

Supporting Information

Copper-Catalyzed C-H Oxidative Radical Functionalization and Annulation of Aniline-Linked 1,7-Enynes: Evidence for a 1,5-Hydride Shift Mechanism

Ming Hu, Hua-Xu Zou, Ren-Jie Song, Jian-Nan Xiang,^{*} and Jin-Heng Li^{*}

State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China, and Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China

jhli@hnu.edu.cn and jnxiang@hnu.edu.cn

List of Contents

(A) General Experimental Procedures	S2-S2
(B) Analytical data	S3-S17
(C) References	S17-S17
(D) Spectra	S18-S45
(E) The X-ray single-crystal diffraction analysis of 4aaa	S46-S65

(A) General Experimental Procedures

(a) Preparation of Substrates 1:

Substrates **1** were prepared according to literature procedures.¹

(b) General Procedures for the Copper-Catalyzed Oxidative Tandem Annulation of Aniline-Linked 1,7-Enynes

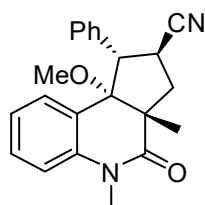
To a Schlenk tube were added 1,7-enyne **1** (0.2 mmol), alkyl nitrile **2** (1.0 mL), alcohol **3** (1.0 mL), Cu(OTf)₂ (10 mol %), Phen **L1** (20 mol %), and DTBP (3 equiv; 0.6 mmol). Then the mixture was stirred at 120 °C (oil bath temperature) under argon atmosphere (1 atm) for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 5:1) to afford the desired products **4** or **5**.

CAUTION: Be careful when performing with larger scale! Peroxides may explode at high temperature!

(B) Analytical data

9b-Methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4aaa):

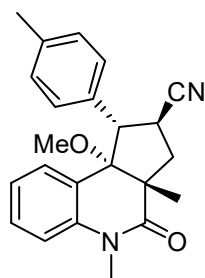
46.4 mg, 67% yield;



Light yellow solid, mp 201.6-203.2 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, *J* = 7.2 Hz, 2H), 7.44-7.32 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.51-3.46 (m, 1H), 3.38 (s, 3H), 3.07 (t, *J* = 12.0 Hz, 1H), 2.17-2.13 (m, 1H), 1.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.3, 141.4, 136.7, 130.1, 129.8, 128.9, 128.3, 127.3, 124.4, 123.0, 122.8, 114.9, 87.1, 55.5, 55.3, 54.7, 35.2, 35.2, 29.6, 22.7; LRMS (EI, 70 eV) *m/z* (%): 346 (M⁺, 13), 331 (100), 202 (58), 188 (30); HRMS *m/z* (ESI) calcd for C₂₂H₂₃N₂O₂ (M+H)⁺ 347.1754, found 347.1758.

9b-Methoxy-3a,5-dimethyl-4-oxo-1-(*p*-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4caa):

50.4 mg, 70% yield;

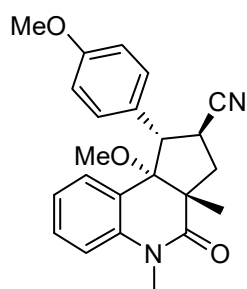


Light yellow solid, mp 180.5-182.2 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.51 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H), 3.48-3.44 (m, 1H), 3.38 (s, 3H), 3.05 (t, *J* = 12.4 Hz, 1H), 2.59 (s, 3H), 2.38 (s, 3H), 2.13 (d, *J* = 13.6 Hz, 1H), 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.4, 141.3, 138.0, 133.5, 130.0, 129.7, 129.6, 127.3, 124.5, 123.1, 122.8, 114.9, 86.9, 55.4, 55.3, 54.3, 35.2, 29.6, 22.7, 21.1; LRMS (EI,

70 eV) m/z (%): 360 (M^+ , 17), 345 (100), 202 (78), 188 (41); HRMS m/z (ESI) calcd for $C_{23}H_{25}N_2O_2$ ($M+H$) $^+$ 361.1911, found 361.1913.

9b-Methoxy-1-(4-methoxyphenyl)-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4daa):

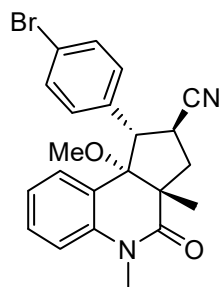
47.4 mg, 63% yield;



Light yellow solid, mp 212.3-213.8 °C (uncorrected); 1H NMR (500 MHz, $CDCl_3$) δ : 7.54 (d, J = 8.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.99-6.94 (m, 3H), 3.86 (d, J = 9.0 Hz, 1H), 3.84 (s, 3H), 3.45-3.40 (m, 1H), 3.38 (s, 3H), 3.04 (t, J = 12.5 Hz, 1H), 2.60 (s, 3H), 2.14-2.11 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 173.4, 159.5, 141.4, 131.1, 129.8, 128.4, 127.3, 124.5, 123.2, 122.8, 114.9, 114.3, 86.7, 55.3, 55.3, 53.9, 35.2, 35.1, 29.7, 22.8; LRMS (EI, 70 eV) m/z (%): 376 (M^+ , 7), 361 (14), 204 (100), 188 (25); HRMS m/z (ESI) calcd for $C_{23}H_{25}N_2O_3$ ($M+H$) $^+$ 377.1860, found 377.1866.

1-(4-Bromophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4eaa):

56.0 mg, 66% yield;

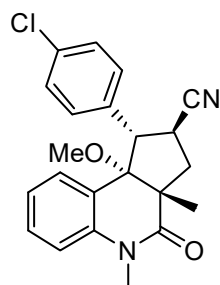


Light yellow solid, mp 212.5-213.8 °C (uncorrected); 1H NMR (400 MHz, $CDCl_3$) δ : 7.58-7.52 (m, 4H), 7.36 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 3.86 (d, J = 8.8 Hz, 1H), 3.48-3.30 (m, 4H), 3.05 (t, J = 12.0 Hz, 1H), 2.60 (s, 3H), 2.16-2.13 (m, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz,

CDCl₃) δ : 173.1, 141.4, 135.9, 132.1, 131.7, 130.0, 127.1, 124.1, 122.9, 122.7, 122.5, 115.0, 87.2, 55.5, 55.2, 54.1, 35.2 (2C), 29.7, 22.8; LRMS (EI, 70 eV) m/z (%): 426 ($M^+ + 2$, 11), 424 (M^+ , 11), 409 (77), 202 (100), 188 (52); HRMS m/z (ESI) calcd for C₂₂H₂₂⁷⁹BrN₂O₂ ($M+H$)⁺ 425.0859, found 425.0867.

1-(4-Chlorophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4faa):

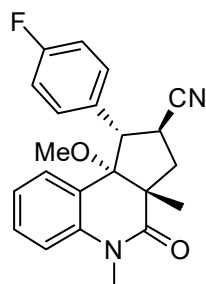
43.3 mg, 57% yield;



Light yellow solid, mp 215.9-217.5 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.59 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 3.88 (d, J = 9.2 Hz, 1H), 3.45-3.38 (m, 4H), 3.06 (t, J = 12.0 Hz, 1H), 2.60 (s, 3H), 2.16-2.12 (m, 1H), 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 173.0, 141.3, 135.3, 134.2, 131.3, 130.0, 129.1, 127.0, 124.0, 122.9, 122.7, 115.0, 87.1, 55.4, 55.2, 54.0, 35.2, 35.1, 29.6, 22.7; LRMS (EI, 70 eV) m/z (%): 382 ($M^+ + 2$, 5), 380 (M^+ , 14), 365 (100), 202 (81), 188 (42); HRMS m/z (ESI) calcd for C₂₂H₂₂³⁵ClN₂O₂ ($M+H$)⁺ 381.1364, found 381.1371.

1-(4-Fluorophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4gaa):

43.7 mg, 60% yield;

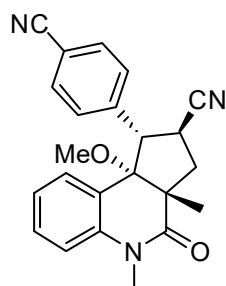


White solid, mp 185.8-187.2 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.64-7.61 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.12 (t, J = 8.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 1H), 6.98

(t, $J = 7.6$ Hz, 1H), 3.89 (d, $J = 9.2$ Hz, 1H), 3.44-3.38 (m, 4H), 3.05 (t, $J = 12.4$ Hz, 1H), 2.60 (s, 3H), 2.16-2.12 (m, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 173.2, 163.7 (d, $J = 246.2$ Hz, 1C), 141.4, 132.5 (d, $J = 3.4$ Hz, 1C), 131.6 (d, $J = 8.0$ Hz, 2C), 130.0, 127.1, 124.2, 122.9, 122.8, 115.9 (d, $J = 21.1$ Hz, 2C), 115.0, 87.0, 55.4, 55.2, 53.9, 35.4, 35.1, 29.6, 22.8; ^{19}F NMR (282 MHz, CDCl_3) δ : -113.6; LRMS (EI, 70 eV) m/z (%): 365 ($\text{M}^+ + 1$, 4), 364 (M^+ , 14), 349 (100), 202 (70), 188 (34); HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{22}^{19}\text{FN}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 365.1660, found 365.1652.

1-(4-Cyanophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4haa):

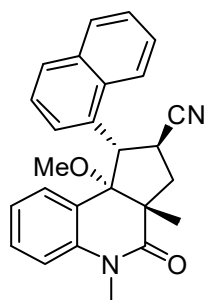
49.0 mg, 66% yield;



Light yellow solid, mp 197.9-199.8 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.79 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 3.94 (d, $J = 8.8$ Hz, 1H), 3.48-3.41 (m, 1H), 3.39 (s, 3H), 3.09 (t, $J = 12.4$ Hz, 1H), 2.60 (s, 3H), 2.18 (d, $J = 13.2$ Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.8, 142.6, 141.3, 132.7, 130.8, 130.3, 126.8, 123.7, 123.0, 122.3, 118.2, 115.2, 112.5, 87.9, 55.6, 55.2, 54.6, 35.3, 35.2, 29.7, 22.8; LRMS (EI, 70 eV) m/z (%): 371 (M^+ , 15), 356 (100), 340 (16), 202 (46); HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 372.1707, found 372.1716.

9b-Methoxy-3a,5-dimethyl-1-(naphthalen-1-yl)-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4iaa):

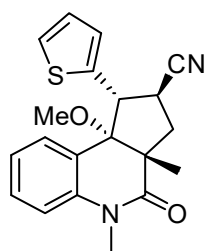
42.0 mg, 53% yield;



Light yellow solid, mp 212.8-214.2 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 1H), 8.01-7.95 (m, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 6.8$ Hz, 1H), 6.70 (t, $J = 7.6$ Hz, 1H), 4.92 (d, $J = 9.2$ Hz, 1H), 3.64-3.59 (m, 1H), 3.39 (s, 3H), 3.19 (t, $J = 12.4$ Hz, 1H), 2.65 (s, 3H), 2.25-2.21 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 173.3, 141.3, 134.1, 132.4 (2C), 129.8, 129.5, 128.8, 127.9, 127.7, 127.2, 125.8, 125.4, 123.9, 123.0, 122.8, 122.4, 114.9, 88.5, 55.8, 55.3, 46.1, 36.2, 35.3, 29.7, 23.1; LRMS (EI, 70 eV) m/z (%): 396 (M^+ , 32), 381 (100), 202 (66), 188 (63); HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 397.1911, found 397.1923.

9b-Methoxy-3a,5-dimethyl-4-oxo-1-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4jaa):

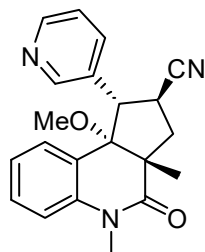
45.1 mg, 64% yield;



Light yellow solid, mp 157.6-159.5 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.29 (m, 4H), 7.07-7.04 (m, 2H), 7.00 (t, $J = 7.6$ Hz, 1H), 4.28 (d, $J = 8.8$ Hz, 1H), 3.42-3.37 (m, 4H), 3.01 (t, $J = 12.4$ Hz, 1H), 2.80 (s, 3H), 2.12-2.08 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.9, 141.6, 139.0, 130.1, 128.1, 127.2, 126.7, 126.5, 123.5, 123.2, 122.7, 115.0, 86.2, 55.1, 54.7, 50.8, 36.9, 34.9, 29.6, 23.1; LRMS (EI, 70 eV) m/z (%): 352 (M^+ , 21), 337 (34), 204 (100), 188 (48); HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 353.1318, found 353.1311.

9b-Methoxy-3a,5-dimethyl-4-oxo-1-(pyridin-3-yl)-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4kaa):

47.9 mg, 69% yield;

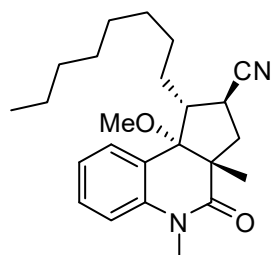


Light yellow solid, mp 165.9-167.5 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.91 (s, 1H), 8.65 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.40-7.36 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 8.8 Hz, 1H),

3.47-3.41 (m, 1H), 3.39 (s, 3H), 3.10 (t, *J* = 12.4 Hz, 1H), 2.60 (s, 3H), 2.21-2.17 (m, 1H), 1.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 172.9, 151.2, 149.7, 141.3, 137.2, 132.8, 130.1, 126.8, 123.8, 123.7, 123.0, 122.4, 115.1, 87.3, 55.5, 55.2, 52.3, 35.2, 35.1, 29.7, 22.7; LRMS (EI, 70 eV) *m/z* (%): 347 (M⁺, 18), 332 (100), 316 (22), 202 (51); HRMS *m/z* (ESI) calcd for C₂₁H₂₂N₃O₂ (M+H)⁺ 348.1707, found 348.1705.

9b-Methoxy-3a,5-dimethyl-1-octyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4laa):

58.1 mg, 76% yield;



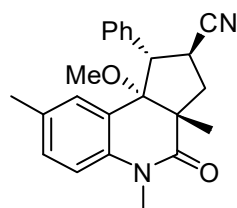
Light yellow solid, mp 99.5-101.2 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.43-7.29 (m, 2H), 7.14-7.07 (m, 2H), 3.43-3.30 (m, 4H), 2.93 (s, 3H), 2.79-2.74 (m, 1H), 2.69-2.63 (m, 1H), 2.22-2.17 (m, 1H), 2.14-2.08 (m, 2H), 1.68-1.26 (m,

12H), 0.90 (t, *J* = 6.4 Hz, 3H), 0.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.4, 141.3, 129.6, 126.5, 124.6, 122.6, 121.0, 115.2, 85.9, 54.8, 53.9, 45.5, 35.5, 31.7, 30.0, 29.8, 29.5, 29.4, 29.2, 28.9, 28.7, 22.5, 21.5, 14.0; LRMS (EI, 70 eV) *m/z* (%): 382

(M⁺, 23), 351 (100), 212 (6), 174 (15); HRMS *m/z* (ESI) calcd for C₂₄H₃₅N₂O₂ (M+H)⁺ 383.2693, found 383.2699.

9b-Methoxy-3a,5,8-trimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4maa):

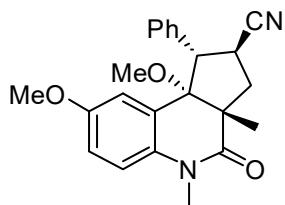
47.5 mg, 66% yield;



White solid, mp 229.6-231.5 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 5.6 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.88 (d, *J* = 8.8 Hz, 1H), 3.47 (t, *J* = 9.6 Hz, 1H), 3.35 (s, 3H), 3.06 (t, *J* = 12.4 Hz, 1H), 2.59 (s, 3H), 2.22 (s, 3H), 2.14 (d, *J* = 13.6 Hz, 1H), 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.2, 138.9, 136.9, 132.4, 130.1, 130.1, 128.8, 128.2, 128.0, 124.3, 123.1, 114.8, 87.1, 55.6, 55.2, 54.6, 35.2 (2C), 29.6, 22.7, 20.7; LRMS (EI, 70 eV) *m/z* (%): 360 (M⁺, 31), 345 (100), 216 (60), 200 (32); HRMS *m/z* (ESI) calcd for C₂₃H₂₅N₂O₂ (M+H)⁺ 361.1911, found 361.1913.

8,9b-Dimethoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4naa):

53.4 mg, 71% yield;

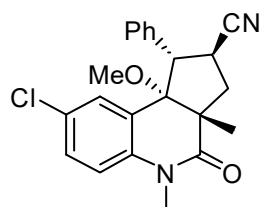


White solid, mp 235.8-137.2 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.64 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.93 (s, 1H), 6.86-6.83 (m, 1H), 3.88 (d, *J* = 9.0 Hz, 1H), 3.69 (s, 3H), 3.51-3.46 (m, 1H), 3.35 (s, 3H), 3.06 (t, *J* = 12.5 Hz, 1H), 2.62 (s, 3H), 2.14 (d, *J* = 13.5 Hz, 1H) 1.21 (s,

3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.8, 155.1, 136.6, 134.8, 130.0, 128.9, 128.3, 125.6, 123.0, 115.9, 113.8, 113.7, 86.9, 55.4, 55.3, 55.2, 54.5, 35.2, 34.9, 29.7, 22.7; LRMS (EI, 70 eV) m/z (%): 376 (M^+ , 4), 351 (100), 234 (62); HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 377.1860, found 377.1863.

8-Chloro-9b-methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[*c*]quinoline-2-carbonitrile (4oaa):

43.3 mg, 57% yield;

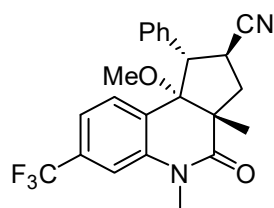


Light yellow solid, mp 196.7-198.2 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (d, J = 7.2 Hz, 2H), 7.46-7.37 (m, 3H), 7.33-7.30 (m, 2H), 6.97 (d, J = 7.6 Hz, 1H), 3.87 (d, J =

8.8 Hz, 1H), 3.52-3.46 (m, 1H), 3.36 (s, 3H), 3.06 (t, J = 12.4 Hz, 1H), 2.61 (s, 3H), 2.17-2.13 (m, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.9, 139.9, 136.0, 130.0, 129.6, 129.0, 128.5, 128.1, 127.4, 126.1, 122.8, 116.1, 86.5, 55.5, 55.3, 54.4, 35.1, 35.0, 29.7, 22.6; LRMS (EI, 70 eV) m/z (%): 382 (M^{++2} , 8), 380 (M^+ , 23), 365 (100), 236 (53), 222 (29); HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{22}^{35}\text{ClN}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 381.1364, found 381.1358.

9b-Methoxy-3a,5-dimethyl-4-oxo-1-phenyl-7-(trifluoromethyl)-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[*c*]quinoline-2-carbonitrile (4paa):

23.2 mg, 28% yield;

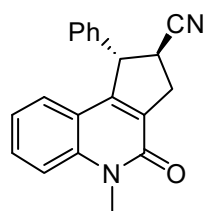


White solid, mp 215.5-217.3 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (d, J = 6.8 Hz, 2H), 7.49-7.39 (m, 4H), 7.28-7.24 (m, 2H), 3.90 (d, J = 8.4 Hz, 1H), 3.51 (t, J = 9.2 Hz,

1H), 3.42 (s, 3H), 3.08 (t, $J = 12.4$ Hz, 1H), 2.59 (s, 3H), 2.18 (d, $J = 14.8$ Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 173.0, 142.0, 136.1, 132.1 (d, $J = 28.9$ Hz, 1C), 130.1, 129.1, 128.6, 127.8, 122.7, 119.6 (d, $J = 3.8$ Hz, 2C), 111.5 (d, $J = 3.7$ Hz, 2C), 111.4, 86.6, 55.6, 55.2, 54.6, 35.1, 35.0, 29.7, 22.68; ^{19}F NMR (282 MHz, CDCl_3) δ : -63.0; LRMS (EI, 70 eV) m/z (%): 415 ($\text{M}^+ + 1$, 2), 414 (M^+ , 9), 399 (100), 270 (60), 142 (19); HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{22}^{19}\text{F}_3\text{N}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 415.1628, found 415.1632.

5-Methyl-4-oxo-1-phenyl-2,3,4,5-tetrahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4qaa):

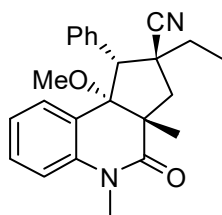
30.0 mg, 50% yield;



Light yellow solid, mp 157.7-159.5 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.50 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 1H), 7.37-7.31 (m, 3H), 7.26 (d, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 6.8$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 4.96 (d, $J = 8.8$ Hz, 1H), 3.85-3.74 (m, 4H), 3.56-3.49 (m, 1H), 3.40-3.34 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.9, 148.7, 140.6, 136.5, 130.7, 130.4, 129.2, 128.5, 128.0, 125.7, 122.4, 119.0, 117.7, 114.8, 53.4, 34.8, 34.4, 29.5; LRMS (EI, 70 eV) m/z (%): 300 (M^+ , 100), 273 (21), 260 (21), 223 (12); HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$ ($\text{M} + \text{H}$) $^+$ 301.1335, found 301.1326.

2-Ethyl-9b-methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4aba):

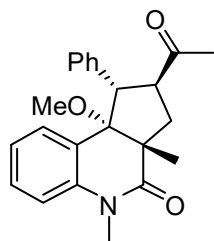
54.6 mg, 73% yield;



White solid, mp 233.9-235.8 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.45-7.30 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 3.42 (s, 1H), 3.40 (s, 3H), 3.23 (d, *J* = 13.6 Hz, 1H), 2.91 (s, 3H), 2.11 (d, *J* = 13.6 Hz, 1H), 1.94-1.85 (m, 1H), 1.69-1.60 (m, 1H), 1.11 (t, *J* = 8.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.5, 141.6, 135.2, 129.7, 128.6 (2C), 128.4, 127.2, 124.4, 123.5, 122.9, 114.9, 88.0, 58.9, 55.2, 53.6, 48.6, 41.2, 33.3, 29.7, 24.3, 10.4; LRMS (EI, 70 eV) *m/z* (%): 374 (M⁺, 30), 359 (100), 316 (14), 202 (74); HRMS *m/z* (ESI) calcd for C₂₄H₂₇N₂O₂ (M+H)⁺ 375.2067, found 375.2073.

2-Acetyl-9b-methoxy-3a,5-dimethyl-1-phenyl-1,2,3,3a,5,9b-hexahydro-4H-cyclopenta[c]quinolin-4-one (4ada):

51.5 mg, 71% yield;

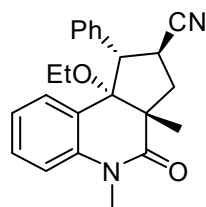


White solid, mp 160.7-162.5 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.67 (d, *J* = 7.6 Hz, 2H), 7.41-7.27 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.67-3.61 (m, 1H), 3.37 (s, 3H), 3.00 (t, *J* = 12.8 Hz, 1H), 2.58 (s, 3H), 2.04 (s, 3H), 1.96-1.92 (m, 1H), 0.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 209.1, 174.6, 141.5, 139.7, 130.6, 129.3, 128.5, 127.4, 127.2, 125.8, 122.5, 114.5, 88.1, 58.9, 55.2, 54.8, 50.3, 33.0, 29.9, 29.6, 22.1; LRMS (EI, 70 eV) *m/z* (%): 363 (M⁺, 18), 348 (90), 203 (52), 117 (100); HRMS *m/z* (ESI) calcd for C₂₃H₂₆NO₃ (M+H)⁺ 364.1907, found 364.1916.

9b-Ethoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta

[c]quinoline-2-carbonitrile (4aab):

36.7 mg, 51% yield;



White solid, mp 226.6-228.2 °C (uncorrected); ¹H NMR (400 MHz,

CDCl₃) δ: 7.65 (d, *J* = 7.6 Hz, 2H), 7.43-7.31 (m, 5H), 7.01 (d, *J* =

8.4 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 3.89 (d, *J* = 9.2 Hz, 1H),

3.54-3.48 (m, 1H), 3.36 (s, 3H), 3.11 (t, *J* = 12.4 Hz, 1H), 2.78-2.71 (m, 1H),

2.50-2.42 (m, 1H), 2.16-2.12 (m, 1H), 1.21 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR

(100 MHz, CDCl₃) δ: 173.4, 141.4, 136.9, 129.9, 129.7, 128.8, 128.3, 127.0, 125.2,

123.2, 122.8, 114.9, 86.7, 62.7, 55.6, 54.7, 35.1, 35.0, 29.6, 22.6, 15.2; LRMS (EI, 70

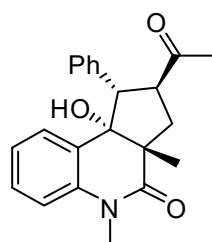
eV) *m/z* (%): 360 (M⁺, 13), 345 (100), 216 (48), 186 (23); HRMS *m/z* (ESI) calcd for

C₂₃H₂₅N₂O₂ (M+H)⁺ 361.1911, found 361.1908.

2-Acetyl-9b-hydroxy-3a,5-dimethyl-1-phenyl-1,2,3,3a,5,9b-hexahydro-4H-cyclop

enta[c]quinolin-4-one (4add):

46.1 mg, 66% yield;



White solid, mp 82.5-83.8 °C (uncorrected); ¹H NMR (400 MHz,

CDCl₃) δ: 7.67 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H),

7.31-7.20 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H),

4.11 (d, *J* = 8.8 Hz, 1H), 3.57-3.51 (m, 1H), 3.36 (s, 3H), 2.97 (t, *J*

= 12.8 Hz, 1H), 2.15 (s, 1H), 2.04 (s, 3H), 1.96-1.92 (m, 1H), 1.01 (s, 3H); ¹³C NMR

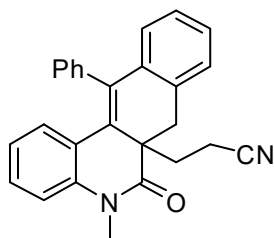
(100 MHz, CDCl₃) δ: 209.0, 174.2, 141.0, 139.6, 130.3, 129.4, 129.0, 128.8, 127.4,

124.9, 122.6, 115.3, 82.5, 58.2, 53.8, 49.9, 33.0, 29.9, 29.6, 21.6; LRMS (EI, 70 eV)

m/z (%): 349 (M^+ , 17), 288 (3), 189 (100), 117 (29); HRMS m/z (ESI) calcd for $C_{22}H_{24}NO_3$ ($M+H$) $^+$ 350.1751, found 350.1755.

3-(5-Methyl-6-oxo-12-phenyl-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)propanenitrile (5ra):

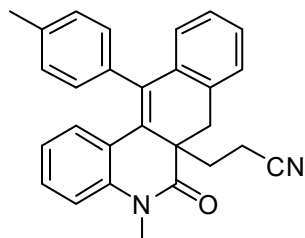
41.3 mg, 53% yield;



Light yellow solid, mp 253.5-255.2 °C (uncorrected); 1H NMR (400 MHz, $CDCl_3$) δ : 7.42-7.35 (m, 3H), 7.28-7.19 (m, 4H), 7.15-7.12 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 3.53 (d, J = 16.8 Hz, 1H), 3.43 (s, 3H), 3.38 (d, J = 17.2 Hz, 1H), 2.36-2.22 (m, 2H), 2.03-1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 171.7, 138.9, 138.2, 137.7, 133.8, 132.0, 130.7, 130.6, 129.1, 128.8, 128.6, 128.3, 128.1, 127.5, 126.9, 126.5, 122.6 (2C), 119.2, 114.5, 45.9, 35.9, 31.8, 30.5, 12.9; LRMS (EI, 70 eV) m/z (%): 390 (M^+ , 7), 336 (100), 320 (8), 167 (6); HRMS m/z (ESI) calcd for $C_{27}H_{23}N_2O$ ($M+H$) $^+$ 391.1805, found 391.1810.

3-(5-Methyl-6-oxo-12-(*p*-tolyl)-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)propanenitrile (5sa):

40.4 mg, 50% yield;

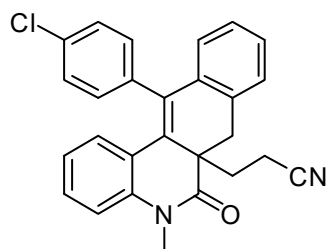


Light yellow solid, mp 203.7-205.5 °C (uncorrected); 1H NMR (400 MHz, $CDCl_3$) δ : 7.27-7.11 (m, 9H), 6.96 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 3.51 (d, J = 16.8 Hz, 1H), 3.42 (s, 3H), 3.37 (d, J = 16.8 Hz, 1H), 2.40 (s, 3H), 2.35-2.21 (m, 2H), 2.03-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 171.8, 138.9,

137.7, 137.1, 135.1, 134.0, 132.0, 130.7, 130.4, 129.5, 128.9, 128.5, 128.2, 128.0, 126.9, 126.4, 122.8, 122.6, 119.2, 114.5, 45.9, 35.9, 31.8, 30.5, 21.3, 12.9; LRMS (EI, 70 eV) m/z (%): 404 (M^+ , 7), 350 (100), 334 (5), 167 (8); HRMS m/z (ESI) calcd for $C_{28}H_{25}N_2O$ ($M+H$)⁺ 405.1961, found 405.1965.

3-(12-(4-Chlorophenyl)-5-methyl-6-oxo-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)propanenitrile (5ta):

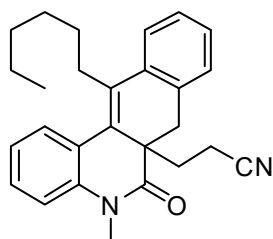
36.5 mg, 43% yield;



Light yellow solid, mp 222.0-223.2 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.40 (d, J = 8.0 Hz, 2H), 7.29-7.12 (m, 6H), 7.05 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 3.52 (d, J = 16.8 Hz, 1H), 3.43 (s, 3H), 3.37 (d, J = 16.8 Hz, 1H), 2.35-2.22 (m, 2H), 2.04-1.90 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.6, 139.0, 136.7, 136.5, 133.5 (2C), 132.1, 132.0, 130.7, 129.7, 129.1, 128.9, 128.5, 128.2, 127.0, 126.2, 122.8, 122.3, 119.1, 114.6, 46.0, 35.8, 31.8, 30.6, 12.9; LRMS (EI, 70 eV) m/z (%): 426 (M^++2 , 7), 424 (M^+ , 20), 370 (100), 354 (8), 167 (6); HRMS m/z (ESI) calcd for $C_{27}H_{22}^{35}ClN_2O$ ($M+H$)⁺ 425.1415, found 425.1421.

3-(12-Hexyl-5-methyl-6-oxo-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)propanenitrile (5ua):

60.5 mg, 76% yield;

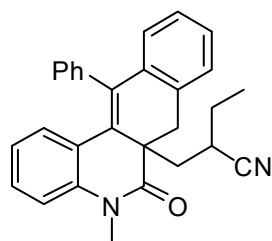


Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 7.45 (d, J = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.29-7.19 (m, 3H), 7.13 (t, J =

7.6 Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 3.40 (s, 3H), 3.22 (s, 2H), 3.18-3.11 (m, 1H), 2.90-2.83 (m, 1H), 2.10 (t, $J = 8.0$ Hz, 2H), 1.73 (t, $J = 8.0$ Hz, 2H), 1.61-1.51 (m, 1H), 1.38-1.29 (m, 1H), 1.22-1.08 (m, 6H), 0.78 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.0, 139.3, 136.9, 134.4, 132.7, 130.3, 129.2, 129.1, 128.1, 127.7, 127.0, 124.6, 123.1, 123.0, 119.2, 114.8, 46.5, 35.7, 31.3, 30.4, 30.1, 29.3 (2C), 28.8, 22.5, 13.9, 12.7; LRMS (EI, 70 eV) m/z (%): 398 (M^+ , 12), 344 (100), 313 (11), 260 (50); HRMS m/z (ESI) calcd for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$ 399.2431, found 399.2441.

2-((5-Methyl-6-oxo-12-phenyl-5,7-dihydrobenzo[*j*]phenanthridin-6a(6*H*)-yl)methyl)butanenitrile (5va):

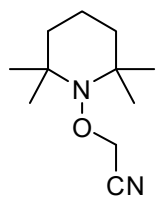
32.6 mg, 39% yield, dr = 2.4:1;



White solid, mp 222.8-224.5 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 7.41-7.11 (m, 10.2H), 6.99-6.91 (m, 1.3H), 6.83 (d, $J = 8.0$ Hz, 0.7H), 6.65-6.60 (m, 1.0H), 3.55-3.37 (m, 5.2H), 2.54-2.48 (m, 1.0H), 2.10-2.03 (m, 1.0H), 1.79 (d, $J = 14.4$ Hz, 0.7H), 1.72 (d, $J = 14.0$ Hz, 0.3H), 1.44-1.40 (m, 2.0H), 0.87 (t, $J = 7.2$ Hz, 3.0H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.5, 171.9, 139.1, 139.0, 138.5, 138.4, 137.7, 137.3, 134.0 (2C), 132.4, 132.0, 131.3, 130.9, 130.7, 129.7, 129.0, 128.8, 128.6, 128.5, 128.2, 128.1 (2C), 127.4 (2C), 126.8, 126.5, 126.4, 122.7 (2C), 122.5, 122.4, 122.1, 121.7, 114.6, 114.3, 46.2, 46.0, 38.7, 37.1, 37.0, 36.2, 30.5 (2C), 28.5, 28.4, 27.3, 27.0, 11.3, 11.1; LRMS

(EI, 70 eV) m/z (%): 418 (M^+ , 5), 336 (100), 320 (7), 291 (3); HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$ 419.2118, found 419.2126.

2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)acetonitrile (7):



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 4.52 (s, 2H), 1.64-1.31 (s, 6H), 1.20 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 116.0, 62.6, 60.3, 39.5, 32.9, 19.8, 16.8; LRMS (EI, 70 eV) m/z (%): 196 (M^+ ,

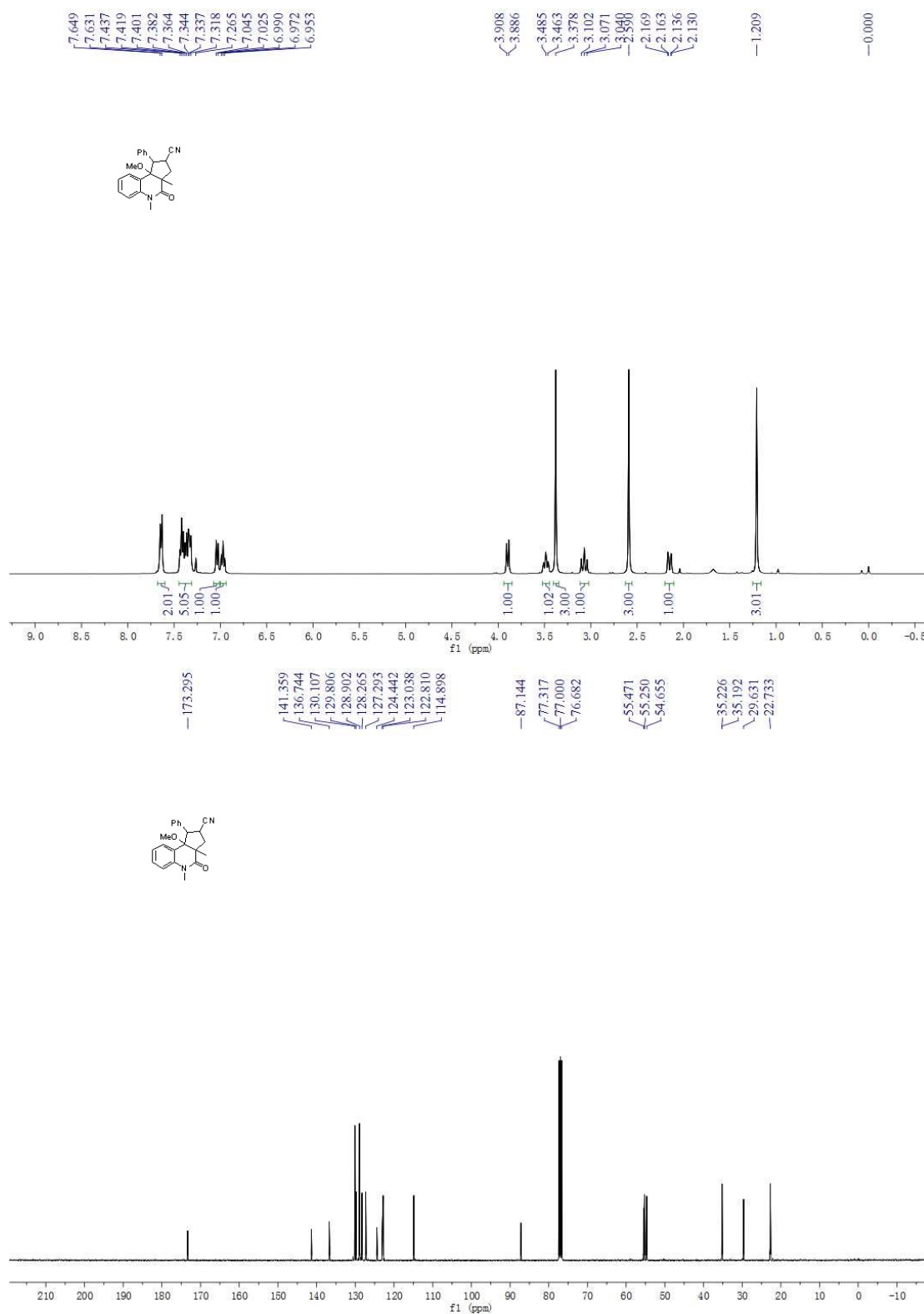
3), 181 (66), 156 (100), 109 (50).

(C) Reference

[1] X. Mu, T. Wu, H.-y. Wang, Y.-l. Guo, G. Liu, *J. Am. Chem. Soc.* **2012**, 134, 878.

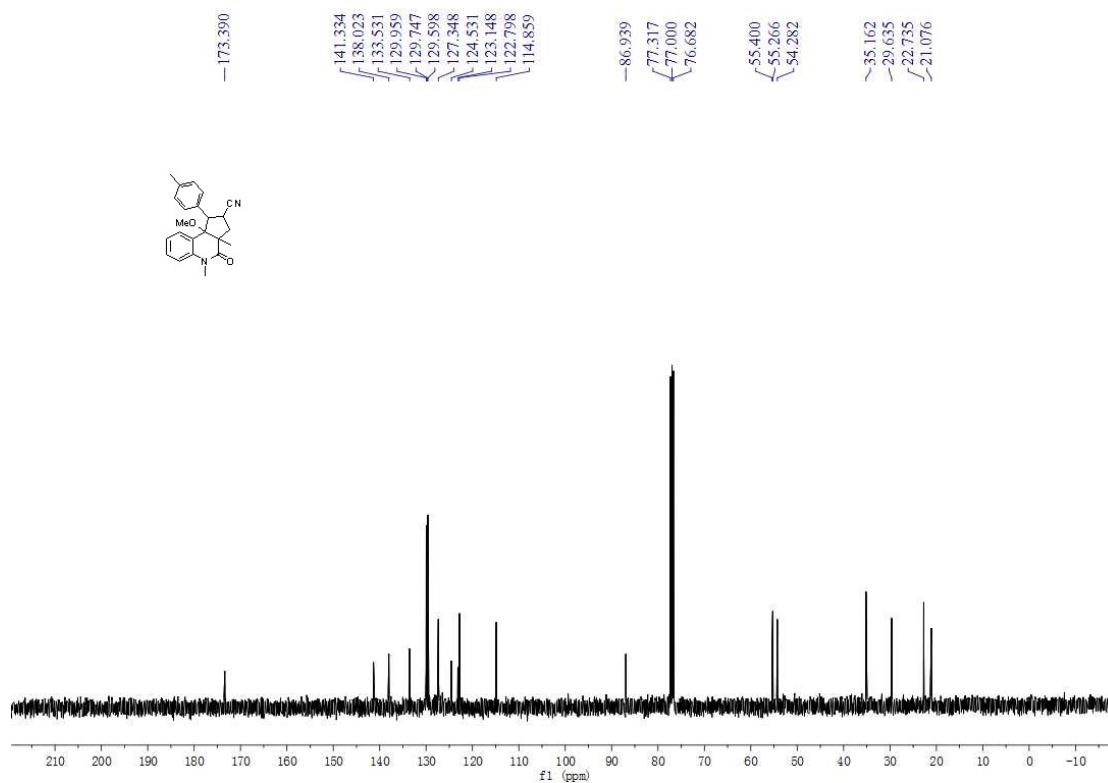
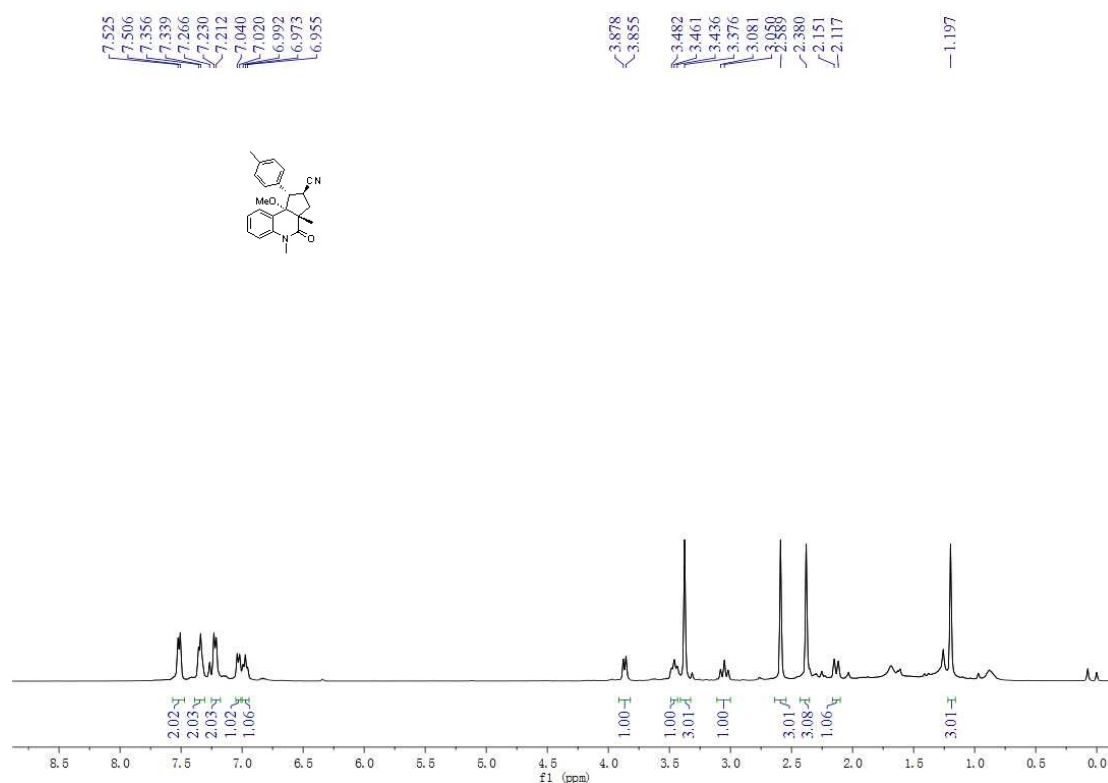
(D) Spectra

9b-Methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]quinoline-2-carbonitrile (4aaa):



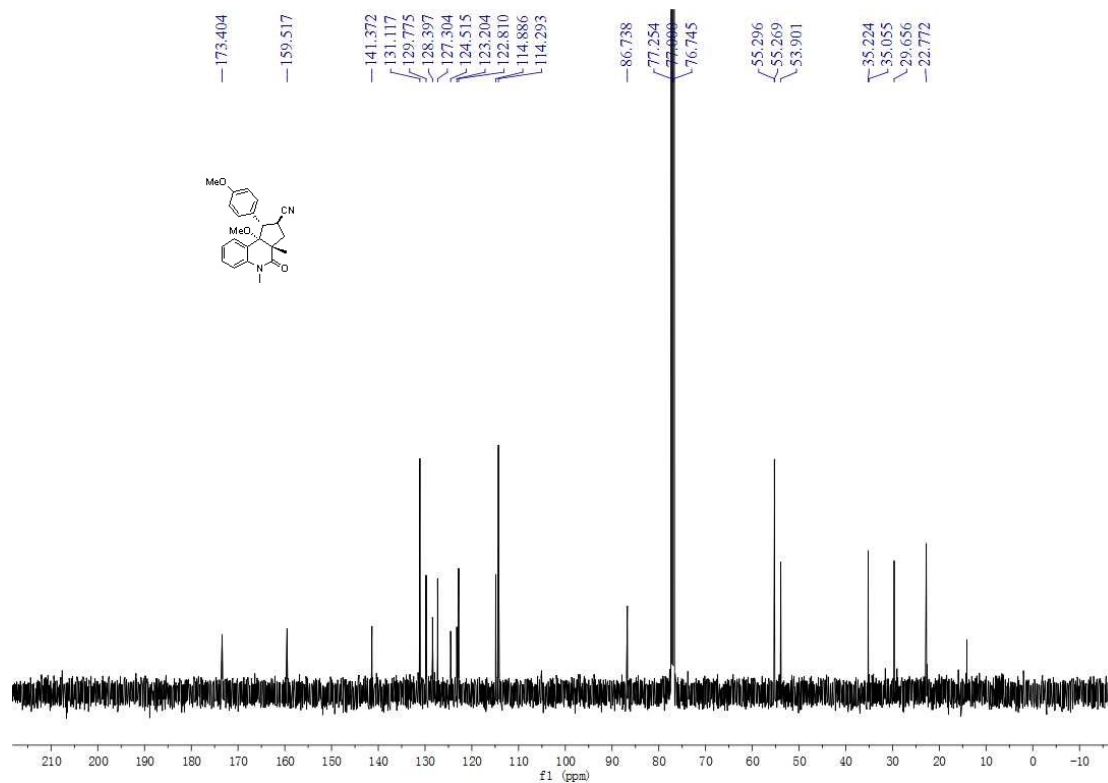
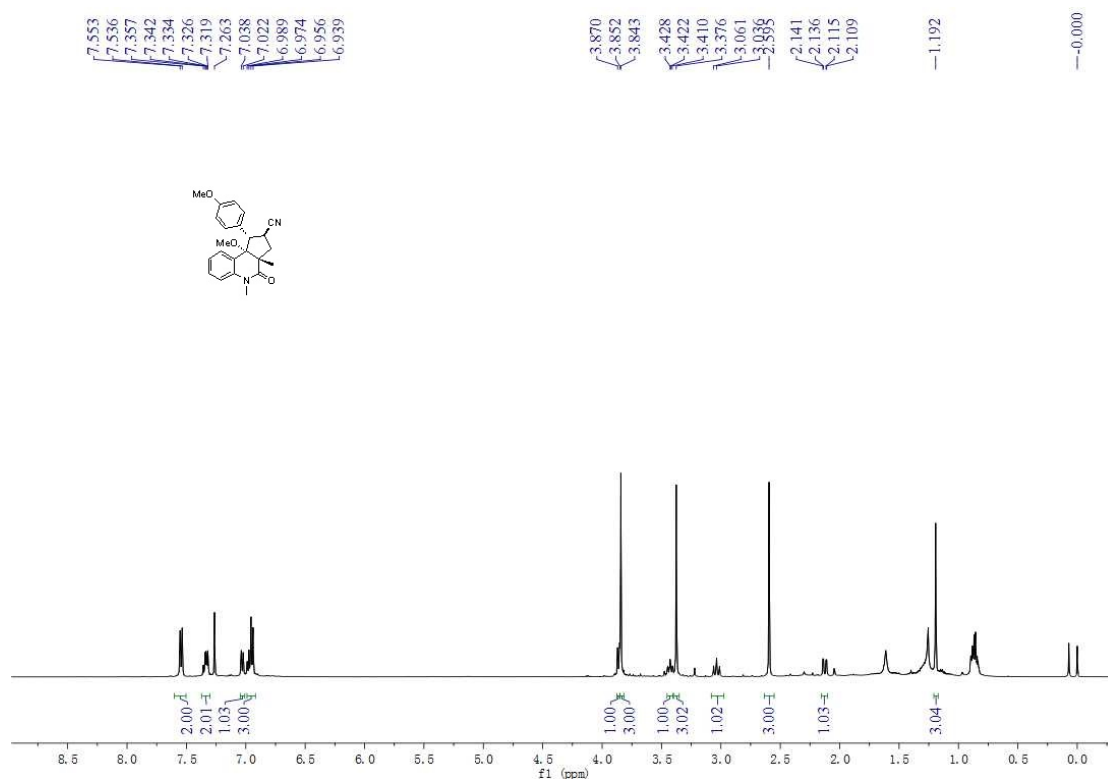
9b-Methoxy-3a,5-dimethyl-4-oxo-1-(*p*-tolyl)-2,3,3a,4,5,9b-hexahydro-1*H*-cyclop

nta[c]quinoline-2-carbonitrile (4caa):



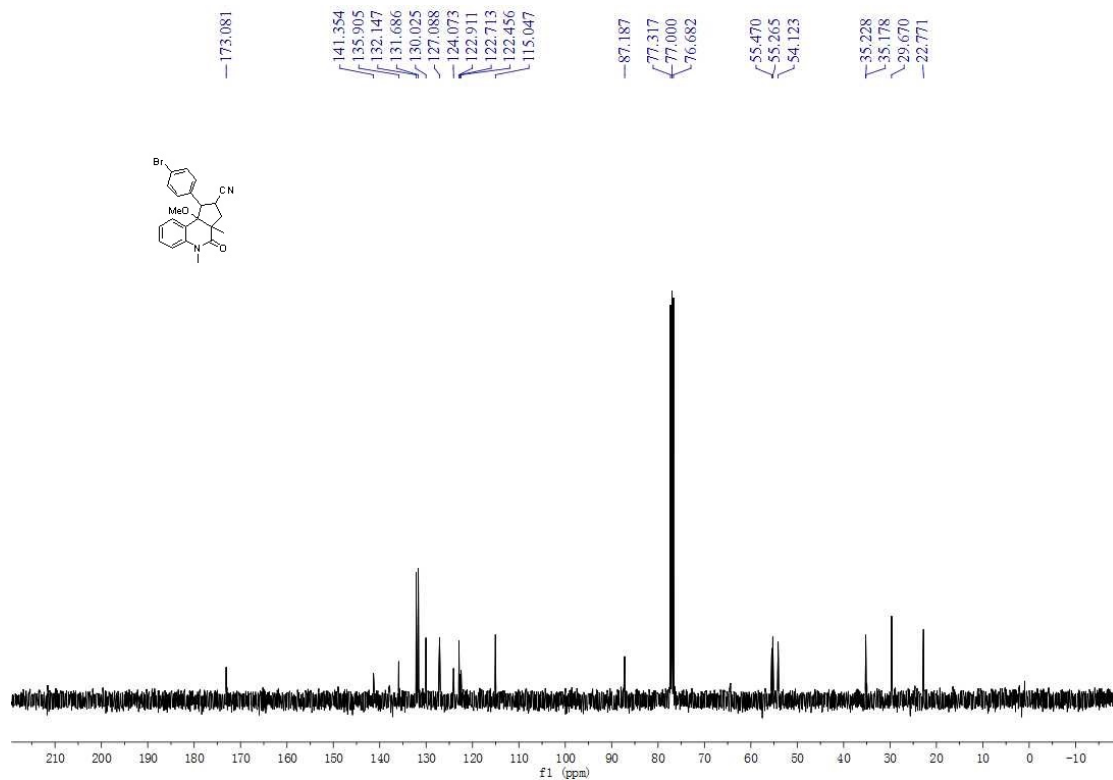
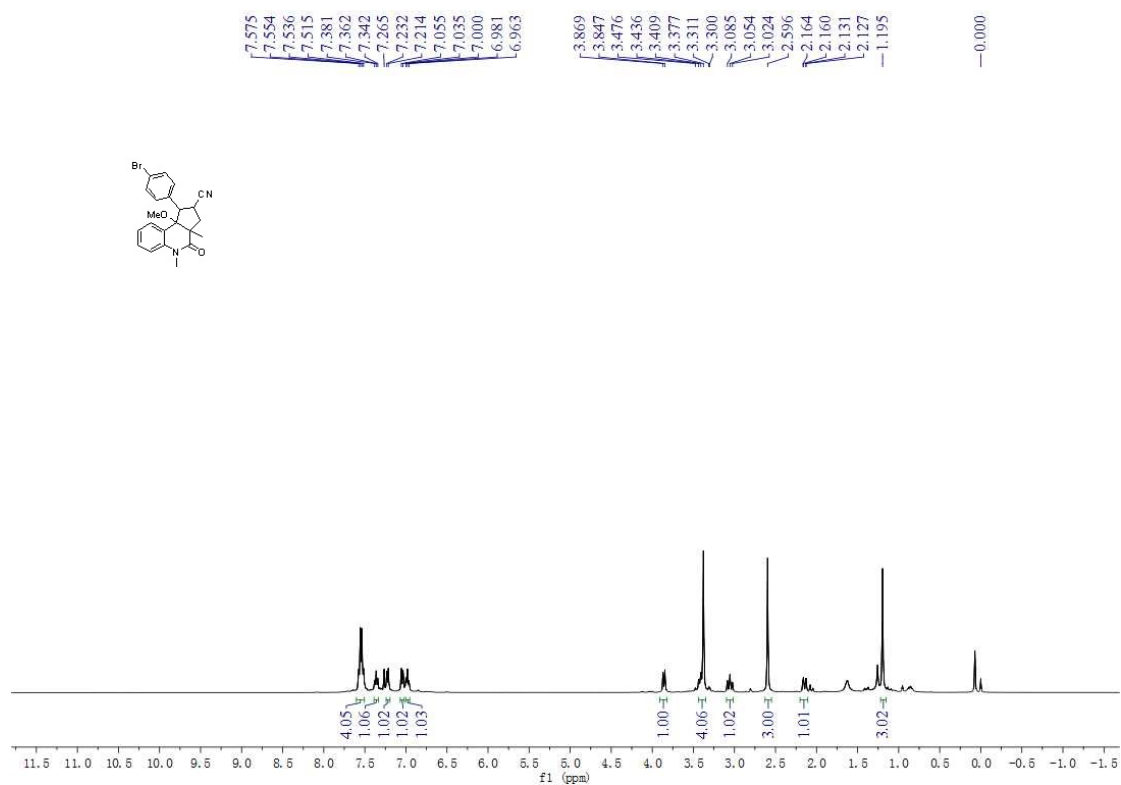
9b-Methoxy-1-(4-methoxyphenyl)-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-

1H-cyclopenta[c]quinoline-2-carbonitrile (4daa):



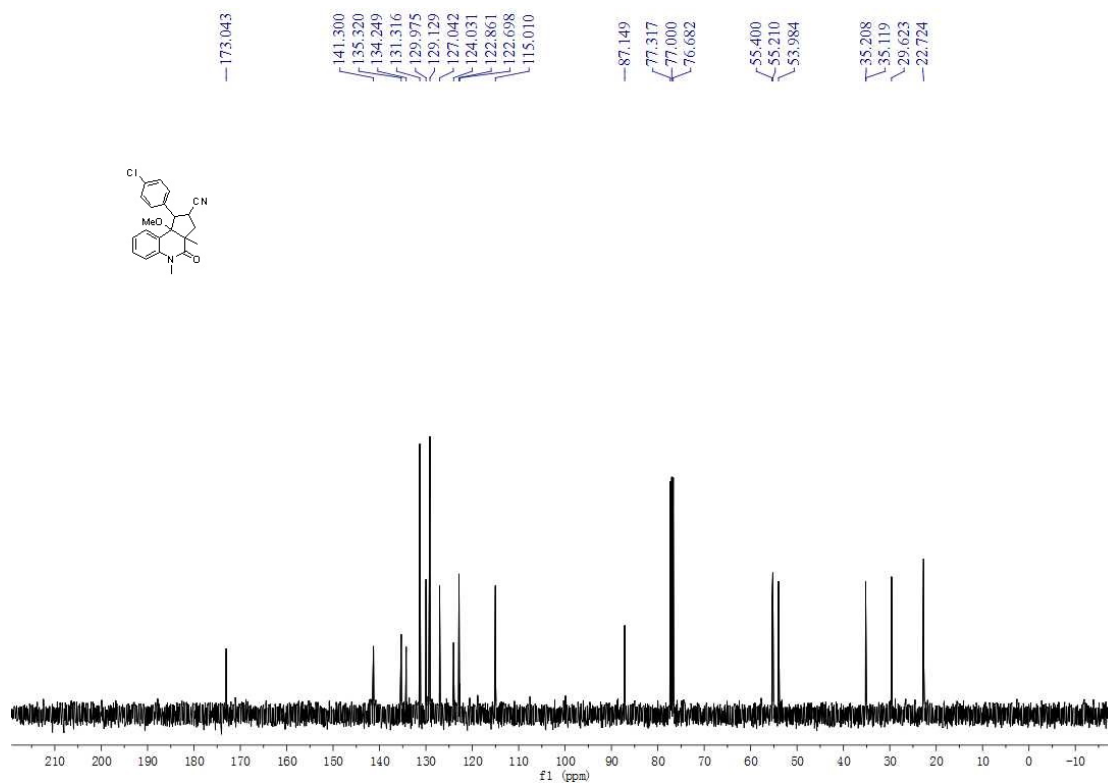
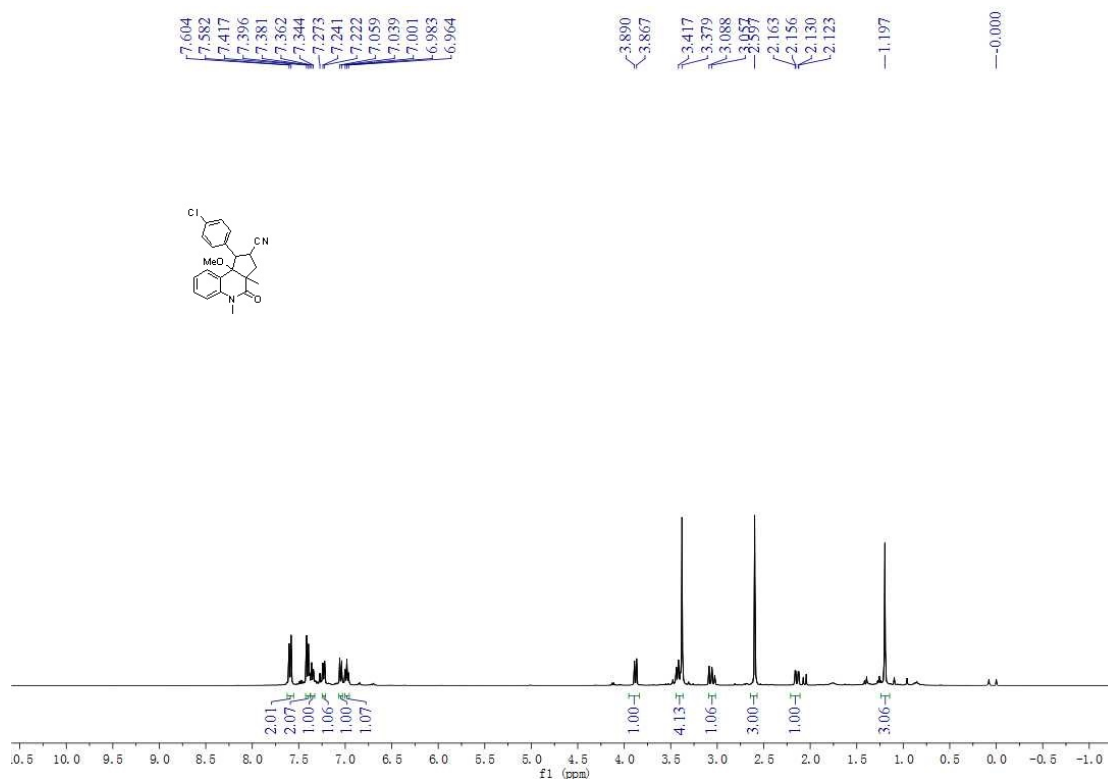
1-(4-Bromophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1*H*

-cyclopenta[c]quinoline-2-carbonitrile (4eaa):



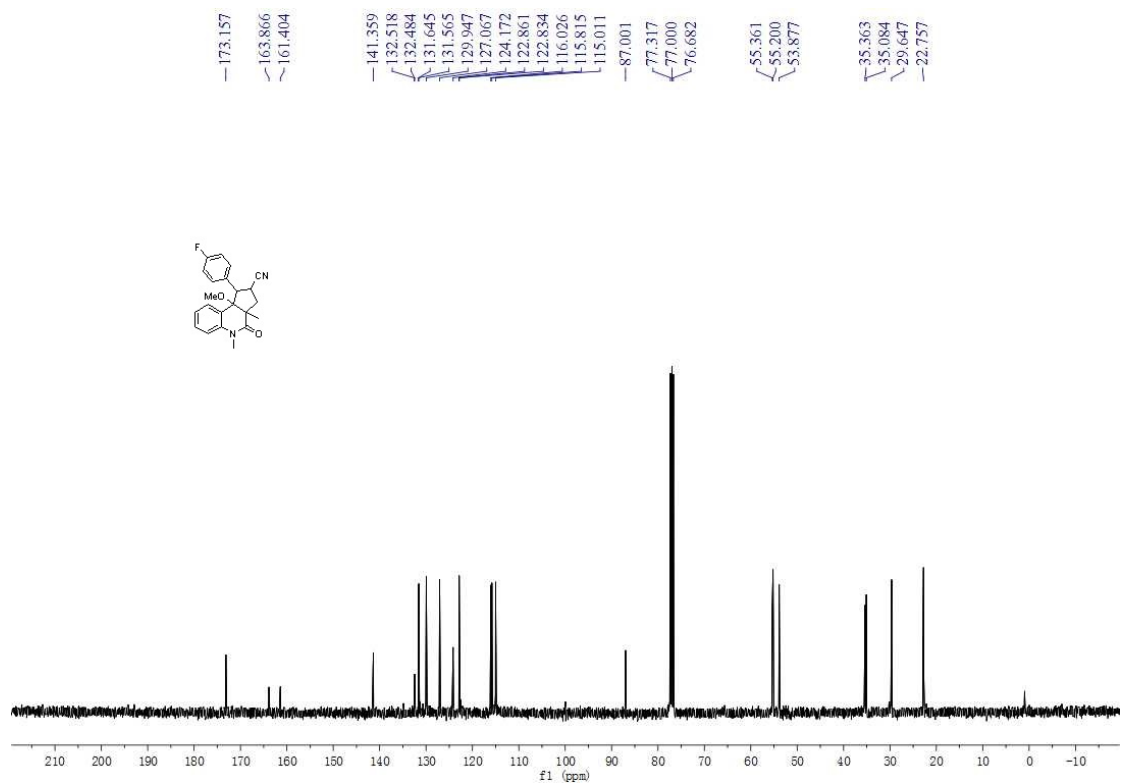
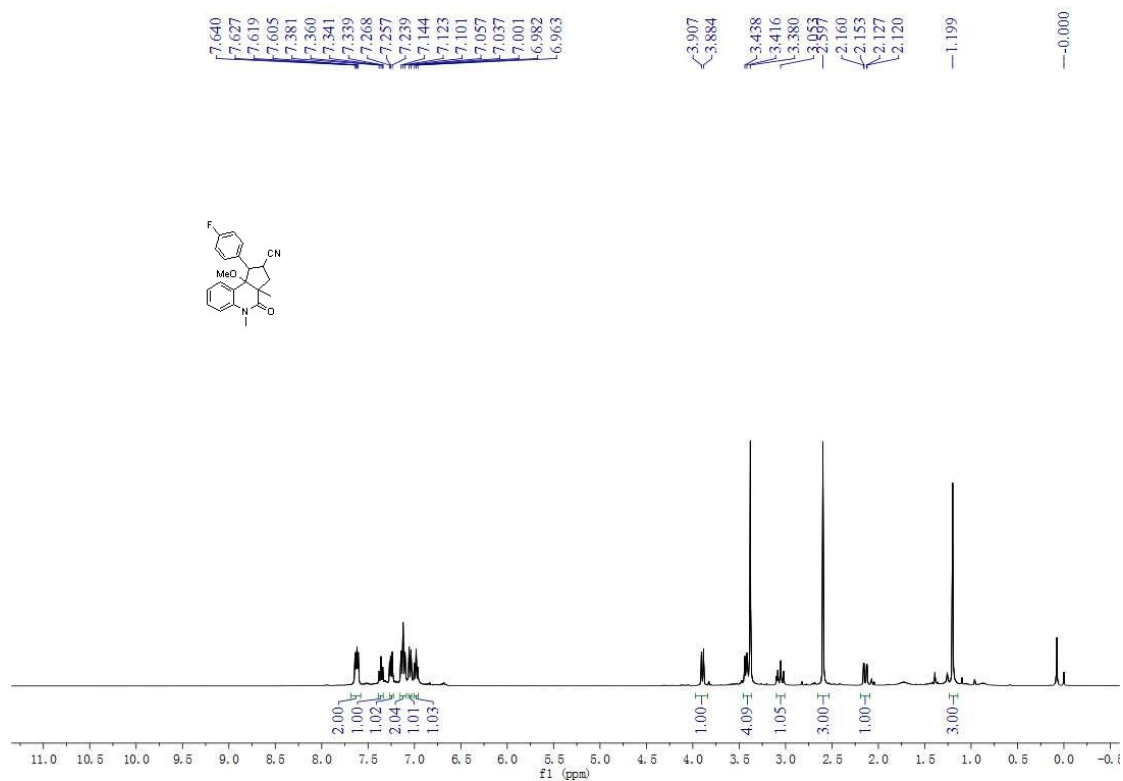
1-(4-Chlorophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1

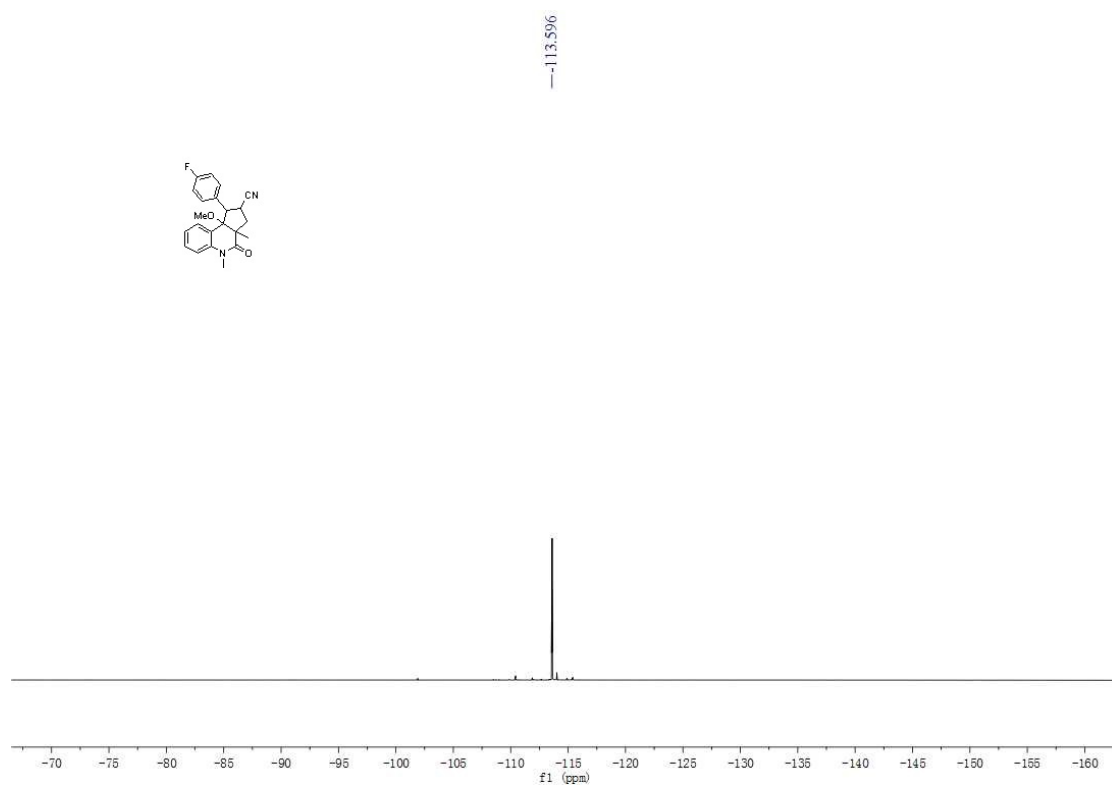
***H*-cyclopenta[*c*]quinoline-2-carbonitrile (4faa):**



1-(4-Fluorophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1*H*

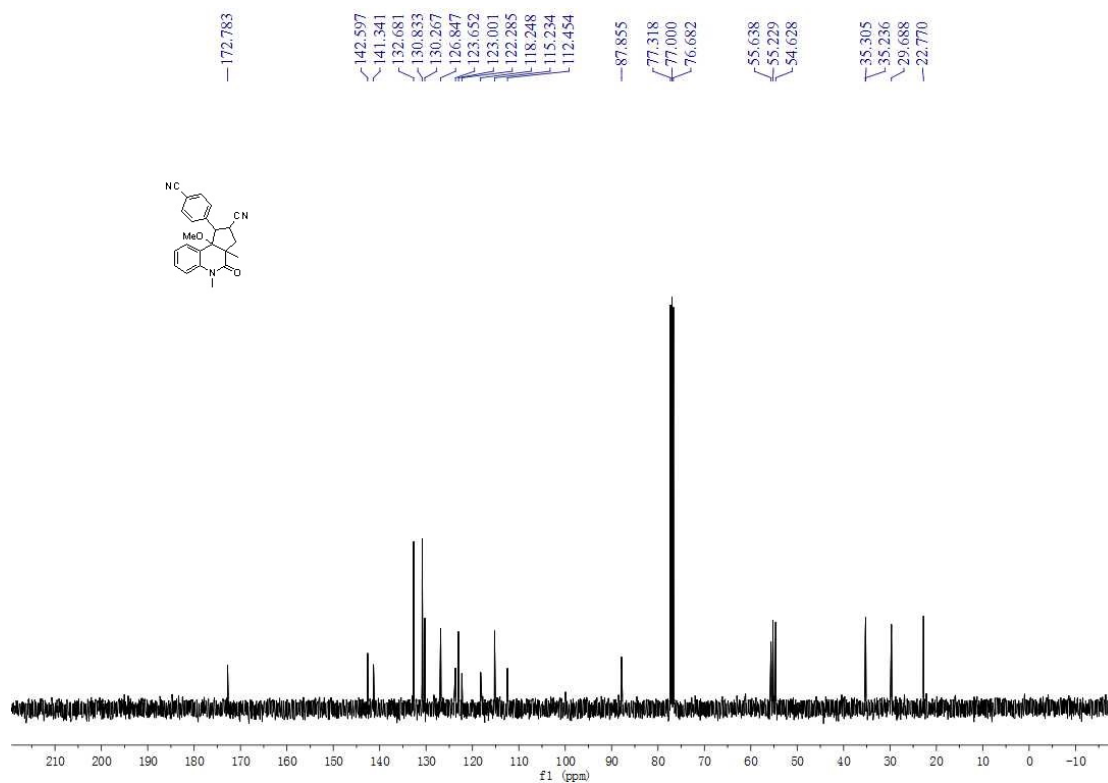
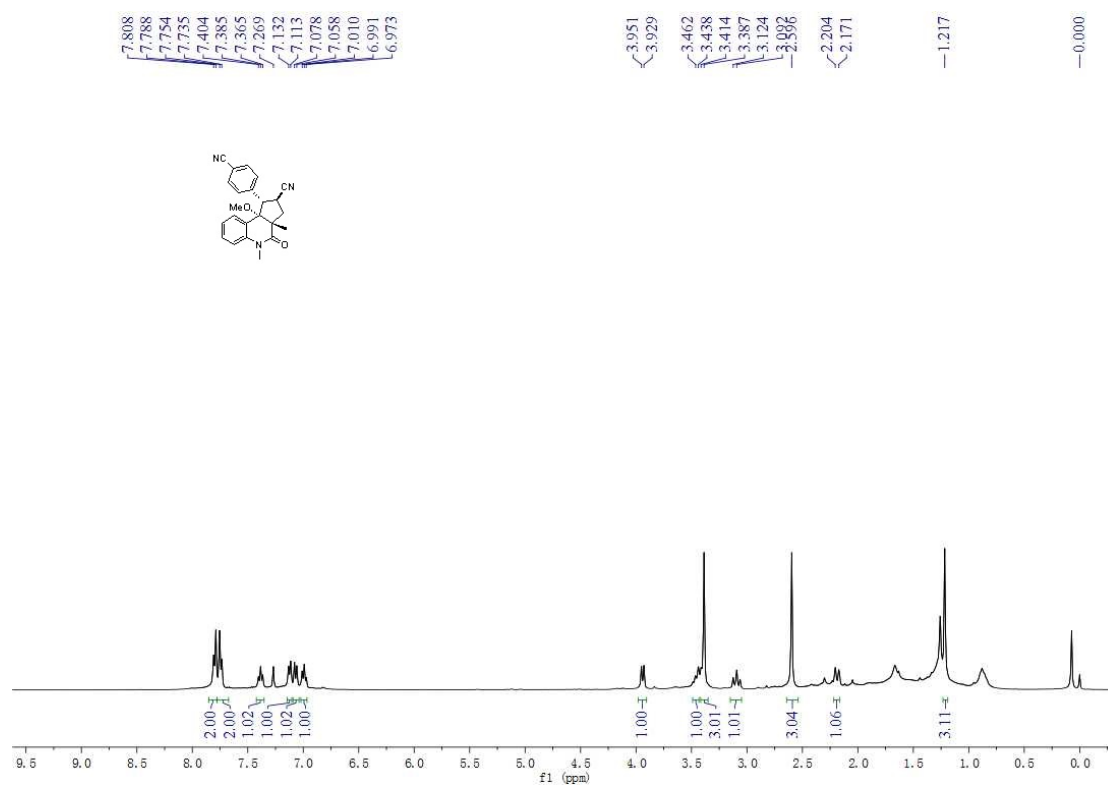
-cyclopenta[*c*]quinoline-2-carbonitrile (4gaa):





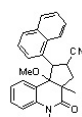
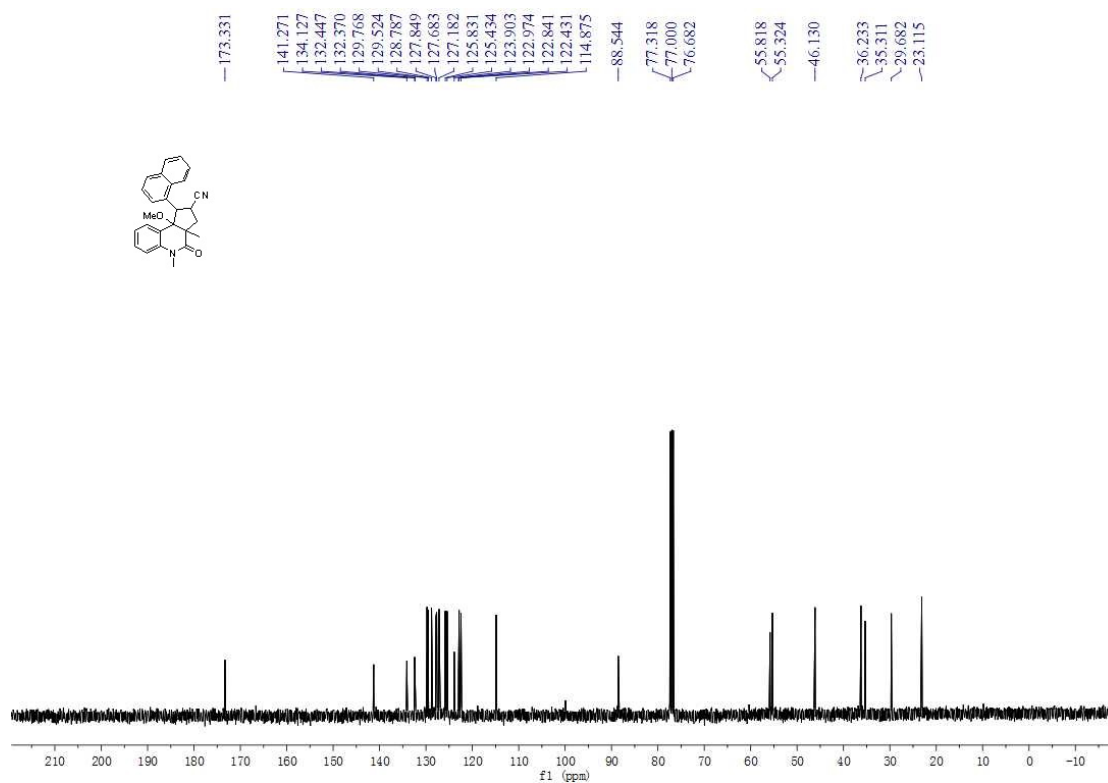
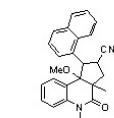
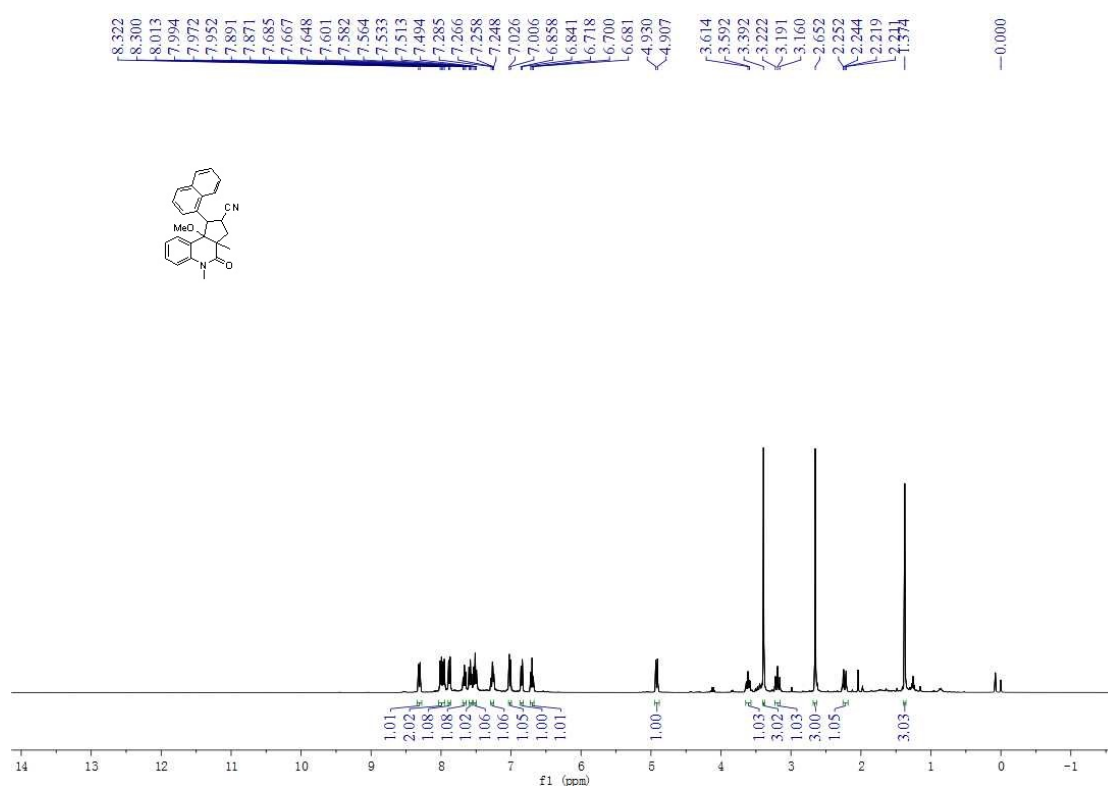
1-(4-Cyanophenyl)-9b-methoxy-3a,5-dimethyl-4-oxo-2,3,3a,4,5,9b-hexahydro-1*H*

-cyclopenta[c]quinoline-2-carbonitrile (4haa):



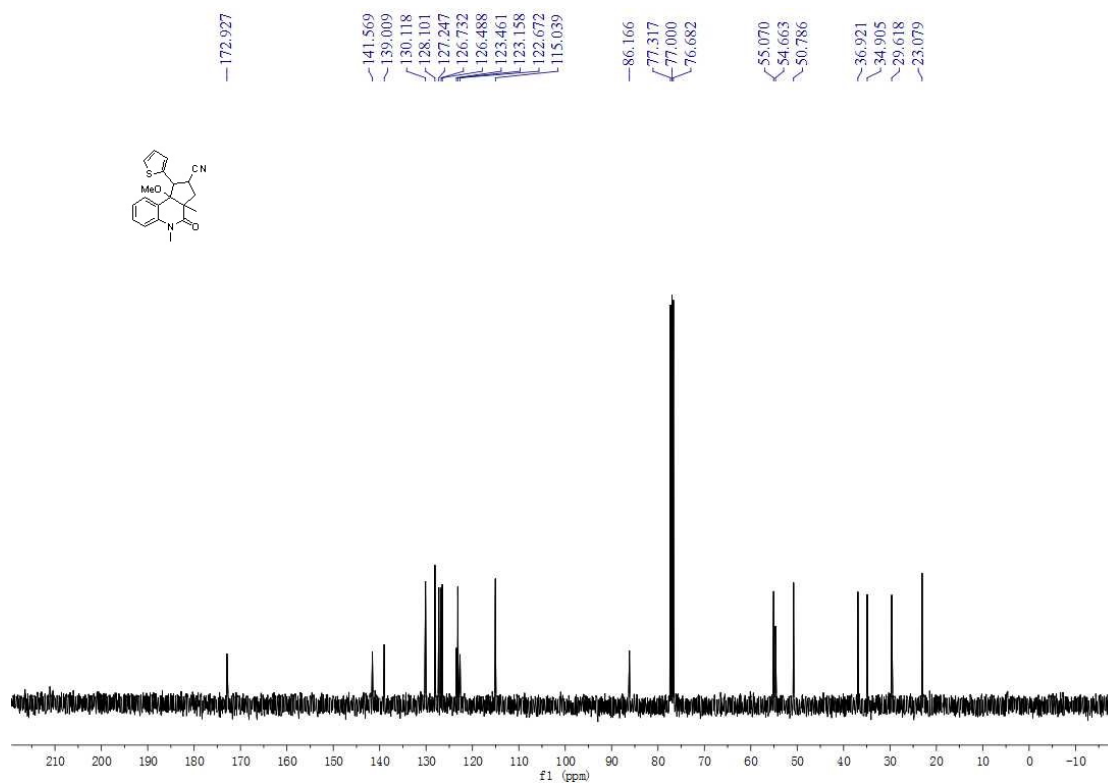
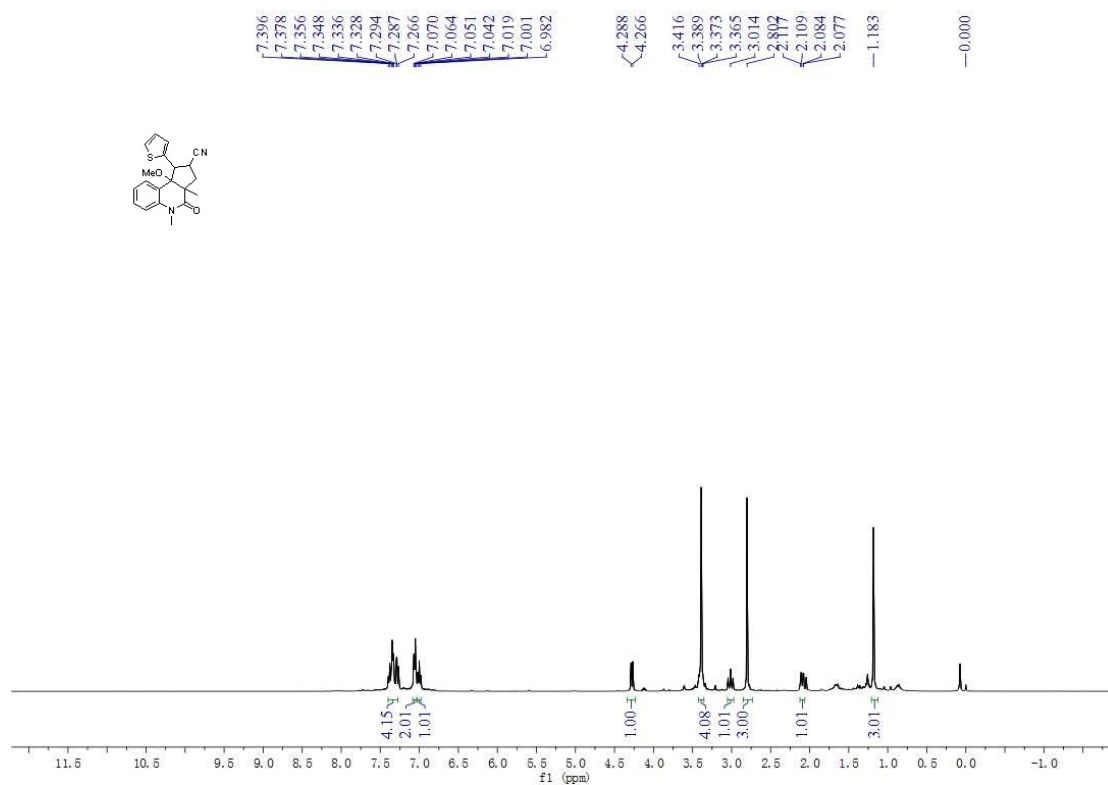
9b-Methoxy-3a,5-dimethyl-1-(naphthalen-1-yl)-4-oxo-2,3,3a,4,5,9b-hexahydro-1

***H*-cyclopenta[*c*]quinoline-2-carbonitrile (4iaa):**



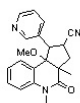
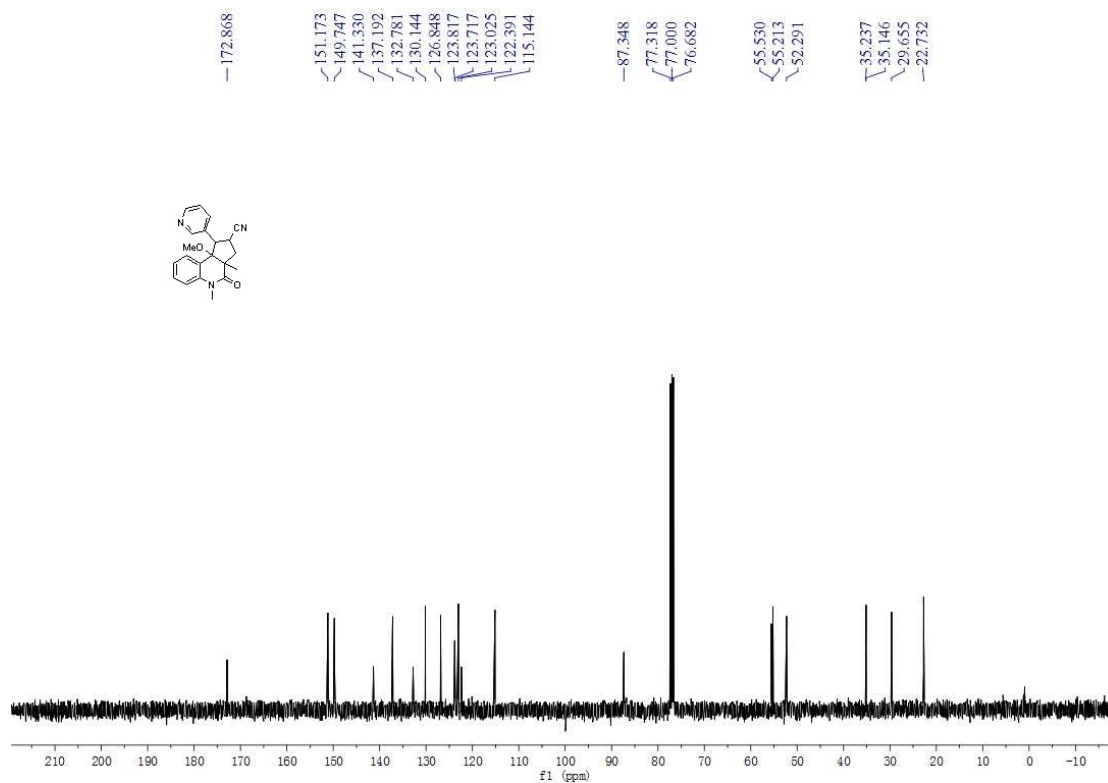
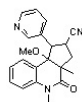
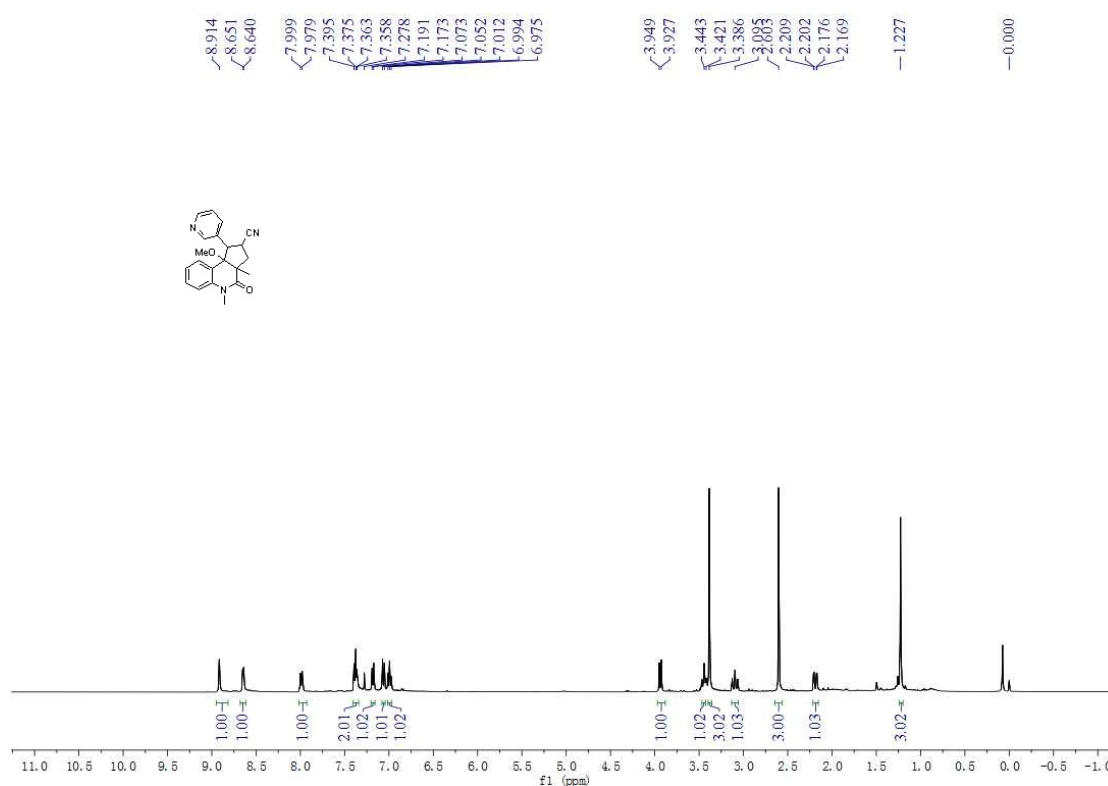
9b-Methoxy-3a,5-dimethyl-4-oxo-1-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-c

yclopenta[c]quinoline-2-carbonitrile (4jaa):



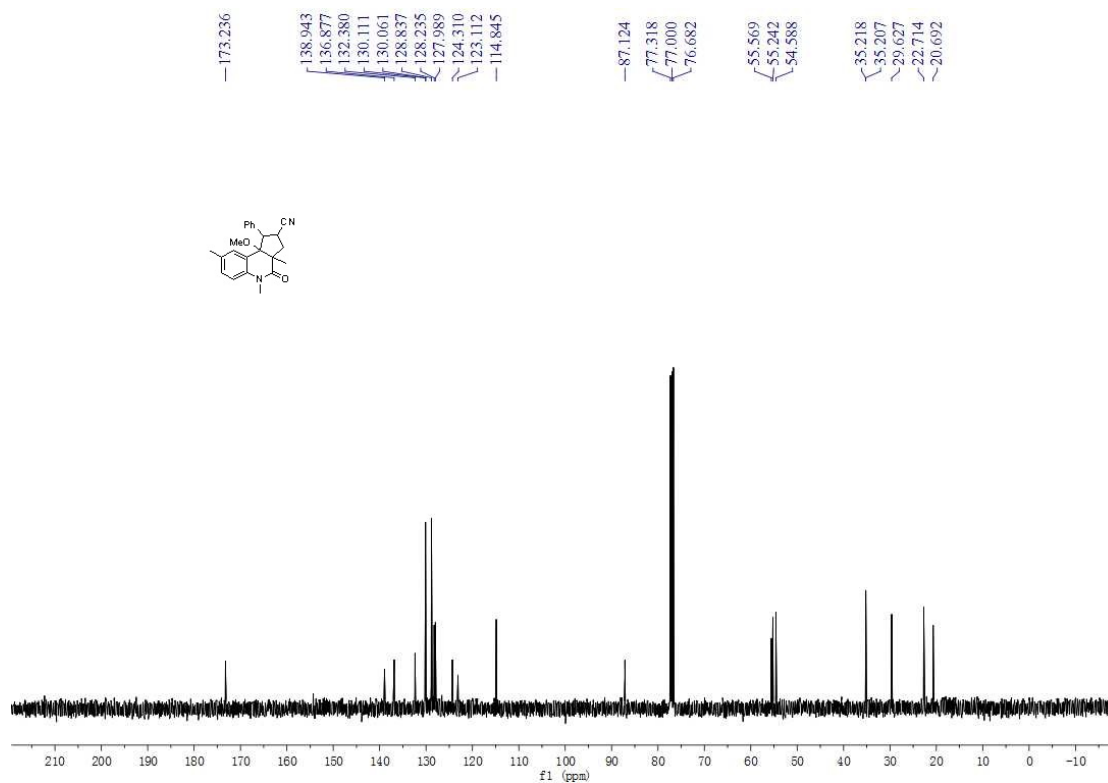
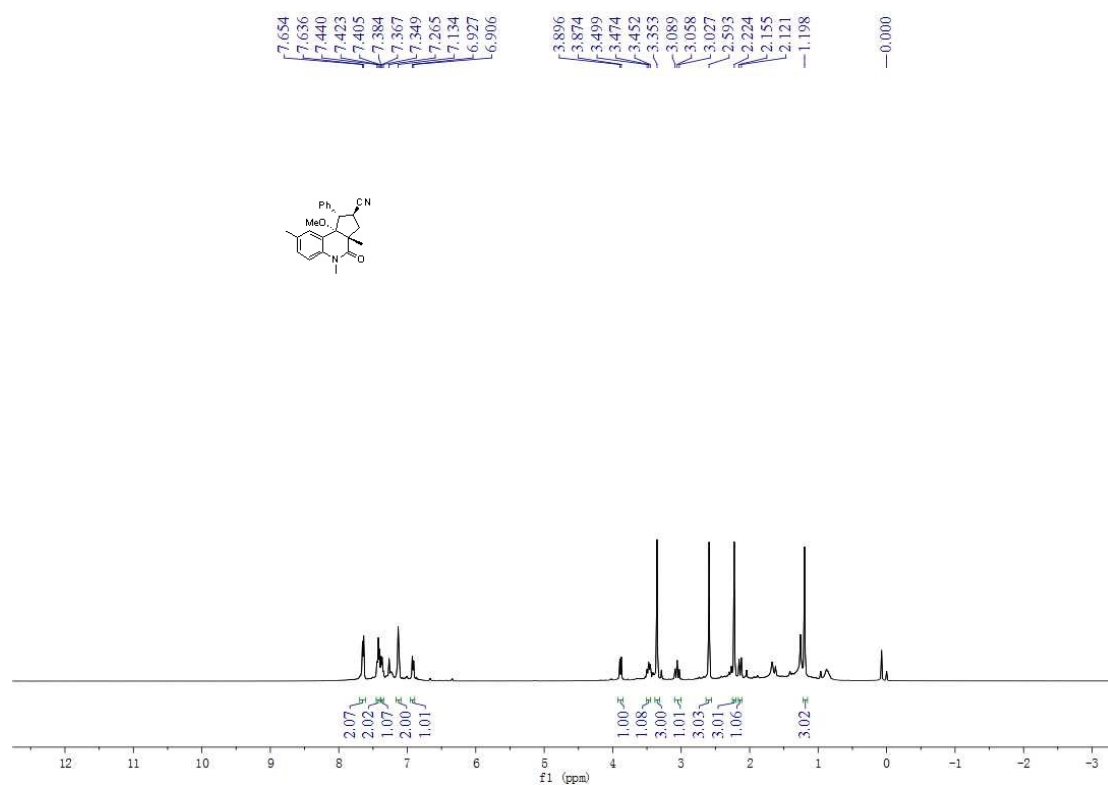
9b-Methoxy-3a,5-dimethyl-4-oxo-1-(pyridin-3-yl)-2,3,3a,4,5,9b-hexahydro-1H-cy

clopenta[c]quinoline-2-carbonitrile (4kaa):



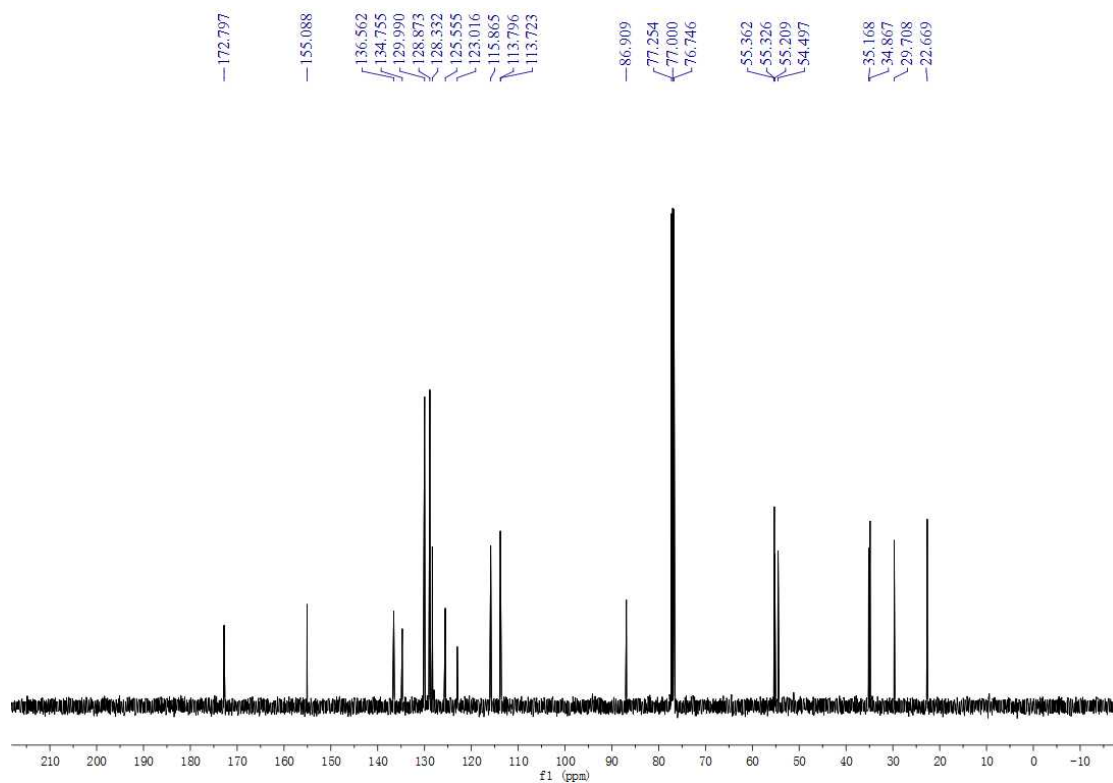
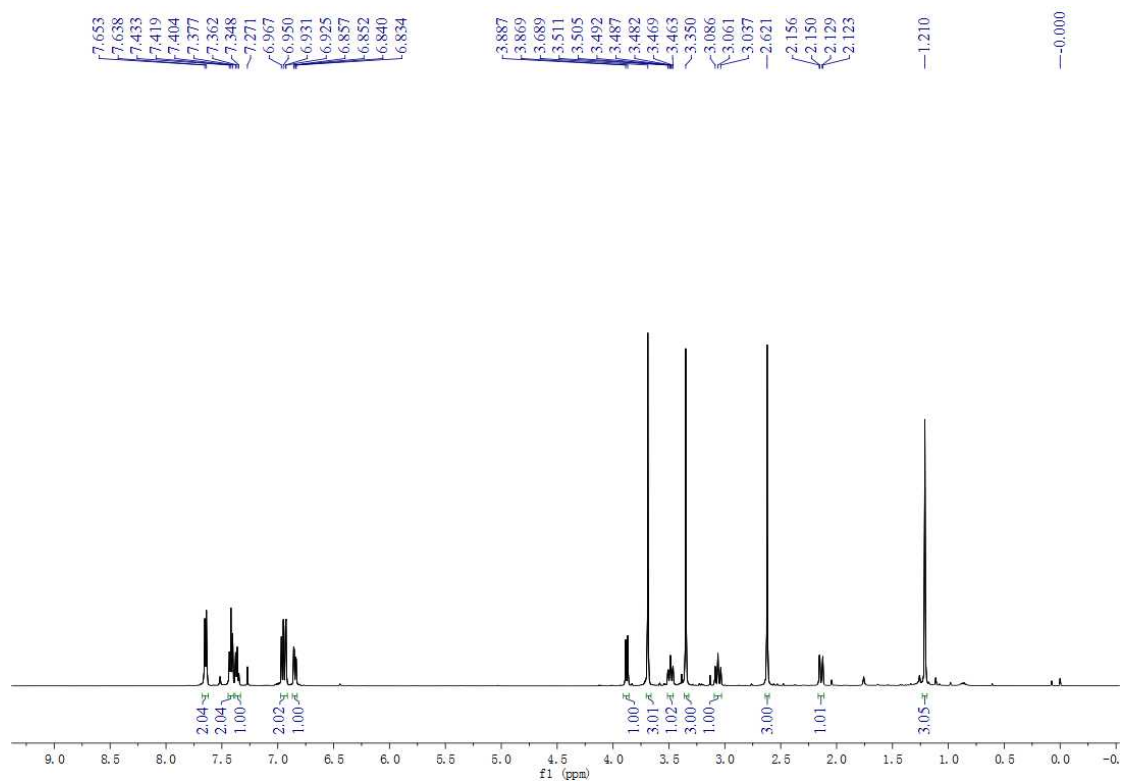
9b-Methoxy-3a,5,8-trimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-cyclop

enta[c]quinoline-2-carbonitrile (4maa):



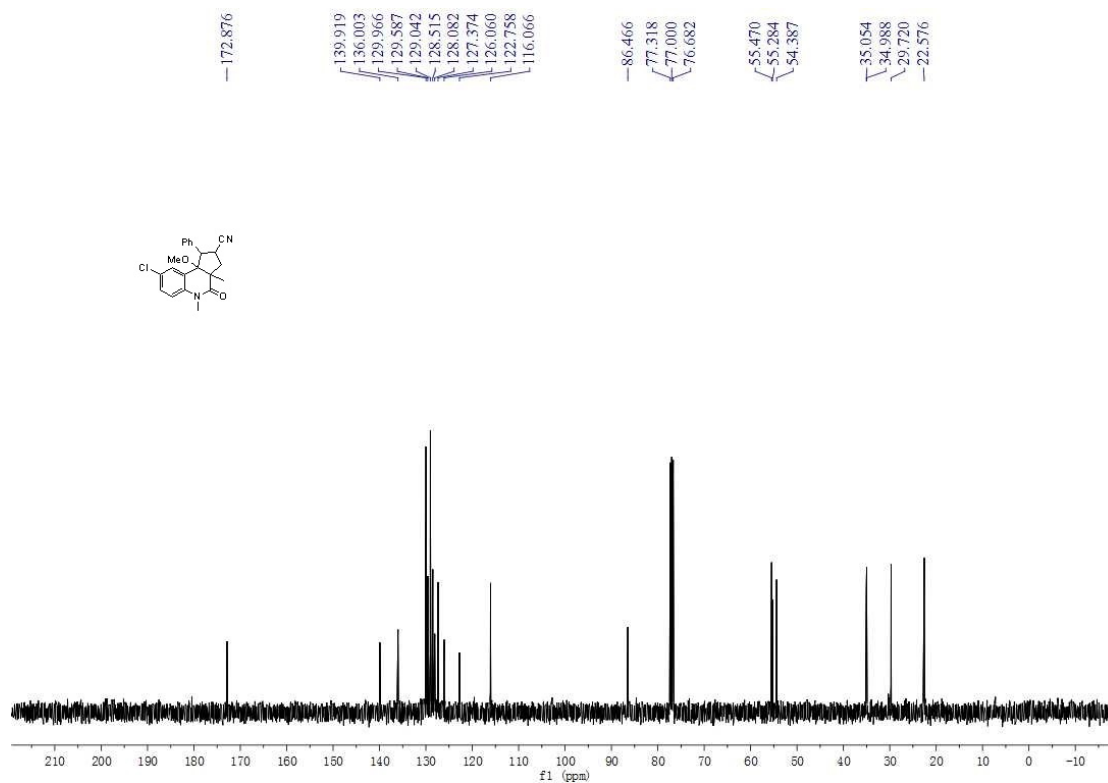
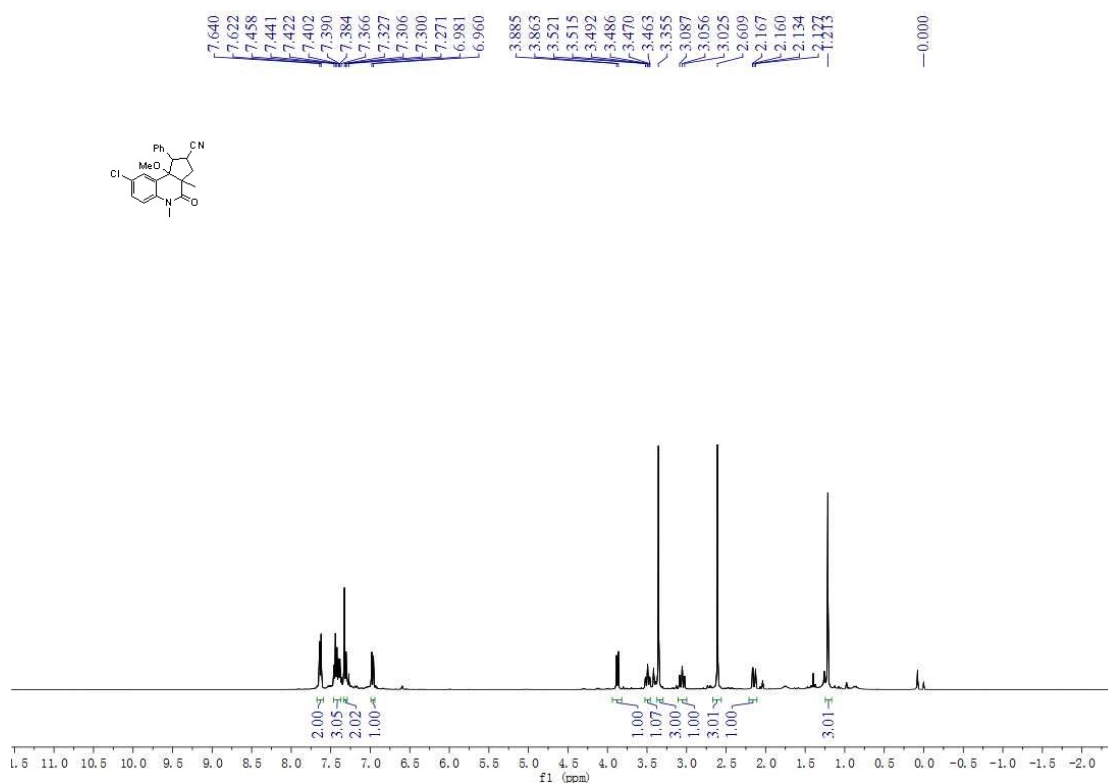
8,9b-Dimethoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclo

penta[*c*]quinoline-2-carbonitrile (4naa):



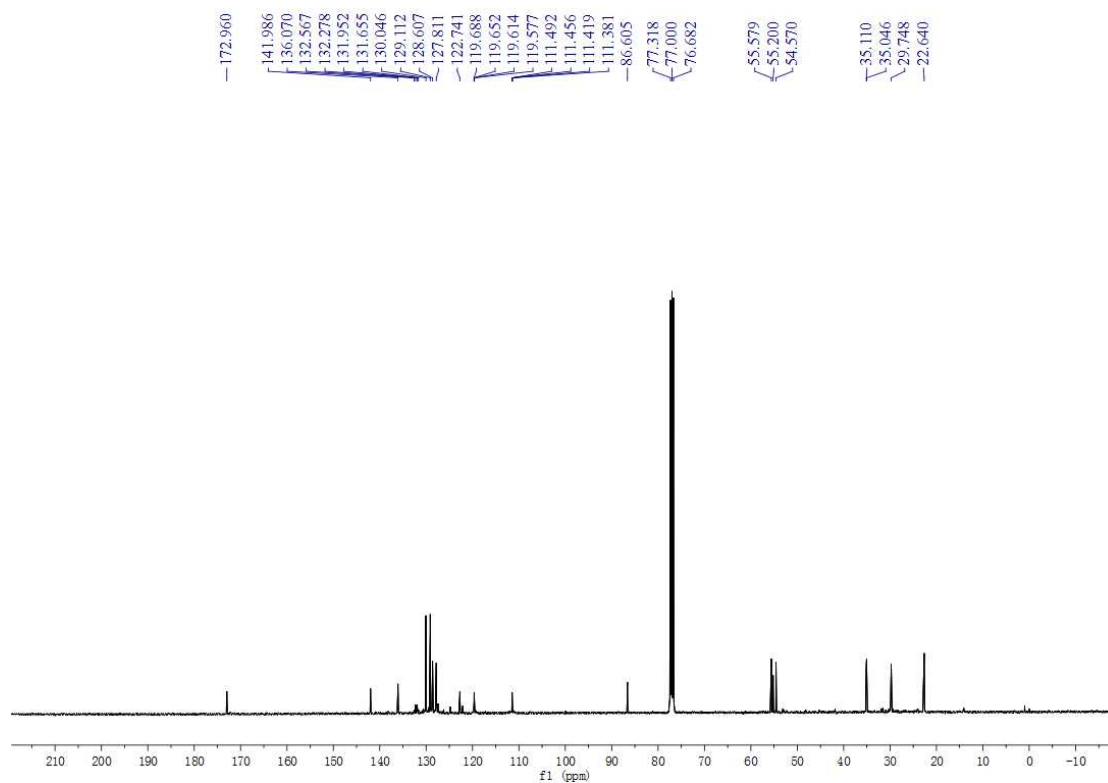
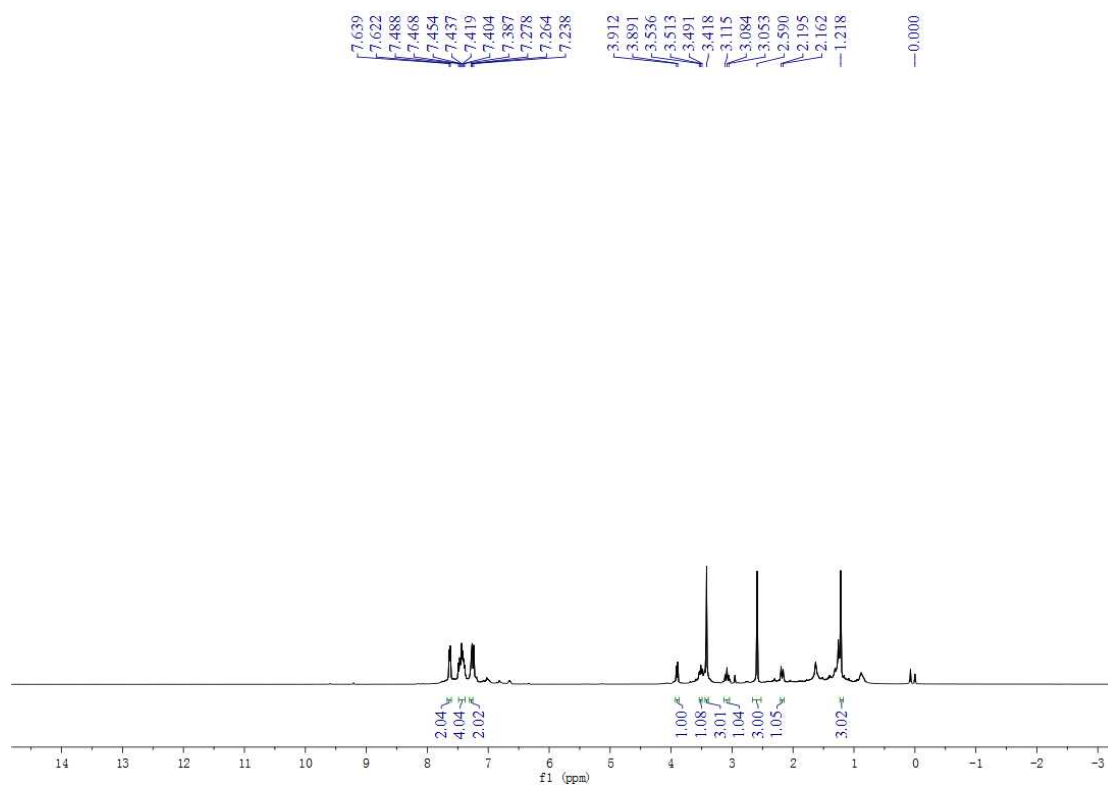
8-Chloro-9b-methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*

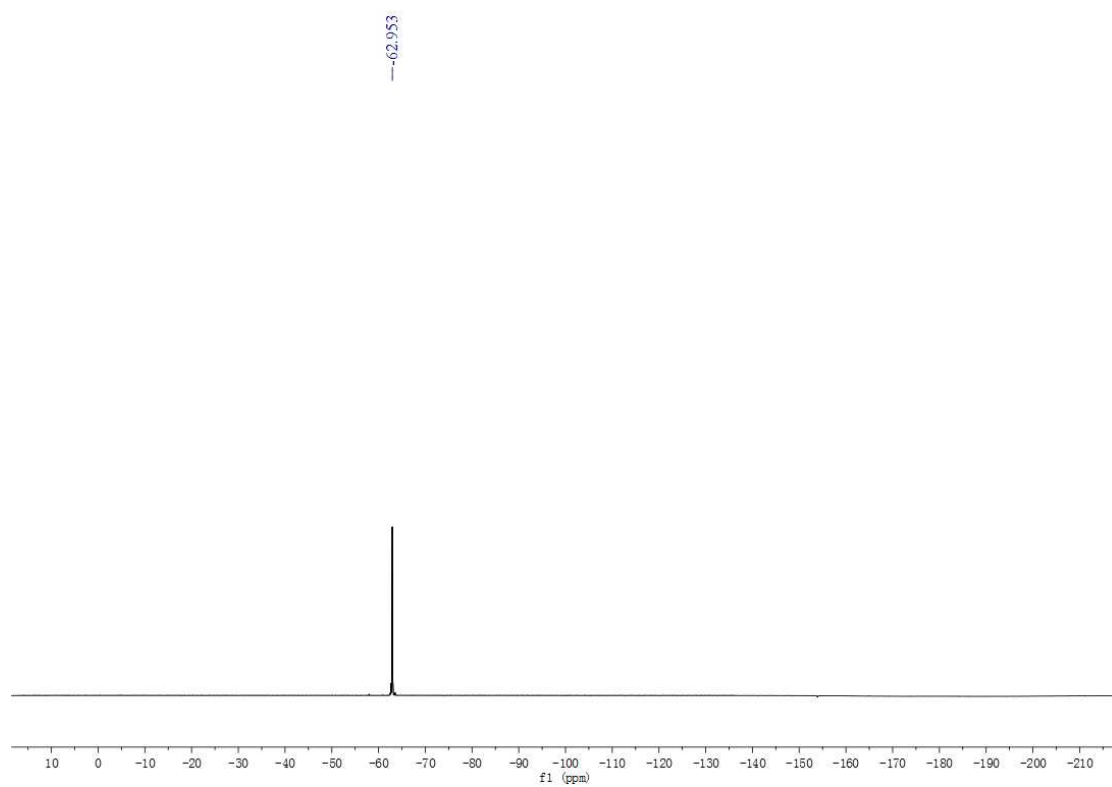
-cyclopenta[*c*]quinoline-2-carbonitrile (4oaa):



9b-Methoxy-3a,5-dimethyl-4-oxo-1-phenyl-7-(trifluoromethyl)-2,3,3a,4,5,9b-hexa

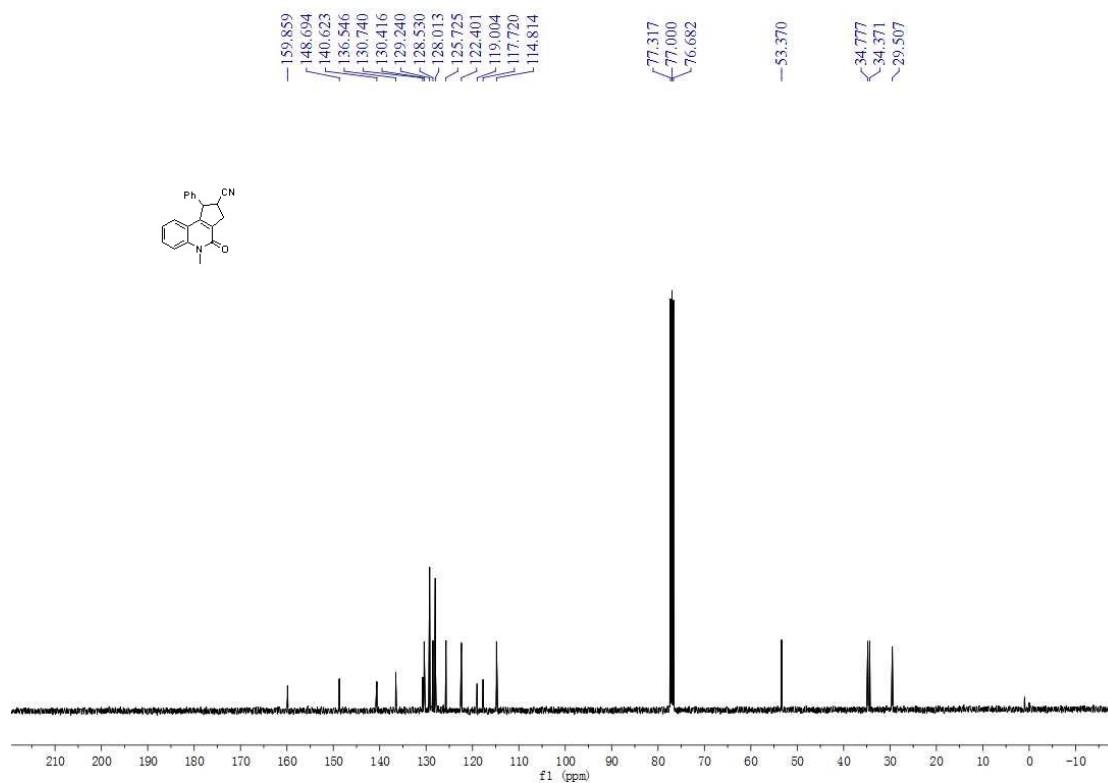
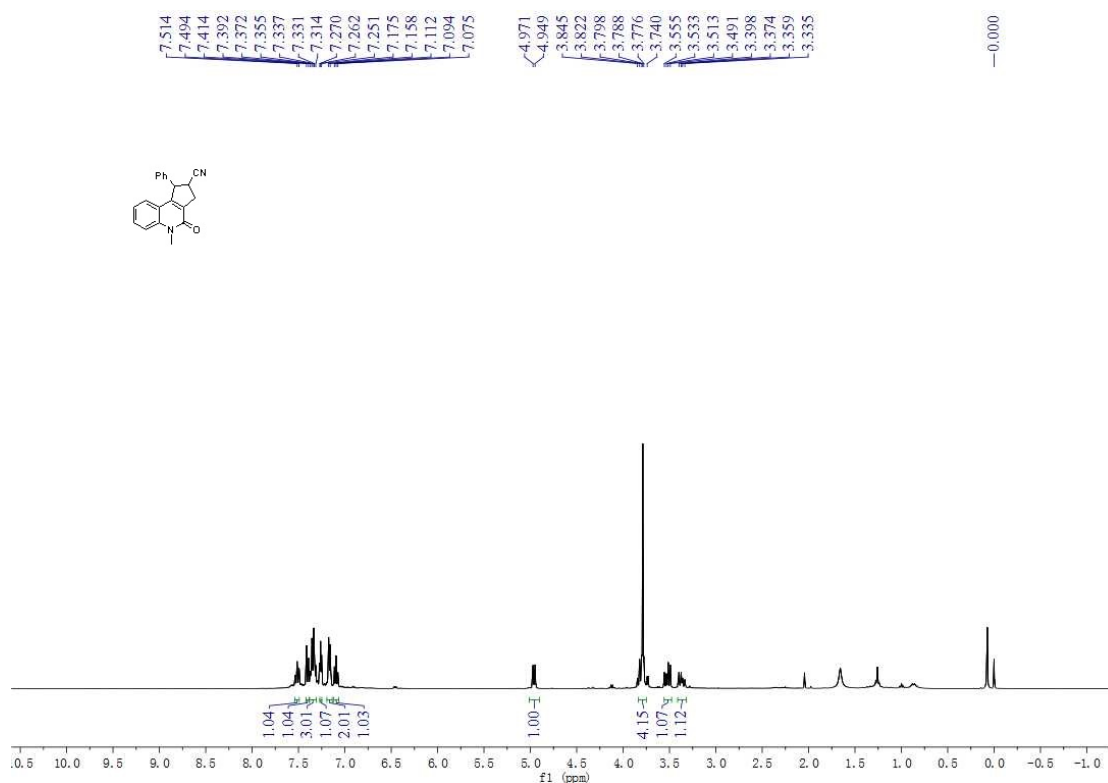
hydro-1*H*-cyclopenta[*c*]quinoline-2-carbonitrile(4paa):





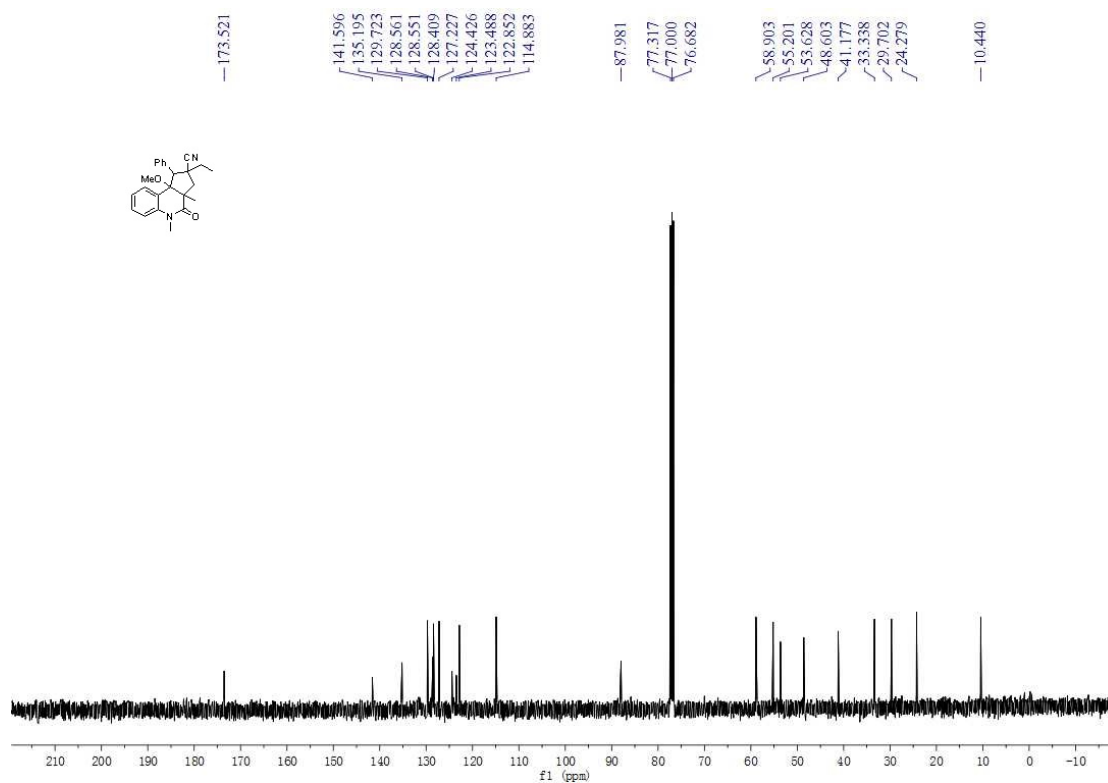
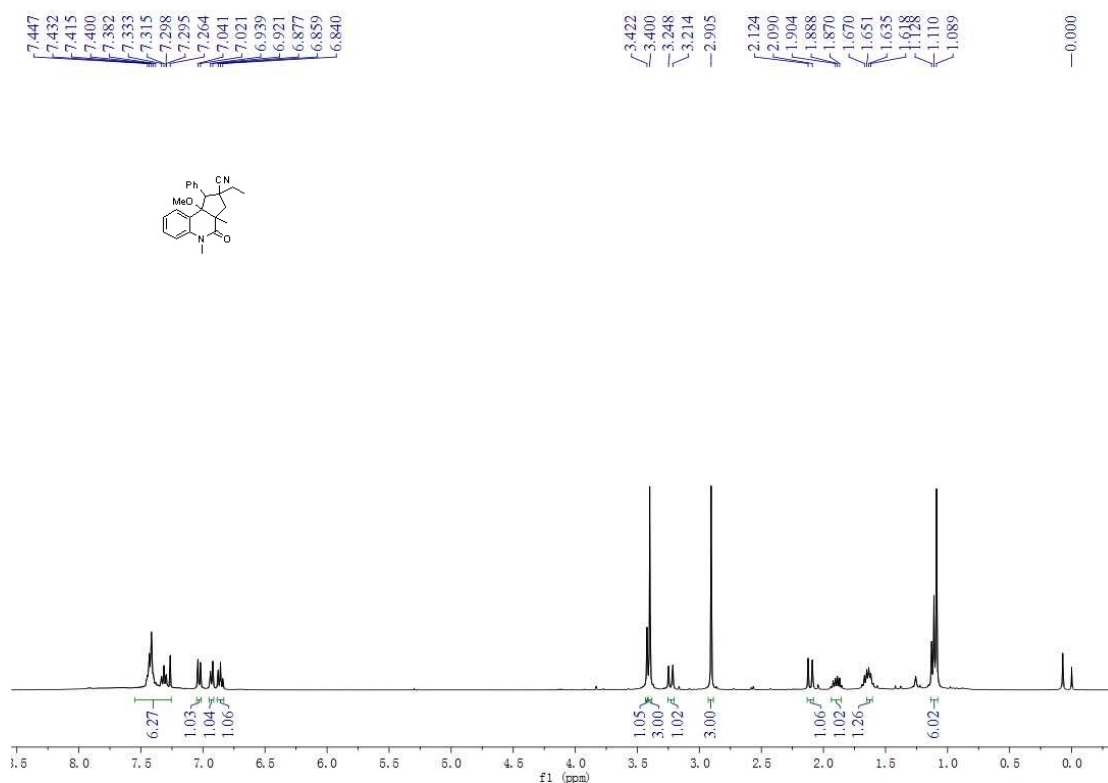
5-Methyl-4-oxo-1-phenyl-2,3,4,5-tetrahydro-1H-cyclopenta[c]quinoline-2-carbon

itrile (4qaa):



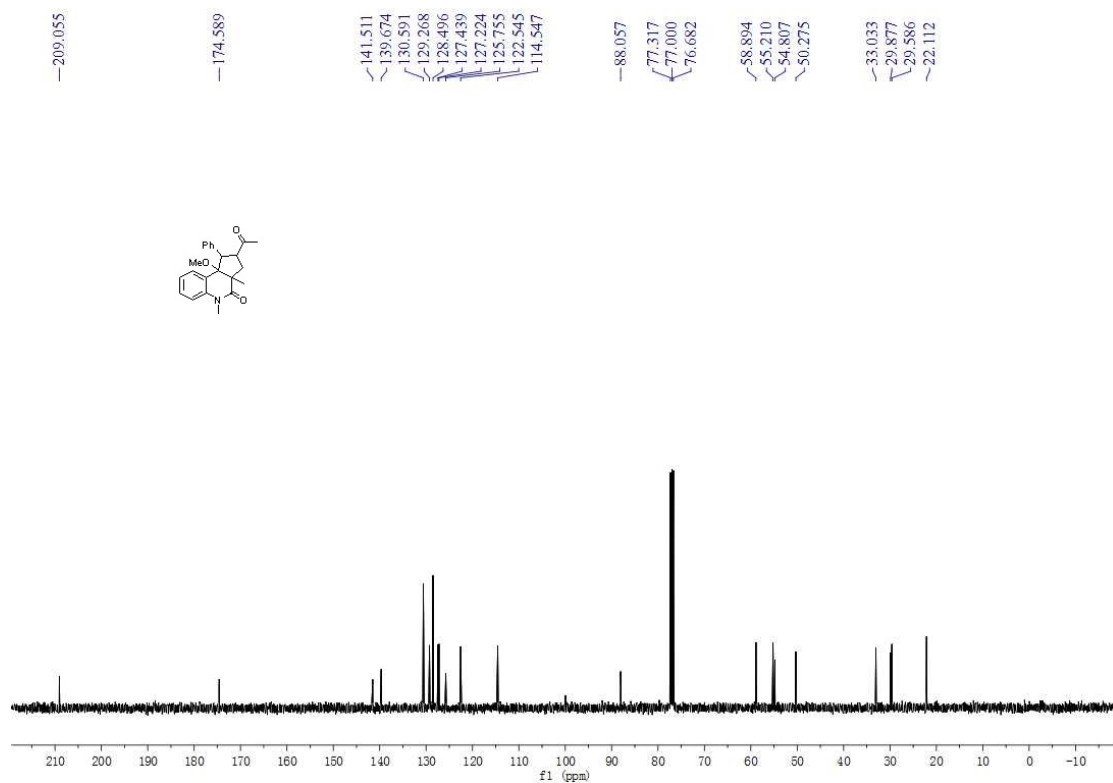
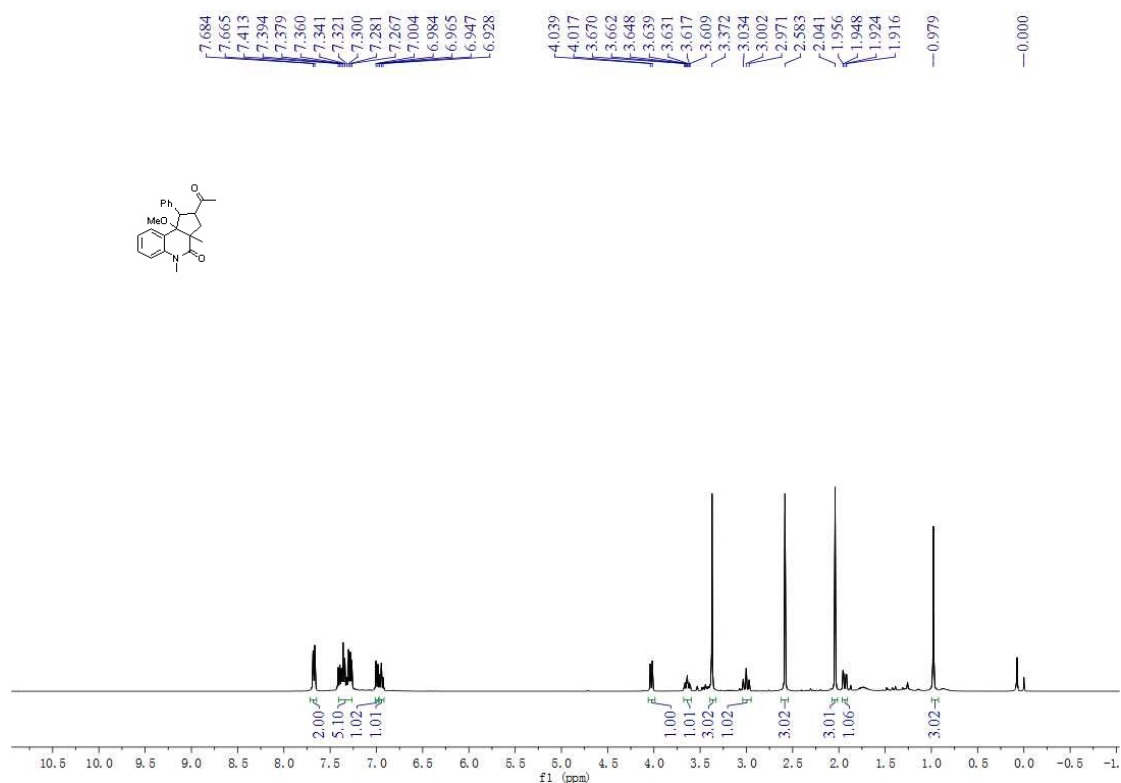
2-Ethyl-9b-methoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1H-c

yclopenta[c]quinoline-2-carbonitrile (4aba):



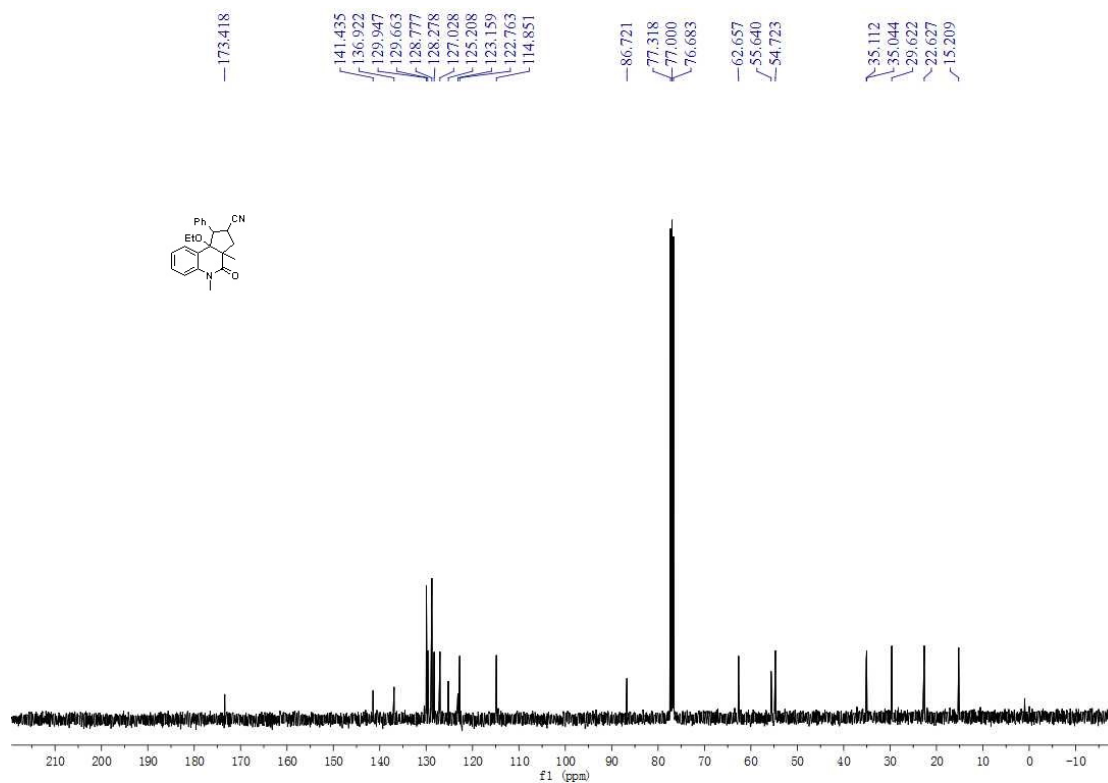
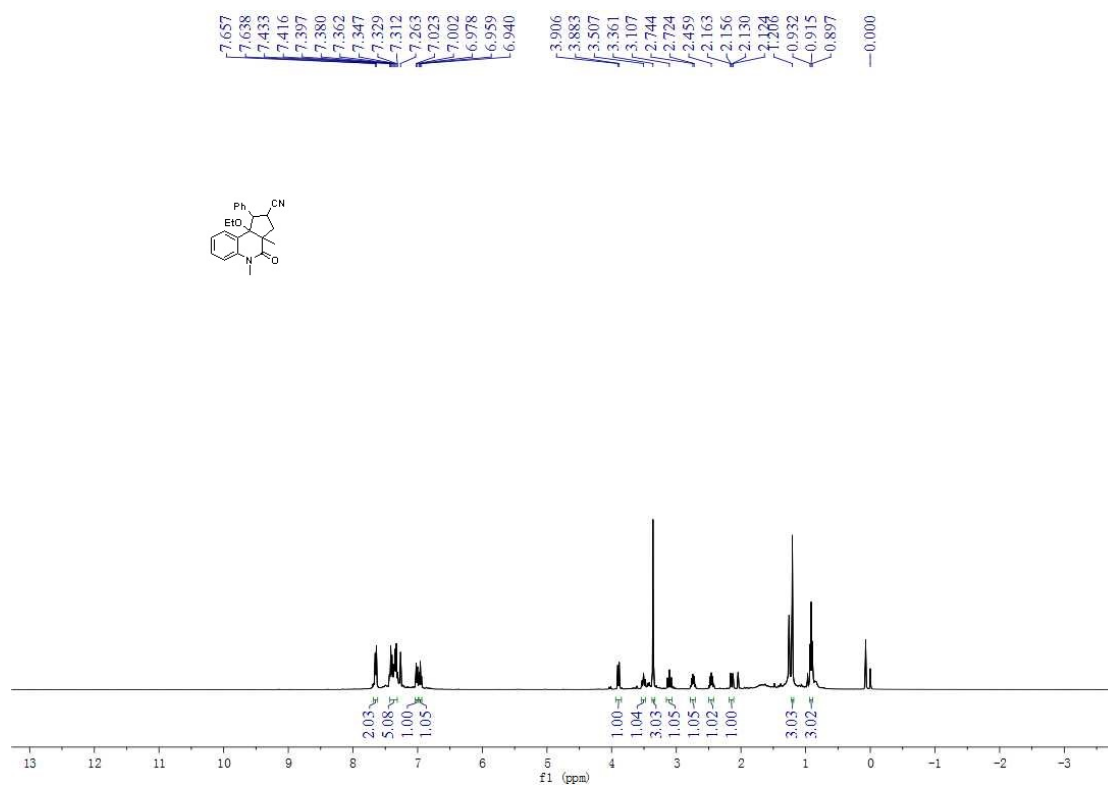
2-Acetyl-9b-methoxy-3a,5-dimethyl-1-phenyl-1,2,3,3a,5,9b-hexahydro-4H-cyclop

enta[c]quinolin-4-one (4ada):



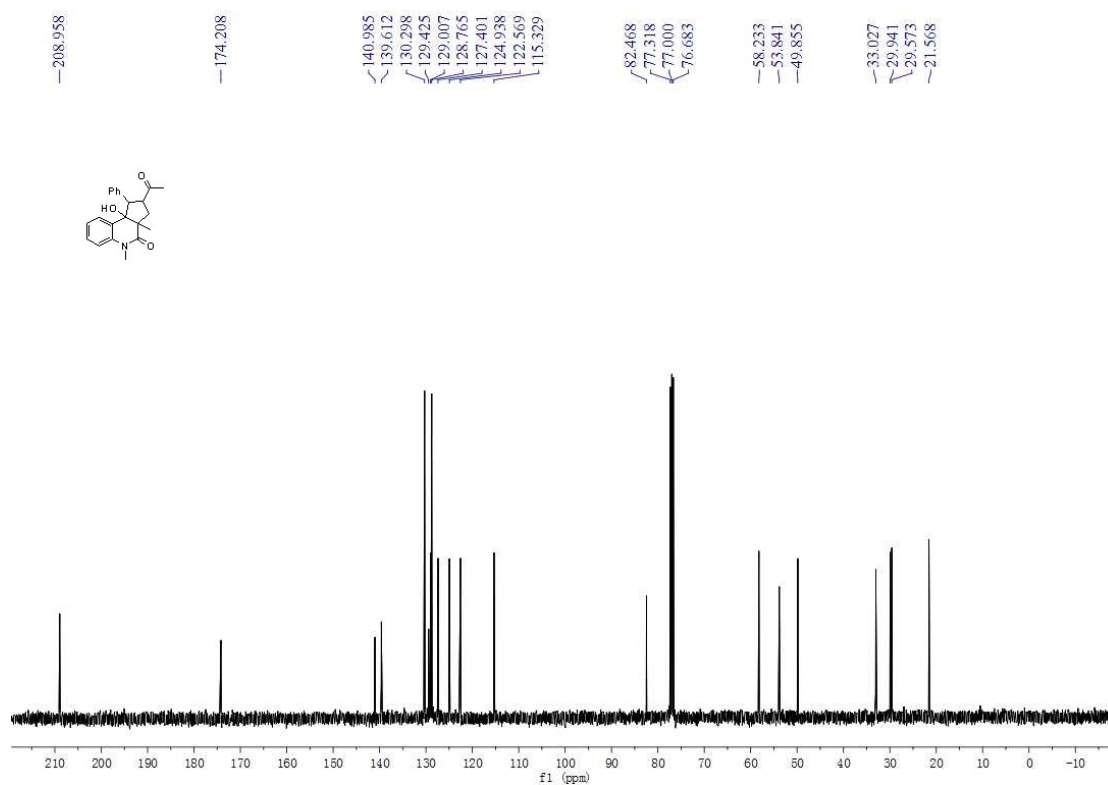
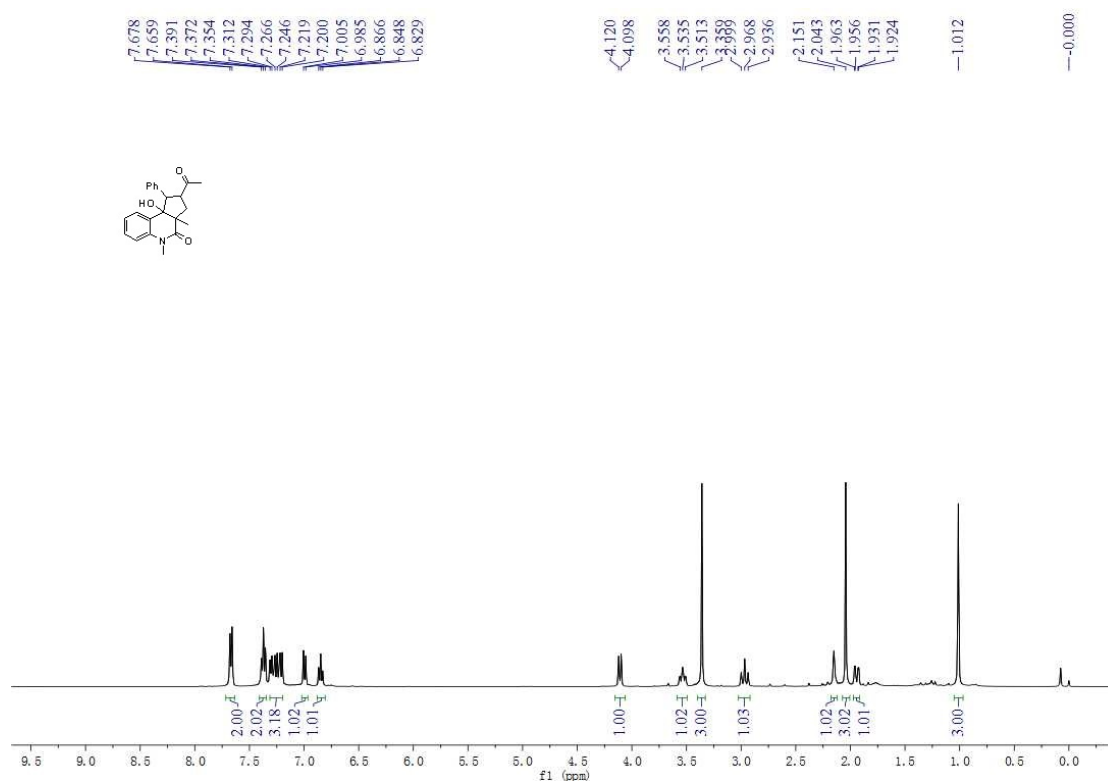
9b-Ethoxy-3a,5-dimethyl-4-oxo-1-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta

[c]quinoline-2-carbonitrile (4aab):

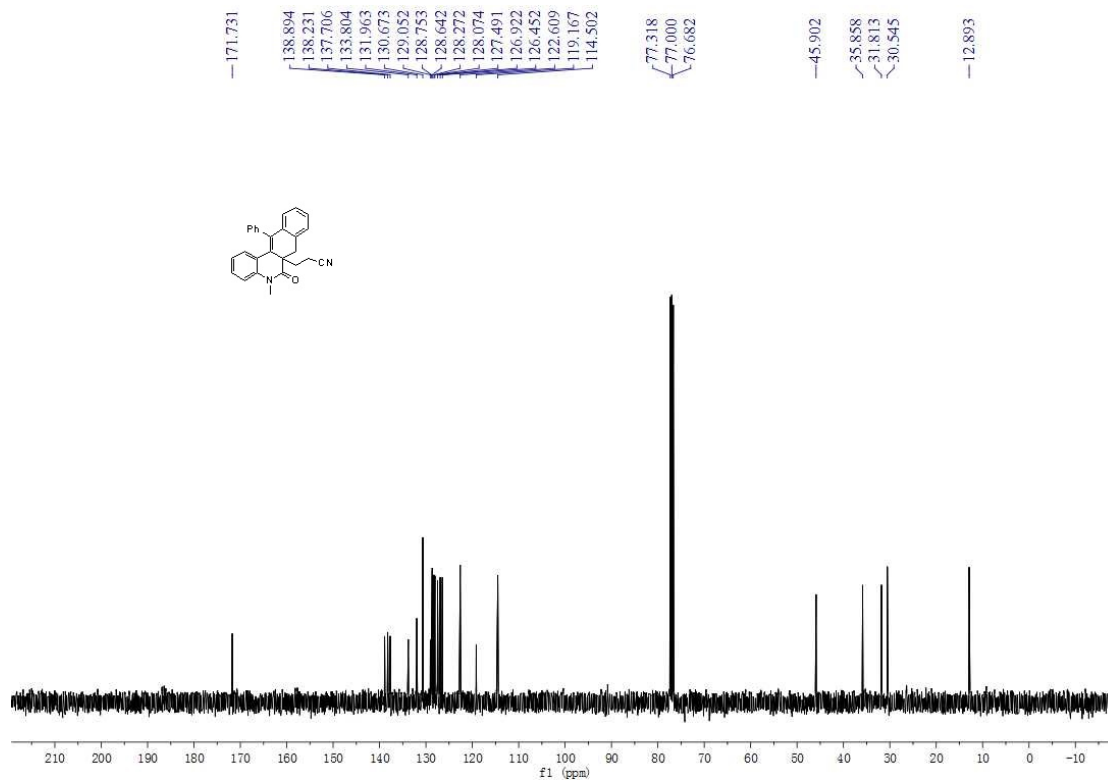
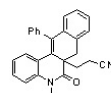


2-Acetyl-9b-hydroxy-3a,5-dimethyl-1-phenyl-1,2,3,3a,5,9b-hexahydro-4H-cyclop

enta[c]quinolin-4-one (4add):

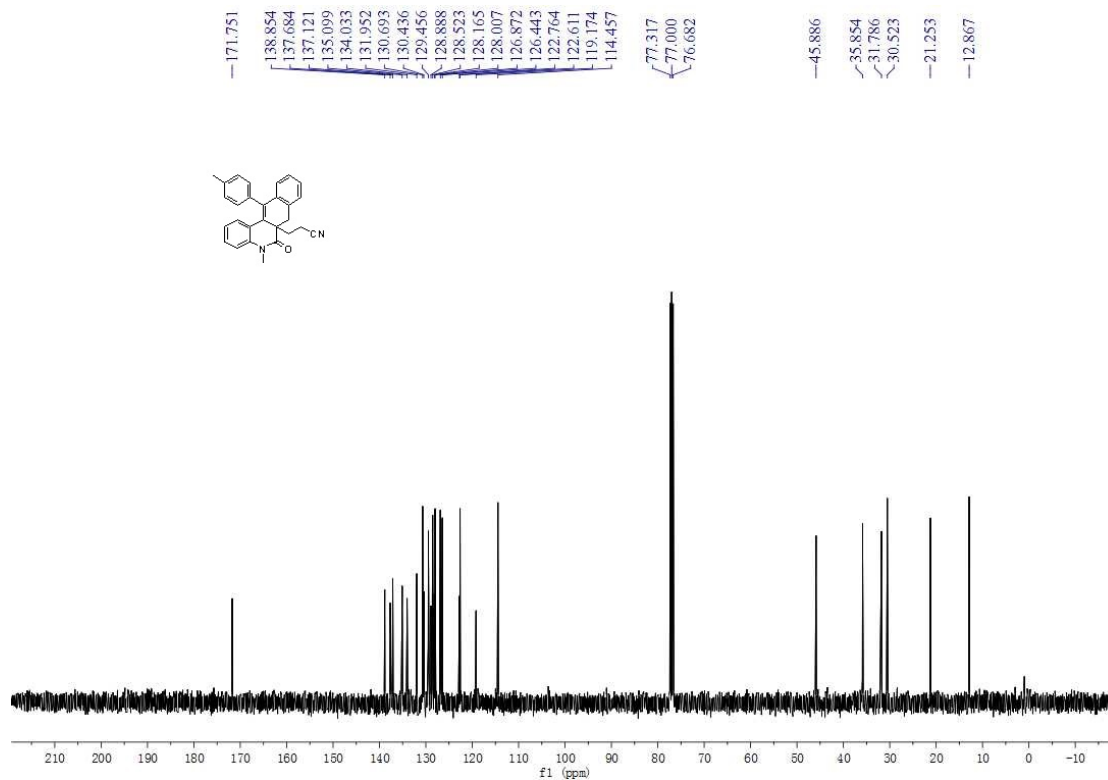
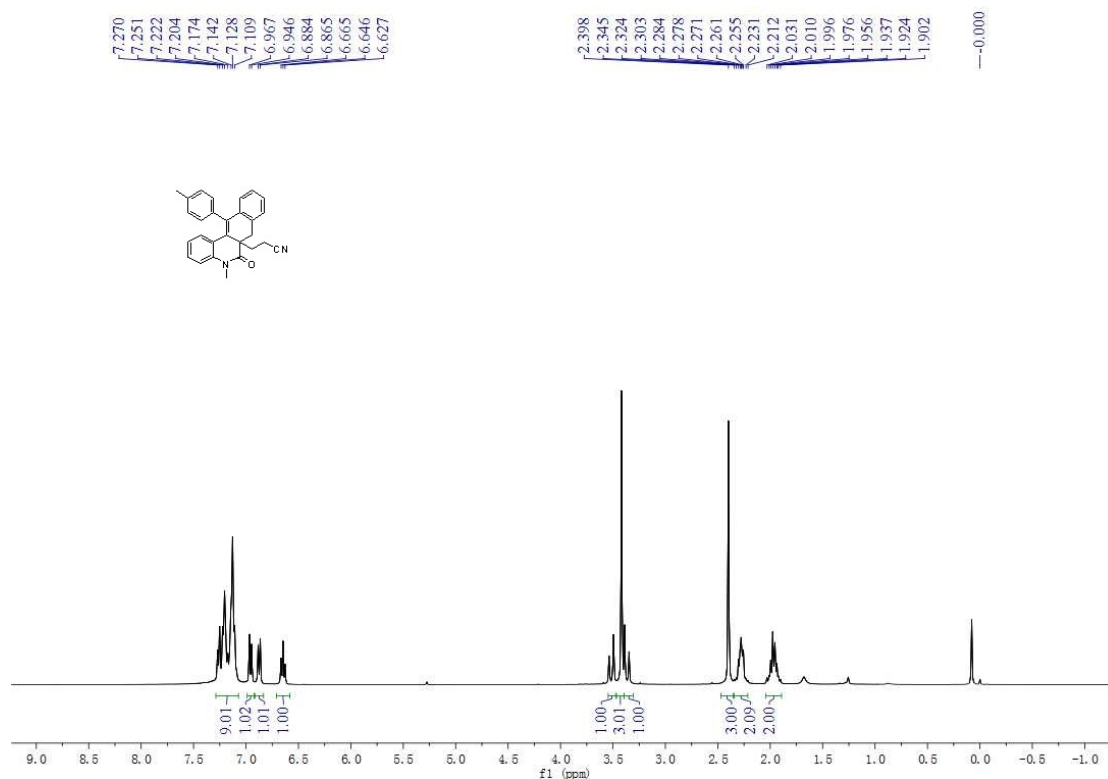


nenitrile (5ra):

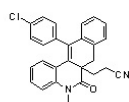
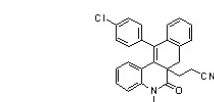


3-(5-Methyl-6-oxo-12-(p-tolyl)-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)prop

anenitrile (5sa):

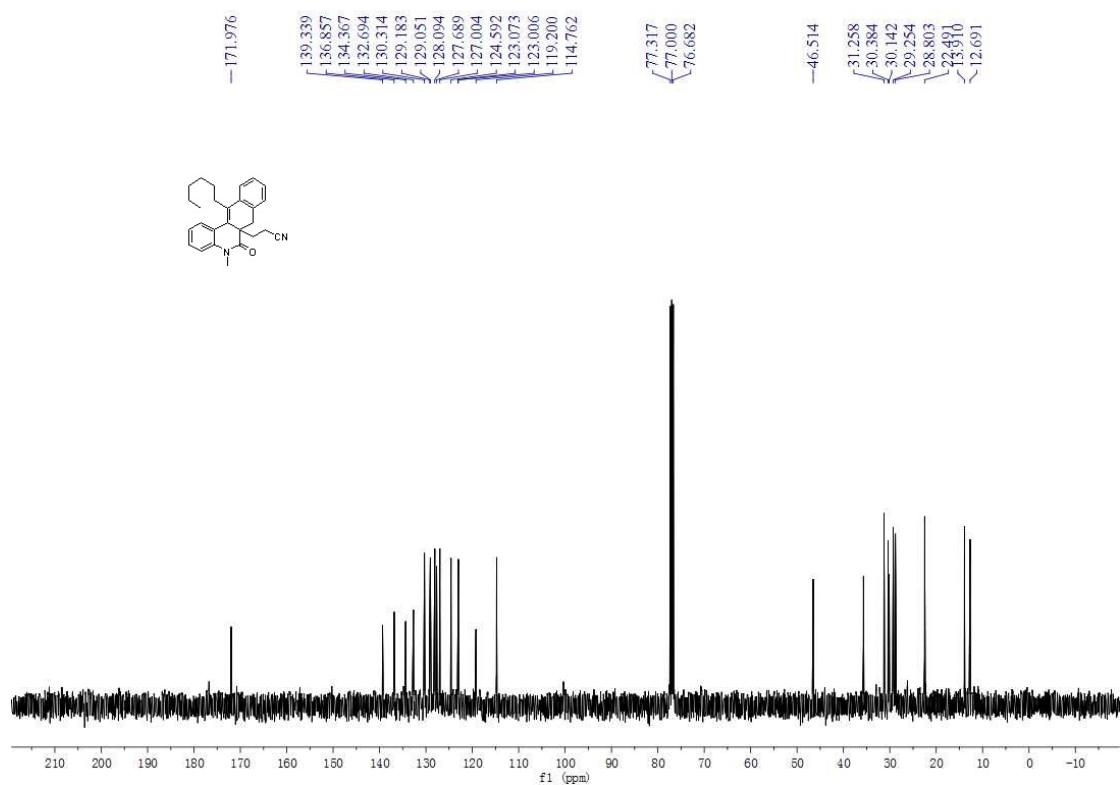
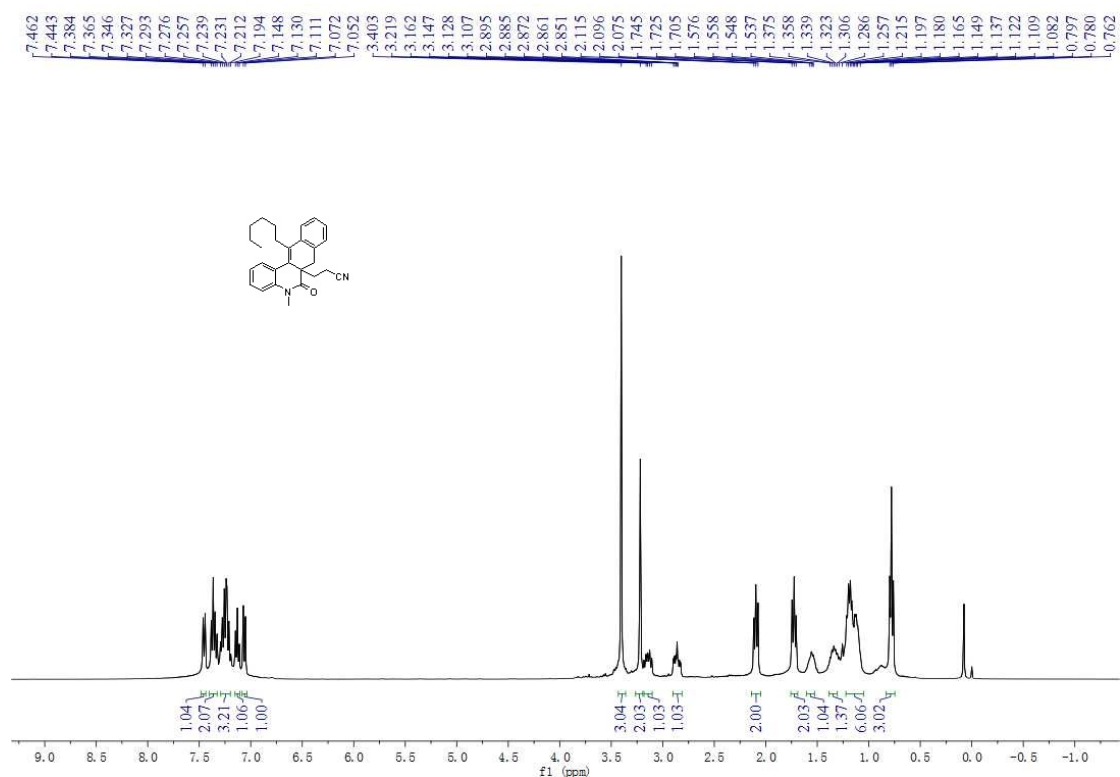


)-yl)propanenitrile (5ta):

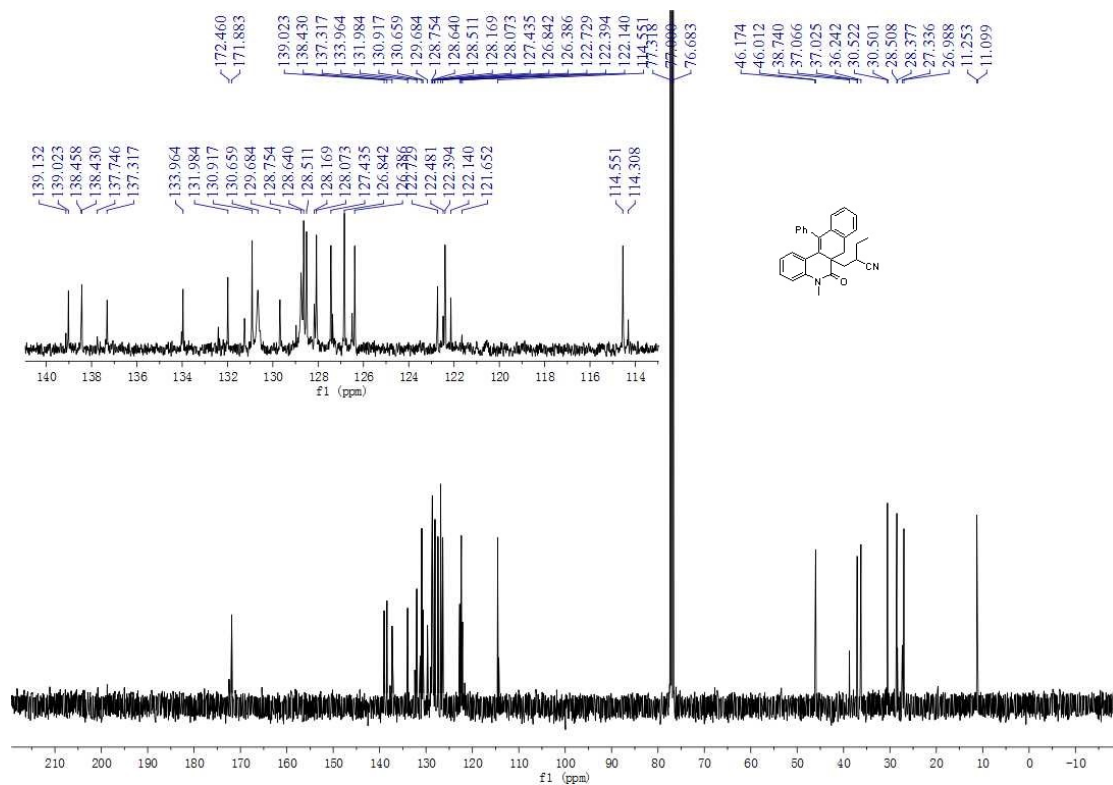
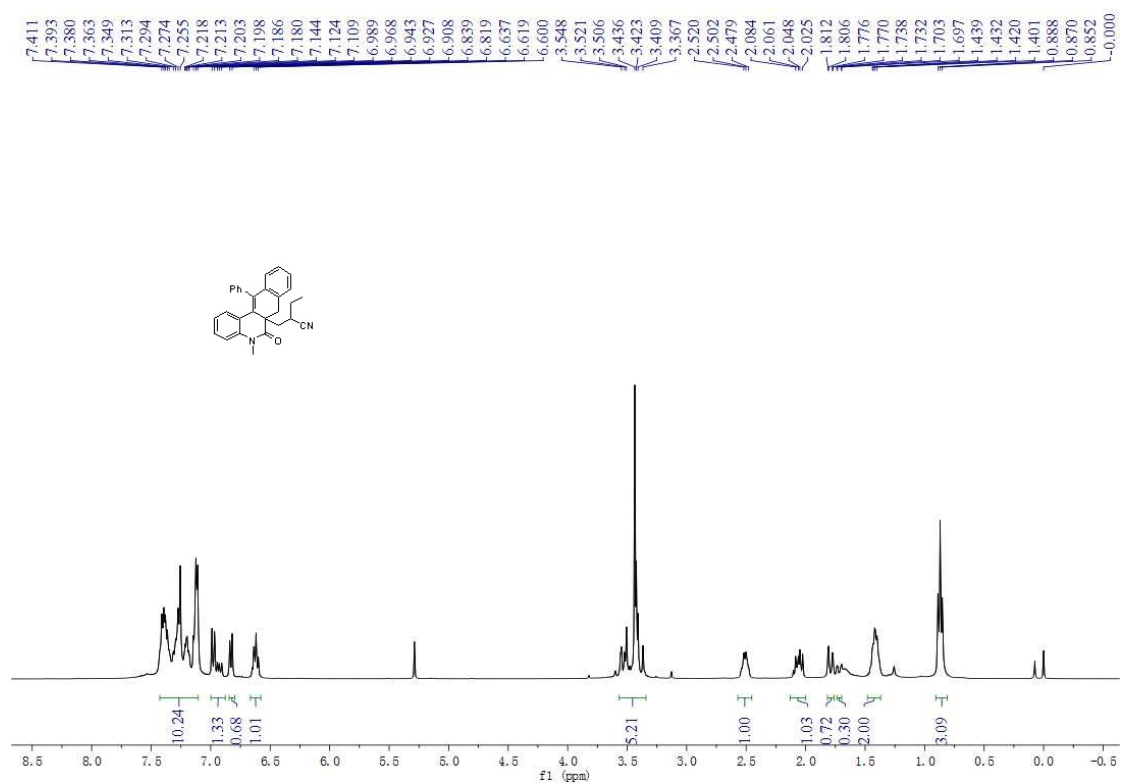


3-(12-Hexyl-5-methyl-6-oxo-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)propan

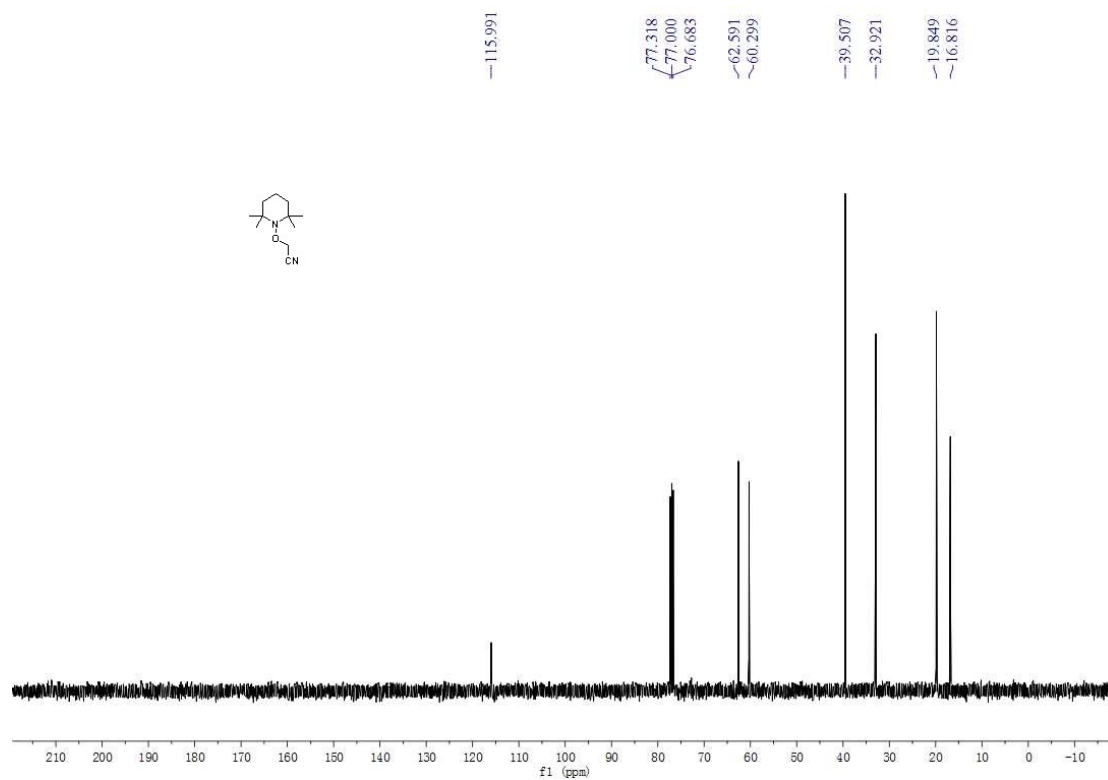
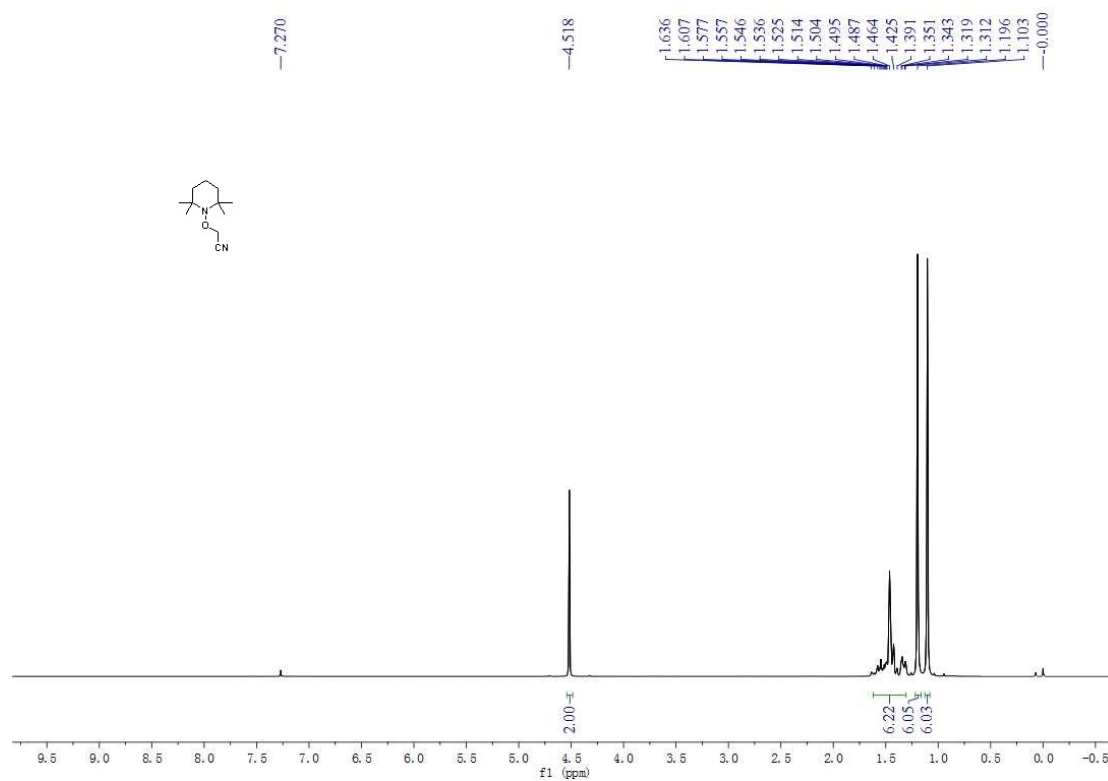
enitrile (5ua):



**2-((5-Methyl-6-oxo-12-phenyl-5,7-dihydrobenzo[j]phenanthridin-6a(6H)-yl)meth
yl)butanenitrile (5va):**



2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)acetonitrile (7):



(E) The X-ray single-crystal diffraction analysis of 4aaa

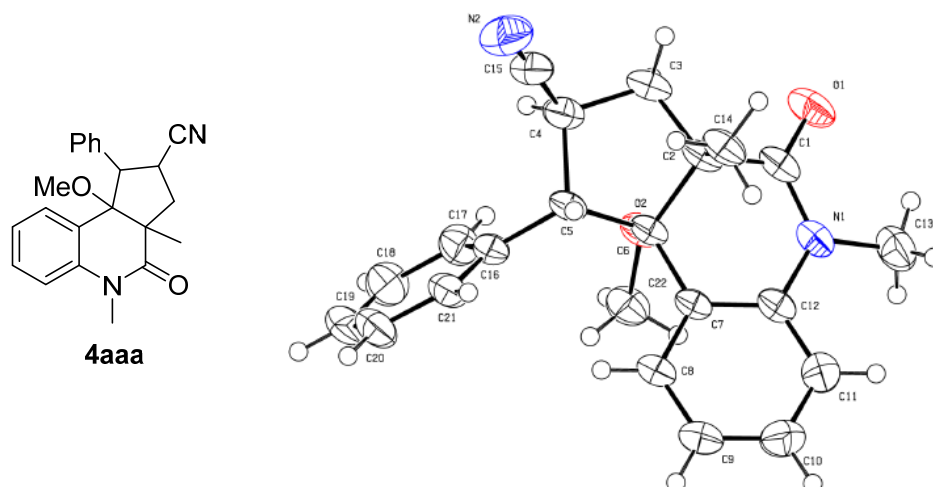


Table 1. Crystal data and structure refinement for ljh015.

Identification code	ljh015
Empirical formula	C ₂₂ H ₂₂ N ₂ O ₂
Formula weight	346.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbc _a
Unit cell dimensions	a = 15.792(3) Å alpha = 90 deg.

$b = 12.080(3) \text{ \AA}$ $\beta = 90 \text{ deg.}$

$c = 19.334(4) \text{ \AA}$ $\gamma = 90 \text{ deg.}$

Volume $3688.5(13) \text{ \AA}^3$

Z, Calculated density 8, 1.248 Mg/m³

Absorption coefficient 0.080 mm^{-1}

F(000) 1472

Crystal size $0.23 \times 0.22 \times 0.21 \text{ mm}$

Theta range for data collection $2.11 \text{ to } 27.41 \text{ deg.}$

Limiting indices $-18 \leq h \leq 20, -14 \leq k \leq 15, -24 \leq l \leq 22$

Reflections collected / unique 19704 / 4141 [$R(\text{int}) = 0.0678$]

Completeness to $\theta = 27.41$ 98.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9833 and 0.9817

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 4141 / 0 / 238

Goodness-of-fit on F^2 1.049

Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0556$, $wR_2 = 0.1371$

R indices (all data) $R_1 = 0.0822$, $wR_2 = 0.1612$

Largest diff. peak and hole 0.270 and -0.280 $e.\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ljh015.

U(eq) is defined as one third of the trace of the orthogonalized

U_{ij} tensor.

	x	y	z	U(eq)
N(1)	7580(1)	300(1)	3377(1)	42(1)
O(1)	8595(1)	-297(1)	2630(1)	57(1)
C(1)	8016(1)	349(2)	2764(1)	40(1)
O(2)	6553(1)	256(1)	2027(1)	39(1)
C(2)	7775(1)	1292(2)	2297(1)	37(1)
N(2)	8030(1)	3711(2)	646(1)	68(1)
C(3)	8026(1)	1147(2)	1540(1)	45(1)
C(4)	7382(1)	1892(2)	1150(1)	42(1)
C(5)	6651(1)	2196(2)	1673(1)	34(1)
C(6)	6796(1)	1347(1)	2261(1)	32(1)
C(7)	6468(1)	1562(1)	2978(1)	33(1)

C(8)	5773(1)	2233(2)	3126(1)	39(1)
C(9)	5486(1)	2350(2)	3798(1)	47(1)
C(10)	5899(1)	1813(2)	4326(1)	52(1)
C(11)	6596(1)	1149(2)	4190(1)	47(1)
C(12)	6881(1)	1013(2)	3519(1)	37(1)
C(13)	7859(1)	-490(2)	3902(1)	56(1)
C(14)	8180(1)	2353(2)	2592(1)	45(1)
C(15)	7755(1)	2908(2)	865(1)	49(1)
C(16)	5799(1)	2268(2)	1315(1)	37(1)
C(17)	5475(1)	1406(2)	913(1)	48(1)
C(18)	4700(1)	1522(2)	581(1)	58(1)
C(19)	4257(1)	2497(2)	630(1)	64(1)
C(20)	4577(1)	3362(2)	1007(1)	60(1)
C(21)	5346(1)	3253(2)	1348(1)	45(1)
C(22)	5731(1)	-128(2)	2224(1)	47(1)

Table 3. Bond lengths [Å] and angles [deg] for ljh015.

N(1)-C(1)	1.372(2)
N(1)-C(12)	1.427(2)
N(1)-C(13)	1.461(3)
O(1)-C(1)	1.230(2)
C(1)-C(2)	1.504(3)
O(2)-C(22)	1.431(2)
O(2)-C(6)	1.445(2)
C(2)-C(3)	1.525(3)
C(2)-C(14)	1.542(3)
C(2)-C(6)	1.549(2)
N(2)-C(15)	1.144(3)
C(3)-C(4)	1.555(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(15)	1.468(3)
C(4)-C(5)	1.578(2)
C(4)-H(4)	0.9800

C(5)-C(16)	1.516(2)
C(5)-C(6)	1.549(2)
C(5)-H(5)	0.9800
C(6)-C(7)	1.502(2)
C(7)-C(8)	1.395(2)
C(7)-C(12)	1.401(3)
C(8)-C(9)	1.384(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.373(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.387(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.383(3)
C(11)-H(11)	0.9300
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(16)-C(21)	1.389(3)
C(16)-C(17)	1.395(3)

C(17)-C(18)	1.389(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.372(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.371(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.388(3)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(1)-N(1)-C(12)	121.90(15)
C(1)-N(1)-C(13)	118.48(16)
C(12)-N(1)-C(13)	119.60(16)
O(1)-C(1)-N(1)	121.85(18)
O(1)-C(1)-C(2)	122.87(18)
N(1)-C(1)-C(2)	115.15(15)
C(22)-O(2)-C(6)	116.92(14)
C(1)-C(2)-C(3)	115.04(15)
C(1)-C(2)-C(14)	107.57(15)

C(3)-C(2)-C(14)	110.04(16)
C(1)-C(2)-C(6)	108.20(14)
C(3)-C(2)-C(6)	102.81(14)
C(14)-C(2)-C(6)	113.29(14)
C(2)-C(3)-C(4)	103.23(14)
C(2)-C(3)-H(3A)	111.1
C(4)-C(3)-H(3A)	111.1
C(2)-C(3)-H(3B)	111.1
C(4)-C(3)-H(3B)	111.1
H(3A)-C(3)-H(3B)	109.1
C(15)-C(4)-C(3)	113.79(16)
C(15)-C(4)-C(5)	109.88(16)
C(3)-C(4)-C(5)	107.58(14)
C(15)-C(4)-H(4)	108.5
C(3)-C(4)-H(4)	108.5
C(5)-C(4)-H(4)	108.5
C(16)-C(5)-C(6)	120.33(14)
C(16)-C(5)-C(4)	111.73(14)
C(6)-C(5)-C(4)	102.02(14)
C(16)-C(5)-H(5)	107.4
C(6)-C(5)-H(5)	107.4
C(4)-C(5)-H(5)	107.4

O(2)-C(6)-C(7)	110.81(14)
O(2)-C(6)-C(2)	103.90(13)
C(7)-C(6)-C(2)	108.08(14)
O(2)-C(6)-C(5)	109.55(13)
C(7)-C(6)-C(5)	120.76(14)
C(2)-C(6)-C(5)	102.07(13)
C(8)-C(7)-C(12)	119.20(16)
C(8)-C(7)-C(6)	124.21(16)
C(12)-C(7)-C(6)	116.55(15)
C(9)-C(8)-C(7)	120.70(18)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(10)-C(9)-C(8)	119.57(18)
C(10)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2
C(9)-C(10)-C(11)	120.68(19)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	120.27(19)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(7)	119.57(17)

C(11)-C(12)-N(1)	120.26(17)
C(7)-C(12)-N(1)	120.16(16)
N(1)-C(13)-H(13A)	109.5
N(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
N(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(2)-C(14)-H(14A)	109.5
C(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(2)-C(15)-C(4)	178.5(2)
C(21)-C(16)-C(17)	118.42(17)
C(21)-C(16)-C(5)	118.99(16)
C(17)-C(16)-C(5)	122.45(17)
C(18)-C(17)-C(16)	120.3(2)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(19)-C(18)-C(17)	120.2(2)

C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	120.2(2)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(21)	120.1(2)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(20)-C(21)-C(16)	120.6(2)
C(20)-C(21)-H(21)	119.7
C(16)-C(21)-H(21)	119.7
O(2)-C(22)-H(22A)	109.5
O(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ljh015.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
N(1)	30(1)	44(1)	53(1)	1(1)	-3(1)	8(1)
O(1)	36(1)	56(1)	80(1)	-1(1)	6(1)	17(1)
C(1)	22(1)	39(1)	59(1)	-7(1)	-3(1)	2(1)
O(2)	26(1)	37(1)	54(1)	-8(1)	2(1)	-5(1)
C(2)	19(1)	38(1)	53(1)	-5(1)	1(1)	0(1)
N(2)	65(1)	72(1)	66(1)	8(1)	21(1)	-8(1)
C(3)	25(1)	51(1)	60(1)	-5(1)	9(1)	3(1)
C(4)	30(1)	51(1)	46(1)	-7(1)	6(1)	-1(1)
C(5)	21(1)	38(1)	44(1)	-4(1)	2(1)	-2(1)
C(6)	19(1)	33(1)	44(1)	-6(1)	1(1)	0(1)
C(7)	21(1)	36(1)	43(1)	-4(1)	1(1)	-2(1)
C(8)	25(1)	42(1)	49(1)	-2(1)	4(1)	3(1)

C(9)	35(1)	51(1)	55(1)	-5(1)	10(1)	6(1)
C(10)	50(1)	58(1)	48(1)	-5(1)	11(1)	1(1)
C(11)	45(1)	50(1)	45(1)	1(1)	-2(1)	3(1)
C(12)	26(1)	38(1)	48(1)	-5(1)	-2(1)	-1(1)
C(13)	45(1)	54(1)	68(1)	9(1)	-7(1)	10(1)
C(14)	24(1)	44(1)	66(1)	-4(1)	-2(1)	-6(1)
C(15)	37(1)	62(1)	49(1)	0(1)	10(1)	0(1)
C(16)	24(1)	46(1)	39(1)	2(1)	2(1)	-4(1)
C(17)	40(1)	52(1)	51(1)	0(1)	-5(1)	-9(1)
C(18)	42(1)	76(2)	55(1)	-2(1)	-8(1)	-19(1)
C(19)	28(1)	106(2)	56(1)	-5(1)	-7(1)	1(1)
C(20)	35(1)	86(2)	59(1)	-7(1)	-3(1)	19(1)
C(21)	30(1)	57(1)	49(1)	-5(1)	1(1)	6(1)
C(22)	32(1)	47(1)	62(1)	-1(1)	-2(1)	-13(1)

—

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ljh015.

	x	y	z	U(eq)
H(3A)	7975	380	1398	54
H(3B)	8603	1393	1461	54
H(4)	7138	1463	768	51
H(5)	6778	2931	1860	41
H(8)	5499	2606	2769	46
H(9)	5016	2790	3893	57
H(10)	5709	1895	4778	62
H(11)	6872	793	4552	56
H(13A)	8281	-971	3708	84
H(13B)	7384	-923	4055	84
H(13C)	8095	-97	4288	84
H(14A)	7964	2487	3048	67
H(14B)	8045	2969	2299	67

H(14C)	8783	2263	2613	67
H(17)	5779	751	869	57
H(18)	4481	938	324	69
H(19)	3738	2570	407	76
H(20)	4278	4024	1034	72
H(21)	5560	3844	1602	54
H(22A)	5745	-378	2695	71
H(22B)	5565	-728	1928	71
H(22C)	5330	466	2181	71

Table 6. Torsion angles [deg] for ljh015.

C(12)-N(1)-C(1)-O(1)	-176.75(17)
C(13)-N(1)-C(1)-O(1)	4.7(3)
C(12)-N(1)-C(1)-C(2)	7.3(2)
C(13)-N(1)-C(1)-C(2)	-171.28(17)
O(1)-C(1)-C(2)-C(3)	23.4(3)
N(1)-C(1)-C(2)-C(3)	-160.68(15)
O(1)-C(1)-C(2)-C(14)	-99.6(2)
N(1)-C(1)-C(2)-C(14)	76.32(18)
O(1)-C(1)-C(2)-C(6)	137.65(18)
N(1)-C(1)-C(2)-C(6)	-46.4(2)
C(1)-C(2)-C(3)-C(4)	155.13(15)
C(14)-C(2)-C(3)-C(4)	-83.21(17)
C(6)-C(2)-C(3)-C(4)	37.76(18)
C(2)-C(3)-C(4)-C(15)	108.04(18)
C(2)-C(3)-C(4)-C(5)	-13.94(19)
C(15)-C(4)-C(5)-C(16)	90.74(19)
C(3)-C(4)-C(5)-C(16)	-144.89(16)
C(15)-C(4)-C(5)-C(6)	-139.43(16)

C(3)-C(4)-C(5)-C(6)	-15.06(18)
C(22)-O(2)-C(6)-C(7)	37.2(2)
C(22)-O(2)-C(6)-C(2)	153.06(15)
C(22)-O(2)-C(6)-C(5)	-98.49(17)
C(1)-C(2)-C(6)-O(2)	-56.41(18)
C(3)-C(2)-C(6)-O(2)	65.70(17)
C(14)-C(2)-C(6)-O(2)	-175.58(15)
C(1)-C(2)-C(6)-C(7)	61.36(18)
C(3)-C(2)-C(6)-C(7)	-176.53(15)
C(14)-C(2)-C(6)-C(7)	-57.8(2)
C(1)-C(2)-C(6)-C(5)	-170.33(14)
C(3)-C(2)-C(6)-C(5)	-48.22(17)
C(14)-C(2)-C(6)-C(5)	70.50(18)
C(16)-C(5)-C(6)-O(2)	52.49(19)
C(4)-C(5)-C(6)-O(2)	-71.78(15)
C(16)-C(5)-C(6)-C(7)	-78.1(2)
C(4)-C(5)-C(6)-C(7)	157.67(14)
C(16)-C(5)-C(6)-C(2)	162.15(15)
C(4)-C(5)-C(6)-C(2)	37.89(16)
O(2)-C(6)-C(7)-C(8)	-103.91(19)
C(2)-C(6)-C(7)-C(8)	142.86(17)
C(5)-C(6)-C(7)-C(8)	26.1(2)

O(2)-C(6)-C(7)-C(12)	73.82(18)
C(2)-C(6)-C(7)-C(12)	-39.4(2)
C(5)-C(6)-C(7)-C(12)	-156.17(15)
C(12)-C(7)-C(8)-C(9)	-0.6(3)
C(6)-C(7)-C(8)-C(9)	177.04(17)
C(7)-C(8)-C(9)-C(10)	1.0(3)
C(8)-C(9)-C(10)-C(11)	-0.5(3)
C(9)-C(10)-C(11)-C(12)	-0.4(3)
C(10)-C(11)-C(12)-C(7)	0.8(3)
C(10)-C(11)-C(12)-N(1)	-177.90(18)
C(8)-C(7)-C(12)-C(11)	-0.3(3)
C(6)-C(7)-C(12)-C(11)	-178.15(16)
C(8)-C(7)-C(12)-N(1)	178.44(16)
C(6)-C(7)-C(12)-N(1)	0.6(2)
C(1)-N(1)-C(12)-C(11)	-163.28(18)
C(13)-N(1)-C(12)-C(11)	15.3(3)
C(1)-N(1)-C(12)-C(7)	18.0(3)
C(13)-N(1)-C(12)-C(7)	-163.48(18)
C(3)-C(4)-C(15)-N(2)	-142(10)
C(5)-C(4)-C(15)-N(2)	-21(10)
C(6)-C(5)-C(16)-C(21)	118.86(19)
C(4)-C(5)-C(16)-C(21)	-121.63(18)

C(6)-C(5)-C(16)-C(17)	-65.5(2)
C(4)-C(5)-C(16)-C(17)	54.1(2)
C(21)-C(16)-C(17)-C(18)	-2.6(3)
C(5)-C(16)-C(17)-C(18)	-178.32(17)
C(16)-C(17)-C(18)-C(19)	1.6(3)
C(17)-C(18)-C(19)-C(20)	0.1(4)
C(18)-C(19)-C(20)-C(21)	-0.8(4)
C(19)-C(20)-C(21)-C(16)	-0.2(3)
C(17)-C(16)-C(21)-C(20)	1.9(3)
C(5)-C(16)-C(21)-C(20)	177.77(18)

Symmetry transformations used to generate equivalent atoms: