Electronic supporting information.

A Convenient and rapid microwave-assisted synthesis of spirooxindoles in aqueous medium and their antibacterial activities

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4b Crystallographic Data

Crystal data for 4b: $C_{24}H_{21}N_3O_4$, M = 415.44, 0.43 x 0.35 x 0.28 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 23.078(5), b = 11.2600(18), c = 17.936(4) Å, β = 118.626(5)°, V = 4091.2(13) Å^3, Z = 8, D_c = 1.349 g/cm^3, F_{000} = 1744, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0°, 17031 reflections collected, 3608 unique (R_{int} = 0.0336), Final *GooF* = 1.047, *R1* = 0.0468, *wR2* = 0.1269, *R* indices based on 2860 reflections with I >2σ(I) (refinement on F^2), 322 parameters, μ = 0.093 mm^{-1}. The crystallographic data at the Cambridge Crystallographic Data Centre has been deposited at the CCDC and obtained a unique depository number, CCDC 1037568. This data can be obtained free of charge from the http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx or by writing to the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk

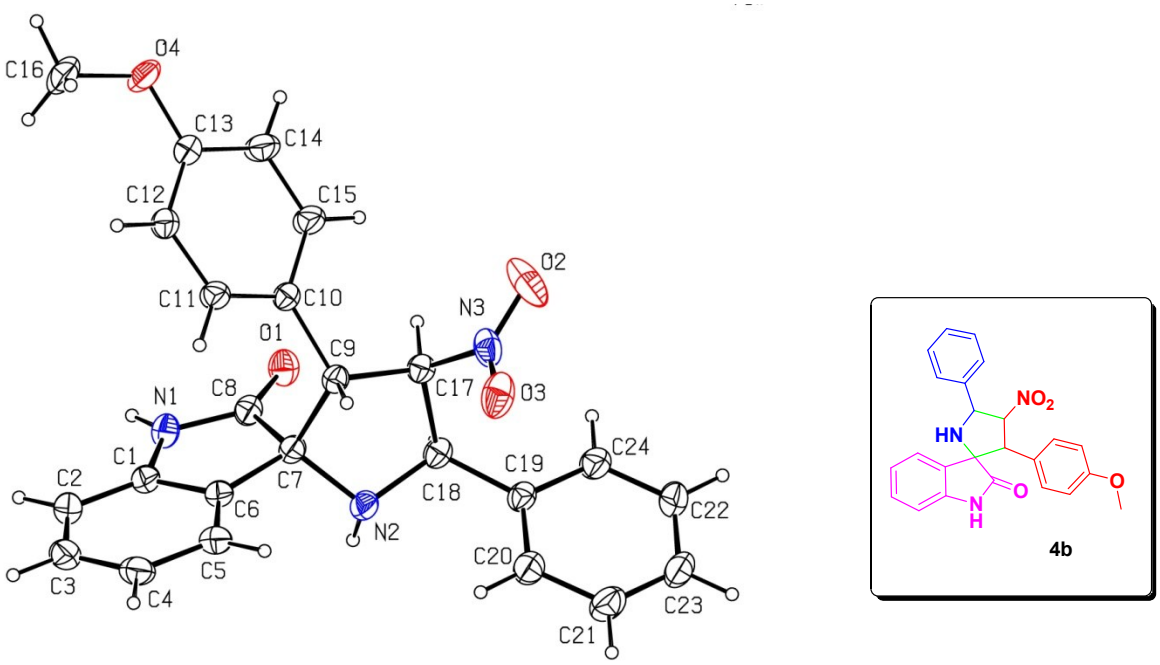


Figure caption: The molecular structure of AX68 with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radius. Only the major component of the disordered *p*-methoxy phenyl ring atoms is shown for clarity.

Data collection and Structure solution: X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 4790 reflections for AX68 data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with U_{iso}(H) = 1.2U_{eq} (C) or 1.5U_{eq} for methyl atoms. The hydrogen atom on nitrogen N1 and N2 were located from the difference Fourier map. The *p*-methoxy phenyl ring atoms were disordered over two sites – 79 % site occupancy for the major component comprising of C10/C11/C12/C13/C14/C15/O4/C16 atoms and 21% site occupancy for the minor component comprising of C10B/C11B/C12B/C13B/C14B/C15B/O4B/C16B atoms. PART and FVAR instructions were invoked for modeling the disorder and estimating the site occupancy factors the disordered atoms, respectively. DFIX was used for restraining the C-C of the phenyl ring bonds to 1.39Å within e.s.d value of 0.01Å. Similarly methoxy group C-C and C-O bonds were restrained to 1.36Å and 1.44 Å, respectively within e.s.d value of 0.01Å

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

General remarks and materials:

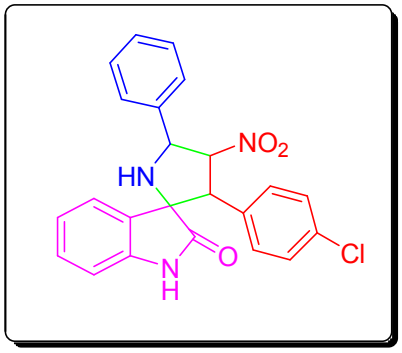
Commercial reagents were purchased from Sigma Aldrich, Fluka or Alfa Aesar and used as received. Anhydrous solvents were purchased from Rankem. All Solvents were distilled before use. Crude mixture was purified by column chromatography using Merck 60-120 mesh silica gel. Thin layer chromatography (TLC) was performed using precoated glass silica gel plates and visualized by UV fluorescence of 254 nm short wavelength ultraviolet light. Reactions were monitored by TLC by exposure to iodine vapours and a solution of *p*-anisaldehyde (3 g of *p*-anisaldehyde, 1mL of AcOH and 3 mL of concentrated H_2SO_4 in 125 mL of HPLC grade MeOH) followed by direct heating on hot plate. Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker Avance 300 MHz, 400 MHz and 500 MHz NMR spectrometer. For ^{1}H NMR, chemical shifts (δ) were expressed in parts per million (ppm) with respective to TMS as internal standard (0.00 ppm), peak multiplicity is indicated as follows: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet and dd-doublet of doublet and $CDCl_3$ (δ = 77.0) used as internal standards for ^{13}C NMR. Coupling constants (*J*) were expressed in Hertz (Hz). Mass spectra were recorded by using 70 eV spectrometer. IR spectra were recorded on Thermo Nicolet FT/IR-5700 spectrometer. High resolution mass spectrums (HRMS) were recorded using Applied Bio-Sciences HRMS spectrometer at national center for mass spectroscopy-IICT. All microwave irradiation experiments were carried out in a dedicated CEM-Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W.

General procedure:

A mixture of isatin (1 mmol), benzyl amine or α-amino acids (1.2 mmol), and aryl β-nitrostyrenes (1 mmol) in water (2 mL) was irradiated under microwave irradiation (150 W power) at 100 °C for 10 minutes. After completion of reaction, the reaction mixture was then extracted with water (60 mL) and ethyl acetate (40 mL). The organic layer was washed with brine solution, dried with anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography with hexane–ethyl acetate (8:2) mixture to get compounds in good yields. All products were characterized by ^{1}H-NMR, ^{13}C-NMR, mass, HRMS data.

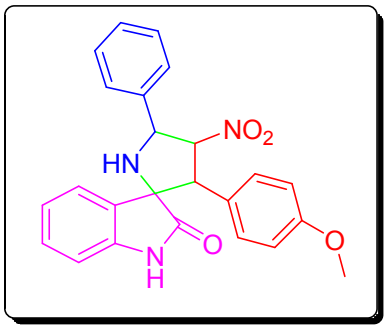
Characteristic data of all compounds:

3'-(4-chlorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4a):



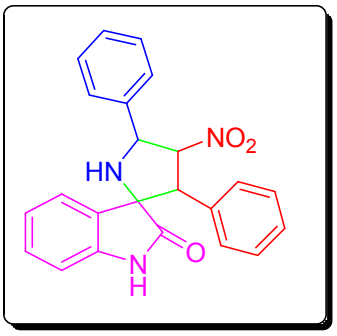
White solid; Mp 239-241 °C; IR (KBr): ν_{max} 3337, 1715, 1620, 1552, 1492, 1368, 1168, 752, 699 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6): δ 9.64 (brs, 1H), 7.74 (d, *J* = 6.78 Hz, 1H), 7.61 (d, *J* = 6.42 Hz, 2H), 7.40-7.30 (m, 3H), 7.19-7.10 (m, 3H), 7.05-6.99 (m, 2H), 6.70 (d, *J* = 7.17 Hz, 1H), 6.38 (t, *J* = 10.00 Hz, 1H), 5.86-5.81 (m, 1H), 4.52 (d, *J* = 10.21 Hz, 1H), 3.02(d, *J* = 5.47 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.0, 141.5, 137.6, 133.0, 130.5, 129.0, 128.0, 127.7, 127.3, 127.1, 123.1, 121.8, 109.5, 90.1, 71.0, 64.9, 60.2, 56.5, 54.3 ppm; MS (ESI) m/z = 420 $[M+H]^+$; HRMS (ESI) Calcd. $C_{23}H_{19}ClN_3O_3$ $[M+H]^+$: 420.11198, found: 420.11185.

3'-(4-methoxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4b):



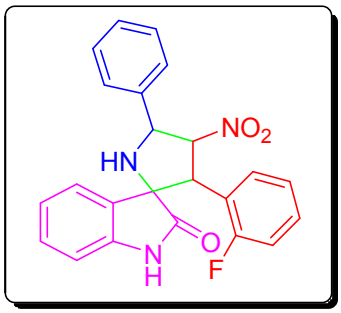
White solid; Mp 210-212 °C; IR (KBr): ν_{max} 3442, 2934, 1713, 1602, 1551, 1469, 1190, 1401, 749, 696 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6): δ 9.80 (brs, 1H), 7.72 (d, *J* = 6.42 Hz, 1H), 7.61-7.57 (m, 3H), 7.39-7.29 (m, 2H), 7.22-7.08 (m, 1H), 6.98 (d, *J* = 8.68 Hz, 2H), 6.66 (d, *J* = 8.87 Hz, 3H), 6.37 (t, *J* = 10.00 Hz, 1H), 5.79 (q, *J* = 5.68 Hz, 1H), 4.44 (d, *J* = 10.38 Hz, 1H), 3.68 (s, 3H), 3.34 (d, *J* = 5.42 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.4, 158.4, 141.5, 137.8, 128.8, 128.7, 128.2, 127.8, 127.6, 127.4, 127.2, 127.1, 123.5, 123.1, 121.7, 112.9, 109.3, 90.5, 71.0, 60.0, 54.3, 54.2, 28.2 ppm; MS (ESI) m/z = 416 $[M+H]^+$; HRMS (ESI) Calcd. $C_{24}H_{22}N_3O_4$ $[M+H]^+$: 416.16160, found: 416.16153.

4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (4c):



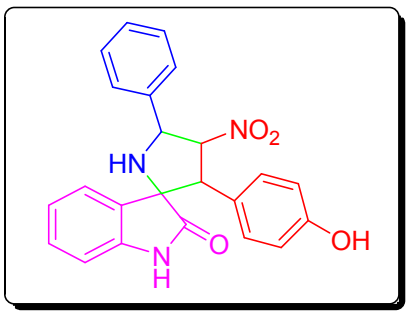
White solid; Mp 236-238 °C; IR (KBr): ν_{max} 3443, 1953, 1704, 1619, 1554, 1320, 1193, 757, 695 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6): δ 9.86 (brs, 1H), 7.75-7.70 (m, 1H), 7.62 (d, *J* = 6.79 Hz, 2H), 7.37-7.29 (m, 3H), 7.22-7.05 (m, 6H), 6.65 (d, *J* = 6.79 Hz, 1H), 6.43 (t, *J* = 10.00 Hz, 1H), 5.83-5.57 (m, 1H), 4.53 (d, *J* = 10.38 Hz, 1H), 3.51 (d, *J* = 5.66 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 178.8, 141.2, 137.6, 131.4, 128.4, 128.3, 127.4, 126.8, 122.8, 121.2, 108.8, 89.8, 70.6, 59.8, 59.7, 59.6, 59.5, 59.4, 54.5 ppm; MS (ESI) m/z = 386 $[M+H]^+$; HRMS (ESI) Calcd. $C_{23}H_{20}N_3O_3$ $[M+H]^+$: 386.15145, found: 386.15123.

3'-(2-fluorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4d);



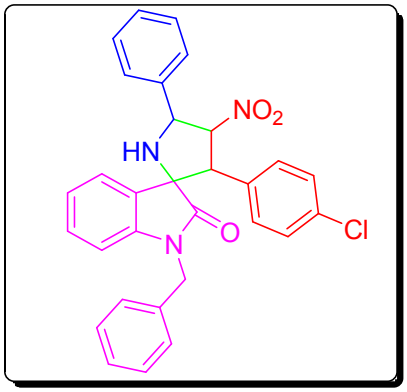
White solid; Mp 220-222 °C; IR (KBr): ν_{max} 3348, 1927, 1725, 1619, 1424, 1373, 836, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (brs, 1H), 7.72-7.36 (m, 1H), 7.61-7.48 (m, 2H), 7.38-7.28 (m, 3H), 7.20-7.02 (m, 5H), 6.94-6.79 (m, 1H), 6.64 (d, *J* = 7.36 Hz, 1H), 6.34 (t, *J* = 9.82 Hz, 1H), 5.88-5.83 (m, 1H), 5.05 (d, *J* = 10.00 Hz, 1H), 3.24 (brs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.2, 161.2, 159.2, 141.2, 137.4, 128.8, 127.8, 127.7, 127.5, 127.3, 127.1, 126.9, 126.8, 123.7, 123.4, 121.6, 119.3, 114.5, 109.1, 90.9, 70.7, 60.5, 46.6 ppm; MS (ESI) m/z = 404 $[M+H]^+$; HRMS (ESI) Calcd. $C_{23}H_{19}N_3O_3F$ $[M+H]^+$: 404.14182, found: 404.14170.

3'-(4-hydroxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4e):



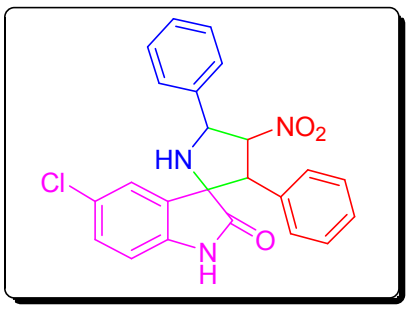
Pale yellow solid; Mp 250-252 °C; IR (KBr): ν_{max} 3541, 3314, 1956, 1759, 1536, 1245, 658, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 8.97 (brs, 1H), 7.64 (d, *J* = 7.17 Hz, 1H), 7.39-7.31 (m, 2H), 7.23-7.12 (m, 4H), 6.86 (d, *J* = 8.30 Hz, 2H), 6.62 (d, *J* = 8.30 Hz, 2H), 6.53-6.39 (m, 2H), 5.91-5.83 (m, 1H), 5.06 (d, *J* = 10.42 Hz, 1H), 4.57 (d, *J* = 10.19 Hz, 1H), 4.27 (d, *J* = 10.19 Hz, 1H), 3.05 (brs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 177.7, 157.1, 142.6, 137.8, 134.1, 129.2, 128.6, 127.7, 127.4, 126.7, 125.9, 123.9, 122.7, 121.9, 115.3, 109.0, 90.8, 71.3, 60.7, 55.1, 42.8 ppm; MS (ESI) m/z = 424 [M+Na]; HRMS (ESI) Calcd. $C_{23}H_{20}N_3O_4$ $[M+H]^+$: 402.14644, found: 402.14629.

1-benzyl-3'-(4-chlorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4f):



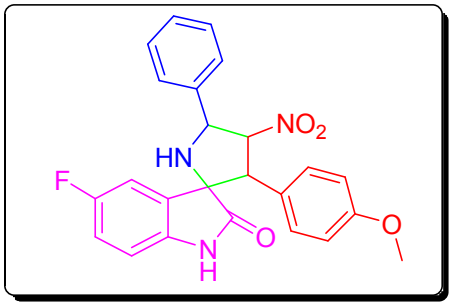
White solid; Mp 220-222 °C; IR (KBr): ν_{max} 3442, 1713, 1612, 1545, 1364, 1178, 748, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81-7.68 (m, 1H), 7.60 (d, *J* = 6.60 Hz, 2H), 7.41-7.38 (m, 2H), 7.25-7.11 (m, 7H), 7.00 (d, *J* = 8.49 Hz, 2H), 6.52-6.39 (m, 3H), 5.95-5.90 (m, 1H), 5.07 (d, *J* = 10.86 Hz, 1H), 4.67 (d, *J* = 9.82 Hz, 1H), 4.24 (d, *J* = 10.86 Hz, 1H), 2.67 (brs, 1H), 1.58 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 177.7, 143.0, 137.5, 134.4, 134.3, 130.6, 130.1, 129.4, 128.9, 128.8, 128.6, 128.3, 127.7, 127.4, 126.3, 123.8, 123.4, 109.6, 90.9, 71.6, 61.3, 55.3, 43.4 ppm; MS (ESI) m/z = 510 $[M+H]^+$; HRMS (ESI) Calcd. $C_{30}H_{25}ClN_3O_3$ $[M+H]^+$: 510.15680, found: 510.15665.

5-chloro-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (4g);



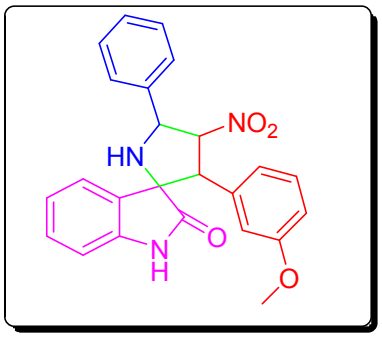
White solid; Mp 255-257 °C; IR (KBr): ν_{max} 3346, 1954, 1745, 1621, 1145, 815, 652, 548 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 9.93 (brs, 1H), 7.80 (d, *J* = 1.88 Hz, 1H), 7.61 (d, *J* = 6.23 Hz, 2H), 7.42-7.36 (m, 3H), 7.25-7.10 (m, 6H), 6.67 (d, *J* = 8.30 Hz, 1H), 6.42 (t, *J* = 9.82 Hz, 1H), 5.93 (d, *J* = 9.63 Hz, 1H), 4.62 (d, *J* = 9.82 Hz, 1H), 2.66 (brs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 178.4, 176.6, 139.9, 138.7, 137.4, 131.4, 131.0, 130.8, 129.4, 128.2, 127.2, 127.0, 126.8, 126.7, 126.0, 124.2, 123.0, 109.9, 89.7, 70.6, 61.2, 59.6, 54.5 ppm.

5-fluoro-3'-(4-methoxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4h):



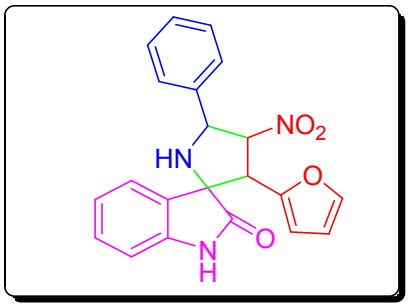
White solid; Mp 212-214 °C; IR (KBr): ν_{max} 3412, 1723, 1695, 1563, 1256, 1198, 836, 648, 542 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 9.49 (brs, 1H), 7.60 (d, *J* = 6.42 Hz, 1H), 7.49-7.25 (m, 4H), 7.02-6.88 (m, 2H), 6.69-6.59 (m, 4H), 6.34 (t, *J* = 10.00 Hz, 1H), 5.86-5.81 (m, 1H), 4.44 (d, *J* = 10.19 Hz, 1H), 3.70 (s, 3H), 2.89 (d, *J* = 5.47 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.56, 160.02, 158.73, 137.72, 137.57, 129.74, 128.45, 127.86, 127.46, 127.26, 123.38, 115.44, 115.13, 113.21, 111.17, 110.85, 110.26, 110.15, 90.57, 71.48, 60.29, 54.77, 54.46 ppm.

3'-(3-methoxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4i);



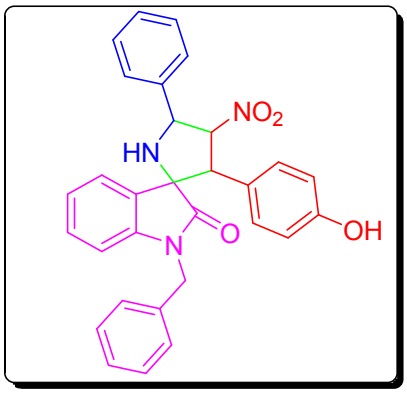
White solid; Mp 167-169 °C; IR (KBr): ν_{max} 3342, 1713, 1602, 1551, 1329, 1118, 749, 696 cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$): δ 9.92 (brs, 1H), 7.75 (d, *J* = 6.98 Hz, 1H), 7.61 (d, *J* = 6.79 Hz, 2H), 7.37-7.26 (m, 3H), 7.23-7.03 (m, 4H), 6.71-6.50 (m, 3H), 6.42 (t, *J* = 10.19 Hz, 1H), 5.80-5.75 (m, 1H), 4.50 (d, *J* = 10.38 Hz, 1H), 3.53 (s, 3H), 3.16 (brs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 178.6, 157.9, 141.3, 137.6, 132.9, 128.2, 128.1, 127.5, 127.0, 126.7, 122.7, 121.0, 118.5, 112.5, 112.0, 108.7, 89.5, 70.3, 59.4, 54.1, 53.0 ppm; MS (ESI) m/z = 416 $[M+H]^+$; HRMS (ESI) Calcd. $C_{24}H_{22}N_3O_4$ $[M+H]^+$: 416.16159, found: 416.16156.

5'-(furan-2-yl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4j):



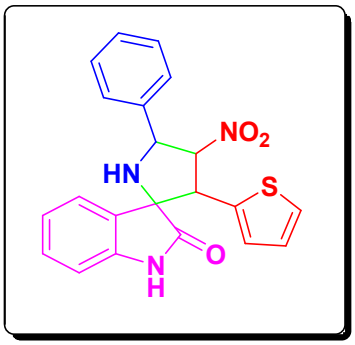
White solid; Mp 190-192 °C; IR (KBr): ν_{max} 3329, 1758, 1654, 1542, 1149, 965, 759, 650 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6): δ 9.83 (brs, 1H), 7.67-7.49 (m, 3H), 7.38-7.08 (m, 5H), 6.82 (d, *J* = 7.55 Hz, 1H), 6.27 (t, *J* = 9.63 Hz, 1H), 6.18-6.06 (m, 1H), 5.96 (d, *J* = 3.02 Hz, 1H), 5.82 (d, *J* = 9.82 Hz, 1H), 5.46 (d, *J* = 7.93 Hz, 1H), 4.69 (d, *J* = 9.44 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.1, 147.1, 141.7, 140.6, 137.2, 136.2, 129.1, 127.8, 127.4, 127.2, 126.9, 123.2, 121.9, 109.8, 109.5, 106.7, 89.9, 69.4, 60.2, 49.0 ppm; MS (ESI) m/z = 376 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{18}N_3O_4$ $[M+H]^+$: 376.13033, found: 376.13009.

1-benzyl-3'-(4-hydroxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2' pyrrolidin]-2-one (4k):



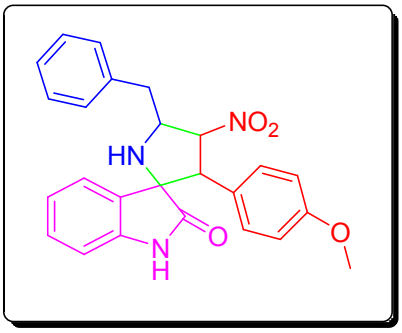
Yellow solid; Mp 189-192 °C; IR (KBr): ν_{max} 3401, 1726, 1643, 1547, 1436, 1478, 1182, 1058, 753, 659 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 6.42 Hz, 1H), 7.61 (d, *J* = 6.42 Hz, 2H), 7.46-7.16 (m, 8H), 6.87 (d, *J* = 8.49 Hz, 2H), 6.64 (d, *J* = 8.49 Hz, 1H), 6.55-6.36 (m, 3H), 5.89 (dd, J_1 = 6.23 Hz, J_2 = 6.04 Hz, 1H), 5.04 (d, *J* = 10.05 Hz, 1H), 4.57 (d, *J* = 10.00 Hz, 1H), 4.25 (d, *J* = 10.05 Hz, 1H), 3.05 (s, 1H), 2.59 (s, 2H) ppm; ^{13}C NMR (75, MHz, $CDCl_3$+DMSO d_6): δ 178.1, 157.5, 153.2, 143.0, 142.9, 138.2, 134.5, 129.6, 129.0, 128.5, 128.1, 127.8, 127.1, 126.3, 123.7, 123.1, 122.3, 115.7, 109.4, 91.2, 71.7, 61.1, 55.4, 43.2 ppm; MS (ESI) m/z = 492 $[M+H]^+$; HRMS (ESI) Calcd. $C_{30}H_{26}N_3O_4$ $[M+H]^+$: 492.19292, found: 492.19277.

4'-nitro-5'-phenyl-3'-(thiophen-2-yl)spiro[indoline-3,2'-pyrrolidin]-2-one (4l) :



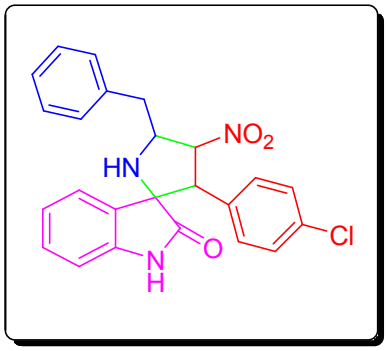
White solid; Mp 245-247 °C; IR (KBr): ν_{max} 3325, 1718, 1625, 1612, 1521, 1506, 1492, 1346, 1160, 896, 742, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 9.90 (brs, 1H), 7.68 (d, *J* = 7.32 Hz, 1H), 7.57 (d, *J* = 6.40 Hz, 2H), 7.37-7.23 (m, 3H), 7.15 (t, *J* = 7.32 Hz, 1H), 7.10 (d, *J* = 5.03 Hz, 1H), 6.84-6.73 (m, 3H), 6.34 (t, *J* = 10.07 Hz, 1H), 5.81 (dd, J_1 = 5.49, J_2 = 5.49 Hz, 1H) 4.78 (d, *J* = 10.07 Hz, 1H), 3.22 (d, *J* = 6.40 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.11, 142.45, 138.25, 138.15, 138.05, 134.89, 129.26, 127.85, 127.53, 127.45, 126.31, 124.97, 124.72, 123.48, 121.89, 109.57, 91.77, 70.78, 64.99, 59.97, 50.66 ppm. MS (ESI) m/z = 392 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{17}N_3O_3S$ $[M+H]^+$: 392.1063, found: 392.1080.

5'-benzyl-3'-(4-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (5a):



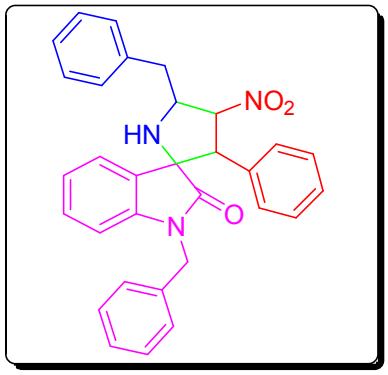
White solid; Mp 242-244 °C; IR (KBr): ν_{max} 3445, 1789, 1625, 1521, 1307, 1145, 943, 654, 548 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 7.64 (d, *J* = 6.79 Hz, 1H), 7.28-7.13 (m, 6H), 7.05-7.00 (m, 1H), 6.96-6.88 (m, 2H), 6.69-6.58 (m, 2H), 6.10 (t, *J* = 9.25 Hz, 1H), 4.86 (t, *J* = 8.87 Hz, 1H), 4.47 (d, *J* = 9.25 Hz, 1H), 3.69 (s, 3H), 2.93 (dd, J_1 = 4.26 Hz, J_2 = 3.58 Hz, 2H), 2.76-2.66 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 178.8, 158.5, 141.5, 136.8, 128.8, 128.6, 128.3, 127.8, 125.9, 123.9, 123.0, 121.7, 113.0, 109.6, 109.3, 90.0, 71.3, 57.5, 56.0, 54.4, 37.6, 37.0, 36.7 ppm; MS (ESI) m/z = 430 $[M+H]^+$; HRMS (ESI) Calcd. $C_{25}H_{24}N_3O_4$ $[M+H]^+$: 430.17602, found: 430.17584.

5'-benzyl-3'-(4-chlorophenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (5b):



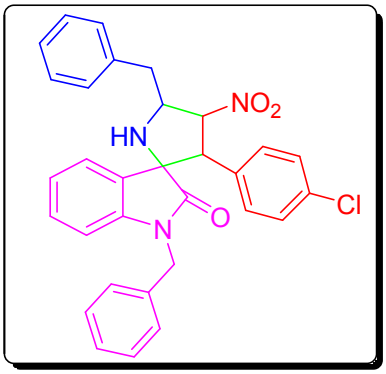
White solid; Mp 160-162 °C; IR (KBr): ν_{max} 3445, 1954, 1706, 1624, 1465, 1305, 1198, 787, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.73 (brs, 1H), 7.61-7.51 (m, 2H), 7.28 (d, *J* = 4.34 Hz, 4H), 7.21-7.06 (m, 5H), 6.98 (d, *J* = 8.49 Hz, 2H), 6.64 (d, *J* = 7.55 Hz, 1H), 6.14 (t, *J* = 9.24 Hz, 1H), 4.47 (d, *J* = 9.44 Hz, 1H), 4.41 (d, *J* = 3.77 Hz, 1H), 2.86 (d, *J* = 3.77 Hz, 1H), 2.71 (q, *J* = 10.38 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 178.2, 141.1, 136.4, 132.6, 130.6, 128.6, 128.3, 128.2, 127.7, 127.4, 127.1, 126.2, 125.5, 125.3, 122.6, 121.4, 109.0, 89.2, 71.0, 57.2, 55.5, 42.1, 37.1 ppm; MS (ESI) m/z = 456 [M+Na] ; HRMS (ESI) Calcd. $C_{24}H_{21}ClN_3O_3$ $[M+H]^+$: 434.12729, found: 434.12735.

1,5'-dibenzyl-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5c):



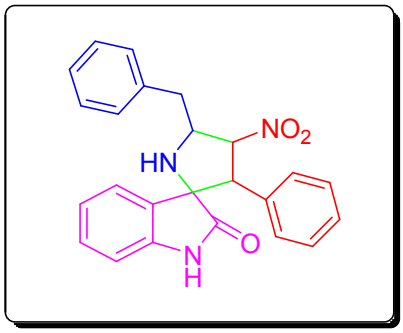
White solid; Mp 165-167 °C; IR (KBr): ν_{max} 3420, 1721, 1645, 1546, 1423, 1375, 1154, 956, 748, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 6.86 Hz, 1H), 7.31-7.24 (m, 6H), 7.19-7.10 (m, 5H), 7.06-7.01 (m, 4H), 6.39 (d, *J* = 7.47 Hz, 2H), 6.32 (d, *J* = 7.32 Hz, 1H), 6.25 (t, *J* = 9.00 Hz, 1H), 5.00-4.94 (m, 2H), 4.60 (d, *J* = 9.00 Hz, 1H), 4.10 (d, *J* = 10.00 Hz, 1H), 2.96 (dd, J_1 = 3.66 Hz, J_2 = 1.25 Hz, 1H), 2.74 (q, *J* = 10.52 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 177.2, 142.9, 137.2, 134.6, 132.4, 130.3, 129.7, 129.4, 129.2, 128.6, 128.5, 128.1, 128.0, 127.8, 127.1, 126.6, 126.2, 123.6, 123.2, 109.3, 90.5, 71.9, 58.7, 57.6, 43.2, 38.1, 26.8 ppm; MS (ESI) m/z = 513 [M+Na]; HRMS (ESI) Calcd. $C_{31}H_{28}N_3O_3$ $[M+H]^+$: 490.21265, found: 490.21252.

1,5'-dibenzyl-3'-(4-chlorophenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (5d):



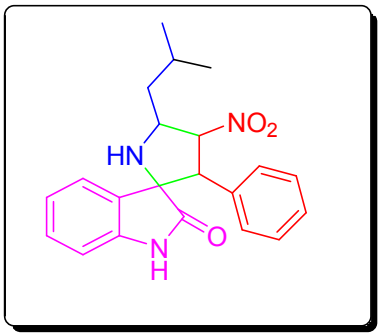
White solid; Mp 159-161 °C; IR (KBr): ν_{max} 3465, 1987, 1723, 1646, 1523, 1437, 1191, 928, 649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.67-7.31 (m, 1H), 7.29-7.23 (m, 7H), 7.19-7.11 (m, 6H), 6.94 (d, J = 4.92 Hz, 2H), 6.41-6.39 (m, 2H), 6.19 (d, J = 9.06 Hz, 1H), 4.97 (d, J = 10.80 Hz, 2H), 4.56 (d, J = 9.2 Hz, 1H), 4.11 (d, J = 10.80 Hz, 1H), 2.96 (dd, J_1 = 3.58 Hz, J_2 = 2.43 Hz, 1H), 2.73 (dd, J_1 = 10.57 Hz, J_2 = 6.57 Hz, 2H), 2.31 (brs,1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.1, 142.9, 137.1, 134.4, 134.3, 130.9, 129.9, 129.4, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 127.5, 127.4, 126.7, 126.3, 123.6, 123.3, 109.4, 90.2, 71.8, 60.5, 58.5, 56.8, 43.3, 38.1 ppm; MS (ESI) m/z = 524 $[M+H]^+$; HRMS (ESI) Calcd. $C_{31}H_{27}N_3O_3Cl$ $[M+H]^+$: 524.17366, found: 524.17355.

5'-benzyl-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5e):



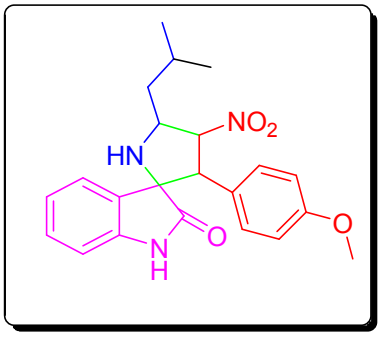
White solid; Mp 174-176 °C; IR (KBr): ν_{max} 3351, 1956, 1720, 1646, 1520, 1356, 1256, 864, 689, 568 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6): δ 7.63-7.40 (m, 2H), 7.34-7.13 (m, 6H), 7.14-7.05 (m, 1H), 6.93 (d, J = 7.93 Hz, 3H), 6.59 (d, J = 6.98 Hz, 1H), 6.12 (t, J = 9.04 Hz, 1H), 4.85 (q, J = 9.04 Hz, 1H), 4.45 (d, J = 9.04 Hz, 1H), 2.94 (dd, J_1 = 3.77 Hz, J_2 = 2.56 Hz, 2H), 2.70-2.21 (m, 1H) ppm; ^{13}C NMR (75 MHz, DMSO d_6): δ 178.4, 141.4, 136.6, 132.0, 128.7, 128.4, 128.3, 127.7, 127.6, 127.5, 127.1, 127.0, 125.8, 122.8, 121.6, 109.5, 109.2, 89.6, 71.2, 57.5, 56.4, 37.4 ppm; MS (ESI) m/z = 400 $[M+H]^+$; HRMS (ESI) Calcd. $C_{24}H_{22}N_3O_3$ $[M+H]^+$: 400.16673, found: 400.16645.

5'-isobutyl-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (6a):



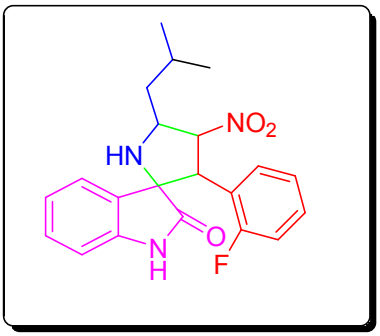
Yellow solid; Mp 205-207 °C; IR (KBr): ν_{max} 3326, 1987, 1715, 1649, 1558, 1359, 1185, 928, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 7.32 Hz, 1H), 7.27-7.21 (m, 3H), 7.19-7.13 (m, 2H), 6.96 (d, J = 7.62 Hz, 2H), 6.65 (d, J = 7.62 Hz, 1H), 5.95 (t, J = 7.93 Hz, 1H), 4.69 (q, J = 5.64 Hz, 1H), 4.42 (d, J = 5.64 Hz, 1H), 1.44 (dd, J_1 = 5.04 Hz, J_2 = 3.25 Hz, 1H), 1.36 (dd, J_1 = 5.04 Hz, J_2 = 2.36 Hz, 1H), 1.27-1.24 (m, 1H), 0.97 (dd, J_1 = 6.67 Hz, J_2 = 2.36 Hz, 6H) ppm; ^{13}C NMR (75 MHz, DMSO d_6): δ 179.2, 159.1, 140.8, 129.7, 128.8, 128.7, 124.9, 123.5, 123.1, 113.8, 109.9, 93.0, 72.8, 58.3, 57.6, 55.0, 39.9, 25.1, 23.6, 21.4 ppm; MS (ESI) m/z = 366 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{24}N_3O_3$ $[M+H]^+$: 366.18122, found: 366.18111.

5'-isobutyl-3'-(4-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (6b):



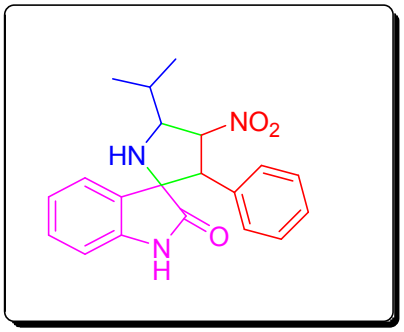
White solid; Mp 165-167 °C; IR (KBr): ν_{max} 3480, 1954, 1748, 1647, 1544, 1487, 1256, 968, 654 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 7.32 Hz, 1H), 7.25-7.20 (m, 1H), 7.16-7.13 (m, 1H), 6.87 (d, J = 8.85 Hz, 2H), 6.65 (d, J = 7.62 Hz, 1H), 6.62 (d, J = 8.85 Hz, 2H), 5.90 (t, J = 8.08 Hz, 1H), 4.67 (q, J = 8.85 Hz, 1H), 4.38 (d, J = 7.62 Hz, 1H), 3.64 (s, 3H), 1.77-1.49 (m, 1H), 1.42 (d, J = 5.04 Hz, 1H), 1.37 (dd, J_1 = 5.04 Hz, J_2 = 2.56 Hz, 1H), 0.94 (dd, J_1 = 6.67 Hz, J_2 = 2.54 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.6, 140.8, 133.0, 130.6, 129.8, 128.6, 128.4, 127.9, 127.7, 123.5, 109.8, 98.1, 92.9, 72.9, 59.0, 58.0, 39.8, 25.2, 23.6, 21.5 ppm; MS (ESI) m/z = 396 $[M+H]^+$; HRMS (ESI) Calcd. $C_{22}H_{26}N_3O_4$ $[M+H]^+$: 396.19178, found: 396.19136.

3'-(2-fluorophenyl)-5'-isobutyl-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (6c):



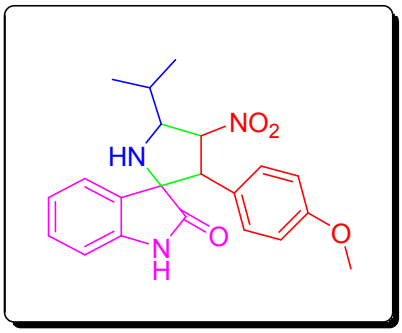
White solid; Mp 176-178 °C; IR (KBr): ν_{max} 3350, 1920, 1723, 1652, 1642, 1290, 1248, 944, 620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.47 Hz, 1H), 7.28-7.23 (m, 2H), 7.18-7.12 (m, 2H), 6.99 (t, *J* = 7.62 Hz, 1H), 6.86-6.81 (m, 1H), 6.69 (d, *J* = 7.78 Hz, 1H), 5.87 (t, *J* = 7.78 Hz, 1H), 4.83 (d, *J* = 6.56 Hz, 1H), 4.72 (q, *J* = 6.56 Hz, 1H), 2.57 (brs, 1H), 1.79-1.72 (m, 1H), 1.42 (dd, J_1 = 4.12 Hz, J_2 = 3.24 Hz, 2H), 0.98 (dd, J_1 = 6.86 Hz, J_2 = 5.45 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.8, 158.3, 141.3, 128.8, 128.5, 127.4, 123.4, 123.0, 121.6, 120.3, 114.8, 109.1, 92.8, 71.9, 60.0, 57.5, 50.1, 24.4, 22.9, 20.8 ppm; MS (ESI) m/z = 384 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{23}N_3O_3F$ $[M+H]^+$: 384.17180, found: 384.17181.

5'-isopropyl-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (7a):



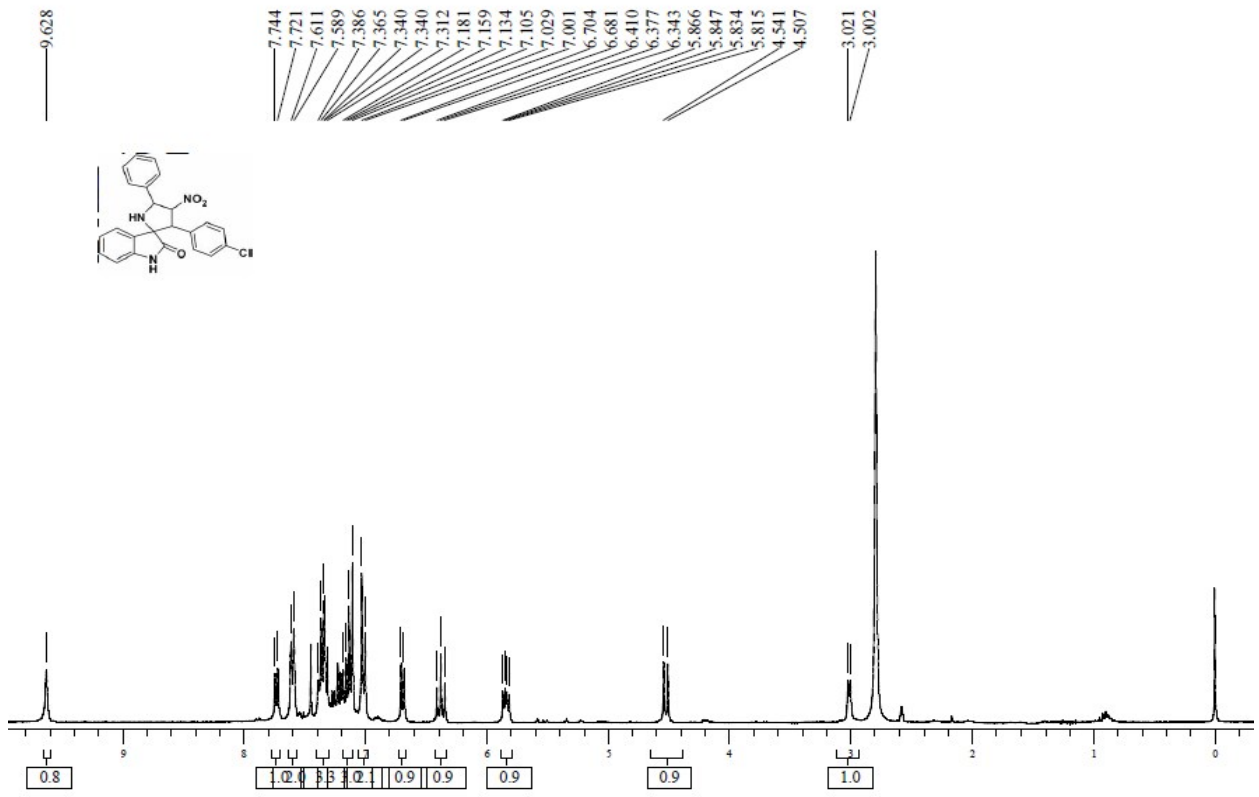
Yellow solid; Mp 199-201 °C; IR (KBr): ν_{max} 3350, 2959, 1712, 1621, 1456, 1365, 1263, 925, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (brs, 1H), 7.57 (d, *J* = 7.36 Hz, 1H), 7.20-7.05 (m, 5H), 6.99-6.96 (m, 2H), 6.63 (d, *J* = 7.55 Hz, 1H), 6.02 (t, *J* = 7.93 Hz, 1H), 4.31 (dd, J_1 = 7.74 Hz, J_2 =6.42 Hz, 1H), 4.31 (brs, 1H), 3.21 (d, *J* = 8.12 Hz, 1H), 1.74 (m, 1H), 1.05 (d, *J* = 6.42 Hz, 3H), 0.99 (d, *J* = 6.42 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 177.9, 141.2, 132.9, 128.6, 128.0, 127.3, 126.9, 126.8, 122.5, 121.4, 108.9, 91.4, 71.4, 65.5, 59.0, 28.8, 28.6, 19.7, 19.0 ppm; MS (ESI) m/z = 352 $[M+H]^+$; HRMS (ESI) Calcd. $C_{20}H_{22}N_3O_3$ $[M+H]^+$: 352.16557, found: 352.16442.

5'-isopropyl-3'-(4-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (7b):



Pale yellow solid; Mp 165-167 °C; IR (KBr): ν_{max} 3320, 2954, 1723, 1621, 1425, 1379, 1189, 956, 619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.93 Hz, 2H), 7.26-7.13 (m, 2H), 6.84 (d, *J* = 8.49 Hz, 2H), 6.66 (t, *J* = 8.87 Hz, 2H), 5.88 (t, *J* = 6.98 Hz, 1H) 4.31 (d, *J* = 6.42 Hz, 1H), 3.64 (s, 3H), 1.83-1.51 (m, 1H), 1.06 (t, *J* = 6.04 Hz, 1H), 0.85 (dd, J_1 = 6.21 Hz, J_2 = 5.22 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.1, 159.0, 140.8, 129.6, 129.0, 128.8, 125.3, 123.6, 123.1, 113.7, 109.8, 93.0, 72.6, 67.3, 60.0, 54.9, 30.8, 29.7, 22.5, 20.6, 20.0 ppm; MS (ESI) m/z = 382 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{24}N_3O_4$ $[M+H]^+$: 382.17613, found: 382.17539.

^1H and ^{13}C NMR spectra: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7.611
7.589
7.386
7.365
7.340
7.340
7.312
7.181
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7.105
7.029
7.001
6.704
6.681
6.410
6.377
6.343
5.866
5.847
5.834
5.815
4.541
4.507
3.021
3.002
NO2
HN
O
N
H
Cl
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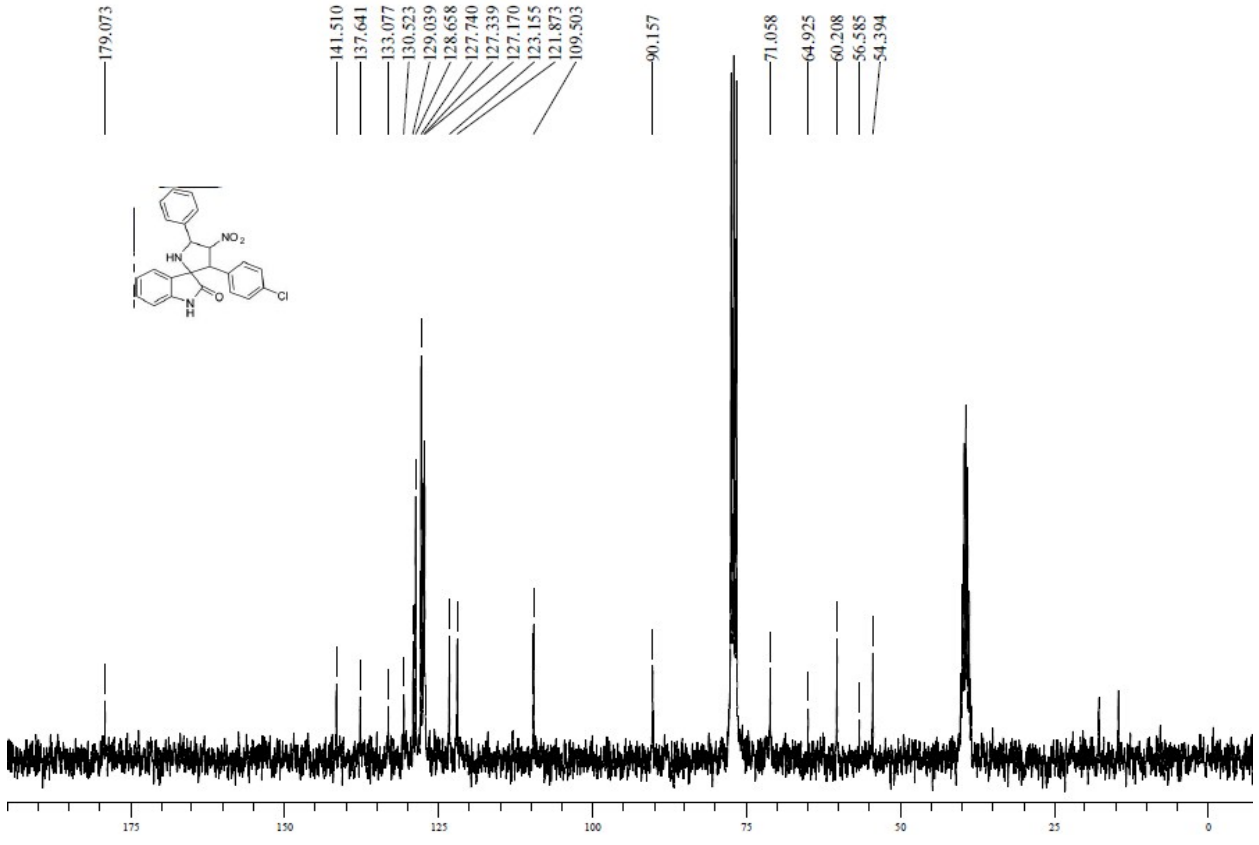
2.0
3.3
3.1
2.1
0.9
0.9
0.9
0.9
1.0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127.740
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54.394
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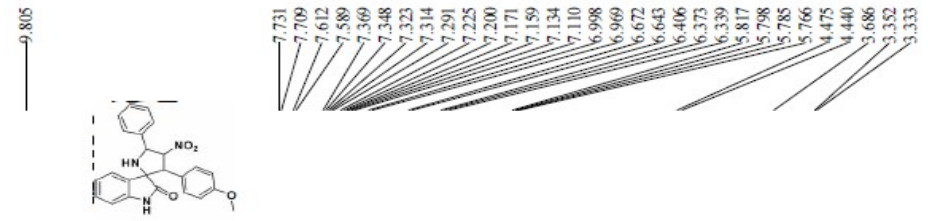
N
H
Cl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6.998
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6.643
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3.333
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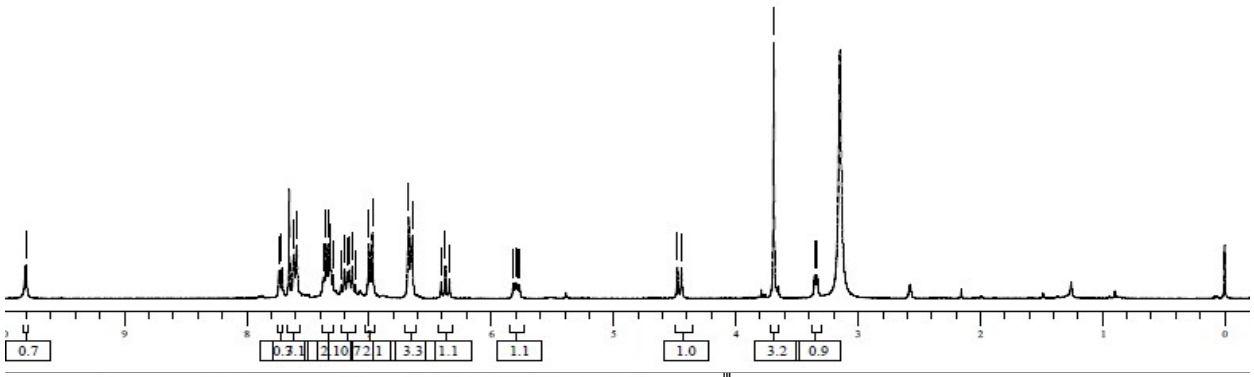
N
H
O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0.3
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2.10
7.2
1
3.3
1.1
1.1
1.0
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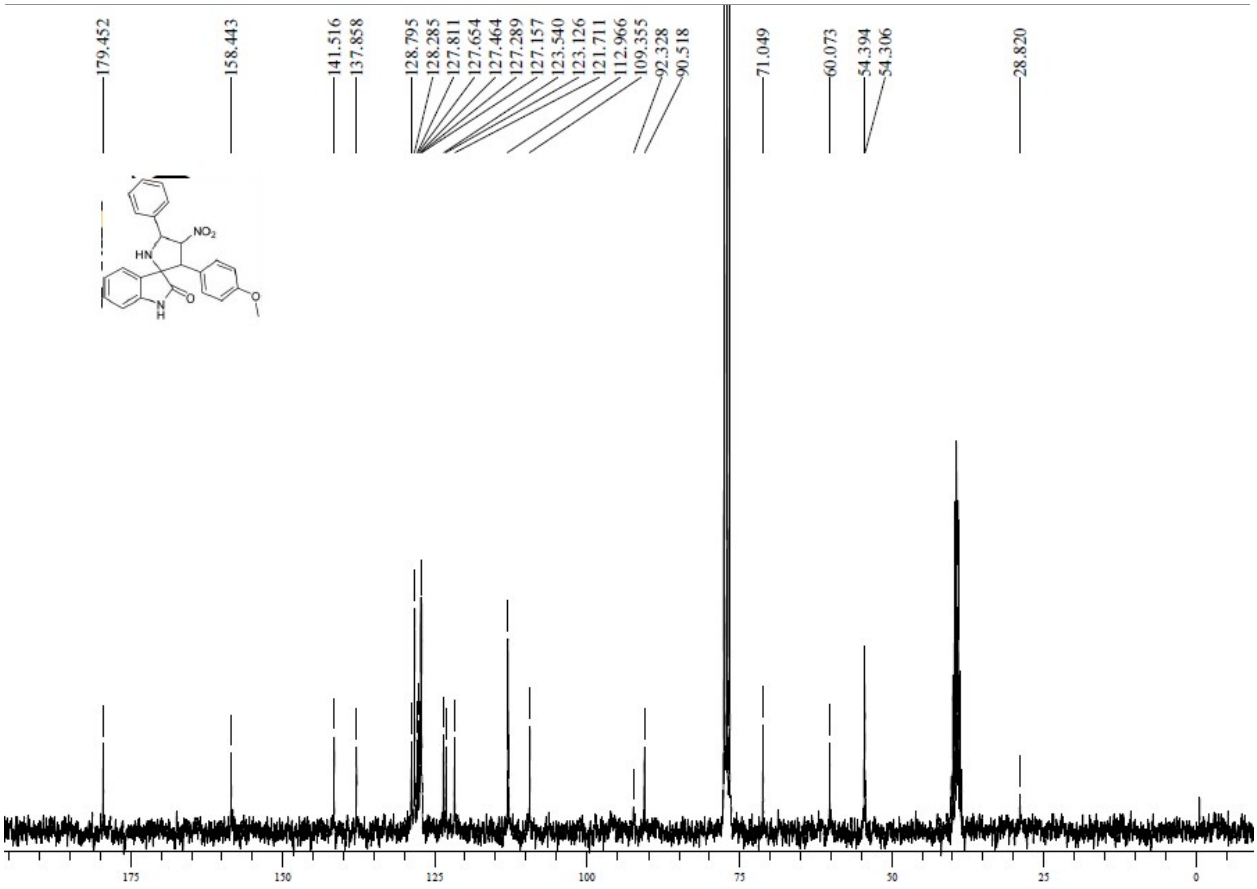
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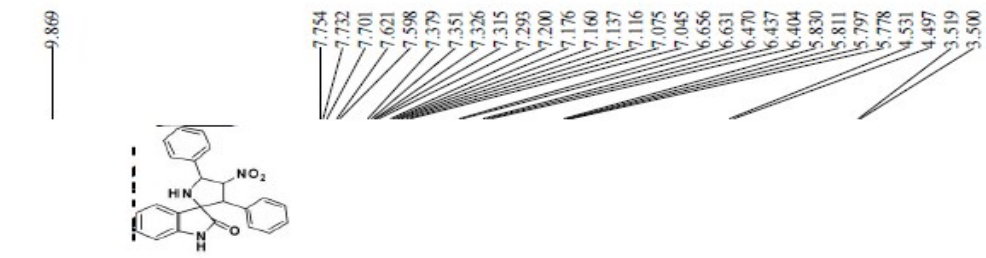
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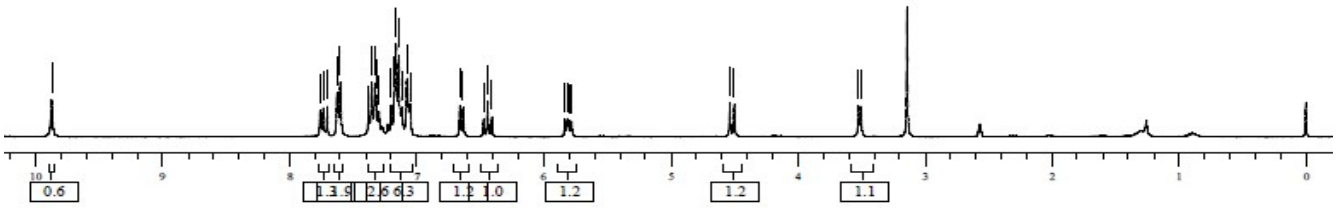
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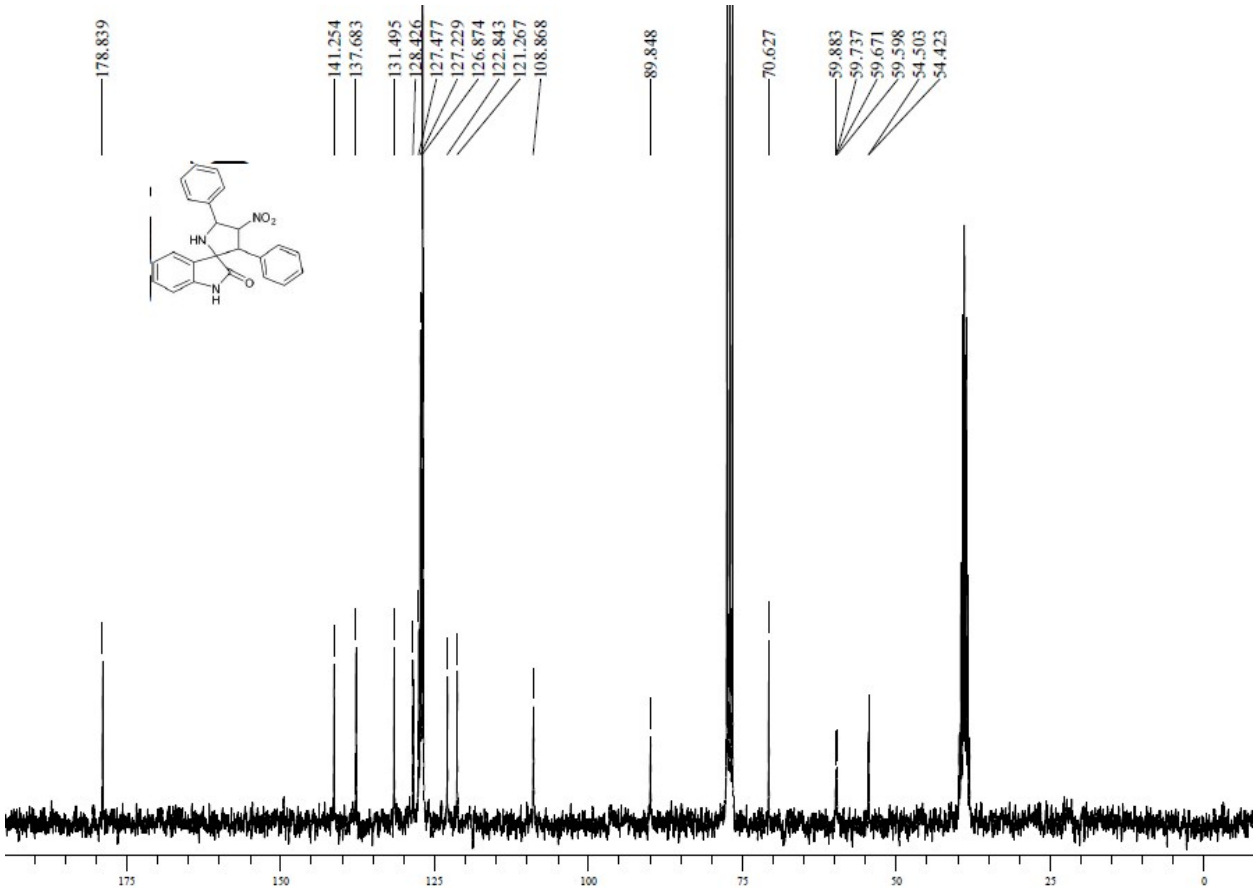
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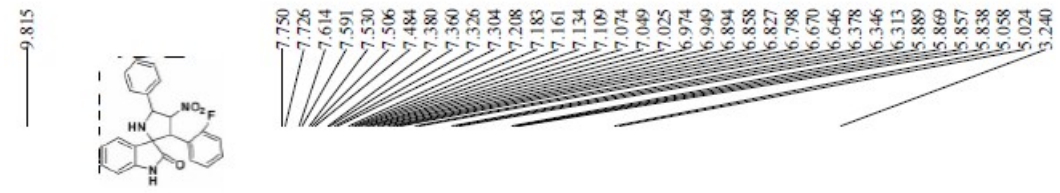
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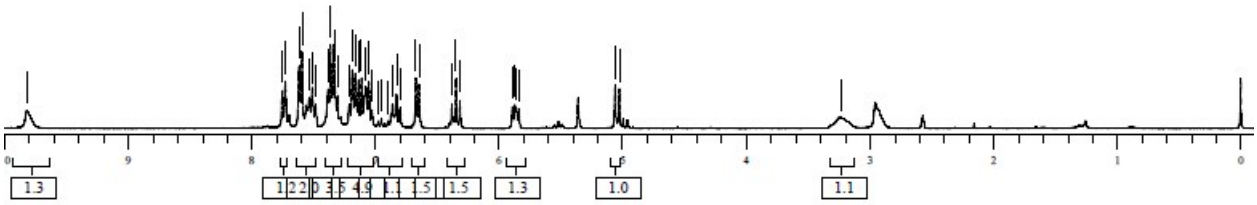
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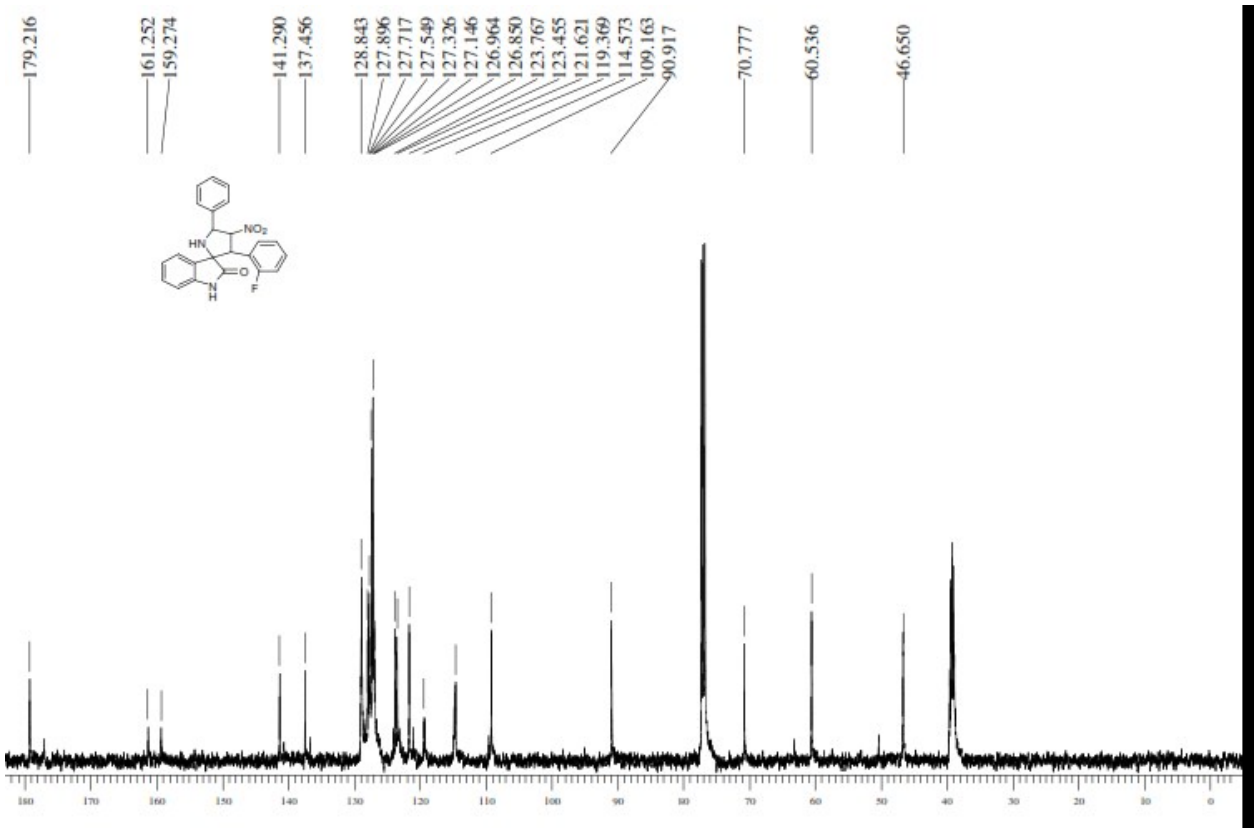
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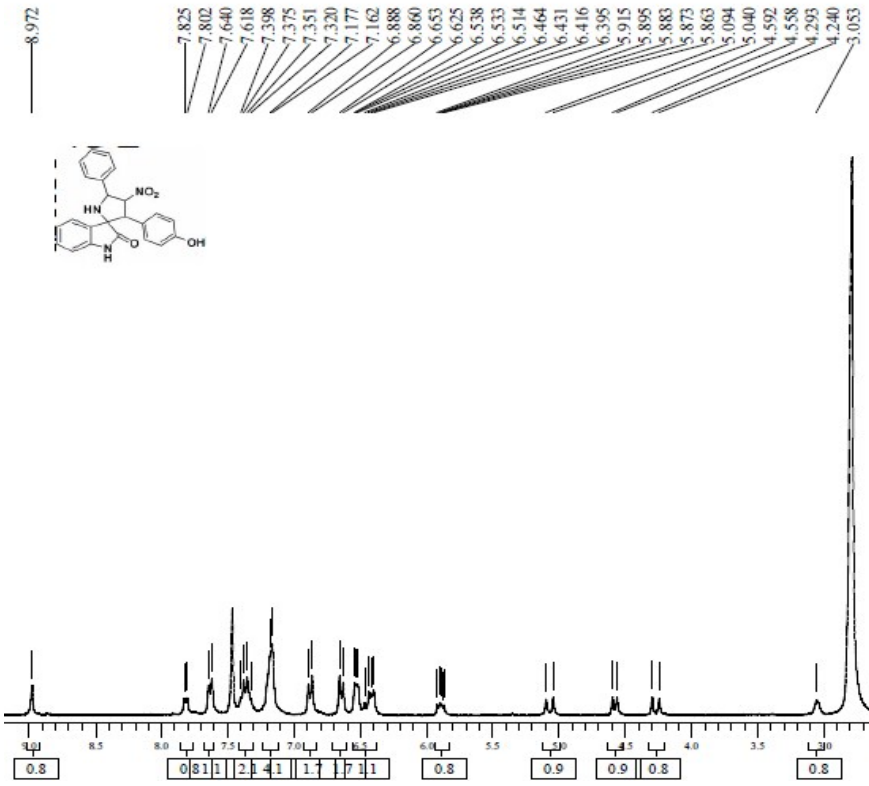
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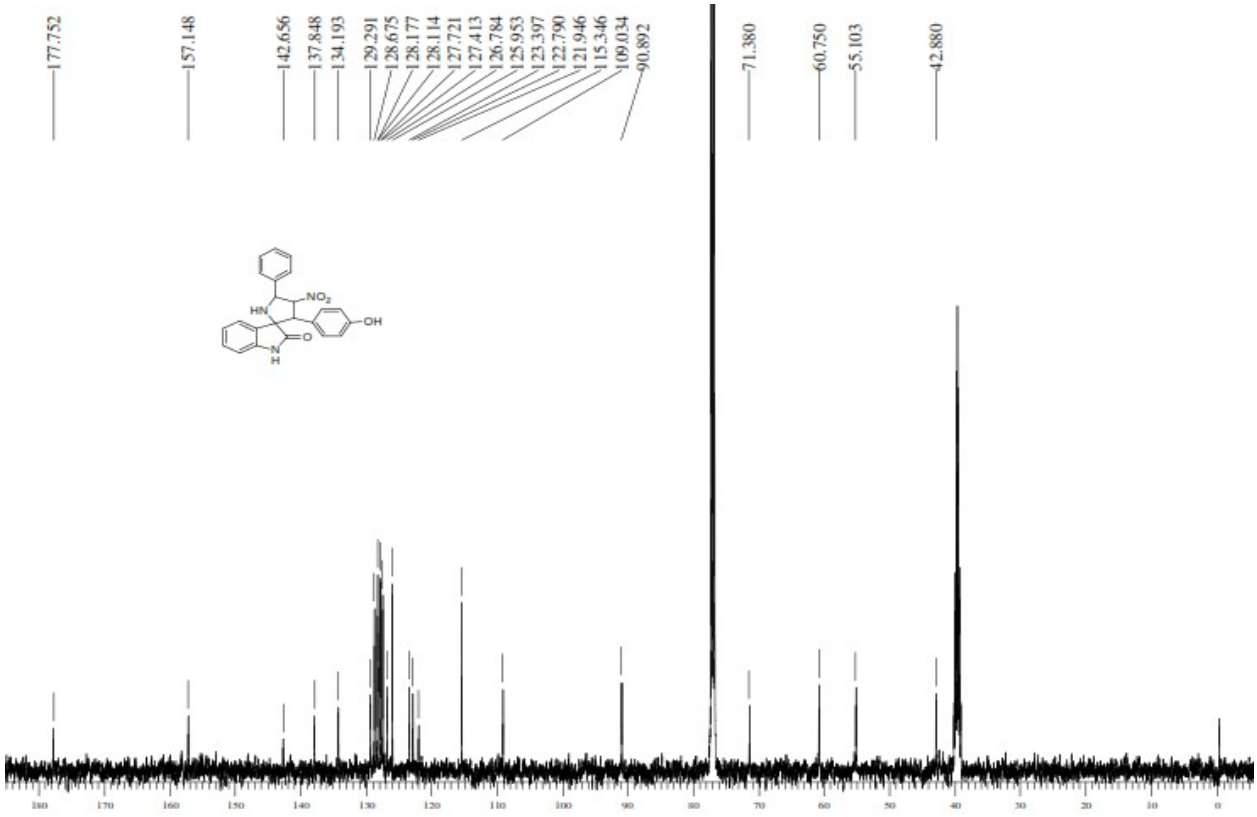
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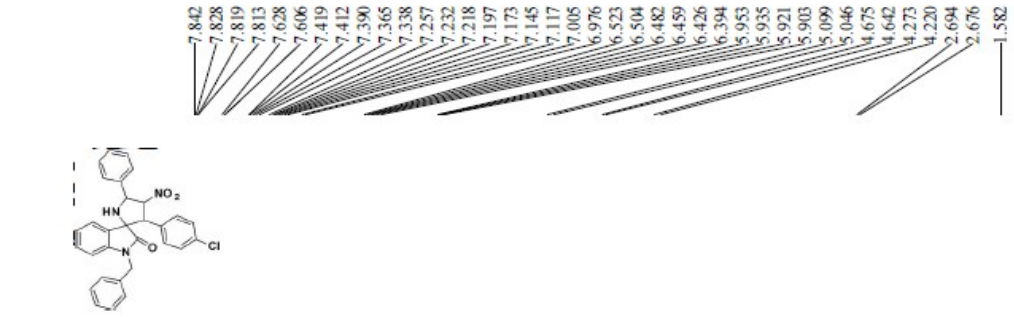
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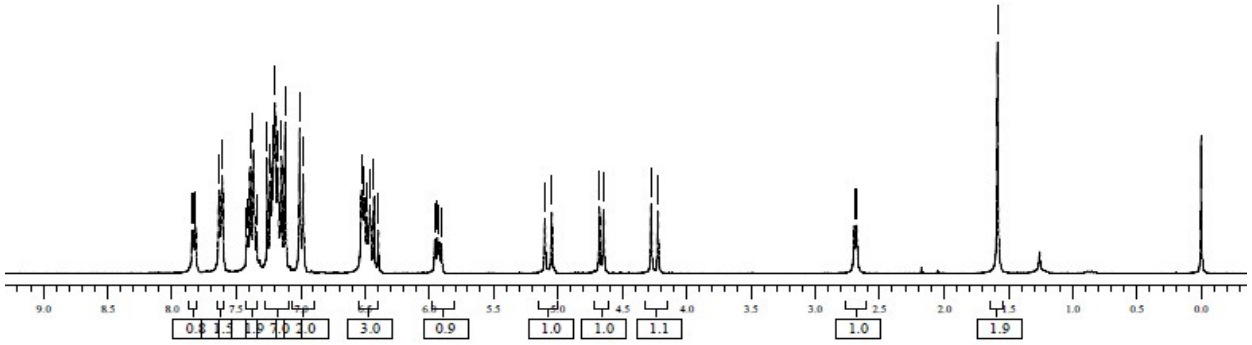
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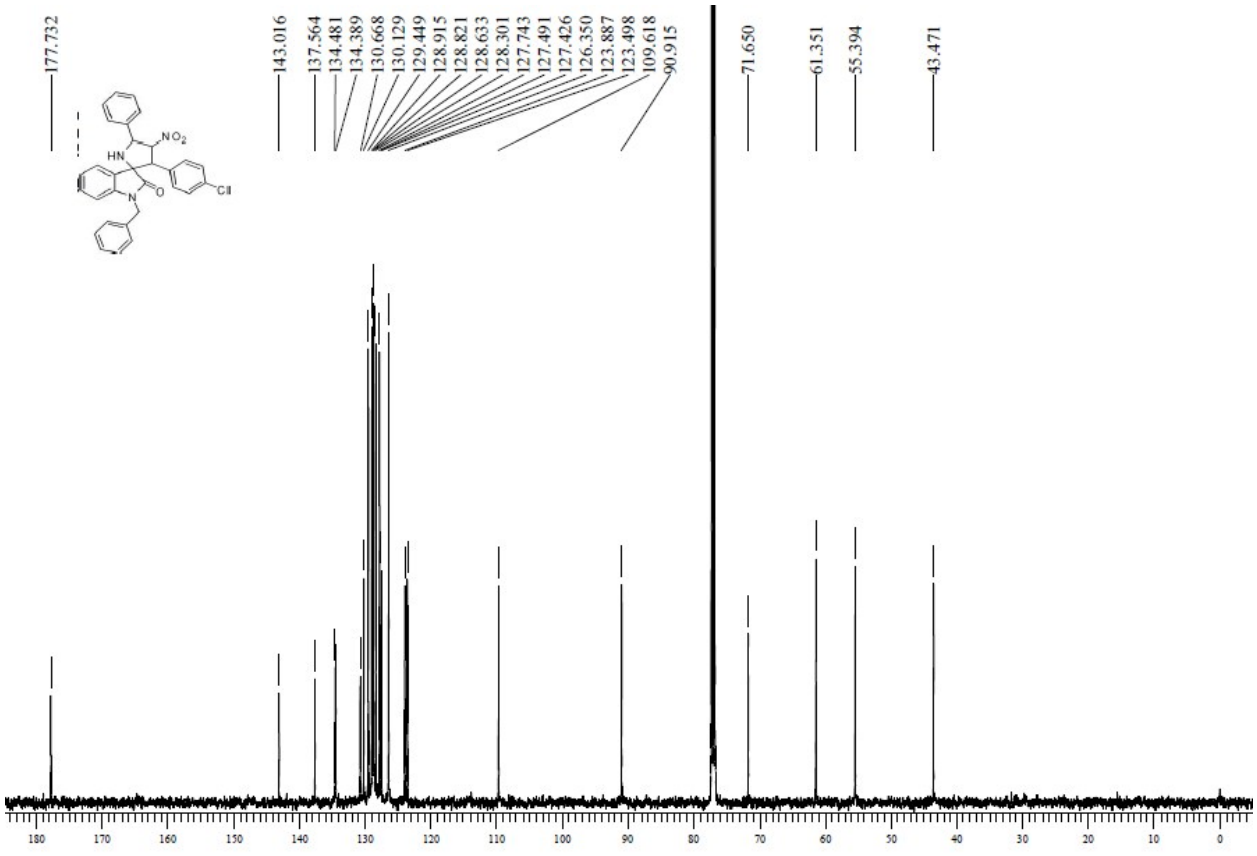
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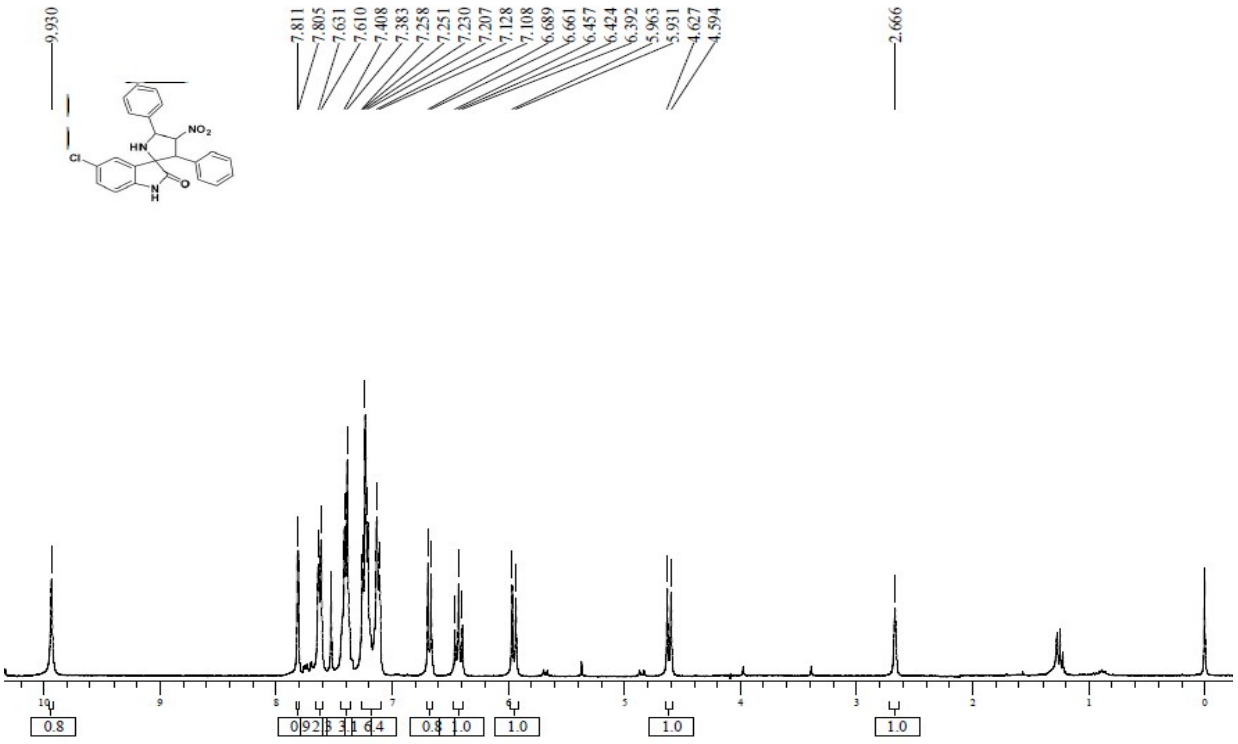
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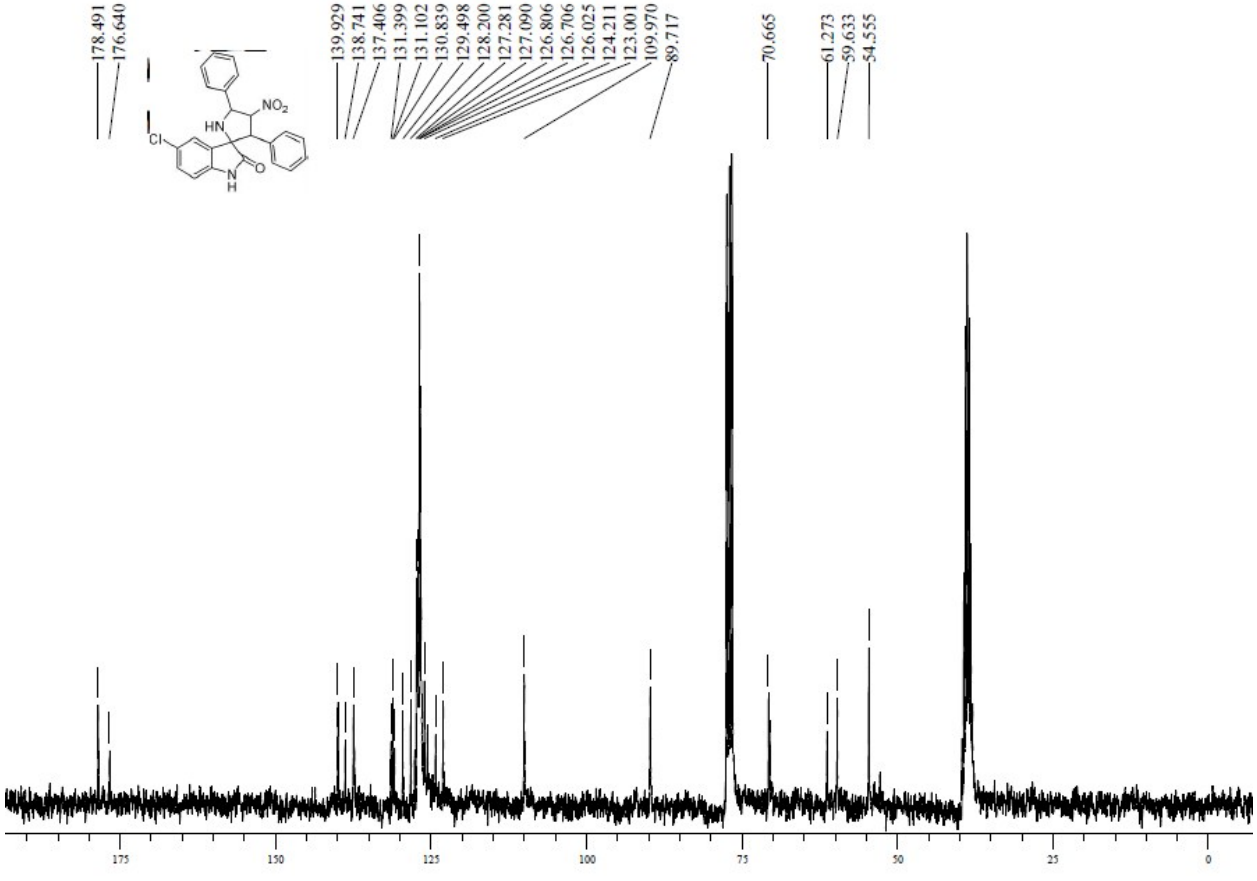
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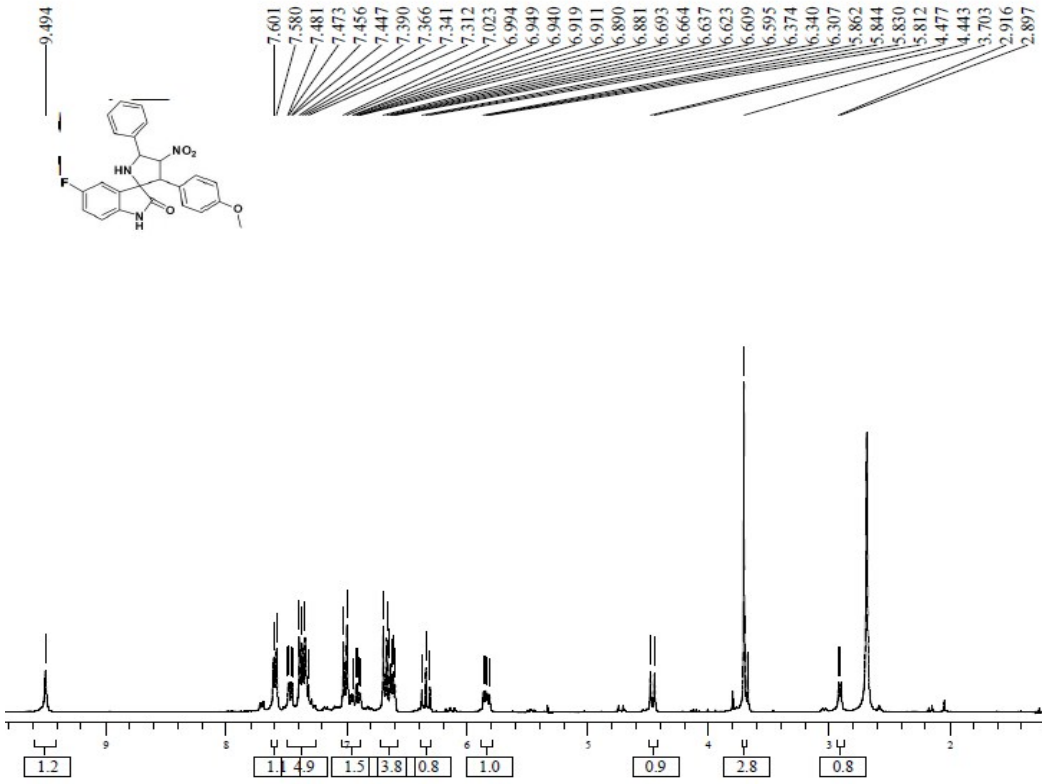
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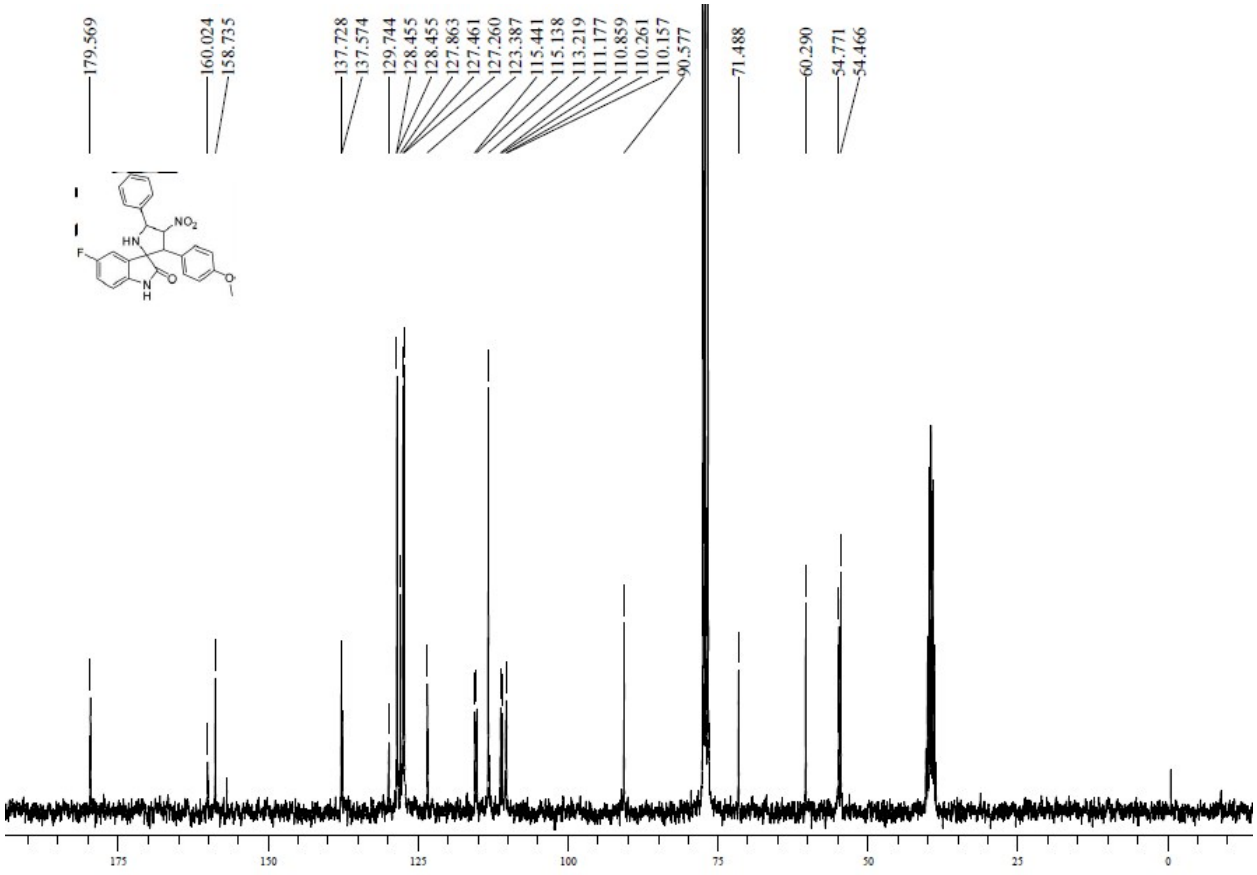
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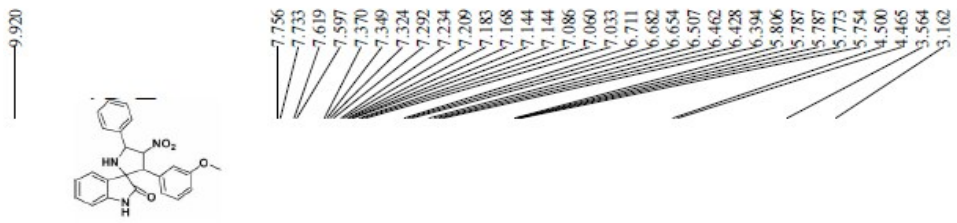
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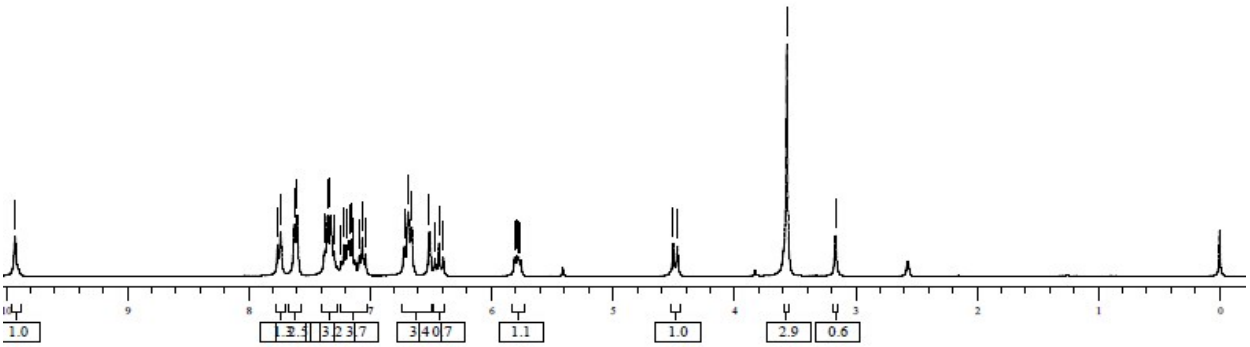
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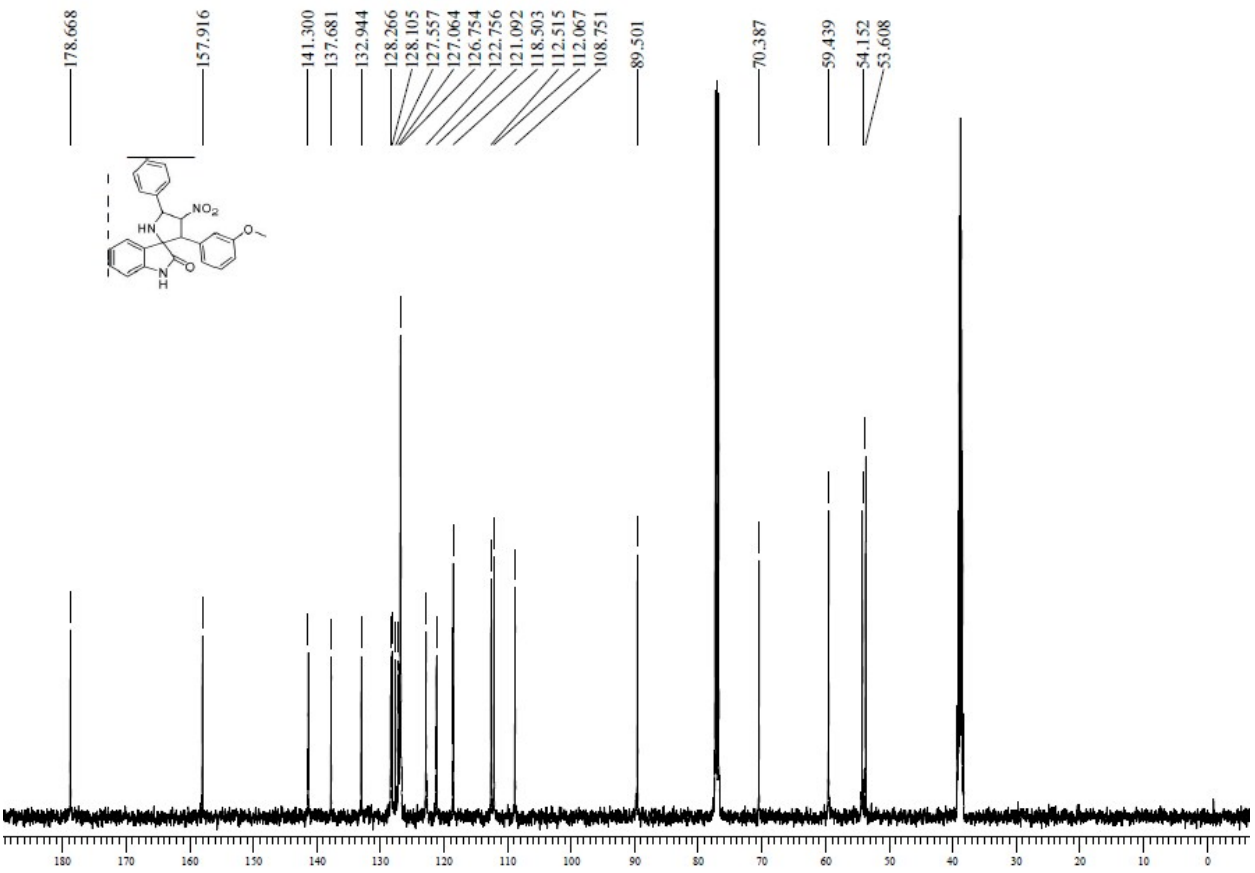
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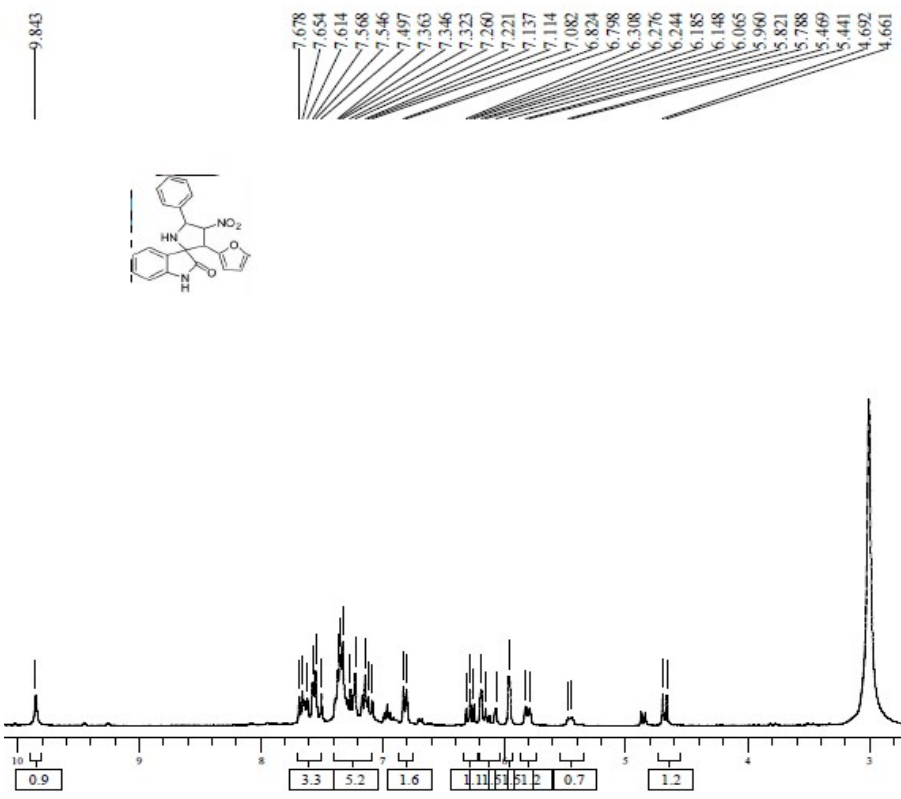
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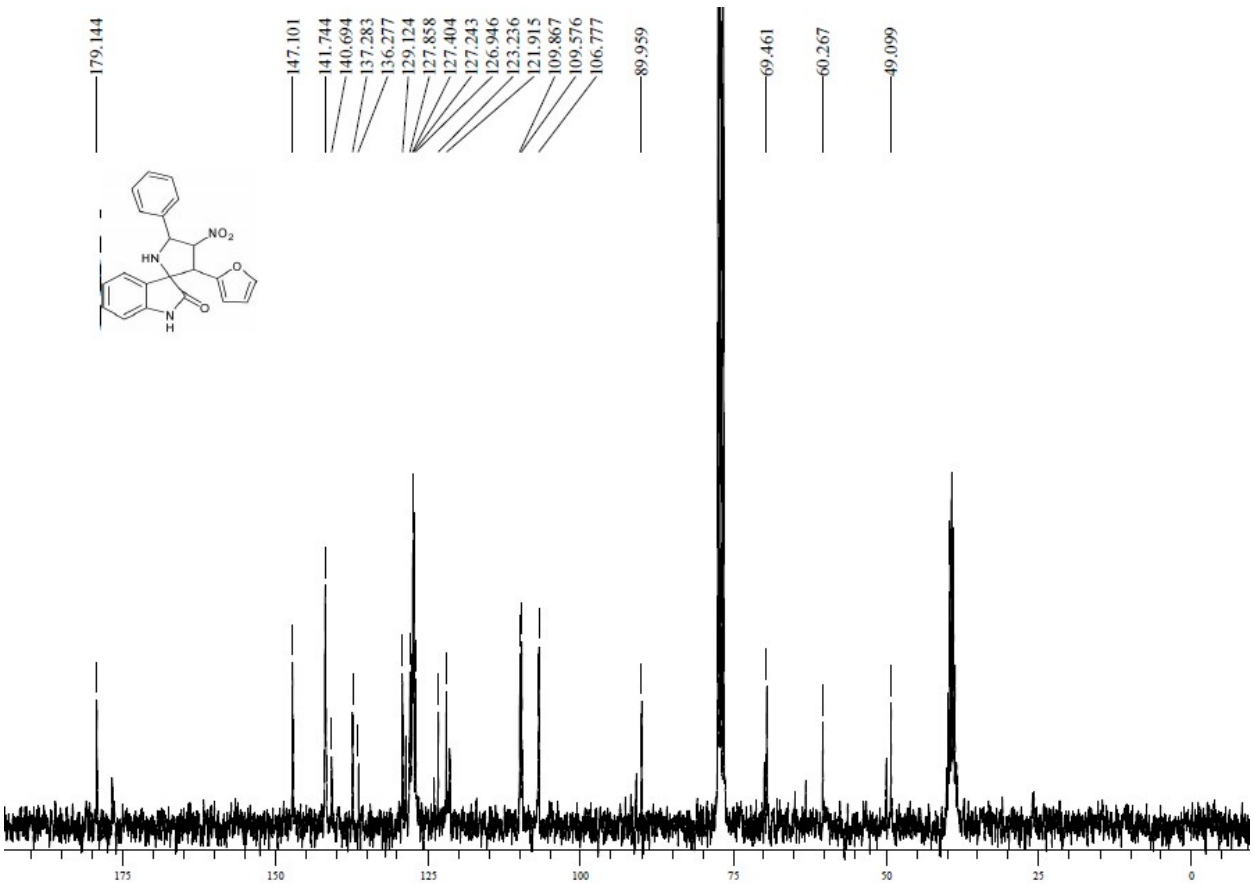
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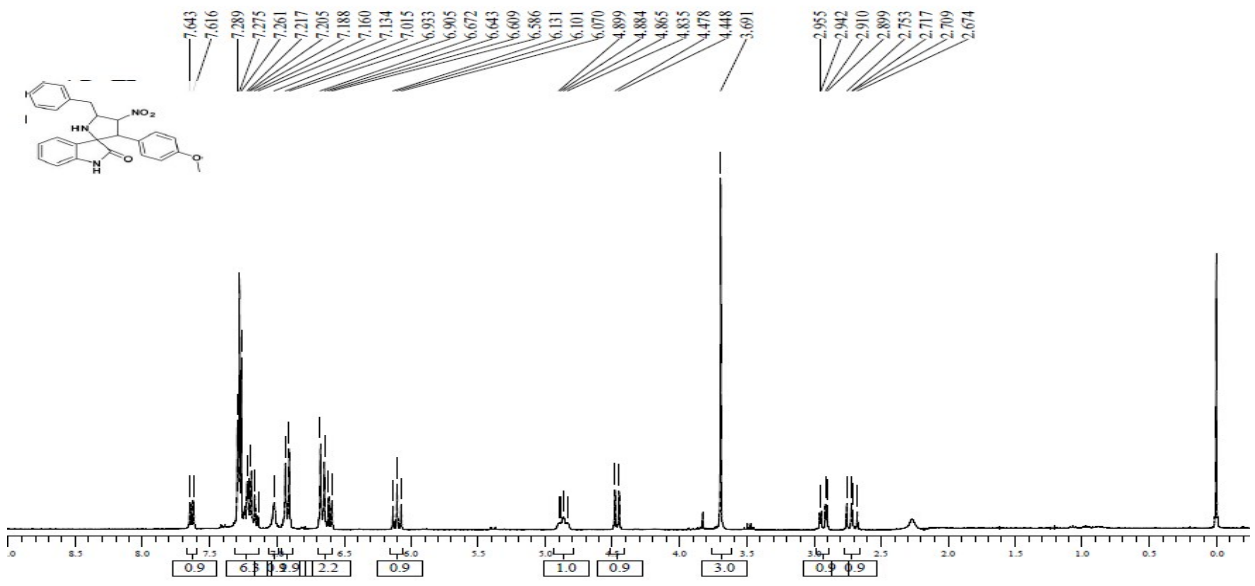
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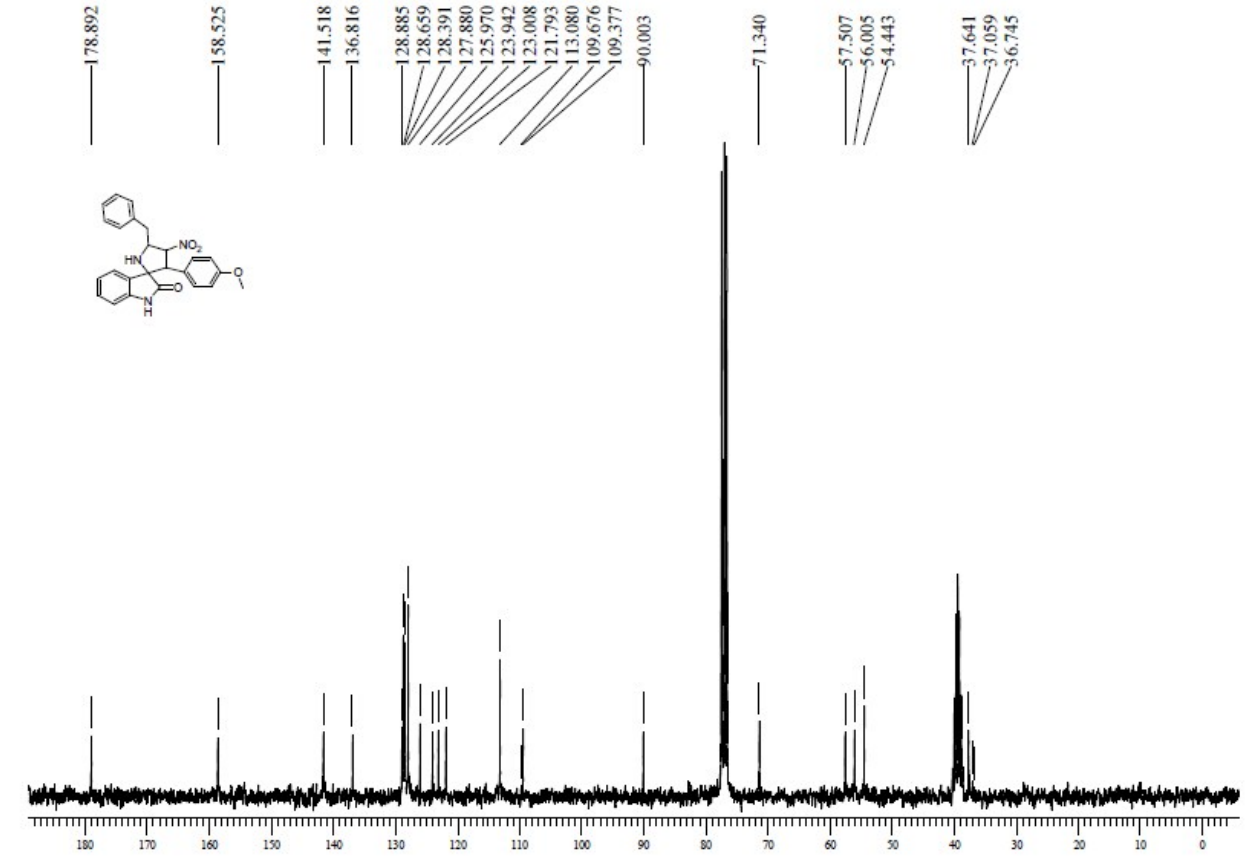
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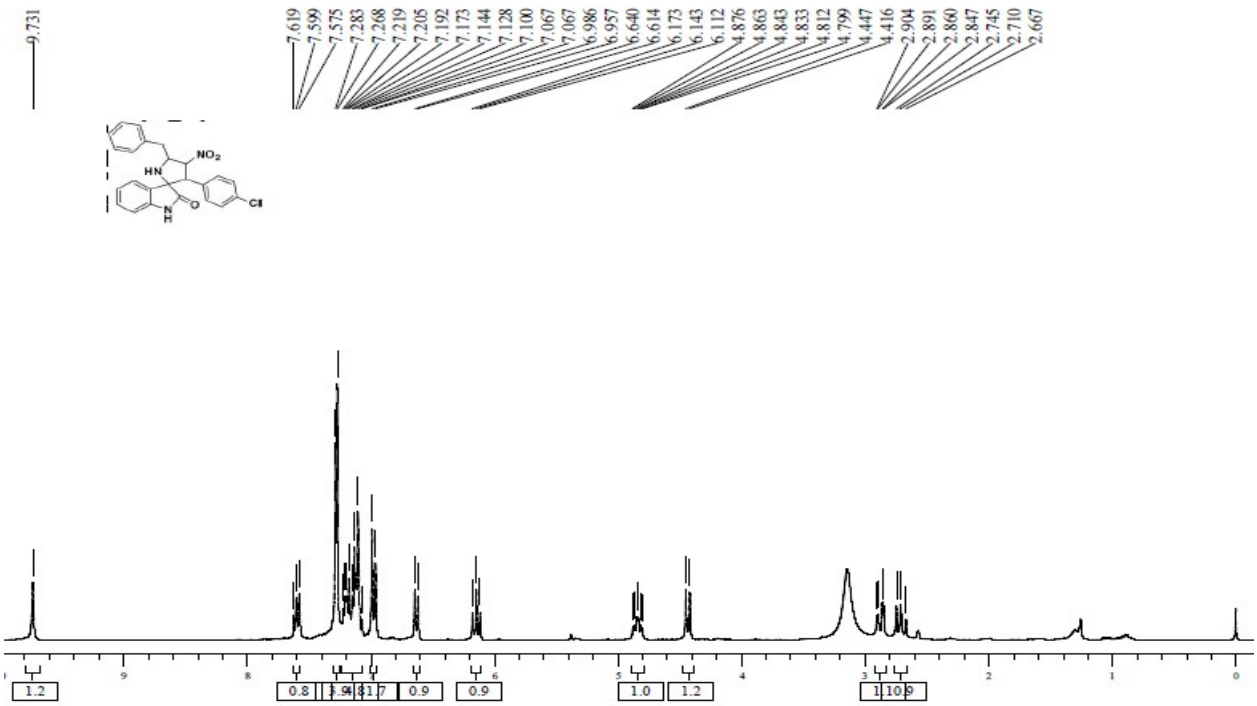
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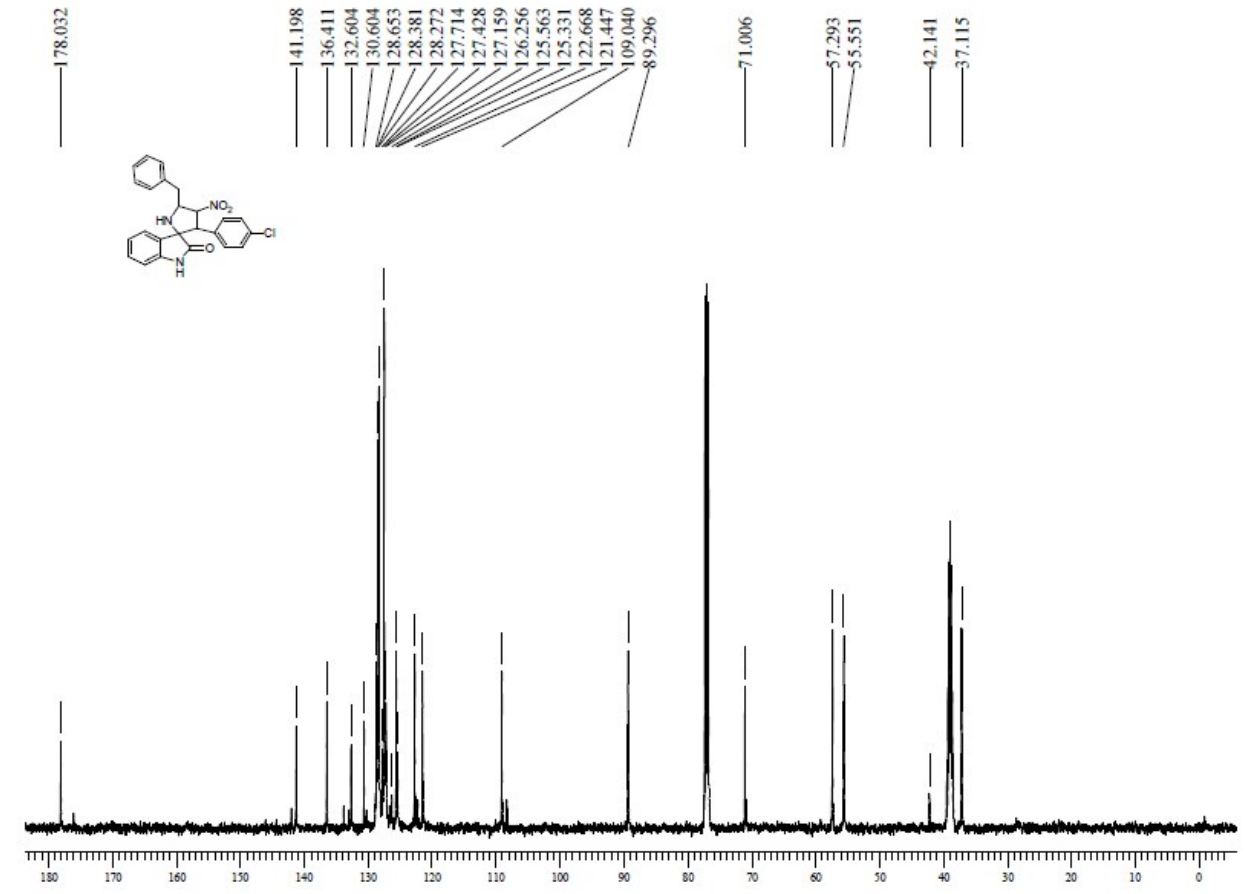
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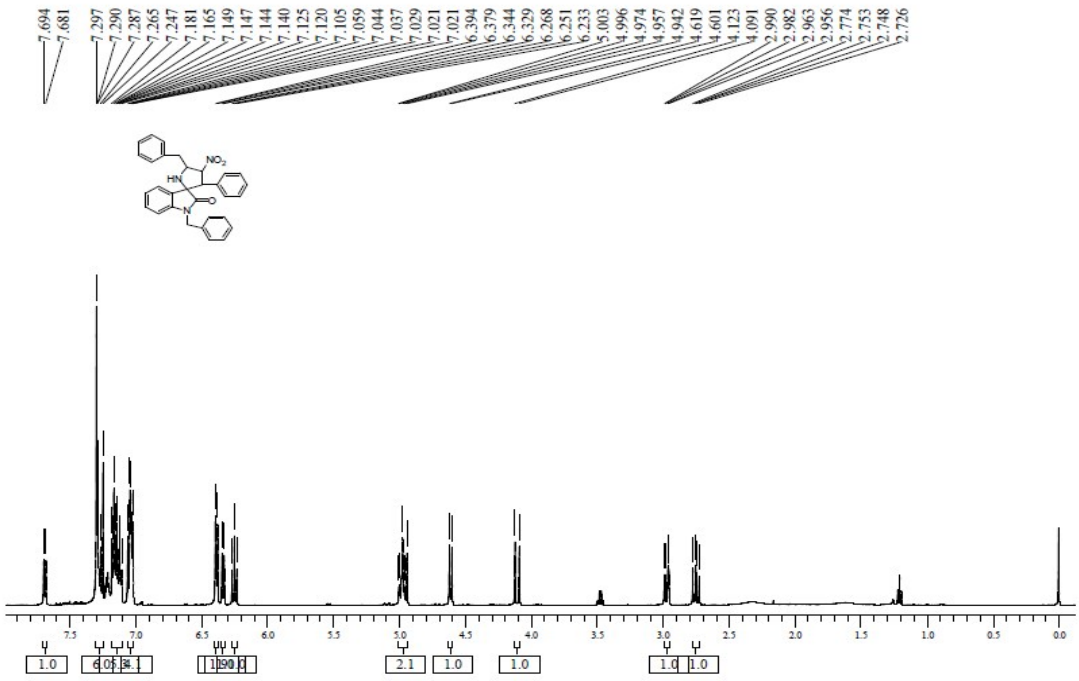
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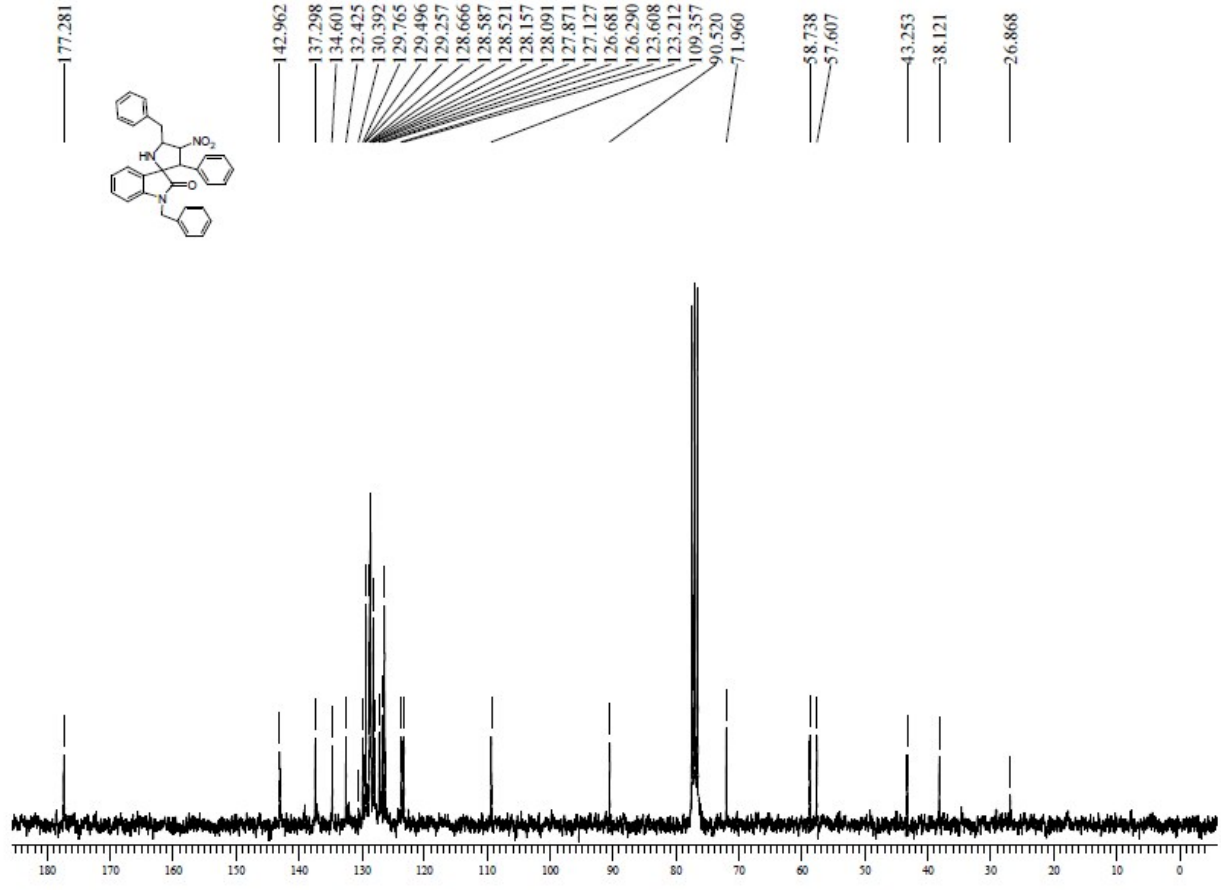
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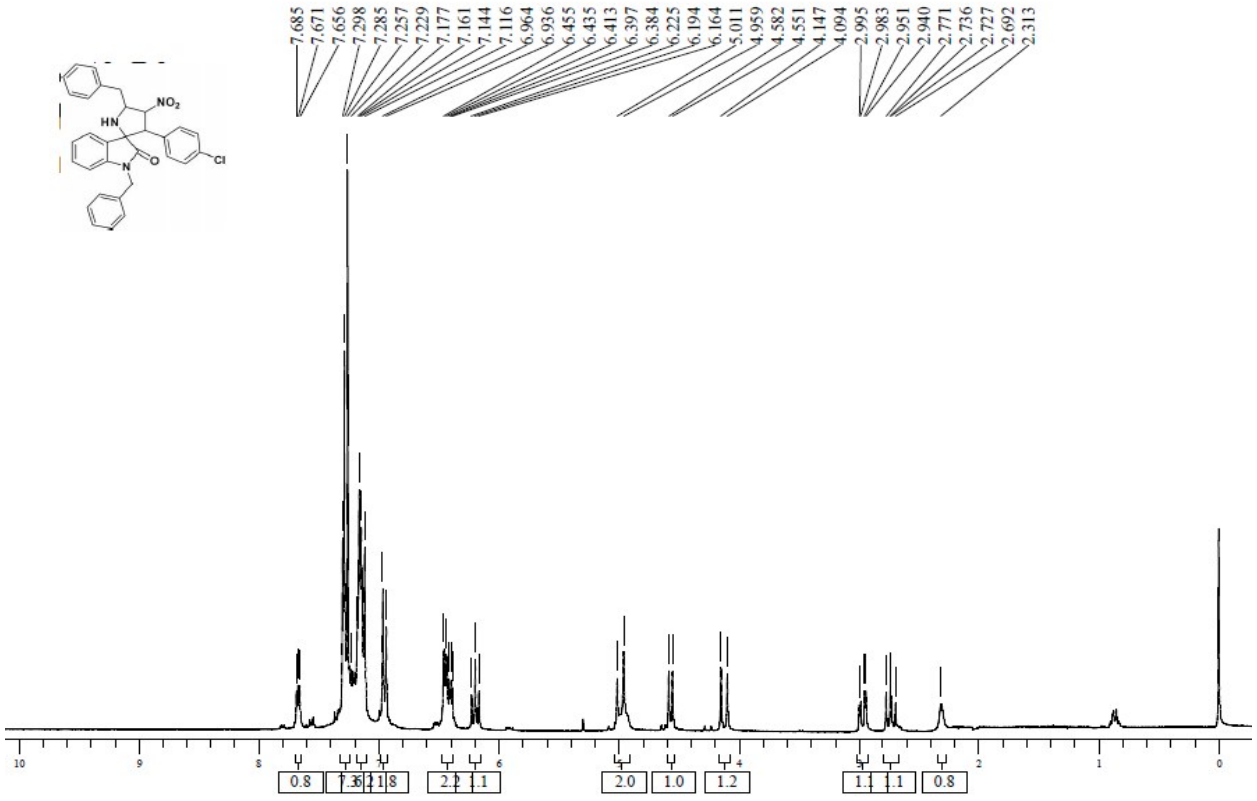
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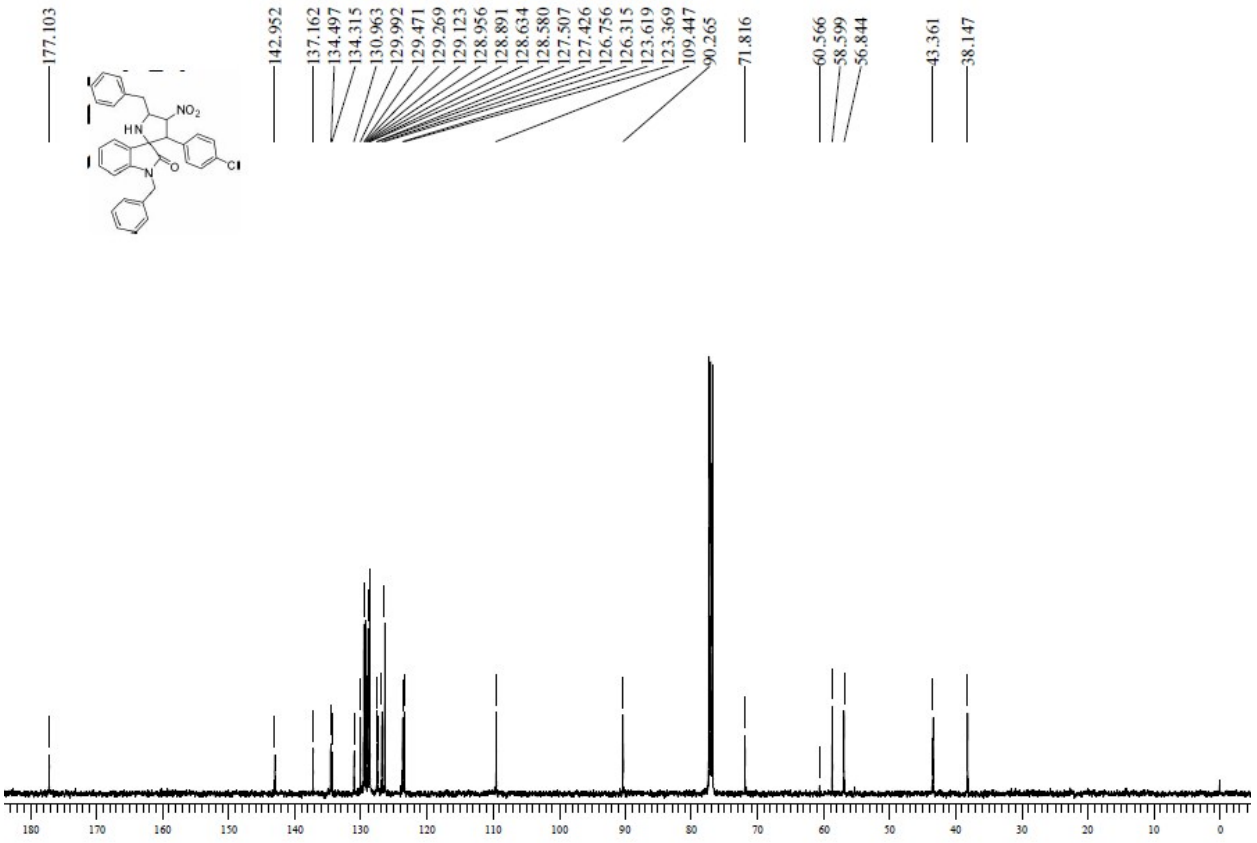
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71.816
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38.147
NO2
HN
O
N
Cl


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6.128
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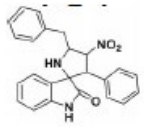
2.671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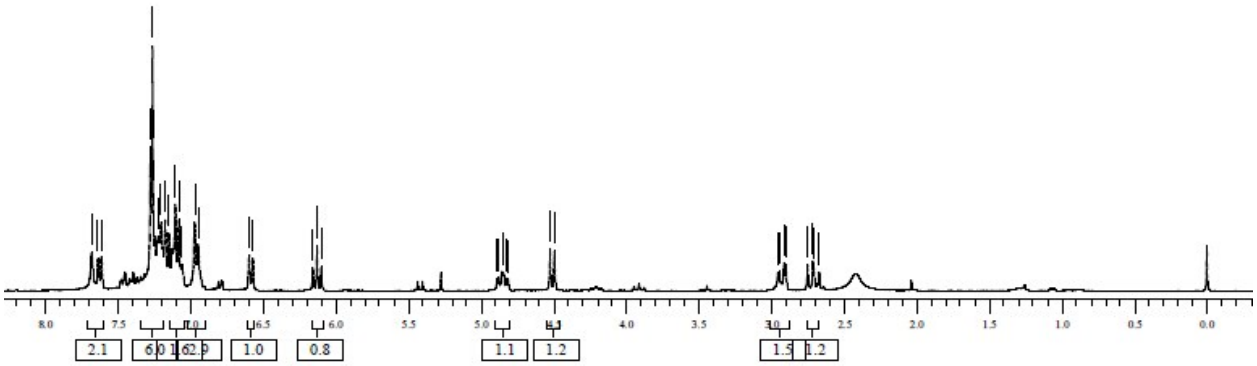
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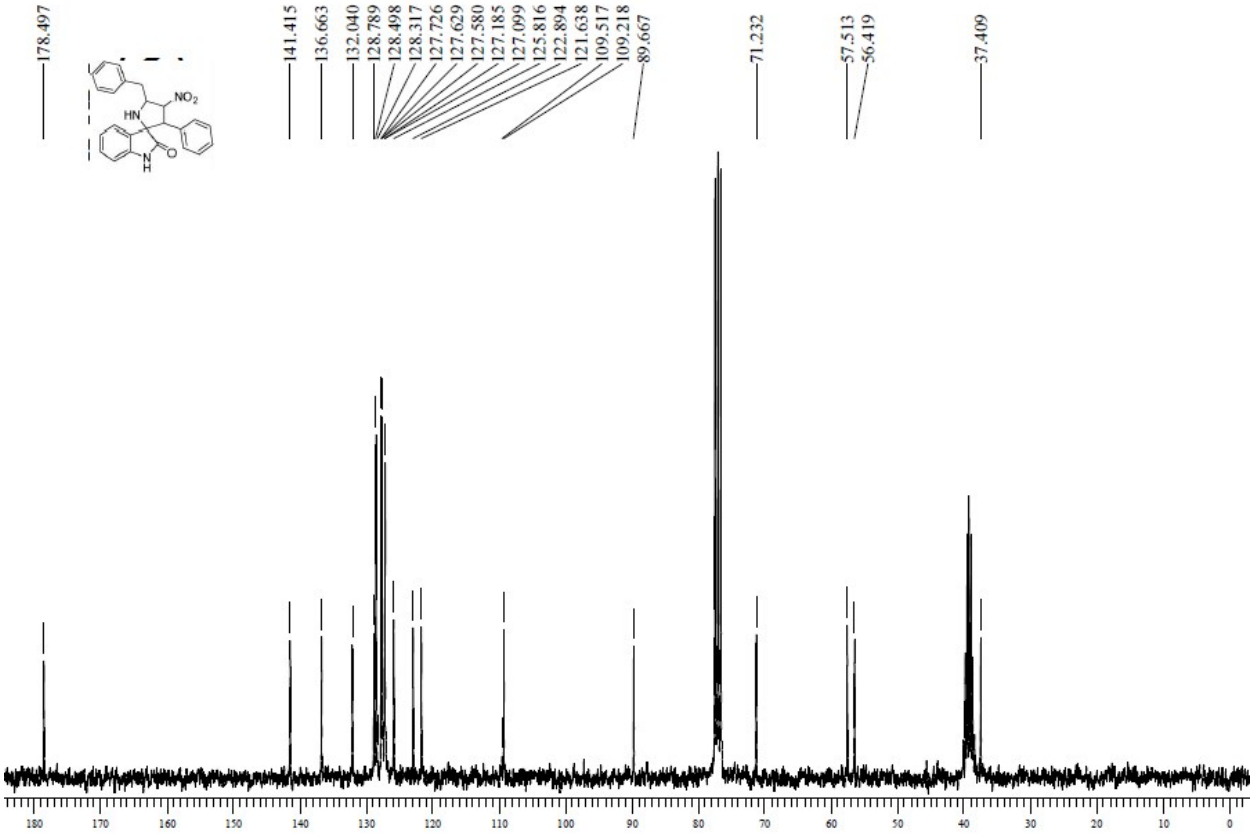
1.2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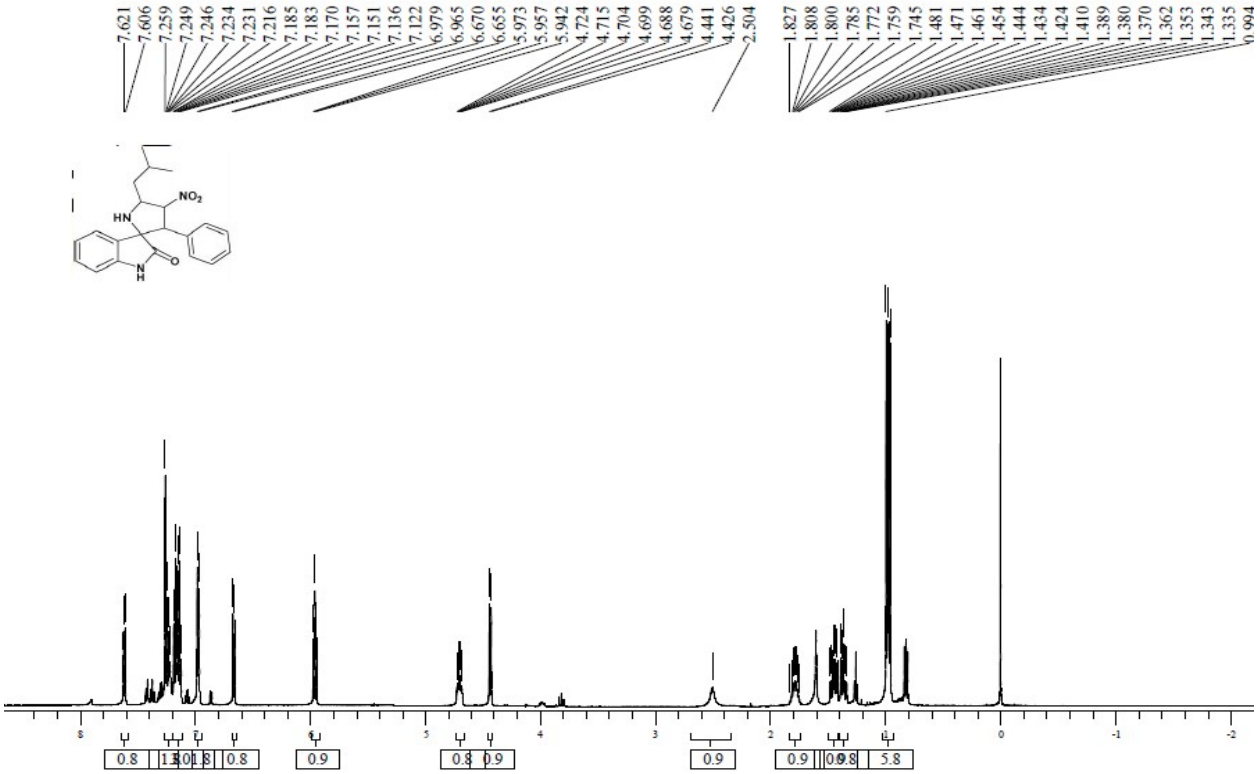
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7.136
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6.655
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4.441
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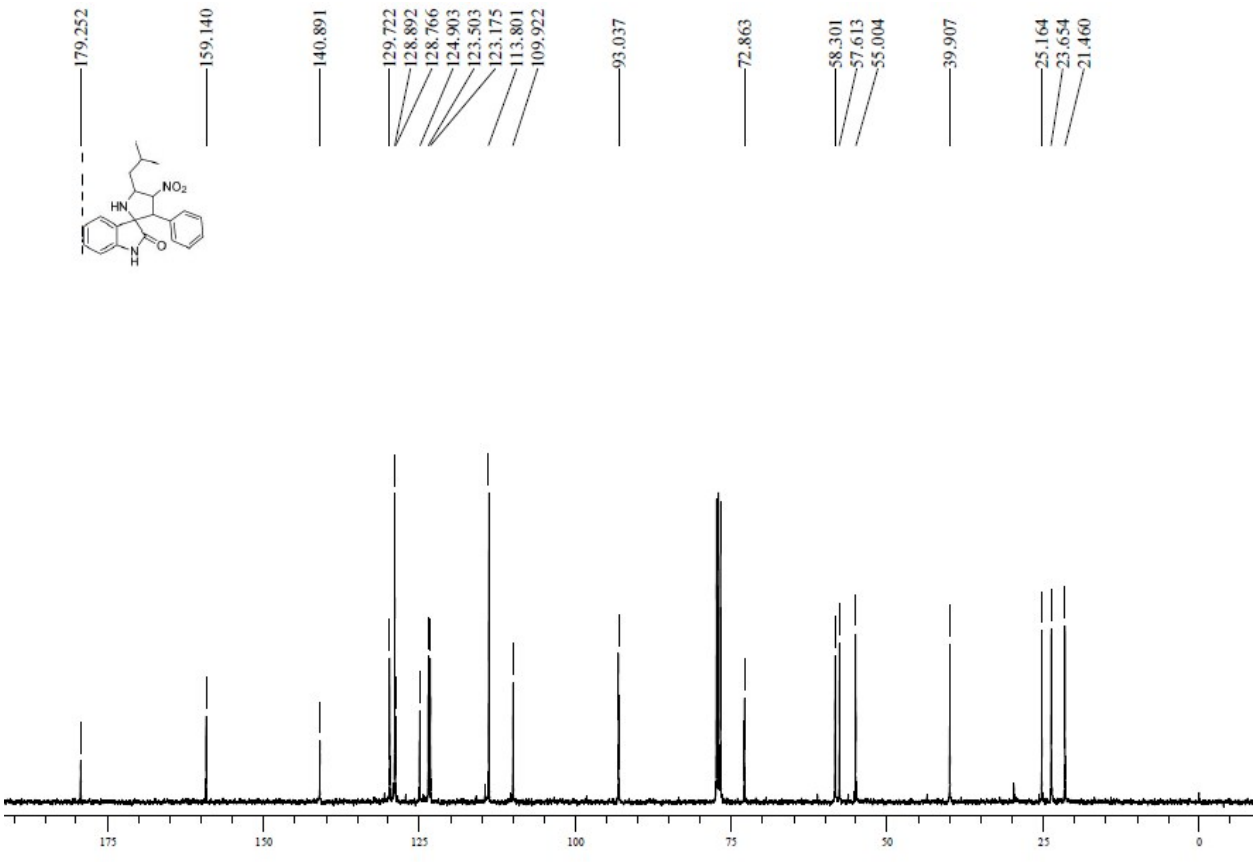
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123.503
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72.863
58.301
57.613
55.004
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23.654
21.460
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O
N
H
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100
75
50
25
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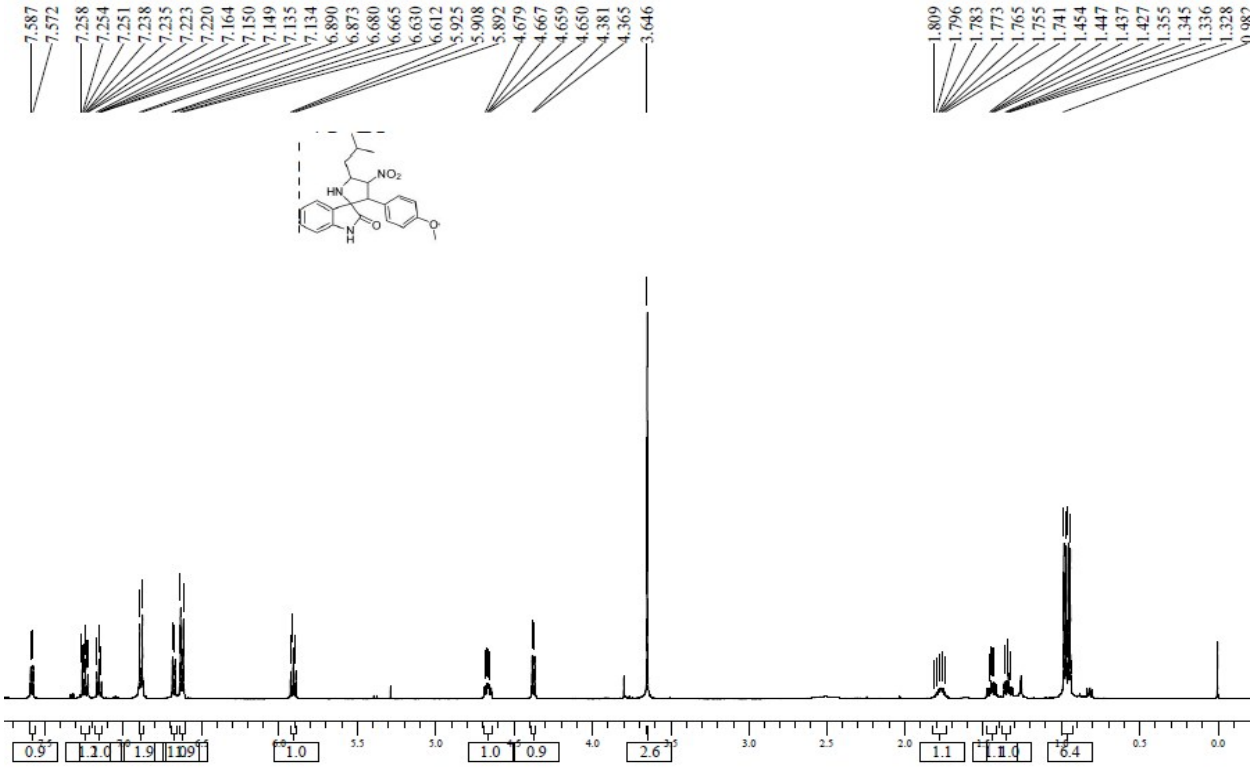
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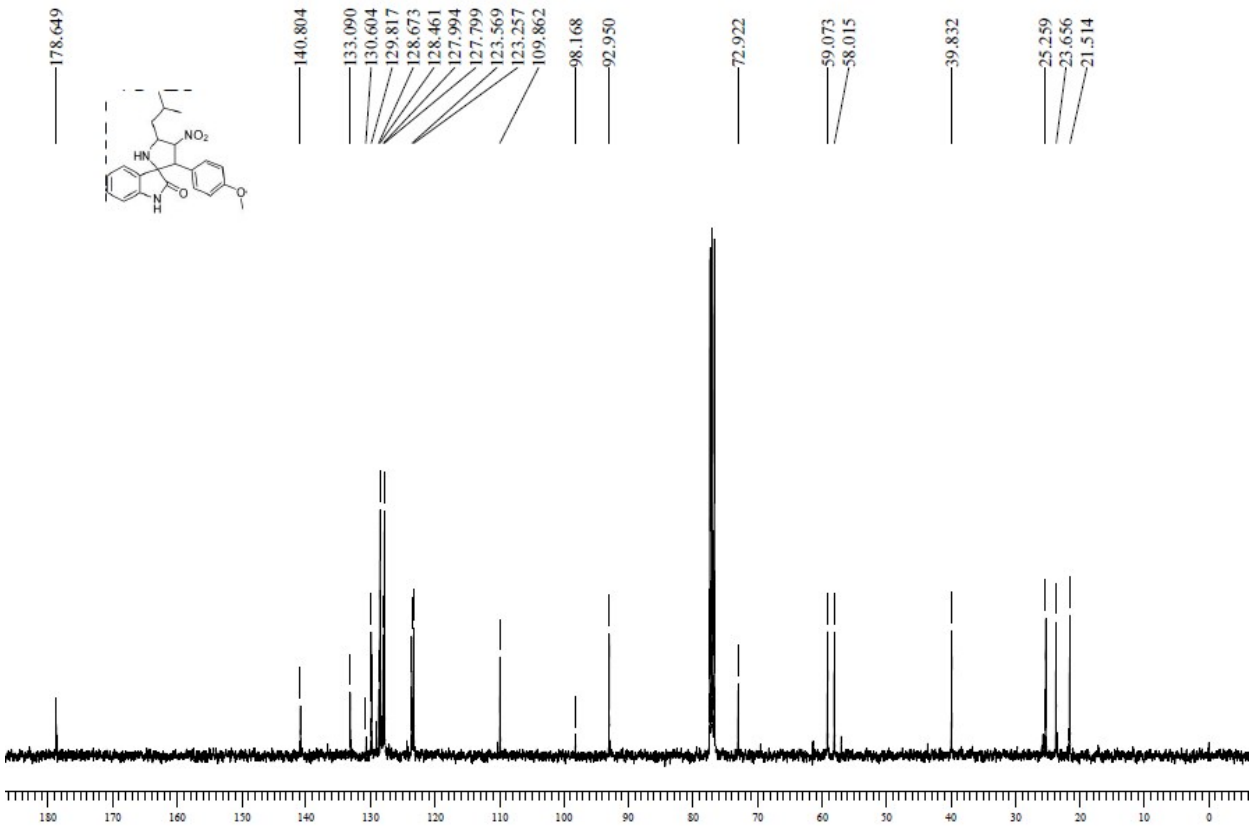
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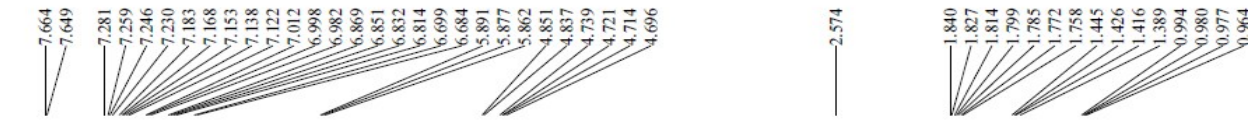
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6.684
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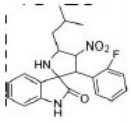
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HN
O
N
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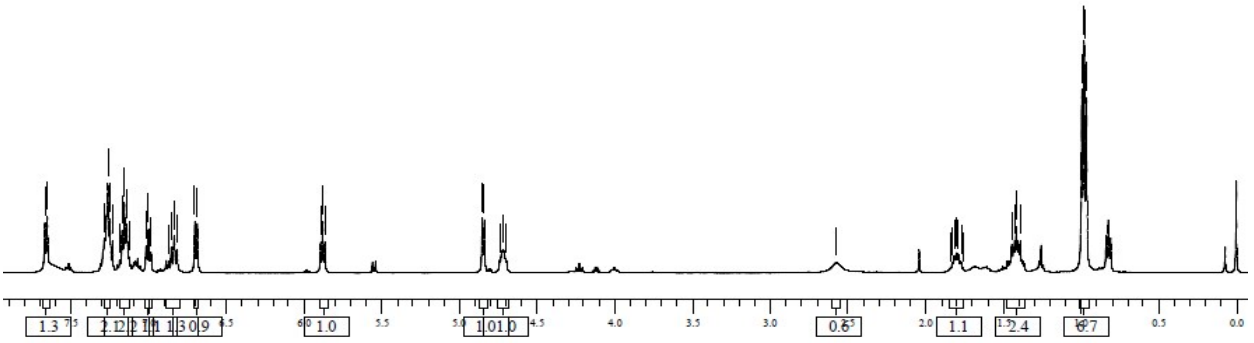
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6.7


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128.883
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127.470
123.416
123.039
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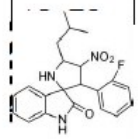
20.882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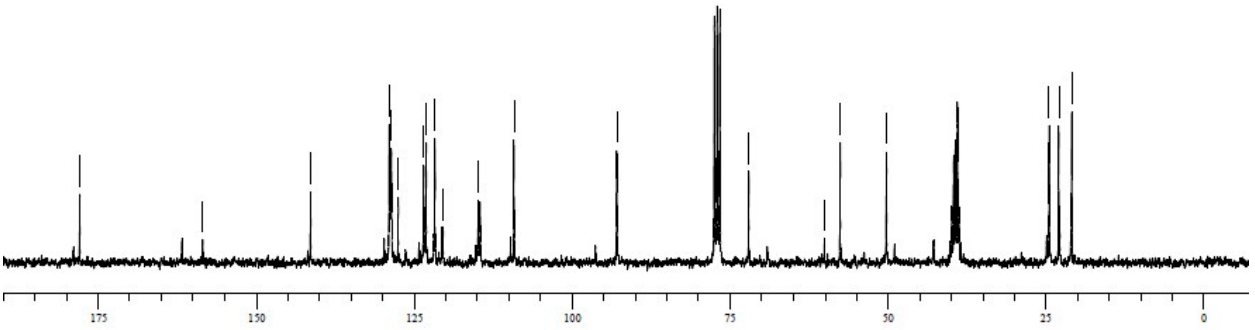
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75
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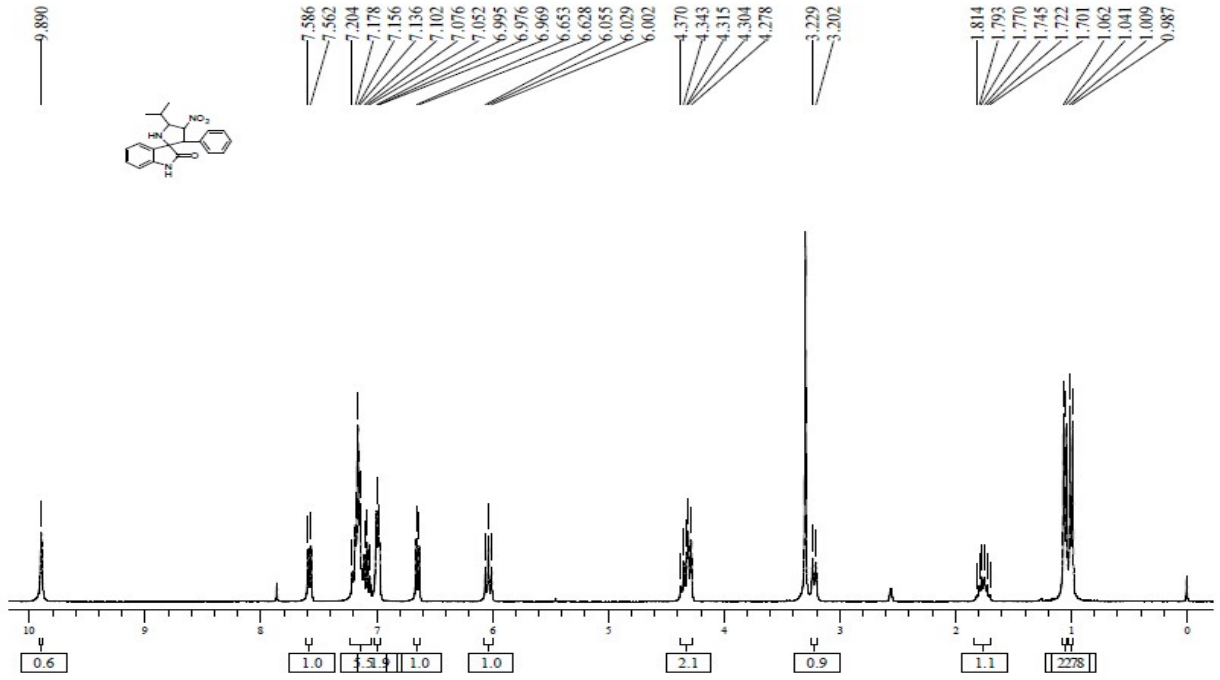
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3.229
3.202
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1.793
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1.745
1.722
1.701
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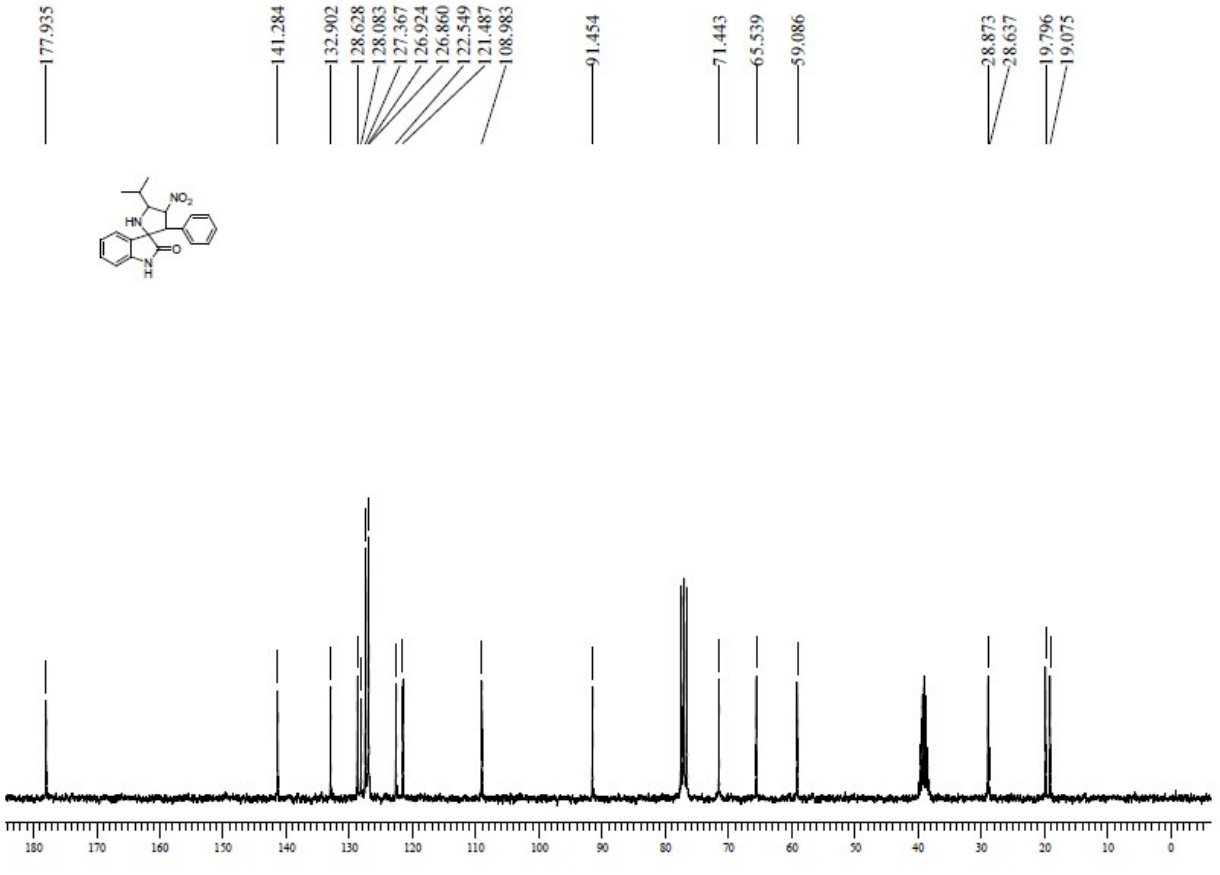
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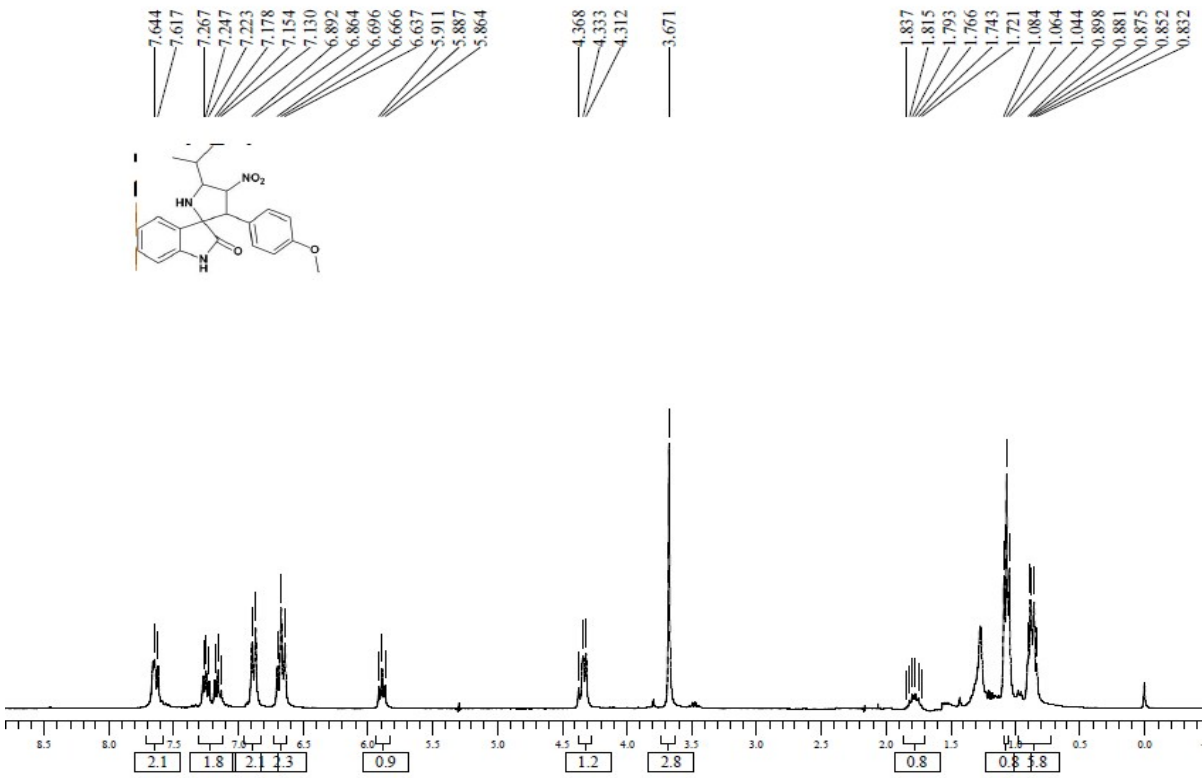
19.075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6.696
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5.911
5.887
5.864
4.368
4.333
4.312
3.671
1.837
1.815
1.793
1.766
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1.084
1.064
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0.898
0.881
0.875
0.852
0.832
NO2
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1.2
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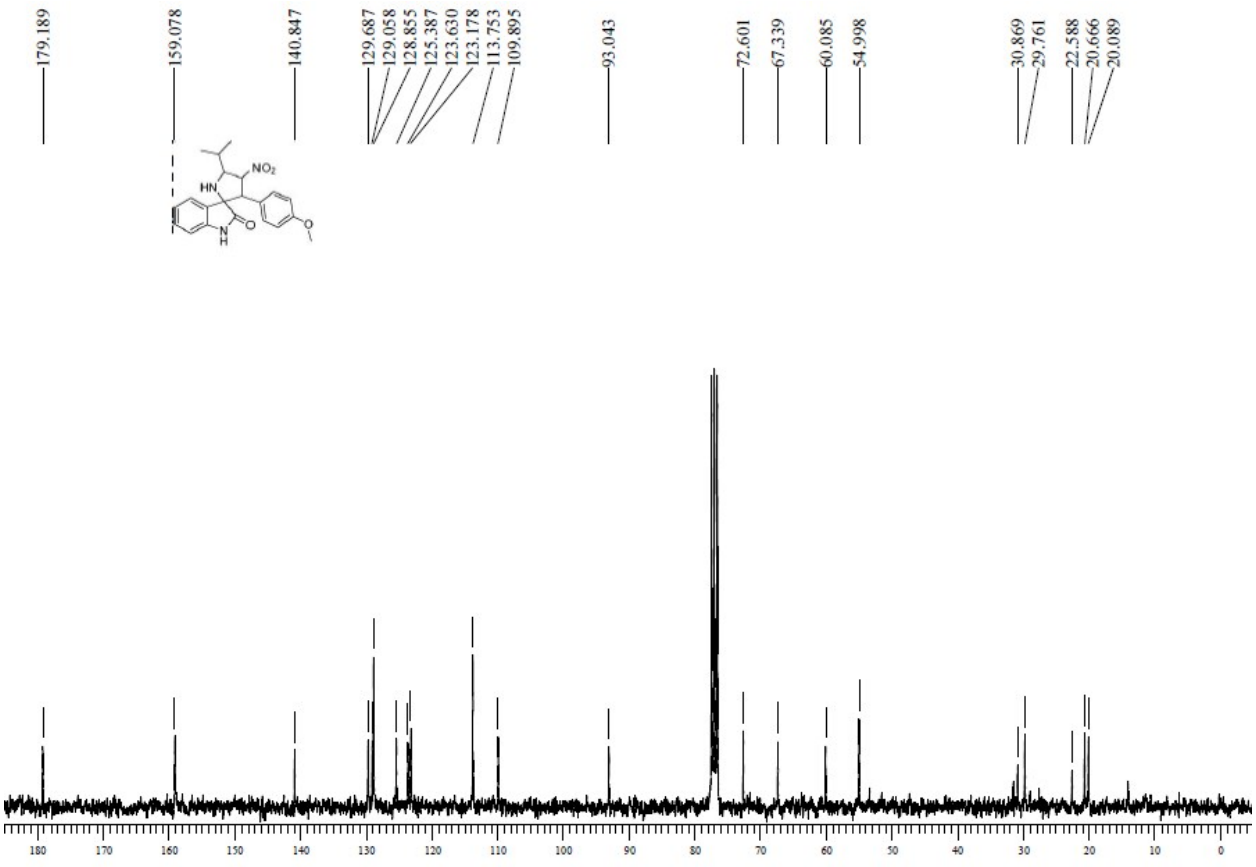
3.8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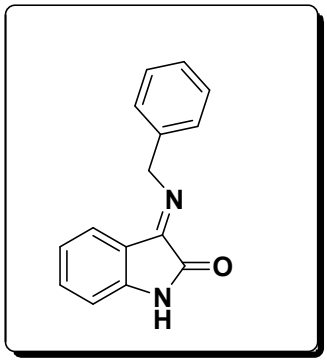
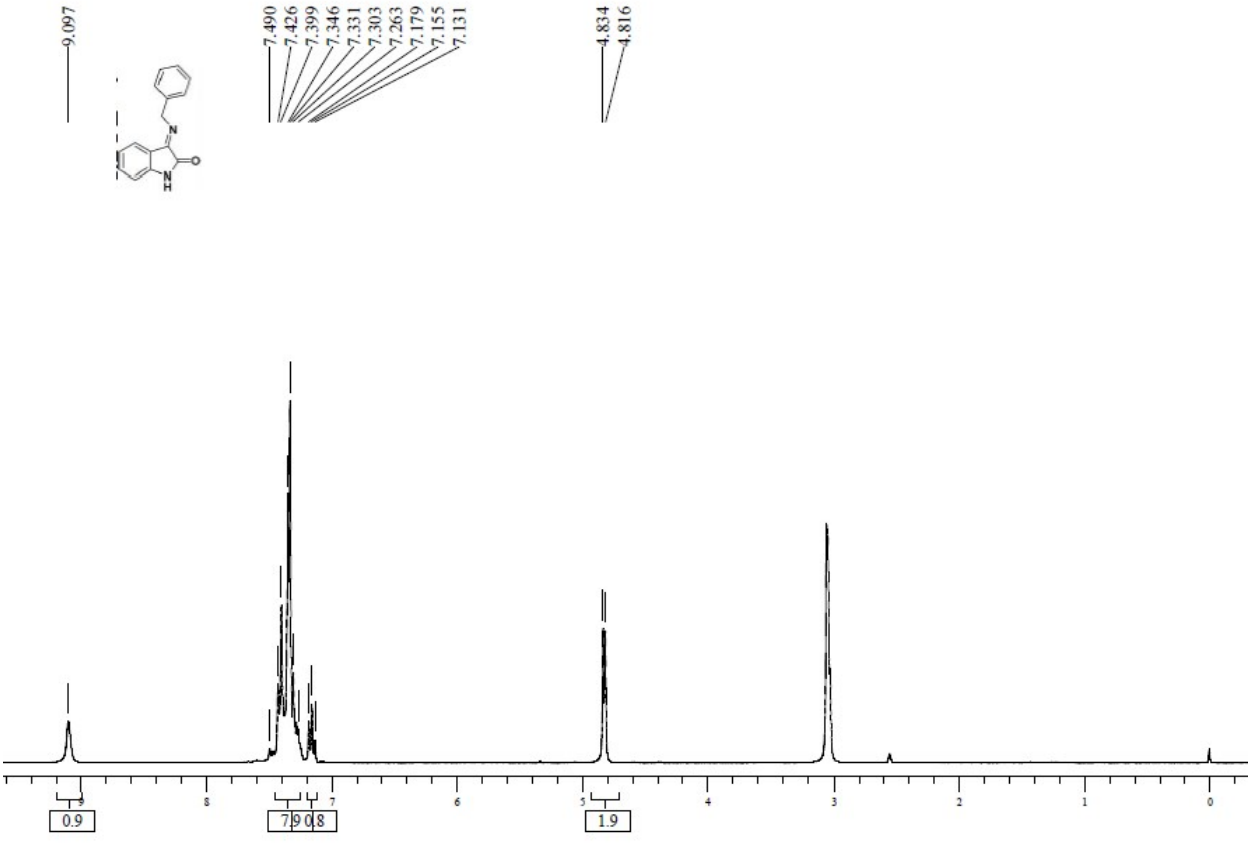
113.753
109.895
93.043
72.601
67.339
60.085
54.998
30.869
29.761
22.588
20.666
20.089
NO2
HN
O
H

3-(2-phenylethylidene)indolin-2-one (I):

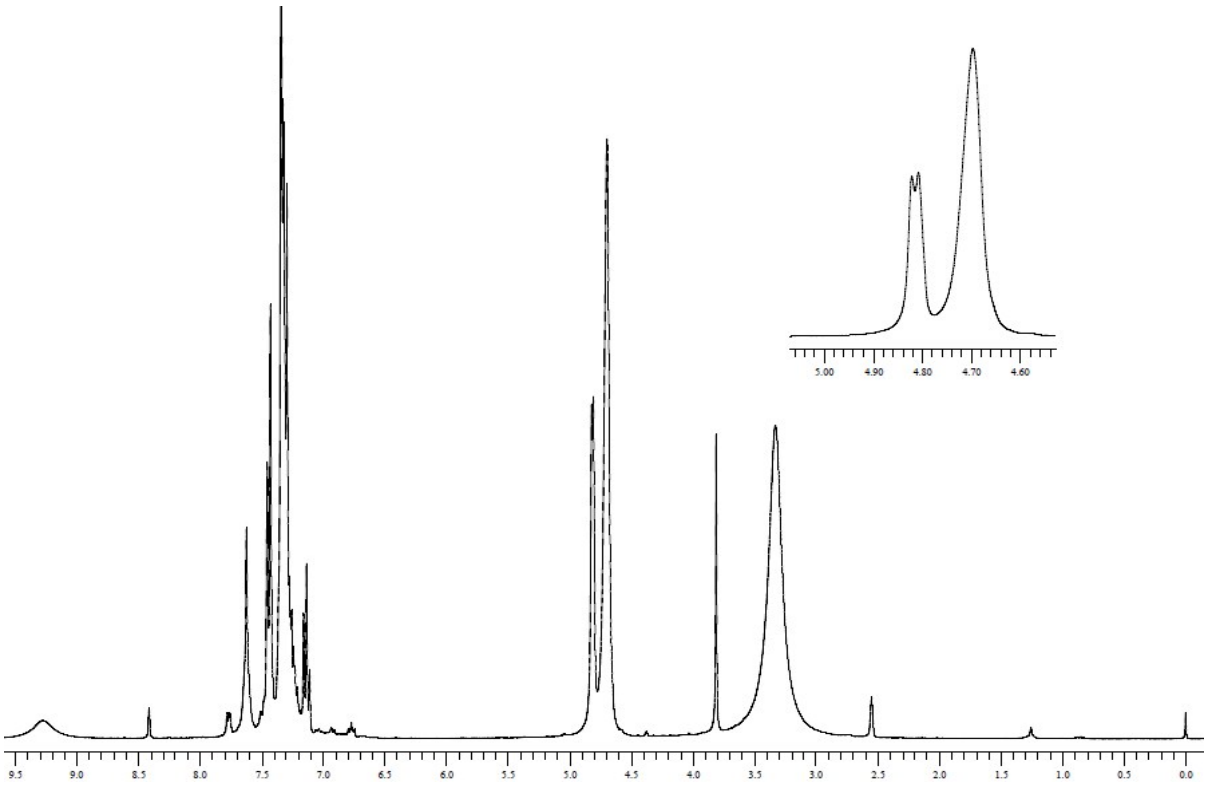


IR (KBr): ν_{max} 3217, 2924, 1717, 1618, 1510, 1472, 1198, 1159, 1019, 835, 752, 674 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 9.09 (brs, 1H), 7.42-7.25 (m, 8H), 7.15 (t, *J* = 7.17 Hz, 1H), 4.83 (d, *J* = 5.28 Hz, 2H), ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 180.79, 138.12, 138.00, 137.76, 128.65, 128.54, 128.11, 127.35, 126.95, 125.08, 124.94, 124.85, 123.88, 123.77, 48.10 ppm. MS (ESI) m/z = 237 $[M+H]^+$; HRMS (ESI) Calcd. $C_{15}H_{12}N_2ONa$ $[M+Na]^+$: 259.0842, found: 259.0857.

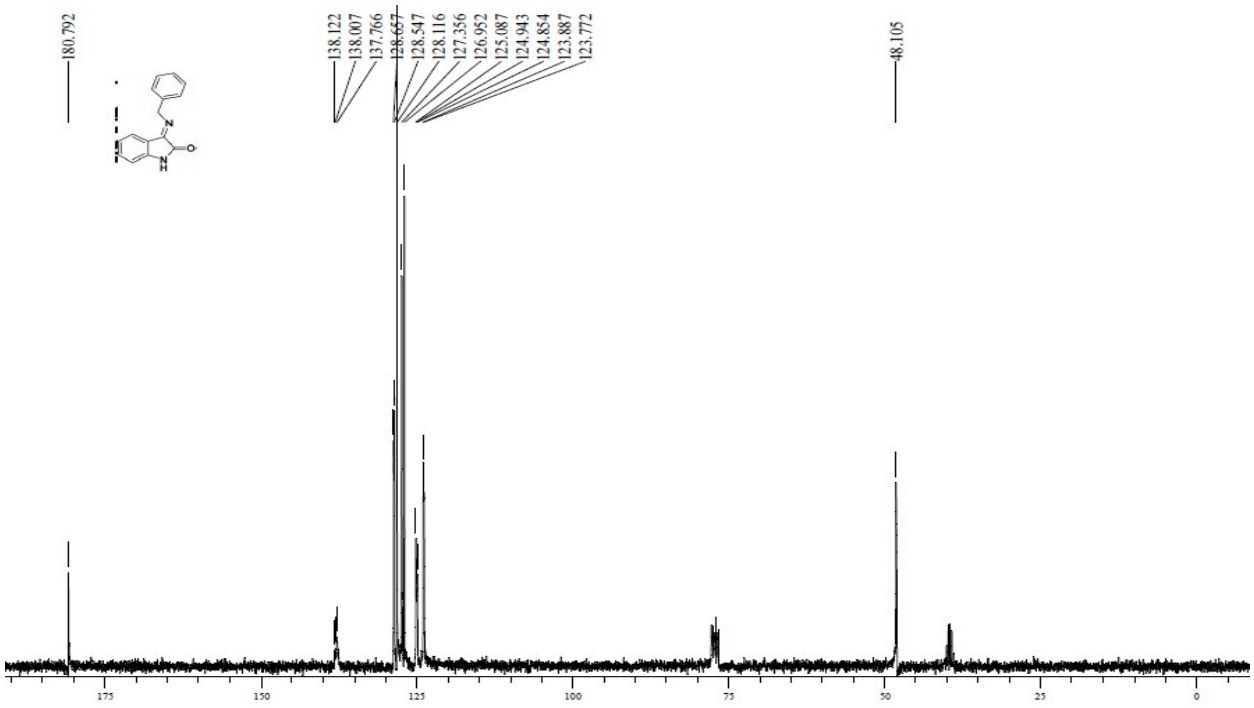
Pure NMR of 3-(2-phenylethylidene)indolin-2-one (I):



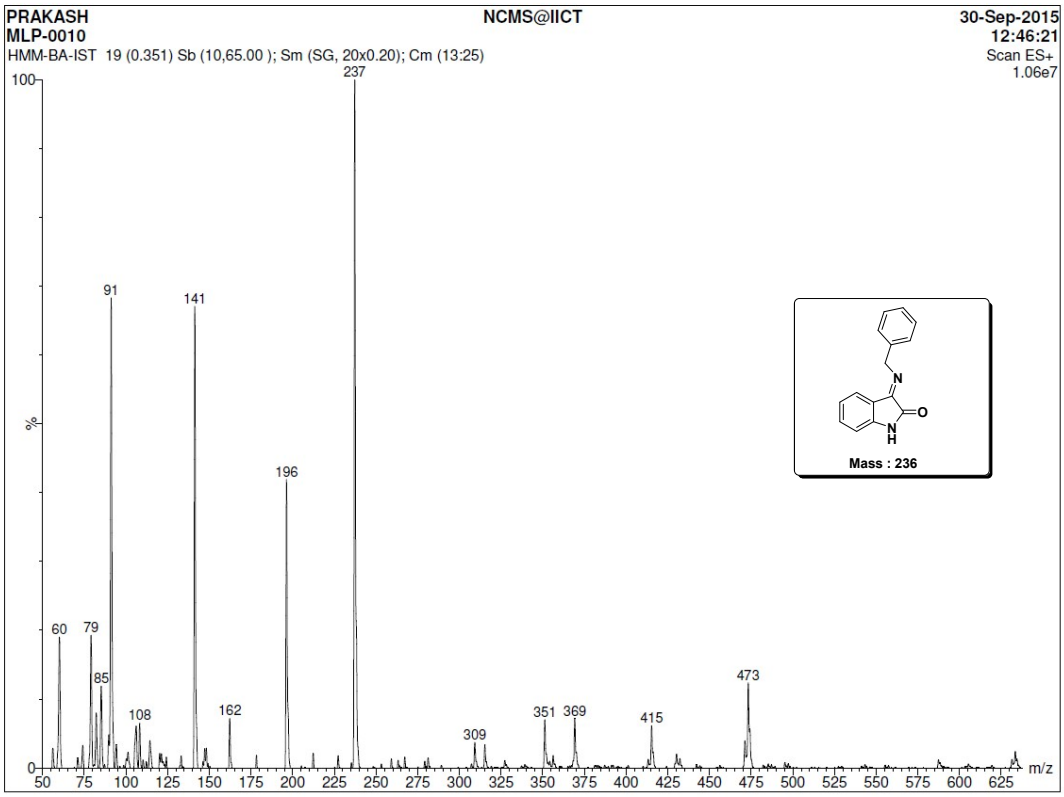
Crude nmr of 3-(2-phenylethylidene)indolin-2-one (I):



13c NMR of 3-(2-phenylethylidene)indolin-2-one (I):

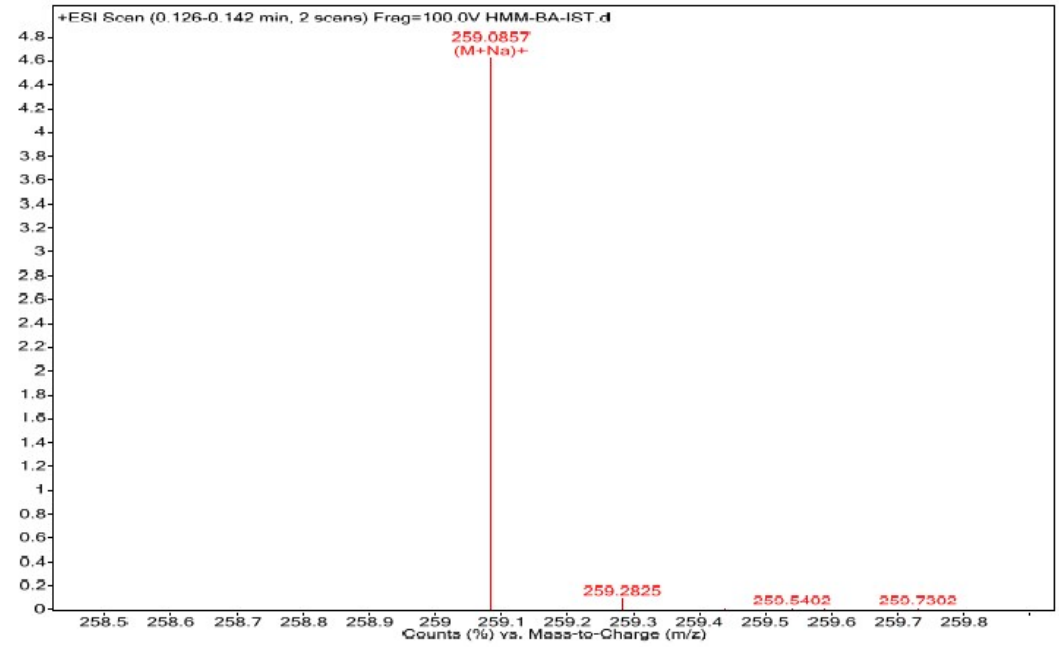


Mass spectra of 3-(2-phenylethylidene)indolin-2-one (I):

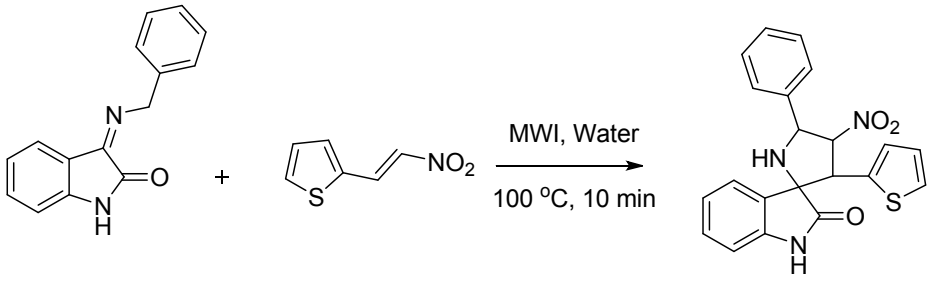


HRMS Spectra of 3-(2-phenylethylidene)indolin-2-one (I):

Sample Name	HMM-BA-IST	**Position**	Vial 71	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	HMM-BA-IST.d	**ACQ Method**		**Comment**		**Acquired Time**	10/2/2015 11:38:48 AM

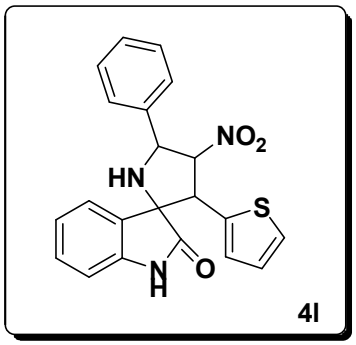


Scheme 3: Synthesis of spirooxindoles starting from imines

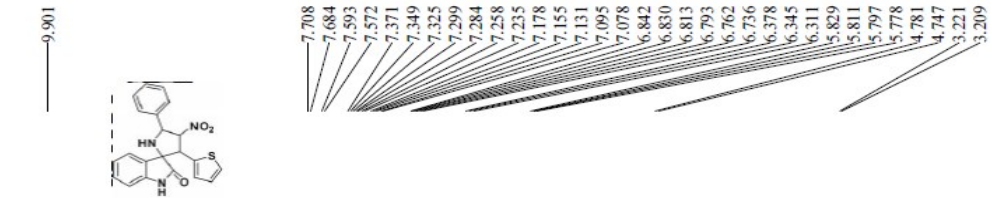


General procedure for the synthesis of (4l): A formed imine from mixture of isatin (1 mmol), benzyl amine (1.2 mmol) in that 2-(2-nitrovinyl)thiophene (1 mmol) and water (2 mL) was added and then this reaction mixture was irradiated under microwave irradiation (150 W power) at 100 °C for 10 minutes. After completion of reaction, the reaction mixture was then extracted with water (60 mL) and ethyl acetate (40 mL). The organic layer was washed with brine solution, dried with anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography with hexane–ethyl acetate (8:2) mixture to get pure product. Then product was characterized by ^{1}H-NMR, ^{13}C-NMR, mass, HRMS and IR data.

4'-nitro-5'-phenyl-3'-(thiophen-2-yl)spiro[indoline-3,2'-pyrrolidin]-2-one (4l):



White solid; Mp 245-247 °C; IR (KBr): ν_{max} 3325, 1718, 1625, 1612, 1521, 1506, 1492, 1346, 1160, 896, 742, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO d_6): δ 9.90 (brs, 1H), 7.68 (d, *J* = 7.32 Hz, 1H), 7.57 (d, *J* = 6.40 Hz, 2H), 7.37-7.23 (m, 3H), 7.15 (t, *J* = 7.32 Hz, 1H), 7.10 (d, *J* = 5.03 Hz, 1H), 6.84-6.73 (m, 3H), 6.34 (t, *J* = 10.07 Hz, 1H), 5.81 (dd, J_1 = 5.49, J_2 = 5.49 Hz, 1H) 4.78 (d, *J* = 10.07 Hz, 1H), 3.22 (d, *J* = 6.40 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO d_6): δ 179.11, 142.45, 138.25, 138.15, 138.05, 134.89, 129.26, 127.85, 127.53, 127.45, 126.31, 124.97, 124.72, 123.48, 121.89, 109.57, 91.77, 70.78, 64.99, 59.97, 50.66 ppm. MS (ESI) m/z = 392 $[M+H]^+$; HRMS (ESI) Calcd. $C_{21}H_{17}N_3O_3S$ $[M+H]^+$: 392.1063, found: 392.1080.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7.131
7.095
7.078
6.842
6.830
6.813
6.793
6.762
6.736
6.378
6.345
6.311
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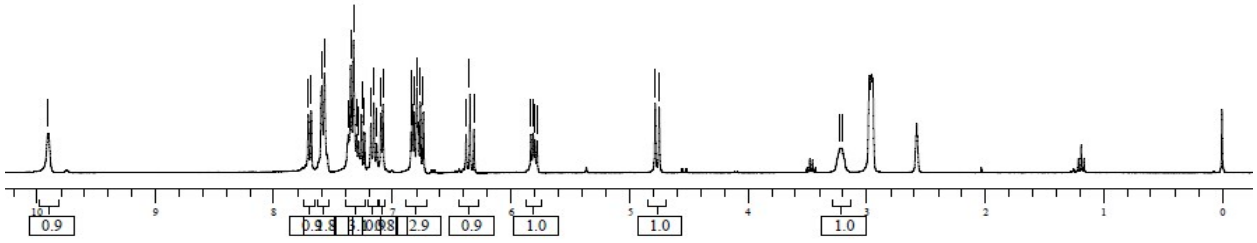
5.778
4.781
4.747
3.221
3.209
NO2
HN
S
N
H
O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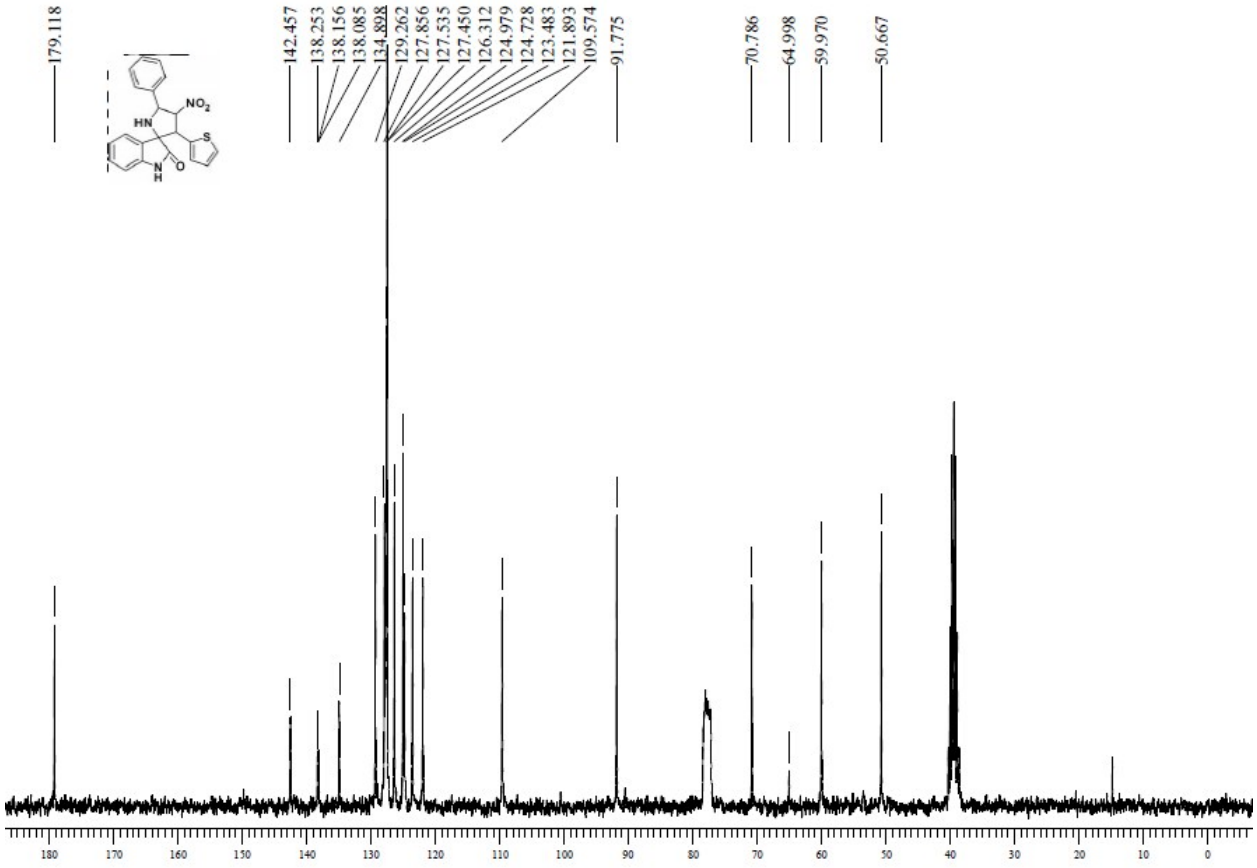
1.0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127.535
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126.312
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124.728
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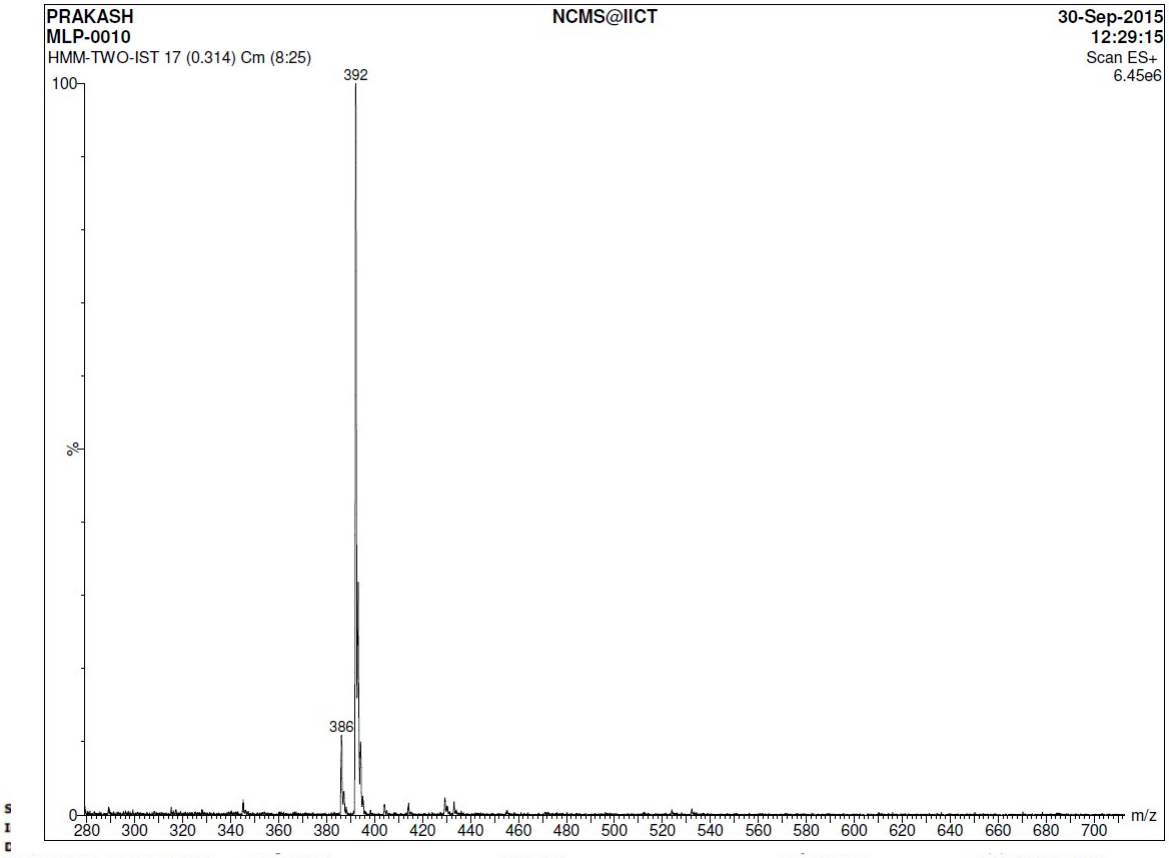
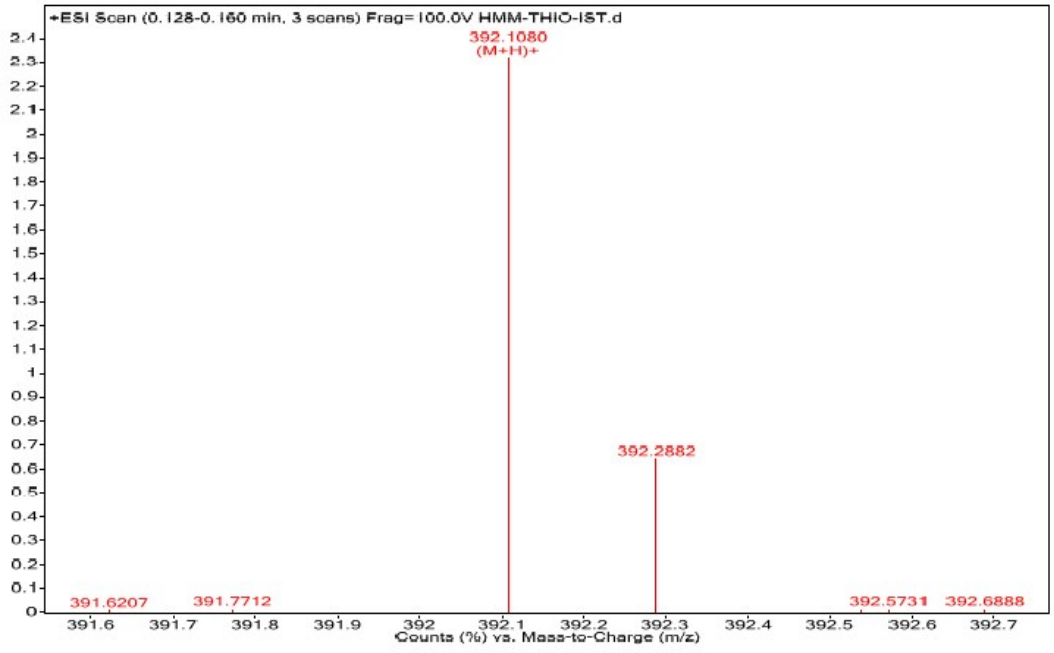
59.970
50.667
NO2
HN
S
N
H
O


PRAKASH
MLP-0010
NCMS@IICT
30-Sep-2015
12:29:15
HMM-TWO-IST 17 (0.314) Cm (8:25)
Scan ES+
6.45e6
100
%
0
392
386
280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700
m/z


+ESI Scan (0.128-0.160 min, 3 scans) Frag=100.0V HMM-THIO-IST.d
392.1080
(M+H)+
392.2882
391.6207
391.7712
392.5731
392.6888
Counts (%) vs. Mass-to-Charge (m/z)