

**Selective construction of polycyclic spirooxindoles via Cu(OTf)₂/HOTf catalyzed
domino reaction of *o*-arylalkynyl acetophenones and 3-phenacylideneoxindoles**

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General Information:

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). The developed chromatogram was analyzed by UV lamp (254 nm). ^1H NMR and ^{13}C NMR spectra were obtained on a Variance 400M. Chemical shifts (δ) are expressed in parts per million and are internally referenced. Infrared spectra were taken on a Perkin Elmer Spectrum 100 FTIR and are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are reported as m/z (relative intensity). X-ray crystallographic data were collected using SMART APEX II X-ray diffractometer. Melting points were measured on a Yanaco Micro Melting Point Apparatus and are uncorrected.

Experiment section:

General Procedure for the Preparation of **1a-1e**. To a solution of 12 mL THF were added $\text{Pd}(\text{PPh}_3)\text{Cl}_2$ (3 mol%), CuI (5 mol%), 2-bromoacetophenone (1.99 g, 10 mmol) phenylacetylene (1.53 g, 15 mmol) and Et_3N (20 mL) in a 100 mL Schleck tube with a magnetic stirrer under N_2 atmosphere. The mixture was heat under reflux or RT overnight. After removal of the solvent under reduce pressure, purification was performed by flash column chromatography on silica gel with light petroleum/ethyl acetate (gradient mixture ratio 50:1) as eluent to afford **1a**.

General Procedure for the Preparation of **1f**. To a solution of 10 mL THF were added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.21 g, 3 mol%), CuI (0.095 g, 5 mol %), 2-iodoacetophenone (2.46 g, 10 mmol), phenylacetylene (2.20 g, 15 mmol) and Et_3N (20 mL) in a 100 mL Schleck tube with a magnetic stirrer under N_2 atmosphere. The mixture was stirred at room temperature overnight. After removal of the solvent under reduce pressure, purification was performed by flash column chromatography on silica gel with light petroleum/ethyl acetate (gradient mixture ratio 50:1) as eluent to afford **1f**.

General Procedure for the Preparation of **3** and **4**:

To a solution of 10 mL DCE were added 3-phenacylideneoxindole (0.5 mmol), *o*-(alkynyl)arylketone (0.5 mmol), HOTf (20 mol%, 0.015 g) and $\text{Cu}(\text{OTf})_2$ (5 mol%, 0.07 g) in a 50 mL flask with a magnetic stirrer. The reaction mixture was stirred under reflux for 15 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with light petroleum/ethyl acetate (gradient mixture ratio is 20:1) or

light petroleum/ CH_2Cl_2 (gradient mixture ratio is 2:1) as eluent to afford **3-4**.

Crystallographic Data for 3j, 3k, 3m, 4r, 4v and F1

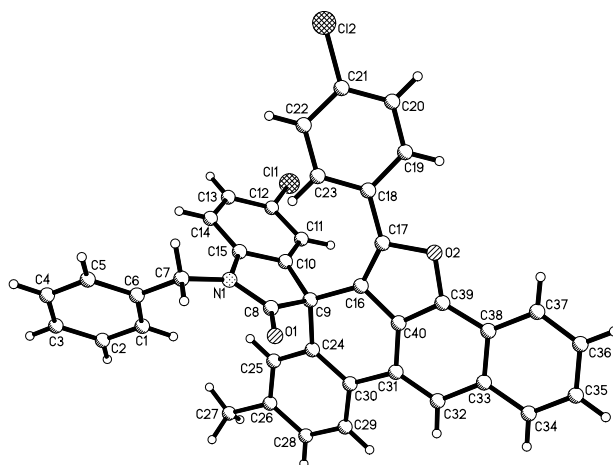


Fig. S1 molecular structure of compound **3j**

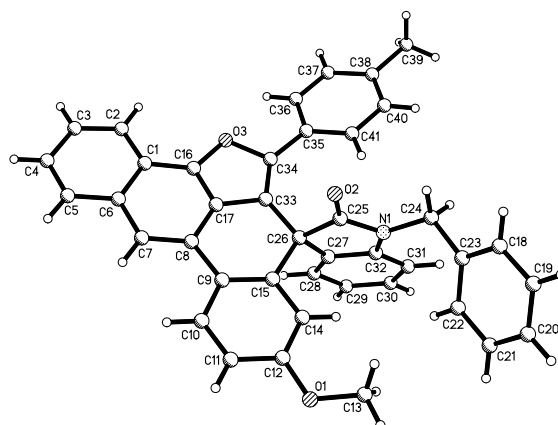


Fig. S2 molecular structure of compound **3k**

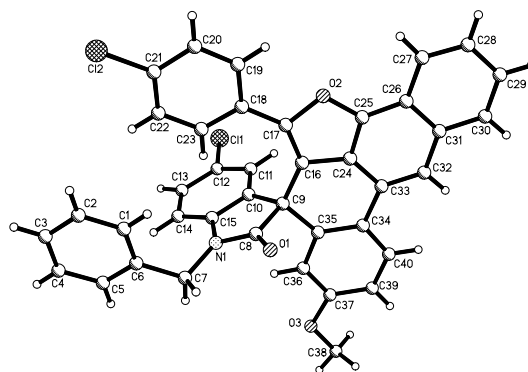


Fig. S3 molecular structure of compound **3m**

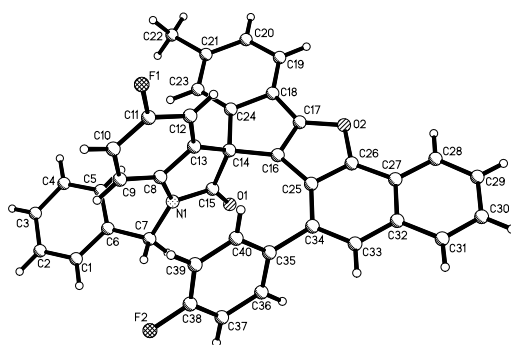


Fig. S4 molecular structure of compound **4r**

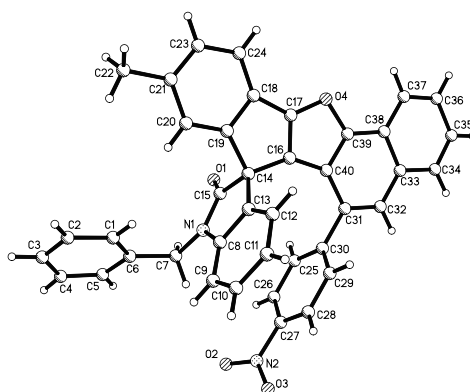


Fig. S5 molecular structure of compound **4v**

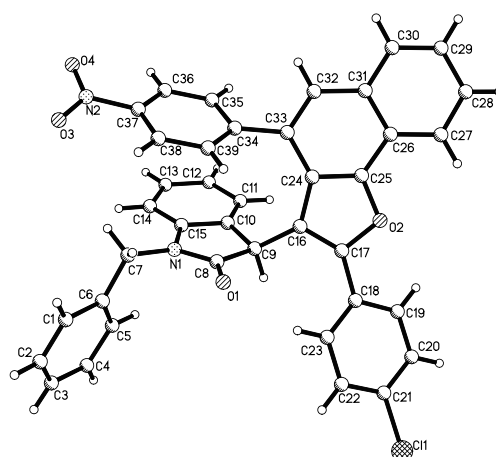
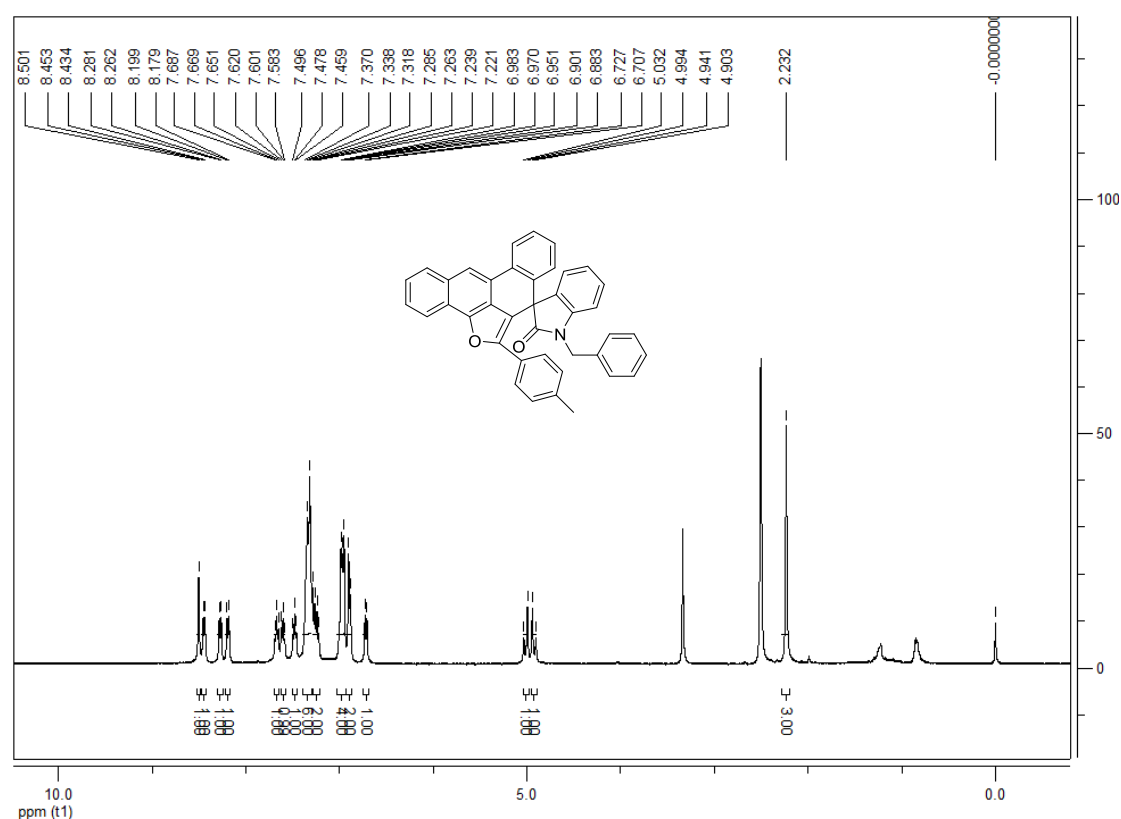
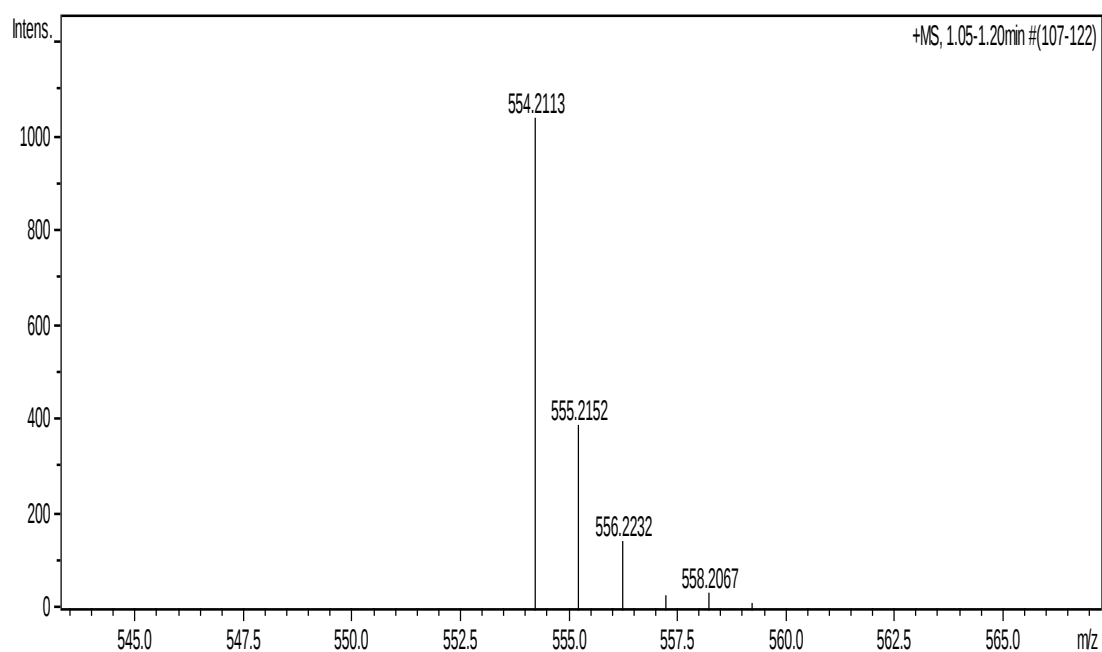
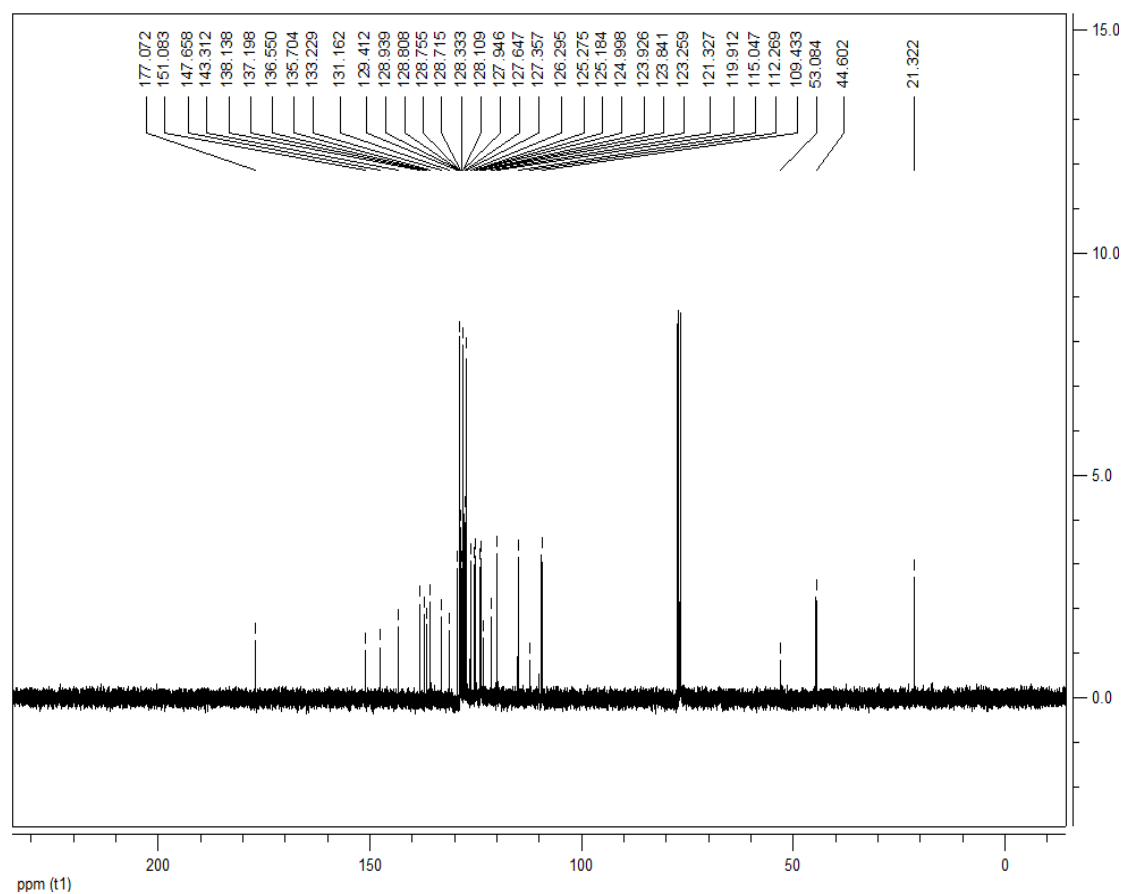


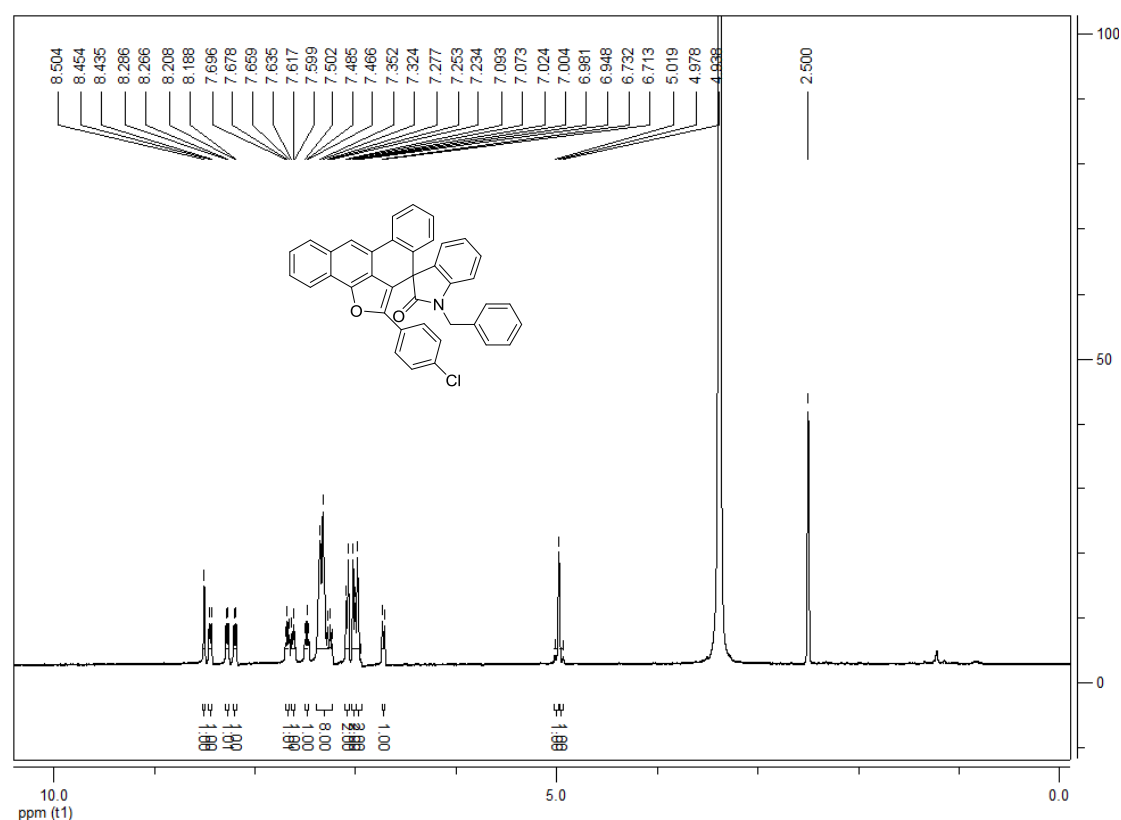
Fig. S6 molecular structure of intermediate **F1**

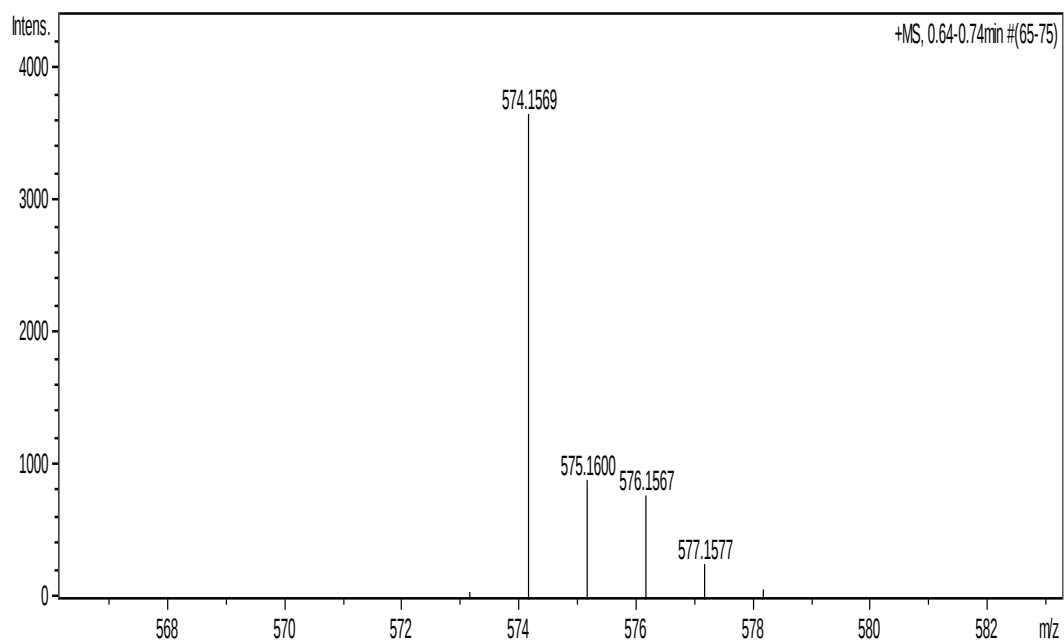
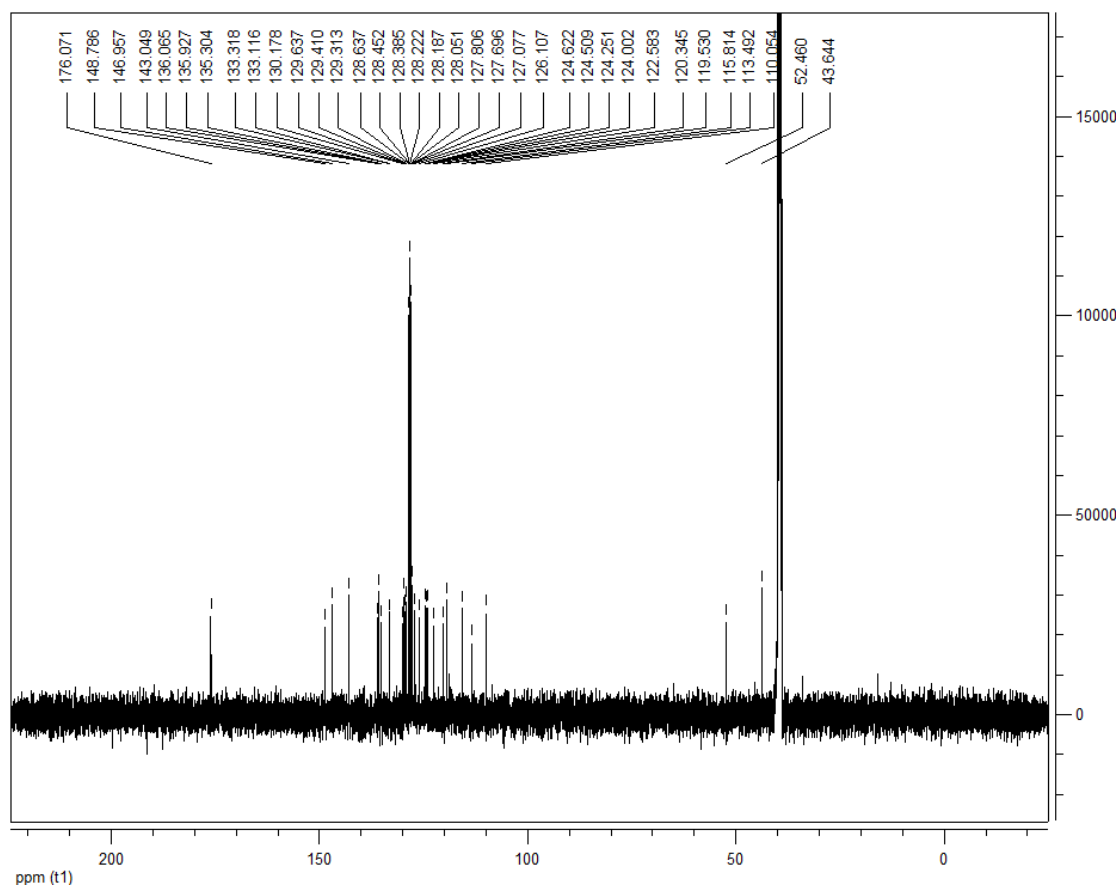
1-benzyl-6'-(*p*-tolyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3a): Yellow solid, 81%, 0.224 g, m.p. 217-219 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.50 (s, 1H, ArH), 8.44 (d, *J* = 7.6 Hz, 1H, ArH), 8.27 (d, *J* = 7.6 Hz, 1H, ArH), 8.19 (d, *J* = 8.0 Hz, 1H, ArH), 7.67 (t, *J* = 7.2 Hz, 1H, ArH), 7.60 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 1H, ArH), 7.37-7.29 (m, 6H, ArH), 7.26-7.22 (m, 2H, ArH), 6.98-6.95 (m, 4H, ArH), 6.89 (d, *J* = 7.2 Hz, 2H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 5.01 (d, *J* = 15.2 Hz, 1H, CH), 4.92 (d, *J* = 15.2 Hz, 1H, CH), 2.23 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 177.0, 151.0, 147.6, 143.3, 138.1, 137.1, 136.5, 135.7, 133.2, 131.1, 129.4, 128.9, 128.8, 128.7, 128.7, 128.3, 128.1, 127.9, 127.6, 127.3, 126.2, 125.2, 125.1, 124.9, 123.9, 123.8, 123.2, 121.3, 119.9, 115.0, 112.2, 109.4, 53.0, 44.6, 21.3; IR (KBr) ν: 3034, 2919, 1719, 1605, 1479, 1346, 1220, 1170, 1077, 1018, 932, 885, 820, 749 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₀H₂₈NO₂ ([M+H]⁺): 554.2115. Found: 554.2113.



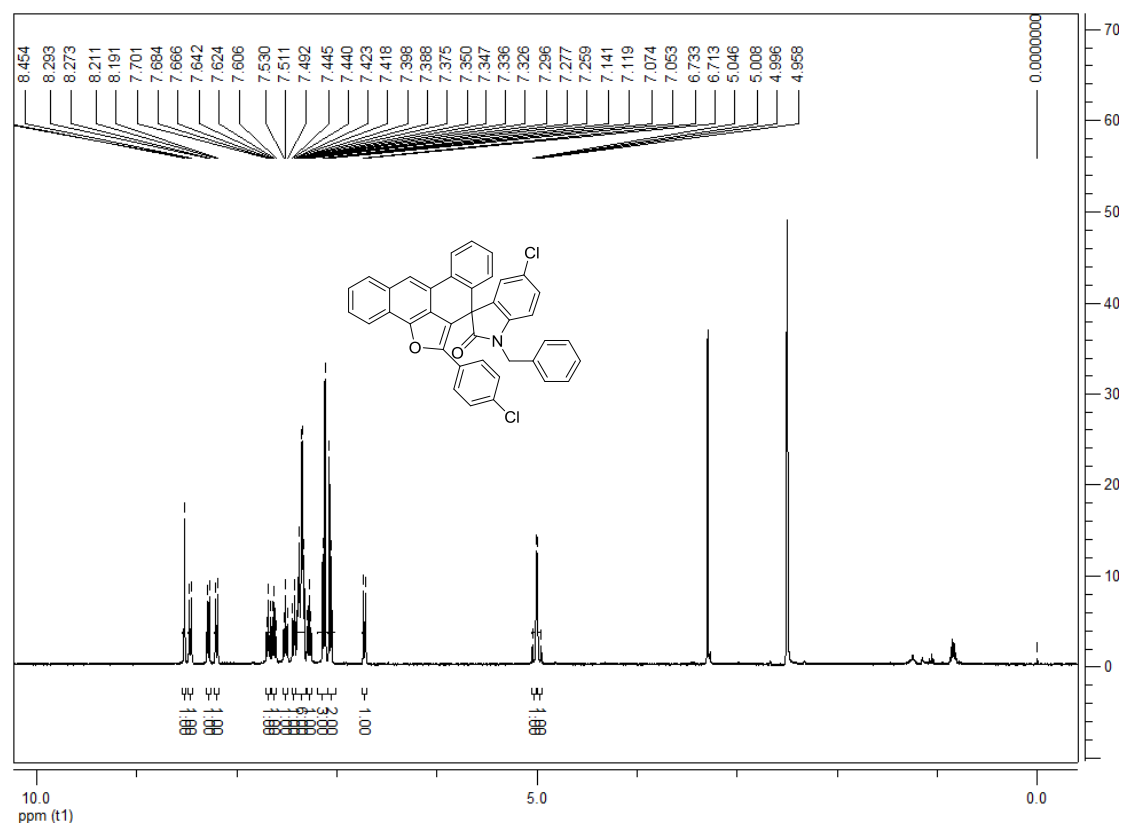


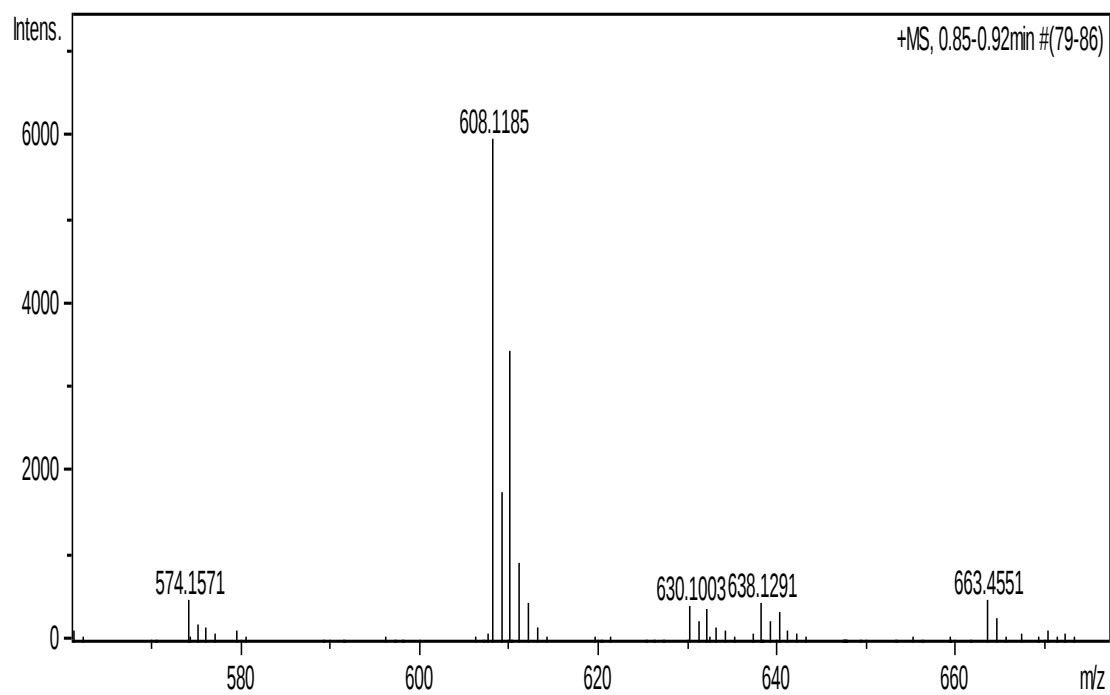
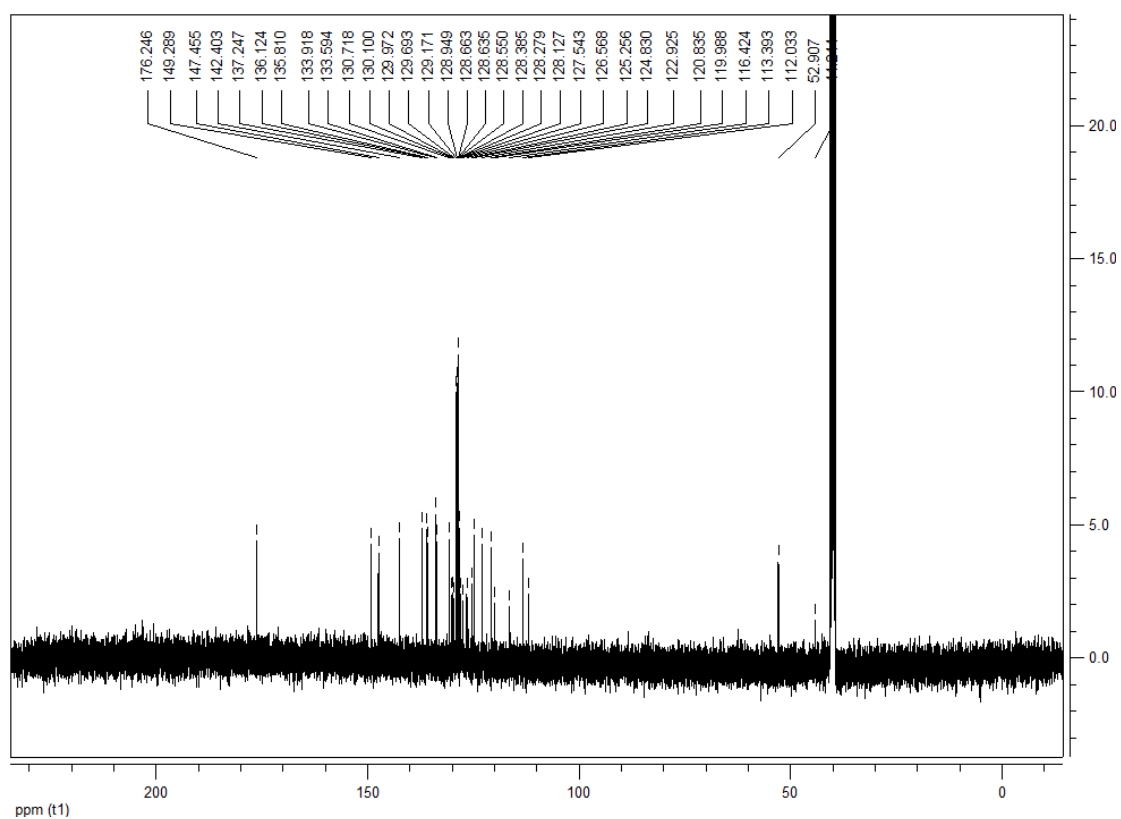
1-benzyl-6'-(4-chlorophenyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3b): Yellow solid, 84%, 0.240 g, m.p. 230-232 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.50 (s, 1H, ArH), 8.44 (d, *J* = 7.6 Hz, 1H, ArH), 8.28 (d, *J* = 8.0 Hz, 1H, ArH), 8.20 (d, *J* = 8.0 Hz, 1H, ArH), 7.68 (t, *J* = 7.2 Hz, 1H, ArH), 7.62 (t, *J* = 7.2 Hz, 1H, ArH), 7.49 (t, *J* = 7.2 Hz, 1H, ArH), 7.35-7.23 (m, 8H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 7.01 (d, *J* = 8.0 Hz, 2H, ArH), 6.98-6.95 (m, 2H, ArH), 6.72 (d, *J* = 7.6 Hz, 1H, ArH), 5.00 (d, *J* = 16.4 Hz, 1H, CH), 4.96 (d, *J* = 16.0 Hz, 1H, CH); ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 176.0, 148.7, 146.9, 143.0, 136.0, 135.9, 135.3, 133.3, 133.1, 130.1, 129.6, 129.4, 129.3, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.0, 126.1, 124.6, 124.5, 124.2, 124.0, 122.5, 120.3, 119.5, 115.8, 113.4, 110.0, 52.4, 43.6; IR (KBr) ν: 3060, 2893, 1717, 1602, 1479, 1343, 1223, 1170, 1083, 1011, 927, 885, 835, 750, 702 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₉H₂₅ClNO₂ ([M+H]⁺): 574.1568. Found: 574.1569.

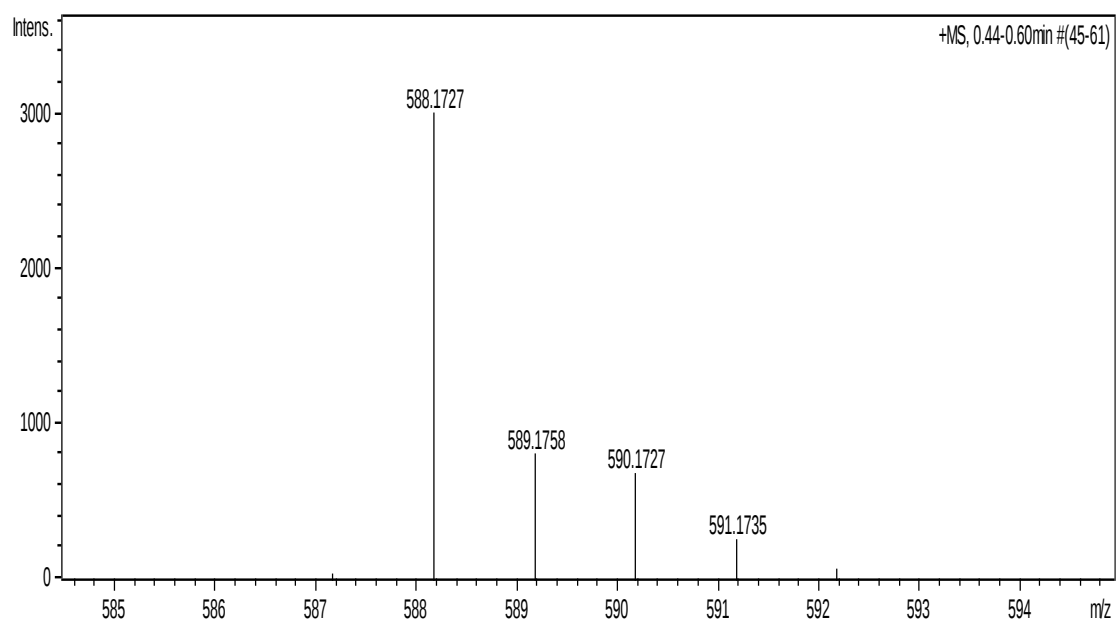
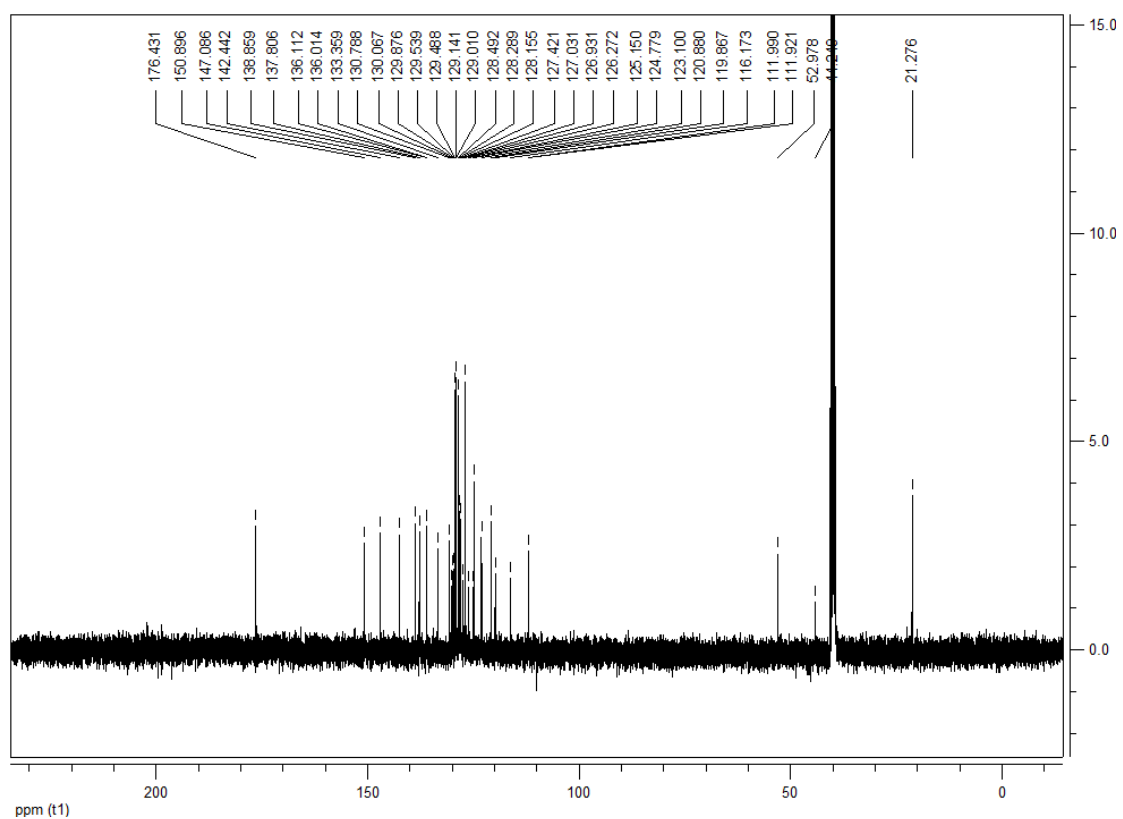




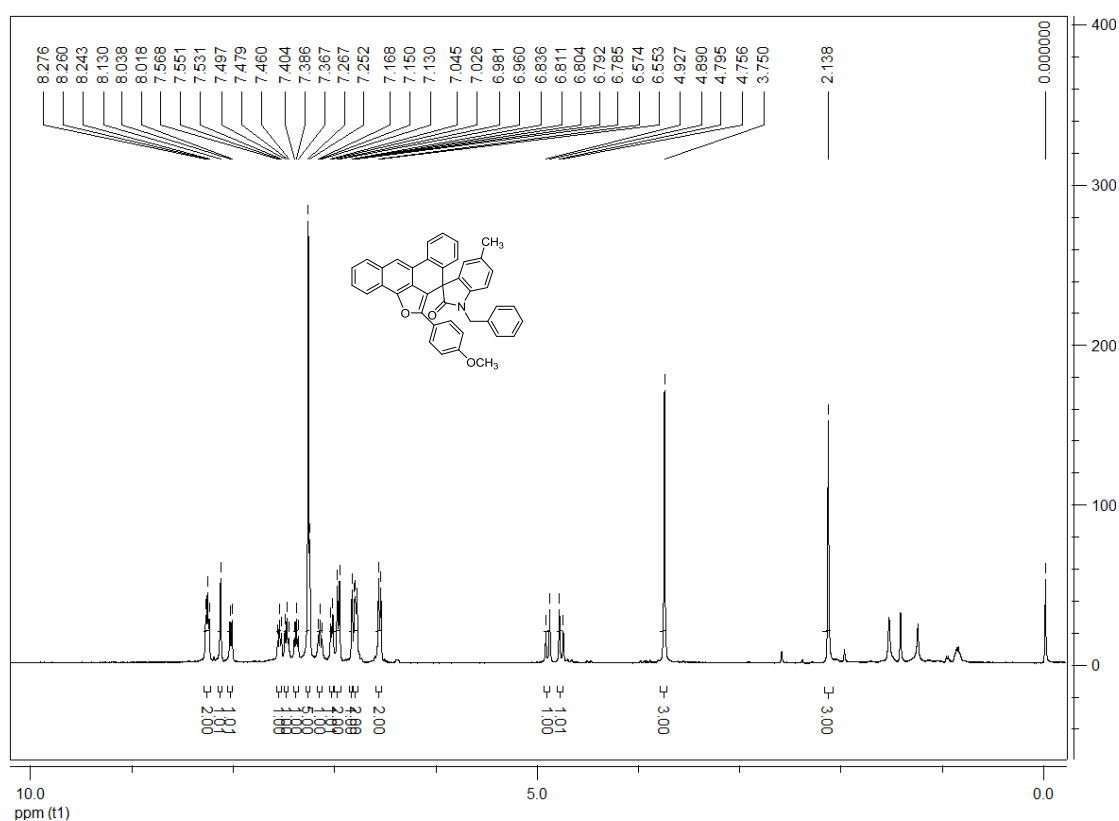
Yellow solid, 80%, 0.243 g, m.p. 213-215°C; ^1H NMR (400 MHz, DMSO- d_6) δ : 8.52 (s, 1H, ArH), 8.46 (d, J = 8.0 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 1H, ArH), 8.20 (d, J = 8.0 Hz, 1H, ArH), 7.68 (t, J = 7.2 Hz, 1H, ArH), 7.62 (t, J = 7.2 Hz, 1H, ArH), 7.51 (t, J = 7.6 Hz, 1H, ArH), 7.43 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.40-7.33 (m, 6H, ArH), 7.28 (t, J = 7.2 Hz, 1H, ArH), 7.14-7.12 (m, 3H, ArH), 7.06 (d, J = 8.4 Hz, 2H, ArH), 6.72 (d, J = 8.0 Hz, 1H, ArH), 5.03 (d, J = 15.2 Hz, 1H, CH), 4.98 (d, J = 15.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO- d_6) δ : 176.2, 149.2, 147.4, 142.4, 137.2, 136.1, 135.8, 133.9, 133.5, 130.7, 130.0, 129.9, 129.6, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.5, 126.5, 125.2, 124.8, 122.9, 120.8, 119.9, 116.4, 113.3, 112.0, 52.9, 44.2; IR (KBr) ν : 3060, 2927, 1719, 1599, 1480, 1426, 1329, 1248, 1167, 1081, 1010, 863, 824, 750, 695 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{39}\text{H}_{24}\text{Cl}_2\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 608.1179. Found: 608.1185.

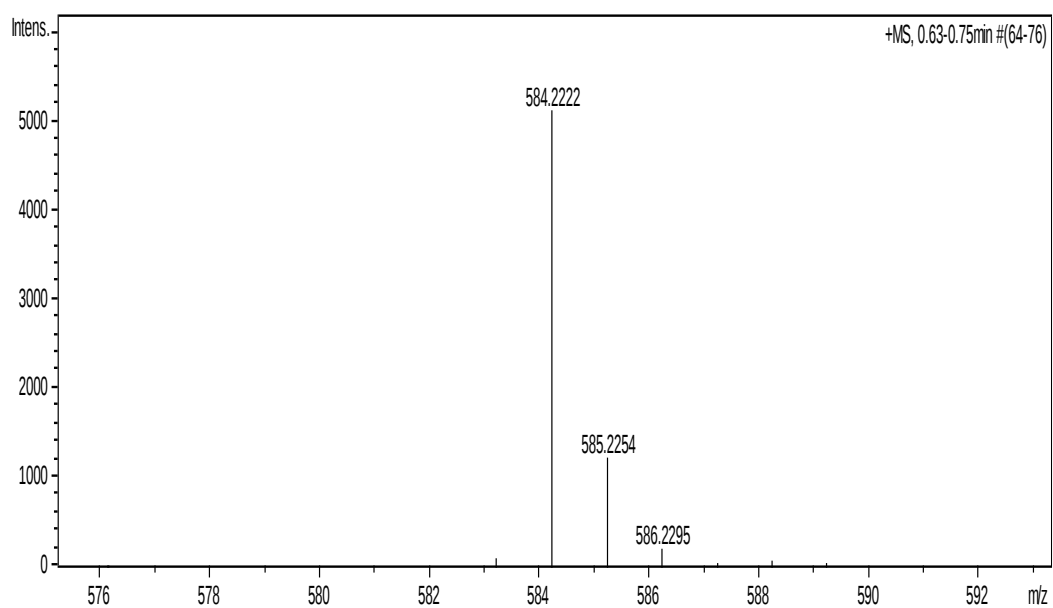
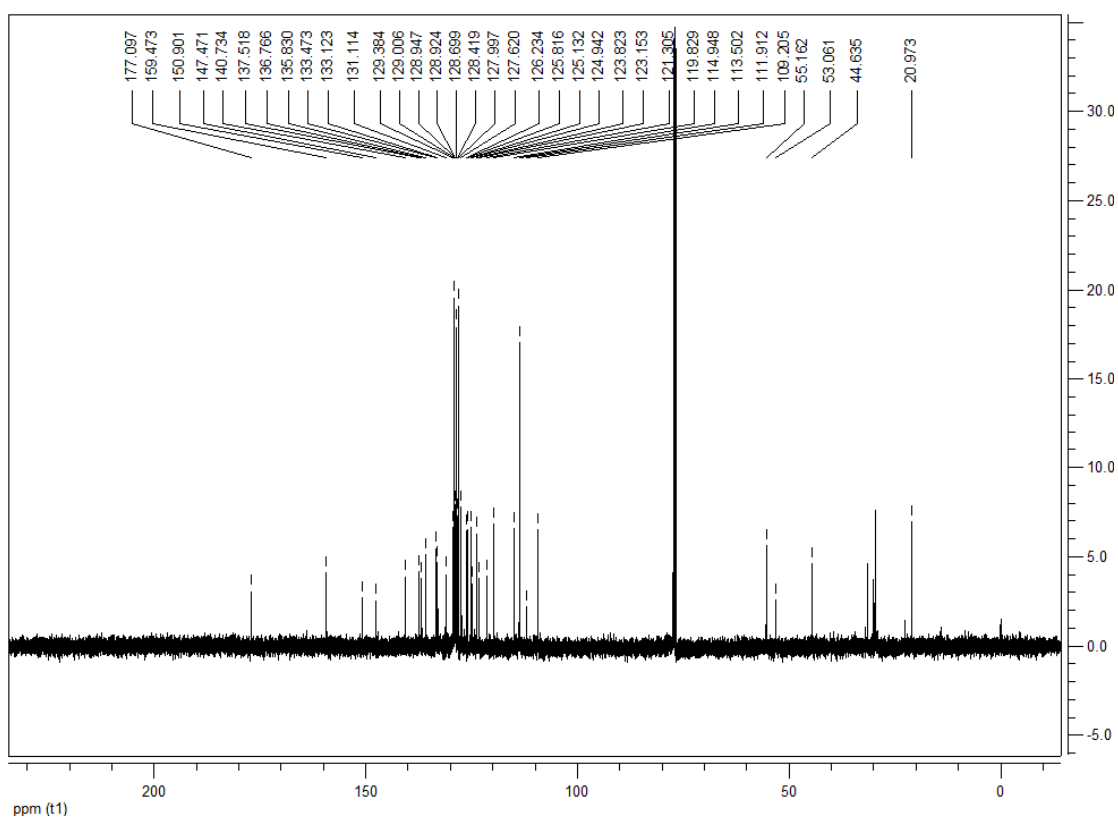


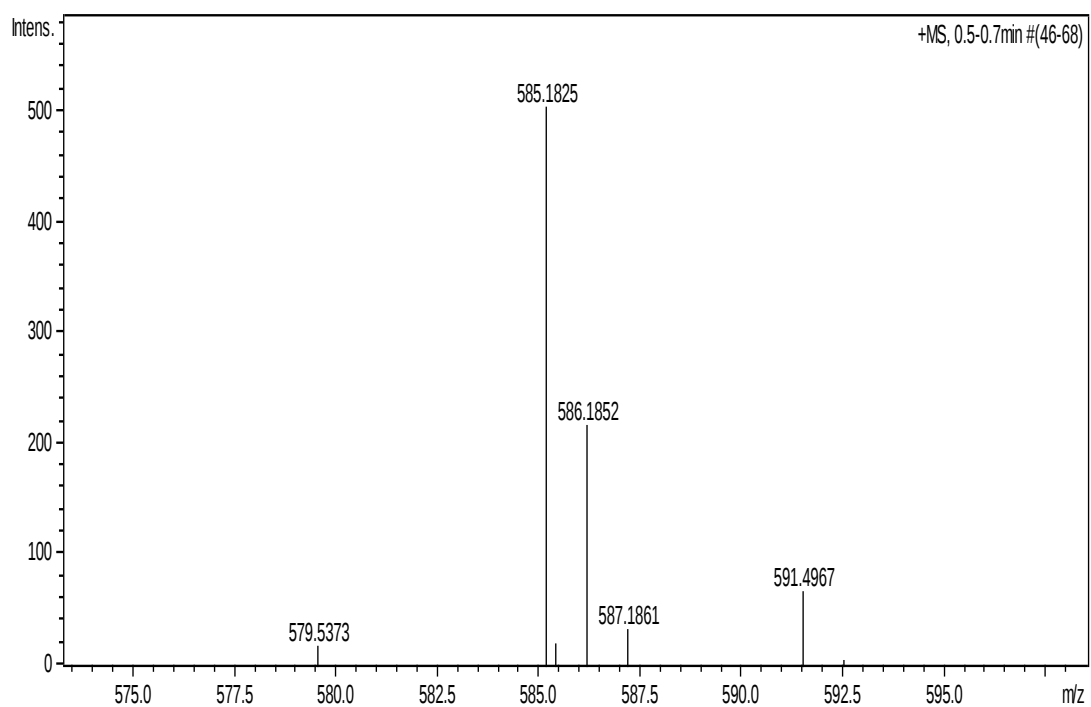
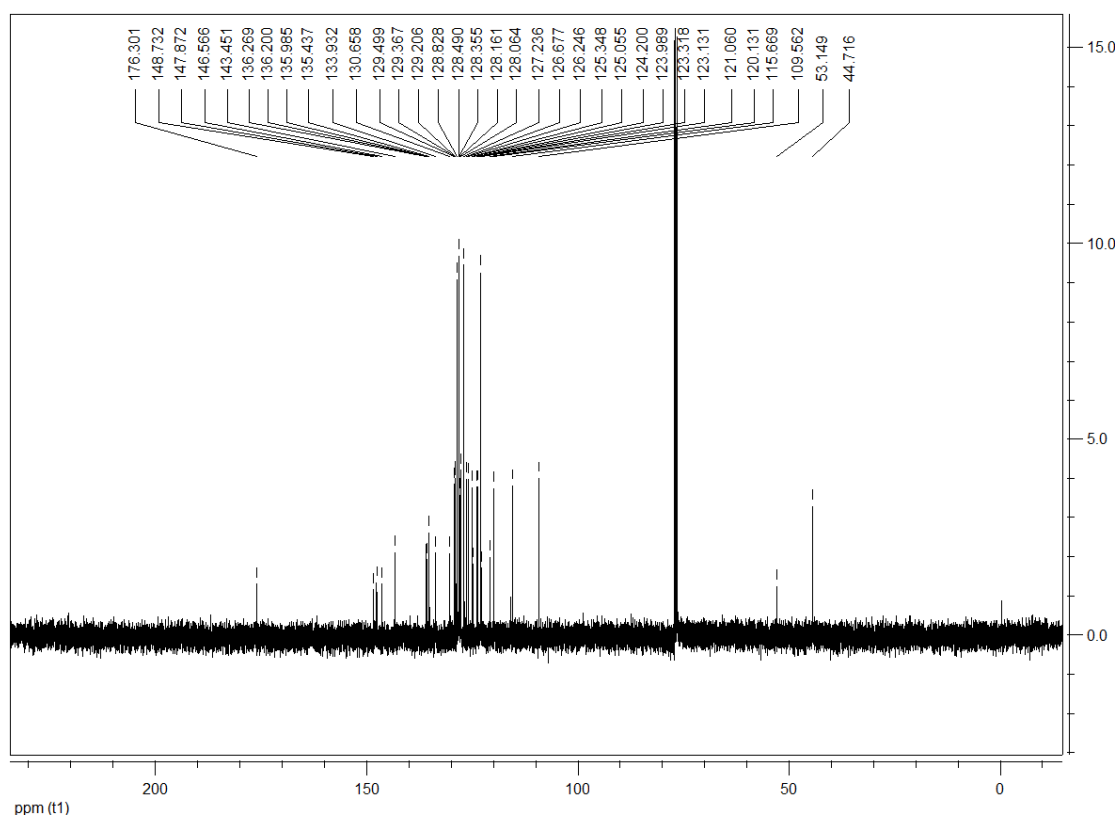




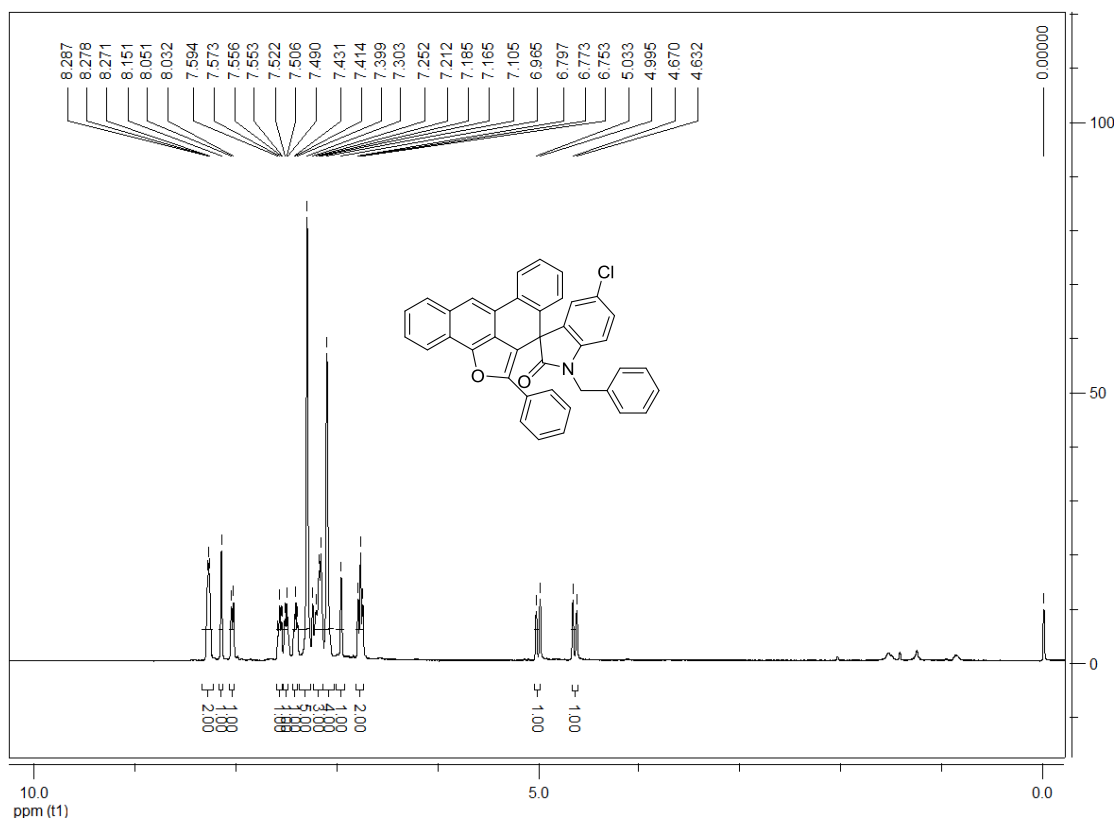
1-benzyl-6'-(4-methoxyphenyl)-5-methylspiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one
(3e): Yellow solid, 76%, 0.221 g, m.p. 223-225 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.28-8.24 (m, 2H, ArH), 8.13 (s, 1H, ArH), 8.03 (d, $J = 8.0$ Hz, 1H, ArH), 7.55 (t, $J = 7.6$ Hz, 1H, ArH), 7.45 (t, $J = 7.6$ Hz, 1H, ArH), 7.39 (t, $J = 7.6$ Hz, 1H, ArH), 7.27-7.25 (m, 5H, ArH), 7.15 (t, $J = 7.6$ Hz, 1H, ArH), 7.04 (d, $J = 7.6$ Hz, 1H, ArH), 6.97 (d, $J = 7.6$ Hz, 2H, ArH), 6.84 (s, 1H, ArH), 6.81-6.79 (m, 2H, ArH), 6.56 (d, $J = 8.4$ Hz, 2H, ArH), 4.91 (d, $J = 14.8$ Hz, 1H, CH), 4.78 (d, $J = 15.6$ Hz, 1H, CH), 3.75 (s, 3H, OCH_3), 2.14 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 177.0, 159.4, 150.9, 147.4, 140.7, 137.5, 136.7, 135.8, 133.4, 133.1, 131.1, 129.3, 129.0, 128.9, 128.9, 128.6, 128.4, 127.9, 127.6, 126.2, 125.8, 125.1, 124.9, 123.8, 123.1, 121.3, 119.8, 114.9, 113.5, 111.9, 109.2, 55.1, 53.0, 44.6, 20.9; IR (KBr) ν : 3057, 2922, 2853, 1718, 1605, 1497, 1448, 1371, 1333, 1250, 1177, 1076, 1027, 963, 884, 834, 753, 696 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. For $\text{C}_{41}\text{H}_{30}\text{NO}_3$ ($[\text{M}+\text{H}]^+$): 584.2226. Found: 584.2222.

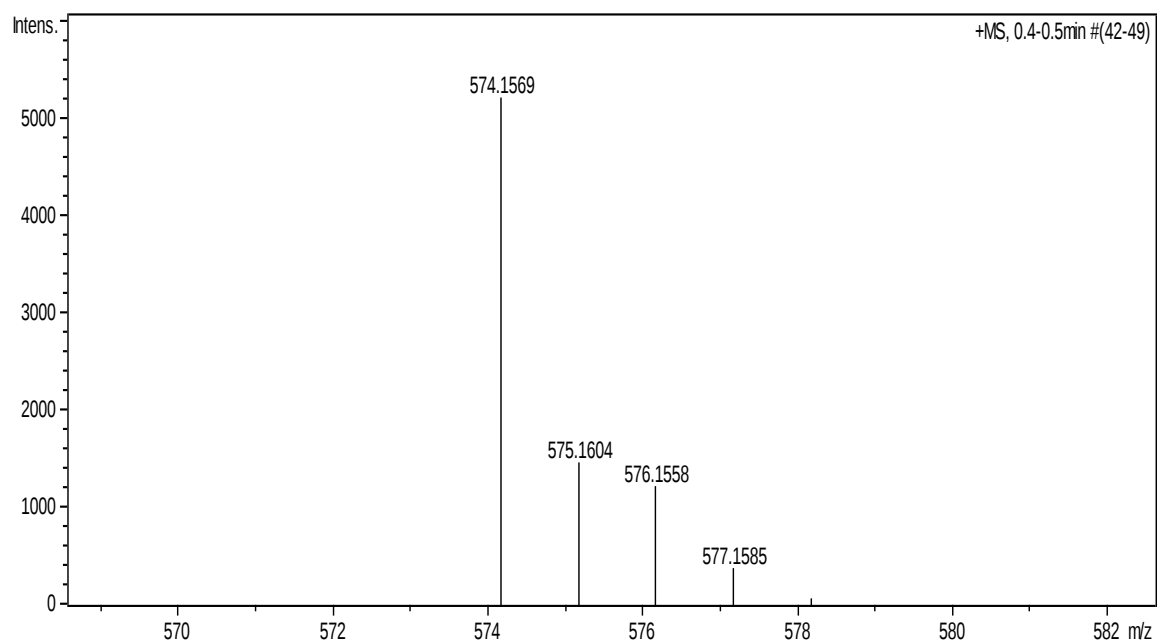
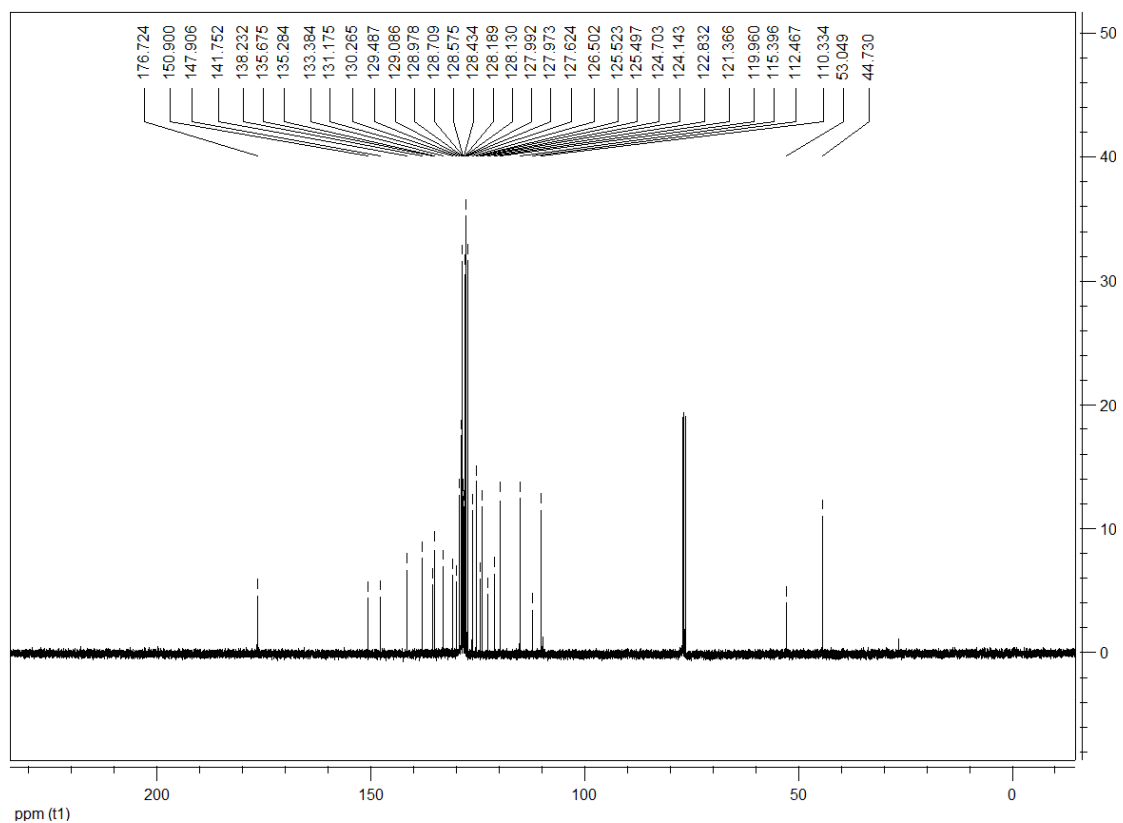




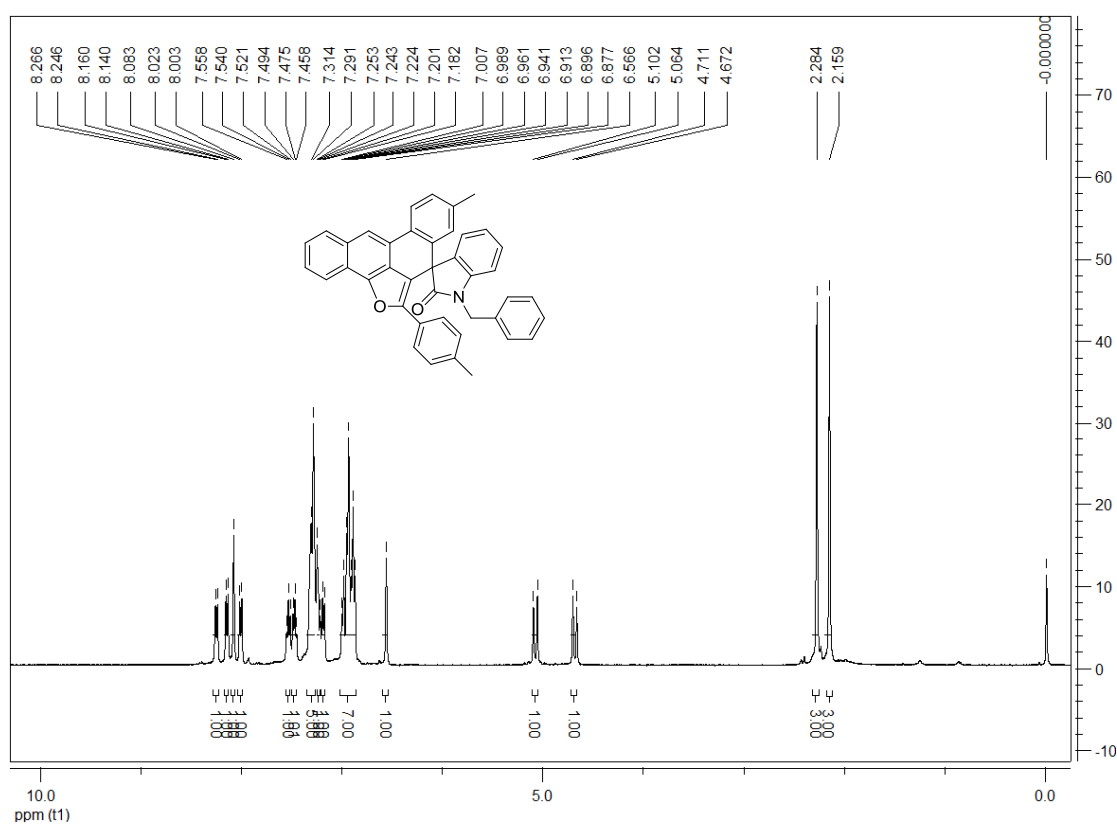


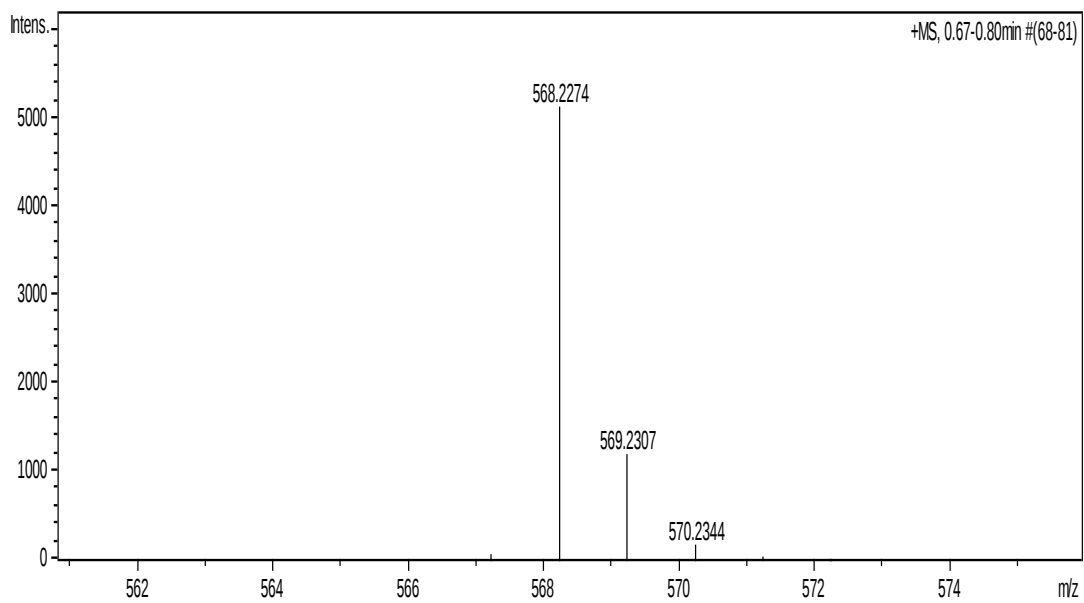
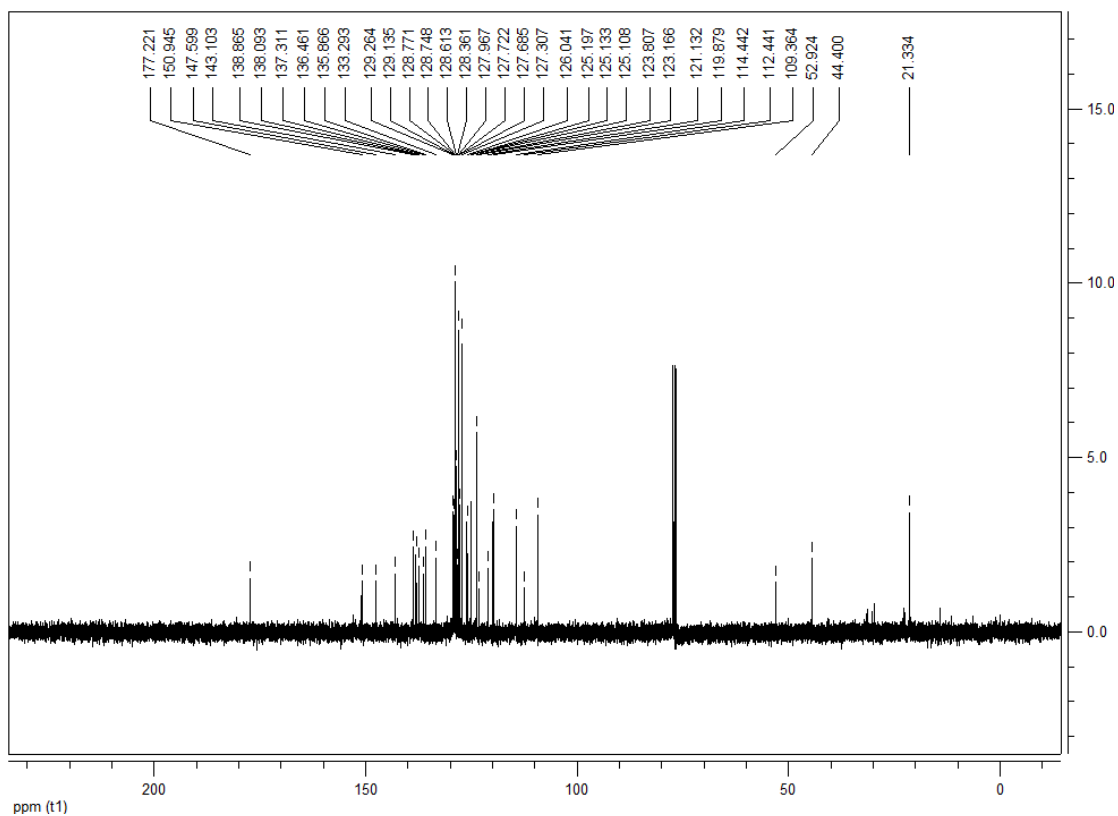
1-benzyl-5-chloro-6'-phenylspiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3g): yellow solid, 91%, 0.260 g, m.p. 236-238 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.29-8.27 (m, 2H, ArH), 8.15 (s, 1H, ArH), 8.04 (d, $J = 7.6$ Hz, 1H, ArH), 7.59-7.57 (m, 1H, ArH), 7.52-7.49 (m, 1H, ArH), 7.43-7.40 (m, 1H, ArH), 7.30 (brs, 5H, ArH), 7.21-7.17 (m, 3H, ArH), 7.11 (brs, 4H, ArH), 6.97 (brs, 1H, ArH), 6.80-6.75 (m, 2H, ArH), 5.01 (d, $J = 15.2$ Hz, 1H, CH), 4.65 (d, $J = 15.6$ Hz, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.7, 150.8, 147.9, 141.7, 138.2, 135.6, 135.2, 133.3, 131.1, 130.2, 129.4, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 126.5, 125.5, 125.4, 124.7, 124.1, 122.8, 121.3, 119.9, 115.3, 112.4, 110.3, 53.0, 44.7; IR (KBr) ν : 3057, 3029, 2928, 1719, 1604, 1481, 1446, 1423, 1368, 1322, 1269, 1219, 1164, 1116, 1067, 1021, 964, 919, 898, 871, 848, 806, 784, 764, 745 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{39}\text{H}_{25}\text{ClNO}_2$ ($[\text{M}+\text{H}]^+$): 574.1574. Found: 574.1569.





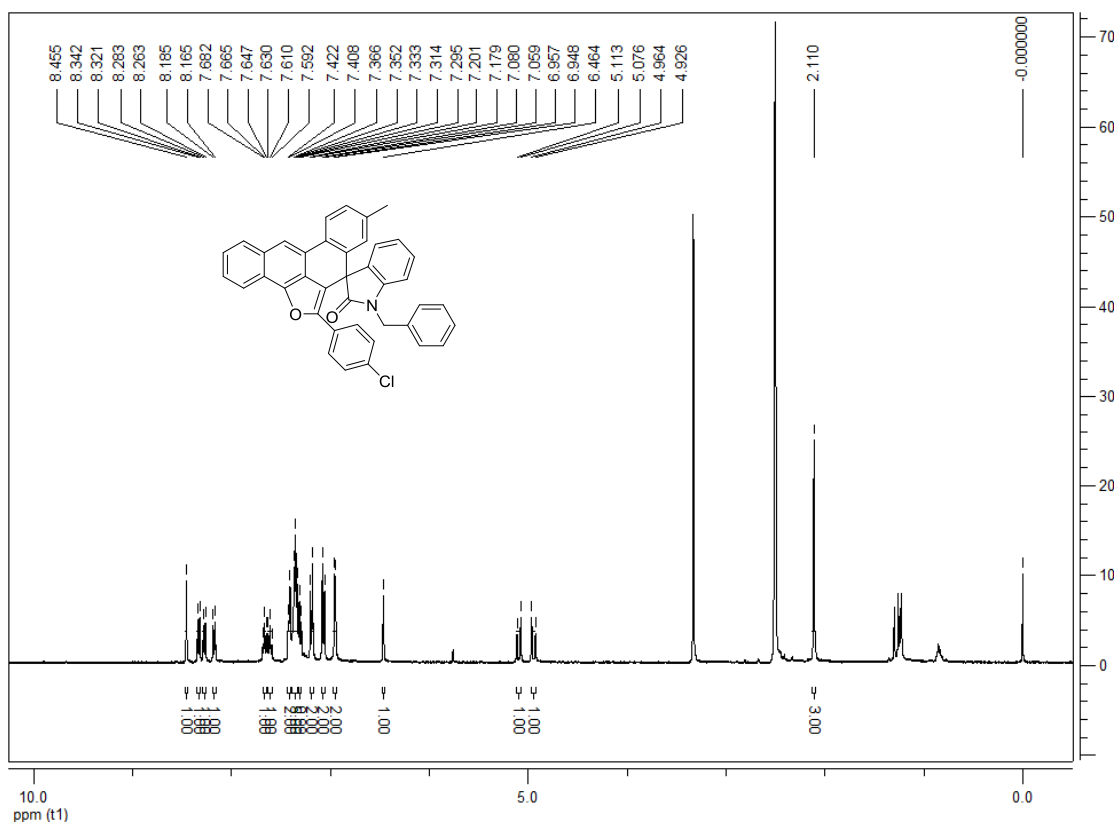
1-benzyl-9'-methyl-6'-(*p*-tolyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3h): Yellow solid, 82%, 0.233 g, m.p. 216-218°C; ¹H NMR (400 MHz, CDCl₃) δ: 8.26 (d, *J* = 8.0 Hz, 1H, ArH), 8.15 (d, *J* = 8.0 Hz, 1H, ArH), 8.08 (s, 1H, ArH), 8.01 (d, *J* = 8.0 Hz, 1H, ArH), 7.54 (t, *J* = 7.6 Hz, 1H, ArH), 7.48 (t, *J* = 7.6 Hz, 1H, ArH), 7.31-7.29 (m, 5H, ArH), 7.23 (d, *J* = 7.6 Hz, 1H, ArH), 7.19 (d, *J* = 7.6 Hz, 1H, ArH), 7.01-6.88 (m, 7H, ArH), 6.57 (s, 1H, ArH), 5.08 (d, *J* = 15.2 Hz, 1H, CH), 4.69 (d, *J* = 15.6 Hz, 1H, CH), 2.28 (s, 3H, CH₃), 2.16 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 177.2, 150.9, 147.5, 143.1, 138.8, 138.0, 137.3, 136.4, 135.8, 133.2, 129.2, 129.1, 128.8, 128.7, 128.6, 128.3, 127.9, 127.7, 127.6, 127.3, 126.0, 125.1, 125.1, 125.1, 123.8, 123.1, 121.1, 119.8, 114.4, 112.4, 109.3, 52.9, 44.4, 21.3; IR (KBr) ν: 3036, 2916, 1717, 1605, 1494, 1456, 1422, 1348, 1224, 1172, 1075, 1018, 961, 901, 820, 742, 694 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₃₀NO₂ ([M+H]⁺): 568.2271. Found: 568.2274.

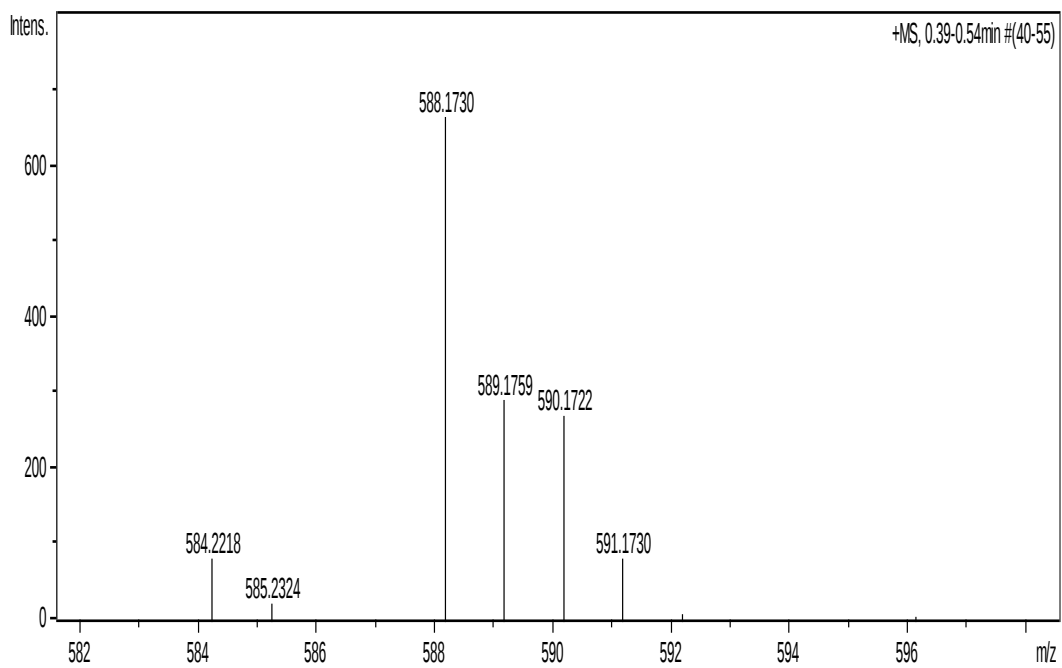
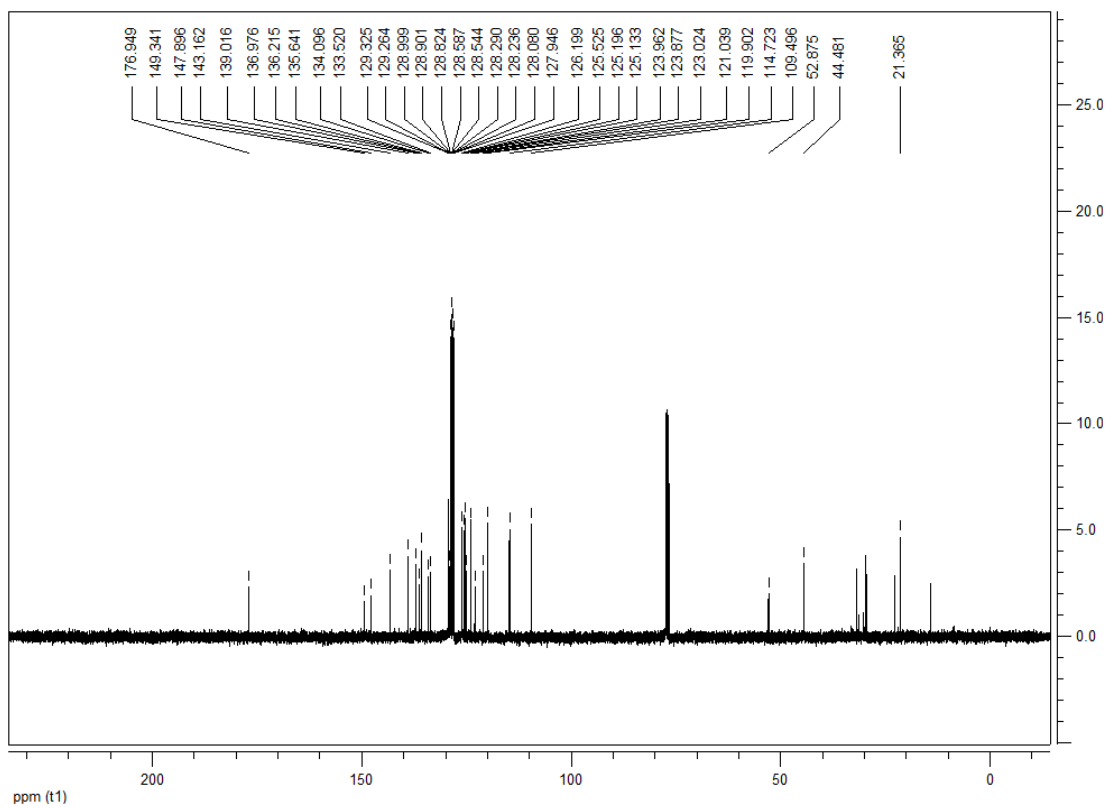


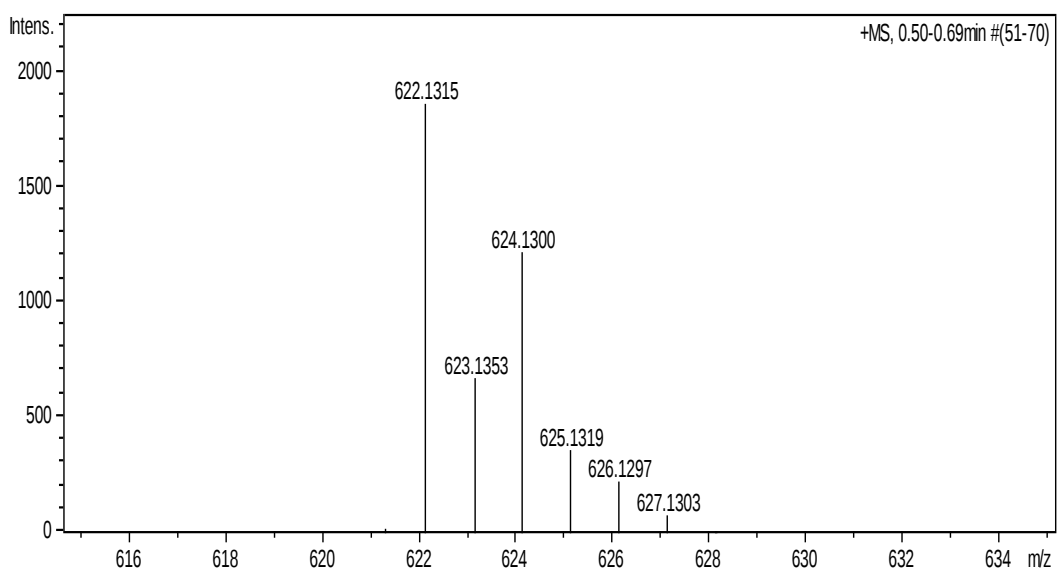
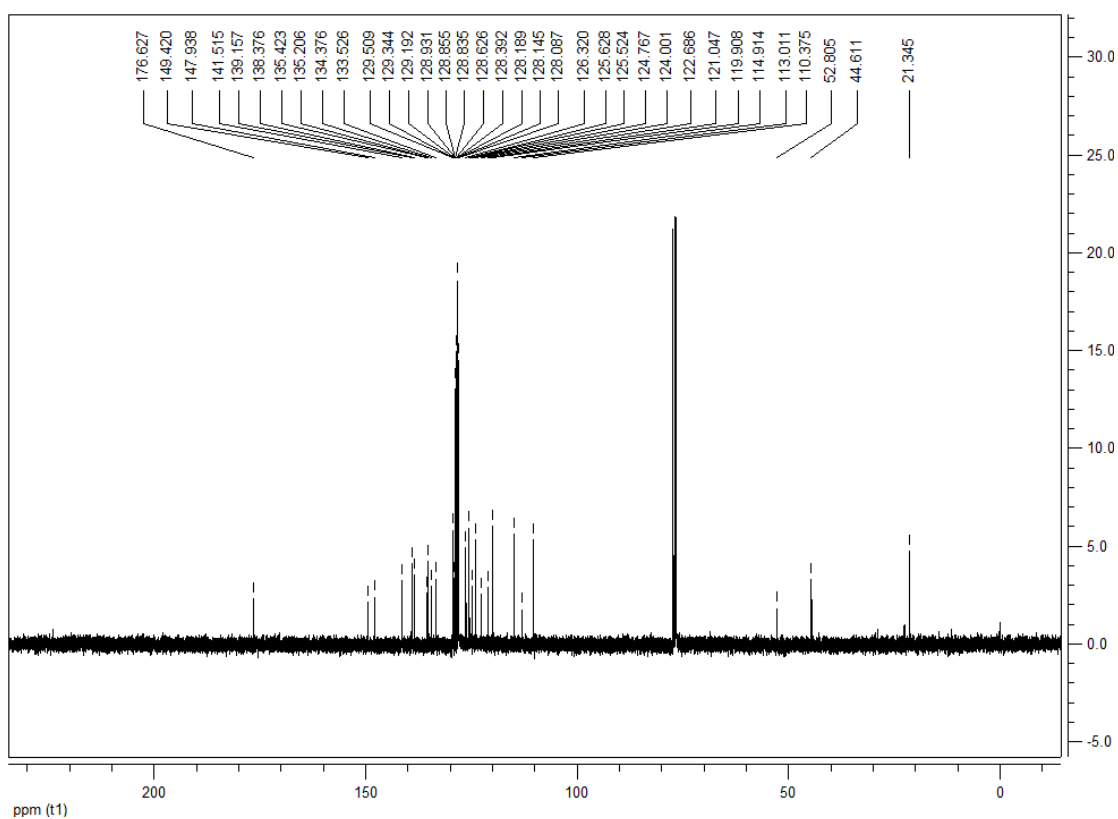


1-benzyl-6'-(4-chlorophenyl)-9'-methylspiro[indoline-3,7'-tetrapheno[7,6-bc]furan]-2-one (3i):

Yellow solid, 87%, 0.255 g, m.p. 268-270°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.46 (s, 1H, ArH), 8.33 (d, $J = 8.4$ Hz, 1H, ArH), 8.27 (d, $J = 8.0$ Hz, 1H, ArH), 8.18 (d, $J = 8.0$ Hz, 1H, ArH), 7.67 (t, $J = 7.2$ Hz, 1H, ArH), 7.61 (t, $J = 7.6$ Hz, 1H, ArH), 7.42-7.41 (m, 2H, ArH), 7.37-7.33 (m, 5H, ArH), 7.30 (d, $J = 7.6$ Hz, 1H, ArH), 7.19 (d, $J = 8.8$ Hz, 2H, ArH), 7.07 (d, $J = 8.4$ Hz, 2H, ArH), 6.95 (d, $J = 3.6$ Hz, 2H, ArH), 6.46 (brs, 1H, ArH), 5.09 (d, $J = 14.8$ Hz, 1H, CH), 4.94 (d, $J = 15.2$ Hz, 1H, CH), 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.9, 149.3, 147.8, 143.1, 139.0, 136.9, 136.2, 135.6, 134.0, 133.5, 129.3, 129.2, 128.9, 128.9, 128.8, 128.5, 128.5, 128.2, 128.2, 128.0, 127.9, 126.1, 125.5, 125.2, 125.1, 123.9, 123.8, 123.0, 121.0, 119.9, 114.7, 109.4, 52.8, 44.4, 21.3; IR (KBr) ν : 3029, 2919, 2852, 1717, 1605, 1477, 1369, 1342, 1221, 1166, 1083, 1014, 962, 909, 826, 749, 705 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{40}\text{H}_{27}\text{ClNO}_2$ ($[\text{M}+\text{H}]^+$): 588.1725. Found: 588.173.

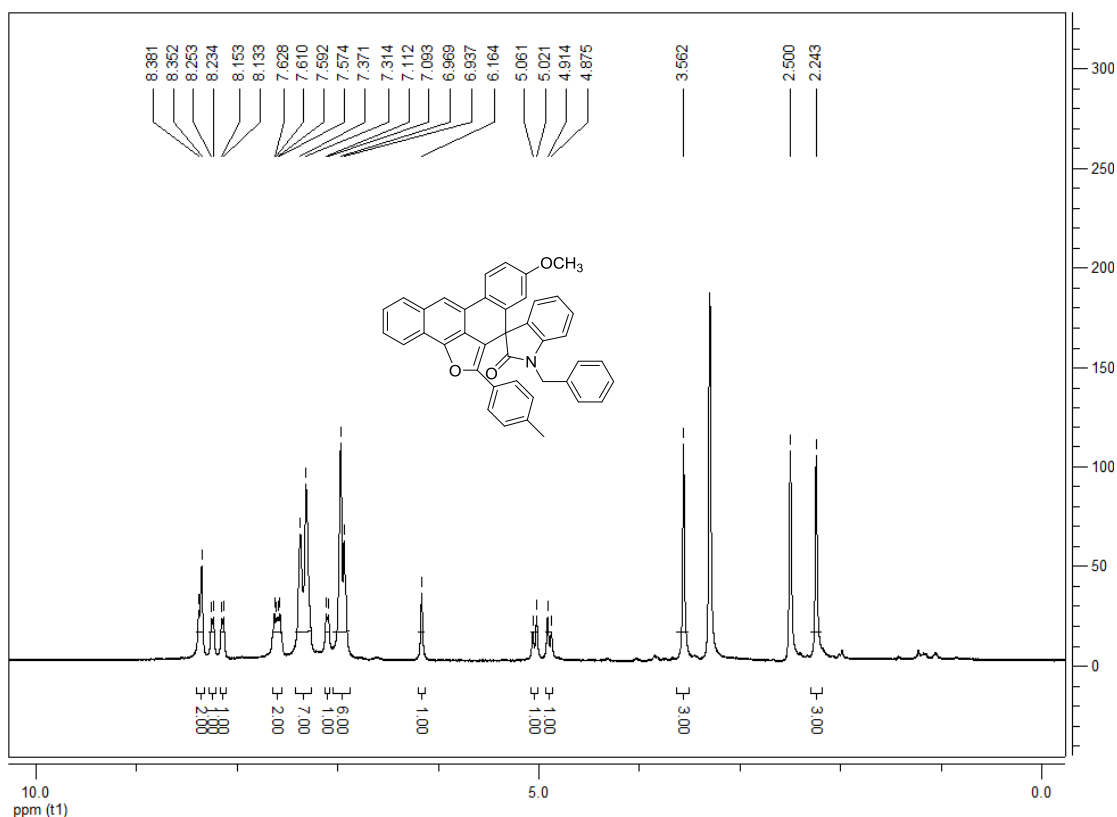


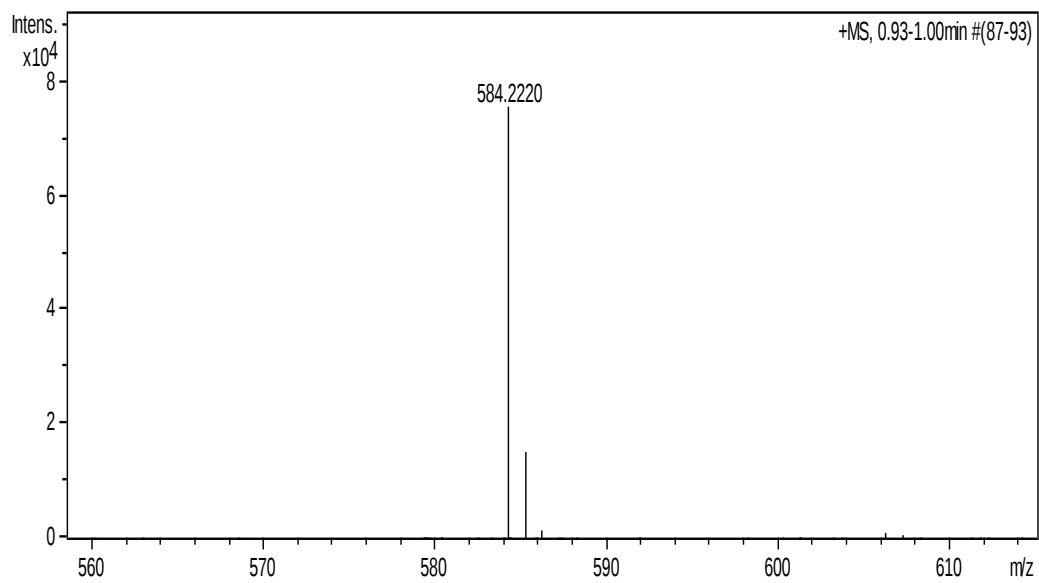
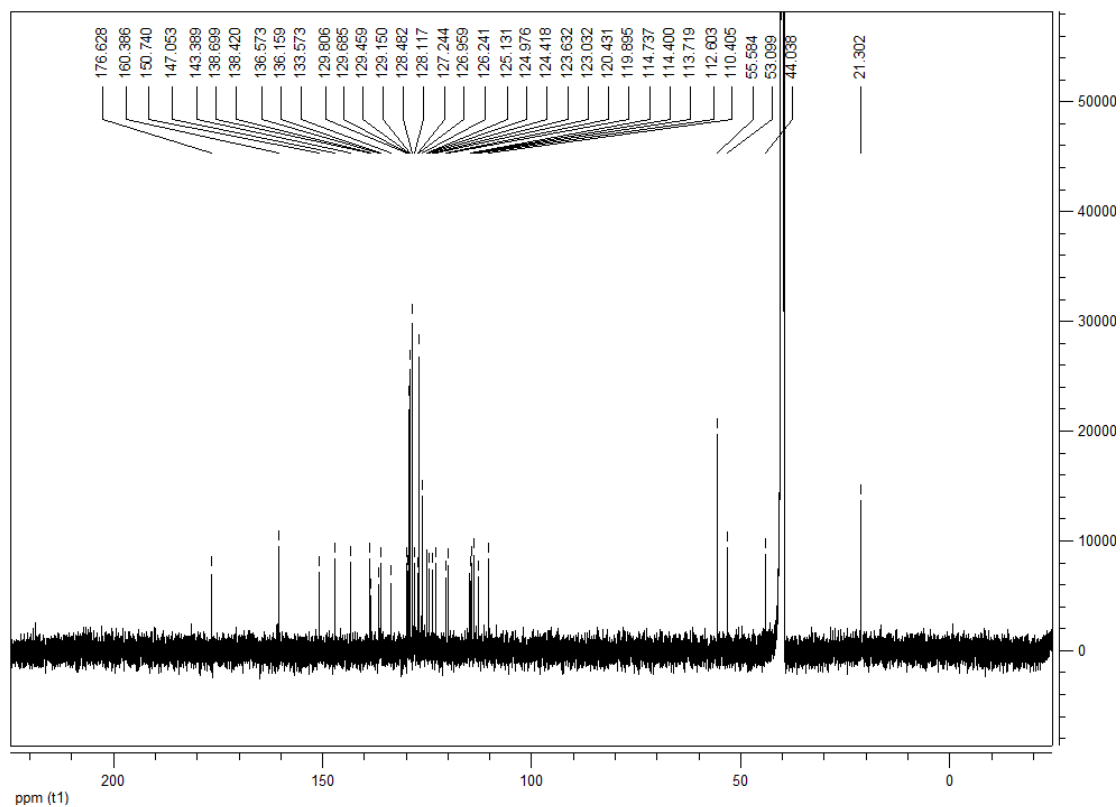




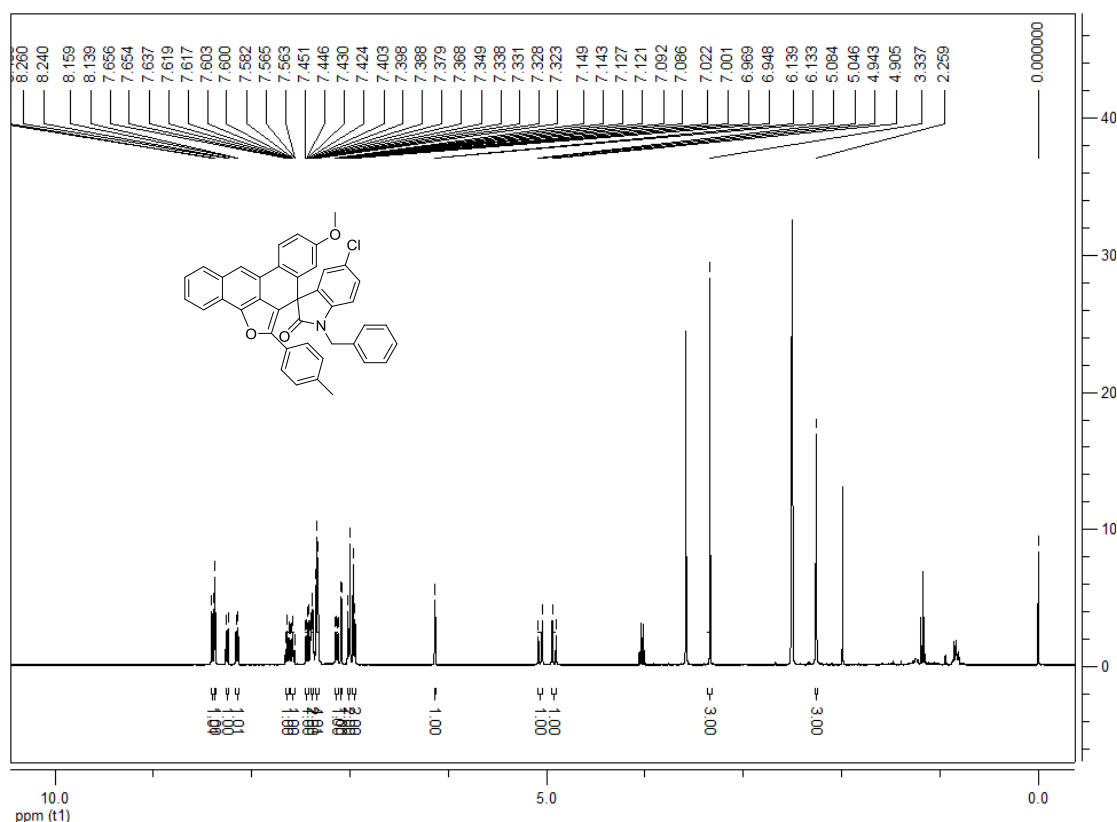
1-benzyl-9'-methoxy-6'-(*p*-tolyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3k):

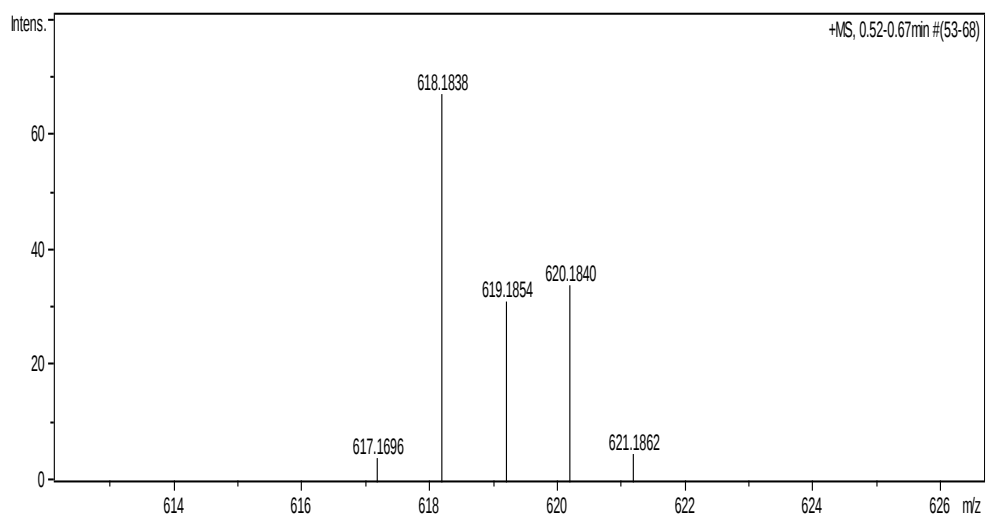
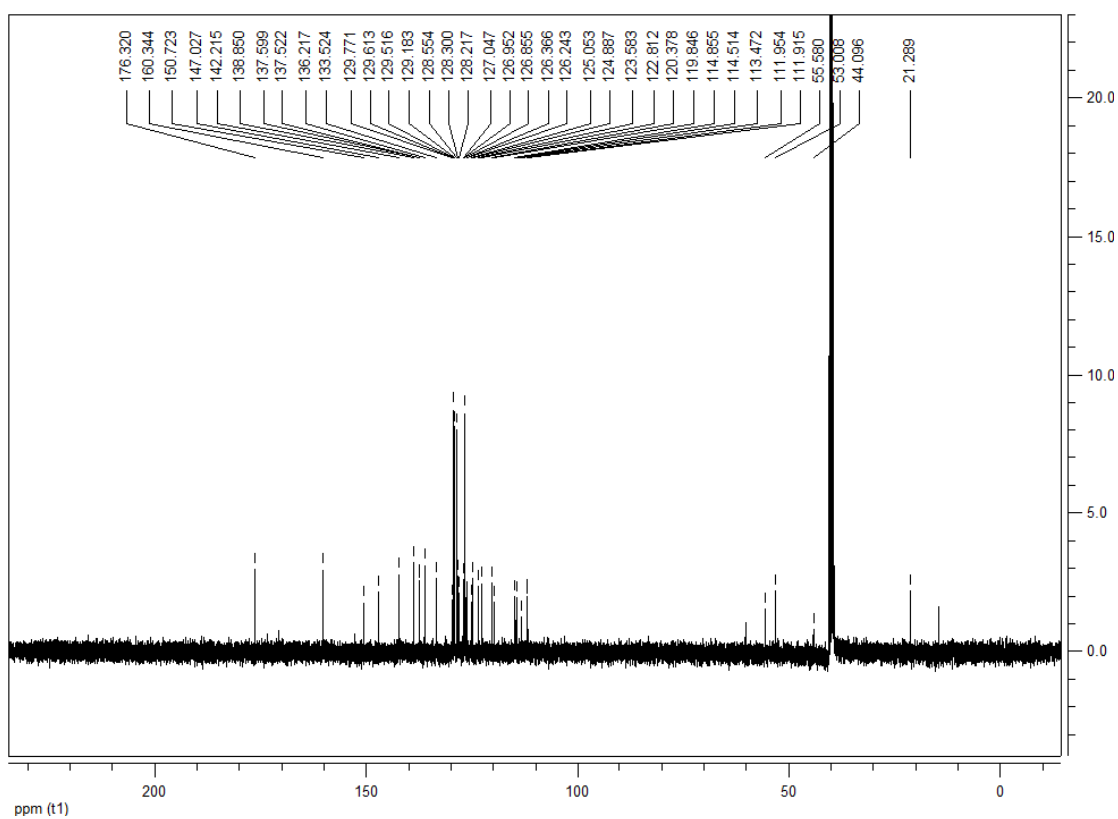
Yellow solid, 83%, 0.242 g, m.p. 239-241 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.38-8.35 (m, 2H, ArH), 8.24 (d, $J = 7.6$ Hz, 1H, ArH), 8.14 (d, $J = 8.0$ Hz, 1H, ArH), 7.63-7.57 (m, 2H, ArH), 7.37-7.31 (m, 7H, ArH), 7.10 (d, $J = 7.6$ Hz, 1H, ArH), 6.97-6.94 (m, 6H, ArH), 6.16 (brs, 1H, ArH), 5.04 (d, $J = 16.0$ Hz, 1H, CH), 4.90 (d, $J = 15.6$ Hz, 1H, CH), 3.56 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 176.6, 160.3, 150.7, 147.0, 143.3, 138.6, 138.4, 136.5, 136.1, 133.5, 129.8, 129.6, 129.4, 129.1, 128.4, 128.1, 127.2, 126.9, 126.2, 125.1, 124.9, 124.4, 123.6, 123.0, 120.4, 119.8, 114.7, 114.3, 113.7, 112.6, 110.4, 55.5, 53.0, 44.0, 21.3; IR (KBr) ν : 3035, 2922, 1722, 1605, 1496, 1469, 1345, 1290, 1246, 1172, 1080, 1036, 911, 825, 748, 698 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{30}\text{NO}_3$ ($[\text{M}+\text{H}]^+$): 584.2220. Found: 584.2220.

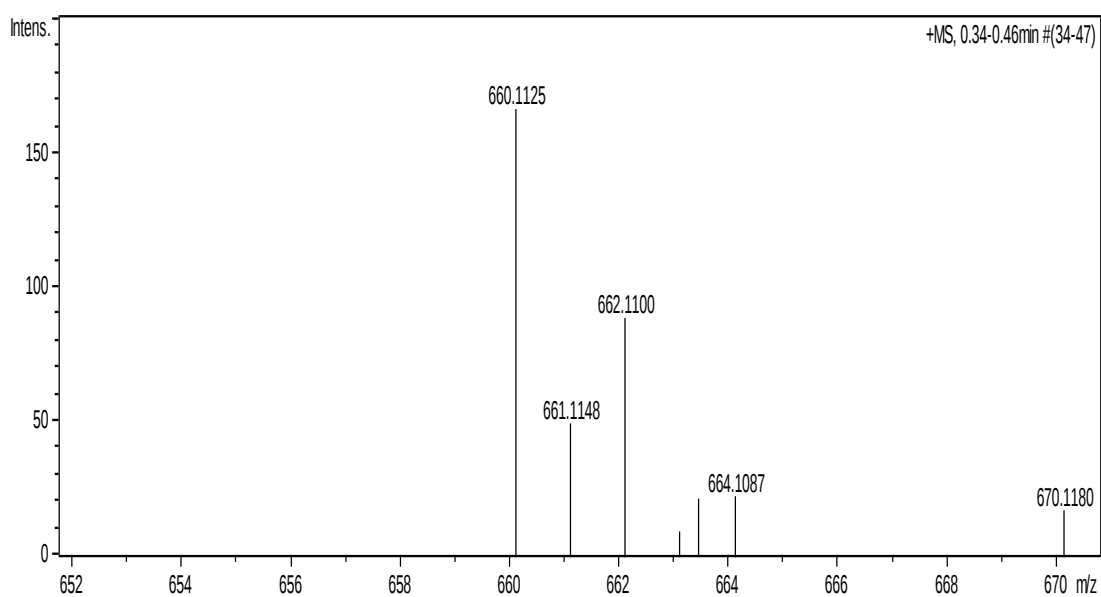
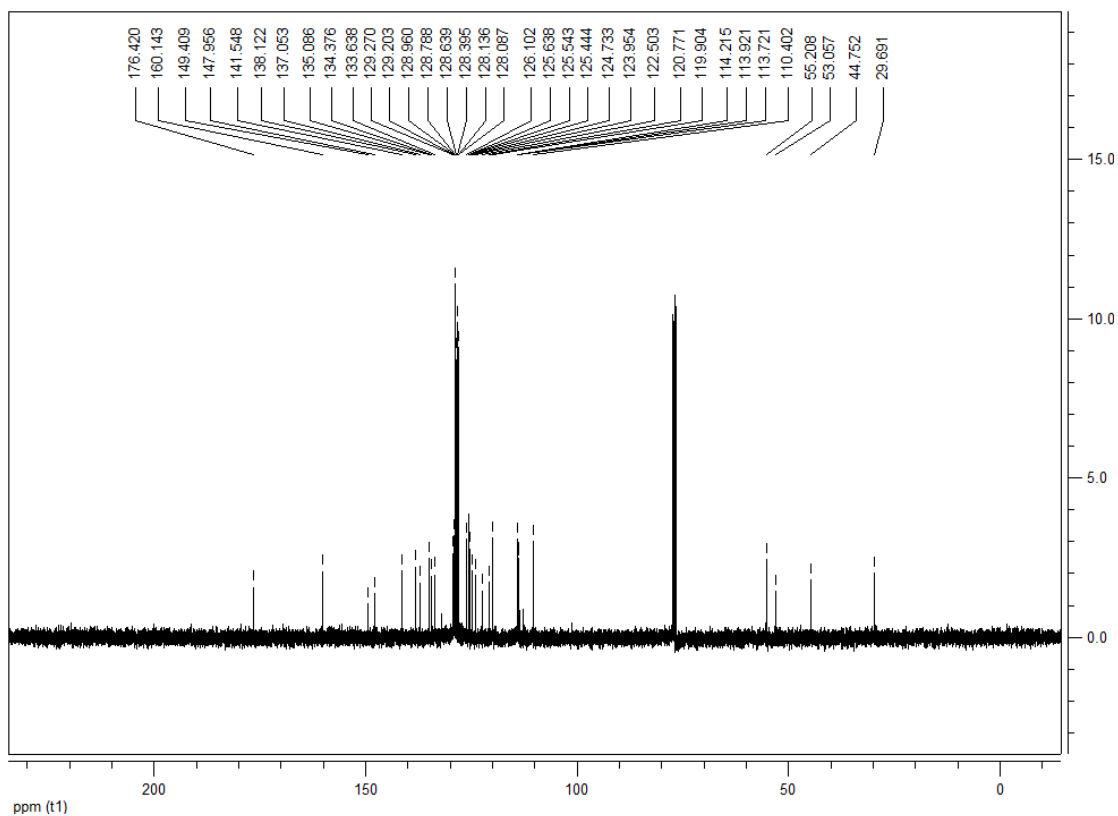




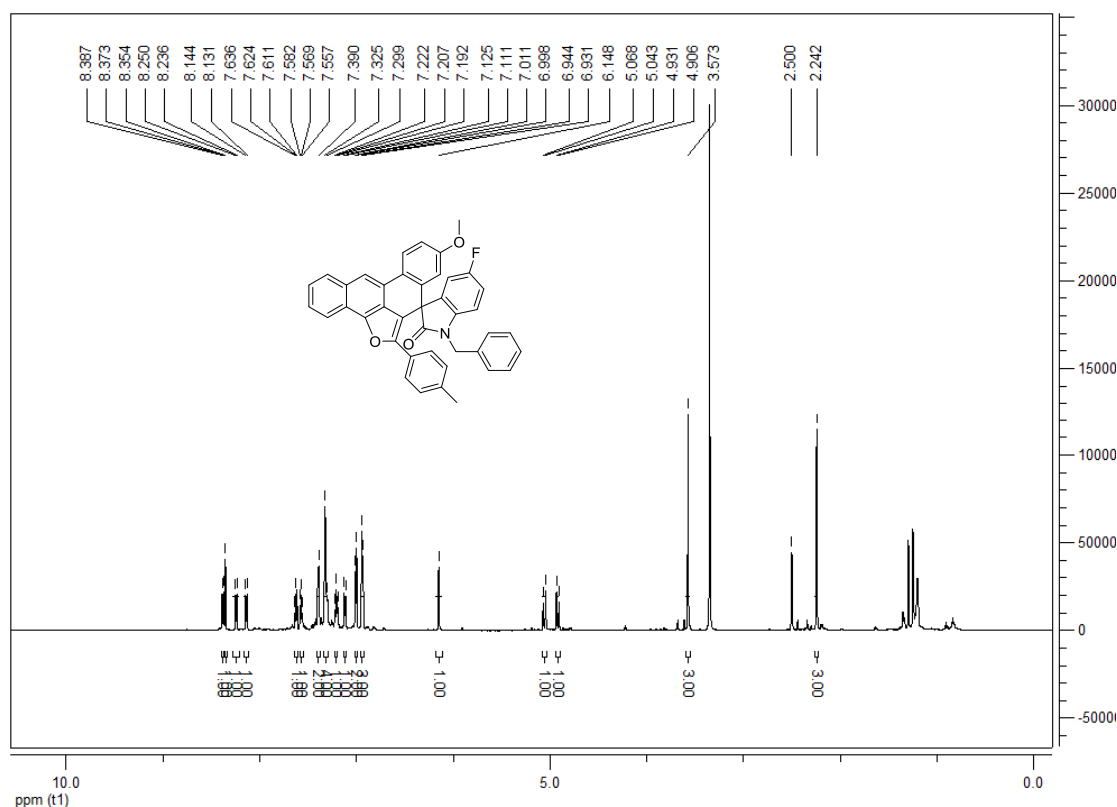
1-benzyl-5-chloro-9'-methoxy-6'-(p-tolyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one
(3l): Yellow solid, 64%, 0.197 g, m.p. 259-261 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.39 (d, *J* = 8.8 Hz, 1H, ArH), 8.37 (s, 1H, ArH), 8.25 (d, *J* = 8.0 Hz, 1H, ArH), 8.15 (d, *J* = 8.0 Hz, 1H, ArH), 7.66-7.62 (m, 1H, ArH), 7.60-7.56 (m, 1H, ArH), 7.44 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.40-7.37 (m, 2H, ArH), 7.35-7.32 (m, 4H, ArH), 7.13 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.09 (d, *J* = 2.4 Hz, 1H, ArH), 7.01 (d, *J* = 8.4 Hz, 2H, ArH), 6.96 (d, *J* = 8.4 Hz, 2H, ArH), 6.14 (d, *J* = 2.4 Hz, 1H, ArH), 5.06 (d, *J* = 15.2 Hz, 1H, CH), 4.93 (d, *J* = 15.2 Hz, 1H, CH), 3.34 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 176.3, 160.3, 150.7, 147.0, 142.2, 138.8, 137.5, 137.5, 136.2, 133.5, 129.7, 129.6, 129.5, 129.1, 128.5, 128.3, 128.2, 127.0, 126.9, 126.8, 126.3, 126.2, 125.0, 124.8, 123.5, 122.8, 120.3, 119.8, 114.8, 114.5, 113.4, 111.9, 111.9, 55.5, 53.0, 44.0, 21.2; IR (KBr) ν: 3037, 2918, 1724, 1604, 1568, 1478, 1425, 1367, 1323, 1244, 1166, 1080, 1042, 887, 814, 748, 700 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₂₉ClNO₃ ([M+H]⁺): 618.1830. Found: 618.1838.

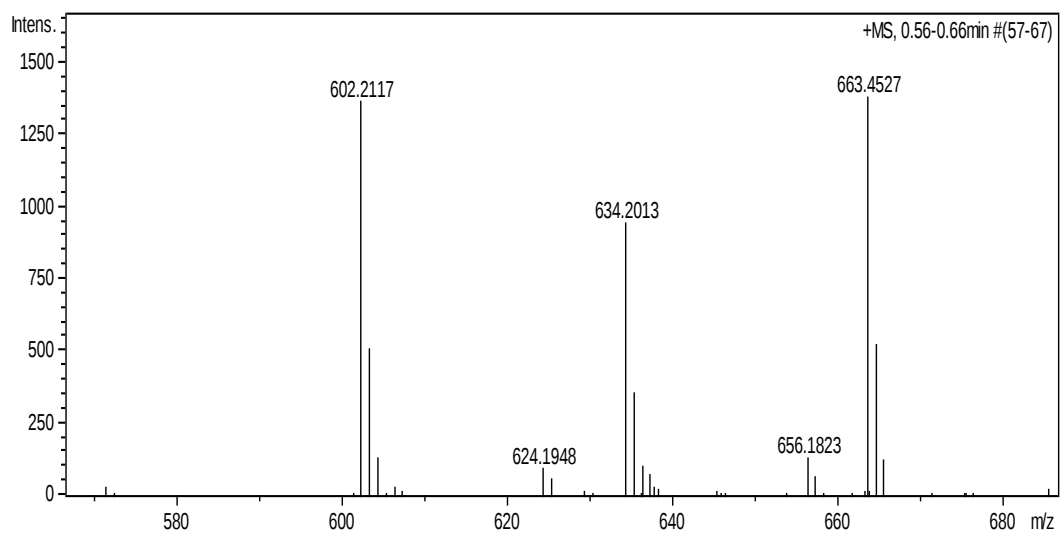
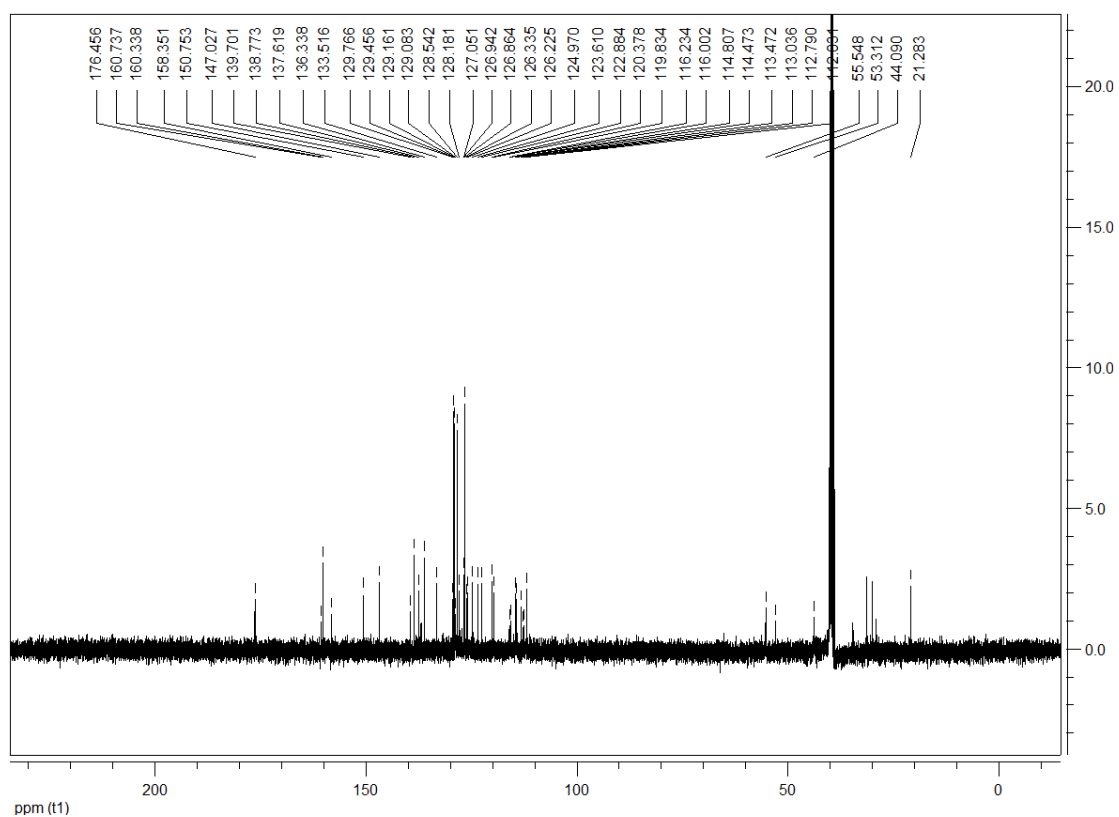






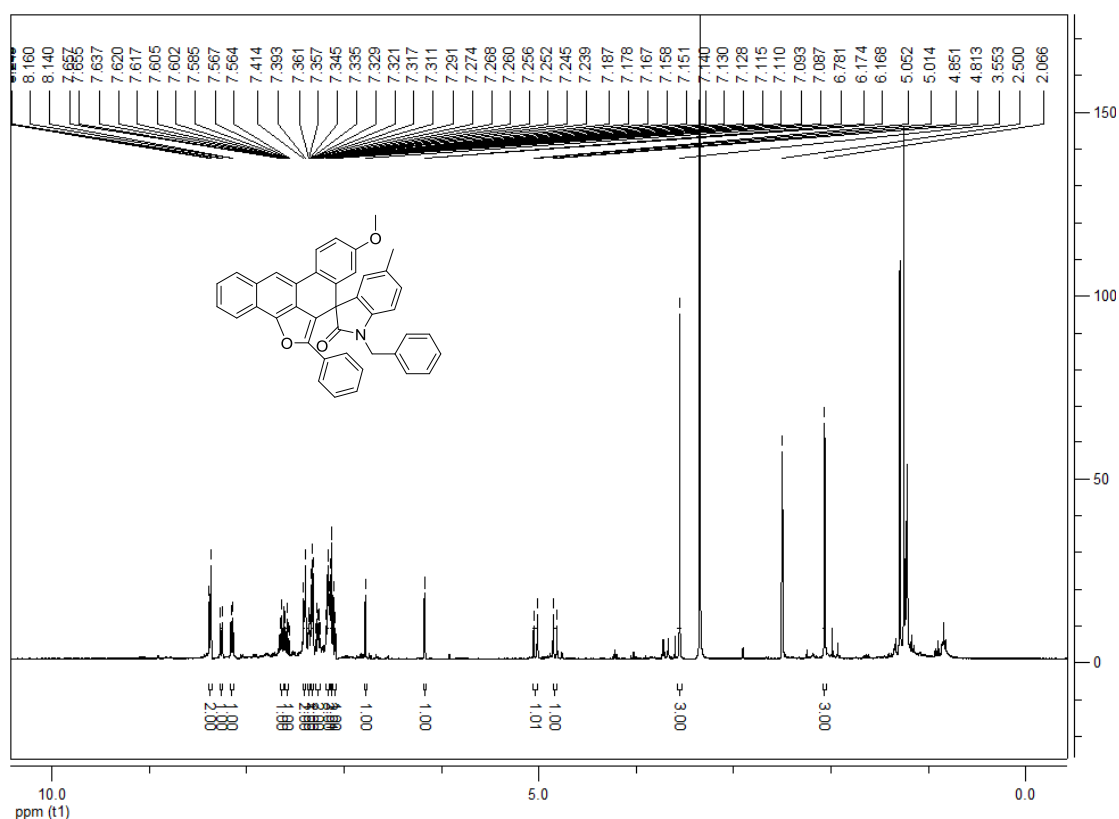
(3n): Yellow solid, 80%, 0.240 g, m.p. 241-243 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ: 8.38 (d, *J* = 8.4 Hz, 1H, ArH), 8.35 (s, 1H, ArH), 8.24 (d, *J* = 8.4 Hz, 1H, ArH), 8.14 (d, *J* = 7.8 Hz, 1H, ArH), 7.62 (t, *J* = 7.8 Hz, 1H, ArH), 7.57 (t, *J* = 7.8 Hz, 1H, ArH), 7.39 (brs, 2H, ArH), 7.33-7.30 (m, 4H, ArH), 7.21 (t, *J* = 9.0 Hz, 1H, ArH), 7.12 (d, *J* = 8.4 Hz, 1H, ArH), 7.00 (d, *J* = 7.8 Hz, 2H, ArH), 6.94-6.93 (m, 3H, ArH), 6.15 (s, 1H, ArH), 5.06 (d, *J* = 15.0 Hz, 1H, CH), 4.92 (d, *J* = 15.0 Hz, 1H, CH), 3.57 (s, 3H, OCH₃), 2.24 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 176.4, 160.3, 159.5 (d, *J* = 238.6 Hz), 150.7, 147.0, 139.7, 138.7, 137.1 (d, *J* = 7.8 Hz), 133.5, 129.7, 129.4, 129.1, 129.0, 128.5, 128.1, 127.0, 126.9, 126.8, 126.3, 126.2, 124.9, 123.6, 122.8, 120.3, 119.8, 116.1 (d, *J* = 23.2 Hz), 114.8, 114.4, 113.4, 112.9 (d, *J* = 24.6 Hz), 112.0, 55.5, 53.3, 44.0, 21.2; IR (KBr) ν: 3060, 2922, 2853, 1724, 1607, 1491, 1447, 1332, 1252, 1170, 1081, 1032, 965, 819, 747, 698 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₂₉FNO₃ ([M+H]⁺): 602.2126. Found: 602.2117.

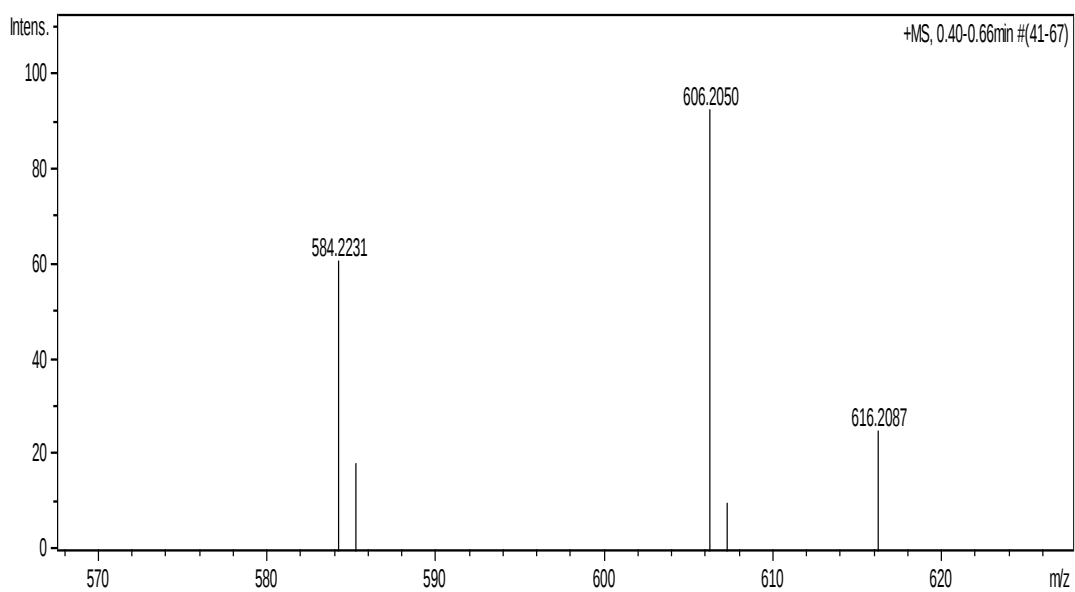
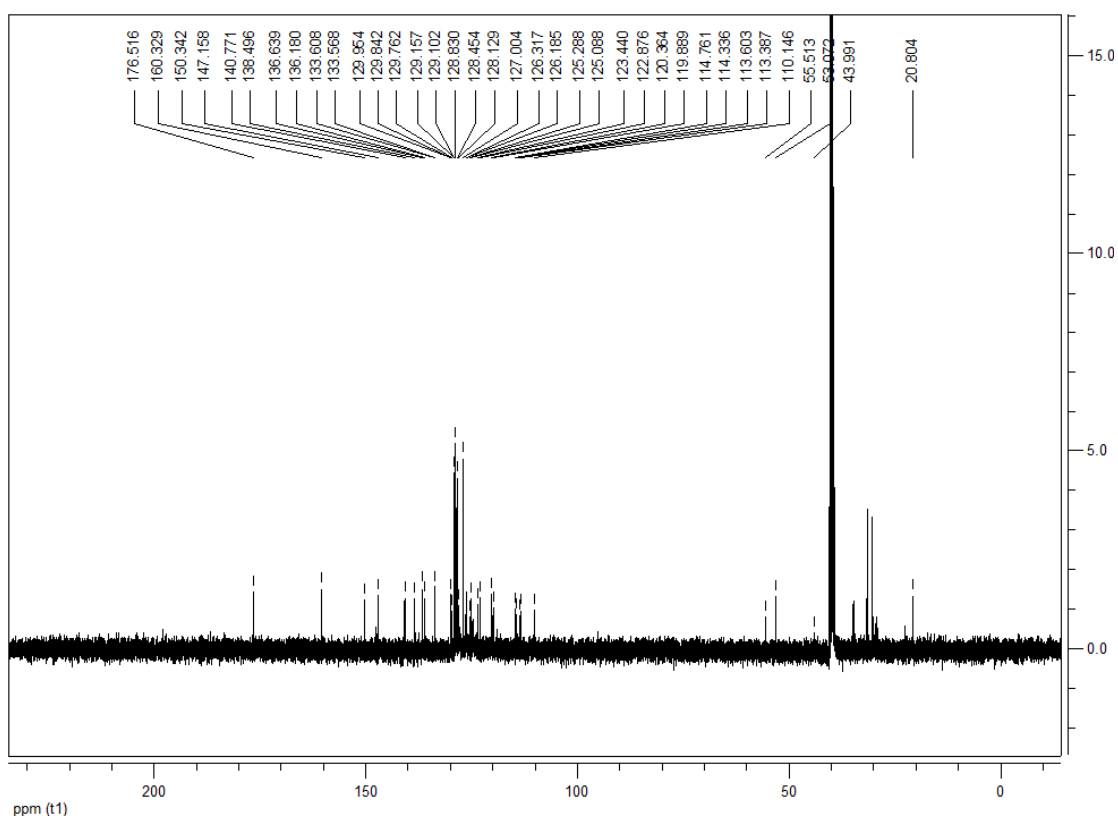


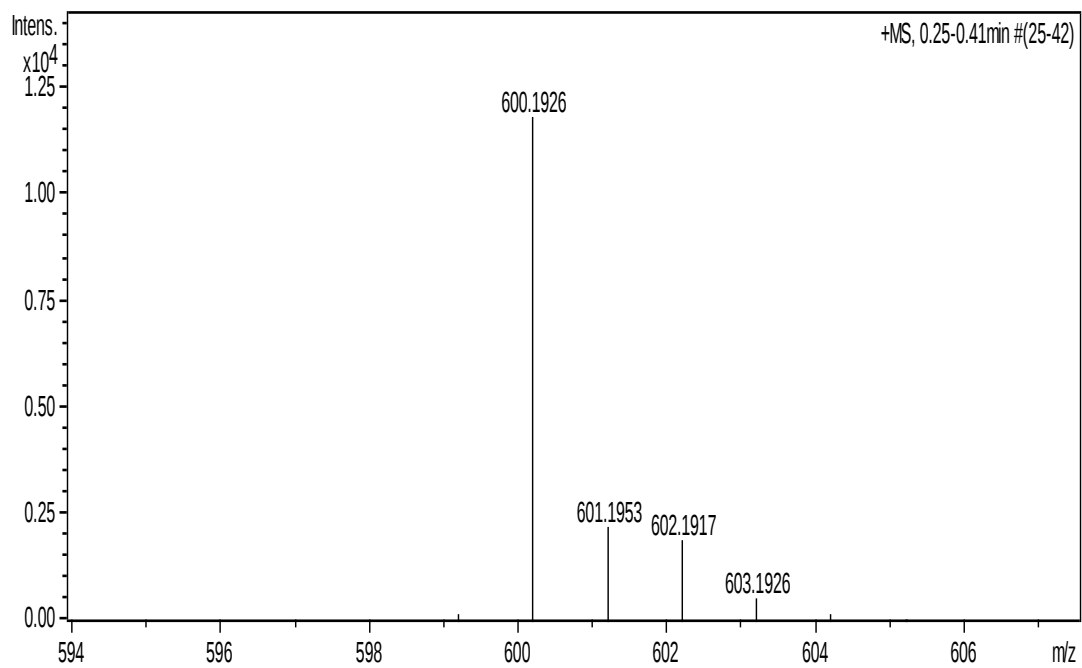
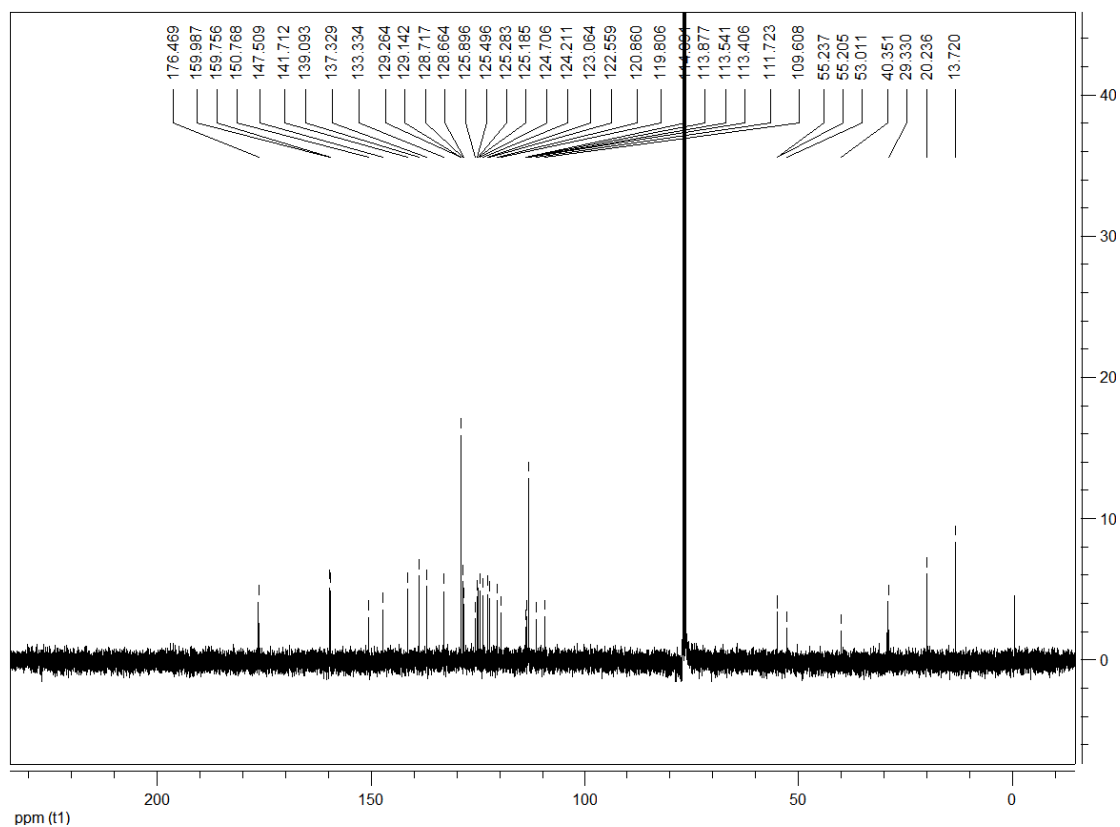


1-benzyl-9'-methoxy-5-methyl-6'-phenylspiro[indoline-3,7'-tetrapheno[7,6-bc]furan]-2-one

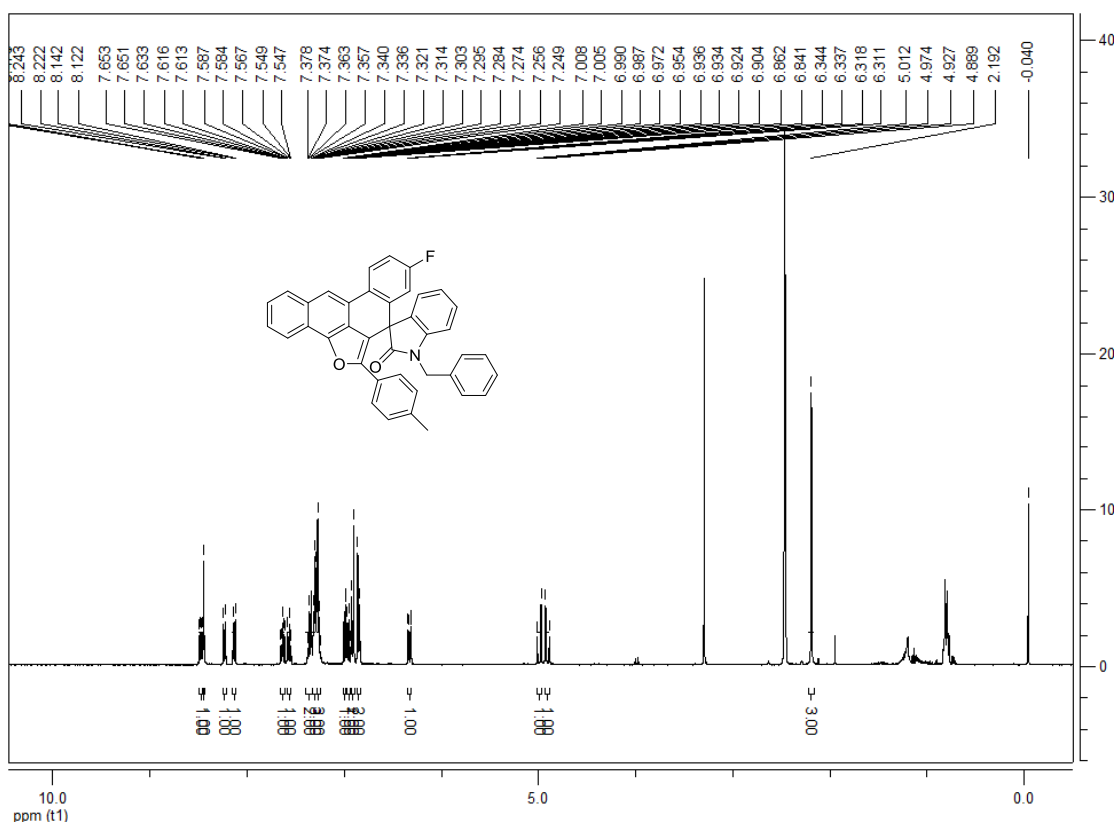
(3o): Yellow solid, 74%, 0.216 g, m.p. 254-256 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.38-8.36 (m, 2H, ArH), 8.26 (d, $J = 7.6$ Hz, 1H, ArH), 8.15 (d, $J = 8.0$ Hz, 1H, ArH), 7.66-7.62 (m, 1H, ArH), 7.61-7.56 (m, 1H, ArH), 7.41-7.39 (m, 2H, ArH), 7.36-7.35 (m, 1H, ArH), 7.34-7.31 (m, 2H, ArH), 7.29-7.24 (m, 2H, ArH), 7.19-7.15 (m, 3H, ArH), 7.14-7.13 (m, 2H, ArH), 7.12-7.09 (m, 1H, ArH), 6.78 (brs, 1H, ArH), 6.17 (d, $J = 2.4$ Hz, 1H, ArH), 5.03 (d, $J = 15.2$ Hz, 1H, CH), 4.83 (d, $J = 15.2$ Hz, 1H, CH), 3.55 (s, 3H, OCH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 176.5, 160.3, 150.3, 147.1, 140.7, 138.4, 136.6, 136.1, 133.6, 133.5, 129.9, 129.8, 129.7, 129.2, 129.1, 128.8, 128.4, 128.1, 127.0, 126.3, 126.1, 125.2, 125.0, 123.4, 122.8, 120.3, 119.8, 114.7, 114.3, 113.6, 113.3, 110.1, 55.5, 53.0, 43.9, 20.8; IR (KBr) ν : 3058, 2923, 2856, 1715, 1604, 1494, 1455, 1368, 1331, 1285, 1242, 1183, 1079, 1033, 960, 817, 754, 696 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{29}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 606.2040. Found: 606.2050.

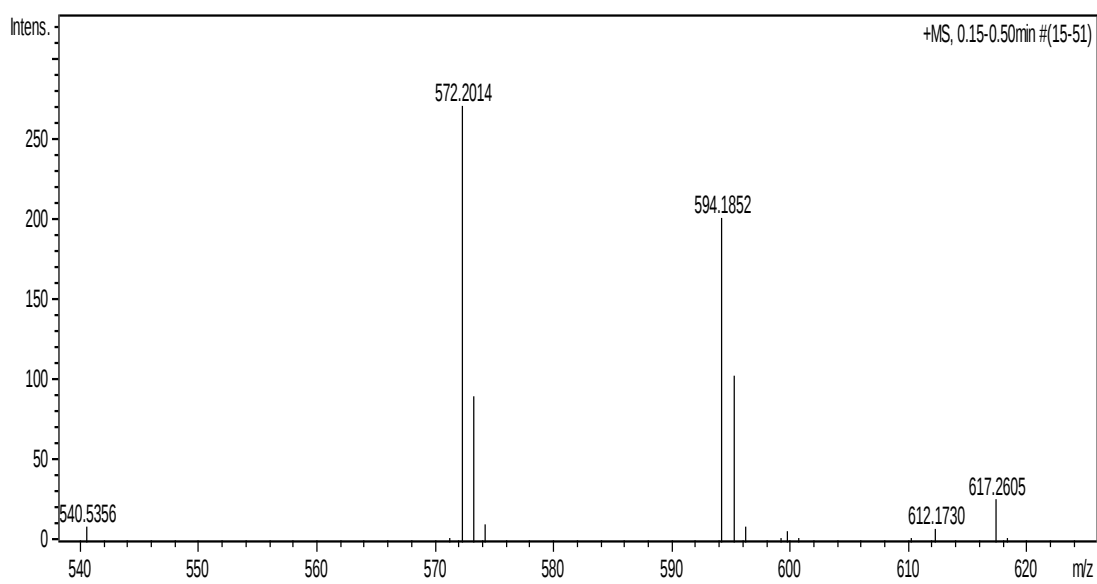
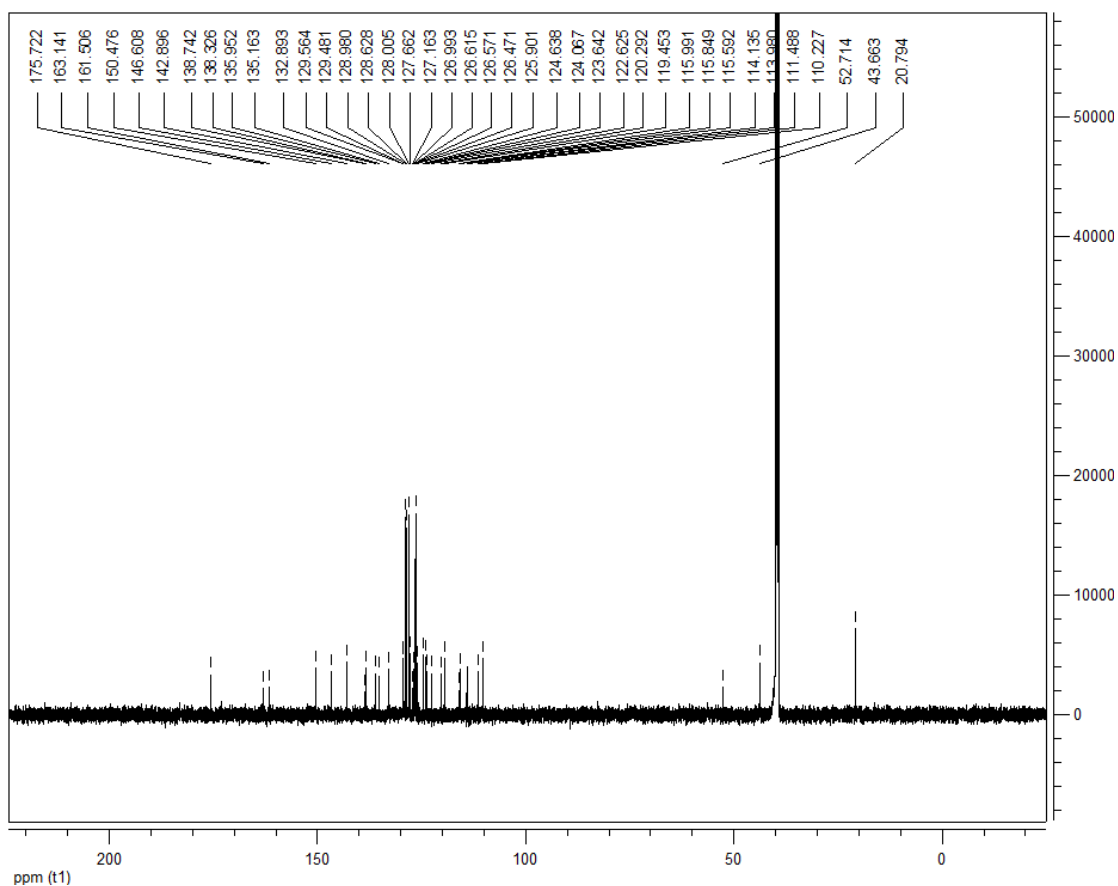


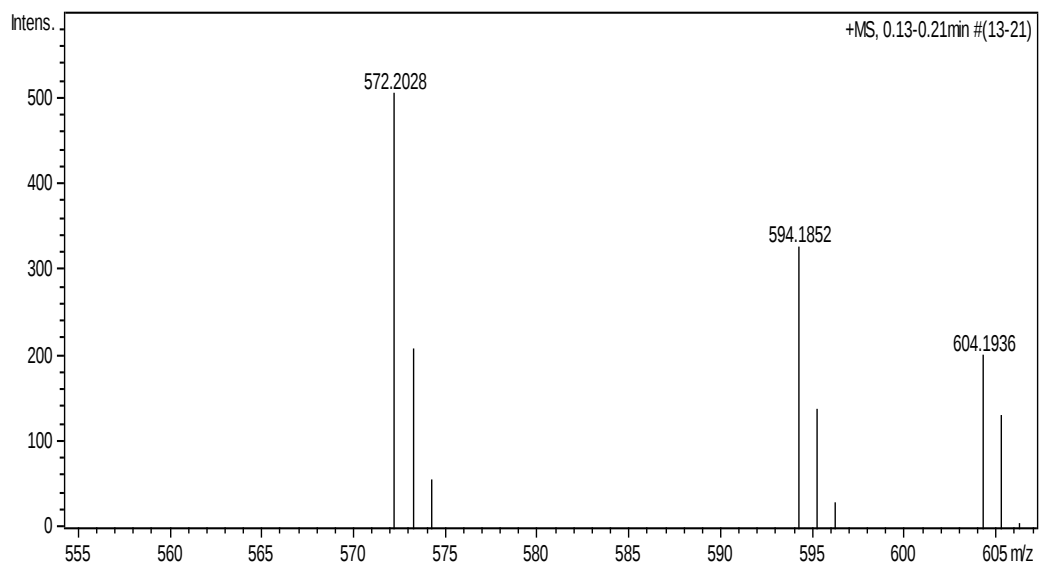
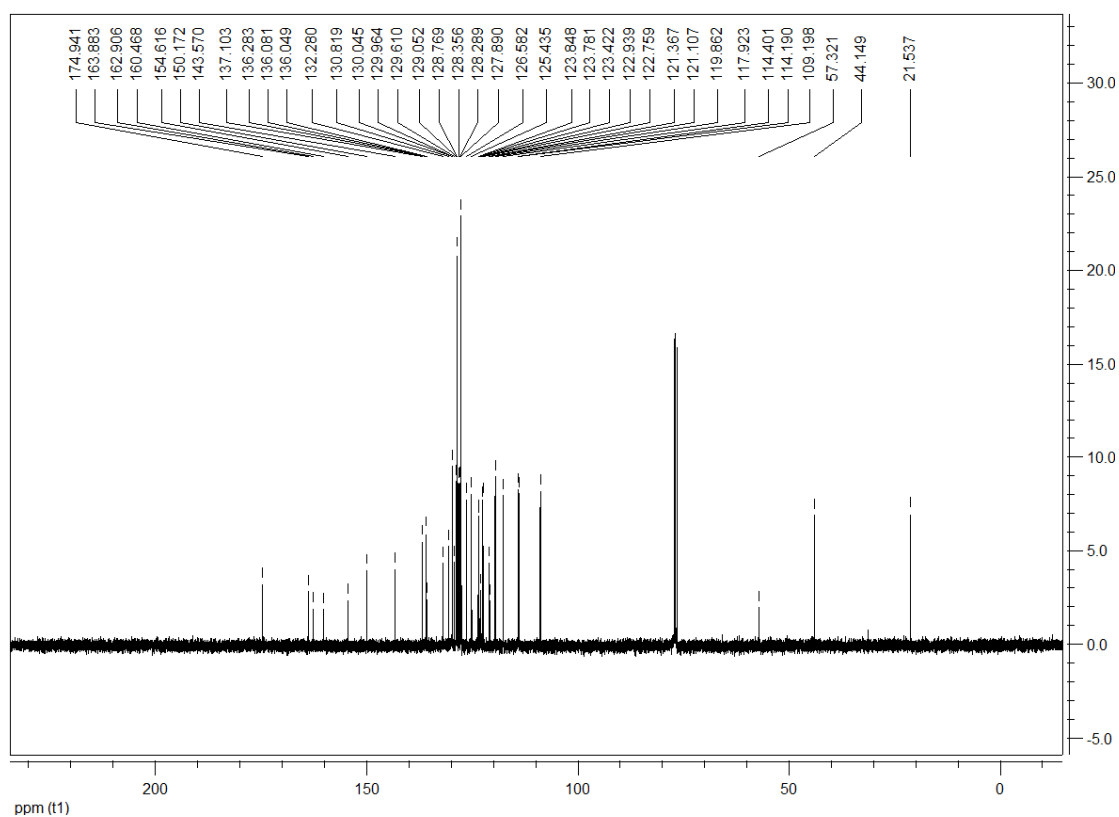




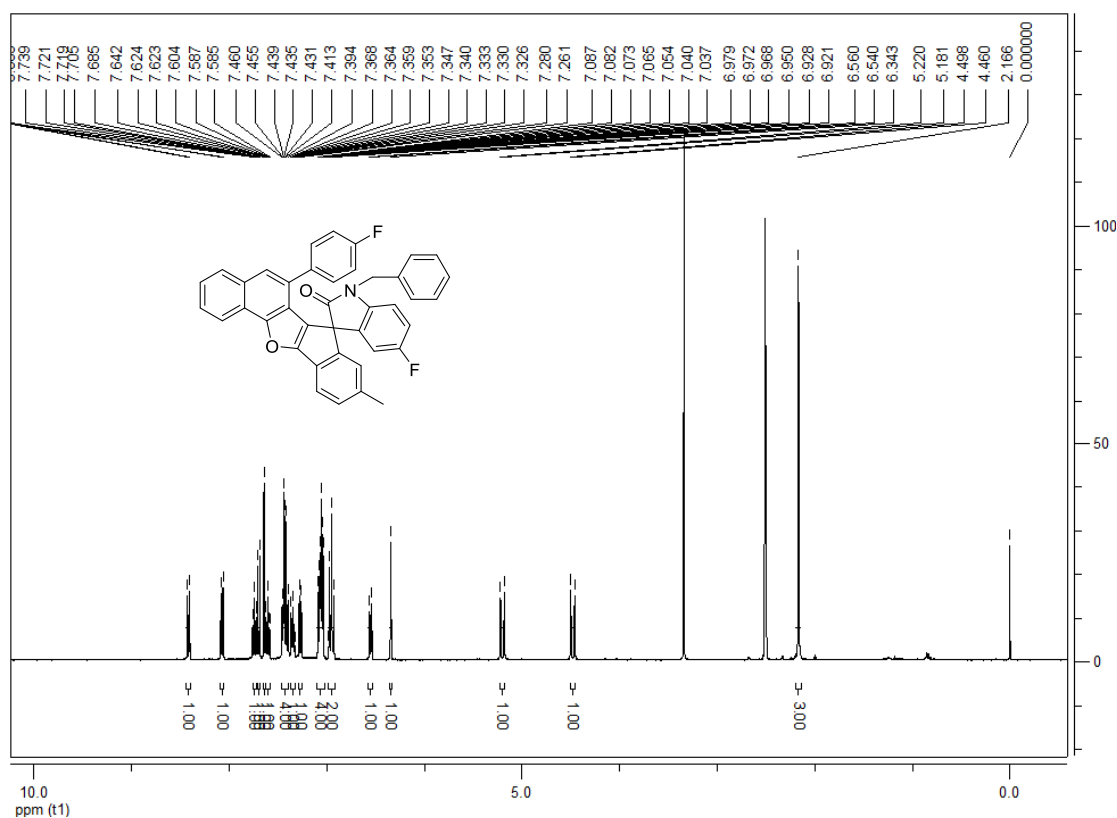
1-benzyl-9'-fluoro-6'-(*p*-tolyl)spiro[indoline-3,7'-tetrapheno[7,6-*bc*]furan]-2-one (3q): Yellow solid, 16%, 0.046 g, m.p. 247-249°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.49-8.46 (m, 1H, ArH), 8.45 (s, 1H, ArH), 8.23 (d, $J = 8.4$ Hz, 1H, ArH), 8.13 (d, $J = 8.0$ Hz, 1H, ArH), 7.65-7.61 (m, 1H, ArH), 7.59-7.55 (m, 1H, ArH), 7.38-7.34 (m, 2H, ArH), 7.32-7.30 (m, 3H, ArH), 7.28-7.25 (m, 3H, ArH), 7.00 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H, ArH), 6.97-6.93 (m, 1H, ArH), 6.91 (d, $J = 8.0$ Hz, 2H, ArH), 6.85 (d, $J = 8.4$ Hz, 2H, ArH), 6.33 (dd, $J_1 = 10.4$ Hz, $J_2 = 2.8$ Hz, 1H, ArH), 4.99 (d, $J = 15.2$ Hz, 1H, CH), 4.91 (d, $J = 15.2$ Hz, 1H, CH), 2.19 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ : 175.7, 162.3 (d, $J = 245.2$ Hz), 150.4, 146.6, 142.8, 138.7, 138.3, 135.9, 135.1, 132.8, 129.5, 129.4, 128.9, 128.6, 128.0, 127.6, 127.1, 126.9, 126.6, 126.5, 126.4, 125.9, 124.6, 124.0, 123.6, 122.6, 120.2, 119.4, 115.9 (d, $J = 21.3$ Hz), 115.5, 114.0 (d, $J = 23.3$ Hz), 111.4, 110.2, 52.7, 43.6, 20.7; IR (KBr) ν : 3061, 2918, 1724, 1605, 1495, 1448, 1337, 1268, 1220, 1167, 1062, 1023, 957, 887, 818, 739, 696 cm^{-1} ; HRMS (ESI) Calcd. for $\text{C}_{40}\text{H}_{27}\text{FNO}_3$ ($[\text{M}+\text{H}]^+$): 572.2020. Found: 572.2014.

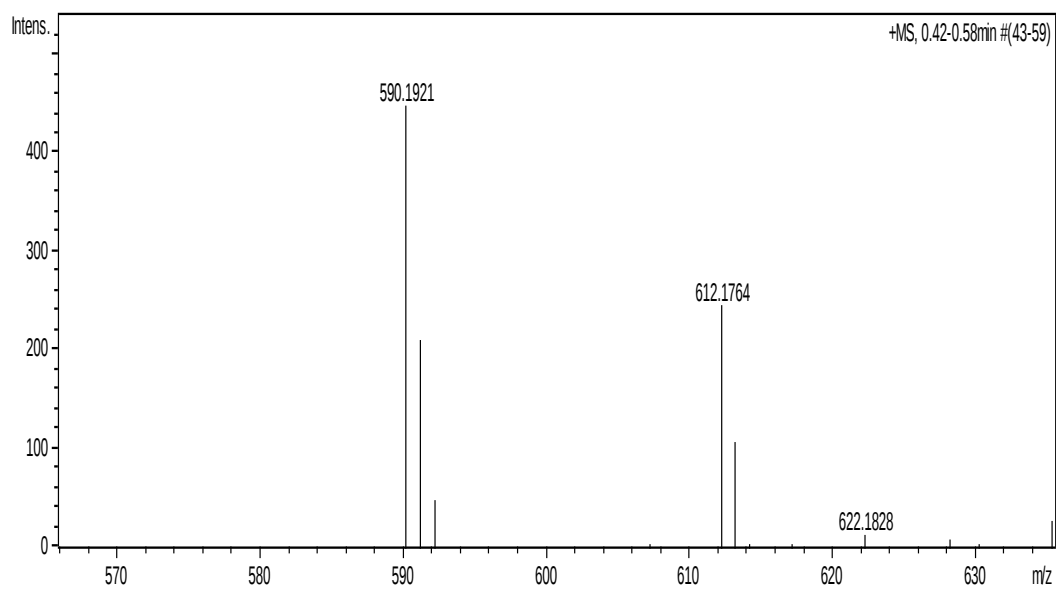
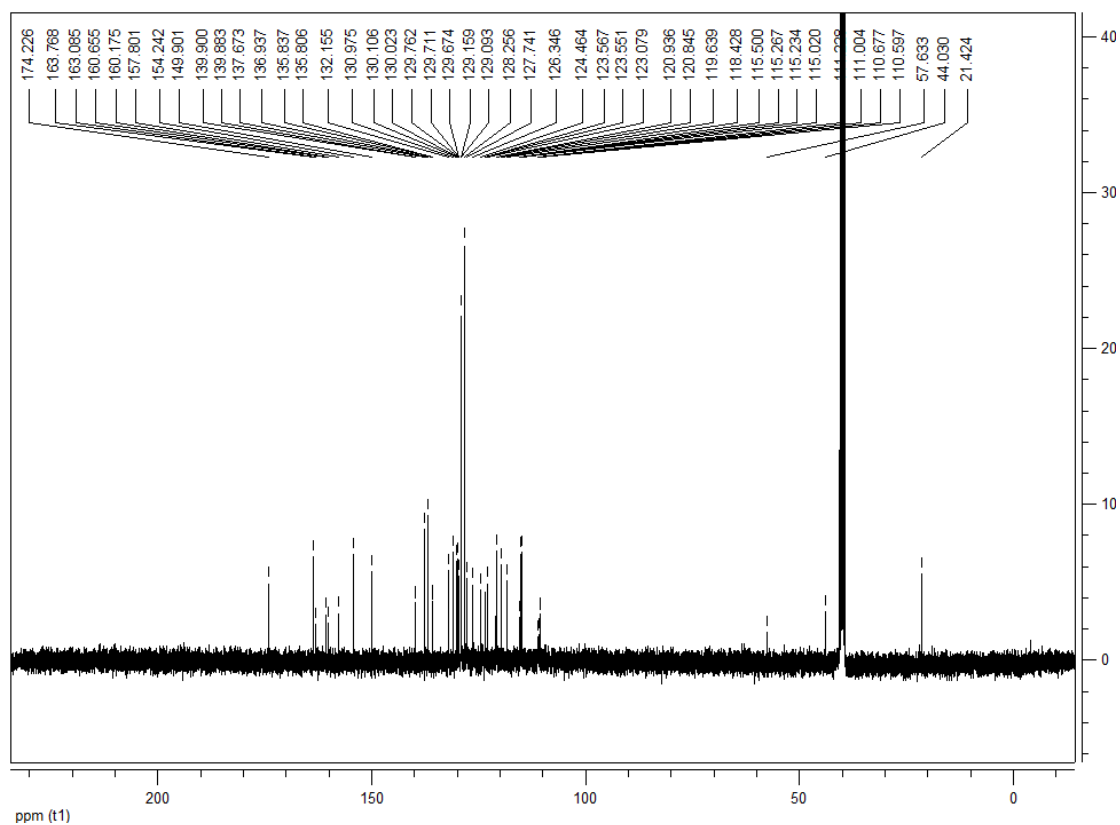


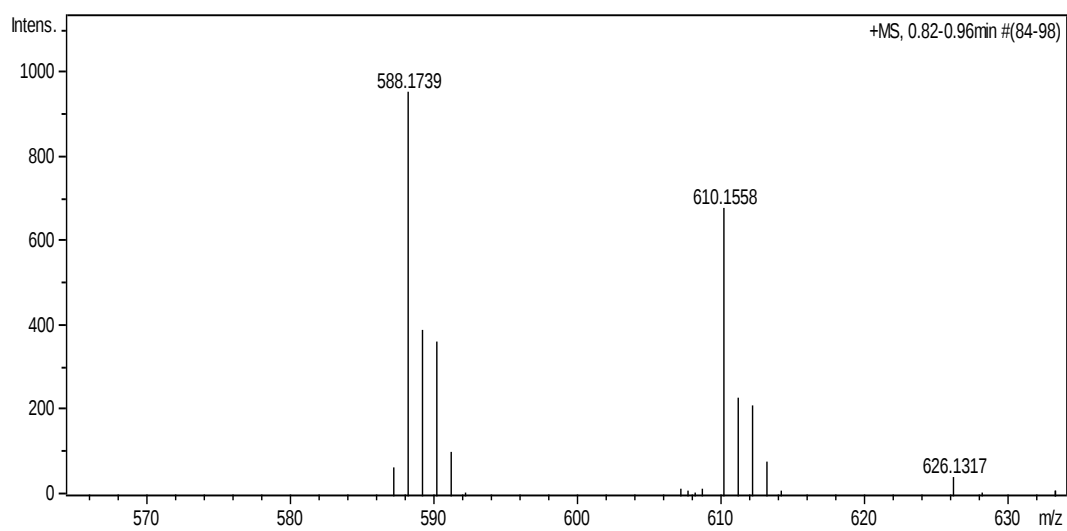
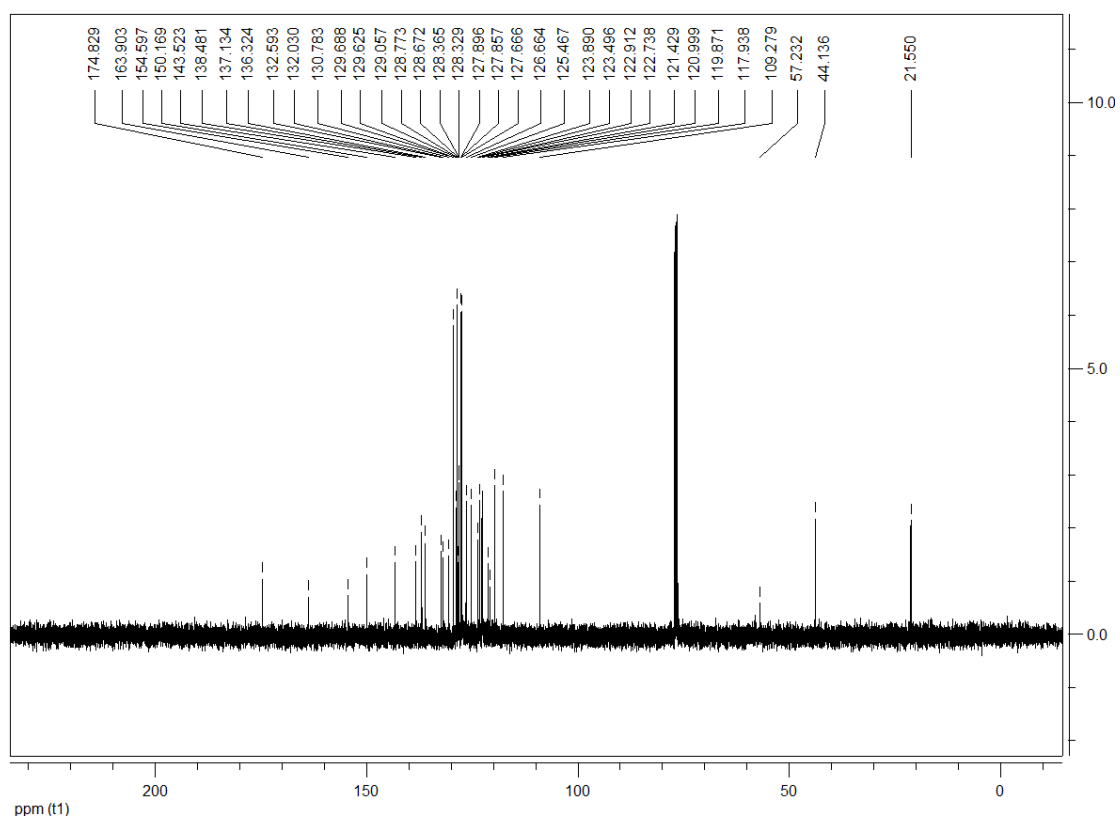




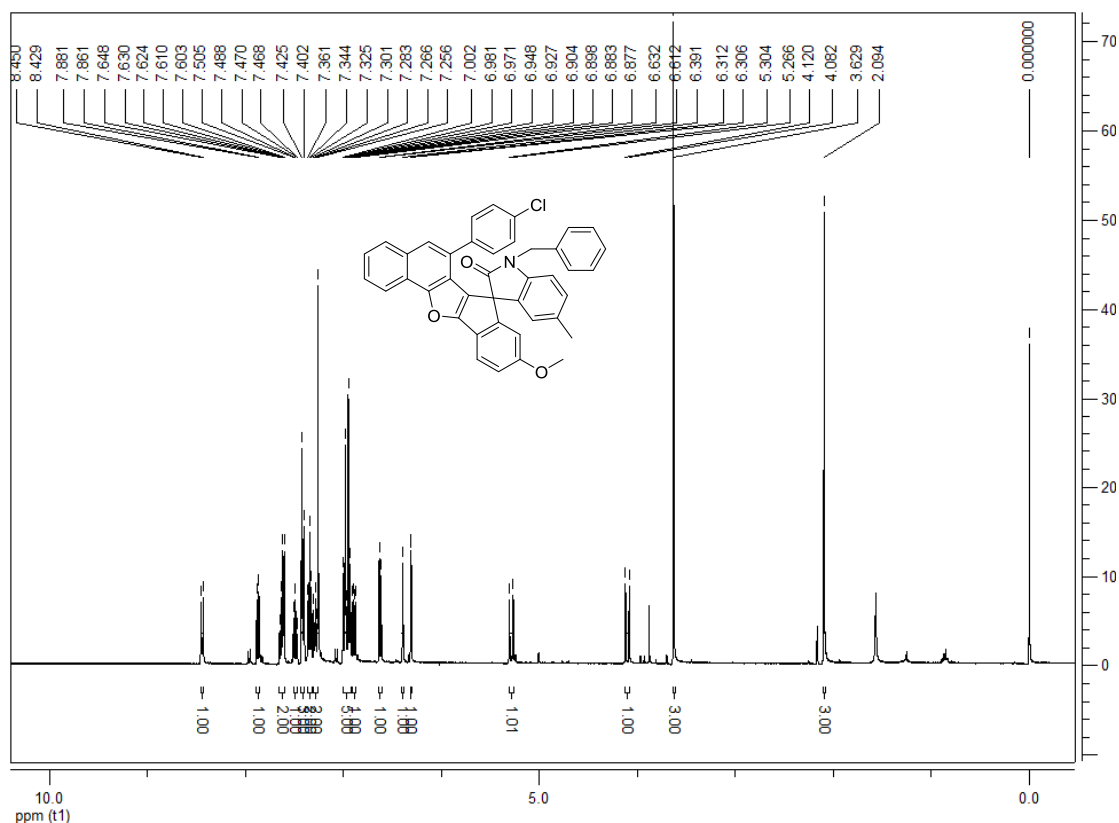
1'-benzyl-5'-fluoro-6-(4-fluorophenyl)-9-methylspiro[indeno[1,2-*b*]naphtho[2,1-*d*]furan-7,3'-indolin]-2'-one (4r): white solid, 43%, 0.126 g, m.p. 240-242 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.42 (d, *J* = 8.0 Hz, 1H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH), 7.76-7.72 (m, 1H, ArH), 7.70 (d, *J* = 8.0 Hz, 1H, ArH), 7.64 (s, 1H, ArH), 7.62-7.59 (m, 1H, ArH), 7.46-7.39 (m, 4H, ArH), 7.37-7.33 (m, 1H, ArH), 7.27 (d, *J* = 7.6 Hz, 1H, ArH), 7.09-7.04 (m, 4H, ArH), 6.98-6.92 (m, 2H, ArH), 6.56-6.54 (m, 1H, ArH), 6.34 (s, 1H, ArH), 5.20 (d, *J* = 15.6 Hz, 1H, CH), 4.48 (d, *J* = 15.2 Hz, 1H, CH), 2.17 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 174.2, 163.7, 161.9 (d, *J* = 243.0 Hz), 160.0 (d, *J* = 237.4 Hz), 154.2, 149.9, 139.9 (d, *J* = 1.7 Hz), 137.6, 136.9, 135.8 (d, *J* = 3.1 Hz), 132.1, 130.9, 130.1, 130.0, 129.7, 129.7, 129.6, 129.1, 129.0, 128.2, 127.7, 126.3, 124.4, 123.5, 123.5, 123.0, 120.9, 120.8, 119.6, 118.4, 115.4 (d, *J* = 23.3 Hz), 115.1 (d, *J* = 21.4 Hz), 111.1 (d, *J* = 22.4 Hz), 110.6, 110.5, 57.6, 44.0, 21.4; IR (KBr) ν: 3040, 2955, 2915, 1717, 1606, 1495, 1348, 1232, 1171, 1072, 1018, 822, 745, 694 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₀H₂₆F₂NO₂ ([M+H]⁺): 590.1926. Found: 590.1921.

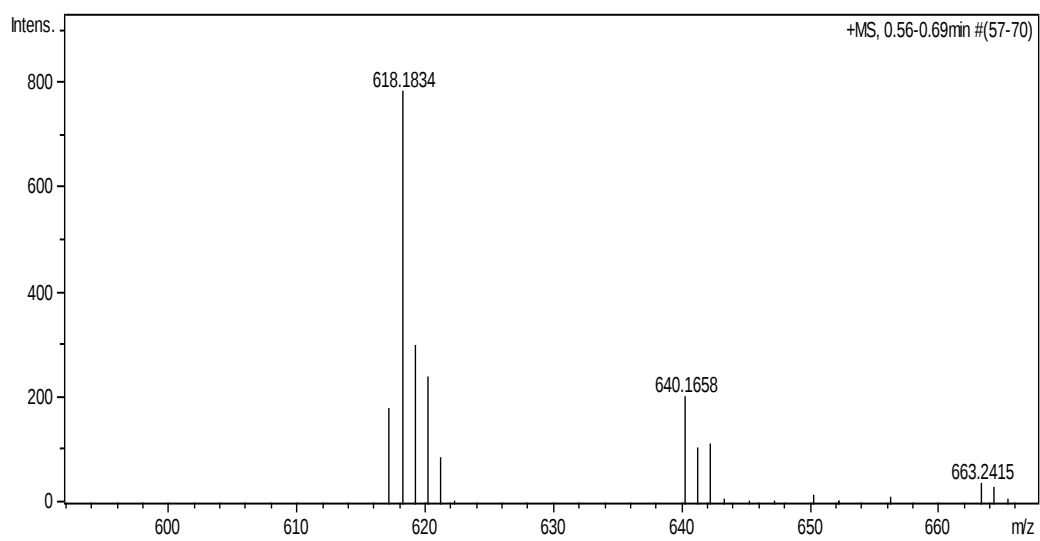
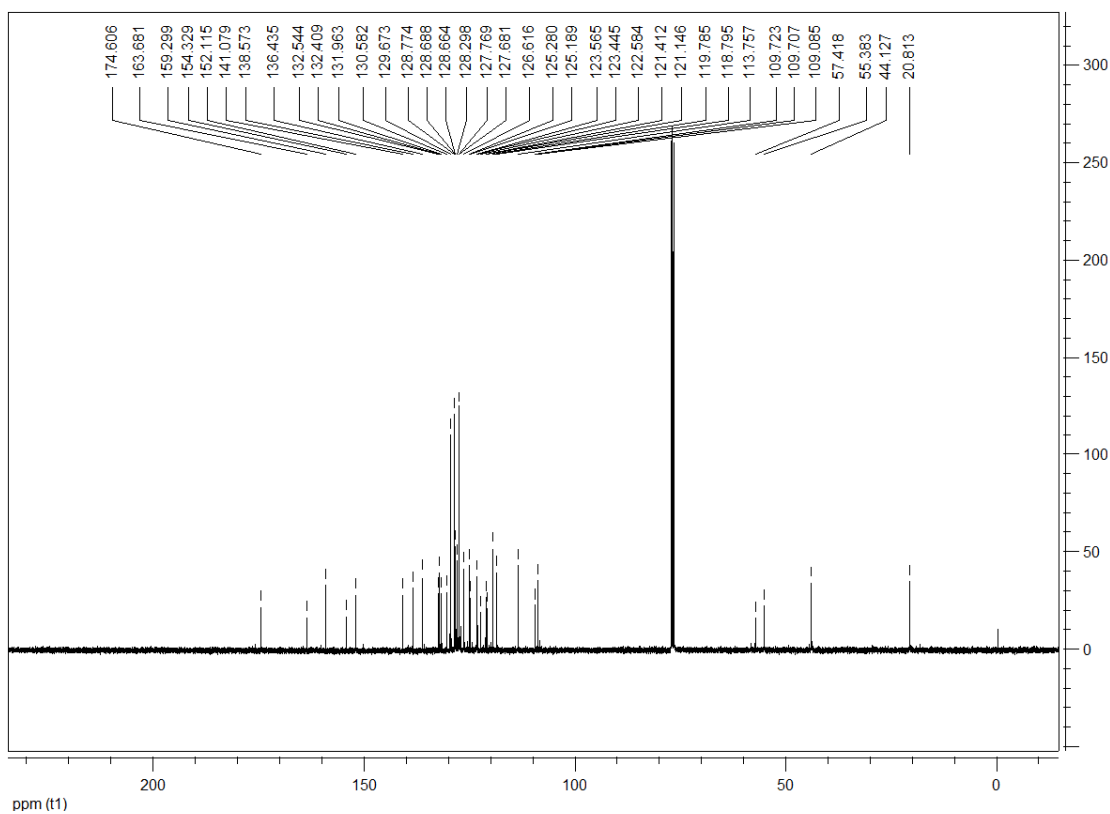




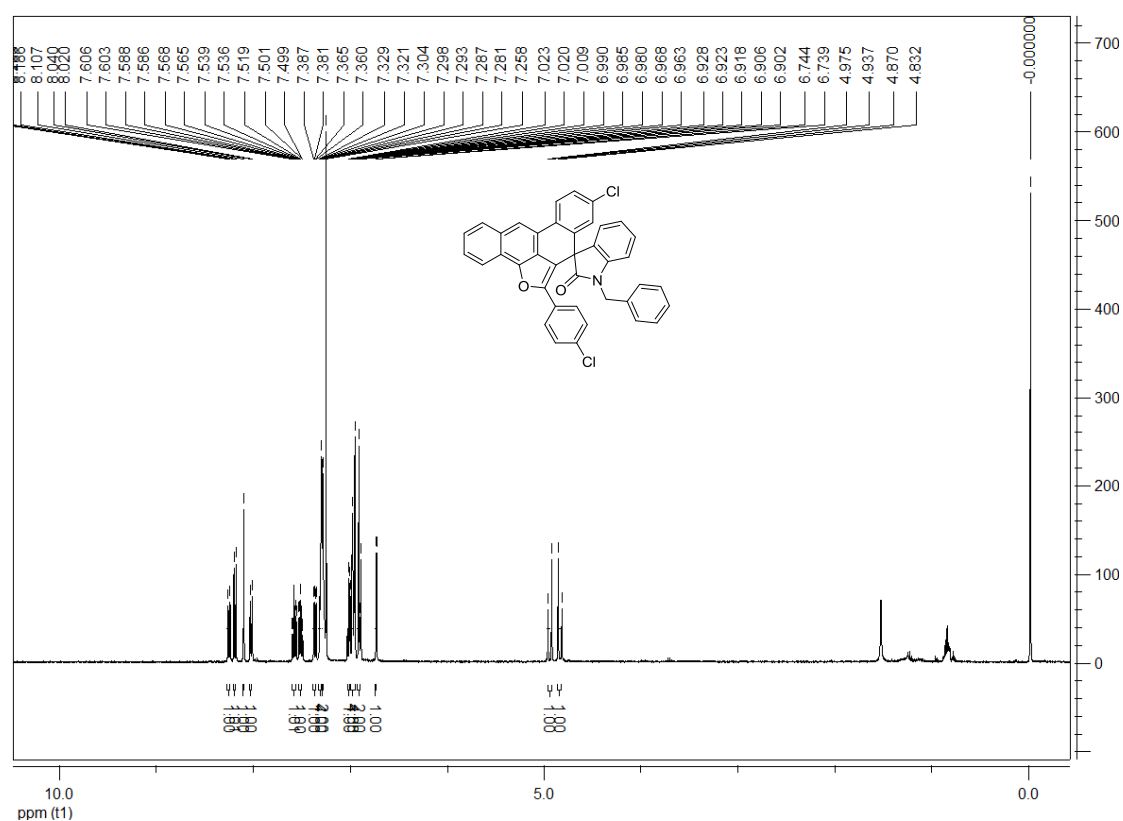


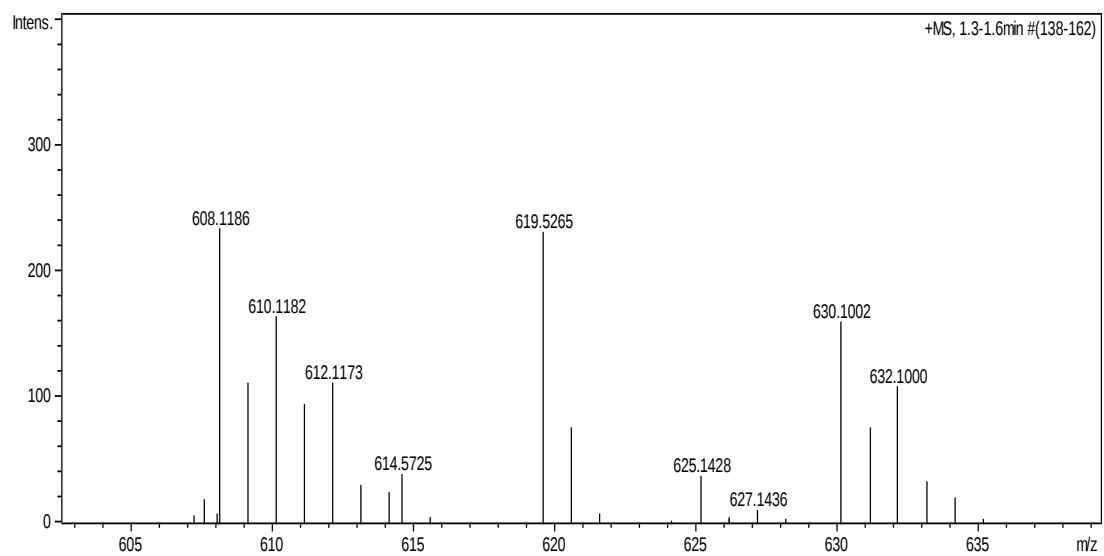
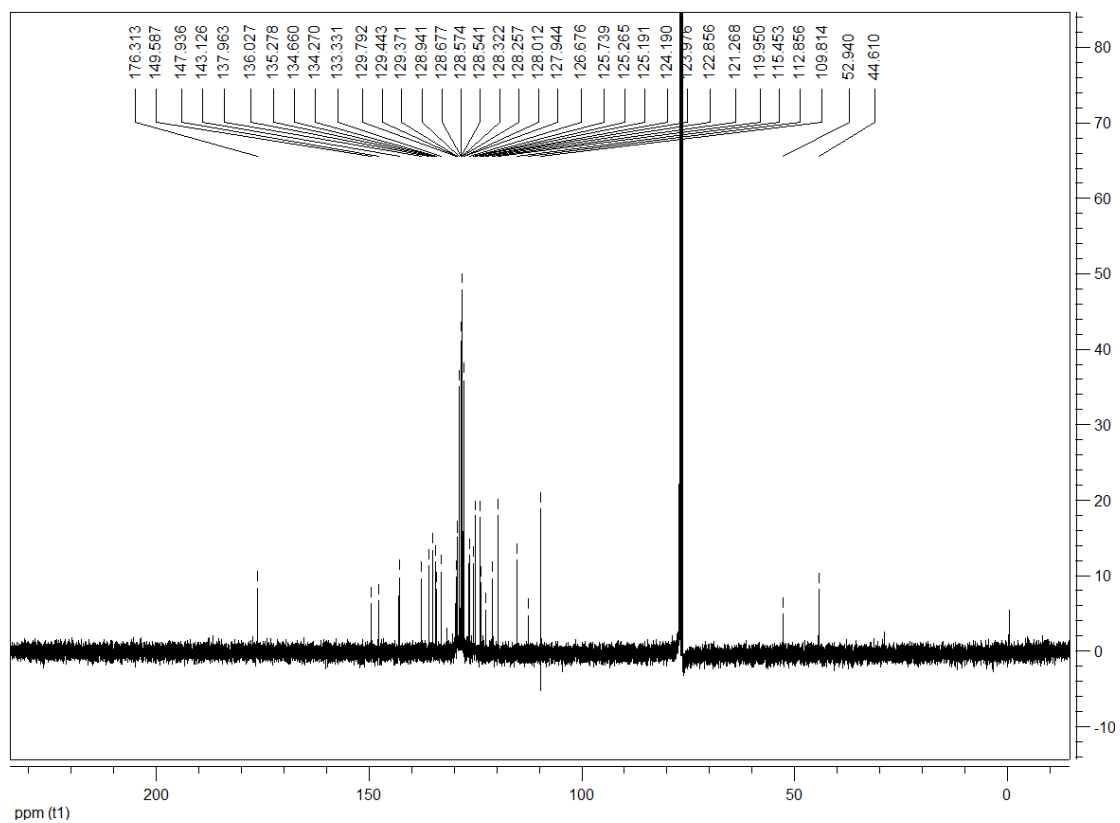
1'-benzyl-6-(4-chlorophenyl)-9-methoxy-5'-methylspiro[indeno[1,2-*b*]naphtho[2,1-*d*]furan-7,3'-indolin]-2'-one (4t): white solid, 62%, 0.191 g, m.p. 230-232°C; ¹H NMR (400 MHz, CDCl₃) δ: 8.44 (d, *J* = 8.4 Hz, 1H, ArH), 7.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.65-7.60 (m, 2H, ArH), 7.51-7.47 (m, 1H, ArH), 7.43-7.40 (m, 3H, ArH), 7.36-7.33 (m, 2H, ArH), 7.30-7.27 (m, 2H, ArH), 7.00-6.93 (m, 5H, ArH), 6.89 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 6.62 (d, *J* = 8.0 Hz, 1H, ArH), 6.31 (d, *J* = 2.4 Hz, 1H, ArH), 5.29 (d, *J* = 15.2 Hz, 1H, CH), 4.10 (d, *J* = 15.2 Hz, 1H, CH), 3.63 (s, 3H, OCH₃), 2.09 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 174.6, 163.6, 159.2, 154.3, 152.1, 141.0, 138.5, 136.4, 132.5, 132.4, 131.9, 130.5, 129.6, 128.7, 128.6, 128.6, 128.2, 127.7, 127.6, 126.6, 125.2, 125.1, 123.5, 123.4, 122.5, 121.4, 121.1, 119.7, 118.7, 113.7, 109.7, 109.7, 109.0, 57.4, 55.3, 44.1, 20.8; IR (KBr) ν: 3057, 2946, 2832, 1715, 1596, 1534, 1492, 1440, 1338, 1278, 1229, 1180, 1126, 1084, 1021, 974, 917, 814, 745, 696 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₂₉ClNO₃ ([M+H]⁺): 618.1830. Found: 618.1834.



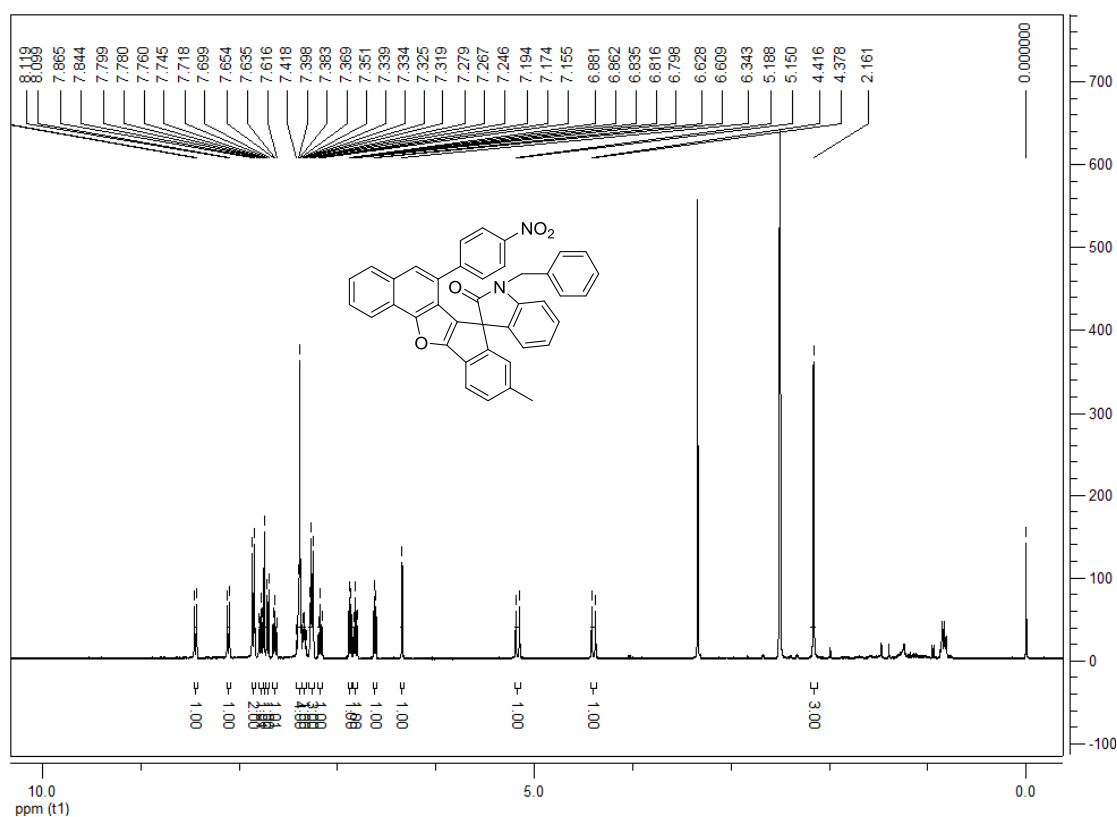


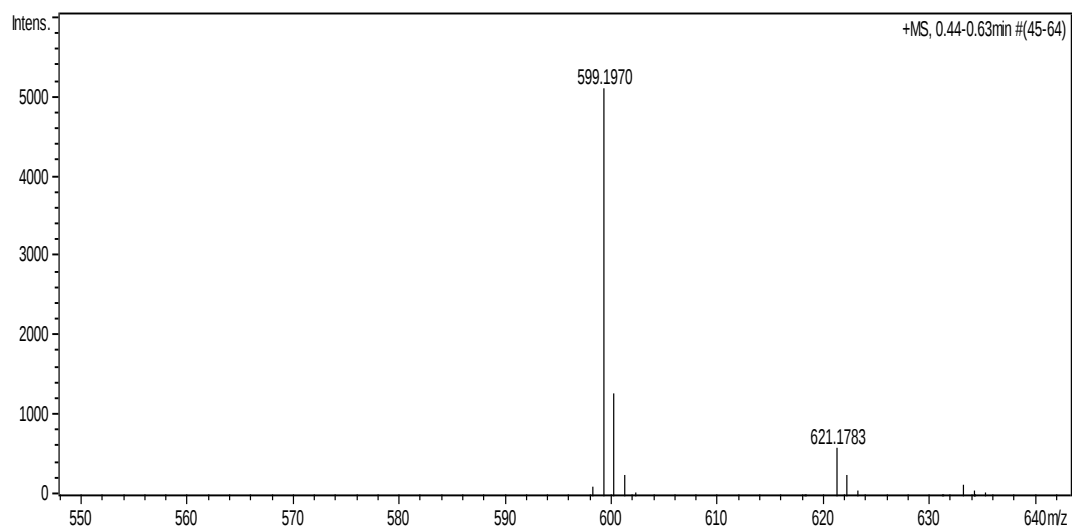
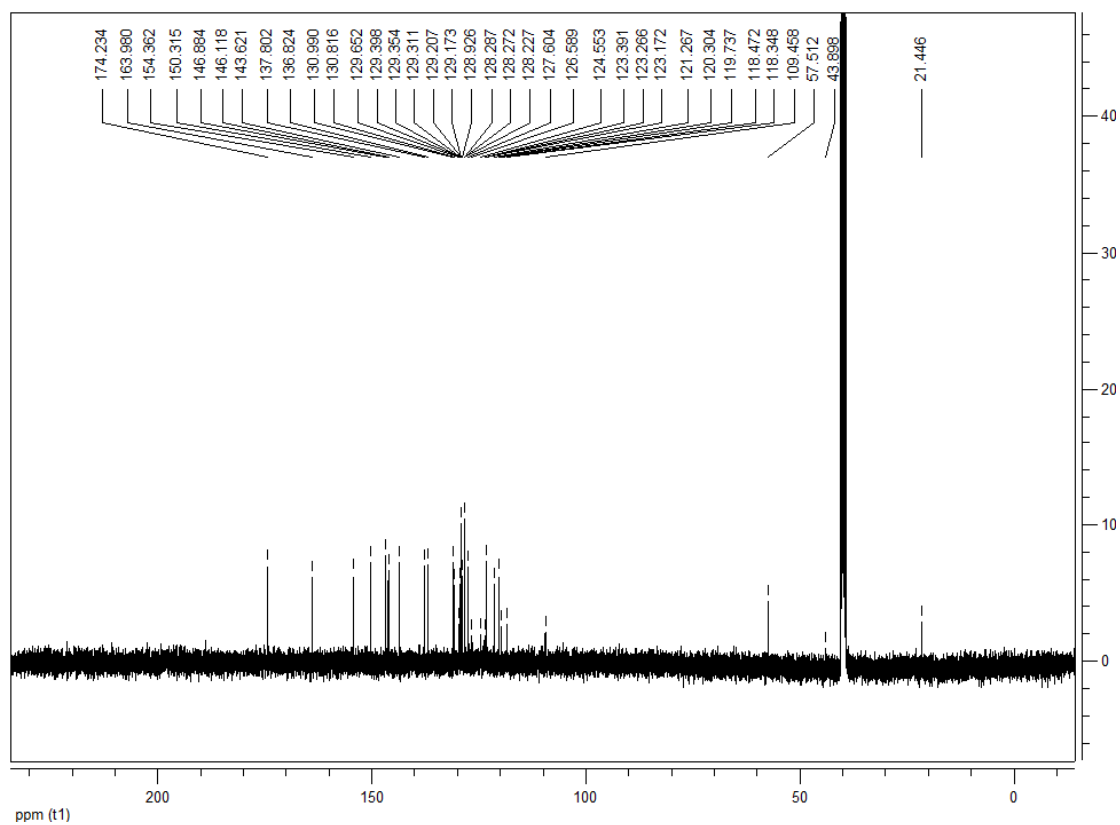
(3u): white solid, 5%, 0.121 g, m.p. 224-226°C; ¹H NMR (400 MHz, CDCl₃) δ: 8.26 (d, *J* = 8.4 Hz, 1H, ArH), 8.20 (d, *J* = 8.4 Hz, 1H, ArH), 8.11 (s, 1H, ArH), 8.03 (d, *J* = 8.0 Hz, 1H, ArH), 7.61-7.59 (m, 1H, ArH), 7.54-7.50 (m, 1H, ArH), 7.37 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.33-7.30 (m, 4H, ArH), 7.29-7.28 (m, 2H, ArH), 7.02-7.01 (m, 1H, ArH), 6.99-6.96 (m, 4H, ArH), 6.93-6.90 (m, 2H, ArH), 6.74 (d, *J* = 2.0 Hz, 1H, ArH), 4.96 (d, *J* = 15.2 Hz, 1H, CH), 4.85 (d, *J* = 15.2 Hz, 1H, CH); ¹³C NMR (100 MHz, CDCl₃) δ: 176.3, 149.5, 147.9, 143.1, 137.9, 136.0, 135.2, 134.6, 134.2, 133.3, 129.7, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 126.6, 125.7, 125.2, 125.1, 124.1, 123.9, 122.8, 121.2, 119.9, 115.4, 112.8, 109.8, 52.9, 44.6; IR (KBr) ν: 3060, 2921, 2850, 1717, 1603, 1482, 1342, 1263, 1221, 1166, 1084, 1011, 941, 909, 830, 746, 704 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₉H₂₄Cl₂NO₂ ([M+H]⁺): 608.1106. Found: 608.1186.



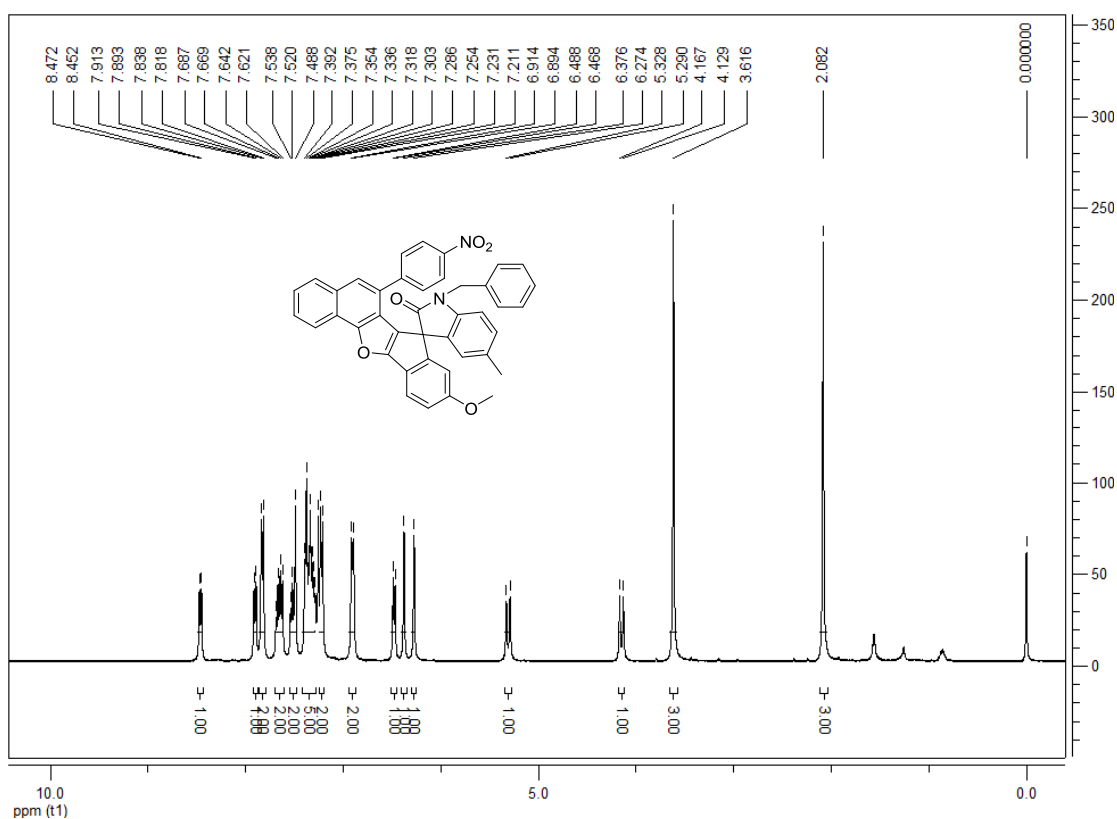


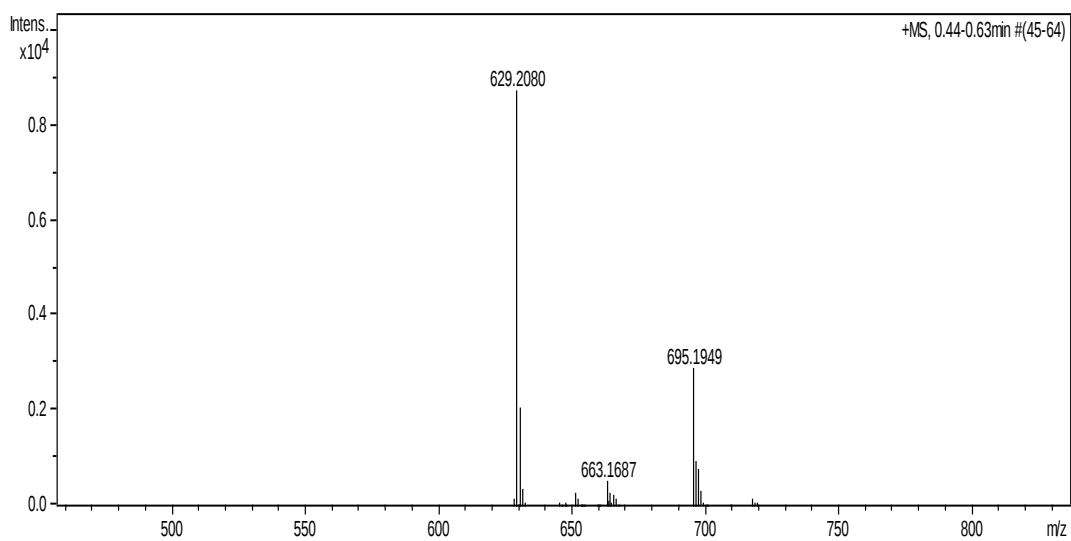
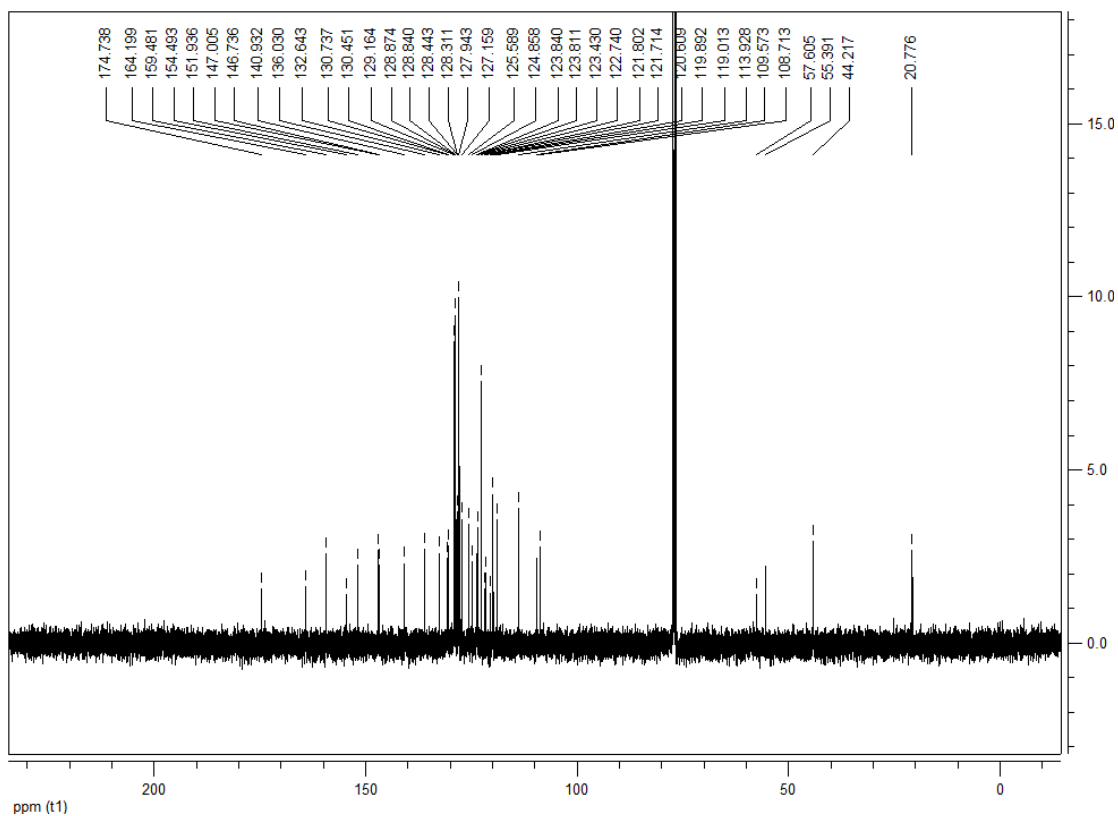
1'-benzyl-9-methyl-6-(4-nitrophenyl)spiro[indeno[1,2-*b*]naphtho[2,1-*d*]furan-7,3'-indolin]-2'-one (4v): Light yellow solid, 66%, 0.210 g, m.p. 226-228°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.44 (d, *J* = 8.0 Hz, 1H, ArH), 8.11 (d, *J* = 8.0 Hz, 1H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 7.78 (t, *J* = 8.0 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.71 (d, *J* = 7.6 Hz, 1H, ArH), 7.64 (d, *J* = 8.0 Hz, 1H, ArH), 7.42-7.37 (m, 4H, ArH), 7.35-7.32 (m, 1H, ArH), 7.28-7.25 (m, 3H, ArH), 7.17 (t, *J* = 8.0 Hz, 1H, ArH), 6.87 (d, *J* = 7.6 Hz, 1H, ArH), 6.82 (t, *J* = 7.6 Hz, 1H, ArH), 6.62 (d, *J* = 7.6 Hz, 1H, ArH), 6.34 (s, 1H, ArH), 5.17 (d, *J* = 15.2 Hz, 1H, CH), 4.40 (d, *J* = 15.2 Hz, 1H, CH), 2.16 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 174.2, 163.9, 154.3, 150.3, 146.8, 146.1, 143.6, 137.8, 136.8, 130.9, 130.8, 129.6, 129.3, 129.3, 129.3, 129.2, 129.1, 128.9, 128.2, 128.2, 128.2, 127.6, 126.5, 124.5, 123.3, 123.2, 123.1, 121.2, 120.3, 119.7, 118.4, 118.3, 109.4, 57.5, 43.8, 21.4; IR (KBr) ν: 3056, 2950, 1717, 1602, 1518, 1481, 1343, 1171, 1106, 1068, 1018, 977, 911, 851, 749 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₀H₂₇N₂O₄ ([M+H]⁺): 599.1965. Found: 599.1970.



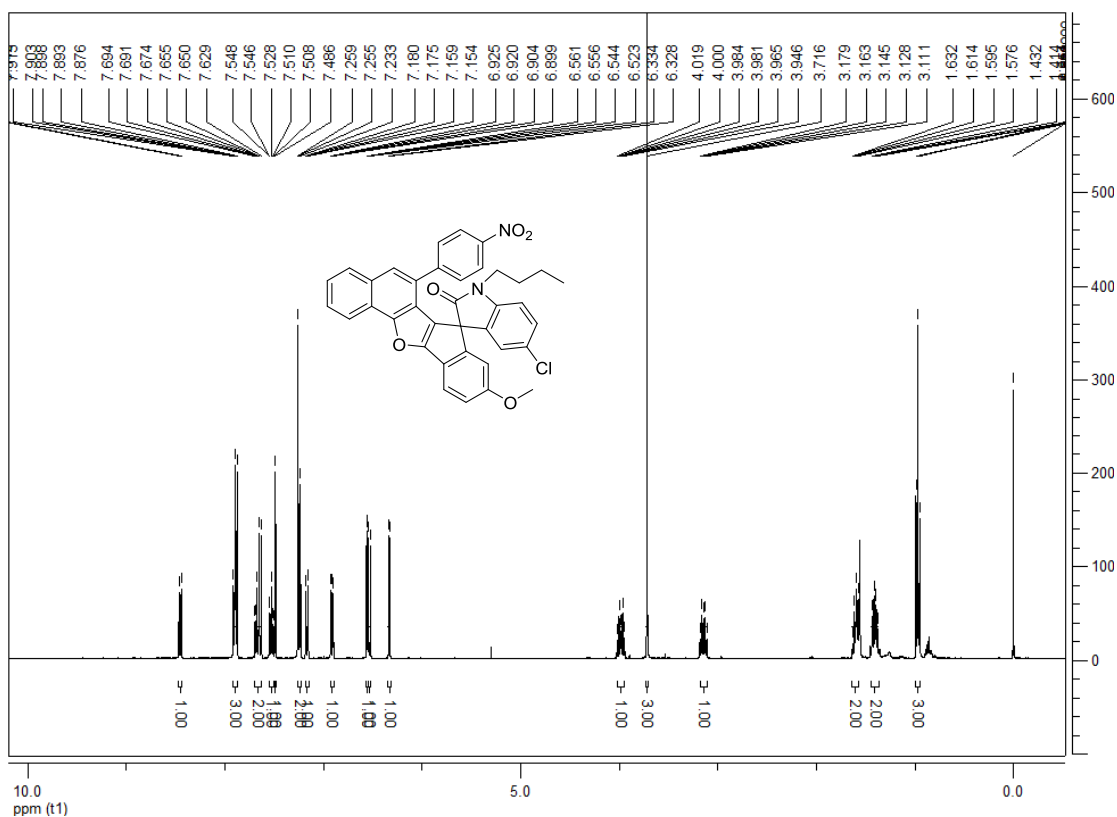


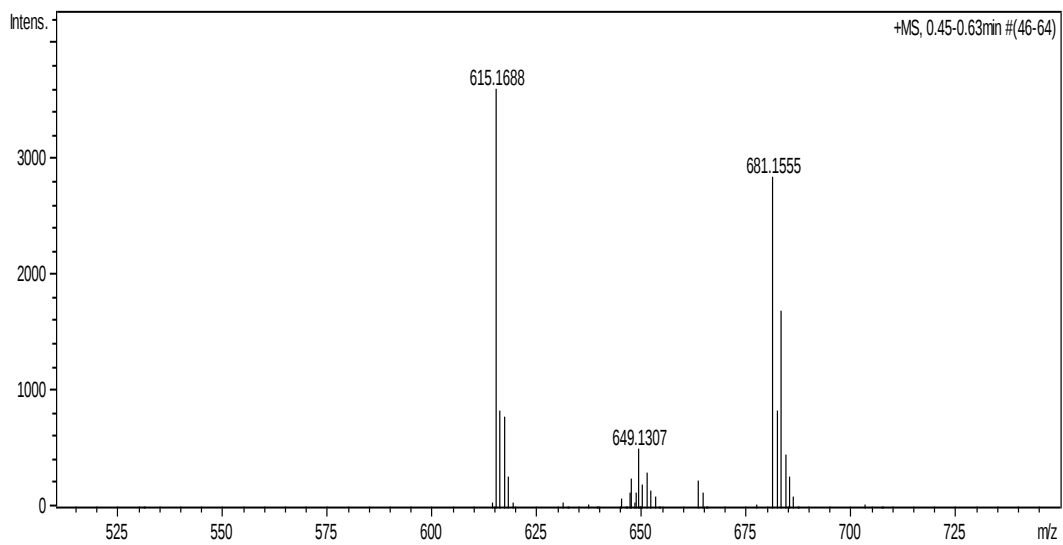
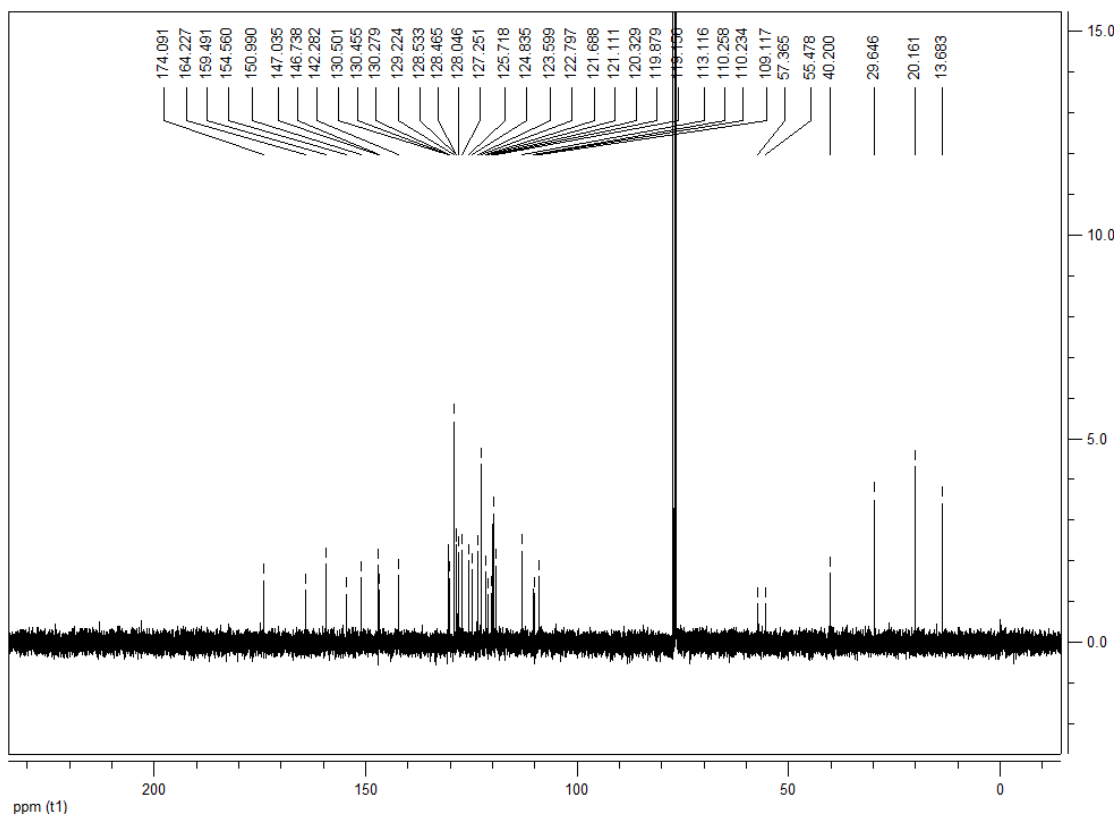
1'-benzyl-9-methoxy-5'-methyl-6-(4-nitrophenyl)spiro[indeno[1,2-*b*]naphtho[2,1-*d*]furan-7,3'-indolin]-2'-one (4w): Light yellow solid, 59%, 0.197 g, m.p. 239-241 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.46 (d, *J* = 8.0 Hz, 1H, ArH), 7.90 (d, *J* = 8.0 Hz, 1H, ArH), 7.83 (d, *J* = 8.0 Hz, 2H, ArH), 7.69-7.62 (m, 2H, ArH), 7.54-7.49 (m, 2H, ArH), 7.39-7.29 (m, 5H, ArH), 7.22 (d, *J* = 8.0 Hz, 2H, ArH), 6.90 (d, *J* = 8.0 Hz, 2H, ArH), 6.48 (d, *J* = 8.0 Hz, 1H, ArH), 6.38 (s, 1H, ArH), 6.27 (s, 1H, ArH), 5.31 (d, *J* = 15.2 Hz, 1H, CH), 4.15 (d, *J* = 15.2 Hz, 1H, CH), 3.62 (s, 3H, OCH₃), 2.08 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 174.7, 164.1, 159.4, 154.4, 151.9, 147.0, 146.7, 140.9, 136.0, 132.6, 130.7, 130.4, 129.1, 128.9, 128.8, 128.4, 128.3, 127.9, 127.1, 125.5, 124.8, 123.9, 123.8, 123.4, 122.7, 121.8, 121.7, 120.6, 119.8, 119.0, 113.9, 109.5, 108.7, 57.6, 55.3, 44.2, 20.7; IR (KBr) ν: 3069, 2943, 2869, 1717, 1597, 1521, 1481, 1432, 1344, 1276, 1228, 1185, 1112, 1071, 1025, 923, 852, 816, 747, 700 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₂₉N₂O₅ ([M+H]⁺): 629.2071. Found: 629.2080.





1'-butyl-5'-chloro-9-methoxy-6-(4-nitrophenyl)spiro[indeno[1,2-*b*]naphtho[2,1-*d*]furan-7,3'-indolin]-2'-one (4x): Light yellow solid, 55%, 0.179 g, m.p. 218-220 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.45 (d, $J = 8.4$ Hz, 1H, ArH), 7.91-7.88 (m, 3H, ArH), 7.69-7.63 (m, 2H, ArH), 7.55-7.51 (m, 1H, ArH), 7.49 (s, 1H, ArH), 7.25-7.23 (m, 2H, ArH), 7.17 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H, ArH), 6.91 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H, ArH), 6.56 (d, $J = 2.0$ Hz, 1H, ArH), 6.53 (d, $J = 8.4$ Hz, 1H, ArH), 6.33 (d, $J = 2.4$ Hz, 1H, ArH), 4.02-3.95 (m, 1H, CH), 3.72 (s, 3H, OCH_3), 3.18-3.11 (m, 1H, CH), 1.63-1.58 (m, 2H, CH), 1.43-1.37 (m, 2H, CH), 0.97 (t, $J = 7.6$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 174.0, 164.2, 159.4, 154.5, 150.9, 147.0, 146.7, 142.2, 130.5, 130.4, 130.2, 129.2, 128.5, 128.4, 128.0, 127.2, 125.7, 124.8, 123.5, 122.7, 121.6, 121.1, 120.3, 119.8, 119.1, 113.1, 110.2, 109.1, 57.3, 55.4, 40.1, 29.6, 20.1, 13.6; IR (KBr) ν : 3069, 2943, 2869, 1717, 1597, 1521, 1481, 1432, 1344, 1276, 1228, 1185, 1112, 1071, 1025, 923, 852, 816, 747, 700 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{37}\text{H}_{28}\text{ClN}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 615.6181. Found: 615.6188.





1-benzyl-3-(2-(4-chlorophenyl)-4-(4-nitrophenyl)naphtho[1,2-*b*]furan-3-yl)indolin-2-one (G): orange solid, 6%, 0.149 g, m.p. 208-210 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.48 (d, $J = 8.0$ Hz, 1H, ArH), 8.02 (d, $J = 8.4$ Hz, 2H, ArH), 7.88 (d, $J = 8.4$ Hz, 1H, ArH), 7.68 (t, $J = 7.6$ Hz, 2H, ArH), 7.62-7.53 (m, 4H, ArH), 7.33-7.27 (m, 5H, ArH), 7.25-7.21 (m, 2H, ArH), 7.00 (t, $J = 7.6$ Hz, 1H, ArH), 6.82 (t, $J = 7.6$ Hz, 2H, ArH), 6.74-6.72 (m, 1H, ArH), 6.21 (d, $J = 7.6$ Hz, 1H, ArH), 5.40 (d, $J = 15.2$ Hz, 1H, CH), 5.01 (s, 1H, CH), 3.90 (d, $J = 15.6$ Hz, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.8, 156.7, 150.9, 147.1, 146.4, 141.9, 135.7, 135.3, 132.1, 130.8, 129.7, 129.3, 129.1, 128.9, 128.8, 128.2, 128.1, 127.7, 127.4, 127.3, 127.1, 126.3, 125.0, 123.7, 123.3, 122.5, 121.2, 120.8, 120.2, 109.6, 108.7, 44.6, 44.0; IR (KBr) ν : 3059, 2922, 2850, 1718, 1602, 1518, 1482, 1343, 1171, 1106, 1069, 1018, 976, 912, 851, 751 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{39}\text{H}_{26}\text{ClN}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$): 621.1503. Found: 621.1566.

