Supporting Information

Green synthesis of glutaramide, piperidino[1,2-a]benzimidazol-1-one and *N*-cyclopentenyl benzimidazolone enabled by microwave assisted domino reactions of cyclic 2-diazo-1,3-diketones with aniline derivatives

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1. General Information

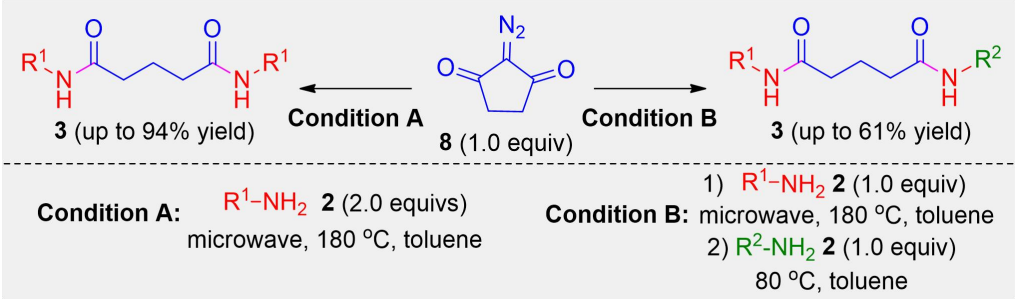
These reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. All reactions under microwave irradiation were performed in an Anton Parr microwave system (800 W) equipped with a build-in pressure measurement sensor and a vertically focused IR temperature sensor. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using Bruker DPX-400 spectrometer or Bruker DPX-500 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$, CD_3OD, DMSO-d_6 with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, sep = septet, dd = doublet of doublets, dt = doublet of triplets, br = broad.

Anhydrous solvents such as toluene, 1,4-dioxane, DMSO, and DMF were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. The cyclic 2-diazo-1,3-diketones **1**[1] and the bromination product **13**[2] were prepared according to the literature procedures.

[1] M. O. Erhunmwunse and P. G. Steel, *J. Org. Chem.*, 2008, **73**, 8675-8677.

[2] Y. Hirose, M. Yamazaki, M. Nogata, A. Nakamura and T. Maegawa, *J. Org. Chem.*, **2019**, *84*, 7405-7410.

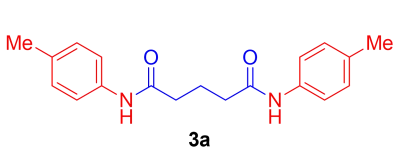
2. General procedure and spectral data of glutaramides 3.



General Procedure A: Amines **2** (R^1-NH_2, 0.20 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 1 h (800 W), after which the reaction mixture was cooled to room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography using petroleum ether/EtOAc (3:1 to 1:1) as the eluent to afford the symmetric *N*^{1}, *N*^{5}-diaryl-glutaramides **3**.

General Procedure B: Amines **2** (R^1-NH_2, 0.10 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 1 h (800 W), after which the reaction mixture was cooled to room temperature. Subsequently, another equivalent of substituted amines **2** (R^2-NH_2, 0.10 mmol) was added to the reaction tube. The resulting mixture was heated to 80 °C by microwave irradiation (1 h, 800 W). After completion of the reaction, the solvent was removed under vacuum, and the residue was purified by column chromatography using petroleum ether/EtOAc (3:1 to 1:1) as the eluent to afford the unsymmetric *N*^{1}, *N*^{5}-diaryl-glutaramides **3**.

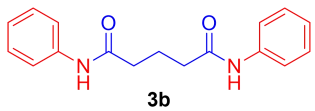
N^1,*N*^{5}-*di*-p-tolylglutaramide (**3a**):



3a

Following general procedure A, the title compound **3a** was obtained as a yellow solid with a 81% yield (25.1 mg, m.p. 151-152 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.89 (p, *J* = 7.2 Hz, 2H), 2.23 (s, 6H), 2.34 (t, *J* = 7.2 Hz, 4H), 7.07 (ABd, *J* = 8.4 Hz, 4H), 7.47 (ABd, *J* = 8.0 Hz, 4H), 9.80 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.62, 136.84, 131.85, 129.03, 119.12, 35.58, 21.03, 20.46; HRMS (ESI): Exact mass calcd for $C_{19}H_{22}N_2O_2Na$ $[M+Na]^+$: 333.3868, Found: 333.3872.

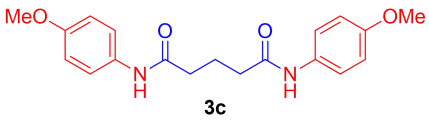
N^1,*N*^{5}-*di*-phenylglutaramide (**3b**):



3b

Following general procedure A, the title compound **3b** was obtained as a yellow solid with a 94% yield (26.5 mg, m.p. 200-201 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.92 (p, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 4H), 7.02 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 4H), 7.60 (ABd, *J* = 8.0 Hz, 4H), 9.90 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 170.79, 139.32, 128.63, 122.95, 119.04, 35.57, 20.92; HRMS (ESI): Exact mass calcd for $C_{17}H_{18}N_2O_2Na$ [M+Na]$^+$: 305.1266, Found: 305.1260.

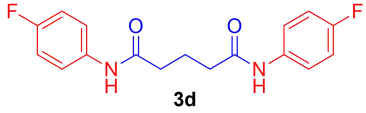
N^1,*N*^{5}-bis(4-methoxyphenyl)glutaramide (**3c**):



3c

Following general procedure A, the title compound **3c** was obtained as a yellow solid with a 84% yield (28.7 mg, m.p. 160-161 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.89 (p, *J* = 7.2 Hz, 2H), 2.33 (t, *J* = 7.6 Hz, 4H), 3.43 (s, 6H), 6.86 (d, *J* = 7.6 Hz, 4H), 7.50 (ABd, *J* = 7.6 Hz, 4H), 9.78 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 170.40, 155.08, 132.57, 120.67, 113.83, 55.20, 35.54, 21.19; HRMS (ESI): Exact mass calcd for $C_{19}H_{22}N_2O_4Na$ [M+Na]$^+$: 365.1478, Found: 365.1472.

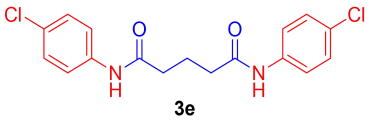
N^1,*N*^{5}-bis(4-fluorophenyl)glutaramide (**3d**):



3d

Following general procedure A, the title compound **3d** was obtained as a yellow solid with a 81% yield (25.8 mg, m.p. 137-138 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.89 (p, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 4H), 7.07-7.15 (m, 4H), 7.58-7.61 (m, 4H), 9.99 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.00, 158.06 (d, *J* = 238 Hz), 135.80 (d, *J* = 2.6 Hz), 121.03 (d, *J* = 7.7 Hz), 115.40 (d, *J* = 22 Hz), 35.61, 21.10; HRMS (ESI): Exact mass calcd for $C_{17}H_{16}F_2N_2O_2Na$ [M+Na]$^+$: 341.1078, Found: 341.1072.

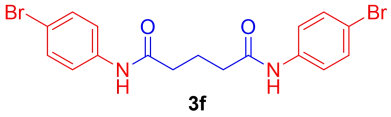
N^1,*N*^{5}-bis(4-chlorophenyl)glutaramide (**3e**):



3e

Following general procedure A, the title compound **3e** was obtained as a yellow solid with a 64% yield (22.4 mg, m.p. 144-145 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.90 (p, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.6 Hz, 4H), 7.33 (ABd, *J* = 8.8 Hz, 4H), 7.63 (ABd, *J* = 8.8 Hz, 4H), 10.04 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.24, 138.33, 128.76, 126.78, 120.81, 35.66, 20.93; HRMS (ESI): Exact mass calcd for $C_{17}H_{16}Cl_2N_2O_2Na$ [M+Na]$^+$: 373.0487, Found: 373.0481.

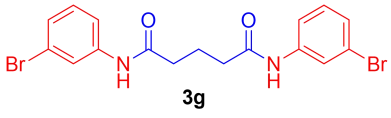
N^1,N^5-bis(4-bromophenyl)glutaramide (**3f**):



3f

Following general procedure A, the title compound **3f** was obtained as a yellow solid with a 66% yield (28.8 mg, m.p. 182-183 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.88 (p, *J* = 7.2 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 4H), 7.45 (ABd, *J* = 8.8 Hz, 4H), 7.56 (ABd, *J* = 8.8 Hz, 4H), 10.07 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.24, 138.74, 131.64, 121.17, 114.74, 35.66, 20.88; HRMS (ESI): Exact mass calcd for $C_{17}H_{16}Br_2N_2O_2Na$ $[M+Na]^+$: 460.9477, Found: 460.9471.

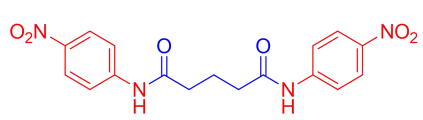
N^1,N^5-bis(3-bromophenyl)glutaramide (**3g**):



3g

Following general procedure A, the title compound **3g** was obtained as a yellow solid with a 63% yield (27.5 mg, m.p. 167-168 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.90 (p, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 4H), 7.19-7.27 (m, 4H), 7.46-7.49 (m, 2H), 7.98 (t, *J* = 2.0 Hz, 2H), 10.09 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.19, 140.87, 130.71, 125.61, 121.55, 121.37, 117.62, 35.47, 20.65; HRMS (ESI): Exact mass calcd for $C_{17}H_{16}Br_2N_2O_2Na$ $[M+Na]^+$: 460.9477, Found: 460.9471.

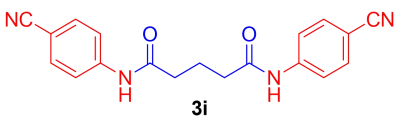
N^1,N^5-bis(4-nitrophenyl)glutaramide (**3h**):



3h

Following general procedure A, the title compound **3h** was obtained as a yellow solid with a 57% yield (21.2 mg, m.p. 140-141 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.94 (p, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 4H), 7.84 (ABd, *J* = 9.2 Hz, 4H), 8.21 (ABd, *J* = 9.2 Hz, 4H), 10.55 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.79, 145.41, 141.99, 124.98, 118.63, 35.54, 20.26; HRMS (ESI): Exact mass calcd for $C_{17}H_{16}N_4O_6Na$ $[M+Na]^+$: 395.0968, Found: 395.0962.

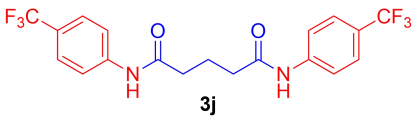
N^1,N^5-bis(4-cyanophenyl)glutaramide (**3i**):



3i

Following general procedure A, the title compound **3i** was obtained as a yellow solid with a 52% yield (17.3 mg, m.p. 178-179 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.91 (p, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 4H), 7.74-7.79 (m, 8H), 10.35 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.68, 143.47, 133.29, 119.15, 119.03, 104.71, 35.56, 20.37; HRMS (ESI): Exact mass calcd for $C_{19}H_{16}N_4O_2Na$ $[M+Na]^+$: 355.1171, Found: 355.1165.

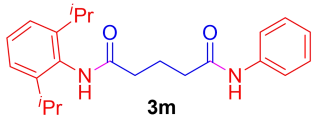
N^1,*N*^{5}-bis(4-(trifluoromethyl)phenyl)glutaramide (**3j**):



3j

Following general procedure A, the title compound **3j** was obtained as a yellow solid with a 50% yield (20.9 mg, m.p. 202-203 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.93 (p, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 4H), 7.65 (ABd, *J* = 8.4 Hz, 4H), 7.80 (ABd, *J* = 8.4 Hz, 4H), 10.30 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.51, 142.85, 126.04 (q, *J* = 3.8 Hz), 124.44 (q, *J* = 269 Hz), 123.01 (q, *J* = 32 Hz), 118.87, 35.54, 20.53; HRMS (ESI): Exact mass calcd for $C_{19}H_{16}F_6N_2O_2Na$ [M+Na]$^+$: 441.1014, Found: 441.1008.

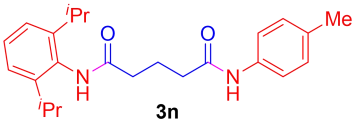
N^1-(2,6-diisopropylphenyl)-*N*^{5}-phenylglutaramide (**3m**):



3m

Following general procedure B, the title compound **3m** was obtained as a white solid with a 58% yield (21.2 mg, m.p. 179-180 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.11 (d, *J* = 6.4 Hz, 12H), 1.93 (p, *J* = 7.2 Hz, 2H), 2.39-2.43 (m, 4H), 3.04 (sep, *J* = 6.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.13 (ABd, *J* = 7.6 Hz, 2H), 7.21-7.25 (m, 1H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.61 (ABd, *J* = 7.6 Hz, 2H), 9.18 (s, 1H), 9.92 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.57, 170.84, 145.95, 139.33, 132.68, 128.65, 127.34, 122.96, 122.76, 119.06, 35.81, 34.72, 28.00, 23.64, 23.25, 21.46; HRMS (ESI): Exact mass calcd for $C_{23}H_{30}N_2O_2Na$ [M+Na]$^+$: 389.2205, Found: 389.2211.

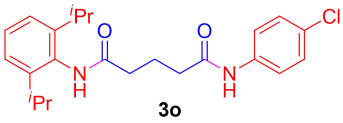
N^1-(2,6-diisopropylphenyl)-*N*^{5}-(p-tolyl)glutaramide (**3n**):



3n

Following general procedure B, the title compound **3n** was obtained as a white solid with a 61% yield (23.2 mg, m.p. 109-110 °C). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 1.11 (d, *J* = 3.0 Hz, 12H), 1.92 (p, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 2.37-2.41 (m, 4H), 3.04 (sep, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.13 (ABd, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.49 (ABd, *J* = 8.5 Hz, 2H), 9.18 (s, 1H), 9.82 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.56, 170.56, 145.94, 136.83, 132.68, 131.79, 129.00, 127.32, 122.74, 119.08, 35.76, 34.74, 27.99, 23.63, 23.23, 21.48, 20.43; HRMS (ESI): Exact mass calcd for $C_{24}H_{32}N_2O_2Na$ [M+Na]$^+$: 403.2362, Found: 403.2368.

N^1-(2,6-diisopropylphenyl)-*N*^{5}-(4-chlorophenyl)glutaramide (**3o**):

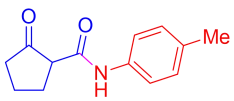


3o

Following general procedure B, the title compound **3o** was obtained as a white solid with a 54% yield (21.6 mg, m.p. 247-248 °C). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 1.11 (d, *J* = 6.0 Hz, 12H), 1.94 (p, *J* = 7.5 Hz, 2H), 2.40-2.44 (m, 4H), 3.04 (sep, *J* = 7.0 Hz, 2H), 7.13 (ABd, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz,1H), 7.35 (ABd, *J* = 9.0 Hz, 2H),

7.66 (ABd, *J* = 8.5 Hz, 2H), 9.19 (s, 1H), 10.07 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.53, 170.99, 145.93, 138.27, 132.67, 128.54, 127.33, 126.49, 122.74, 120.57, 35.77, 34.66, 27.99, 23.63, 23.23, 21.33; HRMS (ESI): Exact mass calcd for $C_{23}H_{29}ClN_2O_2Na$ [M+Na]$^+$: 423.1816, Found: 423.1822.

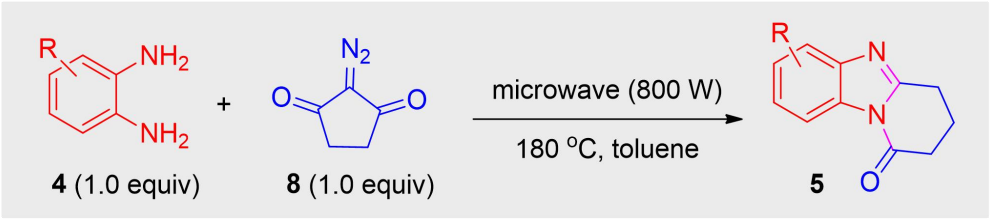
2-oxo-*N*-(*p*-tolyl)cyclopentanecarboxamide (**3s**):



3o
Chemical Formula: $C_{13}H_{15}NO_2$
Exact Mass: 217.1103

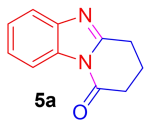
Compound **3s** was obtained as a white solid with a 79% yield (17.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.88 (m, 1H), 2.03-2.12 (m, 1H), 2.30 (s, 3H), 2.34-2.46 (m, 4H), 3.13 (t, *J* = 9.2 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 8.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.96, 164.38, 135.07, 133.81, 129.37, 119.79, 54.58, 39.03, 25.68, 20.80, 20.16; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NO_2Na$ [M + Na]$^+$: 240.1003, Found: 240.1001.

3. General procedure and spectral data of products 5.



General Procedure: *Ortho*-phenylenediamine **4** (0.10 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 1 h (800 W). After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography using petroleum ether/EtOAc (3:1 to 1:1) as the eluent to afford the piperidino[1,2-a]benzimidazol-1-ones **5**.

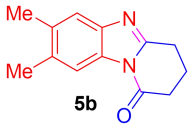
3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5a**):



5a

Following the general procedure, the title compound **5a** was obtained as a yellow solid with a 62% yield (11.5 mg, m.p. 86-87 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (p, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 7.33-7.38 (m, 2H), 7.67-7.69 (m, 1H), 8.20-8.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.86, 154.13, 142.52, 131.16, 125.21, 124.95, 119.27, 115.35, 33.75, 25.16, 20.42; HRMS (ESI): Exact mass calcd for $C_{11}H_{11}N_2O$ [M+H]$^+$: 187.0871, Found: 187.0865.

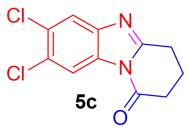
7,8-dimethyl-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5b**):



5b

Following the general procedure, the title compound **5b** was obtained as a yellow solid with a 54% yield (11.6 mg, m.p. 182-183 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (p, *J* = 6.4 Hz, 2H), 2.35 (s, 3H), 2.36 (s, 3H), 2.83 (t, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 6.4 Hz, 2H), 7.40 (s, 1H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.80, 153.25, 140.91, 133.94, 129.43, 119.40, 115.60, 33.69, 25.11, 20.45, 20.30, 20.28; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}N_2O$ $[M+H]^+$:215.1184, Found: 215.1179.

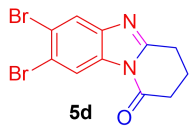
7,8-dichloro-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5c**):



5c

Following the general procedure, the title compound **5c** was obtained as a yellow solid with a 42% yield (10.7 mg, m.p. 129-130 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (p, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 3.18 (t, *J* = 6.4 Hz, 2H), 7.74 (s, 1H), 8.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.42, 155.96, 141.87, 130.13, 129.23, 128.93, 120.53, 116.73, 33.48, 25.08, 20.20; HRMS (ESI): Exact mass calcd for $C_{11}H_9Cl_2N_2O$ $[M+H]^+$: 255.0092, Found: 255.0087.

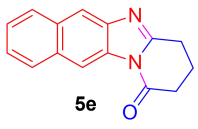
7,8-dibromo-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5d**):



5d

Following the general procedure, the title compound **5d** was obtained as a yellow solid with a 45% yield (15.4 mg, m.p. 159-160 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (p, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 7.92 (s, 1H), 8.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.40, 155.84, 142.77, 131.00, 123.77, 120.73, 120.41, 119.79, 33.51, 25.07, 20.19; HRMS (ESI): Exact mass calcd for $C_{11}H_9Br_2N_2O$ $[M+H]^+$: 342.9081, Found: 342.9065.

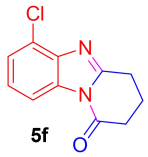
3,4-dihydronaphtho[2',3':4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5e**):



5e

Following the general procedure, the title compound **5e** was obtained as a yellow solid with a 66% yield (15.6 mg, m.p. 169-170 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (p, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 6.0 Hz, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 7.45-7.49 (m, 2H), 7.93-8.00 (m, 2H), 8.07 (s, 1H), 8.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 157.05, 141.86, 131.55, 130.64, 128.41, 128.32, 125.20, 125.03, 116.42, 112.73, 33.57, 25.37, 20.03; HRMS (ESI): Exact mass calcd for $C_{15}H_{13}N_2O$ $[M+H]^+$: 237.1028, Found: 237.1022.

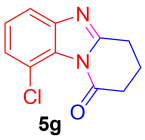
6-chloro-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5f**):



5f

Following the general procedure, the title compound **5f** was obtained as a yellow solid with a 31% yield (6.8 mg, m.p. 138-139 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (p, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.8 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 7.23 (t, *J* = 4.4 Hz, 1H), 7.34 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.09 (dd, *J* = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.76, 154.94, 139.77, 132.20, 125.64, 125.25, 124.18, 113.95, 33.65, 25.19, 20.28; HRMS (ESI): Exact mass calcd for $C_{11}H_{10}ClN_2O$ $[M+H]^+$: 221.0481, Found: 221.0476.

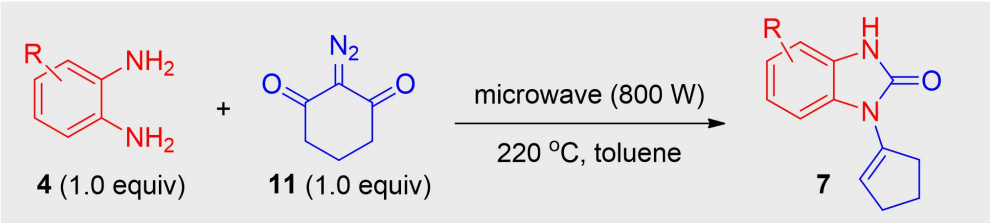
9-chloro-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one (**5g**):



5g

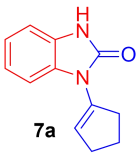
Following the general procedure, the title compound **5g** was obtained as a yellow oil with a 19% yield (4.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (p, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.5 Hz, 2H), 3.20 (t, *J* = 6.5 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.61, 156.29, 145.55, 129.30, 127.34, 126.16, 120.35, 118.05, 34.48, 25.82, 19.96; HRMS (ESI): Exact mass calcd for $C_{11}H_{10}ClN_2O$ $[M+H]^+$: 221.0481, Found: 221.0476.

4. General procedure and spectral data of products 7.



General Procedure: *Ortho*-phenylenediamine **4** (0.10 mmol) was added to a solution of 2-diazocyclohexane-1,3-dione **11** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 220 °C for 1 h (800 W). After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography using petroleum ether/EtOAc (3:1 to 1:1) as the eluent to afford the *N*-cyclopentenyl benzimidazolones **7**.

1-(cyclopent-1-en-1-yl)-1H-benzo[d]imidazol-2(3H)-one (**7a**):

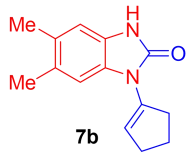


7a

Following the general procedure, the title compound **7a** was obtained as a brown solid with a 73% yield (14.6 mg, m.p. 143-144 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (p, *J* = 7.6 Hz, 2H), 2.56-2.61 (m, 2H), 2.87-2.92 (m, 2H), 5.98 (p, *J* = 2.4 Hz, 1H), 7.06-7.16 (m, 4H), 10.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.58, 135.84, 130.04, 128.19, 123.59, 121.88, 121.29, 109.71,

109.60, 32.01, 30.48, 22.22; HRMS (ESI): Exact mass calcd for $C_{12}H_{12}N_2ONa$ $[M+Na]^+$: 223.0848, Found: 223.0842.

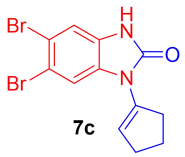
1-(cyclopent-1-en-1-yl)-5,6-dimethyl-1H-benzo[d]imidazol-2(3H)-one (**7b**):



7b

Following the general procedure, the title compound **7b** was obtained as a white solid with a 57% yield (13 mg, m.p. 219-220 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (p, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 2.29 (s, 3H), 2.57-2.61 (m, 2H), 2.89-2.94 (m, 2H), 5.97 (t, *J* = 2.0 Hz, 1H), 6.93 (s, 2H), 10.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.93, 136.12, 130.00, 129.21, 128.08, 126.44, 122.70, 110.90, 110.57, 32.03, 30.43, 22.19, 19.95, 19.70; HRMS (ESI): Exact mass calcd for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$: 251.1161, Found: 251.1160.

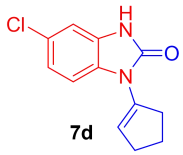
5,6-dibromo-1-(cyclopent-1-en-1-yl)-1H-benzo[d]imidazol-2(3H)-one (**7c**):



7c

Following the general procedure, the title compound **7c** was obtained as a white solid with a 49% yield (17.4 mg, m.p. 239-240 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.96 (p, *J* = 7.6 Hz, 2H), 2.44-2.48 (m, 2H), 2.73-2.78 (m, 2H), 5.95 (p, *J* = 2.0 Hz, 1H), 7.30 (s, 1H), 7.44 (s, 1H), 11.32 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.52, 135.06, 130.19, 129.43, 122.27, 115.13, 114.50, 113.45, 113.10, 31.41, 30.00, 21.63; HRMS (ESI): Exact mass calcd for $C_{12}H_{10}Br_2N_2ONa$ $[M+Na]^+$: 378.9058, Found: 378.9052.

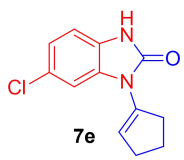
5-chloro-1-(cyclopent-1-en-1-yl)-1H-benzo[d]imidazol-2(3H)-one (**7d**):



7d

Following the general procedure, the title compound **7d** was obtained as a white solid with a 15% yield (3.51 mg, m.p. 195-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (p, *J* = 7.6 Hz, 2H), 2.55-2.60 (m, 2H), 2.85-2.89 (m, 2H), 5.96 (p, *J* = 2.0 Hz, 1H), 7.02-7.06 (m, 2H), 7.12 (s, 1H), 10.35 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.72, 135.49, 129.74, 128.34, 125.62, 120.90, 120.44, 110.55, 108.79, 31.55, 29.94, 21.65; HRMS (ESI): Exact mass calcd for $C_{12}H_{11}ClN_2ONa$ $[M+Na]^+$: 257.0458, Found: 257.0464.

6-chloro-1-(cyclopent-1-en-1-yl)-1H-benzo[d]imidazol-2(3H)-one (**7e**):

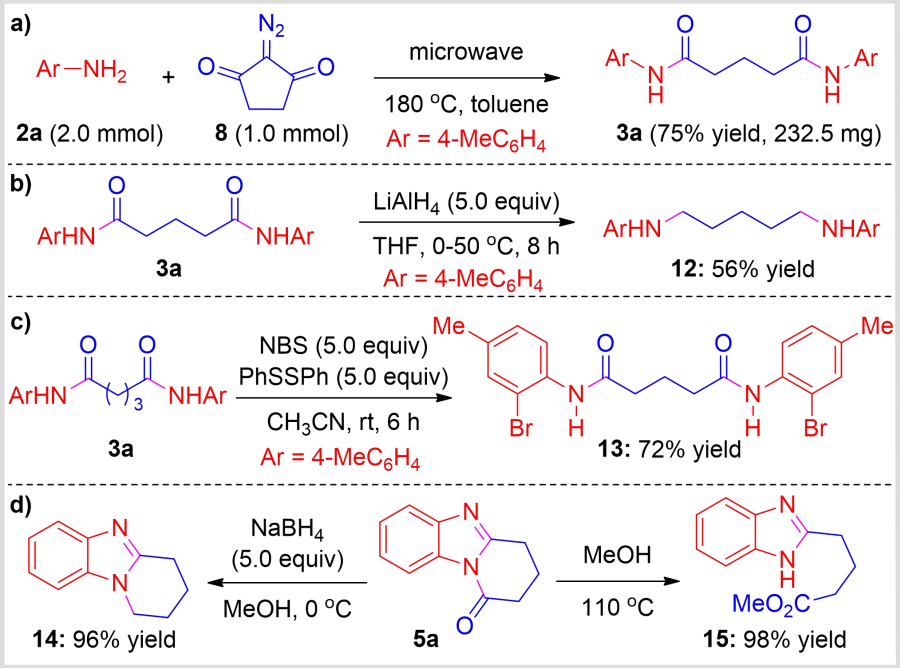


7e

Following the general procedure, the title compound **7e** was obtained as a white solid with a 37% yield (8.7 mg, m.p. 219-220 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (p, *J* = 7.6 Hz, 2H), 2.56-2.61 (m, 2H), 2.84-2.88 (m, 2H), 5.97 (p, *J* = 2.0 Hz, 1H), 7.01-7.06 (m, 2H), 7.12

(s, 1H), 10.74 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.81, 135.42, 130.74, 126.89, 126.84, 124.46, 121.91, 110.51, 109.96, 31.93, 30.47, 22.17; HRMS (ESI): Exact mass calcd for $C_{12}H_{11}ClN_2ONa$ $[M+Na]^+$: 257.0458, Found: 257.0464.

5. Scale-up synthesis and further transformations of the products.



Scale-up synthesis of 3a: *p*-toluidine **2a** (2.0 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (1.0 mmol) in toluene (6.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 1 h (800 W), after which the reaction mixture was cooled to room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 1:1) as the eluent to afford the N^1, N^5-di(*p*-tolyl)-glutaramide **3a** with 75% yield (232.5 mg).

The preparation of 12: Under N_2 atmosphere, **3a** (31 mg, 0.10 mmol) and dry THF (2.0 mL) were added to an oven-dried 10 mL Schlenk tube. Subsequently, $LiAlH_4$ (19 mg, 0.5 mmol) was added in three portions to the reaction mixture at 0 °C. The reaction was stirred at 50 °C for 2 h. After the full consumption of **3a** (monitored by TLC), saturated NH_4Cl aqueous solution was added to quench the reaction. The resulting solution was extracted with ethyl acetate (8 mL × 3), the combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 2:1) as the eluent to afford the desired product **12** in 56 % yield as a pink solid (15.8 mg, m.p. 59-60 °C).

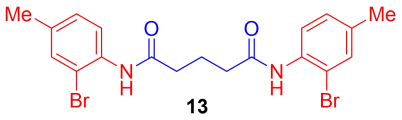
N^1,*N*^{5}-di-p-tolylpentane-1,5-diamine (**12**):

12

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49-1.57 (m, 2H), 1.68 (p, *J* = 7.6 Hz, 4H), 2.28 (s, 6H), 3.14 (t, *J* = 6.8 Hz, 6H), 6.57 (ABd, *J* = 8.0 Hz, 4H), 7.03 (ABd, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.05, 129.67, 126.39, 112.91, 44.21, 29.36, 24.69, 20.33; HRMS (ESI): Exact mass calcd for $C_{19}H_{27}N_2$ [M+H]$^+$: 283.2174, Found: 283.2169.

The preparation of 13: Under N_2 atmosphere, **3a** (31.0 mg, 0.10 mmol), PhSSPh (109 mg, 0.50 mmol), dry CH_3CN (2 mL) and NBS (89 mg, 0.5 mmol) were successively added to an oven-dried 10 mL Schlenk tube. The reaction mixture was allowed to stir at room temperature for 4 h. After the full consumption of **3a** (monitored by TLC), saturated $NaHCO_3$ and $Na_2S_2O_3$ (v/v = 1:1) aqueous solution was added to quench the reaction. The resulting mixture was extracted with ethyl acetate (8 mL × 3), and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 1:1) as the eluent to afford the desired product **13** in 72% yield as a white solid (33.5 mg, m.p. 184-185 °C).

N^1,*N*^{5}-bis(2-bromo-4-methylphenyl)glutaramide (**13**):

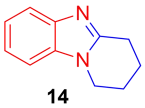


13

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.91 (p, *J* = 7.2 Hz, 2H), 2.28 (s, 6H), 2.41 (t, *J* = 6.8 Hz, 4H), 7.16 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.41 (ABd, *J* = 8.0 Hz, 2H), 7.47 (s, 2H), 9.38 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.05, 136.86, 133.77, 132.67, 128.56, 127.43, 118.41, 34.98, 20.10; HRMS (ESI): Exact mass calcd for $C_{19}H_{20}Br_2N_2O_2Na$ [M+Na]$^+$: 488.9790, Found: 488.9784.

The preparation of 14: Under N_2 atmosphere, **5a** (55.8 mg, 0.30 mmol) and MeOH (3 mL) were added to an oven-dried 10 mL Schlenk tube. Subsequently, $NaBH_4$ (57 mg, 1.5 mmol) was added in three portions to the reaction mixture at 0 °C. The reaction mixture was stir at 0 °C for 3 h. After the full consumption of **5a** (monitored by TLC), saturated NH_4Cl aqueous solution was added to quench the reaction. The resulting solution was extracted with ethyl acetate (20 mL × 3), the combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using DCM/MeOH (v/v = 20:1) as the eluent to afford the desired product **14** in 96 % yield as a yellow solid (49.5 mg, m.p. 113-114 °C).

1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (**14**):



14

^{1}H NMR (400 MHz, CD_3OD) δ 1.60 (p, *J* = 6.8 Hz, 2H), 1.89 (p, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 3.59 (t, *J* = 6.4 Hz, 2H), 7.15-7.19 (m, 2H), 7.46-7.50 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 156.70, 139.45, 123.15, 115.27, 62.39, 33.05, 29.47, 25.71; HRMS (ESI): Exact mass calcd for $C_{11}H_{13}N_2$ $[M+H]^+$: 173.1078, Found: 173.1073.

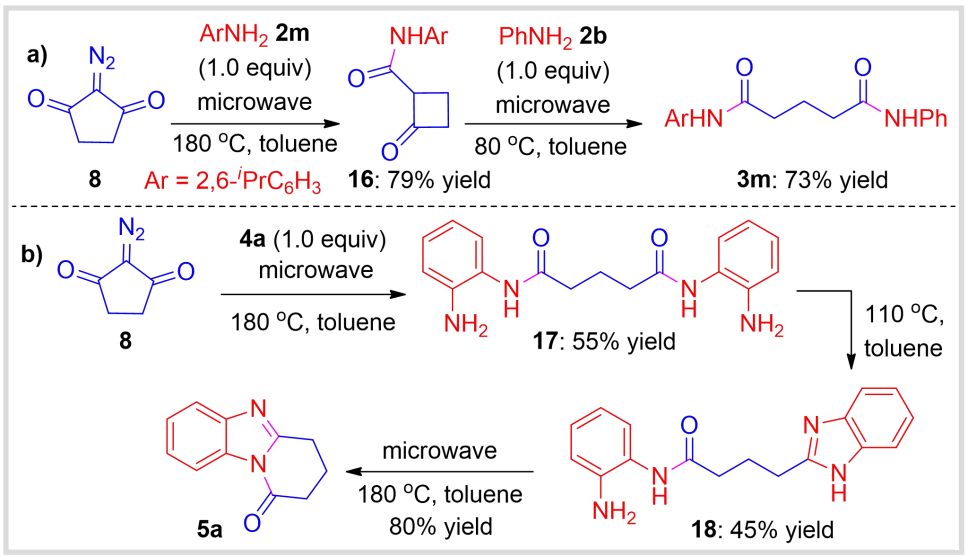
The preparation of 15: 5a (18.6 mg, 0.10 mmol) and MeOH (3 mL) were added to a 25 mL sealed tube at room temperature. The reaction mixture was stirred at 100 °C for 10 h. After the full consumption of **5a** (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 3:2) as the eluent to afford the desired product **15** in 98 % yield as a yellow solid (21.3 mg, m.p. 81-82 °C).

methyl 4-(1*H*-benzo[d]imidazol-2-yl)butanoate (**15**):

15

^{1}H NMR (400 MHz, DMSO-d_6) δ 2.03 (p, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 3.58 (s, 3H), 7.10-7.12 (m, 2H), 7.46 (s, 2H), 12.17 (brs, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 172.96, 154.23, 136.37, 122.55, 114.25, 51.36, 32.54, 27.03, 22.45; HRMS (ESI): Exact mass calcd for $C_{12}H_{15}N_2O_2$ $[M+H]^+$: 219.1133 Found: 219.1128.

6. Mechanism experiments.

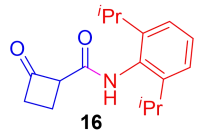


The preparation of 16:

2,6-Diisopropylaniline **2m** (0.10 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a

temperature of 180 °C for 1 h (800 W), after which the reaction mixture was cooled to room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 4:1) as the eluent to afford the cyclic *β*-keto amide **16** in 79 % yield as a white solid (21.6 mg, m.p. 194-195 °C).

N-(2,6-diisopropylphenyl)-2-oxocyclobutanecarboxamide (**16**):



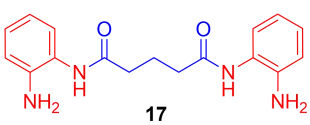
16

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (d, *J* = 7.0 Hz, 6H), 1.20 (d, *J* = 7.0 Hz, 6H), 2.33-2.41 (m, 1H), 2.47-2.54 (m, 1H), 2.99 (p, *J* = 7.0 Hz, 2H), 3.09-3.16 (m, 1H), 3.20-3.27 (m, 1H), 4.35-4.39 (m, 1H), 7.17 (ABd, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.48, 164.78, 145.98, 130.53, 128.38, 123.38, 64.37, 45.66, 28.72, 23.35, 13.63; HRMS (ESI): Exact mass calcd for $C_{17}H_{23}NO_2Na$ [M+Na]$^+$: 296.1627, Found: 296.1633.

The preparation of 3m: Aniline **2b** (0.10 mmol) was added to a solution of cyclic *β*-keto amide **16** (0.10 mmol) in toluene (1.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 80 °C for 6 min (800 W), after which the reaction mixture was cooled to room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography using petroleum ether/EtOAc (v/v = 2:1) as the eluent to afford the desired product **3m** in 73 % yield as a white solid (26.7 mg, m.p. 179-180 °C). The NMR data of compound **3m** are the same as described in page S6.

The preparation of 17: Benzene-1,2-diamine **4a** (1.0 mmol) was added to a solution of 2-diazocyclopentane-1,3-dione **8** (1.0 mmol) in toluene (6.0 mL), the resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 15 min (800 W), after which the reaction mixture was cooled to room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography using DCM/MeOH (v/v = 12:1) as the eluent to afford the desired product **17** in 55 % yield as a brown solid (171.6 mg, m.p. 183-184 °C).

N^1,*N*^{5}-bis(2-aminophenyl)glutaramide (**17**):

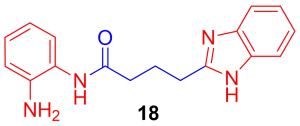


17

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.93 (p, *J* = 7.2 Hz, 2H), 2.40 (t, *J* = 7.6 Hz, 4H), 4.84 (s, 4H), 6.55 (t, *J* = 7.6 Hz, 2H), 6.72 (ABd, *J* = 7.6 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 2H), 7.19 (ABd, *J* = 7.2 Hz, 2H), 9.14 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.88, 141.98, 125.79, 125.47, 123.50, 116.17, 115.87, 35.12, 21.52; HRMS (ESI): Exact mass calcd for $C_{25}H_{18}N_3Na$ [M+Na]$^+$: 335.1484, Found: 335.1490.

The preparation of 18: Compound **17** (0.1 mmol) and toluene (1.0 mL) were added to an oven-dried 10 mL microwave tube. The resulting mixture was subjected to microwave irradiation at a temperature of 110 °C for 30 min (800 W). After completion, the reaction mixture was cooled down to room temperature and concentrated in vacuo. The residue was purified by column chromatography using DCM/MeOH (12:1) as the eluent to afford the desired product **18** in 45% yield as a white solid (13.2 mg, m.p. 139-140 ºC).

N-(2-aminophenyl)-4-(1*H*-benzo[d]imidazol-2-yl)butanamide (**18**):



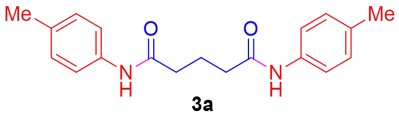
18

^{1}H NMR (500 MHz, DMSO-d_6) δ 1.92 (p, *J* = 7.5 Hz, 2H), 2.38-2.44 (m, 4H), 4.83 (s, 2H), 6.53 (td, *J* = 7.5, 1.0 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.87-6.91 (m, 1H), 7.12-7.18 (m, 3H), 7.56 (dd, *J* = 5.5, 3.5 Hz, 2H), 9.13 (s, 1H), 9.33 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.23, 170.86, 141.97, 130.51, 125.80, 125.47, 124.87, 124.68, 123.43, 116.15, 115.85, 35.41, 35.02, 21.29; HRMS (ESI): Exact mass calcd for $C_{17}H_{18}N_4ONa$ $[M+Na]^+$: 317.1379, Found: 317.1385.

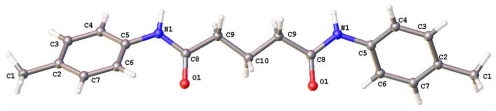
The preparation of 5a: Compound **18** (0.045 mmol) and toluene (1.0 mL) were successively added to an oven-dried 10 mL microwave tube. The resulting mixture was subjected to microwave irradiation at a temperature of 180 °C for 30 min (800 W). After completion, the reaction mixture was cooled down to room temperature and concentrated in vacuo. The residue was purified by column chromatography using DCM/MeOH (12:1) as the eluent to afford the desired product **5a** in 80% yield as a white solid (6.7 mg).

7. X-Ray crystallographic data for compounds 3a, 5b, 5g, 7a and 7e.

Data intensity of compound **3a** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 150.00 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically (CCDC 2270422).



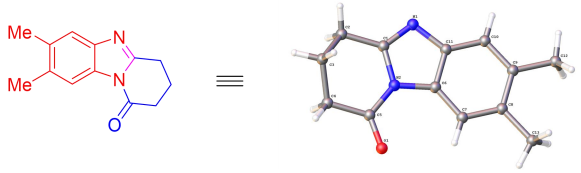
3a



X-ray structure of product **3a**
CCDC 2270422

Empirical formula	$C_{19}H_{22}N_2O_2$
Formula weight	310.38
Temperature/K	150.00 (10)
Crystal system	monoclinic
Space group	P2/c
a/Å	17.2708(7)
b/Å	4.7852(2)
c/Å	9.9268(4)
α/°	90
β/°	95.928(4)
γ/°	90
Volume/Å^3	816.01(6)
Z	2
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.656
F(000)	332.0
Crystal size/mm^3	0.14 × 0.12 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.144 to 146.856
Index ranges	-19 ≤ h ≤ 21, -3 ≤ k ≤ 5, -11 ≤ l ≤ 12
Reflections collected	2646
Independent reflections	1597 [R_{int} = 0.0194, R_{sigma} = 0.0273]
Data/restraints/parameters	1597/0/107
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1251
Largest diff. peak/hole / e Å^{-3}	0.23/-0.18

Data intensity of compound **5b** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 170.00 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. (CCDC 2242165).

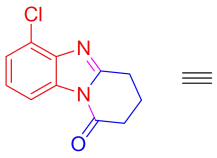


5b

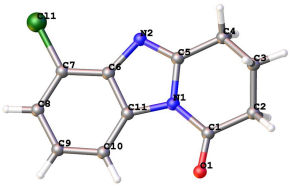
X-ray structure of product **5b**
CCDC 2242165

Empirical formula	$C_{13}H_{14}N_2O$
Formula weight	214.26
Temperature/K	170.00 (10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.33660(10)
b/Å	15.1353(2)
c/Å	11.4895(2)
α/°	90
β/°	98.0090(10)
γ/°	90
Volume/Å^3	1091.17(3)
Z	4
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.670
F(000)	456.0
Crystal size/mm^3	0.13 × 0.17 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.162 to 154.924
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 14, -18 ≤ l ≤ 17
Reflections collected	5140
Independent reflections	2095 [R_{int} = 0.0136, R_{sigma} = 0.0167]
Data/restraints/parameters	2095/0/148
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1209
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1224
Largest diff. peak/hole / e Å^{-3}	0.40/-0.17

Data intensity of compound **5g** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 297.24 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. (CCDC 2289773).



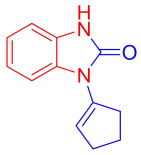
5g



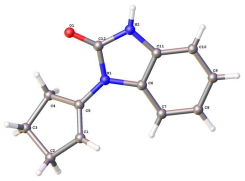
X-ray structure of product **5g**
CCDC 2289773

Empirical formula	$C_{11}H_9ClN_2O$
Formula weight	220.65
Temperature/K	297.24 (10)
Crystal system	monoclinic
Space group	I2/a
a/Å	10.8166(3)
b/Å	13.6079(4)
c/Å	14.4431(6)
α/°	90
β/°	108.571(4)
γ/°	90
Volume/Å^3	2015.20(13)
Z	8
ρ_{calc}g/cm^3	1.455
μ/mm^{-1}	3.130
F(000)	912.0
Crystal size/mm^3	912.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.162 to 154.924
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 14, -18 ≤ l ≤ 17
Reflections collected	6739
Independent reflections	2009 [R_{int} = 0.0725, R_{sigma} = 0.0638]
Data/restraints/parameters	2009/0/137
Goodness-of-fit on F^2	1.285
Final R indexes [I>=2σ (I)]	R_1 = 0.0817, wR_2 = 0.3097
Final R indexes [all data]	R_1 = 0.1094, wR_2 = 0.3239
Largest diff. peak/hole / e Å^{-3}	0.45/-0.30

Data intensity of compound **7a** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 169.99 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically (CCDC 2242071).



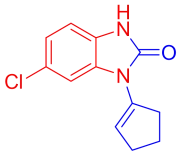
7a



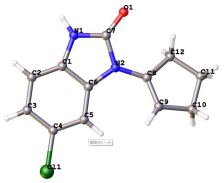
X-ray structure of product **7a**
CCDC 2242071

Empirical formula	$C_{12}H_{12}N_2O$
Formula weight	200.24
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	4.2516(9)
b/Å	8.8641(13)
c/Å	13.329(3)
α/°	83.536(16)
β/°	81.034(19)
γ/°	87.099(15)
Volume/Å^3	492.76(18)
Z	2
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	0.705
F(000)	212.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.752 to 151.916
Index ranges	-3 ≤ h ≤ 5, -8 ≤ k ≤ 10, -16 ≤ l ≤ 16
Reflections collected	2840
Independent reflections	1911 [R_{int} = 0.0868, R_{sigma} = 0.1103]
Data/restraints/parameters	1911/0/137
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.1267, wR_2 = 0.3372
Final R indexes [all data]	R_1 = 0.1740, wR_2 = 0.3806
Largest diff. peak/hole / e Å^{-3}	0.49/-0.48

Data intensity of compound **7e** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 169.99 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically (CCDC 2289775).



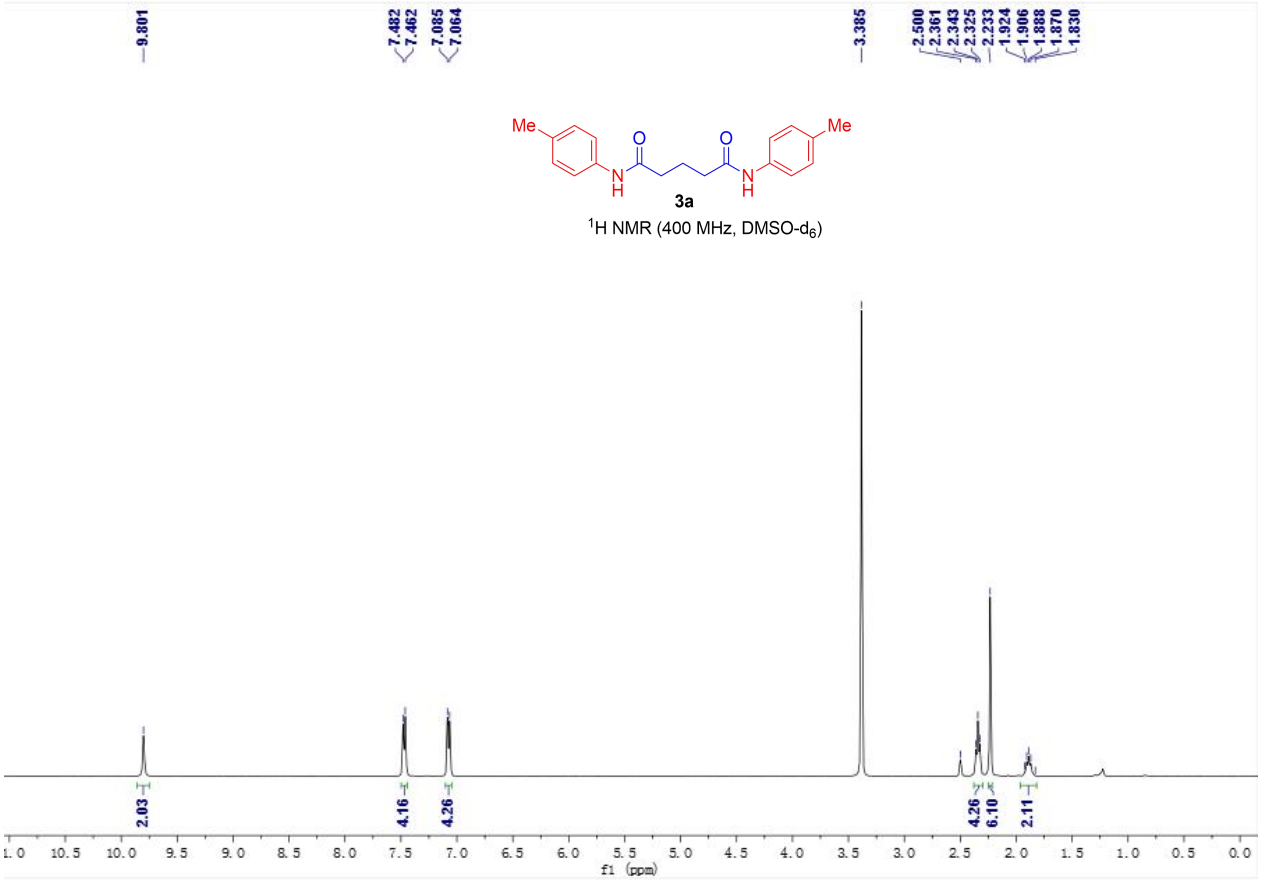
7e



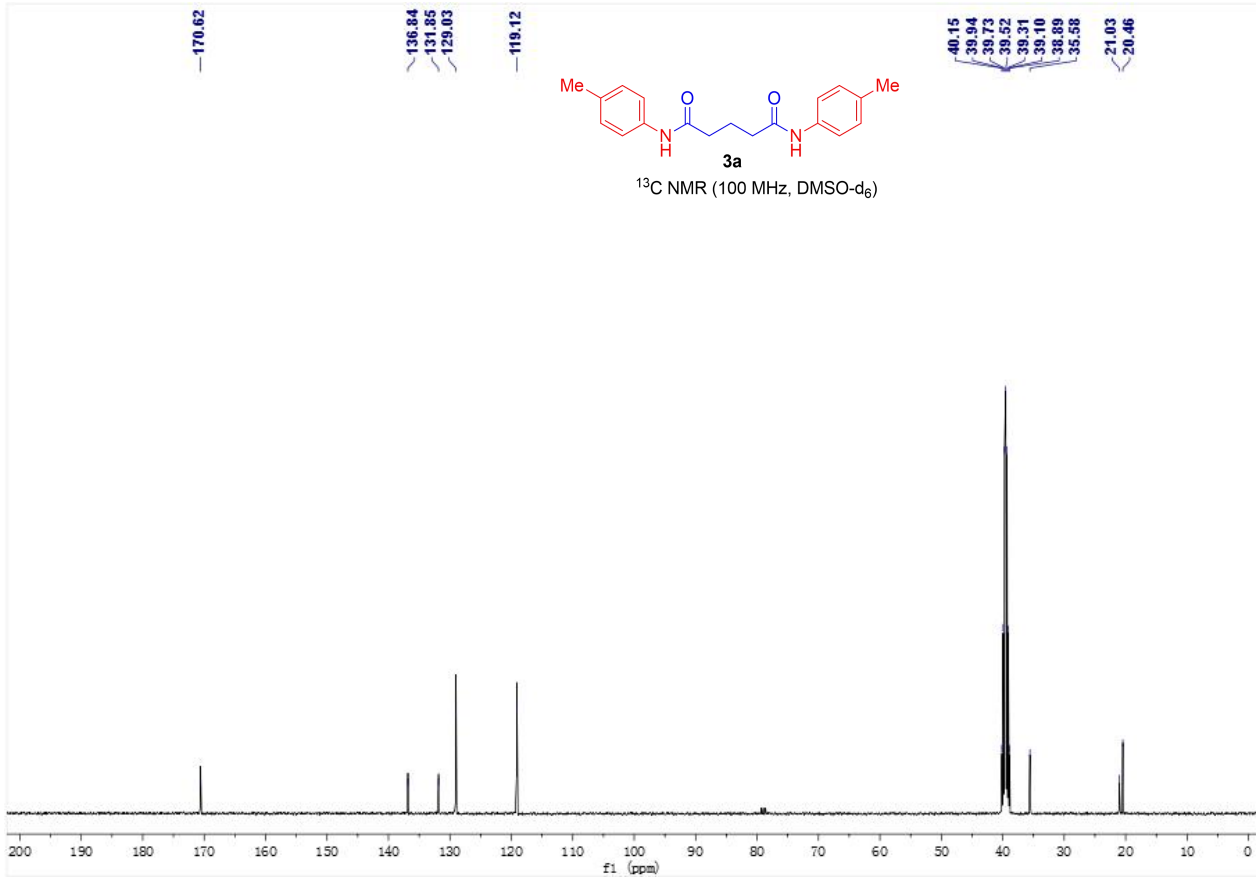
X-ray structure of product **7e**
CCDC 2289775

Empirical formula	$C_{12}H_{11}ClN_2O$
Formula weight	234.68
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.9222(8)
b/Å	8.8334(11)
c/Å	8.9454(9)
α/°	98.054(9)
β/°	98.509(9)
γ/°	95.175(10)
Volume/Å^3	532.18(11)
Z	2
ρ_{calc}g/cm^3	1.465
μ/mm^{-1}	0.336
F(000)	244.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.662 to 58.682
Index ranges	-9 ≤ h ≤ 8, -8 ≤ k ≤ 12, -12 ≤ l ≤ 11
Reflections collected	4032
Independent reflections	2467 [R_{int} = 0.0282, R_{sigma} = 0.0623]
Data/restraints/parameters	2467/0/145
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1212
Final R indexes [all data]	R_1 = 0.0872, wR_2 = 0.1420
Largest diff. peak/hole / e Å^{-3}	0.33/-0.27

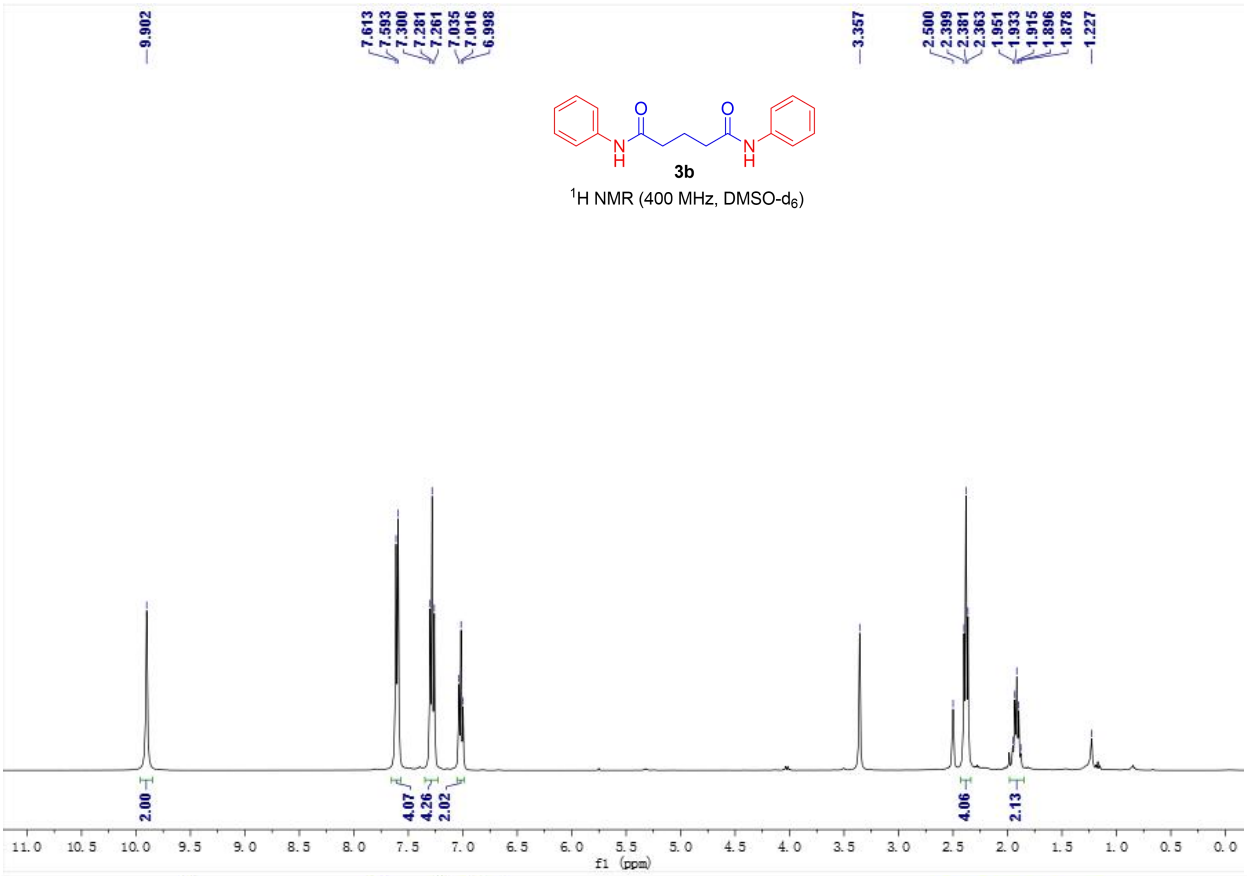
8. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Compounds 3-18.



^{1}H NMR (400 MHz, DMSO-d_6)

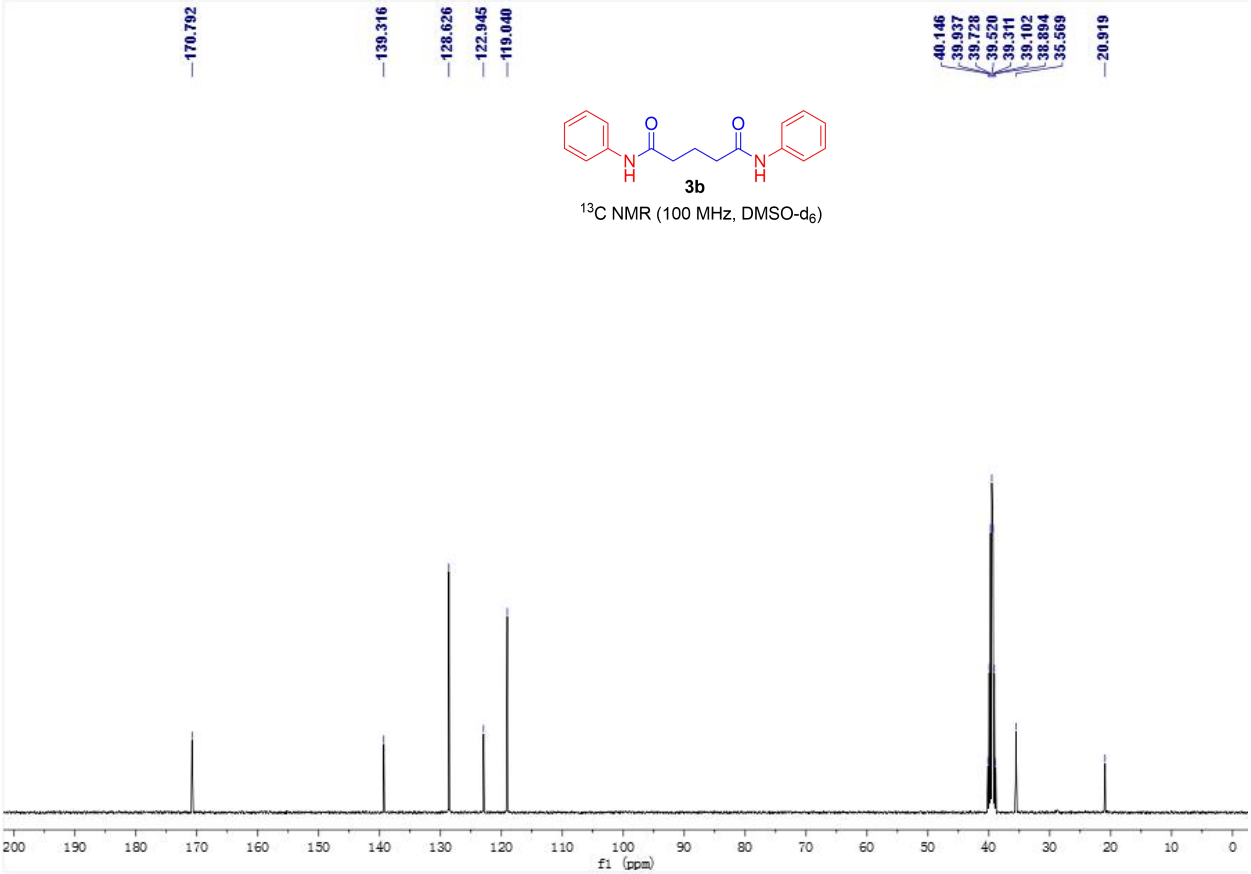


^{13}C NMR (100 MHz, DMSO-d_6)



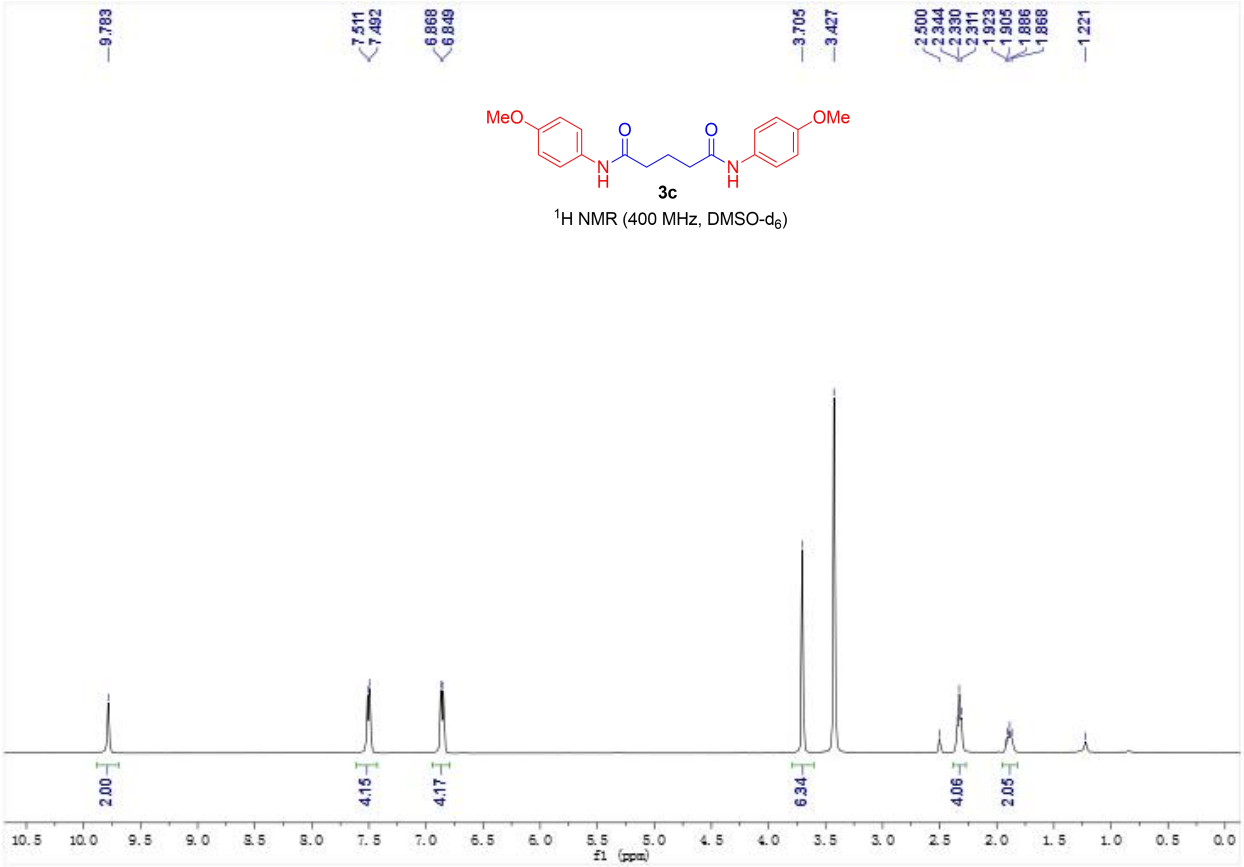
3b

^{1}H NMR (400 MHz, DMSO-d_6)

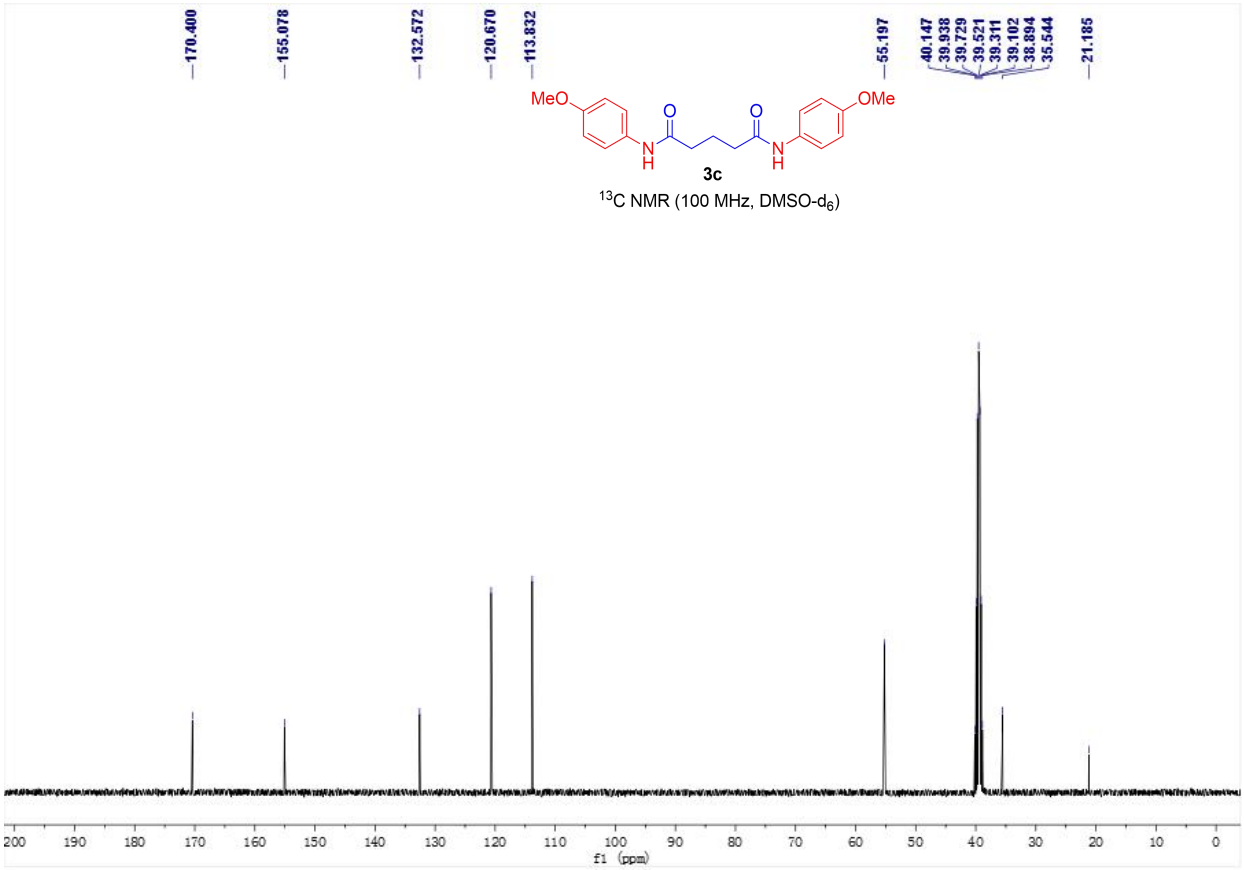


3b

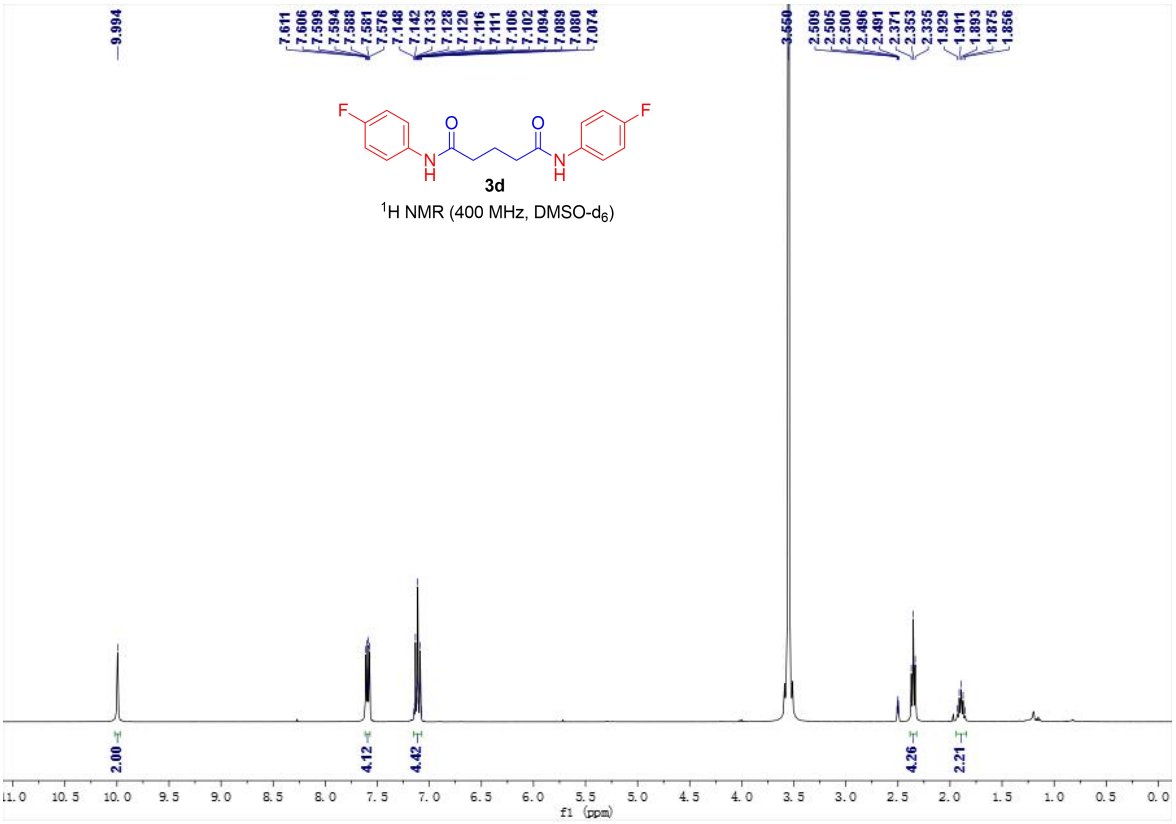
^{13}C NMR (100 MHz, DMSO-d_6)



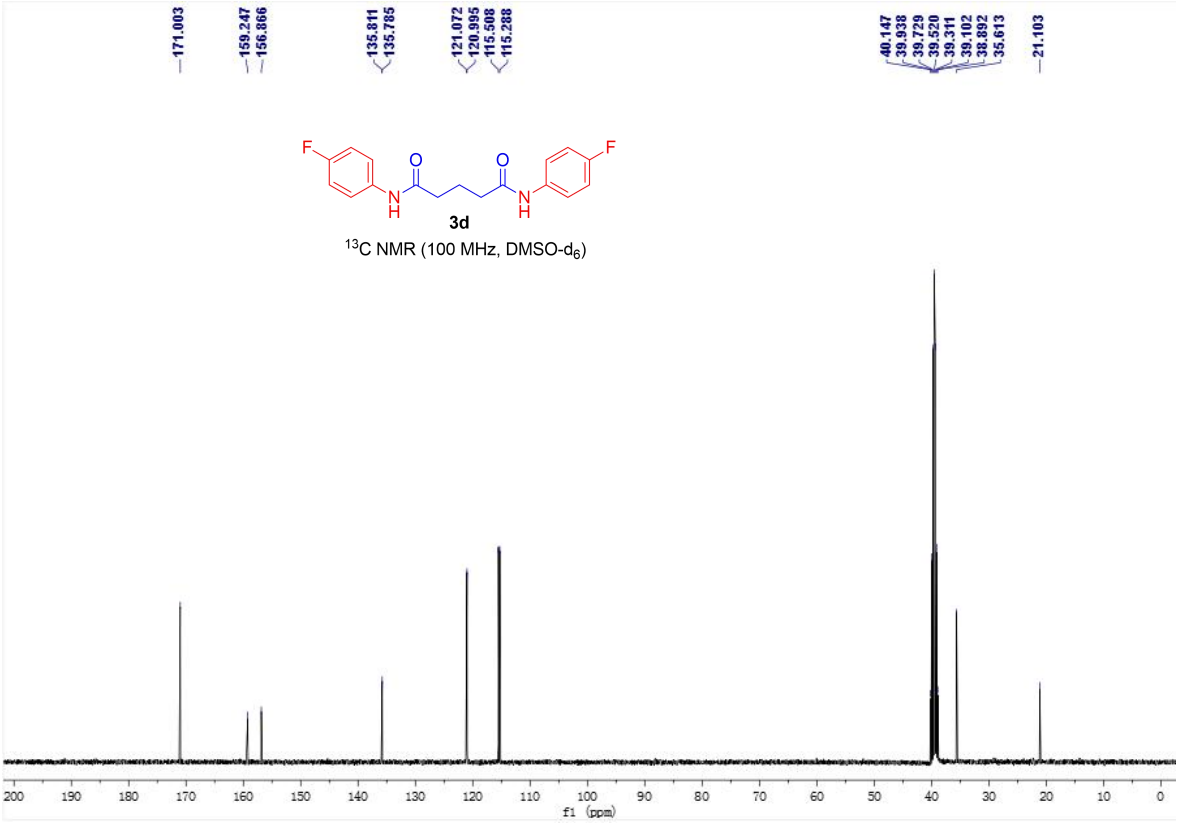
^{1}H NMR (400 MHz, DMSO-d_6)



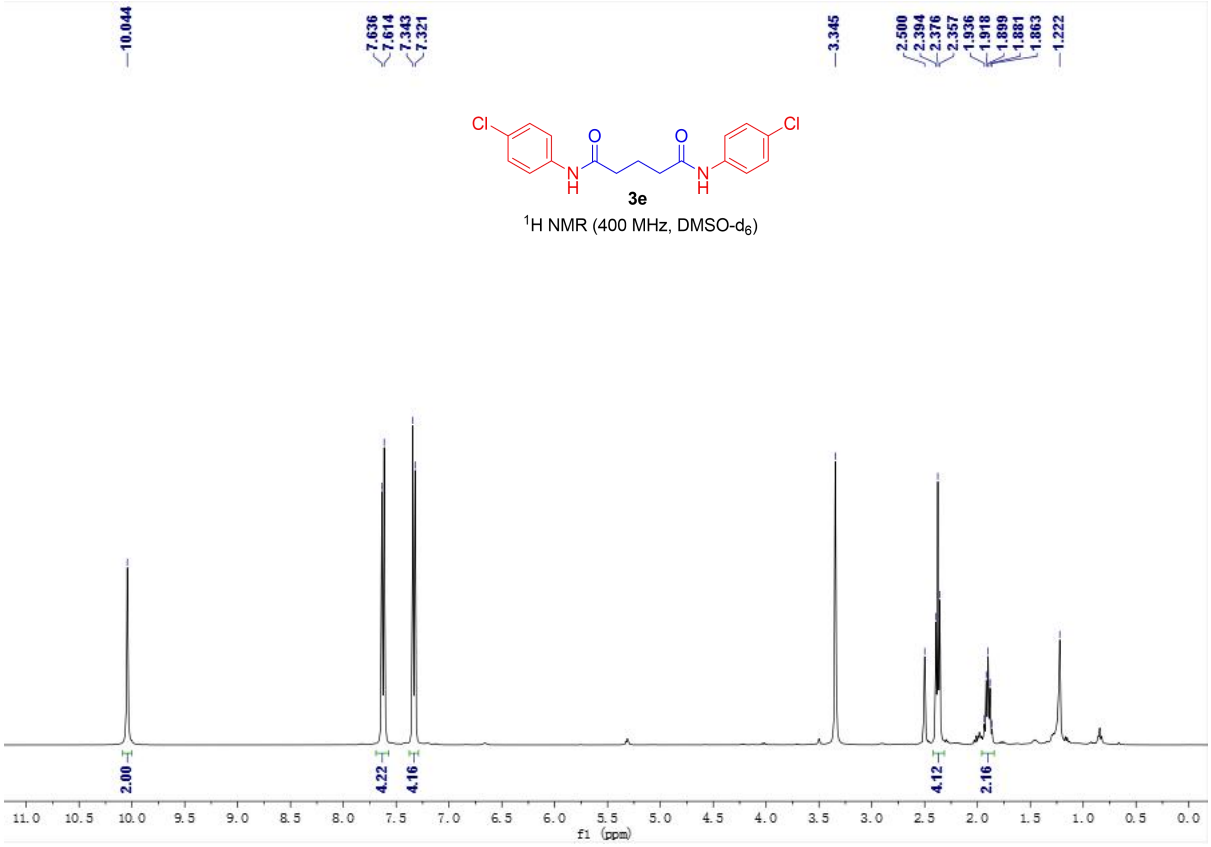
^{13}C NMR (100 MHz, DMSO-d_6)



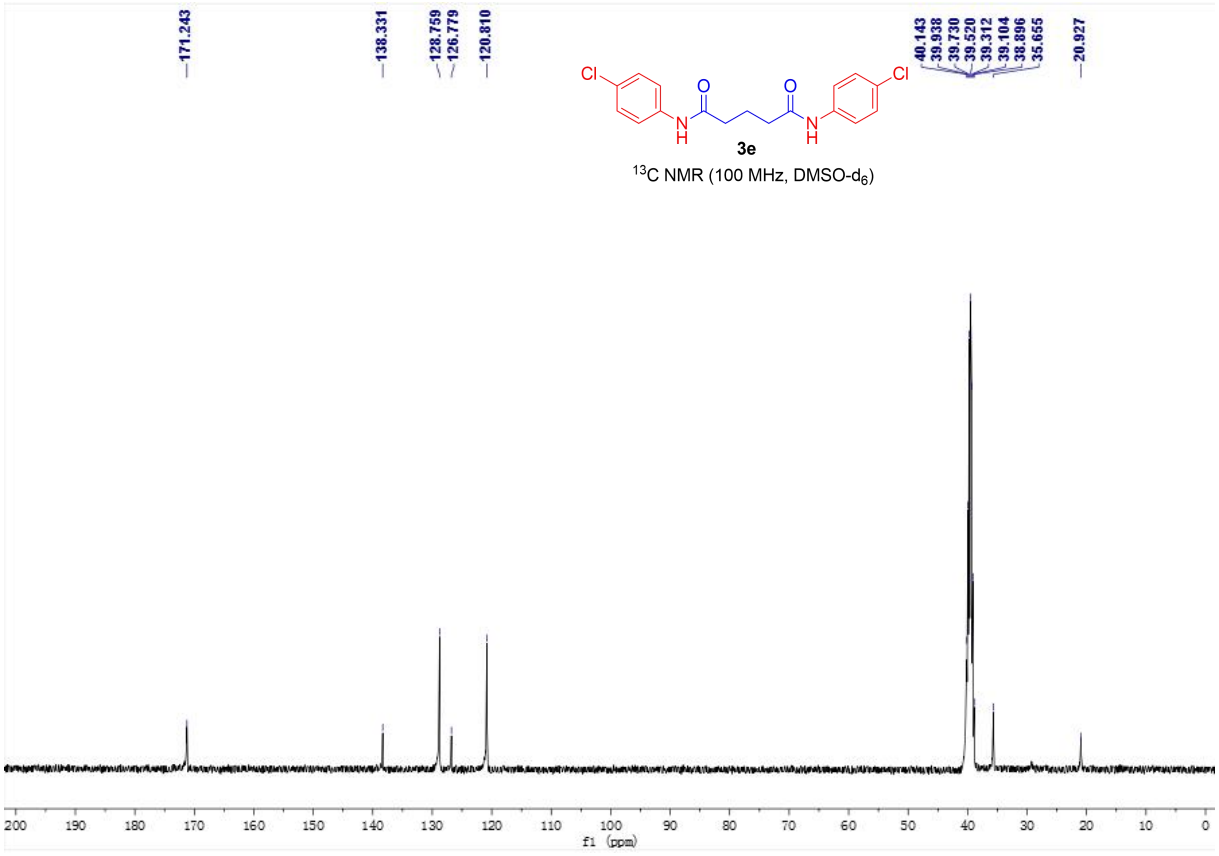
^{1}H NMR (400 MHz, DMSO-d_6)



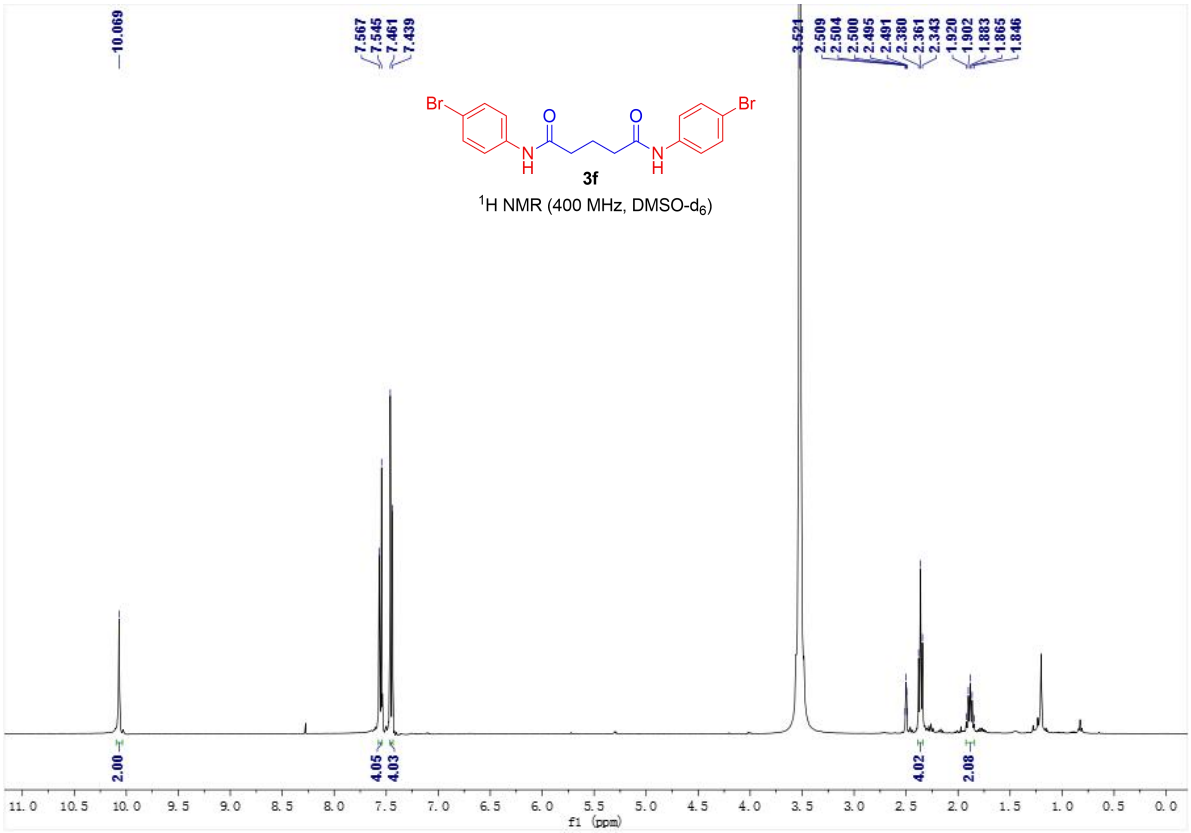
^{13}C NMR (100 MHz, DMSO-d_6)



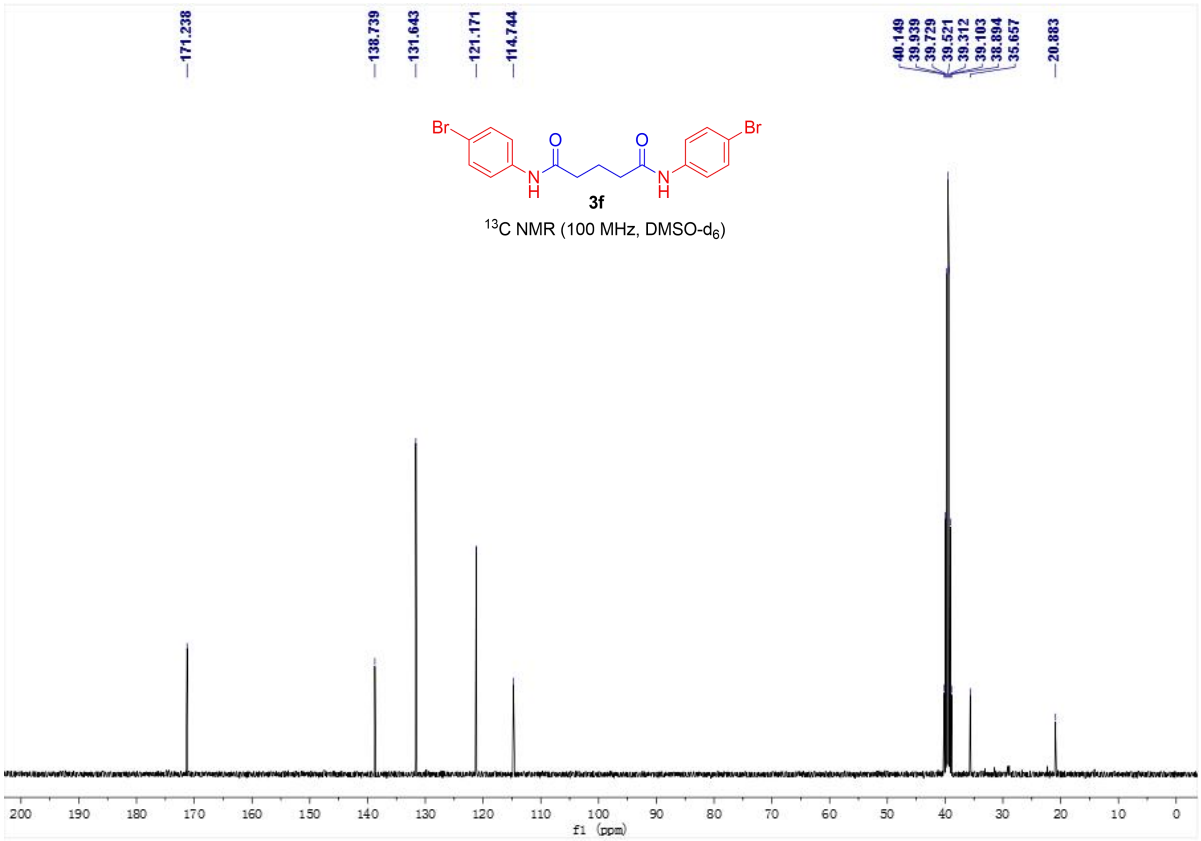
^{1}H NMR (400 MHz, DMSO-d_6)



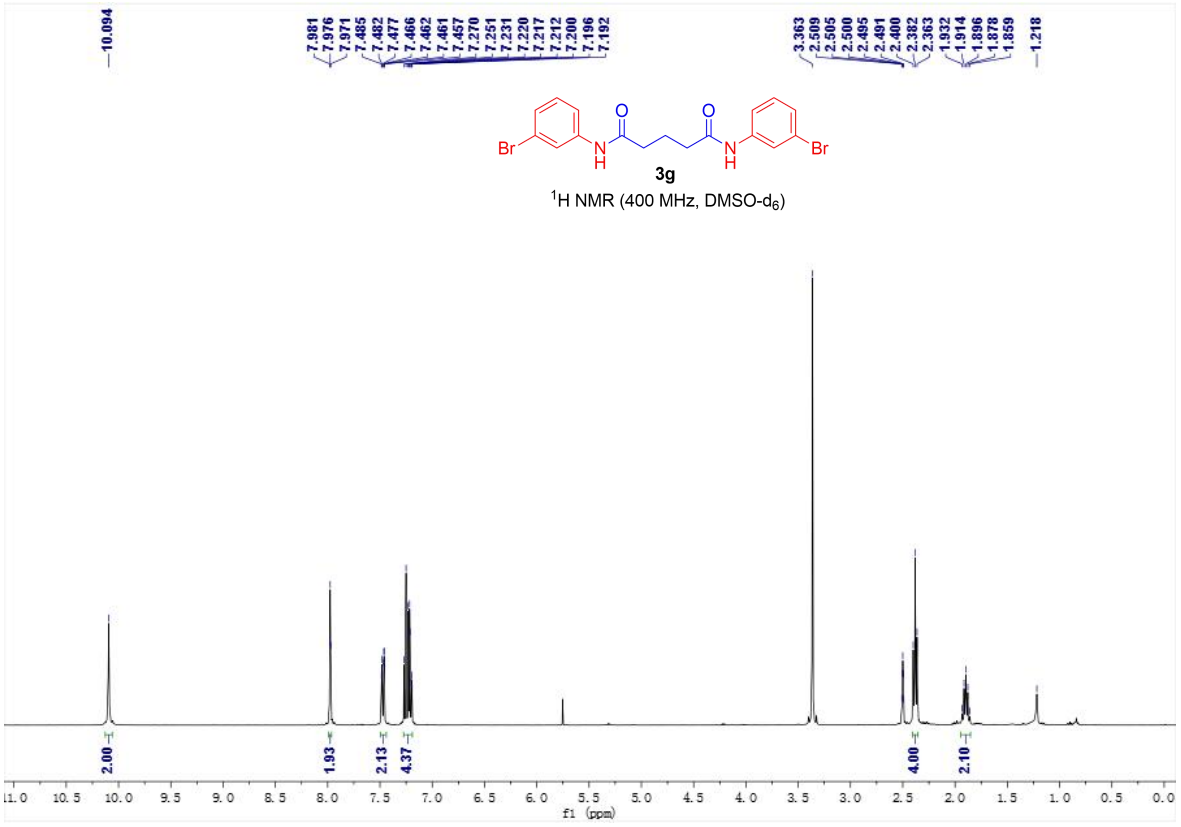
^{13}C NMR (100 MHz, DMSO-d_6)



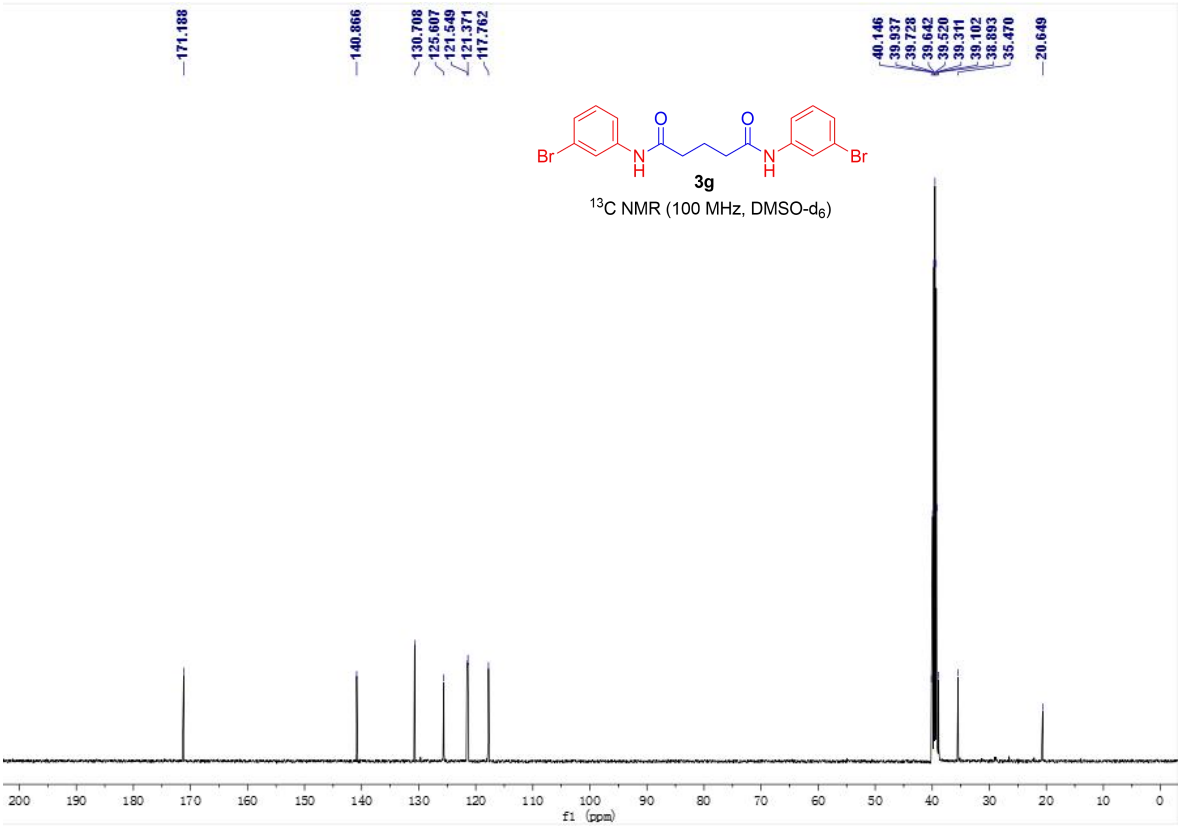
^{1}H NMR (400 MHz, DMSO-d_6)



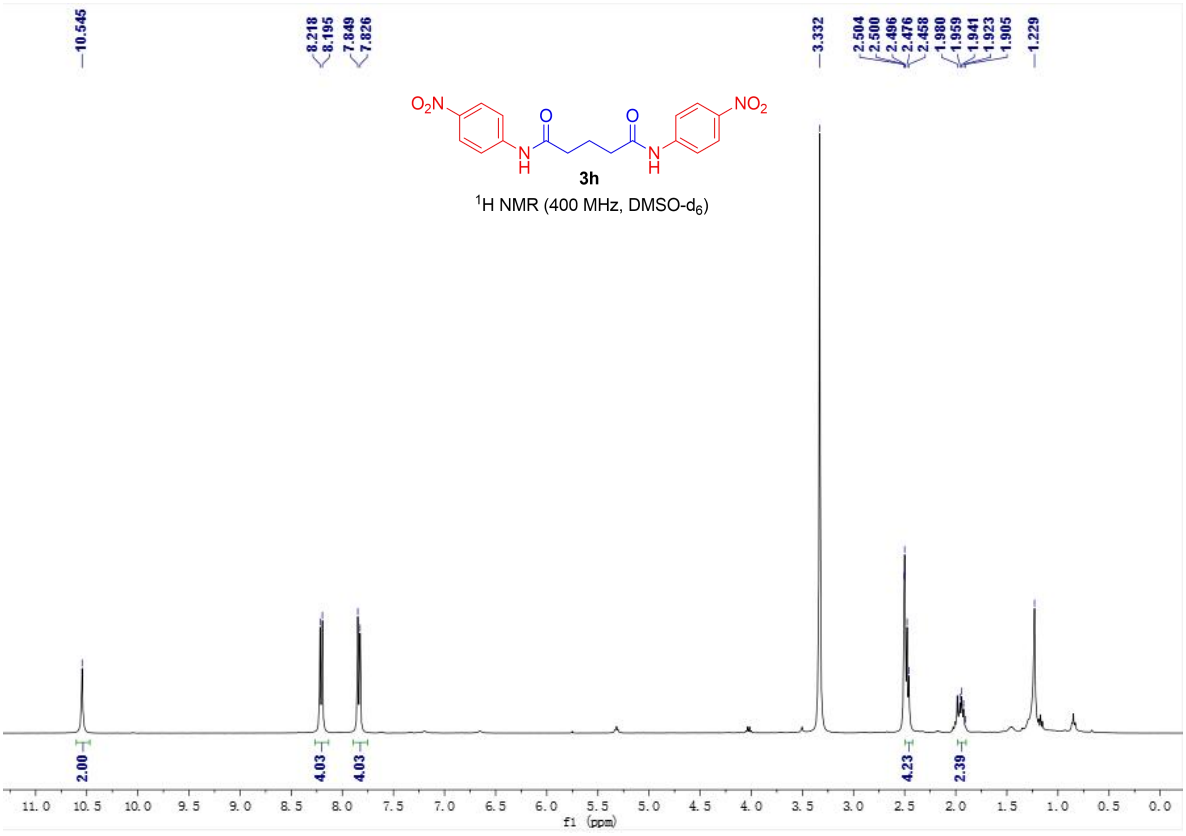
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)

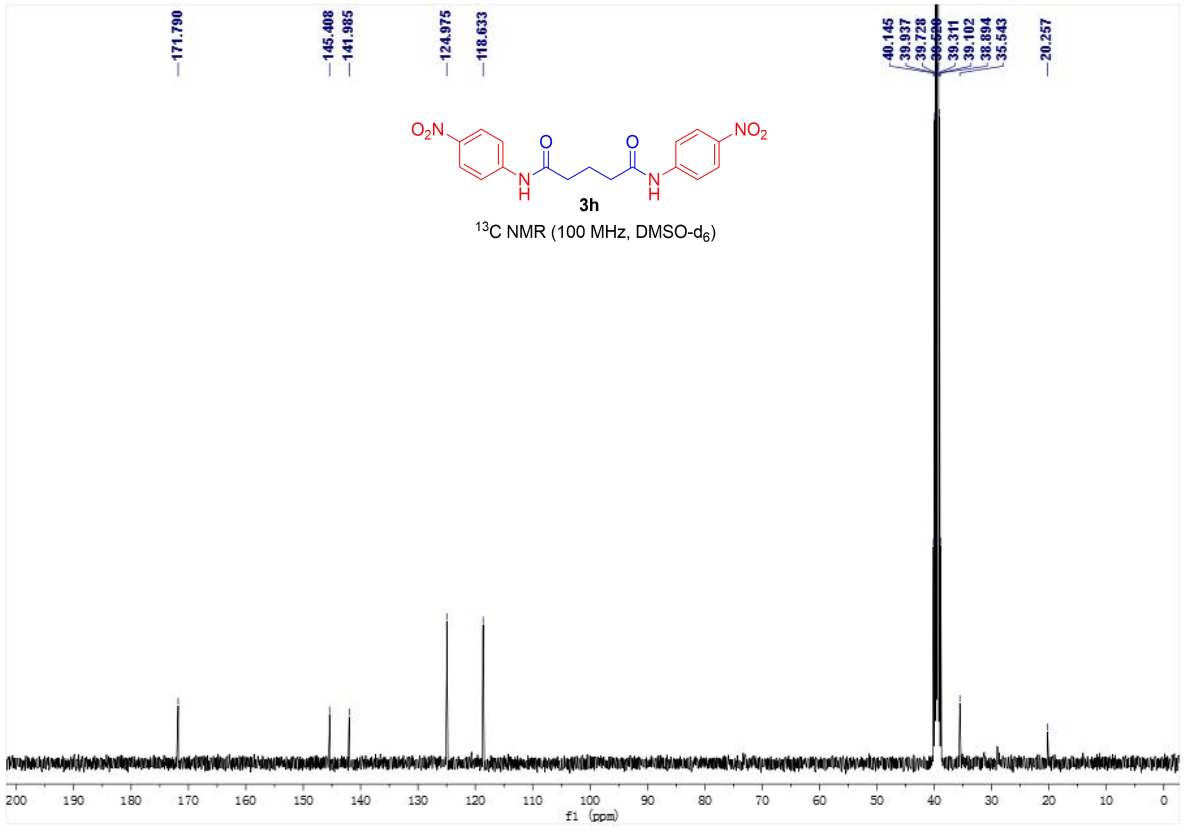


^{13}C NMR (100 MHz, DMSO-d_6)



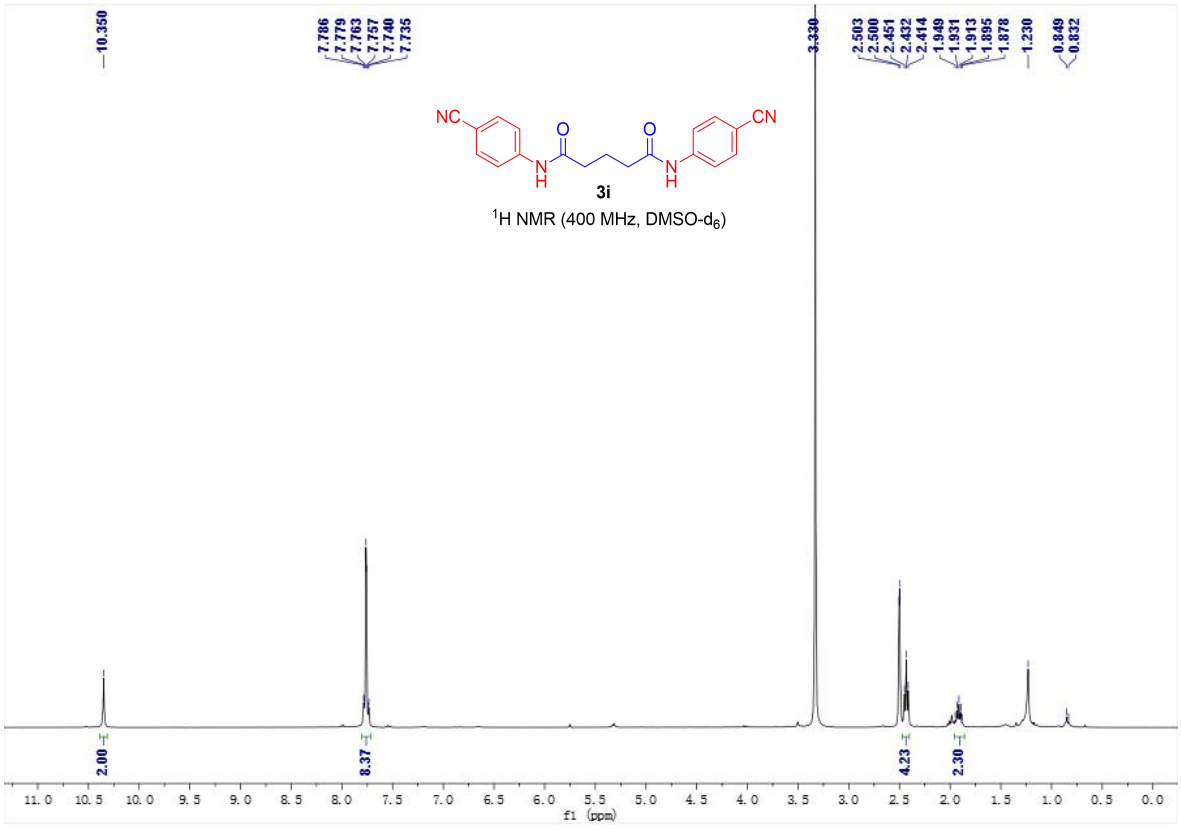
3h

^{1}H NMR (400 MHz, DMSO-d_6)



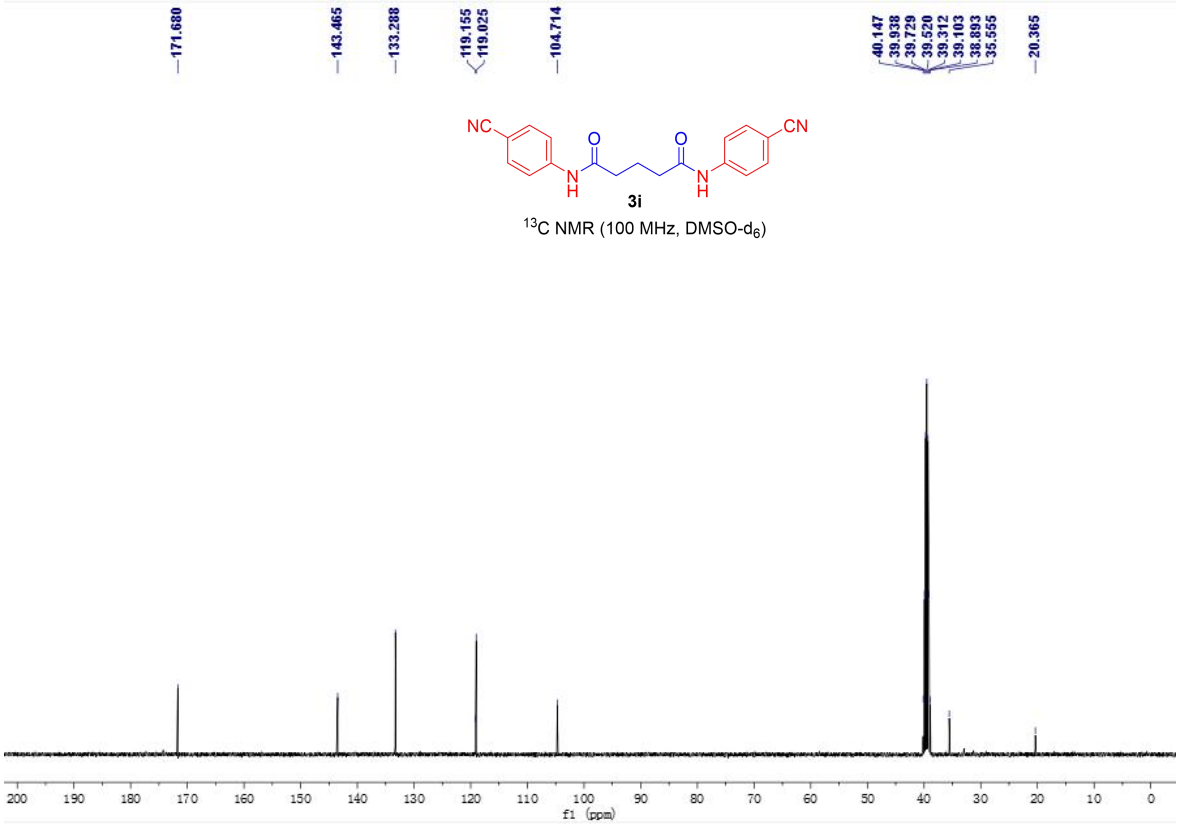
3h

^{13}C NMR (100 MHz, DMSO-d_6)



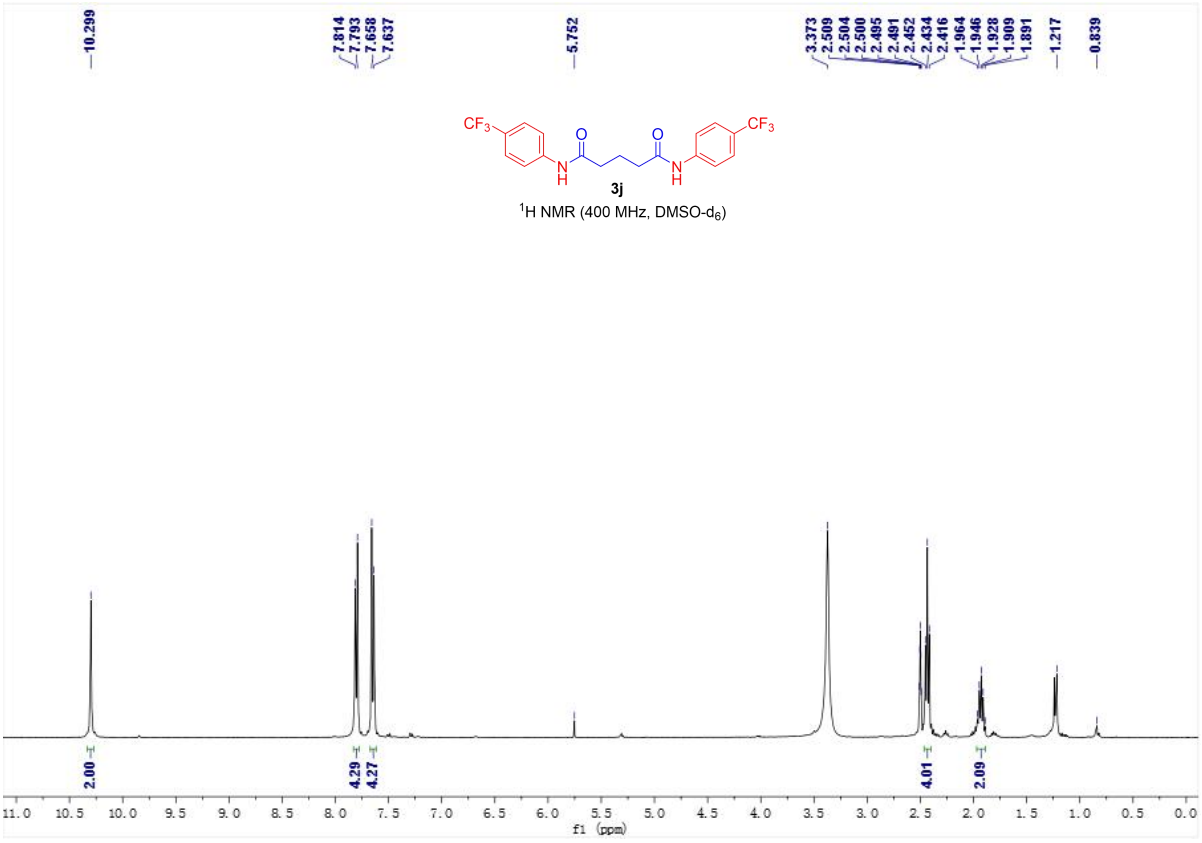
3i

^{1}H NMR (400 MHz, DMSO-d_6)



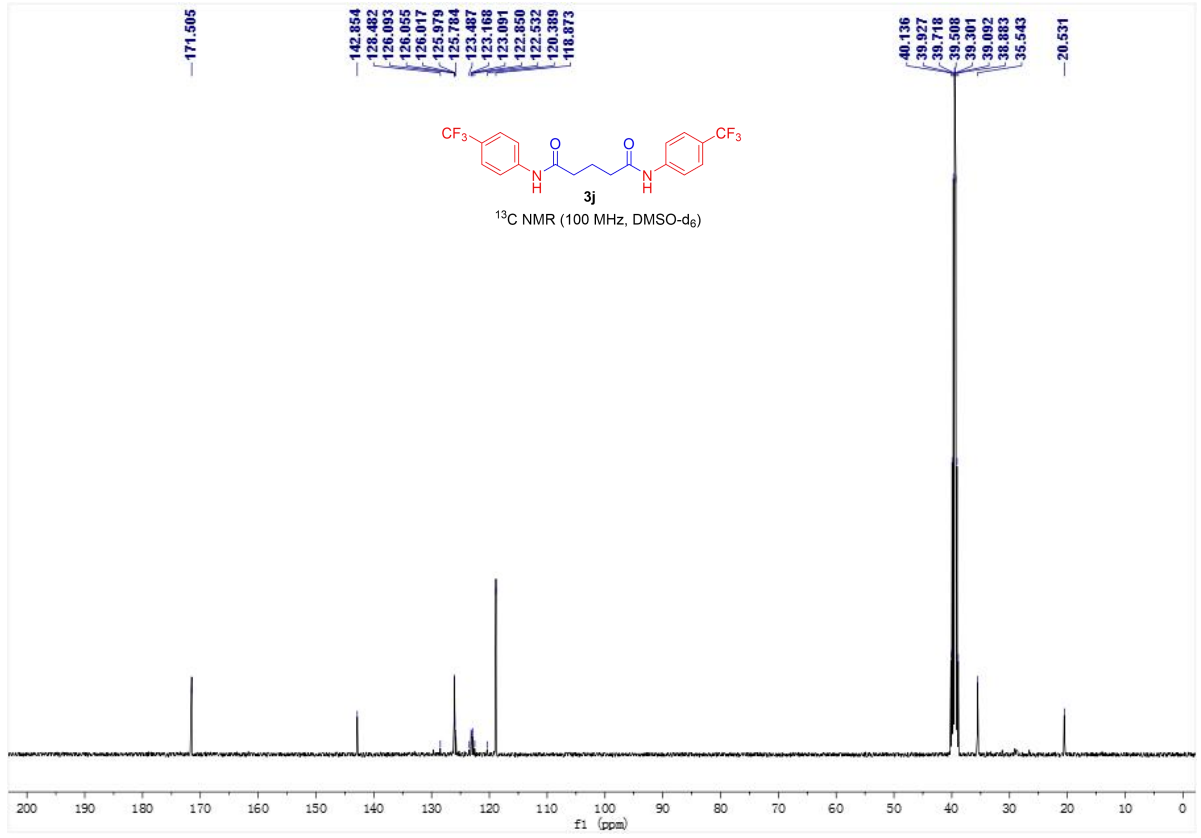
3i

^{13}C NMR (100 MHz, DMSO-d_6)



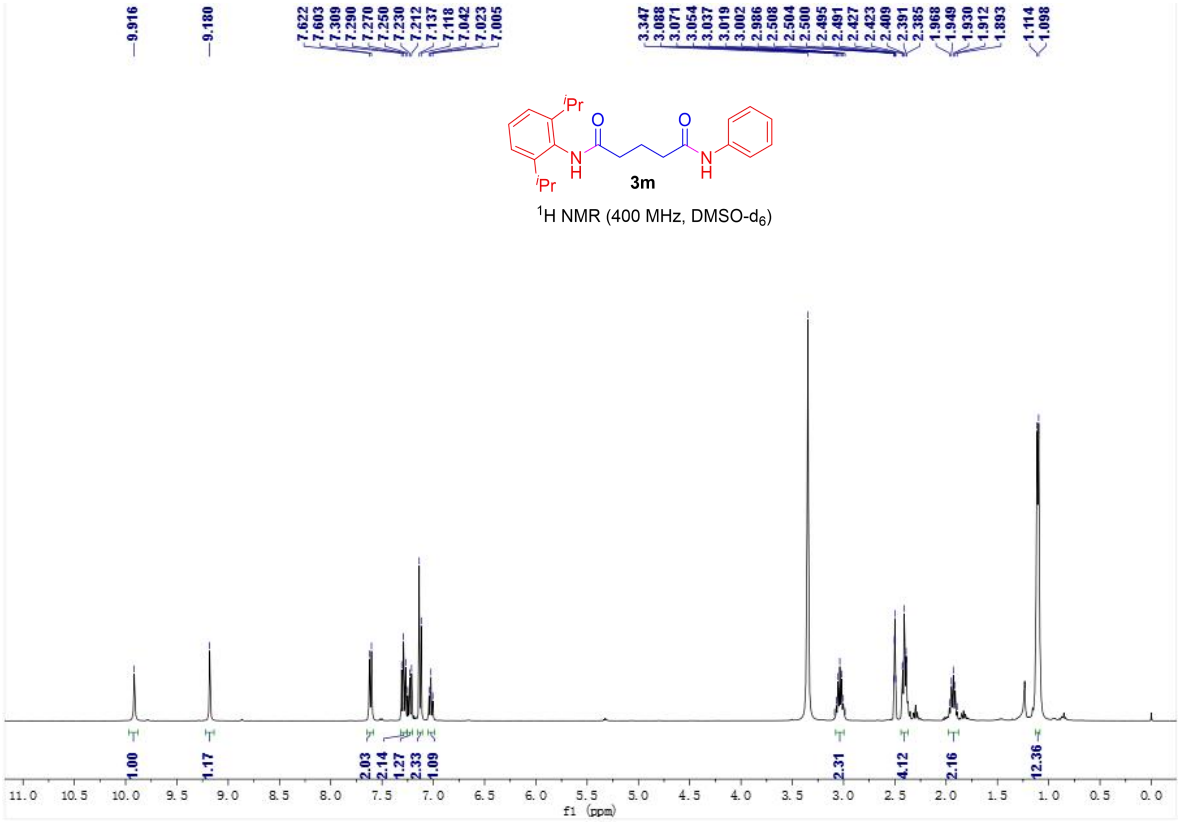
3j

^{1}H NMR (400 MHz, DMSO-d_6)

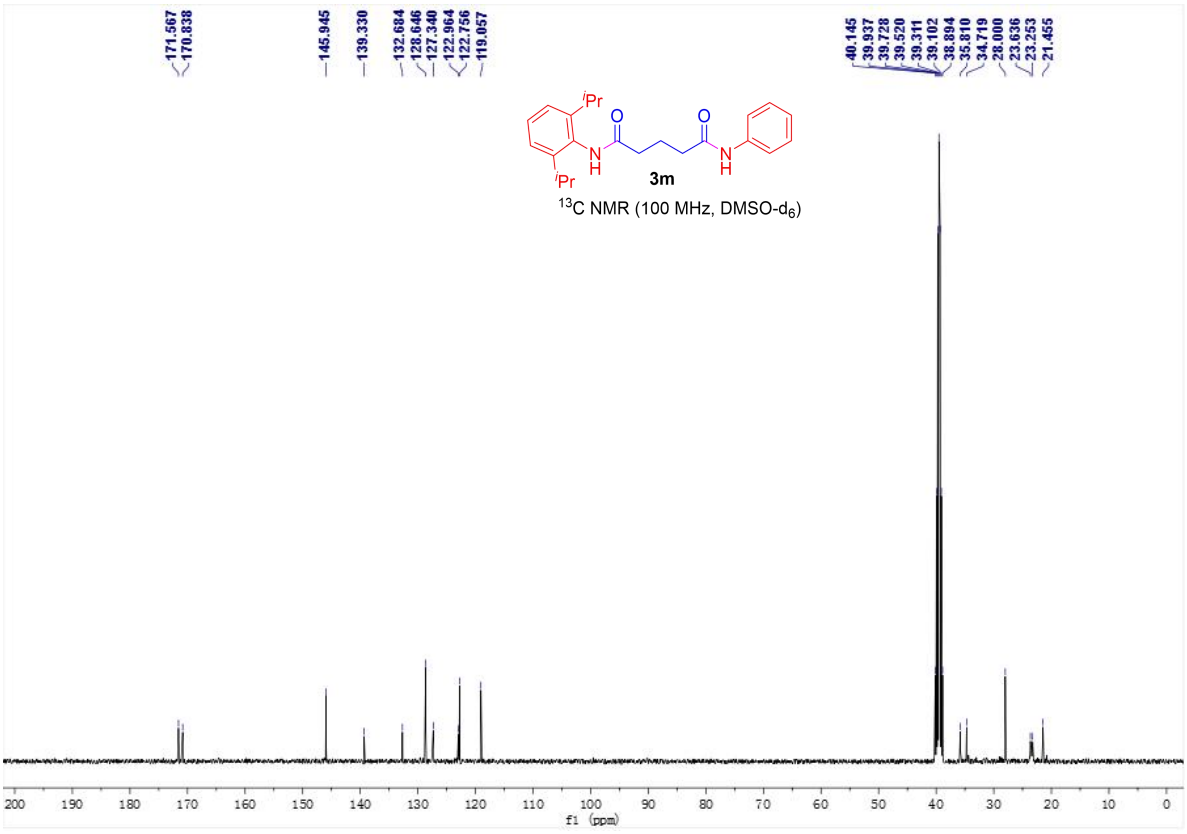


3j

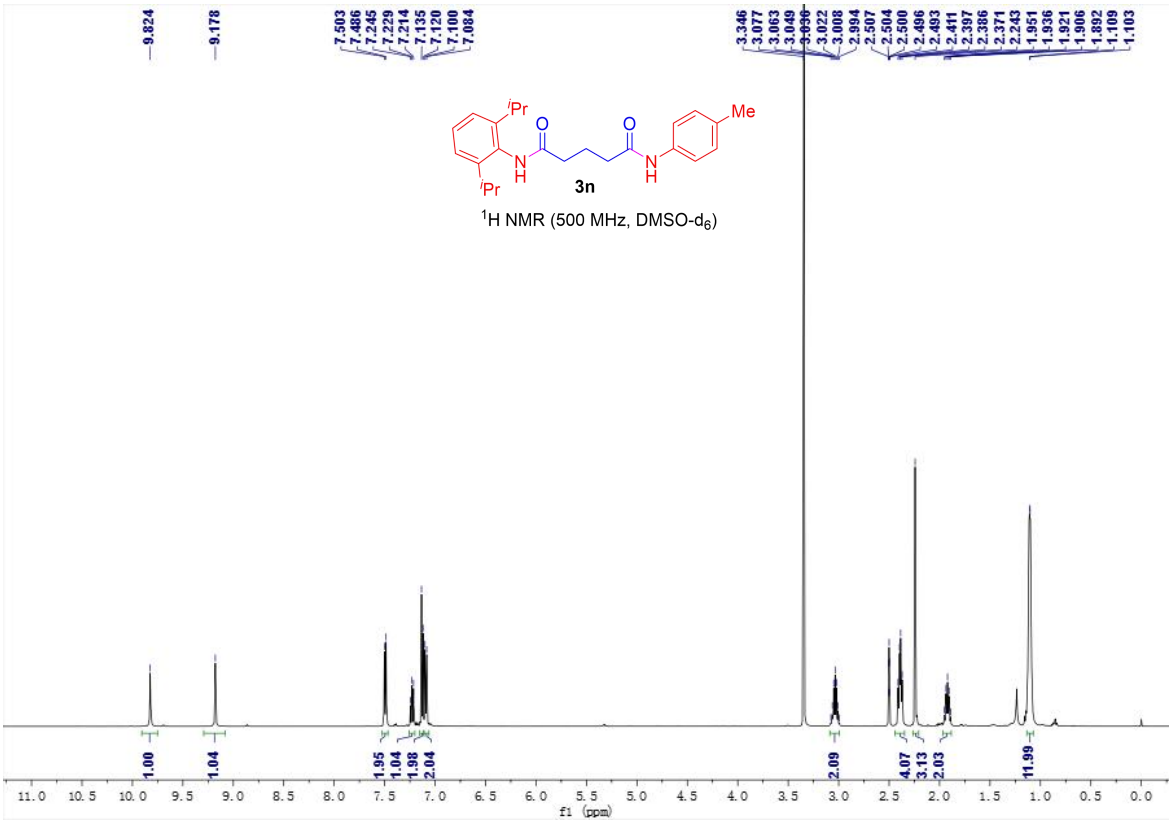
^{13}C NMR (100 MHz, DMSO-d_6)



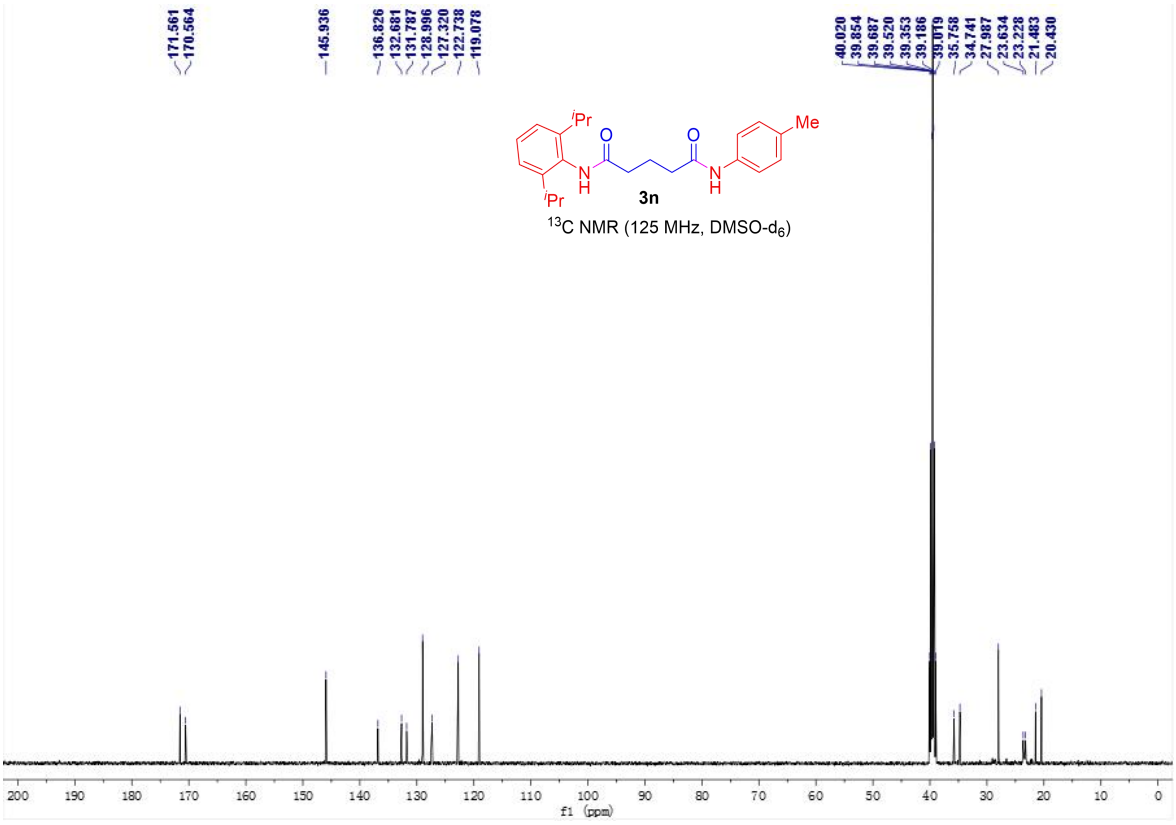
^{1}H NMR (400 MHz, DMSO-d_6)



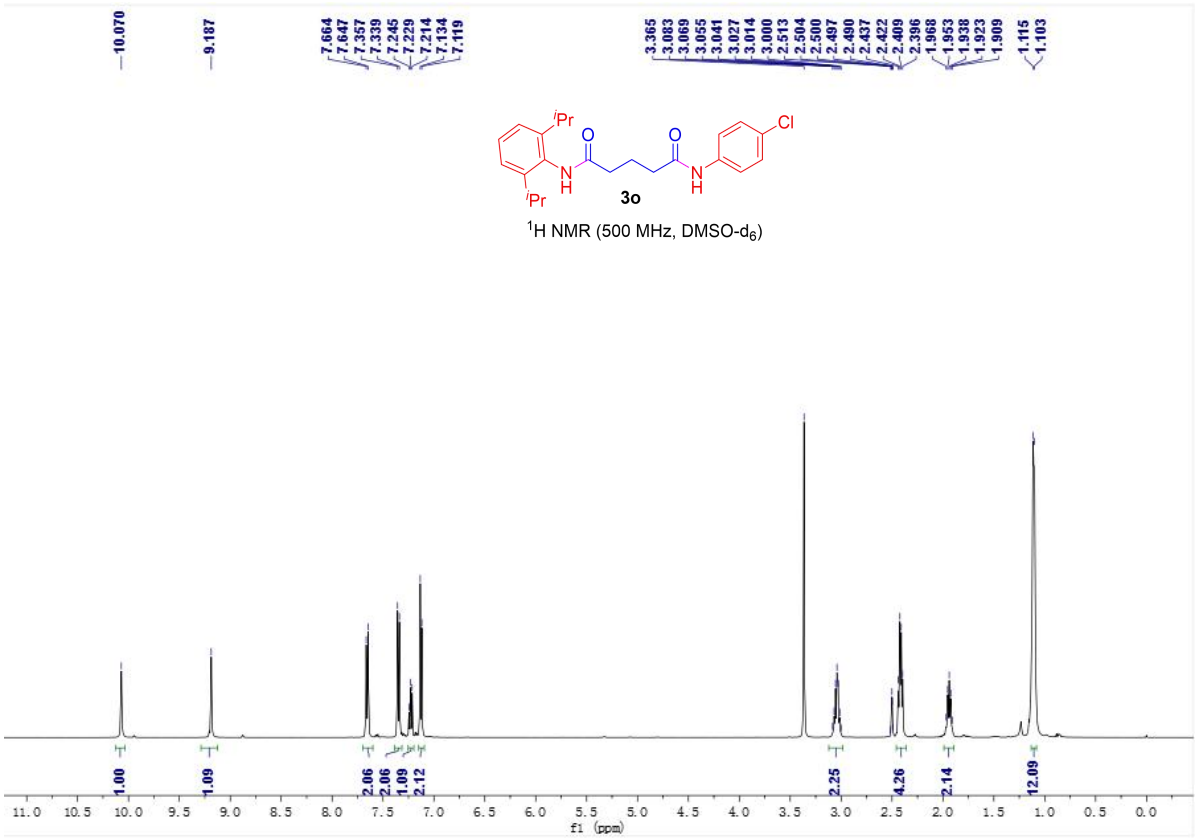
^{13}C NMR (100 MHz, DMSO-d_6)



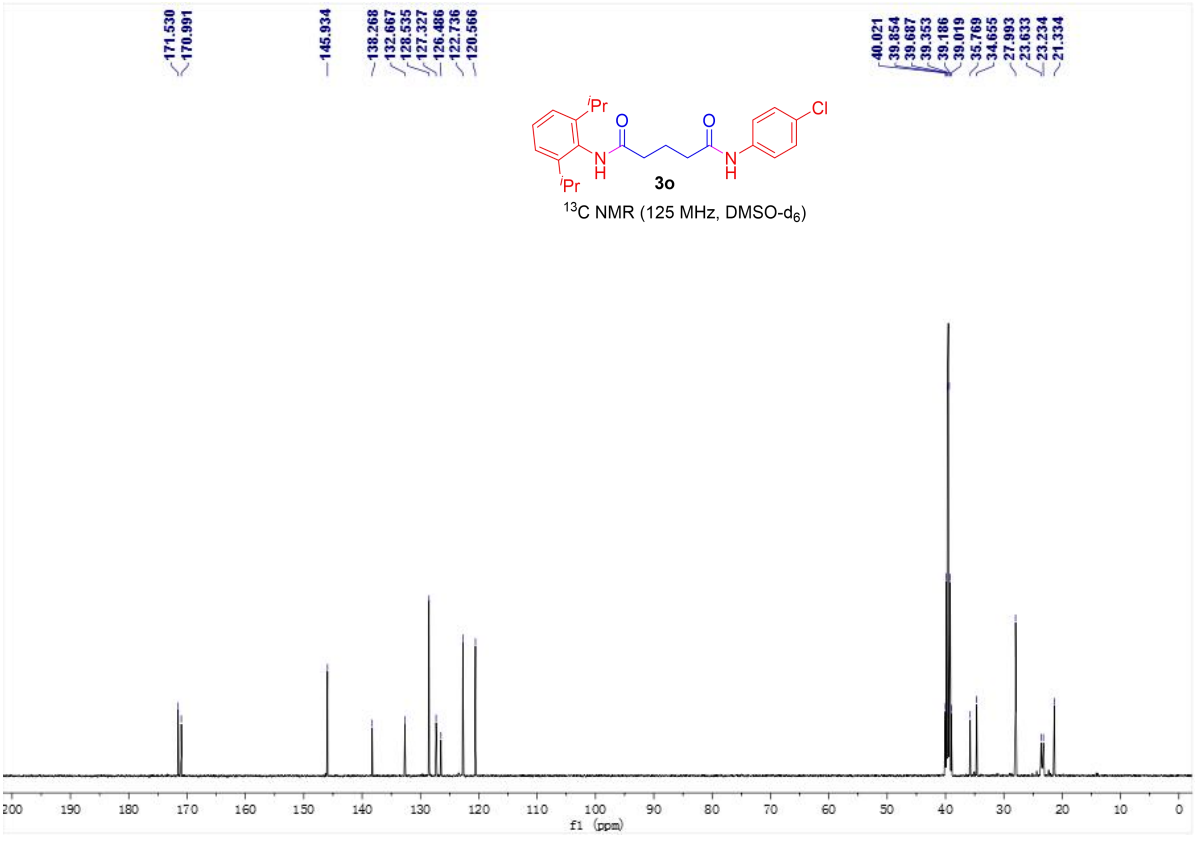
^{1}H NMR (500 MHz, DMSO-d_6)



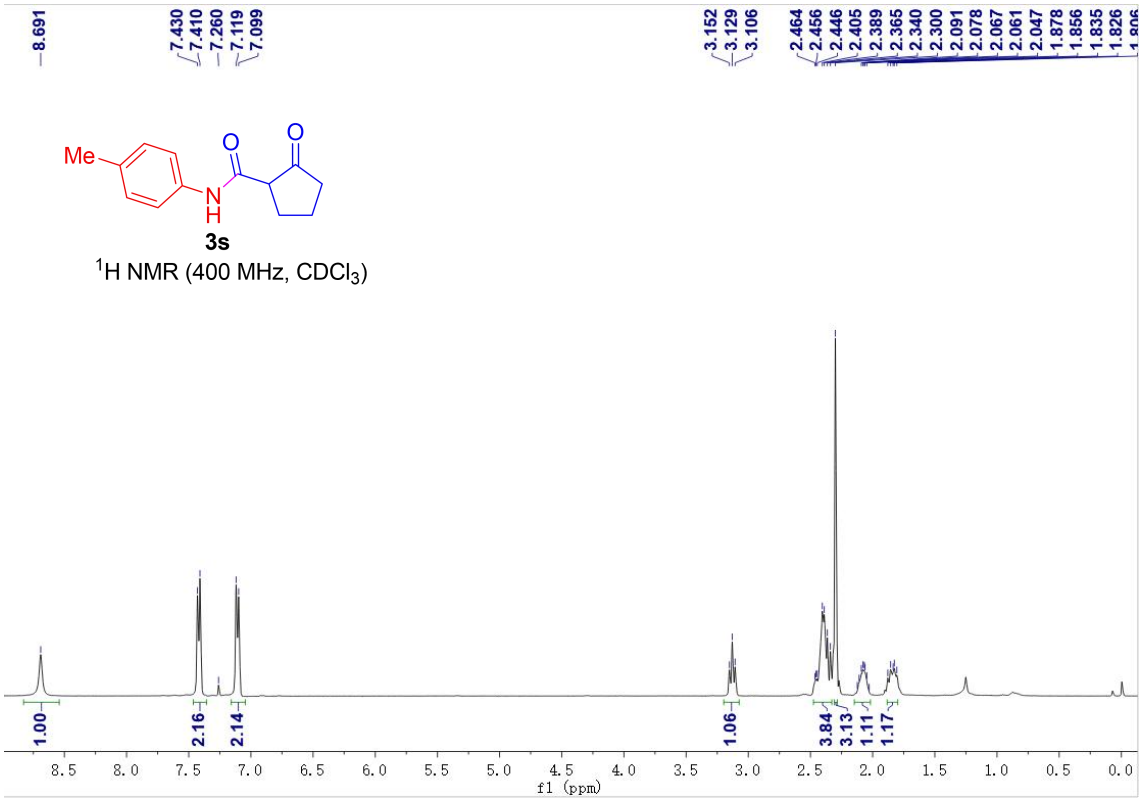
^{13}C NMR (125 MHz, DMSO-d_6)



^{1}H NMR (500 MHz, DMSO-d_6)

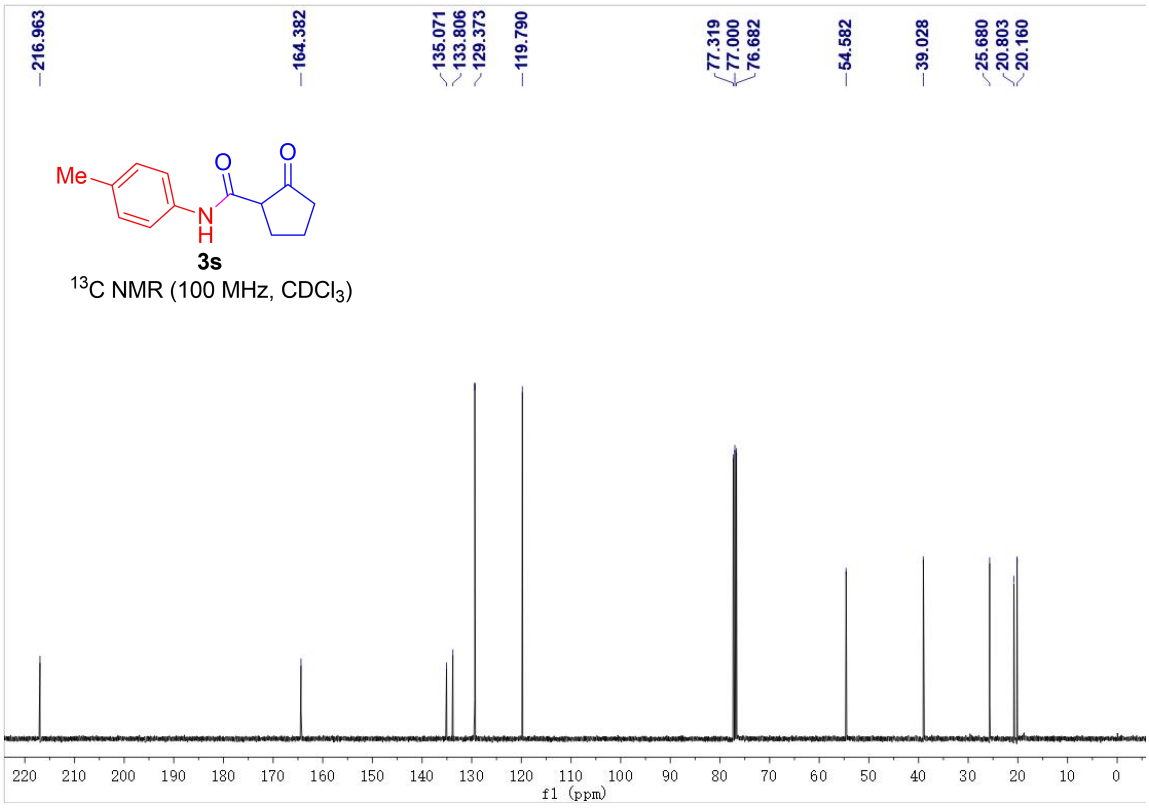


^{13}C NMR (125 MHz, DMSO-d_6)



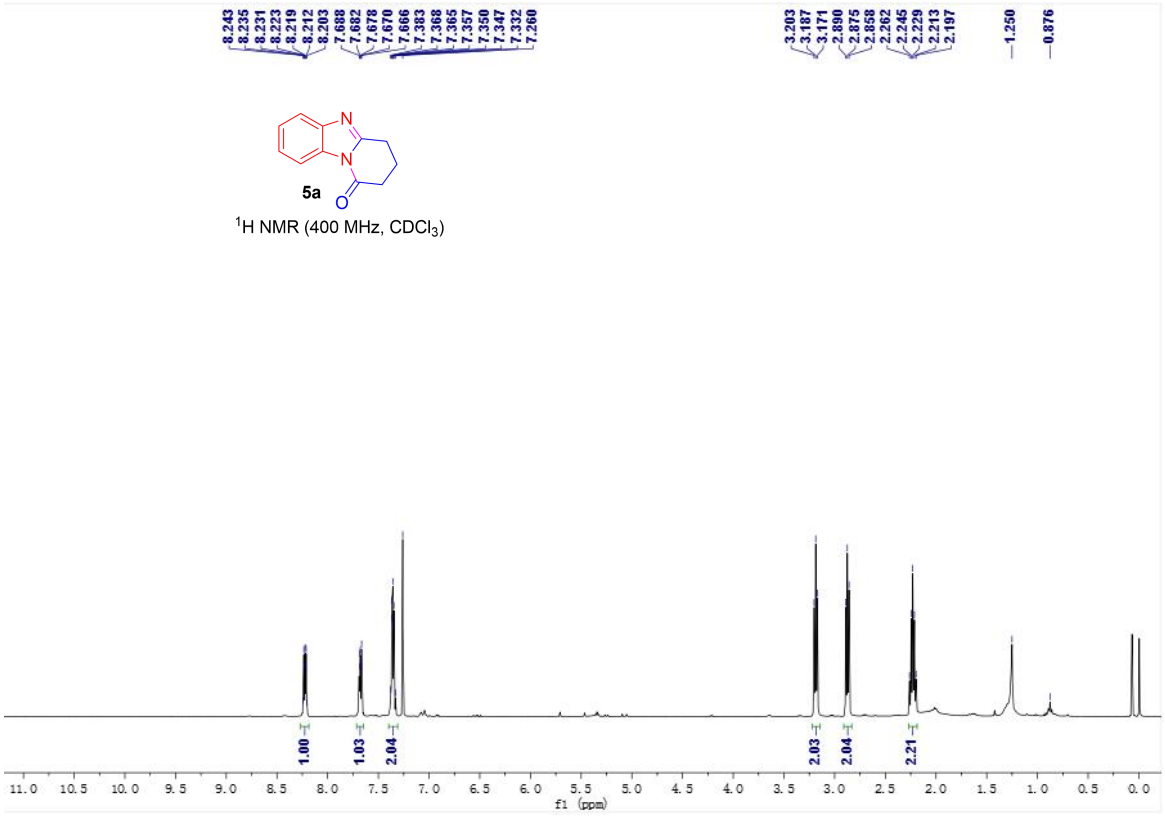
3s

^{1}H NMR (400 MHz, $CDCl_3$)

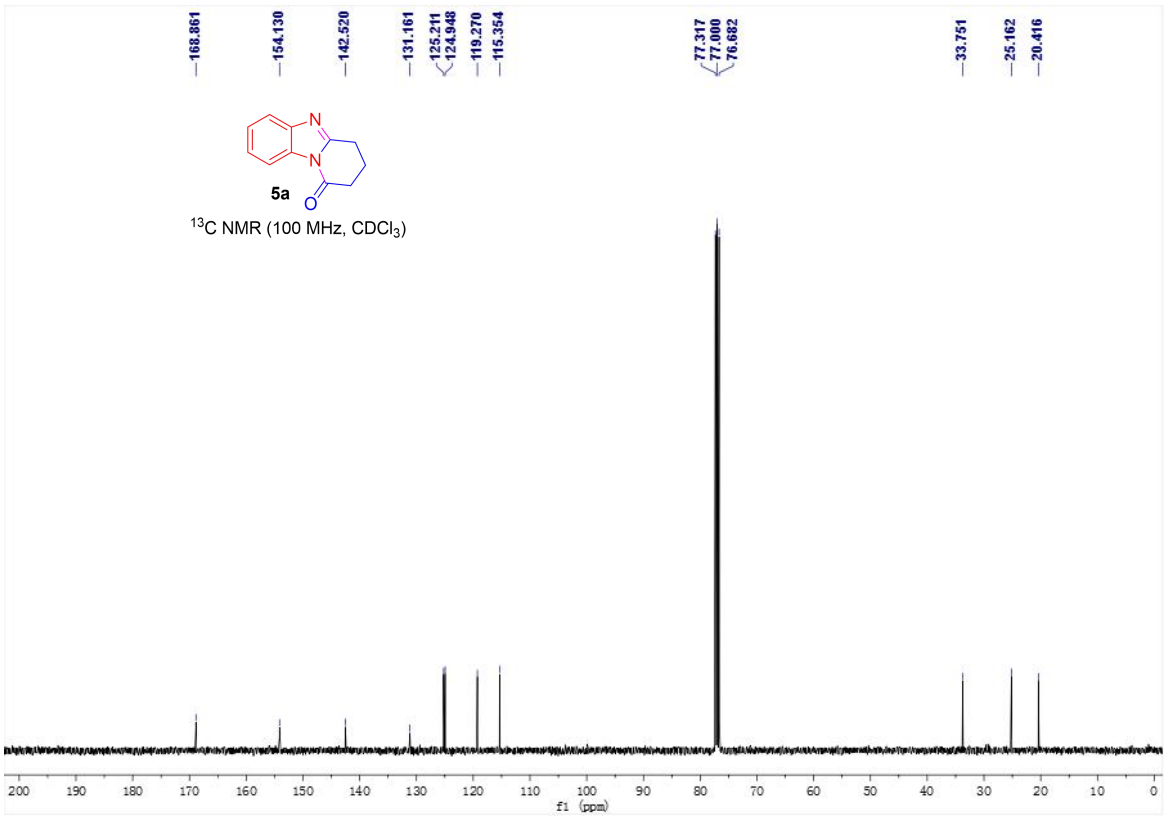


3s

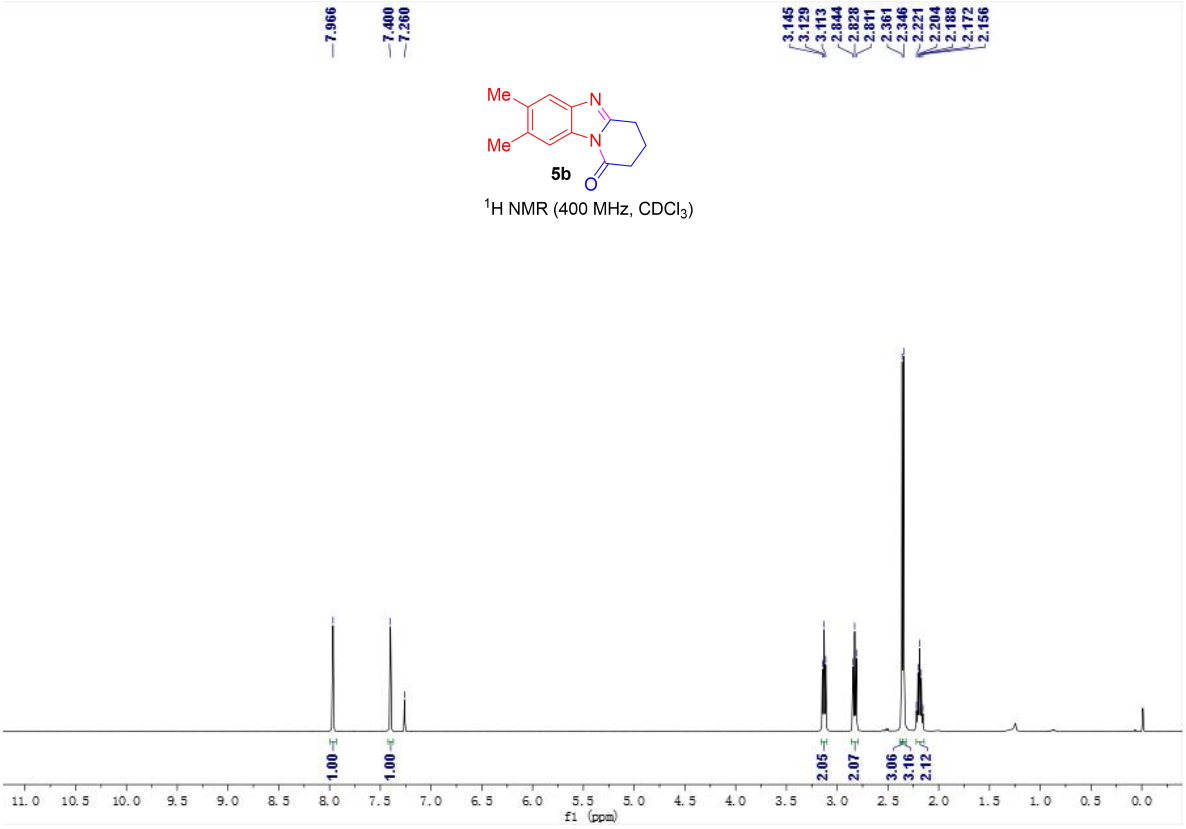
^{13}C NMR (100 MHz, $CDCl_3$)



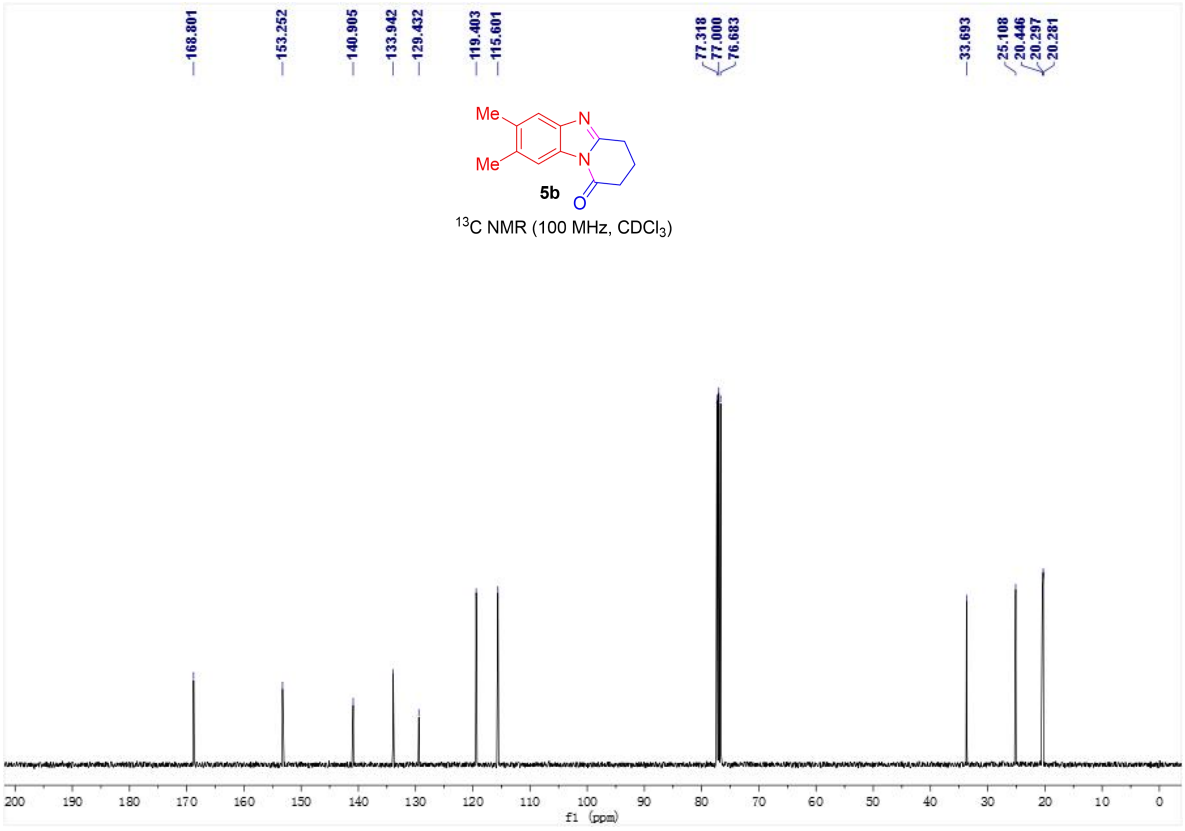
^{1}H NMR (400 MHz, $CDCl_3$)



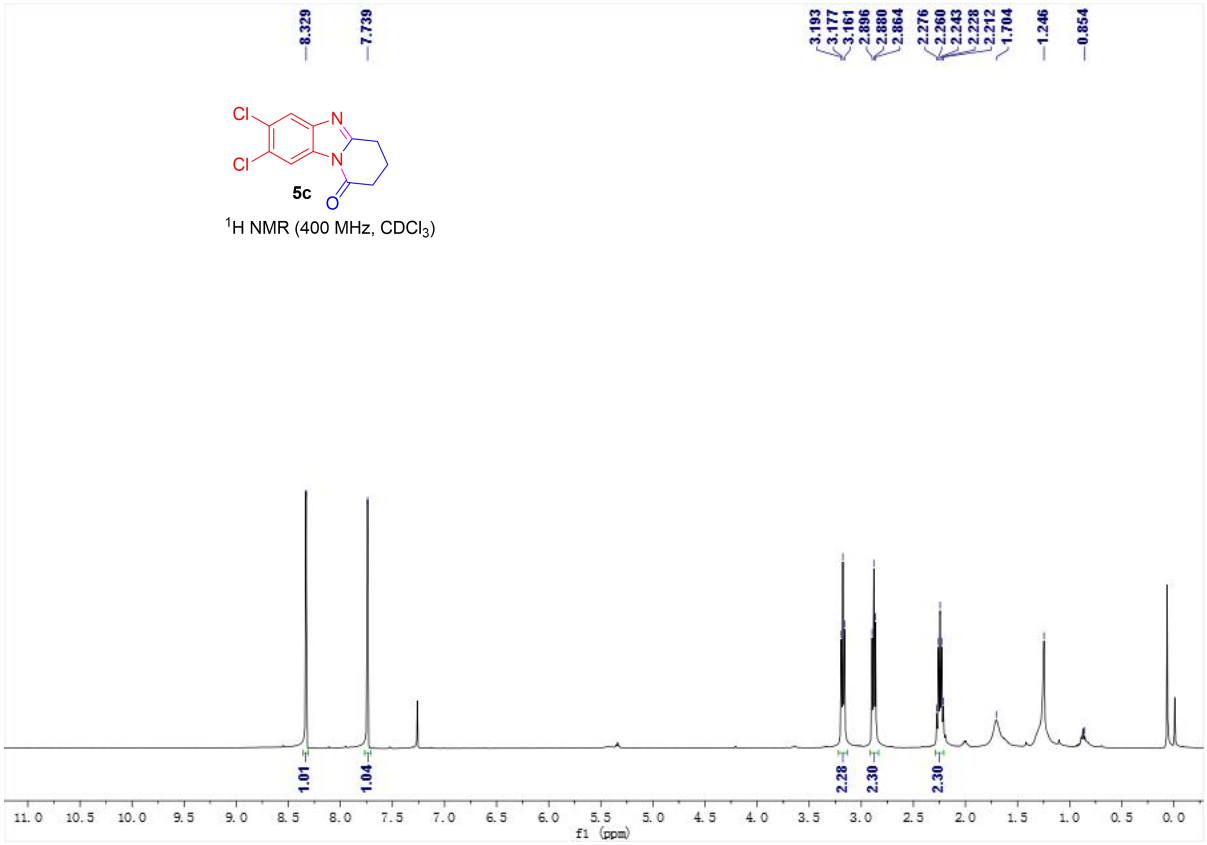
^{13}C NMR (100 MHz, $CDCl_3$)



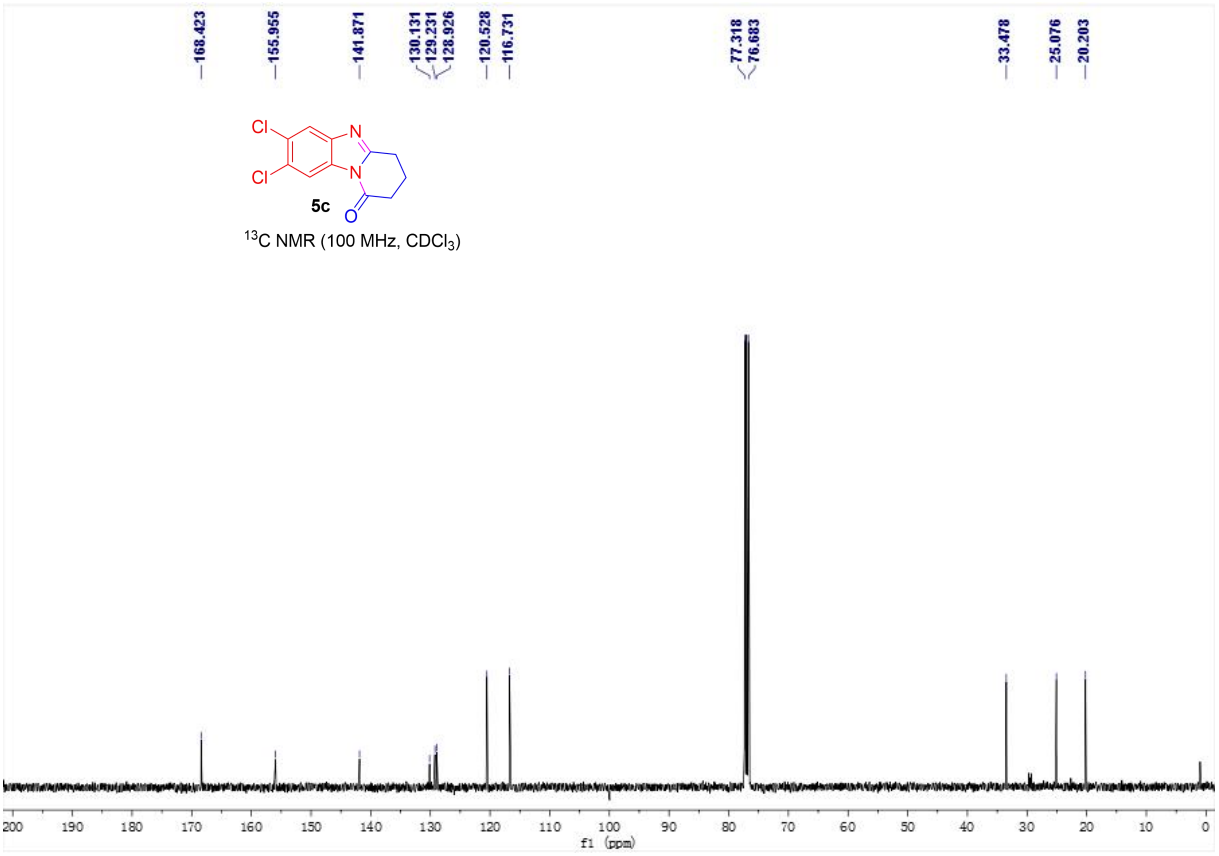
^{1}H NMR (400 MHz, $CDCl_3$)



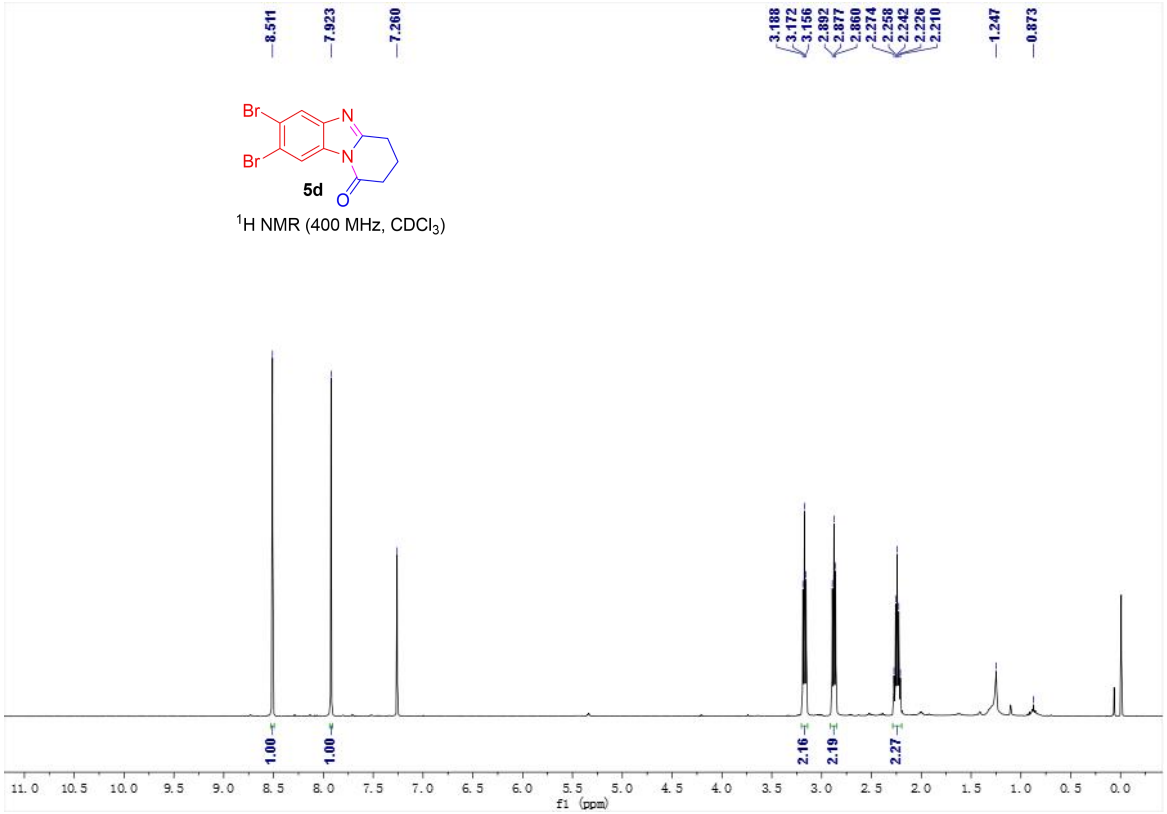
^{13}C NMR (100 MHz, $CDCl_3$)



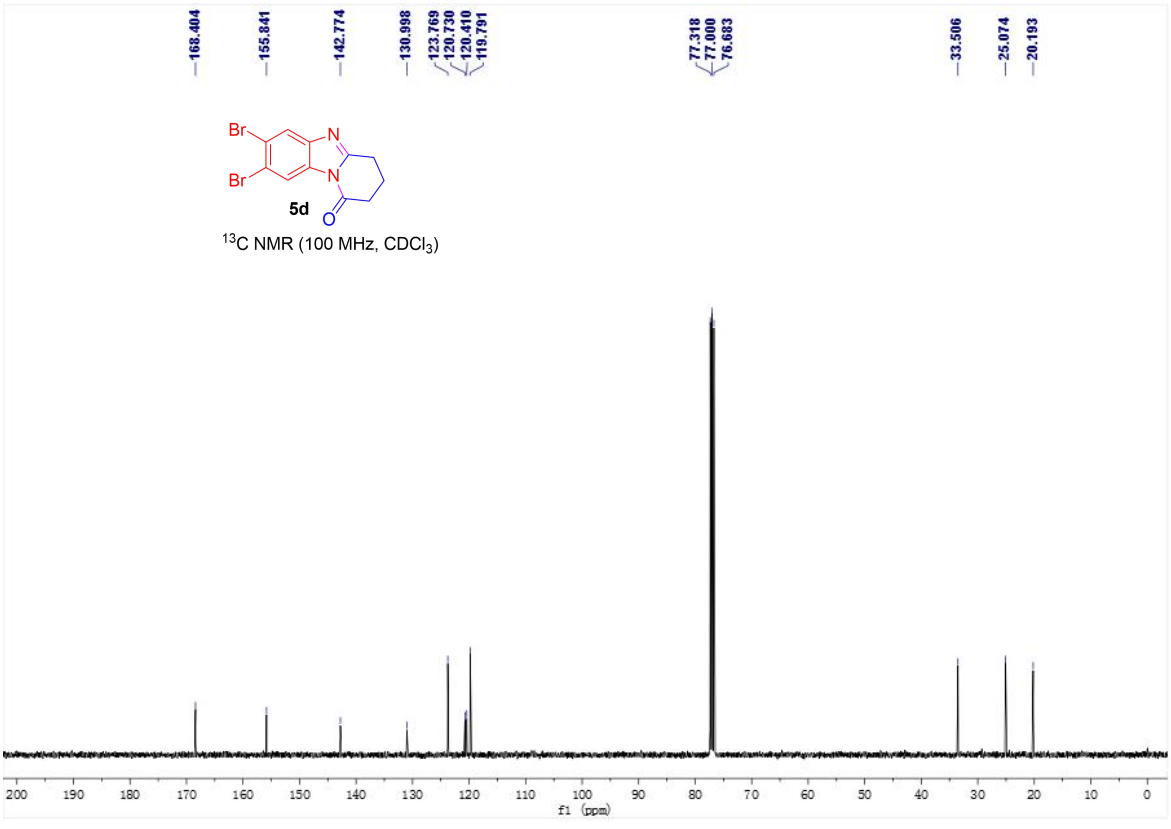
^{1}H NMR (400 MHz, $CDCl_3$)



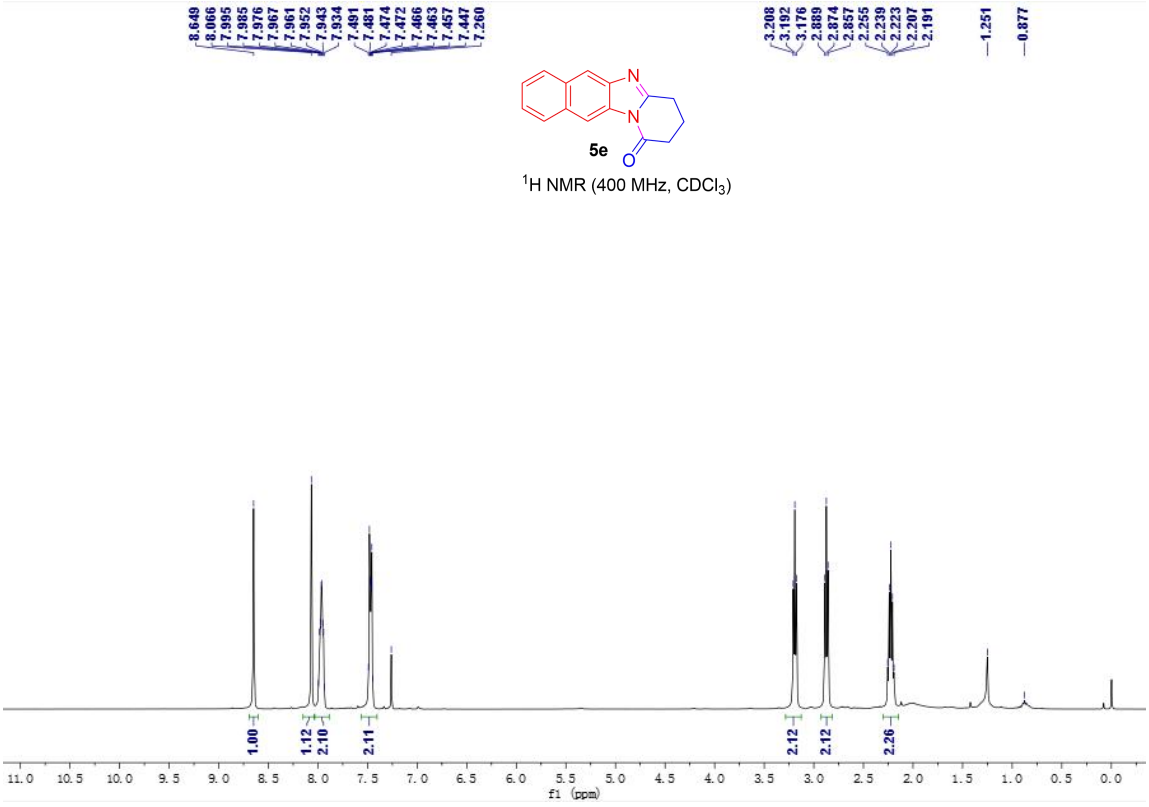
^{13}C NMR (100 MHz, $CDCl_3$)



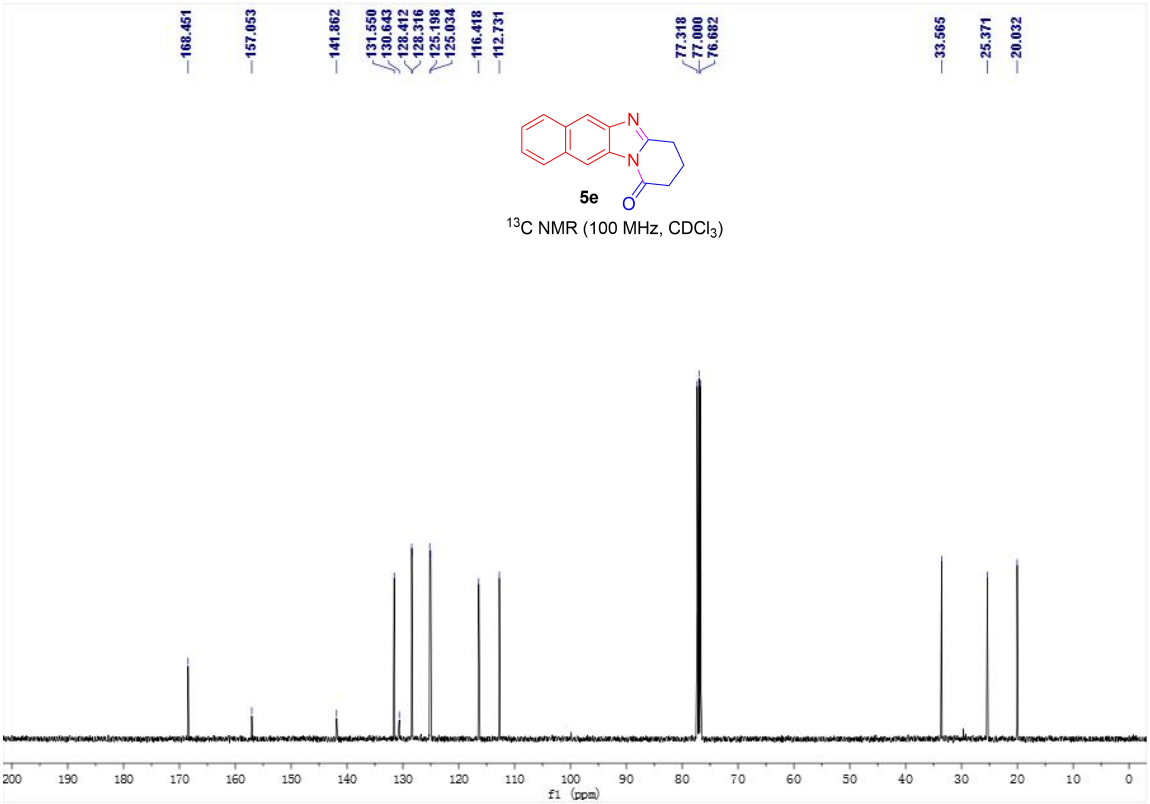
^{1}H NMR (400 MHz, $CDCl_3$)



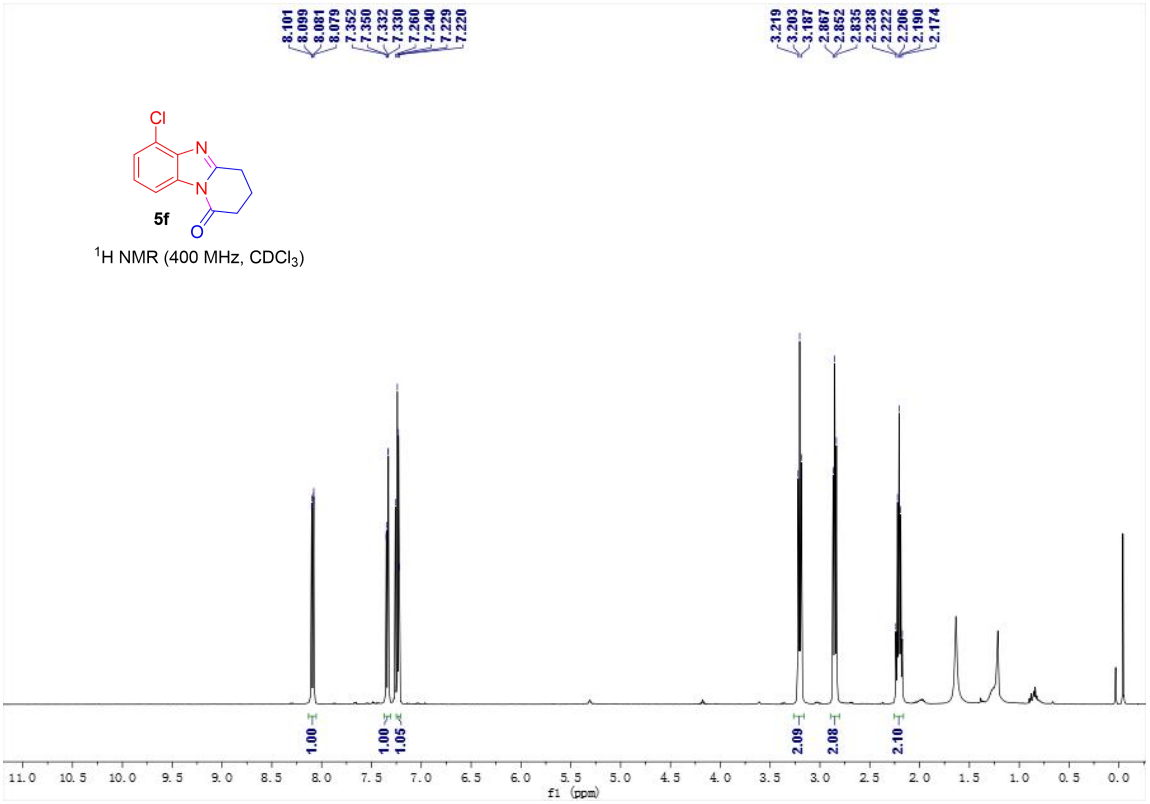
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

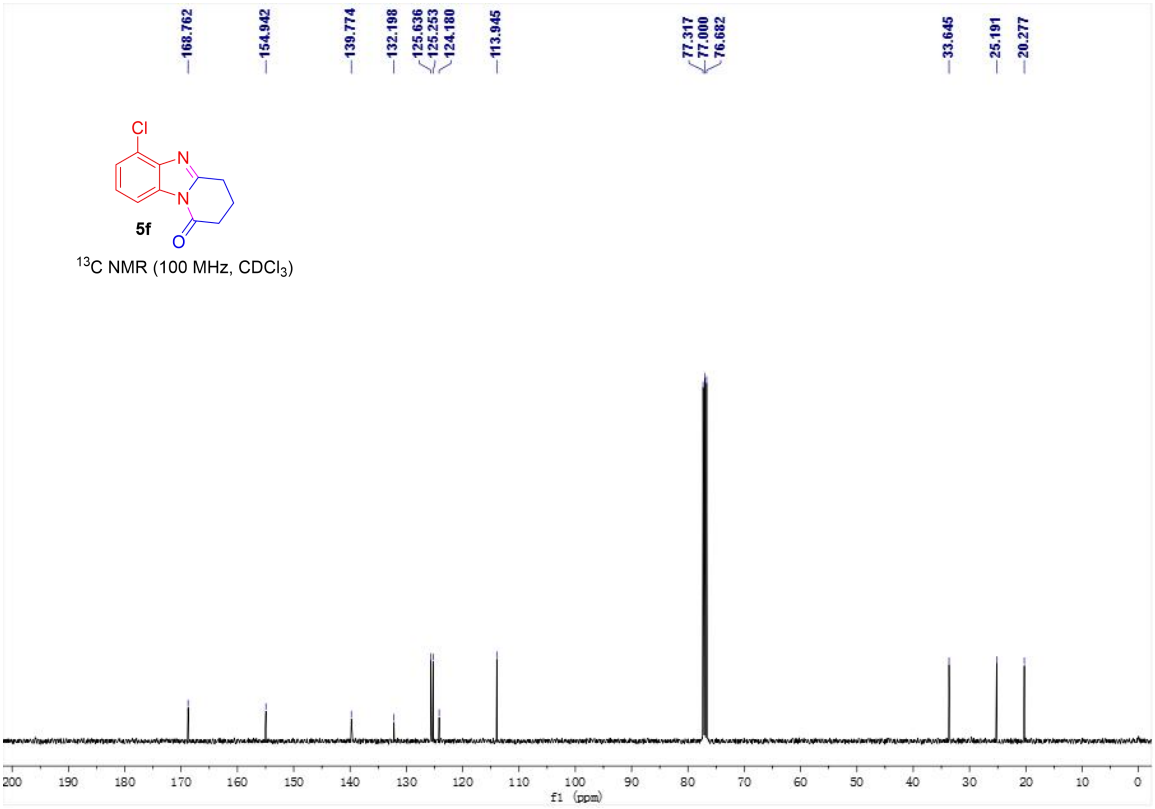


^{13}C NMR (100 MHz, $CDCl_3$)



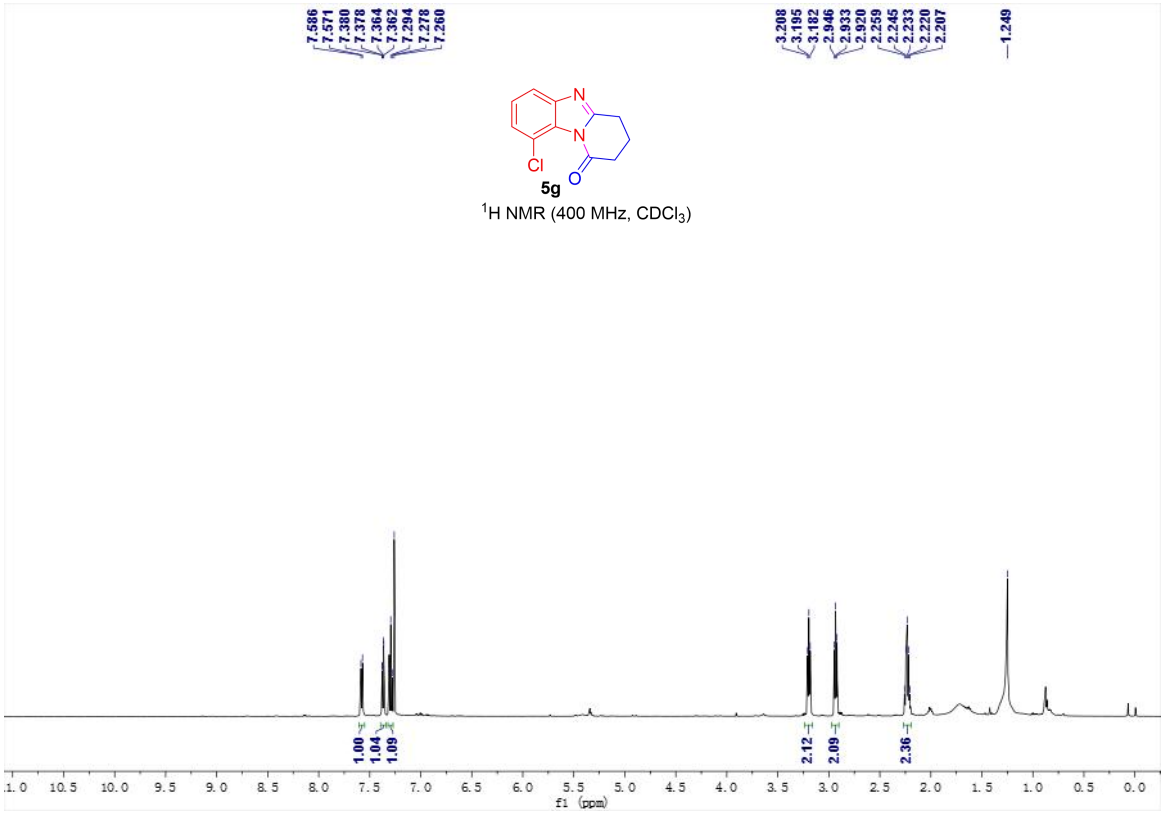
5f

^{1}H NMR (400 MHz, $CDCl_3$)



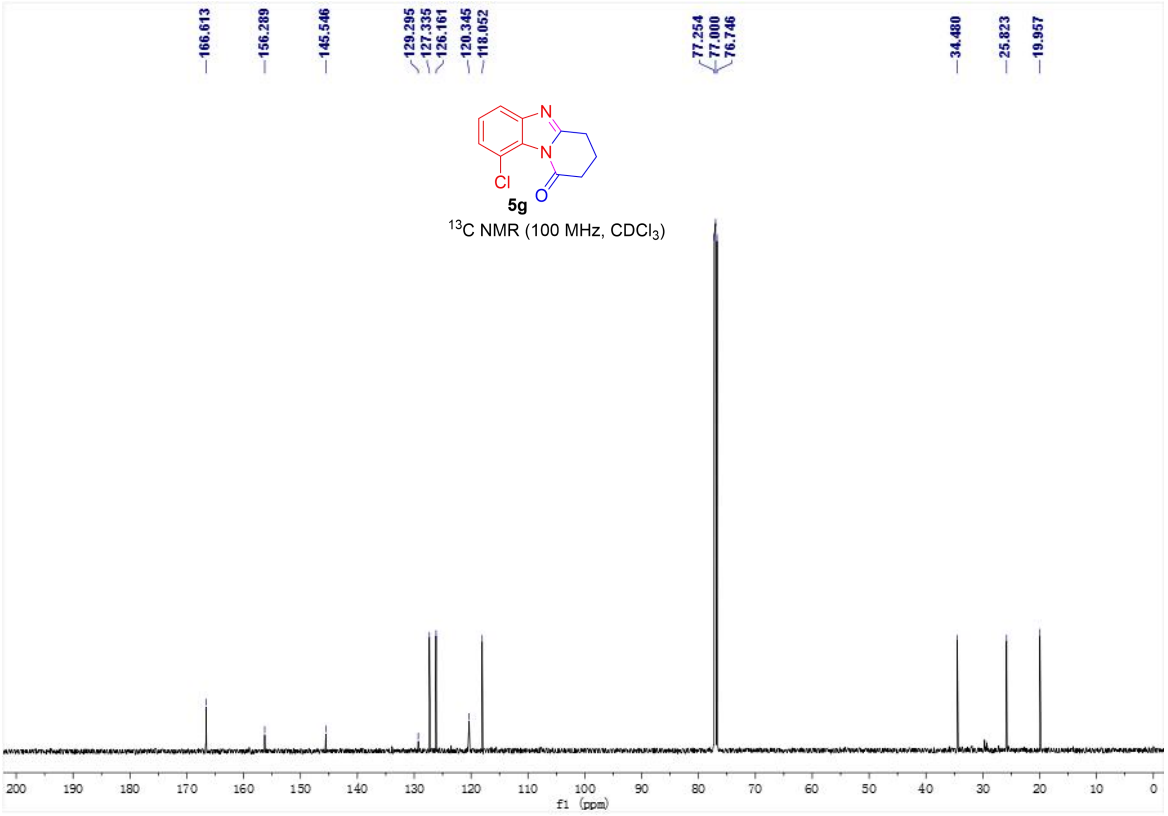
5f

^{13}C NMR (100 MHz, $CDCl_3$)



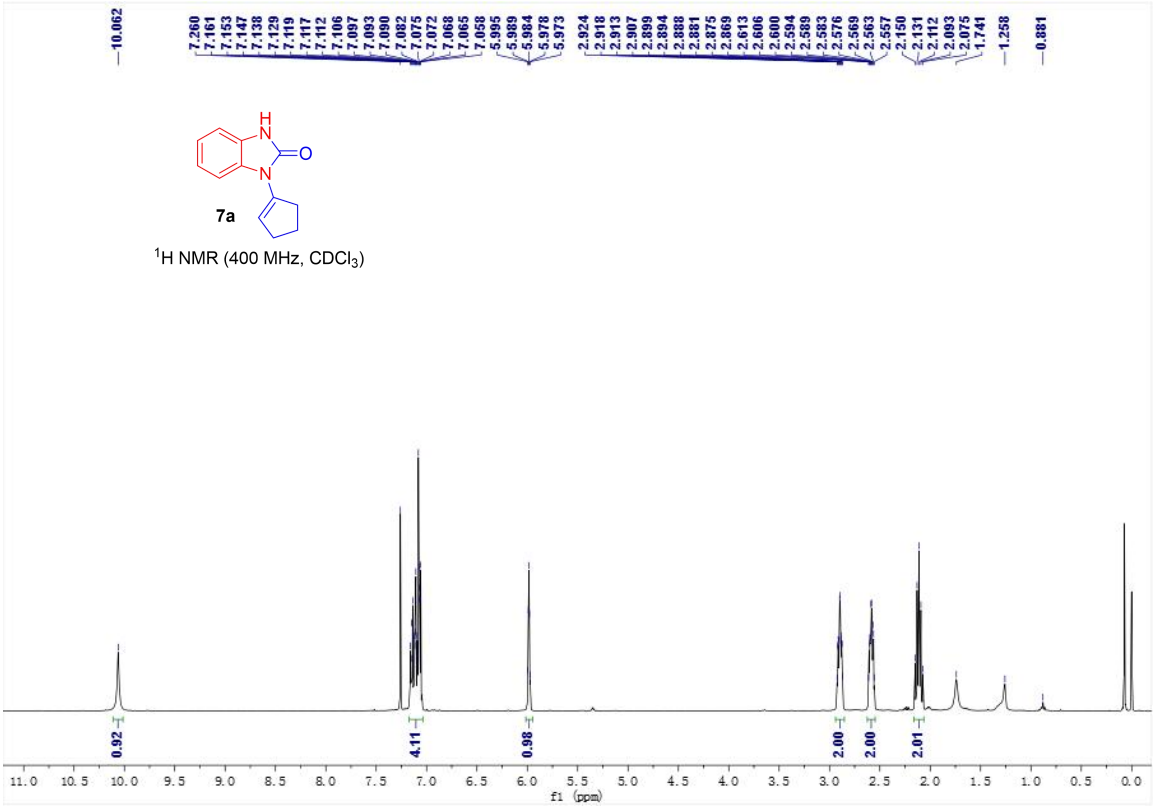
5g

^{1}H NMR (400 MHz, $CDCl_3$)



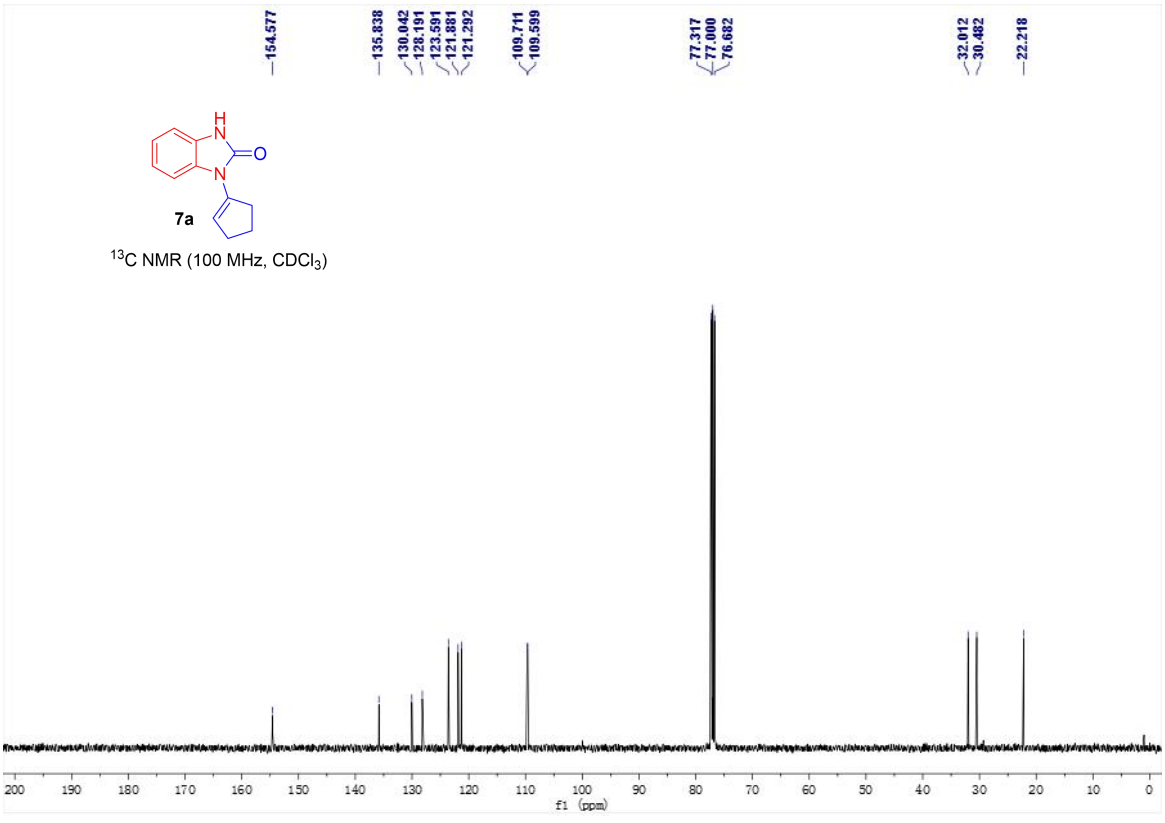
5g

^{13}C NMR (100 MHz, $CDCl_3$)



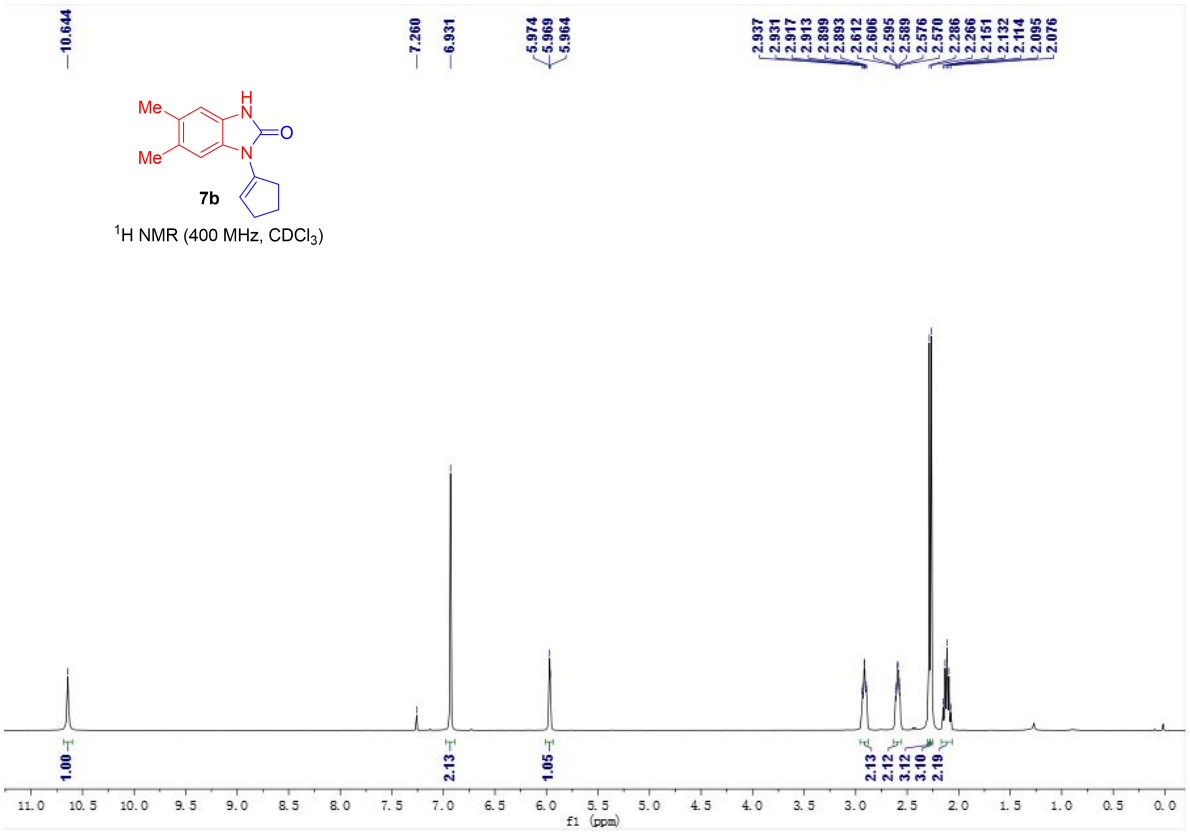
7a

^{1}H NMR (400 MHz, $CDCl_3$)

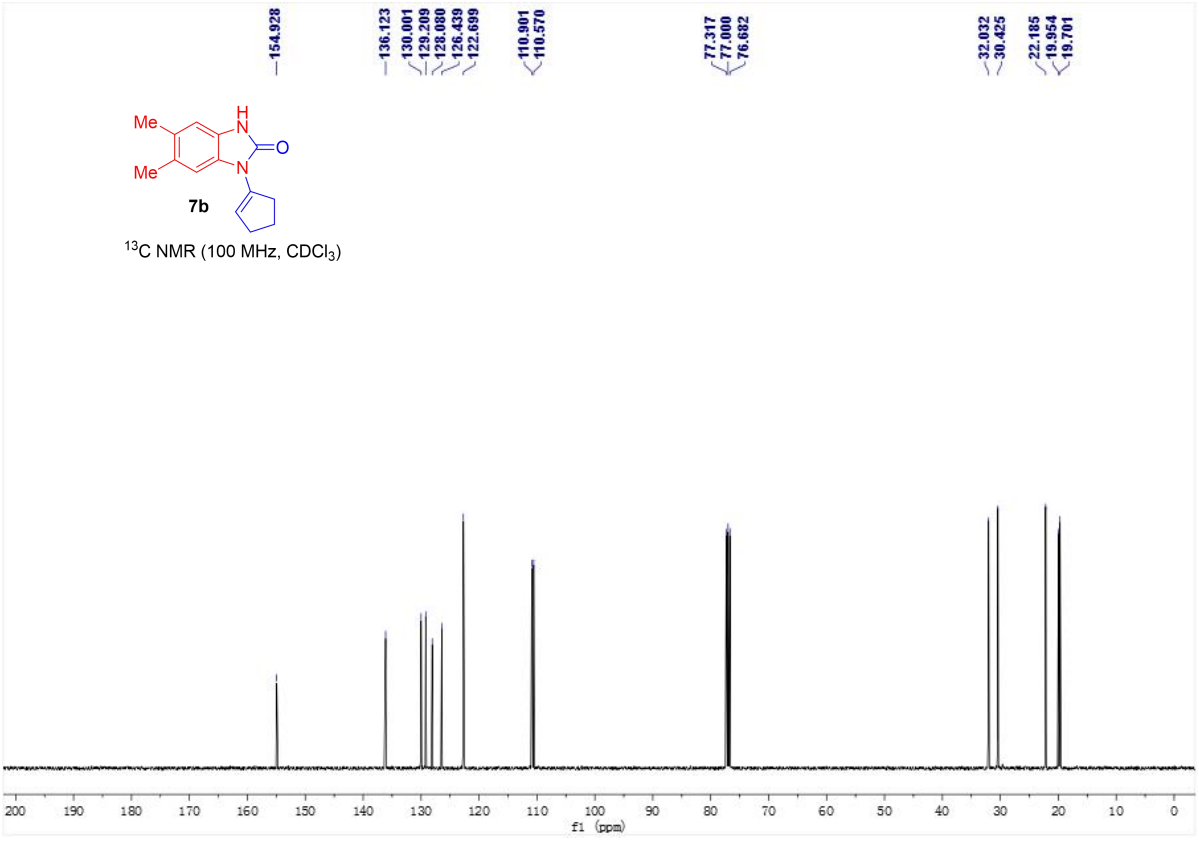


7a

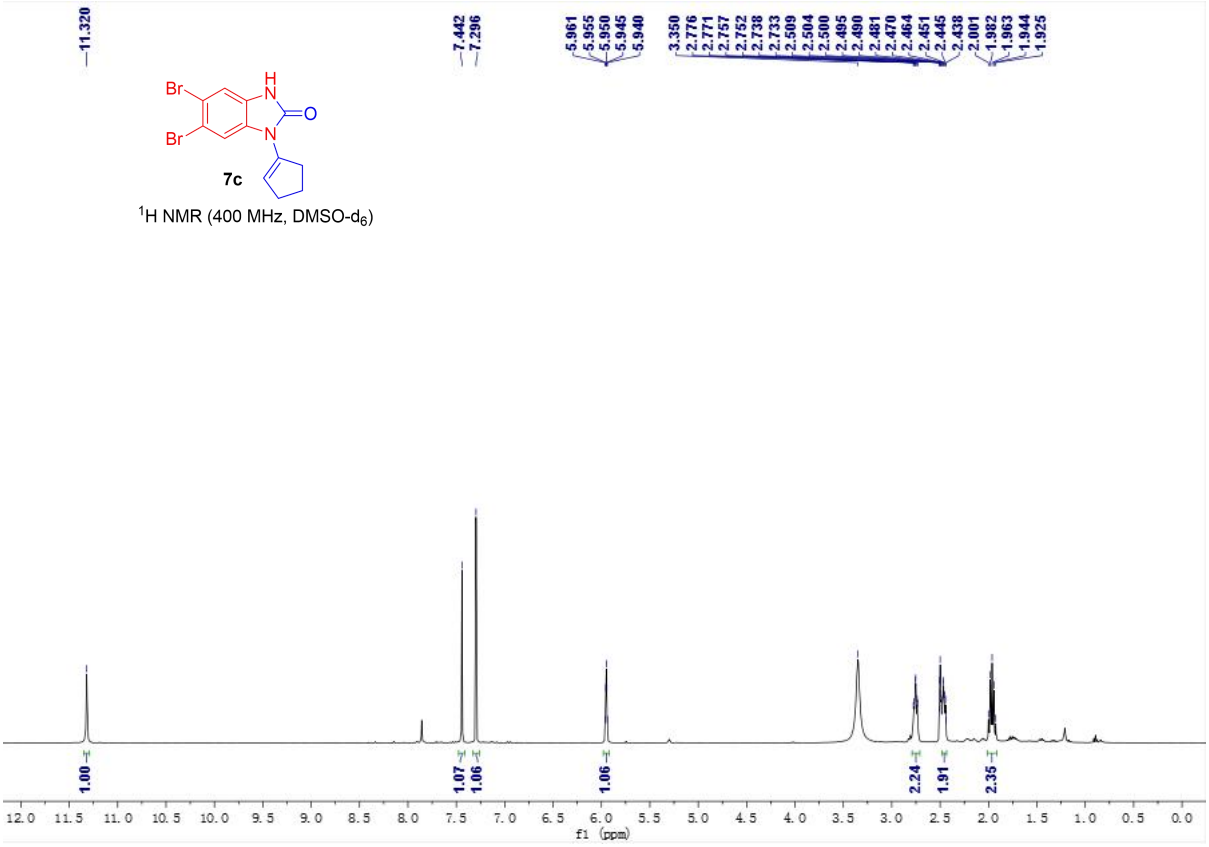
^{13}C NMR (100 MHz, $CDCl_3$)



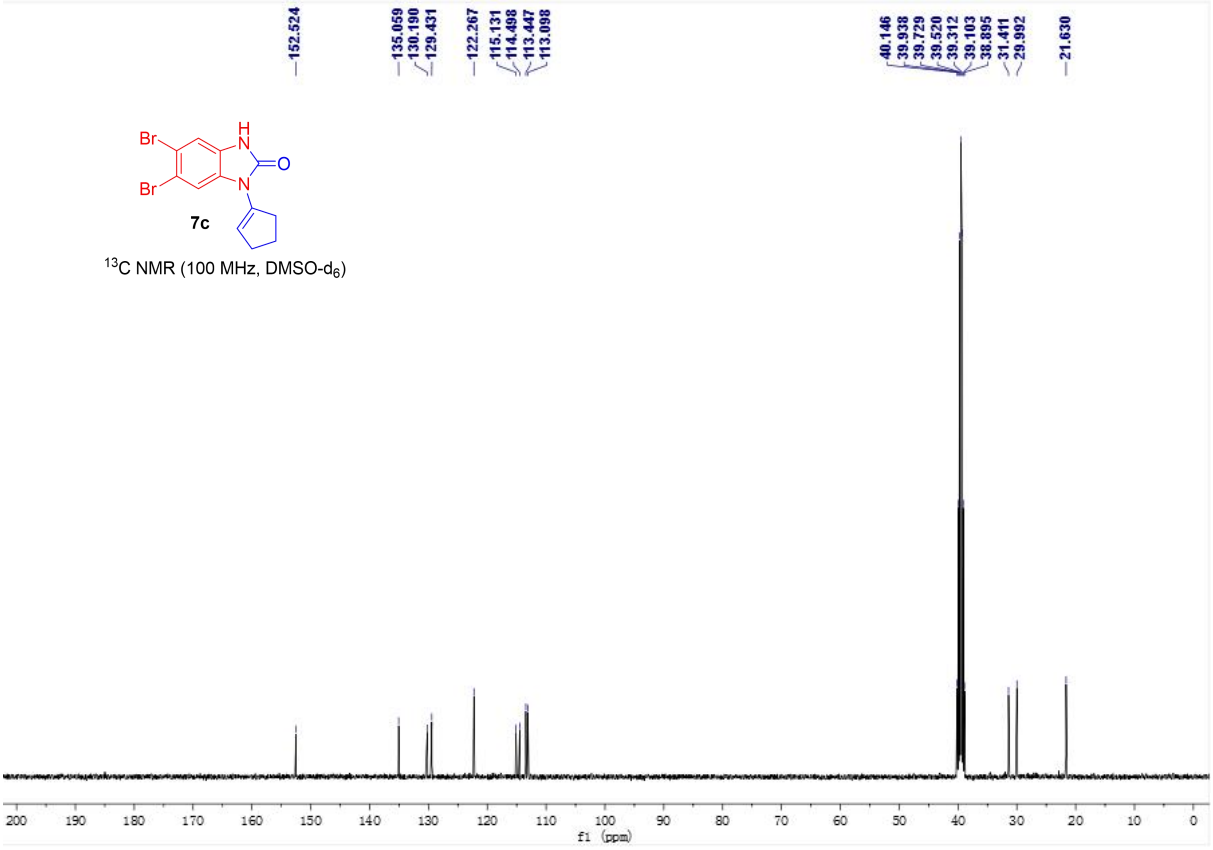
^{1}H NMR (400 MHz, $CDCl_3$)



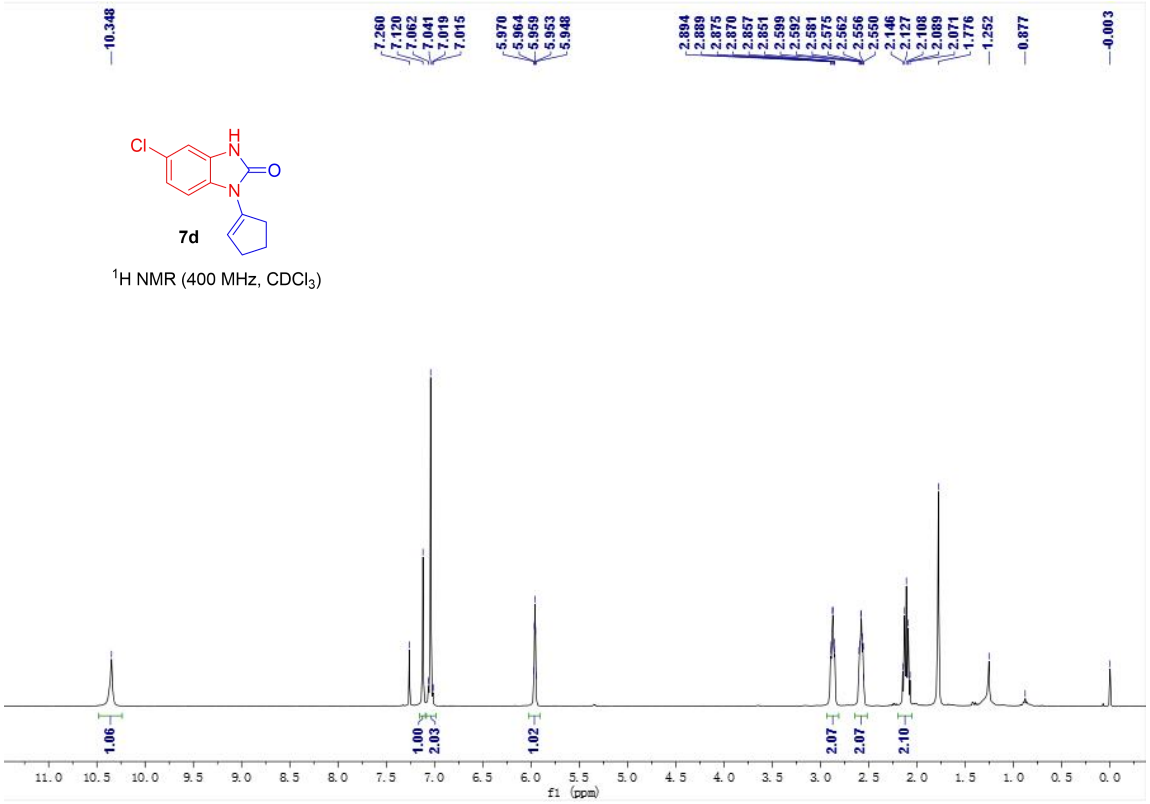
^{13}C NMR (100 MHz, $CDCl_3$)



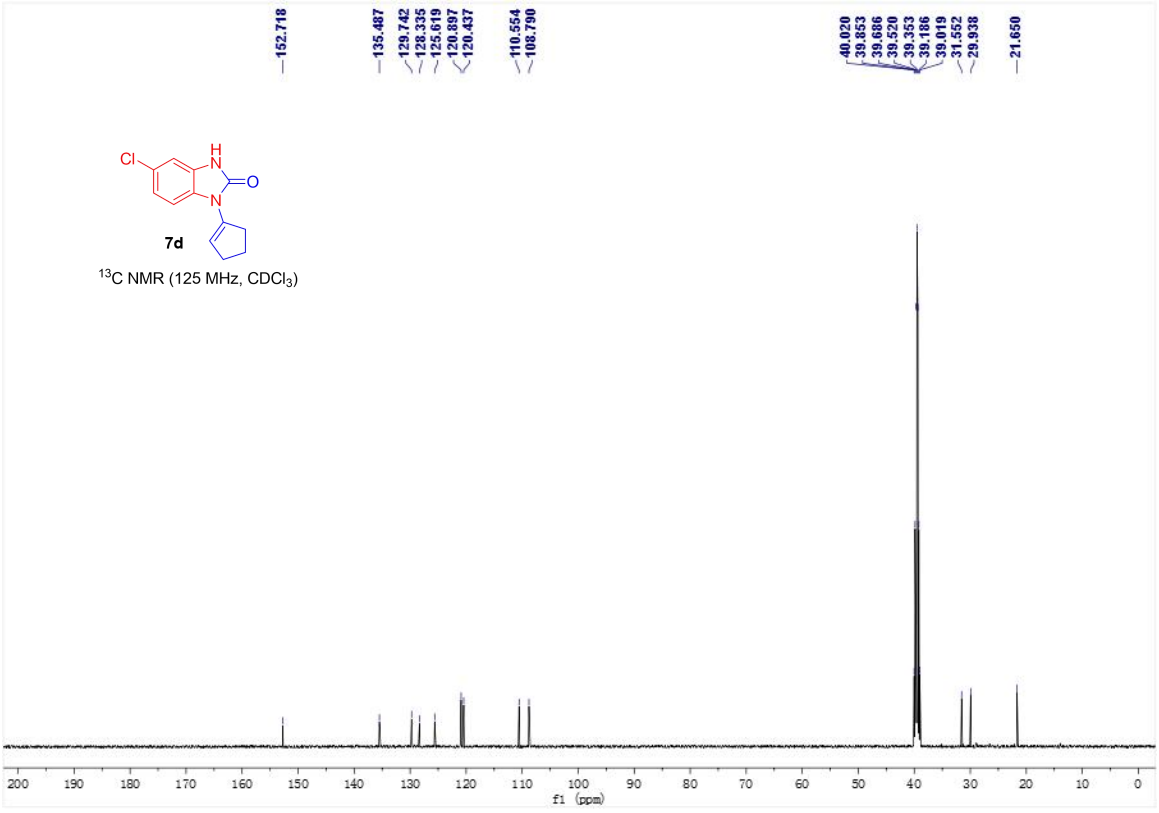
^{1}H NMR (400 MHz, DMSO-d_6)



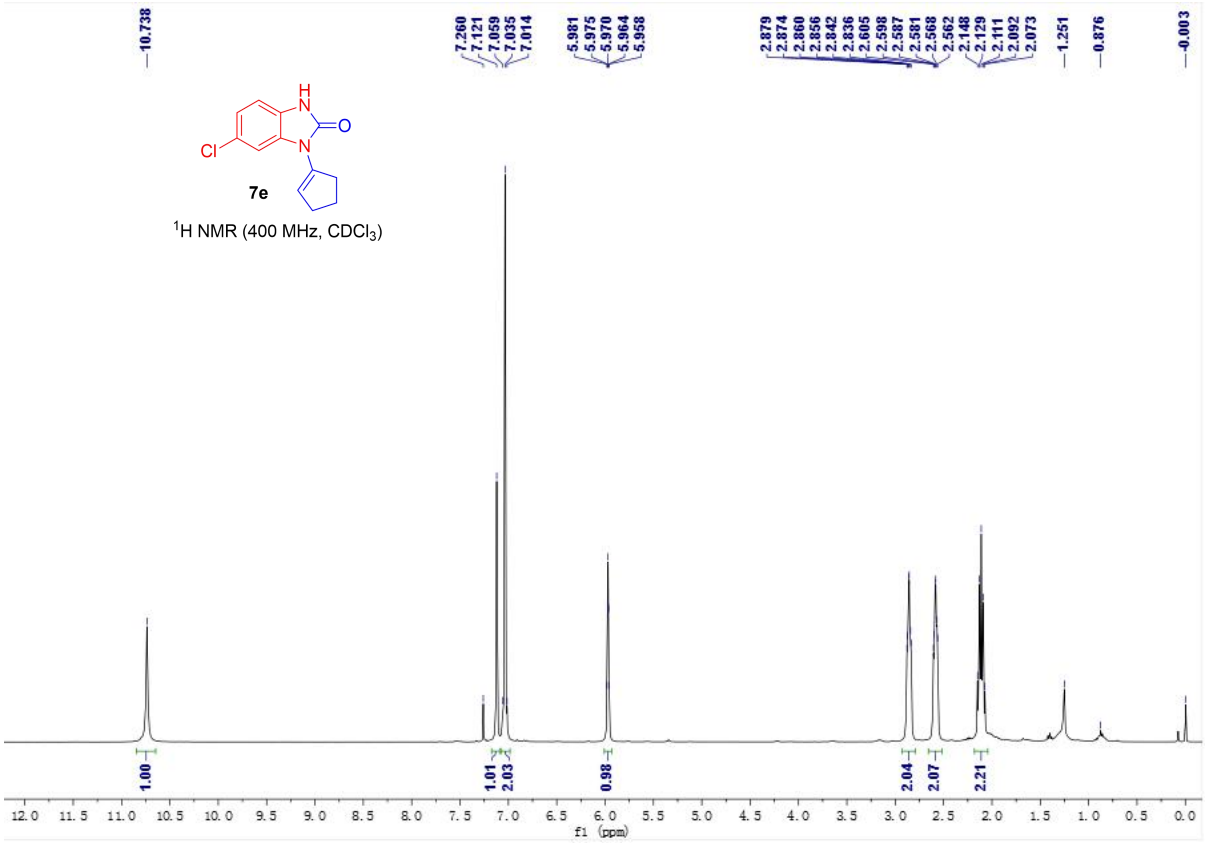
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, $CDCl_3$)

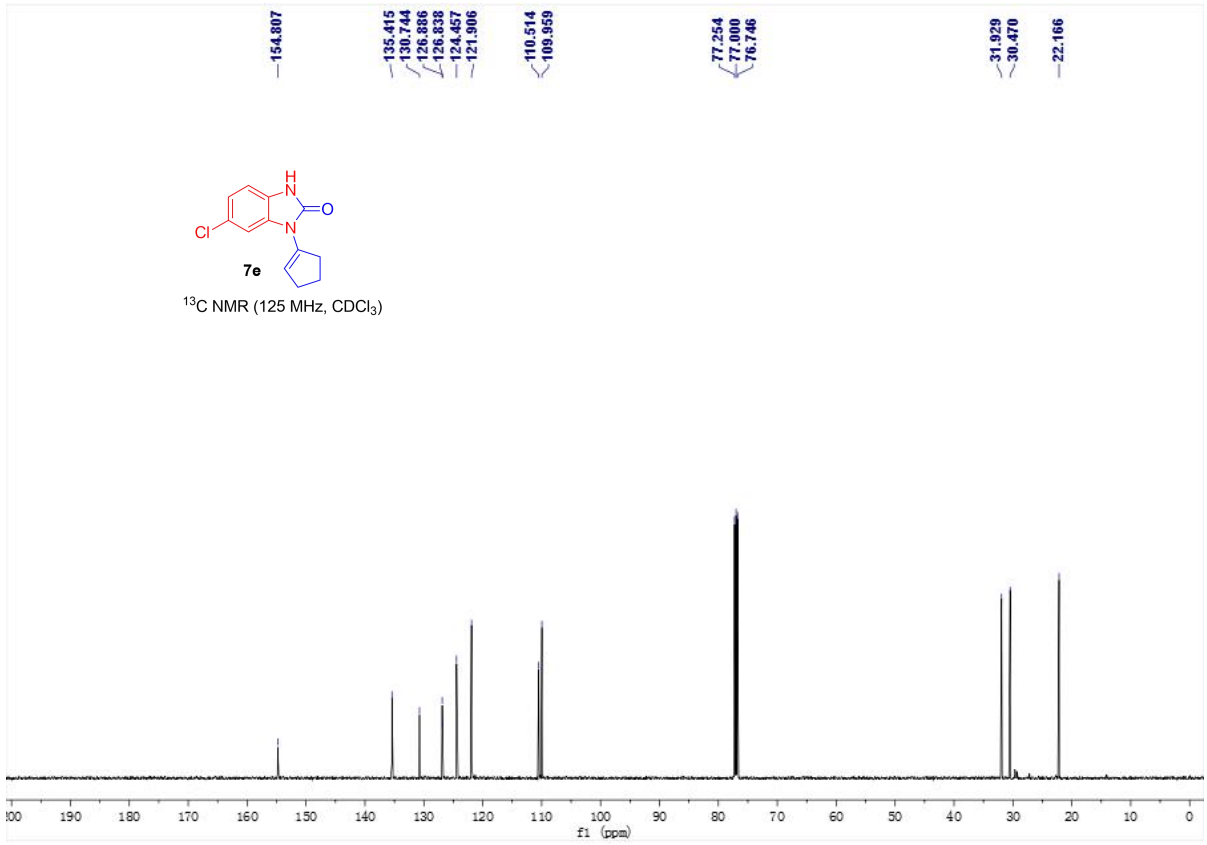


^{13}C NMR (125 MHz, $CDCl_3$)



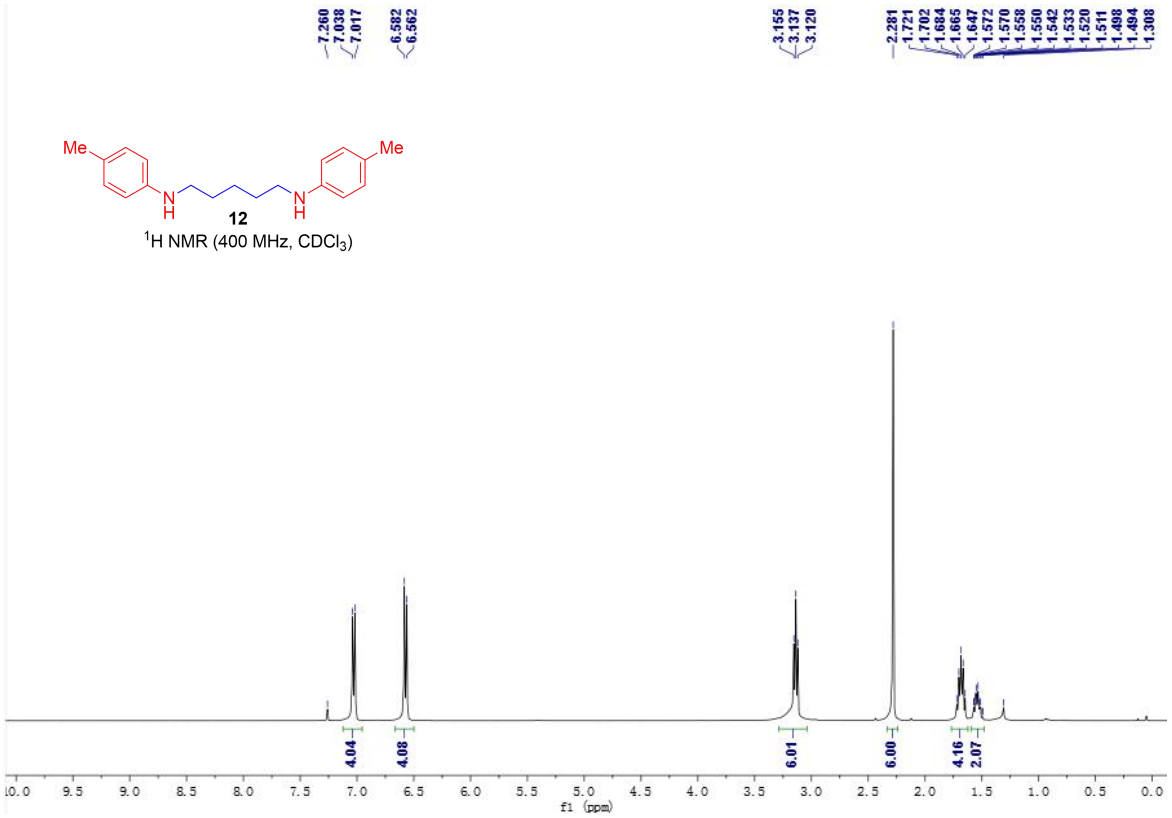
7e

^{1}H NMR (400 MHz, $CDCl_3$)

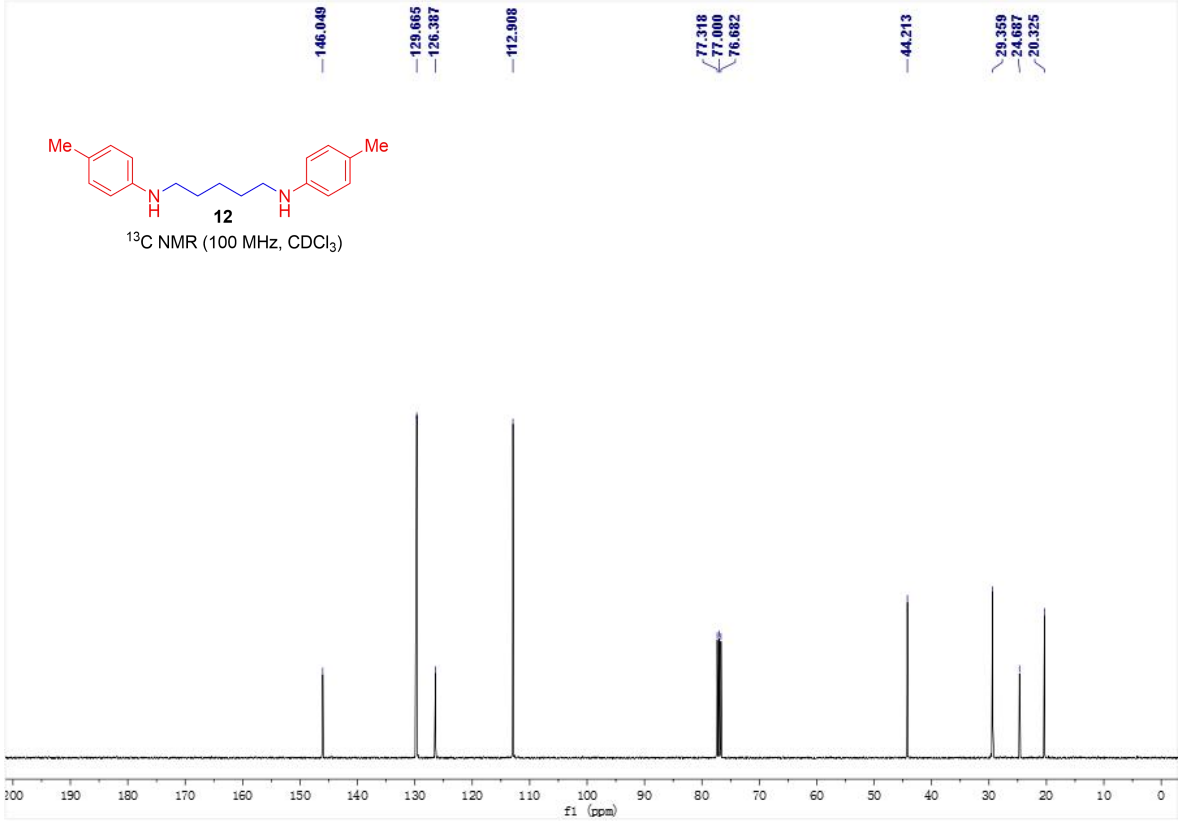


7e

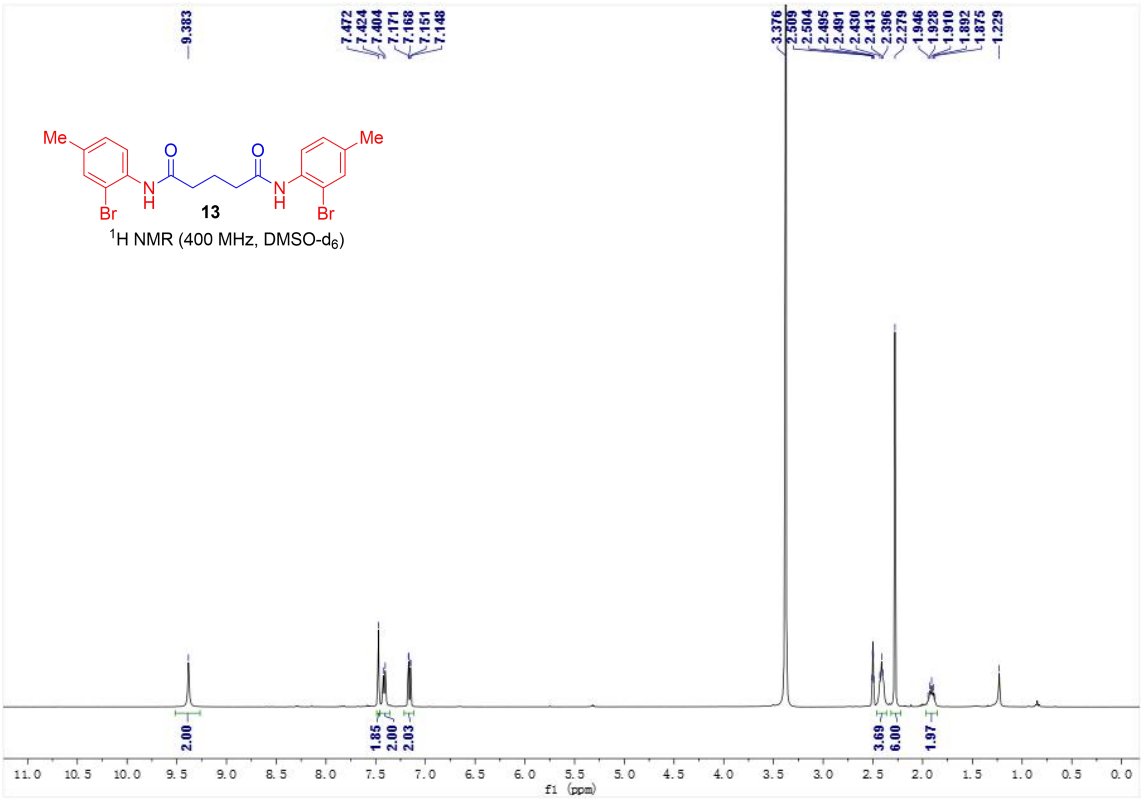
^{13}C NMR (125 MHz, $CDCl_3$)



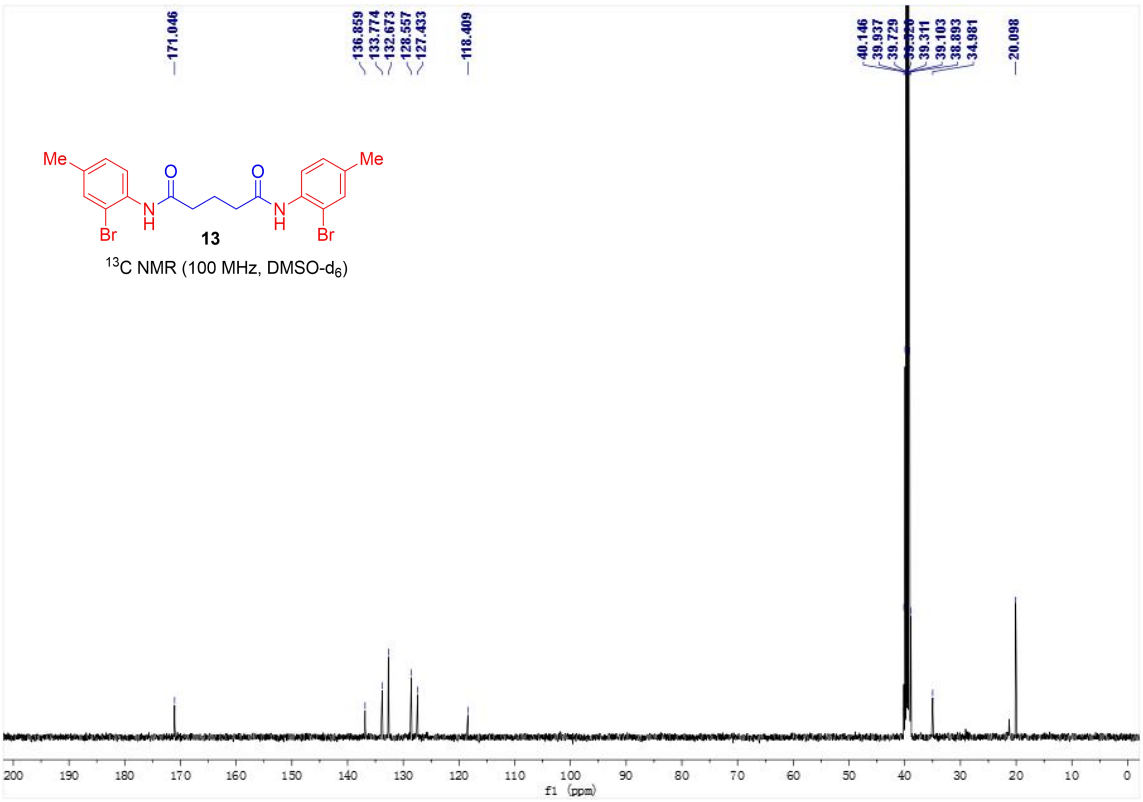
^{1}H NMR (400 MHz, $CDCl_3$)



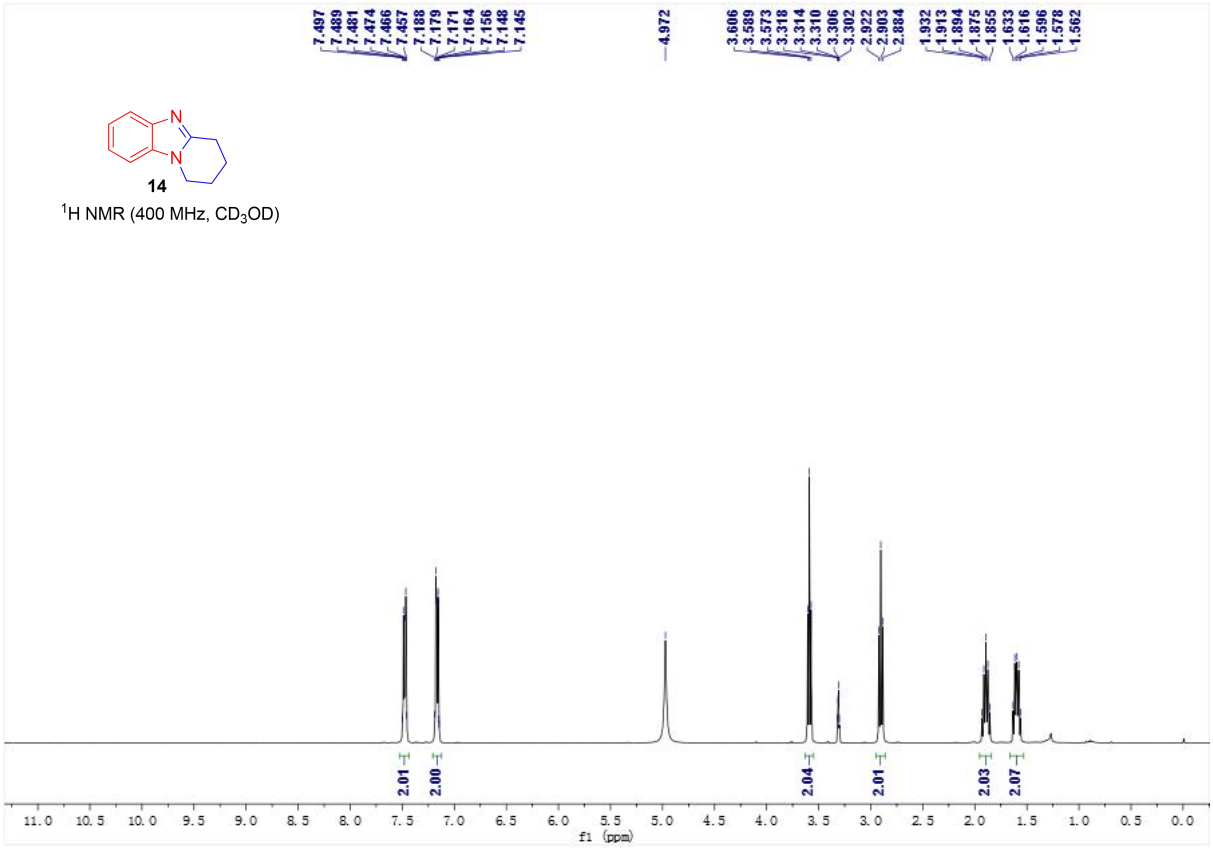
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, DMSO-d_6)

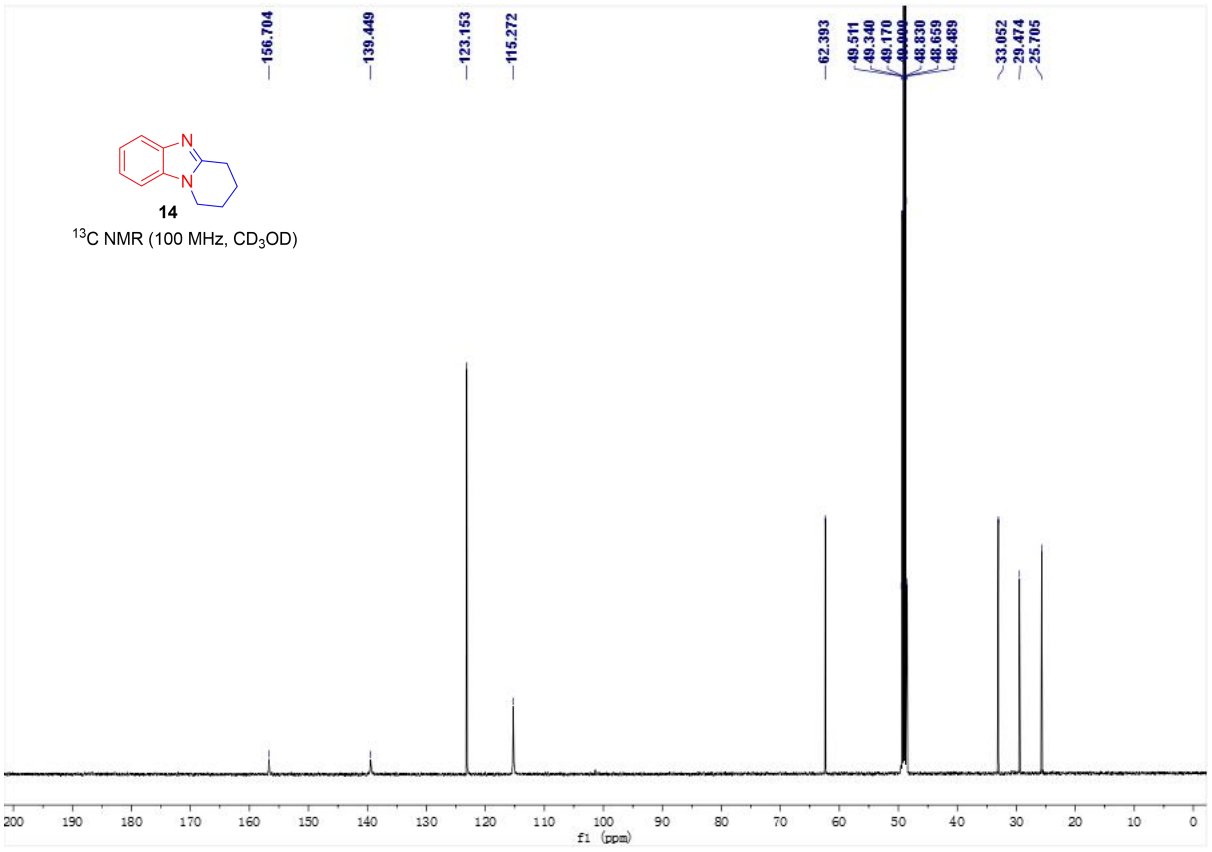


^{13}C NMR (100 MHz, DMSO-d_6)



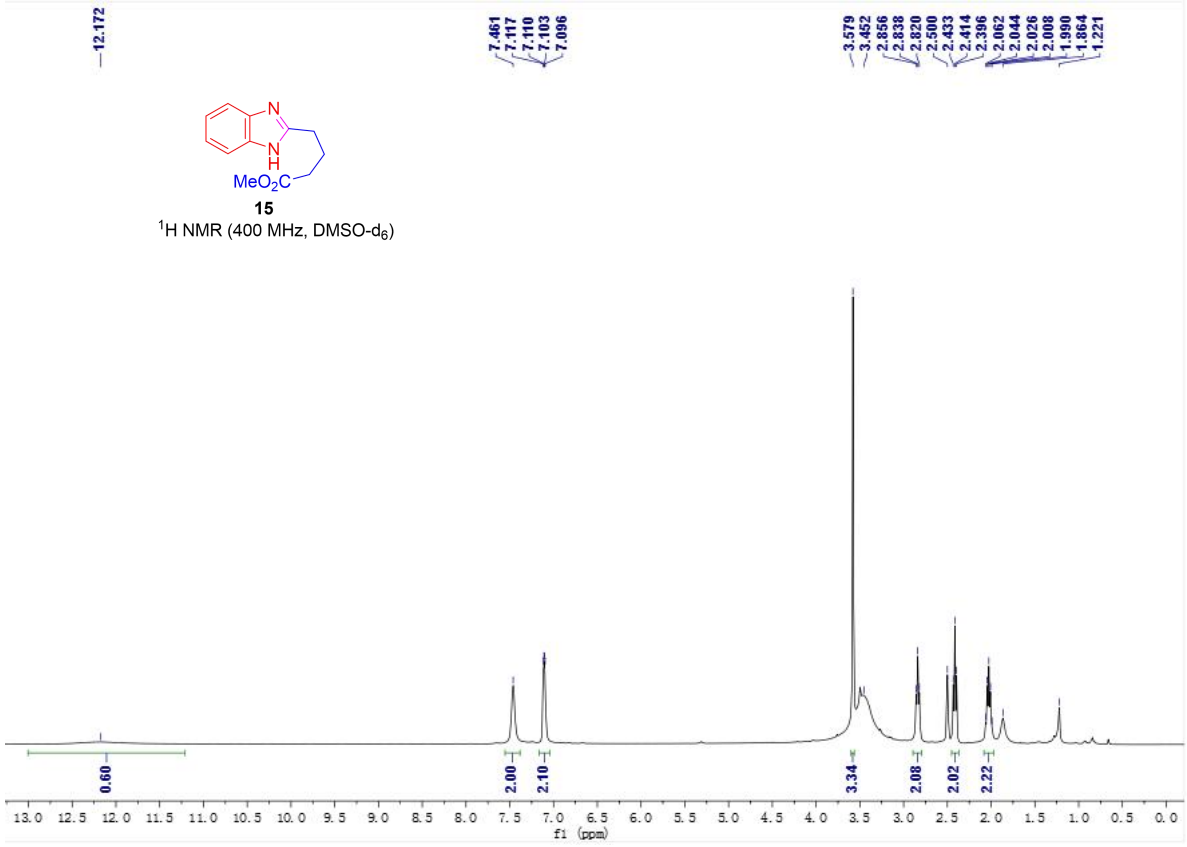
14

^{1}H NMR (400 MHz, CD_3OD)



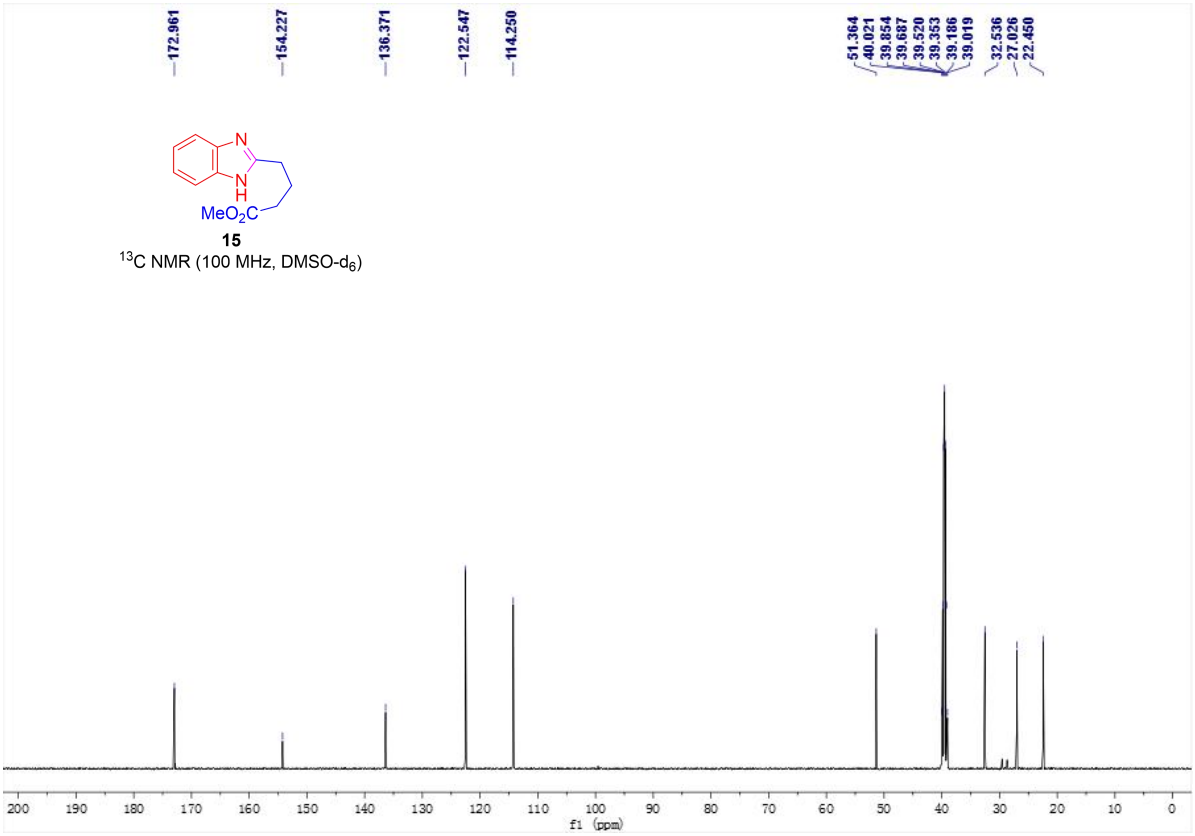
14

^{13}C NMR (100 MHz, CD_3OD)



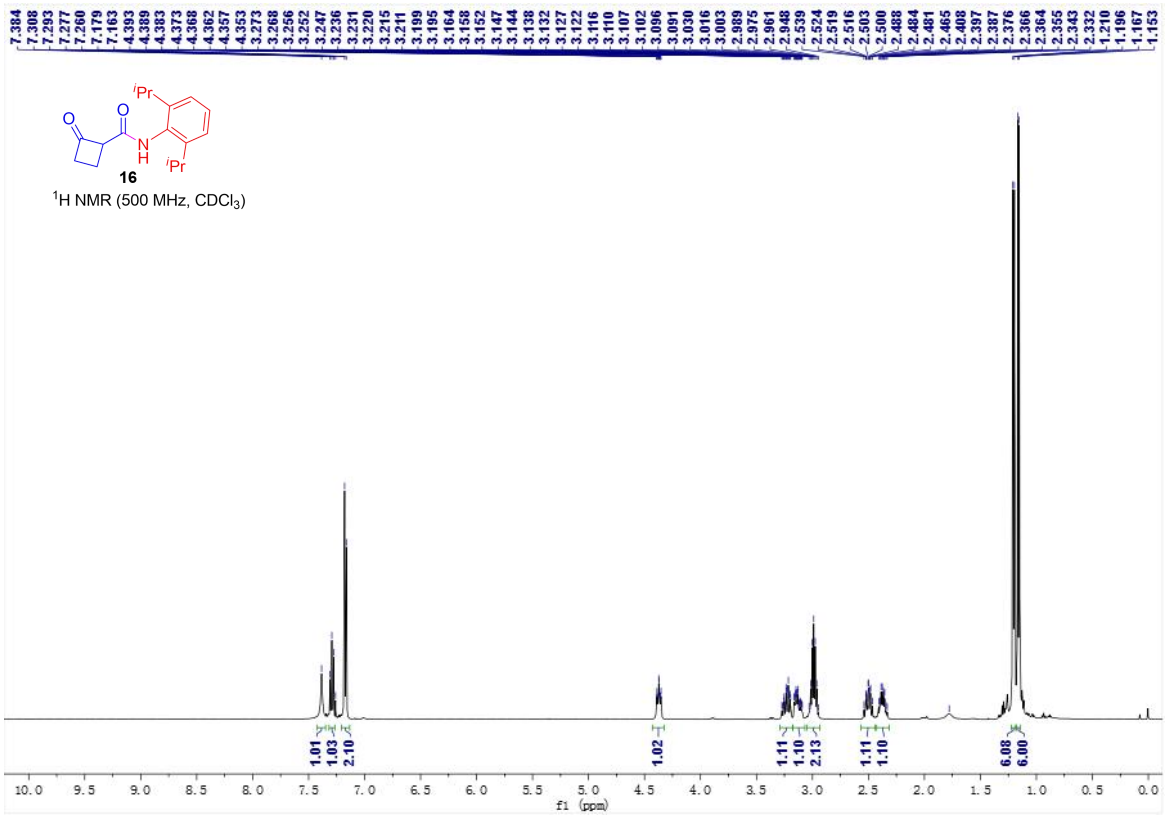
15

^{1}H NMR (400 MHz, DMSO-d_6)

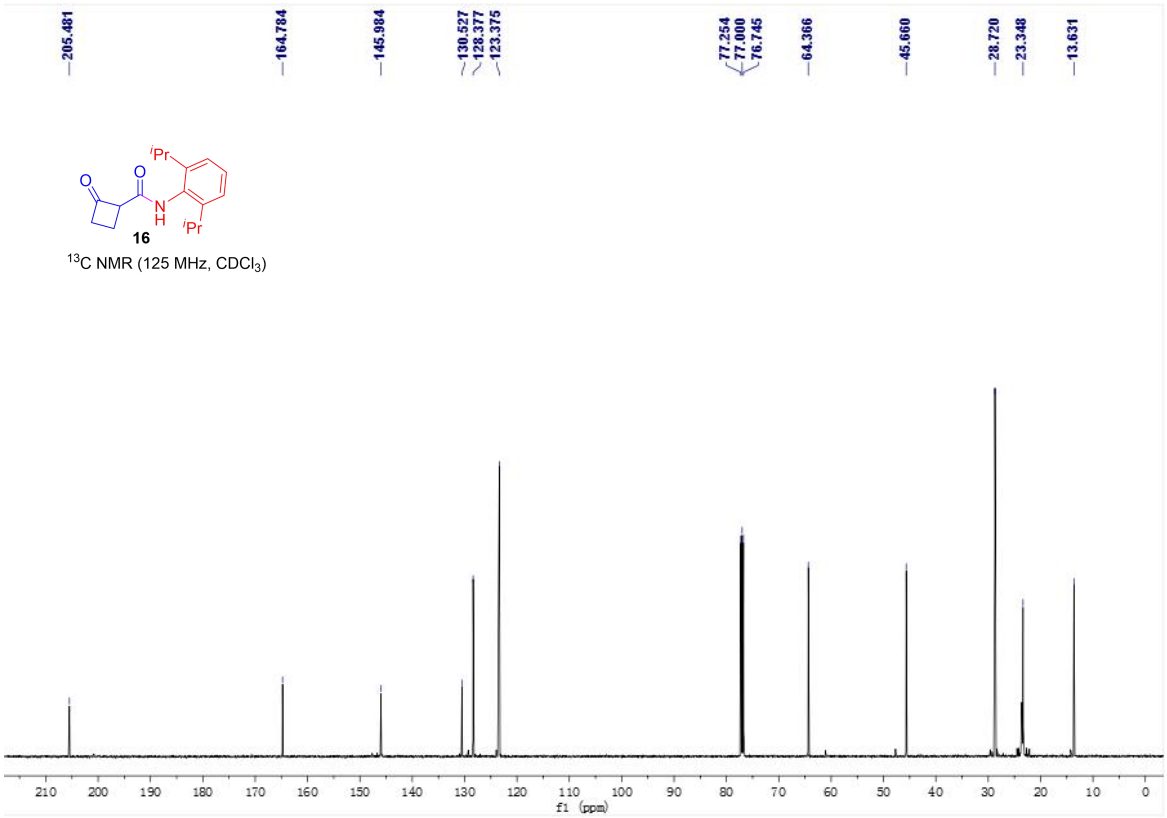


15

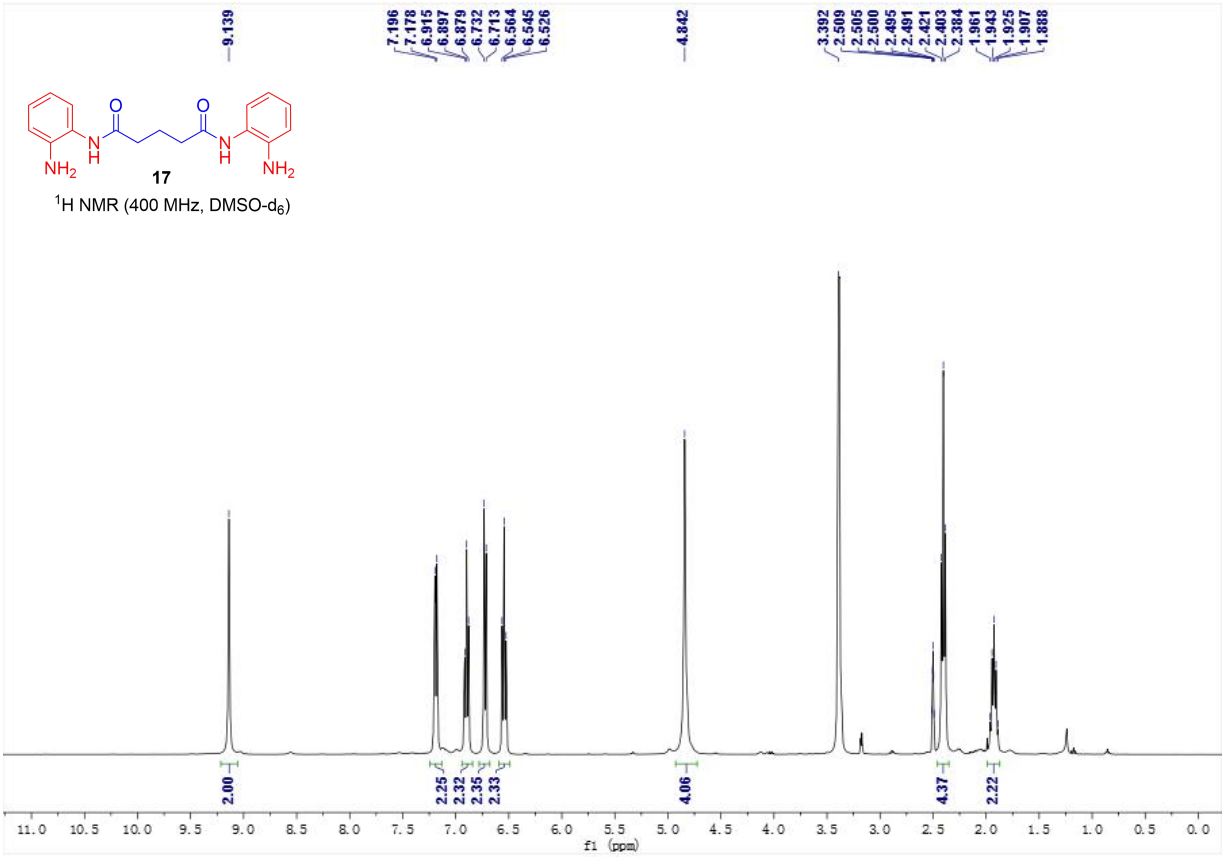
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (500 MHz, $CDCl_3$)

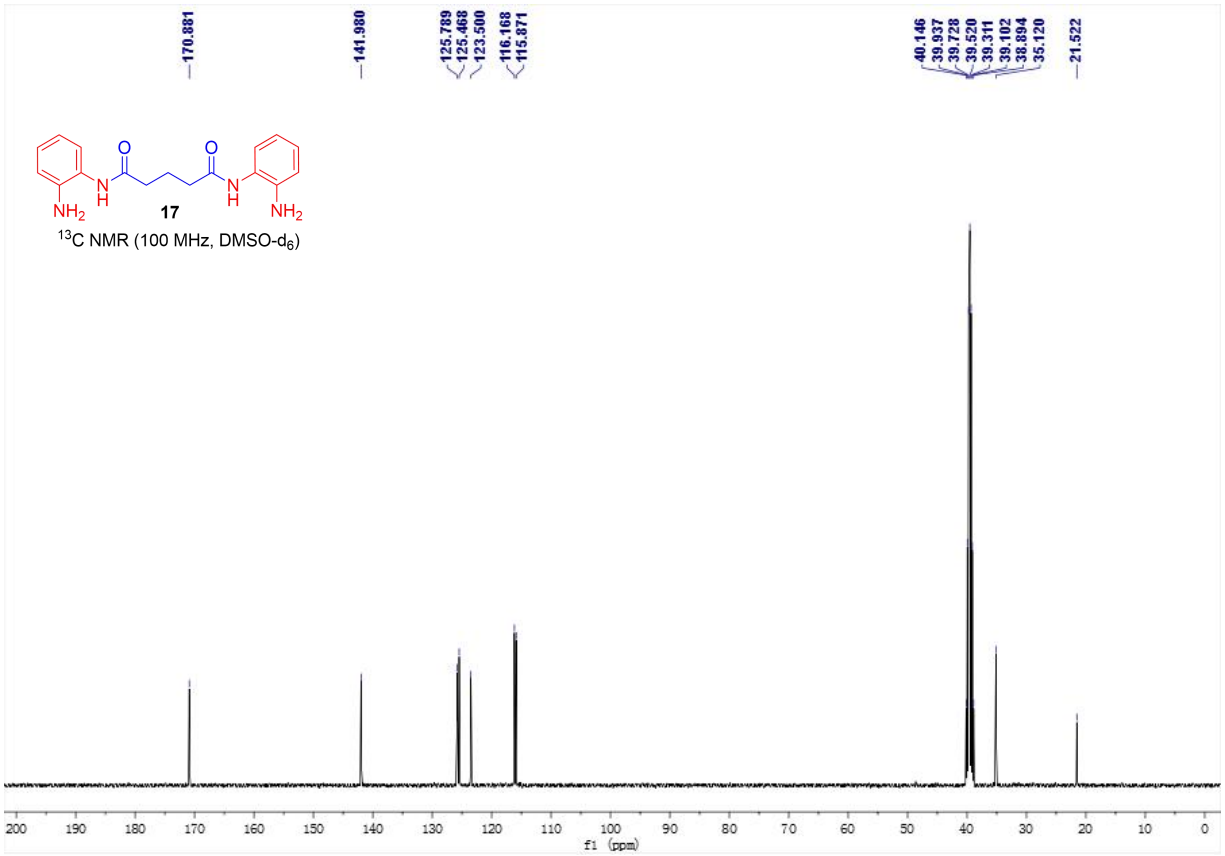


^{13}C NMR (125 MHz, $CDCl_3$)



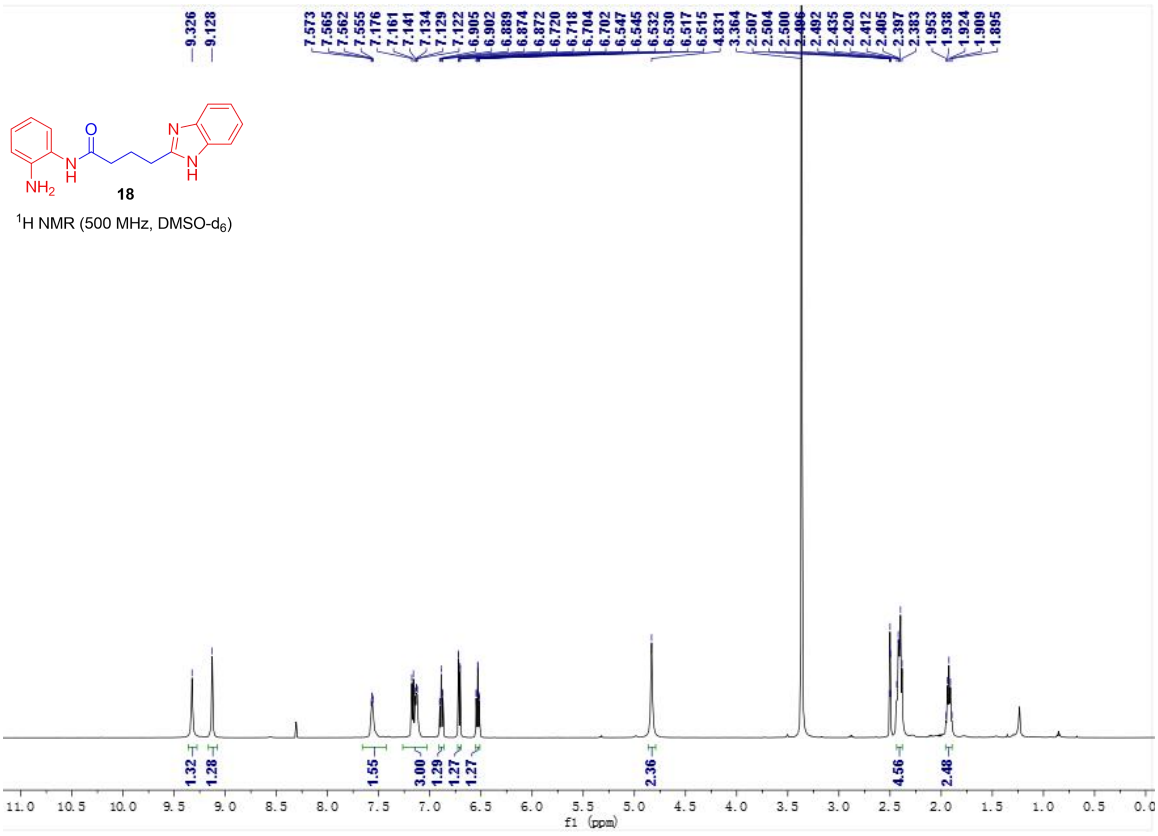
17

^{1}H NMR (400 MHz, DMSO-d_6)



17

^{13}C NMR (100 MHz, DMSO-d_6)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7.565
7.562
7.555
7.176
7.161
7.141
7.134
7.129
7.122
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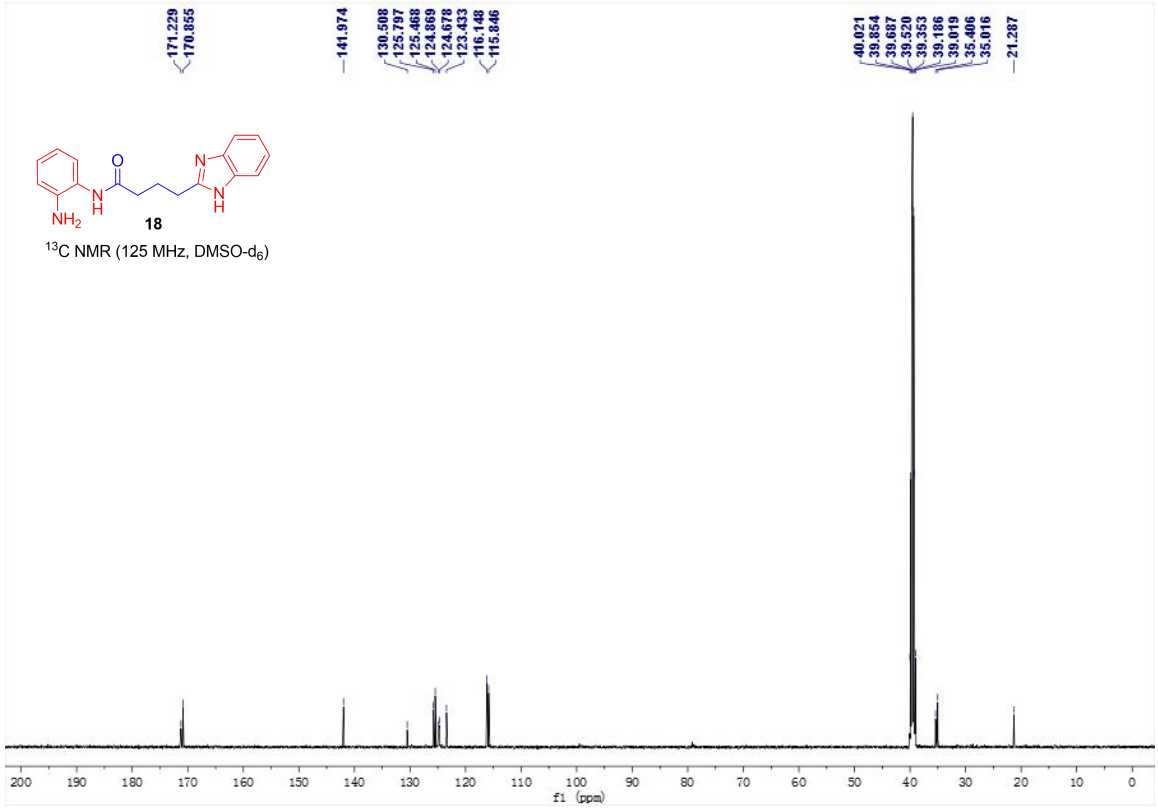
6.902
6.889
6.874
6.872
6.720
6.718
6.704
6.702
6.547
6.545
6.532
6.530
6.517
6.515
4.831
3.364
2.507
2.504
2.500
2.492
2.435
2.420
2.412
2.405
2.397
2.383
1.953
1.938
1.924
1.909
1.895
NH2
N
H
O
N
H
18
1H NMR (500 MHz, DMSO-d6)
1.32
1.28
1.55
3.00
1.29
1.27
1.27
2.36
4.56
2.48
f1 (ppm)


171.229
170.855
141.974
130.508
125.797
125.468
124.869
124.678
123.433
116.148
115.846
40.021
39.854
39.687
39.520
39.353
39.186
39.019
35.406
35.016
21.287
NH2
N
H
O
N
H
18
13C NMR (125 MHz, DMSO-d6)
f1 (ppm)