Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Ultrasound-assisted ionic liquid-mediated green method for synthesis of 1,3-diphenylpyrazole-based spirooxindolopyrrolizidines, their anti-tubercular activity, molecular docking study and ADME predictions

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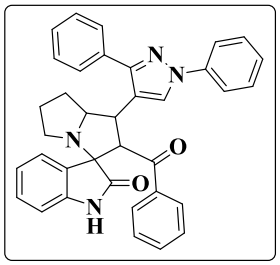
1. General information

The chemicals isatin with purity 98% was purchased from Spectrochem, Mumbai and L-proline with purity 99% was purchased from Sisco Research Laboratories (SRL) Pvt. Ltd., Mumbai. The ionic liquid [Bmim]BF_4 with purity >98.0% was purchased from Tokyo Chemical Industry (TCI), Tokyo, Japan. All the acetophenones with purity 99% were purchased from Finar chemicals Ltd., Ahmedabad, India. Phenyhydrazine with purity 98% was purchased from AVRA synthesis Pvt. Ltd., Hyderabad, India. All the solvents were purchased from Merck chemicals, Mumbai. The compounds were used without further purification. All the melting points were determined by using Stuart SMP30 melting point apparatus (Bibby Scientific Ltd. United Kingdom) and were uncorrected. Ultrasonication irradiation was performed on PCi-Analytics-6.5L200H1DTC ultrasonic cleaner, the frequency of ultrasonic cleaner is 25 kHz, input voltage range of 170–270VAC at 50 Hz and output power is 250 W (Mumbai, India). The reaction progress was checked with TLC plates (E. Merck, Mumbai, India). IR spectra were recorded on KBr disc by using Perkin-Elmer 100S spectrophotometer (Perkin-Elmer Ltd. United Kingdom) from 400-4000 cm^{-1} and Bruker spectrometer. ^1H and ^{13}C NMR spectra were recorded on Avance-III Bruker-400 MHz spectrometer (Bruker Corporation Ltd., Germany) using DMSO-*d*6 and $CDCl_3$ as solvents and TMS as an internal standard, chemical shifts were expressed in ppm. Mass spectra were recorded on a Jeol JMSD-300 spectrometer (Jeol Ltd., Tokyo, Japan) in acetonitrile solvent. The single crystal X-ray diffraction data of the compound **4b** was collected and solved by using Bruker Kappa Apex II CCD diffractometer and ShelXT software. Molecular docking studies were performed by using AutoDock Tools-1.5.6 software and visualized by Discovery studio.

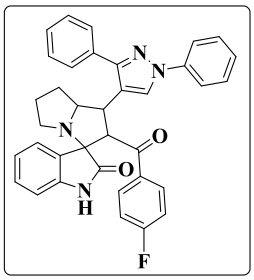
2. Spectral data for compounds

(dl)-2'-benzoyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one (4a). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3248, 1731, 1674, 1598.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.42 (t, *J* = 7.2 Hz, 4H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.25 (s, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.12 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.23 (t, *J* = 11.6 Hz, 1H), 4.04 (q, *J* = 6.4 Hz, 1H), 2.56 (dd, *J* = 12.8, 7.2 Hz, 2H), 1.85 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.74 (dd, *J* = 9.6, 7.2 Hz, 2H), 1.45 (dd, *J* = 12.4, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.19, 180.74, 153.15, 140.49, 139.97, 137.12, 133.75, 132.99, 129.47, 129.36, 129.10, 128.59, 128.21, 128.10, 127.93, 127.45, 126.29, 125.04, 124.98, 122.42, 120.61, 118.95, 110.08, 73.61, 64.11, 48.11, 42.73, 30.26, 27.07. HRMS (ESI, m/z): $[M+H]^+$ calcd. For $C_{36}H_{30}N_4O_2$: 551.2442; Found: 535.2126.

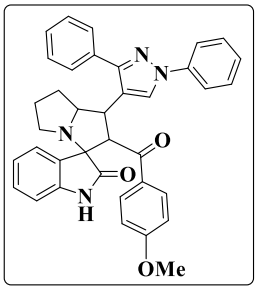
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoli- ne-3,3'-pyrrolizin]-2-one (4b). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3221, 1725, 1676, 1597. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.11 (s, 1H), 8.97 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 4H), 7.62 (t, *J* = 7.2 Hz, 2H), 7.56 – 7.46 (m, 5H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 8.8 Hz, 3H), 7.00 (dd, *J* = 13.6, 7.2 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.07 (t, *J* = 11.2 Hz, 1H), 3.75 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.38 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.29 (dd, *J* = 11.2, 6.0 Hz, 1H), 1.62 (dt, *J* = 12.4, 6.4 Hz, 3H), 1.21 (dd, *J* = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 196.90, 179.41, 166.58, 164.08, 152.41, 142.36, 139.98, 134.15, 131.33, 131.23, 129.91, 129.39, 129.11, 128.87, 128.53, 126.96, 126.49, 125.05, 121.65, 120.75, 118.46, 115.69, 115.48, 110.17, 73.41, 73.11, 63.55, 47.71, 42.42, 30.03, 27.12. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{36}H_{29}FN_4O_2$: 569.2347; Found: 569.2347.



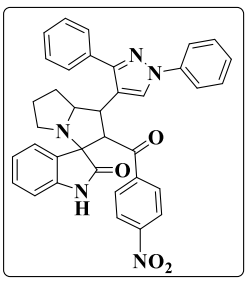
(dl)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoli ne-3, 3'-pyrrolizin]-2-one (4c). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.14 (s, 1H), 8.97 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 3H), 7.69 (t, *J* = 5.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.00 (dd, *J* = 11.2, 6.4 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 1H), 5.14 (d, *J* = 11.2 Hz, 1H), 4.06 (t, *J* = 10.8 Hz, 1H), 3.75 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.37 (t, *J* = 8.0 Hz, 1H), 2.29 (dd, *J* = 10.8, 4.0 Hz, 1H), 1.66 (dd, *J* = 11.2, 5.2 Hz, 1H), 1.61 – 1.54 (m, 2H), 1.21 (dd, *J* = 12.0, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.39, 179.34, 152.41, 142.35, 139.97, 138.46, 136.14, 134.13, 130.59, 130.24, 130.15, 129.91, 129.43, 129.40, 129.12, 128.95, 128.87, 128.68, 128.54, 126.97, 126.51, 124.99, 121.70, 121.55, 120.70, 119.22, 118.46, 110.21, 73.42, 73.07, 63.61, 47.69, 42.38, 30.04, 27.13. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{36}H_{29}ClN_4O_2$: 585.2052; Found: 585.2059.

(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro

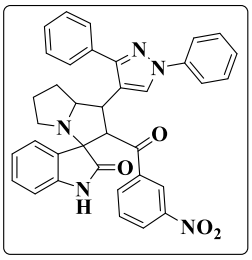
***[indoline-3,3'-pyrrolizin]-2-one (4d)*.** White Solid. mp: 179-180 °C**.** IR (KBr, cm^{-1}): 3391, 1721, 1668, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.13 (s, 1H), 8.93 (s, 1H), 7.90 (t, J = 7.6 Hz, 4H), 7.60 (d, J = 7.6 Hz, 2H), 7.50 (dd, J = 10.8, 8.8 Hz, 5H), 7.28 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 6.8 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 7.6 Hz, 1H), 5.10 (d, J = 11.8 Hz, 1H), 4.14 – 4.07 (m, 1H), 3.77 (s, 3H), 3.75 – 3.70 (m, 1H), 2.37 (t, J = 8.4 Hz, 1H), 2.29 (dd, J = 10.4, 5.2 Hz, 1H), 1.66 (dd, J = 12.1, 5.5 Hz, 1H), 1.61 – 1.55 (m, 2H), 1.21 (dd, J = 12.4, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.97, 179.54, 163.51, 152.42, 142.32, 139.95, 134.13, 130.85, 130.30, 129.90, 129.65, 129.08, 128.87, 128.52, 127.14, 126.89, 126.47, 125.26, 121.52, 120.86, 118.44, 113.83, 110.09, 73.34, 62.73, 55.92, 47.73, 42.70, 30.03, 27.12. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{37}H_{32}N_4O_3$: 581.2547; Found: 581.2556.



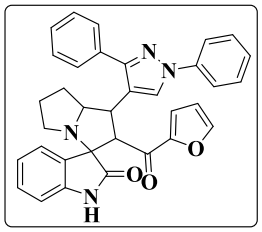
***(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indolin e-3,3'-pyrrolizin]-2-one (4e)*.** White Solid. mp: 179-180 °C**.** IR (KBr, cm^{-1}): 3383, 1719, 1661, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.02 (s, 1H), 9.00 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.90 (s, 4H), 7.64 (t, J = 11.6 Hz, 4H), 7.51 (d, J = 4.8 Hz, 4H), 7.33 (t, J = 13.2 Hz, 1H), 7.16 (s, 1H), 7.02 (s, 1H), 6.48 (d, J = 7.2 Hz, 1H), 5.22 (d, J = 10.8 Hz, 1H), 4.04 (t, J = 10.0 Hz, 1H), 3.76 (d, J = 6.4 Hz, 1H), 2.37 (dd, J = 15.6, 8.0 Hz, 1H), 2.29 (d, J = 5.2 Hz, 1H), 1.67 (dd, J = 11.2, 5.2 Hz, 1H), 1.60 (d, J = 5.6 Hz, 2H), 1.23 (dd, J = 11.2, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 198.09, 198.09, 179.18, 179.18, 152.41, 152.41, 150.11, 142.33, 139.98, 134.12, 130.14, 129.93, 129.56, 129.15, 128.88, 128.58, 127.05, 126.80, 126.54, 124.80, 123.54, 121.91, 120.58, 118.47, 110.42, 73.51, 72.95, 64.62, 47.65, 42.20, 30.12, 27.20. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{36}H_{29}N_5O_4$: 596.2292; Found: 596.2297.



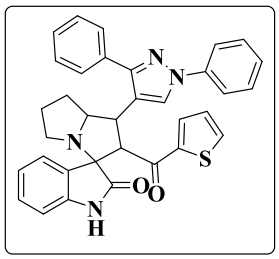
***(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indolin e-3,3'-pyrrolizin]-2-one (4f)*.** White Solid. mp: 179-180 °C**.** IR (KBr, cm^{-1}): 3382, 1719, 1669, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.09 (s, 1H), 9.01 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.08 (s, 1H), 7.90 (d, J = 8.4 Hz, 4H), 7.78 (d, J = 7.8 Hz, 1H), 7.60 (dt, J = 12.4, 7.2 Hz, 3H), 7.53 – 7.47 (m, 3H), 7.29 (t, J = 7.2 Hz, 1H), 7.14 – 7.07 (m, 1H), 7.04 – 6.97 (m, 2H), 6.42 (d, J = 8.0 Hz, 1H), 5.20 (d, J = 11.2 Hz, 1H), 4.11 – 4.00 (m, 1H), 3.77 (dd, J = 14.4, 6.8 Hz, 1H), 2.39 (dd, J = 11.2, 4.8 Hz, 1H), 2.30 (dd, J = 10.0, 5.6 Hz, 1H), 1.66 (dd, J = 12.4, 5.6 Hz, 1H), 1.62 – 1.53 (m, 2H), 1.23 (dd, J = 12.4, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.32, 179.29, 152.42, 147.75, 142.36, 140.00, 138.53, 134.28, 134.17, 130.33, 130.05, 129.92, 129.13, 128.90, 128.56, 127.66, 127.14, 126.76, 126.52, 124.85, 122.81, 121.88, 120.52, 118.50, 110.21, 73.37, 72.87, 64.39, 47.75, 42.28, 29.94, 27.04. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{36}H_{29}N_5O_4$: 596.2292; Found: 596.2290.



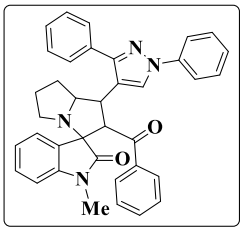
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(furan-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indo line-3,3'-pyrrolizin]-2-one (4g). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3214, 1719, 1669, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.36 (s, 1H), 8.85 (s, 1H), 7.86 (dd, J = 11.6, 8.0 Hz, 4H), 7.80 (s, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.51 (dd, J = 13.6, 7.6 Hz, 3H), 7.29 (dd, J = 15.2, 7.2 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 6.62 (s, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.08 (t, J = 11.2 Hz, 1H), 3.78 (dd, J = 16.4, 7.6 Hz, 1H), 2.45 (dd, J = 12.0, 7.6 Hz, 1H), 2.35 (dd, J = 12.0, 5.6 Hz, 1H), 1.74 (dd, 11.6, 5.2 Hz, 1H), 1.65 – 1.55 (m, 2H), 1.24 (dd, 12.0, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 184.07, 179.64, 152.41, 152.07, 148.98, 142.31, 139.90, 133.93, 129.93, 129.80, 129.06, 128.84, 128.55, 128.19, 127.29, 127.01, 126.57, 125.13, 121.65, 120.68, 120.43, 118.50, 112.85, 110.31, 73.60, 73.18, 63.32, 47.65, 42.29, 29.93, 27.10. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{34}H_{28}N_4O_3$: 541.2234; Found: 541.2232.



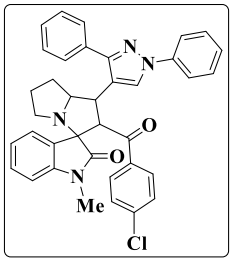
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(thiophene-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro [indoline-3,3'-pyrrolizin]-2-one (4h). White Solid. mp: 179-180 ℃. IR (KBr, cm^{-1}): 3203, 1719, 1657, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.30 (s, 1H), 8.90 (s, 1H), 7.86 (dd, J = 13.6, 7.2 Hz, 4H), 7.81 (d, J = 3.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.49 (dd, J = 15.2, 8.0 Hz, 4H), 7.28 (t, J = 7.6 Hz, 1H), 7.13 (dd, J = 8.8, 5.2 Hz, 2H), 7.08 (d, J = 7.2 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 4.98 (d, J = 12.0 Hz, 1H), 4.16 (t, J = 11.6 Hz, 1H), 3.77 (dd, J = 16.0, 6.4 Hz, 1H), 2.41 (dd, J = 16.4, 6.8 Hz, 1H), 2.32 (dd, J = 10.4, 5.2 Hz, 1H), 1.68 (dd, J = 12.0, 5.4 Hz, 1H), 1.60 (dd, J = 13.6, 6.4 Hz, 2H), 1.22 (dd, J = 12.0, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 189.54, 179.69, 152.43, 144.14, 142.22, 139.89, 136.29, 134.37, 133.95, 129.93, 129.79, 129.09, 128.84, 128.57, 127.24, 127.01, 126.56, 125.13, 121.74, 120.41, 118.47, 110.26, 79.62, 73.74, 73.30, 63.89, 47.75, 42.62, 29.97, 27.11. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{34}H_{28}N_4O_2S$: 557.2006; Found: 557. 2010.



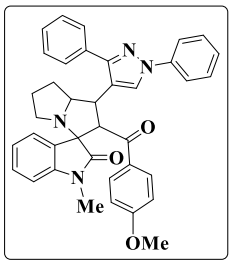
(dl)-2'-benzoyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-1',2',5',6',7',7a'-hexahydrospiro[indo line-3,3'-pyrrolizin]-2-one (4i). White Solid. mp: 179-180 ℃. IR (KBr, cm^{-1}): 1713, 1682, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.97 (s, 1H), 7.93 – 7.90 (m, 4H), 7.69 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 4H), 7.27 (dd, J = 5.6, 2.8 Hz, 4H), 7.21 (dd, J = 8.0, 2.8 Hz, 1H), 7.05 (dd, J = 9.6, 7.6 Hz, 2H), 6.60 (d, J = 8.0 Hz, 1H), 5.14 (d, J = 11.6 Hz, 1H), 4.08 (t, 1H), 3.80 – 3.73 (m, 1H), 2.59 (s, 3H), 2.38 (dd, J = 16.8, 7.2 Hz, 1H), 2.27 (dd, J = 11.6, 6.0 Hz, 1H), 1.65 (dd, J = 12.4, 5.6 Hz, 1H) 1.63 (dd, J = 15.2, 7.2 Hz, 2H), 1.24 (dd, J = 12.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 198.26, 177.67, 152.40, 143.56, 140.00, 137.43, 134.22, 133.22, 129.90, 129.11, 128.91, 128.52, 128.29, 128.05, 126.94, 126.47, 126.35, 124.50, 122.33, 120.79, 118.46, 108.98, 73.55, 72.95, 64.52, 47.79, 42.11, 30.17, 27.29, 26.14. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{37}H_{32}N_4O_2$: 565.2598; Found: 565.2605.



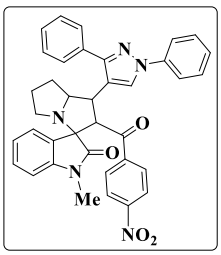
(dl)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4j). White Solid. mp: 179-180 ℃. IR (KBr, cm^{-1}): 1714, 1682, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.96 (s, 1H), 7.89 (d, J = 7.6 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.50 (dd, J = 16.0, 8.4 Hz, 3H), 7.37 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.8 Hz, 3H), 7.23 (dd, J = 7.6, 4.0 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.67 (d, J = 7.6 Hz, 1H), 5.12 (d, J = 11.6 Hz, 1H), 4.03 (t, J = 11.6, Hz, 1H), 3.76 (dd, J = 16.0, 6.4 Hz, 1H), 2.66 (s, 3H), 2.37 (dd, J = 13.2, 6.4 Hz, 1H), 2.27 (dd, J = 15.2, 5.6 Hz, 1H) 1.72 – 1.54 (m, 3H), 1.23 (dd, J = 11.6, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.27, 177.61, 152.38, 143.48, 139.98, 138.28, 136.03, 134.17, 130.10, 129.91, 129.12, 128.88, 128.54, 128.44, 127.02, 126.51, 126.37, 124.36, 122.46, 120.62, 118.46, 109.11, 73.53, 72.88, 64.56, 47.78, 42.06, 30.14, 27.27, 26.20. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{37}H_{31}ClN_4O_2$: 599.2208; Found: 599.2221.



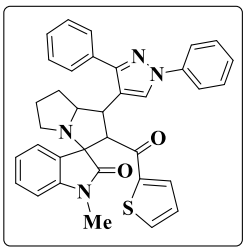
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1-methyl-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4k). White Solid. mp: 179-180 ℃. IR (KBr, cm^{-1}): 1712, 1671, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.93 (s, 1H), 7.91 (t, J = 8.0 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.34 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.20 (dd, J = 7.6, 4.0 Hz, 1H), 7.05 (d, J = 4.4 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 7.6 Hz, 1H), 5.07 (d, J = 11.2 Hz, 1H), 4.10 – 4.00 (m, 1H), 3.77 (s, 3H), 3.64 – 3.50 (m, 1H), 2.70 (s, 3H), 2.39 (dd, J = 15.2, 8.0 Hz, 1H), 2.27 (dd, J = 15.4, 5.6 Hz, 1H), 1.67 (dd, J = 12.0, 5.2 Hz, 1H), 1.60 (dd, J = 14.0, 8.8 Hz, 2H), 1.23 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.98, 177.91, 163.39, 152.40, 143.51, 139.98, 134.21, 130.53, 130.20, 129.99, 129.89, 129.82, 129.08, 128.90, 128.50, 128.19, 126.93, 126.46, 124.61, 122.25, 120.84, 118.85, 118.44, 113.58, 108.93, 73.48, 73.16, 63.95, 55.98, 47.82, 42.26, 30.13, 27.27, 26.33. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{38}H_{34}N_4O_3$: 595.2704; Found: 595.2720.



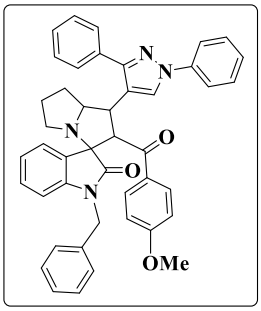
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4l). White Solid. mp: 179-180 ℃. IR (KBr, cm^{-1}): 1715, 1610, 1531. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.00 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.90 (dd, J = 8.8, 3.2 Hz, 5H), 7.71 (d, J = 7.6 Hz, 1H), 7.61 (q, J = 8.0 Hz, 3H), 7.53-7.48 (m, 3H), 7.30 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.59 (d, J = 7.8 Hz, 1H), 5.21 (d, J = 11.6 Hz, 1H), 4.04 (t, J = 11.2 Hz, 1H), 3.78 (dd, J = 16.0, 6.4 Hz, 1H), 2.60 (s, 3H), 2.39 (dd, J = 16.4, 6.8 Hz, 1H), 2.27 (dd, J = 15.2, 5.6 Hz, 1H), 1.67 (dd, J = 12.4, 5.6 Hz, 1H), 1.60 (dd, J = 13.2, 6.4 Hz, 2H), 1.24 (dd, J = 12.0, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.68, 178.51, 153.06, 147.91, 143.28, 139.92, 138.46, 133.64, 133.20, 129.88, 129.38, 129.12, 129.08, 128.61, 128.17, 126.97, 126.69, 126.37, 125.28, 124.27, 122.68, 122.66, 120.34, 118.92, 108.19, 73.41, 72.90, 65.56, 48.39, 42.52, 29.71, 26.62, 26.16. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{37}H_{31}N_5O_4$: 610.2449; Found: 610.2455.



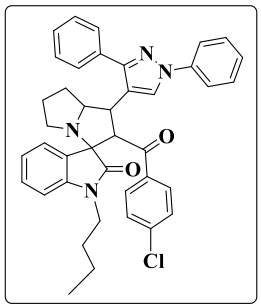
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-2'-(thiophene-2-carbonyl)-1',2',5',6',7',7a'-hexa hydrospiro[indoline-3,3'-pyrrolizin]-2-one (4m). White Solid. mp: 179-180 ℃. IR (KBr, cm-1): 1712, 1655, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.91 (s, 1H), 7.88 (d, J = 8.4 Hz, 4H), 7.82 (d, J = 4.4 Hz, 1H), 7.65 (d, J = 3.2 Hz, 1H), 7.60 (t, J = 8.0 Hz, 2H), 7.49 (dd, J = 14.8, 7.2 Hz, 4H), 7.29 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 4.8 Hz, 1H), 7.08 (t, J = 5.6 Hz, 2H), 6.75 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 12.0 Hz, 1H), 4.10 (t, J = 12.0 Hz, 1H), 3.79 (dd, J = 16.4, 6.4 Hz, 1H), 2.84 (s, 3H), 2.42 (dd, J = 13.6, 6.8 Hz, 1H), 2.31 (dd, J = 11.2, 6.0 Hz, 1H), 1.71 – 1.58 (m, 3H), 1.24 (dd, J = 12.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 189.32, 178.03, 152.42, 143.72, 143.45, 139.91, 136.09, 134.01, 133.87, 129.92, 129.09, 128.86, 128.56, 128.45, 127.04, 126.63, 126.54, 124.46, 122.49, 120.33, 118.47, 109.08, 79.62, 73.64, 73.42, 64.88, 47.85, 42.20, 30.08, 27.27, 26.40. HRMS (ESI, m/z): $[M+H]^+$calcd. For $C_{35}H_{30}N_4O_2S$: 571.2162; Found: 571.2173.



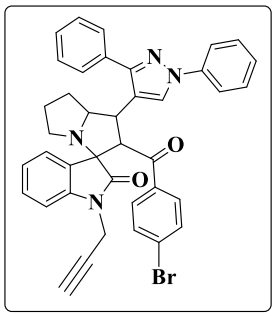
***(dl)-1-benzyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4n)*.** White Solid. mp: 179-180 ℃**.** IR (KBr, cm-1): 1714, 1668, 1600. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.98 (s, 1H), 7.91 (t, J = 7.6 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.54 – 7.46 (m, 6H), 7.27 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 6.4 Hz, 2H), 7.12 (t, J = 9.6 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.2 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 7.6 Hz, 1H), 5.24 (d, J = 11.6 Hz, 1H), 4.71 (d, J = 16.0 Hz, 1H), 4.45 (d, J = 16.0 Hz, 1H), 4.17 (t, J = 10.8 Hz, 1H), 3.83 (t, J = 9.2 Hz, 1H), 3.79 (s, 3H), 2.37 – 2.27 (m, 2H), 1.69 (dd, J = 11.6, 5.6 Hz, 1H), 1.64 – 1.56 (m, 2H), 1.23 (dd, J = 11.6, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.61, 178.08, 163.75, 152.44, 142.73, 139.96, 136.33, 134.11, 130.92, 130.07, 129.91, 129.74, 129.10, 128.94, 128.89, 128.54, 127.65, 127.16, 127.00, 126.50, 124.74, 122.39, 120.68, 118.46, 113.97, 109.70, 73.33, 72.98, 62.56, 56.00, 47.61, 43.18, 42.85, 30.10, 27.27. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{44}H_{38}N_4O_3$: 671.3017; Found: 671.3022.



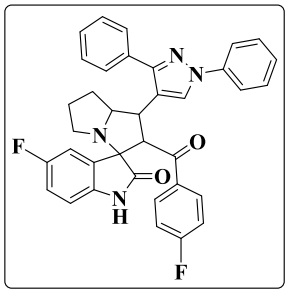
***(dl)-1-butyl-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4o)*.** White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 1710, 1681, 1600. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.99 (s, 1H), 7.89 (t, J = 6.8 Hz, 4H), 7.62 (t, J = 8.0 Hz, 2H), 7.50 (dd, J = 16.0, 8.8 Hz, 4H), 7.37 (d, J = 1.2 Hz, 3H), 7.28 (t, J = 7.6 Hz, 1H), 7.24 (dd, J = 8.8, 4.0 Hz, 1H), 7.07 (d, J = 4.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 1H), 5.20 (d, J = 12.0 Hz, 1H), 4.08 (t, J = 11.2 Hz, 1H), 3.76 (dd, J = 16.0, 6.4 Hz, 1H), 3.22 (dd, J = 13.6, 7.6 Hz, 1H), 2.28 (dd, J = 13.6, 6.4 Hz, 2H), 1.67 (dd, J = 12.0, 5.6 Hz, 1H), 1.59 (t, J = 6.8 Hz, 2H), 1.25-1.19 (m, 2H), 1.07 (dd, J = 16.0, 6.4 Hz, 3H), 0.92 (dd, J = 13.6, 6.4 Hz, 1H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.25, 177.27, 152.41, 142.99, 139.95, 138.58, 136.13, 134.10, 130.10, 129.92, 129.13, 128.88, 128.73, 128.57, 127.03, 126.77, 126.53, 124.45, 122.23, 120.49, 118.45, 109.29, 73.41, 72.65, 63.52, 47.56, 42.39, 30.16, 28.99, 27.30, 19.84, 14.12. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{40}H_{37}ClN_4O_2$: 641.2678; Found: 641. 2693.



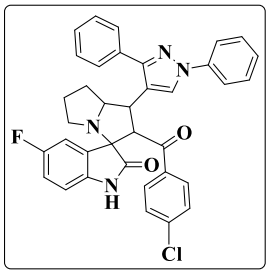
(dl)-2'-(4-bromobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-(prop-2-yn-1-yl)-1',2',5',6',7',7a'-hex -ahydrospiro[indoline-3,3'-pyrrolizin]-2-one (4p). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 1721, 1680, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.96 (s, 1H), 7.89 (d, J = 8.0 Hz, 4H), 7.60 (t, J = 8.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 5H), 7.28 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 6.4 Hz, 2H), 6.82 (d, J = 7.6 Hz, 1H), 5.16 (d, J = 12.0 Hz, 1H), 4.29 (dd, J = 17.6, 2.4 Hz, 1H), 4.10 – 3.99 (m, 3H), 3.79 (dd, J = 16.0, 6.4 Hz, 1H), 2.37 (d, J = 6.4 Hz, 1H), 2.27 (dd, J = 10.8, 5.6 Hz, 1H), 1.68 (dd, J = 12.4, 5.6 Hz, 1H), 1.60 (dd, J = 12.0, 6.4 Hz, 2H), 1.24 (dd, J = 12.4, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.13, 177.81, 153.10, 141.40, 139.93, 135.76, 133.73, 131.65, 129.58, 129.37, 129.31, 129.11, 128.60, 128.13, 127.09, 126.34, 125.06, 124.28, 122.82, 120.28, 118.95, 109.37, 73.47, 73.05, 72.33, 64.22, 48.24, 42.62, 30.04, 29.71, 29.37, 26.88. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{39}H_{31}BrN_4O_2$: 667.1703; Found: 667. 1718.



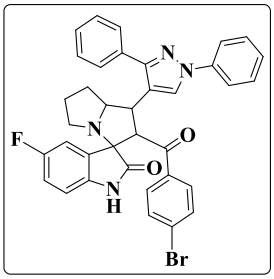
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrospi -ro[indoline-3,3'-pyrrolizin]-2-one (4q). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3210, 1723, 1681, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.18 (s, 1H), 8.97 (s, 1H), 7.88 (dd, J = 7.6, 5.6 Hz, 4H), 7.60 (t, J = 7.6 Hz, 4H), 7.50 (dd, J = 15.2, 7.6 Hz, 3H), 7.29 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 8.8 Hz, 2H), 7.00 (t, J = 8.4 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.53 (dd, J = 8.4, 4.4 Hz, 1H), 5.17 (d, J = 12.0 Hz, 1H), 4.01 (t, J = 11.2 Hz, 1H), 3.83 – 3.70 (m, 1H), 2.42 – 2.36 (m, 1H), 2.34 (d, J = 4.8 Hz, 1H), 1.87 – 1.67 (m, 1H), 1.64 (dd, J = 12.0, 5.6 Hz, 2H), 1.24 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 196.67, 179.22, 166.75, 164.24, 158.92, 156.56, 152.43, 139.94, 138.59, 134.05, 133.94, 131.46, 131.37, 129.93, 129.07, 128.90, 128.61, 127.09, 126.54, 120.36, 118.45, 116.56, 116.33, 115.86, 115.64, 114.50, 114.25, 111.07, 110.99, 73.45, 73.33, 63.53, 47.57, 42.42, 30.10, 27.44. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}F_2N_4O_2$: 587.2253; Found: 587.2266.



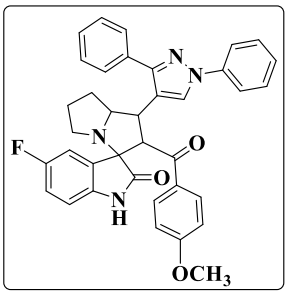
(dl)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-1',2',5',6',7',7a'-hexahydrospi -ro[indoline-3,3'-pyrrolizin]-2-one (4r). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3210, 1722, 1681, 1597. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.23 (s, 1H), 8.98 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 3H), 7.68 (dd, J = 8.4, 4.4 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.51 (dd, J = 8.4, 6.4 Hz, 3H), 7.40 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.55 (dd, J = 8.4, 4.4 Hz, 1H), 5.17 (d, J = 11.2 Hz, 1H), 4.02 (t, J = 10.4 Hz, 1H), 3.80 (d, J = 8.0 Hz, 1H), 2.41 (d, J = 7.6 Hz, 1H), 2.35 (d, J = 6.4 Hz, 1H), 1.79 – 1.68 (m, 1H), 1.65 (dd, J = 12.0, 6.4 Hz, 2H), 1.26 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.12, 188.08, 179.05, 158.94, 156.58, 152.42, 139.94, 138.78, 136.80, 135.86, 135.21, 134.03, 130.60, 130.24, 129.93, 129.43, 129.40, 129.08, 128.94, 128.90, 128.83, 128.62, 127.12, 126.55, 121.53, 120.25, 119.21, 118.46, 118.24, 116.67, 116.44, 114.52, 114.27, 111.15, 111.07, 73.41, 73.35, 63.54, 47.63, 42.35, 30.07, 27.42. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}ClFN_4O_2$: 603.1958; Found: 603.1968.



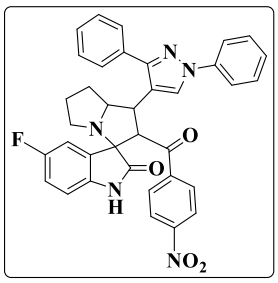
***(dl)-2'-(4-bromobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-1',2',5',6',7',7a'-hexahydrospi -ro[indoline-3,3'-pyrrolizin]-2-one (4s)*.** White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3213, 1719, 1682, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.20 (s, 1H), 8.97 (s, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 3H), 7.59 (d, J = 7.6 Hz, 2H), 7.56 – 7.51 (m, 4H), 7.43 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.01 (t, J = 10.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.54 (dd, J = 8.8, 4.4 Hz, 1H), 5.16 (d, J = 11.6 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.77 (dd, J = 14.8, 7.6 Hz, 1H), 2.39 (dd, J = 10.4, 7.6 Hz, 1H), 2.33 (dd, J = 10.4, 5.2 Hz, 1H), 1.69 (dd, J = 11.6, 5.2 Hz, 1H), 1.66 – 1.60 (m, 2H), 1.24 (dd, J = 11.6, 6.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.35, 188.34, 179.22, 158.95, 156.58, 153.59, 153.57, 152.44, 139.92, 138.56, 136.17, 134.02, 132.37, 131.77, 130.70, 130.31, 130.24, 129.93, 129.40, 129.07, 128.94, 128.90, 128.63, 128.02, 127.07, 126.77, 126.70, 126.57, 120.31, 119.23, 118.47, 116.62, 116.38, 114.47, 114.22, 111.14, 111.07, 105.53, 73.43, 73.31, 63.56, 47.53, 42.40, 30.11, 27.44. HRMS (ESI, m/z): [M+H]$^+$ calcd. for $C_{36}H_{28}BrFN_4O_2$: 647.1452; Found: 647.1458.



***(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4t)*.** White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3209, 1722, 1669, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.19 (s, 1H), 8.94 (s, 1H), 7.89 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 8.8 Hz, 4H), 7.49 (dd, J = 15.6, 8.0 Hz, 3H), 7.28 (t, J = 7.2 Hz, 1H), 6.99 (t, J = 10.8 Hz, 1H), 6.83 (t, J = 9.2 Hz, 3H), 6.55 (dd, J = 8.4, 4.4 Hz, 1H), 5.13 (d, J = 11.6 Hz, 1H), 4.04 (t, J = 11.2 Hz, 1H), 3.88 (s, 1H), 3.78 (s, 3H), 2.40 (dd, J = 10.8, 7.6 Hz, 1H), 2.34 (dd, J = 10.4, 5.2 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.63 (dd, J = 12.4, 6.2 Hz, 2H), 1.23 (dd, J = 11.6, 6.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.77, 179.38, 163.71, 158.84, 156.49, 152.45, 139.94, 138.59, 134.06, 130.94, 130.11, 129.91, 129.03, 128.90, 128.59, 127.00, 126.51, 120.49, 118.45, 116.33, 116.09, 114.68, 114.44, 113.96, 110.93, 110.85, 73.67, 73.27, 62.78, 55.96, 47.57, 42.72, 30.11, 27.43. HRMS (ESI, m/z): [M+H]$^+$ calcd. for $C_{37}H_{31}FN_4O_3$: 599.2453; Found: 599.2464.



***(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospir o[indoline-3,3'-pyrrolizin]-2-one (4u)*.** White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3124, 1736, 1693, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.09 (s, 1H), 9.01 (s, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.89 (t, J = 8.4 Hz, 4H), 7.66 (d, J = 8.8 Hz, 2H), 7.60 (t, J = 7.6 Hz, 2H), 7.51 (dd, J = 15.6, 8.0 Hz, 3H), 7.30 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 9.2 Hz, 1H), 6.82 (d, J = 10.0 Hz, 1H), 6.50 (dd, J = 8.4, 4.4 Hz, 1H), 5.25 (d, J = 11.6 Hz, 1H), 3.99 (t, J = 11.2 Hz,1H), 3.79 (dd, J = 16.0, 9.2 Hz, 1H), 2.37 (dd, J = 12.4, 6.2 Hz, 2H), 1.65 (dd, J = 13.2, 6.2 Hz, 3H), 1.26 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.87, 179.04, 159.05, 156.69, 152.43, 150.27, 142.00, 139.95, 138.60, 138.58, 134.04, 132.25, 130.25, 130.01, 129.94, 129.70, 129.42, 127.16, 126.57, 124.42, 123.68, 120.22, 120.18, 119.26, 118.47, 116.87, 116.64, 114.34, 114.12, 111.35, 111.27, 73.41, 73.32, 64.62, 47.48, 42.21, 30.22, 27.55. HRMS (ESI, m/z): [M+H]$^+$calcd. For $C_{36}H_{28}FN_5O_4$: 614.2198; Found: 614.2206.

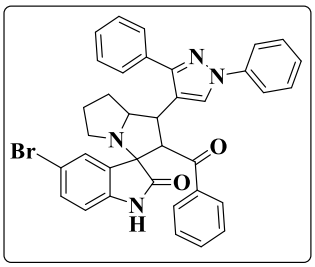


(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one (4v). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3179, 1717, 1689, 1600. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.15 (s, 1H), 9.01 (s, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.17 (t, J = 7.6 Hz, 1H), 7.88 (dd, J = 7.6, 5.6 Hz, 4H), 7.84 (d, J = 7.6 Hz, 1H), 7.61 (dd, J = 14.0, 8.0 Hz, 3H), 7.53 – 7.47 (m, 3H), 7.29 (t, J = 7.6 Hz, 1H), 6.99 (td, J = 9.2, 2.4 Hz, 1H), 6.81 (dd, J = 8.8, 4.4 Hz, 1H), 6.44 (dd, J = 8.8, 4.4 Hz, 1H), 5.23 (d, J = 11.6 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.84 – 3.76 (m, 1H), 2.40 (dt, J = 12.4, 6.4 Hz, 1H), 2.34 (dd, J = 12.0, 5.6 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.64 (dd, J = 12.4, 6.4 Hz, 2H), 1.26 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.04, 179.15, 159.05, 156.68, 152.45, 147.85, 139.97, 138.60, 138.24, 134.36, 134.09, 130.52, 129.93, 129.08, 128.94, 128.62, 127.95, 127.25, 126.61, 126.55, 122.92, 120.17, 118.50, 116.76, 116.53, 114.32, 114.07, 111.17, 111.09, 73.27, 73.25, 64.38, 47.56, 42.30, 30.03, 27.39. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}FN_5O_4$: 614.2198; Found: 614.2194.

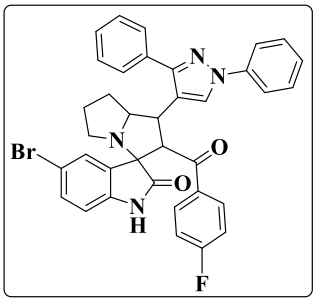
(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(furan-2-carbonyl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4w). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3222, 1723, 1669, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.40 (s, 1H), 8.86 (s, 1H), 7.87 (dd, J = 20.4, 8.0 Hz, 4H), 7.57 (t, J = 7.2 Hz, 2H), 7.49 (dd, J = 13.2, 7.6 Hz, 4H), 7.34 (d, J = 3.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 9.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.68 (dd, J = 8.4, 4.4 Hz, 1H), 6.61 (s, 1H), 4.80 (d, J = 11.6 Hz, 1H), 4.02 (t, J = 11.2 Hz, 1H), 3.80 (dd, J = 15.6, 6.8 Hz, 1H), 2.40 (dd, J = 24.4, 8.4 Hz, 2H), 1.66 (dd, J = 13.2, 7.6 Hz, 2H), 1.26 (dd, J = 11.2, 6.4 Hz, 1H), 1.13 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.89, 179.44, 158.88, 156.52, 152.42, 151.99, 149.27, 139.88, 138.55, 133.86, 129.94, 129.22, 129.02, 128.87, 128.62, 128.19, 127.13, 126.96, 126.89, 126.60, 125.93, 121.04, 120.05, 118.49, 114.86, 114.61, 112.95, 111.15, 111.07, 73.90, 73.13, 63.40, 47.50, 42.30, 30.01, 27.41. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{34}H_{27}FN_4O_3$: 559.2140; Found: 559.2142.

(dl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(thiophene-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one (4x). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 1722, 1656, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.36 (s, 1H), 8.92 (s, 1H), 7.90 – 7.85 (m, 4H), 7.83 (s, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.49 (dd, J = 15.2, 7.6 Hz, 4H), 7.30 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 4.8 Hz, 1H), 7.01 (td, J = 10.4, 4.0 Hz, 1H), 6.85 (dd, J = 8.4, 2.4 Hz, 1H), 6.63 (dd, J = 8.8, 4.4 Hz, 1H), 5.01 (d, J = 11.2 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.80 (dd, J = 15.6, 6.4 Hz, 1H), 2.43 (dd, J = 11.6, 4.4 Hz, 1H), 2.36 (dd, J = 10.4, 5.2 Hz, 1H), 1.74 – 1.69 (m, 1H), 1.65 (dd, J = 13.2, 5.6 Hz, 2H), 1.25 (dd, J = 11.2, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 189.43, 179.48, 156.58, 152.45, 144.02, 139.90, 138.52, 136.63, 134.63, 133.91, 129.92, 129.03, 128.95, 128.87, 128.62, 127.14, 126.99, 126.92, 126.57, 120.06, 118.48, 116.48, 116.24, 114.81, 114.57, 111.09, 111.02, 74.04, 73.25, 64.01, 47.59, 42.62, 30.05, 27.43. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{34}H_{27}FN_4O_2S$: 575.1912; Found: 575.1917.

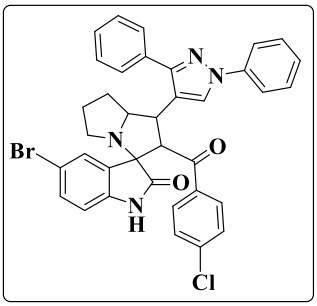
(dl)-2'-benzoyl-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indolin -e-3,3'-pyrrolizin]-2-one (4y). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 33209, 1726, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.16 (s, 1H), 8.96 (s, 1H), 7.89 (dd, J = 7.6, 4.0 Hz, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.54 – 7.48 (m, 6H), 7.31 (dd, 15.6, 8.0 Hz, 3H), 6.99 (t, J = 11.6 Hz, 1H), 6.80 (dd, J = 8.4, 2.4 Hz, 1H), 6.50 (dd, J = 8.4, 4.4 Hz, 1H), 5.18 (d, J = 11.6 Hz, 1H), 4.03 (t, J = 11.6 Hz, 1H), 3.79 (dd, J = 16.0, 6.4 Hz, 1H), 2.41 (dd, J = 9.2, 7.6 Hz, 1H), 2.33 (dd, J = 11.2, 6.0 Hz, 1H), 1.70 (dd, J = 12.4, 5.6 Hz, 1H), 1.63 (dd, J = 13.6, 7.2 Hz, 2H), 1.24 (dd, J = 12.0, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 198.09, 178.73, 152.50, 141.72, 139.94, 137.19, 134.03, 133.83, 132.55, 129.92, 129.62, 129.01, 128.95, 128.72, 128.64, 128.40, 127.72, 127.04, 126.53, 120.21, 118.45, 113.28, 112.14, 73.26, 73.15, 63.18, 47.65, 42.66, 29.91, 27.31. HRMS (ESI, m/z): $[M+H]^+$calcd. for $C_{36}H_{29}BrN_4O_2$: 629.1547; Found: 629.1516.



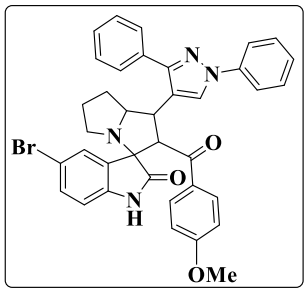
(dl)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrosp -ro[indoline-3,3'-pyrrolizin]-2-one (4z). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3198, 1740, 1683, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.29 (s, 1H), 8.99 (s, 1H), 7.89 (dd, J = 11.6, 8.0 Hz, 4H), 7.60 (s, 4H), 7.49 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 6.0 Hz, 1H), 7.18 (t, J = 8.4 Hz, 2H), 7.13 (s, 1H), 6.52 (d, J = 7.6 Hz, 1H), 5.18 (d, J = 11.2 Hz, 1H), 4.01 (t, J = 12.0 Hz, 1H), 3.81 – 3.70 (m, 1H), 2.38 – 2.30 (m, 2H), 1.69 – 1.53 (m, 3H), 1.16 (dd, J = 10.4, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 196.72, 178.67, 168.34, 166.79, 152.49, 141.66, 139.94, 134.03, 133.95, 133.93, 132.64, 131.48, 131.38, 129.94, 129.56, 129.02, 128.94, 128.65, 127.63, 127.10, 126.54, 120.13, 118.43, 115.91, 115.69, 113.35, 112.21, 73.35, 73.20, 63.35, 47.63, 42.52, 30.00, 27.41. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}BrFN_4O_2$: 647.1452; Found: 647.1459.



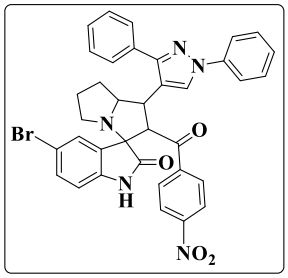
(dl)-5-bromo-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrosp -iro[indoline-3,3'-pyrrolizin]-2-one (4aa). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3208, 1724, 1679, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.30 (s, 1H), 8.99 (s, 1H), 7.89 (dd, 10.4, 7.2 Hz, 4H), 7.60 (t, J = 6.8 Hz, 3H), 7.50 – 7.47 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.12 (s, 1H), 6.53 (d, J = 7.6 Hz, 1H), 5.17 (d, J = 11.6 Hz, 1H), 4.00 (t, J = 11.2 Hz, 1H), 3.77 (d, J = 7.6 Hz, 1H), 2.34 (s, 2H), 1.62 (dd, J = 10.4, 6.4 Hz, 3H), 1.17 (dd, J = 10.4, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.24, 178.60, 153.24, 152.48, 141.65, 139.93, 139.42, 138.85, 136.79, 135.87, 134.01, 132.70, 132.33, 130.60, 130.25, 129.95, 129.40, 129.03, 128.94, 128.87, 128.67, 127.56, 127.11, 126.56, 121.54, 120.07, 119.21, 118.43, 113.38, 112.26, 73.32, 73.21, 63.41, 47.64, 42.48, 30.00, 27.42. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}BrClN_4O_2$: 663.1157; Found: 663.1165.



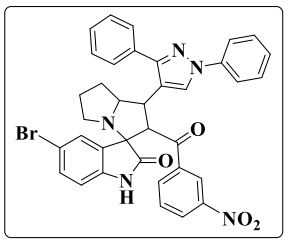
(dl)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydro spiro[indoline-3,3'-pyrrolizin]-2-one (4ab). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3118, 1721, 1668, 1598. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.31 (s, 1H), 8.96 (s, 1H), 7.90 (dd, J = 22.4, 7.2 Hz, 4H), 7.59 (d, J = 6.4 Hz, 4H), 7.49 (d, J = 8.4 Hz, 3H), 7.31 (dd, 16.4, 7.2 Hz, 2H), 7.17 (s, 1H), 6.86 (d, J = 7.6 Hz, 2H), 6.54 (d, J = 7.6 Hz, 1H), 5.14 (d, J = 11.6 Hz, 1H), 4.04 (t, J = 104 Hz, 1H), 3.88 (s, 1H), 3.78 (s, 3H), 2.34 (s, 2H), 1.61 (s, 3H), 1.16 (dd, J = 11.2, 10.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.77, 178.80, 163.77, 152.50, 141.64, 139.93, 134.02, 132.44, 130.97, 130.09, 129.92, 129.78, 128.98, 128.94, 128.63, 127.85, 127.02, 126.51, 120.24, 118.42, 113.99, 113.25, 112.11, 73.59, 73.16, 62.56, 55.97, 47.65, 42.79, 30.01, 27.41. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{37}H_{31}BrN_4O_3$: 659.1652; Found: 659.1658.



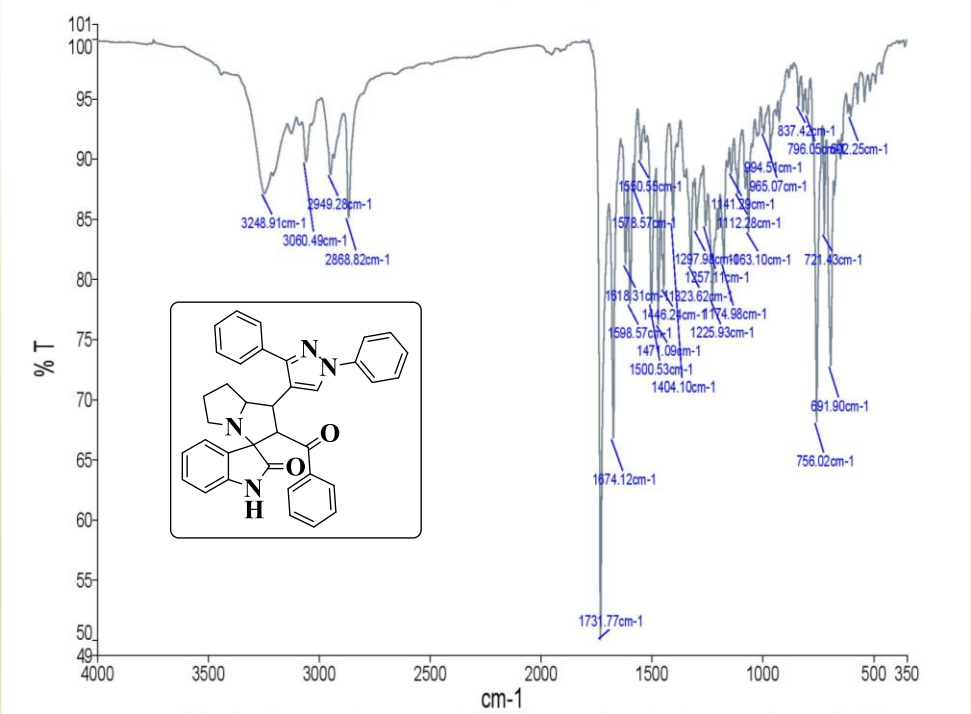
(dl)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one (4ac). White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3379, 1719, 1615, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.20 (s, 1H), 9.03 (s, 1H), 8.15 (d, J = 4.8 Hz, 2H), 7.89 (s, 4H), 7.63 (dd, J = 22.8, 7.6 Hz, 4H), 7.51 (d, J = 6.4 Hz, 3H), 7.38 (d, J = 6.8 Hz, 1H), 7.30 (t, J = 6.4 Hz, 1H), 7.12 (s, 1H), 6.49 (d, J = 6.4 Hz, 1H), 5.27 (d, J = 9.2 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.81 – 3.72 (m, 1H), 2.34 (d, J = 4.0 Hz, 2H), 1.62 (dd, J = 3.6, 2.4 Hz, 3H), 1.19 (dd, J = 6.4, 4.0 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.92, 178.46, 152.51, 150.33, 141.96, 141.65, 139.94, 134.00, 132.94, 129.96, 129.69, 129.36, 129.06, 128.95, 128.70, 127.36, 127.17, 126.60, 123.74, 119.95, 118.46, 113.56, 112.48, 73.27, 73.21, 64.40, 47.59, 42.33, 30.07, 27.48. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}BrN_5O_4$: 674.1397; Found: 674.1409.



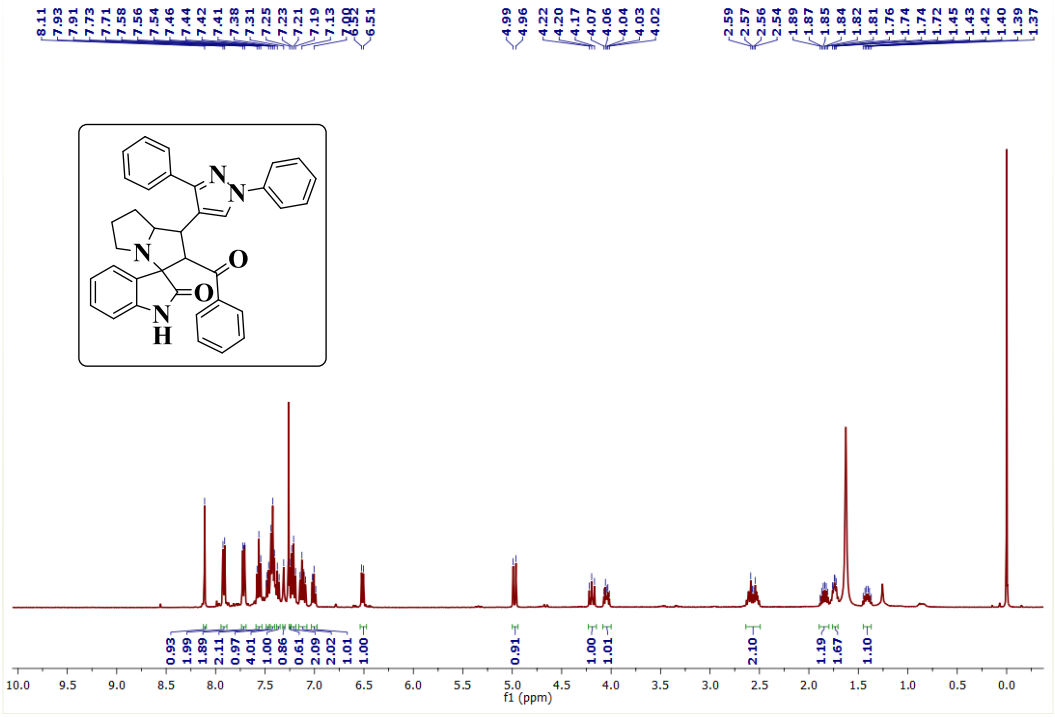
(dl)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospir -o[indoline-3,3'-pyrrolizin]-2-one (4ad)**:** White Solid. mp: 179-180 ℃**.** IR (KBr, cm^{-1}): 3168, 1719, 1689, 1599. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.28 (s, 1H), 9.02 (s, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 7.89 (t, J = 8.8 Hz, 4H), 7.84 (d, J = 7.6 Hz, 1H), 7.5– 7.58 (m, 3H), 7.51 (dd, J = 15.6, 8.0 Hz, 3H), 7.31 (dd, J = 15.6, 8.8 Hz, 2H), 7.12 (s, 1H), 6.44 (d, J = 8.4 Hz, 1H), 5.24 (d, J = 11.6 Hz, 1H), 4.00 (t, J = 11.2 Hz, 1H), 3.80 (dd, J = 15.6, 6.4 Hz, 1H), 2.35 (d, J = 3.2 Hz, 2H), 1.72 – 1.57 (m, 3H), 1.19 (dd, J = 11.6, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 197.11, 178.57, 152.51, 147.88, 141.65, 139.97, 138.23, 134.33, 134.06, 132.84, 130.58, 129.94, 129.34, 129.04, 128.97, 128.67, 128.02, 127.42, 127.28, 126.57, 122.94, 119.92, 118.49, 113.53, 112.28, 73.14, 73.10, 64.17, 47.66, 42.38, 29.87, 27.33. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{36}H_{28}BrN_5O_4$: 674.1397; Found: 674.1409.



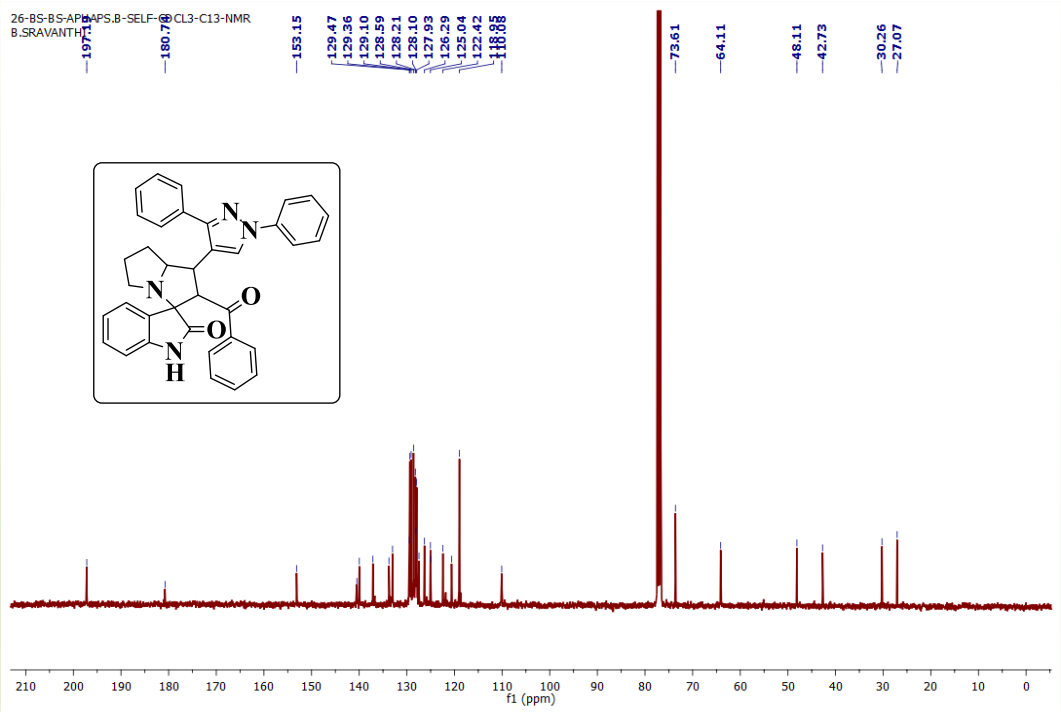
3. FT-IR, ^{1}H-NMR, ^{13}C-NMR and Mass Spectra of the Compounds



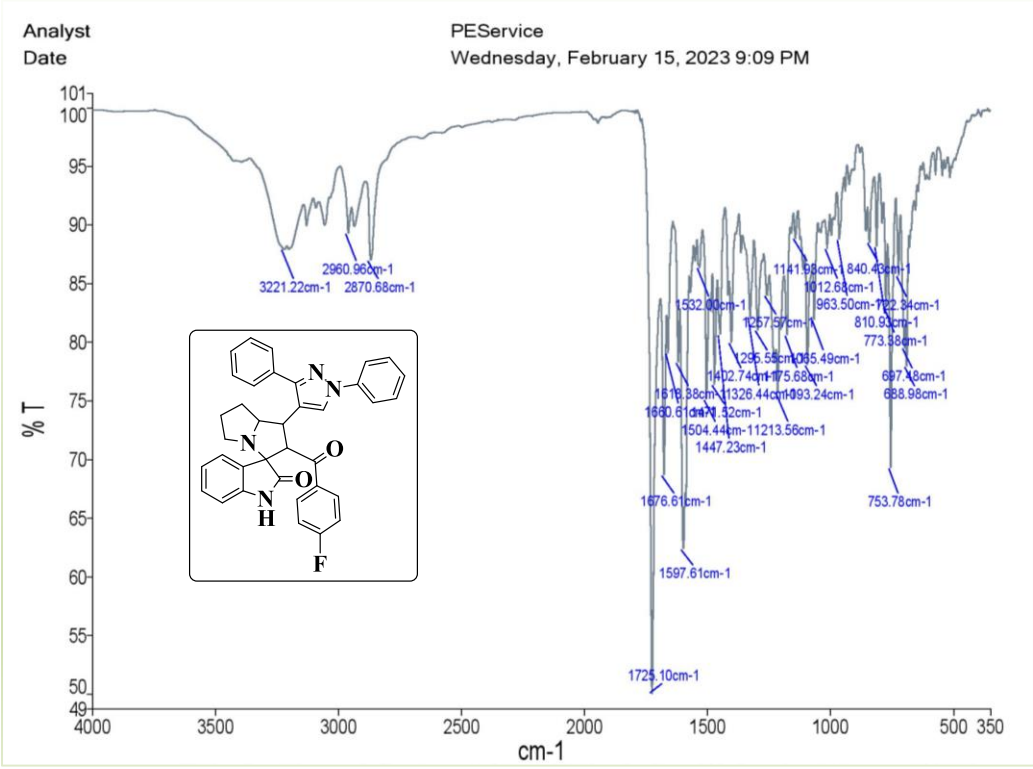
FT-IR Spectrum of the compound 4a



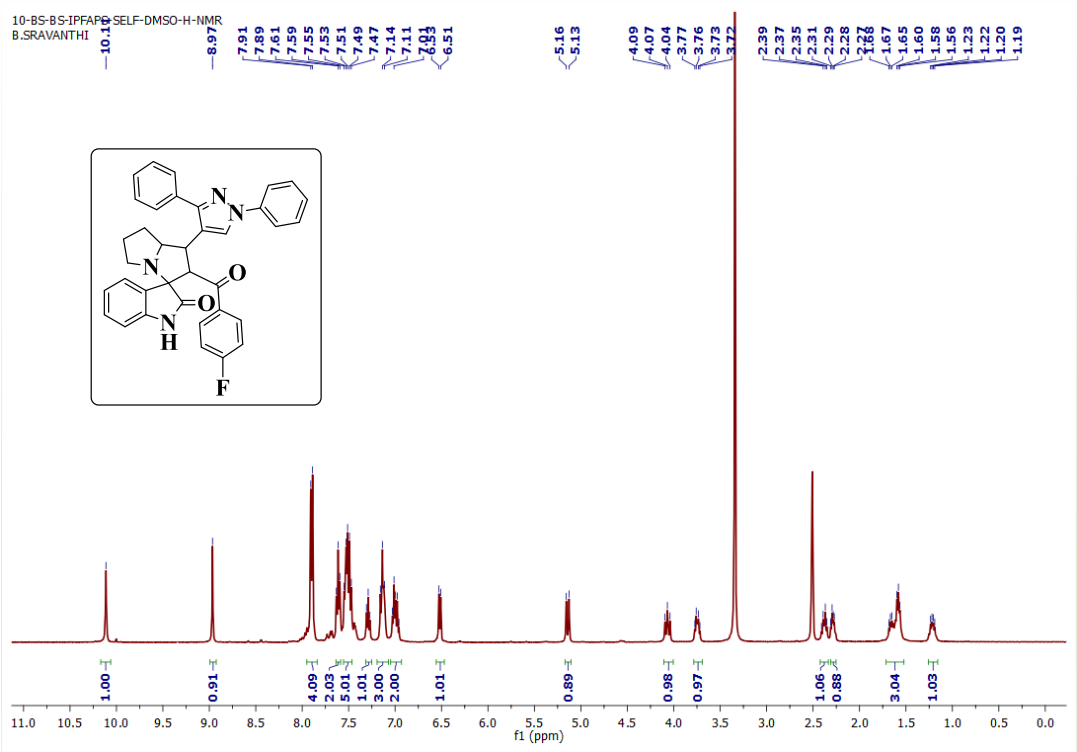
^{1}H NMR Spectrum of the compound 4a



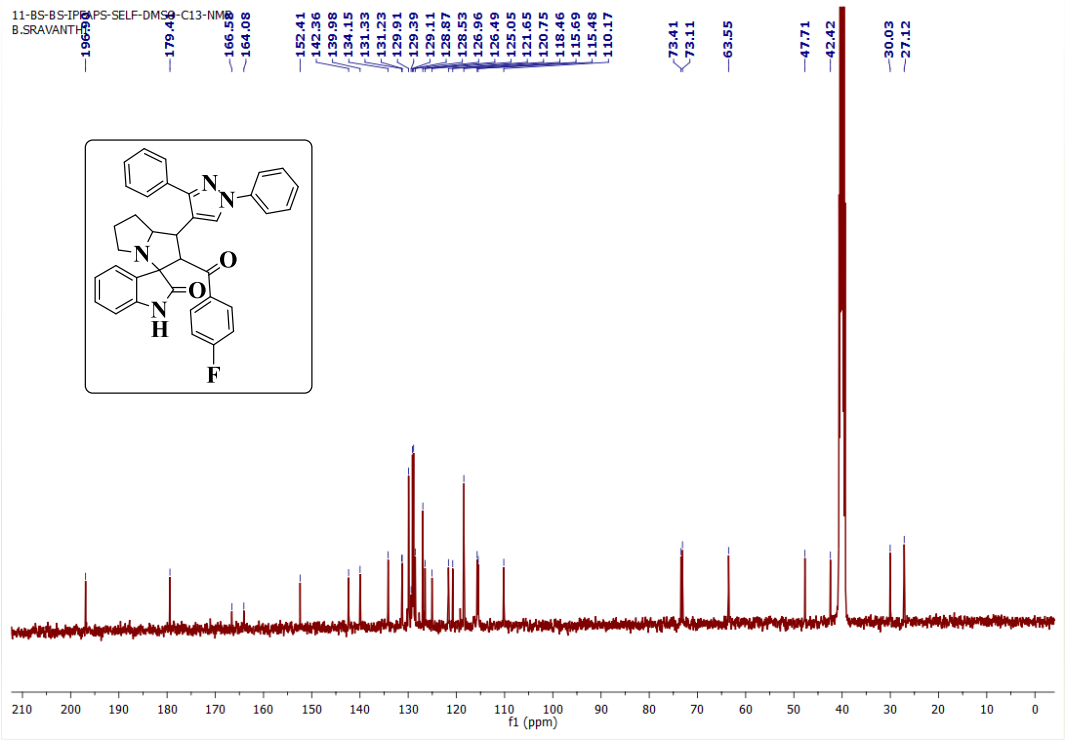
^{13}C NMR Spectrum of the compound 4a



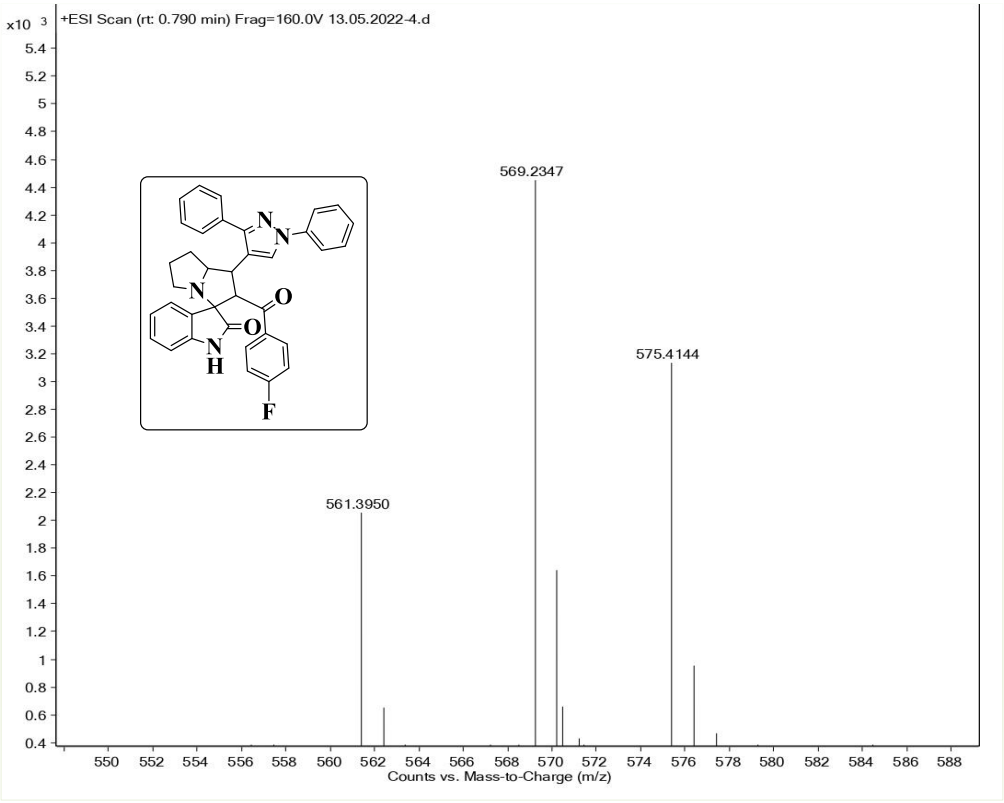
FT-IR Spectrum of the compound 4b



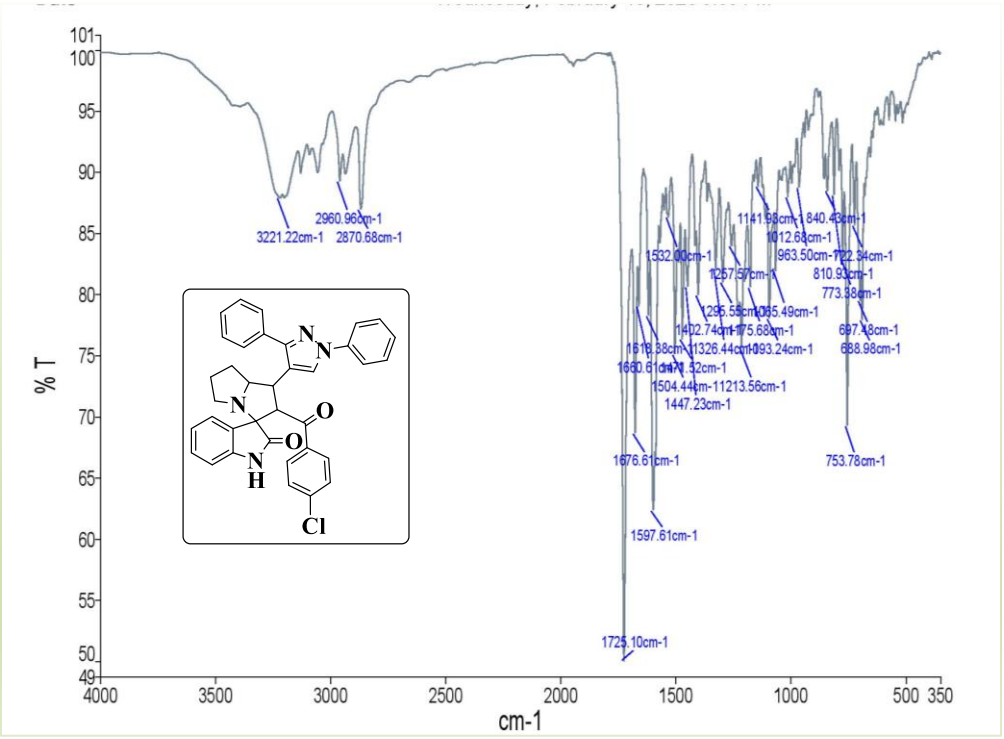
^{1}H NMR Spectrum of the compound 4b



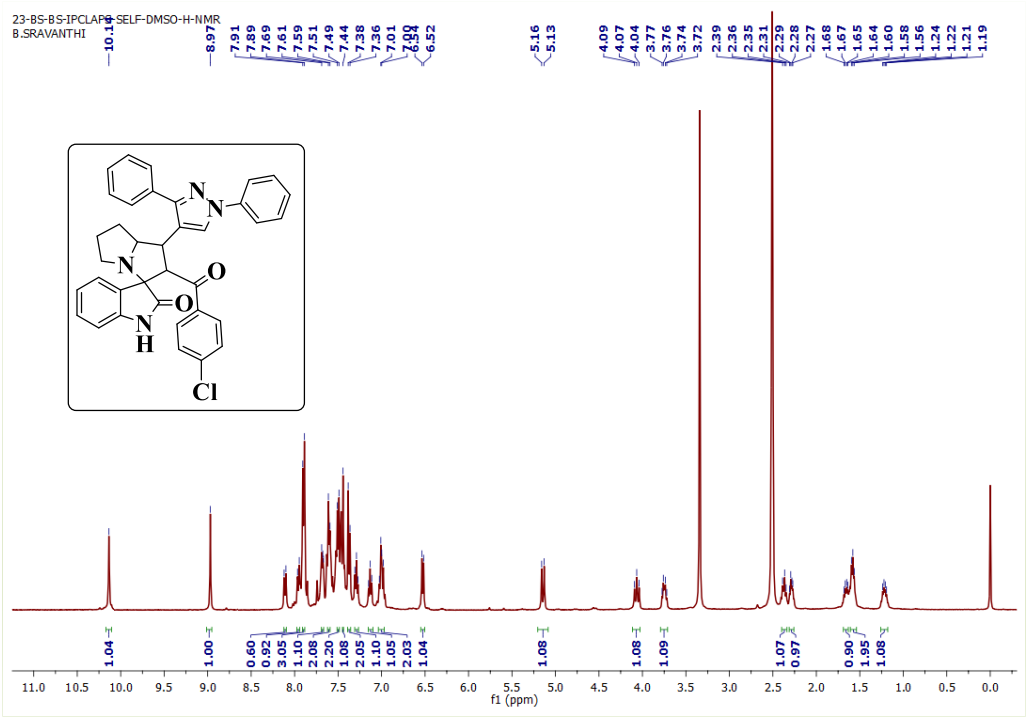
^{13}C NMR Spectrum of the compound 4b



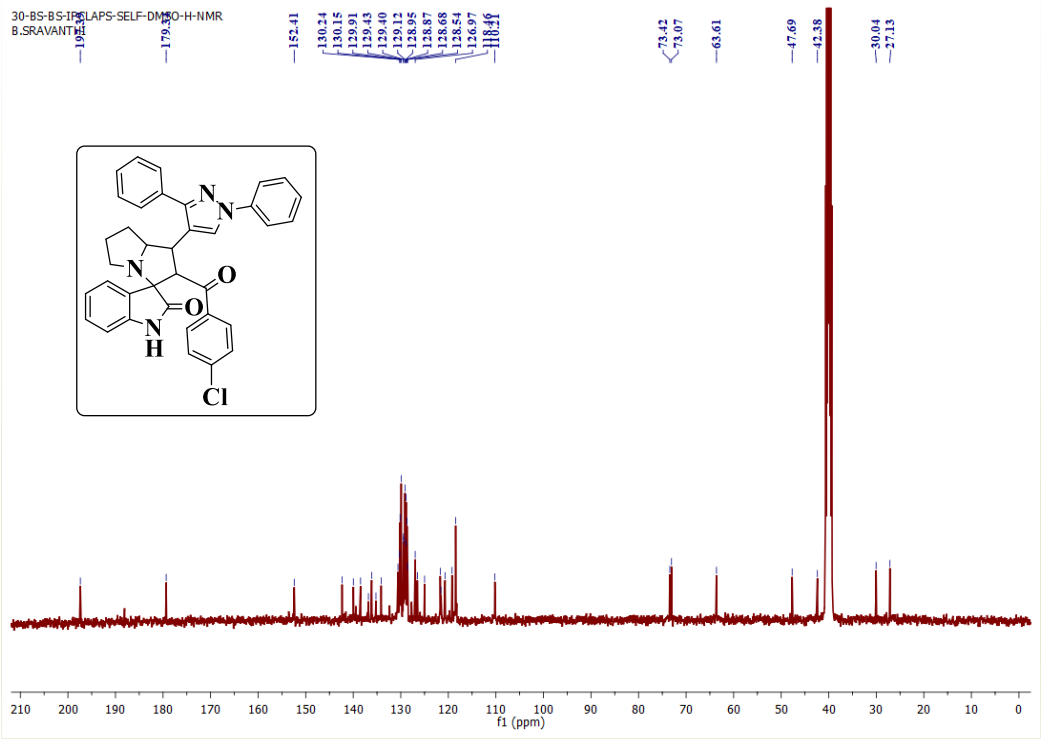
Mass spectrum of the compound 4b



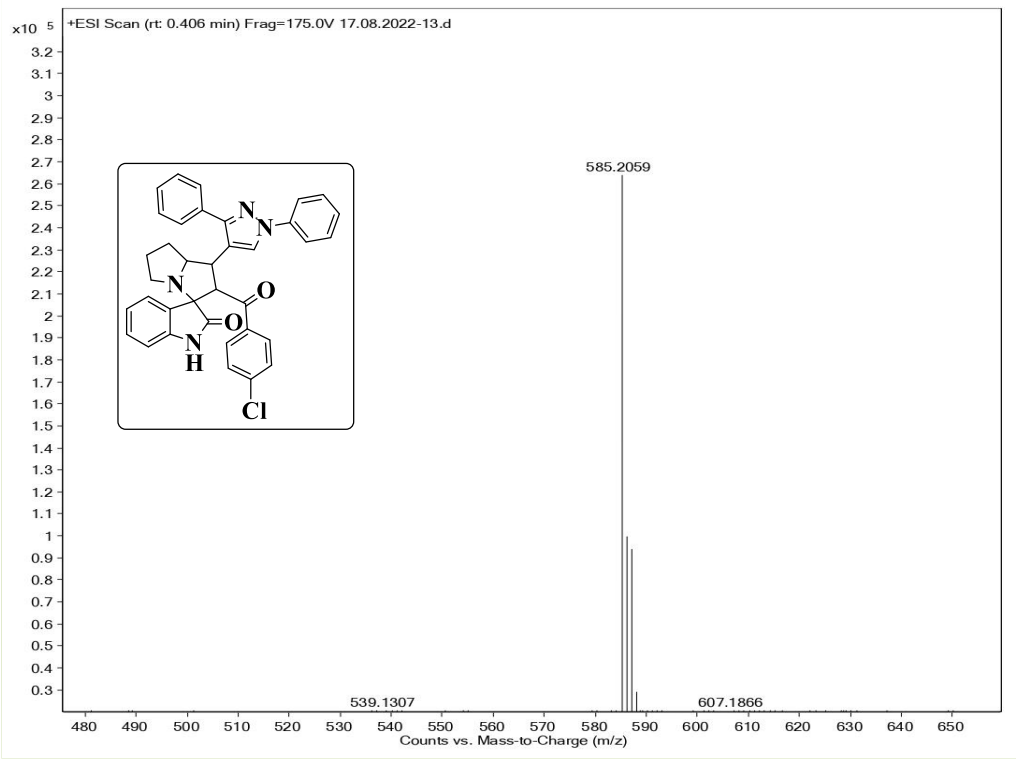
FT-IR Spectrum of the compound 4c



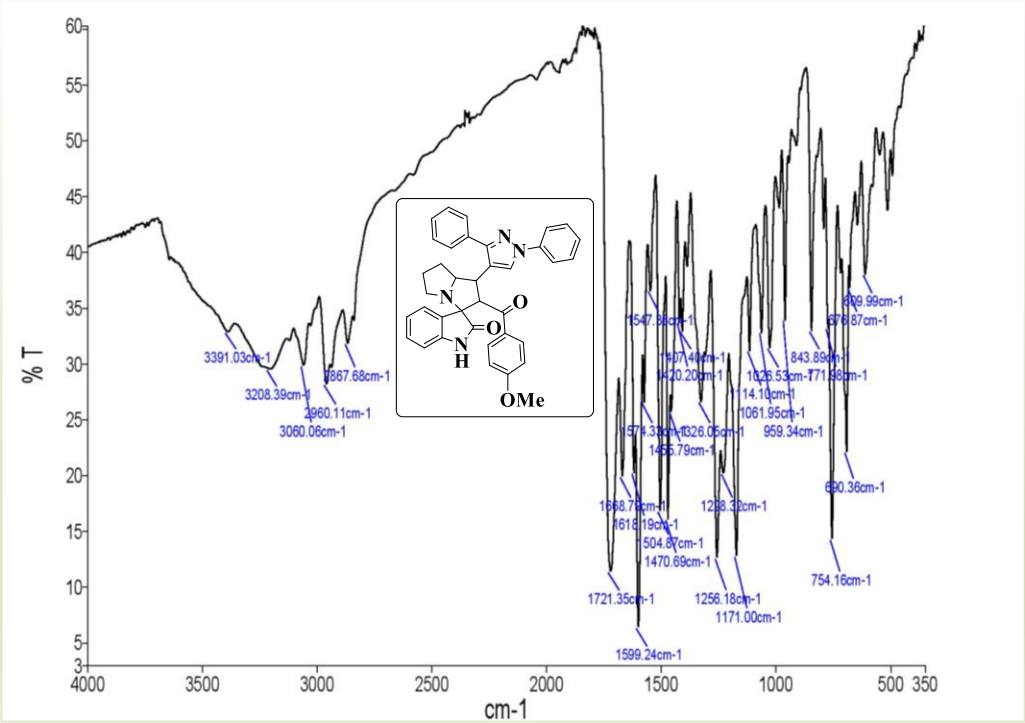
^{1}H NMR Spectrum of the compound 4c



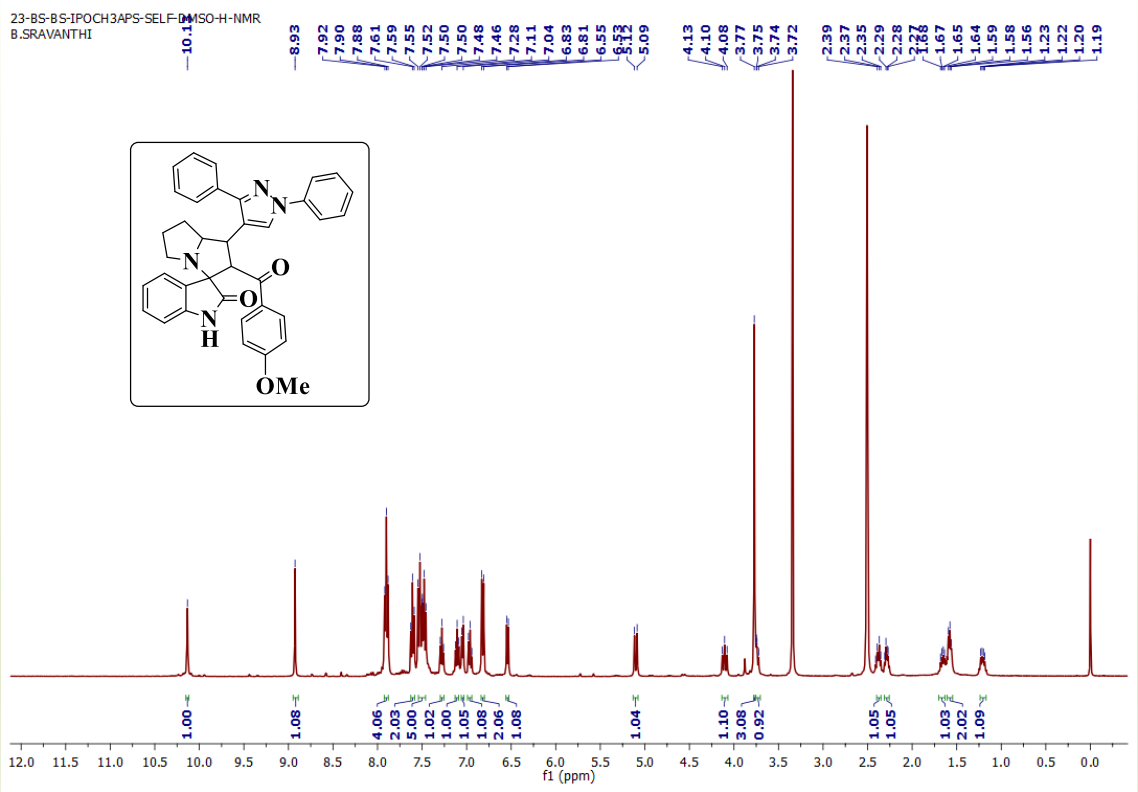
^{13}C NMR Spectrum of the compound 4c



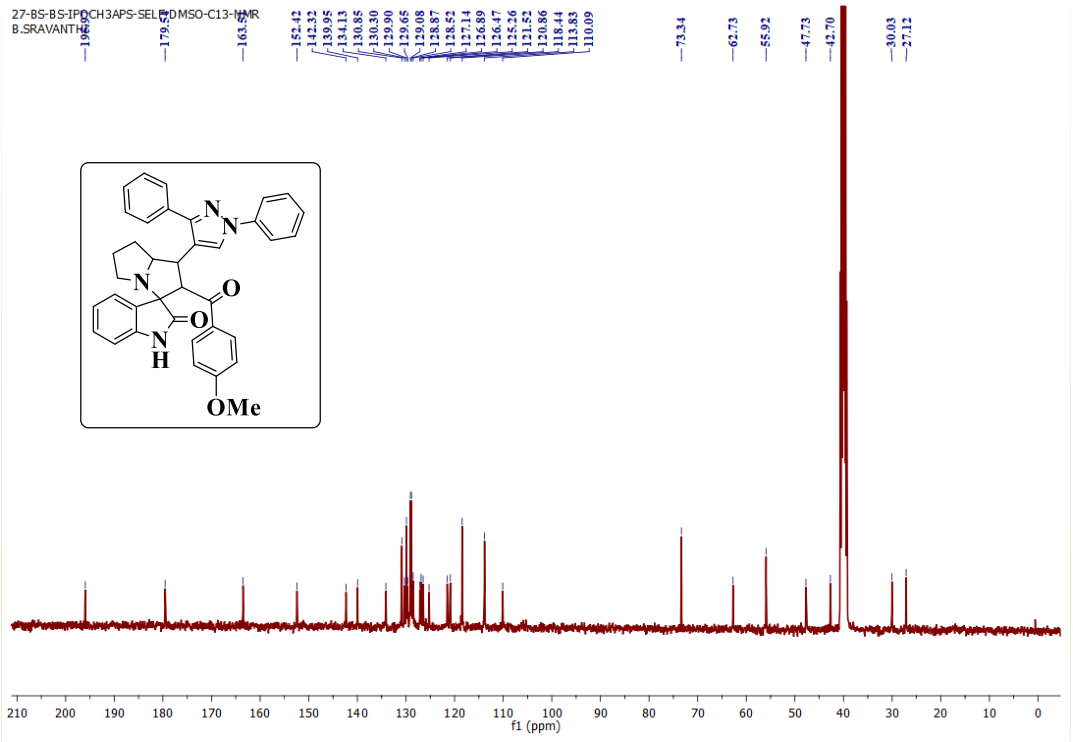
Mass spectrum of the compound 4c



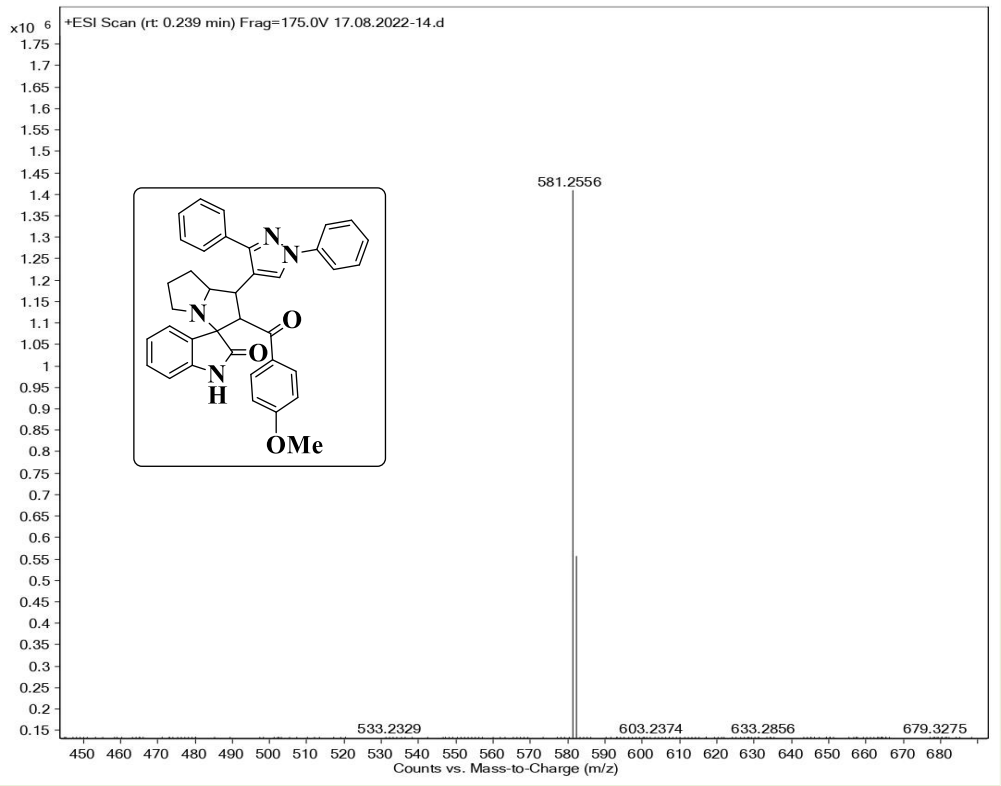
FT-IR Spectrum of the compound 4d



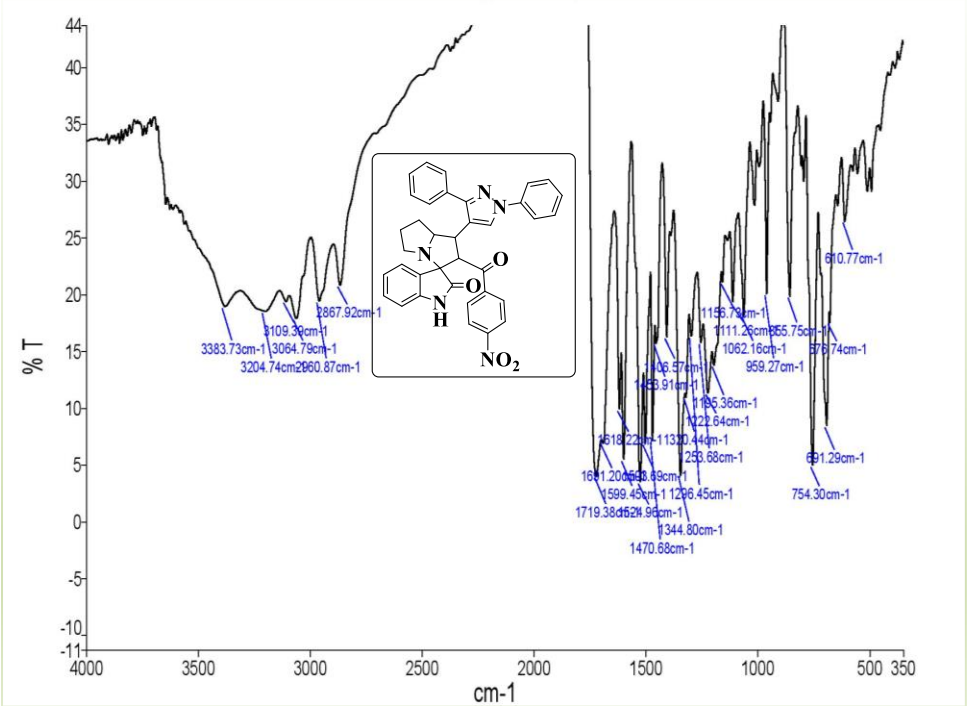
^{1}H NMR Spectrum of the compound 4d



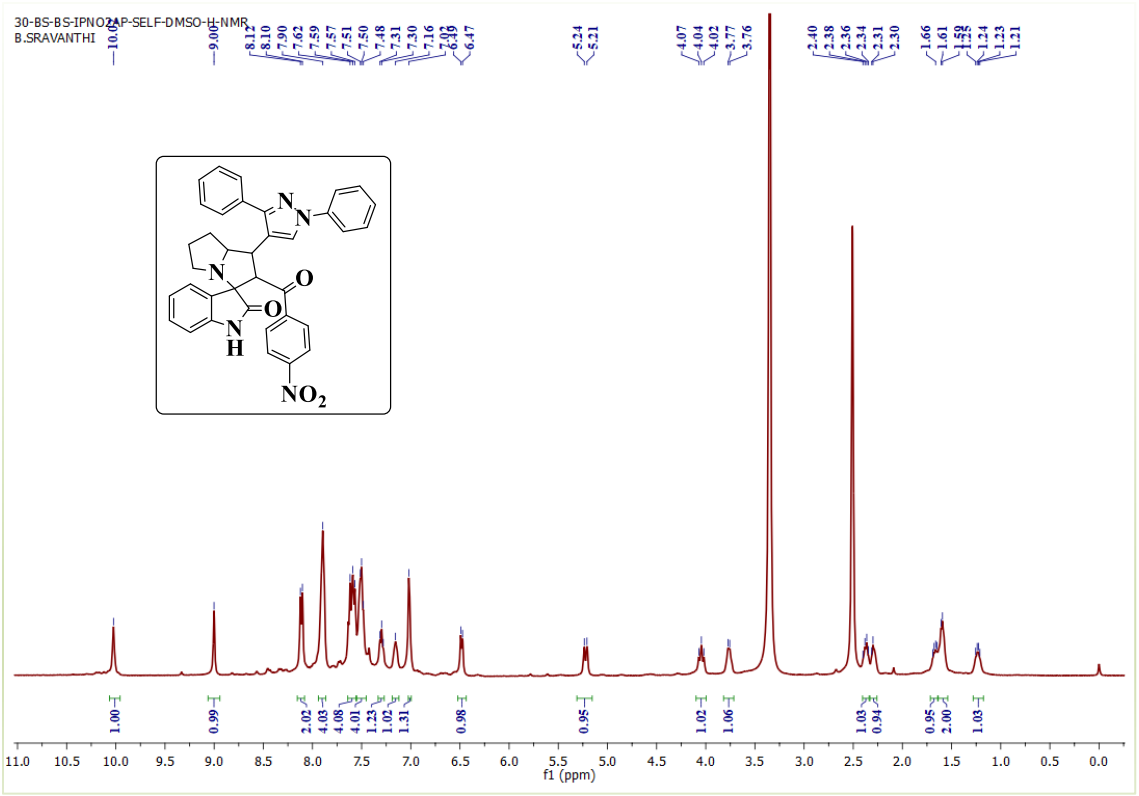
^{13}C NMR Spectrum of the compound 4d



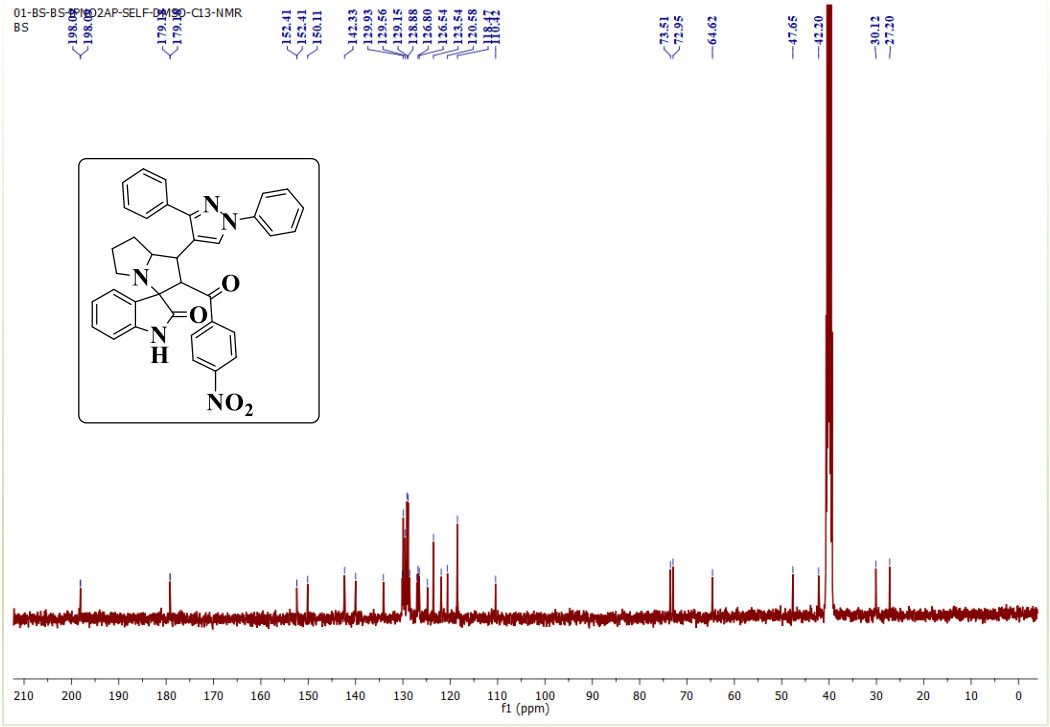
Mass spectrum of the compound 4d



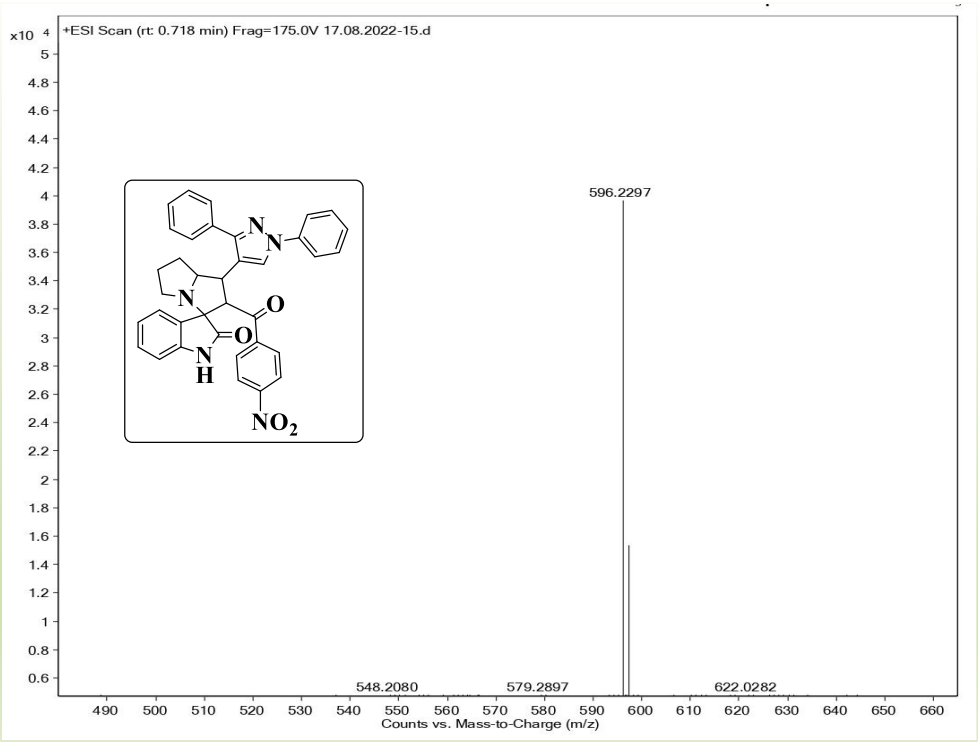
FT-IR Spectrum of the compound 4e



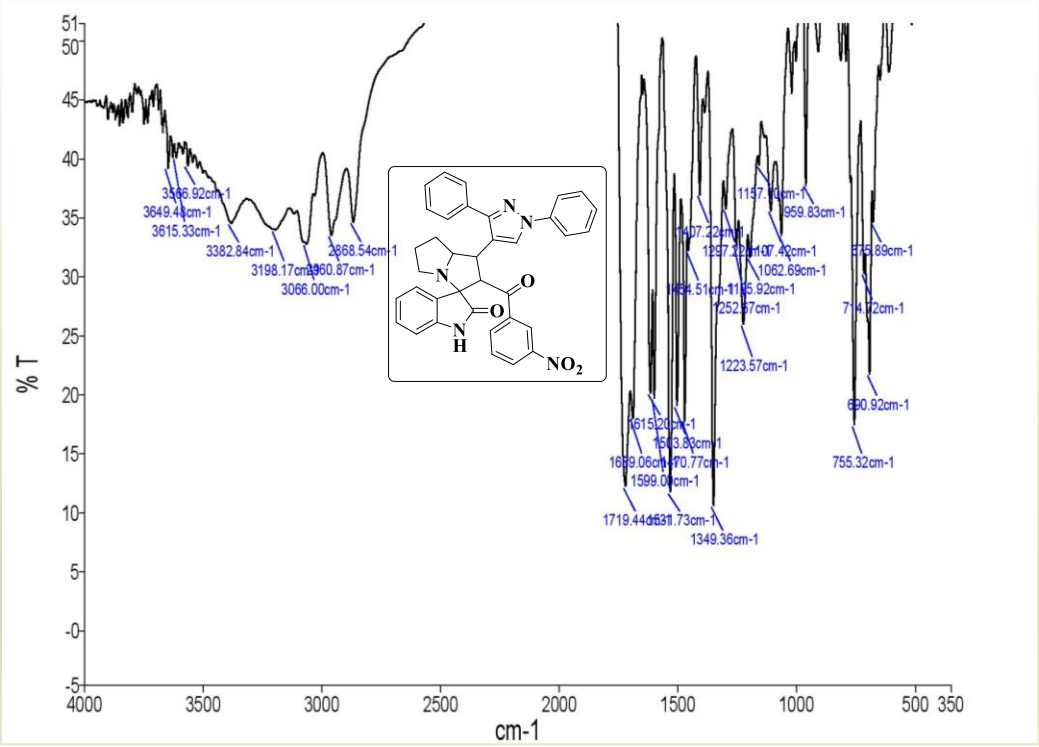
^{1}H NMR Spectrum of the compound 4e



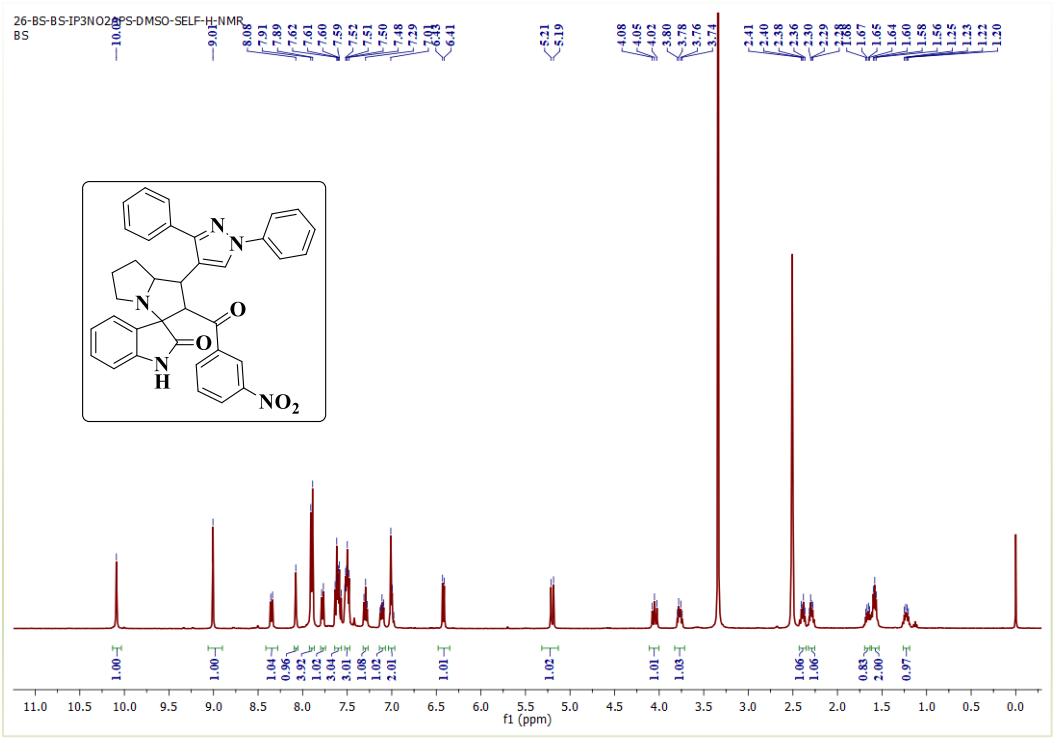
^{13}C NMR Spectrum of the compound 4e



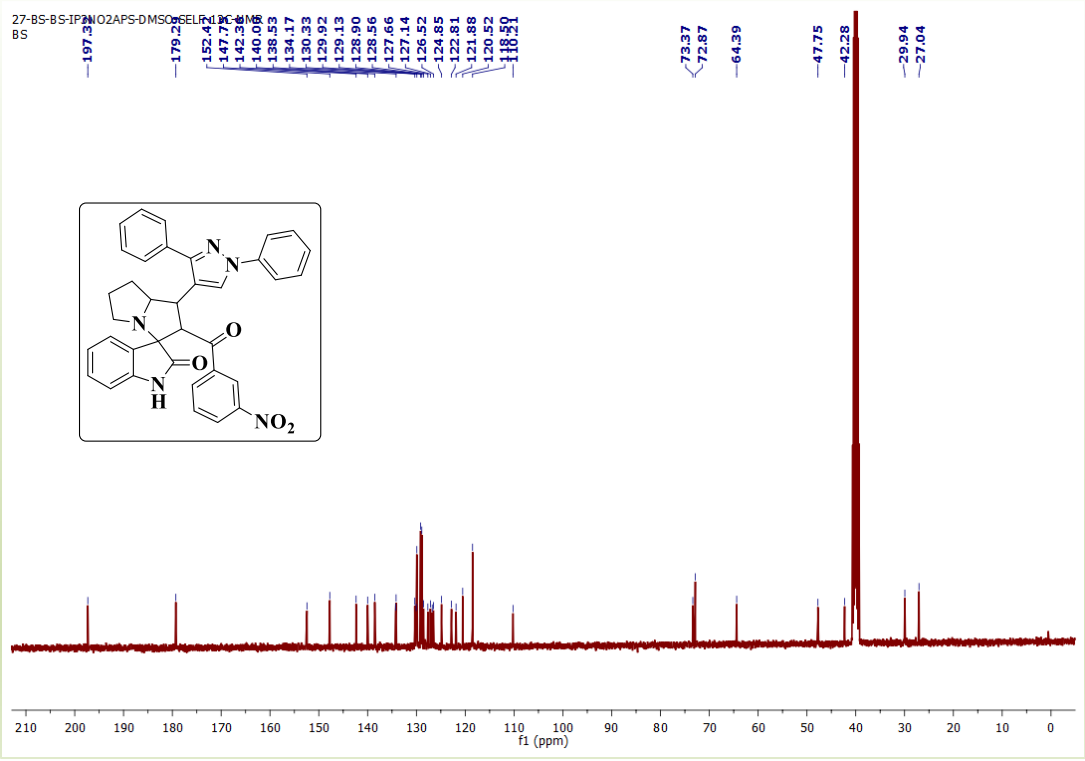
Mass spectrum of the compound 4e



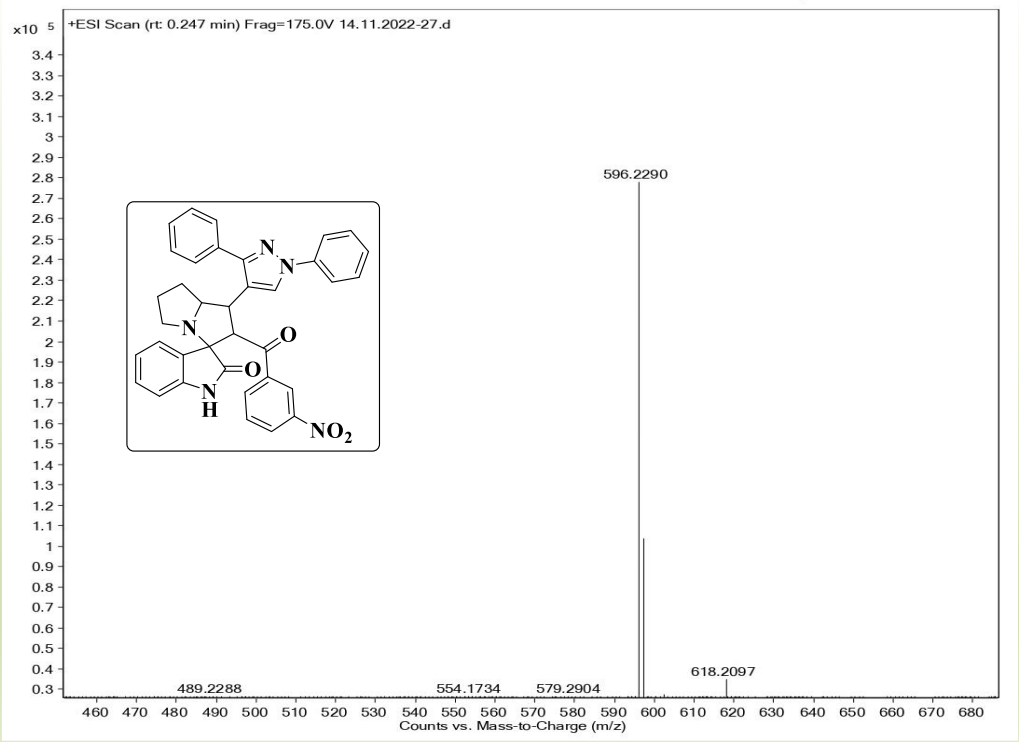
FT-IR Spectrum of the compound 4f



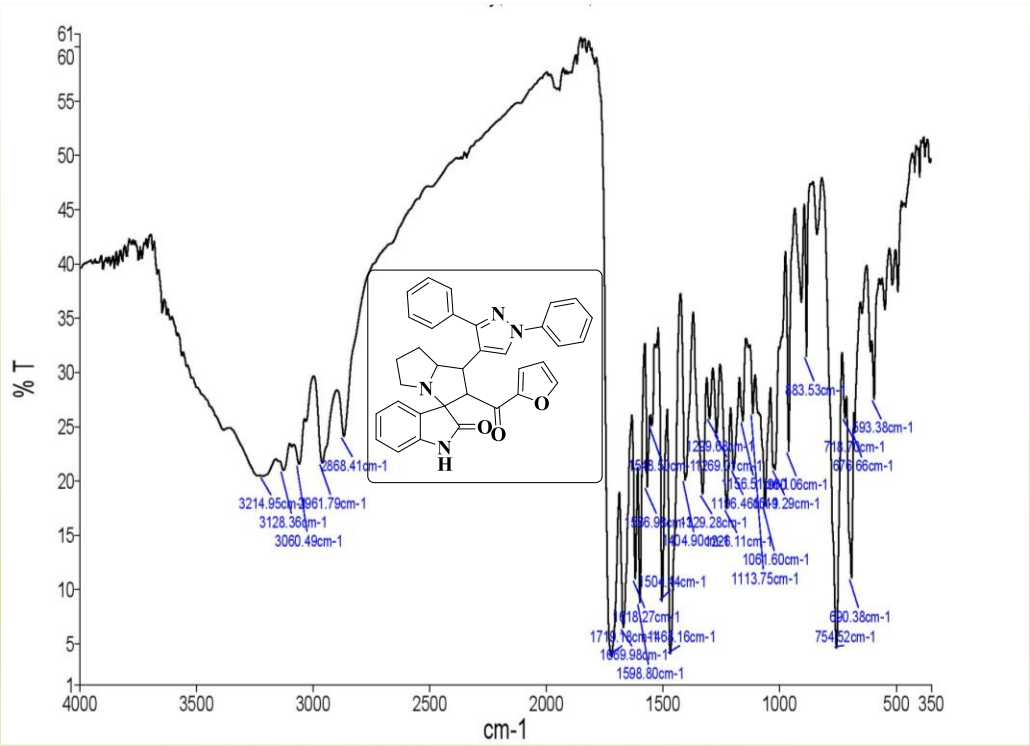
^{1}H NMR Spectrum of the compound 4f



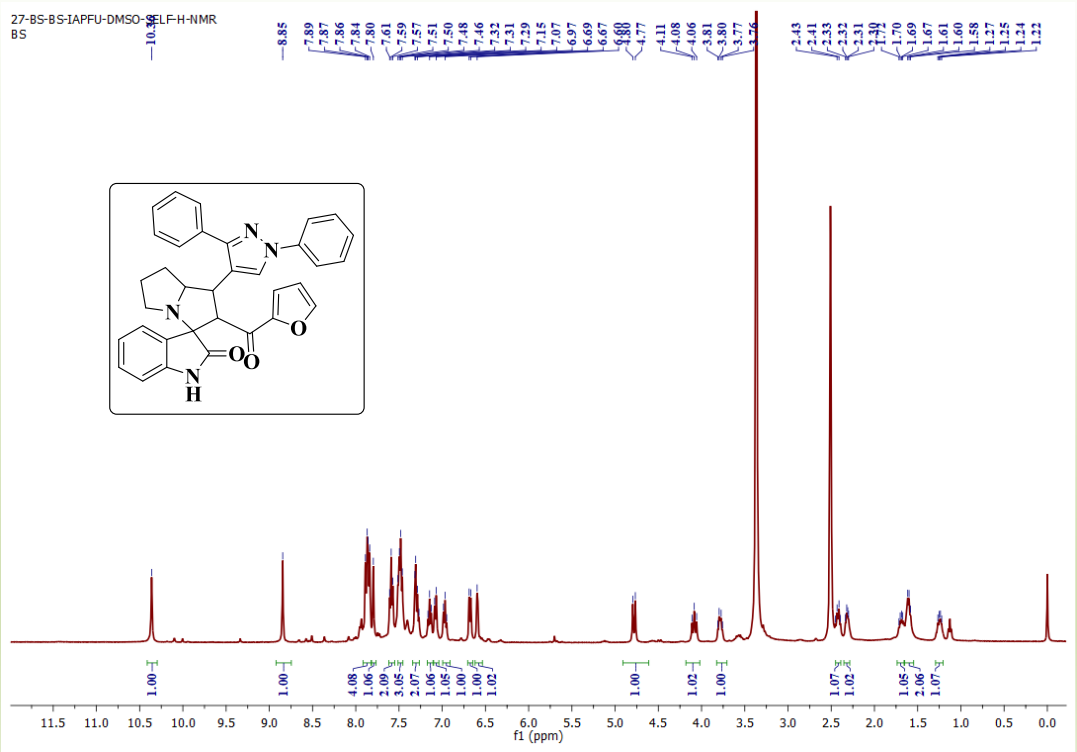
^{13}C NMR Spectrum of the compound 4f



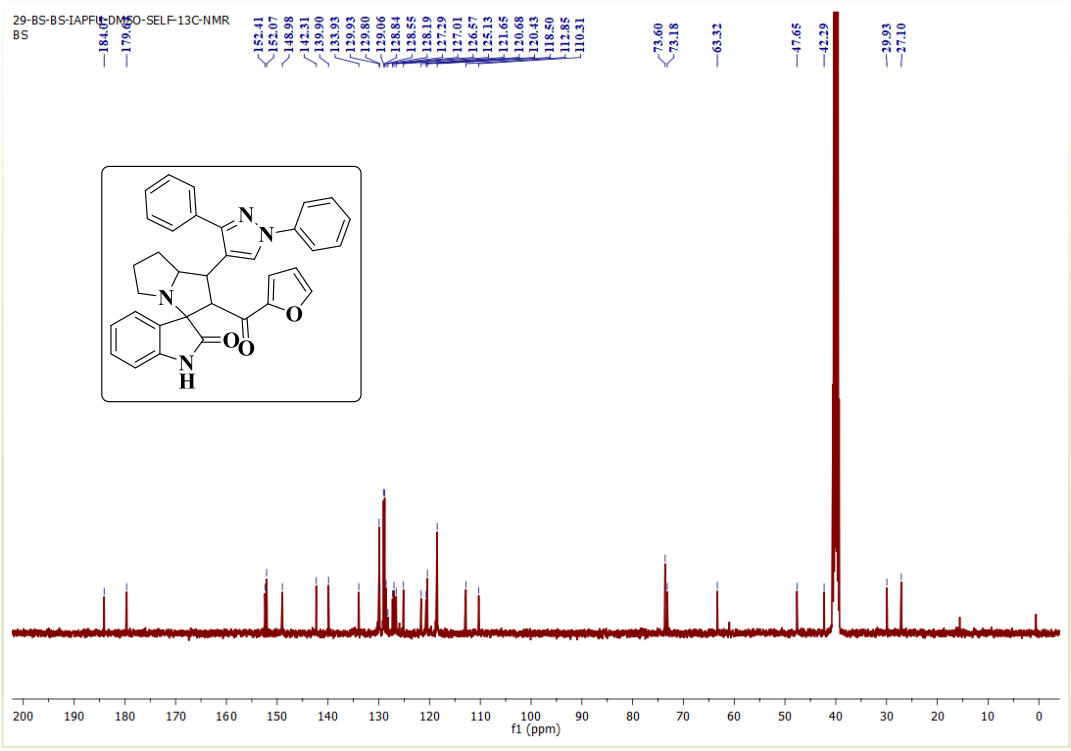
Mass spectrum of the compound 4f



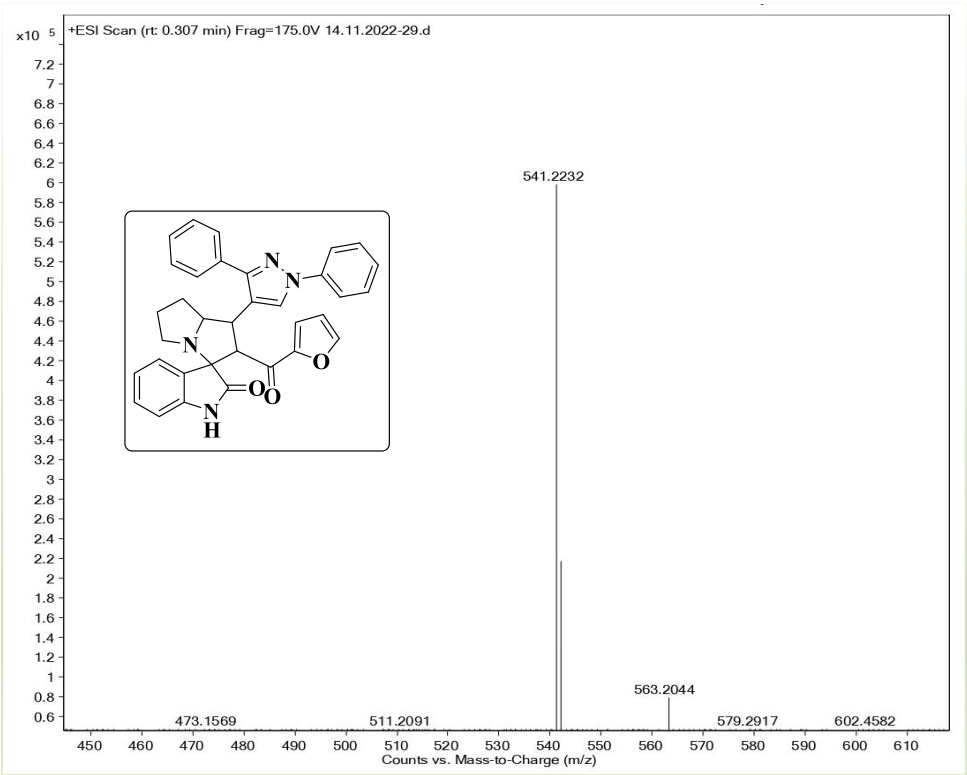
FT-IR Spectrum of the compound 4g



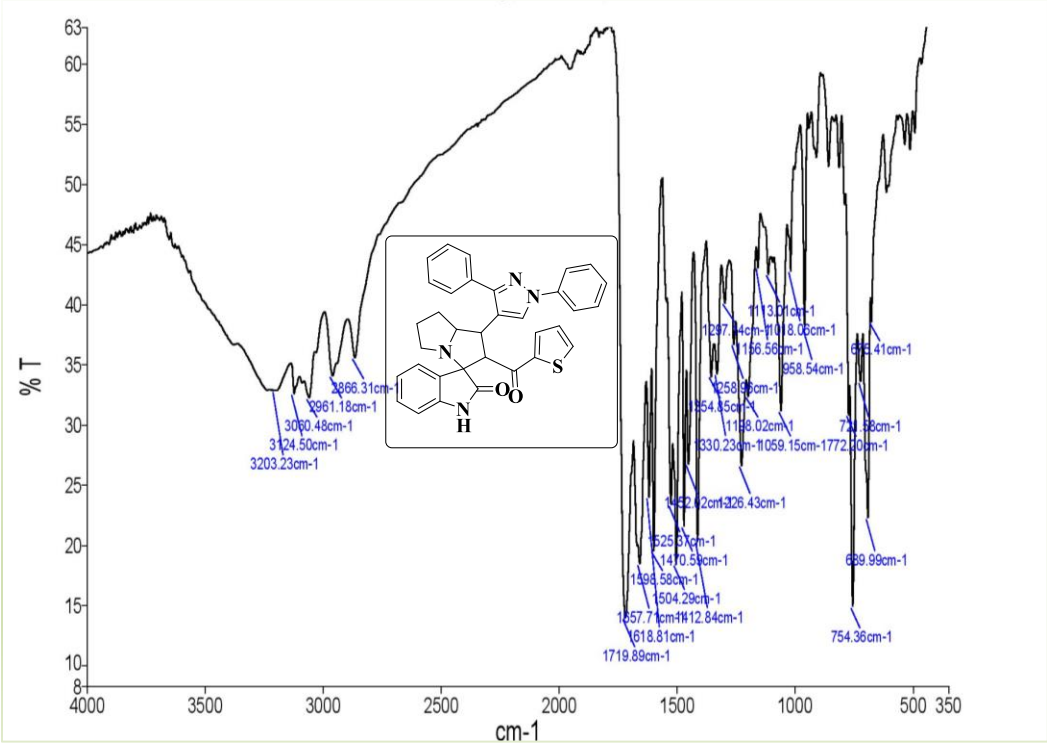
^{1}H NMR Spectrum of the compound 4g



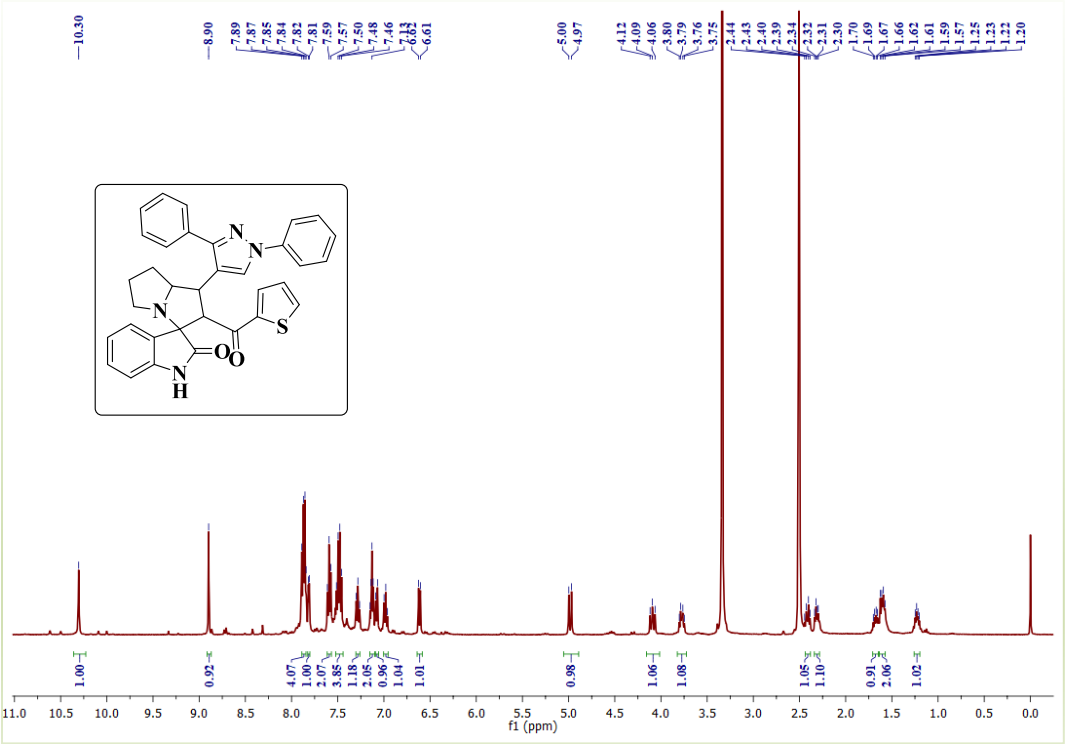
^{13}C NMR Spectrum of the compound 4g



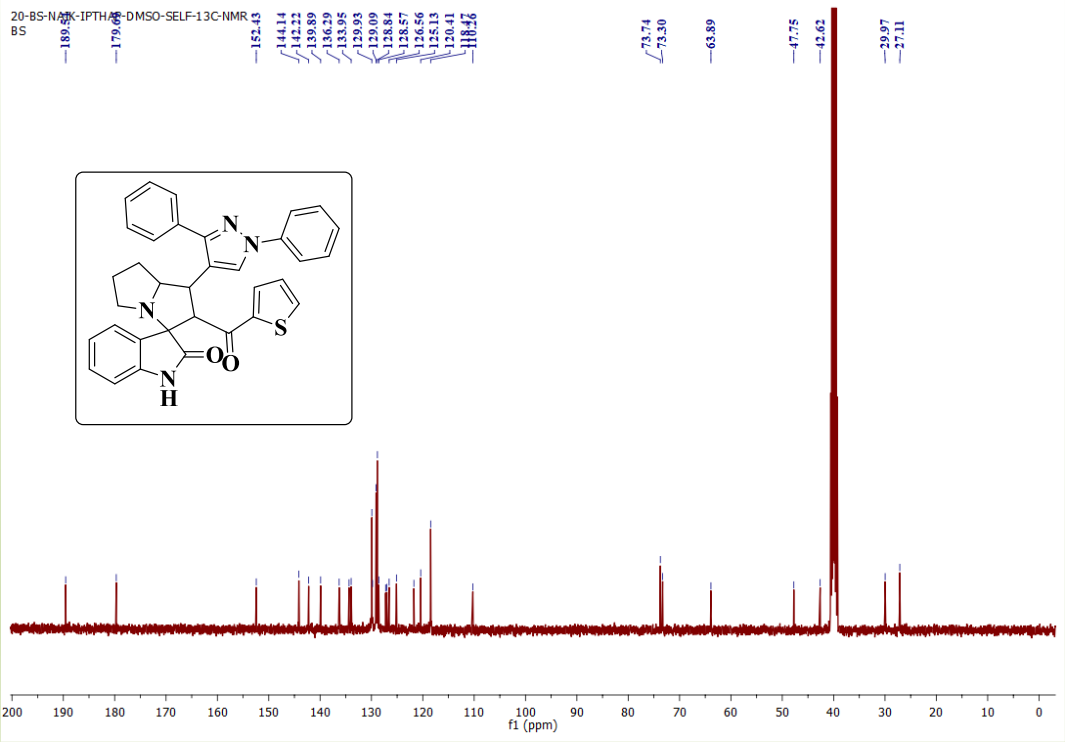
Mass spectrum of the compound 4g



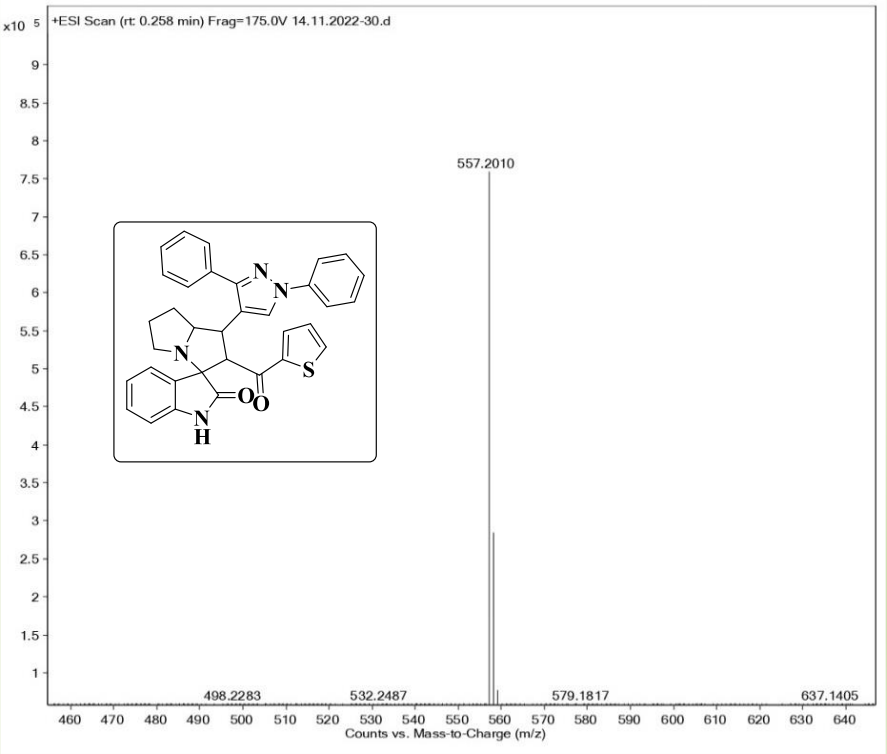
FT-IR Spectrum of the compound 4h



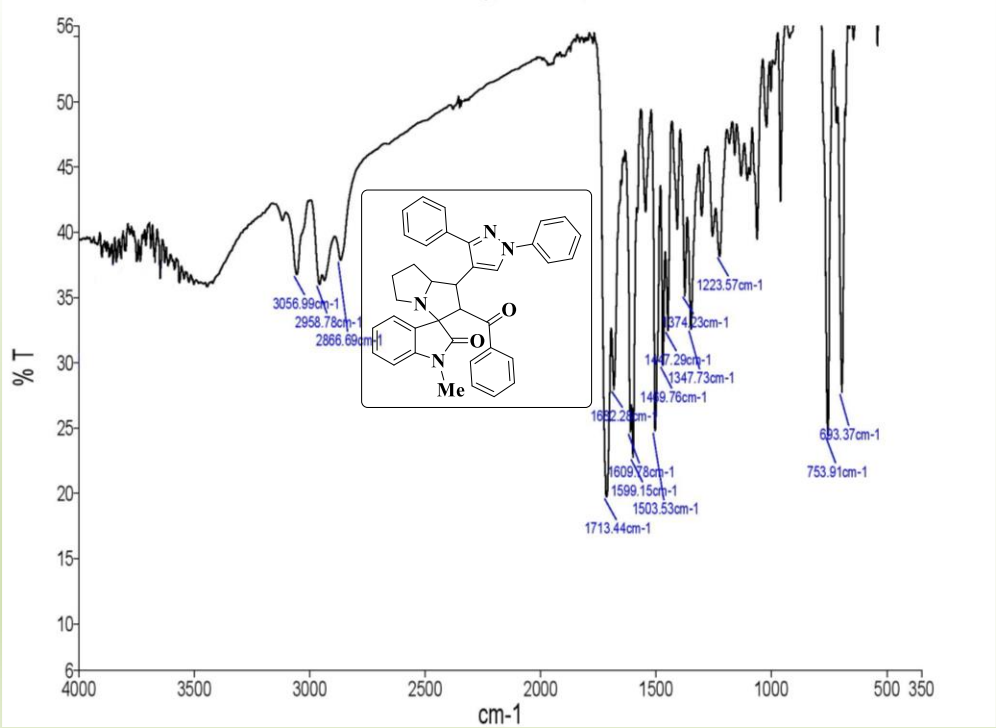
^{1}H NMR Spectrum of the compound 4h



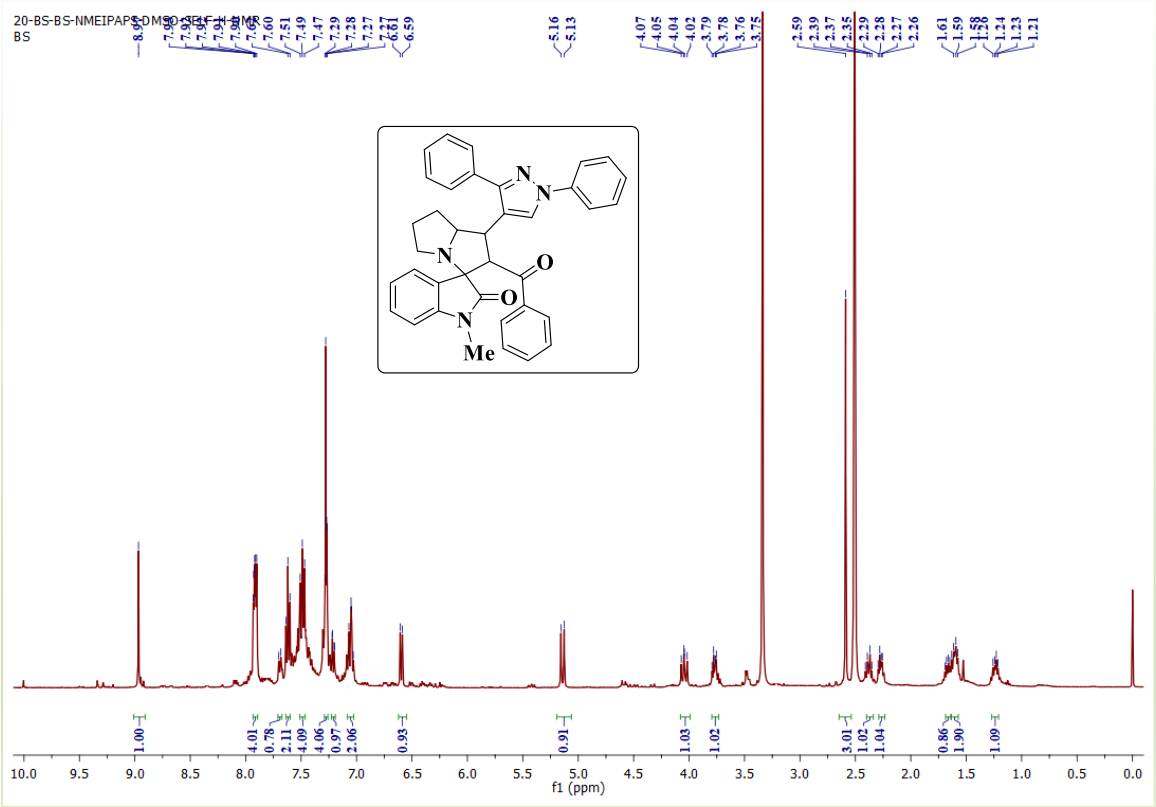
^{13}C NMR Spectrum of the compound 4h



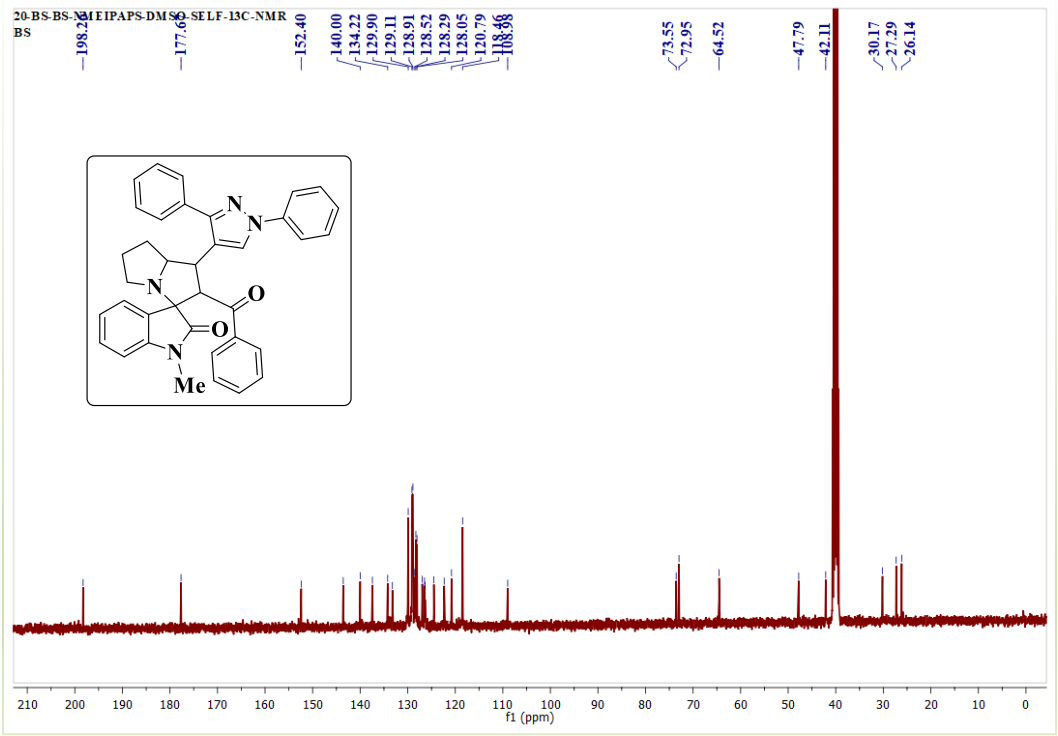
Mass spectrum of the compound 4h



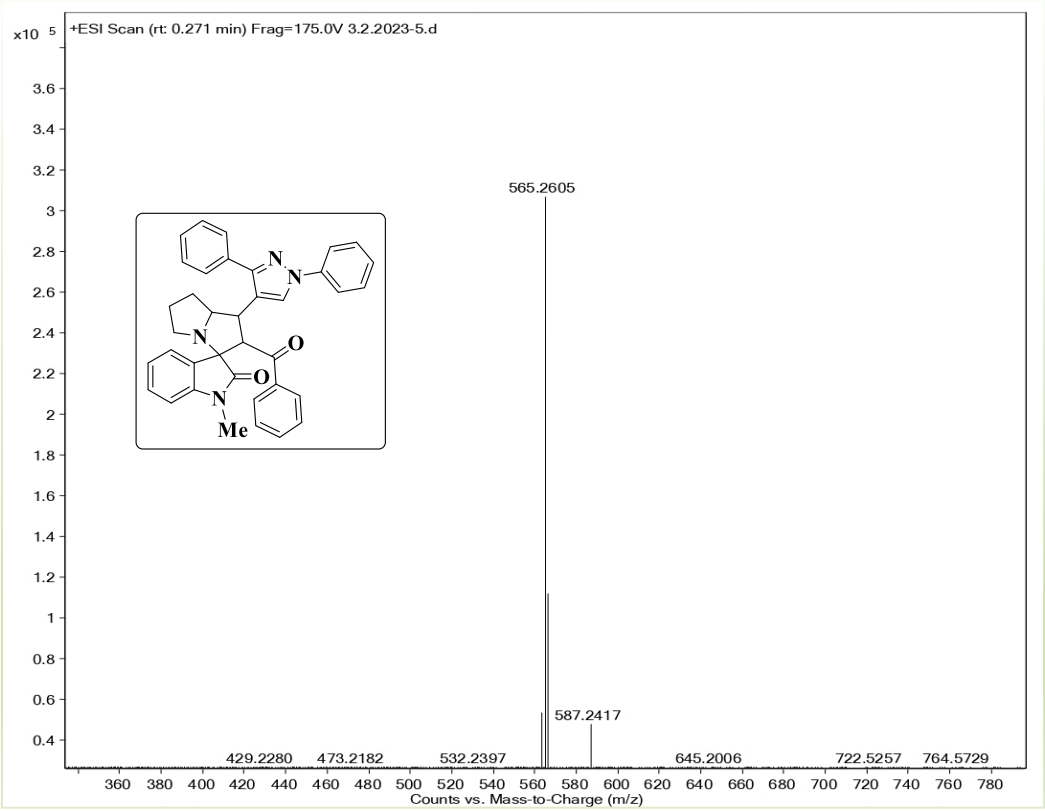
FT-IR Spectrum of the compound 4i



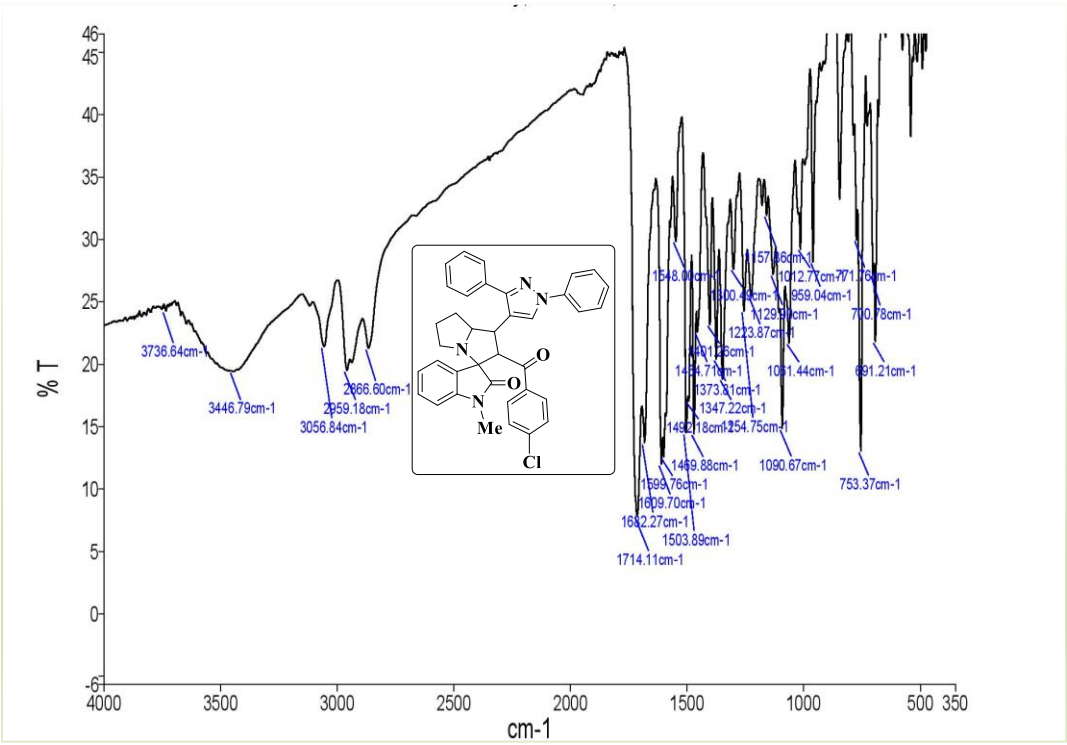
^{1}H NMR Spectrum of the compound 4i



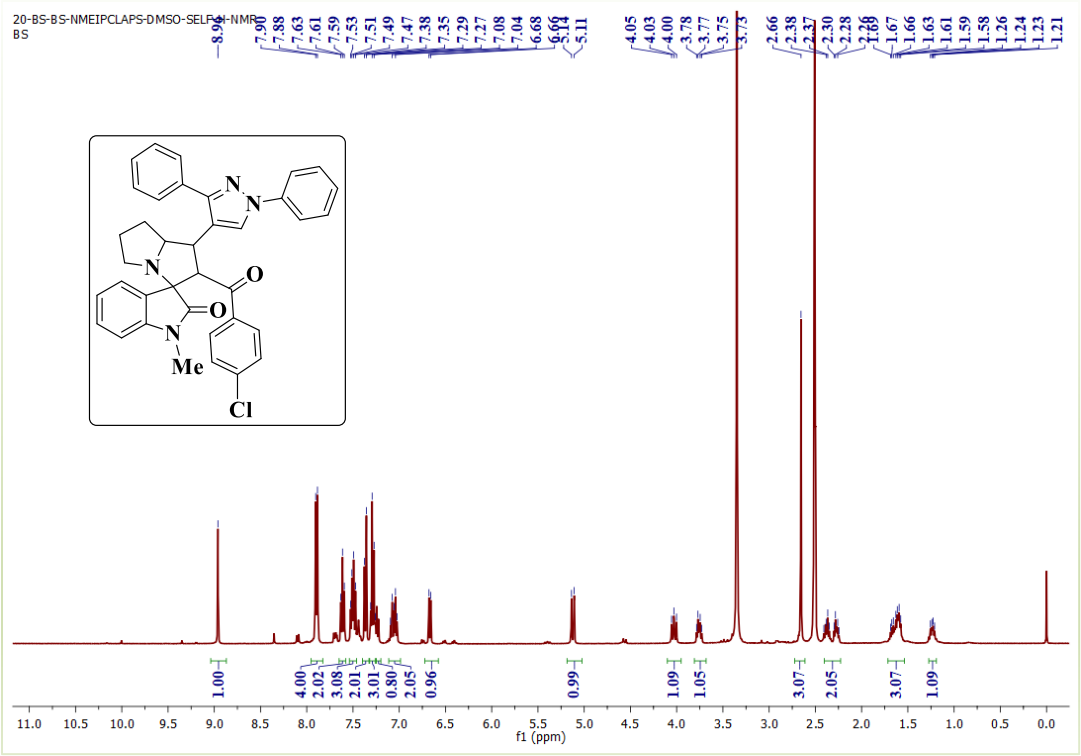
^{13}C NMR Spectrum of the compound 4i



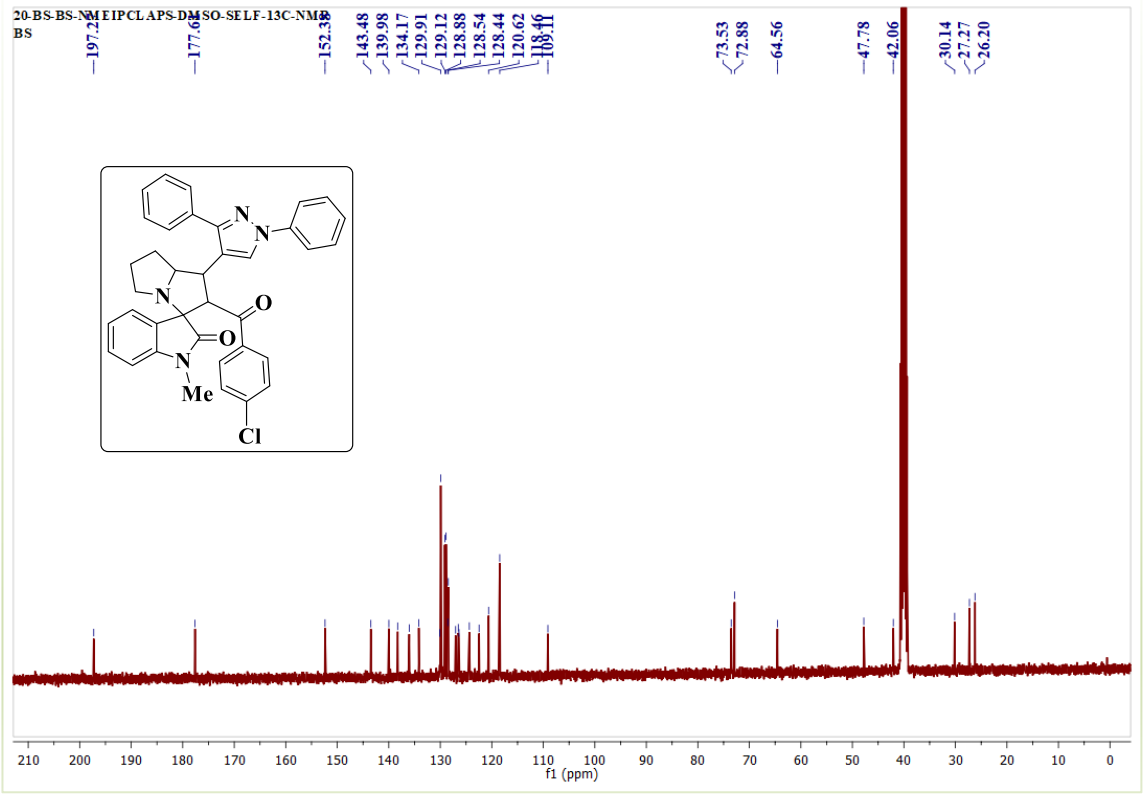
Mass spectrum of the compound 4i



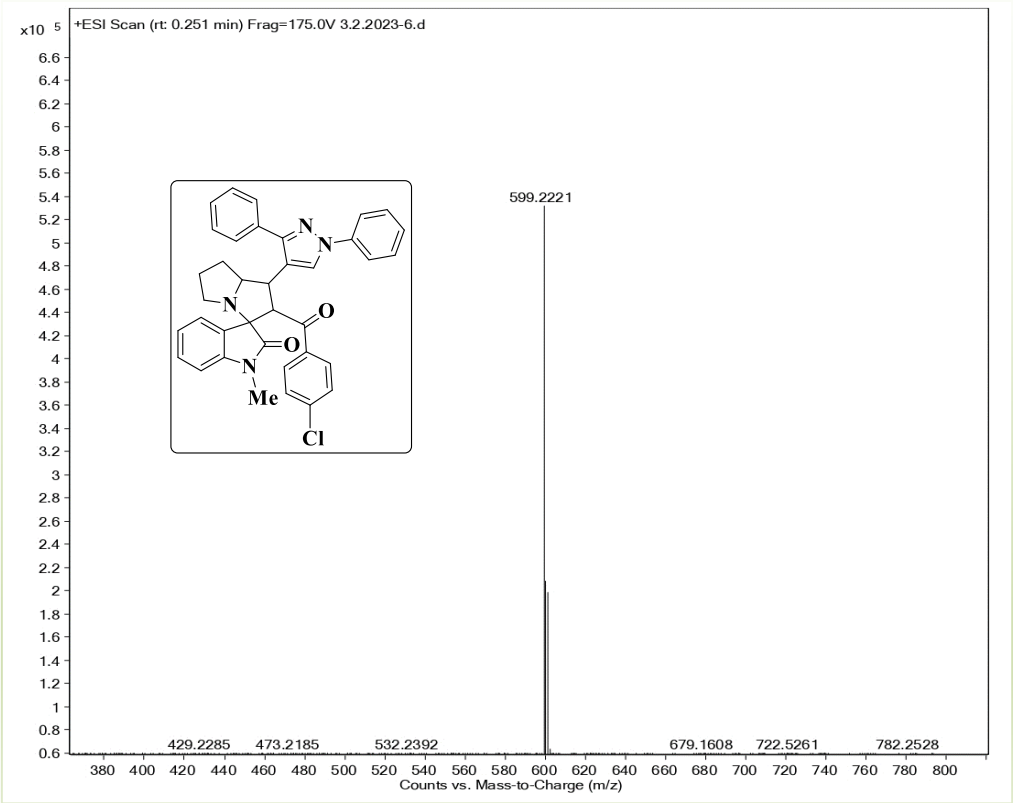
FT-IR Spectrum of the compound 4j



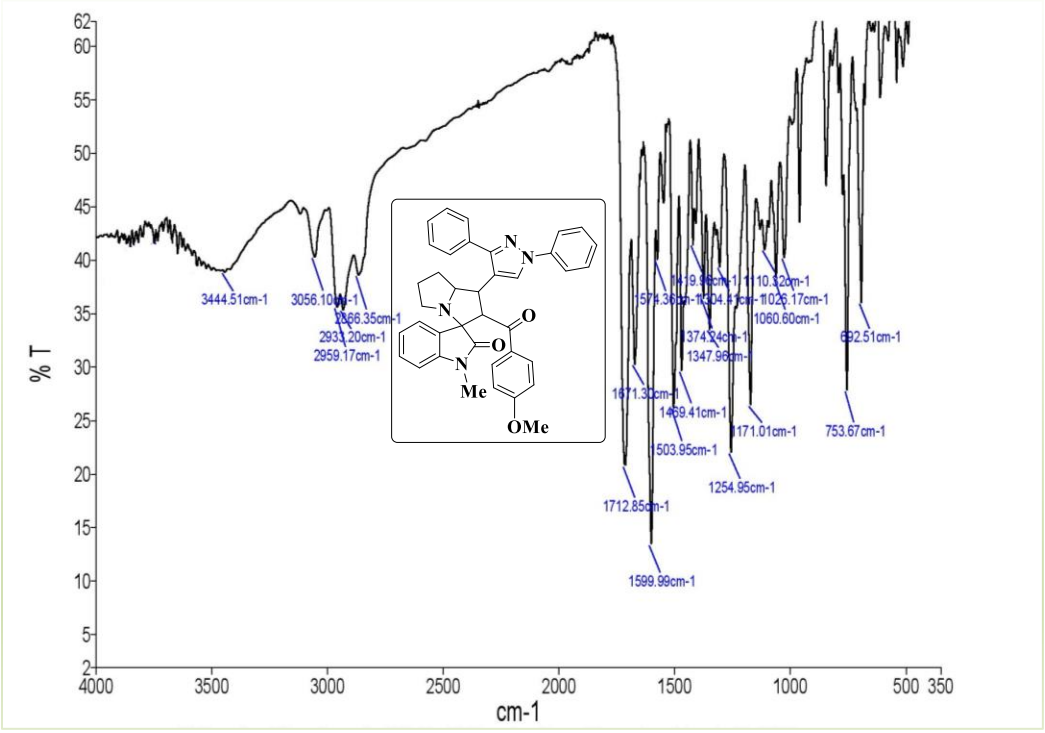
^{1}H NMR Spectrum of the compound 4j



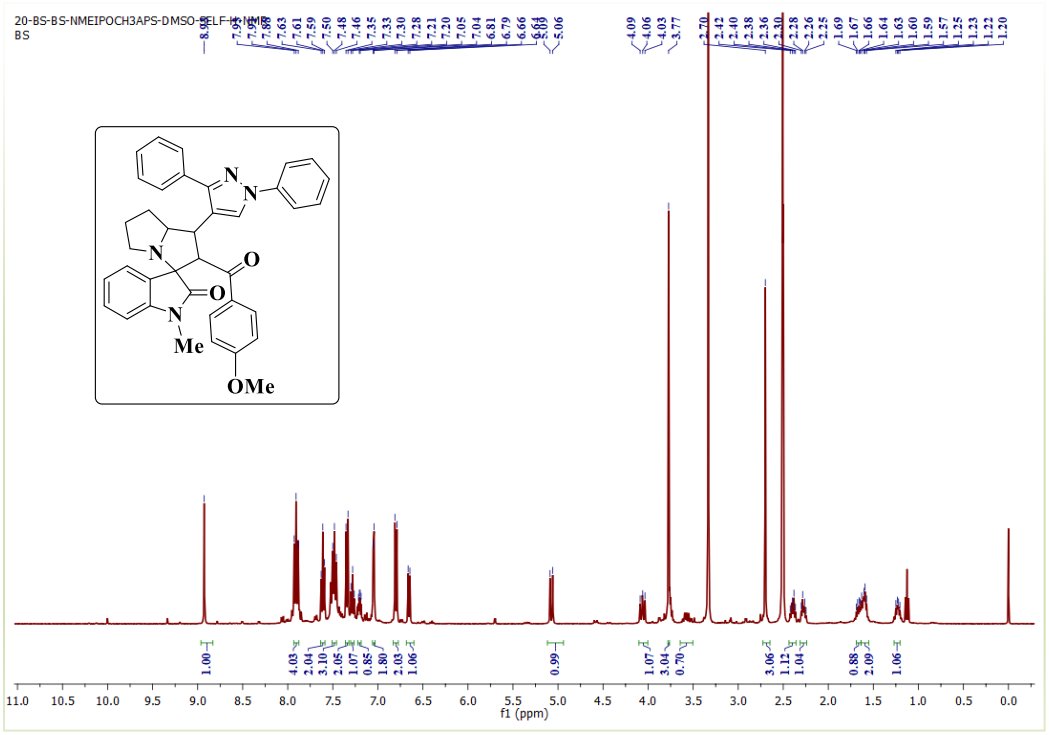
^{13}C NMR Spectrum of the compound 4j



Mass spectrum of the compound 4j



FT-IR Spectrum of the compound 4k



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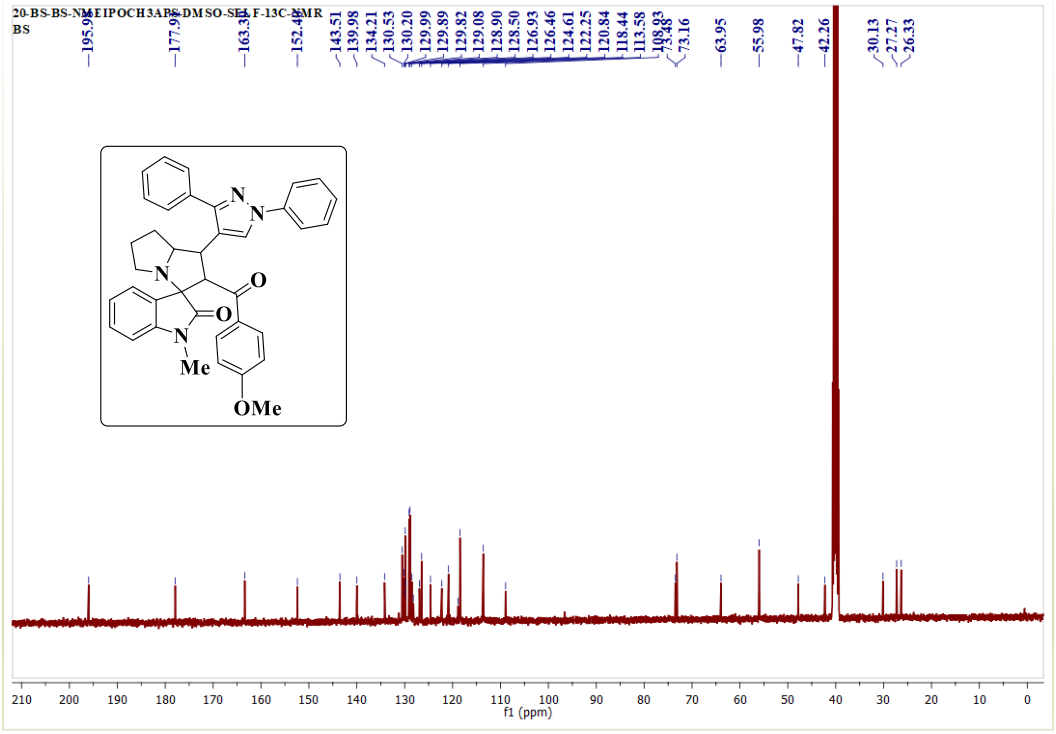
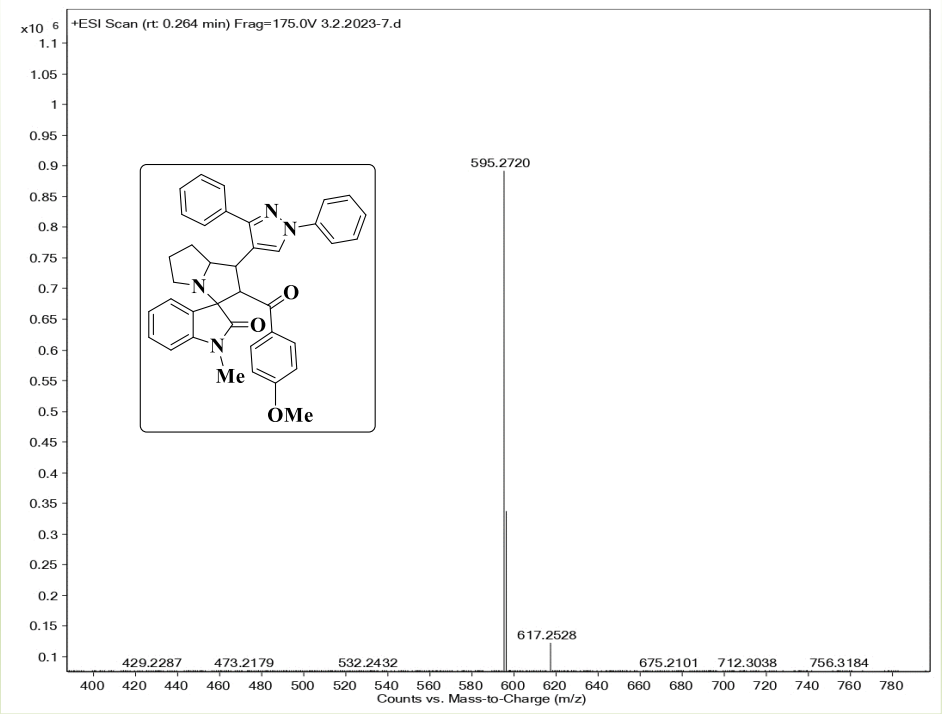
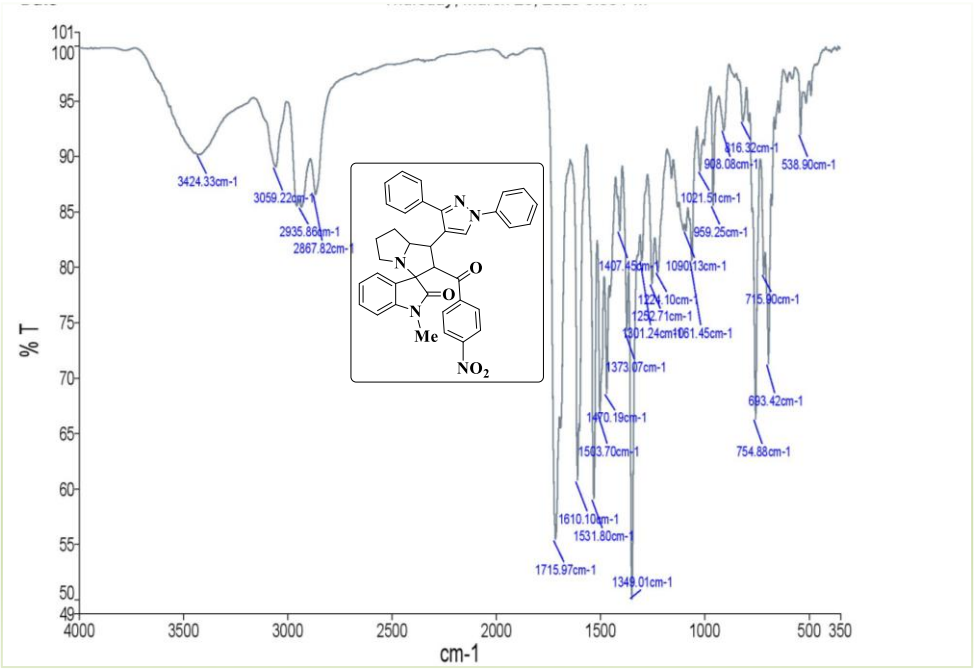


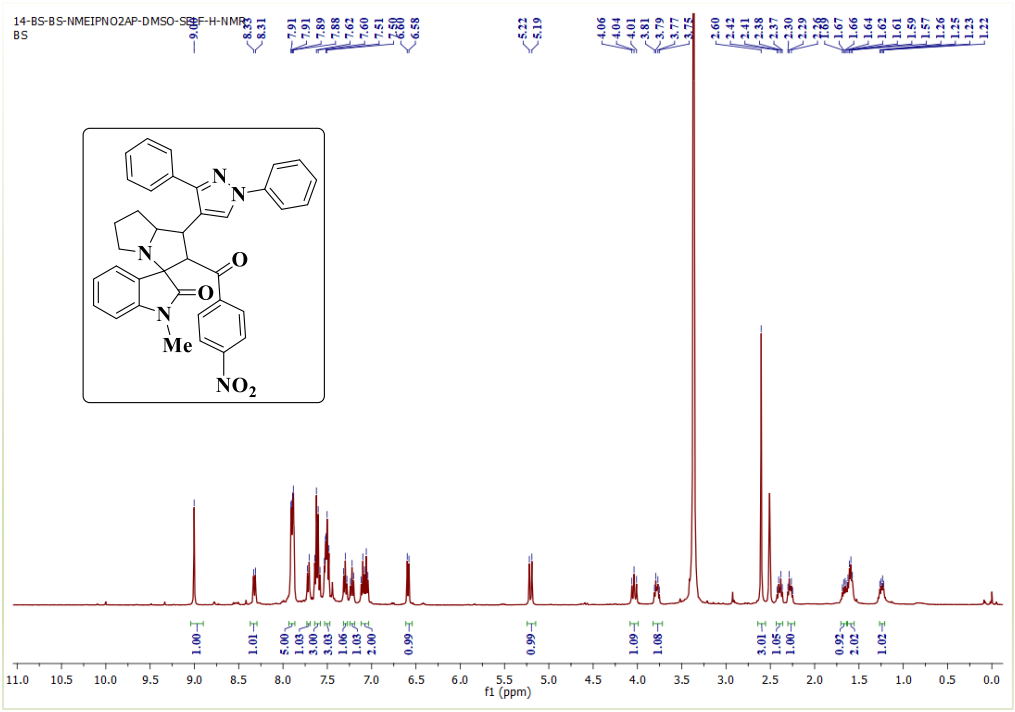
^{13}C NMR Spectrum of the compound 4k



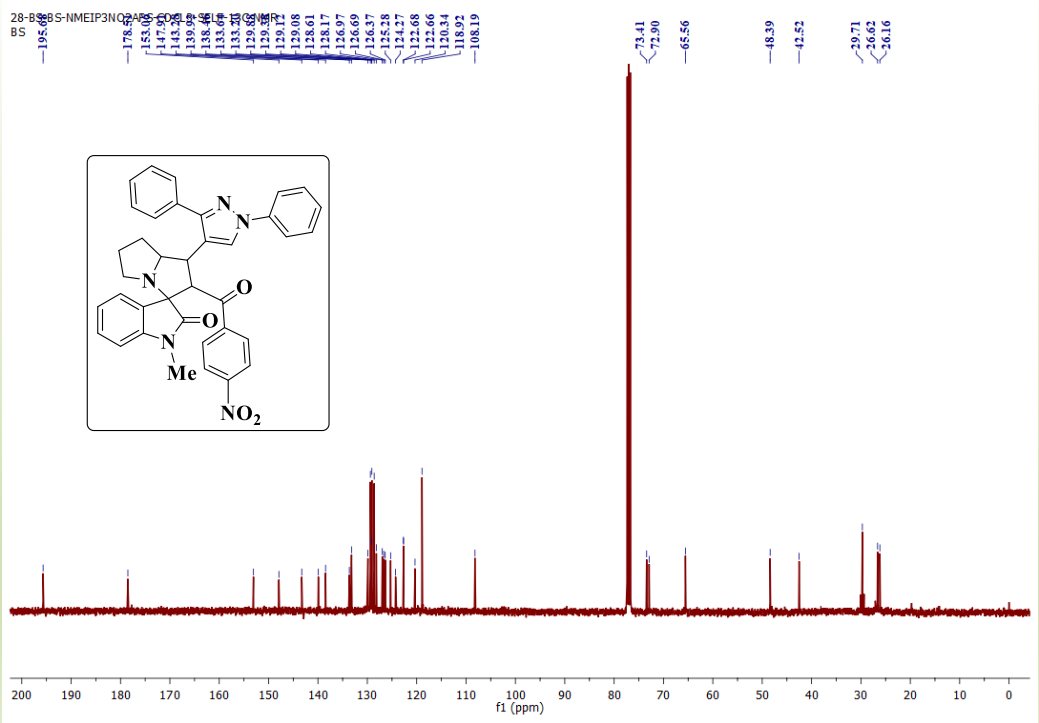
Mass spectrum of the compound 4k



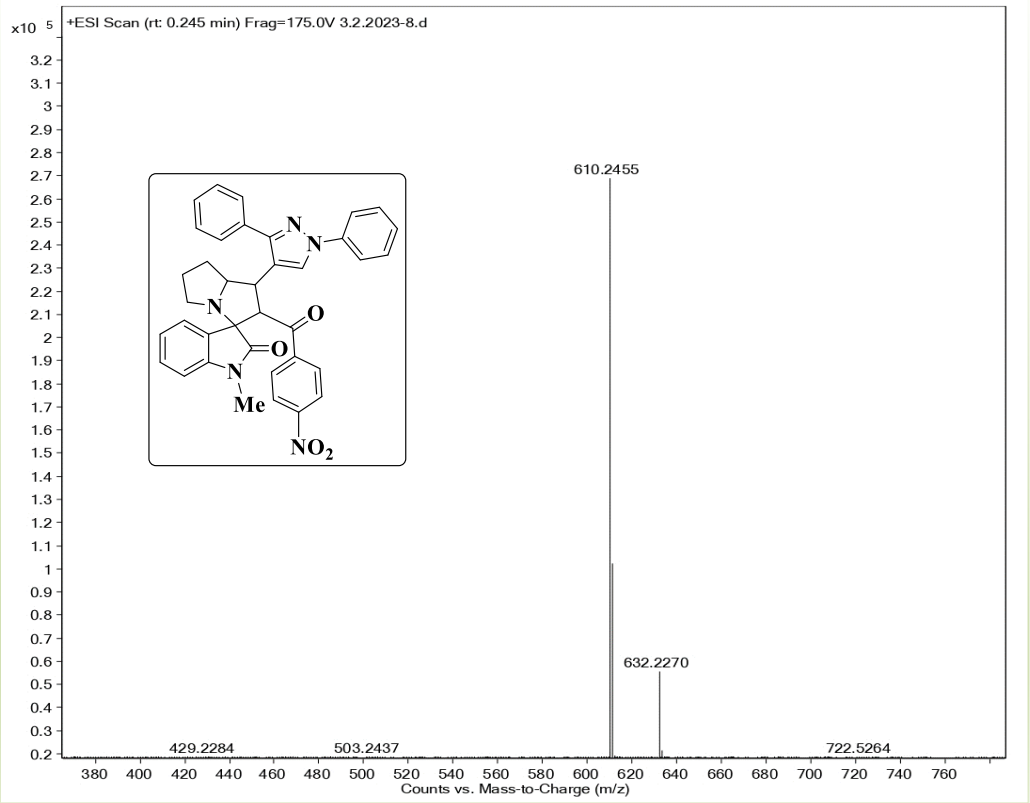
FT-IR Spectrum of the compound 4l



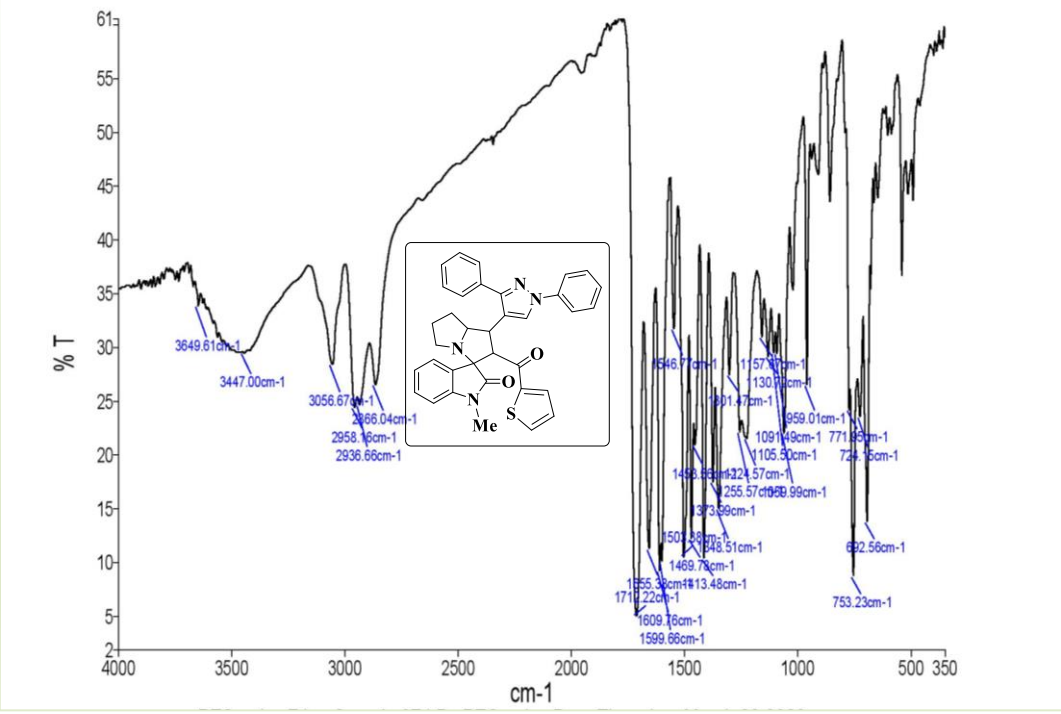
^{1}H NMR Spectrum of the compound 4l



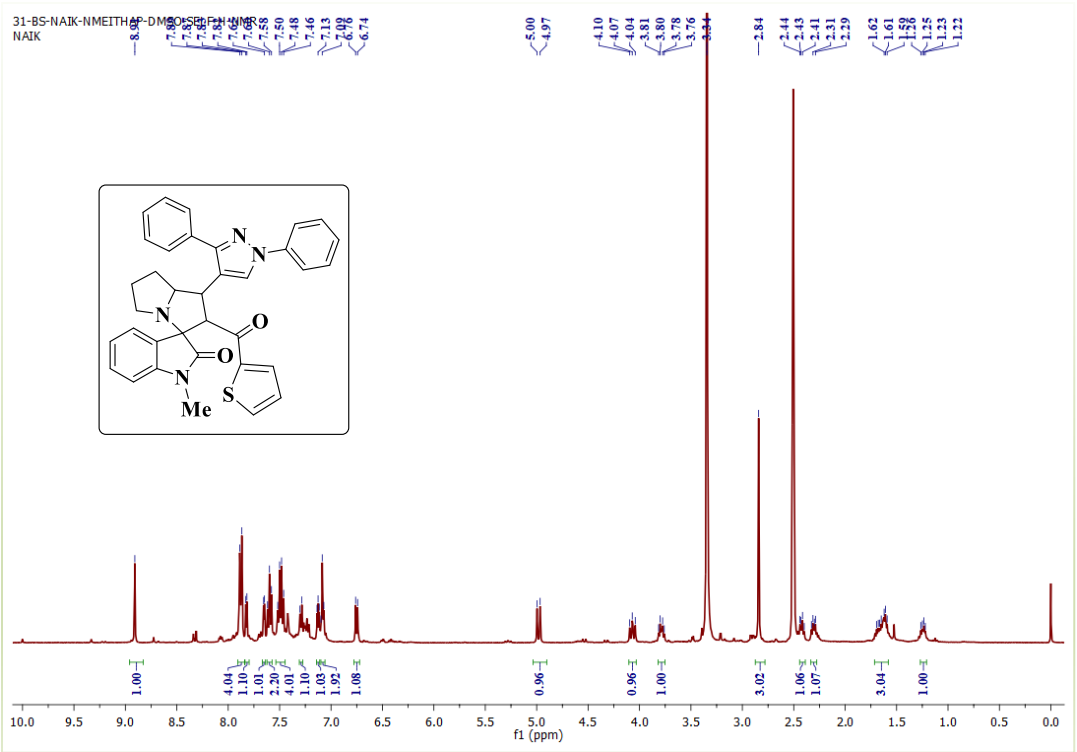
^{13}C NMR Spectrum of the compound 4l



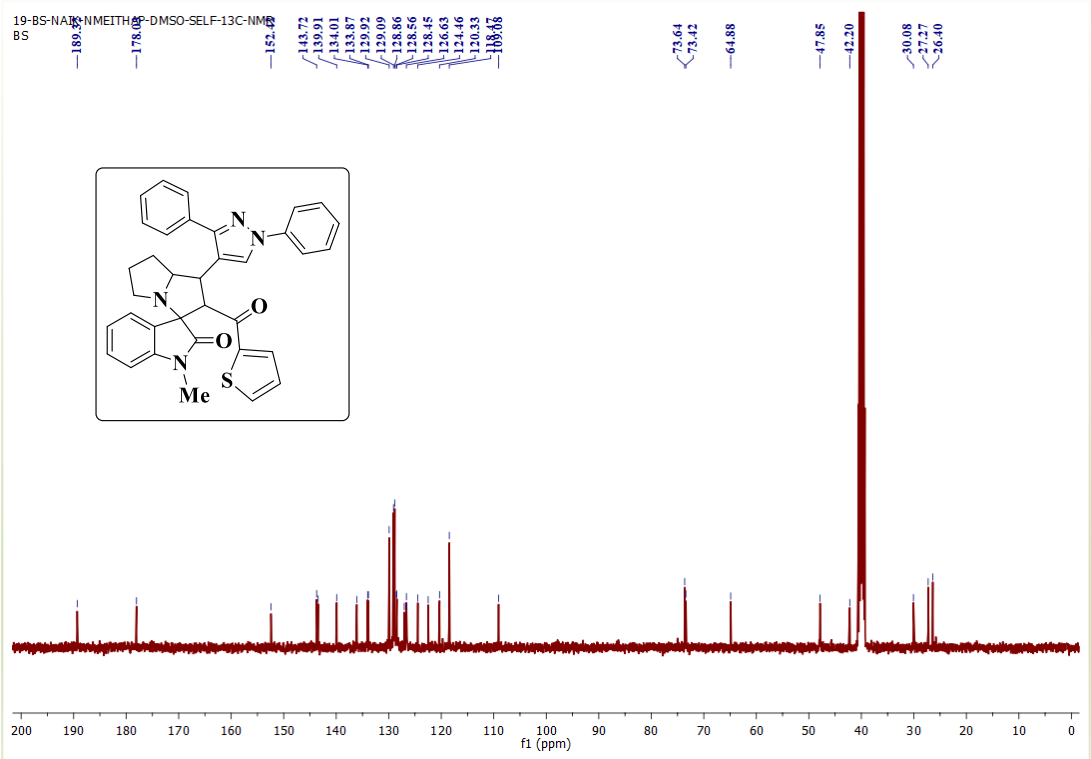
Mass spectrum of the compound 4l



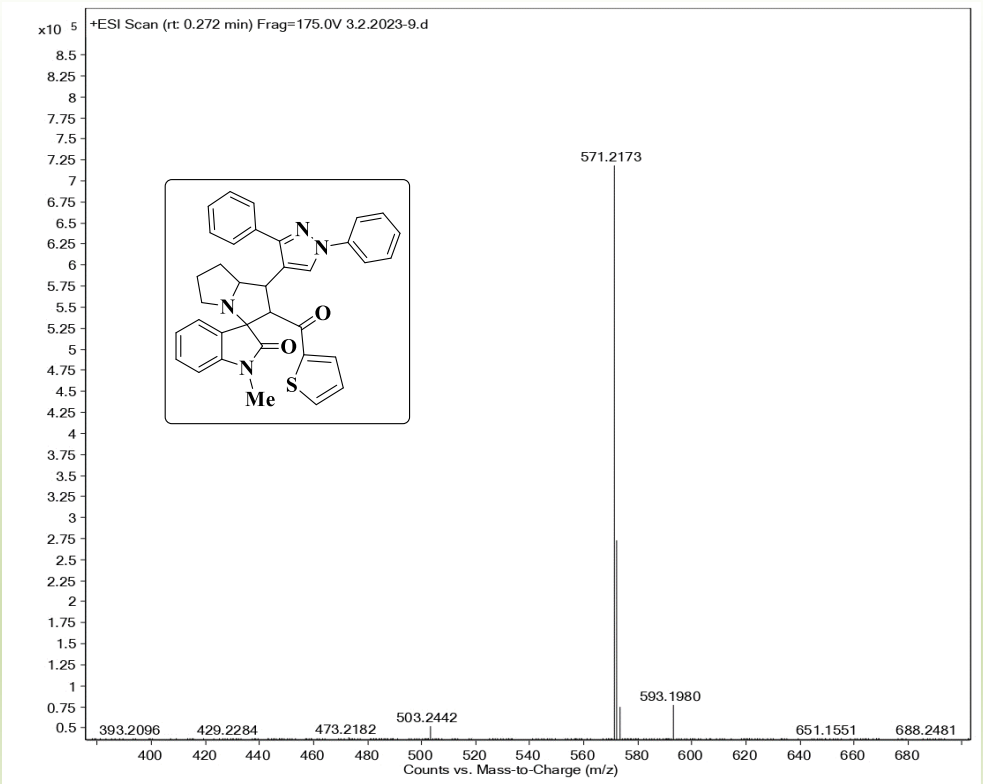
FT-IR Spectrum of the compound 4m



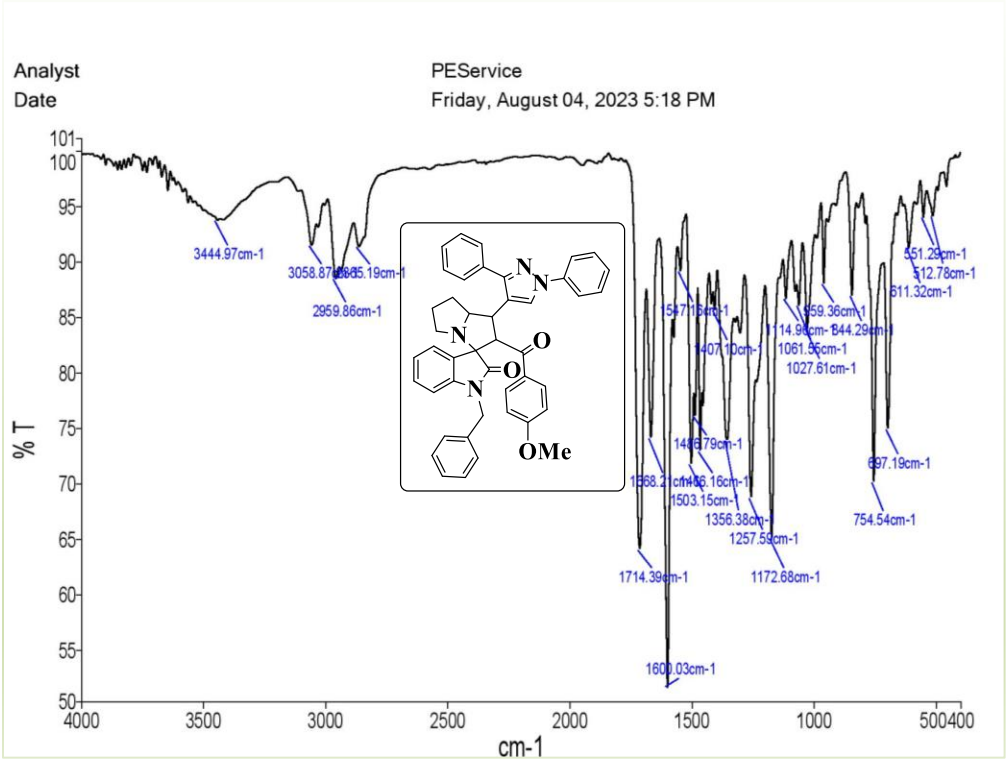
^{1}H NMR Spectrum of the compound 4m



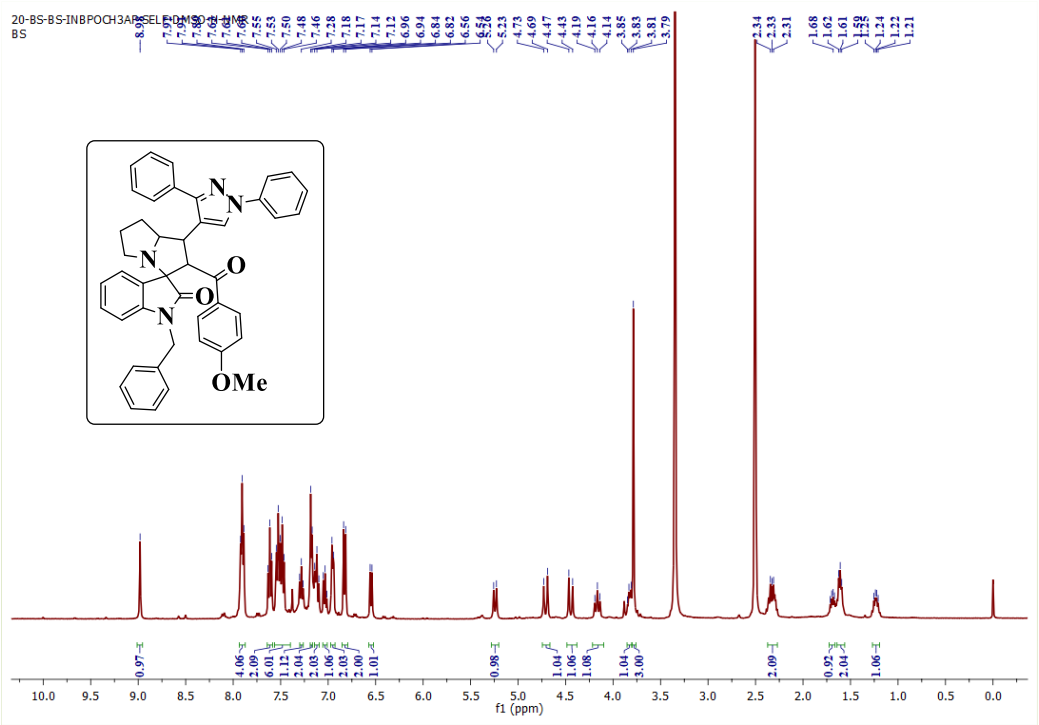
^{13}C NMR Spectrum of the compound 4m



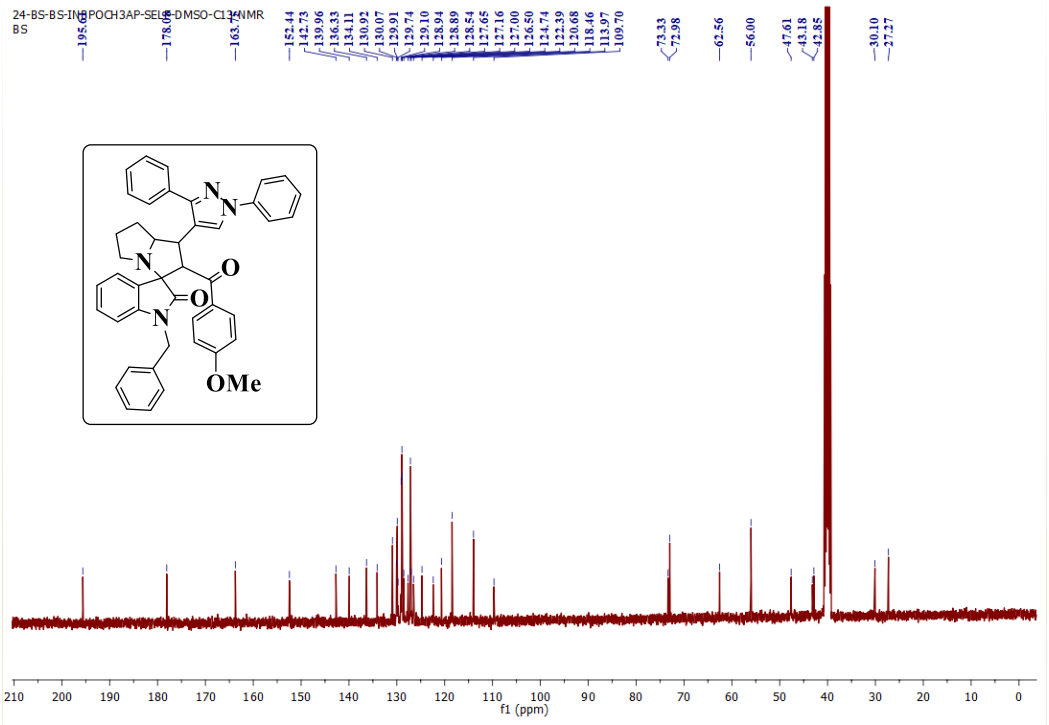
Mass spectrum of the compound 4m



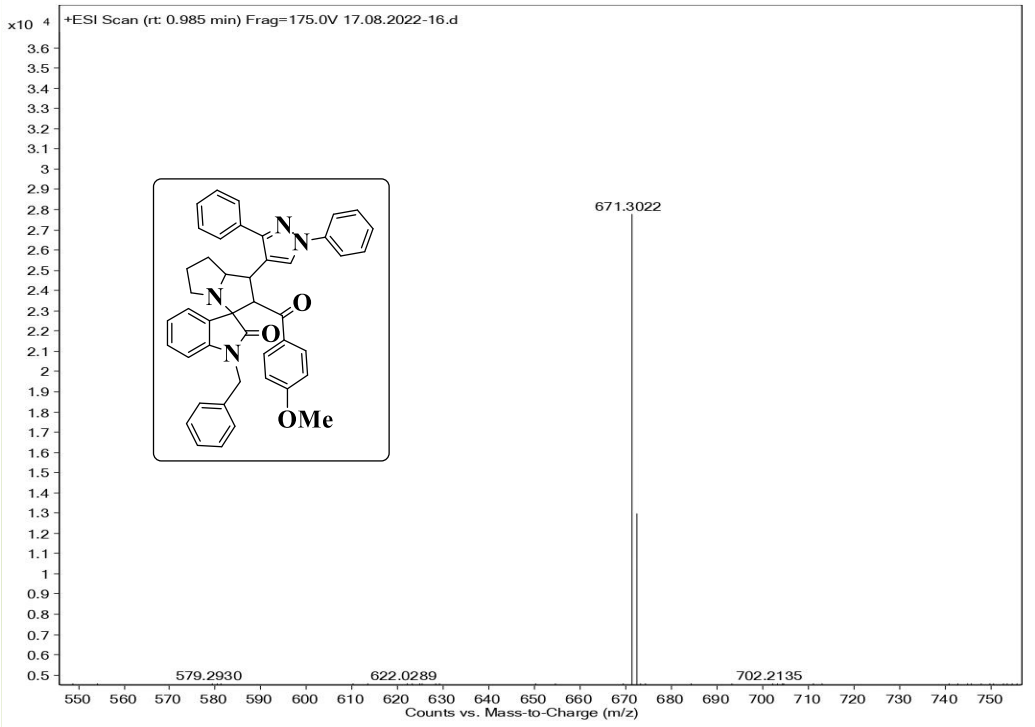
FT-IR Spectrum of the compound 4n



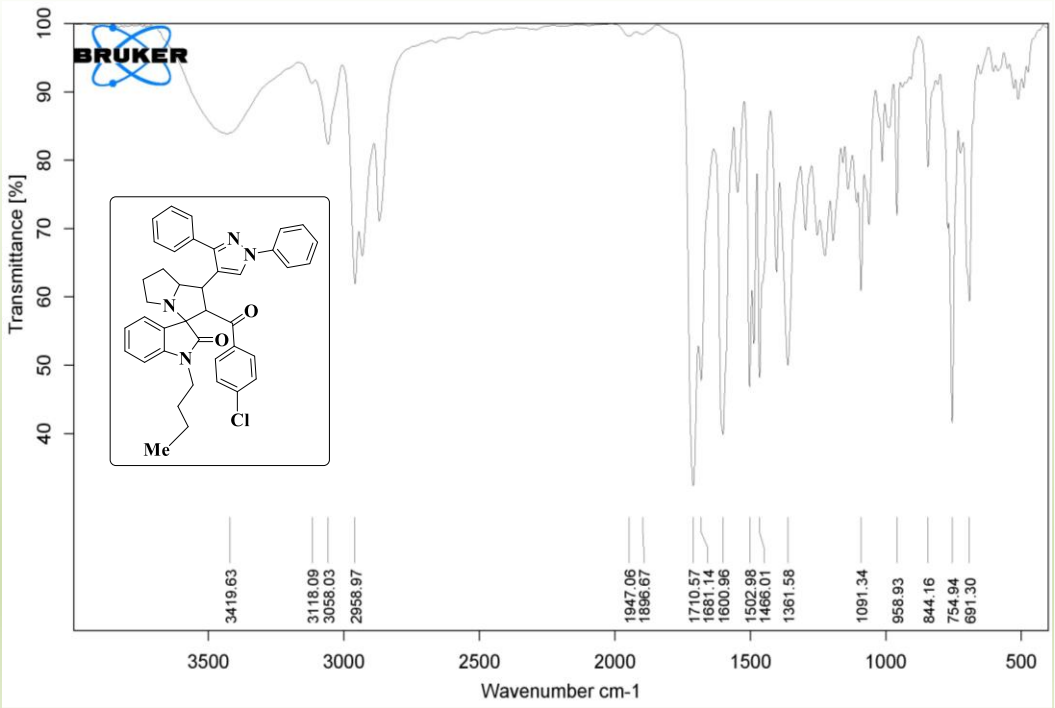
^{1}H NMR Spectrum of the compound 4n



^{13}C NMR Spectrum of the compound 4n



Mass spectrum of the compound 4n



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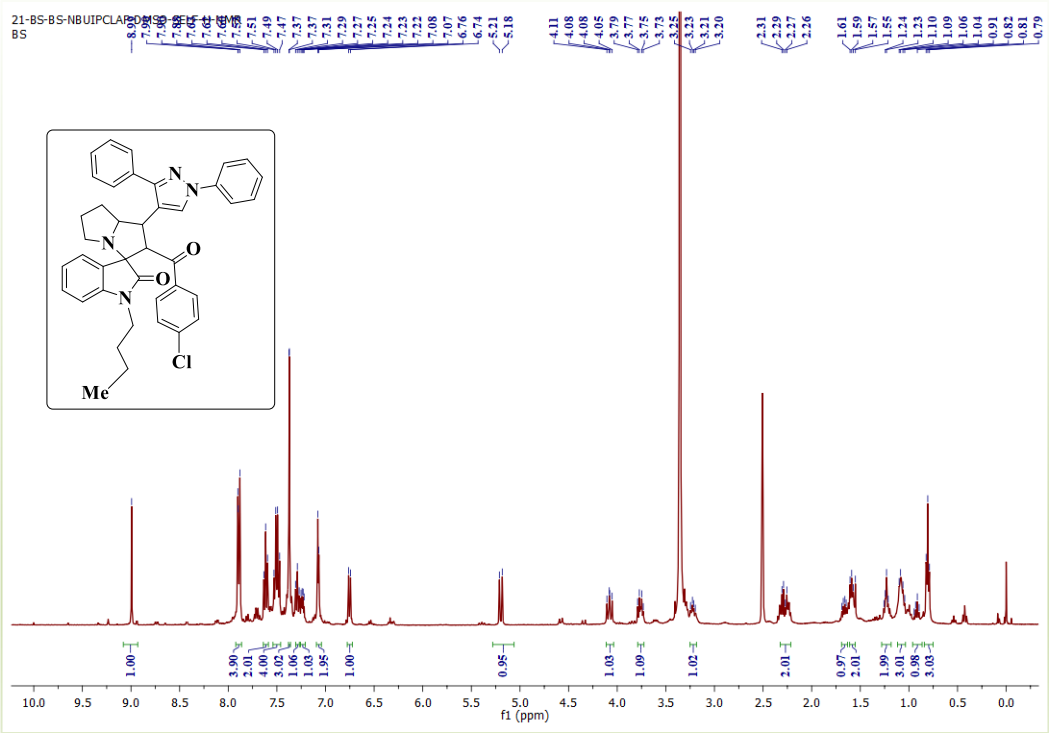
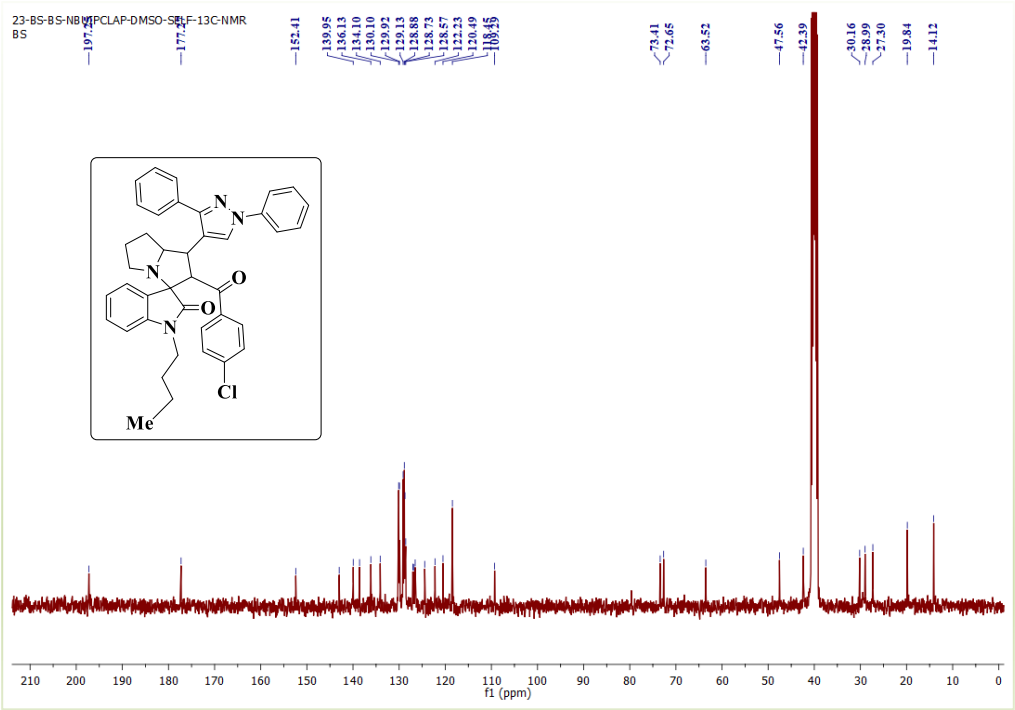
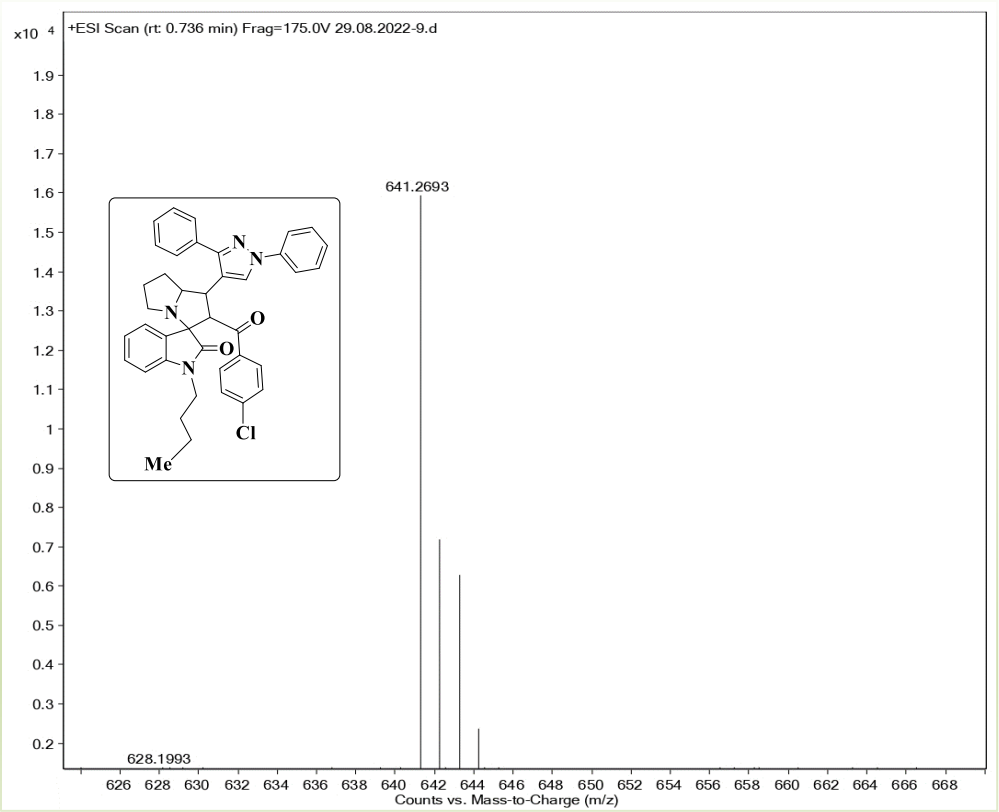


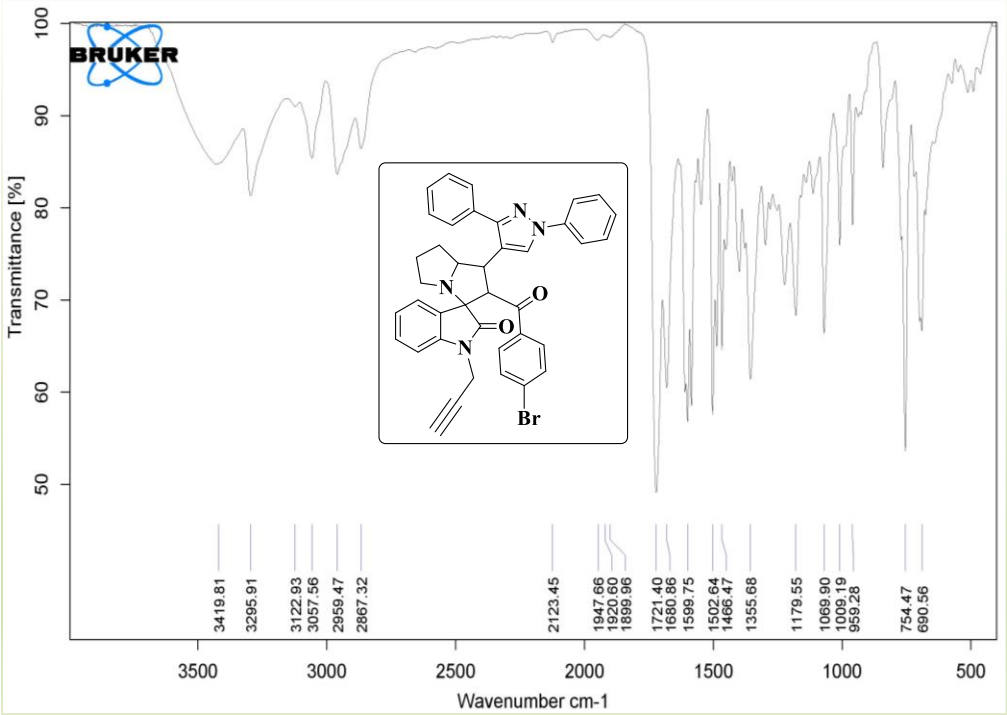
^{1}H NMR Spectrum of the compound 4o



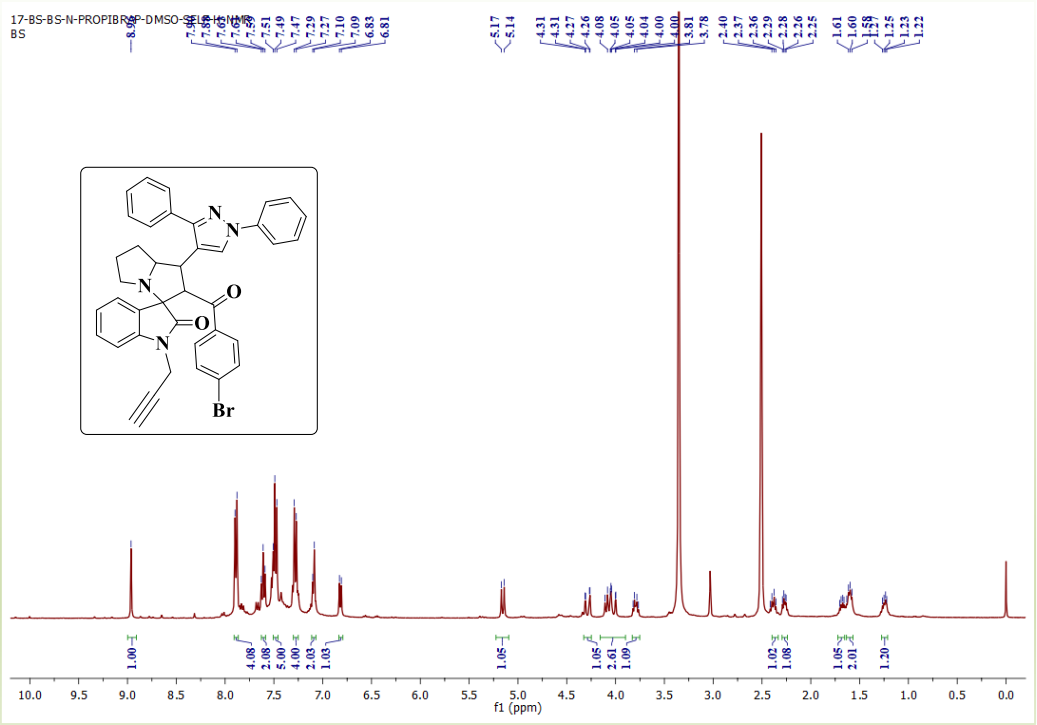
^{13}C NMR Spectrum of the compound 4o



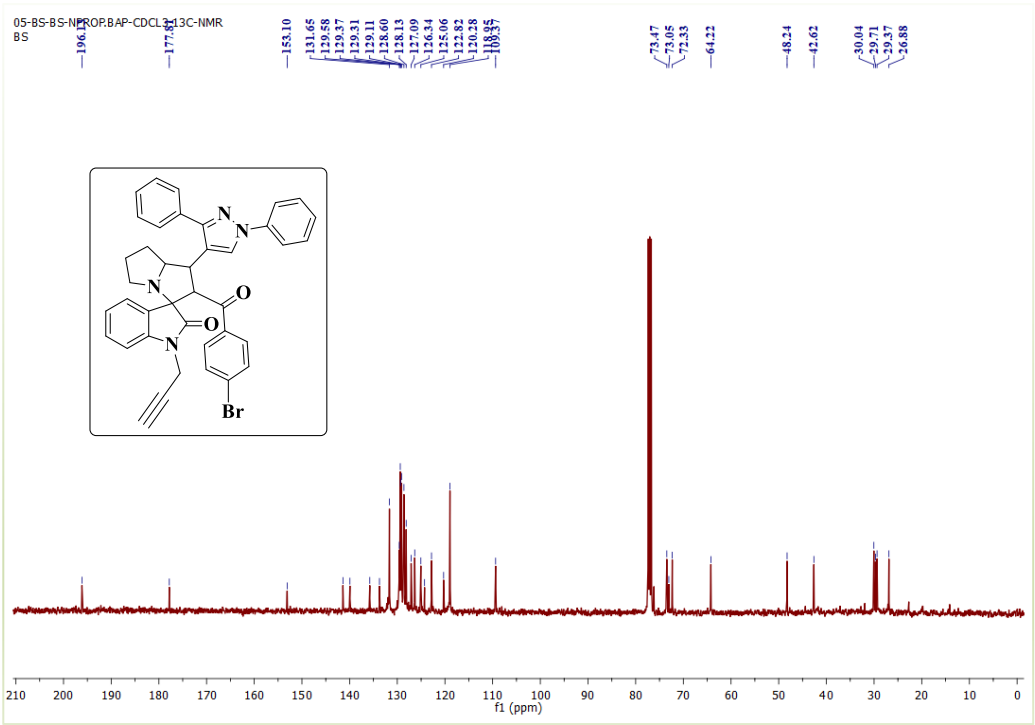
Mass spectrum of the compound 4o



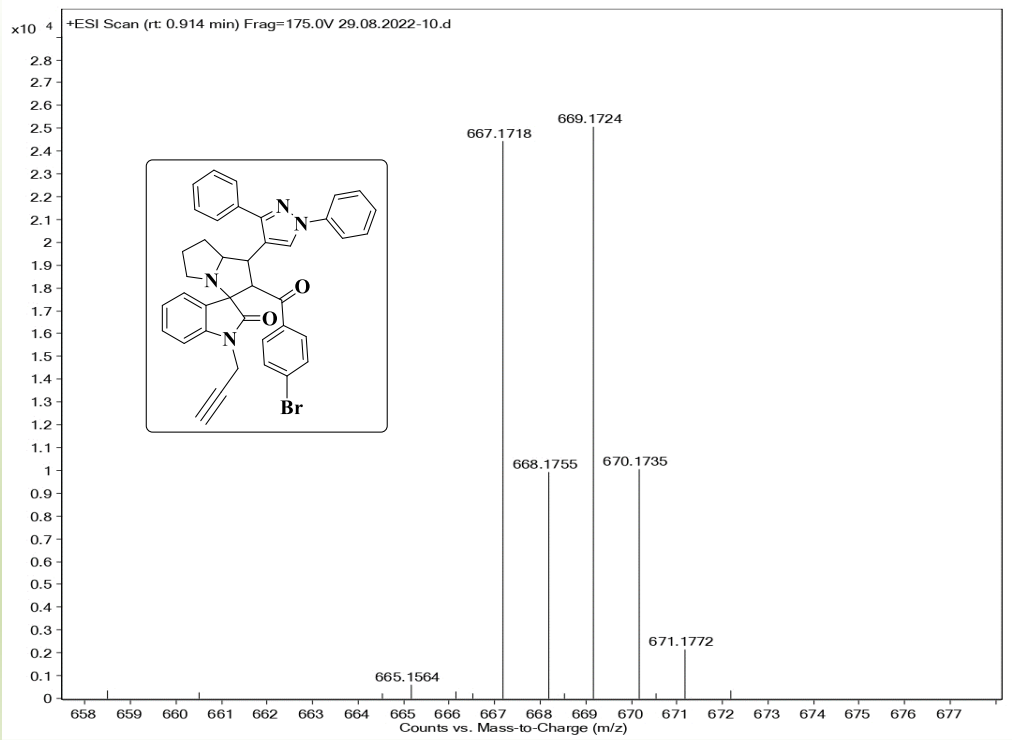
FT-IR Spectrum of the compound 4p



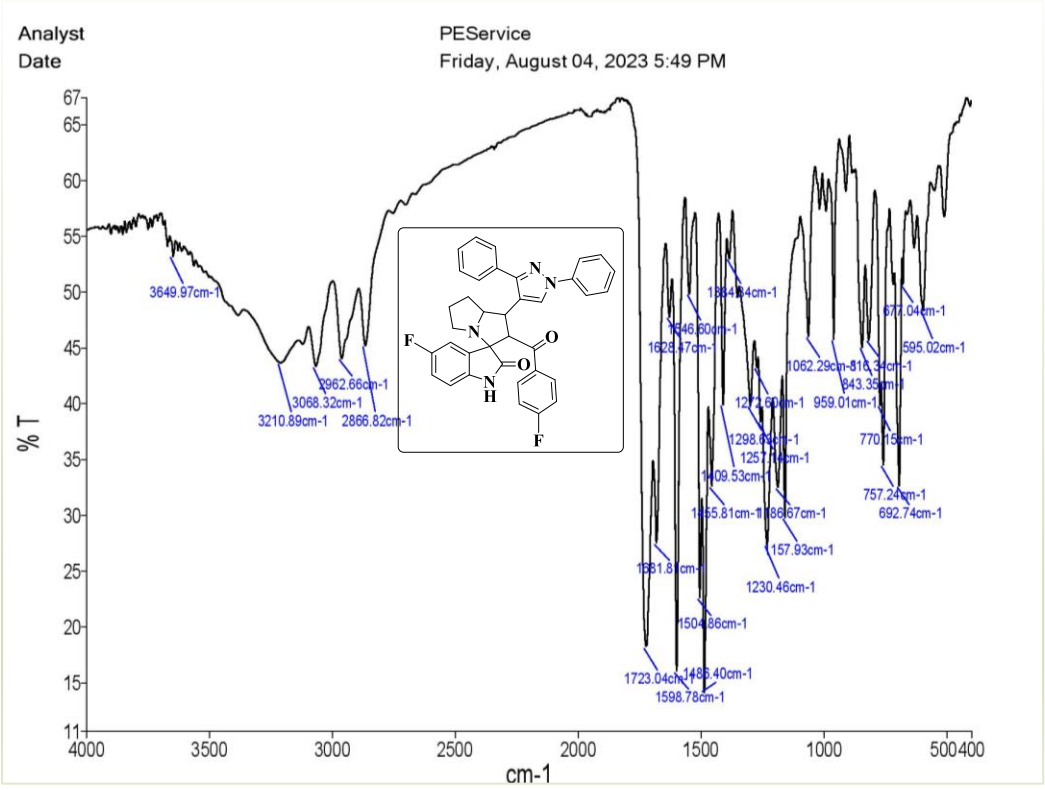
^{1}H NMR Spectrum of the compound 4p



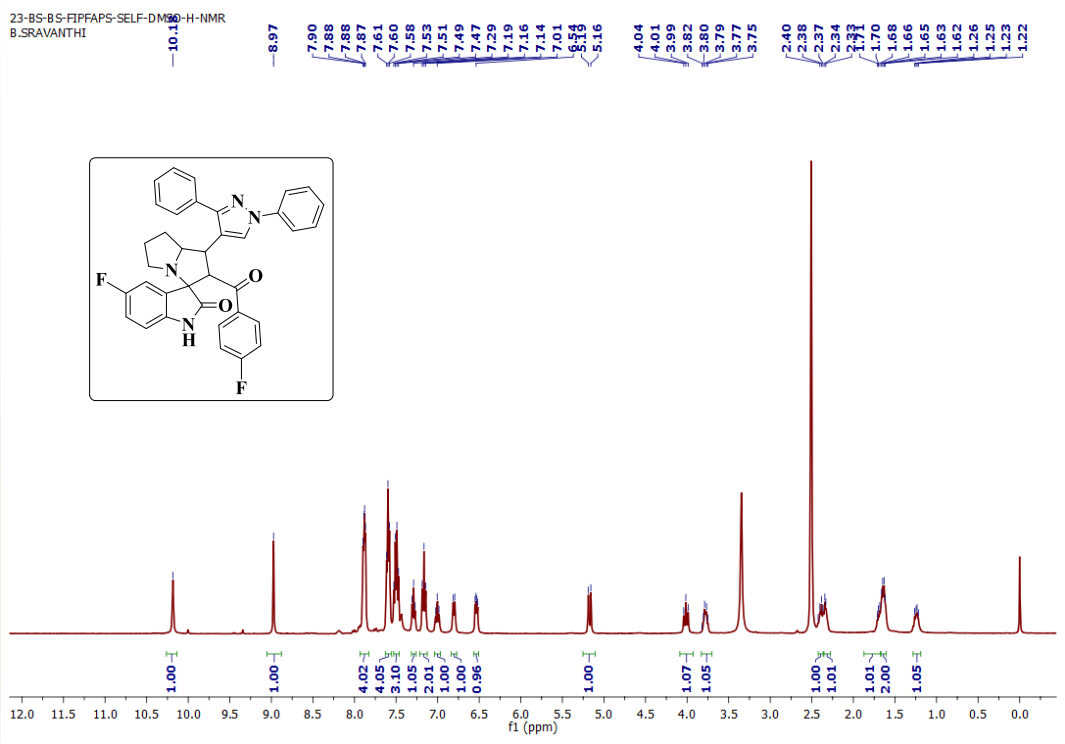
^{13}C NMR Spectrum of the compound 4p



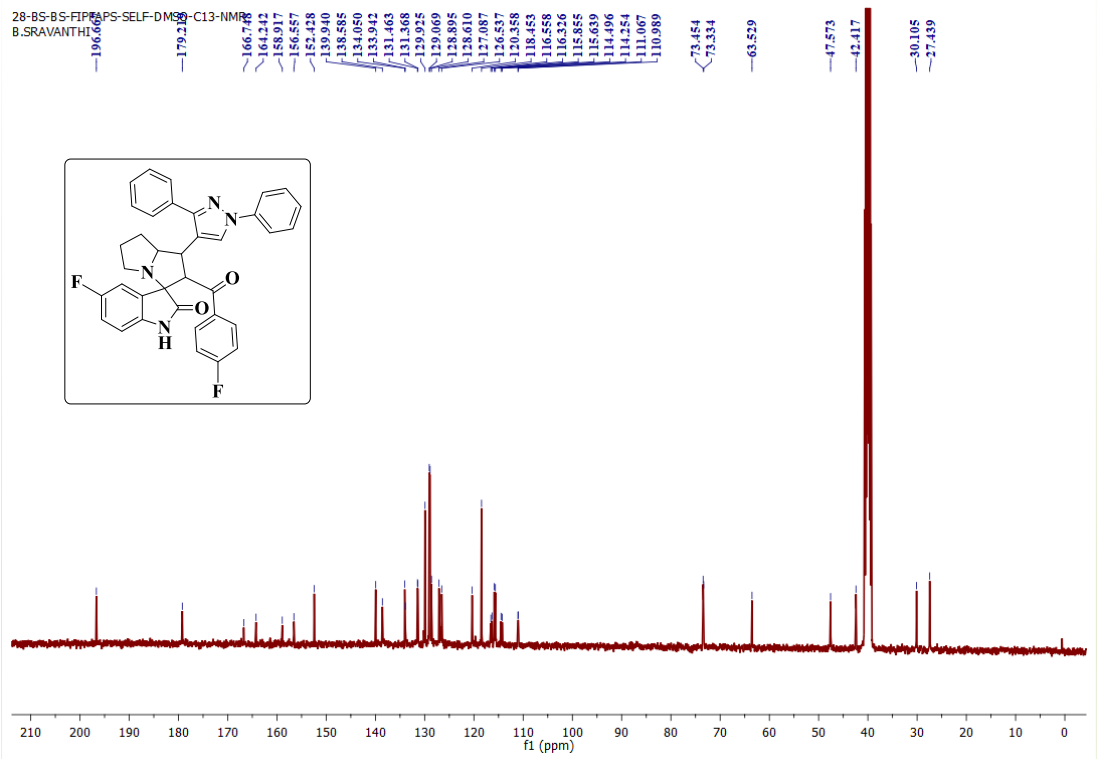
Mass spectrum of the compound 4p



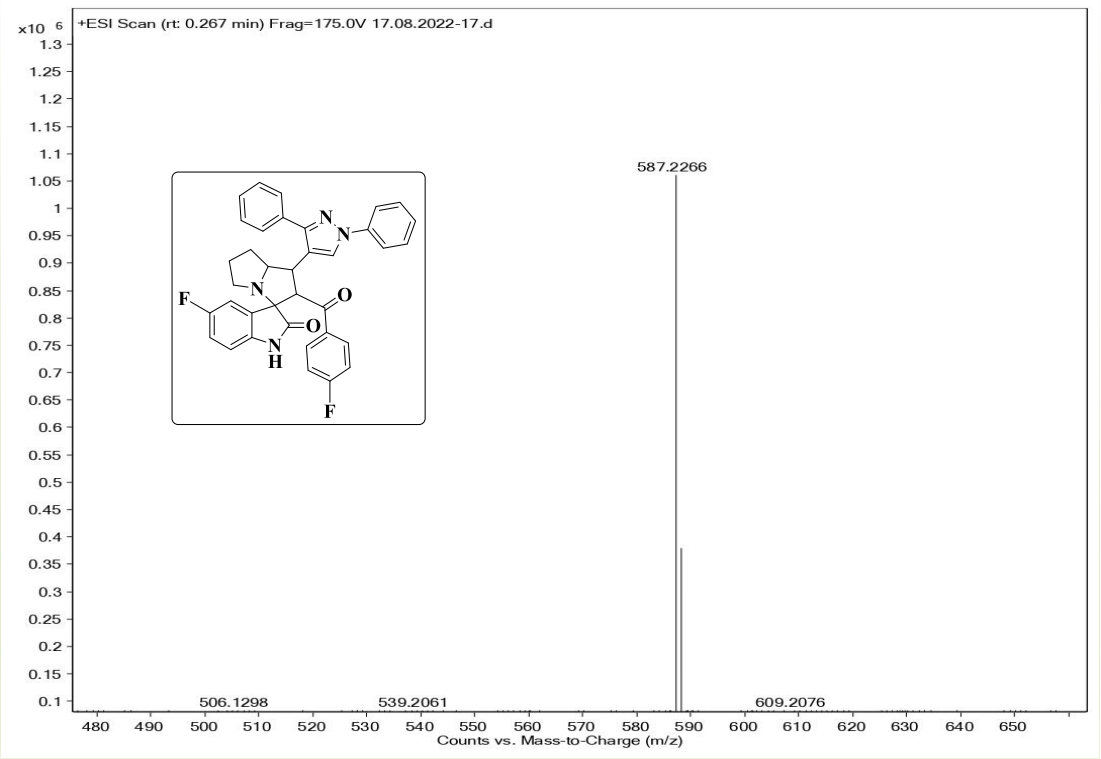
FT-IR Spectrum of the compound 4q



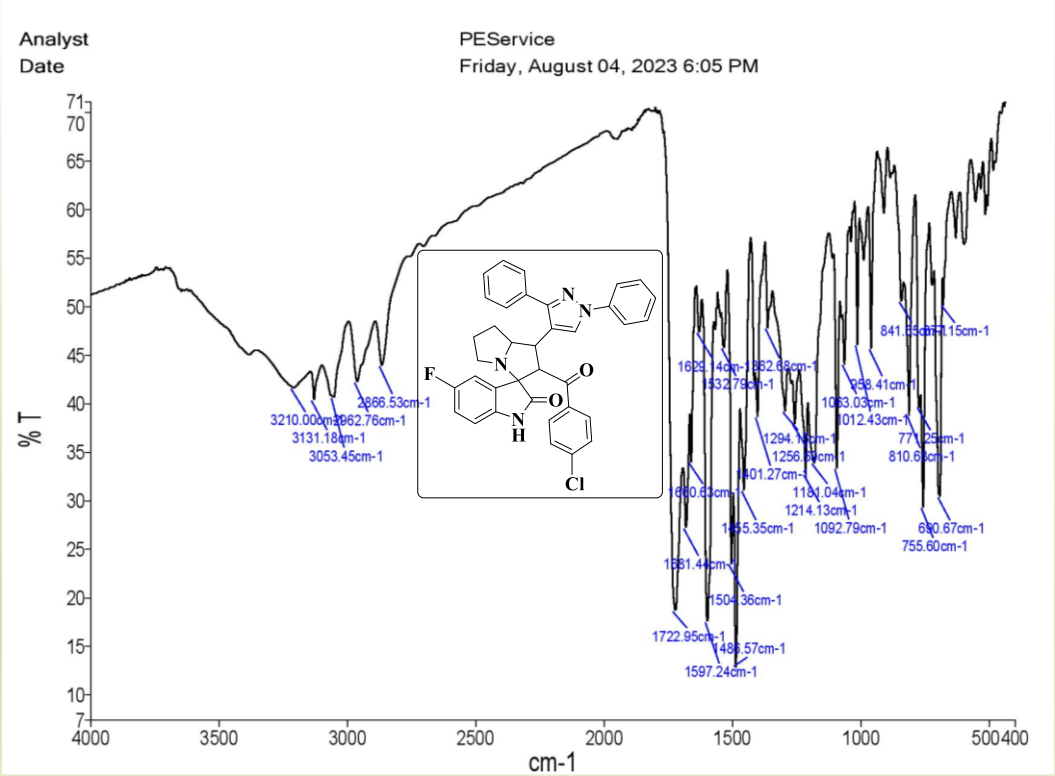
^{1}H NMR Spectrum of the compound 4q



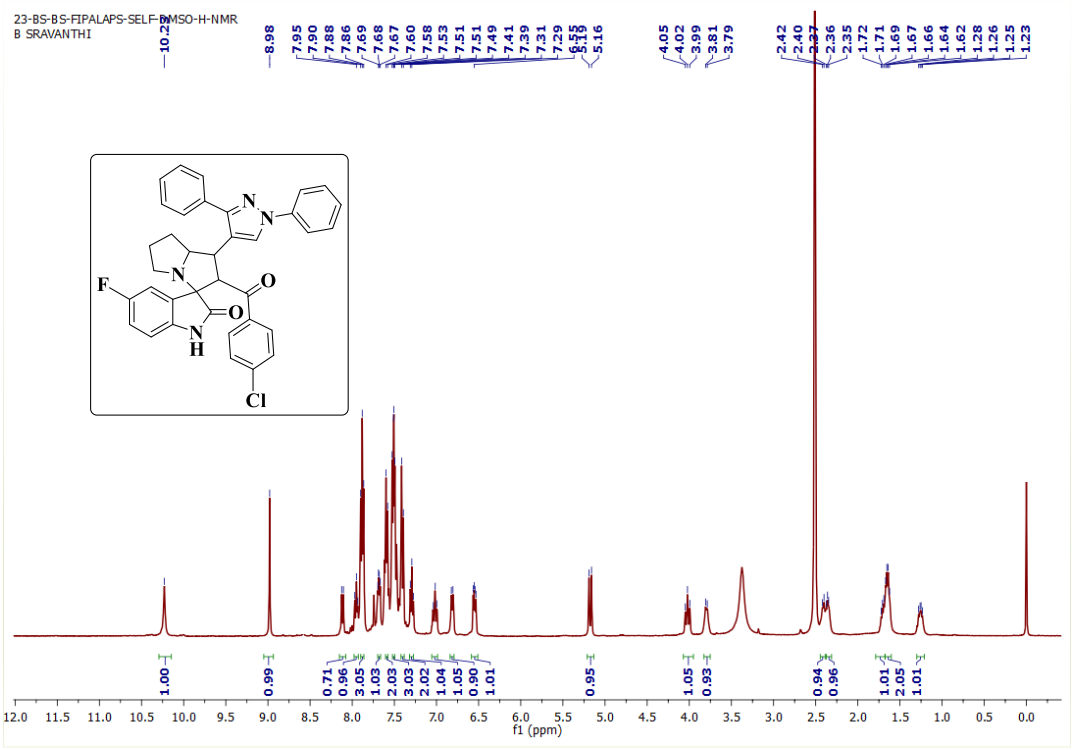
^{13}C NMR Spectrum of the compound 4q



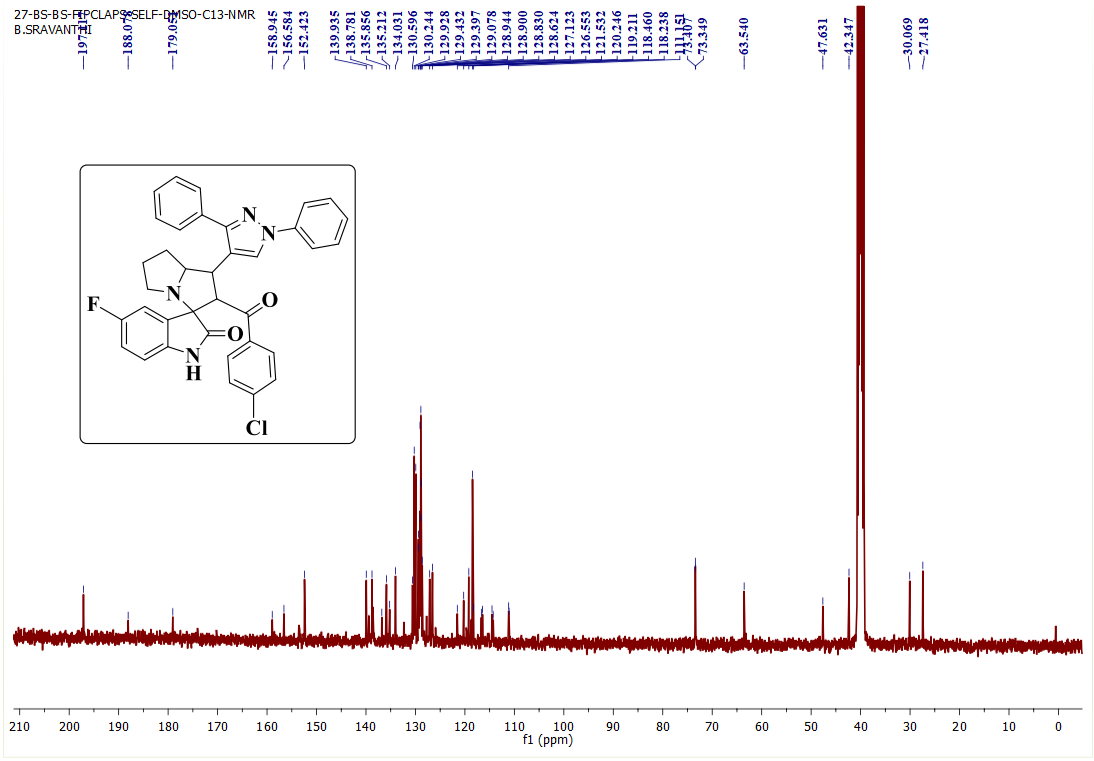
Mass spectrum of the compound 4q



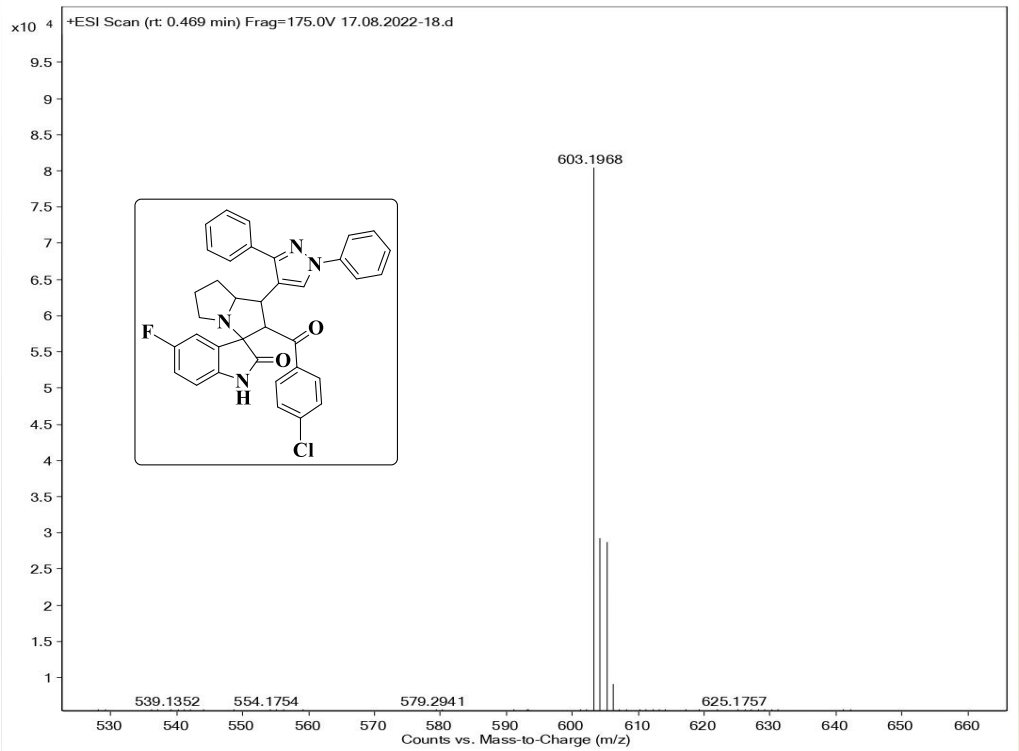
FT-IR Spectrum of the compound 4r



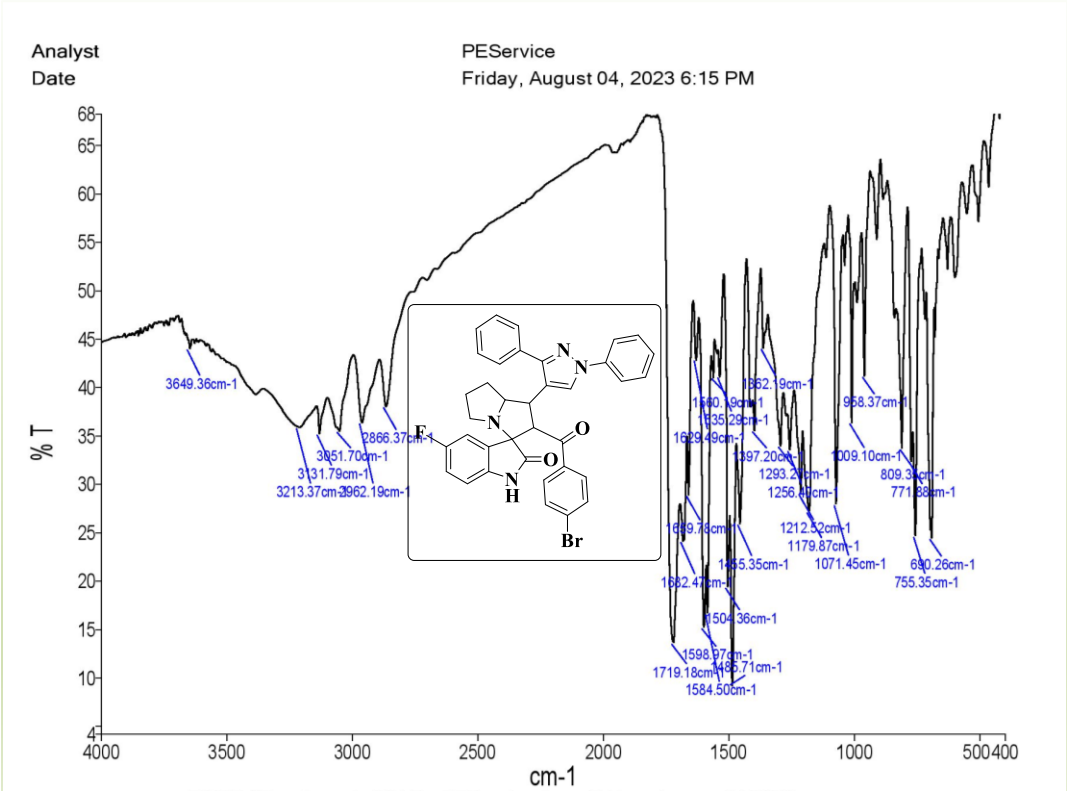
^{1}H NMR Spectrum of the compound 4r



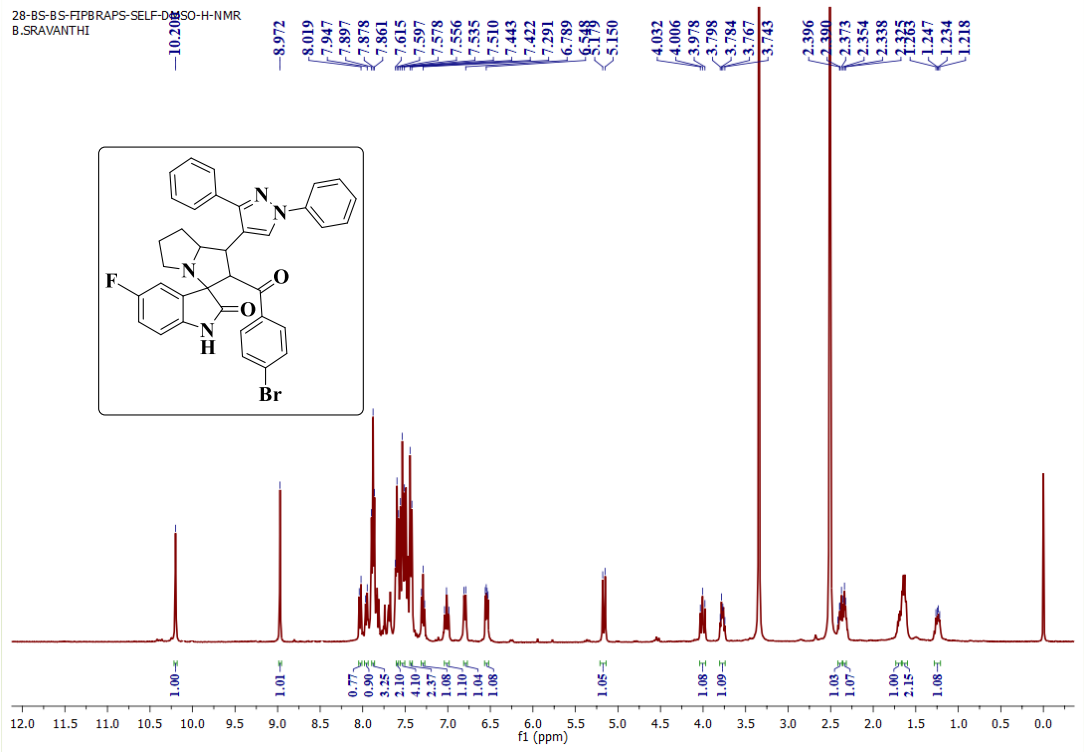
^{13}C NMR Spectrum of the compound 4r



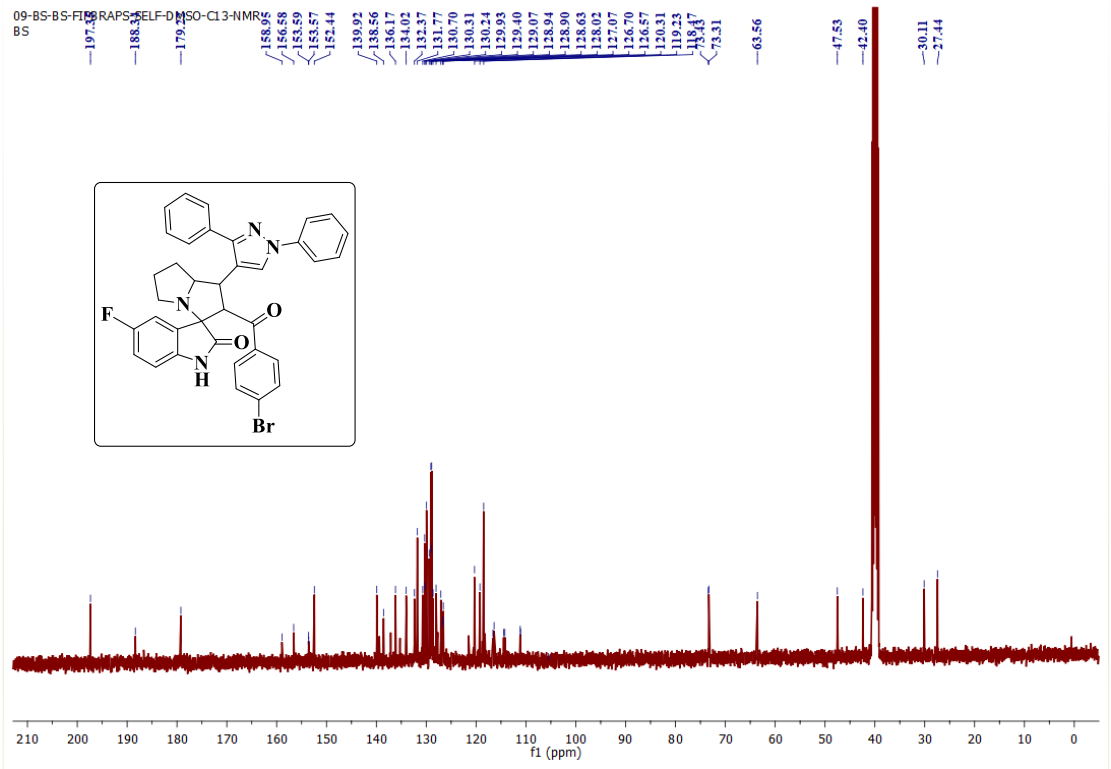
Mass spectrum of the compound 4r



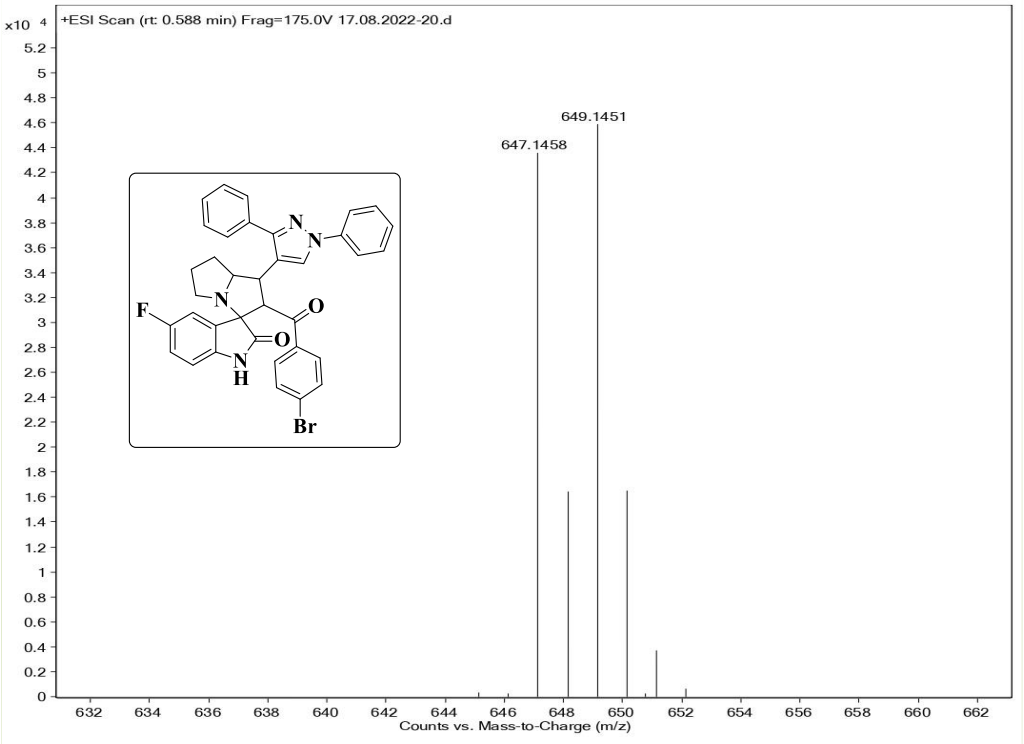
FT-IR Spectrum of the compound 4s



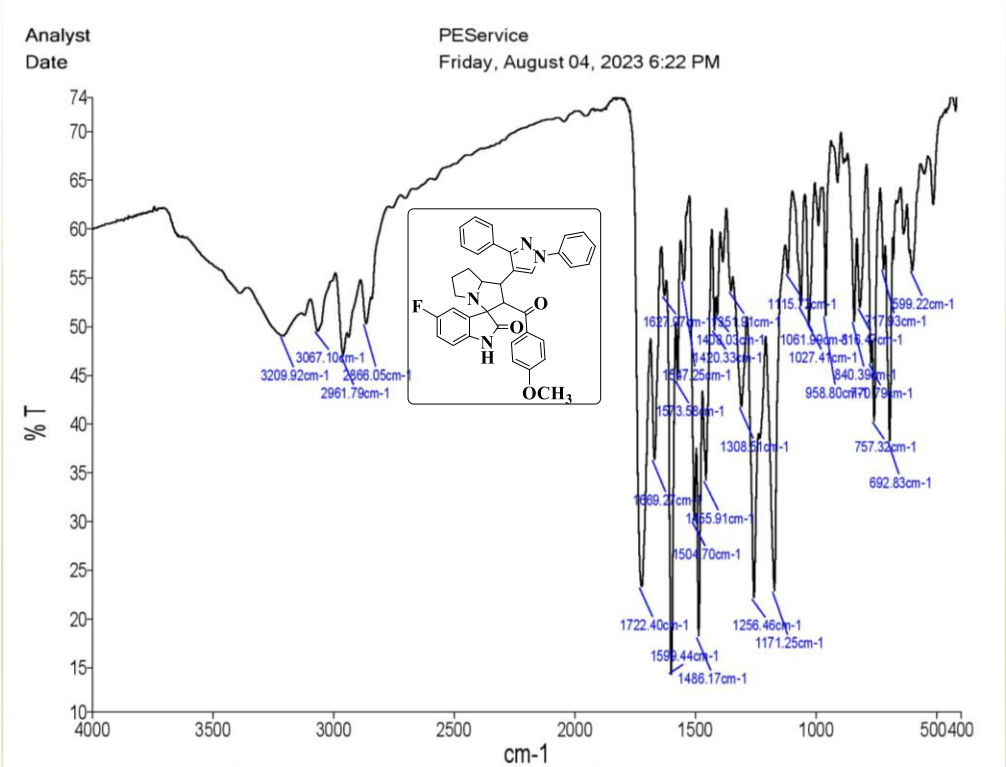
^{1}H NMR Spectrum of the compound 4s



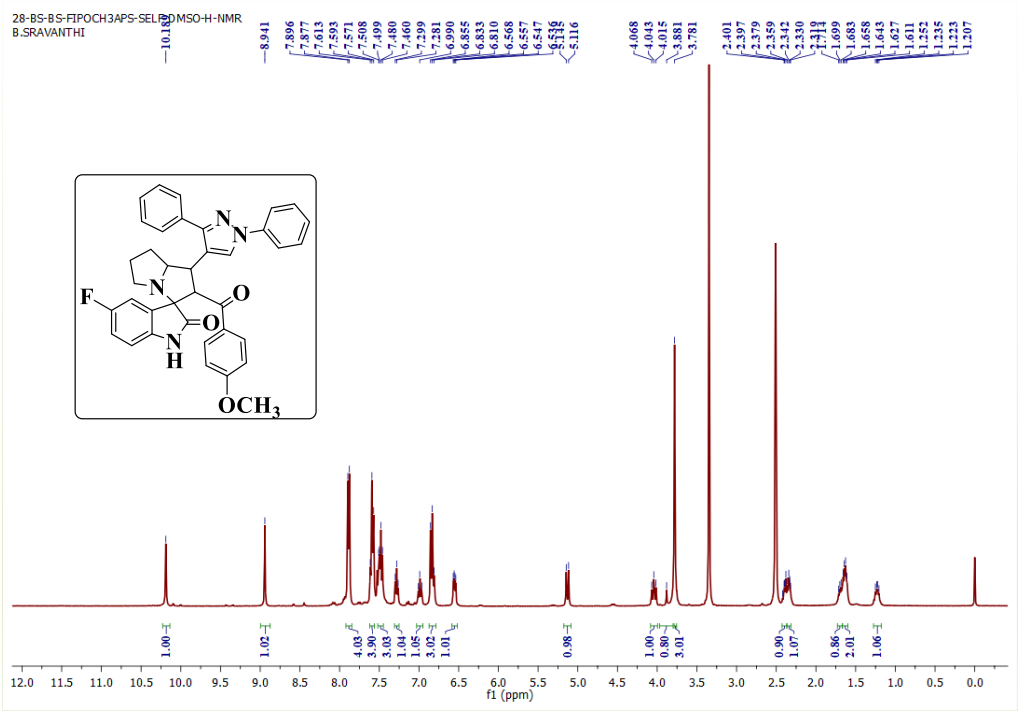
^{13}C NMR Spectrum of the compound 4s



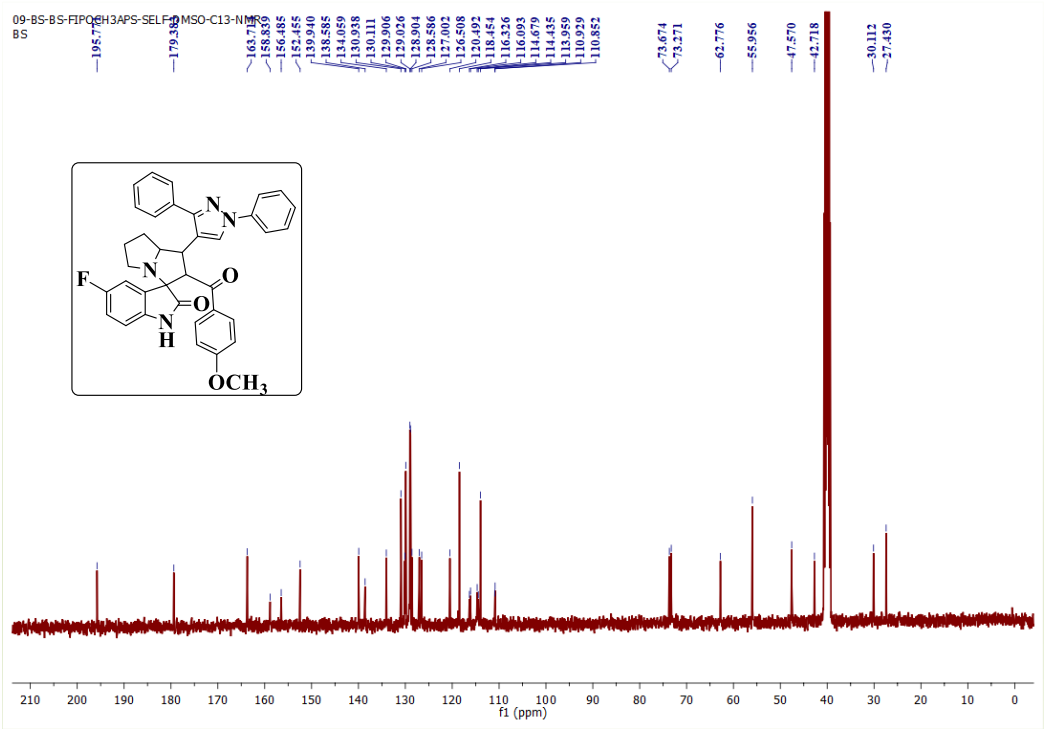
Mass spectrum of the compound 4s



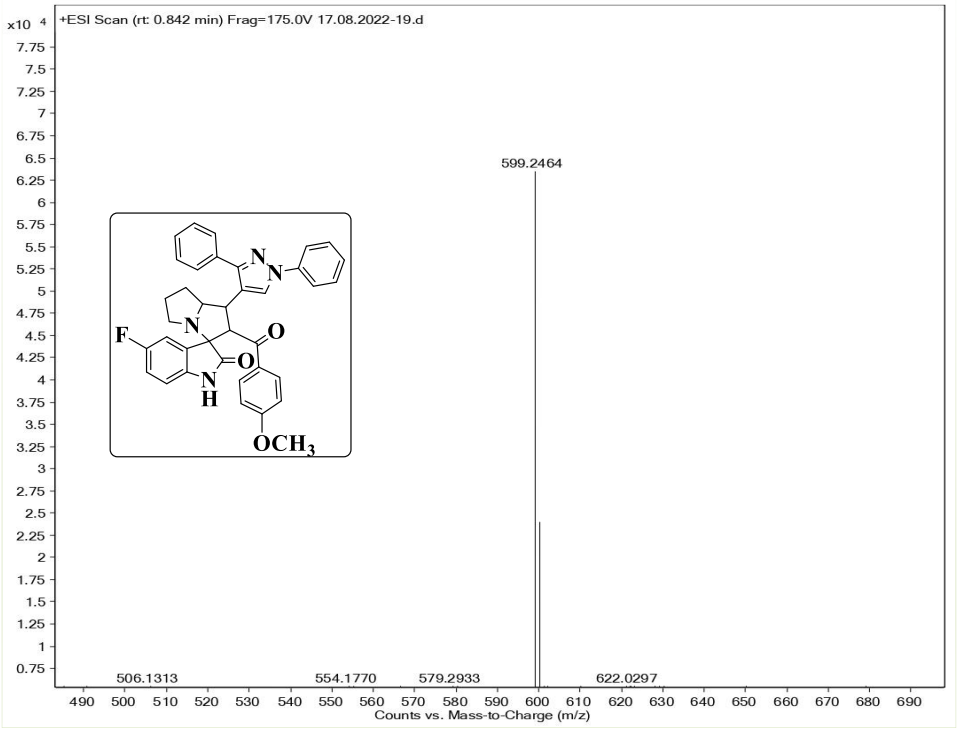
FT-IR Spectrum of the compound 4t



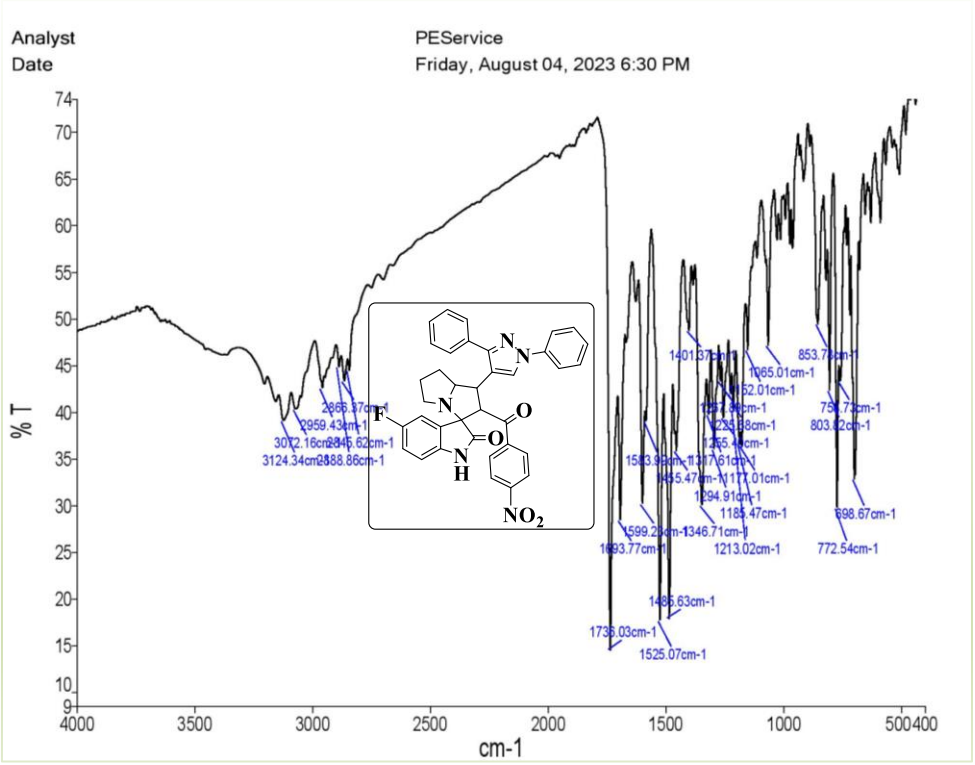
^{1}H NMR Spectrum of the compound 4t



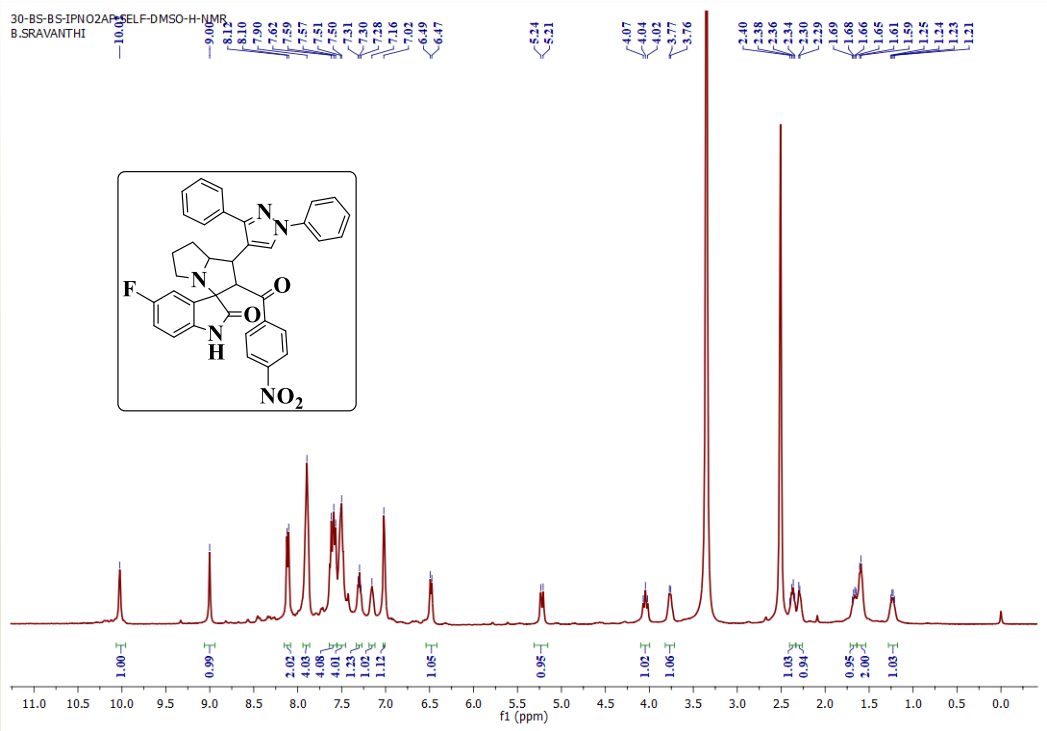
^{13}C NMR Spectrum of the compound 4t



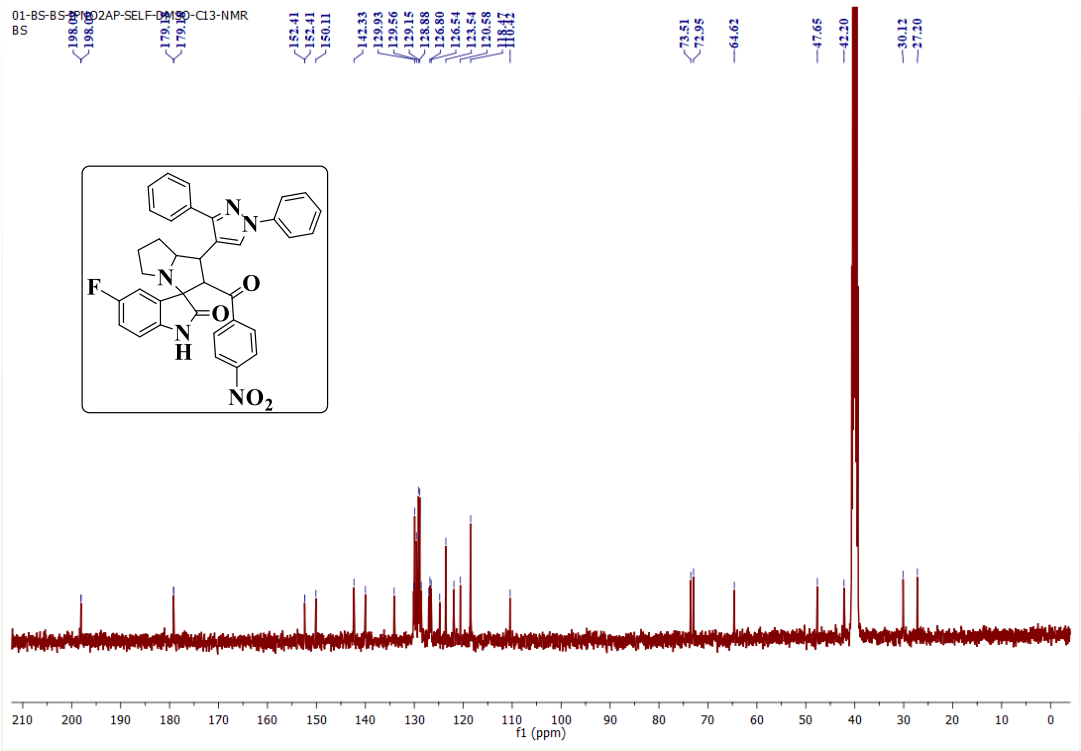
Mass spectrum of the compound 4t



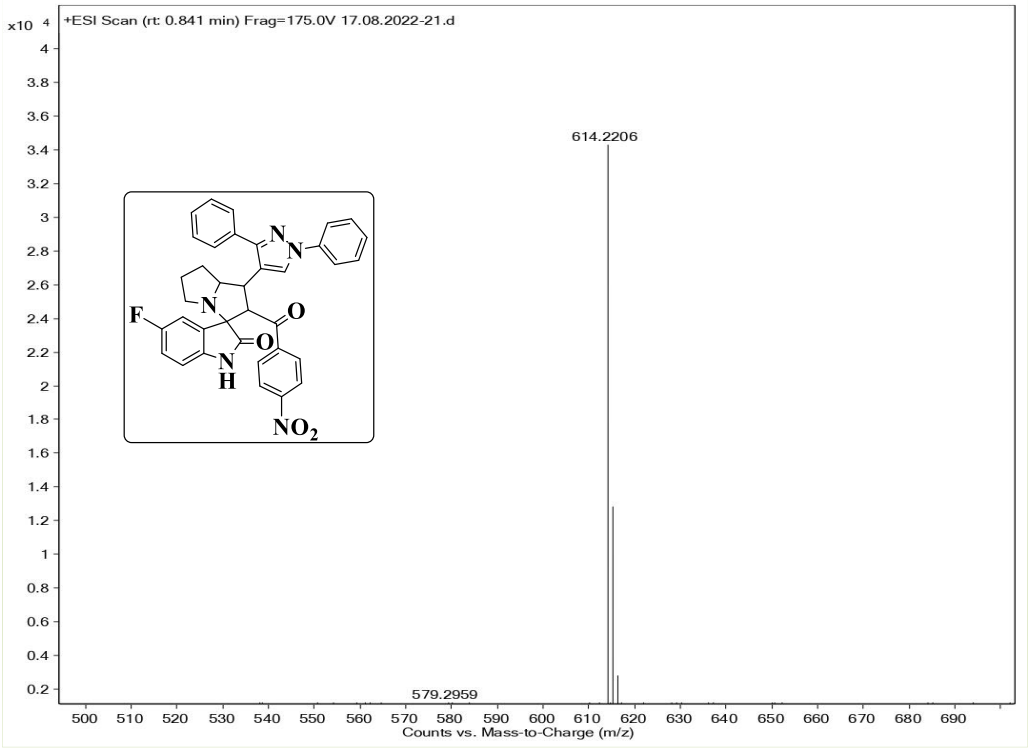
FT-IR Spectrum of the compound 4u



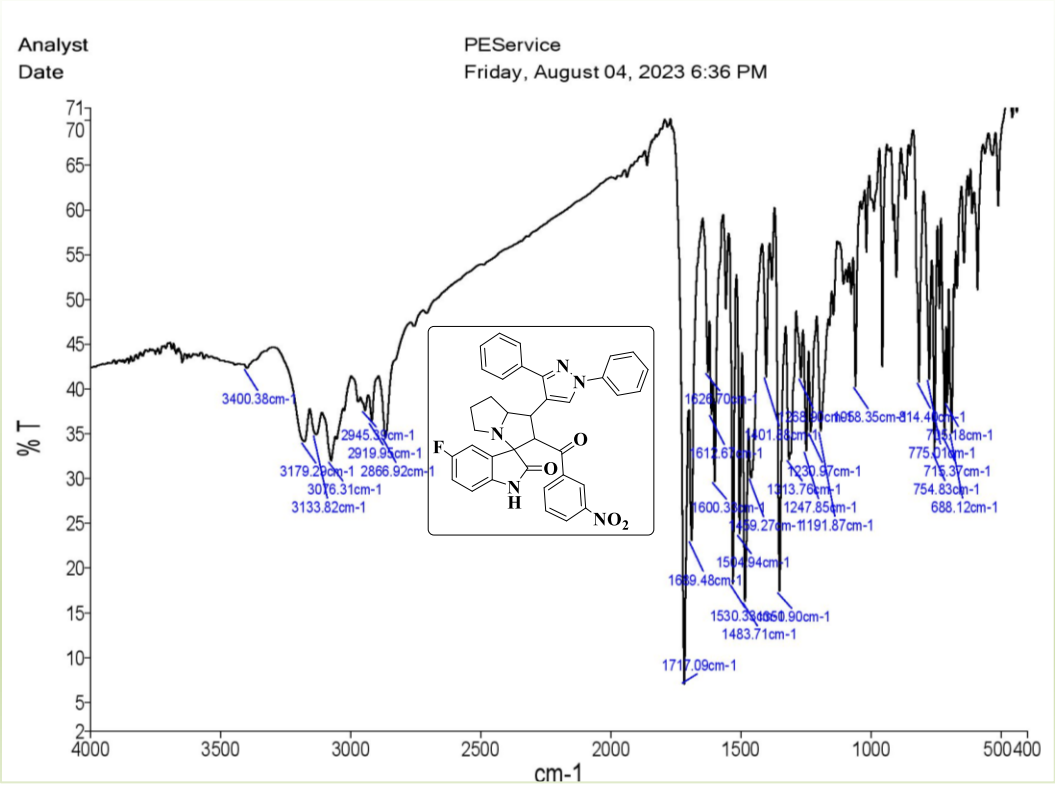
^{1}H NMR Spectrum of the compound 4u



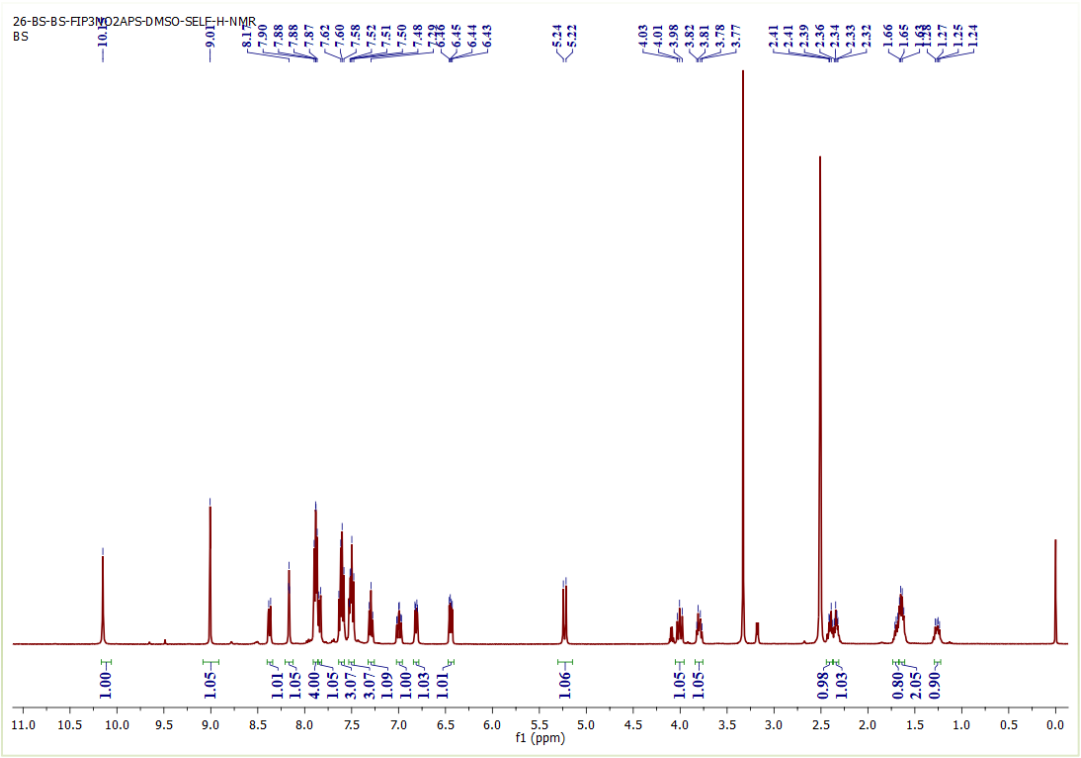
^{13}C NMR Spectrum of the compound 4u



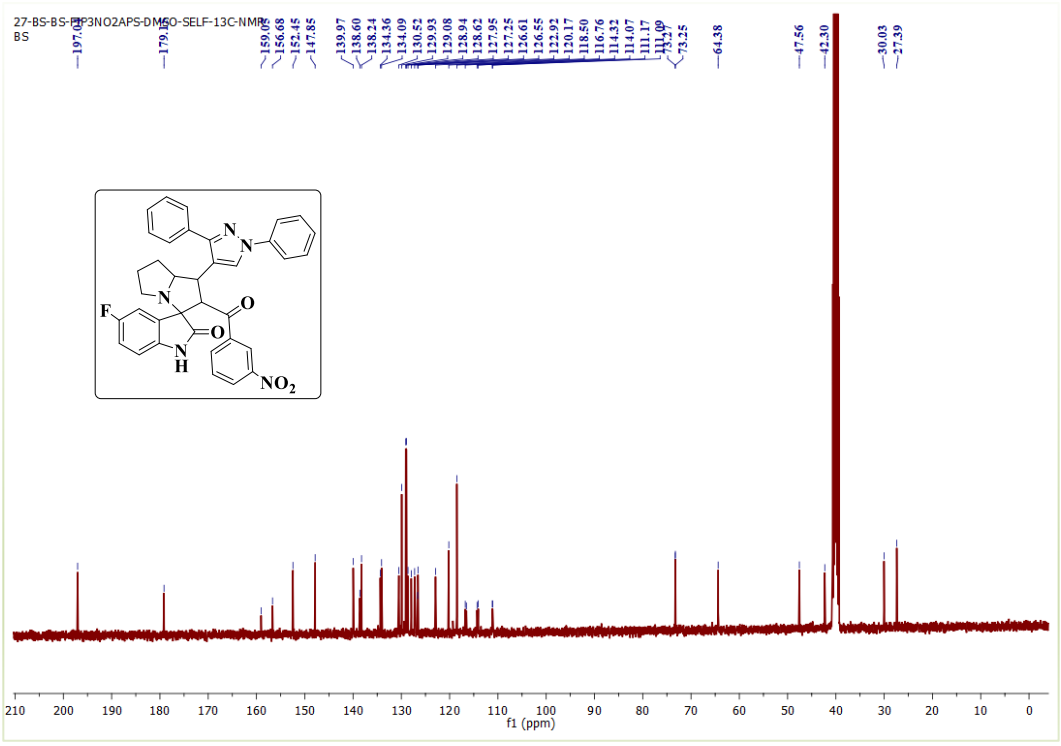
Mass spectrum of the compound 4u



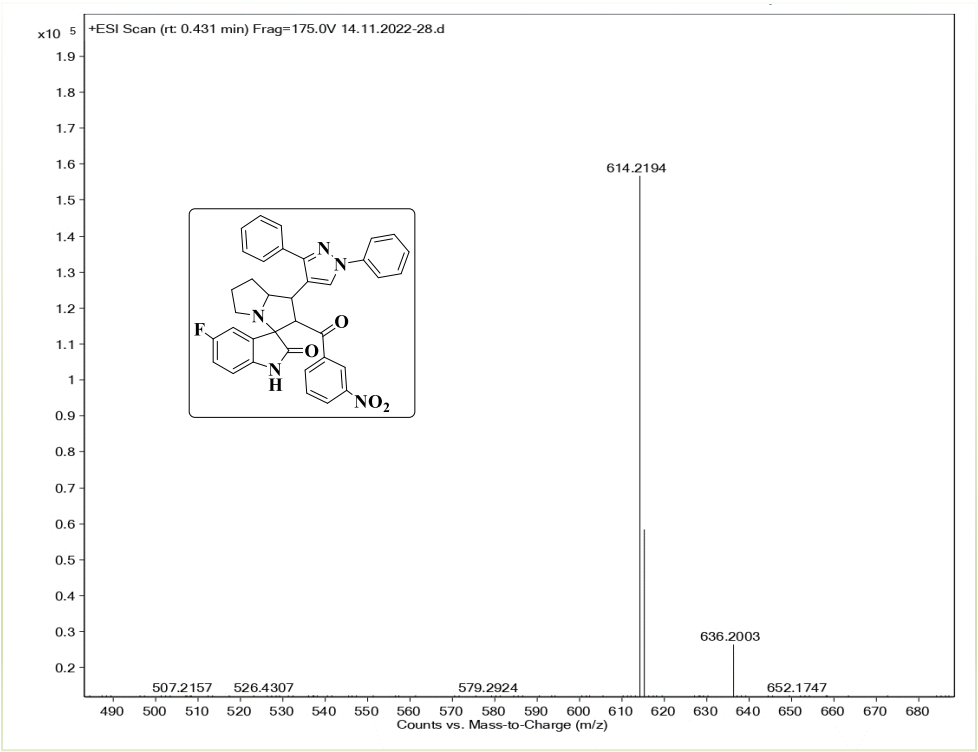
FT-IR Spectrum of the compound 4v



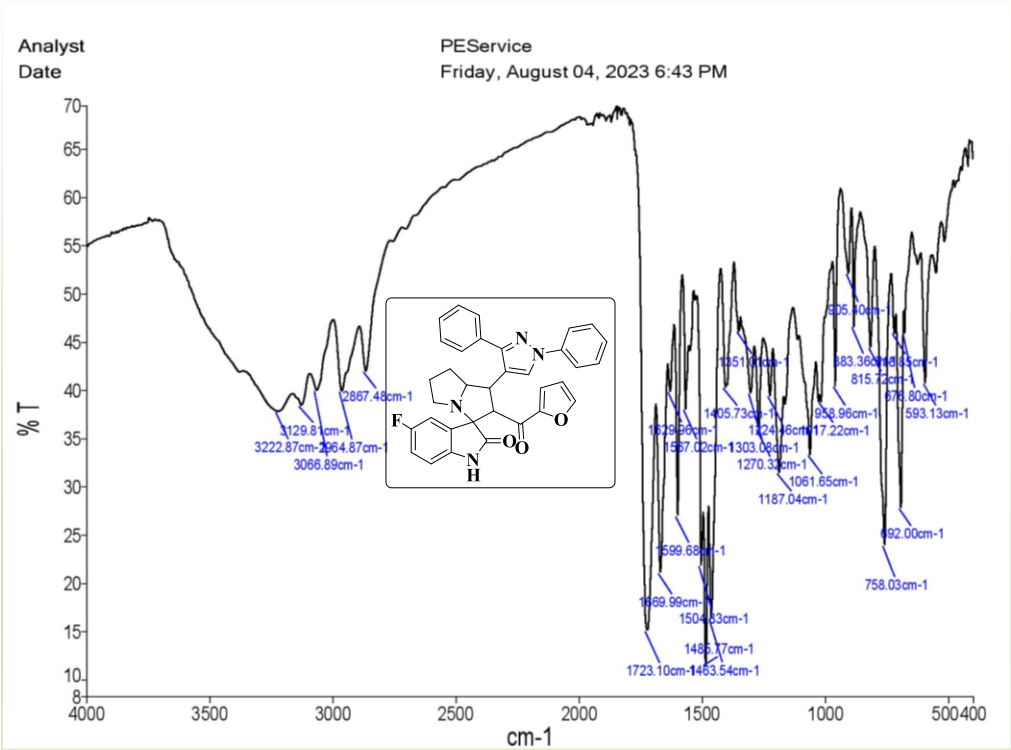
^{1}H NMR Spectrum of the compound 4v



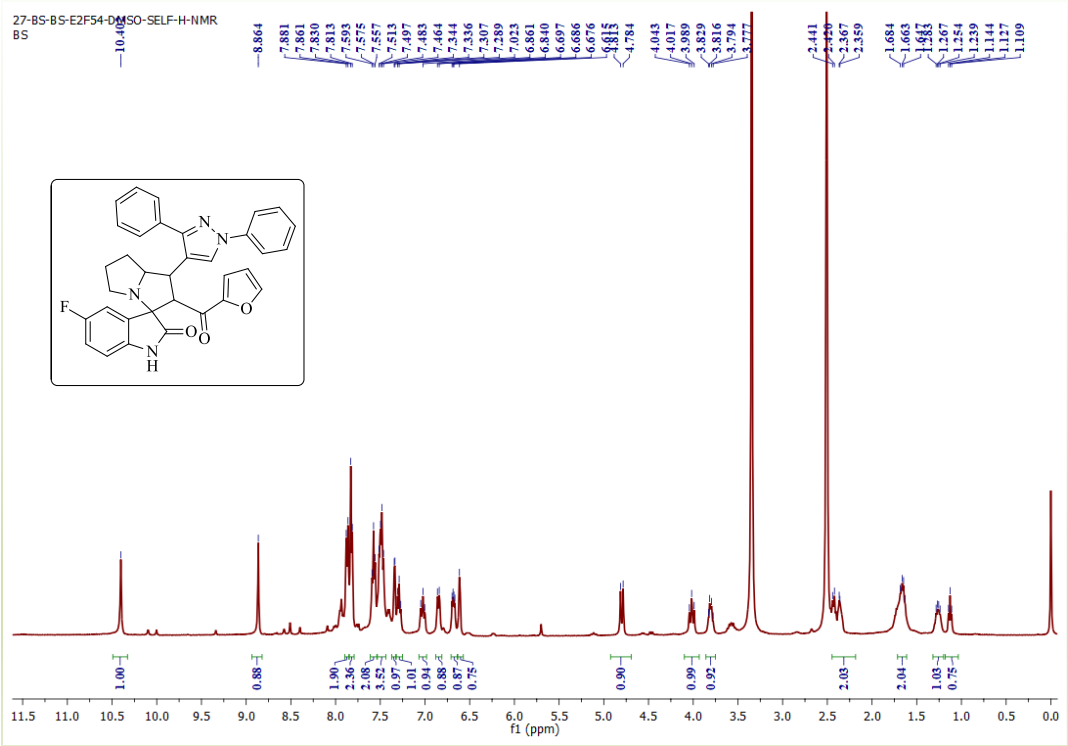
^{13}C NMR Spectrum of the compound 4v



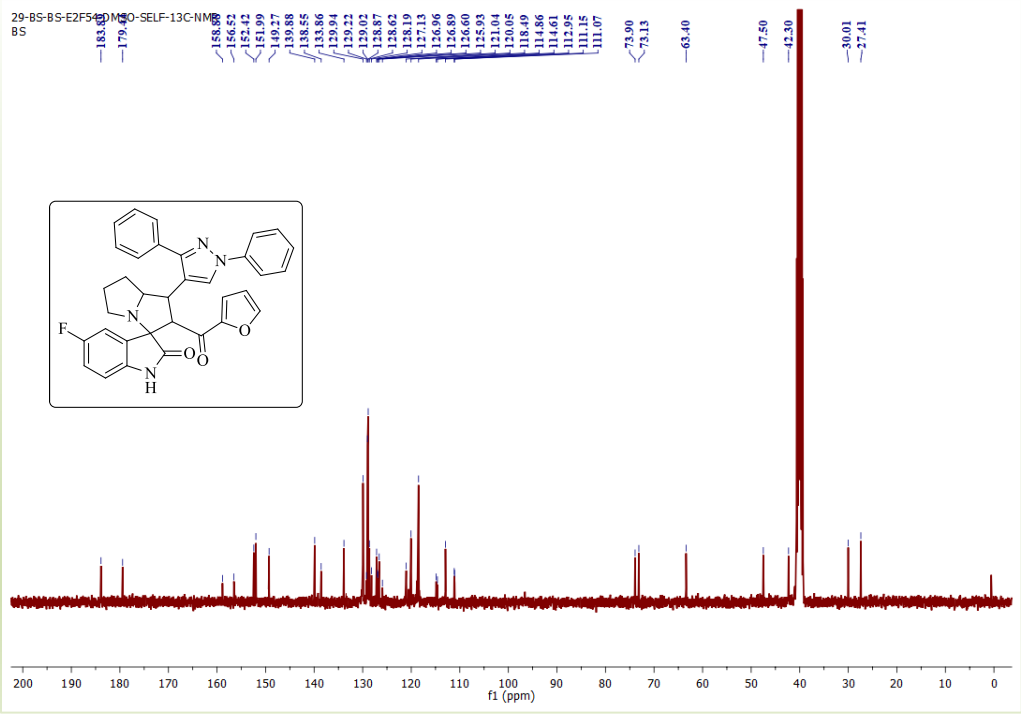
Mass spectrum of the compound 4v



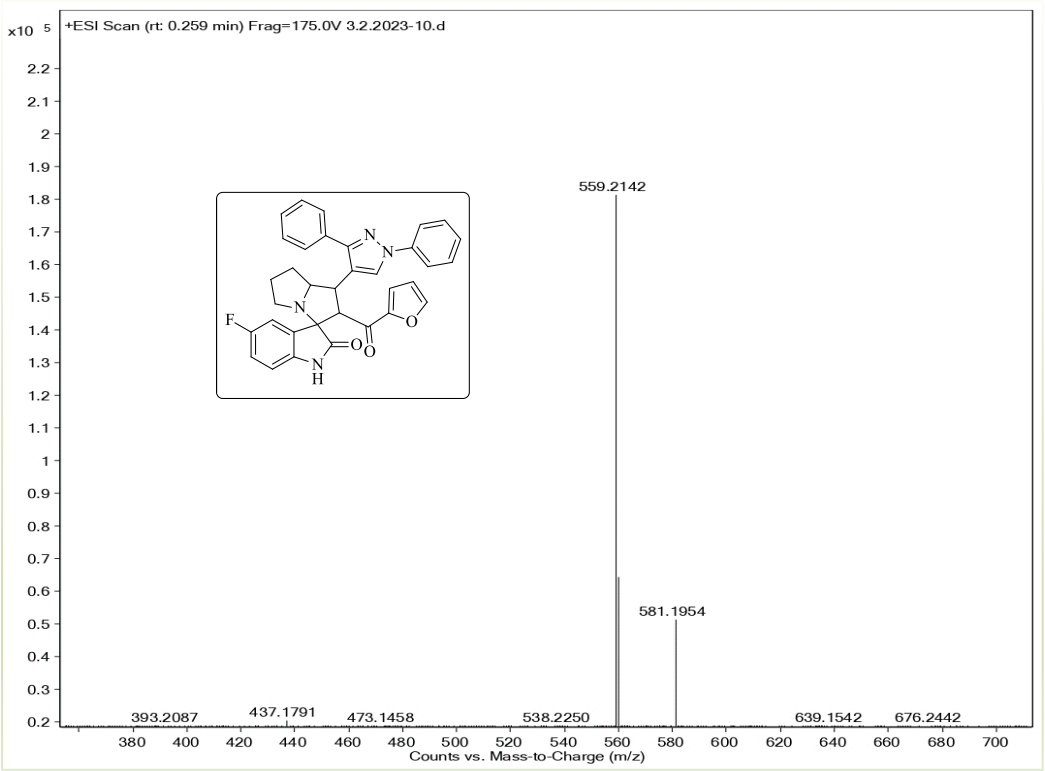
FT-IR Spectrum of the compound 4w



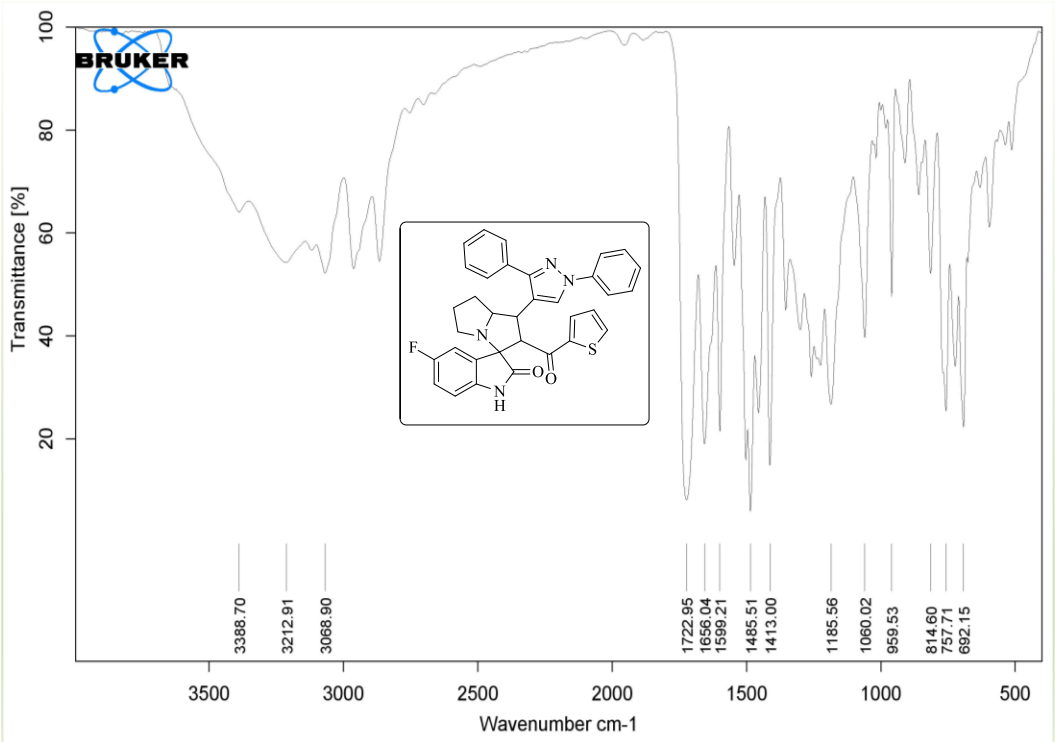
^{1}H NMR Spectrum of the compound 4w



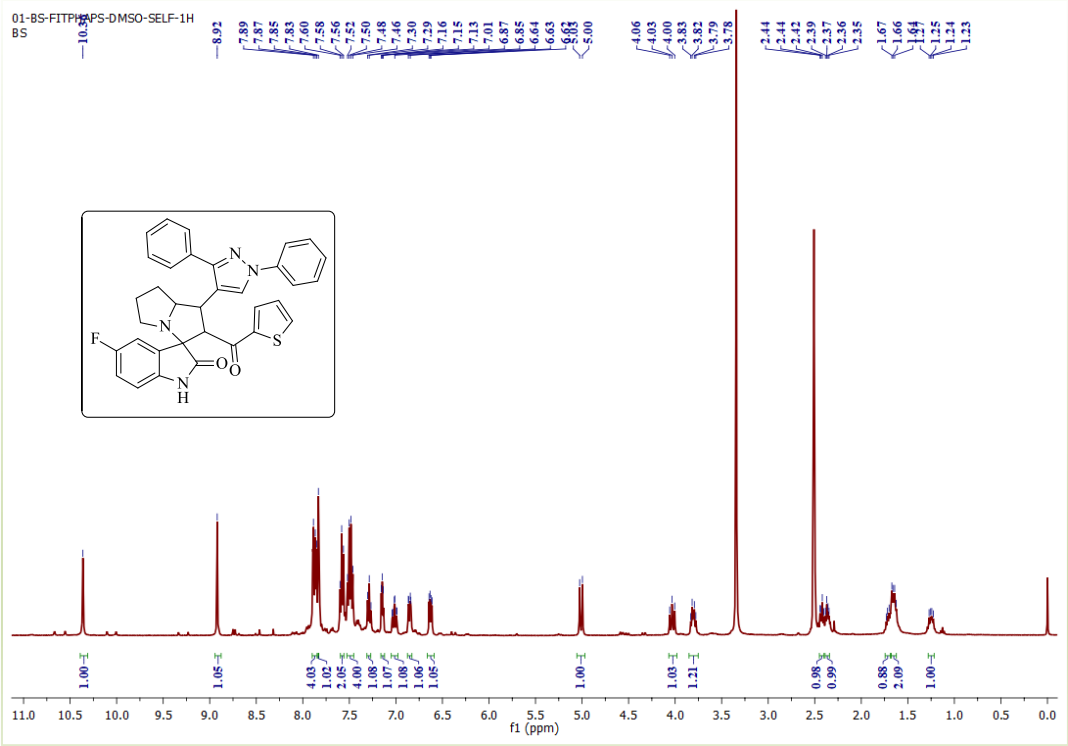
^{13}C NMR Spectrum of the compound 4w



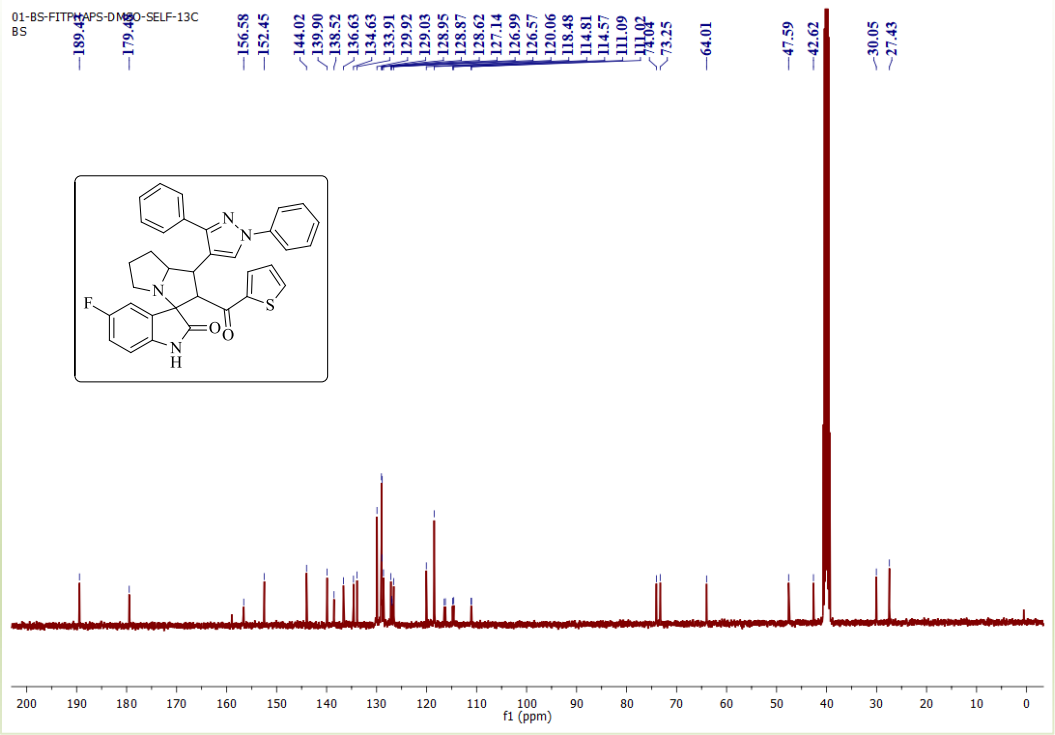
Mass spectrum of the compound 4w



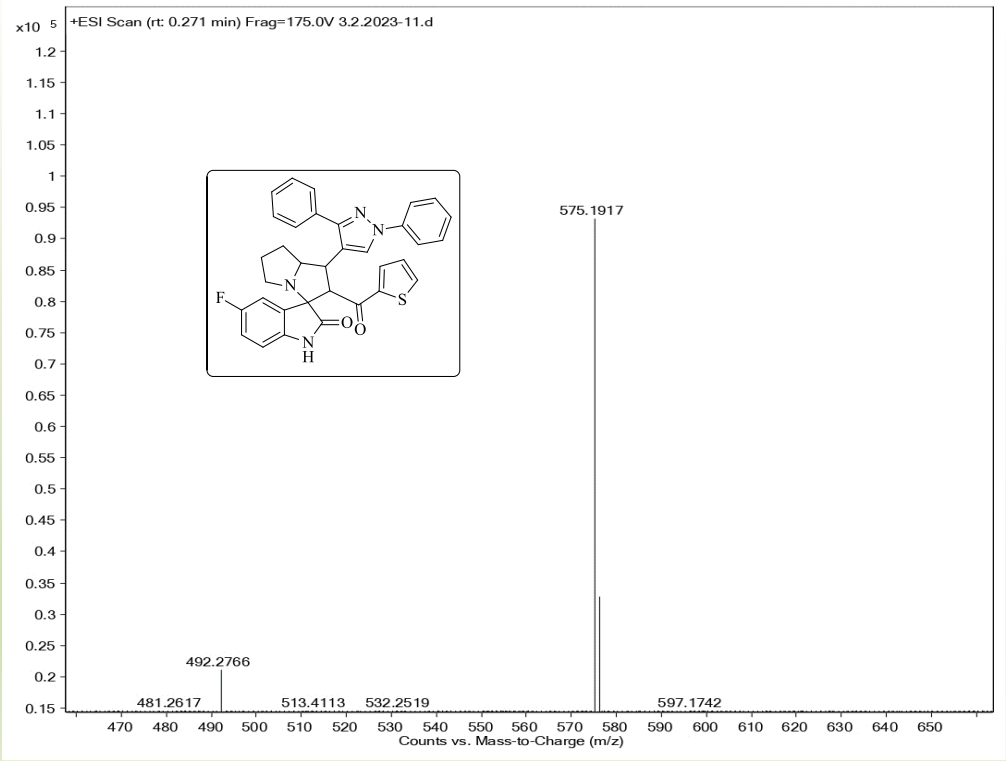
FT-IR Spectrum of the compound 4x



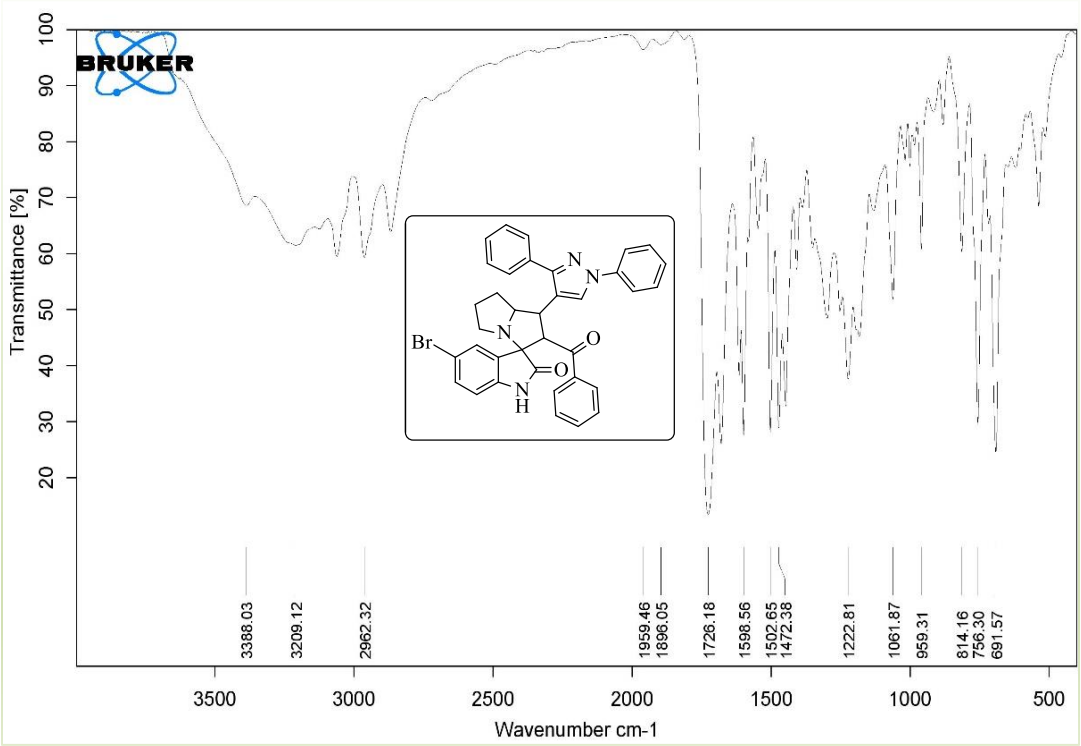
^{1}H NMR Spectrum of the compound 4x



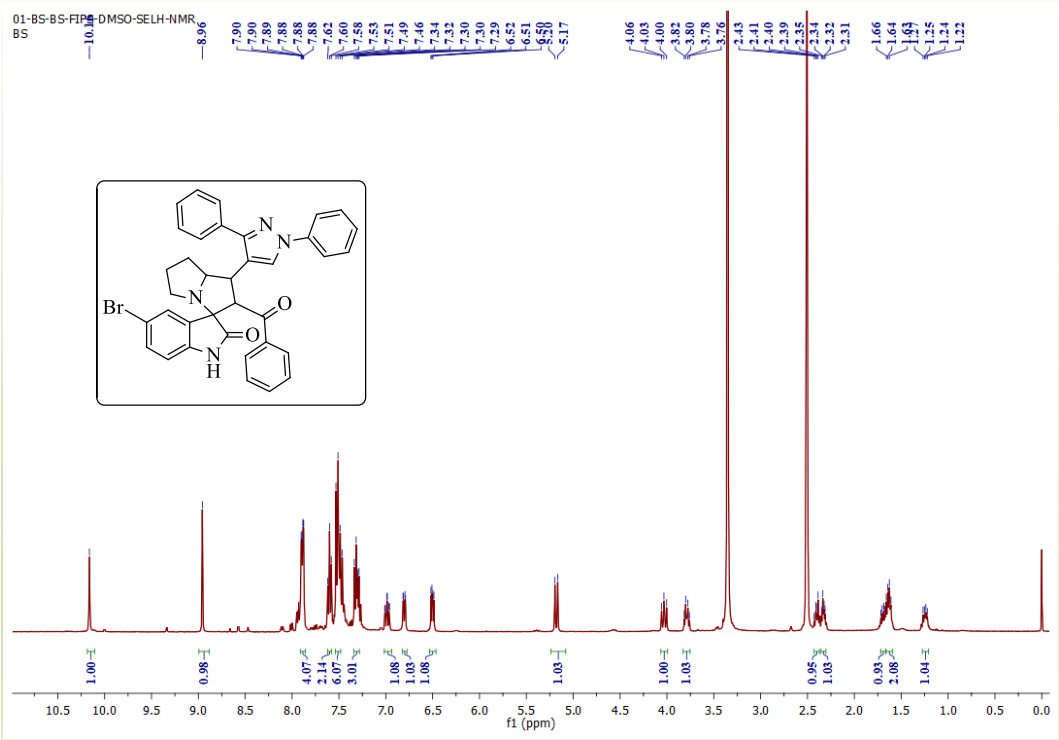
^{13}C NMR Spectrum of the compound 4x



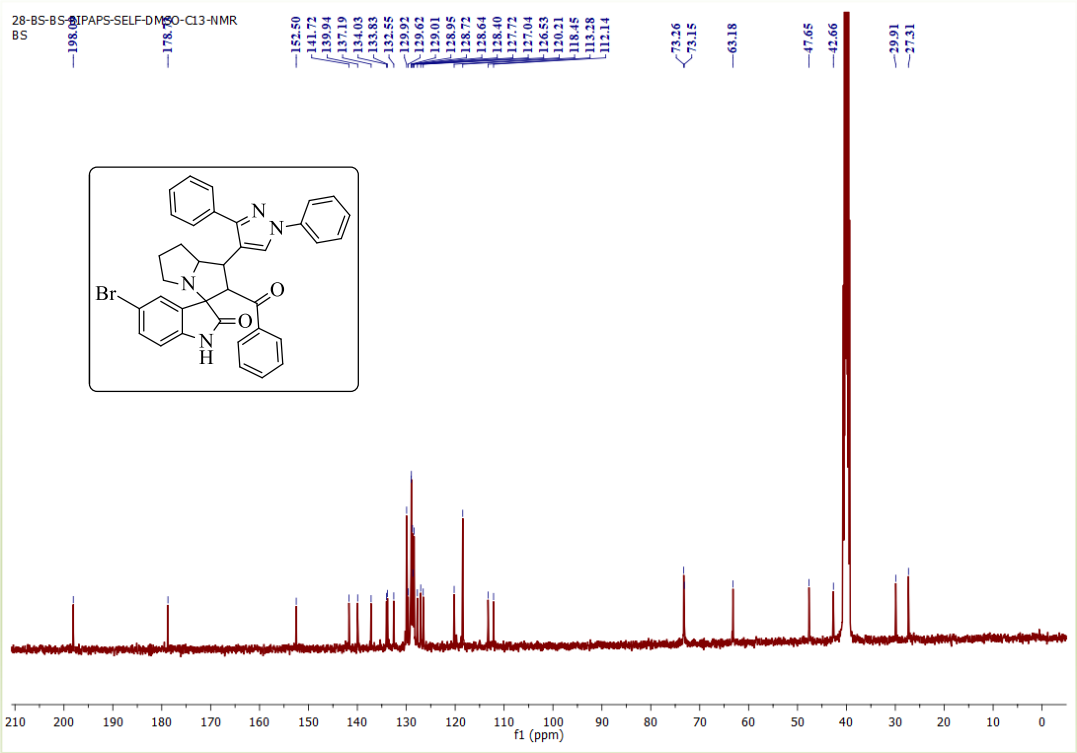
Mass spectrum of the compound 4x



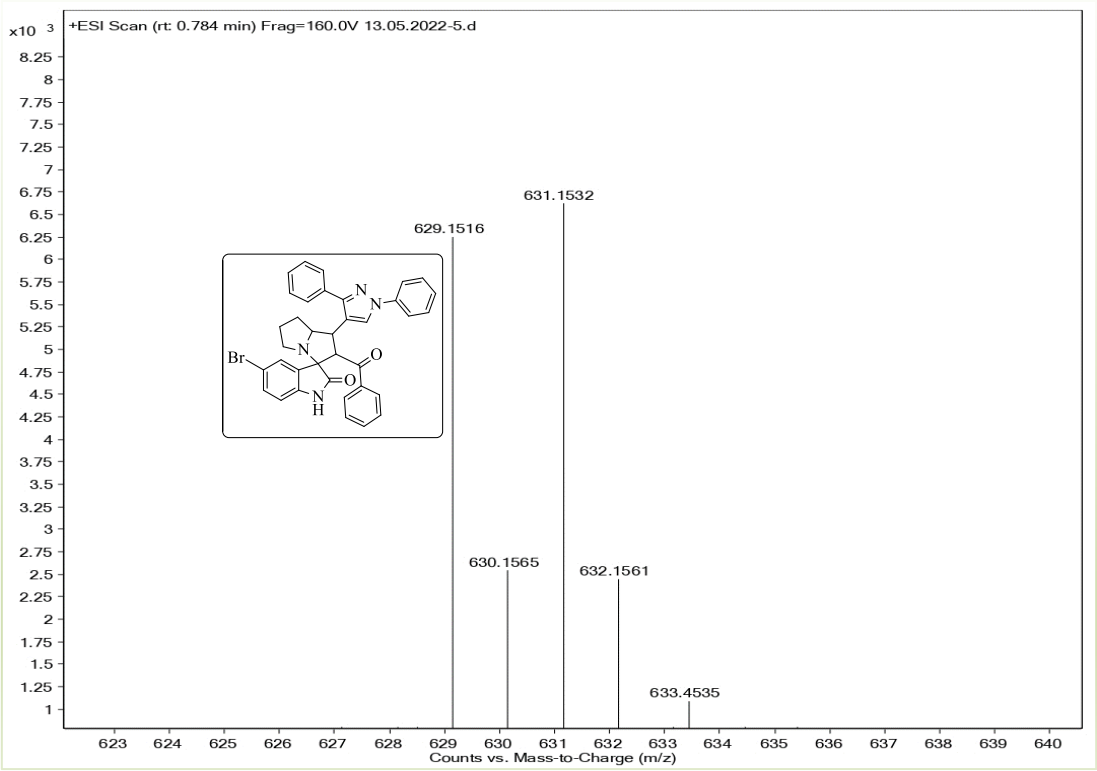
FT-IR Spectrum of the compound 4y



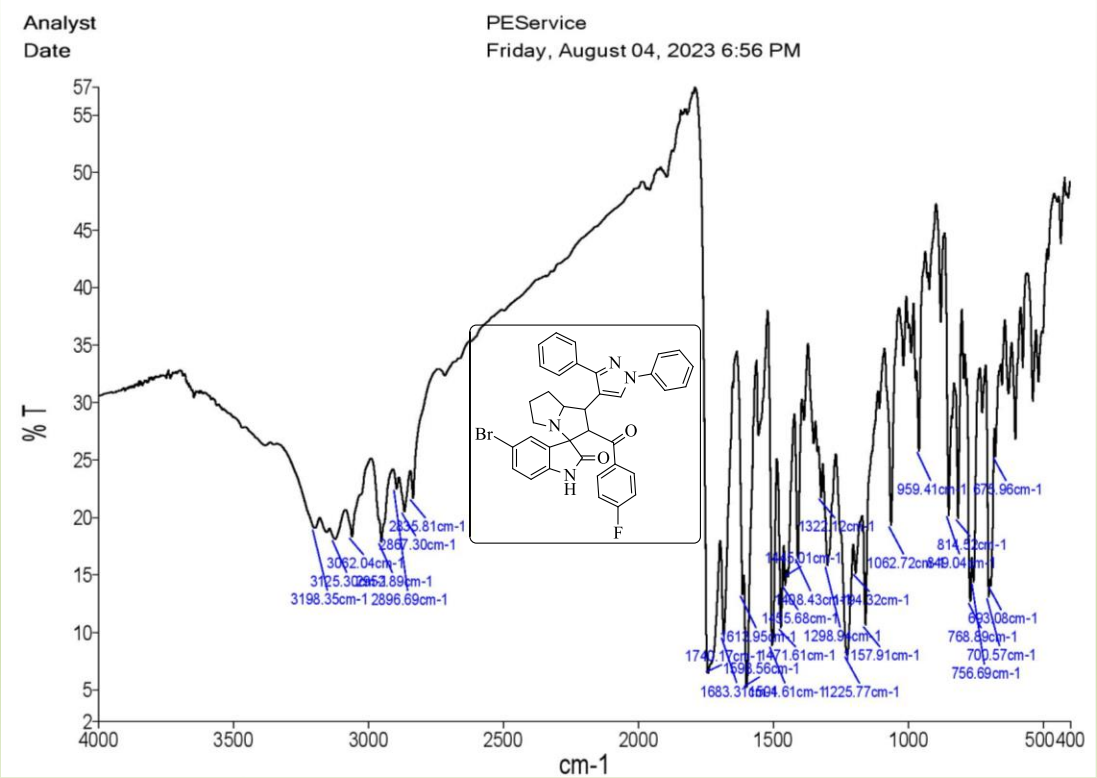
^{1}H NMR Spectrum of the compound 4y



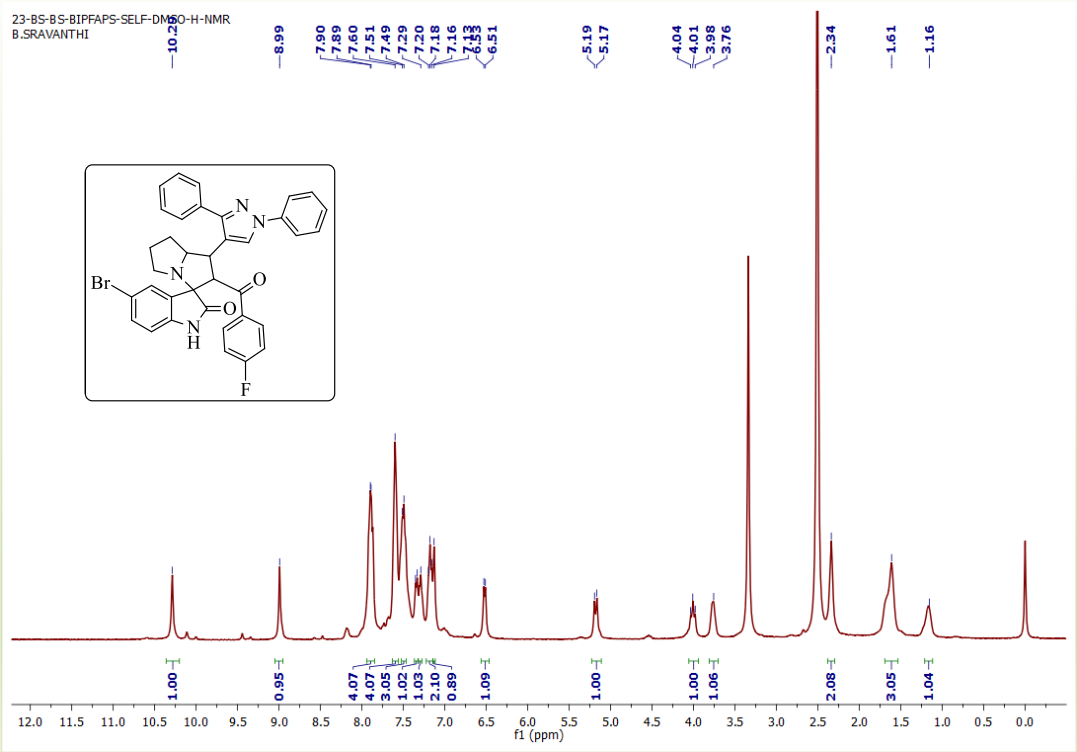
^{13}C NMR Spectrum of the compound 4y



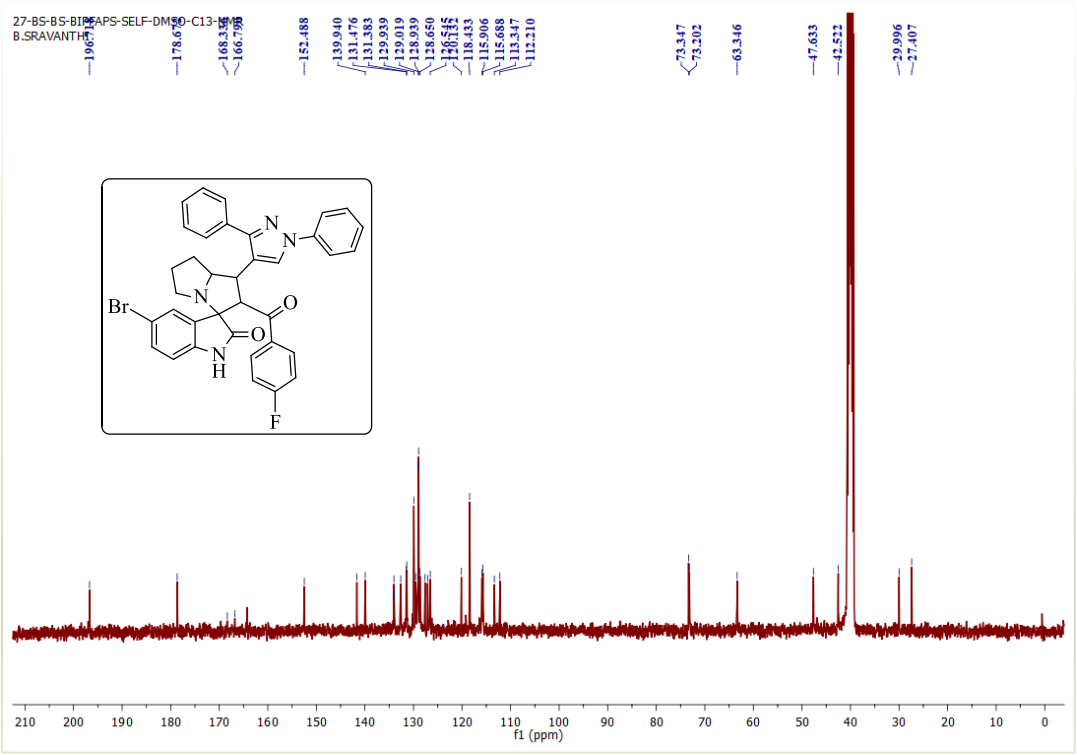
Mass spectrum of the compound 4y



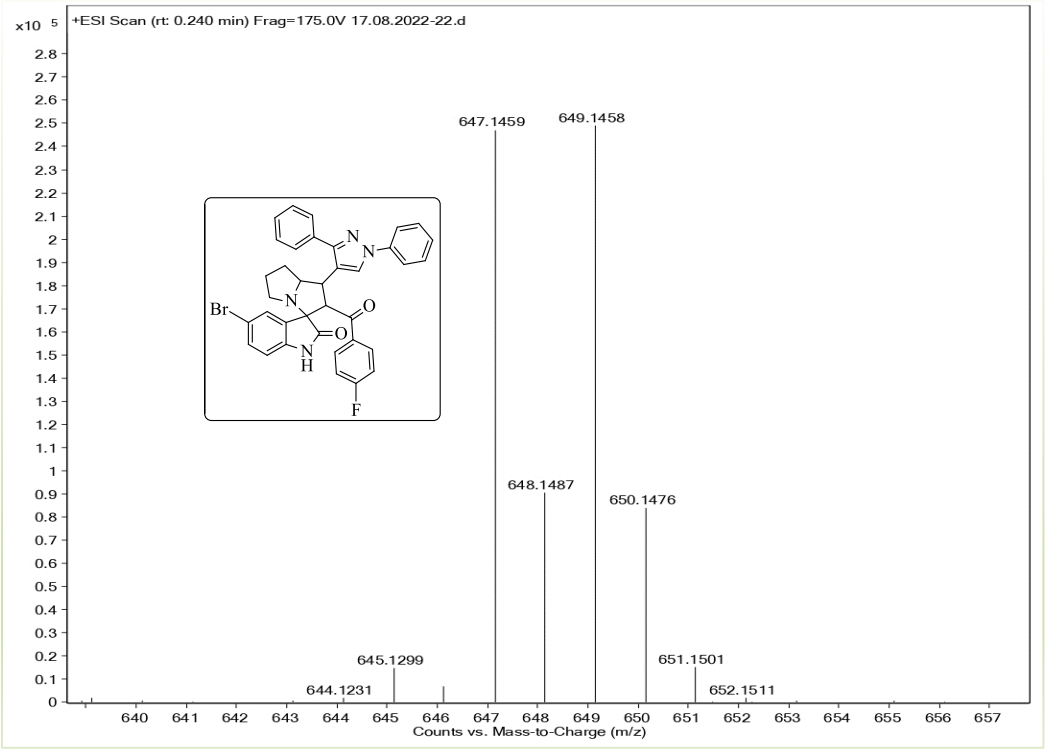
FT-IR Spectrum of the compound 4z



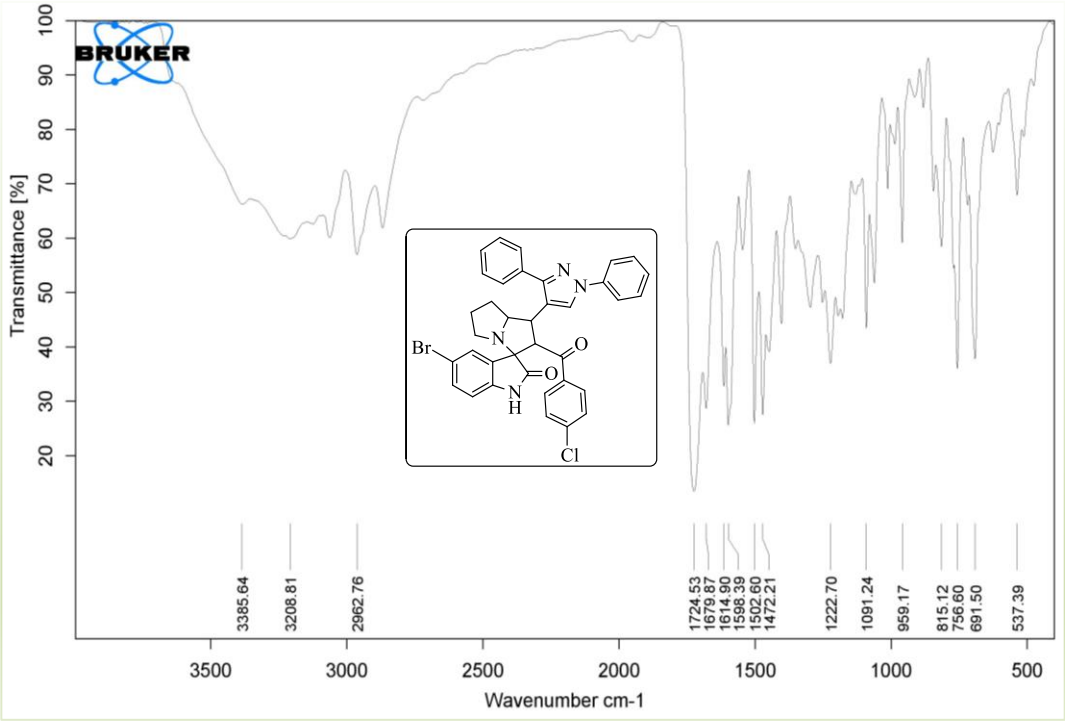
^{1}H NMR Spectrum of the compound 4z



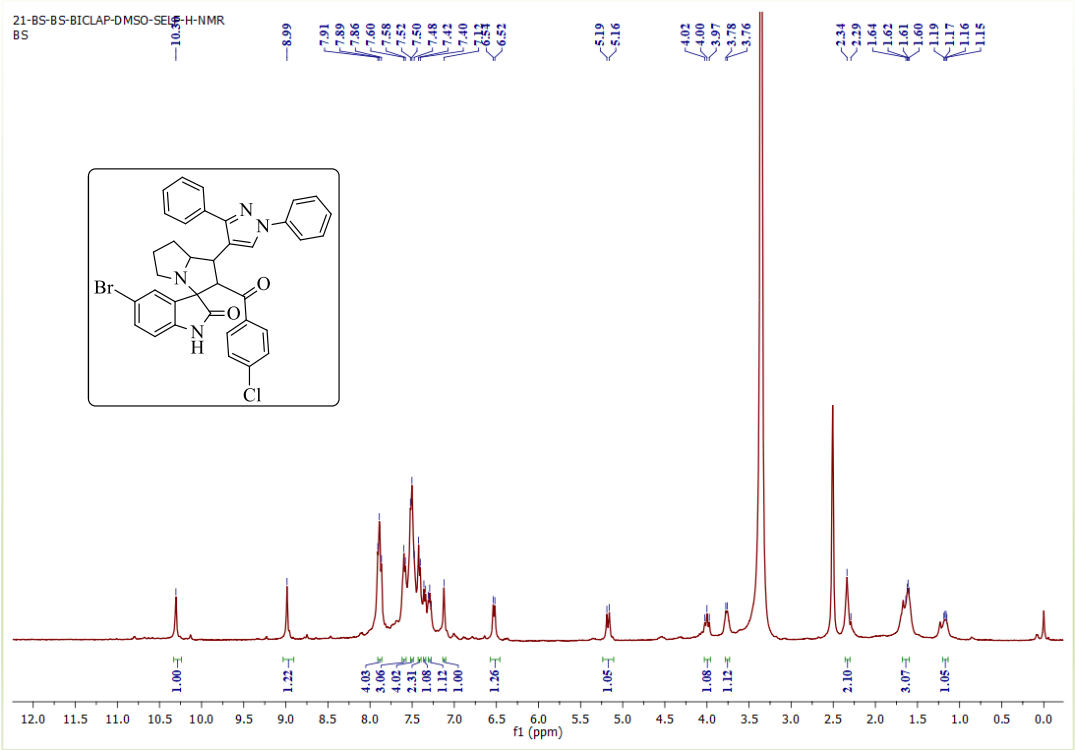
^{13}C NMR Spectrum of the compound 4z



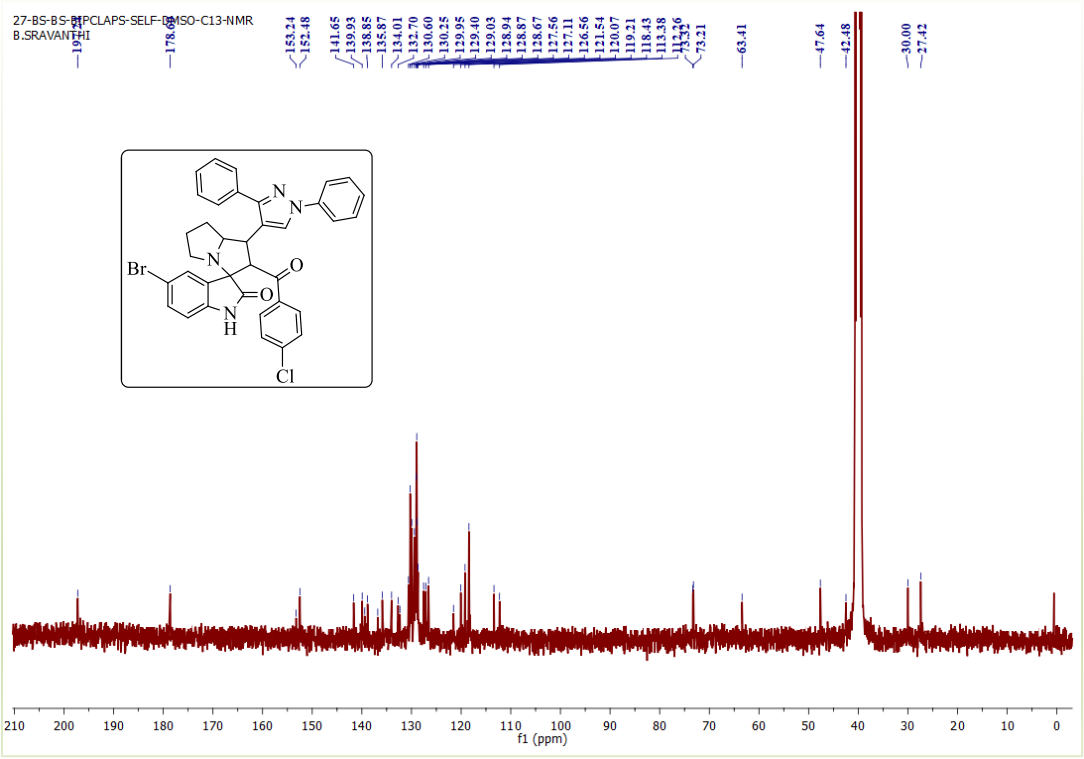
Mass spectrum of the compound 4z



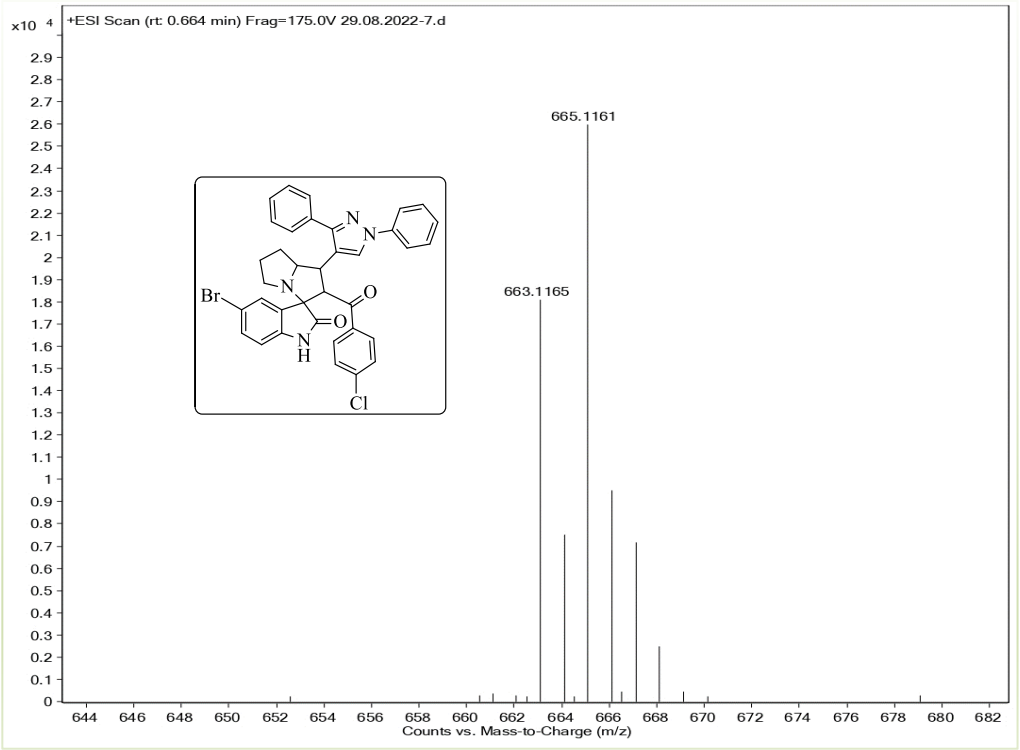
FT-IR Spectrum of the compound 4aa



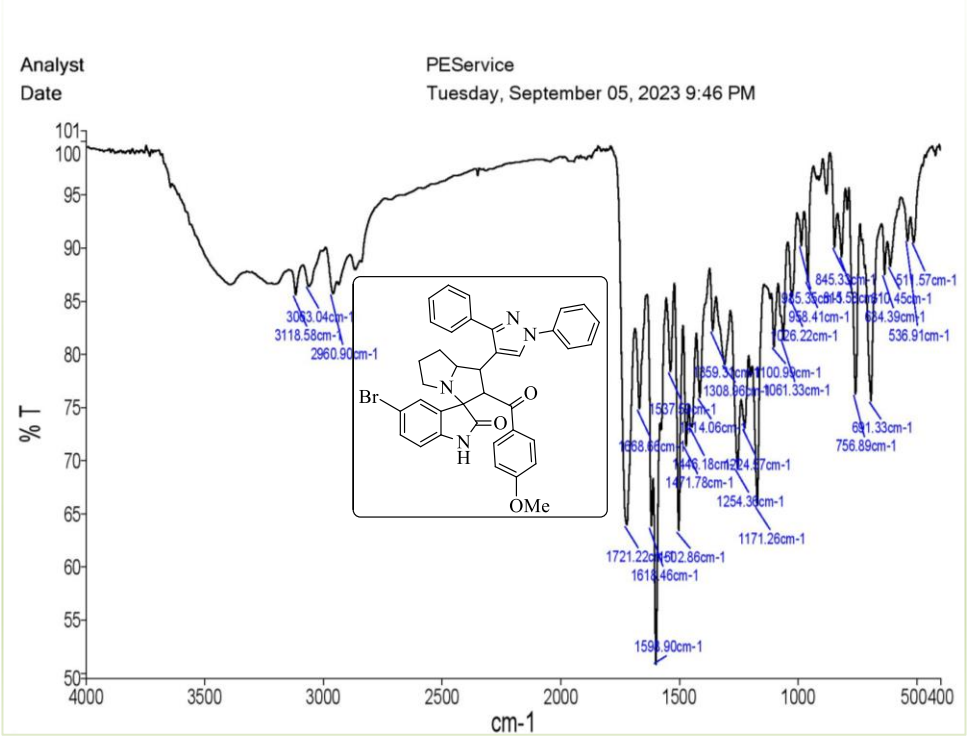
^{1}H NMR Spectrum of the compound 4aa



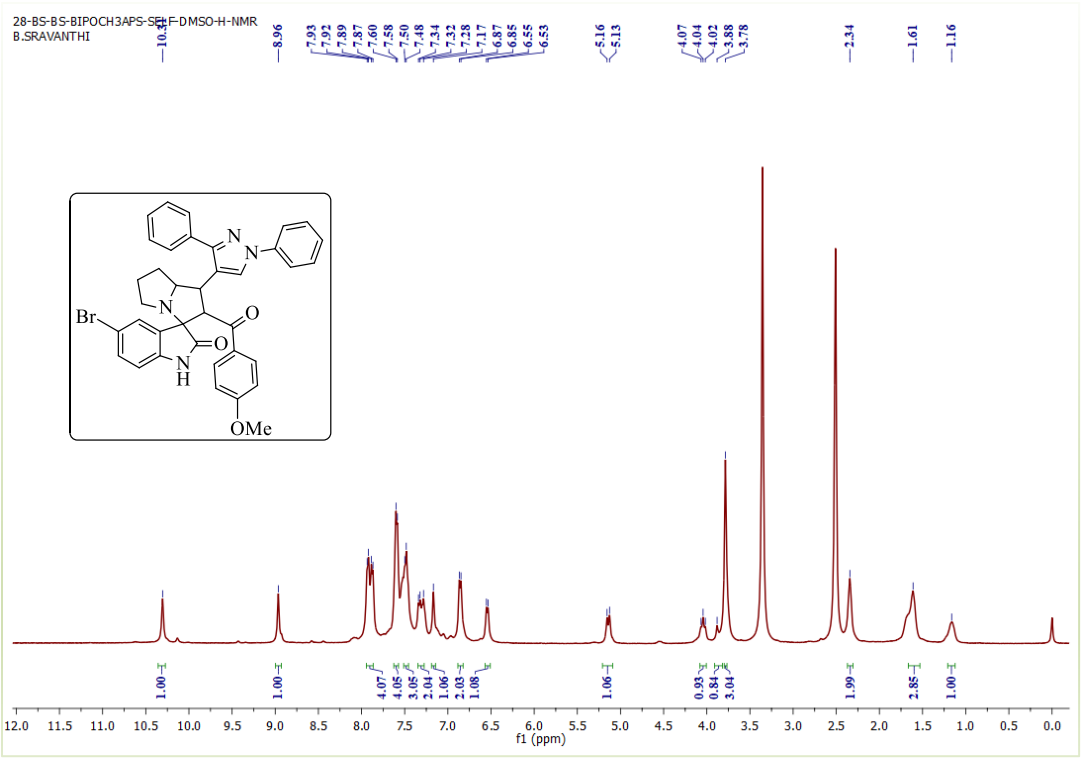
^{13}C NMR Spectrum of the compound 4aa



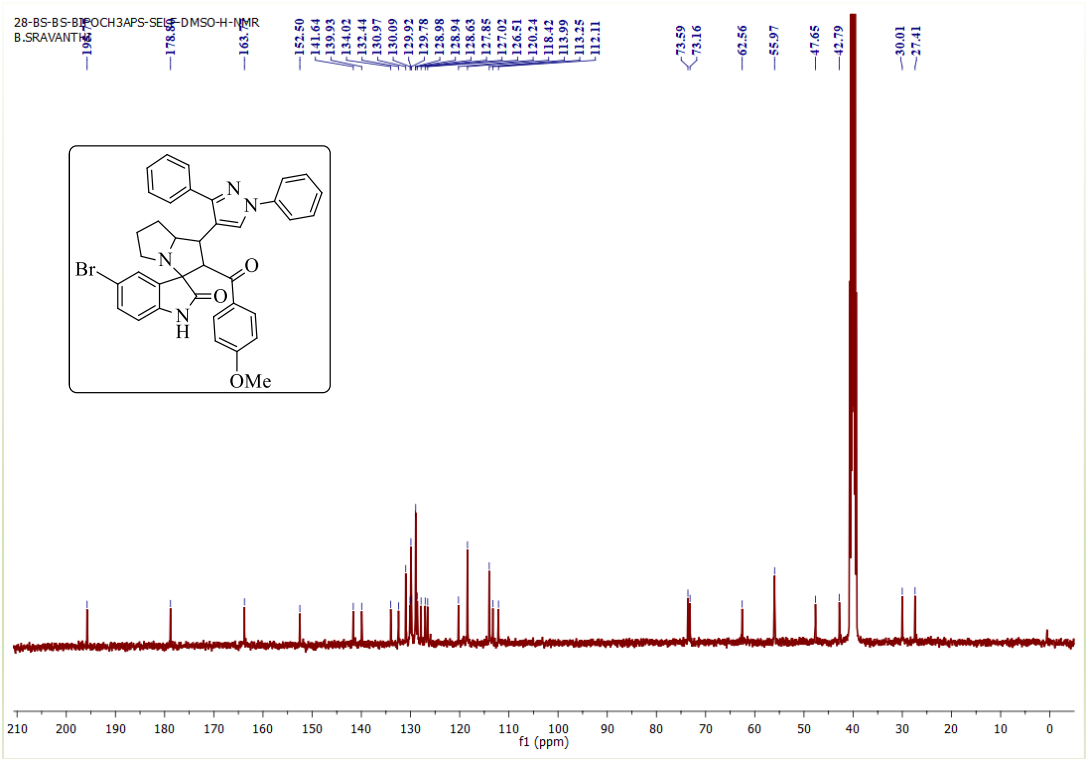
Mass spectrum of the compound 4aa



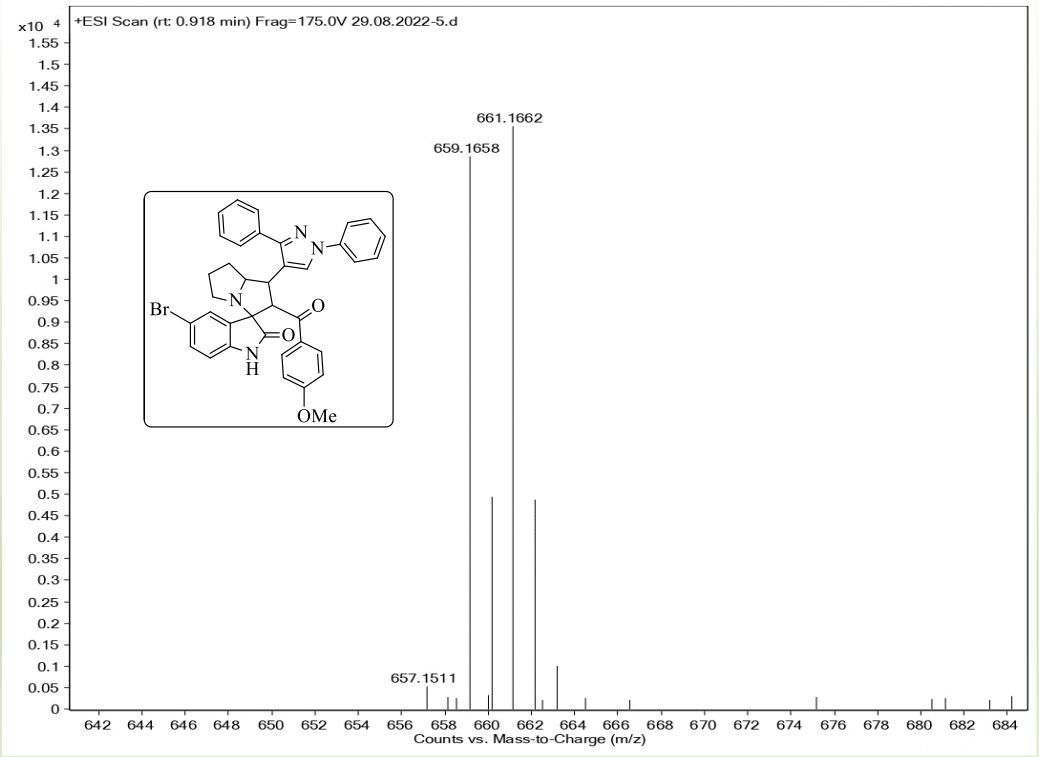
FT-IR Spectrum of the compound 4ab



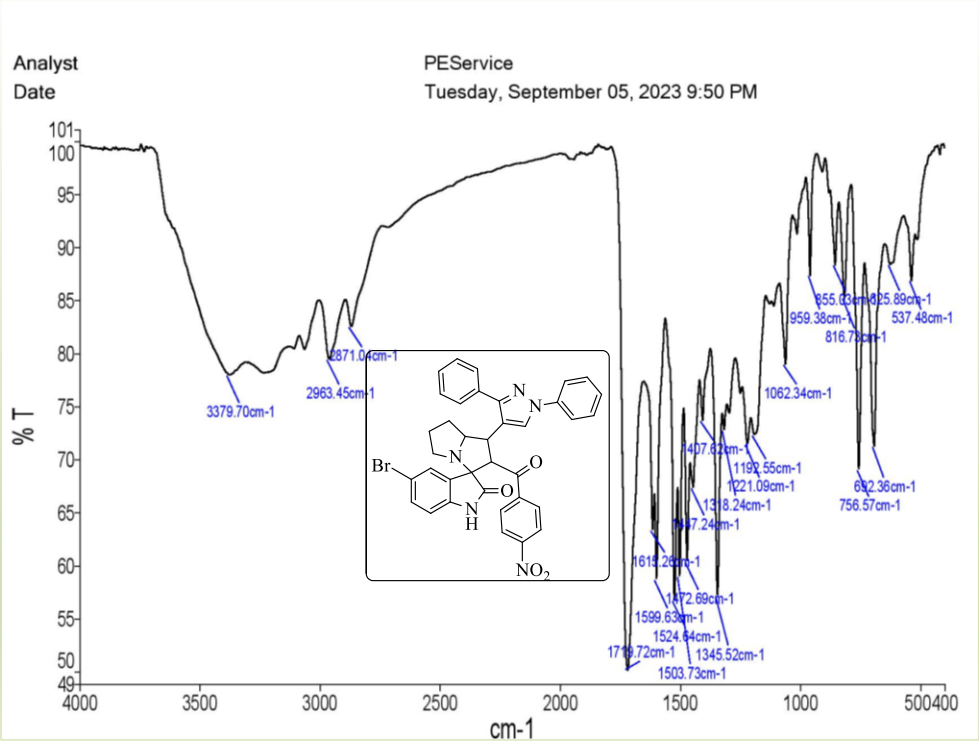
^{1}H NMR Spectrum of the compound 4ab



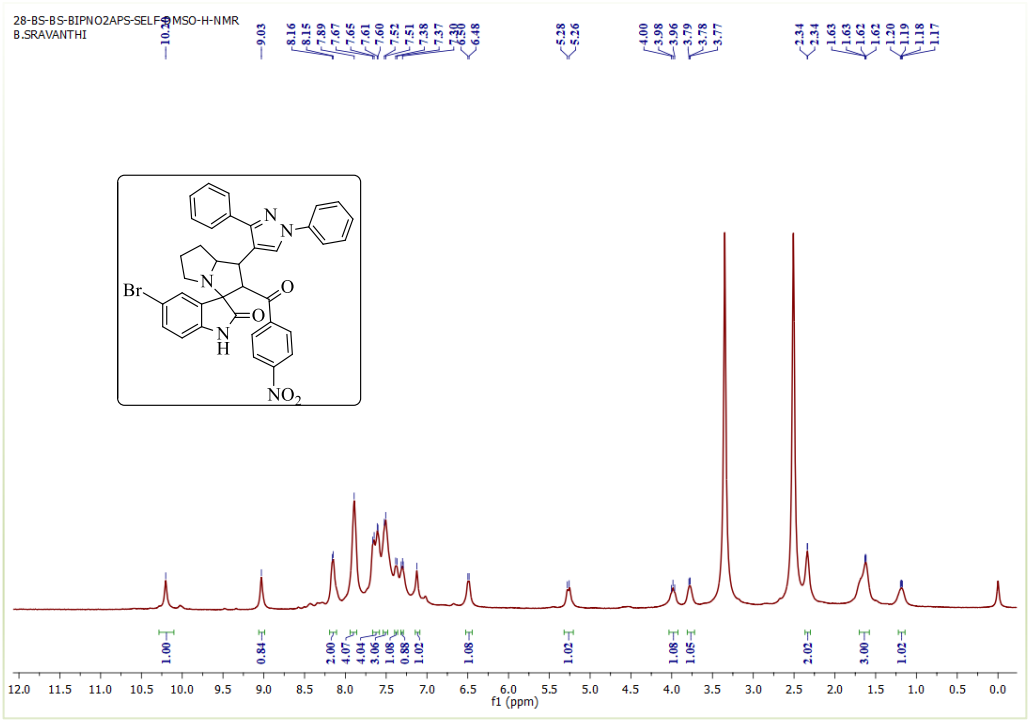
^{13}C NMR Spectrum of the compound 4ab



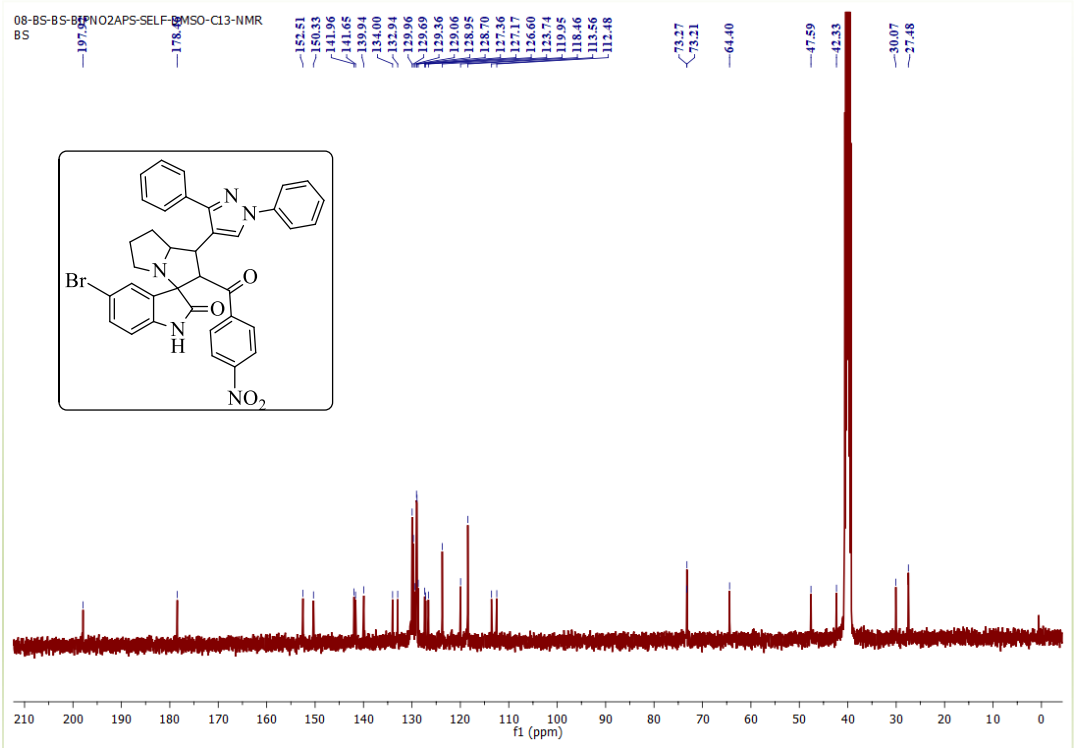
Mass spectrum of the compound 4ab



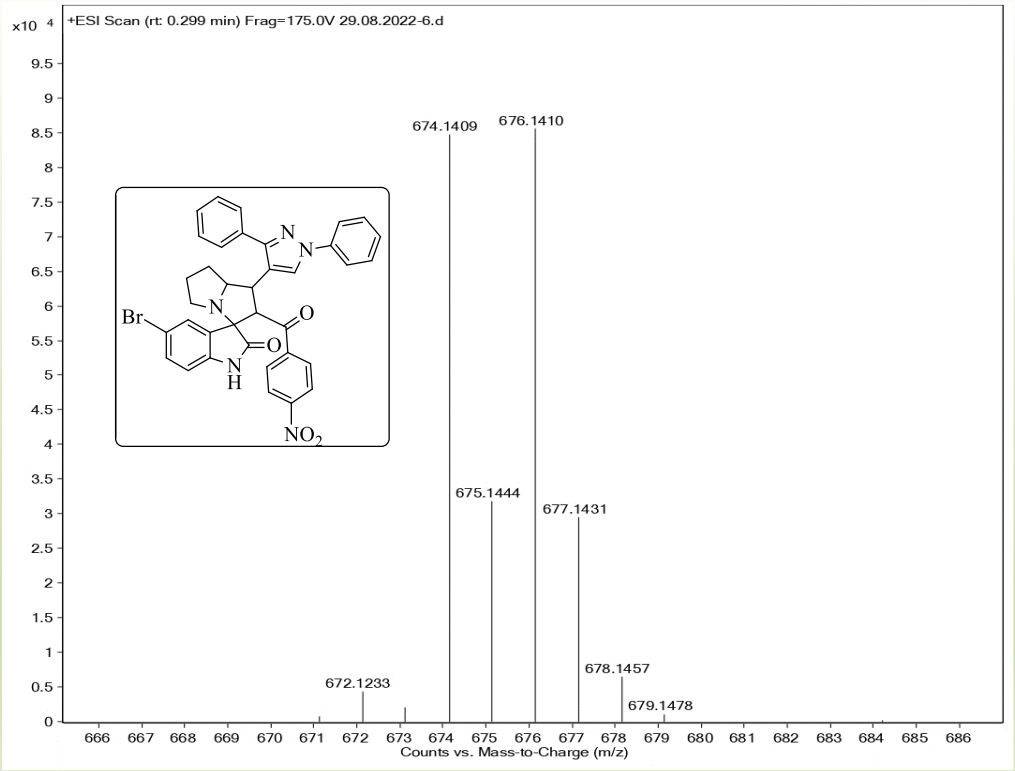
FT-IR Spectrum of the compound 4ac



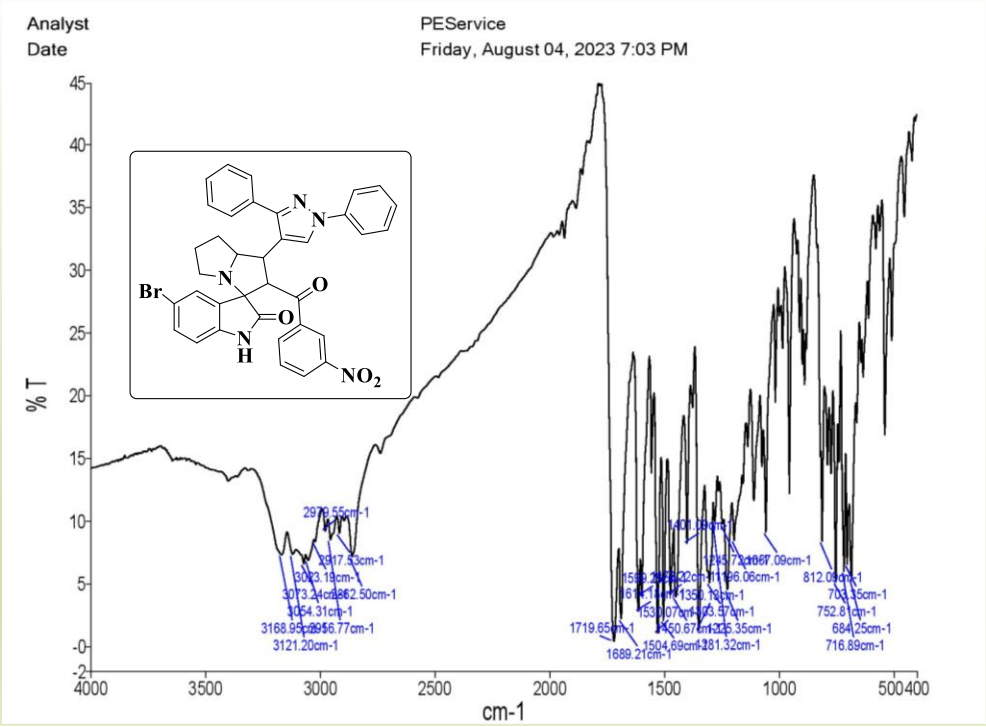
^{1}H NMR Spectrum of the compound 4aC



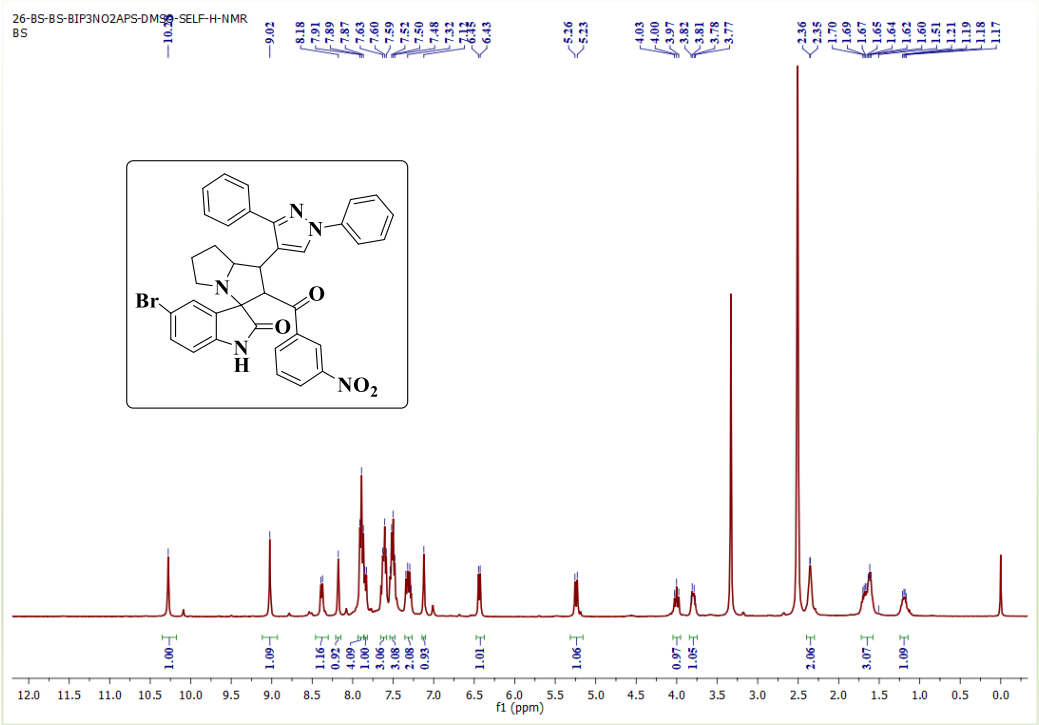
^{13}C NMR Spectrum of the compound 4ac



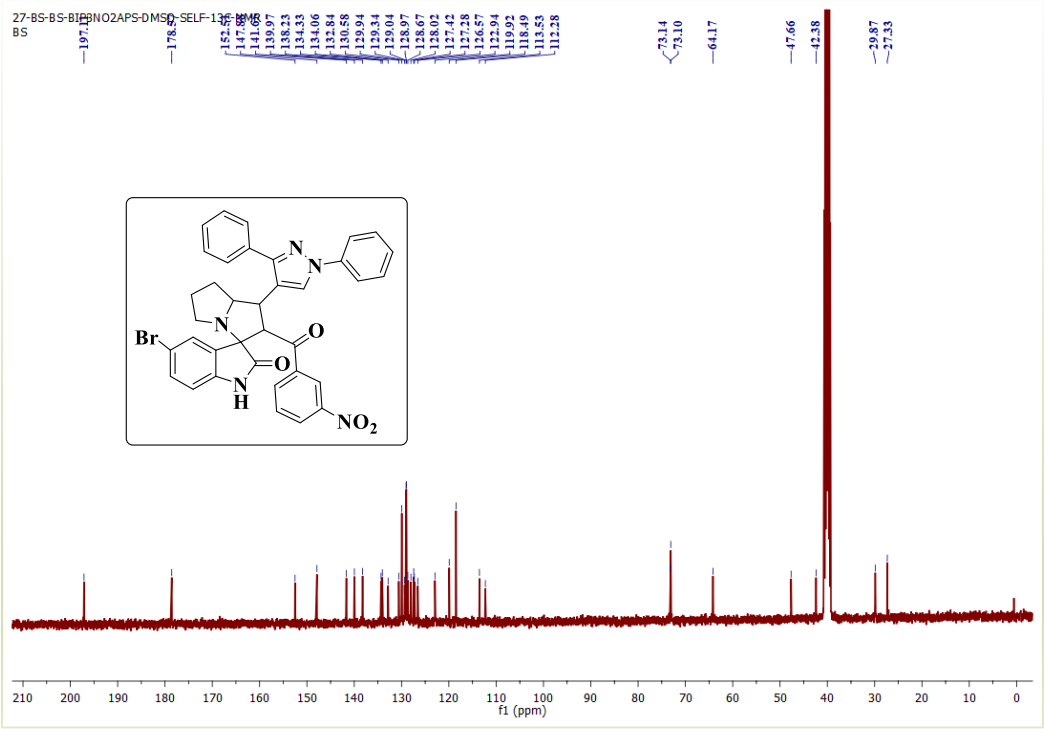
Mass spectrum of the compound 4ac



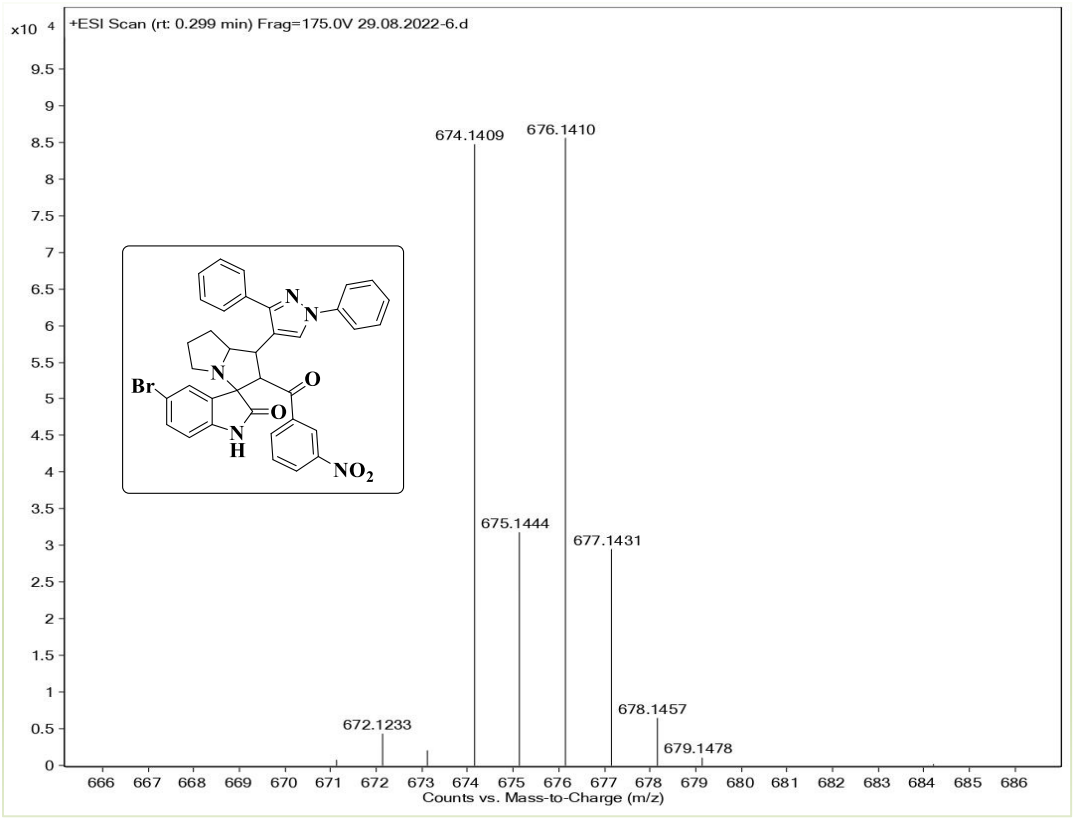
FT-IR Spectrum of the compound 4ad



^{1}H NMR Spectrum of the compound 4ad



^{13}C NMR Spectrum of the compound 4ad



Mass spectrum of the compound 4ad

4. Salient features of crystallographic data of compound 4b

Identification code	**4b**
Empirical formula	$C_{36}H_{29}FN_4O_2$
Formula weight	568.65
Crystal system	Monoclinic
Space group	P 21/n
T (K)	293 K
a (Å)	11.1333(10)
b (Å)	11.4934(10)
c (Å)	22.104(2)
α (°)	90
β (°)	91.270(4)
γ (°)	90
Z	4
V (Å^3)	2827.7 (4)
D_{calc} (g/cm^3)	1.336
F (000)	1192.0
μ (mm^{-1})	0.089
Θ (°)	26.998
Index ranges	-14 ≤ h ≤ 14 -14 ≤ k ≤ 14 -28 ≤ k ≤ 28
N-total	6177
Parameters	389
R_1 *[I > 2 σ (I)]*	0.0414
wR_2 (all data)	0.1027
GOF	1.066
CCDC	2330349

5. In-vitro *MTB* MABA assay

Briefly, the inoculum was prepared from fresh LJ medium re-suspended in 7H9-S medium (7H9 broth, 0.1% casitone, 0.5% glycerol, supplemented oleic acid, albumin, dextrose, and catalase [OADC]), adjusted to a OD_{590} 1.0, and diluted 1:20; 100 µl was used as inoculum. Each drug stock solution was thawed and diluted in 7H9-S at four-fold the final highest concentration tested. Serial two-fold dilutions of each drug were prepared directly in a sterile 96-well microtiter plate using 100 µl 7H9-S. A growth control containing no antibiotic and a sterile control were also prepared on each plate. Sterile water was added to all perimetre wells to avoid evaporation during the incubation. The plate was covered, sealed in plastic bags and incubated at 37ºC in normal atmosphere. After 7 days incubation, 30 µl of alamar blue solution was added to each well, and the plate was re-incubated overnight. A change in colour from blue (oxidised state) to pink (reduced) indicated the growth of bacteria, and the MIC was defined as the lowest concentration of drug that prevented this change in colour.

6. Cytotoxicity, % of inhibition assay

Cytotoxicity was carried out in mouse macrophage cell line (RAW 264.7) at 25 µg/mL concentration. After 48 h of exposure, viability was assessed on the basis of cellular conversion of MTT into a formazan product using the cell proliferation assay. Cells were grown in RPMI medium supplemented with 10% fetal bovine serum (FBS), 10,000 units penicillin and 10 mg streptomycin per mL in T25 flasks to attain 80-90% confluency. Cells were scraped and seeded into wells approx 5,000 cells per well in poly-L-lysine coated plates. The microtiter plates were incubated at 37 ºC, 5% CO_2 and 100% relative humidity for 24 h prior to addition of experimental drugs. The test compounds at 50 µg/mL concentrations were then added to cells and incubated at 37 °C for 48 h; later 10 µL of 0.5 mg/mL concentration of MTT was added and incubated for 3 h at 37 ºC and the final product formazan crystals were measured at 595nm and 625nm.

7. Molecules 4a-4ad with their stereochemical configurations used in silico studies

S. No.	Compound	Name
1	**4a**	(1'S,2'R,3R,7a'R)-2'-benzoyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
2	**4b**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
3	**4c**	(1'S,2'R,3R,7a'R)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
4	**4d**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
5	**4e**	(1'S,2'R,3S,7a'R)-1'-(1,3-dicyclohexyl-1H-pyrazol-4-yl)-2'-(4-nitrobenzoyl)dodecahydrospiro[indole-3,3'-pyrrolizin]-2(1H)-one
6	**4f**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
7	**4g**	(1'R,2'S,3R,7a'R)-1'-(3-(cyclohexa-2,5-dien-1-ylidene)-1-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2'-(tetrahydrofuran-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
8	**4h**	(1'R,2'S,3R,7a'R)-1'-(3-(cyclohexa-2,5-dien-1-ylidene)-1-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2'-(thiophene-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
9	**4i**	(1'S,2'R,3R,7a'R)-2'-benzoyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
10	**4j**	(1'S,2'R,3R,7a'R)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
11	**4k**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1-methyl-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
12	**4l**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
13	**4m**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-methyl-2'-(tetrahydrothiophene-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one

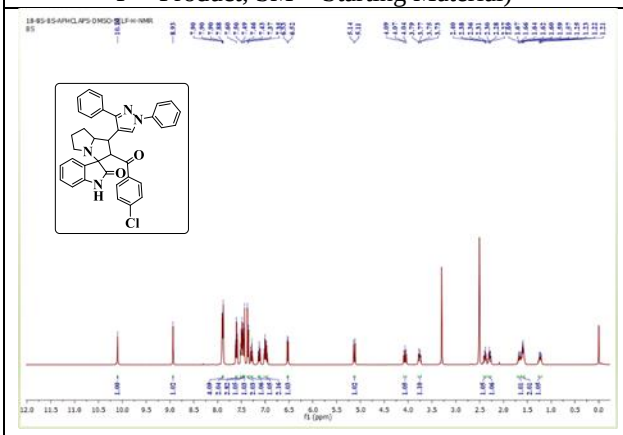
14	**4n**	(1'S,2'R,3R,7a'R)-1-benzyl-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
15	**4o**	(1'S,2'R,3R,7a'R)-1-butyl-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
16	**4p**	(1'S,2'R,3R,7a'R)-2'-(4-bromobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-(prop-2-yn-1-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
17	**4q**	(1'S,2'R,3R,7a'R)-2'-(4-bromobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1-(prop-2-yn-1-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
18	**4r**	(1'S,2'R,3R,7a'R)-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
19	**4s**	(1'S,2'R,3R,7a'R)-2'-(4-bromobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
20	**4t**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
21	**4u**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
22	**4v**	(1'S,2'R,3R,7a'R)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-5-fluoro-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
23	**4w**	(1'R,2'S,3R,7a'R)-1'-(3-(cyclohexa-2,5-dien-1-ylidene)-1-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-5-fluoro-2'-((Z)-furan-2(5H)-ylidene(hydroxy)methyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
24	**4x**	(1'R,2'S,3R,7a'R)-1'-(3-(cyclohexa-2,5-dien-1-ylidene)-1-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-5-fluoro-2'-(thiophene-2-carbonyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
25	**4y**	(1'S,2'R,3R,7a'R)-2'-benzoyl-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
26	**4z**	(1'S,2'R,3R,7a'R)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one

27	**4aa**	(1'S,2'R,3R,7a'R)-5-bromo-2'-(4-chlorobenzoyl)-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
28	**4ab**	(1'S,2'R,3R,7a'R)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
29	**4ac**	(1'S,2'R,3R,7a'R)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(4-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one
30	**4ad**	(1'S,2'R,3R,7a'R)-5-bromo-1'-(1,3-diphenyl-1H-pyrazol-4-yl)-2'-(3-nitrobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one

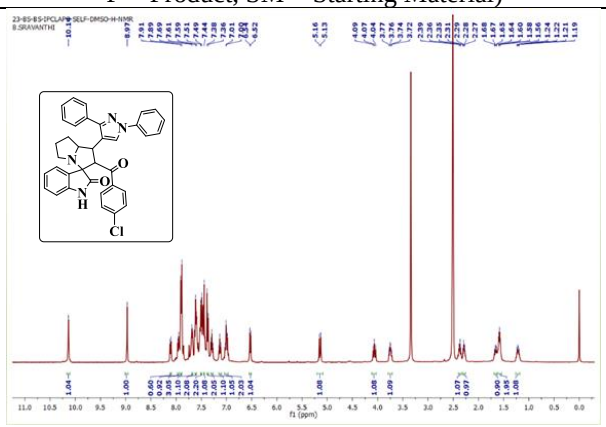
Bulk purity of the synthesized compound 4c; (500 mg and 100 mg scale reactions)

500 mg scale reaction
(TLC: Solvent system: *n*-hexane : EtOAc (7:3)
P = Product, SM = Starting Material)

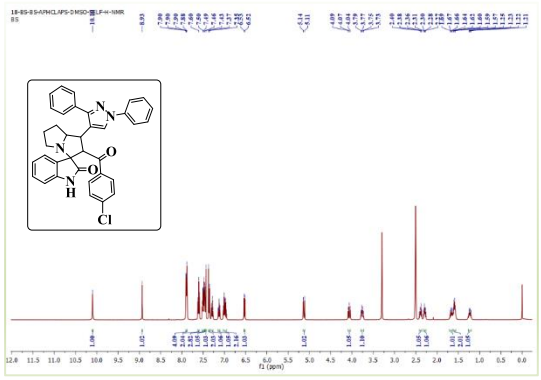
100 mg scale reaction
(TLC: Solvent system: *n*-hexane : EtOAc (7:3)
P = Product, SM = Starting Material)



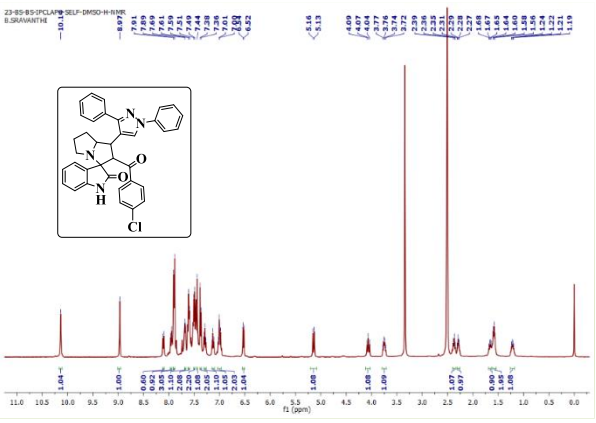
^{1}H NMR Spectrum of the compound **4c**



^{13}C NMR Spectrum of the compound **4c**



^{1}H NMR Spectrum of the compound **4c**



^{13}C NMR Spectrum of the compound **4c**