

Persulfate promoted carbamoylation of *N*-arylacrylamides and *N*-arylcinnamamides with 4-carbamoyl-Hantzsch esters

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1. General methods

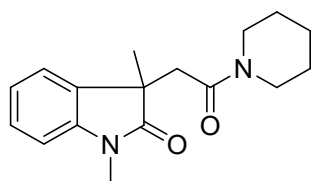
Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD 400 instrument. HRMS (ESI) determinations were carried out on a Bruker Daltonics MicrOTOF II spectrometer. Melting points were determined on a Shanghai Shengguang WRS-3 melting point instrument. The 4-carbamoyl-Hantzsch esters and N-arylacrylamides were prepared according to the published procedures¹⁻⁶.

2. General procedure for the carbamoylation

4-Carbamoyl Hantzsch ester **1** (0.24 mmol), N-arylacrylamides **2** or N-arylcinnamamides **4** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol), and $\text{CH}_3\text{CN-H}_2\text{O}$ (2 mL, v/v, 1:1) were added to a 10 mL Schlenk tube under N_2 . The mixture was heated at 50 °C for 12 h and then cooled to room temperature. After the reaction was completed, the mixture was concentrated under reduced pressure, the resulting mixture was dissolved with ethyl acetate (5 mL) and washed with H_2O (3 x 5 mL). The organic phase was concentrated under vacuum, the residue was purified by column chromatography on silica gel to give the corresponding products **3** or **5**.

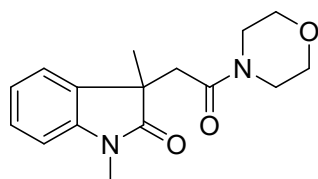
3. Characteristic data of compounds

1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3a**)⁷



Yield (88%), white solid, mp 140.5-141.3 °C, PE/EA = 3/1 to EA as the eluent; ^1H NMR (400 MHz, CDCl_3) δ : 7.25-7.19 (m, 1H), 7.17-7.11 (m, 1H), 7.02-6.96 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.38-3.28 (m, 4H), 3.26 (s, 3H), 2.99 (d, J = 16.0 Hz, 1H), 2.94 (d, J = 16.0 Hz, 1H), 1.61-1.47 (m, 4H), 1.46-1.35 (m, 2H), 1.34 (s, 3H).

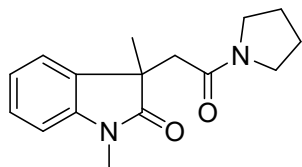
1,3-dimethyl-3-(2-morpholino-2-oxoethyl)indolin-2-one (**3b**)⁷



Yield (82%), white solid, mp 180.9-181.2 °C, PE/EA = 3/1 to EA as the eluent; ^1H NMR (400

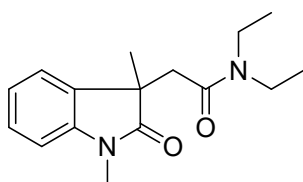
MHz, CDCl₃) δ : 7.27-7.22 (m, 1H), 7.17-7.13 (m, 1H), 7.04-6.98 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 3.66-3.48 (m, 4H), 3.48-3.28 (m, 4H), 3.26 (s, 3H), 3.00 (d, J = 16.0 Hz, 1H), 2.92 (d, J = 16.0 Hz, 1H), 1.36 (s, 3H).

1,3-dimethyl-3-(2-oxo-2-(pyrrolidin-1-yl)ethyl)indolin-2-one (**3c**)



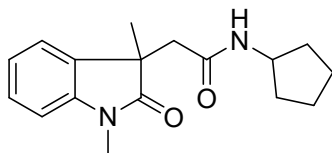
Yield (80%), viscous liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.25-7.19 (m, 1H), 7.18-7.15 (m, 1H), 7.01-6.94 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.37-3.27 (m, 3H), 3.25 (s, 3H), 3.23-3.17 (m, 1H), 2.91 (d, J = 16.0 Hz, 1H), 2.84 (d, J = 16.0 Hz, 1H), 1.89-1.82 (m, 2H), 1.78-1.70 (m, 2H), 1.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 180.8, 167.4, 143.8, 134.1, 127.6, 121.9, 121.7, 108.0, 46.5, 45.6, 45.4, 41.9, 26.3, 26.0, 24.5, 24.2; HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₆H₂₁N₂O₂ 273.1598; found 273.1598.

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N,N-diethylacetamide (**3d**)⁷



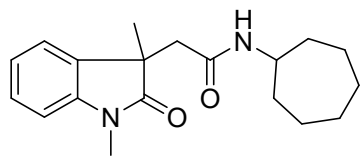
Yield (75%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.25-7.18 (m, 1H), 7.17-7.11 (m, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.30-3.21 (m, 5H), 3.21-3.11 (m, 2H), 2.96 (d, J = 16.0 Hz, 1H), 2.91 (d, J = 16.0 Hz, 1H), 1.36 (s, 3H), 1.14 (t, J = 8.0 Hz, 3H), 0.90 (t, J = 8.0 Hz, 3H).

N-cyclopentyl-2-(1,3-dimethyl-2-oxoindolin-3-yl)acetamide (**3e**)⁷



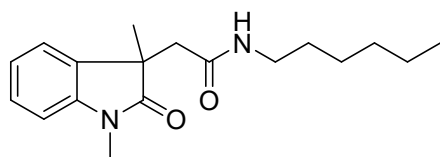
Yield (88%), yellow solid, 118.6-119.2 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.32-7.24 (m, 2H), 7.08 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.33 (s, 1H), 4.11-3.98 (m, 1H), 3.24 (s, 3H), 2.75 (d, J = 16.0 Hz, 1H), 2.62 (d, J = 16.0 Hz, 1H), 1.92-1.74 (m, 2H), 1.68-1.46 (m, 4H), 1.43 (s, 3H), 1.33-1.17 (m, 2H).

N-cycloheptyl-2-(1,3-dimethyl-2-oxoindolin-3-yl)acetamide (**3f**)⁷



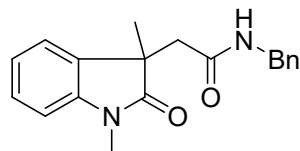
Yield (70%), yellow liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.28-7.22 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 3.83-3.71 (m, 1H), 3.22 (s, 3H), 2.73 (d, *J* = 16.0 Hz, 1H), 2.59 (d, *J* = 16.0 Hz, 1H), 1.78-1.64 (m, 2H), 1.59-1.45 (m, 6H), 1.43-1.38 (m, 4H), 1.33-1.21 (m, 3H).

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-hexylacetamide (**3g**)⁷



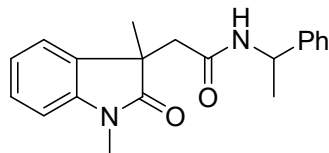
Yield (85%), yellow liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.30-7.22 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 3.23 (s, 3H), 3.13-3.03 (m, 2H), 2.77 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* = 16.0 Hz, 1H), 1.41 (s, 3H), 1.38-1.29 (m, 2H), 1.28-1.16 (m, 6H), 0.85 (t, *J* = 8.0 Hz, 3H).

N-benzyl-2-(1,3-dimethyl-2-oxoindolin-3-yl)acetamide (**3h**)⁸



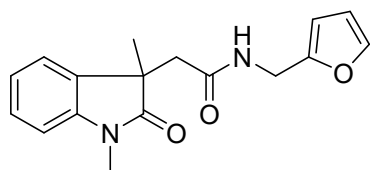
Yield (70%), yellow liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.31-7.19 (m, 5H), 7.10-6.99 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.60-6.50 (m, 1H), 4.34-4.14 (m, 2H), 3.09 (s, 3H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.68 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H).

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-(1-phenylethyl)acetamide (**3i**)⁷



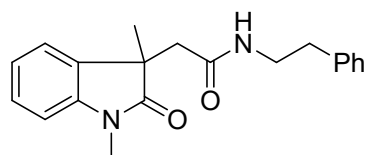
Yield (41%), yellow solid, mp 171.7-172.5 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.33-7.23 (m, 5H), 7.21-7.15 (m, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.03-4.89 (m, 1H), 3.24 (s, 3H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.65 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H), 1.34 (d, *J* = 8.0 Hz, 3H).

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-(furan-2-ylmethyl)acetamide (**3j**)



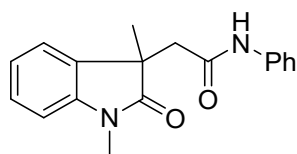
Yield (50%), white solid, mp 100.7-101.1 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.32-7.28 (m, 1H), 7.28-7.22 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.29-6.23 (m, 1H), 6.12-6.04 (m, 1H), 4.38-4.20 (m, 2H), 3.18 (s, 3H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.68 (d, *J* = 16.0 Hz, 1H), 1.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 180.5, 168.7, 151.3, 142.8, 141.9, 133.1, 128.1, 122.3, 110.3, 108.3, 107.1, 46.1, 43.6, 36.3, 26.3, 23.5; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₇H₁₉N₂O₃ 299.1390; found 299.1387.

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-phenethylacetamide (**3k**)⁷



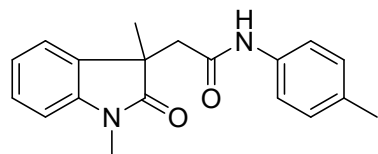
Yield (83%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.30-7.24 (m, 4H), 7.21-7.16 (m, 1H), 7.14-7.09 (m, 2H), 7.09-7.03 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.26 (s, 1H), 3.44-3.27 (m, 2H), 3.21 (s, 3H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.61 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H).

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-phenylacetamide (**3l**)⁸



Yield (75%), white solid, mp 98.2-99.1 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 8.87 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.15-7.03 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.26 (s, 3H), 2.91 (d, *J* = 16.0 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 1.51 (s, 3H).

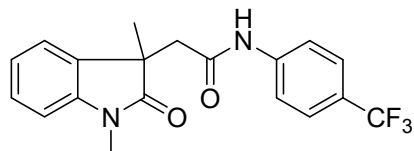
2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-(p-tolyl)acetamide (**3m**)⁸



Yield (76%), yellow solid, mp 111.8-112.5 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400

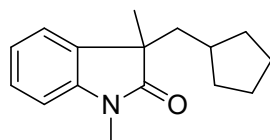
MHz, CDCl₃) δ : 8.73 (s, 1H), 7.37-7.27 (m, 4H), 7.13-7.05 (m, 3H), 6.86 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H), 2.90 (d, J = 16.0 Hz, 1H), 2.82 (d, J = 16.0 Hz, 1H), 2.29 (s, 3H), 1.50 (s, 3H).

2-(1,3-dimethyl-2-oxoindolin-3-yl)-N-(4-(trifluoromethyl)phenyl)acetamide (**3n**)⁸



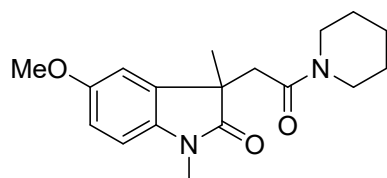
Yield (51%), white solid, mp 72.1-72.9 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 9.52 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.34-7.26 (m, 2H), 7.12 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 3.27 (s, 3H), 2.95 (d, J = 16.0 Hz, 1H), 2.89 (d, J = 16.0 Hz, 1H), 1.50 (s, 3H).

3-(cyclopentylmethyl)-1,3-dimethylindolin-2-one (**3o**)⁹



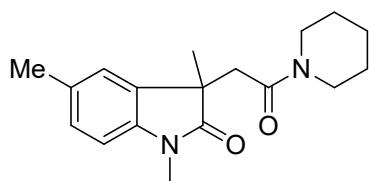
Yield (81%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.29-7.22 (m, 1H), 7.18-7.14 (m, 1H), 7.08-7.02 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H), 2.11-2.00 (m, 1H), 1.92-1.82 (m, 1H), 1.51-1.18 (m, 10H), 1.06-0.94 (m, 1H), 0.89-0.75 (m, 1H).

5-methoxy-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3p**)



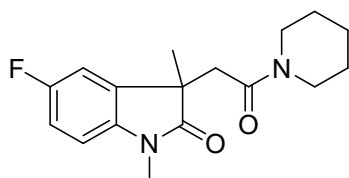
Yield (71%), yellow solid, mp 134.5-135.2 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 6.78-7.76 (m, 1H), 6.74-6.72 (m, 2H), 3.76 (s, 3H), 3.36-3.30 (m, 4H), 3.23 (s, 3H), 2.98 (d, J = 16.0 Hz, 1H), 2.90 (d, J = 16.0 Hz, 1H), 1.59-1.47 (m, 4H), 1.43-1.33 (m, 2H), 1.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 180.5, 166.9, 155.5, 137.4, 135.9, 110.9, 109.9, 108.0, 55.6, 46.5, 46.0, 42.5, 40.5, 26.4, 26.2, 25.3, 25.0, 24.3; HRMS (ESI) calcd for C₁₈H₂₅N₂O₃⁺: [M+H]⁺ 317.1860, found: 317.1860.

1,3,5-trimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3q**)⁷



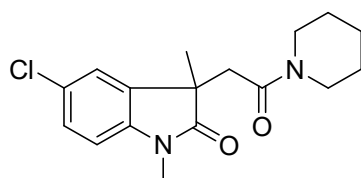
Yield (81%), white solid, mp 112.3-112.8 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.02 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.42-3.26 (m, 4H), 3.23 (s, 3H), 2.97 (d, *J* = 16.0 Hz, 1H), 2.91 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H), 1.60-1.46 (m, 4H), 1.45-1.34 (m, 2H), 1.33 (s, 3H).

5-fluoro-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3r**)⁷



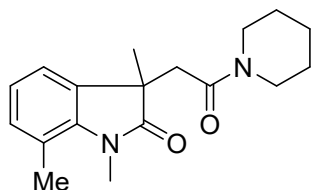
Yield (70%), yellow solid, mp 115.4-116.2 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 6.95-6.87 (m, 2H), 6.78-6.72 (m, 1H), 3.40-3.28 (m, 4H), 3.25 (s, 3H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 1.62-1.48 (m, 4H), 1.48-1.34 (m, 2H), 1.33 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ: -121.7.

5-chloro-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3s**)⁷



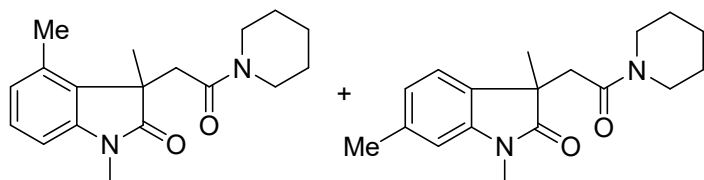
Yield (86%), white solid, mp 131.5-132.2 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.22-7.16 (m, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.41-3.28 (m, 4H), 3.24 (s, 3H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 1.64-1.48 (m, 4H), 1.46-1.34 (m, 2H), 1.32 (s, 3H).

1,3,7-trimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3u**)⁷



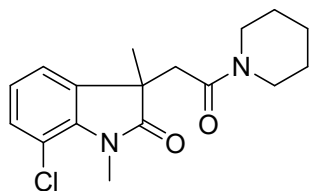
Yield (75%), colorless liquid, PE/EA = 3/1 to EA as the eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 6.96-6.91 (m, 2H), 6.89-6.83 (m, 1H), 3.54 (s, 3H), 3.40-3.28 (m, 4H), 3.00 (d, $J = 16.0$ Hz, 1H), 2.93 (d, $J = 16.0$ Hz, 1H), 2.58 (s, 3H), 1.60-1.47 (m, 4H), 1.45-1.32 (m, 2H), 1.30 (s, 3H).

1,3,4-trimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one and 1,3,6-trimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3v** + **3v'**)⁷



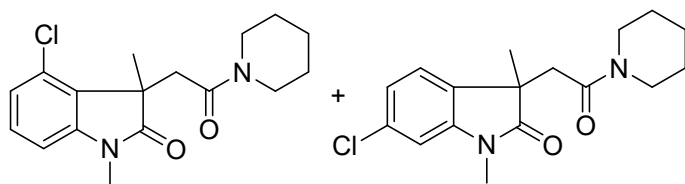
Yield (85%), colorless liquid, PE/EA = 3/1 to EA as the eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.13 (t, $J = 8.0$ Hz, 0.66H), 7.02 (d, $J = 7.6$ Hz, 0.34H), 6.80 (d, $J = 7.6$ Hz, 0.34H), 6.75 (d, $J = 7.6$ Hz, 0.67H), 6.72-6.65 (m, 1H), 3.42-3.27 (m, 4H), 3.24 (s, 3H), 3.20 (d, $J = 16.8$ Hz, 0.65H), 3.06 (d, $J = 16.8$ Hz, 0.65H), 2.98 (d, $J = 16.4$ Hz, 0.35H), 2.92 (d, $J = 16.4$ Hz, 0.35H), 2.35 (s, 1H), 2.33 (s, 2H), 1.61-1.46 (m, 4H), 1.43-1.30 (m, 5H).

7-chloro-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3w**)⁷



Yield (51%), viscous liquid, PE/EA = 3/1 to EA as the eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.14-7.08 (m, 1H), 6.98-6.94 (m, 1H), 6.87 (t, $J = 8.0$ Hz, 1H), 3.62 (s, 3H), 3.39-3.27 (m, 4H), 3.04 (d, $J = 16.4$ Hz, 1H), 2.93 (d, $J = 16.4$ Hz, 1H), 1.59-1.47 (m, 4H), 1.45-1.31 (m, 2H), 1.29 (s, 3H).

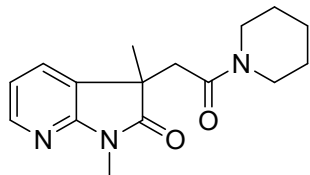
4-chloro-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one and 6-chloro-1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3x**+**3x'**)⁷



Yield (70%), colorless liquid, PE/EA = 3/1 to EA as the eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.15 (t, $J = 7.6$ Hz, 0.81H), 7.03 (d, $J = 8.0$ Hz, 0.19H), 6.96-6.02 (m, 0.19H), 6.91-6.85 (m, 0.80H), 6.82 (d, $J = 2.0$ Hz, 0.19H), 6.76-6.71 (m, 0.81H), 3.62 (d, $J = 16.4$ Hz, 0.83H), 3.48-3.29

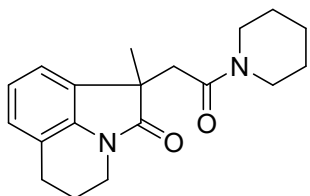
(m, 3H), 3.27-3.18 (m, 4H), 3.00 (d, $J = 16.4$ Hz, 0.22H), 2.98 (d, $J = 16.4$ Hz, 0.83H), 2.93 (d, $J = 16.4$ Hz, 0.22H), 1.61-1.48 (m, 4H), 1.46-1.28 (m, 5H).

1,3-dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (**3y**)⁷



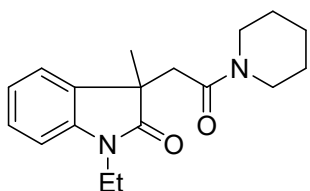
Yield (75%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 8.15-8.11 (m, 1H), 7.42-7.38 (m, 1H), 6.89-6.85 (m, 1H), 3.37-3.30 (m, 7H), 3.00 (d, $J = 16.4$ Hz, 1H), 2.94 (d, $J = 16.4$ Hz, 1H), 1.60-1.47 (m, 4H), 1.46-1.37 (m, 2H), 1.36 (s, 3H).

1-methyl-1-(2-oxo-2-(piperidin-1-yl)ethyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (**3z**)



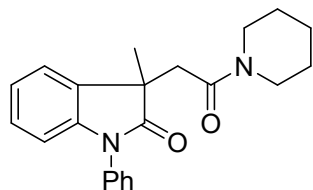
Yield (88%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.05-6.94 (m, 2H), 6.91-6.84 (m, 1H), 3.80-3.71 (m, 2H), 3.40-3.30 (m, 4H), 2.94 (s, 2H), 2.87-2.69 (m, 2H), 2.12-1.92 (m, 2H), 1.60-1.50 (m, 4H), 1.49-1.39 (m, 2H), 1.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 179.7, 167.2, 139.5, 132.8, 126.5, 121.4, 119.8, 119.7, 47.0, 46.6, 42.5, 40.2, 38.8, 26.3, 25.4, 24.6, 24.3, 21.2; HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₉H₂₅N₂O₂ 313.1911; found 313.1910.

1-ethyl-3-methyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3ab**)⁷



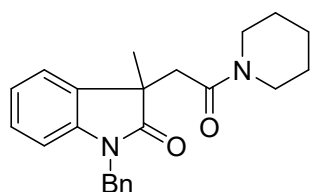
Yield (82%), colorless liquid, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ : 7.24-7.12 (m, 2H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.6$ Hz, 1H), 3.90-3.70 (m, 2H), 3.42-3.23 (m, 4H), 2.95 (s, 2H), 1.59-1.45 (m, 4H), 1.45-1.35 (m, 2H), 1.34 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H).

3-methyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)-1-phenylindolin-2-one (**3ac**)⁷



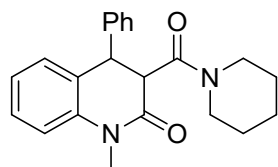
Yield (79%), white solid, mp 88.9-89.5 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.57-7.45 (m, 4H), 7.42-7.33 (m, 1H), 7.22-7.11 (m, 2H), 7.06-6.98 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 3.44-3.31 (m, 4H), 3.12 (d, *J* = 16.4 Hz, 1H), 3.05 (d, *J* = 16.0 Hz, 1H), 1.62-1.50 (m, 4H), 1.48-1.36 (m, 5H).

1-benzyl-3-methyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (**3ad**)⁷



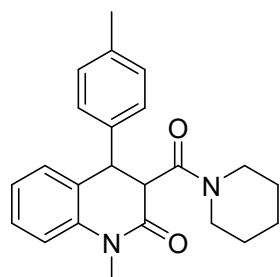
Yield (72%), white solid, mp 133.1-133.8 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.39-7.34 (m, 2H), 7.33-7.28 (m, 2H), 7.25-7.20 (m, 1H), 7.19-7.16 (m, 1H), 7.13-7.08 (m, 1H), 7.00-6.94 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 16.0 Hz, 1H), 4.85 (d, *J* = 16.0 Hz, 1H), 3.41-3.34 (m, 4H), 3.09 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 1.62-1.53 (m, 2H), 1.51-1.44 (m, 4H), 1.43 (s, 3H).

1-methyl-4-phenyl-3-(piperidine-1-carbonyl)-3,4-dihydroquinolin-2(1*H*)-one (**5a**)



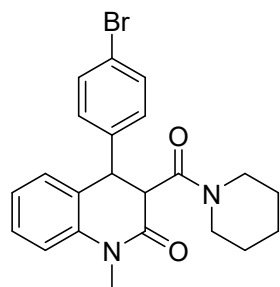
Yield (56%), white solid, mp 196.9-197.3 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.36-7.29 (m, 2H), 7.29-7.20 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.20 (d, *J* = 10.8 Hz, 1H), 3.69-3.57 (m, 1H), 3.48-3.31 (m, 5H), 3.30-3.21 (m, 1H), 1.64-1.44 (m, 4H), 1.22-1.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 166.7, 166.3, 140.2, 139.4, 128.7, 128.6, 128.2, 127.7, 127.2, 123.1, 114.5, 50.7, 47.3, 45.1, 43.2, 29.9, 26.3, 25.4, 24.4; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₅N₂O₂ 349.1911; found 313.1911.

1-methyl-3-(piperidine-1-carbonyl)-4-(p-tolyl)-3,4-dihydroquinolin-2(1H)-one (**5b**)



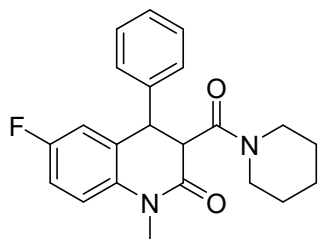
Yield (48%), yellow solid, mp 163.8-164.9 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.28-7.24 (m, 1H), 7.16-7.08 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 3.69-3.57 (m, 1H), 3.48-3.38 (m, 5H), 3.35-3.27 (m, 1H), 2.33 (s, 3H), 1.60-1.52 (m, 4H), 1.28-1.21 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 166.8, 166.4, 139.4, 137.1, 136.8, 129.4, 128.5, 128.4, 128.3, 127.6, 123.1, 114.4, 50.7, 47.3, 44.6, 43.2, 29.9, 26.2, 25.4, 24.4, 21.0; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₃H₂₇N₂O₂ 363.2067; found 363.2069.

4-(4-bromophenyl)-1-methyl-3-(piperidine-1-carbonyl)-3,4-dihydroquinolin-2(1H)-one (**5c**)



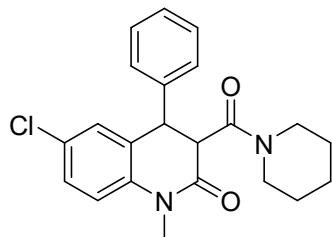
Yield (48%), yellow solid, mp 185.6-186.4 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.48-7.46 (m, 2H), 7.30-7.26 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.15 (d, *J* = 10.2 Hz, 1H), 3.62-3.54 (m, 1H), 3.48-3.31 (m, 5H), 3.30-3.21 (m, 1H), 1.64-1.50 (m, 4H), 1.26-1.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 166.4, 166.0, 139.4, 139.3, 131.8, 130.5, 128.0, 127.9, 127.8, 123.2, 121.1, 114.6, 50.5, 47.3, 44.4, 43.3, 30.0, 26.3, 25.5, 24.4; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₄BrN₂O₂ 427.1016; found 427.1011.

6-fluoro-1-methyl-4-phenyl-3-(piperidine-1-carbonyl)-3,4-dihydroquinolin-2(1H)-one (**5d**)



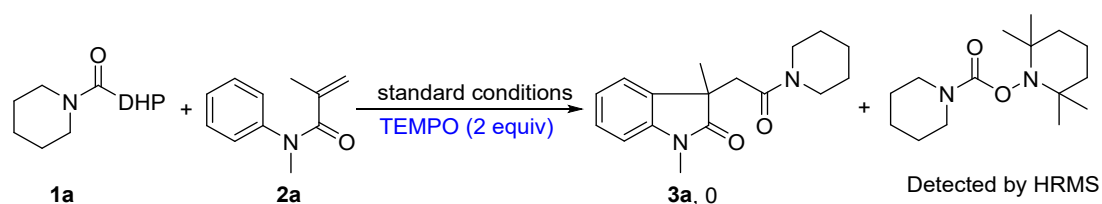
Yield (48%), yellow solid, mp 154.2-155.1 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.38-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.22-7.18 (m, 2H), 6.97-6.95 (m, 2H), 6.58-6.50 (m, 1H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.19 (d, *J* = 8.0 Hz, 1H), 3.69-3.61 (m, 1H), 3.48-3.40 (m, 5H), 3.34-3.26 (m, 1H), 1.56-1.50 (m, 4H), 1.22-1.14 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 166.3, 166.1, 158.8 (d, *J* = 242.0 Hz), 139.6, 135.7 (d, *J* = 2.0 Hz), 130.6 (d, *J* = 7.0 Hz), 128.9, 128.6, 127.5, 115.7 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 25.0 Hz), 114.0 (d, *J* = 22.0 Hz), 50.5, 47.4, 45.1, 43.3, 30.2, 26.2, 25.5, 24.4; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₄FN₂O₂ 367.1816; found 367.1819.

6-chloro-1-methyl-4-phenyl-3-(piperidine-1-carbonyl)-3,4-dihydroquinolin-2(1H)-one (**5e**)

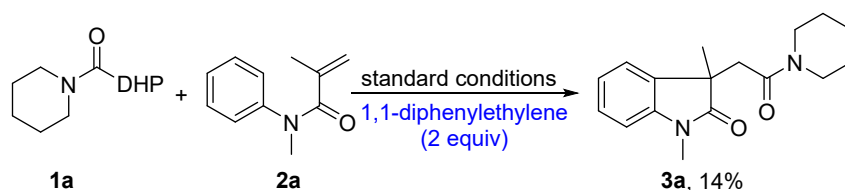
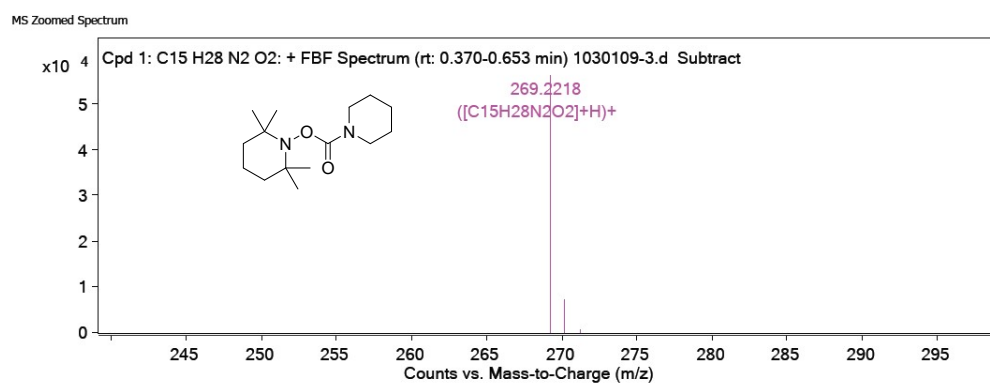


Yield (26%), white solid, mp 162.3-162.9 °C, PE/EA = 3/1 to EA as the eluent; ¹H NMR (400 MHz, CDCl₃) δ: 7.38-7.32 (m, 2H), 7.30-7.28 (m, 1H), 7.25-7.17 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.82-6.78 (m, 1H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 8.0 Hz, 1H), 3.69-3.57 (m, 1H), 3.48-3.41 (m, 5H), 3.34-3.26 (m, 1H), 1.55-1.47 (m, 4H), 1.22-1.12 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 166.3, 166.1, 139.6, 138.1, 130.0, 129.0, 128.6, 128.5, 128.3, 127.7, 127.6, 115.8, 50.6, 47.4, 45.1, 43.4, 30.0, 26.2, 25.5, 24.4; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₄ClN₂O₂ 383.1521; found 383.1517.

4. Mechanistic Investigations



1a (0.24 mmol), **2a** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol), TEMPO (0.4 mmol), and degassed $\text{CH}_3\text{CN-H}_2\text{O}$ (2 mL, 1:1, v/v) were added to a 10 mL Schlenk tube under N_2 . The mixture was heated at 50 °C for 12 h and then cooled to room temperature. After the reaction was completed, the reaction mixture was monitored by TLC, and no desired product was observed. Then the mixture was concentrated under reduced pressure, the resulting mixture was dissolved with ethyl acetate (5 mL) and washed with H_2O (3 x 5 mL). The organic phase was concentrated under vacuum, the residue was measured by HRMS. The HRMS below indicated the formation of carbamoyl-TEMPO adduct.



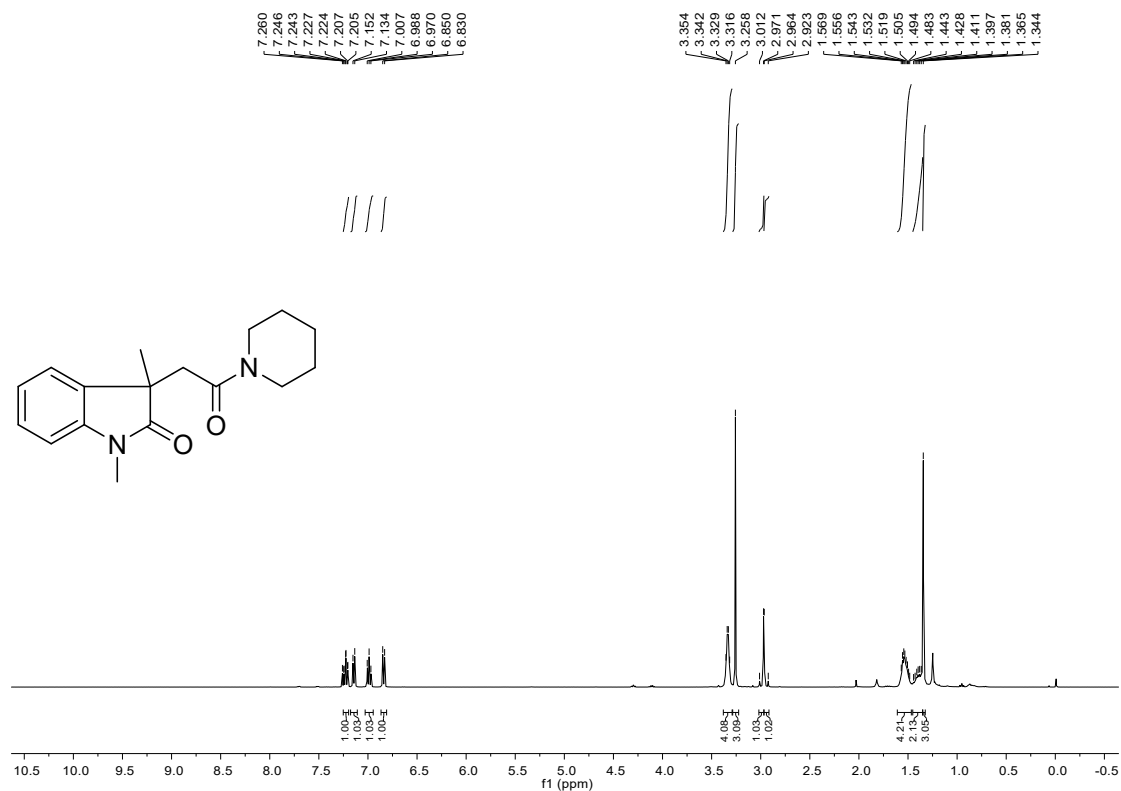
1a (0.24 mmol), **2a** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol), 1,1-diphenylethylene (0.4 mmol), and degassed $\text{CH}_3\text{CN-H}_2\text{O}$ (2 mL, 1:1, v/v) were added to a 10 mL Schlenk tube under N_2 . The mixture was heated at 50 °C for 12 h and then cooled to room temperature. After the reaction was completed, the mixture was concentrated under reduced pressure, the resulting mixture was dissolved with ethyl acetate (5 mL) and washed with H_2O (3 x 5 mL). The organic phase was concentrated under vacuum, the yield was determined by ^1H NMR with CH_2Br_2 as internal standard.

5. References

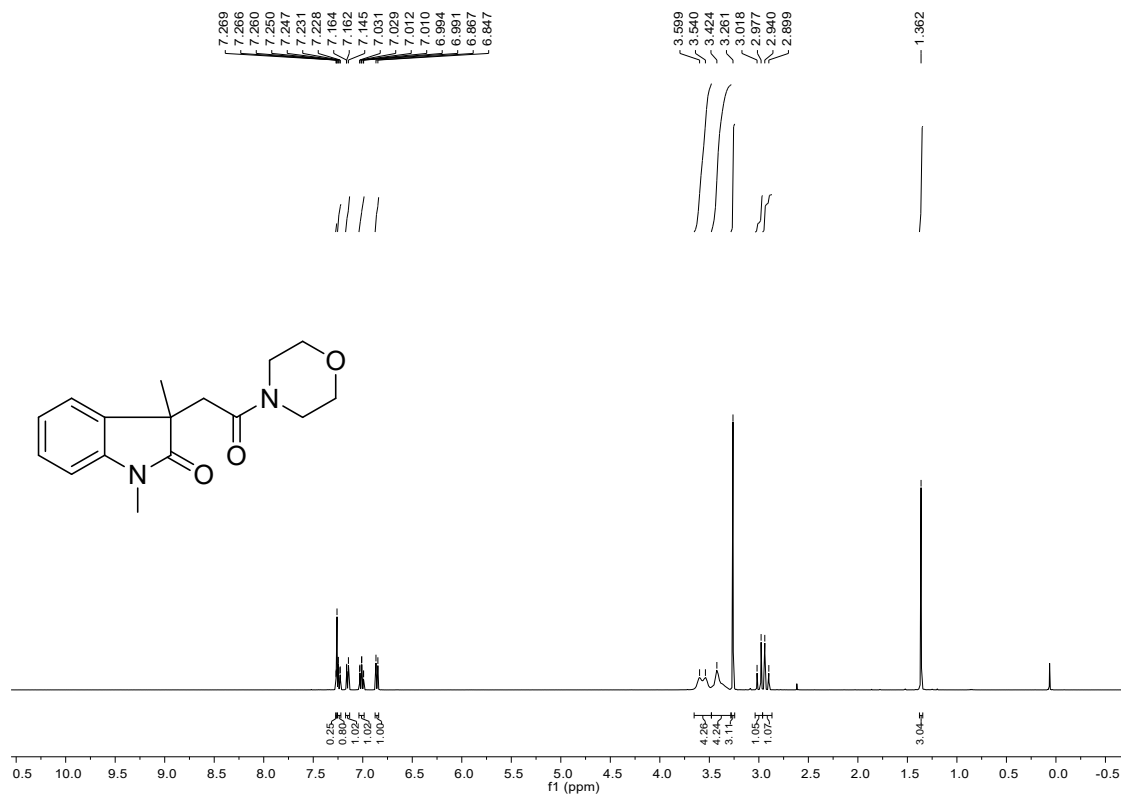
- (1) N. Alandini , L. Buzzetti, G. Favi, T. Schulte, L. Candish, K.D. Collins, P. Melchiorre. *Angew. Chem. Int. Ed.* 2020, 59, 5248-5253.
- (2) L. Cardinale, M. O. Konev, A. J. Wangelin. *Chem. Eur. J.* 2020, 26, 8239-8243.
- (3) B.T. Matsuo, P.H.R. Pliveira, J.T.M. Correia, M.W. Paixão. *Org. Lett.* 2021, 23, 6775-6779.
- (4) L. Cardinale, M.W.S. Schmotz, M.O. Konev. A. J. Wangelin. *Org. Lett.* 2022, 24, 506-510.
- (5) D.C. Fabry, M. Stodulski, D.C.S. Hoerner, T. Gulder. *Chem. Eur. J.* 2012, 18, 10834-10838.
- (6) Z. He, J. Guo, S. Tian. *Adv. Synth. Catal.* 2018, 360, 1544-1548.
- (7) Q. Gao, Q. Jing, Y. Chen, J. Sun, M. Zhou. *Chin. J. Org. Chem.* 2022, 42, 257-265.
- (8) Z. He, J. Guo, S. Tian. *Adv. Synth. Catal.* 2018, 360, 1544-1548.
- (9) K. Muralirajan, R. Kancherla, A. Gimnkhan, R. Magnus. *Org. Lett.* 2021, 23, 6905-6910.

6. NMR spectra

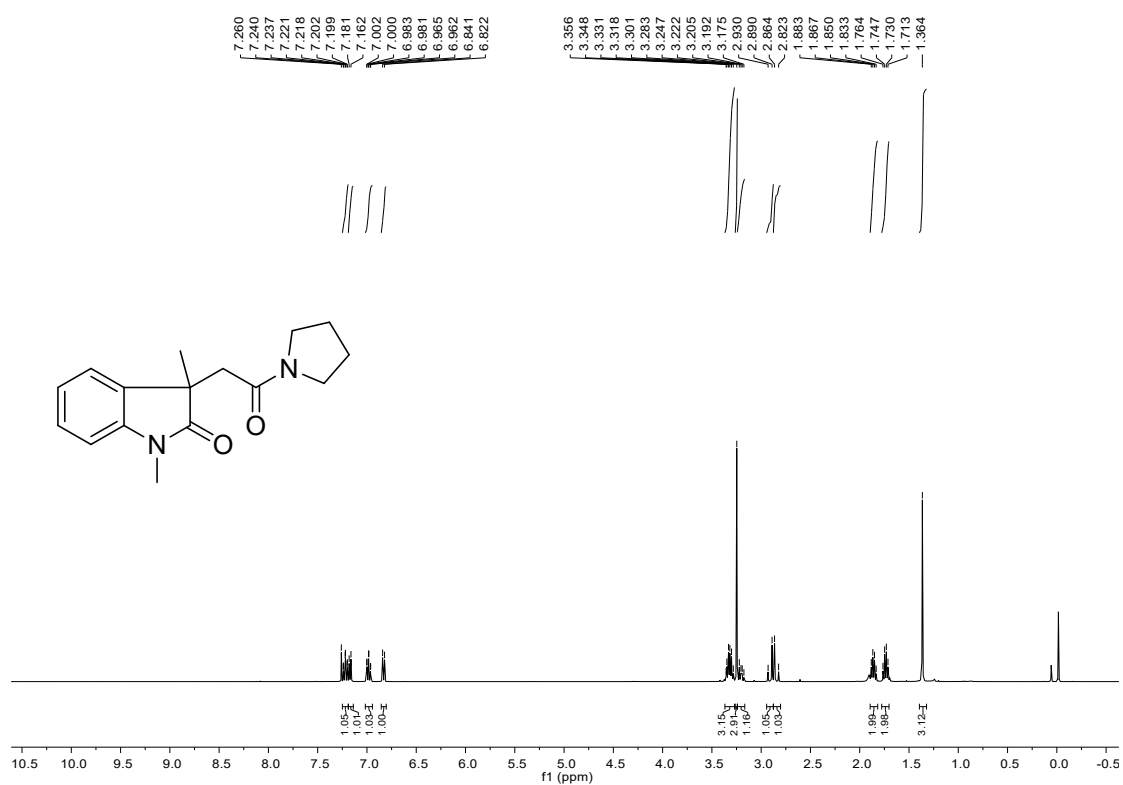
¹H NMR (400 MHz, CDCl₃) spectra of **3a**



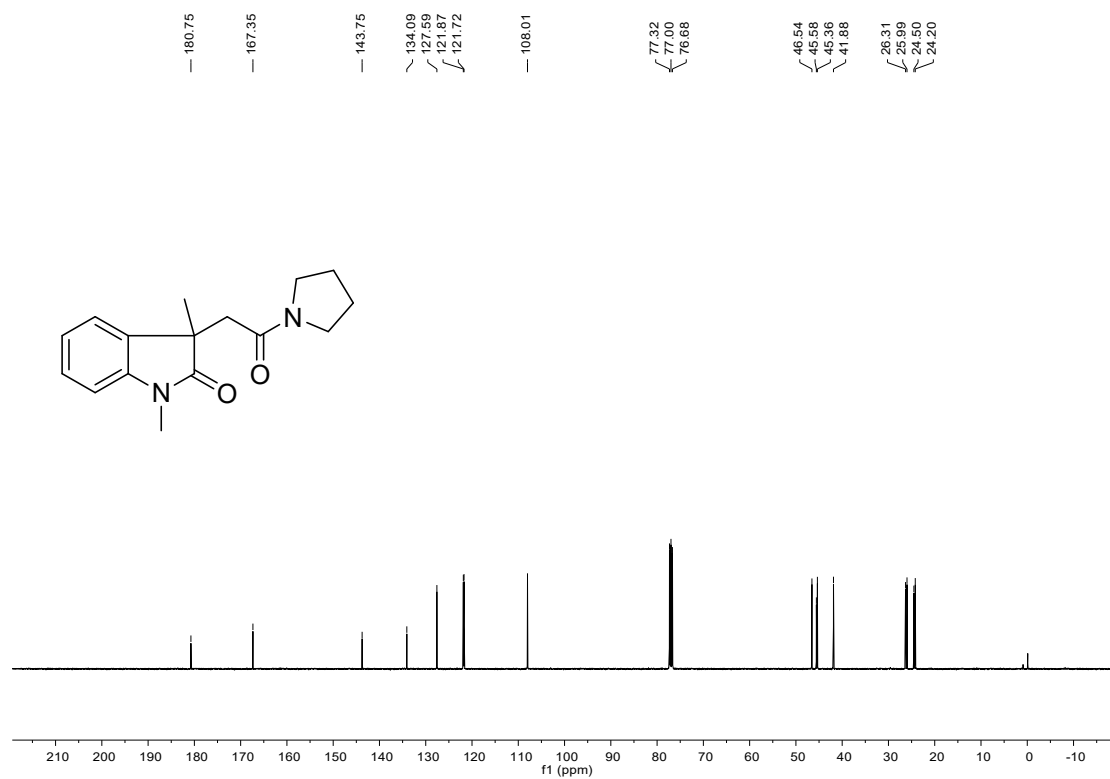
¹H NMR (400 MHz, CDCl₃) spectra of **3b**



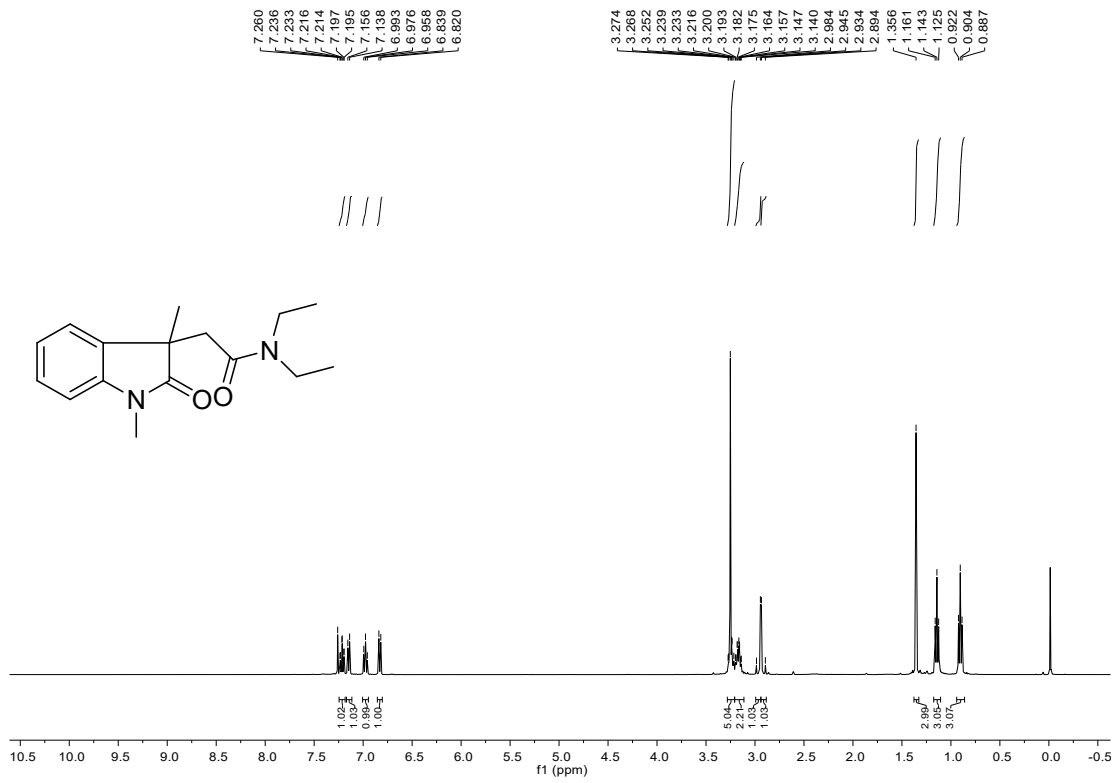
¹H NMR (400 MHz, CDCl₃) spectra of **3c**



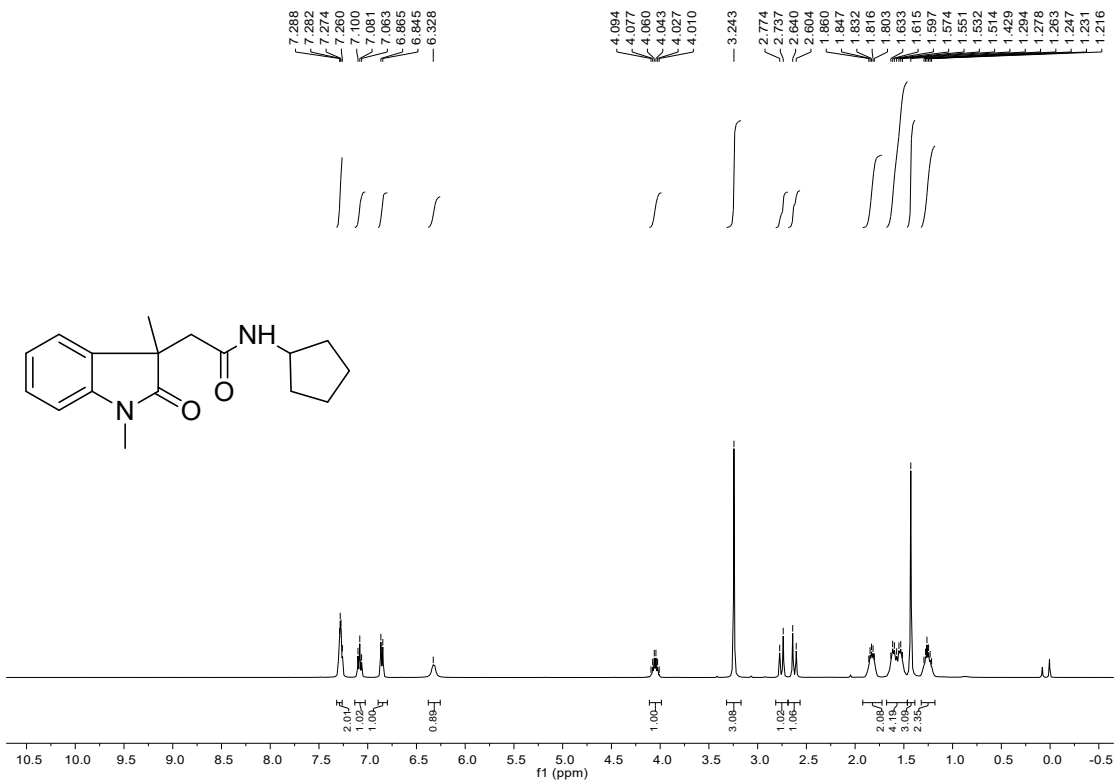
¹³C NMR (100 MHz, CDCl₃) spectra of **3c**



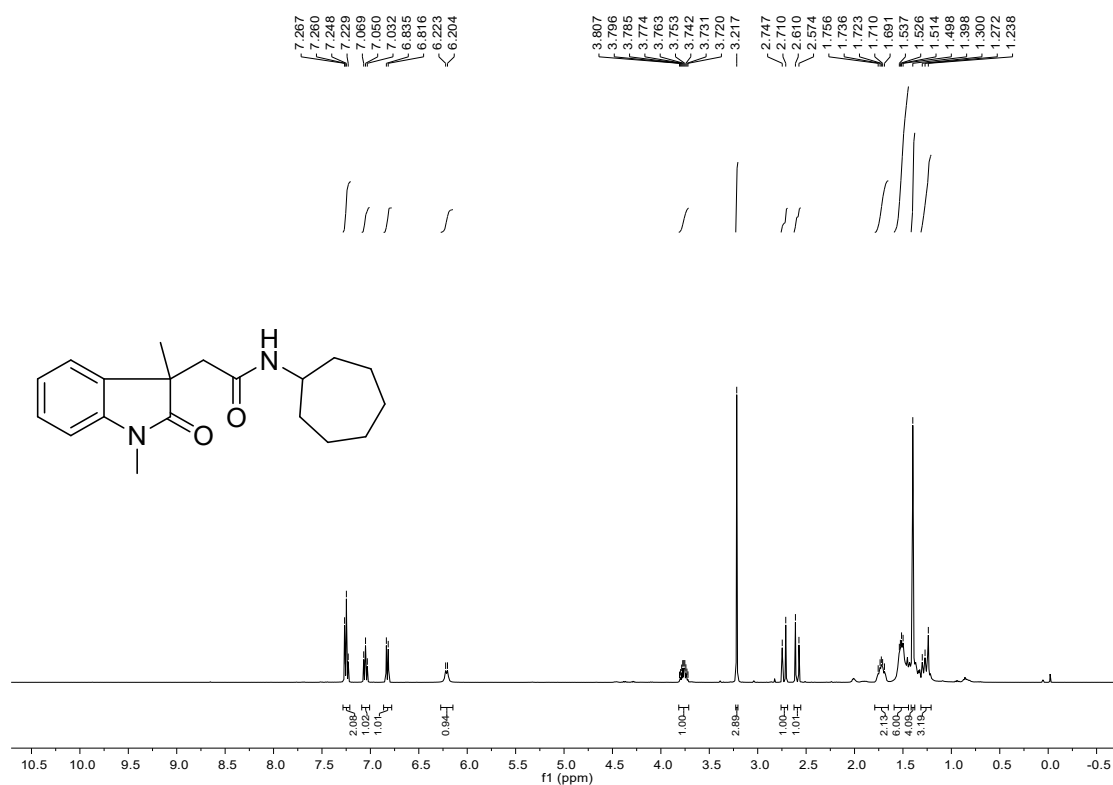
¹H NMR (400 MHz, CDCl₃) spectra of **3d**



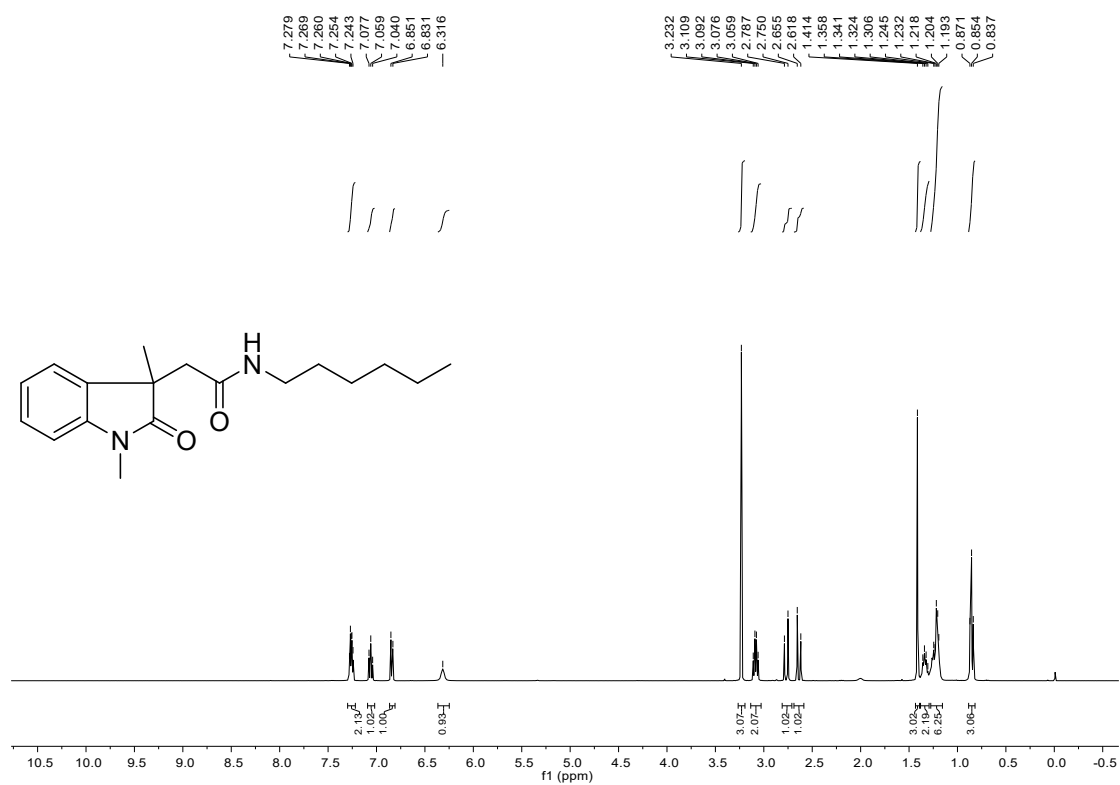
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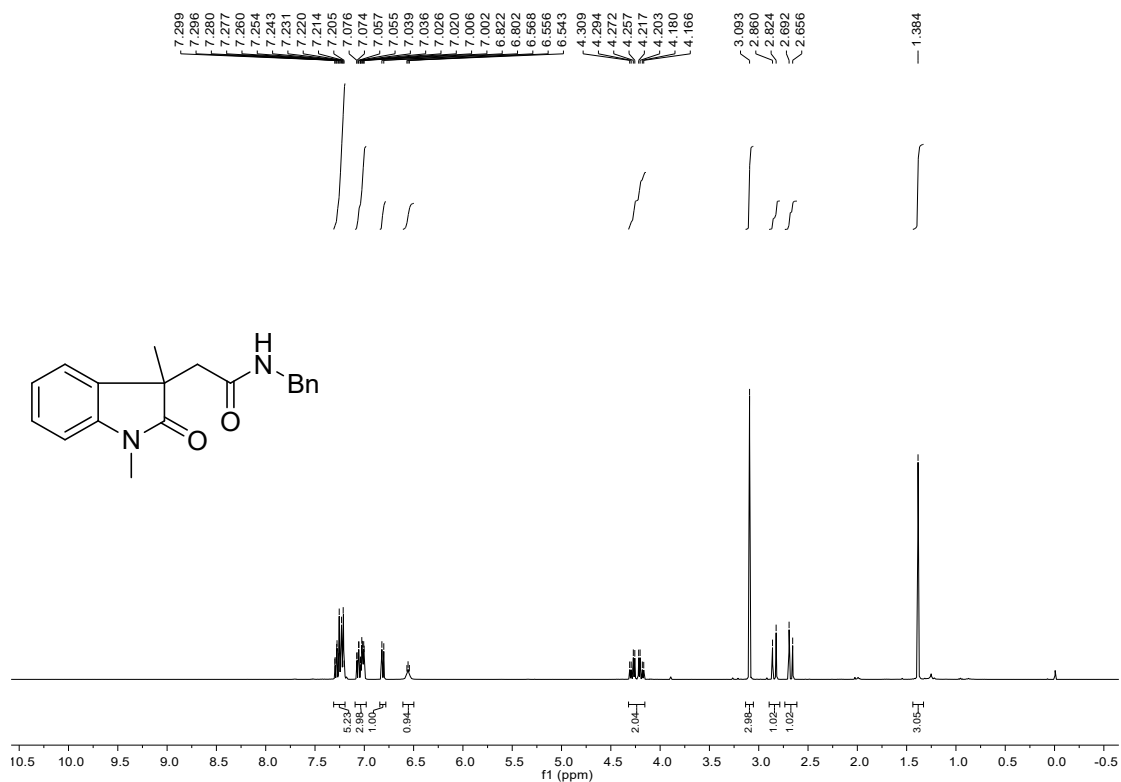
¹H NMR (400 MHz, CDCl₃) spectra of **3f**



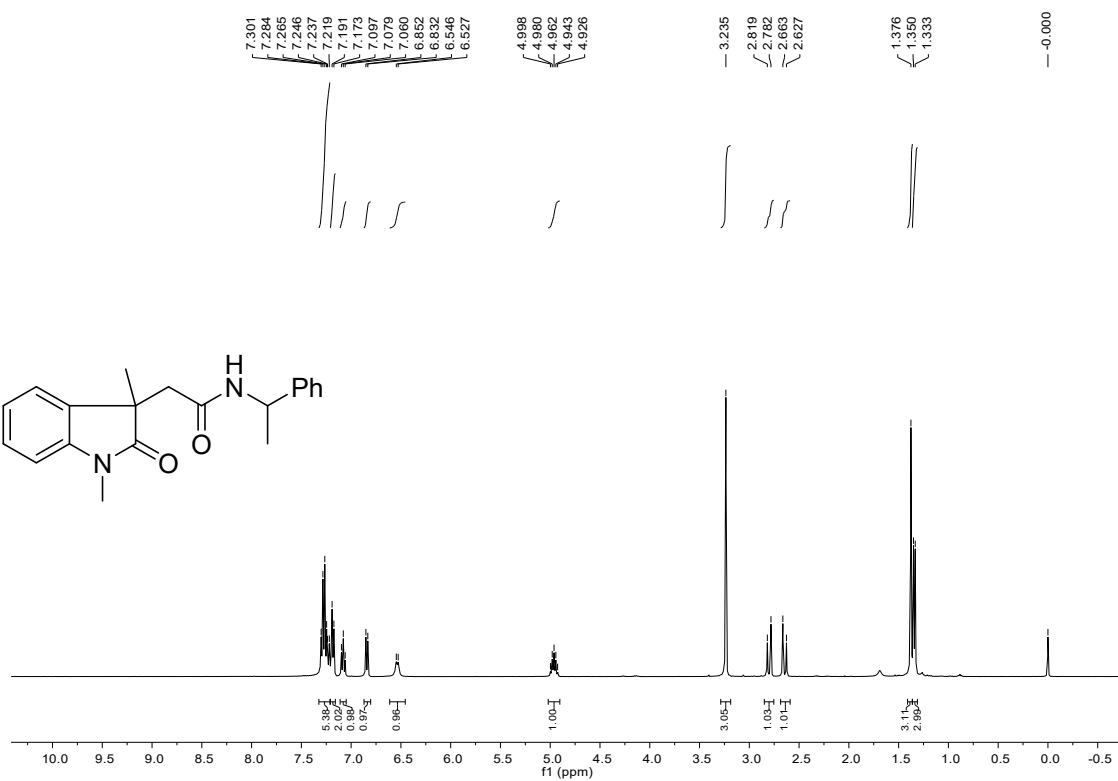
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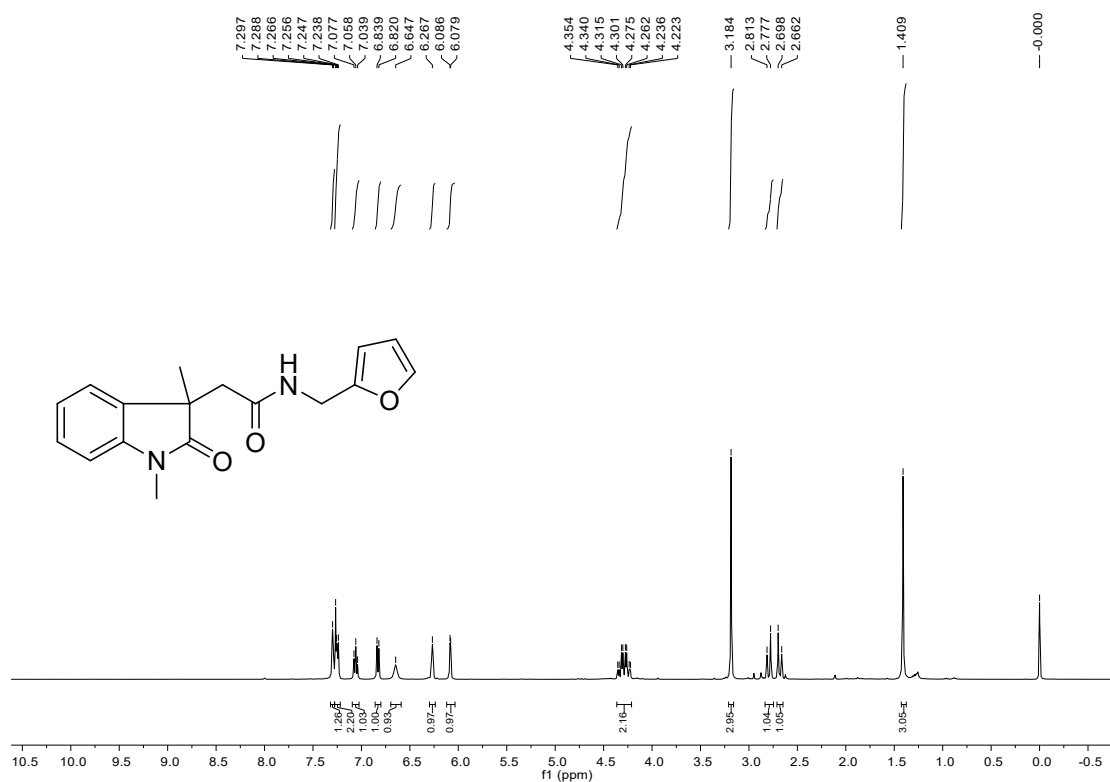
¹H NMR (400 MHz, CDCl₃) spectra of **3h**



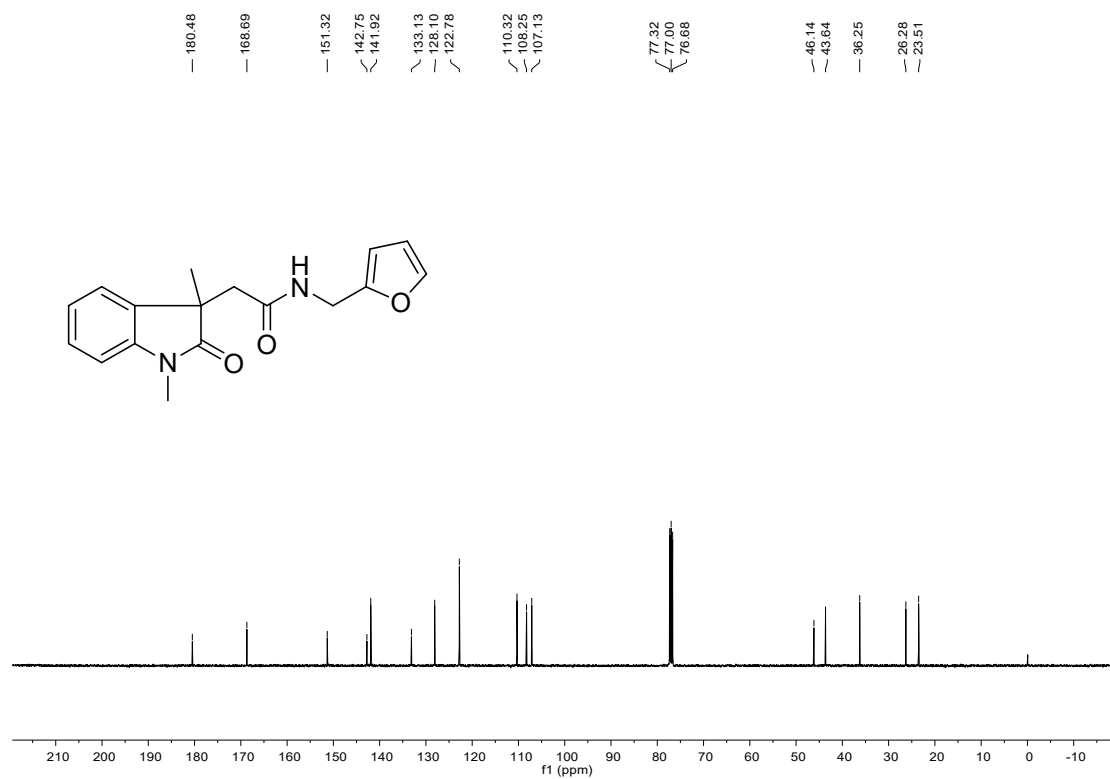
¹H NMR (400 MHz, CDCl₃) spectra of **3i**



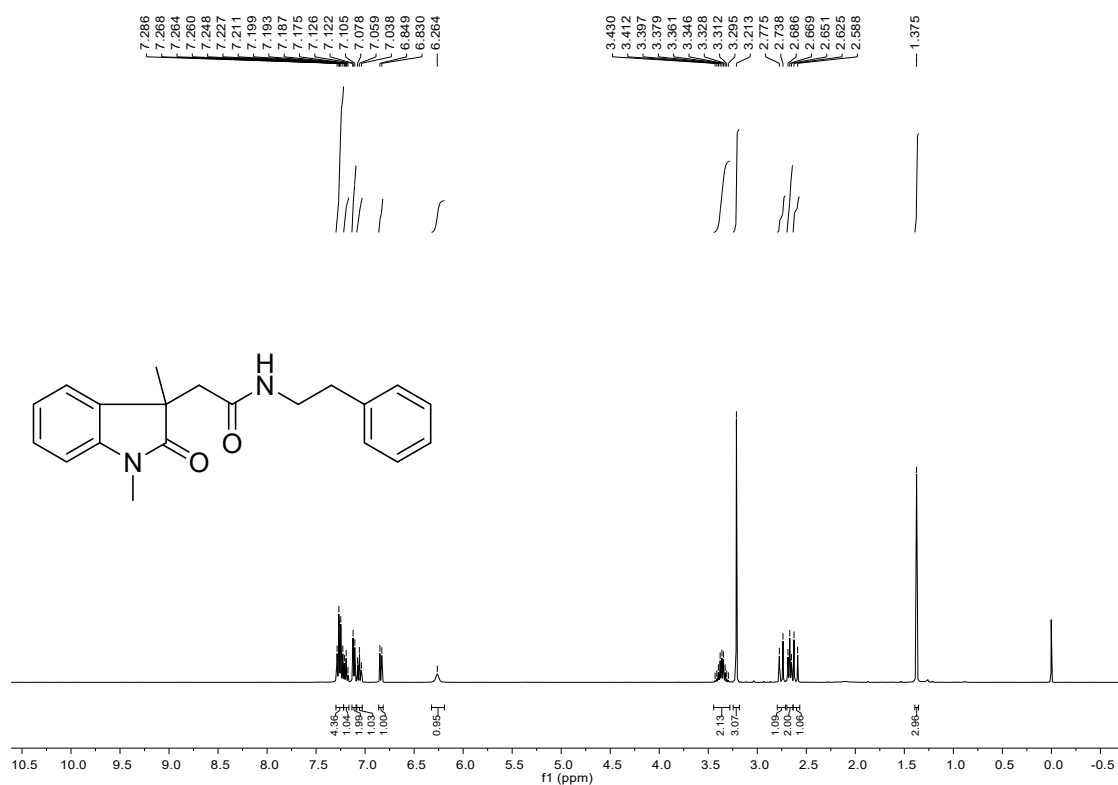
¹H NMR (400 MHz, CDCl₃) spectra of **3j**



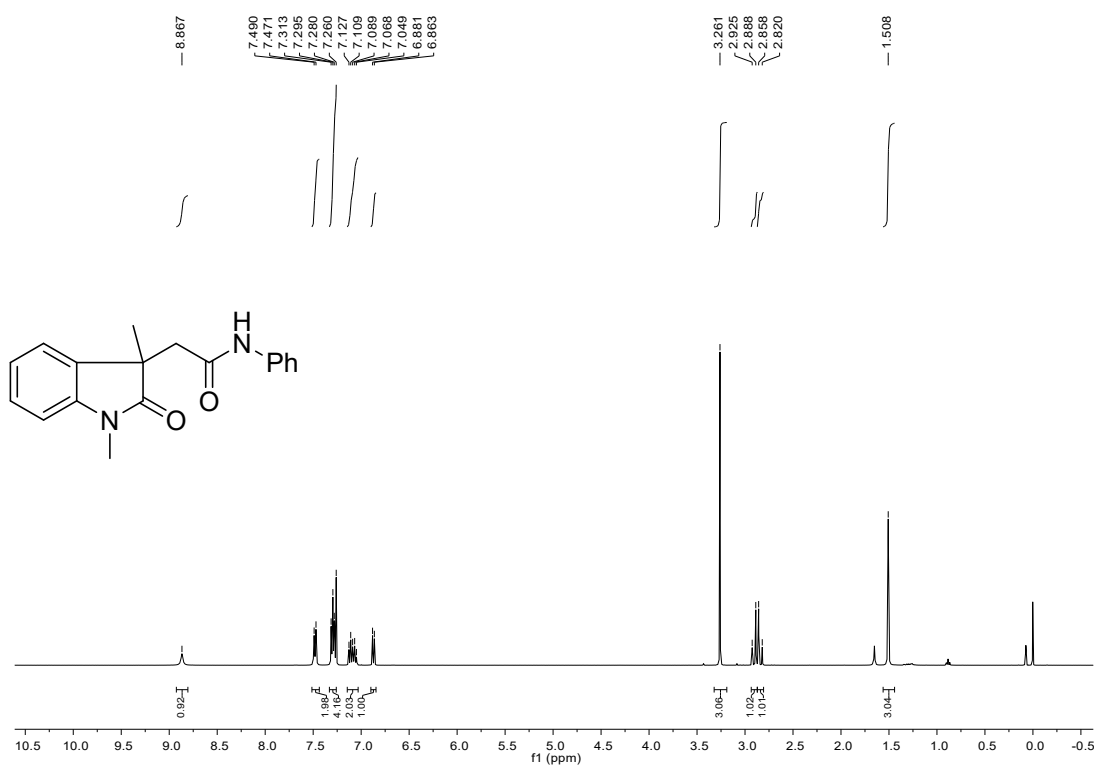
¹³C NMR (100 MHz, CDCl₃) spectra of **3j**



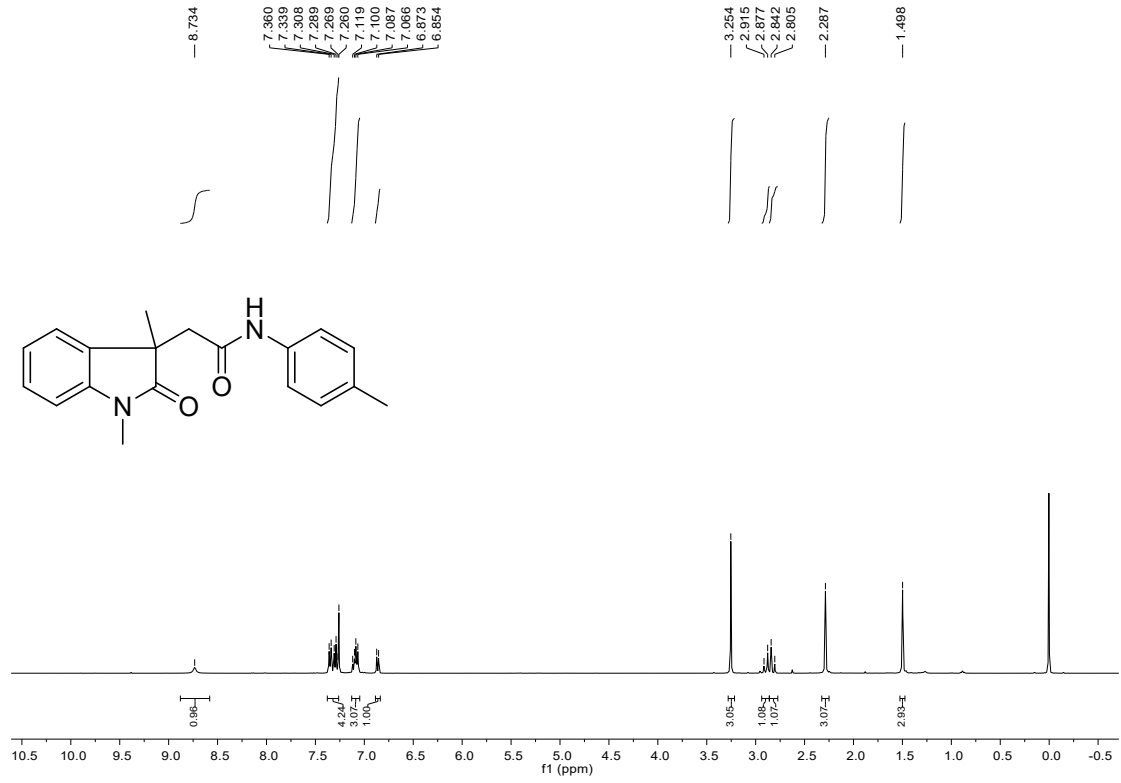
¹H NMR (400 MHz, CDCl₃) spectra of **3k**



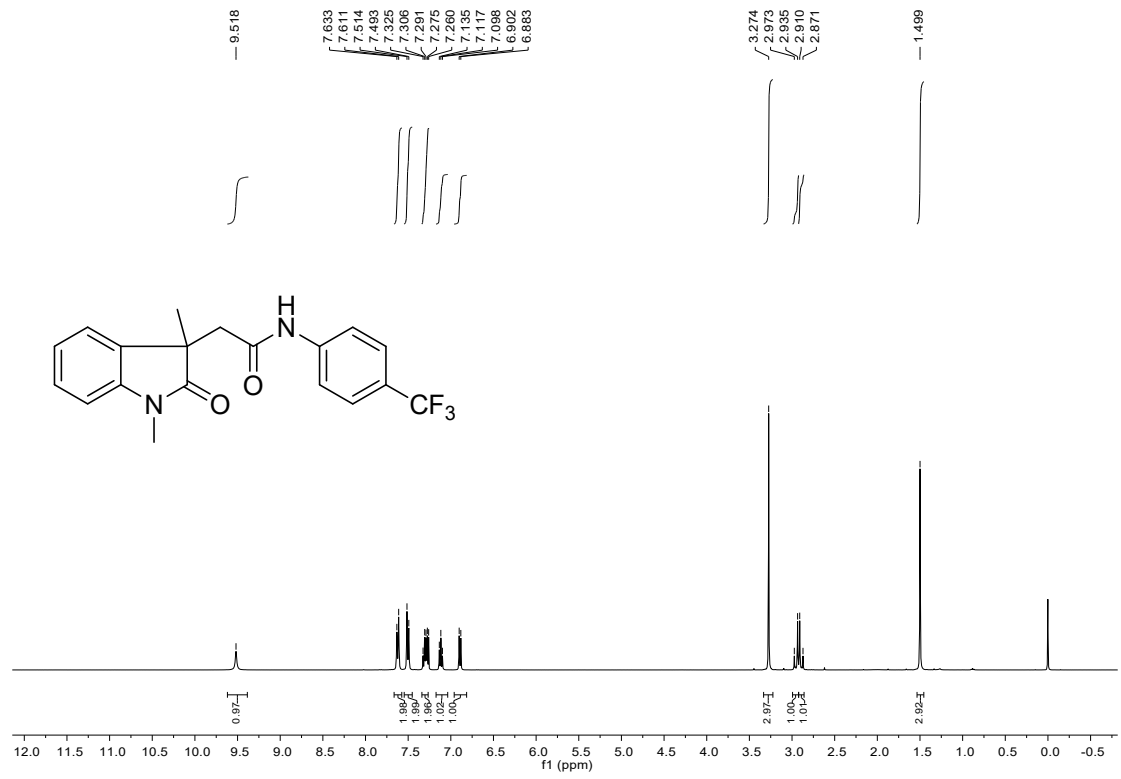
¹H NMR (400 MHz, CDCl₃) spectra of **3l**



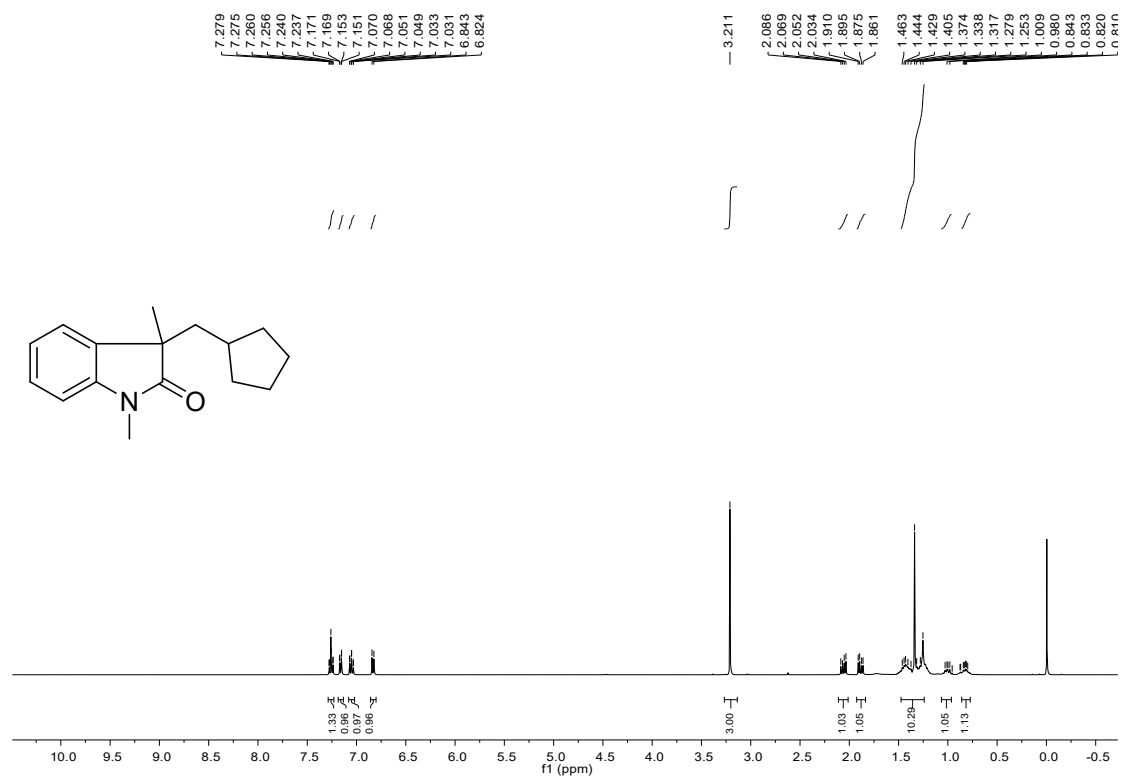
¹H NMR (400 MHz, CDCl₃) spectra of **3m**



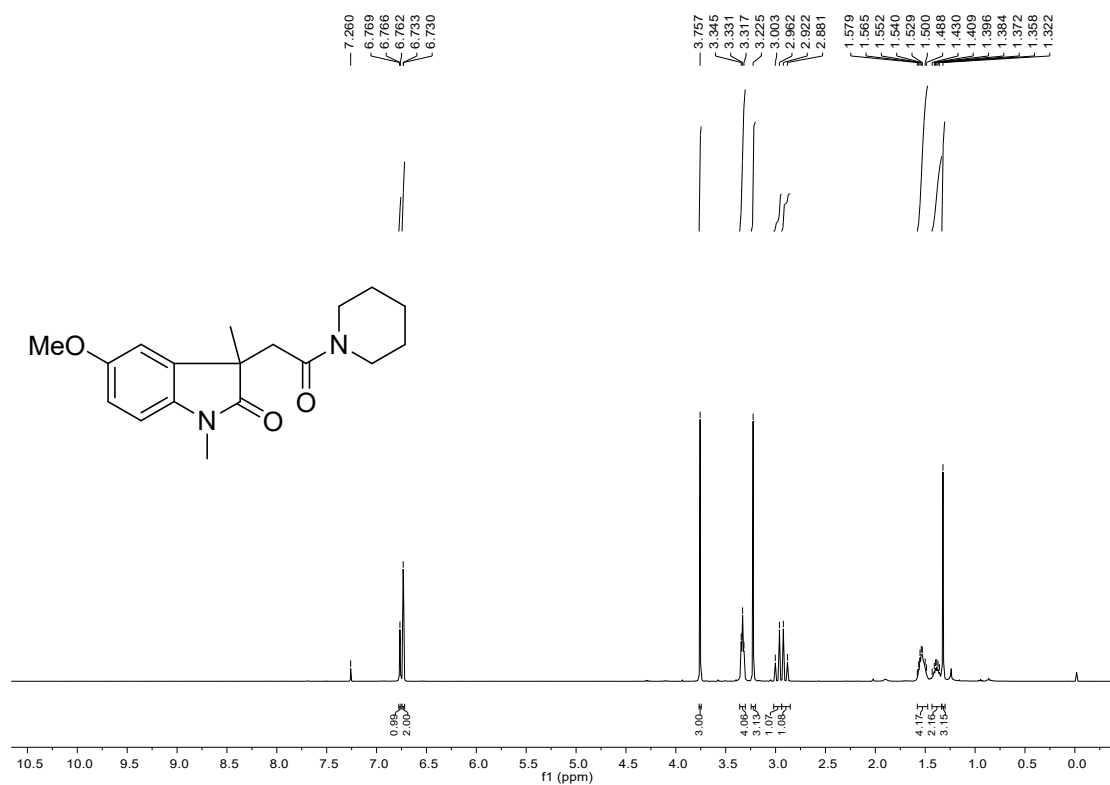
¹H NMR (400 MHz, CDCl₃) spectra of **3n**



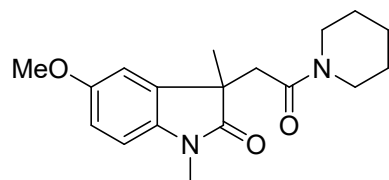
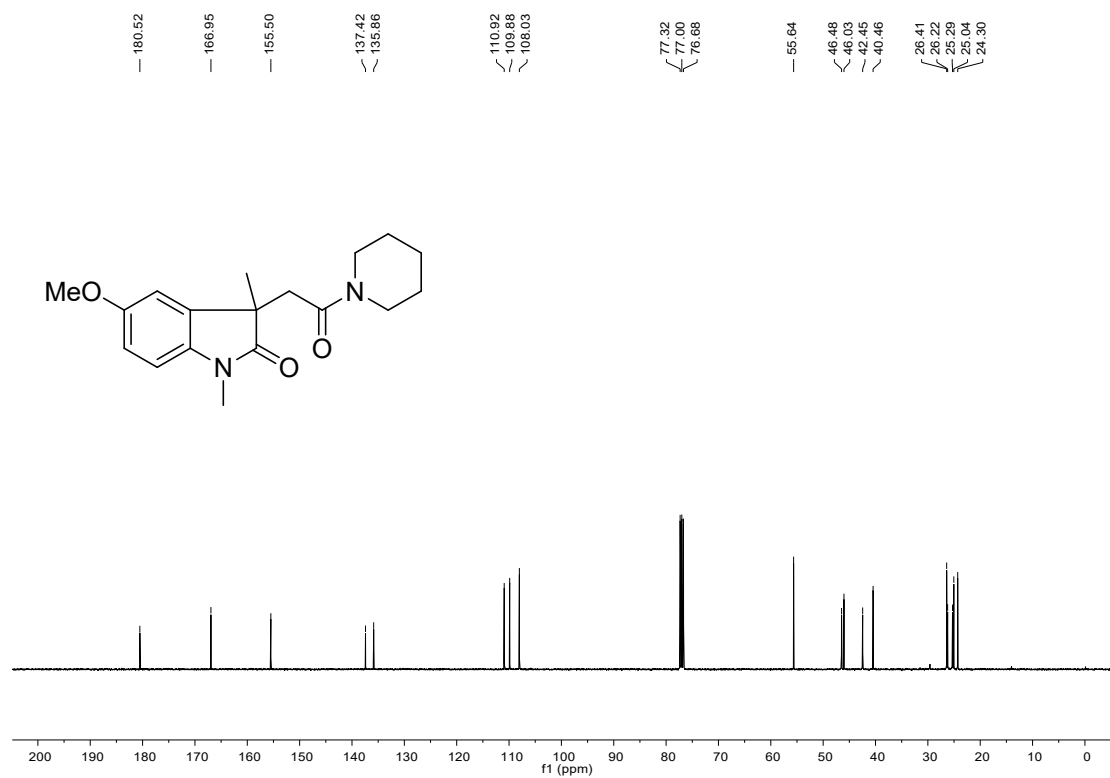
¹H NMR (400 MHz, CDCl₃) spectra of **3o**



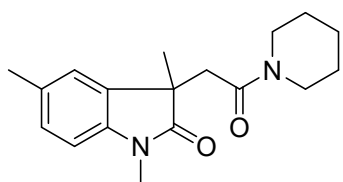
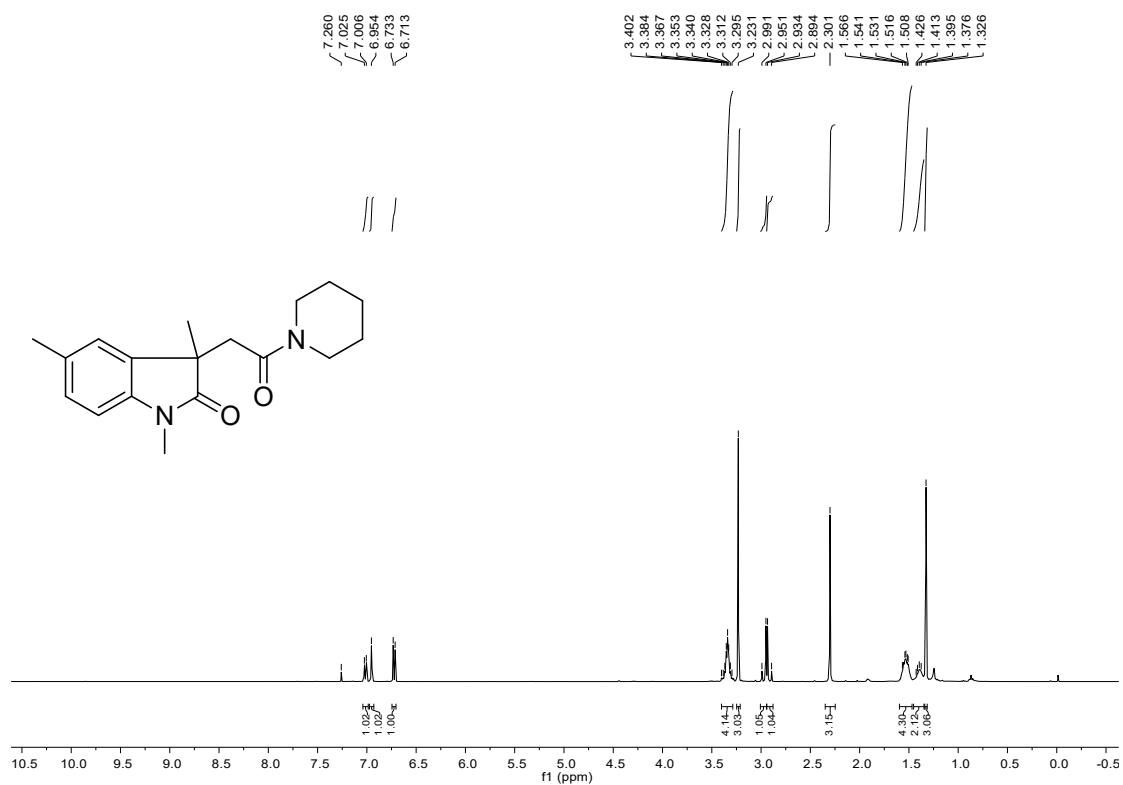
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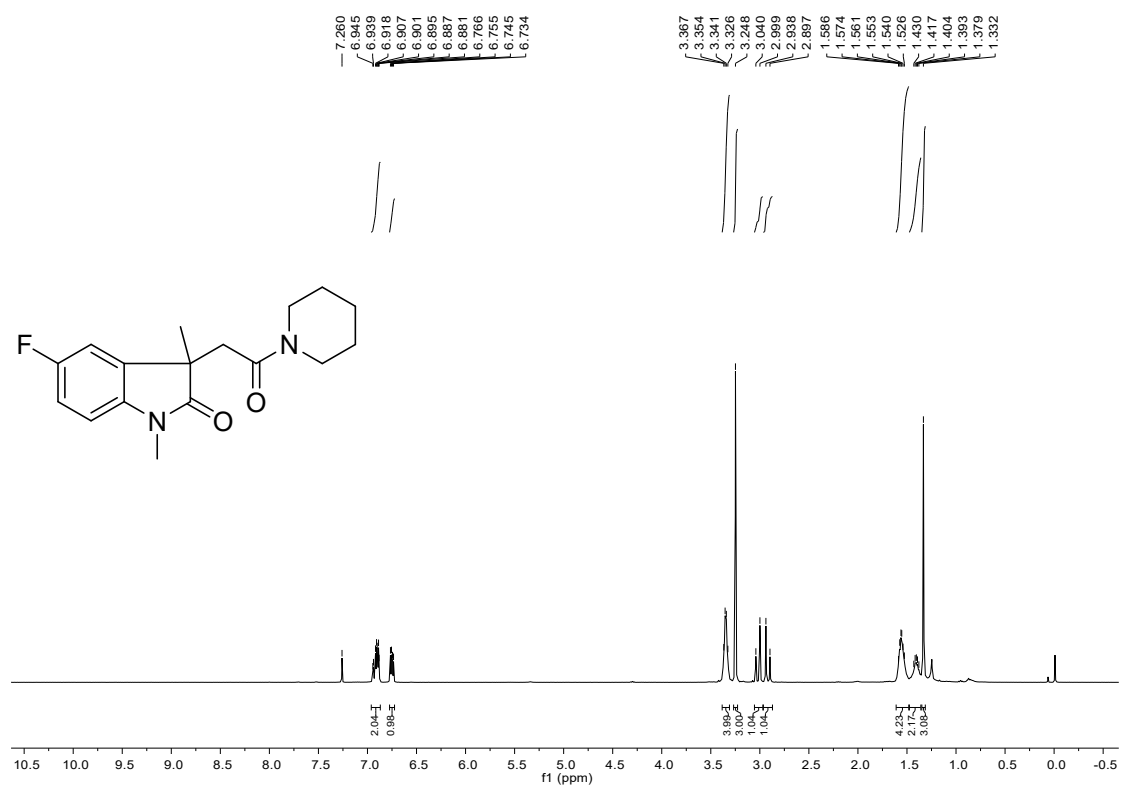
¹³C NMR (100 MHz, CDCl₃) spectra of **3p**



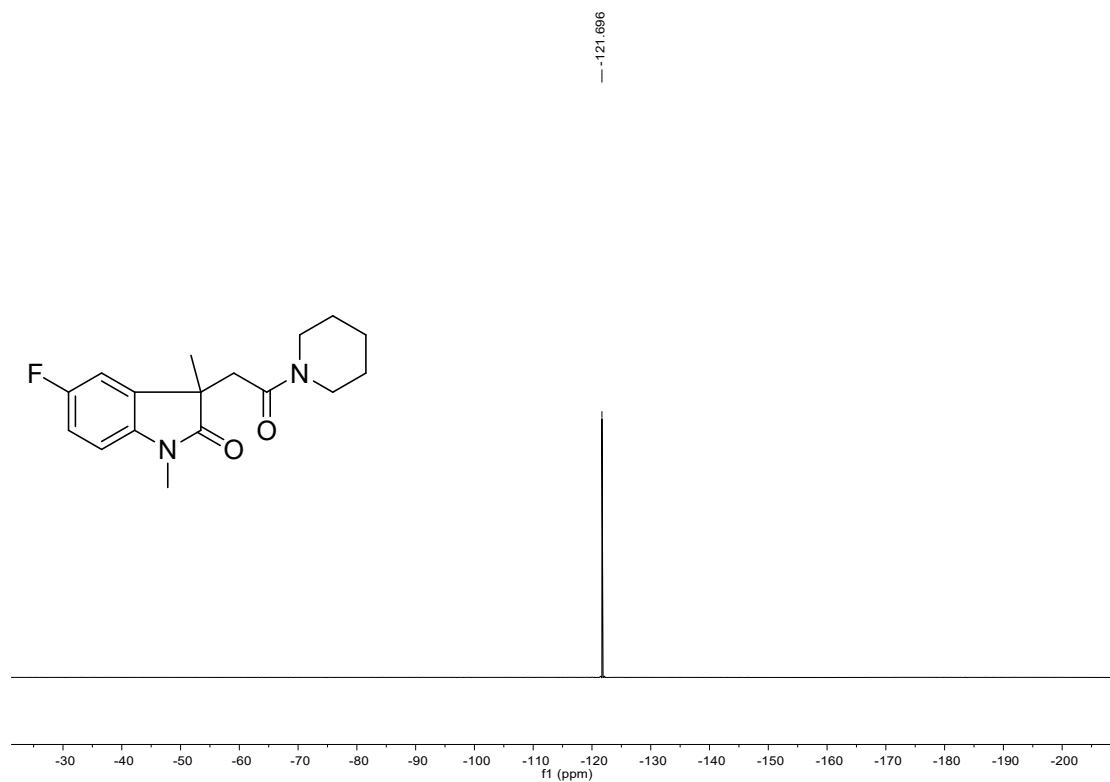
¹H NMR (400 MHz, CDCl₃) spectra of **3q**



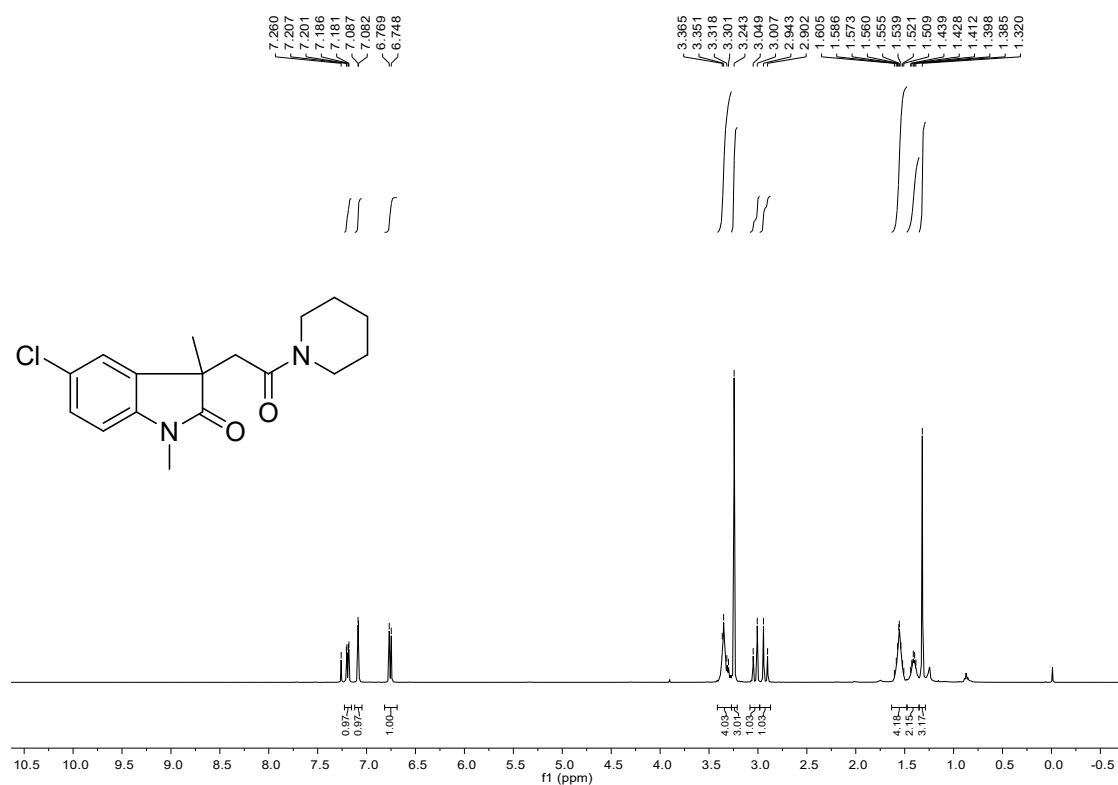
¹H NMR (400 MHz, CDCl₃) spectra of **3r**



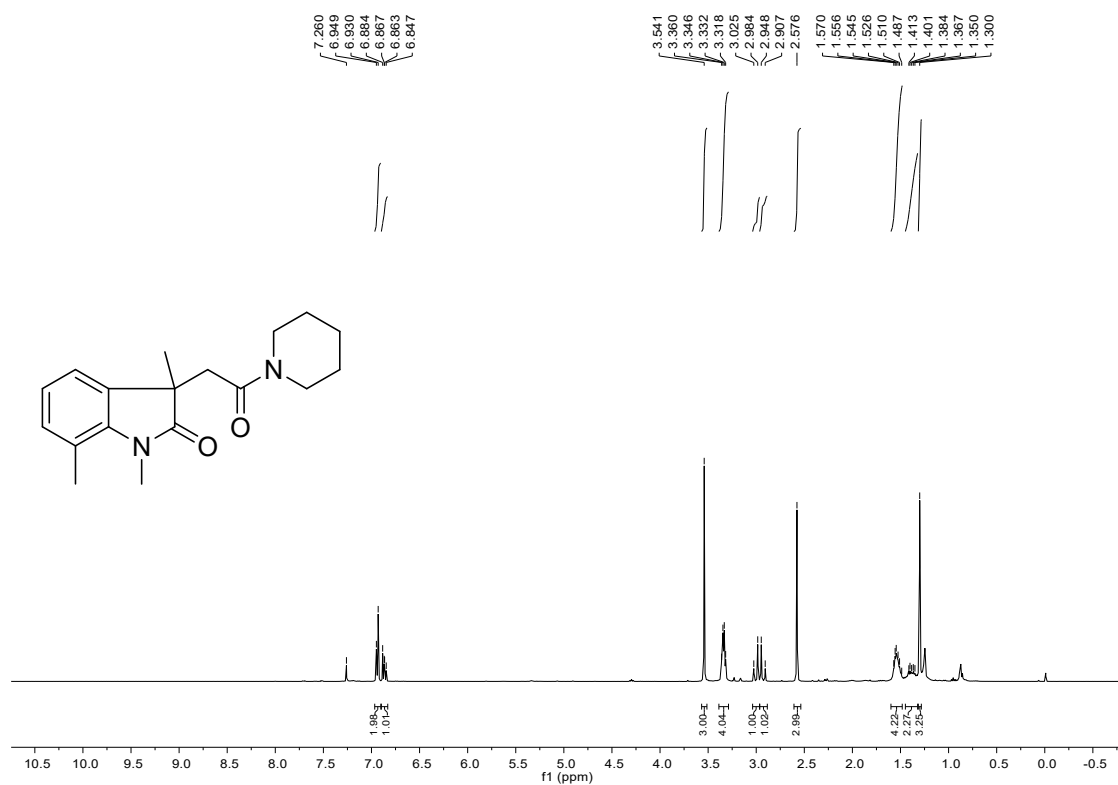
¹⁹F NMR (376 MHz, CDCl₃) spectra of **3r**



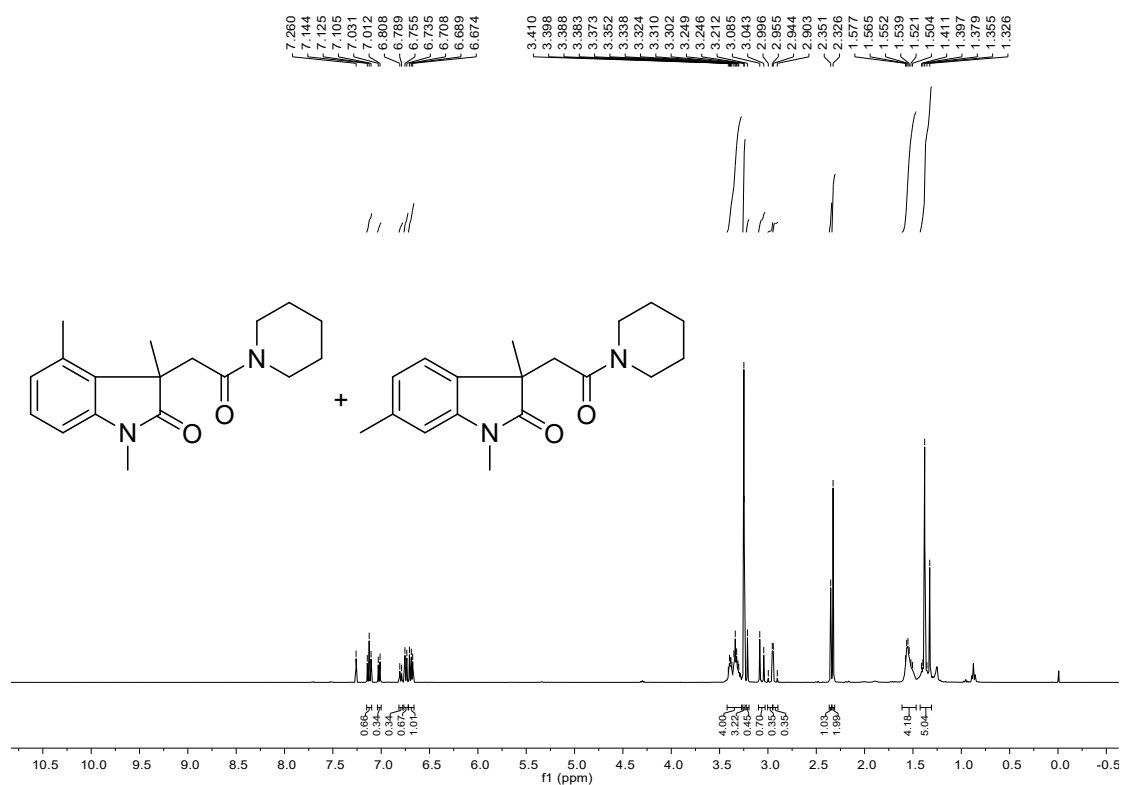
¹H NMR (400 MHz, CDCl₃) spectra of **3s**



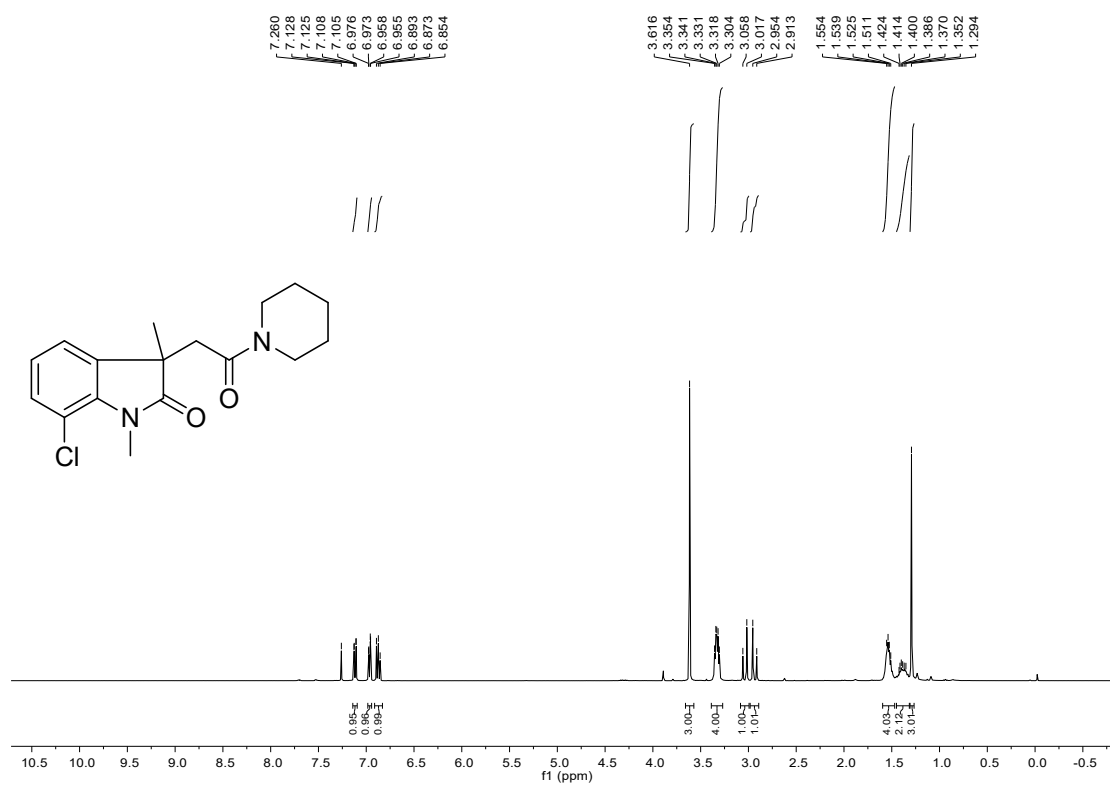
¹H NMR (400 MHz, CDCl₃) spectra of **3u**



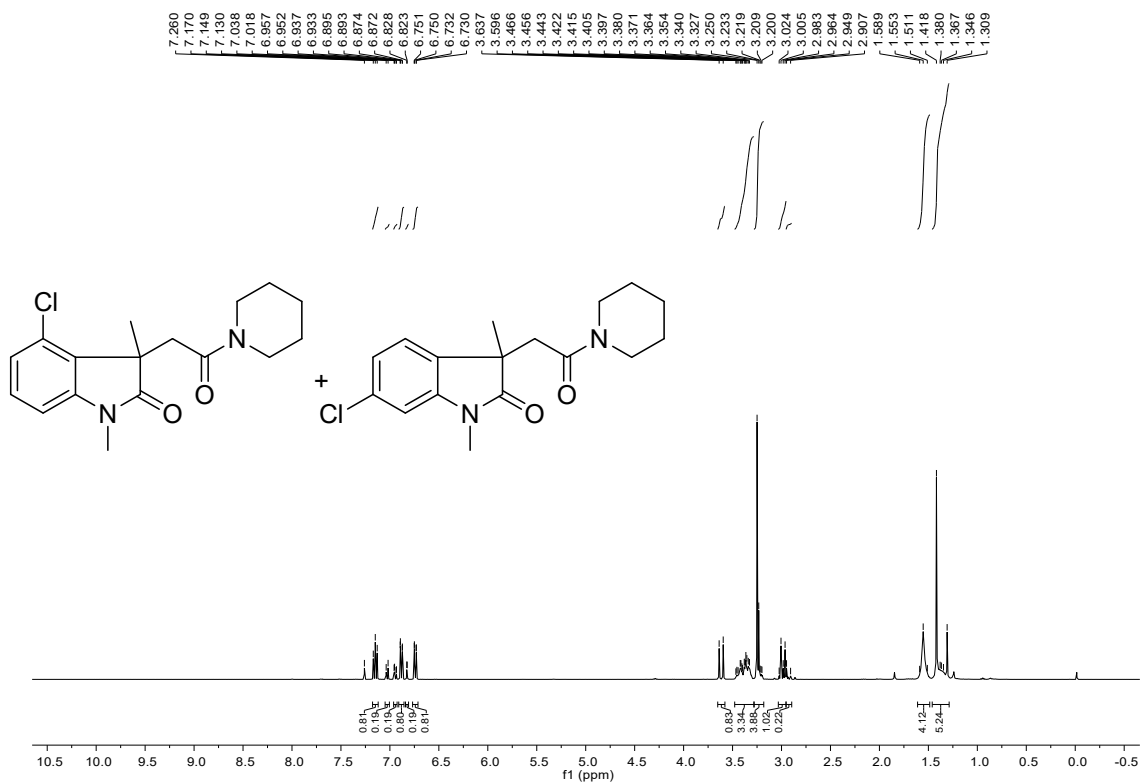
¹H NMR (400 MHz, CDCl₃) spectra of **3v+3v'**



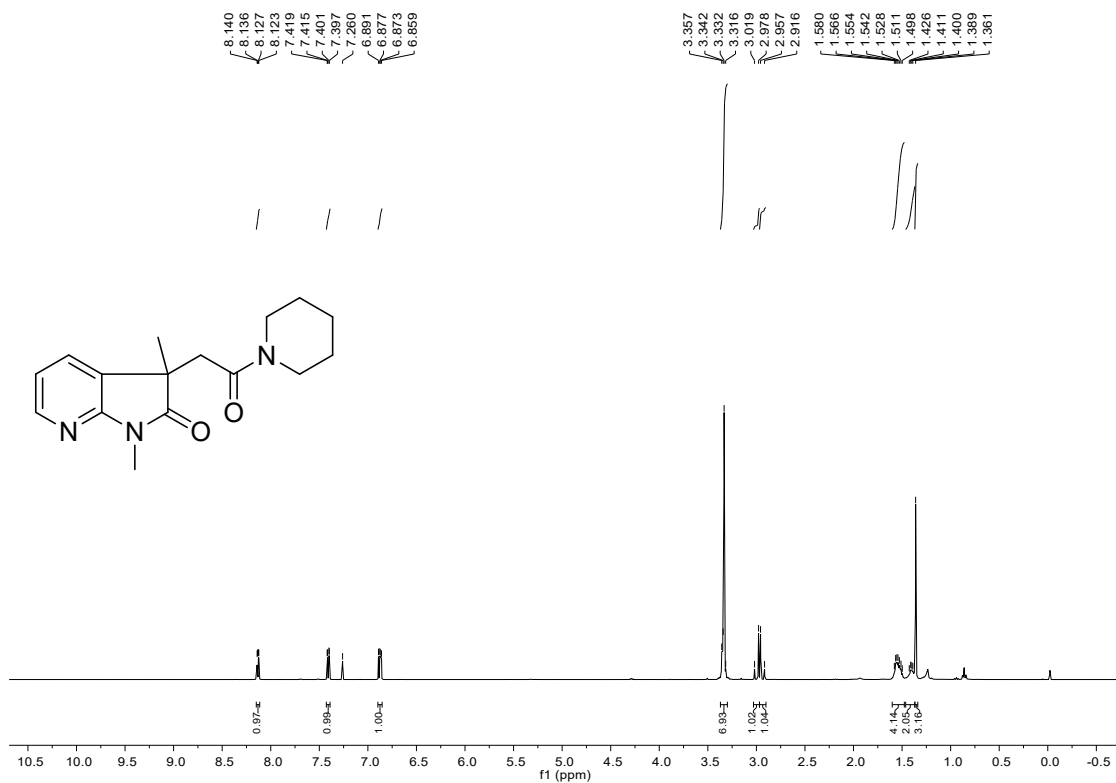
¹H NMR (400 MHz, CDCl₃) spectra of **3w**



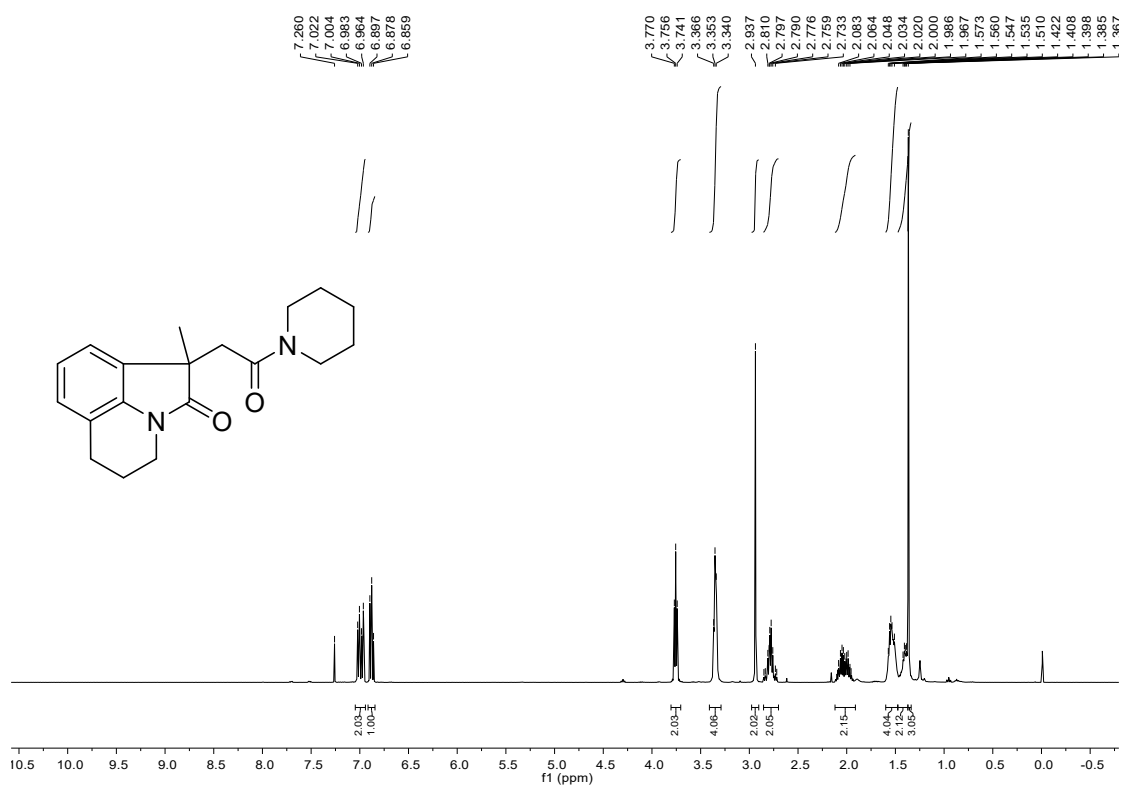
¹H NMR (400 MHz, CDCl₃) spectra of **3x** + **3x'**



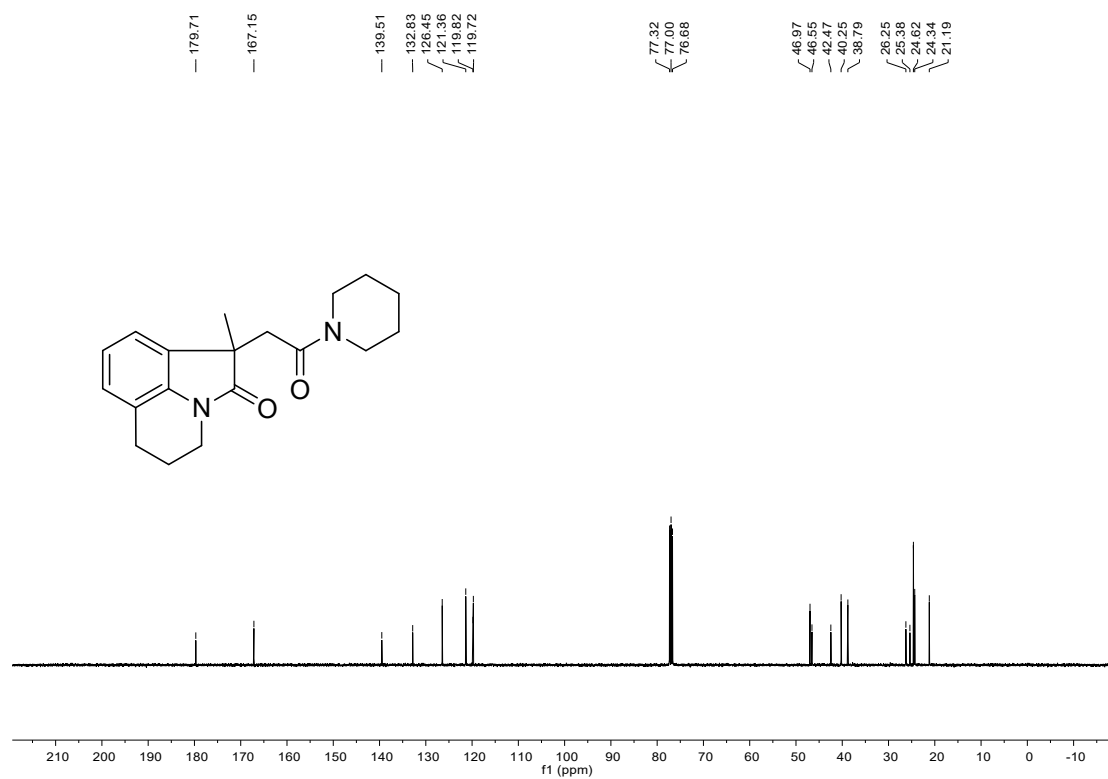
¹H NMR (400 MHz, CDCl₃) spectra of **3y**



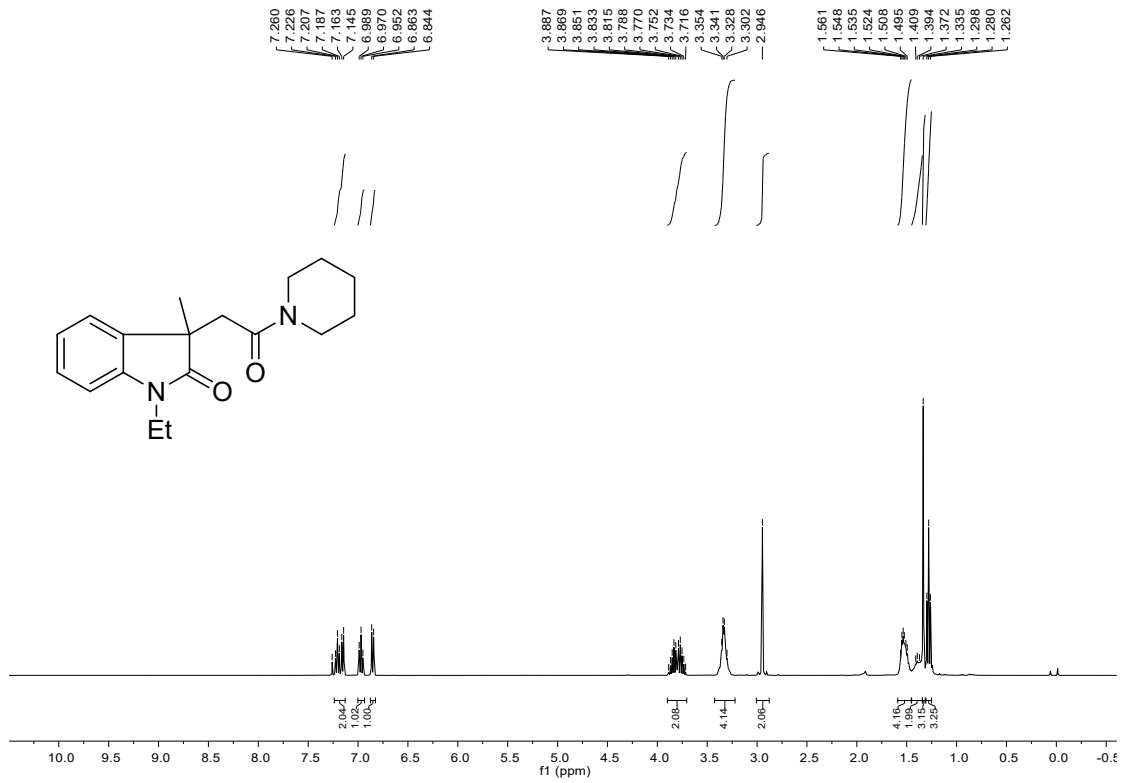
¹H NMR (400 MHz, CDCl₃) spectra of **3z**



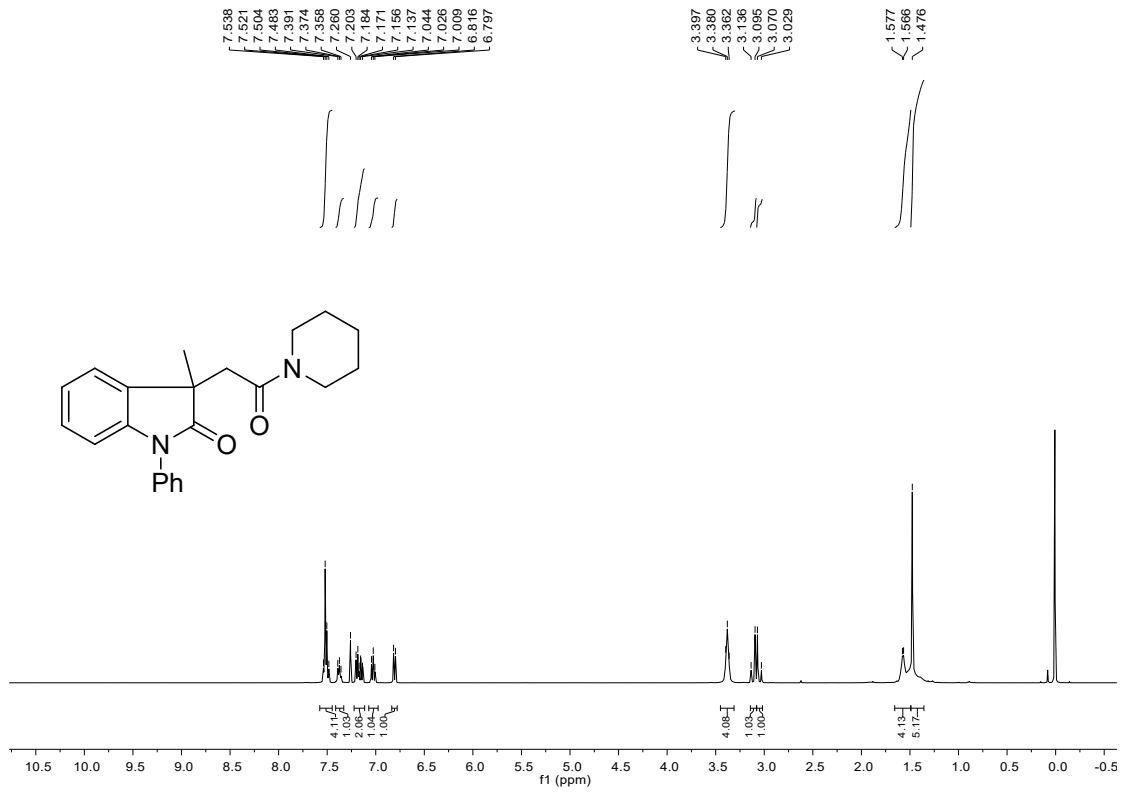
¹³C NMR (100 MHz, CDCl₃) spectra of **3z**



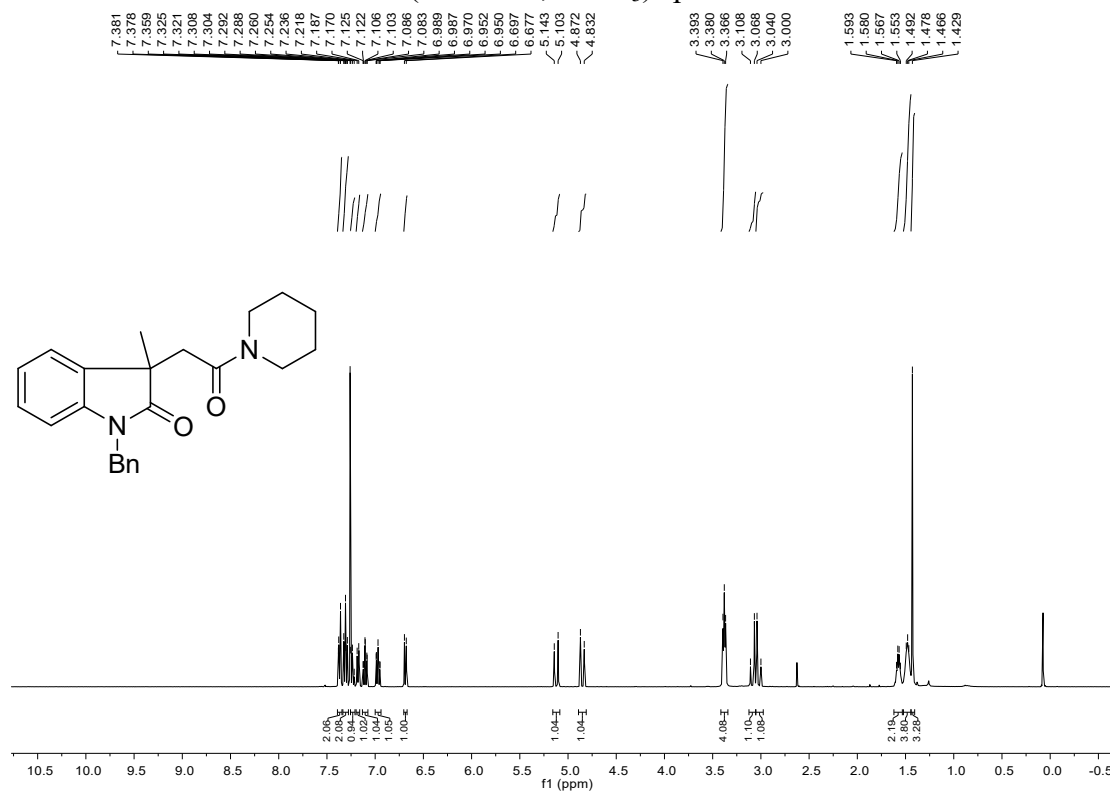
¹H NMR (400 MHz, CDCl₃) spectra of **3ab**



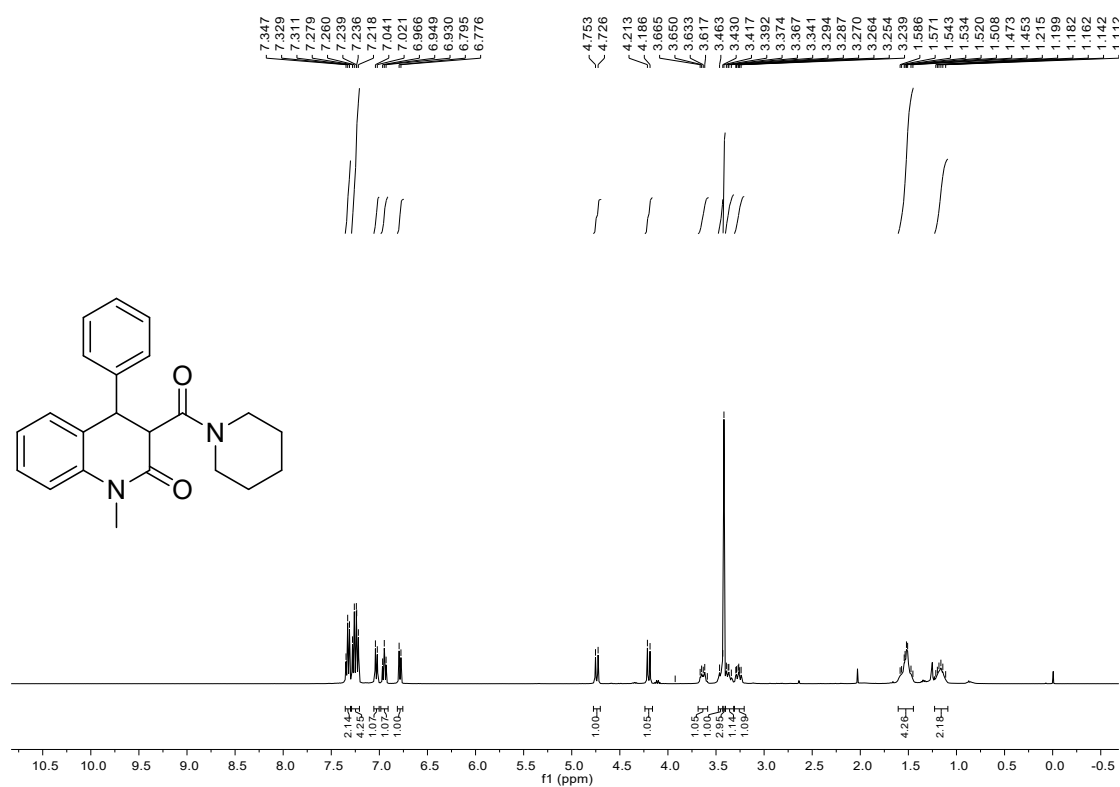
¹H NMR (400 MHz, CDCl₃) spectra of **3ac**



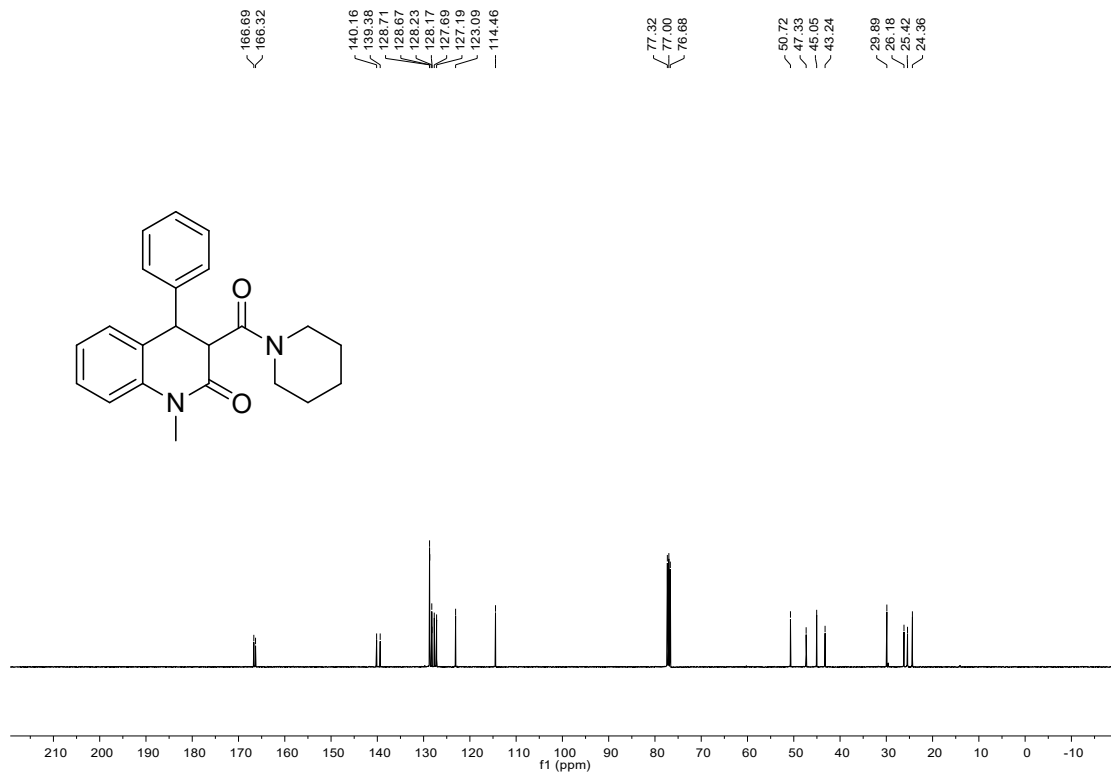
¹H NMR (400 MHz, CDCl₃) spectra of **3ad**



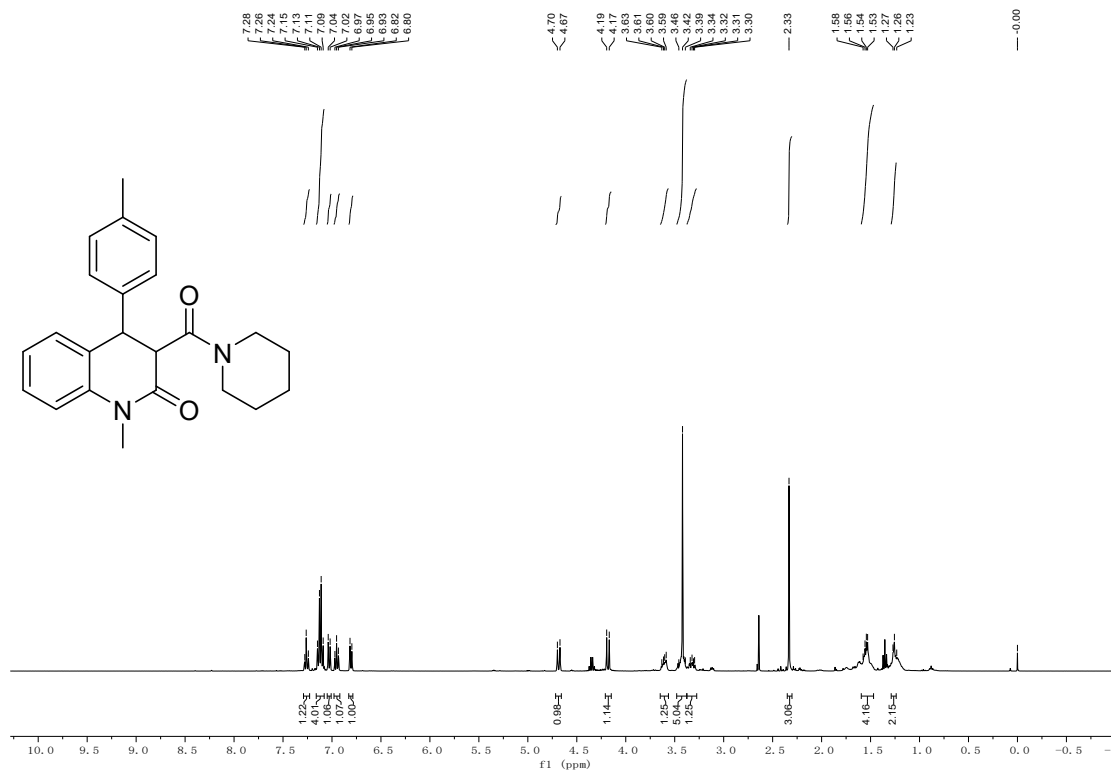
¹H NMR (400 MHz, CDCl₃) spectra of **5a**



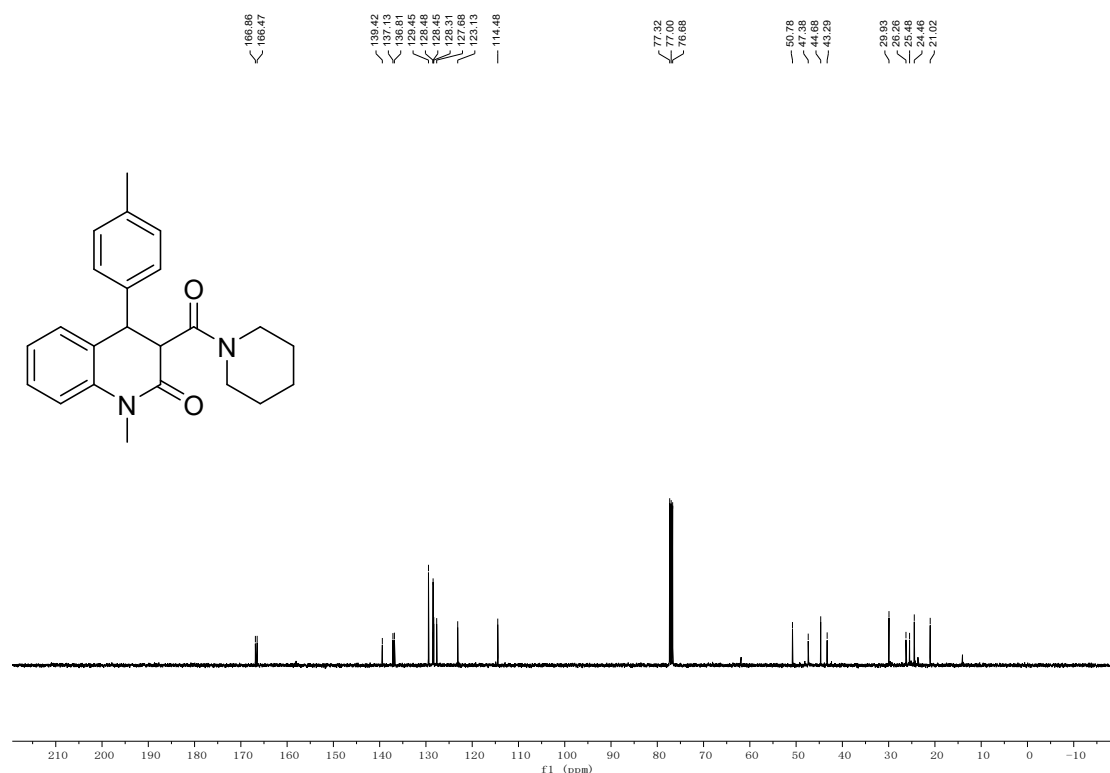
¹³C NMR (100 MHz, CDCl₃) spectra of **5a**



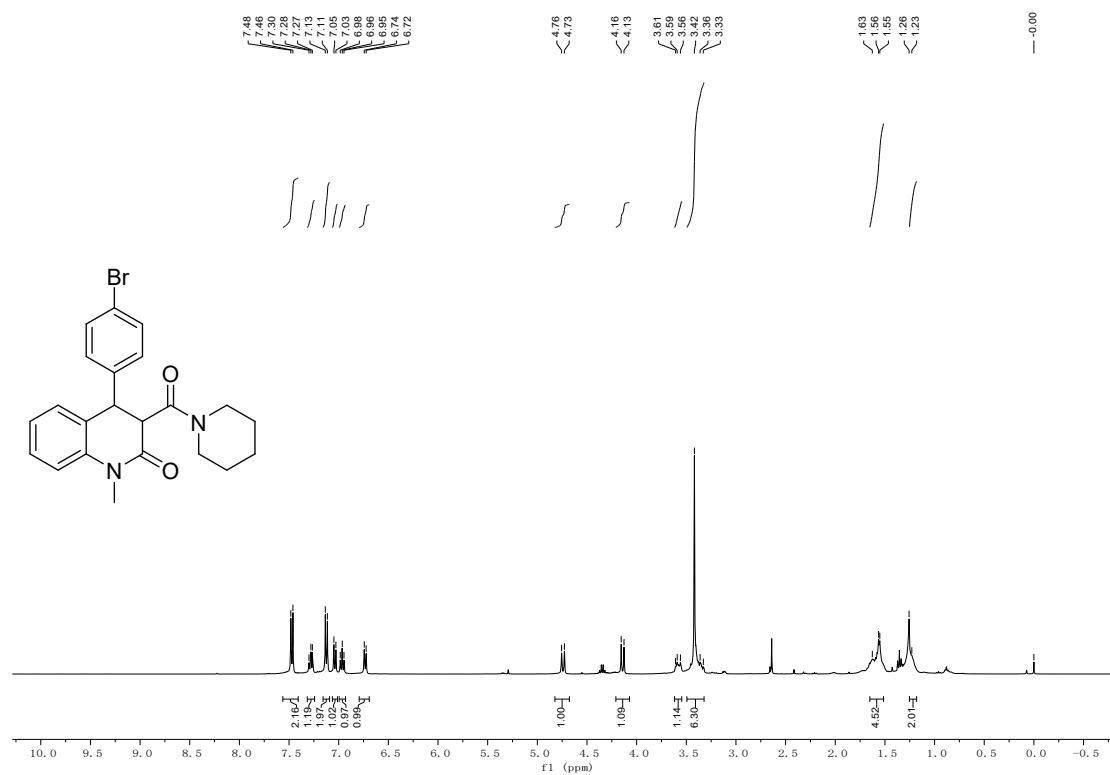
¹H NMR (400 MHz, CDCl₃) spectra of **5b**



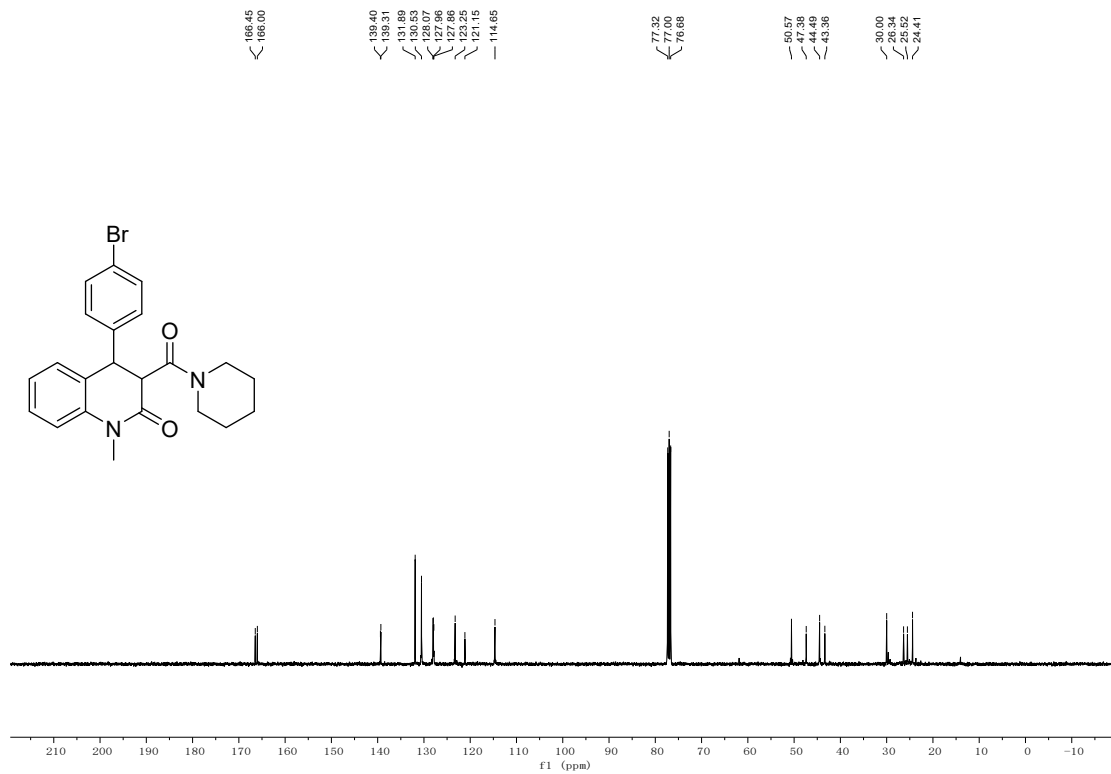
¹³C NMR (100 MHz, CDCl₃) spectra of **5b**



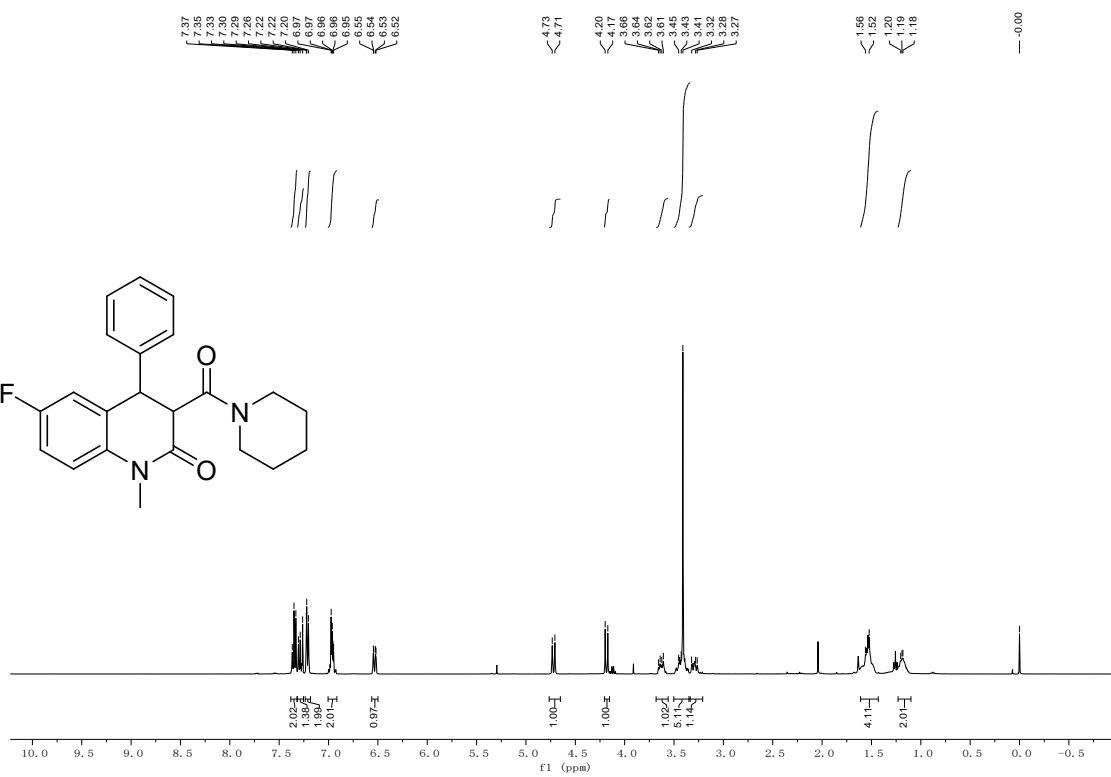
¹H NMR (400 MHz, CDCl₃) spectra of **5c**



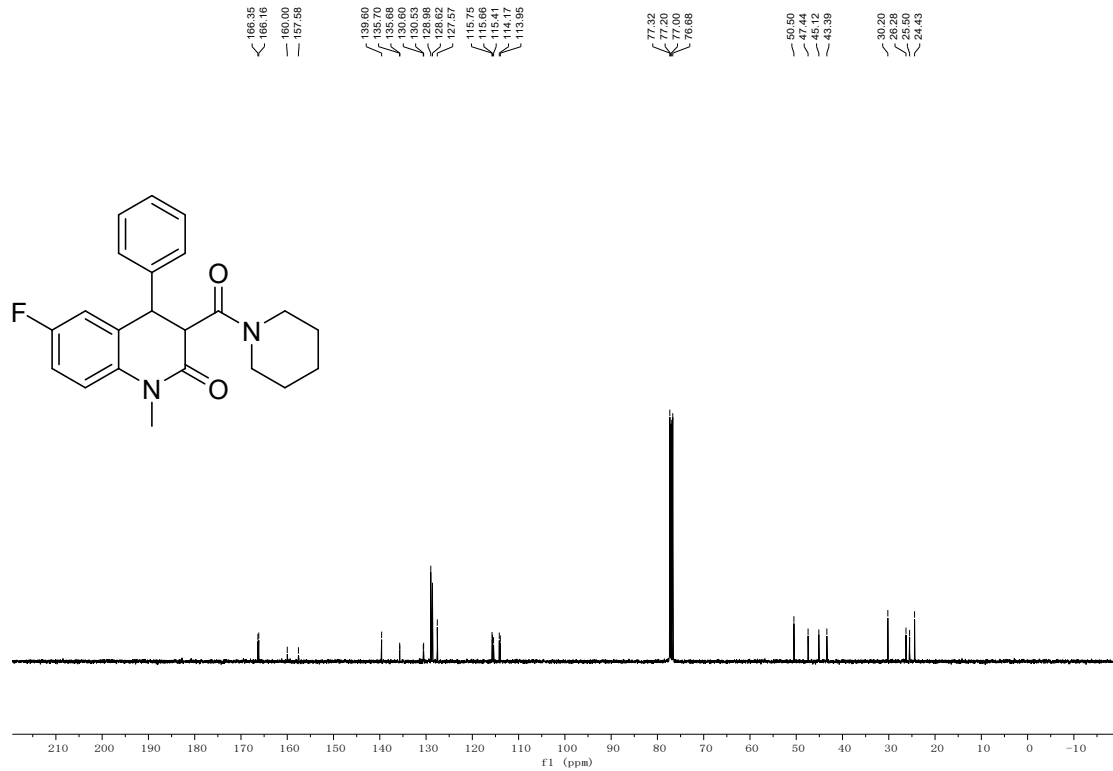
¹³C NMR (100 MHz, CDCl₃) spectra of **5c**



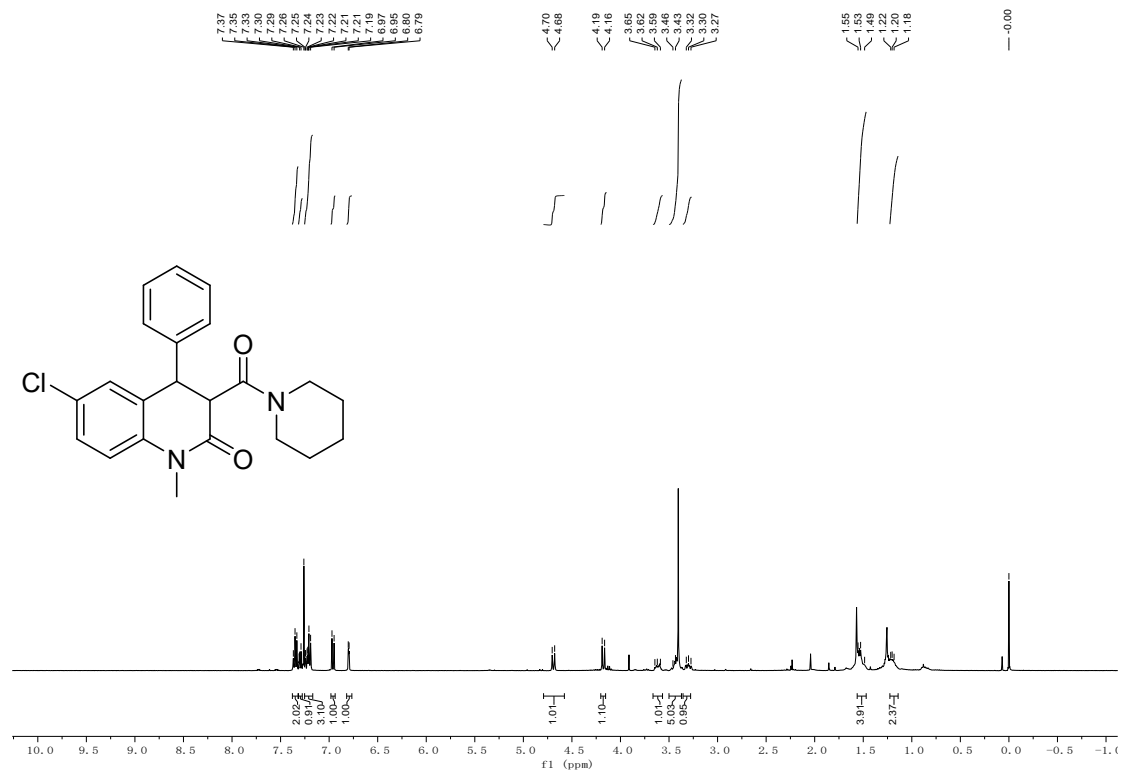
¹H NMR (400 MHz, CDCl₃) spectra of **5d**



¹³C NMR (100 MHz, CDCl₃) spectra of **5d**



¹H NMR (400 MHz, CDCl₃) spectra of **5e**



¹³C NMR (100 MHz, CDCl₃) spectra of **5e**

