Tandem double [3+2] cycloaddition reactions at both C-1 and C-3 atoms of *N*-cyanomethylisoquinolinium ylide

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Supporting Information

1. General procedure for the preparation of spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinolines] 1a-1f: A mixture of *N*-cyanomethylisoquinolinium chloride (0.5 mmol), 2-arylidene-1,3-indanedione (0.5 mmol) and triethylamine (0.6 mmol) in dry tetrahydrofuran (15.0 mL) was stirred at room temperature for ten hour. The solvent was removed at reduced pressure by rotatory evaporation. The residue was titrated with a mixture of light petroleum and methylene dichloride to give the pure solid.

2. General procedure for the preparation of spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indenes] 2a-2y: A mixture of *N*-cyanomethylisoquinolinium chloride (0.5 mmol), aromatic aldehyde (0.5 mmol), 1,3-indanedione (1.1 mmol) and triethylamine (1.2 mmol) in acetonitrile (15.0 mL) was stirred at room temperature for eight hours. The resulting precipitates were collected by filtration and washed with cold ethanol to give pure products **2a-2v** for analysis. In the cases of reactions with n-heptanal, the crude products were subjected to column chromatography with a mixture of light petroleum and ethyl acetate (V/V = 2:1) as eluent to give the pure products **2x-2y** for analysis.

1,3-Dioxo-2'-phenyl-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1a): yellow solid, 81%, m.p. 161-163 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78-7.76 (m, 4H, ArH), 7.20-7.16 (m, 5H, ArH), 6.94 (t, *J* = 7.2 Hz, 1H, ArH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 6.59-6.35 (m, 2H, ArH), 6.23 (d, *J* = 7.6 Hz, 1H, CH), 5.84 (s, 1H, CH), 5.68 (d, *J* = 10.0 Hz, 1H, CH), 5.36 (d, *J* = 7.6 Hz, 1H, CH), 4.29 (d, *J* = 10.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 142.6, 137.0, 134.0, 132.5, 132.1, 129.3, 129.2, 129.0, 128.5, 125.7, 125.2, 125.1, 125.0, 123.2, 119.3, 100.3, 71.1, 71.0, 57.1, 53.9; IR (KBr) υ: 3061, 2924, 2860, 2238, 1810, 1696, 1592, 1491, 1420, 1244, 1033, 854, 760 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{19}N_2O_2$([M+H]$^+$): 403.1441, Found: 403.1452.

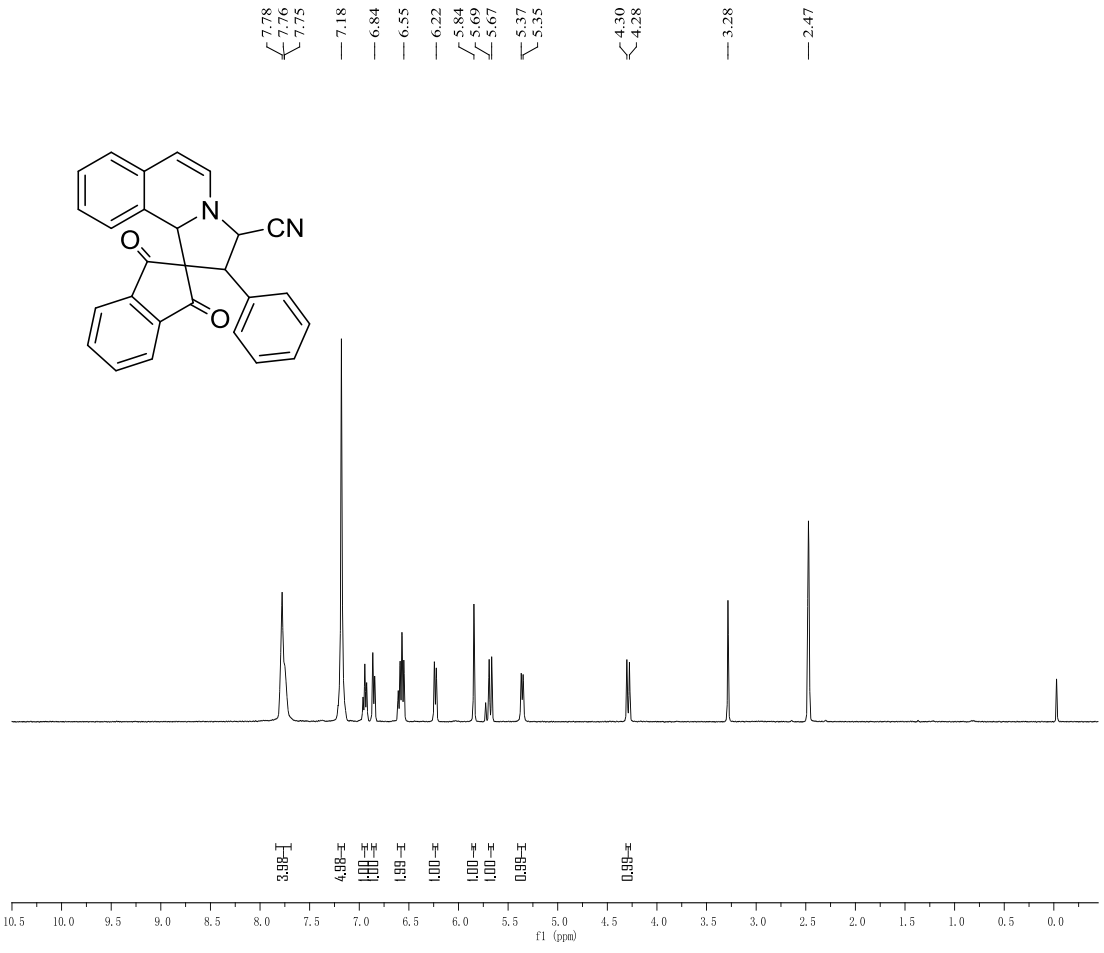

Figure S1 ^{1}H NMR spectra of the compound **1a**

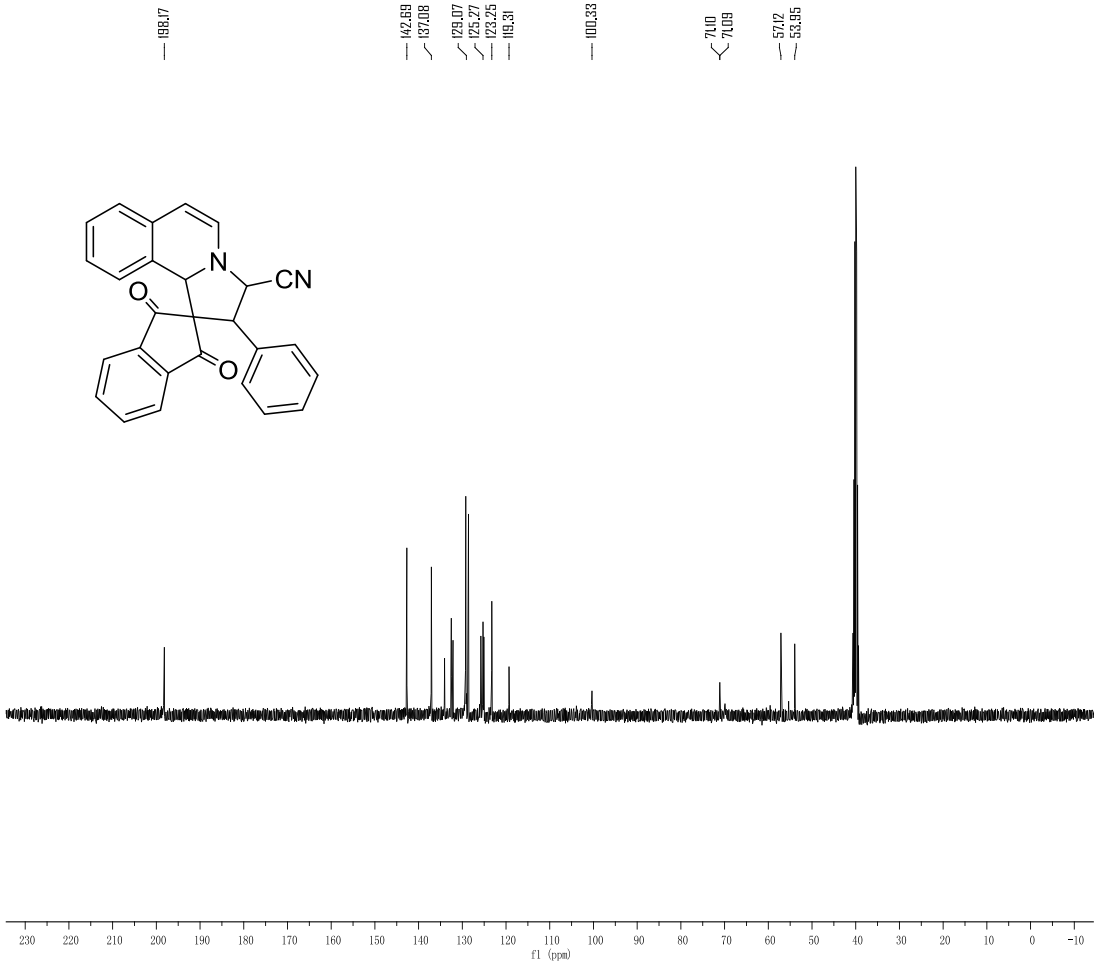

Figure S2 ^{13}C NMR spectra of the compound **1a**

2'-(2-Methoxyphenyl)-1,3-dioxo-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1b): yellow solid, 84%, m.p. 162-164 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.79-7.71 (m, 4H, ArH), 7.41 (d, J = 7.2 Hz, 1H, ArH), 7.15 (t, J = 7.6 Hz, 1H, ArH), 6.98-6.91 (m, 3H, ArH), 6.65 (d, J = 7.6 Hz, 1H, CH), 6.61-6.56 (m, 2H, ArH), 6.19 (d, J = 7.6 Hz, 1H, ArH), 5.66 (d, J = 7.6 Hz, 1H, CH), 5.47-5.45 (m 2H, CH), 4.23-4.22 (m, 1H, CH), 3.12 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 156.7, 142.2, 136.5, 132.6, 129.7, 128.9, 127.9, 125.6, 125.2, 124.9, 122.9, 120.8, 110.7, 69.8, 68.2, 56.0, 54.6, 49.4; IR (KBr) υ: 3031, 2928, 2269, 1738, 1704, 1593, 1548, 1540, 1359, 1262, 836, 813, 769, 675 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}N_2O_3$([M+H]$^+$): 433.1547, Found: 433.1560.

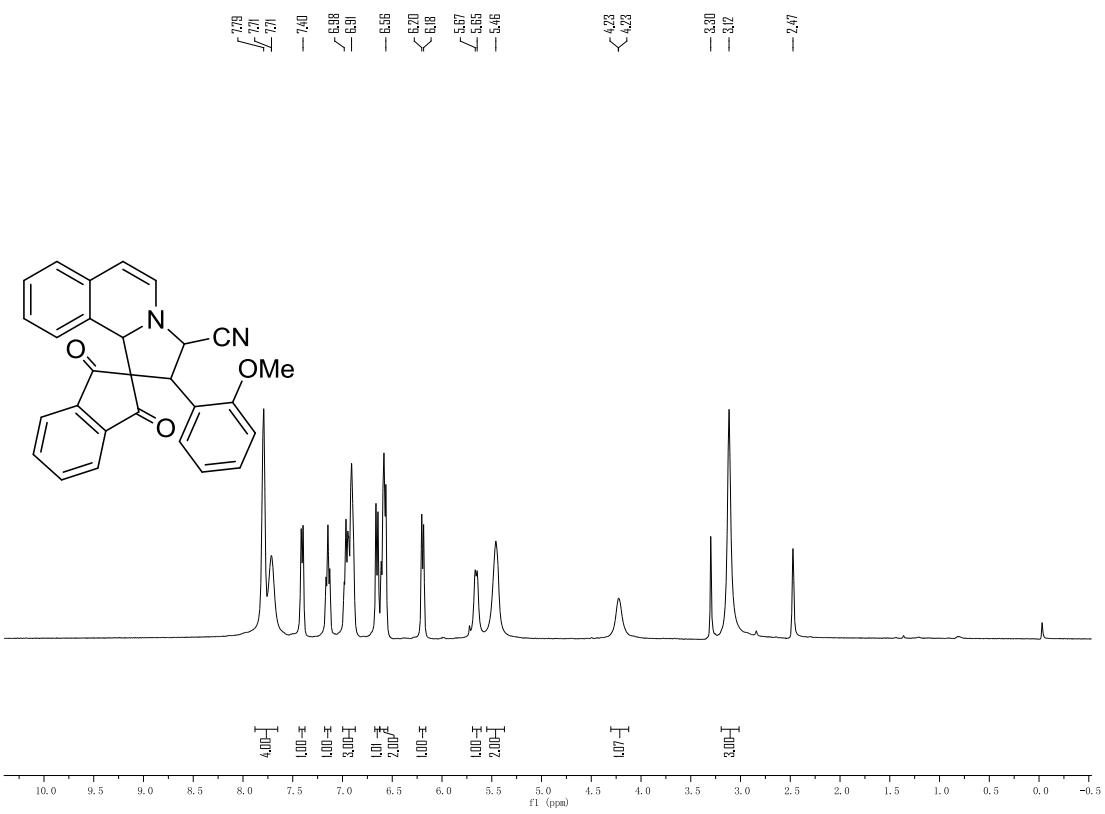

Figure S3 ^{1}H NMR spectra of the compound **1b**

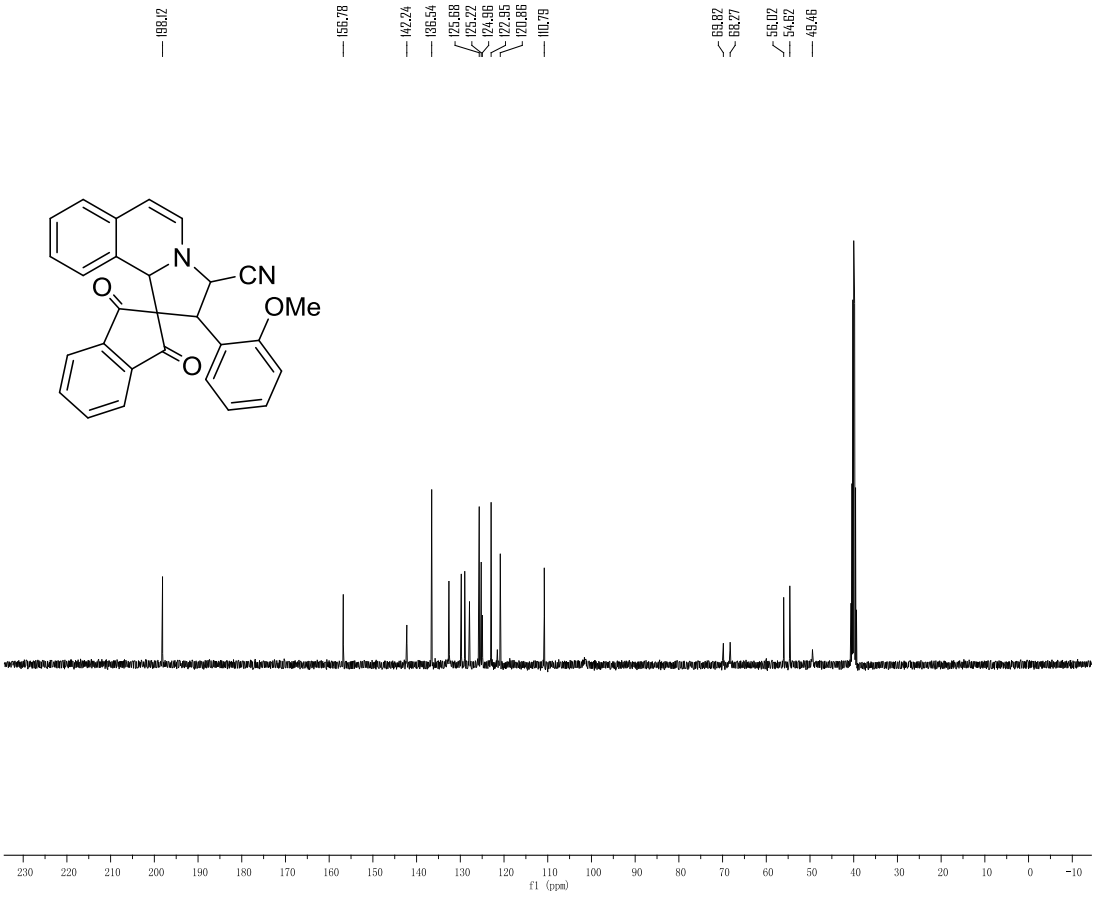

Figure S4 ^{13}C NMR spectra of the compound **1b**

1,3-Dioxo-2'-(p-tolyl)-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1c): yellow solid, 79%, m.p. 181-183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.90 (m, 1H, ArH), 7.73-7.69 (m, 1H, ArH), 7.63-7.62 (m, 2H, ArH), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 6.97-6.92 (m, 3H, ArH), 6.83 (d, *J* = 7.2 Hz, 1H, ArH), 6.54 (d, *J* = 7.6 Hz, 1H, ArH), 6.33 (d, *J* = 7.2 Hz, 1H, CH), 6.25 (d, *J* = 7.6 Hz, 1H, ArH), 5.84 (s, 1H, CH), 5.39 (d, *J* = 7.2 Hz, 1H, CH), 5.16 (d, *J* = 10.4 Hz, 1H, CH), 4.29 (d, *J* = 10.8 Hz, 1H, CH), 2.18 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.2, 142.7, 138.4, 137.1, 134.1, 132.4, 129.7, 129.1, 128.9, 128.4, 125.6, 125.2, 125.1, 125.0, 123.2, 119.3, 100.1, 70.9, 69.4, 57.2, 53.7, 20.9; IR (KBr) υ: 3059, 2916, 2275, 1740, 1704, 1591, 1562, 1540, 1353, 878, 803, 772, 680 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}N_2O_2$([M+H]$^+$): 417.1598, Found: 417.1611.

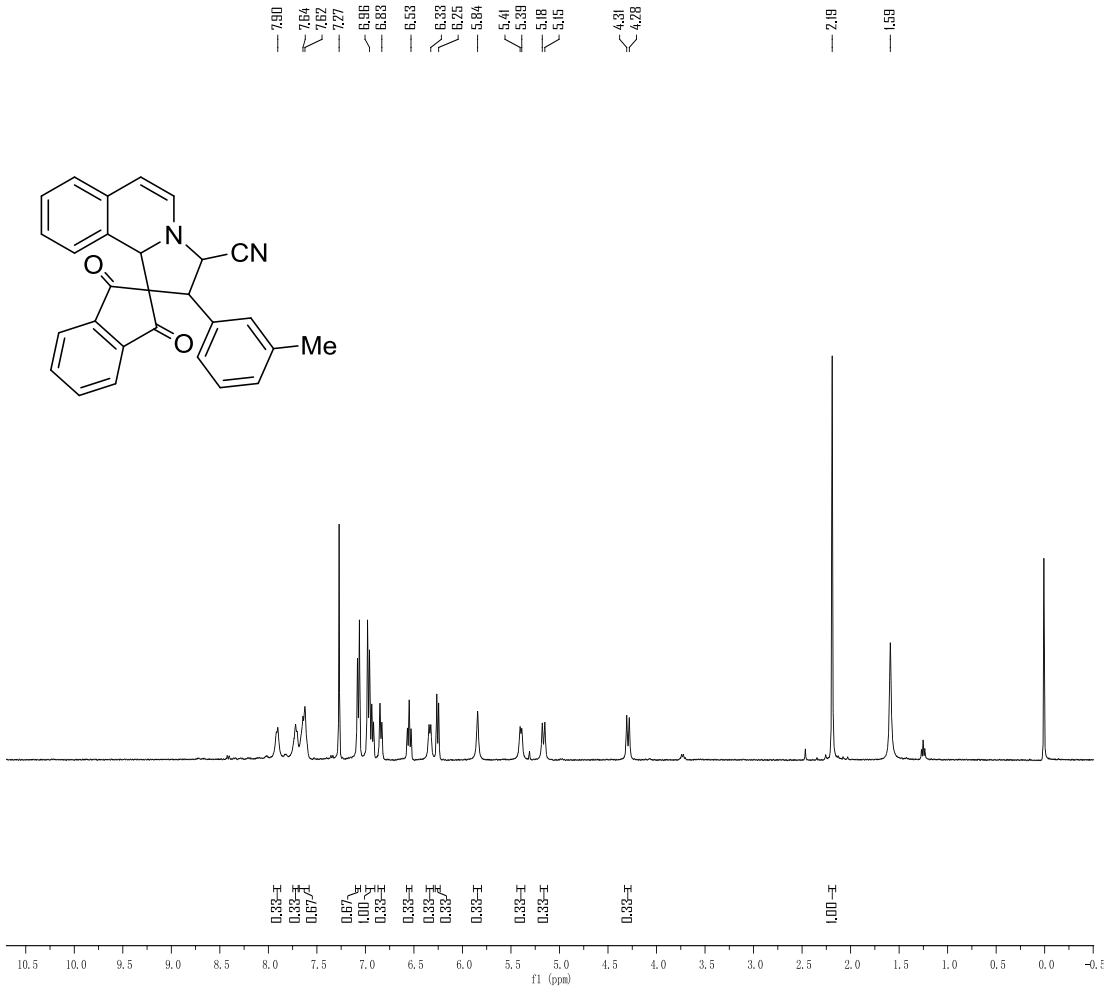

Figure S5 ^{1}H NMR spectra of the compound **1c**

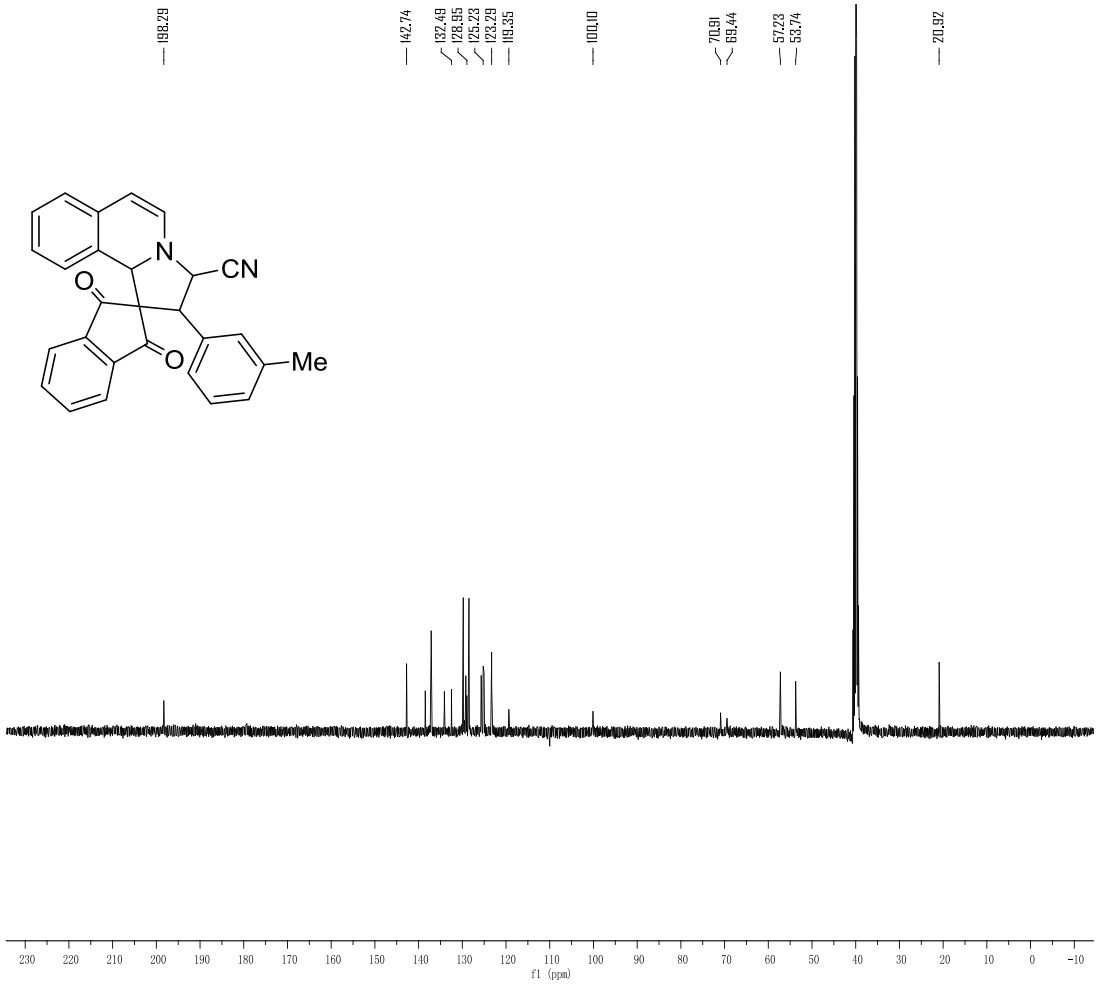

Figure S6 ^{13}C NMR spectra of the compound **1c**

2'-(4-Bromophenyl)-1,3-dioxo-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1d): yellow solid, 83%, m.p. 177-179 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78-7.75 (m, 4H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.16 (d, J = 8.0 Hz, 2H, ArH), 6.98 (d, J = 7.2 Hz, 1H, ArH), 76.89 (d, J = 7.6 Hz, 1H, ArH), 6.64-6.60 (m, 2H, ArH), 6.29 (d, J = 7.6 Hz, 1H, CH), 5.91 (s, 1H, CH), 5.73 (d, J = 10.0 Hz, 1H, CH), 5.44 (d, J = 7.6 Hz, 1H, CH), 4.31 (d, J = 10.4 Hz, 1H, CH),; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.7, 142.5, 137.0, 133.9, 132.5, 132.1, 131.9, 130.8, 129.5, 125.9, 125.3, 125.3, 125.0, 123.1, 122.3, 119.0, 101.0, 71.7, 71.7, 57.2, 52.9; IR (KBr) υ: 3060, 2911, 2231, 1736, 1702, 1593, 1489, 1418, 1248, 766, 718 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{18}BrN_2O_2$([M+H]$^+$): 781.0546, Found: 481.0542.

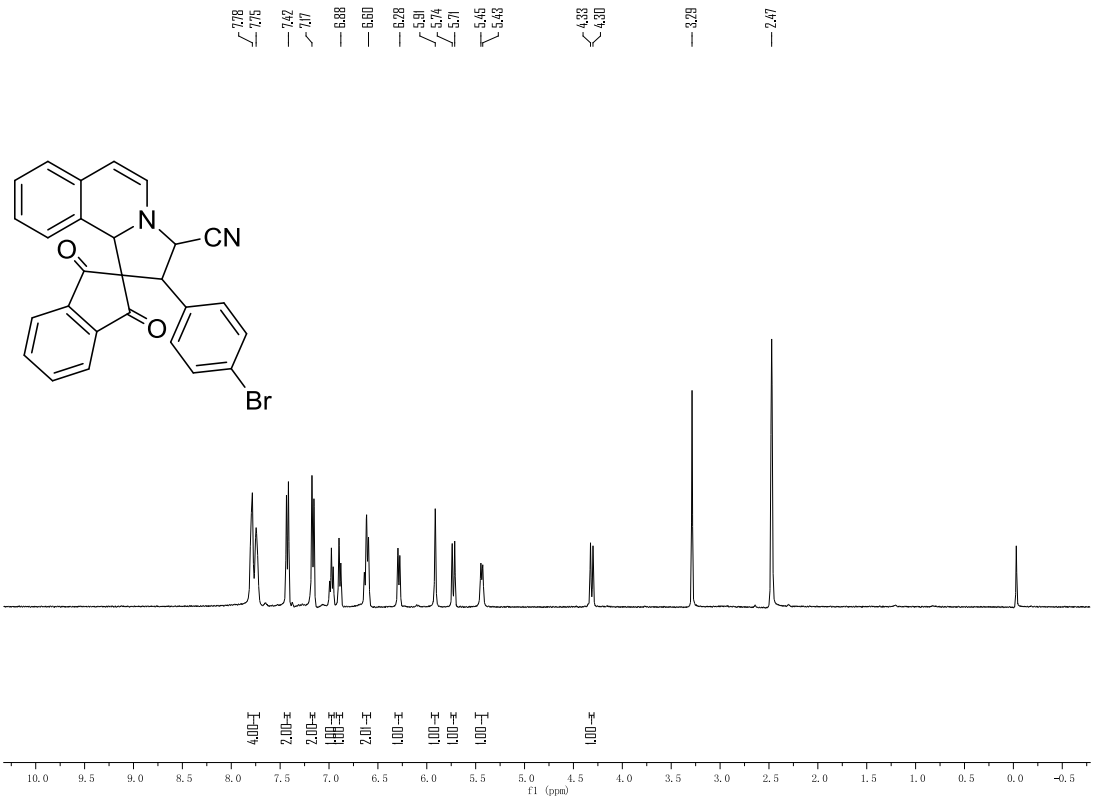

Figure S7 ^{1}H NMR spectra of the compound **1d**

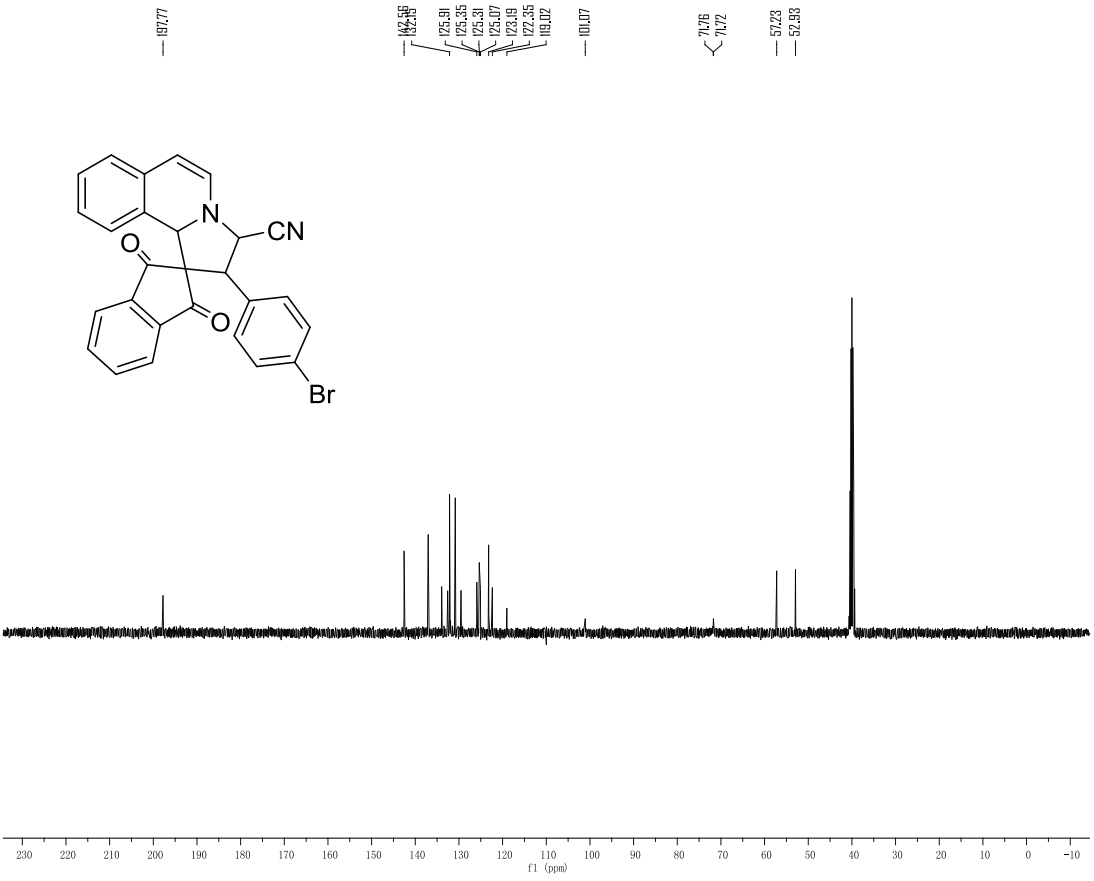

Figure S8 ^{1}H NMR spectra of the compound **1d**

2'-(4-Chlorophenyl)-1,3-dioxo-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1e): yellow solid, 81%, m.p. 180-183 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.91-7.90 (m, 1H, ArH), 7.74-7.73 (m, 1H, ArH), 7.67-7.62 (m, 2H, ArH), 7.17-7.13 (m, 4H, ArH), 6.93 (t, *J* = 7.2 Hz, 1H, ArH), 6.84 (d, *J* = 7.2 Hz, 1H, ArH), 6.54 (d, *J* = 7.2 Hz, 1H, ArH), 6.32 (d, *J* = 6.6 Hz, 1H, CH), 6.24 (d, *J* = 7.8 Hz, 1H, ArH), 5.81 (s, 1H, CH), 5.41 (d, *J* = 6.0 Hz, 1H, CH), 5.14 (d, *J* = 10.2 Hz, 1H, CH), 4.28 (d, *J* = 10.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.1, 142.9, 136.0, 136.0, 134.8, 132.3, 131.8, 129.7, 129.6, 129.1, 128.7, 125.4, 125.3, 124.8, 124.8, 123.1, 109.9, 101.1, 70.1, 68.6, 57.7, 53.6; IR (KBr) υ: 3064, 2914, 2240, 1739, 1704, 1590, 1489, 1456, 1276, 1095, 849, 737 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{18}ClN_2O_2$([M+H]$^+$): 437.1051, Found: 437.1045.

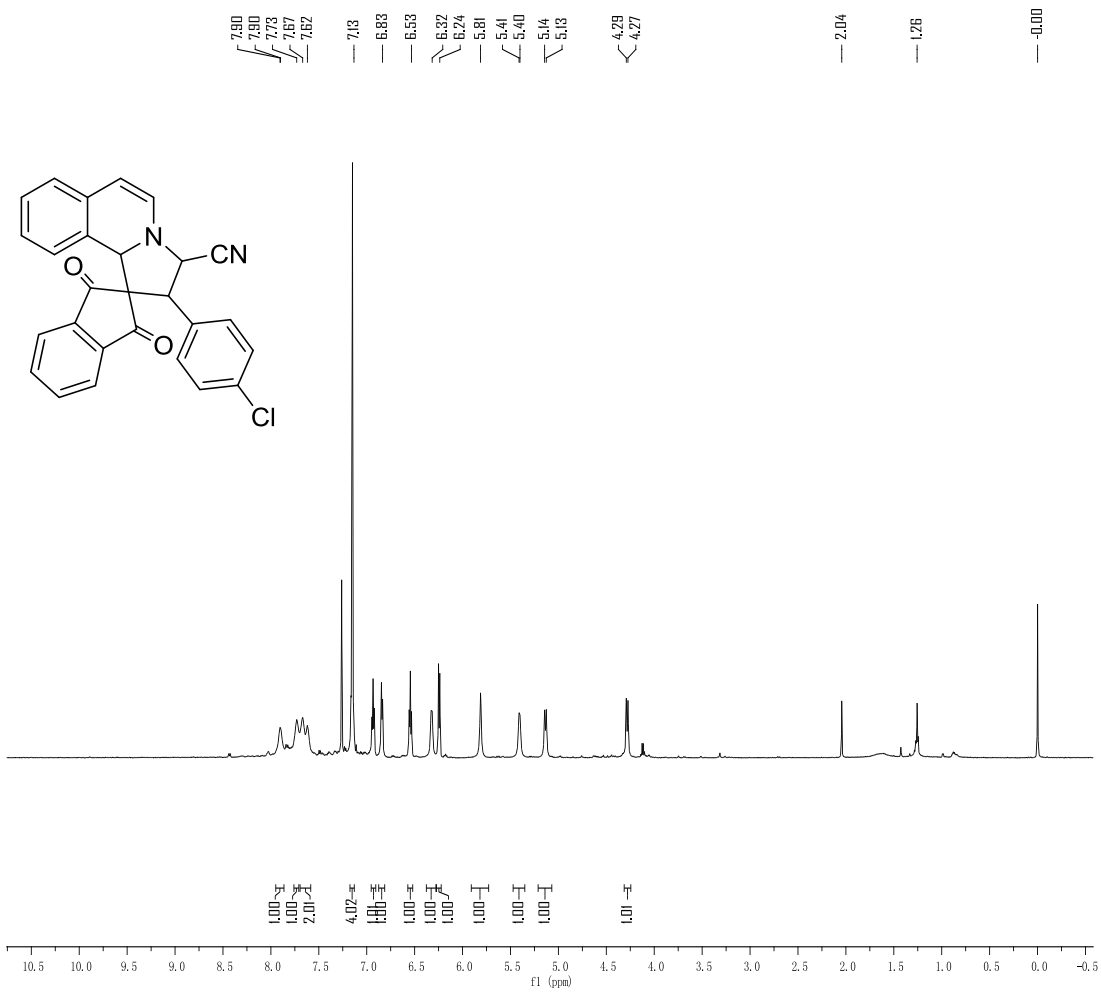

Figure S9 ^{1}H NMR spectra of the compound **1e**

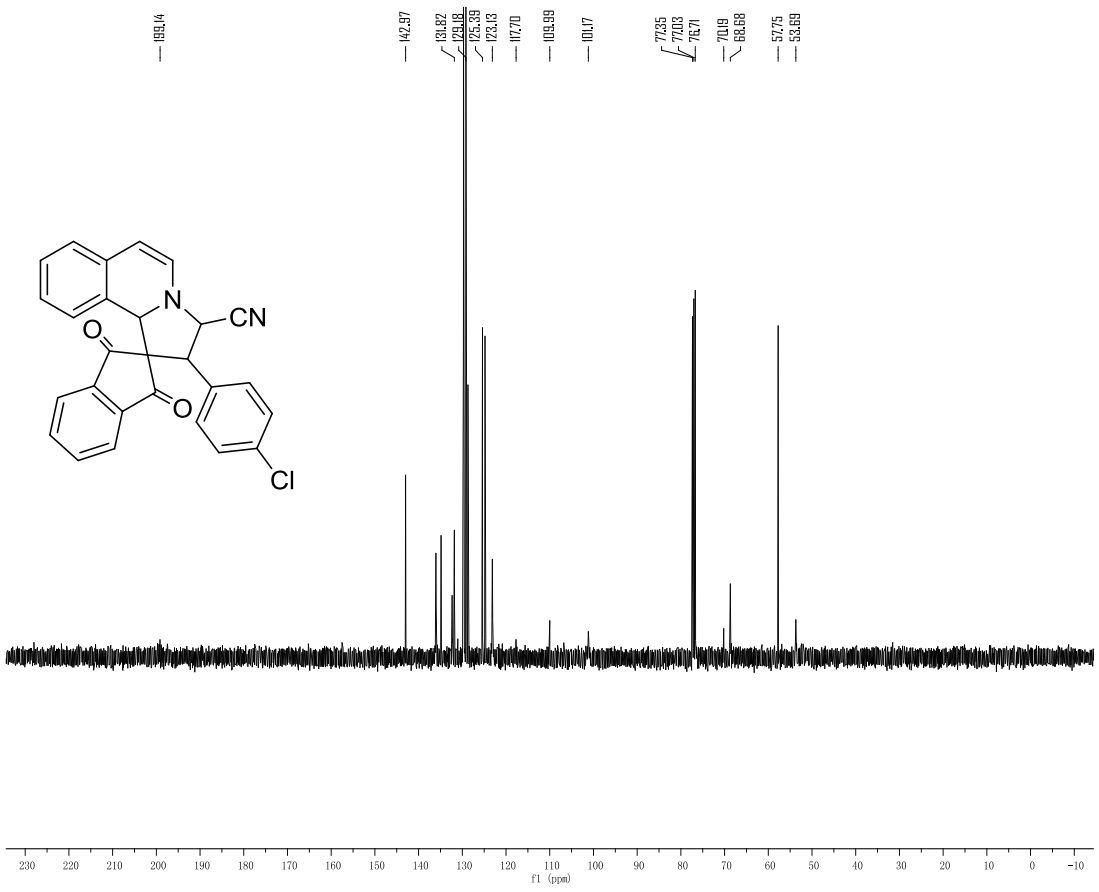

Figure S10 ^{13}C NMR spectra of the compound **1e**

2'-(4-(tert-Butyl)phenyl)-1,3-dioxo-1,2',3,3'-tetrahydro-10b'*H*-spiro[indene-2,1'-pyrrolo[2,1-*a*]isoquinoline]-3'-carbonitrile (1f): yellow solid, 61%, m.p. 176-178 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.90 (m, 1H, ArH), 7.72-7.69 (m, 1H, ArH), 7.63-7.62 (m, 2H, ArH), 7.16 (d, *J* = 8.4 Hz, 2H, ArH), 7.09 (d, *J* = 8.4 Hz, 2H, ArH), 6.93 (t, *J* = 7.6 Hz, 1H, ArH), 6.83 (d, *J* = 7.2 Hz, 1H, ArH), 6.54 (t, *J* = 7.6 Hz, 1H, ArH), 6.33 (d, *J* = 7.2 Hz, 1H, CH), 6.25 (d, *J* = 7.6 Hz, 1H, ArH), 5.83 (s, 1H, CH), 5.39 (d, *J* = 6.8 Hz, 1H, CH), 5.16 (d, *J* = 10.4 Hz, 1H, CH), 4.30 (d, *J* = 10.8 Hz, 1H, CH), 1.16 (s, 9H, $3CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 151.4, 142.7, 137.0, 134.2, 132.4, 129.2, 129.1, 128.3, 126.0, 125.6, 125.2, 125.1, 125.0, 123.2, 119.4, 100.2, 100.1, 71.1, 70.0, 57.4, 53.4, 34.6, 31.2; IR (KBr) υ: 3057, 2961, 2867, 2257, 1739, 1700, 1595, 1500, 1267, 1084, 951, 805, 762, 721 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}N_2O_2$([M+H]$^+$): 459.2067, Found: 459.2081.

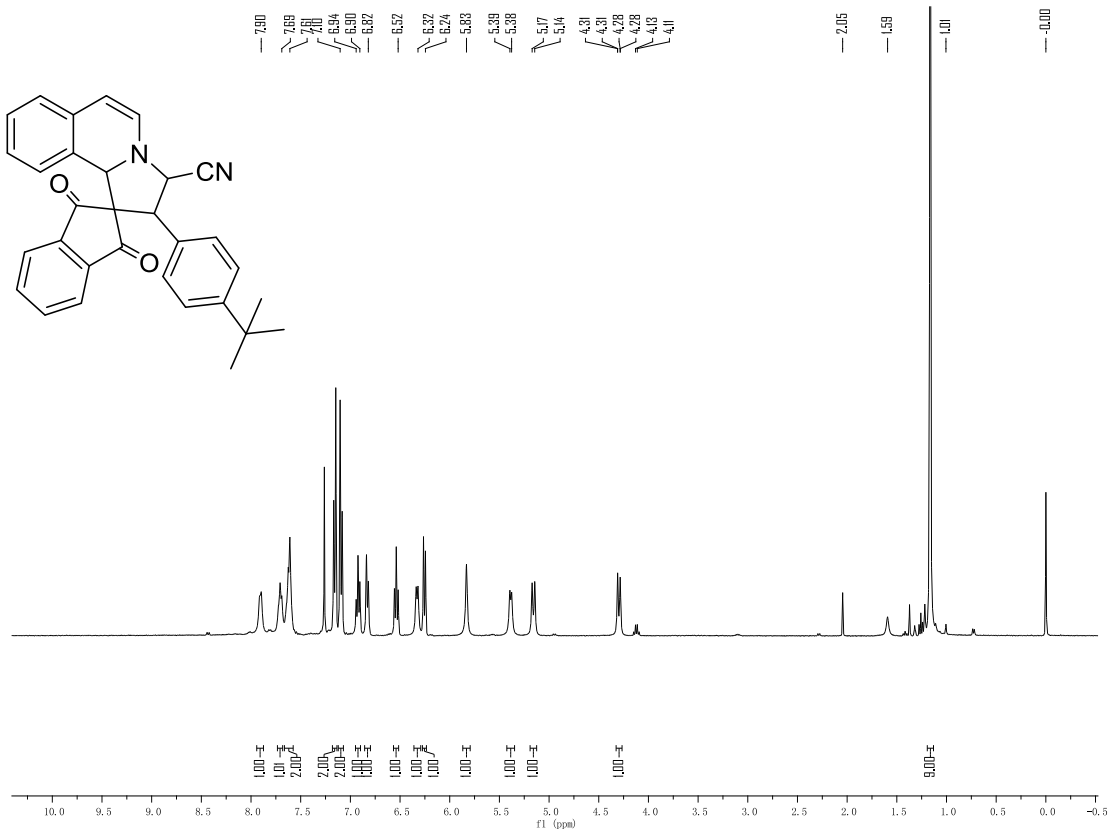

Figure S11 ^{1}H NMR spectra of the compound **1f**

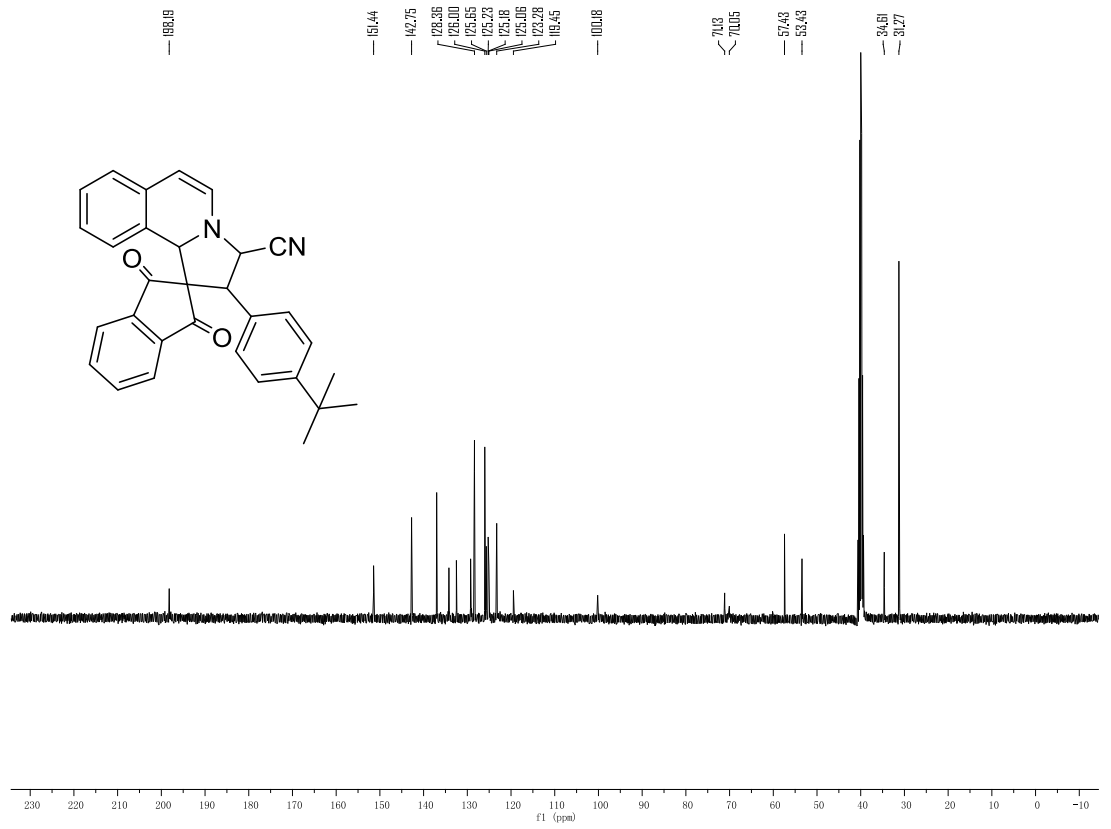

Figure S12 ^{13}C NMR spectra of the compound **1f**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-phenyl-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2a): white solid, 83%, m.p. 249-251 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.29 (s, 1H, NH), 7.39 (d, *J* = 7.6 Hz, 1H, ArH), 7.76 (t, *J* = 7.6 Hz, 1H, ArH), 7.72-7.65 (m, 3H, ArH), 7.61 (d, *J* = 6.8 Hz, 1H, ArH), 7.57-7.51 (m, 2H, ArH), 7.44 (d, *J* = 7.2 Hz, 1H, ArH), 7.33 (t, *J* = 7.6 Hz, 1H, ArH), 7.27 (t, *J* = 7.6 Hz, 1H, ArH), 7.19-7.11 (m, 5H, ArH), 7.01 (d, *J* = 7.2 Hz, 1H, ArH), 5.99 (s, 1H, CH), 5.44 (d, *J* = 6.8 Hz, 1H, CH), 4.66-4.65 (m, 1H, CH), 3.54 (d, *J* = 10.4 Hz, 1H, CH), 2.93 (t, *J* = 12.4 Hz, 1H, CH), 2.41-2.36 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 197.5, 194.0, 188.7, 165.7, 142.9, 141.5, 139.9, 139.7, 137.6, 136.1, 135.5, 134.8, 133.2, 132.8, 129.7, 129.1, 129.0, 128.0, 127.9, 127.3, 127.1, 123.1, 123.0, 122.0, 121.2, 100.9, 77.3, 74.5, 67.8, 62.4, 56.3, 30.1; IR (KBr) υ: 3276, 3026, 2916, 1738, 1703, 1570, 1457, 1273, 1087, 859, 739 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{25}N_2O_4$([M+H]$^+$): 549.1809, Found: 549.1818.

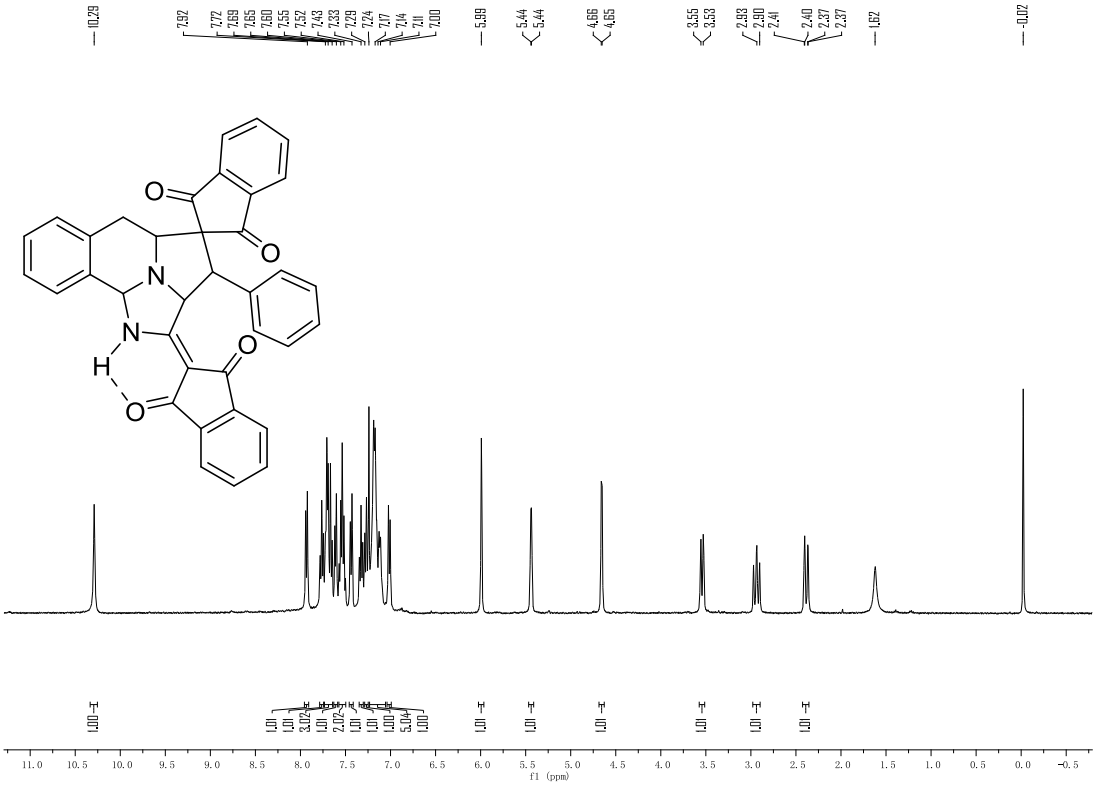

Figure S13 ^{1}H NMR spectra of the compound **2a**

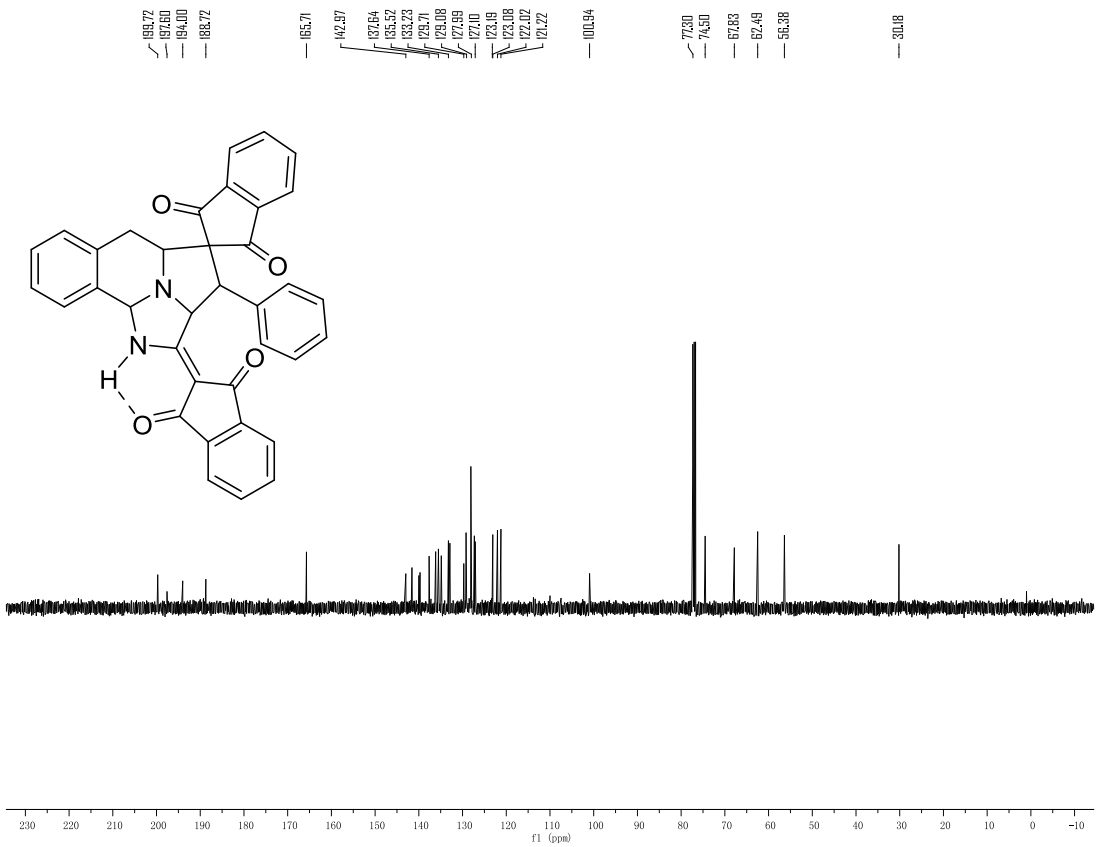

Figure S14 ^{13}C NMR spectra of the compound **2a**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(2-hydroxyphenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2b): white solid, 78%, m.p. 247-249 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (s, 1H, NH), 9.00 (s, 1H, OH), 7.91-7.88 (m, 3H, ArH), 7.83-7.80 (m, 1H, ArH), 7.66-7.60 (m, 4H, ArH), 7.50-7.45 (m, 2H, ArH), 7.34 (t, J = 7.6 Hz, 1H, ArH), 7.29-7.26 (m, 1H, ArH), 7.08 (d, J = 7.6 Hz, 1H, ArH), 6.90-6.86 (m, 1H, ArH), 6.74 (t, J = 7.2 Hz, 1H, ArH), 6.38 (d, J = 8.0 Hz, 1H, ArH), 5.95 (s, 1H, CH), 5.51-5.50 (m, 1H, CH), 4.64 (d, J = 3.6 Hz, 1H, CH), 3.21 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 1H, CH), 2.62-2.55 (m, 1H, CH), 2.35 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.4, 191.9, 188.2, 167.3, 154.3, 142.3, 141.4, 139.7, 139.5, 136.4, 136.2, 135.4, 133.8, 133.6, 130.4, 129.7, 129.3, 129.1, 128.5, 127.5, 127.2, 125.8, 123.2, 122.9, 121.6, 121.2, 118.7, 114.4, 100.0, 77.7, 73.7, 65.9, 63.4, 48.7, 29.9; IR (KBr) υ: 3265, 3069, 2910, 1745, 1707, 1566, 1457, 1206, 1139, 997, 862, 741, 694, 655 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{25}N_2O_5$([M+H]$^+$): 565.1758, Found: 565.1757.

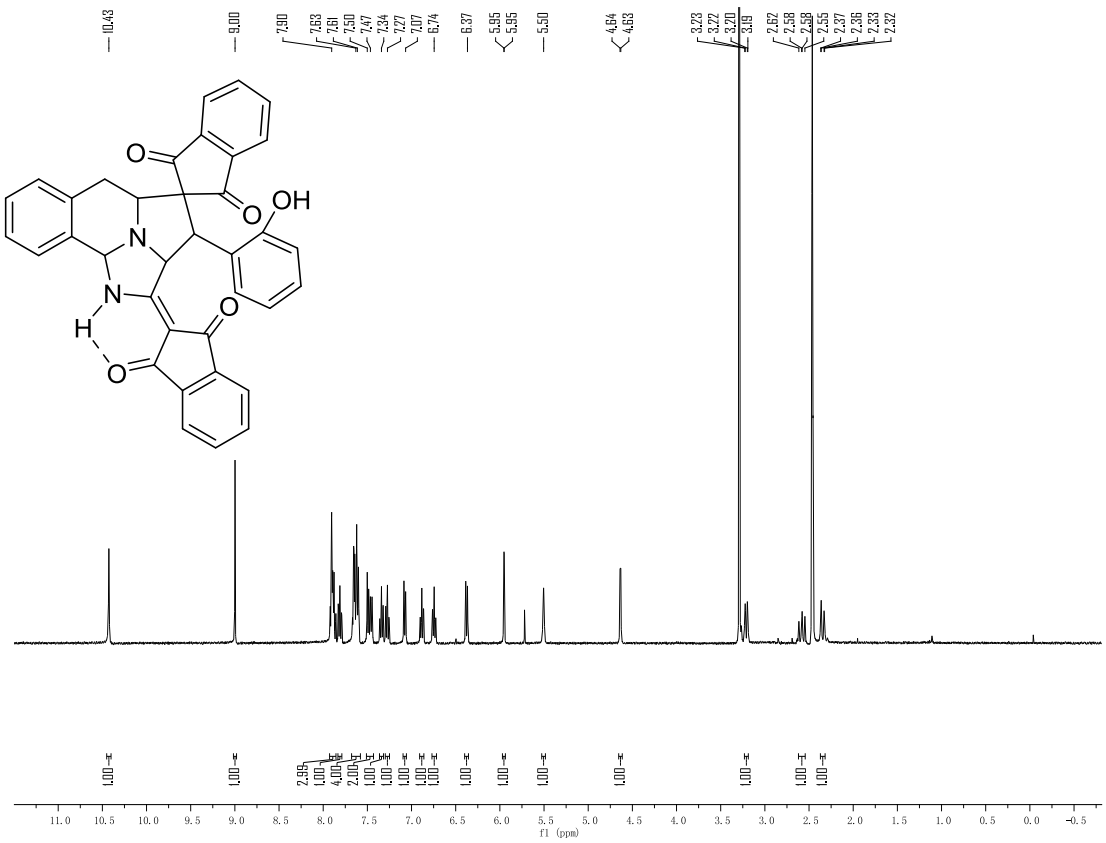

Figure S15 ^{1}H NMR spectra of the compound **2b**

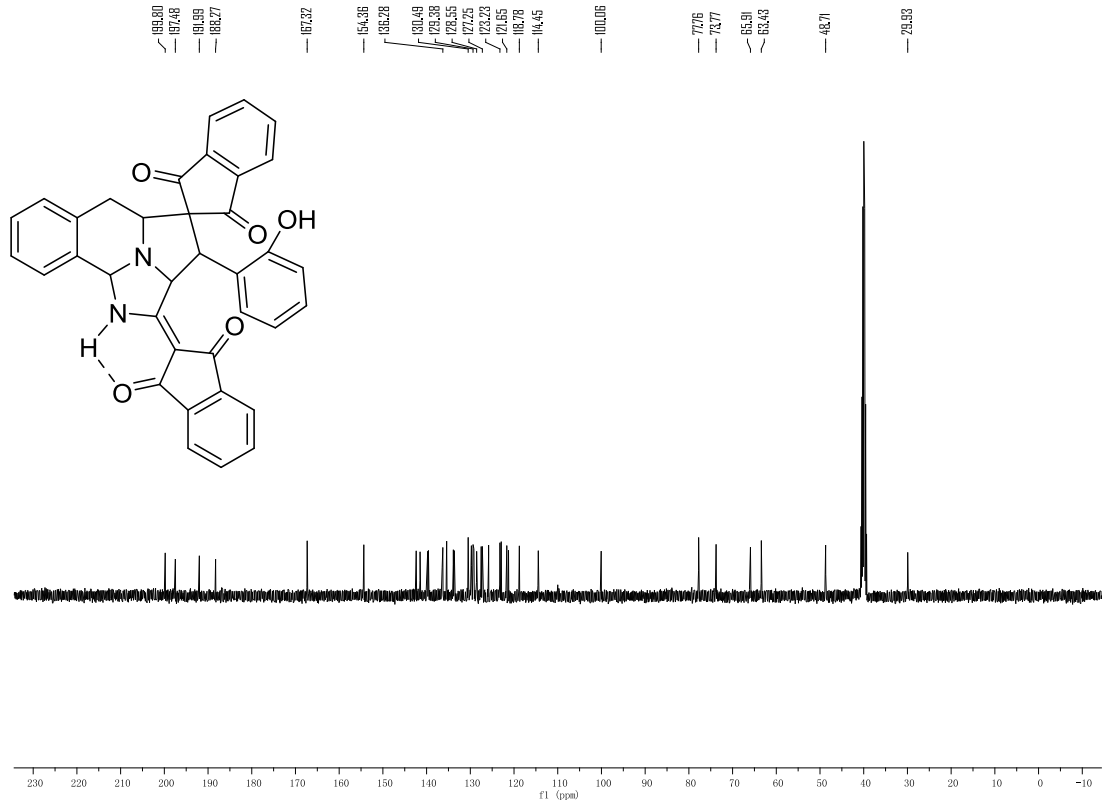

Figure S16 ^{13}C NMR spectra of the compound **2b**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(2-methoxyphenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2c): white solid, 87%, m.p. 266-268 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.45 (s, 1H, NH), 8.02 (d, J = 7.2 Hz, 1H, ArH), 7.94-7.92 (m, 2H, ArH), 7.85 (t, J = 7.2 Hz, 1H, ArH), 7.68-7.60 (m, 5H, ArH), 7.52 (d, J = 6.8 Hz, 1H, ArH), 7.37 (t, J = 7.6 Hz, 1H, ArH), 7.31 (t, J = 7.6 Hz, 1H, ArH), 7.12-7.10 (m, 2H, ArH), 6.97 (t, J = 7.6 Hz, 1H, ArH), 6.58 (d, J = 8.0 Hz, 1H, ArH), 6.00 (s, 1H, CH), 5.63 (s, 1H, CH), 4.67-4.66 (m, 1H, CH), 3.30-3.28 (m, 1H, CH), 2.95 (s, 3H, CH_3), 2.64 (t, J = 7.2 Hz, 1H, CH), 2.43 (d, J = 10.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 197.2, 191.9, 188.4, 167.1, 155.5, 142.1, 141.1, 139.7, 139.5, 136.5, 136.3, 135.4, 133.8, 133.7, 130.4, 129.7, 129.3, 129.1, 128.1, 128.0, 127.4, 127.2, 123.1, 122.9, 121.6, 121.2, 120.5, 110.2, 100.0, 77.8, 73.0, 65.6, 63.1, 54.3, 49.1, 29.8; IR (KBr) υ: 3252, 3072, 2833, 1746, 1708, 1649, 1567, 1492, 1462, 1360, 1275, 1206, 1029, 933, 853, 697 cm^{-1}; HRMS (ESI) Calcd. for $C_{37}H_{27}N_2O_5$([M+H]$^+$): 579.1914, Found: 579.1920.

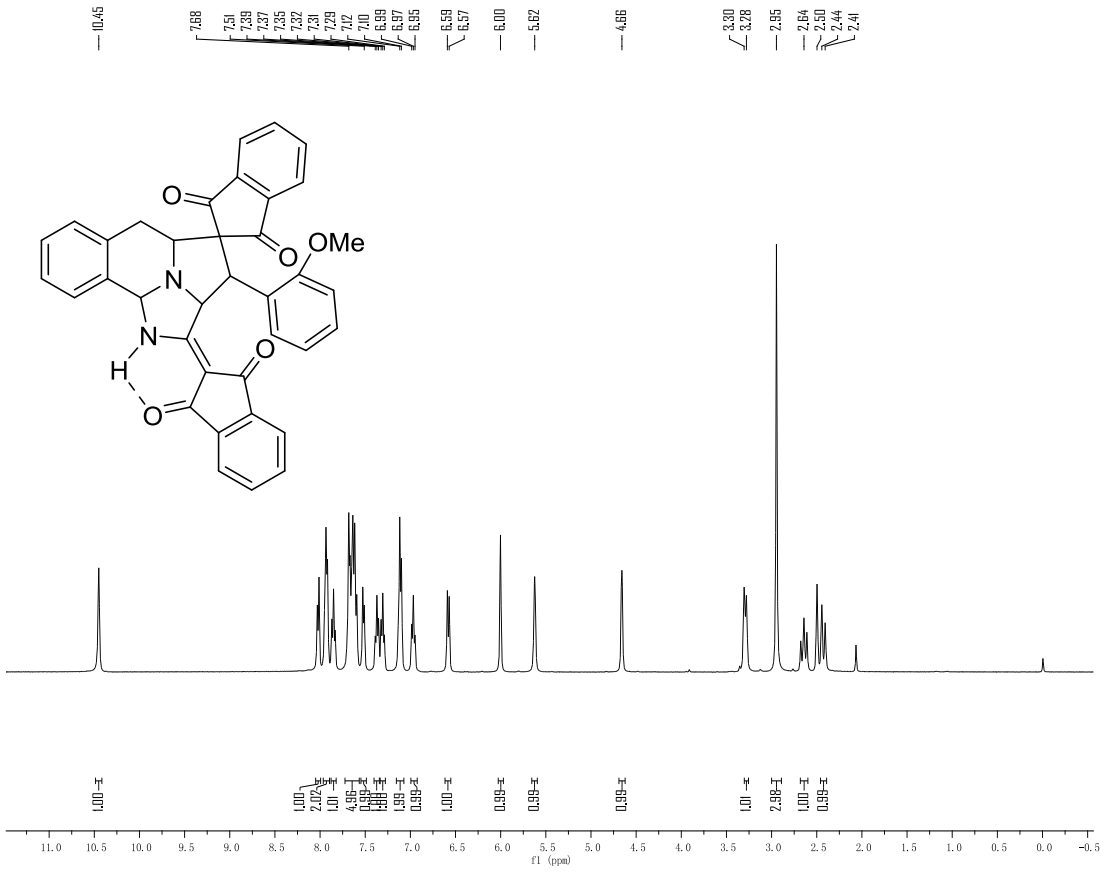

Figure S17 ^{1}H NMR spectra of the compound **2c**

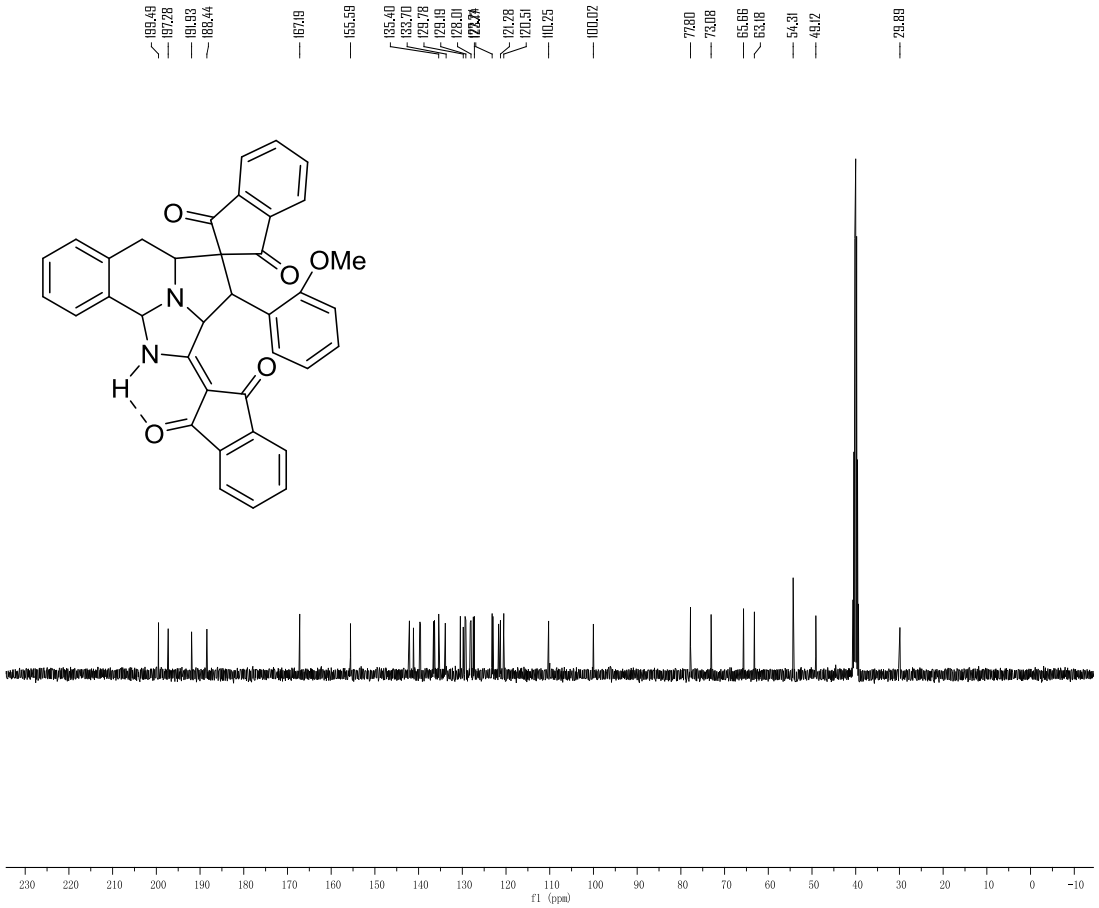

Figure S18 ^{13}C NMR spectra of the compound **2c**

3-(2-Chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2d): white solid, 89%, m.p. 264-266 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.46 (s, 1H, NH), 7.98-7.92 (m, 3H, ArH), 7.88 (t, J = 7.2 Hz, 1H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.70-7.65 (m, 4H, ArH), 7.56-7.55 (m, 1H, ArH), 7.38-7.32 (m, 3H, ArH), 7.17-7.12 (m, 3H, ArH), 6.02 (s, 1H, CH), 5.46 (s, 1H, CH), 4.84-4.83 (m, 1H, CH), 3.37-3.34 (m, 1H, CH), 2.74 (t, J = 12.4 Hz, 1H, CH), 2.52-2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.9, 196.9, 191.6, 188.5, 166.0, 141.9, 141.8, 139.7, 139.5, 137.3, 136.8, 136.7, 135.3, 133.9, 133.7, 133.4, 131.0, 130.3, 129.9, 129.3, 129.2, 129.0, 128.7, 127.2, 127.0, 123.6, 123.1, 121.6, 121.3, 99.9, 78.0, 76.1, 65.8, 63.4, 52.1, 29.7; IR (KBr) υ: 3279, 3069, 2907, 2836, 1746, 1709, 1659, 1572, 1461, 1436, 1205, 1036, 891, 850, 792, 685 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}ClN_2O_4$([M+H]$^+$): 583.1419, Found: 583.1421.

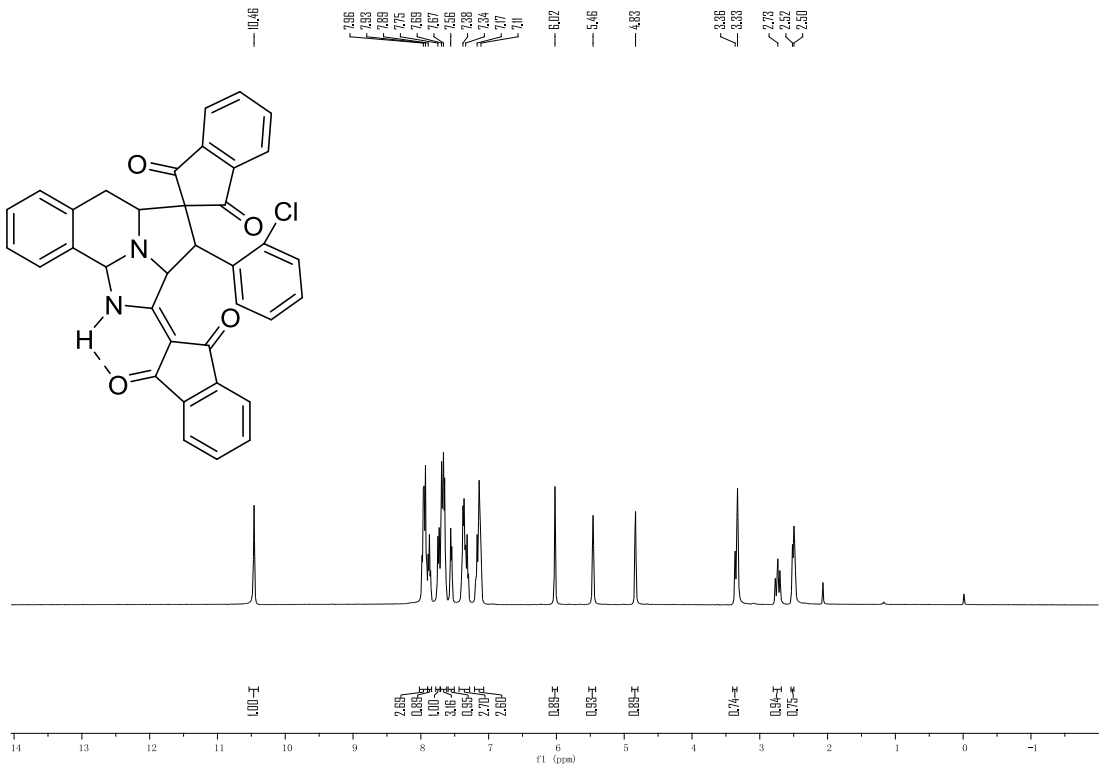

Figure S19 ^{1}H NMR spectra of the compound **2d**

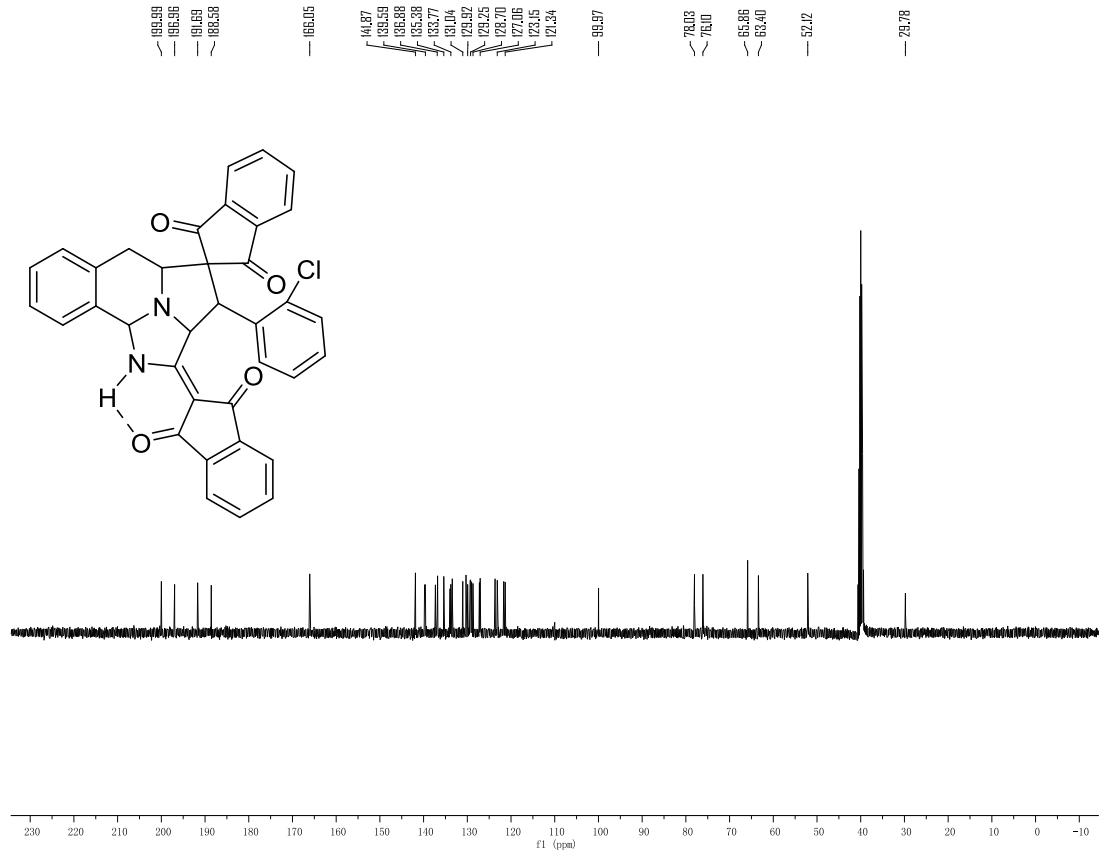

Figure S20 ^{13}C NMR spectra of the compound **2d**

3-(2-Bromophenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2e): white solid, 85%, m.p. 270-272 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.21 (s, 1H, NH), 8.42-8.37 (m, 2H, ArH), 7.97 (d, *J* = 7.2 Hz, 1H, ArH), 7.83-7.73 (m, 5H, ArH), 7.63-7.55 (m, 3H, ArH), 7.46 (d, *J* = 7.8 Hz, 1H, ArH), 7.36 (t, *J* = 7.8 Hz, 1H, ArH), 7.30 (t, *J* = 7.2 Hz, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.03 (d, *J* = 7.2 Hz, 1H, ArH), 6.00 (s, 1H, CH), 5.39-5.38 (m, 1H, CH), 4.65-4.64 (m, 1H, CH), 3.56 (d, *J* = 12.0 Hz, 1H, CH), 2.91 (t, *J* = 13.2 Hz, 1H, CH), 2.40 (d, *J* = 15.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.5, 188.5, 165.9, 142.1, 141.9, 139.8, 139.6, 138.5, 137.2, 136.8, 135.4, 133.9, 133.7, 132.3, 131.4, 130.3, 129.9, 129.3, 129.2, 128.9, 127.5, 127.2, 124.9, 123.7, 123.1, 121.6, 121.3, 100.0, 78.1, 76.8, 65.8, 63.3, 54.7, 29.7; IR (KBr) υ: 3278, 3066, 2914, 2836, 1741, 1703, 1584, 1464, 1431, 1265, 1132, 852, 746 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}BrN_2O_4$([M+H]$^+$): 627.0914, Found: 627.0900.

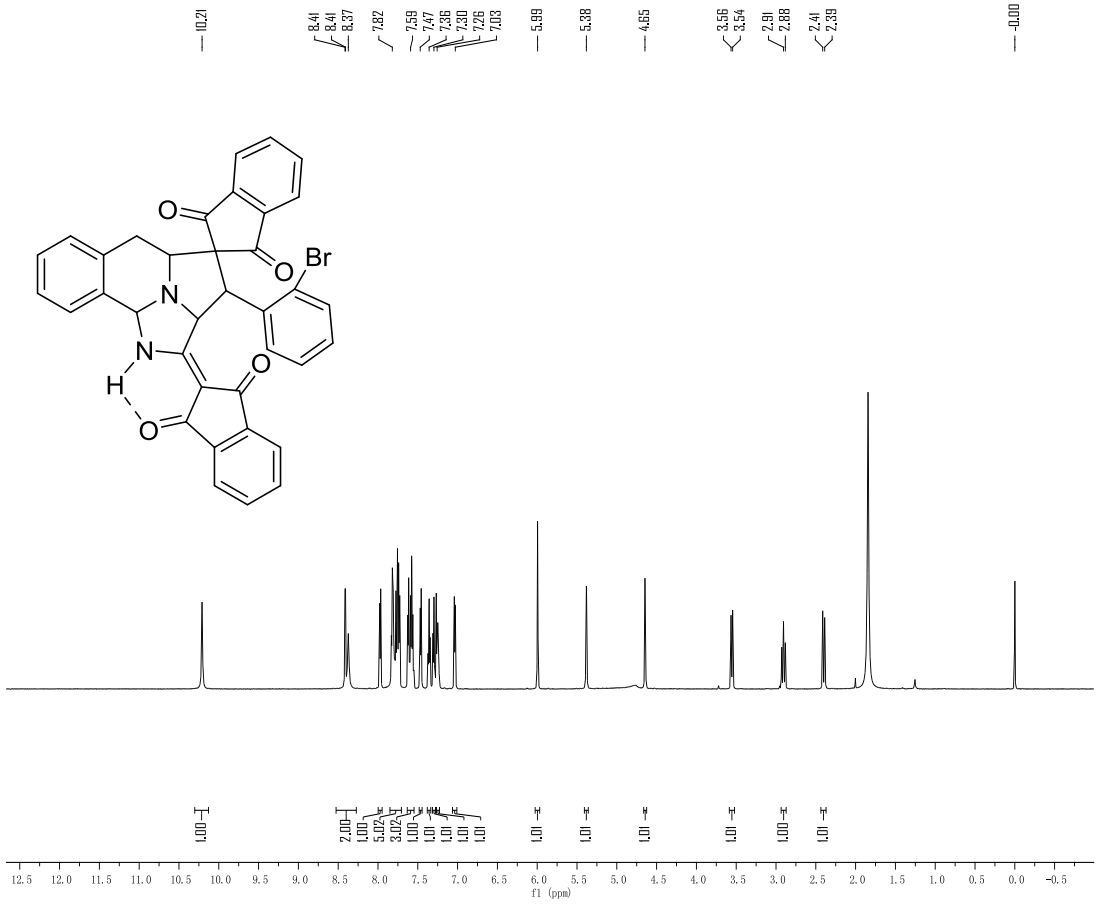

Figure S21 ^{1}H NMR spectra of the compound **2e**

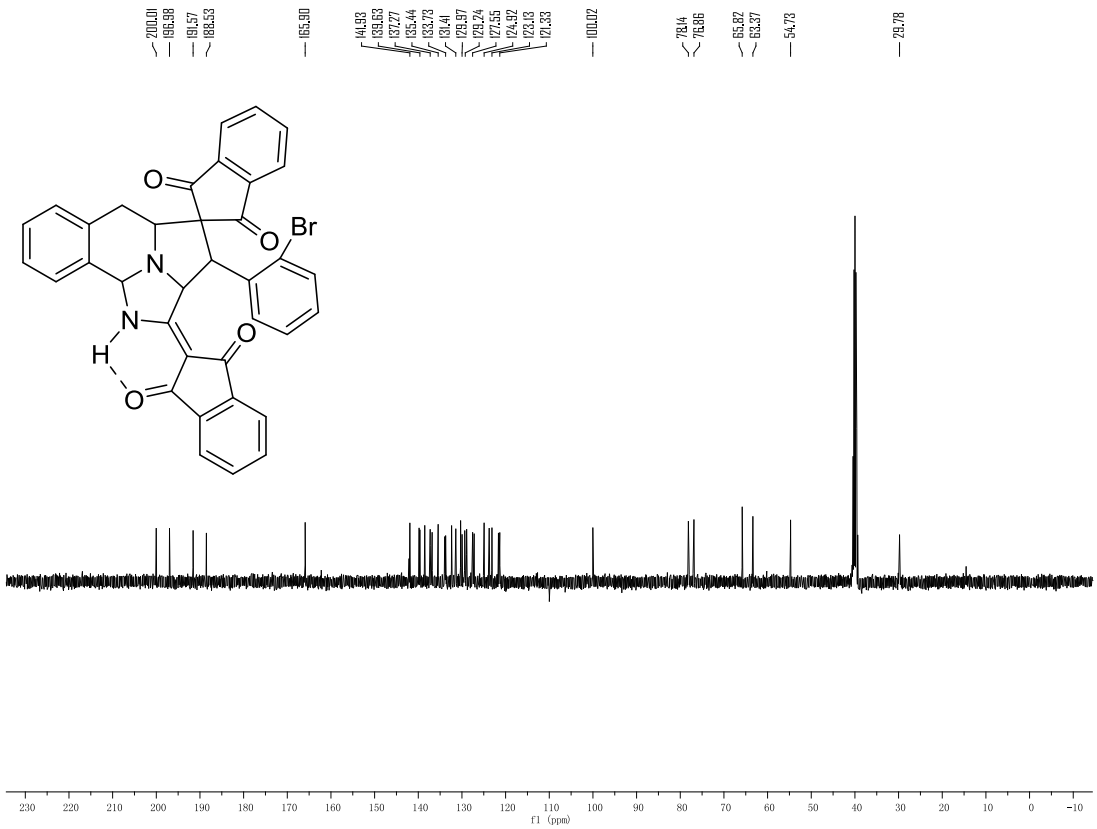

Figure S22 ^{13}C NMR spectra of the compound **2e**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(m-tolyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2f): white solid, 86%, m.p. 233-235 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.23 (s, 1H, NH), 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.76 (t, *J* = 7.2 Hz, 1H, ArH), 7.72-7.69 (m, 2H, ArH), 7.66 (d, *J* = 8.0 Hz, 1H, ArH), 7.62 (d, *J* = 6.8 Hz, 1H, ArH), 7.57-7.50 (m, 1H, ArH), 7.44 (d, *J* = 7.6 Hz, 1H, ArH), 7.32 (t, *J* = 7.6 Hz, 1H, ArH), 7.28-7.25 (m, 1H, ArH), 7.04-7.00 (m, 3H, ArH), 6.92-6.89 (m, 2H, ArH), 6.00 (s, 1H, CH), 5.45 (d, *J* = 3.6 Hz, 1H, CH), 4.63 (d, *J* = 4.0 Hz, 1H, CH), 3.55-3.52 (m, 1H, CH), 2.99-2.92 (m, 1H, CH), 2.39 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH), 2.20 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 197.5, 193.9, 188.7, 165.7, 143.0, 141.6, 139.9, 139.7, 137.5, 137.4, 136.0, 135.4, 134.9, 133.2, 132.8, 129.7, 129.1, 129.0, 128.5, 127.9, 127.8, 127.2, 125.1, 123.1, 123.0, 122.0, 121.2, 100.9, 77.3, 77.0, 76.7, 74.4, 67.8, 62.3, 56.3, 30.1, 21.4; IR (KBr) υ: 3273, 3099, 3018, 2918, 1741, 1706, 1570, 1489, 1461, 1365, 1278, 1137, 1062, 934, 868, 730, 700, 653 cm^{-1}; HRMS (ESI) Calcd. for $C_{37}H_{26}KN_2O_4$([M+K]$^+$): 601.1524, Found: 601.1527.

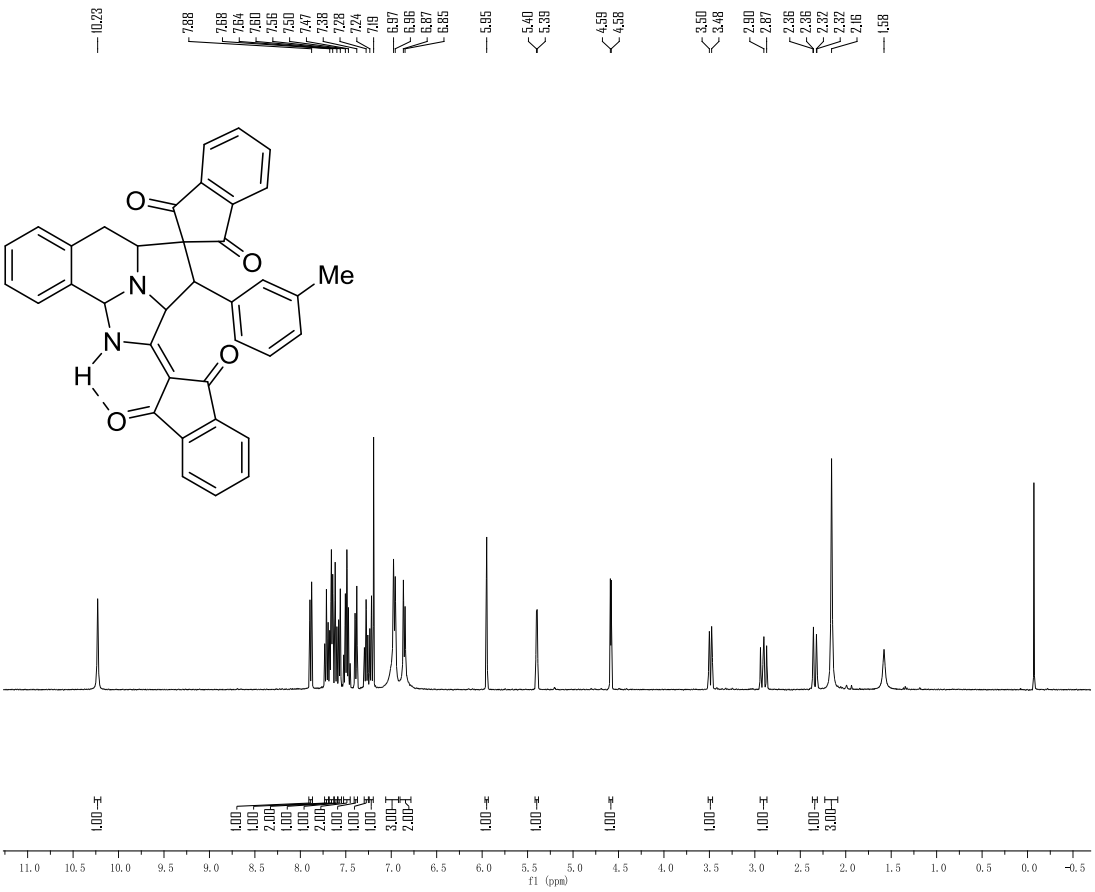

Figure S23 ^{1}H NMR spectra of the compound **2f**

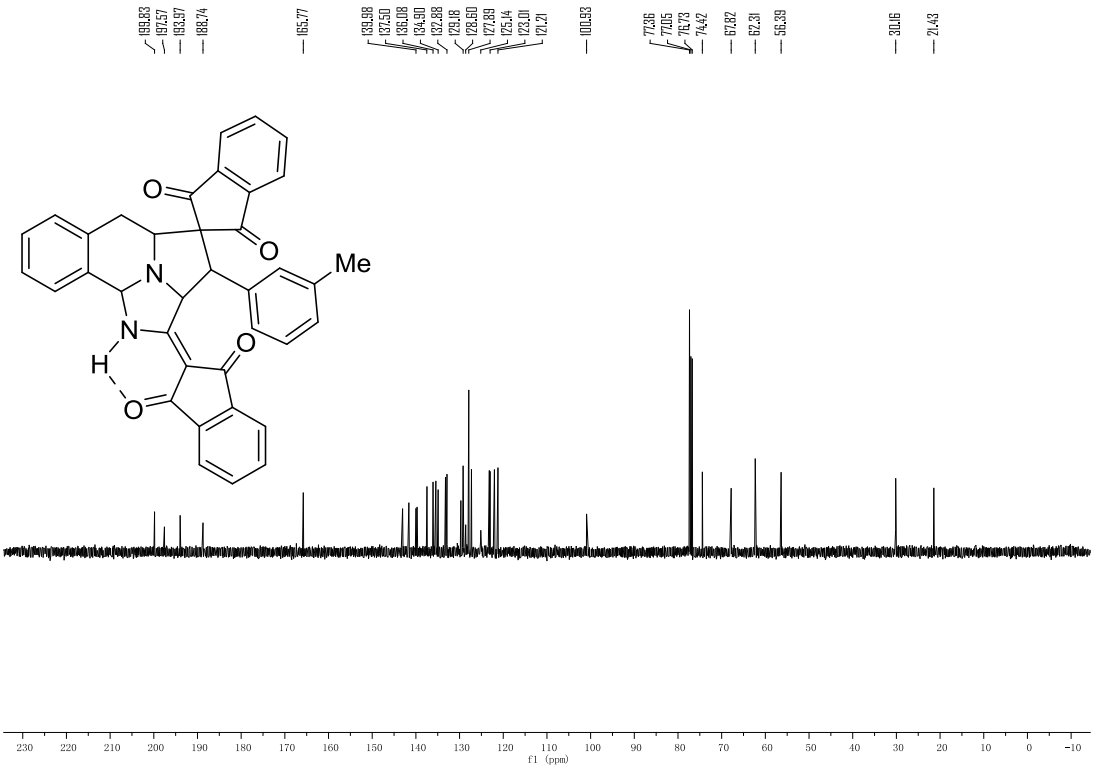

Figure S24 ^{13}C NMR spectra of the compound **2f**

2-(1,3-Bioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(3-fluorophenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2g): white solid, 81%, m.p. 259-261 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.24 (s, 1H, NH), 7.95 (d, J = 7.6 Hz, 1H, ArH), 7.82-7.70 (m, 4H, ArH), 7.63-7.61 (m, 1H, ArH), 7.58-7.54 (m, 2H, ArH), 7.44 (d, J = 7.6 Hz, 1H, ArH), 7.33 (t, J = 7.6 Hz, 1H, ArH), 7.29-7.25 (m, 1H, ArH), 7.16-7.12 (m, 1H, ArH), 7.02-6.93 (m, 3H, ArH), 6.85-6.80 (m, 1H, ArH), 5.98 (s, 1H, CH), 5.39 (d, J = 3.6 Hz, 1H, CH), 4.64 (d, J = 4.4 Hz, 1H, CH), 3.51 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 1H, CH), 2.94-2.87 (m, 1H, CH), 2.37 (dd, J_1 = 15.2 Hz, J_2 = 2.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 197.3, 193.8, 188.8, 165.3, 162.4 (d, J = 244.5 Hz), 142.8, 141.4, 140.4, 140.3, 139.9, 139.7, 134.6, 133.3, 133.0, 129.5, 129.5, 129.2, 129.1, 128.0, 127.3, 123.7, 123.3, 123.2, 121.9, 121.2, 115.2 (d, J = 22.6 Hz), 114.1 (d, J = 20.9 Hz), 109.9, 100.8, 77.2, 74.3, 67.6, 62.7, 55.6, 30.1; IR (KBr) υ: 3280, 3067, 3020, 2916, 2838, 1742, 1709, 1659, 1589, 1488, 1202, 1090, 959, 828, 739 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}FN_2O_4$([M+H]$^+$): 567.1715, Found: 567.1709.

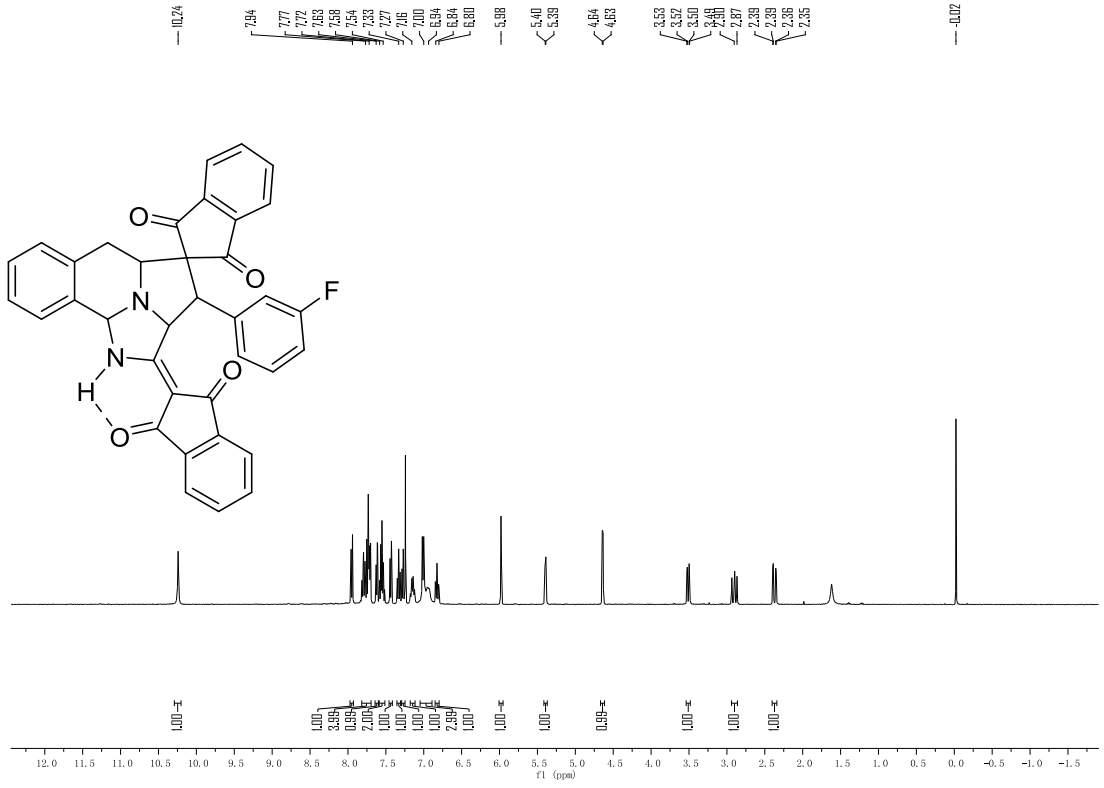

Figure S25 ^{1}H NMR spectra of the compound **2g**

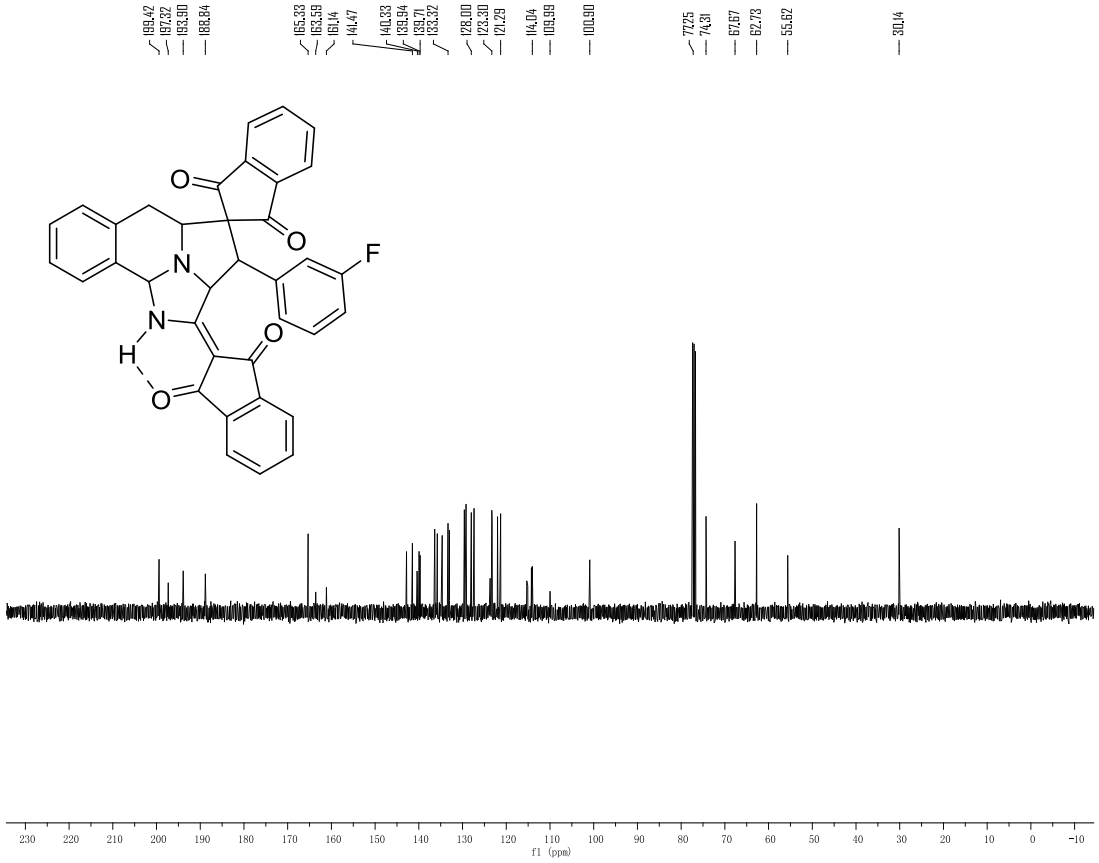

Figure S26 ^{13}C NMR spectra of the compound **2g**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(3-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2h): white solid, 82%, m.p. 252-254 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.18 (s, 1H, NH), 8.16-8.15 (m, 1H, ArH), 8.04-8.01 (m, 1H, ArH), 7.97 (d, J = 7.6 Hz, 1H, ArH), 7.84-7.80 (m, 1H, ArH), 7.78-7.74 (m, 1H, ArH), 7.72-7.71 (m, 1H, ArH), 7.60-7.53 (m, 4H, ArH), 7.45 (d, J = 7.2 Hz, 1H, ArH), 7.41-7.33 (m, 2H, ArH), 7.30-7.26 (m, 1H, ArH), 7.01 (d, J = 7.6 Hz, 1H, ArH), 5.99 (s, 1H, CH), 5.44 (d, J = 3.6 Hz, 1H, CH), 4.73 (d, J = 4.0 Hz, 1H, CH), 3.53 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H, CH), 2.91-4.84 (m, 1H, CH), 2.37 (dd, J_1 = 14.8 Hz, J_2 = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.8, 197.2, 193.7, 189.0, 164.8, 147.8, 142.5, 141.3, 140.2, 139.8, 139.6, 136.6, 136.1, 134.4, 134.3, 133.4, 133.1, 129.4, 129.2, 129.0, 128.0, 127.4, 123.4, 123.3, 123.2, 122.2, 121.9, 121.3, 100.8, 77.2, 74.3, 67.6, 63.2, 55.0, 30.1; IR (KBr) υ: 3282, 3068, 2911, 2835, 1743, 1708, 1660, 1569, 1529, 1462, 1203, 994, 831, 737 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}N_3O_6$([M+H]$^+$): 594.1660, Found: 594.1651.

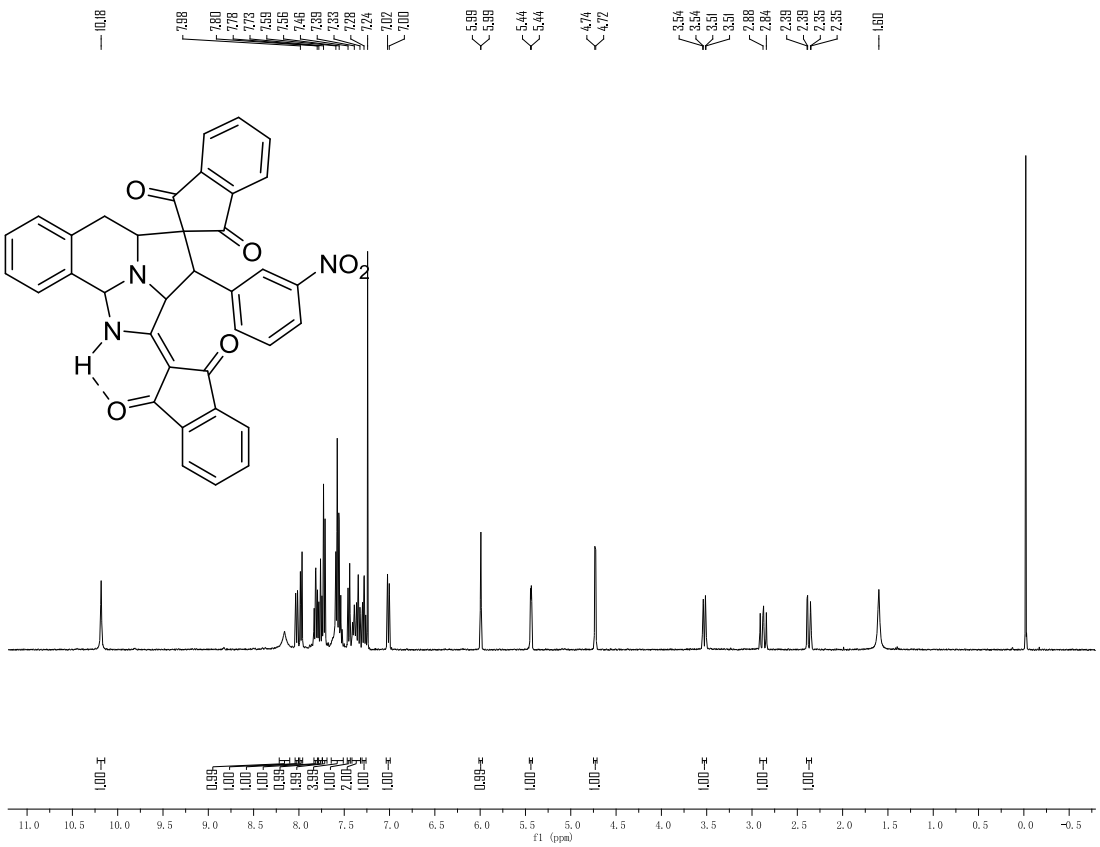

Figure S27 ^{1}H NMR spectra of the compound **2h**

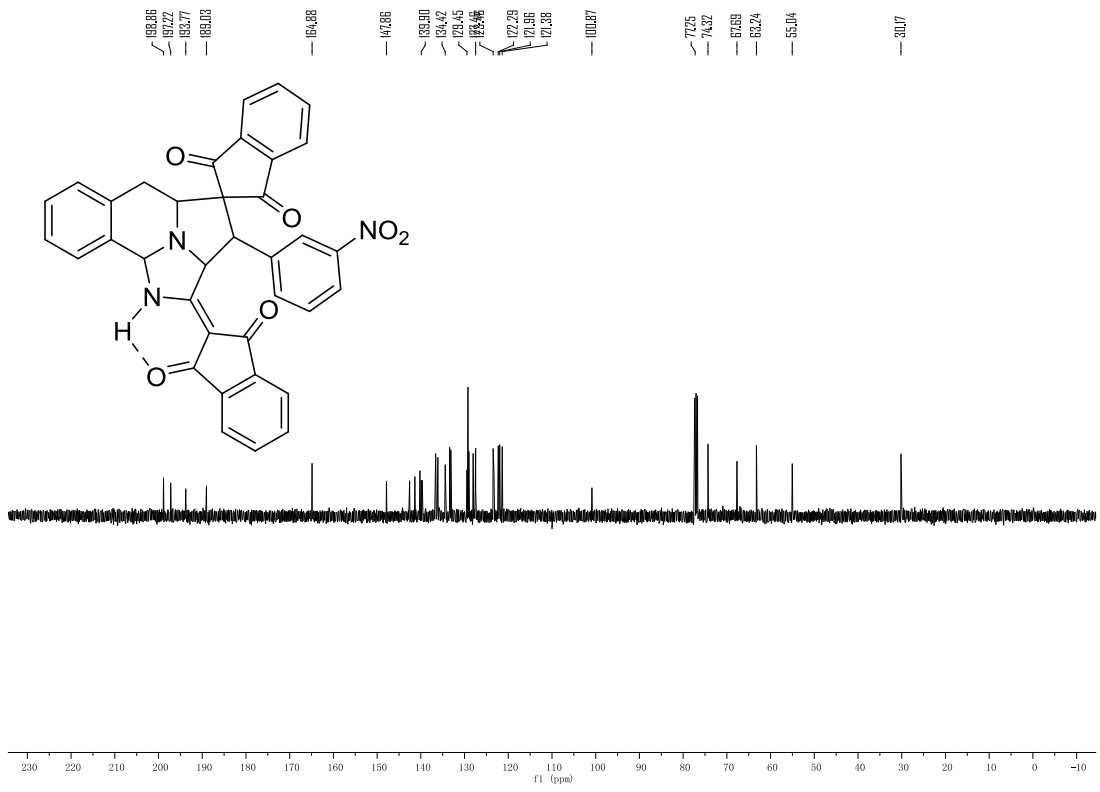

Figure S28 ^{13}C NMR spectra of the compound **2h**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(p-tolyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2i): white solid, 92%, m.p. 233-235 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.48 (s, 1H, NH), 7.97-7.95 (m, 1H, ArH), 7.92-7.86 (m, 3H, ArH), 7.68-7.62 (m, 4H, ArH), 7.50 (d, J = 6.4 Hz, 1H, ArH), 7.34 (t, J = 7.2 Hz, 1H, ArH), 7.27 (t, J = 6.4 Hz, 1H, ArH), 7.07 (d, J = 7.2 Hz, 1H, ArH), 6.92-6.90 (m, 3H, ArH), 5.96-5.95 (m, 1H, CH), 5.47-5.45 (m, 1H, CH), 4.37 (d, J = 4.0 Hz, 1H, CH), 3.18 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH), 2.64-2.57 (m, 1H, CH), 2.45-2.42 (m, 1H, CH), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.5, 196.9, 192.0, 188.3, 166.7, 142.7, 141.3, 139.6, 139.5, 137.5, 136.7, 135.9, 135.7, 135.1, 133.9, 133.7, 130.3, 129.6, 129.4, 129.2, 128.7, 128.0, 127.3, 123.7, 123.3, 121.7, 121.2, 100.0, 77.3, 74.6, 67.6, 63.0, 55.4, 29.8, 21.0; IR (KBr) υ: 3275, 3018, 2918, 1738, 1704, 1569, 1459, 1357, 1274, 1135, 861, 740 cm^{-1}; HRMS (ESI) Calcd. for $C_{37}H_{27}N_2O_4$([M+H]$^+$): 563.1965, Found: 563.1979.

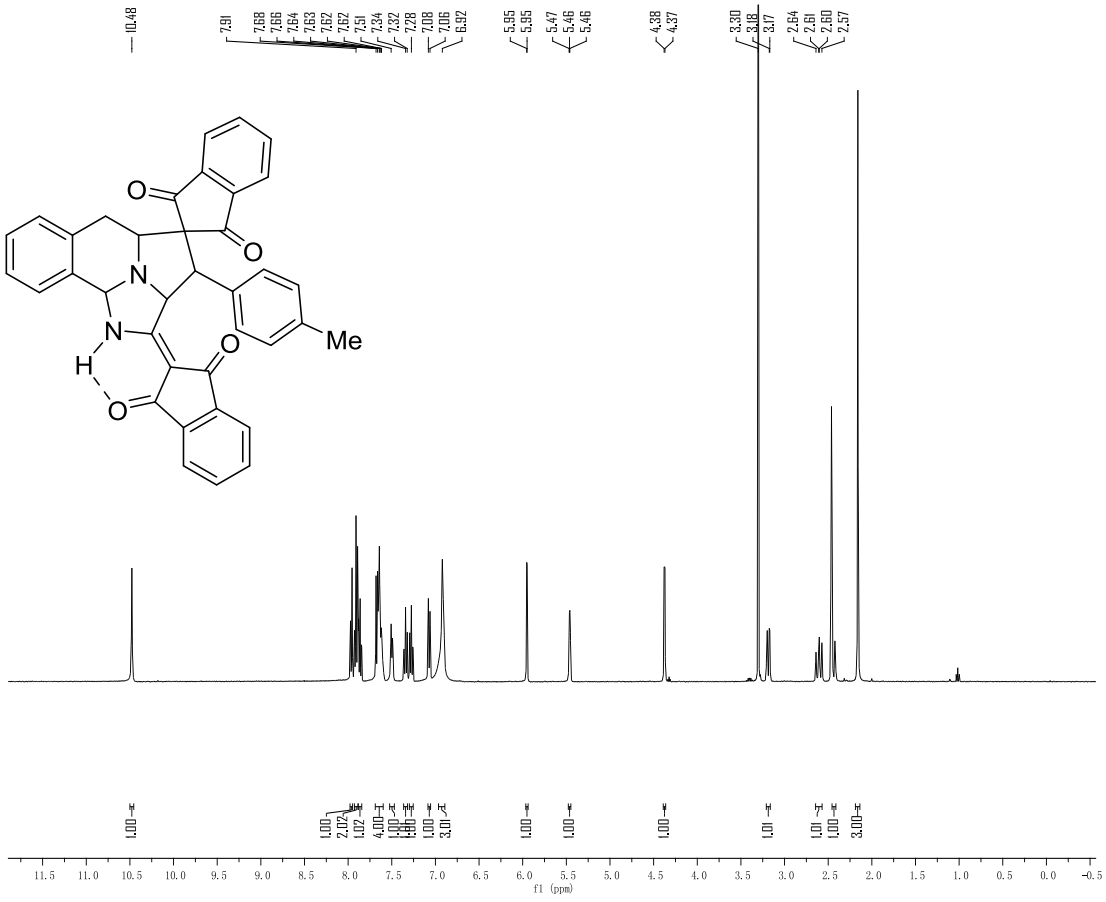

Figure S29 ^{1}H NMR spectra of the compound **2i**

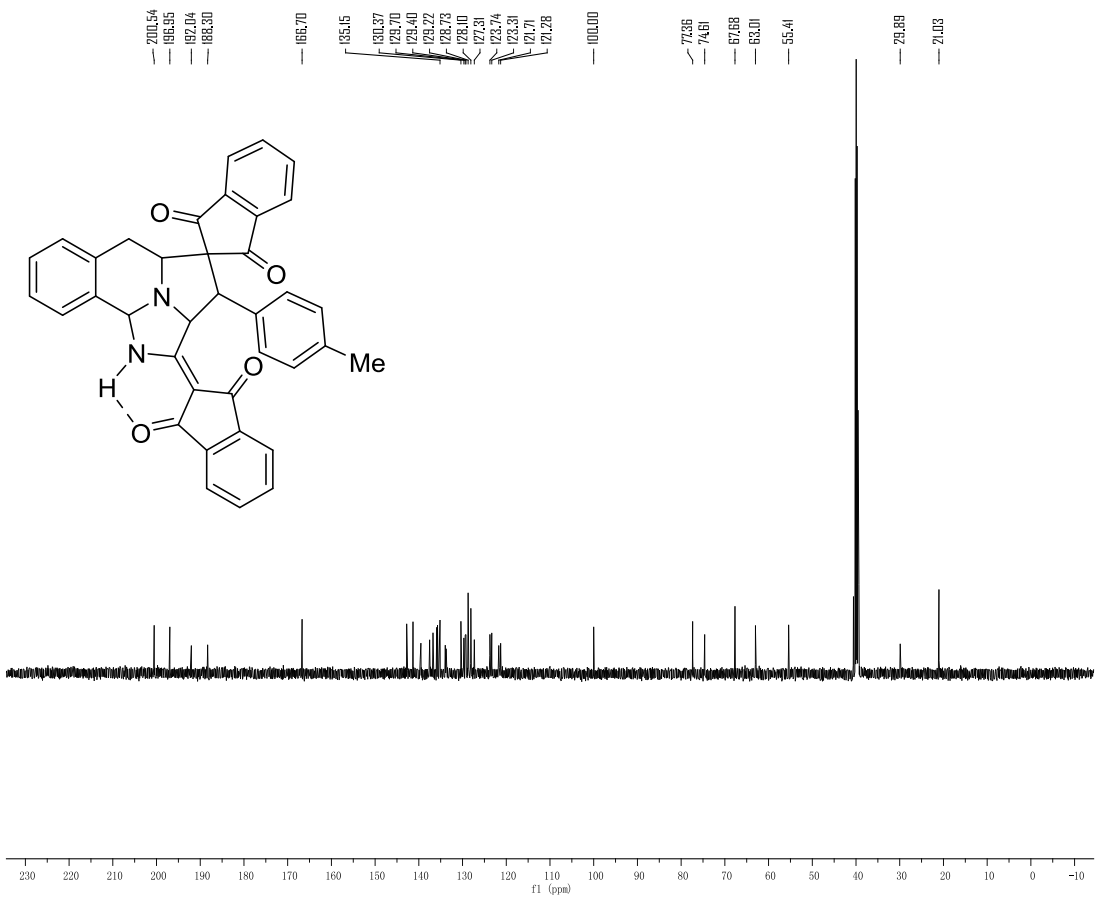

Figure S30 ^{13}C NMR spectra of the compound **2i**

3-(4-(Bimethylamino)phenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2j): white solid, 73%, m.p. 262-264 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H, NH), 7.92-7.91 (m, 1H, ArH), 7.74-7.69 (m, 4H, ArH), 7.62-7.61 (m, 1H, ArH), 7.53-7.52 (m, 2H, ArH), 7.43-7.41 (m, 1H, ArH), 7.32-7.30 (m, 2H, ArH), 7.04-7.01 (m, 3H, ArH), 6.54-6.51 (m, 2H, ArH), 5.98 (s, 1H, CH), 5.34 (s, 1H, CH), 4.60 (s, 1H, CH), 3.51 (d, *J* = 12.4 Hz, 1H, CH), 2.96 (t, *J* = 10.4 Hz, 1H, CH), 2.84 (s, 6H, $2CH_3$), 2.37 (d, *J* = 13.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.1, 197.9, 194.1, 188.6, 166.0, 149.2, 143.1, 141.7, 139.9, 139.7, 135.9, 135.2, 135.0, 133.1, 132.7, 129.8, 129.1, 129.0, 128.8, 127.9, 127.2, 125.3, 123.2, 122.9, 122.0, 121.1, 112.1, 101.0, 77.1, 75.2, 68.0, 62.1, 56.0, 40.4, 30.2; IR (KBr) υ: 3270, 3071, 2903, 2832, 1744, 1708, 1665, 1568, 1520, 1459, 1362, 1340, 1246, 1058, 858, 743, 693 cm^{-1}; HRMS (ESI) Calcd. for $C_{38}H_{29}N_3NaO_4$([M+Na]$^+$): 614.2050, Found: 614.2041.

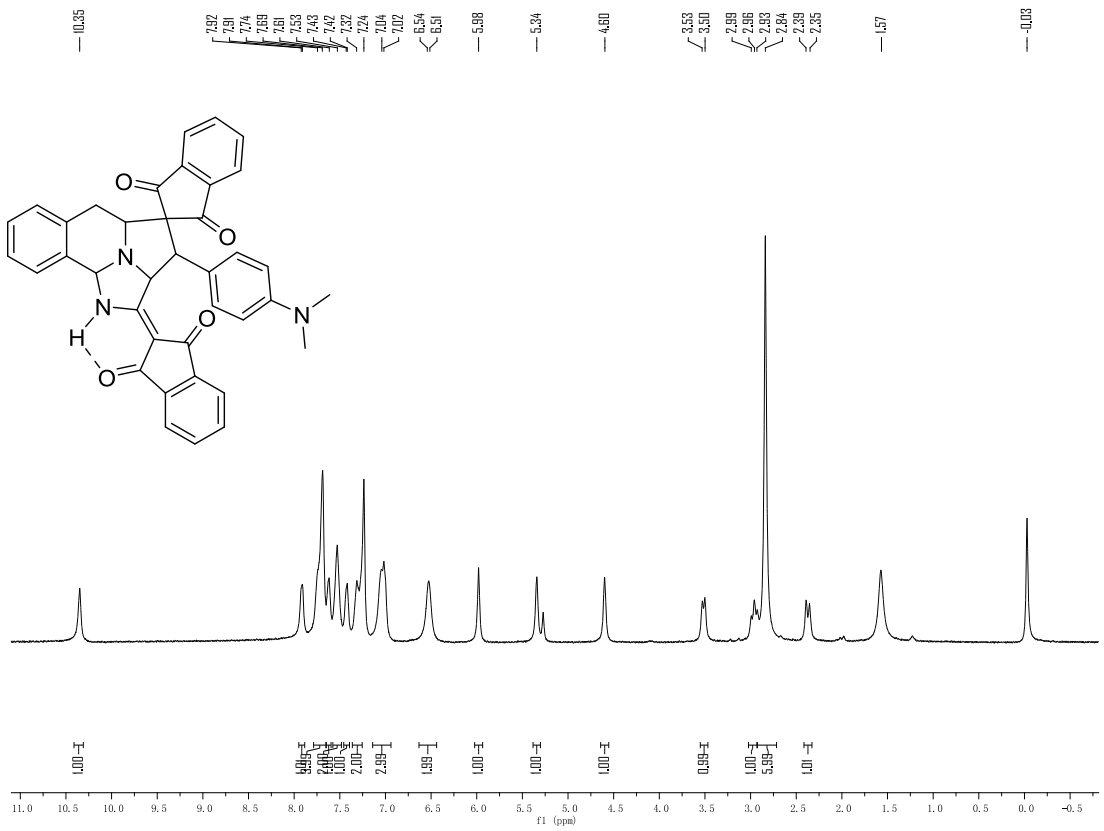

Figure S31 ^{1}H NMR spectra of the compound **2j**

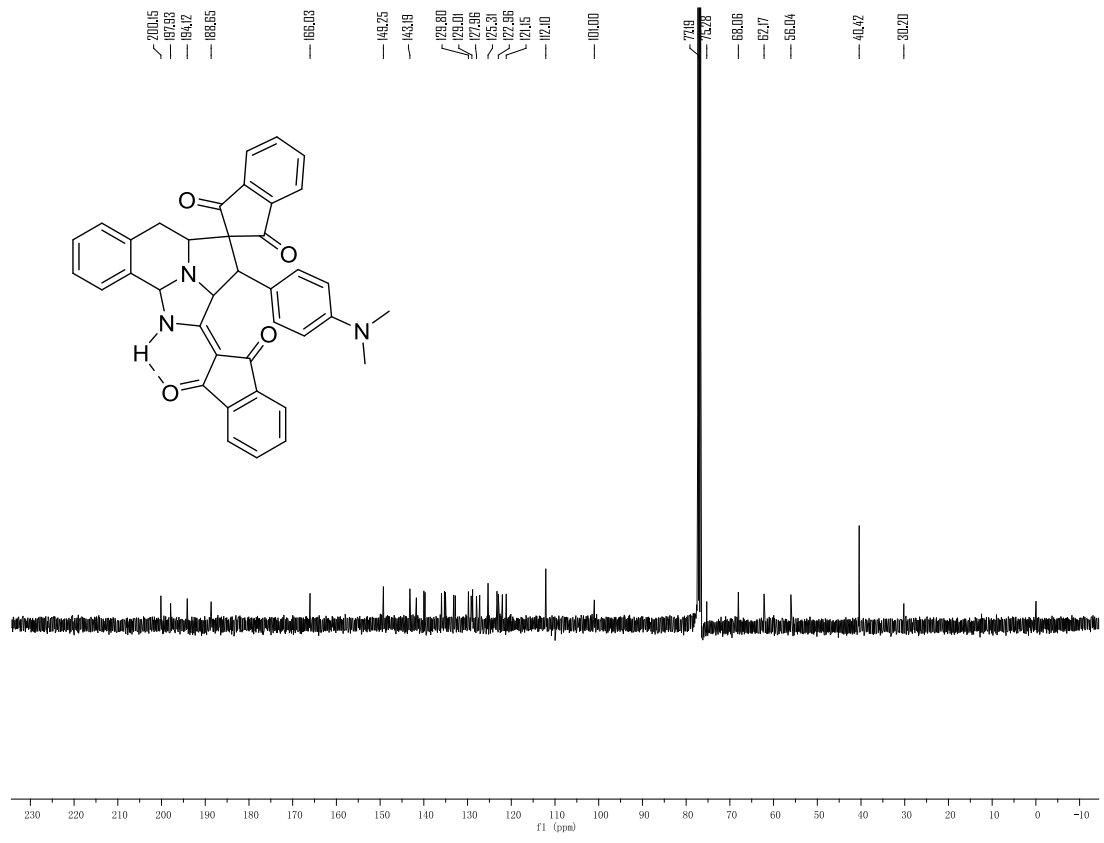

Figure S32 ^{13}C NMR spectra of the compound **2j**

3-(4-Bromophenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2k): white solid, 81 %, m.p. 278-281 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.46 (s, 1H, NH), 7.98-7.89 (m, 4H, ArH), 7.73-7.71 (m, 1H, ArH), 7.62-7.57 (m, 4H, ArH), 7.36-7.30 (m, 3H, ArH), 7.28 (t, *J* = 7.6 Hz, 1H, ArH), 7.08-6.95 (m, 3H, ArH), 5.93 (s, 1H, CH), 5.48 (s, 1H, CH), 4.36-4.35 (m, 1H, CH), 3.19 (d, *J* = 10.4 Hz, 1H, CH), 2.58 (t, *J* = 12.4 Hz, 1H, CH), 2.45-2.43 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.9, 191.9, 191.9, 188.5, 188.4, 188.4, 166.3, 142.6, 141.3, 138.4, 137.6, 136.9, 135.0, 133.9, 133.9, 133.8, 133.8, 133.8, 131.0, 130.4, 130.3, 129.7, 129.4, 129.2, 127.3, 123.8, 123.3, 120.0, 100.0, 77.4, 74.3, 67.5, 63.2, 54.9, 40.4, 40.2, 39.9, 29.9； IR (KBr) υ: 3279, 3066, 2902, 1738, 1704, 1569, 1488, 1279, 1137, 1003, 934, 862, 744 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{23}BrKN_2O_4$([M+K]$^+$): 665.0473, Found: 665.0460.

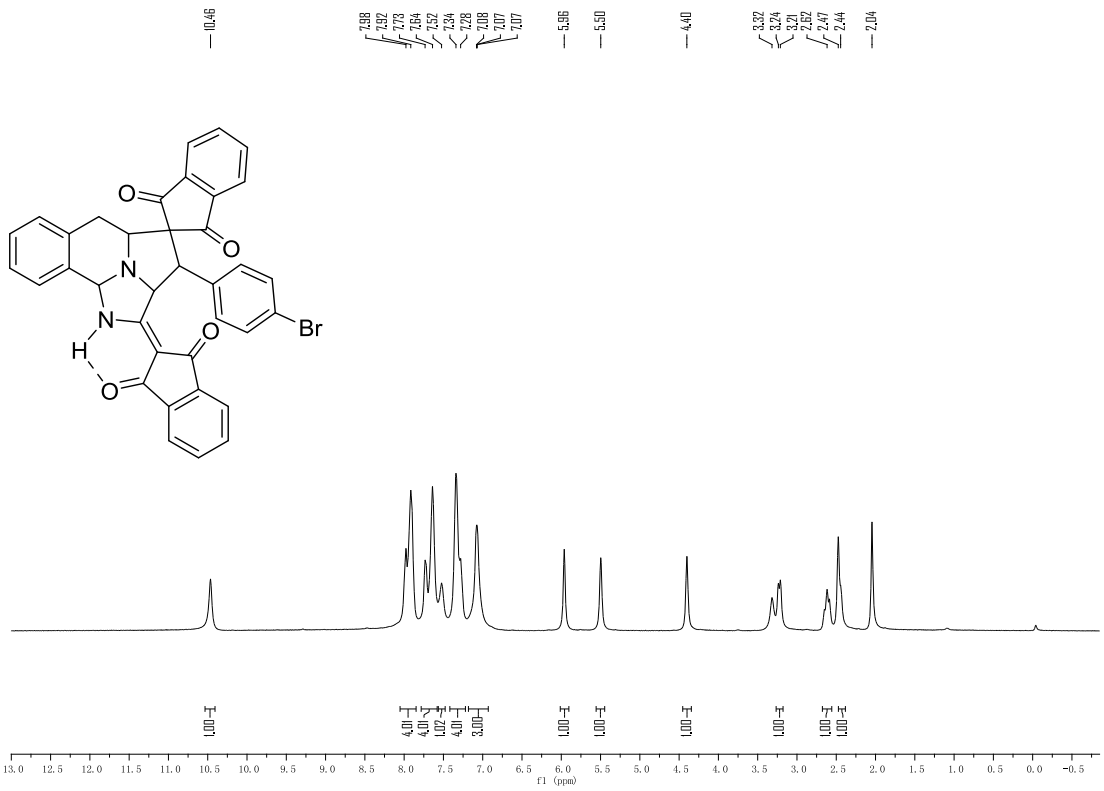

Figure S33 ^{1}H NMR spectra of the compound **2k**

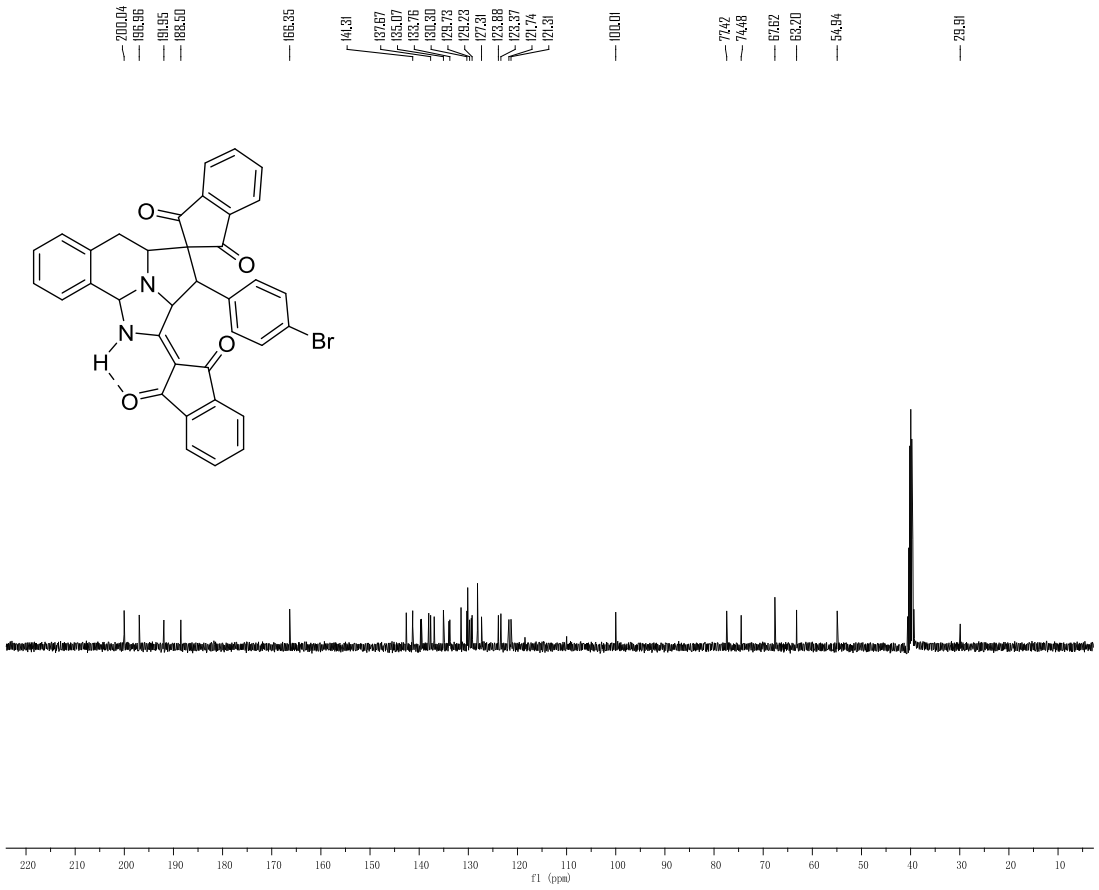

Figure S34 ^{13}C NMR spectra of the compound **2k**

3-(4-Chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2l): white solid, 91 %, m.p. 269-272 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.02-8.00 (m, 2H, ArH), 7.97-7.94 (m, 2H, ArH), 7.75 (d, J = 7.2 Hz, 1H, ArH), 7.70-7.68 (m, 2H, ArH), 7.54 (d, J = 6.8 Hz, 1H, ArH), 7.42-7.40 (m, 1H, ArH), 7.33-7.29 (m, 2H, ArH), 7.24-7.22 (m, 3H, ArH), 7.12-7.08 (m, 2H, ArH), 5.98 (s, 1H, CH), 5.54-5.50 (m, 1H, CH), 4.42-4.41 (m, 1H, CH), 3.24 (d, J = 10.8 Hz, 1H, CH), 2.64 (t, J = 12.4 Hz, 1H, CH), 2.49-2.47 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.9, 188.4, 166.3, 142.6, 141.3, 139.7, 139.5, 138.0, 137.6, 136.9, 135.0, 133.9, 133.7, 131.4, 130.3, 130.1, 129.7, 129.3, 129.2, 128.1, 127.3, 123.8, 123.3, 121.7, 121.3, 100.0, 77.4, 74.4, 67.6, 63.2, 54.9, 29.9； IR (KBr) υ: 3287, 3042, 2938, 1739, 1704, 1661, 1568, 1487, 1283, 1141, 1020, 936, 897, 732 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}ClN_2O_4$([M+H]$^{+}$): 583.1419, Found: 583.1421.

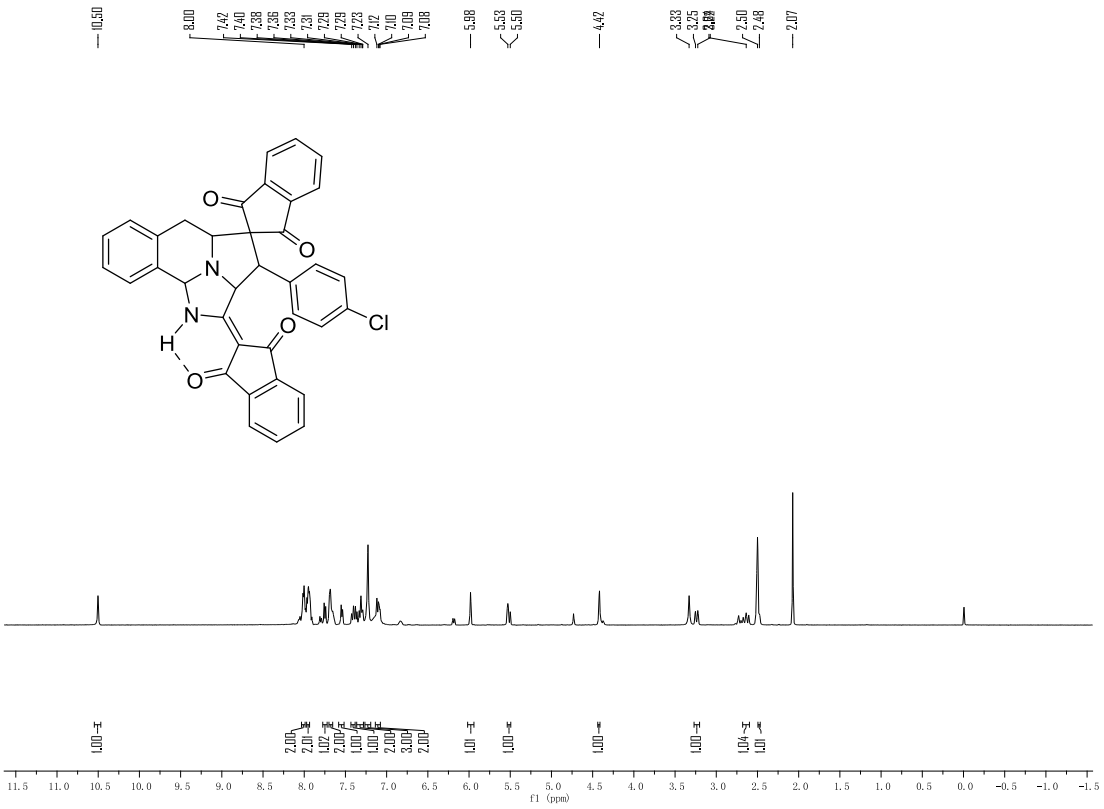

Figure S35 ^{1}H NMR spectra of the compound **2l**

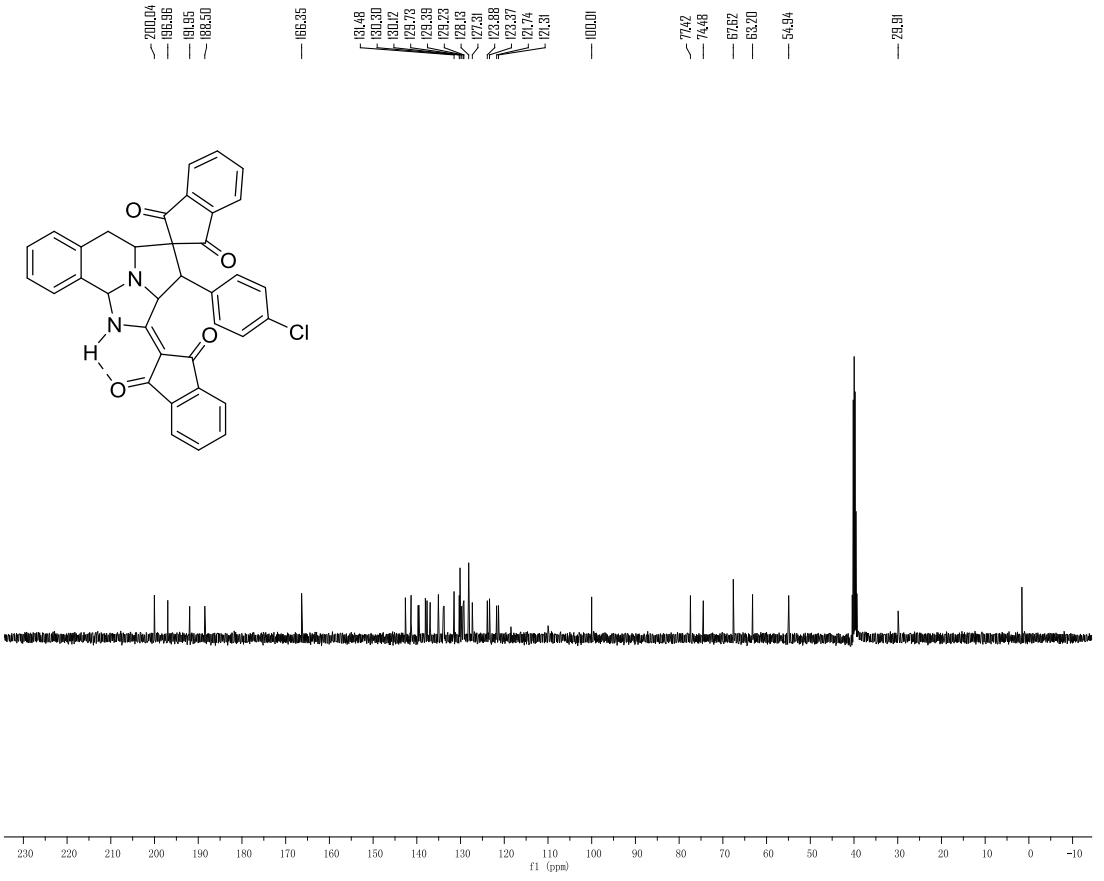

Figure S34 ^{13}C NMR spectra of the compound **2l**

3-(4-(tert-Butyl)phenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2m): white solid, 81%, m.p. 255-257 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H, NH), 7.92 (d, *J* = 7.6 Hz, 1H, ArH), 7.76-7.73 (m, 1H, ArH), 7.71-7.65 (m, 2H, ArH), 7.63-7.61 (m, 1H, ArH), 7.58-7.56 (m, 1H, ArH), 7.55-7.50 (m, 2H, ArH), 7.44 (d, *J* = 7.2 Hz, 1H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 7.29-7.25 (m, 1H, ArH), 7.15-7.06 (m, 4H, ArH), 7.03 (d, *J* = 7.6 Hz, 1H, ArH), 6.01 (s, 1H, CH), 5.40-5.38 (m, 1H, CH), 4.63 (d, *J* = 4.0 Hz, 1H, CH), 3.55 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH), 3.03-2.96 (m, 1H, CH), 2.40 (dd, J_1 = 15.6 Hz, J_2 = 2.4 Hz, 1H, CH), 1.20 (s, 9H, $3CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 197.6, 197.6, 194.0, 188.8, 165.7, 149.5, 143.1, 141.6, 139.9, 139.6, 135.8, 135.3, 135.0, 134.4, 133.1, 132.8, 129.7, 129.2, 129.0, 127.9, 127.7, 127.2, 124.9, 122.9, 122.0, 121.2, 100.9, 77.3, 74.7, 68.0, 61.8, 56.4, 34.3, 31.2, 30.1; IR (KBr) υ: 3280, 3063, 3019, 2960, 2872, 1741, 1703, 1569, 1461, 1356, 1274, 1136, 931, 824, 742 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{33}N_2O_4$([M+H]$^+$): 605.2435, Found: 605.2432.

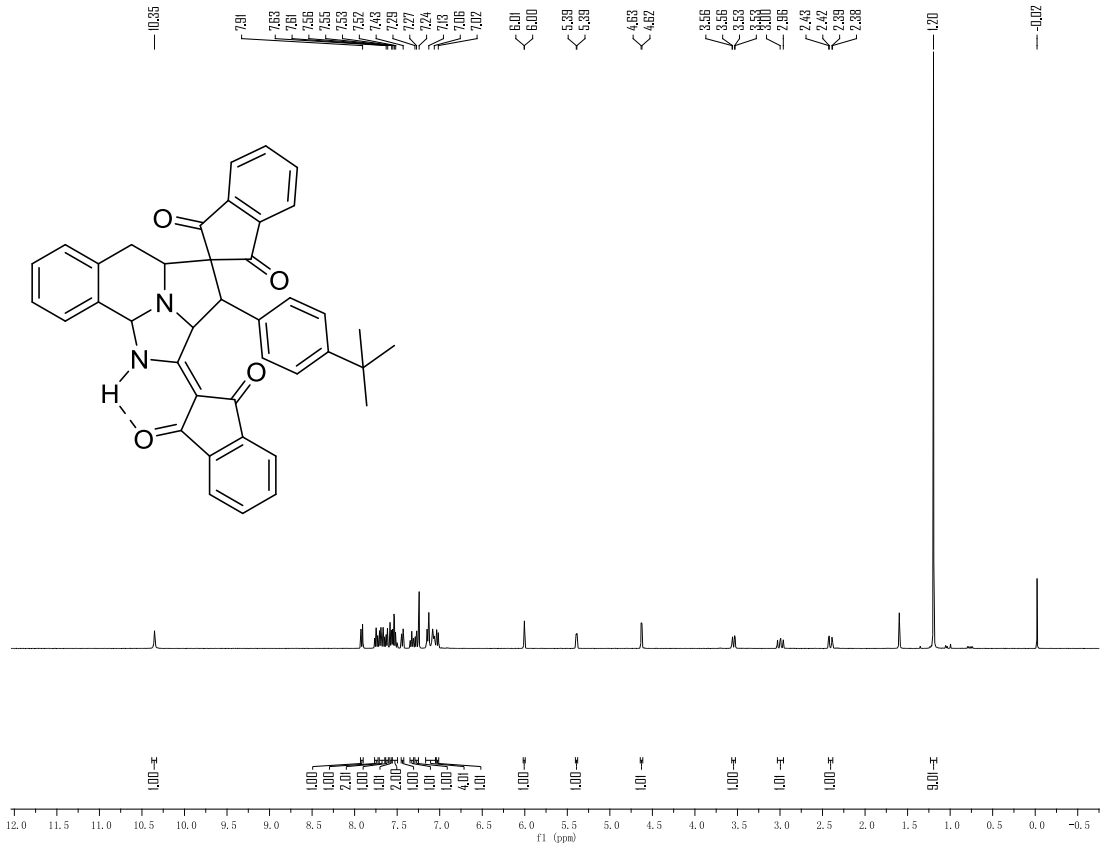

Figure S35 ^{1}H NMR spectra of the compound **2m**

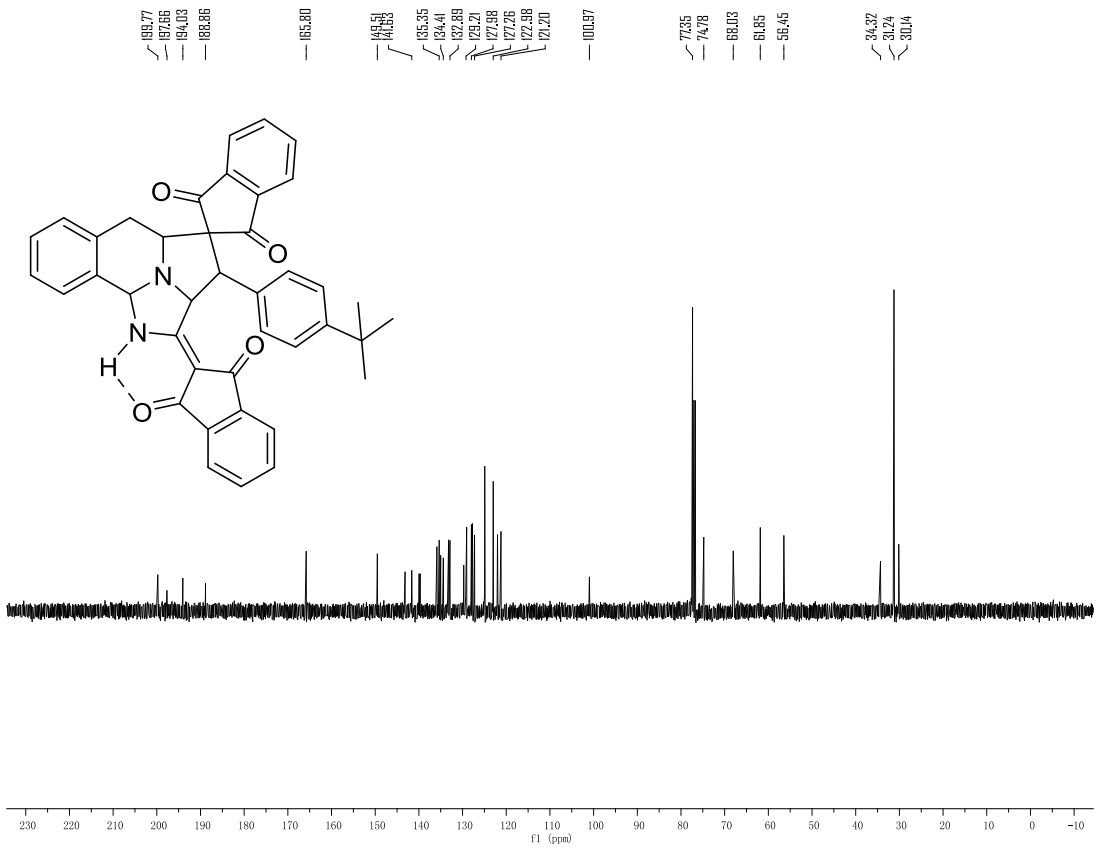

Figure S36 ^{13}C NMR spectra of the compound **2m**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(4-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2n): white solid, 79 %, m.p. 265-267 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.48 (s, 1H, NH), 8.12-8.00 (m, 4H, ArH), 7.98-7.92 (m, 3H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.70-7.65 (m, 3H, ArH), 7.52 (d, J = 6.8 Hz, 1H, ArH), 7.44-7.43 (m, 1H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.32 (t, J = 7.6 Hz, 1H, ArH), 7.11 (d, J = 7.6 Hz, 1H, ArH), 6.00 (s, 1H, CH), 5.66 (s, 1H, CH), 4.56 (d, J = 3.6 Hz, 1H, CH), 3.26-3.25 (m, 1H, CH), 2.62 (t, J = 12.0 Hz, 1H, CH), 2.52-2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 196.7, 191.8, 188.6, 166.0, 147.0, 146.5, 142.4, 141.2, 139.6, 139.5, 137.8, 137.1, 134.9, 133.9, 133.8, 130.2, 129.7, 129.5, 129.4, 129.2, 127.3, 124.0, 123.4, 123.3, 121.7, 121.3, 99.9, 77.4, 74.0, 67.7, 63.6, 54.7, 29.9; IR (KBr) υ: 3245, 3017, 2900, 2832, 1741, 1704, 1571, 1571, 1460, 1206, 1050, 896, 789, 698 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{23}KN_3O_4$([M+K]$^+$): 632.1218, Found: 632.1216.

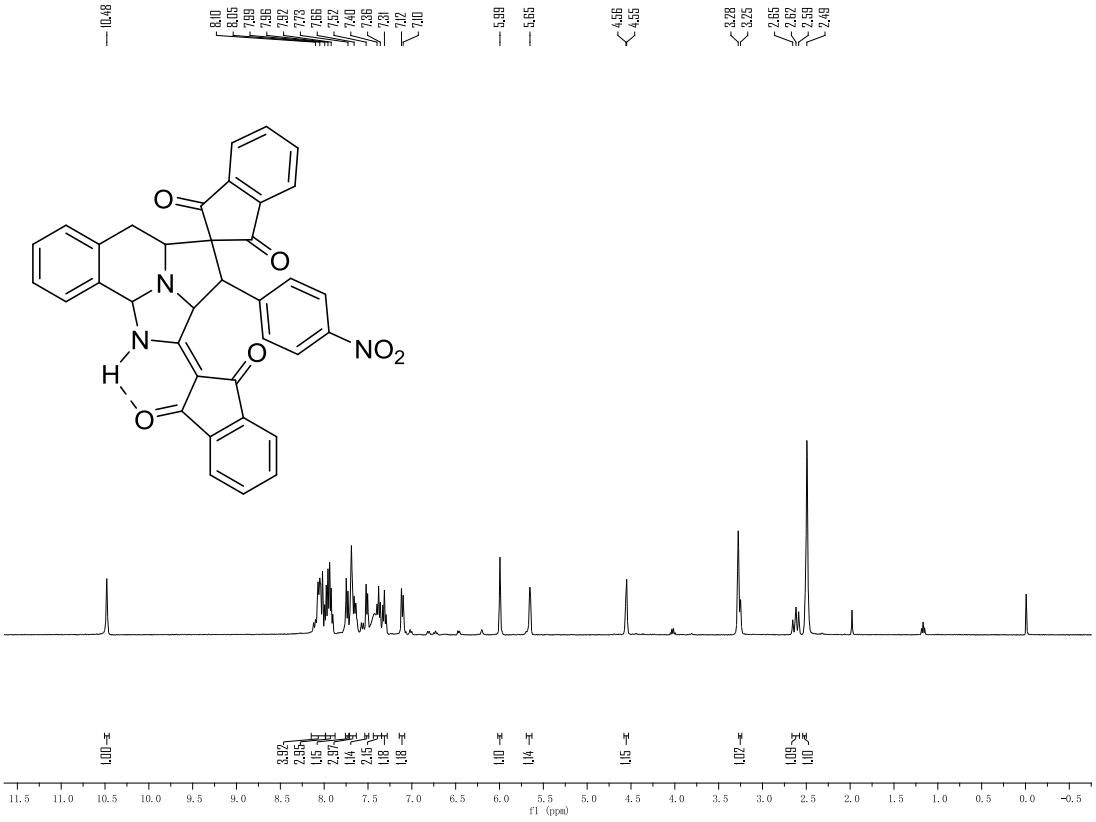

Figure S37 ^{1}H NMR spectra of the compound **2n**

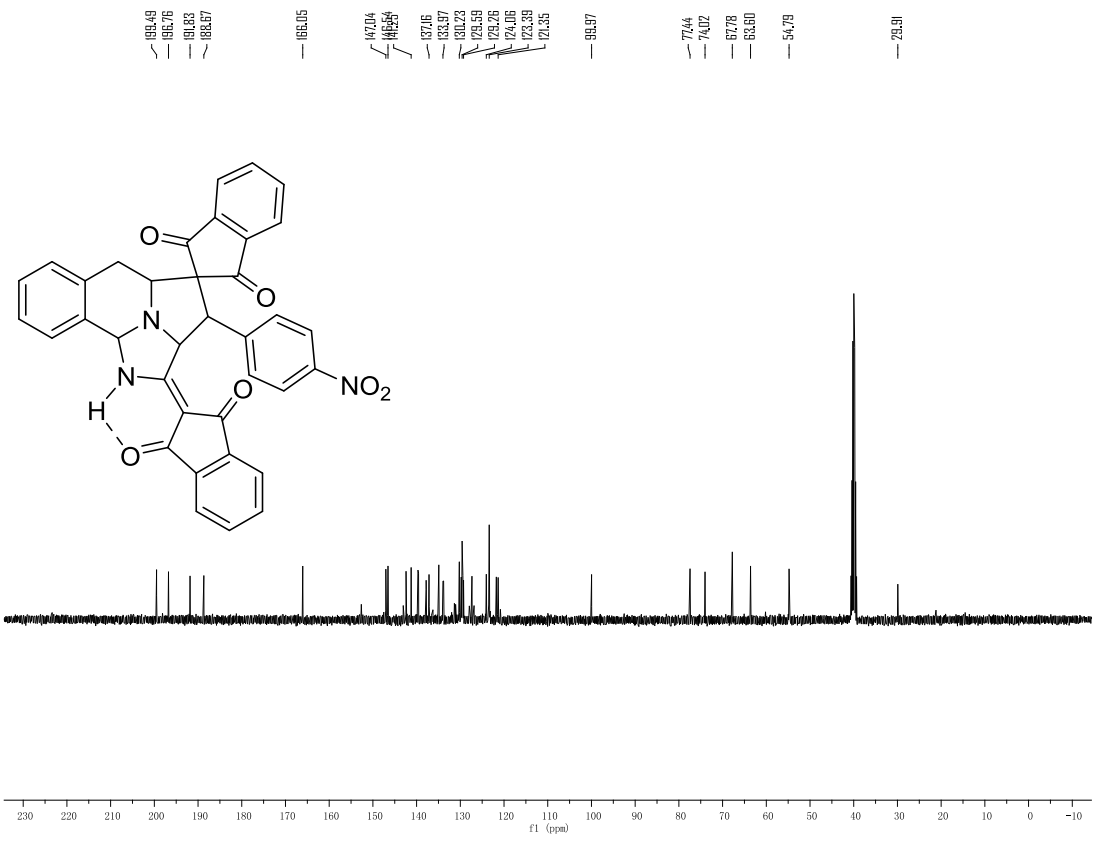

Figure S38 ^{13}C NMR spectra of the compound **2n**

3-(4-Chloro-2-hydroxyphenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2o): white solid, 72 %, m.p. 240-242 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.45 (s, 1H, NH), 9.44 (s, 1H, OH), 7.98-7.92 (m, 3H, ArH), 7.88 (t, *J* = 7.2 Hz, 1H, ArH), 7.75-7.73 (m, 1H, ArH), 7.69-7.66 (m, 3H, ArH), 7.55-7.54 (m, 2H, ArH), 7.37 (t, *J* = 7.6 Hz, 1H, ArH), 7.31 (t, *J* = 7.6 Hz, 1H, ArH), 7.11 (d, *J* = 7.6 Hz, 1H, ArH), 7.00-6.97 (m, 1H, ArH), 6.45 (d, *J* = 8.8 Hz, 1H, ArH), 5.98 (s, 1H, CH), 5.59 (s, 1H, CH), 4.61 (d, *J* = 3.6 Hz, 1H, CH), 3.24-3.21 (m, 1H, CH), 2.63-2.56 (m, 1H, CH), 2.40-2.37 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 197.5, 191.8, 188.5, 167.0, 153.3, 142.2, 141.3, 139.7, 136.6, 136.5, 135.2, 133.7, 130.4, 129.8, 129.3, 129.2, 128.3, 127.3, 127.2, 123.3, 123.1, 122.6, 121.6, 115.9, 100.0, 77.8, 73.4, 65.7, 63.7, 48.3, 29.9; IR (KBr) υ: 3351, 3304, 3058, 2926, 1741, 1705, 1667, 1570, 1490, 1462, 1203, 1033, 928, 869, 787, 740, 700, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{24}ClN_2O_5$([M+H]$^+$): 599.1368, Found: 599.1364.

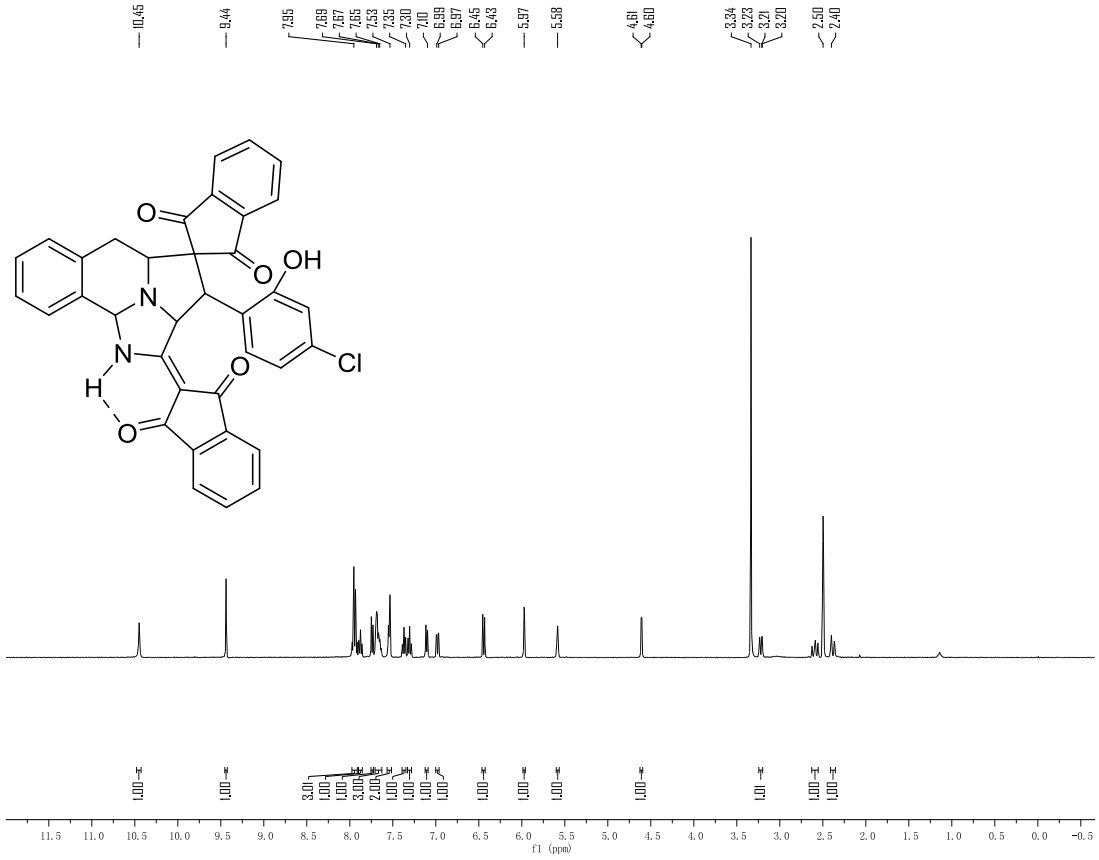

Figure S39 ^{1}H NMR spectra of the compound **2o**

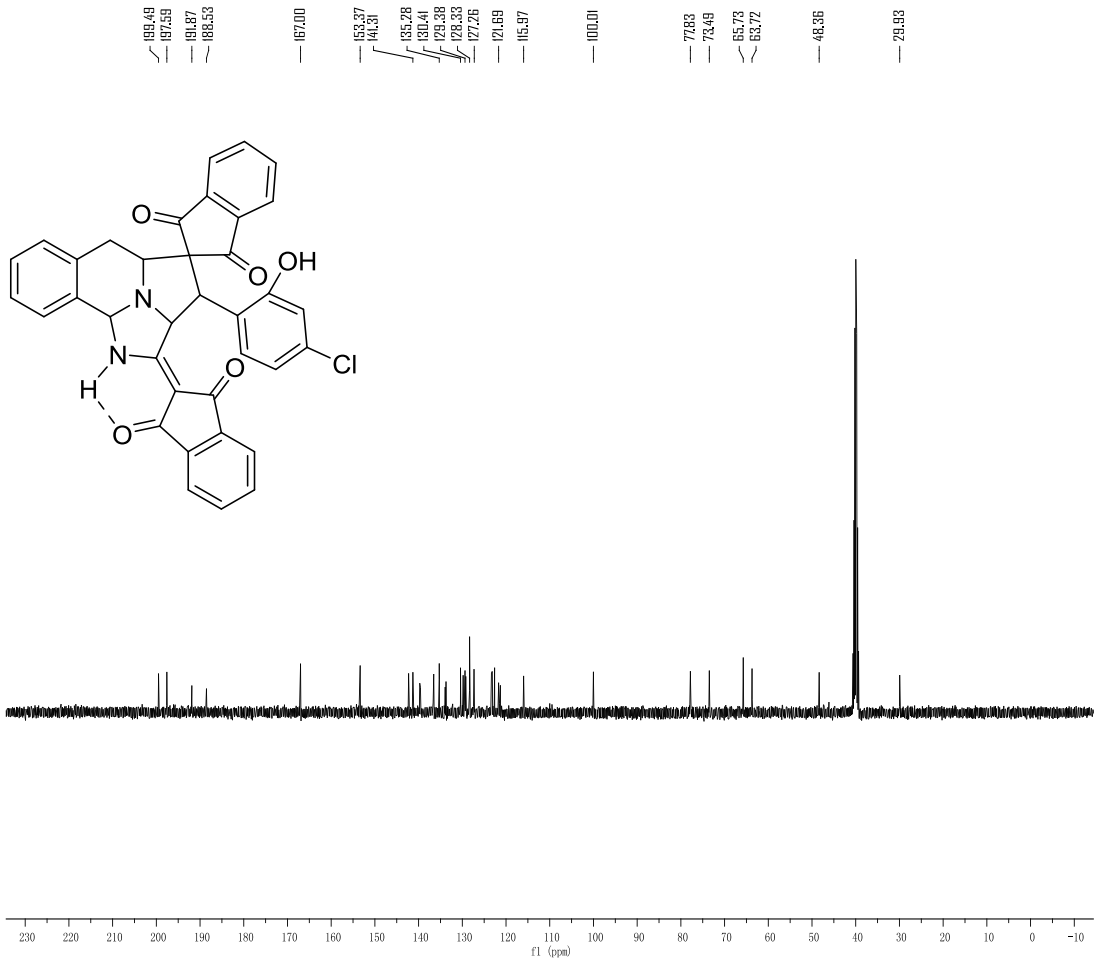

Figure S40 ^{13}C NMR spectra of the compound **2o**

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(furan-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2'-indene]-1',3'-dione (2p): white solid, 69 %, m.p. 221-223 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 10.54 (s, 1H, NH), 8.08-8.04 (m, 3H, ArH), 7.96-7.92 (m, 2H, ArH), 7.75-7.71 (m, 3H, ArH), 7.62-7.60 (m, 1H, ArH), 7.39-7.34 (m, 2H, ArH), 7.26-7.25 (m, 1H, ArH), 7.12-7.11 (m, 1H, ArH), 6.38-6.34 (m, 2H, ArH), 5.97 (s, 1H, CH), 5.56 (s, 1H, CH), 4.50-4.48 (m, 1H, CH), 3.16-3.10 (m, 1H, CH), 2.60-2.58 (m, 1H, CH), 2.50-2.46 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d6) δ: 199.3, 195.7, 191.5, 188.2, 165.4, 152.3, 142.0, 141.2, 140.6, 139.2, 139.0, 137.2, 136.4, 134.3, 133.6, 133.4, 129.8, 129.2, 129.0, 128.8, 126.9, 123.5, 122.9, 121.3, 120.9, 110.5, 106.4, 99.6, 76.6, 72.5, 65.6, 62.7, 47.7, 39.5, 29.2； IR (KBr) υ: 3278, 3069, 2913, 2831, 1744, 1707, 1680, 1593, 1564, 1462, 1244, 1135, 888, 697 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{23}N_2O_5$([M+H]+): 539.1601, Found: 539.1620.

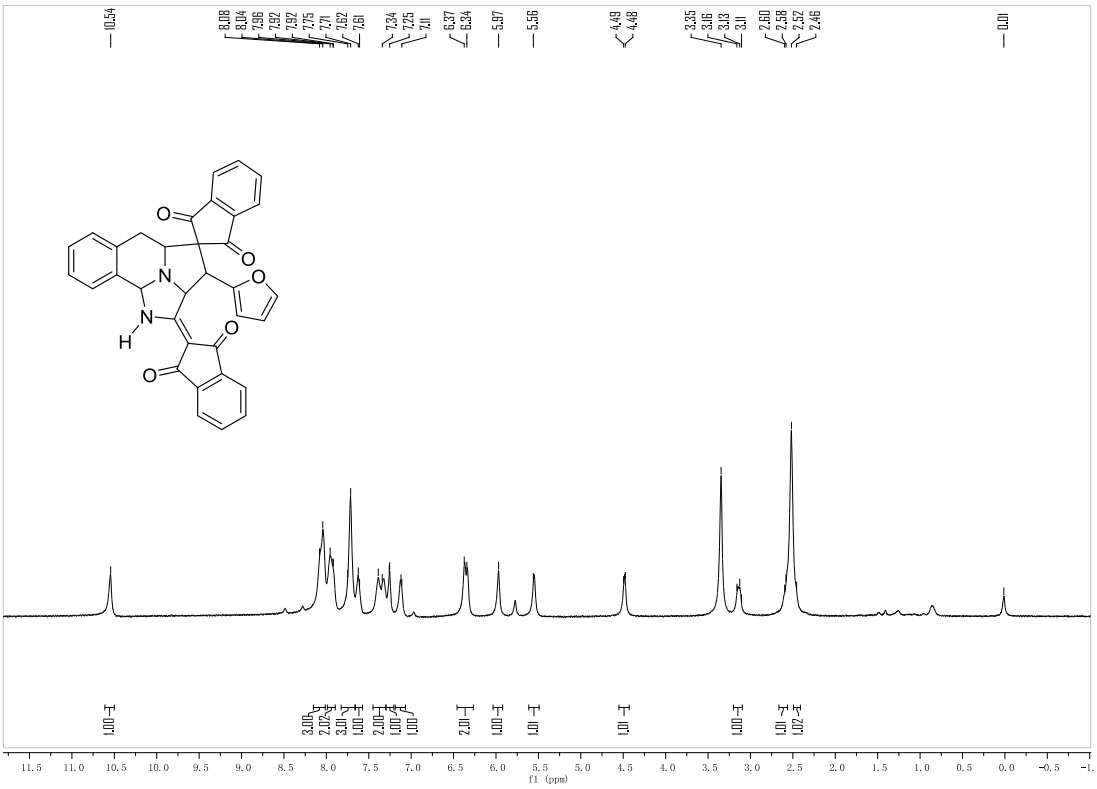

Figure S41 ^{1}H NMR spectra of the compound **2p**

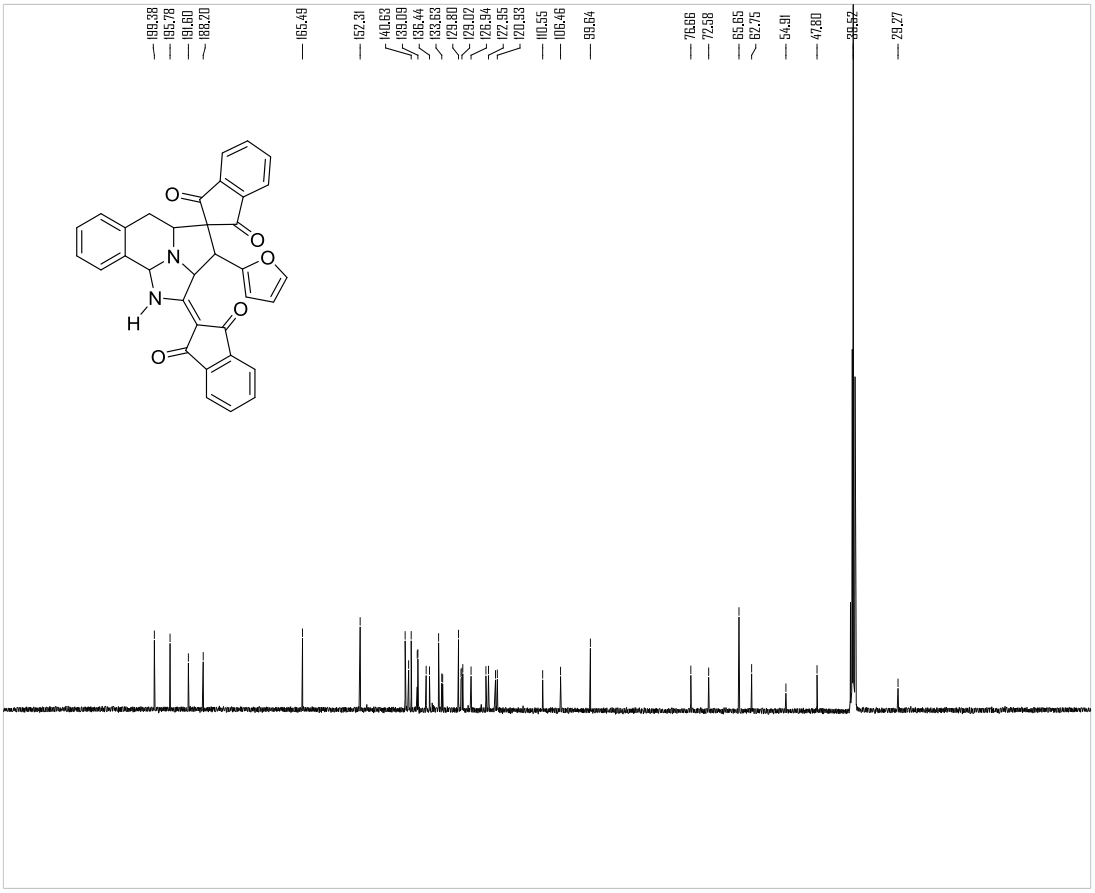

Figure S42 ^{13}C NMR spectra of the compound **2p**

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(thiophen-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2'-indene]-1',3'-dione (2q): white solid, 78 %, m.p. 233-235 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.55 (s, 1H, NH), 8.06-8.04 (m, 1H, ArH), 7.99-7.97 (m, 2H, ArH), 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.82 (d, *J* = 8.0 Hz, 1H, ArH), 7.69-7.67 (m, 3H, ArH), 7.59-7.57 (m, 3H, ArH), 7.37 (t, *J* = 8.0 Hz, 1H, ArH), 7.32 (t, *J* = 7.6 Hz, 1H, ArH), 7.21 (d, *J* = 4.4 Hz, 1H, ArH), 7.11 (d, *J* = 7.6 Hz, 1H, ArH), 6.87-6.86 (m, 2H, ArH), 5.99 (s, 1H, CH), 5.53 (s, 1H, CH), 4.67 (d, *J* = 4.0 Hz, 1H, CH), 3.21-3.18 (m, 1H, CH), 2.62-2.59 (m, 1H, CH), 2.50-2.48 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.2, 192.0, 188.3, 165.8, 142.8, 142.0, 141.4, 139.6, 139.5, 137.6, 136.8, 134.8, 134.0, 133.8, 130.2, 129.6, 129.4, 129.2, 127.3, 126.9, 125.5, 124.1, 123.8, 123.3, 121.7, 121.3, 100.1, 77.1, 75.6, 67.6, 63.0, 50.3, 29.8； IR (KBr) υ: 3277, 3068, 2915, 2836, 1742, 1705, 1568, 1462, 1245, 1203, 1060, 892, 738, 692 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{23}N_3O_2S$ ([M+H]+): 555.1373, Found: 555.1383.

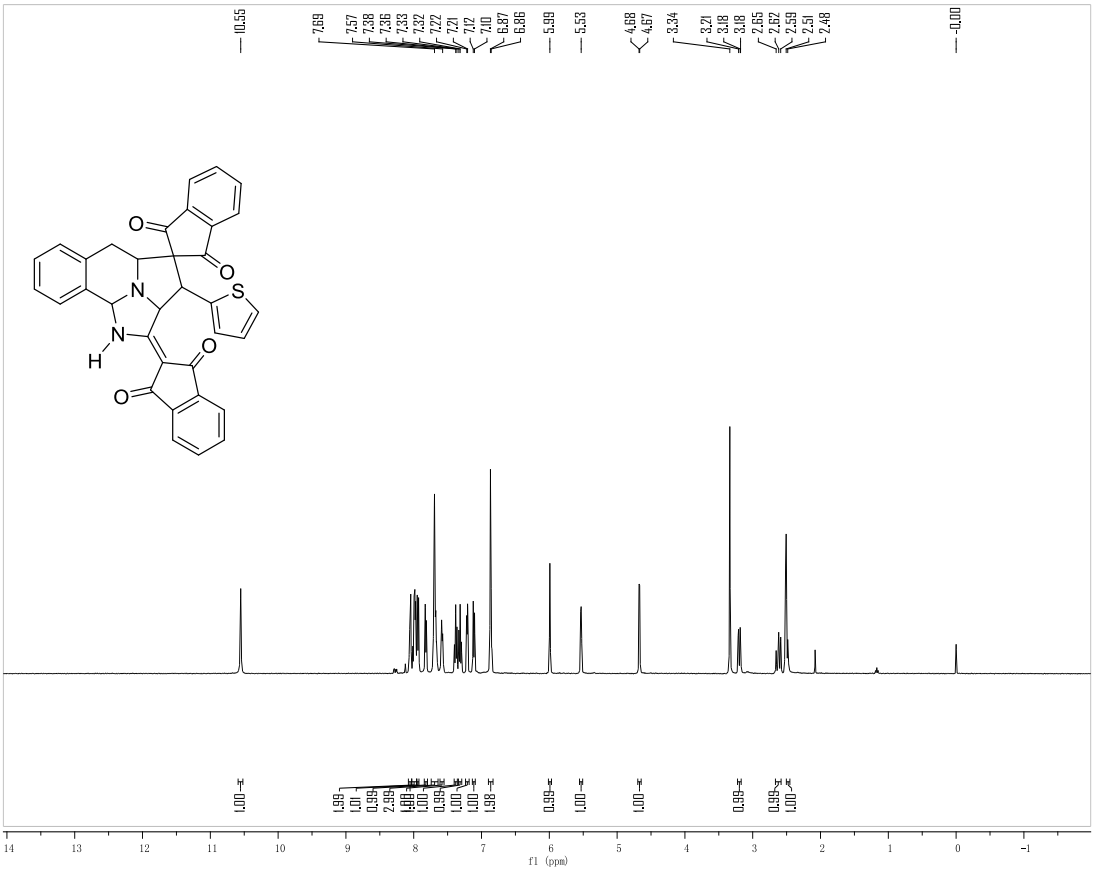

Figure S43 ^{1}H NMR spectra of the compound **2q**

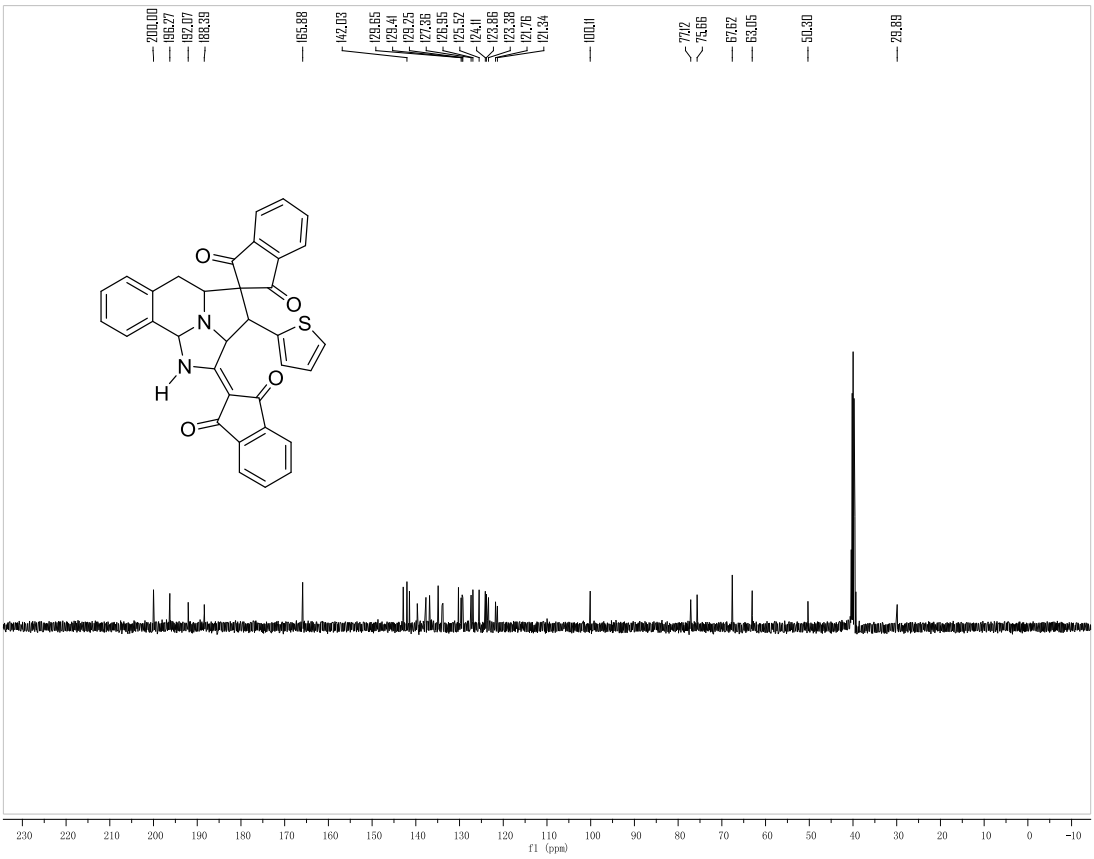

Figure S44 ^{13}C NMR spectra of the compound **2q**

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(pyridin-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2'-indene]-1',3'-dione (2r): white solid, 83 %, m.p. 270-272 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.55 (s, 1H, NH), 8.07 (d, *J* = 7.6 Hz, 1H, ArH), 8.01-7.94 (m, 4H, ArH), 7.89 (d, *J* = 6.8 Hz, 1H, ArH), 7.75 (d, *J* = 7.6 Hz, 1H, ArH), 7.70-7.64 (m, 4H, ArH), 7.55 (d, *J* = 6.8 Hz, 1H, ArH), 7.37 (t, *J* = 7.6 Hz, 1H, ArH), 7.30 (t, *J* = 7.6 Hz, 1H, ArH), 7.13-7.09 (m, 2H, ArH), 5.97 (s, 1H, CH), 5.91 (s, 1H, CH), 4.73 (d, *J* = 4.0 Hz, 1H, CH), 3.15-3.11 (m, 1H, CH), 2.48-2.45 (m, 1H, CH), 2.42-2.38 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.7, 192.0, 188.7, 167.0, 158.6, 147.9, 147.9, 142.8, 141.4, 139.6, 139.5, 137.0, 136.5, 136.4, 134.7, 134.0, 133.8, 130.3, 129.6, 129.4, 129.2, 127.3, 123.9, 122.9, 122.4, 121.9, 121.7, 121.3, 100.0, 77.0, 77.0, 71.4, 67.5, 63.1, 55.8, 55.7, 29.8, 29.8； IR (KBr) υ: 3271, 3062, 2925, 1745, 1710, 1648, 1568, 1466, 1338, 1212, 935, 682 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{24}N_3O_4$ ($[M+H]^+$): 550.1761, Found: 550.1769.

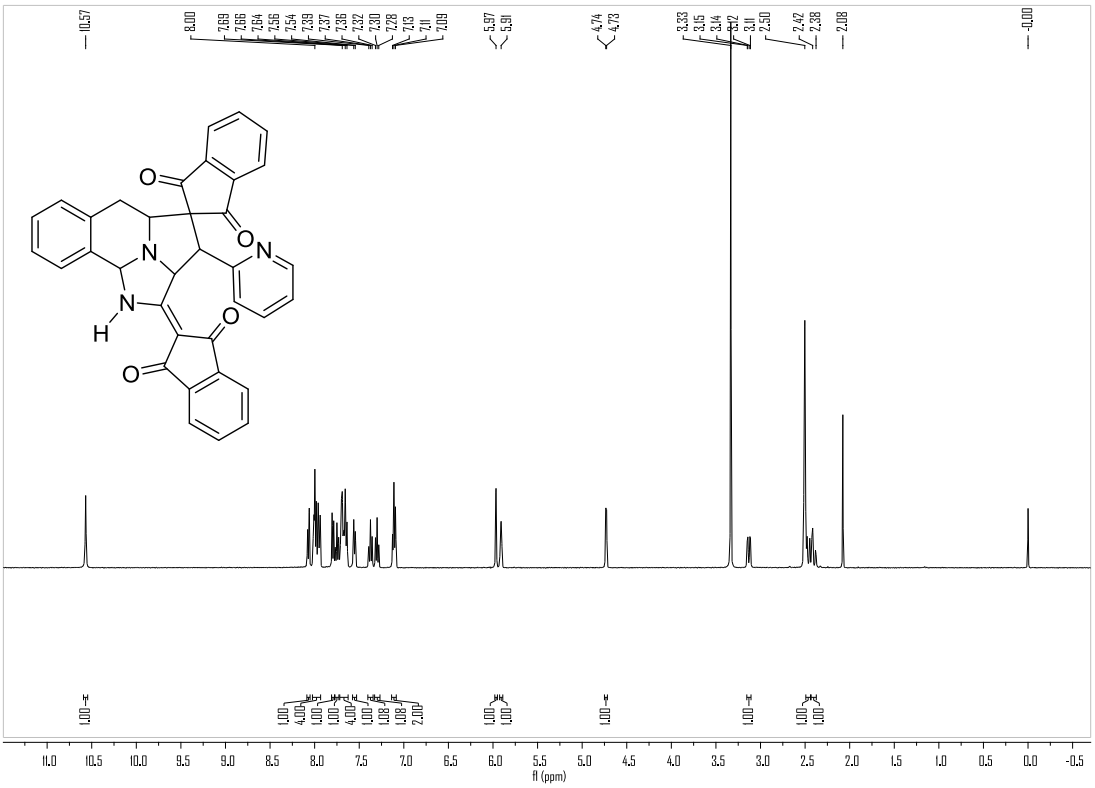

Figure S45 ^{1}H NMR spectra of the compound **2r**

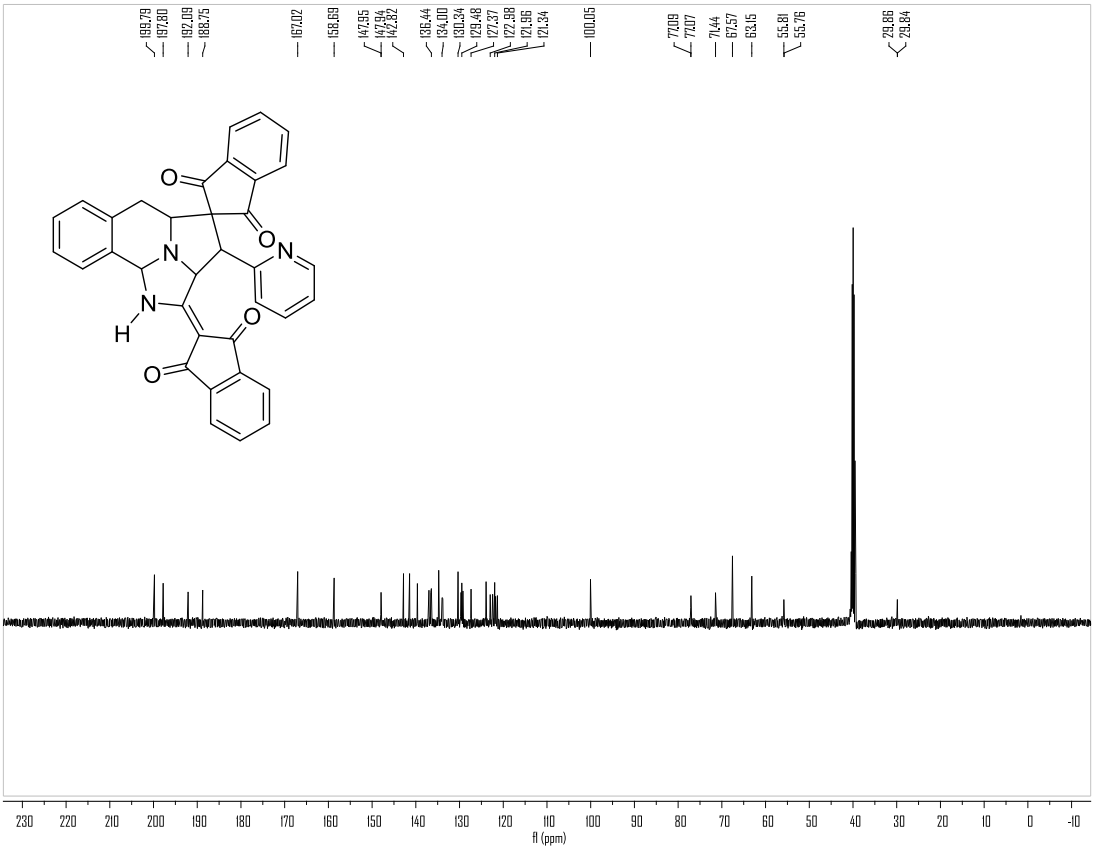

Figure S46 ^{13}C NMR spectra of the compound **2r**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(pyridin-3-yl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2s): white solid, 76%, m.p. 255-257 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.33-8.32 (m, 1H, ArH), 8.25-8.24 (m, 1H, ArH), 8.02 (d, *J* = 7.2 Hz, 1H, ArH), 7.99-7.92 (m, 3H, ArH), 7.74-7.68 (m, 5H, ArH), 7.55-7.53 (m, 1H, ArH), 7.38 (t, *J* = 7.6 Hz, 1H, ArH), 7.32 (t, *J* = 7.2 Hz, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.12 (d, *J* = 7.6 Hz, 1H, ArH), 5.99 (s, 1H, CH), 5.58 (s, 1H, CH), 4.43 (d, *J* = 3.2 Hz, 1H, CH), 3.28 (d, *J* = 12.0 Hz, 1H, CH), 2.66 (t, *J* = 12.0 Hz, 1H, CH), 2.54-2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.0, 191.8, 188.5, 166.1, 149.4, 148.1, 142.5, 141.3, 139.7, 139.5, 137.7, 137.1, 135.8, 135.0, 134.6, 133.9, 133.8, 130.2, 129.7, 129.4, 129.2, 127.3, 123.9, 123.3, 123.2, 121.7, 121.3, 99.9, 77.4, 74.2, 67.5, 63.3, 53.1, 29.8; IR (KBr) υ: 3284, 3070, 2969, 2916, 1741, 1704, 1571, 1484, 1202, 1089, 932, 713, 682, 618 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{24}N_3O_4$([M+H]$^+$): 550.1761, Found: 550.1783.

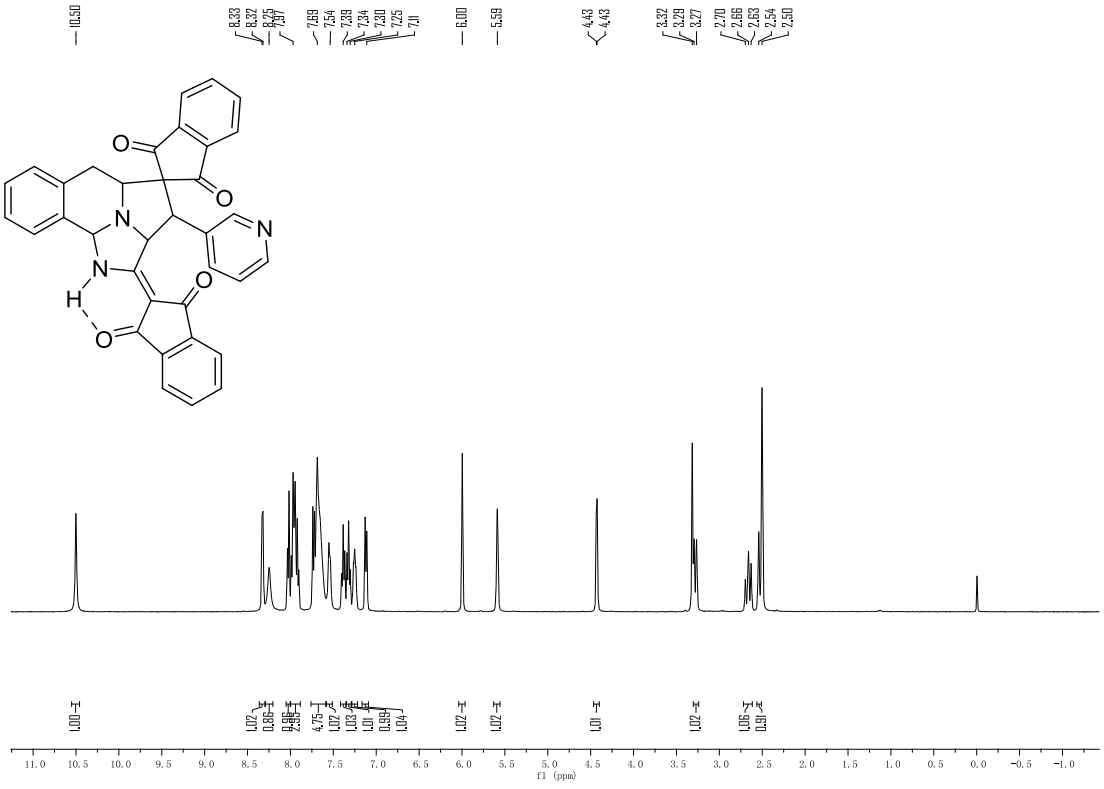

Figure S47 ^{1}H NMR spectra of the compound **2s**

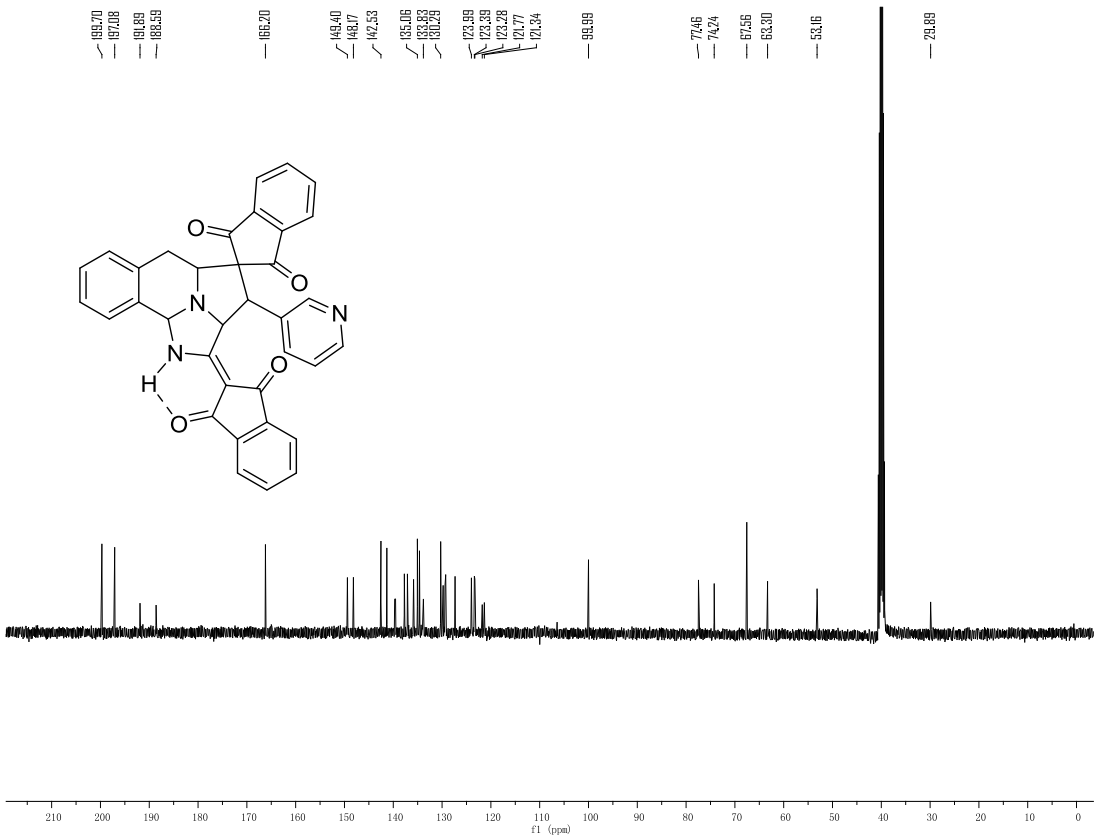

Figure S48 ^{13}C NMR spectra of the compound **2s**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(pyridin-4-yl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2t): white solid, 74%, m.p. 265-267 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.37-8.36 (m, 2H, ArH), 8.05 (d, J = 6.8 Hz, 1H, ArH), 8.01-7.95 (m, 3H, ArH), 7.75 (t, J = 7.2 Hz, 1H, ArH), 7.69-7.66 (m, 3H, ArH), 7.55-7.53 (m, 1H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.32 (t, J = 7.2 Hz, 1H, ArH), 7.12-7.10 (m, 3H, ArH), 5.98 (s, 1H, CH), 5.66 (s, 1H, CH), 4.41 (d, J = 3.2 Hz, 1H, CH), 3.24 (d, J = 11.2 Hz, 1H, CH), 2.59 (t, J = 11.6 Hz, 1H, CH), 2.49-2.48 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.5, 196.6, 191.8, 188.6, 166.1, 149.6, 147.8, 142.5, 141.2, 139.6, 137.8, 137.1, 134.9, 133.9, 133.8, 130.2, 129.7, 129.4, 129.2, 127.3, 124.0, 123.4, 123.2, 121.7, 121.3, 99.9, 77.3, 73.0, 67.4, 63.4, 54.2, 29.8; IR (KBr) υ: 3293, 3071, 3038, 2901, 2834, 1742, 1705, 1668, 1567, 1461, 1203, 1140, 1054, 892, 815, 740, 680 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{24}N_3O_4$([M+H]$^+$): 550.1761, Found: 550.1783.

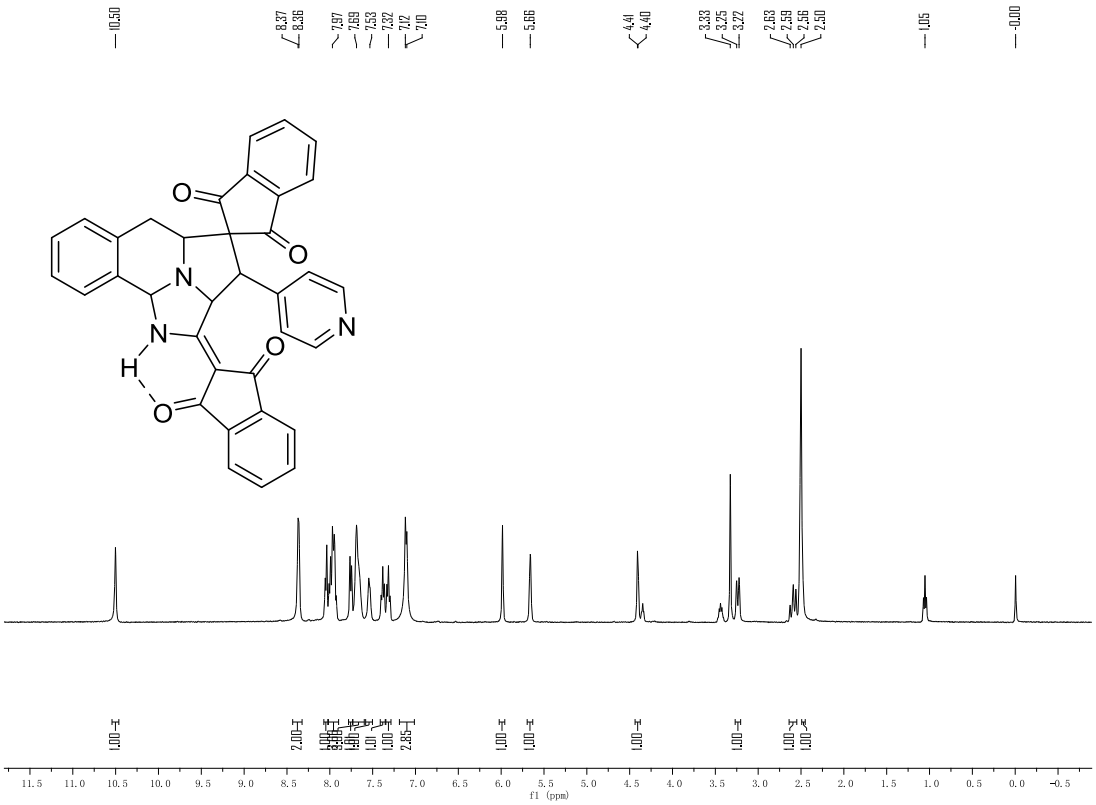

Figure S49 ^{1}H NMR spectra of the compound **2t**

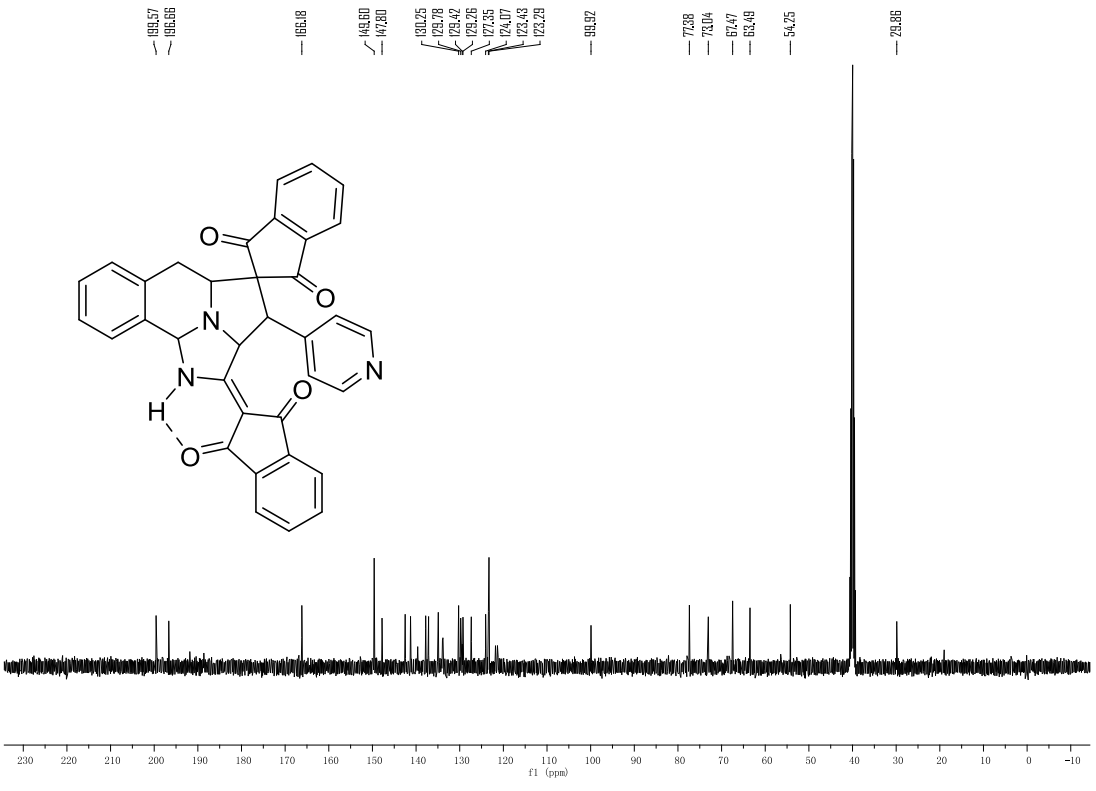

Figure S50 ^{1}H NMR spectra of the compound **2t**

3-Benzoyl-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2'-indene]-1',3'-dione (**2u**): white solid, 85 %, m.p. 284-286 ℃; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 10.68 (s, 1H, NH), 8.18 (d, J = 7.6 Hz, 1H, ArH), 8.10-8.05 (m, 3H, ArH), 7.99-7.91 (m, 4H, ArH), 7.82 (d, *J* = 6.4 Hz, 1H, ArH), 7.63-7.58 (m, 6H, ArH), 7.52 (t, *J* = 7.2 Hz, 2H, ArH), 7.41 (t, *J* = 7.2 Hz, 2H, ArH), 7.30 (d, *J* = 7.6 Hz, 1H, ArH), 6.26 (s, 1H, CH), 6.10 (s, 1H, CH), 5.27 (d, *J* = 3.6 Hz, 1H, CH), 3.40-3.37 (m, 1H, CH), 2.68-2.65 (m, 1H, CH), 2.61-2.57 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 199.5, 196.7, 193.8, 191.8, 189.4, 166.4, 141.5, 140.8, 139.8, 139.4, 137.5, 136.9, 136.5, 134.6, 134.0, 133.9, 133.3, 130.2, 129.8, 129.4, 129.1, 128.8, 128.2, 127.3, 123.6, 123.2, 121.8, 121.3, 99.7, 77.6, 69.7, 64.9, 64.7, 55.8, 29.6; IR (KBr) υ: 3239, 3065, 2913, 2828, 1739, 1708, 1653, 1580, 1461, 1266, 1144, 792, 704, 637 cm^{-1}; HRMS (ESI) Calcd. for $C_{37}H_{25}N_2O_5$ ([M+H]$^+$): 577.1758, Found: 577.1765.

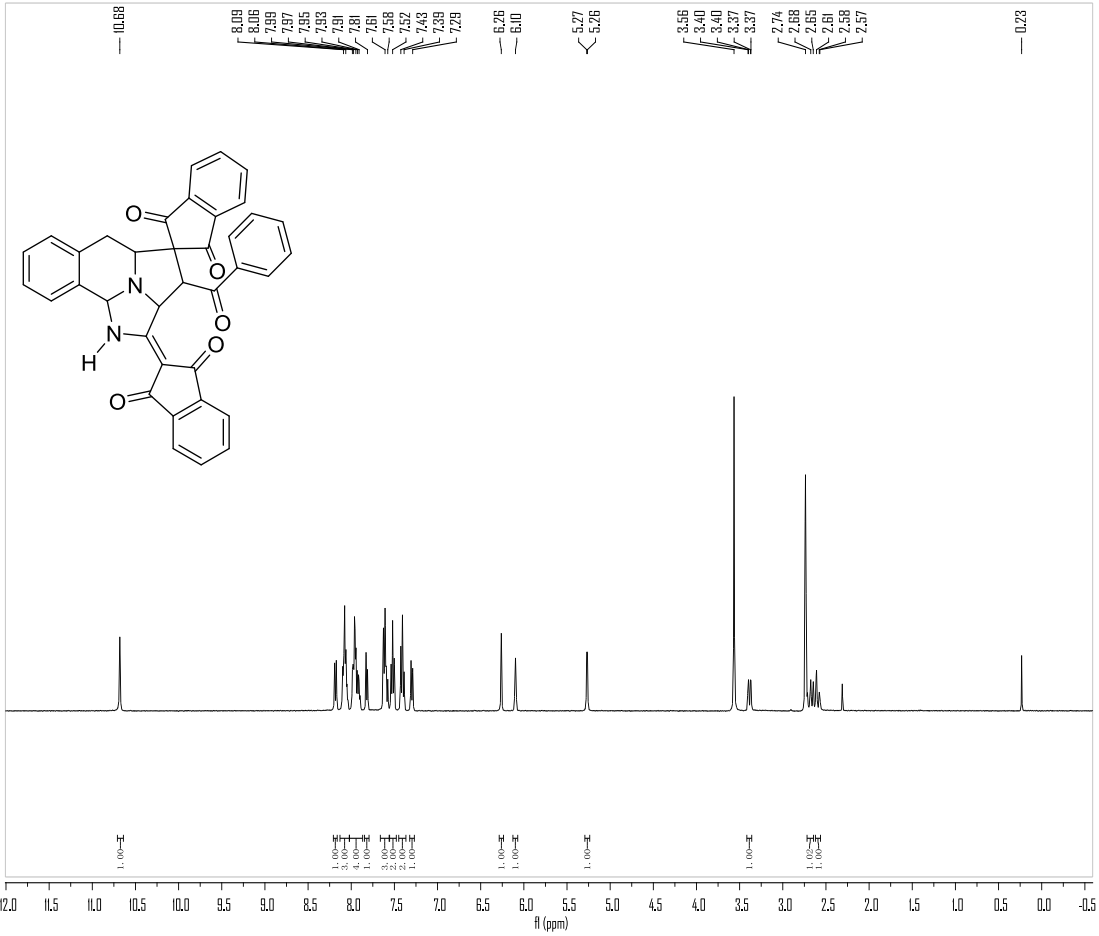

Figure S51 ^{1}H NMR spectra of the compound **2u**

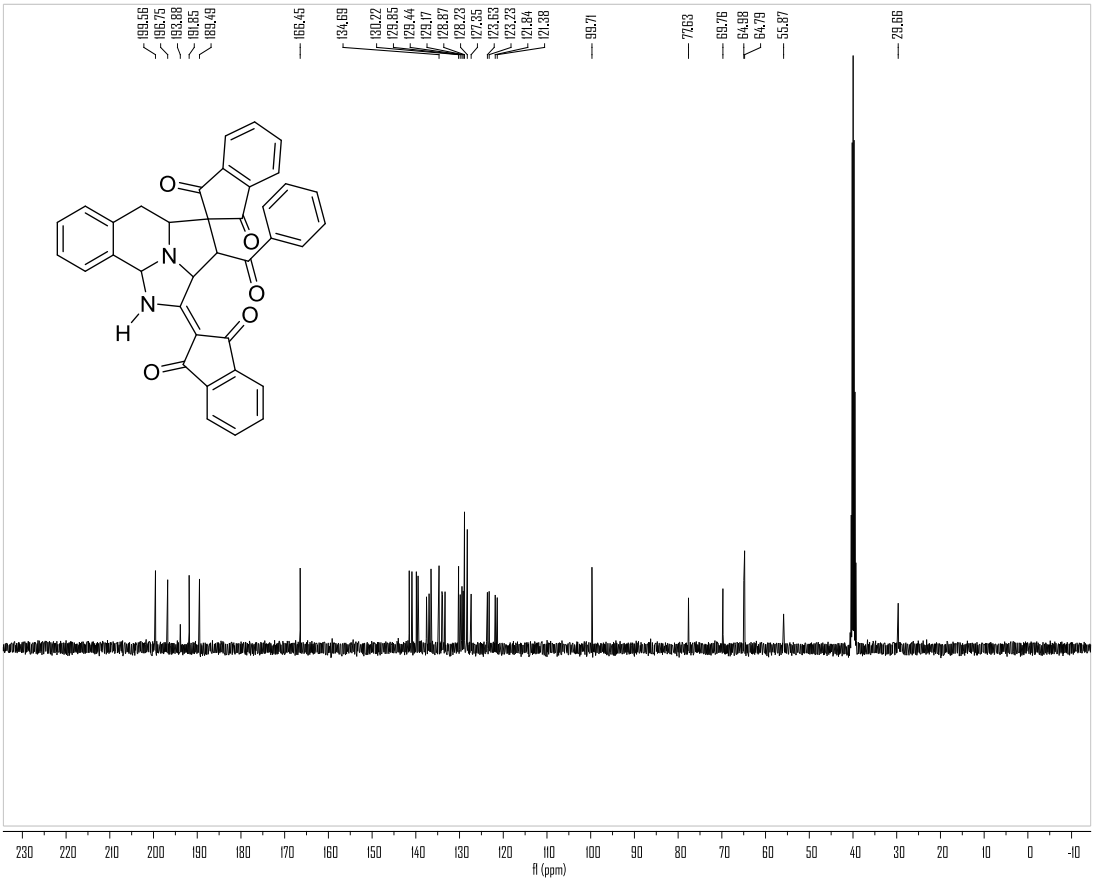

Figure S52 ^{13}C NMR spectra of the compound **2u**

6-Bromo-3-(4-chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2v): white solid, 81 %, m.p. 266-268 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.56 (s, 1H, NH), 8.04 (d, J = 7.8 Hz, 1H, ArH), 8.01 (d, J = 7.8 Hz, 1H, ArH), 7.97 (d, J = 7.8 Hz, 1H, ArH), 7.93 (d, J = 7.2 Hz, 1H, ArH), 7.73 (d, J = 7.8 Hz, 1H, ArH), 7.71-7.67 (m, 4H, ArH), 7.56 (d, J = 7.2 Hz, 1H, ArH), 7.38 (t, J = 7.8 Hz, 1H, ArH), 7.24-7.23 (m, 2H, ArH), 7.12-7.11 (m, 1H, ArH), 6.00 (s, 1H, CH), 5.51 (s, 1H, CH), 4.40 (d, J = 3.6 Hz, 1H, CH), 3.29 (dd, J_1 = 11.4 Hz, J_2 = 2.4 Hz, 1H, CH), 2.61-2.58 (m, 1H, CH), 2.53-2.52 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.5, 196.8, 191.6, 188.4, 165.9, 134.6, 132.8, 131.4, 130.1, 129.6, 128.9, 127.9, 124.3, 123.8, 123.2, 100.0, 77.0, 74.5, 67.1, 62.2, 55.4, 30.9; IR (KBr) υ: 3288, 3066, 2927, 1738, 1702, 1652, 1571, 1492, 1452, 1280, 1136, 1012, 892, 819, 779, 698 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{22}BrClN_2NaO_4$ ([M+Na]$^+$): 683.0344, Found: 683.0351.

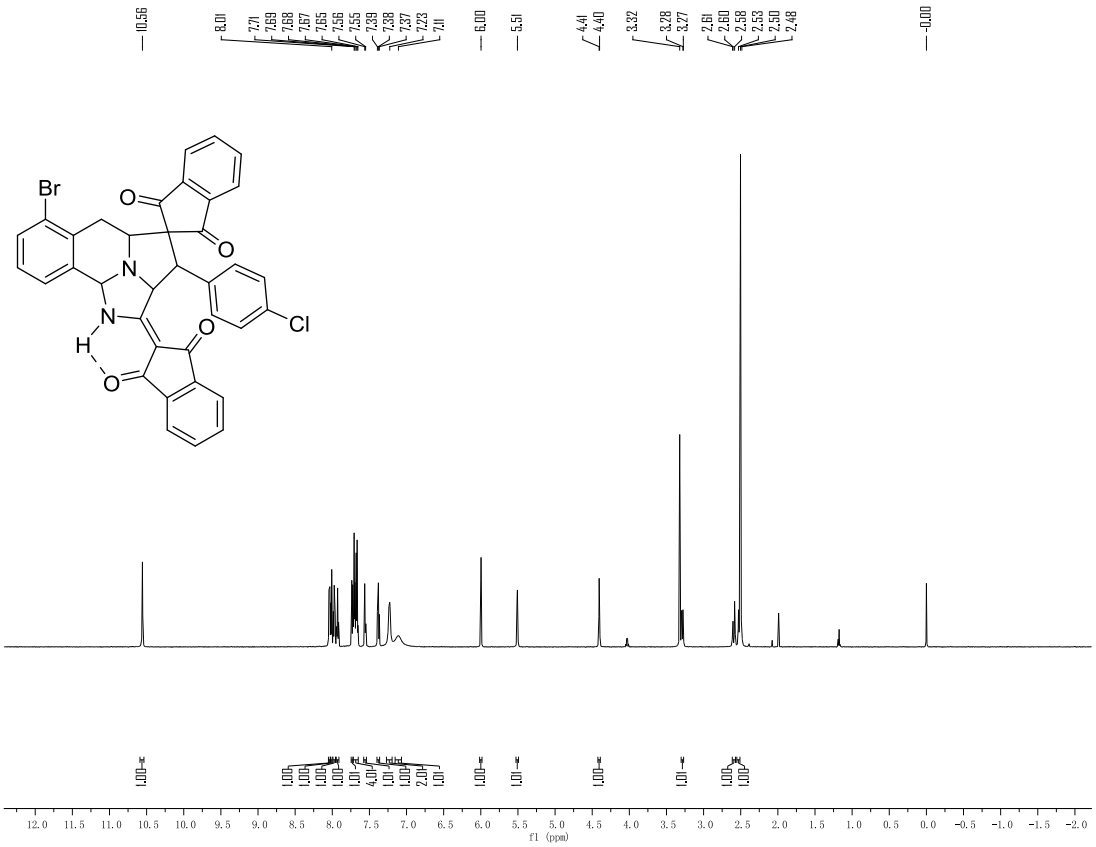

Figure S53 ^{1}H NMR spectra of the compound **2v**

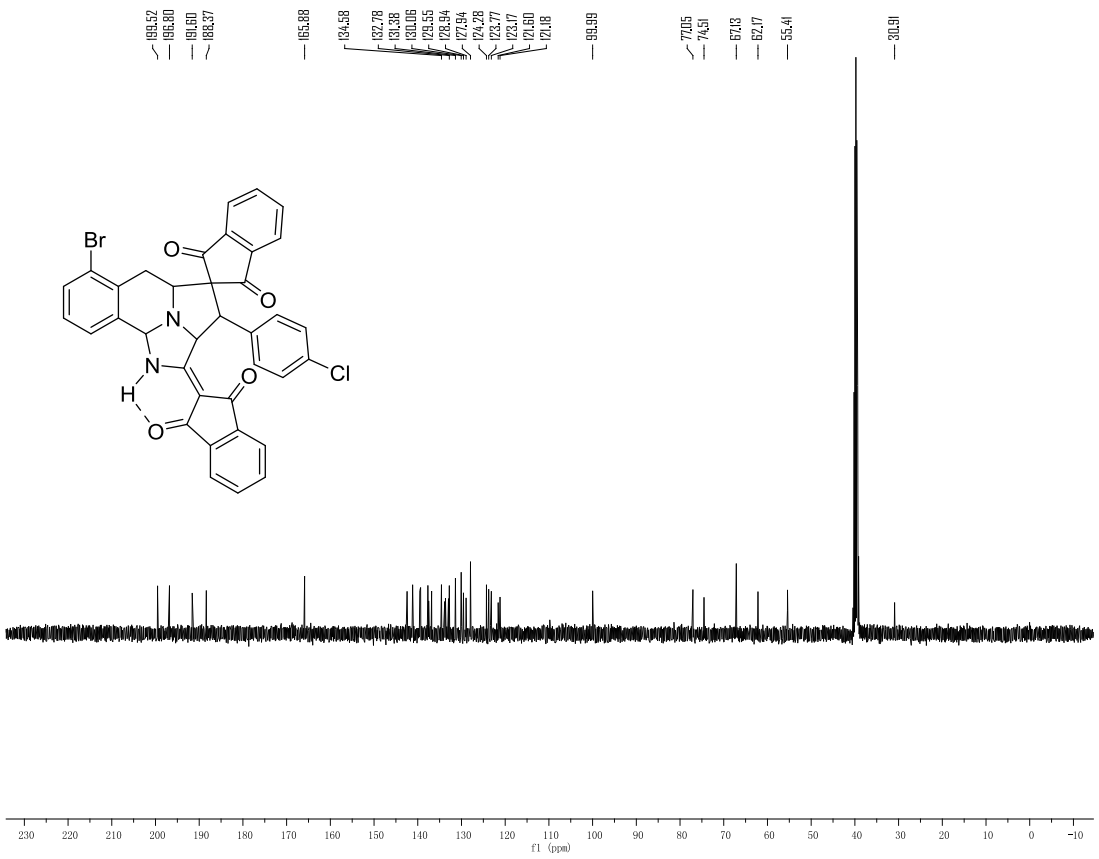

Figure S54 ^{13}C NMR spectra of the compound **2v**

6-Bromo-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-(4-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2w): white solid, 83 %, m.p. 275-277 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.59 (s, 1H, NH), 8.08-8.03 (m, 4H, ArH), 7.99 (t, J = 7.2 Hz, 1H, ArH), 7.93 (t, J = 7.2 Hz, 1H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.67-7.65 (m, 3H, ArH), 7.61-7.60 (m, 2H, ArH), 7.40-7.35 (m, 3H, ArH), 5.99 (s, 1H, CH), 5.62 (s, 1H, CH), 4.53 (d, J = 3.6 Hz, 1H, CH), 3.31 (dd, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 1H, CH), 2.61-2.58 (m, 1H, CH), 2.48-2.44 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.2, 196.8, 165.8, 147.0, 146.5, 142.4, 141.2, 139.7, 137.8, 137.2, 134.6, 133.7, 133.0, 129.7, 129.7, 129.1, 124.4, 124.1, 123.4, 123.3, 121.3, 100.1, 78.0, 77.9, 77.9, 74.5, 67.5, 62.7, 55.4, 31.1； IR (KBr) υ: 3288, 3074, 2912, 1744, 1704, 1658, 1578, 1518, 1421, 1214, 1011, 942, 839, 706, 690 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{22}BrKN_3O_6$([M+K]$^+$): 710.0324, Found: 710.0319.

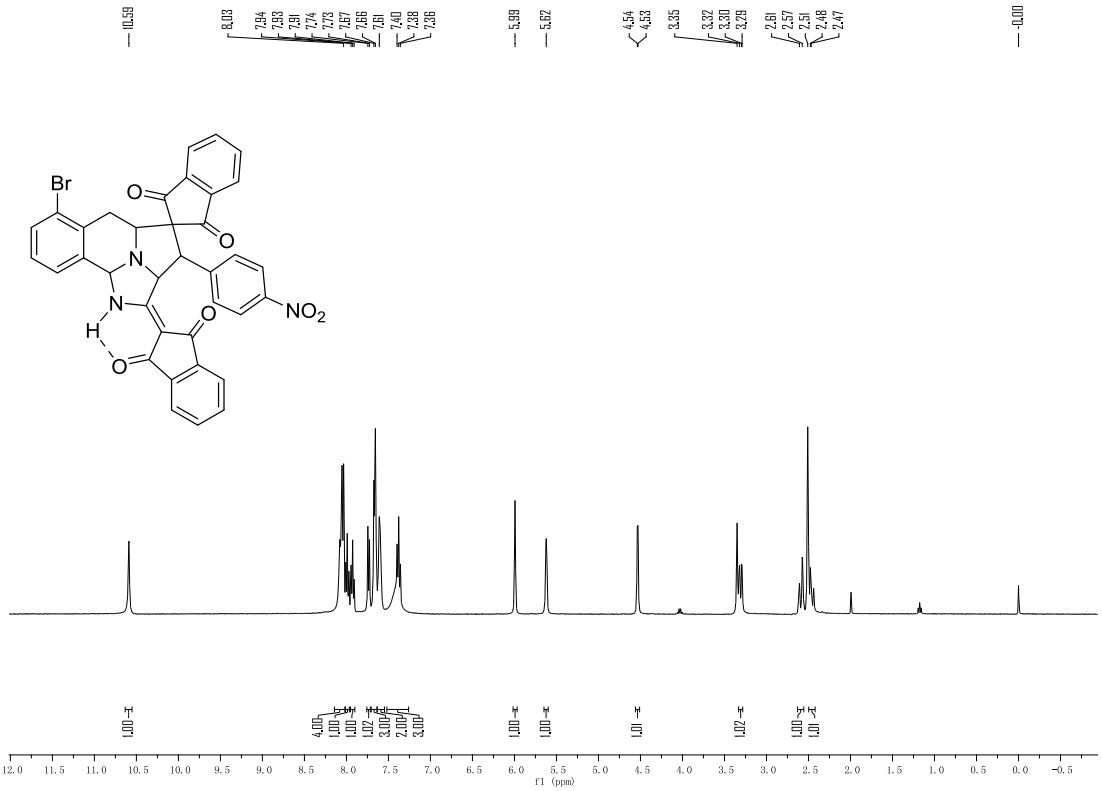

Figure S55 ^{1}H NMR spectra of the compound **2w**

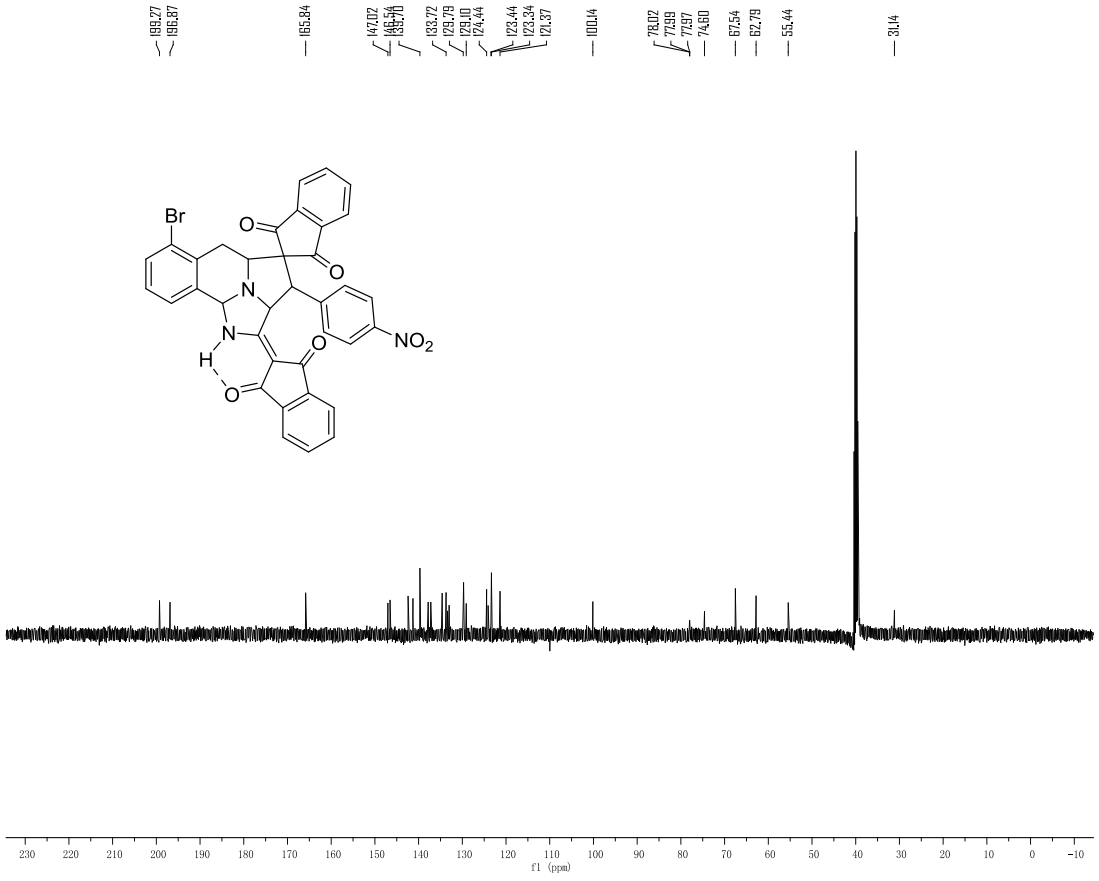

Figure S56 ^{13}C NMR spectra of the compound **2w**

2-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-hexyl-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2x): white solid, 70 %, m.p. 275-277 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.52 (s, 1H, NH), 8.10-8.03 (m, 4H, ArH), 7.86 (t, *J* = 8.0 Hz, 1H, ArH), 7.71-7.70 (m, 4H, ArH), 7.35 (t, *J* = 7.6 Hz, 1H, ArH), 7.28 (d, *J* = 7.2 Hz, 1H, ArH), 7.08 (d, *J* = 7.2 Hz, 1H, ArH), 5.86(s, 1H, CH), 4.70 (s, 1H, CH), 3.19 (d, *J* = 12.0 Hz, 1H, CH), 2.97 (d, *J* = 11.6 Hz, 1H, CH), 2.70-2.69 (m, 1H, CH), 2.49-2.46 (m, 1H, CH), 2.37 (d, *J* = 10.8 Hz, 1H, CH), 1.99-1.91 (m, 1H, CH), 1.10-1.05 (m, 2H, CH), 0.96-0.94 (m, 4H, CH), 0.79-0.78 (m, 1H, CH), 0.69 (t, *J* = 5.6 Hz, 3H, CH_3), 0.51-0.50 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.8, 198.3, 192.3, 188.9, 167.1, 142.3, 140.3, 139.7, 139.3, 137.6, 137.1, 134.7, 134.0, 133.8, 130.2, 129.4, 129.1, 127.3, 123.9, 123.3, 121.7, 121.3, 100.2, 76.9, 76.7, 65.0, 64.3, 49.3, 31.1, 31.0, 29.6, 28.4, 28.1, 21.8, 14.1； IR (KBr) υ: 3237, 3071, 2952, 2849, 1741, 1703, 1647, 1593, 1493, 1359, 1334, 1273, 1203, 1002, 897, 785, 737, 685 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{32}N_2NaO_4$([M+Na]$^+$): 579.2254, Found: 579.2254.

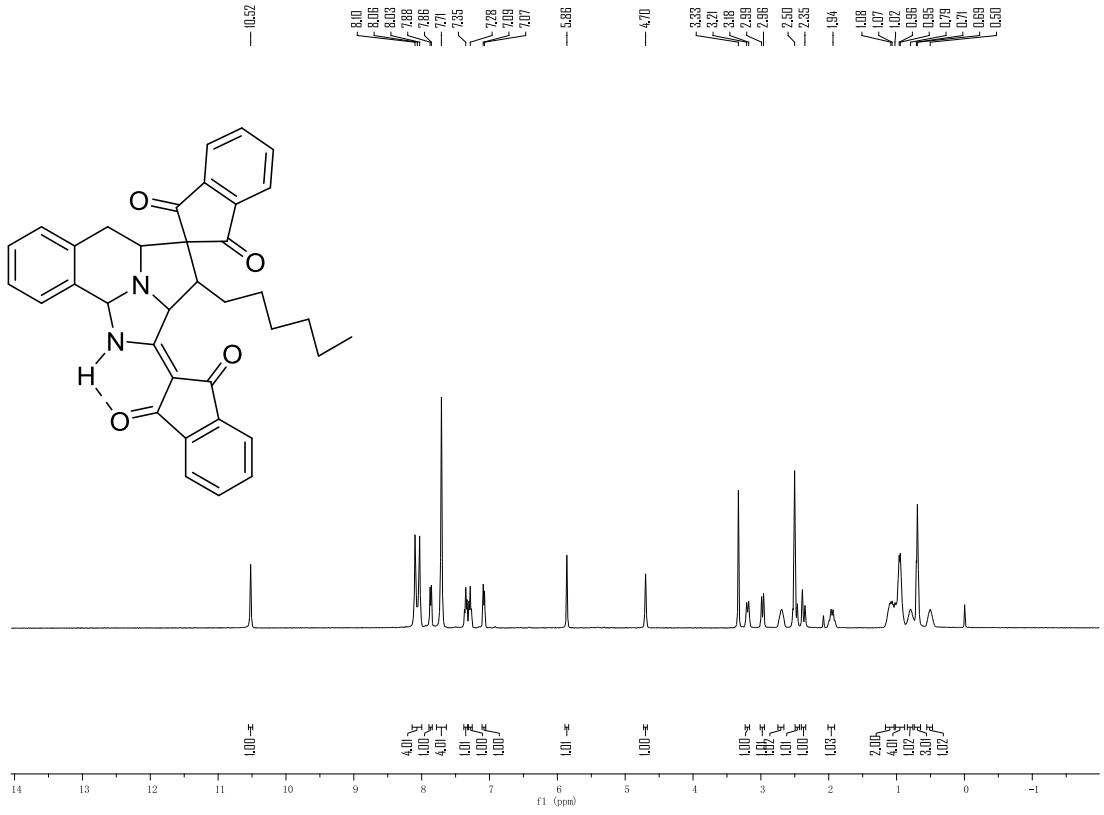

Figure S57 ^{1}H NMR spectra of the compound **2x**

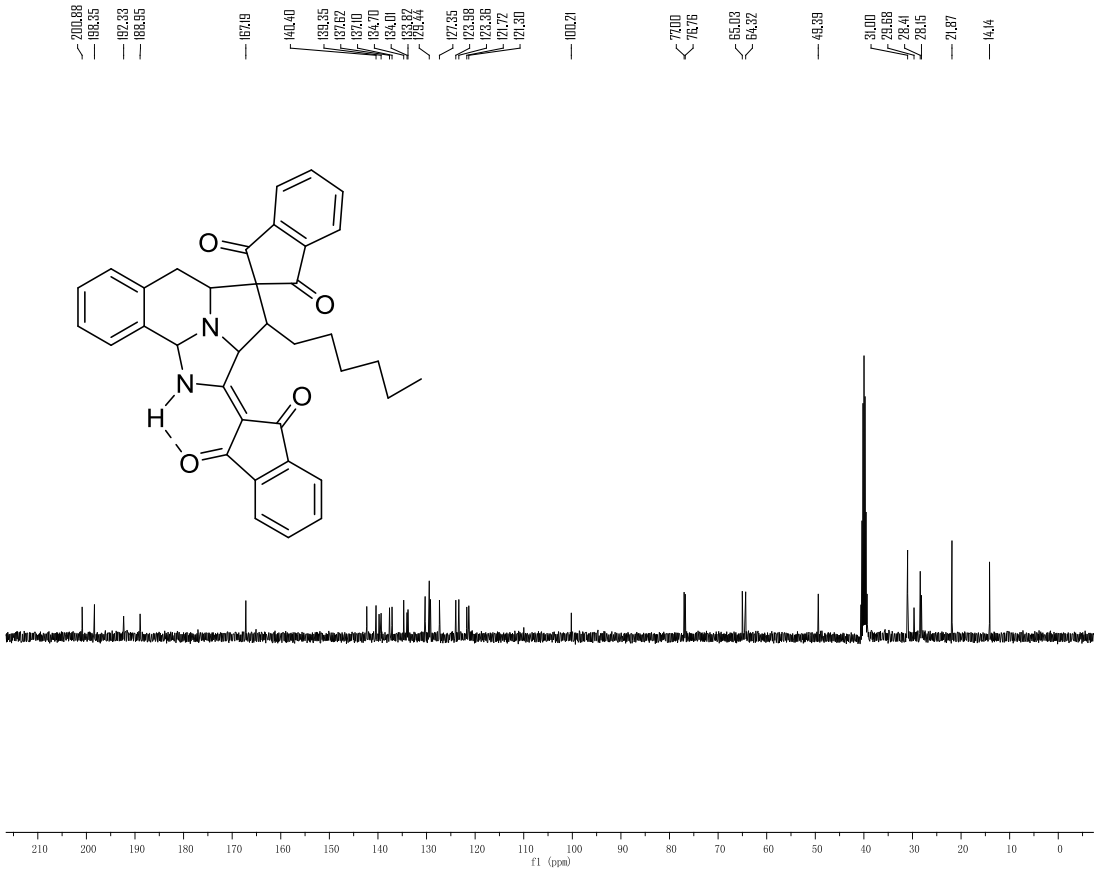

Figure S58 ^{13}C NMR spectra of the compound **2x**

6-Bromo-2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)-3-hexyl-1,2a,3,4a,5,9b-hexahydro-2*H*-spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2'-indene]-1',3'-dione (2y): white solid, 63 %, m.p. 251-253 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.54 (s, 1H, NH), 8.12-8.04 (m, 4H, ArH), 7.95 (t, *J* = 7.2 Hz, 1H, ArH), 7.72-7.70 (m, 4H, ArH), 7.62 (d, *J* = 7.6 Hz, 1H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 5.86(s, 1H, CH), 4.71 (s, 1H, CH), 3.21 (d, *J* = 11.6 Hz, 1H, CH), 3.01 (d, *J* = 11.2 Hz, 1H, CH), 2.68-2.66 (m, 1H, CH), 2.41 (d, *J* = 15.0 Hz, 1H, CH), 2.33 (d, *J* = 12.4 Hz, 1H, CH), 1.98-1.95 (m, 1H, CH), 1.09-1.06 (m, 2H, CH), 0.96-0.92 (m, 4H, CH), 0.80-0.78 (m, 1H, CH), 0.70 (t, *J* = 5.6 Hz, 3H, CH_3), 0.52-0.50 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.6, 198.2, 192.2, 188.9, 166.9, 142.2, 140.4, 139.7, 139.3, 137.7, 137.2, 134.2, 134.0, 133.8, 133.0, 132.9, 129.4, 129.1, 124.5, 124.0, 123.3, 121.7, 121.3, 100.4, 76.7, 64.8, 63.8, 49.7, 31.1, 31.0, 30.8, 28.4, 28.1, 21.8, 14.1； IR (KBr) υ: 3247, 3071, 2925, 2853, 1742, 1707, 1669, 1569, 1451, 1359, 1276, 1215, 1090, 953, 833, 777, 696, 652 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{32}BrN_2NaO_4$([M+H]$^+$): 635.1540, Found: 635.1544.

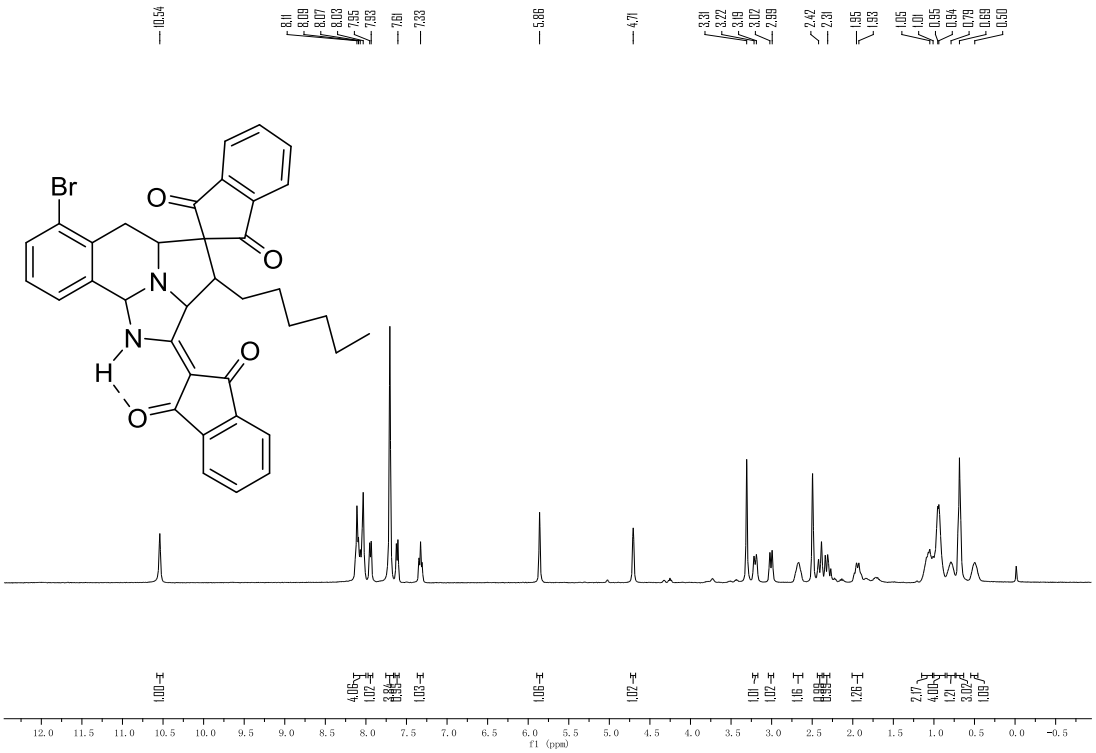

Figure S59 ^{1}H NMR spectra of the compound **2y**

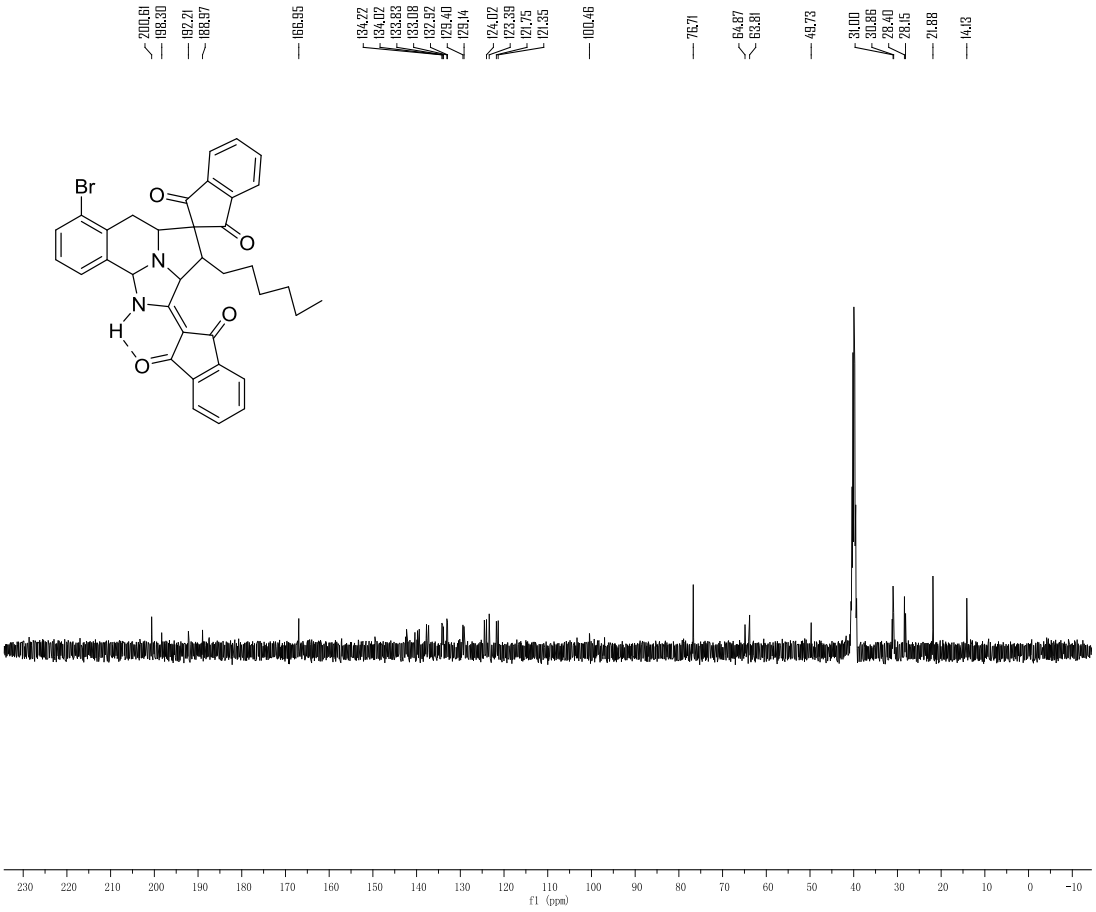

Figure S60 ^{13}C NMR spectra of the compound **2y**