Supporting information

Graphite Oxide catalyzed one-pot synthesis of highly functionalized spirodibenzo[1,4]diazepine derivatives in aqueous ethanol medium

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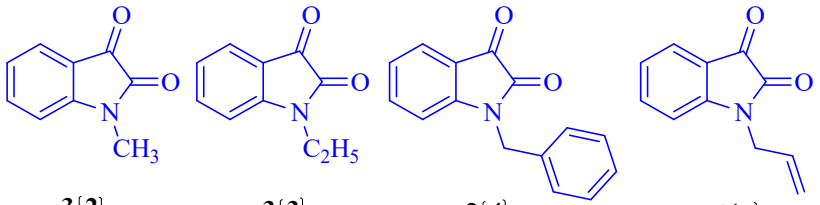
1. General Information

All the necessary chemicals required were purchased from Sigma-Aldrich, Alfa Aesar and Spectrochem and utilized without further purification. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (υ_{max} in cm^{-1}) on KBr disk. ^{1}H NMR and ^{13}C NMR (400, 500 MHz and 100, 125 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in DMSO-d6 and $CDCl_3$ (chemical shifts in δ with TMS as internal standard). ESI-MS spectra were recorded on Xevo TQ-XS, Water mass spectrometer. HRMS spectra were recorded on Waters, Xevo G2-XS QTof Mass Spectrometer. Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis were carried out using a JSM-6360 (JEOL) system. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Powder XRD was recorded on BRUKER AXS, D8 FOCUS instrument. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. Raman analysis was carried out on a Renishaw Basis Series with 514 lasers.

2. Experimental Section

2.1. General procedure for the one-pot two step synthesis of spirodibenzo[1,4]diazepine derivatives. In a 25 ml round bottomed flask, a mixture of 1.2-phenylenediamine (1 mmol) and cyclohexane-1,3-dione (1 mmol) in 4 ml of ethanol:water (1:1) were first stirred at 50 ^{o}C for 2 h. Subsequently, isatin (1 mmol) was added to the same reaction vessel and the reaction mixture was further stirred at that temperature for another 3-6 h to obtain the desired product. After completion of the reaction as monitored by TLC, solvent was removed by evaporation and the reaction mixture was diluted using ethyl acetate (20 ml), and the catalyst was removed by centrifugation followed by filtration. The recovered catalyst was washed with ethyl acetate (3 × 5 ml), ethanol (3 × 5 ml), followed by diethyl ether (3 × 5 ml), and dried at 40 ^{o}C for 6 h, and reused in the next cycle of reaction. The ethyl acetate extracts were washed with water (2 × 10 ml), brine solution (1 × 10 ml) and dried over anhydrous sodium sulphate. Finally, the solvent was removed and the crude product was purified by column chromatography (silica gel 60-120 mesh) using ethylacetate/hexane as eluent.

2.2. General procedure for the synthesis of N-substituted isatin derivatives



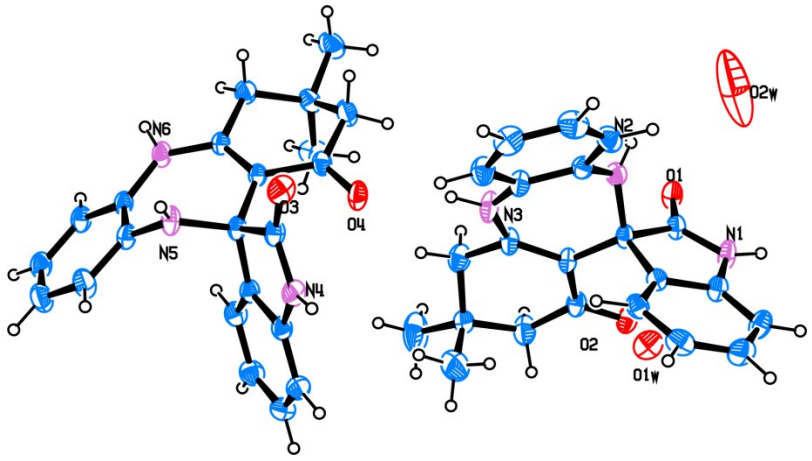
3{2} **3{3}** **3{4}** **3{5}**

The desired isatin derivatives were synthesized by following the previous reported method.[1] Typically, a mixture of isatin (1.5 g, 10.20 mmol), K_2CO_3 (1.68 g, 12.24 mmol) and appropriate alkyl iodide (12.24 mmol for the compound 3{2}), alkyl bromide (12.24 mmol, for the compounds 3{3} and 3{4}) or allyl chloride (12.24 mmol for the compound 3{5}) in 30 ml of acetonitrile was refluxed at 82 ^oC for 24 h. After completion of the reaction time, the reaction mixture was cooled to room temperature and filtered. The filtrate was then concentrated under reduced pressure and the crude solid product was purified by column chromatography (silica gel 60-120 mesh) using ethylacetate/hexane as eluent.

2.3. Single crystal X-ray data for compound 4{121}:

Single crystal for compound **4{121}** was grown from ethanol**.** The X-ray diffraction data were collected at 293 K using BRUKER D8 VENTURE SC-XRD system, equipped with dual X-ray sources (Mo and Cu), Photon II detector. The software's used for data collection was APEX3 and structure confirmation and refinement was SHEXLTL. The structure were solved by using the program SIR-9240 and refined by full matrix least-squares calculations (F2) by using the SHELXL-2018/3 software 41 in WinGX-Version 2021.3.

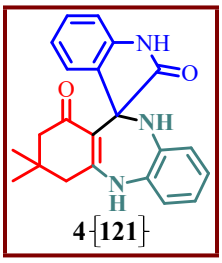
Table S1. X-ray Crystallography data for compound **4{121}** (CCDC 2169839).



Empirical formula	$C_{44}H4_{46}N_6O_6$
Formula weight	754.87
Crystal system	Monoclinic
Space group	P21/n
a(Å)	12.921 (3)
b(Å)	22.128 (5)
c(Å)	14.966 (4)
α(°)	90
β(°)	113.873 (7)
γ(°)	90
Volume ($Å^3$)	3912.8 (16)
ρ (calculated) ($mg\ mm^{-3}$)	1.281
T(K)	293 (2)
Absorption coefficient (μ/mm^{-1})	0.087
Total reflection collected	80405

Independent reflection	10174
θ range (°)	1.753 to 29.029
Final R Indexes [I>=2σ(I)]	R_1 = 0.0838, wR_2 = 0.220
Final R indexes [all data]	R_1 = 0.1501, wR_2 = 0.2658
Goodness-of-fit on F^2	1.023

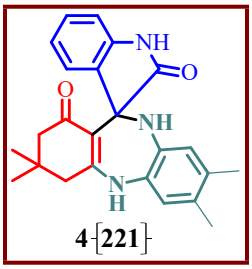
3. Characterization data for products.



4{121}

3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(*2H*)-dione 4{121}.[2]

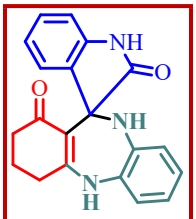
White solid
IR (KBr): 904, 1187, 1231, 1473, 1580, 1612, 3295 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.01 (s, 3H), 1.14 (s, 3H), 1.95-1.92 (m, 1H), 2.09-2.03 (m, 1H), 2.69-2.60 (m, 2H), 5.42 (s, 1H), 6.25 (d, *J* = 7 Hz, 1H), 6.61 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.81-6.77 (m, 2H), 6.91-6.88 (m, 1H), 7.06 (t, *J* = 7.75 Hz, 1H), 7.18 (d, *J* = 8 Hz, 1H), 9.07 (s, 1H), 10.15 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.9, 28.06, 31.8, 45.4, 50.2, 66.4, 108.6, 109.4, 120.33, 120.38, 122.01, 122.09, 123.1, 123.7, 127.6, 133.6, 135.5, 137.7, 143.3, 154.9, 176.6, 192.7
HRMS (ESI, M^+ + H) calcd for $C_{22}H_{21}N_3O_2$ 360.1712, found 360.1706.



4{221}

3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(*2H*)-dione 4{221}.

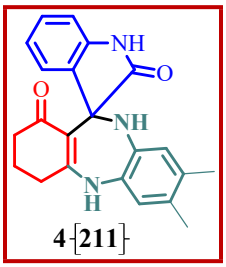
White solid
IR (KBr): 906, 1189, 1238, 1471, 1536, 1625, 3298 cm^{-1}
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 0.93 (s, 3H), 1.07 (s, 3H), 1.87-1.84 (m, 1H), 1.95 (s, 3H), 1.99-1.98 (m, 1H), 2.10 (s, 3H), 2.60-2.54 (m, 2H), 5.12 (s, 1H), 6.21 (d, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 7.00 (t, *J* = 7.75 Hz, 1H), 8.93 (s, 1H), 10.06 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.10, 19.14, 27.8, 28.1, 31.9, 45.4, 50.2, 66.4, 108.4, 109.3, 120.3, 121.3, 122.1, 123.9, 127.5,129.3, 131.1, 131.2, 135.3, 135.6, 143.2, 155.0, 176.7, 192.5.
HRMS (ESI, M^+ + H) calcd for $C_{24}H_{25}N_3O_2$ 388.2025, found 388.2005.



4{111}

3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(*2H*)-dione 4{111}.[2]

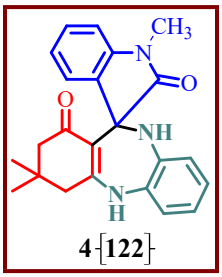
Light brown solid
IR (KBr): 830, 1197, 1259, 1470, 1535, 1619, 3320 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.87-1.84 (m, 2H), 2.01-1.94 (m, 1H), 2.13-2.07 (m, 1H), 2.74-2.67 (m, 2H), 5.39 (s, 1H), 6.21 (d, *J* = 7.5 Hz, 1H), 6.55 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.75-6.71 (m, 2H), 6.86 (t, *J* = 7.25 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8 Hz, 1H), 9.08 (s, 1H), 10.13 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 21.1, 32.0, 36.7, 66.2, 109.2, 109.8, 120.2, 120.3, 122.0, 122.2, 123.1, 123.6, 127.5, 133.6, 135.5, 137.9, 143.3, 156.8, 176.6, 192.9.
HRMS (ESI, M^+ + H) calcd for $C_{20}H_{17}N_3O_2$ 332.1399, found 332.1398.



4{211}

7,8-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{211}.

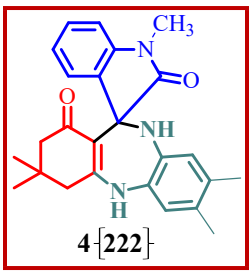
Off white solid
IR (KBr): 880, 1149, 1234, 1471, 1528, 1625, 3327 cm^{-1}
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 1.85-1.82 (m, 2H), 1.93-1.90 (m, 1H), 1.96 (s, 3H), 2.07-2.05 (m, 1H), 2.10 (s, 3H), 2.69-2.64 (m, 2H), 5.11 (s, 1H), 6.23 (d, *J* = 7.2 Hz, 1H), 6.40 (s, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 8.97 (s, 1H), 10.07 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.10, 19.13, 21.1, 32.0, 36.7, 66.2, 109.2, 109.6, 120.3, 121.3, 122.3, 123.9, 127.4, 129.3, 131.0, 131.2, 135.4, 135.6, 143.2, 156.7, 176.8, 192.7.
HRMS (ESI, M^+ + H) calcd for $C_{22}H_{21}N_3O_2$ 360.1712, found 360.1706.



4{122}

1',3,3-trimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{122}.[2]

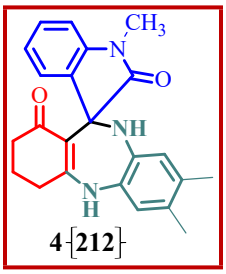
Brown solid
IR (KBr): 900, 1155, 1257, 1495, 1547, 1610, 3304 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 0.95 (s, 3H), 1.10 (s, 3H), 1.89-1.85 (m, 1H), 2.02-1.99 (m, 1H), 2.65-2.57 (m, 2H), 3.14 (s, 3H), 5.47 (s, 1H), 6.20 (d, *J* = 7 Hz, 1H), 6.63-6.59 (m, 2H), 6.75 (t, *J* = 7 Hz, 1H), 6.90-6.84 (m, 2H), 7.11 (t, *J* = 7.25 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 9.07 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 26.6, 27.8, 28.0, 31.9, 45.3, 50.1, 65.9, 108.1, 108.7, 120.5, 120.9, 121.7, 122.0, 123.0, 123.7, 127.6, 133.5, 134.7, 137.8, 144.8, 154.9, 175.1, 192.6.



4{222}

1',3,3,7,8-pentamethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{222}.[4]

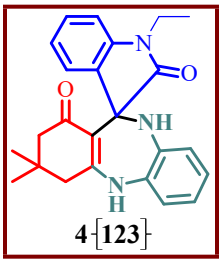
Off white solid
IR (KBr): 896, 1158, 1259, 1528, 1609, 3309 cm^{-1}
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 0.92 (s, 3H), 1.08 (s, 3H), 1.87-1.83 (m, 1H), 1.97 (s, 3H), 2.01-1.99 (m, 1H), 2.11 (s, 3H), 2.62-2.50 (m, 2H), 3.13 (s, 3H), 5.24 (s, 1H), 6.22 (d, *J* = 7 Hz, 1H), 6.37 (s, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8 Hz, 1H), 6.92 (s, 1H), 7.10 (t, *J* = 7.75 Hz, 1H), 8.97 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.13, 19.16, 26.6, 27.9, 28.01, 31.9, 45.4, 50.2, 65.9, 108.06, 108.5, 120.9, 121.4, 121.7, 123.8, 127.5, 129.3, 130.9, 131.3, 134.8, 135.4, 144.8, 154.9, 175.2, 192.3.
HRMS (ESI, M^+ + H) calcd for $C_{25}H_{27}N_3O_2$ 402.2181, found 402.2198.



4{212}

1',7,8-trimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{212}.

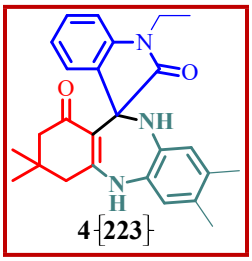
Off white solid
IR (KBr): 883, 1199, 1228, 1473, 1589, 1609, 3296 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.84-1.83 (m, 2H), 1.94-1.90 (m, 1H), 1.96 (s, 3H), 2.08-2.04 (m, 1H), 2.11 (s, 3H), 2.73-2.63 (m, 2H), 3.13 (s, 3H), 5.23 (s, 1H), 6.22 (d, *J* = 7 Hz, 1H), 6.36 (s, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H), 6.91 (s, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 9.03 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.14, 19.15, 21.1, 26.6, 32.0, 36.6, 65.7, 107.9, 109.6, 120.9, 121.4, 121.9, 123.8, 127.5, 129.3, 130.9, 131.3, 134.8, 135.5, 144.8, 156.7, 175.3, 192.5.
HRMS (ESI, M^+ + H) calcd for $C_{23}H_{23}N_3O_2$ 374.1869, found 374.1805.



4{123}

1'-ethyl-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{123}.[2]

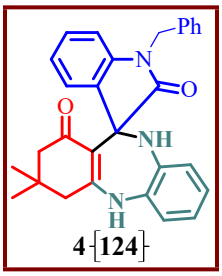
White solid
IR (KBr): 849, 1198, 1234, 1466, 1541, 1608, 3306cm^{-1}
^{1}H NMR (DMSO-d$_6$, 400 MHz)**:** δ 0.79 (s, 3H), 0.94 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.73-1.69 (m, 1H), 1.89-1.85 (m, 1H), 2.51-2.40 (m, 2H), 3.52-3.43 (m, 1H), 3.69-3.60 (m, 1H), 5.29 (s, 1H), 6.07 (d, *J* = 7.2 Hz, 1H), 6.47-6.44 (m, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8 Hz, 1H), 8.93 (s, 1H).
^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 11.7, 27.4, 27.5, 31.4, 33.9, 44.8, 49.5, 65.4, 107.8, 108.1, 119.9, 120.2, 121.4, 121.5, 122.5, 123.2, 127.1, 133.0, 134.3, 137.2, 143.2, 154.3, 174.1, 192.2



4{223}

1'-ethyl-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{223}.

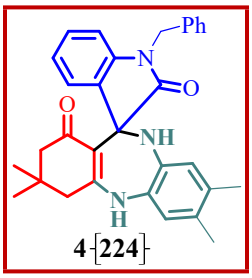
White solid
IR (KBr): 866, 1198, 1232, 1462, 1536, 1613, 3306 cm^{-1}
^{1}H NMR (DMSO-d$_6$, 400 MHz)**:** δ 0.66 (s, 3H), 0.82 (s, 3H), 1.00 (t, *J* = 7.00 Hz, 3H), 1.60-1.56 (m, 1H), 1.70 (s, 3H), 1.77-1.73 (m, 1H), 1.85 (s, 3H), 2.41-2.29 (m, 2H), 3.40-3.31 (m, 1H), 3.56-3.47 (m, 1H), 4.93 (s, 1H), 5.97 (d, *J* = 7.2 Hz, 1H), 6.11 (s, 1H), 6.37 (t, *J* = 7.4 Hz, 1H), 6.65-6.64 (m, 2H), 6.83 (t, *J* = 7.6 Hz, 1H), 8.71 (s, 1H).
^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 12.2, 19.1, 27.8, 28.1, 31.9, 34.4, 45.4, 50.1, 65.9, 108.1, 108.5, 120.7, 121.4, 122.0, 123.8, 127.5, 129.3, 131.0, 131.3, 135.0, 135.2, 143.7, 154.8, 174.7, 192.4
HRMS (ESI, M^{+} + H) calcd for $C_{26}H_{29}N_3O_2$ 416.2338, found 416.2326.



4{124}

1'-benzyl-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{124}.[2]

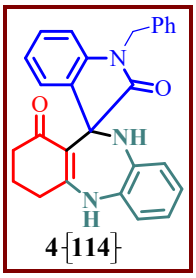
Off white solid
IR (KBr): 856, 1178, 1227, 1486, 1533, 1630, 3318 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.04 (s, 3H), 1.17 (s, 3H), 1.99-1.96 (m, 1H), 2.15-2.12 (m, 1H), 2.75-2.67 (m, 2H), 4.81 (d, *J* = 16.5 Hz, 1H), 5.10 (d, *J* = 16 Hz, 1H), 5.55 (s, 1H), 6.36 (d, *J* = 7 Hz, 1H), 6.60 (d, *J* = 8 Hz, 1H), 6.69-6.65 (m, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8 Hz, 1H), 7.33 (t, *J* = 7.25 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 9.17 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.8, 28.2, 31.8, 43.8, 45.4, 50.1, 66.2, 108.3, 109.0, 120.4, 121.7, 121.8, 122.1, 123.2, 123.8, 127.4, 127.6, 127.8, 128.7, 133.7, 134.6, 137.6, 143.7, 155.2, 175.2, 192.8.



4{224}

1'-benzyl-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{224}.[4]

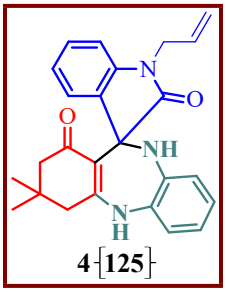
Off white solid
IR (KBr): 847, 1168, 1224, 1491, 1534, 1613, 3311 cm^{-1}
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 0.72 (s, 3H), 0.85 (s, 3H), 1.68-1.64 (m, 1H), 1.73 (s, 3H), 1.84-1.80 (m, 1H), 1.87 (s, 3H), 2.43-2.30 (m, 2H) 4.49 (d, *J* = 16.4 Hz, 1H), 4.80 (d, *J* = 16 Hz, 1H), 5.05 (s, 1H), 6.06 (d, *J* = 7.2 Hz, 1H), 6.15 (s, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 6.40 (t, *J* = 7.6 Hz, 1H), 6.73-6.68 (m, 2H), 7.03-7.00 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 8.79 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 18.6, 27.2, 27.7, 31.4, 43.3, 44.9, 49.6, 65.6, 107.6, 108.4, 120.6, 120.9, 121.3, 123.4, 126.9, 127.3, 128.2, 129.0, 130.7, 130.9, 134.3, 134.6, 136.9, 143.2, 154.7, 174.7, 192.0.
HRMS (ESI, $M^+ + H$) calcd for $C_{31}H_{31}N_3O_2$ 478.2495, found 478.2460.



4{114}

1'-benzyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{114}.

White solid
IR (KBr): 825, 1170, 1221, 1466, 1598, 1616, 3297 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.89 (s, 2H), 2.05-1.99 (m, 1H), 2.17-2.12 (m, 1H), 2.75 (s, 2H), 4.76 (d, *J* = 16.5 Hz, 1H), 5.05-5.02 (d, *J* = 16 Hz, 1H), 5.48 (s, 1H), 6.34 (d, *J* = 7 Hz, 1H), 6.55 (d, *J* = 8 Hz, 1H), 6.65-6.60 (m, 2H), 6.77 (t, *J* = 7.25 Hz, 1H), 6.89 (t, *J* = 7.25 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8 Hz, 1H), 7.27-7.24 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 9.18 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 14.5, 21.0, 32.1, 36.6, 43.8, 66.0, 108.9, 109.4, 120.4, 121.1, 121.9, 122.2, 123.2, 123.8, 127.3, 127.6, 127.7, 128.7, 133.7, 134.6, 137.3, 137.7, 143.7, 157.1, 175.3, 193.1.
HRMS (ESI, M^+ + H) calcd for $C_{27}H_{23}N_3O_2$ 422.1869, found 422.1847.



4{125}

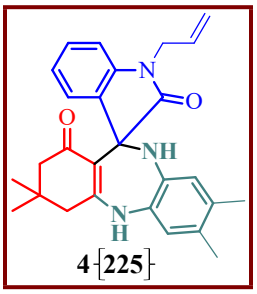
1'-allyl-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{125}.

Off white solid
IR (KBr): 1180, 1221, 1534, 1609, 3304 cm^{-1}
^{1}H NMR (DMSO-d_6 400 MHz)**:** δ 0.96 (s, 3H), 1.09 (s, 3H), 1.90-1.86 (m, 1H), 2.05-2.01 (m, 1H), 2.67-2.56 (m, 2H), 4.22 (dd, *J* = 5.6, 16.4 Hz, 1H), 4.42-4.36 (m, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.46 (brs, 1H), 5.58-5.53 (m, 1H), 5.98-5.89 (m, 1H), 6.25 (d, *J* = 7.2 Hz, 1H), 6.64-6.59 (m,

2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 9.11 (s, 1H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 27.8, 28.1, 31.9, 42.4, 45.3, 50.0, 66.0, 108.4, 109.0, 117.5, 120.4, 121.0, 121.8, 122.1, 123.1, 123.8, 127.6, 133.1, 133.6, 134.6, 137.6, 143.7, 155.1, 174.8, 192.8.

HRMS (ESI, M^+ + H) calcd for $C_{25}H_{27}N_3O_2$ 402.2181, found 402.2162.



4{225}

1'-allyl-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{225}.

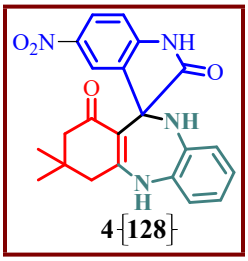
Off white solid

IR (KBr): 868, 1178, 1225, 1593, 1615, 3321 cm^{-1}

^{1}H NMR (DMSO-d_6 400 MHz)**:** δ 0.93 (s, 3H), 1.08 (s, 3H), 1.88-1.84 (m, 1H), 1.96 (s, 3H), 2.04-2.00 (m, 1H), 2.11 (s, 3H), 2.64-2.56 (m, 2H), 4.22-4.17 (m, 1H), 4.40 (d, *J* = 14.8 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 2H), 5.58-5.53 (m, 1H), 5.97-5.91 (m, 1H), 6.26 (d, *J* = 7.2 Hz, 1H), 6.37 (s, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 9.02 (s, 1H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.1, 27.8, 28.1, 31.9, 42.4, 45.4, 50.1, 66.0, 108.3, 108.9, 117.5, 120.9, 121.4, 121.8, 123.9, 127.4, 129.5, 131.0, 131.4, 133.2, 134.8, 135.2, 143.8, 155.1, 174.9, 192.5.

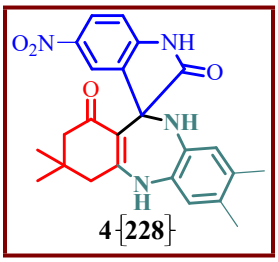
HRMS (ESI, M^+ + H) calcd for $C_{27}H_{29}N_3O_2$ 428.2338, found 428.2337.



4{128}

3,3-dimethyl-5'-nitro-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{128}.[3]

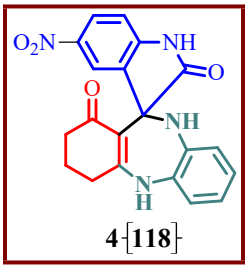
Light yellow solid
IR (KBr): 896, 1185, 1226, 1582, 1610, 3305 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.04 (s, 3H), 1.15 (s, 3H), 2.07-1.96 (m, 2H), 2.73-2.65 (m, 2H), 5.72 (s, 1H), 6.68 (d, *J* = 8 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9 Hz, 2H), 7.24 (d, *J* = 8 Hz, 1H), 8.11-8.09 (m, 1H), 9.30 (s, 1H), 10.98 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.5, 28.2, 31.7, 45.1, 49.8, 66.3, 107.2, 109.4, 116.9, 120.8, 122.8, 123.3, 124.3, 125.4, 133.7, 136.0, 137.2, 141.0, 150.0, 156.1, 176.8, 193.4



4{228}

3,3,7,8-tetramethyl-5'-nitro-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{228}.

Light yellow solid
IR (KBr): 874, 1179, 1224, 1453, 1622, 3328 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.03 (s, 3H), 1.14 (s, 3H), 1.99-1.96 (m, 1H), 2.02 (s, 3H), 2.06-2.03 (m, 1H), 2.17 (s, 3H), 2.70-2.63 (m, 2H), 5.52 (s, 1H), 6.48 (s, 1H), 7.01-6.99 (m, 2H), 7.09-7.08 (m, 1H), 8.11-8.08 (m, 1H), 9.14 (s, 1H), 10.92 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.11, 19.16, 27.8, 28.1, 31.7, 45.2, 49.9, 66.3, 107.1, 109.3, 117.0, 121.7, 124.0, 125.3, 130.0, 131.2, 131.8, 134.8, 136.3, 140.9, 150.1, 155.9, 176.9, 193.0
HRMS (ESI, $M^+ + H$) calcd for $C_{24}H_{24}N_4O_4$ 433.1876, found 433.1868.

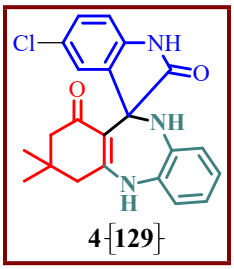


4{118}

5'-nitro-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{118}.

Off white solid
IR (KBr): 839, 1195, 1230, 1456, 1622, 3321 cm^{-1}

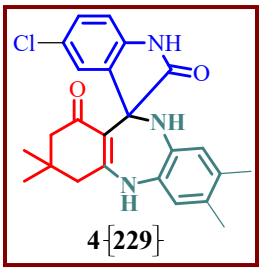
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.93 (s, 2H), 2.17-2.04 (m, 2H), 2.82-2.80 (m, 2H), 5.74 (s, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 7.04-6.96 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 8.10-8.08 (m, 1H), 9.34 (s, 1H), 10.98 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.9, 31.9, 36.4, 66.0, 108.4, 109.3, 117.1, 120.8, 122.7, 123.3, 124.2, 125.3, 133.7, 136.1, 137.4, 141.0, 150.0, 157.9, 176.8, 193.5.
HRMS (ESI, M^+ + H) calcd for $C_{20}H_{16}N_4O_4$ 377.1250, found 377.1172.



4{129}

5'-chloro-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{129}.[2]

Off white solid
IR (KBr): 817, 1184, 1288, 1584, 1620, 3305 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.03 (s, 3H), 1.14 (s, 3H), 2.07-1.96 (m, 2H), 2.66 (s, 2H), 5.58 (s, 1H), 6.157-6.153 (m, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.85-6.81 (m, 2H), 6.96 (t, *J* = 7 Hz, 1H), 7.12-7.10 (m, 1H), 7.20 (d, *J* = 8 Hz, 1H), 9.15 (s, 1H), 10.33 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.7, 28.2, 31.7, 45.2, 50.0, 66.6, 107.9, 110.6, 120.5, 121.9, 122.3, 123.2, 123.9, 124.1, 127.2, 133.6, 137.4, 137.5, 142.2, 155.4, 176.2, 193.0.
HRMS (ESI, M^+ + H) calcd for $C_{22}H_{20}ClN_3O_2$ 394.1322, 396.1302 found 394.1333, 396.1261.

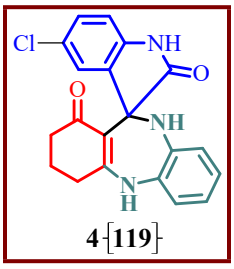


4{229}

5'-chloro-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{229}.

Off white solid
IR (KBr): 814, 1180, 1290, 1585, 1620, 3303 cm^{-1}

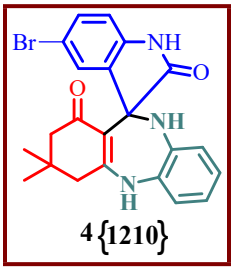
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 0.71 (s, 3H), 0.82 (s, 3H), 1.71-1.62 (m, 2H), 1.73 (s, 3H), 1.86 (s, 3H), 2.32 (s, 2H), 5.08 (s, 1H), 5.90-5.89 (m, 1H), 6.18 (s, 1H), 6.49 (d, *J* = 8 Hz, 1H), 6.65 (s, 1H), 6.81-6.78 (m, 1H), 8.73 (s, 1H), 9.99 (s, 1H)
^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.11, 19.19, 27.9, 28.0, 31.7, 45.3, 50.1, 66.7, 107.7, 110.6, 121.4, 121.9, 123.9, 124.1, 127.2, 129.6, 131.1, 131.5, 134.9, 137.6, 142.3, 155.3, 176.4, 192.7
HRMS (ESI, M^+ + H) calcd for $C_{24}H_{24}ClN_3O_2$ 422.1635, 424.1616, found 422.1695, 424.1605.



4{119}

5'-chloro-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{119}.

Off white solid
IR (KBr): 874, 1196, 1234, 1582, 1617, 3338 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 1.86 (s, 2H), 2.08-1.98 (m, 2H), 2.72 (s, 2H), 5.53 (s, 1H), 6.13 (s, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.78-6.74 (m, 2H), 6.90 (t, *J* = 7.25 Hz, 1H), 7.14-7.04 (m, 2H), 9.15 (s, 1H), 10.29 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.9, 31.9, 36.6, 66.4, 109.0, 110.5, 120.5, 122.0, 122.3, 123.2, 123.9, 124.2, 127.2, 133.6, 137.4, 137.6, 142.2, 157.3, 176.3, 193.2.
HRMS (ESI, M^+ + H) calcd for $C_{20}H_{16}N_3O_2$ 332.1399, found 332.1398.

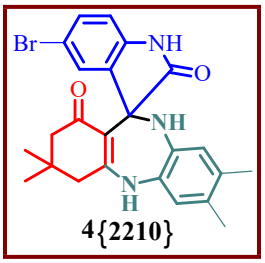


4{1210}

5'-bromo-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{1210}.[2]

White solid
IR (KBr): 875, 1181, 1228, 1474, 1583, 1613, 3300 cm^{-1}

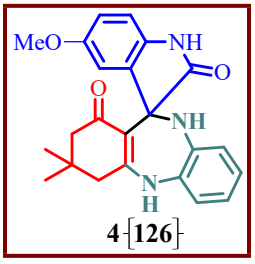
^{1}H NMR (DMSO-d_6, 400 MHz)**:** δ 0.98 (s, 3H), 1.09 (s, 3H), 2.02-1.91 (m, 2H), 2.616-2.613 (m, 2H), 5.55 (s, 1H), 6.226-6.221 (m, 1H), 6.67-6.65 (m, 1H), 6.73-6.71 (m, 1H), 6.81-6.77 (m, 1H), 6.91-6.87 (m, 1H), 7.15-7.12 (m, 1H), 7.19-7.17 (m, 1H), 9.09 (s, 1H), 10.30 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 27.7, 28.2, 31.7, 45.2, 50.0, 66.6, 107.8, 111.2, 111.9, 120.5, 122.3, 123.3, 123.9, 124.6, 130.1, 133.6, 137.5, 137.8, 142.6, 155.3, 176.1, 192.9.



4{2210}

5'-bromo-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{2210}.

White solid
IR (KBr): 873, 1182, 1227, 1475, 1586, 1616, 3328 cm^{-1}
^{1}H NMR ($CDCl_3$, 500 MHz)**:** δ 1.08 (s, 3H), 1.16 (s, 3H), 2.04 (s, 1H), 2.08 (s, 3H), 2.10 (s, 1H), 2.17 (s, 3H), 2.46-2.43 (m, 1H), 2.63-2.60 (m, 1H), 6.30 (s, 1H), 6.50 (s, 1H), 6.57 (s, 1H), 6.68 (s, 1H), 6.73 (d, J = 8.0 Hz, 1H), 7.23-7.21 (m, 1H), 7.36 (s, 1H), 8.03 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.9, 19.0, 27.9, 28.2, 31.8, 47.1, 49.7, 67.0, 111.2, 114.2, 121.1, 124.6, 125.9, 128.3, 130.9, 131.9, 132.9, 133.4, 135.7, 140.2, 154.5, 176.8, 194.2.
HRMS (ESI, M^+ + H) calcd for $C_{24}H_{24}BrN_3O_2$ 466.1130, 468.1113 found 466.1072, 468.1018.

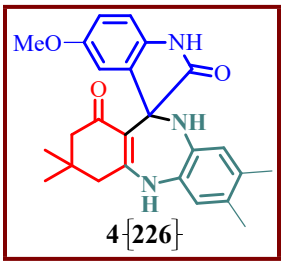


4{126}

5'-methoxy-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{126}.

White solid
IR (KBr): 846, 1162, 1203, 1473, 1584, 1605, 3328 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 0.97 (s, 3H), 1.09 (s, 3H), 1.91-1.88 (m, 1H), 2.04-1988 (m, 1H), 2.63-2.55 (m, 2H), 3.41 (s, 3H), 5.36 (s, 1H), 5.786-5.782 (m, 1H), 6.59-6.56 (m, 1H), 6.66

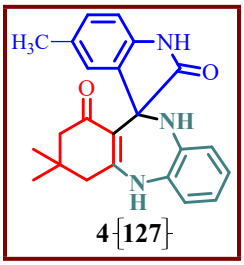
(t, J = 9 Hz, 2H), 6.77 (t, J = 7.25 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 9.01 (s, 1H), 9.94 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.9, 28.0, 31.8, 45.3, 50.2, 55.4, 66.7, 108.5, 109.3, 109.8, 111.5, 120.3, 122.0, 123.2, 123.7, 133.6, 136.7, 136.8, 137.7, 153.8, 154.9, 176.5, 192.7.
HRMS (ESI, M^+ + H) calcd for $C_{23}H_{23}N_3O_2$ 390.1818, found 390.1804.



4{226}

5'-methoxy-3,3,7,8-tetramethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{226}.

White solid
IR (KBr): 884, 1165, 1293, 1494, 1628, 3326 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz)**:** δ 0.95 (s, 3H), 1.07 (s, 3H), 1.88-1.84 (m, 1H), 1.98 (s, 3H), 2.03 (s, 1H), 2.10 (s, 3H), 2.61-2.54 (m, 2H), 3.43 (s, 3H), 5.09 (s, 1H), 5.82 (s, 1H), 6.42 (s, 1H), 6.59-6.56 (m, 1H), 6.65-6.63 (m, 1H), 6.89 (s, 1H), 8.88 (s, 1H), 9.89 (s, 1H)
^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.0, 19.1, 27.8, 28.2, 31.8, 45.4, 50.2, 55.5, 66.8, 108.3, 109.2, 110, 111.3, 121.3, 124.0, 129.3, 131.2, 135.2, 136.8, 136.9, 153.8, 154.8, 176.7, 192.4.
HRMS (ESI, M^+ + H) calcd for $C_{25}H_{27}N_3O_2$ 418.2131, found 418.2108.

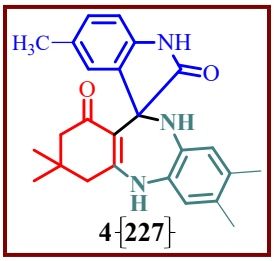


4{127}

3,3,5'-trimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{127}.[2]

White solid
IR (KBr): 883, 1158, 1206, 1583, 1619, 3303 cm^{-1}
^{1}H NMR (DMSO-d_6+$CDCl_3$, 400 MHz)**:** δ 0.99 (s, 3H), 1.10 (s, 3H), 1.91-1.87 (m, 1H), 1.97 (s, 3H), 2.03-1.99 (m, 1H), 2.59-2.58 (m, 2H), 5.21 (s, 1H), 6.03 (s, 1H), 6.64-6.60 (m, 2H), 6.73 (t, J = 8 Hz, 1H), 6.84-6.77 (m, 2H), 7.11 (d, J = 7.6 Hz, 1H), 8.95 (s, 1H), 9.98 (s, 1H).

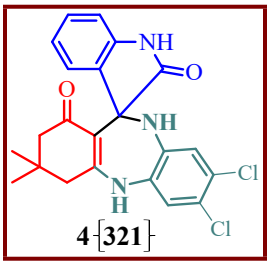
^{13}C NMR (DMSO-d_6, 100 MHz): δ 21.1, 27.8, 31.7, 45.5, 50.2, 66.7, 108.5, 108.9, 120.3, 121.8, 123.0, 123.1, 123.5, 127.6, 128.7, 133.6, 135.5, 137.7, 140.8, 154.8, 176.8, 192.6.



4{227}

3,3,5',7,8-pentamethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{227}.

White solid
IR (KBr): 885, 1158, 1204, 1585, 1621, 3298 cm^{-1}
^{1}H NMR (DMSO-d_6 400 MHz)**:** δ 0.97 (s, 3H), 1.07 (s, 3H), 1.89-1.84 (m, 1H), 1.97 (s, 3H), 1.98 (s, 3H), 2.00-1.99 (m, 1H), 2.11 (s, 3H), 2.56-2.55 (m, 2H), 5.05 (s, 1H), 6.07 (s, 1H), 6.41 (s, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.81-6.79 (m, 1H), 6.88 (s, 1H), 8.87 (s, 1H), 9.96 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 19.14, 19.19, 21.2, 27.9, 28.1, 31.7, 45.4, 50.2, 66.7, 108.3, 108.9, 121.2, 123.0, 123.9, 127.7, 128.6, 129.1, 131.10, 131.17, 135.3, 135.8, 140.9, 154.7, 176.9, 192.5.
HRMS (ESI, M^+ + H) calcd for $C_{25}H_{27}N_3O_2$ 402.2181, found 402.2162.

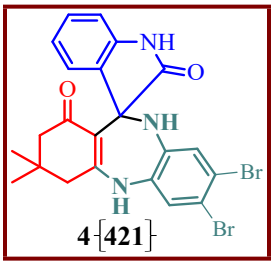


4{321}

7,8-dichloro-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{321}.

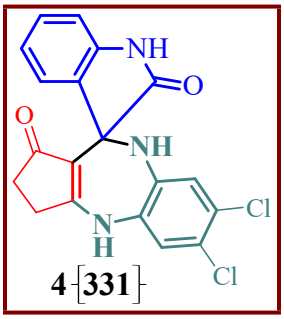
Off white solid
IR (KBr): 582, 746, 841, 1542, 1619, 3301 cm^{-1}
^{1}H NMR (DMSO-d_6 500 MHz)**:** δ 0.97 (s, 3H), 1.08 (s, 3H), 1.92-1.89 (m, 1H), 2.06-2.03 (m, 1H), 2.63-2.53 (m, 2H), 5.88 (s, 1H), 6.36 (d, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.34 (s, 1H), 9.14 (s, 1H), 10.24 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.7, 28.1, 31.8, 45.2, 50.1, 66.1, 109.2, 109.6, 120.7, 121.1, 122.0, 122.7, 123.3, 124.3, 128.0, 133.9, 135.0, 138.1, 143.4, 154.1, 176.3, 193.2.

HRMS (ESI, $M^+ + H$) calcd for $C_{22}H_{19}Cl_2N_3O_2$ 428.0933, found 428.0932, 430.0897.



7,8-dibromo-3,3-dimethyl-3,4,5,10-tetrahydrospiro[dibenzo[b,e][1,4]diazepine-11,3'-indoline]-1,2'(2H)-dione 4{421}.

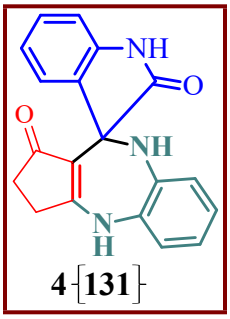
Light orange solid
IR (KBr): 575, 748, 803, 1571, 1615, 3311 cm^{-1}
^{1}H NMR (DMSO-d_6 500 MHz)**:** δ 0.96 (s, 3H), 1.07 (s, 3H), 1.91-1.88 (m, 1H), 2.06-1.99 (m, 1H), 2.62-2.55 (m, 2H), 5.86 (s, 1H), 6.36 (d, *J* = 7.0 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 7.07-7.04 (m, 2H), 7.46 (s, 1H), 9.13 (s, 1H), 10.22 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.6, 28.1, 31.1, 31.8, 45.2, 50.1, 66.1, 109.2, 114.6, 116.4, 120.8, 122.0, 124.0, 126.3, 128.0, 134.4, 135.0, 138.6, 143.4, 154.1, 176.3, 193.2.
ESI-MS, m/z 517 (M^+) and 519 ($M^+ + 2$).



6,7-dichloro-2,3-dihydro-1H-spiro[benzo[b]cyclopenta[e][1,4]diazepine-10,3'-indoline]-1,2'(4H,9H)-dione 4{331}

White solid
IR (KBr): 557, 826, 1187, 1226, 1552, 1675, 3319 cm^{-1}
^{1}H NMR (DMSO-d_6 400 MHz)**:** δ 2.22-2.17 (m, 2H), 2.77-2.75 (m, 2H), 6.08 (s, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 6.82-6.76 (m, 2H), 7.08 (s, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 10.08 (s, 1H), 10.47 (s, 1H).
^{13}C NMR (DMSO-d_6, 100 MHz): δ 27.5, 33.2, 64.0, 109.8, 112.4, 120.6, 121.5, 122.4, 123.4, 123.7, 124.1, 128.6, 132.6, 132.7, 137.4, 143.3, 166.3, 175.5, 199.1.

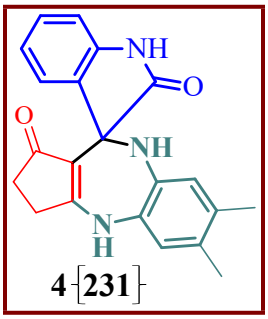
ESI-MS, m/z 386 (M^+) and 388 ($M^+ + 2$).



4{131}

2,3-dihydro-1H-spiro[benzo[b]cyclopenta[e][1,4]diazepine-10,3'-indoline]-1,2'(4H,9H)-dione 4{131}.

Off white solid
IR (KBr): 826, 1157, 1228, 1555, 1661, 3289 cm^{-1}
^{1}H NMR (DMSO-d_6 500 MHz)**:** δ 2.40-2.22 (m, 2H), 2.86 (brs, 2H), 5.74 (s, 1H), 6.46 (d, *J* = 7.0 Hz, 1H), 6.79 (t, *J* = 7.0 Hz, 1H), 6.89 (brs, 3H), 6.98 (brs, 1H), 7.22-7.16 (m, 2H), 10.01 (s, 1H), 10.45 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 32.3, 37.9, 68.9, 114.4, 117.0, 124.7, 125.8, 126.4, 127.9, 128.2, 128.4, 132.9, 137.4, 138.3, 141.9, 148.1, 171.6, 180.3, 203.5.
ESI-MS, m/z 318 ($M^+ + H$).



4{231}

6,7-dimethyl-2,3-dihydro-1H-spiro[benzo[b]cyclopenta[e][1,4]diazepine-10,3'-indoline]-1,2'(4H,9H)-dione 4{231}

Off wzhite solid
IR (KBr): 871, 1186, 1246, 1557, 1660, 3335 cm^{-1}
^{1}H NMR (DMSO-d_6 500 MHz)**:** δ 2.0 (s, 3H), 2.12 (s, 3H), 2.28-2.18 (m, 2H), 2.74-2.70 (m, 2H), 5.39 (s, 1H), 6.35 (d, *J* = 7.5 Hz, 1H), 6.55 (s, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 9.78 (s, 1H), 10.31 (s, 1H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.07, 19.12, 27.5, 33.0, 64.2, 112.2, 120.9, 121.0, 123.2, 124.5, 128.0, 129.1, 130.2, 131.0, 133.8, 134.7, 143.3, 166.8, 175.5, 198.6.

HRMS (ESI, $M^+ + H$) calcd for $C_{21}H_{19}N_3O_2$ 346.1556, found 346.1552.

4. References

1 S. Lee, Y. Lim, Y. Jeon, M. A. Hossain, H. Jang, Y. Cho and W.-G. Kim, *Int. J. Hydrog. Energy* 2015, **40,** 5390-5395.

2 K. De, P. Bhanja, A. Bhaumik and C. Mukhopadhyay, *ChemCatChem.*, 2018, **10,** 590-600.

3 S. K. Maury, D. Kumar, A. Kamal, H. K. Singh, S. Kumari and S. Singh, *Mol. Divers.,* 2021, **25,** 131-142.

4 Y. Wang, F. Shi, X.-X. Yao, M. Sun, L. Dong and S.-J. Tu, *Chem. Eur. J.,* 2014, **20,** 15047-15052.

5. ^{1}H and ^{13}C NMR Spectra

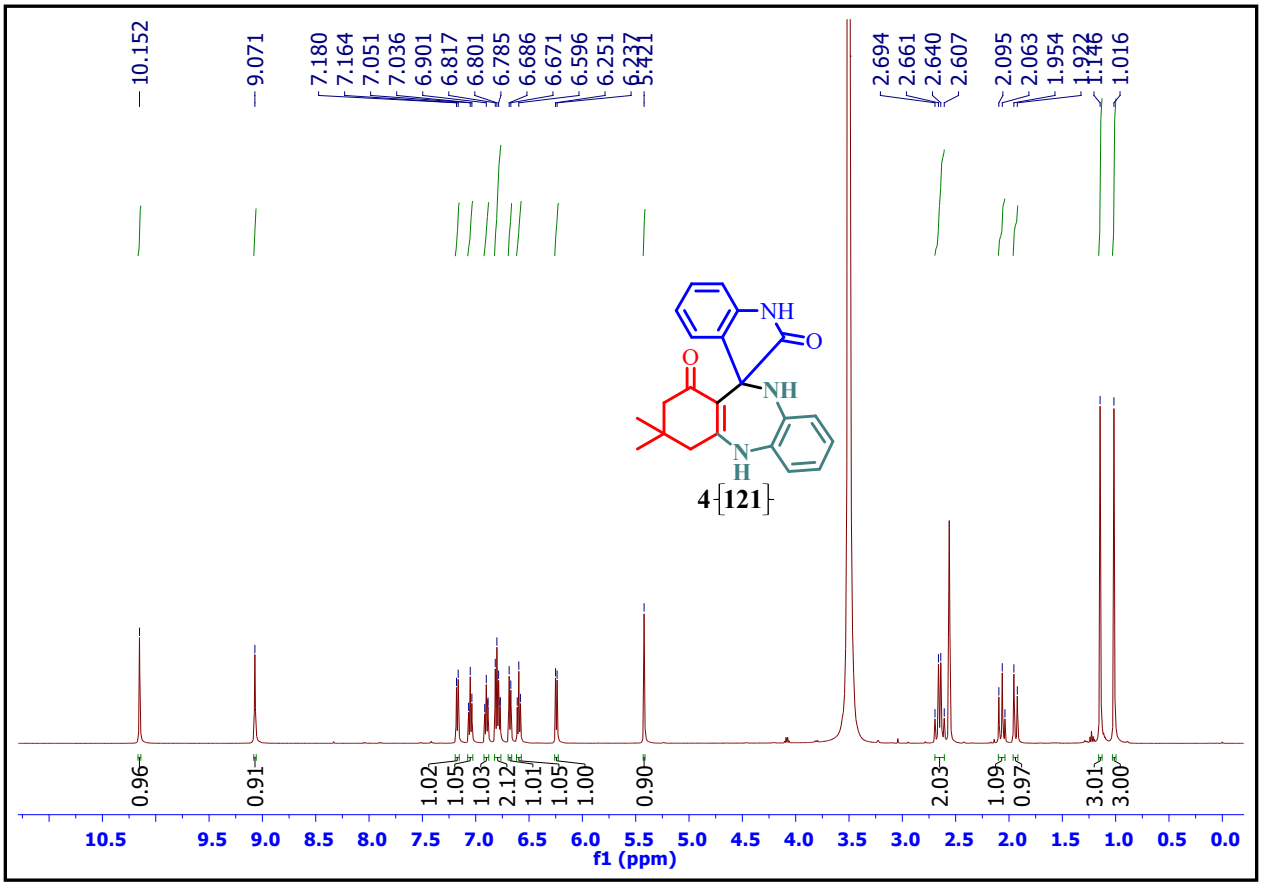


Figure S1.^{1}H NMR spectra of **4{121}** in DMSO-d6.

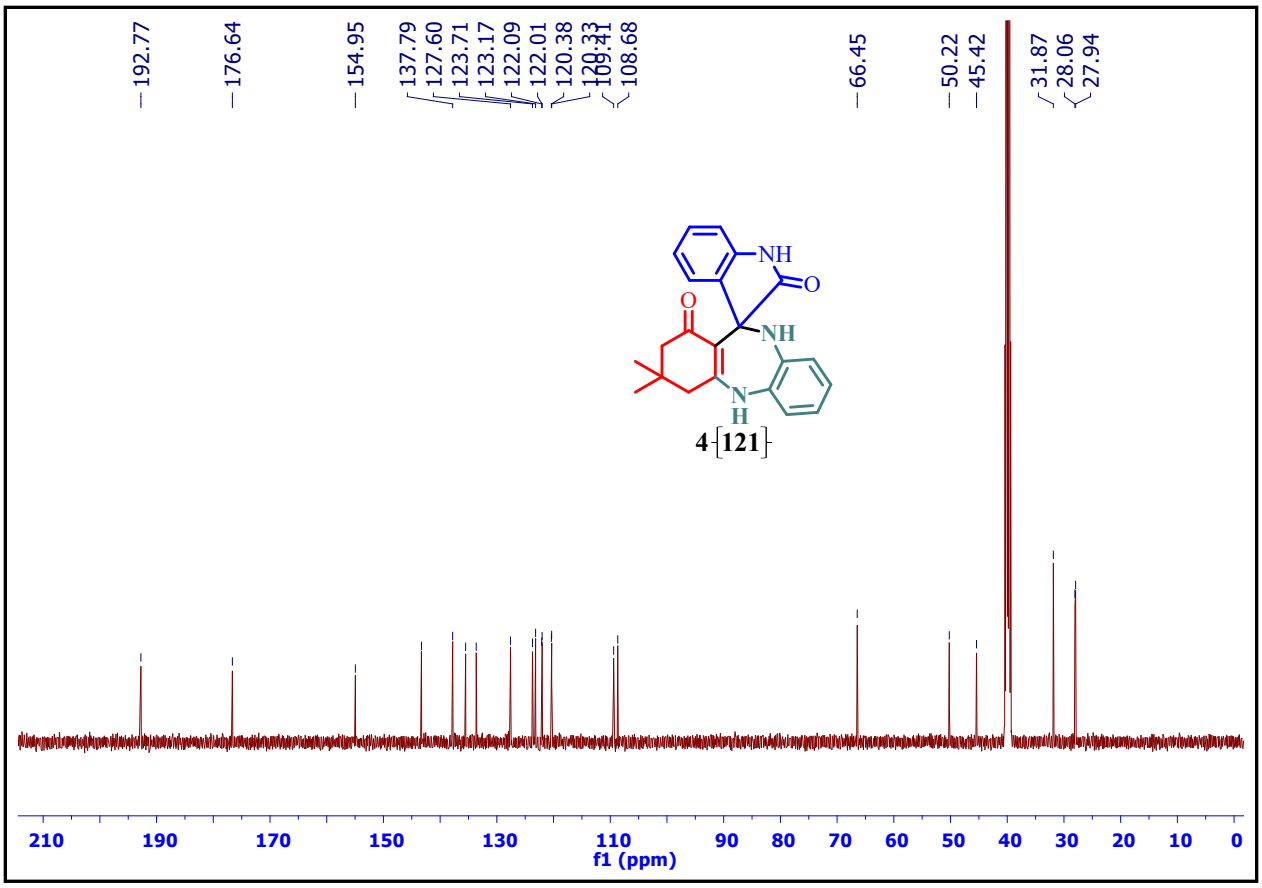


Figure S2.^{13}C NMR spectra of**4 {121}** in DMSO-d6.

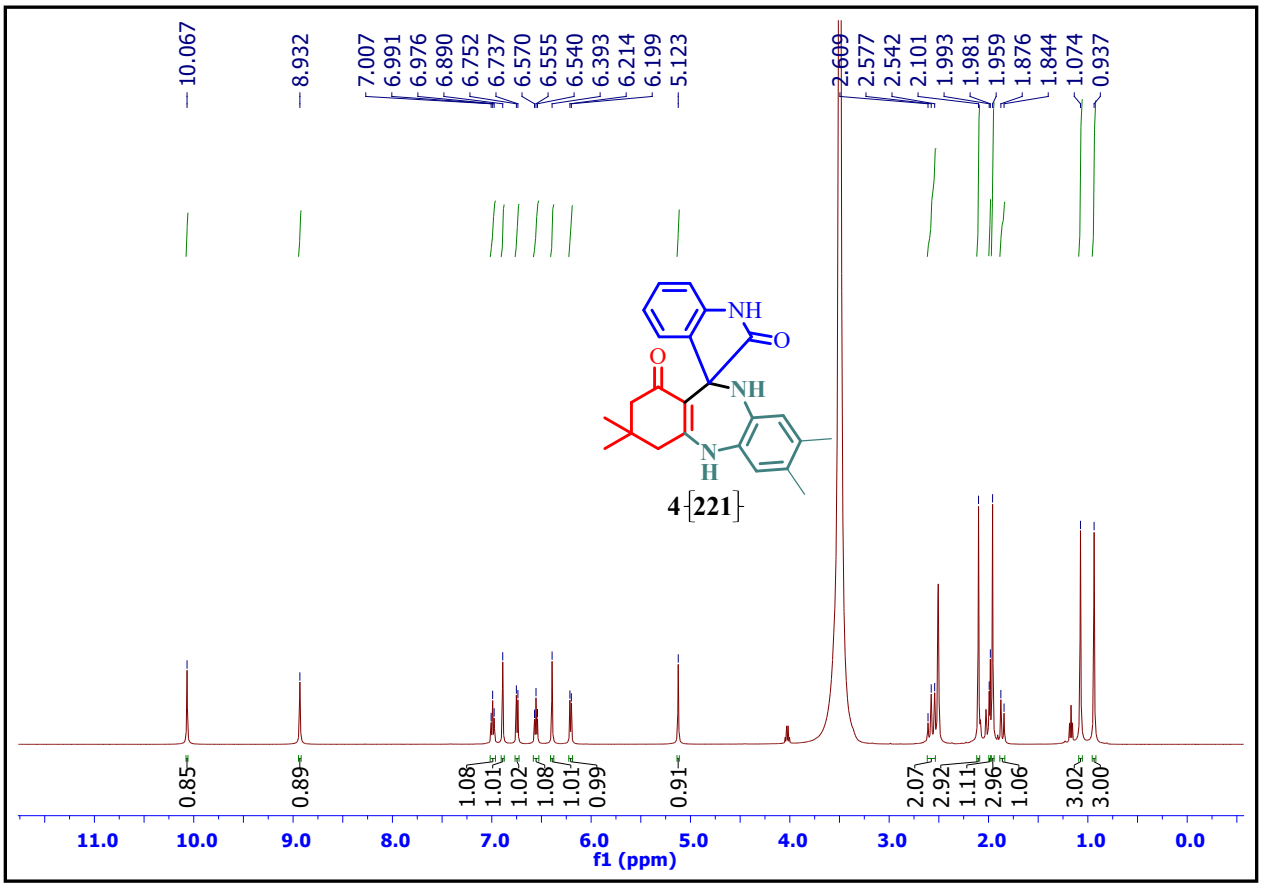


Figure S3.[1]H NMR spectra of **4{221}** in DMSO-d6.

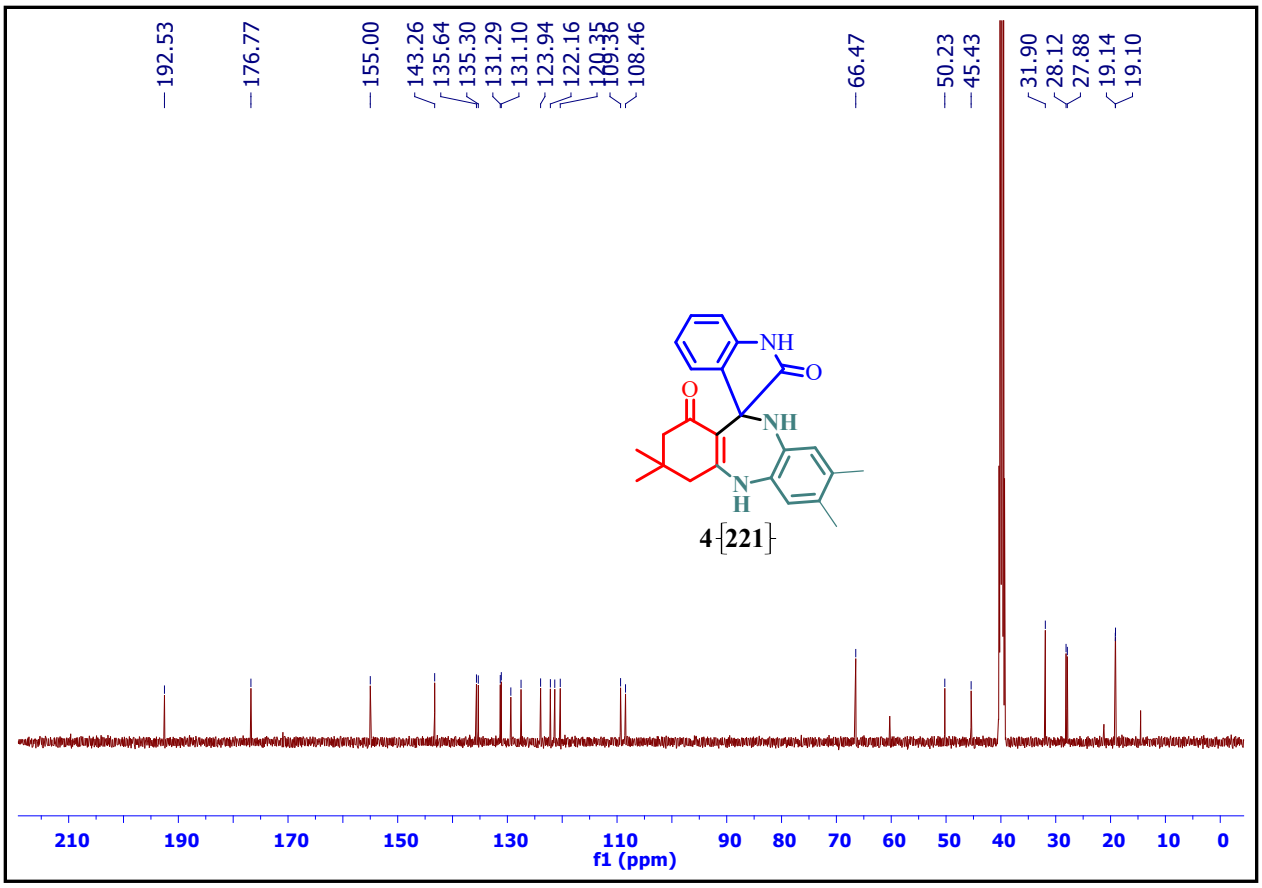


Figure S4. ^{13}C NMR spectra of in **4{221}** DMSO-d6.

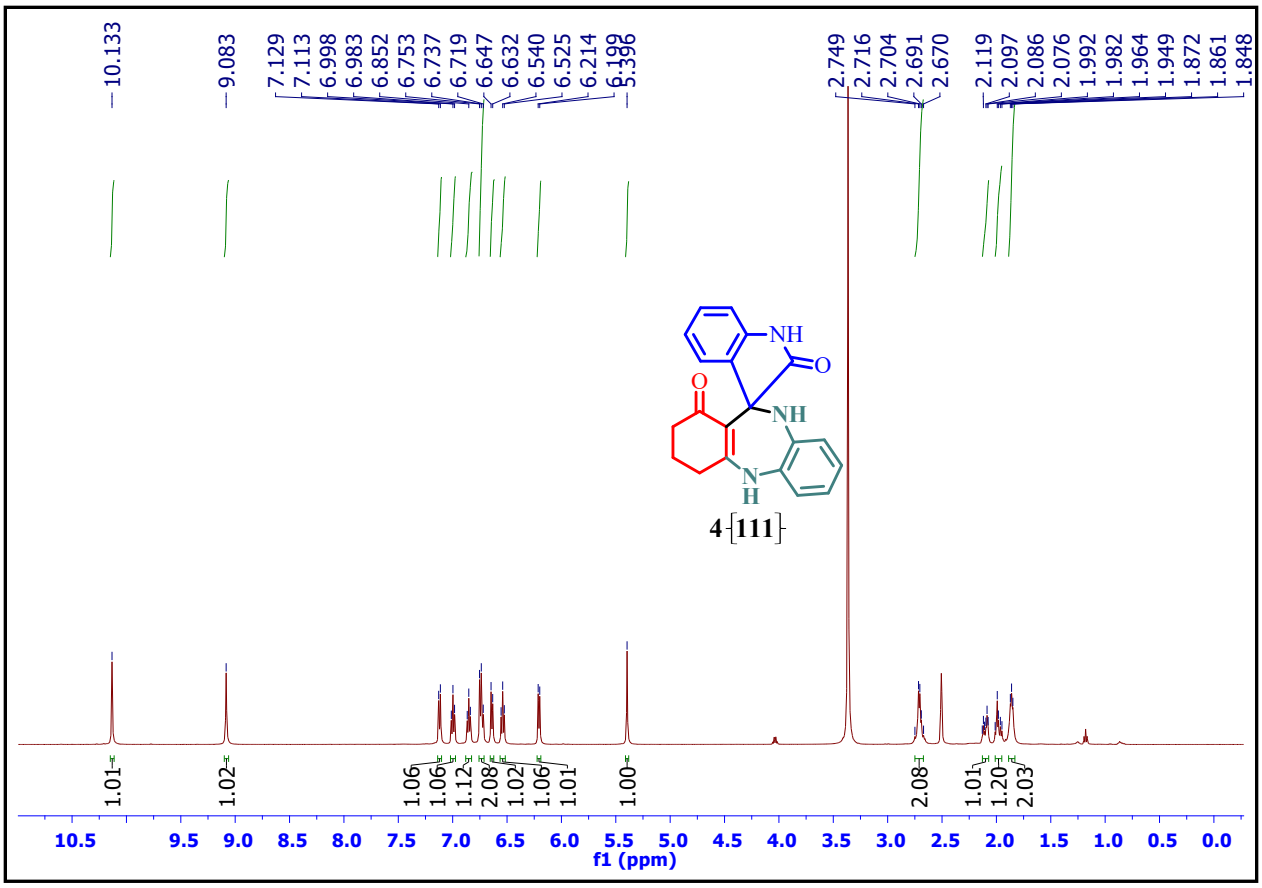


Figure S5. ^{1}H NMR spectra of **4{111}** in DMSO-d6.

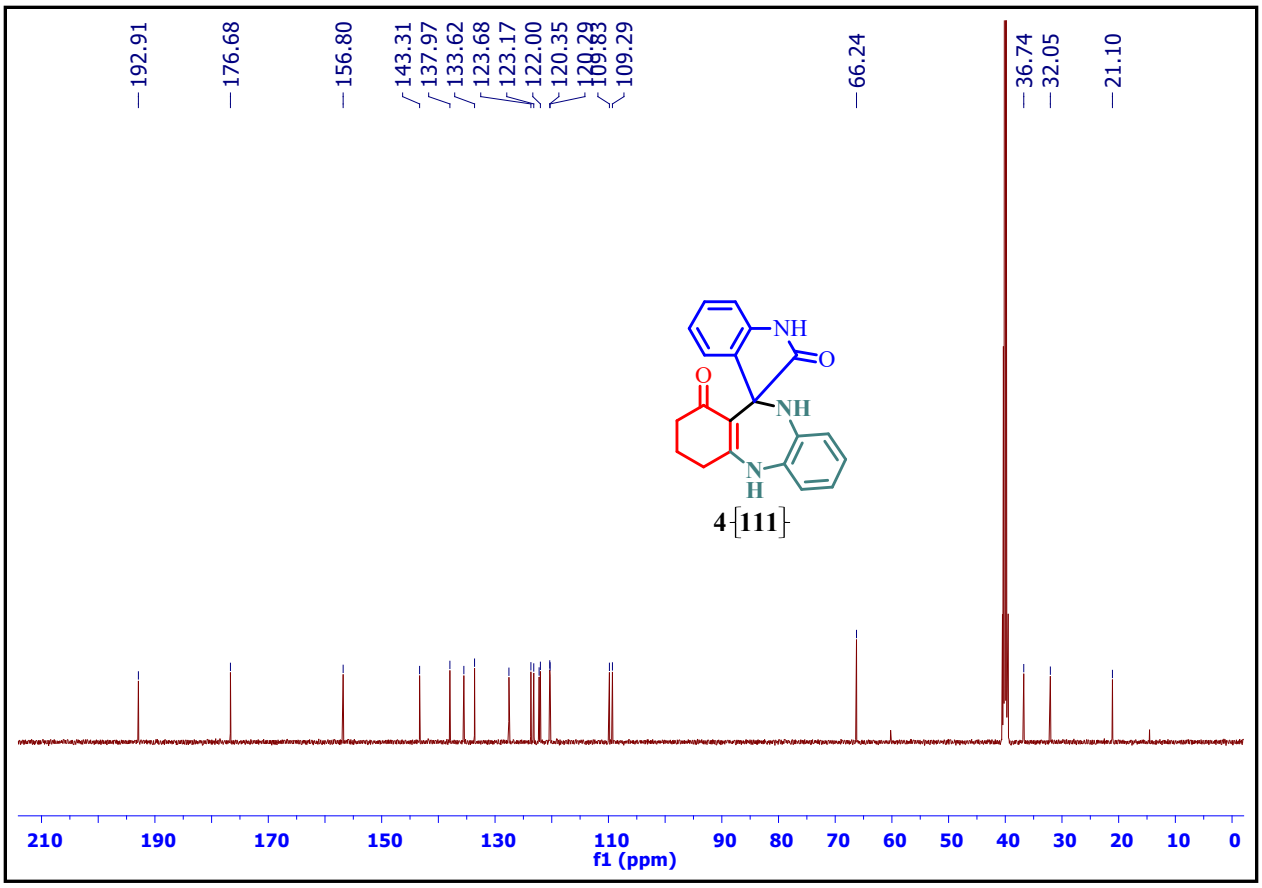


Figure S6. ^{13}C NMR spectra of **4{111}** in DMSO-d6.

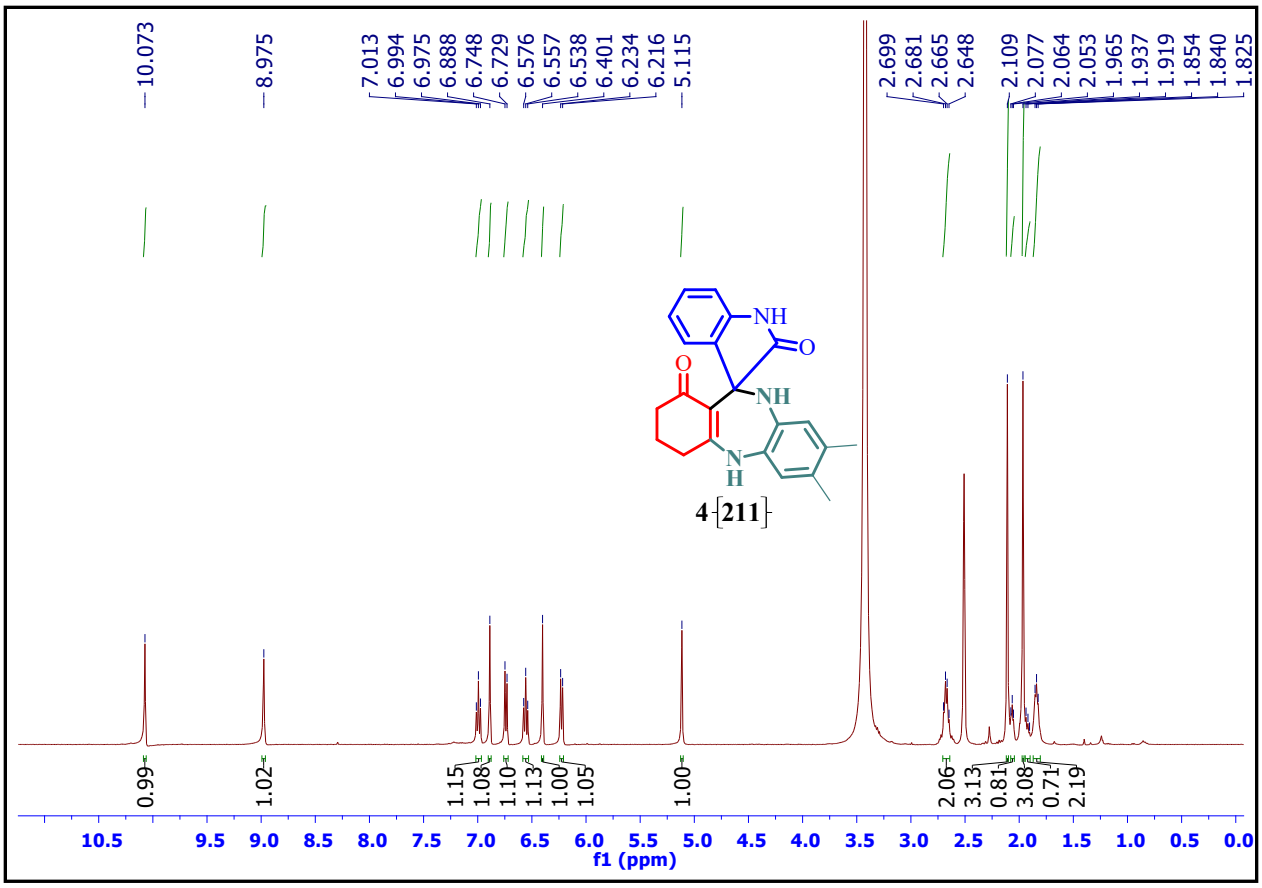


Figure S7.[1]H NMR spectra of **4{211}** in DMSO-d6.

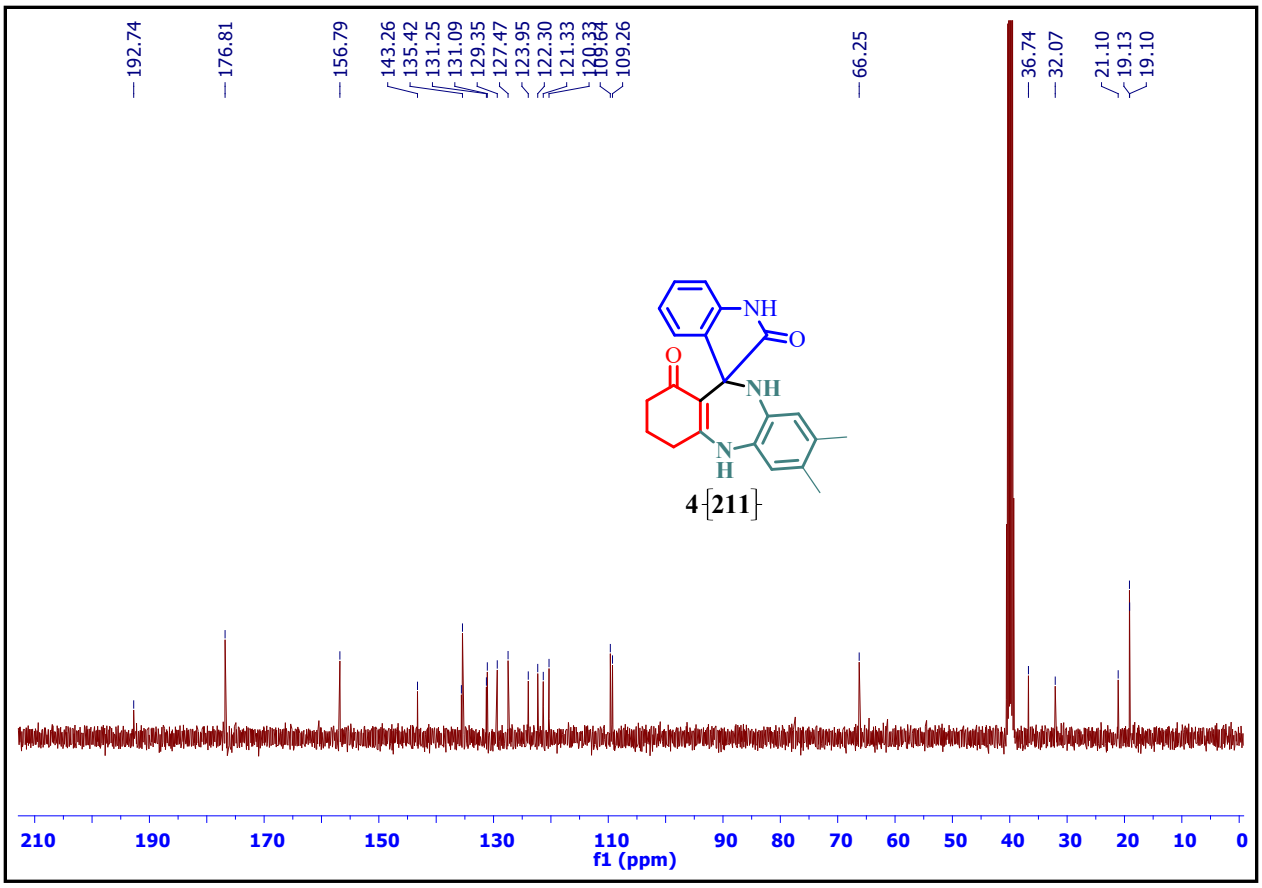


Figure S8. ^{13}C NMR spectra of **4{211}** in DMSO-d6.

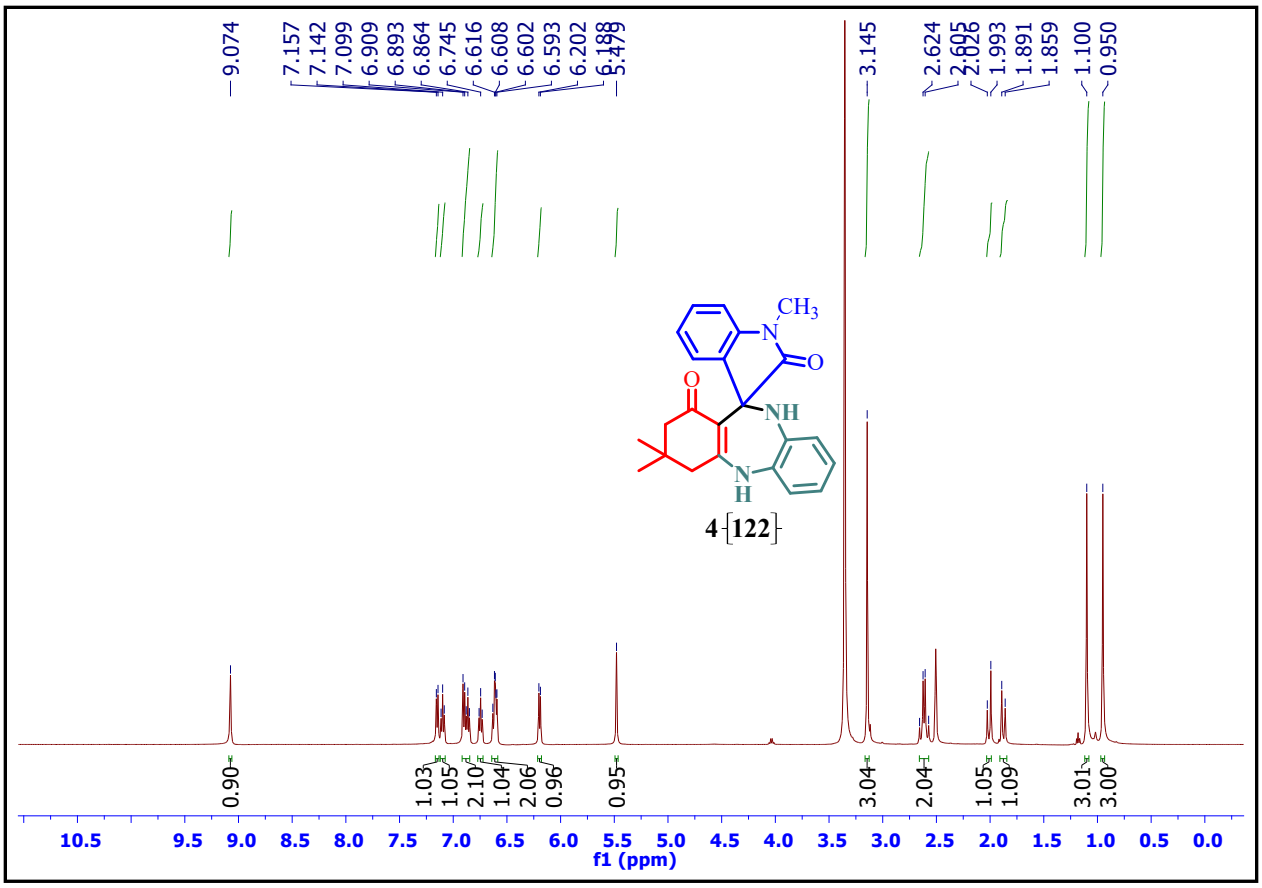


Figure S9.[1]H NMR spectra of **4{122}** in DMSO-d6.

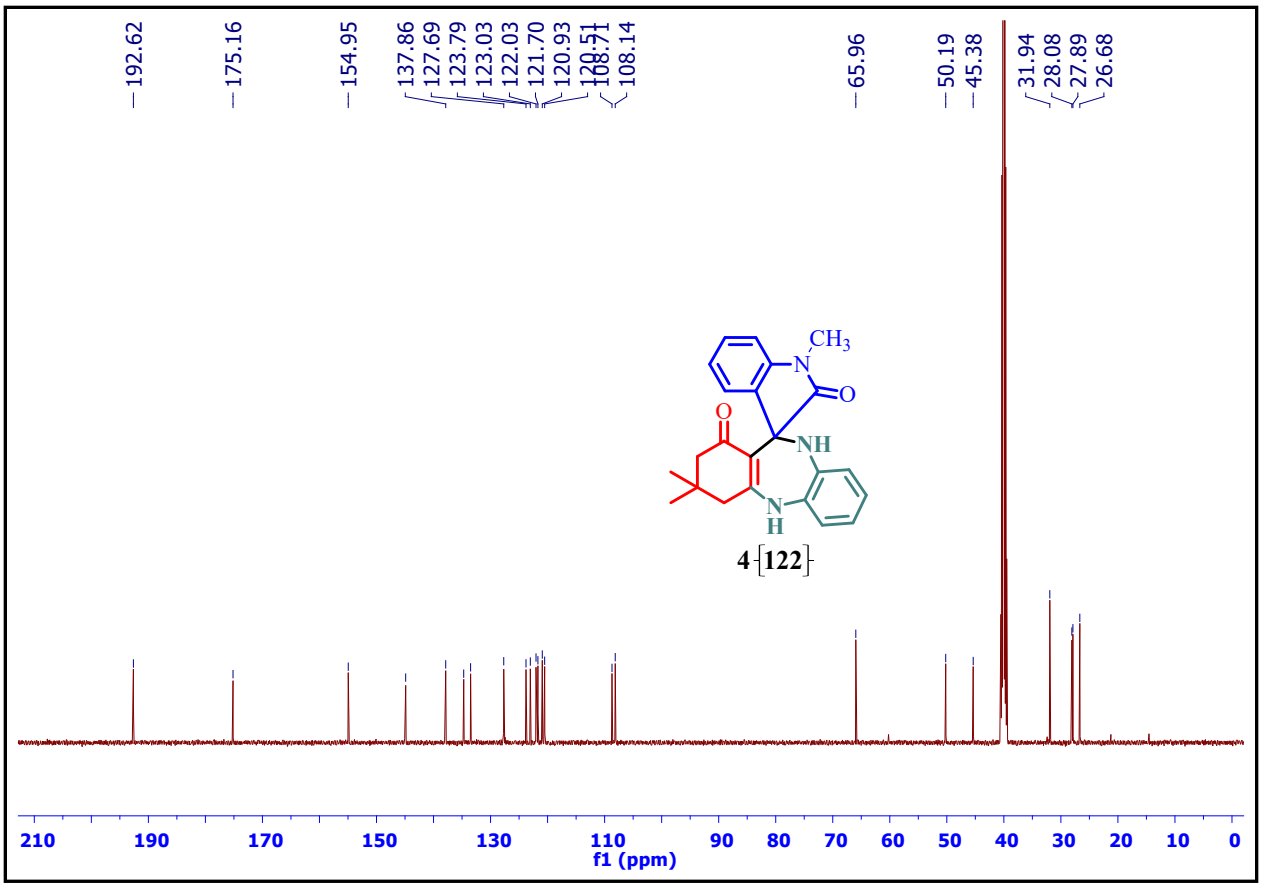


Figure S10.^{13}C NMR spectra of **4{122}** in DMSO-d6.

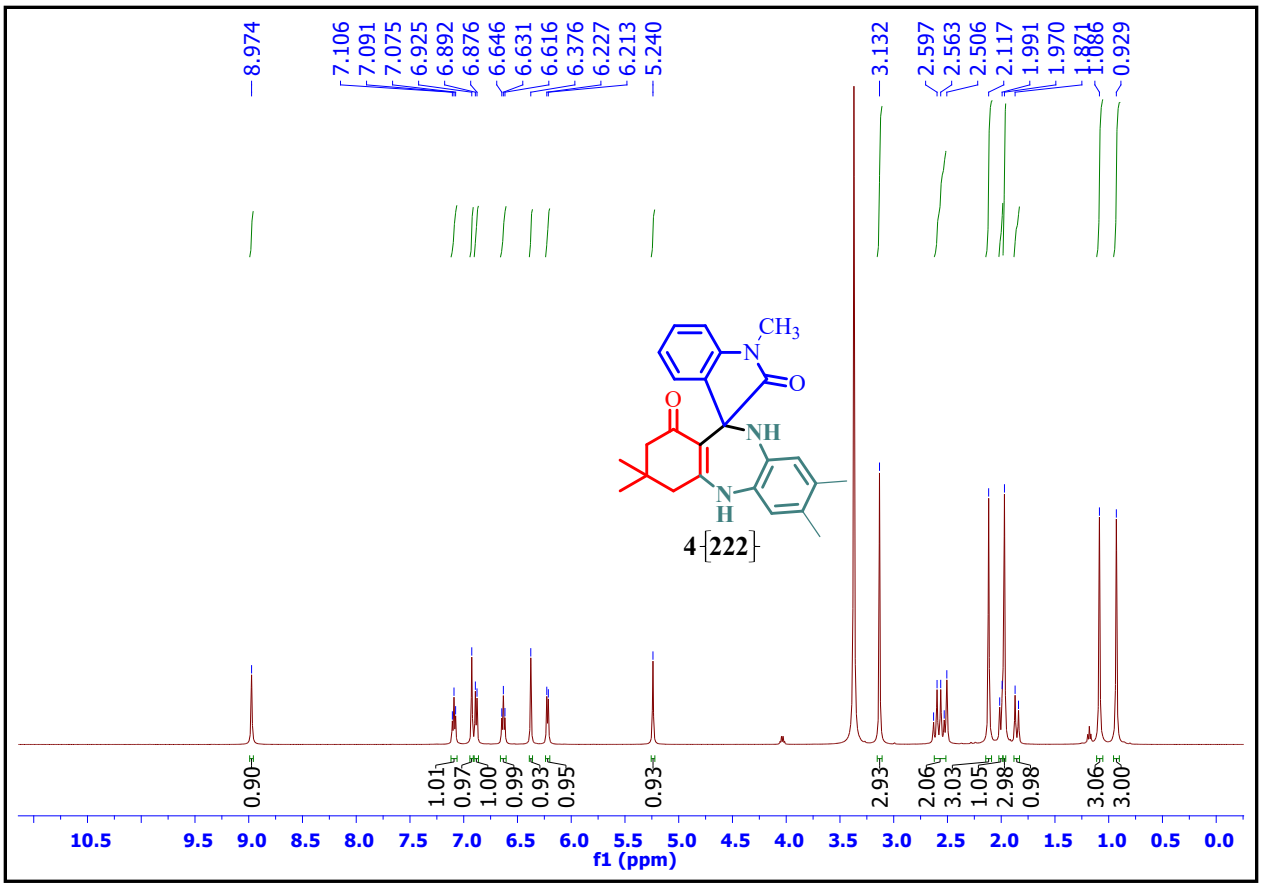


Figure S11.[1]H NMR spectra of **4{222}** in DMSO-d6.

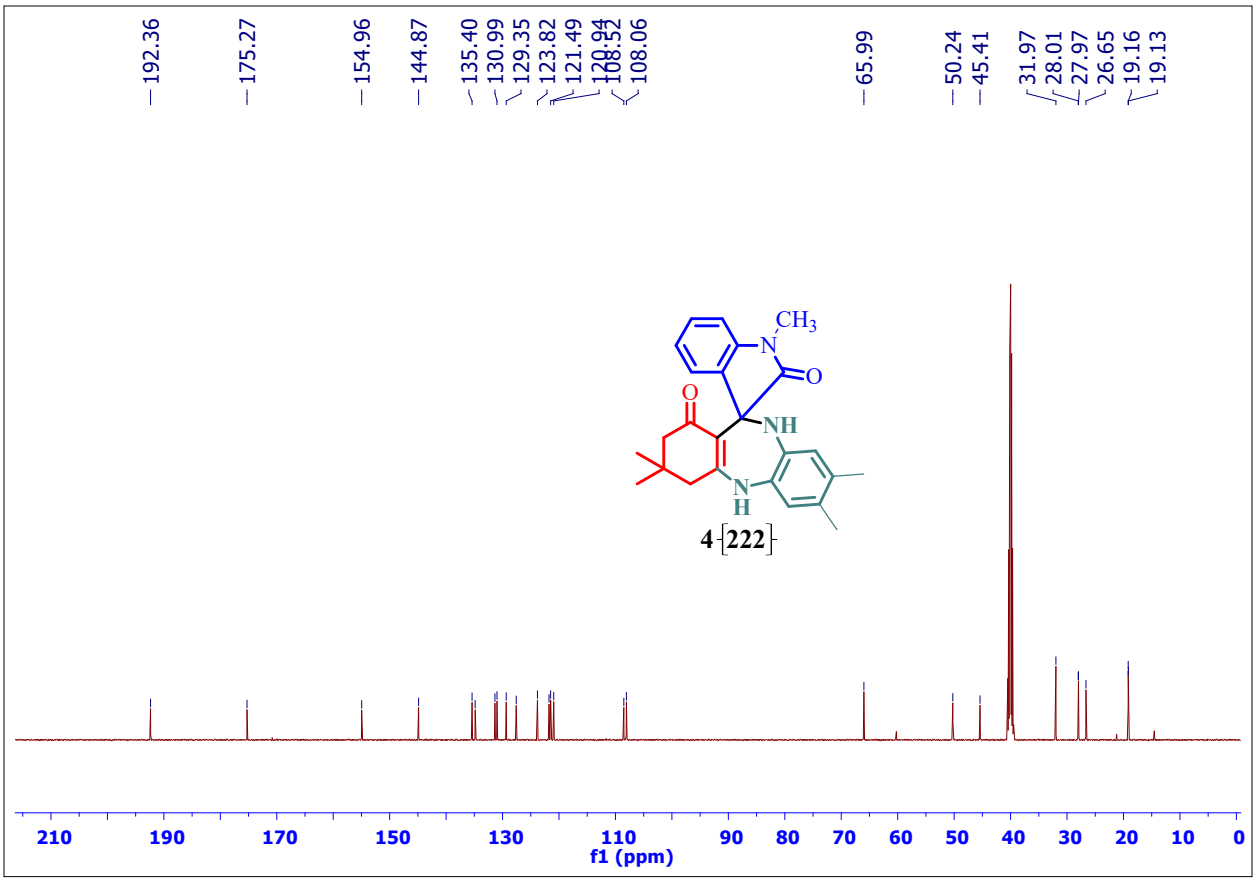


Figure S12. ^{13}C NMR spectra of **4{222}** in DMSO-d6.

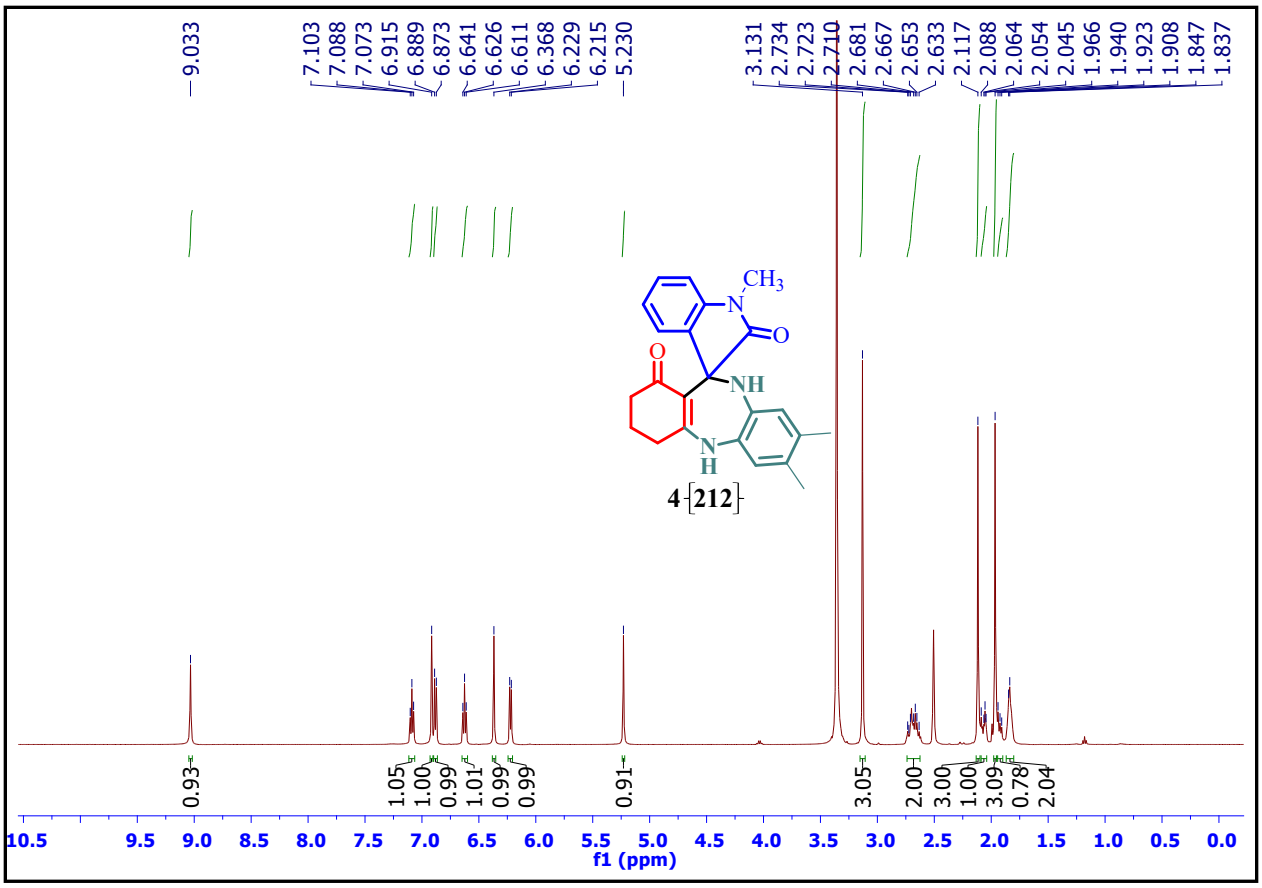


Figure S13.[1]H NMR spectra of **4{212}** in DMSO-d6.

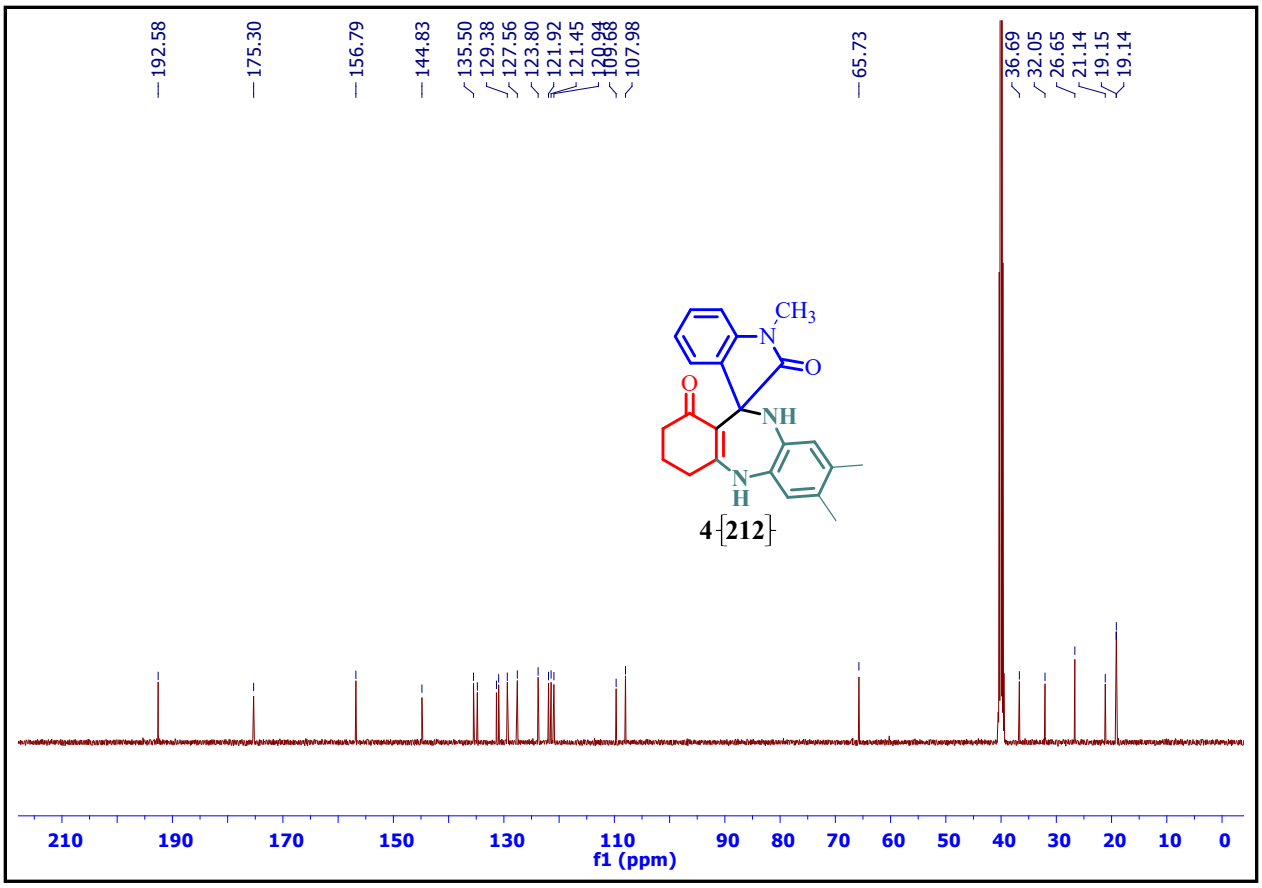


Figure S14.[13]C NMR spectra of **4{212}** in DMSO-d6.

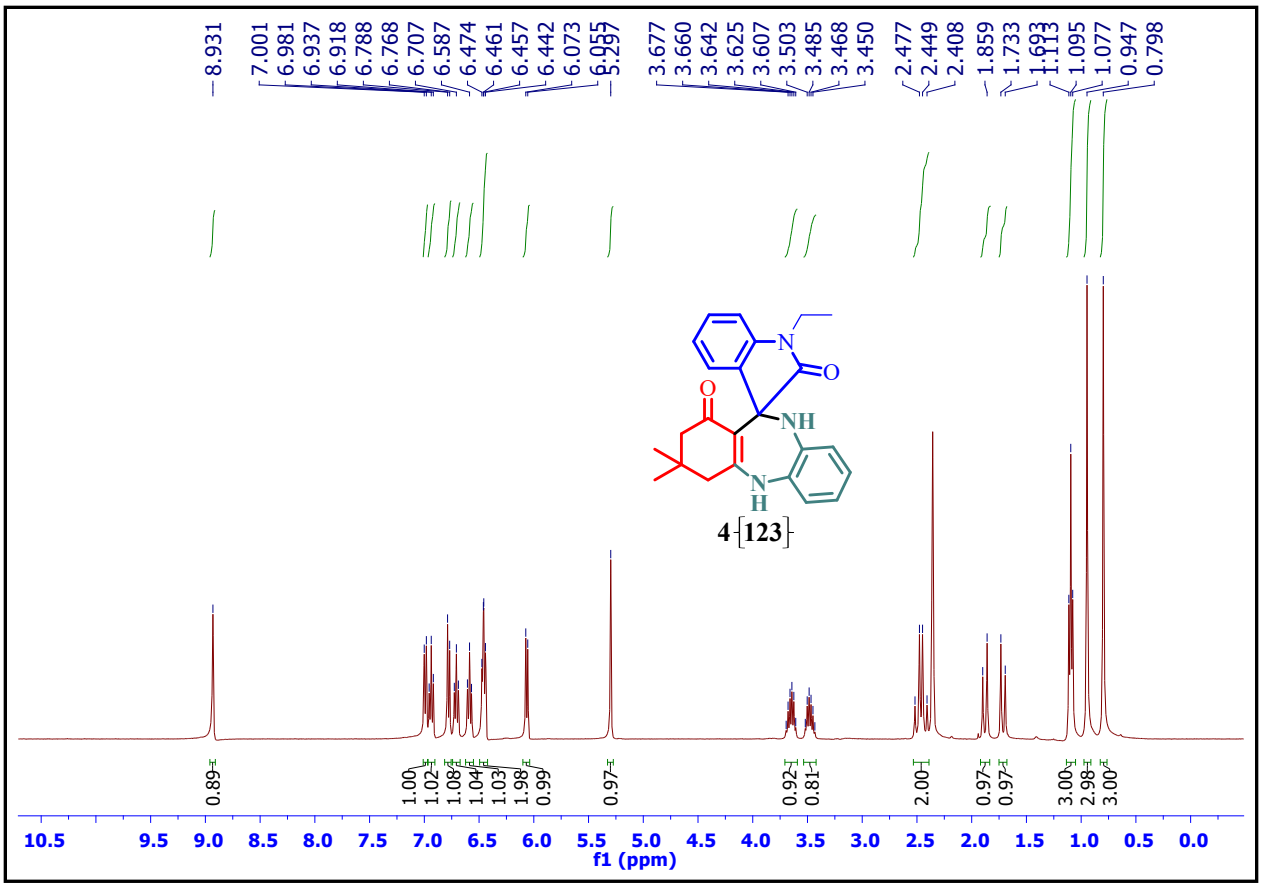


Figure S15.[1]H NMR spectra of **4{123}** in DMSO-d6.

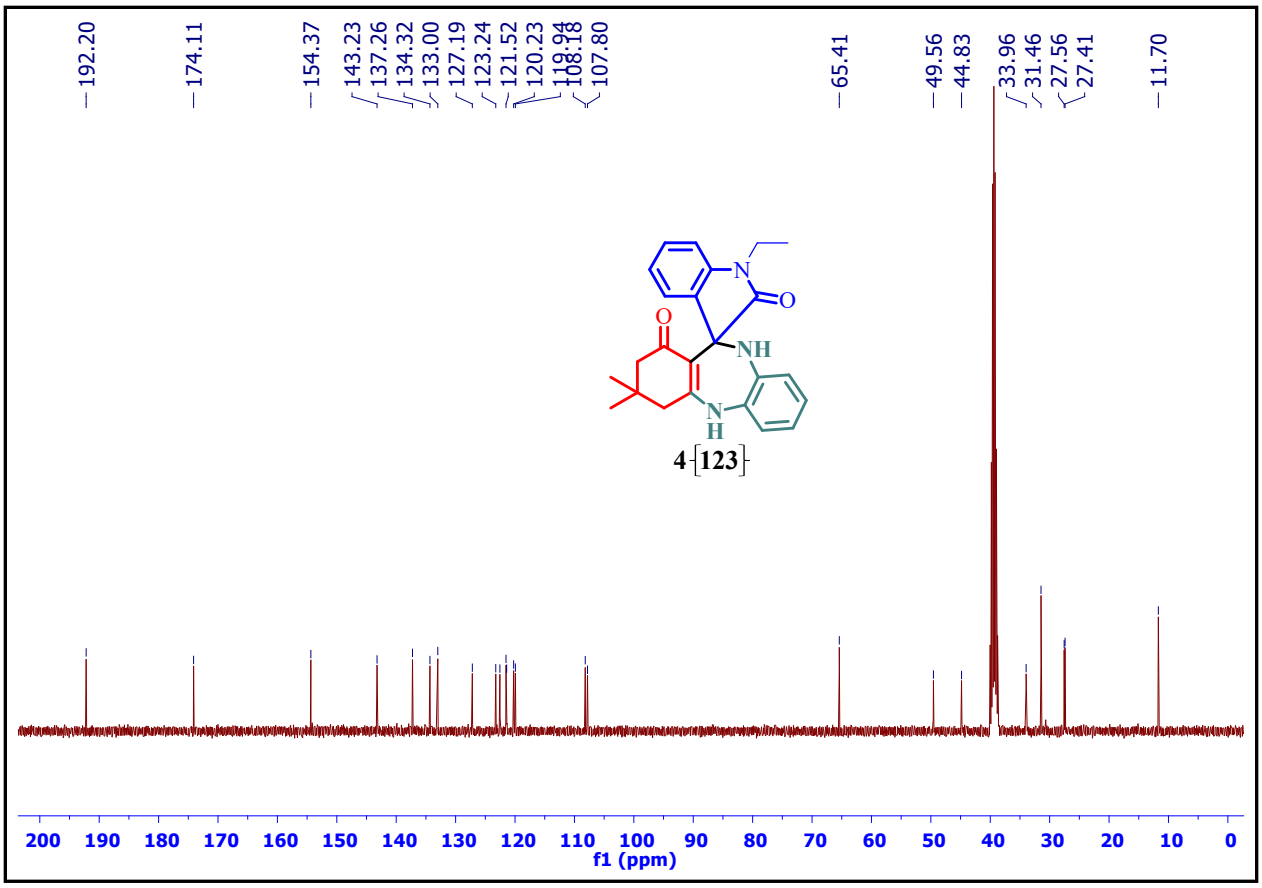


Figure S16. ^{13}C NMR spectra of **4{123}** in DMSO-d6.

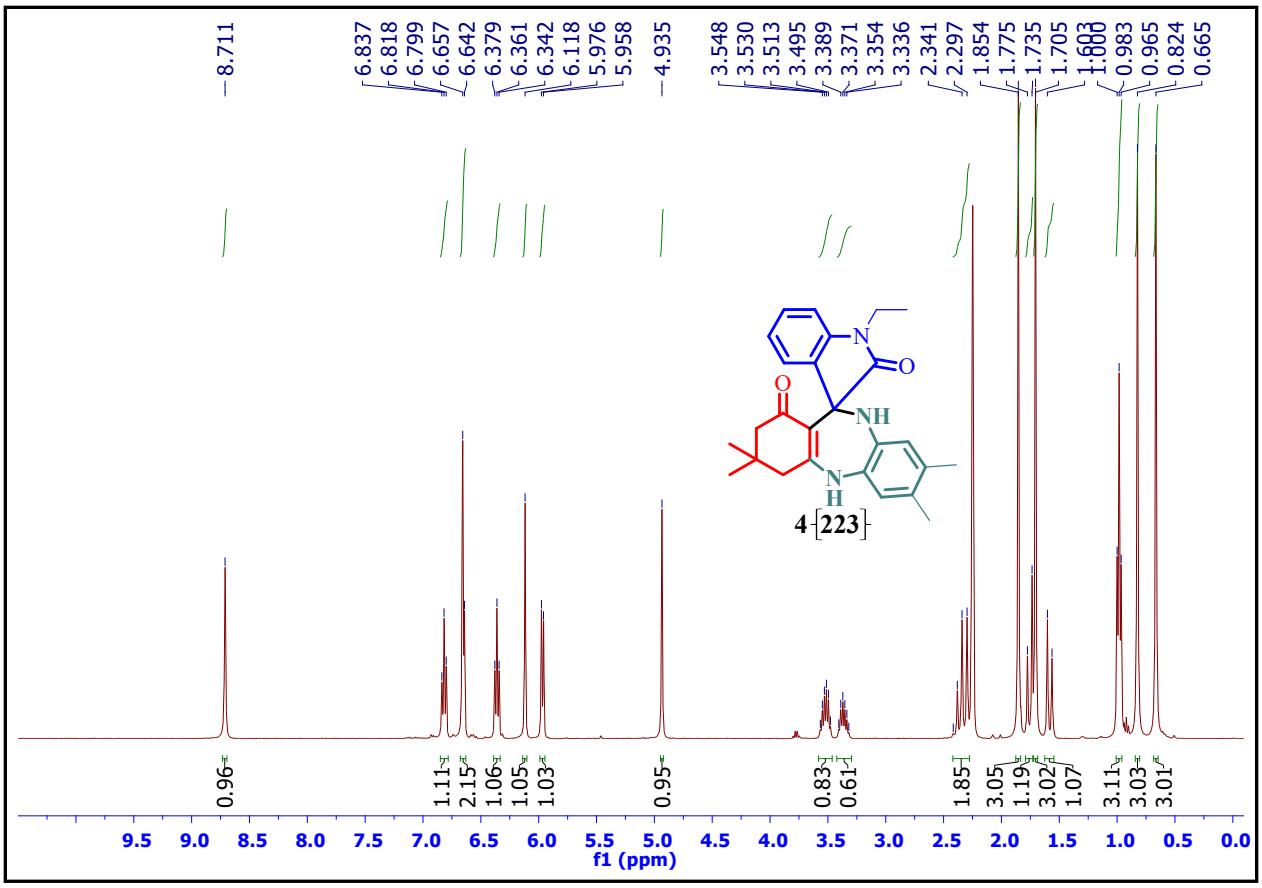


Figure S17.[1]H NMR spectra of **4{223}** in DMSO-d6.

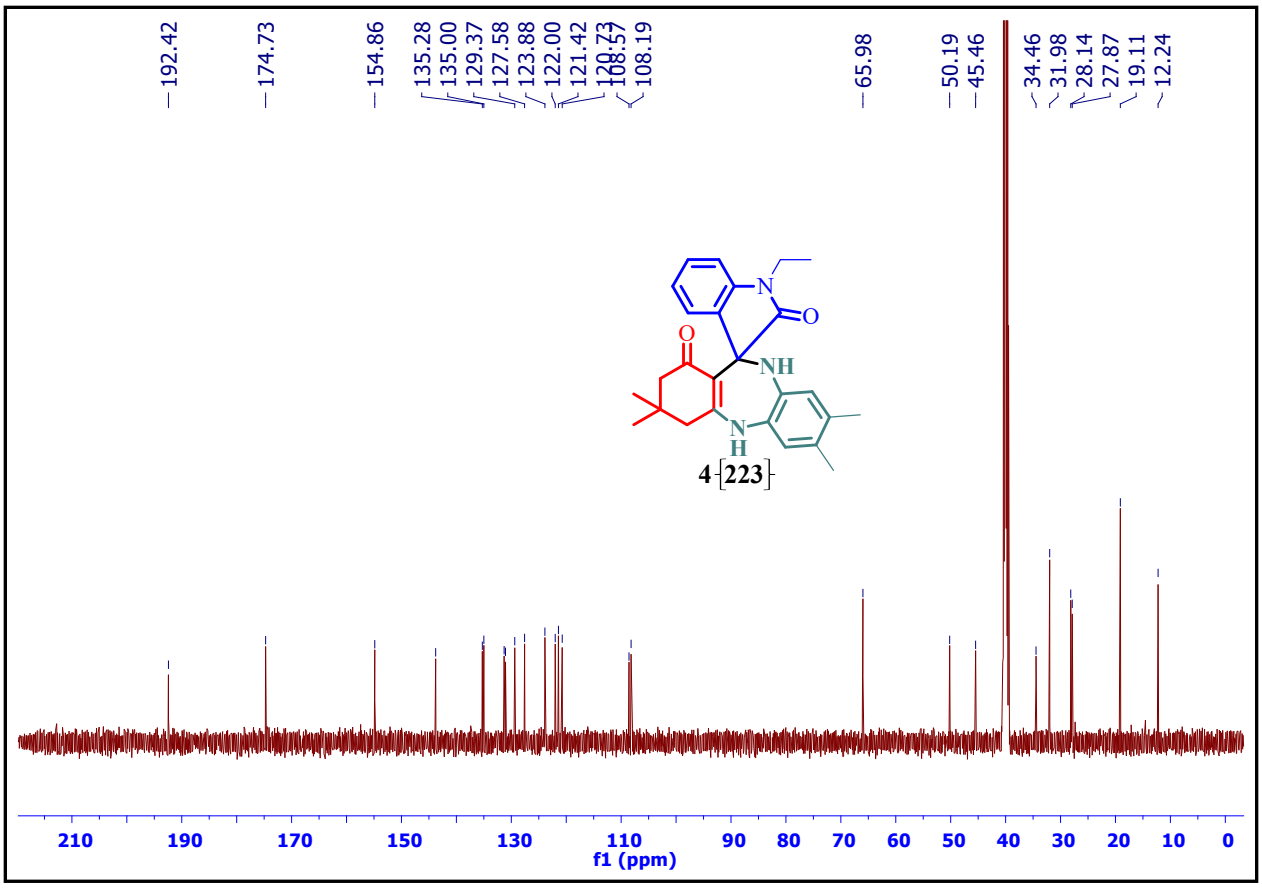


Figure S18.[13]C NMR spectra of **4{223}** in DMSO-d6.

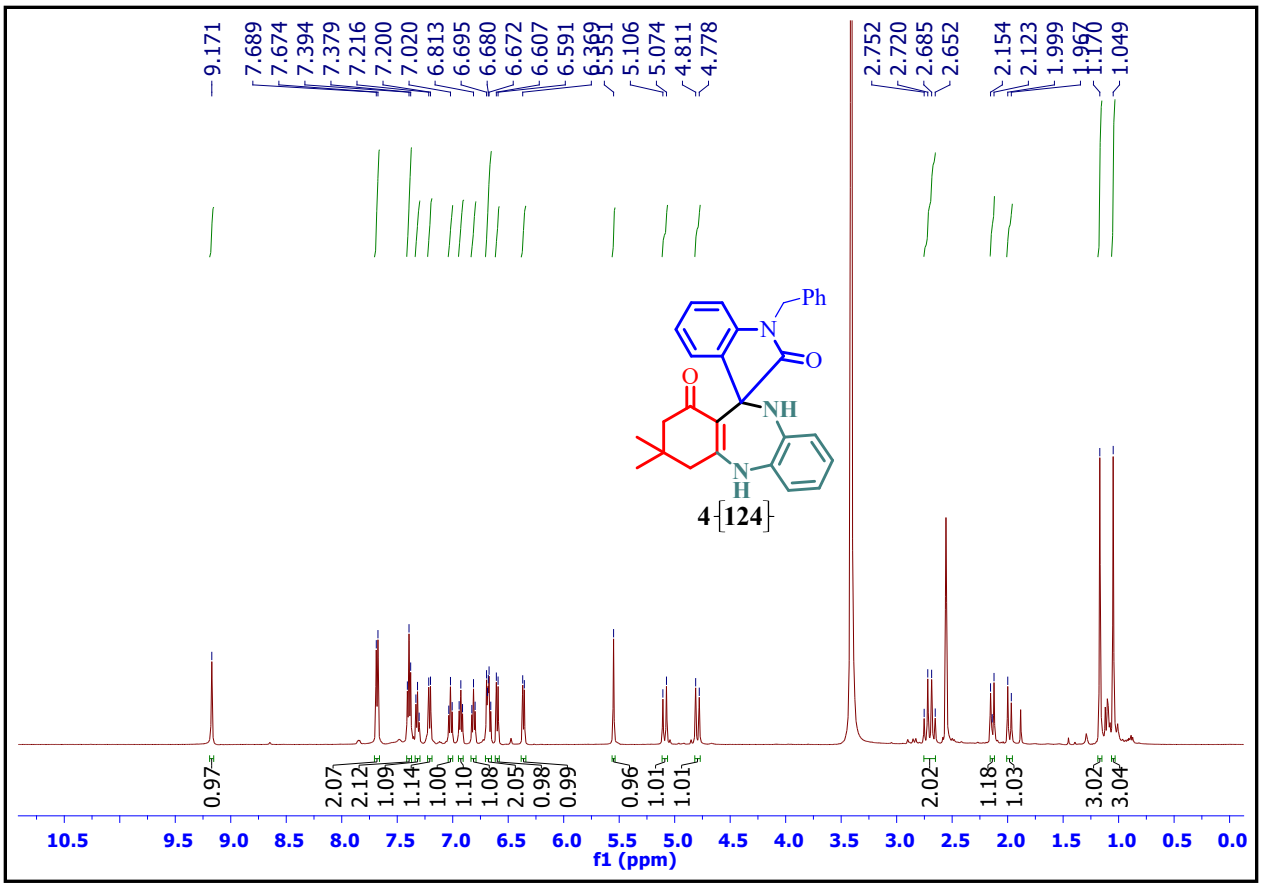


Figure S19.[1]H NMR spectra of **4{124}** in DMSO-d6.

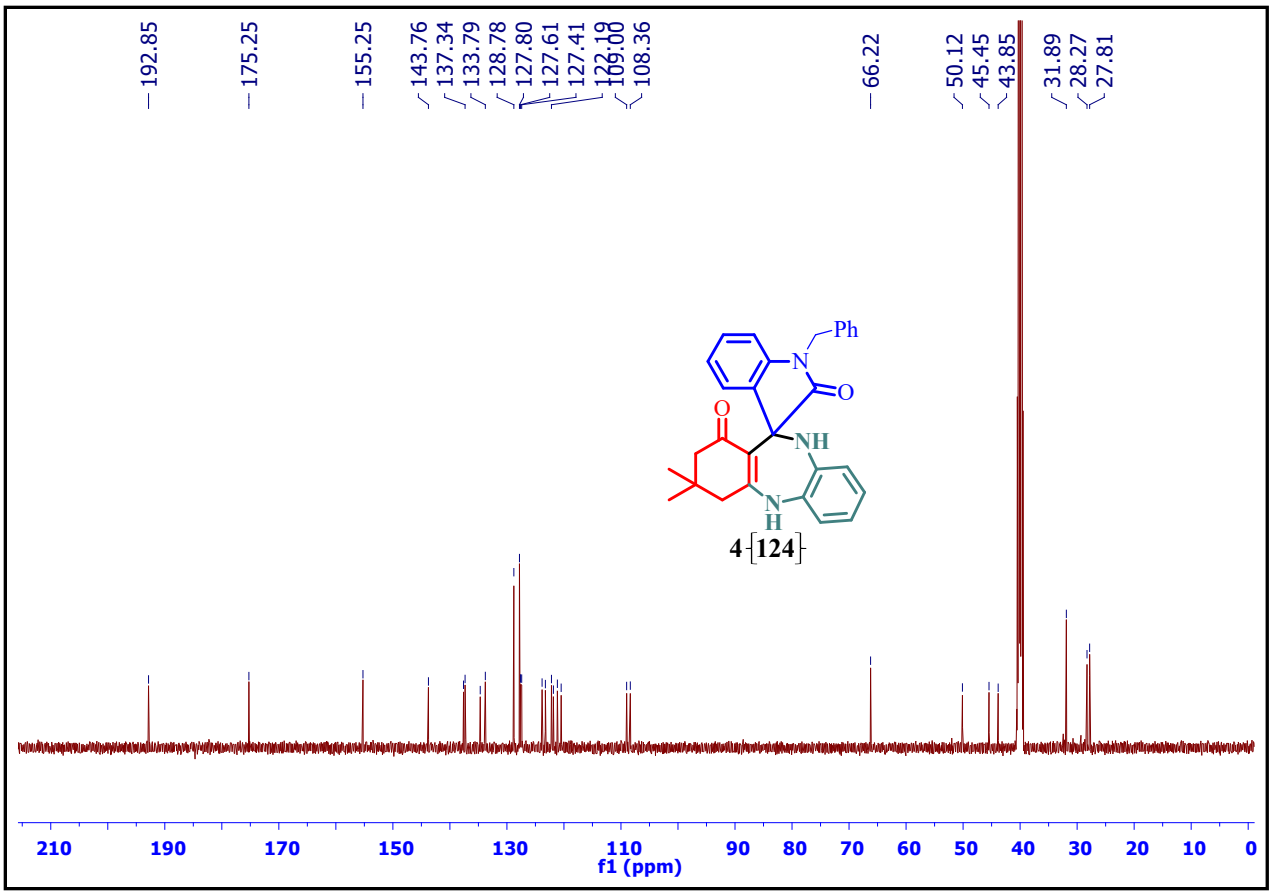


Figure S20.[13]C NMR spectra of **4{124}** in DMSO-d6.

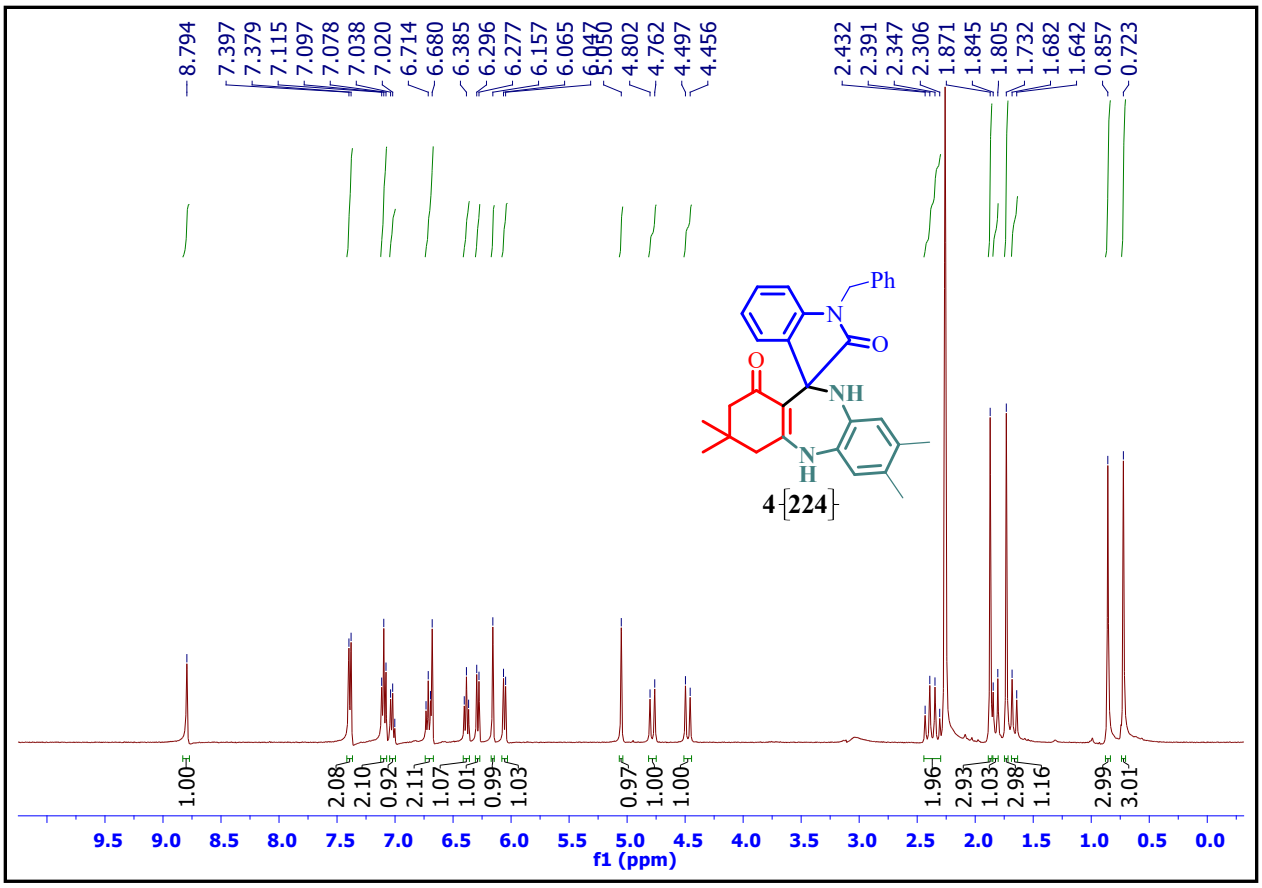


Figure 21. ^{1}H NMR spectra of **4{224}** in DMSO-d6.

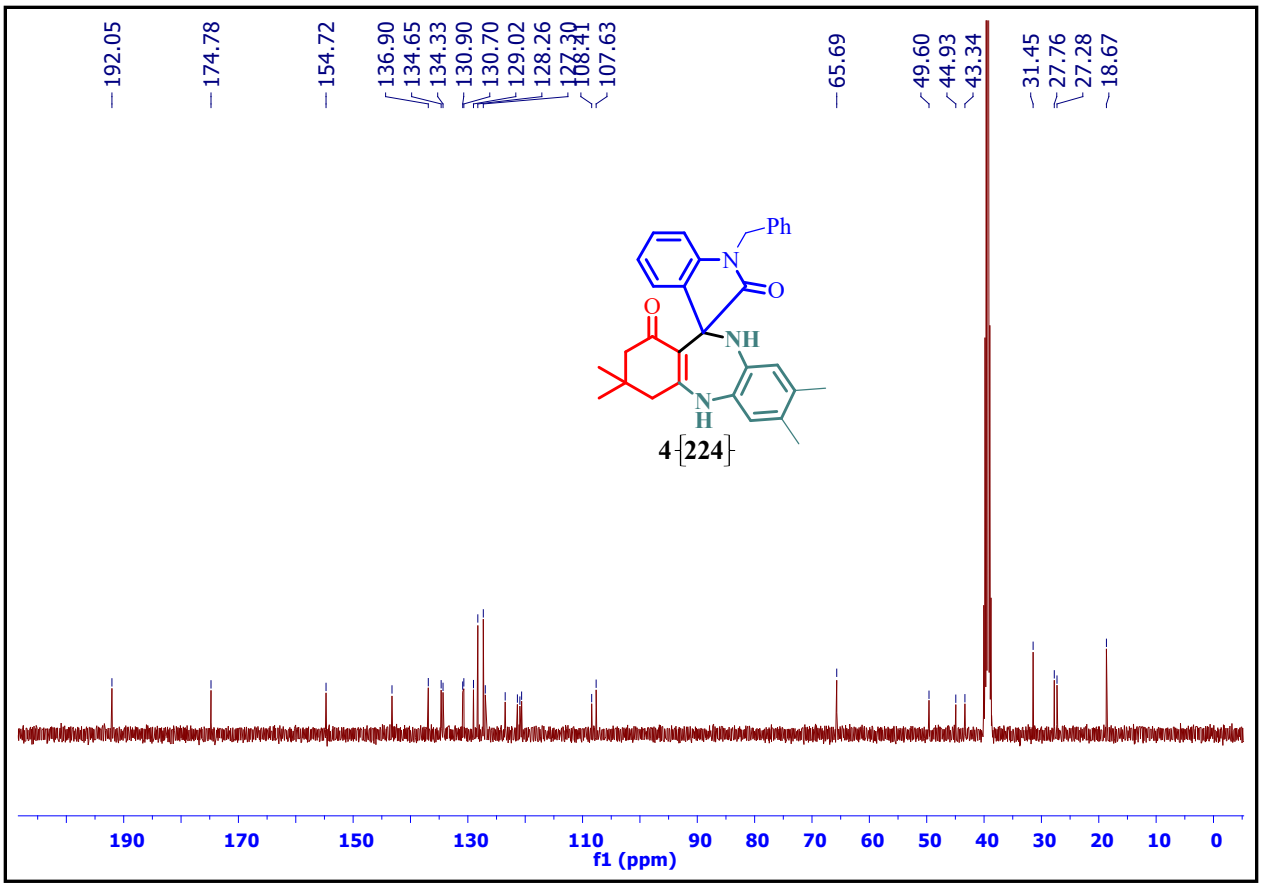


Figure S22. ^{13}C NMR spectra of **4{224}** in DMSO-d6.

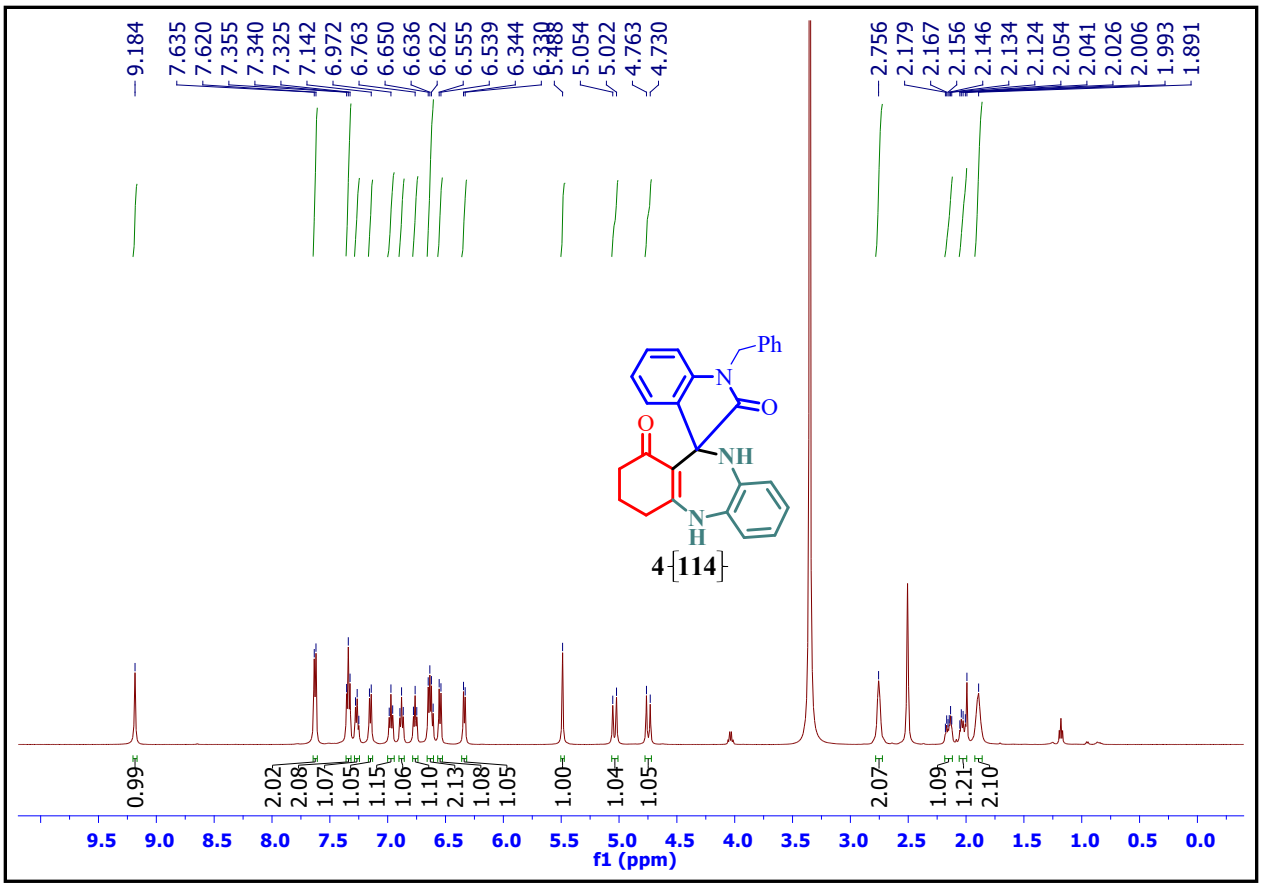


Figure S23.[1]H NMR spectra of **4{114}** in DMSO-d6.

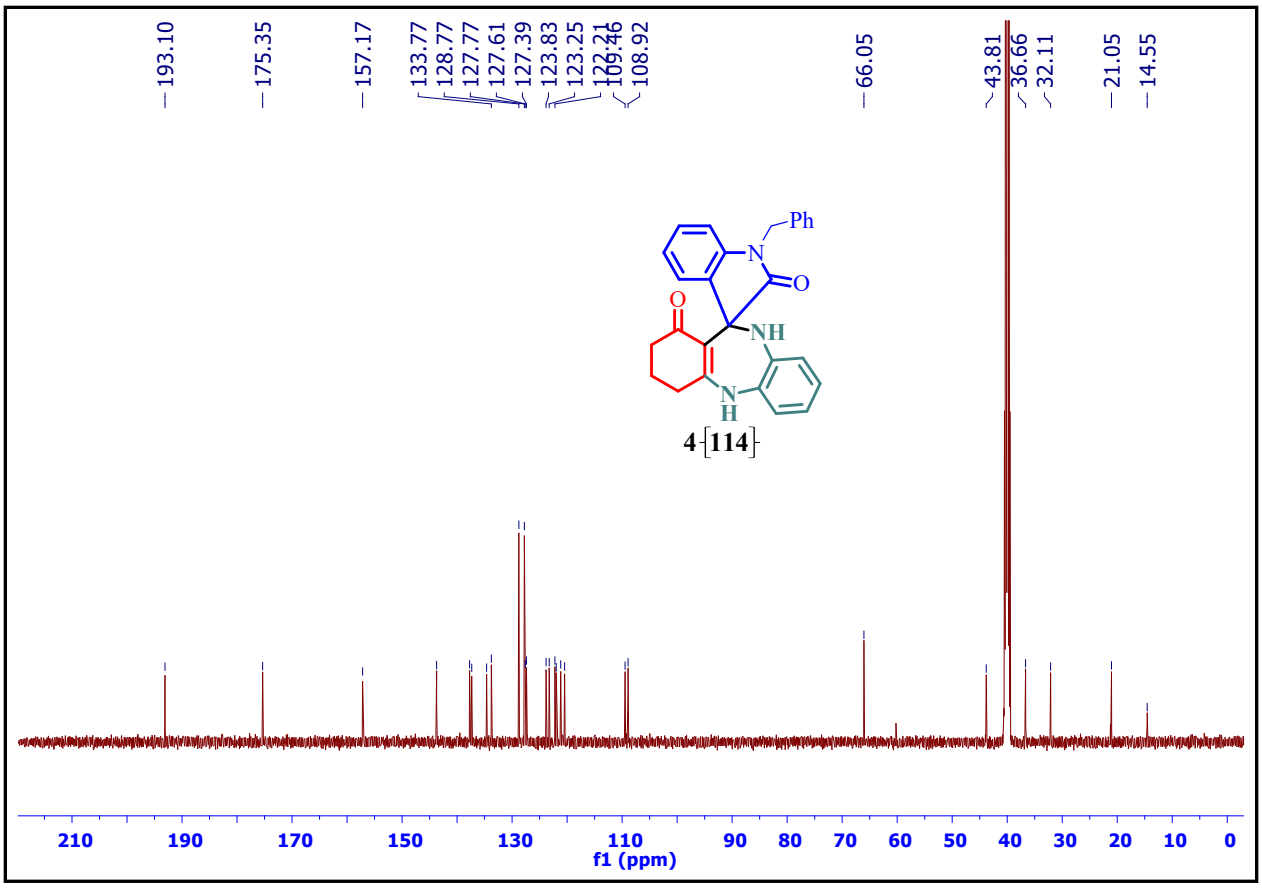


Figure S24. ^{13}C NMR spectra of **4{114}** in DMSO-d6.

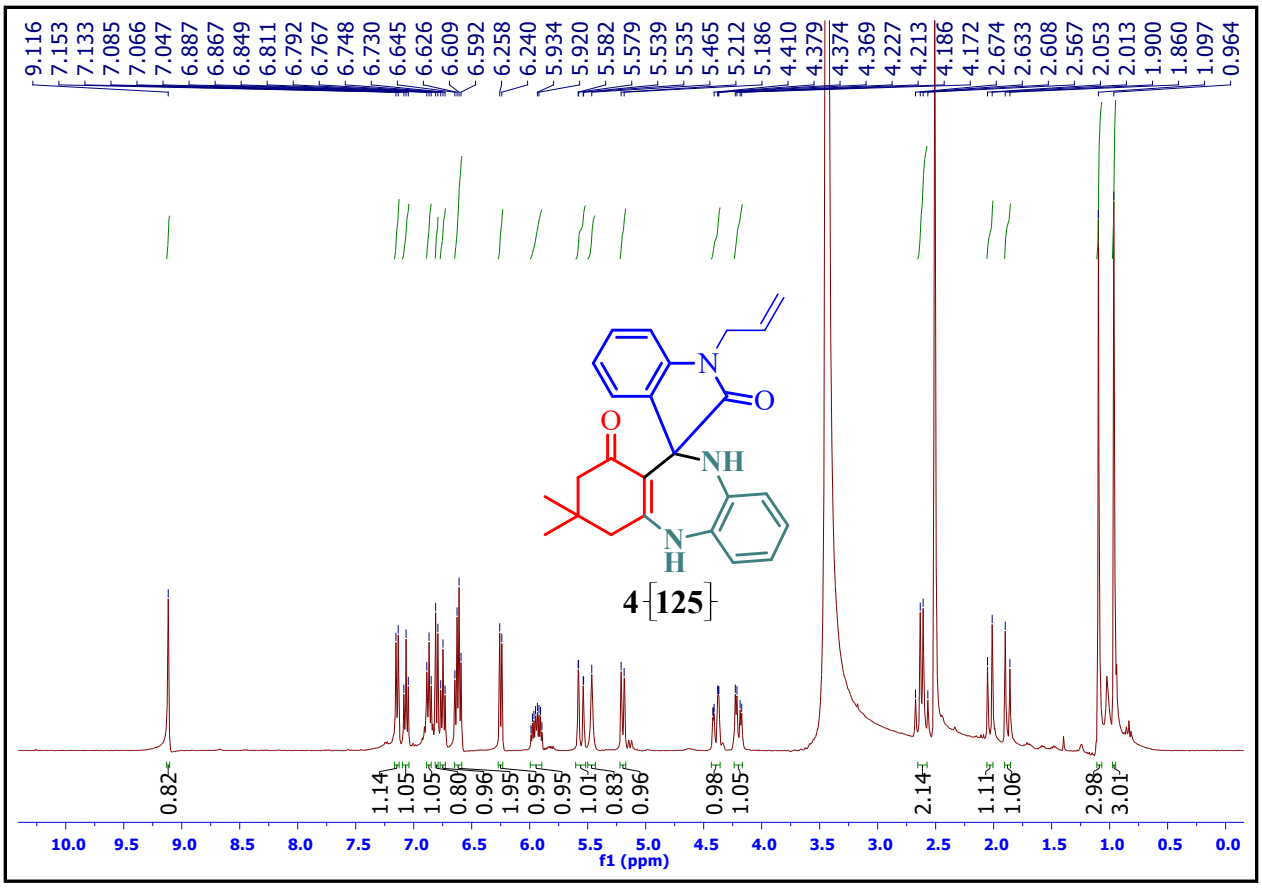


Figure S25. ^{1}H NMR spectra of **4{125}** in DMSO-d6.

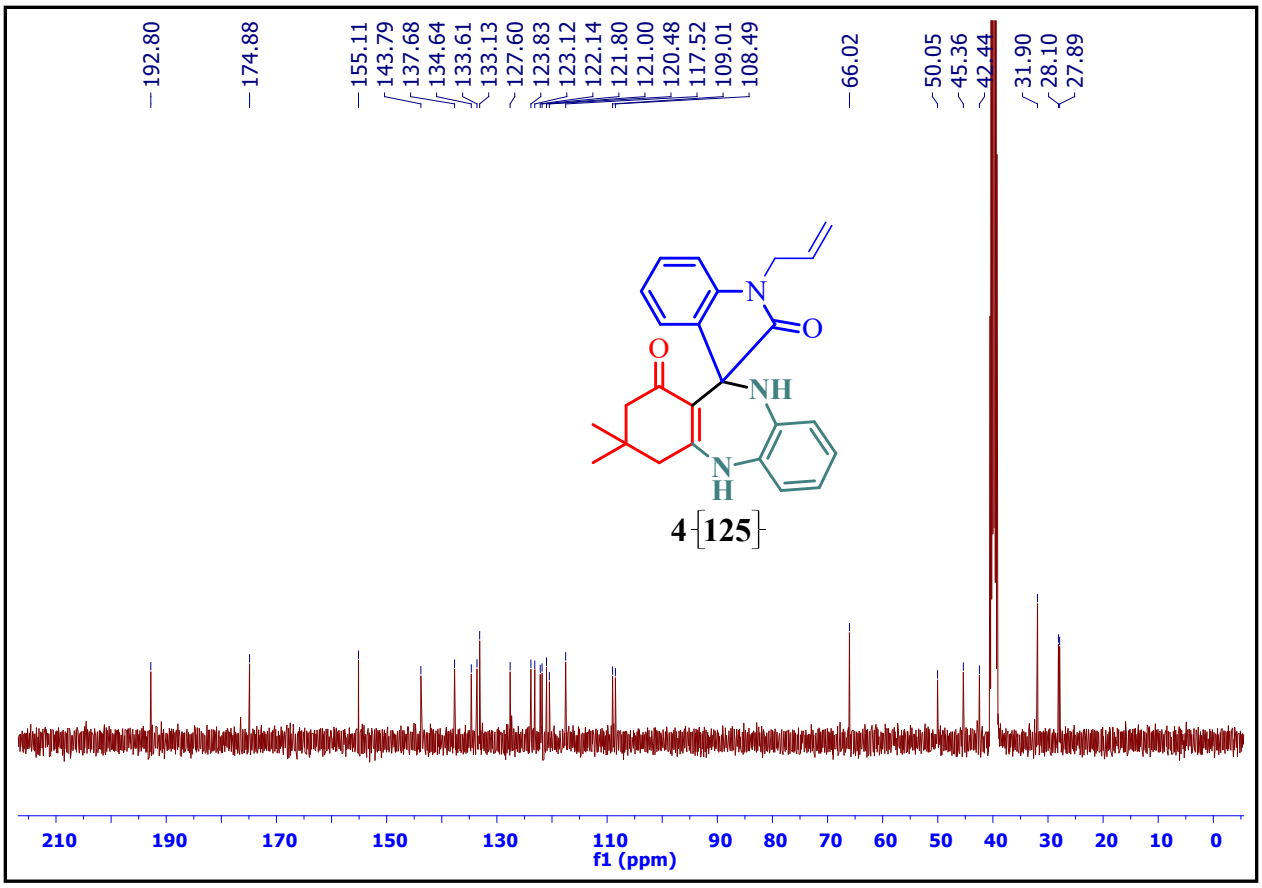


Figure S26. ^{13}C NMR spectra of **4{125}** in DMSO-d6.

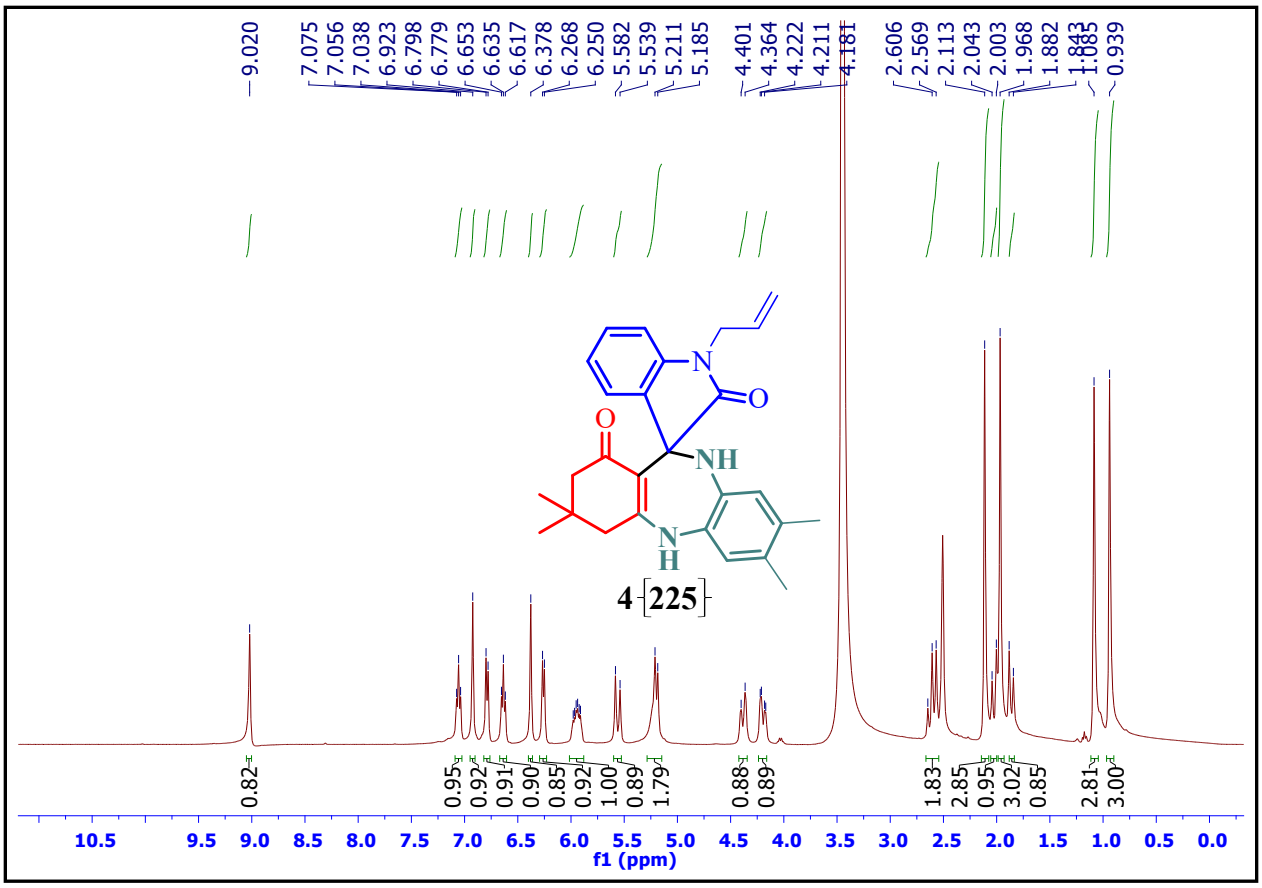


Figure S27.[1]H NMR spectra of **4{225}** in DMSO-d6.

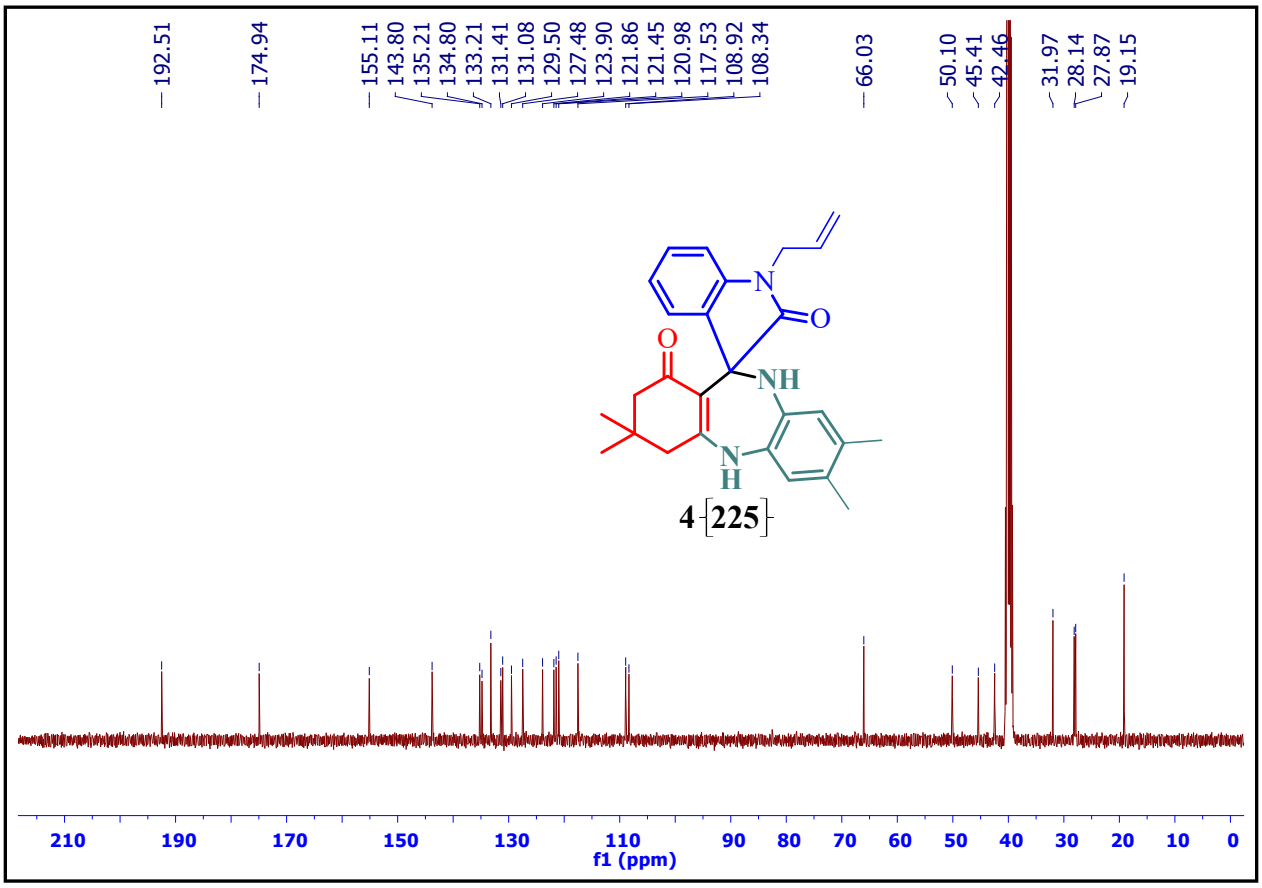


Figure S28. ^{13}C NMR spectra of **4{225}** in DMSO-d6.

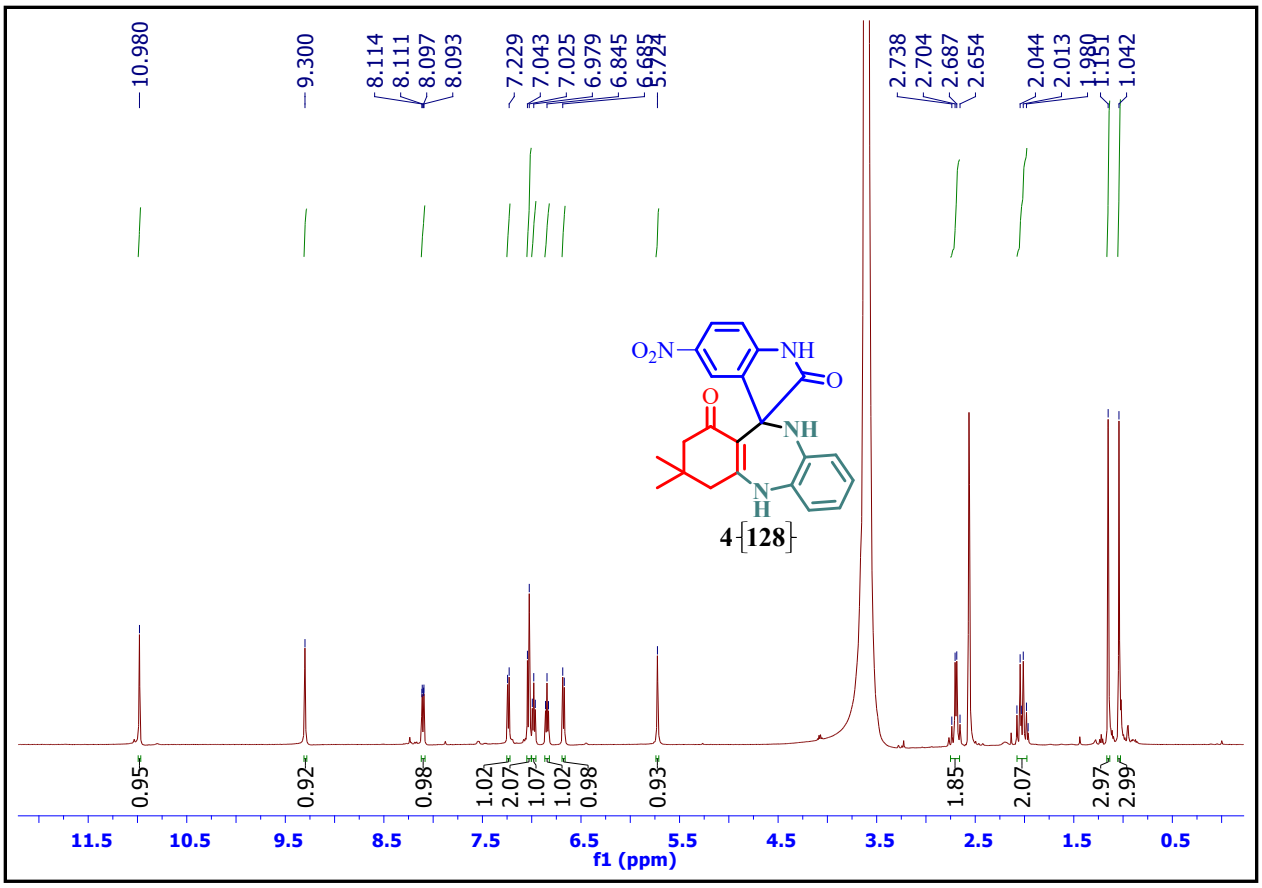


Figure S29.[1]H NMR spectra of **4{128}** in DMSO-d6.

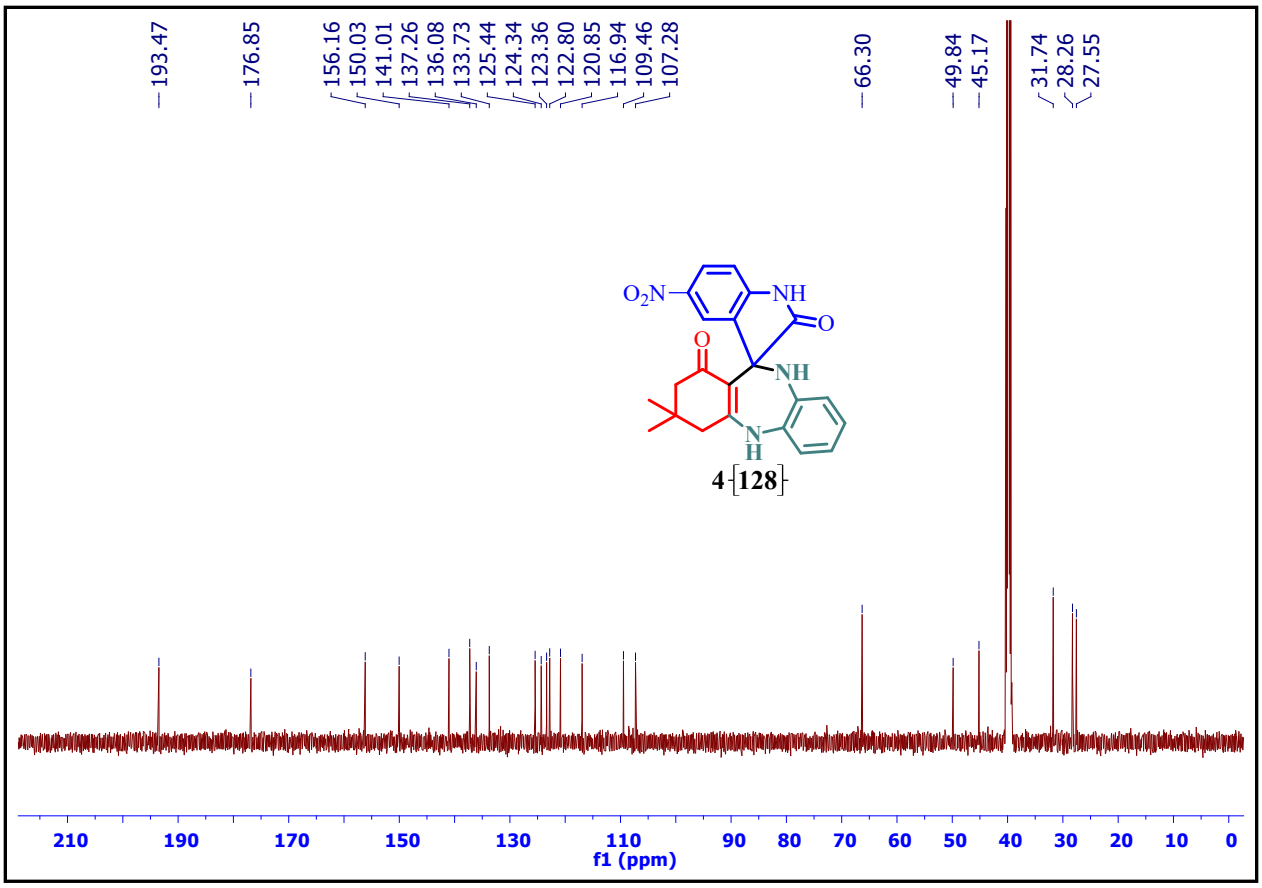


Figure S30.[13]C NMR spectra of **4{128}** in DMSO-d6.

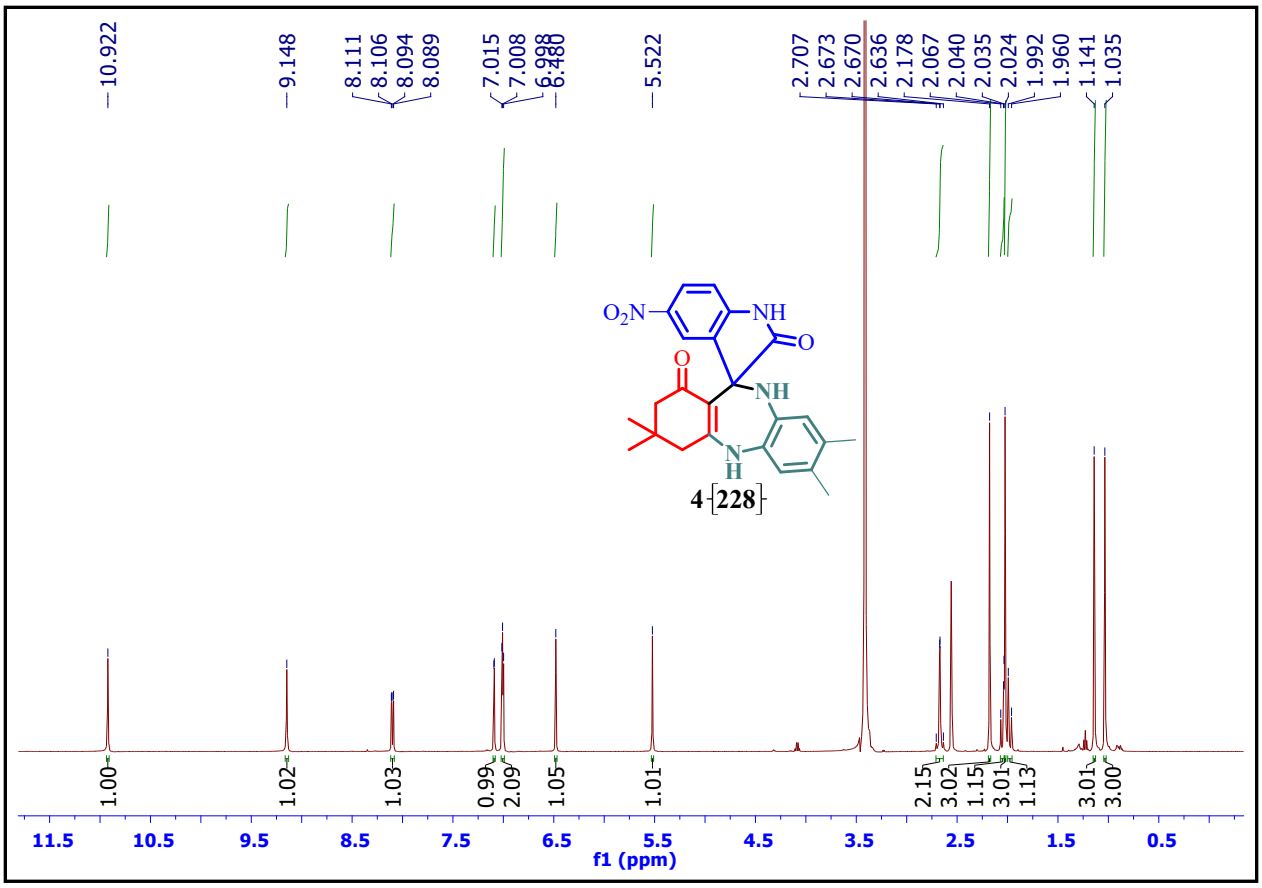


Figure S31.[1]H NMR spectra of **4{228}** in DMSO-d6.

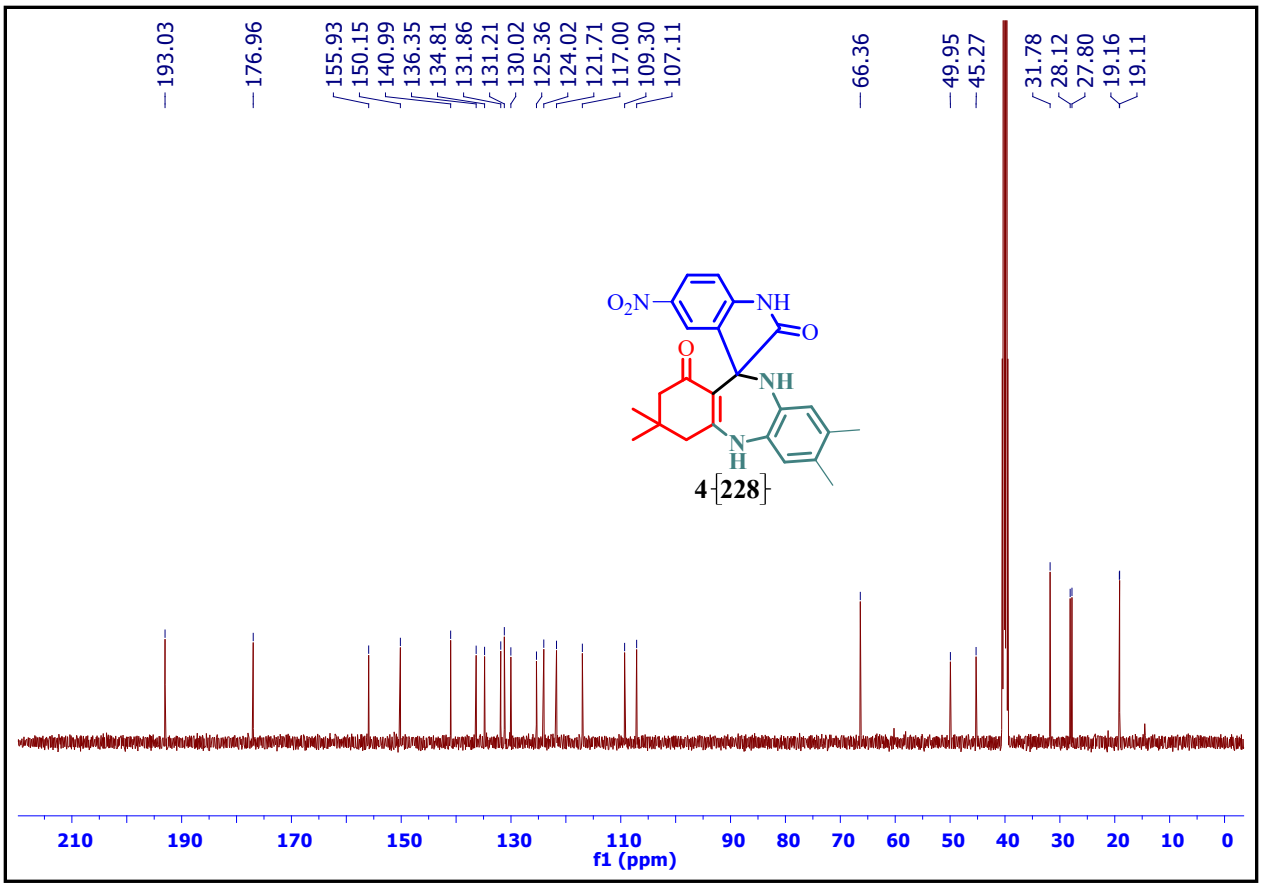


Figure S32.[13]C NMR spectra of **4{228}** in DMSO-d6.

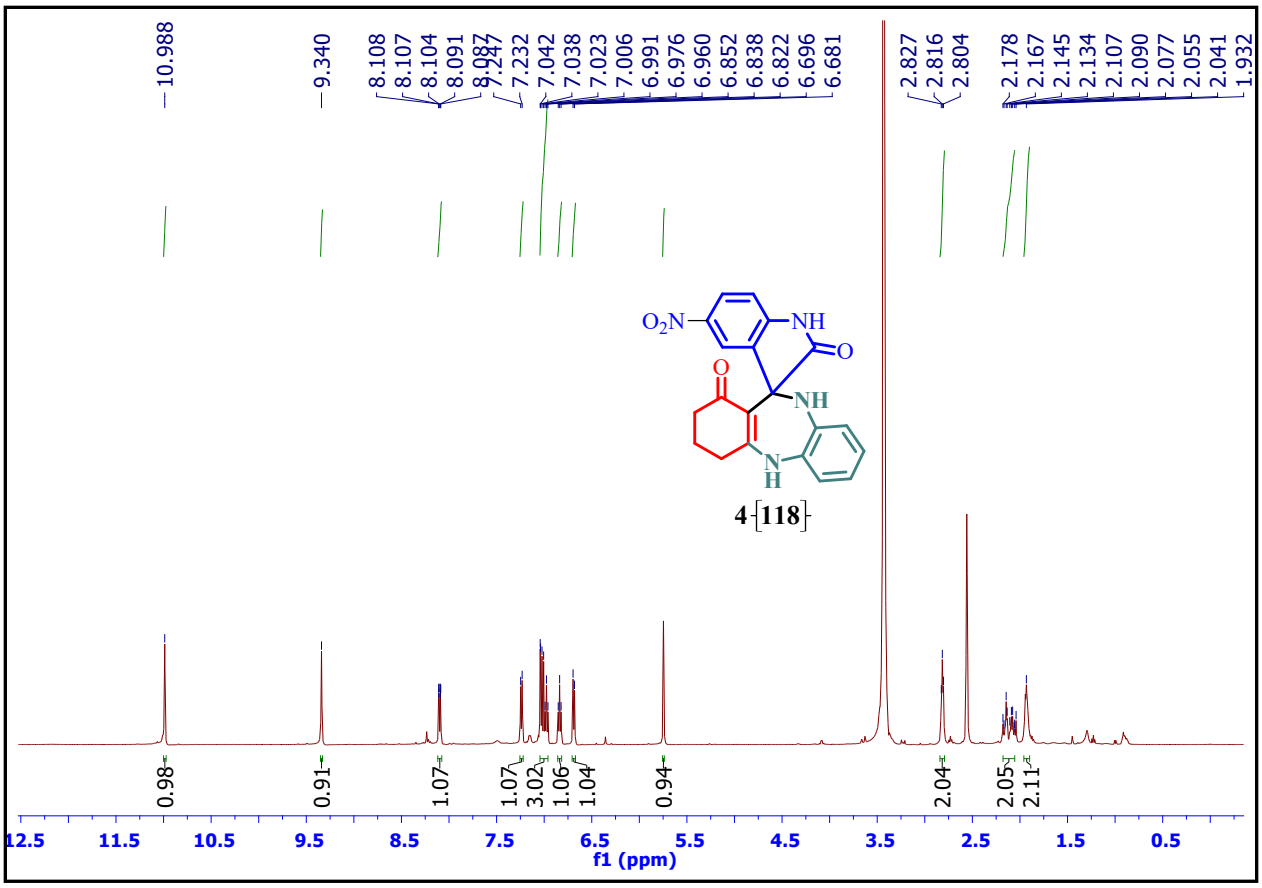


Figure S33.[1]H NMR spectra of **4{118}** in DMSO-d6.

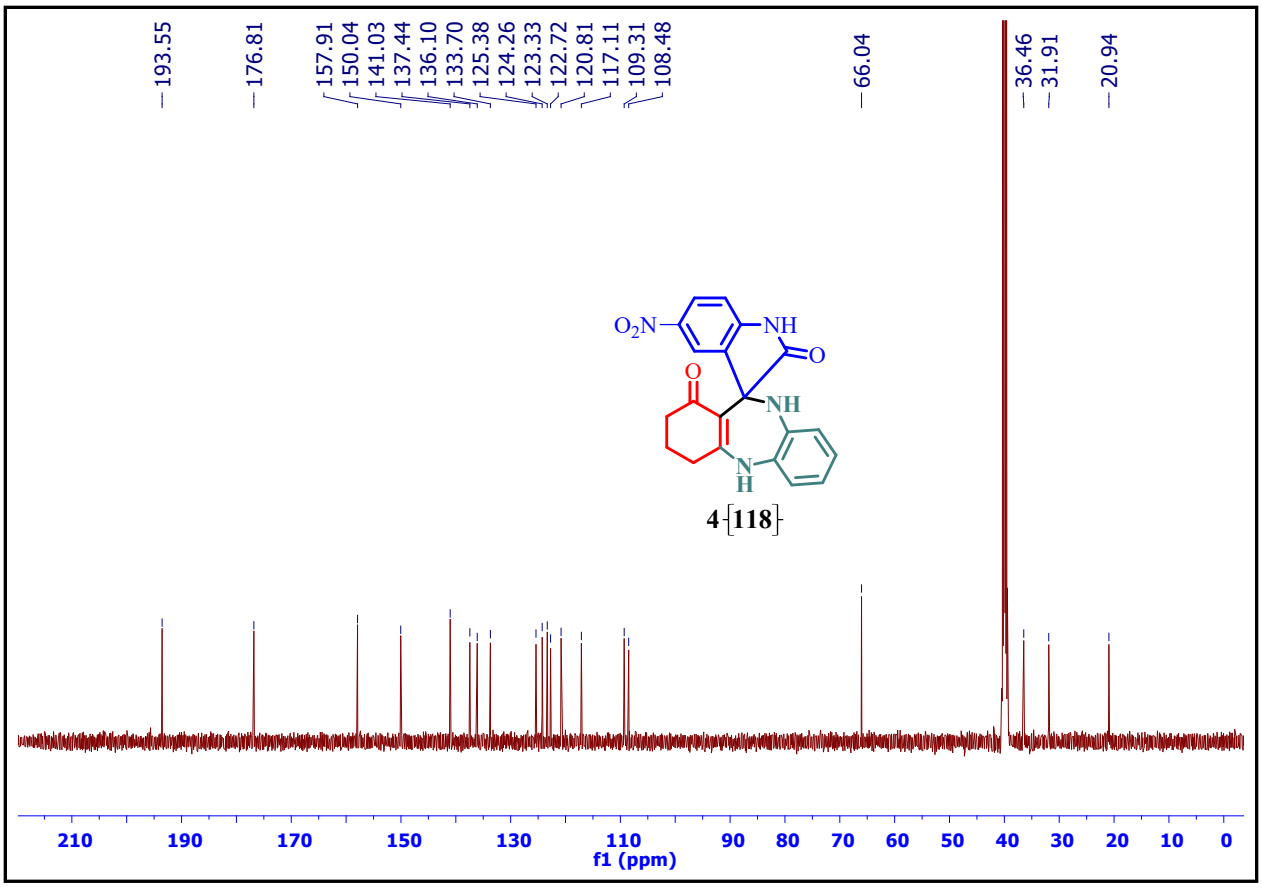


Figure S34.[13]C NMR spectra of **4{118}** in DMSO-d6.

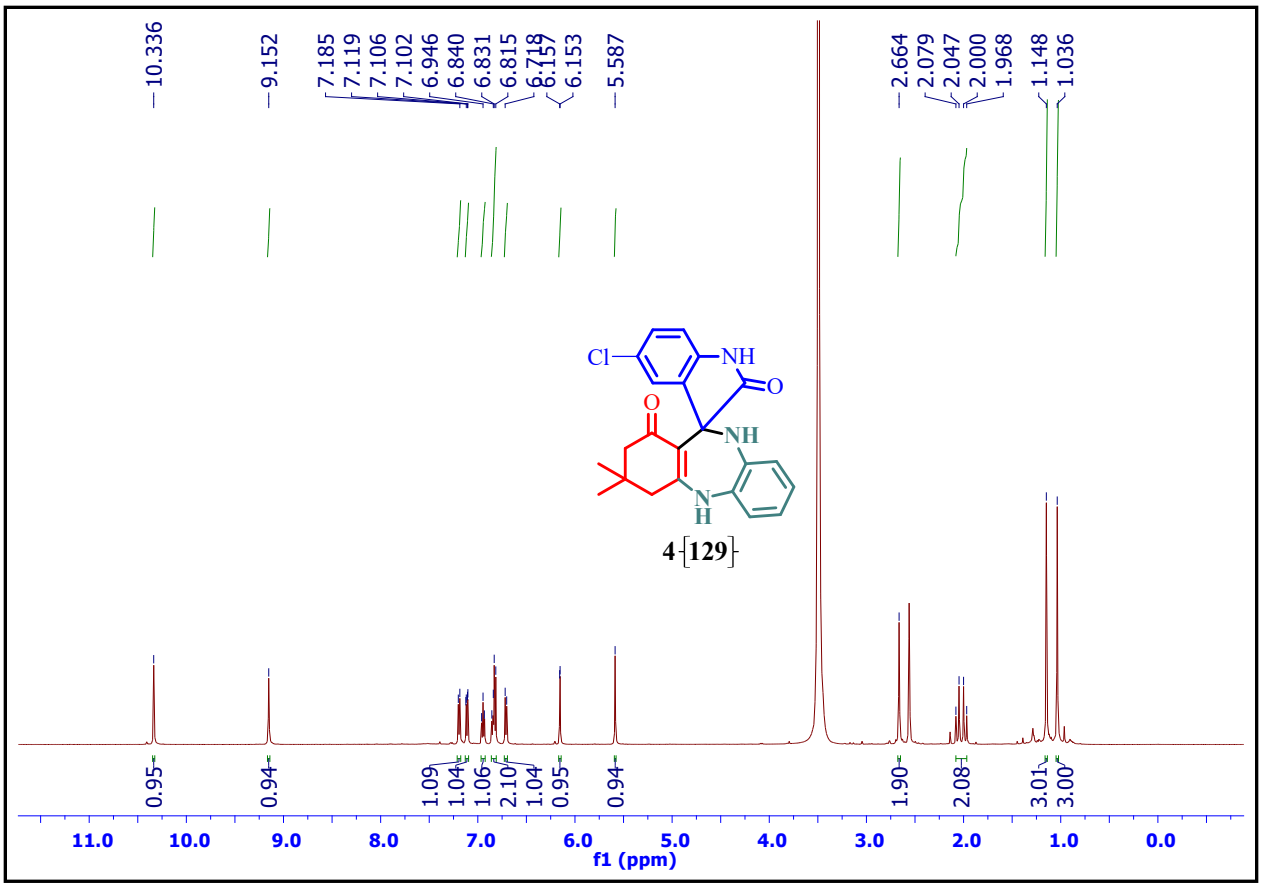


Figure S35.[1]H NMR spectra of **4{129}** in DMSO-d6.

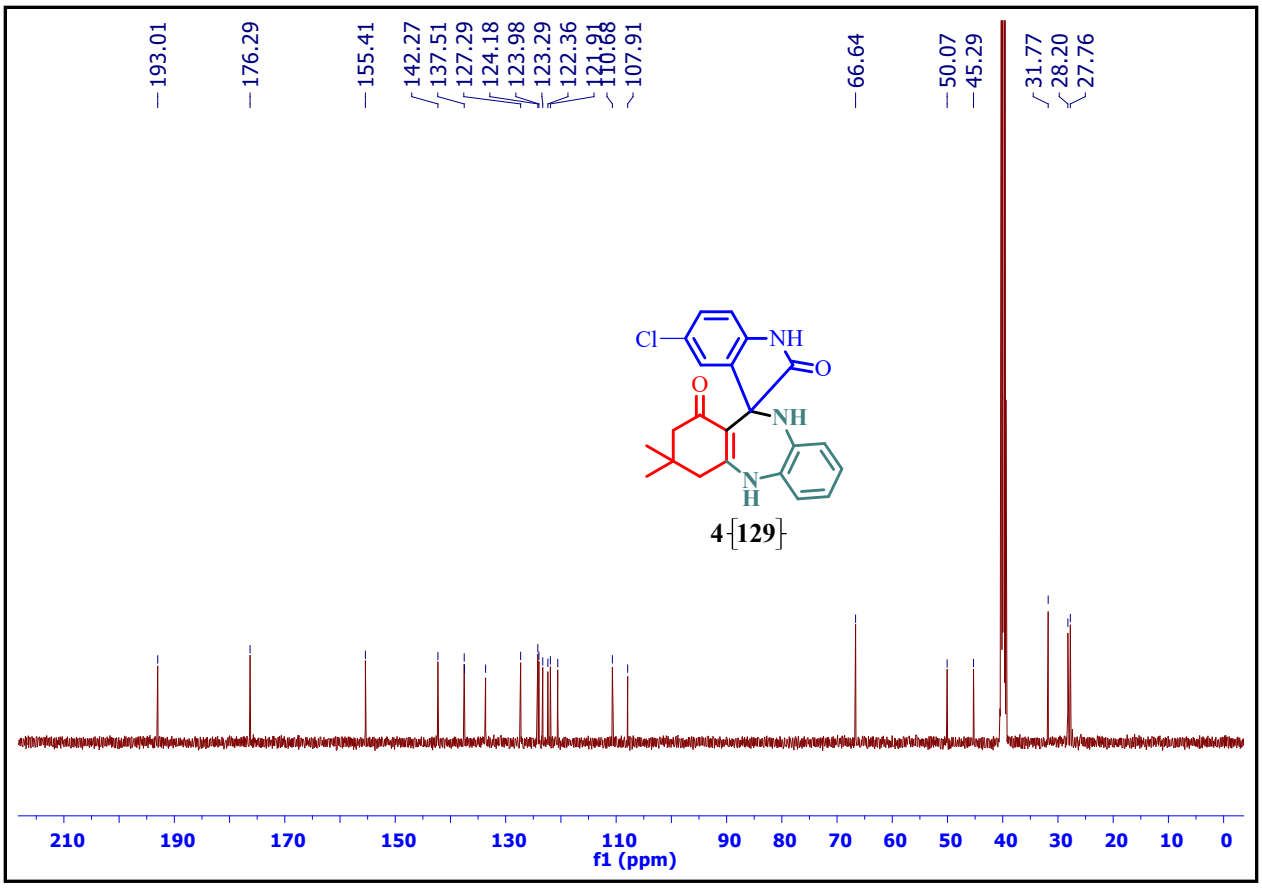


Figure S36. ^{13}C NMR spectra of **4{129}** in DMSO-d6.

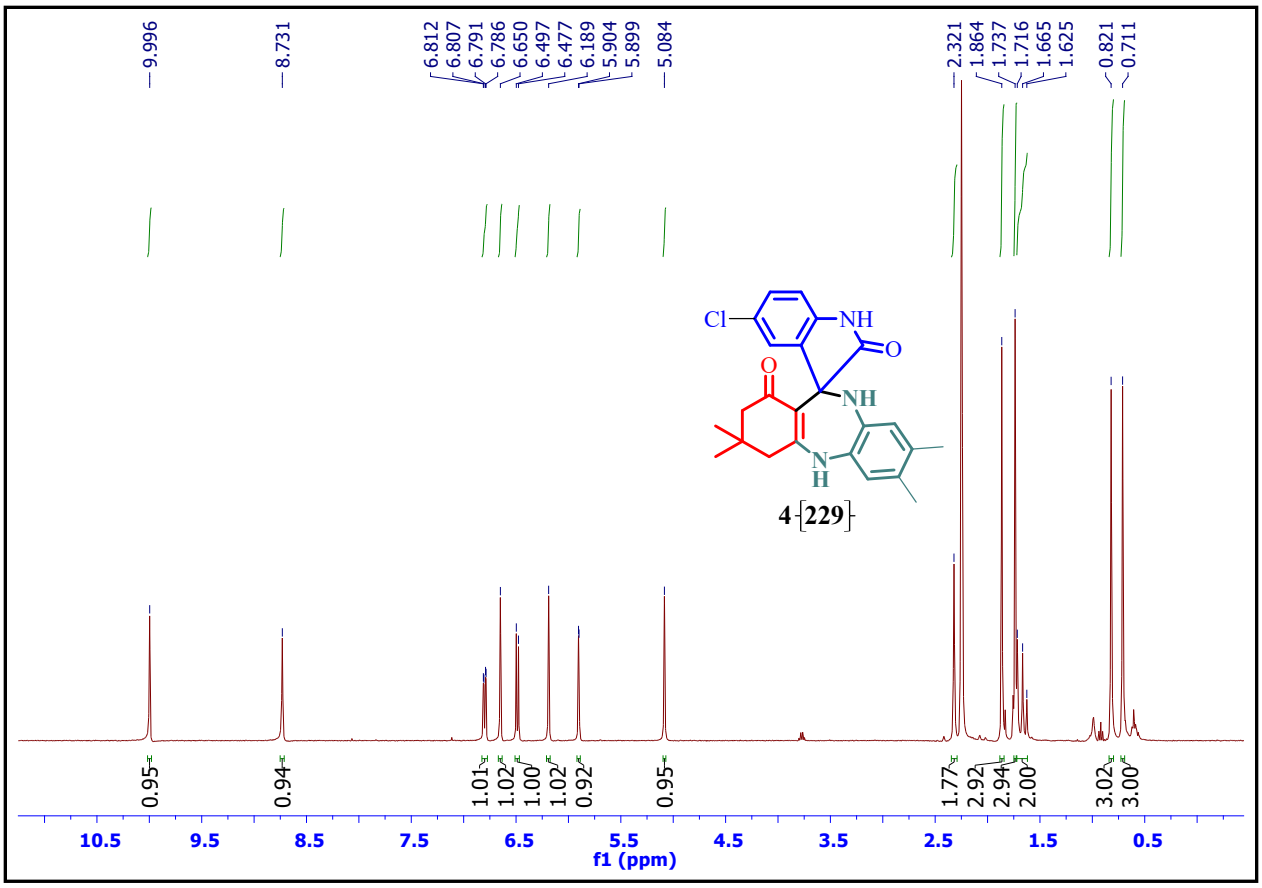


Figure S37.[1]H NMR spectra of **4{229}** in DMSO-d6.

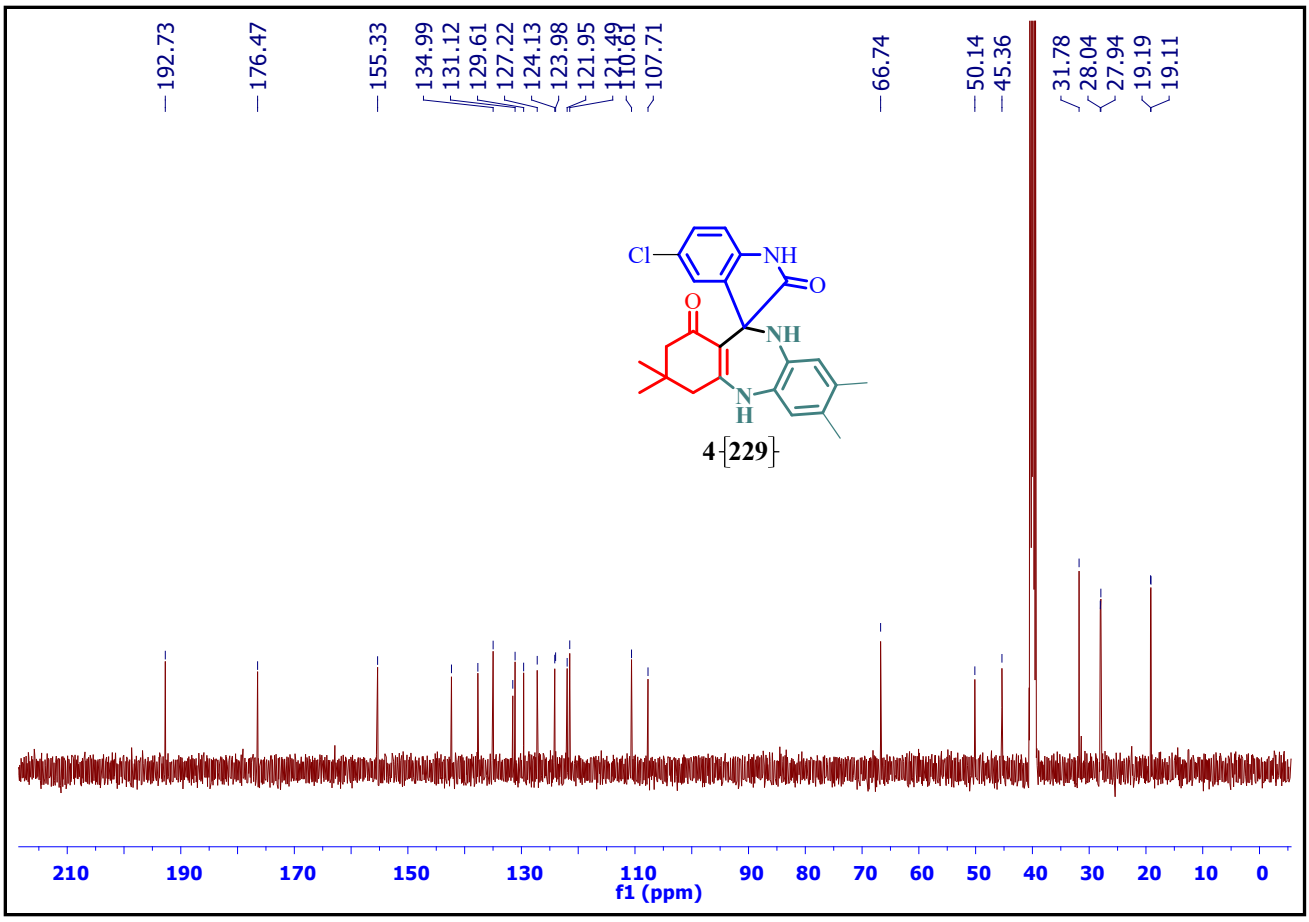


Figure S38. ^{13}C NMR spectra of **4{229}** in DMSO-d6.

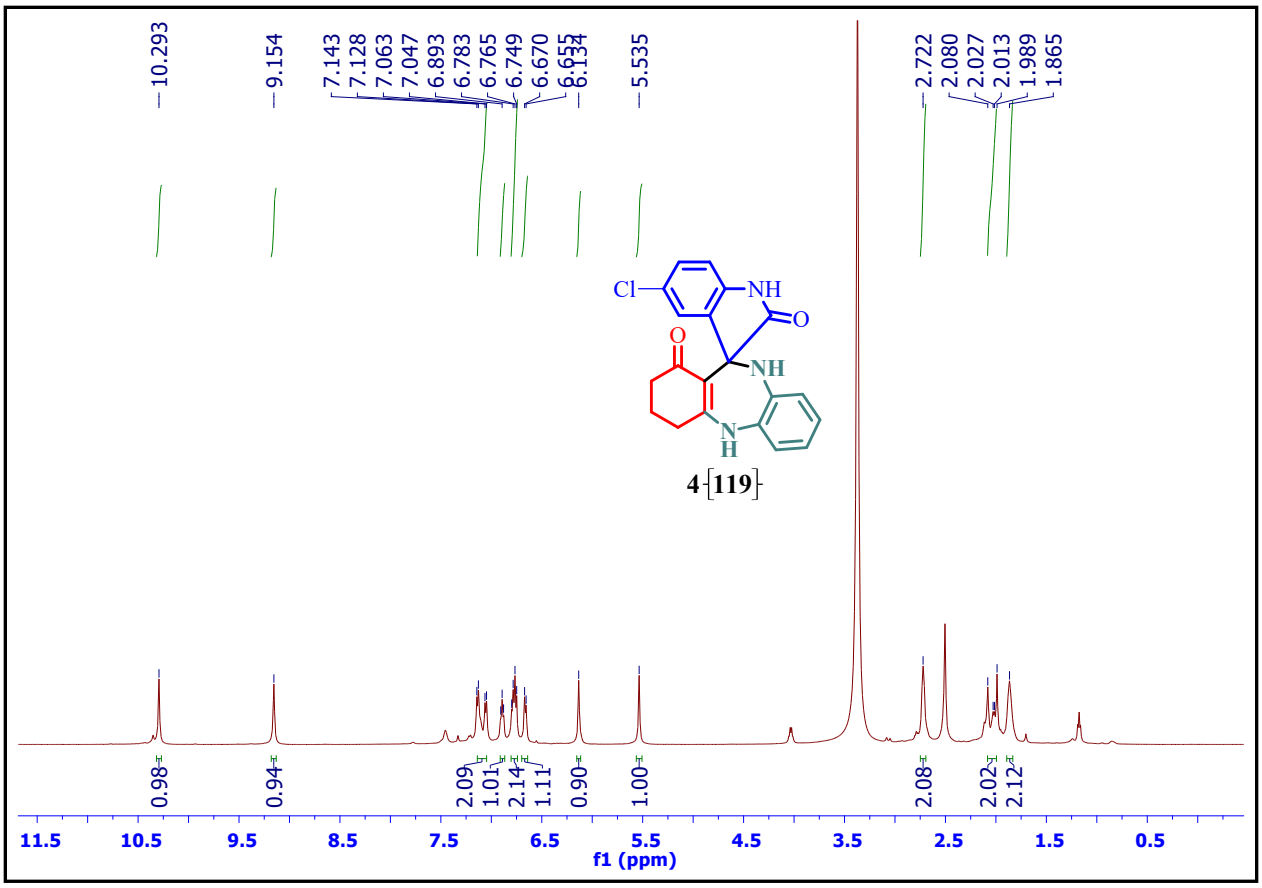


Figure S39.[1]H NMR spectra of **4{119}** in DMSO-d6.

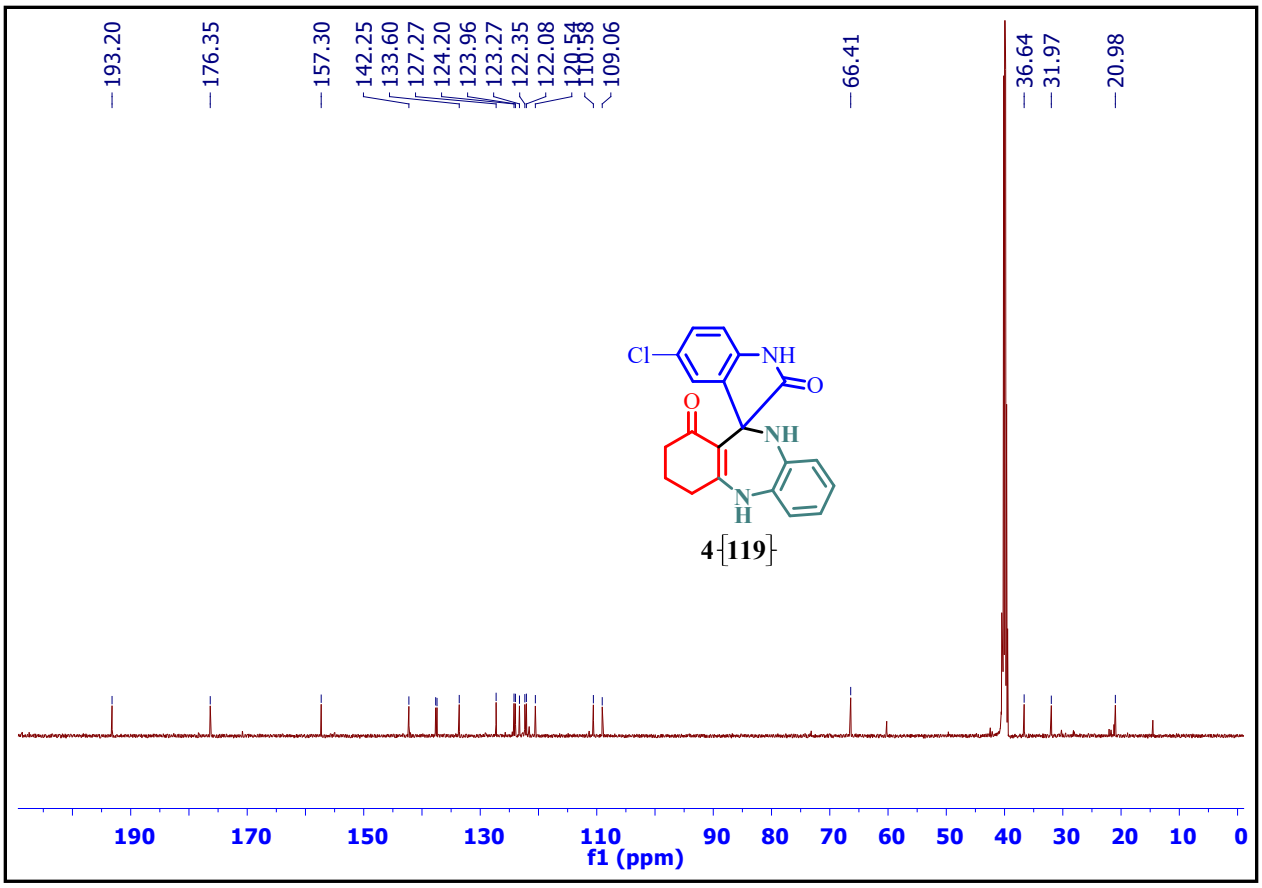


Figure S40.^{13}C NMR spectra of **4{119}** in DMSO-d6.

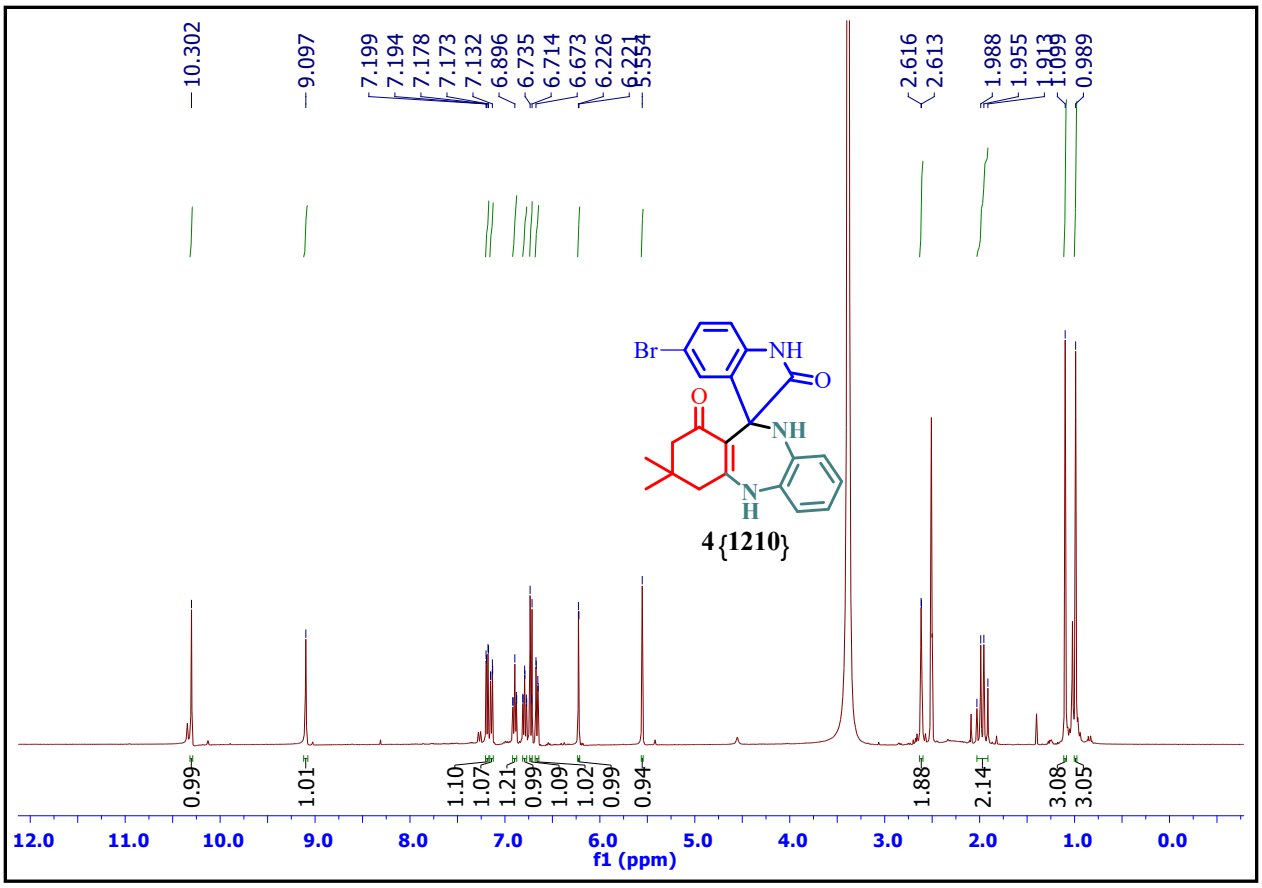


Figure S41.[1]H NMR spectra of **4{1210}** in DMSO-d6.

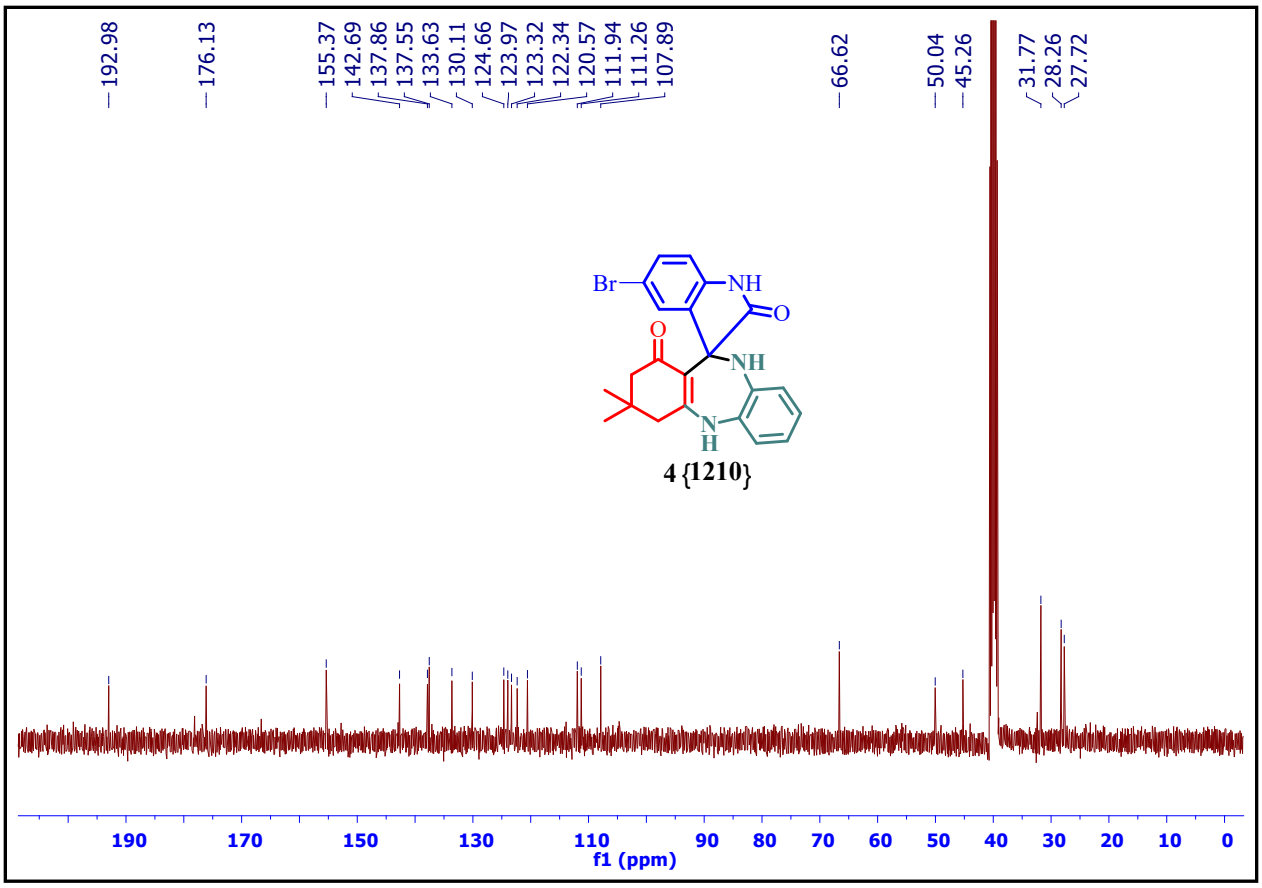


Figure S42.[13]C NMR spectra of **4{1210}** in DMSO-d6.

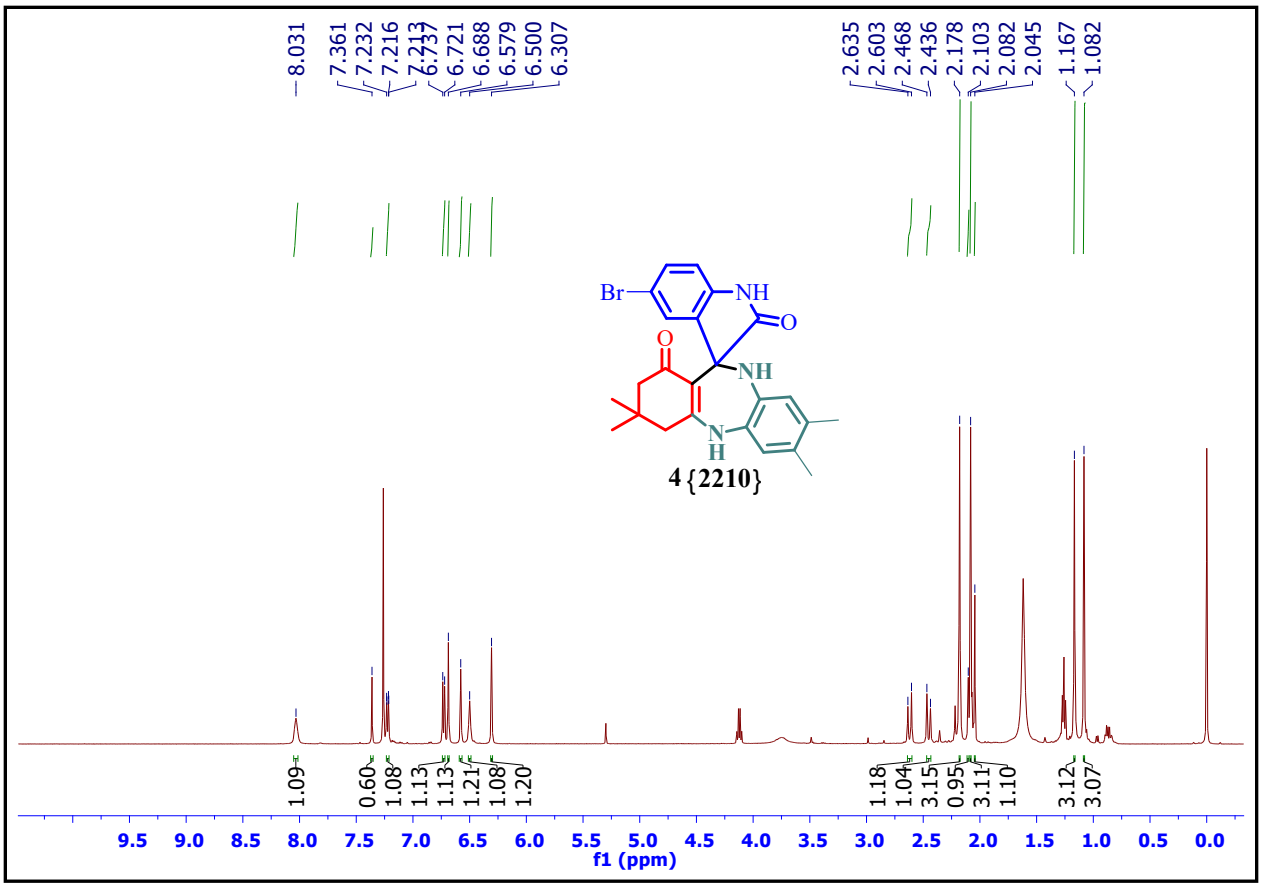


Figure S43. ^{1}H NMR spectra of **4{2210}** in $CDCl_3$.

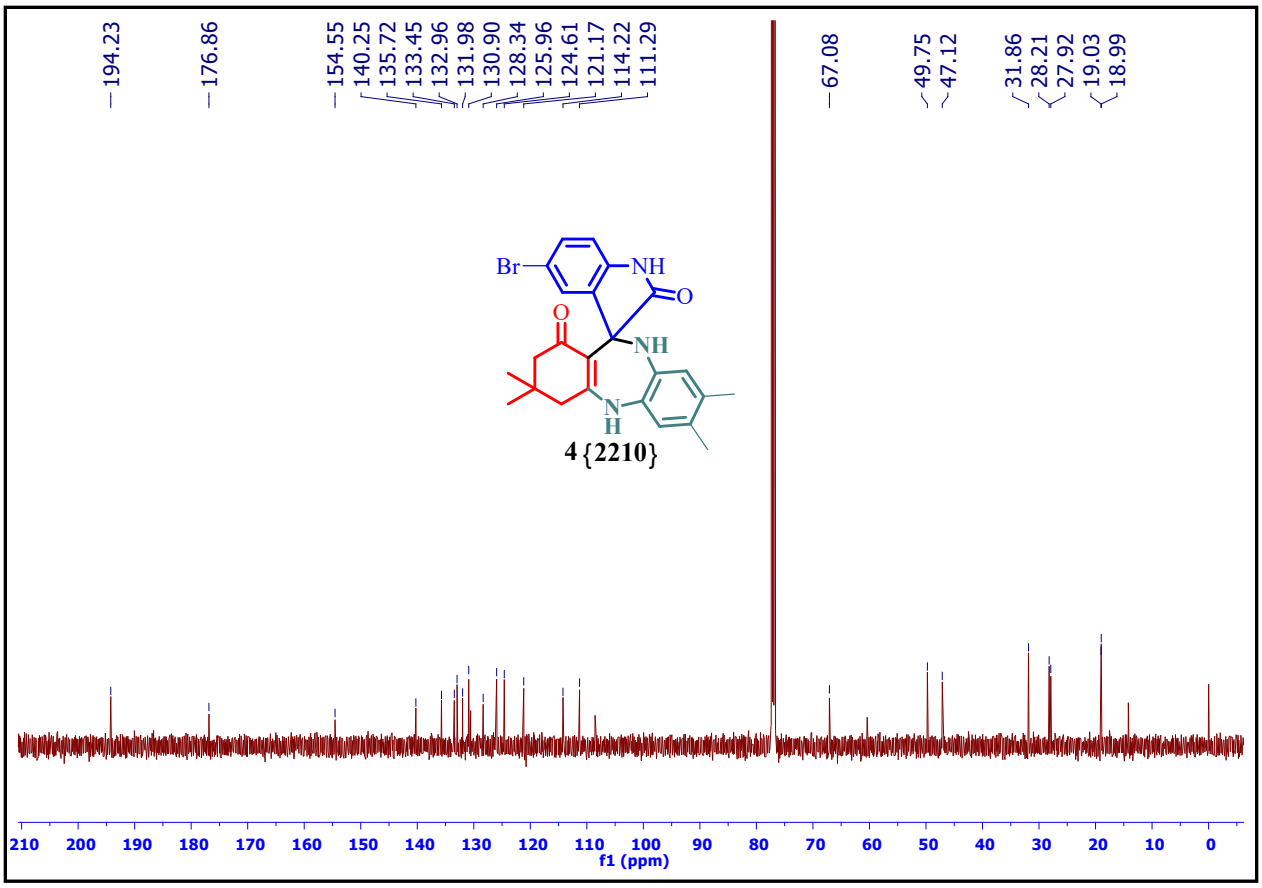


Figure S44. ^{13}C NMR spectra of **4{2210}** in $CDCl_3$.

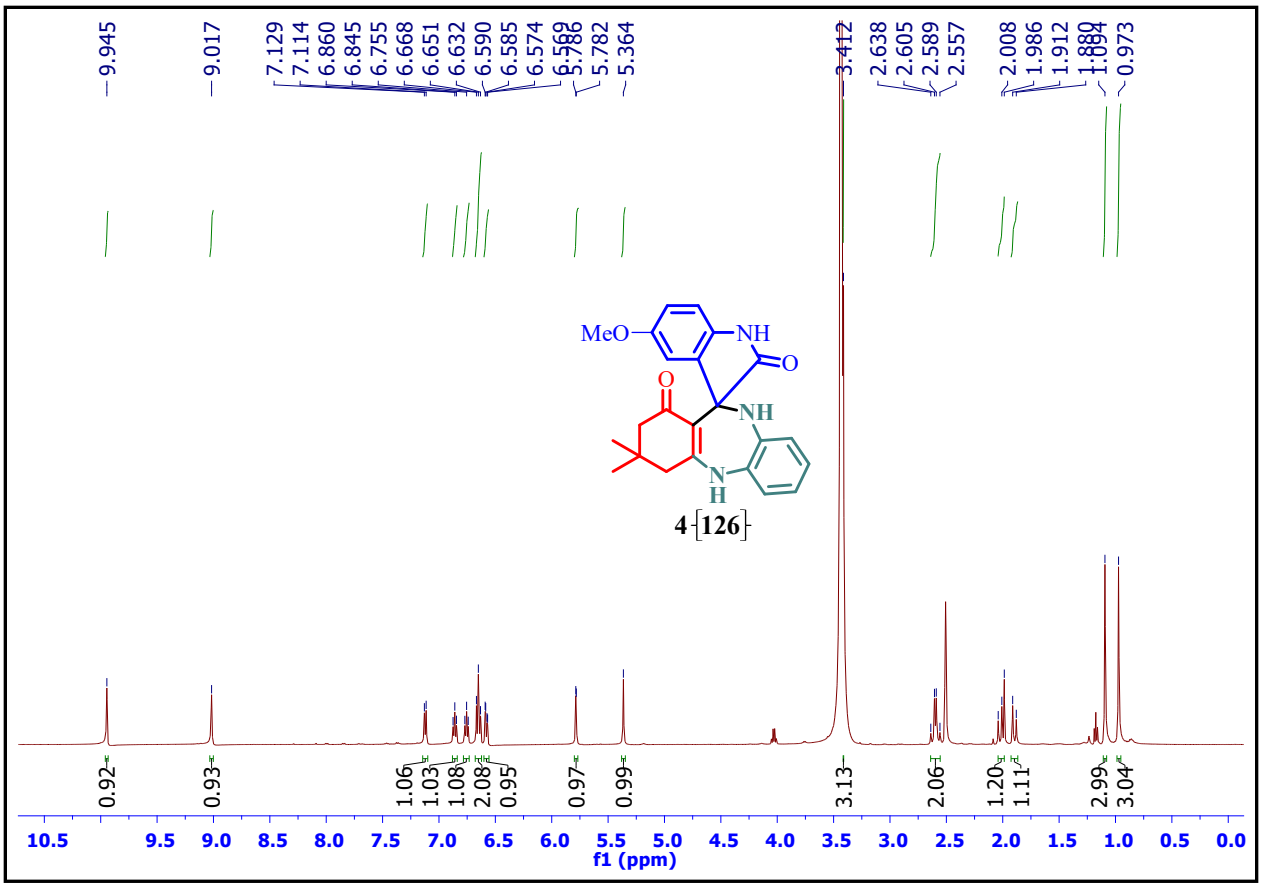


Figure 45. ^{1}H NMR spectra of **4{126}** in DMSO-d6.

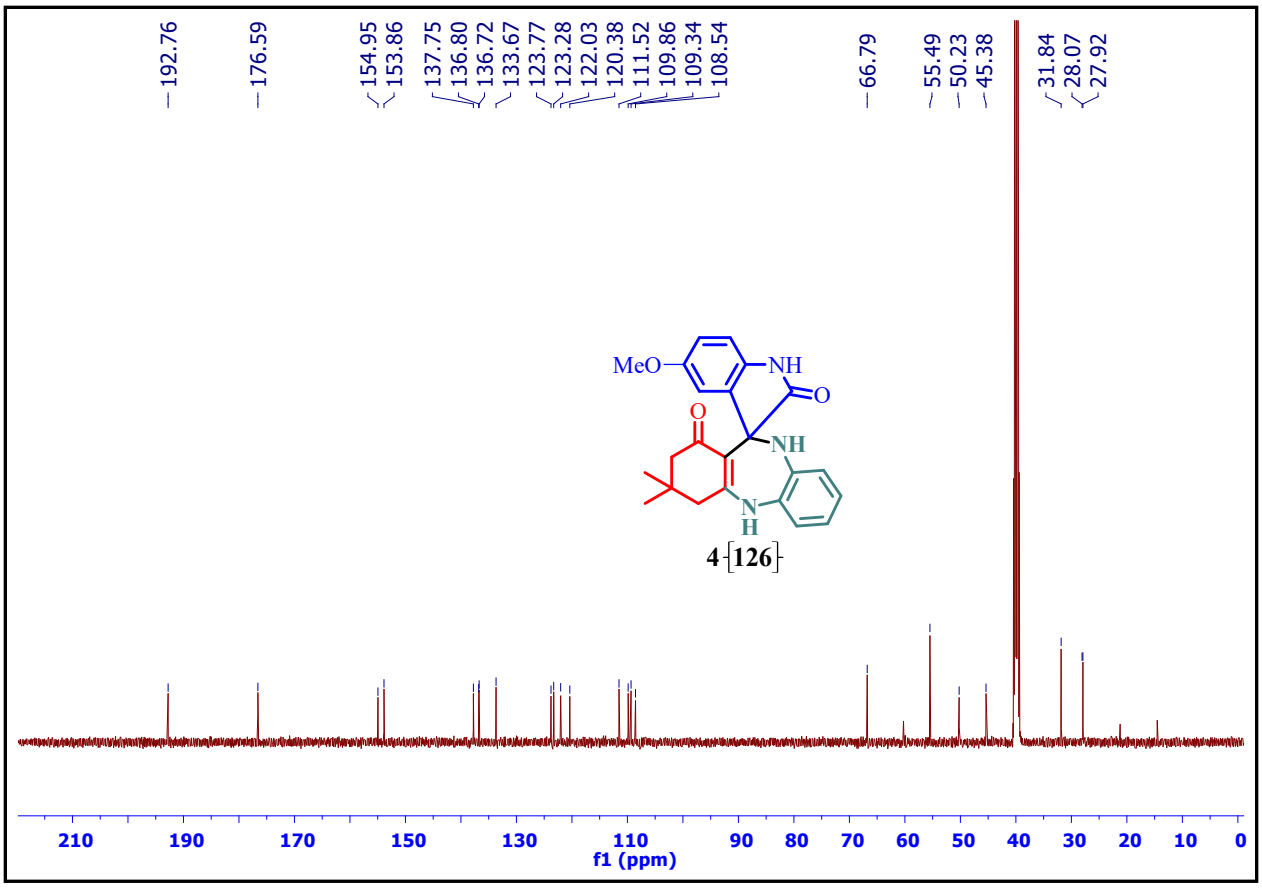


Figure S46. ^{13}C NMR spectra of **4{126}** in DMSO-d6.

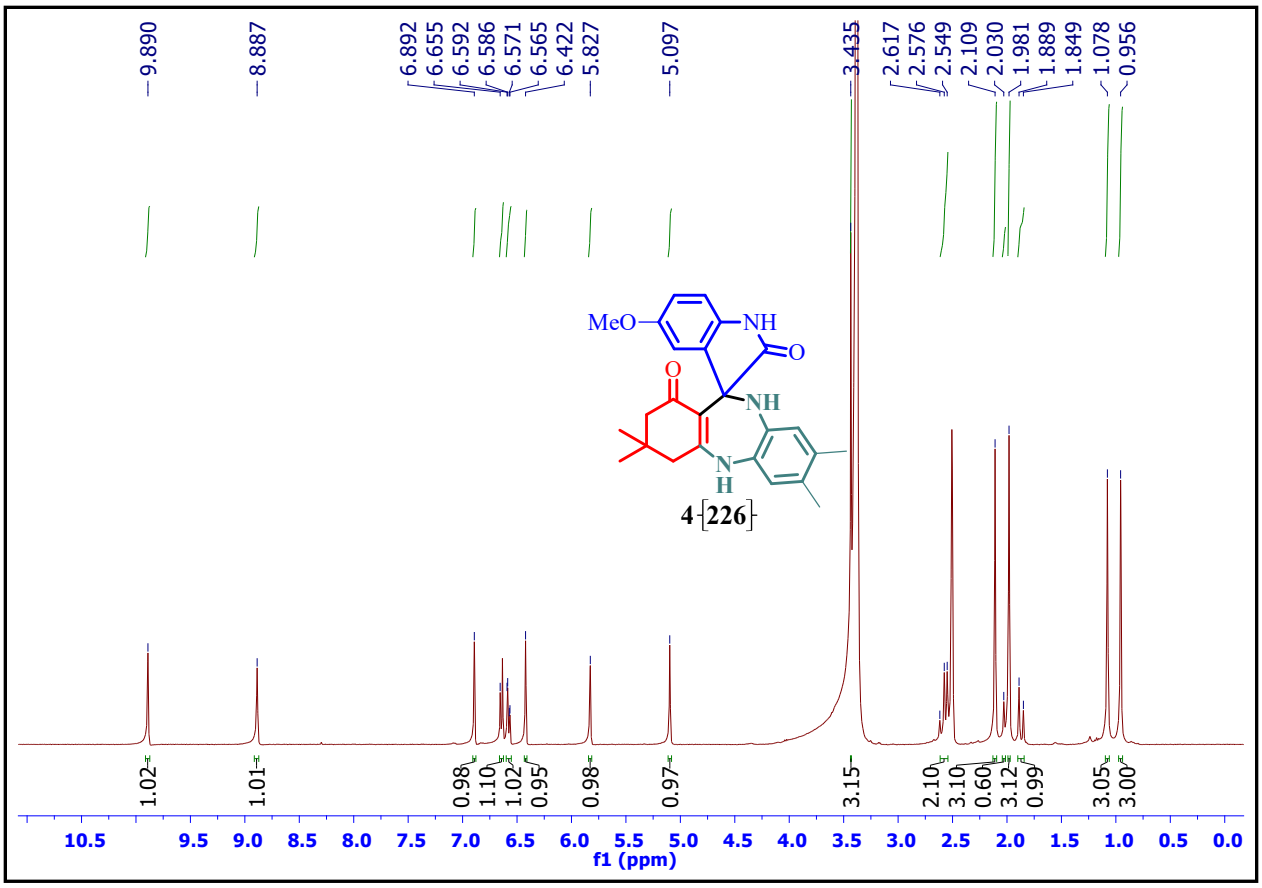


Figure S47.[1]H NMR spectra of **4{226}** in DMSO-d6.

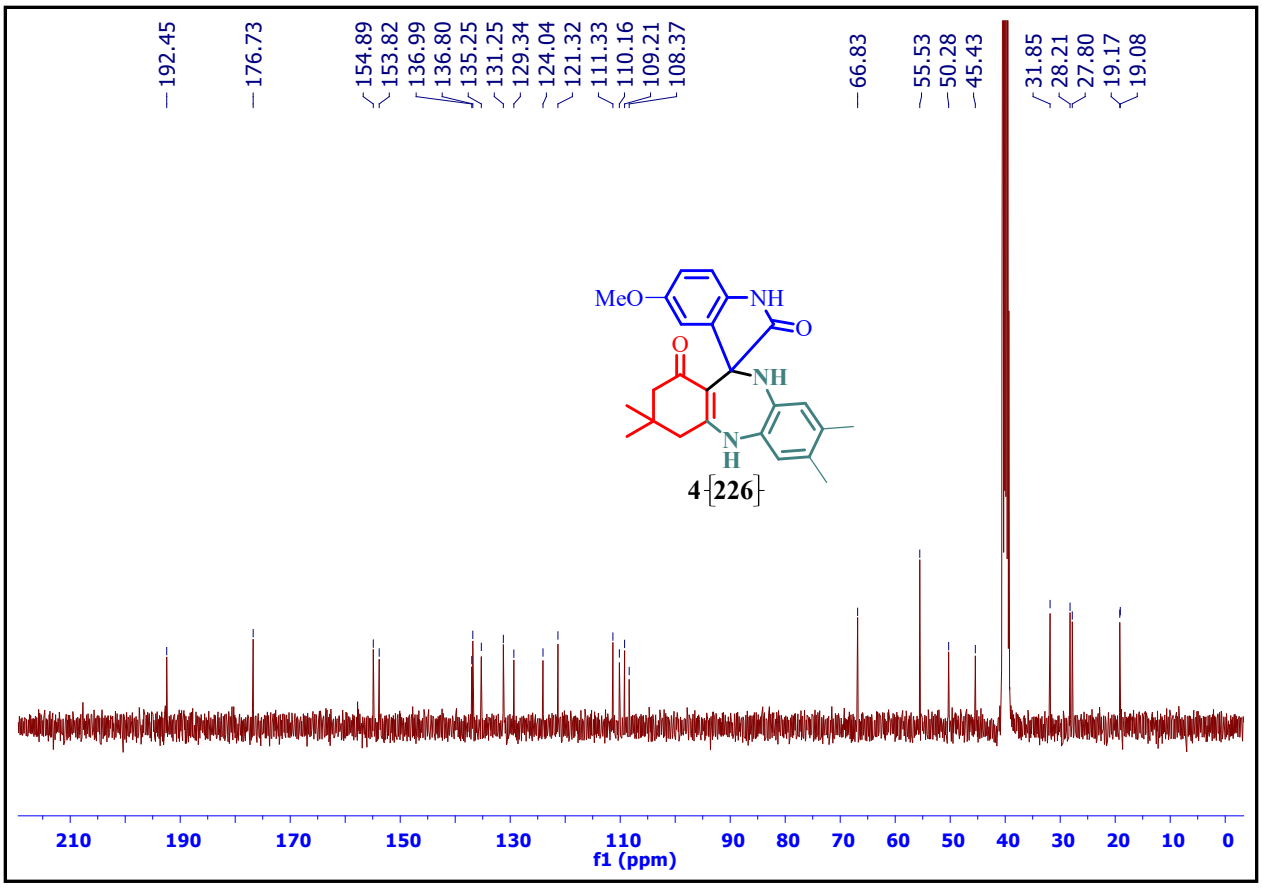


Figure S48. ^{13}C NMR spectra of **4{226}** in DMSO-d6.

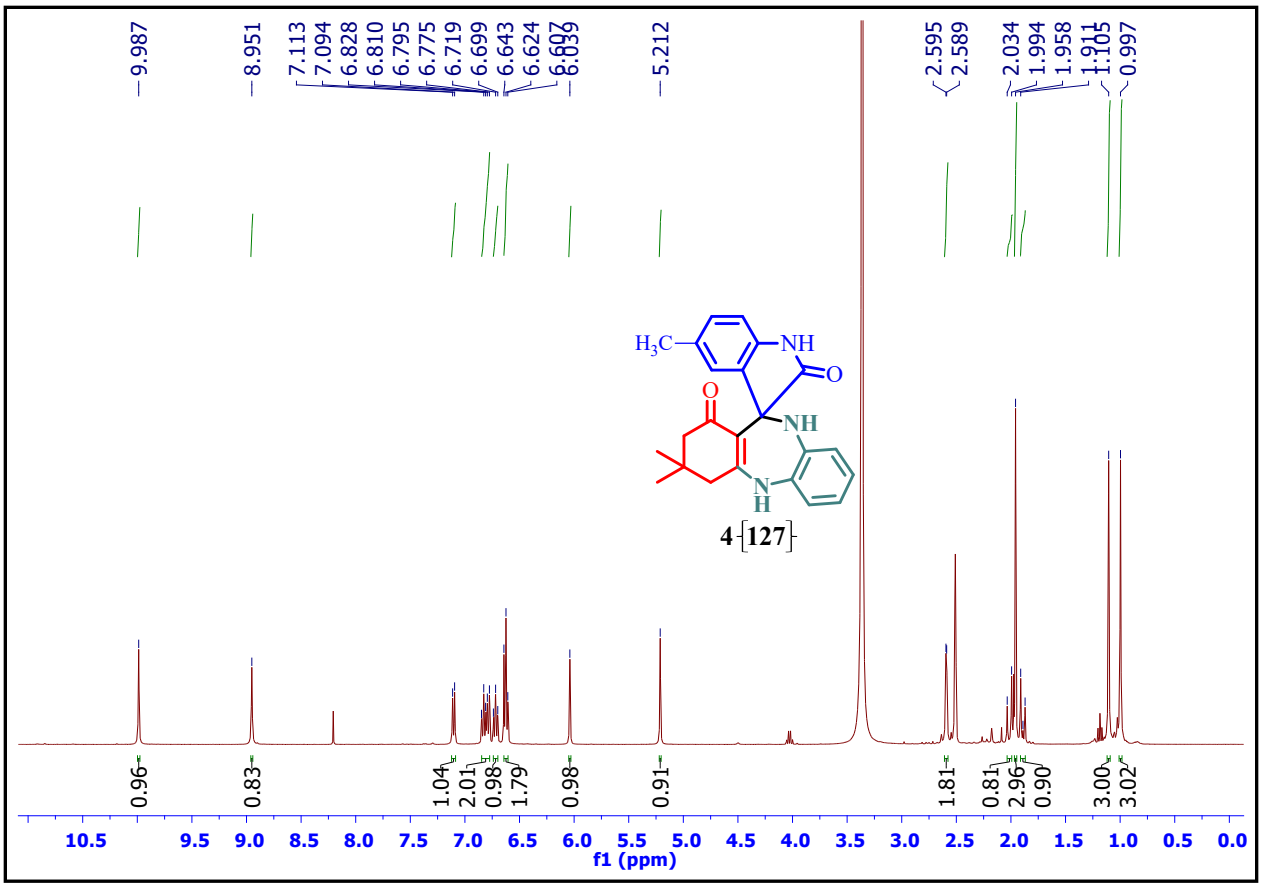


Figure S49.[1]H NMR spectra of **4{127}** in DMSO-d6.

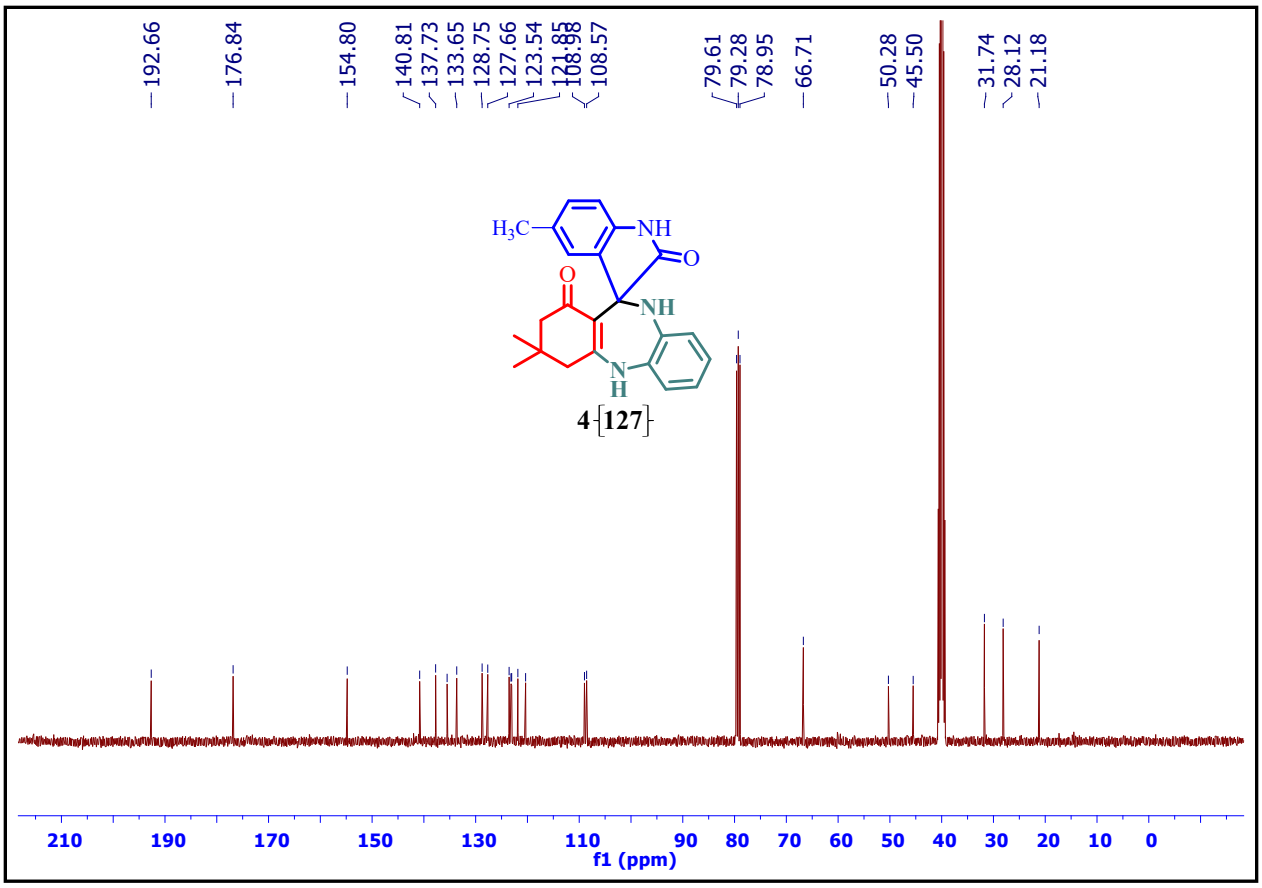


Figure S50.[13]C NMR spectra of **4{127}** in DMSO-d6.

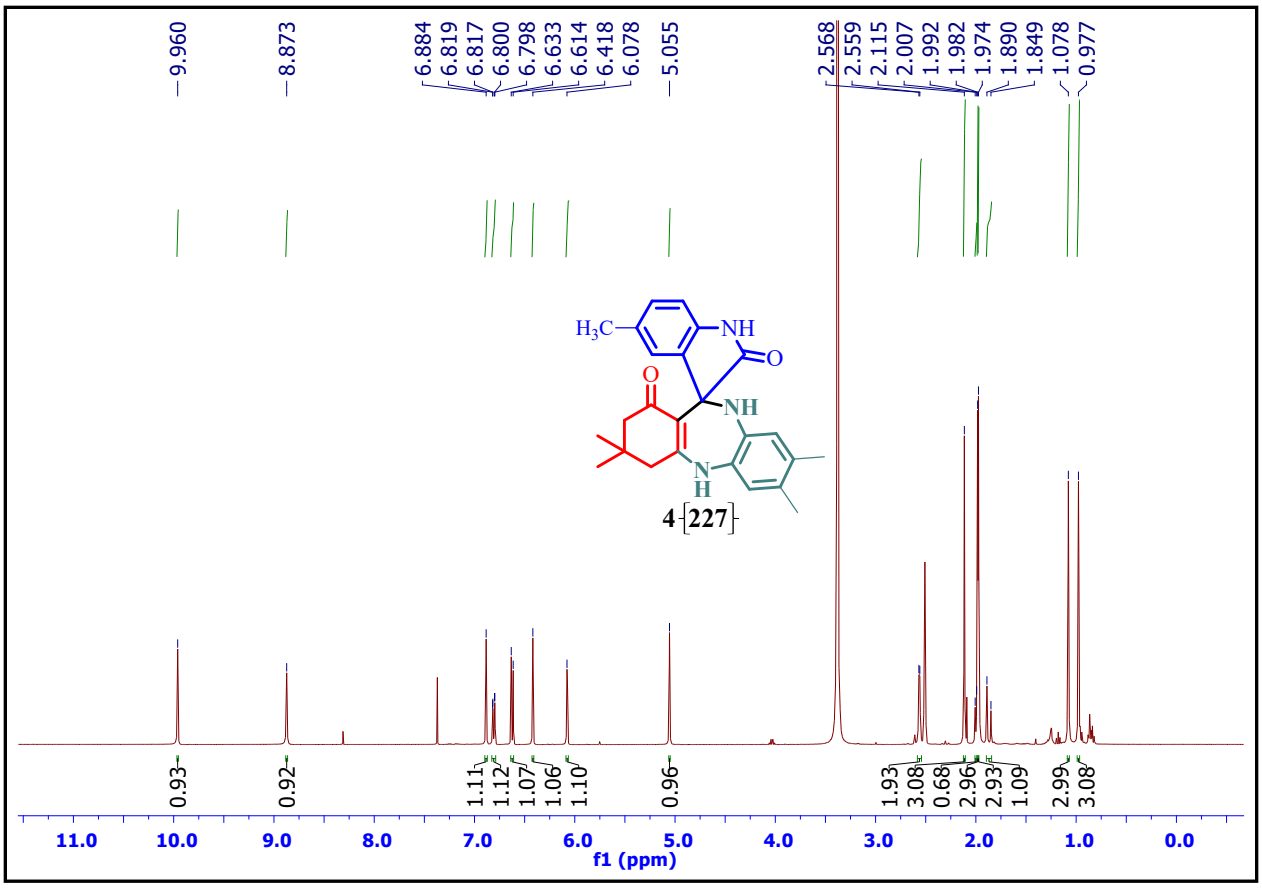


Figure 51. ^{1}H NMR spectra of **4{227}** in DMSO-d6.

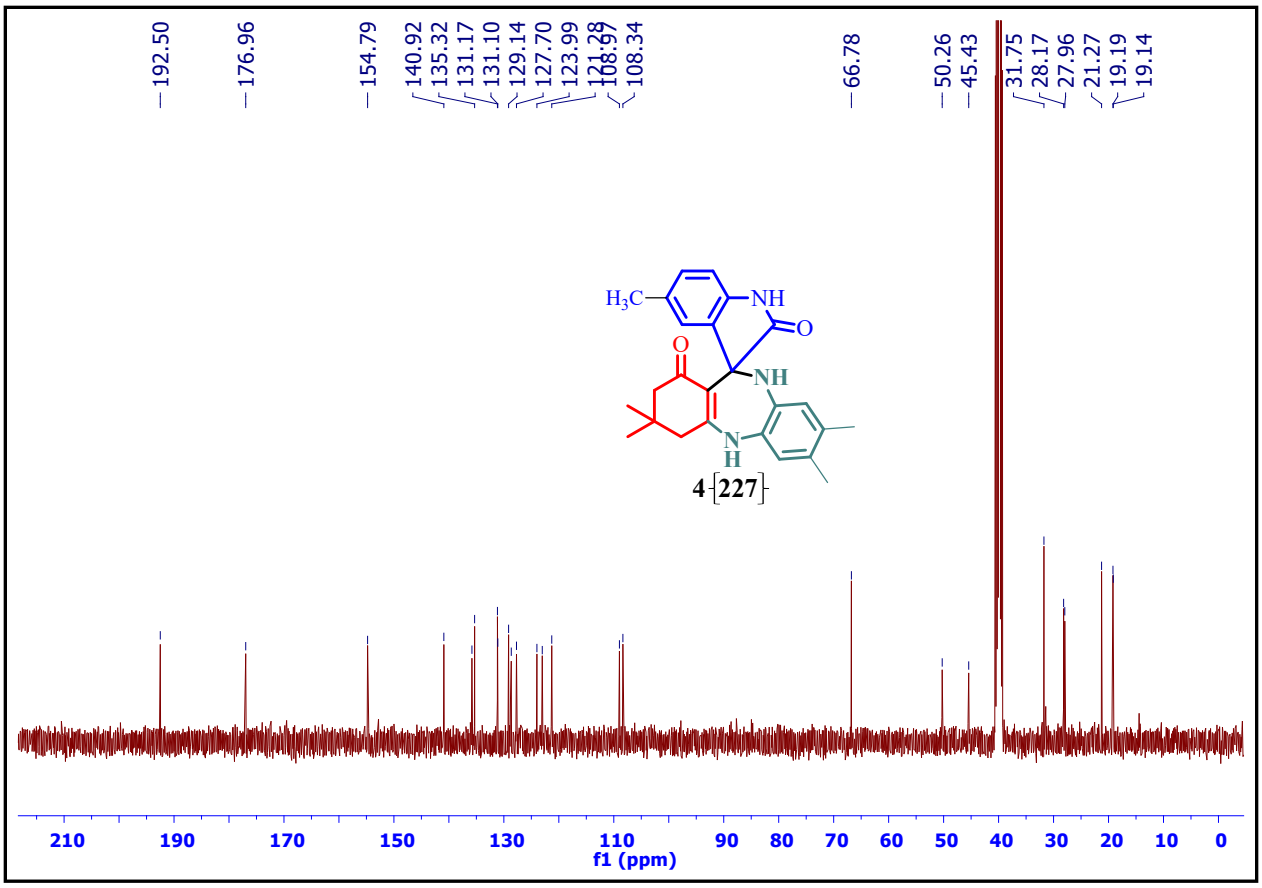


Figure S52.[13]C NMR spectra of **4{227}** in DMSO-d6.

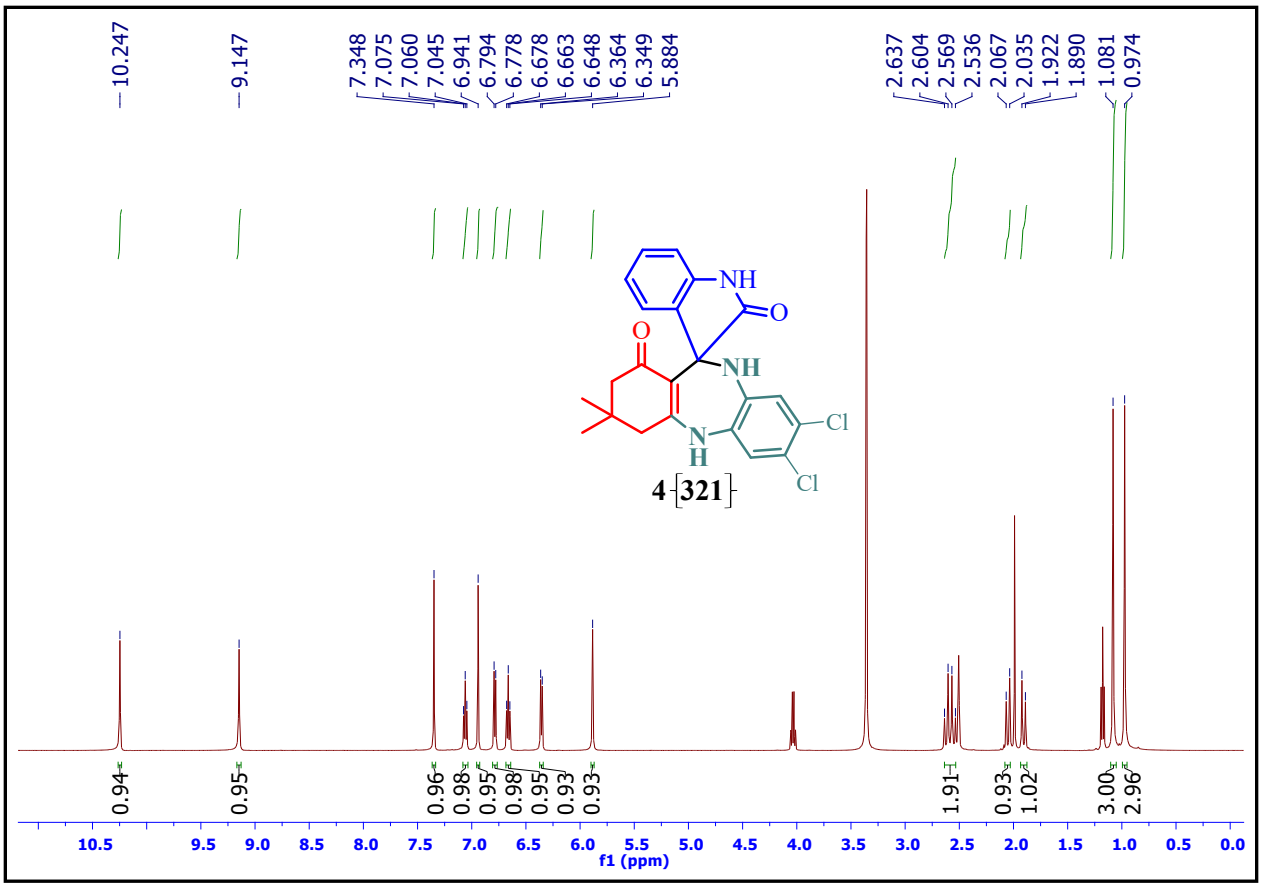


Figure S53.[1]H NMR spectra of **4{321}** in DMSO-d6.

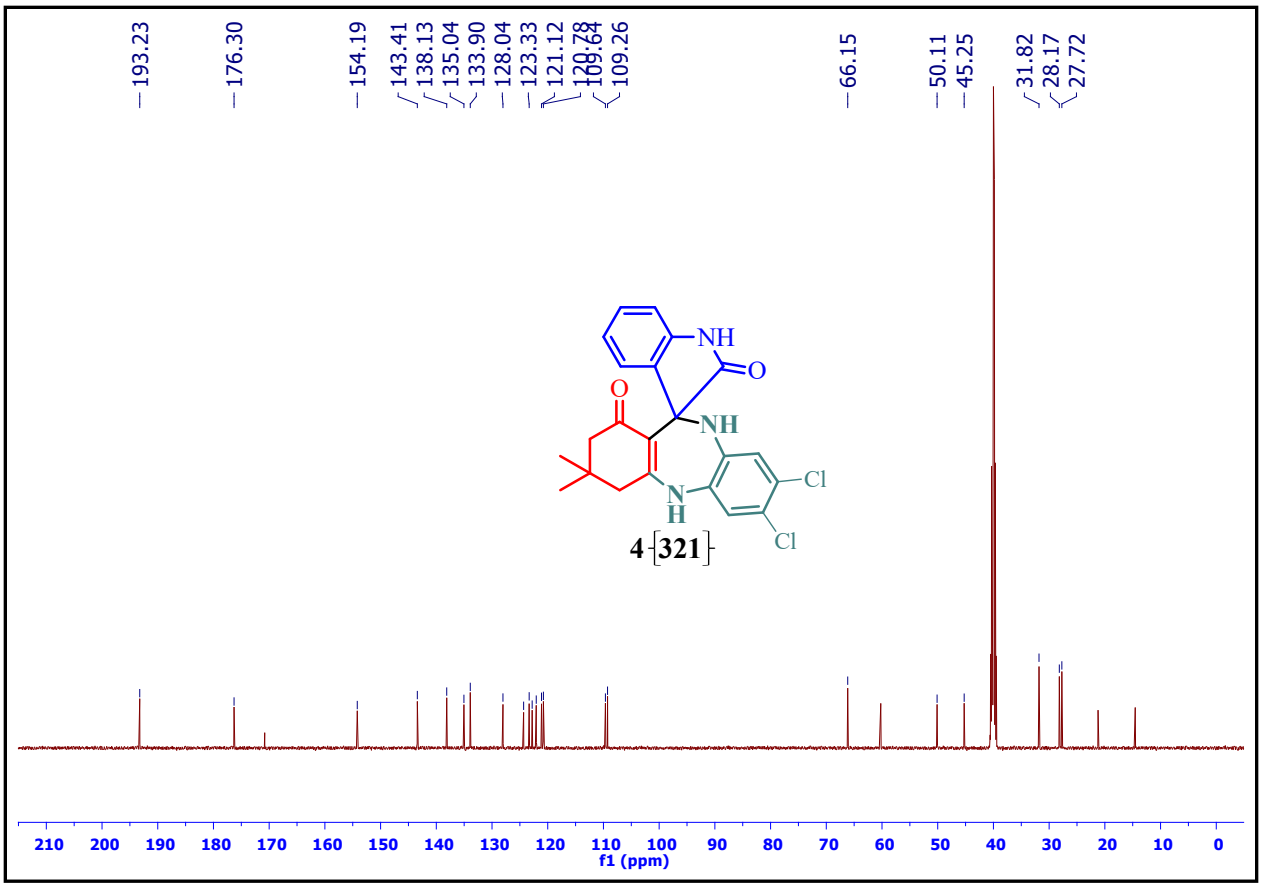


Figure S54.[13]C NMR spectra of **4{321}** in DMSO-d6.

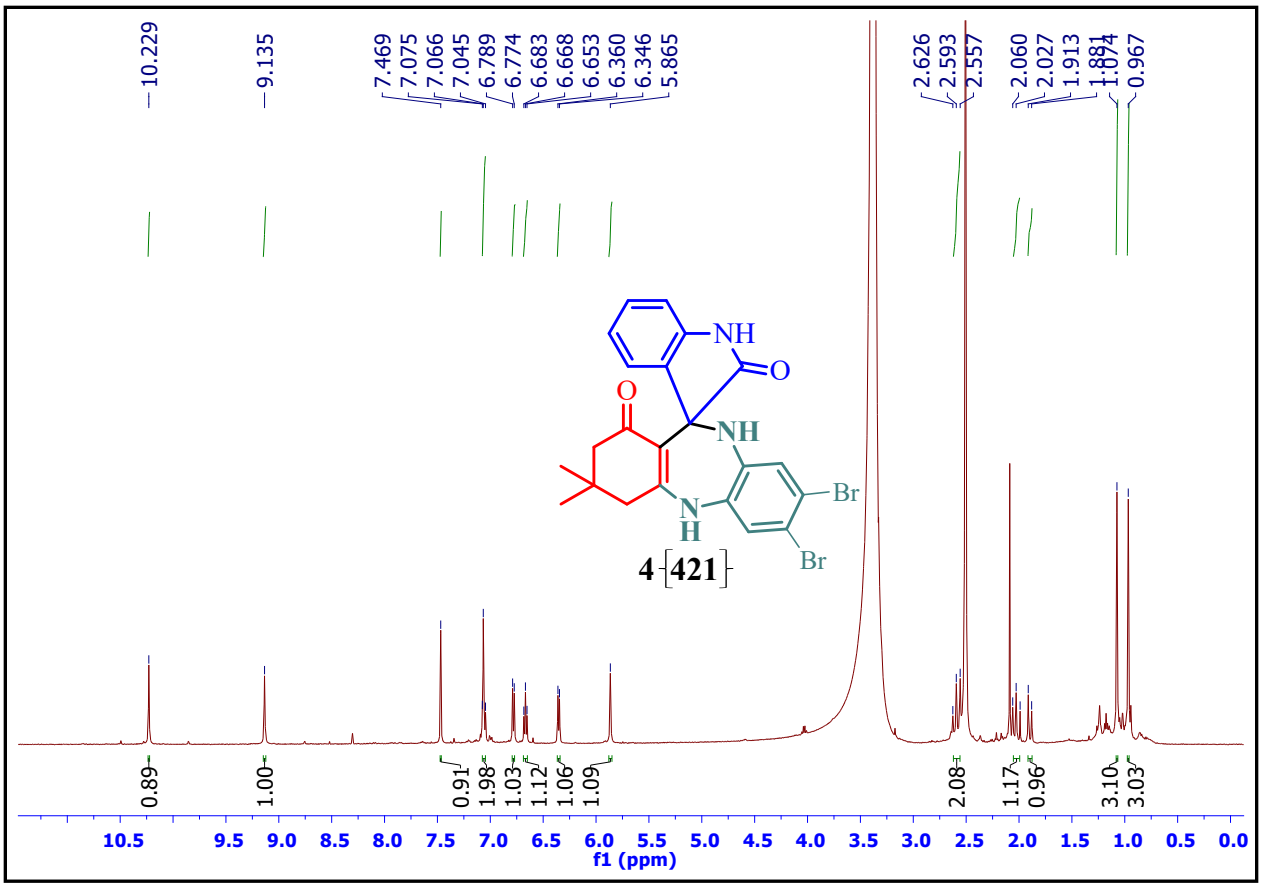


Figure S55.[1]H NMR spectra of **4{421}** in DMSO-d6.

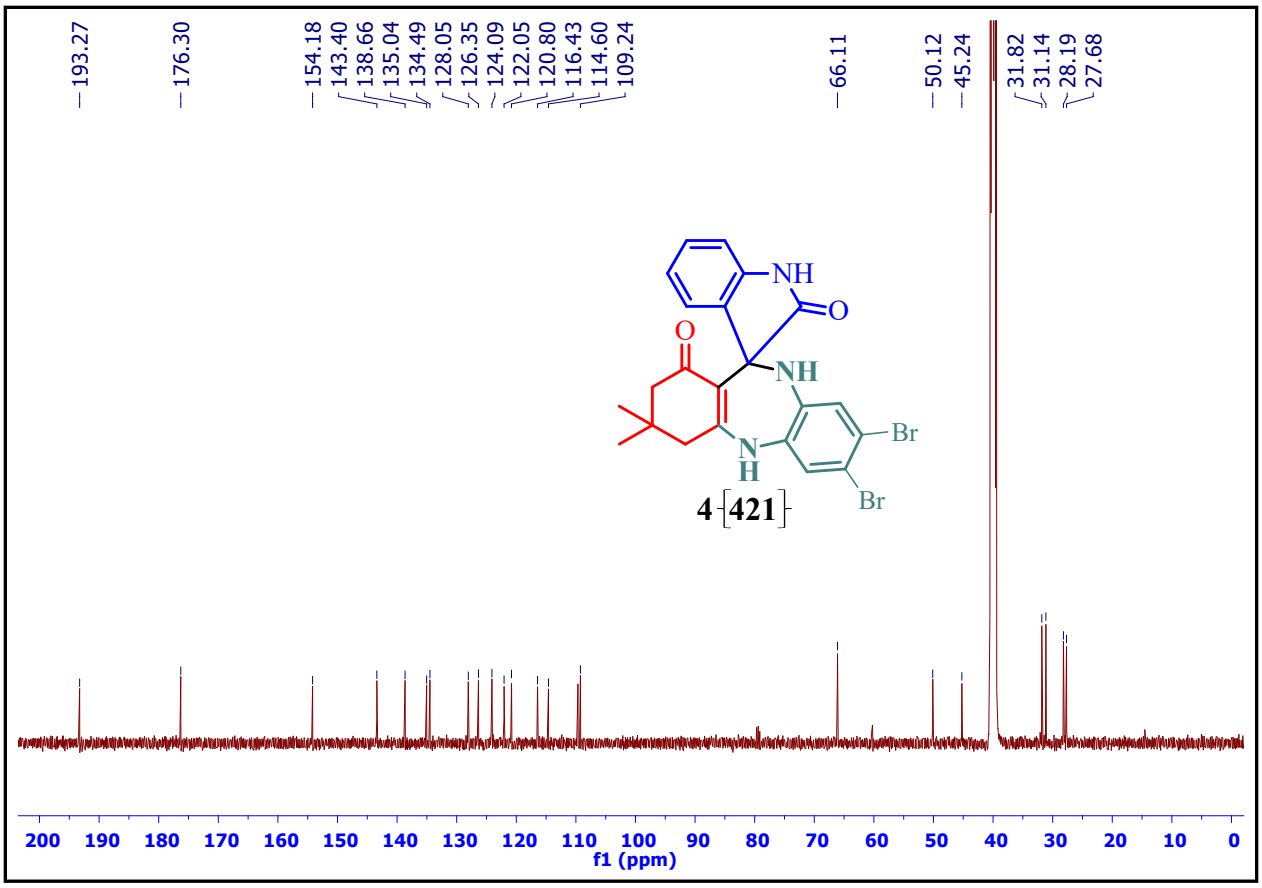


Figure S56.[13]C NMR spectra of **4{421}** in DMSO-d6.

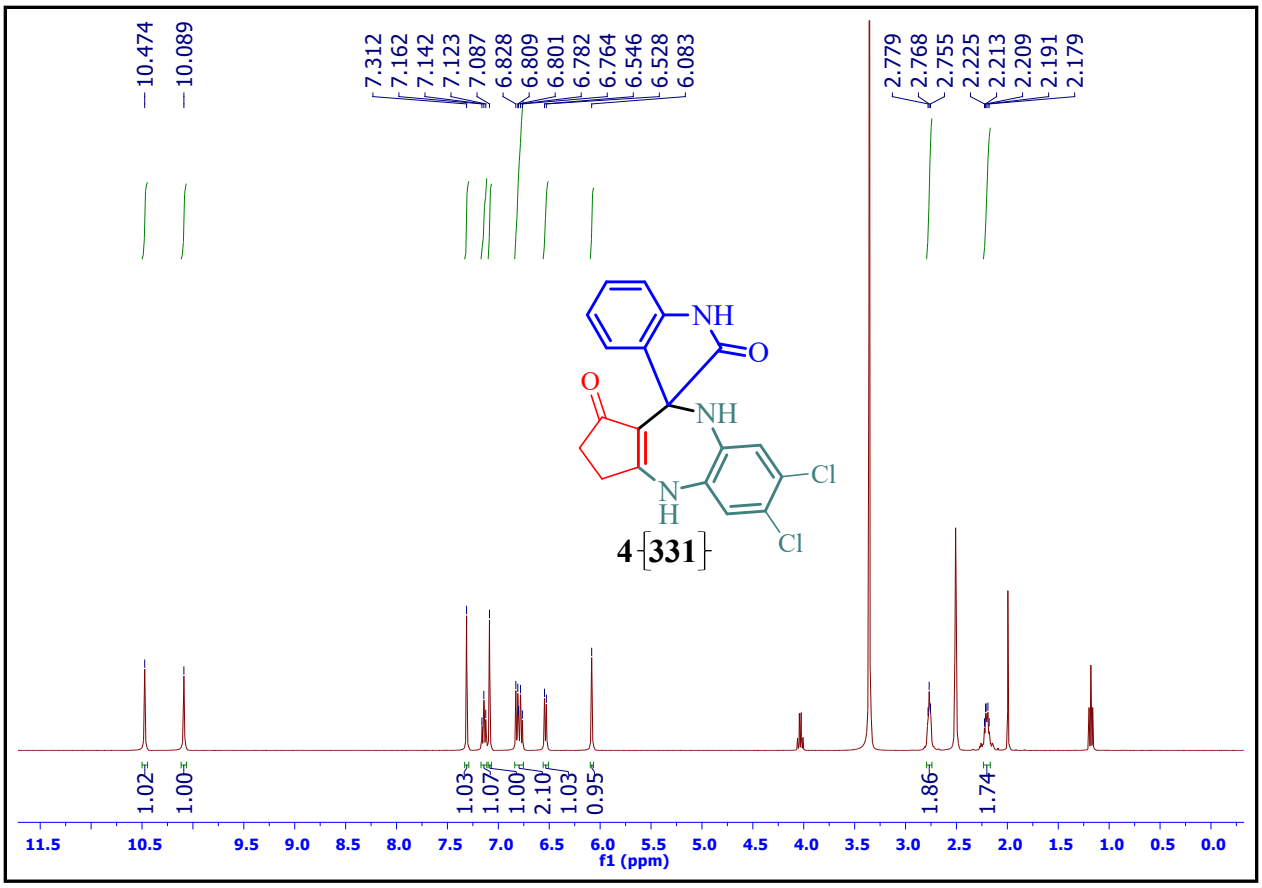


Figure S57.[1]H NMR spectra of **4{331}** in DMSO-d6.

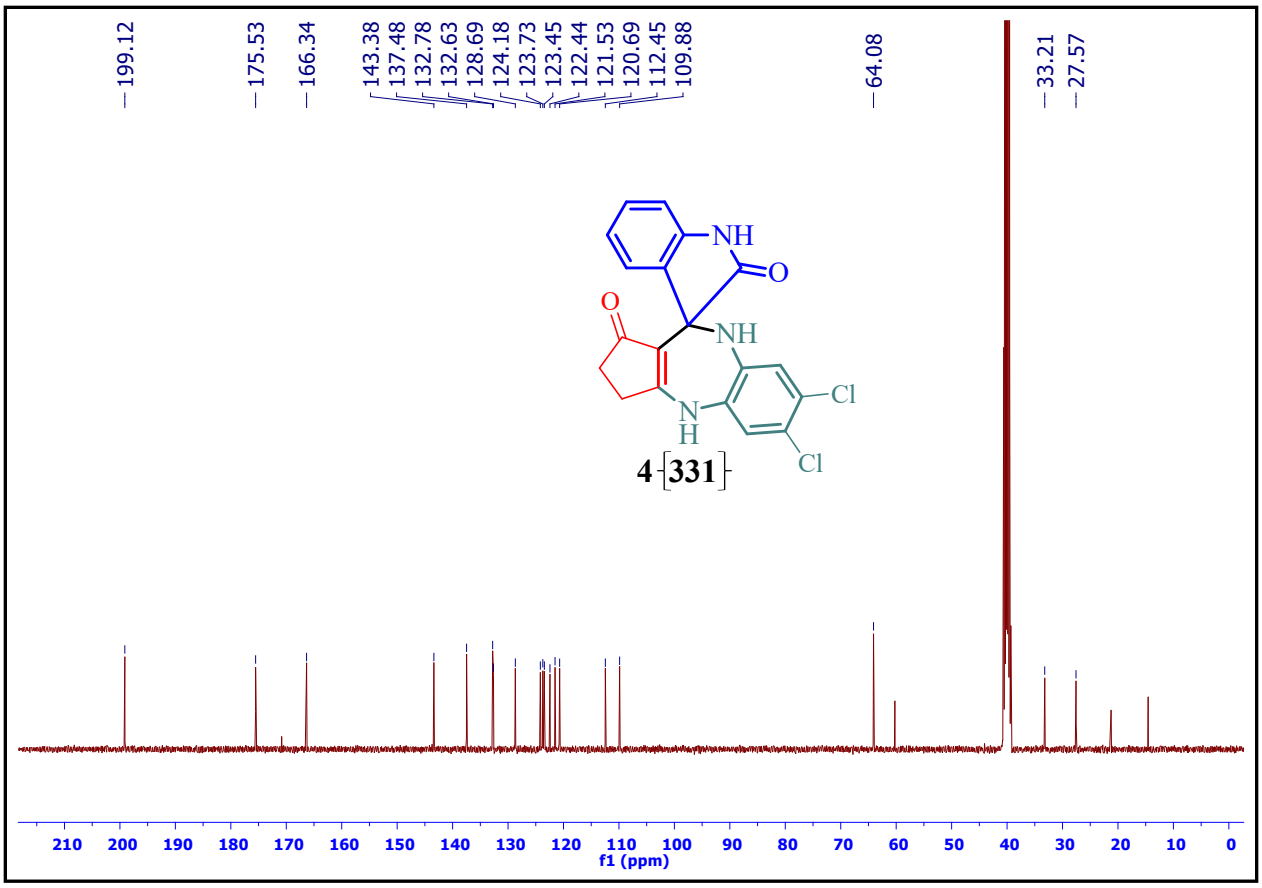


Figure S58.[13]C NMR spectra of **4{331}** in DMSO-d6.

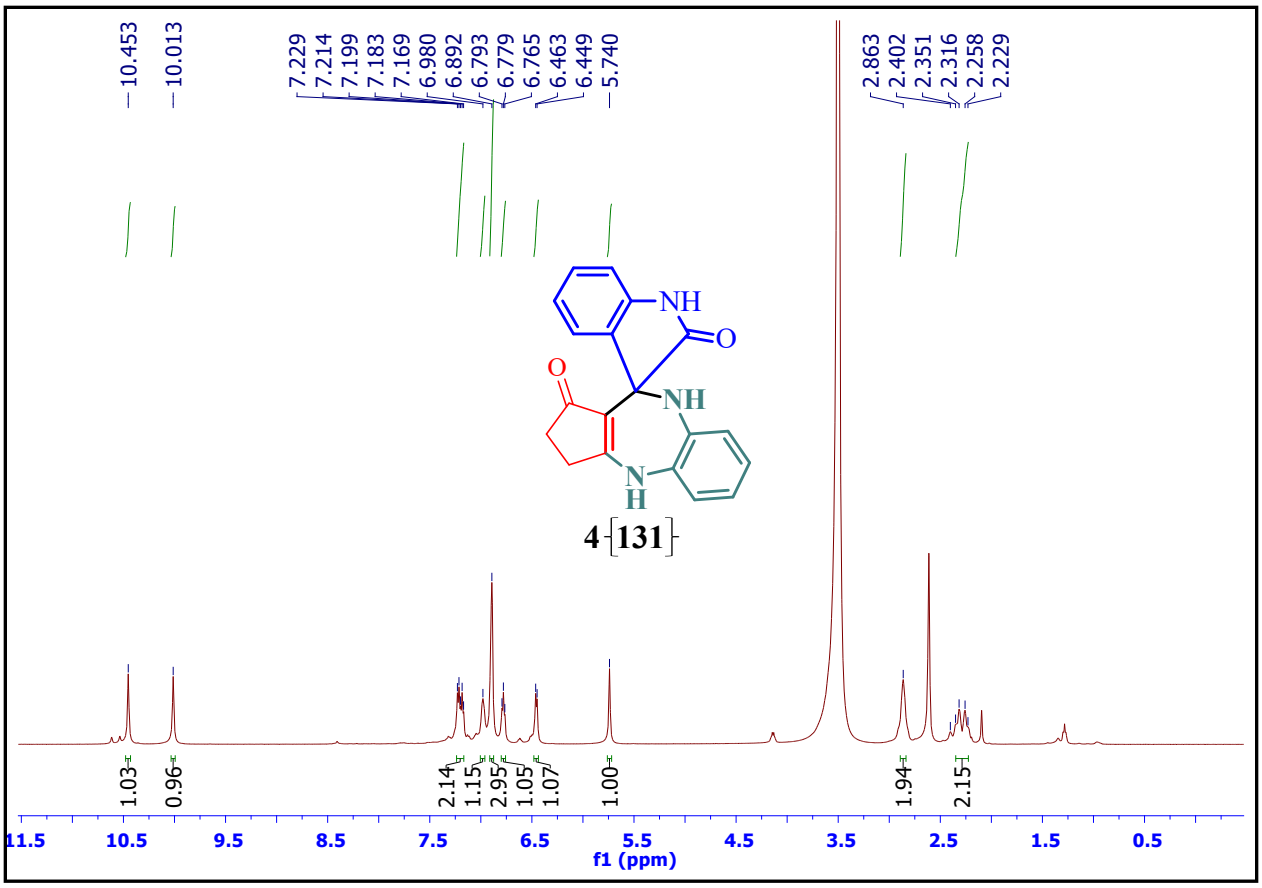


Figure S59.[1]H NMR spectra of **4{131}** in DMSO-d6.

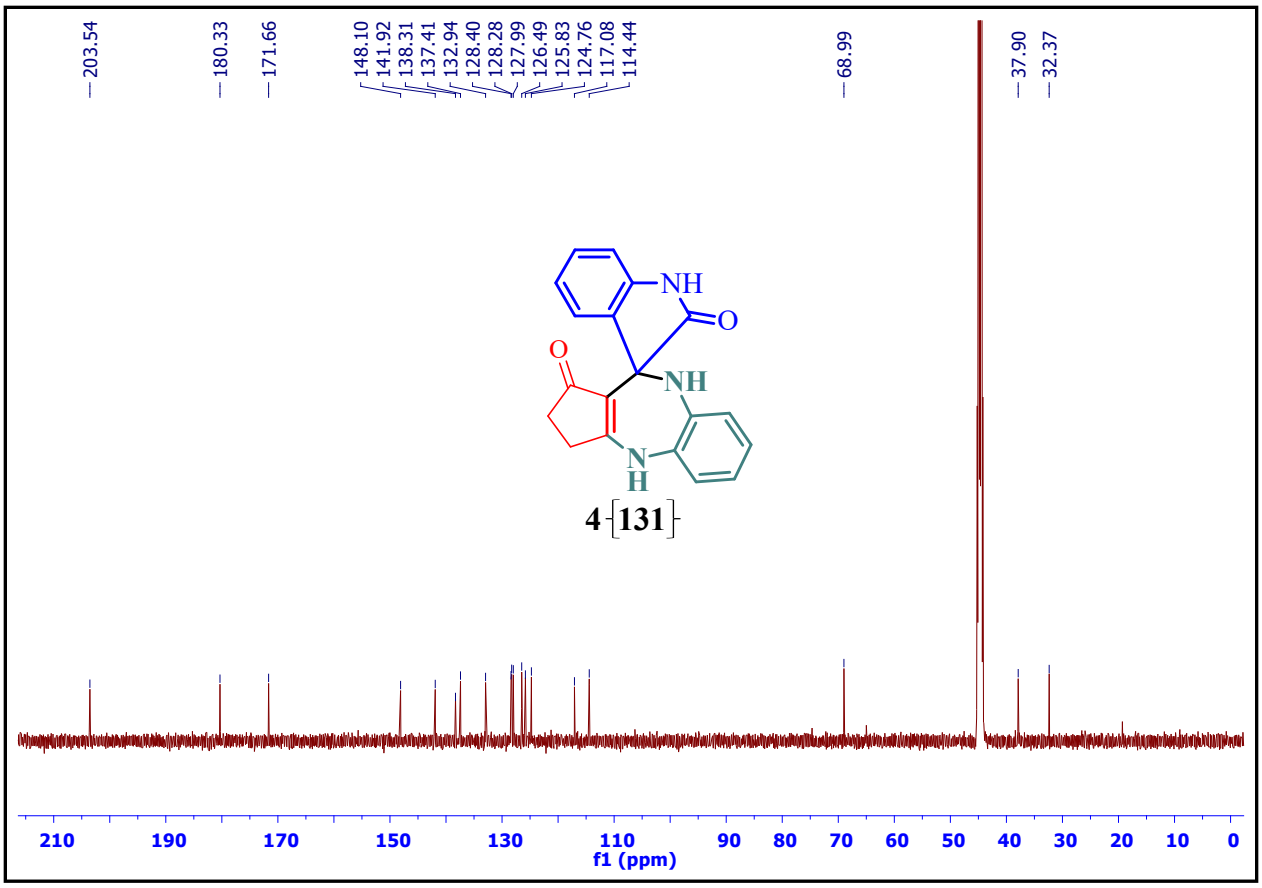


Figure S60. ^{13}C NMR spectra of **4{131}** in DMSO-d6.

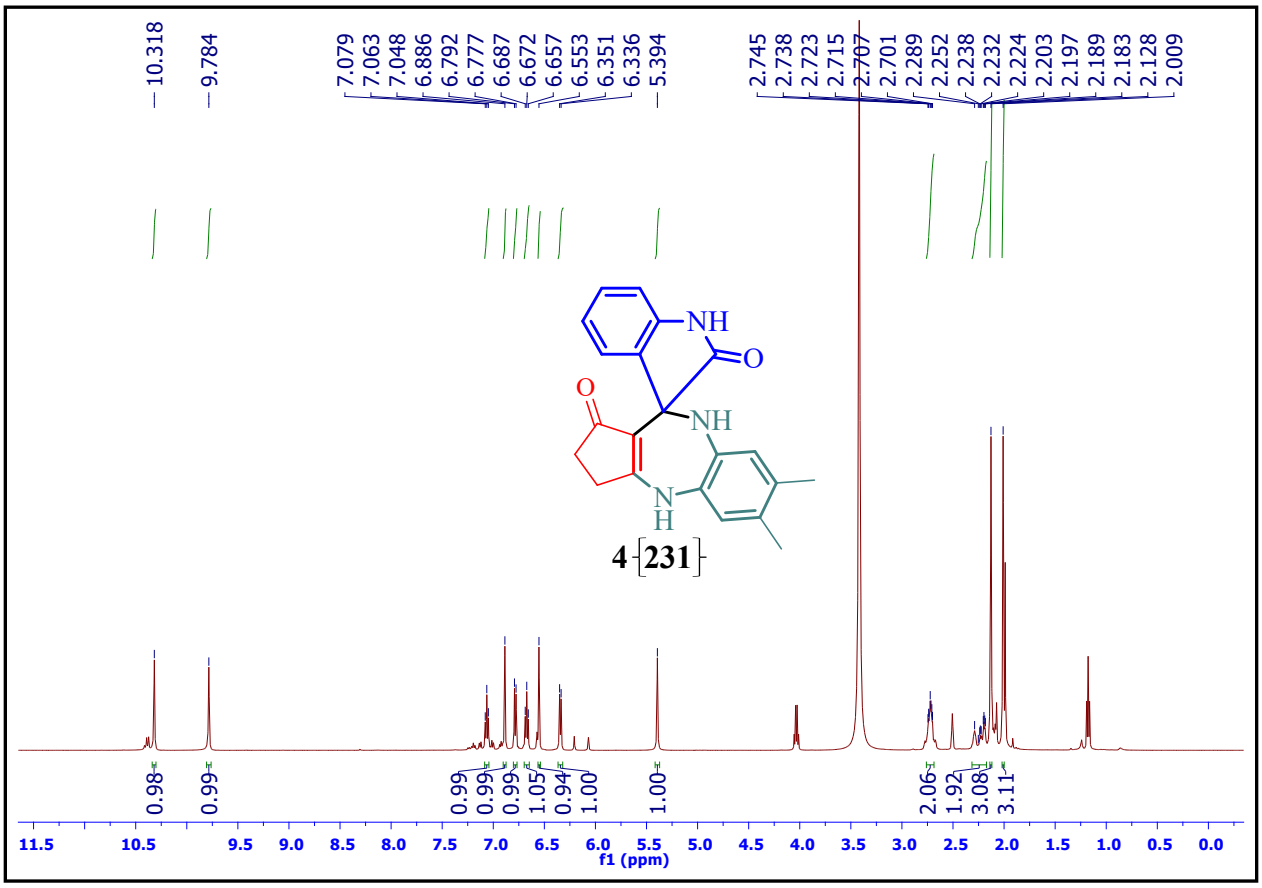


Figure S61. ^{1}H NMR spectra of **4{231}** in DMSO-d6.

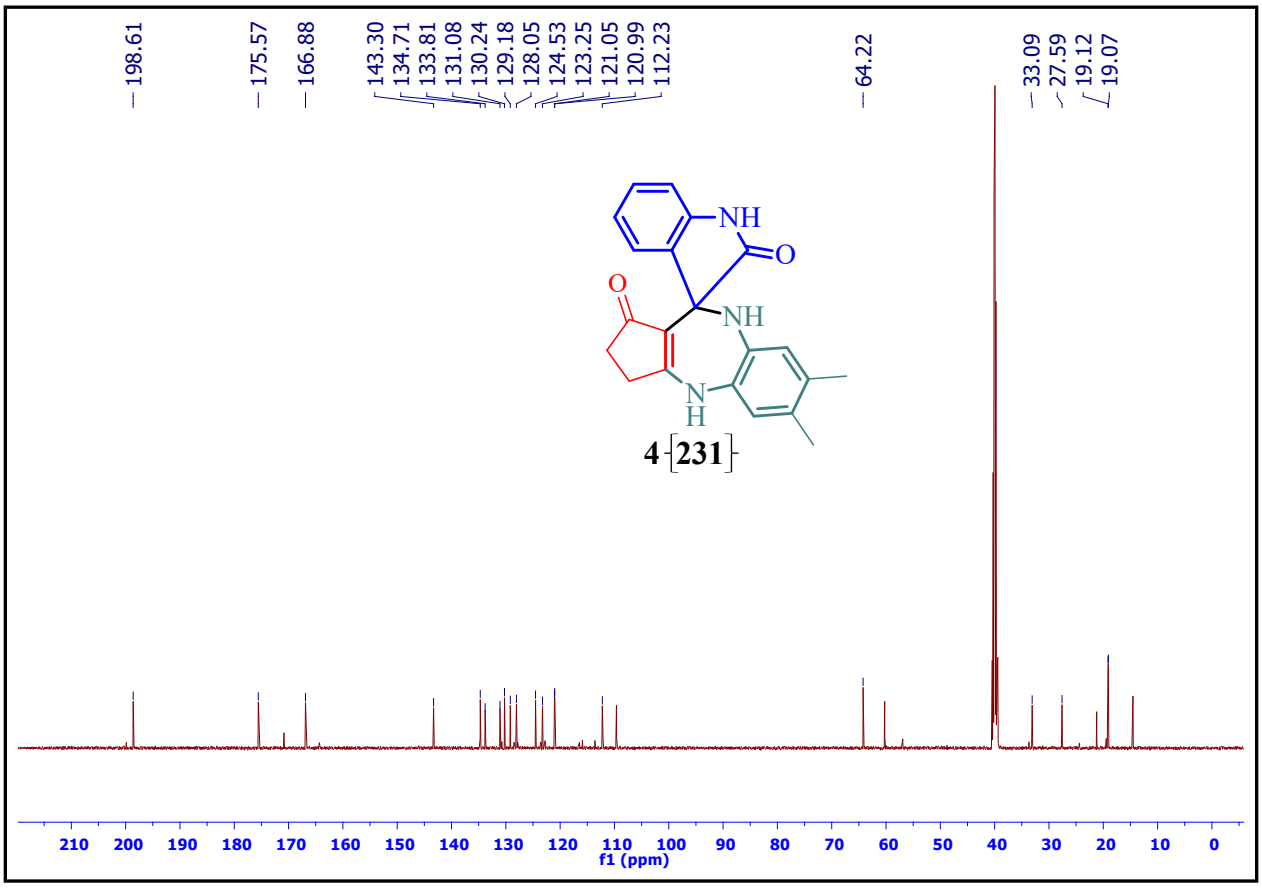


Figure S62. ^{13}C NMR spectra of **4{231}** in DMSO-d6.