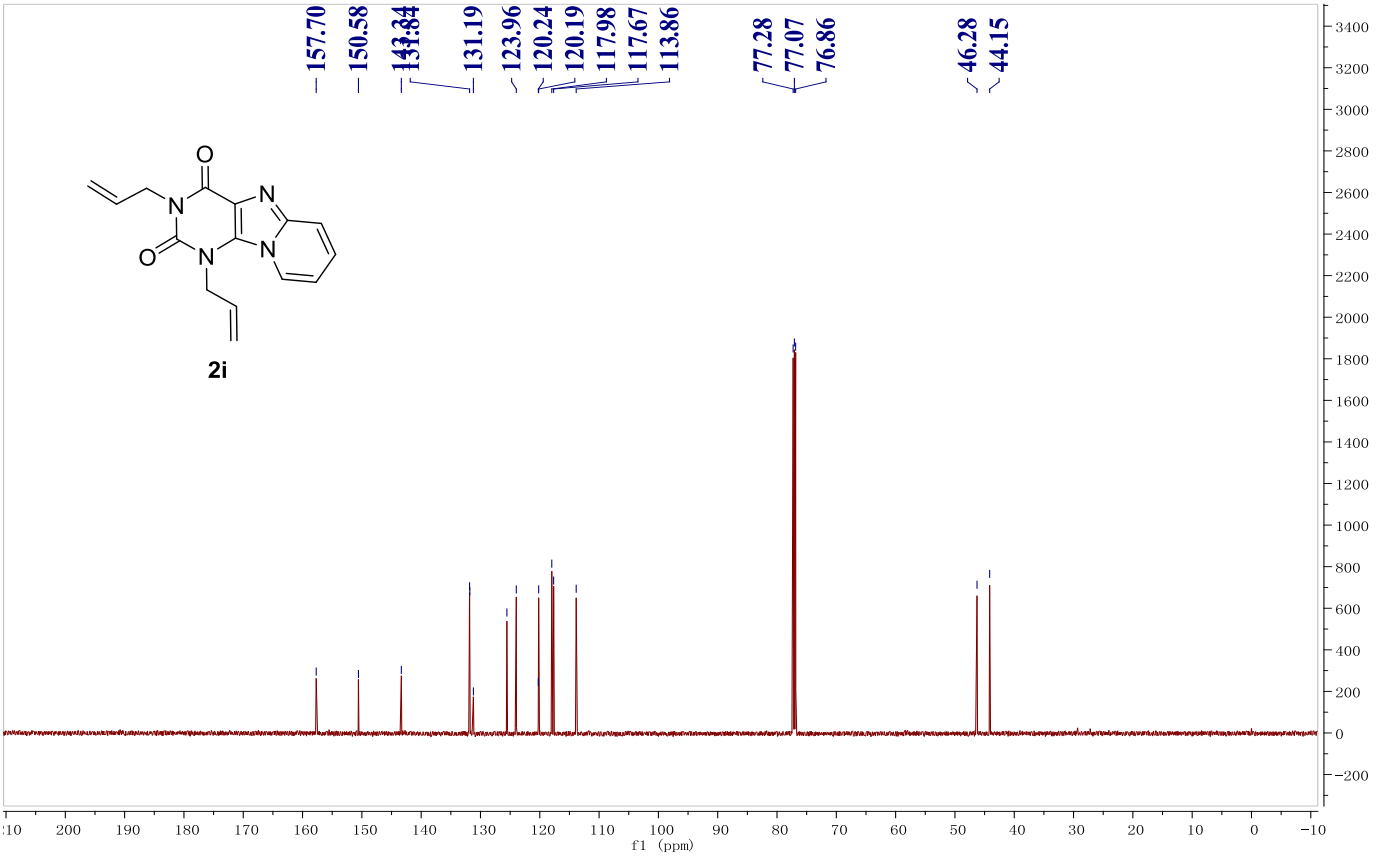
^{13}C NMR Spectrum of 2h at 25 °C ($CDCl_3$, 150 MHz)



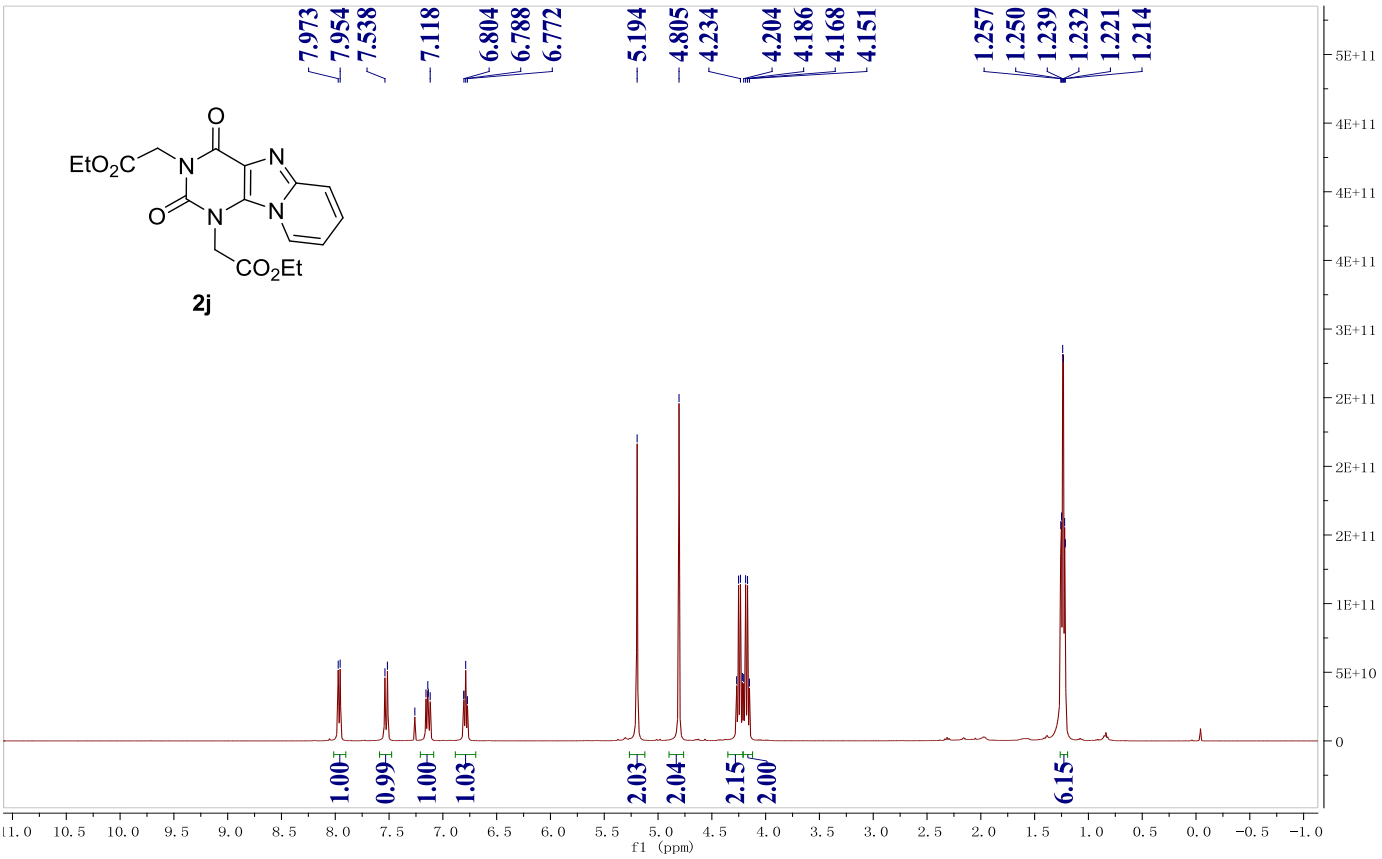
^{1}H NMR Spectrum of 2i at 25 °C ($CDCl_3$, 600 MHz)



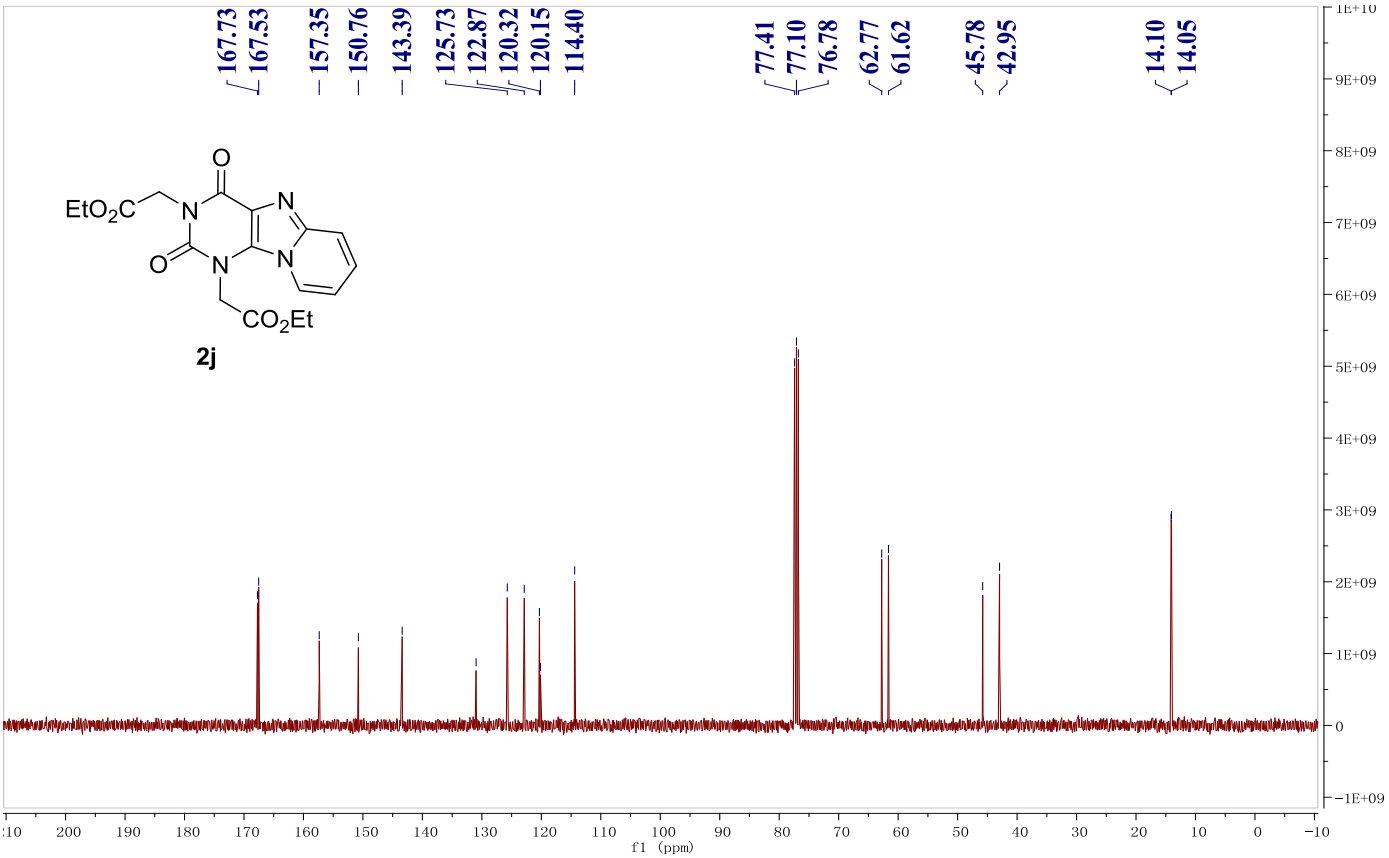
^{13}C NMR Spectrum of 2i at 25 °C ($CDCl_3$, 150 MHz)



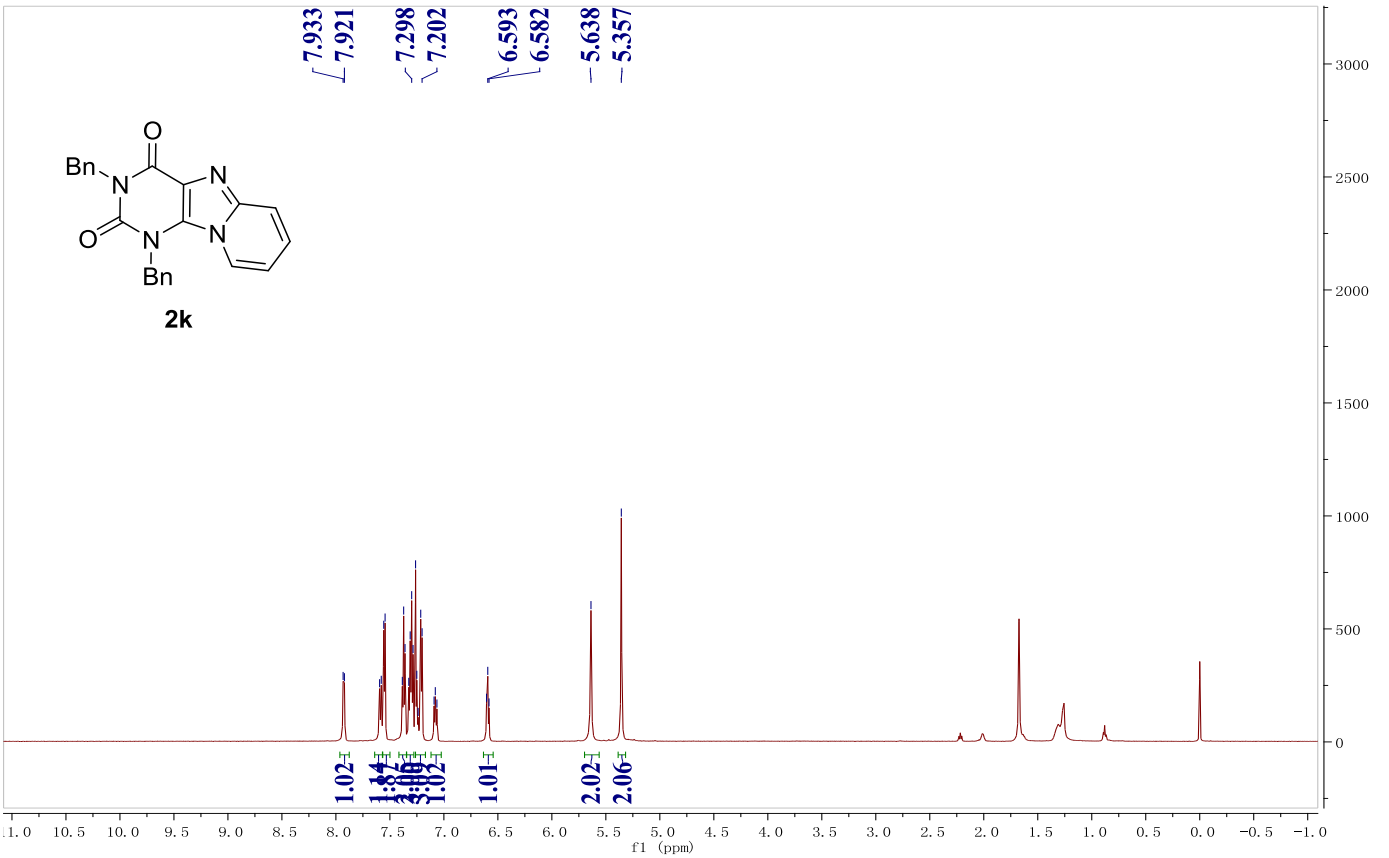
^{1}H NMR Spectrum of 2j at 25 °C ($CDCl_3$, 400 MHz)



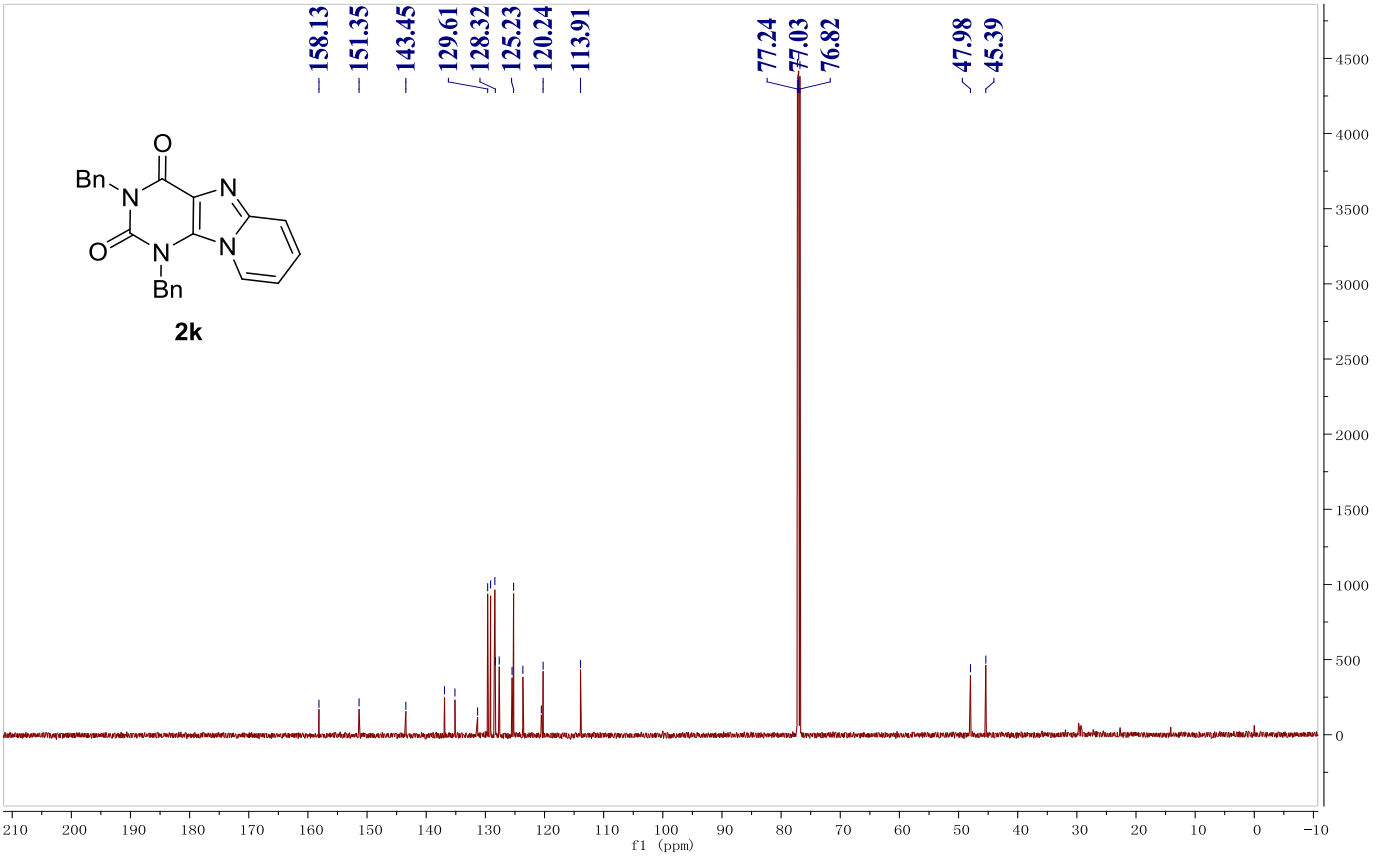
^{13}C NMR Spectrum of 2j at 25 °C ($CDCl_3$, 100 MHz)



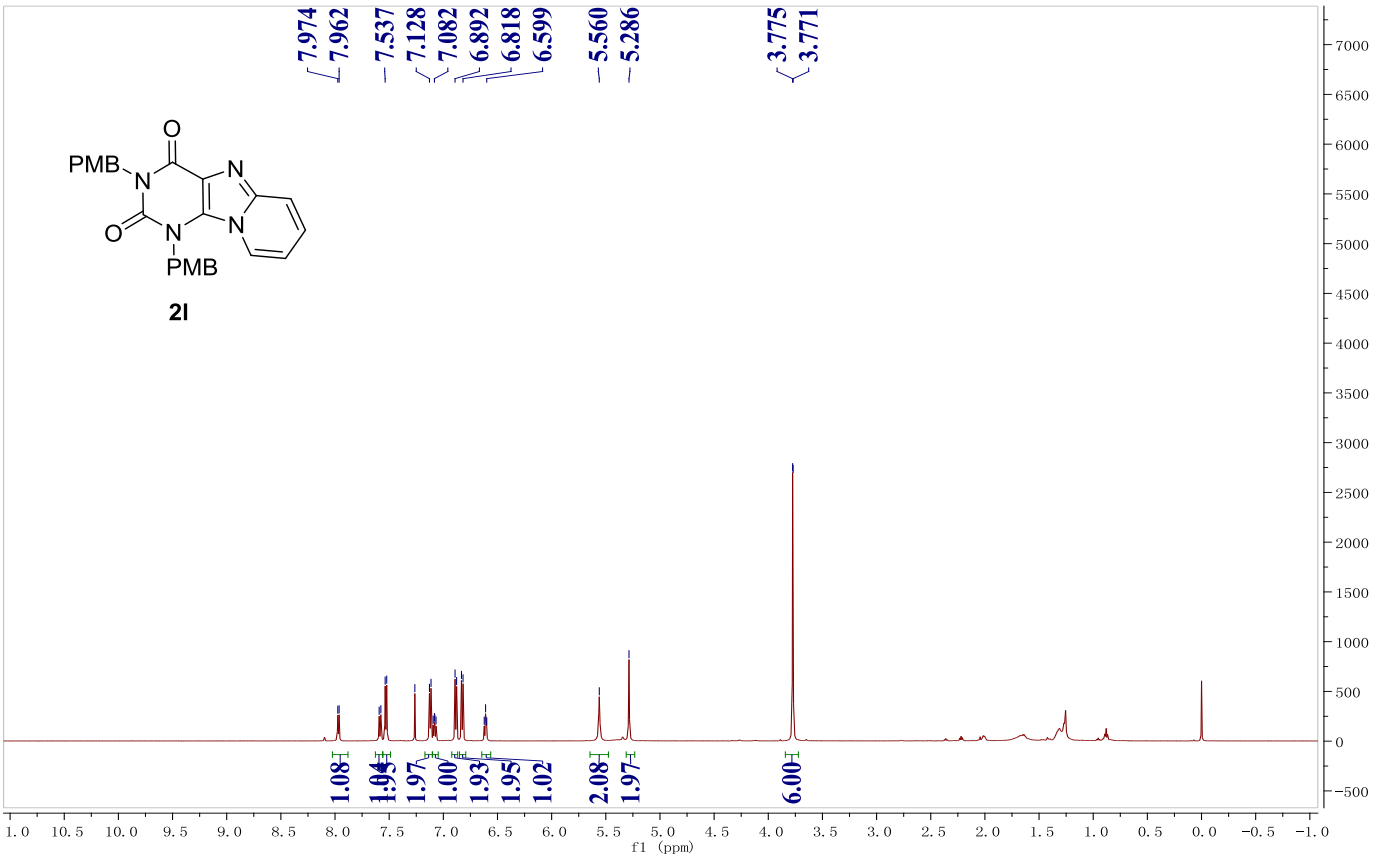
^{1}H NMR Spectrum of 2k at 25 °C ($CDCl_3$, 600 MHz)



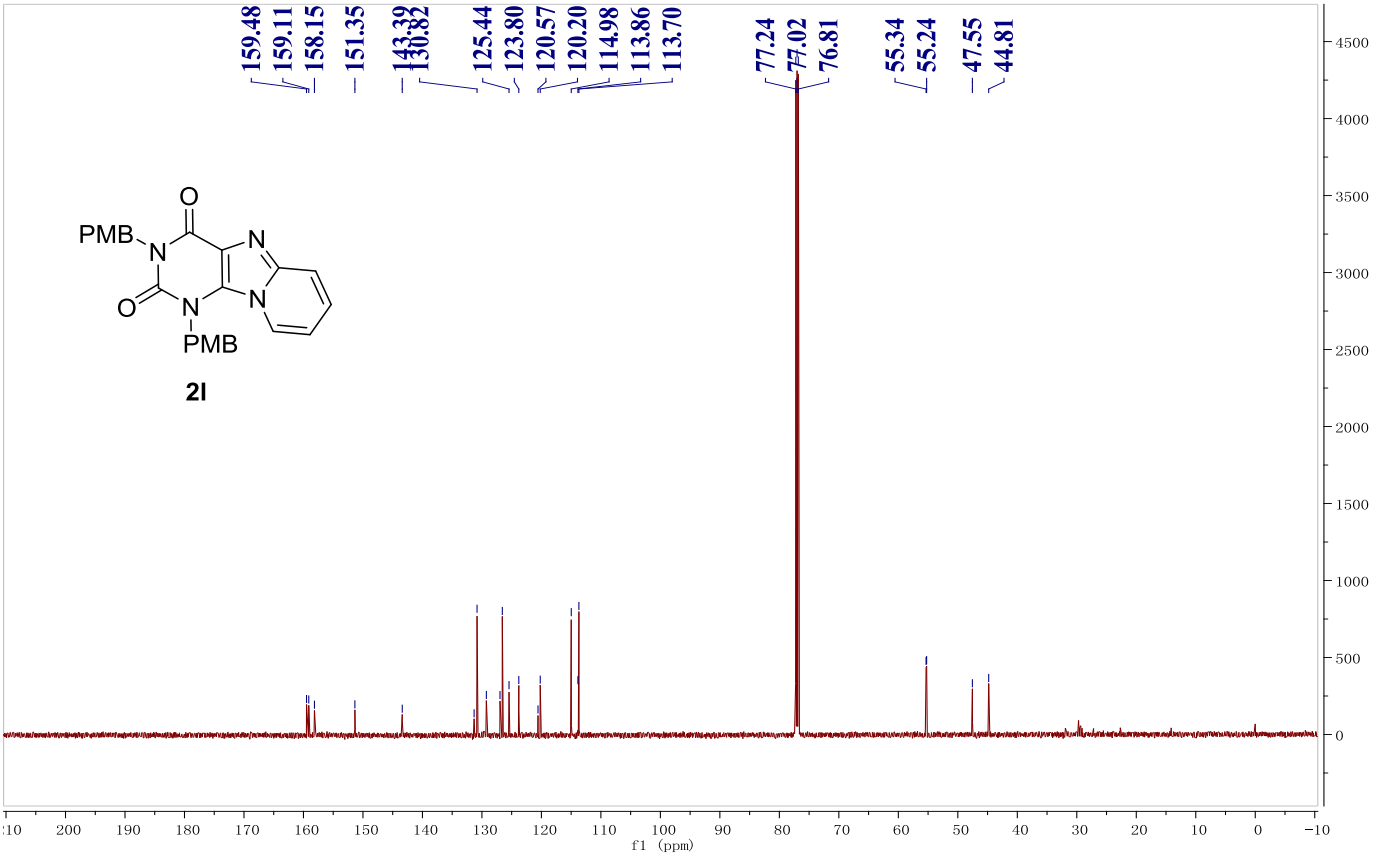
^{13}C NMR Spectrum of 2k at 25 °C ($CDCl_3$, 150 MHz)



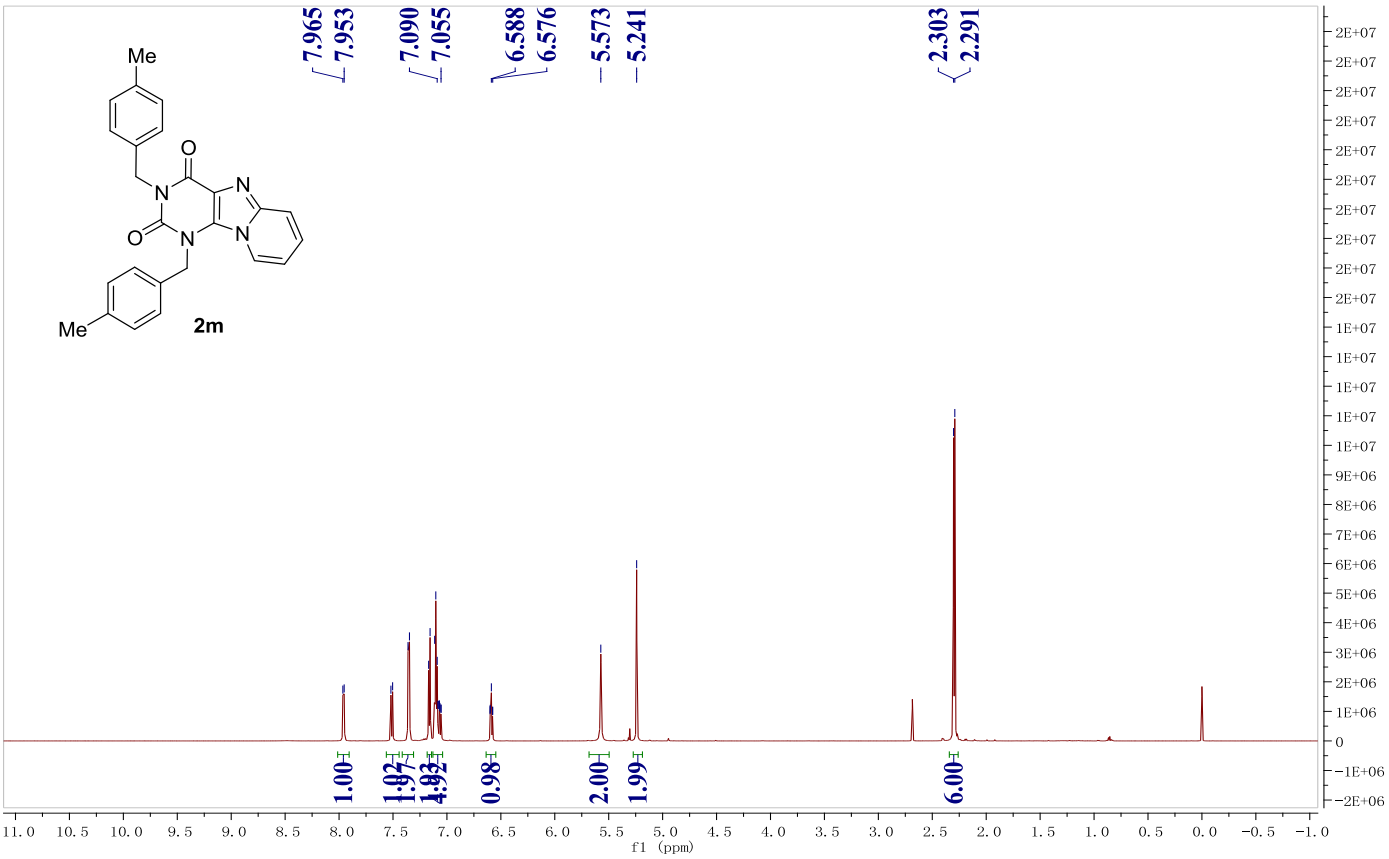
^{1}H NMR Spectrum of 2l at 25 °C ($CDCl_3$, 600 MHz)



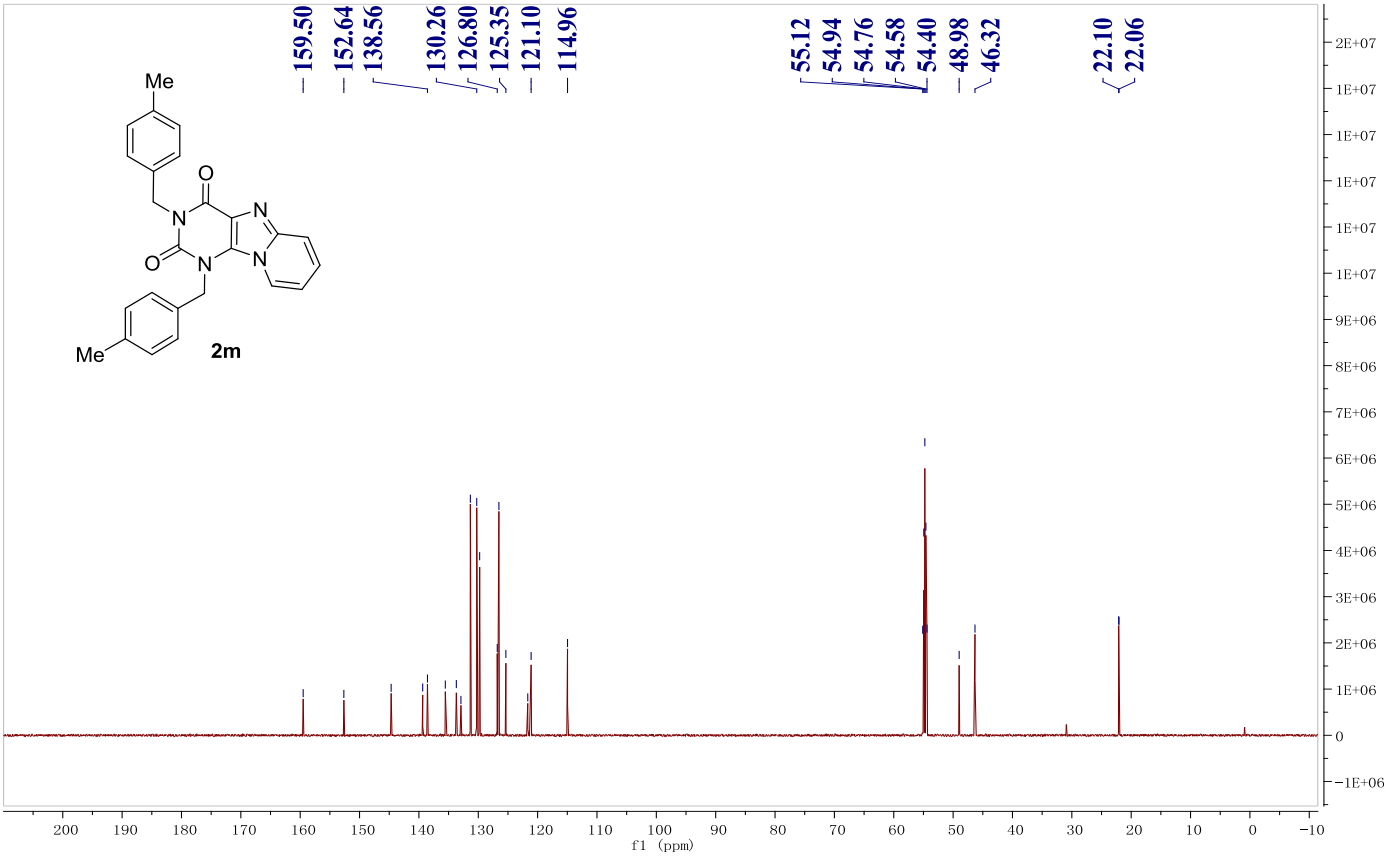
^{13}C NMR Spectrum of 2l at 25 °C ($CDCl_3$, 150 MHz)



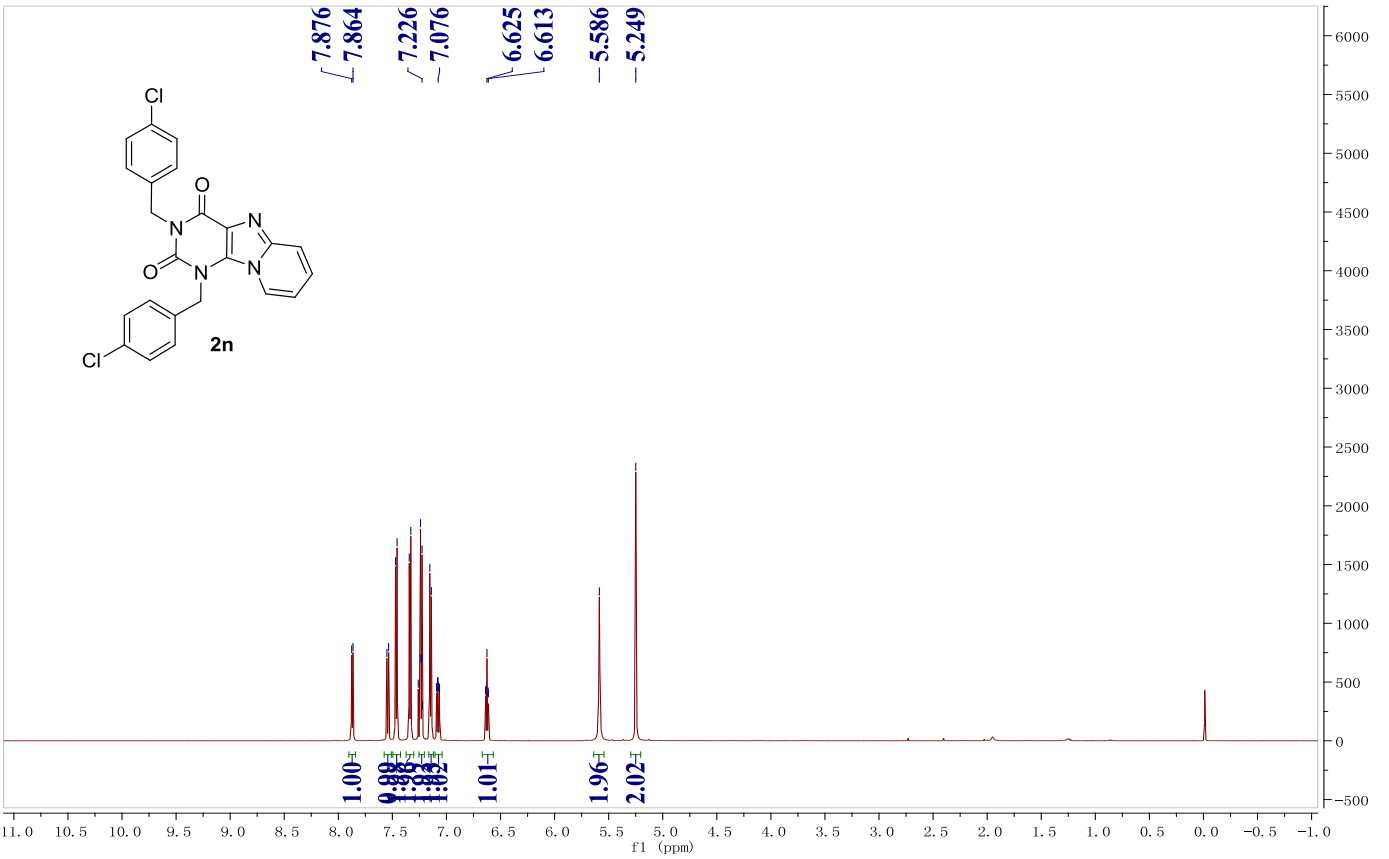
^{1}H NMR Spectrum of 2m at 25 °C ($CDCl_3$, 600 MHz)



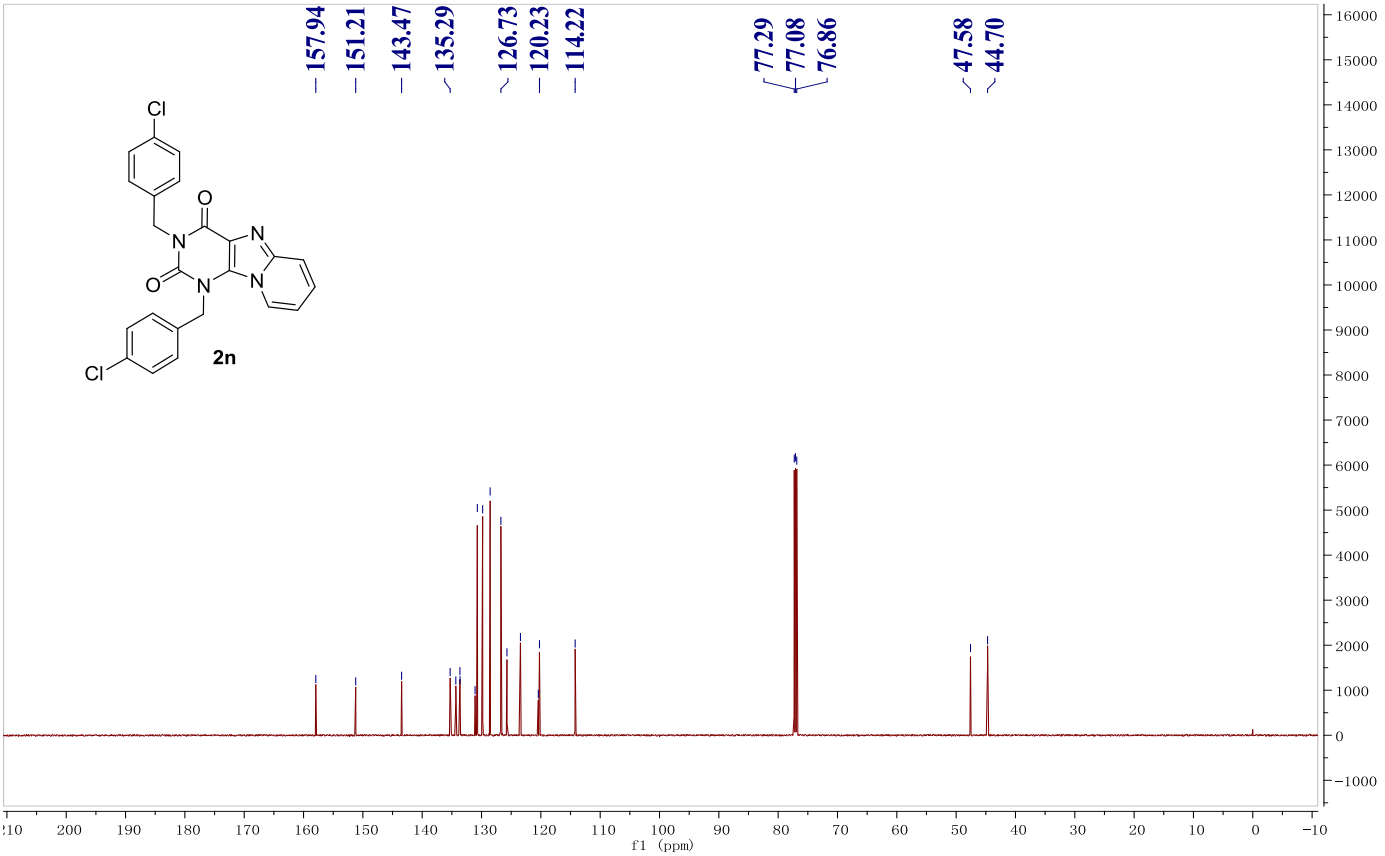
^{13}C NMR Spectrum of 2m at 25 °C ($CDCl_3$, 150 MHz)



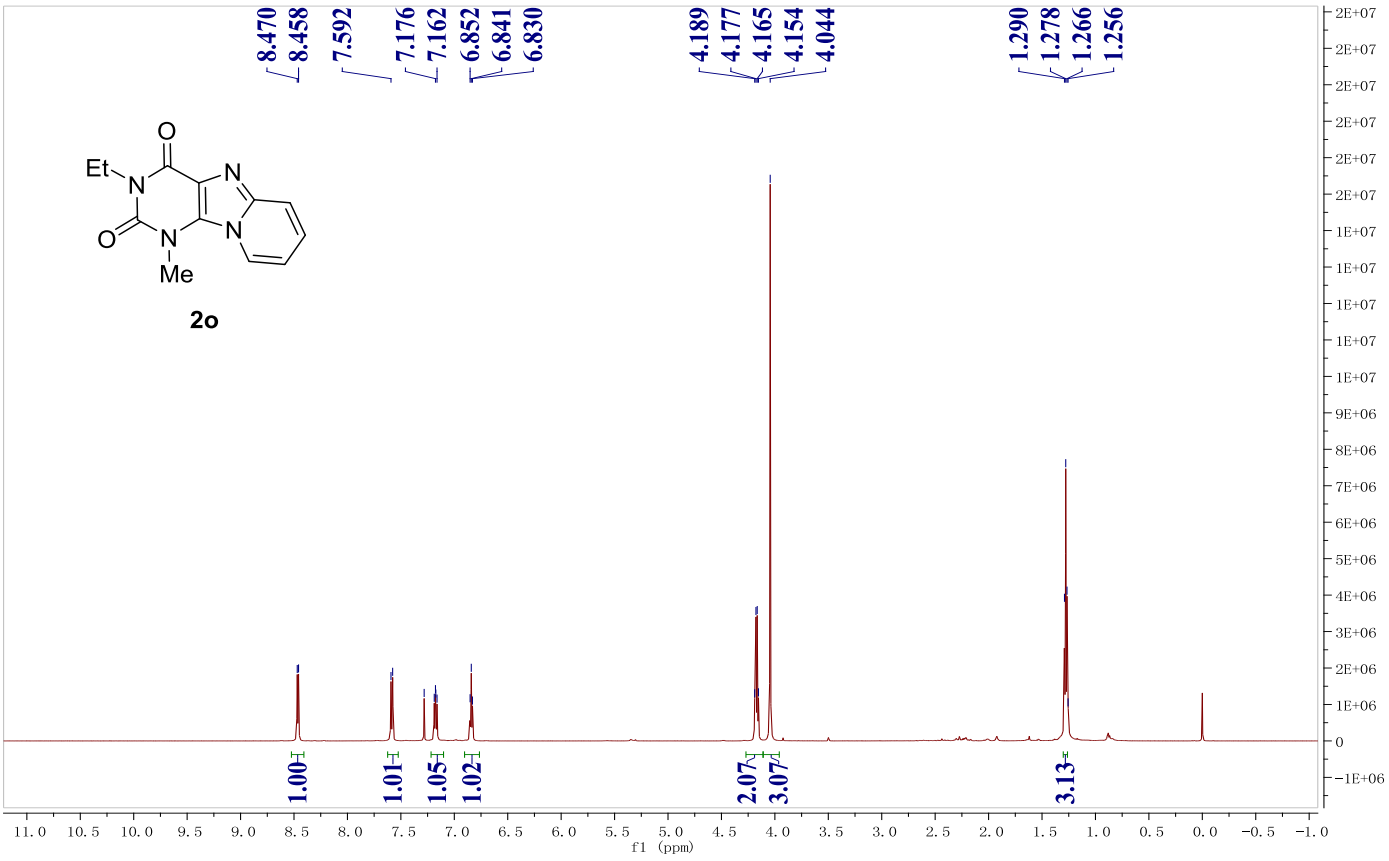
^{1}H NMR Spectrum of 2n at 25 °C ($CDCl_3$, 600 MHz)



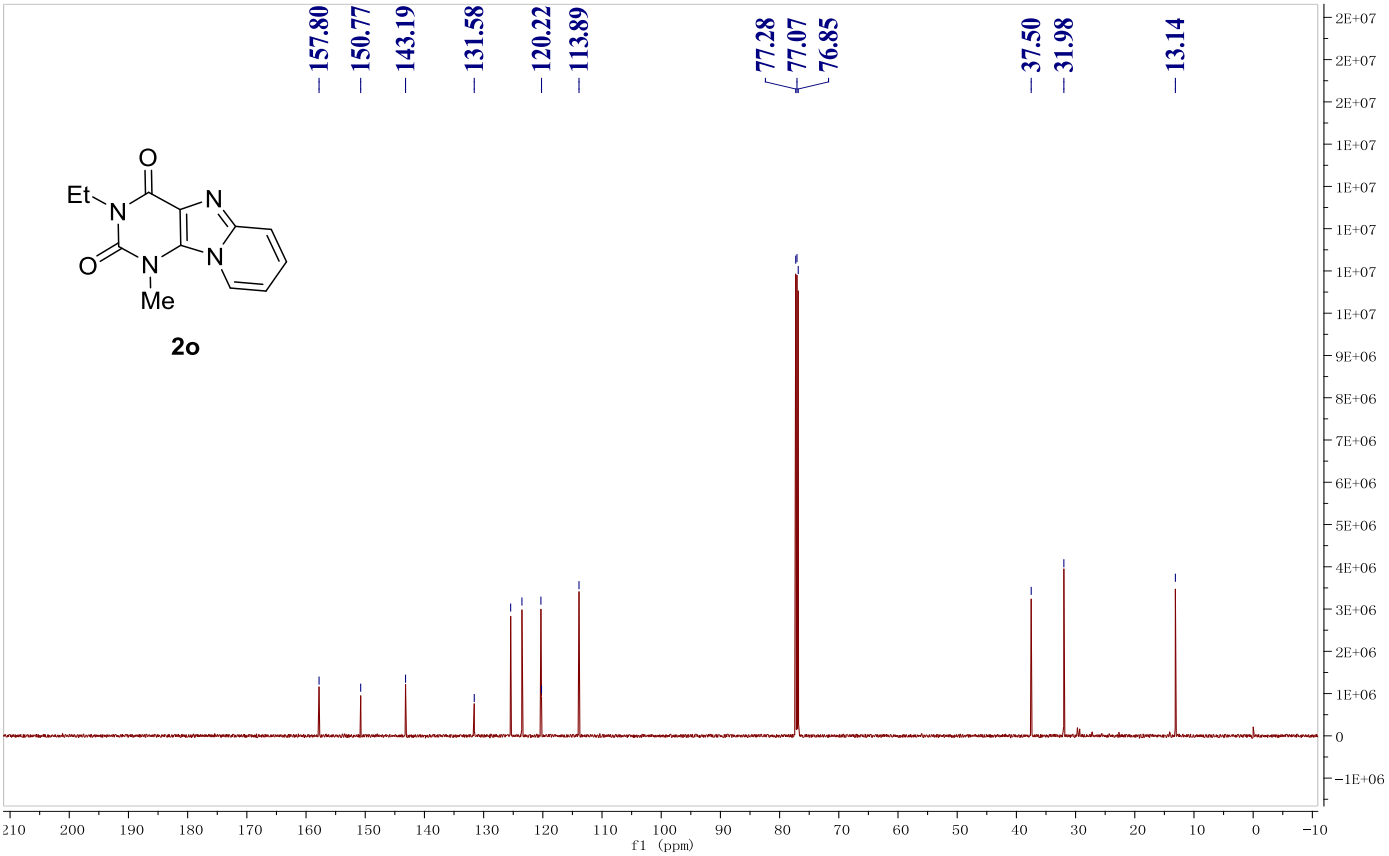
^{13}C NMR Spectrum of 2n at 25 °C ($CDCl_3$, 150 MHz)



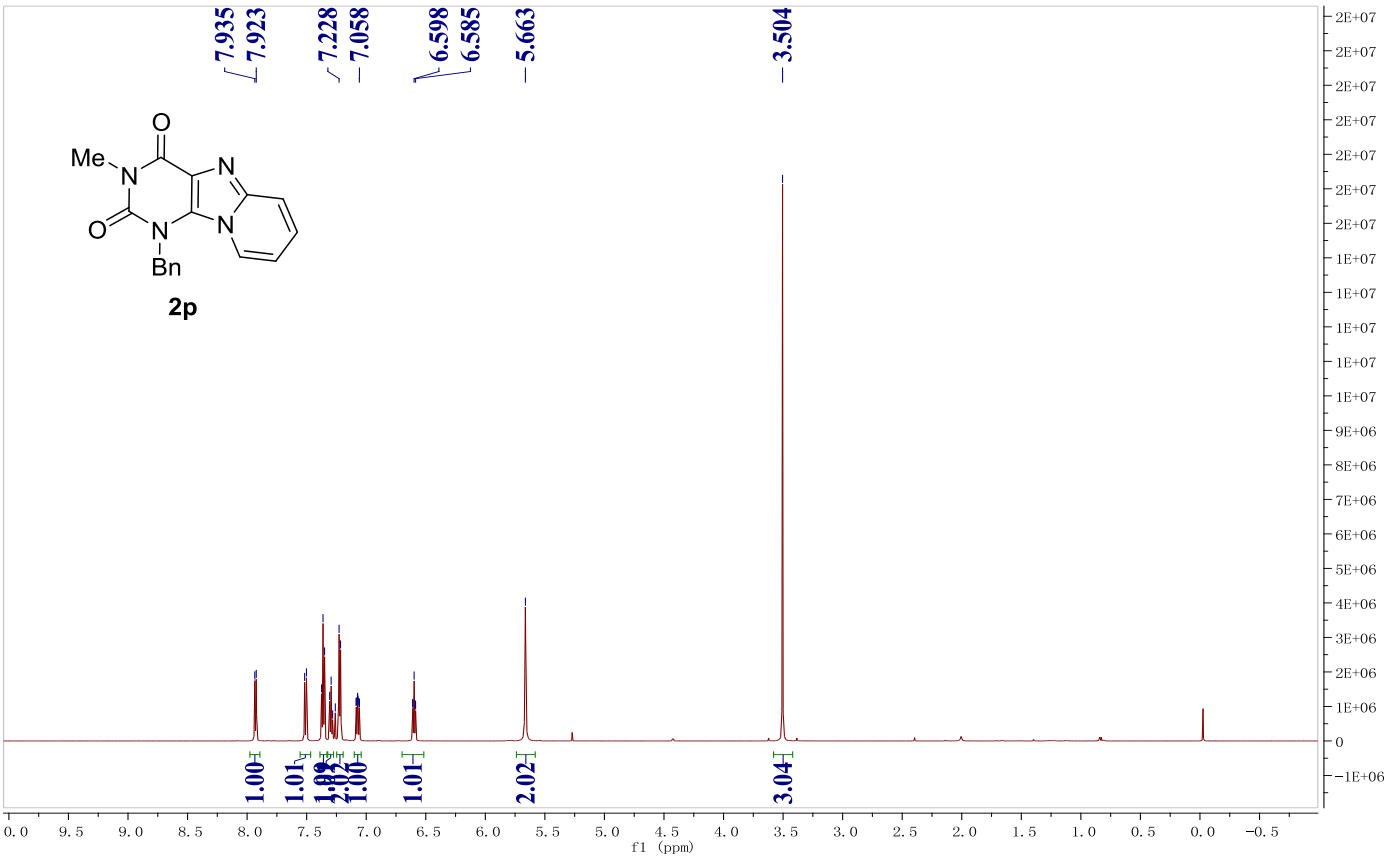
^{1}H NMR Spectrum of 2o at 25 °C ($CDCl_3$, 600 MHz)



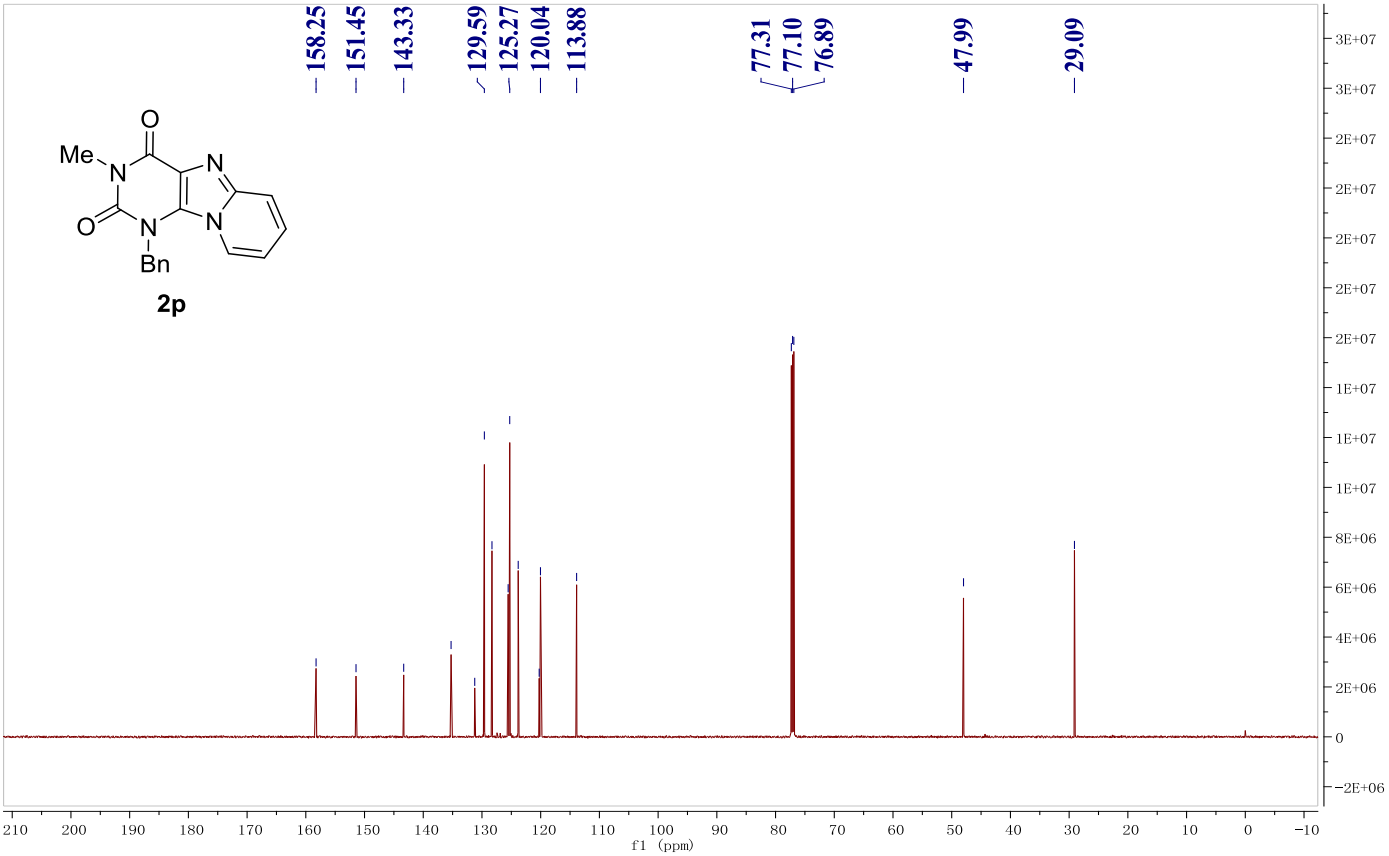
^{13}C NMR Spectrum of 2o at 25 °C ($CDCl_3$, 150 MHz)



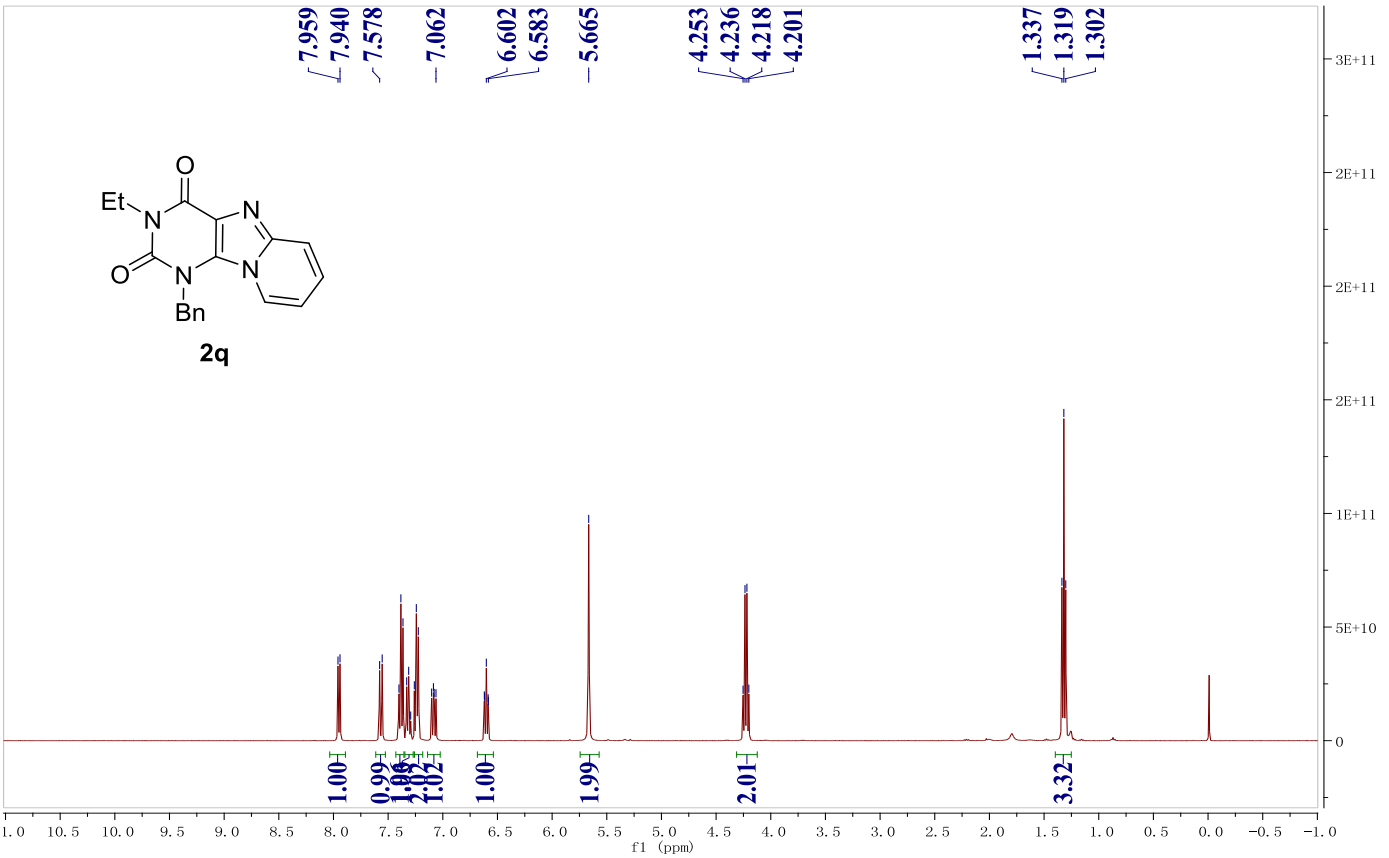
^{1}H NMR Spectrum of 2p at 25 °C ($CDCl_3$, 600 MHz)



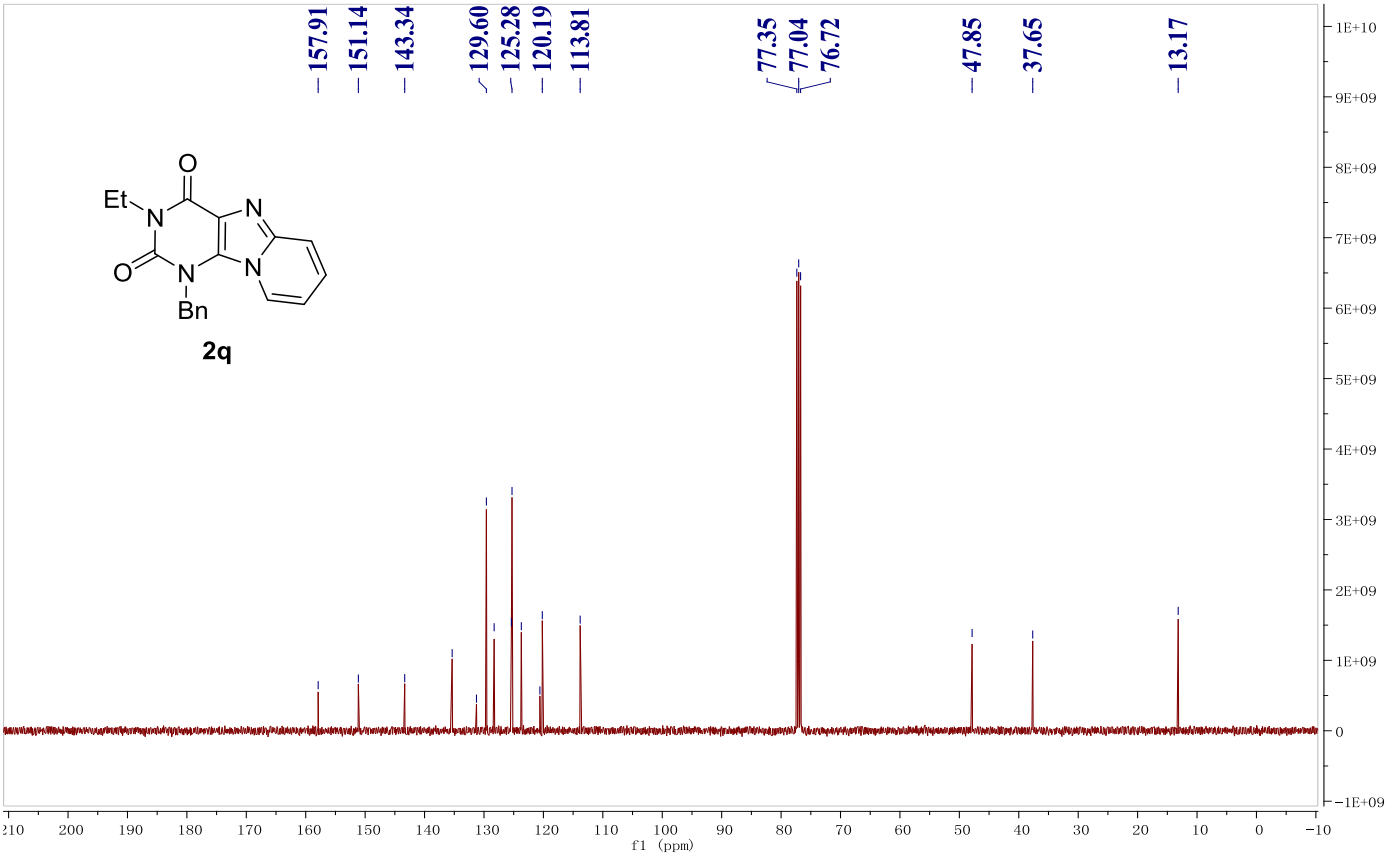
^{13}C NMR Spectrum of 2p at 25 °C ($CDCl_3$, 150 MHz)



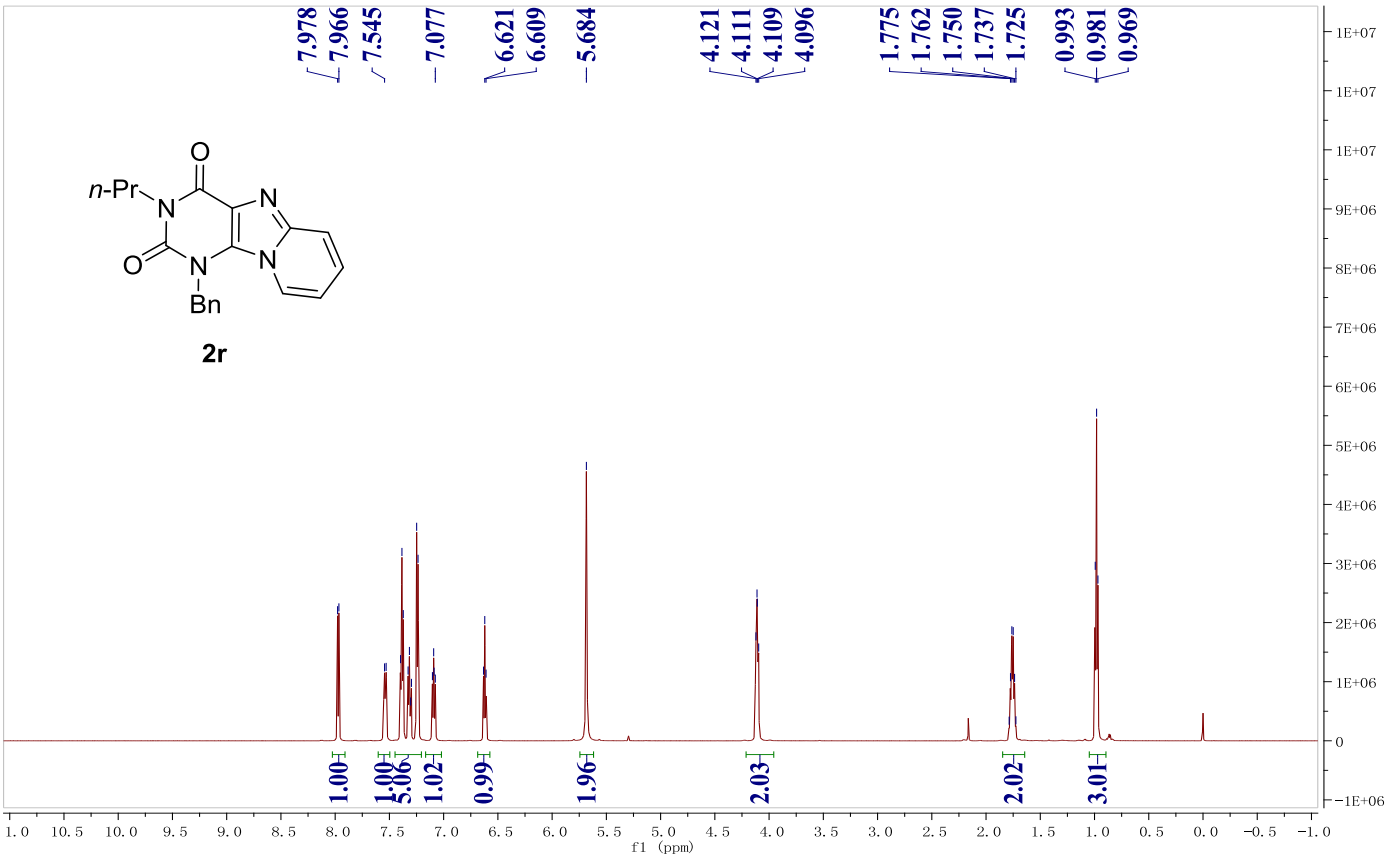
^{1}H NMR Spectrum of 2q at 25 °C ($CDCl_3$, 600 MHz)



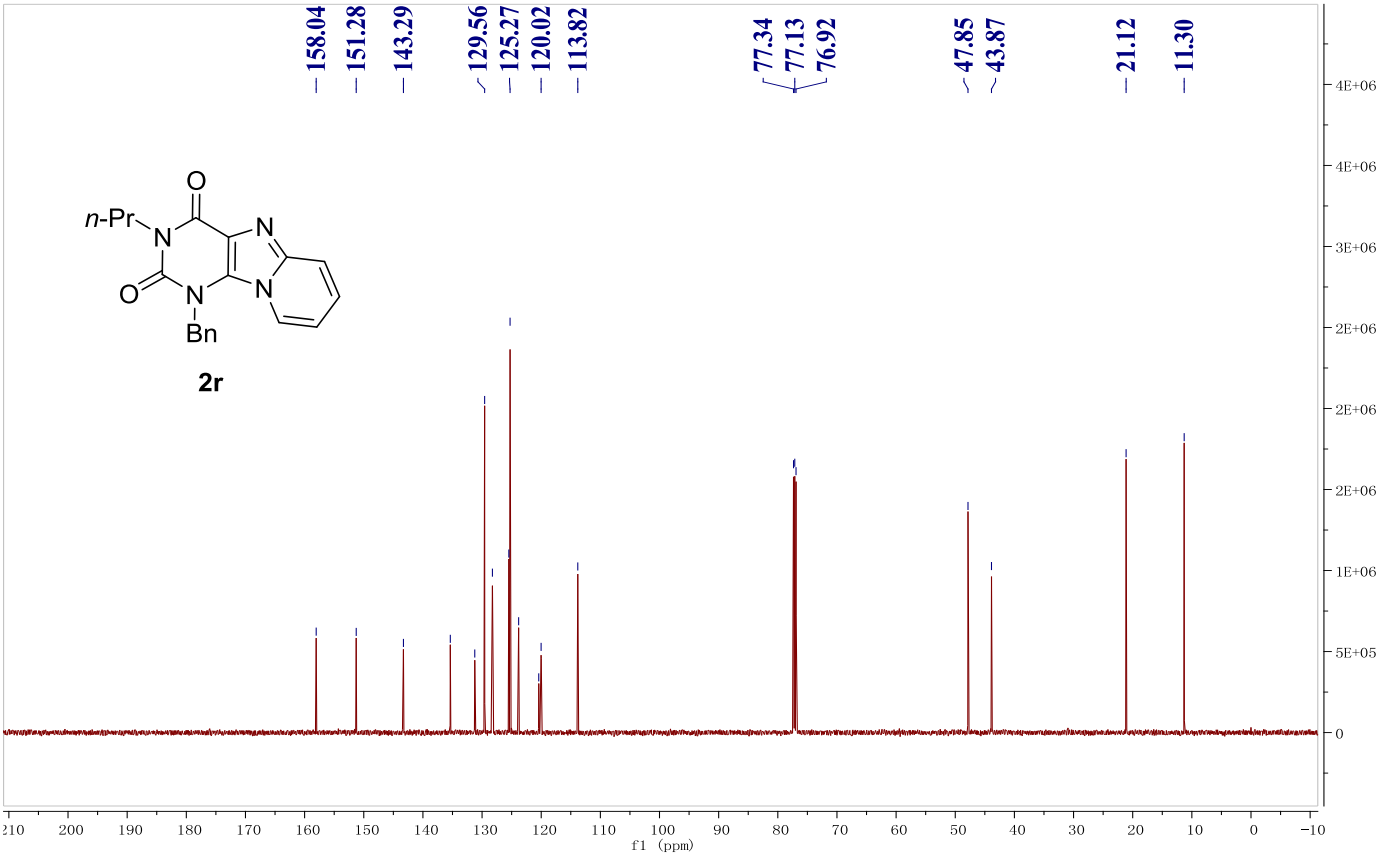
^{13}C NMR Spectrum of 2q at 25 °C ($CDCl_3$, 150 MHz)



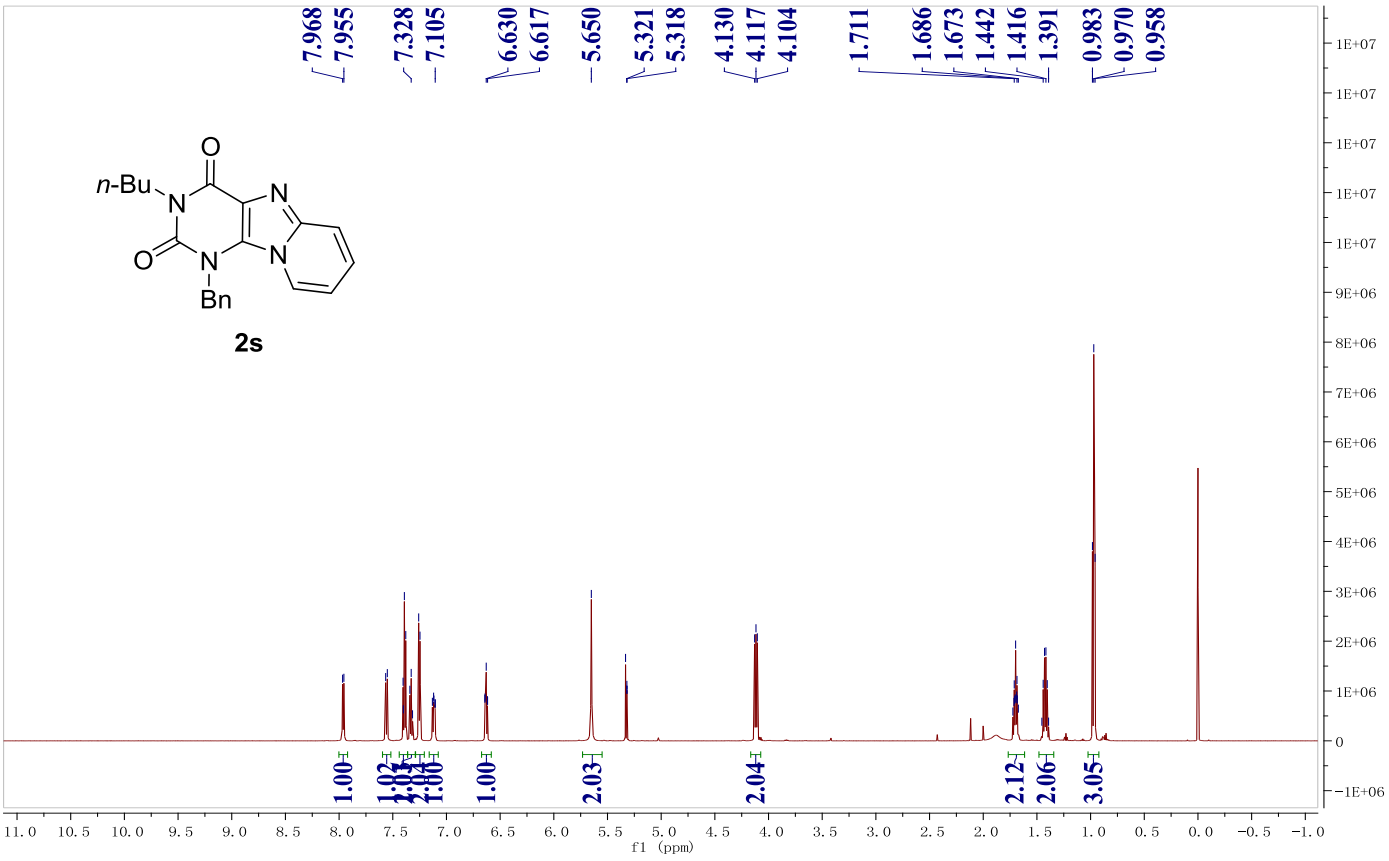
^{1}H NMR Spectrum of 2r at 25 °C ($CDCl_3$, 600 MHz)



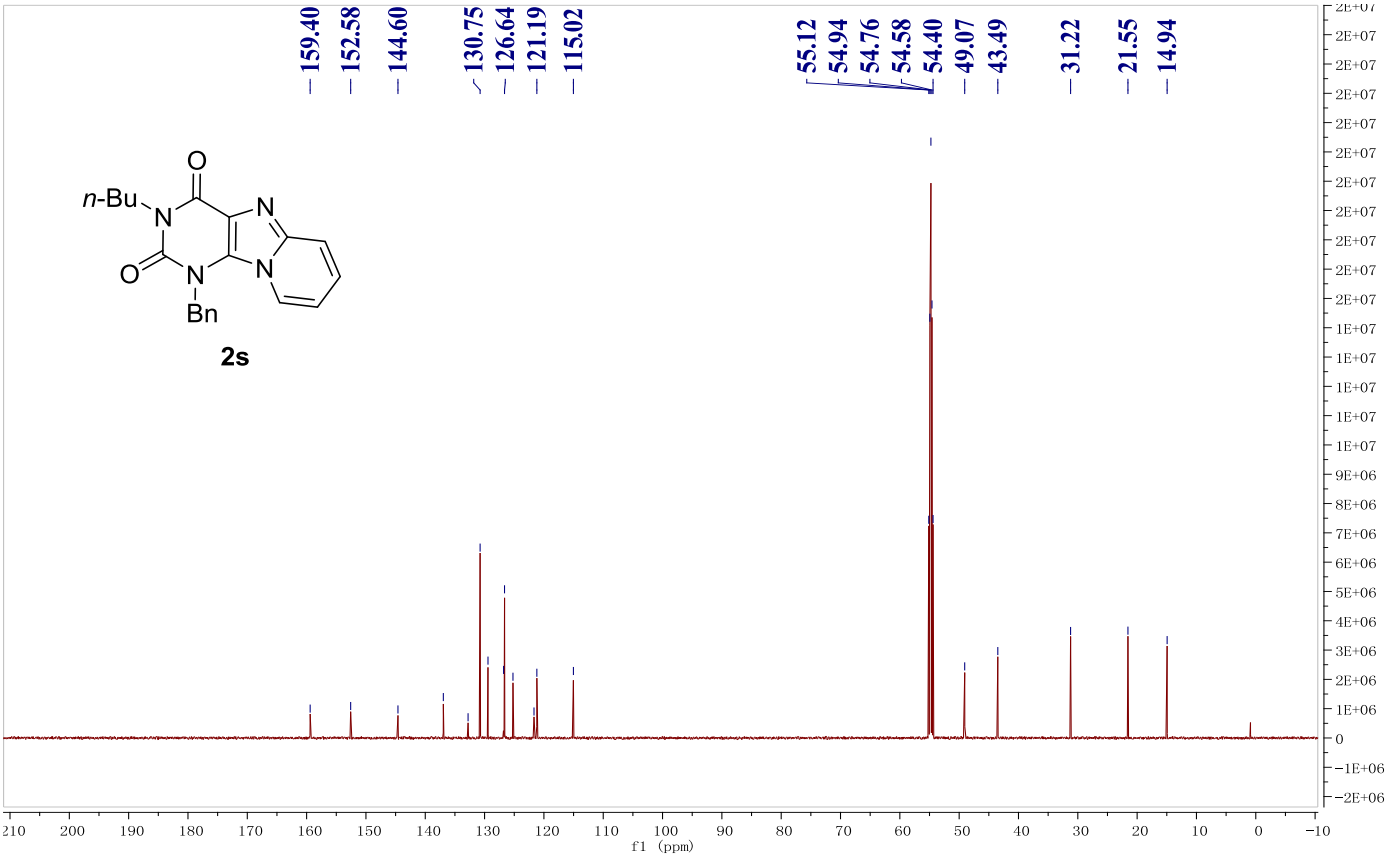
^{13}C NMR Spectrum of 2r at 25 °C ($CDCl_3$, 150 MHz)



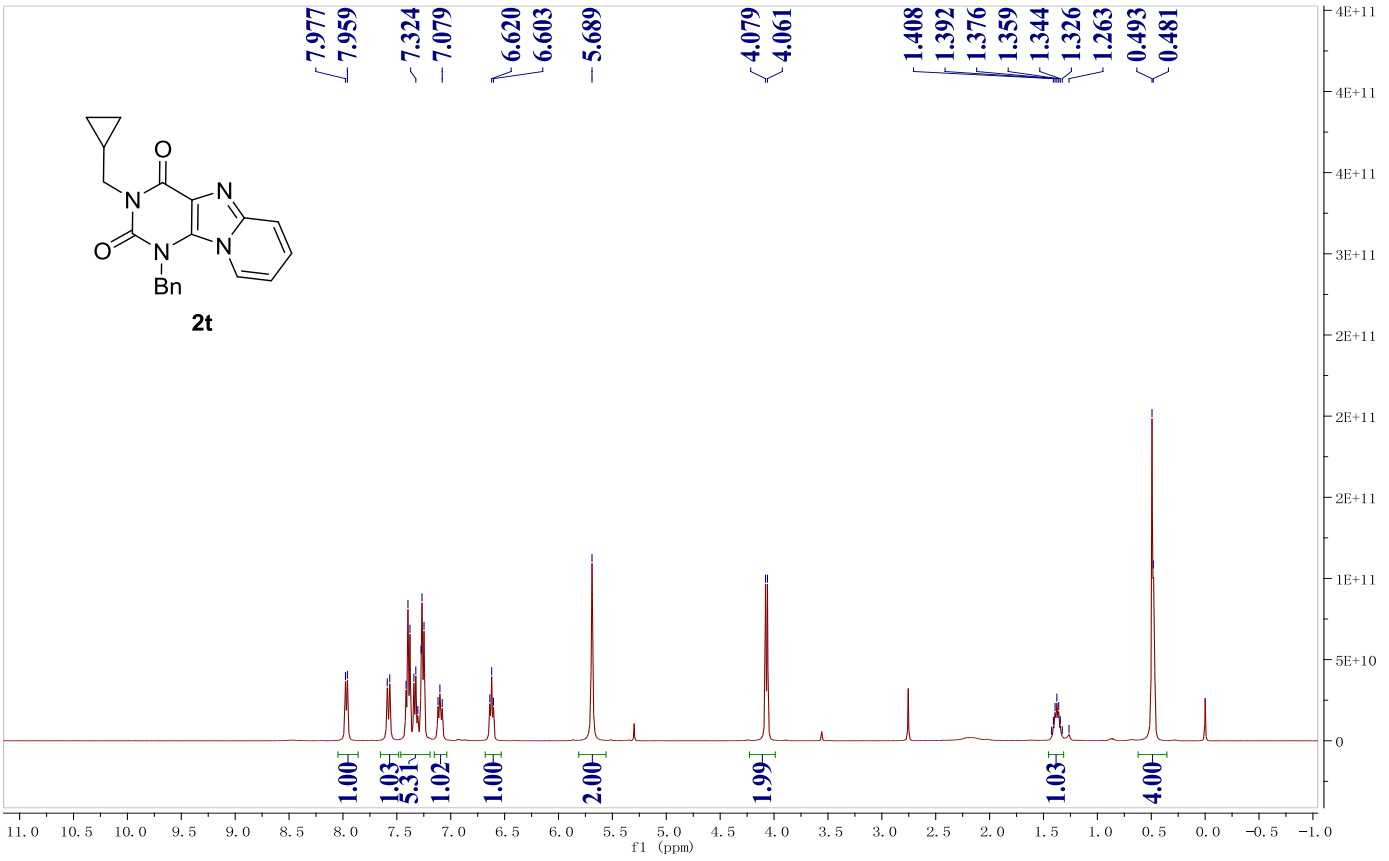
^{1}H NMR Spectrum of 2s at 25 °C (CD_2Cl_2, 600 MHz)



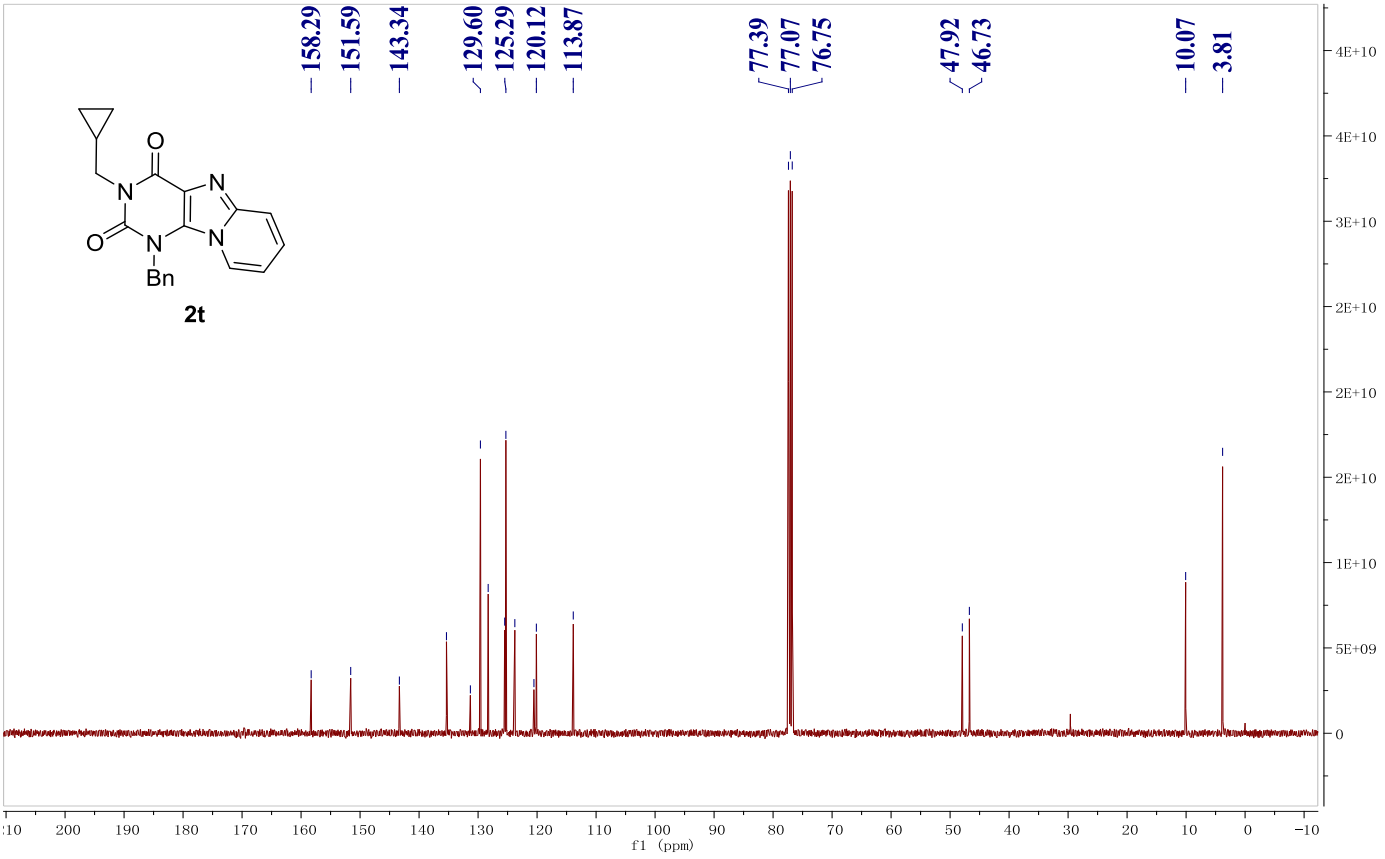
^{13}C NMR Spectrum of 2s at 25 °C (CD_2Cl_2, 150 MHz)



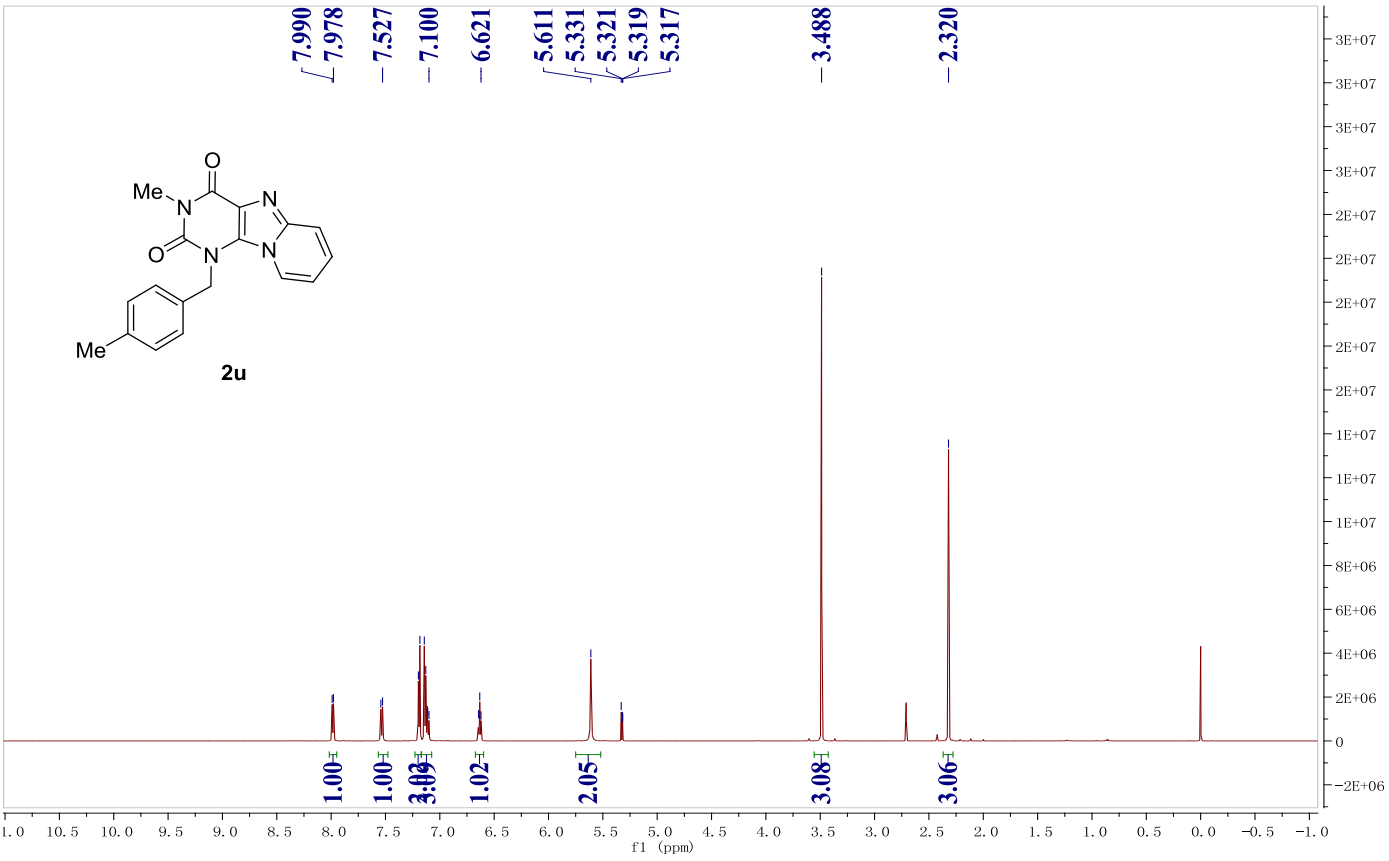
^{1}H NMR Spectrum of 2t at 25 °C ($CDCl_3$, 400 MHz)



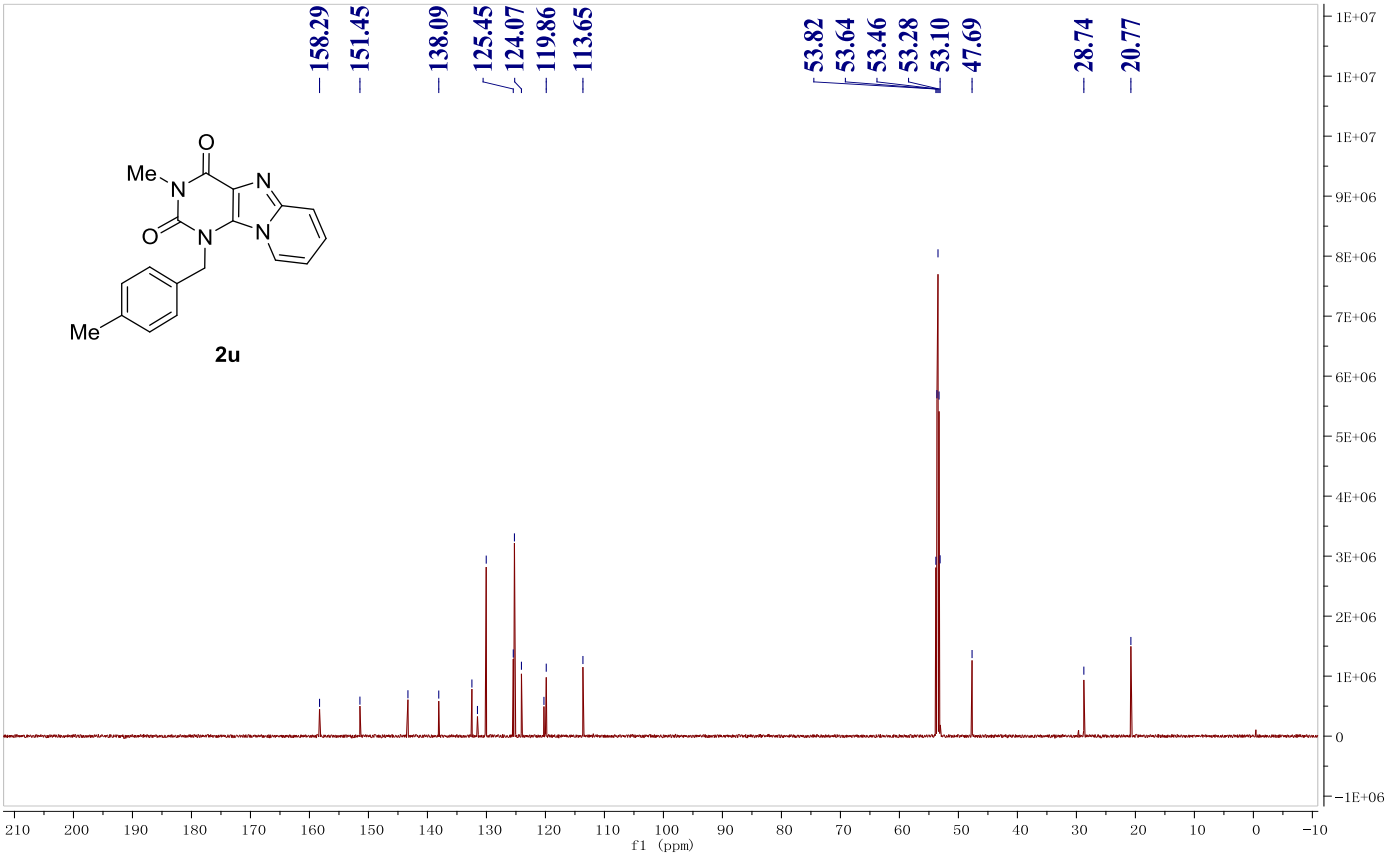
^{13}C NMR Spectrum of 2t at 25 °C ($CDCl_3$, 100 MHz)



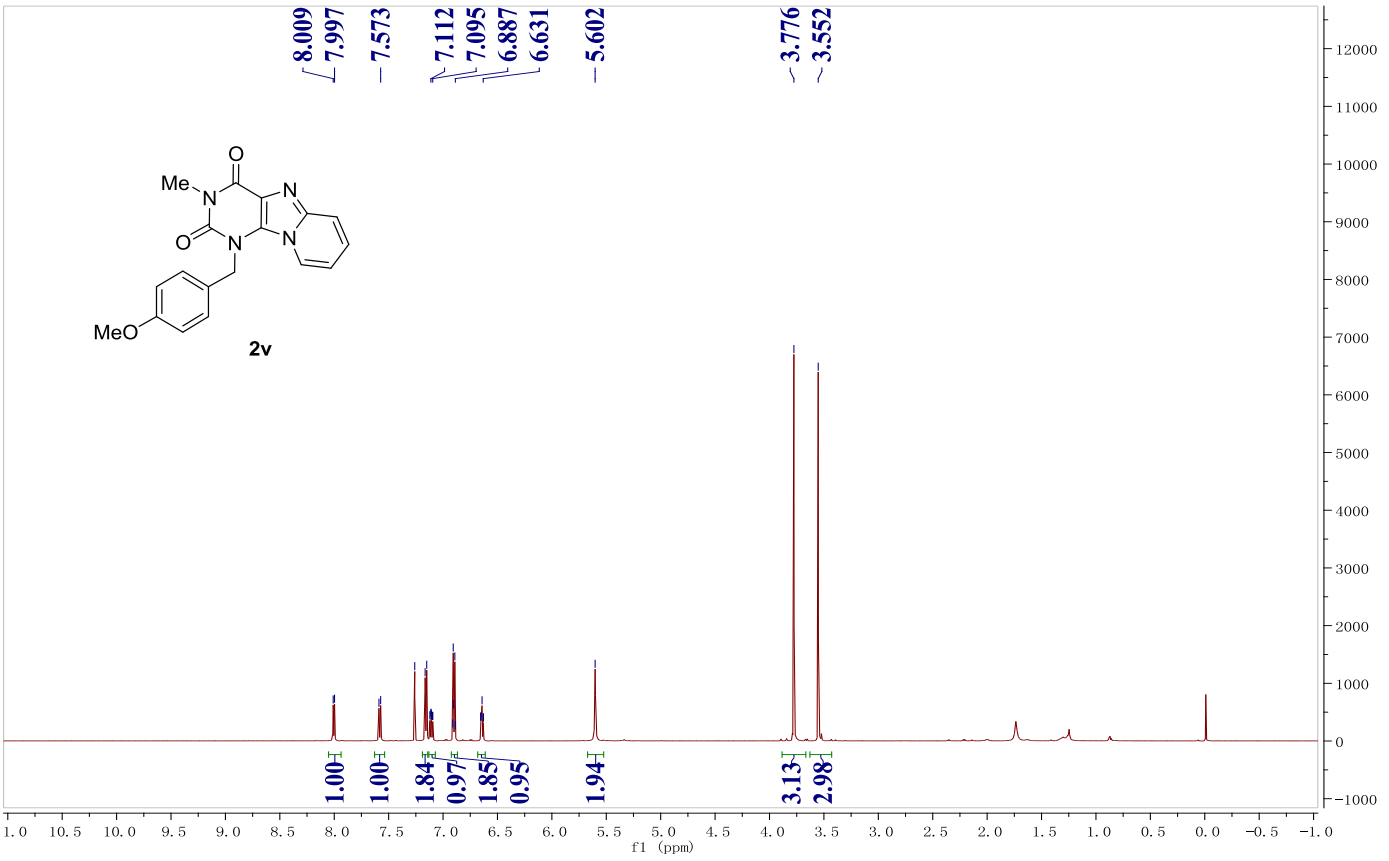
^{1}H NMR Spectrum of 2u at 25 °C (CD_2Cl_2, 600 MHz)



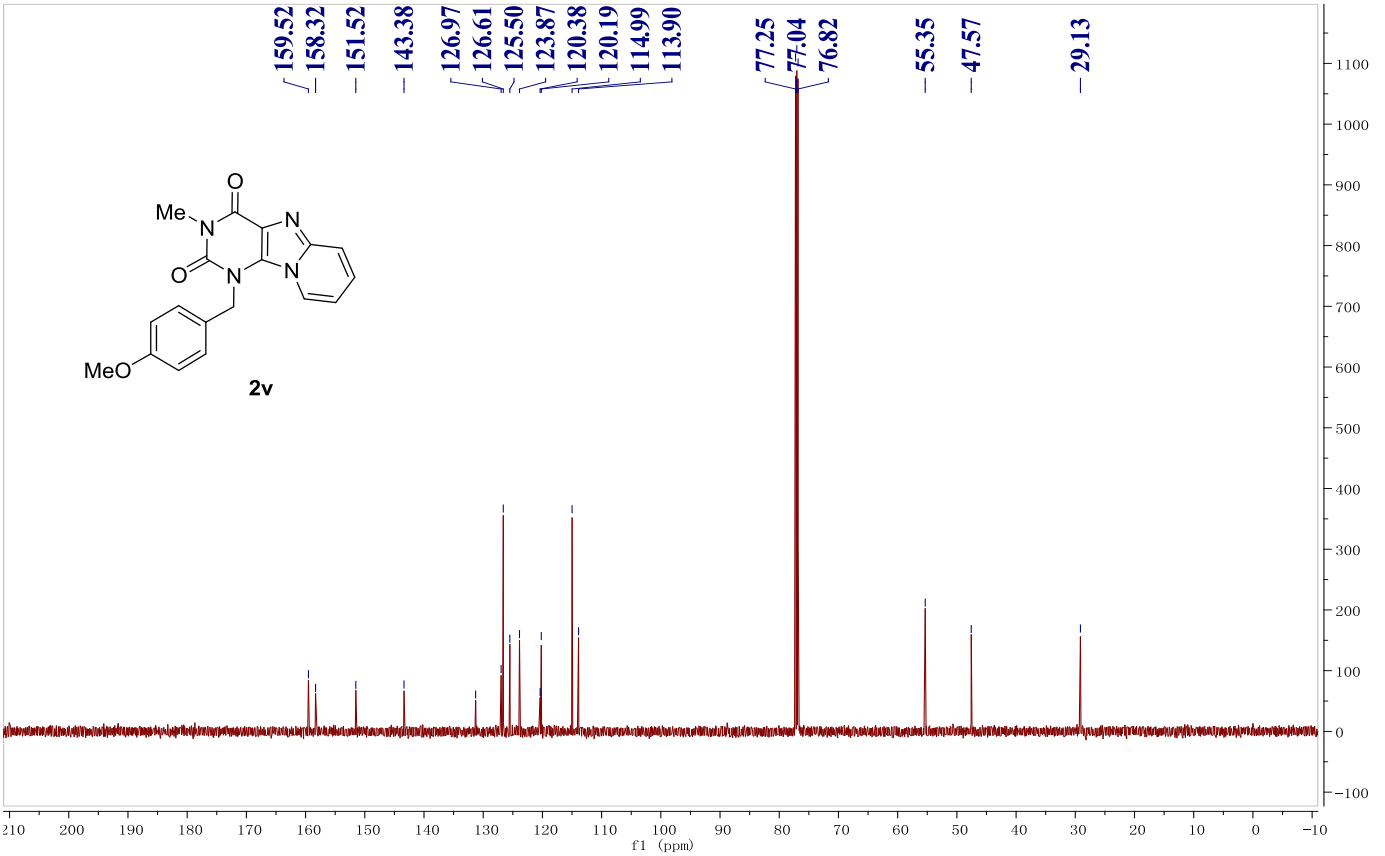
^{13}C NMR Spectrum of 2u at 25 °C (CD_2Cl_2, 150 MHz)



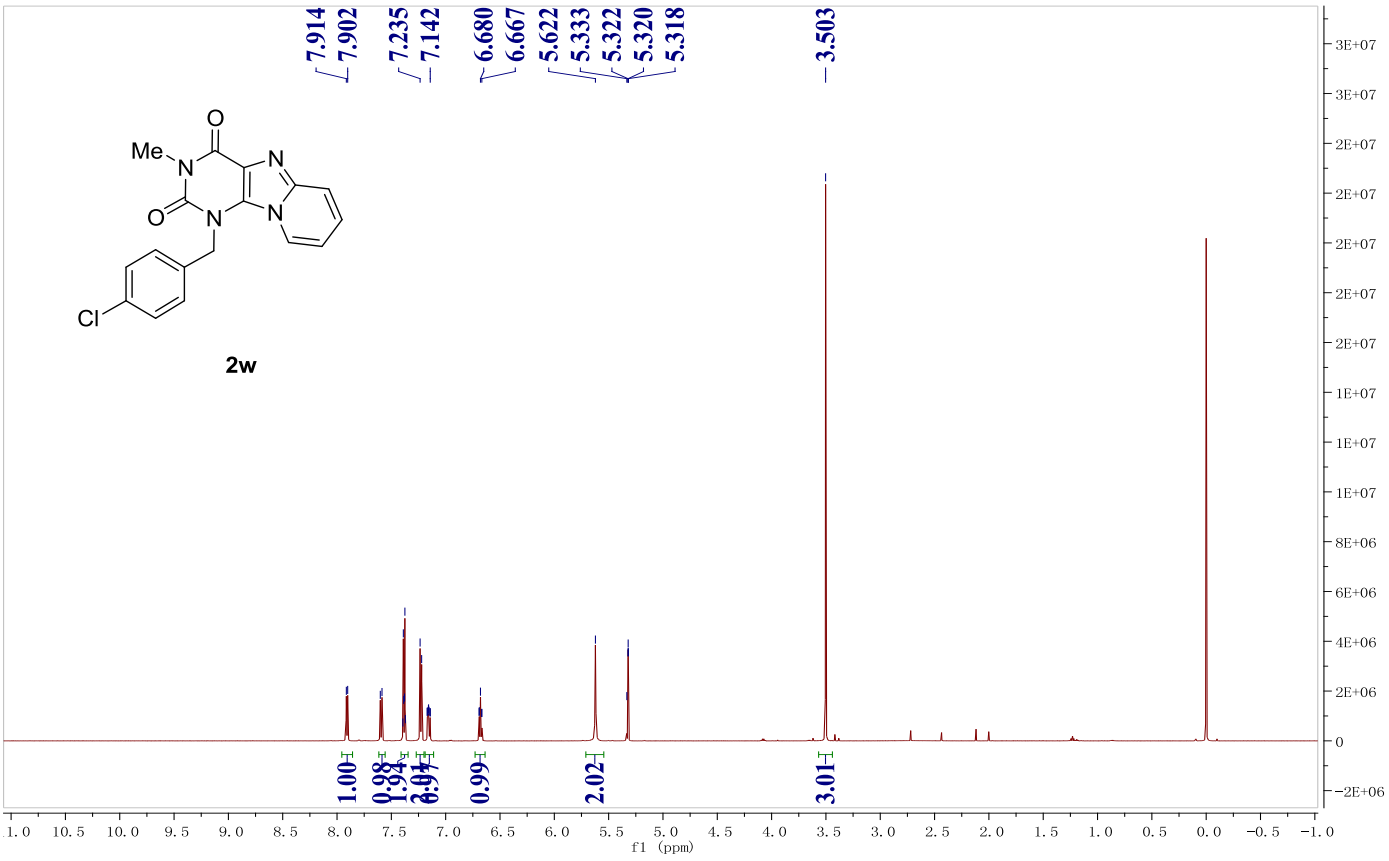
^{1}H NMR Spectrum of 2v at 25 °C ($CDCl_3$, 600 MHz)



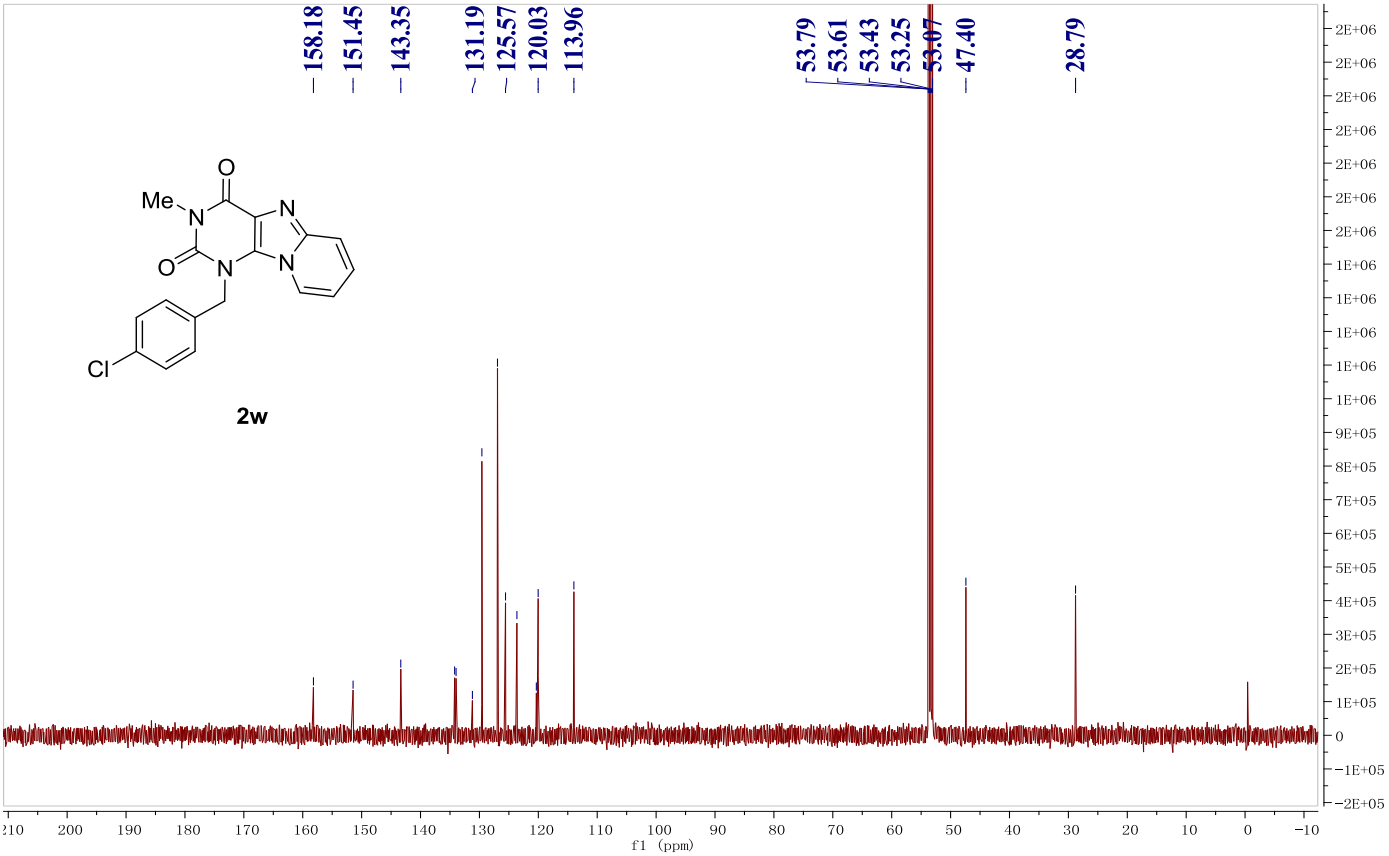
^{13}C NMR Spectrum of 2v at 25 °C ($CDCl_3$, 150 MHz)



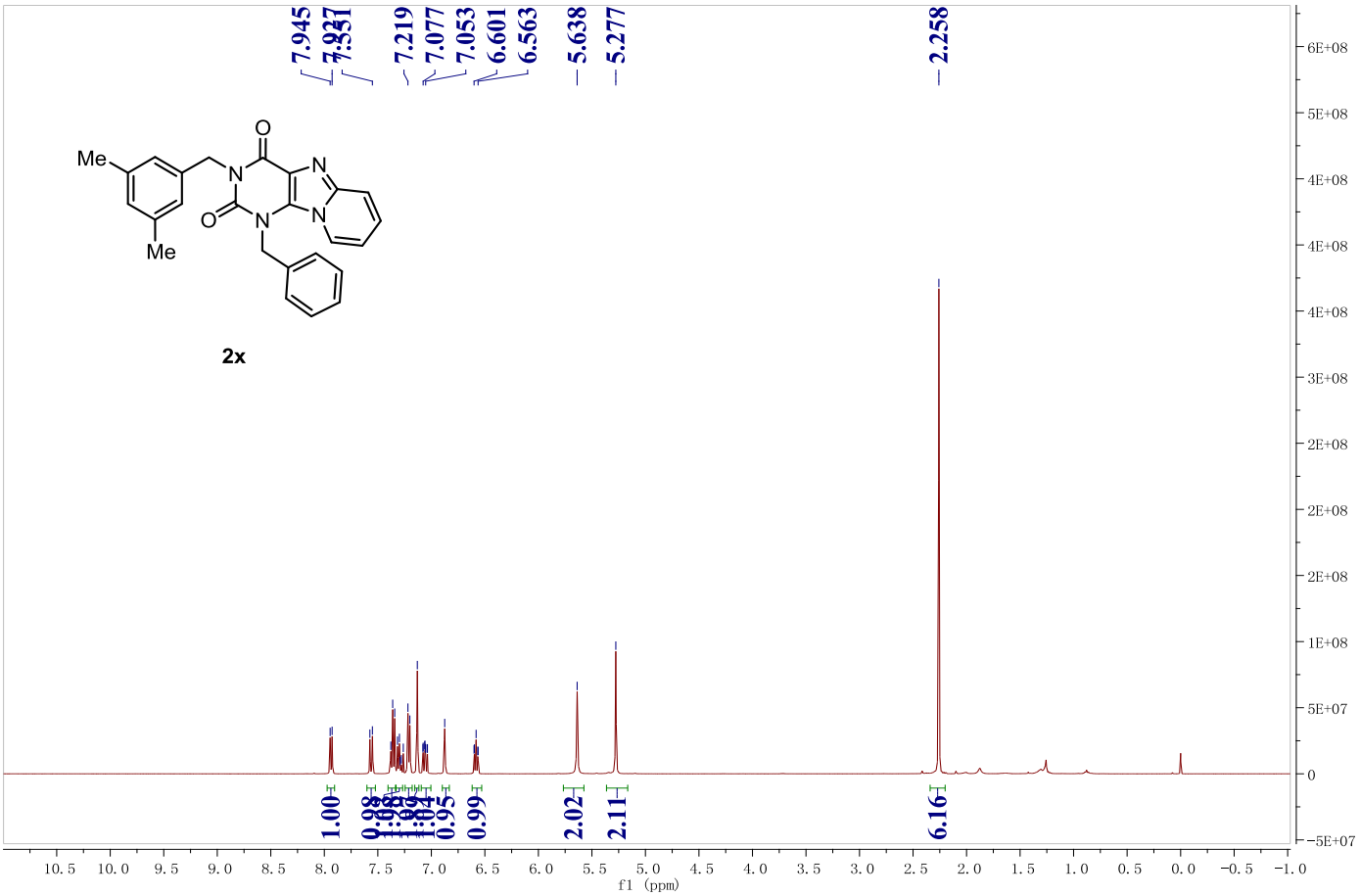
^{1}H NMR Spectrum of 2w at 25 °C ($CDCl_3$, 600 MHz)



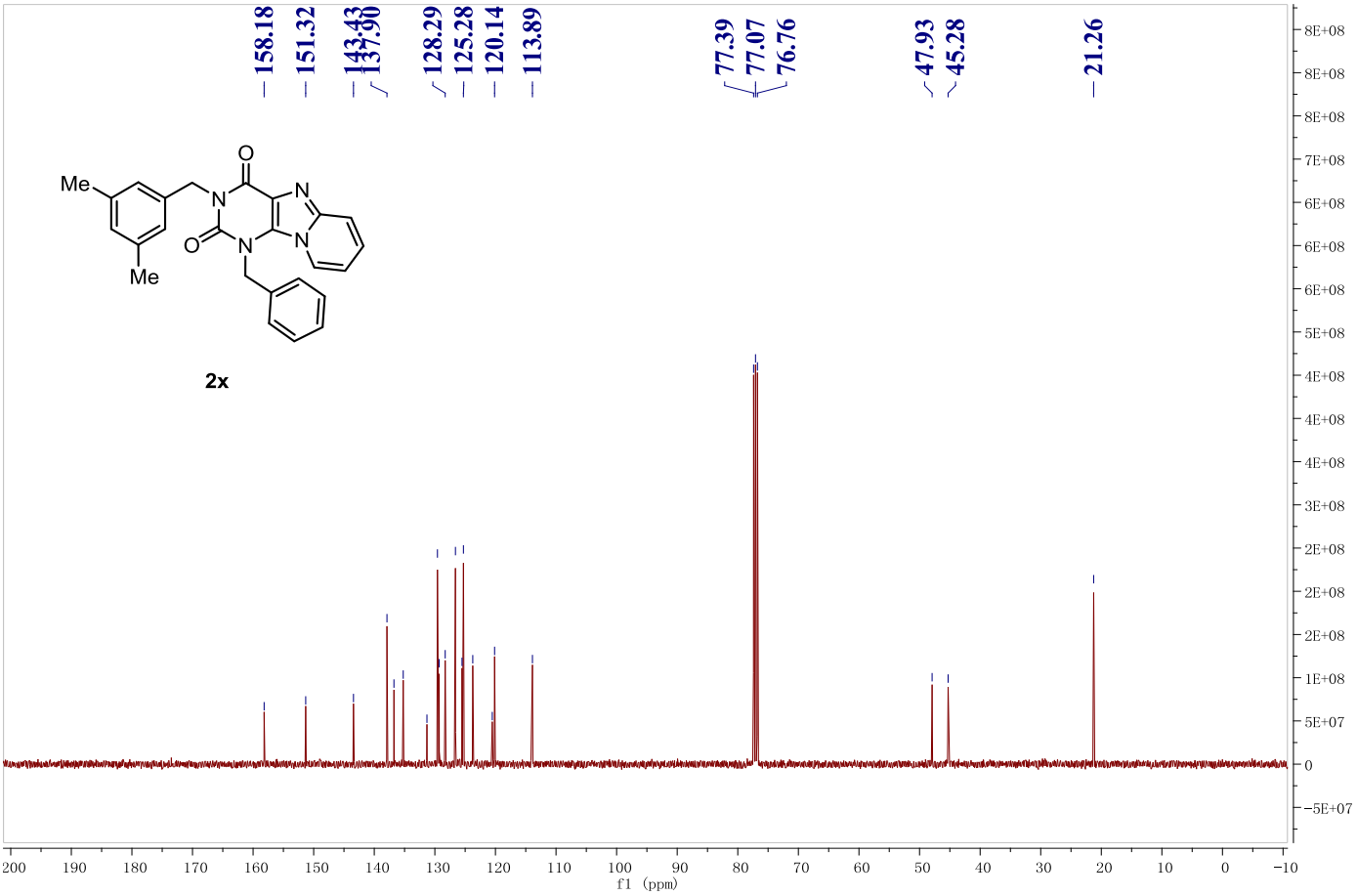
^{13}C NMR Spectrum of 2w at 25 °C ($CDCl_3$, 150 MHz)



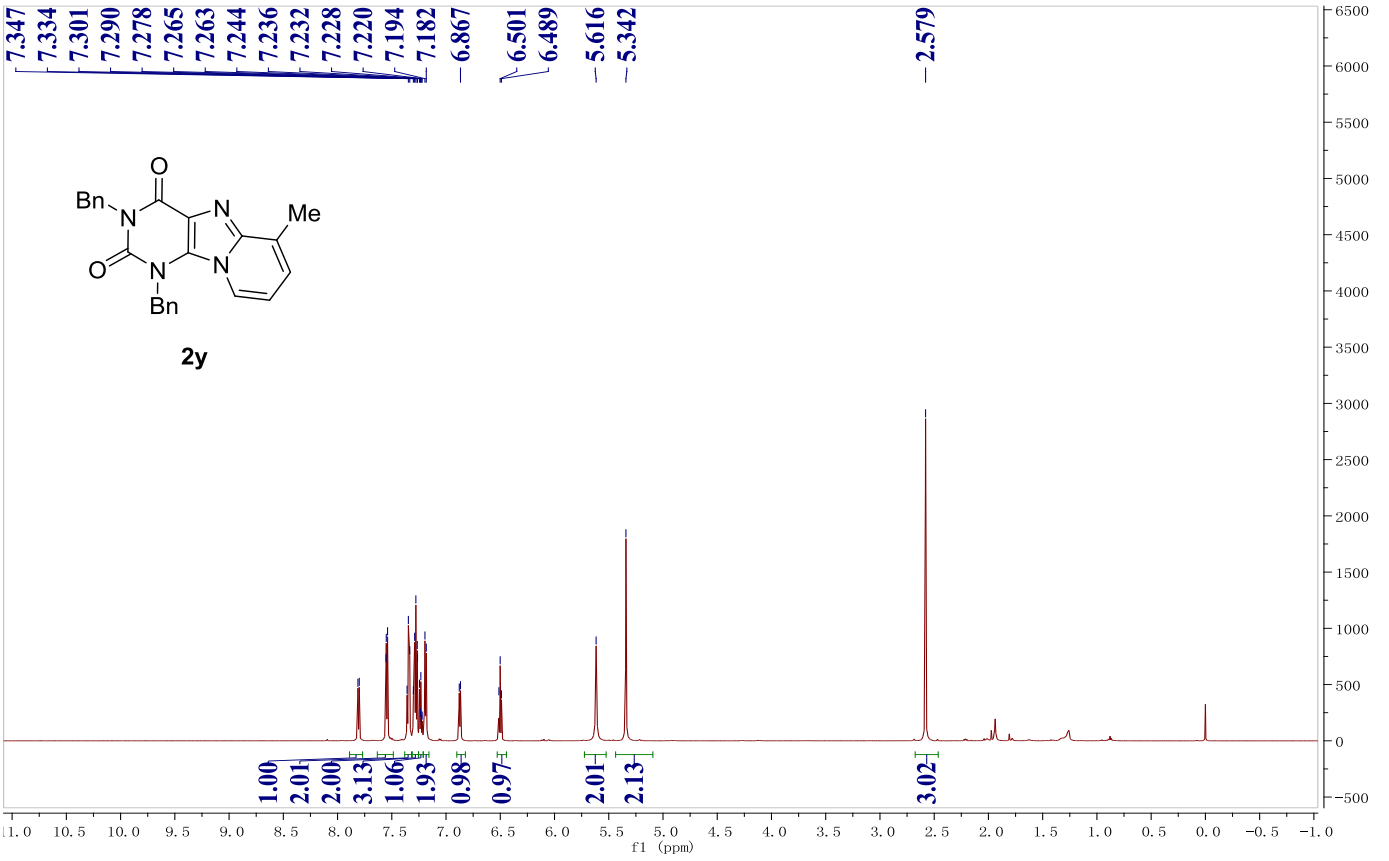
^{1}H NMR Spectrum of 2x at 25 °C ($CDCl_3$, 400 MHz)



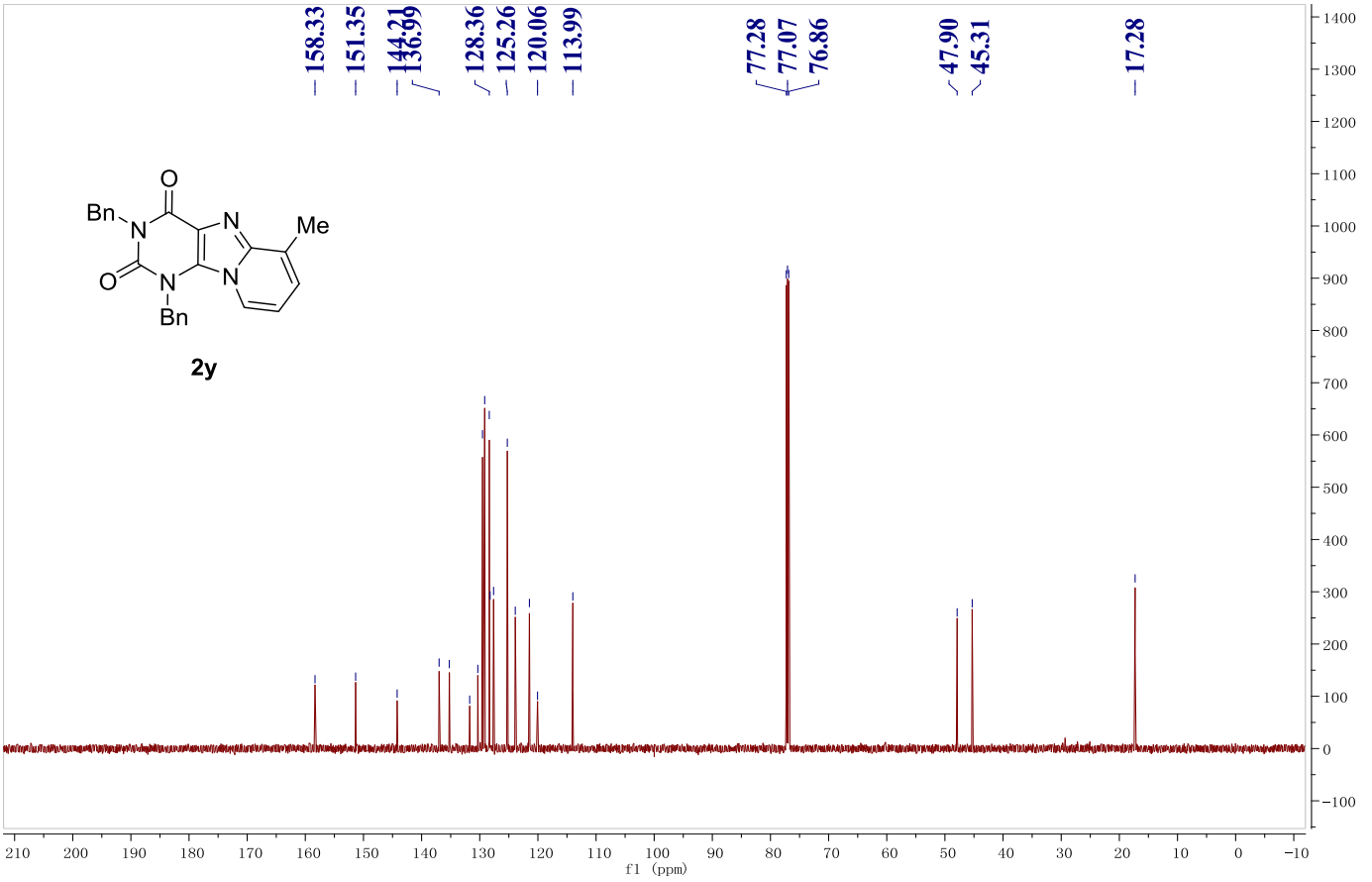
^{13}C NMR Spectrum of 2x at 25 °C ($CDCl_3$, 100 MHz)



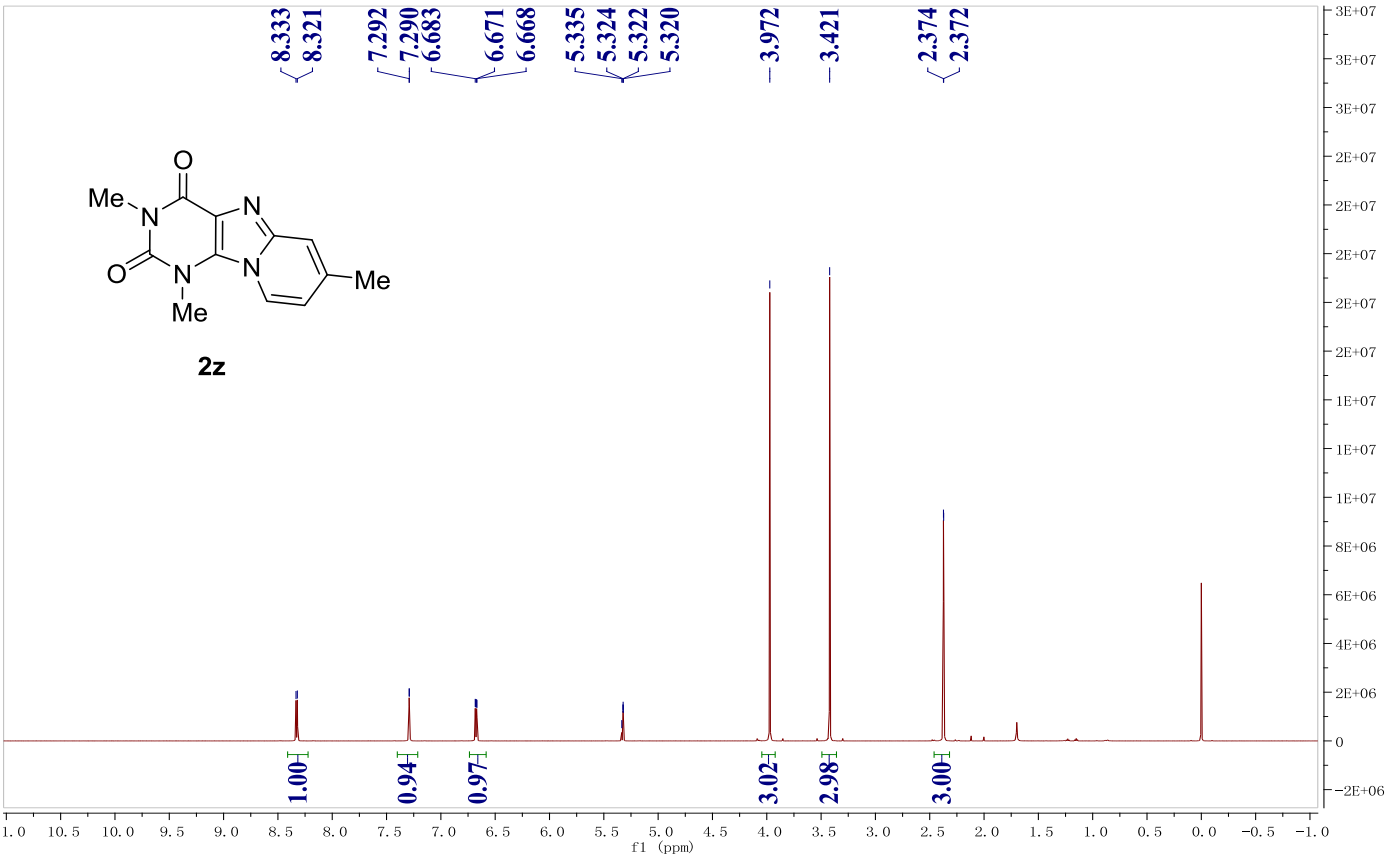
^{1}H NMR Spectrum of 2y at 25 °C ($CDCl_3$, 600 MHz)



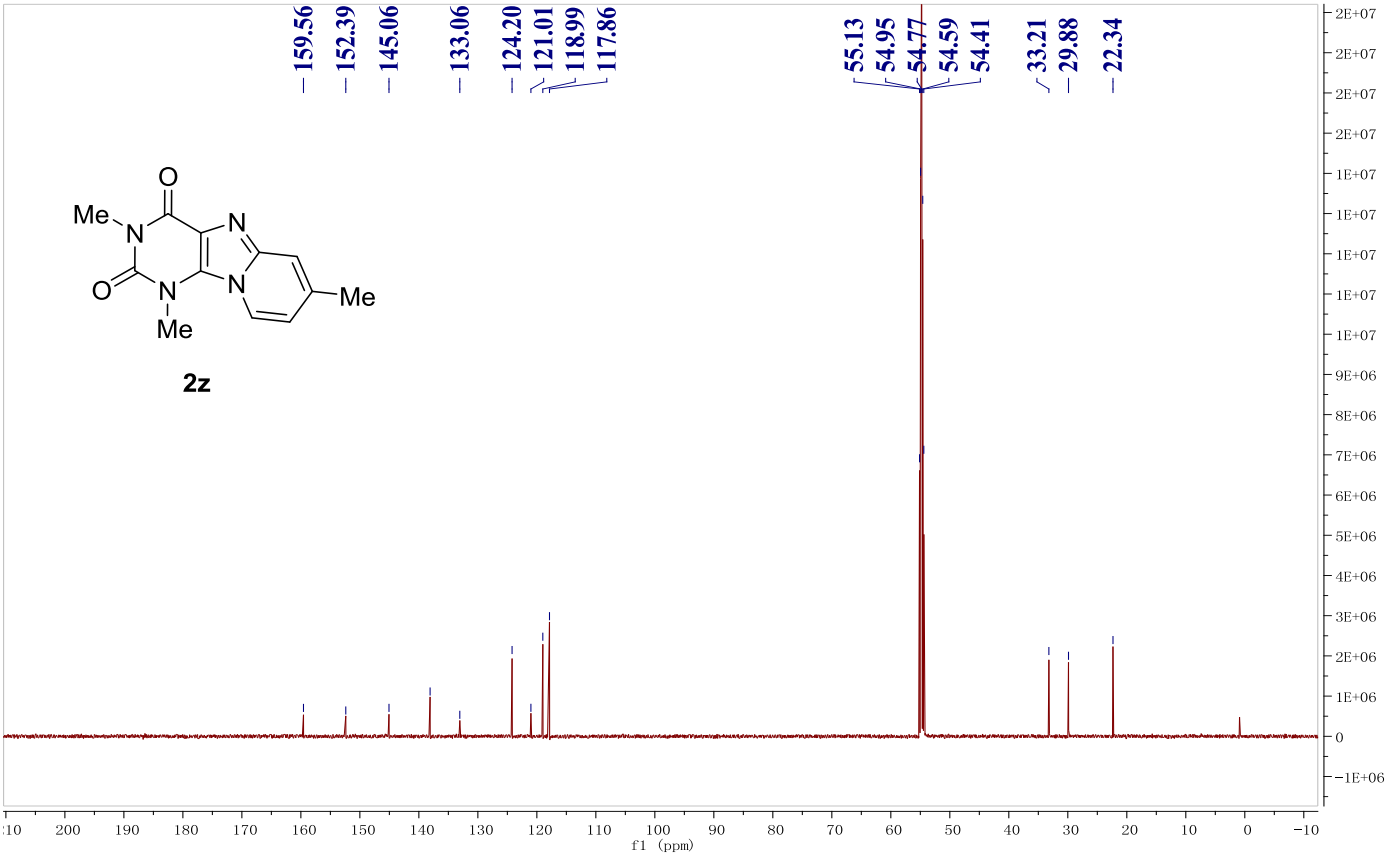
^{13}C NMR Spectrum of 2ay at 25 °C ($CDCl_3$, 150 MHz)



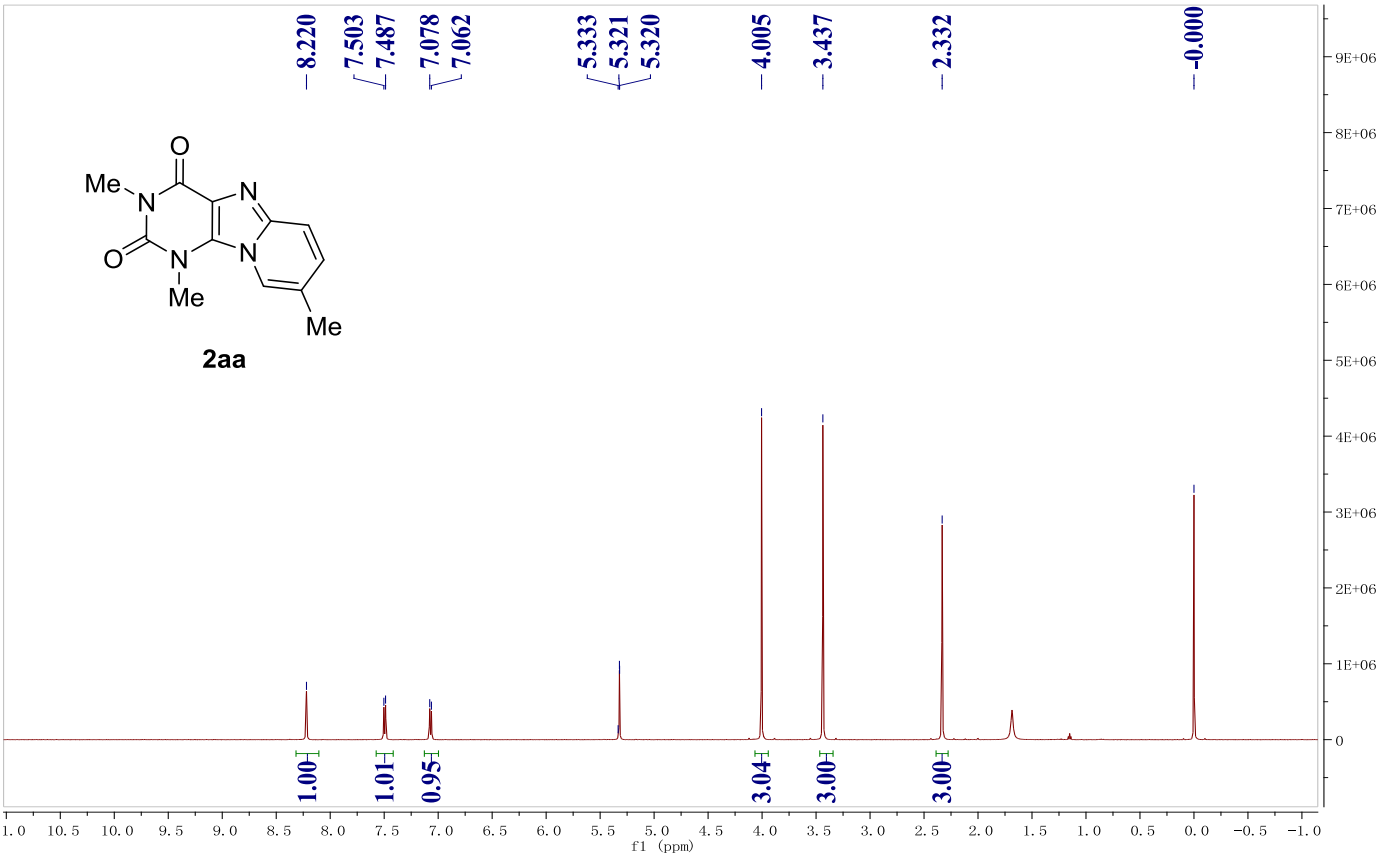
^{1}H NMR Spectrum of 2z at 25 °C ($CDCl_3$, 600 MHz)



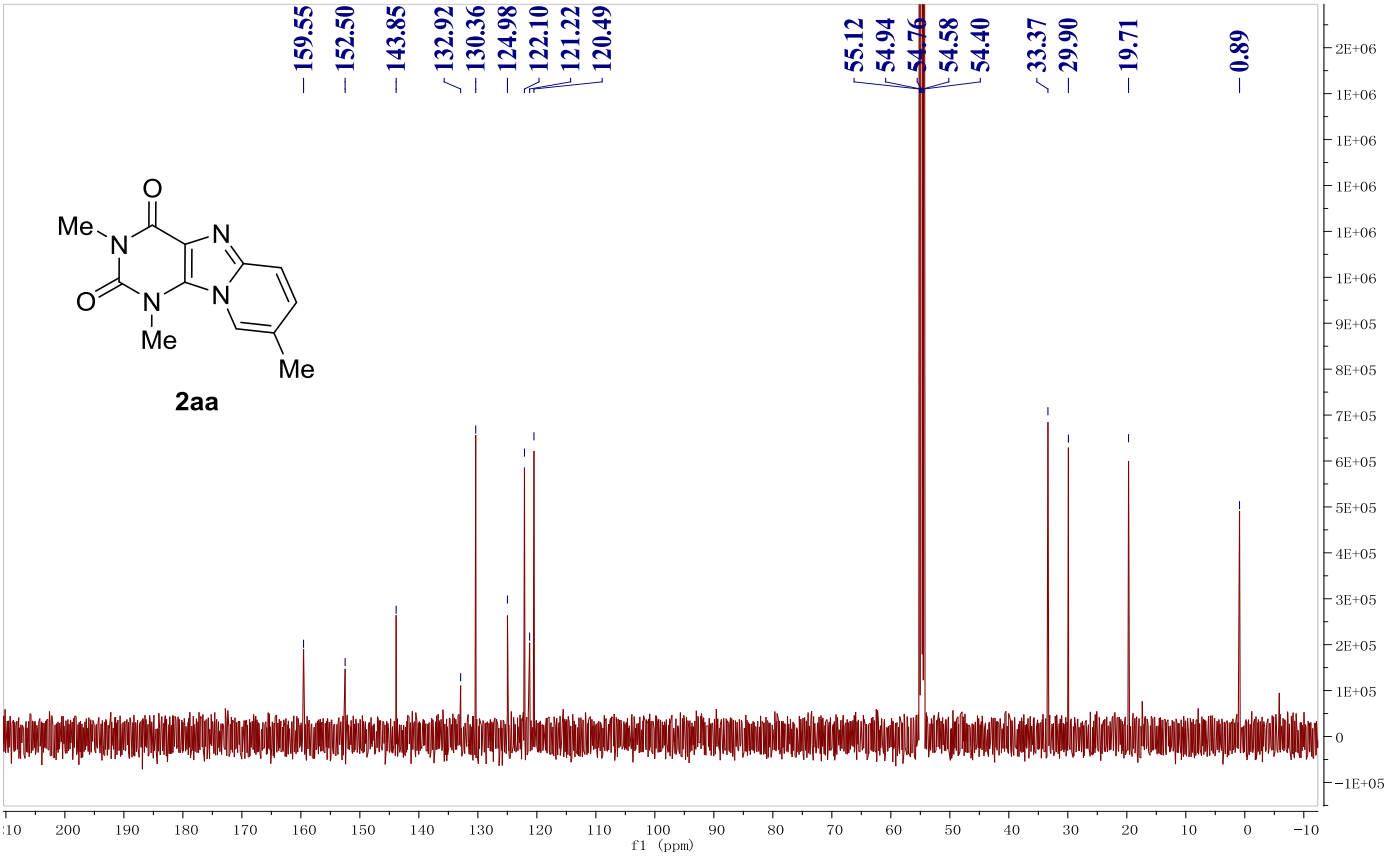
^{13}C NMR Spectrum of 2z at 25 °C ($CDCl_3$, 150 MHz)



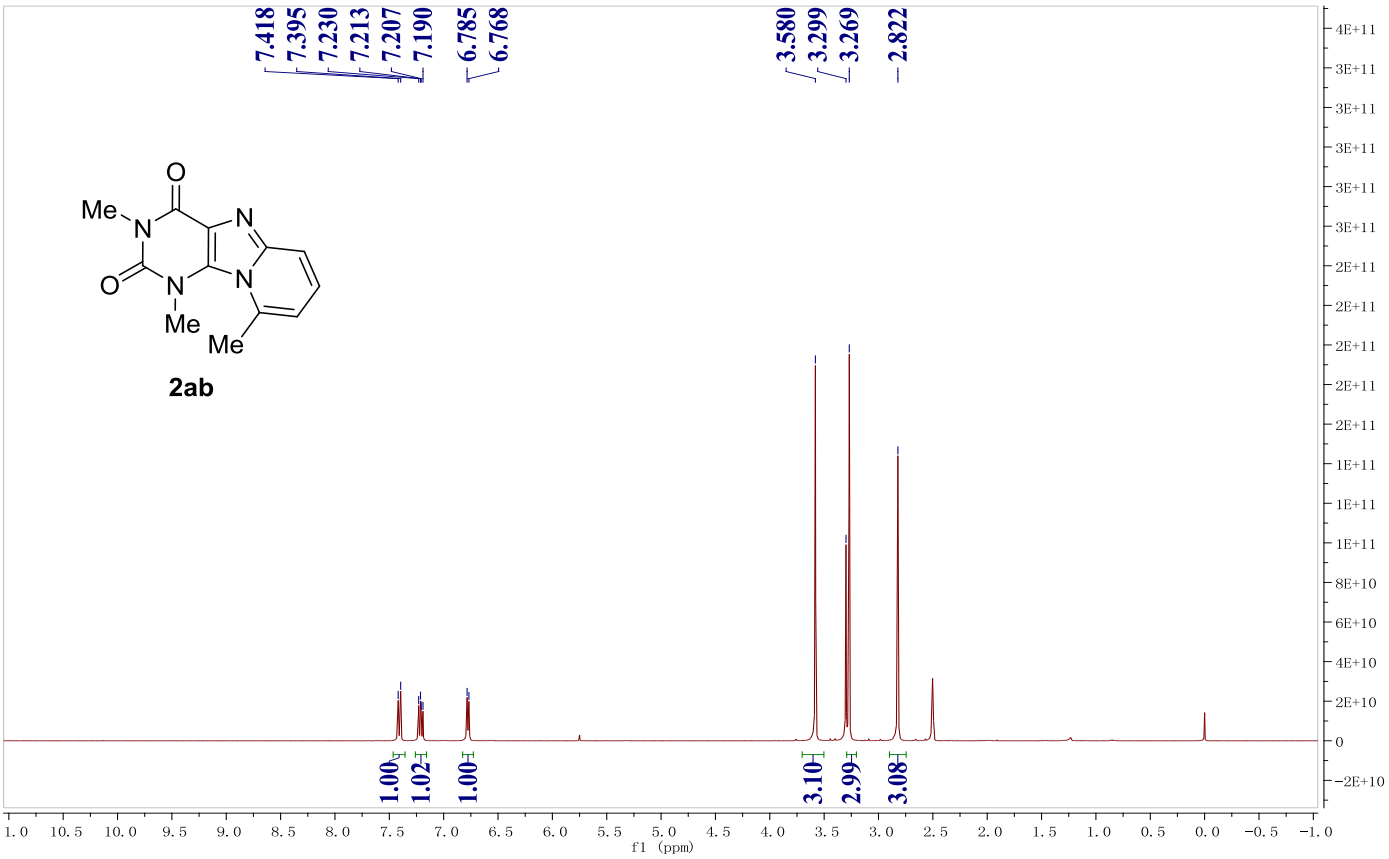
^{1}H NMR Spectrum of 2aa at 25 °C ($CDCl_3$, 600 MHz)



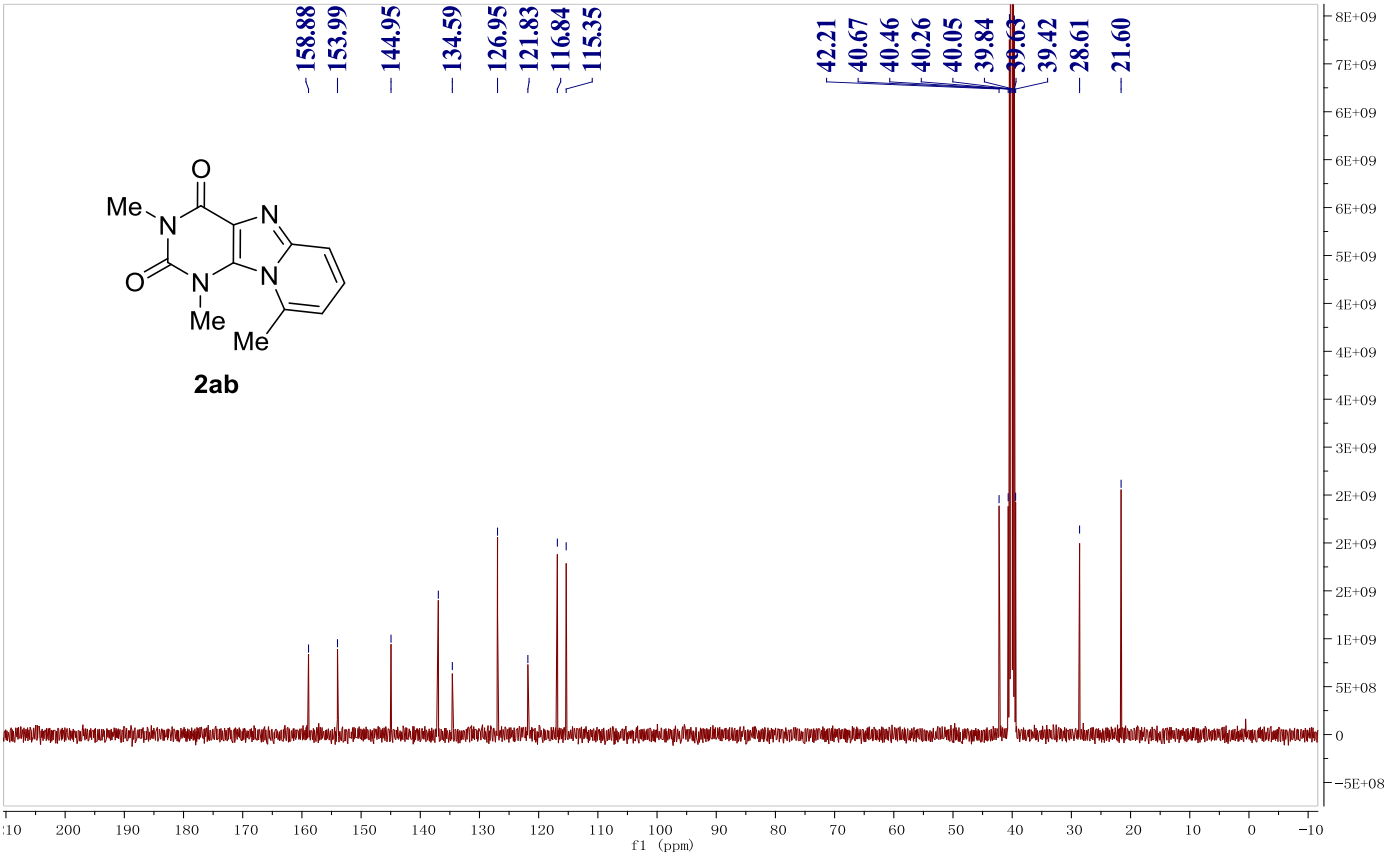
^{13}C NMR Spectrum of 2aa at 25 °C ($CDCl_3$, 150 MHz)



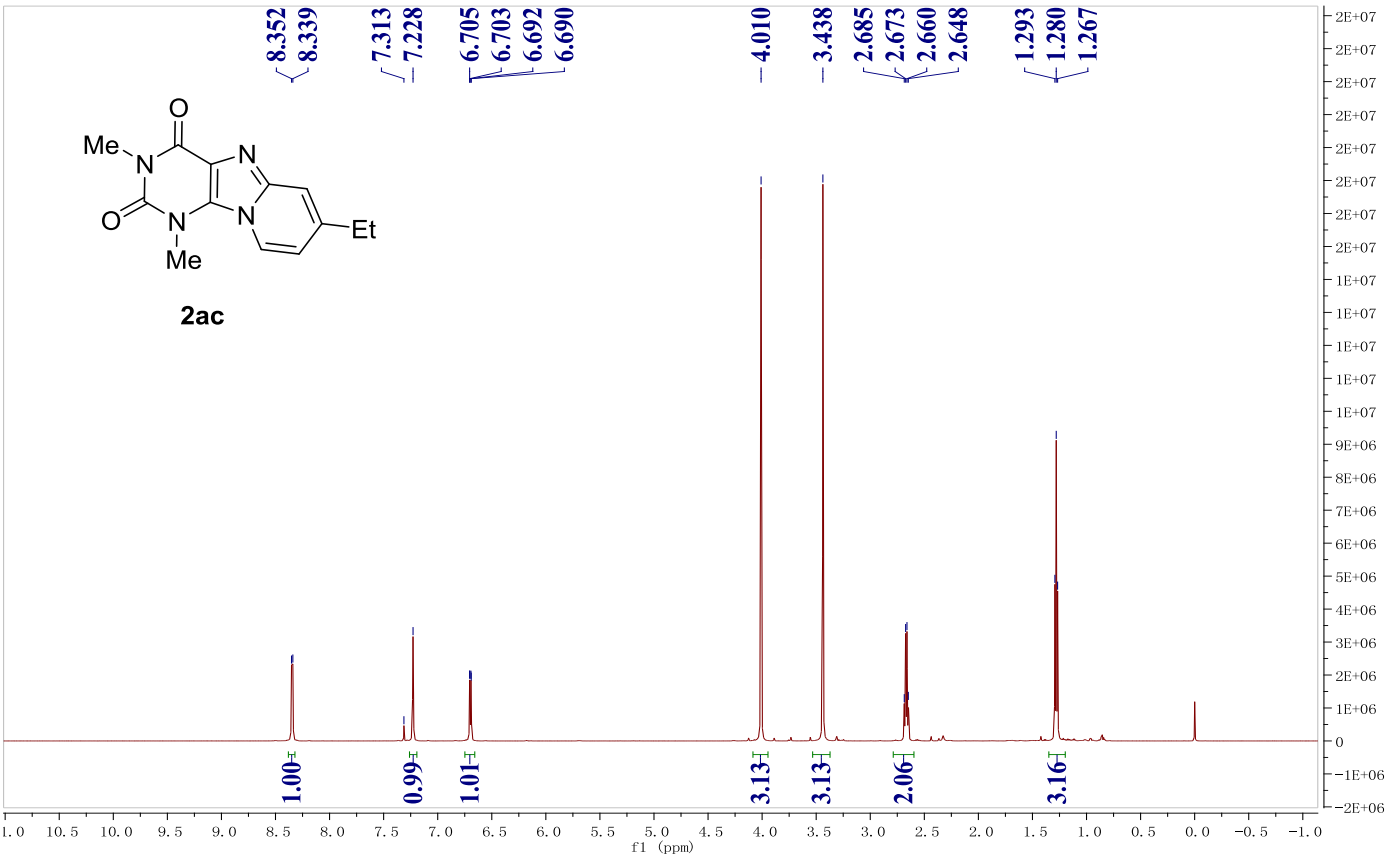
^{1}H NMR Spectrum of 2ab at 25 °C ($CDCl_3$, 600 MHz)



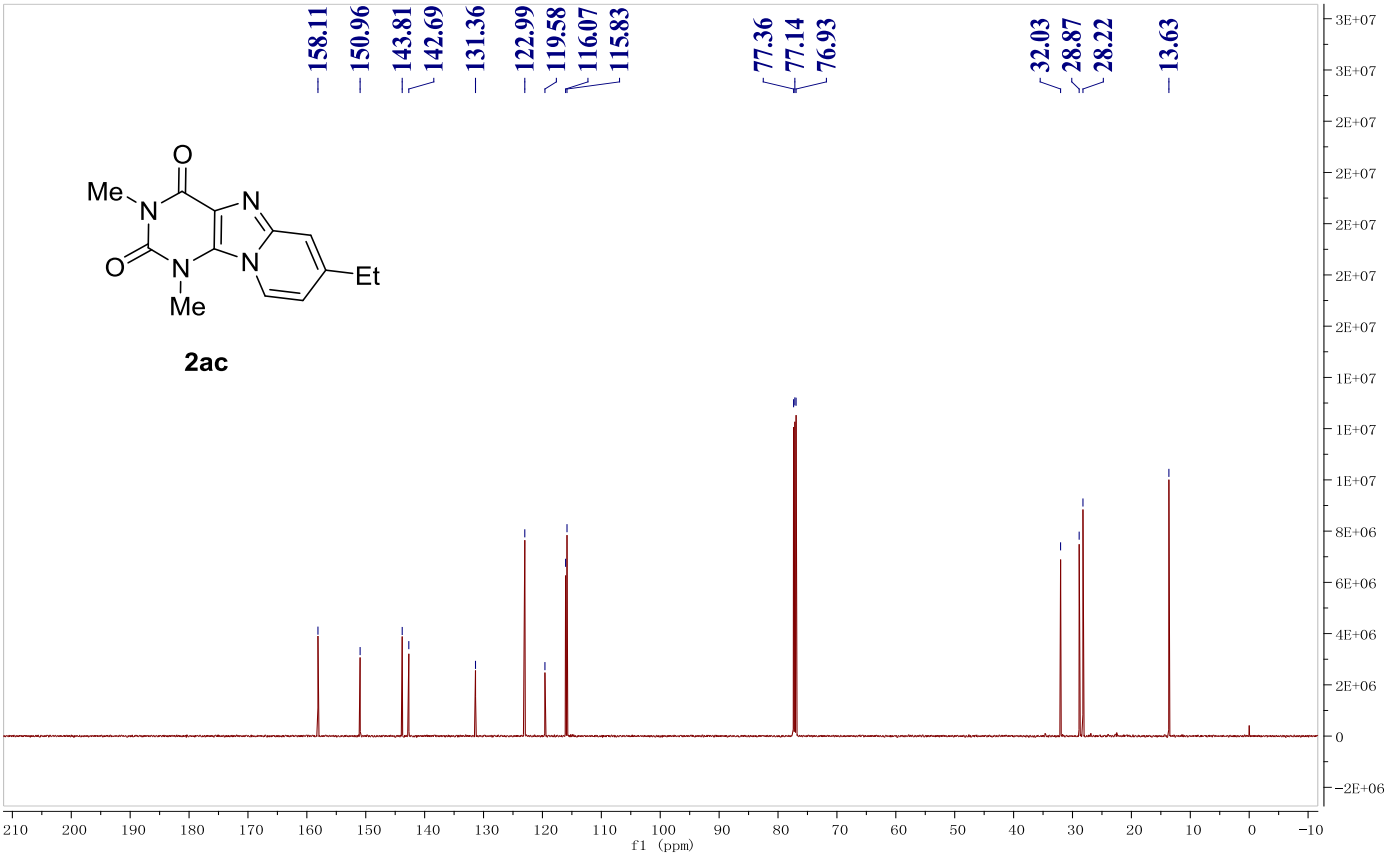
^{13}C NMR Spectrum of 2ab at 25 °C ($CDCl_3$, 150 MHz)



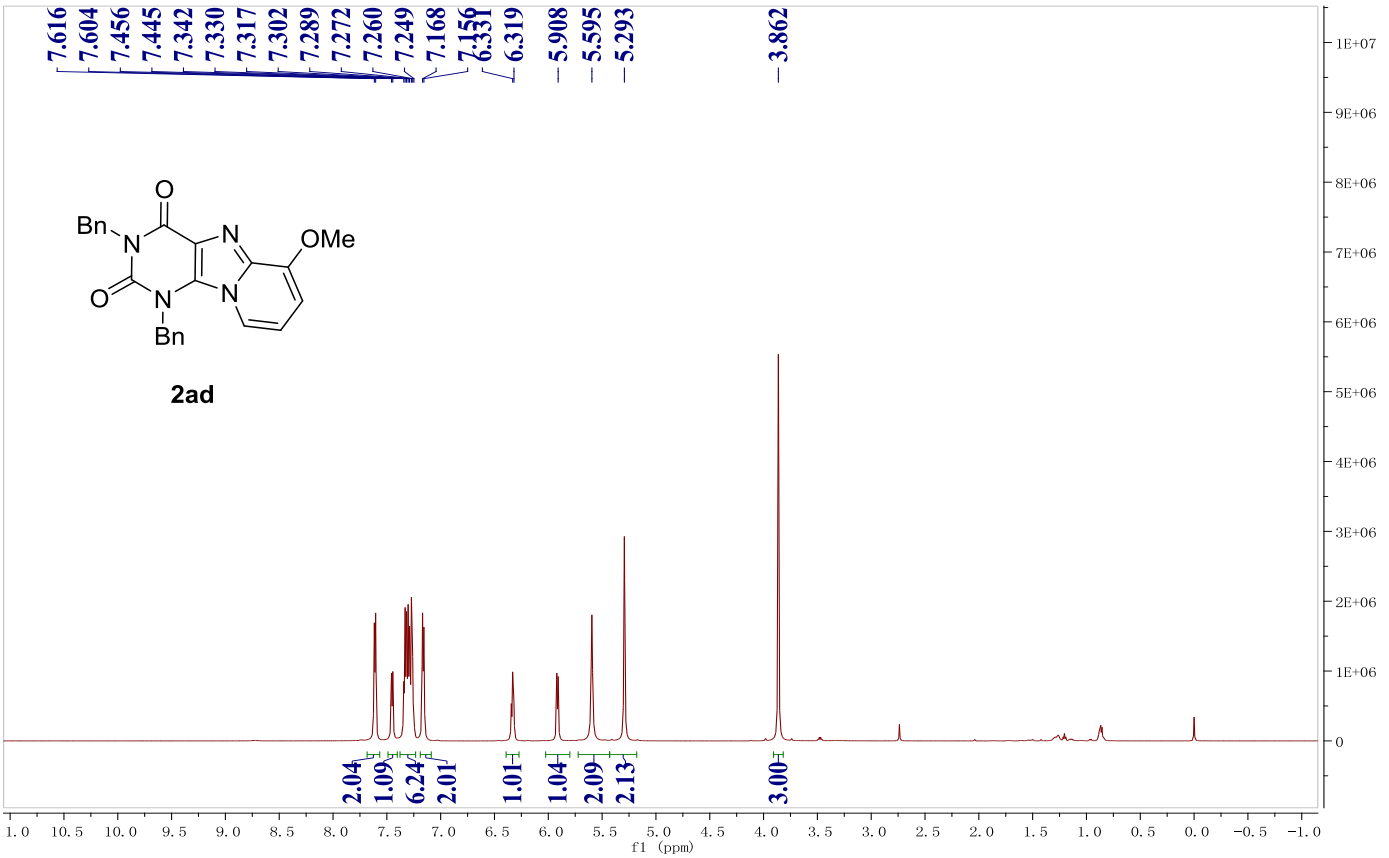
^{1}H NMR Spectrum of 2ac at 25 °C ($CDCl_3$, 600 MHz)



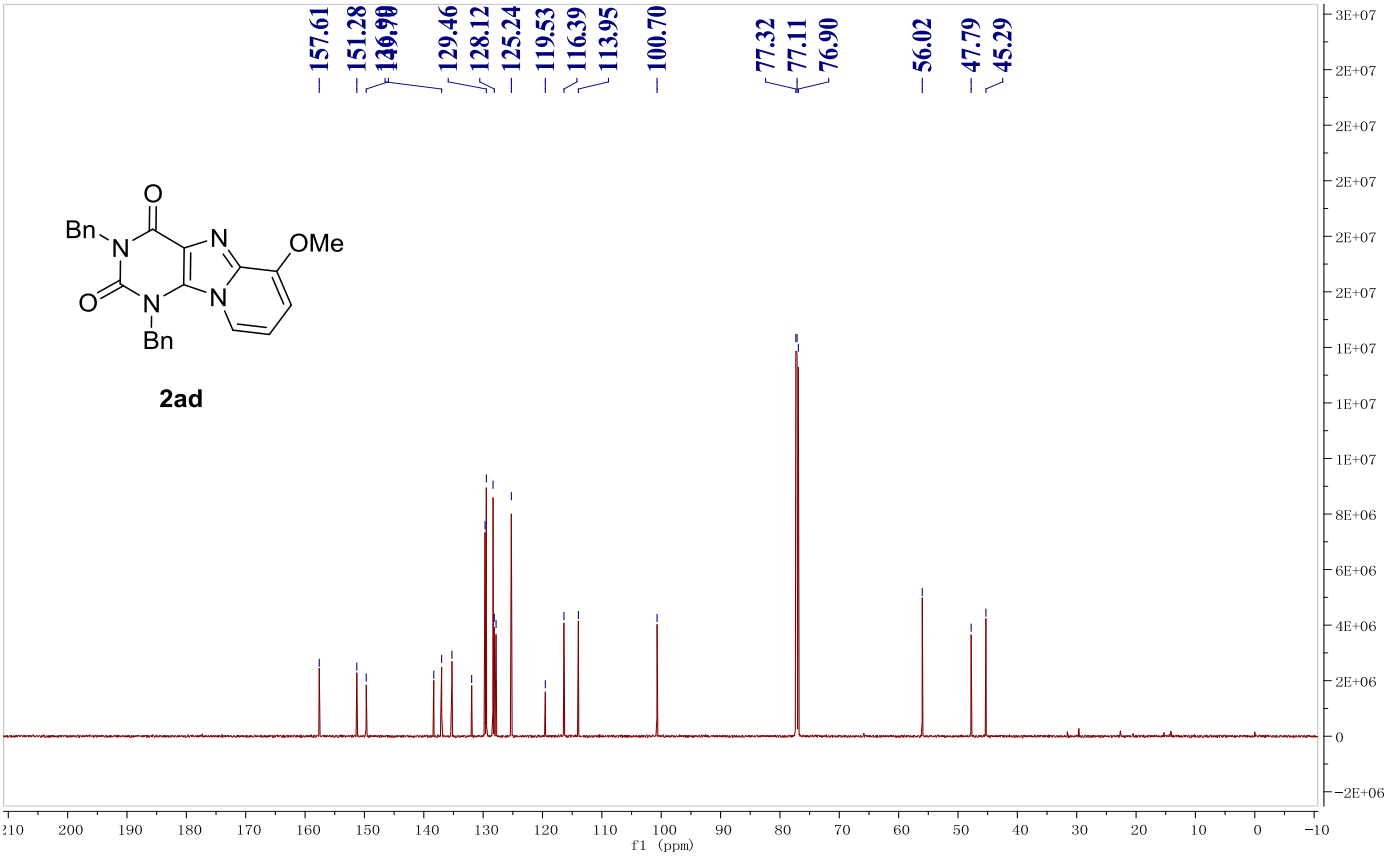
^{13}C NMR Spectrum of 2ac at 25 °C ($CDCl_3$, 150 MHz)



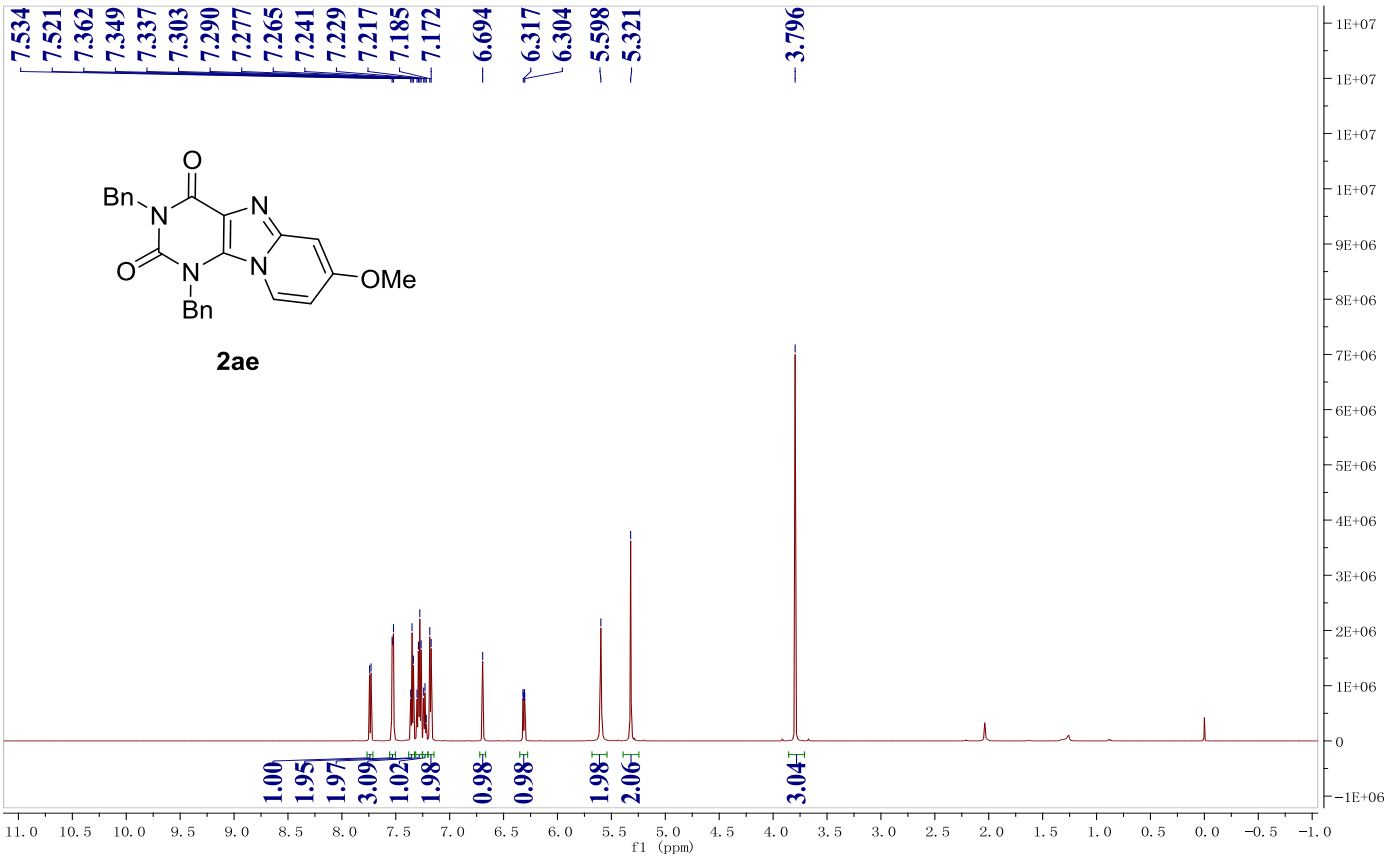
^{1}H NMR Spectrum of 2ad at 25 °C ($CDCl_3$, 600 MHz)



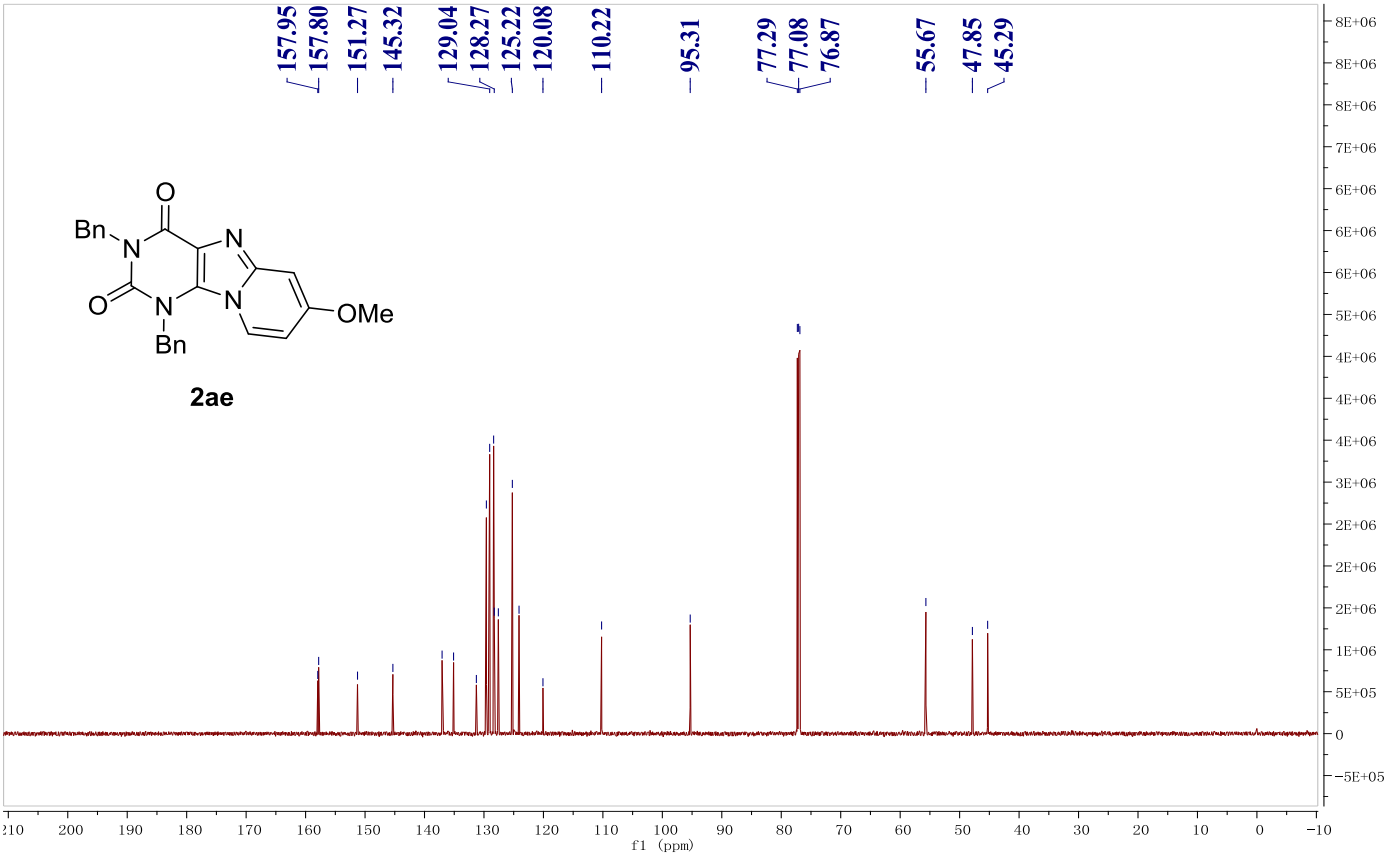
^{13}C NMR Spectrum of 2ad at 25 °C ($CDCl_3$, 150 MHz)



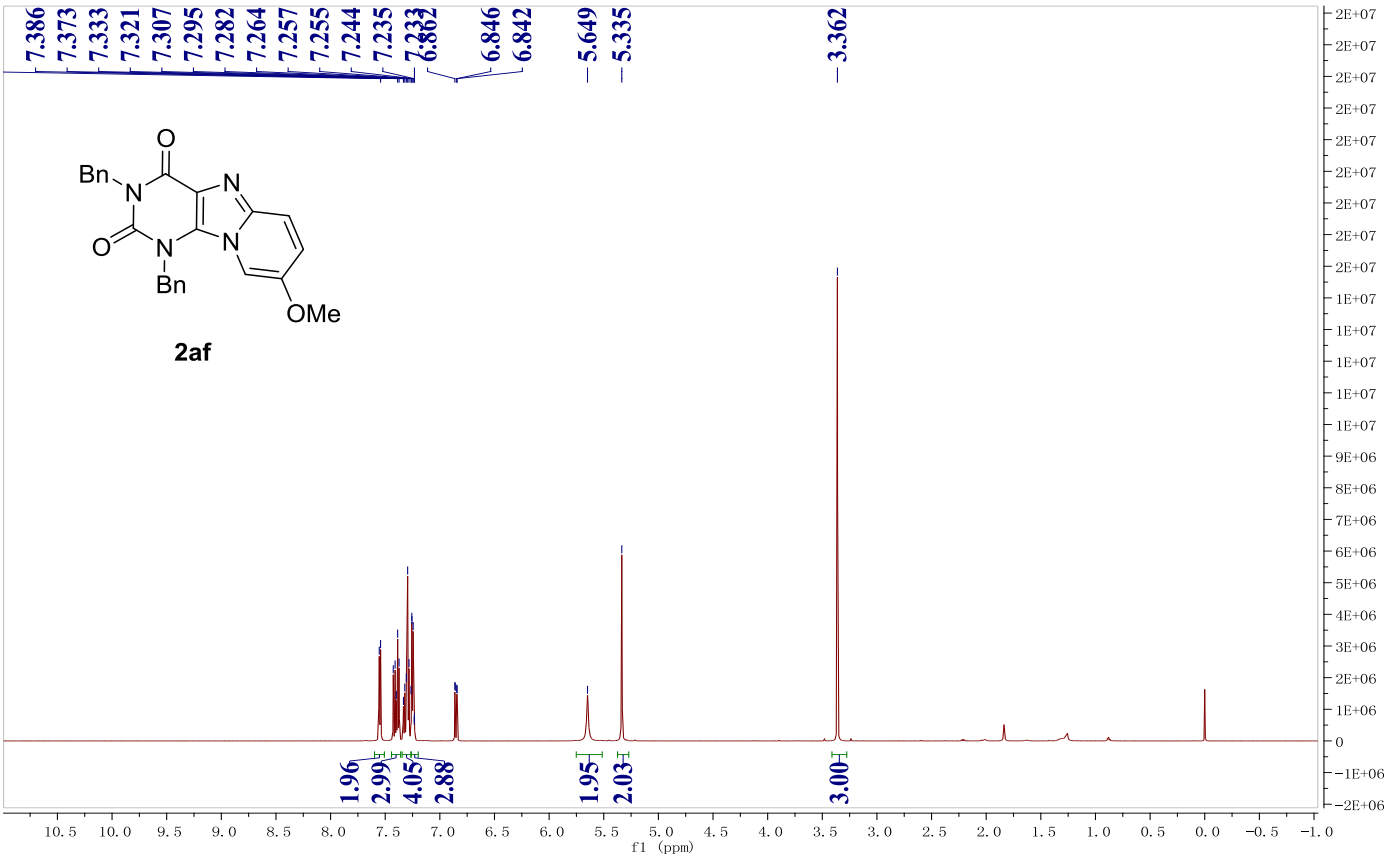
^{1}H NMR Spectrum of 2ae at 25 °C ($CDCl_3$, 600 MHz)



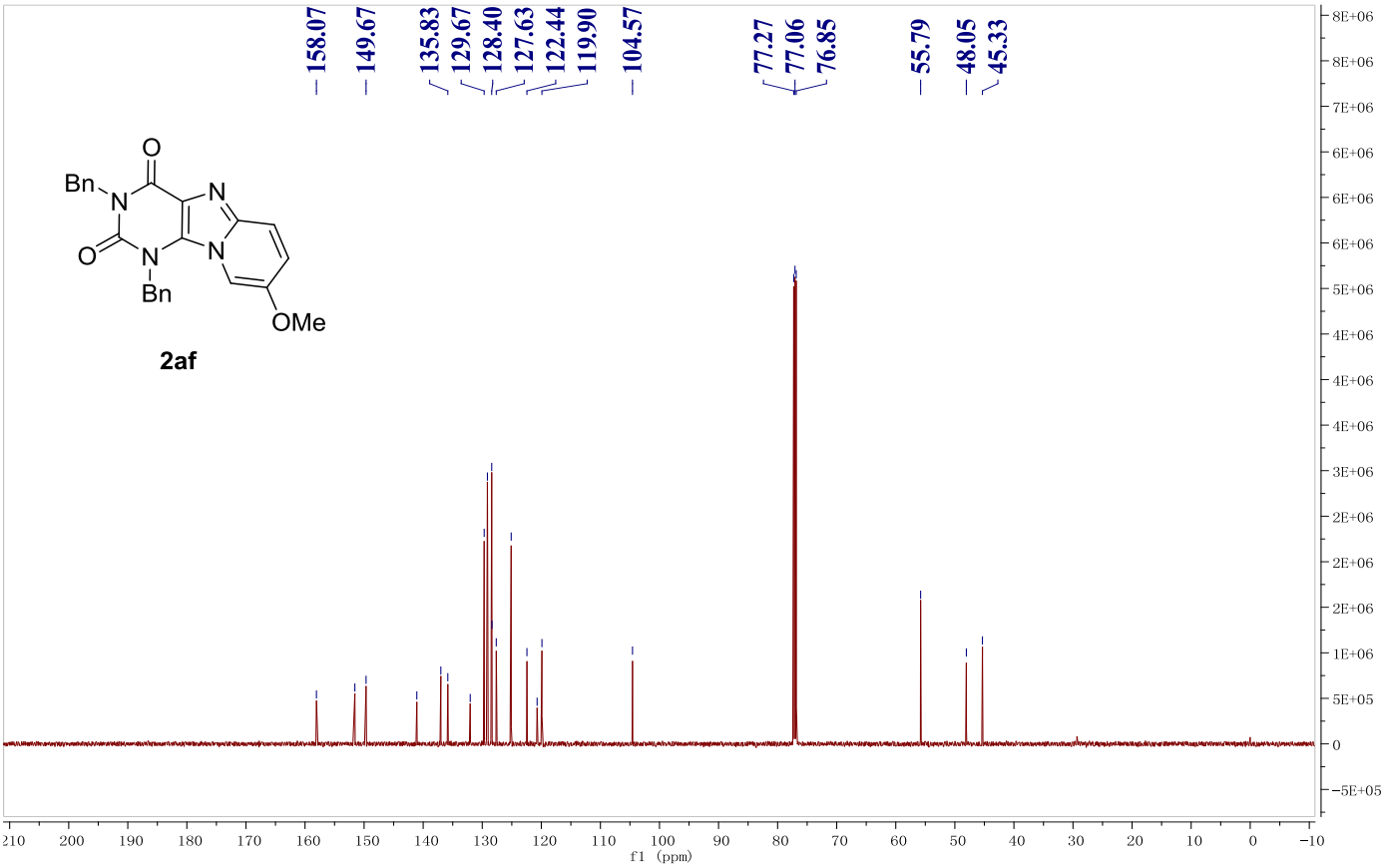
^{13}C NMR Spectrum of 2ae at 25 °C ($CDCl_3$, 150 MHz)



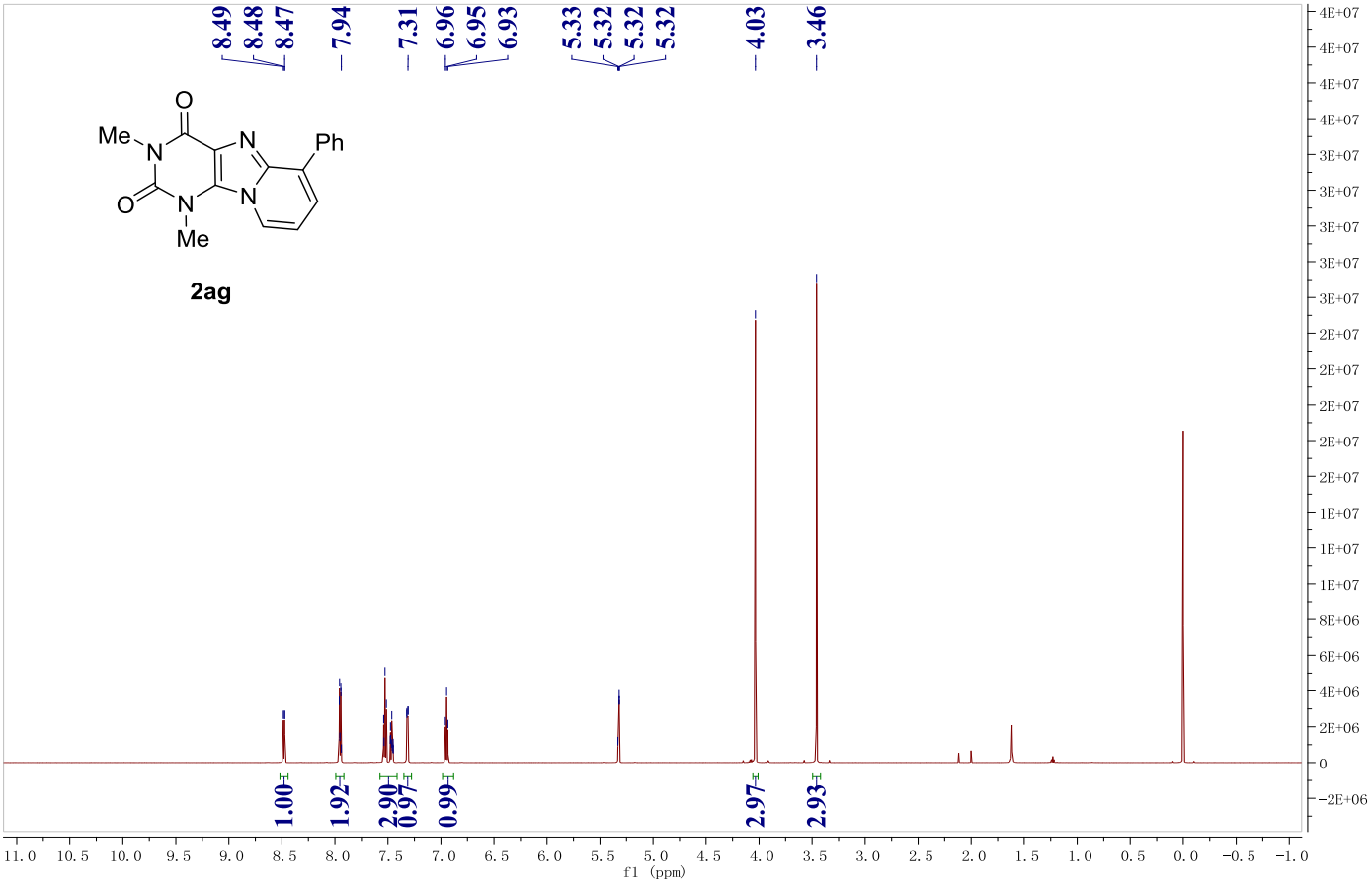
^{1}H NMR Spectrum of 2af at 25 °C ($CDCl_3$, 600 MHz)



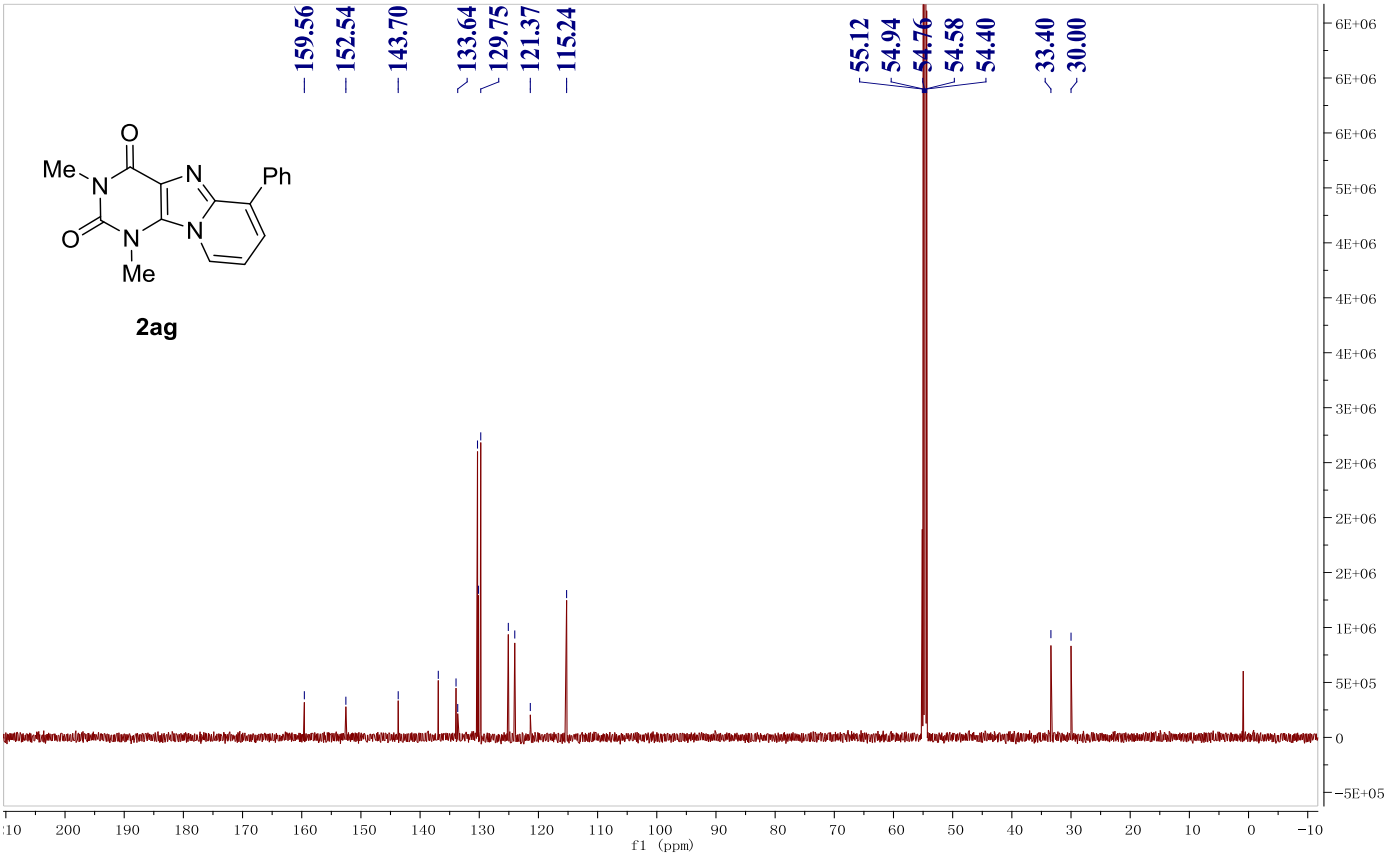
^{13}C NMR Spectrum of 2af at 25 °C ($CDCl_3$, 150 MHz)



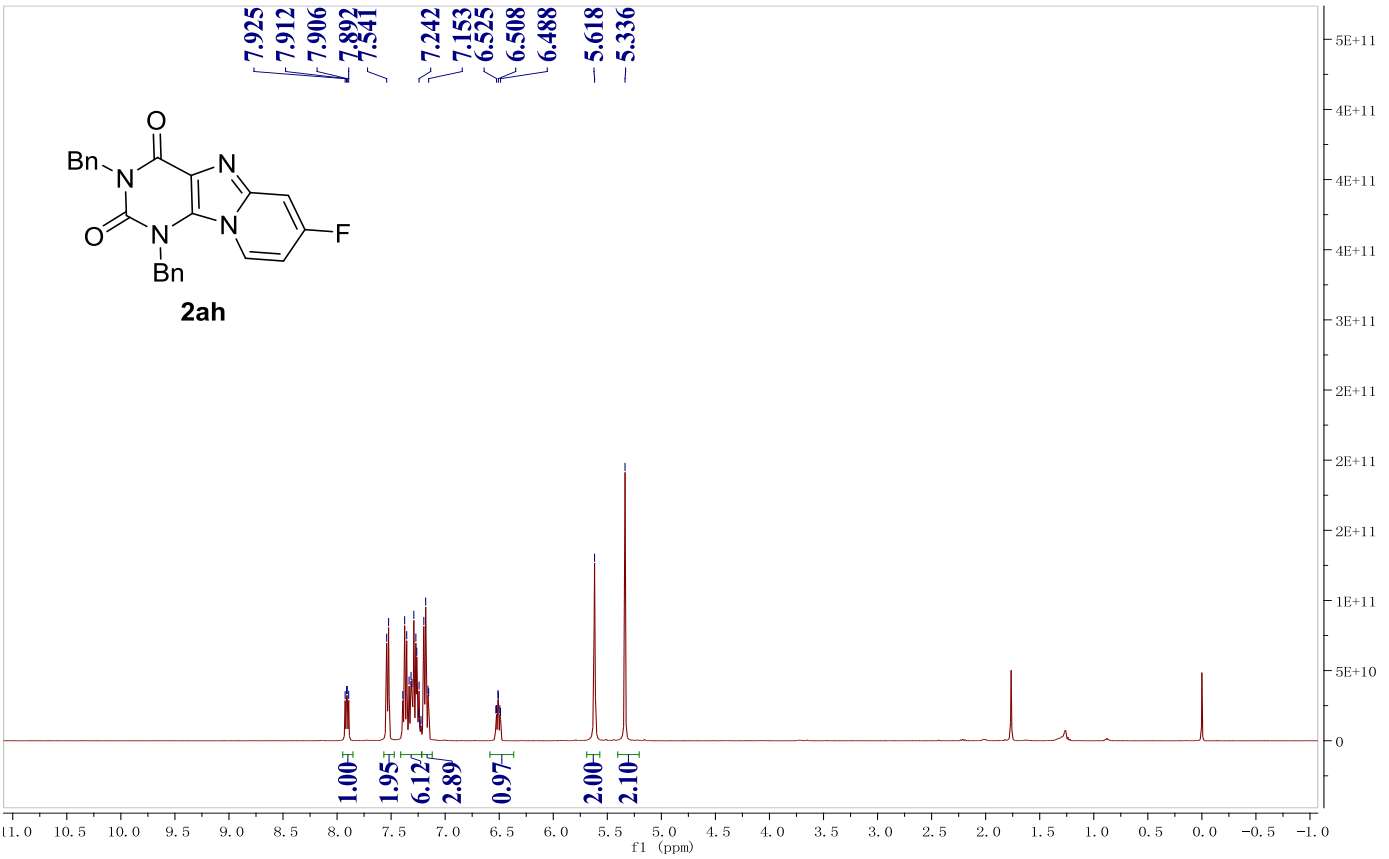
^{1}H NMR Spectrum of 2ag at 25 °C ($CDCl_3$, 600 MHz)



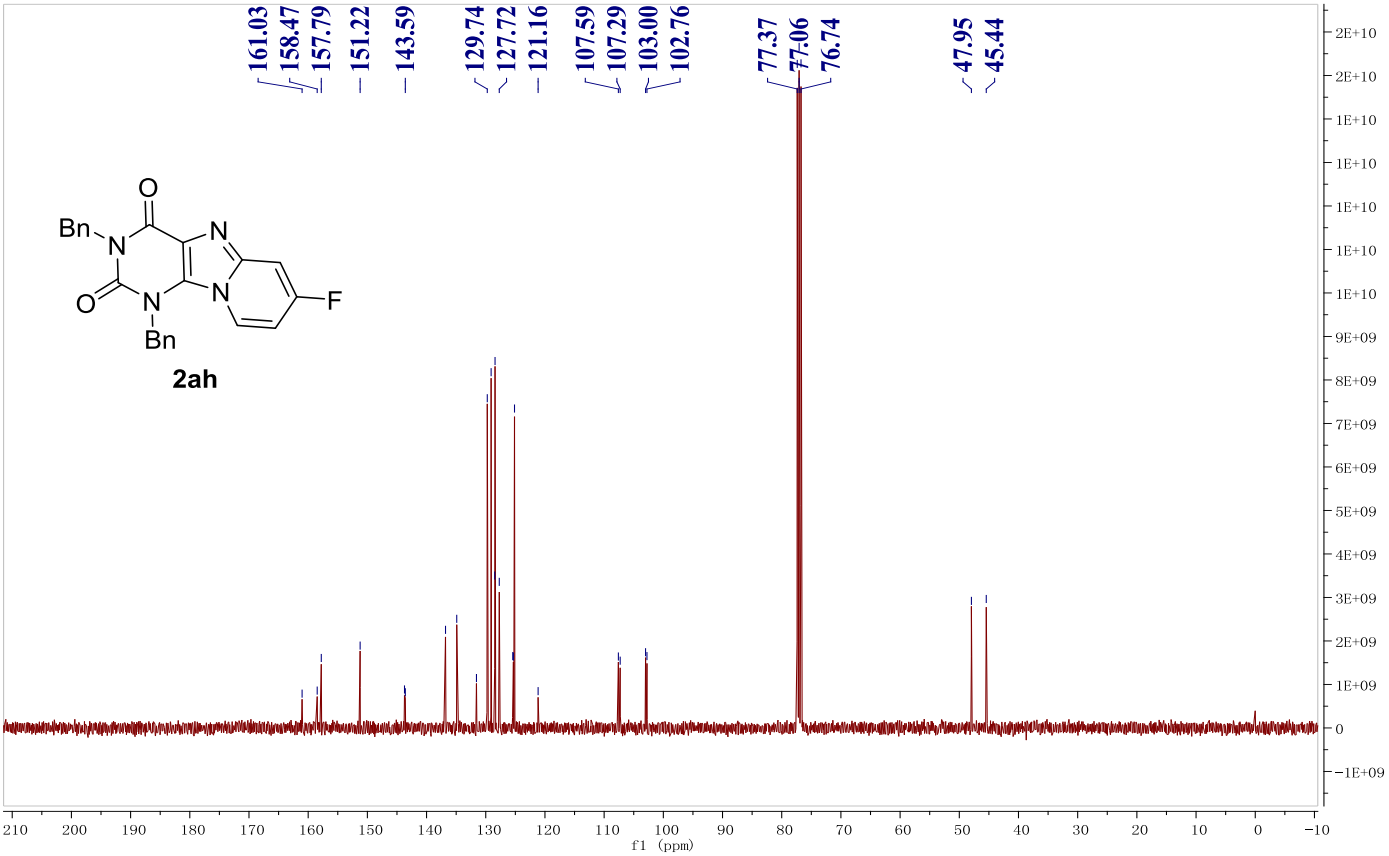
^{13}C NMR Spectrum of 2ag at 25 °C ($CDCl_3$, 150 MHz)



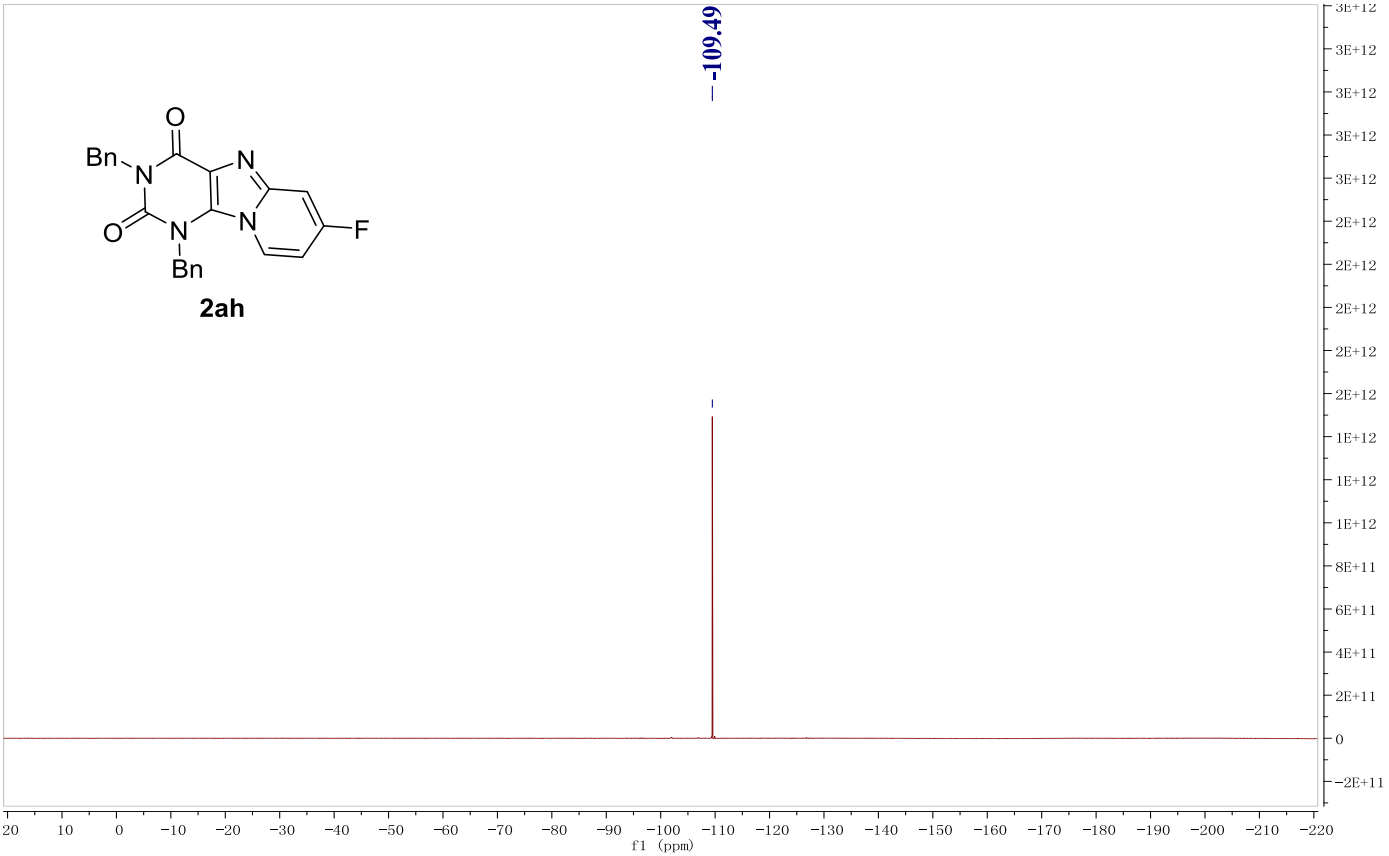
^{1}H NMR Spectrum of 2ah at 25 °C ($CDCl_3$, 400 MHz)



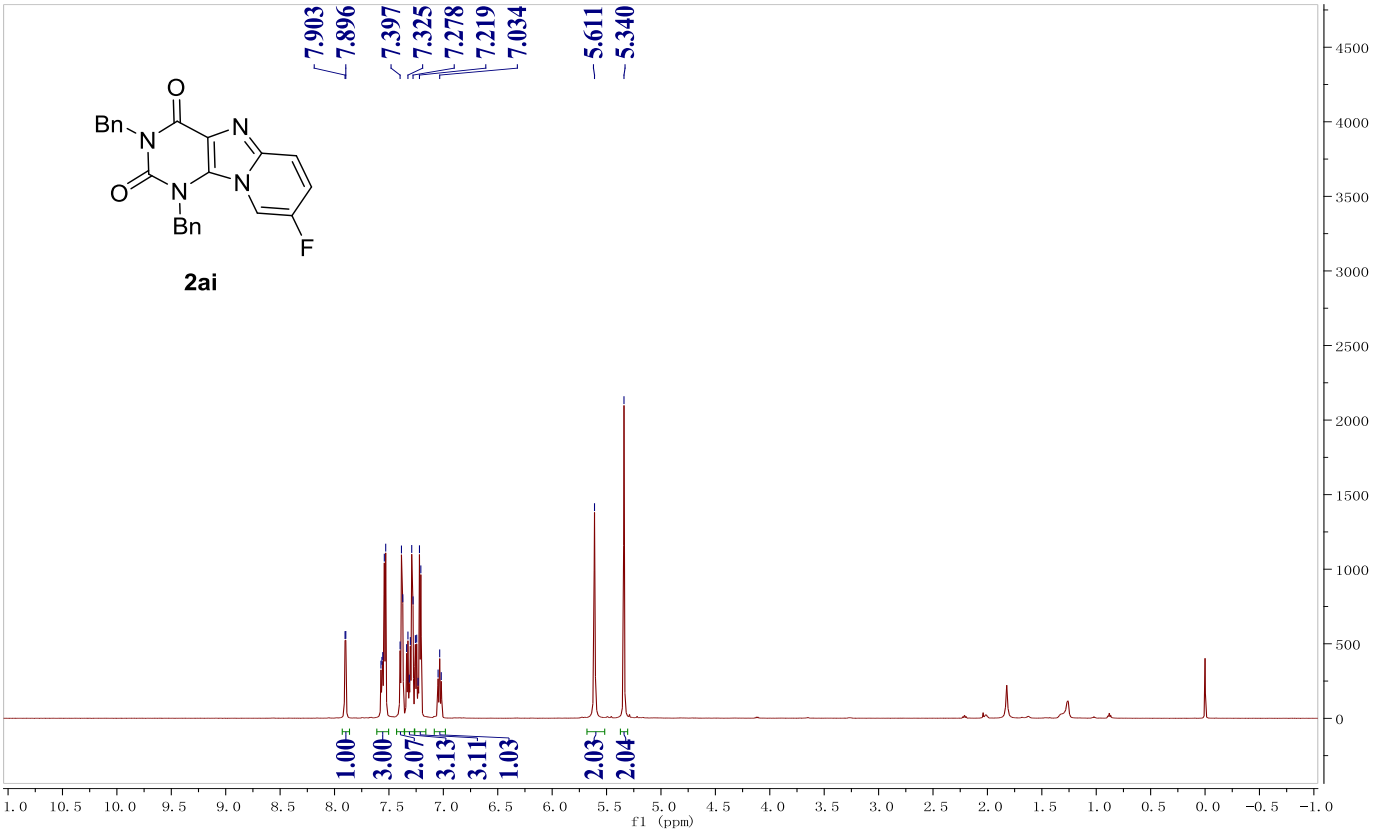
^{13}C NMR Spectrum of 2ah at 25 °C ($CDCl_3$, 100 MHz)



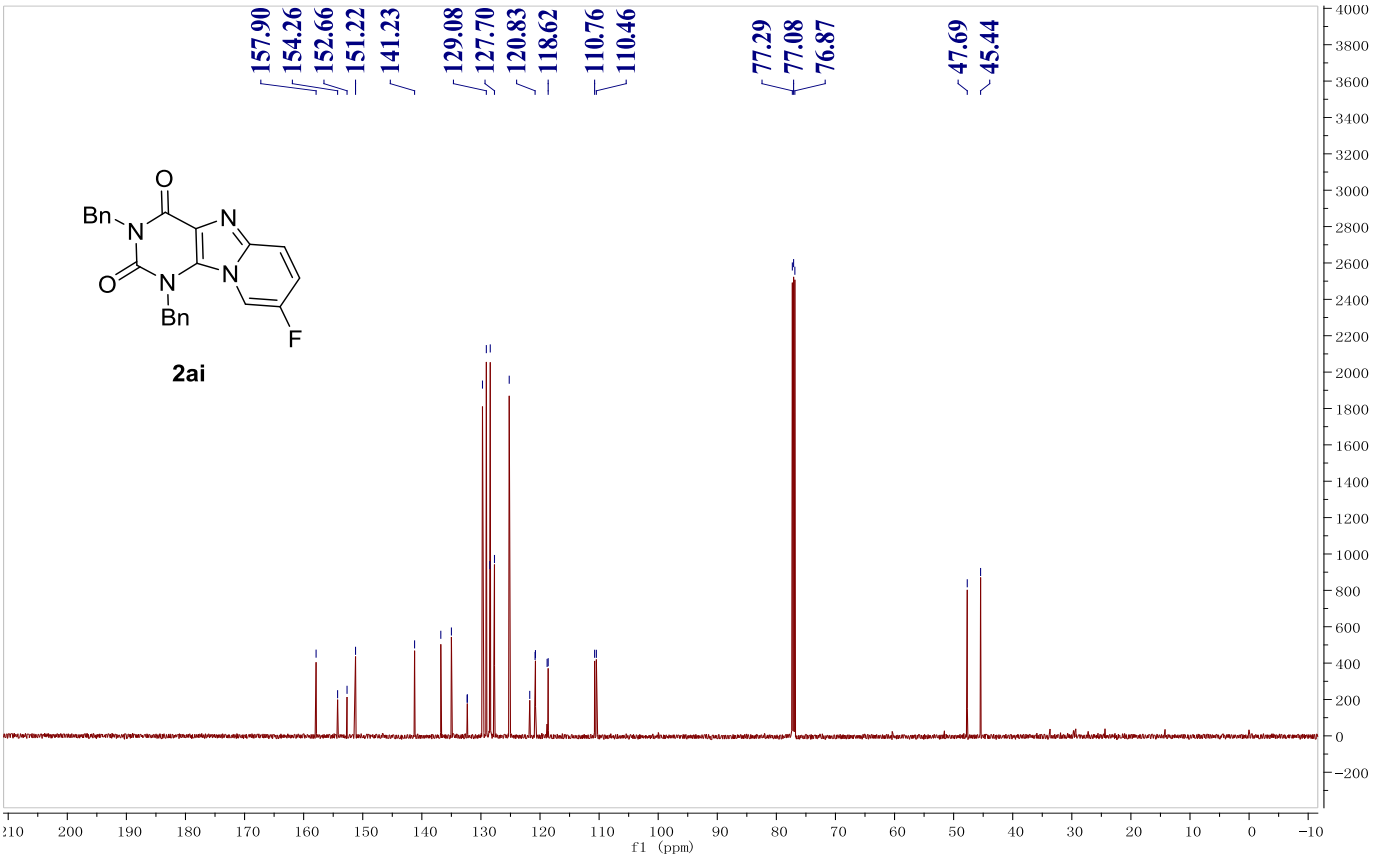
^{19}F NMR Spectrum of 2ah at 25 °C ($CDCl_3$, 376 MHz)



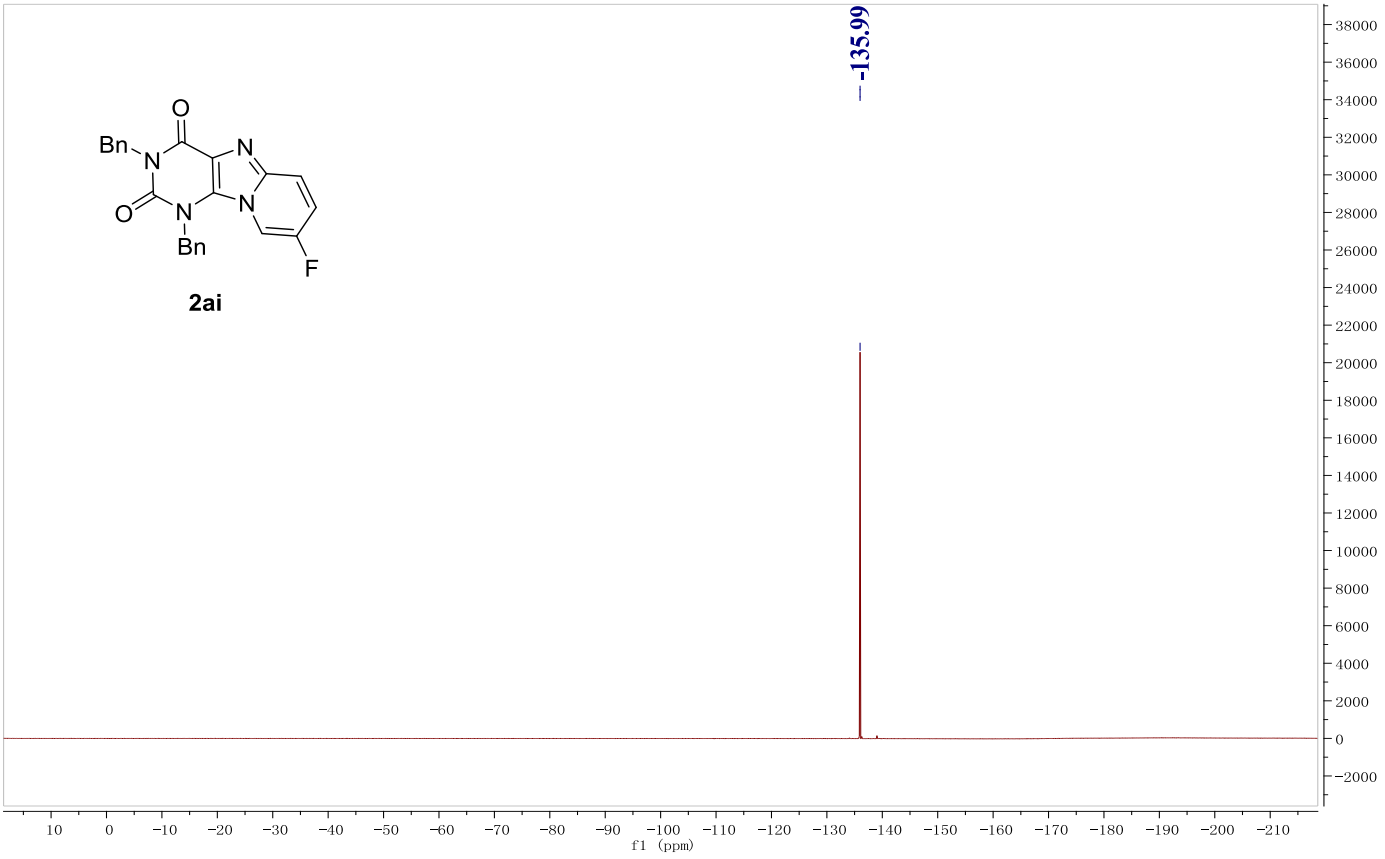
^{1}H NMR Spectrum of 2ai at 25 °C ($CDCl_3$, 600 MHz)



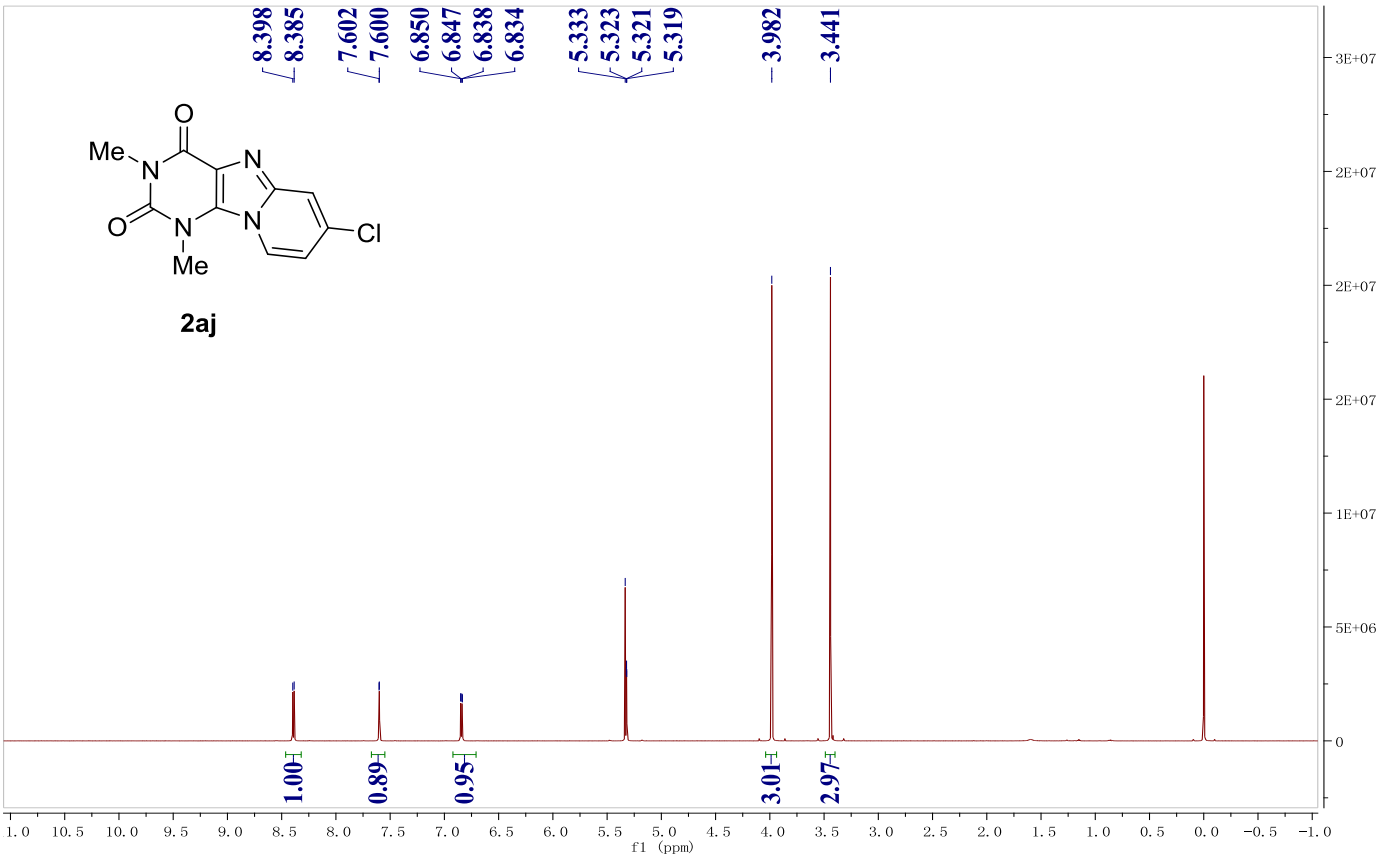
^{13}C NMR Spectrum of 2ai at 25 °C ($CDCl_3$, 150 MHz)



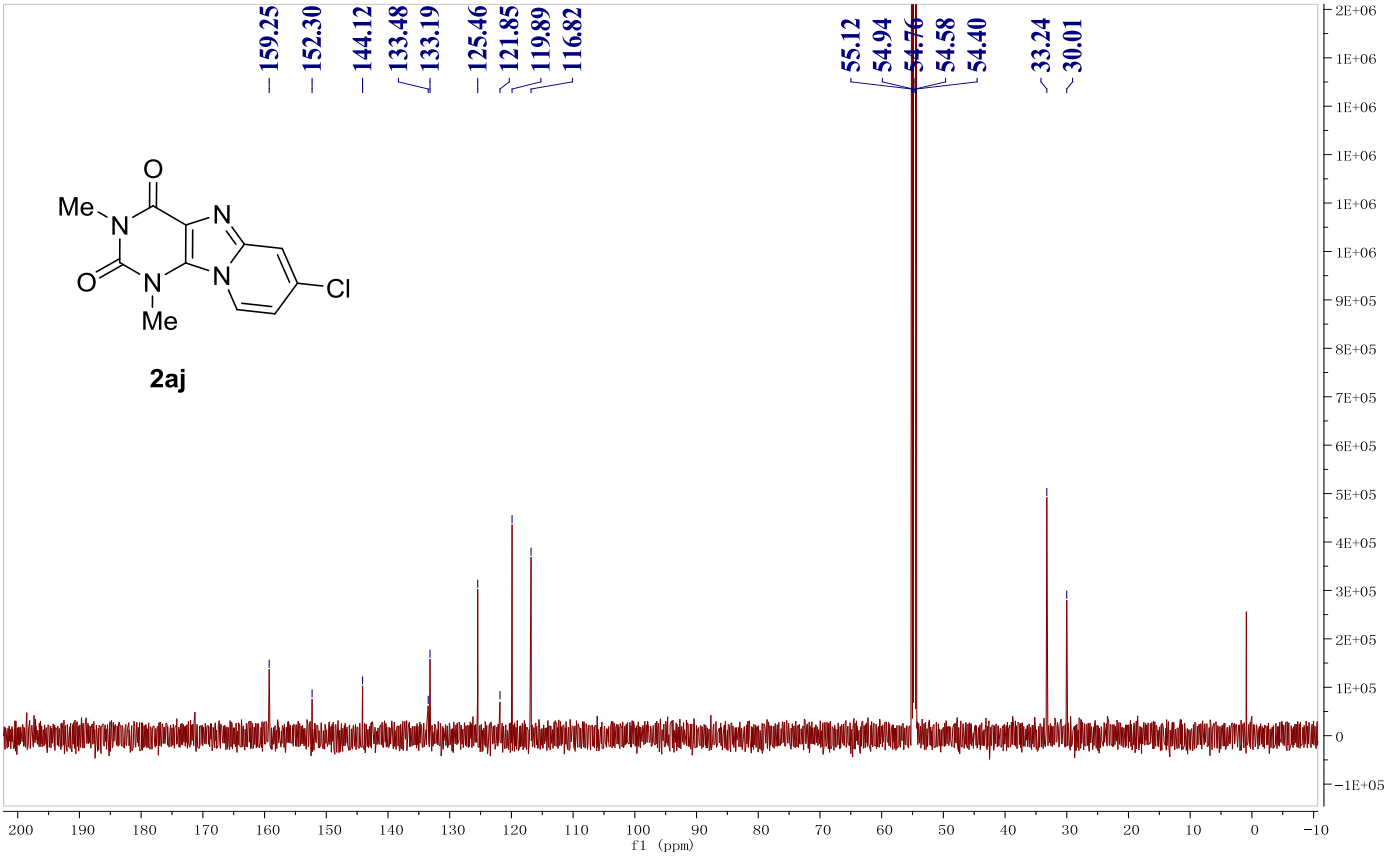
^{19}F NMR Spectrum of 2ai at 25 °C ($CDCl_3$, 565 MHz)



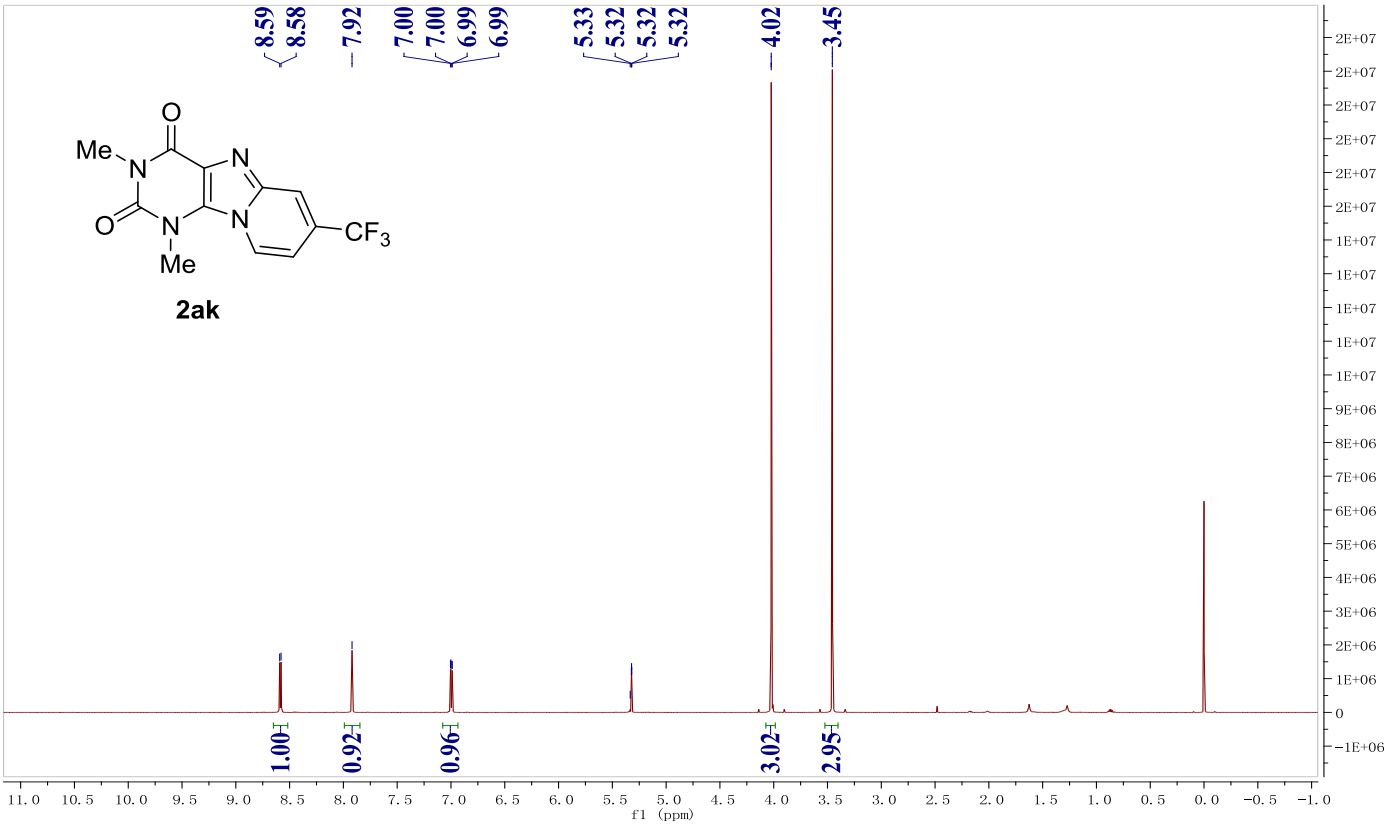
^{1}H NMR Spectrum of 2aj at 25 °C (CD_2Cl_2, 600 MHz)



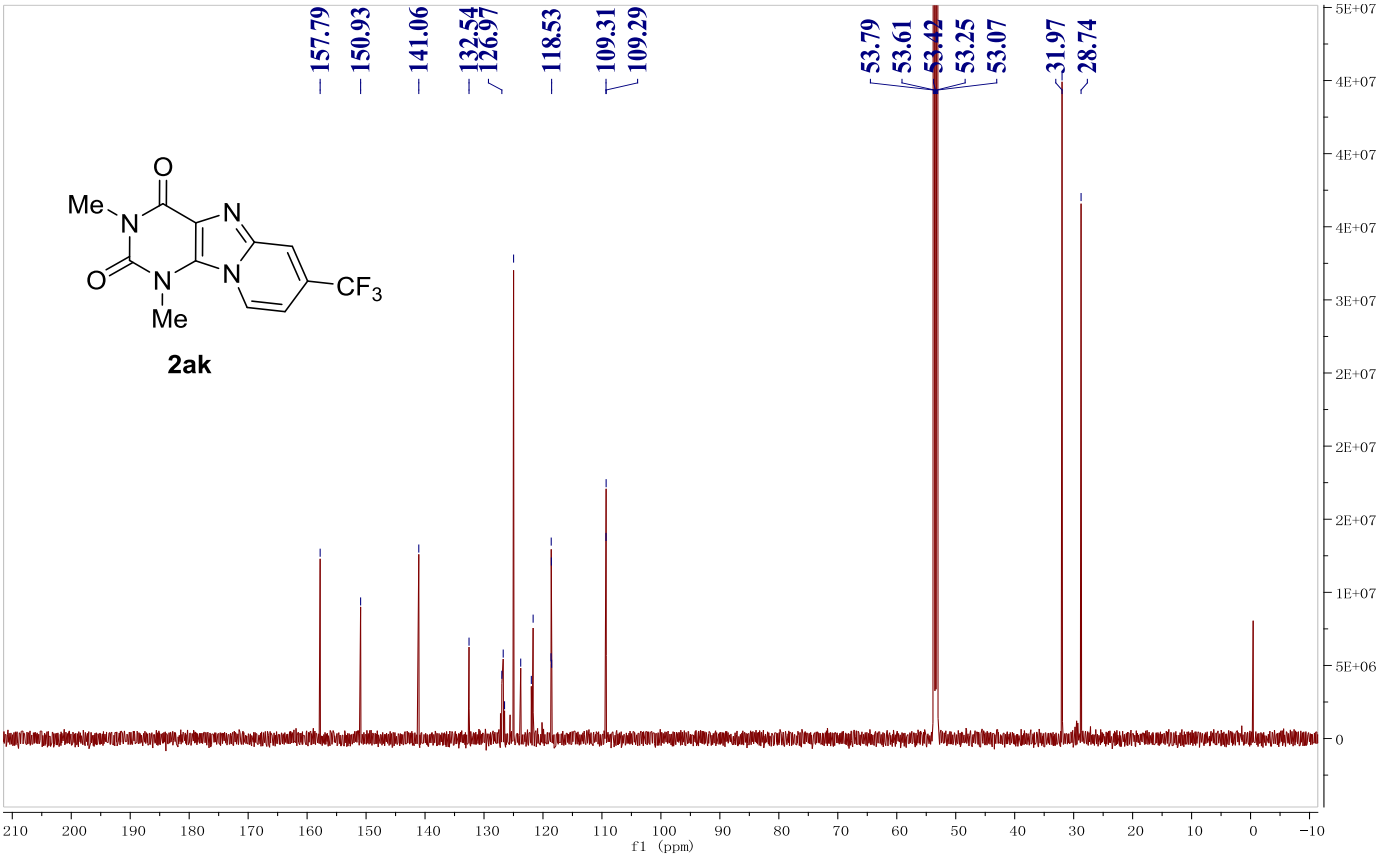
^{13}C NMR Spectrum of 2aj at 25 °C (CD_2Cl_2, 150 MHz)



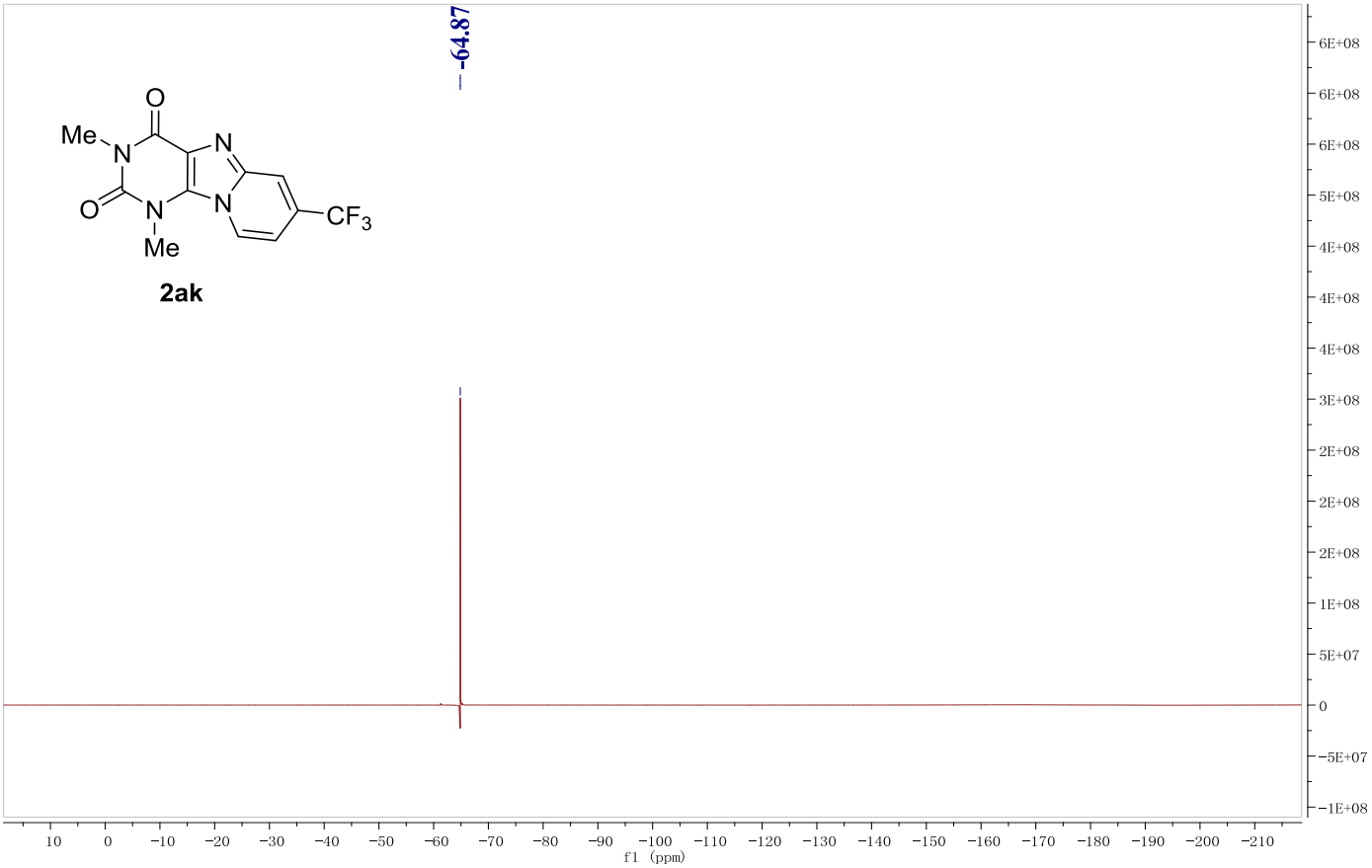
^{1}H NMR Spectrum of 2ak at 25 °C (CD_2Cl_2, 600 MHz)



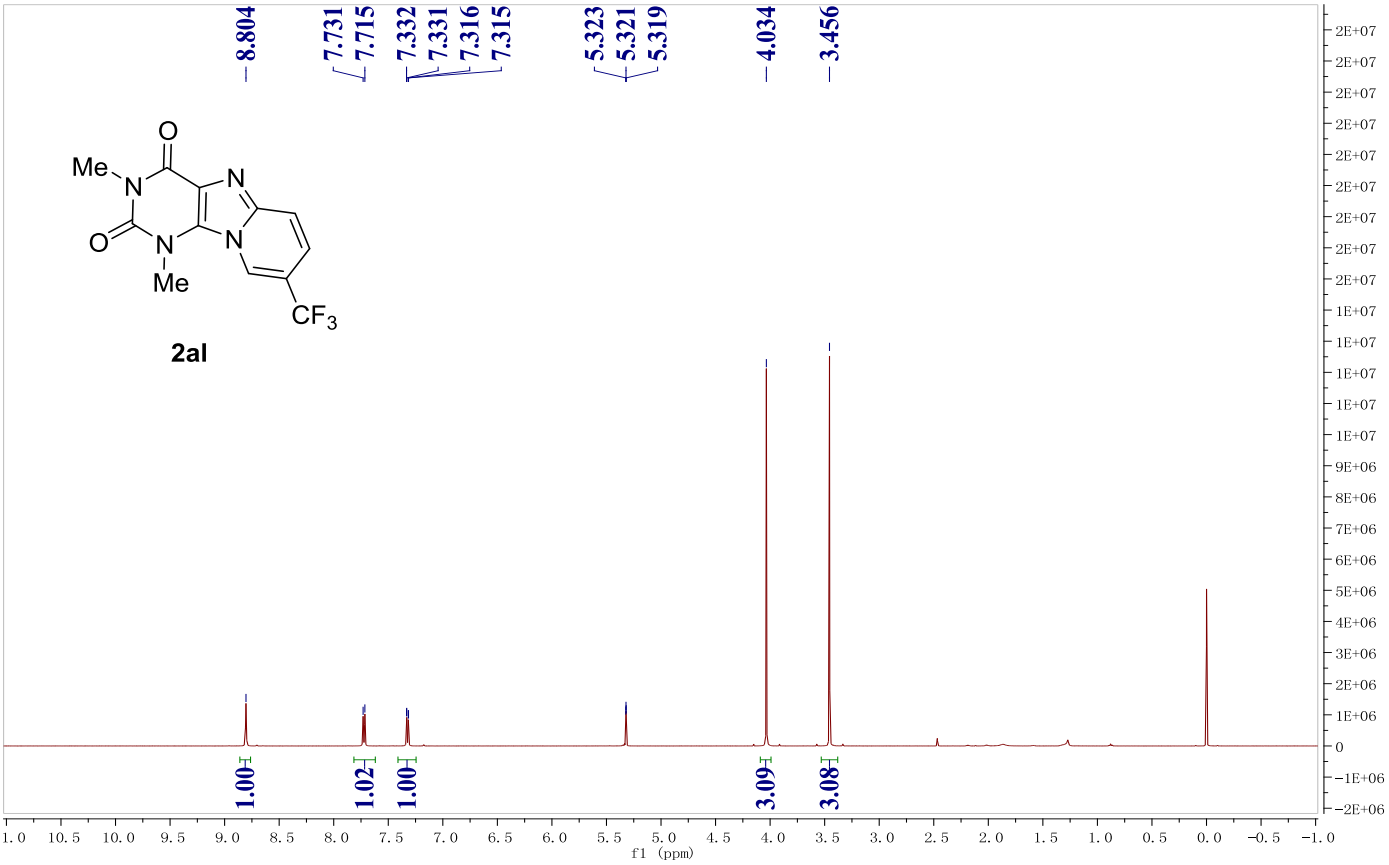
^{13}C NMR Spectrum of 2ak at 25 °C (CD_2Cl_2, 150 MHz)



^{19}F NMR Spectrum of 2ak at 25 °C (CD_2Cl_2, 565 MHz)

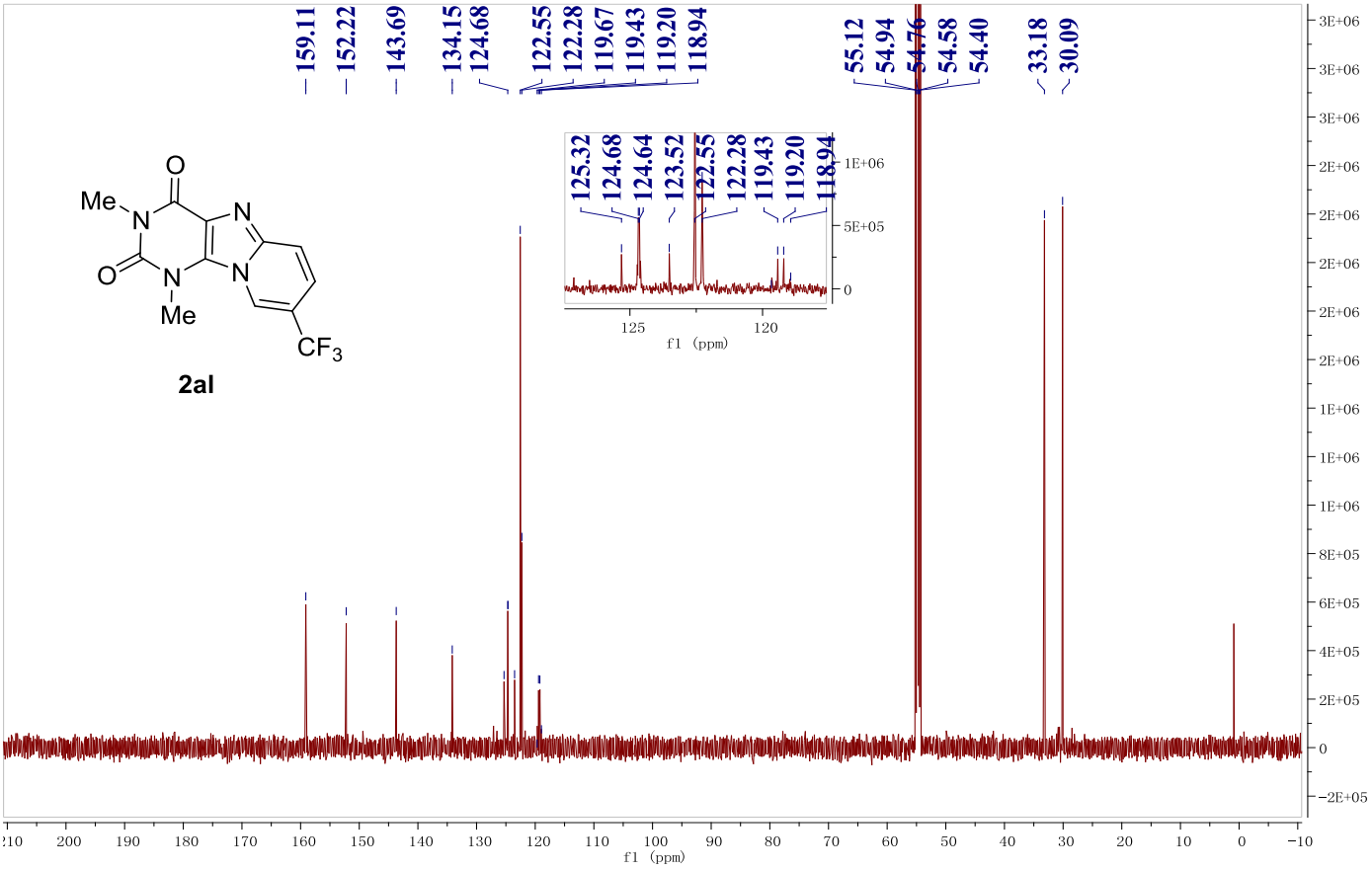


^{1}H NMR Spectrum of 2al at 25 °C ($CDCl_3$, 600 MHz)



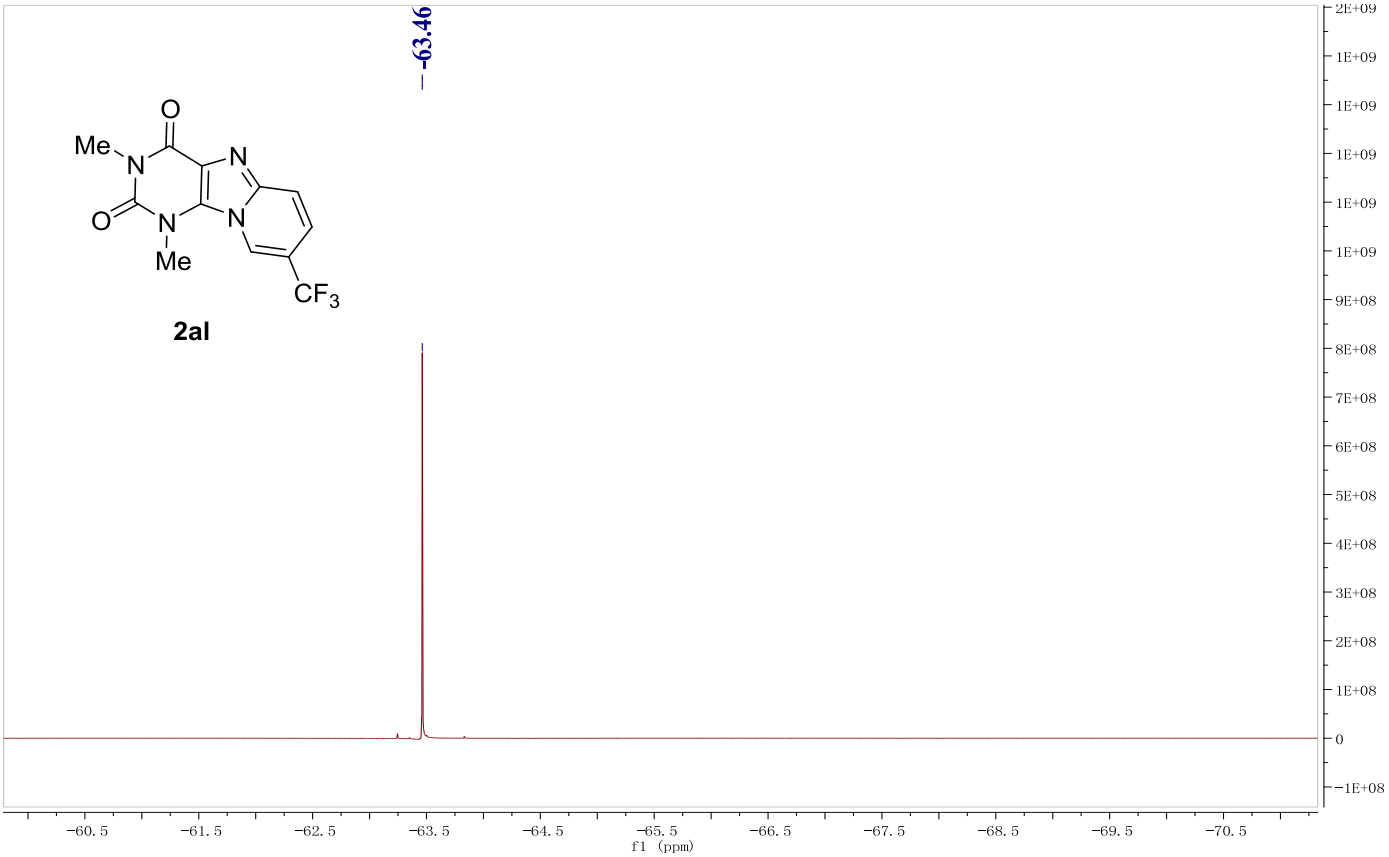
2al

^{13}C NMR Spectrum of 2al at 25 °C ($CDCl_3$, 150 MHz)

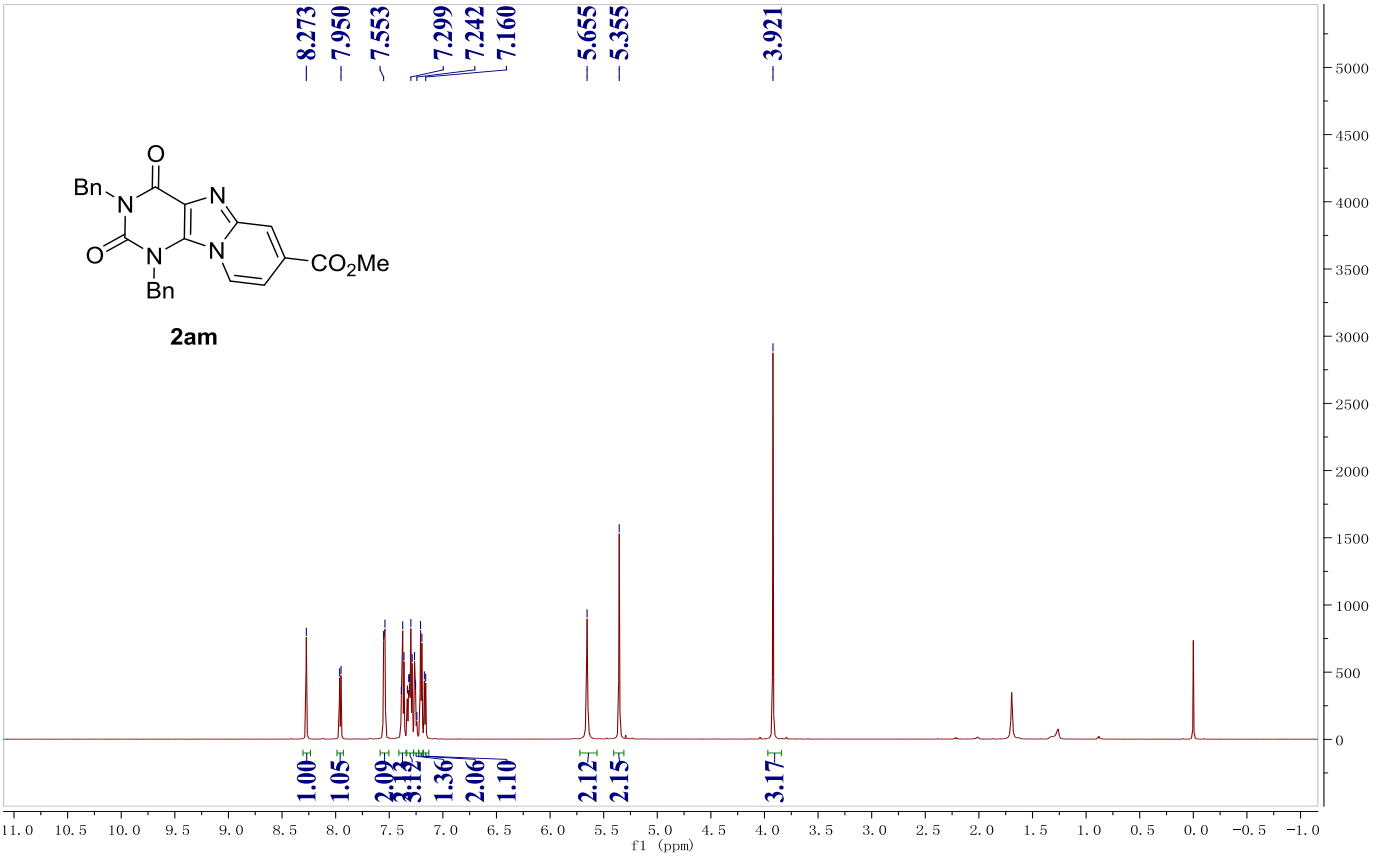


2al

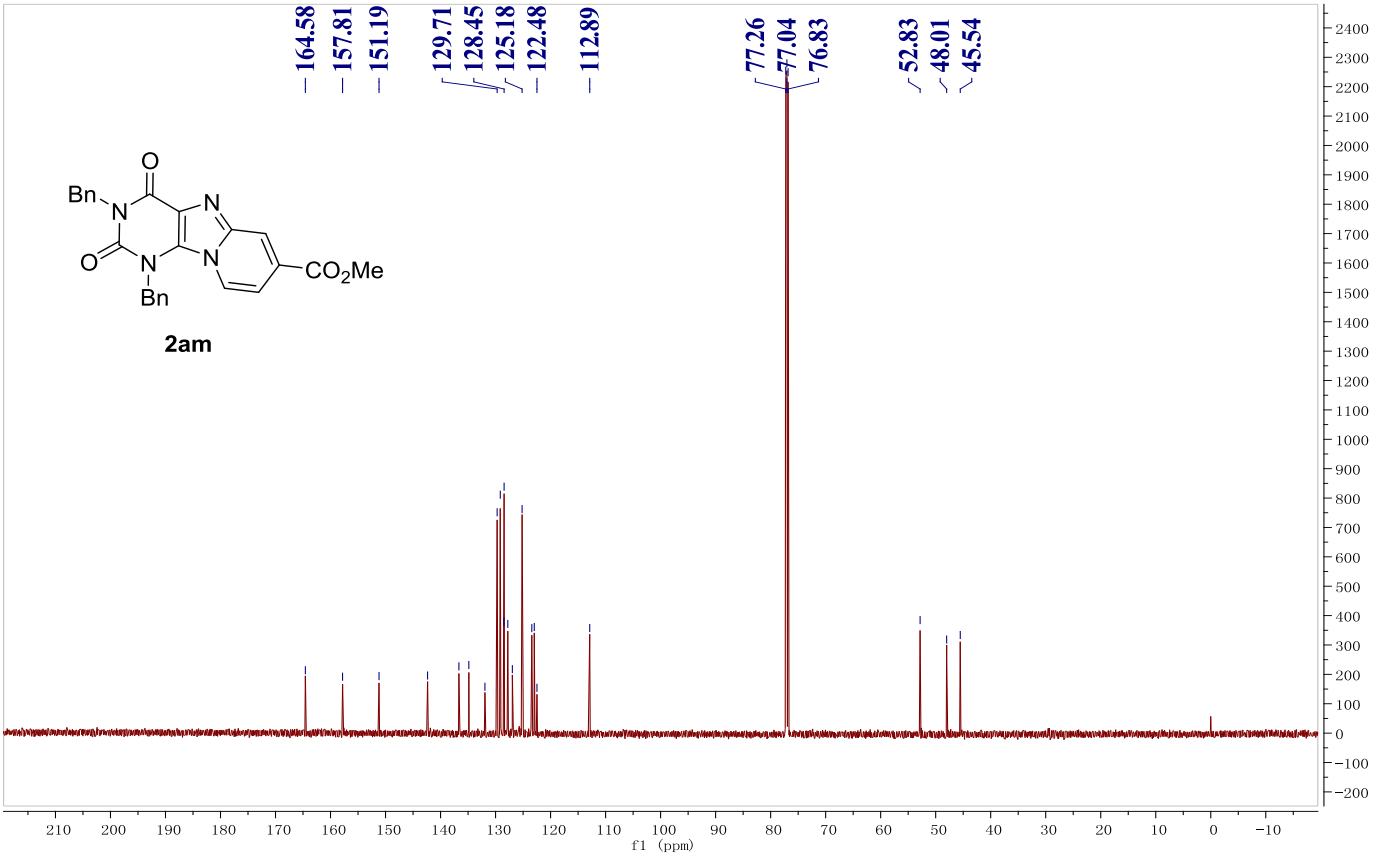
^{19}F NMR Spectrum of 2al at 25 °C ($CDCl_3$, 565 MHz)



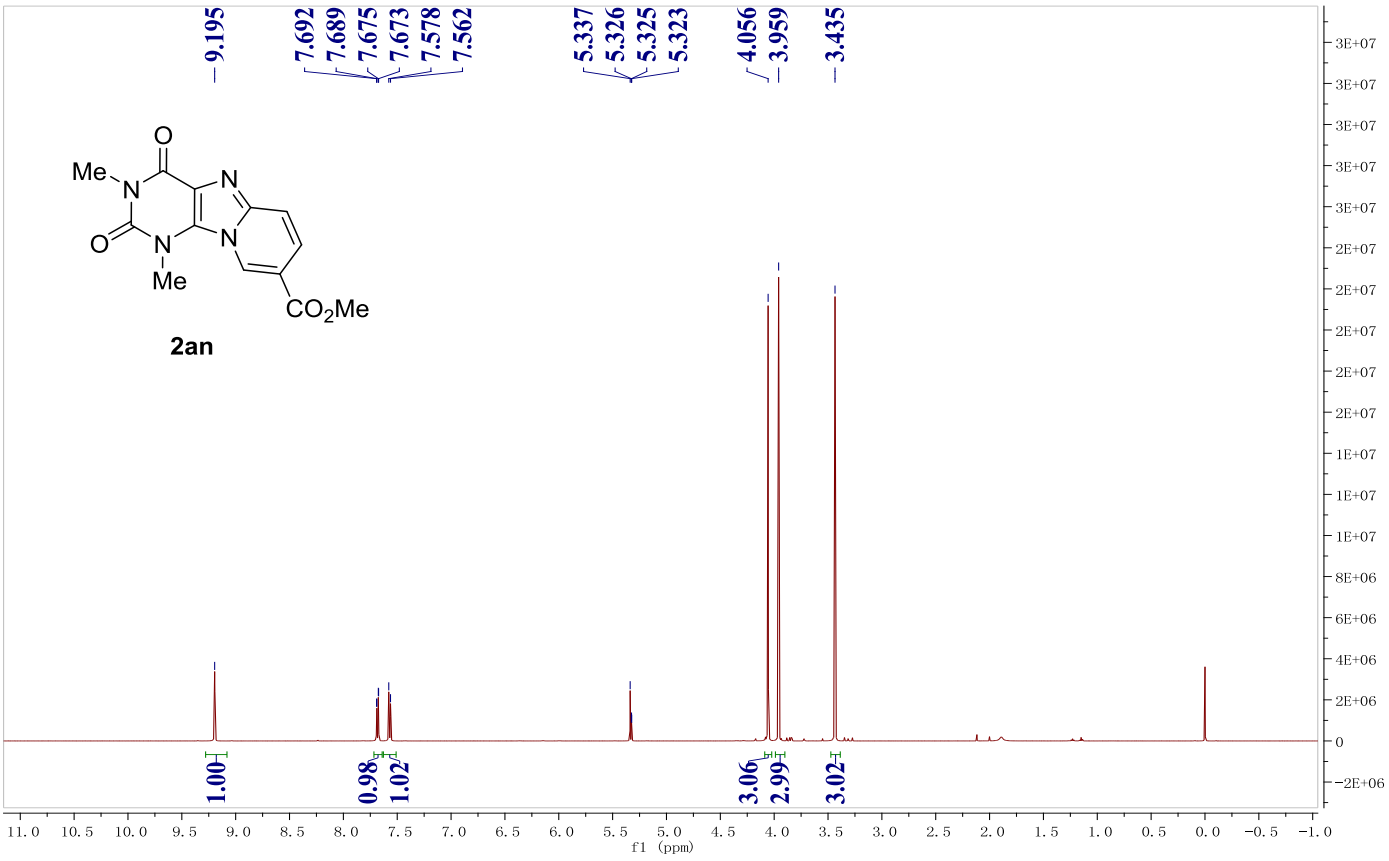
^{1}H NMR Spectrum of 2am at 25 °C ($CDCl_3$, 600 MHz)



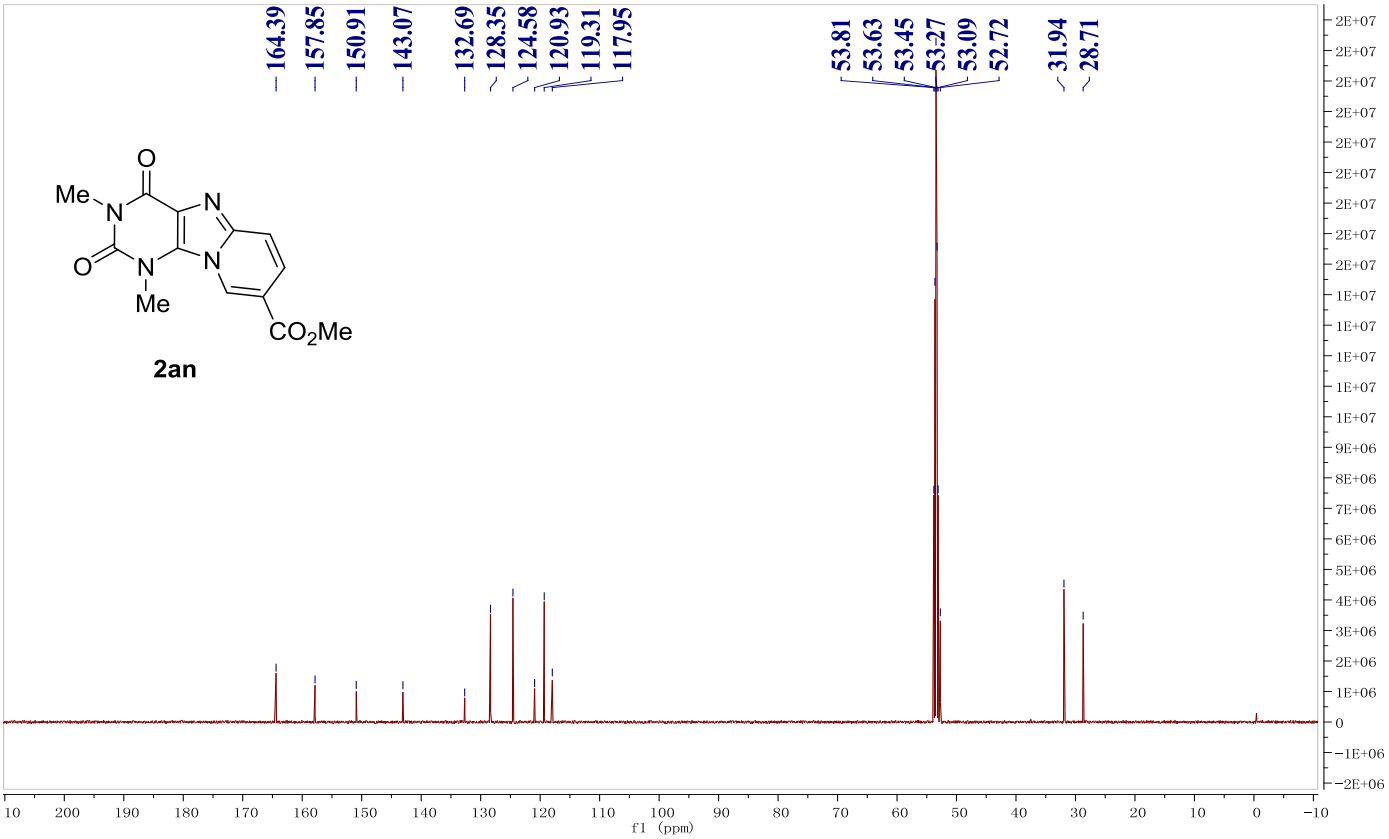
^{13}C NMR Spectrum of 2am at 25 °C ($CDCl_3$, 150 MHz)



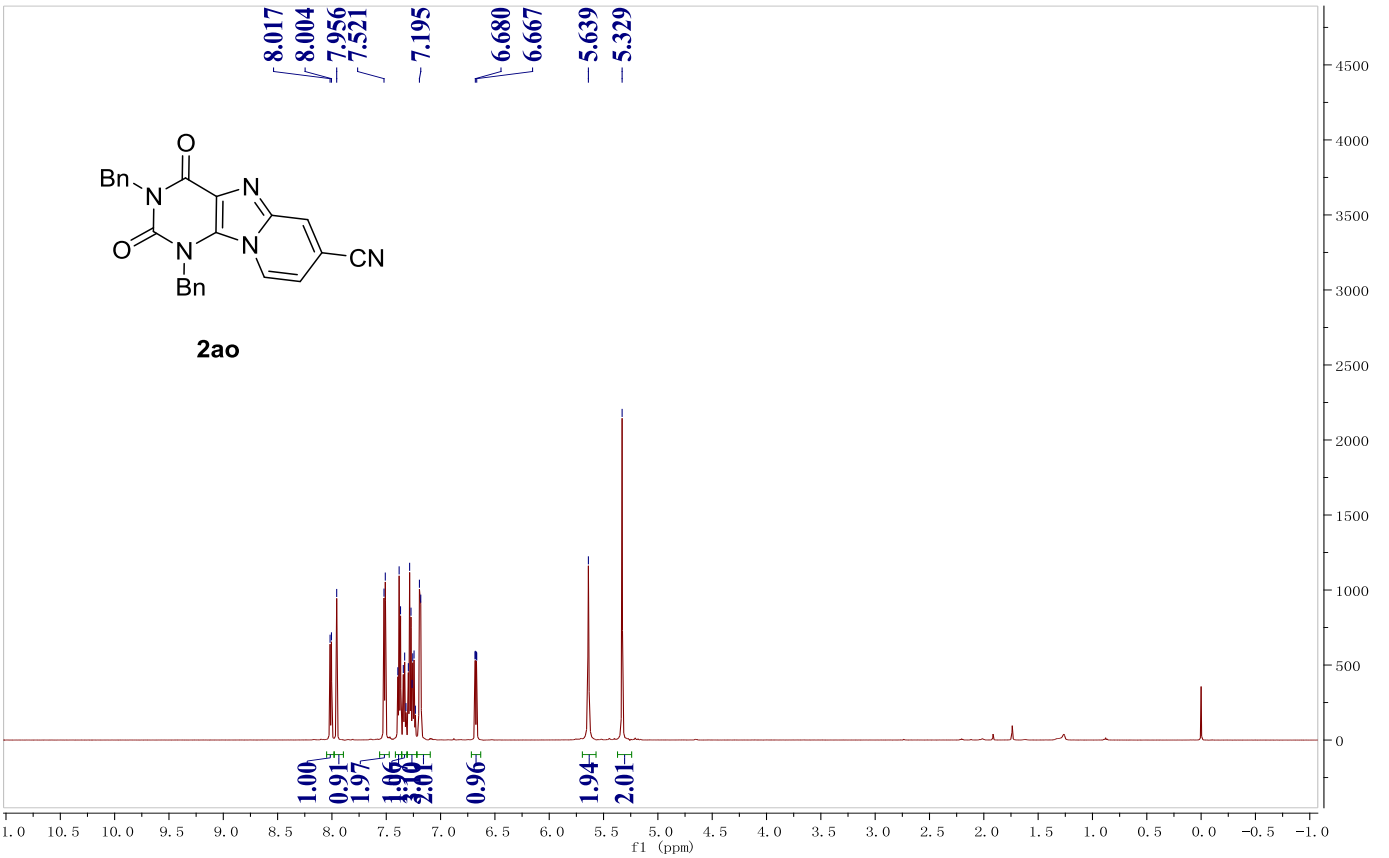
^{1}H NMR Spectrum of 2an at 25 °C ($CDCl_3$, 600 MHz)



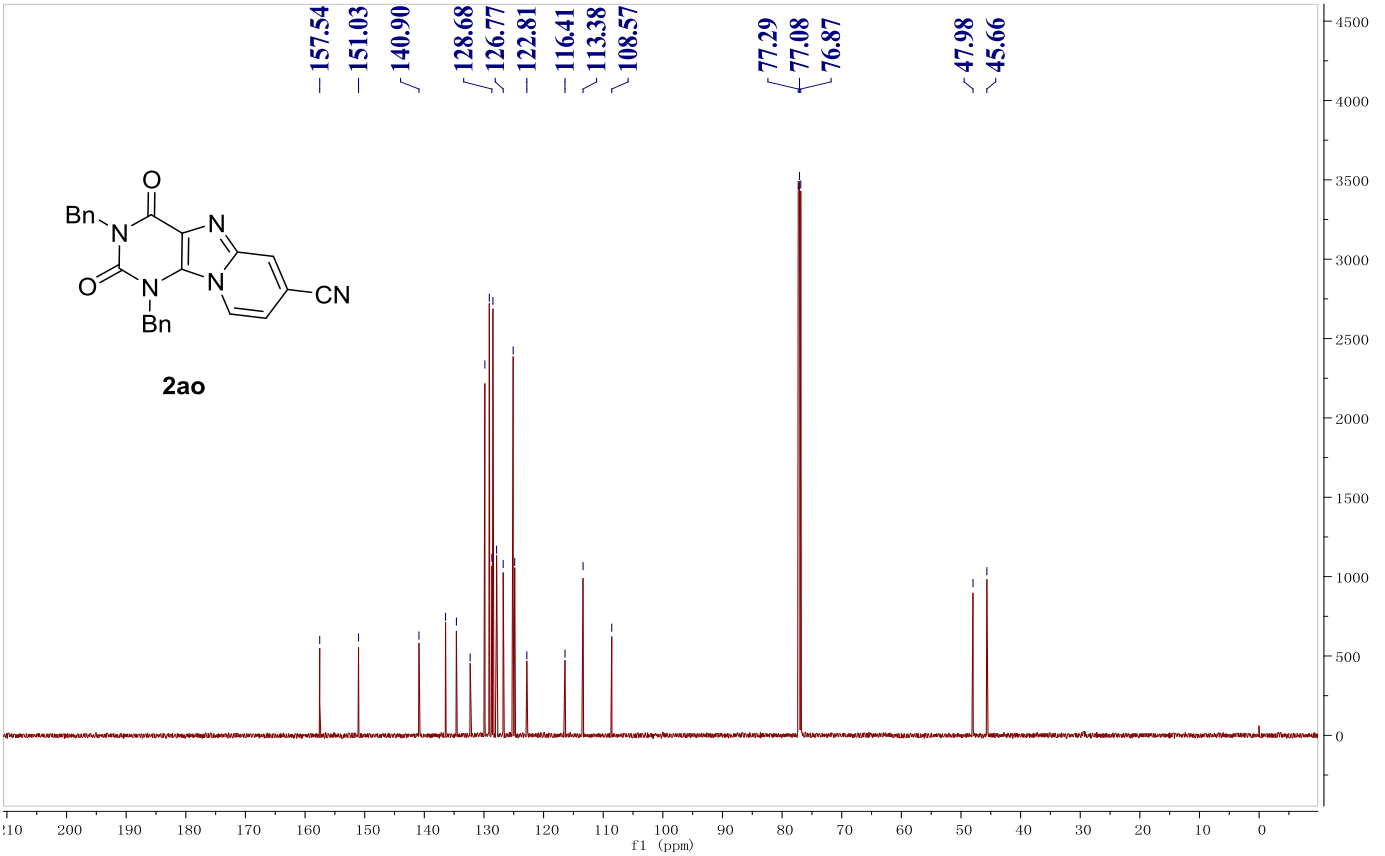
^{13}C NMR Spectrum of 2an at 25 °C ($CDCl_3$, 150 MHz)



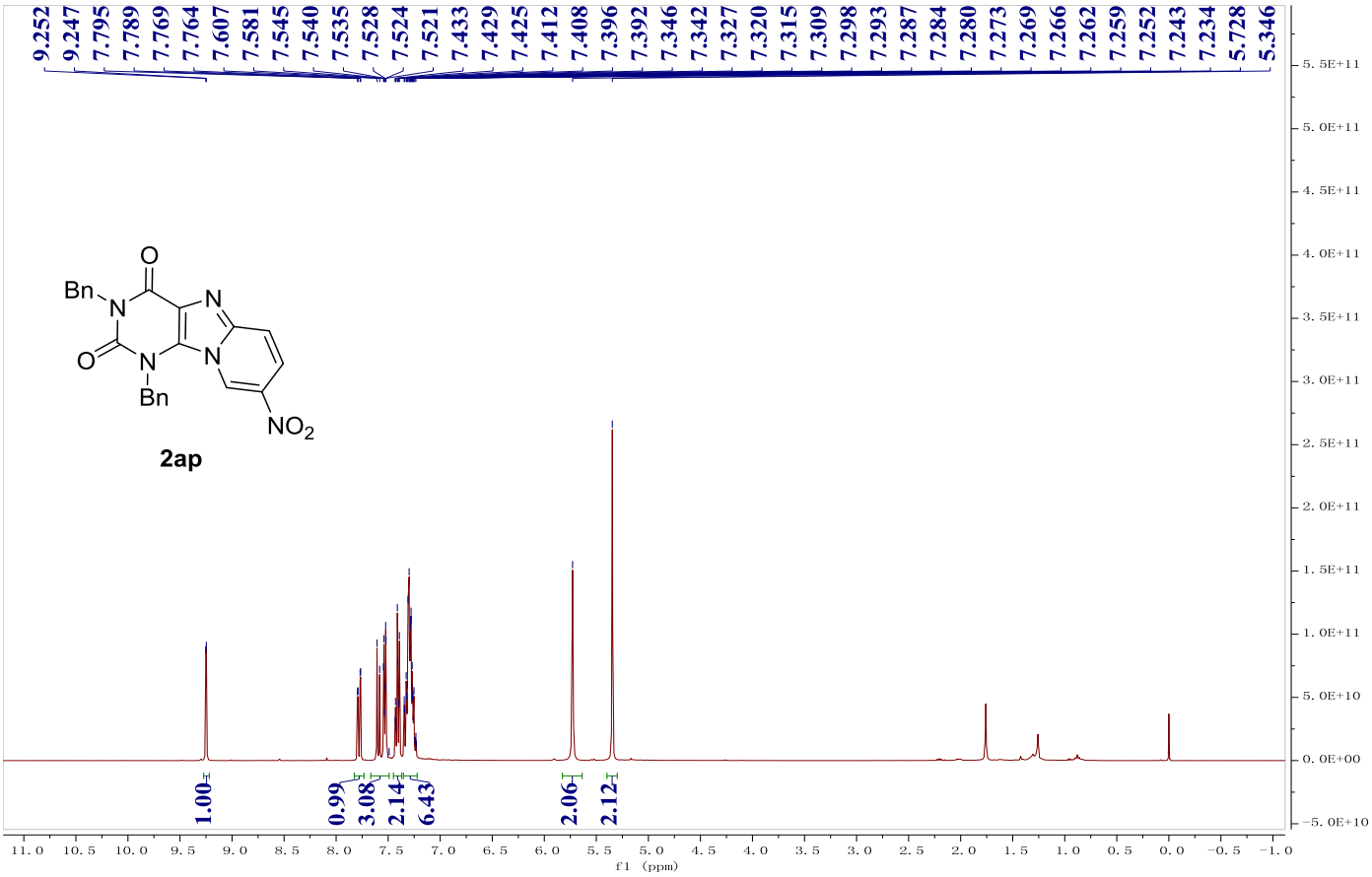
^{1}H NMR Spectrum of 2ao at 25 °C ($CDCl_3$, 600 MHz)



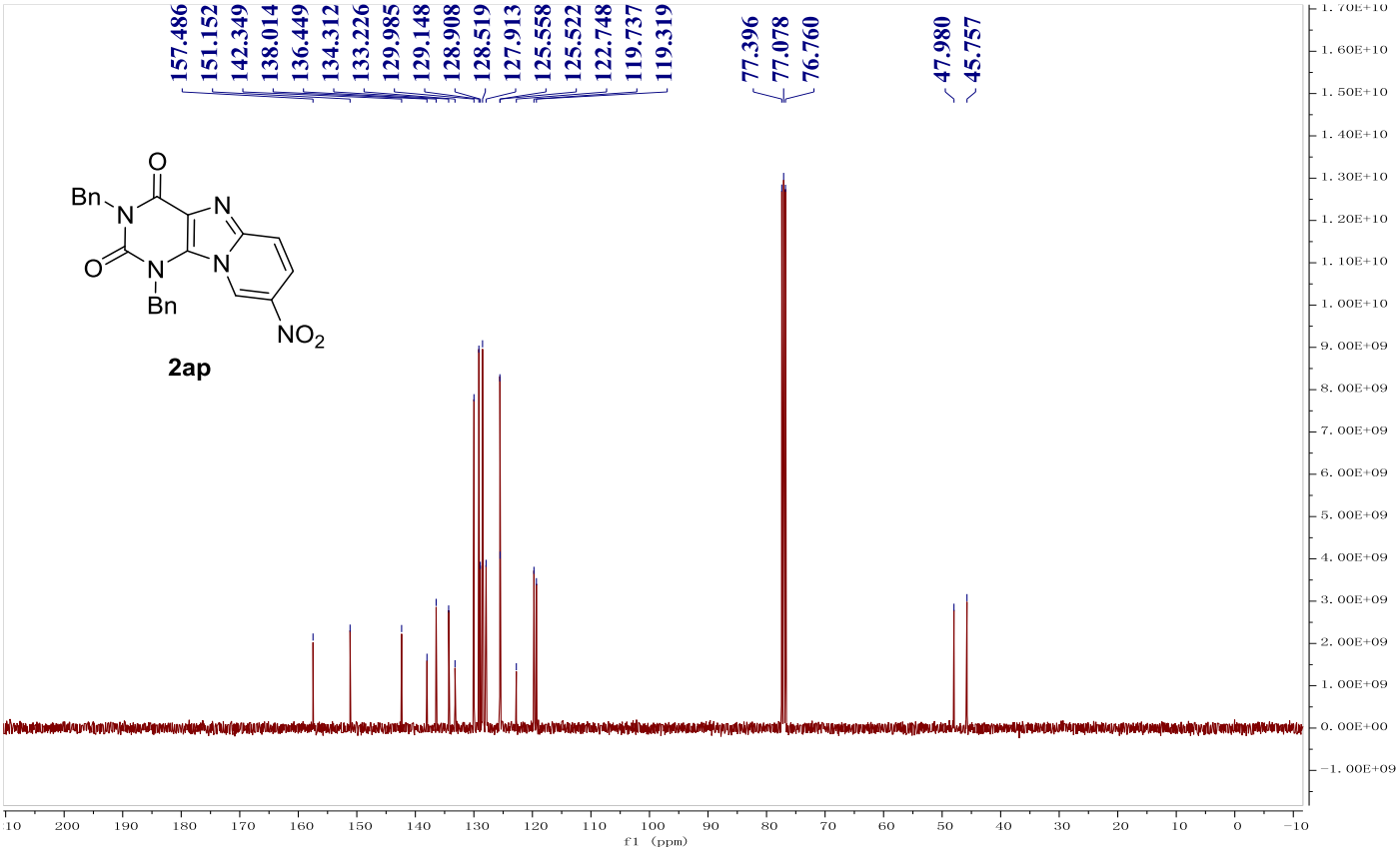
^{13}C NMR Spectrum of 2ao at 25 °C ($CDCl_3$, 150 MHz)



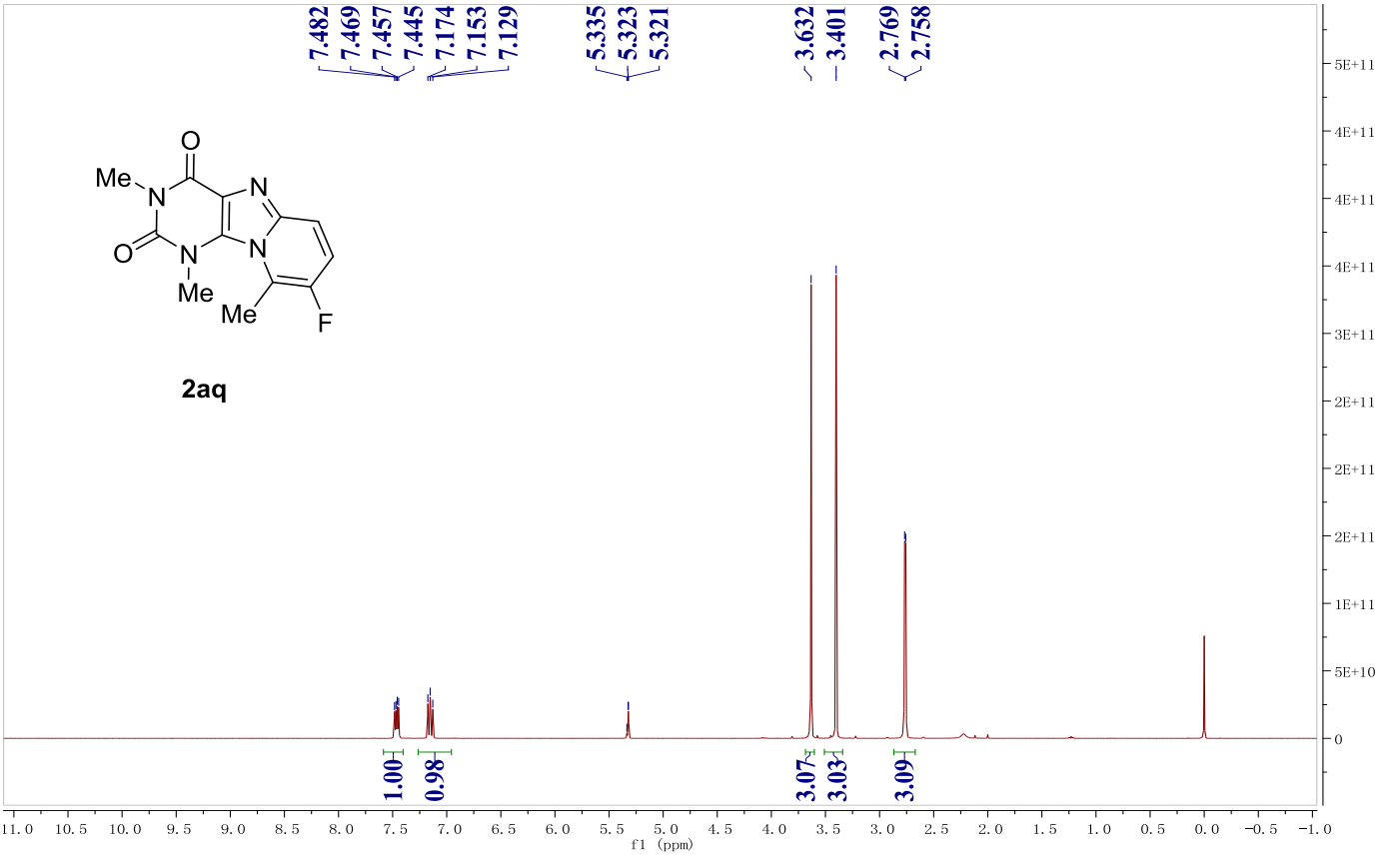
^{1}H NMR Spectrum of 2ap at 25 °C (CD_2Cl_2, 400 MHz)



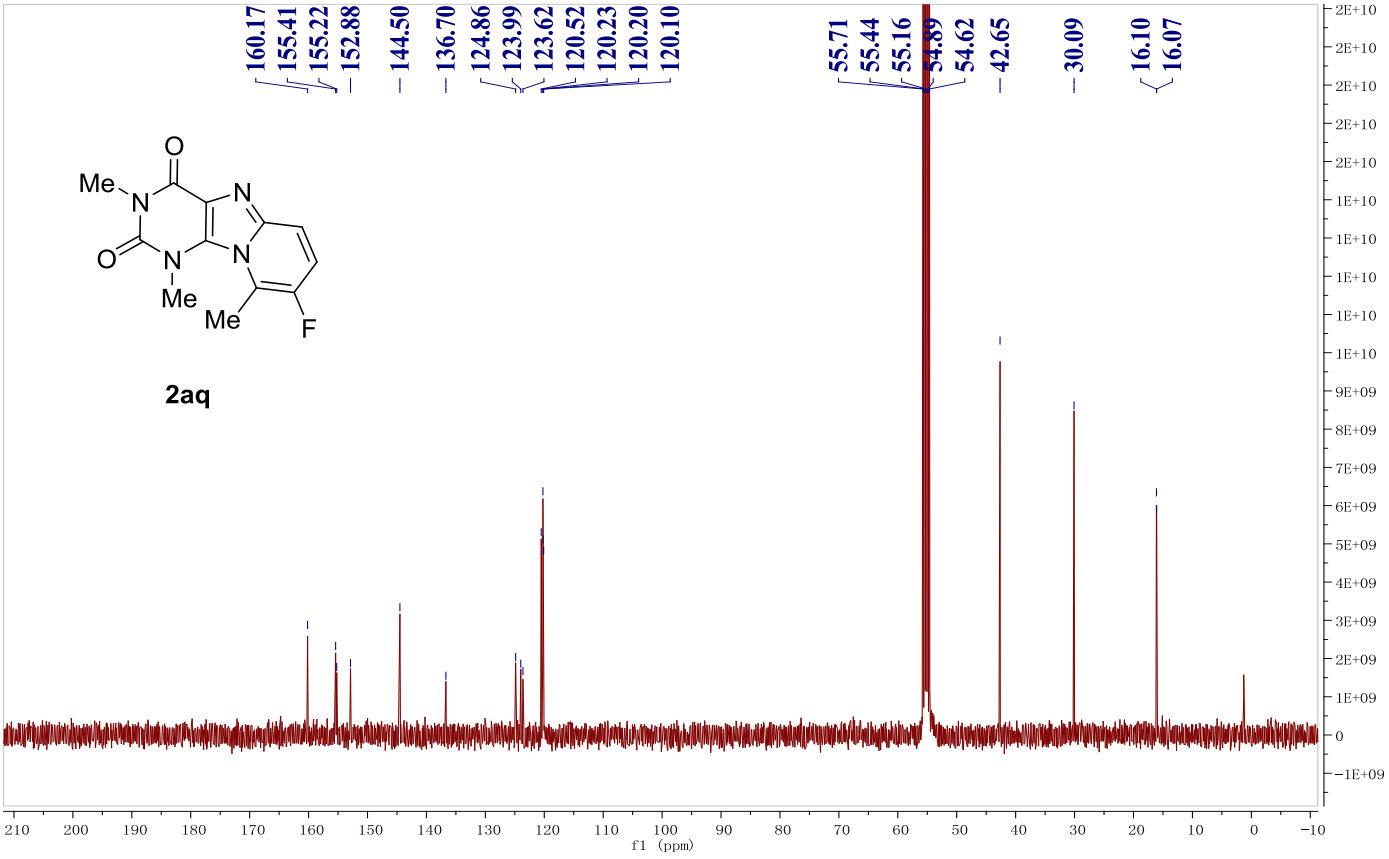
^{13}C NMR Spectrum of 2aq at 25 °C (CD_2Cl_2, 100 MHz)



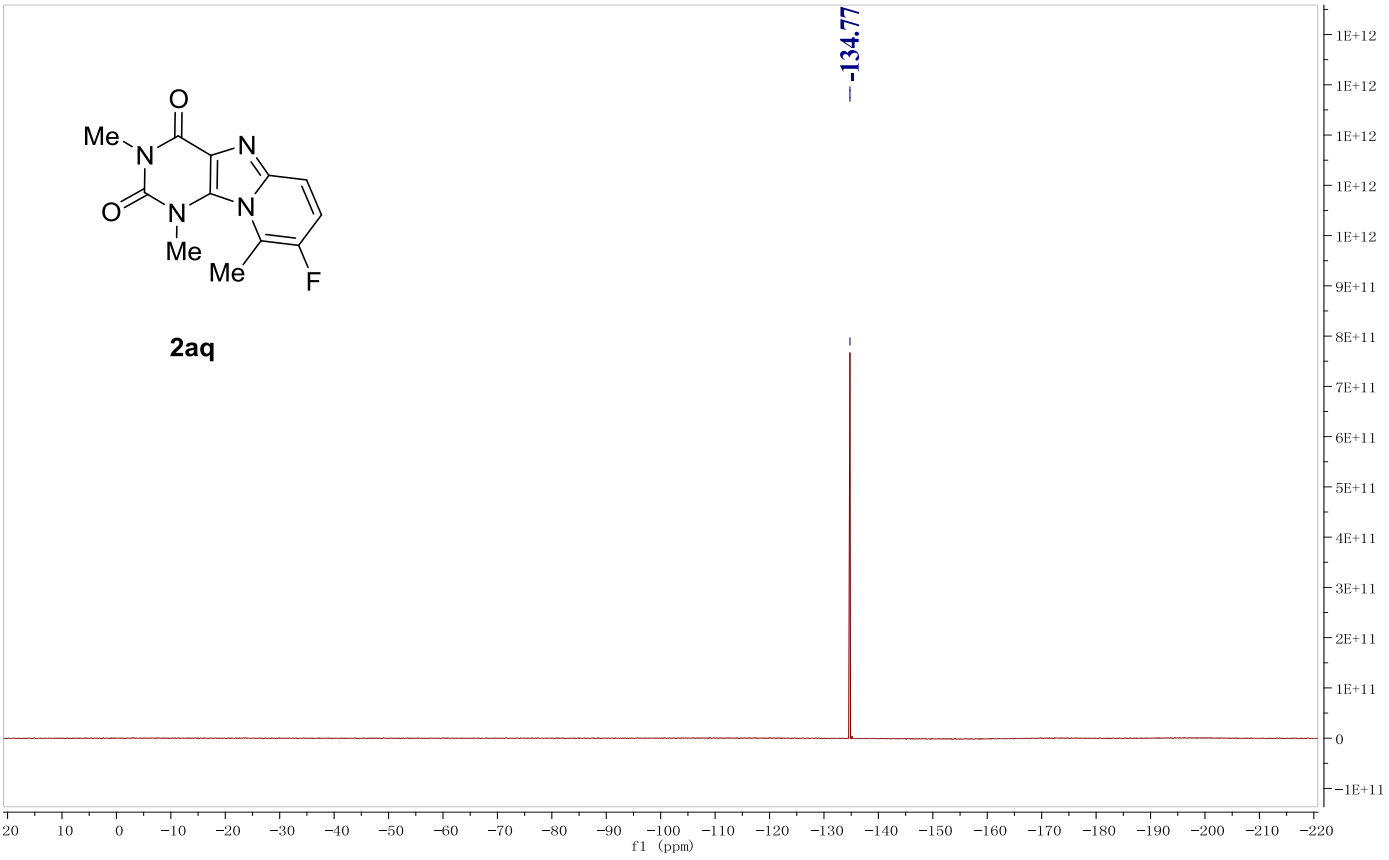
^{1}H NMR Spectrum of 2aq at 25 °C (CD_2Cl_2, 400 MHz)



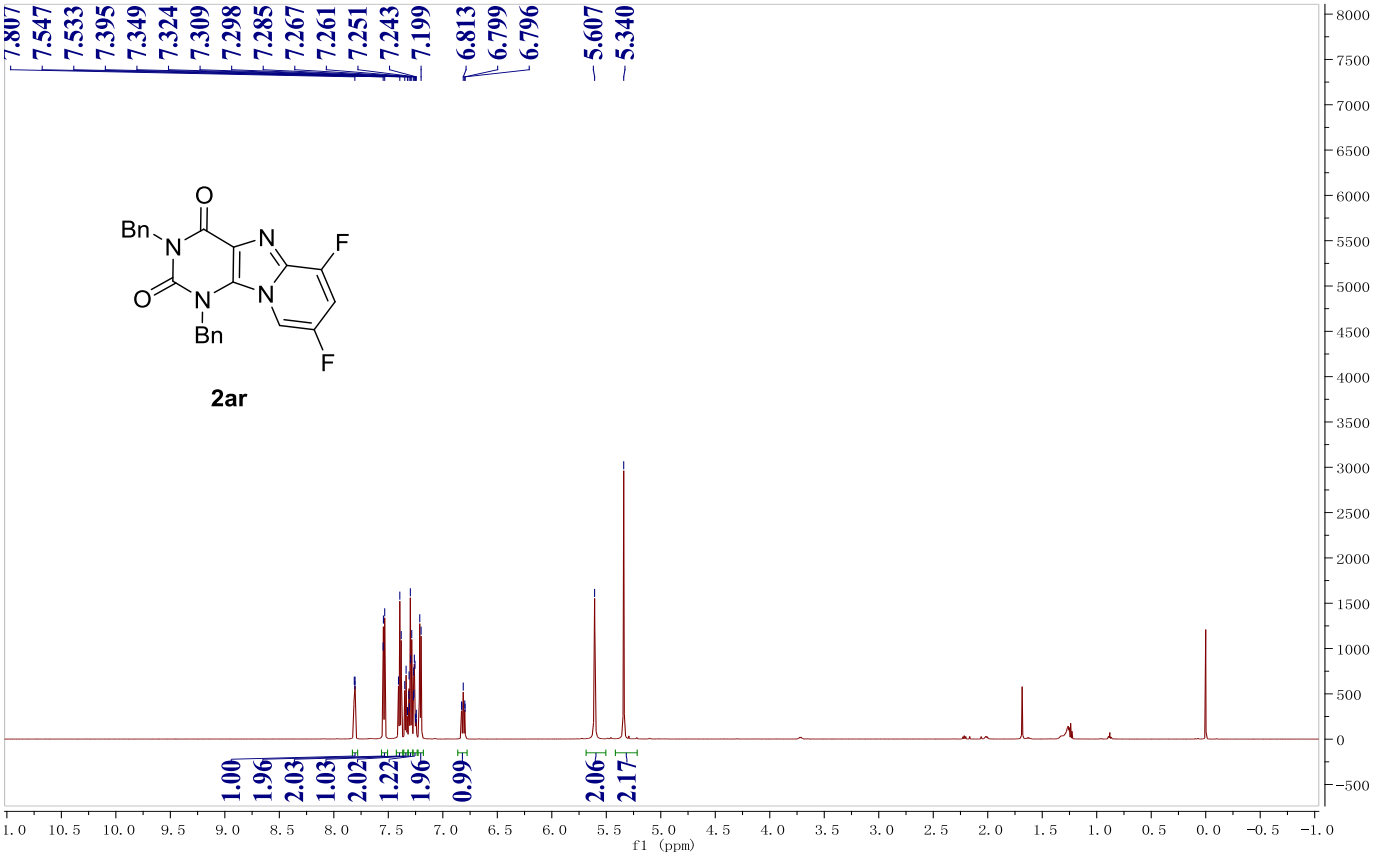
^{13}C NMR Spectrum of 2aq at 25 °C (CD_2Cl_2, 100 MHz)



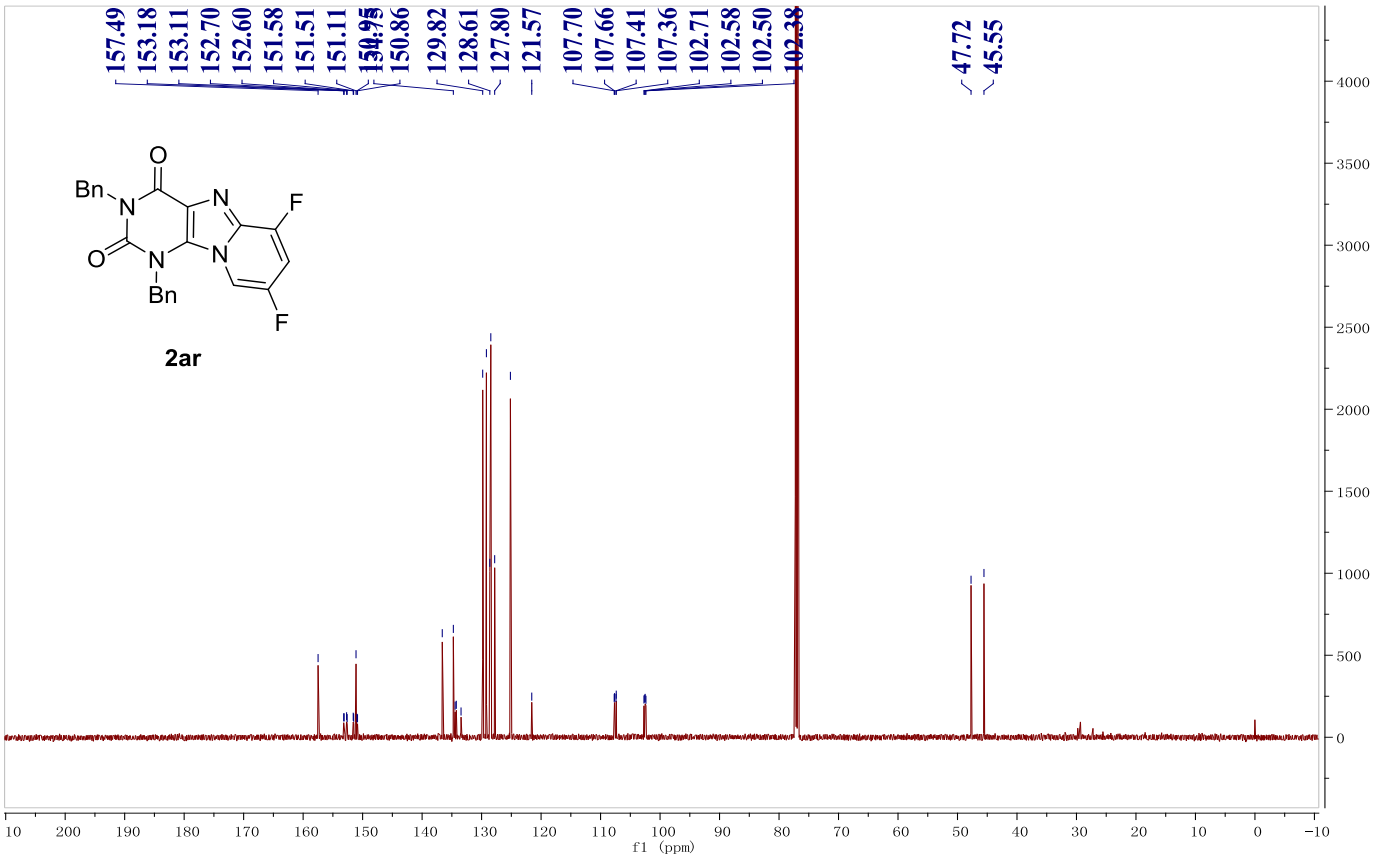
^{19}F NMR Spectrum of 2aq at 25 °C (CD_2Cl_2, 376 MHz)



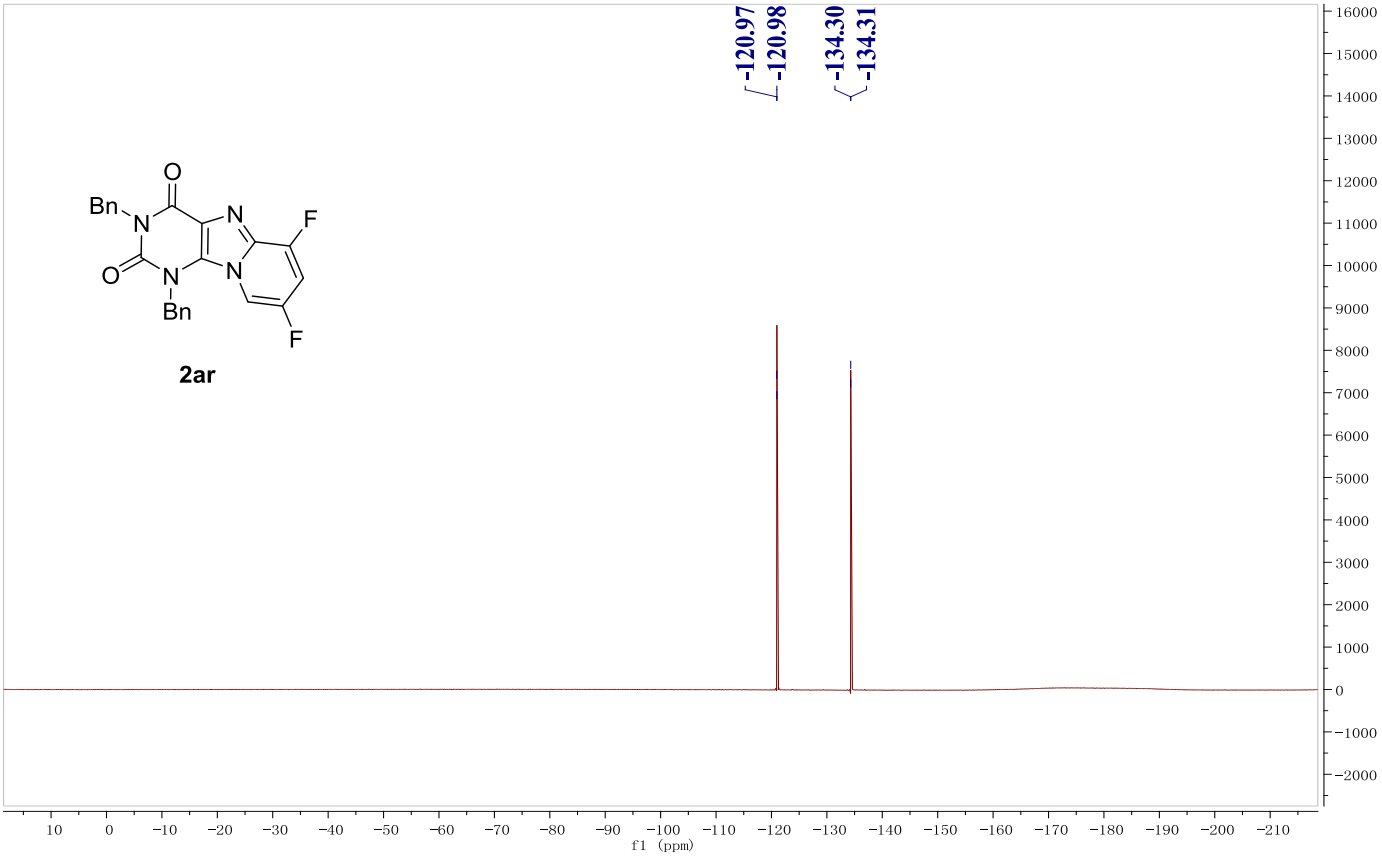
^{1}H NMR Spectrum of 2ar at 25 °C ($CDCl_3$, 600 MHz)



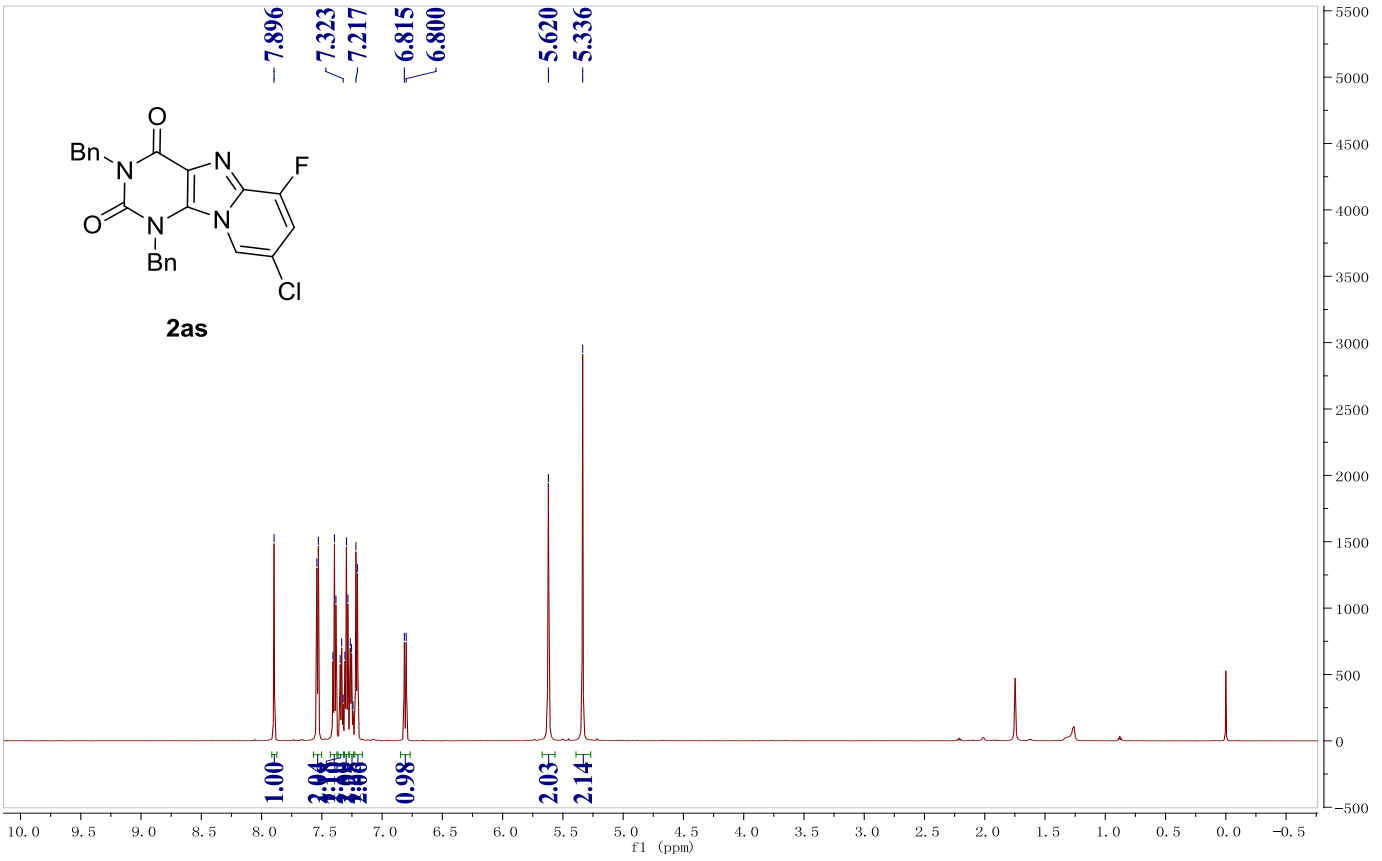
^{13}C NMR Spectrum of 2ar at 25 °C ($CDCl_3$, 150 MHz)



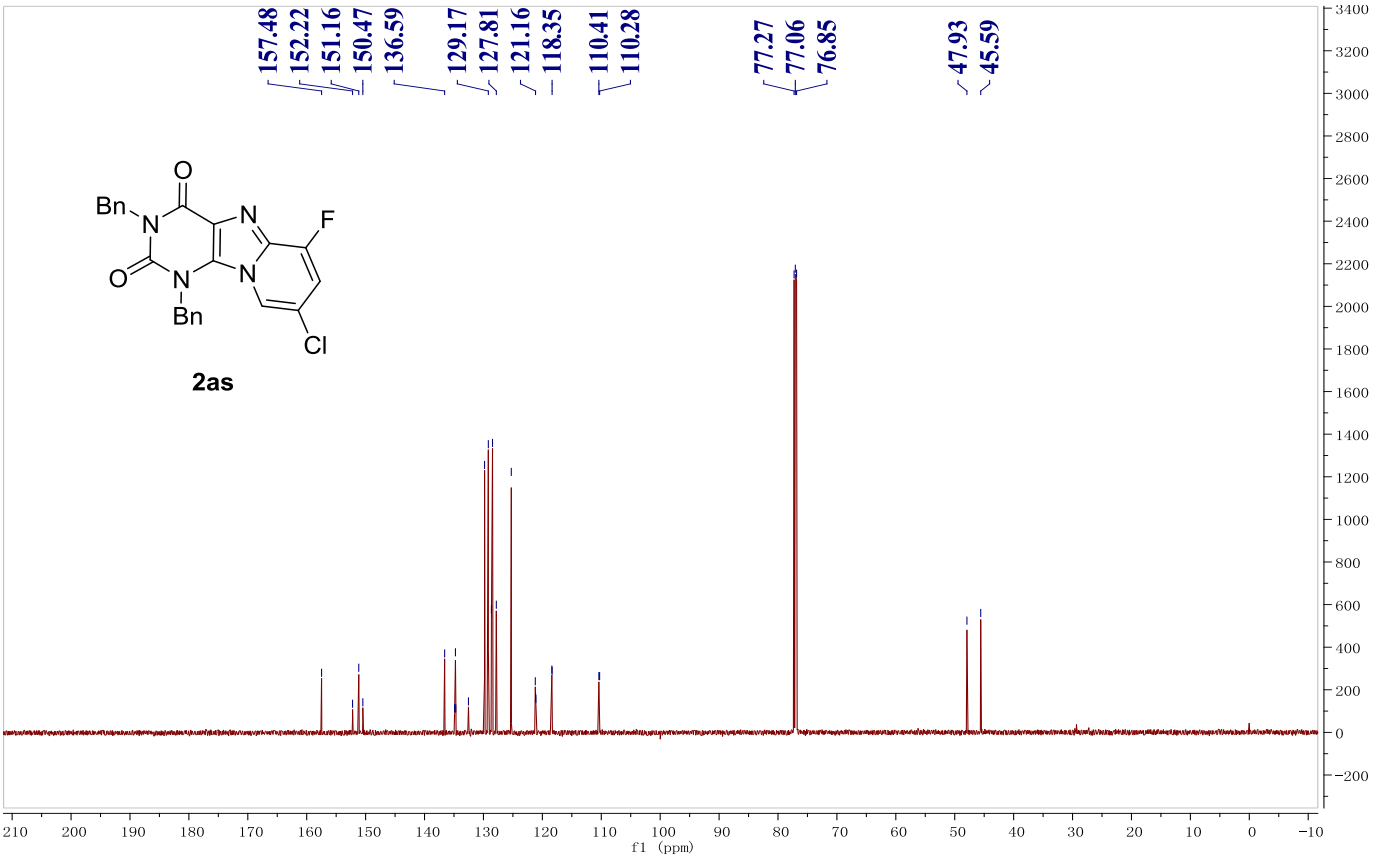
^{19}F NMR Spectrum of 2ar at 25 °C ($CDCl_3$, 565 MHz)



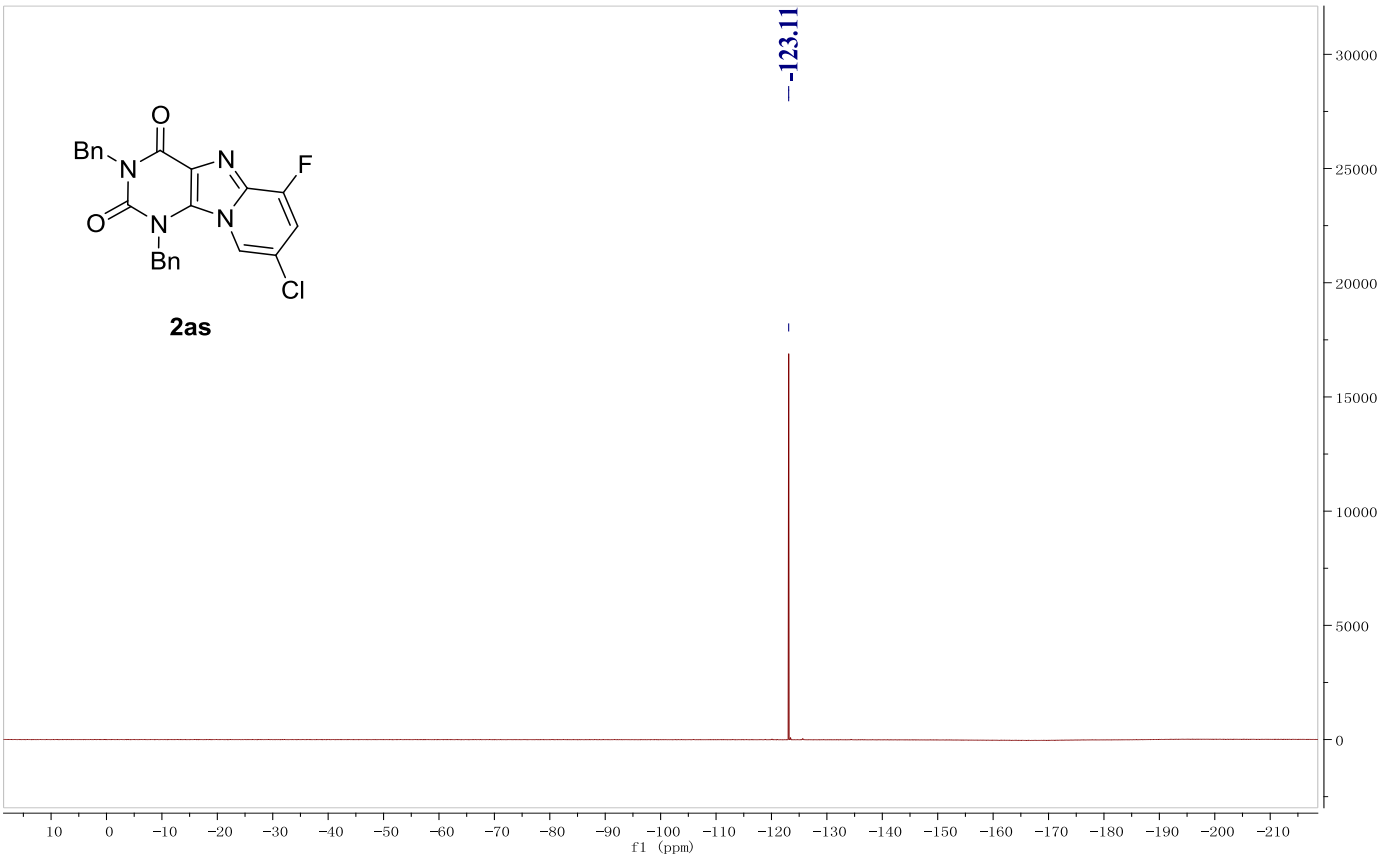
^{1}H NMR Spectrum of 2as at 25 °C ($CDCl_3$, 600 MHz)



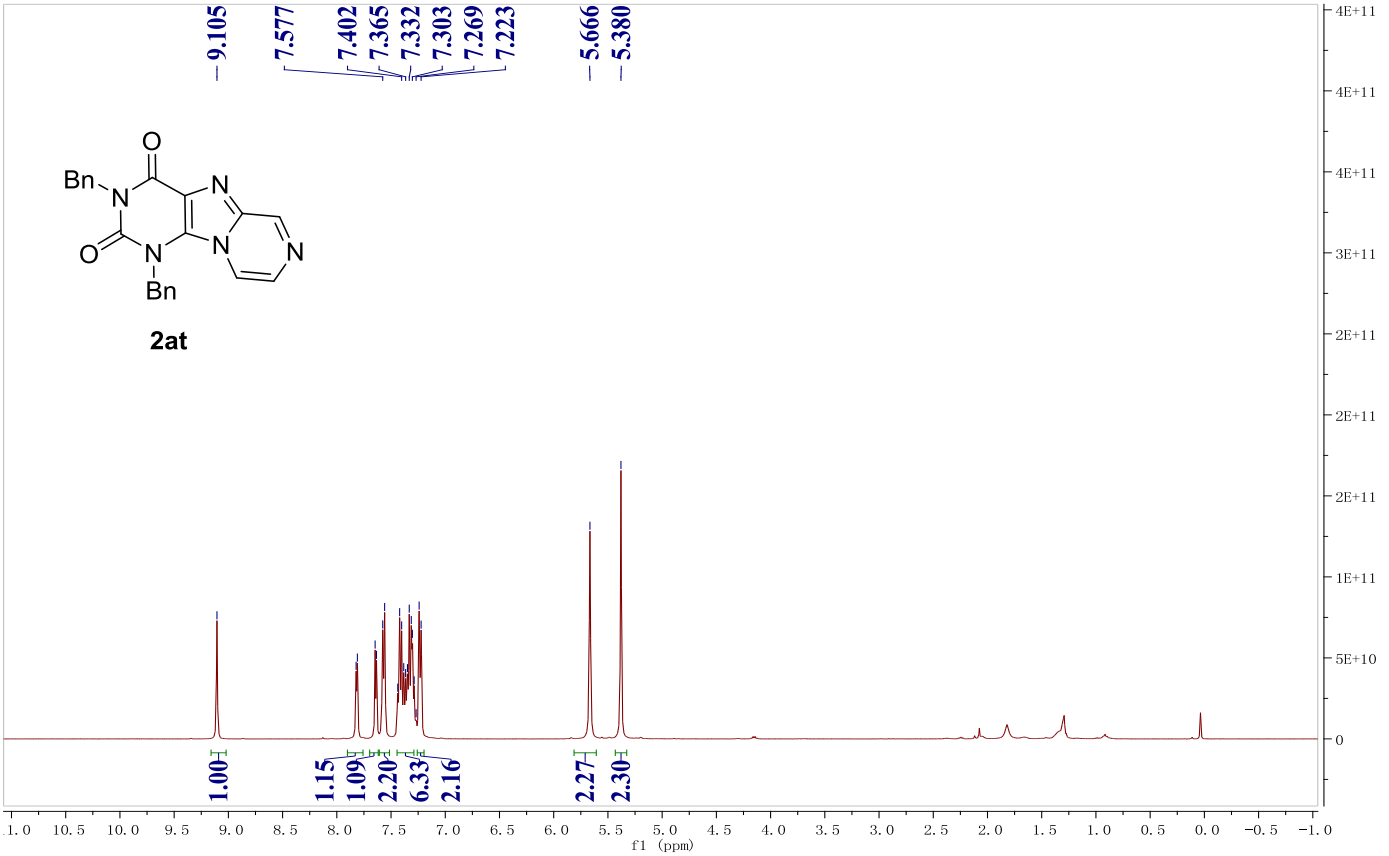
^{13}C NMR Spectrum of 2as at 25 °C ($CDCl_3$, 150 MHz)



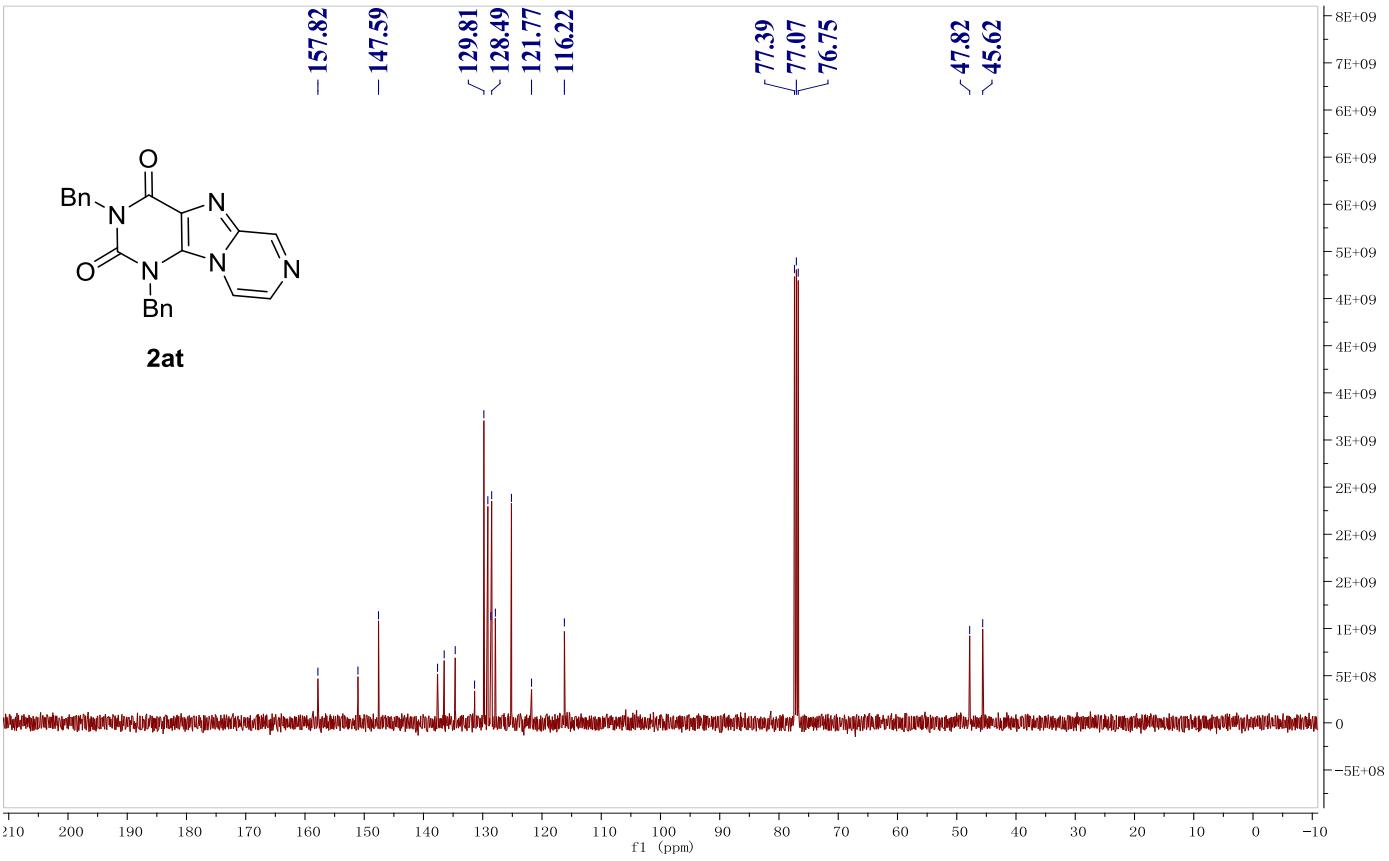
^{13}C NMR Spectrum of 2as at 25 °C ($CDCl_3$, 565 MHz)



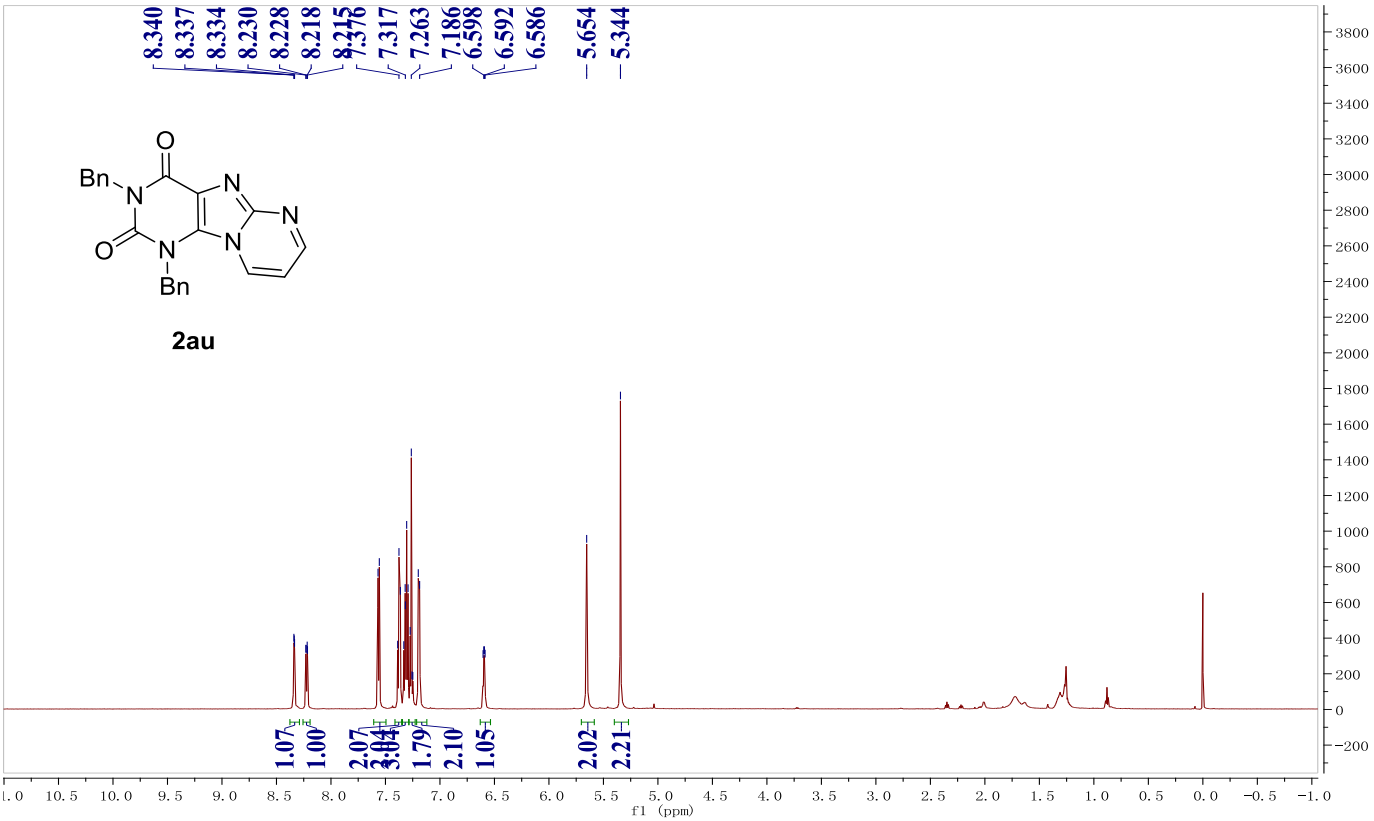
^{1}H NMR Spectrum of 2at at 25 °C ($CDCl_3$, 400 MHz)



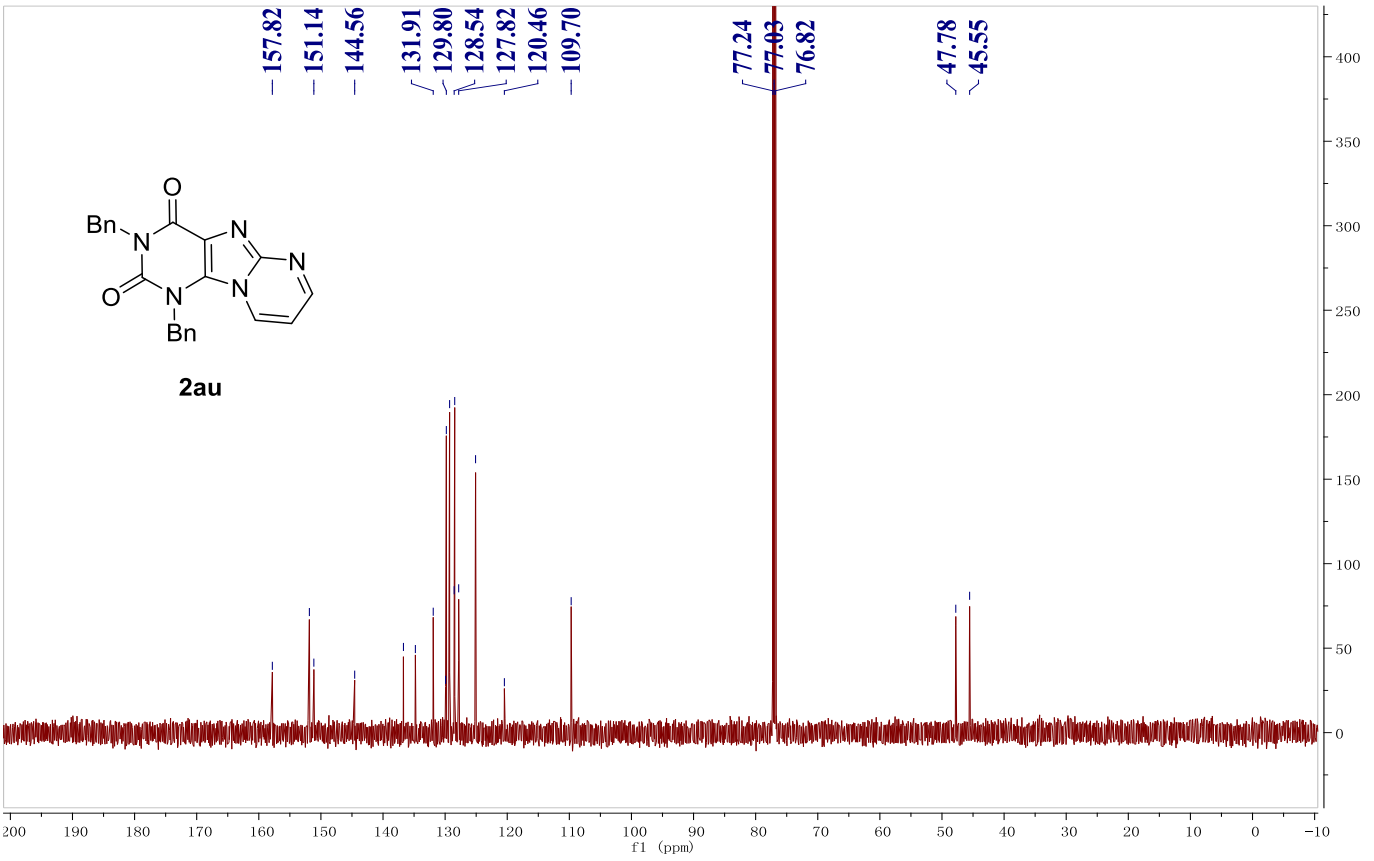
^{13}C NMR Spectrum of 2at at 25 °C ($CDCl_3$, 100 MHz)



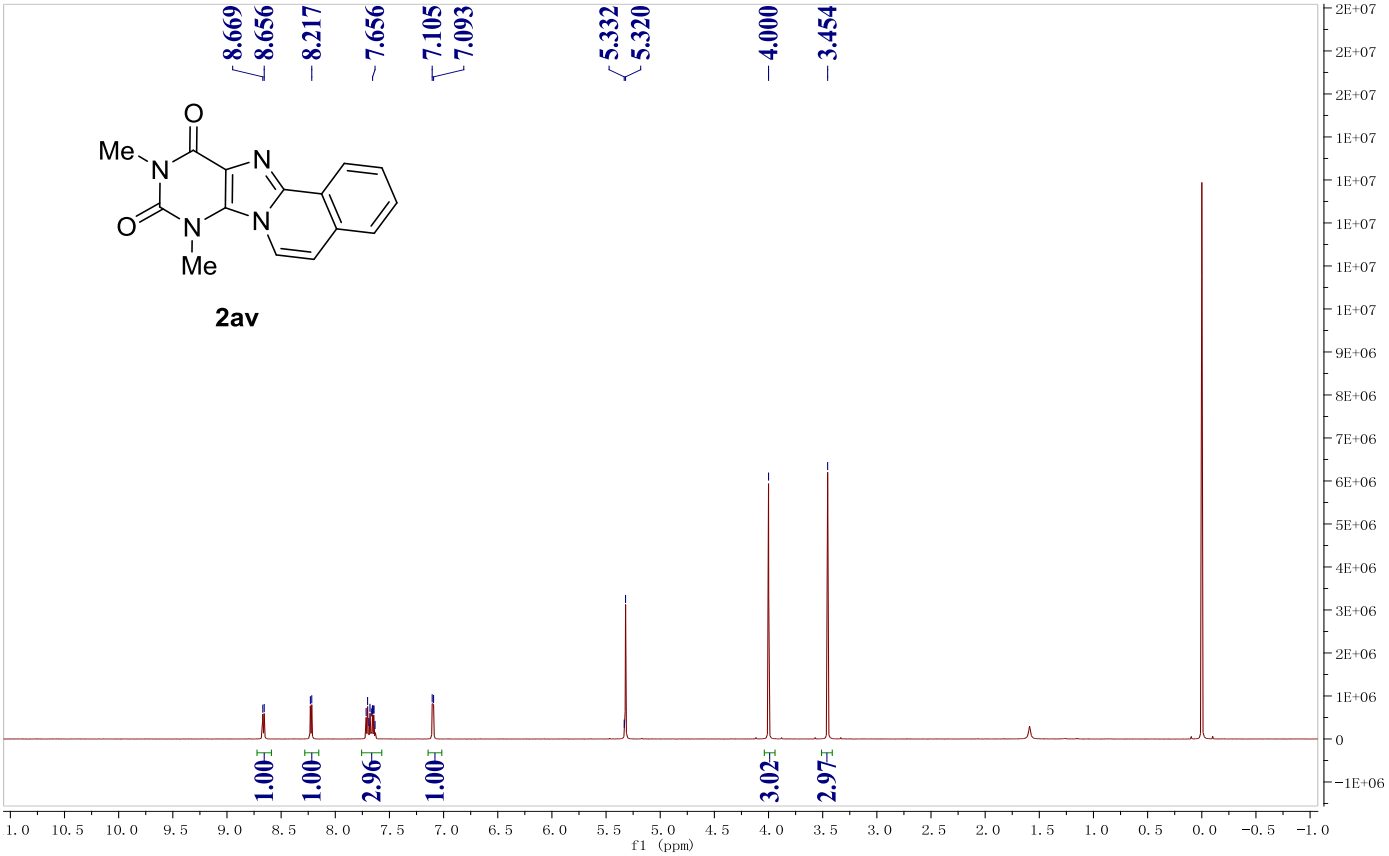
^{1}H NMR Spectrum of 2au at 25 °C ($CDCl_3$, 600 MHz)



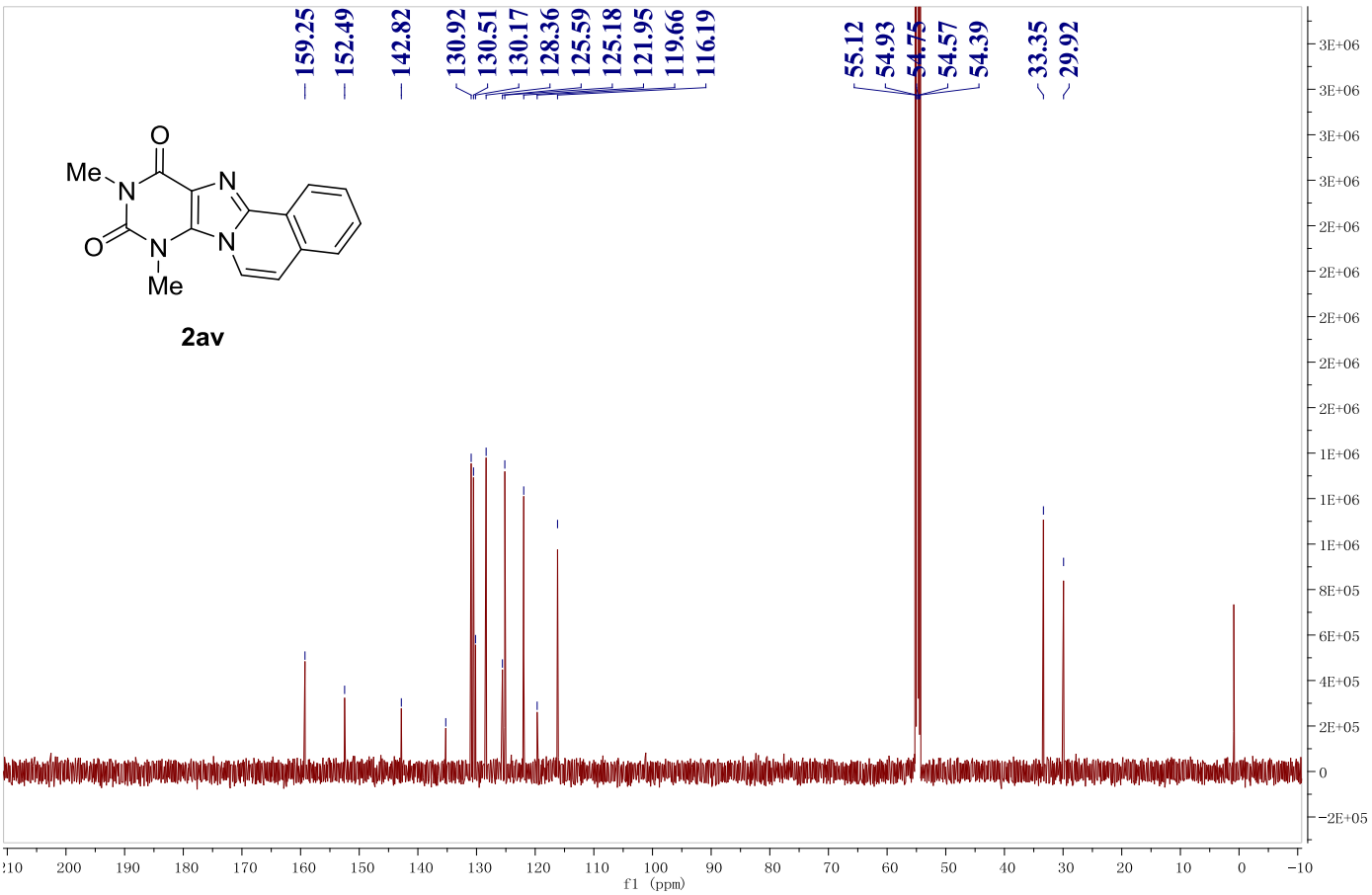
^{13}C NMR Spectrum of 2au at 25 °C ($CDCl_3$, 150 MHz)



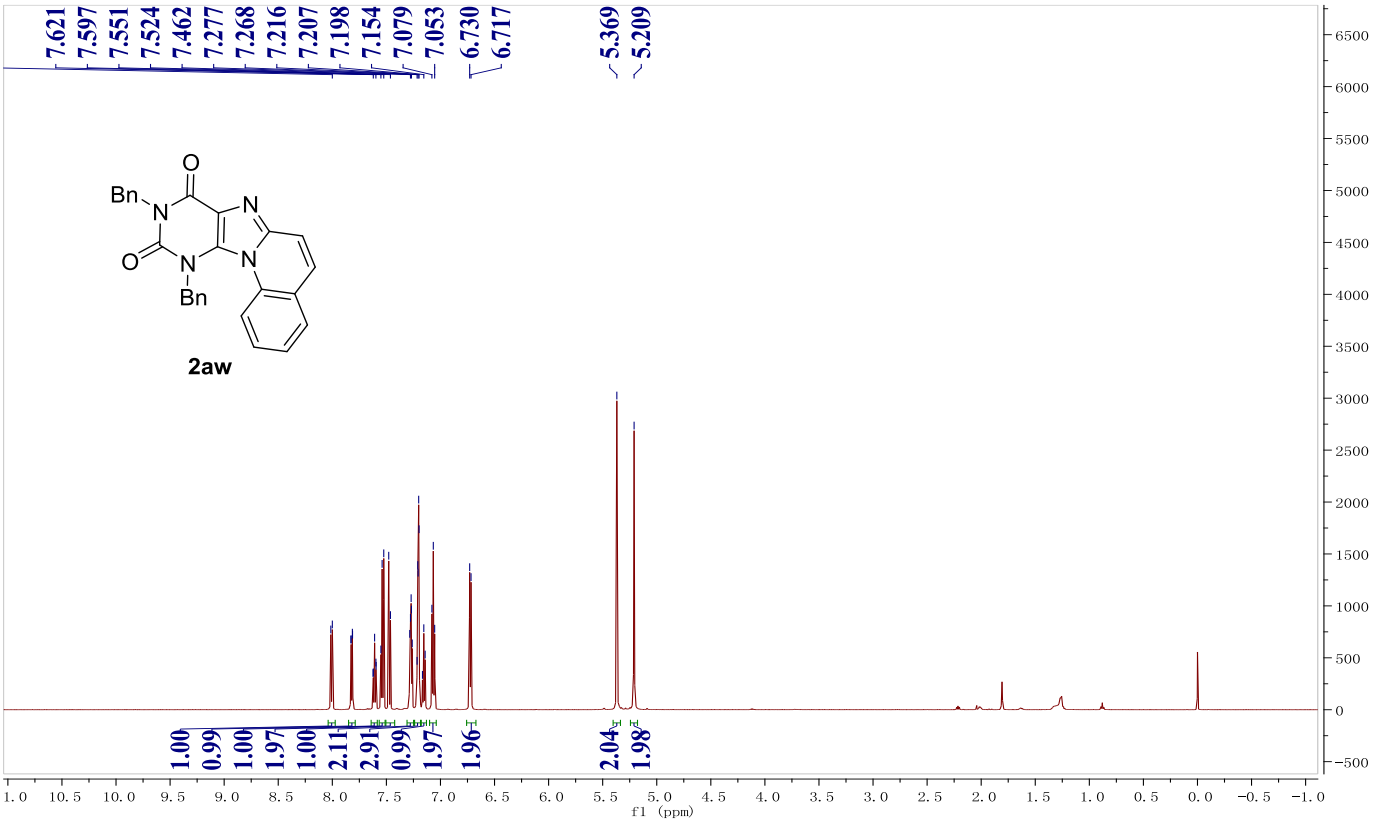
^{1}H NMR Spectrum of 2av at 25 °C ($CDCl_3$, 600 MHz)



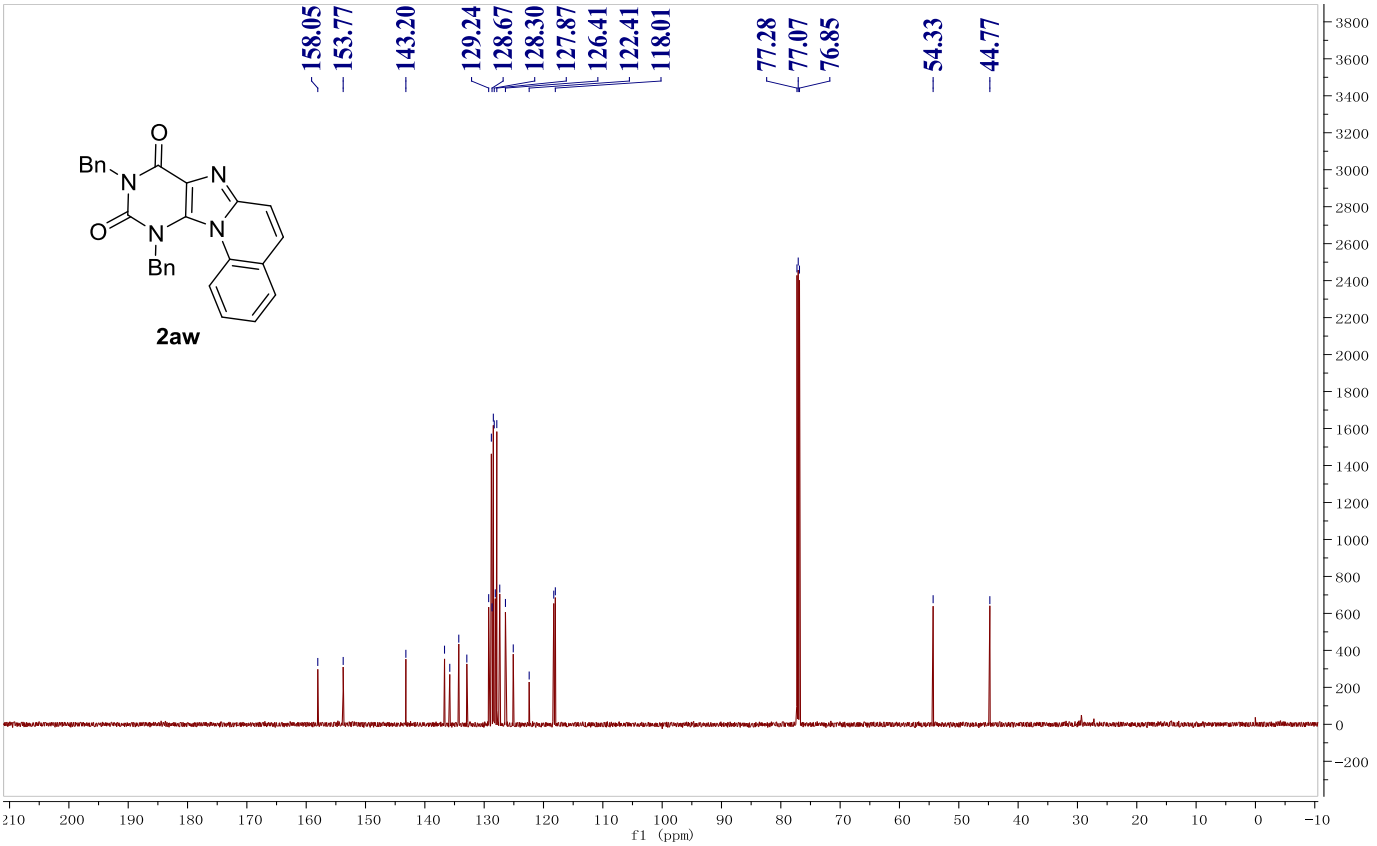
^{13}C NMR Spectrum of 2av at 25 °C ($CDCl_3$, 150 MHz)



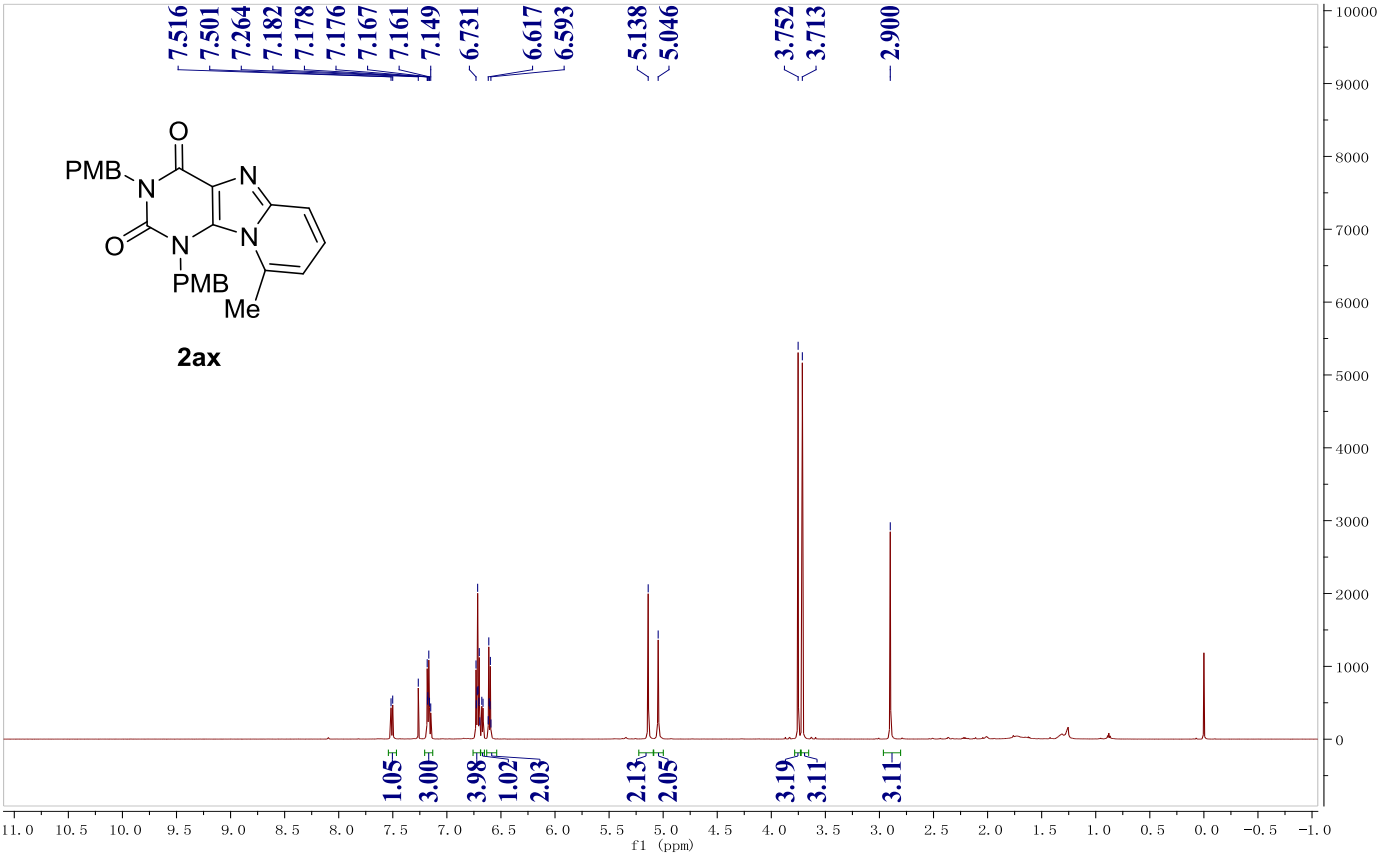
^{1}H NMR Spectrum of 2aw at 25 °C ($CDCl_3$, 600 MHz)



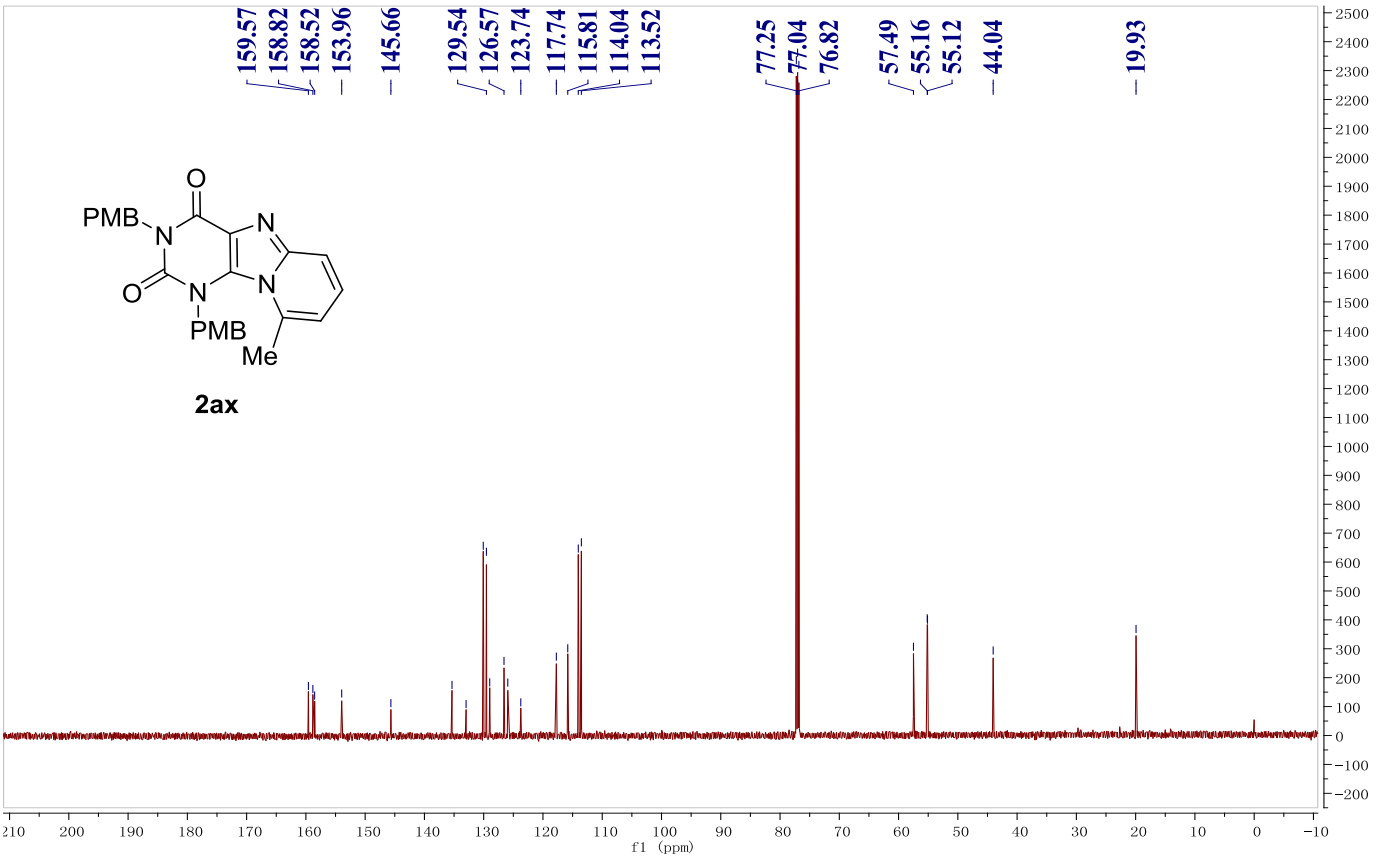
^{13}C NMR Spectrum of 2aw at 25 °C ($CDCl_3$, 150 MHz)



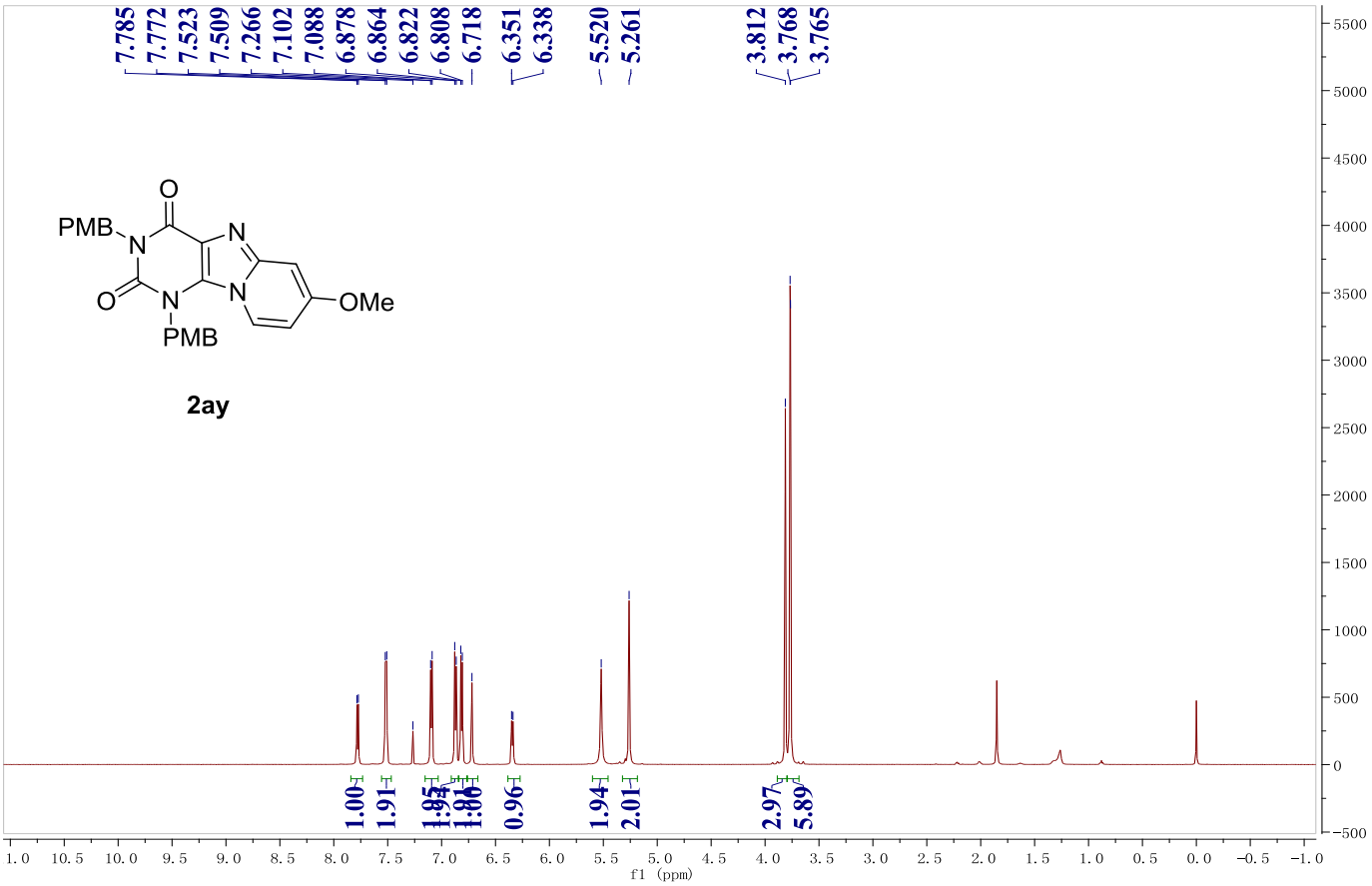
^{1}H NMR Spectrum of 2ax at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 2ax at 25 °C ($CDCl_3$, 150 MHz)



^{1}H NMR Spectrum of 2ay at 25 °C ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of 2ay at 25 °C ($CDCl_3$, 150 MHz)