

Efficient Construction of Pyrrolo[1',2':1,2]azocino[4,5-*c*]quinolines via Cascade Cycloaddition and Annulation Reaction

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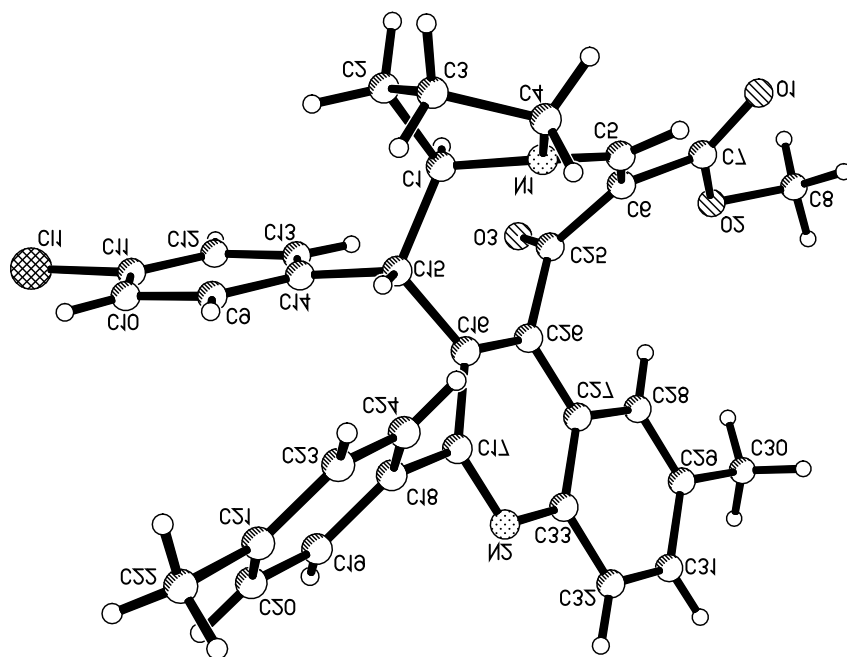


Fig. 1 The single crystal structure of the compound **1e**

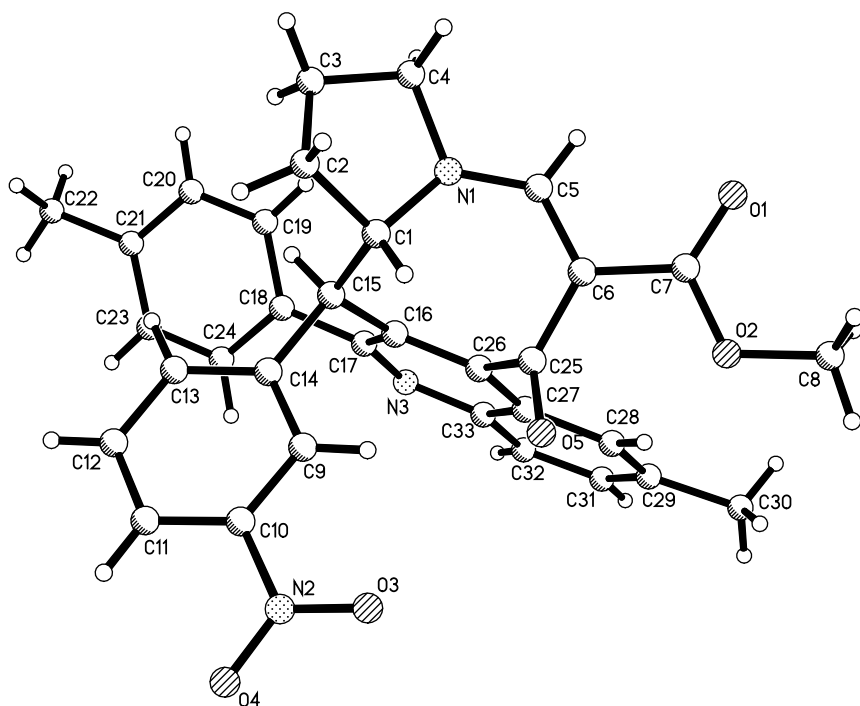


Fig. 2 The single crystal structure of the compound **1i**

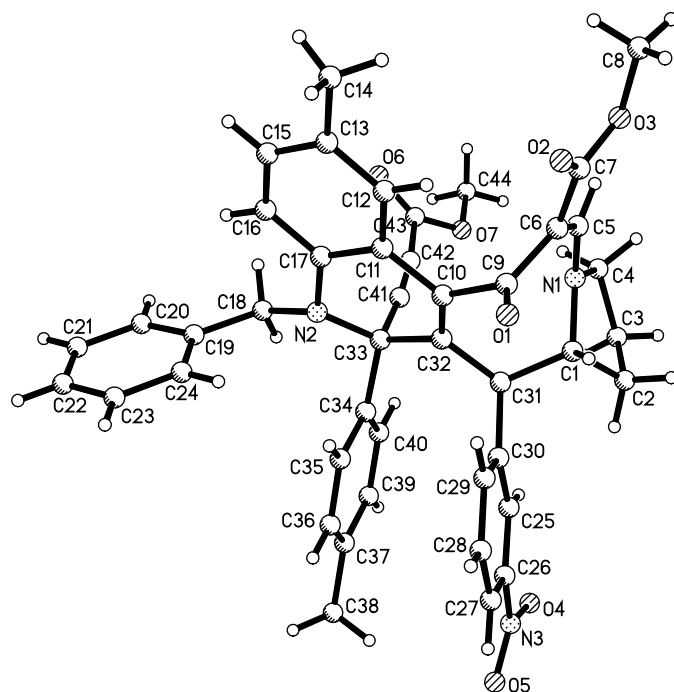


Fig. 3 The single crystal structure of the compound **2f**

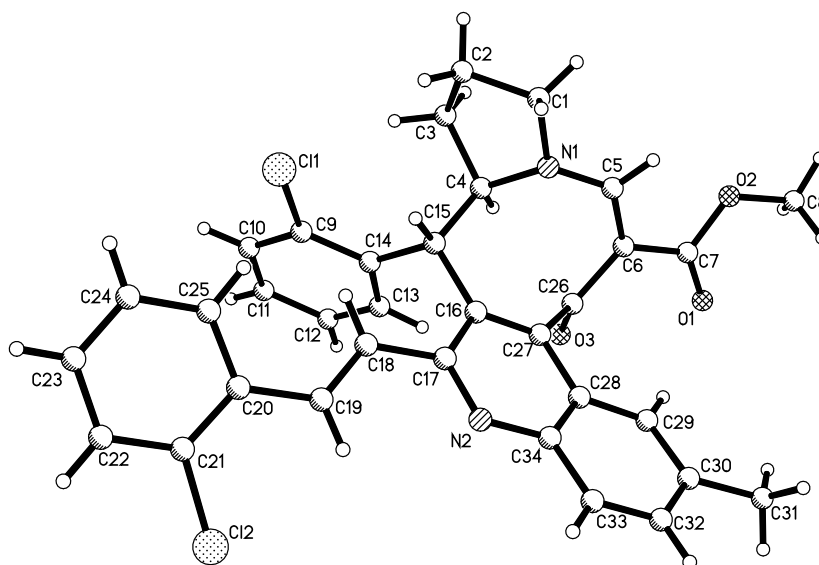


Fig. 3 The single crystal structure of the compound **3f**

Experimental section

1. General procedure for the preparation of

hexahydropyrrolo[1',2':1,2]azocino-[4,5-c]quinolines 1a-1k: To a round flask was added L-proline (0.5 mmol), isatin (0.5 mmol), chalcone (0.5 mmol), and methanol (10.0 mL). The mixture was refluxed for two hours. The solvent was removed by rotatory evaporation at reduced pressure. Then, methyl propiolate (0.6 mmol) and acetonitrile (10.0 mL) was added. The mixture was refluxed for eight hours. After removing the solvent, the residue was subjected to column chromatography with light petroleum and ethyl acetate (V/V = 5:1) as eluent to give the pure product for analysis.

2. General procedure for the preparation of octahydropyrrolo[1',2':1,2]azocino[4,5-c]-

quinolines 2a-2p: To a round flask was added L-proline (0.5 mmol), isatin (0.5 mmol), chalcone (0.5 mmol), and methanol (10.0 mL). The mixture was refluxed for two hours. The solvent was removed by rotatory evaporation at reduced pressure. Then, methyl propiolate (1.2 mmol) and acetonitrile (10.0 mL) was added. The mixture was refluxed for twenty-four hours. After removing the solvent, the residue was subjected to column chromatography with light petroleum and ethyl acetate (V/V = 5:1) as eluent to give the pure product for analysis.

3. General procedure for the preparation of hexahydropyrrolo[1',2':1,2]azocino[4,5-c]-

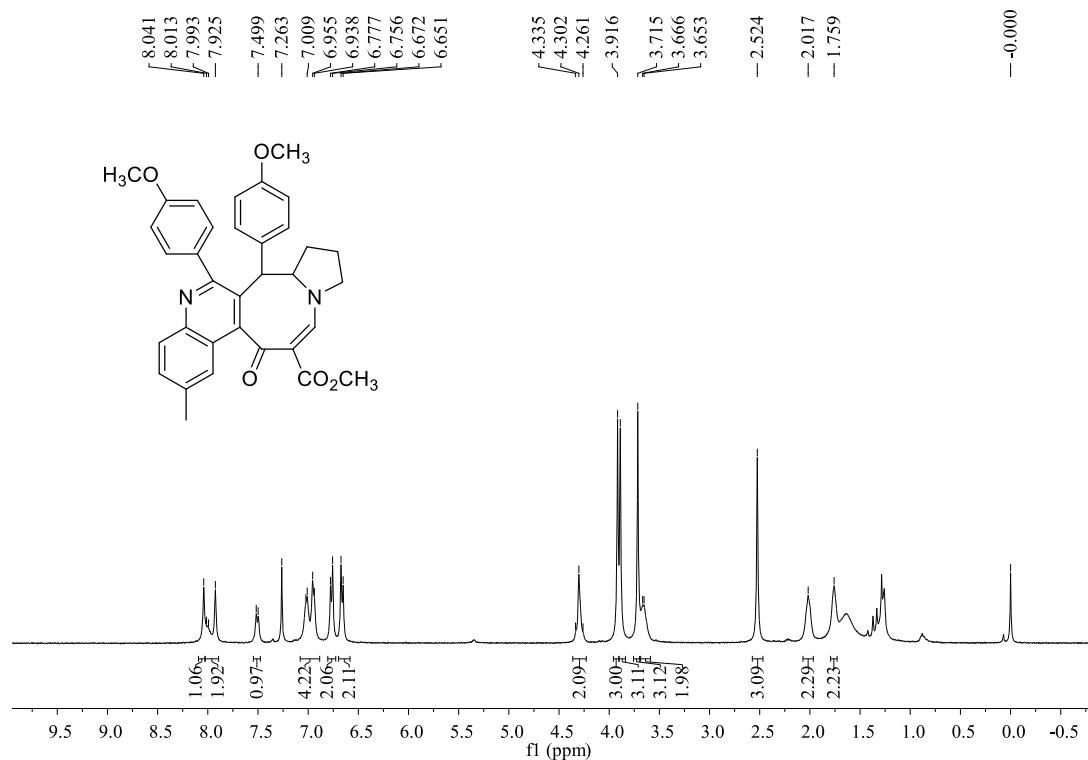
quinolines 3a-3h: To a round flask was added L-proline (0.5 mmol), isatin (0.5 mmol), bis-chalcone (0.5 mmol), and methanol (10.0 mL). The mixture was refluxed for two hours. The solvent was removed by rotatory evaporation at reduced pressure. Then, methyl propiolate (0.6 mmol) and acetonitrile (10.0 mL) was added. The mixture was refluxed for eight hours. After removing the solvent, the residue was subjected to column chromatography with light petroleum

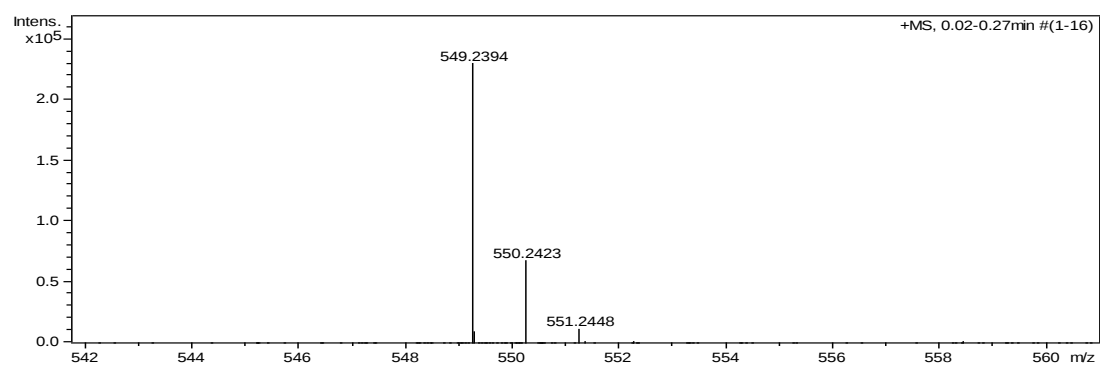
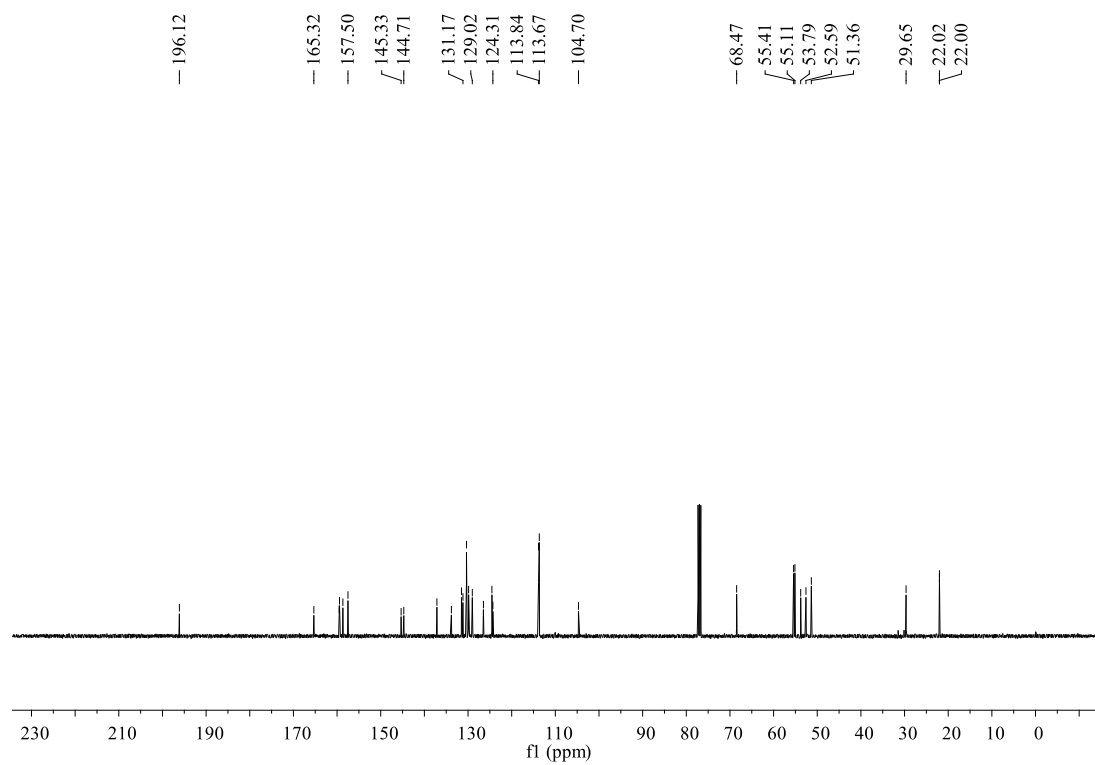
and ethyl acetate (V/V = 5:1) as eluent to give the pure product for analysis.

Methyl

(*E*)-1,14-bis(4-methoxyphenyl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (**1a**):

yellow solid, 70%, m.p. 295~297°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (s, 1H, CH), 8.01~7.92 (m, 2H, ArH), 7.51 (d, $J = 8.0$ Hz, 1H, ArH), 7.02~6.94 (m, 4H, ArH), 6.76 (d, $J = 8.4$ Hz, 2H, ArH), 6.66 (d, $J = 8.4$ Hz, 2H, ArH), 4.26~4.34 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.66 (d, $J = 6.8$ Hz, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.02 (s, 2H, CH_2), 1.76 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 165.2, 159.5, 159.4, 158.6, 157.5, 145.3, 144.6, 137.1, 133.7, 131.5, 131.1, 130.3, 129.8, 128.9, 126.5, 124.5, 124.3, 113.8, 113.6, 110.0, 104.6, 68.4, 55.4, 55.1, 53.7, 52.5, 51.3, 31.3, 29.6, 22.0; IR (KBr) ν : 3300, 2951, 2840, 1737, 1704, 1681, 1649, 1606, 1577, 1512, 1460, 1344, 1271, 1179, 1149, 1063, 1032, 947, 885, 840, 806, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 549.2384, found: 549.2394.

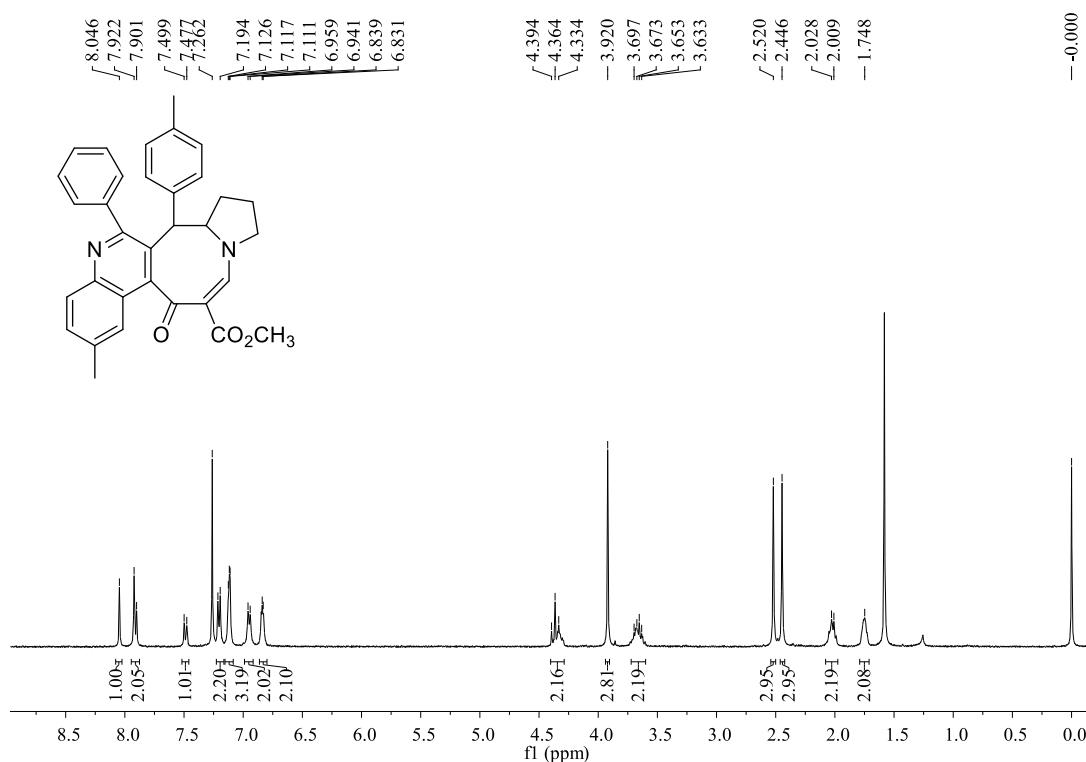


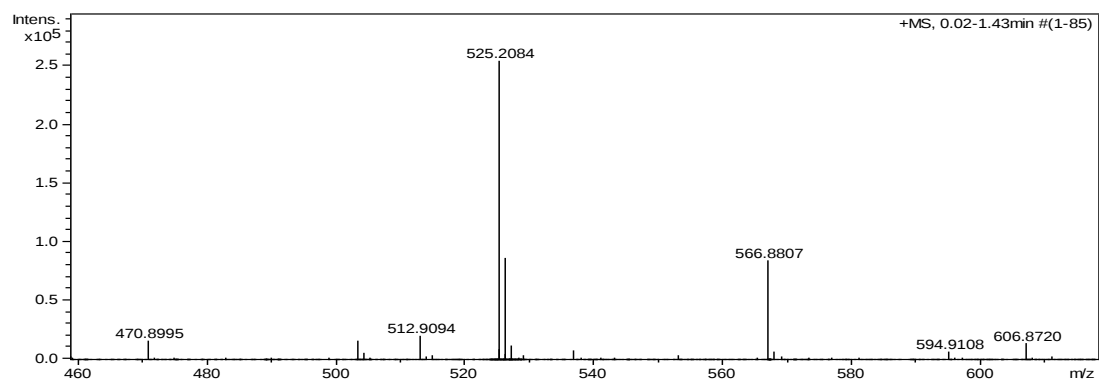
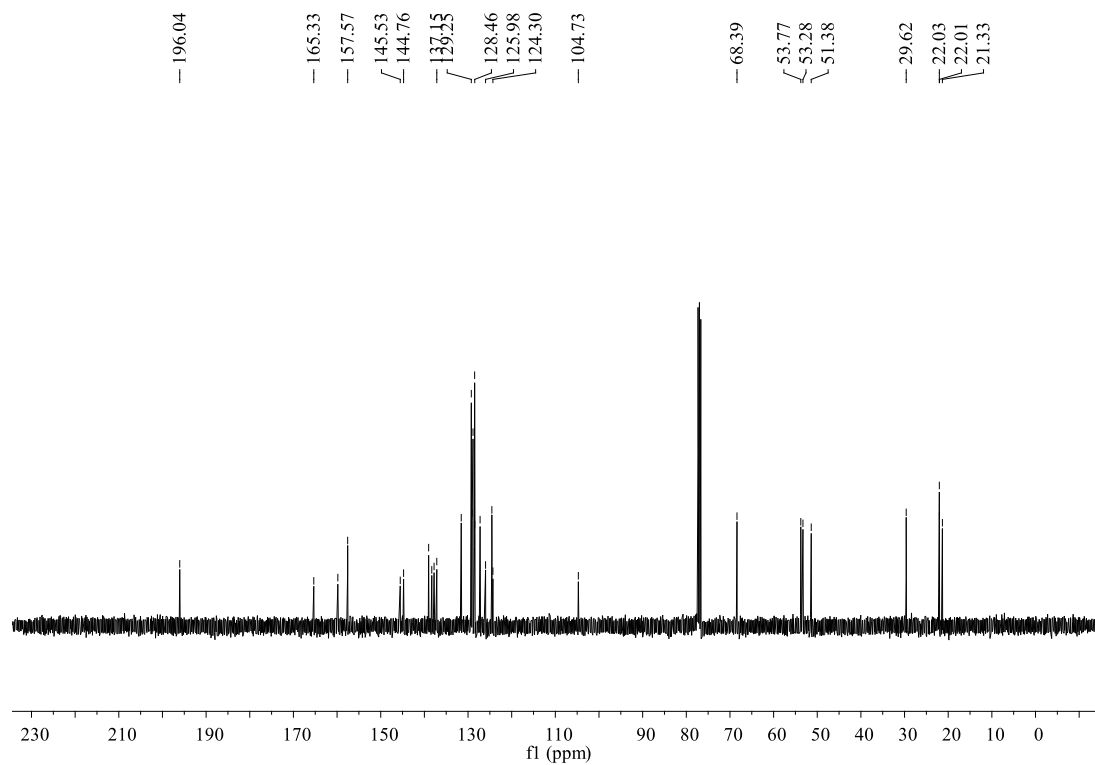


Methyl

(*E*)-5-methyl-7-oxo-1-phenyl-14-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (1b):

yellow solid, 72%, m.p. 287~289°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (s, 1H, CH), 7.91 (d, J = 8.4 Hz, 2H, ArH), 7.49 (d, J = 8.8 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.15~7.08 (m, 3H, ArH), 6.95 (d, J = 7.2 Hz, 2H, ArH), 6.84~6.94 (m, 2H, ArH), 4.36 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.66 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.02 (m, 2H, CH_2), 1.75 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 165.3, 159.8, 157.5, 145.5, 144.7, 139.0, 138.3, 137.7, 137.1, 131.5, 129.2, 129.0, 128.8, 128.5, 128.4, 127.2, 125.9, 124.5, 124.3, 104.7, 68.3, 53.7, 53.2, 51.3, 29., 22.0, 22.0, 21.3; IR(KBr) ν : 3298, 2953, 1703, 1585, 1493, 1451, 1409, 1358, 1321, 1272, 1186, 1148, 1059, 980, 944, 912, 885, 824, 807, 758, 703 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{30}\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 525.2149, found: 525.2084.

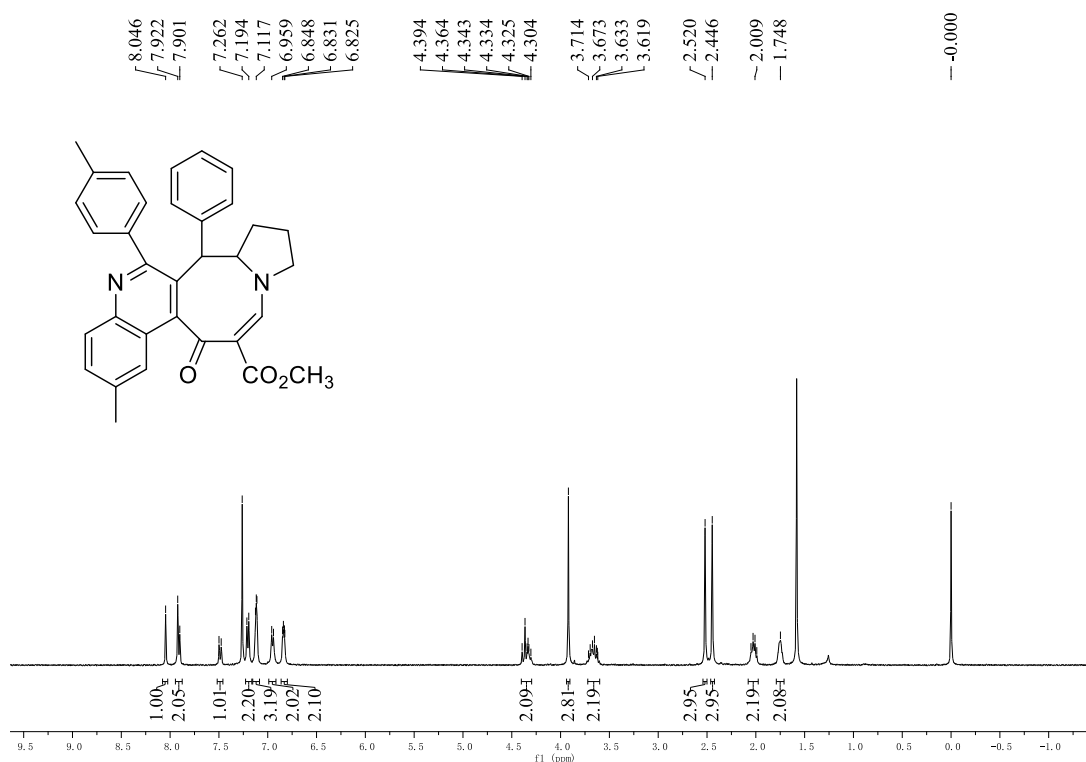


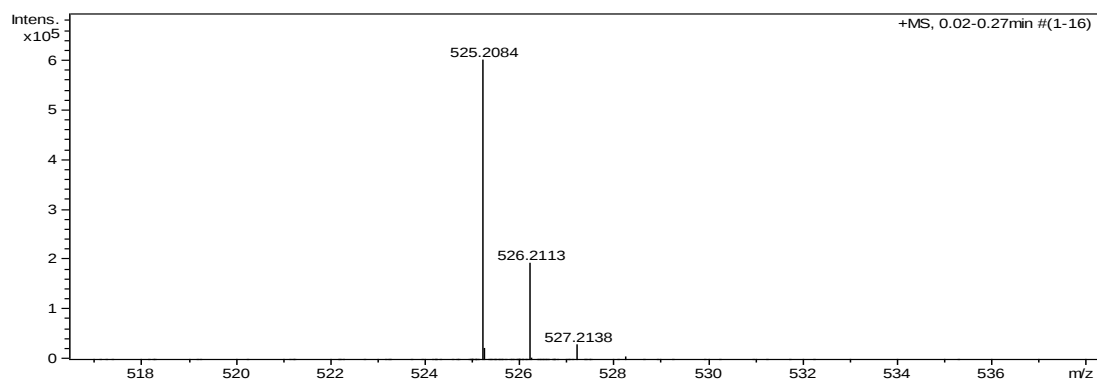
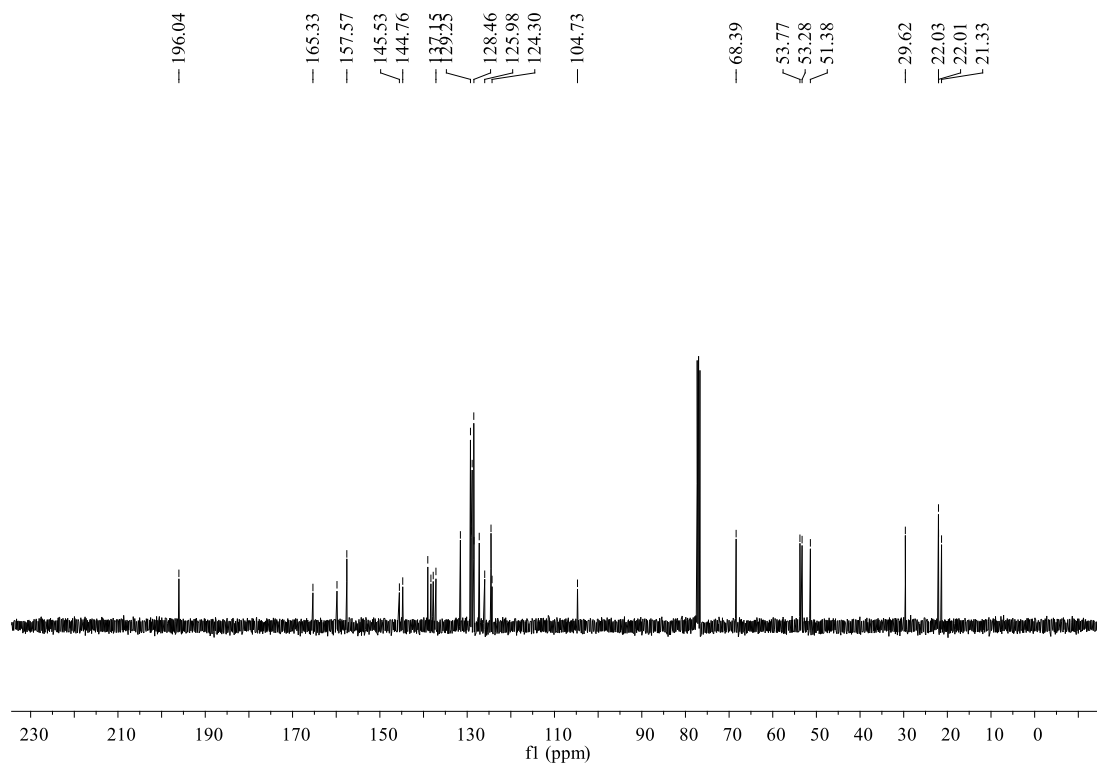


Methyl

(E)-5-methyl-7-oxo-14-phenyl-1-(p-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (1c):

yellow solid, 43%, m.p. 293~297°C; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H, CH), 7.91 (d, J = 8.4 Hz, 2H, ArH), 7.49 (d, J = 8.8 Hz, 1H, ArH), 7.20 (d, J = 7.8 Hz, 2H, ArH), 7.15~7.08 (m, 3H, ArH), 6.95 (d, J = 7.2 Hz, 2H, ArH), 6.85~6.82 (m, 2H, ArH), 4.369~4.32 (m, 2H, CH), 3.92 (s, 3H, CH_3), 3.71~3.62 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.05~1.99 (m, 2H, CH_2), 1.75 (s, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 196.0, 165.3, 159.8, 157.5, 145.5, 144.7, 139.0, 138.3, 137.7, 137.1, 131.5, 129.2, 129.0, 128.8, 128.4, 128.4, 127.2, 125.98, 124.5, 124.3, 104.7, 68.3, 53.7, 53.2, 51.3, 29.6, 22.0, 22.0, 21.3; IR (KBr) ν : 3298, 2954, 1703, 1586, 1494, 1451, 1410, 1359, 1321, 1272, 1186, 1149, 1060, 980, 944, 912 885, 825, 807, 759, 703 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{30}\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 525.2149, found: 525.2084.

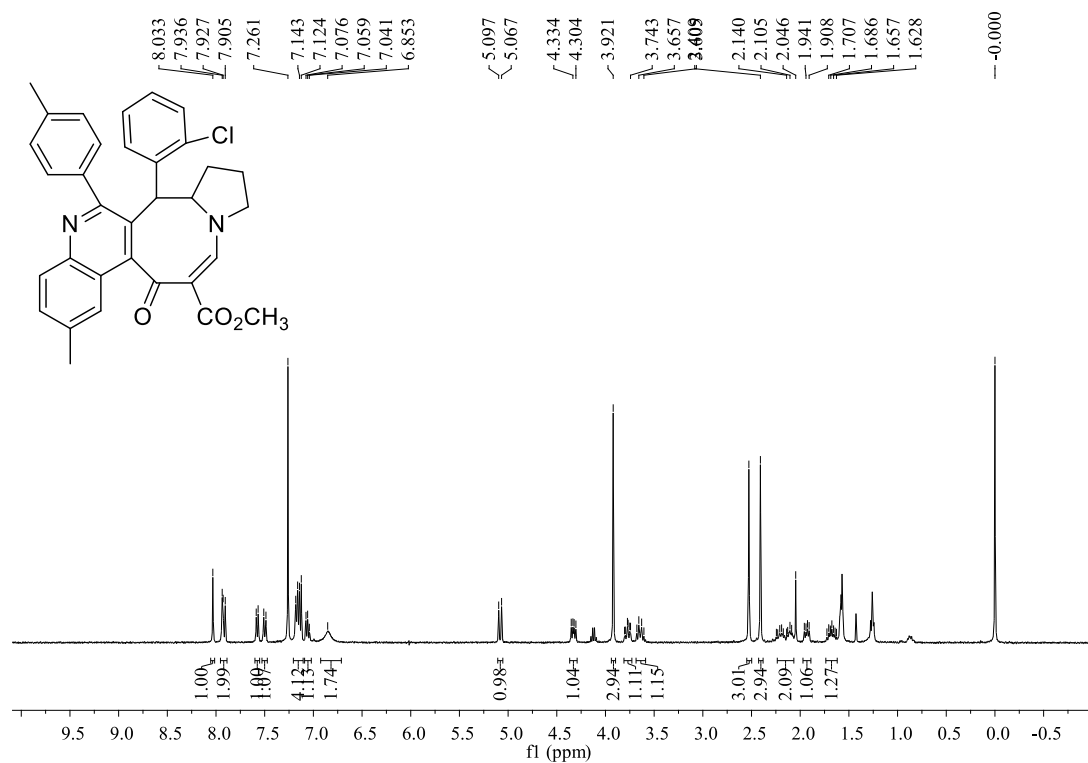


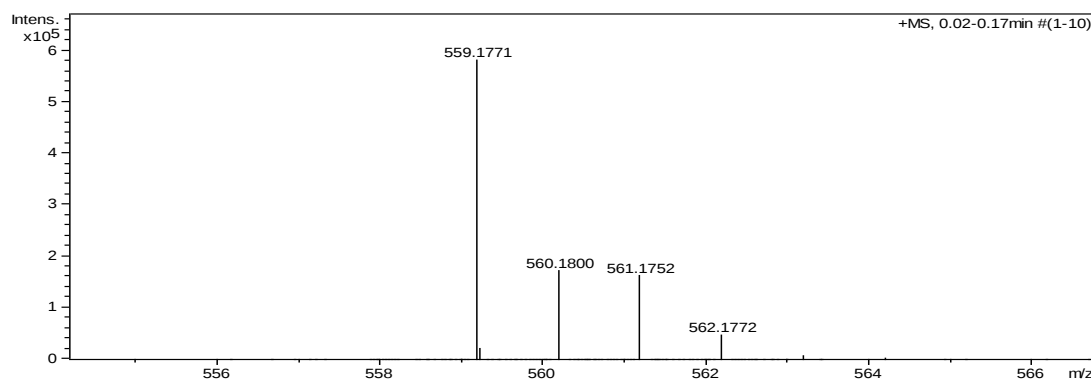
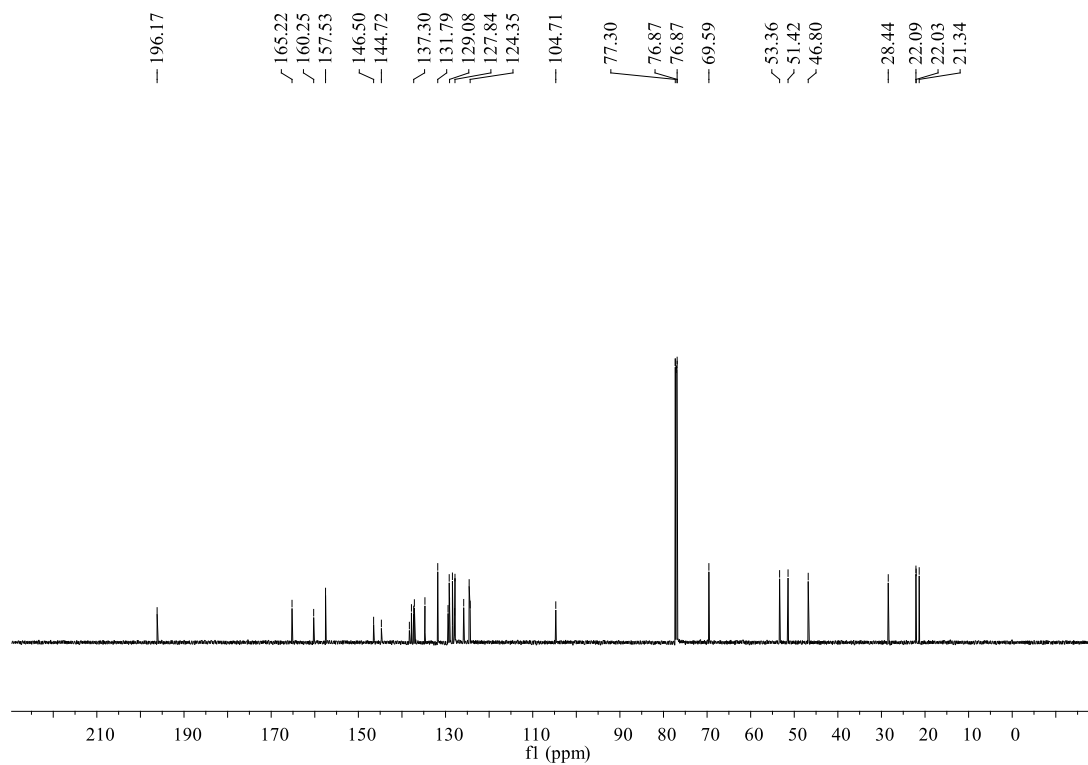


Methyl

(*E*)-14-(3-chlorophenyl)-5-methyl-7-oxo-1-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (1d):

yellow solid, 55%, m.p. 300~302 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.03 (s, 1H, CH), 7.95~7.89 (m, 2H, ArH), 7.58 (d, $J = 8.0$ Hz, 1H, ArH), 7.50 (d, $J = 8.8$ Hz, 1H, ArH), 7.15 (dd, $J_1 = 15.2$ Hz, $J_2 = 7.6$ Hz, 4H, ArH), 7.09~7.02 (m, 1H, ArH), 6.85 (s, 2H, ArH), 5.08 (d, $J = 12.0$ Hz, 1H, CH), 4.33 (dd, $J_1 = 12.0$ Hz, $J_2 = 7.2$ Hz, 1H, CH), 3.92 (s, 3H, OCH_3), 3.80~3.74 (m, 1H, CH), 3.64 (dd, $J_1 = 20.0$ Hz, $J_2 = 8.0$ Hz, 1H, CH_2), 2.53 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.28~2.08 (m, 2H, CH_2), 1.93 (m, 1H, CH_2), 1.72~1.62 (m, 1H, CH_2); ^{13}C NMR (151 MHz, CDCl_3) δ : 196.2, 165.2, 160.2, 157.5, 146.5, 144.7, 138.3, 137.8, 137.3, 137.1, 134.7, 131.8, 129.4, 129.1, 129.0, 128.4, 127.9, 127.8, 125.8, 124.5, 124.3, 104.7, 69.5, 53.3, 51.4, 46.8, 28.4, 22.0, 22.0, 21.3; IR (KBr) ν : 3301, 3061, 3019, 2981, 1680, 1639, 1568, 1512, 1473, 1442, 1350, 1320, 1276, 1188, 1152, 1062, 1047, 1032, 980, 961, 912, 883, 863, 821, 795, 761 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 559.1759, found: 559.1771.

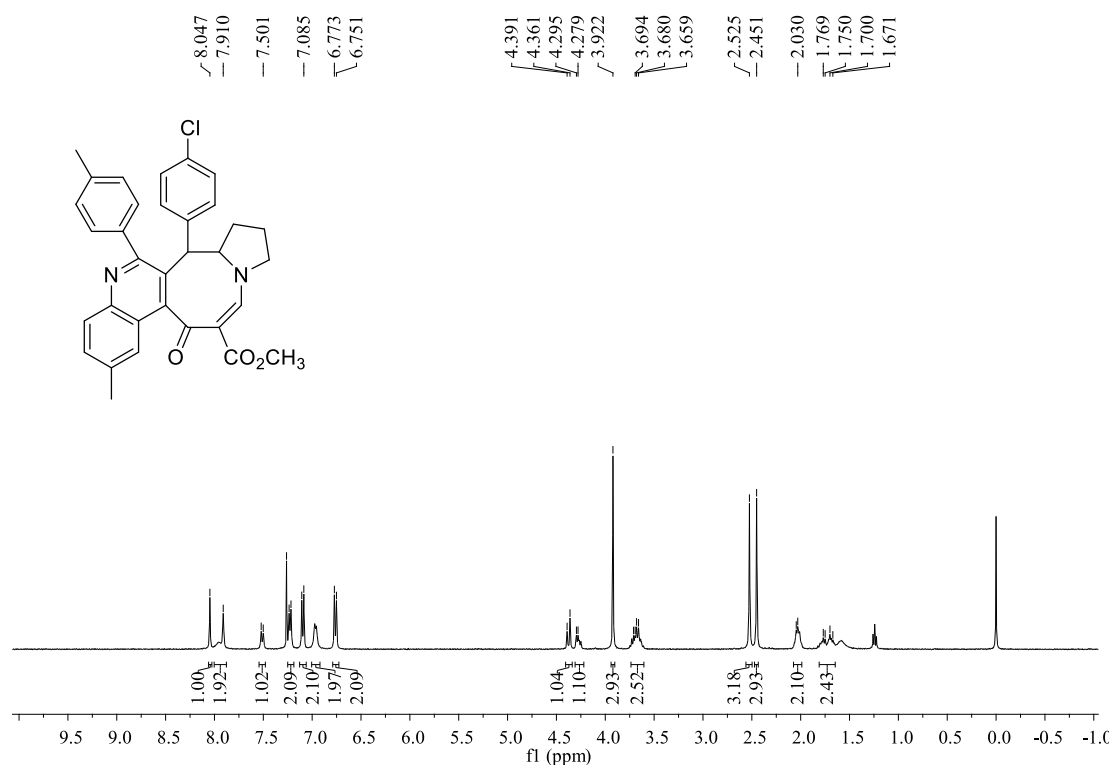


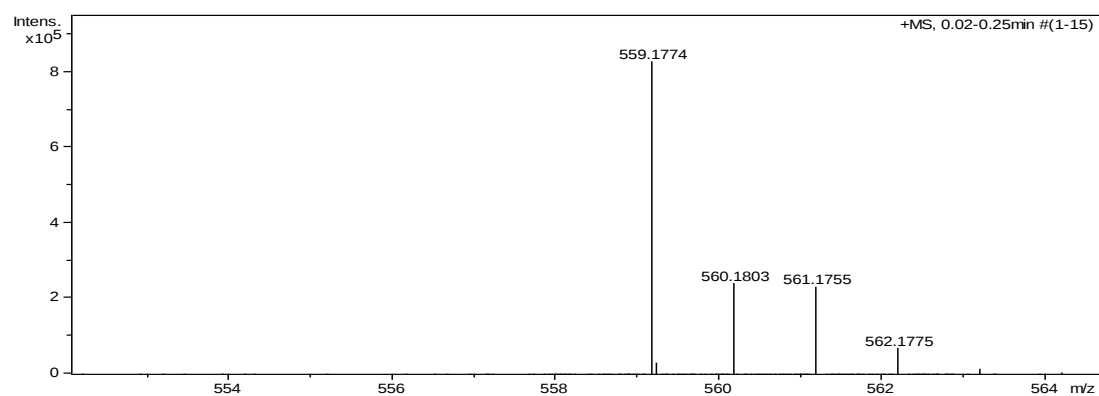
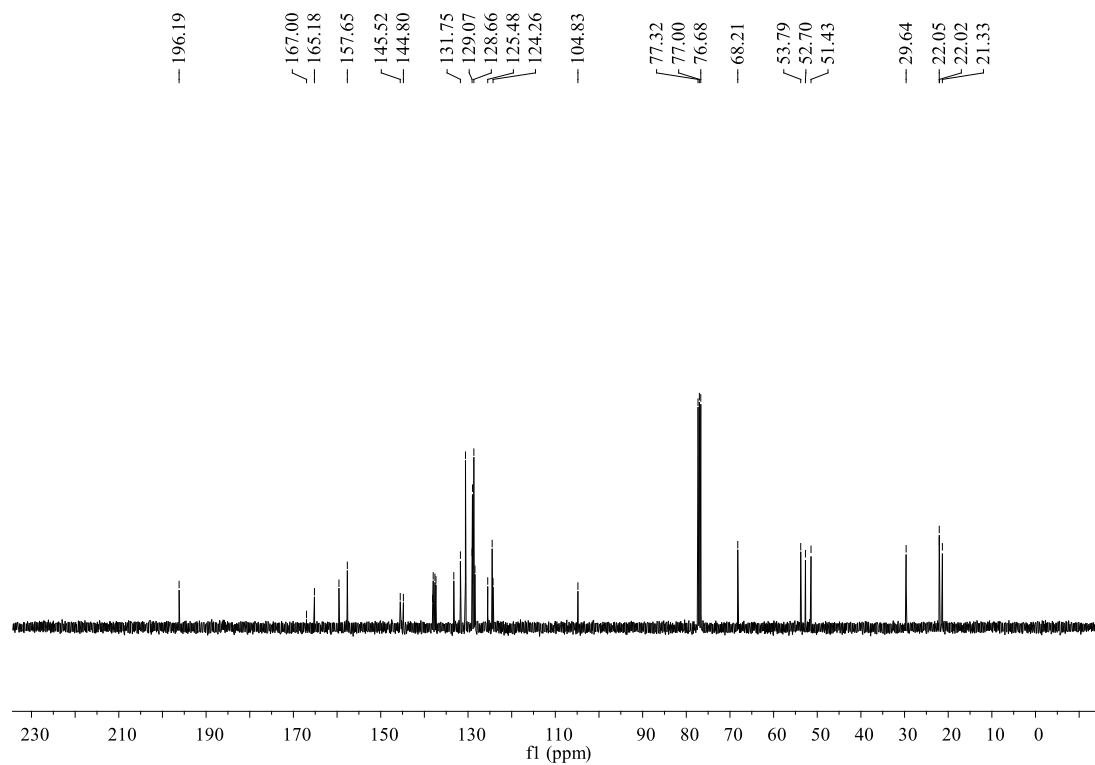


Methyl

(E)-14-(4-chlorophenyl)-5-methyl-7-oxo-1-(p-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (1e):

yellow solid, 59%, m.p. 290~292 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (s, 1H, CH), 7.91 (s, 2H, ArH), 7.51 (d, $J = 8.4$ Hz, 1H, ArH), 7.23 (d, $J = 7.6$ Hz, 2H, ArH), 7.10 (d, $J = 8.4$ Hz, 2H, ArH), 6.97 (d, $J = 6.4$ Hz, 2H, ArH), 6.76 (d, $J = 8.5$ Hz, 2H, ArH), 4.38 (d, $J = 12.0$ Hz, 1H, CH), 4.31~4.22 (m, 1H, CH), 3.92 (s, 3H, OCH_3), 3.72~3.60 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.06~1.99 (m, 2H, CH_2), 1.82~1.66 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 165.2, 159.5, 157.6, 145.5, 144.8, 138.1, 137.9, 137.5, 137.3, 133.2, 131.7, 130.5, 129.0, 128.9, 128.6, 128.4, 125.4, 124.4, 124.2, 104.8, 68.2, 53.7, 52.7, 51.4, 29.6, 22.0, 22.0, 21.3; IR (KBr) ν : 3299, 2951, 1688, 1647, 1573, 1492, 1457, 1345, 1323, 1271, 1201, 1149, 1089, 1062, 1046, 1015, 949, 885, 827, 805, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 559.1759, found: 559.1774.

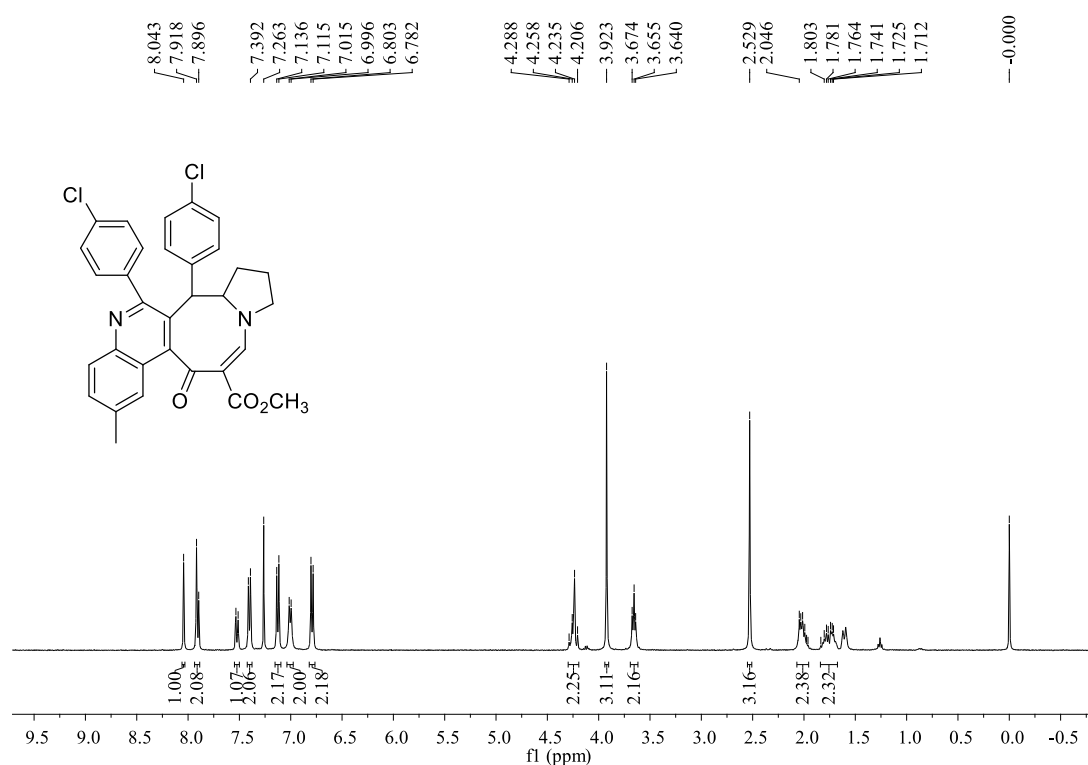


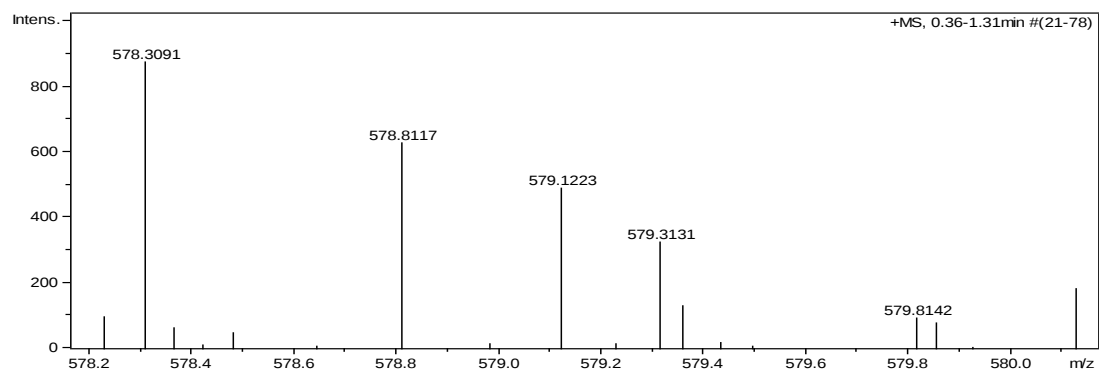
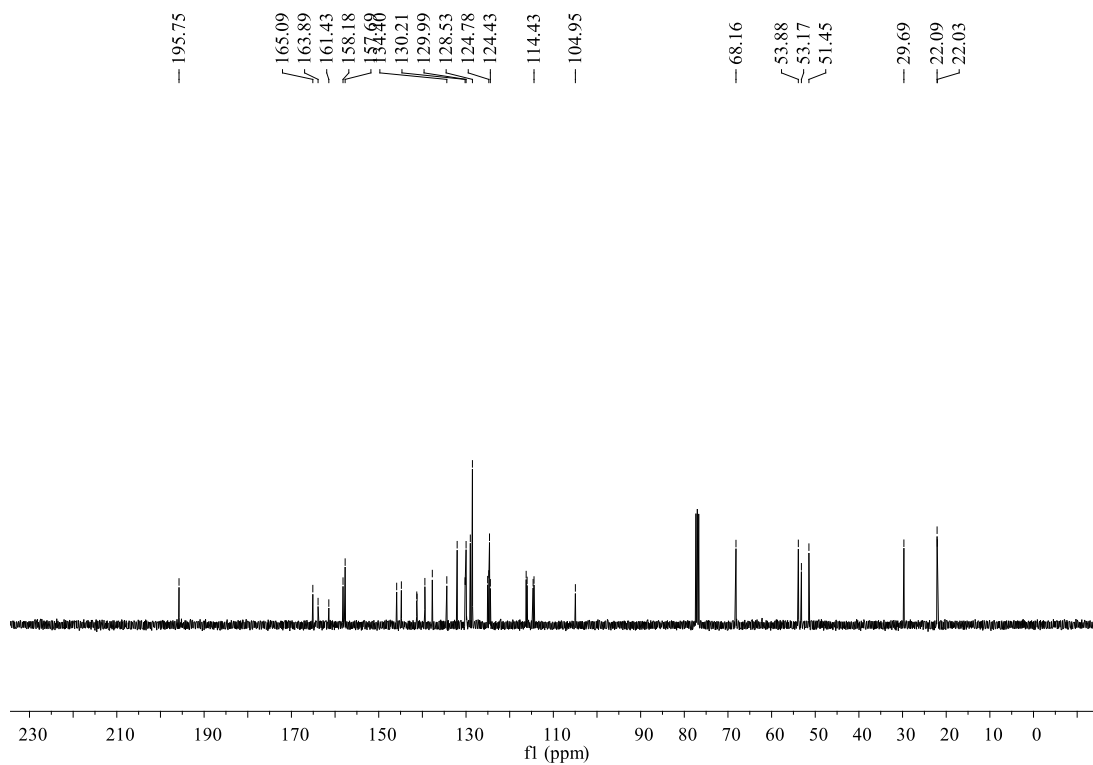


Methyl

(*E*)-1,14-bis(4-chlorophenyl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (1f):

yellow solid, 43%, m.p. 312~314°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (s, 1H, CH), 7.91 (d, J = 8.8 Hz, 2H, ArH), 7.52 (d, J = 8.8 Hz, 1H, ArH), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.13 (d, J = 8.4 Hz, 2H, ArH), 7.01 (d, J = 7.6 Hz, 2H, ArH), 6.79 (d, J = 8.4 Hz, 2H, ArH), 4.28~4.20 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.66 (t, J = 6.9 Hz, 2H, CH), 2.53 (s, 3H, CH_3), 2.04~1.96 (m, 2H, CH_2), 1.84~1.67 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.7, 165.0, 163.8, 161.4, 158.1, 157.6, 145.8, 144.1, 141.2, 141.2, 139.4, 137.7, 134.4, 132.0, 130.2, 130.1, 129.9, 129.0, 128.5, 125.0, 124.7, 124.6, 124.4, 116.2, 116.0, 114.6, 114.4, 104.9, 68.1, 53.8, 53.1, 51.4, 29.6, 22.9, 22.0; IR (KBr) ν : 3295, 3066, 2952, 1683, 1641, 1574, 1491, 1444, 1354, 1320, 1275, 1220, 1190, 1153, 1087, 1047, 1014, 961, 891, 859, 827, 789, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 579.1213, found: 579.1223.

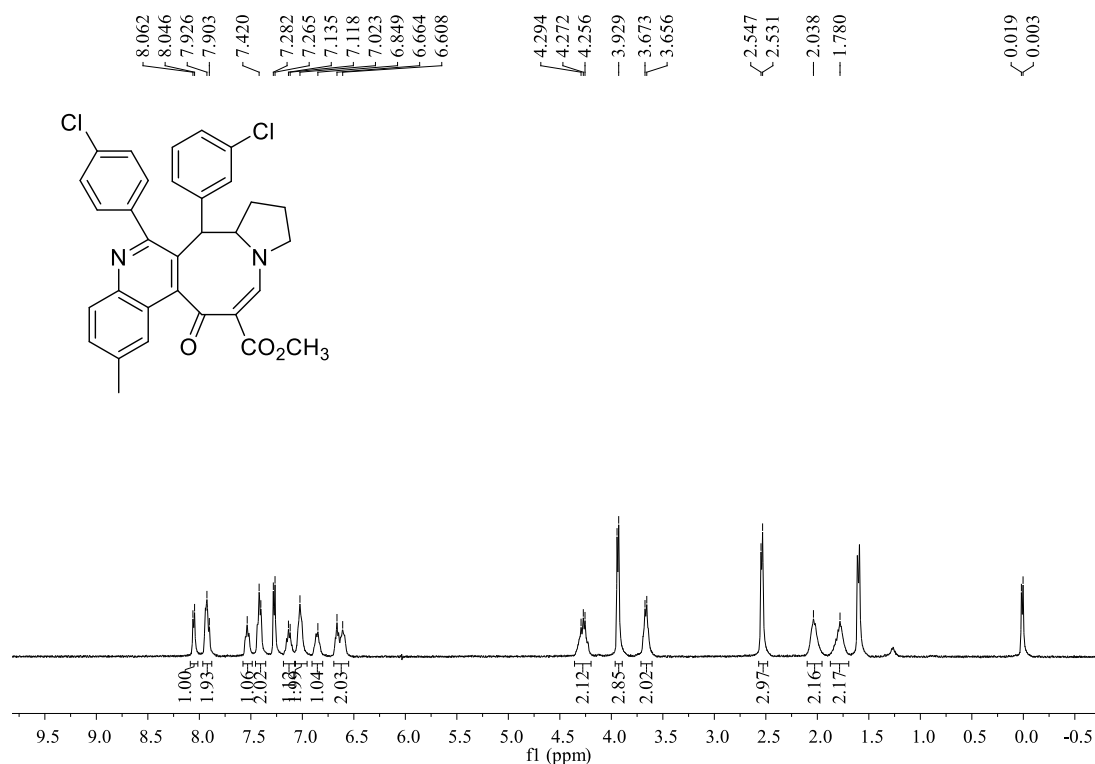


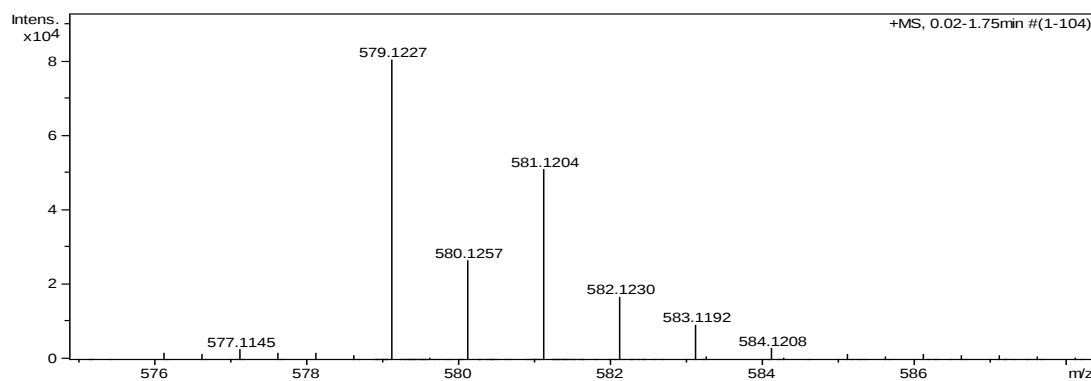
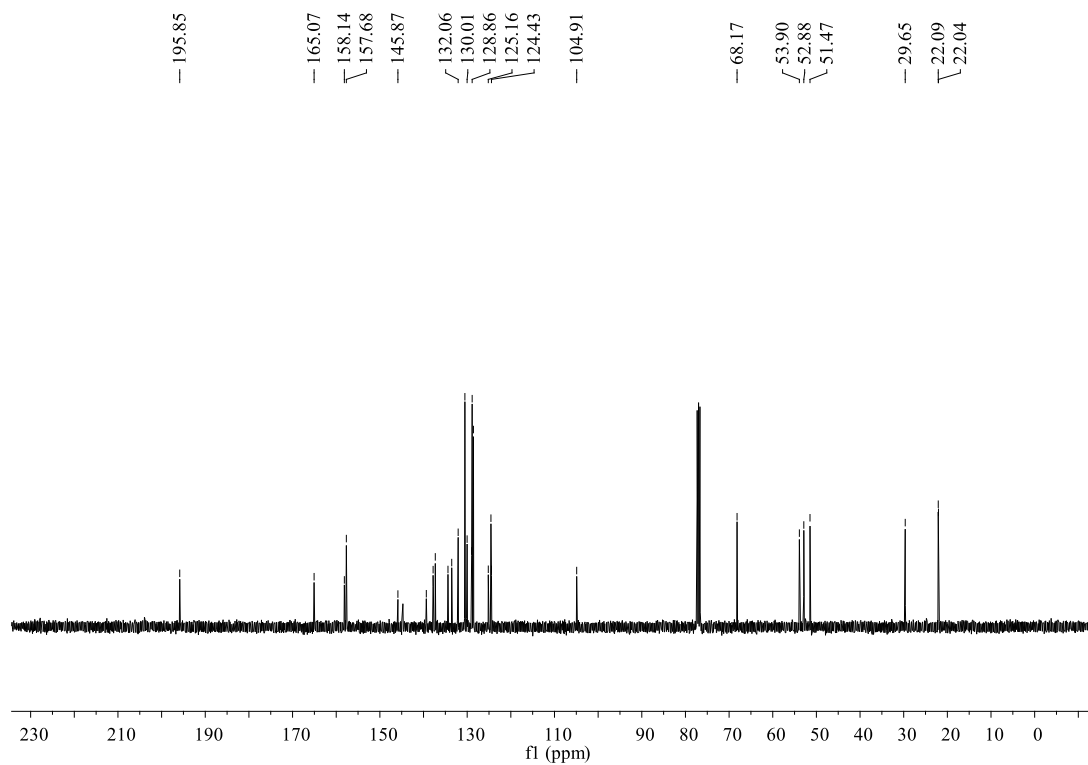


Methyl

(E)-14-(3-chlorophenyl)-1-(4-chlorophenyl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (1g):

yellow solid, 40%, m.p. 288~290 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (d, $J = 6.4$ Hz, 1H), 7.94~7.90(m, 2H, ArH), 7.54 (s, 1H, ArH), 7.41 (d, $J = 6.6$ Hz, 2H, ArH), 7.13 (d, $J = 6.6$ Hz, 1H, ArH), 7.02 (s, 2H, ArH), 6.85 (s, 1H, ArH), 6.64 (d, $J = 22.2$ Hz, 2H, ArH), 4.36~4.20 (m, 2H, CH), 3.94 (s, 3H, OCH_3), 3.66 (d, $J = 6.9$ Hz, 2H, CH_2), 2.54 (s, 3H, CH_3), 2.04 (s, 2H, CH_2), 1.78 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.8, 165.0, 158.1, 157.6, 145.8, 139.3, 137.8, 137.3, 134.4, 133.5, 132.0, 130.5, 130.0, 128.9, 128.8, 128.5, 125.1, 124.5, 124.4, 104.9, 68.1, 53.9, 52.8, 51.4, 29.6, 22.0, 22.0; IR (KBr) ν : 3439, 3297, 3021, 2950, 1684, 1573, 1492, 1460, 1357, 1321, 1273, 1189, 1150, 1090, 1047, 1014, 981, 885, 838, 806, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 579.1213, found: 579.1227.

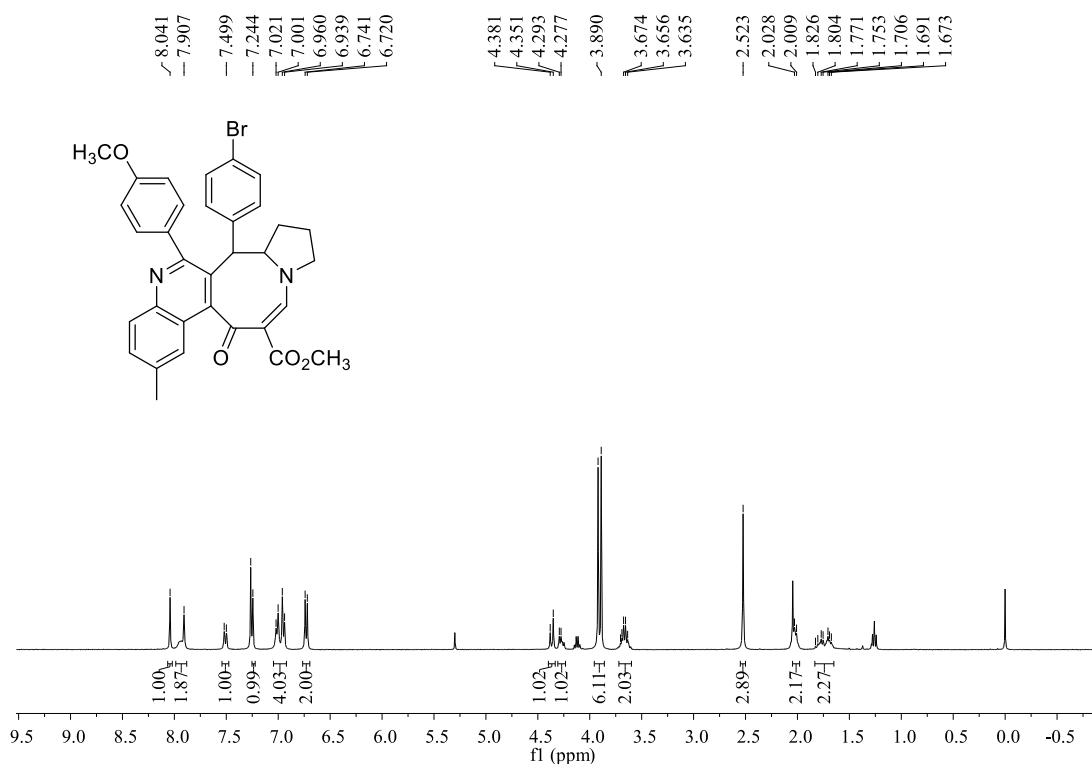


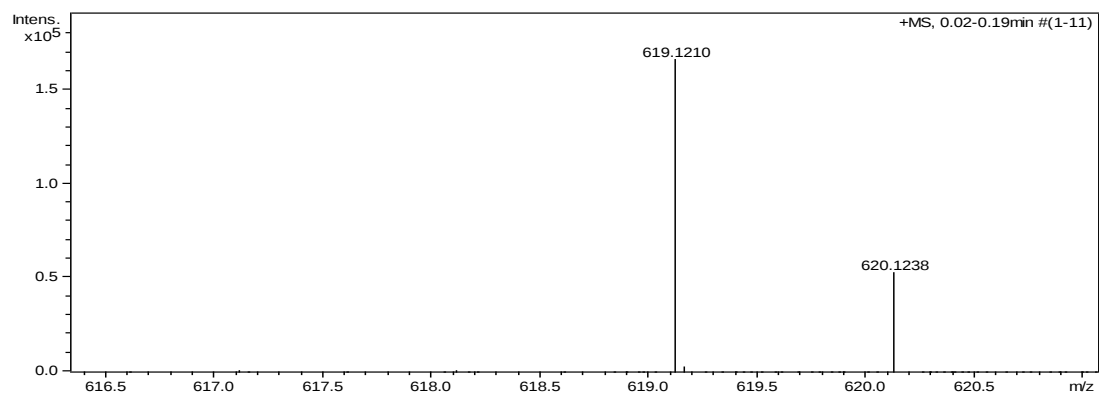
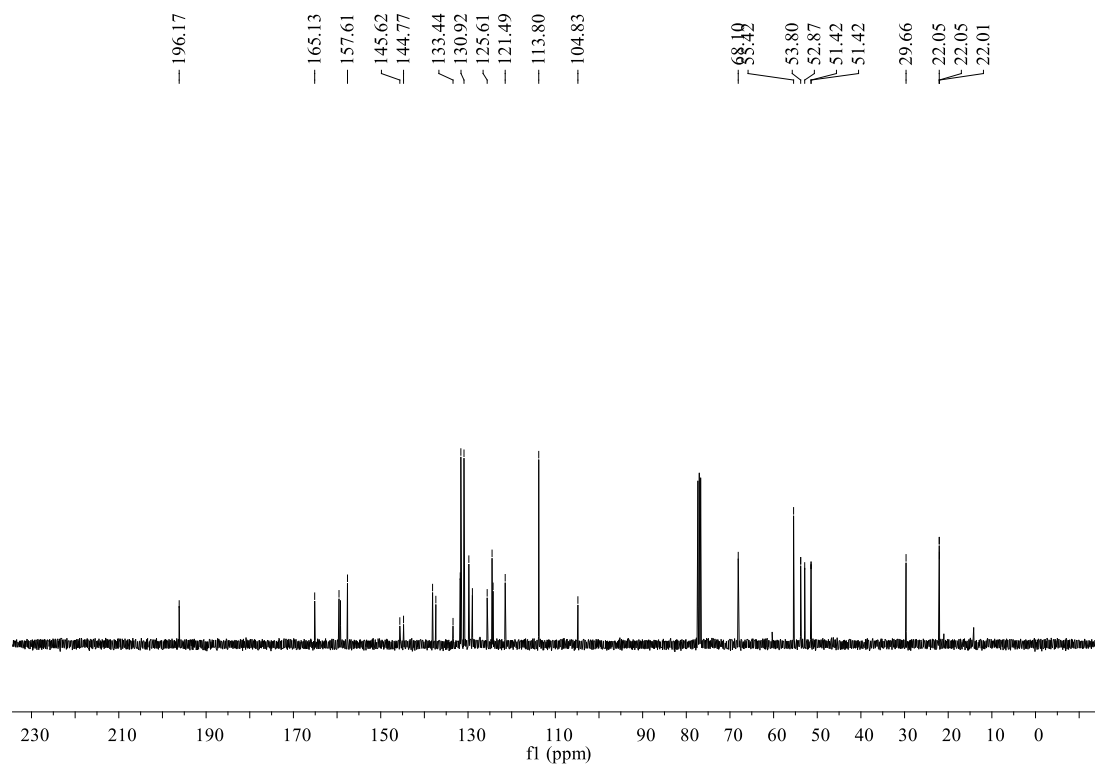


Methyl

(E)-14-(4-bromophenyl)-1-(4-methoxyphenyl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydro-yrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (1h):

yellow solid, 67%, m.p. 289~291 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (s, 1H, CH), 7.92 (s, 2H, ArH), 7.51 (d, $J = 8.4$ Hz, 1H, ArH), 7.24 (s, 1H, ArH), 7.02~7.64 (m, 4H, ArH), 6.73 (d, $J = 8.4$ Hz, 2H, ArH), 4.37 (d, $J = 12.0$ Hz, 1H, CH), 4.3~4.23 (m, 1H, CH), 3.90 (s, 6H, OCH_3), 3.72~3.60 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.05~1.98 (m, 2H, CH_2), 1.83~1.65 (m, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 196.1, 165.1, 159.5, 159.2, 157.6, 145.6, 144.7, 138.1, 137.3, 133.4, 131.7, 131.6, 130.9, 129.8, 129.0, 125.6, 124.5, 124.2, 121.4, 113.8, 104.8, 68.1, 55.4, 53.8, 52.87, 51.4, 29.6, 22.0, 22.0; IR (KBr) ν : 3299, 2951, 1739, 1686, 1647, 1575, 1511, 1489, 1459, 1345, 1322, 1271, 1188, 1149, 1064, 1030, 1009, 949, 885, 839, 804, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{29}\text{BrN}_2\text{NaO}_4$ ($[\text{M}+\text{Na}]^+$): 619.1203, found: 619.1210.

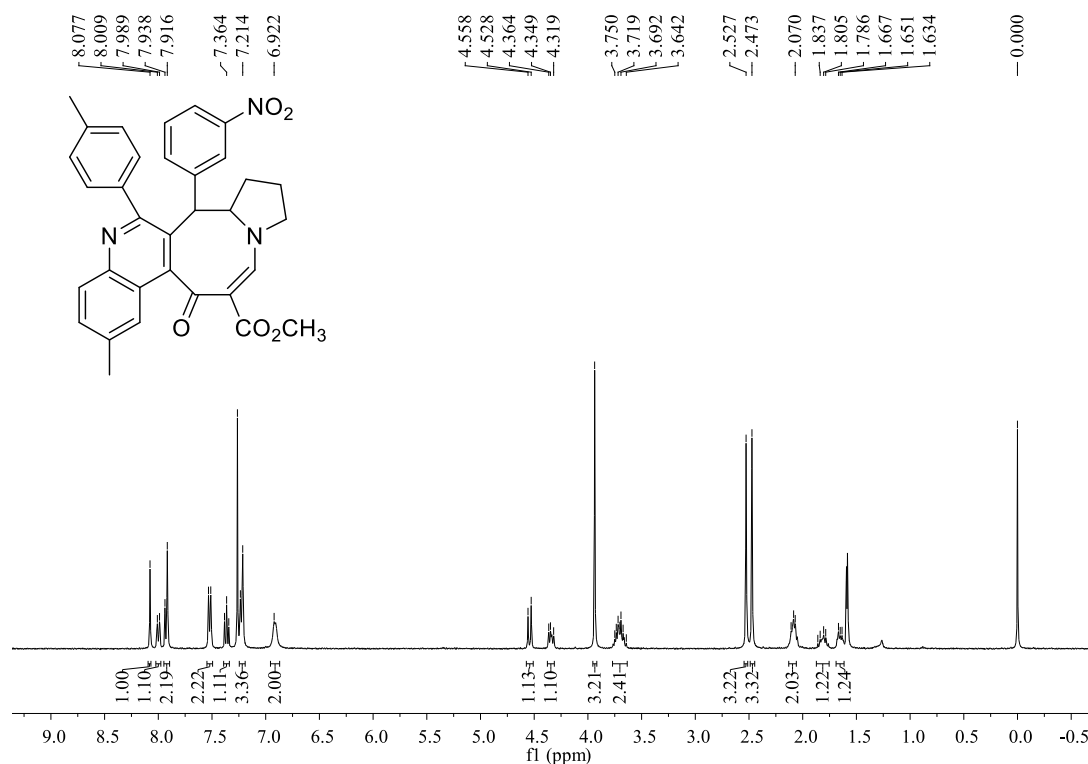


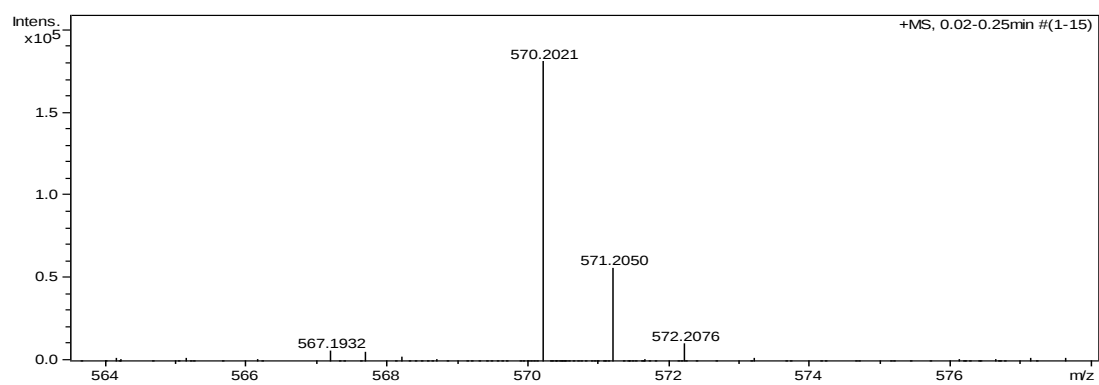
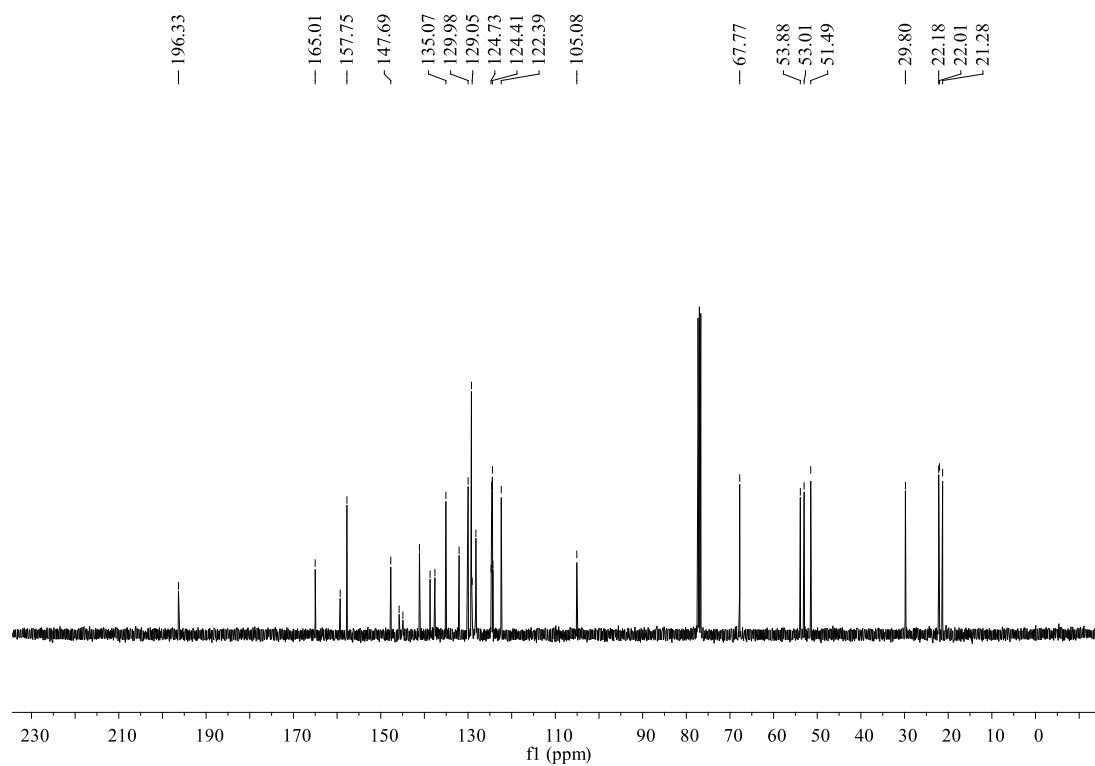


Methyl

(*E*)-5-methyl-14-(3-nitrophenyl)-7-oxo-1-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (**1i**):

yellow solid, 61%, m.p. 310~312 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.08 (s, 1H, CH), 8.00 (d, J = 8.0 Hz, 1H, ArH), 7.99~7.93 (m, 2H, ArH), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.36 (t, J = 8.0 Hz, 1H, ArH), 7.24~7.21 (m, 3H, ArH), 6.92 (s, 2H, ArH), 4.54 (d, J = 12.0 Hz, 1H, CH), 4.38~4.31 (m, 1H, CH), 3.94 (s, 3H, OCH_3), 3.77~3.63 (m, 2H, CH_2), 2.53 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.13~2.04 (m, 2H, CH_2), 2.12~2.07 (m, 1H, CH_2), 1.69~1.61 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.3, 165.0, 159.2, 157.7, 147.7, 145.7, 144.9, 141.1, 138.7, 137.5, 135.0, 132.0, 129.9, 129.2, 129.0, 128.2, 124.7, 124.5, 124.4, 124.3, 122.4, 105.1, 67.7, 53.9, 53.0, 51.4, 29.8, 22.2, 22.0, 21.3; IR (KBr) ν : 3302, 2923, 1684, 1652, 1579, 1531, 1459, 1436, 1350, 1270, 1188, 1151, 1063, 1047, 988, 958, 905, 877, 857, 829, 806, 758, 734 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{29}\text{N}_3\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 570.1999, found: 570.2021.

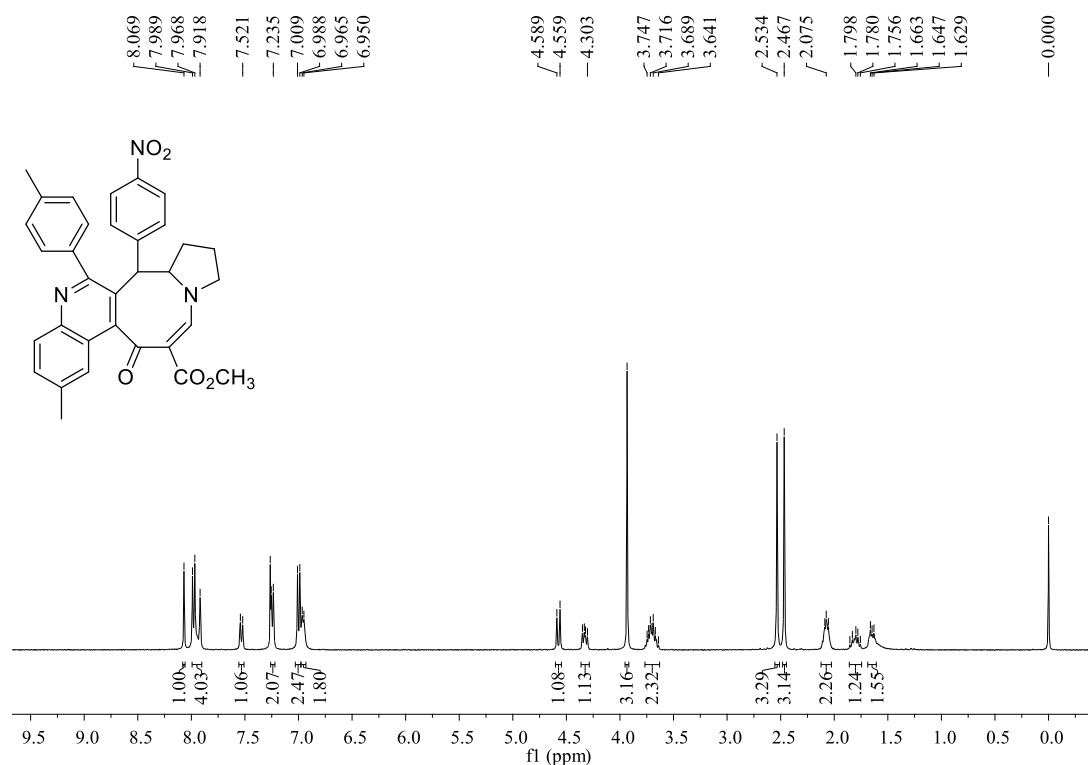


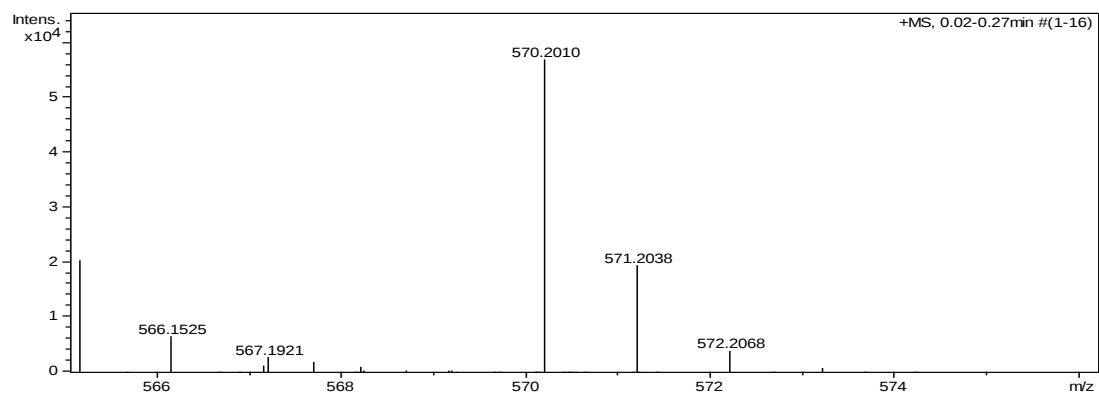
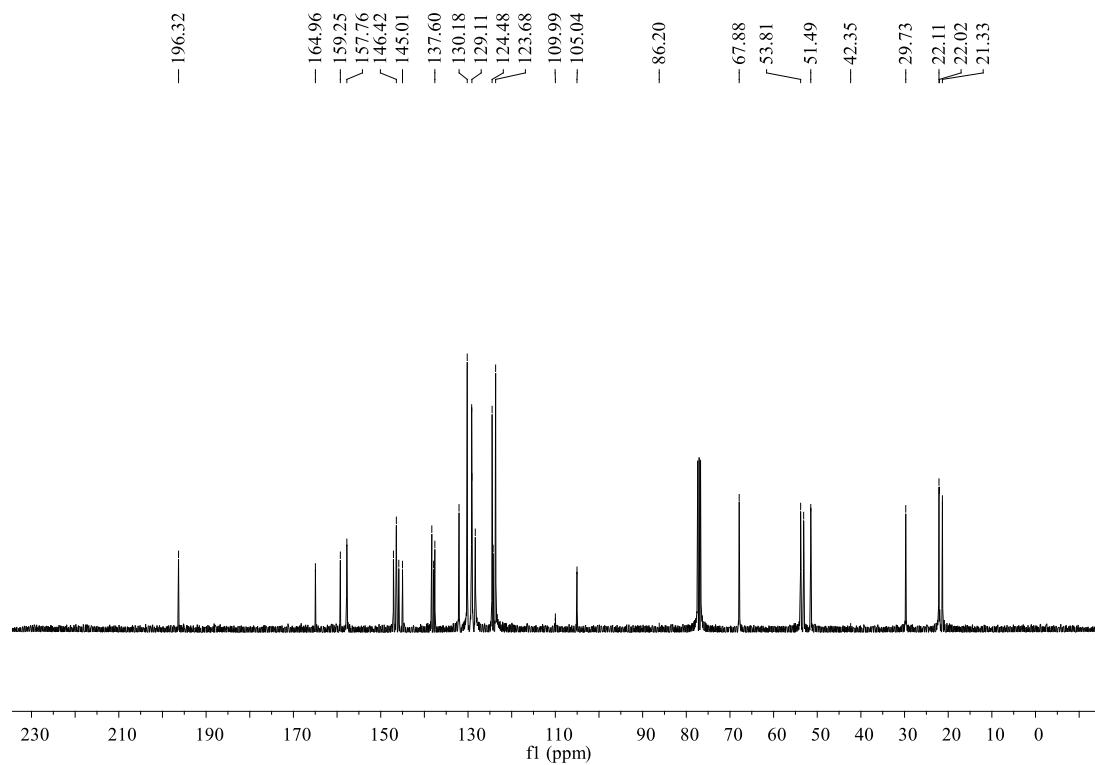


Methyl

(E)-5-methyl-14-(4-nitrophenyl)-7-oxo-1-(p-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (1j):

yellow solid, 65%, m.p. 298~300°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.07 (s, 1H, CH), 7.99~7.90 (m, 4H, ArH), 7.53 (d, J = 8.4 Hz, 1H, ArH), 7.00 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8.0 Hz, 2H ArH), 6.96 (d, J = 6.0 Hz, 2H, ArH), 4.57 (d, J = 12.0 Hz, 1H, CH), 4.33 (dd, J_1 = 11.2 Hz, J_2 = 7.2 Hz, 1H, CH), 3.93 (s, 3H, OCH_3), 3.77~3.63 (m, 2H, CH_2), 2.53 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.12~2.03 (m, 2H, CH_2), 1.86~1.74 (m, 1H, CH_2), 1.69~1.61 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.3, 164.9, 159.2, 157.7, 147.0, 146.4, 145.8, 145.0, 138.2, 137.8, 137.6, 132.0, 130.1, 129.1, 129.1, 128.3, 124.4, 124.2, 123.6, 109.9, 105.0, 67.8, 53.8, 53.1, 51.4, 29.7, 22.1, 22.0, 21.3; IR (KBr) ν : 3440, 3298, 2948, 1710, 1584, 1523, 1460, 1433, 1346, 1324, 1272, 1188, 1150, 1063, 1019, 946, 889, 827, 810, 744 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{29}\text{N}_3\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 570.1999, found: 570.2010.

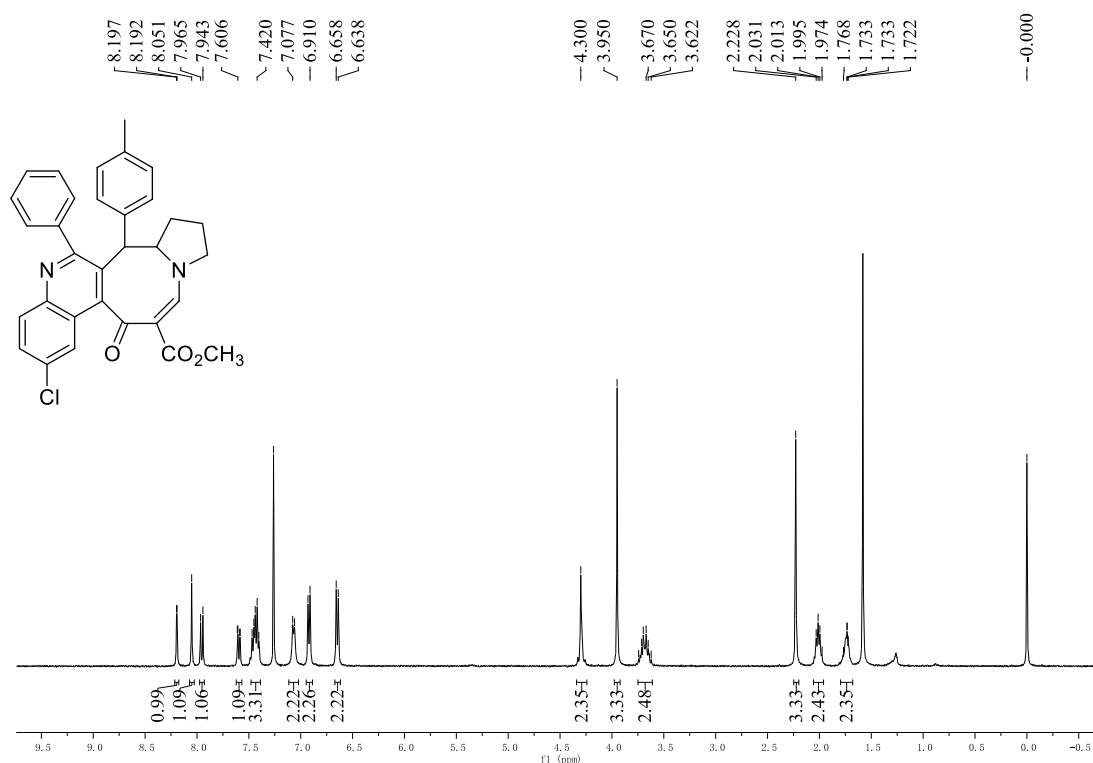


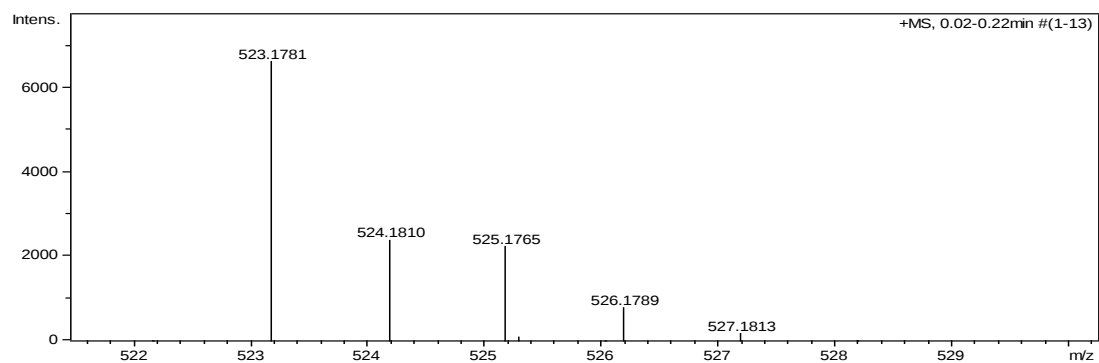
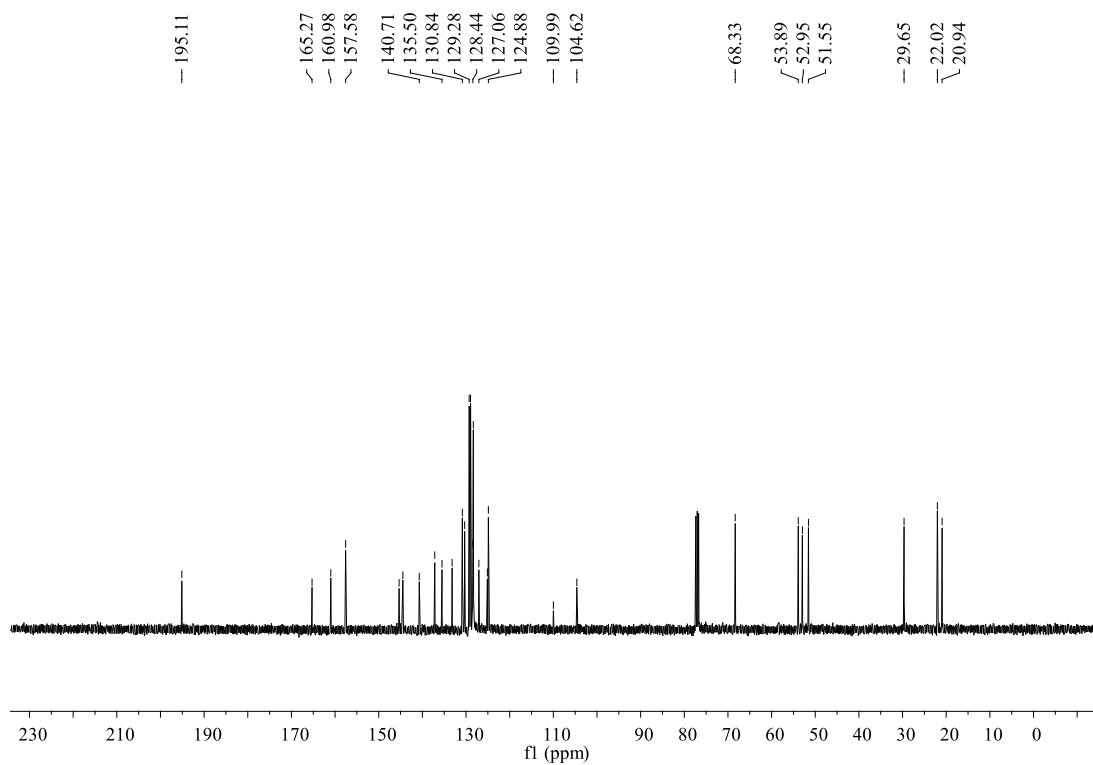


Methyl

(*E*)-5-chloro-7-oxo-1-phenyl-14-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocin o[4,5-*c*]quinoline-8-carboxylate (1k):

yellow solid, 55%, m.p. 231~233 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (d, $J = 2.0$ Hz, 1H, ArH), 8.05 (s, 1H, CH), 7.95 (d, $J = 8.8$ Hz, 1H, ArH), 7.60 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H, ArH), 7.45~7.40 (m, 3H, ArH), 7.07 (d, $J = 7.2$ Hz, 2H, ArH), 6.92 (d, $J = 8.0$ Hz, 2H, ArH), 6.65 (d, $J = 8.0$ Hz, 2H, ArH), 4.30 (s, 2H, CH), 3.95 (s, 3H, OCH_3), 3.75~3.61 (m, 2H, CH_2), 2.23 (s, 3H, CH_3), 2.06~1.96 (m, 2H, CH_2), 1.77~1.72 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.1, 165.2, 160.9, 157.5, 145.3, 144.4, 140.7, 137.1, 135.5, 133.1, 130.8, 130.3, 129.2, 128.9, 128.4, 128.3, 127.0, 125.1, 124.8, 109.9, 104.6, 68.3, 53.8, 52.9, 51.5, 29.6, 22.0, 20.9; IR (KBr) ν : 3296, 2948, 2883, 1699, 1658, 1577, 1514, 1480, 1438, 1348, 1323, 1271, 1192, 1153, 1061, 1028, 981, 950, 886, 834, 807, 766, 728, 705 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{28}\text{ClN}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 523.1783, found: 523.1781.

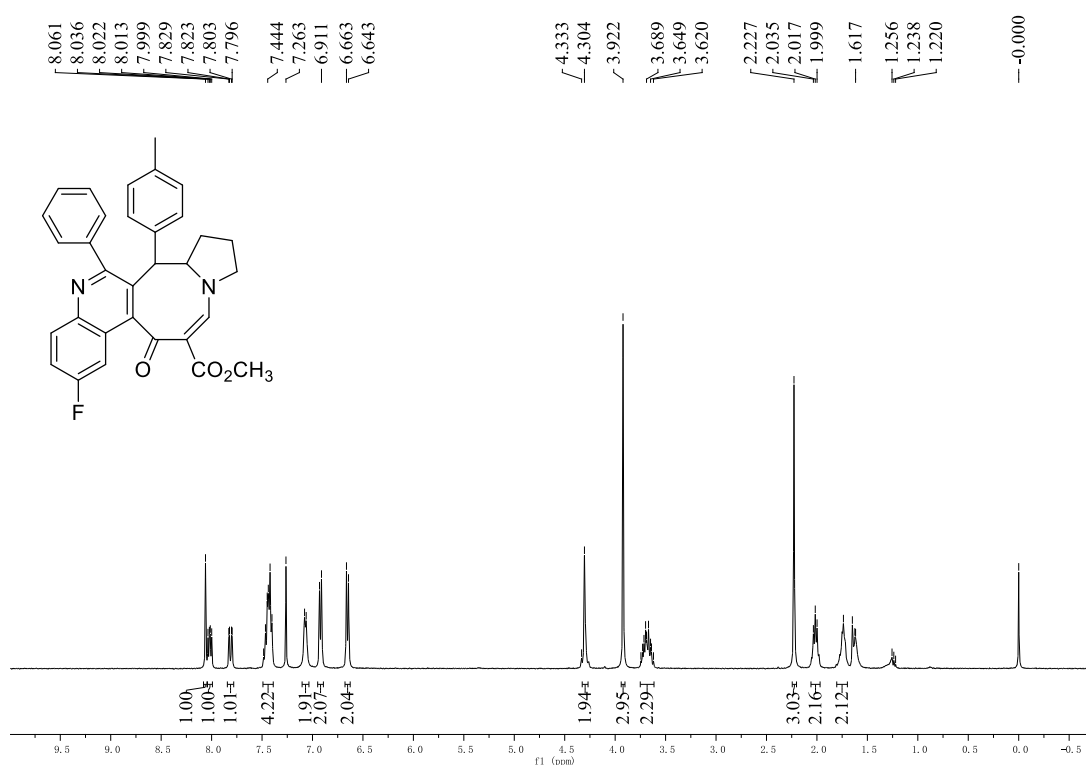


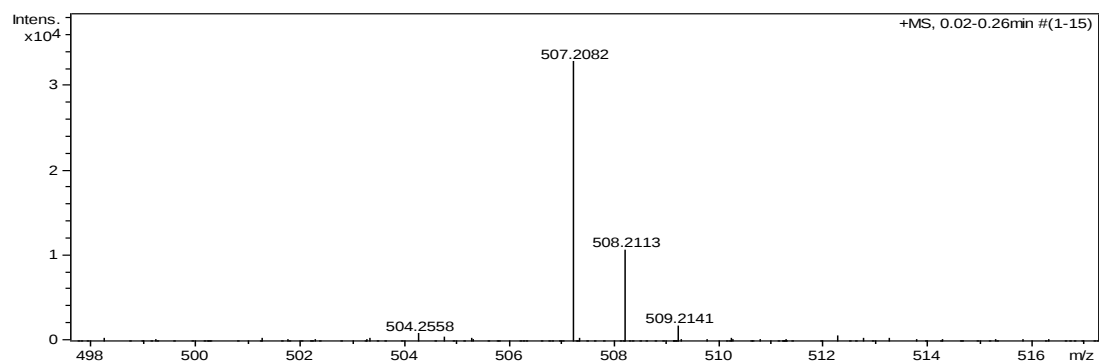
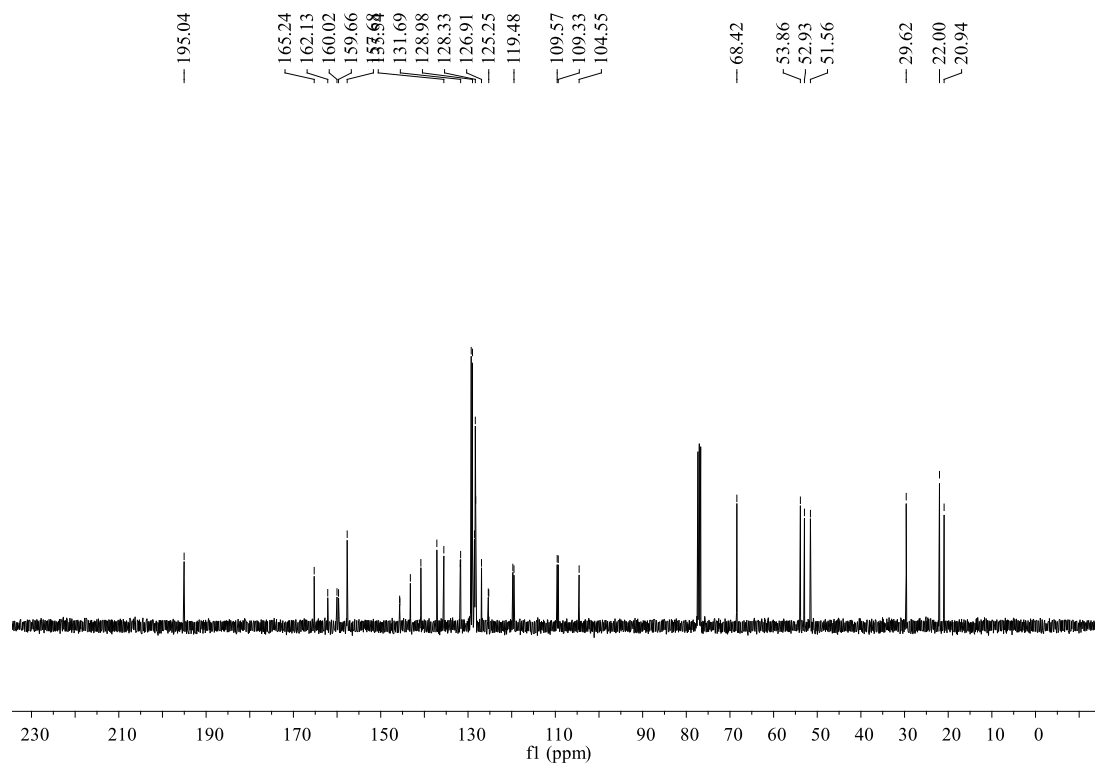


Methyl

(*E*)-5-fluoro-7-oxo-1-phenyl-14-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocin o[4,5-*c*]quinoline-8-carboxylate (11):

yellow solid, 55%, m.p. 253~255°C; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H, CH), 8.02 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H, ArH), 7.81 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H, ArH), 7.49~7.39 (m, 4H, ArH), 7.07 (d, J = 6.4 Hz, 2H, ArH), 6.92 (d, J = 7.6 Hz, 2H, ArH), 6.65 (d, J = 8.0 Hz, 2H, ArH), 4.32 (d, J = 11.3 Hz, 2H, CH), 3.92 (s, 3H, OCH_3), 3.75~3.61 (m, 2H, CH_2), 2.23 (s, 3H, CH_3), 2.06~1.97 (m, 2H, CH_2), 1.74 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.0, 165.2, 162.1, 160.0, 159.6, 157.6, 145.6, 145.6, 143.2, 140.8, 137.1, 135.5, 131.7, 131.6, 129.2, 128.9, 128.5, 128.3, 128.2, 126.9, 125.3, 125.2, 119.7, 119.4, 109.5, 109.3, 104.5, 68.4, 53.8, 52.9, 51.5, 29.6, 22.0, 20.9; IR (KBr) ν : 3440, 3299, 3059, 2950, 1702, 1648, 1625, 1587, 1558, 1495, 1436, 1414, 1360, 1318, 1271, 1235, 1202, 1151, 1064, 1047, 1030, 983, 951, 916, 886, 834, 810, 761 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{28}\text{FN}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 507.2084, found: 507.2082.

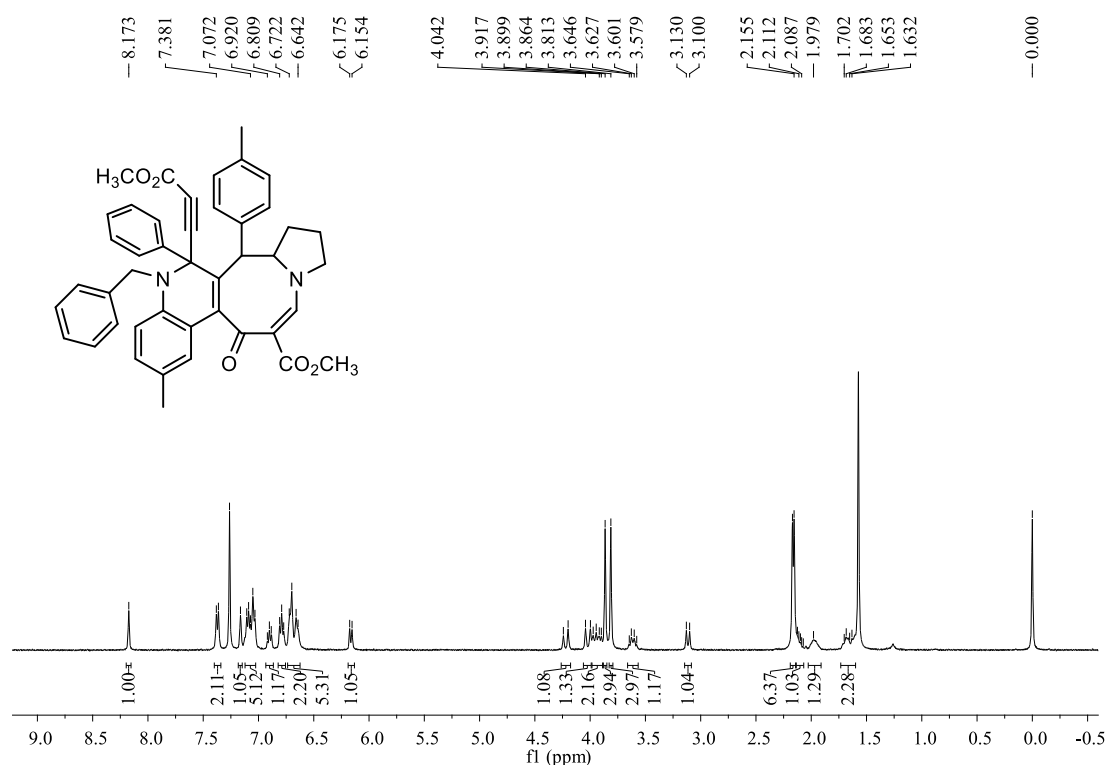


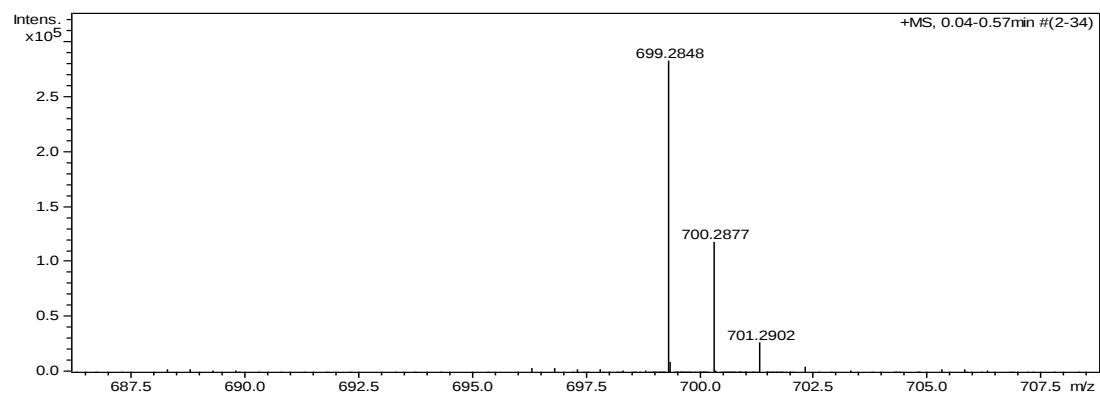
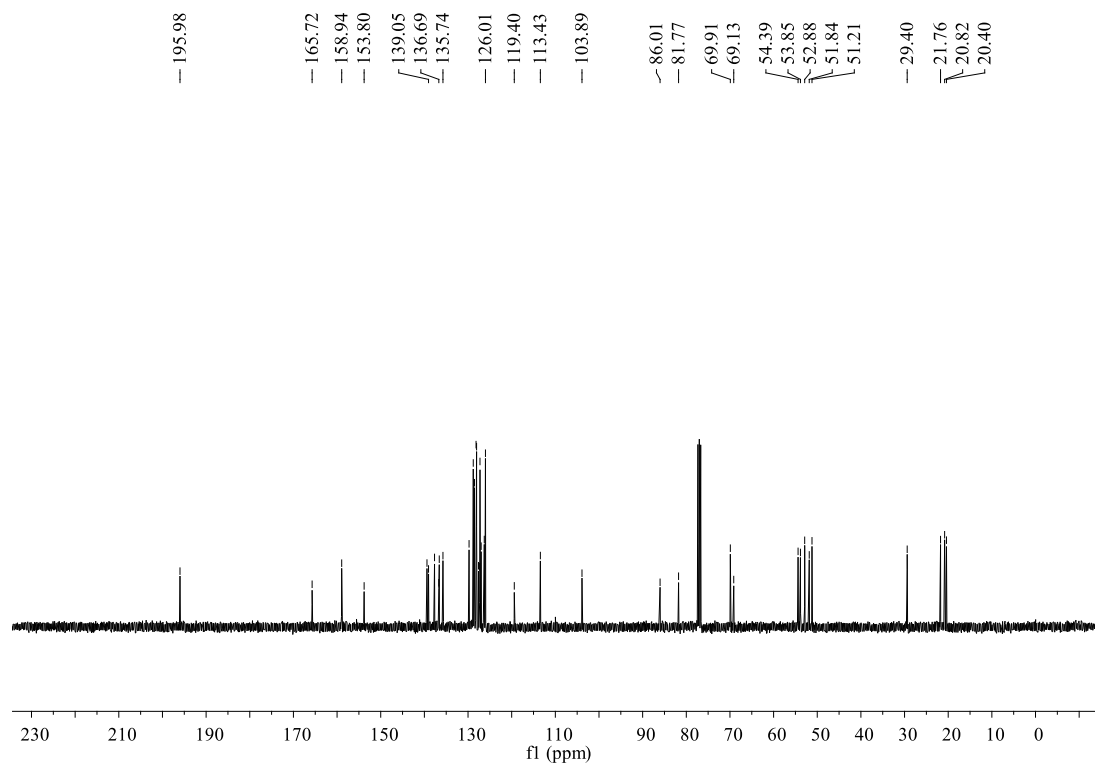


Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1-phenyl-14-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2a):

yellow solid, 78%, m.p. 171~173°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.37 (d, J = 7.6 Hz, 2H, ArH), 7.16 (s, 1H, ArH), 7.12~7.03 (m, 5H, ArH), 6.89 (t, J = 7.2 Hz, 1H, ArH), 6.79 (t, J = 7.2 Hz, 2H, ArH), 6.72~6.64 (m, 5H, ArH), 6.16 (d, J = 8.4 Hz, 1H, ArH), 4.22 (d, J = 17.2 Hz, 1H, CH_2), 4.02 (d, J = 18.0 Hz, 1H, CH_2), 3.97~3.89 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.61 (dd, J_1 = 19.0 Hz, J_2 = 8.6 Hz, 1H, CH), 3.11 (d, J = 12.0 Hz, 1H, CH), 2.16 (s, 6H, CH_3), 2.112~2.07 (m, 1H, CH_2), 1.98 (s, 1H, CH_2), 1.70~1.63 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.9, 165.7, 158.9, 153.8, 139.4, 139.0, 137.6, 136.6, 136.5, 135.7, 129.7, 128.8, 128.5, 128.1, 128.0, 127.6, 127.3, 127.2, 126.9, 126.2, 126.0, 119.4, 113.4, 103.9, 86.0, 81.7, 69.9, 69.1, 54.39, 53.8, 52.8, 51.8, 51.2, 29.4, 21.7, 20.8, 20.4; IR (KBr) ν : 3302, 3002, 2949, 2218, 1711, 1683, 1646, 1606, 1568, 1506, 1456, 1433, 1347, 1249, 1175, 1146, 1118, 1028, 946, 865, 835, 799, 786, 744, 723 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{44}\text{H}_{40}\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 699.2829, found: 699.2848.

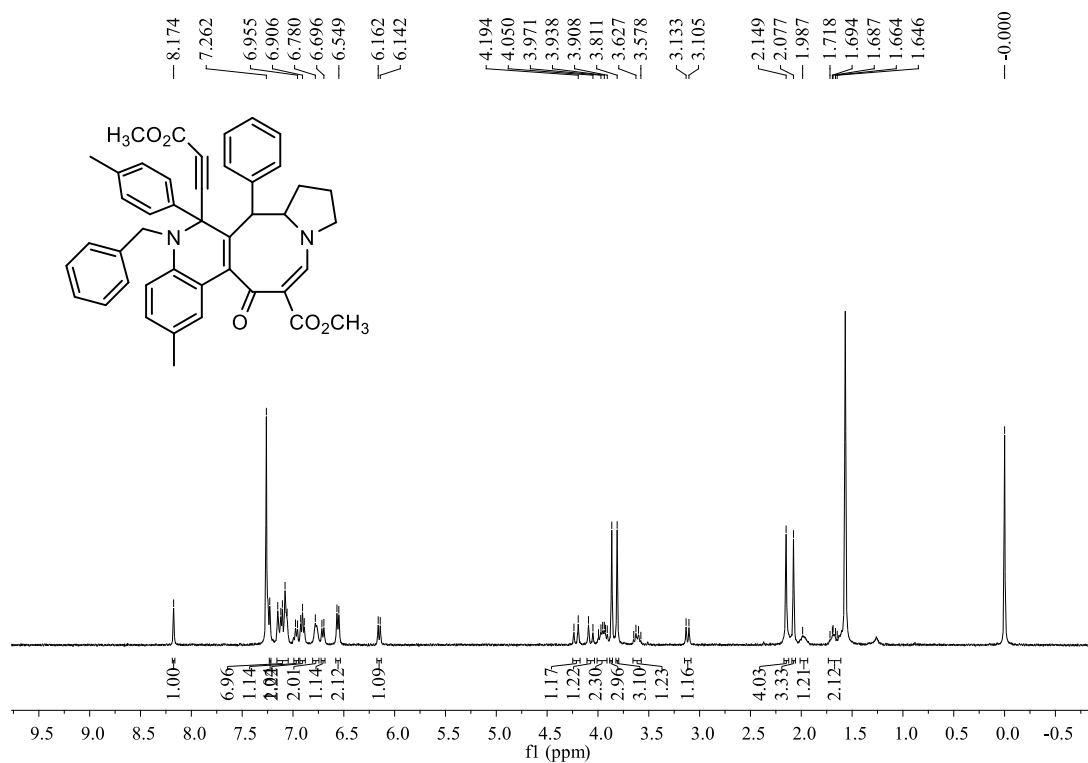


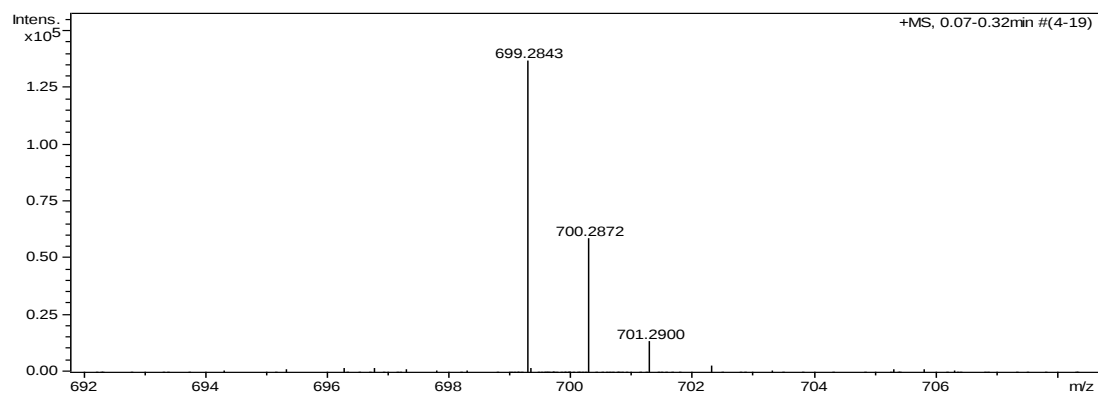
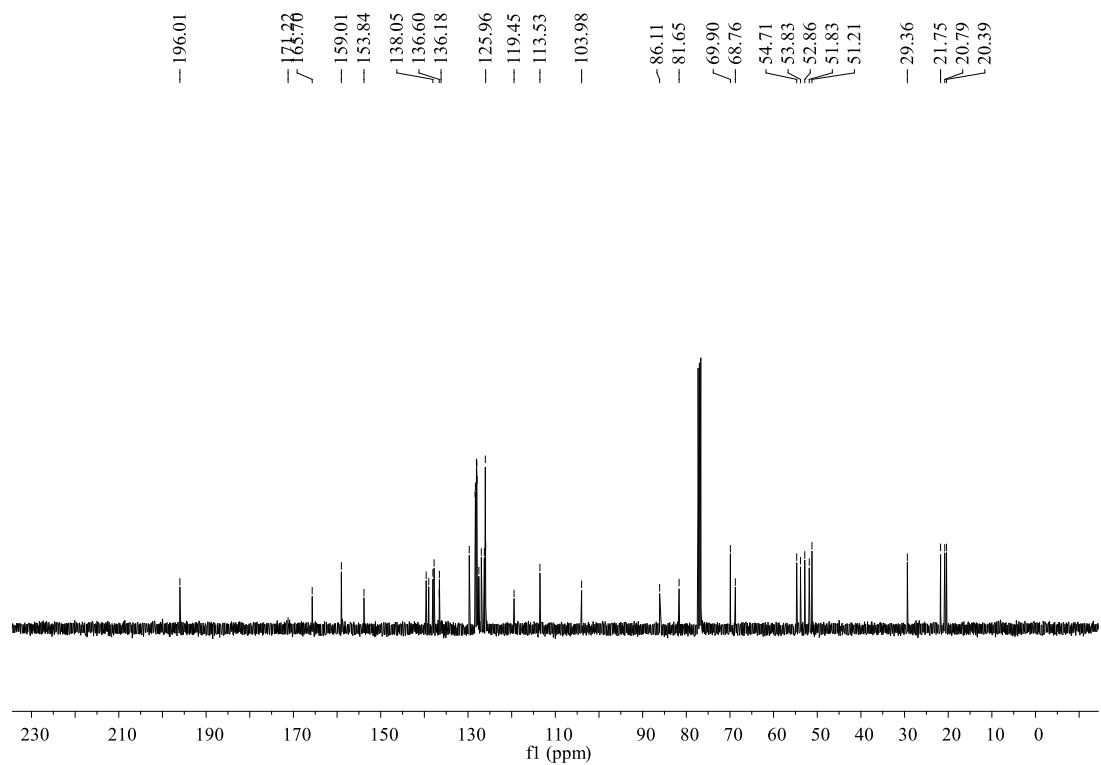


Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-14-phenyl-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2b):

yellow solid, 82%, m.p. 170~172°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.23 (s, 1H, ArH), 7.15~7.06 (m, 7H, ArH), 6.97 (d, $J = 8.0$ Hz, 1H, ArH), 6.91 (t, $J = 7.2$ Hz, 2H, ArH), 6.78 (s, 2H, ArH), 6.71 (d, $J = 8.0$ Hz, 1H, ArH), 6.56 (d, $J = 7.6$ Hz, 2H, ArH), 6.15 (d, $J = 8.0$ Hz, 1H, ArH), 4.22 (d, $J = 16.8$ Hz, 1H, CH_2), 4.07 (d, $J = 17.2$ Hz, 1H, CH_2), 4.01~3.90 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.61 (dd, $J_1 = 19.1$, $J_2 = 9.0$ Hz, 1H, CH), 3.12 (d, $J = 11.2$ Hz, 1H, CH), 2.15 (s, 4H, CH_3 , CH_2), 2.08 (s, 3H, CH_2), 1.99 (s, 1H, CH_2), 1.72~1.65 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 171.2, 165.7, 162.8, 159.0, 153.8, 139.5, 139.0, 138.0, 137.7, 136.6, 136.5, 136.1, 129.7, 128.3, 128.3, 128.0, 127.9, 127.9, 127.6, 127.5, 126.9, 126.2, 126.0, 125.9, 119.4, 113.5, 103.9, 86.1, 81.6, 69.9, 68.7, 54.7, 53.8, 52.8, 51.8, 51.2, 29.3, 21.7, 20.7, 20.3; IR (KBr) ν : 3300, 2951, 2221, 1735, 1710, 1681, 1575, 1502, 1437, 1348, 1247, 1193, 1149, 1043, 1021, 944, 918, 810, 786, 747 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{44}\text{H}_{40}\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 699.2829, found: 699.2843.



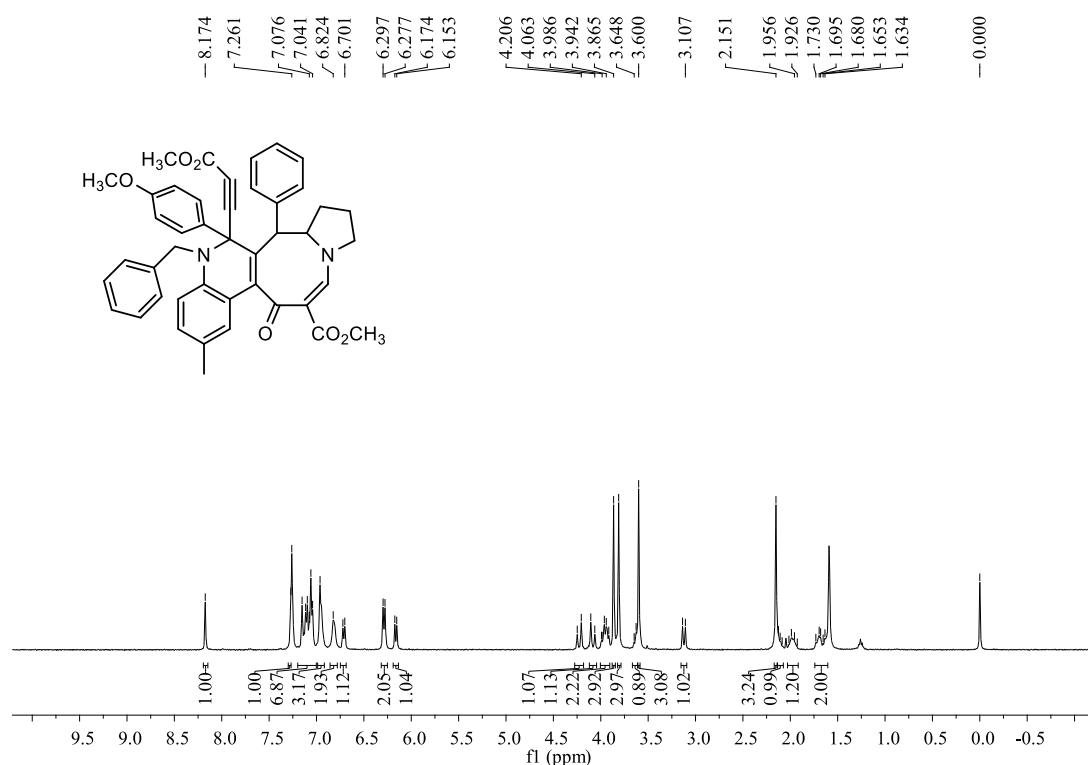


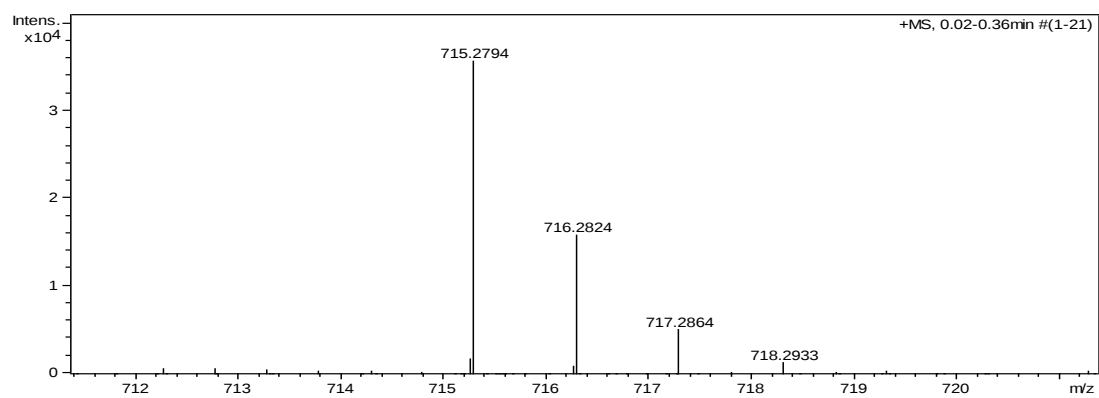
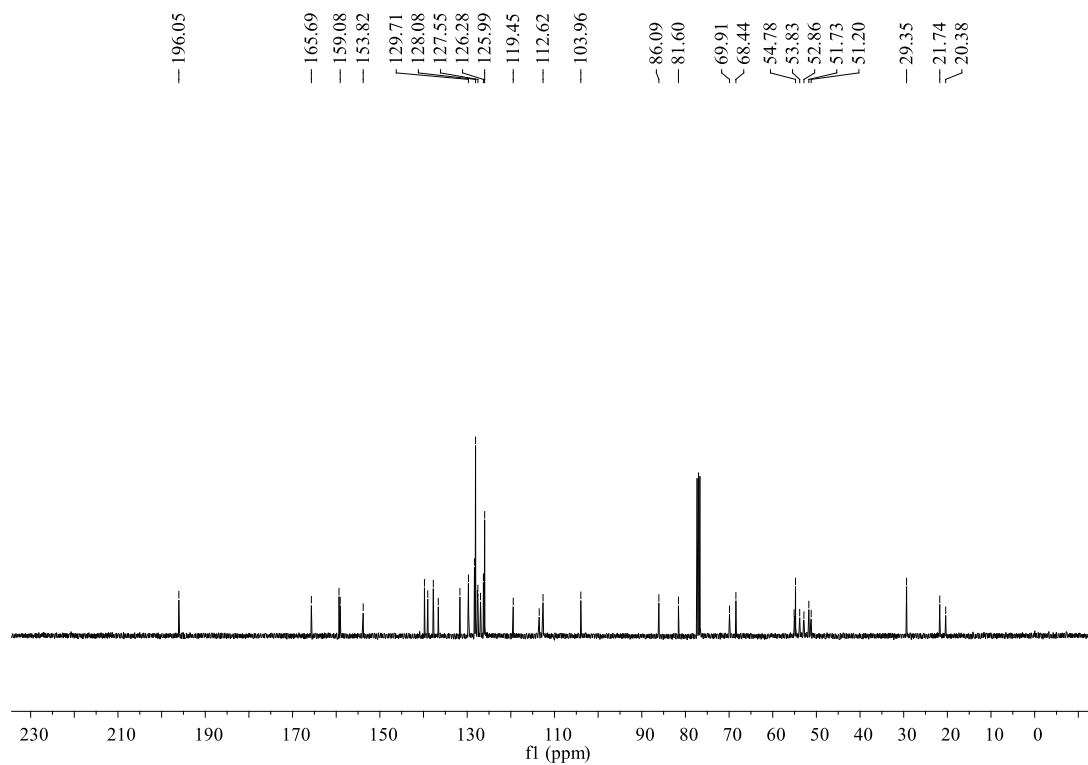
Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-1-(4-methoxyphenyl)-5-methyl-7-oxo-14-phenyl-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate

(2c):

yellow solid, 84%, m.p. 233~235°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.27 (s, 1H, ArH), 7.20~7.00 (m, 7H, ArH), 6.96 (s, 3H, ArH), 6.82 (s, 2H, ArH), 6.71 (d, $J = 8.4$ Hz, 1H, ArH), 6.29 (d, $J = 8.0$ Hz, 2H, ArH), 6.16 (d, $J = 8.4$ Hz, 1H, ArH), 4.23 (d, $J = 16.8$ Hz, 1H, CH_2), 4.08 (d, $J = 16.8$ Hz, 1H, CH_2), 4.00~3.90 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.65~3.63 (m, 1H, CH), 3.60 (s, 3H, OCH_3), 3.12 (d, $J = 12.0$ Hz, 1H, CH), 2.15 (s, 3H, CH_3), 2.14~2.07 (m, 1H, CH_2), 2.04~1.94 (m, 1H, CH_2), 1.74~1.60 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 165.6, 159.3, 159.0, 153.8, 139.7, 139.0, 137.7, 136.6, 131.6, 129.7, 128.3, 128.1, 127.7, 127.5, 126.9, 126.2, 126.1, 125.9, 119.5, 113.5, 112.6, 103.9, 86.0, 81.6, 69.9, 68.4, 55.1, 54.8, 53.8, 52.8, 51.7, 51.2, 29.3, 21.7, 20.3; IR (KBr) ν : 3299, 3084, 2222, 1712, 1571, 1502, 1454, 1347, 1259, 1194, 1145, 1043, 944, 822, 751 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{45}\text{H}_{42}\text{N}_2\text{NaO}_6$ ($[\text{M}+\text{Na}]^+$): 715.2779, found: 715.2794.

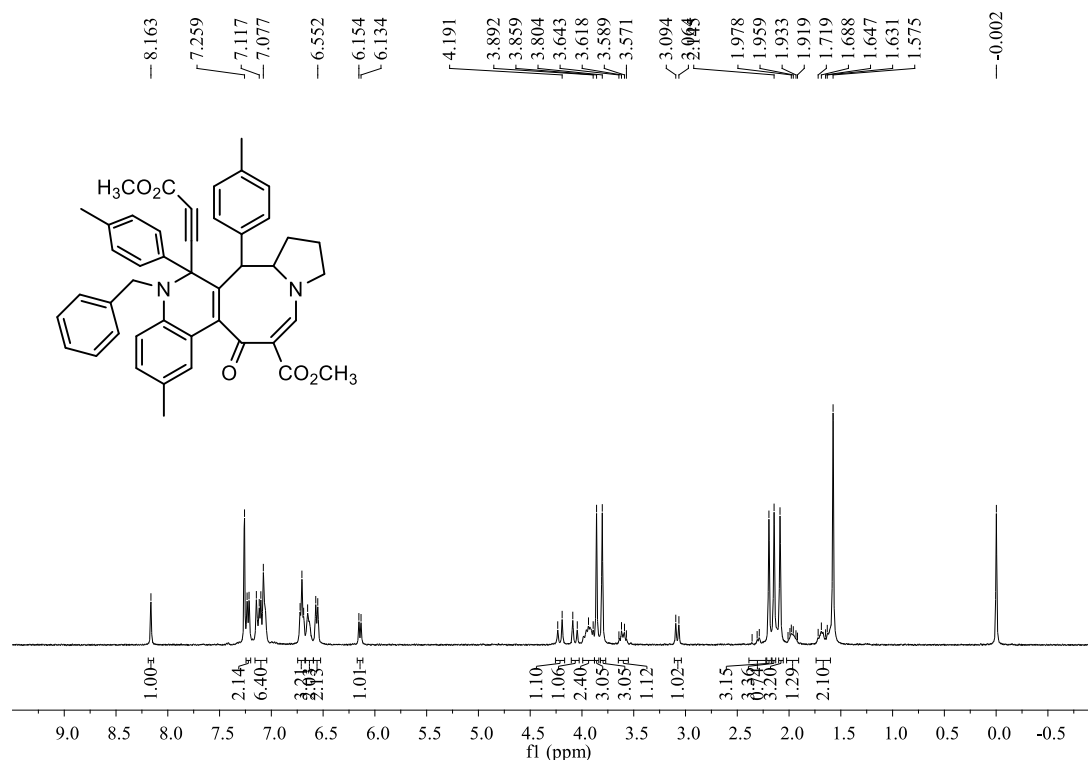


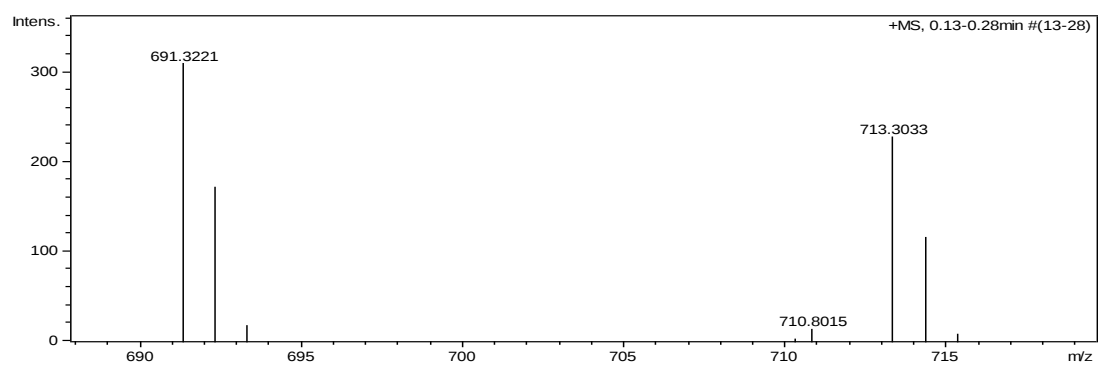
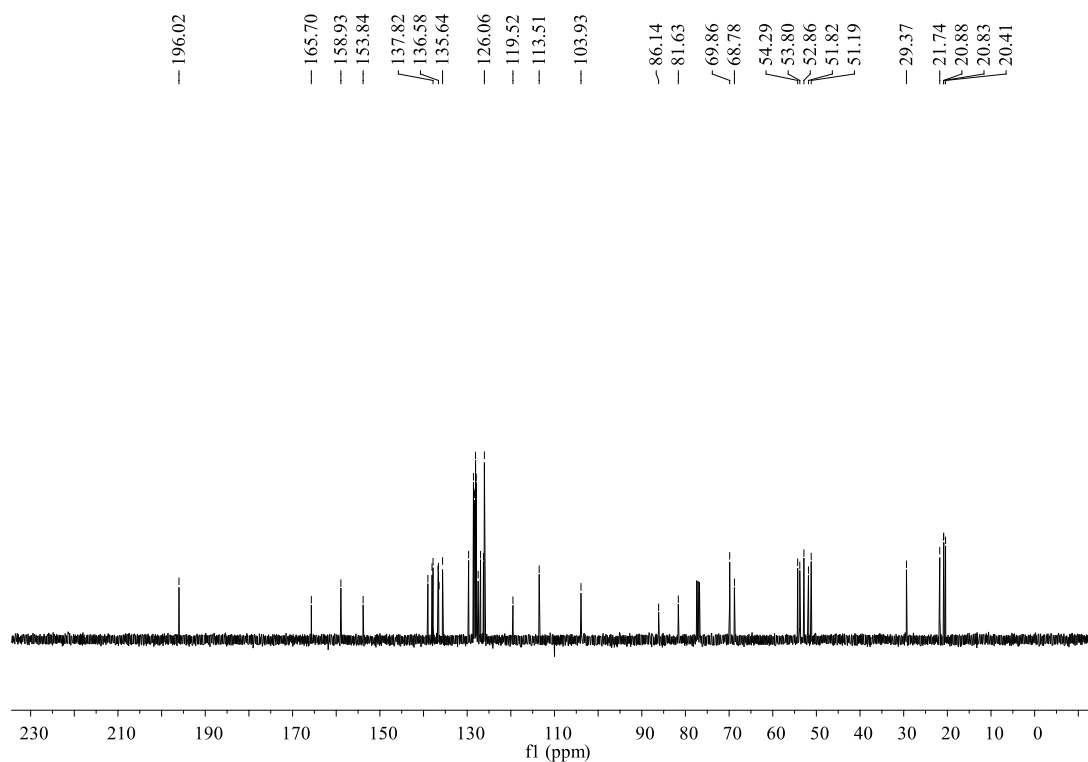


Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1,14-di-p-tolyl-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2d):

yellow solid, 70%, m.p. 165~167°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.16 (s, 1H, CH), 7.22 (d, J = 7.6 Hz, 2H, ArH), 7.14~7.08 (m, 6H, ArH), 6.71 (t, J = 6.8 Hz, 3H, ArH), 6.65 (s, 2H, ArH), 6.56 (d, J = 7.6 Hz, 2H), 6.14 (d, J = 8.0 Hz, 1H, ArH), 4.21 (d, J = 17.2 Hz, 1H, CH_2), 4.07 (d, J = 17.6 Hz, 1H, CH_2), 3.98~3.86 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.64~3.57 (m, 1H, CH), 3.08 (d, J = 12.0 Hz, 1H, CH), 2.36~2.29 (m, 1H, CH_2), 2.19 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.01~1.92 (m, 1H, CH_2), 1.72~1.57 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 165.7, 159.0, 153.8, 138.9, 138.0, 137.82, 136.6, 136.5, 136.4, 135.6, 129.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 126.9, 126.3, 126.0, 119.5, 113.5, 109.9, 103.9, 86.1, 81.6, 69.9, 68.7, 54.2, 53.8, 52.9, 51.8, 51.2, 29.3, 21.7, 20.9, 20.8, 20.4; IR (KBr) ν : 3550, 3480, 3415, 2945, 2217, 1709, 1579, 1503, 1425, 1332, 1261, 1149, 1037, 948, 885, 803, 753, 723 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{45}\text{H}_{42}\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 713.2986, found: 713.3033.



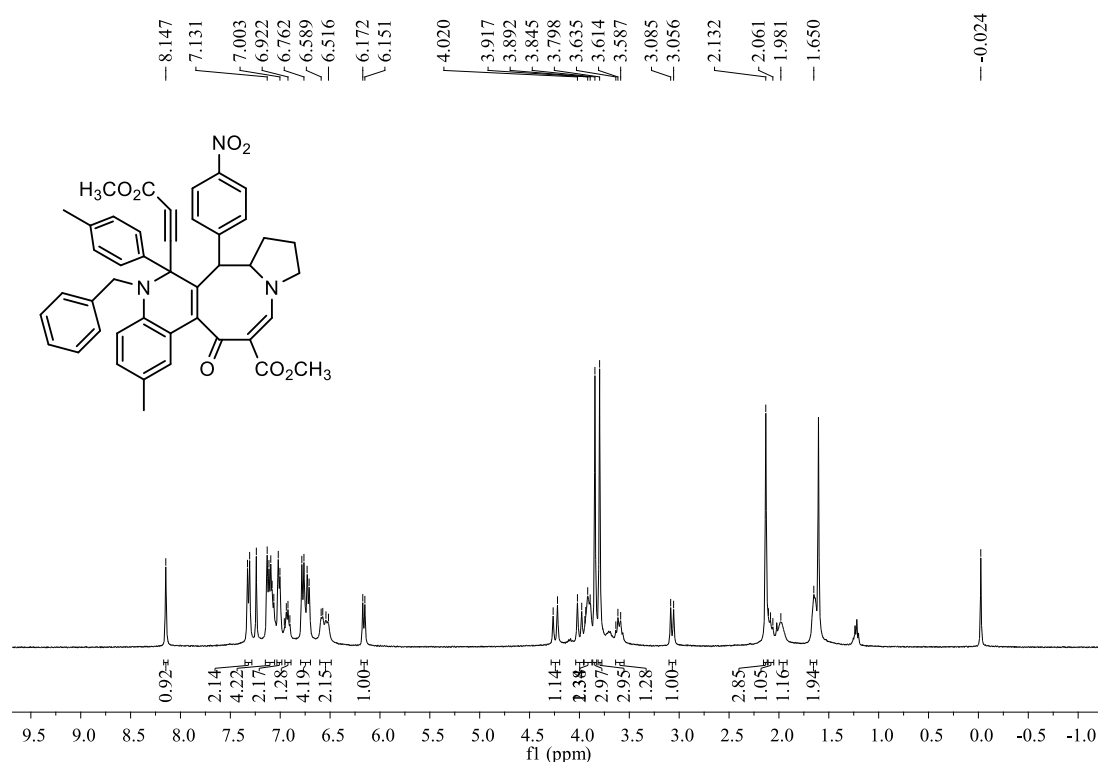


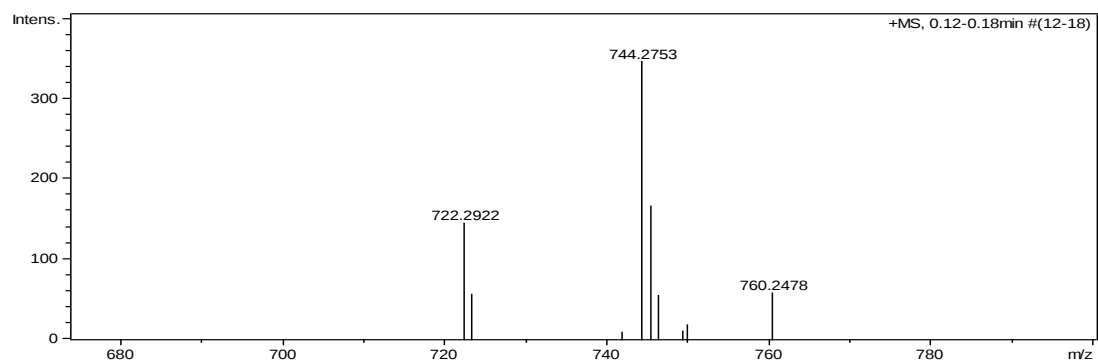
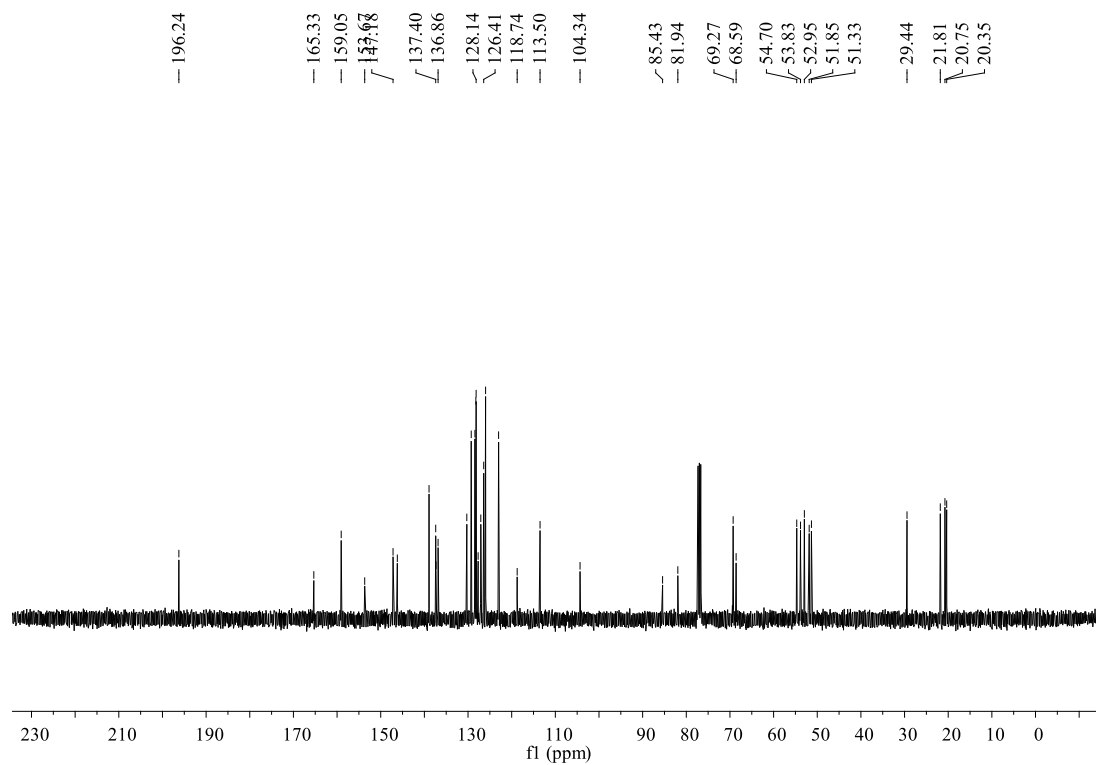
Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-14-(4-nitrophenyl)-7-oxo-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate

(2e):

yellow solid, 59%, m.p. 232~234°C; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H, CH), 7.32 (d, J = 8.8 Hz, 2H, ArH), 7.13~7.06 (m, 4H, ArH), 7.01 (d, J = 6.8 Hz, 2H, ArH), 6.95~6.89 (m, 1H, ArH), 6.75 (dd, J = 16.8 Hz, J = 8.0 Hz, 4H, ArH), 6.60~6.52 (m, 2H, ArH), 6.16 (d, J = 8.4 Hz, 1H, ArH), 4.24 (d, J = 17.6 Hz, 1H, CH_2), 4.00 (d, J = 17.2 Hz, 1H, CH_2), 3.92 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.64~3.55 (m, 1H, CH), 3.07 (d, J = 11.6 Hz, 1H, CH), 2.13 (s, 3H, CH_3), 2.11~2.05 (m, 1H, CH_2), 1.98 (s, 1H, CH_2), 1.65 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 165.3, 159.0, 153.6, 147.1, 146.2, 138.9, 137.4, 137.3, 136.8, 130.2, 129.2, 128.4, 128.2, 128.1, 127.6, 127.0, 126.4, 125.9, 123.0, 118.7, 113.5, 104.3, 85.4, 81.9, 69.2, 68.5, 54.70, 53.8, 52.9, 51.8, 51.3, 29.4, 21.8, 20.7, 20.3; IR (KBr) ν : 3549, 3477, 3412, 2950, 2879, 2227, 1913, 1711, 1648, 1580, 1514, 1416, 1350, 1252, 1176, 1138, 1036, 943, 854, 811, 753, 731 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{44}\text{H}_{39}\text{N}_3\text{NaO}_7$ ($[\text{M}+\text{Na}]^+$): 744.2680, found: 744.2753.



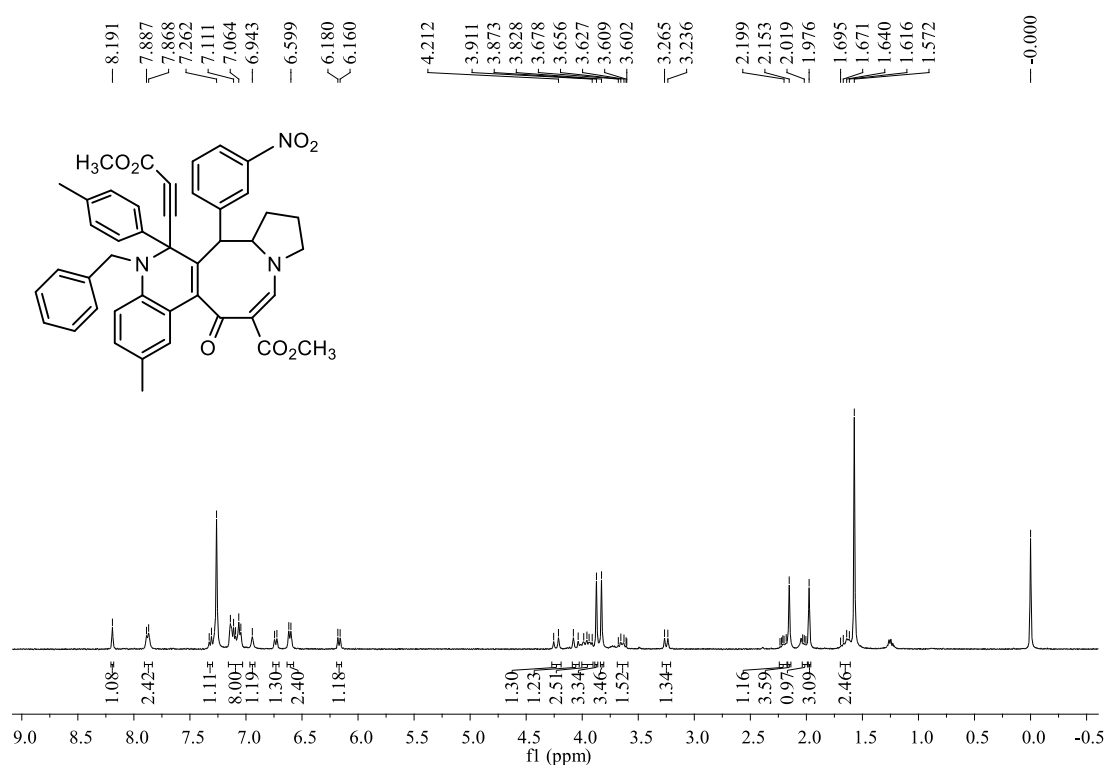


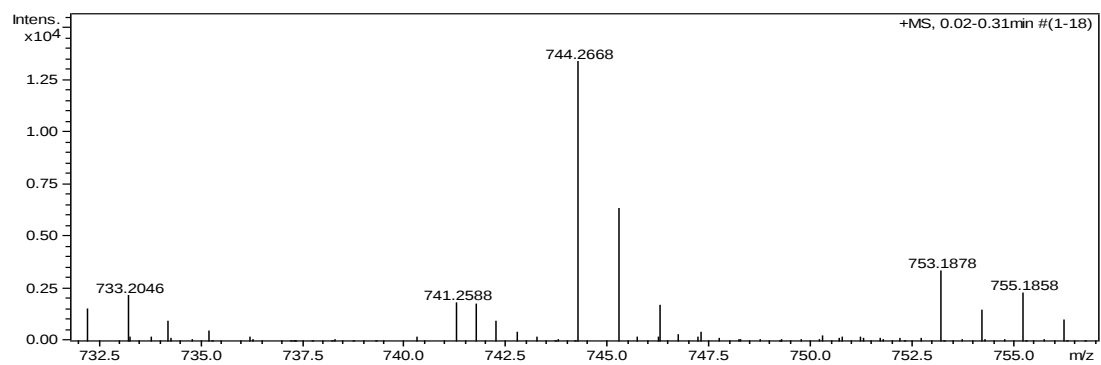
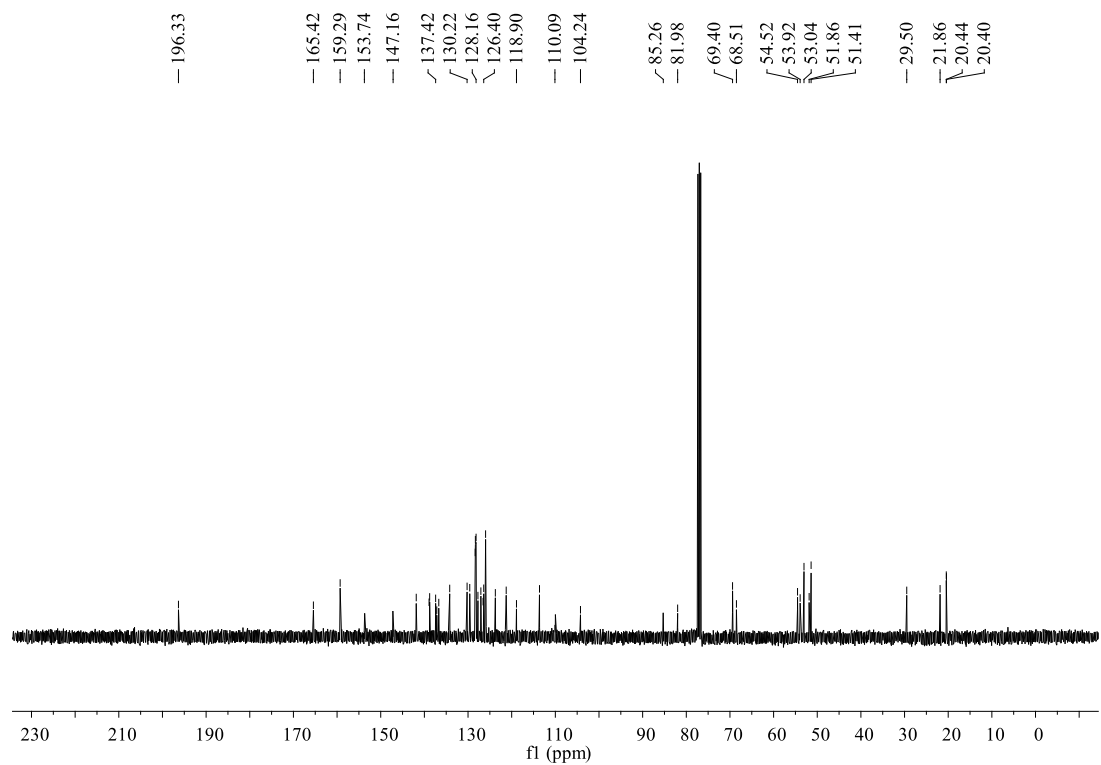
Methyl

(E)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-14-(3-nitrophenyl)-7-oxo-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate

(2f):

yellow solid, 69%, m.p. 215~217°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (s, 1H, CH), 7.88 (d, J = 7.6 Hz, 2H, ArH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.17~7.02 (m, 8H, ArH), 6.94 (s, 1H, ArH), 6.73 (d, J = 8.2 Hz, 1H, ArH), 6.61 (d, J = 7.6 Hz, 2H, ArH), 6.17 (d, J = 8.0 Hz, 1H, ArH), 4.23 (d, J = 17.2 Hz, 1H, CH_2), 4.06 (d, J = 17.2 Hz, 1H, CH_2), 3.95-3.91 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.68~3.60 (m, 1H, CH), 3.25 (d, J = 11.6 Hz, 1H, CH), 2.25~2.18 (m, 1H, CH_2), 2.15 (s, 3H, CH_3), 2.05 (s, 1H, CH_2), 2.03~2.00 (m, 1H, CH_2), 1.98 (s, 3H, CH_3), 1.69~1.57 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.3, 165.4, 159.2, 153.7, 147.1, 141.8, 138.9, 138.7, 137.4, 137.1, 136.7, 134.1, 130.2, 129.6, 128.3, 128.3, 128.1, 127.7, 127.0, 126.5, 126.4, 125.9, 123.7, 121.2, 118.9, 113.6, 110.0, 104.2, 85.2, 81.9, 69.4, 68.5, 54.5, 53.9, 53.0, 51.8, 51.4, 29.5, 21.8, 20.5, 20.4; IR (KBr) ν : 3549, 3477, 3412, 2950, 2879, 2227, 1913, 1711, 1648, 1580, 1514, 1416, 1350, 1252, 1176, 1138, 1036, 943, 854, 811, 753, 731 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{39}\text{N}_3\text{NaO}_7$ ($[\text{M}+\text{Na}]^+$): 744.2680, found: 744.2668.

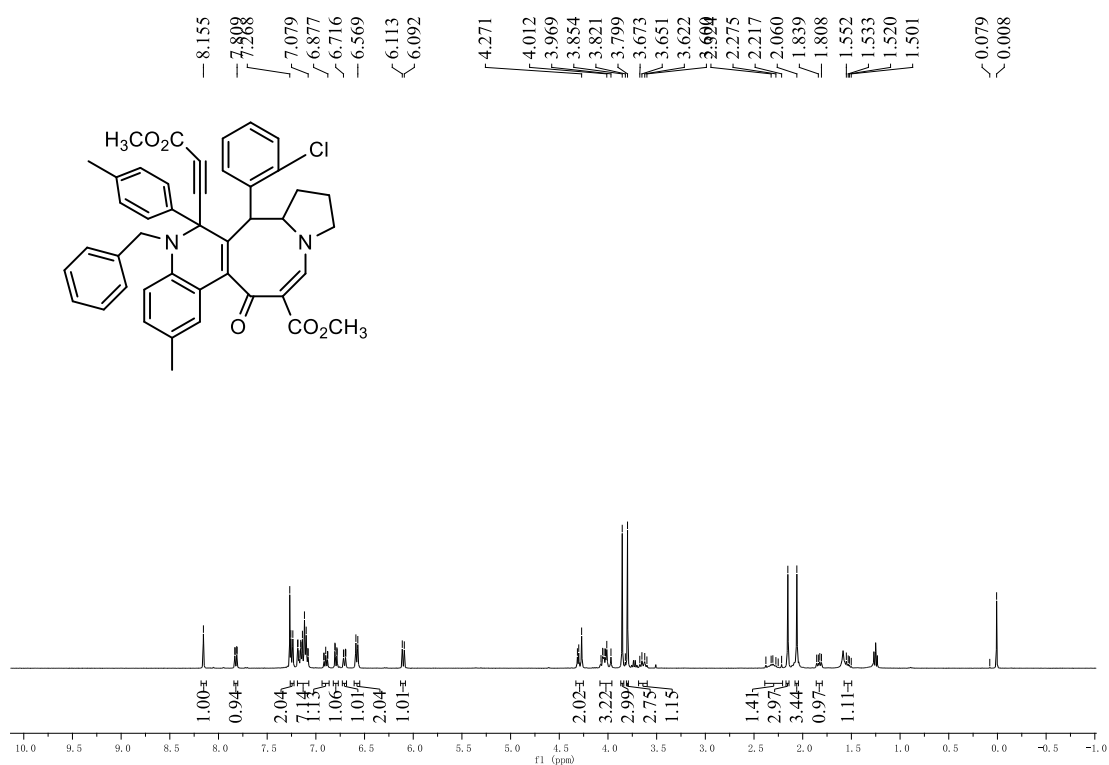


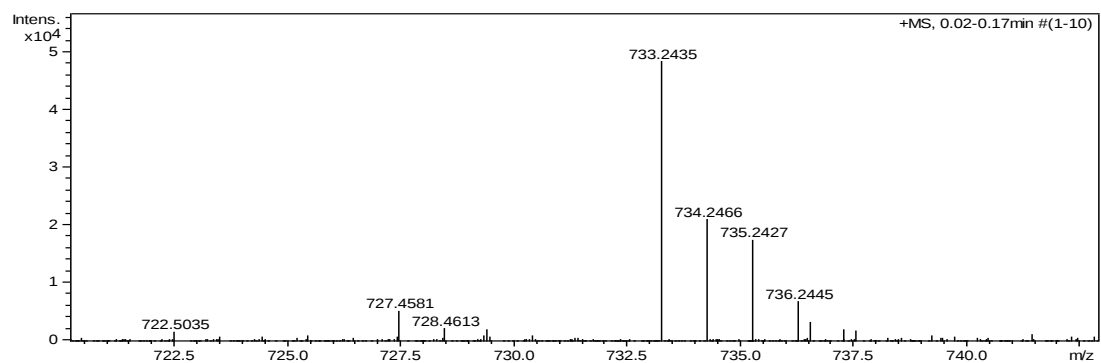
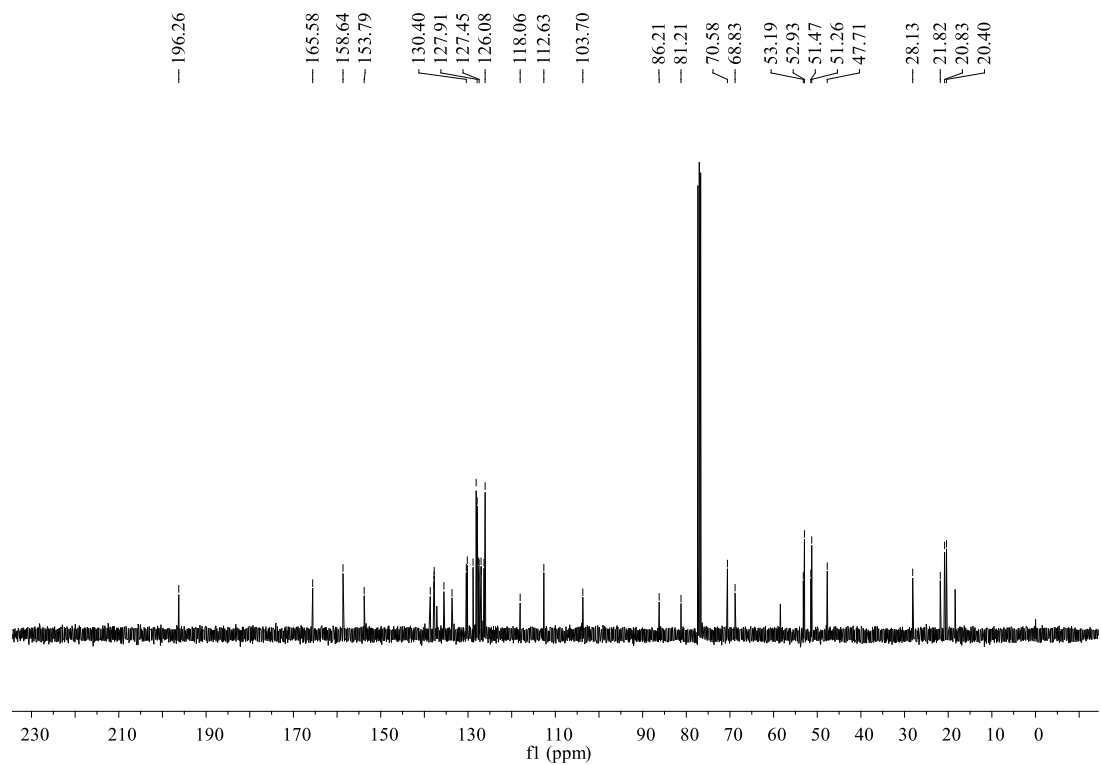


Methyl

(E)-2-benzyl-14-(2-chlorophenyl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2g):

yellow solid, 71%, m.p. 173~175°C; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.81 (d, $J = 6.8$ Hz, 1H, ArH), 7.24 (d, $J = 8.1$ Hz, 2H, ArH), 7.12 (d, $J = 13.4$, 7.9 Hz, 8H, ArH), 6.89 (t, $J = 7.6$ Hz, 1H, ArH), 6.78 (d, $J = 7.8$ Hz, 1H, ArH), 6.70 (d, $J = 7.2$ Hz, 1H, ArH), 6.57 (d, $J = 7.8$ Hz, 2H, ArH), 6.09 (d, $J = 8.3$ Hz, 1H, ArH), 4.29 (d, $J = 6.7$ Hz, 1H, CH_2), 4.26 (s, 1H, CH_2), 4.04~3.96 (m, 3H, CH_2), 3.85 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.63 (dd, $J_1 = 20.4$ Hz, $J_2 = 8.8$ Hz, 1H), 2.42~2.18 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 2.09 (d, $J = 7.2$ Hz, 1H, CH_2), 2.05 (s, 3H, CH_3), 1.86~1.81 (m, 1H, CH_2), 1.56~1.50 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 165.5, 158.6, 153.7, 138.6, 137.8, 137.7, 137.7, 135.5, 133.6, 130.4, 130.1, 128.8, 128.1, 127.9, 127.8, 127.5, 127.5, 127.4, 127.0, 126.9, 126.3, 126.0, 118.0, 112.6, 103.7, 86.2, 81.2, 70.5, 68.8, 53.1, 52.9, 51.4, 51.2, 47.7, 28.1, 21.8, 20.8, 20.4; IR (KBr) ν : 3479, 3415, 2950, 2219, 1710, 1579, 1527, 1434, 1350, 1266 1154, 1038, 953, 896, 809, 734 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{39}\text{ClN}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 733.2440, found: 733.2435.

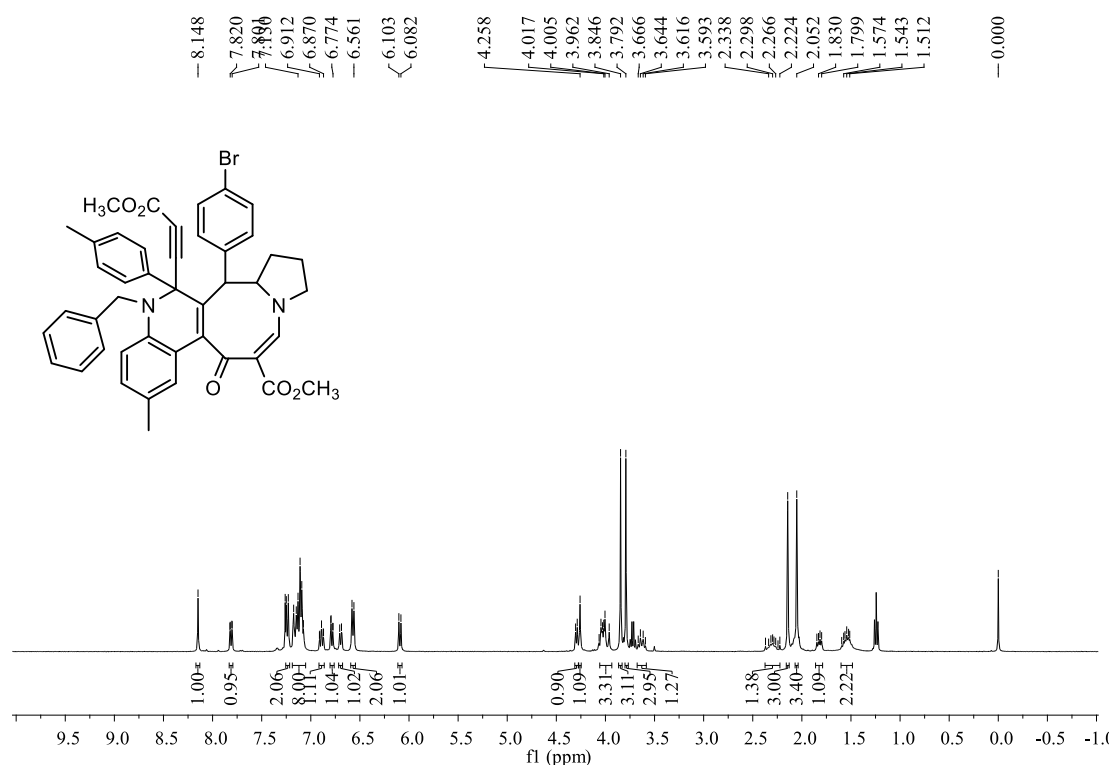


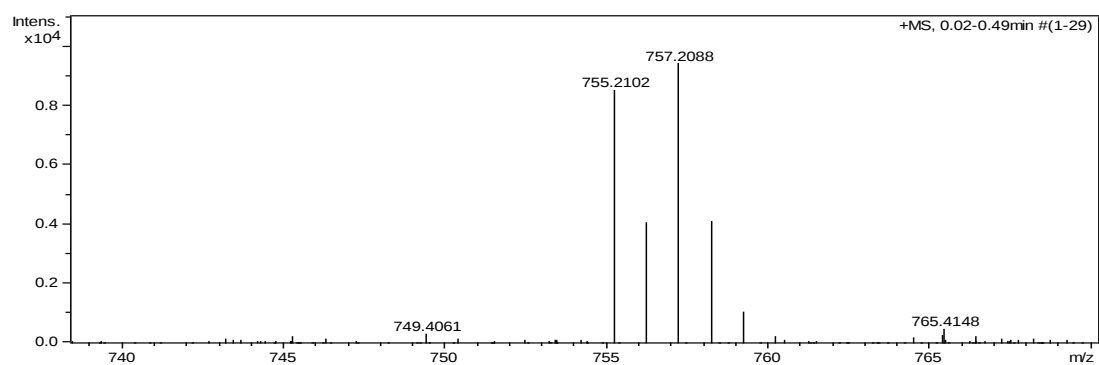
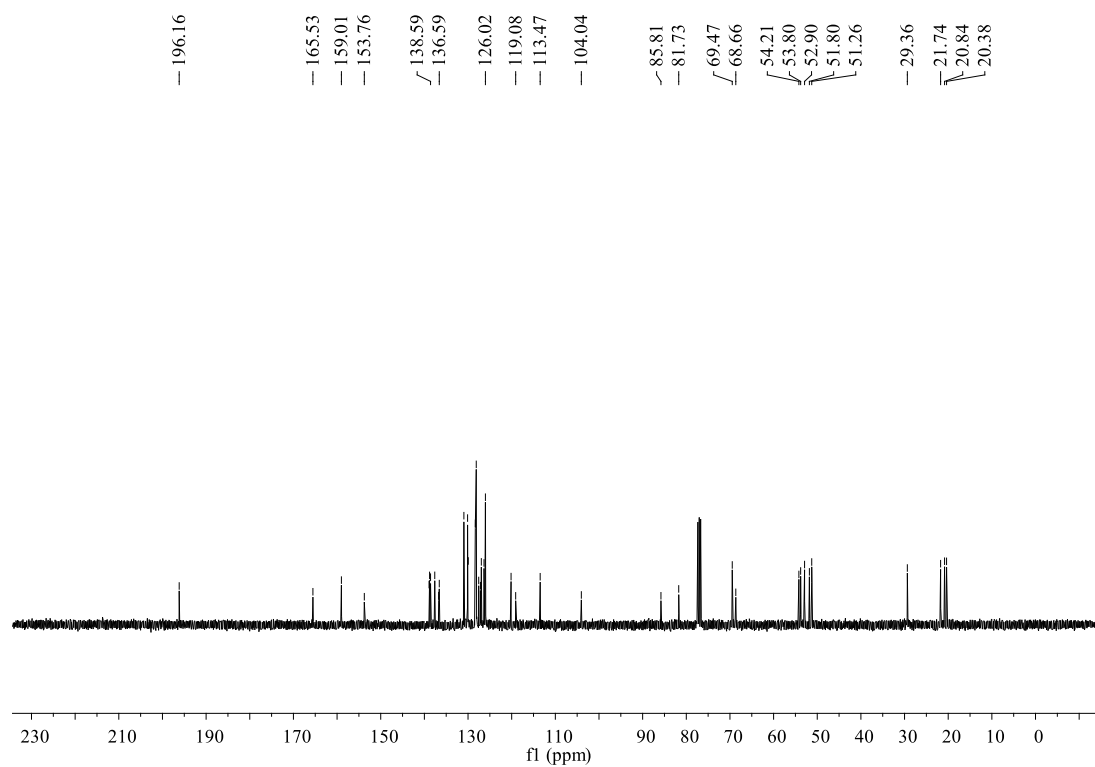


Methyl

(E)-2-benzyl-14-(4-bromophenyl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1-(p-to ly)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2h):

yellow solid, 50%, m.p. 170~172°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.15 (s, 1H), 7.83–7.79 (m, 1H, ArH), 7.23 (d, $J = 8.0$ Hz, 1H, ArH), 7.12 (m, 8H, ArH), 6.91–6.87 (m, 1H, ArH), 6.80~6.76 (m, 1H, ArH), 6.70 (d, $J = 7.6$ Hz, 1H, ArH), 6.57 (d, $J = 8.0$ Hz, 2H, ArH), 6.09 (d, $J = 8.4$ Hz, 1H, ArH), 4.30 (d, $J = 6.8$ Hz, 1H, CH_2), 4.26 (s, 1H, CH_2), 4.02 (m, 3H, CH_2 , CH), 3.85 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.63 (dd, $J_1 = 20.0$, $J_2 = 9.0$ Hz, 1H, CH), 2.37~2.22 (m, 1H, CH_2), 2.14 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.82 (dd, $J = 12.8$, $J = 6.8$ Hz, 1H, CH_2), 1.60~1.49 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 165.5, 159.0, 153.7, 138.9, 138.8, 138.5, 137.6, 136.7, 136.5, 130.9, 130.1, 129.9, 128.3, 128.1, 127.5, 127.1, 126.9, 126.3, 126.0, 120.1, 119.1, 113.5, 104.0, 85.8, 81.7, 69.4, 68.6, 54.2, 53.8, 52.9, 51.8, 51.2, 29.3, 21.7, 20.8, 20.3; IR (KBr) ν : 3530, 3415, 2958, 2881, 2229, 1711, 1653, 1578, 1501, 1444, 1345, 1252, 1156, 1036, 948, 874, 797, 755 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{40}\text{BrN}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 755.2115, found: 755.2102.

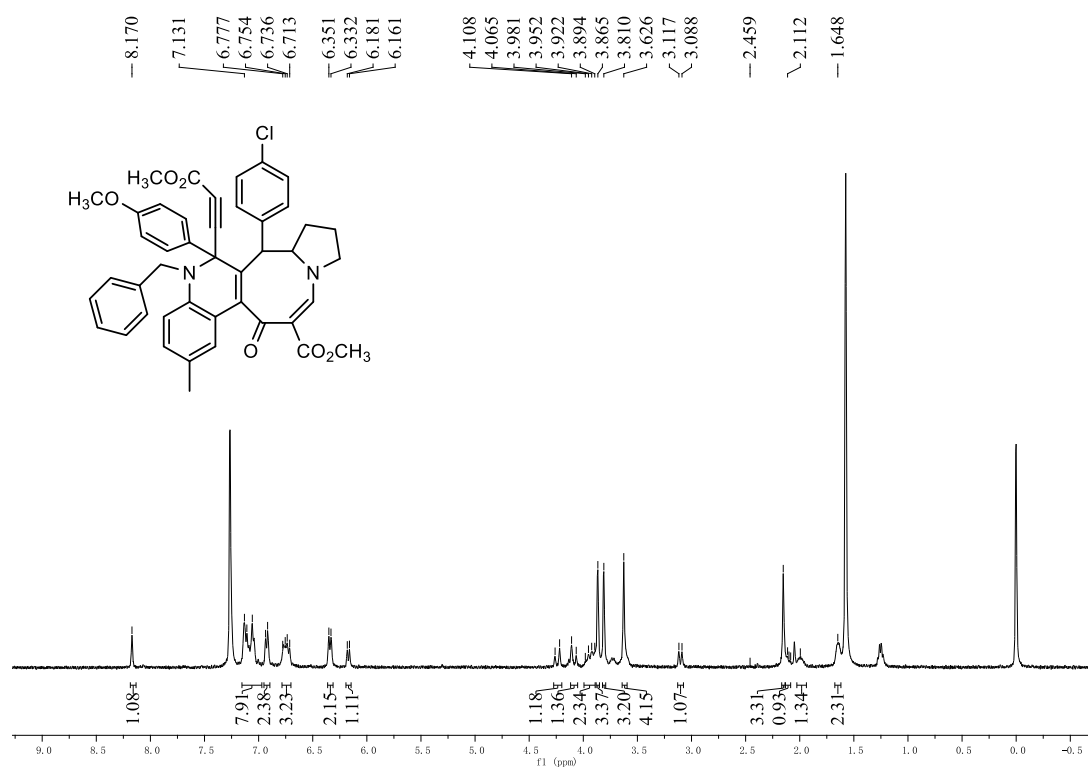


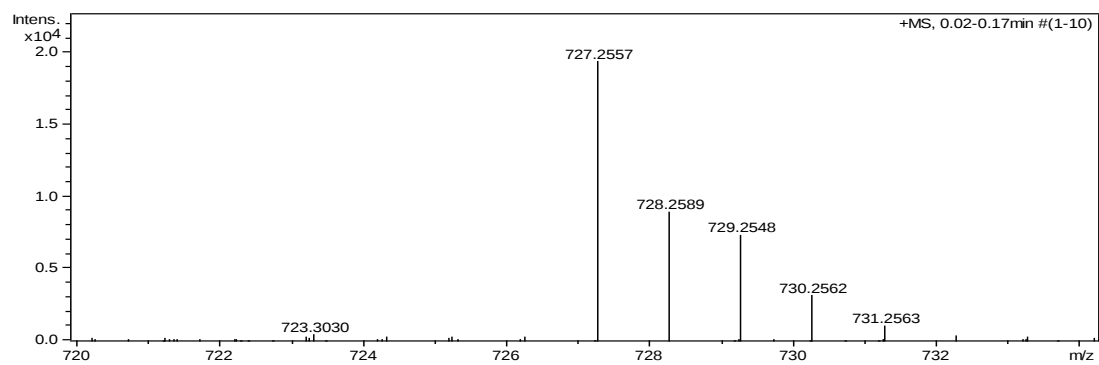
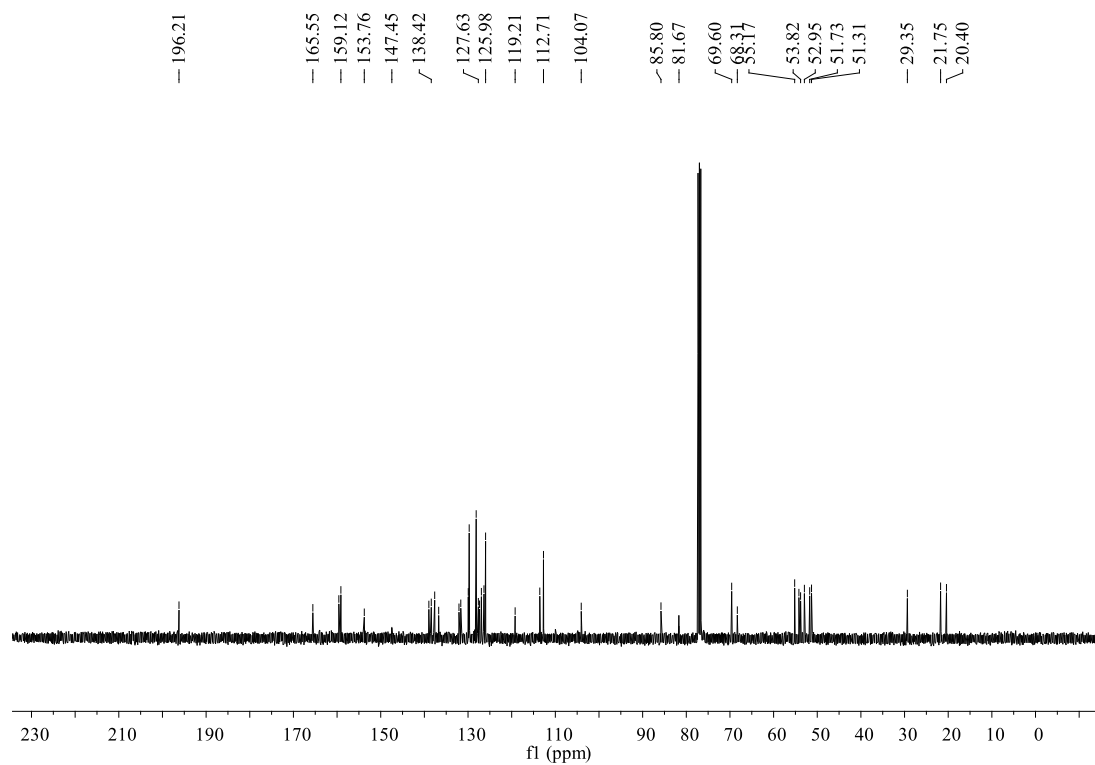


Methyl

(E)-2-benzyl-14-(4-chlorophenyl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-1-(4-methoxyphenyl)-5-methyl-7-oxo-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2i):

yellow solid, 74%, m.p. 169~171°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.15~7.02 (m, 8H, ArH), 6.93 (d, $J = 7.6$ Hz, 2H, ArH), 6.8-6.7 (m, 3H, ArH), 6.34 (d, $J = 7.6$ Hz, 2H, ArH), 6.17 (d, $J = 8.0$ Hz, 1H, ArH), 4.24 (d, $J = 16.8$ Hz, 1H, CH_2), 4.09 (d, $J = 17.2$ Hz, 2H, CH_2), 4.0~3.9 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.63 (s, 1H, OCH_3 , CH), 3.10 (d, $J = 11.6$ Hz, 1H, CH), 2.15 (s, 3H, CH_3), 2.1~2.0 (m, 1H, CH_2), 1.99 (s, 1H, CH_2), 1.65 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 165.5, 159.5, 159.1, 153.7, 147.4, 138.9, 138.4, 137.6, 136.7, 132.0, 131.6, 129.9, 129.7, 128.1, 127.6, 127.3, 126.9, 126.3, 125.9, 119.2, 113.5, 112.7, 104.0, 85.8, 81.6, 69.6, 68.3, 55.1, 54.2, 53.8, 52.9, 51.7, 51.3, 29.3, 21.7, 20.4; IR (KBr) ν : 3553, 3477, 3414, 3237, 2949, 2220, 2028, 1711, 1623, 1578, 1501, 1427, 1252, 1155, 1034, 950, 807, 736 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{44}\text{H}_{40}\text{ClN}_2\text{O}_6$ ($[\text{M}+\text{H}]^+$): 727.2569, found: 727.2557.

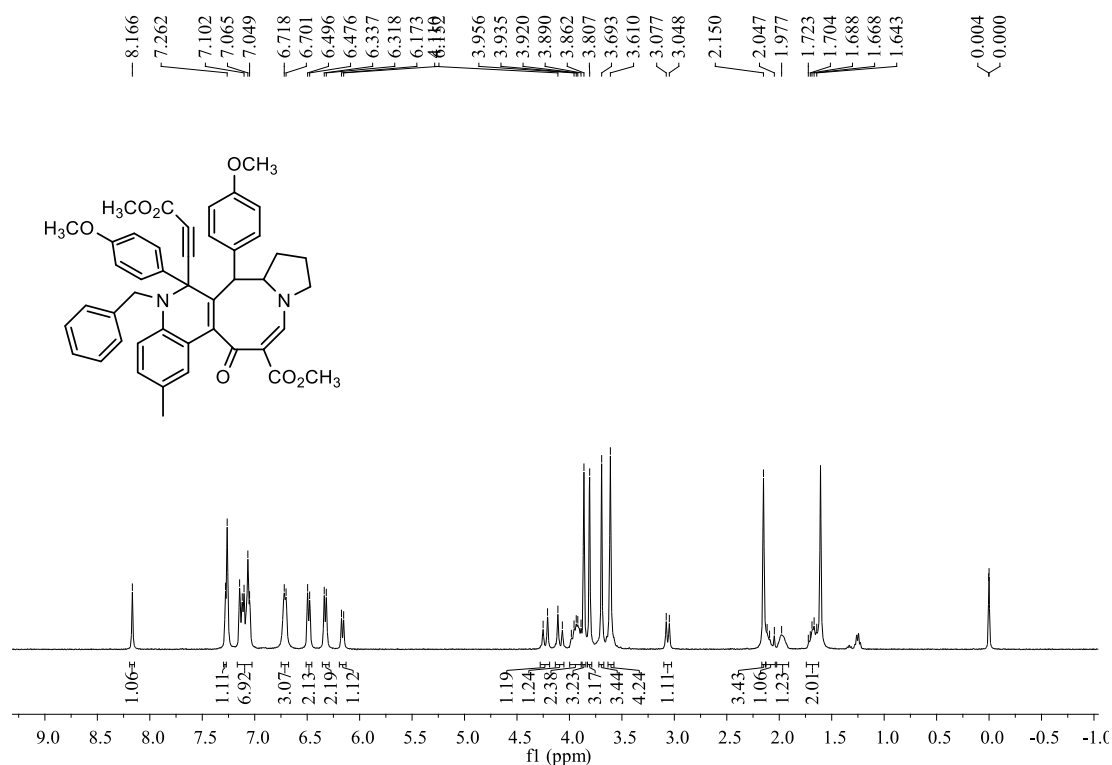


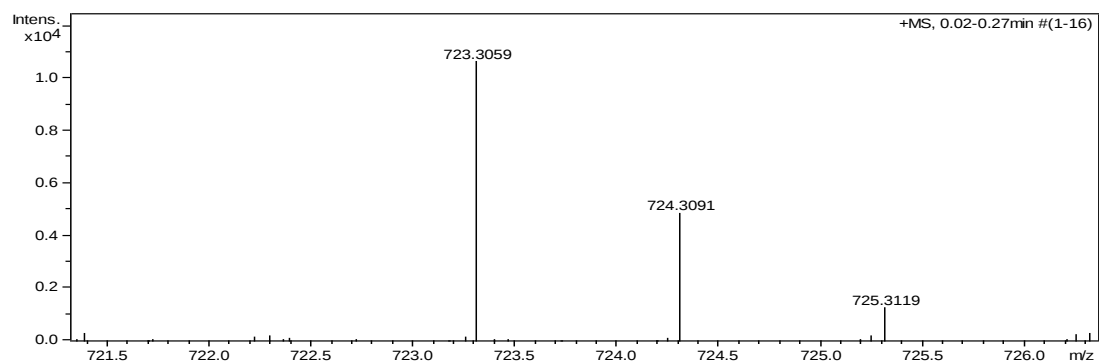
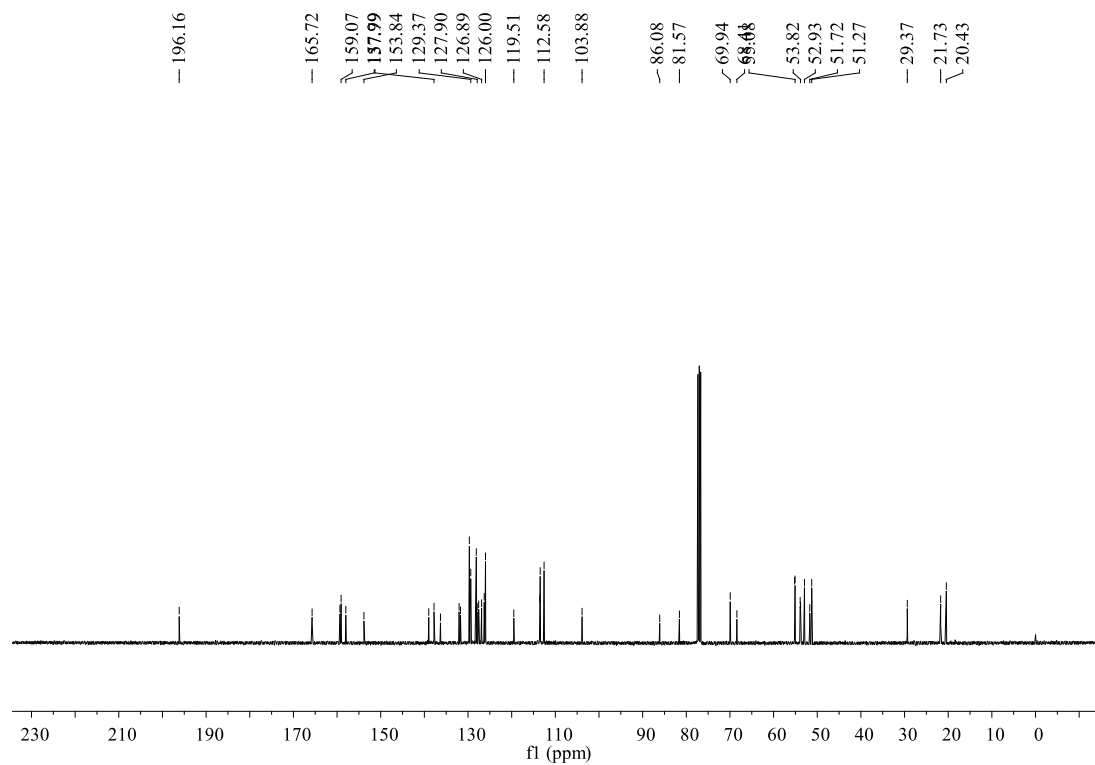


Methyl

(*E*)-2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-1,14-bis(4-methoxyphenyl)-5-methyl-7-oxo-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (2j):

yellow solid, 73%, m.p. 165~167 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.28 (s, 1H, ArH), 7.17~7.01 (m, 7H, ArH), 6.71 (d, $J = 2.8$ Hz, 3H, ArH), 6.49 (d, $J = 8.0$ Hz, 2H, ArH), 6.33 (d, $J = 7.6$ Hz, 2H, ArH), 6.16 (d, $J = 8.4$ Hz, 1H, ArH), 4.23 (d, $J = 16.8$ Hz, 1H, CH_2), 4.09 (d, $J = 17.2$ Hz, 1H, CH_2), 4.00~3.89 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.69 (s, 4H, OCH_3), 3.61 (s, 1H, CH), 3.06 (d, $J = 11.6$ Hz, 1H, CH_2), 2.15 (s, 3H, CH_3), 2.16~2.05 (m, 1H, CH_2), 1.98 (s, 1H, CH_2), 1.74~1.62 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.1, 165.7, 159.3, 159.0, 157.9, 153.8, 139.0, 137.7, 136.3, 132.0, 131.7, 129.7, 129.3, 128.1, 127.9, 127.5, 126.8, 126.2, 126.0, 119.5, 113.5, 113.4, 112.5, 103.8, 86.0, 81.5, 69.9, 68.4, 55.1, 55.0, 53.9, 53.8, 52.9, 51.7, 51.2, 29.3, 21.7, 20.4; IR (KBr) ν : 3551, 3412, 2962, 2889, 2214, 1711, 1653, 1578, 1506, 1433, 1245, 1156, 1113, 1076, 1032, 953, 887, 839, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{45}\text{H}_{43}\text{N}_2\text{O}_7$ ($[\text{M}+\text{H}]^+$): 723.3065, found: 723.3059.

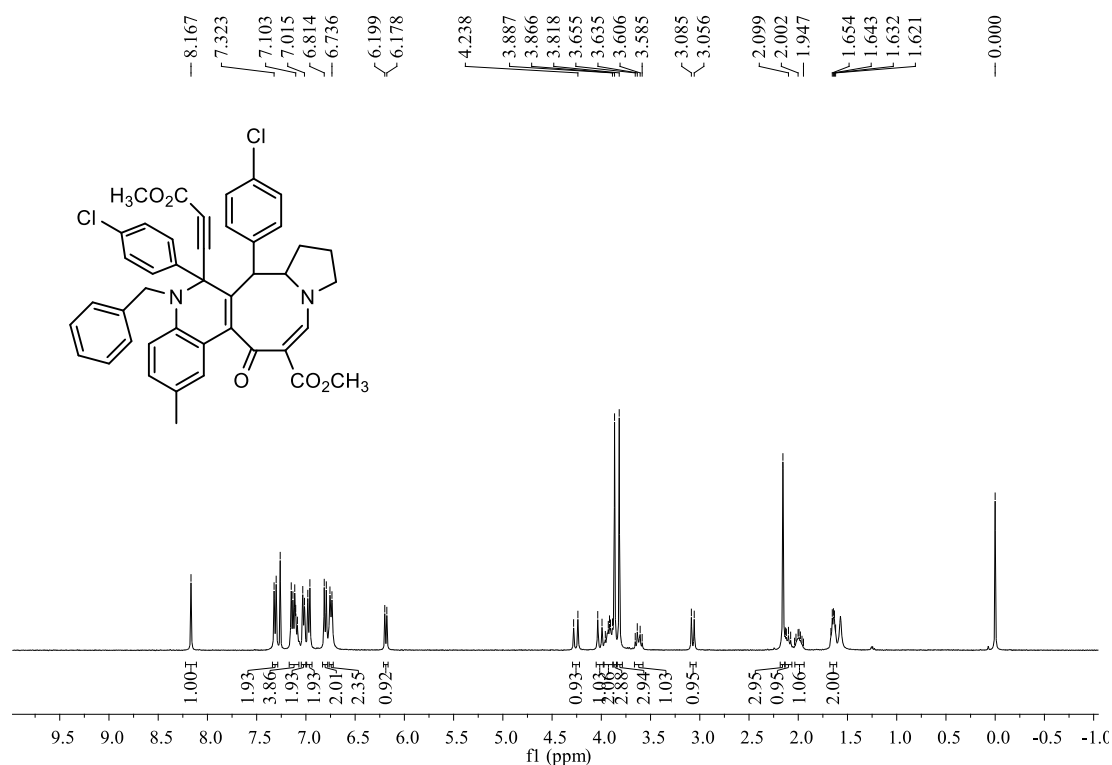


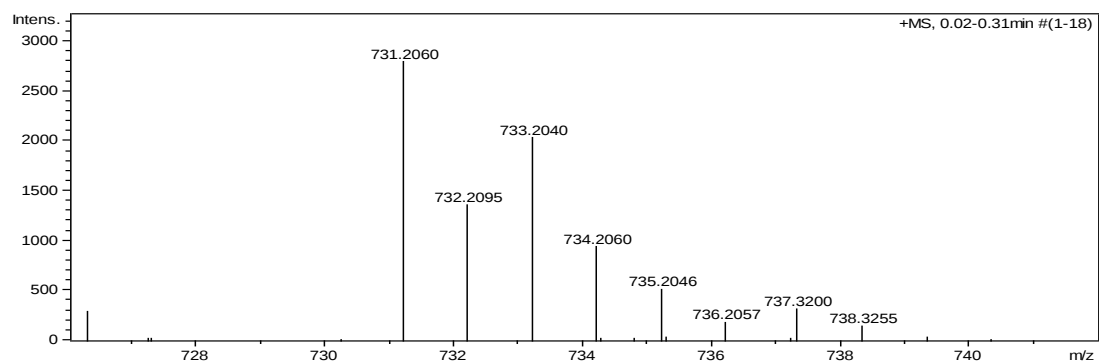
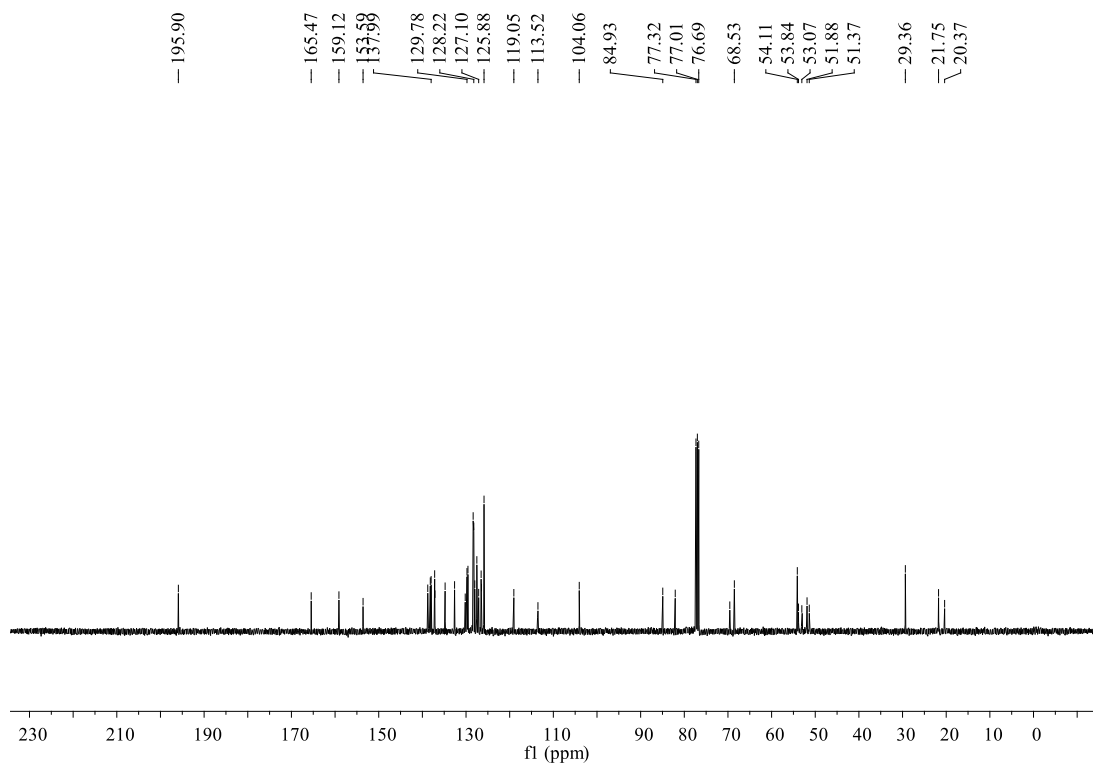


Methyl

(E)-2-benzyl-1,14-bis(4-chlorophenyl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2k):

yellow solid, 48%, m.p. 174~176°C; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H, CH), 7.31 (d, J = 8.4 Hz, 2H, ArH), 7.17~7.07 (m, 4H, ArH), 7.02 (d, J = 6.8 Hz, 2H, ArH), 6.97 (d, J = 8.8 Hz, 2H, ArH), 6.80 (d, J = 8.4 Hz, 2H, ArH), 6.75 (d, J = 8.4 Hz, 3H, ArH), 6.19 (d, J = 8.4 Hz, 1H, ArH), 4.26 (d, J = 17.2 Hz, 1H, CH_2), 4.01 (d, J = 17.2 Hz, 1H, CH_2), 3.97~3.88 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.66~3.59 (m, 1H, CH), 3.07 (d, J = 11.6 Hz, 1H, CH), 2.16 (s, 3H, CH_3), 2.12~2.07 (m, 1H, CH_2), 2.04~1.95 (m, 1H, CH_2), 1.68~1.61 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.9, 165.4, 159.1, 153.5, 138.7, 138.1, 137.9, 137.1, 137.1, 134.7, 132.6, 130.1, 129.7, 129.5, 128.3, 128.2, 128.0, 127.5, 127.1, 126.5, 126.4, 125.8, 119.0, 113.5, 104.0, 84.9, 82.0, 69.5, 68.5, 54.1, 53.8, 53.0, 51.8, 51.3, 29.3, 21.7; IR (KBr) ν : 3478, 3415, 2953, 2218, 1707, 1625, 1579, 1499, 1424, 1357, 1261, 1152, 1040, 950, 885, 810, 754, 731 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{37}\text{Cl}_2\text{N}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 731.2074, found: 731.2060.

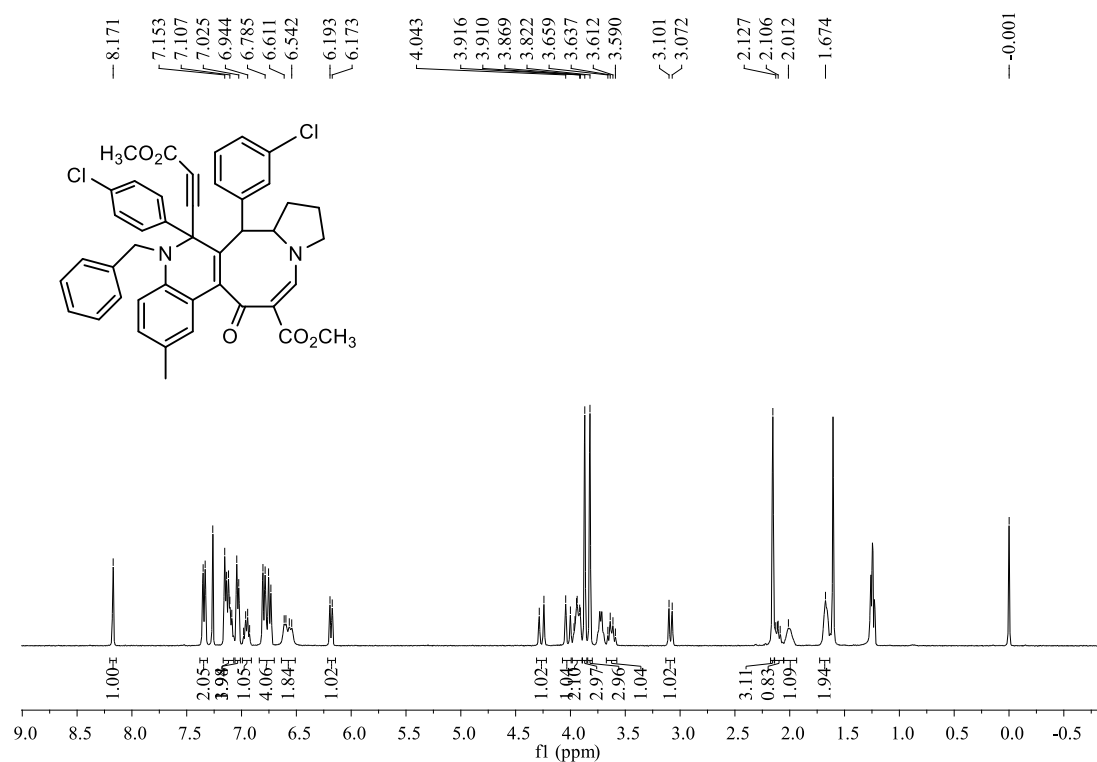


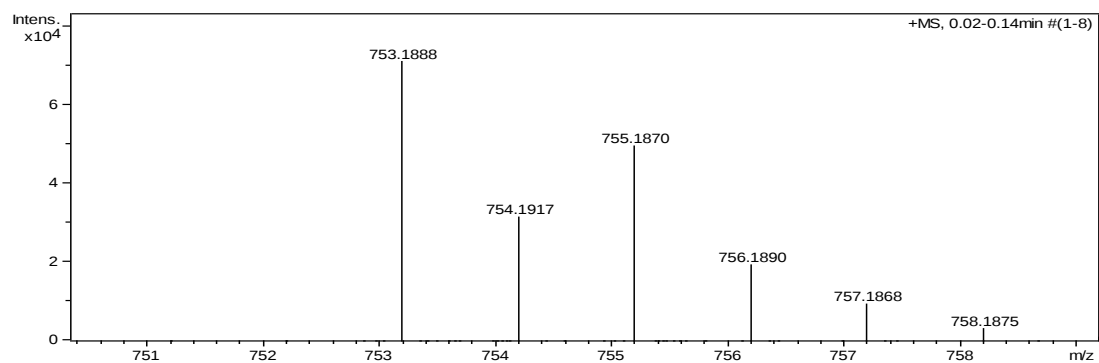
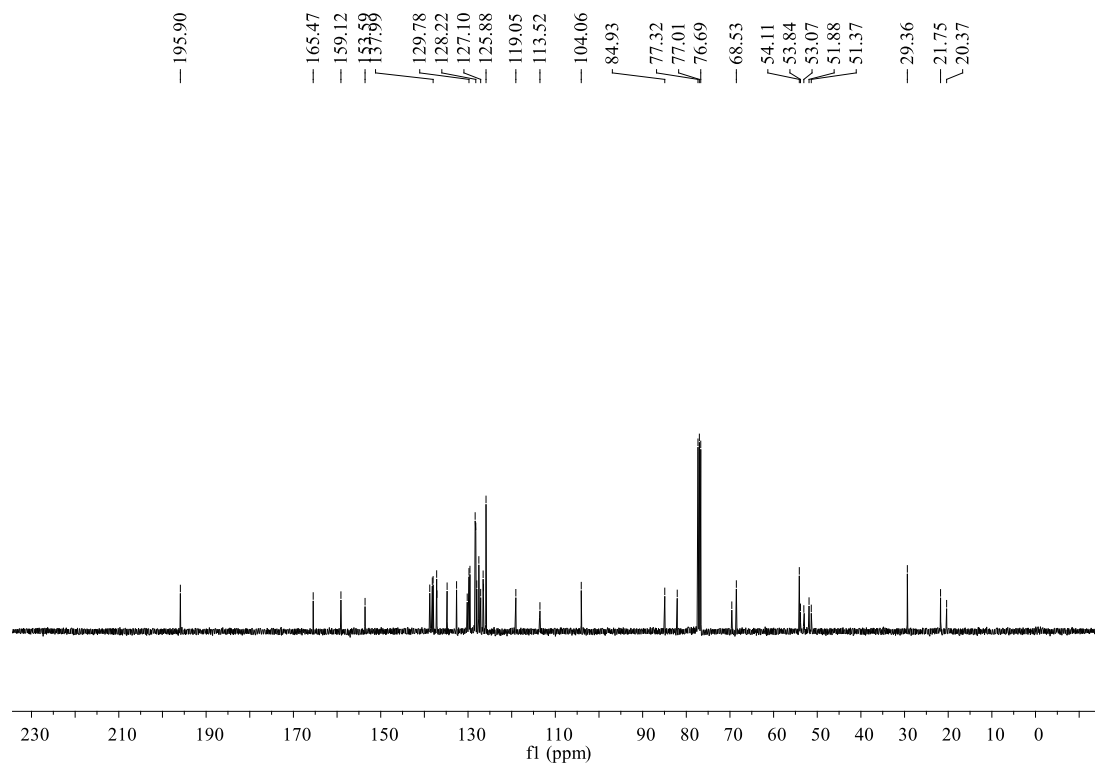


Methyl

(E)-2-benzyl-14-(3-chlorophenyl)-1-(4-chlorophenyl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2l):

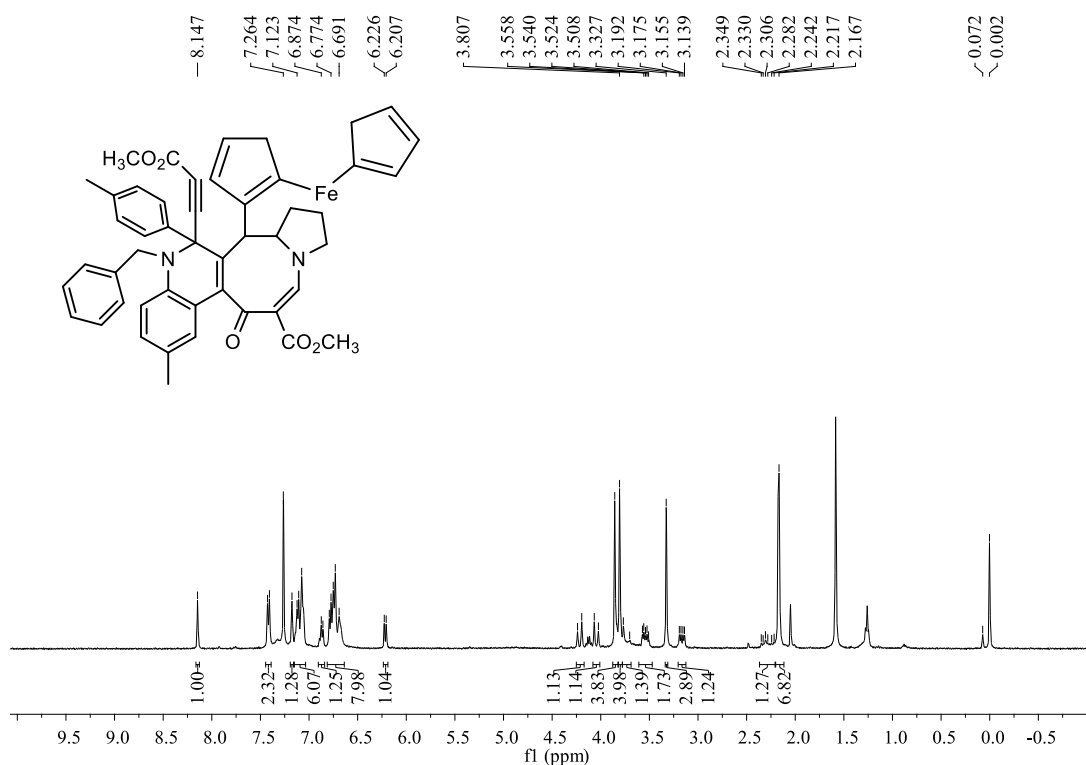
yellow solid, 47%, m.p. 170~172°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H, CH), 7.34 (d, J = 7.2 Hz, 2H, ArH), 7.15~7.09 (m, 4H, ArH), 7.03 (d, J = 7.6 Hz, 2H, ArH), 6.98~6.92 (dd, J_1 = 14.8 Hz, J_2 = 7.2 Hz, 1H, ArH), 6.81~6.73 (m, 4H, ArH), 6.61~6.54 (m, 2H, ArH), 6.18 (d, J = 8.0 Hz, 1H, ArH), 4.26 (d, J = 16.8 Hz, 1H, CH_2), 4.02 (d, J = 17.2 Hz, 1H, CH_2), 3.97~3.91 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.62 (dd, J_1 = 18.8 Hz, J_2 = 8.0 Hz, 1H, CH), 3.09 (d, J = 11.6 Hz, 1H, CH), 2.15 (s, 3H, CH_3), 2.16~2.09 (m, 1H, CH_2), 2.01 (s, 1H, CH_2), 1.67 (s, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ 195.9, 165.4, 159.1, 153.5, 138.7, 138.1, 137.9, 137.1, 137.1, 134.7, 132.6, 130.1, 129.7, 129.5, 128.3, 128.2, 128.0, 127.5, 127.1, 126.5, 126.4, 125.8, 119.0, 113.5, 104.0, 84.9, 82.0, 69.5, 68.5, 54.1, 53.8, 53.0, 51.8, 51.3, 29.3, 21.7; IR (KBr) ν : 3478, 3415, 2953, 2218, 1707, 1625, 1579, 1499, 1424, 1357, 1261, 1152, 1040, 950, 885, 810, 754, 731 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{36}\text{Cl}_2\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 753.1893, found: 753.1888.

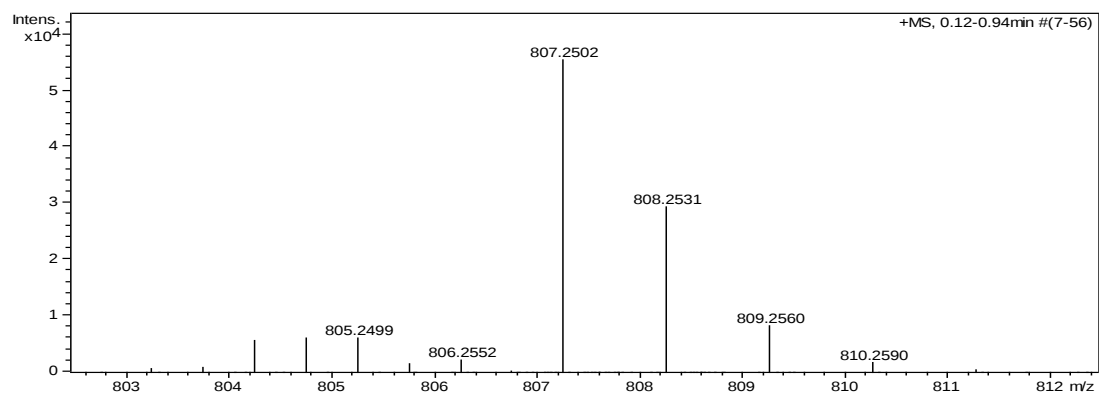
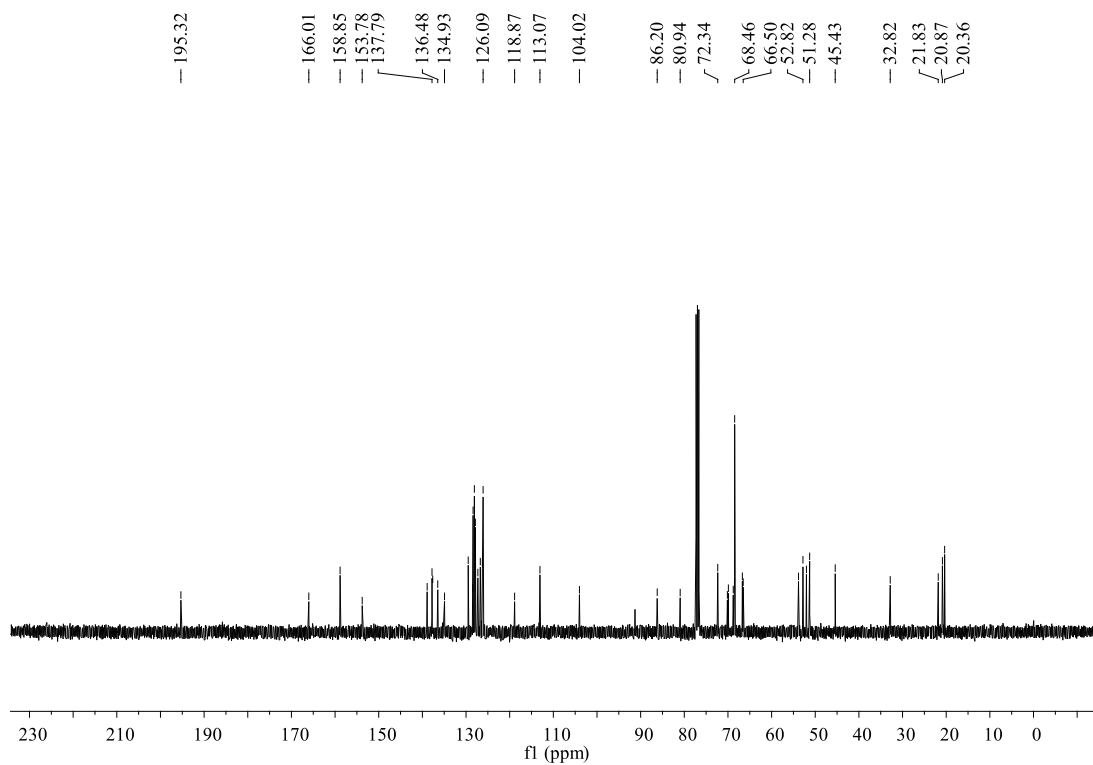




(E)-(2-(2-benzyl-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-8-(methoxycarbonyl)-5-methyl-7-oxo-1-(*p*-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinolin-14-yl)cyclopenta-1,3-dien-1-yl)(cyclopenta-1,3-dien-1-yl)iron (2m):

yellow solid, 50%, m.p. 260~262 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.15 (s, 1H, CH), 7.42 (d, *J* = 7.6 Hz, 2H, ArH), 7.18 (s, 1H, ArH), 7.15 ~7.04 (m, 6H, ArH), 6.87 (d, *J* = 6.6 Hz, 1H, ArH), 6.81 ~6.64 (m, 8H, ArH, CH), 6.22 (d, *J* = 8.0 Hz, 1H, CH), 4.22 (d, *J* = 17.2 Hz, 1H, CH₂), 4.05 (d, *J* = 17.2 Hz, 1H, CH₂), 3.86 (s, 3H, OCH₃), 3.81 (s, 4H, OCH₃, CH), 3.77 (s, 1H, CH), 3.57 ~3.51 (m, 2H, CH₂), 3.33 (s, 3H, CH₃), 3.17 (dd, *J*₁ = 14.6, *J*₂ = 6.7 Hz, 1H, CH₂), 2.37 ~2.21 (m, 1H, CH₂), 2.17 (s, 6H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ: 195.3, 166.0, 158.8, 153.8, 138.9, 137.8, 137.6, 136.4, 134.9, 129.5, 128.4, 128.3, 128.0, 127.8, 127.2, 126.7, 126.2, 126.0, 118.8, 113.0, 104.0, 86.2, 80.9, 72.3, 70.1, 69.9, 68.7, 68.4, 66.7, 66.5, 53.8, 52.8, 52.0, 51.2, 45.4, 32.8, 21.8, 20.8, 20.3; IR (KBr) ν: 3300, 3085, 2220, 1710, 1685, 1649, 1571, 1498, 1455, 1435, 1350, 1277, 1253, 1201, 1149, 1037, 950, 877, 799, 745 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₈H₄₄FeN₂NaO₅ ([M+Na]⁺): 807.2492, found: 807.2502.

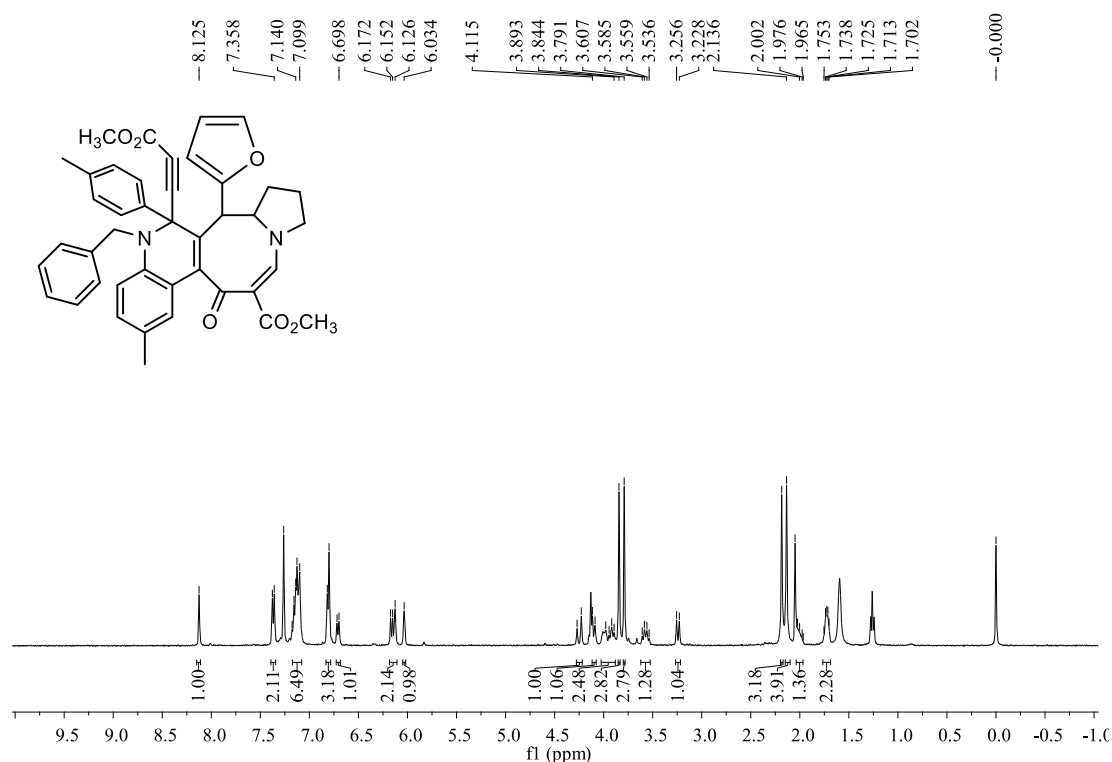


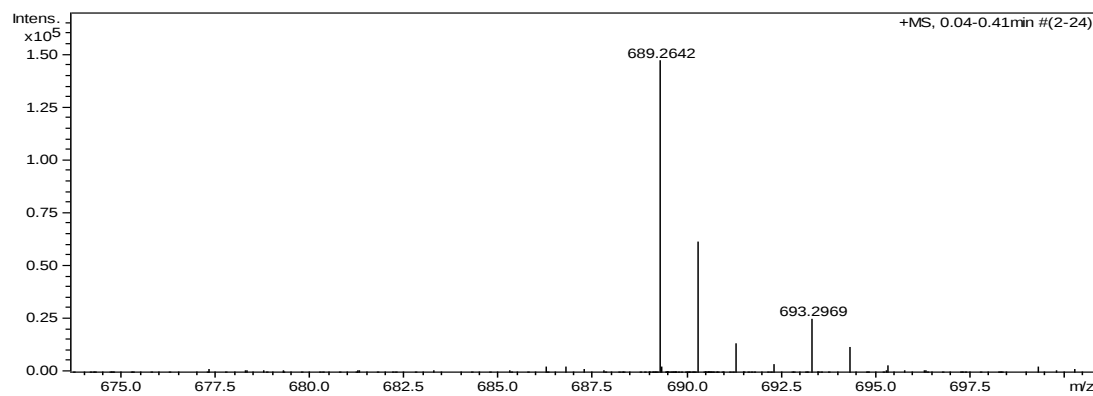
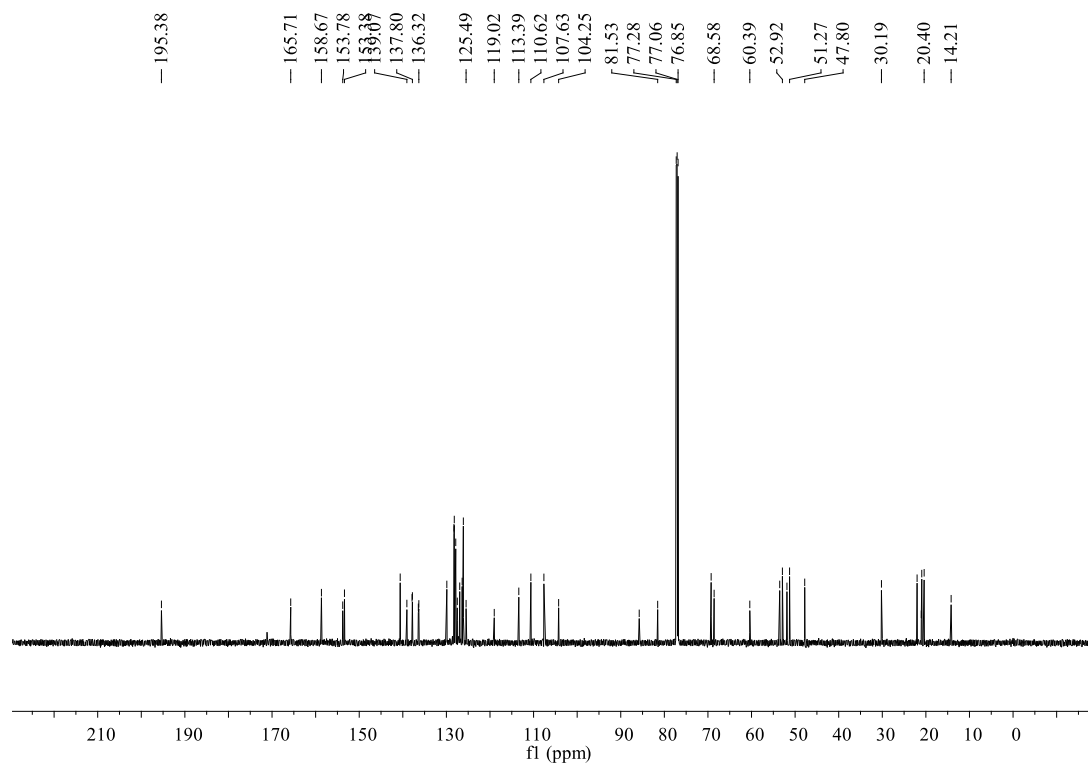


Methyl

(*E*)-2-benzyl-14-(furan-2-yl)-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-5-methyl-7-oxo-1-(*p*-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate(2n):

yellow solid, 85%, m.p. 190~192°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (s, 1H, CH), 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.13 (m, 6H, ArH), 6.82~6.80 (m, 3H, ArH), 6.71 (d, J = 8.0 Hz, 1H, ArH), 6.18~6.11 (m, 2H, ArH), 6.03 (s, 1H, ArH), 4.25 (d, J = 17.2 Hz, 1H, CH_2), 4.10 (d, J = 10.8 Hz, 1H, CH_2), 3.93 (m, 2H, CH_2), 3.84 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.57 (dd, J_1 = 19.2 Hz, J_2 = 8.9 Hz, 1H, CH), 3.24 (d, J = 11.2 Hz, 1H, CH), 2.18 (s, 3H, CH_3), 2.14 (s, 4H, CH_3 , CH_2), 2.04~1.97 (m, 1H, CH_2), 1.77~1.69 (m, 2H, CH_2); ^{13}C NMR (151 MHz, CDCl_3) δ : 195.3, 165.7, 158.6, 153.7, 153.3, 140.6, 139.0, 137.8, 137.8, 136.4, 136.3, 129.9, 128.2, 128.2, 127.8, 127.5, 126.9, 126.3, 126.1, 125.4, 119.0, 113.4, 110.6, 107.6, 104.2, 85.7, 81.5, 77.2, 77.0, 76.8, 69.2, 68.5, 53.5, 52.9, 51.8, 51.2, 47.8, 30.1, 22.0, 21.0, 20.9, 20.4; IR (KBr) ν : 3299, 2951, 2218, 1711, 1685, 1647, 1571, 1493, 1455, 1434, 1349, 1272, 1251, 1189, 1146, 1036, 946, 867 823, 799, 746. cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{42}\text{H}_{38}\text{N}_2\text{NaO}_6$ ($[\text{M}+\text{Na}]^+$): 689.2622, found: 689.2642.

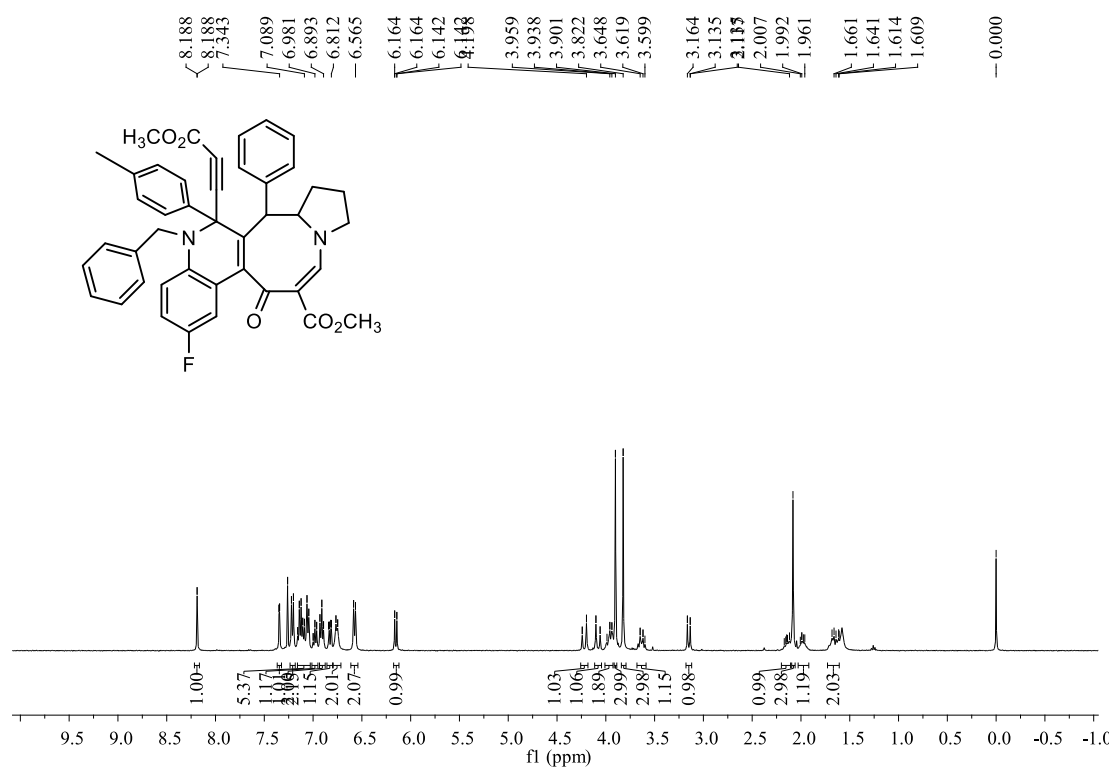


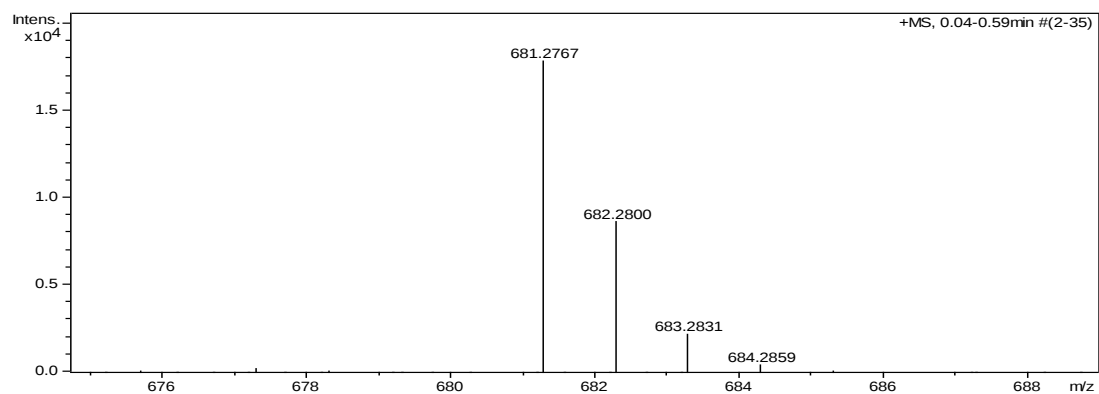
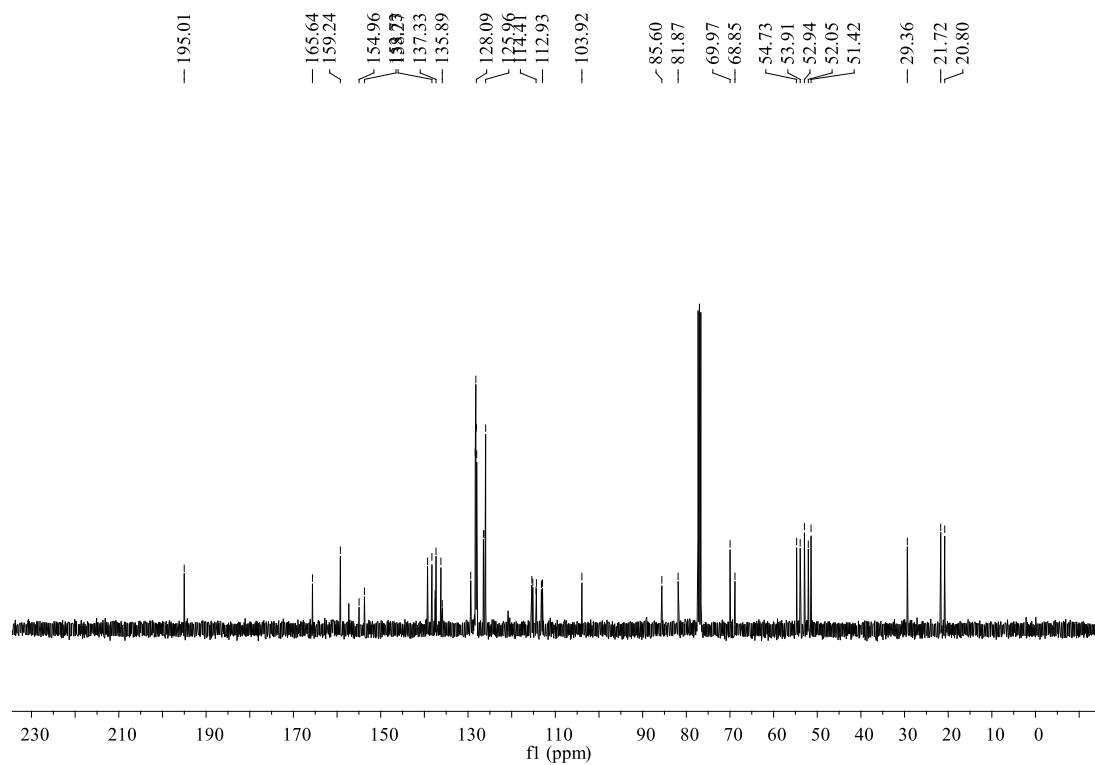


Methyl

(E)-2-benzyl-5-fluoro-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-7-oxo-14-phenyl-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2o):

yellow solid, 64%, m.p. 259~261 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (s, 1H, CH), 7.35 (d, J = 2.3 Hz, 1H, ArH), 7.21 (d, J = 8.1 Hz, 2H, ArH), 7.16~7.03 (m, 6H, ArH), 6.98 (t, J = 7.2 Hz, 1H, ArH), 6.91 (t, J = 7.4 Hz, 2H, ArH), 6.83 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.76 (d, J = 7.1 Hz, 2H, ArH), 6.58 (d, J = 7.8 Hz, 2H, ArH), 6.15 (d, J = 8.8 Hz, 1H, ArH), 4.22 (d, J = 17.3 Hz, 1H, CH_2), 4.08 (d, J = 17.2 Hz, 1H, CH_2), 4.01~3.92 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.67~3.60 (m, 1H, CH), 3.15 (d, J = 11.6 Hz, 1H, CH), 2.18~2.11 (m, 1H, CH_2), 2.08 (s, 3H, CH_3), 1.99 (s, 1H, CH_2), 1.656~1.61 (m, 2H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.0, 165.6, 159.2, 157.36, 154.9, 153.7, 139.2, 138.2, 137.5, 137.3, 136.2, 135.9, 129.3, 128.3, 128.2, 128.0, 128.0, 126.4, 126.1, 125.9, 115.3, 115.1, 114.4, 114.3, 113.1, 112.9, 103.9, 85.6, 81.8, 69.9, 68.8, 54.7, 53.9, 52.9, 52.0, 51.4, 29.3, 21.72, 20.8; IR (KBr) ν : 3298, 2959, 1688, 1658, 1581, 1514, 1438, 1346, 1272, 1191, 1151, 1064, 1032, 953, 887, 851, 830, 808, 766, 706 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{43}\text{H}_{38}\text{FN}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 681.2759, found: 681.2767.

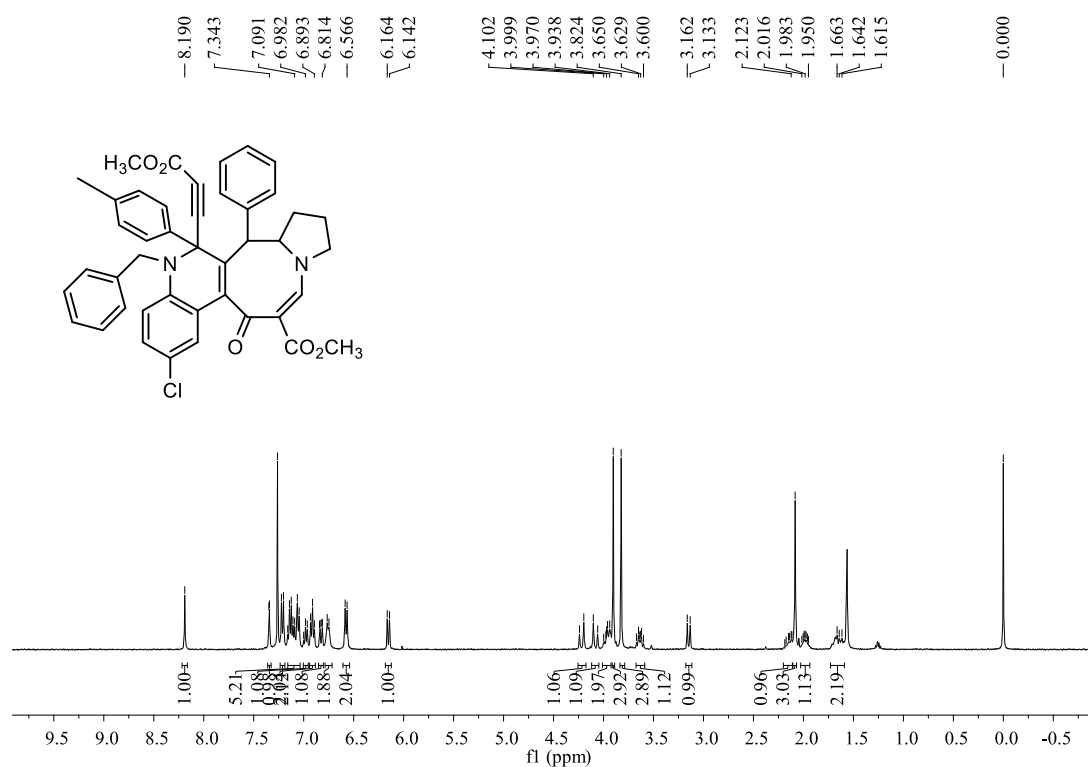


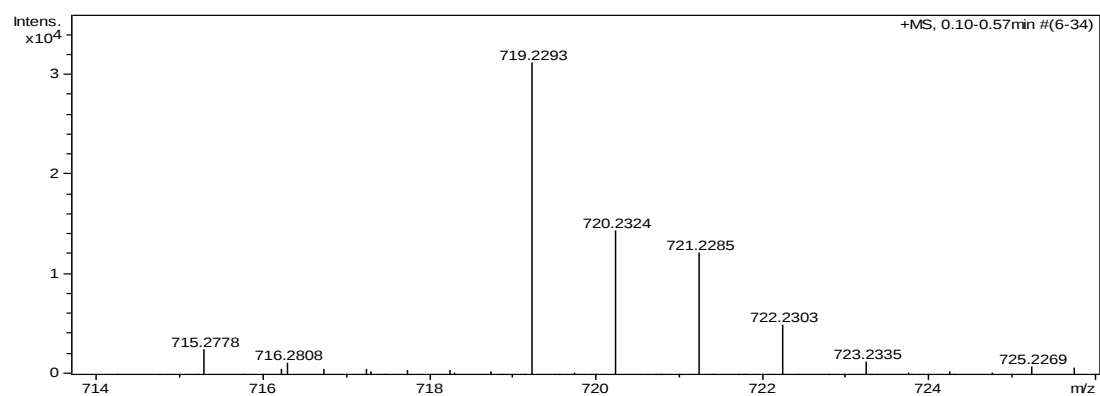
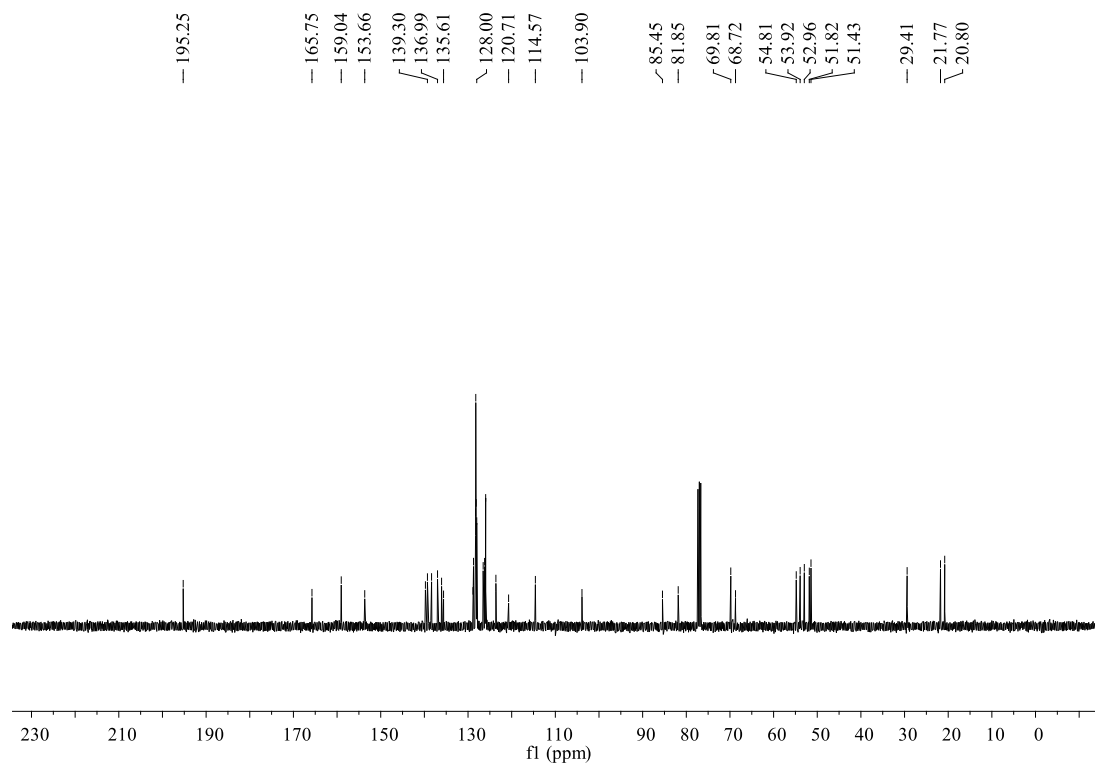


Methyl

(E)-2-benzyl-5-chloro-1-(3-methoxy-3-oxoprop-1-yn-1-yl)-7-oxo-14-phenyl-1-(p-tolyl)-1,2,7,11,12,13,13a,14-octahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (2p):

yellow solid, 58%, m.p. 261~263 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.19 (s, 1H, CH), 7.35 (d, *J* = 2.0 Hz, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 2H, ArH), 7.16~7.04 (m, 5H, ArH), 6.98 (t, *J* = 7.2 Hz, 1H, ArH), 6.91 (t, *J* = 7.6 Hz, 2H, ArH), 6.83 (dd, *J*₁ = 8.8, *J*₂ = 2.4 Hz, 1H, ArH), 6.75 (d, *J* = 7.2 Hz, 2H, ArH), 6.58 (d, *J* = 7.6 Hz, 2H, ArH), 6.15 (d, *J* = 8.8 Hz, 1H, ArH), 4.22 (d, *J* = 17.2 Hz, 1H, CH₂), 4.08 (d, *J* = 17.2 Hz, 1H, CH₂), 4.01~3.92 (m, 2H, CH₂), 3.90 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 3.67~3.64 (m, 1H), 3.15 (d, *J* = 11.6 Hz, 1H), 2.20~2.11 (m, 1H, CH₂), 2.08 (s, 3H, CH₃), 2.03~1.94 (m, 1H, CH₂), 1.73~1.59 (m, 2H, CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 195.2, 165.7, 159.0, 153.6, 139.7, 139.3, 138.3, 136.9, 136.0, 135.6, 128.8, 128.7, 128.2, 128.2, 128.1, 128.0, 126.5, 126.1, 126.1, 125.9, 123.6, 120.7, 114.5, 103.9, 85.4, 81.8, 69.8, 68.7, 54.8, 53.9, 52.9, 51.8, 51.4, 29.4, 21.7, 20.8; IR (KBr) ν: 3300, 2956, 2221, 1714, 1683, 1579, 1502, 1453, 1355, 1324, 1248, 1190, 1149, 1119, 1042, 951, 809, 750 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₃H₃₇ClN₂NaO₅ ([M+Na]⁺): 719.2283, found: 719.2293.

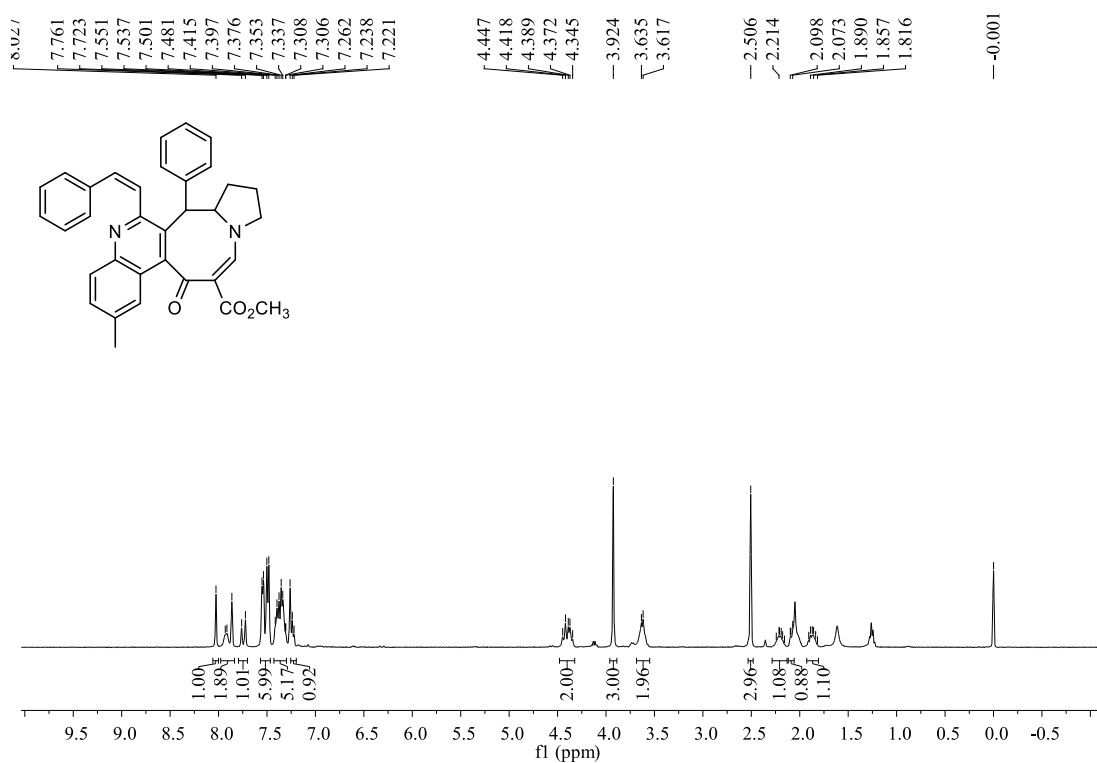


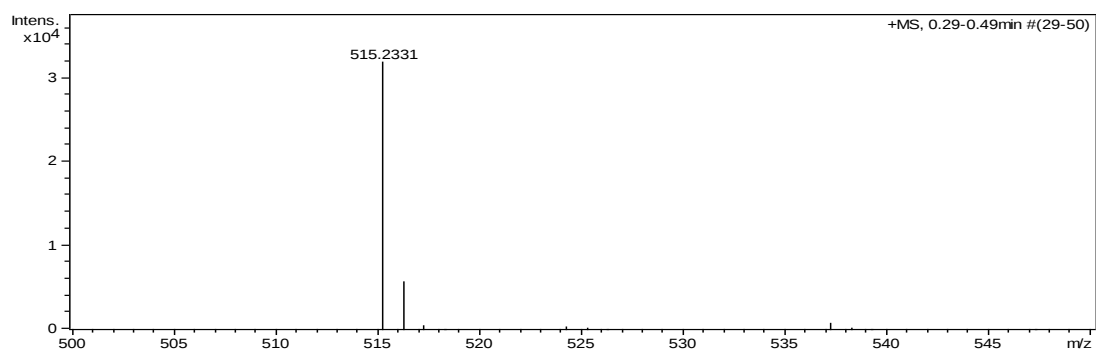
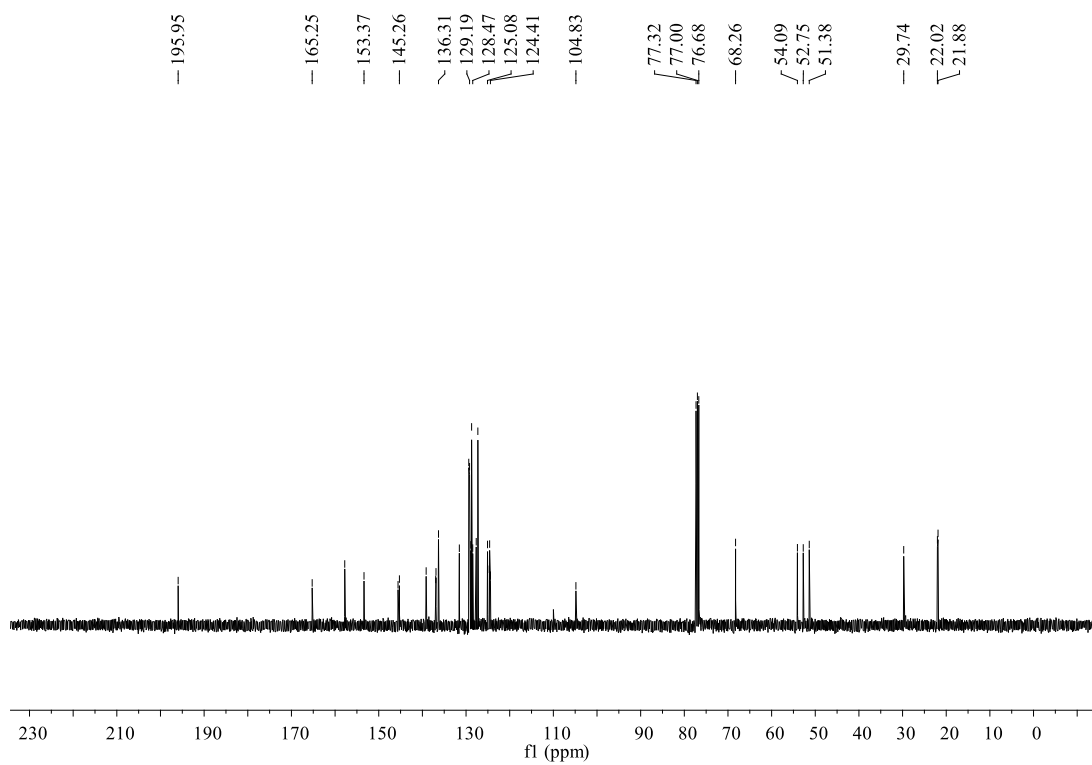


Methyl

(*E*)-5-methyl-7-oxo-14-phenyl-1-((*Z*)-styryl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (3a):

yellow solid, 63%, m.p. 260~262 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (s, 1H, CH), 7.93~7.86 (m, 2H, ArH), 7.74 (d, $J = 15.2$ Hz, 1H, ArH), 7.55~7.48 (m, 6H, ArH), 7.37 (m, 5H, ArH, CH), 7.23 (d, $J = 6.8$ Hz, 1H, CH), 4.48~4.32 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.63 (d, $J = 7.0$ Hz, 2H, CH), 2.51 (s, 3H, CH_2), 2.24~2.15 (m, 1H, CH_2), 2.12~2.06 (m, 1H, CH_2), 1.93~1.81 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.9, 165.2, 157.8, 153.3, 139.1, 136.9, 136.4, 131.5, 129.37, 129.1, 128.8, 128.7, 128.5, 127.6, 127.3, 125.0, 124.6, 124.4, 104.7, 68.2, 54.1, 52.7, 51.3, 29.7, 22.0, 21.8; IR (KBr) ν : 2945, 1701, 1645, 1547, 1512, 1460, 1324, 1269, 1182, 1190, 1109, 1029, 968, 946, 908, 887 812, 780, 772, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 515.2335, found: 515.2331.

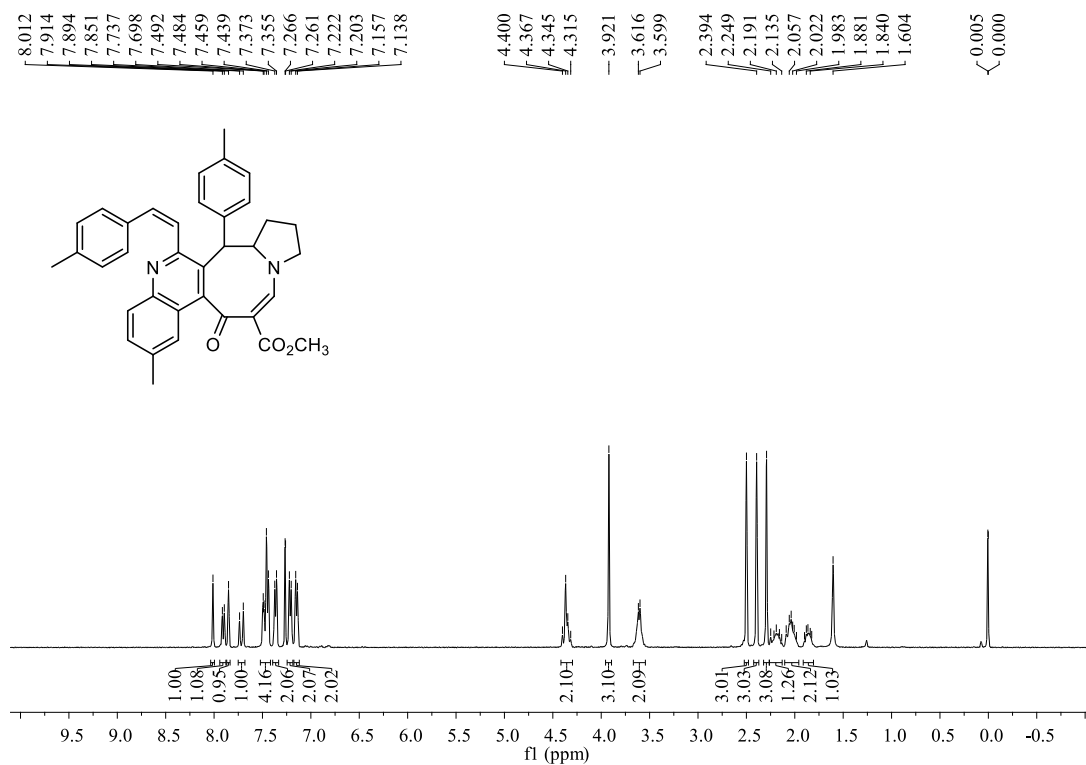


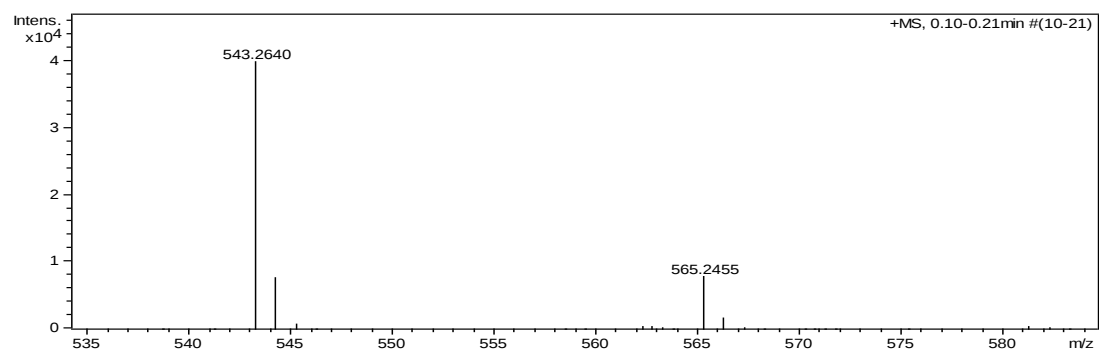
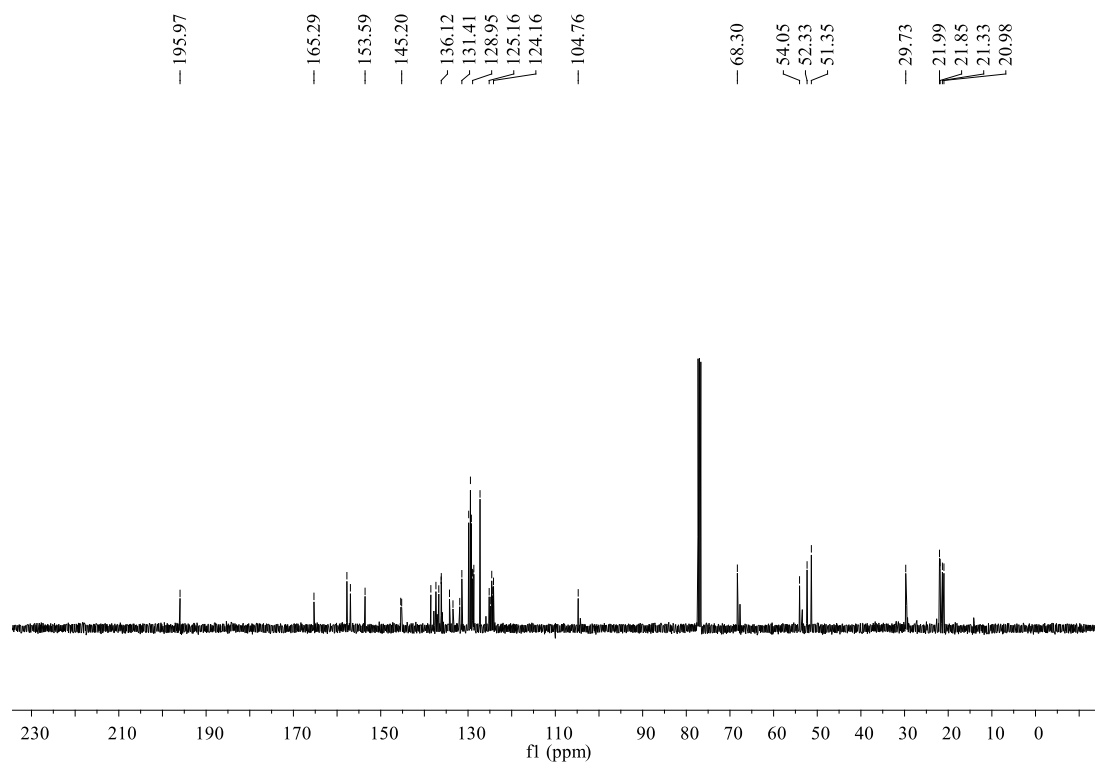


Methyl

(*E*)-5-methyl-1-((*Z*)-4-methylstyryl)-7-oxo-14-(*p*-tolyl)-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (**3b**):

yellow solid, 70%, m.p. 293~295 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (s, 1H, CH), 7.90 (d, J = 8.0 Hz, 1H, ArH), 7.85 (s, 1H), 7.72 (d, J = 15.4 Hz, 1H, ArH), 7.47 (dd, J_1 = 15.6 Hz, J_2 = 5.8 Hz, 4H, ArH), 7.36 (d, J = 7.2 Hz, 2H, ArH), 7.27 (s, 1H, ArH), 7.21 (d, J = 7.5 Hz, 2H, ArH), 7.15 (d, J = 7.3 Hz, 2H, CH), 4.42~4.30 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.61 (d, J = 6.7 Hz, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.22~2.13 (m, 1H, CH_2), 2.09~1.98 (m, 2H, CH_2), 1.90~1.82 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.9, 165.3, 157.8, 153.6, 145.2, 138.5, 137.3, 136.2, 136.1, 136.4, 134.2, 129.8, 129.1, 128.9, 128.8, 128.6, 127.2, 125.2, 124.8, 124.6, 124.3, 124.1, 104.7, 68.3, 54.0, 52.3, 51.3, 29.7, 22.0, 21.8, 21.3, 20.9; IR (KBr) ν : 2945, 1701, 1645, 1547, 1512, 1460, 1324, 1269, 1182, 1190, 1109, 1029, 968, 946, 908, 887, 812, 780, 772, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 543.2642, found: 543.2640.

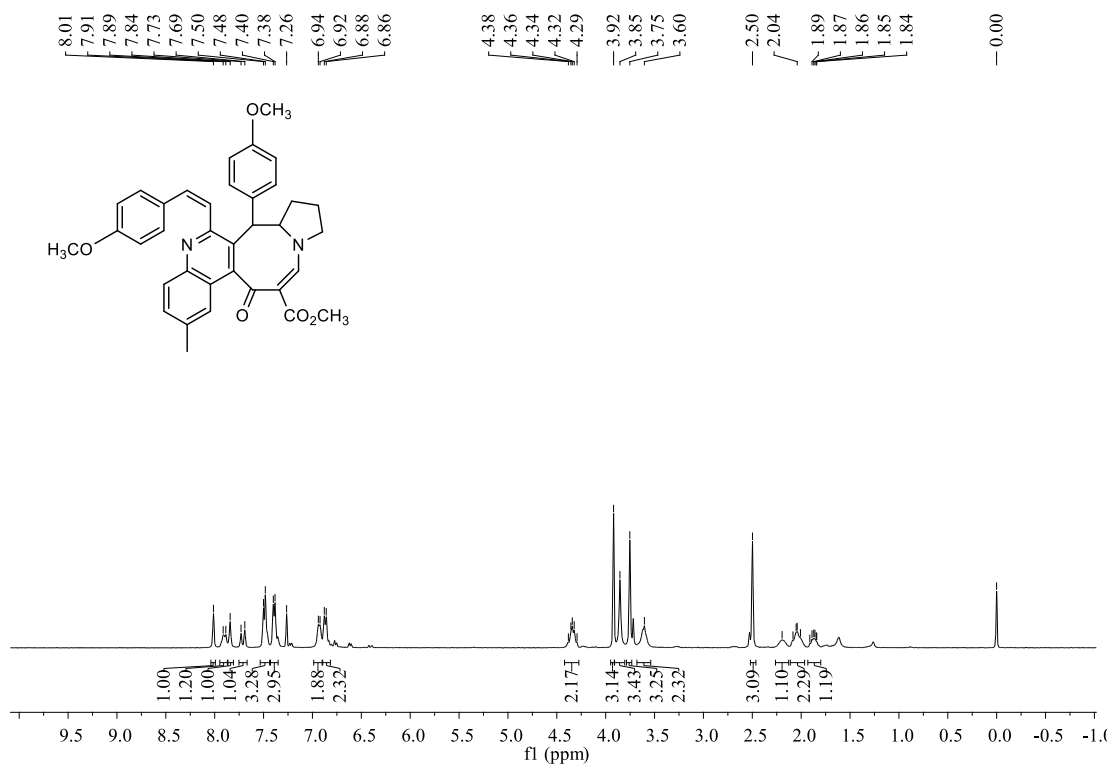


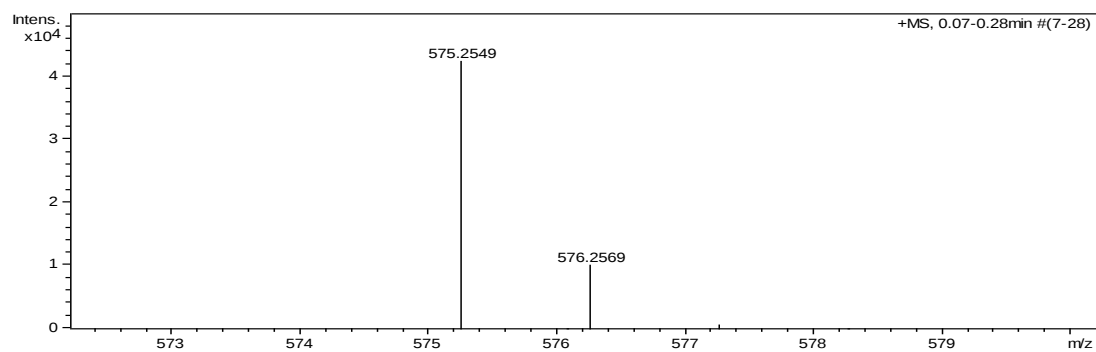
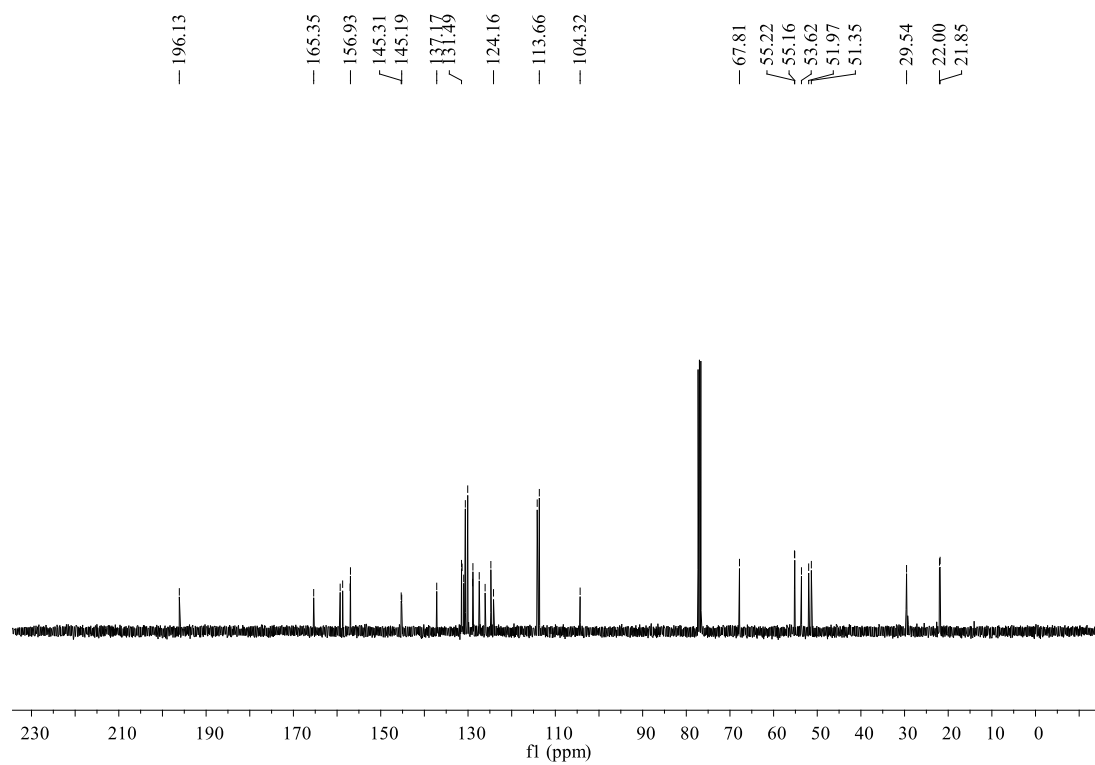


Methyl

(E)-14-(4-methoxyphenyl)-1-((Z)-4-methoxystyryl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (3c):

yellow solid, 80%, m.p. 265~267°C; ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (s, 1H, CH, ArH), 7.90 (d, $J = 10.8$ Hz, 1H, ArH), 7.84 (s, 1H, ArH), 7.71 (d, $J = 15.3$ Hz, 1H, ArH), 7.49 (d, $J = 7.4$ Hz, 3H, ArH), 7.39 (d, $J = 7.0$ Hz, 3H, ArH), 6.93 (d, $J = 7.0$ Hz, 2H, ArH), 6.87 (d, $J = 7.9$ Hz, 2H, CH), 4.38~4.29 (m, 2H, CH), 3.92 (s, 3H, OCH_3), 3.85 (s, 3H), 3.75 (s, 3H, OCH_3), 3.60 (s, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.20 (s, 1H, CH_2), 2.04 (s, 2H, CH_2), 1.91~1.84 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : ^{13}C NMR (101 MHz, CDCl_3) δ : 196.1, 165.2, 160.0, 158.7, 157.0, 156.9, 145.3, 145.2, 137.1, 131.5, 131.2, 131.0, 130.6, 130.0, 129.0, 128.9, 127.4, 126.1, 124.8, 124.2, 114.1, 113.7, 104.3, 67.8, 55.2, 55.1, 53.6, 52.0, 51.3, 29.5, 22.0, 21.8; IR (KBr) ν : 2948, 2836, 1706, 1637, 1604, 1583, 1548, 1511, 1460, 1423, 1357, 1325, 1302, 1253, 1176, 1150, 1111, 1034, 966, 823, 776 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 575.2540, found: 575.2549.

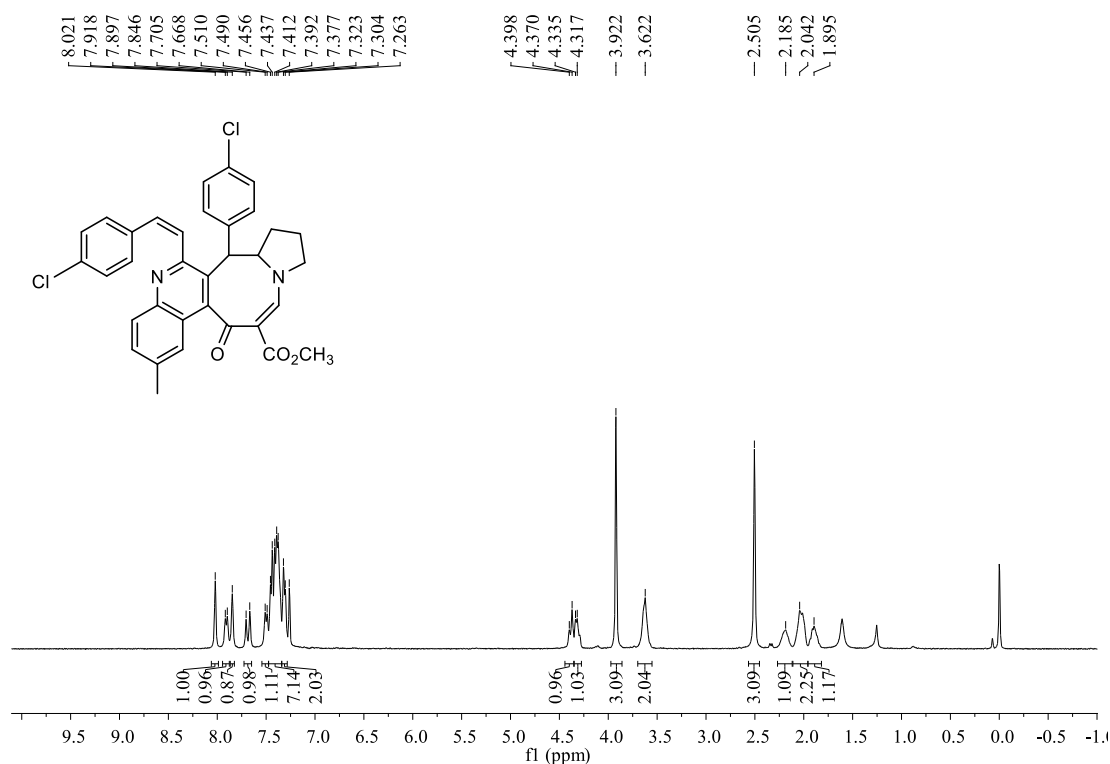


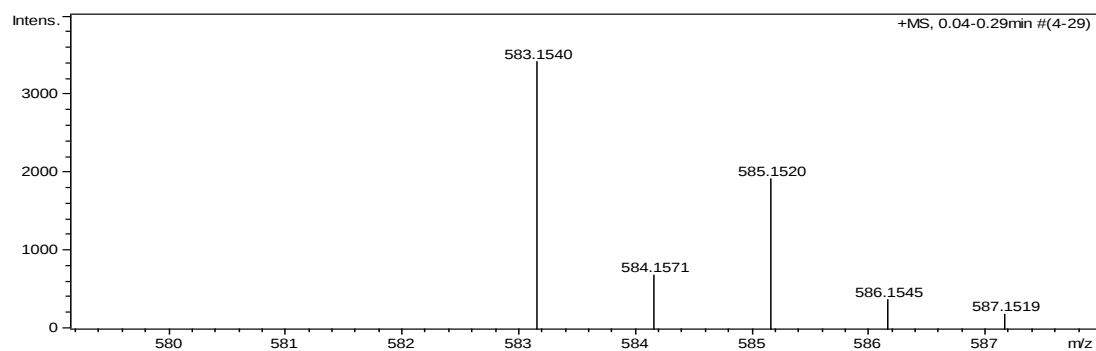
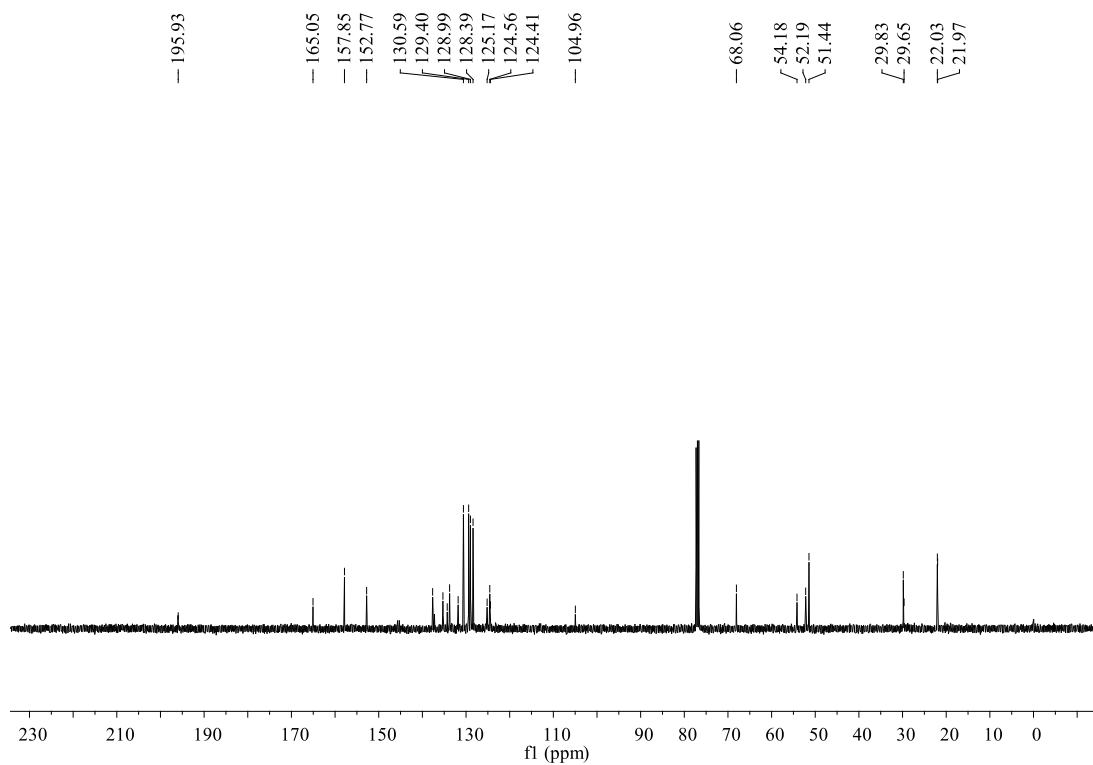


Methyl

(*E*)-14-(4-chlorophenyl)-1-((*Z*)-4-chlorostyryl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydro-*yrrolo*[1',2':1,2]azocino[4,5-*c*]quinoline-8-carboxylate (**3d**):

yellow solid, 52%, m.p. 265~267 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.02 (s, 1H, CH), 7.91 (d, J = 8.4 Hz, 1H, ArH), 7.85 (s, 1H, ArH), 7.69 (d, J = 14.8 Hz, 1H, ArH), 7.50 (d, J = 8.0 Hz, 1H, ArH), 7.48~7.34 (m, 7H, ArH), 7.31 (d, J = 7.6 Hz, 2H, CH), 4.38 (d, J = 11.4 Hz, 1H, CH), 4.34~4.28 (m, 1H, CH), 3.92 (s, 3H, OCH_3), 3.62 (s, 2H, CH_2), 2.51 (s, 3H, CH_3), 2.23~2.16 (m, 1H, CH_2), 2.04~2.01 (m, 2H, CH_2), 1.94~1.84 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 195.9, 165.0, 157.8, 152.7, 137.6, 137.4, 135.3, 134.3, 133.7, 131.8, 130.5, 129.4, 128.9, 128.3, 125.1, 124.5, 124.4, 104.9, 68.0, 54.2, 52.2, 51.4, 29.8, 29.6, 22.0, 21.9; IR (KBr) ν : 2943, 1705, 1632, 1582, 1547, 1471, 1433, 1356, 1324, 1270, 1201, 1180, 1148, 1105, 1037, 1001, 968, 946, 908, 885, 833, 776, 755 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{Cl}_2\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 583.1550, found: 583.1540.

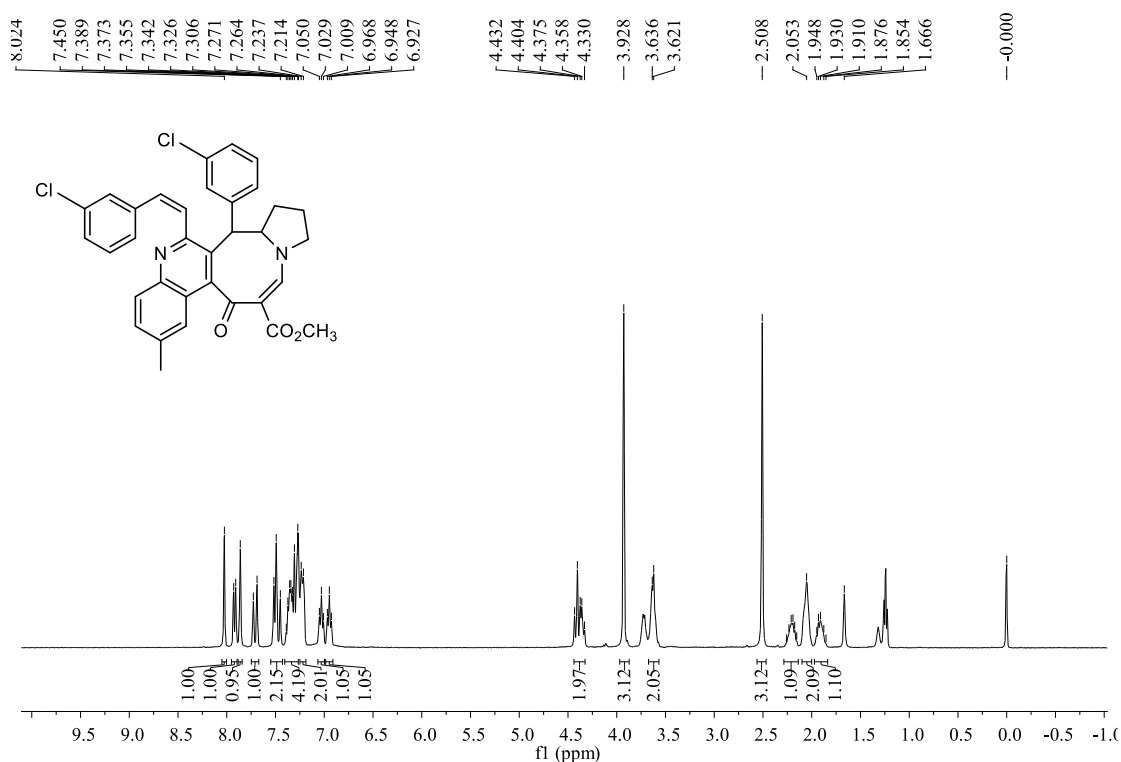


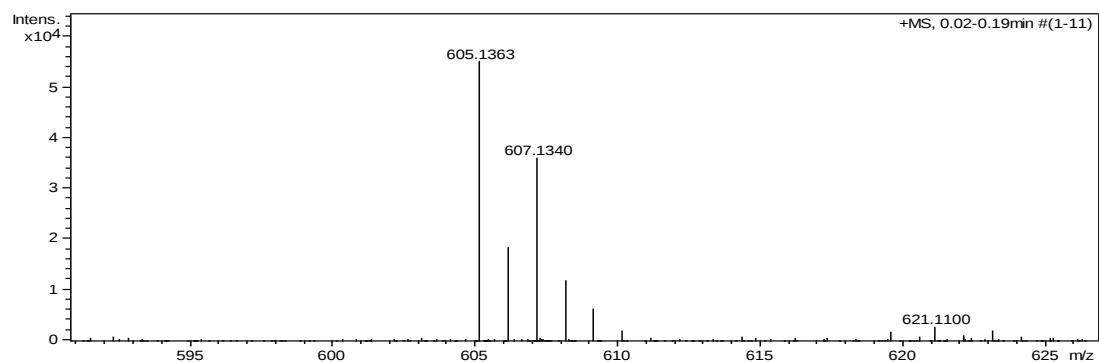
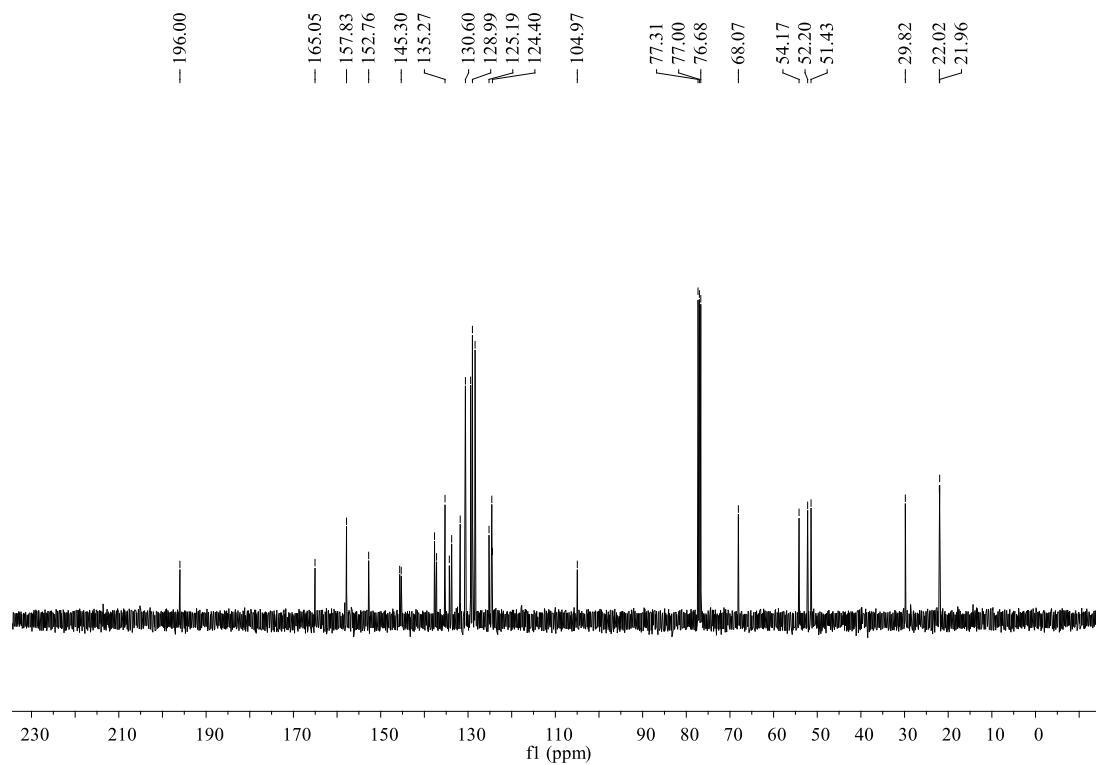


Methyl

(E)-14-(3-chlorophenyl)-1-((Z)-3-chlorostyryl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydro-*yrrolo*[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (3e):

yellow solid, 48%, m.p. 265~267°C; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1H, CH), 7.92 (d, J = 8.4 Hz, 1H, ArH), 7.86 (s, 1H, ArH), 7.71 (d, J = 15.2 Hz, 1H, ArH), 7.50~7.45 (m, 2H, ArH), 7.41~7.27 (m, 4H, ArH), 7.23 (d, J = 9.2 Hz, 2H, ArH), 7.03 (t, J = 8.2 Hz, 1H, CH), 6.95 (t, J = 8.2 Hz, 1H, CH), 4.44~4.32 (m, 2H, CH), 3.93 (s, 3H, OCH_3), 3.64~3.62 (m, 2H, CH_2), 2.51 (s, 3H, CH_3), 2.26~2.15 (m, 1H, CH_2), 2.05 (s, 2H, CH_2), 1.95~1.85 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.0, 165.0, 157.8, 152.7, 145.6, 145.3, 137.6, 137.2, 135.2, 134.2, 133.7, 131.7, 130.6, 129.4, 128.9, 128.3, 125.1, 124.5, 124.4, 104.9, 68.0, 54.1, 52.2, 51.4, 29.8, 22.0, 21.9; IR (KBr) ν : 2949, 1705, 1630, 1587, 1547, 1490, 1458, 1415, 1358, 1324, 1269, 1182, 1148, 1108, 1091, 1037, 1010, 962, 887, 812, 772 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 605.1369, found: 605.1363.

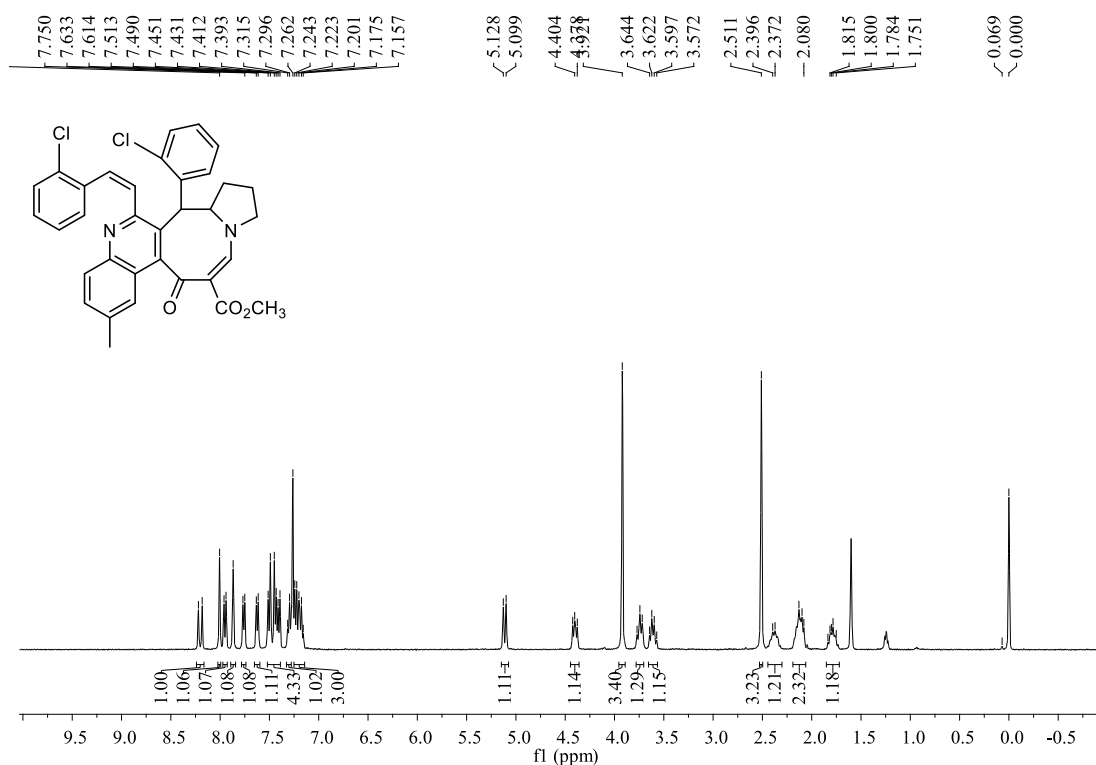


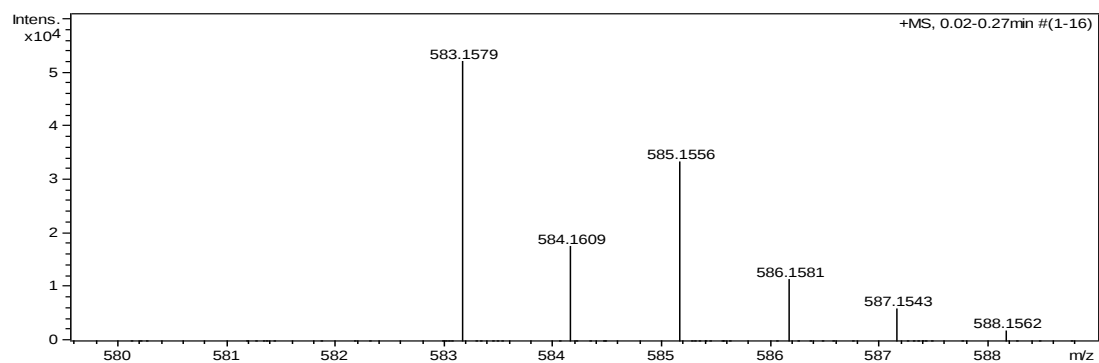
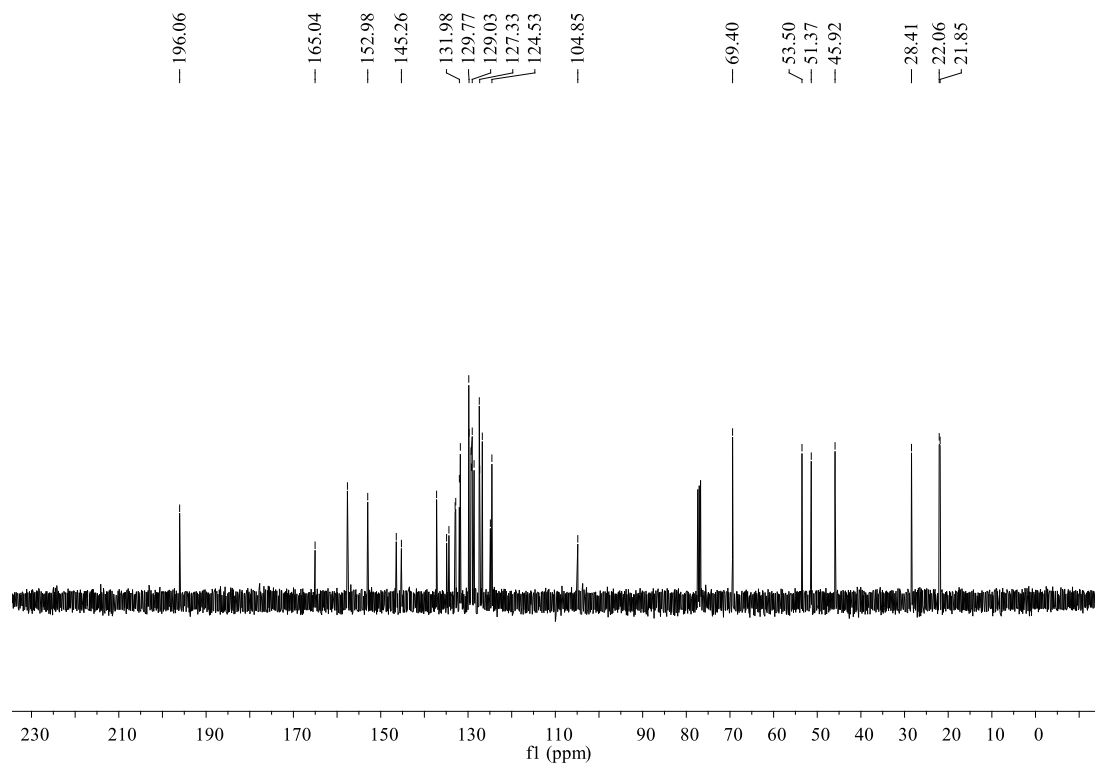


Methyl

(E)-14-(2-chlorophenyl)-1-((Z)-2-chlorostyryl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydro-*yrrolo*[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (3f):

yellow solid, 53%, m.p. 262~264 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.20 (d, $J = 15.2$ Hz, 1H, ArH), 8.01 (s, 1H, CH), 7.95 (d, $J = 8.0$ Hz, 1H, ArH), 7.87 (s, 1H, ArH), 7.76 (d, $J = 7.6$ Hz, 1H, ArH), 7.62 (d, $J = 7.6$ Hz, 1H), 7.50~7.42 (m, 4H, ArH), 7.31 (d, $J = 7.6$ Hz, 1H, ArH), 7.25~7.14 (m, 3H, ArH, CH), 5.11 (d, $J = 11.6$ Hz, 1H, CH), 4.45~4.36 (m, 1H, CH), 3.92 (s, 3H, OCH_3), 3.77~3.72 (m, 1H, CH_2), 3.64~3.57 (m, 1H, CH_2), 2.51 (s, 3H, CH_3), 2.38 (d, $J = 9.6$ Hz, 1H, CH_2), 2.19~2.06 (m, 2H, CH_2), 1.81~1.75 (m, 1H, CH_2); ^{13}C NMR (101MHz, CDCl_3) δ : 196.0, 165.0, 157.6, 152.9, 146.4, 145.2, 137.2, 134.9, 134.3, 132.9, 132.8, 131.9, 131.7, 129.8, 129.7, 129.3, 129.2, 129.0, 128.6, 127.4, 127.3, 126.7, 124.8, 124.5, 104.8, 69.4, 53.5, 51.3, 45.9, 28.4, 22.0, 21.8; IR (KBr) ν : 2947, 1702, 1677, 1635, 1581, 1547, 1512, 1460, 1430, 1329, 1275, 1184, 1149, 1109, 1039, 999, 970, 824, 808, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{Cl}_2\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 583.1550, found: 583.1579.

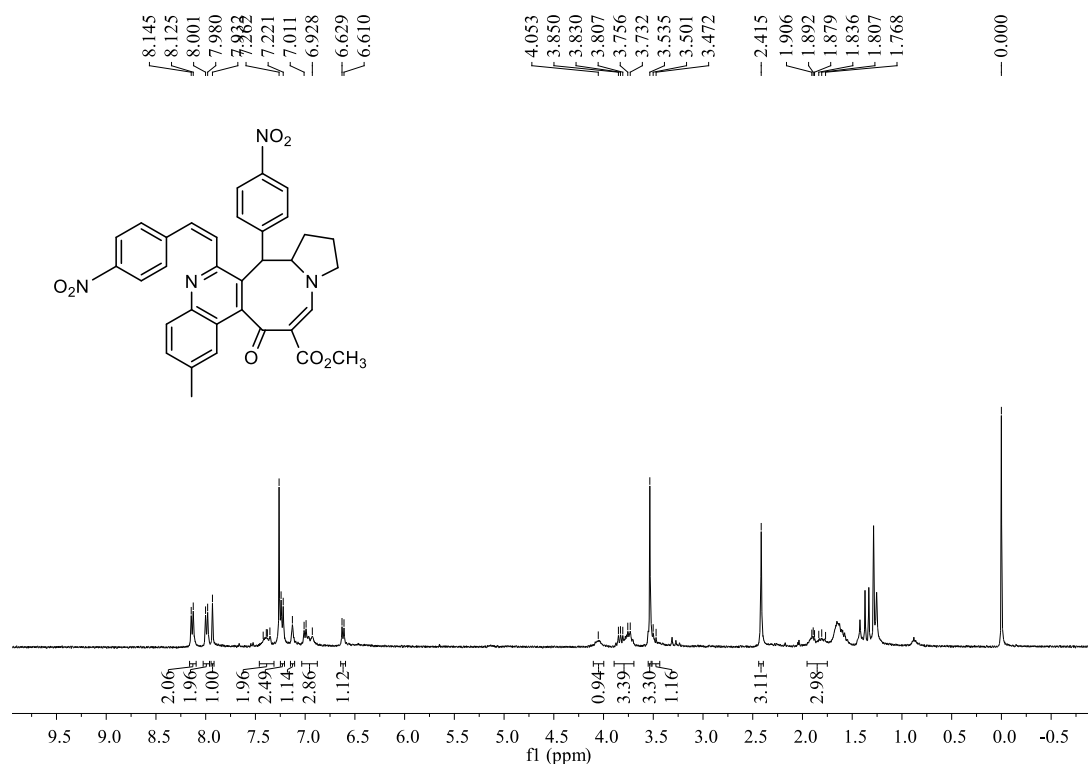


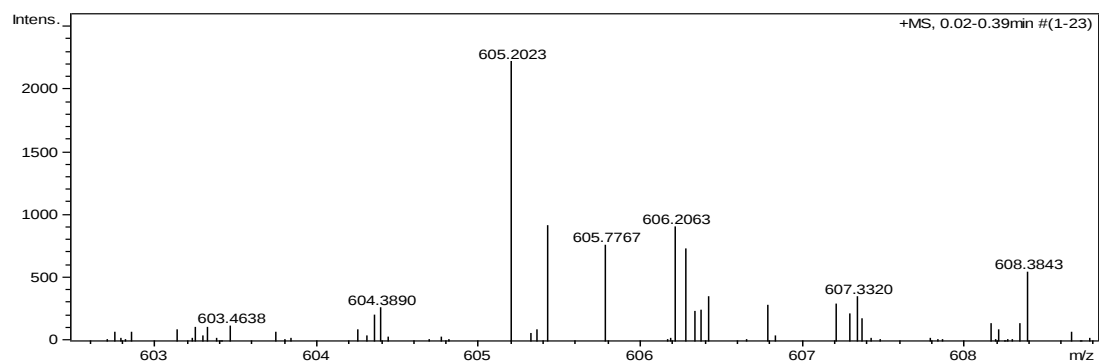
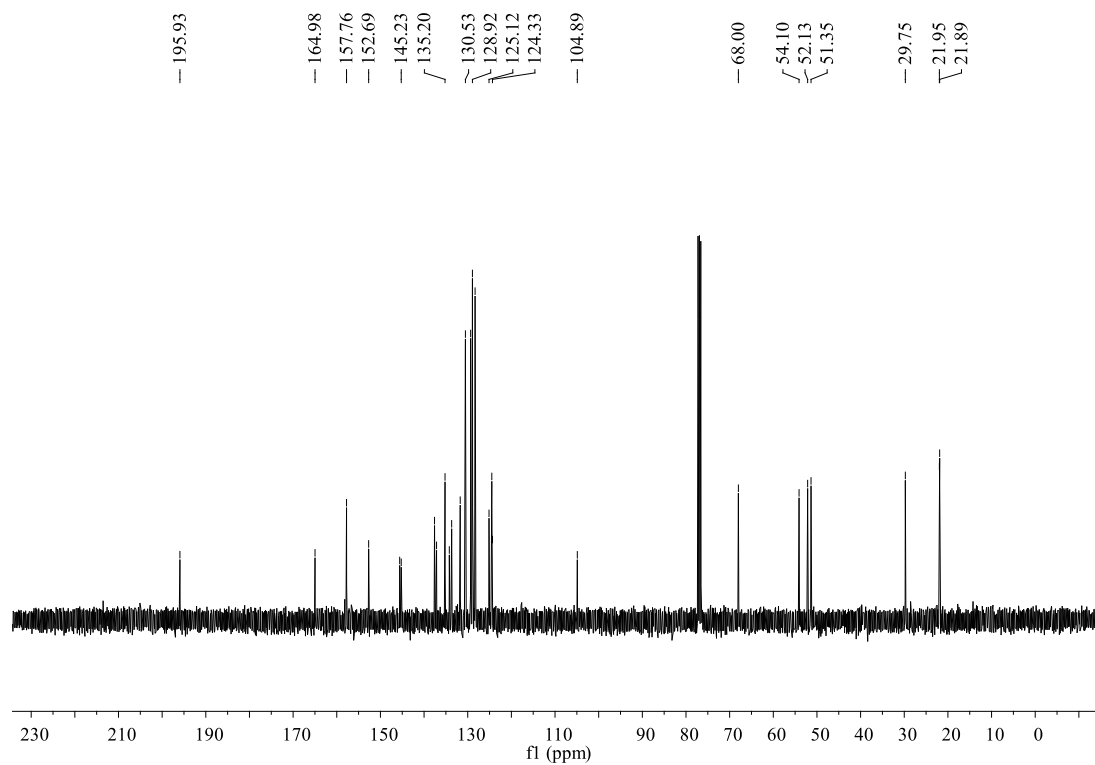


Methyl

(E)-5-methyl-14-(4-nitrophenyl)-1-((Z)-4-nitrostyryl)-7-oxo-7,11,12,13,13a,14-hexahydropyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (3g):

yellow solid, 50%, m.p. 278~280°C; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.2$ Hz, 2H, ArH), 7.99 (d, $J = 8.4$ Hz, 2H, ArH), 7.93 (s, 1H, CH), 7.42~7.35 (m, 2H, ArH), 7.23 (d, $J = 8.6$ Hz, 2H, ArH), 7.13 (s, 1H, ArH), 7.03~6.88 (m, 3H, ArH, CH), 6.62 (d, $J = 7.9$ Hz, 1H, CH), 4.05 (s, 1H, CH), 3.89~3.69 (m, 3H, CH_2), 3.53 (s, 3H OCH_3), 3.49 (d, $J = 11.8$ Hz, 1H, CH_2), 2.41 (s, 3H CH_3), 1.95~1.75 (m, 3H, CH_2); ^{13}C NMR (101MHz, CDCl_3) δ : 195.9, 164.9, 157.7, 152.7, 145.6, 145.2, 137.6, 137.1, 135.2, 134.2, 133.7, 131.7, 130.5, 129.3, 128.9, 128.3, 125.1, 124.4, 124.3, 104.8, 68.0, 54.1, 52.1, 51.3, 29.7, 21.9, 21.8; IR (KBr) ν : 2951, 1717, 1614, 1520, 1491, 1432, 1346, 1274, 1238, 1190, 1109, 1029, 976, 851, 779, 738, 701 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{N}_4\text{O}_7$ ($[\text{M}+\text{H}]^+$): 605.2031, found: 605.2023.





Methyl

(E)-14-(4-bromophenyl)-1-((Z)-4-bromostyryl)-5-methyl-7-oxo-7,11,12,13,13a,14-hexahydro pyrrolo[1',2':1,2]azocino[4,5-c]quinoline-8-carboxylate (3h):

yellow solid, 40%, m.p. 284~286°C; ^1H NMR (400 MHz, CDCl_3) δ : 7.67 (d, $J = 14.4$ Hz, 1H, CH), 7.46 (d, $J = 8.4$ Hz, 2H, ArH), 7.40 (d, $J = 8.4$ Hz, 2H, ArH), 7.35 (d, $J = 8.4$ Hz, 2H, ArH), 7.11~7.07 (m, 4H, ArH), 6.95 (d, $J = 5.6$ Hz, 1H, ArH), 6.72 (d, $J = 14.4$ Hz, 1H, CH), 6.10 (d, $J = 16.2$ Hz, 1H, CH), 4.47 (d, $J = 11.6$ Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 2.57 (t, $J = 6.4$ Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.03~1.98 (m, 1H, CH_2), 1.936~1.90 (m, 2H, CH_2), 1.72~1.63 (m, 1H, CH_2); ^{13}C NMR (101 MHz, CDCl_3) δ : 196.2, 169.6, 144.1, 140.2, 139.8, 136.0, 135.1, 134.4, 133.9, 133.6, 132.4, 131.5, 131.4, 129.8, 127.2, 126.7, 122.7, 111.8, 108.2, 74.0, 69.6, 53.5, 5.3, 49.4, 32.7, 29.5, 23.1; IR (KBr) ν : 945, 1710, 1684, 1626, 1601, 1488, 1432, 1399, 1324, 1271, 1197, 1107, 1071, 1008, 815, 760 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{Br}_2\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 671.0539, found: 671.0528.

