Highly Efficient Construction of Pentacyclic Benzo[*b*]indeno[1,2,3-*de*][1,8]-naphthyridine Derivatives via Four-Component Domino Reaction

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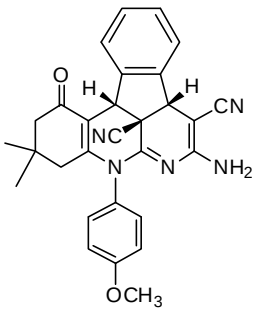
1. General methods

Microwave irradiation was carried out with Initiator 2.5 Microwave Synthesizers from Biotage, Uppsala, Sweden. All reagents were purchased from commercial suppliers and used without further purification. Melting Points are uncorreted. IR spectra were recorded on a Tensor 27 spectrometer in KBr with absorptions in cm^{-1}. ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz or 100 MHz) spectra were recorded on a Varian Inova-400 MHz in DMSO-d_6 solution. *J* values are in hertz. Chemical shifts are expressed in parts per million downfield from interal standard TMS. High-resolution mass spectra (HRMS) for all the compounds were determined on Bruker MicrOTOF-QII mass spertrometer with ESI resource. X-Ray diffraction analysis was recorded on a Smart-1000 diffractomrter.

2. General procedure for the synthesis of products 4 and 6 are represented as follows

An equimolar mixture of enaminone **1** (1.0 mmol), malononitrile **2** (2.2 mmol, 2.2 equiv) and OPA **3** (1.0 mmol) or glutaraldehyde **5** (1.0 mmol) was introduced in a 5 mL vial with DMF (2 mL) as solution. The reaction vial was closed and prestirred for 20 s. The mixture was irradiated at 110 ^{o}C. The reaction was monitored by TLC. After the completion, the reaction mixture was then cooled to room temperature and diluted with cold water (40 mL), then filtered, the precipitate was collected and purified by recrystallization from 95% EtOH or by flash column chromatography (petroleum ether : ethyl acetate = 5:1), The analytical data for represent compounds are shown below.

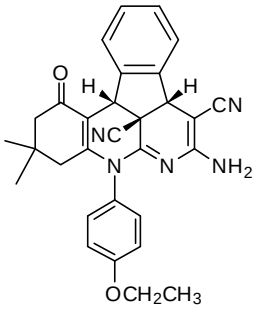
3. Characterizations for all compounds



7-Amino-5-(4-methoxyphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^{1},8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^{1},8-dicarbonitrile (4a)

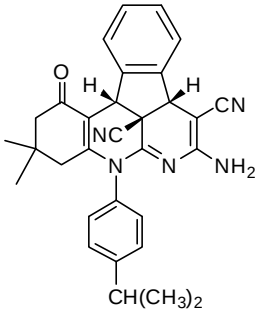
The crude products **4a** purified by recrystallization from 95% ethanol, yellow solid 419 mg (yield 88%); The obtained final

products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3332, 2953, 2174, 1634, 1595, 1564, 1528, 1381, 1343, 1259, 1264, 1023, 823, 735 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.37-7.29 (m, 2H, ArH), 7.26 (d, J = 6.8 Hz, 1H, ArH), 7.15-7.13 (m, 1H, ArH), 7.06-7.03 (m, 1H, ArH), 6.95-6.89 (m, 2H, ArH), 6.55 (s, 2H, NH_2), 6.52-6.51 (m, 1H, ArH), 4.99 (s, 1H, CH), 4.67 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 2.50-2.46 (m, 1H, CH-H), 2.37-2.33 (m, 1H, CH-H), 2.05 (s, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 195.1, 158.4, 156.8, 153.5, 152.3, 140.6, 140.2, 129.6, 129.2, 128.6, 128.1, 127.8, 122.3, 122.2, 121.0, 116.1, 114.5, 114.0, 111.0, 54.8, 51.3, 48.5, 44.9, 41.3, 41.2 40.5, 32.3, 27.6, 26.3 ppm; HRMS calcd for $C_{29}H_{24}N_5O_2$ $[M-H]^-$: 474.1930 , found: 474.1935.



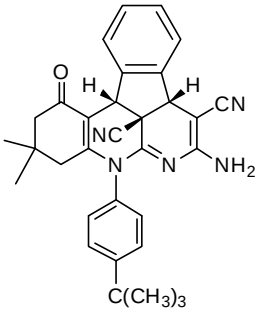
7-Amino-5-(4-ethoxyphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a[1],8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a[1],8-dicarbonitrile (4b)

The crude products **4b** purified by recrystallization from 95% ethanol, yellow solid 455 mg (yield 93%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3332, 2963, 2175, 1633, 1594, 1564, 1508, 1383, 1343, 1299, 1260, 1245, 1221, 1164, 1127, 1044, 995, 822, 736, 610 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.35-7.24 (m, 3H, ArH), 7.12 (d, J = 7.2 Hz, 1H, ArH), 7.02 (d, J = 8.0 Hz, 1H, ArH), 6.93 (d, J = 6.8 Hz, 1H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH), 6.56 (s, 2H, NH_2), 6.49 (d, J = 7.6 Hz, 1H, ArH), 4.99 (s, 1H, CH), 4.67 (s, 1H, CH), 4.01-4.00 (m, 2H, CH_2), 2.46-2.33 (m, 2H, CH_2), 2.05 (s, 2H, CH_2), 1.32 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 195.1, 157.7, 156.8, 153.5, 152.3, 140.6, 140.2, 129.2, 129.1, 128.6, 128.1, 127.8, 122.3, 122.2, 121.0, 116.1, 114.9, 114.3, 110.9, 62.8, 51.3, 48.5, 44.9, 41.3, 41.2, 40.5, 32.3, 27.6, 26.3, 14.0 ppm; HRMS calcd for $C_{30}H_{26}N_5O_2$ $[M-H]^-$: 488.2087, found: 488.2083.



7-Amino-5-(4-isopropylphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4c)

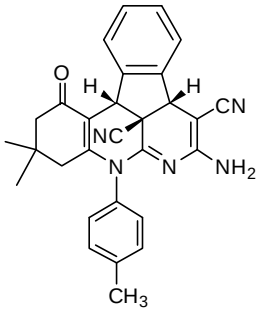
The crude products **4c** purified by recrystallization from 95% ethanol, yellow solid 419 mg (yield 86%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 217 -219°C; IR (KBr) *v* : 3329, 2959, 2187, 1629, 1567, 1508, 1461, 1338, 1332, 1253, 1203, 1050, 997, 845, 748, 731, 687 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.38-7.29 (m, 3H, ArH), 7.24 (d, J = 6.8 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 1H, ArH), 6.94 (d, J = 7.2Hz, 1H, CH), 6.55 (s, 2H, NH_2), 6.50 (d, J = 8.0Hz, 1H, ArH), 4.77 (s, 1H, CH), 4.66 (s, 1H, CH), 2.93-2.89 (m,1H, CH), 2.47-2.32 (m, 2H, CH_2), 2.07-1.95 (m, 2H, CH_2), 1.19 (d, J = 6.8 Hz, 6H, 2 × CH_3), 0.99 (s, 3H, CH_3), 0.94 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.2, 157.9, 154.4, 153.2, 149.3, 141.6, 141.2, 135.5, 129.2, 129.0, 128.9, 128.2, 128.1, 127.9, 123.4, 123.2, 122.0, 117.1, 112.3, 52.3, 49.6, 45.9, 42.4, 42.2, 41.6, 33.5, 33.4, 28.7, 27.1, 24.2, 24.0 ppm; HRMS calcd for $C_{31}H_{28}N_5O$ $[M-H]^-$: 486.2294, found: 486.2287 .



7-Amino-5-(4-(*tert*-butyl)phenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4d)

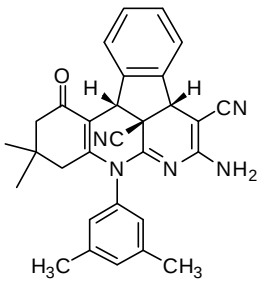
The crude products **4d** purified by recrystallization from 95% ethanol, yellow solid 441 mg (yield 88%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 278-280 °C; IR (KBr) *v* : 3330, 2961, 2180, 1661, 1627, 1567, 1509, 1461, 1381, 1332, 1253, 1204, 1108, 1049, 1019, 995, 742, 726 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.51-7.16 (m, 6H, ArH), 6.95-6.94 (m, 1H, ArH), 6.57-6.50 (m, 3H, NH_2+ArH), 5.00 (s, 1H, CH), 4.67 (s, 1H, CH), 2.36-2.33 (m, 2H, CH_2), 2.03-2.00 (m, 2H, CH_2), 1.27 (s, 9H, 3 × CH_3), 0.99 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 195.1, 156.8, 153.3,

152.2, 150.5, 140.5, 140.1, 134.2, 128.1, 127.8, 127.7, 126.8, 125.9, 125.8, 122.3, 122.2, 121.0, 116.1, 111.3, 51.2, 48.5, 44.9, 41.4, 41.2, 40.5, 33.9, 32.4, 30.5, 27.7, 26.0 ppm; HRMS calcd for $C_{32}H_{30}N_5O$ $[M-H]^-$: 500.2450, found: 500.2444.



7-Amino-3,3-dimethyl-1-oxo-5-(*p*-tolyl)-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4e)

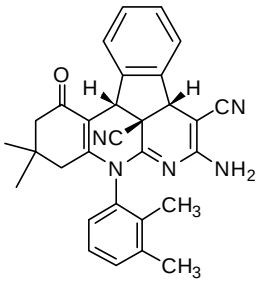
The crude products **4e** purified by recrystallization from 95% ethanol, yellow solid 381 mg (yield 83%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 275-277 °C; IR (KBr) *v* : 3328, 2956, 2180, 1633, 1612, 1563, 1509, 1461, 1382, 1333, 1283, 1251, 1203, 1161, 997, 908, 835, 767, 734, 647 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.35-7.31 (m, 3H, ArH), 7.24 (d, J = 6.8 Hz, 1H, ArH), 7.17 (d, J = 7.2 Hz, 1H, ArH), 7.10 (d, J = 7.2 Hz, 1H, ArH), 6.93 (d, J = 6.8 Hz, 1H, ArH), 6.54 (s, 2H, NH_2), 6.49 (d, J = 6.8 Hz, 1H, ArH), 4.99 (s, 1H, CH), 4.67 (s, 1H, CH), 2.46 (s,1H, CH-H), 2.36 (s, 1H, CH-H), 2.31 (s, 3H, CH_3), 2.02 (s, 2H, CH_2), 0.99 (s, 3H, CH_3), 0.94 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.1, 156.7, 153.3, 152.0, 140.6, 140.1, 137.7, 134.3, 129.8, 129.5, 128.1, 127.8, 127.3, 122.3, 122.0 120.8, 116.0, 111.0, 55.5, 51.3, 48.5, 44.9, 41.3, 41.2, 40.5, 32.3, 27.6, 26.2, 20.2, 18.0 ppm; HRMS calcd for $C_{29}H_{24}N_5O$ $[M-H]^-$: 458.1981, found: 458.1988.



7-Amino-5-(3,5-dimethylphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4f)

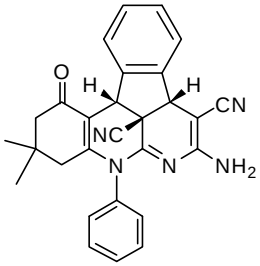
The crude products **4f** purified by recrystallization from 95% ethanol, yellow solid 388 mg (yield 82%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3413, 3327, 2958, 2175, 1632, 1605, 1565, 1470, 1380, 1336, 1283, 1257, 1221, 1106, 933, 925, 849, 737, 688 cm^{-1}; ^1H NMR

(400 MHz, DMSO-d_6) δ : 7.38-7.32 (m, 2H, ArH), 7.28 (d, J = 7.2 Hz, 1H, ArH), 7.06 (s, 1H, ArH), 6.97 (d, J = 7.2 Hz, 1H, ArH), 6.84 (s, 1H, ArH), 6.60 (s, 2H, NH_2), 6.27 (s, 1H, ArH), 5.02 (s, 1H, CH), 4.70 (s, 1H, CH), 2.54-2.53 (m,1H, CH-H), 2.39 (s, 1H, CH-H), 2.35 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.15-2.11 (m, H, CH-H), 2.04-2.01 (m, 1H, CH-H), 1.03 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.2, 157.8, 154.2, 153.0, 141.6, 141.2, 139.6, 139.4, 137.7, 130.9, 129.2, 128.9, 126.5, 125.9, 123.4, 123.3, 122.0, 117.2, 111.9, 52.4, 49.6, 45.9, 42.4, 42.3, 41.5, 33.4, 28.8, 27.1, 21.3, 21.0 ppm; HRMS calcd for $C_{30}H_{26}N_5O$ $[M-H]^-$: 472.2137, found: 472.2134.



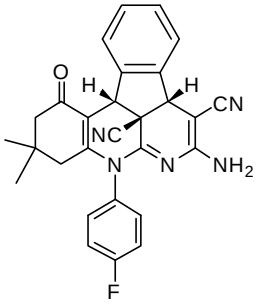
7-Amino-5-(2,3-dimethylphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4g)

The crude products **4g** purified by recrystallization from 95% ethanol, yellow solid 360 mg (yield 76%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 292-294 °C; IR (KBr) v : 3331, 2958, 2175, 1654, 1631, 1600, 1564, 1469, 1381, 1338, 1258, 1212, 1160, 735 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.37-7.29 (m, 2H, ArH), 7.25 (d, J = 7.6 Hz, 1H, ArH), 7.20 (d, J = 7.6 Hz, 1H, ArH), 7.06 (t, J = 7.6 Hz, 1H, ArH), 6.95 (d, J = 6.8 Hz, 1H, ArH), 6.62(s, 2H, NH_2), 6.31 (d, J = 7.6 Hz, 1H, ArH), 5.01 (s, 1H, CH), 4.68 (s, 1H, CH), 2.54-2.53 (m, 1H, CH-H), 2.36-2.32 (m, 1H, CH-H), 2.30 (s, 3H, CH_3), 2.13-2.09 (m, H, CH-H), 2.00 (s, 3H, CH_3), 1.78-1.74 (m, 1H, CH-H), 1.01 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.1, 158.1, 153.1, 152.8, 141.6, 141.1, 138.8, 136.4, 135.2, 130.9, 129.2, 128.9, 126.9, 125.7, 123.4, 123.2, 122.0, 117.1, 112.3, 52.1, 49.6, 45.8, 42.3, 42.1, 41.2, 33.6, 29.0, 26.6, 20.4, 13.6 ppm; HRMS calcd for $C_{30}H_{26}N_5O$ $[M-H]^-$: 472.2137, found: 472.2124 .



7-Amino-3,3-dimethyl-1-oxo-5-phenyl-1,2,3,4,5,5a[1],8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a[1],8-dicarbonitrile (4h)

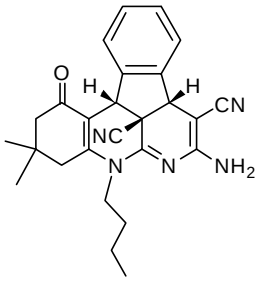
The crude products **4h** purified by recrystallization from 95% ethanol, yellow solid 339 mg (yield 76%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 274-276 °C; IR (KBr) *v* : 3349, 2960, 2172, 1657, 1628, 1558, 1490, 1457, 1378, 1334, 1278, 1247, 1202, 1188, 1045, 764, 732, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.52 (t, J = 7.2 Hz, 1H, ArH), 7.45-7.29 (m, 4H, ArH), 7.26-7.23 (m, 2H, ArH), 6.95 (d, J = 7.2 Hz, 1H, ArH), 6.60 (d, J = 7.6 Hz, 1H, ArH), 6.55 (s, 2H, NH_2),5.01 (s, 1H, CH), 4.68 (s, 1H, CH), 2.48-2.46 (m,1H, CH-H), 2.38-2.33 (m, 1H, CH-H), 2.01-1.98 (m, 2H, CH_2), 0.99 (s, 3H, CH_3),0.93 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.2, 157.8, 154.3, 153.0, 141.6, 141.2, 138.0, 130.3, 130.2, 129.4, 129.3, 129.2, 128.9, 128.6, 123.4, 123.3, 122.0, 117.1, 112.2, 52.4, 49.5, 45.9, 42.4, 42.3, 41.6, 33.4, 28.6, 27.3 ppm; HRMS calcd for $C_{28}H_{22}N_5O$ $[M-H]^-$:444.1824, found: 444.1833.



7-Amino-5-(4-fluorophenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a[1],8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a[1],8-dicarbonitrile (4i)

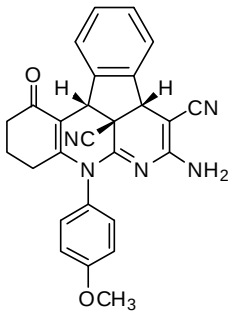
The crude products **4i** purified by flash column chromatography (petroleum ether : ethyl acetate = 5:1), yellow solid 329 mg (yield 71%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3335, 2963, 2176, 1659, 1629, 1561, 1504, 1379, 1246, 1218, 1189, 1152, 991, 842, 739 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.35-7.19 (m, 6H, ArH), 6.94 (d, J = 7.2 Hz, 1H, ArH), 6.67-6.66 (m, 1H, ArH), 6.60 (s, 2H, NH_2), 5.01 (s, 1H, CH), 4.68 (s, 1H, CH), 2.46-2.43 (m, 2H, CH_2), 2.05 (s, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.96 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.2, 163.3, 160.9, 157.6, 154.4, 152.8, 141.5, 141.1, 134.1, 131.5, 131.4, 130.8, 130.7, 129.9, 128.9, 123.4, 123.3, 121.9, 117.5, 117.2,

117.1, 117.0, 116.9, 112.1, 52.4, 49.6, 45.9, 42.4, 42.3, 41.5, 33.4, 28.6, 27.3 ppm; HRMS calcd for $C_{28}H_{21}FN_5O$ $[M-H]^-$: 462.1730, found: 462.1732 .



7-Amino-5-butyl-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4j)

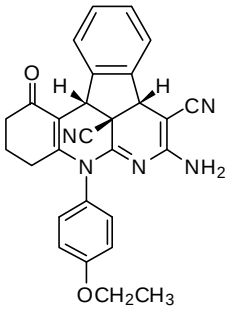
The crude products **4j** purified by recrystallization from 95% ethanol, yellow solid 370 mg (yield 87%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: 216-218 °C; IR (KBr) *v* : 3339, 2957, 2174, 1621, 1593, 1560, 1385, 1348, 1265, 1202, 1126, 998, 734, 605 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.29-7.17 (m, 3H, ArH), 6.83 (s, 2H, NH_2), 6.79 (d, J = 7.2Hz, 1H, ArH), 4.83 (s, 1H, CH), 4.56 (s, 1H, CH), 3.94-3.93 (m, 1H, CH-H), 3.69-3.67 (m, 1H, CH-H), 2.74-2.69 (m, 1H, CH-H), 2.60-2.55 (m, 1H, CH-H), 2.46 (s, 1H, CH-H), 2.34-2.30 (m, 1H, CH-H), 1.25-1.24 (m, 2H, CH_2), 1.10 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.94-0.87 (m, 2H, CH_2), 0.65 (t, J = 6.8 Hz, 3H,CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.0, 158.4, 153.3, 152.8, 141.8, 141.1, 128.9, 128.7, 122.3, 117.2, 112.5, 51.6, 49.4, 46.1, 44.3, 42.1, 41.8, 33.3, 30.3, 29.1, 27.0, 19.3, 14.1 ppm; HRMS calcd for $C_{26}H_{26}N_5O$ $[M-H]^-$: 424.2137, found: 424.2144 .



7-Amino-5-(4-methoxyphenyl)-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahyd-robenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4k)

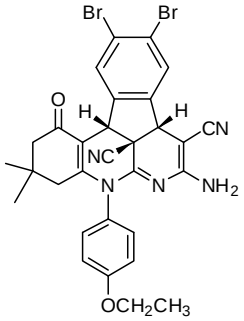
The crude products **4k** purified by flash column chromatography (petroleum ether : ethyl acetate = 5:1), yellow solid 304 mg (yield 68%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3333, 2962, 2174, 1654, 1626, 1601, 1561, 1507, 1378, 1252, 1183, 1202, 983, 739 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.35-7.28 (m, 2H, ArH), 7.24 (d, J = 6.8 Hz, 1H, ArH), 7.16 (d, J = 8.8 Hz, 1H, ArH), 7.03 (d, J = 9.2 Hz, 1H, ArH), 6.95

(d, J = 7.2Hz, 1H, ArH), 6.89 (d, J = 8.4 Hz, 1H, ArH), 6.55 (s, 3H, ArH+NH_2), 4.97 (s, 1H, CH), 4.66 (s, 1H, CH), 3.75 (s, 3H, OCH_3), 2.46-2.43 (m, 2H, CH_2), 2.12-2.11 (m, 2H, CH_2), 1.92-1.91 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.4, 159.5, 157.9, 155.5, 154.2, 141.5, 141.3, 130.5, 129.7, 129.1, 128.8, 123.5, 123.3, 122.0, 117.2, 115.5, 114.9, 112.8, 56.5, 55.8, 52.8, 46.1, 42.3, 36.1, 28.4, 21.9, 19.1 ppm; HRMS calcd for $C_{27}H_{20}N_5O_2$ $[M-H]^-$: 446.1617, found: 446.1637.



7-Amino-5-(4-ethoxyphenyl)-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4l)

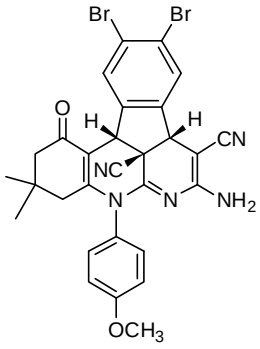
The crude products **4l** by flash column chromatography (petroleum ether : ethyl acetate = 5:1), yellow solid 300 mg (yield 65%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) v : 3335, 2888, 2171, 1629, 16-7, 1562, 1527, 1377, 1332, 1256, 1185, 1168, 1041, 923, 836, 741 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.35-7.29 (m, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.14 (d, J = 8.0 Hz, 1H, ArH), 7.00 (d, J = 8.8 Hz, 1H, ArH), 6.95 (d, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 8.4 Hz, 1H, ArH), 6.54 (s, 2H, NH_2), 6.53-6.51 (m, 1H, ArH), 4.96 (s, 1H, CH), 4.65 (s, 1H, CH), 4.02-3.97 (m, 2H, CH_2), 2.46-2.41 (m, 2H, CH_2), 2.12-2.09 (m, 2H, CH_2), 1.92-1.91 (m, 2H, CH_2), 1.31 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.4, 158.8, 157.9, 155.5, 154.2, 141.5, 141.3, 130.4, 130.1, 129.7, 129.1, 128.8, 123.5, 123.3, 121.1, 117.2, 115.8, 115.3, 112.8, 63.8, 52.3, 46.1, 42.3, 36.1, 28.4, 21.8, 15.1 ppm; HRMS calcd for $C_{28}H_{22}N_5O_2$ $[M-H]^-$: 460.1773, found : 460.1776.



(5a^{1}S,8aR,12bR)-7-amino-10,11-dibromo-5-(4-ethoxyphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a^1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile (4m)

The crude products **4m** by flash column chromatography

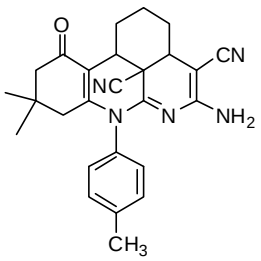
(petroleum ether : ethyl acetate = 5:1), yellow solid 453 mg (yield 70%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3332, 2930, 2185, 1630, 1569, 1509, 1453, 1383, 1329, 1252, 1114, 1046, 825, 755 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.44 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.10-7.08 (m, 1H, ArH), 7.03-7.01 (m, 1H, ArH), 6.91-6.89 (m, 1H, ArH), 6.73-6.71 (m, 1H, ArH), 6.69 (s, 2H, NH_2), 5.00 (s, 1H, CH), 4.70 (s, 1H, CH), 4.01 (s, 2H, CH_2), 2.55-2.50 (m, 1H, CH-H), 2.31-2.27 (m, 1H, CH-H), 2.16-2.12 (m, 1H, CH-H), 1.96-1.92 (m, 1H, CH-H), 1.34-1.35 (m, 3H, CH_3), 0.98 (s, 3H, CH_3), 0.93 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.4, 158.8, 158.0, 154.0, 143.5, 142.6, 130.0, 130.1, 129.9, 128.5, 128.3, 124.4, 124.1, 121.6, 116.5, 115.9, 115.3, 110.8, 63.8, 63.6, 51.2, 49.3, 45.2, 42.3, 41.8, 41.7, 33.4, 29.1, 26.7, 15.1 ppm; HRMS calcd for $C_{30}H_{25}Br_2N_5O_2$ $[M+Na]^+$: 668.0273, found: 668.0235.



(5a^{1}S,8aR,12bR)-7-amino-10,11-dibromo-5-(4-methoxyphenyl)-3,3-dimethyl-1-oxo-1,2,3,4,5,5a1,8a,12b-octahydrobenzo[*b*]indeno[1,2,3-*de*][1,8]naphthyridine-5a^1,8-dicarbonitrile(4n)

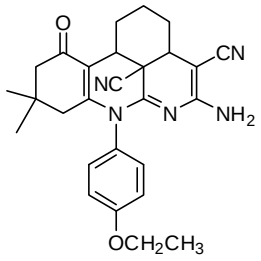
The crude products **4n** by flash column chromatography (petroleum ether : ethyl acetate = 5:1), yellow solid 411 mg (yield 67%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3332, 2955, 2182, 1630, 1568, 1509, 1509, 1454, 1379, 1252, 1191, 1026, 911, 889, 755 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.45 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.13-7.10 (m, 1H, ArH), 7.06-7.03 (m, 1H, ArH), 6.94-6.91 (m, 1H, ArH), 6.76-6.74 (m, 1H, ArH), 6.71 (s, 2H, NH_2), 5.01 (s, 1H, CH), 4.72 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 2.56-2.52 (m, 1H, CH-H), 2.32-2.28 (m, 1H, CH-H), 2.17-2.12 (m, 1H, CH-H), 1.96-1.92 (m, 1H, CH-H), 0.99 (s, 3H, CH_3), 0.94 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 196.4, 159.5, 158.0, 154.0, 143.5, 142.6, 130.1, 129.9, 128.5, 128.3, 124.4, 124.1, 121.6, 121.6, 116.5, 115.6, 114.9, 110.8, 55.8, 51.2, 49.3, 45.2, 42.3, 41.8, 41.7, 36.4, 33.4, 29.1, 26.7 ppm; HRMS calcd for $C_{29}H_{23}Br_2N_5O_2[M+Na]^+$:

654.0116, found: 654.0101.



5-amino-9,9-dimethyl-11-oxo-7-(*p*-tolyl)-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6a)

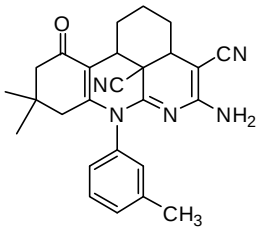
The crude products **6a** purified by recrystallization from 95% ethanol, yellow solid 366 mg (yield 86%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3336, 2954, 2167, 1662, 1639, 1589, 1561, 1382, 1336, 1248, 1125, 1009, 879, 742 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.34-7.32 (m, 2H, ArH), 7.18-7.16 (m, 2H, ArH), 6.29 (s, 2H, NH_2), 3.32-3.29 (m, 1H, CH), 2.85-2.83 (m, 1H, CH), 2.38 (s, 3H, CH_3), 2.23 (s, 2H, CH_2), 2.02-1.91 (m, 2H, CH_2), 1.80-1.77 (m, 1H, CH), 1.69-1.67 (m, 1H, CH), 1.46-1.44 (m, 1H, CH), 1.34-1.25 (m, 2H, CH_2),1.04-1.01 (m, 1H, CH), 0.95 (s, 3H, CH_3), 0.86 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.6, 157.5, 155.1, 152.3, 138.8, 135.0, 130.5, 121.4, 119.1, 117.1, 58.6, 49.5, 41.3, 37.2, 33.2, 32.9, 29.7, 28.4, 27.4, 21.2, 20.1 ppm; HRMS calcd for $C_{26}H_{26}N_5O$ $[M-H]^-$: 424.2137, found: 424.2162.



5-amino-7-(4-ethoxyphenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6b)

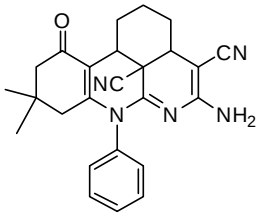
The crude products **6b** purified by recrystallization from 95% ethanol, yellow solid 396 mg (yield 87%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3327, 2929, 2167, 1663, 1638, 1589, 1561, 1507, 1383, 1249, 1110, 1043, 921, 879 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.19-7.18 (m, 2H, ArH), 7.03-7.01(m, 2H, ArH), 6.26 (s, 2H, NH_2), 4.08-4.07 (m, 2H, CH_2), 3.31-3.28 (m, 1H, CH), 2.85-2.82 (m, 1H, CH), 2.23 (s, 2H, CH_2), 2.05-1.97 (m, 2H, CH_2), 1.81-1.79 (m, 1H, CH), 1.69-1.67 (m, 1H, CH), 1.47-1.44 (m, 1H, CH), 1.36 (t, J = 6.8 Hz, 3H, CH_3), 1.30-1.27 (m, 2H, 2×CH), 1.08-1.04 (m, 1H, CH), 0.96

(s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.9, 159.0, 157.0, 155.5, 152.8, 130.1, 121.6, 119.3, 117.2, 115.6, 64.0, 58.5, 49.7, 41.5, 37.5, 33.4, 33.0, 29.0, 28.6, 27.6, 20.3, 15.3 ppm; HRMS calcd for $C_{27}H_{28}N_5O_2$ $[M-H]^-$: 454.2243, found: 454.2243.



5-amino-9,9-dimethyl-11-oxo-7-(*m*-tolyl)-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6c)

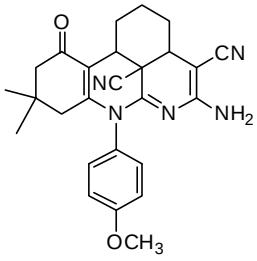
The crude products **6c** purified by recrystallization from 95% ethanol, yellow solid 370 mg (yield 87%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3333, 2953, 2167, 1661, 1636, 1597, 1561, 1383, 1335, 1249, 1159, 1124, 1023, 739, 690 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.41-7.40 (m, H, ArH), 7.29 (s, 1H, ArH), 7.10-7.08 (m, 2H, ArH), 6.30 (s, 2H, NH_2), 3.37-3.28 (m, 1H, CH), 2.84-2.82 (m, 1H, CH), 2.38 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 1.97 (s, 2H, CH_2), 1.79-1.78 (m, 1H, CH), 1.70-1.68 (m, 1H, CH), 1.45-1.44 (m, 1H, CH), 1.31-1.29 (m, 2H, CH_2), 1.05-1.02 (m, 1H, CH), 0.95 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.7, 157.5, 154.9, 152.2, 139.7, 137.4, 130.0, 129.7, 121.1, 119.1, 127.1, 58.5, 49.5, 41.2, 37.2, 33.3, 32.8, 29.7, 28.5, 27.4, 27.3, 21.3, 20.1 ppm; HRMS calcd for $C_{26}H_{26}N_5O$ $[M-H]^-$: 424.2137, found: 424.2139.



5-amino-9,9-dimethyl-11-oxo-7-phenyl-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6d)

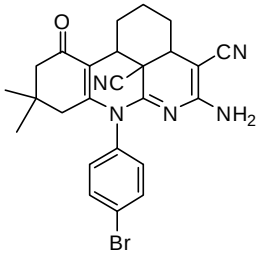
The crude products **6d** purified by recrystallization from 95% ethanol, yellow solid 362 mg (yield 88%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3328, 2952, 2169, 1660, 1637, 1602, 1563, 1381, 1335, 1249, 1126, 1073, 1017, 878, 733 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.54-7.48 (m, 3H, ArH), 7.31-7.29 (m, 2H, ArH), 6.30 (s, 2H, NH_2), 3.31-3.30 (m, 1H, CH),

2.86-2.83 (m, 1H, CH), 2.24 (s, 2H, CH_2), 2.01-1.89 (m, 2H, CH_2), 1.80-1.77 (m, 1H, CH), 1.70-1.67 (m, 1H, CH), 1.46-1.45 (m, 1H, CH), 1.34-1.26 (m, 2H, CH_2), 1.05-1.02 (m, 1H, CH), 0.95 (s, 3H, CH_3), 0.86 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.7, 157.5, 155.0, 152.2, 137.5, 130.0, 129.4, 121.4, 119.1, 117.2, 58.7, 49.5, 41.3, 37.2, 33.3, 32.9, 29.7, 28.4, 27.5, 27.4, 20.1 ppm; HRMS calcd for $C_{25}H_{24}N_5O$ $[M-H]^-$: 410.1981, found: 410.1980.



5-amino-7-(4-methoxyphenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6e)

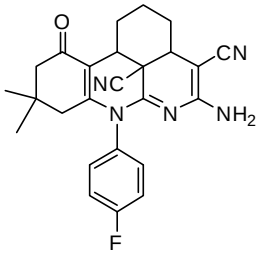
The crude products **6e** purified by recrystallization from 95% ethanol, yellow solid 384 mg (yield 87%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3333, 2933, 2167, 1661, 1637, 1591, 1562, 1508, 1383, 1248, 1224, 1026, 878, 747 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.21-7.20 (m, 2H, ArH), 7.05-7.04 (m, 2H, ArH), 6.30 (s, 2H, NH_2), 3.82 (s, 3H, OCH_3), 3.29-3.26 (m, 1H, CH), 2.83-2.80 (m, 1H, CH), 2.23-2.22 (m, 2H, CH_2), 2.00-1.97 (m, 2H, CH_2), 1.80-1.77 (m, 1H, CH), 1.68-1.65 (m, 1H, CH), 1.44 (s, 1H, CH), 1.30-1.28 (m, 2H, CH_2),1.04-1.01 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 199.6, 164.4, 162.5, 160.2, 157.5, 135.0, 126.3, 124.3, 121.9, 120.0, 63.5, 60.8, 54.4, 46.2, 45.6, 42.2, 38.1, 37.8, 34.7, 33.3, 32.4, 25.0 ppm; HRMS calcd for $C_{26}H_{26}N_5O_2$ $[M-H]^-$: 440.2086, found: 440.2104].



5-amino-7-(4-bromophenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6f)

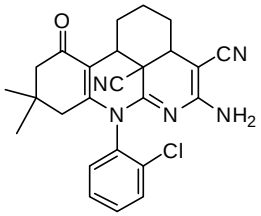
The crude products **6f** purified by recrystallization from 95% ethanol, yellow solid 421.7 mg (yield 86%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3334, 2955, 2167, 1664, 1641, 1591, 1561,

1486, 1379, 1334, 1149, 1071, 1010, 920, 737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.72-7.71 (m, 2H, ArH), 7.30-6.29 (m, 2H, ArH), 6.36 (s, 2H, NH_2), 3.29-3.28 (m, 1H, CH), 2.85-2.83 (m, 1H, CH), 2.24 (s, 2H, CH_2), 1.99-1.94 (m, 2H, CH_2), 1.79-1.78 (m, 1H, CH), 1.67-1.65 (m, 1H, CH), 1.44 (s, 1H, CH), 1.30 (s, 2H, CH_2), 1.05-1.01 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.6, 157.2, 154.9, 151.6, 136.8, 132.9, 122.5, 121.3, 119.0, 117.2, 58.6, 49.5, 41.2, 37.2, 33.2, 32.8, 29.7, 28.3, 27.4, 20.0 ppm; HRMS calcd for $C_{25}H_{23}BrN_5O$ $[M-H]^-$: 488.1086, found: 488.1093.



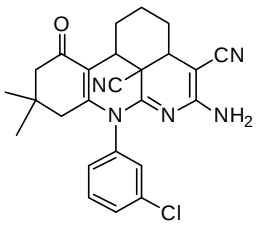
5-amino-7-(4-fluorophenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6g)

The crude products **6g** purified by recrystallization from 95% ethanol, yellow solid 374 mg (yield 87%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3325, 2953, 2168, 1661, 1641, 1590, 1564, 1504, 1379, 1335, 1250, 1013, 879, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.37-7.36 (m, 4H, ArH), 6.33 (s, 2H, NH_2), 3.32-3.30 (m, 1H, CH), 2.86-2.82 (m, 1H, CH), 2.24 (s, 2H, CH_2), 2.05-1.92 (m, 2H, CH_2), 1.80-1.77 (m, 1H, CH), 1.69-1.66 (m, 1H, CH), 1.45-1.44 (m, 1H, CH), 1.32-1.27 (m, 2H, CH_2), 1.05-1.03 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.7, 194.6, 157.3, 157.0, 154.8, 153.7, 151.3, 151.1, 135.2, 134.8, 133.5, 132.4, 132.1, 131.5, 130.9, 130.8, 130.7, 129.2, 129.1, 121.3, 121.2, 119.0, 118.6, 116.4, 116.2, 59.2, 59.0, 49.5, 37.4, 37.1, 33.3, 33.1, 33.0, 32.8, 30.0, 29.0, 28.7, 27.1, 26.9, 20.0, 19.8 ppm; HRMS calcd for $C_{25}H_{23}FN_5O$ $[M-H]^-$: 428.1887, found : 428.1898.



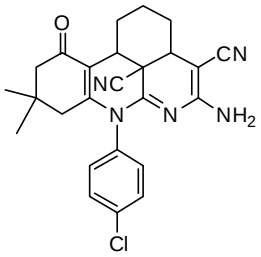
5-amino-7-(2-chlorophenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6h)

The crude products **6h** purified by recrystallization from 95% ethanol, yellow solid 375 mg (yield 84%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3326, 2935, 2172, 1666, 1648, 1632, 1599, 1563, 1383, 1326, 1247, 1112, 1057, 770, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.56-7.51 (m, 3H, ArH), 7.30 (s, 1H, ArH), 6.35 (s, 2H, NH_2), 3.31-3.30 (m, 1H, CH), 2.86-2.83 (m, 1H, CH), 2.24 (m, 2H, CH_2), 2.03-1.91 (m, 2H, CH_2), 1.79-1.76 (m, 1H, CH), 1.67-1.66 (m, 1H, CH), 1.45-1.44 (m, 1H, CH), 1.33-1.32 (m, 2H, CH_2), 1.10-1.07 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.6, 157.4, 155.1, 152.0, 133.7, 121.3, 119.1,117.1, 117.0, 116.8, 58.7, 49.5, 41.2, 37.3, 33.2, 32.9, 31.2, 29.7, 28.3, 27.5, 27.4, 20.1 ppm; HRMS calcd for $C_{25}H_{23}ClN_5O$ $[M-H]^-$: 444.1591, found : 444.1606.



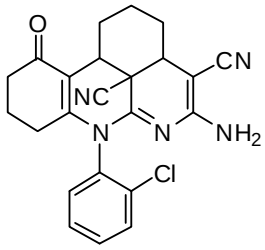
5-amino-7-(3-chlorophenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7 ,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridin e-3a^1,4-dicarbonitrile (6i)

The crude products **6i** purified by recrystallization from 95% ethanol, yellow solid 366 mg (yield 82%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3332, 2953, 2169, 1662, 1638, 1602, 1563, 1383, 1335, 1249, 1127, 1076, 881, 739, 682 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ : 7.57-7.52 (m, 3H, ArH), 7.31 (s, 1H, ArH), 6.35 (s, 2H, NH_2), 3.34-3.26 (m, 1H, CH), 2.86-2.83 (m, 1H, CH), 2.24 (s, 2H, CH_2), 2.07-1.92 (m, 2H, CH_2), 1.80-1.77 (m, 1H, CH), 1.66-1.65 (m, 1H, CH), 1.44 (s, 1H, CH), 1.32 (s, 2H, CH_2), 1.09-1.05 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.9, 157.5, 155.1, 151.8, 138.9, 134.3, 131.6, 129.8, 121.5, 119.2, 117.4, 110.0, 59.0, 49.7, 41.3, 37.5, 33.5, 33.1, 29.8, 28.5, 27.6, 20.3 ppm; HRMS calcd for $C_{25}H_{23}ClN_5O$ $[M-H]^-$: 444.1591, found: 444.1613.



5-amino-7-(4-chlorophenyl)-9,9-dimethyl-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6j)

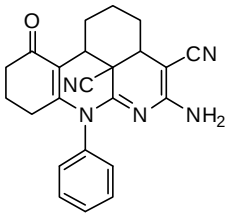
The crude products **6j** purified by recrystallization from 95% ethanol, yellow solid 384 mg (yield 86%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3333, 2955, 2167, 1663, 1641, 1600, 1562, 1489, 1381, 1334, 1247, 1125, 1089, 1014, 878, 745 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.59-7.58 (m, 2H, ArH), 7.37-7.36 (m, 2H, ArH), 6.36 (s, 2H, NH_2), 3.30-3.27 (m, 1H, CH), 2.86-2.83 (m, 1H, CH), 2.24 (s, 2H, CH_2), 2.05-1.93 (m, 2H, CH_2), 1.79-1.77 (m, 1H, CH), 1.68-1.67 (m, 1H, CH), 1.45-1.44 (m, 1H, CH), 1.31-1.29 (m, 2H, CH_2), 1.05-1.02 (m, 1H, CH), 0.96 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.6, 157.3, 155.0, 151.7, 136.4, 133.9, 130.0, 121.3, 119.0, 117.2, 58.7, 49.5, 41.2, 37.2, 33.3, 32.9, 31.2, 29.7, 28.3, 27.5, 27.4, 20.1 ppm; HRMS calcd for $C_{25}H_{23}ClN_5O$ $[M-H]^-$: 444.1591, found : 444.1593.



5-amino-7-(2-chlorophenyl)-11-oxo-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6k)

The crude products **6k** purified by recrystallization from 95% ethanol, yellow solid 309.2 mg (yield 74%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) ν : 3323, 2935, 2167, 1658, 1630, 1600, 1549, 1480, 1379, 1328, 1250, 1180, 1061, 956, 773, 751 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.69-7.68 (m, 1H, ArH), 7.54-7.53 (m, 3H, ArH), 6.30 (s, 2H, NH_2), 3.34-3.29 (m, 1H, CH), 2.87-2.83 (m, 1H, CH), 2.35-2.33 (m, 2H, CH_2), 2.02-2.00 (m, 2H, CH_2), 1.82-1.79 (m, 3H, CH_2+CH), 1.69-1.68 (m, 1H, CH), 1.45-1.44 (m, 1H, CH), 1.34-1.29 (m, 2H, CH_2), 1.09-1.02 (m, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 194.7, 157.3, 153.6, 153.2, 135.4, 133.4, 131.5, 131.1, 130.8, 129.1, 121.3, 118.5, 117.3, 59.0, 37.3, 36.0, 33.0, 29.9, 27.4, 26.7, 21.6, 20.0 ppm; HRMS calcd for

$C_{23}H_{19}ClN_5O$ [M-H]$^-$: 416.1278, found : 416.1282.



5-amino-11-oxo-7-phenyl-2,3,3a,3a^1,7,8,9,10,11,11b-decahydro-1H-pyrido[2,3,4-*gh*]phenanthridine-3a^1,4-dicarbonitrile (6l)

The crude products **6l** purified by recrystallization from 95% ethanol, yellow solid 288 mg (yield 75%); The obtained final products are directedly use as the specific sample for the NMR spectra without further purfication; m.p.: > 300 °C; IR (KBr) *v* : 3325, 2934, 2168, 1662, 1632, 1601, 1563, 1474, 1380, 1331, 1253, 1181, 1057, 954, 772, 750 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 7.52-7.48 (m, 3H, ArH), 7.32-7.31 (m, 2H, ArH), 6.27 (s, 2H, NH_2), 3.31-3.29 (m, 1H, CH), 2.86-2.80 (m, 1H, CH), 2.33-2.32 (m, 2H, CH_2), 2.18-2.14 (m, 1H, CH), 1.98-1.96 (m, 1H, CH), 1.80-1.78 (m, 3H, CH_2+CH), 1.70-1.67 (m, 1H, CH), 1.46-1.44 (m, 1H, CH), 1.33-1.27 (m, 2H, CH_2), 1.09-1.02 (m, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ : 195.0, 157.7, 155.0, 154.0, 137.9, 130.1, 129.5, 121.5, 119.2, 118.1, 58.9, 37.5, 36.2, 33.1, 29.9, 28.2, 27.8, 21.8, 20.3 ppm; HRMS calcd for $C_{23}H_{20}N_5O$ [M-H]$^-$: 382.1668, found : 382.1660.

4. Crystal date of compound 4a

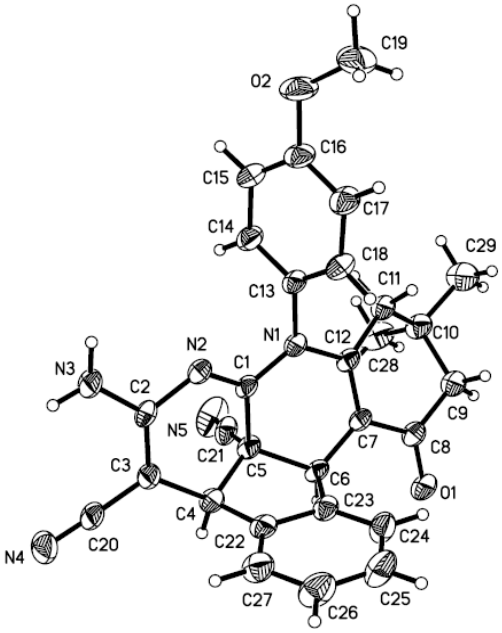


Figure 1. The Crystal Structure of **4a**.

Table 1. Crystallographic Data of Compound **4a**

Empirical formula	$C_{29}H_{25}N_5O_2$
Formula weight	475.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P2(1)/c
Unit cell dimensions	a = 14.6432(17) Å α = 90 °
	b = 7.6244(9) Å β = 104.693(2) °
	c = 23.275(3) Å γ = 90 °
Volume	2513.6(5) $Å^3$
Z	4
Calculated density	1.257 Mg/m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	1000
Crystal size	0.38 × 030 × 0.21 mm
Theta range for data collection	2.82 to 25. 02°
Limiting indices	-17≤h≤17, -7≤k≤9, -27≤l≤26
Reflections collected	13947
Independent reflections	4428 [R(int) = 0.0925]
Data / restraints / parameters	4428 / 0 / 328
Goodness-of-fit on F^2	1.052
Final R indices [I>2σ(I)]	R_1 = 0.0840, wR_2 = 0.1996
R indices (all data)	R_1 = 0.1522, wR_2 = 0.2565
Largest diff. peak and hole	0.244 and -0.296 e. $Å^{-3}$

Table 2 Selected bond lengths (Å) of compound **4a**

Bond	Bond Lengths	Bond	Bond Lengths	Bond	Bond Lengths
N(1)-C(1)	1.363(5)	C(4)-C(22)	1.507(6)	C(13)-C(18)	1.349(6)
N(1)-C(12)	1.424(5)	C(4)-C(5)	1.538(6)	C(13)-C(14)	1.373(6)
N(1)-C(13)	1.458(5)	C(5)-C(21)	1.456(6)	C(14)-C(15)	1.387(6)
N(2)-C(1)	1.289(5)	C(5)-C(6)	1.535(5)	C(15)-C(16)	1.372(7)
N(2)-C(2)	1.395(5)	C(6)-C(7)	1.490(5)	C(16)-C(17)	1.369(7)
N(4)-C(20)	1.154(5)	C(6)-C(23)	1.513(6)	C(17)-C(18)	1.412(6)
N(5)-C(21)	1.141(6)	C(7)-C(12)	1.349(5)	C(22)-C(27)	1.377(6)
O(1)-C(8)	1.236(5)	C(7)-C(8)	1.461(5)	C(22)-C(23)	1.408(6)
O(2)-C(16)	1.376(5)	C(8)-C(9)	1.487(6)	C(23)-C(24)	1.362(6)
O(2)-C(19)	1.422(7)	C(9)-C(10)	1.517(6)	C(24)-C(25)	1.383(7)
C(1)-C(5)	1.535(5)	C(10)-C(28)	1.523(7)	C(25)-C(26)	1.383(7)
C(2)-C(3)	1.352(6)	C(10)-C(29)	1.533(7)	C(26)-C(27)	1.374(7)
C(3)-C(20)	1.410(6)	C(10)-C(11)	1.538(5)		

C(3)-C(4)	1.511(5)	C(11)-C(12)	1.496(6)

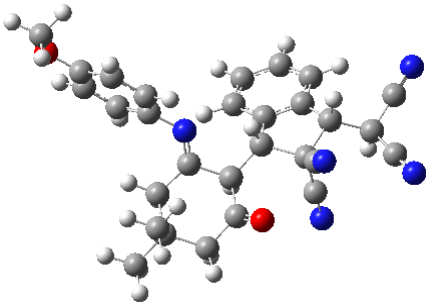
Table 3 Selected bond angles (°) of compound **4a**

Angles	(°)	Angles	(°)
C(1)-N(1)-C(12)	122.8(3)	C(9)-C(10)-C(28)	110.4(4)
C(1)-N(1)-C(13)	119.3(3)	C(9)-C(10)-C(29)	109.7(4)
C(12)-N(1)-C(13)	117.8(3)	C(28)-C(10)-C(29)	110.3(4)
C(1)-N(2)-C(2)	119.0(3)	C(9)-C(10)-C(11)	108.1(3)
C(16)-O(2)-C(19)	117.8(5)	C(28)-C(10)-C(11)	110.6(4)
N(2)-C(1)-N(1)	119.4(4)	C(29)-C(10)-C(11)	107.7(4)
N(2)-C(1)-C(5)	124.1(4)	C(12)-C(11)-C(10)	113.0(4)
N(1)-C(1)-C(5)	116.5(3)	C(7)-C(12)-N(1)	119.4(4)
C(3)-C(2)-N(3)	124.8(4)	C(7)-C(12)-C(11)	123.7(3)
C(3)-C(2)-N(2)	122.9(3)	N(1)-C(12)-C(11)	116.8(3)
N(3)-C(2)-N(2)	112.2(4)	C(18)-C(13)-C(14)	121.2(4)
C(2)-C(3)-C(20)	120.1(4)	C(18)-C(13)-N(1)	118.9(4)
C(2)-C(3)-C(4)	118.8(4)	C(14)-C(13)-N(1)	119.9(4)
C(20)-C(3)-C(4)	121.1(4)	C(13)-C(14)-C(15)	119.1(5)
C(22)-C(4)-C(3)	117.4(3)	C(16)-C(15)-C(14)	120.0(5)
C(22)-C(4)-C(5)	100.4(3)	C(17)-C(16)-C(15)	120.9(5)
C(3)-C(4)-C(5)	111.6(3)	C(17)-C(16)-O(2)	124.0(5)
C(21)-C(5)-C(1)	107.0(3)	C(15)-C(16)-O(2)	115.1(5)
C(21)-C(5)-C(6)	110.2(3)	C(16)-C(17)-C(18)	118.4(5)
C(1)-C(5)-C(6)	109.9(3)	C(13)-C(18)-C(17)	120.2(4)
C(21)-C(5)-C(4)	115.8(4)	N(4)-C(20)-C(3)	178.2(5)
C(1)-C(5)-C(4)	108.6(3)	N(5)-C(21)-C(5)	176.1(5)
C(6)-C(5)-C(4)	105.2(3)	C(27)-C(22)-C(23)	119.1(4)
C(7)-C(6)-C(23)	120.1(4)	C(27)-C(22)-C(4)	129.8(4)
C(7)-C(6)-C(5)	111.8(3)	C(23)-C(22)-C(4)	111.0(3)
C(23)-C(6)-C(5)	101.0(3)	C(24)-C(23)-C(22)	121.2(4)
C(12)-C(7)-C(8)	119.6(4)	C(24)-C(23)-C(6)	129.6(4)
C(12)-C(7)-C(6)	120.9(3)	C(22)-C(23)-C(6)	109.1(4)
C(8)-C(7)-C(6)	119.4(4)	C(23)-C(24)-C(25)	119.3(5)
O(1)-C(8)-C(7)	119.6(4)	C(24)-C(25)-C(26)	119.6(5)
O(1)-C(8)-C(9)	122.5(4)	C(27)-C(26)-C(25)	121.6(5)
C(7)-C(8)-C(9)	118.0(4)	C(26)-C(27)-C(22)	119.1(5)
C(8)-C(9)-C(10)	113.0(4)		

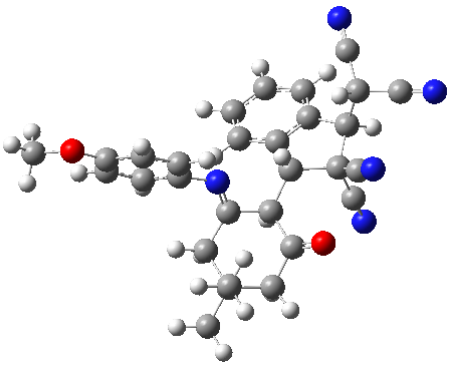
5. The theory calculation of intermediate B

We have calculated possible configurations of the intermediate *syn*-**B** and *anti*-**B** at the DFT level of theory, and all the calculations were performed at the B3LYP/6-31G level of theory. First, the geometrical optimizations of the two possible configurations

were obtained, and then the lowest energy minimum corresponds to the configurations were calculated. The results are shown in Figure 2. From Figure 2, we found that the most stable configuration of *syn*-**B** is 4.9 kJ/mol lower in energy than configuration of *anti*-**B**.



syn-**B**: E = -1543.275878 hartree

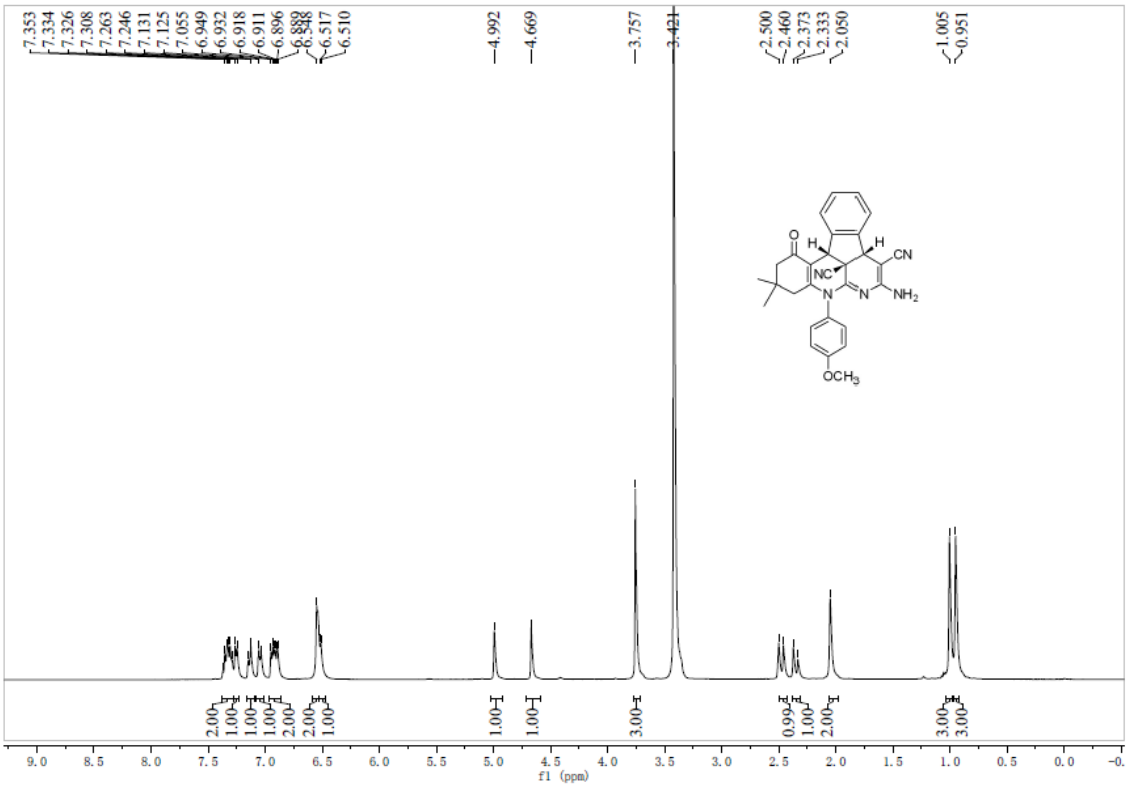


anti-**B** : E = -1543.274009 hartree

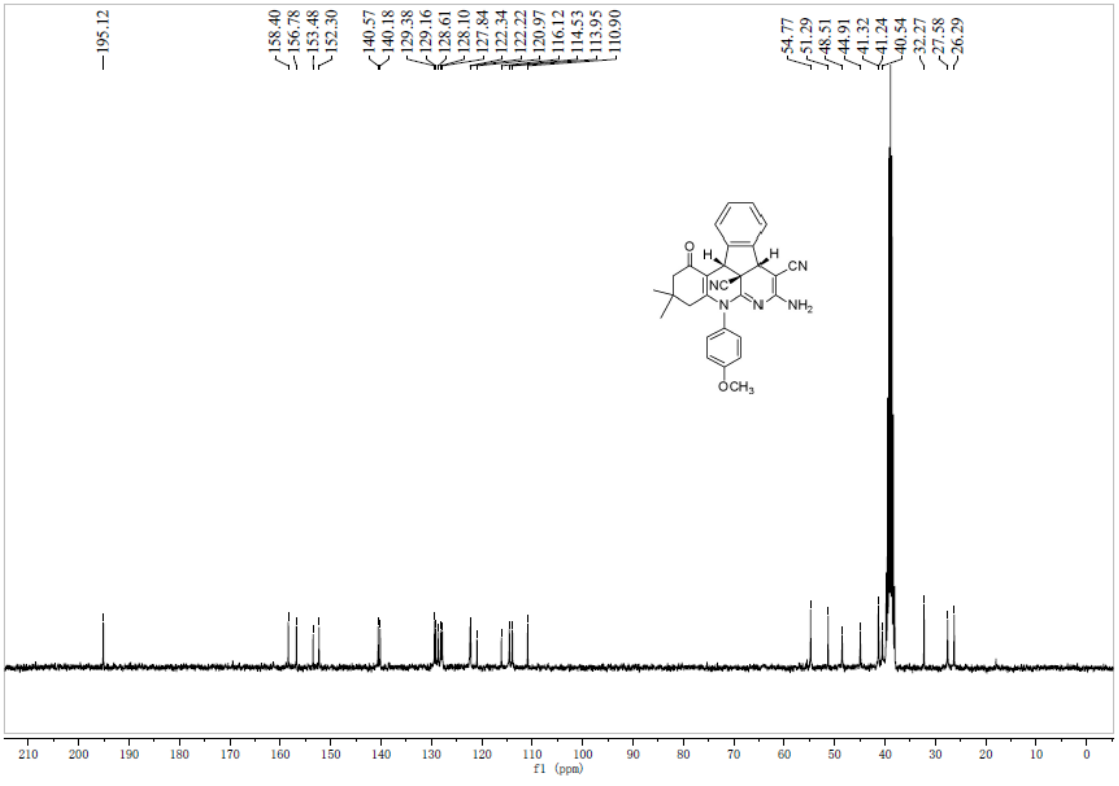
Figure 2. The lowest energy minimum of the intermediate *syn*-**B** and *anti*-**B**

6. ^{1}H NMR and ^{13}C NMR Spectra of all compounds

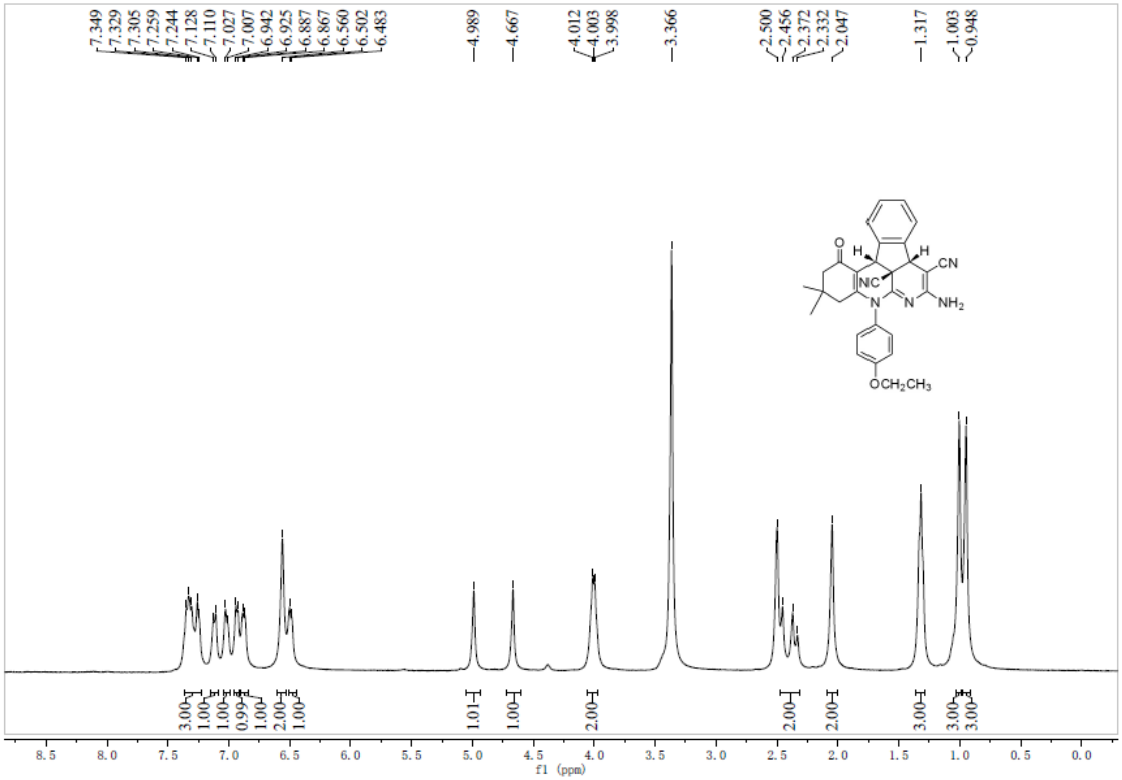
^{1}H NMR of compound **4a**



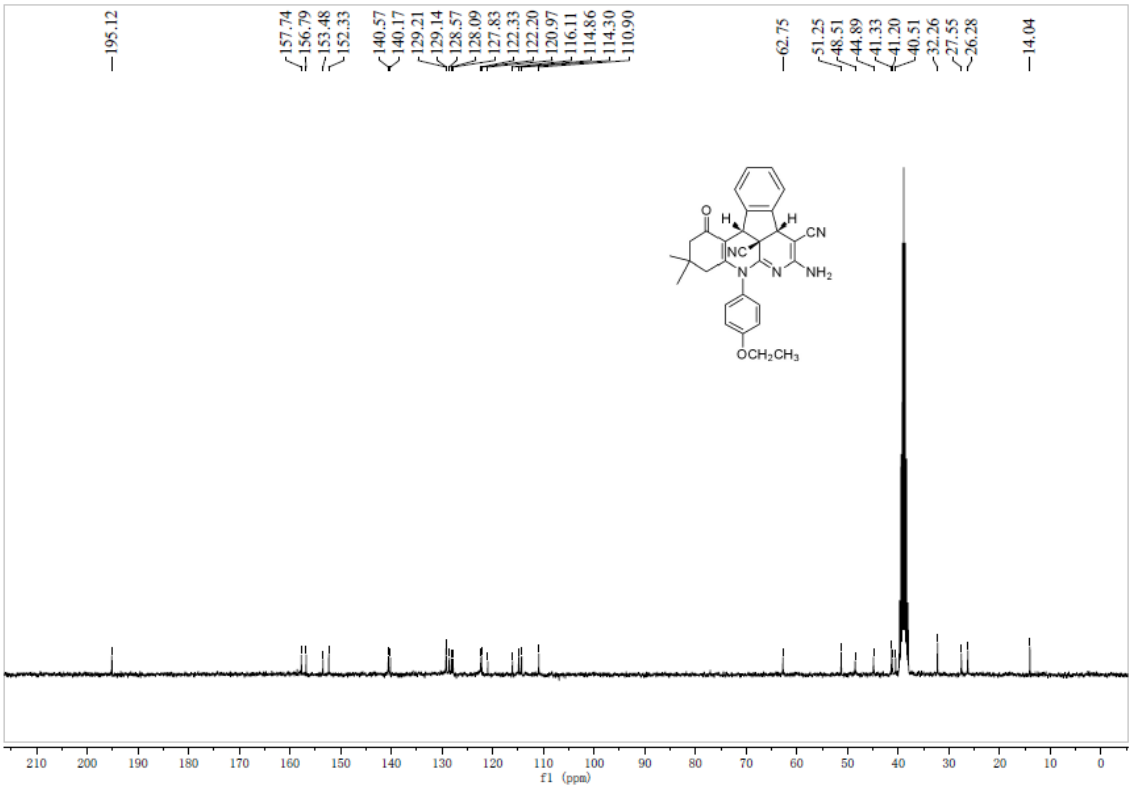
^{13}C NMR of mpound **4a**



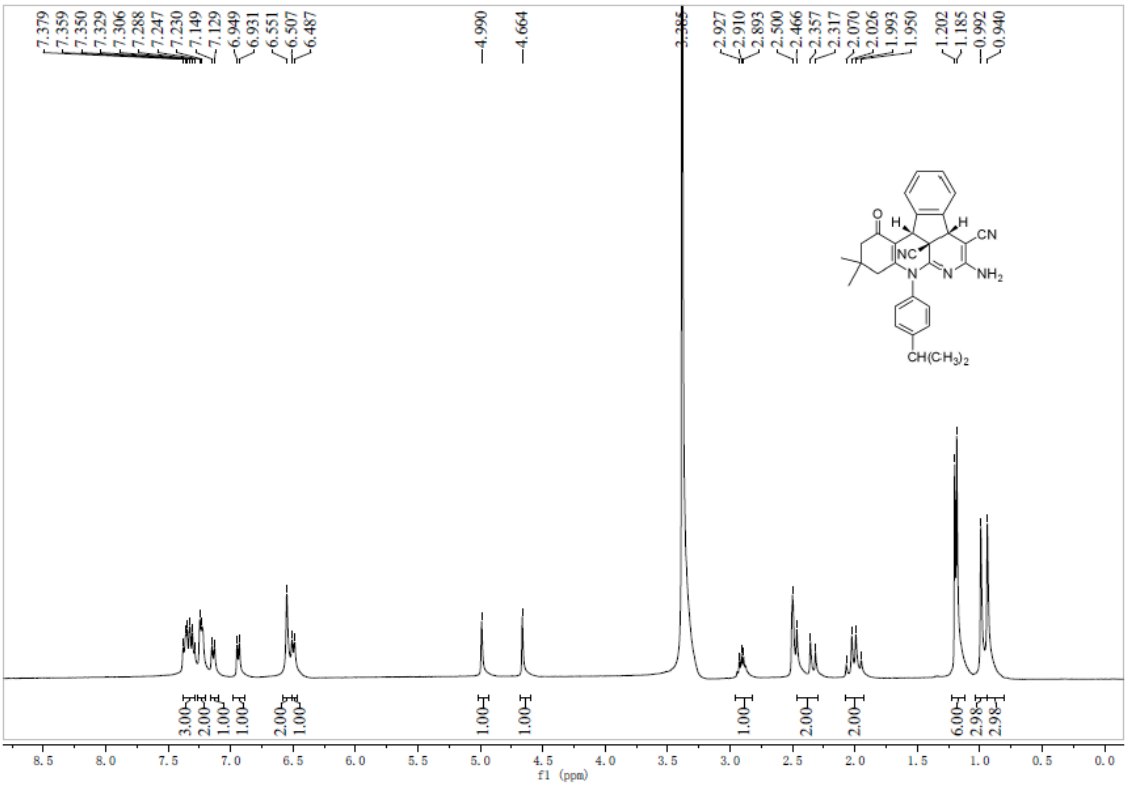
^{1}H NMR of compound **4b**



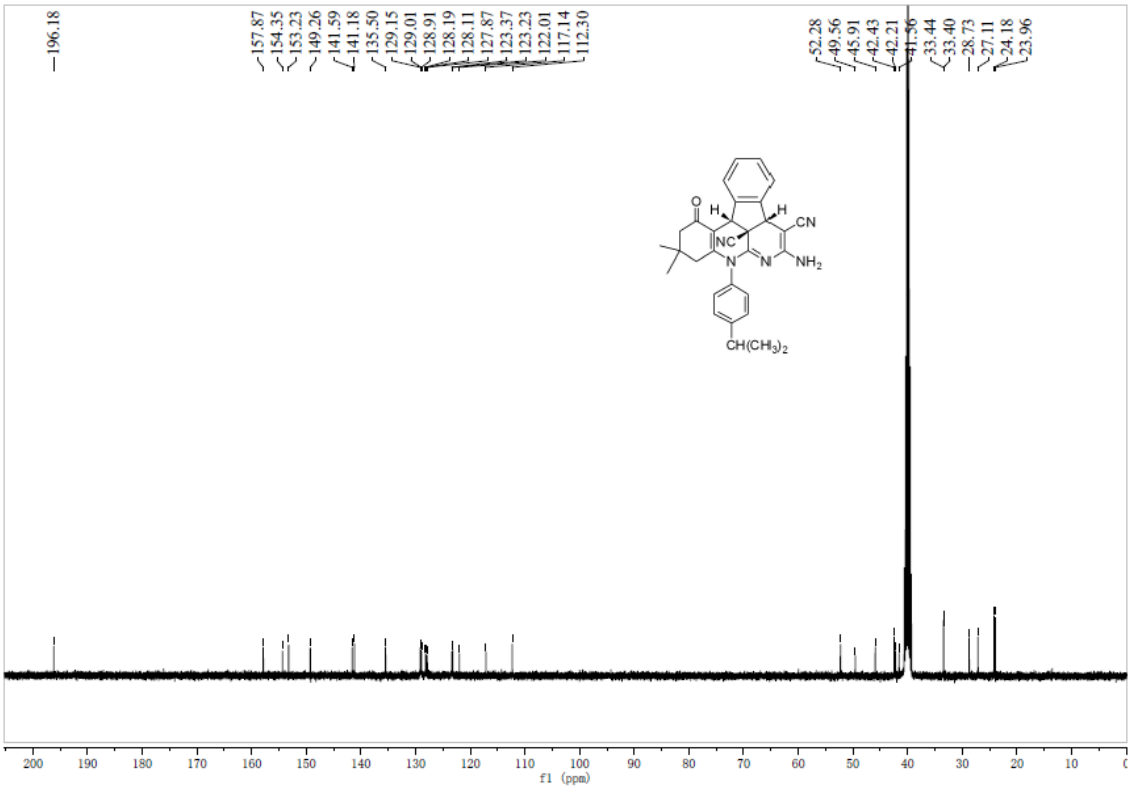
^{13}C NMR of compound **4b**



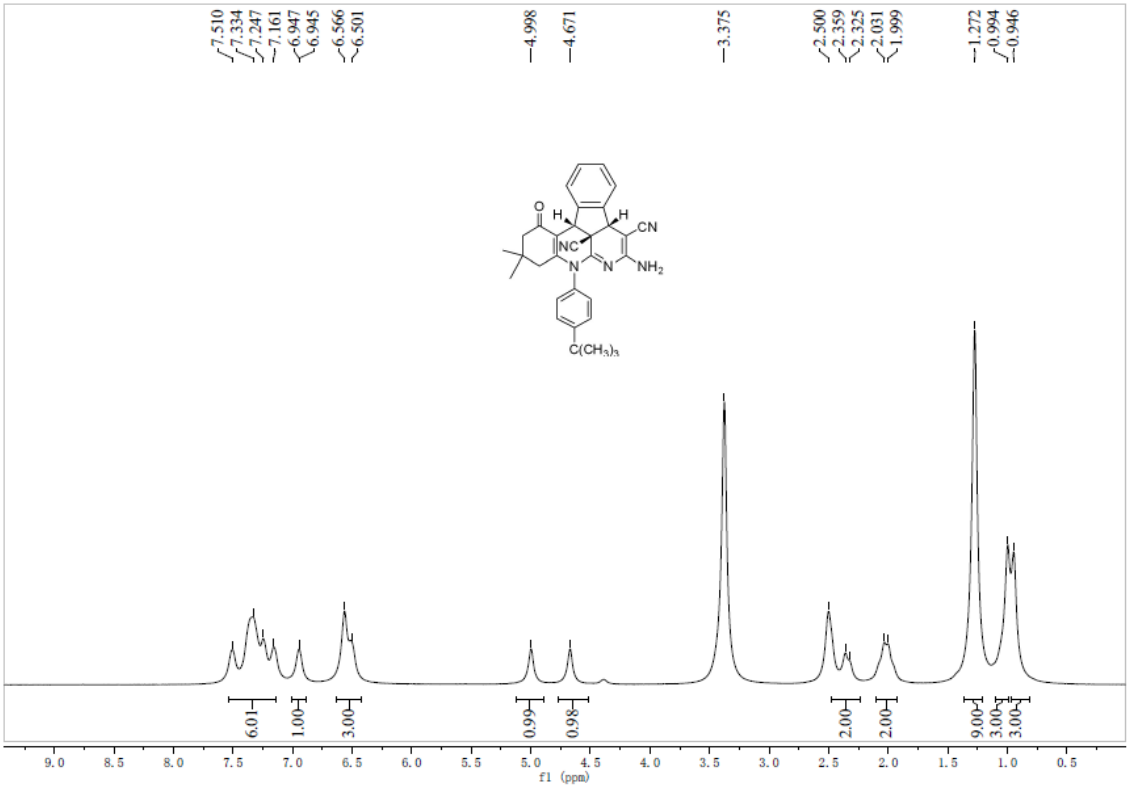
^{1}H NMR of compound **4c**



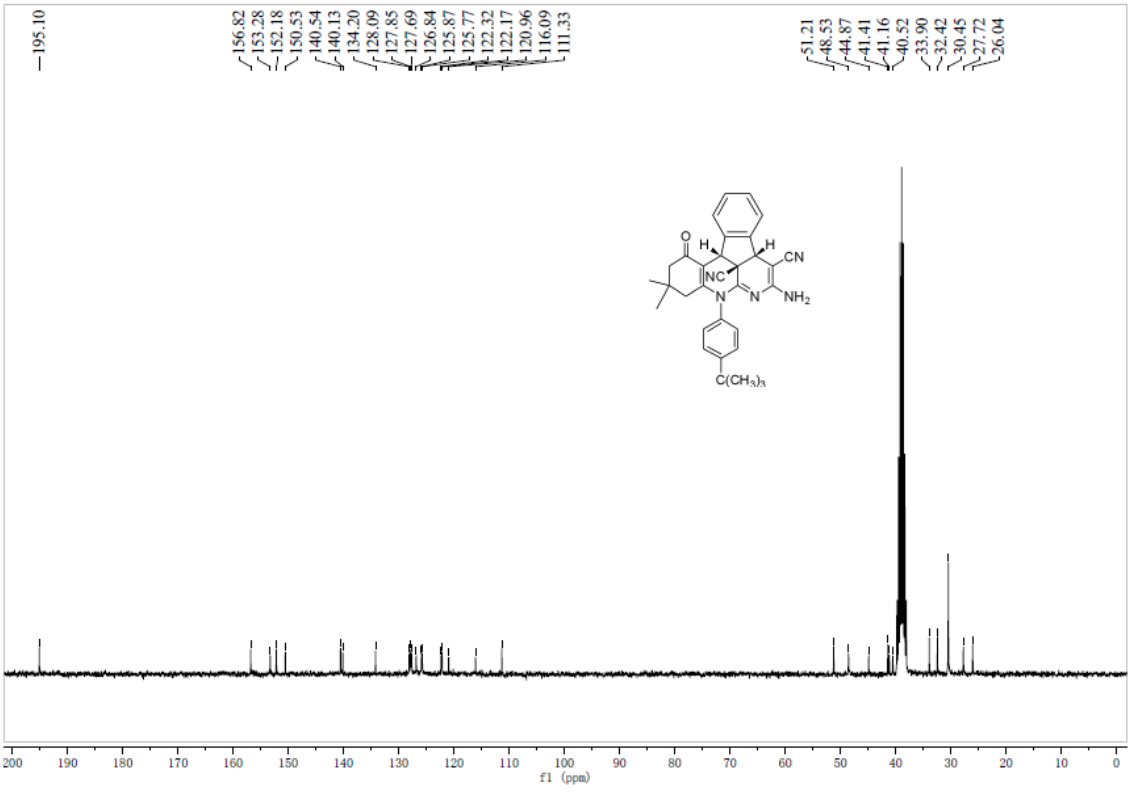
^{13}C NMR of compound **4c**



^{1}H NMR of compound **4d**



^{13}C NMR of compound **4d**



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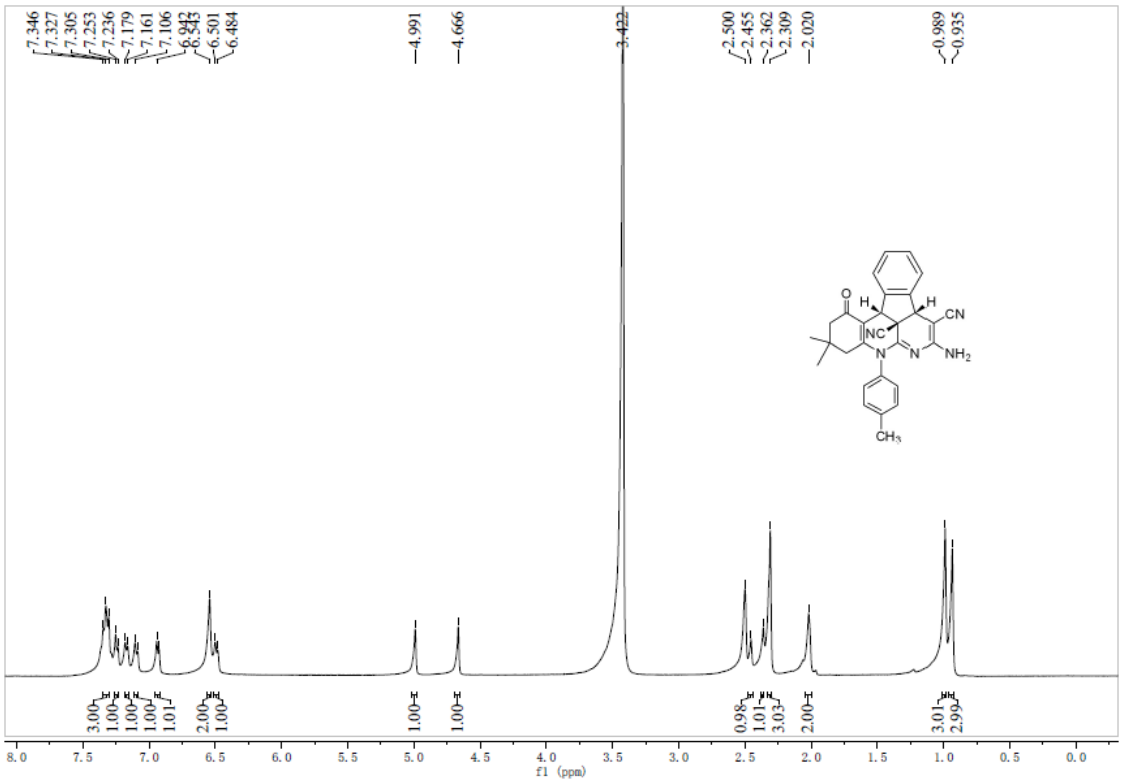

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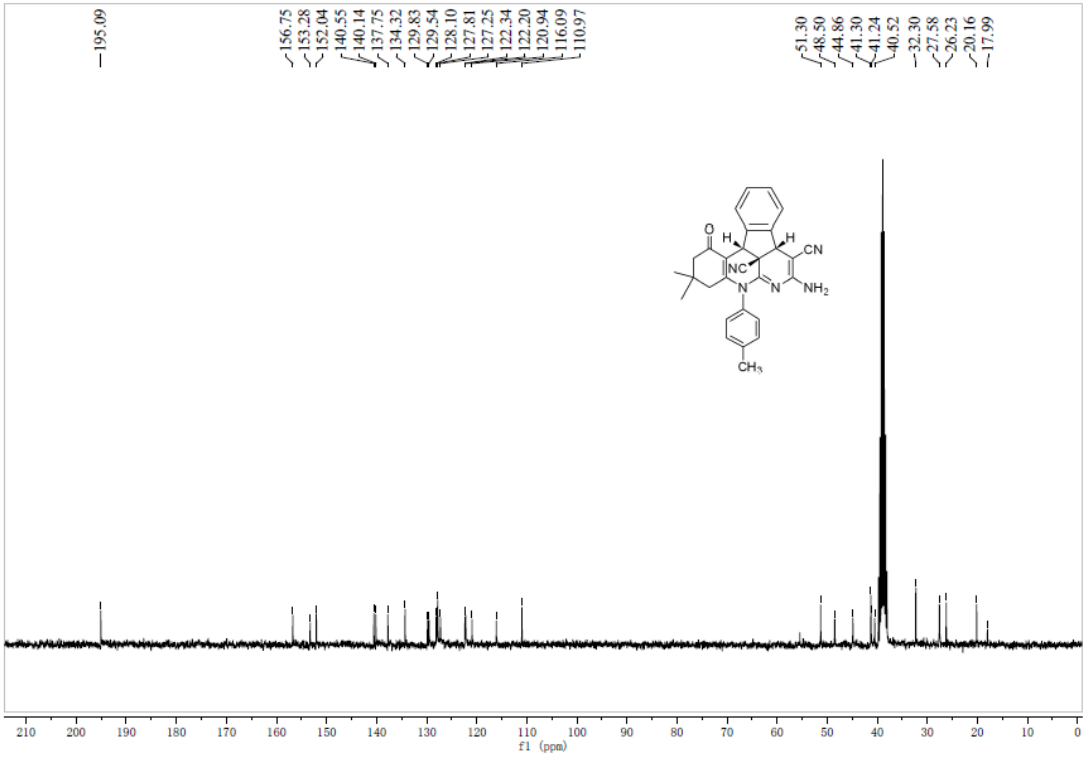
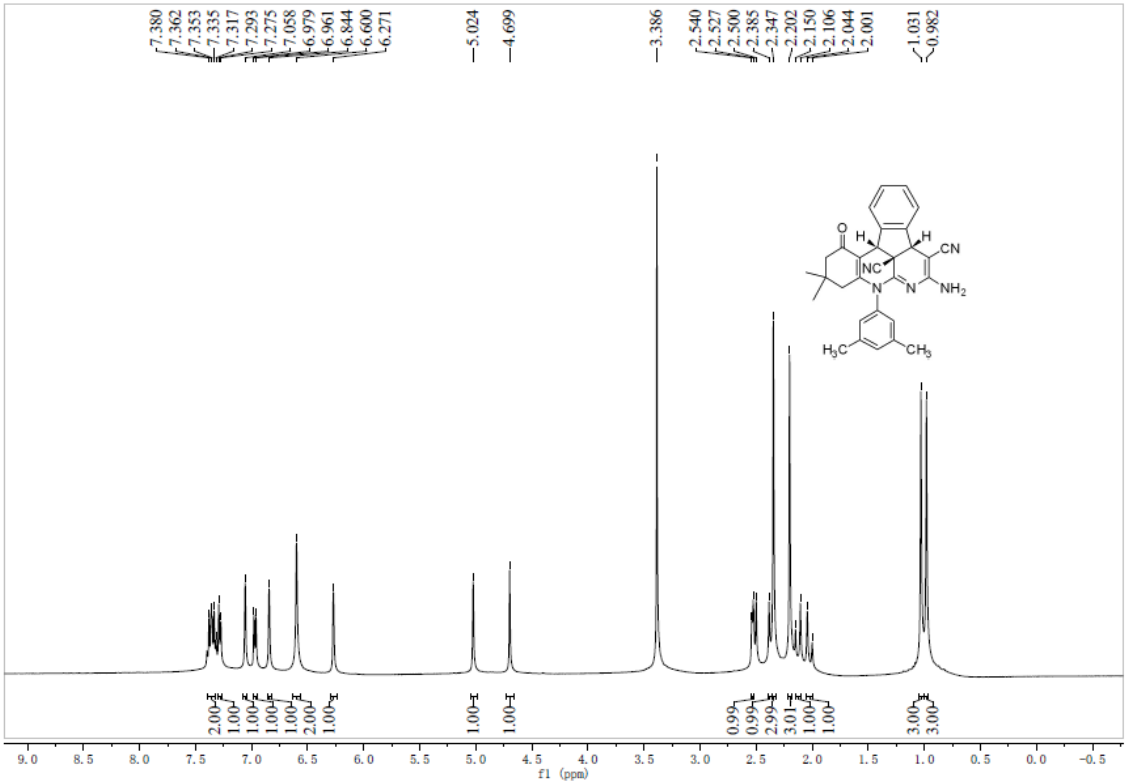
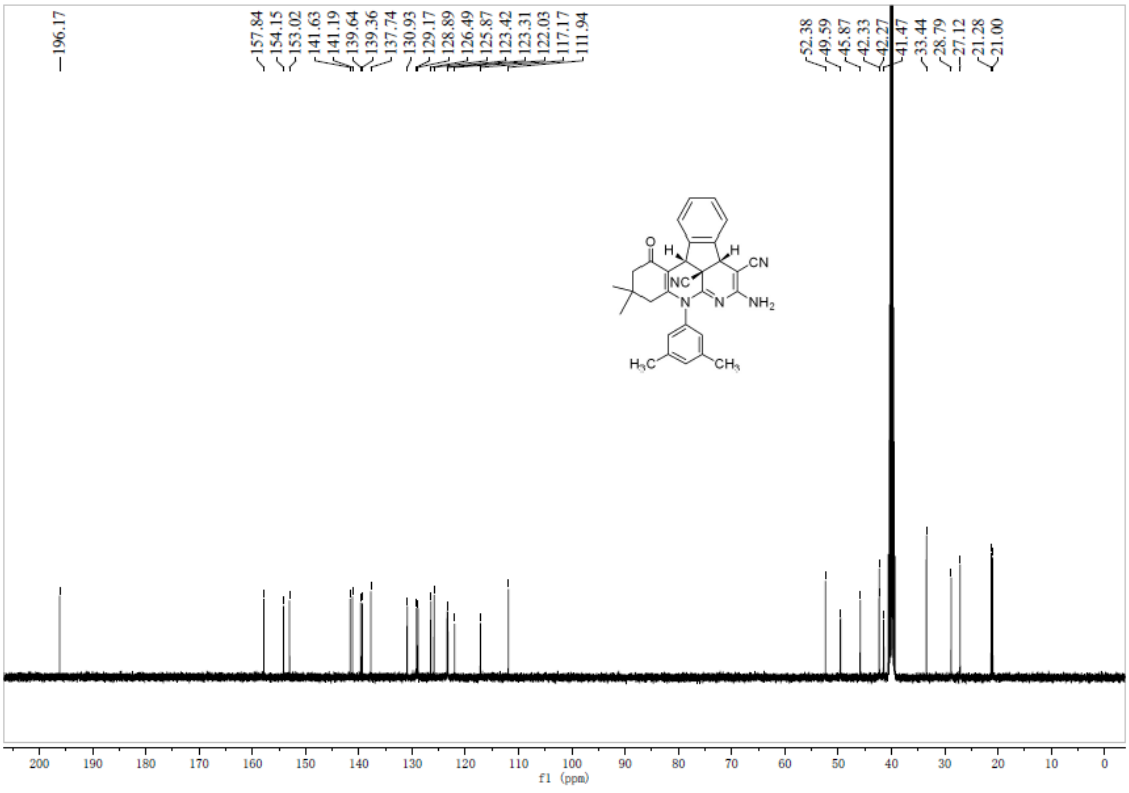


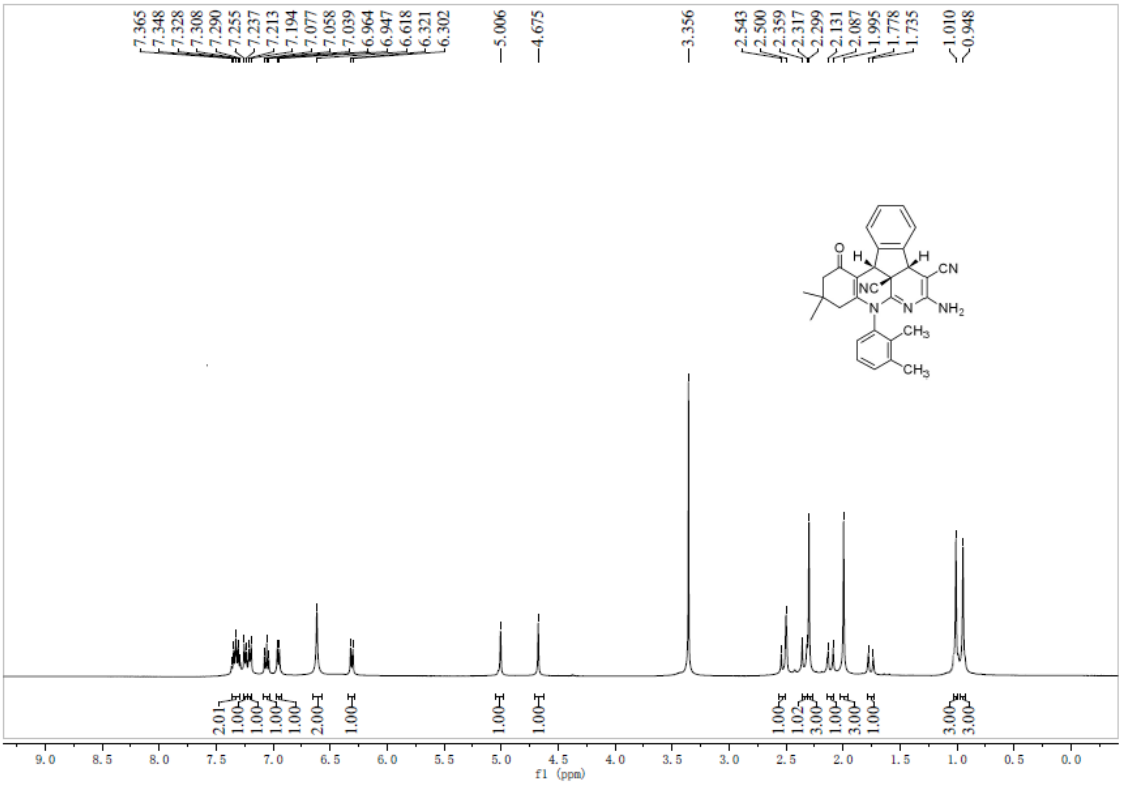
^{1}H NMR of compound **4f**



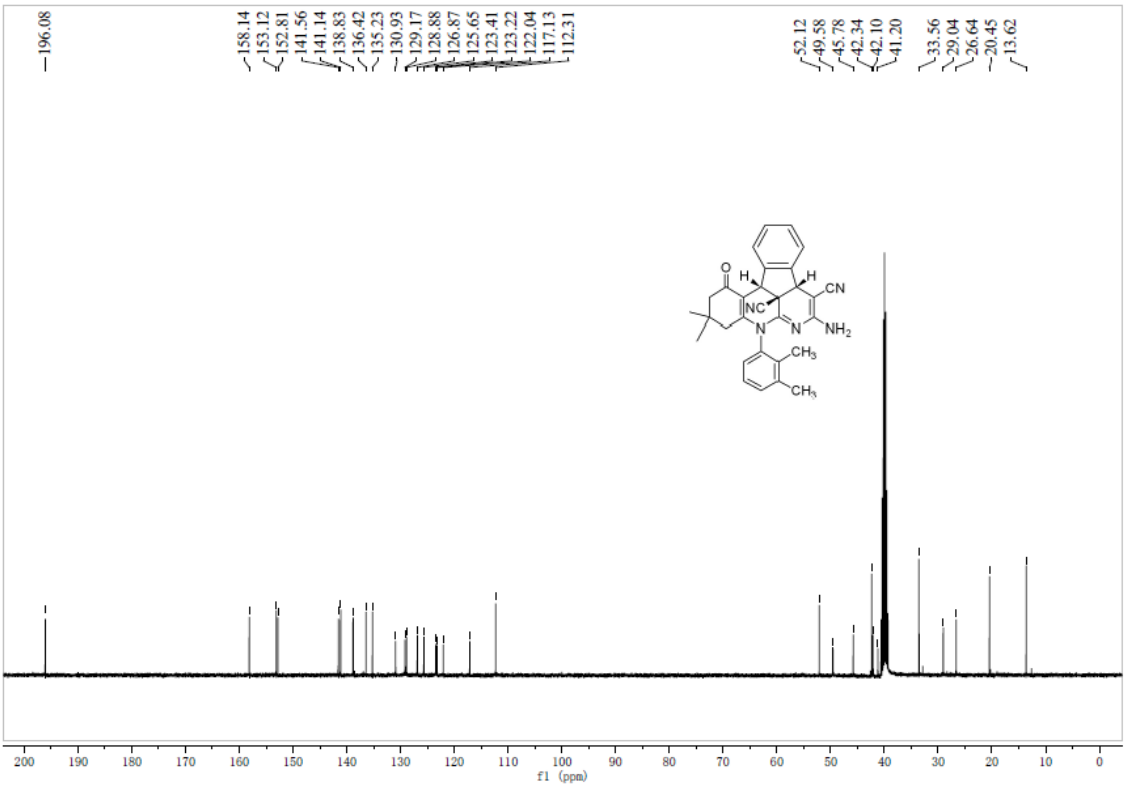
^{13}C NMR of compound **4f**



^{1}H NMR of compound **4g**



^{13}C NMR of compound **4g**



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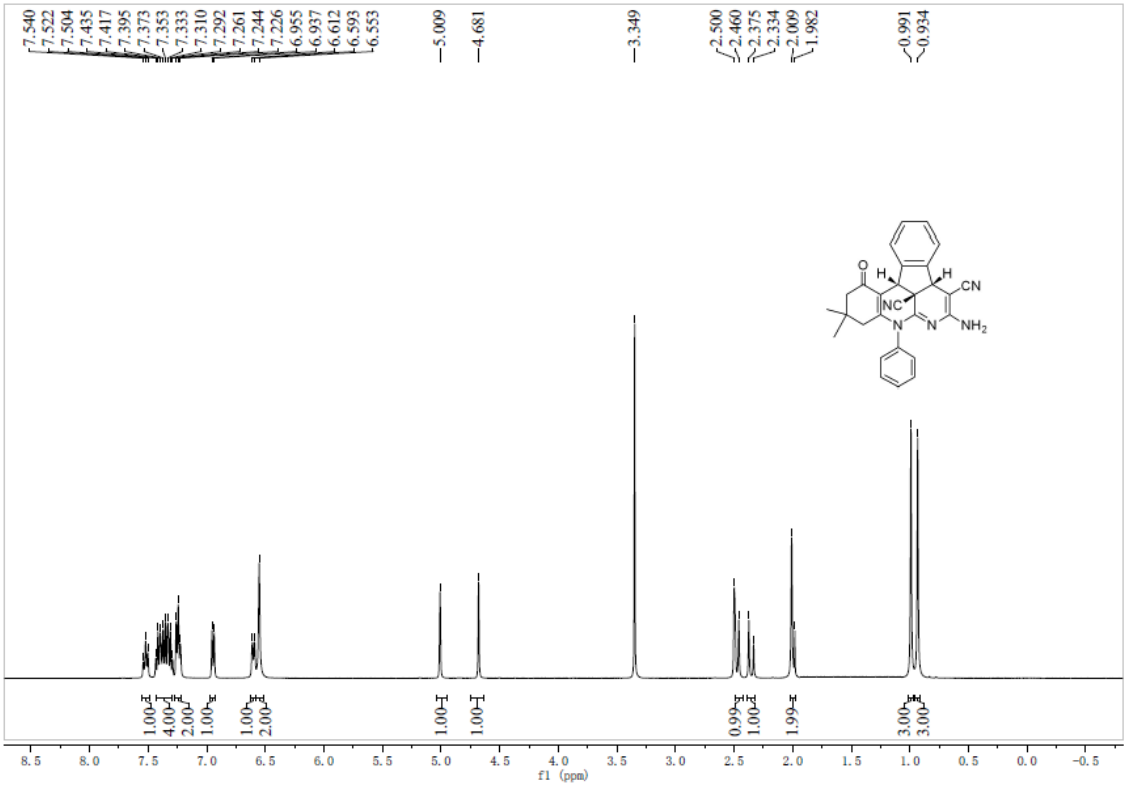

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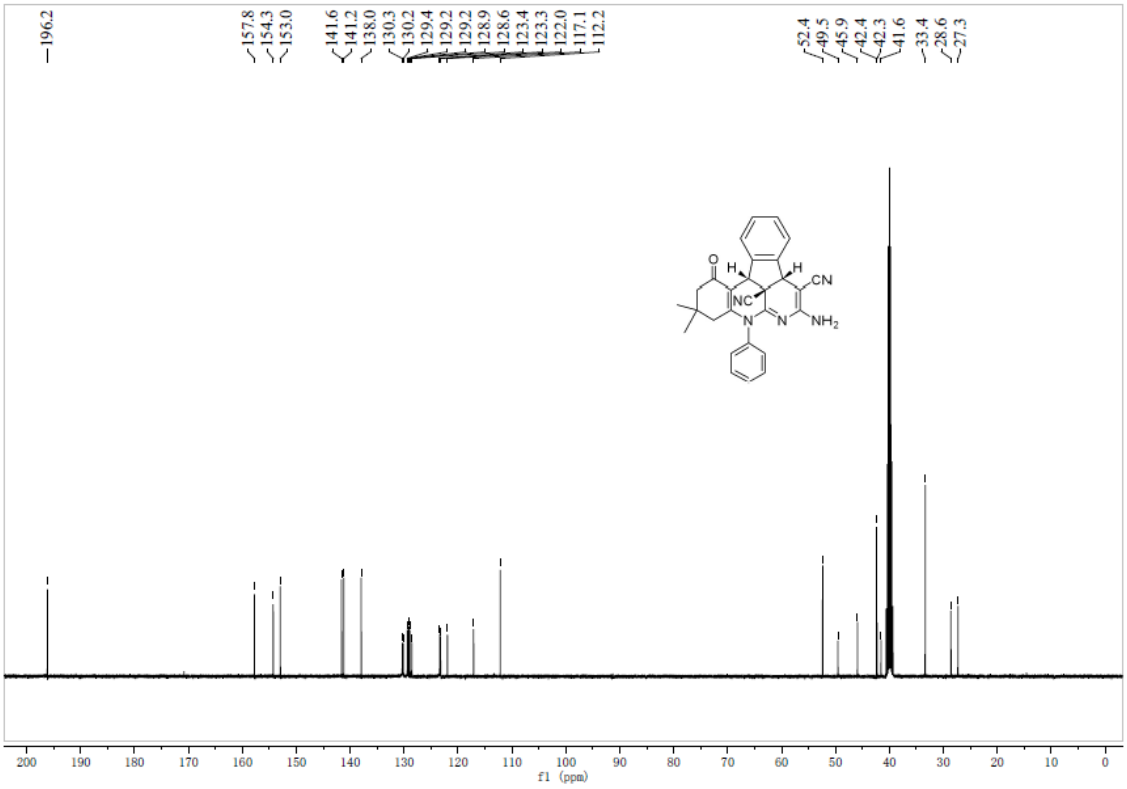
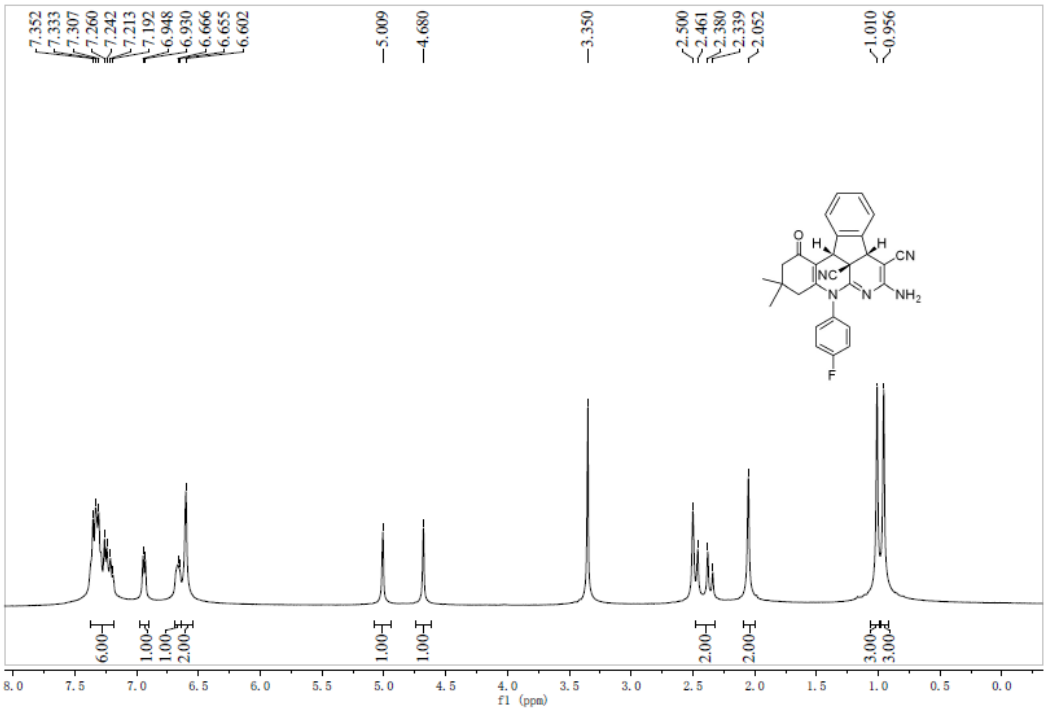
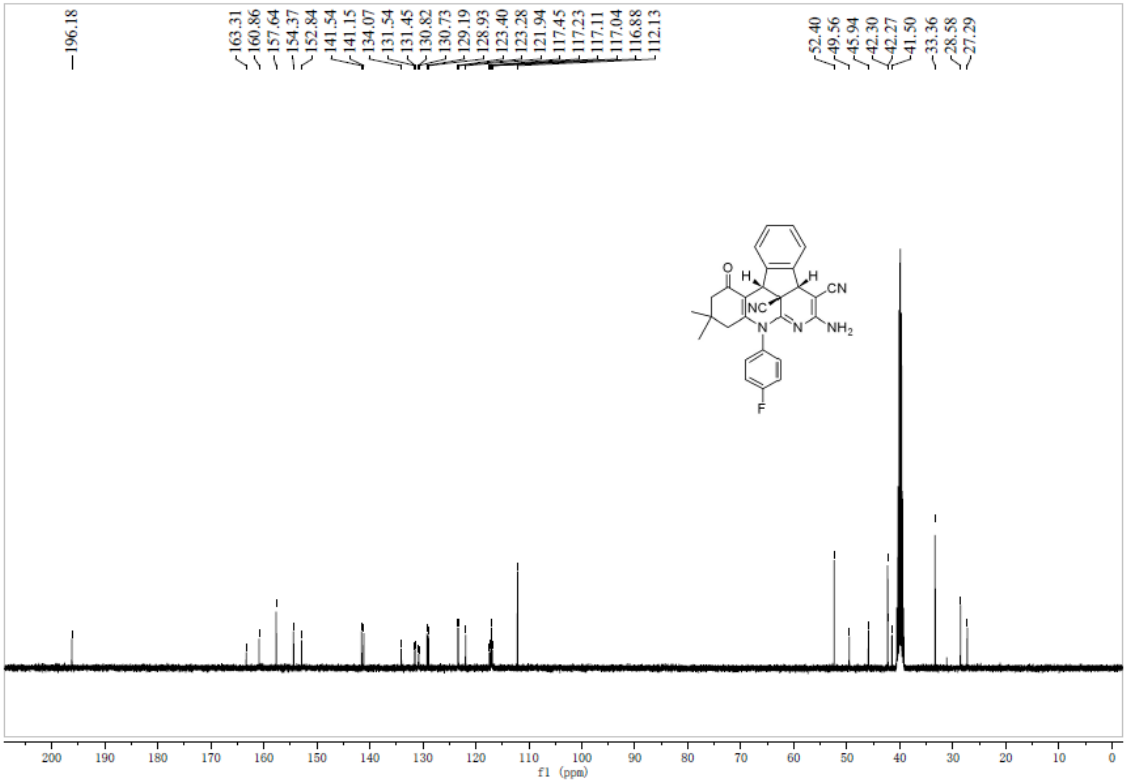


^{1}H NMR of compound **4i**



^{13}C NMR of compound **4i**



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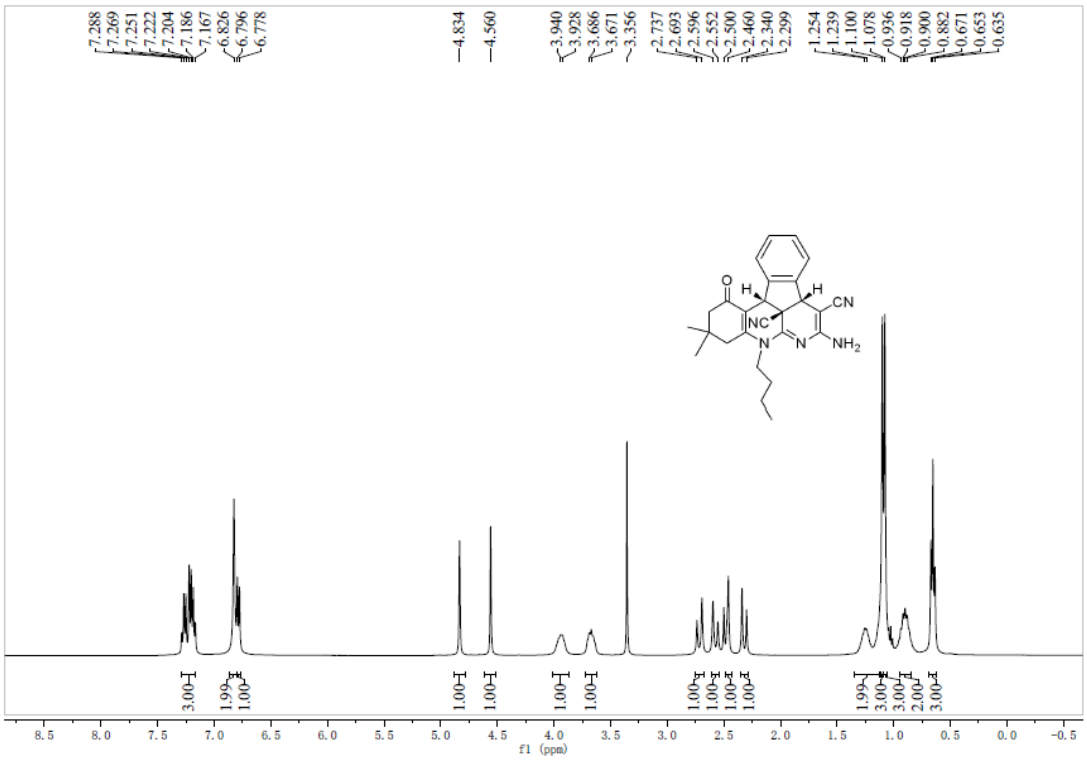

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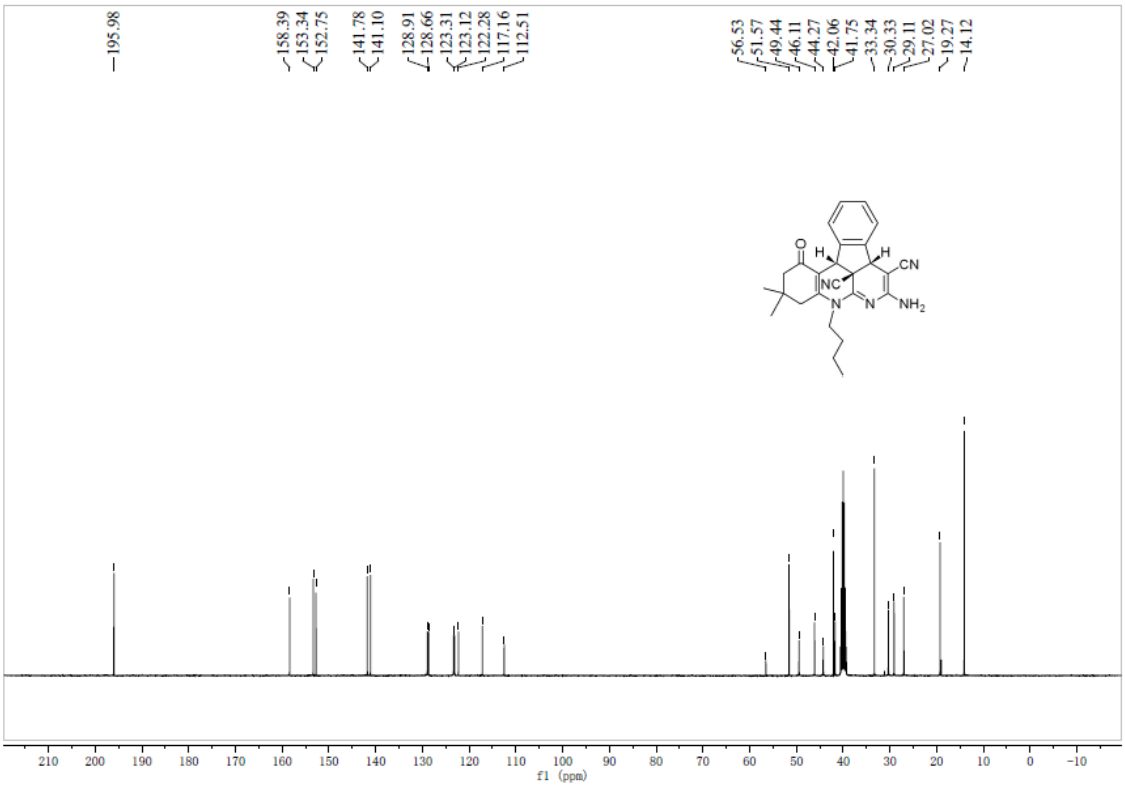
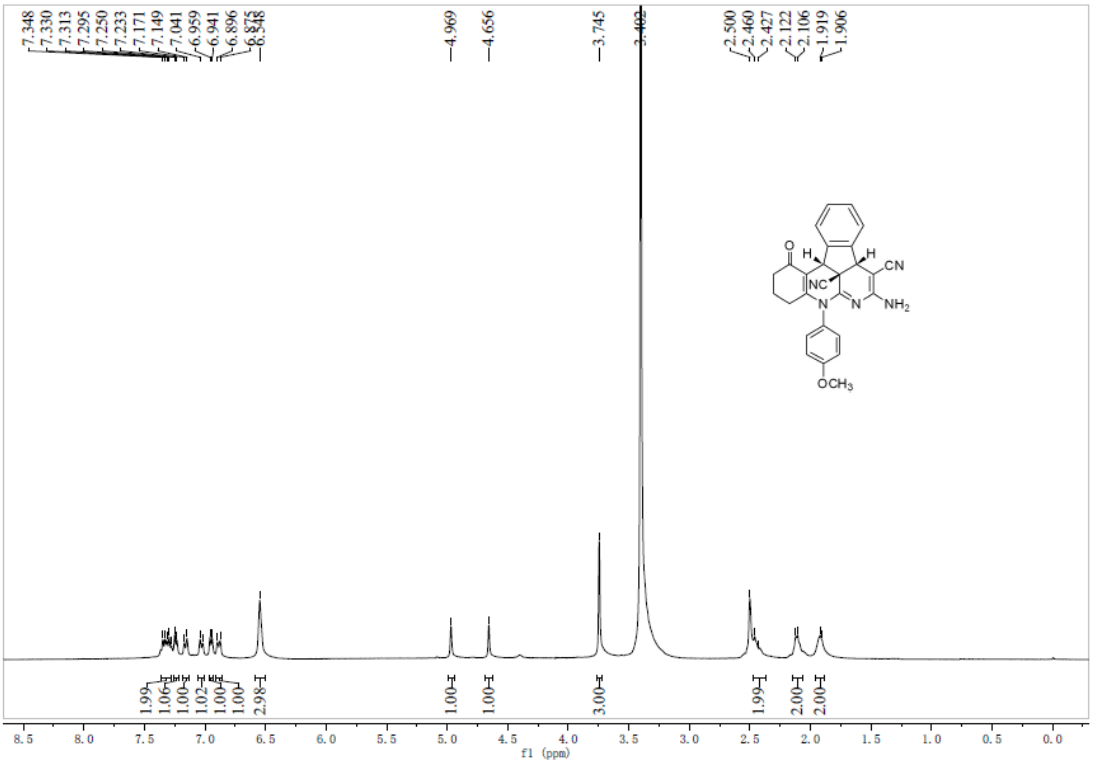
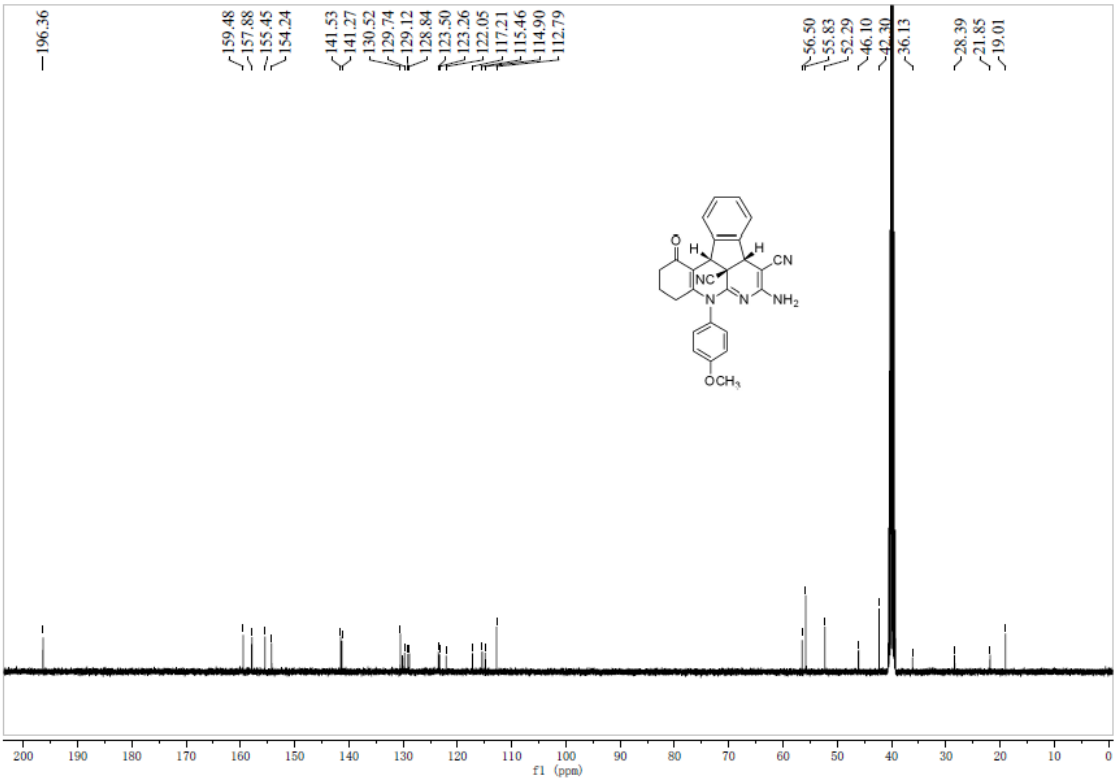


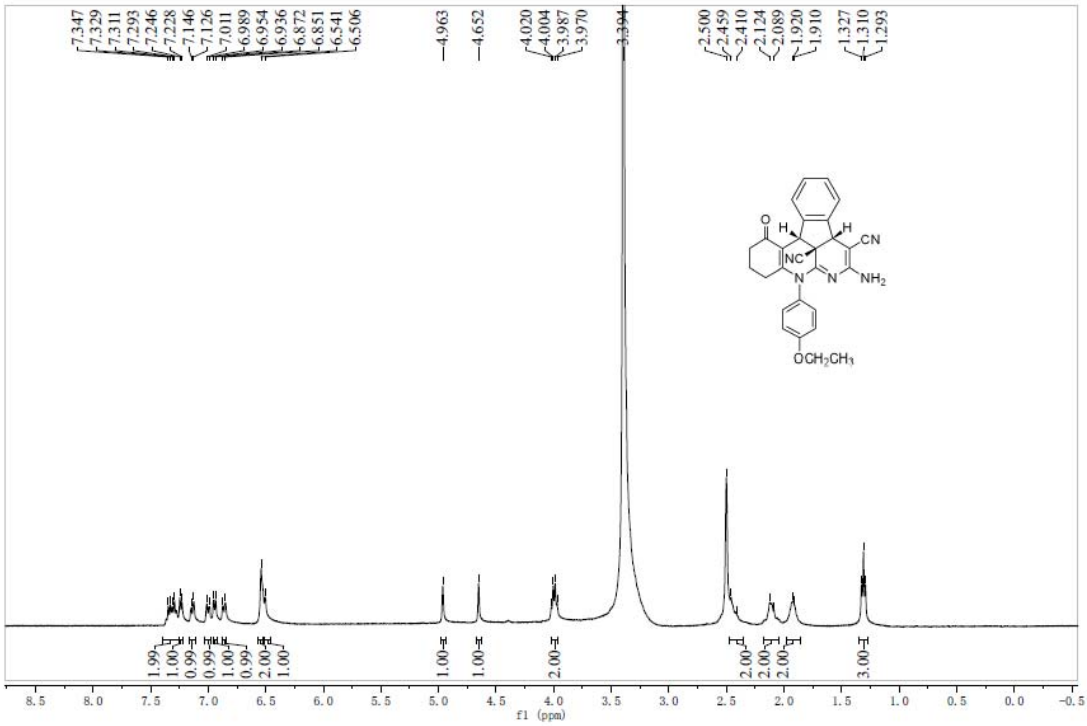
^{1}H NMR of compound **4k**



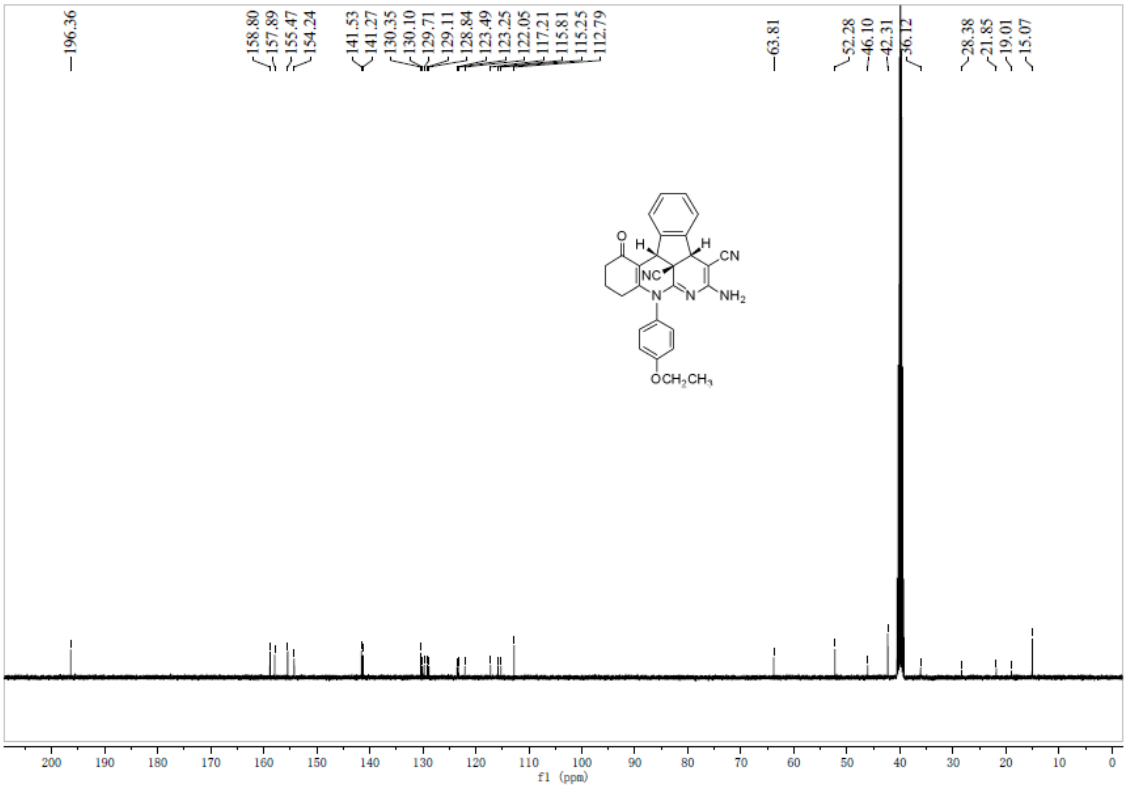
^{13}C NMR of compound **4k**



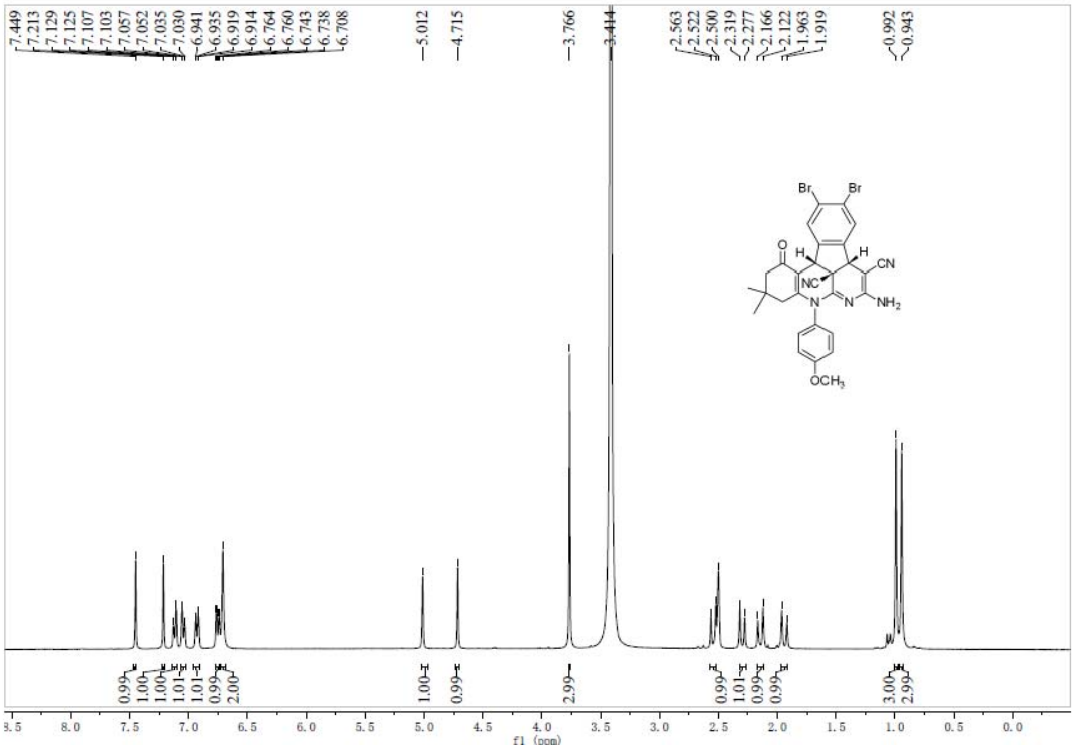
^{1}H NMR of compound **4l**



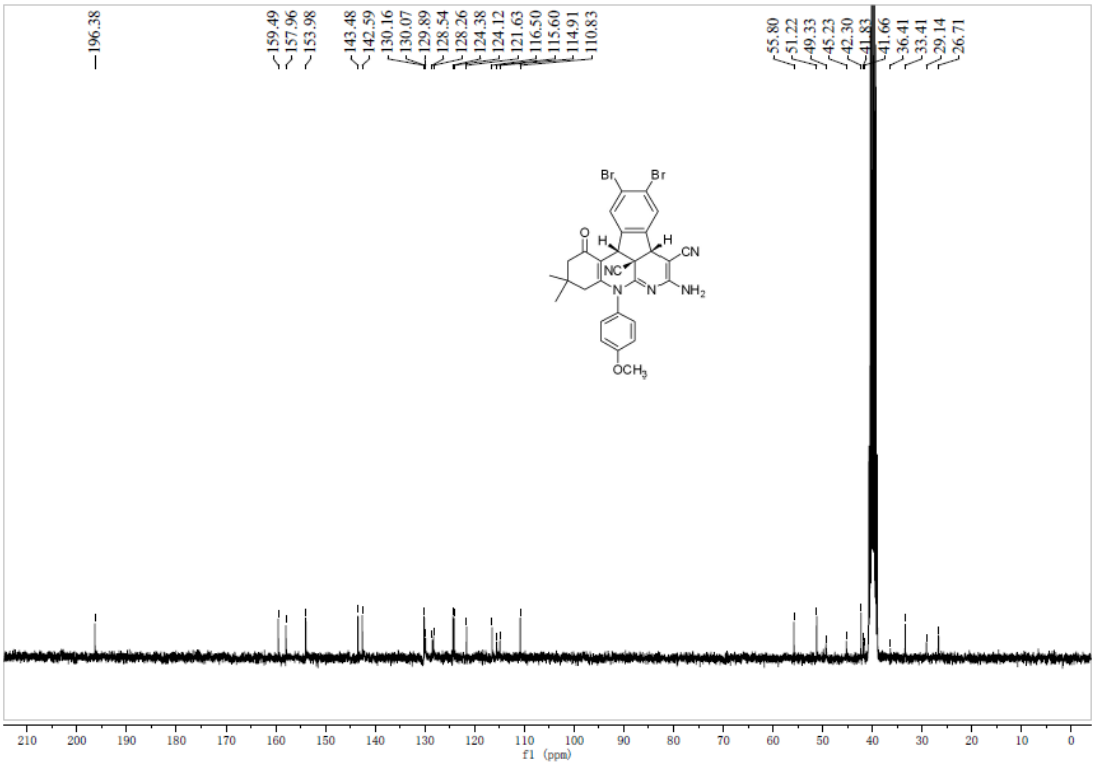
^{13}C NMR of compound **4l**



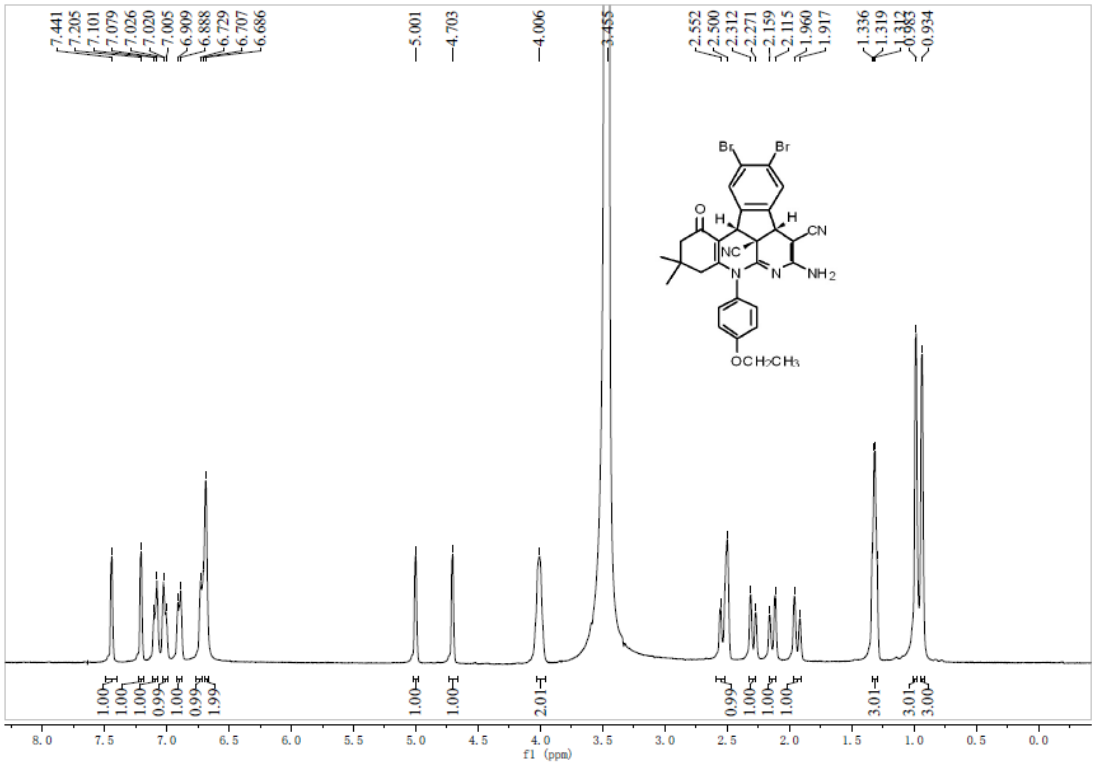
^{1}H NMR of compound **4m**



^{13}C NMR of compound **4m**



^{1}H NMR of compound **4n**



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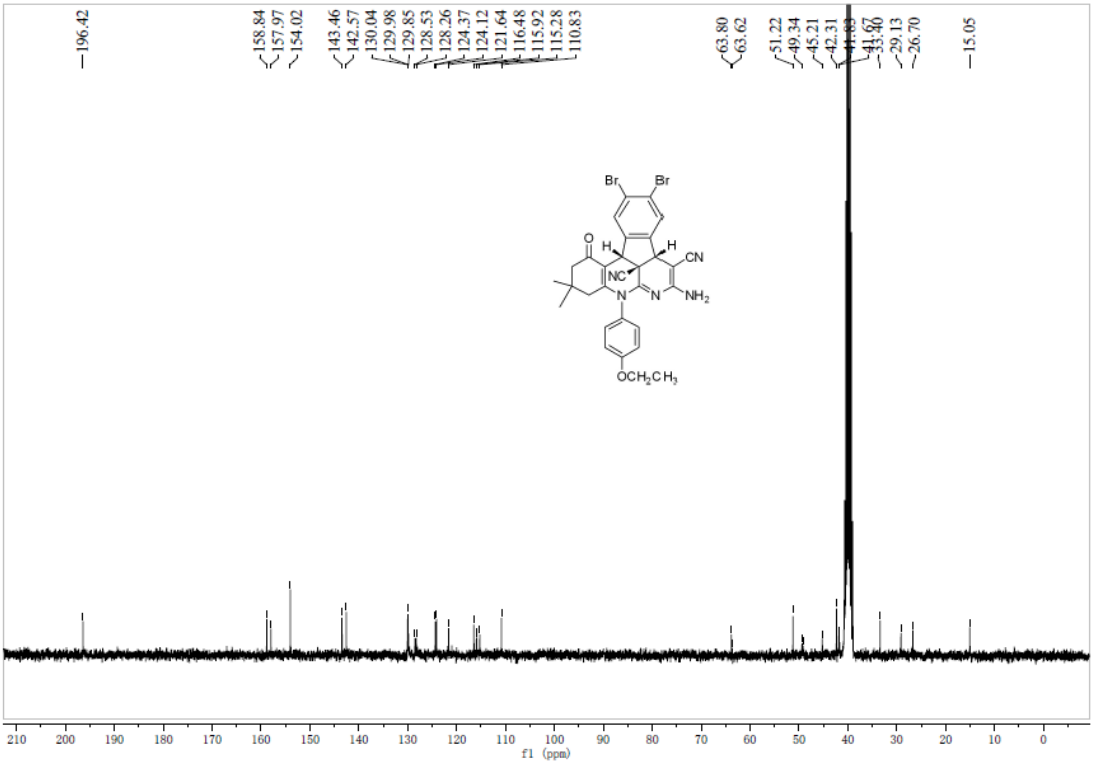
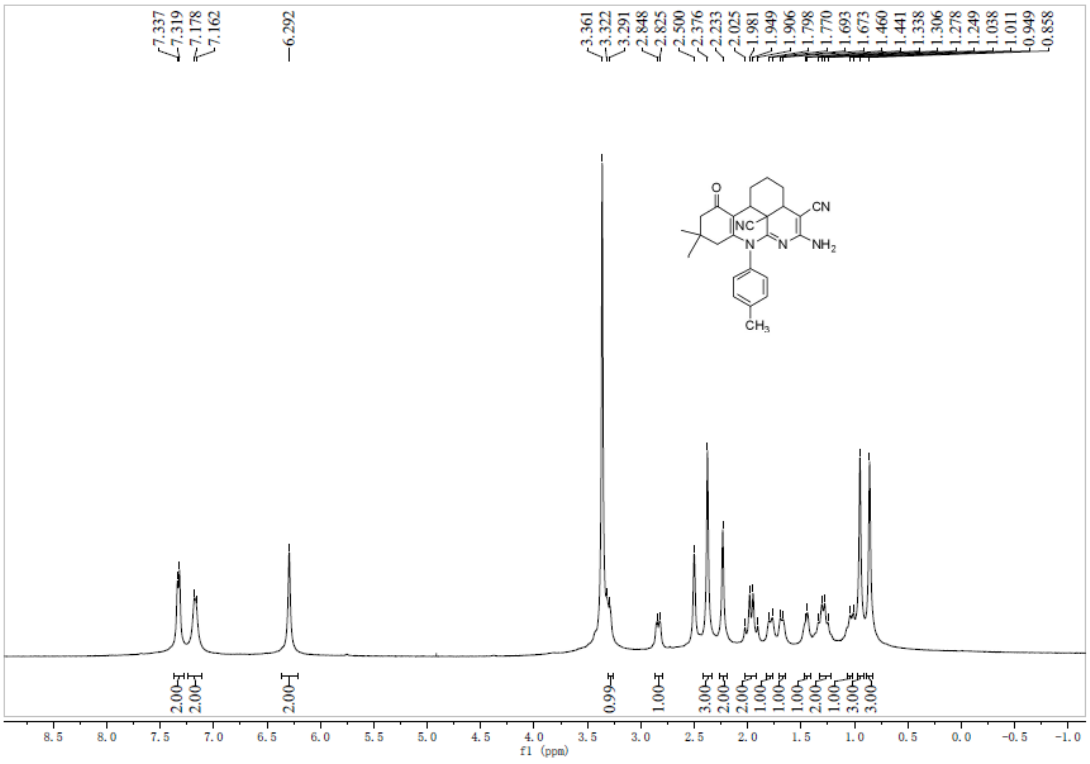
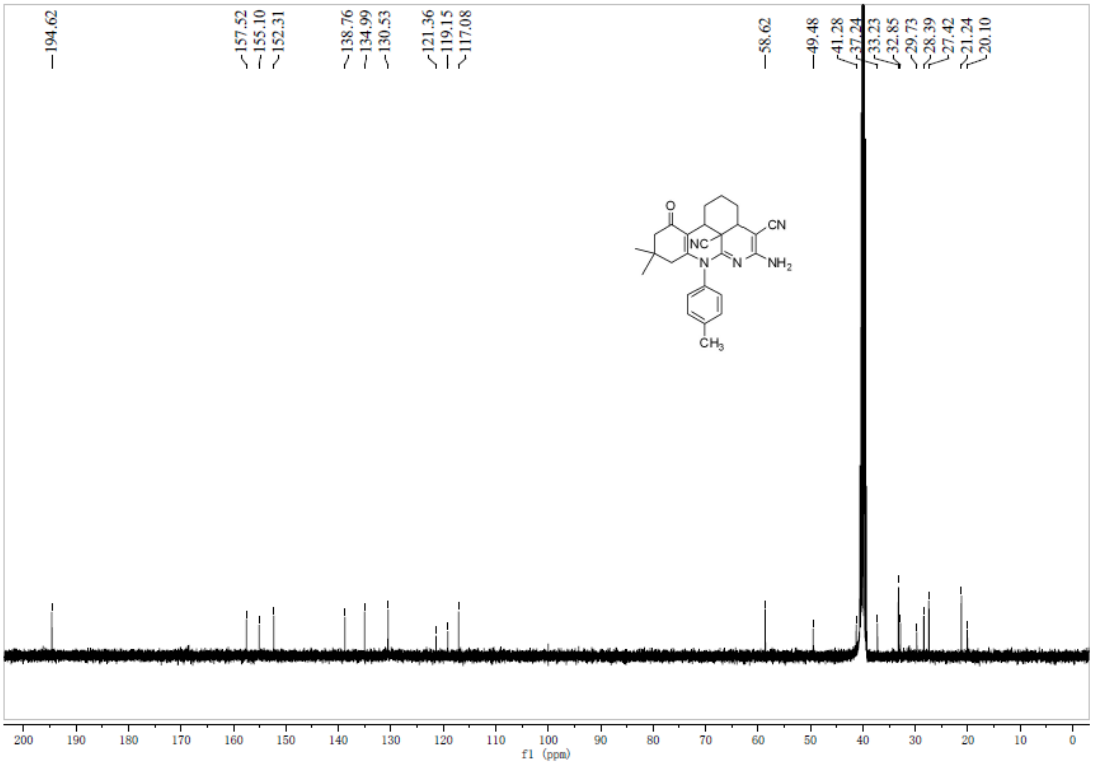


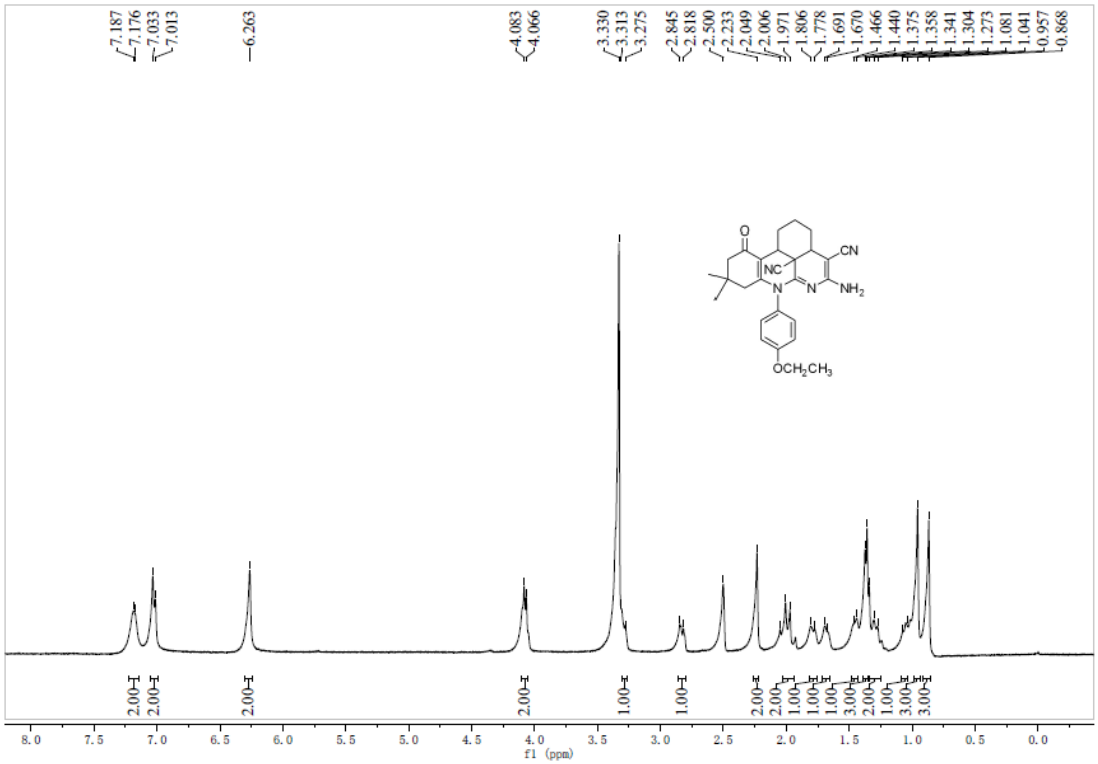
^{1}H NMR of compound **6a**



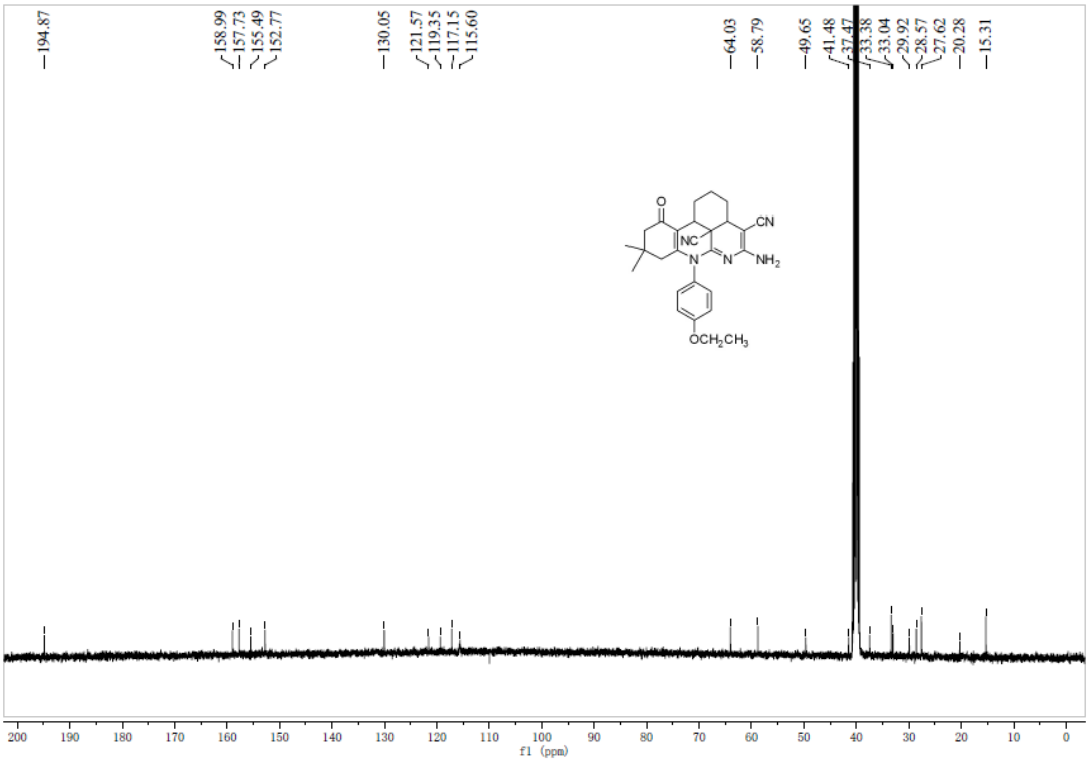
^{13}C NMR of compound **6a**



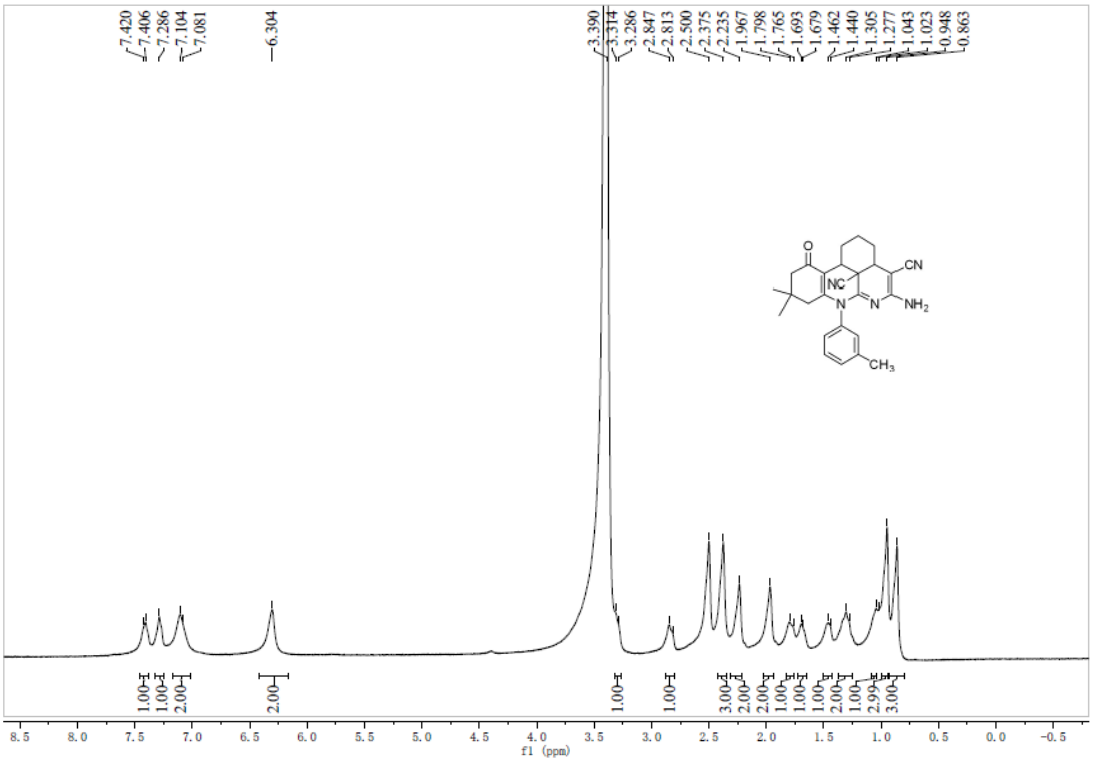
^{1}H NMR of compound **6b**



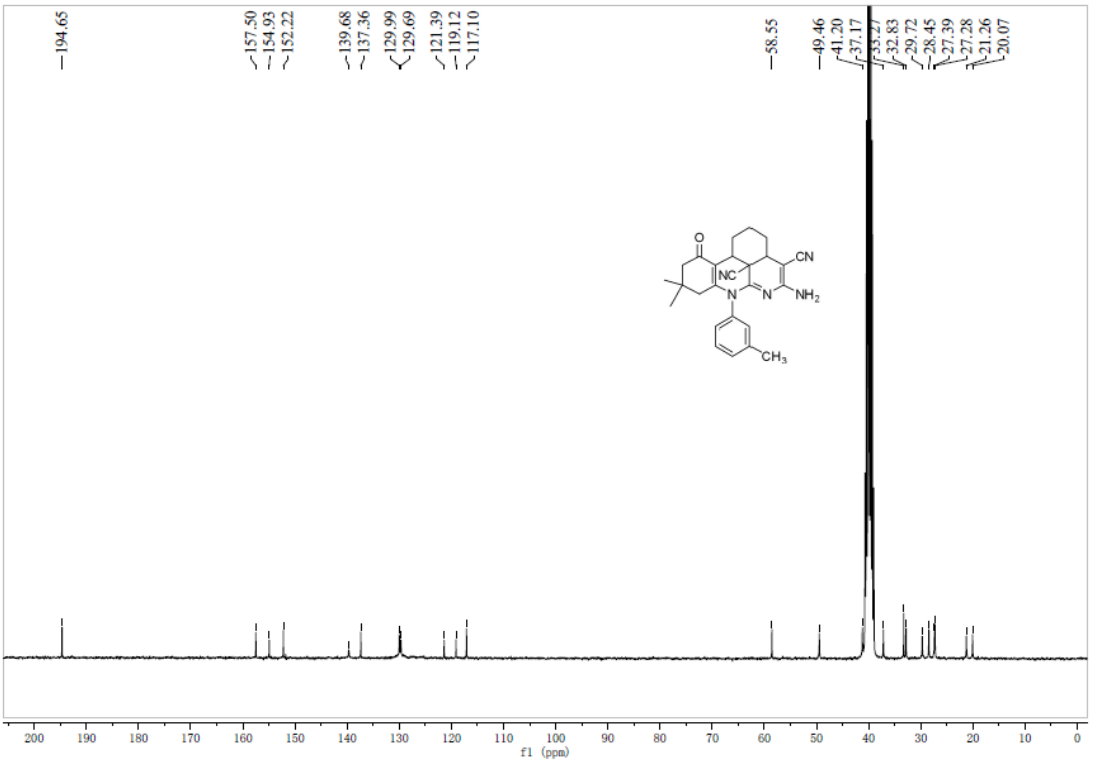
^{13}C NMR of compound **6b**



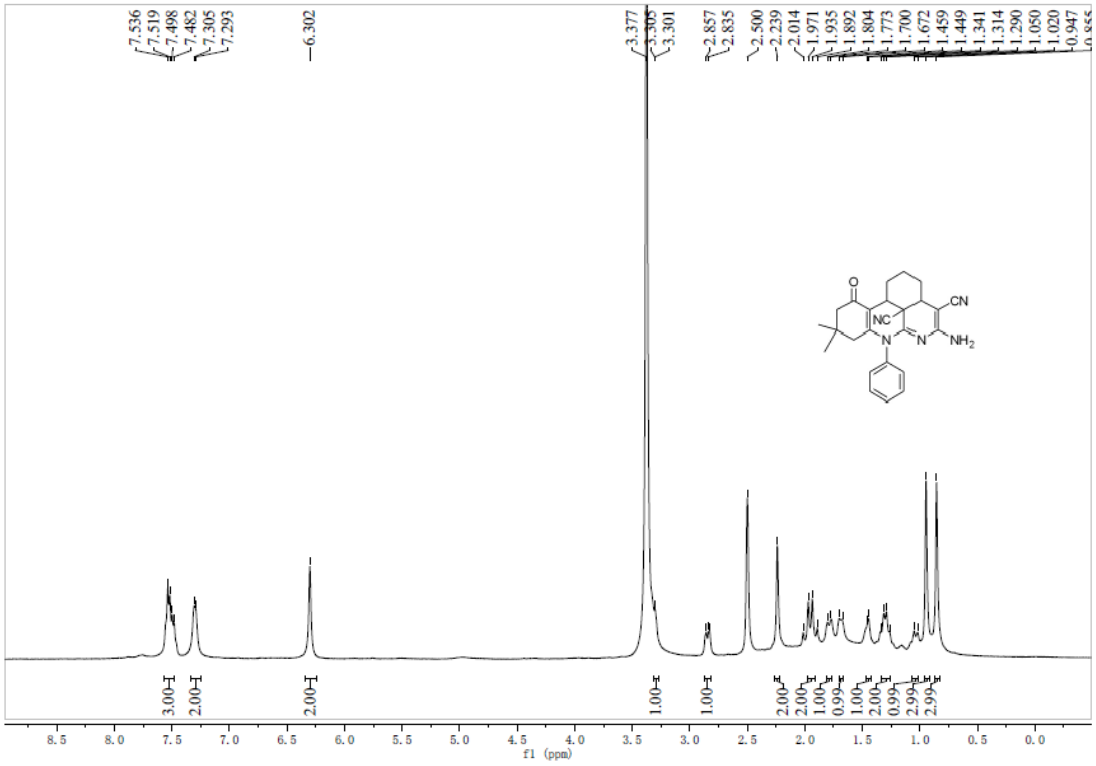
^{1}H NMR of compound **6c**



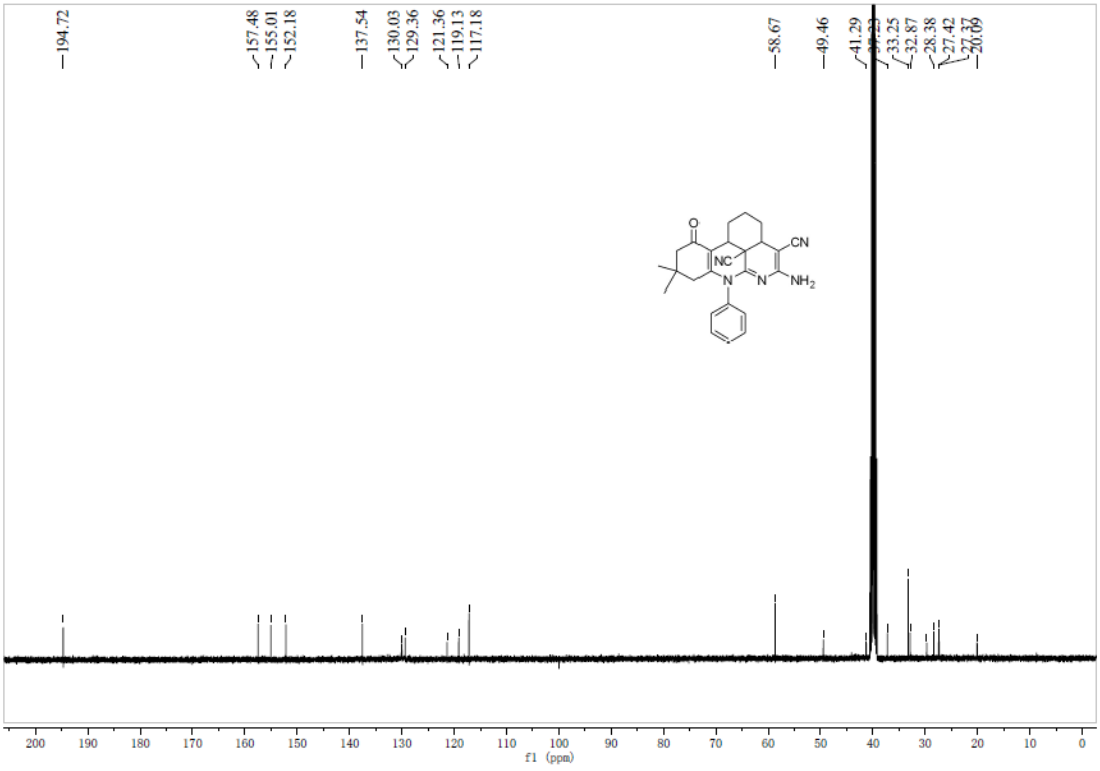
^{13}C NMR of compound **6c**



^{1}H NMR of compound **6d**



^{13}C NMR of compound **6d**



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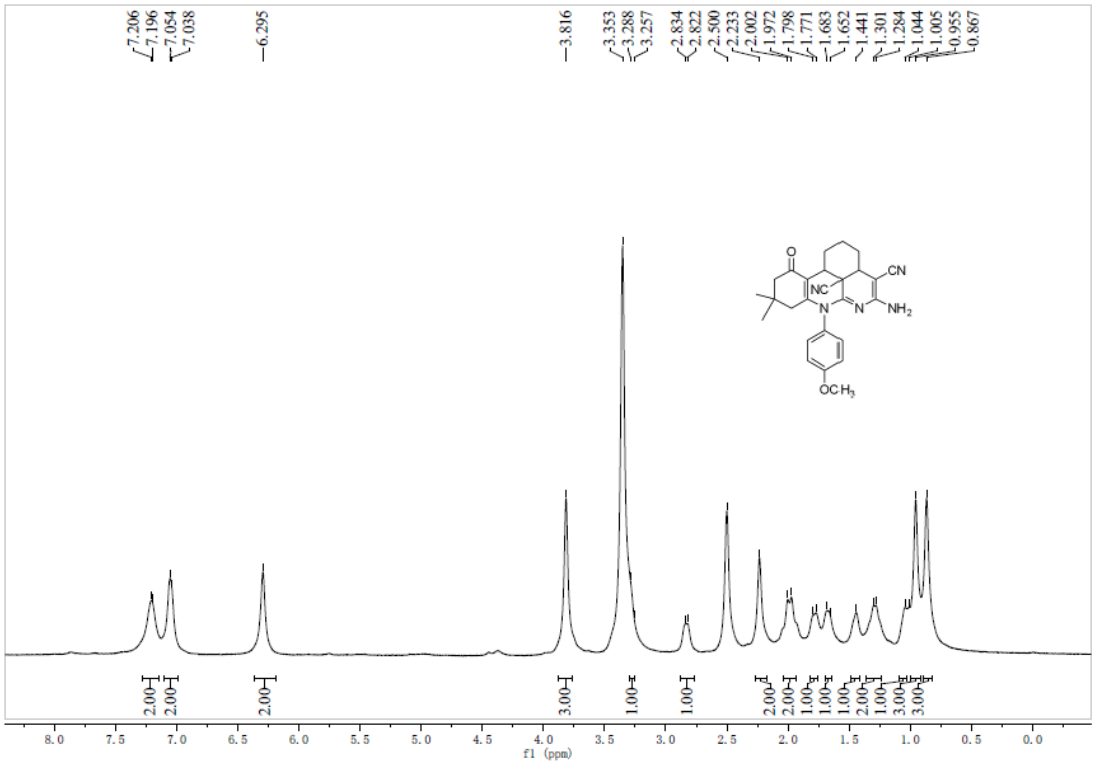

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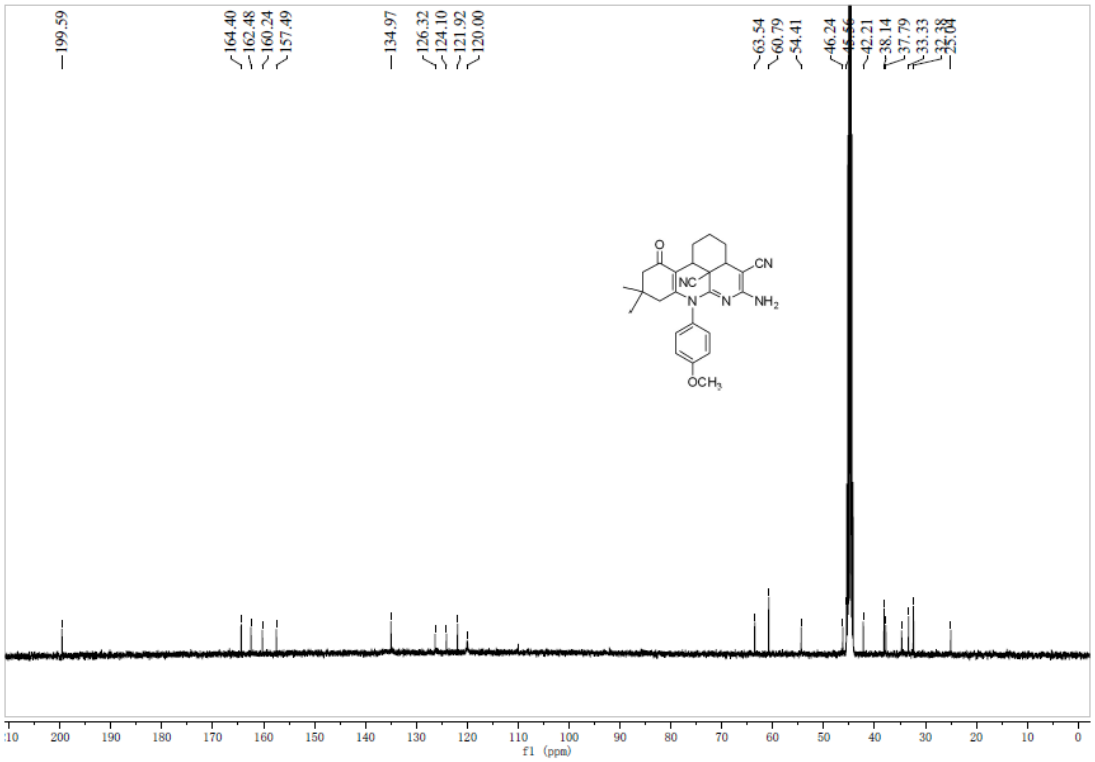
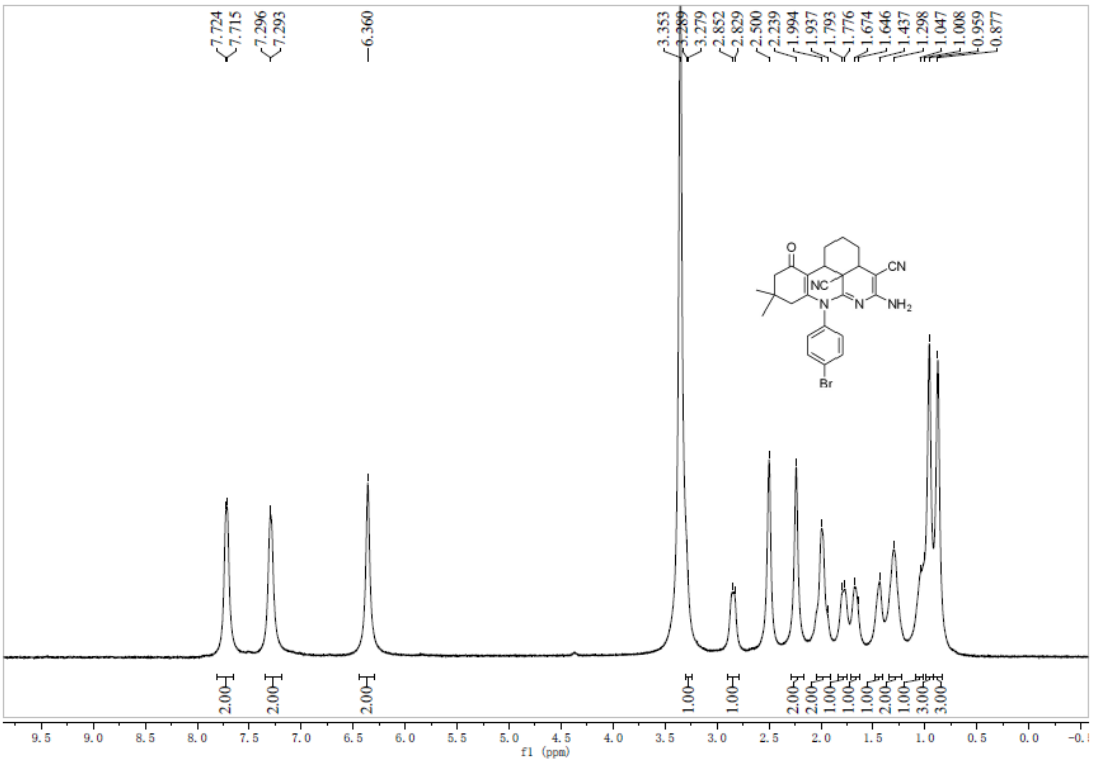
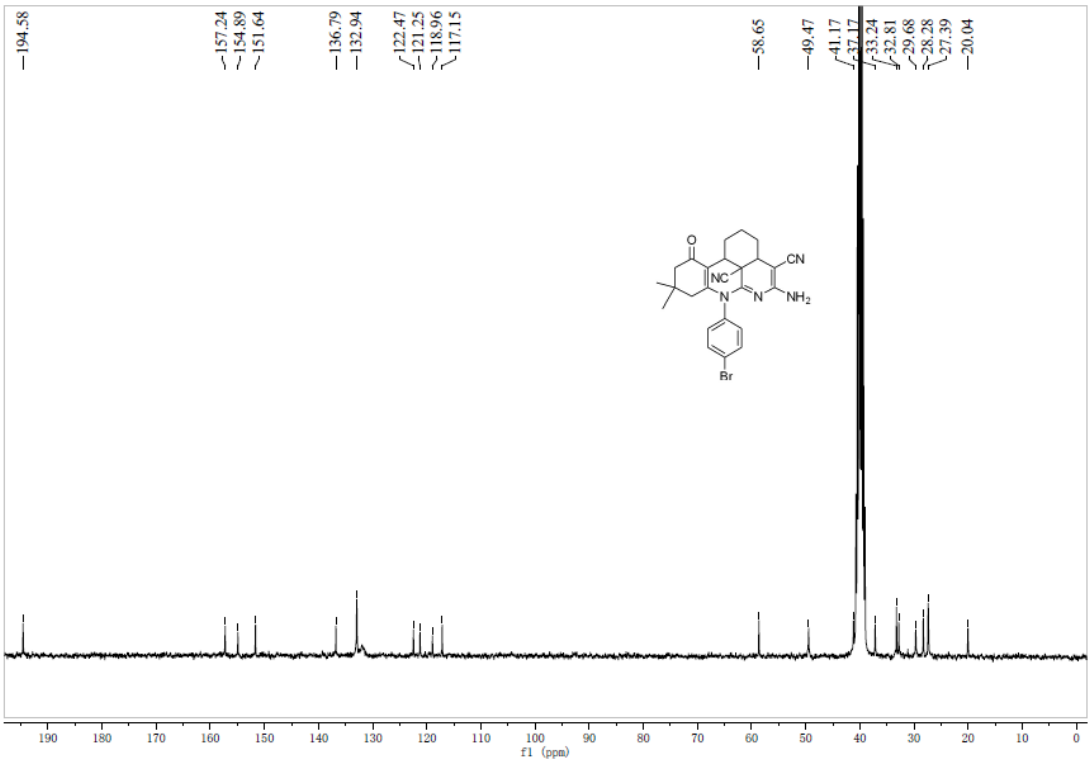


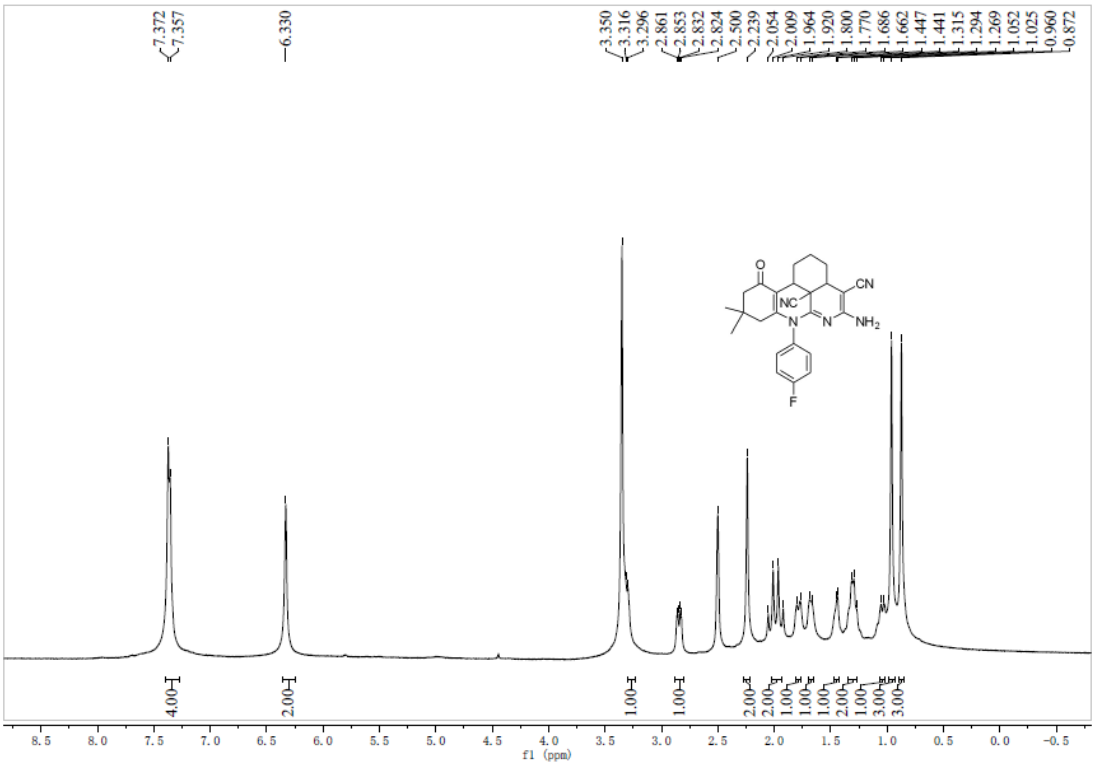
^{1}H NMR of compound **6f**



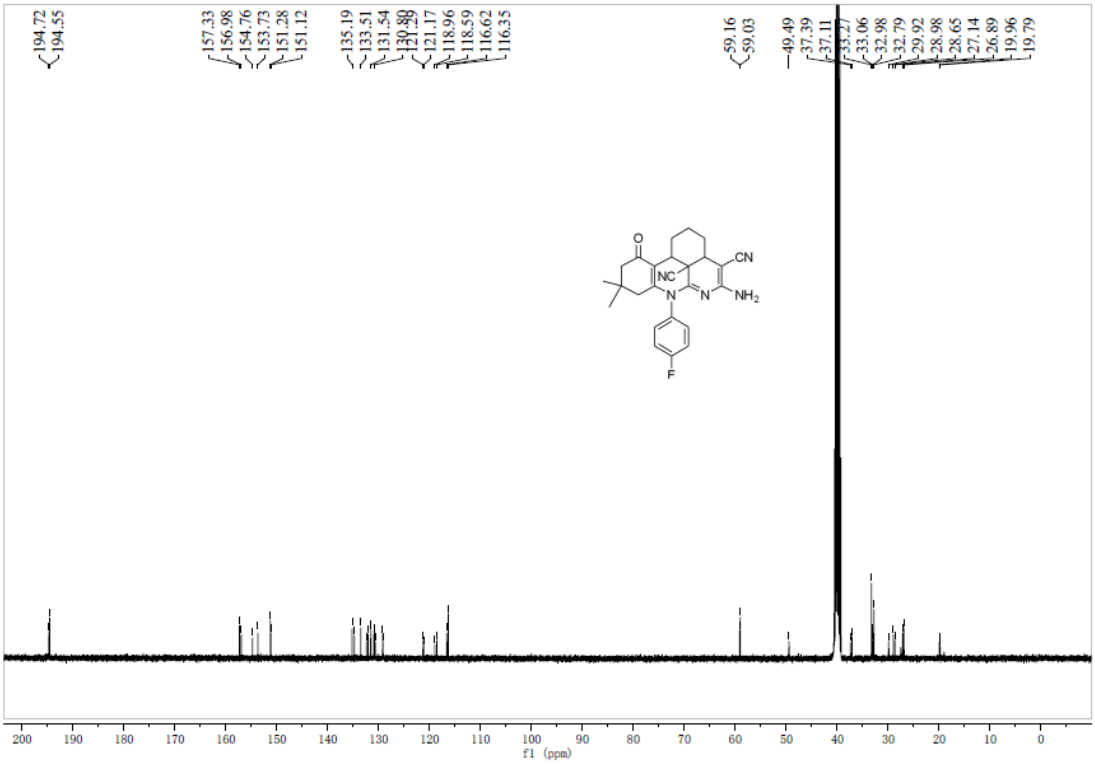
^{13}C NMR of compound **6f**



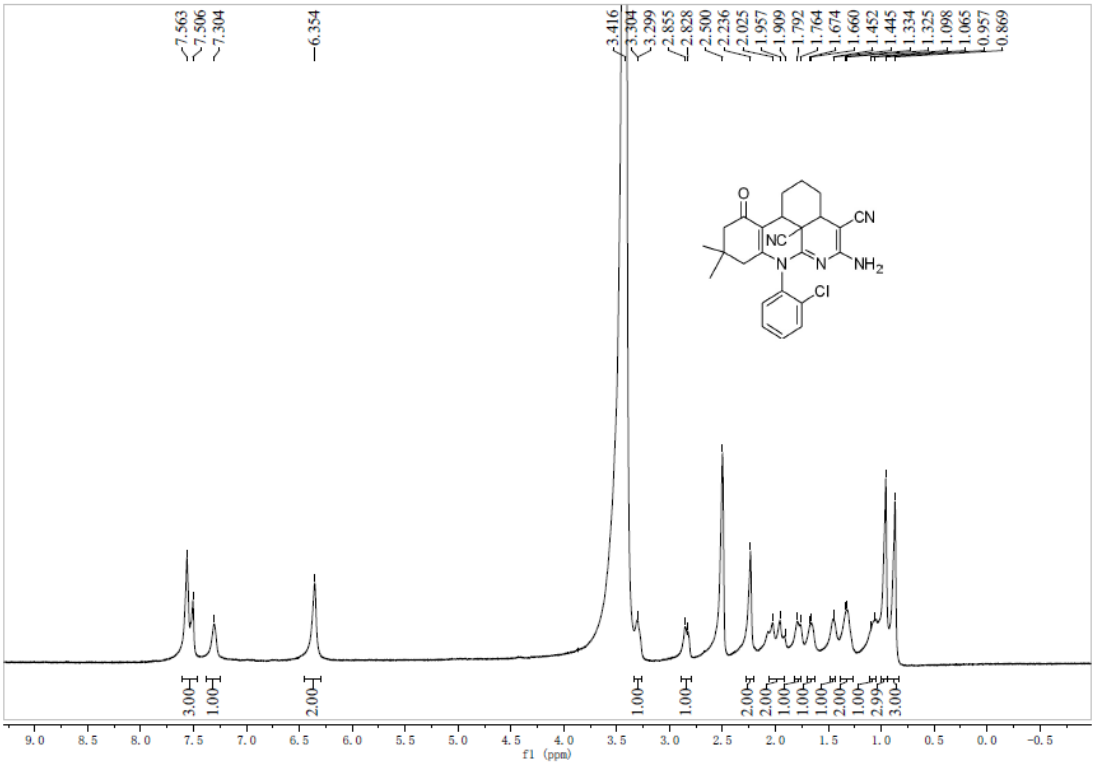
^{1}H NMR of compound **6g**



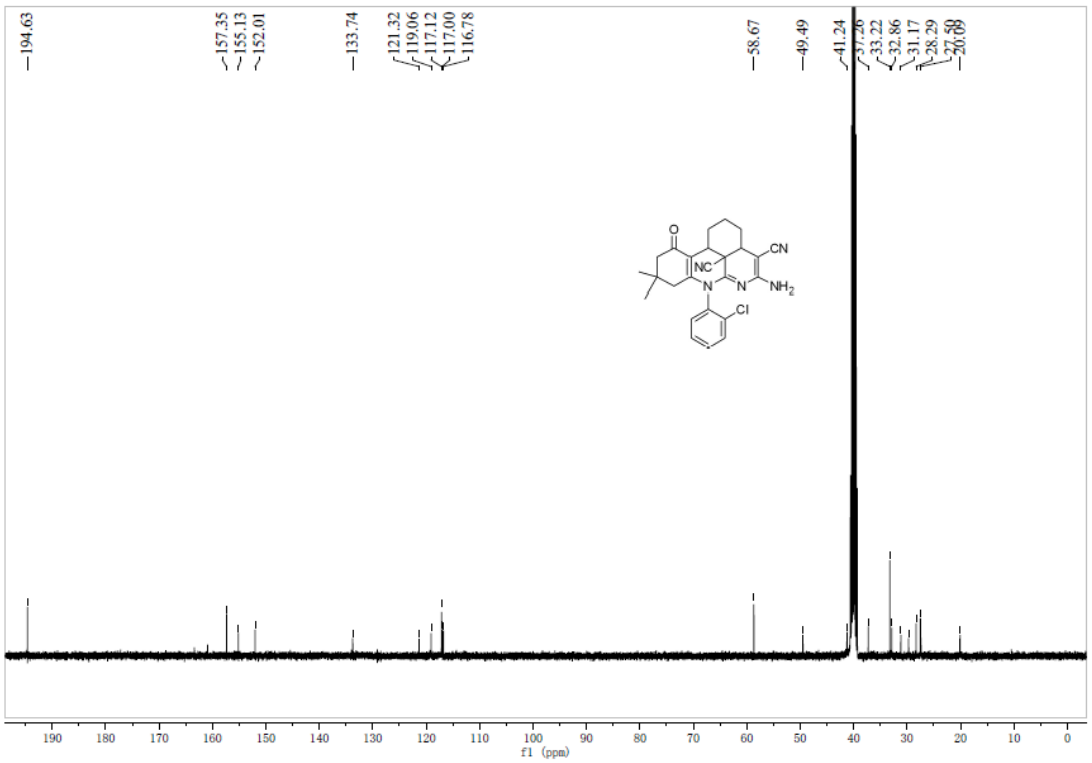
^{13}C NMR of compound **6g**



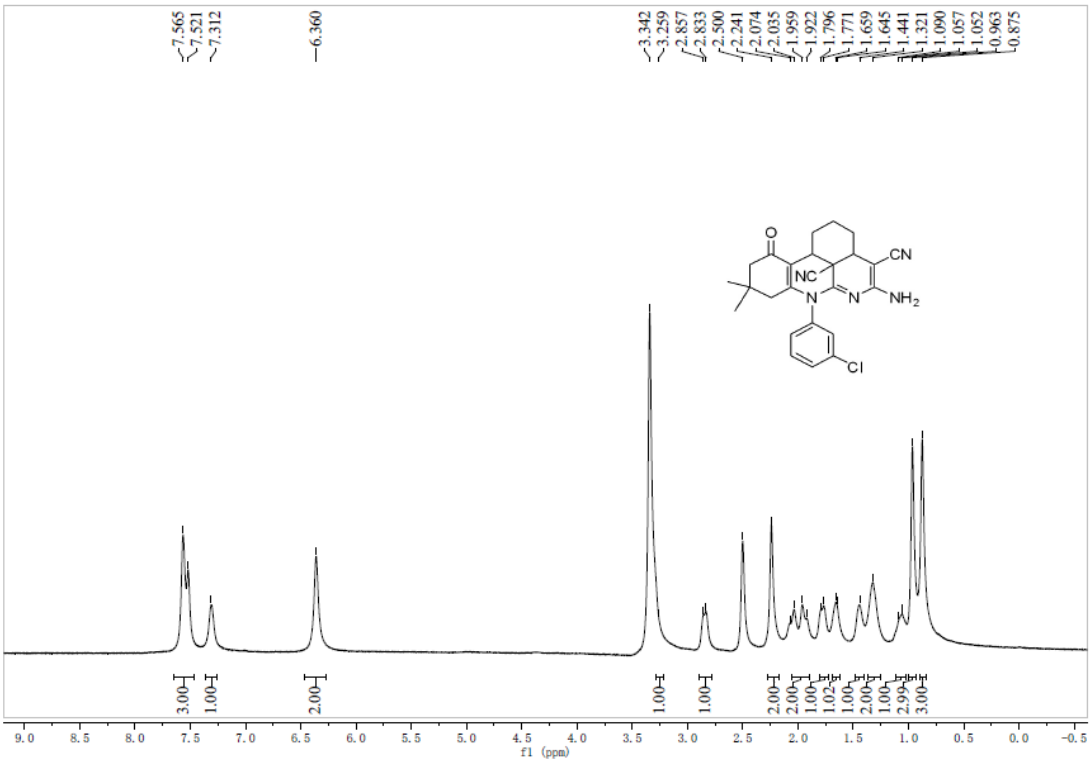
^{1}H NMR of compound 6**h**



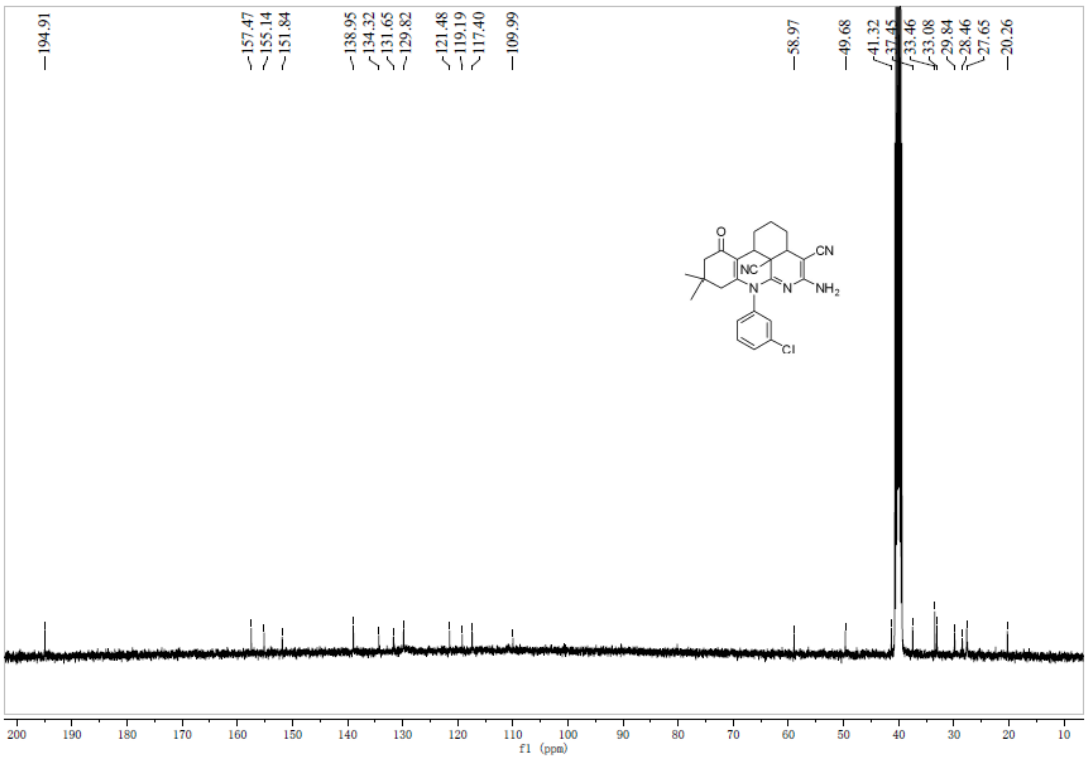
^{13}C NMR of compound **6h**



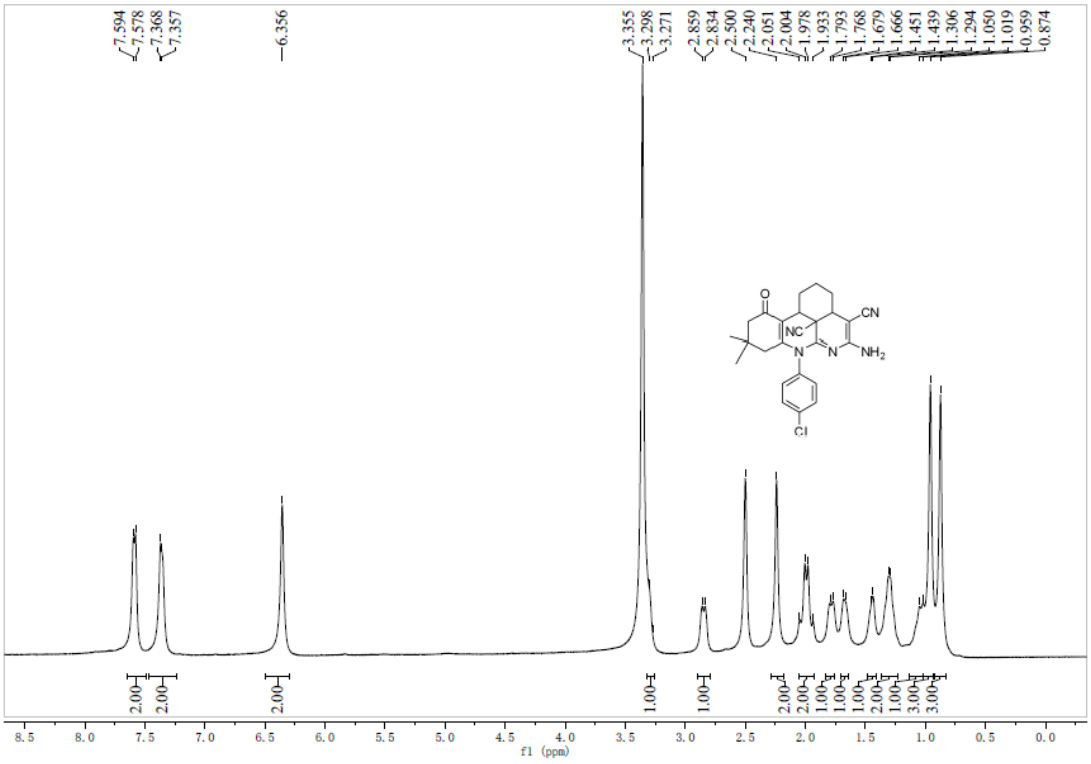
^{1}H NMR of compound **6i**



^{13}C NMR of compound **6i**



^{1}H NMR of compound **6j**



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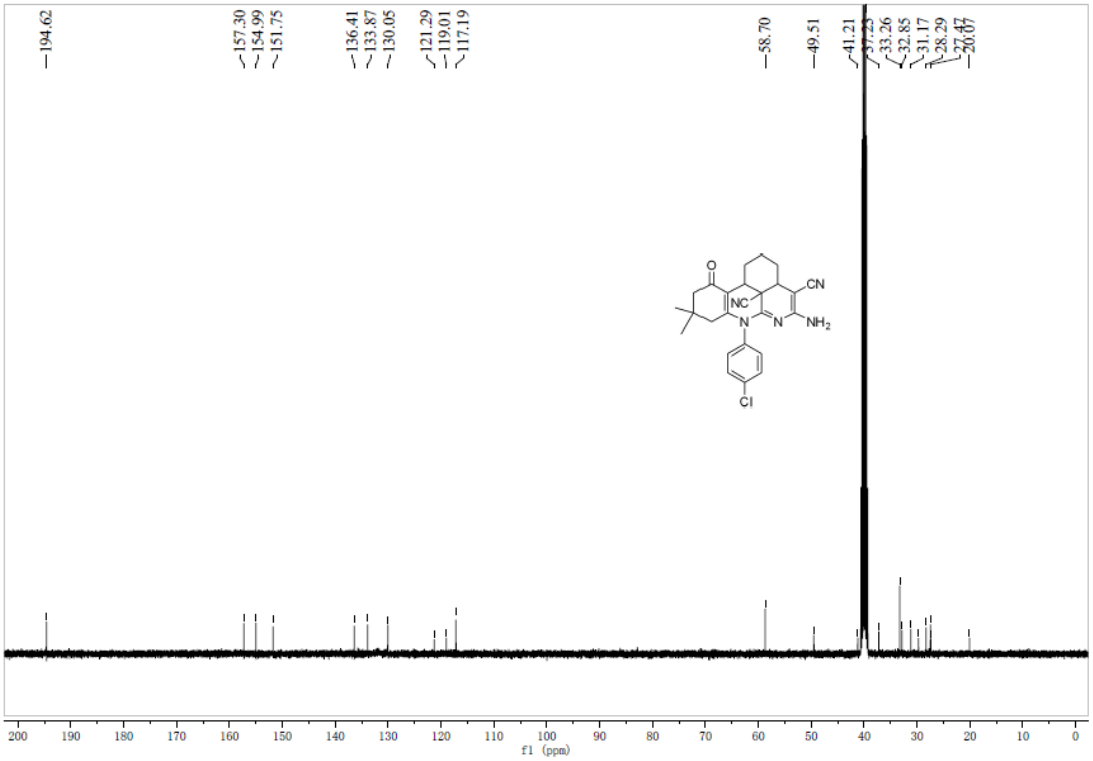

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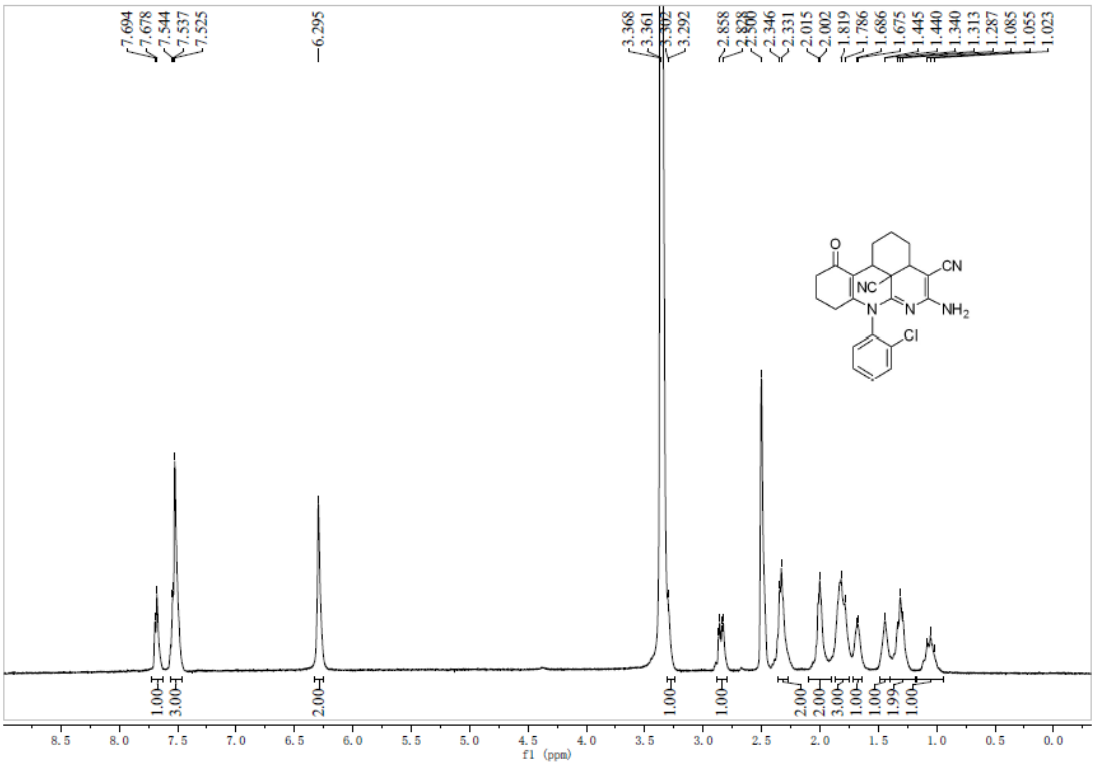

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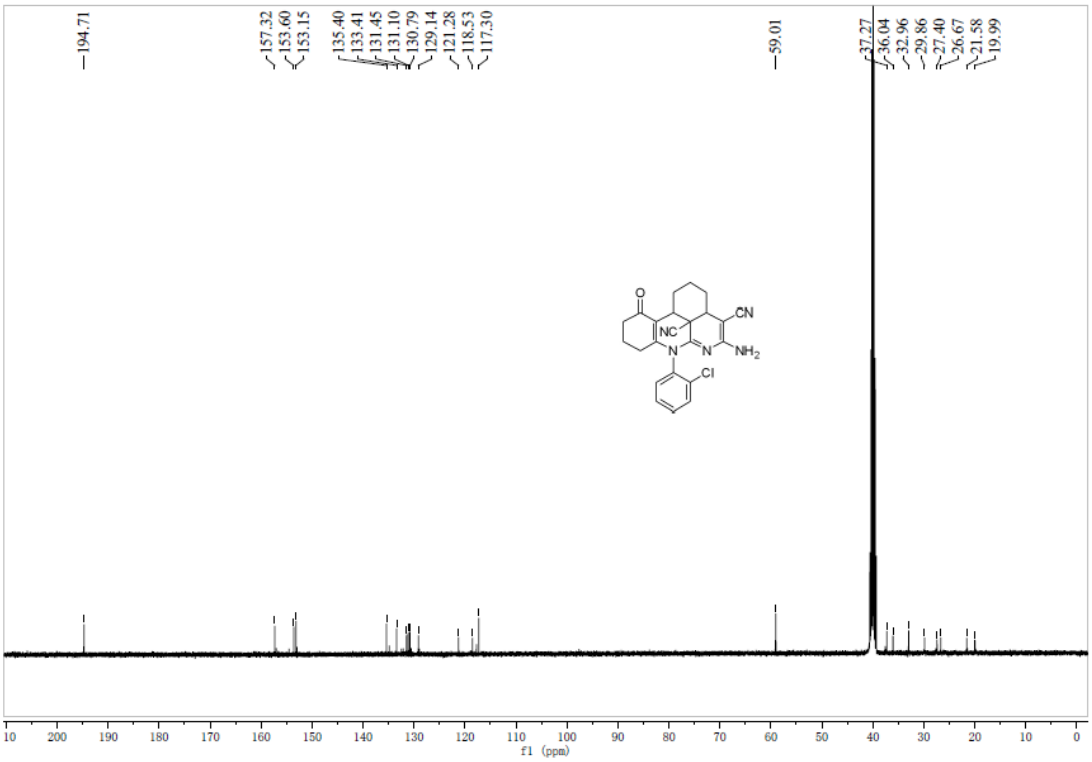

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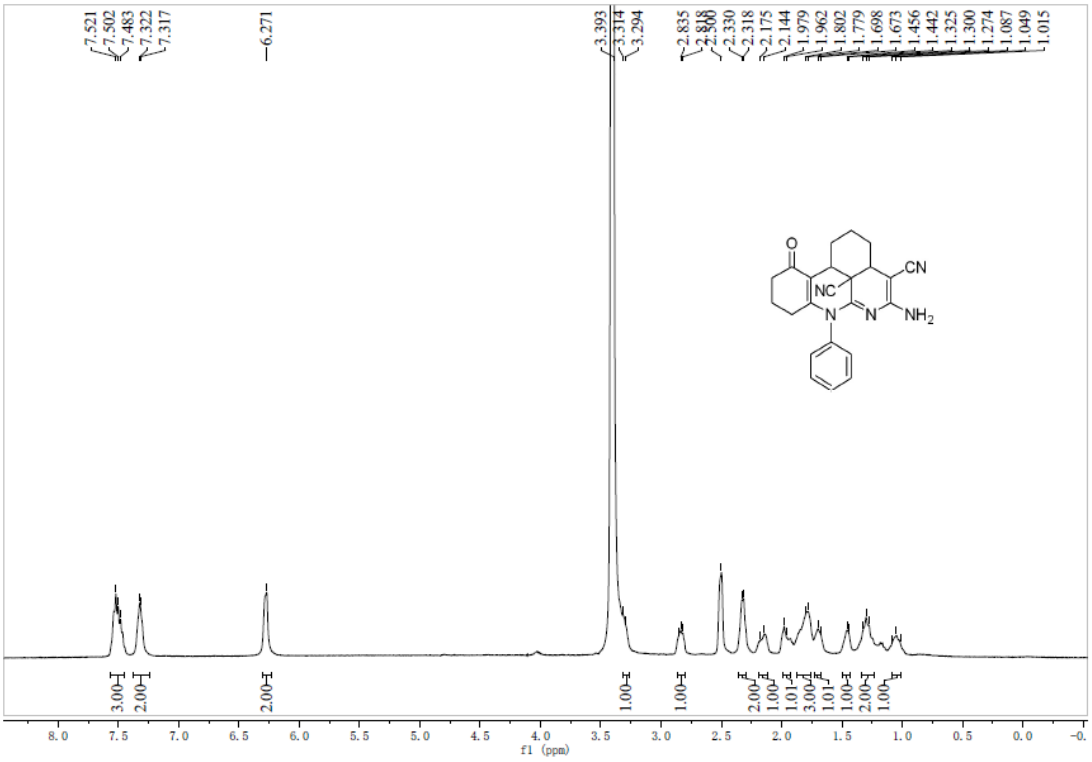

^{13}C NMR of compound **6l**