Supporting Information

Facile Construction of Hydrogenated Azepino[3,2,1-*hi*]indoles by Rh(III)-catalyzed C-H Activation/[5 + 2] Annulation of *N*-Cyanoacetylindolines with Sulfoxonium Ylides

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Contents

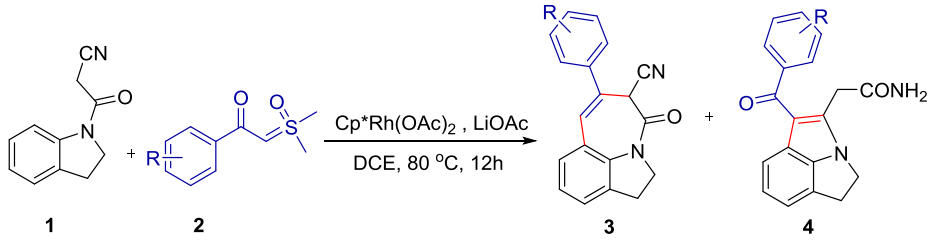
Experimental Section

General Considerations: All the reactions were carried out under argon atmosphere using standard Schlenk technique. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. The coupling constants were given in Hz. HRMS data were obtained using a TOF mode. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized under UV light (254 and 365 nm). Column chromatography was performed on silica gel 200-300 mesh. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification.

General Procedure: Preparation of the Substrates

The substrates **1a-1m**,[1] **2a-2v,**[2] were prepared according to the literature reports.

General Procedure of Rh(III)-Catalyzed C-H Activation and Annulation with Sulfoxonium Ylides



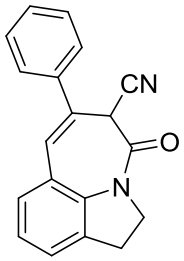
General procedure A for synthesis of 3 and 4:

A mixture of **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), Cp*Rh(OAc)$_2$·H$_2$O (6.0 mg, 0.016 mmol, 8.0 mol%), and LiOAc (3.3 mg, 0.25 equiv) were added to a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 ^{o}C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: **3**: DCM ,**4** : DCM:EA = 4:1).

Gram-scale synthesis of 3aa

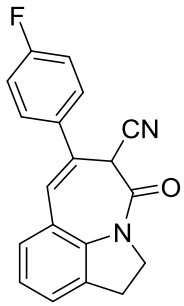
A mixture of **1** (4 mmol), **2** (6 mmol, 1.5 equiv), Cp*Rh(OAc)$_2$·H$_2$O (120.0 mg, 0.32 mmol, 8.0 mol%), and LiOAc (66 mg, 0.25 equiv) were added to a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (40 mL) was added and the mixture was stirred at 80 ^{o}C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel and moderate yield of **3aa** 60% (0.68 g) was still attained (eluent: DCM), The purification was performed by flash column chromatography on silica gel and moderate yield of **4aa** 21% (0.25 g) was still attained (eluent: DCM : EA = 4:1)

Preparation and Characterization of Product 3



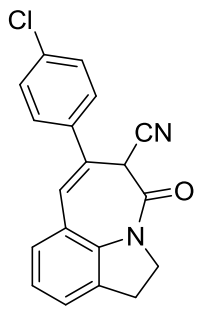
4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3aa)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 43.6 mg, 70%). M.p.: 165 - 166. ℃.^{1}H NMR (600 MHz, CDCl3) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31 - 7.27 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 4.89 (s, 1H), 4.47 - 4.44 (m, 1H), 4.12 - 4.07 (m, 1H), 3.38 – 3.26 (m, 1H), 3.16 – 3.07 (m, 1H).^{13}C NMR (151 MHz, CDCl3) δ 158.9, 138.7, 137.9, 134.1, 129.3, 128.8, 128.7, 128.6, 128.5, 126.3, 125.3, 124.5, 123.3, 114.0, 50.1, 42.8, 27.8.HRMS (ESI): Calcd for $C_{19}H_{14}N_2O$ [M+Na] $^{+}$ 309.0098, Found: 309.0098.



2-(4-fluorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ab)

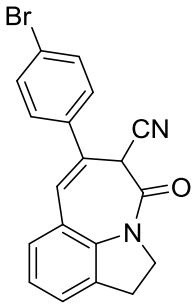
The title compound was isolated as a white solid (eluent: DCM, 34.9 mg, 57%). M.p.: 166 - 167 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 2H), 7.02 (s, 1H), 4.81 (s, 1H), 4.47 - 4.44 (m, 1H), 4.20 – 4.10 (m, 1H), 3.37 – 3.27 (m, 1H), 3.20 – 3.10 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1 (d, *J* = 248.5 Hz), 159.1, 138.1, 134.3, 131.9 (d, *J* = 2.0 Hz), 130.7 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 2.8 Hz), 128.7, 127.1 (d, *J* = 13.5 Hz), 125.7, 124.9, 124.6 (d, *J* = 3.6 Hz), 124.5, 122.9, 116.2 (d, *J* = 21.7 Hz), 113.9, 50.2, 42.9, 42.9, 27.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.2, -112.2, -112.2, -112.2. HRMS (ESI): Calcd for $C_{19}H_{13}FN_2O$ [M+Na] $^{+}$ 327.0904, Found: 327.0902.



2-(4-chlorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ac)

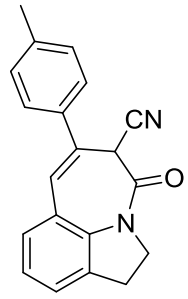
The title compound was isolated as a pale-yellow solid (eluent: DCM, 30.9 mg, 48%). M.p.: 164 - 165 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 - 7.32 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 4.79 (s, 1H), 4.446 - 4.42 (m, 1H), 4.17 - 4.12 (m, 1H), 3.35- 3.29 (m, 1H), 3.18 – 3.11 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 138.1, 137.2, 134.8, 134.3, 129.1, 129.1, 128.6, 128.2, 127.8, 125.6, 124.7, 123.2,

113.9, 50.2, 42.3, 27.9. HRMS (ESI): Calcd for $C_{19}H_{13}ClN_2O$ $[M+Na]^+$ 343.0609, Found: 343.0610.



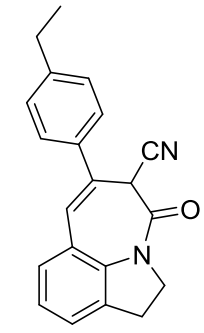
2-(4-bromophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ad)

The title compound was isolated as a white solid (eluent: DCM, 39.6 mg, 54%). M.P.: 159 - 160 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 4.81 (s, 1H), 4.51 – 4.42 (m, 1H), 4.20 - 4.15 (m, 1H), 3.40 – 3.28 (m, 1H), 3.22 – 3.14 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 138.1, 137.6, 134.3, 132.1, 129.2, 128.6, 128.3, 128.0, 125.6, 124.7, 123.2, 123.0, 113.9, 50.2, 42.2, 27.9. HRMS (ESI): Calcd for $C_{19}H_{13}BrN_2O$ $[M+Na]^+$ 387.0104, Found: 387.0104.



4-oxo-2-(p-tolyl)-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ae)

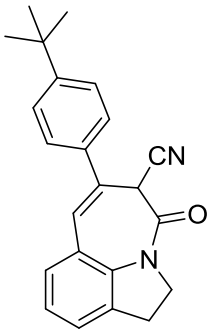
The title compound was isolated as a pale-yellow solid (eluent: DCM, 36.0 mg, 60%). M.p.: 122 - 123 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 4.89 (s, 1H), 4.50 - 4.46 (m, 1H), 4.13 - 4.08 (m, 1H), 3.36 - 3.30 (m, 1H), 3.15 - 3.10 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 138.9, 137.9, 136.0, 134.2, 129.6, 129.4, 128.5, 128.0, 126.4, 125.2, 124.5, 123.6, 114.2, 50.2, 42.4, 27.9, 21.2. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ $[M+H]^+$ 301.1135 Found: 301.1136.



2-(4-ethylphenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3af)

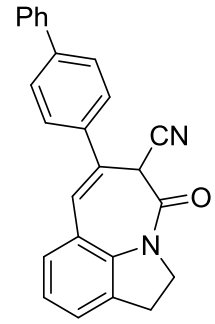
The title compound was isolated as a pale-yelow solid (eluent: DCM, 38.4 mg, 61%). M.p.: 122 - 123 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 4.91 (s, 1H), 4.50 - 4.47 (m, 1H), 4.12 - 4.07 (m, 1H), 3.39 – 3.27 (m, 1H), 3.14 - 3.10 (m, 1H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 145.2, 137.8, 136.2, 134.1, 129.4, 128.5, 128.4, 128.0, 126.4, 125.2, 124.5, 123.6,

114.2, 50.2, 42.3, 28.5, 27.9, 15.4. HRMS (ESI): Calcd for $C_{21}H_{18}N_2O$ [M+Na]$^+$ 337.1311, Found: 337.1307.



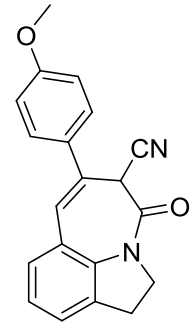
2-(4-(tert-butyl)phenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ag)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 47.5 mg, 69%). M.p.: 80 - 81 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.32 - 7.28 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.07 (s, 1H), 4.93 (s, 1H), 4.52 - 4.48 (m, 1H), 4.12 - 4.07 (m, 1H), 3.39 – 3.30 (m, 1H), 3.16 – 3.08 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 152.1, 137.9, 136.0, 134.2, 129.3, 128.6, 128.1, 126.2, 125.9, 125.2, 124.5, 123.6, 114.2, 50.2, 42.3, 34.7, 31.2, 27.9. HRMS (ESI): Calcd for $C_{23}H_{22}N_2O$ [M+Na]$^+$ 365.1624, Found: 365.1628.



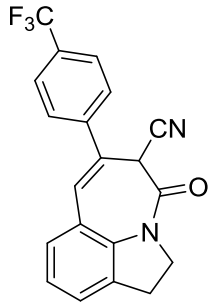
2-([1,1'-biphenyl]-4-yl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ah)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 48.8 mg, 67%). M.p.: 152 - 153 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.53 - 7.50 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 4.85 (s, 1H), 4.41 - 4.37 (m, 1H), 4.07 – 3.99 (m, 1H), 3.29 – 3.19 (m, 1H), 3.06 - 3.02 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 141.5, 140.0, 137.9, 137.6, 134.2, 128.9, 128.8, 128.6, 128.6, 127.7, 127.5, 127.0, 126.8, 125.4, 124.6, 123.4, 114.1, 50.2, 42.2, 27.8. HRMS (ESI): Calcd for $C_{25}H_{18}N_2O$ [M+Na]$^+$ 385.1311, Found: 385.1309.



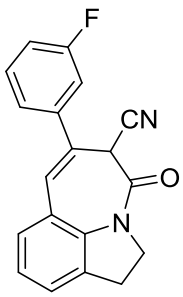
2-(4-methoxyphenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ai)

The title compound was isolated as a white solid (eluent: DCM, 29.4 mg, 46%). M.p.: 145 - 146 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.31 - 7.26 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 7.3 Hz, 2H), 4.88 (s, 1H), 4.49 - 4.46 (m, 1H), 4.13 - 4.08 (m, 1H), 3.84 (s, 3H), 3.39 – 3.26 (m, 1H), 3.15 - 3.11 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 158.9, 137.8, 134.1, 131.3, 129.0, 128.4, 127.9, 127.2, 125.1, 124.5, 123.7, 114.3, 114.2, 55.4, 50.2, 42.4, 27.9. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O_2$ [M+Na]$^+$ 339.1104, Found: 339.1100.



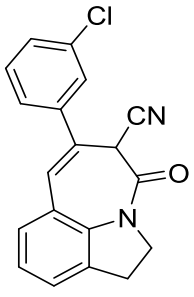
4-oxo-2-(4-(trifluoromethyl)phenyl)-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3aj)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 37.1 mg, 52%). M.p.: 160 - 161 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.37 - 7.35 (m, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 4.81 (s, 1H), 4.47 - 4.43 (m, 1H), 4.21 - 4.16 (m, 1H), 3.36 - 3.31 (m, 1H), 3.22 – 3.13 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) 158.8, 142.2, 138.3, 134.4, 130.7 (q, *J* = 33.0 Hz), 130.5, 128.7, 128.0, 126.8, 126.0, 125.9 (q, *J* = 3.2 Hz), 124.8, 123.0, 122.2 (q, *J* = 272.5 Hz), 113.8, 50.3, 42.3, 27.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.68. HRMS (ESI): Calcd for $C_{20}H_{13}F_3N_2O$ $[M+Na]^+$ 377.0872, Found: 377.0879.



2-(3-fluorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ak)

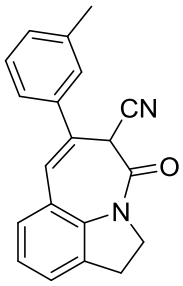
The title compound was isolated as a pale-yellow solid (eluent: DCM, 37.4 mg, 61%). M.p.: 149 - 150 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 - 7.41 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 9.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.07 (m, 2H), 4.87 (s, 1H), 4.52 - 4.48 (m, 1H), 4.18 - 4.13 (m, 1H), 3.42 – 3.31 (m, 1H), 3.22 – 3.13 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.6 Hz), 158.7, 140.9 (d, *J* = 7.7 Hz), 138.1, 134.3, 130.5 (d, *J* = 8.4 Hz), 129.7, 128.7, 128.1, 125.7, 124.7, 123.1, 122.1 (d, *J* = 2.8 Hz), 115.7 (d, *J* = 21.2 Hz), 113.8, 113.6 (d, *J* = 22.6 Hz), 50.2, 42.3, 27.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.73, -111.75, -111.76, -111.77. HRMS (ESI): Calcd for $C_{19}H_{13}FN_2O$ $[M+Na]^+$ 327.0904, Found: 327.0903.



2-(3-chlorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3al)

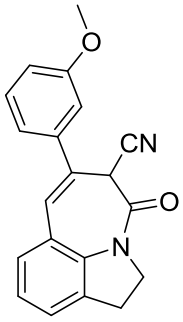
The title compound was isolated as a pale-yellow solid (eluent: DCM, 38.3 mg, 60%). M.p.: 154 - 155 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 - 7.50 (m, 1H), 7.43 – 7.32 (m, 4H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 4.82 (s, 1H), 4.47 - 4.44 (m, 1H), 4.15 - 4.10 (m, 1H), 3.35 - 3.30 (m, 1H), 3.17 - 3.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 140.5, 138.0, 134.9, 134.3, 130.1, 129.8,

128.8, 128.6, 127.9, 126.7, 125.7, 124.7, 124.6, 123.0, 113.8, 50.2, 42.2, 27.8. HRMS (ESI): Calcd for $C_{19}H_{13}ClN_2O$ [M+Na] $^+$343.0609, Found: 343.0606.



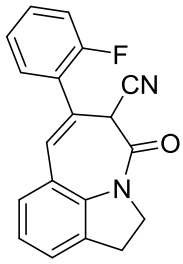
4-oxo-2-(m-tolyl)-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3am)

The title compound was isolated as a white solid (eluent: DCM, 36.1mg, 60%). M.p.: 133 - 134 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 - 7.34 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.22 - 719 (m, 2H), 7.10 (s, 1H), 4.94 (s, 1H), 4.54 - 4.51 (m, 1H), 4.15 - 4.10 (m, 1H), 3.43 – 3.31 (m, 1H), 3.18 - 3.14 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 138.9, 138.7, 137.9, 134.2, 129.6, 129.5, 128.8, 128.6, 128.6, 127.1, 125.3, 124.6, 123.6, 123.5, 114.1, 50.2, 42.4, 27.9, 21.4. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ [M+Na] $^+$ 323.1155, Found: 323.1154.



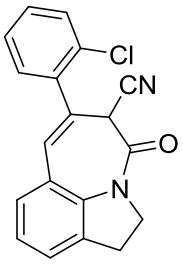
2-(3-methoxyphenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3an)

The title compound was isolated as a pale-yelow solid (eluent: DCM, 29.7 mg, 47%). M.p.: 117 - 118 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 - 7.28 (m, 3H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.03 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 4.89 (s, 1H), 4.50 - 4.46 (m, 1H), 4.13 - 7.08 (m, 1H), 3.85 (s, 3H), 3.39 – 3.28 (m, 1H), 3.15 - 3.11 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 158.9, 140.3, 137.9, 134.2, 129.9, 129.3, 128.9, 128.6, 125.4, 124.6, 123.3, 118.8, 114.3, 114.0, 112.1, 55.4, 50.2, 42.4, 27.8. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O_2$ [M+Na] $^+$ 339.1104, Found: 339.1102.



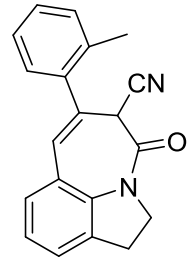
2-(2-fluorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ao)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 42.2mg, 69%). M.p.: 142 - 143 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 - 7.36 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.20 - 7.14 (m, 3H), 7.04 (s, 1H), 4.75 (s, 1H), 4.51 – 4.42 (m, 1H), 4.18 - 4.13 (m, 1H), 3.38 – 3.25 (m, 1H), 3.19 – 3.10 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 249.4 Hz), 158.9, 138.0, 134.9 (d, *J* = 3.4 Hz), 134.3, 128.7, 128.5, 128.4, 128.4 (d, *J* = 8.3 Hz), 125.5, 124.6, 123.3, 115.9 (d, *J* = 21.9 Hz), 114.0, 50.2, 42.5, 27.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.92, -112.93, -112.94. HRMS (ESI): Calcd for $C_{19}H_{13}FN_2O$ [M+Na] $^+$ 327.0904, Found: 327.096.



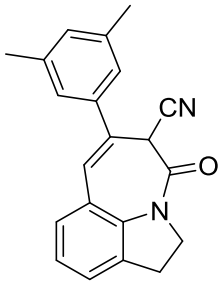
2-(2-chlorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ap)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 24.8 mg, 39%). M.P.: 132 - 133 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.34 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.94 (s, 1H), 4.67 (s, 1H), 4.50 - 4.46 (m, 1H), 4.21 - 4.16 (m, 1H), 3.37 – 3.30 (m, 1H), 3.19 – 3.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 138.5, 138.2, 134.3, 133.2, 132.0, 131.2, 130.2, 130.0, 128.6, 128.6, 127.1, 125.7, 124.5, 122.7, 114.0, 50.3, 43.4, 27.8. HRMS (ESI): Calcd for $C_{19}H_{13}ClN_2O$ $[M+Na]^+$ 343.0609, Found: 343.0611.



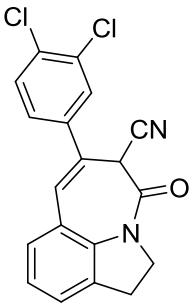
4-oxo-2-(o-tolyl)-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3aq)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 21.6 mg, 36%). M.p.: 68 - 69 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.31 (m, 1H), 7.30 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 7.20 – 7.15 (m, 1H), 6.84 (s, 1H), 4.50 (s, 1H), 4.46 - 4.40 (m, 1H), 4.28 - 4.21 (m, 1H), 3.36 - 3.27 (m, 1H), 3.23 – 3.14 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 139.7, 138.1, 135.8, 134.3, 130.8, 130.7, 130.5, 129.3, 128.8, 128.4, 126.1, 125.4, 124.5, 123.2, 114.1, 50.3, 44.0, 27.9, 20.5. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ $[M+Na]^+$ 323.1155, Found: 323.1157.



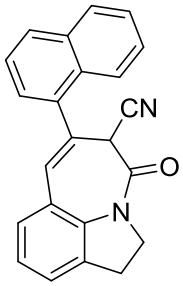
2-(3,5-dimethylphenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ar)

The title compound was isolated a white solid (eluent: DCM, 40.1 mg, 64%). M.p.: 166 - 167 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 - 7.28 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 2H), 7.06 (s, 1H), 7.02 (s, 1H), 4.92 (s, 1H), 4.54 – 4.46 (m, 1H), 4.11 - 4.06 (m, *J* = 20.9, 9.5 Hz, 1H), 3.37 - 3.31 (m, 1H), 3.14 - 3.09 (m, 1H), 2.36 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 138.9, 138.5, 137.8, 134.1, 130.4, 129.7, 128.5, 128.3, 125.2, 124.5, 124.3, 123.5, 114.2, 50.2, 42.4, 27.8, 21.3. HRMS (ESI): Calcd for $C_{21}H_{18}N_2O$ $[M+Na]^+$ 337.1311, Found: 337.1313.



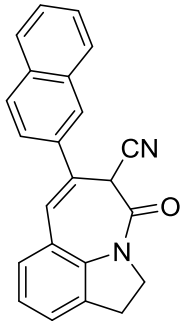
2-(3,4-dichlorophenyl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3as)

The title compound was isolated a white solid (eluent: DCM, 43.2 mg, 61%). M.p.: 180 - 181 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.36 - 7.34 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 4.75 (s, 1H), 4.45 - 4.42 (m, 1H), 4.18 - 4.13 (m, 1H), 3.37 – 3.29 (m, 1H), 3.20 – 3.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 138.6, 138.1, 134.4, 133.2, 133.0, 130.8, 130.0, 128.6, 128.4, 126.9, 125.9, 125.7, 124.7, 122.9, 113.7, 50.3, 42.1, 27.9. HRMS (ESI): Calcd for $C_{19}H_{12}ClN_2O_2$ $[M+Na]^+$ 377.0219, Found: 377.0216.



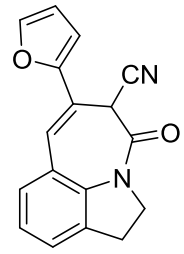
2-(naphthalen-1-yl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3at)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 39.3 mg, 58%). M.P.: 83 - 84 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 7.88 – 7.79 (m, 3H), 7.53 – 7.45 (m, 2H), 7.40 (m, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 1H), 4.65 (s, 1H), 4.45 (t, *J* = 8.6 Hz, 1H), 4.16 (dd, *J* = 19.5, 9.5 Hz, 1H), 3.34 – 3.25 (m, 1H), 3.15 – 3.07 (m, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 159.2, 138.2, 137.8, 134.3, 133.9, 131.7, 130.8, 129.4, 129.4, 128.8, 128.5, 127.1, 127.1, 126.4, 125.5, 125.3, 125.0, 124.6, 123.2, 114.2, 50.4, 44.3, 27.9. HRMS (ESI): Calcd for $C_{23}H_{16}N_2O$ $[M+Na]^+$ 359.1155, Found: 359.1157.



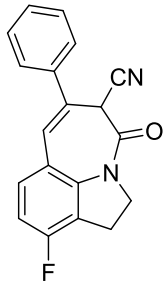
2-(naphthalen-2-yl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3au)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 45.8 mg, 68%). M.P.: 185 - 186 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.21 - 7.18 (m, 2H), 5.06 (s, 1H), 4.53 - 4.50 (m, 1H), 4.15 - 4.10 (m, 1H), 3.42 – 3.30 (m, 1H), 3.17 - 3.13 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 138.0, 136.1, 134.2, 133.2, 133.1, 129.3, 129.2, 128.8, 128.6, 128.3, 127.7, 126.8, 126.8, 125.7, 125.4, 124.6, 124.0, 123.5, 114.1, 50.2, 42.4, 27.9. HRMS (ESI): Calcd for $C_{23}H_{16}N_2O$ $[M+Na]^+$ 359.1155, Found: 359.1159.



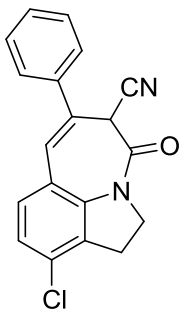
2-(furan-2-yl)-4-oxo-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3av)

The title compound was isolated a pale-yellow solid (eluent: DCM, 31.5 mg, 57%). M.p.: 167 - 168 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.41 – 7.30 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 6.52 (s, 1H), 4.97 (s, 1H), 4.60 - 4.56 (m, 1H), 4.04 - 3.99 (m, 1H), 3.46 – 3.32 (m, 1H), 3.13 - 3.09 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 151.3, 143.8, 137.6, 134.2, 128.8, 125.4, 124.6, 124.6, 123.2, 118.2, 113.7, 112.2, 108.7, 50.3, 39.5, 27.8. HRMS (ESI): Calcd for $C_{17}H_{12}N_2O_2$ $[M+Na]^+$ 299.0791, Found: 299.0792.



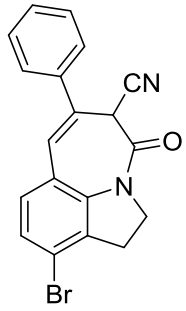
8-fluoro-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ba)

The title compound was isolated a white solid (eluent: DCM, 19.9 mg, 33%). M.p.: 157 - 158 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 8.6, 5.2 Hz, 1H), 6.97 (s, 1H), 6.85 (t, *J* = 8.4 Hz, 1H), 4.85 (s, 1H), 4.50 – 4.44 (m, 1H), 4.08 (dd, *J* = 21.0, 9.5 Hz, 1H), 3.29 – 3.20 (m, 1H), 3.16 – 3.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0 (d, *J* = 250.1 Hz), 158.8, 140.2 (d, *J* = 9.2 Hz), 138.8 (d, *J* = 8.2 Hz), 130.8, 129.0, 128.8, 128.8, 128.1, 126.4, 119.8 (d, *J* = 3.0 Hz), 119.8 (d, *J* = 22.7 Hz), 113.9, 112.6 (d, *J* = 1.8 Hz), 50.7, 42.4, 24.2. ^{19}F NMR (376 MHz, CDCl3) δ -116.09, -116.11, -116.13. HRMS (ESI): Calcd for $C_{19}H_{13}N_2O$ $[M+Na]^+$ 327.0904, Found: 327.0905.



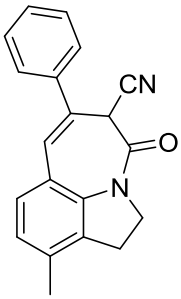
8-chloro-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile(3ca)

The title compound was isolated as a white solid (eluent: DCM, 39.7 mg, 62%). M.p.: 130 - 131 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 4.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 4.93 (s, 1H), 4.55 – 4.48 (m, 1H), 4.13 (dd, *J* = 20.9, 9.6 Hz, 1H), 3.35 – 3.29 (m, 1H), 3.22 – 3.17 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 138.9, 138.7, 132.4, 131.3, 130.0., 129.7, 129.0, 129.0, 128.0, 126.4, 124.8, 121.8, 113.8, 49.9, 42.4, 27.3. HRMS (ESI): Calcd for $C_{19}H_{13}ClN_2O$ $[M+Na]^+$ 343.0609, Found: 343.0608.



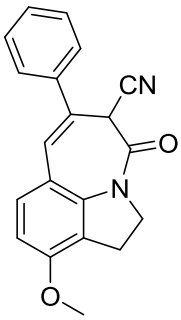
8-bromo-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3da)

The title compound was isolated as a white solid (eluent: DCM, 45.7 mg, 63%). M.p.: 149 - 150 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.1 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.05 (s, 1H), 4.95 (s, 1H), 4.55 - 4.51 (m, 1H), 4.18 - 4.13 (m, 1H), 3.38 – 3.28 (m, 1H), 3.24 – 3.16 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 138.6, 138.5, 134.7, 130.0, 129.7, 129.0, 129.0, 128.1, 127.6, 126.4, 122.2, 120.1, 113.8, 49.5, 42.3, 29.3. HRMS (ESI): Calcd for $C_{19}H_{13}BrN_2O$ $[M+Na]^+$ 387.0104, Found: 387.0104.



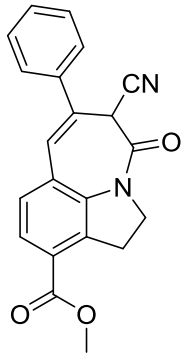
8-methyl-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ea)

The title compound was isolated a white solid (eluent: DCM, 35.8 mg, 60%). M.p.: 151 - 152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.44 - 7.34 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 4.90 (s, 1H), 4.50 - 4.46 (m, 1H), 4.13 - 4.06 (m, 1H), 3.25 - 3.17 (m, 1H), 3.11 – 2.99 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 139.0, 137.6, 135.4, 132.5, 128.9, 128.6, 128.5, 128.2, 126.4, 126.0, 121.1, 114.2, 49.9, 42.3, 26.6, 18.7. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ $[M+Na]^+$ 323.1155, Found: 323.1153.



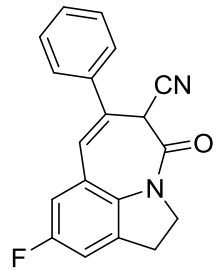
8-methoxy-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3fa)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 26.3 mg, 42%). M.p.: 156 - 157 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.03 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 4.91 (s, 1H), 4.51 - 4.48 (m, 1H), 4.12 - 4.07 (m, 1H), 3.92 (s, 3H), 3.23 – 3.15 (m, 1H), 3.11 - 3.07 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 156.4, 139.4, 139.2, 130.6, 128.9, 128.8, 128.4, 126.9, 126.4, 120.5, 117.0, 114.4, 107.9, 55.7, 50.6, 42.4, 24.8. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O_2$ $[M+Na]^+$ 339.1104, Found: 339.1103.



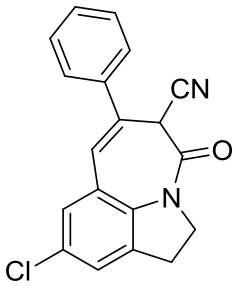
Methyl 3-cyano-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-8-carboxylate (3ga)

The title compound was isolated as a white solid (eluent: DCM, 46.3 mg, 67%). M.p.: 175 - 176 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.14 (s, 1H), 4.97 (s, 1H), 4.59 – 4.51 (m, 1H), 4.13 (dd, *J* = 20.8, 9.5 Hz, 1H), 3.98 (s, 3H), 3.68 – 3.60 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 158.8, 138.7, 138.5, 137.7, 131.9, 129.2, 129.1, 128.7, 128.1, 126.9, 126.7, 126.5, 125.6, 113.7, 52.2, 50.2, 42.4, 29.2. HRMS (ESI): Calcd for $C_{21}H_{16}N_2O_3$ $[M+Na]^+$ 367.1053, Found: 367.1058.



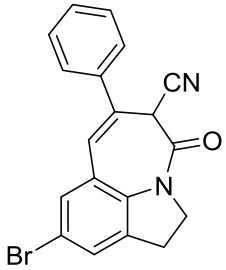
9-fluoro-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ha)

The title compound was isolated as a white solid (eluent: DCM, 42.6 mg, 70%). M.p.: 163 - 164 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 13.2 Hz, 2H), 4.93 (s, 1H), 4.56 - 4.53 (m, 1H), 4.19 - 4.14 (m, 1H), 3.42 – 3.32 (m, 1H), 3.18 - 3.14 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (d, *J* = 242.9 Hz), 158.6, 138.5, 136.6 (d, *J* = 9.2 Hz), 134.3, 130.8, 129.1, 129.0, 127.7 (d, *J* = 1.9 Hz), 126.4, 124.2 (d, *J* = 9.0 Hz), 113.9 (d, *J* = 2.9 Hz), 113.7, 113.6 (d, *J* = 25.0 Hz), 50.5, 42.2, 28.0. ^{19}F NMR (376 MHz, CDCl3) δ -117.73, -117.76, -117.78. HRMS (ESI): Calcd for $C_{19}H_{13}N_2OF$ $[M+Na]^+$ 327.0904, Found: 327.0903.



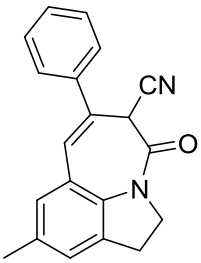
9-chloro-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ia)

The title compound was isolated as a pale-yellow solid (eluent: DCM, 47.7 mg, 74%). M.p.: 204 - 205 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.31 - 7.28 (m, 2H), 7.00 (s, 1H), 4.92 (s, 1H), 4.53 - 4.49 (m, 1H), 4.15 - 4.10 (m, 1H), 3.40 – 3.29 (m, 1H), 3.18 – 3.08 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 138.5, 136.6, 136.2, 130.8, 129.8, 129.1, 129.0, 127.9, 127.6, 126.5, 125.7, 124.3, 113.8, 50.4, 42.4, 27.8. HRMS (ESI): Calcd for $C_{19}H_{13}N_2OCl$ $[M+Na]^+$ 343.0609, Found: 343.0611.



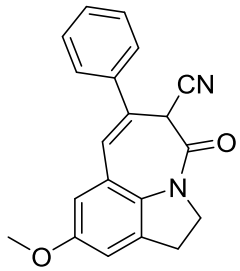
9-bromo-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ja)

The title compound was isolated as a white solid (eluent: DCM, 41.5 mg, 57%). M.p.: 201 - 202 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.48 - 7.46 (m, 4H), 7.45 – 7.41 (m, 1H), 7.02 (s, 1H), 4.95 (s, 1H), 4.54 - 4.51 (m, 1H), 4.17 - 4.12 (m, 1H), 3.43 – 3.33 (m, 1H), 3.20 – 3.11 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 138.5, 137.0, 136.4, 130.8, 130.7, 129.1, 129.0, 128.4, 127.5, 126.4, 124.7, 117.3, 113.7, 50.4, 42.3, 27.7. HRMS (ESI): Calcd for $C_{19}H_{13}BrN_2O$ $[M+Na]^+$ 387.0104, Found: 387.0100.



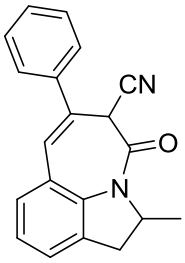
9-methyl-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3ka)

The title compound was isolated as a white solid (eluent: DCM, 34.7 mg, 58%). M.p.: 179 - 180 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 750 (m, 2H), 7.46 – 7.34 (m, 3H), 7.14 (s, 1H), 7.09 (s, 1H), 7.03 (s, 1H), 4.89 (s, 1H), 4.49 - 4.44 (m, 1H), 4.12 - 4.05 (m, 1H), 3.37 – 3.23 (m, 1H), 3.12 - 3.05 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 139.0, 135.8, 134.4, 134.3, 129.2, 128.9, 128.8, 128.7, 128.6, 126.5, 126.4, 123.1, 114.2, 50.3, 42.4, 27.8, 21.0. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ $[M+Na]^+$ 323.1155, Found: 323.1155.



9-methoxy-4-oxo-2-phenyl-3,4,6,7-tetrahydroazepino[3,2,1-hi]indole-3-carbonitrile (3la)

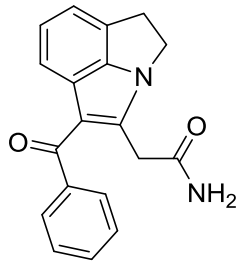
The title compound was isolated as a white solid (eluent: DCM, 30.4 mg, 48%). M.p.: 171 - 172 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.05 (s, 1H), 6.96 (s, 1H), 6.78 (s, 1H), 4.91 (s, 1H), 4.52 - 4.48 (m, 1H), 4.15 - 4.10 (m, 1H), 3.86 (s, 3H), 3.38 – 3.29 (m, 1H), 3.14 - 3.10 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 156.7, 138.8, 136.0, 132.0, 129.7, 128.9, 128.8, 128.5, 126.4, 123.9, 114.2, 113.5, 110.9, 55.7, 50.3, 42.3, 28.1. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O_2$ $[M+Na]^+$ 339.1104, Found: 339.1103.



(±)-2-hydroxy-5-methoxy-2,8-diphenyl-2,3-dihydrobenzo[de]chromene-9-carbonitrile (3ma)

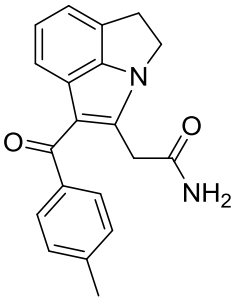
The mixtures were isolated as pale-yellow solids in 71% overall yield (DCM, 42.5 mg) dr =1:2.4. M.p.: 150 - 151 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.1 Hz, 0.88H), 7.46 (d, *J* = 7.2 Hz, 2.06H), 7.38 – 7.29 (m, 4.67H), 7.26 – 7.17 (m, 3.11H), 7.11 (t, *J* = 7.7 Hz, 1.46H), 7.07 (s, 1H), 6.87 (s, 0.43H), 4.99 (s, 1H), 4.95 – 4.86 (m, 1.47H), 4.09 (s, 0.42H), 3.51 - 3.41 (M, 1.51H), 2.62 (t, *J* = 14.9 Hz, 1.50H), 1.22 – 1.18 (m, 4.59H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 158.5, 139.2, 137.9, 137.5, 136.2, 133.3, 132.9, 130.4, 129.3, 129.0, 129.0, 128.9, 128.7, 128.7, 128.6, 128.2, 127.9, 126.9, 126.3, 125.9, 125.5, 124.6, 124.5, 123.9, 123.8, 114.8, 113.9, 58.7, 58.2, 43.0, 42.4, 36.0, 35.6, 20.3, 20.2. HRMS (ESI): Calcd for $C_{20}H_{16}N_2O$ $[M+Na]^+$ 323.1155, Found: 323.1151.

Preparation and Characterization of Products 4



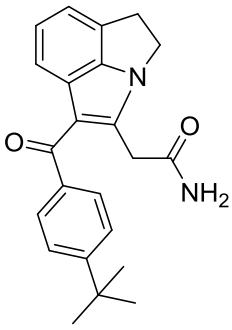
2-(5-benzoyl-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4aa)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 9.1 mg, 15%). M.p.: 245 - 246 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.28 (d, *J* = 9.3 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.33 (s, 2H), 3.22 (s, 2H), 3.19 (s, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 167.0, 156.8, 141.6, 138.7, 133.0, 130.9, 129.8, 128.6, 127.5, 126.3, 123.0, 121.9, 104.1, 48.3, 44.9, 28.7. HRMS (ESI): Calcd for $C_{19}H_{16}N_2O_2$ $[M+Na]^+$ 327.1104, Found: 327.1100.



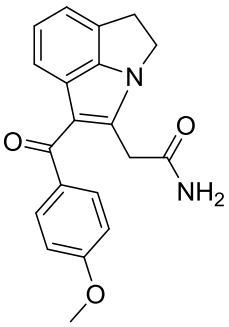
2-(5-(4-methylbenzoyl)-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ae)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 11.2 mg, 18%). M.p.: 220 - 221 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 2H), 6.95 - 6.86 (m, 5H), 6.61 – 6.54 (m, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 4.23 (t, *J* = 7.3 Hz, 2H), 3.14 – 3.07 (m, 4H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 167.0, 156.1, 140.2, 138.7, 138.6, 133.0, 130.9, 128.8, 128.2, 126.5, 123.1, 121.9, 104.3, 48.3, 45.1, 28.7, 21.4. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_2$ $[M+Na]^+$ 341.1261, Found: 341.1265.



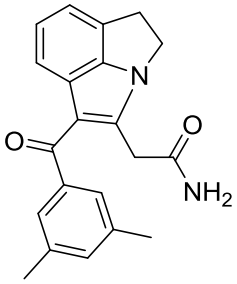
2-(5-(4-(tert-butyl)benzoyl)-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ag)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 16.8 mg, 23%). M.p.: 195 - 196 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.96 - 6.93 (m, 3H), 6.60 – 6.49 (m, 2H), 4.23 (t, *J* = 7.3 Hz, 2H), 3.16 – 3.06 (m, 4H), 1.18 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 167.0, 156.1, 153.3, 138.7, 138.5, 132.9, 130.9, 128.6, 126.5, 124.4, 123.0, 121.9, 104.3, 48.3, 45.0, 34.7, 31.13, 28.7. HRMS (ESI): Calcd for $C_{23}H_{24}N_2O_2$ $[M+Na]^+$ 383.1730, Found: 383.1734.



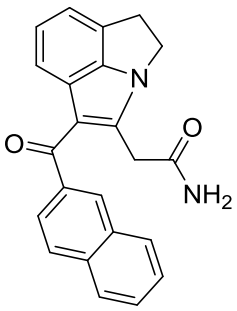
2-(5-(4-methoxybenzoyl)-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ai)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 22.2 mg, 33%). M.p.: 215 - 216 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.96 - 6.94 (m, 1H), 6.65 – 6.51 (m, 4H), 4.23 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 3H), 3.15 – 3.06 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 167.1, 161.0, 155.8, 138.6, 133.8, 133.0, 130.9, 130.8, 126.7, 123.2, 121.9, 112.8, 104.1, 55.2, 48.3, 44.9, 28.7. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_3$ $[M+Na]^+$ 357.1210, Found: 357.1212.



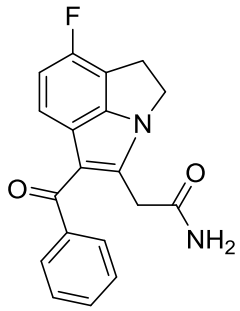
2-(5-(3,5-dimethylbenzoyl)-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ar)

The title compound was isolated a pale-yellow solid (eluent: DCM:EA, 10.7 mg, 17%). M.P.: 246 - 247 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 6.93 (d, *J* = 7.1 Hz, 1H), 6.81 (s, 1H), 6.60 - 6.55 (m, 3H), 6.50 (d, *J* = 7.8 Hz, 1H), 4.28 – 4.16 (m, 2H), 3.17 – 3.06 (m, 4H), 2.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.9, 167.0, 156.4, 141.3, 138.6, 136.8, 132.8, 131.4, 130.9, 126.5, 122.9, 121.8, 104.3, 48.3, 44.8, 28.6, 21.1. HRMS (ESI): Calcd for $C_{21}H_{20}N_2O_2$ $[M+Na]^+$ 355.1417, Found: 355.1419.



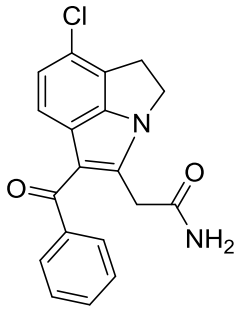
2-(5-(2-naphthoyl)-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4au)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 16.8 mg, 24%). M.P.: >290 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.70 – 7.60 (m, 3H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.33 (m, 2H), 6.99 – 6.89 (m, 2H), 6.51 (d, *J* = 7.7 Hz, 1H), 6.48 – 6.42 (m, 1H), 4.28 (t, *J* = 6.9 Hz, 2H), 3.21 – 3.09 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 167.0, 156.7, 138.9, 138.8, 133.9, 133.1, 132.5, 130.9, 129.3, 128.9, 127.5, 127.1, 126.8, 126.3, 126.1, 125.6, 123.3, 122.0, 104.4, 100.0, 48.4, 45.1, 28.7. HRMS (ESI): Calcd for $C_{23}H_{18}N_2O_2$ $[M+Na]^+$ 377.1261, Found: 377.1257.



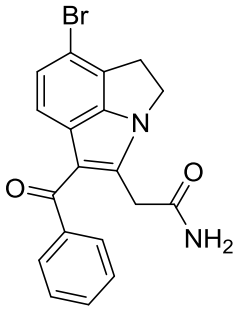
2-(5-benzoyl-8-fluoro-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ba)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 12.9 mg, 20%). M.P.: 102 - 103 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 8.06 (s, 2H), 7.21 – 7.18 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.45 – 6.43 (m, 1H), 6.29 (t, *J* = 8.5 Hz, 1H), 4.27 (s, 2H), 3.17 (s, 2H), 3.12 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, CDCl3) δ 194.3, 167.1, 157.7, 156.6, 156.1, 141.4, 140.6, 140.5, 132.6, 132.5, 129.8, 128.5, 127.6, 122.4, 122.4, 118.4, 118.3, 110.7, 110.5, 103.5, 48.7, 44.7, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.4. HRMS (ESI): Calcd for $C_{19}H_{15}FN_2O_2$ $[M+Na]^+$ 345.1010, Found: 345.1002.



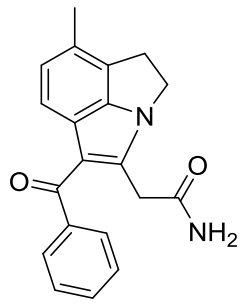
2-(5-benzoyl-8-chloro-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ca)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 10.6 mg, 16%). M.P.: 118 - 119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.31 – 7.27 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 4.33 (t, *J* = 6.8 Hz, 2H), 3.21 – 3.16 (m, 4H). ^{13}C NMR (151 MHz, CDCl3) δ 194.5, 167.0, 156.6, 141.3, 139.6, 132.2, 131.3, 130.0, 128.5, 127.7, 127.6, 124.7, 123.1, 103.5, 48.1, 44.9, 28.2. HRMS (ESI): Calcd for $C_{19}H_{15}N_2O_2Cl$ $[M+Na]^+$ 361.0714, Found: 361.0716.



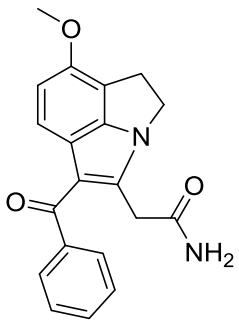
2-(5-benzoyl-8-bromo-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4da)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 8.9 mg, 12%). M.P.: 190 - 191 ℃. ^{1}H NMR (600 MHz, CDCl3) δ 8.08 (s, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 4.25 (s, 2H), 3.16 (s, 2H), 3.09 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, CDCl3) δ 194.3, 167.2, 156.9, 141.3, 139.4, 133.5, 132.4, 129.9, 128.5, 127.7, 125.9, 125.4, 116.0, 103.4, 47.7, 44.7, 30.1. HRMS (ESI): Calcd for $C_{19}H_{15}N_2O_2Br$ $[M+Na]^+$ 405.0209, Found: 405.0209.



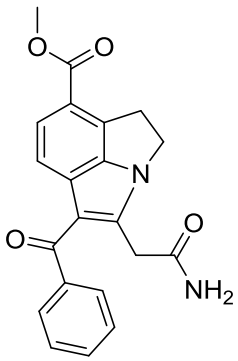
2-(5-benzoyl-8-methyl-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ea)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 16.3 mg, 26%). M.P.: 124 - 125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.27 - 7.23 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.45 (s, 2H), 4.31 - 4.29 (m, 2H), 3.19 (s, 2H), 3.07 (t, *J* = 7.8 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 167.1, 156.4, 141.7, 138.4, 131.5, 131.4, 130.9, 129.7, 128.6, 127.5, 124.3, 123.6, 104.2, 48.1, 45.0, 27.5, 18.3. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_2$ $[M+Na]^+$ 341.1261, Found: 341.1263.



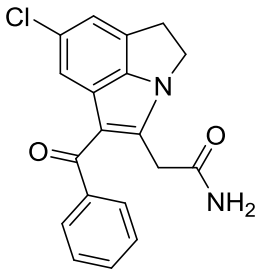
2-(5-benzoyl-8-methoxy-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4fa)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 26.0 mg, 39%). M.P.: 99 - 100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.51 (d, *J* = 8.7 Hz, 1H), 6.23 (d, *J* = 8.7 Hz, 1H), 4.33 - 4.28 (m, 2H), 3.74 (s, 3H), 3.22 (s, 2H), 3.09 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 156.2, 153.9, 141.7, 140.1, 132.2, 129.6, 128.6, 127.6, 127.5, 119.3, 119.2, 106.3, 103.9, 55.5, 48.7, 44.9, 25.8. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_2$ $[M+Na]^+$ 357.1210, Found: 357.1213.



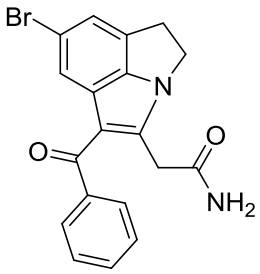
Methyl 4-(2-amino-2-oxoethyl)-5-benzoyl-1,2-dihydropyrrolo [3,2,1-hi]indole-8-carboxylate (4ga)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 11.4 mg, 16%). M.P.: 123 - 124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.27 – 7.24 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.32 (s, 2H), 3.86 (s, 3H), 3.53 (t, *J* = 7.8 Hz, 2H), 3.21 (s, 2H). ^{13}C NMR (151 MHz, CDCl3) δ 194.6, 166.8, 166.5, 157.6, 141.2, 139.2, 136.6, 130.9, 130.6, 130.1, 128.5, 127.7, 124.1, 123.5, 51.9, 48.4, 44.8, 29.9. HRMS (ESI): Calcd for $C_{21}H_{18}N_2O_4$ $[M+Na]^+$ 385.1159, Found: 385.1156.



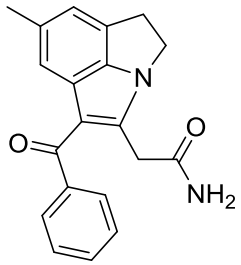
2-(5-benzoyl-7-chloro-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ia)

The title compound was isolated a pale-yellow solid (eluent: DCM:EA, 8.4 mg, 12%). M.P.:231 - 232 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.98 – 6.95 (m, 1H), 6.48 (d, *J* = 1.9 Hz, 1H), 4.31 (s, 2H), 3.18 (s, 2H), 3.15 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 166.6, 156.8, 141.04 1374, 134.8, 130.4, 130.1, 128.3, 128.3, 127.7, 127.4, 122.1, 103.4, 48.5, 45.0, 28.6. HRMS (ESI): Calcd for $C_{19}H_{15}N_2O_2Cl$ $[M+Na]^+$ 361.0714, Found: 361.0719.



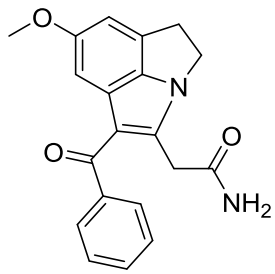
2-(5-benzoyl-7-bromo-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ja)

The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 9.1 mg, 12%). M.P.: >280 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.27 - 7.23 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.04 – 7.00 (m, 3H), 6.57 (d, *J* = 1.8 Hz, 1H), 4.23 (s, 2H), 3.12 – 3.06 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 166.5, 156.9, 141.0, 137.8, 135.1, 133.4, 130.1, 128.3, 127.9, 127.7, 124.9, 115.8, 103.4, 48.5, 45.0, 28.5. HRMS (ESI): Calcd for $C_{19}H_{15}N_2O_2Br$ $[M+Na]^+$ 405.0209, Found: 405.0211.



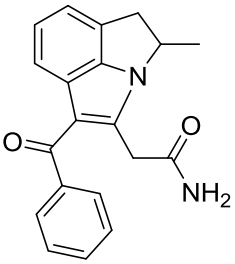
2-(5-benzoyl-7-methyl-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ka)

The title compound was isolated a pale-yellow solid (eluent: DCM:EA, 10.4 mg, 16%). M.P.:210 - 211 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.24 (s, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.81 (s, 1H), 6.30 (s, 1H), 4.28 (s, 2H), 3.17 (s, 2H), 3.11 (t, *J* = 7.4 Hz, 2H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.8, 166.6, 156.4, 141.6, 136.7, 133.0, 132.7, 131.4, 129.7, 128.4, 127.4, 125.8, 122.9, 104.3, 48.4, 45.2, 28.6, 20.7. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_2$ $[M+Na]^+$ 341.1261, Found: 341.1267.



2-(5-benzoyl-7-methoxy-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4la)

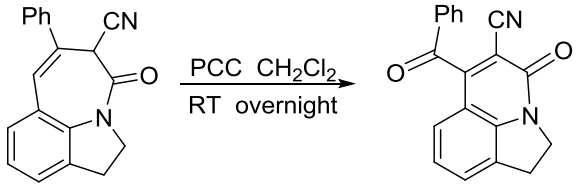
The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 15.3 mg, 23%). M.P.: 204 - 205 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 2H), 7.26 – 7.23 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.08 (m, 2H), 6.60 – 6.57 (m, 1H), 5.97 (d, *J* = 2.4 Hz, 1H), 4.28 (s, 2H), 3.24 (s, 2H), 3.20 (s, 3H), 3.11 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 166.5, 157.4, 155.4, 141.9, 134.5, 132.7, 129.6, 128.3, 127.6, 126.8, 114.1, 110.6, 104.1, 55.3, 48.5, 44.7, 28.9. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_3$ $[M+Na]^+$ 357.1210, Found: 357.1210.



2-(5-benzoyl-2-methyl-1,2-dihydropyrrolo[3,2,1-hi]indol-4-yl)acetamide (4ma)

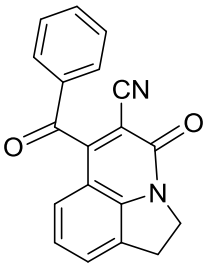
The title compound was isolated as a pale-yellow solid (eluent: DCM:EA, 12.6 mg, 20%). M.P.: 216 - 217 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.25 - 7.22 (m, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.02 (m, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.67 – 6.59 (m, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 5.03 - 4.96 (m, 1H), 3.48 - 3.42 (m, 1H), 3.24 (d, *J* = 12.9 Hz, 1H), 3.15 (d, *J* = 12.9 Hz, 1H), 2.64 (d, *J* = 15.8 Hz, 1H), 1.36 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 166.3, 156.7, 141.7, 137.4, 131.9, 130.8, 129.7, 128.5, 127.5, 126.8, 123.1, 122.4, 104.2, 56.1, 45.0, 36.2, 21.0. HRMS (ESI): Calcd for $C_{20}H_{18}N_2O_2$ $[M+Na]^+$ 341.1261, Found: 341.1262.

Derivatization of 3aa



3aa **5aa**

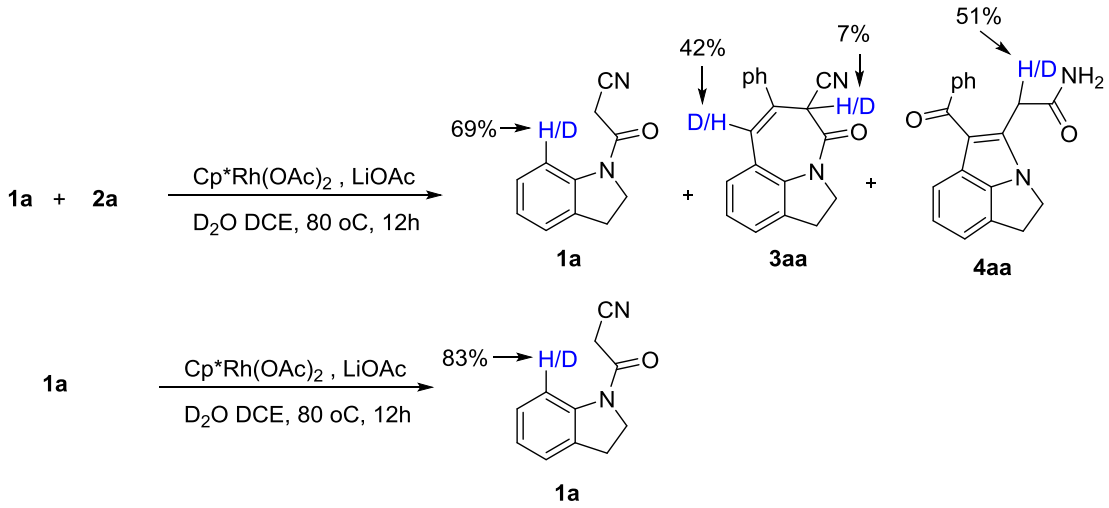
A mixture of **3aa** (0.2 mmol) and pcc (0.4 mmol) were added to a Schlenk tube equipped with a stir bar. Dry DCM (2.0 mL) was added and the mixture was stirred at rt for overnight. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: DCM).



6-benzoyl-4-oxo-1,2-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carbonitrile (5aa)

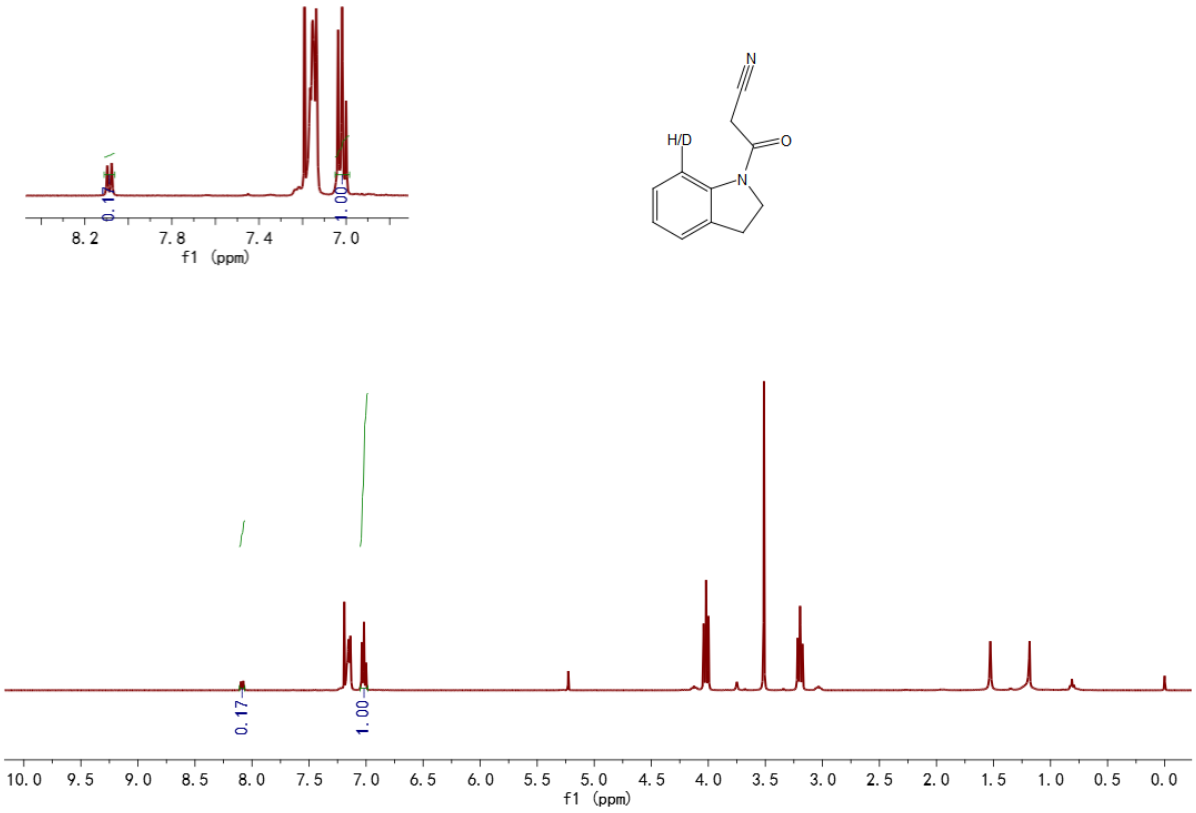
The title compound was isolated as a yellow solid (eluent: DCM, 27.6 mg, 46%). M.P.: 244 -245 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 - 7.55 (m, 1H), 7.50 – 7.44 (m, 3H), 7.42 - 7.40 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 1H), 4.52 – 4.31 (m, 2H), 3.30 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 185.8, 158.3, 157.1, 138.9, 135.2, 134.4, 131.4, 130.4, 128.8, 128.6, 128.4, 125.4, 124.6, 118.3, 114.9, 50.3, 26.4. HRMS (ESI): Calcd for $C_{19}H_{12}N_2O_2$ $[M+Na]^+$ 323.0791, Found: 323.0786.

H/D exchange experiments:

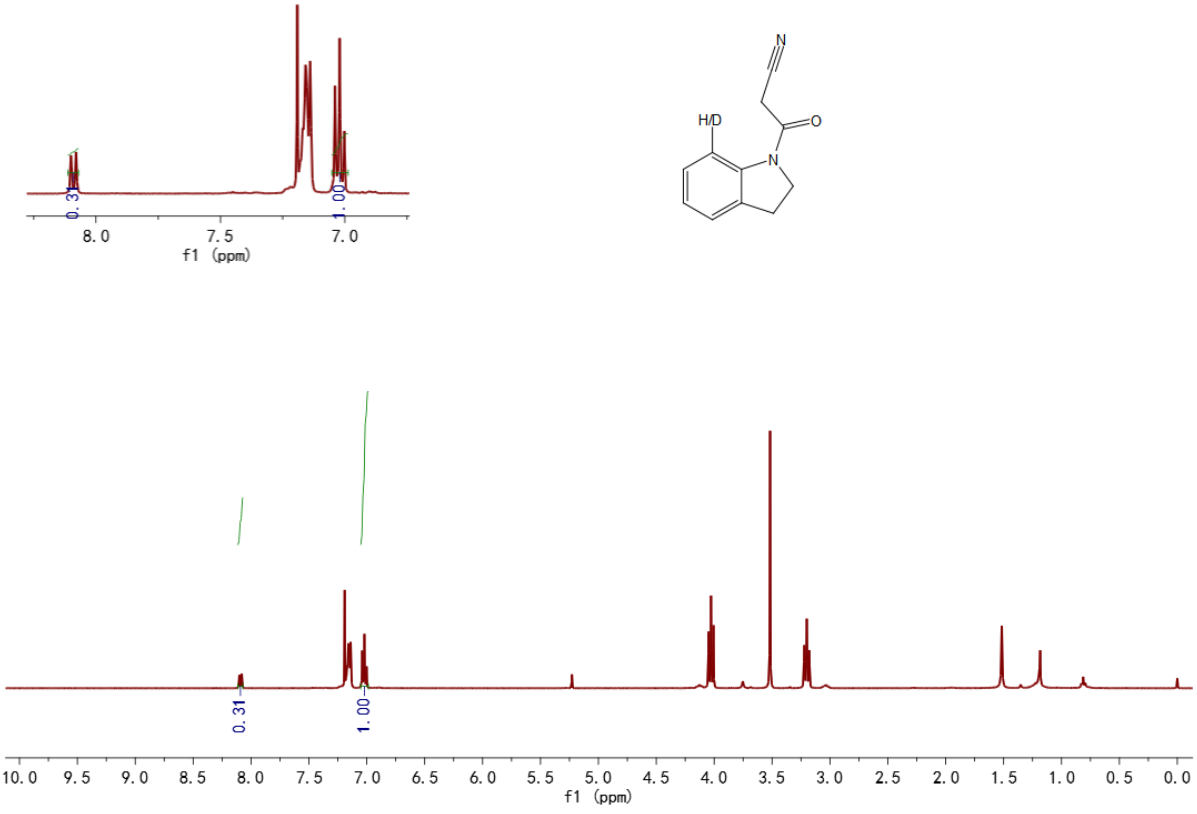


Procedures for the reaction without 2a: A mixture of **1** (0.2 mmol), Cp*Rh(OAc)$_2$·H$_2$O (6.0 mg, 0.016 mmol, 8.0 mol%), D$_2$O (10 equiv), and LiOAc (3.3 mg, 0.25 equiv) were added to a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 ^{o}C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: DCM **4**).

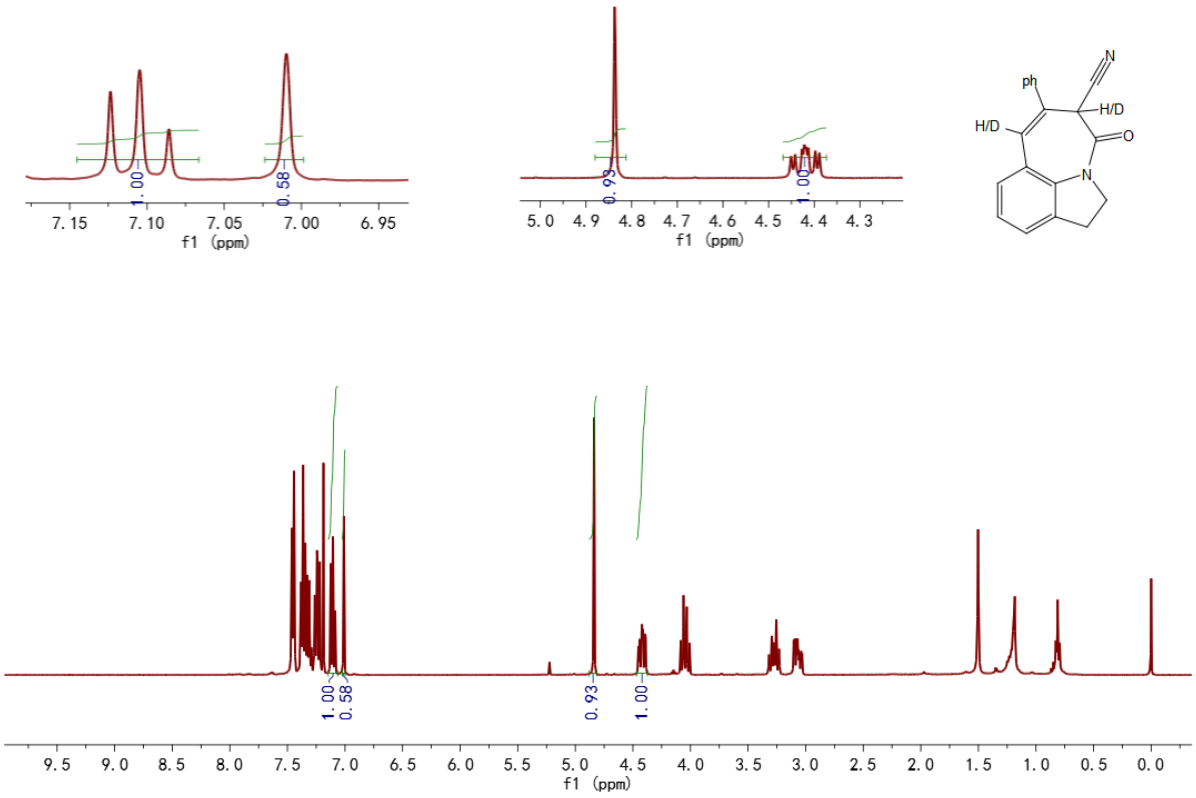
Procedures for the reaction in the presence of 2a: A mixture of **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), Cp*Rh(OAc)$_2$·H$_2$O (6.0 mg, 0.016 mmol, 8.0 mol%), D$_2$O (10 equiv), and LiOAc (3.3 mg, 0.25 equiv) were added to a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (2.0 mL) was added and the mixture was stirred at 80 ^{o}C for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: PE:EA = 4:1 - 1:1).



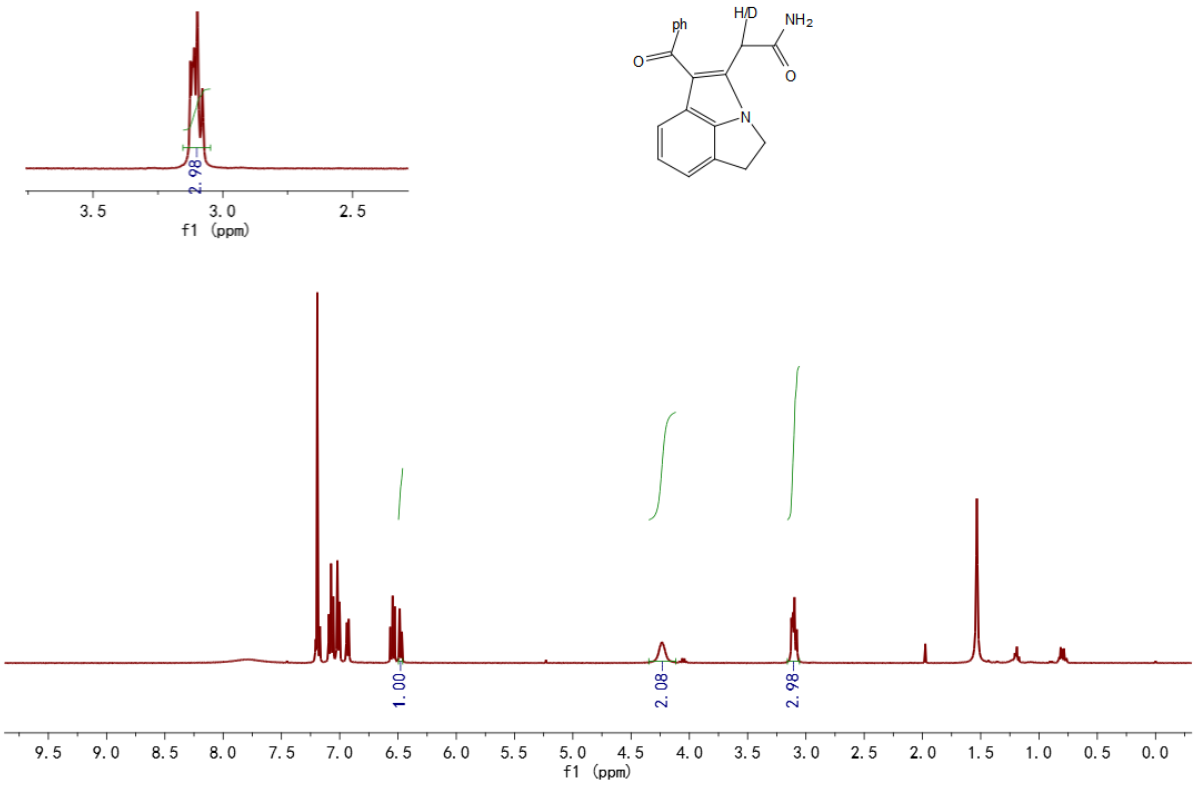
^{1}H NMR of the recovered **1a** of the reaction without **2a**



^{1}H NMR of the recovered **1a** of the reaction in presence of **2a**

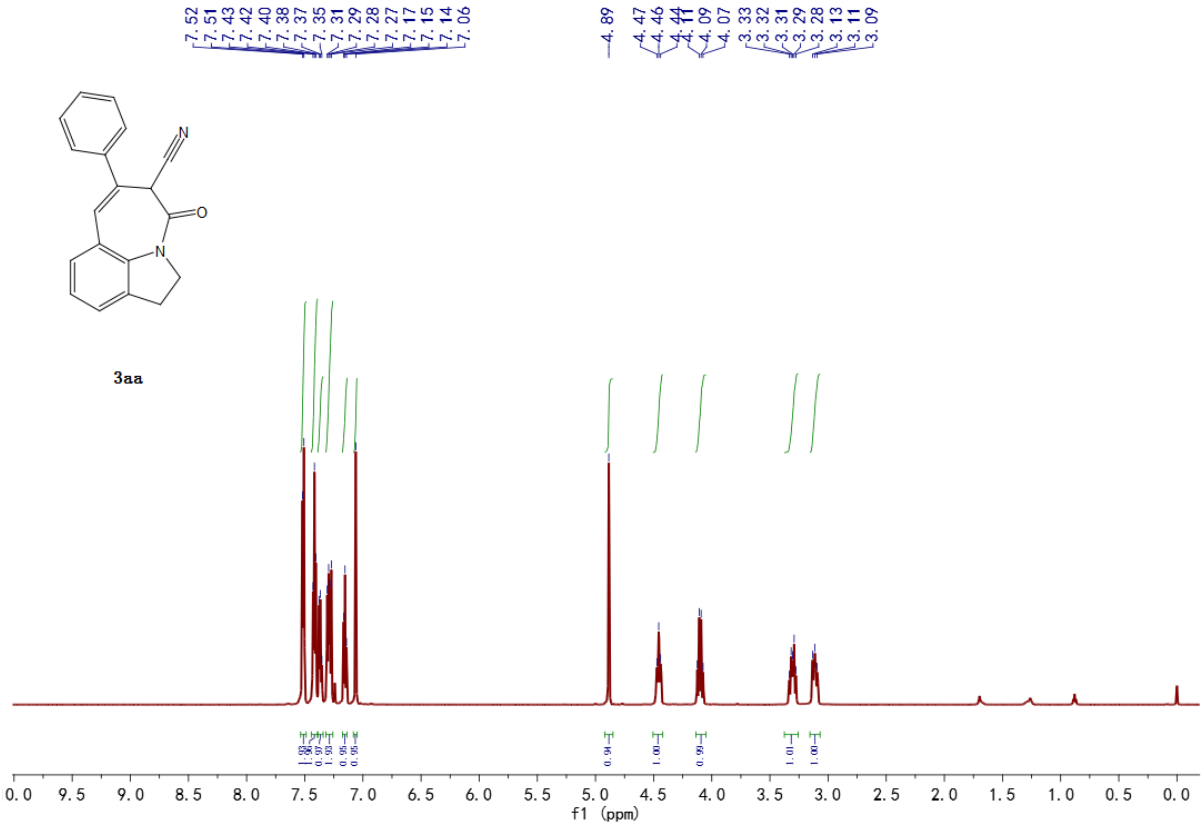


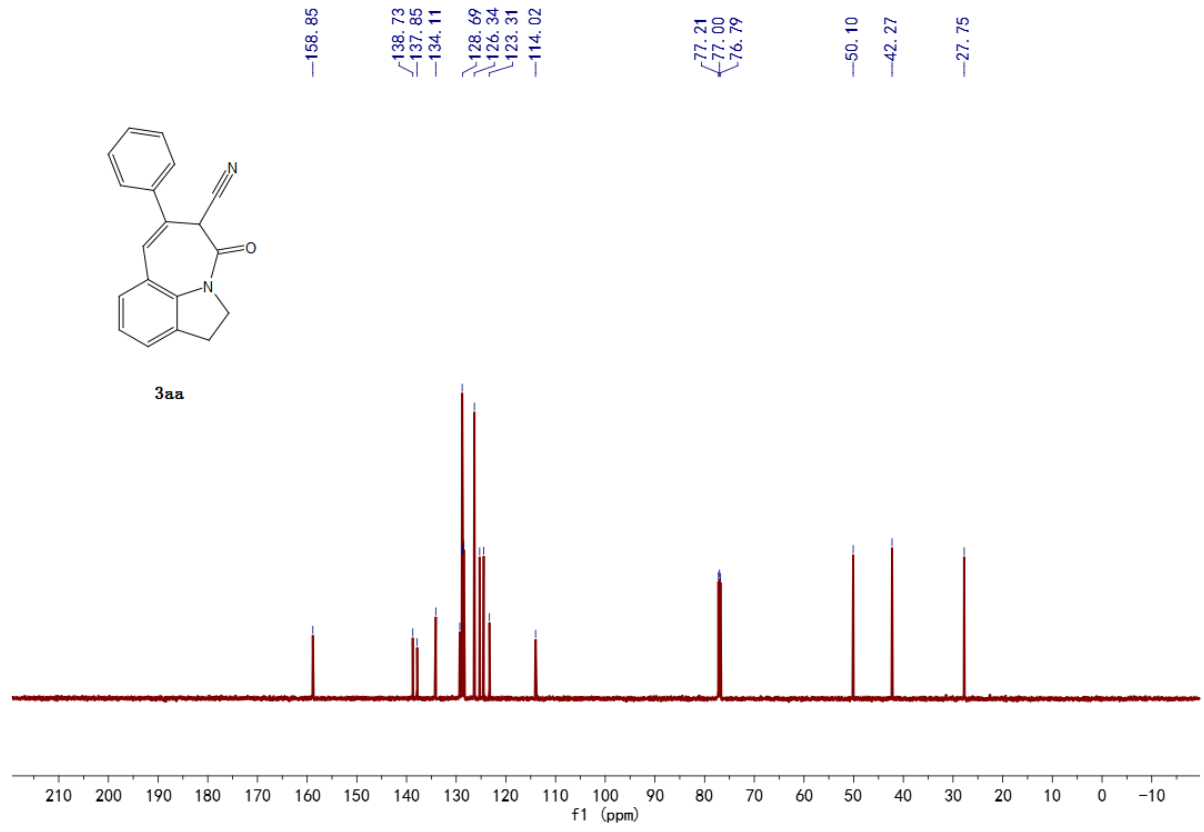
^{1}H NMR of the product **3aa** for the H/D exchange reaction in presence of **2a**

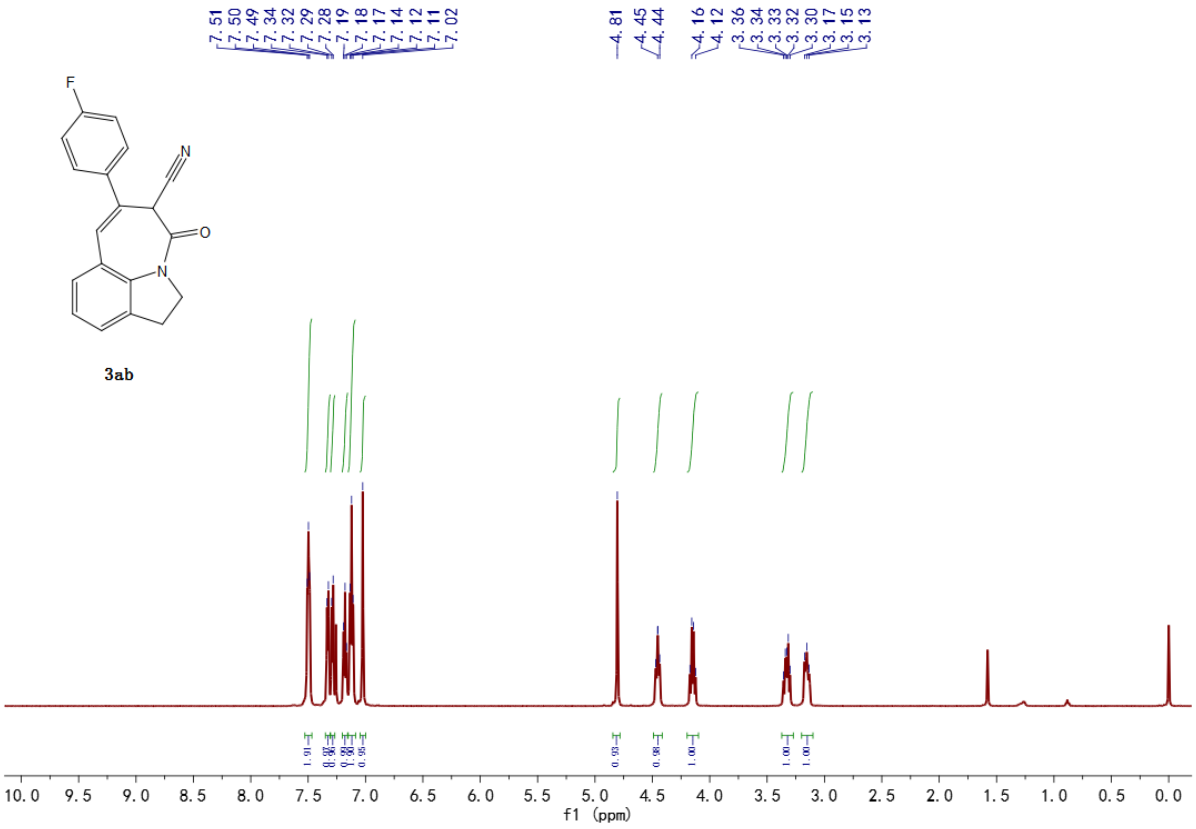


^{1}H NMR of the product **4aa** for the H/D exchange reaction in presence of **2a**.

Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra of the products



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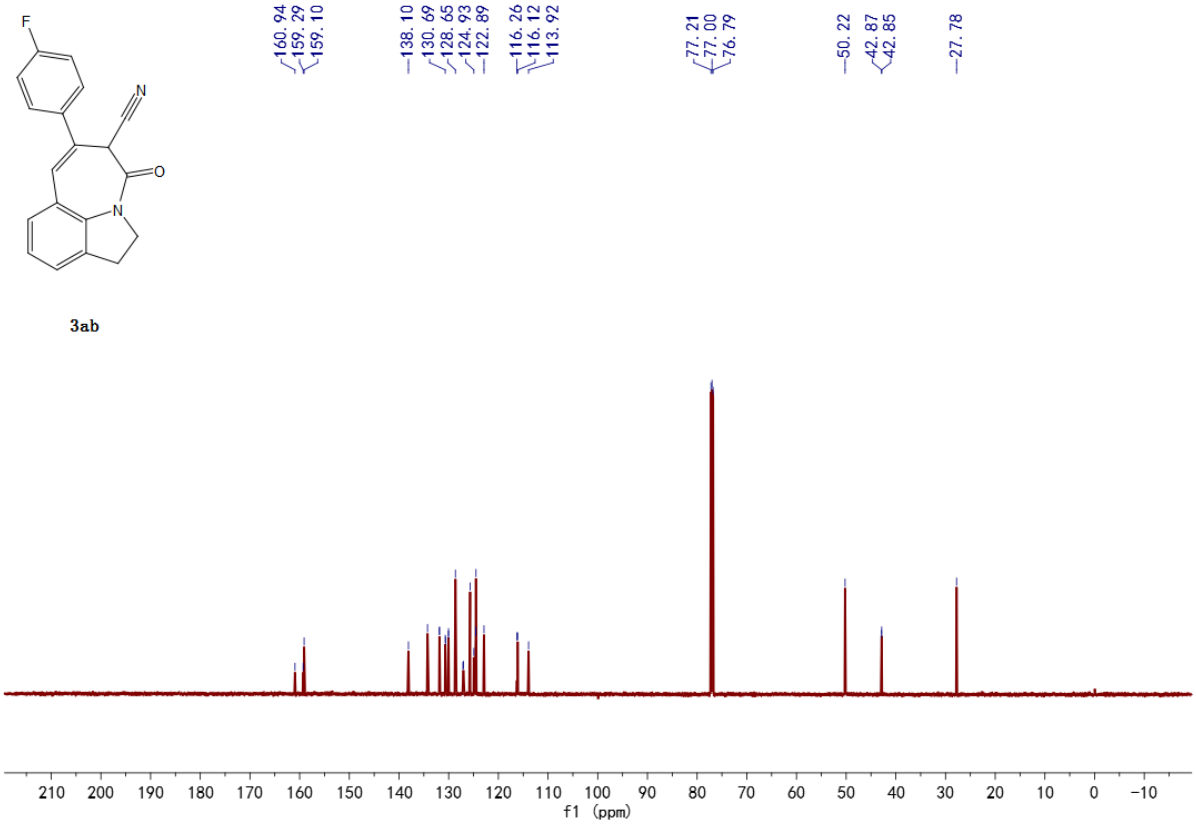
7.11
7.02
4.81
4.45
4.44
4.16
4.12
3.36
3.34
3.33
3.32
3.30
3.17
3.15
3.13
F
N
O
N
3ab
1.91
0.93
0.88
0.98
1.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.10
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122.89
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116.12
113.92
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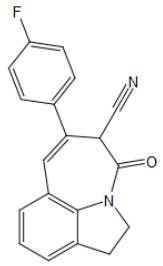
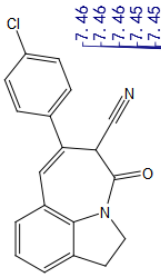
77.00
76.79
50.22
42.87
42.85
27.78
F
N
O
N
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
N
O
N

3ab

112.19
112.20
112.21
112.21
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)


Cl
N
O
N

3ac

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7.45
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7.39
7.39
7.34
7.34
7.33
7.32
7.29
7.28
7.19
7.18
7.16
7.05
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4.44
4.42
4.15
4.12
3.35
3.33
3.32
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3.16
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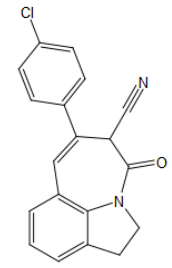
3.14
3.13
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
O
N

3ac

158.81
138.05
137.16
134.78
134.27
129.08
125.58
123.18
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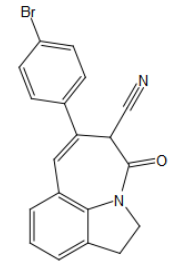
77.21
77.00
76.79
50.21
42.29
27.86
f1 (ppm)


Br
N
O
N

3ad

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7.20
7.19
7.09
4.81
4.47
4.45
4.18
4.15
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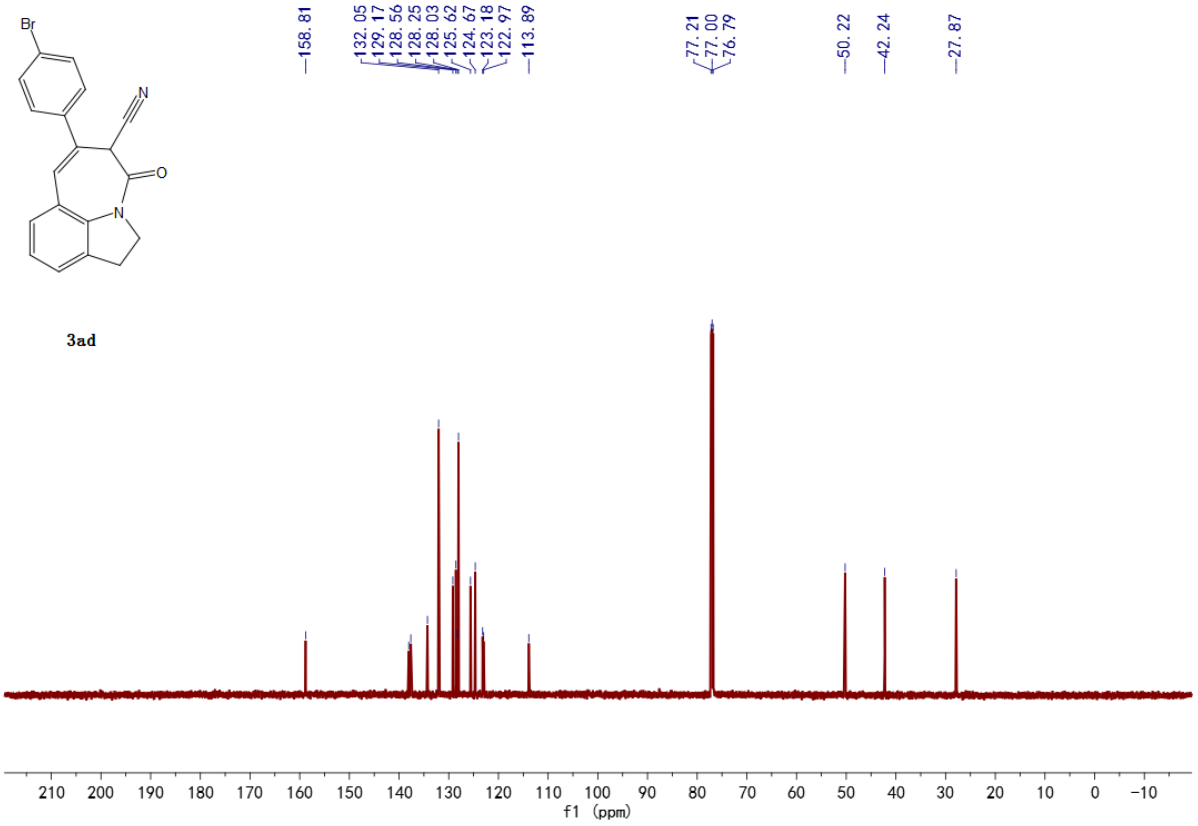
3.34
3.32
3.20
3.20
3.19
3.18
3.17
3.16
f1 (ppm)


Br
N
O
N
158.81
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128.56
128.25
128.03
125.62
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123.18
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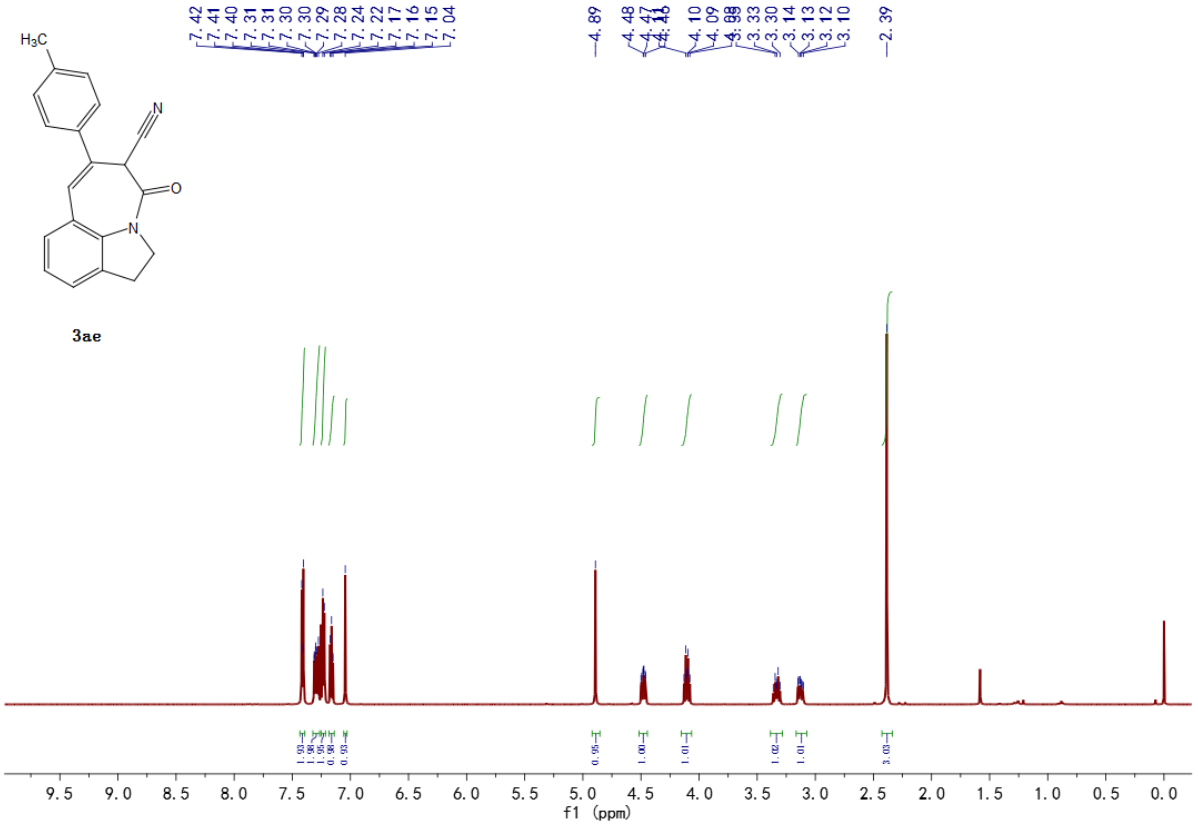
76.79
50.22
42.24
27.87
f1 (ppm)

3ad


H3C
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O
N
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7.30
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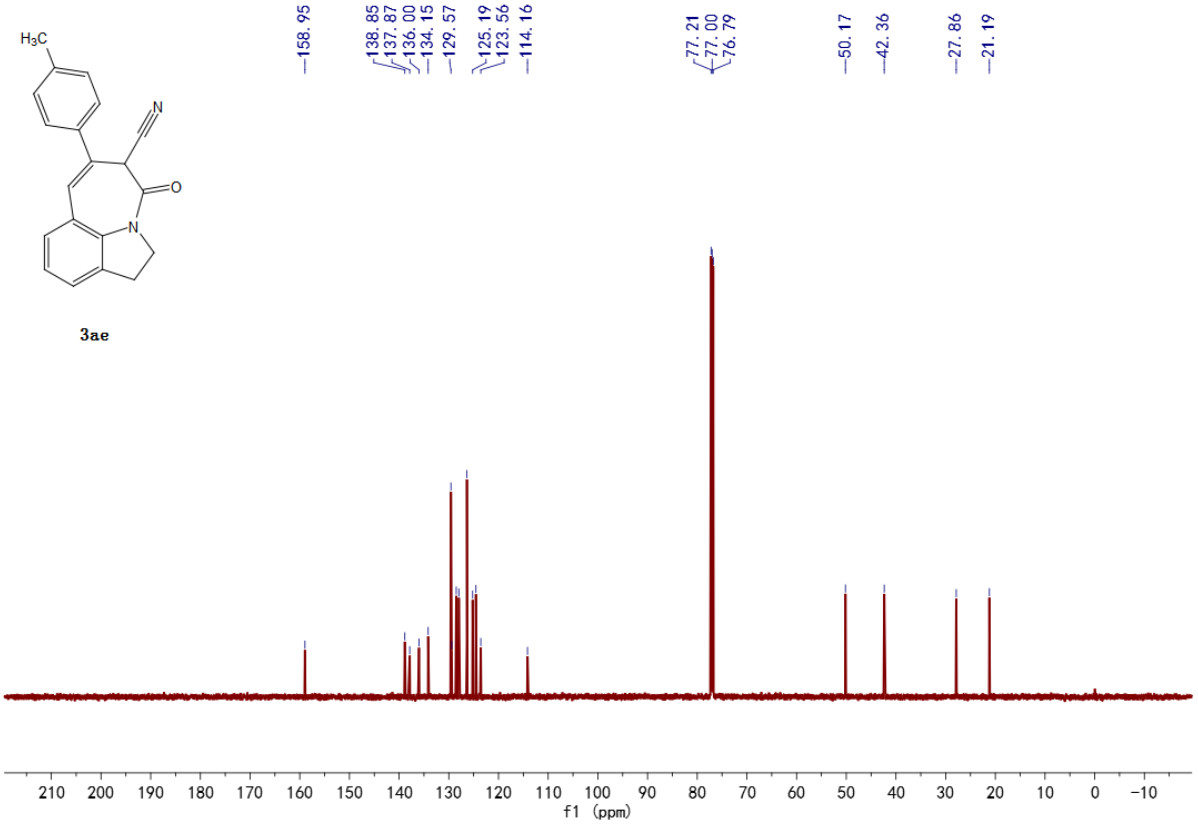
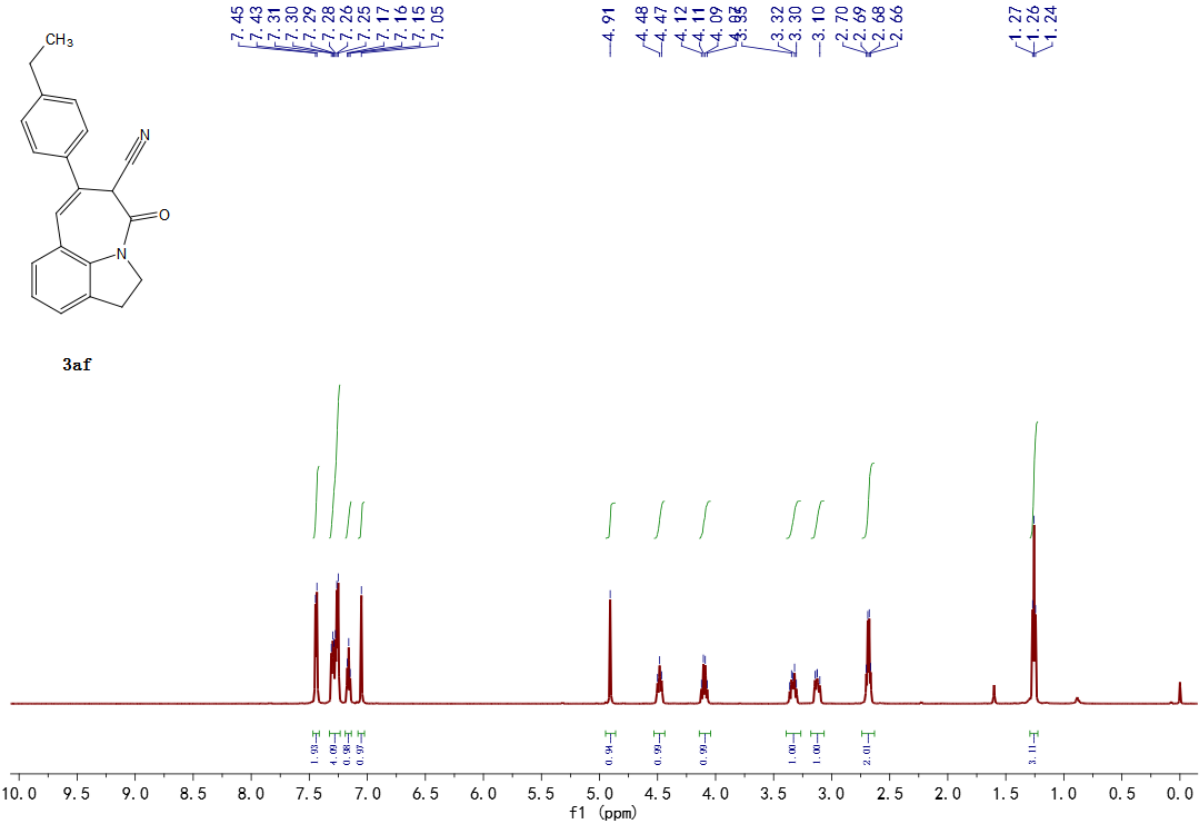
7.24
7.22
7.17
7.16
7.15
7.04
4.89
4.48
4.47
4.10
4.09
3.33
3.30
3.14
3.13
3.12
3.10
2.39
f1 (ppm)

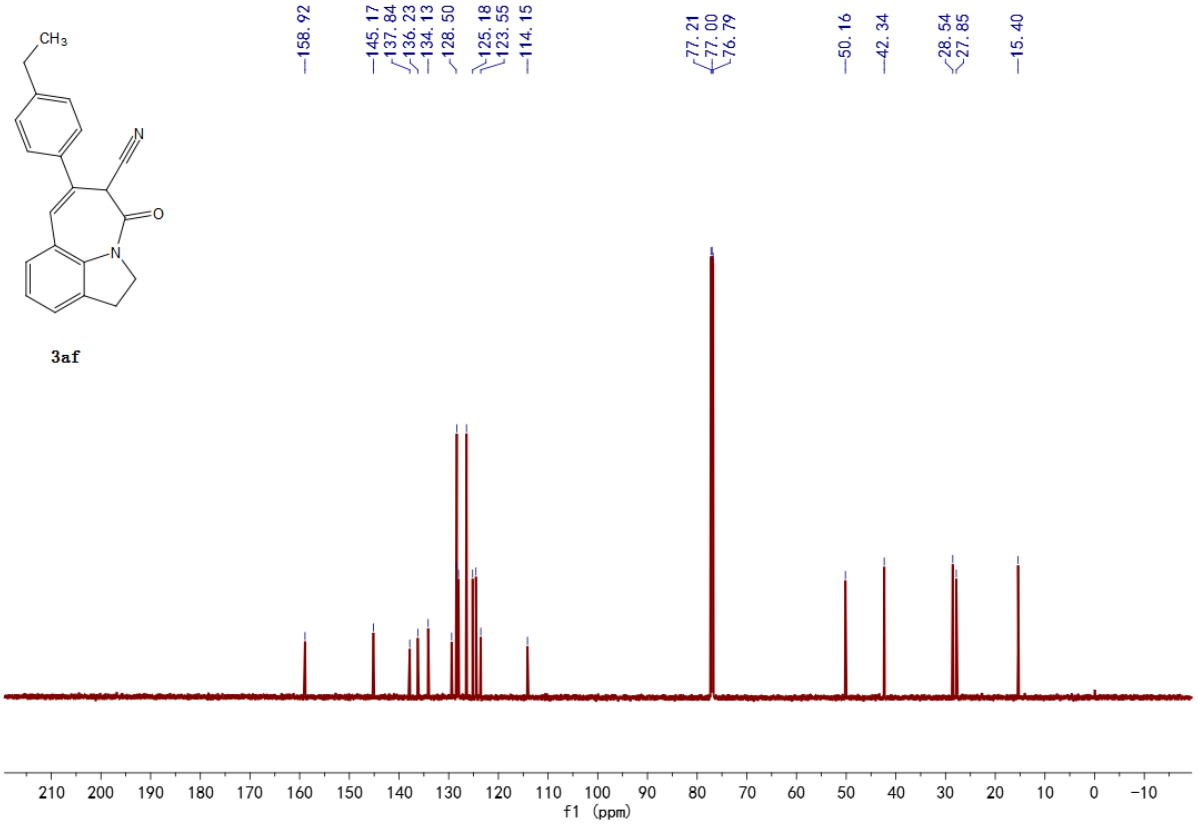
3ae


H3C
N
O
N
158.95
138.85
137.87
136.00
134.15
129.57
125.19
123.56
114.16
77.21
77.00
76.79
50.17
42.36
27.86
21.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

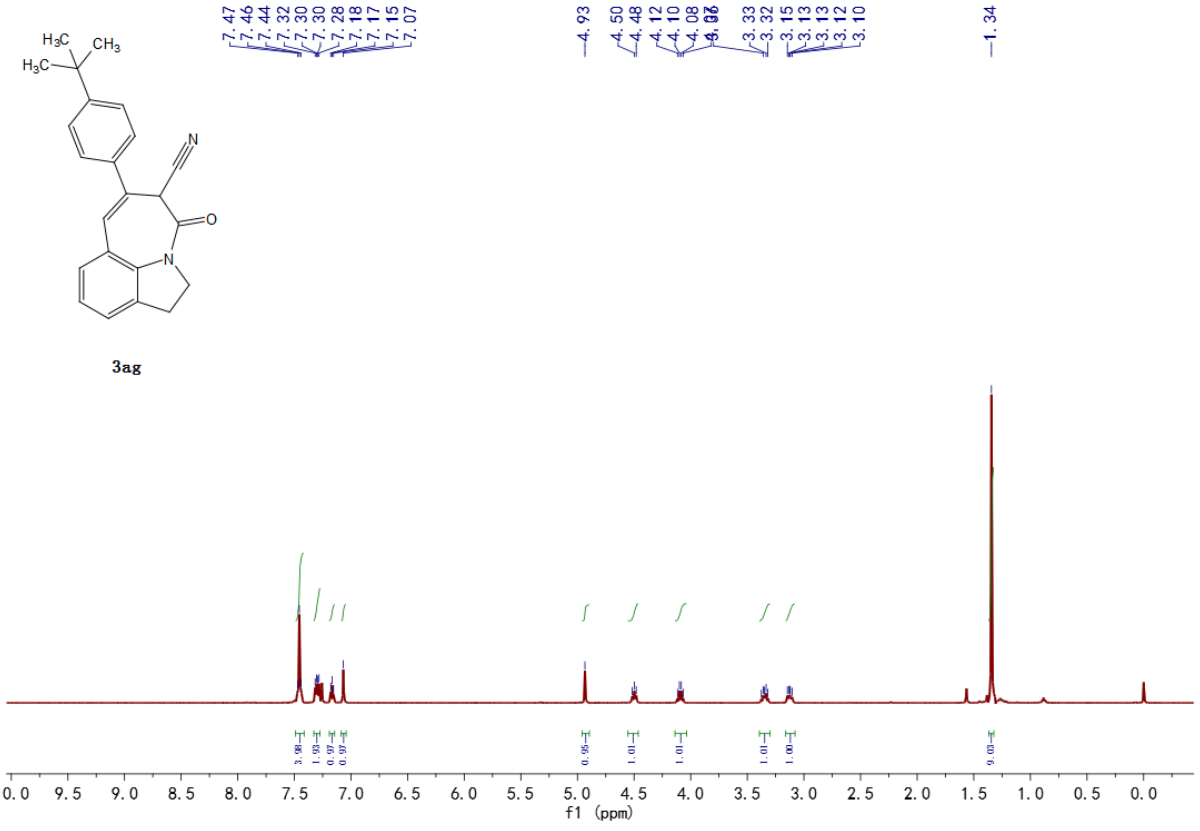
3ae


CH3
N
O
N
7.45
7.43
7.31
7.30
7.29
7.28
7.26
7.25
7.17
7.16
7.15
7.05
4.91
4.48
4.47
4.12
4.11
4.09
3.32
3.30
3.10
2.70
2.69
2.68
2.66
1.27
1.26
1.24
1.93
4.09
0.98
0.97
0.94
0.99
0.99
1.00
1.00
2.01
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

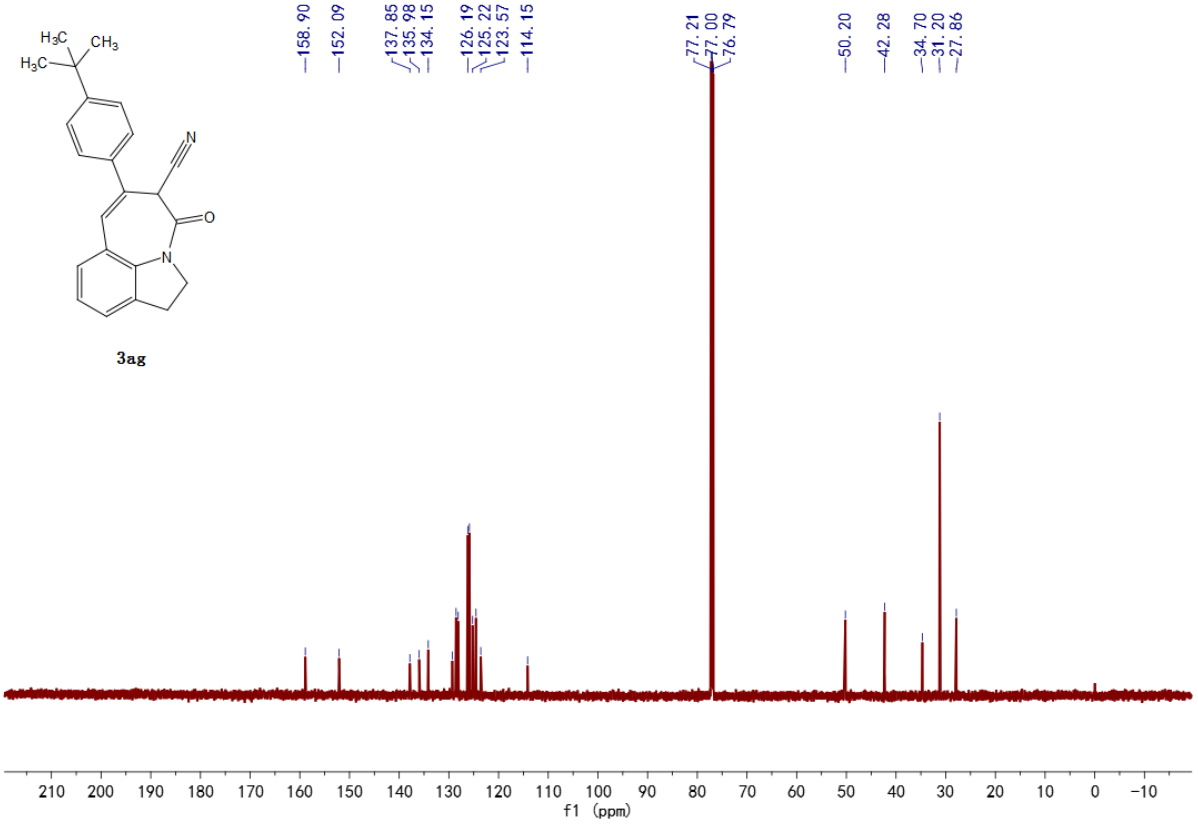
3af


158.92
145.17
137.84
136.23
134.13
128.50
125.18
123.55
114.15
77.21
77.00
76.79
50.16
42.34
28.54
27.85
15.40
CH3
N
O
N
f1 (ppm)

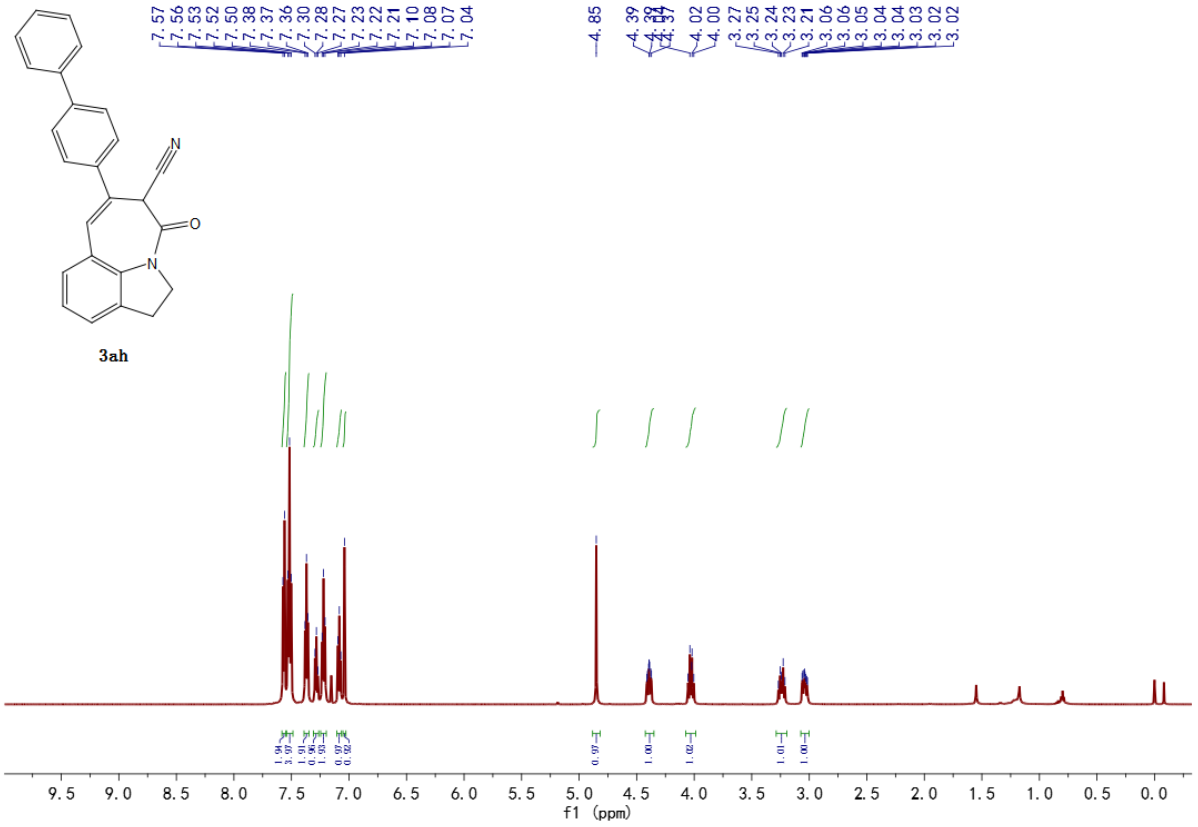
3af


7.47
7.46
7.44
7.32
7.30
7.30
7.28
7.18
7.17
7.15
7.07
4.93
4.50
4.48
4.12
4.10
4.08
3.33
3.32
3.15
3.13
3.13
3.12
3.10
1.34
H3C
CH3
H3C
N
O
N
3.98
1.93
0.97
0.97
0.96
1.01
1.01
1.01
1.00
9.03
f1 (ppm)

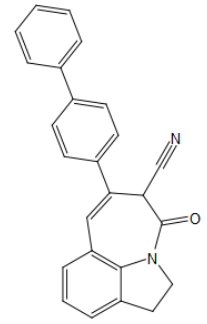
3ag


158.90
152.09
137.85
135.98
134.15
126.19
125.22
123.57
114.15
77.21
77.00
76.79
50.20
42.28
34.70
31.20
27.86
f1 (ppm)

3ag

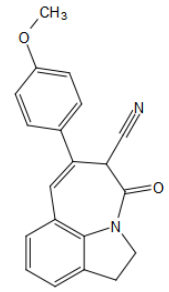

7.57
7.56
7.53
7.52
7.50
7.38
7.37
7.36
7.30
7.28
7.27
7.23
7.22
7.21
7.10
7.08
7.07
7.04
4.85
4.39
4.02
4.00
3.27
3.25
3.24
3.23
3.21
3.06
3.05
3.04
3.03
3.02
f1 (ppm)

3ah


N
O
N

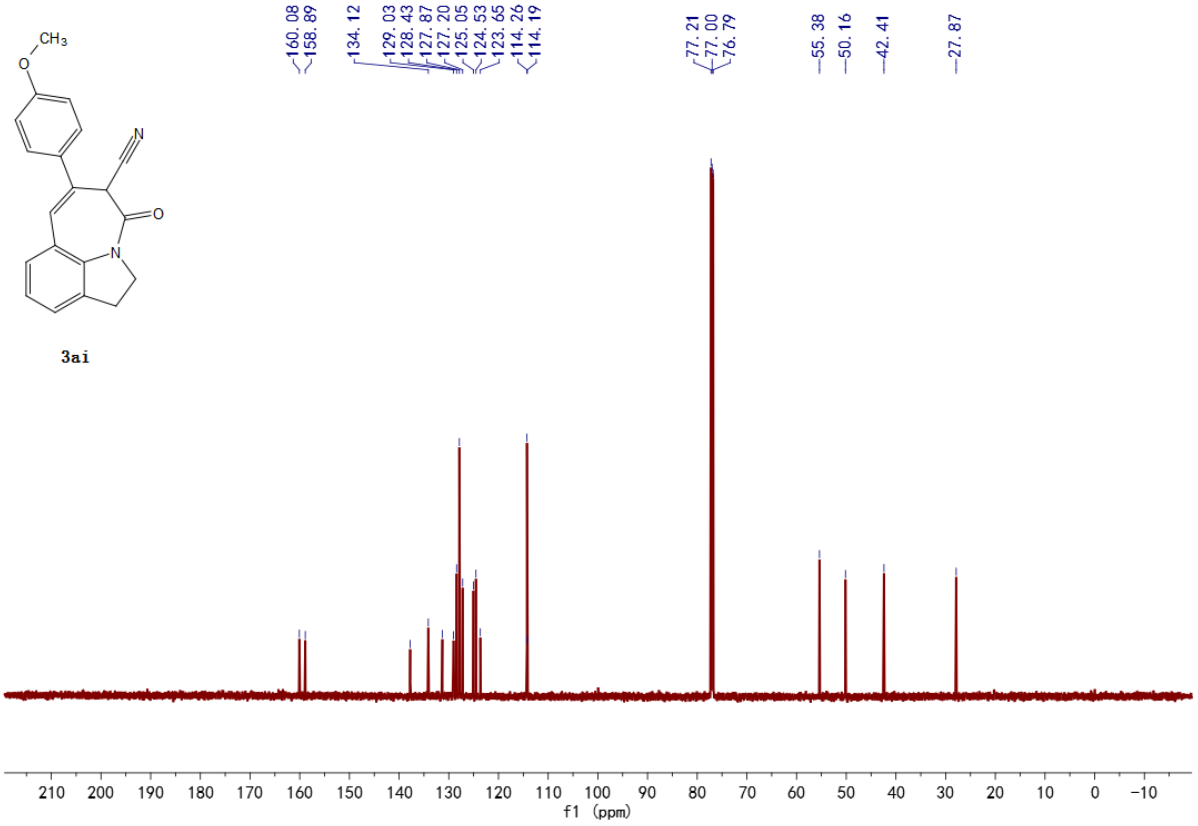
3ah

158.86
141.50
140.01
137.93
137.57
134.18
128.84
126.84
123.42
114.08
77.21
77.00
76.79
50.17
42.22
27.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

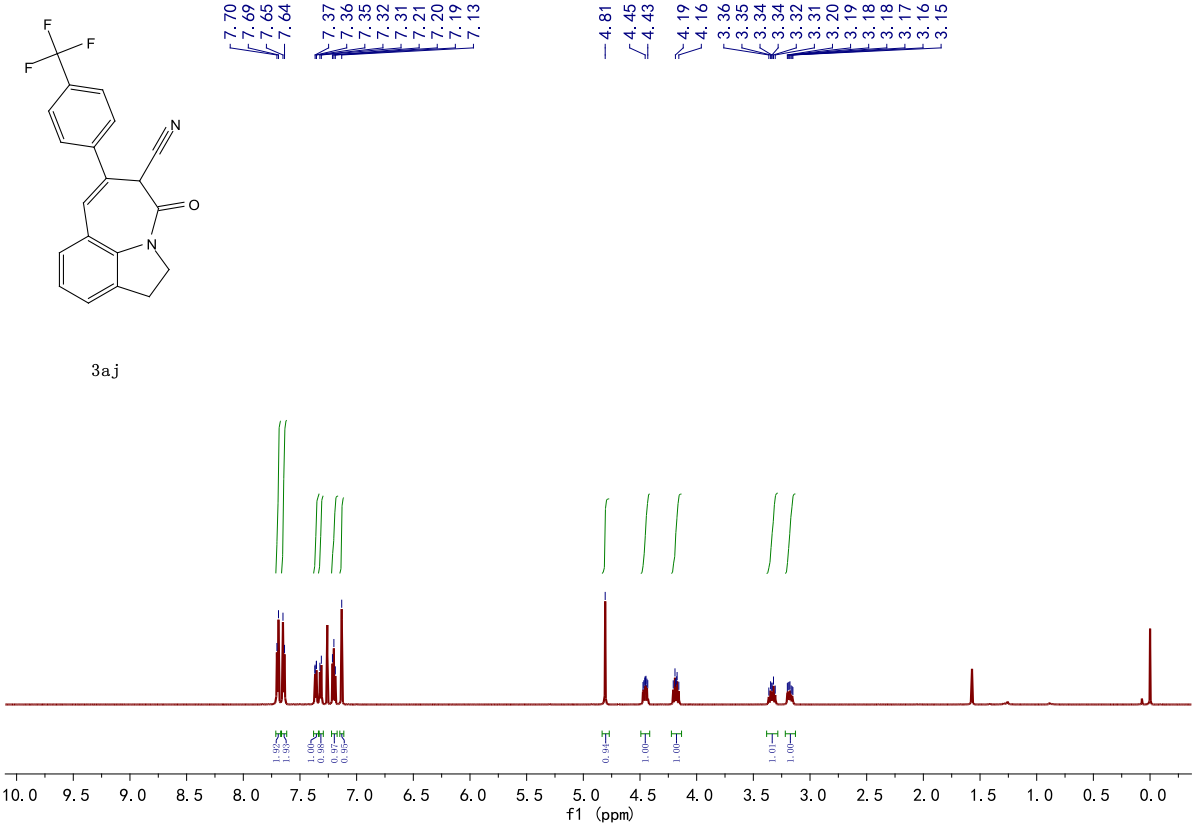

CH3
O
N
O
N

3ai

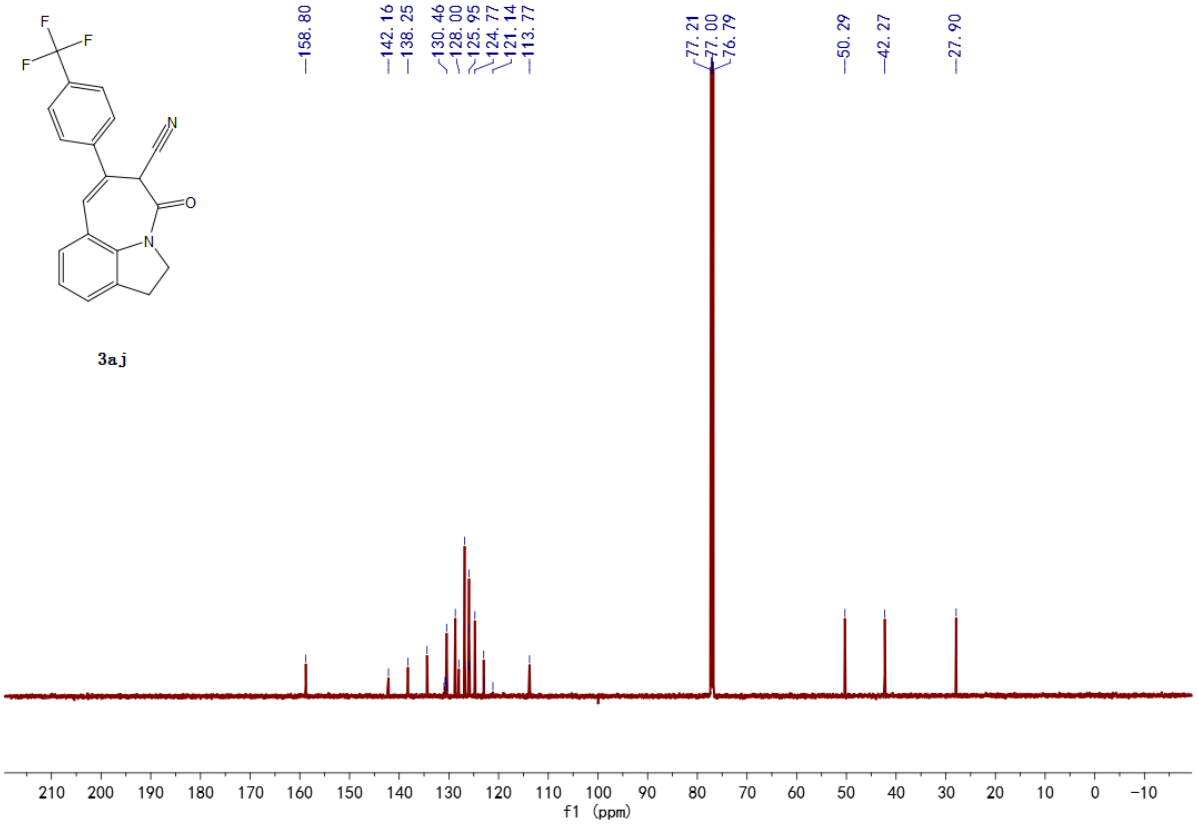
7.46
7.45
7.31
7.29
7.28
7.27
7.26
7.17
7.16
7.15
7.00
6.95
6.94
4.88
4.48
4.47
4.08
3.84
3.33
3.30
3.15
3.13
3.11
1.90
1.95
0.98
1.94
1.91
0.98
1.00
1.01
3.02
1.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

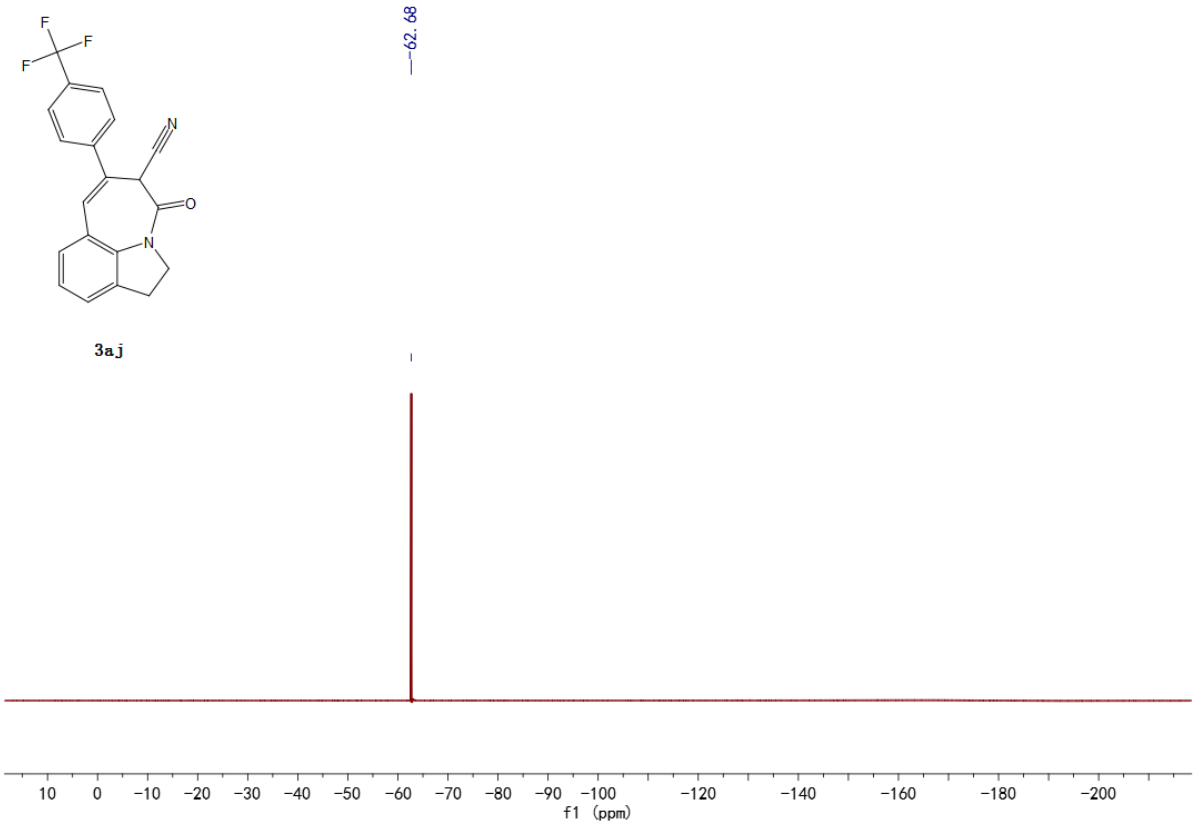

160.08
158.89
134.12
129.03
128.43
127.87
127.20
125.05
124.53
123.65
114.26
114.19
77.21
77.00
76.79
55.38
50.16
42.41
27.87
CH3
O
N
O
N
f1 (ppm)

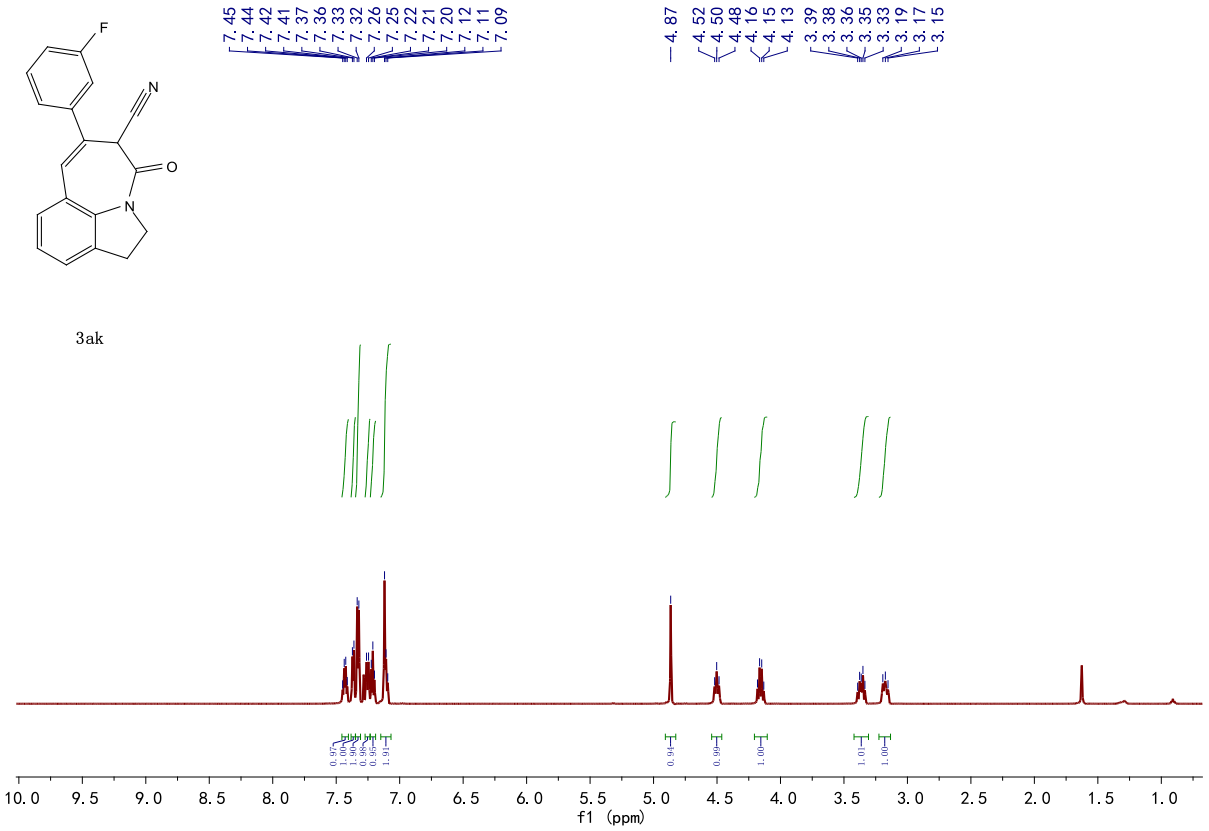
3ai

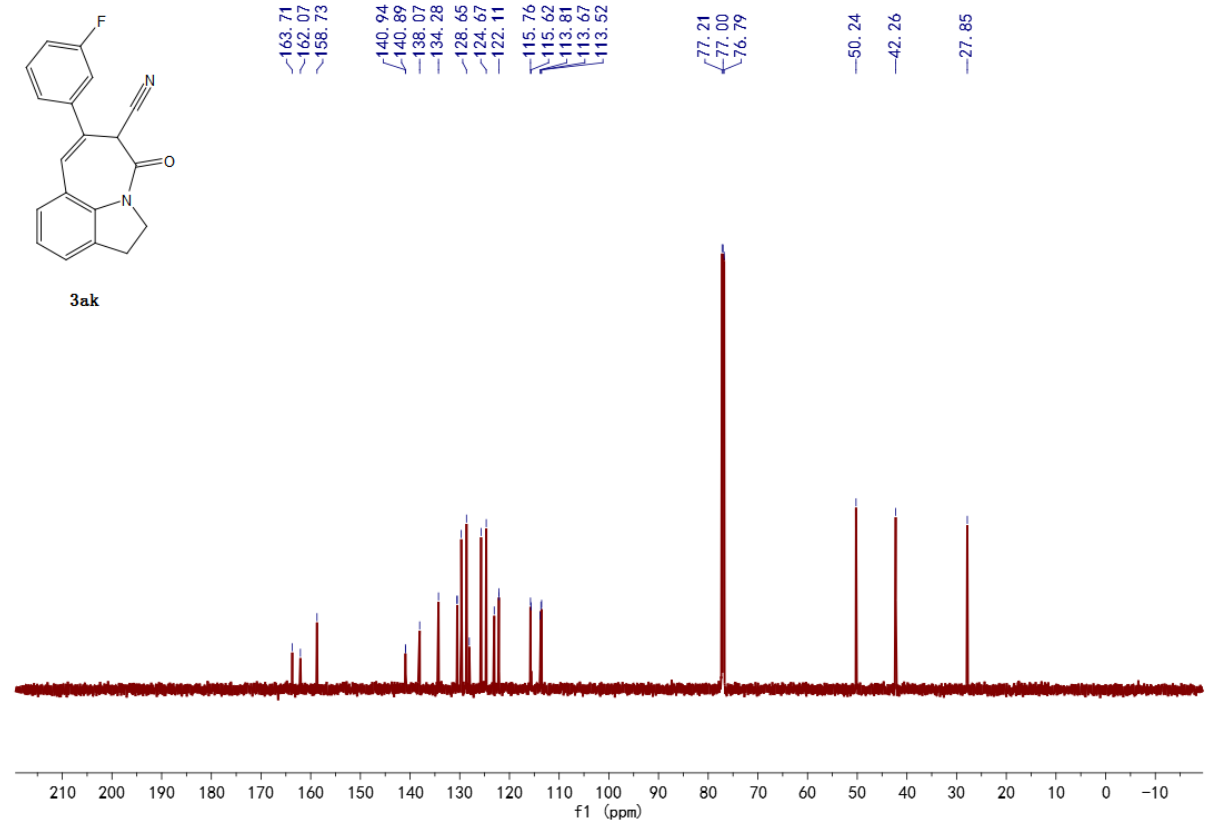

7.70
7.69
7.65
7.64
7.37
7.36
7.35
7.32
7.31
7.21
7.20
7.19
7.13
4.81
4.45
4.43
4.19
4.16
3.36
3.35
3.34
3.34
3.32
3.31
3.20
3.19
3.18
3.18
3.17
3.16
3.15
F
F
F
N
O
N
f1 (ppm)

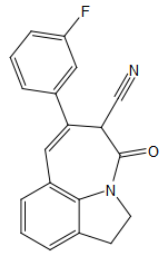
3aj


158.80
142.16
138.25
130.46
128.00
125.95
124.77
121.14
113.77
77.21
77.00
76.79
50.29
42.27
27.90
F
F
F
N
O
N
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

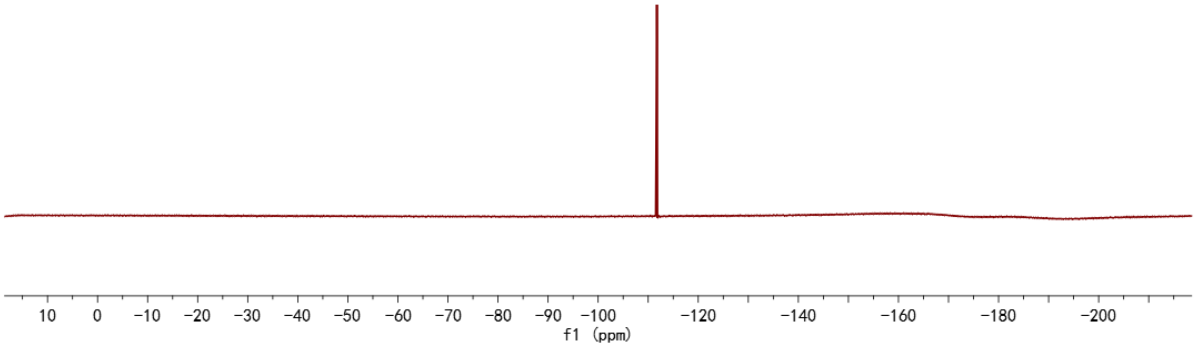

62.68
F
F
F
N
O
N
3aj
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)


7.45
7.44
7.42
7.41
7.37
7.36
7.33
7.32
7.26
7.25
7.22
7.21
7.20
7.12
7.11
7.09
4.87
4.52
4.50
4.48
4.16
4.15
4.13
3.39
3.38
3.36
3.35
3.33
3.19
3.17
3.15
F
N
O
N
3ak
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

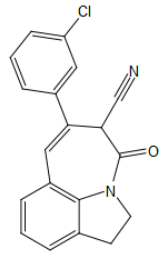

163.71
162.07
158.73
140.94
140.89
138.07
134.28
128.65
124.67
122.11
115.76
115.62
113.81
113.67
113.52
77.21
77.00
76.79
50.24
42.26
27.85
F
N
O
N
3ak
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
N
O
N

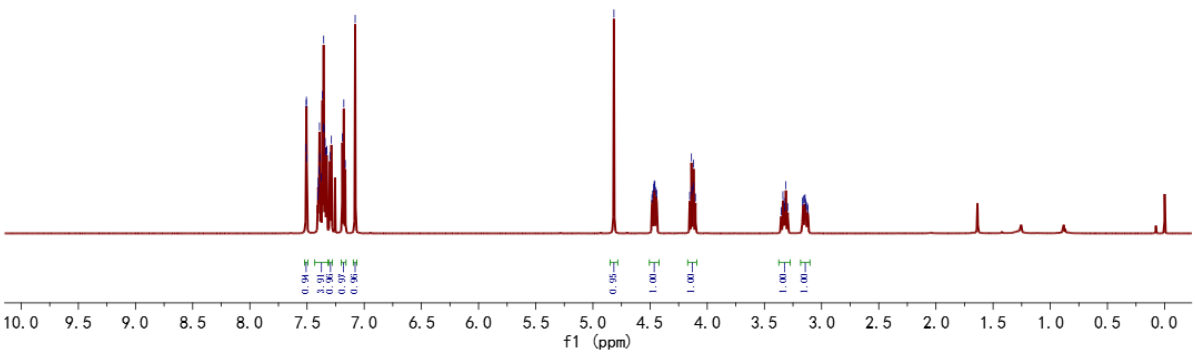
3ak

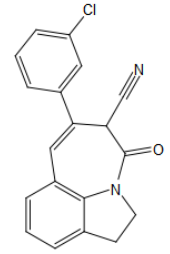

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)


7.51 7.51 7.51 7.50 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.30 7.29 7.19 7.18 7.17 7.08
4.82 4.46 4.44 4.13 4.10 3.35 3.34 3.33 3.32 3.31 3.30 3.17 3.16 3.15 3.14 3.14 3.13 3.12 3.12


Cl
N
O
N

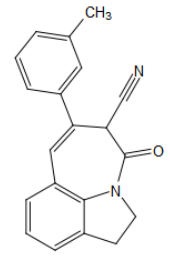
3al


0.94 3.91 0.96 0.97 0.96 0.95 1.00 1.00 1.00 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
O
N

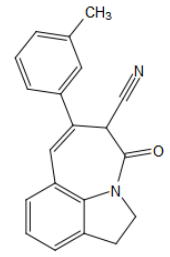
3al

158.69
140.51
138.04
134.87
126.65
124.65
123.02
113.77
77.21
77.00
76.79
50.22
42.20
27.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


CH3
N
O
N

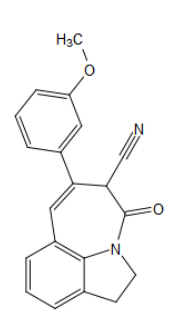
3am

7.35
7.33
7.31
7.22
7.21
7.20
7.19
7.10
4.94
4.52
4.51
4.15
4.14
4.12
4.10
3.38
3.36
3.34
3.16
3.16
3.14
2.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


CH3
N
O
N

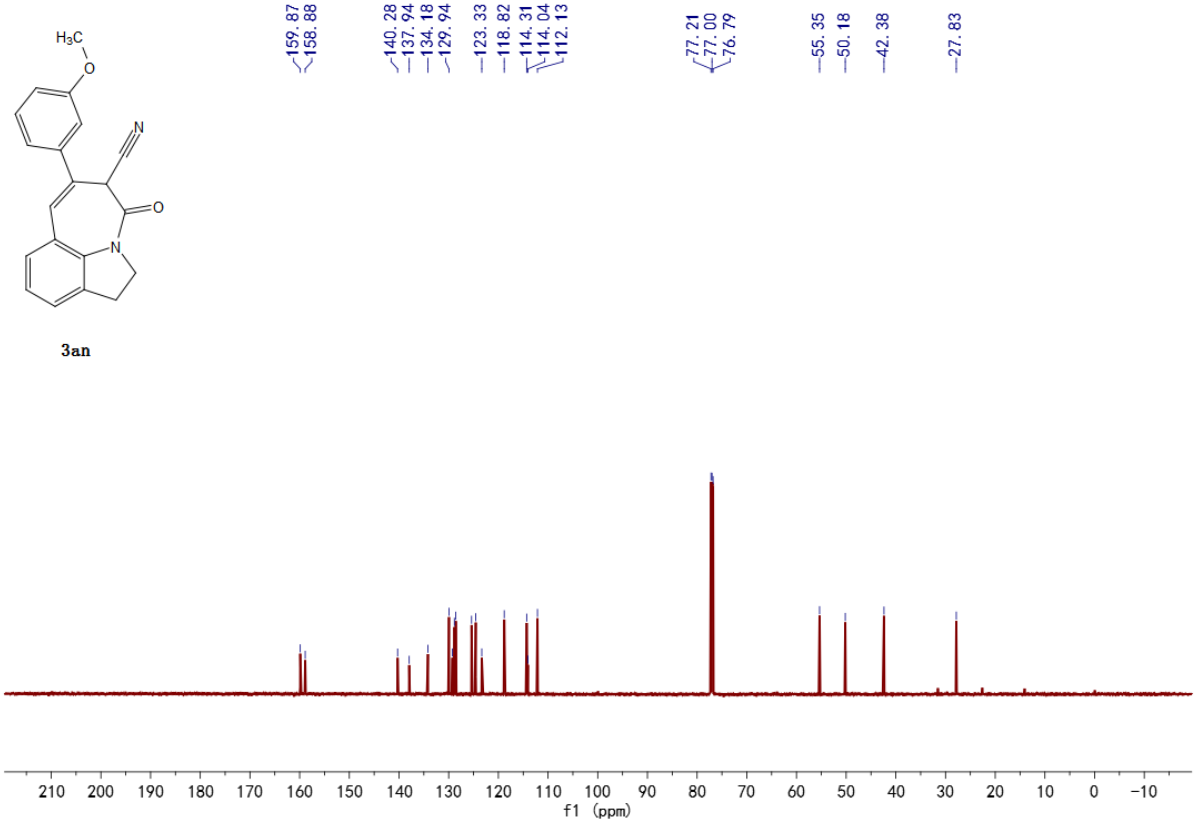
3am

158.95
138.90
138.65
137.88
134.16
128.57
125.30
123.49
114.11
77.21
77.00
76.79
50.19
42.38
27.85
21.43
f1 (ppm)

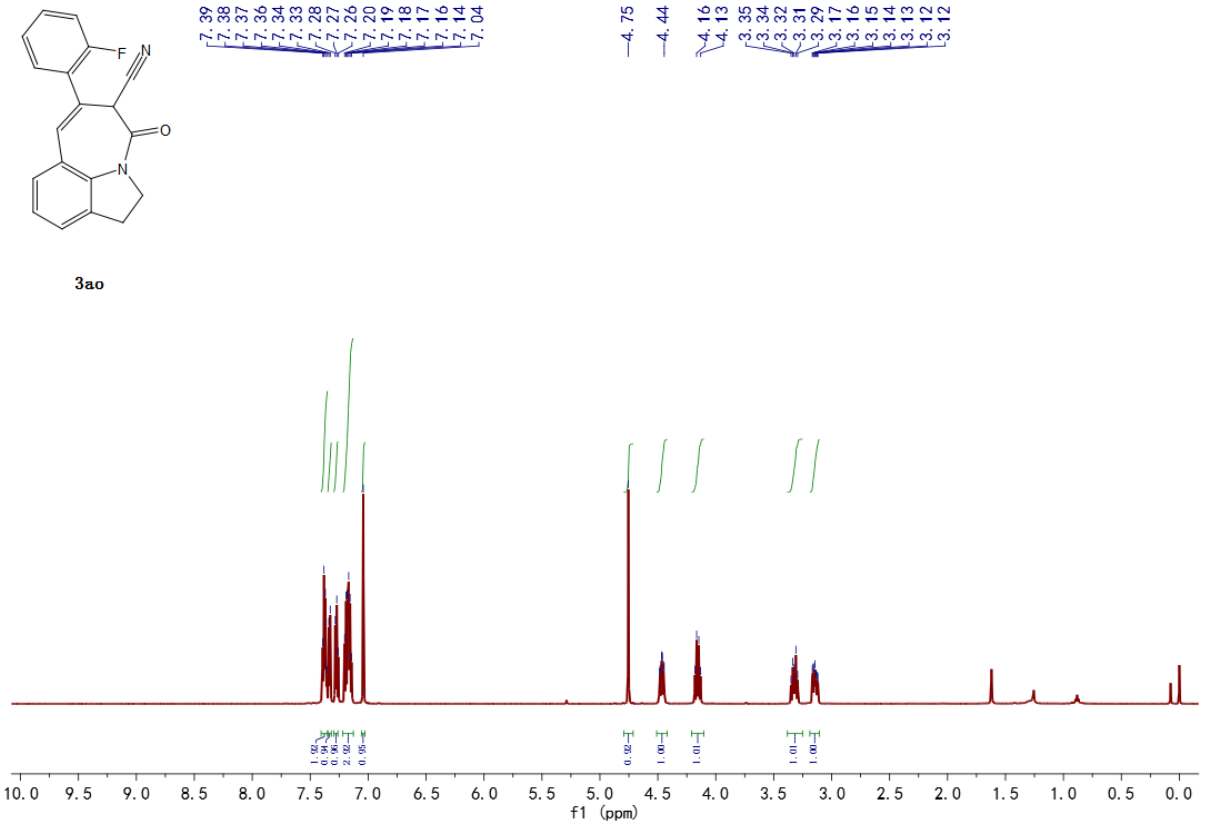

H3C
O
N
O
N

3an

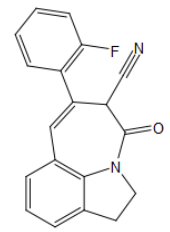
7.35
7.34
7.32
7.31
7.30
7.28
7.18
7.17
7.16
7.11
7.09
7.08
7.03
6.93
6.91
4.89
4.50
4.48
4.08
3.85
3.36
3.35
3.33
3.32
3.30
3.15
3.13
3.13
3.11
f1 (ppm)


159.87
158.88
140.28
137.94
134.18
129.94
123.33
118.82
114.31
114.04
112.13
77.21
77.00
76.79
55.35
50.18
42.38
27.83
f1 (ppm)

3an

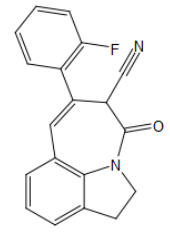

7.39
7.38
7.37
7.36
7.34
7.33
7.28
7.27
7.26
7.20
7.19
7.18
7.17
7.16
7.14
7.04
4.75
4.44
4.16
4.13
3.35
3.34
3.32
3.31
3.29
3.17
3.16
3.15
3.14
3.13
3.12
3.12
f1 (ppm)

3ao



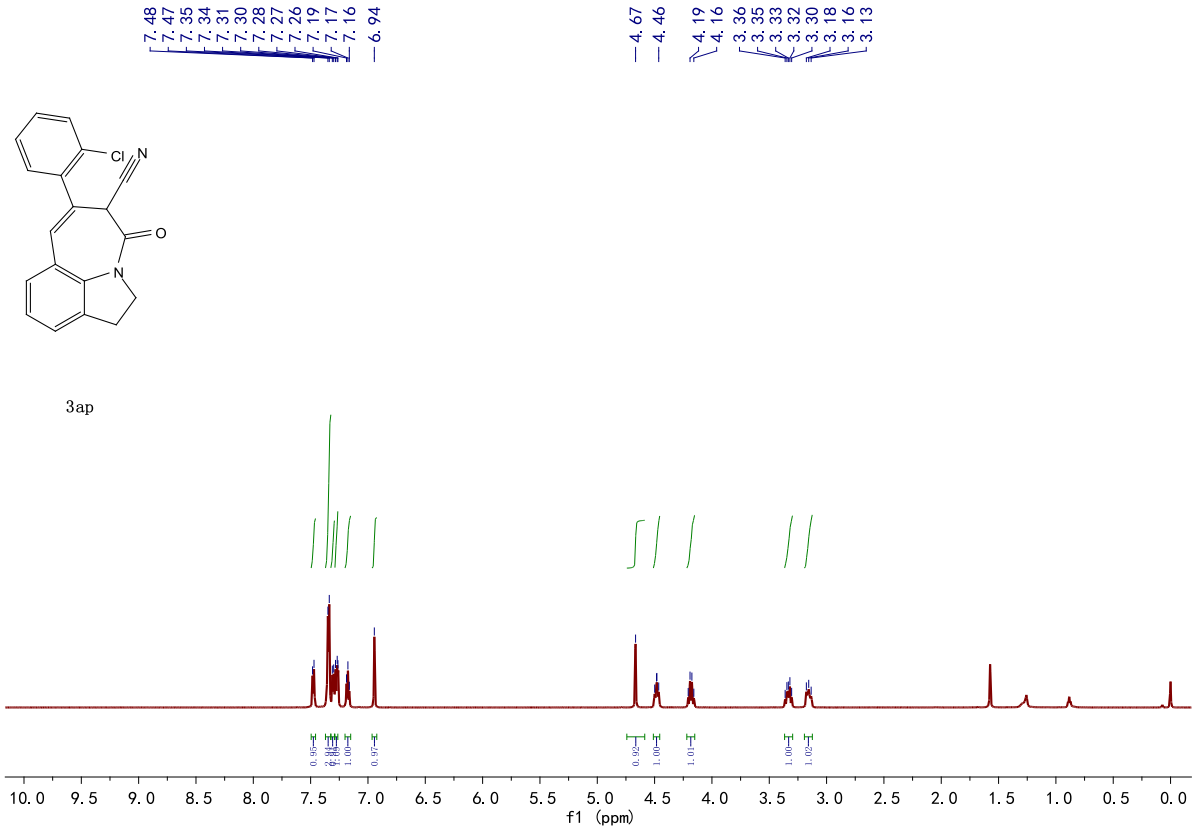
3ao

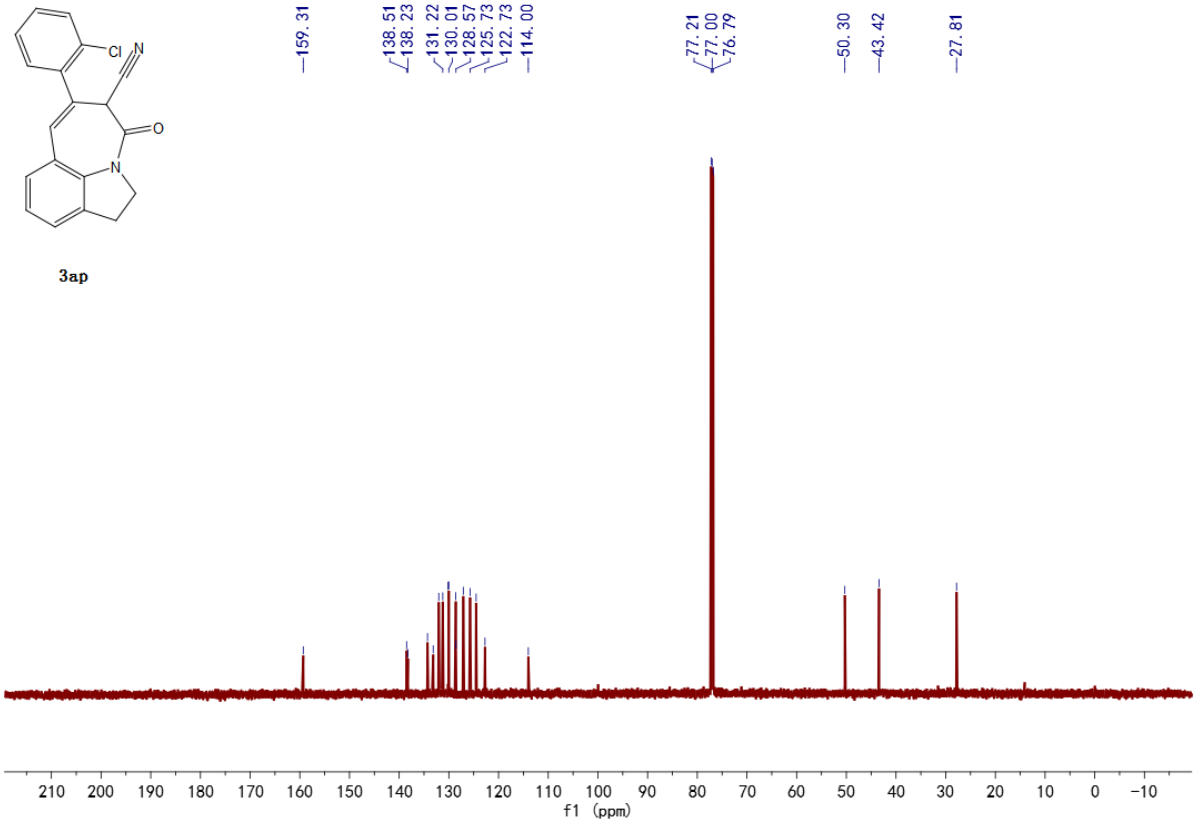
163.75
162.09
158.85
137.99
134.95
134.92
134.25
128.39
123.28
116.00
115.85
113.96
77.21
77.00
76.79
50.21
42.53
27.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

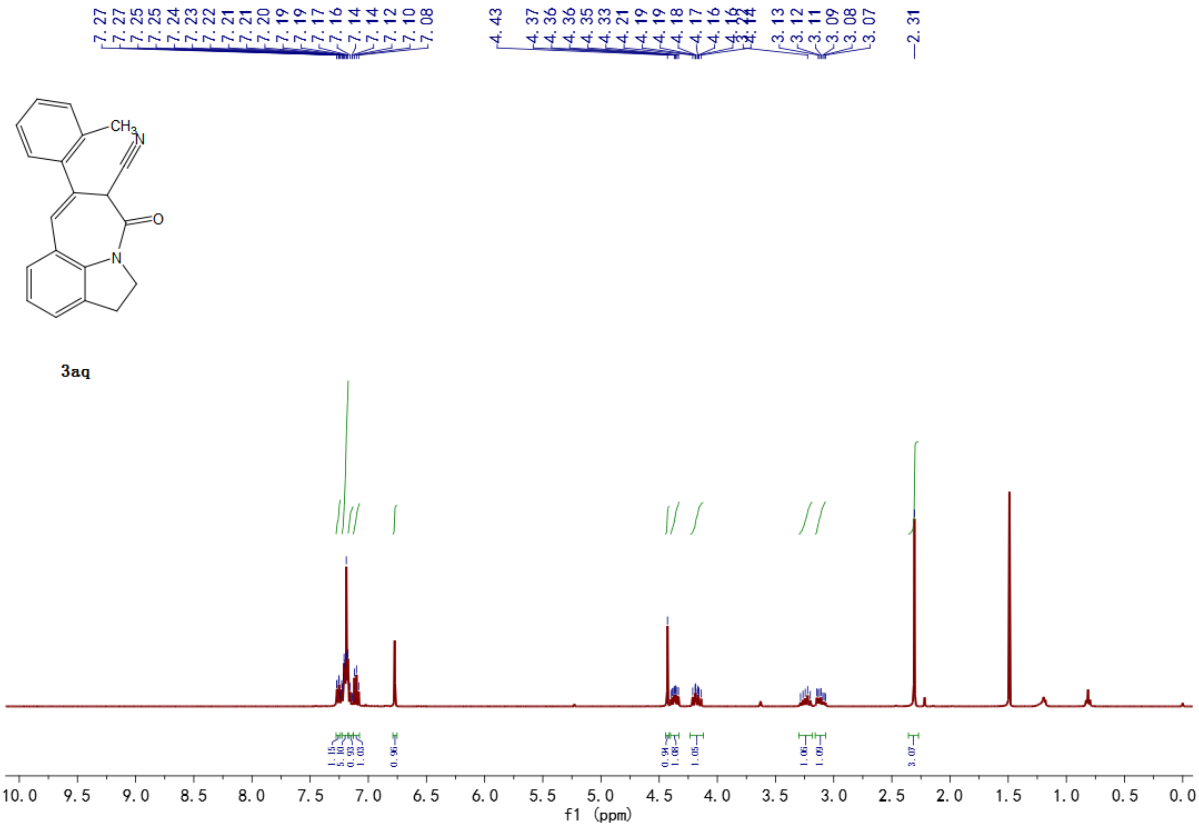


3ao

112.92
112.93
112.94
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.48
7.47
7.35
7.34
7.31
7.30
7.28
7.27
7.26
7.19
7.17
7.16
6.94
4.67
4.46
4.19
4.16
3.36
3.35
3.33
3.32
3.30
3.18
3.16
3.13
Cl
N
O
N
3ap
f1 (ppm)


159.31
138.51
138.23
131.22
130.01
128.57
125.73
122.73
114.00
77.21
77.00
76.79
50.30
43.42
27.81
Cl
N
O
N
3ap
f1 (ppm)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7.27
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7.25
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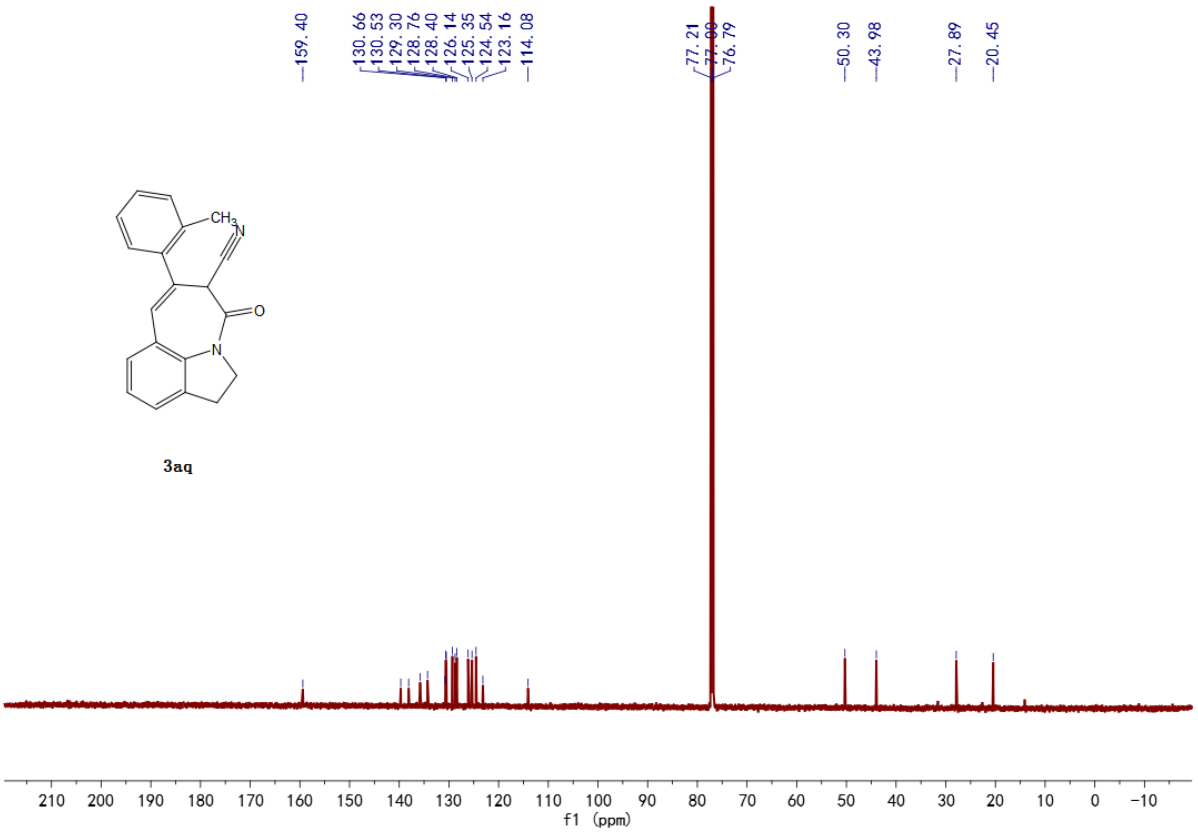
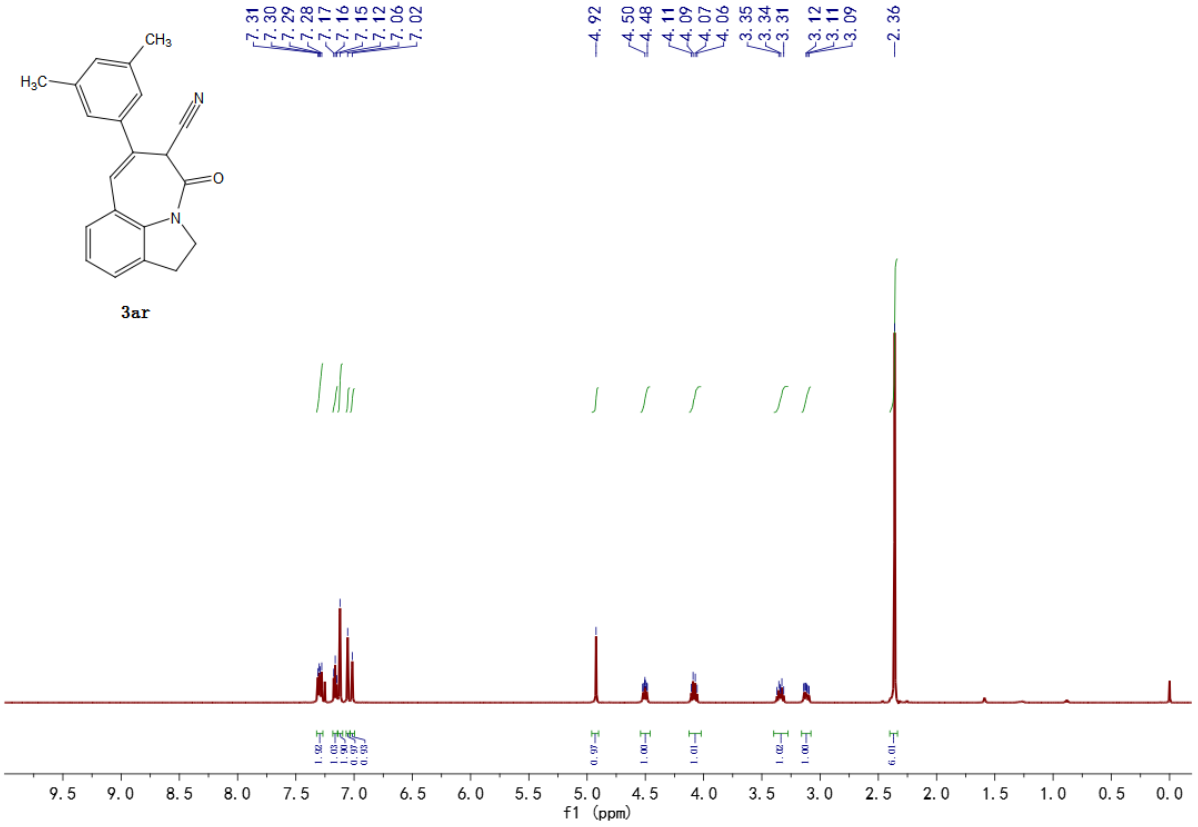
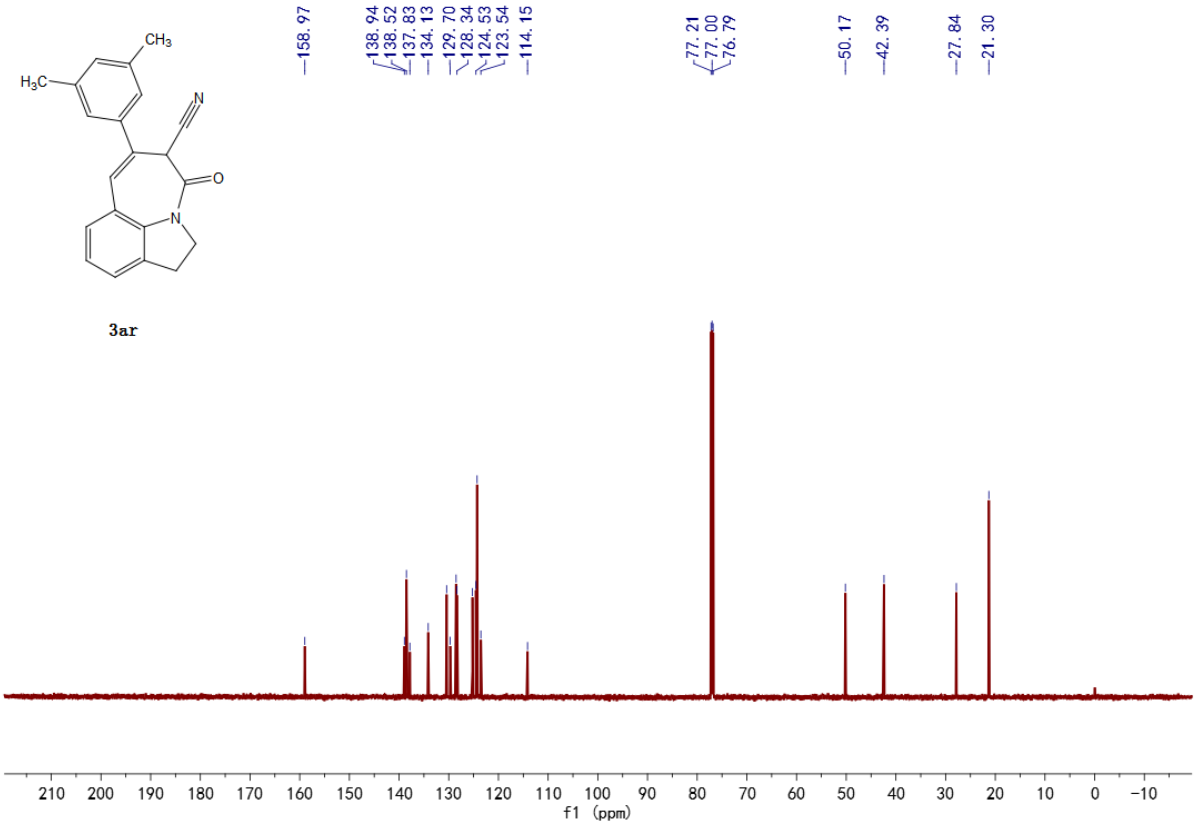
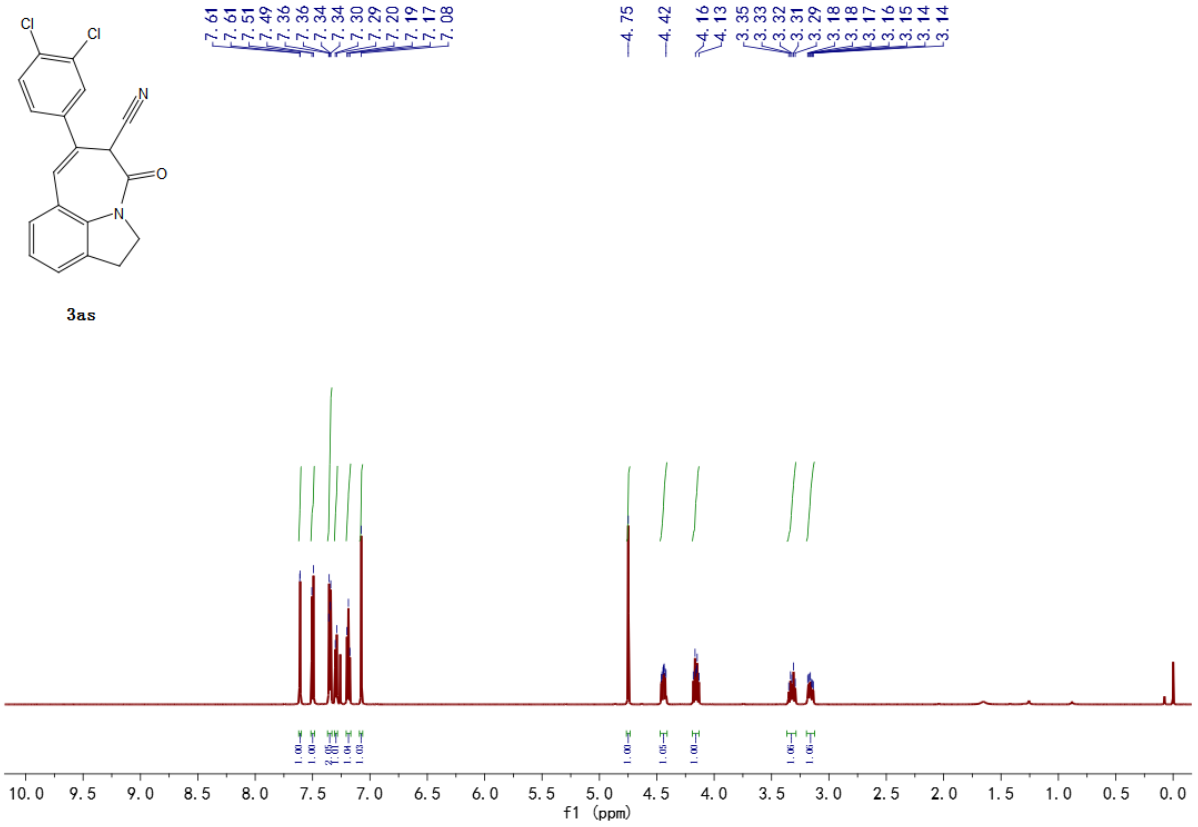
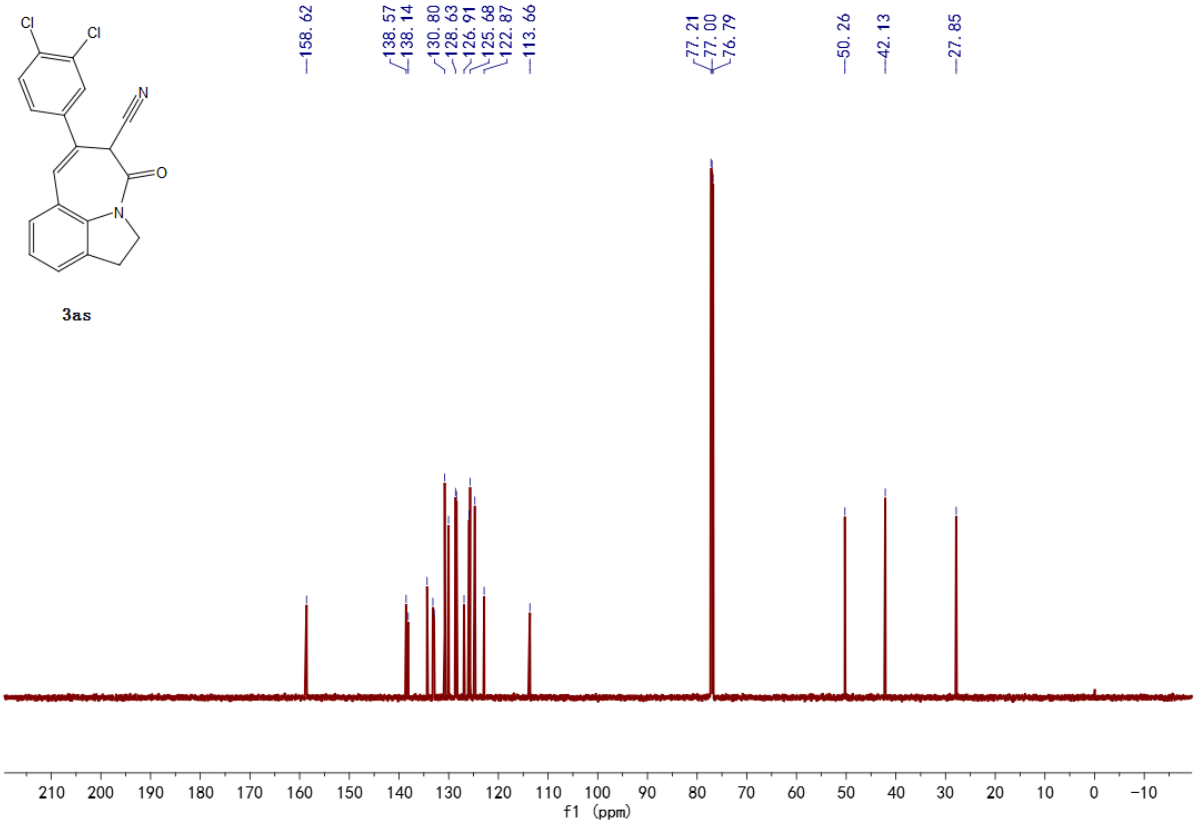
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.16
7.14
7.14
7.12
7.10
7.08
4.43
4.37
4.36
4.36
4.35
4.33
4.21
4.19
4.19
4.18
4.17
4.16
4.16
4.14
4.14
3.13
3.12
3.11
3.09
3.08
3.07
2.31
CH3
N
O
N
3aq
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

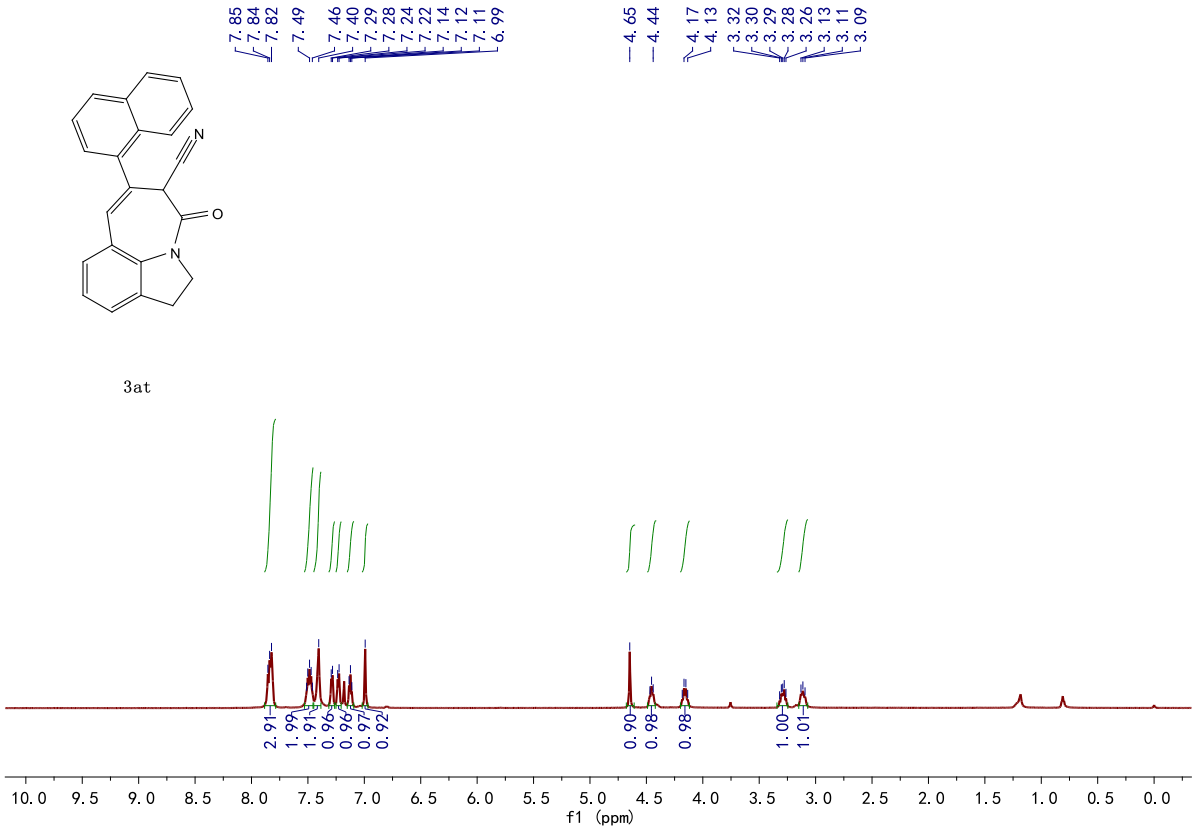

159.40
130.66
130.53
129.30
128.76
128.40
126.14
125.35
124.54
123.16
114.08
77.21
77.00
76.79
50.30
43.98
27.89
20.45
CH3
N
O
N
3aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.31
7.30
7.29
7.28
7.17
7.16
7.15
7.12
7.06
7.02
4.92
4.50
4.48
4.11
4.09
4.07
4.06
3.35
3.34
3.31
3.12
3.11
3.09
2.36
CH3
H3C
N
O
N
3ar
f1 (ppm)

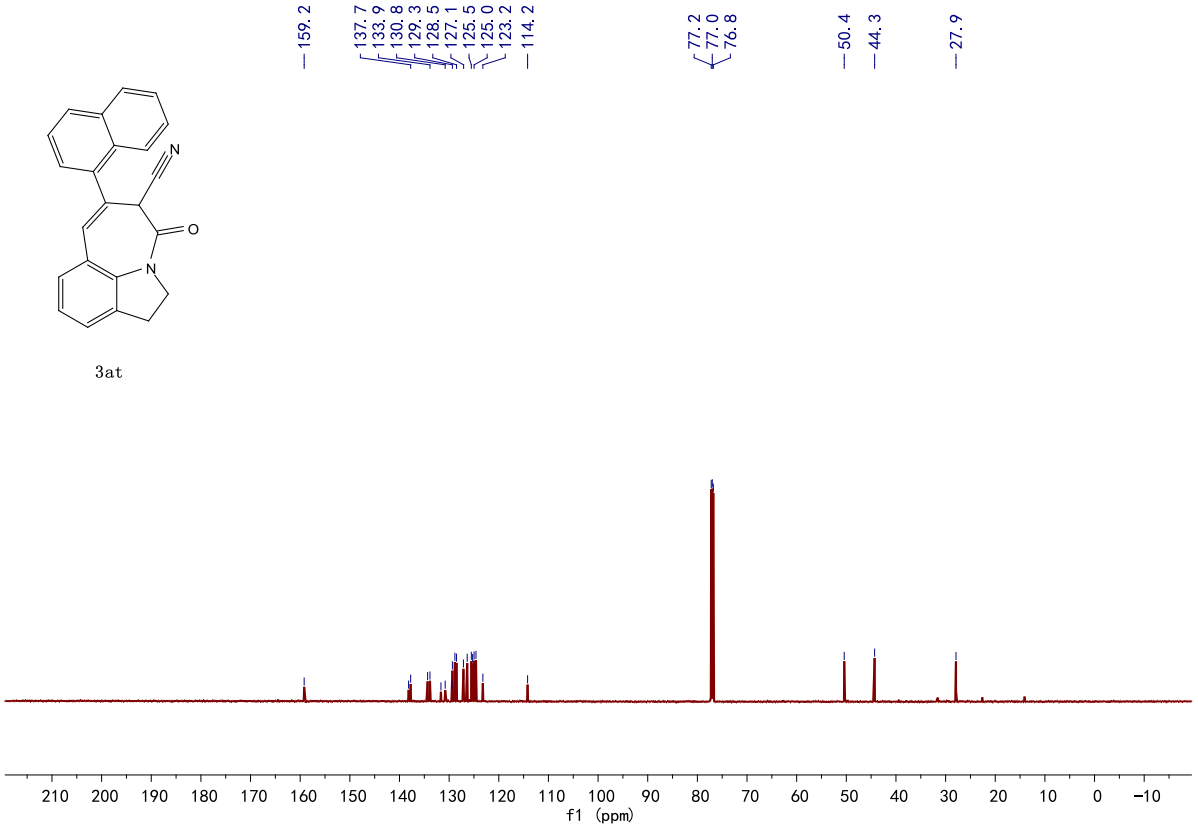

158.97
138.94
138.52
137.83
134.13
129.70
128.34
124.53
123.54
114.15
77.21
77.00
76.79
50.17
42.39
27.84
21.30
CH3
H3C
N
O
N
3ar
f1 (ppm)


7.61
7.61
7.51
7.49
7.36
7.36
7.34
7.34
7.30
7.29
7.20
7.19
7.17
7.08
4.75
4.42
4.16
4.13
3.35
3.33
3.32
3.31
3.29
3.18
3.18
3.17
3.16
3.15
3.14
3.14
Cl
Cl
N
O
N
3as
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

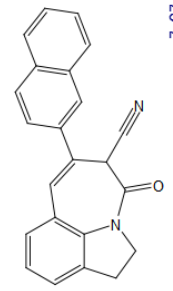

158.62
138.57
138.14
130.80
128.63
126.91
125.68
122.87
113.66
77.21
77.00
76.79
50.26
42.13
27.85
Cl
Cl
N
O
N
3as
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.85
7.84
7.82
7.49
7.46
7.40
7.29
7.28
7.24
7.22
7.14
7.12
7.11
6.99
4.65
4.44
4.17
4.13
3.32
3.30
3.29
3.28
3.26
3.13
3.11
3.09
N
O
N
2.91
1.99
1.91
0.96
0.96
0.97
0.92
0.90
0.98
0.98
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3at

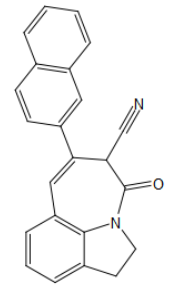

159.2
137.7
133.9
130.8
129.3
128.5
127.1
125.5
125.0
123.2
114.2
77.2
77.0
76.8
50.4
44.3
27.9
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3at



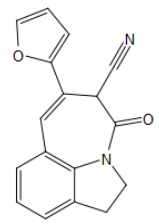
3au

7.97
7.90
7.89
7.86
7.84
7.52
7.34
7.33
7.21
7.20
7.19
7.18
5.06
4.52
4.50
4.15
4.14
4.12
3.34
3.33
3.17
3.15
3.13
f1 (ppm)



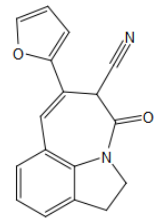
3au

158.95
137.97
136.05
134.23
133.15
133.09
128.32
125.68
123.51
114.14
77.21
77.00
76.79
50.23
42.38
27.88
f1 (ppm)



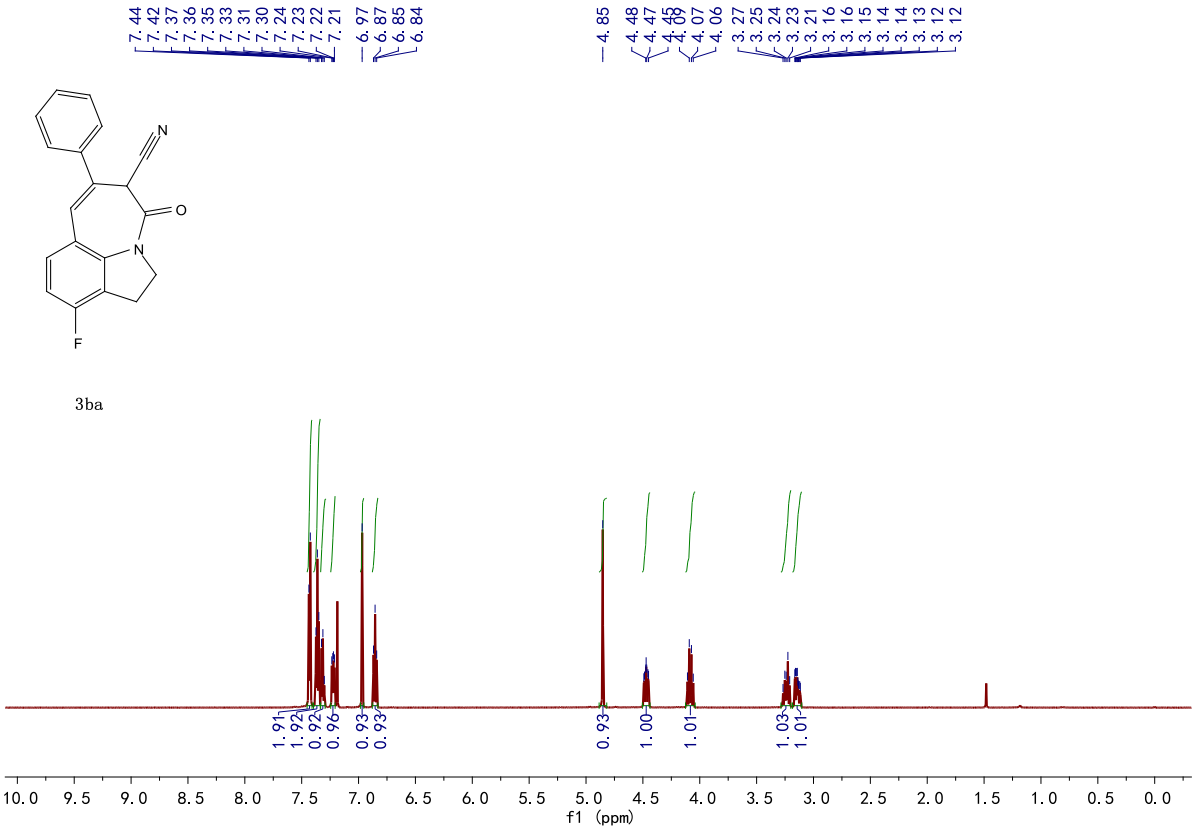
3av

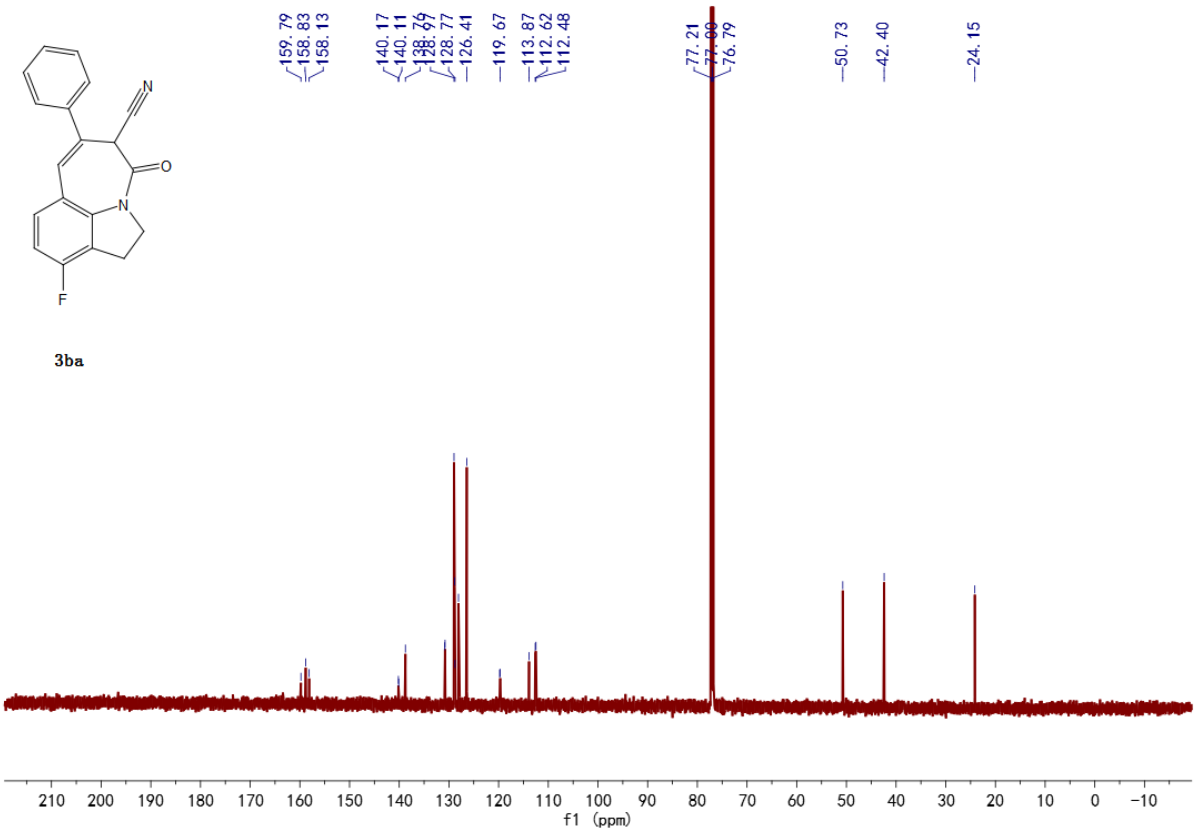
7.50
7.36
7.33
7.32
7.20
7.19
7.18
6.68
6.52
4.97
4.58
4.56
4.04
4.03
4.01
3.99
3.38
3.36
3.13
3.12
3.11
3.09
0.92
2.90
0.97
0.97
0.93
0.93
0.99
0.99
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

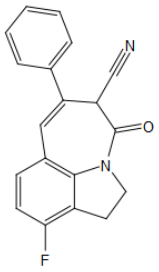


3av

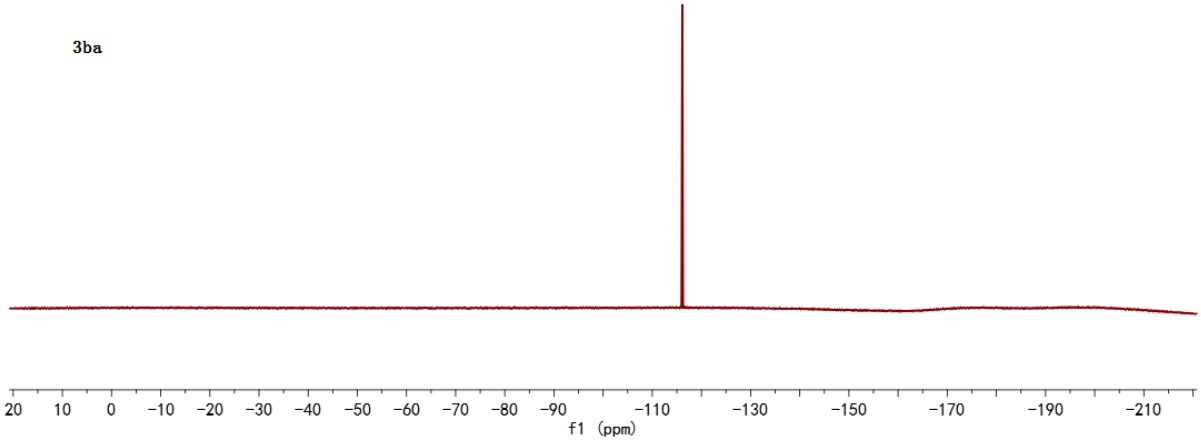
158.17
151.32
143.83
134.22
124.64
123.17
118.19
113.66
112.22
108.65
77.21
77.00
76.79
50.34
39.50
27.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

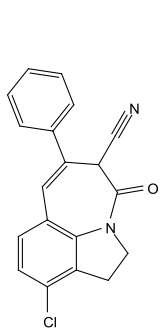

7.44
7.42
7.37
7.36
7.35
7.33
7.31
7.30
7.24
7.23
7.22
7.21
6.97
6.87
6.85
6.84
4.85
4.48
4.47
4.45
4.09
4.07
4.06
3.27
3.25
3.24
3.23
3.21
3.16
3.15
3.14
3.13
3.12
3.12
N
O
N
F
3ba
1.91
1.92
0.92
0.96
0.93
0.93
0.93
1.00
1.01
1.03
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.79
158.83
158.13
140.17
140.11
138.76
138.69
128.77
126.41
119.67
113.87
112.62
112.48
77.21
77.00
76.79
50.73
42.40
24.15
N
O
N
F
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
O
N
F

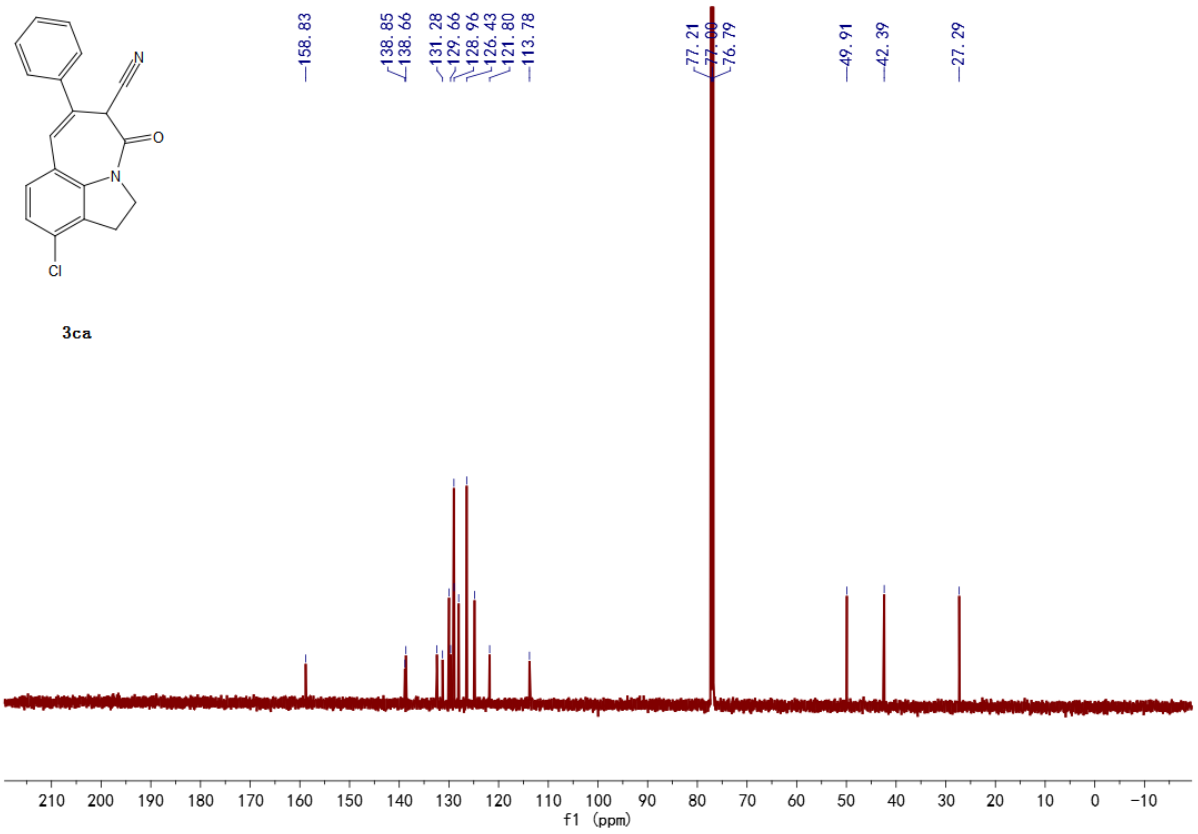
3ba


20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)

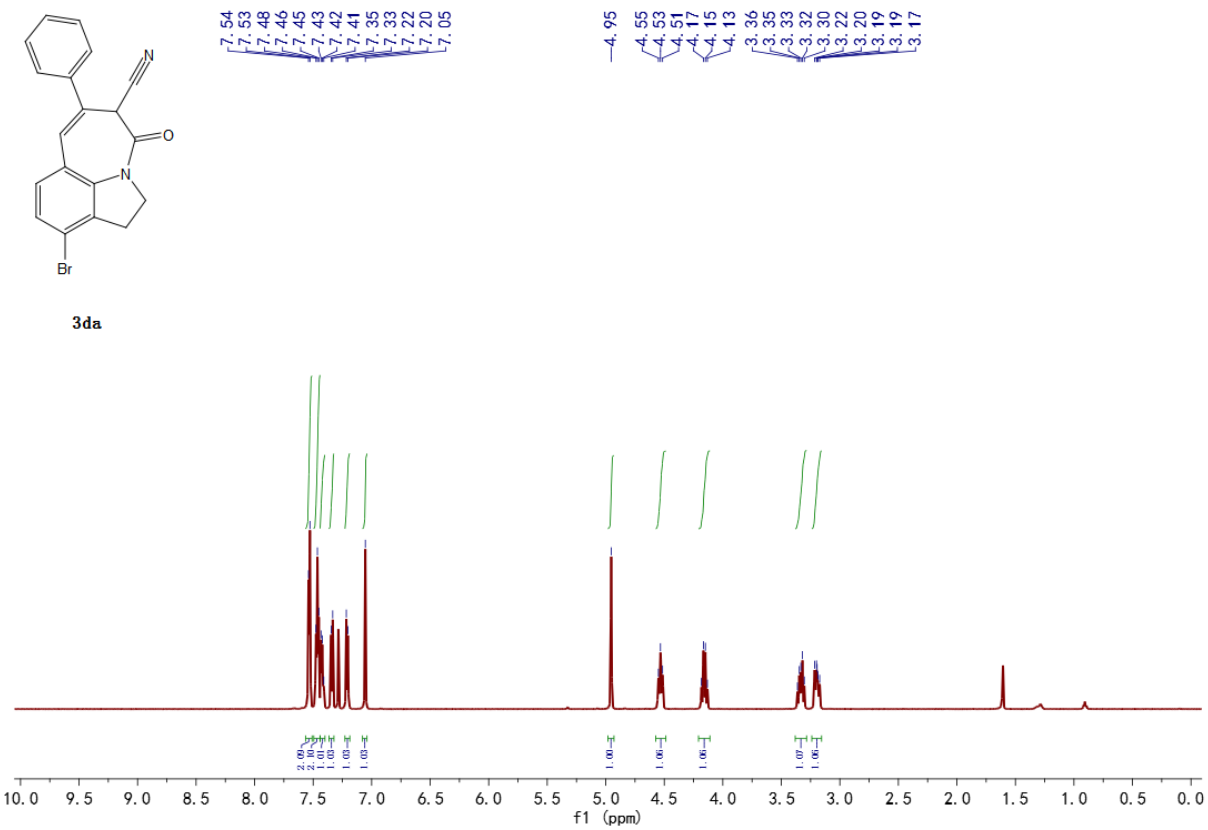

N
O
N
Cl

3ca

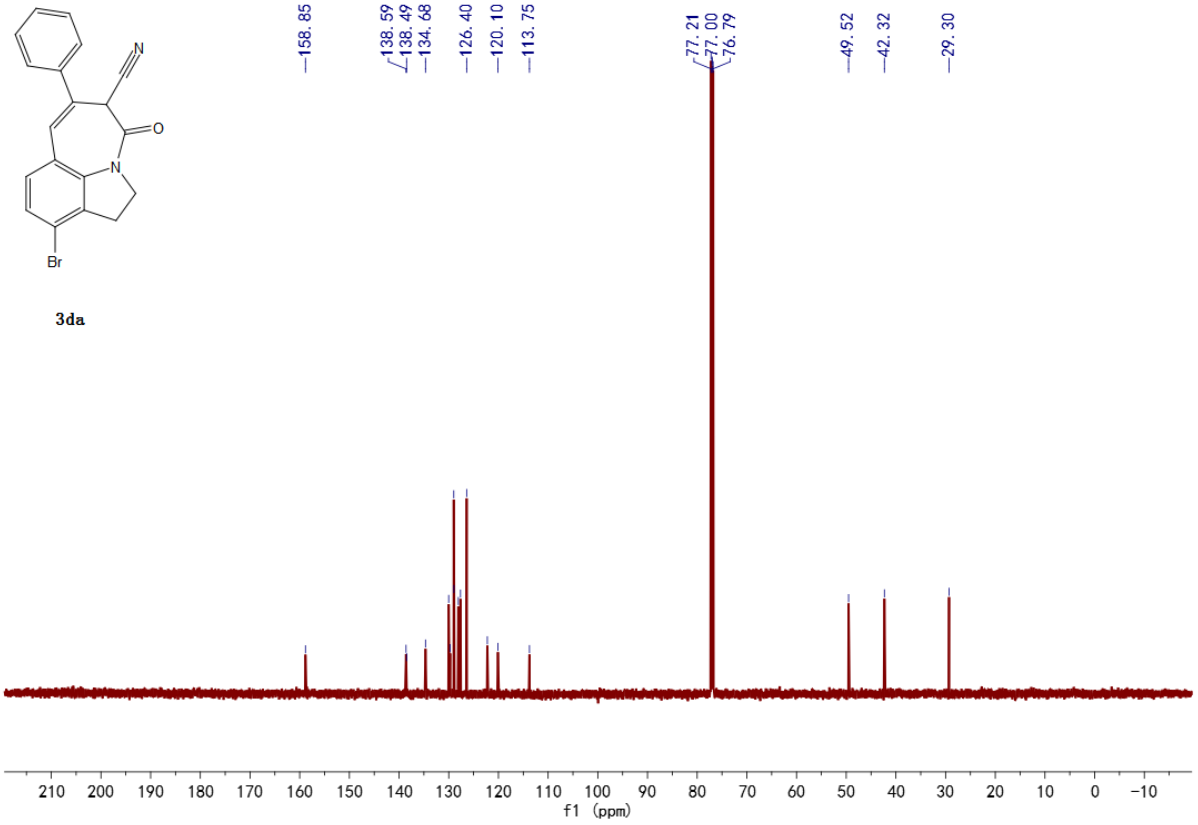
7.51 7.50 7.45 7.43 7.42 7.40 7.39 7.38 7.25 7.25 7.17 7.15 7.04
4.93 4.52 4.50 4.50 4.14 4.12 4.11
3.35 3.34 3.33 3.31 3.29 3.22 3.22 3.21 3.20 3.20 3.19 3.18 3.17
1.90 1.90 0.93 1.02 0.92 0.92
0.91 1.00 1.04 1.04 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.83
138.85
138.66
131.28
129.66
128.96
126.43
121.80
113.78
77.21
77.00
76.79
49.91
42.39
27.29
N
O
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

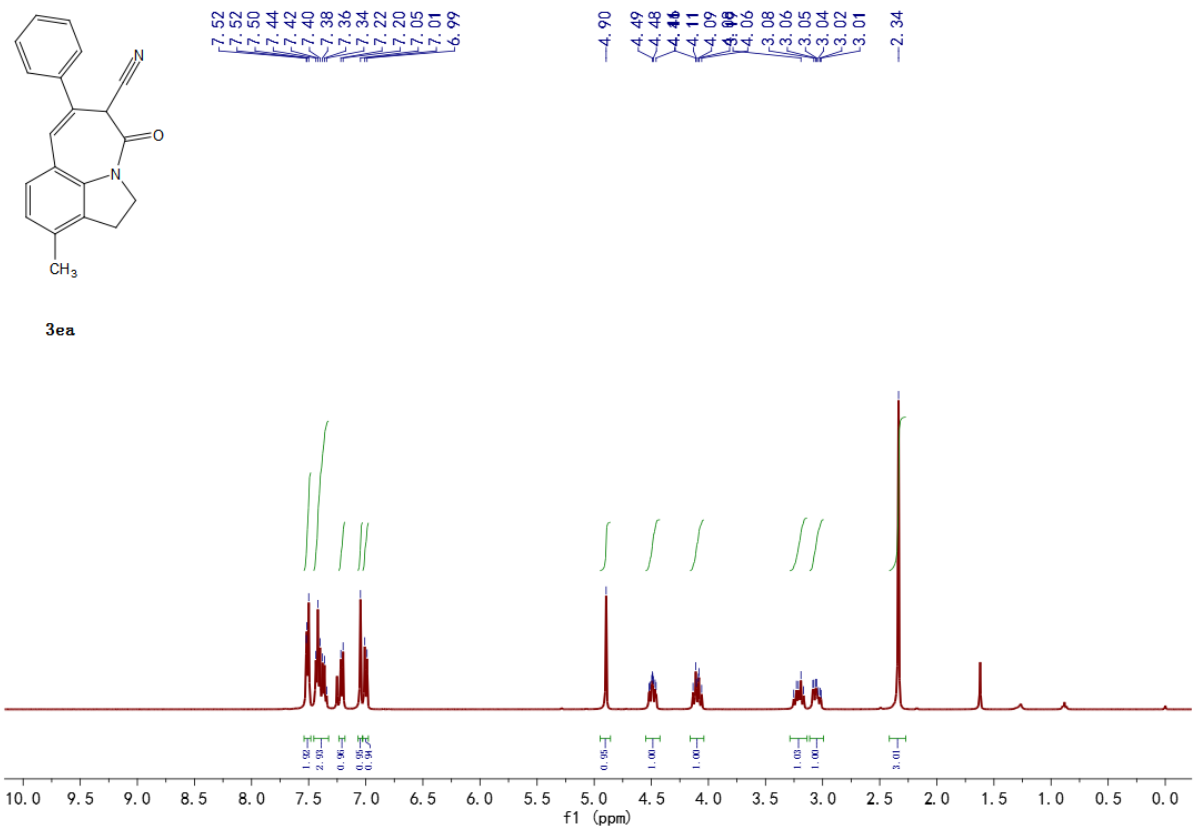
3ca


7.54
7.53
7.48
7.46
7.45
7.43
7.42
7.41
7.35
7.33
7.22
7.20
7.05
4.95
4.55
4.53
4.51
4.17
4.15
4.13
3.36
3.35
3.33
3.32
3.30
3.22
3.20
3.19
3.19
3.17
N
O
N
Br
2.09
2.10
1.01
1.03
1.03
1.00
1.00
1.00
1.07
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

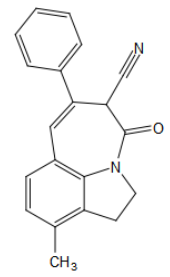
3da

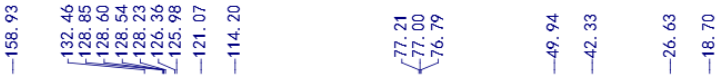

158.85
138.59
138.49
134.68
126.40
120.10
113.75
77.21
77.00
76.79
49.52
42.32
29.30
N
O
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3da

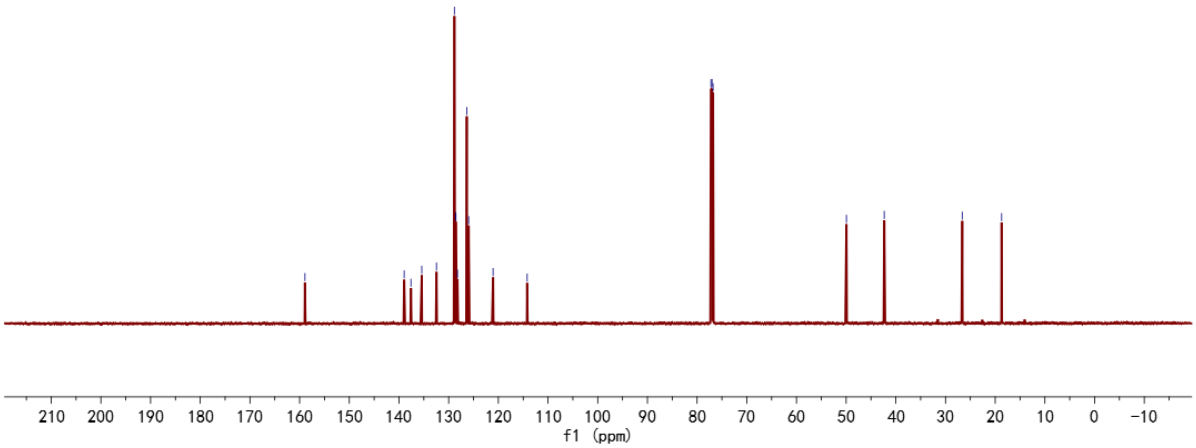

7.52
7.52
7.50
7.44
7.42
7.40
7.38
7.36
7.34
7.22
7.20
7.05
7.01
6.99
4.90
4.49
4.48
4.11
4.09
4.06
3.08
3.06
3.05
3.04
3.02
3.01
2.34
N
O
N
CH3
1.92
2.93
0.90
0.95
0.94
0.95
1.00
1.00
1.03
1.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

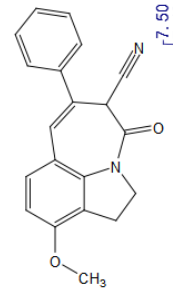
3ea


N
O
N
CH3


158.93
132.46
128.85
128.60
128.54
128.23
126.36
125.98
121.07
114.20
77.21
77.00
76.79
49.94
42.33
26.63
18.70

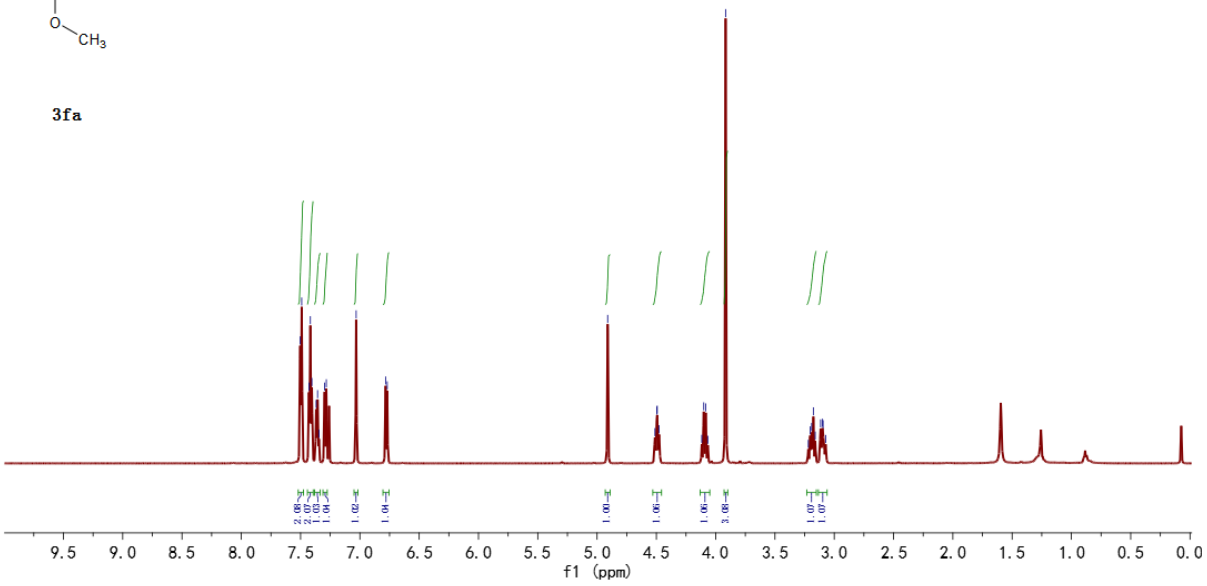
3ea

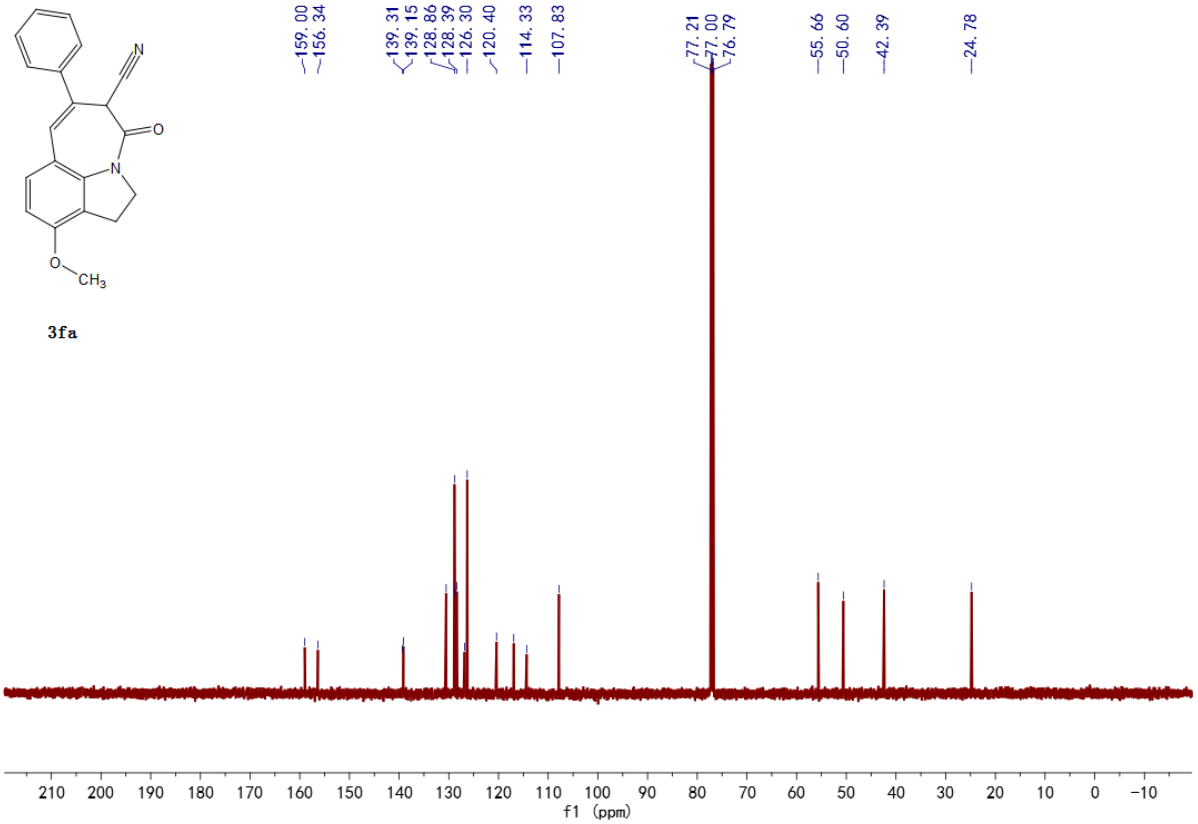

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


N
O
N
O
CH3

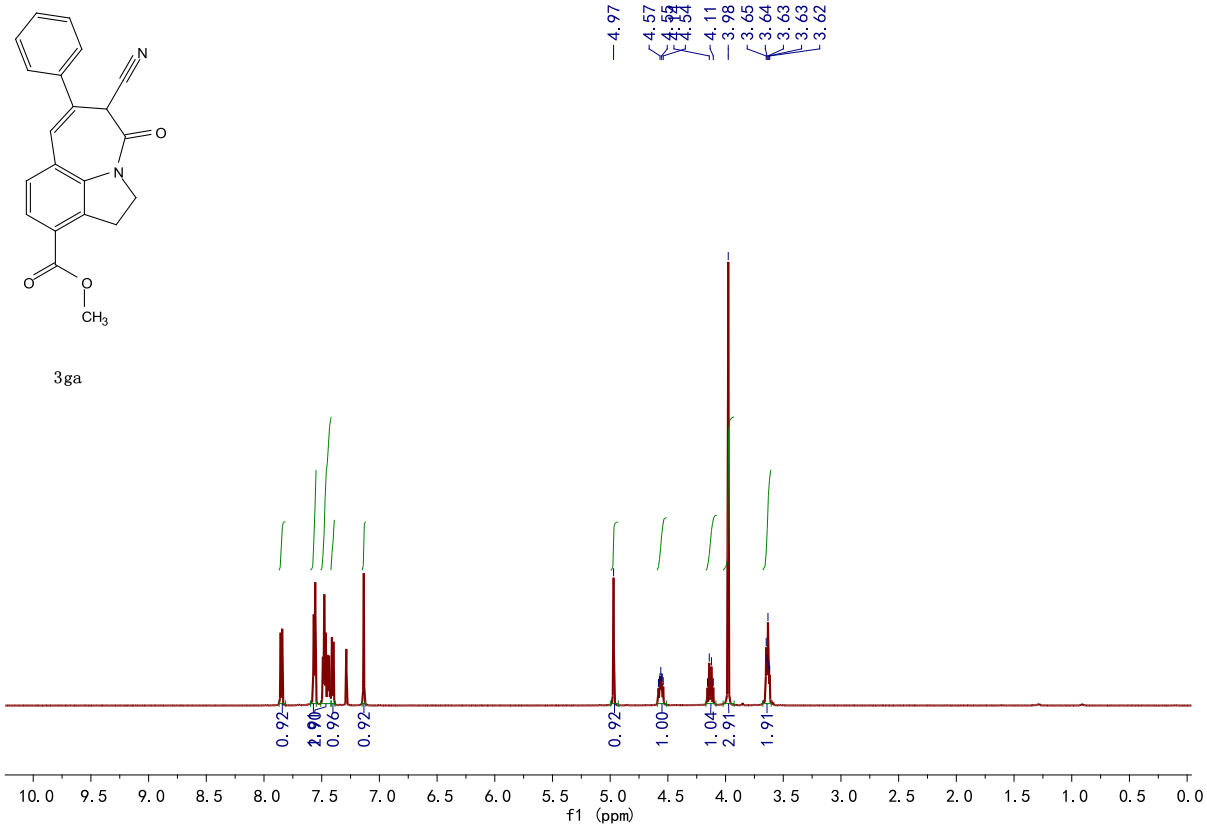

7.50
7.49
7.43
7.42
7.41
7.37
7.36
7.34
7.30
7.28
7.03
6.78
6.77
4.91
4.50
4.49
4.48
4.10
4.08
4.07
3.92
3.22
3.20
3.19
3.18
3.16
3.11
3.10
3.09
3.07

3fa

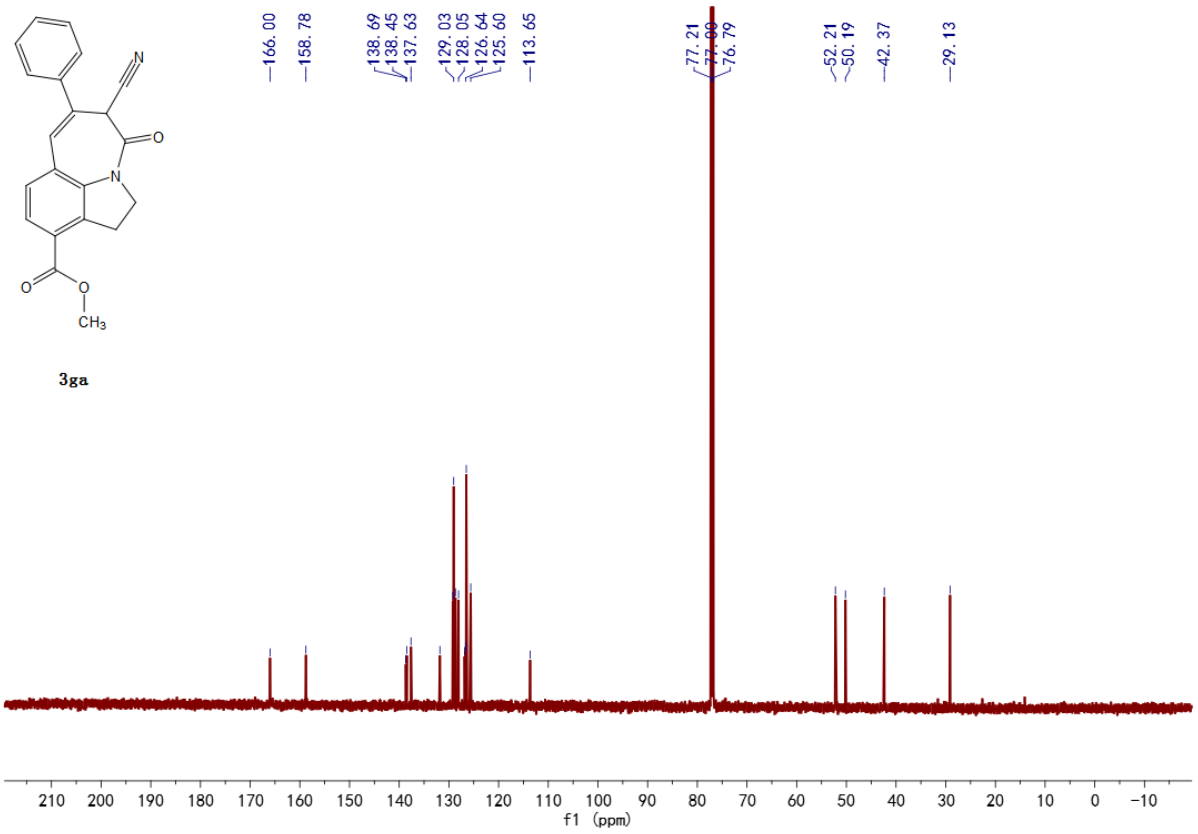

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.00
156.34
139.31
139.15
128.86
128.39
126.30
120.40
114.33
107.83
77.21
77.00
76.79
55.66
50.60
42.39
24.78
f1 (ppm)

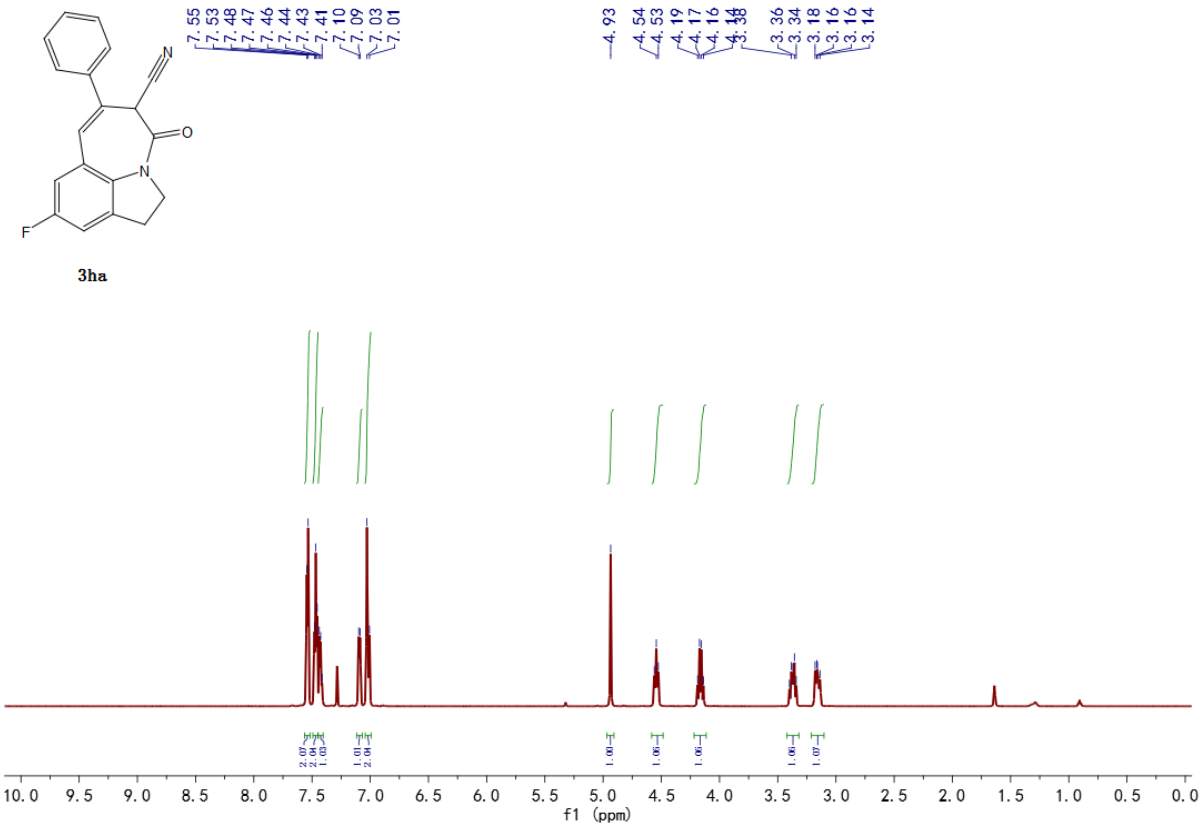
3fa


4.97
4.57
4.54
4.11
3.98
3.65
3.64
3.63
3.63
3.62
0.92
2.90
0.96
0.92
0.92
1.00
1.04
2.91
1.91
f1 (ppm)

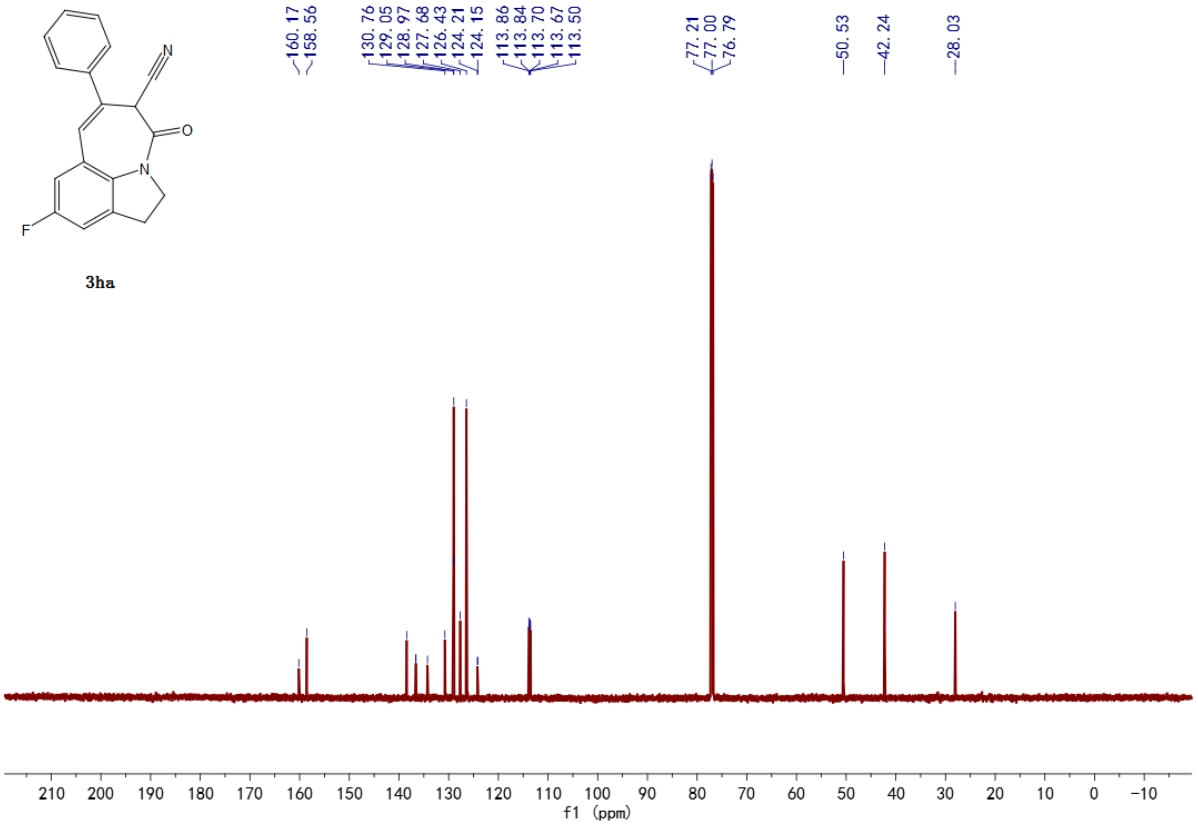
3ga


166.00
158.78
138.69
138.45
137.63
129.03
128.05
126.64
125.60
113.65
77.21
77.00
76.79
52.21
50.19
42.37
29.13
N
O
O
O
CH3
f1 (ppm)

3ga


7.55
7.53
7.48
7.47
7.46
7.44
7.43
7.41
7.10
7.09
7.03
7.01
4.93
4.54
4.53
4.19
4.17
4.16
4.14
3.38
3.36
3.34
3.18
3.16
3.16
3.14
N
O
F
f1 (ppm)

3ha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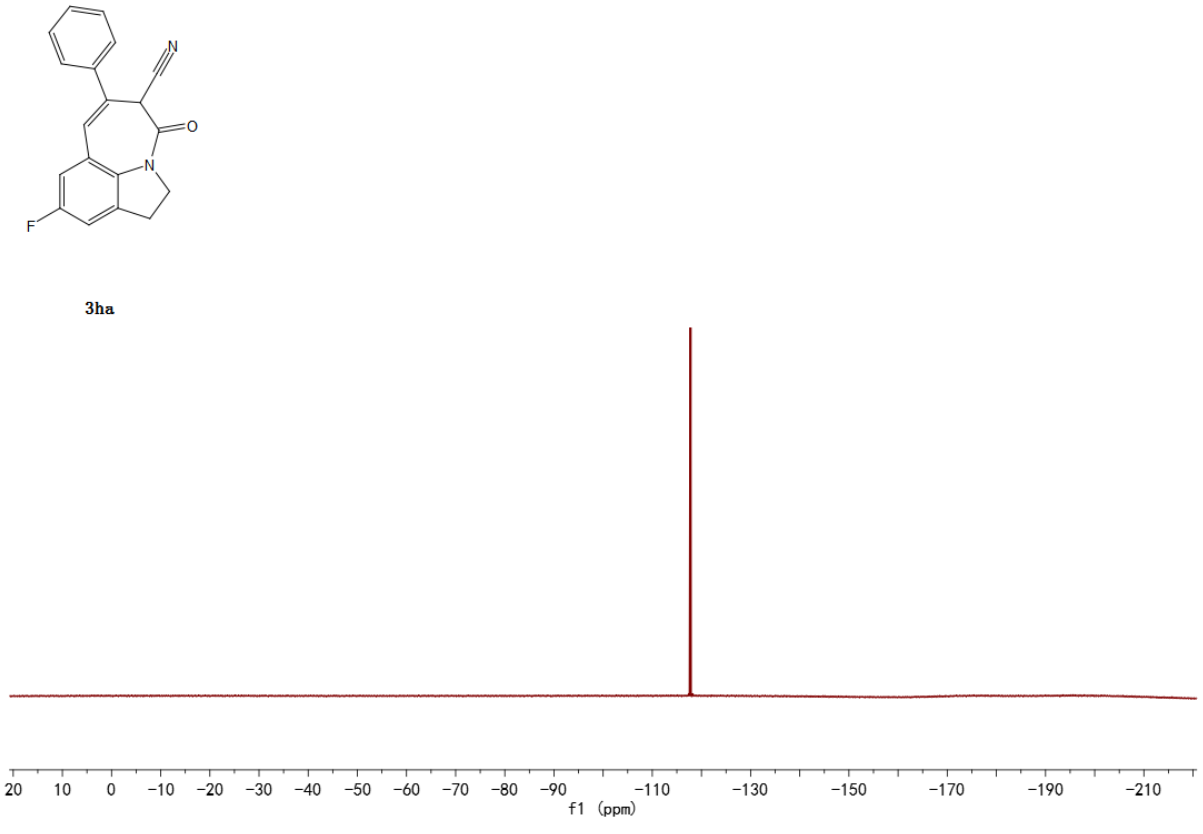
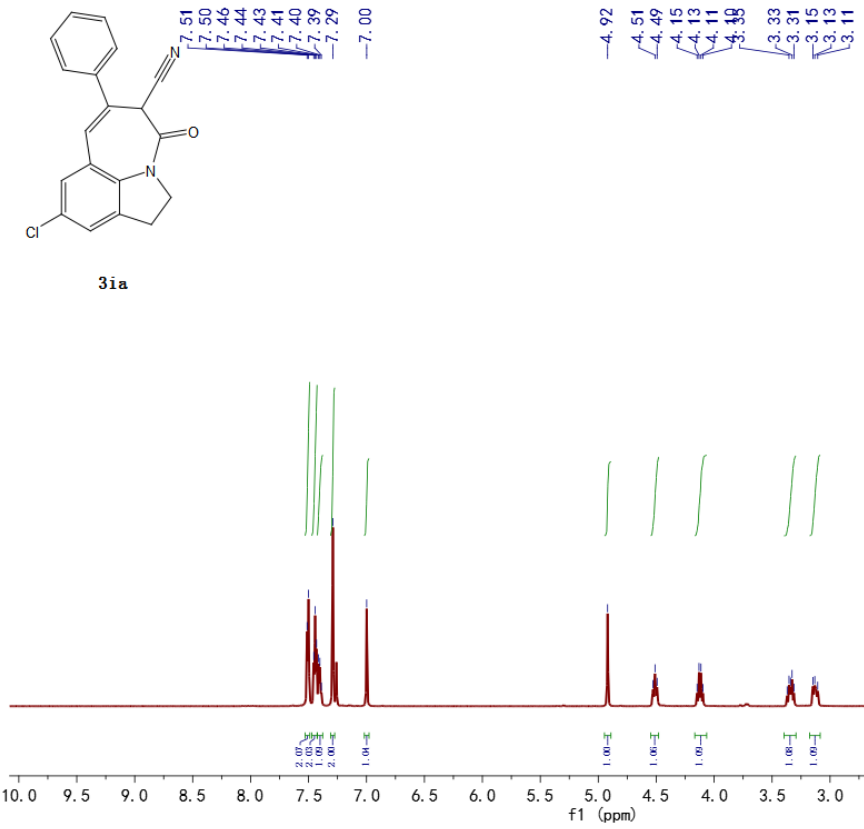
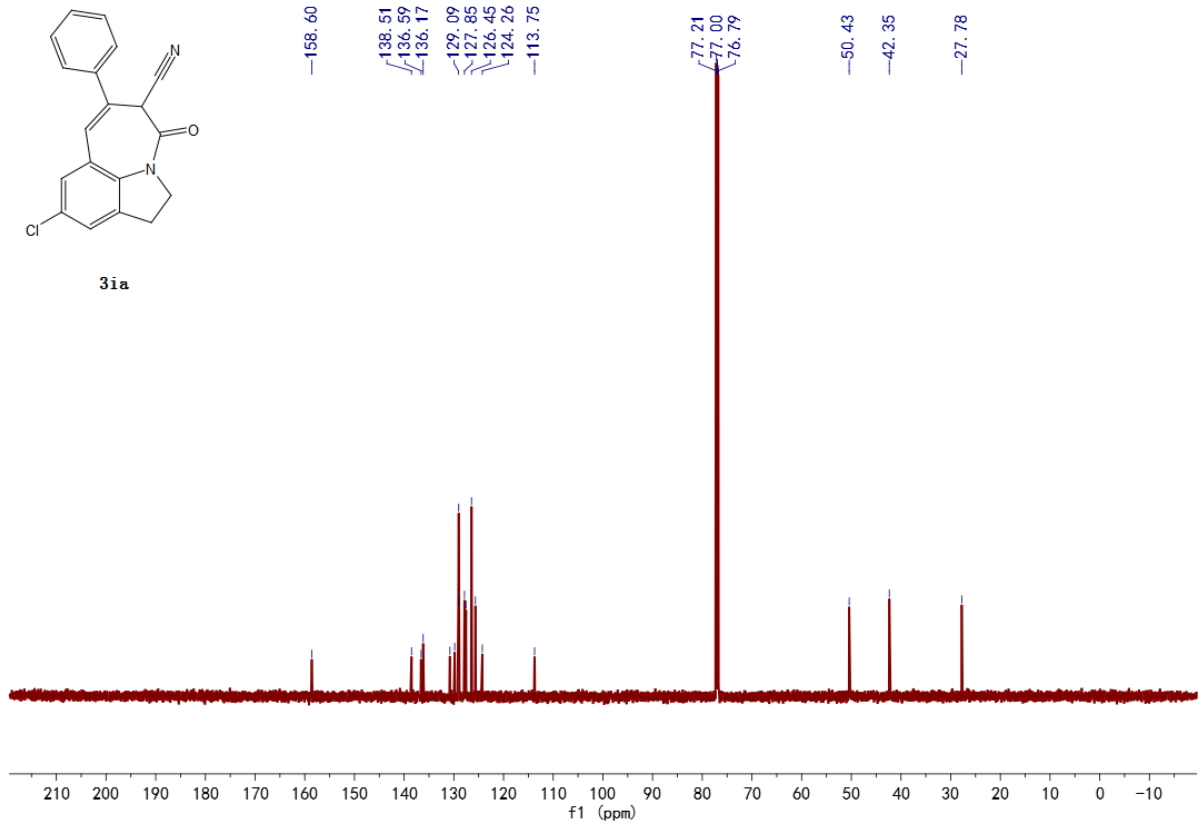
158.56
130.76
129.05
128.97
127.68
126.43
124.21
124.15
113.86
113.84
113.70
113.67
113.50
77.21
77.00
76.79
50.53
42.24
28.03
N
O
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

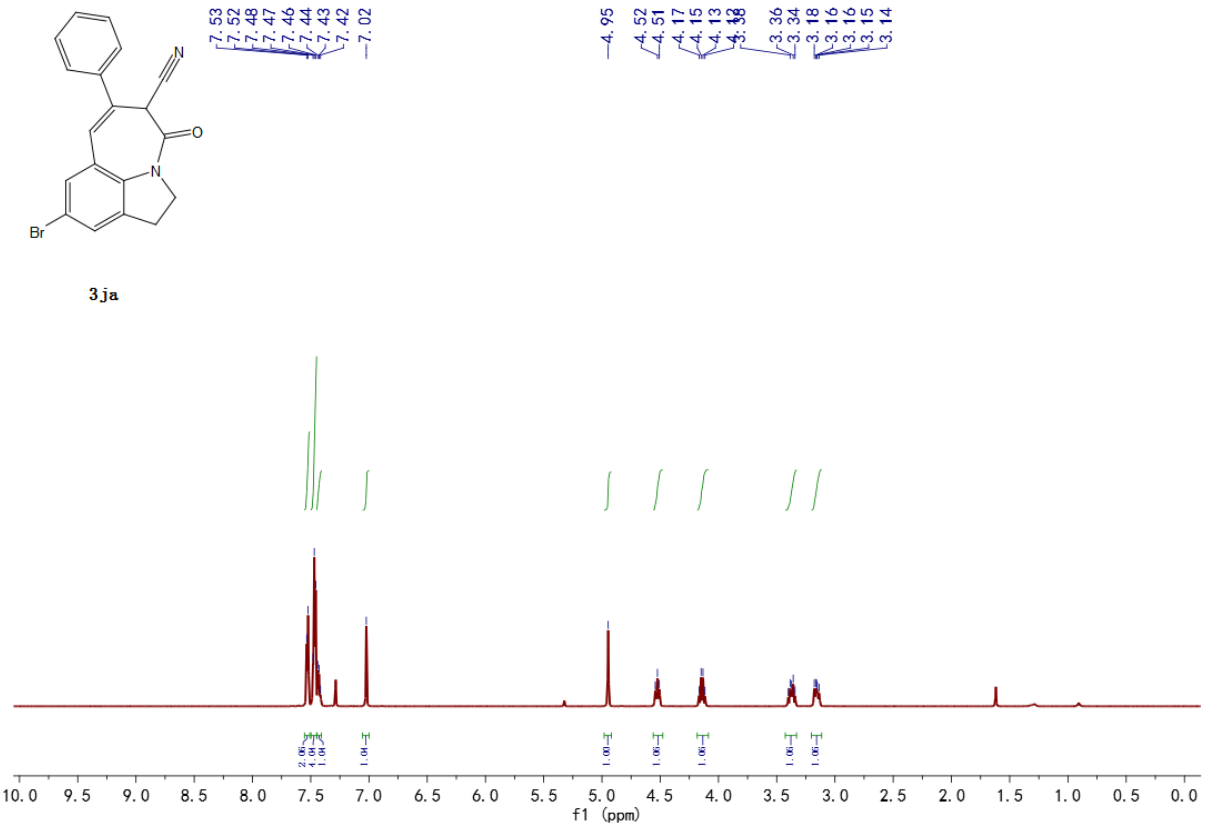
3ha

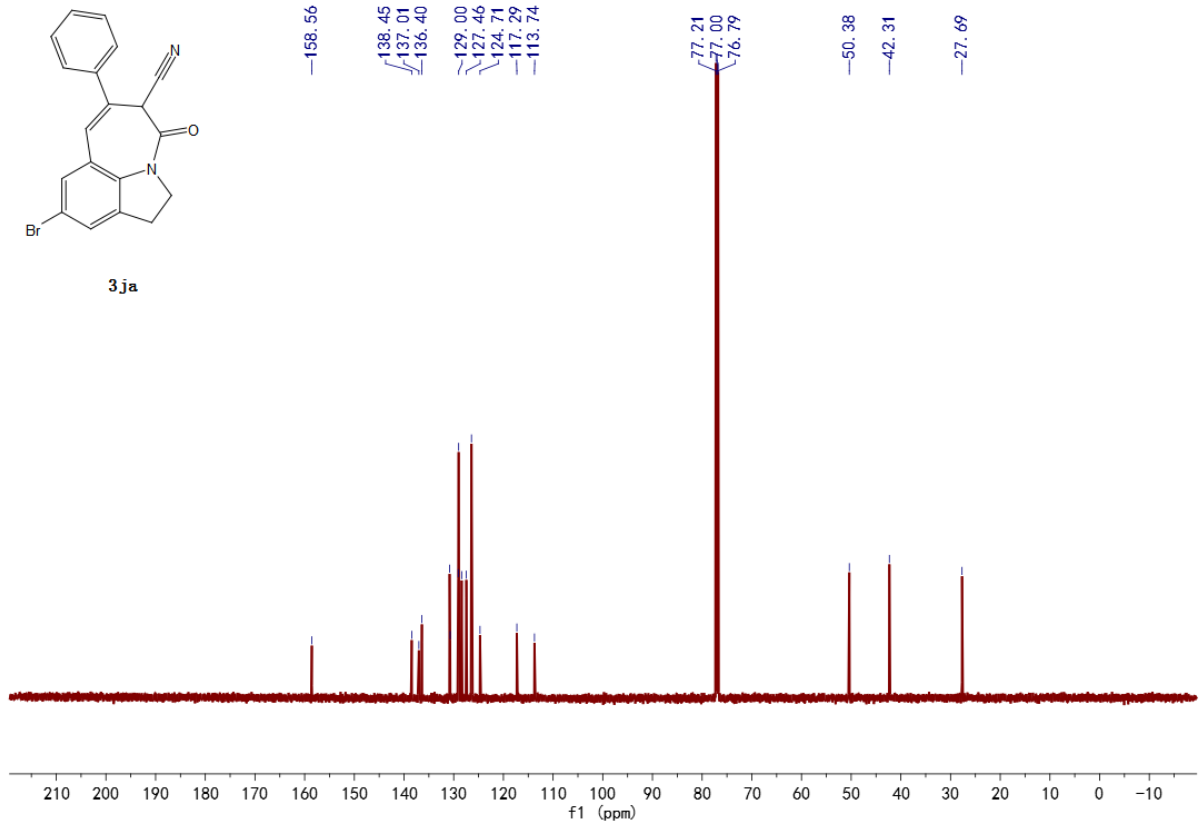

N
O
N
F
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)

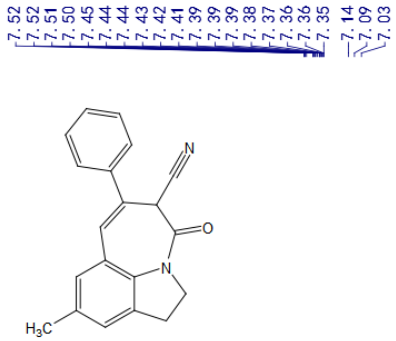
3ha


7.51
7.50
7.46
7.44
7.43
7.41
7.40
7.39
7.29
7.00
4.92
4.51
4.49
4.15
4.13
4.11
3.33
3.31
3.15
3.13
3.11
N
O
N
Cl
3ia
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

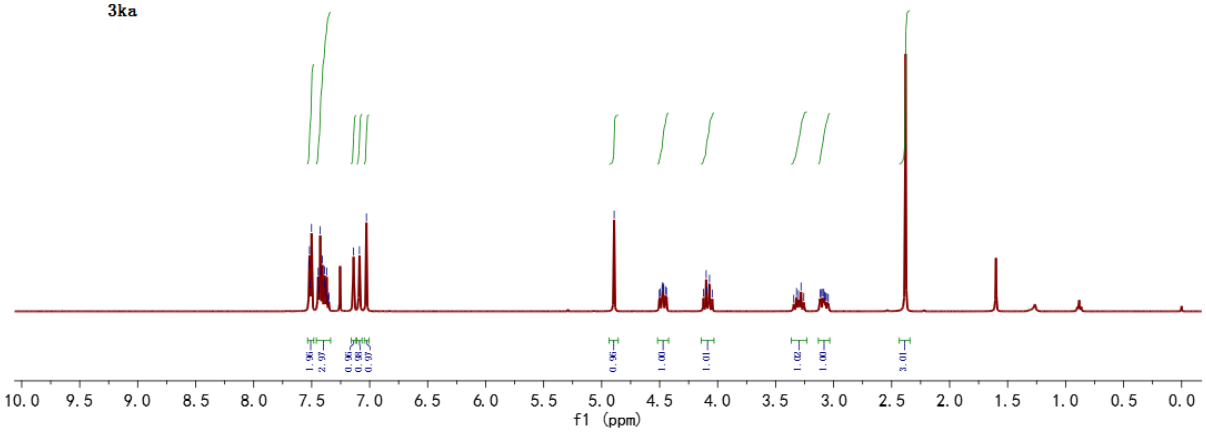

158.60
138.51
136.59
136.17
129.09
127.85
126.45
124.26
113.75
77.21
77.00
76.79
50.43
42.35
27.78
N
O
N
Cl
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

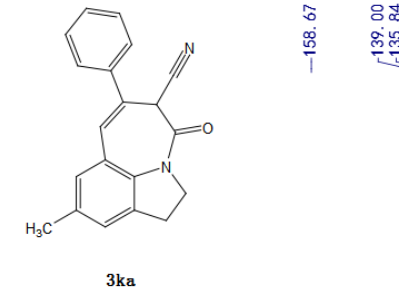

7.53
7.52
7.48
7.47
7.46
7.44
7.43
7.42
7.02
4.95
4.52
4.51
4.17
4.15
4.13
3.36
3.34
3.18
3.16
3.15
3.14
N
O
N
Br
3ja
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.56
138.45
137.01
136.40
129.00
127.46
124.71
117.29
113.74
77.21
77.00
76.79
50.38
42.31
27.69
N
O
N
Br
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

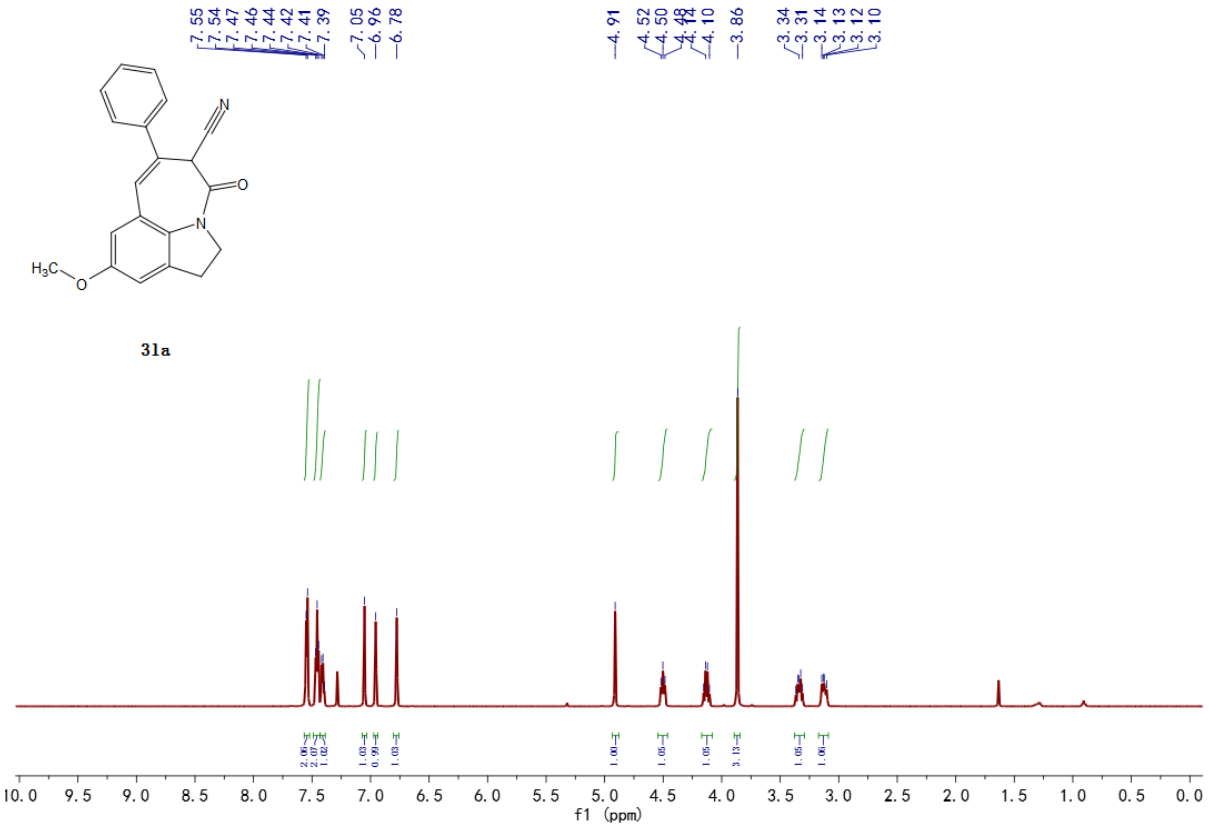


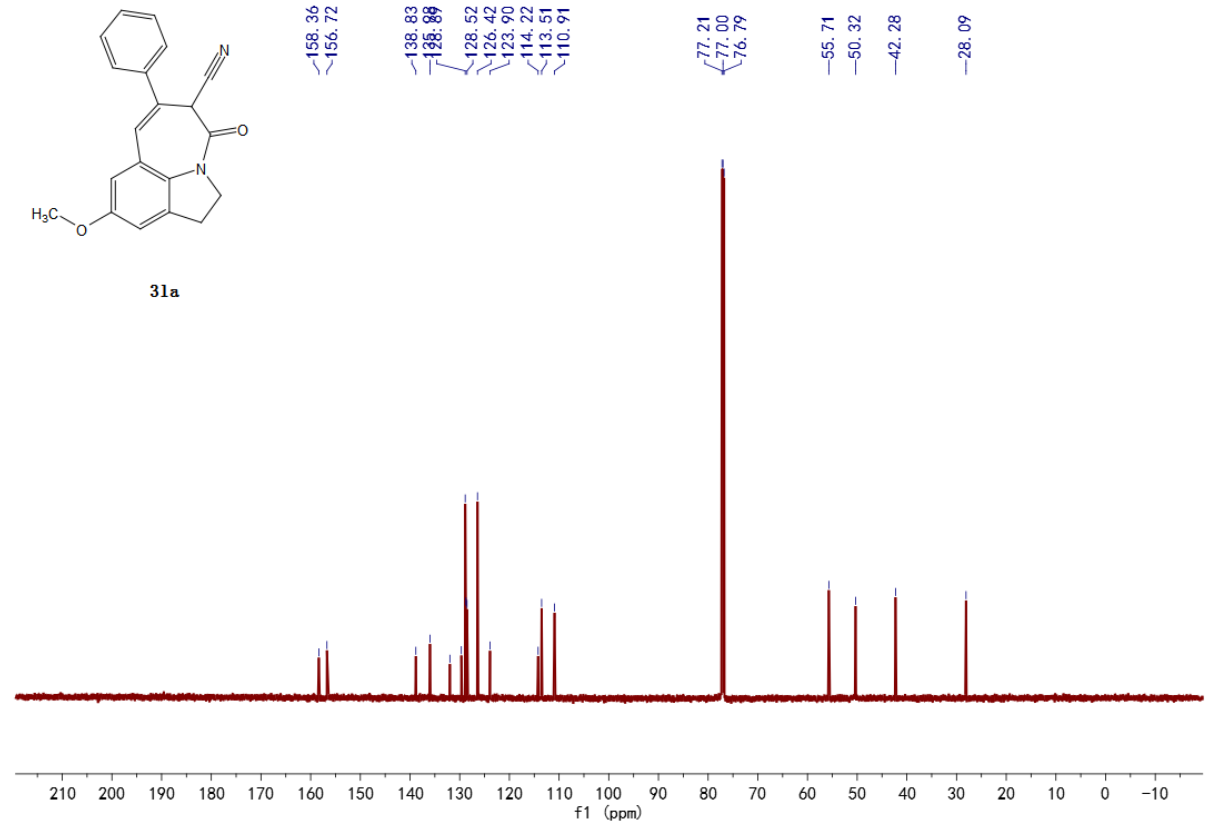
3ka

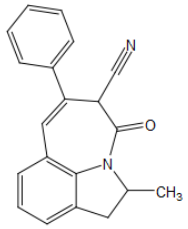




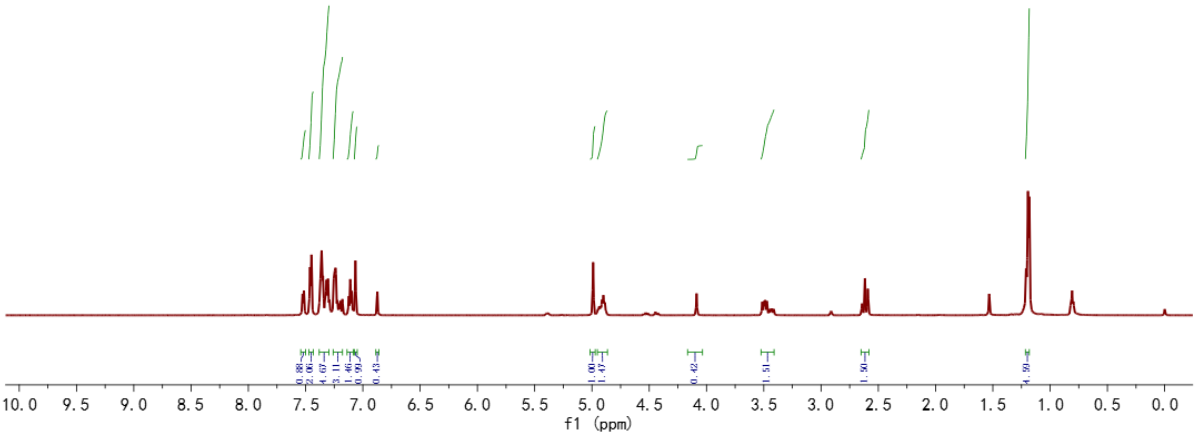
3ka

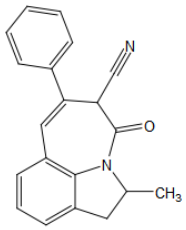

7.55
7.54
7.47
7.46
7.44
7.42
7.41
7.39
7.05
6.96
6.78
4.91
4.52
4.50
4.10
3.86
3.34
3.31
3.14
3.13
3.12
3.10
N
O
N
H3C
O
31a
f1 (ppm)


158.36
156.72
138.83
128.52
126.42
123.90
114.22
113.51
110.91
77.21
77.00
76.79
55.71
50.32
42.28
28.09
N
O
N
H3C
O
31a
f1 (ppm)

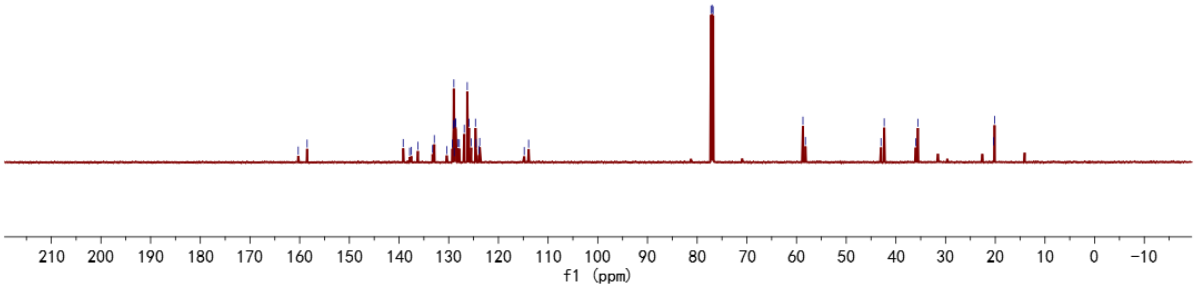


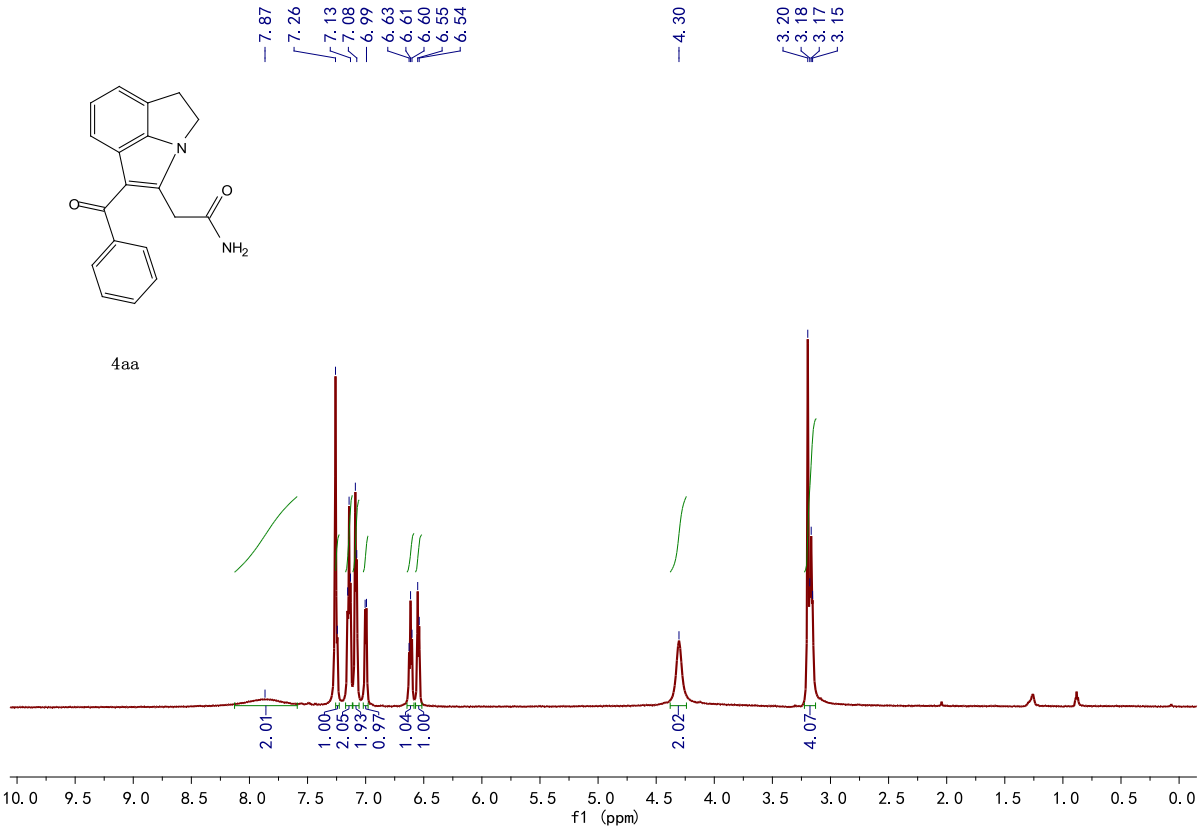
3ma, d. r. =1:2.4

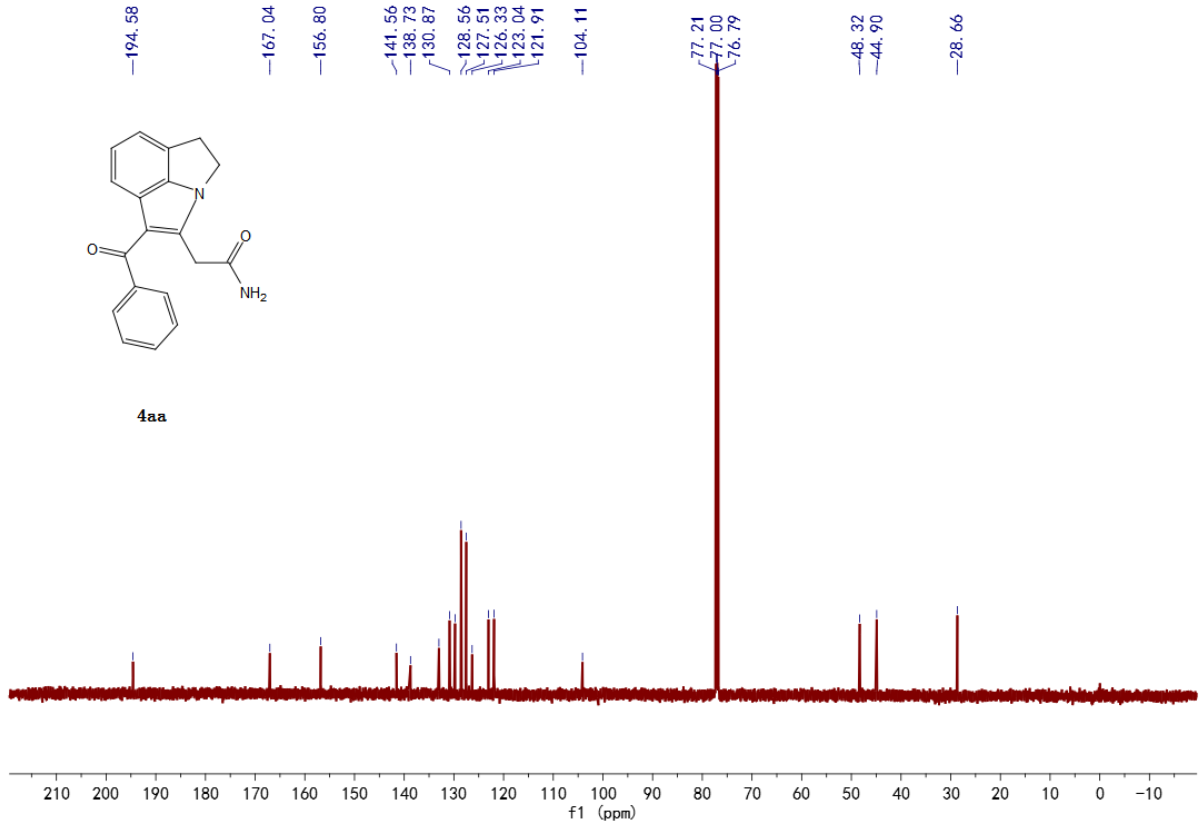


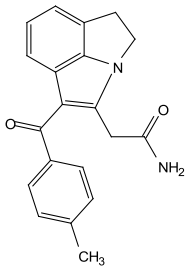


3ma, d. r. =1:2.4



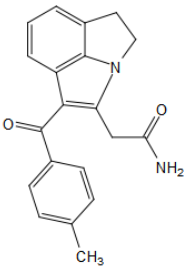

7.87
7.26
7.13
7.08
6.99
6.63
6.61
6.60
6.55
6.54
4.30
3.20
3.18
3.17
3.15
O
N
O
NH2
4aa
2.01
1.00
2.05
1.93
0.97
1.04
1.00
2.02
4.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.58
167.04
156.80
141.56
138.73
130.87
128.56
127.51
126.33
123.04
121.91
104.11
77.21
77.00
76.79
48.32
44.90
28.66
O
N
O
NH2
4aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
O
O
NH2
CH3

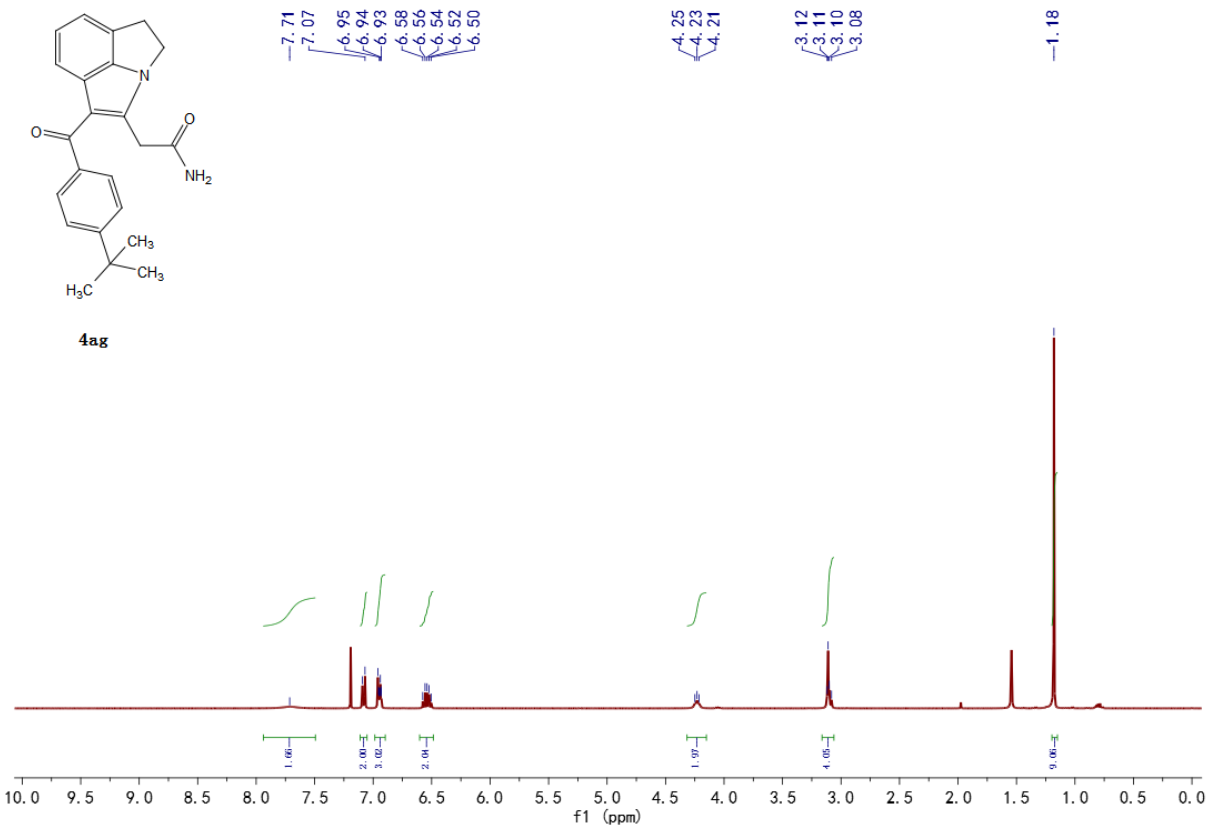
4ae

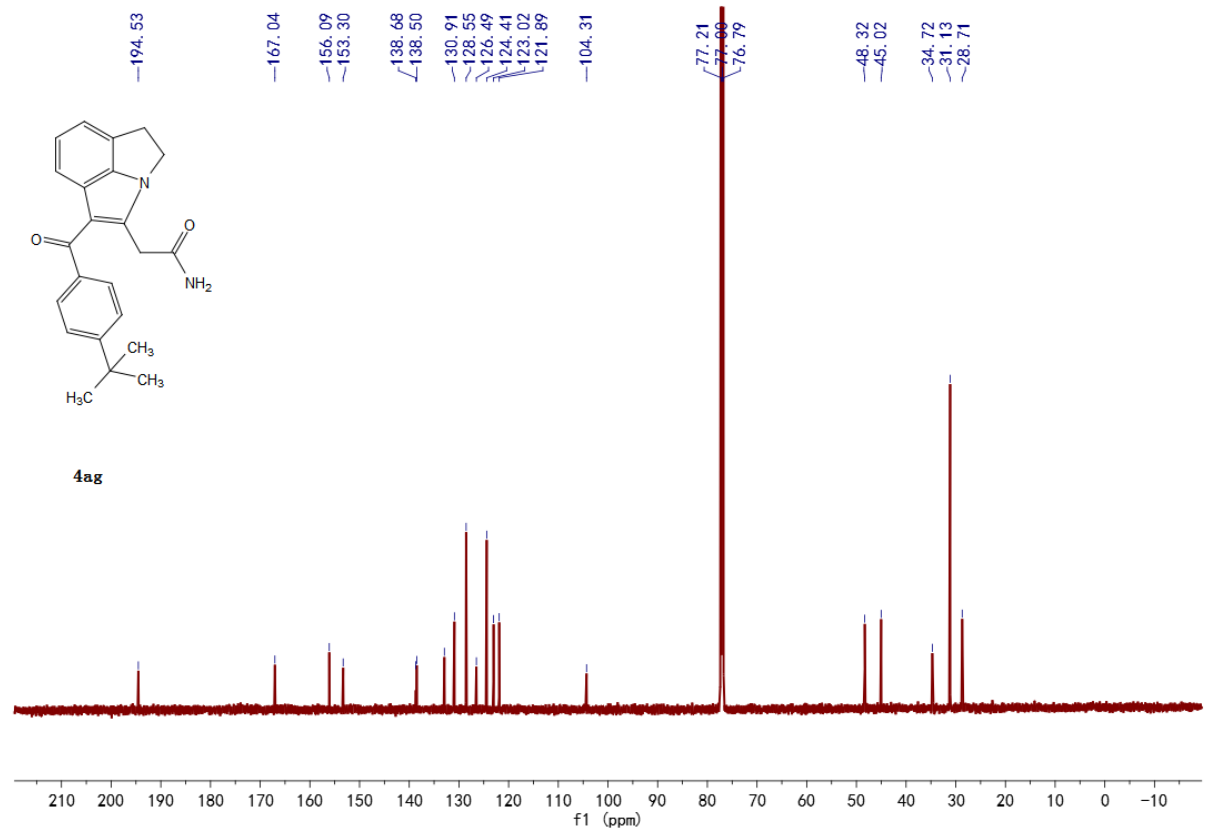
7.70
7.26
6.93
6.66
6.64
6.63
6.59
6.57
4.32
4.30
4.28
3.18
3.17
3.15
2.28
1.89
5.06
1.08
1.00
2.06
4.12
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

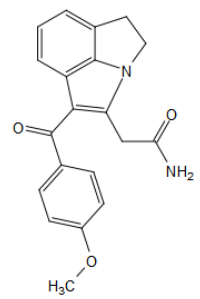

N
O
O
NH2
CH3

4ae

194.53
167.02
156.08
140.19
138.72
138.62
130.85
128.79
128.20
126.49
123.09
121.87
104.27
77.21
77.00
76.79
48.31
45.05
28.69
21.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

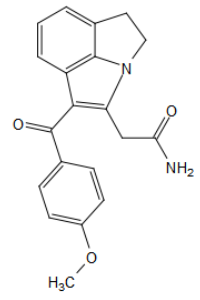

7.71
7.07
6.95
6.94
6.93
6.58
6.56
6.54
6.52
6.50
4.25
4.23
4.21
3.12
3.11
3.10
3.08
1.18
O
N
O
NH2
CH3
CH3
H3C
4ag
f1 (ppm)


194.53
167.04
156.09
153.30
138.68
138.50
130.91
128.55
126.49
124.41
123.02
121.89
104.31
77.21
77.00
76.79
48.32
45.02
34.72
31.13
28.71
O
N
O
NH2
CH3
CH3
H3C
4ag
f1 (ppm)



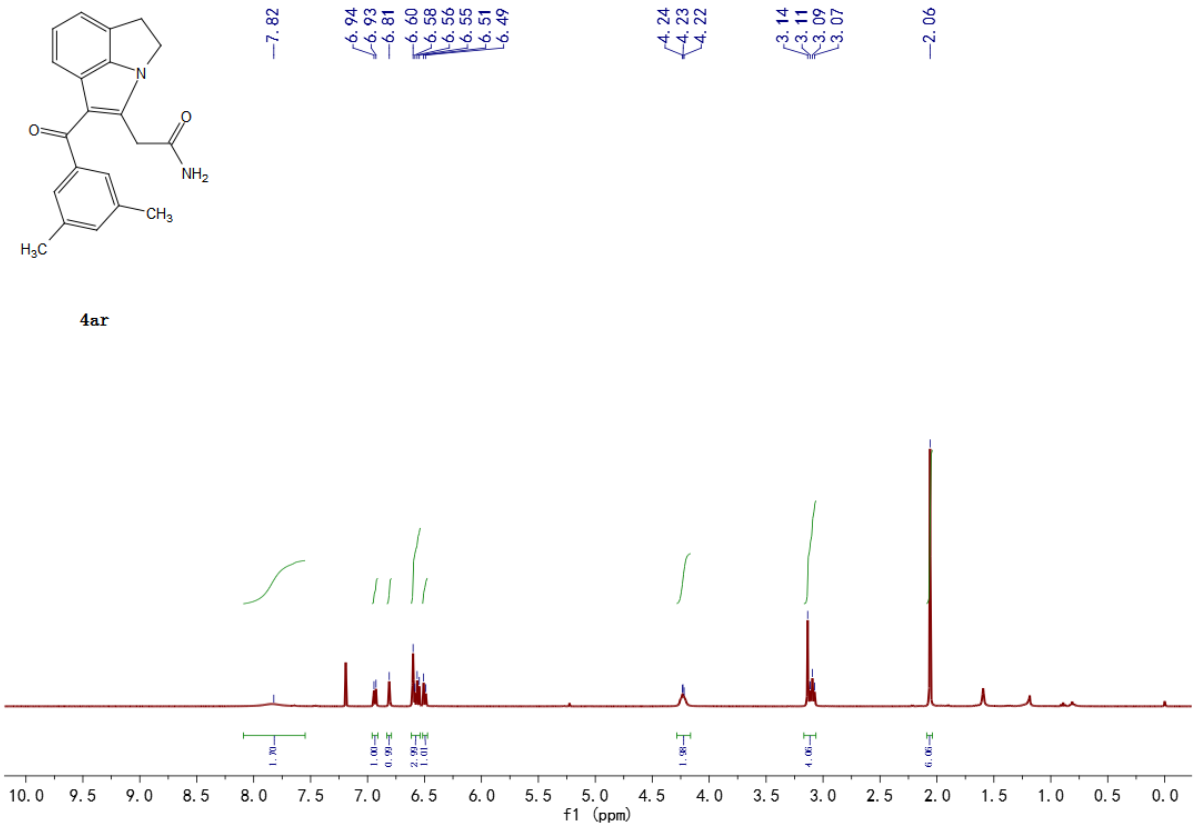
4ai

7.63
6.98
6.95
6.94
6.62
6.60
6.59
6.57
6.56
6.55
6.53
4.25
4.23
4.21
3.70
3.12
3.11
3.10
3.08
1.02
1.98
1.00
4.02
1.02
3.03
3.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4ai

193.66
167.10
161.02
155.80
138.64
130.83
126.67
123.16
121.85
112.76
104.11
77.21
77.00
76.79
55.20
48.32
44.94
28.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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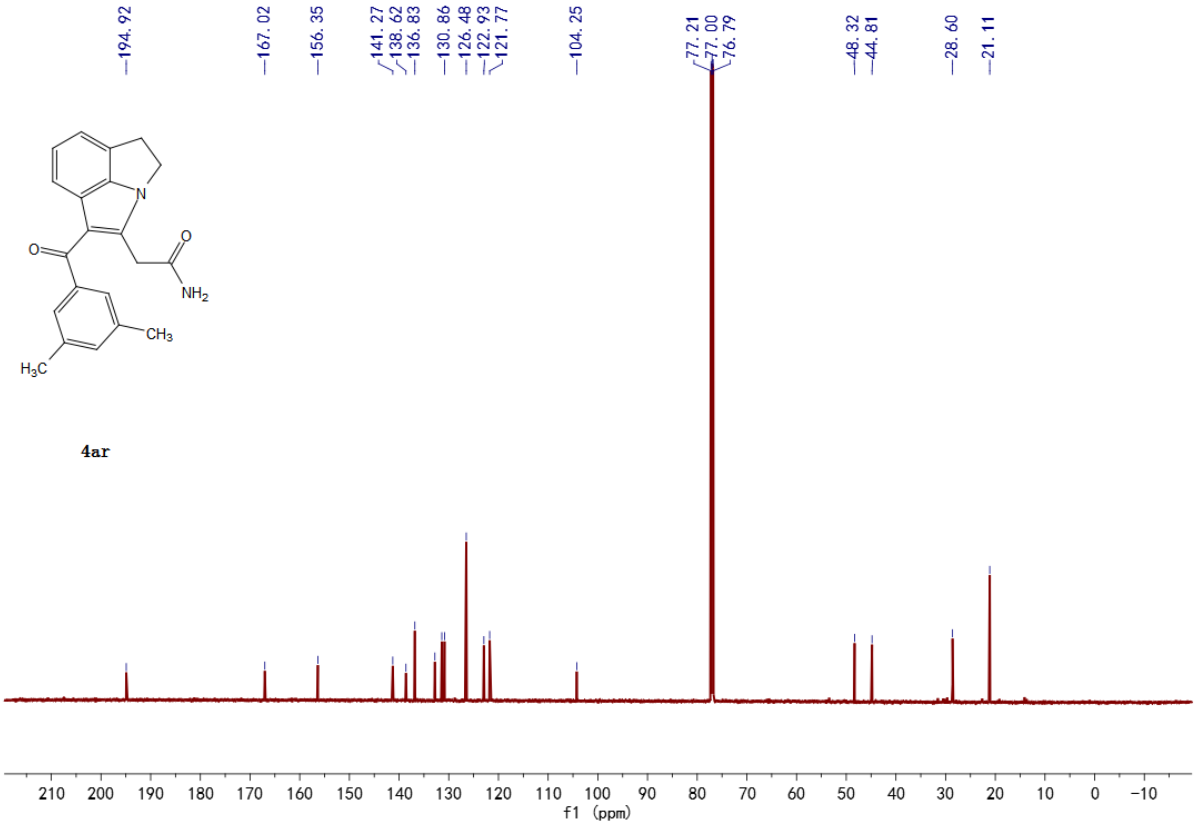
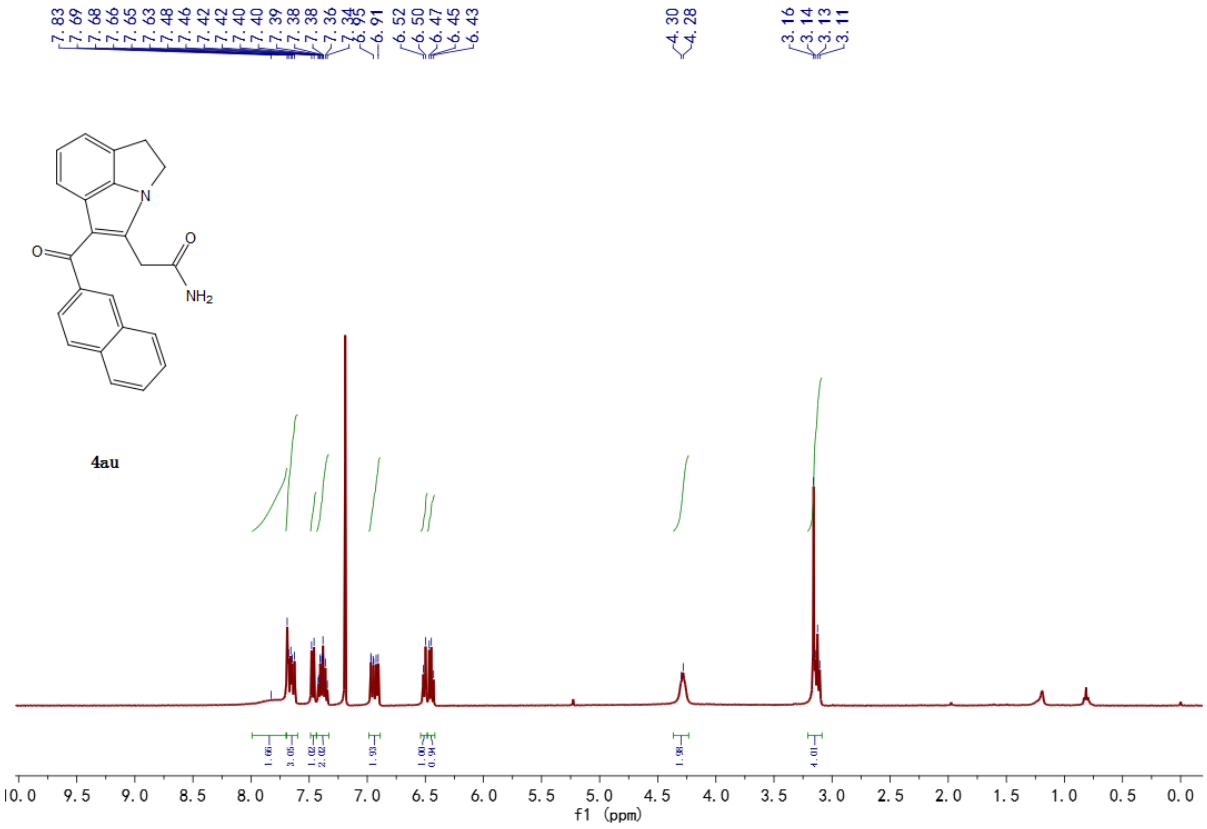
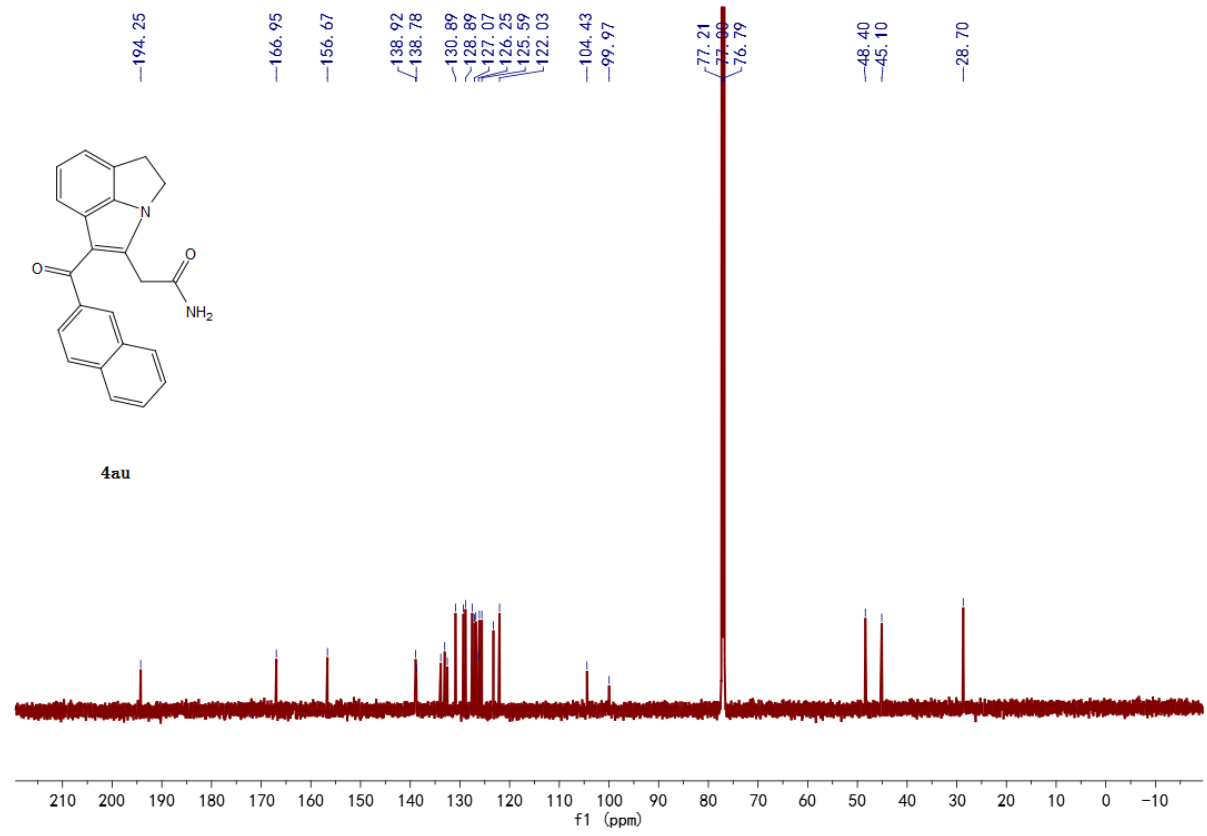
6.94
6.93
6.81
6.60
6.58
6.56
6.55
6.51
6.49
4.24
4.23
4.22
3.14
3.11
3.09
3.07
2.06
O
N
O
NH2
CH3
H3C
1.00
0.99
2.99
1.01
1.98
4.06
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

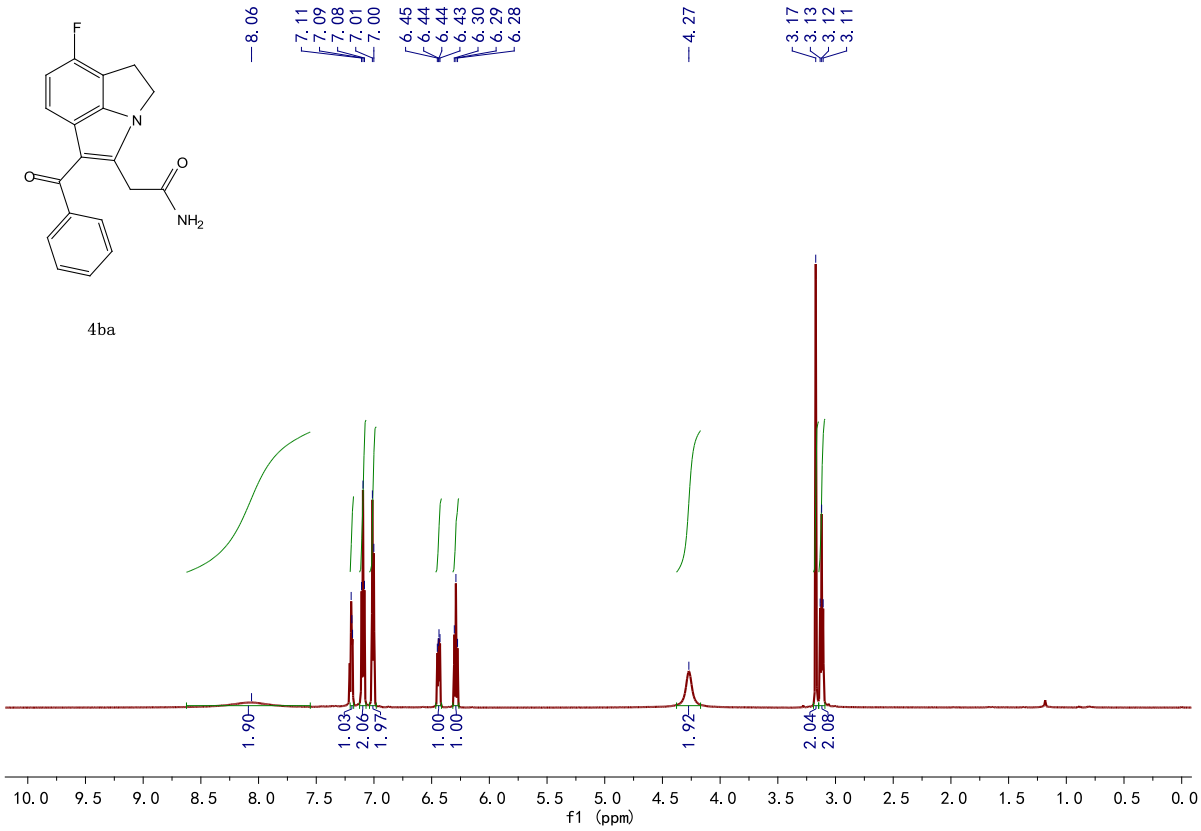
4ar


194.92
167.02
156.35
141.27
138.62
136.83
130.86
126.48
122.93
121.77
104.25
77.21
77.00
76.79
48.32
44.81
28.60
21.11
O
N
O
NH2
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

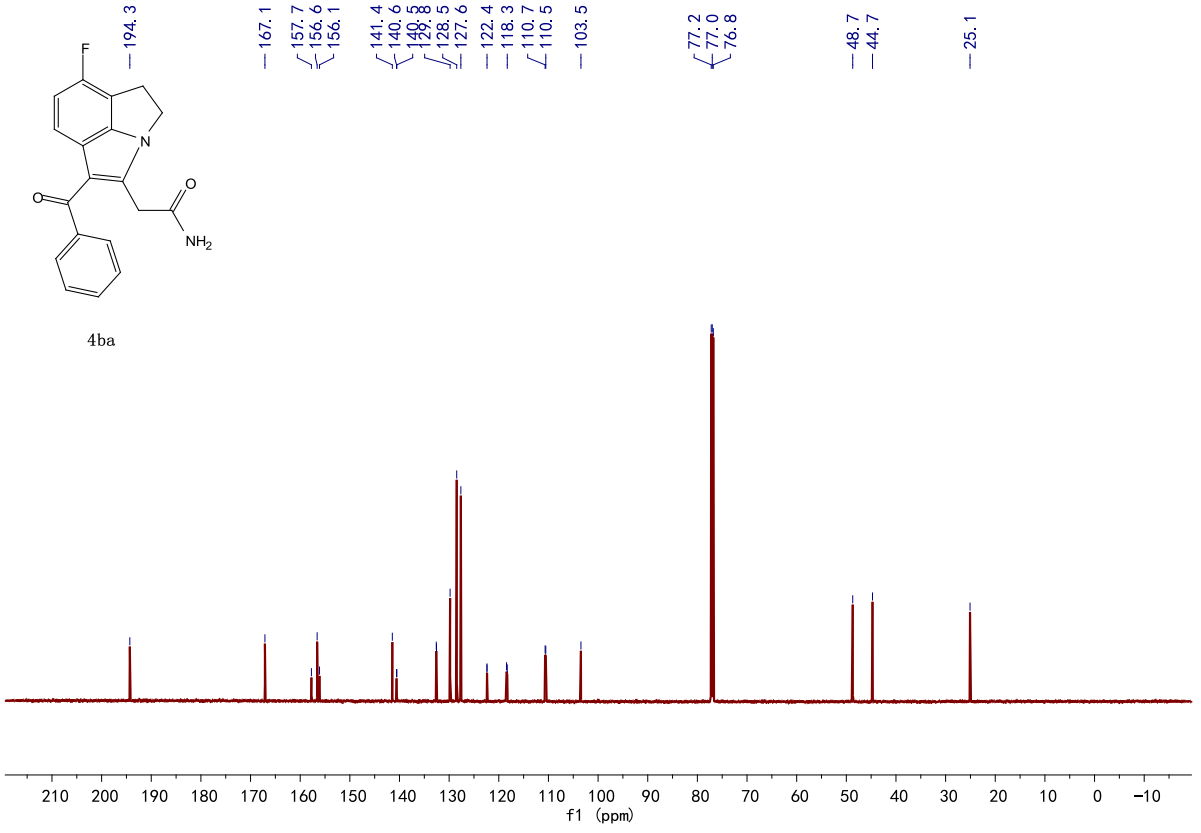
4ar


7.83
7.69
7.68
7.66
7.65
7.63
7.48
7.46
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.36
7.34
6.91
6.52
6.50
6.47
6.45
6.43
4.30
4.28
3.16
3.14
3.13
3.11
O
N
O
NH2
4au
f1 (ppm)

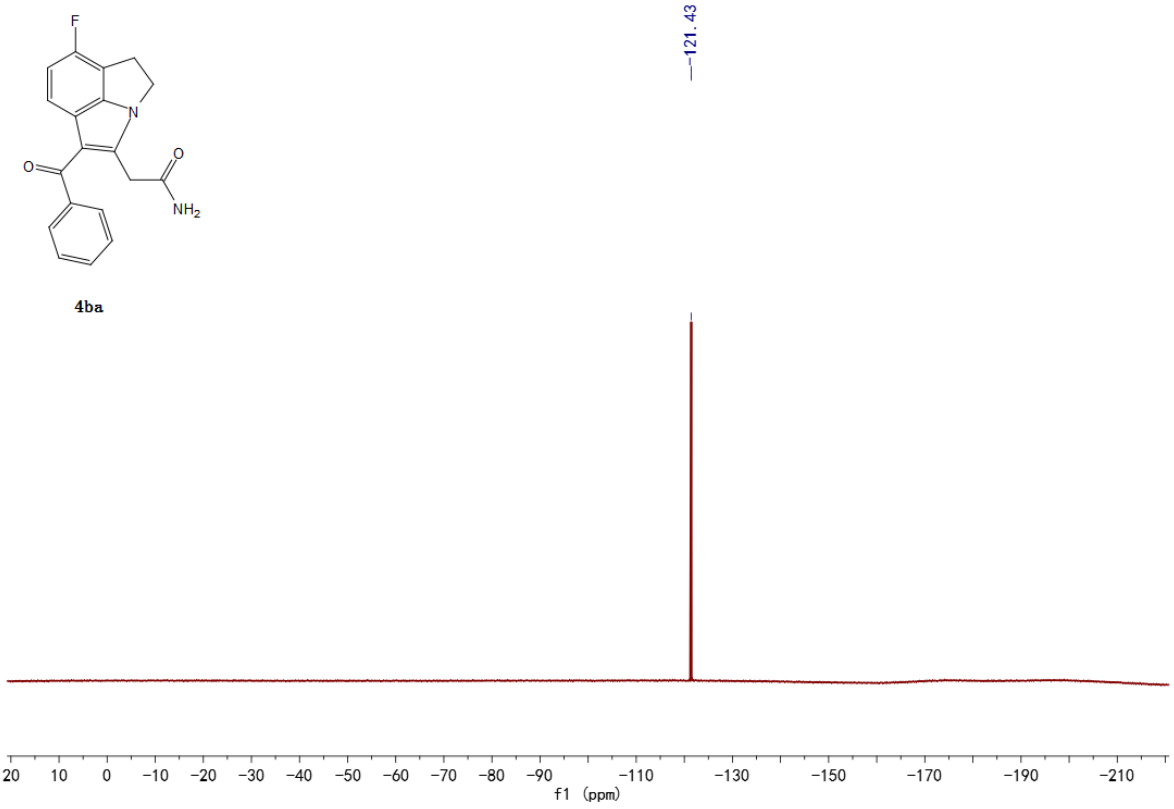

194.25
166.95
156.67
138.92
138.78
130.89
128.89
127.07
126.25
125.59
122.03
104.43
99.97
77.21
77.00
76.79
48.40
45.10
28.70
O
N
O
NH2
4au
f1 (ppm)


F
N
O
O
NH2
8.06
7.11
7.09
7.08
7.01
7.00
6.45
6.44
6.44
6.43
6.30
6.29
6.28
4.27
3.17
3.13
3.12
3.11
1.90
1.03
2.06
1.97
1.00
1.00
1.92
2.04
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

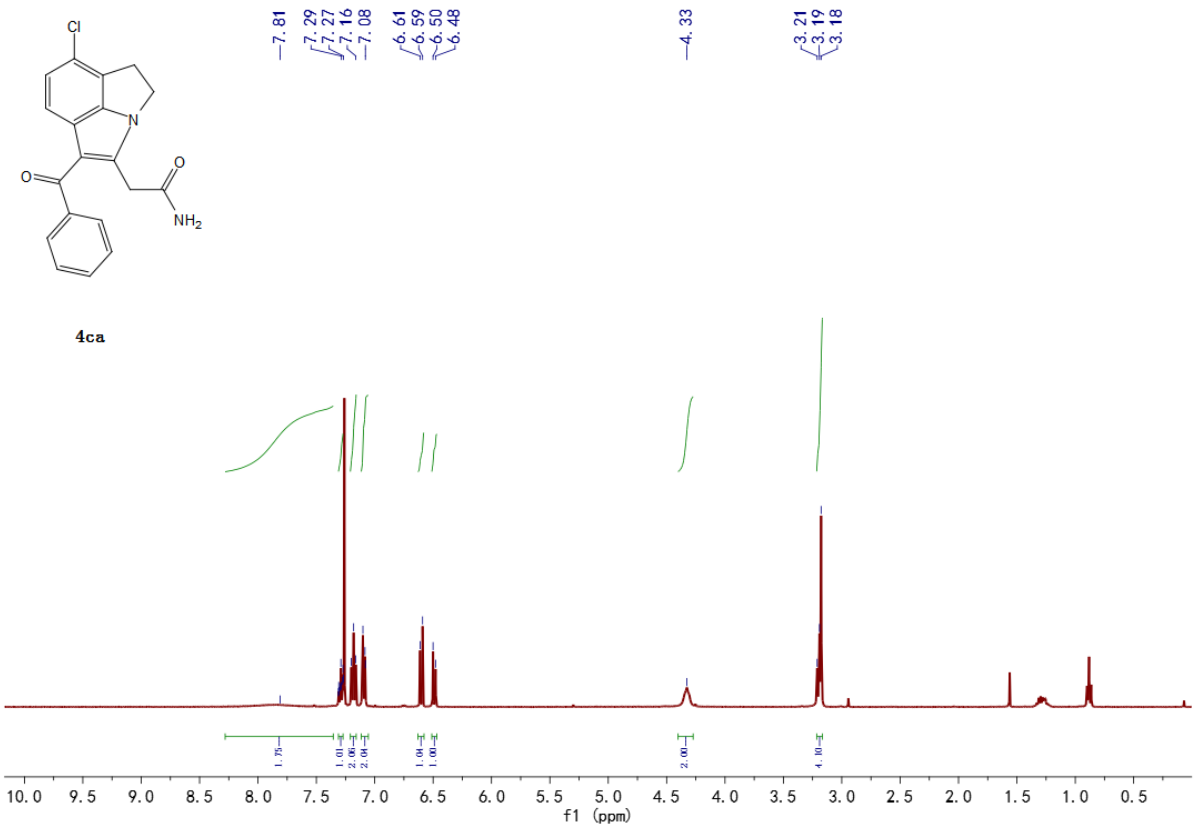
4ba


F
N
O
O
NH2
194.3
167.1
157.7
156.6
156.1
141.4
140.6
129.8
128.5
127.6
122.4
118.3
110.7
110.5
103.5
77.2
77.0
76.8
48.7
44.7
25.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

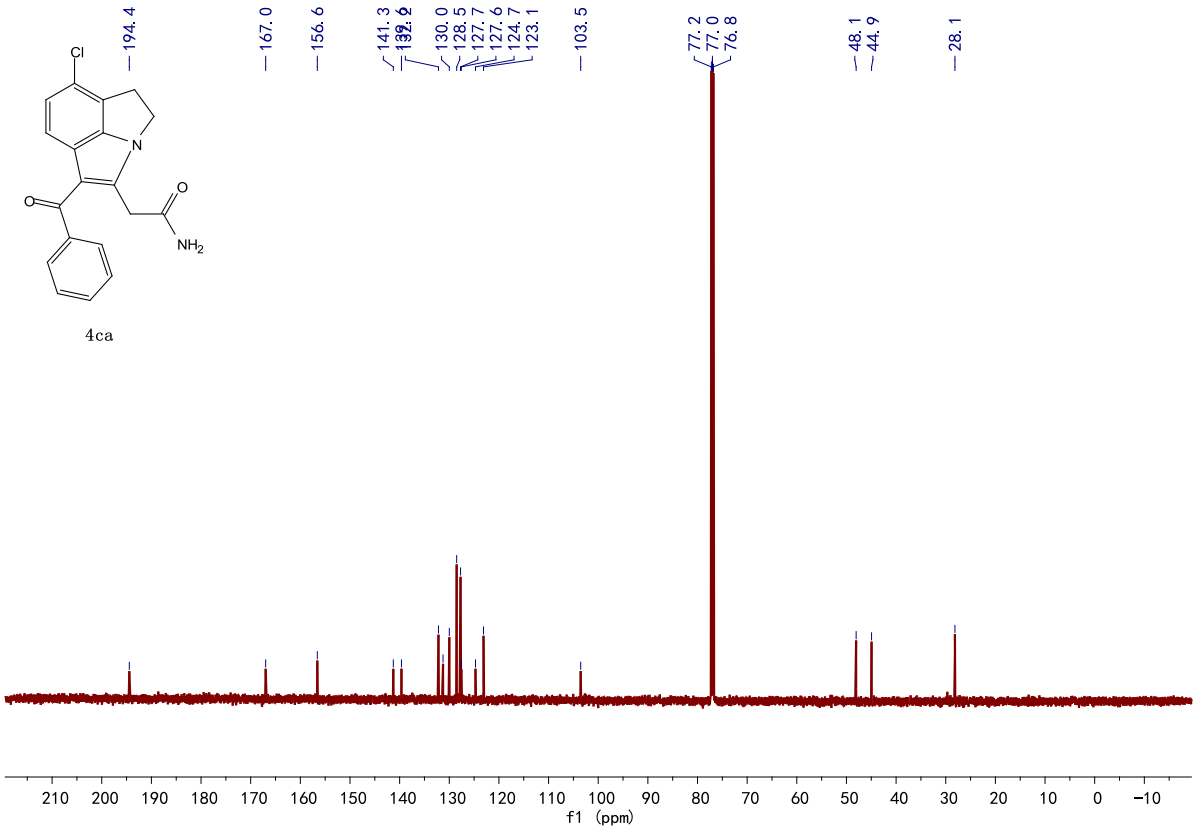
4ba

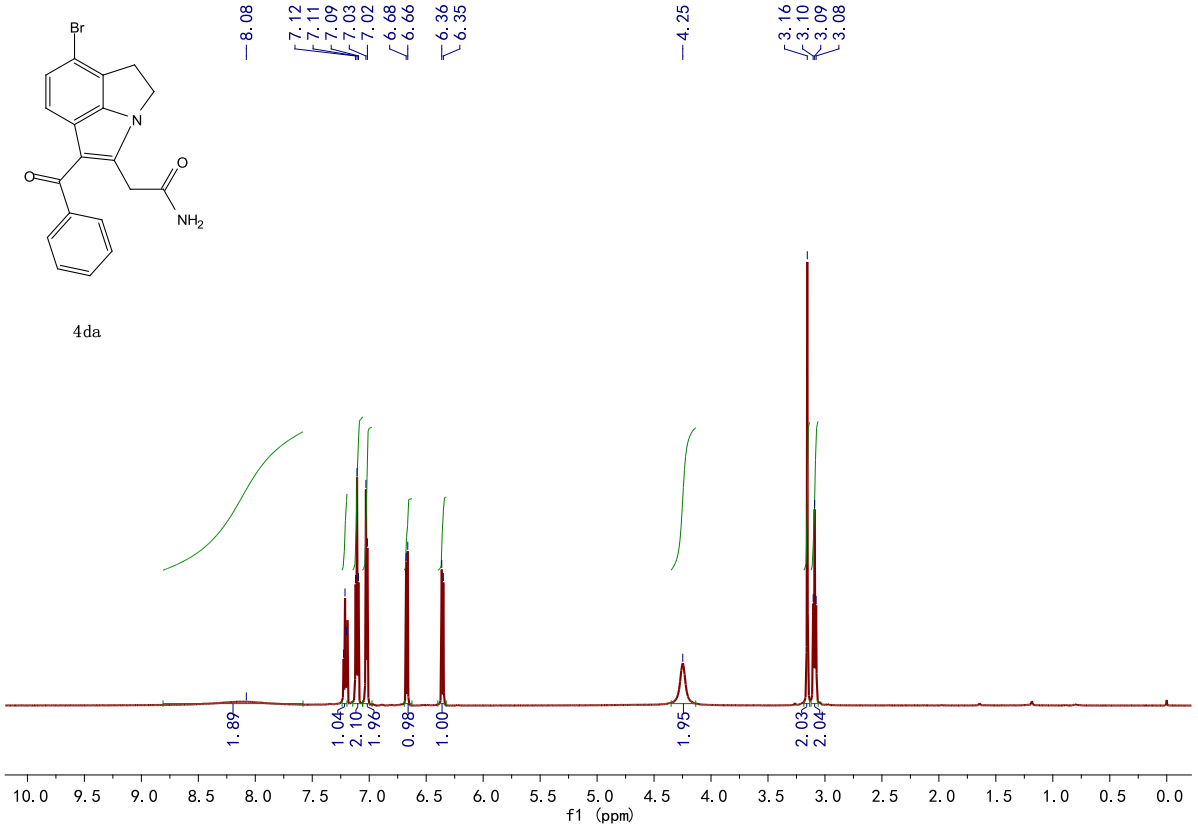

F
N
O
O
NH2
-121.43
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

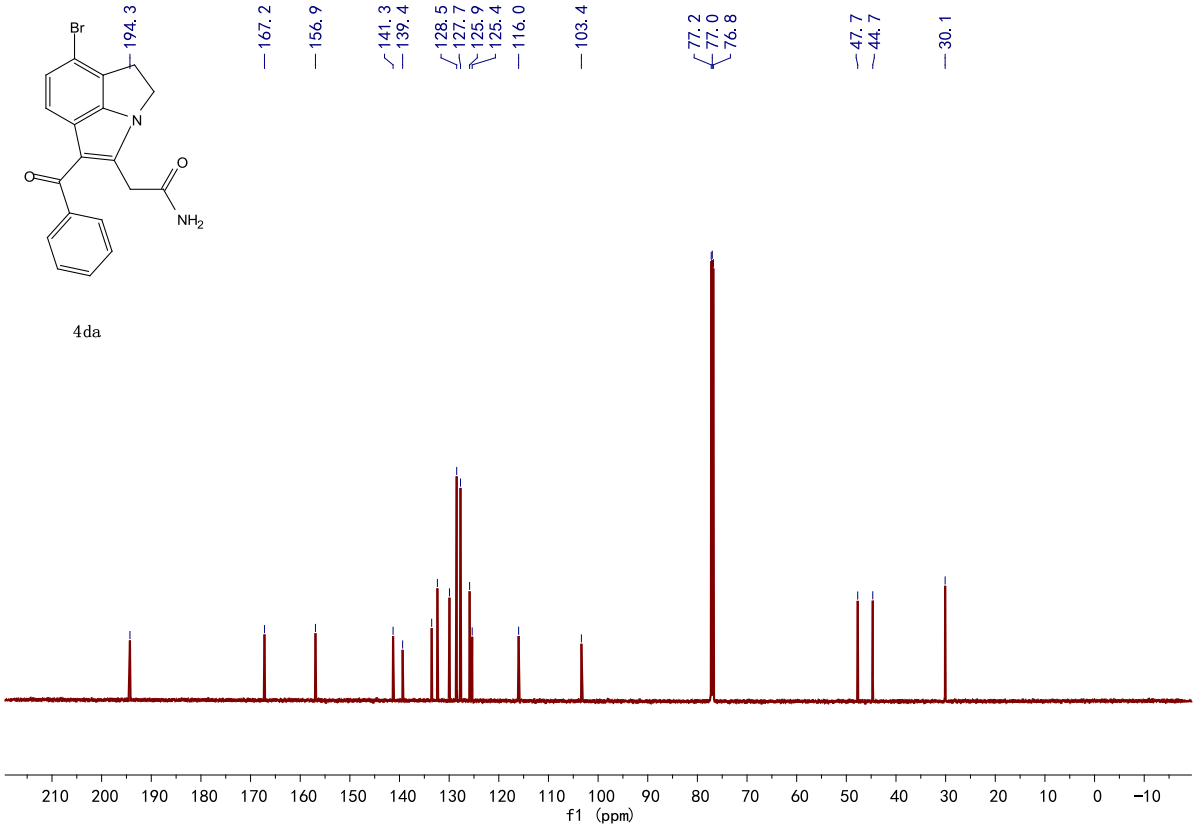
4ba


Cl
N
O
O
NH2
7.81
7.29
7.27
7.16
7.08
6.61
6.59
6.50
6.48
4.33
3.21
3.19
3.18
1.75
1.01
2.06
2.04
1.04
1.00
2.00
4.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

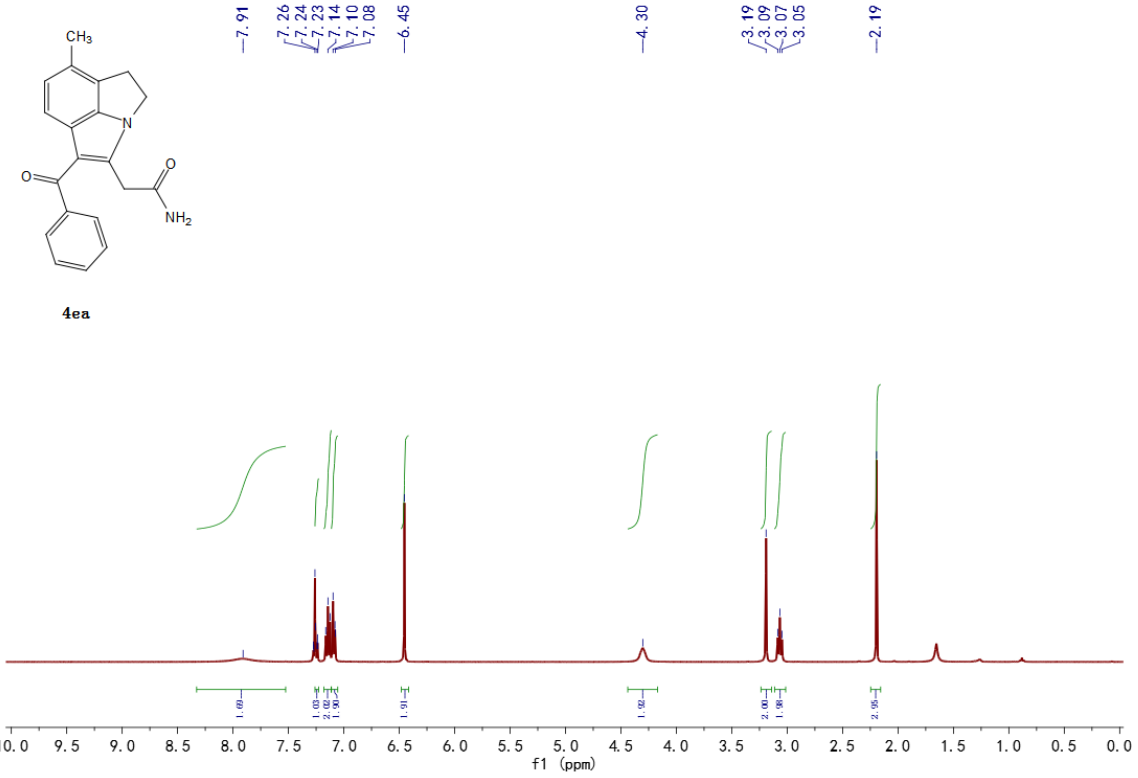
4ca


194.4
167.0
156.6
141.3
130.0
128.5
127.7
127.6
124.7
123.1
103.5
77.2
77.0
76.8
48.1
44.9
28.1
Cl
N
O
O
NH2
4ca
f1 (ppm)

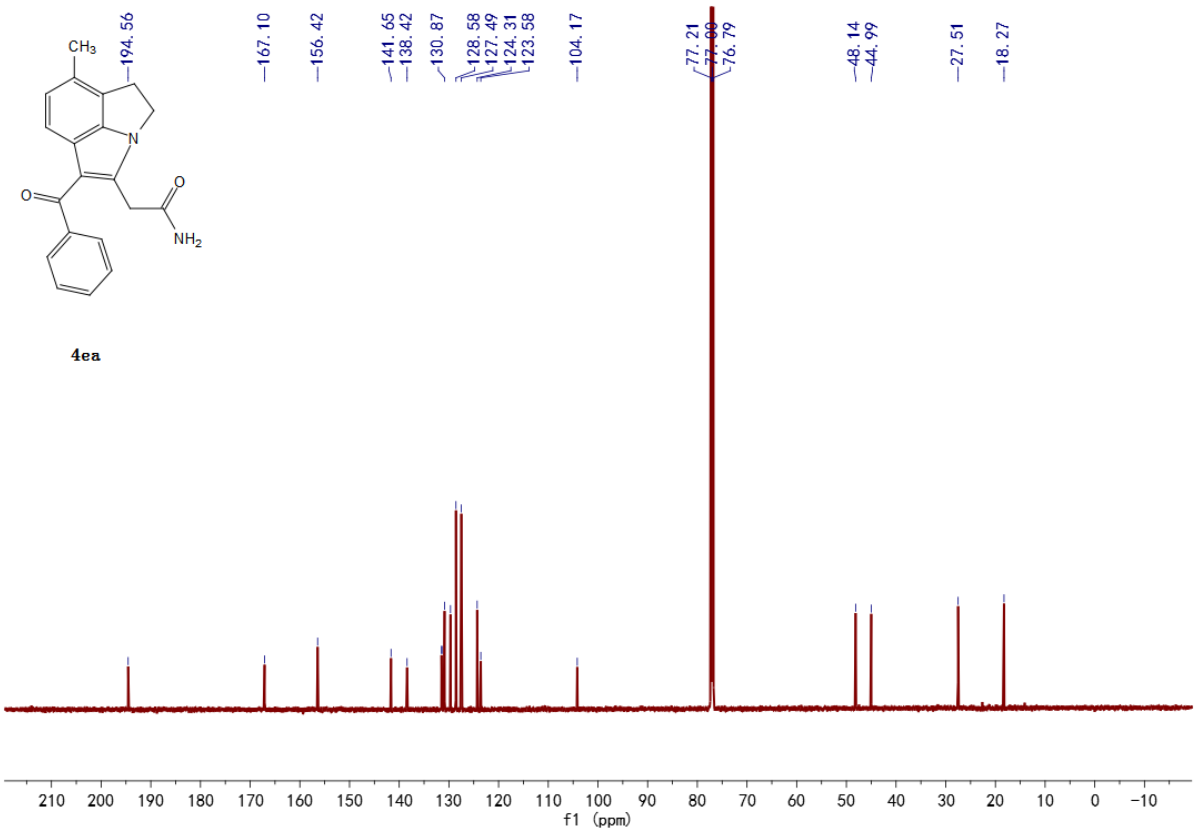

8.08
7.12
7.11
7.09
7.03
7.02
6.68
6.66
6.36
6.35
4.25
3.16
3.10
3.09
3.08
Br
N
O
O
NH2
4da
1.89
1.04
2.10
1.96
0.98
1.00
1.95
2.03
2.04
f1 (ppm)


Br
O
N
O
NH2
194.3
167.2
156.9
141.3
139.4
128.5
127.7
125.9
125.4
116.0
103.4
77.2
77.0
76.8
47.7
44.7
30.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

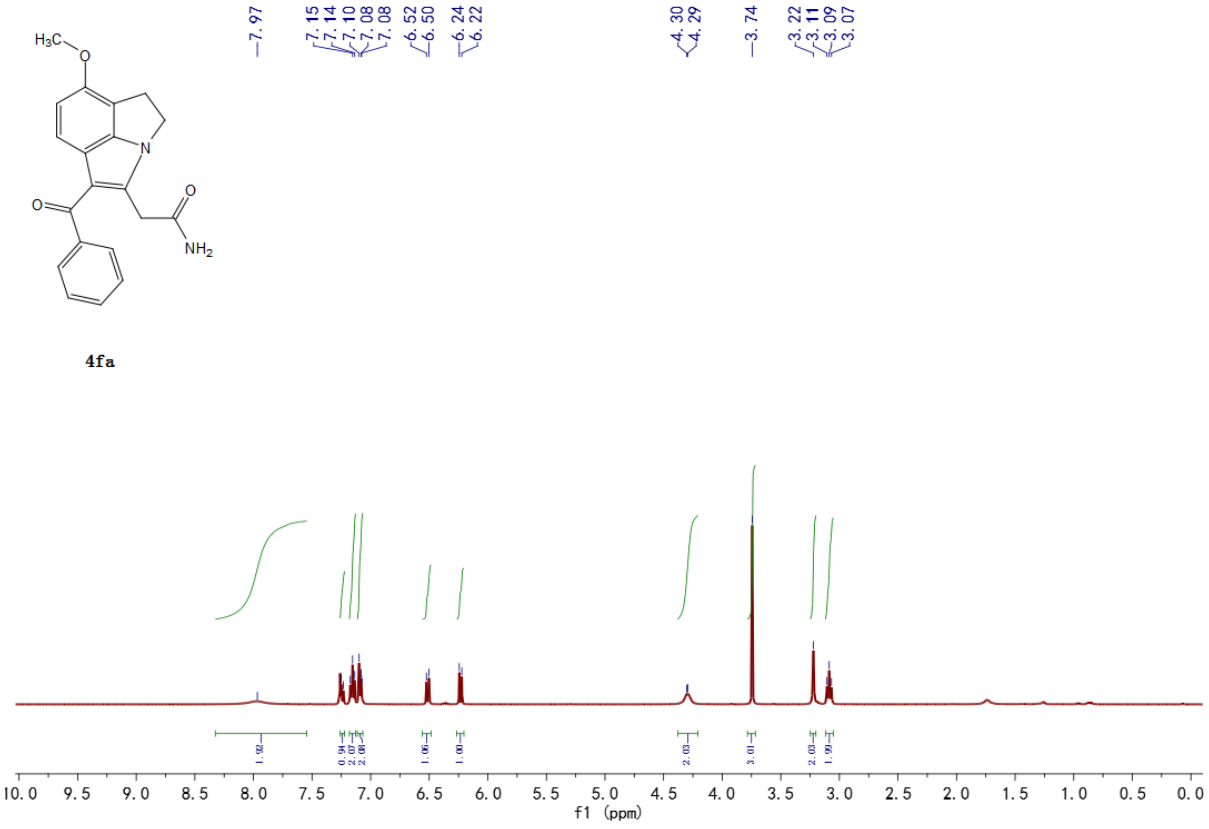
4da


CH3
N
O
O
NH2
7.91
7.26
7.24
7.23
7.14
7.10
7.08
6.45
4.30
3.19
3.09
3.07
3.05
2.19
1.69
1.03
2.02
1.93
1.91
1.92
2.00
1.98
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

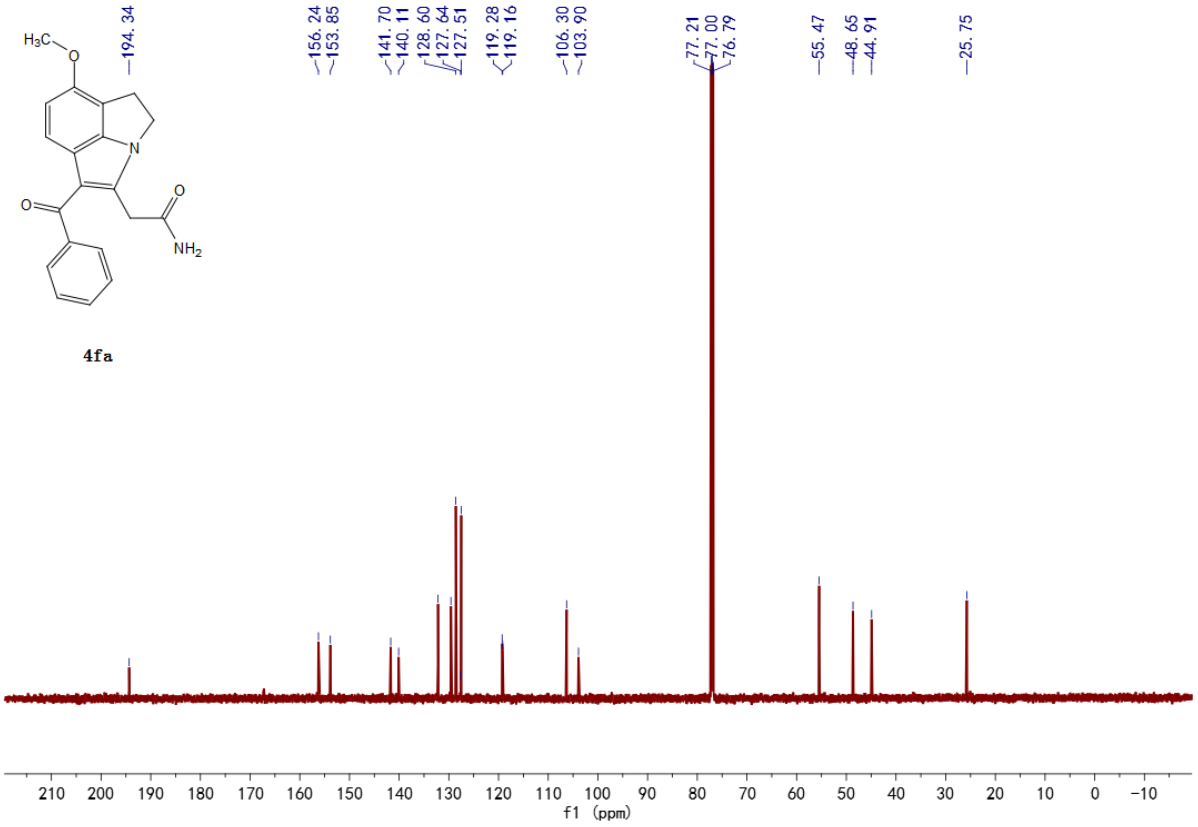
4ea


194.56
167.10
156.42
141.65
138.42
130.87
128.58
127.49
124.31
123.58
104.17
77.21
77.00
76.79
48.14
44.99
27.51
18.27
CH3
N
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

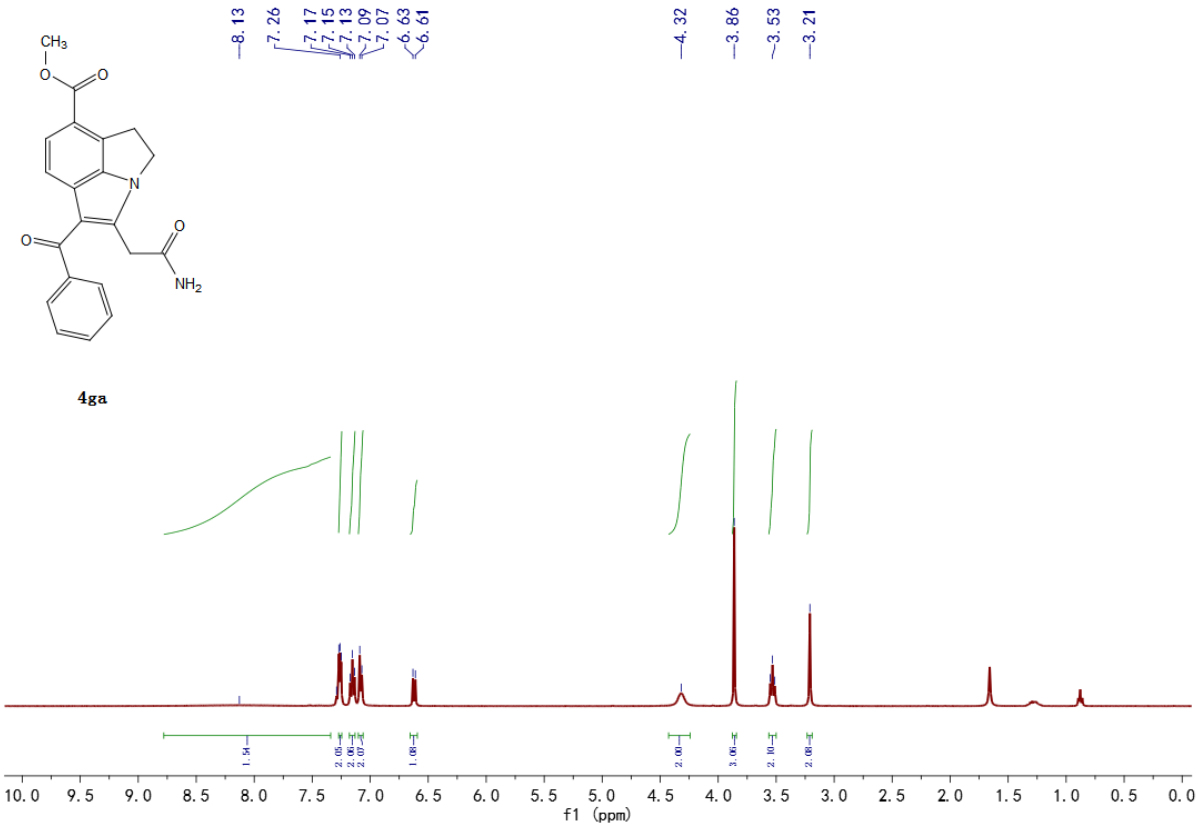
4ea


7.97
7.15
7.14
7.10
7.08
7.08
6.52
6.50
6.24
6.22
4.30
4.29
3.74
3.22
3.11
3.09
3.07
H3C
O
N
O
O
NH2
1.92
0.94
2.07
2.00
1.06
1.00
2.03
3.01
2.03
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

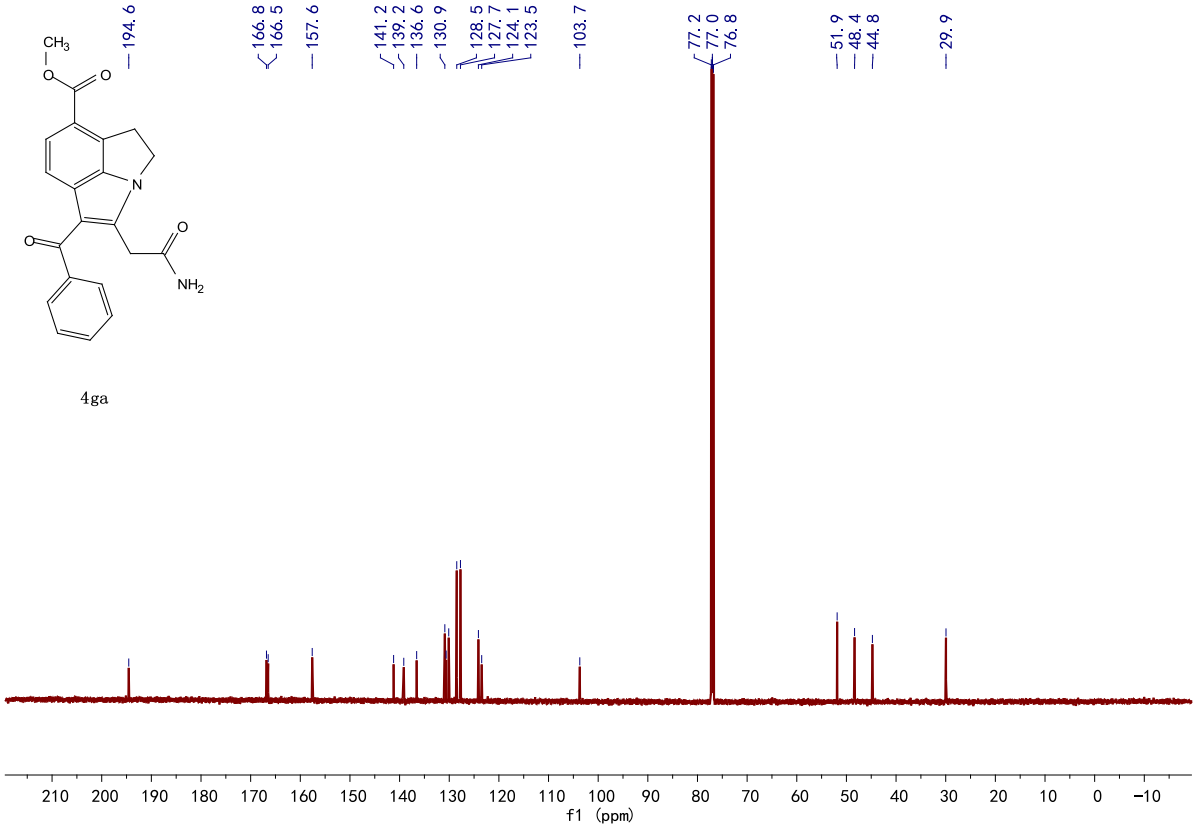
4fa


194.34
156.24
153.85
141.70
140.11
128.60
127.64
127.51
119.28
119.16
106.30
103.90
77.21
77.00
76.79
55.47
48.65
44.91
25.75
H3C
O
N
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

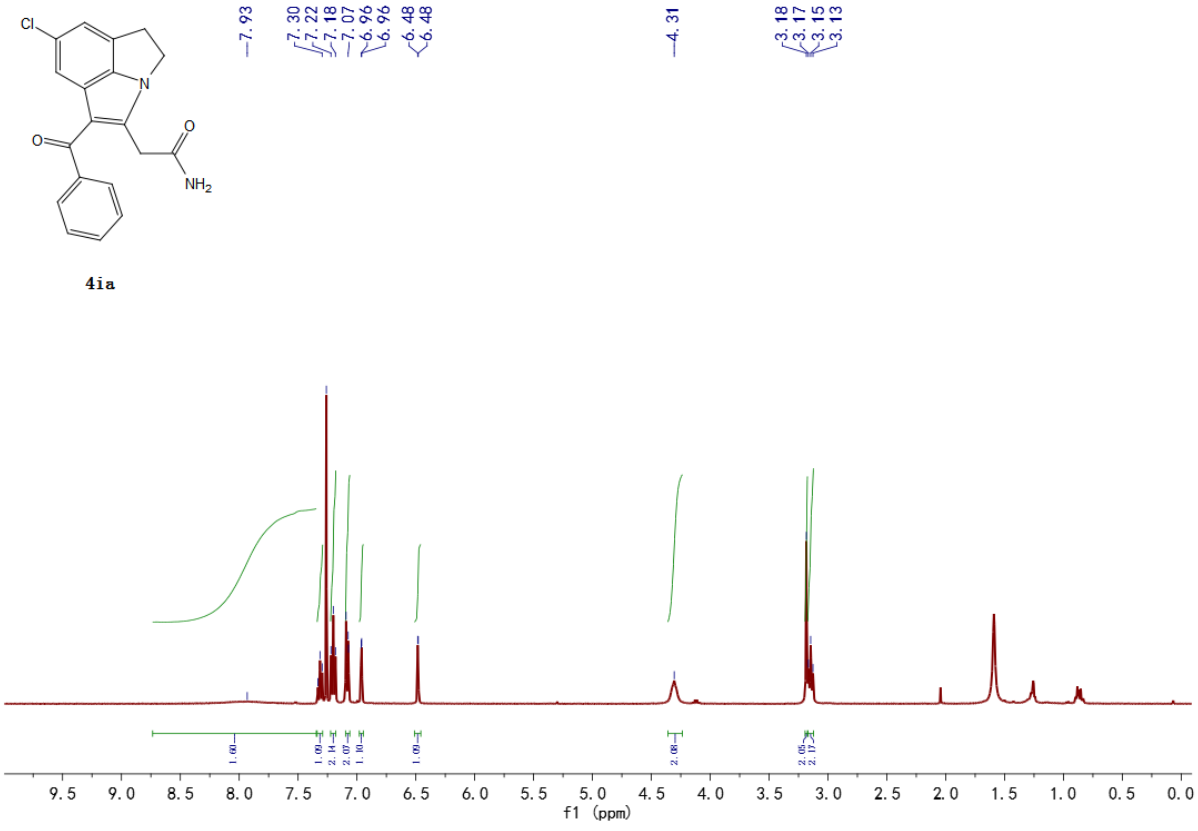
4fa


8.13
7.26
7.17
7.15
7.13
7.09
7.07
6.63
6.61
4.32
3.86
3.53
3.21
CH3
O
O
O
N
O
O
NH2
1.54
2.05
2.04
2.07
1.00
2.00
3.00
2.10
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

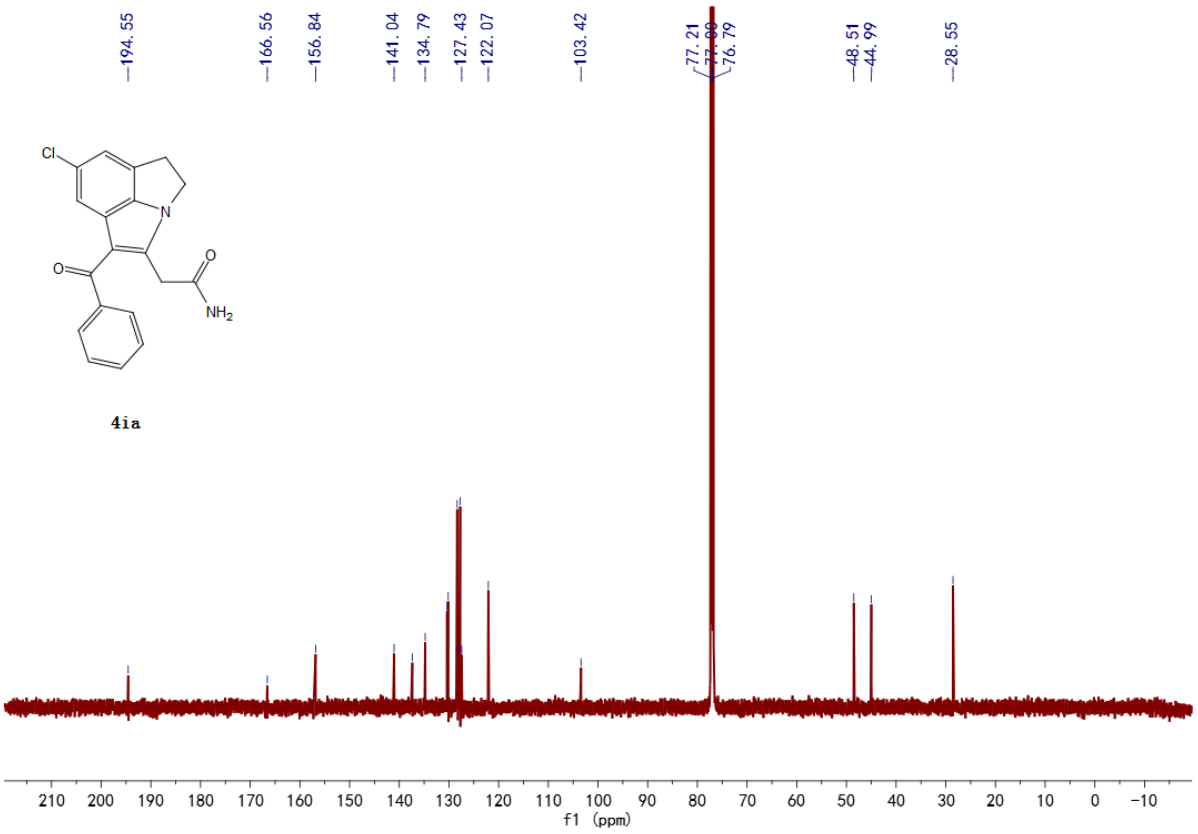
4ga


194.6
166.8
166.5
157.6
141.2
139.2
136.6
130.9
128.5
127.7
124.1
123.5
103.7
77.2
77.0
76.8
51.9
48.4
44.8
29.9
f1 (ppm)

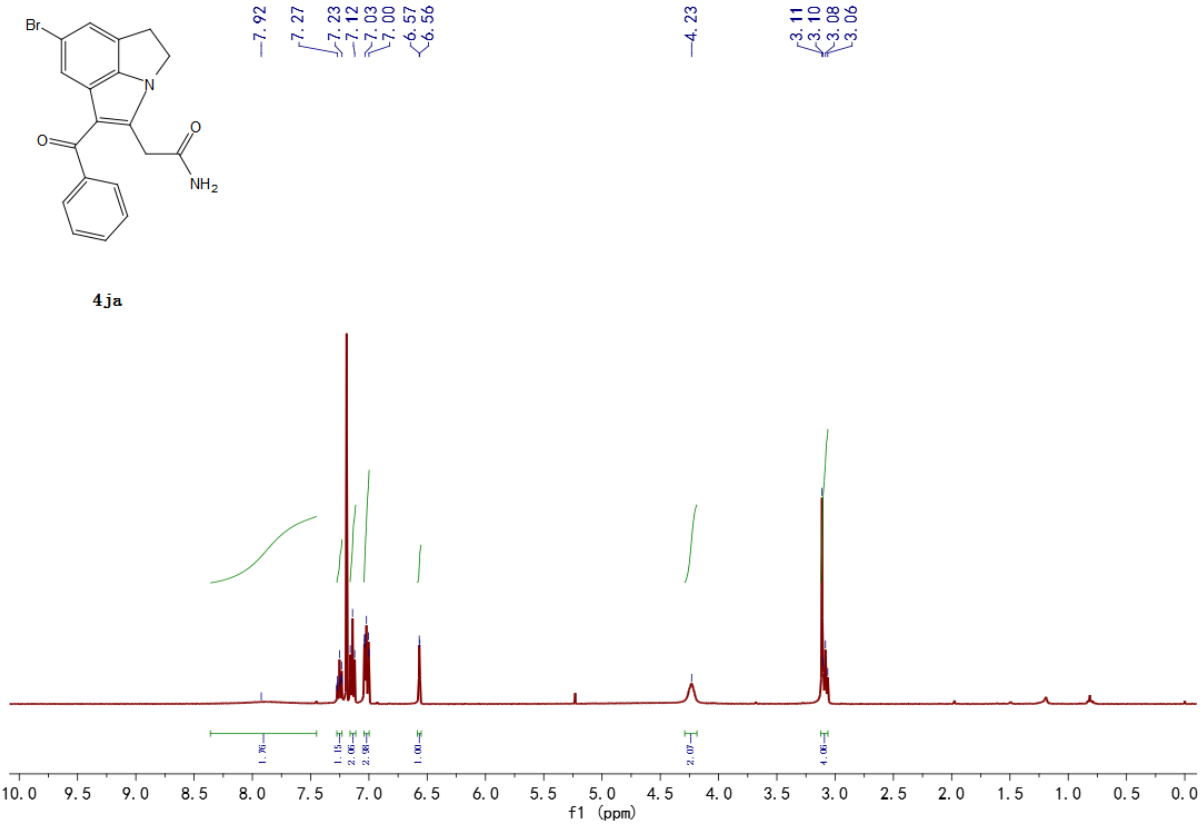
4ga


7.93
7.30
7.22
7.18
7.07
6.96
6.96
6.48
6.48
4.31
3.18
3.17
3.15
3.13
f1 (ppm)

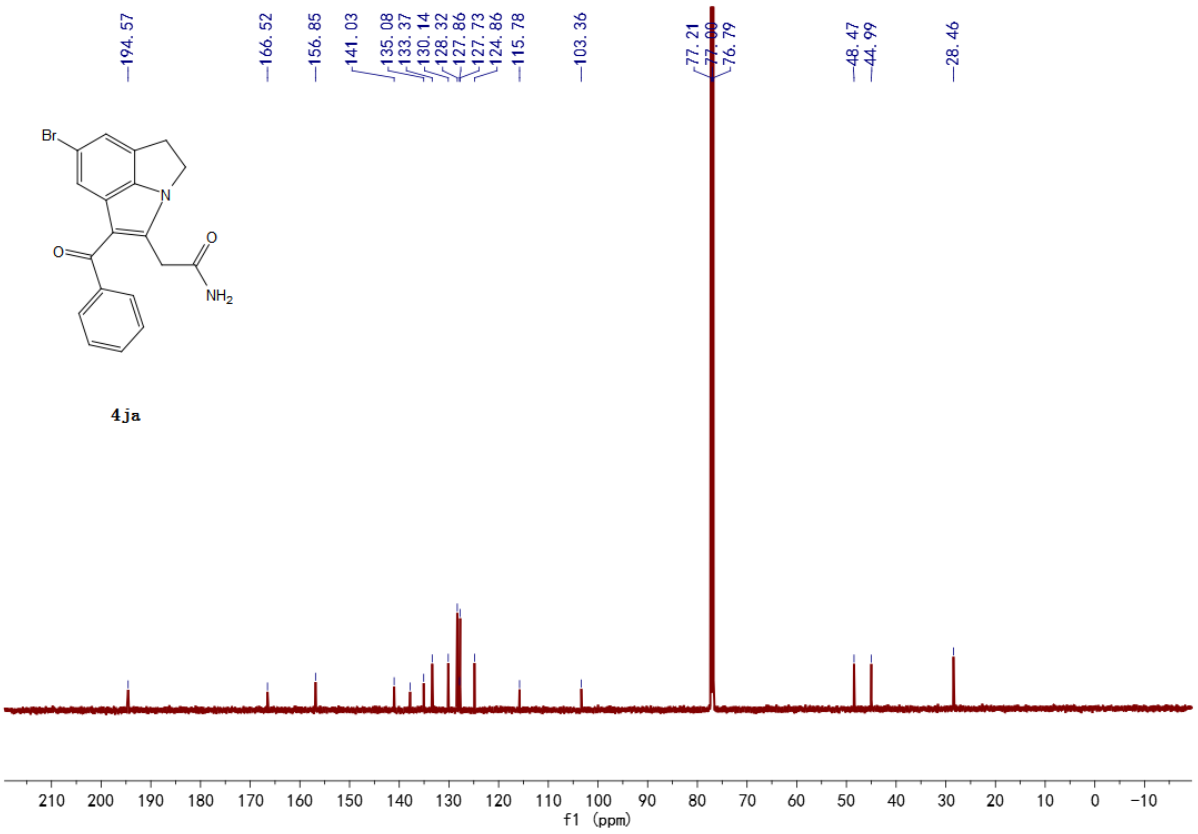
4ia


194.55
166.56
156.84
141.04
134.79
127.43
122.07
103.42
77.21
77.00
76.79
48.51
44.99
28.55
Cl
N
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

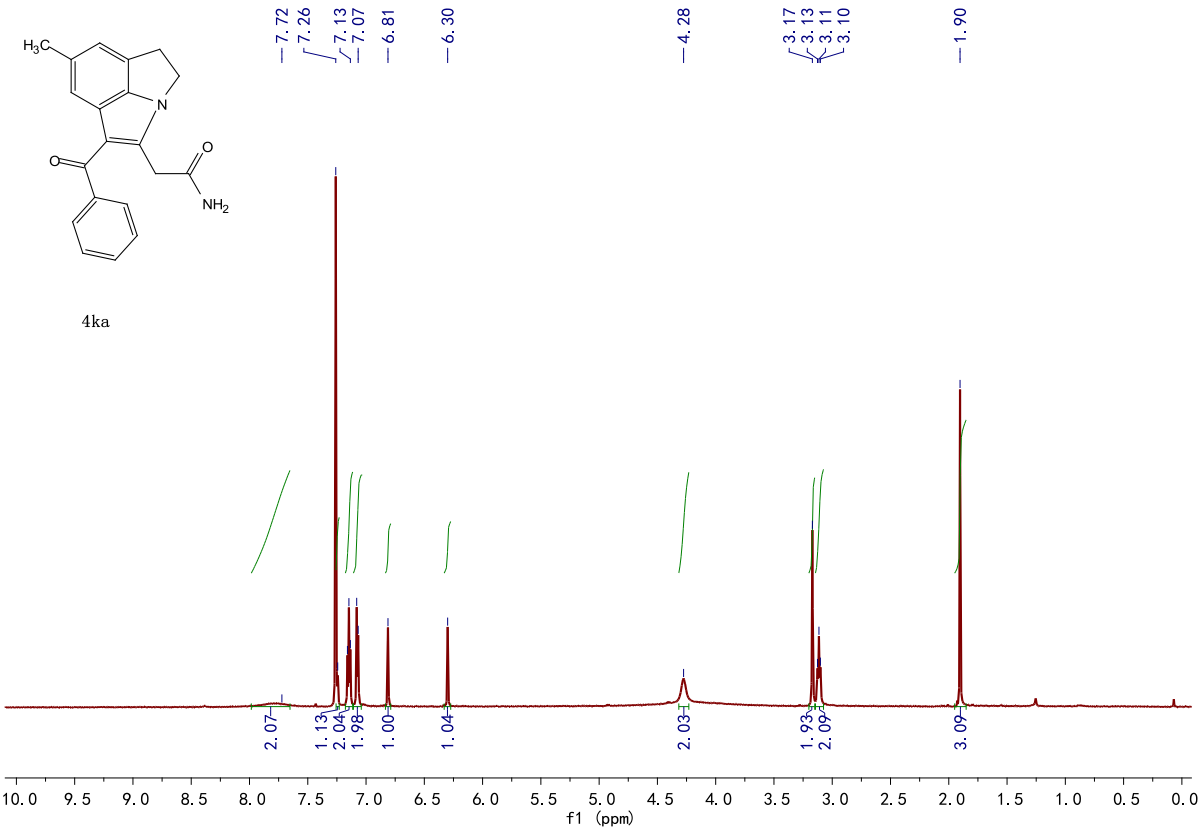
4ia


7.92
7.27
7.23
7.12
7.03
7.00
6.57
6.56
4.23
3.11
3.10
3.08
3.06
Br
N
O
O
NH2
1.70
1.15
2.06
2.98
1.00
2.07
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

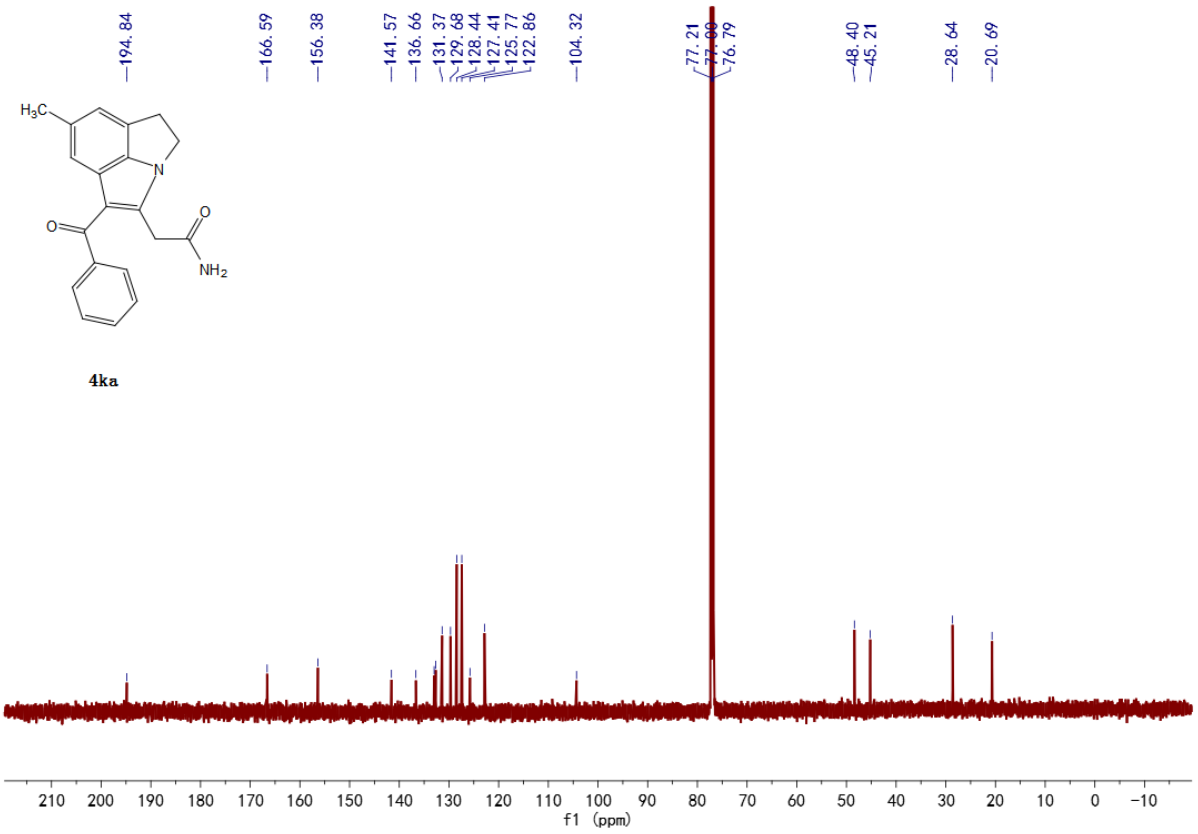
4ja


194.57
166.52
156.85
141.03
135.08
133.37
130.14
128.32
127.86
127.73
124.86
115.78
103.36
77.21
77.00
76.79
48.47
44.99
28.46
Br
N
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

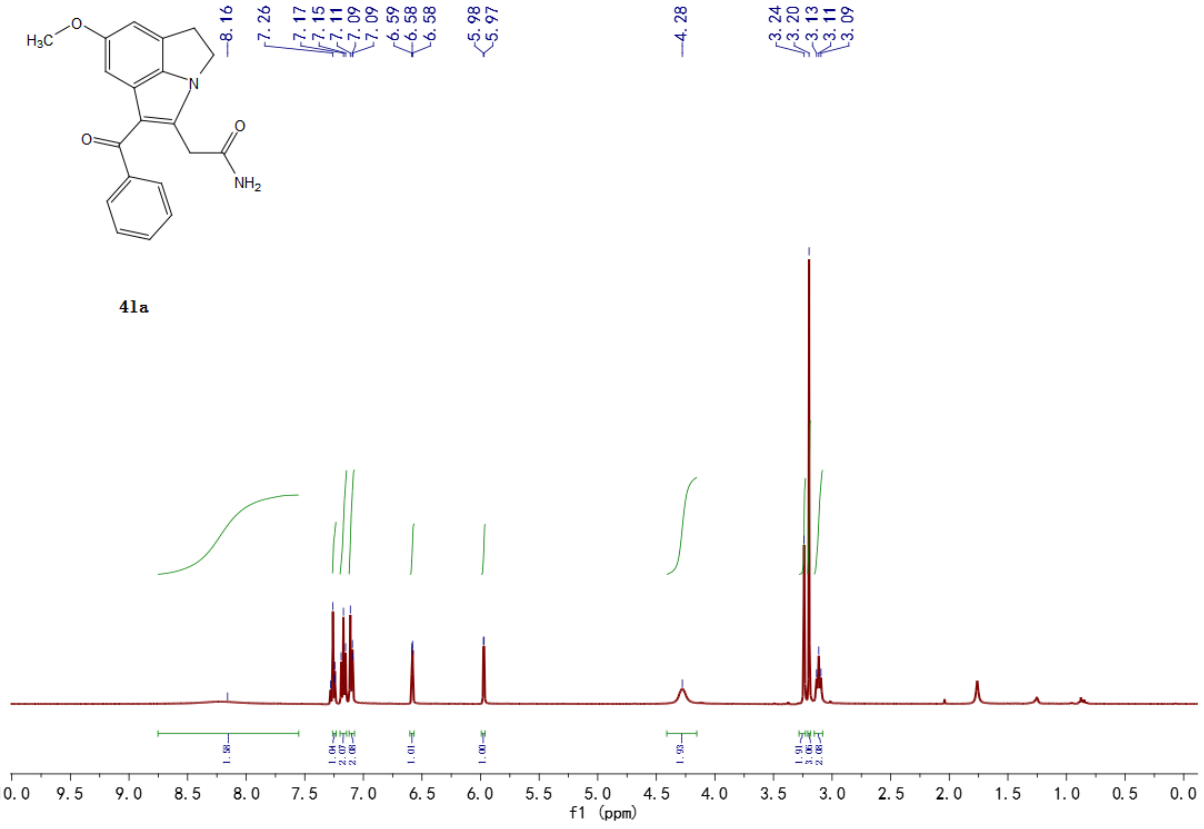
4ja


7.72
7.26
7.13
7.07
6.81
6.30
4.28
3.17
3.13
3.11
3.10
1.90
H3C
N
O
O
NH2
2.07
1.13
2.04
1.98
1.00
1.04
2.03
1.93
2.09
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

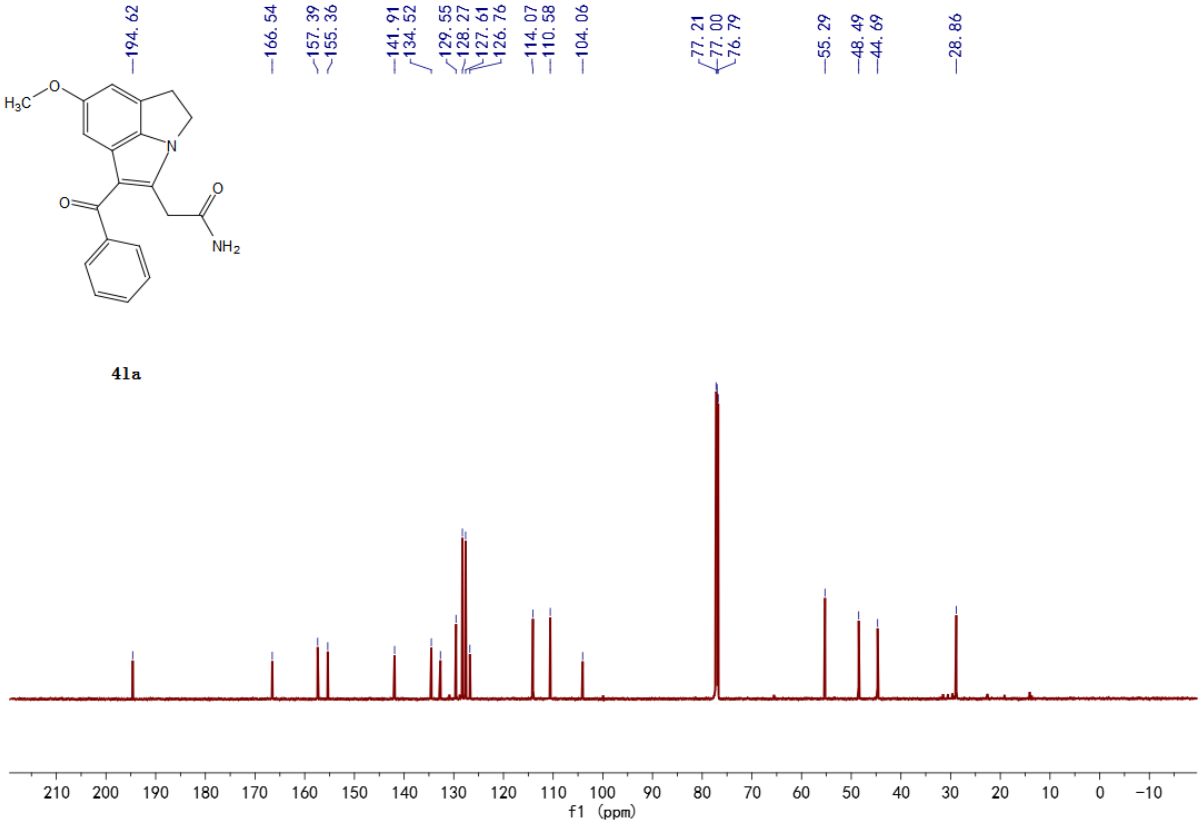
4ka


194.84
166.59
156.38
141.57
136.66
131.37
129.68
128.44
127.41
125.77
122.86
104.32
77.21
77.00
76.79
48.40
45.21
28.64
20.69
H3C
N
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

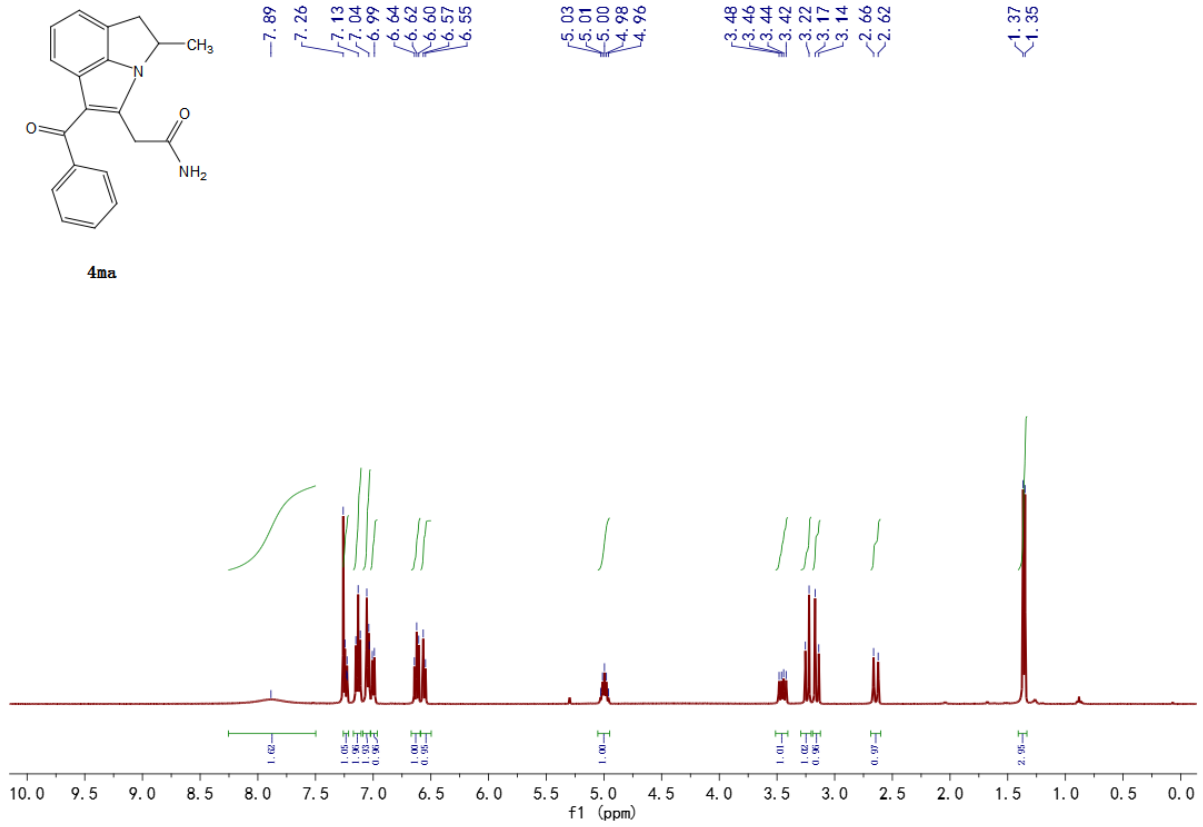
4ka


8.16
7.26
7.17
7.15
7.11
7.09
7.09
6.59
6.58
6.58
5.98
5.97
4.28
3.24
3.20
3.13
3.11
3.09
H3C
O
N
O
O
NH2
1.90
1.04
2.03
2.00
1.01
1.00
1.93
1.91
3.00
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

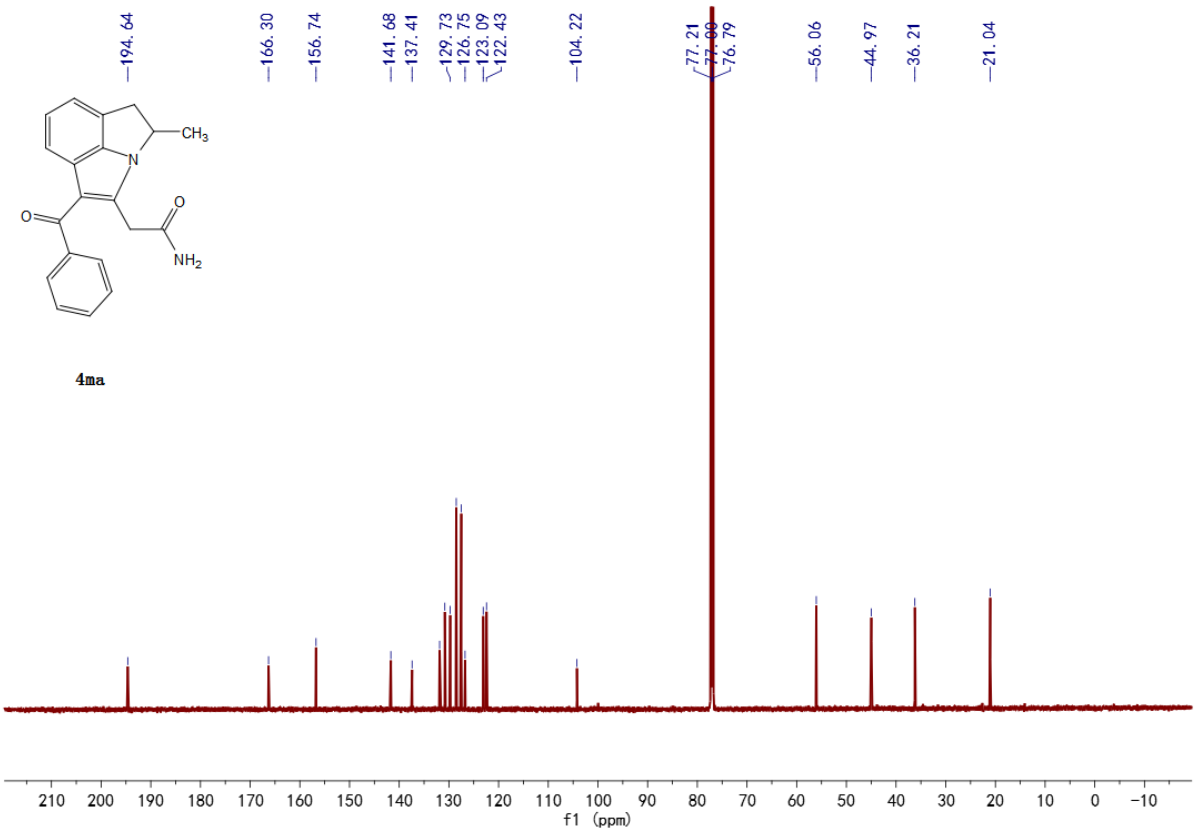
41a

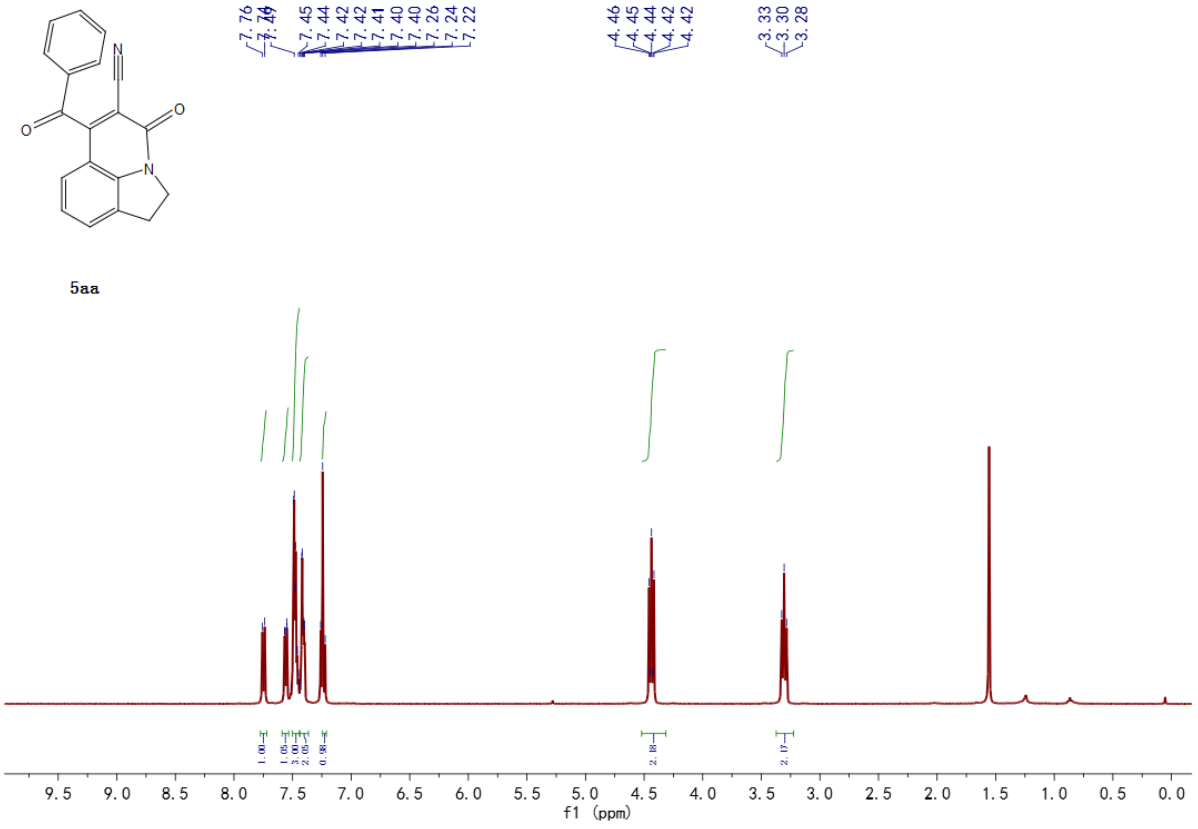

194.62
166.54
157.39
155.36
141.91
134.52
129.55
128.27
127.61
126.76
114.07
110.58
104.06
77.21
77.00
76.79
55.29
48.49
44.69
28.86
H3C
O
N
O
O
NH2
f1 (ppm)

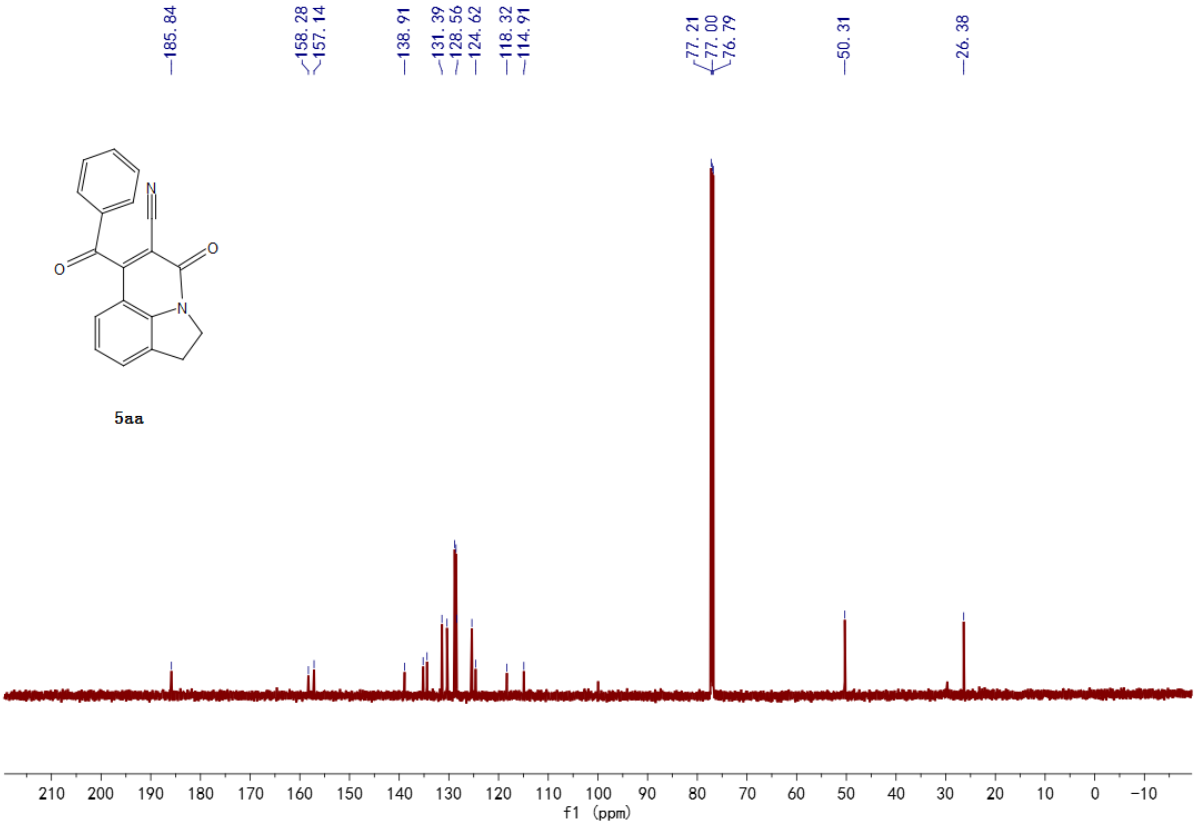
41a


7.89
7.26
7.13
7.04
6.99
6.64
6.62
6.60
6.57
6.55
5.03
5.01
5.00
4.98
4.96
3.48
3.46
3.44
3.42
3.22
3.17
3.14
2.66
2.62
1.37
1.35
CH3
N
O
O
NH2
f1 (ppm)

4ma


194.64
166.30
156.74
141.68
137.41
129.73
126.75
123.09
122.43
104.22
77.21
77.00
76.79
56.06
44.97
36.21
21.04
CH3
N
O
O
NH2
4ma
f1 (ppm)


7.76
7.45
7.44
7.42
7.42
7.41
7.40
7.40
7.26
7.24
7.22
4.46
4.45
4.44
4.42
4.42
3.33
3.30
3.28
N
O
O
N
5aa
f1 (ppm)



References:

[1] Zhou, T.; Li, B.; Wang, B. Chem. Commun. 2016, 52, 14117.

[2] Vaitla, J.; Bayer, A.; Hopmann, K. H. *Angew. Chem., Int.* Ed. **2017**, *56*, 4277.