

Molecular diversity of cyclization reaction of 3-methyleneoxindoles with 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitriles

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Supporting Information

Figures of single crystal structures s1-17	2-4
¹H and ¹³C NMR spectra of the prepared compounds	5-33

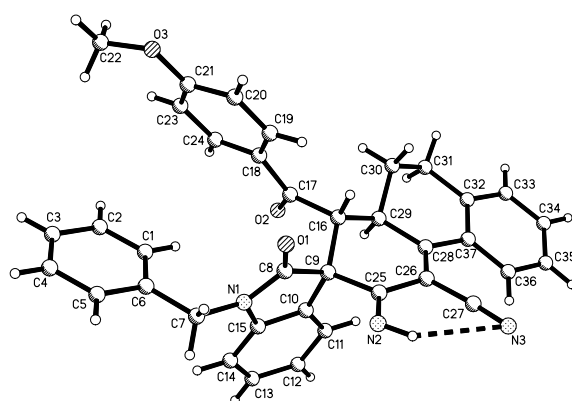


Fig. s1 Molecular structure of compound **1b** (*cis*-isomer)

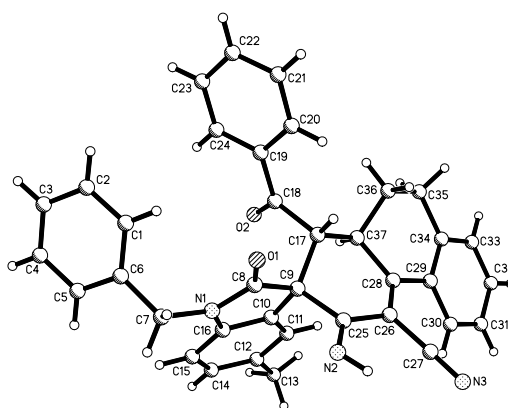


Fig. s2 Molecular structure of compound **1c** (*cis*-isomer)

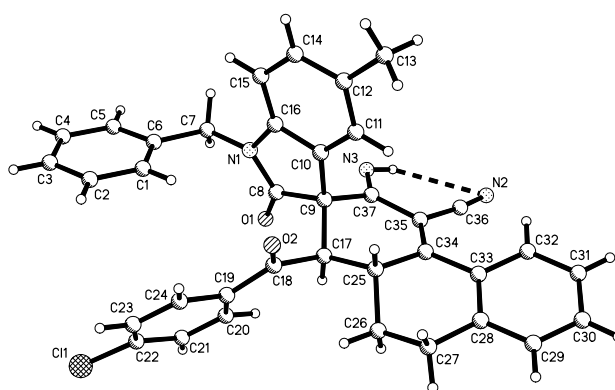


Fig. s3 Molecular structure of compound **1d** (*cis*-isomer)

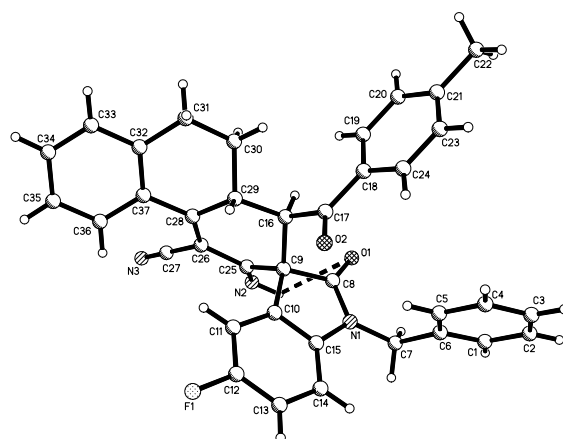


Fig. s4 Molecular structure of compound **1e** (*cis*-isomer)

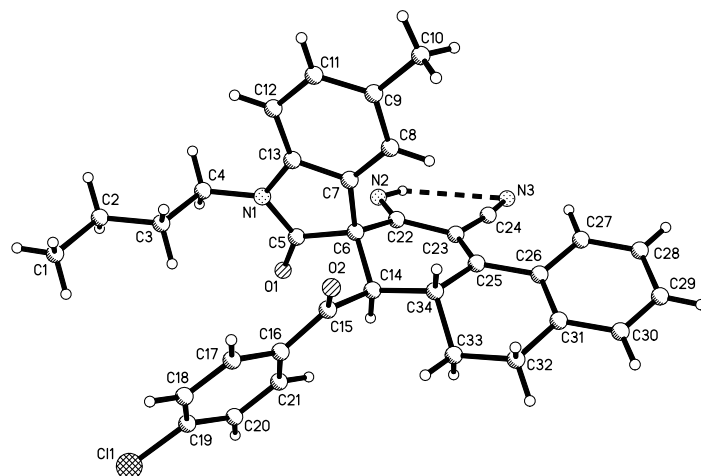


Fig. s5 Molecular structure of compound **1j** (*cis*-isomer)

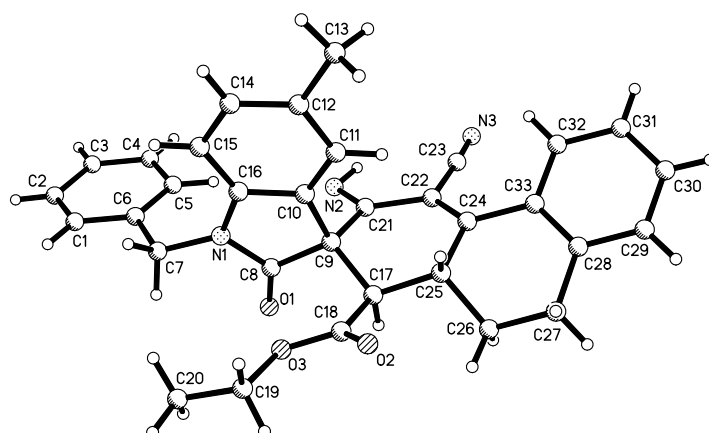


Fig. s6 Molecular structure of compound **2b** (*cis*-isomer)

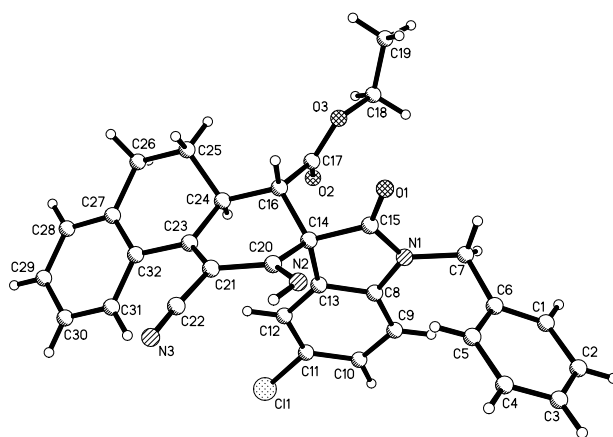


Fig. s7 Molecular structure of compound **2c** (*cis*-isomer)

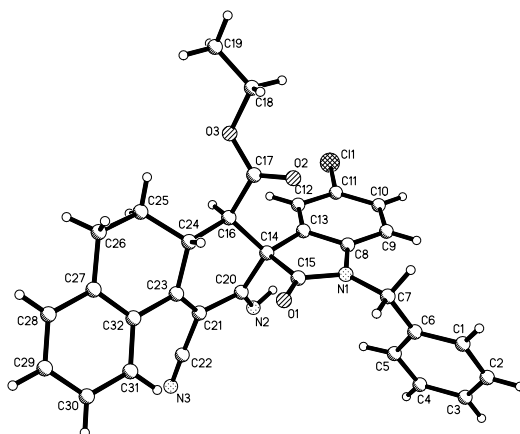


Fig. s8 Molecular structure of compound **2c'** (*trans*-isomer)

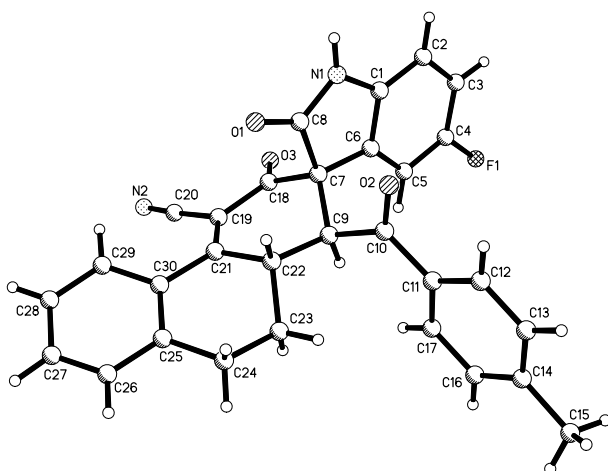
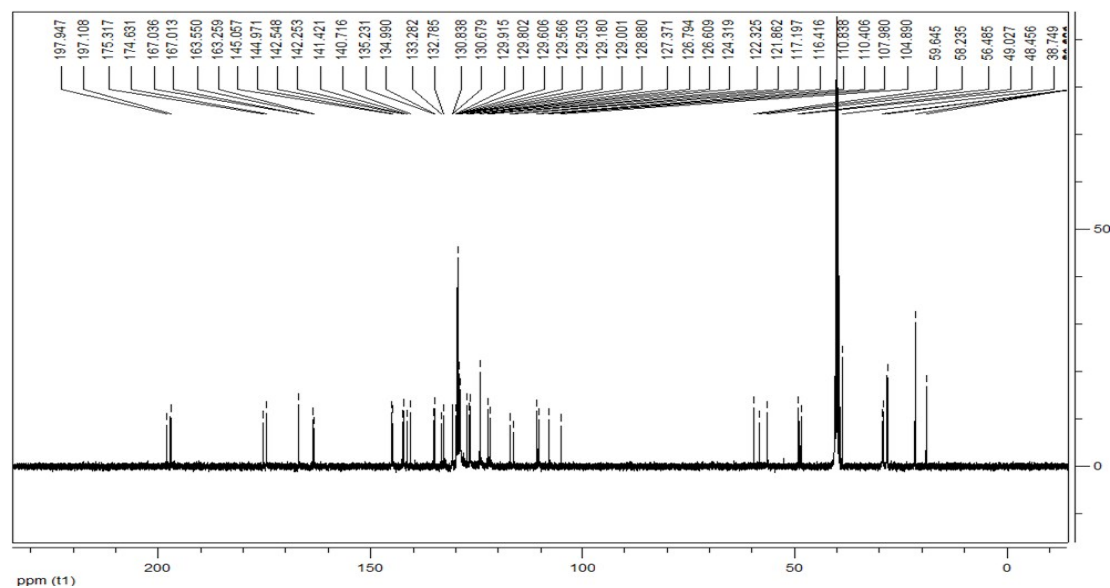
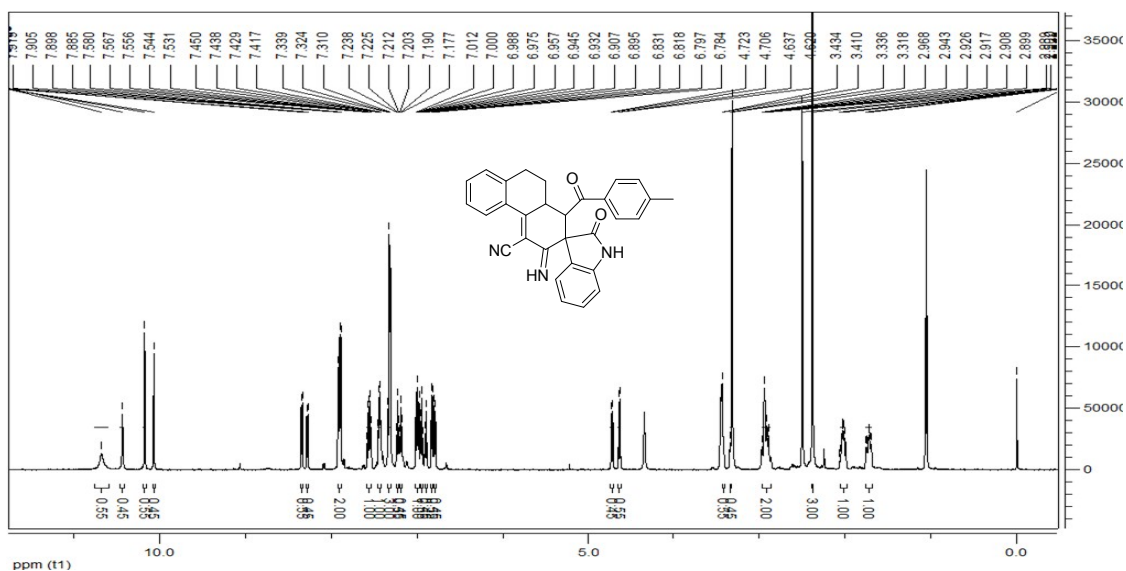
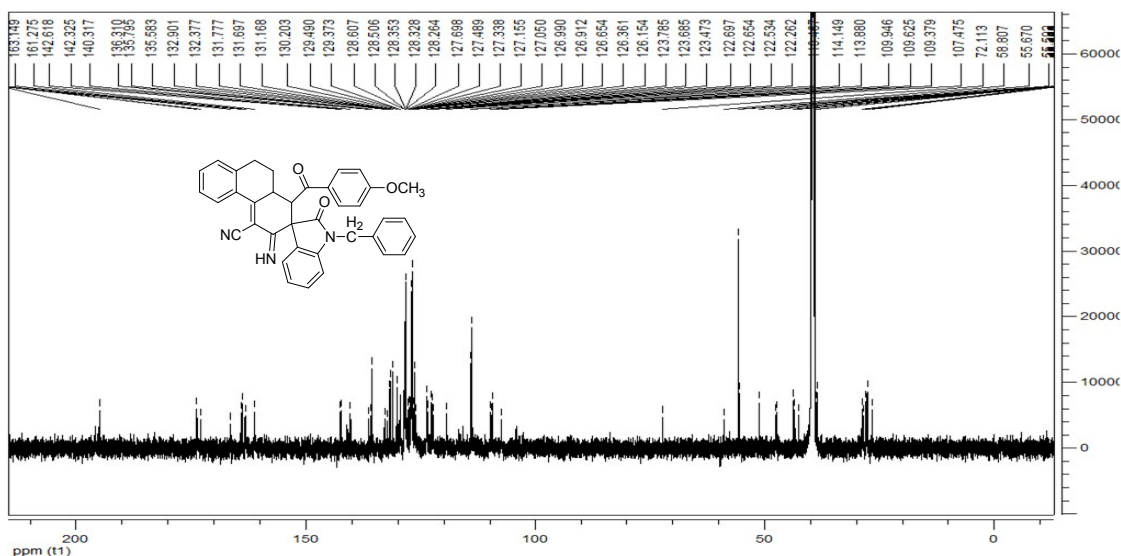
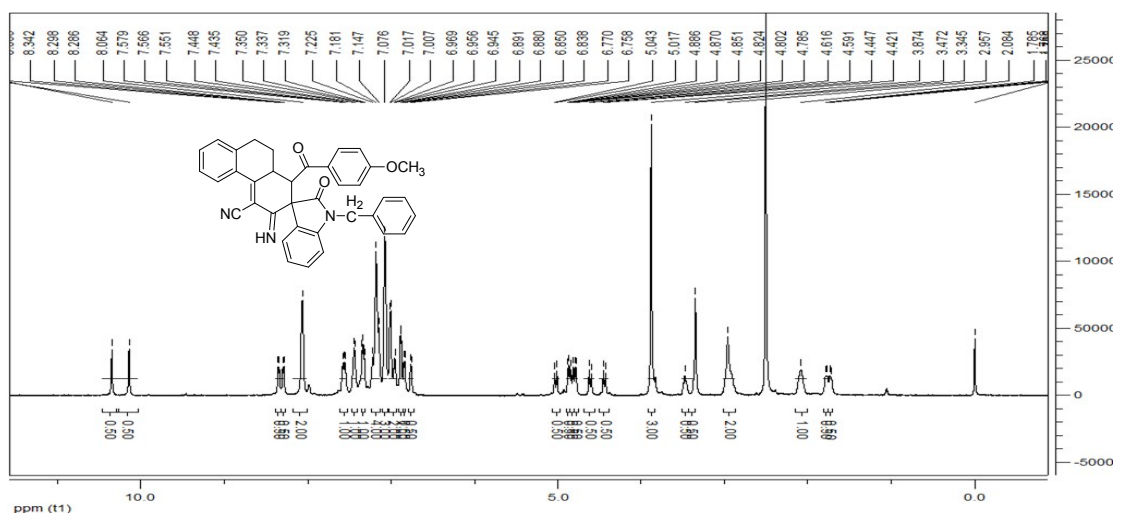


Fig. s9 Molecular structure of compound **4d** (*trans*-isomer)

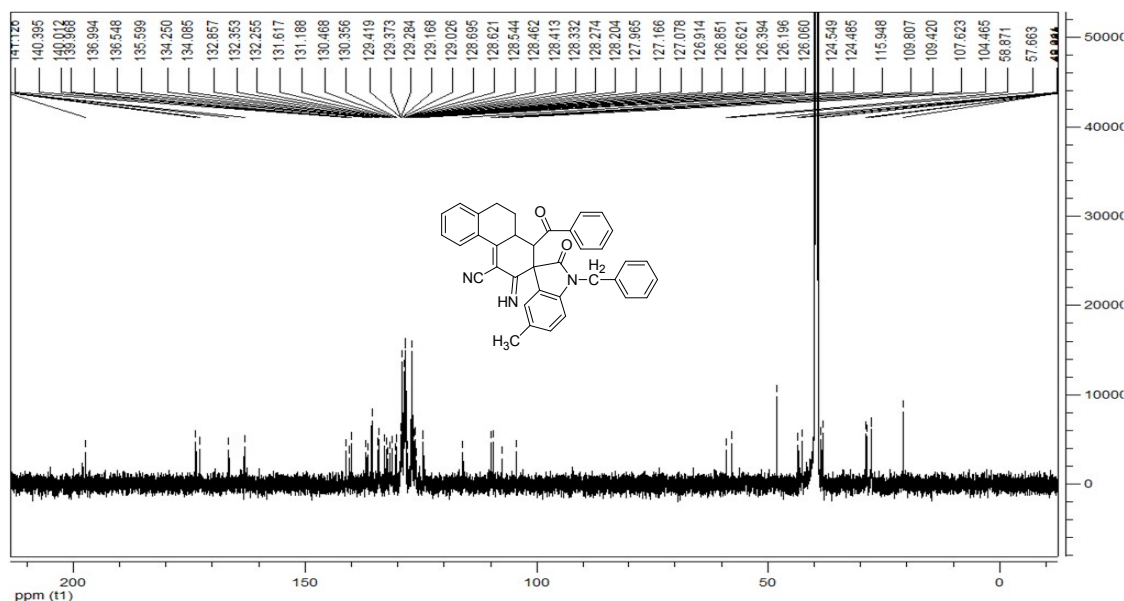
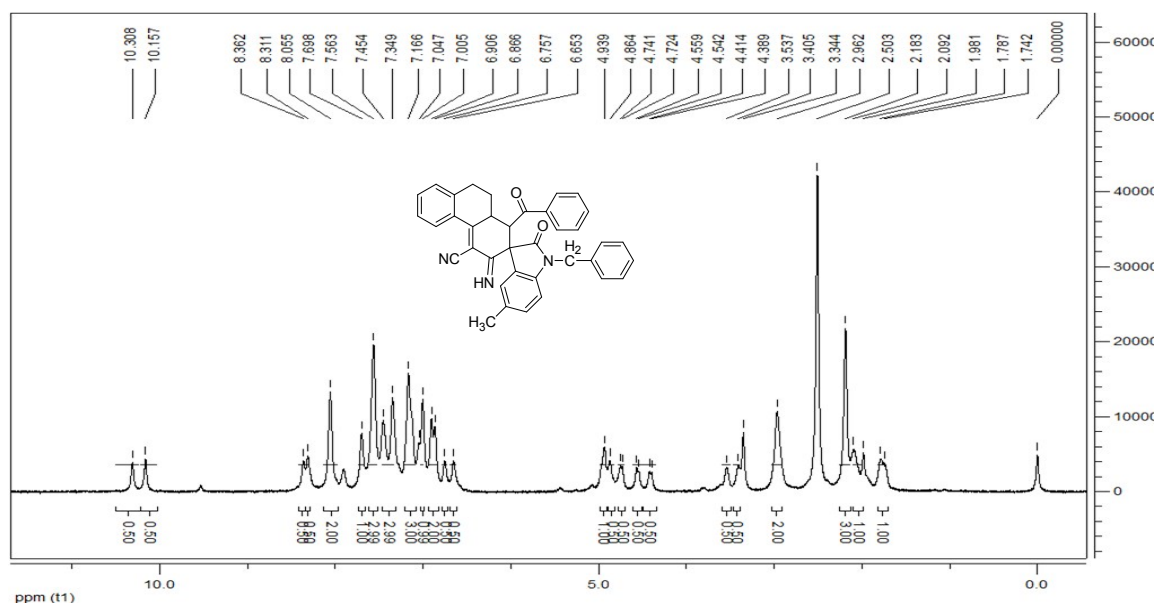
3'-imino-1'-(4-methylbenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1a): white solid, 76%, m.p. 221-223 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.67 (brs, 1H, NH), 10.17 (s, 1H, NH), 8.34 (d, *J* = 7.8Hz, 1H, ArH), 7.92~7.88 (m, 2H, ArH), 7.58~7.53 (m, 1H, ArH), 7.45~7.42 (m, 1H, ArH), 7.34~7.31 (m, 3H, ArH), 7.22 (t, *J* = 7.8Hz, 1H, ArH), 7.01~6.98 (m, 1H, ArH), 6.96~6.93 (m, 1H, ArH), 6.82 (d, *J* = 7.8Hz, 1H, ArH), 4.63 (d, *J* = 10.2Hz, 1H, CH), 3.43~3.41 (m, 1H, CH), 2.97~2.89 (m, 2H, CH), 2.38 (s, 3H, CH₃), 2.06~1.99 (m, 1H, CH), 1.76~1.70 (m, 1H, CH); *trans*-isomer: 10.43 (s, 1H, NH), 10.06 (s, 1H, NH), 8.28 (d, *J* = 7.8Hz, 1H, ArH), 7.19 (t, *J* = 7.8Hz, 1H, ArH), 6.91~6.88 (m, 1H, ArH), 6.79 (d, *J* = 7.8Hz, 1H, ArH), 4.71 (d, *J* = 10.2Hz, 1H, CH), 3.34~3.32 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 197.9, 197.1, 175.3, 174.6, 167.0, 163.6, 163.3, 145.1, 145.0, 142.5, 142.3, 141.4, 140.7, 135.2, 135.0, 133.3, 132.8, 130.8, 130.7, 129.9, 129.8, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 127.4, 126.8, 126.6, 124.3, 122.3, 121.9, 117.2, 116.4, 110.8, 110.4, 108.0, 104.9, 59.6, 58.2, 56.5, 49.0, 48.5, 38.7, 29.4, 29.1, 28.2, 21.6, 19.0; IR (KBr) ν: 3241, 2925, 2208, 1736, 1671, 1604, 1470, 1448, 1405, 1379, 1356, 1329, 1301, 1268, 1228, 1203, 1180, 1120, 1093, 1060, 1046, 997, 958, 931, 887, 818, 781, 754 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₃N₃NaO₂ ([M+Na]⁺): 480.1682. Found: 480.1675.



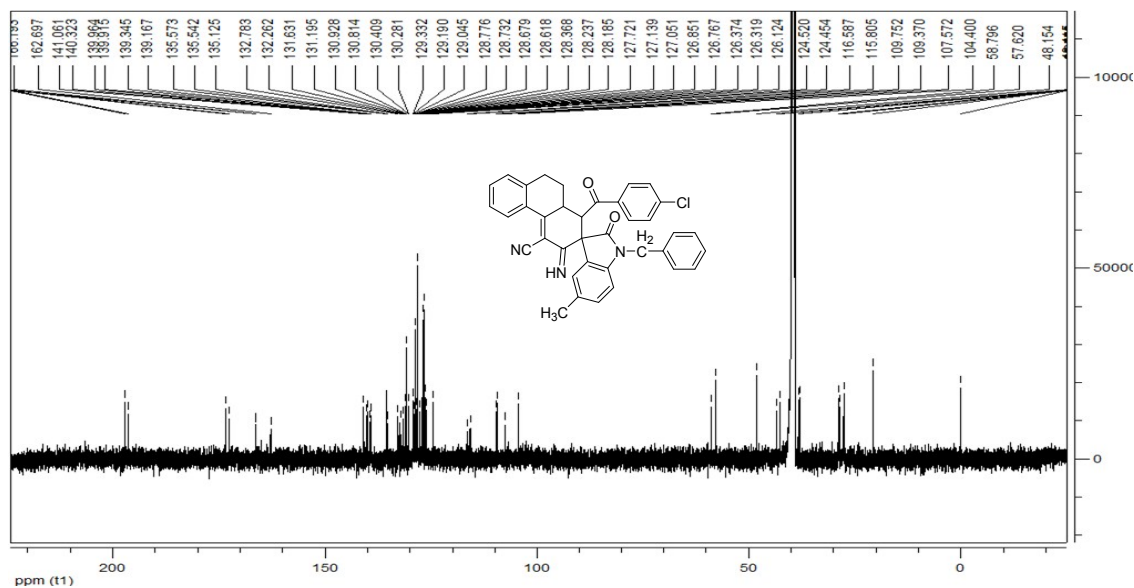
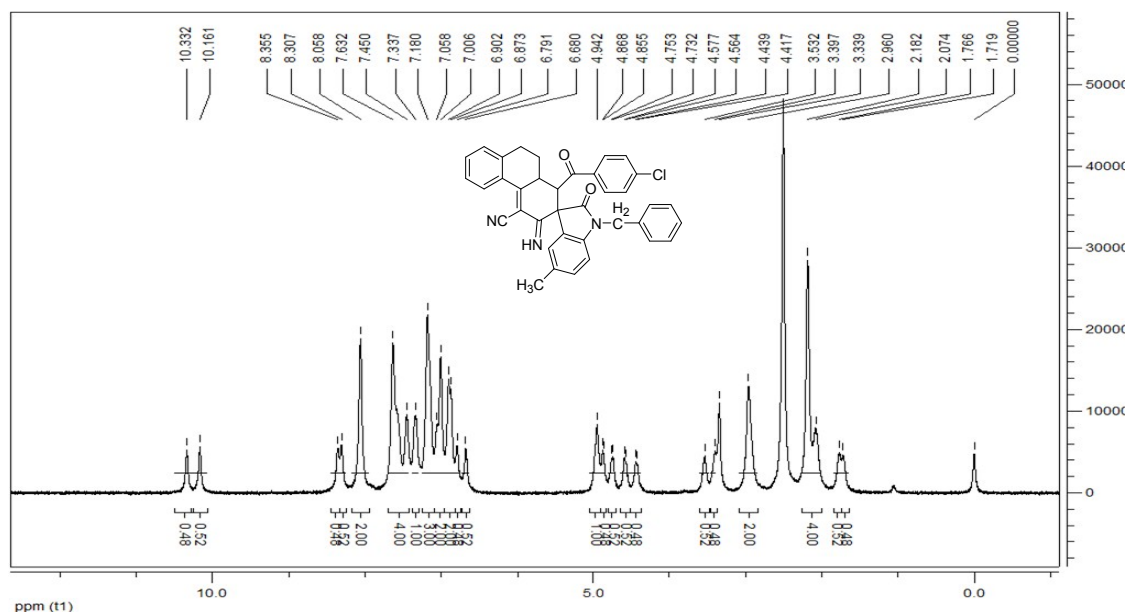
1-benzyl-3'-imino-1'-(4-methoxybenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1b): yellow solid, 80%, m.p. 209~211 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.14 (s, 1H, NH), 8.29 (d, *J* = 7.2Hz, 1H, ArH), 8.06 (brs, 2H, ArH), 7.58~7.55 (m, 1H, ArH), 7.45~7.44 (m, 1H, ArH), 7.35~7.32 (m, 1H, ArH), 7.22~7.15 (m, 4H, ArH), 7.08 (brs, 3H, ArH), 7.02~6.94 (m, 2H, ArH), 6.89 (d, *J* = 6.6Hz, 1H, ArH), 6.76 (d, *J* = 7.2Hz, 1H, ArH), 4.88 (d, *J* = 9.6Hz, 1H, CH), 4.84 (d, *J* = 16.2Hz, 1H, CH), 4.60 (d, *J* = 15.0Hz, 1H, CH), 3.87 (brs, 3H, OCH₃), 3.47 (brs, 1H, CH), 2.96 (brs, 2H, CH), 2.08 (brs, 1H, CH), 1.78~1.76 (m, 1H, CH); *trans*-isomer: 10.34 (s, 1H, NH), 8.35(d, *J* = 7.8Hz, 1H, ArH), 6.84 (d, *J* = 7.2Hz, 1H, ArH), 5.03(d, *J* = 15.6Hz, 1H, CH), 4.79 (d, *J* = 10.2Hz, 1H, CH), 4.43 (d, *J* = 15.6Hz, 1H, CH), 3.34 (brs, 1H, CH), 1.74~1.72 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 194.8, 173.8, 172.9, 166.5, 166.3, 164.0, 163.8, 163.1, 161.3, 142.6, 142.3, 140.3, 136.3, 135.8, 135.6, 132.9, 132.4, 131.8, 131.7, 131.2, 130.2, 129.5, 129.4, 128.6, 128.5, 128.4, 128.3, 127.7, 127.5, 127.3, 127.2, 127.0, 126.9, 126.7, 126.4, 126.2, 123.8, 123.7, 123.5, 122.7, 122.5, 122.3, 119.5, 114.1, 113.9, 109.9, 109.6, 109.4, 107.5, 72.1, 58.8, 55.7, 55.6, 51.1, 47.7, 47.4, 43.7, 43.4, 42.6, 38.7, 38.5, 28.8, 28.5, 27.9, 27.6, 26.5; IR (KBr) ν: 3438, 3060, 2931, 2206, 1725, 1662, 1595, 1508, 1485, 1464, 1421, 1348, 1300, 1258, 1230, 1175, 1129, 1027, 849, 781, 751 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₃₀N₃O₃ ([M+H]⁺): 564.2282. Found: 564.2272.



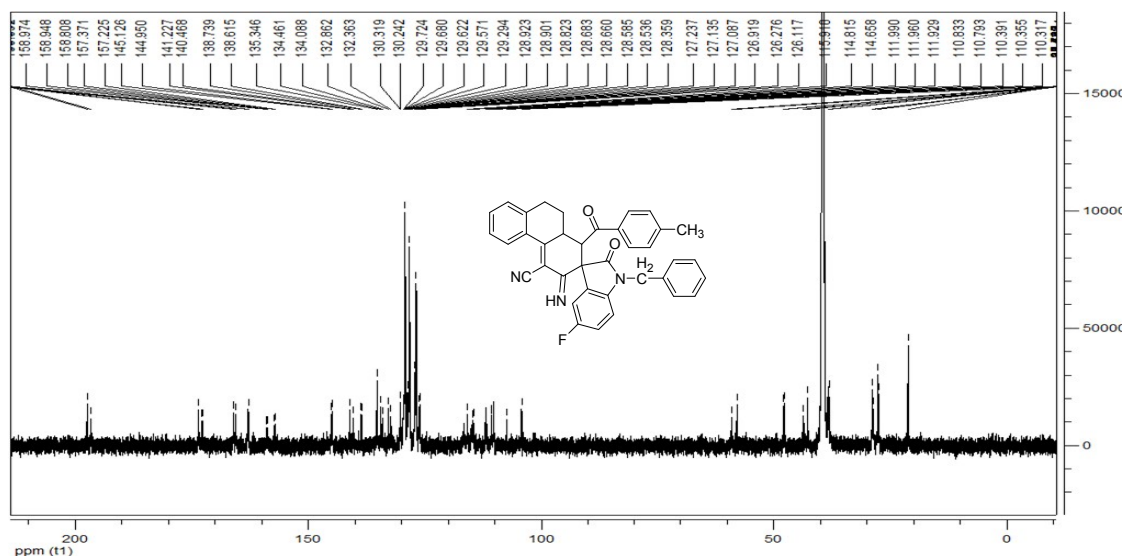
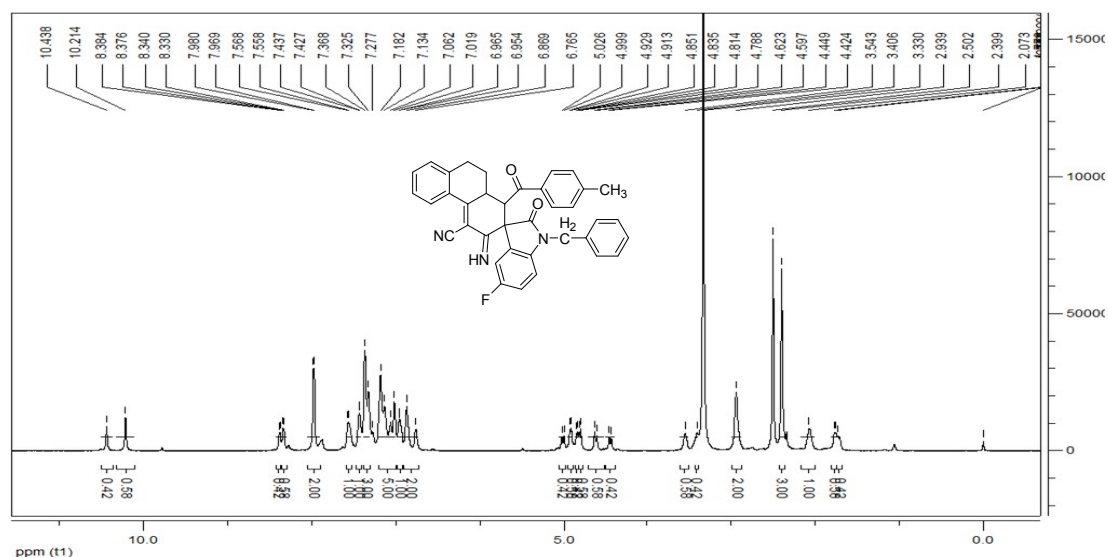
1'-benzoyl-1-benzyl-3'-imino-5-methyl-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1c**):** yellow solid, 76%, m.p. 199~202°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.16 (s, 1H, NH), 8.31 (brs, 1H, ArH), 8.06 (brs, 2H, ArH), 7.70 (s, 1H, ArH), 7.56 (brs, 3H, ArH), 7.45~7.35 (m, 3H, ArH), 7.17 (brs, 3H, ArH), 7.05~7.00 (m, 1H, ArH), 6.91~6.87 (m, 2H, ArH), 6.53 (brs, 1H, ArH), 4.94 (brs, 1H, CH), 4.86 (brs, 1H, CH), 4.73 (d, *J* = 10.2Hz, 1H, CH), 3.54 (brs, 1H, CH), 2.96 (brs, 2H, CH), 2.18 (s, 3H, CH₃), 2.09~1.98 (m, 1H, CH), 1.79~1.74 (m, 1H, CH); *trans*-isomer: 10.31 (s, 1H, NH), 8.36 (brs, 1H, ArH), 6.76 (brs, 1H, ArH), 4.40 (d, *J* = 15.0Hz, 1H, CH), 4.55 (d, *J* = 10.2Hz, 1H, CH), 3.40 (brs, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 197.3, 173.5, 172.8, 166.5, 162.9, 141.1, 140.4, 140.0, 137.0, 136.5, 135.6, 134.2, 134.1, 132.9, 132.4, 132.3, 131.6, 131.2, 130.5, 130.4, 129.4, 129.3, 129.2, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.2, 127.1, 126.9, 126.6, 126.4, 126.2, 126.1, 124.5, 115.9, 109.8, 109.4, 107.6, 104.5, 58.9, 57.7, 48.0, 43.4, 42.6, 38.5, 38.2, 28.9, 28.6, 27.6, 20.8; IR (KBr) ν: 3259, 2921, 2211, 1719, 1674, 1597, 1495, 1449, 1343, 1225, 1197, 1161, 1078, 1000, 889, 807, 772 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₃₀N₃O₂ ([M+H]⁺): 548.2333. Found: 548.2328.



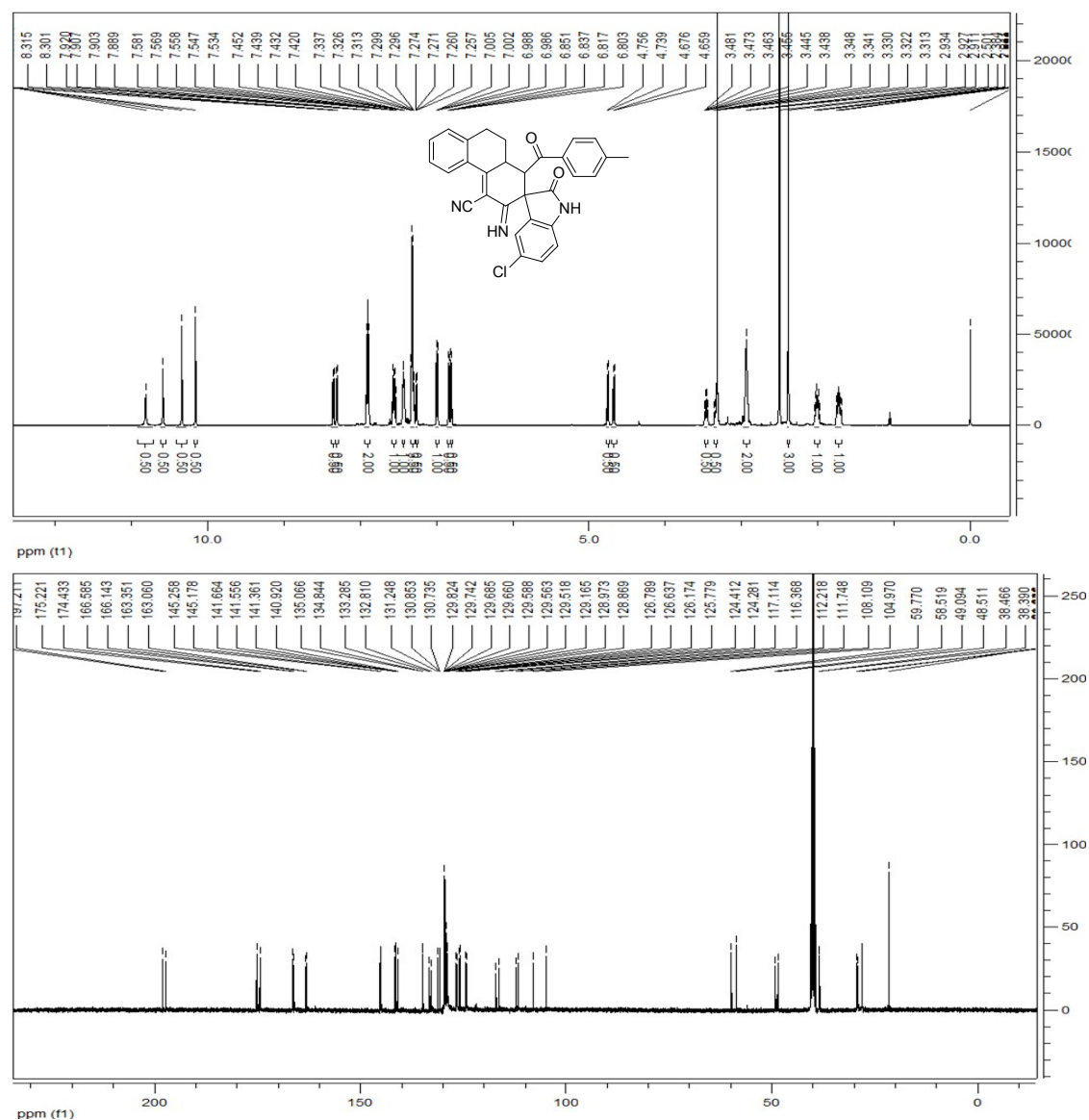
1-benzyl-1'-(4-chlorobenzoyl)-3'-imino-5-methyl-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1d): yellow solid, 72%, m.p. 196~198 °C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ *cis*-isomer: 10.16 (s, 1H, NH), 8.31 (brs, 1H, ArH), 8.06 (s, 2H, ArH), 7.63~7.45 (m, 4H, ArH), 7.34 (brs, 1H, ArH), 7.18 (brs, 3H, ArH), 7.06~7.01 (m, 2H, ArH), 6.90~6.87 (m, 2H, ArH), 6.68 (brs, 1H, ArH), 4.94 (brs, 1H, CH), 4.74 (d, $J = 12.6\text{Hz}$, 1H, CH), 4.57 (d, $J = 7.8\text{Hz}$, 1H, CH), 3.53 (brs, 1H, CH), 2.96 (brs, 2H, CH), 2.18~2.07 (m, 4H, CH_3 , CH), 1.77 (brs, 1H, CH); *trans*-isomer: 10.33 (s, 1H, NH), 8.34 (brs, 1H, ArH), 6.79 (brs, 1H, ArH), 4.86 (d, $J = 7.8\text{Hz}$, 1H, CH), 4.43 (d, $J = 13.2\text{Hz}$, 1H, CH), 3.40 (brs, 1H, CH), 1.72 (brs, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 197.1, 196.2, 173.4, 172.7, 116.3, 116.2, 162.7, 141.1, 140.3, 140.0, 139.9, 139.3, 139.2, 135.6, 135.5, 135.1, 132.8, 132.3, 131.6, 131.2, 130.9, 130.8, 130.4, 130.3, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.2, 127.1, 126.9, 126.8, 126.4, 126.3, 126.1, 124.5, 116.6, 115.8, 109.8, 109.4, 107.6, 104.4, 58.8, 57.2, 48.2, 43.4, 42.6, 38.3, 38.0, 28.7, 28.4, 27.6, 27.5, 20.8, 20.7; IR (KBr) ν : 3421, 2926, 2208, 1718, 1671, 1601, 1492, 1344, 1166, 1091, 996, 805, 775 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{37}\text{H}_{29}\text{ClN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$): 582.1943. Found: 582.1924.



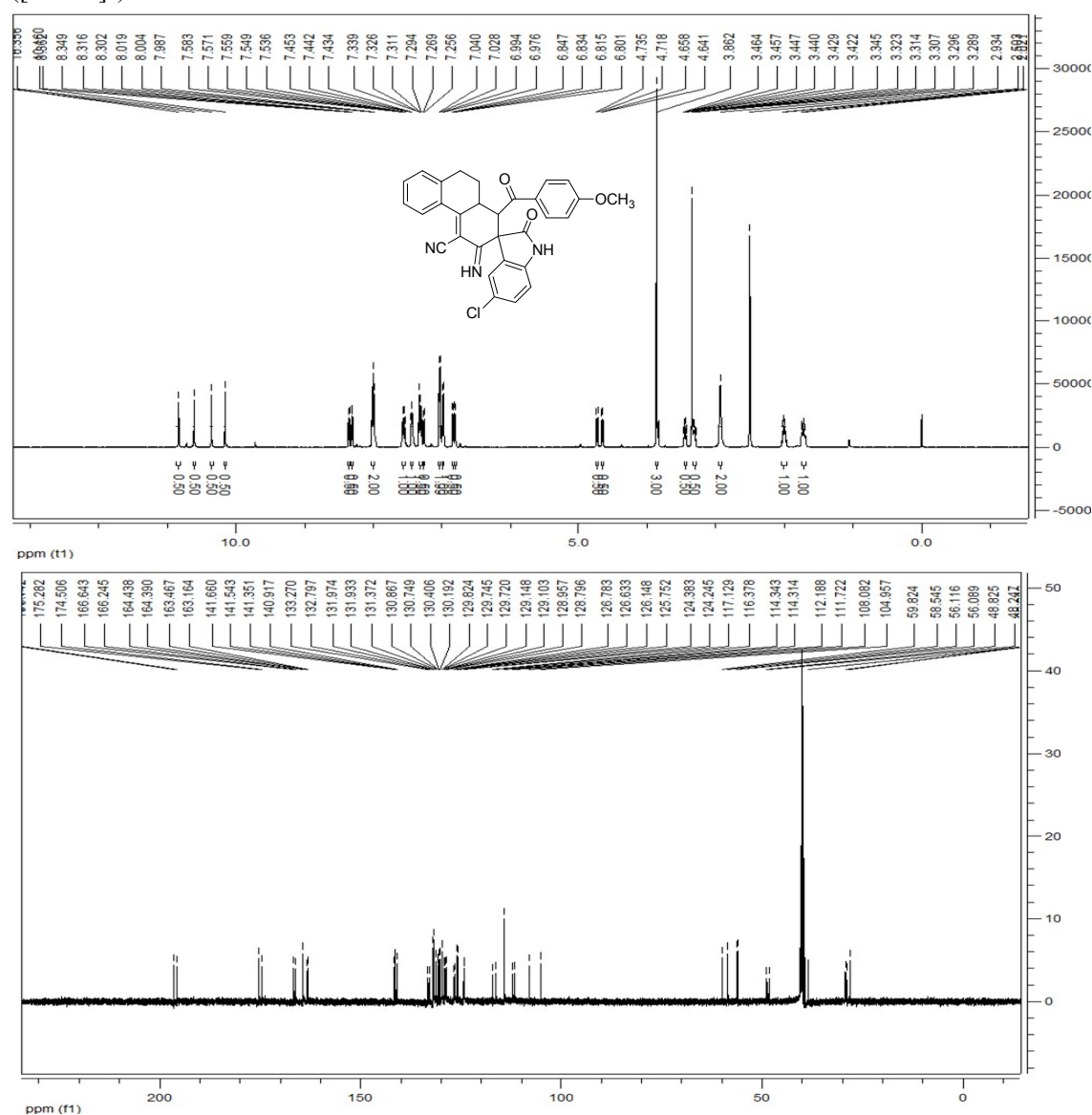
1-benzyl-5-fluoro-3'-imino-1'-(4-methylbenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1e): yellow solid, 85%, m.p. 212~214°C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ *cis*-isomer: 10.21 (s, 1H, NH), 8.34 (d, $J = 6.0\text{Hz}$, 1H, ArH), 7.97 (d, $J = 6.6\text{Hz}$, 2H, ArH), 7.57~7.56 (m, 1H, ArH), 7.44~7.43 (m, 1H, ArH), 7.37~7.28 (m, 3H, ArH), 7.18~7.02 (m, 5H, ArH), 6.96~6.95 (m, 1H, ArH), 6.87~6.76 (m, 2H, ArH), 4.92 (d, $J = 9.6\text{Hz}$, 1H, CH), 4.80 (d, $J = 15.6\text{Hz}$, 1H, CH), 4.61 (d, $J = 15.6\text{Hz}$, 1H, CH), 3.54 (brs, 1H, CH), 2.94 (brs, 2H, CH), 2.40 (s, 3H, CH_3), 2.07 (brs, 1H, CH), 1.77~1.76 (m, 1H, CH); *trans*-isomer: 10.44 (s, 1H, NH), 8.38(d, $J = 4.8\text{Hz}$, 1H, ArH), 5.01(d, $J = 16.2\text{Hz}$, 1H, CH), 4.84 (d, $J = 9.6\text{Hz}$, 1H, CH), 4.44 (d, $J = 15.0\text{Hz}$, 1H, CH), 3.41 (brs, 1H, CH), 1.74~1.73 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 197.5, 196.7, 173.5, 172.8, 166.1, 165.7, 163.1, 162.9, 159.0, 158.9, 158.8, 157.4, 157.2, 145.1, 145.0, 141.2, 140.5, 138.7, 138.6, 135.3, 134.5, 134.1, 132.9, 132.4, 130.3, 130.2, 129.7, 129.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.2, 127.1, 126.9, 126.3, 126.1, 115.9, 114.8, 114.7, 112.0, 111.9, 110.8, 110.4, 110.3, 107.5, 104.3, 59.0, 57.9, 47.9, 47.7, 43.6, 42.7, 38.4, 38.2, 28.9, 28.6, 27.6, 21.2; IR (KBr) ν : 3430, 2926, 2221, 1712, 1661, 1603, 1488, 1452, 1344, 1271, 1244, 1165, 1123, 1028, 1005, 969, 891, 869, 812, 776 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{37}\text{H}_{29}\text{FN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$): 566.2238. Found: 566.2231.



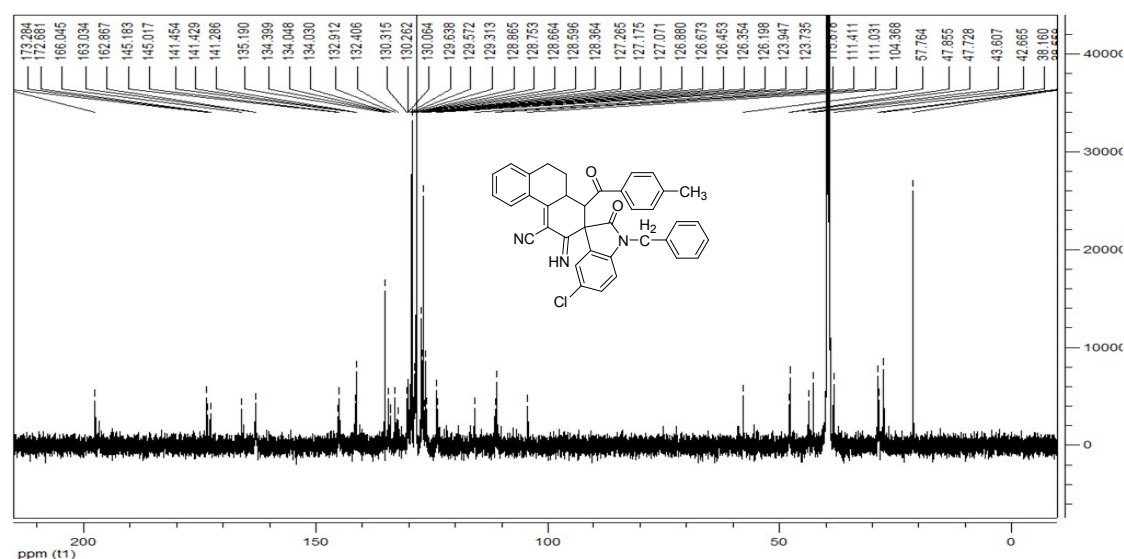
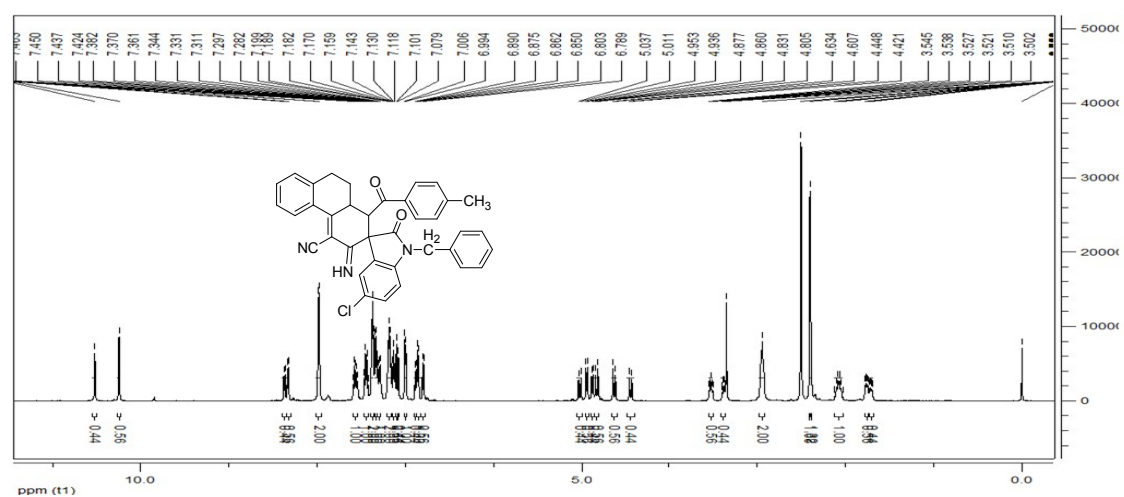
5-chloro-3'-imino-1'-(4-methylbenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1f): white solid, 73%, m.p. 212-214°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.81 (brs, 1H, NH), 10.34 (s, 1H, NH), 8.36 (d, *J* = 8.4Hz, 1H, ArH), 7.92~7.89 (m, 2H, ArH), 7.58~7.53 (m, 1H, ArH), 7.45~7.42 (m, 1H, ArH), 7.34~7.30 (m, 4H, ArH), 7.00~6.99 (m, 1H, ArH), 6.84 (d, *J* = 8.4Hz, 1H, ArH), 4.67 (d, *J* = 10.2Hz, 1H, CH), 3.48~3.44 (m, 1H, CH), 2.93~2.91 (m, 2H, CH), 2.38 (brs, 3H, CH₃), 2.04~1.97 (m, 1H, CH), 1.75~1.69 (m, 1H, CH); *trans*-isomer: 10.59 (s, 1H, NH), 10.16 (s, 1H, NH), 8.31 (d, *J* = 8.4Hz, 1H, ArH), 7.27~7.26 (m, 1H, ArH), 6.81 (d, *J* = 8.4Hz, 1H, ArH), 4.75 (d, *J* = 10.2Hz, 1H, CH), 3.35~3.32 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 198.0, 197.2, 175.2, 174.4, 166.6, 166.1, 163.4, 163.1, 145.3, 145.2, 141.7, 141.6, 141.4, 140.9, 135.1, 134.8, 133.3, 132.8, 131.2, 130.9, 130.7, 129.8, 129.7, 129.6, 129.5, 129.2, 129.0, 128.9, 126.8, 126.6, 126.2, 125.8, 124.4, 124.3, 117.1, 116.4, 112.2, 111.7, 108.1, 105.0, 59.8, 58.5, 49.1, 48.5, 38.5, 38.4, 29.3, 29.0, 28.1, 28.0, 21.6; IR (KBr) ν: 3250, 2924, 2731, 2213, 1730, 1671, 1606, 1574, 1476, 1451, 1379, 1340, 1307, 1268, 1231, 1184, 1163, 1123, 1085, 1046, 1000, 876, 822, 776 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₂ClN₃NaO₂ ([M+Na]⁺): 514.1293. Found: 514.1285.



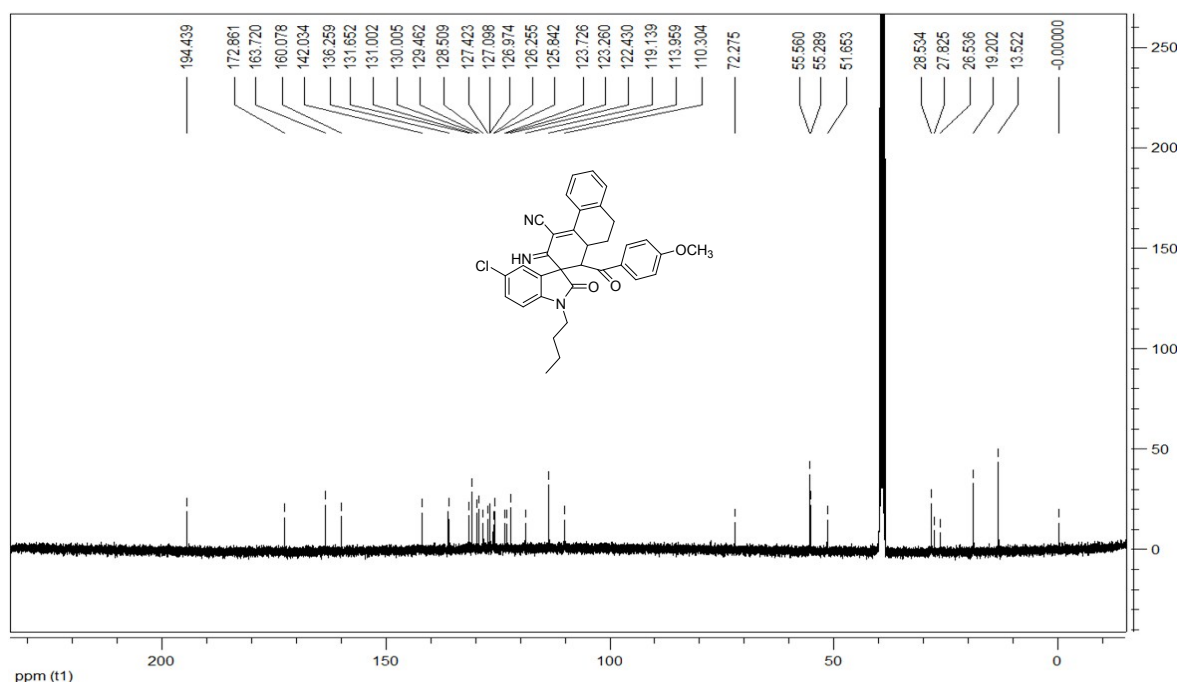
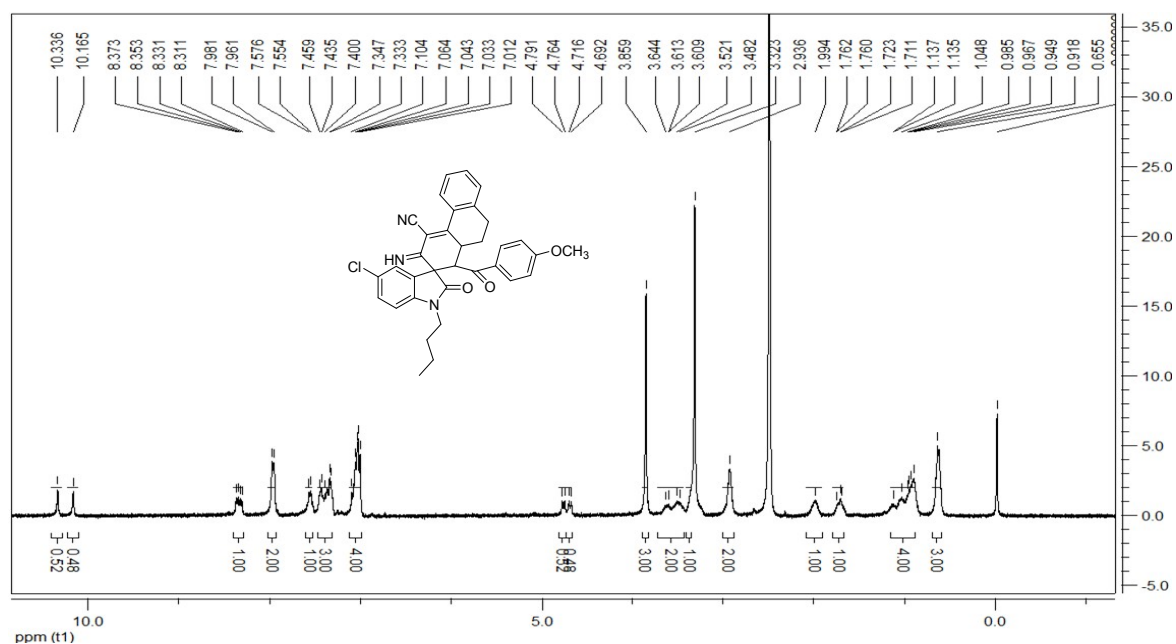
5-chloro-3'-imino-1'-(4-methoxybenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1g): white solid, 78%, m.p. 198-200°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.84 (brs, 1H, NH), 10.36 (s, 1H, NH), 8.35 (d, *J* = 7.8Hz, 1H, ArH), 8.02-7.99 (m, 2H, ArH), 7.58~7.54 (m, 1H, ArH), 7.45~7.43 (m, 1H, ArH), 7.34~7.29 (m, 2H, ArH), 7.03 (d, *J* = 7.2Hz, 2H, ArH), 6.99 (d, *J* = 10.8Hz, 1H, ArH), 6.84 (d, *J* = 7.8Hz, 1H, ArH), 4.65 (d, *J* = 10.2Hz, 1H, CH), 3.86 (s, 3H, OCH₃), 3.46~3.42 (m, 1H, CH), 2.93 (brs, 2H, CH), 2.02~1.99 (m, 1H, CH), 1.75~1.70 (m, 1H, CH); *trans*-isomer: 10.61 (s, 1H, NH), 10.16 (s, 1H, NH), 8.31 (d, *J* = 8.4Hz, 1H, ArH), 7.26 (d, *J* = 7.8Hz, 1H, ArH), 6.81 (d, *J* = 8.4Hz, 1H, ArH), 4.73 (d, *J* = 10.2Hz, 1H, CH), 3.32~3.29 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 196.5, 195.7, 175.3, 174.5, 166.6, 166.2, 164.4, 164.3, 163.5, 163.2, 141.7, 141.5, 141.4, 140.9, 133.3, 132.8, 132.0, 131.9, 131.4, 130.9, 130.7, 130.4, 130.2, 129.8, 129.7, 129.1, 129.0, 128.8, 126.8, 126.6, 126.1, 125.8, 124.4, 124.2, 117.1, 116.4, 114.3, 112.2, 111.7, 108.1, 105.0, 59.8, 58.5, 56.1, 48.8, 48.2, 38.5, 38.4, 29.3, 29.0, 28.1, 28.0; IR (KBr) ν: 3194, 2931, 2838, 2214, 1734, 1670, 1596, 1510, 1475, 1450, 1377, 1351, 1304, 1260, 1231, 1170, 1054, 1026, 995, 878, 858, 825, 802 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₂ClN₃NaO₃ ([M+Na]⁺): 530.1242. Found: 530.1238.



1-benzyl-5-chloro-3'-imino-1'-(4-methylbenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1h): yellow solid, 79%, m.p. 151~153 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.24 (s, 1H, NH), 8.33 (d, *J* = 7.8Hz, 1H, ArH), 7.98 (d, *J* = 7.8Hz, 2H, ArH), 7.59~7.54 (m, 1H, ArH), 7.46~7.42 (m, 1H, ArH), 7.38~7.36 (m, 2H, ArH), 7.34~7.33 (m, 1H, ArH), 7.31~7.28 (m, 1H, ArH), 7.20~7.16 (m, 2H, ArH), 7.14~7.12 (m, 1H, ArH), 7.10 (s, 1H, ArH), 7.00 (d, *J* = 7.2Hz, 1H, ArH), 6.86 (d, *J* = 7.2Hz, 1H, ArH), 6.80 (d, *J* = 8.4Hz, 1H, ArH), 4.94 (d, *J* = 10.2Hz, 1H, CH), 4.82 (d, *J* = 15.6Hz, 1H, CH), 4.67 (d, *J* = 16.2Hz, 1H, CH), 3.54~3.50 (m, 1H,CH), 2.94 (brs, 2H, CH), 2.40 (s, 3H, CH₃), 2.12~2.03 (m, 1H, CH), 1.78~1.75 (m, 1H, CH); *trans*-isomer: 10.52 (s, 1H, NH), 8.37 (d, *J* = 7.8Hz, 1H, ArH), 7.08 (s, 1H, ArH), 6.88 (d, *J* = 9.0Hz, 1H, ArH), 5.02 (d, *J* = 15.6Hz, 1H, CH), 4.87 (d, *J* = 10.2Hz, 1H, CH), 4.43 (d, *J* = 16.2Hz, 1H, CH), 3.40~3.36 (m, 1H,CH), 2.39 (s, 3H, CH₃), 1.72~1.70 (m, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 197.5, 173.5, 173.3, 172.7, 166.0, 163.0, 162.9, 145.2, 145.0, 141.5, 141.4, 141.3, 135.2, 134.4, 134.0, 132.9, 132.4, 130.3, 130.1, 129.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 127.3, 127.2, 127.0, 126.9, 126.7, 126.4, 126.2, 123.9, 123.7, 115.9, 111.4, 111.0, 104.4, 57.8, 47.9, 47.7, 43.6, 42.7, 38.2, 28.8, 28.6, 27.6, 27.5, 21.2; IR (KBr) ν: 3253, 2925, 2213, 1723, 1670, 1605, 1483, 1429, 1341, 1268, 1232, 1183, 1124, 1079, 1028, 1002, 883, 811, 770 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₂₉ClN₃O₂ ([M+H]⁺): 582.1943. Found: 582.1933.

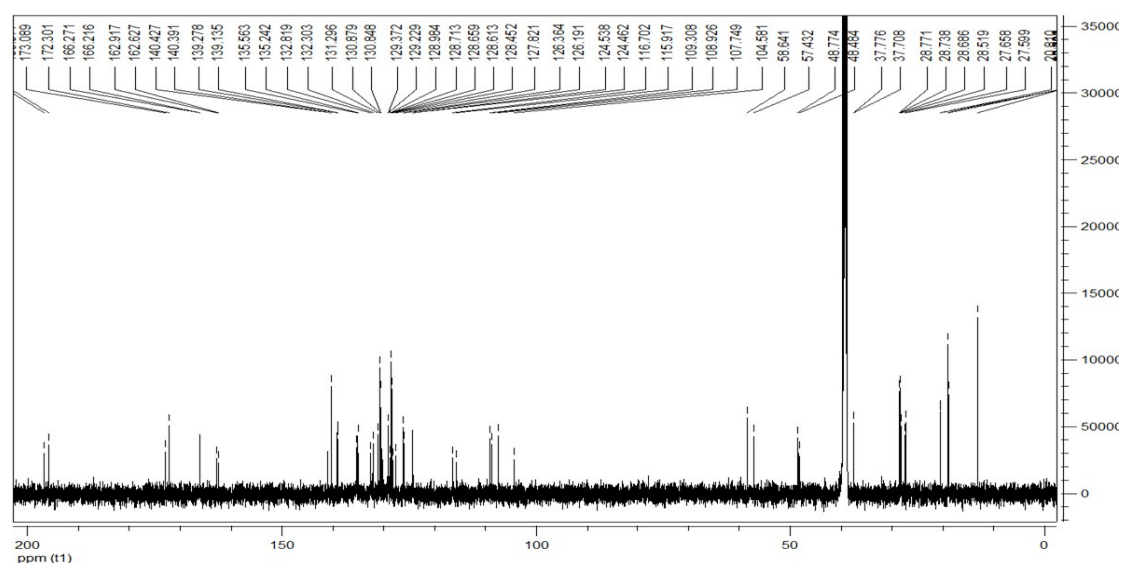
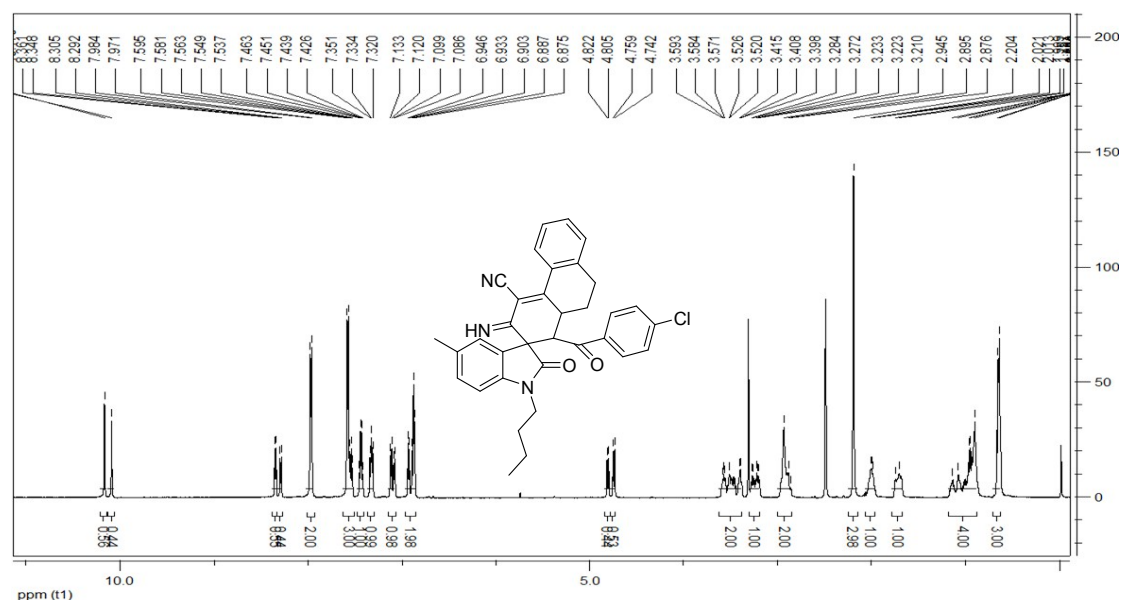


1-butyl-5-chloro-3'-imino-1'-(4-methoxybenzoyl)-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1i**):** white solid, 66%, m.p. 209-211°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.34 (s, 1H, NH), 8.37-8.31 (m, 1H, ArH), 7.98-7.96 (m, 2H, ArH), 7.58-7.55 (m, 1H, ArH), 7.46-7.33 (m, 3H, ArH), 7.10-7.01 (m, 4H, ArH), 7.48 (d, *J* = 10.8Hz, 1H, CH), 3.86 (s, 3H, OCH₃), 3.64-3.48 (m, 2H, CH), 3.32 (brs, 1H, CH), 2.94 (brs, 2H, CH), 1.99 (brs, 1H, CH), 1.76-1.71 (m, 1H, CH), 1.14-0.92 (m, 4H, CH), 0.66 (brs, 3H, CH₃); *trans*-isomer: 10.16 (s, 1H, NH), 4.70 (d, *J* = 9.6Hz, 1H, CH). Ratio of *cis/trans* isomers = 1:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 194.4, 172.9, 163.7, 160.1, 142.0, 136.3, 131.7, 131.0, 129.5, 128.5, 127.4, 127.1, 127.0, 126.3, 125.8, 123.7, 123.3, 122.4, 119.1, 114.0, 110.3, 72.3, 55.6, 55.3, 51.7, 28.5, 27.8, 26.5, 19.2, 13.5; IR (KBr) ν: 3690, 2950, 2212, 1719, 1667, 1596, 1477, 1430, 1343, 1258, 1172, 1021, 887, 846, 776 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₀ClN₃NaO₃ ([M+Na]⁺): 586.1868. Found: 586.1864.

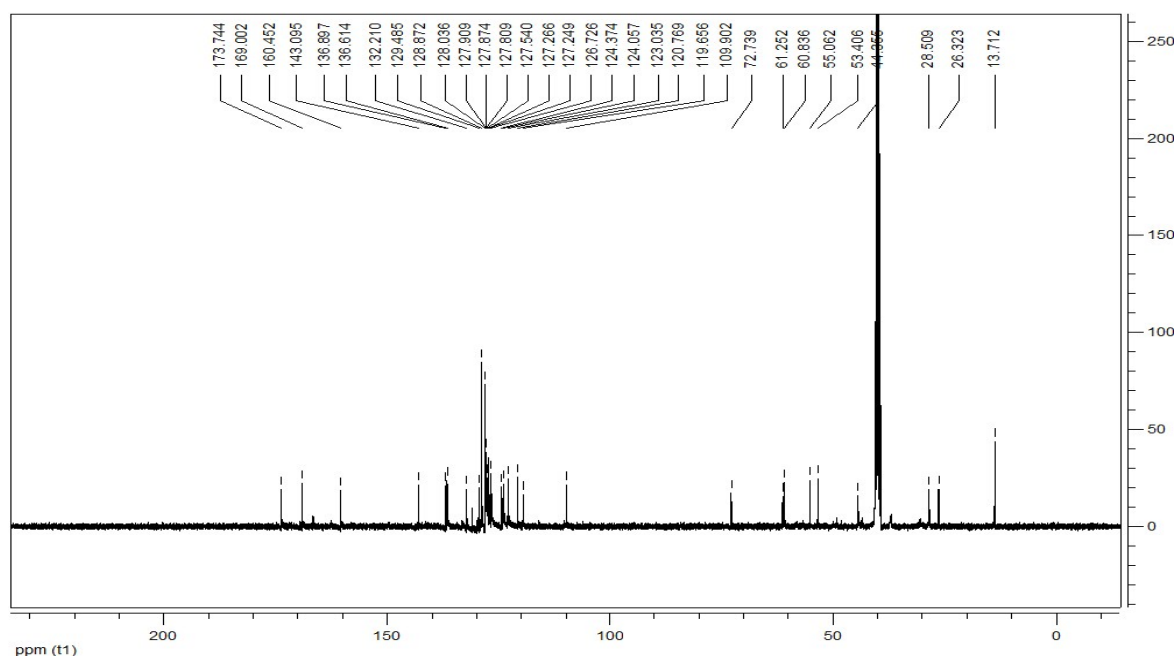
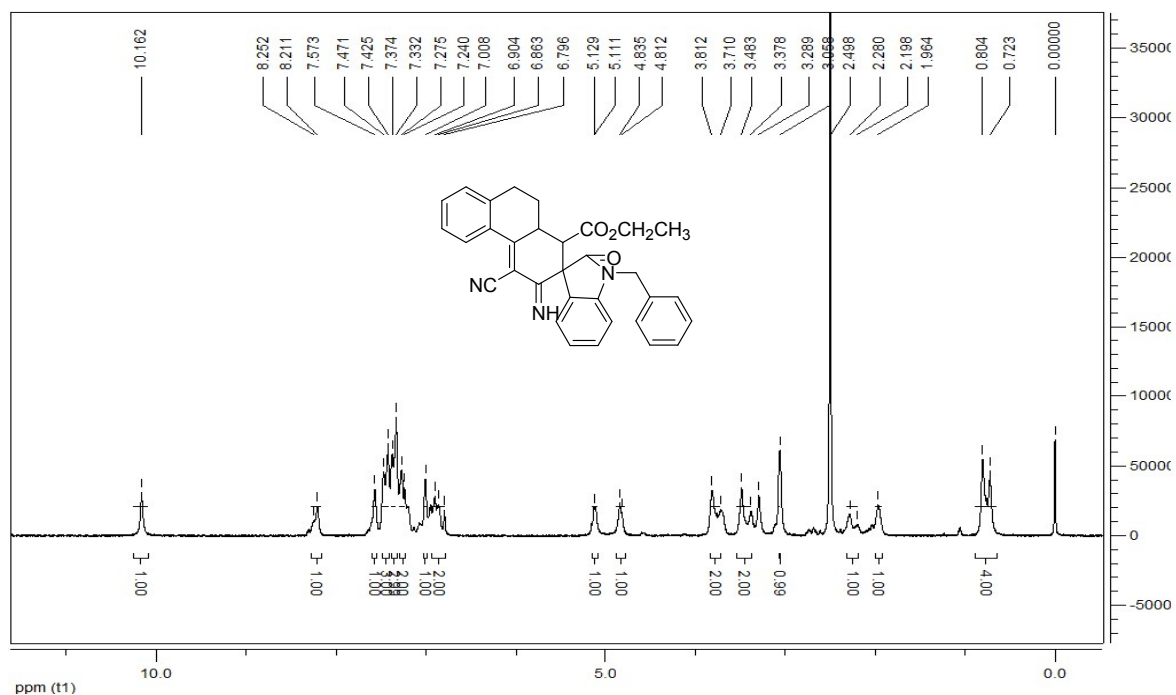


1-butyl-1'-(4-chlorobenzoyl)-3'-imino-5-methyl-2-oxo-3',9',10',10a'-tetrahydro-1'H-

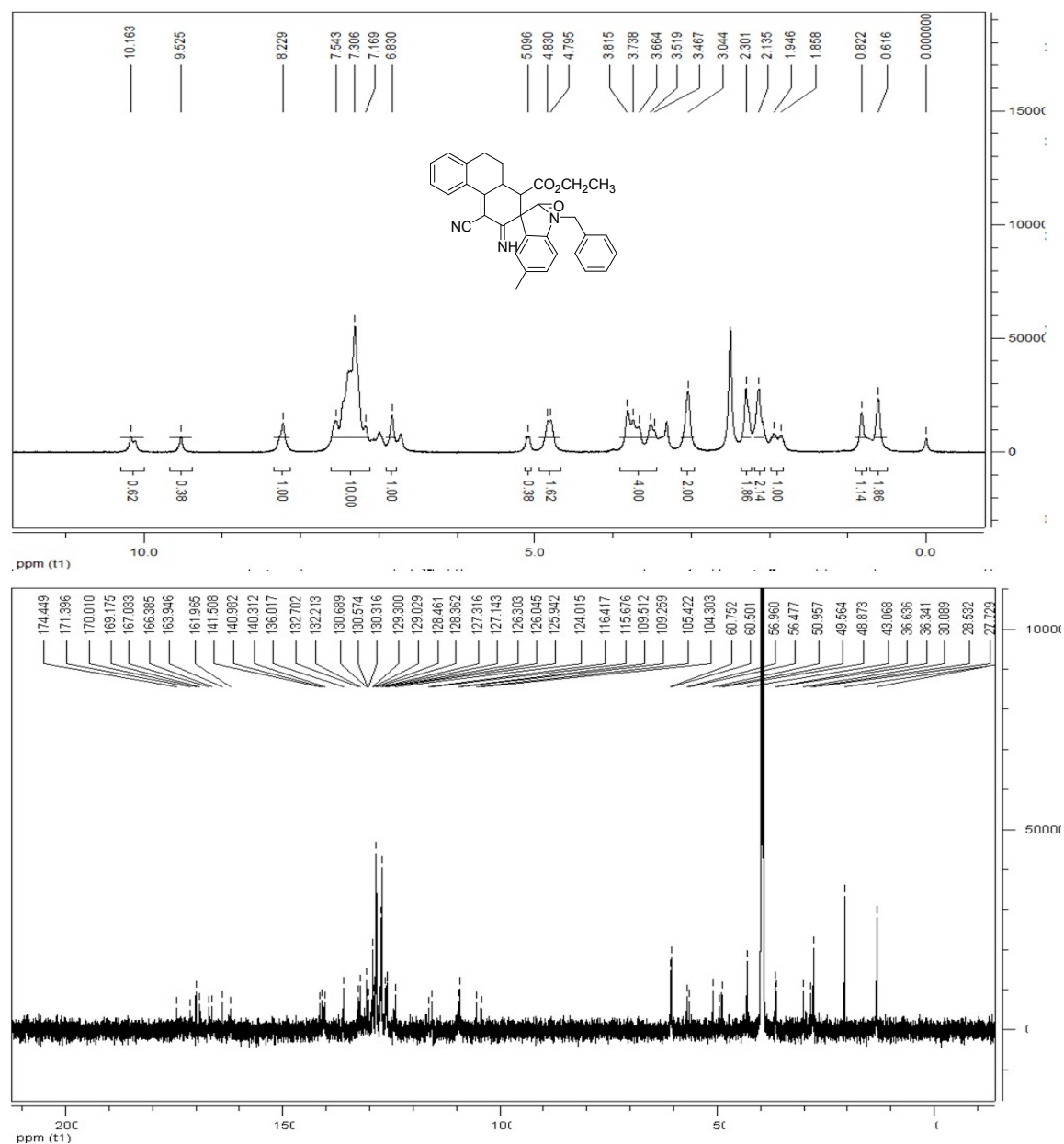
spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (1j**):** white solid, 76%, m.p. 226-228°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.17 (s, 1H, NH), 8.35 (d, *J* = 7.2Hz, 1H, ArH), 7.98 (d, *J* = 7.2Hz, 2H, ArH), 7.60-7.54 (m, 3H, ArH), 7.46-7.43 (m, 1H, ArH), 7.35-7.32 (m, 1H, ArH), 7.13-7.09 (m, 1H, ArH), 6.95-6.88 (m, 2H, ArH), 4.75 (d, *J* = 10.4Hz, 1H, CH), 3.59-3.52 (m, 2H, CH), 3.28-3.21 (m, 1H, CH), 2.95-2.88 (m, 2H, CH), 2.20 (s, 3H, CH₃), 2.02-2.00 (m, 1H, CH), 1.76-1.72 (m, 1H, CH), 1.16-0.92 (m, 4H, CH), 0.67-0.66 (m, 3H, CH₃); *trans*-isomer: 10.10 (s, 1H, NH), 8.30 (d, *J* = 7.2Hz, 1H, ArH), 4.81 (d, *J* = 10.4Hz, 1H, CH) Ratio of *cis/trans* isomers = 11:9. ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 196.87, 195.98, 173.09, 172.30, 166.27, 166.22, 162.92, 162.63, 140.43, 140.39, 139.28, 139.13, 135.56, 135.24, 132.82, 132.30, 131.29, 130.88, 130.85, 129.37, 129.23, 128.98, 128.71, 128.66, 128.61, 128.45, 127.82, 126.19, 124.54, 124.46, 116.70, 115.92, 109.31, 108.93, 107.75, 104.58, 58.64, 57.43, 48.77, 48.48, 37.78, 37.71, 28.77, 28.74, 28.69, 28.52, 27.66, 27.60, 20.81, 20.79, 19.24, 19.07, 13.47; IR (KBr) ν: 3454, 3260, 3064, 2952, 2928, 2868, 2209, 1715, 1674, 1592, 1565, 1491, 1459, 1344, 1284, 1221, 1200, 1170, 1135, 189, 993, 887, 862, 837, 799, 779 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₀ClN₃NaO₂([M+Na]⁺): 570.1919. Found: 570.1923.



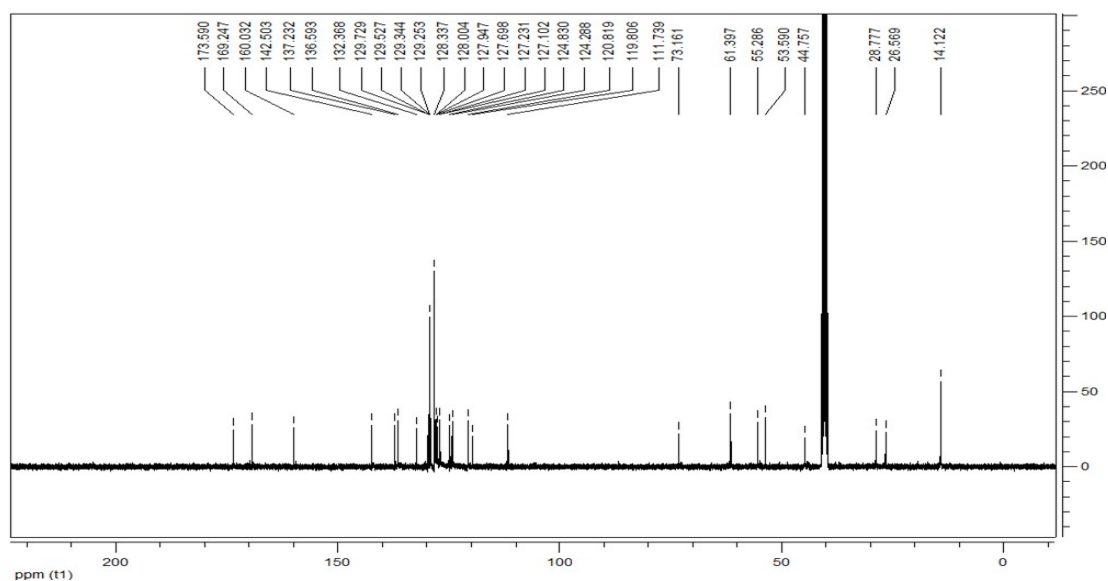
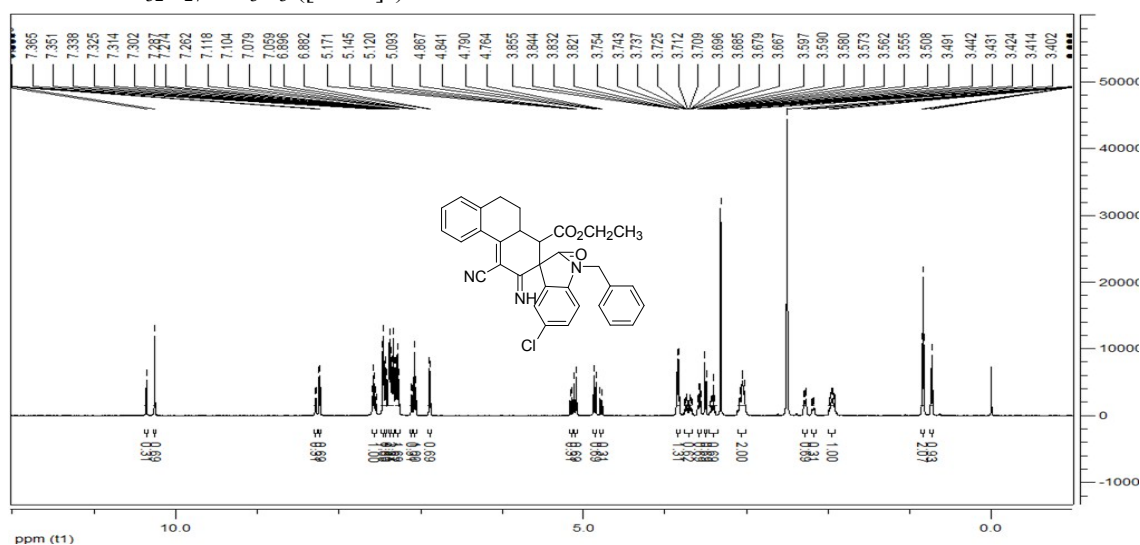
Ethyl 1-benzyl-4'-cyano-3'-imino-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (2a): yellow solid, 66%, m.p. 192~194°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 10.16 (s, 1H, NH), 8.25~8.21 (m, 1H, ArH), 7.57 (s, 1H, ArH), 7.47~7.42 (m, 3H, ArH), 7.37~7.33 (m, 3H, ArH), 7.28~7.24 (m, 2H, ArH), 7.01 (brs, 1H, ArH), 6.90~6.80 (m, 2H, ArH), 5.13~5.11 (m, 1H, CH), 4.84~4.81 (m, 1H, CH), 3.81~3.71 (m, 2H, CH), 3.48~3.38 (m, 2H, CH), 3.06 (brs, 1H, CH), 2.28~2.20 (m, 1H, CH), 1.96 (brs, 3H, CH), 0.80~0.72 (m, 4H, CH, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 173.7, 169.0, 160.5, 143.1, 136.9, 136.6, 132.2, 129.5, 128.9, 128.0, 127.9, 127.8, 127.5, 127.3, 127.2, 126.7, 124.4, 124.1, 123.0, 120.8, 119.7, 109.9, 72.7, 61.3, 60.8, 55.1, 53.4, 44.4, 28.5, 26.3, 13.7; IR (KBr) ν: 3279, 3062, 3024, 2964, 2938, 2906, 2216, 1732, 1610, 1488, 1363, 1338, 1312, 1282, 1242, 1221, 1180, 1159, 1097, 1028, 1010, 928, 878, 762 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₈N₃O₃ ([M+H]⁺): 502.2125. Found: 502.2122.



Ethyl 1-benzyl-4'-cyano-3'-imino-5-methyl-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (2b): yellow solid, 59%, m.p. 168~170 °C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ *cis*-isomer: 10.16 (s, 1H, NH), 8.23 (brs, 1H, ArH), 7.54~7.17 (m, 10H, ArH), 6.83 (s, 1H, ArH), 4.83~4.80 (m, 2H, CH), 3.82~3.47 (m, 4H, CH), 3.04 (brs, 2H, CH), 2.30 (brs, 3H, CH_3), 2.14 (brs, 1H, CH), 1.95~1.86 (m, 1H, CH), 0.62 (brs, 3H, CH_3); *trans*-isomer: 9.52 (s, 1H, NH), 5.10 (brs, 1H, CH), 0.82 (brs, 3H, CH_3). Ratio of *cis/trans* isomers = 1.6:1. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 174.4, 171.4, 170.0, 169.2, 167.0, 166.4, 163.9, 162.0, 141.5, 141.0, 140.3, 136.0, 132.7, 132.2, 130.7, 130.6, 130.3, 129.3, 129.0, 128.5, 128.4, 127.3, 127.1, 126.3, 126.0, 125.9, 124.0, 116.4, 115.7, 109.5, 109.2, 105.4, 104.3, 60.8, 60.5, 57.0, 56.5, 50.9, 49.6, 48.9, 43.1, 36.6, 36.3, 30.1, 28.5, 27.7, 20.6, 13.2; IR (KBr) ν : 3248, 3064, 3028, 2979, 2922, 2208, 1733, 1705, 1602, 1573, 1497, 1454, 1432, 1257, 1192, 1160, 1077, 1020, 957, 887, 860, 811, 773 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{30}\text{N}_3\text{O}_3$ ($[\text{M}+\text{H}]^+$): 516.2282. Found: 516.2280.

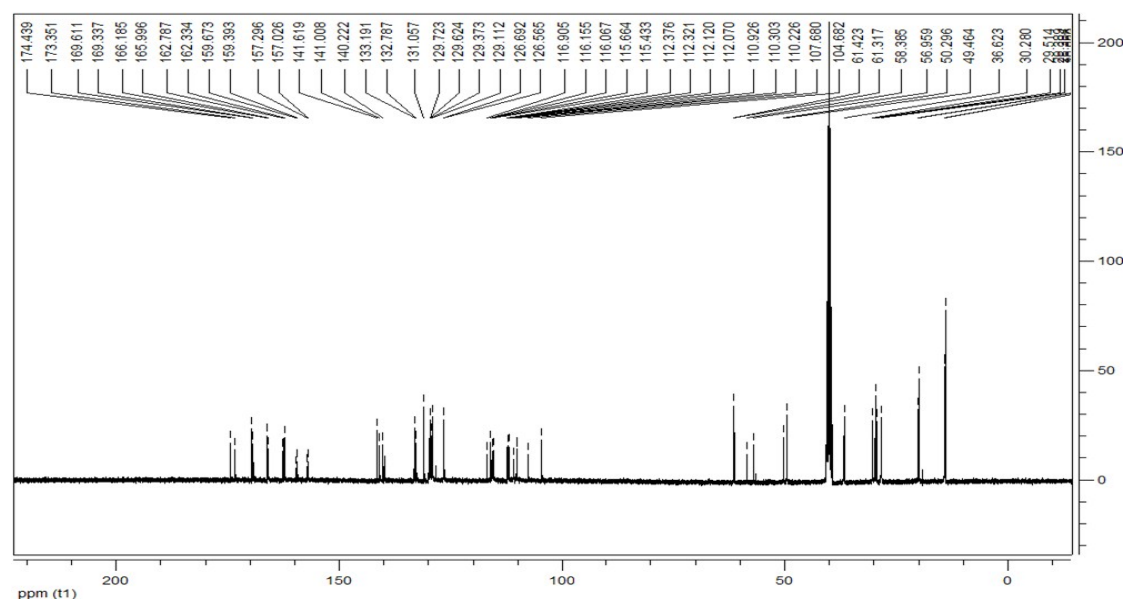
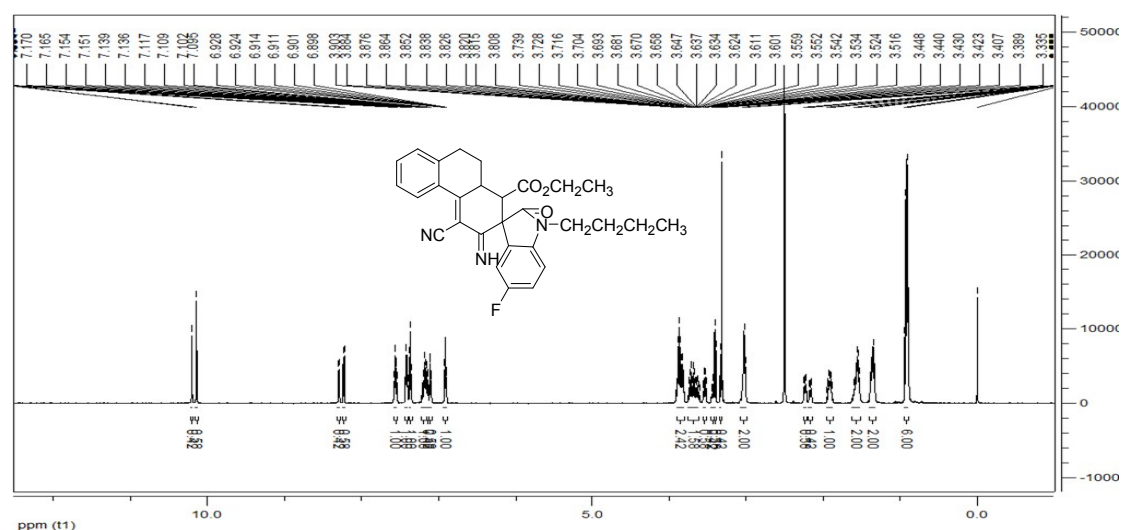


Ethyl 1-benzyl-5-chloro-4'-cyano-3'-imino-2-oxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (2c): yellow solid, 51%, m.p. 171~173 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: *cis*-isomer: 10.26 (s, 1H, NH), 8.24 (d, *J* = 7.8 Hz, 1H, ArH), 7.59~7.54 (m, 1H, ArH), 7.47~7.45 (m, 2H, ArH), 7.43~7.42 (m, 1H, ArH), 7.39~7.36 (m, 2H, ArH), 7.35~7.32 (m, 1H, ArH), 7.31~7.26 (m, 2H, ArH), 7.08~7.06 (m, 1H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 5.11 (d, *J* = 16.2 Hz, 1H, ArH), 4.85 (d, *J* = 15.6 Hz, 1H, CH), 3.86~3.82 (m, 1H, CH), 3.60~3.56 (m, 1H, CH), 3.51~3.49 (m, 1H, CH), 3.44~3.38 (m, 1H, CH), 3.08~3.02 (m, 1H, CH), 2.30~2.27 (m, 1H, CH), 1.99~1.91 (m, 1H, CH), 0.84 (t, *J* = 7.2 Hz, 3H, CH₃); *trans*-isomer: 10.36 (s, 1H, NH), 8.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.11 (d, *J* = 8.4 Hz, 1H, ArH), 5.16 (d, *J* = 15.6 Hz, 1H, CH), 4.78 (d, *J* = 15.6 Hz, 1H, CH), 3.75~3.67 (m, 2H, CH), 2.20~2.17 (m, 1H, CH), 0.73 (t, *J* = 7.2 Hz, 3H, CH₃). Ratio of *cis/trans* isomers = 2.2:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 173.6, 169.2, 160.0, 142.5, 137.2, 136.6, 132.4, 129.7, 129.5, 129.3, 128.3, 128.0, 127.9, 127.7, 127.2, 127.1, 124.8, 124.3, 120.8, 119.8, 111.7, 73.2, 61.4, 55.3, 53.6, 44.8, 22.8, 26.6, 14.1; IR (KBr) ν: 3253, 3065, 2979, 2929, 2862, 2214, 1732, 1607, 1579, 1556, 1482, 1454, 1431, 1338, 1271, 1225, 1189, 1157, 1119, 1080, 1027, 955, 884, 824, 767 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇ClN₃O₃ ([M+H]⁺): 536.1735. Found: 536.1726.

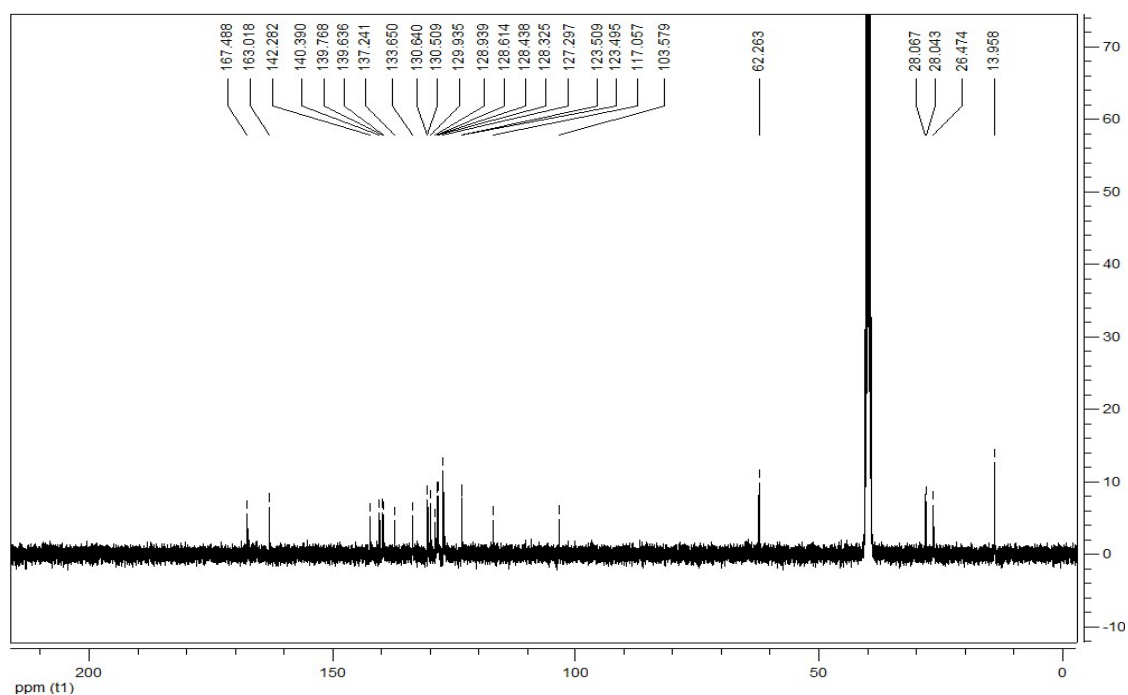
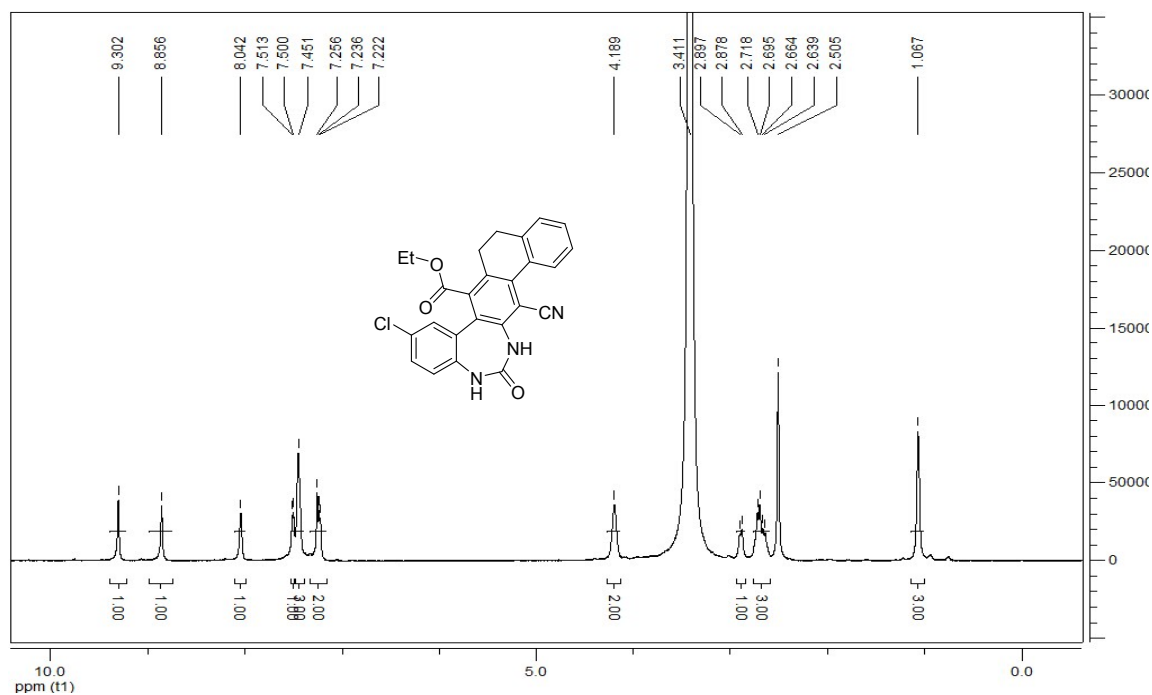


Ethyl 1-benzyl-5-fluoro-4'-cyano-3'-imino-2-oxo-3',9',10',10a'-tetrahydro-1'H-

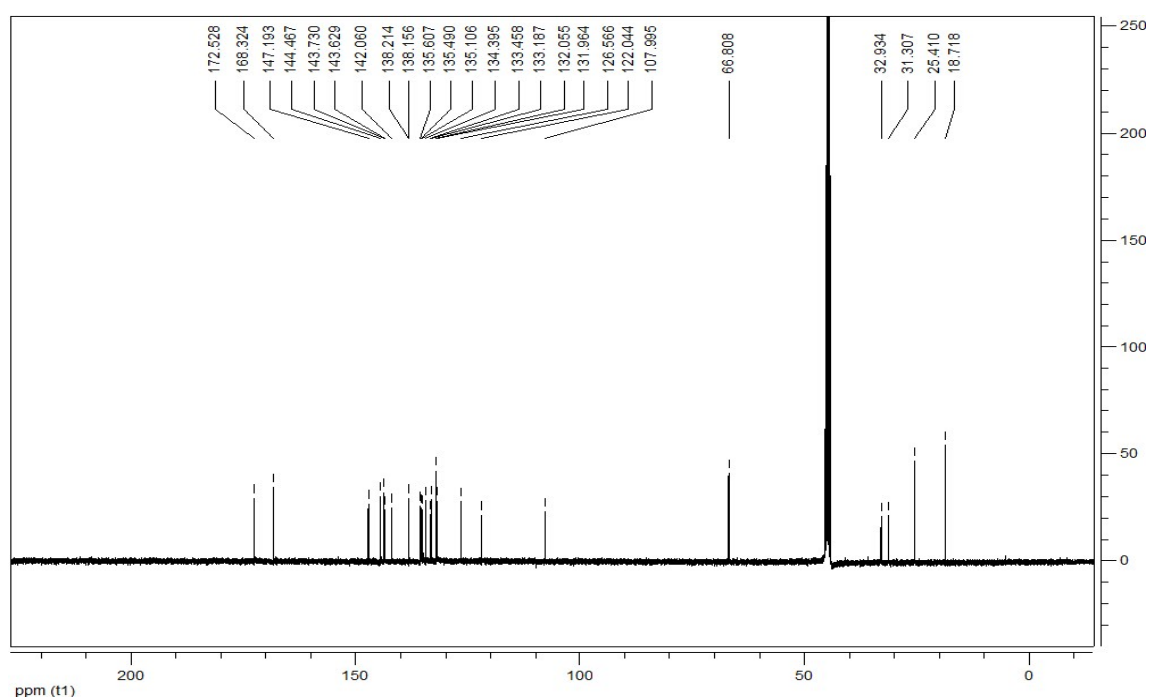
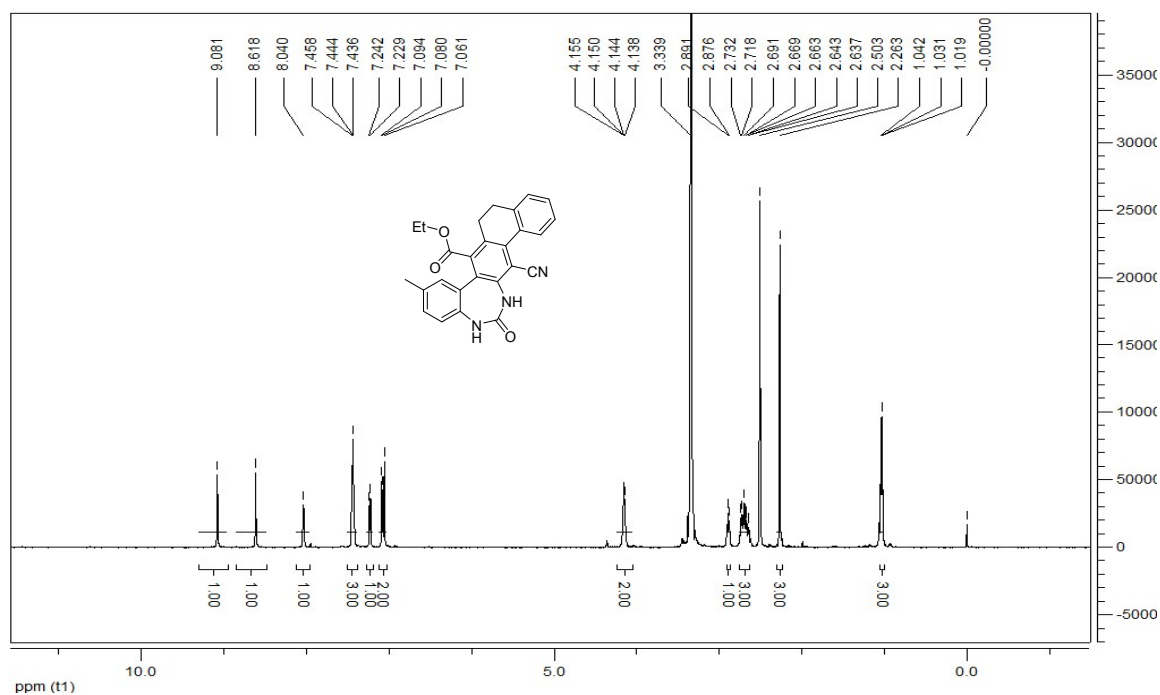
spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (2d): yellow solid, 72%, m.p. 180~182 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ *cis*-isomer: 10.14 (s, 1H, NH), 8.23 (d, *J* = 8.4Hz, 1H, ArH), 7.58~7.54 (m, 1H, ArH), 7.43~7.40 (m, 1H, ArH), 7.37 (t, *J* = 7.8Hz, 1H, ArH), 7.22~7.16 (m, 1H, ArH), 7.12~7.10 (m, 1H, ArH), 6.91 (td, *J*₁ = 8.4Hz, *J*₂ = 1.8Hz, 1H, ArH), 3.90~3.81 (m, 2H, CH), 3.74~3.60 (m, 2H, CH), 3.54 (td, *J*₁ = 10.2Hz, *J*₂ = 4.8Hz, 1H, CH), 3.40 (d, *J* = 10.8Hz, 1H, CH), 3.05~3.01 (m, 2H, CH), 2.25~2.22 (m, 1H, CH), 1.95~1.88 (m, 1H, CH), 1.60~1.53 (m, 2H, CH), 1.39~1.33 (m, 2H, CH), 0.94~0.89 (m, 6H, CH₃); *trans*-isomer: 10.20 (s, 1H, NH), 8.29 (d, *J* = 7.8Hz, 1H, ArH), 7.15~7.14 (m, 1H, ArH), 3.45~3.41 (m, 1H, CH), 3.34~3.31 (m, 1H, CH), 2.18~2.15 (m, 1H, CH). Ratio of *cis/trans* isomers = 1.6:1. ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 174.4, 173.4, 169.6, 169.3, 166.2, 166.0, 162.8, 162.3, 159.7, 159.4, 157.3, 157.0, 141.6, 141.0, 140.2, 139.9, 133.2, 132.8, 131.1, 129.9 (*J* = 12.6Hz), 129.7, 129.6, 129.4, 129.1, 128.4 (*J* = 12.3Hz), 126.7, 126.6, 116.9, 116.2, 115.8, 115.7, 115.4, 112.4, 112.3, 112.1, 111.0 (*J* = 11.8Hz), 110.3 (*J* = 11.5Hz), 107.7, 104.7, 61.4, 61.3, 58.4, 57.0, 50.3, 49.5, 36.8, 36.6, 30.3, 29.8, 29.5, 29.4, 28.4, 20.1, 19.9, 14.2, 14.1, 14.0; IR (KBr) ν: 3250, 3075, 2958, 2934, 2871, 2216, 1730, 1606, 1577, 1556, 1489, 1450, 1344, 1273, 1190, 1159, 1094, 1055, 1011, 952, 888, 866, 832, 776 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₈FN₃NaO₃ ([M+Na]⁺): 508.2007. Found: 508.2008.



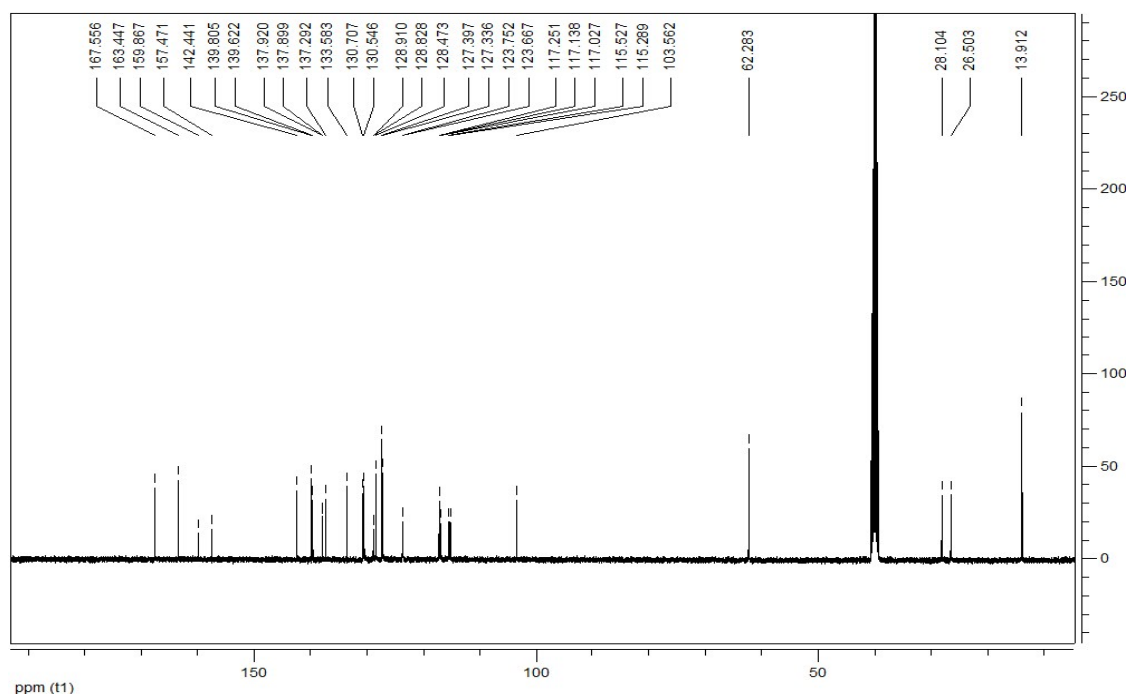
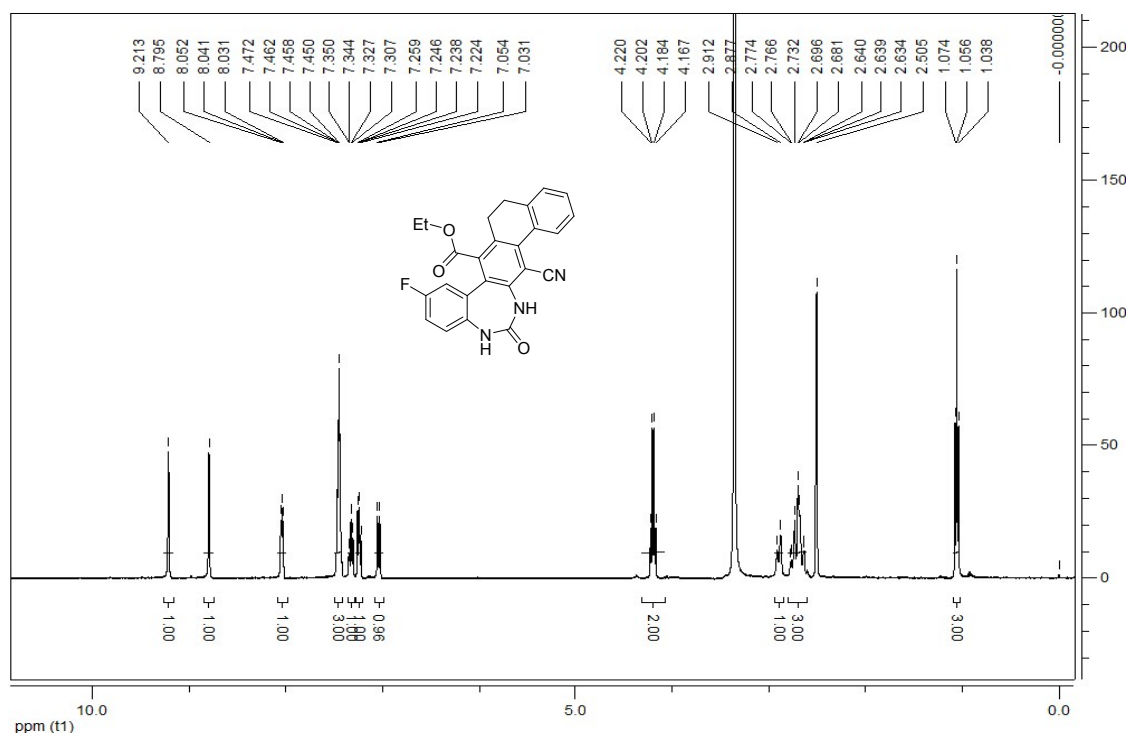
Ethyl 1-benzyl-5-chloro-4'-cyano-3'-imino-2-oxo-9',10'-dihydro-3'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (3a): yellow solid, 65%, 0.288g, m.p. 156~158°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 9.30 (s, 1H, NH), 8.84 (s, 1H, NH), 8.04 (s, 1H, ArH), 7.51 (d, *J* = 7.2 Hz, 1H, ArH), 7.45 (brs, 3H, ArH), 7.26~7.23 (m, 2H, ArH), 4.19 (s, 2H, CH₂), 2.90~2.88 (m, 1H, CH), 2.73~2.64 (m, 3H, CH), 1.09 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 167.5, 163.0, 142.3, 140.4, 139.8, 139.6, 137.2, 133.6, 130.6, 130.5, 129.9, 128.9, 128.6, 128.4, 128.3, 127.3, 123.5, 117.1, 103.6, 62.3, 28.1, 28.0, 26.5, 14.0; IR (KBr) ν: 3374, 3238, 3137, 2940, 2222, 1703, 1603, 1574, 1550, 1494, 1469, 1441, 1403, 1365, 1279, 1250, 1197, 1160, 1103, 1050, 1008, 946, 927, 895, 834, 772 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₅H₁₈ClN₃NaO₃ ([M+Na]⁺): 466.0929. Found: 466.0930.



Ethyl 1-benzyl-4'-cyano-3'-imino-5-methyl-2-oxo-9',10'-dihydro-3'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (3b): yellow solid, 66%, 0.279g, m.p. 202~204°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 9.08 (s, 1H, NH), 8.62 (s, 1H, NH), 8.04 (brs, 1H, ArH), 7.46~7.44 (m, 3H, ArH), 7.23 (d, *J* = 7.8Hz, 1H, ArH), 7.09~7.06 (m, 2H, ArH), 4.16~4.14 (m, 2H, CH₂), 2.89~2.88 (m, 1H, CH), 2.73~2.64 (m, 3H, CH), 2.26 (s, 3H, CH₃), 1.03 (t, *J* = 6.6Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 172.5, 168.3, 147.2, 144.5, 143.7, 143.6, 142.1, 138.2, 135.6, 135.5, 135.1, 134.4, 133.5, 133.2, 132.1, 132.0, 126.6, 122.0, 108.0, 66.8, 32.9, 31.3, 25.4, 18.7; IR (KBr) ν: 3243, 3133, 2940, 2222, 1693, 1585, 1551, 1506, 1467, 1441, 1409, 1368, 1336, 1285, 1252, 1196, 1101, 1051, 1009, 954, 895, 829, 775 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₁N₃NaO₃ ([M+Na]⁺): 446.1475. Found: 446.1476.

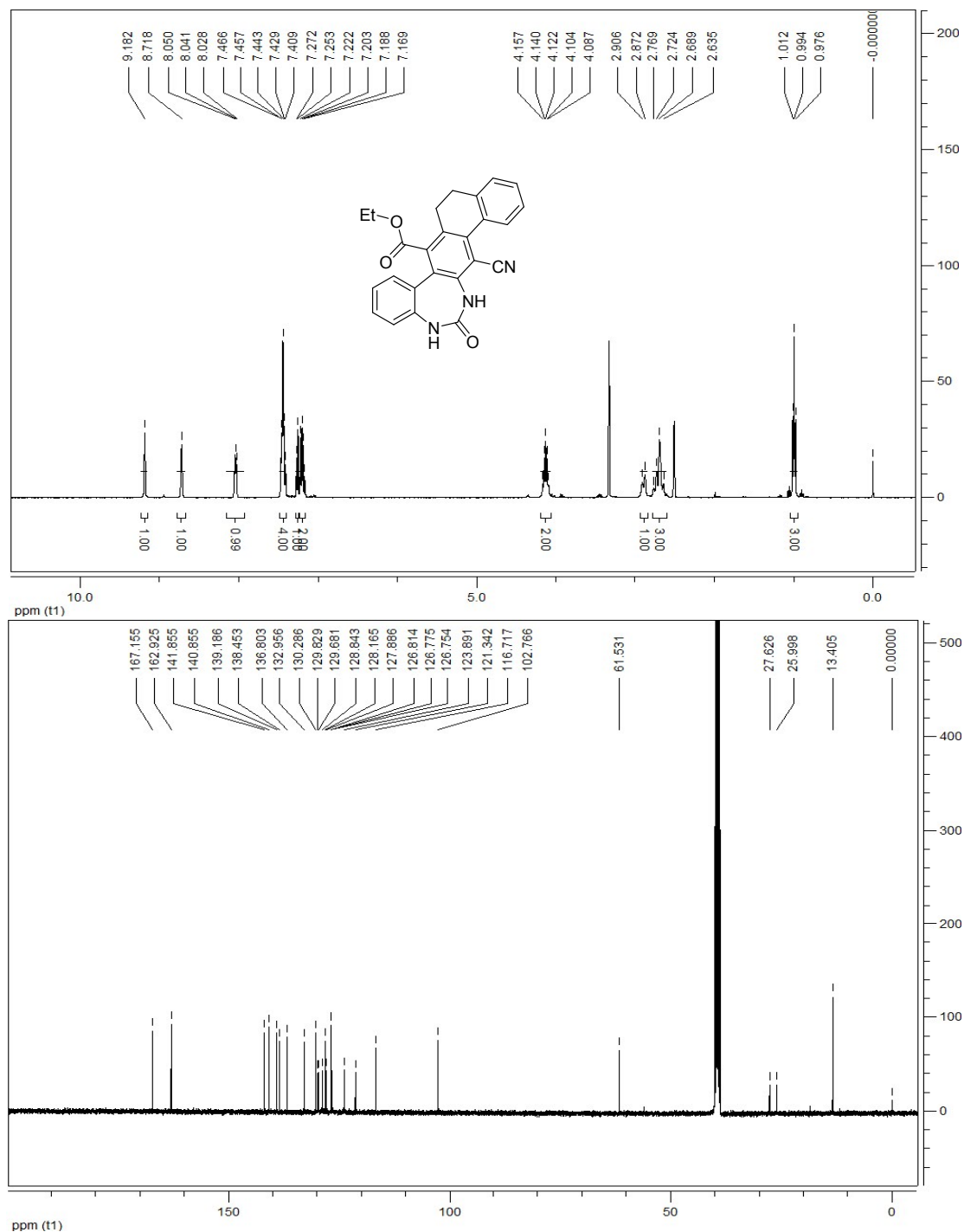


Ethyl 1-benzyl-4'-cyano-5-fluoro-3'-imino-2-oxo-9',10'-dihydro-3'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (3c): yellow solid, 63%, 0.269g, m.p. 168~170°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.21 (s, 1H, NH), 8.80 (s, 1H, NH), 8.05~8.03 (m, 1H, ArH), 7.47~7.45 (m, 3H, ArH), 7.35~7.31 (m, 1H, ArH), 7.26~7.22 (m, 1H, ArH), 7.05~7.03 (m, 1H, ArH), 4.19 (q, *J* = 7.2Hz, 2H, CH₂), 2.91~2.88 (m, 1H, CH), 2.77~2.63 (m, 3H, CH), 1.06 (t, *J* = 7.2Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 167.6, 163.4, 159.9, 157.5, 142.4, 139.8, 139.6, 137.9, 137.3, 133.6, 130.7, 130.5, 128.9, 128.8, 128.5, 127.4, 127.3, 123.8, 123.7, 117.3, 117.1, 117.0, 115.5, 115.3, 103.6, 62.3, 28.1, 26.5, 13.9; IR (KBr) ν: 3271, 3162, 2952, 2853, 2206, 1718, 1631, 1593, 1574, 1508, 1461, 1444, 1408, 1374, 1316, 1282, 1225, 1167, 1146, 1104, 972, 901, 870, 831, 778 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₅H₁₈FN₃NaO₃ ([M+Na]⁺): 450.1224. Found: 450.1224.

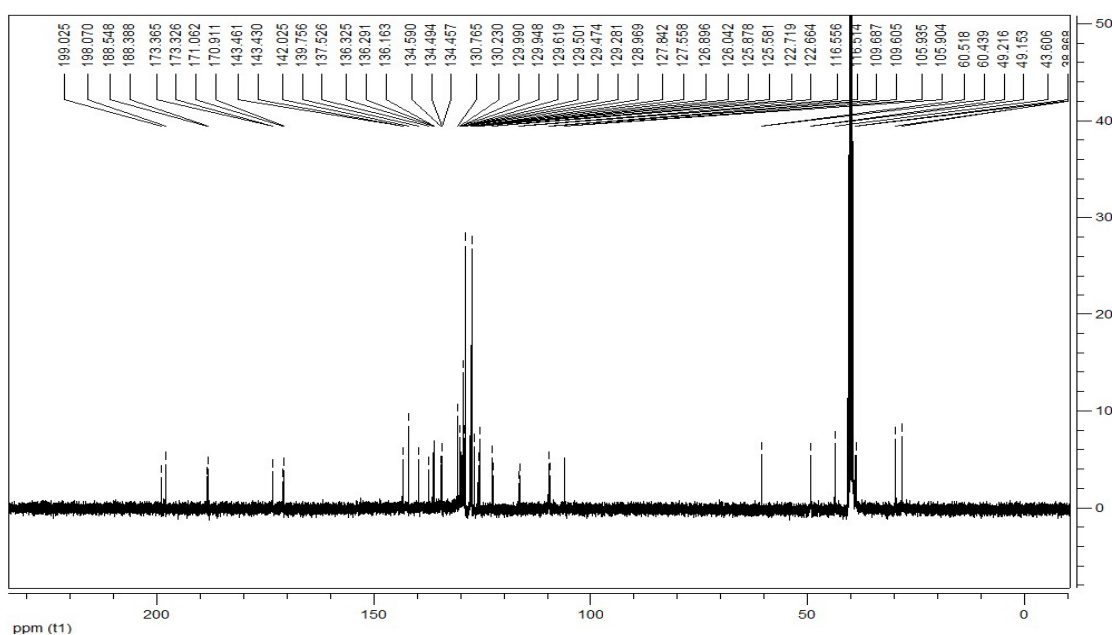
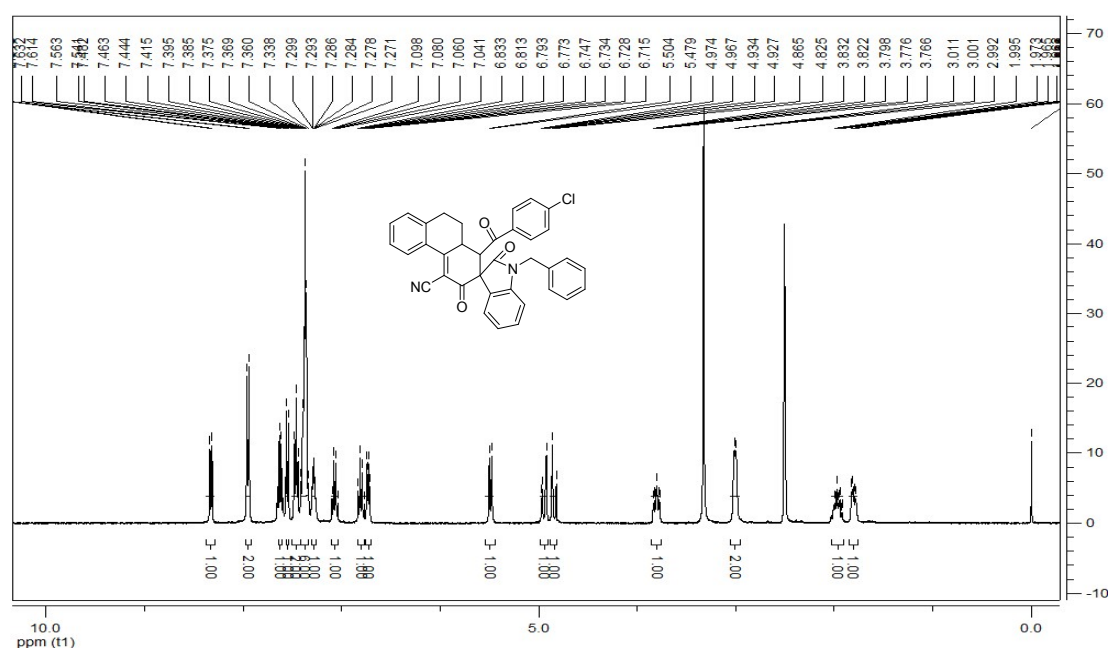


Ethyl

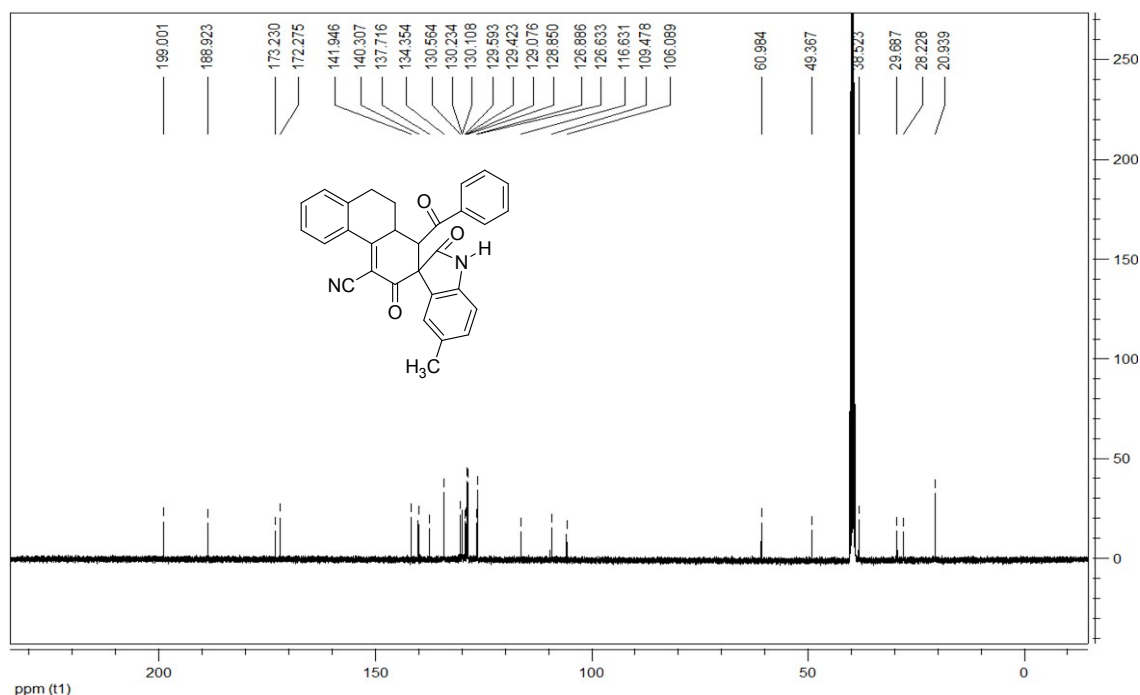
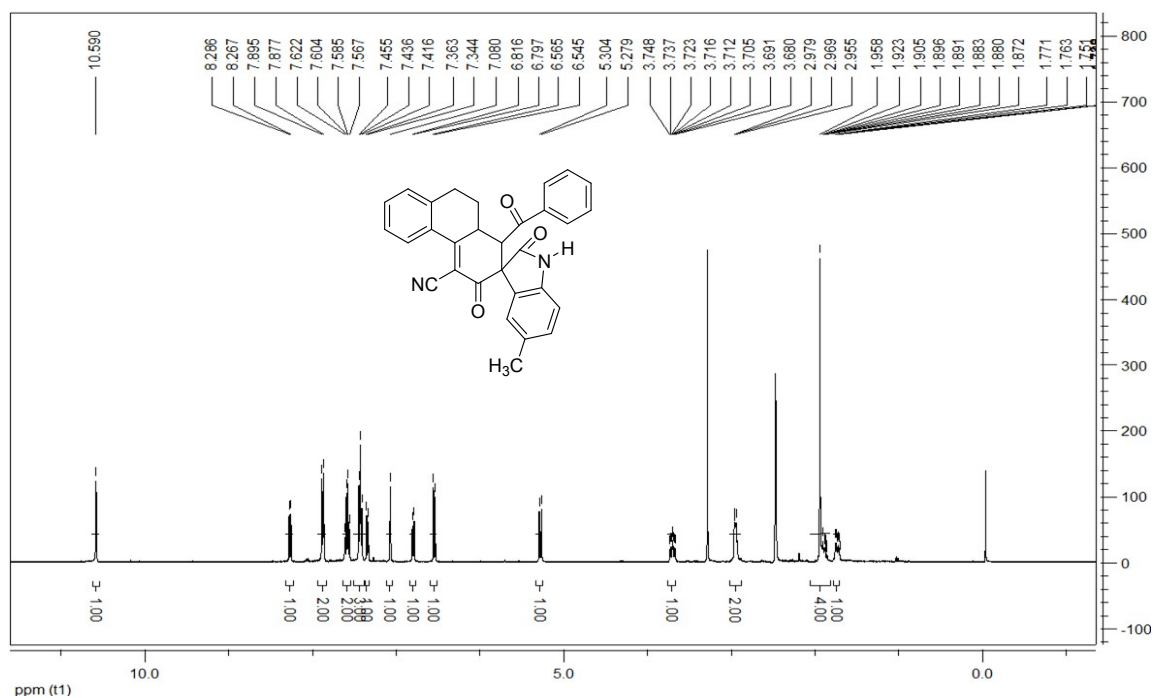
1-benzyl-4'-cyano-3'-imino-2-oxo-9',10'-dihydro-3'H-spiro[indoline-3,2'-phenanthrene]-1'-carboxylate (3d): yellow solid, 64%, 0.262g, m.p. 218~220°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.18 (s, 1H, NH), 8.72 (s, 1H, NH), 8.05~8.03 (m, 1H, ArH), 7.47~7.41 (m, 4H, ArH), 7.27~7.25 (m, 1H, ArH), 7.22~7.17 (m, 2H, ArH), 4.16~4.09 (m, 2H, CH₂), 2.91~2.87 (m, 1H, CH), 2.77~2.64 (m, 3H, CH), 0.99 (t, *J* = 7.2Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 167.2, 162.9, 141.9, 140.9, 139.2, 138.5, 136.8, 133.0, 130.3, 129.8, 129.7, 128.8, 128.2, 127.9, 126.8, 126.7, 123.9, 121.3, 116.7, 102.8, 61.5, 27.6, 26.0, 13.4; IR (KBr) ν: 3303, 3241, 2957, 2219, 1709, 1639, 1583, 1548, 1501, 1439, 1397, 1354, 1298, 1256, 1232, 1201, 1161, 1050, 813, 754 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₅H₁₉N₃NaO₃ ([M+Na]⁺): 432.1319. Found: 432.1322.



1-benzyl-1'-(4-chlorobenzoyl)-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4a): white solid, 70%, m.p. 218~220°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.32 (d, *J* = 8.0Hz, 1H, ArH), 7.95 (d, *J* = 8.4Hz, 2H, ArH), 7.63~7.61 (m, 1H, ArH), 7.55 (d, *J* = 8.8Hz, 1H, ArH), 7.48~7.44 (m, 2H, ArH), 7.42~7.34 (m, 6H, ArH), 7.30~7.27 (m, 1H, ArH), 7.07 (q, *J* = 7.6Hz, 1H, ArH), 6.83~6.77 (m, 1H, ArH), 6.75~6.72 (m, 1H, ArH), 5.49 (d, *J* = 10.0Hz, 1H, CH), 4.97~4.93 (m, 1H, CH), 4.85 (d, *J* = 16.0Hz, 1H, CH), 3.83~3.77 (m, 1H, CH), 3.01~2.99 (m, 2H, CH), 2.00~1.92 (m, 1H, CH), 1.82~1.78 (m, 1H, CH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 199.0, 198.1, 188.5, 188.4, 173.4, 173.3, 171.1, 170.9, 143.5, 143.4, 142.0, 139.8, 137.5, 136.3, 136.2, 134.6, 134.5, 130.8, 130.2, 130.0, 129.9, 129.6, 129.5, 129.3, 129.0, 127.8, 127.6, 126.9, 126.0, 125.9, 125.6, 122.7, 116.6, 116.5, 109.7, 109.6, 105.9, 60.5, 60.4, 49.2, 43.6, 38.9, 38.8, 29.7, 28.2; IR (KBr) ν: 3063, 2926, 2225, 1712, 1679, 1611, 1574, 1491, 1467, 1454, 1403, 1353, 1310, 1280, 1250, 1227, 1177, 1094, 1002, 895, 862, 806, 752 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₅ClN₂NaO₃ ([M+Na]⁺): 591.1446. Found: 591.1443.

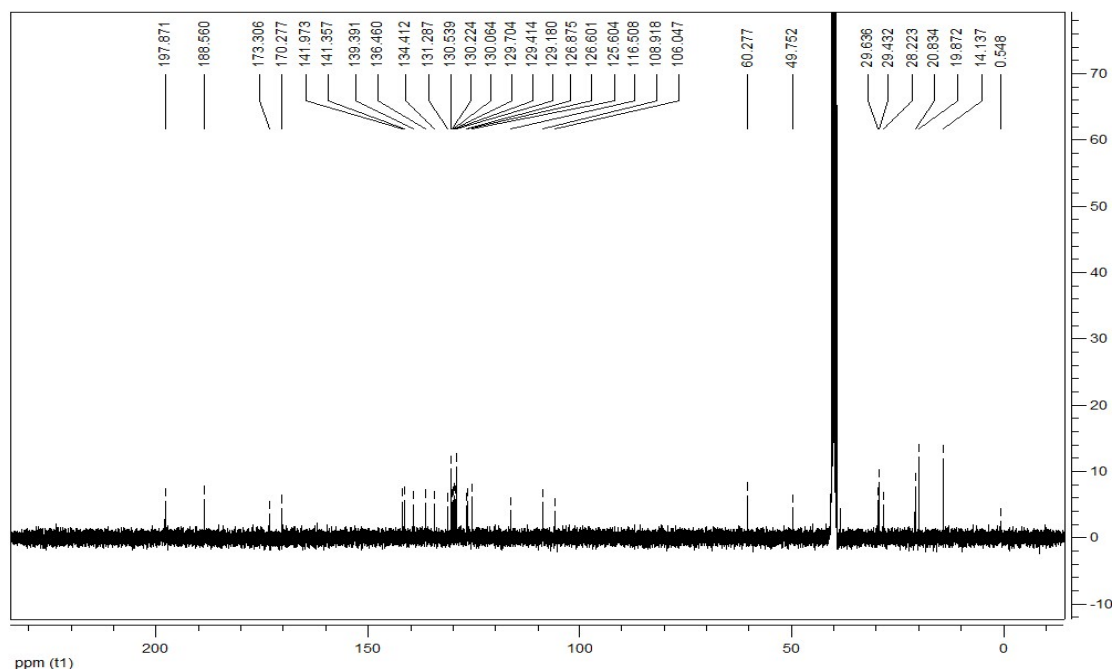
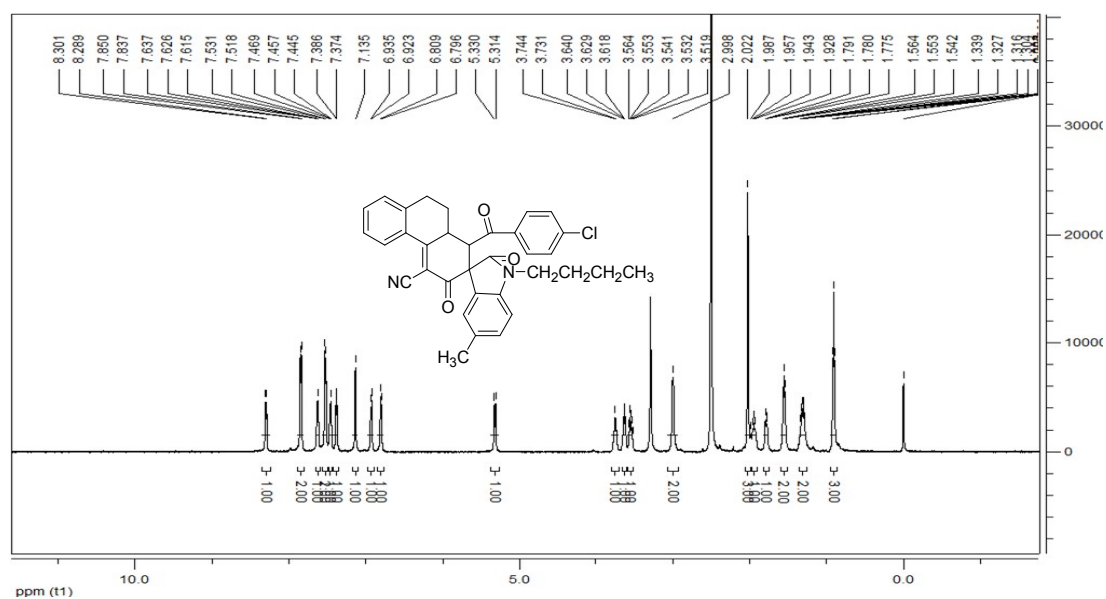


1'-benzoyl-5-methyl-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4b): white solid, 63%, m.p. 243-245°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 10.59 (s, 1H, NH), 8.28 (d, *J* = 7.6Hz, 1H, ArH), 7.89 (d, *J* = 7.2Hz, 2H, ArH), 7.62-7.57 (m, 2H, ArH), 7.46-7.42 (m, 3H, ArH), 7.36-7.34 (m, 1H, ArH), 7.08 (s, 1H, ArH), 6.81 (d, *J* = 7.6Hz, 1H, ArH), 6.56 (d, *J* = 8.0Hz, 1H, ArH), 5.29 (d, *J* = 10.0Hz, 1H, CH), 3.75-3.68 (m, 1H, CH), 2.98-2.96 (m, 2H, CH), 1.96-1.87 (m, 1H, CH), 1.77-1.72 (m, 1H, CH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 199.0, 188.9, 173.2, 172.3, 141.9, 140.3, 137.7, 134.4, 130.6, 130.2, 130.1, 129.6, 129.4, 129.1, 128.8, 126.9, 126.6, 116.6, 109.5, 106.1, 61.0, 49.4, 38.5, 29.7, 28.2, 20.9; IR (KBr) ν: 3630, 3036, 2219, 1716, 1680, 1651, 1550, 1493, 1444, 1355, 1312, 1277, 1215, 1163, 1057, 1002, 866, 810, 774 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₂N₂NaO₃ ([M+Na]⁺): 481.1523. Found: 481.1518.

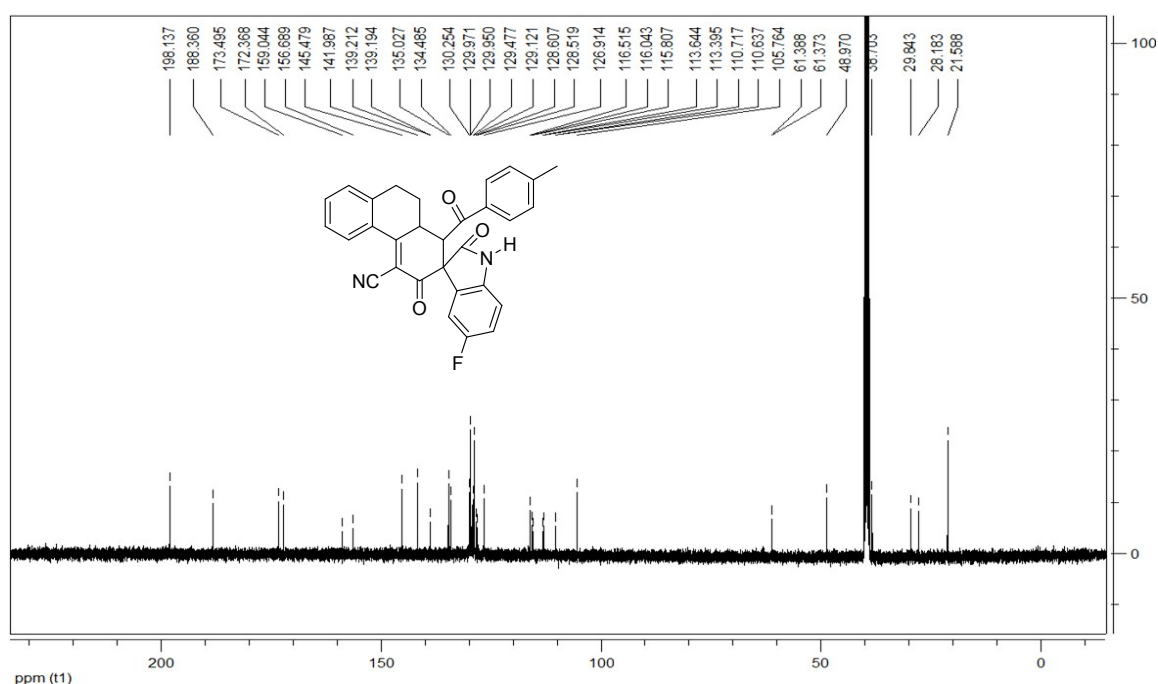
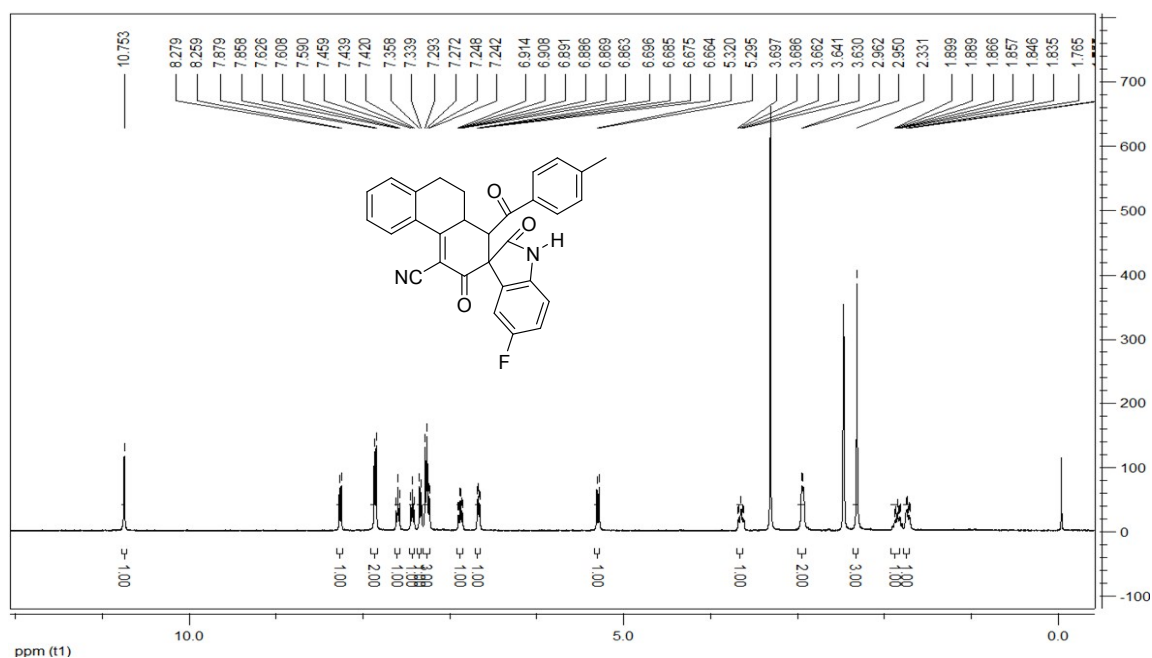


1-Butyl-1'-(4-chlorobenzoyl)-5-methyl-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-

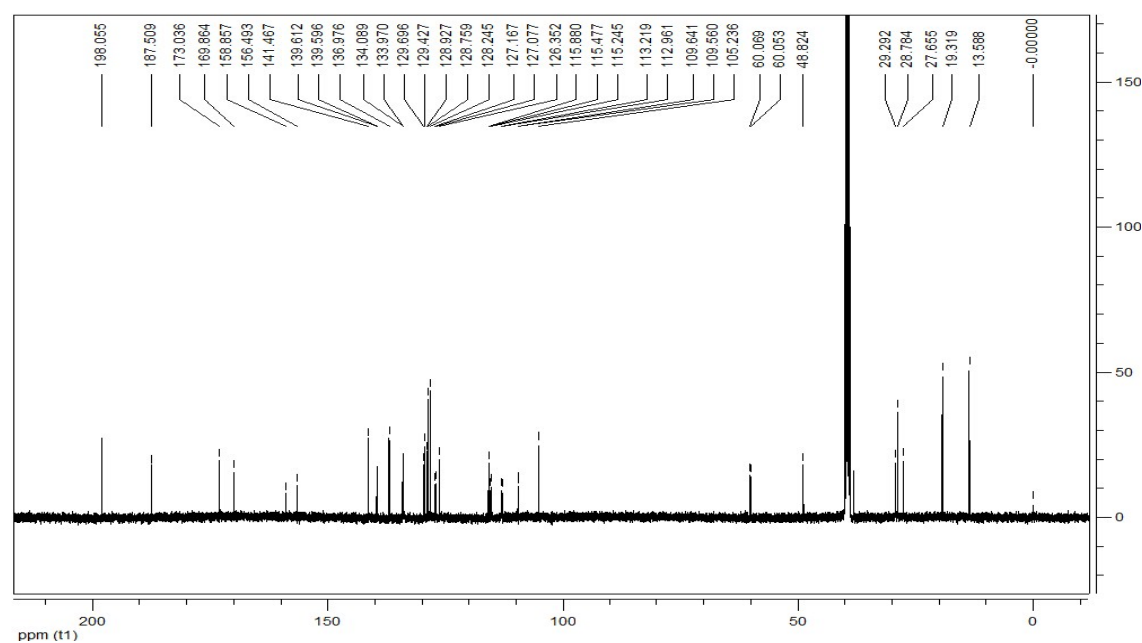
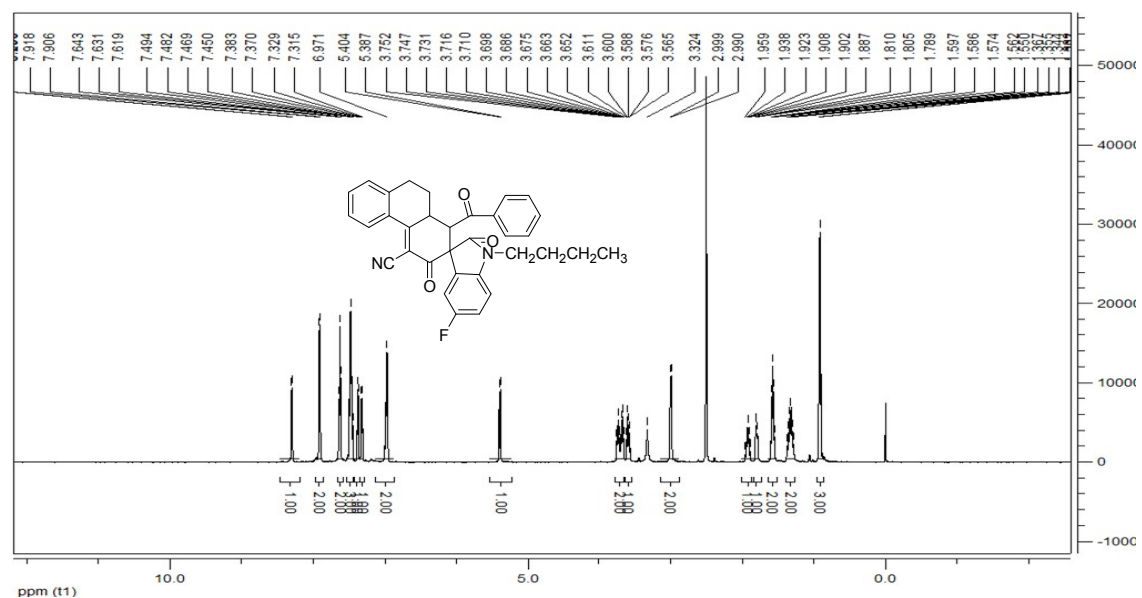
spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4c): yellow solid, 77%, m.p. 201~203 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 8.30 (d, *J* = 7.2Hz, 1H, ArH), 7.84 (d, *J* = 7.8Hz, 2H, ArH), 7.64~7.62 (m, 1H, ArH), 7.52 (d, *J* = 7.8Hz, 2H, ArH), 7.47~7.44 (m, 1H, ArH), 7.38 (d, *J* = 7.2Hz, 1H, ArH), 7.14 (s, 1H, ArH), 6.93 (d, *J* = 7.2Hz, 1H, ArH), 6.80 (d, *J* = 7.8Hz, 1H, ArH), 5.32 (d, *J* = 15.6Hz, 1H, CH), 3.74~3.73 (m, 1H, CH), 3.64~3.62 (m, 1H, CH), 3.56~3.52 (m, 1H, CH), 3.00 (brs, 2H, CH), 2.02 (s, 3H, CH₃), 1.96~1.93 (m, 1H, CH), 1.79~1.78 (m, 1H, CH), 1.56~1.54 (m, 2H, CH), 1.34~1.28 (m, 2H, CH), 0.91 (t, *J* = 6.6Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 197.9, 188.6, 173.3, 170.3, 142.0, 141.4, 139.4, 136.5, 134.4, 131.3, 130.5, 130.2, 130.1, 129.7, 129.4, 129.2, 126.9, 126.6, 125.6, 116.5, 108.9, 106.0, 60.3, 49.8, 29.6, 29.4, 28.2, 20.8, 19.9, 14.1; IR (KBr) ν: 2934, 2871, 2222, 1715, 1681, 1576, 1496, 1454, 1402, 1346, 1312, 1280, 1224, 1197, 1170, 1095, 998, 918, 844, 814, 775 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₂₉ClN₂NaO₃ ([M+Na]⁺): 571.1759. Found: 571.1751.



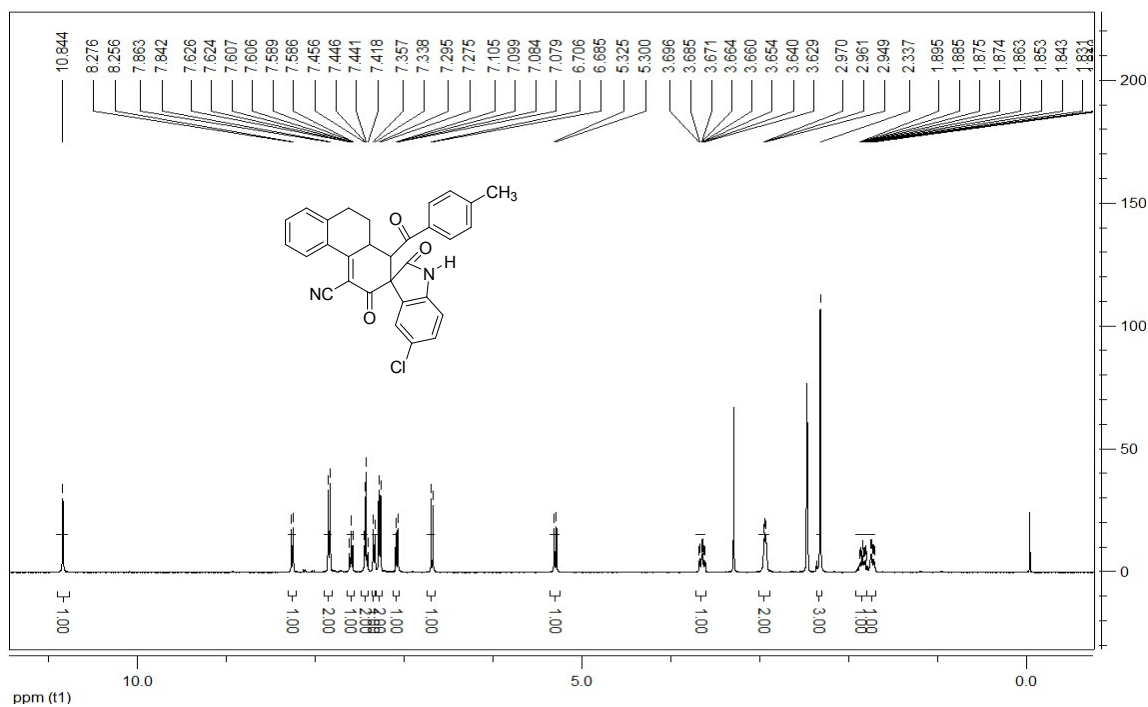
5-fluoro-1'-(4-methylbenzoyl)-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4d): white solid, 62%, m.p. 234-236°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 10.75 (s, 1H, NH), 8.27 (d, *J* = 8.0Hz, 1H, ArH), 7.87 (d, *J* = 8.4Hz, 2H, ArH), 7.61 (t, *J* = 7.2Hz, 1H, ArH), 7.44 (t, *J* = 8.0Hz, 1H, ArH), 7.35 (d, *J* = 7.6Hz, 1H, ArH), 7.29-7.24 (m, 3H, ArH), 6.89 (td, *J*₁ = 8.8Hz, *J*₂ = 2.4Hz, 1H, ArH), 6.70-6.66 (m, 1H, ArH), 5.31 (d, *J* = 10.0Hz, 1H, CH), 3.70-3.63 (m, 1H, CH), 2.96-2.95 (m, 2H, CH), 2.33 (s, 3H, CH₃), 1.90-1.84 (m, 1H, CH), 1.76-1.72 (m, 1H, CH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 198.1, 188.4, 173.5, 172.4, 157.9 (d, *J* = 235.5Hz), 145.5, 142.0, 139.2, 139.1, 135.0, 134.5, 130.3, 130.0, 129.5, 129.1, 128.6, 128.5, 126.9, 116.5, 115.9 (d, *J* = 23.6Hz), 113.5 (d, *J* = 24.9Hz), 110.7 (d, *J* = 8.0Hz), 105.8, 61.4, 61.3, 48.8, 38.7, 29.8, 28.2, 21.6; IR (KBr) ν: 3657, 3078, 2222, 1717, 1678, 1605, 1561, 1488, 1358, 1311, 1279, 1191, 1124, 1052, 1005, 818, 770 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₁FN₂NaO₃ ([M+Na]⁺): 499.1428. Found: 499.1431.

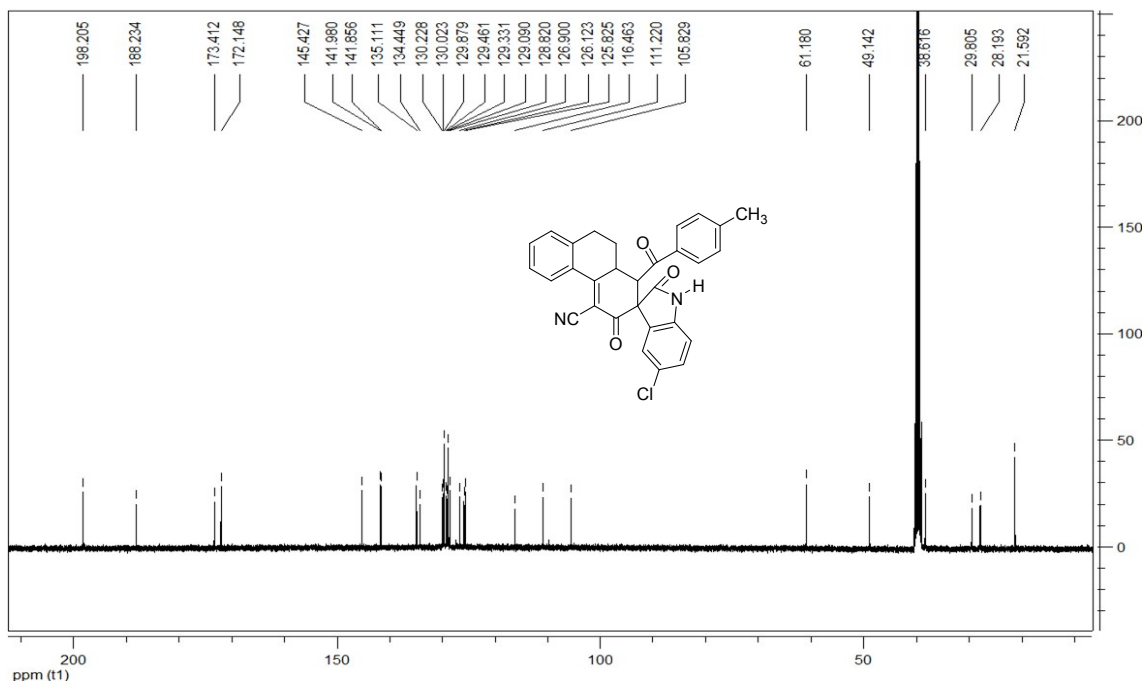


1'-benzoyl-1-butyl-5-fluoro-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4e): yellow solid, 79%, m.p. 208~210°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 8.30 (d, *J* = 7.8Hz, 1H, ArH), 7.91 (d, *J* = 7.2Hz, 2H, ArH), 7.63 (t, *J* = 7.2Hz, 2H, ArH), 7.49~7.45 (m, 3H, ArH), 7.38 (d, *J* = 7.8Hz, 1H, ArH), 7.32 (d, *J* = 8.4Hz, 1H, ArH), 6.99~6.97 (m, 2H, ArH), 5.40 (d, *J* = 10.2Hz, 1H, CH), 3.75~3.65 (m, 2H, CH), 3.61~3.56 (m, 1H, CH), 3.00 (d, *J* = 5.4Hz, 2H, CH), 1.96~1.89 (m, 1H, CH), 1.81~1.80 (m, 1H, CH), 1.60~1.55 (m, 2H, CH), 1.37~1.29 (m, 2H, CH), 0.92 (t, *J* = 7.2Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 198.1, 187.5, 173.0, 169.9, 158.9, 156.5, 141.5, 139.6 (*J* = 1.6Hz), 137.0, 134.1 (*J* = 12.1Hz), 129.7, 129.4, 128.9, 128.8, 128.2, 127.1 (*J* = 9.0Hz), 126.4, 115.9, 115.4 (*J* = 23.2Hz), 113.2 (*J* = 25.8Hz), 109.6 (*J* = 8.1Hz), 105.2, 60.1, 48.8, 29.3, 28.8, 27.7, 19.3, 13.6; IR (KBr) ν: 3067, 2960, 2933, 2874, 2221, 1706, 1680, 1616, 1593, 1570, 1552, 1493, 1450, 1425, 1347, 1307, 1275, 1252, 1223, 1186, 1136, 1074, 1045, 999, 956, 934, 888, 856, 818, 792, 771 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₂₇FN₂NaO₃ ([M+Na]⁺): 541.1898. Found: 541.1888.

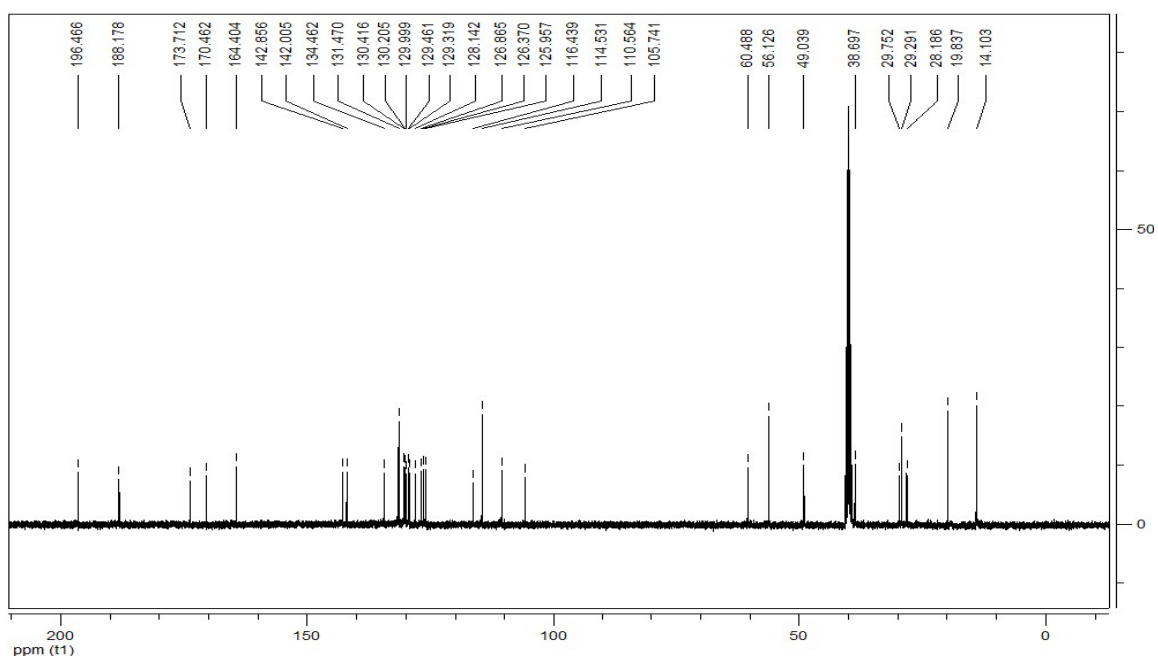
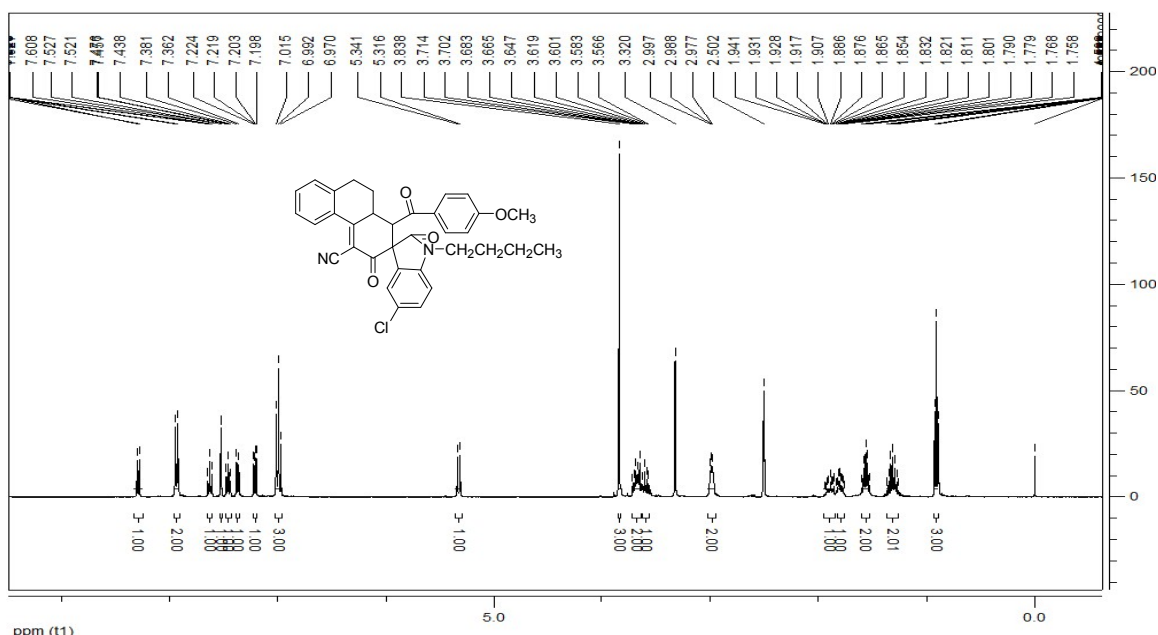


5-chloro-1'-(4-methylbenzoyl)-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4f): white solid, 70%, 0.344g, m.p. 238-240°C; ^1H NMR (400 MHz, DMSO- d_6) δ : 10.84 (s, 1H, NH), 8.27 (d, $J = 8.0\text{Hz}$, 1H, ArH), 7.85 (d, $J = 8.4\text{Hz}$, 2H, ArH), 7.61 (td, $J_1 = 7.6\text{Hz}$, $J_2 = 0.8\text{Hz}$, 1H, ArH), 7.46-7.42 (m, 2H, ArH), 7.35 (d, $J = 7.6\text{Hz}$, 1H, ArH), 7.28 (d, $J = 8.0\text{Hz}$, 2H, ArH), 7.09 (dd, $J_1 = 8.0\text{Hz}$, $J_2 = 2.0\text{Hz}$, 1H, ArH), 6.70 (d, $J = 8.4\text{Hz}$, 1H, ArH), 5.31 (d, $J = 10.0\text{Hz}$, 1H, CH), 3.70-3.63 (m, 1H, CH), 2.97-2.95 (m, 2H, CH), 2.34 (s, 3H, CH₃), 1.90-1.81 (m, 1H, CH), 1.77-1.73 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO- d_6) δ : 198.2, 188.2, 173.4, 172.1, 145.4, 142.0, 141.9, 135.1, 134.4, 130.2, 130.0, 129.9, 129.5, 129.3, 129.1, 128.8, 126.9, 126.1, 125.8, 116.5, 111.2, 105.8, 61.2, 49.1, 38.6, 29.8, 28.2, 21.6; IR (KBr) ν : 3640, 3187, 2221, 1718, 1678, 1609, 1563, 179, 1357, 1312, 1278, 1190, 1052, 1002, 818, 772 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 515.1133. Found: 515.1130.





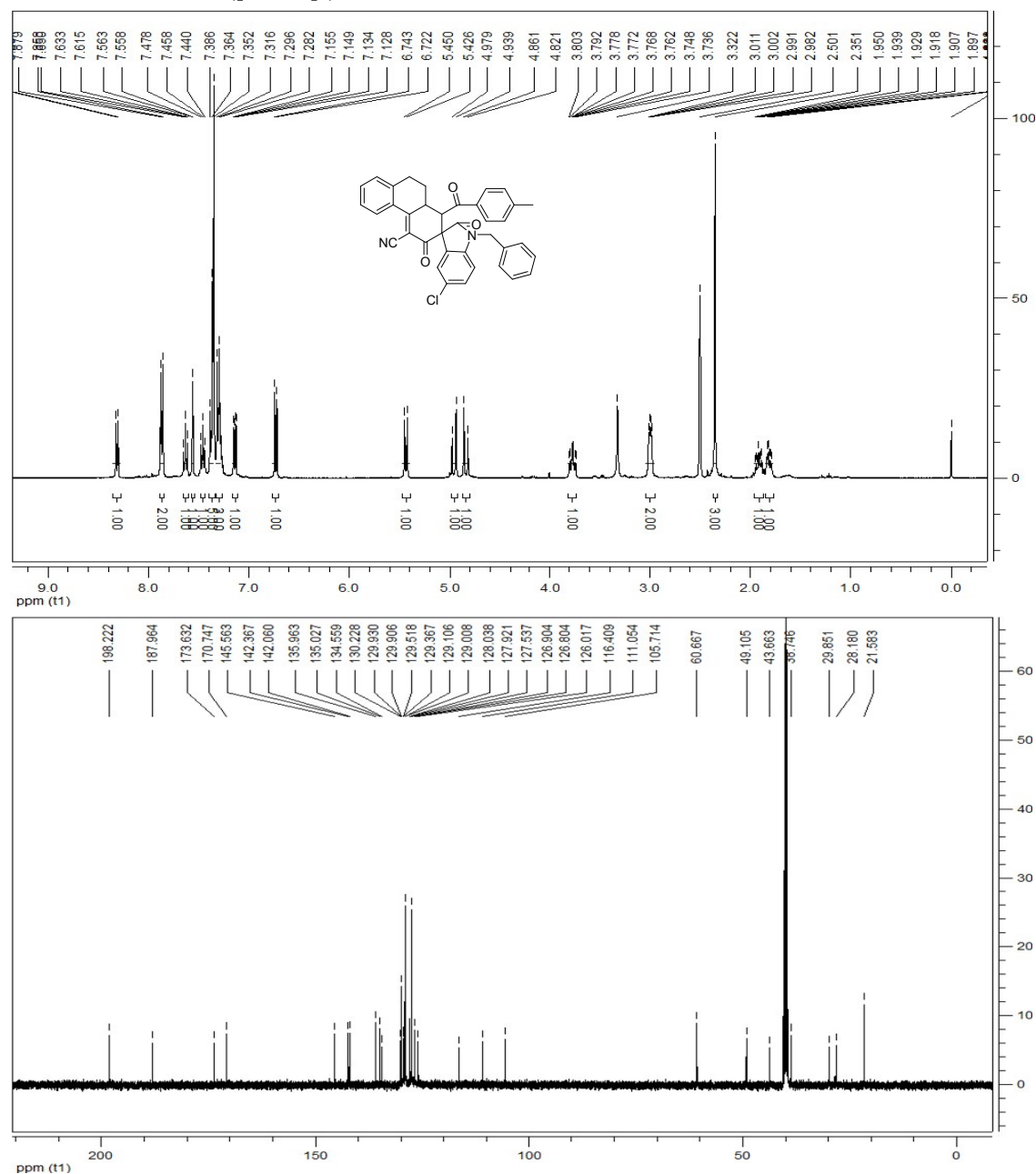
1-Butyl-5-fluoro-2,3'-dioxo-1'-(4-methoxybenzoyl)-3',9',10',10a'-tetrahydro-1'H-spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4g): white solid, 76%, m.p. 206–208 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.29 (d, *J* = 7.6 Hz, 1H, ArH), 7.93 (d, *J* = 8.8 Hz, 2H, ArH), 7.63 (t, *J* = 7.6 Hz, 1H, ArH), 7.52 (d, *J* = 2.4 Hz, 1H, ArH), 7.46 (d, *J* = 7.6 Hz, 1H, ArH), 7.37 (d, *J* = 7.6 Hz, 1H, ArH), 7.21 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.02–6.97 (m, 3H, ArH), 5.33 (d, *J* = 10.0 Hz, 1H, CH), 3.84 (s, 3H, OCH₃), 3.71–3.65 (m, 2H, CH), 3.62–3.57 (m, 1H, CH), 3.00–2.98 (m, 2H, CH), 1.94–1.85 (m, 1H, CH), 1.83–1.76 (m, 1H, CH), 1.60–1.53 (m, 2H, CH), 1.36–1.26 (m, 2H, CH), 0.91 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 196.5, 188.2, 173.7, 170.5, 164.4, 142.9, 142.0, 134.5, 131.5, 130.4, 130.2, 130.0, 129.5, 129.3, 128.1, 12.9, 126.4, 126.0, 116.4, 114.5, 110.6, 105.7, 60.5, 56.1, 49.0, 38.7, 29.8, 29.3, 28.2, 19.8, 14.1; IR (KBr) ν: 3071, 2935, 2870, 2224, 1713, 1684, 1596, 1572, 1552, 1512, 1486, 1457, 1427, 1345, 1311, 1273, 1231, 1177, 1128, 1075, 1028, 942, 904, 867, 842, 815, 777 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₂₉ClN₂NaO₄ ([M+Na]⁺): 587.1708. Found: 587.1706.



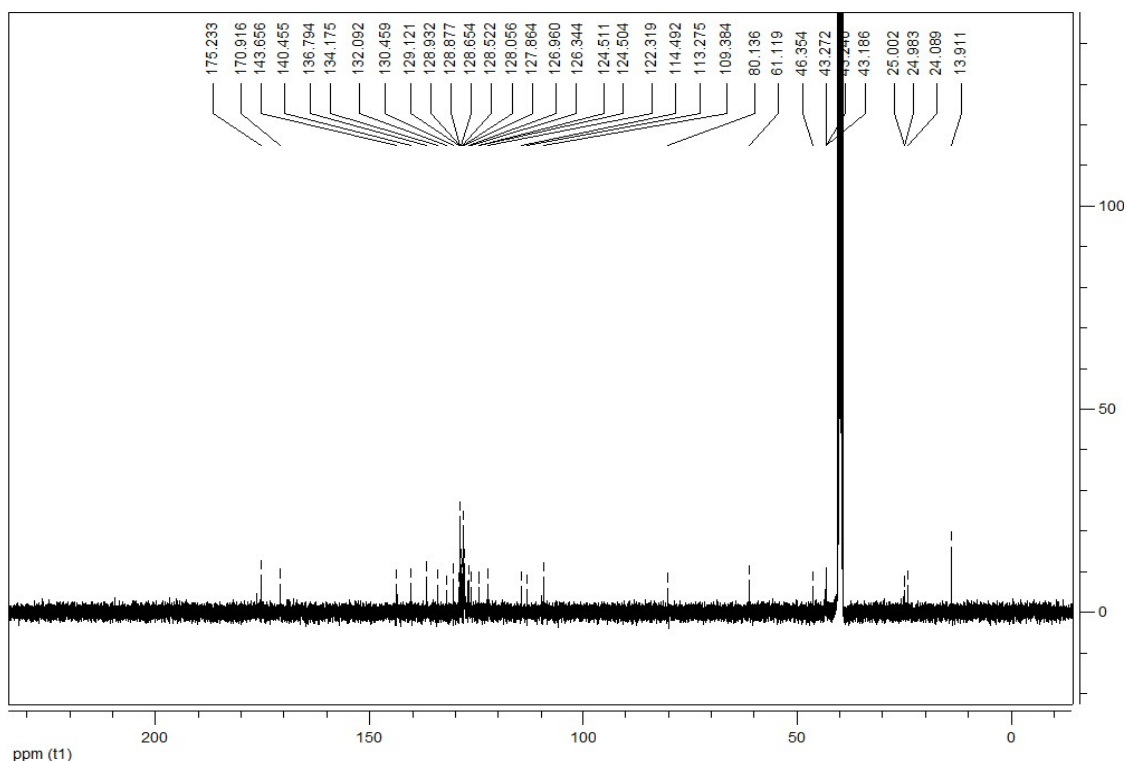
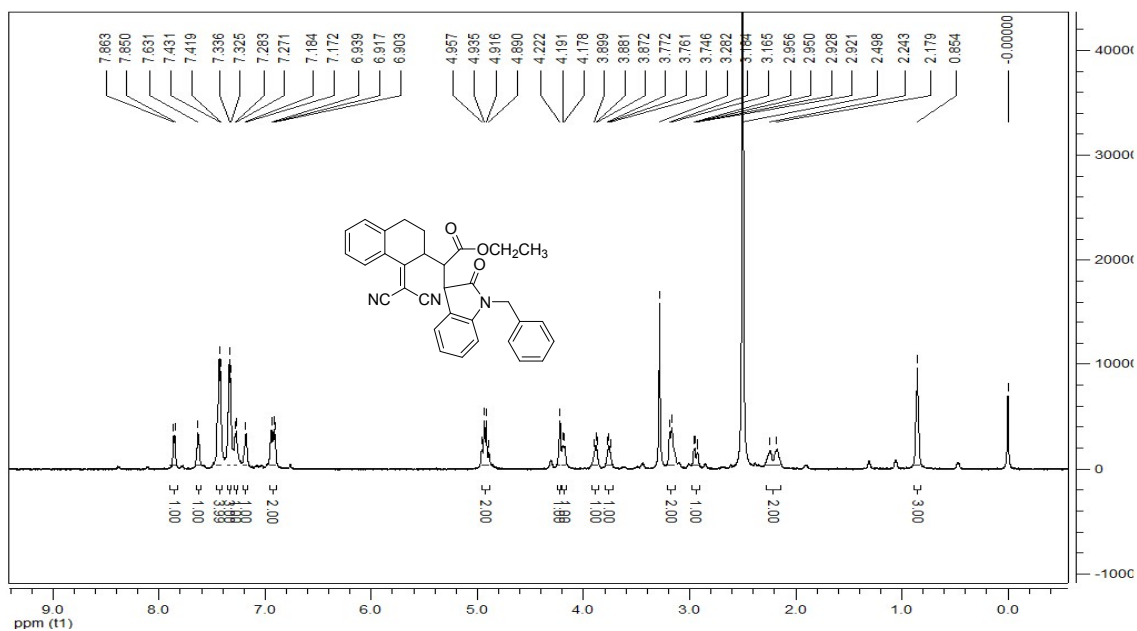
1-benzyl-5-chloro-1'-(4-methylbenzoyl)-2,3'-dioxo-3',9',10',10a'-tetrahydro-1'H-

spiro[indoline-3,2'-phenanthrene]-4'-carbonitrile (4h): white solid, 81%, m.p. 222~224 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.31 (d, *J* = 7.6 Hz, 1H, ArH), 7.87 (d, *J* = 8.4 Hz, 2H, ArH), 7.63 (t, *J* = 7.2 Hz, 1H, ArH), 7.56 (d, *J* = 2.0 Hz, 1H, ArH), 7.46 (t, *J* = 7.2 Hz, 1H, ArH), 7.39~7.35 (m, 5H, ArH), 7.32~7.28 (m, 3H, ArH), 7.14 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 5.44 (d, *J* = 9.6 Hz, 1H, CH), 4.96 (d, *J* = 16.0 Hz, 1H, CH), 4.84 (d, *J* = 16.0 Hz, 1H, CH), 3.80~3.74 (m, 1H, CH), 3.01~2.98 (m, 2H, CH), 2.35 (s, 3H, CH₃), 1.95~1.89 (m, 1H, CH), 1.83~1.79 (m, 1H, CH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 198.2, 188.0, 173.6, 170.7, 145.6, 142.4, 142.1, 136.0, 135.0, 134.6, 130.2, 129.9, 129.5, 129.4, 129.1, 129.0, 128.0, 127.9, 127.5, 126.9, 126.8, 126.0, 116.4, 111.0, 105.7, 60.7, 49.1, 43.7, 38.7, 29.9, 28.2, 21.6; IR (KBr) ν: 3067, 2921, 2225, 1718, 1678, 1606, 1574, 1559, 1486, 1453, 1429, 1344, 1312, 1279, 1232, 1174, 1129, 1078, 1032, 1010, 952, 869, 823, 765 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd.

for C₃₇H₂₇ClN₂NaO₃ ([M+Na]⁺): 605.1602. Found: 605.1598.

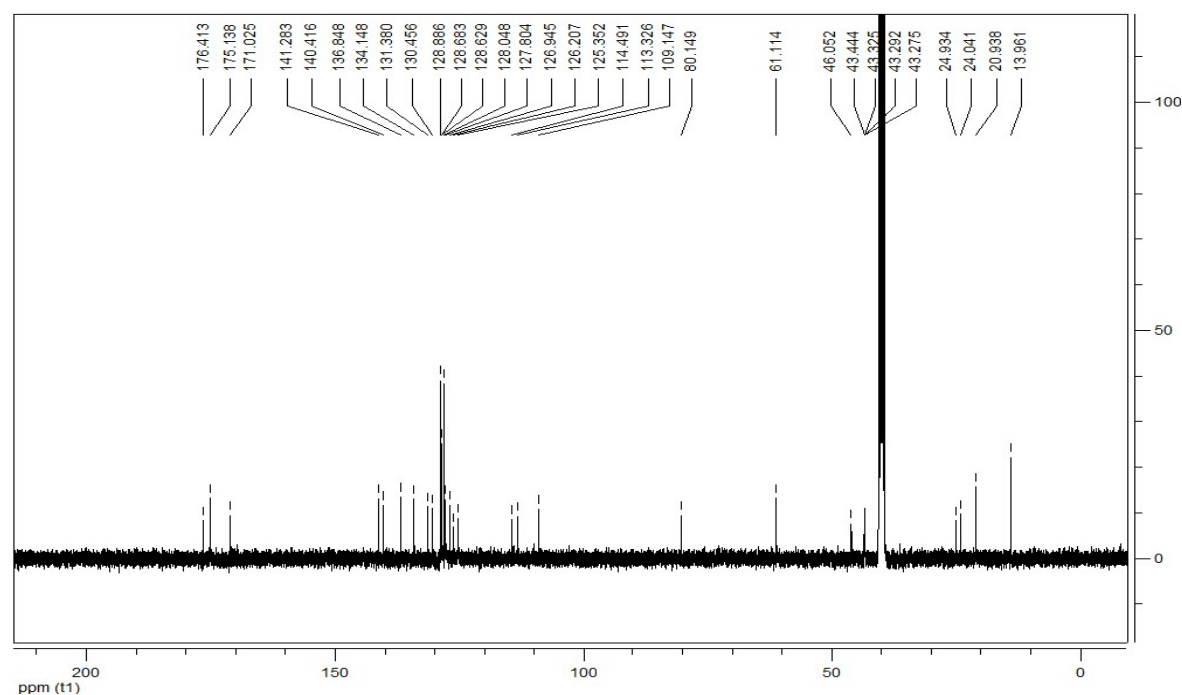
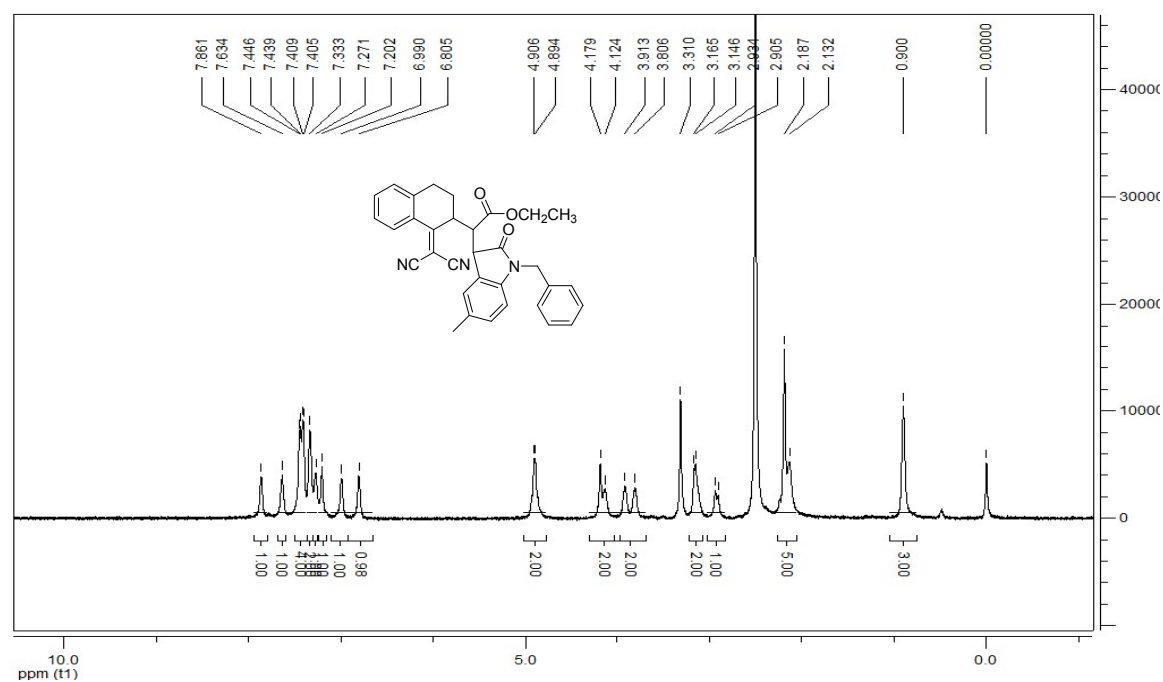


Ethyl 2-(1-benzyl-2-oxoindolin-3-yl)-2-(1-(dicyanomethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (B1): yellow solid, 37%, m.p. 158~160°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 7.86 (d, *J* = 7.8 Hz, 1H, ArH), 7.63 (brs, 1H, ArH), 7.43~7.42 (m, 4H, ArH), 7.34~7.32 (m, 3H, ArH), 7.28~7.27 (m, 1H, ArH), 7.18~7.17 (m, 1H, ArH), 6.94~6.90 (m, 2H, ArH), 4.96~4.89 (m, 2H, CH₂), 4.22 (s, 1H, CH), 4.19~4.18 (m, 1H, CH), 3.90~3.87 (m, 1H, CH), 3.77~3.75 (m, 1H, CH), 3.18~3.16 (m, 2H, CH), 2.96~2.92 (m, 1H, CH), 2.24~2.18 (m, 2H, CH), 0.85 (brs, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 175.2, 170.9, 143.7, 140.5, 136.8, 134.2, 132.1, 130.5, 129.1, 128.9, 128.7, 128.5, 128.1, 27.9, 127.0, 126.3, 124.5, 122.3, 114.5, 113.3, 109.4, 80.1, 61.1, 46.4, 43.3, 43.2, 25.0, 24.1, 13.9; IR (KBr) ν: 2957, 2220, 1739, 1699, 1583, 1558, 1502, 1439, 1387, 1355, 1298, 1266, 1212, 1151, 1050, 817, 774 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₃NaO₃ ([M+Na]⁺): 524.1945. Found: 524.1944.



Ethyl 2-(1-benzyl-5-methyl-2-oxindolin-3-yl)-2-(1-(dicyanomethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (B2): yellow solid, 44%, 0.227g, m.p. 161~153 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 7.86 (s, 1H, ArH), 7.63 (s, 1H, ArH), 7.45~7.40 (m, 4H, ArH), 7.33 (brs, 2H, ArH), 7.27 (s, 1H, ArH), 7.20 (s, 1H, ArH), 6.99 (brs, 1H, ArH), 6.80 (brs, 1H, ArH), 4.91~4.89 (m, 2H, CH₂), 4.18~4.12 (m, 2H, CH), 3.91~3.81 (m, 2H, CH), 3.16~3.15 (m, 2H, CH), 2.93~2.90 (m, 1H, CH), 2.19~2.13 (m, 5H, CH₃, CH), 0.90 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 176.4, 175.1, 171.0, 141.3, 140.4, 136.8, 134.1, 131.4, 130.5, 128.9, 128.7, 128.6, 128.0, 127.8, 126.9, 125.4, 114.5, 113.3, 109.1, 80.1, 61.1, 46.1, 43.4, 43.3, 24.9, 24.0, 20.9, 14.0; IR (KBr) ν: 2978, 2933, 2225, 1734, 1701, 1618, 1599, 1570, 1557, 1493, 1455, 1365, 1340, 1266, 1184, 1121, 1035, 940, 873, 828, 772 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₂₉N₃NaO₃

$[M+Na]^+$: 538.2101. Found: 538.2092.



Ethyl 2-(1-benzyl-5-fluoro-2-oxindolin-3-yl)-2-(1-(dicyanomethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (B3): white solid, 50%, m.p. 202-204°C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ : 7.88 (d, $J = 7.2\text{Hz}$, 1H, ArH), 7.64 (t, $J = 7.2\text{Hz}$, 1H, ArH), 7.45-7.39 (m, 5H, ArH), 7.35-7.33 (m, 2H, ArH), 7.29-7.26 (m, 1H, ArH), 7.03 (t, $J = 9.0\text{Hz}$, 1H, ArH), 6.89-6.87 (m, 1H, ArH), 4.96-4.89 (m, 2H, CH), 4.28-4.23 (m, 2H, CH), 3.91-3.88 (m, 1H, CH), 3.77-3.74 (m, 1H, CH), 3.27 (td, $J_1 = 3.6\text{Hz}$, $J_2 = 7.2\text{Hz}$, 1H, CH), 3.23-3.17 (m, 1H, CH), 2.96-2.92 (m, 1H, CH), 2.36-2.29 (m, 1H, CH), 2.24-2.19 (m, 1H, CH), 0.85 (t, $J = 6.6\text{Hz}$, 3H, CH); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 175.93, 174.61, 170.39, 157.37, 140.23, 139.49, 136.21, 133.65, 130.12, 128.48, 128.18, 127.62, 127.51, 127.43, 127.24, 126.45, 114.20, 114.09, 112.87, 112.41, 109.49, 79.70,

60.67, 60.53, 45.76, 42.98, 42.88, 27.70, 24.76, 23.69, 13.45, 13.24; IR (KBr) ν : 33260, 3070, 2941, 2221, 1728, 1656, 1621, 1493, 1453, 1340, 1261, 1093, 1025, 933, 876, 829, 772, 727 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{26}\text{FN}_3\text{NaO}_3$ ([M+Na]⁺): 542.1850. Found: 542.1867.

