Electronic Supplementary Material (ESI) for ChemComm.

Two-carbon ring expansion of isatin: a convenient construction of dibenzo[*b,d*]azepinone scaffold

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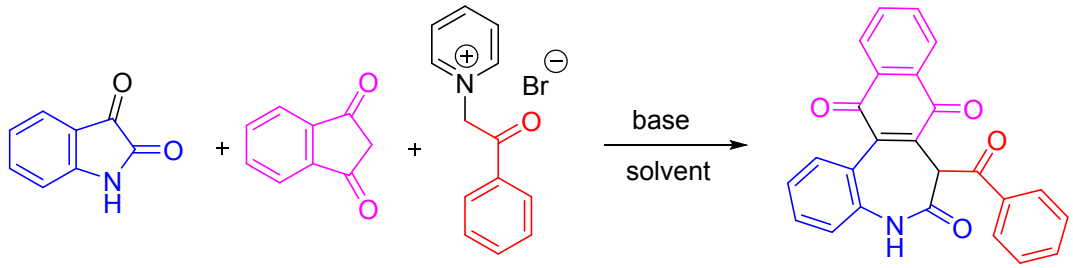
Supporting Information

Table S1 Condition optimization for the ring expansion to compound 1a.



1.0 mmol 1.0 mmol 1.2 mmol 20 mL **1a**

Entry	Conditions	Yield (%)
1	DBU (1.5 mmol), EtOH, rt, 8h	0
2	Et_3N (1.0 mmol), EtOH, rt, 6h	0
3	Et_3N (1.0 mmol), EtOH, reflux, 6h	29
4	Et_3N (1.5 mmol), EtOH, 60 ℃, 6h	12
5	Et_3N (1.5 mmol), EtOH, reflux, 5h	45
6	Piperidine (1.0 mmol), EtOH, reflux, 7h	23
7	Piperidine (1.5 mmol), EtOH, reflux, 6h	31
8	Et_3N (1.5 mmol), DMF, 80 ℃, 6h	32
9	Et_3N (1.5 mmol), DMF, reflux, 6h	31
10	DBU (1.5 mmol), EtOH, reflux, 8h	30
11	Piperidine (1.5 mmol), DMF, reflux, 8h	33
12	Et_3N (1.5 mmol), MeOH, reflux, 7h	24
13	Et_3N (1.5 mmol), MeCN, reflux, 5h	13
14	Et_3N (1.5 mmol), EtOH, reflux, 12h	51
15	Et_3N (1.5 mmol), DMF, reflux, 12h	42
16	DBU (1.5 mmol), EtOH, reflux, 24h	52
17	Piperidine (1.5 mmol), DMF, reflux, 24h	43
18	Et_3N (1.5 mmol), EtOH, reflux, 24h	69
19	Piperidine (1.5 mmol), EtOH, reflux, 24h	61

ORTEP-drawings of the crystal structures of compounds 1e, 1k, 1l, 2c, 2h, 4b

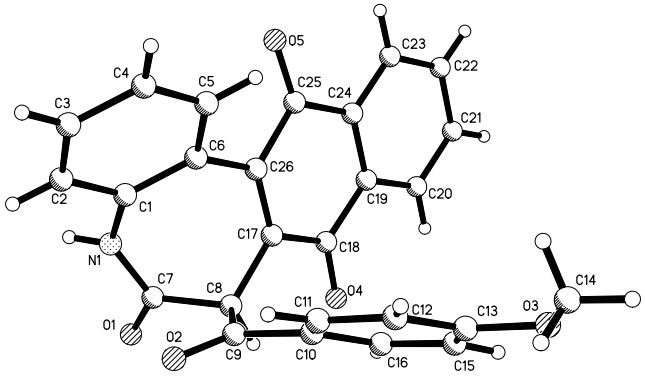


Figure s1 ORTEP-drawings of the crystal structure of compound **1e**

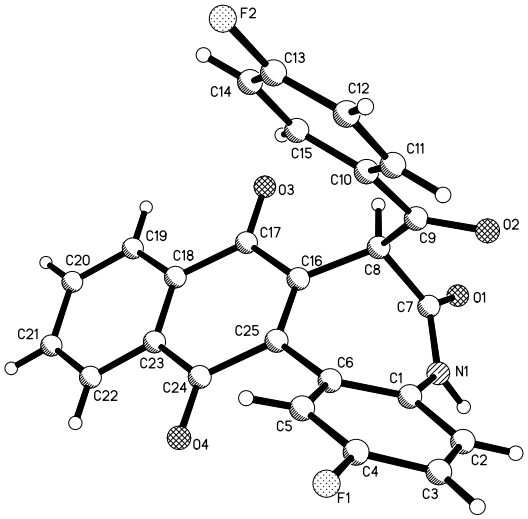


Figure s2 ORTEP-drawings of the crystal structure of compound **1k**

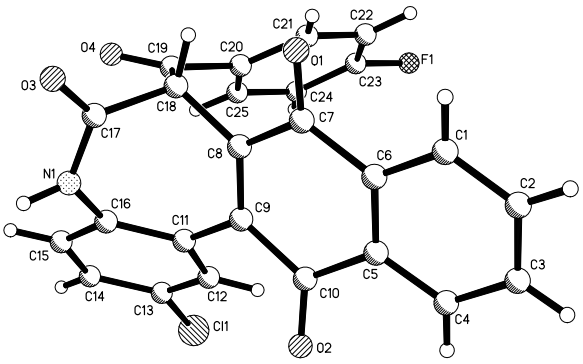


Figure s3 ORTEP-drawings of the crystal structure of compound **1l**

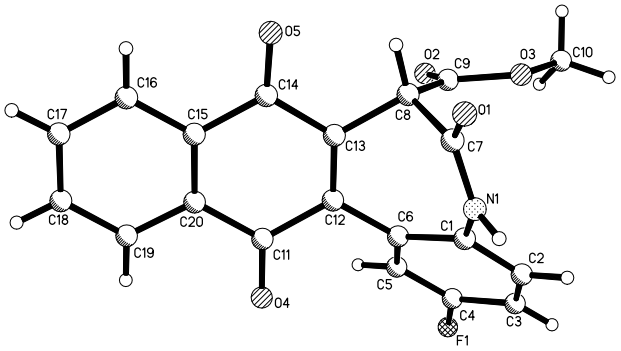


Figure s4 ORTEP-drawings of the crystal structure of compound **2c**

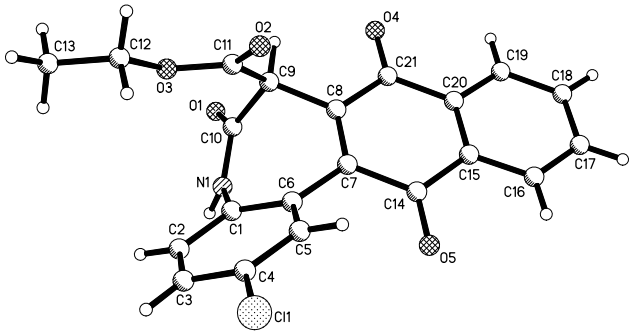


Figure s5 ORTEP-drawings of the crystal structure of compound **2h**

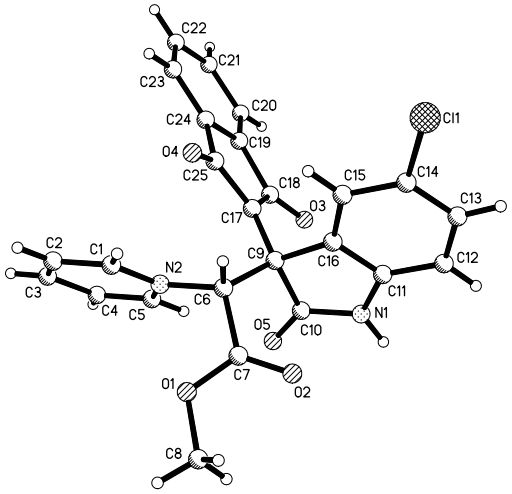
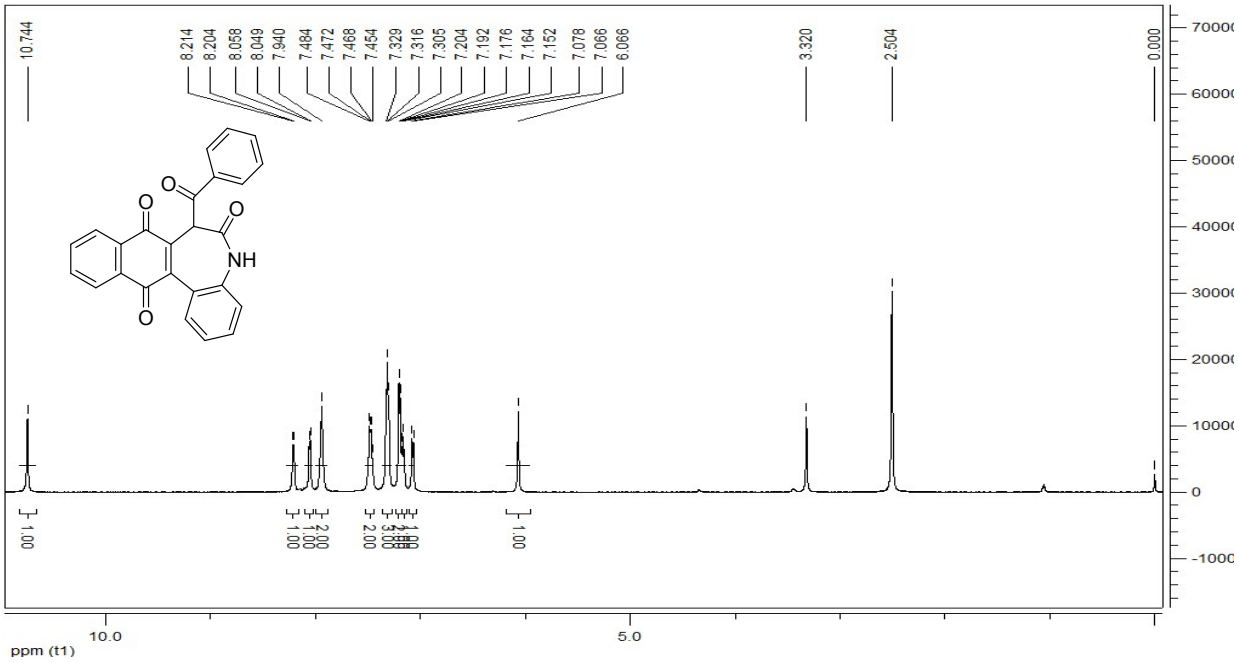


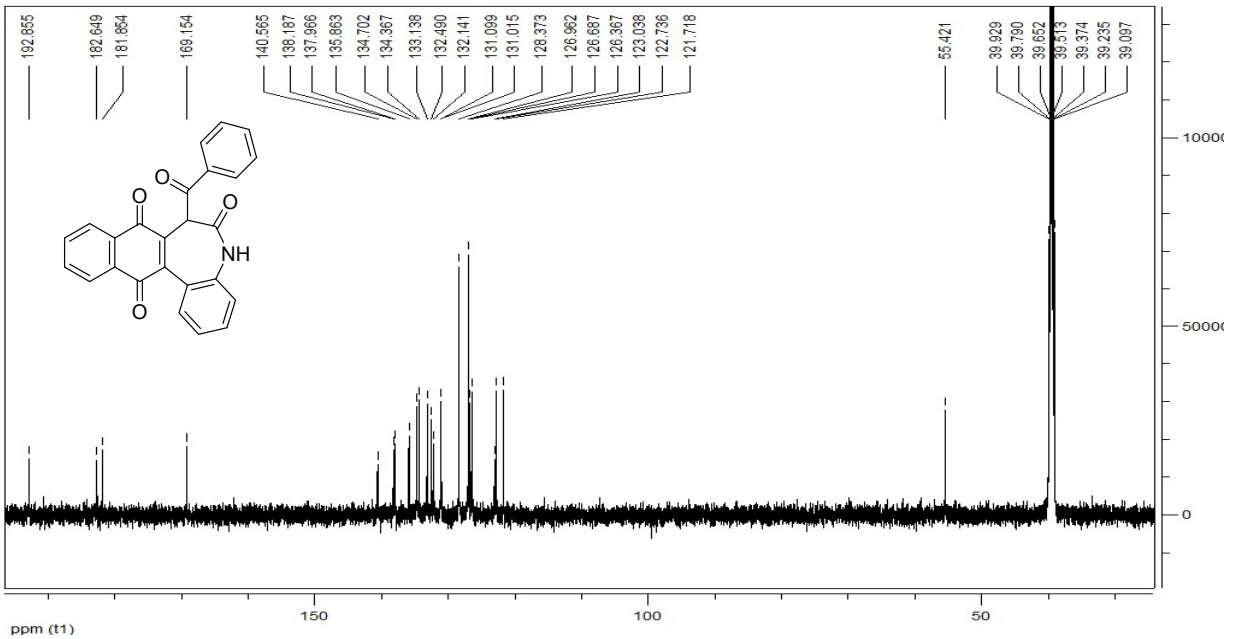
Figure s6 ORTEP-drawings of the crystal structure of compound **4b**

Experimental section

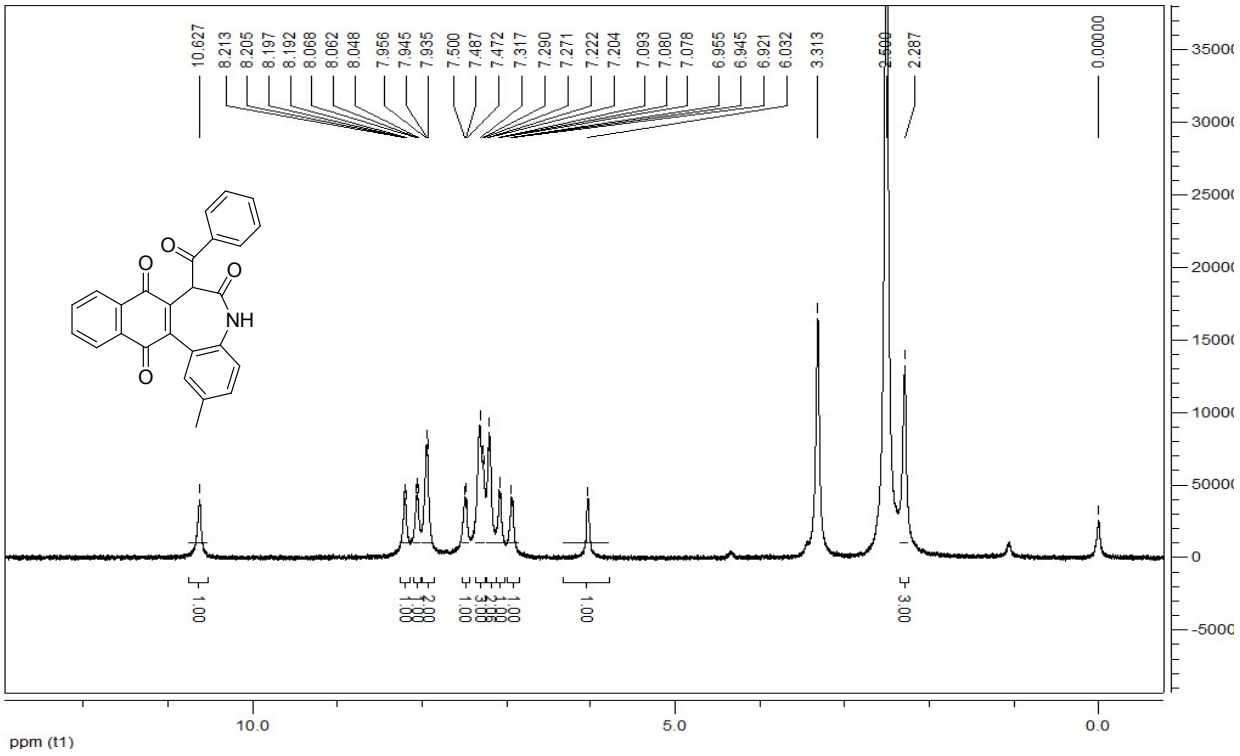
1. General procedure for the syntheses of 5*H*-benzo[*b*]naphtho[2,3-*d*]azepines 1a-1p and 2a-2l from the reaction of isatins, pyridinium salts and indene-1,3-dione: A mixture of isatin (1.0 mmol), pyridinium salt (1.2 mmol), indene-1,3-dione (1.0 mmol) and triethylamine (1.5 mmol) in ethanol (20 mL) was stirred at room temperature for 1h. Then the mixture was refluxed for 24h. After removing the solvent, the resulting residue was titrated with cold ethanol to give pure product for analysis.

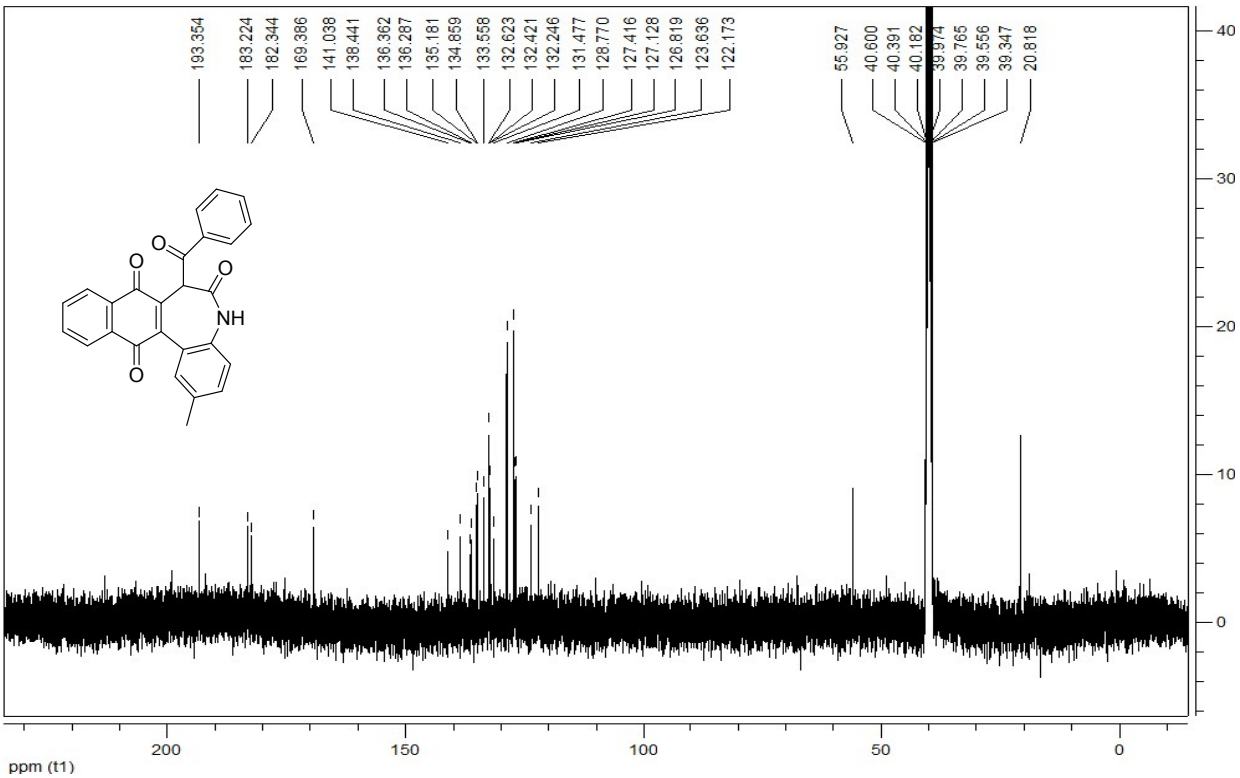
7-Benzoyl-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (**1a**): yellow solid, 69%, m.p. 250 – 252 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.74 (br, 1H, NH), 8.21 (d, J = 6.0 Hz, 1H, ArH), 8.05 (d, J = 5.4 Hz, 1H, ArH), 7.96 – 7.92 (m, 2H, ArH), 7.48 – 7.45 (m, 2H, ArH), 7.33 – 7.31 (m, 3H, ArH), 7.20 – 7.15 (m, 3H, ArH), 7.07 (d, J = 7.2 Hz, 1H, ArH), 6.07 (s, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 192.9, 182.6, 181.9, 169.2, 140.6, 138.2, 138.0, 135.9, 134.7, 134.4, 133.1, 132.5, 132.1, 131.1, 131.0, 128.4, 127.0, 126.7, 126.4, 123.0, 122.7, 121.7, 55.4; IR (KBr) υ: 3063, 2975, 1681, 1609, 1593, 1484, 1448, 1073, 876, 779, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{15}NNaO_4$ ([M+Na]$^+$): 416.0893, Found: 416.0891.



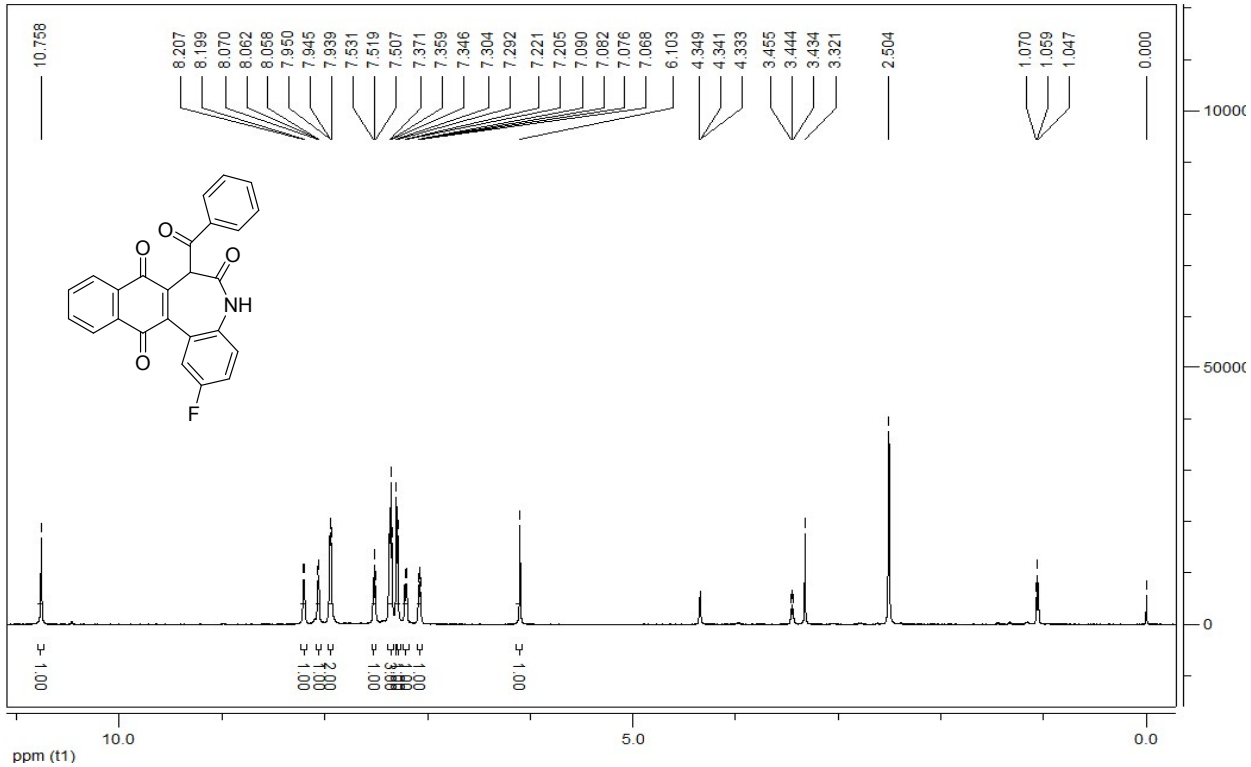


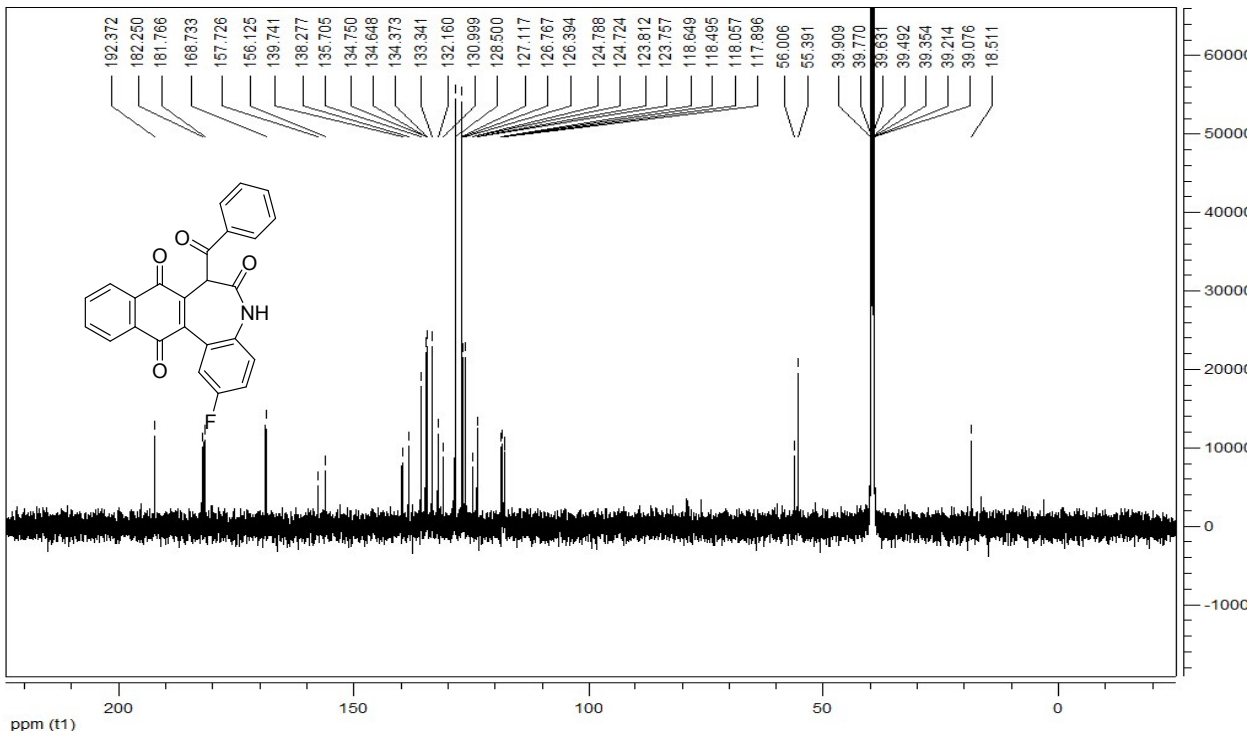
7-Benzoyl-2-methyl-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1b): yellow solid, 70%, m.p. 232 – 234 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.63 (br, 1H, NH), 8.21 – 8.19 (m, 1H, ArH), 8.07 – 8.05 (m, 1H, ArH), 7.96 – 7.93 (m, 2H, ArH), 7.50 – 7.47 (m, 1H, ArH), 7.32 – 7.27 (m, 3H, ArH), 7.22 – 7.20 (m, 2H, ArH), 7.09 – 7.08 (m, 1H, ArH), 6.96 – 6.92 (m, 1H, ArH), 6.03 (s, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 193.4, 183.2, 182.3, 169.4, 141.0, 138.4, 136.4, 136.3, 135.2, 134.9, 133.6, 132.6, 132.4, 132.2, 131.5, 128.8, 127.4, 127.1, 126.8, 123.6 (2C), 122.2, 55.9, 20.8; IR (KBr) υ: 3188, 3063, 2923, 1666, 1595, 1502, 1451, 1383, 843 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{17}NNaO_4$ ([M+Na]$^{+}$): 430.1050, Found: 430.1050.



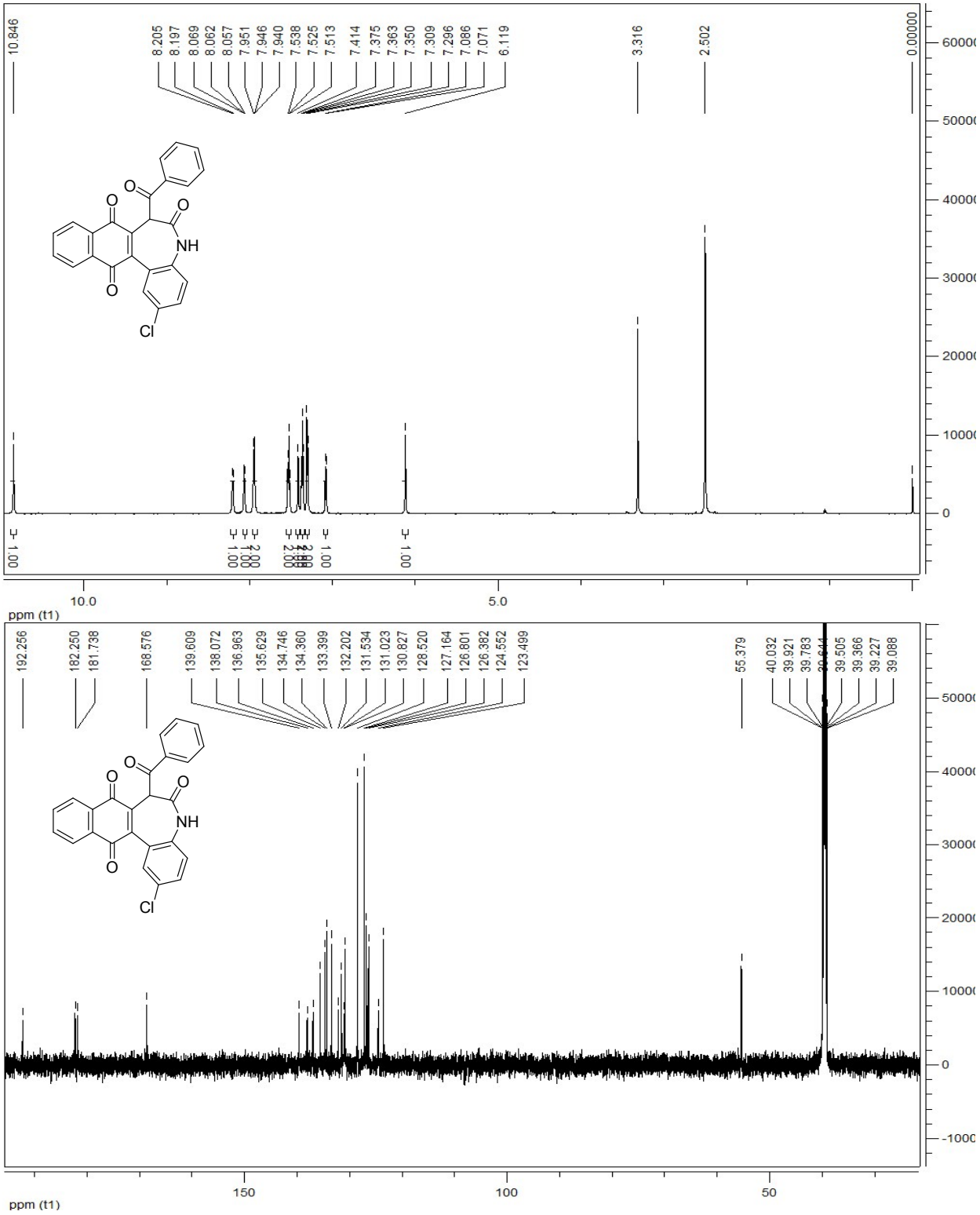


7-Benzoyl-2-fluoro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1c): yellow solid, 63%, m.p. 234 – 236 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.76 (br, 1H, NH), 8.20 (d, J = 4.8 Hz, 1H, ArH), 8.07 – 8.06 (m, 1H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.52 (t, J = 7.2 Hz, 1H, ArH), 7.36 (t, J = 7.4 Hz, 3H, ArH), 7.30 (d, J = 7.2 Hz, 2H, ArH), 7.21 (d, J = 9.6 Hz, 1H, ArH), 7.09 – 7.07 (m, 1H, ArH), 6.10 (s, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 192.4, 182.3, 181.8, 168.7, 156.9 (d, J = 240.2 Hz), 139.7, 138.3, 135.7, 134.8, 134.6, 134.4, 133.3, 132.2, 131.0, 128.5, 127.1, 126.8, 126.4, 124.8 (d, J = 9.6 Hz), 123.8 (d, J = 8.3 Hz), 118.6 (d, J = 23.1 Hz), 118.0 (d, J = 24.1 Hz), 55.4; IR (KBr) υ: 3084, 2971, 1681, 1609, 1591, 1449, 864, 773, 738 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{14}FNNaO_4$ ([M+Na]$^+$): 434.0799, Found: 434.0798.

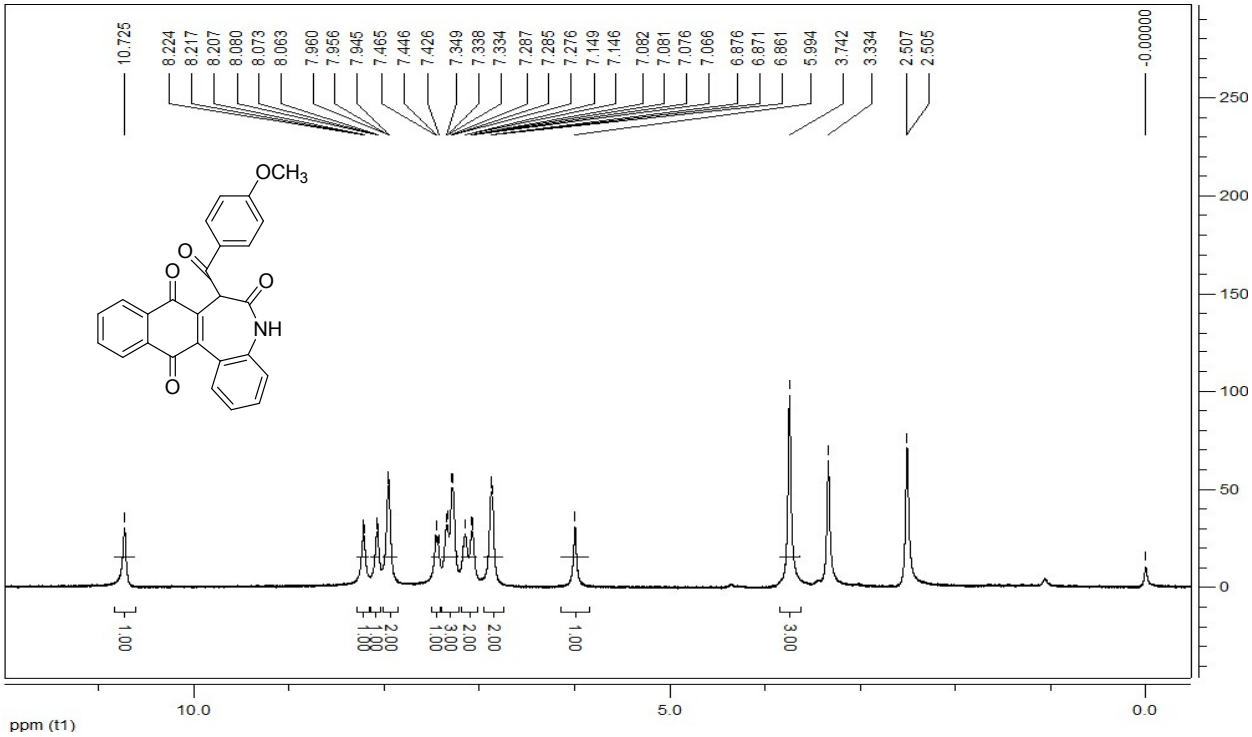


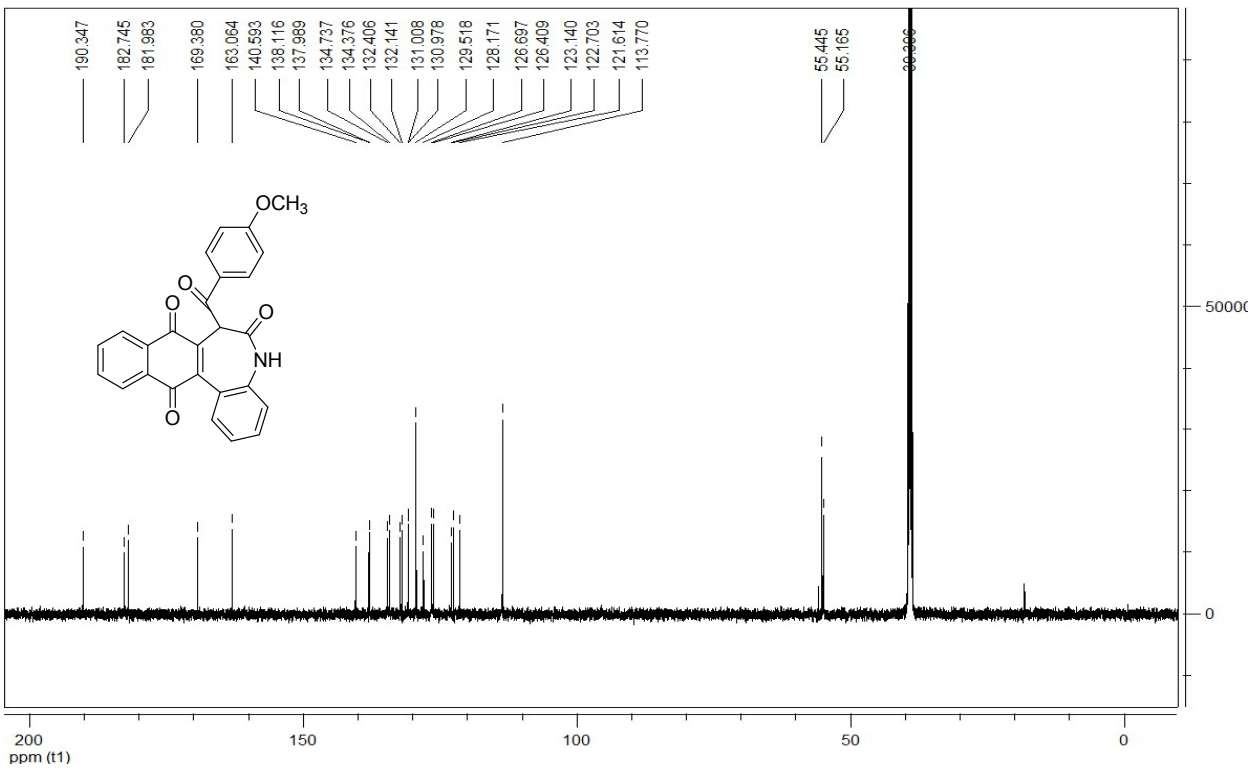


7-Benzoyl-2-chloro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1d): yellow solid, 64%, m.p. 248 – 250 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.85 (br, 1H, NH), 8.20 (d, J = 4.8 Hz, 1H, ArH), 8.07 – 8.06 (m, 1H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.53 (t, J = 7.2 Hz, 2H, ArH), 7.42 – 7.40 (m, 1H, ArH), 7.36 (t, J = 7.2 Hz, 2H, ArH), 7.30 (d, J = 7.8 Hz, 2H, ArH), 7.08 (d, J = 9.0 Hz, 1H, ArH), 6.12 (s, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 192.3, 182.3, 181.7, 168.6, 139.6, 138.1, 137.0, 135.6, 134.7, 134.4, 133.4, 132.2, 131.5, 131.0, 130.8, 128.5, 127.2, 126.8, 126.4, 124.6, 123.5 (2C), 55.4; IR (KBr) υ: 3079, 2948, 1684, 1665, 1592, 829, 775 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{14}ClNNaO_4$ ([M+Na]$^+$): 450.0504, Found: 450.0501.

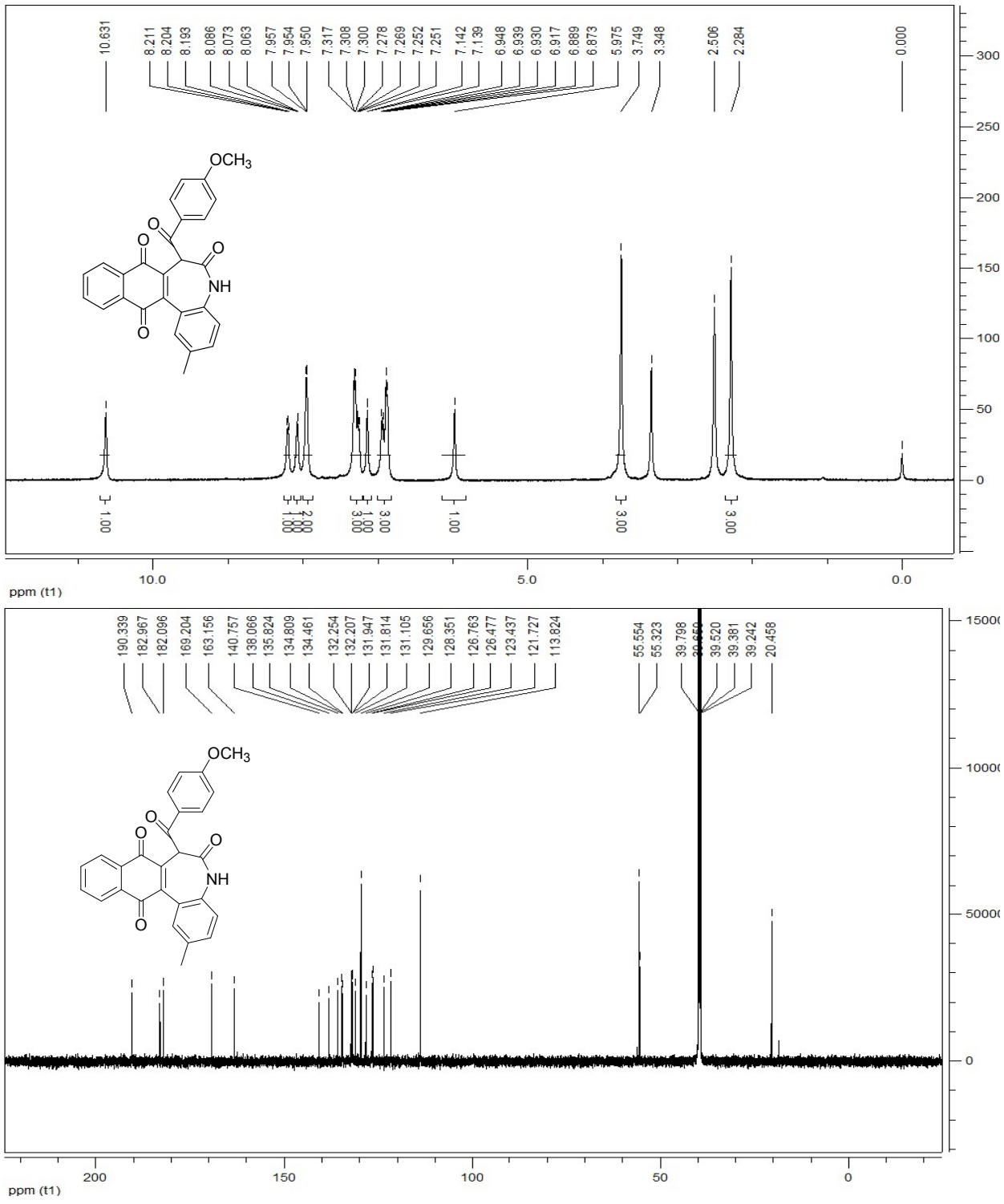


7-(4-Methoxybenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1e): Yellow Solid, 65%, m.p. 236 – 237 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.72 (br, 1H, NH), 8.22 – 8.21 (m, 1H, ArH), 8.08 – 8.06 (m, 1H, ArH), 7.96 – 7.94 (m, 2H, ArH), 7.46 – 7.43 (m, 1H, ArH), 7.35 – 7.28 (m, 3H, ArH), 7.15 – 7.07 (m, 2H, ArH), 6.89 – 6.86 (m, 2H, ArH), 5.99 (s, 1H, CH), 3.74 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 190.3, 182.7, 182.0, 169.4, 163.1, 140.6, 138.1, 138.0, 134.7, 134.4, 132.4, 132.1, 131.0, 130.9, 129.5, 128.2, 126.7, 126.4, 123.1, 122.7, 121.6, 113.8, 55.4, 55.2; IR (KBr) υ: 3441, 2910, 1665, 1600, 1574, 1509, 1476, 838, 757, 711 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{17}NNaO_5$ ([M+Na]$^{+}$): 446.0999, Found: 446.1001.

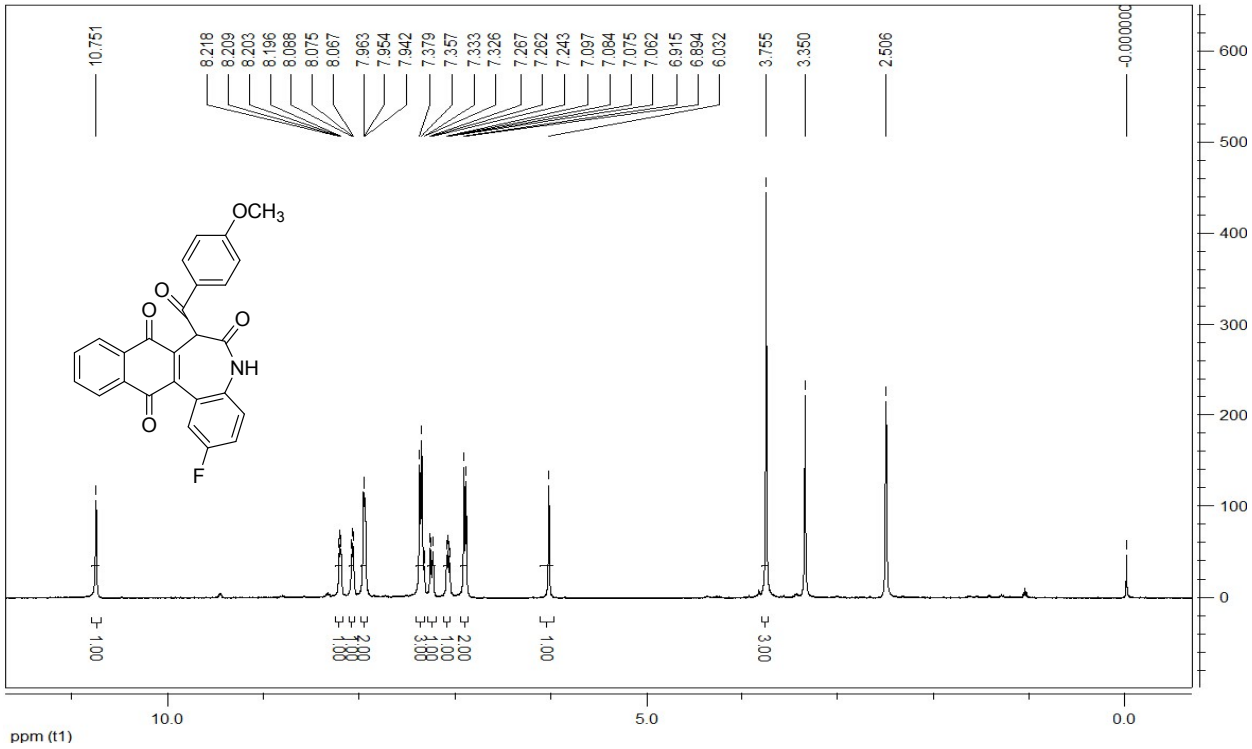


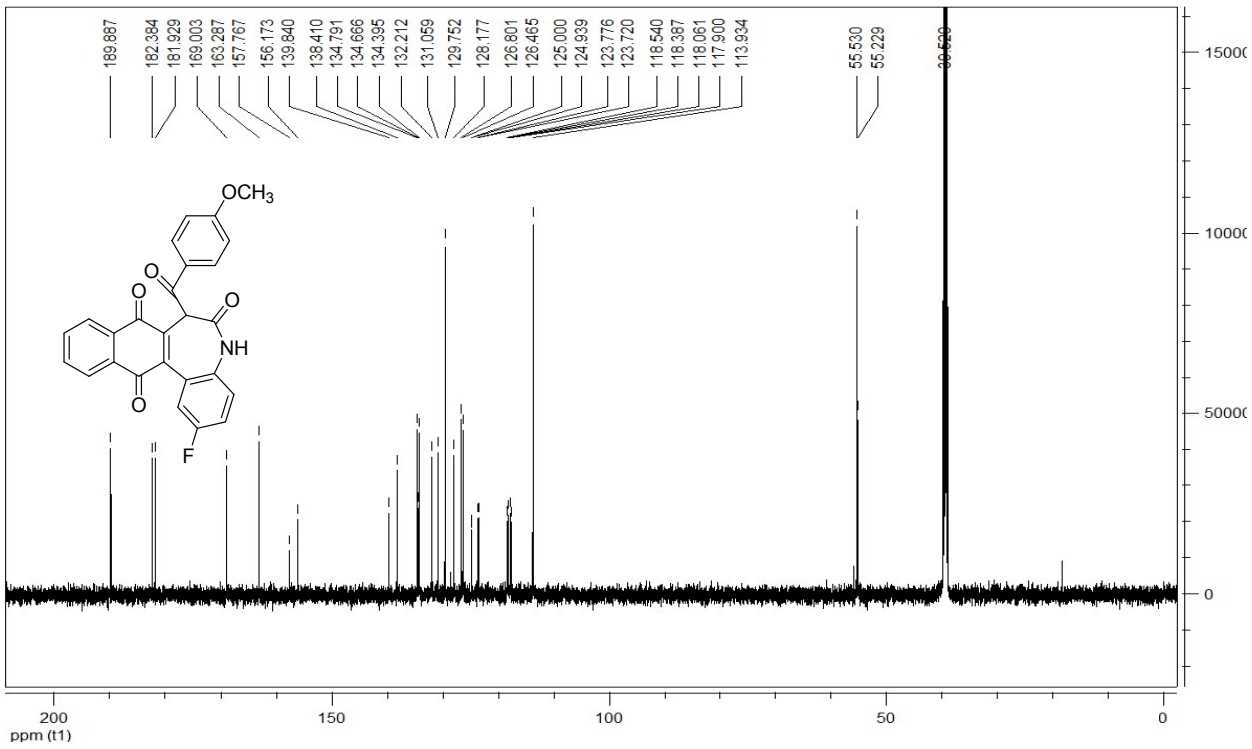


7-(4-Methoxybenzoyl)-2-methyl-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1f): Yellow Solid, 58%, m.p. 238 – 241 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.63 (br, 1H, NH), 8.21 – 8.19 (m, 1H, ArH), 8.09 – 8.06 (m, 1H, ArH), 7.96 – 7.95 (m, 2H, ArH), 7.32-7.25 (m, 3H, ArH), 7.14 – 7.13 (m, 1H, ArH), 6.95-6.87 (m, 3H, ArH), 5.98 (s, 1H, CH), 3.75 (s, 3H, OCH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 190.3, 183.0, 182.1, 169.2, 163.2, 140.8, 138.1, 135.8, 134.8, 134.5, 132.3, 132.2, 131.9, 131.8, 131.1, 129.7, 128.4, 126.8, 126.5, 123.4, 121.7, 113.8, 55.6, 55.3, 20.5; IR (KBr) υ: 3195, 3055, 2946, 1678, 1600, 1510, 1463, 1371, 830, 786, 745 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{19}NNaO_5$ ([M+Na]$^{+}$): 460.1155, Found: 460.1165.

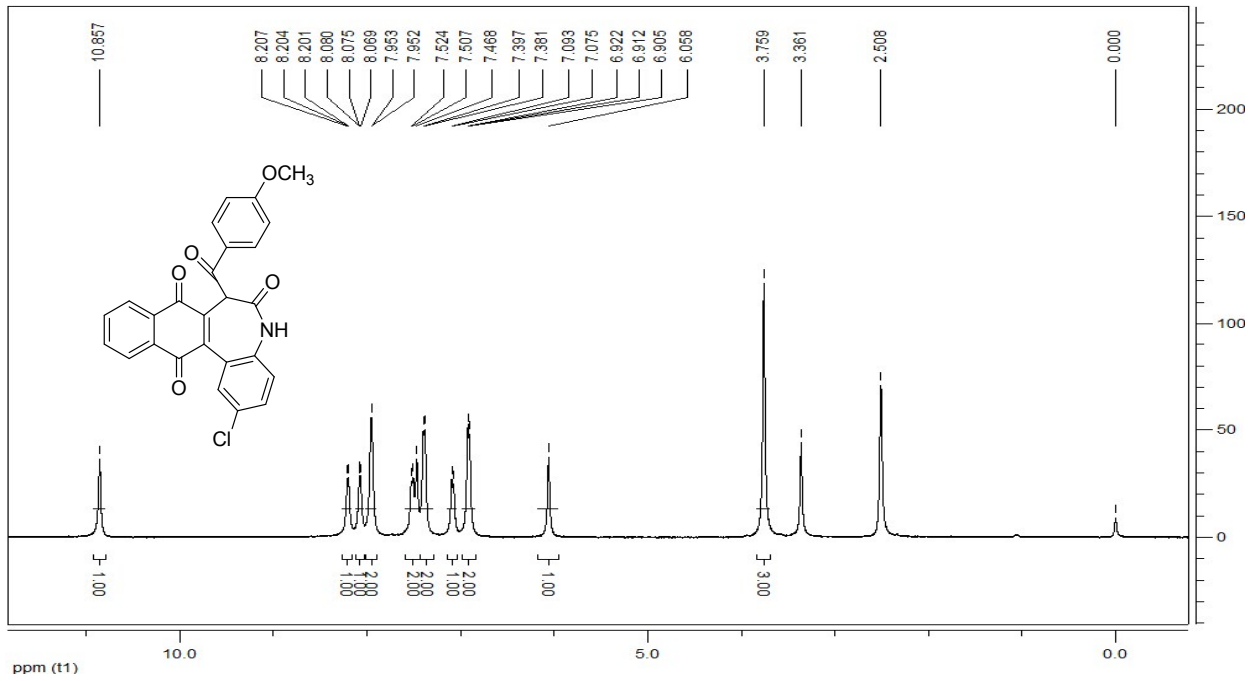


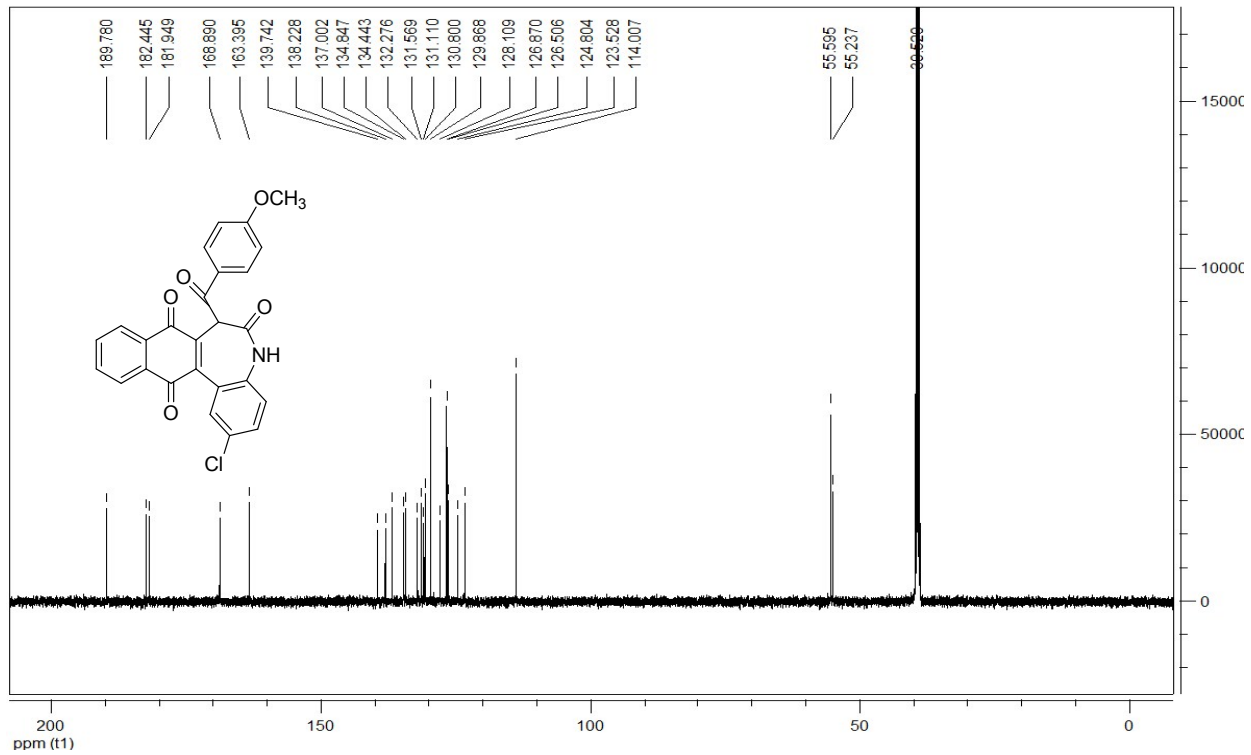
2-Fluoro-7-(4-methoxybenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1g): Yellow Solid, 62%, m.p. 242 – 244 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.75 (br, 1H, NH), 8.22 – 8.20 (m, 1H, ArH), 8.09 – 8.07 (m, 1H, ArH), 7.96 – 7.94 (m, 2H, ArH), 7.38 – 7.33 (m, 3H, ArH), 7.27 – 7.24 (m, 1H, ArH), 7.10 – 7.06 (m, 1H, ArH), 6.90 (d, J = 8.4 Hz, 2H, ArH), 6.03 (s, 1H, CH), 3.76 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 189.9, 182.4, 181.9, 169.0, 163.3, 157.0 (d, J = 239.1 Hz), 139.8, 138.4, 134.8, 134.7, 134.4, 132.2, 131.1, 129.8, 128.2, 126.8, 126.5, 125.0 (d, J = 9.1 Hz), 123.7 (d, J = 8.4 Hz), 118.5 (d, J = 23.0 Hz), 118.0 (d, J = 24.1 Hz), 113.9, 55.5, 55.2; IR (KBr) υ: 3244, 3077, 2914, 1668, 1599, 1575, 1498, 1363, 878, 788, 741 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{16}FNNaO_5$ ([M+Na]$^{+}$): 464.0905, Found: 464.0905.



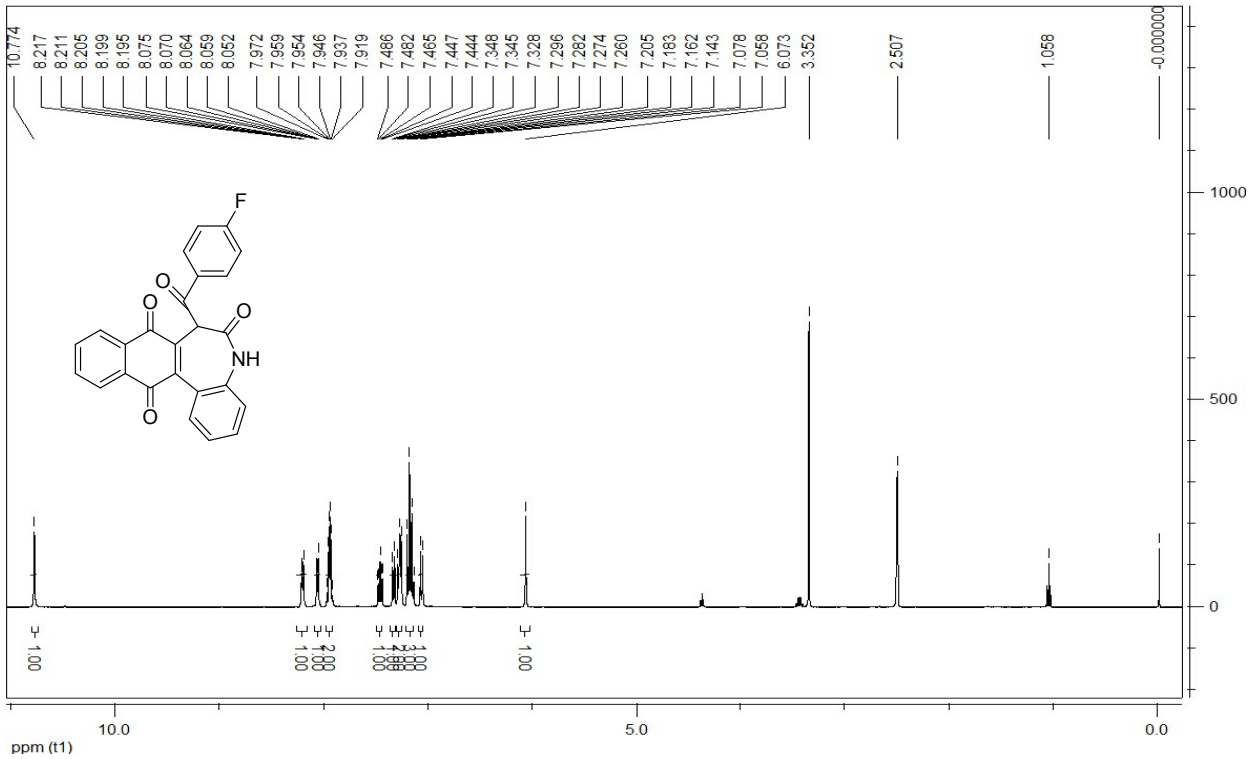


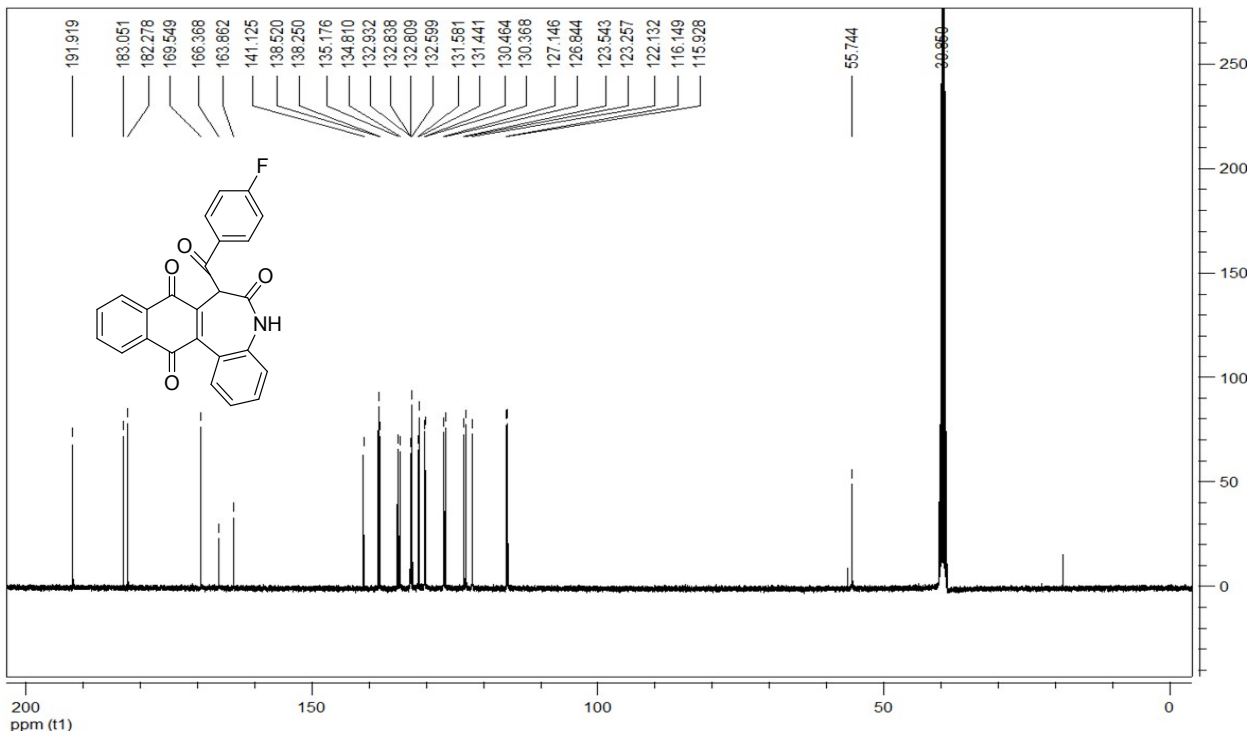
2-Chloro-7-(4-methoxybenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1h): Yellow Solid, 63%, m.p. 226 – 228 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.86 (br, 1H, NH), 8.21 – 2.20 (m, 1H, ArH), 8.08 – 8.07 (m, 1H, ArH), 7.96 – 7.95 (m, 2H, ArH), 7.52 – 7.47 (m, 2H, ArH), 7.40 – 7.38 (m, 2H, ArH), 7.08 (d, *J* =7.6 Hz, 1H, ArH), 6.92 – 6.90 (m, 2H, ArH), 6.06 (s, 1H, CH), 3.76 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 189.8, 182.4, 181.9, 168.9, 163.4, 139.7, 138.2, 137.0, 134.8, 134.4, 132.3, 131.6, 131.1, 130.8, 129.9, 128.1, 126.9, 126.5, 124.8, 123.5, 114.0, 55.6, 55.2; IR (KBr) υ: 3045, 2934, 1669, 1597, 1511, 1484, 1390, 1364, 910, 850, 809, 743 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{16}ClNNaO_5$ ([M+Na]$^+$): 480.0609, Found: 480.0617.



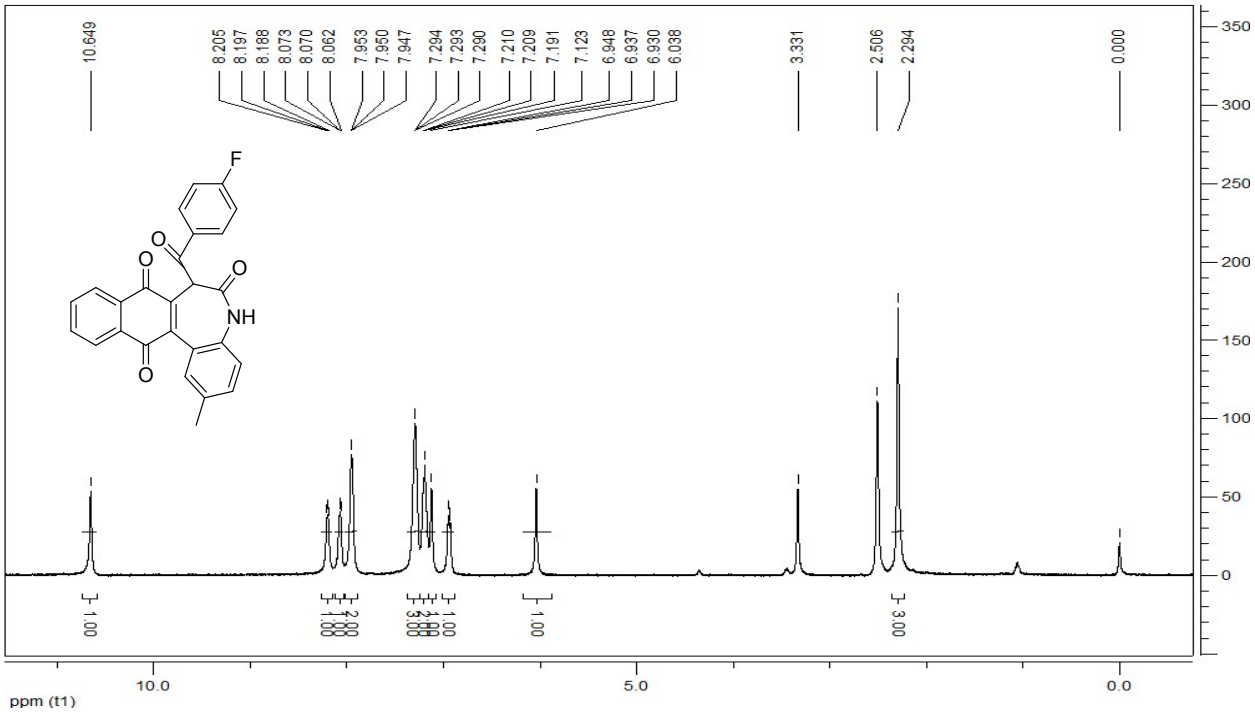


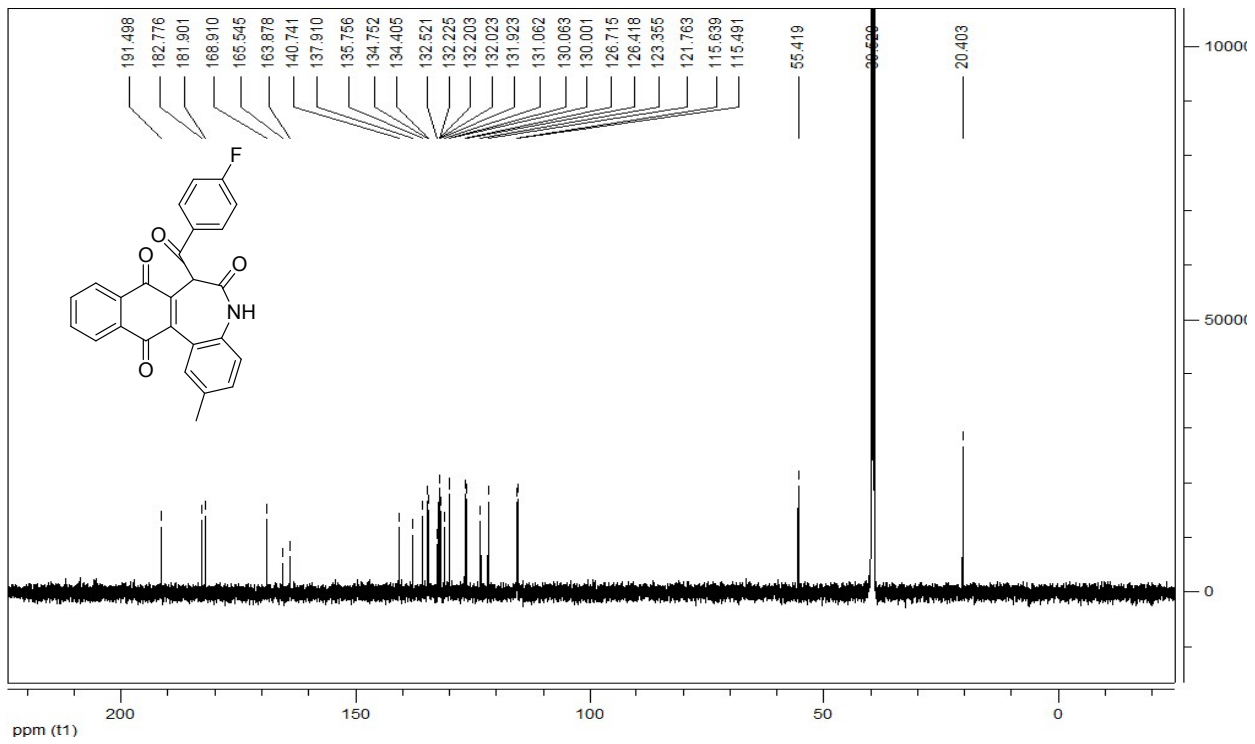
7-(4-Fluorobenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1i): Yellow Solid, 59%, m.p. 248 – 250 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.77 (br, 1H, NH), 8.22 – 8.20 (m, 1H, ArH), 8.08 – 8.05 (m, 1H, ArH), 7.97 – 7.92 (m, 2H, ArH), 7.50 – 7.44 (m, 1H, ArH), 7.35 – 7.33 (m, 1H, ArH), 7.30 – 7.26 (m, 2H, ArH), 7.20 – 7.14 (m, 3H, ArH), 7.07 (d, J = 8.0 Hz, 1H, ArH), 6.07 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 191.9, 183.1, 182.3, 169.5, 165.1 (d, J = 250.6 Hz), 141.1, 138.5, 138.3, 135.2, 134.8, 132.9, 132.8 (d, J = 2.9 Hz), 132.6, 131.6, 131.4, 130.4 (d, J = 9.6 Hz), 127.1, 126.8, 123.5, 123.3, 122.1, 116.0 (d, J = 22.1 Hz), 55.7; IR (KBr) υ: 3198, 3073, 2974, 1669, 1597, 1505, 1483, 1430, 846, 757, 713 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{14}FNNaO_4$ ([M+Na]$^{+}$): 434.0799, Found: 450.0801.



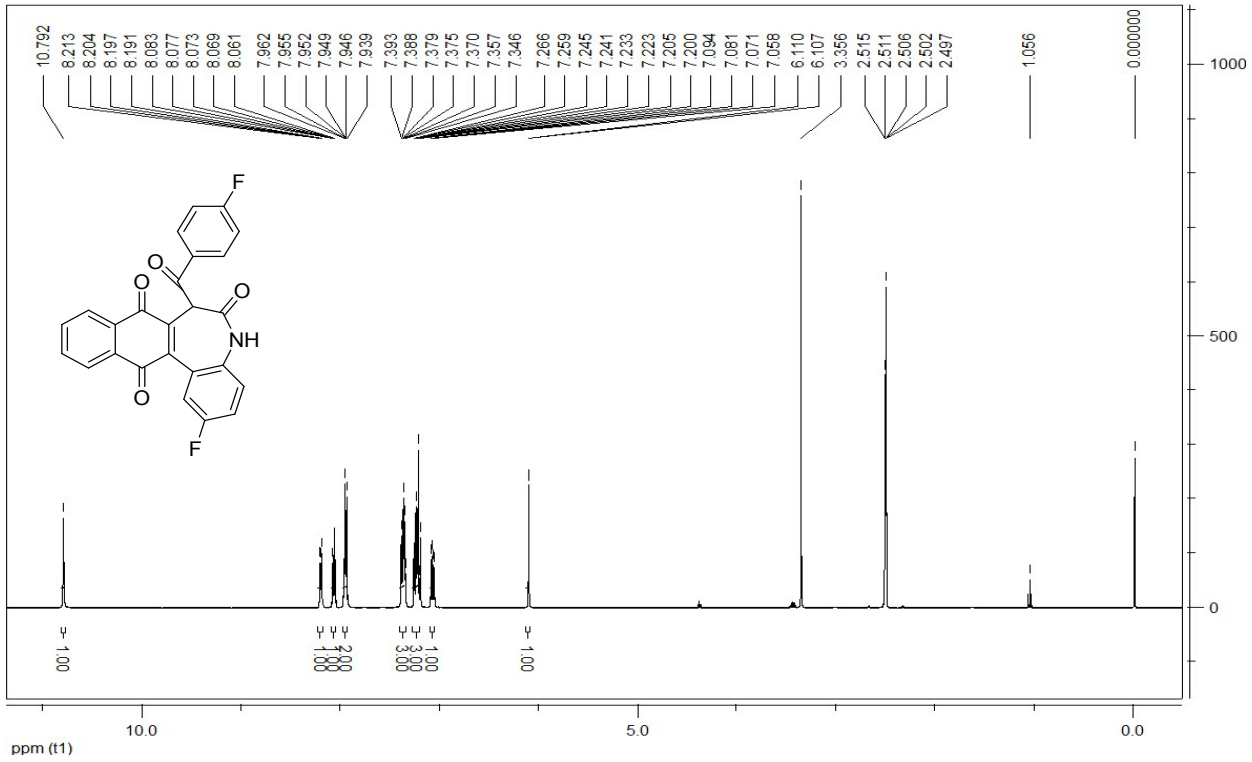


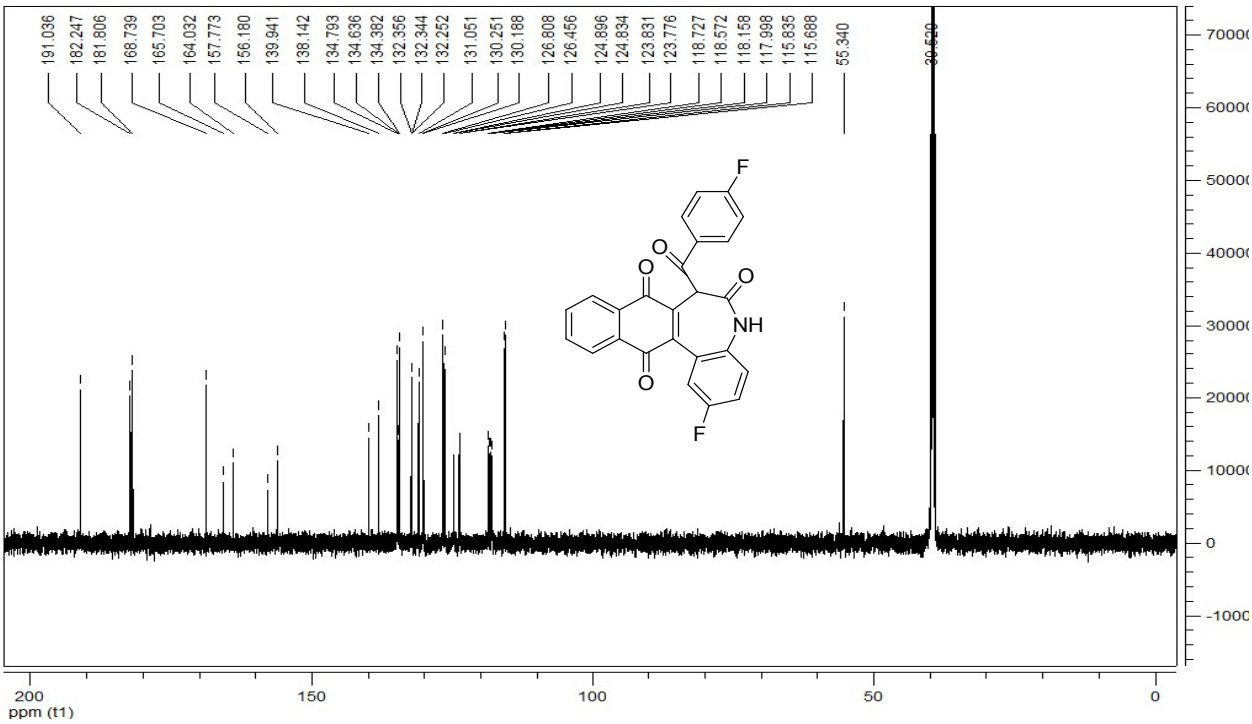
7-(4-Fluorobenzoyl)-2-methyl-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1j): Yellow Solid, 61%, m.p. 236 – 238 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.65 (br, 1H, NH), 8.21 – 8.19 (m, 1H, ArH), 8.07 – 8.06 (m, 1H, ArH), 7.96 – 7.95 (m, 2H, ArH), 7.30 – 7.28 (m, 3H, ArH), 7.21 – 7.19 (m, 2H, ArH), 7.13 – 7.11 (m, 1H, ArH), 6.95 – 6.93 (m, 1H, ArH), 6.04 (s, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 191.5, 182.8, 181.9, 168.9, 164.7 (d, J = 245.5 Hz), 140.7, 137.9, 135.8, 134.8, 134.4, 132.5, 132.23, 132.20, 132.0, 131.9, 131.1, 130.0 (d, J = 9.3 Hz), 126.7, 126.4, 123.4, 121.8, 115.6 (d, J = 22.2 Hz), 55.4, 20.4; IR (KBr) υ: 3169, 3070, 2947, 1685, 1597, 1501, 1454, 1368, 937, 871, 824, 764, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{16}FNNaO_4$ ([M+Na]$^{+}$): 448.0956, Found: 448.0966.



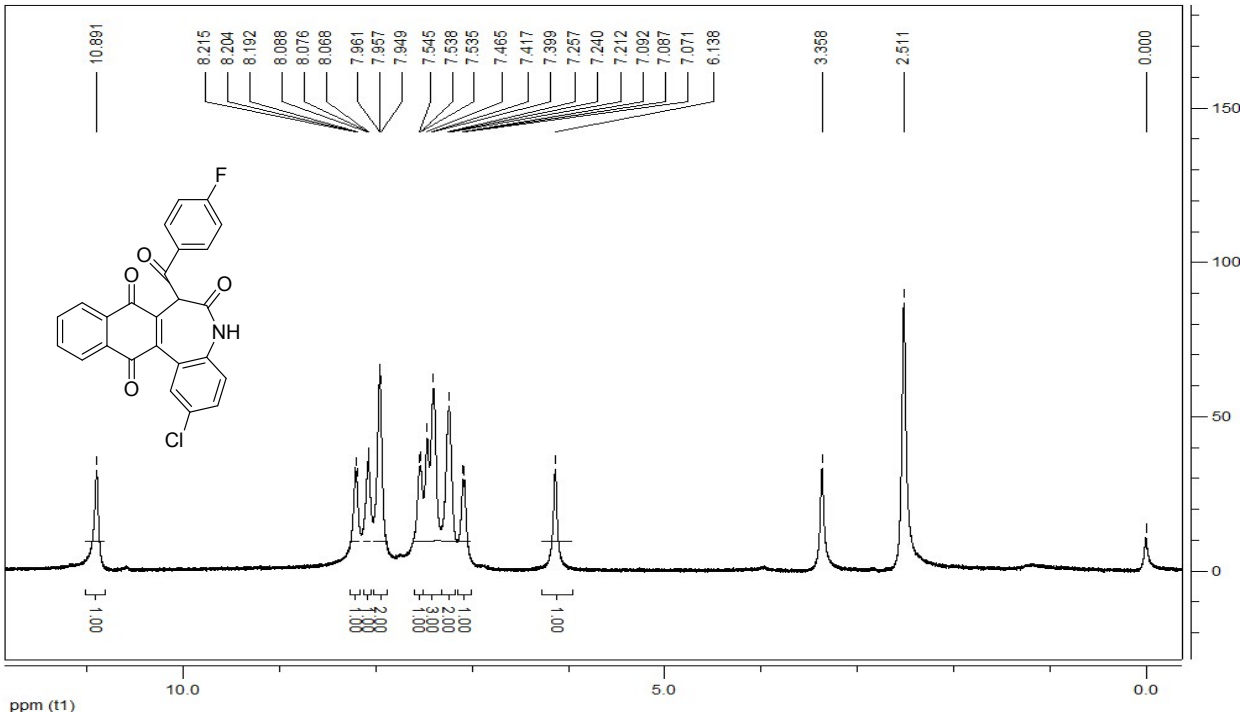


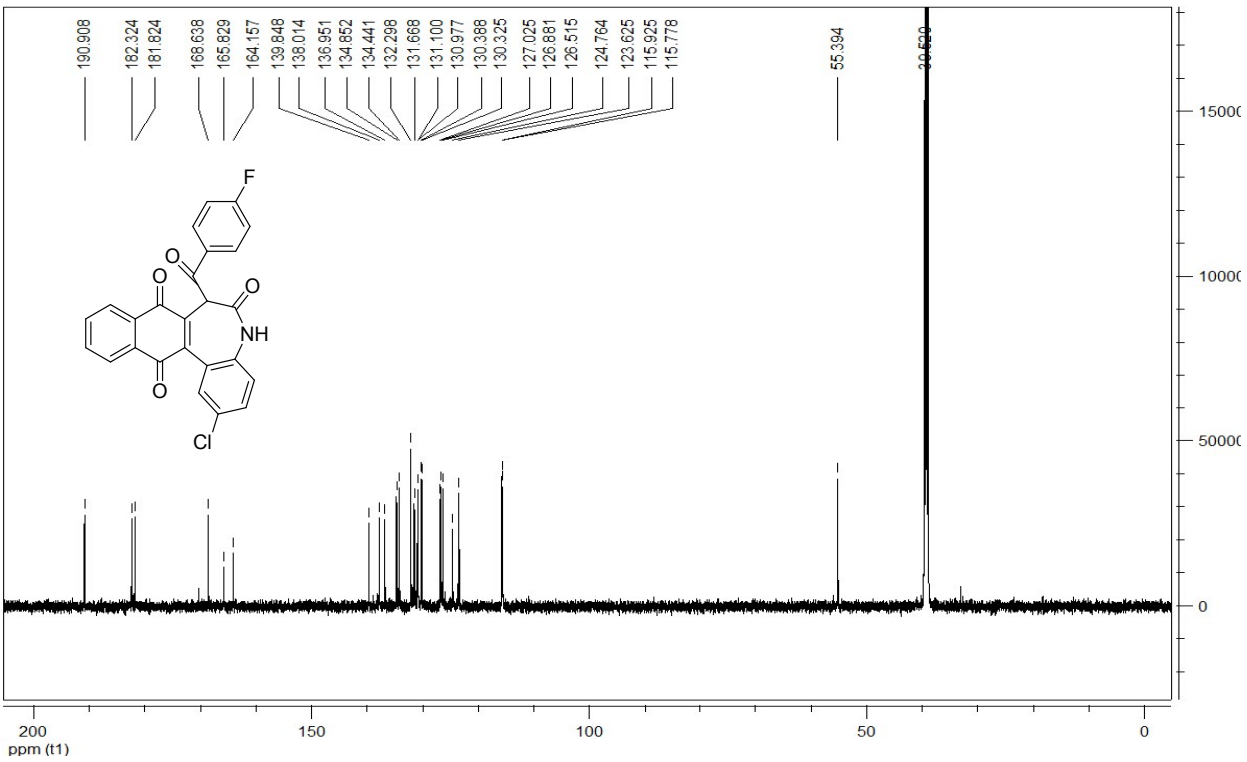
2-Fluoro-7-(4-fluorobenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1k): Yellow Solid, 65%, m.p. 240 – 241 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.79 (br, 1H, NH), 8.21 – 8.19 (m, 1H, ArH), 8.08 – 8.06 (m, 1H, ArH), 7.96 – 7.94 (m, 2H, ArH), 7.39 – 7.35 (m, 3H, ArH), 7.27 – 7.20 (m, 3H, ArH), 7.09 – 7.06 (m, 1H, ArH), 6.11 – 6.10 (m, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 191.0, 182.2, 181.8, 168.7, 164.9 (d, J = 250.6 Hz), 157.0 (d, J = 234.0 Hz), 139.9, 138.1, 134.8, 134.6, 134.4, 132.4 (d, J = 3.3 Hz), 132.3, 131.1, 130.2 (d, J = 9.4 Hz), 126.8, 126.5, 124.9 (d, J = 9.3 Hz), 123.8 (d, J = 8.3 Hz), 118.6 (d, J = 23.2 Hz), 118.1 (d, J = 24.0 Hz), 115.8 (d, J = 22.0 Hz), 55.3; IR (KBr) υ: 3181, 3087, 2973, 1685, 1597, 1498, 951, 826, 738, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{13}F_2NNaO_4$ ([M+Na]$^+$): 452.0705, Found: 452.0707.



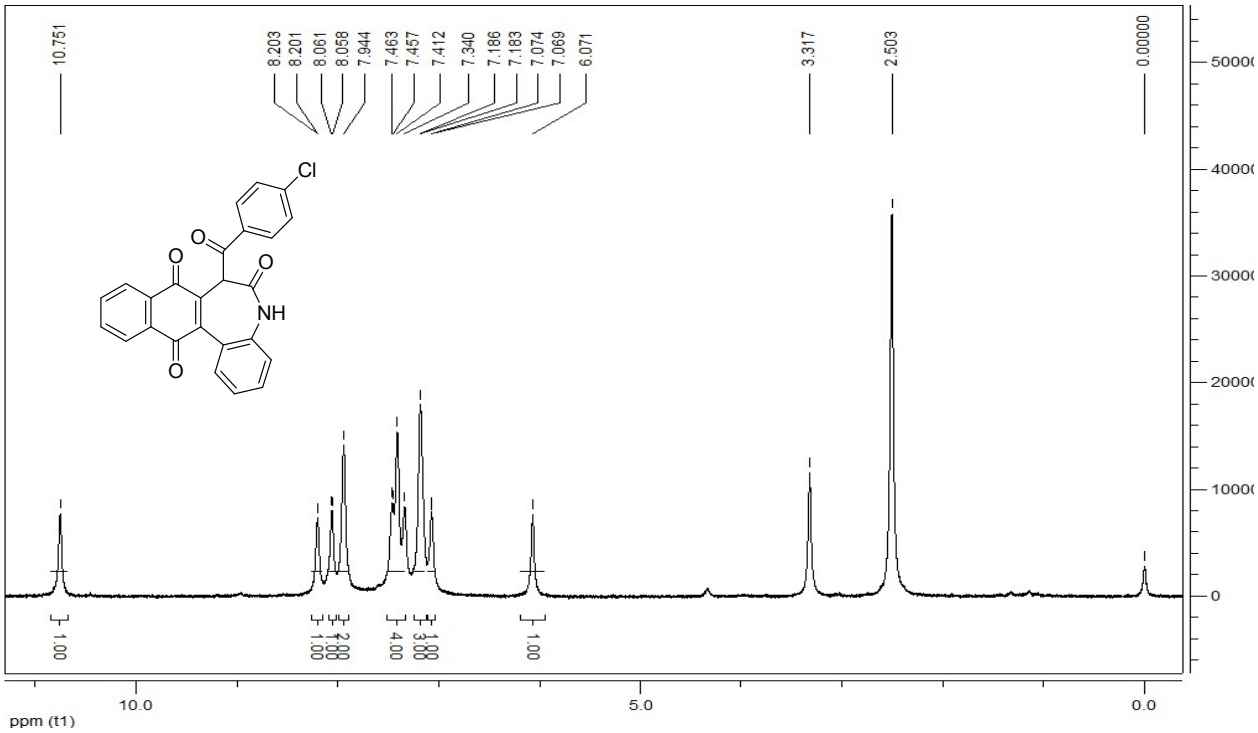


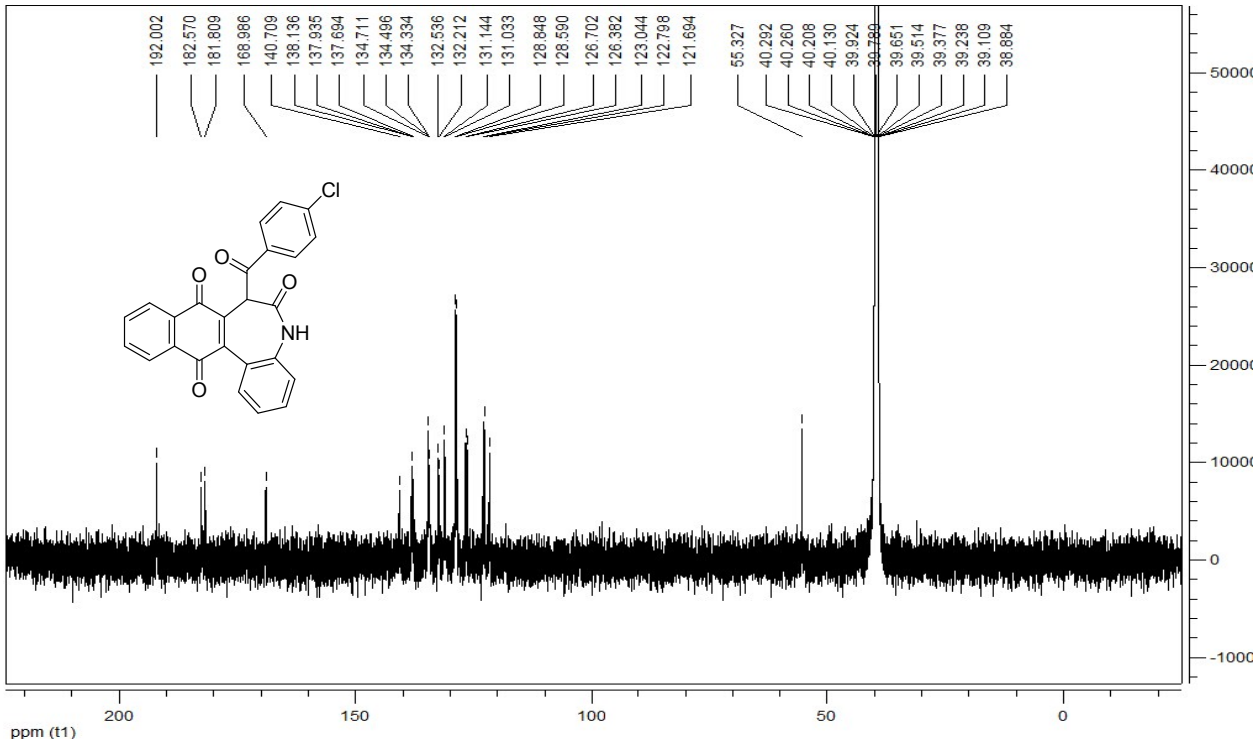
2-Chloro-7-(4-fluorobenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1l): Yellow Solid, 62%, m.p. 233 – 235 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.89 (br, 1H, NH), 8.22 – 8.19 (m, 1H, ArH), 8.09 – 8.07 (m, 1H, ArH), 7.96 – 7.95 (m, 2H, ArH), 7.55 – 7.53 (m, 1H, ArH), 7.46-7.40 (m, 3H, ArH), 7.26 – 7.21 (m, 2H, ArH), 7.09 – 7.07 (m, 1H, ArH), 6.14 (s, 1H, CH); ^{13}C NMR(150 MHz, DMSO-d_6) δ: 190.9, 182.3, 181.8, 168.6, 165.0 (d, J = 250.8 Hz), 139.8, 138.0, 137.0, 134.9, 134.4, 132.3 (2C), 131.7, 131.1, 131.0, 130.4 (d, J = 9.4 Hz), 127.0, 126.9, 126.5, 124.8, 123.6, 115.9 (d, J = 22.0 Hz), 55.4; IR (KBr) υ: 3197, 3076, 2949, 1682, 1596, 1505, 1481, 1390, 784, 724 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{13}ClFNNaO_4$ ([M+Na]$^+$): 468.0409, Found: 468.0409.



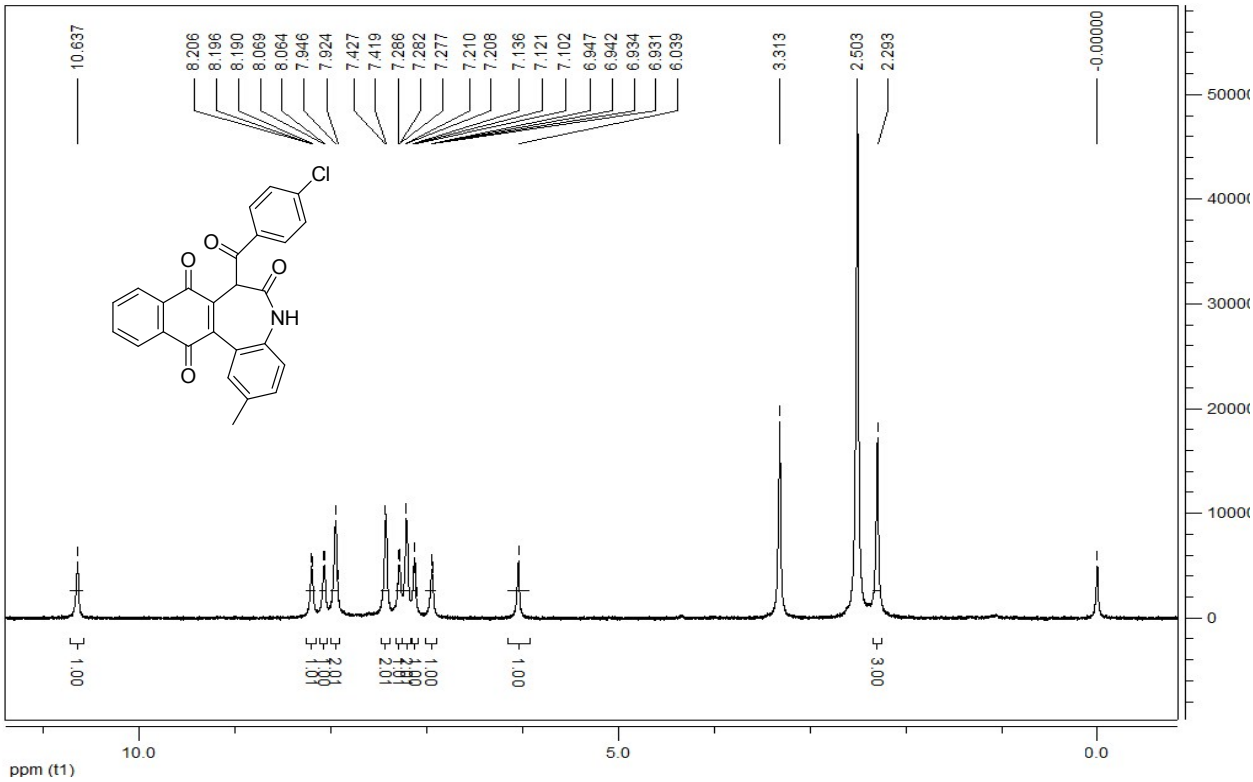


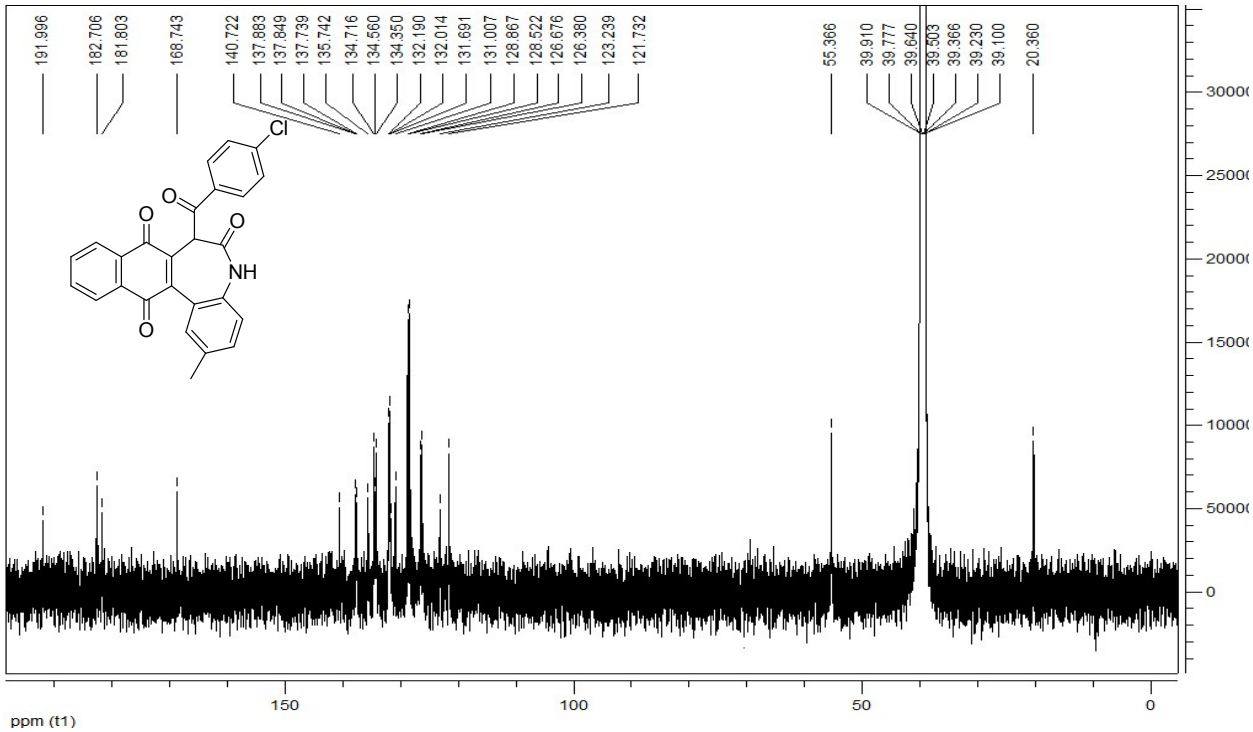
7-(4-Chlorobenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1m): yellow solid, 67%, m.p. 249 – 251 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.75 (br, 1H, NH), 8.21 – 8.20 (m, 1H, ArH), 8.06 – 8.05 (m, 1H, ArH), 7.96 – 7.93 (m, 2H, ArH), 7.46 – 7.34 (m, 4H, ArH), 7.19 – 7.18 (m, 3H, ArH), 7.08 – 7.06 (m, 1H, ArH), 6.07 (s, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 192.0, 182.6, 181.8, 169.0, 140.7, 138.1, 137.9, 137.7, 134.7, 134.5, 134.3, 132.5, 132.2, 131.1, 131.0, 128.8, 128.6, 126.7, 126.4, 123.0, 122.8, 121.7, 55.3; IR (KBr) υ: 3075, 2973, 1682, 1611, 1592, 1483, 859, 830, 755 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{14}ClNNaO_4$ ([M+Na]$^{+}$): 450.0504, Found: 450.0500.



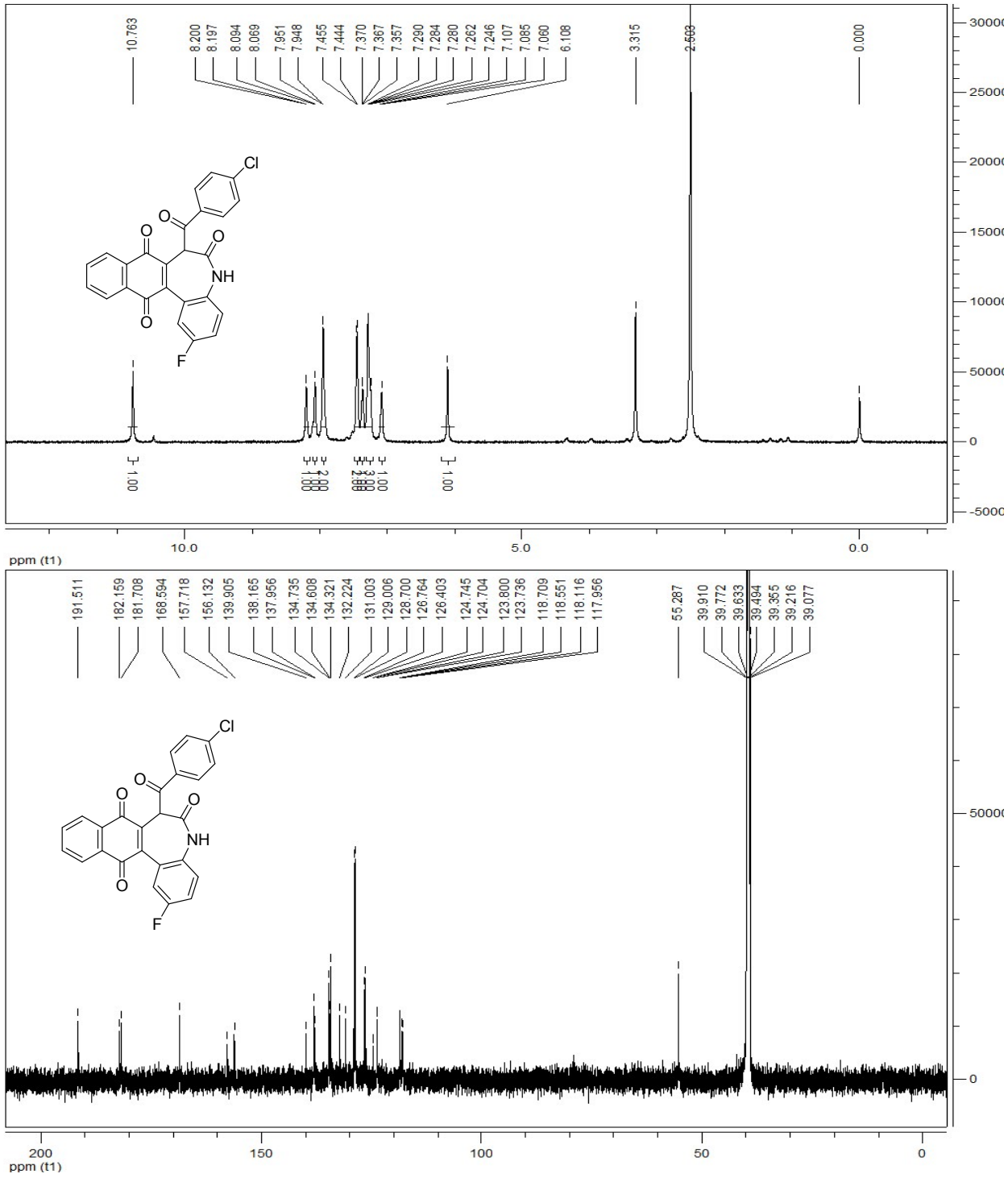


7-(4-Chlorobenzoyl)-2-methyl-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1n): yellow solid, 63%, m.p. 249 – 251 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.64 (br, 1H, NH), 8.21 – 8.19 (m, 1H, ArH), 8.07 – 8.06 (m, 1H, ArH), 7.95 – 7.92 (m, 2H, ArH), 7.43 – 7.42 (m, 2H, ArH), 7.29 – 7.28 (m, 1H, ArH), 7.22 – 7.20 (m, 2H, ArH), 7.14 – 7.10 (m, 1H, ArH), 6.95 – 6.93 (m, 1H, ArH), 6.04 (s, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 192.0, 182.7, 181.8, 168.7, 140.7, 137.9, 137.8, 137.7, 135.7, 134.7, 134.6, 134.4, 132.2, 132.0, 131.7, 131.0, 128.9, 128.5, 126.7, 126.4, 123.2, 121.7, 55.4, 20.4; IR (KBr) υ: 3205, 3069, 2941, 1685, 1592, 1499, 1363, 822 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{16}ClNNaO_4$ ([M+Na]$^+$): 464.0660, Found: 464.0659.

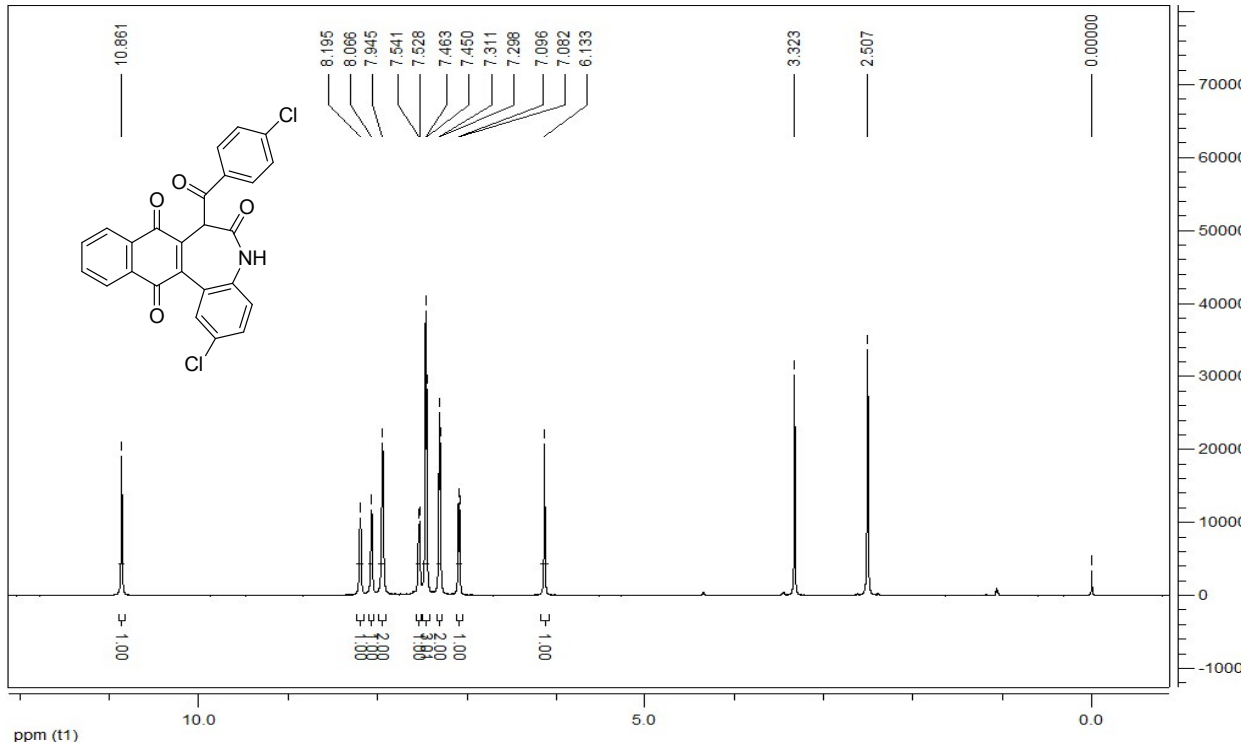


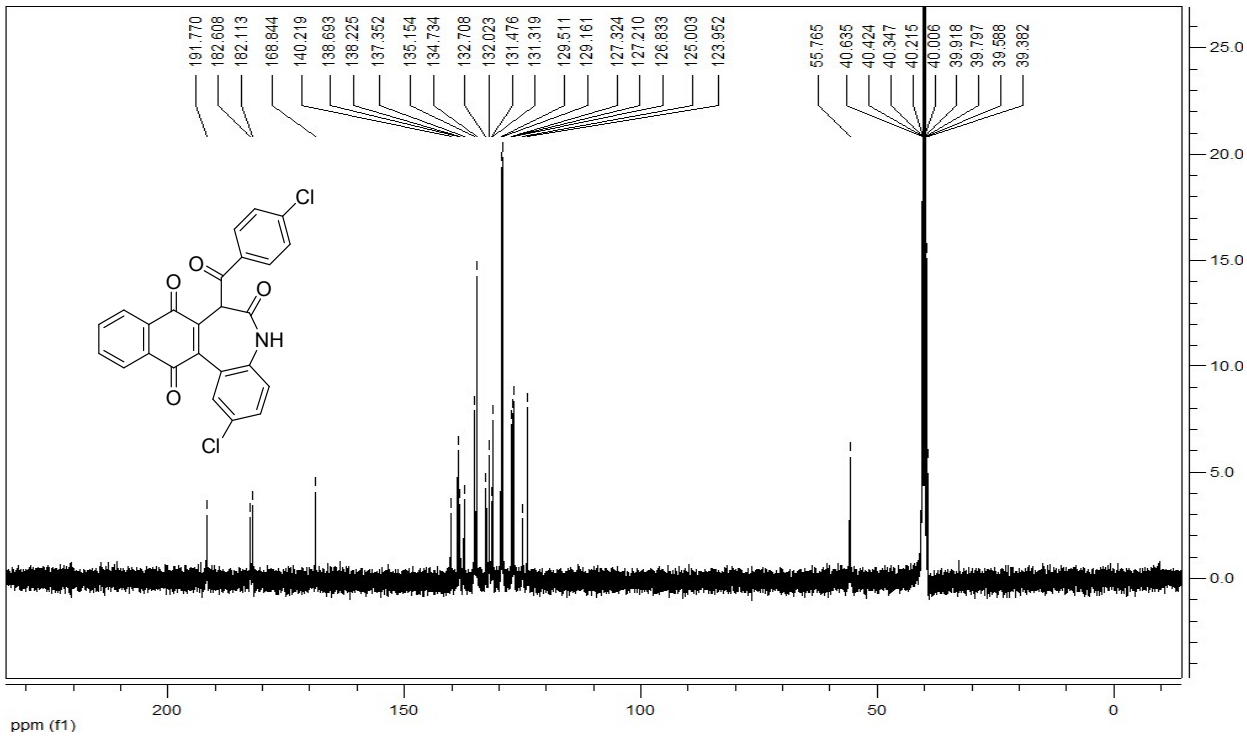


7-(4-Chlorobenzoyl)-2-fluoro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1o): yellow solid, 65%, m.p. 250 – 252 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.76 (br, 1H, NH), 8.20 – 8.19 (m, 1H, ArH), 8.09 – 8.07 (m, 1H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.45 (d, J = 6.6 Hz, 2H, ArH), 7.37 – 7.36 (m, 1H, ArH), 7.29 – 7.25 (m, 3H, ArH), 7.11 – 7.06 (m, 1H, ArH), 6.11 (s, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 191.5, 182.2, 181.7, 168.6, 156.9 (d, J = 237.9 Hz), 139.9, 138.2, 138.0, 134.7, 134.6, 134.4, 134.3, 132.2, 131.0, 129.0, 128.7, 126.8, 126.4, 124.7 (d, J = 6.2 Hz), 123.8 (d, J = 9.6 Hz), 118.6 (d, J = 22.7 Hz), 118.0 (d, J = 24.0 Hz), 55.3; IR (KBr) υ: 3096, 2958, 1679, 1664, 1591, 1496, 875, 821, 776 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{13}ClFNNaO_4$ ([M+Na]$^+$): 468.0409, Found: 468.0409.

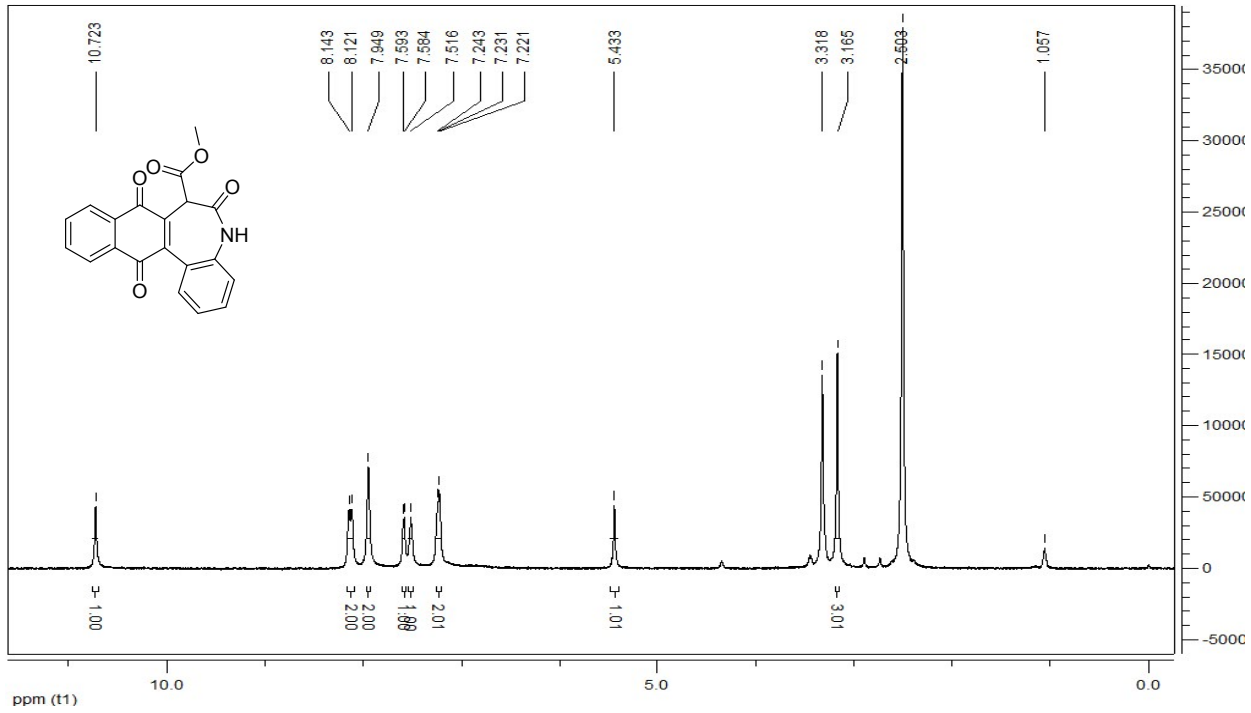


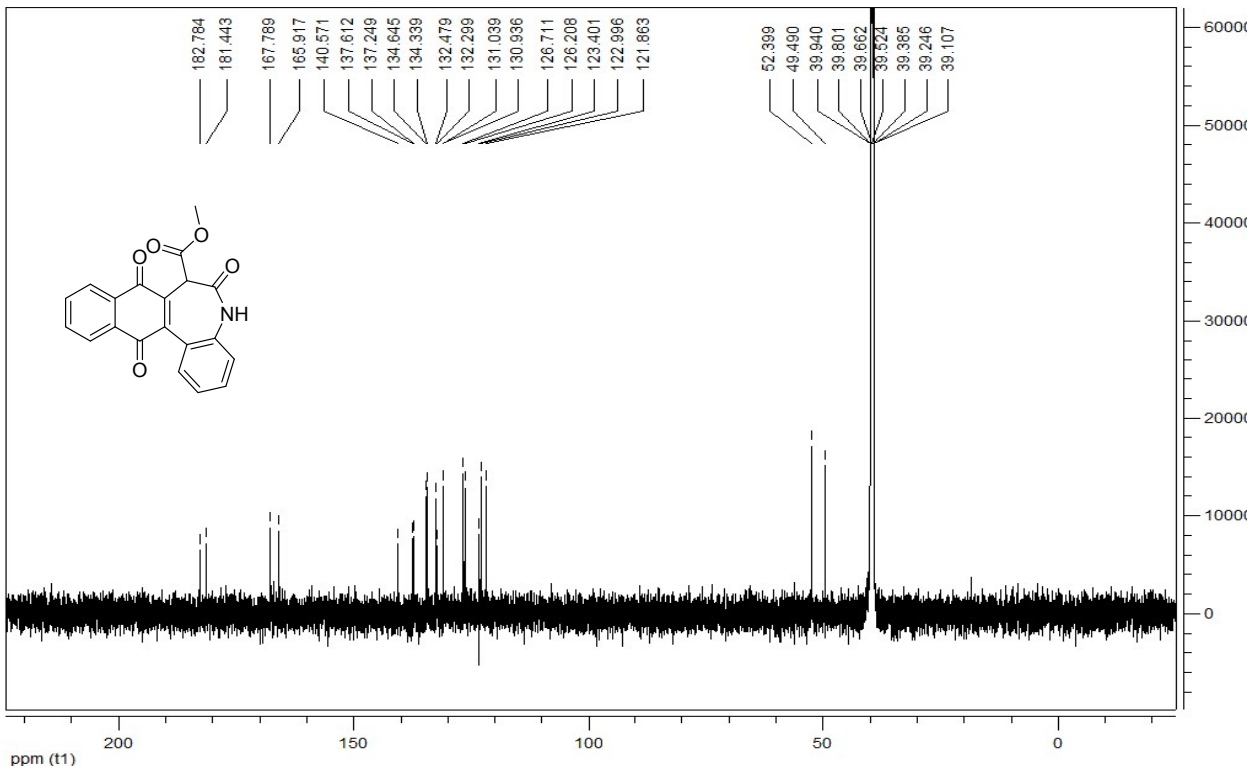
2-Chloro-7-(4-chlorobenzoyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (1p): yellow solid, 68%, m.p. 272 – 274 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.86 (br, 1H, NH), 8.20 – 8.19 (m, 1H, ArH), 8.07 – 8.06 (m, 1H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.53 (d, J = 7.8 Hz, 1H, ArH), 7.46 – 7.45 (m, 3H, ArH), 7.30 (d, J = 7.8 Hz, 2H, ArH), 7.09 (d, J = 8.4 Hz, 1H, ArH), 6.13 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 191.8, 182.6, 182.1, 168.8, 140.2, 138.7, 138.2, 137.4, 135.2, 134.7, 132.7, 132.0, 131.5, 131.3, 129.5, 129.2, 127.3, 127.2, 126.8, 125.0, 124.0, 55.8; IR (KBr) υ: 3081, 2928, 1681, 1592, 1485, 919, 826 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{13}Cl_2NNaO_4$ ([M+Na]$^+$): 484.0114, Found: 484.0110.



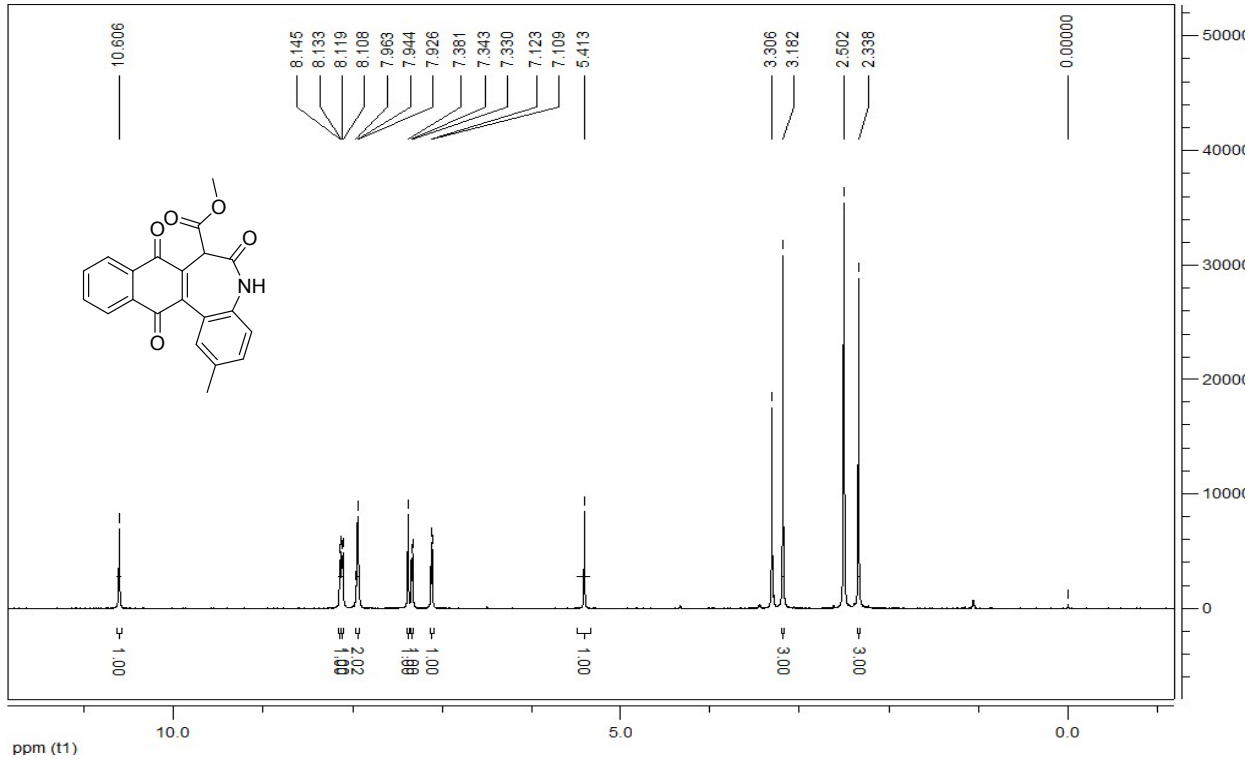


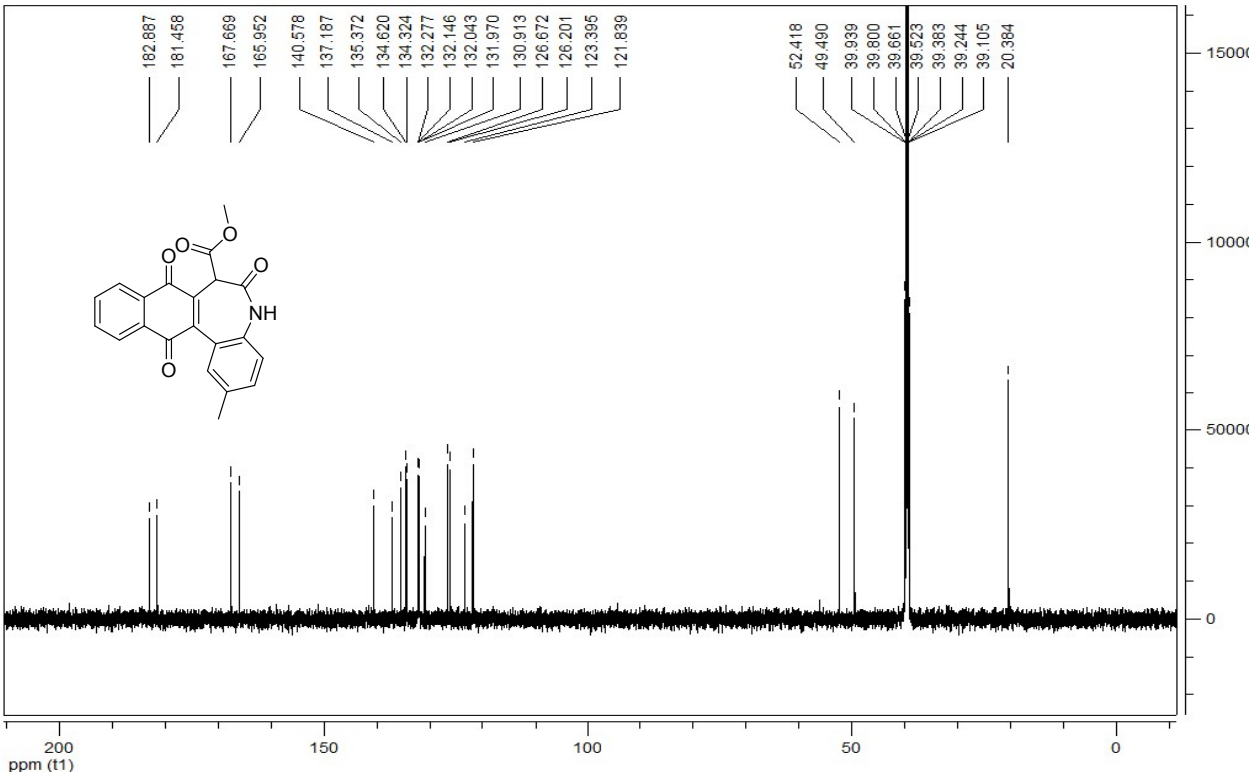
Methyl 6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (**2a**): Yellow Solid, 53%, m.p. 233 – 235 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.72 (br, 1H, NH), 8.15 – 8.11 (m, 2H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.59 – 7.58 (m, 1H, ArH), 7.52 – 7.51 (m, 1H, ArH), 7.24 – 7.22 (m, 2H, ArH), 5.43 (s, 1H, CH), 3.16 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.8, 181.4, 167.8, 165.9, 140.6, 137.6, 137.2, 134.6, 134.3, 132.5, 132.3, 131.0, 130.9, 126.7, 126.2, 123.4, 123.0, 121.9, 52.4, 49.5; IR (KBr) υ: 3193, 3070, 2952, 1746, 1674, 1605, 1474, 1370, 754, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{13}NNaO_5$ ([M+Na]$^{+}$): 370.0686, Found: 370.0696.



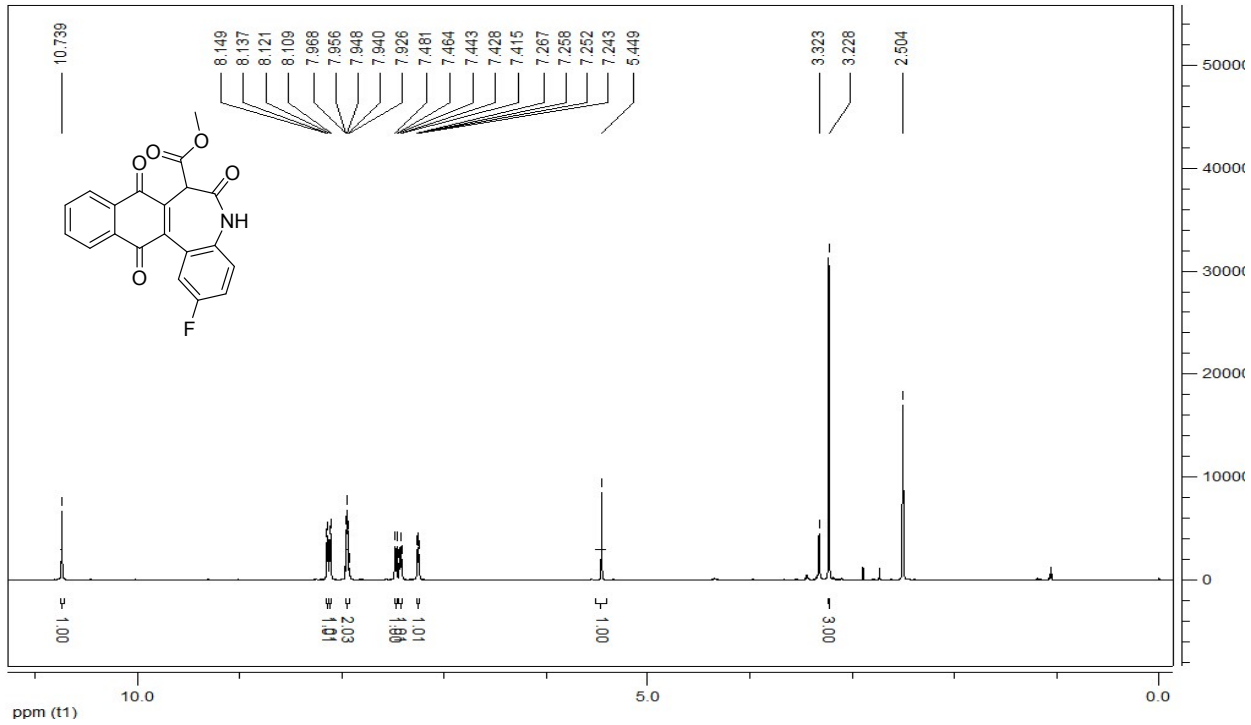


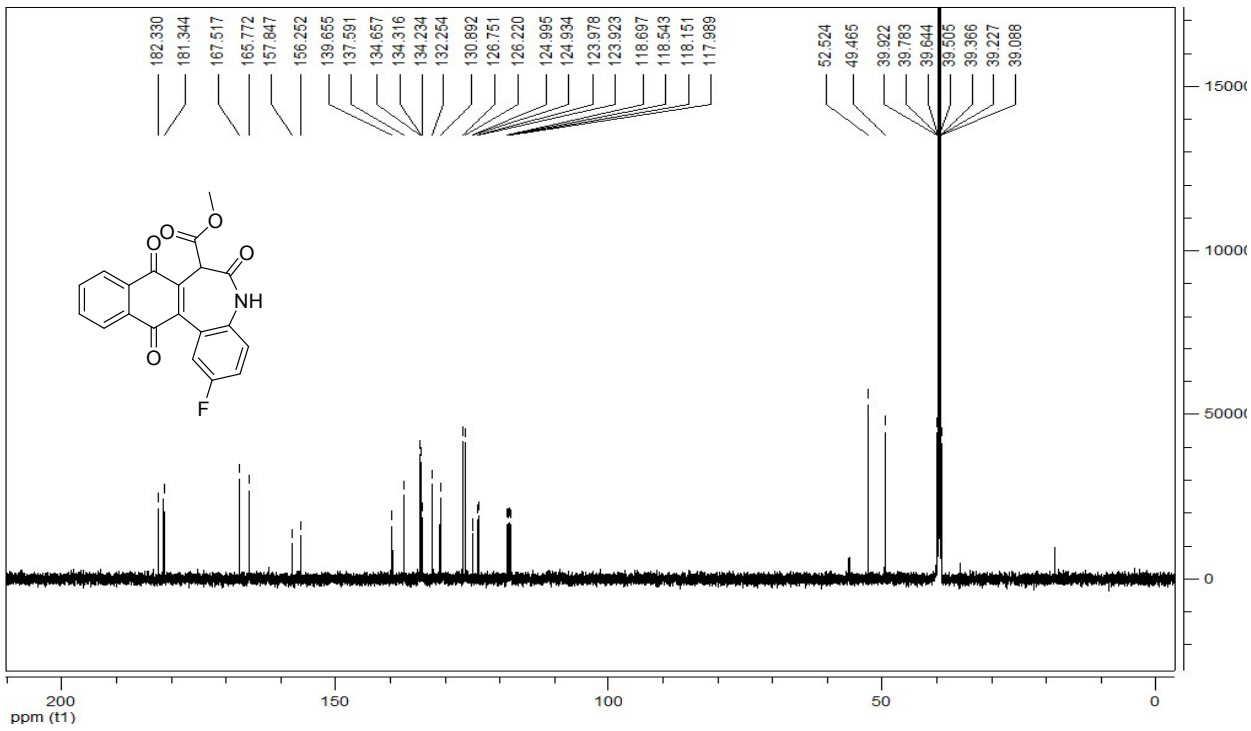
Methyl 2-methyl-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (**2b**): Yellow Solid, 70%, m.p. 216 – 218 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.61 (br, 1H, NH), 8.14 (d, *J* = 7.2 Hz, 1H, ArH), 8.11 (d, *J* = 6.6 Hz, 1H, ArH), 7.96 – 7.93 (m, 2H, ArH), 7.39 – 7.38 (m, 1H, ArH), 7.34 (d, *J* = 7.8 Hz, 1H, ArH), 7.12 (d, *J* = 8.4 Hz, 1H, ArH), 5.41 (s, 1H, CH), 3.18 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.3, 181.5, 167.7, 166.0, 140.6, 137.2, 135.4, 134.6, 134.3, 132.3, 132.1, 132.0, 131.9, 130.9, 126.7, 126.2, 123.4, 121.8, 52.4, 49.5, 20.4; IR (KBr) υ: 3278, 2944, 1730, 1694, 1589, 1449, 1360, 815, 708 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{15}NNaO_5$ ([M+Na]$^{+}$): 384.0842, Found: 384.0859.



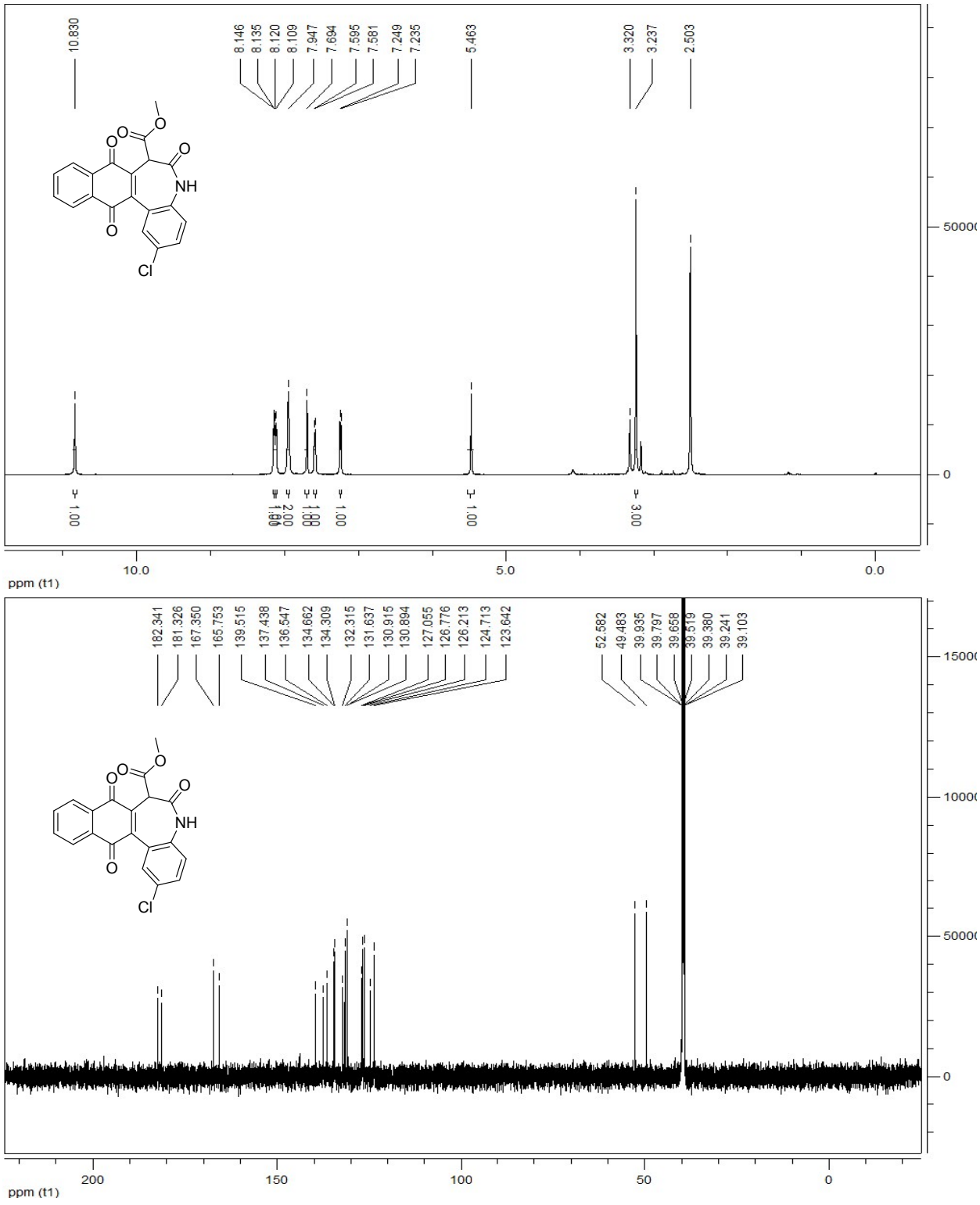


Methyl 2-fluoro-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (**2c**): Yellow Solid, 73%, m.p. 233 – 236 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.74 (br, 1H, NH), 8.14 (d, J = 7.2 Hz, 1H, ArH), 8.12 (d, J = 6.6 Hz, 1H, ArH), 7.97 – 7.93 (m, 2H, ArH), 7.47 (d, 1H, J = 10.2 Hz, ArH), 7.44 – 7.42 (m, 1H, ArH), 7.27 – 7.24 (m, 1H, ArH), 5.45 (s, 1H, CH), 3.23 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.3, 181.3, 167.5, 165.8, 157.0 (d, J = 239.2 Hz), 139.7, 137.6, 134.7, 134.3, 134.2, 132.3, 130.9, 126.8, 126.2, 125.0 (d, J = 9.1 Hz), 124.0 (d, J = 8.2 Hz), 118.6 (d, J = 23.1 Hz), 118.0 (d, J = 24.3 Hz), 52.5, 49.5; IR (KBr) υ: 3195, 3080, 2955, 1747, 1673, 1584, 1492, 1364, 890, 745, 702 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{12}FNNaO_5$ ([M+Na]$^+$): 388.0592, Found: 388.0610.

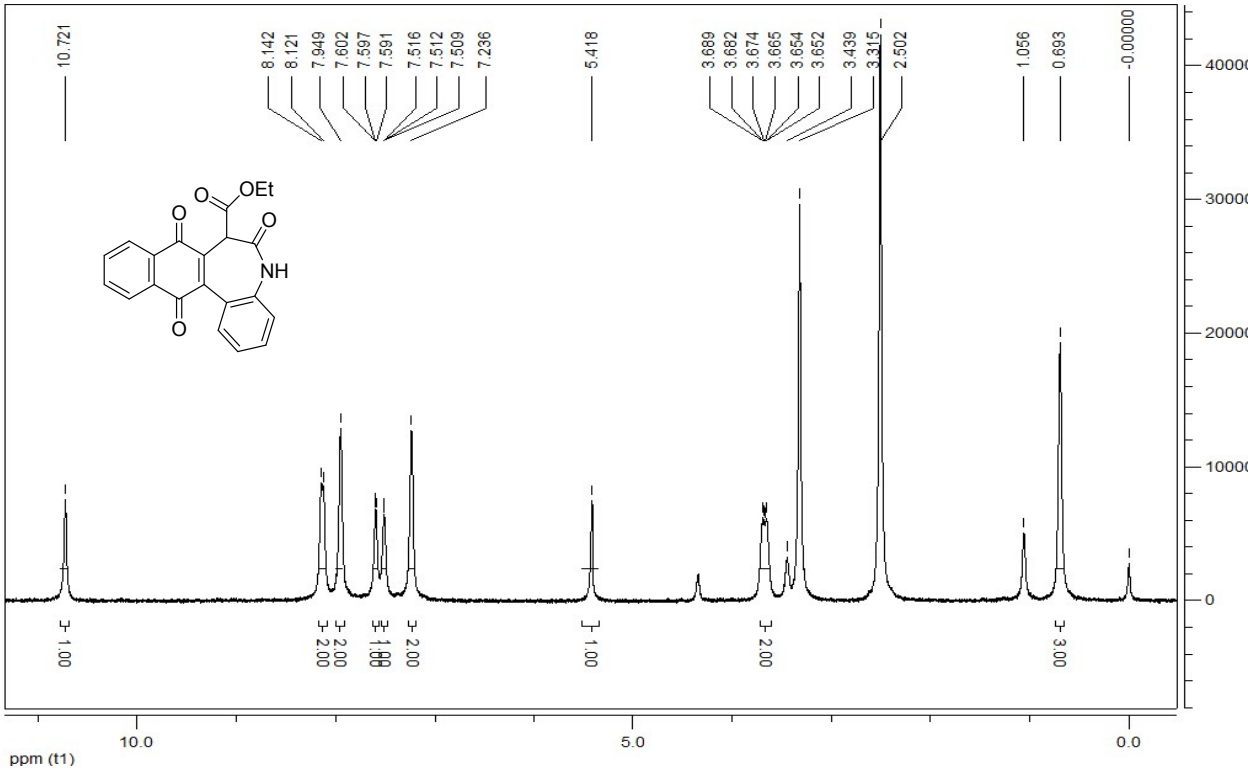


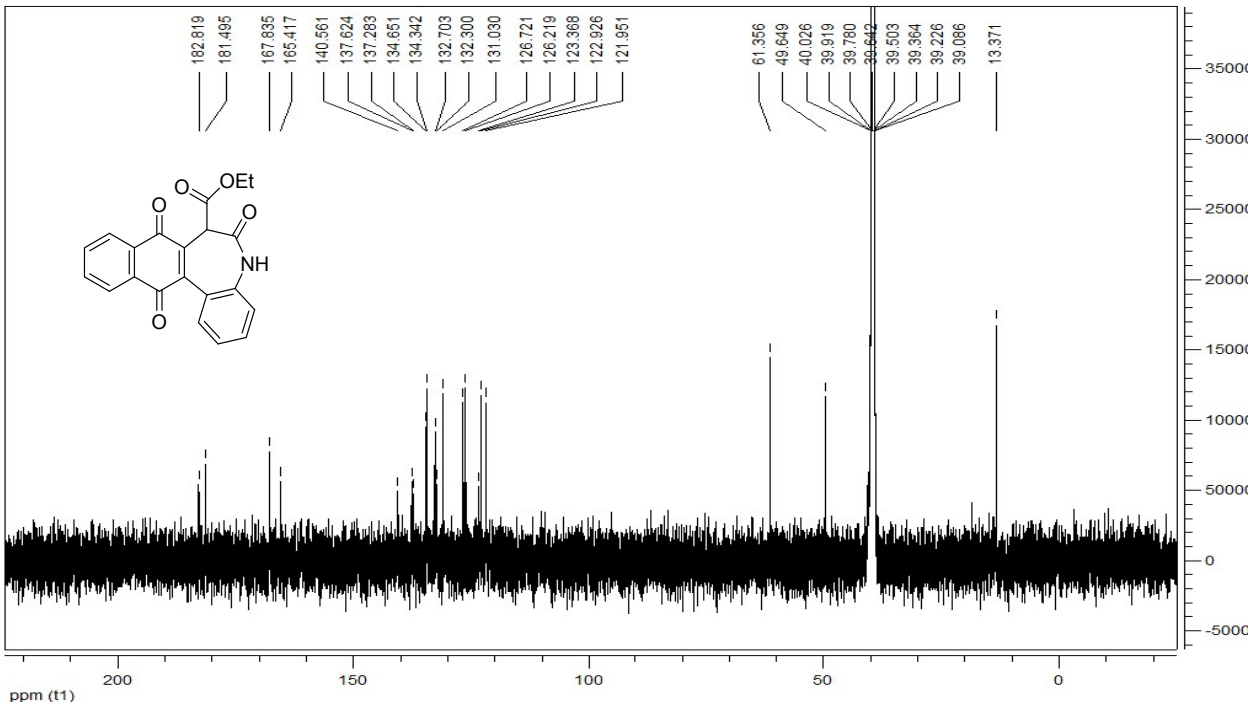


Methyl 2-chloro-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (**2d**): Yellow Solid, 75%, 230 – 232 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.83 (br, 1H, NH), 8.14 (d, J = 6.6 Hz, 1H, ArH), 8.11 (d, J = 6.6 Hz, 1H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.70 – 7.69 (m, 1H, ArH), 7.59 (d, J = 8.4 Hz, 1H, ArH), 7.24 (d, J = 8.4 Hz, 1H, ArH), 5.46 (s, 1H, CH), 3.24 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.3, 181.3, 167.3, 165.8, 139.5, 137.4, 136.5, 134.7, 134.3, 132.3, 131.6, 130.9, 130.8, 127.1, 126.8, 126.2, 124.7, 123.6, 52.6, 49.5; IR (KBr) υ: 3195, 3105, 2947, 1748, 1681, 1596, 1476, 1362, 828, 735 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{15}ClNNaO_5$ ([M+Na]$^{+}$): 404.0296, Found: 404.0310.

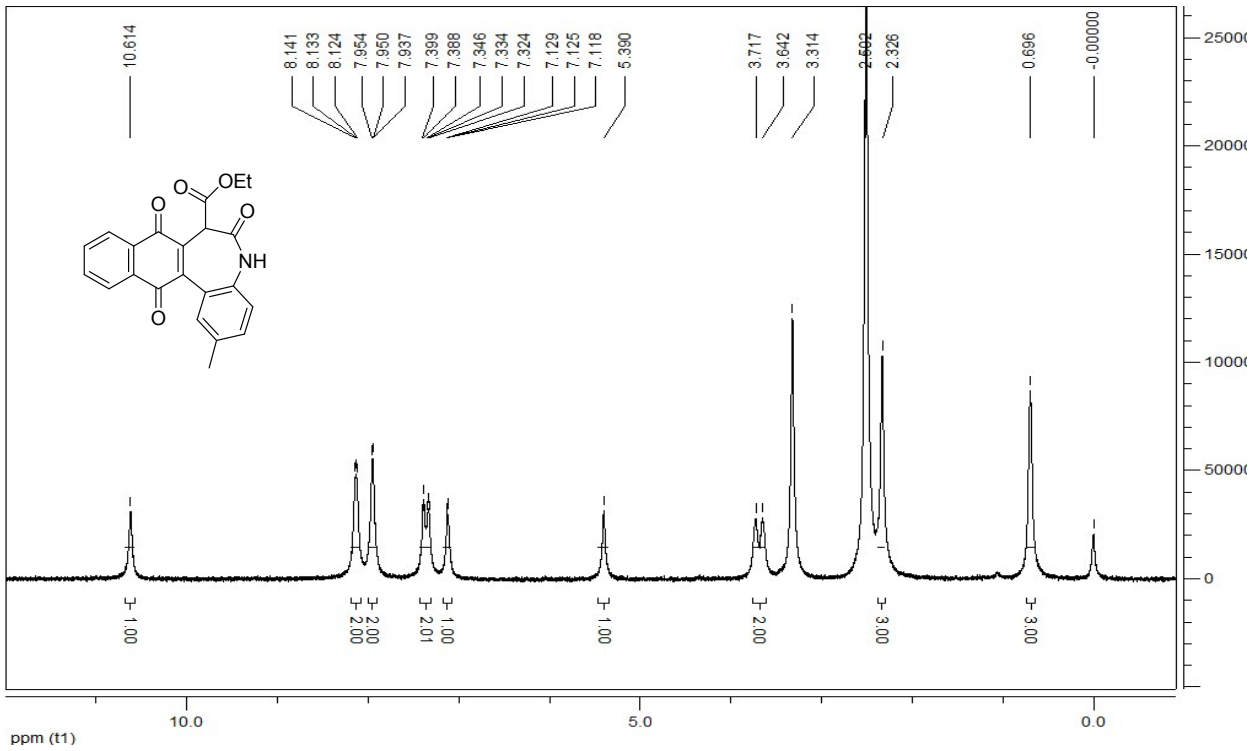


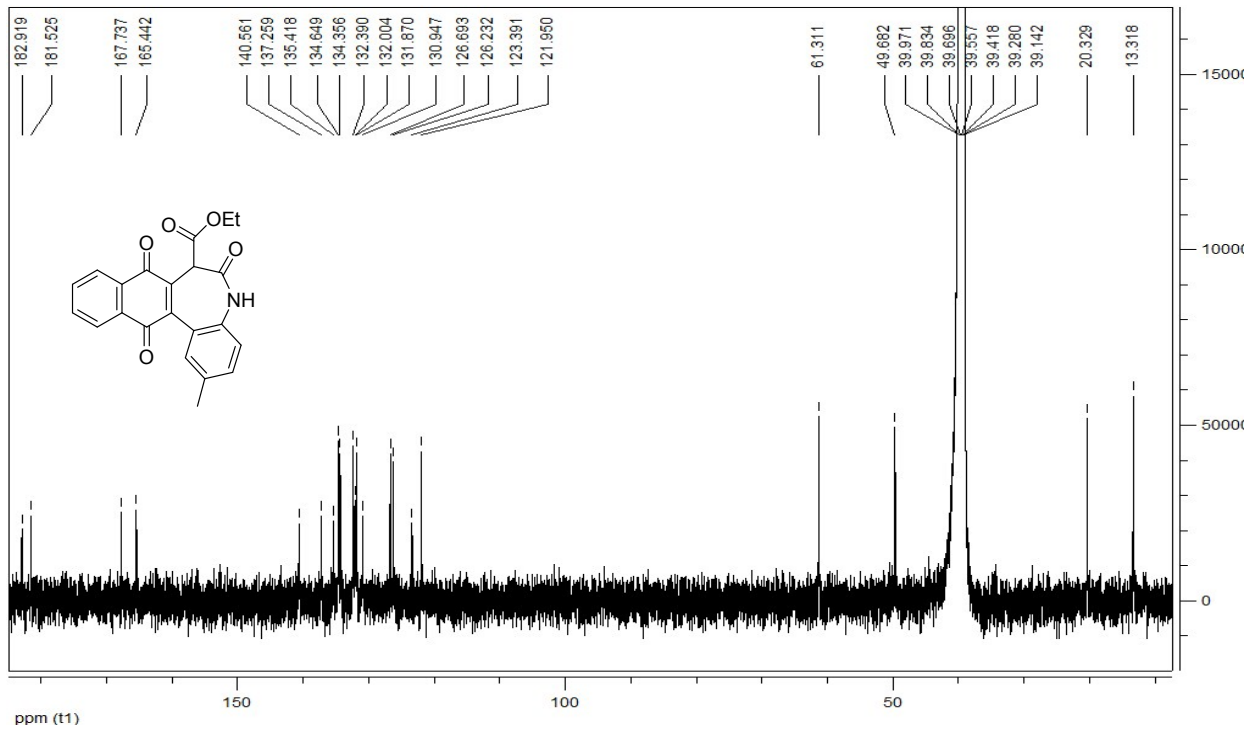
Ethyl 6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (2e): yellow solid, 64%, m.p. 230 – 232 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.72 (br, 1H, NH), 8.14 – 8.13 (m, 2H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.60 – 7.59 (m, 1H, ArH), 7.52 – 7.51 (m, 1H, ArH), 7.24 – 7.23 (m, 2H, ArH), 5.42 (s, 1H, CH), 3.69 – 3.65 (m, 2H, CH_2), 0.71 – 0.67 (m, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.8, 181.5, 167.8, 165.4, 140.6, 137.6, 137.3, 134.7, 134.3, 132.7, 132.3, 131.0, 130.9, 126.7, 126.2, 123.4, 122.9, 122.0, 61.4, 49.6, 13.4; IR (KBr) υ: 3069, 2971, 1739, 1675, 1567, 1429, 1382, 852, 826, 755 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{15}NNaO_5$ ([M+Na]$^{+}$): 384.0842, Found: 384.0841.



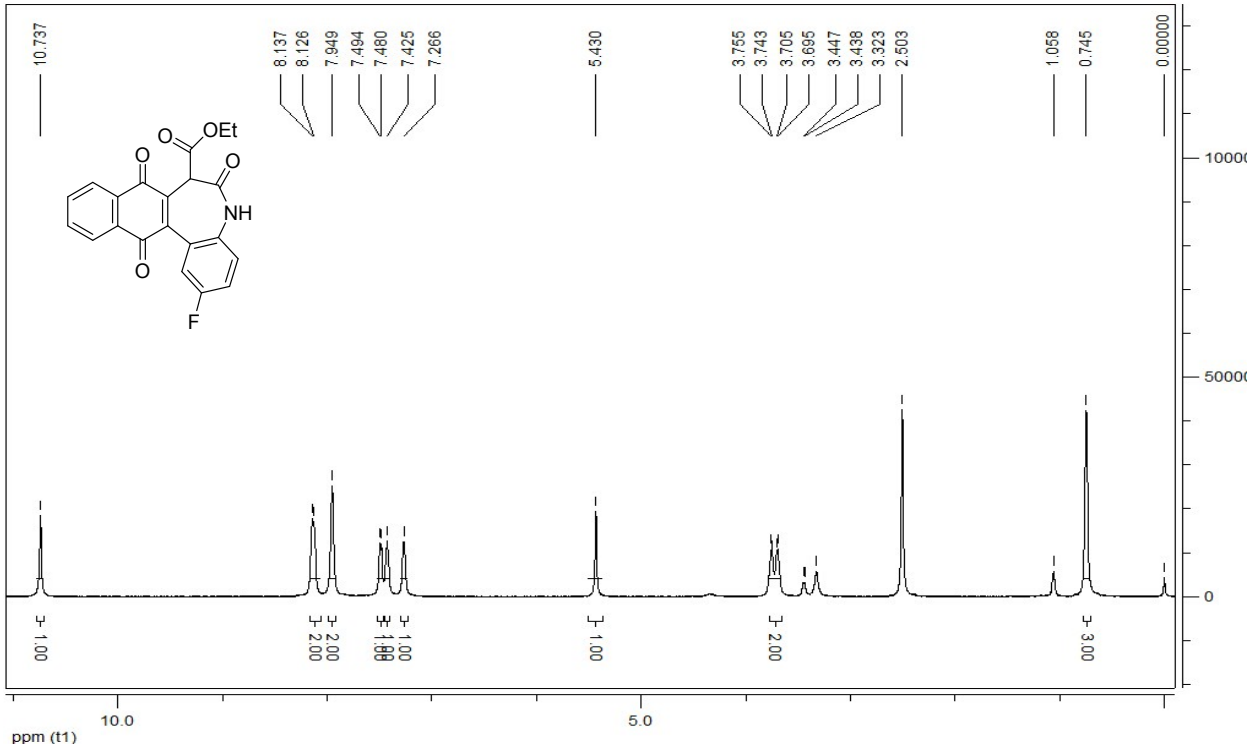


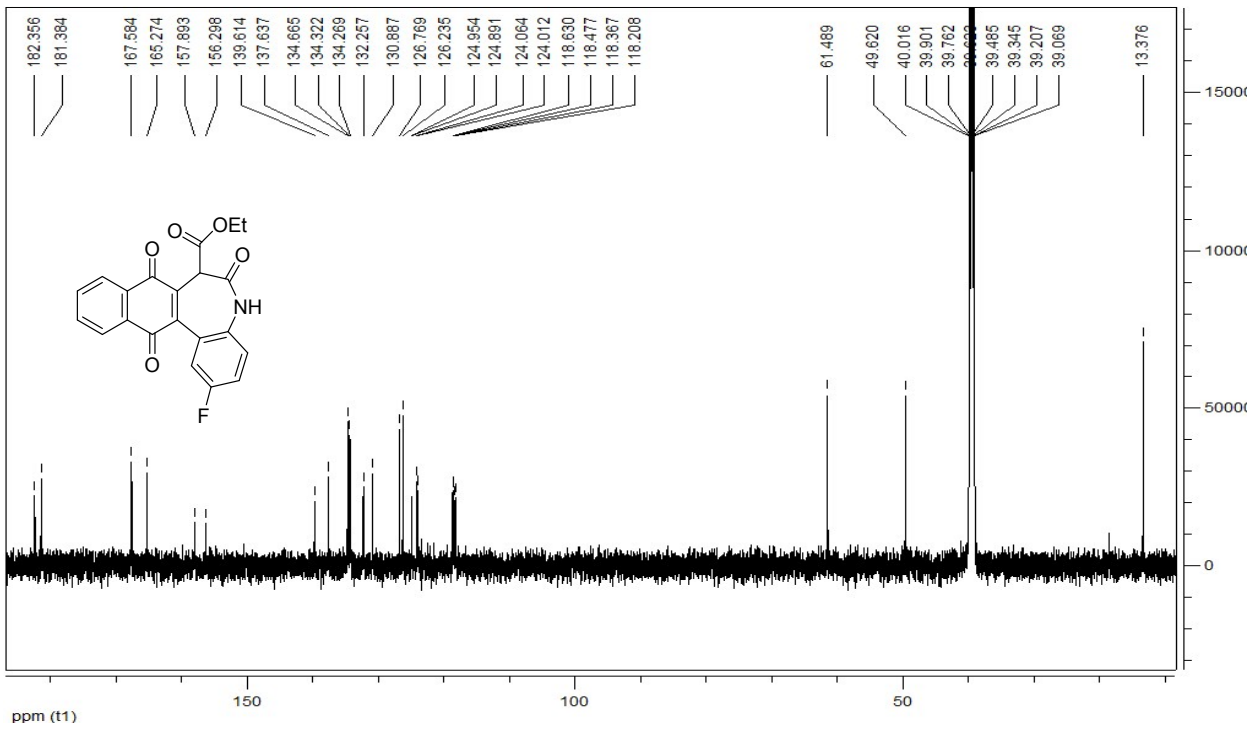
Ethyl 2-methyl-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (2f): yellow solid, 69%, m.p. 238 – 240 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.61 (br, 1H, NH), 8.14 – 8.12 (m, 2H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.40 – 7.32 (m, 2H, ArH), 7.13 – 7.12 (m, 1H, ArH), 5.39 (s, 1H, CH), 3.72 – 3.64 (m, 2H, CH_2), 2.33 (s, 3H, CH_3), 0.72 – 0.68 (m, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.9, 181.5, 167.7, 165.4, 140.6, 137.3, 135.4, 134.6, 134.4, 132.4, 132.3, 132.0, 131.9, 130.9, 126.7, 126.2, 123.4, 122.0, 61.3, 49.7, 20.3, 13.3; IR (KBr) υ: 3183, 3053, 2933, 1747, 1713, 1682, 1612, 1574, 1464, 1372, 868 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{17}NNaO_5$ ([M+Na]$^{+}$): 398.0999, Found: 398.1001.



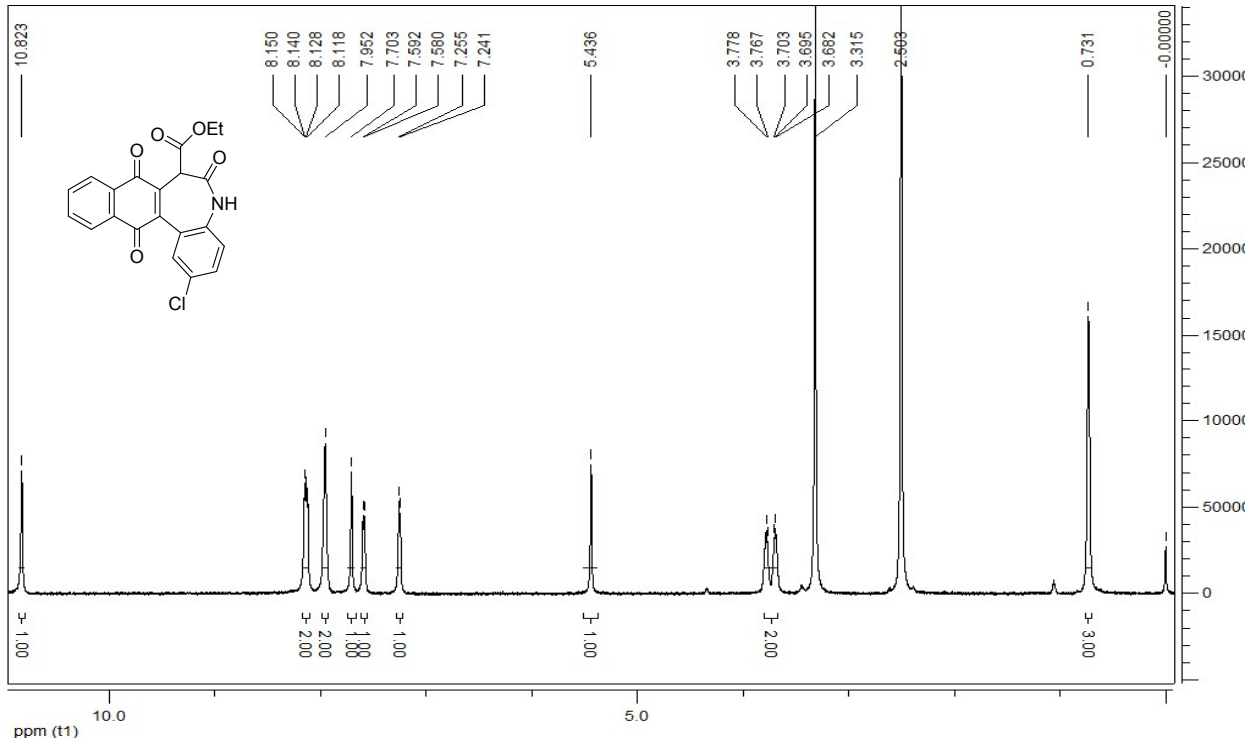


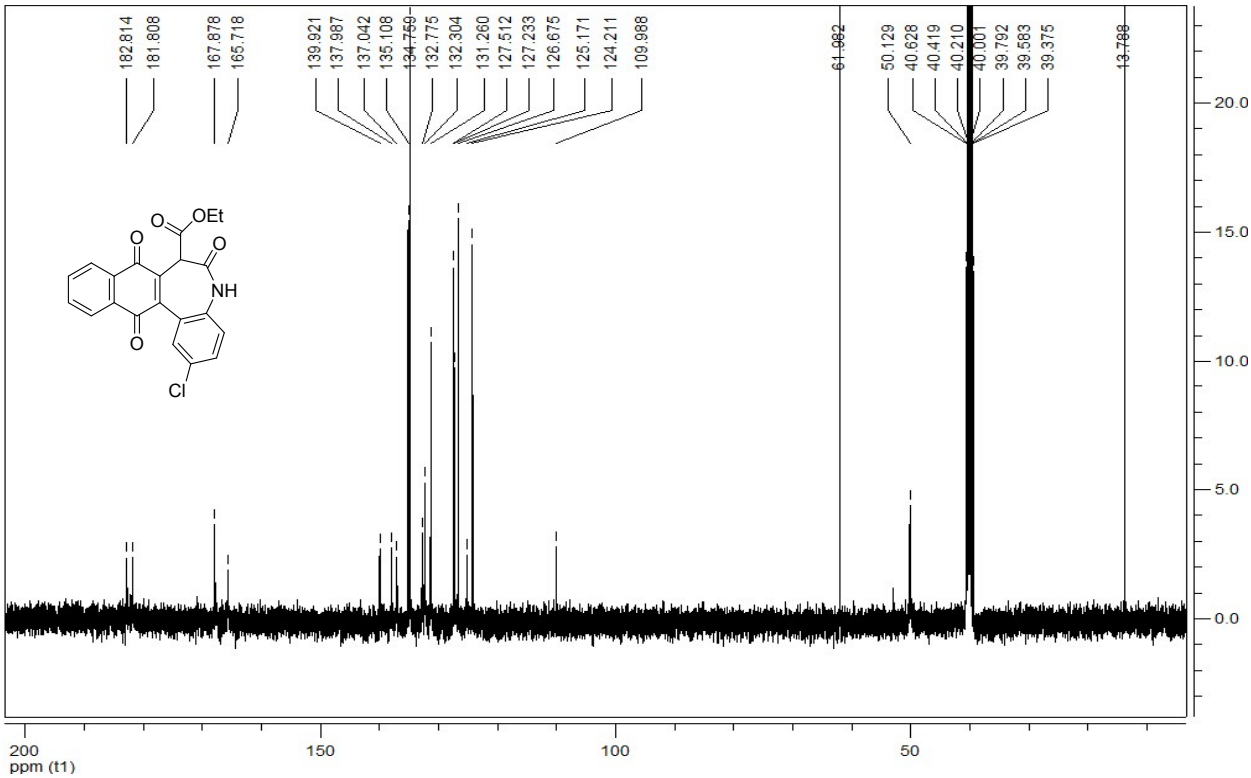
Ethyl 2-fluoro-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (2g): yellow solid, 68%, m.p. 276 – 278 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.74 (br, 1H, NH), 8.15 – 8.11 (m, 2H, ArH), 7.95 – 7.94 (m, 2H, ArH), 7.49 (d, J = 8.4 Hz, 1H, ArH), 7.43 – 7.42 (m, 1H, ArH), 7.27 – 7.26 (m, 1H, ArH), 5.43 (s, 1H, CH), 3.76 – 3.70 (m, 2H, CH_2), 0.76 – 0.72 (m, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.4, 181.4, 167.6, 165.3, 157.1 (d, J = 239.2 Hz), 139.6, 137.6, 134.7, 134.3, 134.2, 132.3, 130.9, 126.8, 126.2, 124.9 (d, J = 9.4 Hz), 124.0 (d, J = 7.8 Hz), 118.6 (d, J = 21.0 Hz), 118.3 (d, J = 23.8 Hz), 61.5, 49.6, 13.4; IR (KBr) υ: 3194, 3092, 2969, 2901, 1751, 1684, 1670, 1592, 1501, 1483, 1373, 1328, 933, 830, 771 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{14}FNNaO_5$ ([M+Na]$^{+}$): 402.0748, Found: 402.0749.



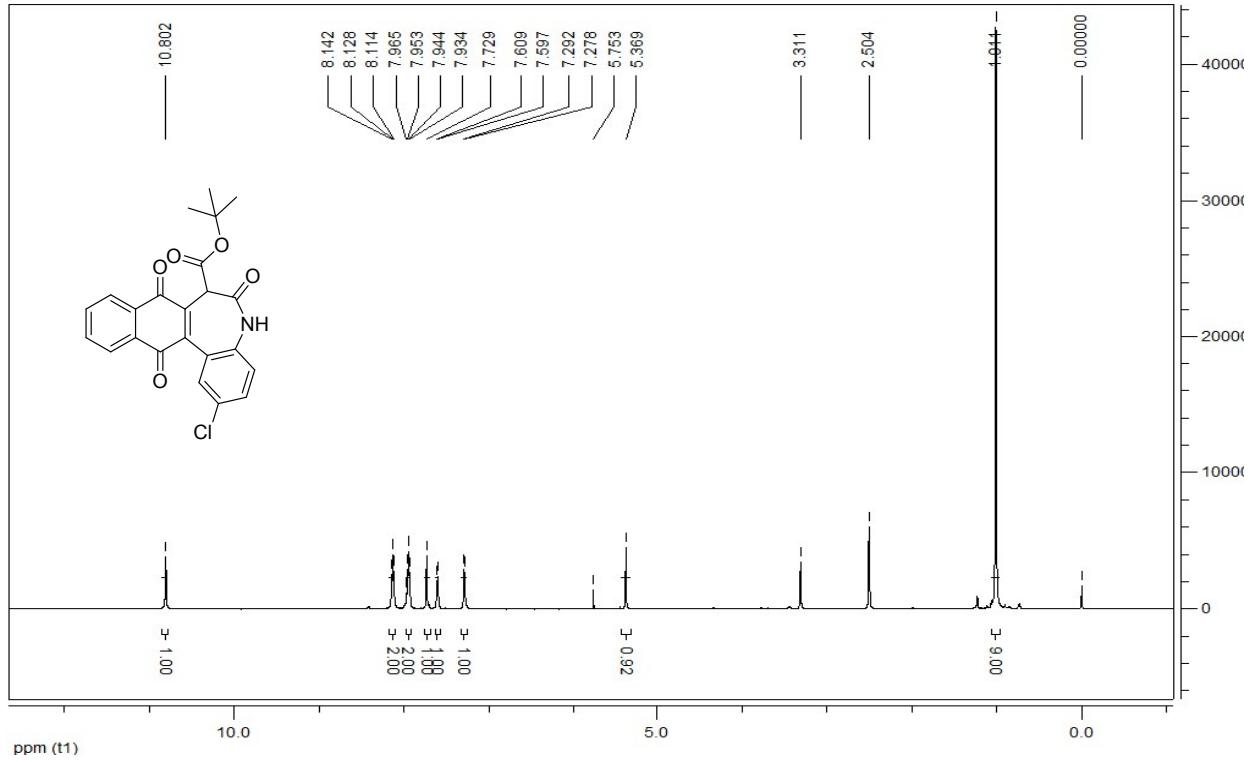


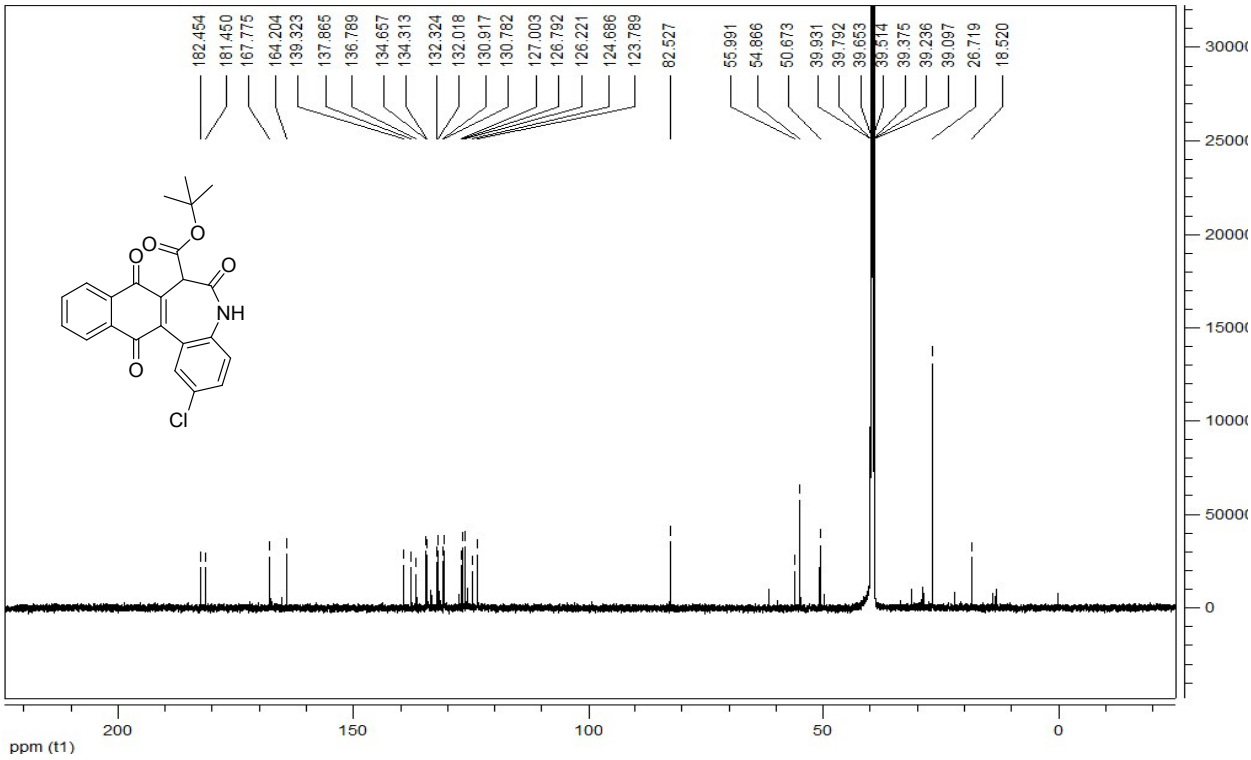
Ethyl 2-chloro-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (2h): yellow solid, 70%, m.p. 232 – 234 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.82 (br, 1H, NH), 8.15 – 8.12 (m, 2H, ArH), 7.96 – 7.95 (m, 2H, ArH), 7.77 – 7.70 (m, 1H, ArH), 7.59 (d, J = 7.2 Hz, 1H, ArH), 7.25 (d, J = 8.4 Hz, 1H, ArH), 5.44 (s, 1H, CH), 3.78 – 3.69 (m, 2H, CH_2), 0.75 – 0.71 (m, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 182.8, 181.8, 167.9, 165.7, 139.9, 138.0, 137.0, 135.1, 134.8, 132.8, 132.3, 131.3, 127.5, 127.2, 126.7, 125.2, 124.2, 110.0, 61.1, 50.1, 13.8; IR (KBr) υ: 3069, 2948, 1751, 1688, 1669, 1594, 1479, 1390, 1365, 1324, 941, 827 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{14}ClNNaO_5$ ([M+Na]$^{+}$): 418.0453, Found: 418.0453.



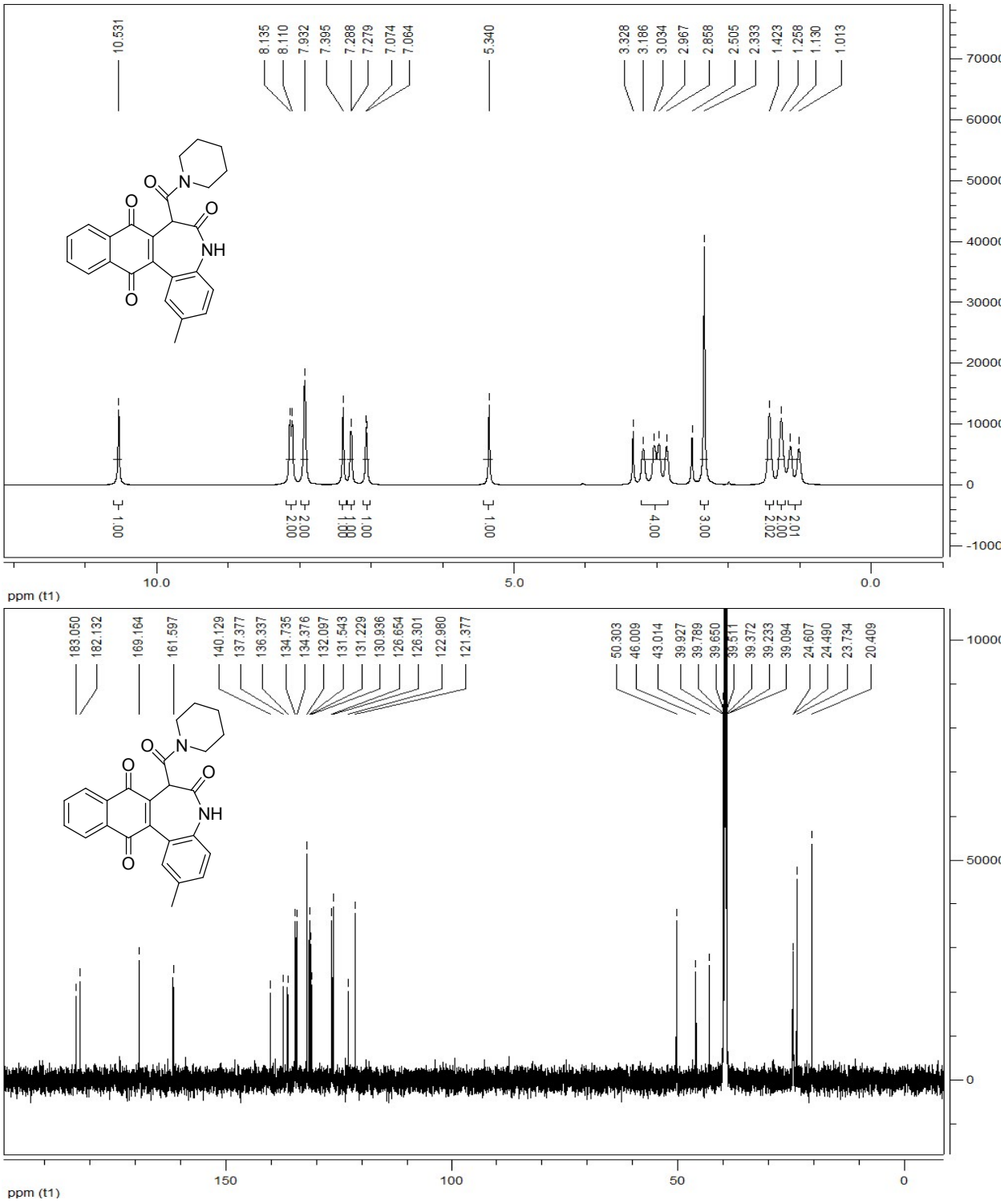


***t*-Butyl 2-chloro-6,8,13-trioxo-6,7,8,13-tetrahydro-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-7-carboxylate (2i):** Yellow Solid, 53%, m.p. 238 – 240 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.80 (br, 1H, NH), 8.14 – 8.11 (m, 2H, ArH), 7.96 – 7.93 (m, 2H, ArH), 7.73 – 7.72 (m, 1H, ArH), 7.60 (d, J = 7.2 Hz, 1H, ArH), 7.28 (d, J = 8.4 Hz, 1H, ArH), 5.37 (s, 1H, CH), 1.01 (s, 9H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.5, 181.4, 167.8, 164.2, 139.3, 137.9, 136.8, 134.7, 134.3, 132.3, 132.0, 130.9, 130.8, 127.0, 126.8, 126.2, 124.7, 123.8, 82.5, 50.7, 26.7; IR (KBr) υ: 3191, 3102, 2940, 1743, 1684, 1605, 1477, 1390, 1362, 1323, 943, 910, 828, 731 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}ClNNaO_5$ ([M+Na]$^{+}$): 446.0766, Found: 446.0771.

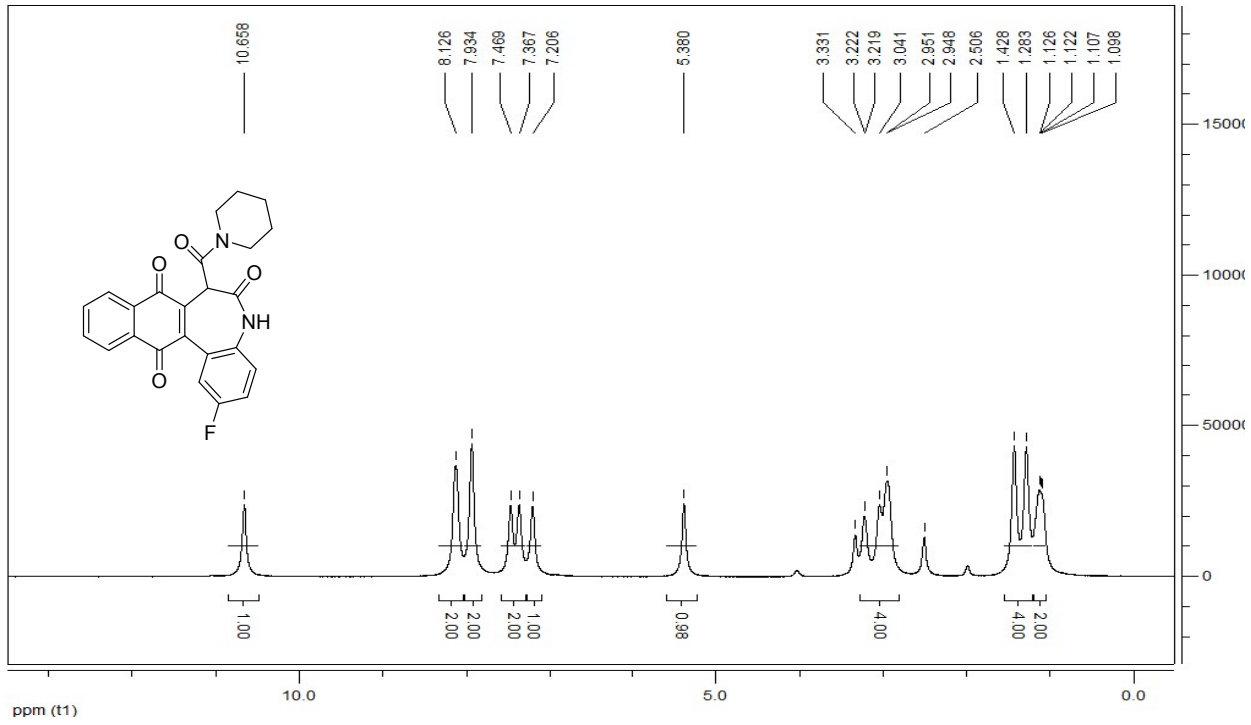


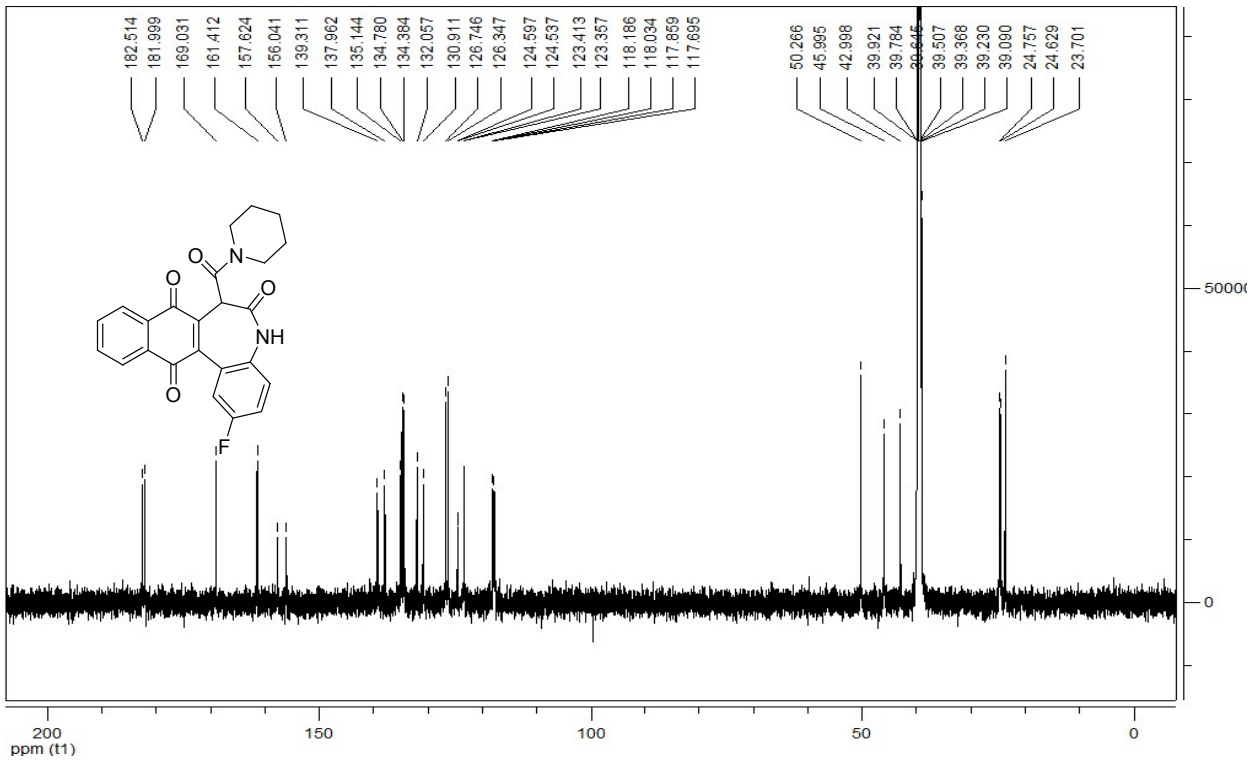


2-Methyl-7-(piperidine-1-carbonyl)- 5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (2j): yellow solid, **49**%, m.p. 238 – 240 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.53 (br, 1H, NH), 8.14 – 8.10 (m, 2H, ArH), 7.94 – 7.93 (m, 2H, ArH), 7.40 – 7.39 (m, 1H, ArH), 7.28 (d, J = 5.4 Hz, 1H, ArH), 7.07 (d, J = 6.0 Hz, 1H, ArH), 5.34 (s, 1H, CH), 3.19 – 2.86 (m, 4H, CH), 2.33 (s, 3H, CH_3), 1.44 – 1.40 (m, 2H, CH), 1.28 – 1.22 (m, 2H, CH), 1.13 – 1.01 (m, 2H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.0, 182.1, 169.2, 161.6, 140.1, 137.4, 136.3, 134.7, 134.4, 132.1 (2C), 131.5, 131.2, 130.9, 126.7, 126.3, 123.0, 121.4, 50.3, 46.0, 43.0, 24.6, 24.5, 23.7, 20.4; IR (KBr) υ: 3195, 3103, 2949, 2859, 1683, 1629, 1395, 1362, 823, 739, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{22}N_2NaO_4$ ([M+Na]$^+$): 437.1472, Found: 437.1479.

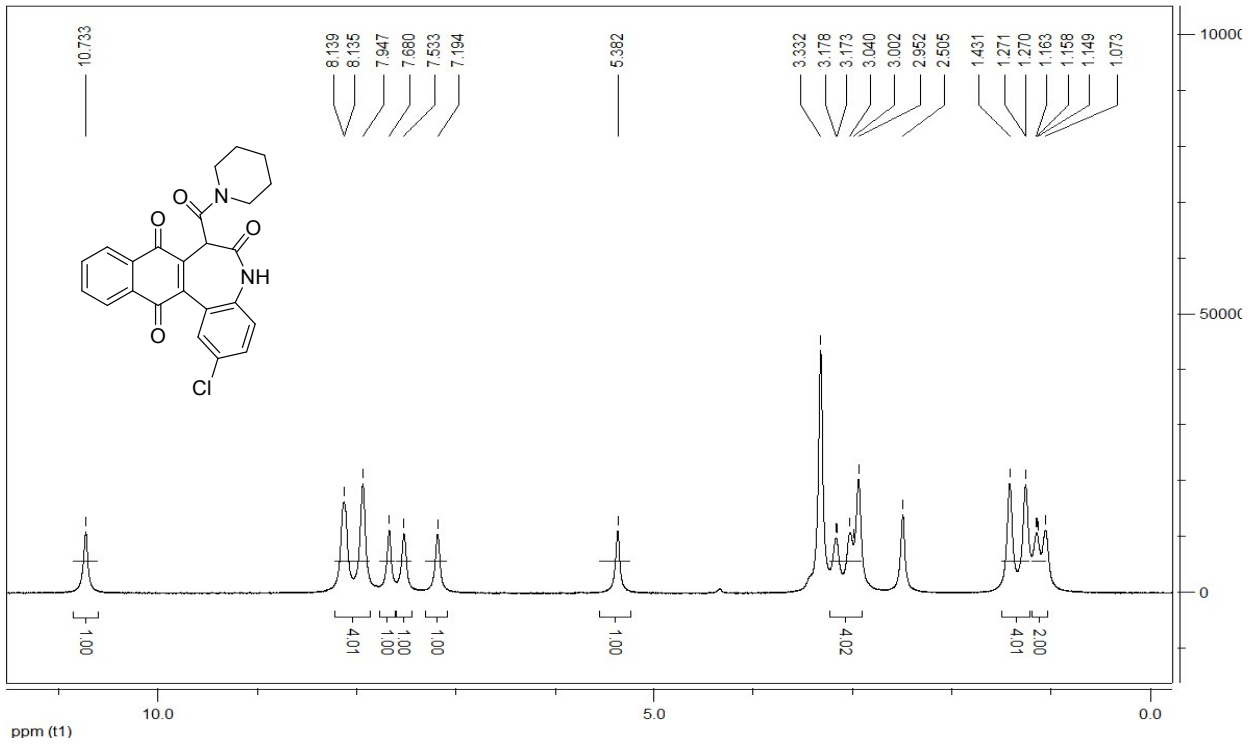


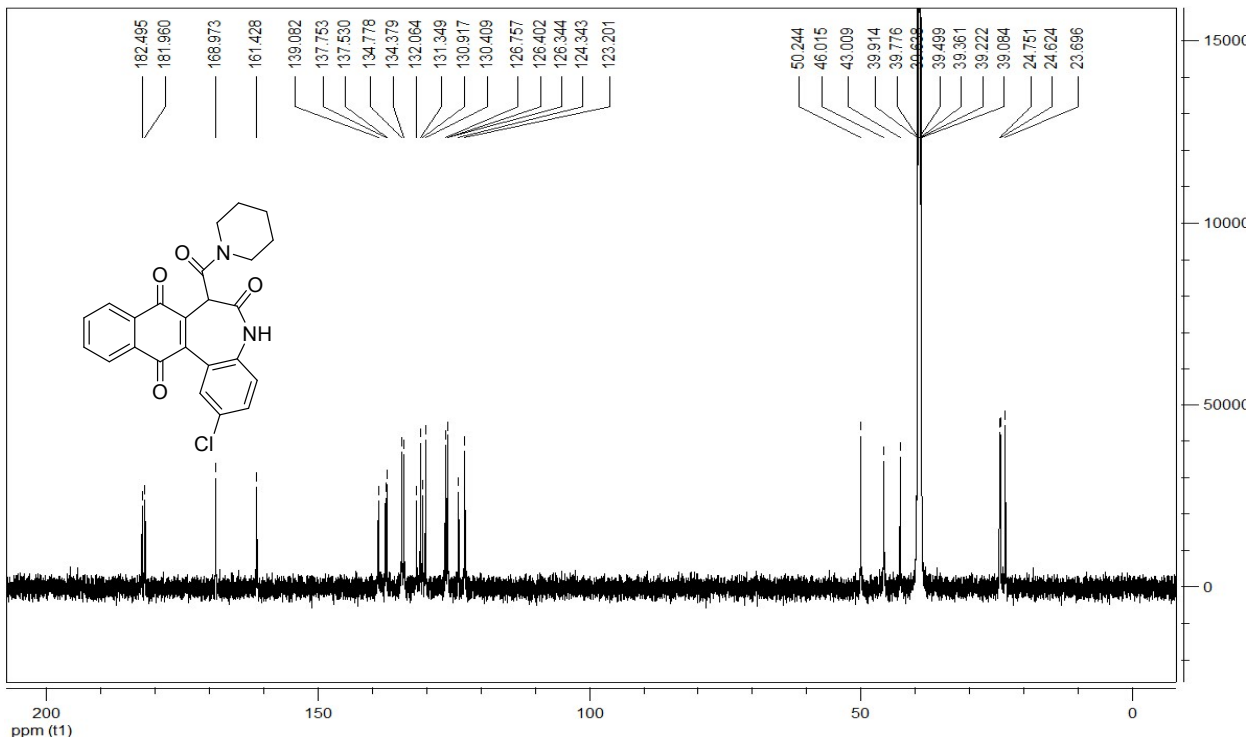
2-Fluoro-7-(piperidine-1-carbonyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (2k): yellow solid, 47%, m.p. 243 – 246 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.66 (br, 1H, NH), 8.13 – 8.12 (m, 2H, ArH), 7.94 – 7.93 (m, 2H, ArH), 7.47 – 7.37 (m, 2H, ArH), 7.21 – 7.20 (m, 1H, ArH), 5.38 (s, 1H, CH), 3.22 – 2.95 (m, 4H, CH), 1.43 – 1.28 (m, 4H, CH), 1.13 – 1.10 (m, 2H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.5, 182.0, 169.0, 161.4, 156.8 (d, J = 237.3 Hz), 139.3, 138.0, 135.1, 134.8, 134.4, 132.1, 130.9, 126.7, 126.3, 124.6 (d, J = 9.0 Hz), 123.4 (d, J = 8.4 Hz), 118.1 (d, J = 22.8 Hz), 117.8 (d, J = 24.6 Hz), 50.3, 46.0, 43.0, 24.8, 24.6, 23.7; IR (KBr) υ: 3467, 3160, 2943, 2855, 1705, 1665, 1616, 1495, 1447, 1356, 1293, 1132, 1066, 944, 867, 823, 796, 740 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{19}FN_2NaO_4$ ([M+Na]$^+$): 441.1221, Found: 441.1226.





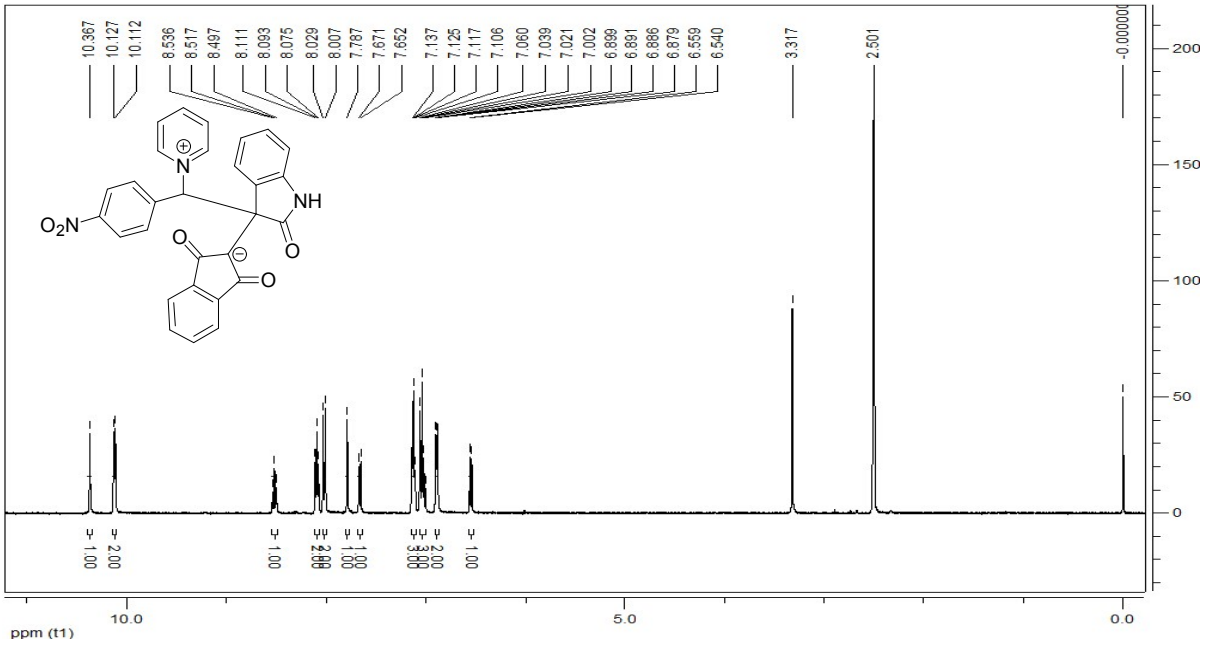
2-Chloro-7-(piperidine-1-carbonyl)-5*H*-benzo[*b*]naphtho[2,3-*d*]azepine-6,8,13(7*H*)-trione (2l): yellow solid, **55**%, m.p. 239 – 241 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.73 (br, 1H, NH), 8.14 – 7.95 (m, 4H, ArH), 7.69 – 7.67 (m, 1H, ArH), 7.54 – 7.53 (m, 1H, ArH), 7.20 – 7.19 (m, 1H, ArH), 5.38 (s, 1H, CH), 3.18 – 2.95 (m, 4H, CH), 1.43 – 1.27 (m, 4H, CH), 1.16 – 1.07 (m, 2H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.5, 182.0, 169.0, 161.4, 139.1, 137.8, 137.6, 134.8, 134.4, 132.1, 131.3, 130.9, 130.4, 126.8, 126.4, 126.3, 124.3, 123.2, 50.2, 46.0, 43.0, 24.8, 24.6, 23.7; IR (KBr) υ: 3197, 3107, 2949, 2857, 1687, 1628, 1485, 1452, 1387, 854, 783, 741 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{19}ClN_2NaO_4$ ([M+Na]$^{+}$): 457.0926, Found: 457.0926.

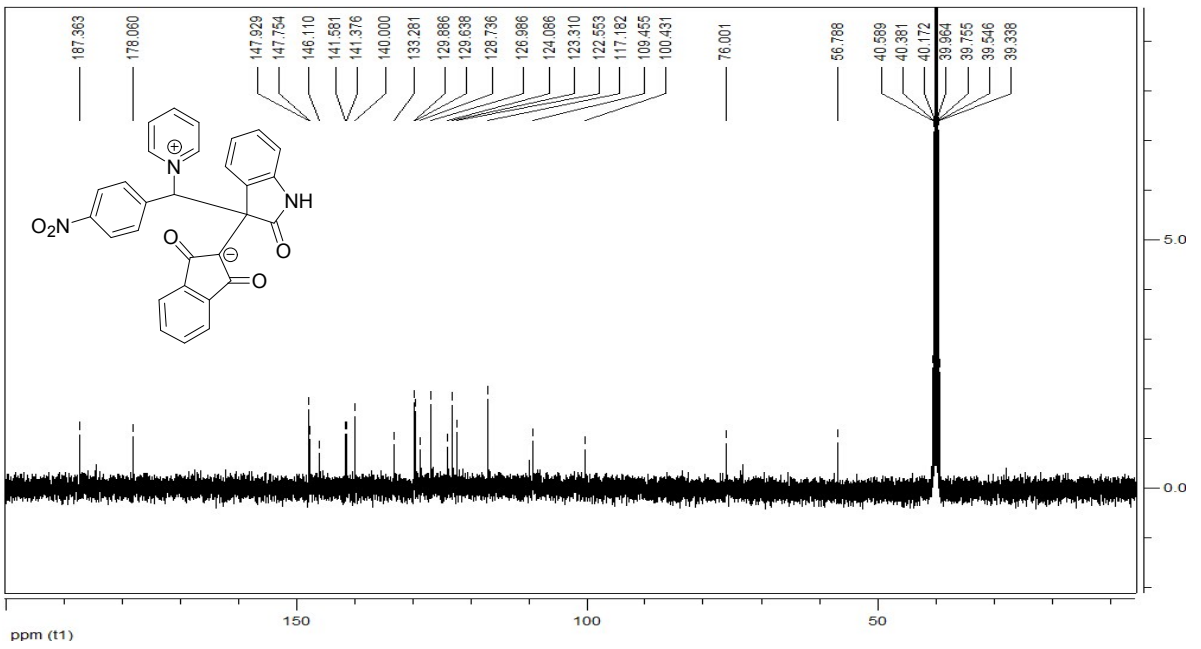




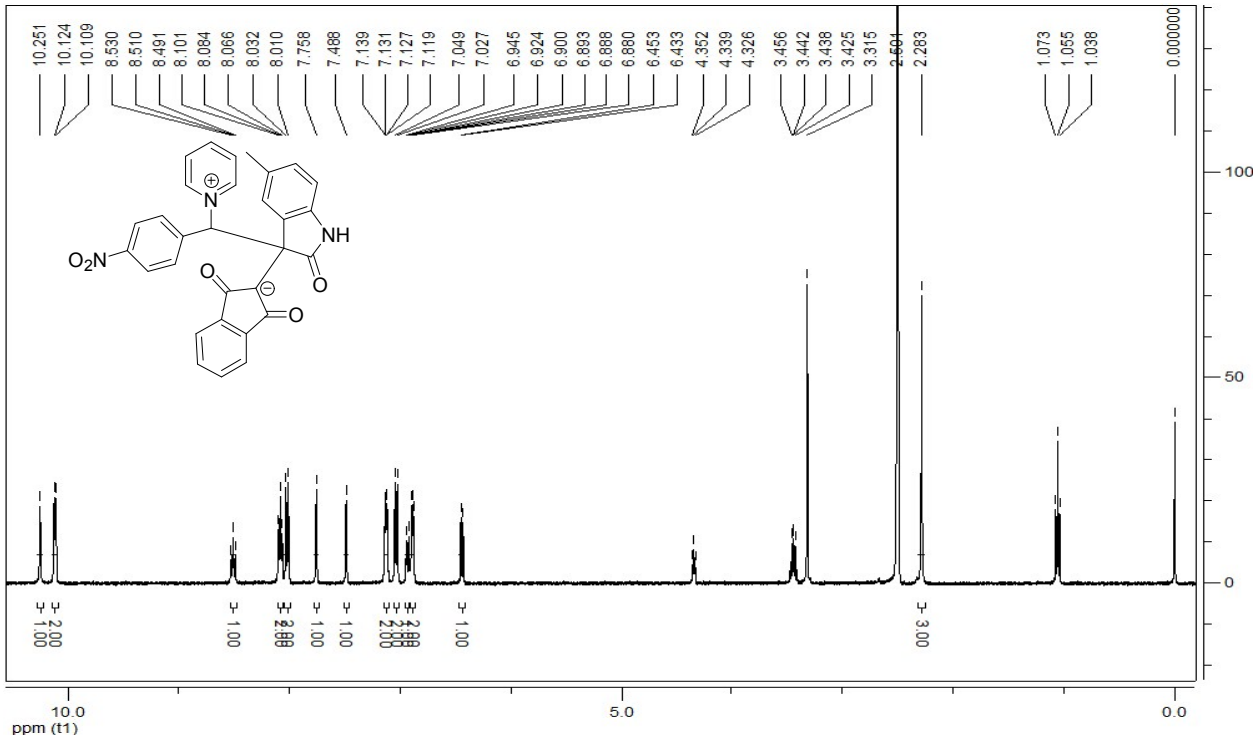
2. General procedure for synthesis of zwitterionic compounds 3a-3d from the reaction of pyridinium salts with isatins and indene-1,3-dione: A mixture of *N*-(4-nitrobenyl)pyridinium salts (0.6 mmol), isatin (0.5 mmol), indene-1,3-dione (0.5 mmol) and triethylamine (0.5 mmol) in ethanol (20 mL) was stirred at room temperature for about one hour. Then the mixture was refluxed for 24 hours. After cooling, the resulting precipitates were collected by filtration and washed with cold alcohol to give pure product for analysis.

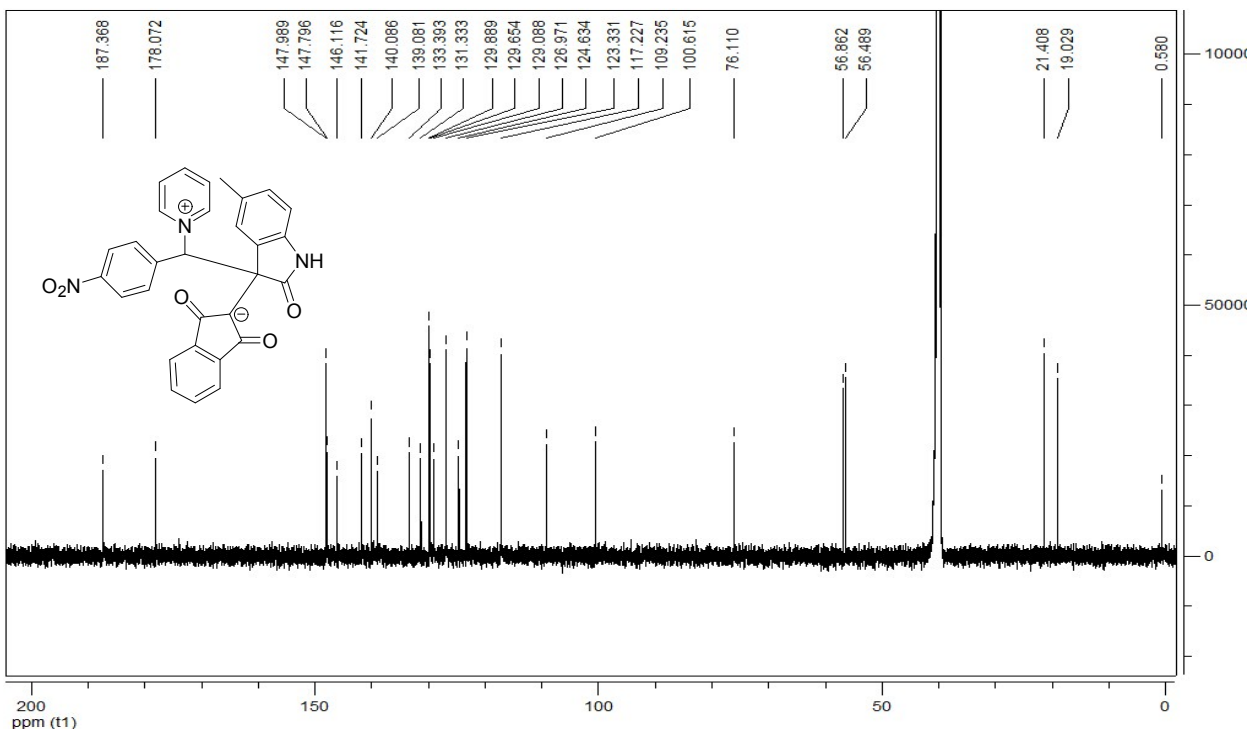
2-(3-((4-Nitrophenyl)(pyridin-1-ium-1-yl)methyl)-2-oxoindolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (3a): yellow solid, 81%, m.p. 230 – 231 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.37 (br, 1H, NH), 10.12 (d, *J* = 6.0 Hz, 2H, ArH), 8.52 (t, *J* = 7.6 Hz, 1H, ArH), 8.09 (t, *J* = 7.2 Hz, 2H, ArH), 8.02 (d, *J* = 8.8 Hz, 2H, ArH), 7.79 (s, 1H, CH), 7.66 (d, *J* = 7.6 Hz, 1H, ArH), 7.14 – 7.11 (m, 3H, ArH), 7.06 – 7.00 (m, 3H, ArH), 6.90 – 6.88 (m, 2H, ArH), 6.55 (d, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 187.4, 178.1, 147.9, 147.8, 146.1, 141.6, 141.4, 140.0, 133.3, 129.9, 129.6, 128.7, 127.0, 124.1, 123.3, 122.6, 117.2, 109.5, 100.4, 76.0, 56.8; IR (KBr) υ: 3168, 3087, 1716, 1652, 1616, 1540, 1473, 1398, 1346, 1264, 1226, 1160, 1099, 940, 876, 842, 754 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{19}N_3NaO_5$ ([M+Na]$^+$): 512.1217, Found: 512.1219.



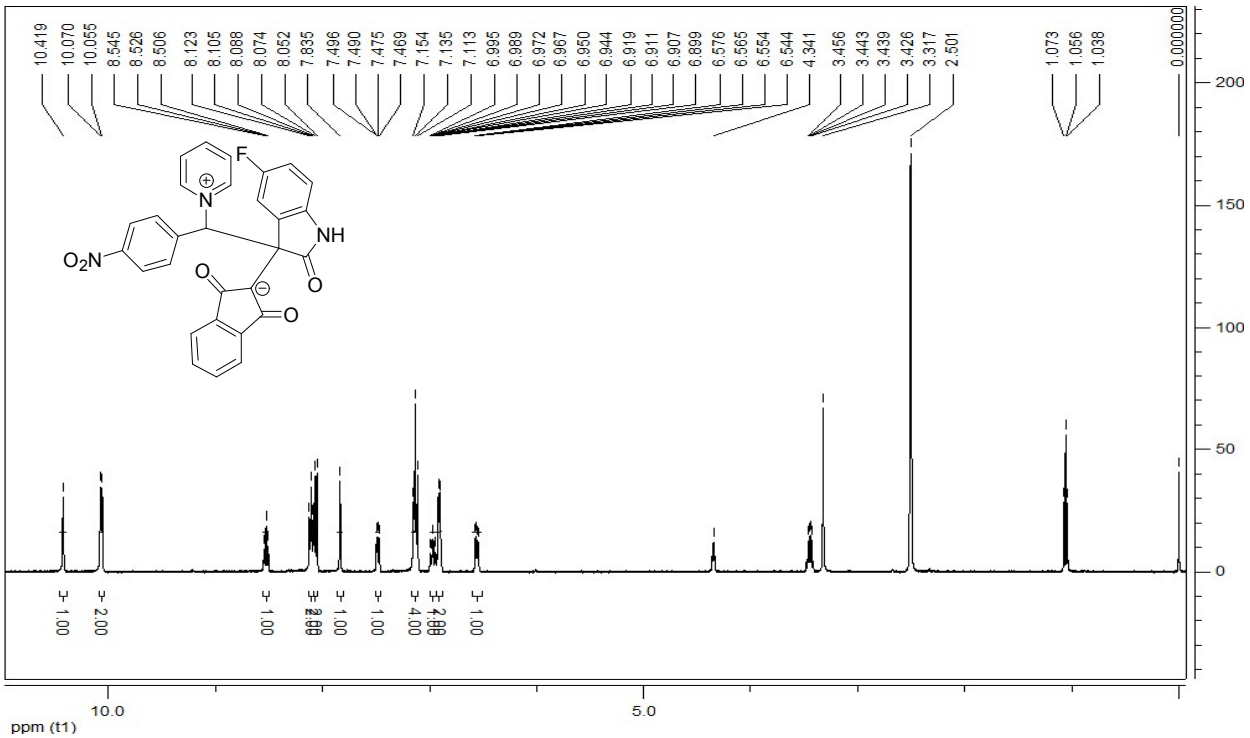


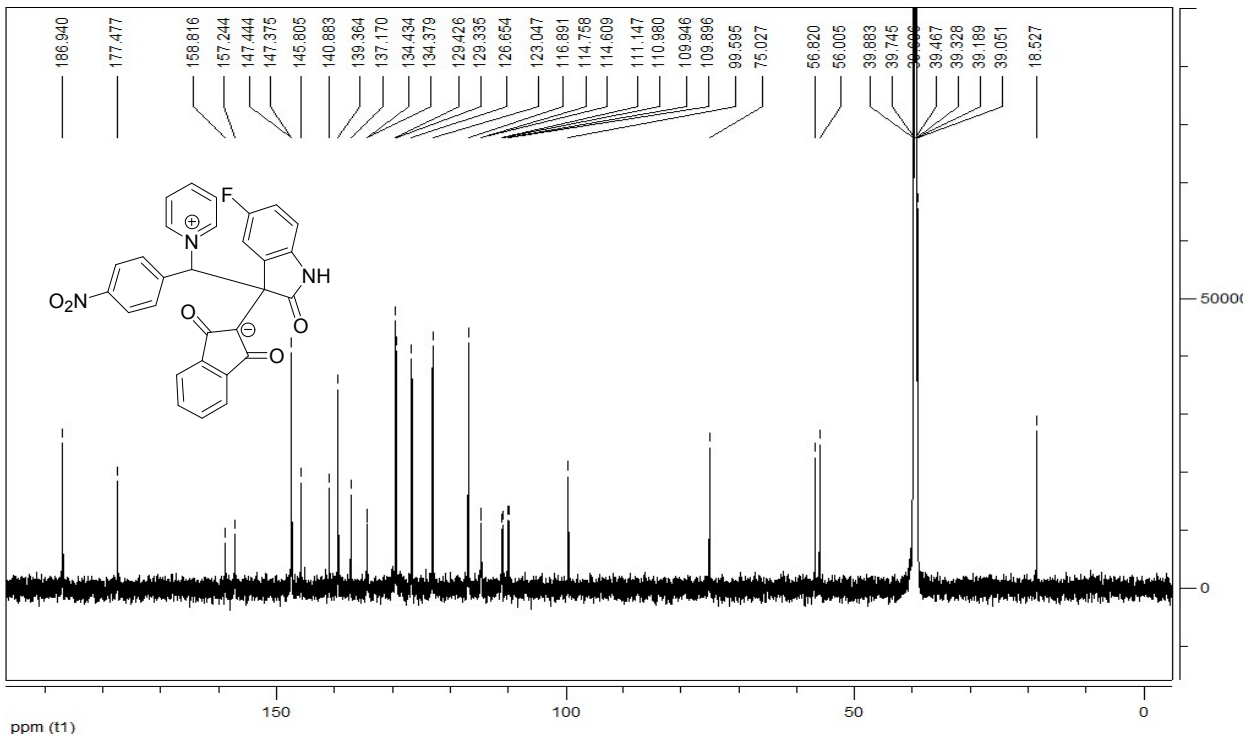
2-(5-Methyl-3-((4-nitrophenyl)(pyridin-1-ium-1-yl)methyl)-2-oxoindolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (3b): yellow solid, 75%, m.p. 225 – 226 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.25 (br, 1H, NH), 10.11 (d, J = 6.0 Hz, 2H, ArH), 8.51 (t, J = 7.6 Hz, 1H, ArH), 8.08 (t, J = 7.2 Hz, 2H, ArH), 8.02 (d, J = 8.8 Hz, 2H, ArH), 7.76 (s, 1H, CH), 7.49 – 7.48 (m, 1H, ArH), 7.14 – 7.12 (m, 2H, ArH), 7.04 (d, J = 8.8 Hz, 2H, ArH), 6.94 (d, J = 8.4 Hz, 1H, ArH), 6.90 – 6.88 (m, 2H, ArH), 6.44 (d, J = 8.0 Hz, 1H, ArH), 2.28 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 187.4, 178.1, 148.0, 147.8, 146.1, 141.7, 140.1, 139.1, 133.4, 131.3, 129.9, 129.7, 129.1, 127.0, 124.7, 123.3, 117.2, 109.2, 100.6, 76.1, 56.8, 21.4; IR (KBr) υ: 3166, 3021, 2962, 1714, 1610, 1575, , 1494, 1411, 1344, 876, 811, 769 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{21}N_3NaO_5$ ([M+Na]$^+$): 526.1373, Found: 526.1370.



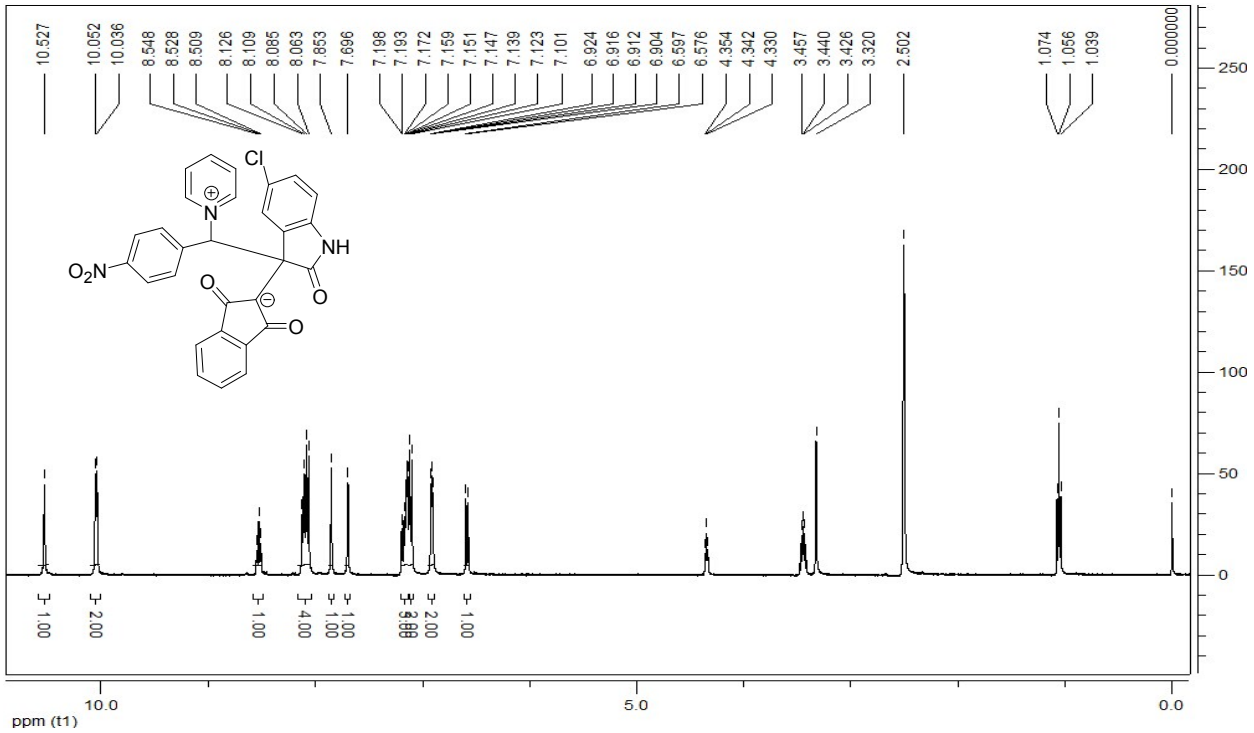


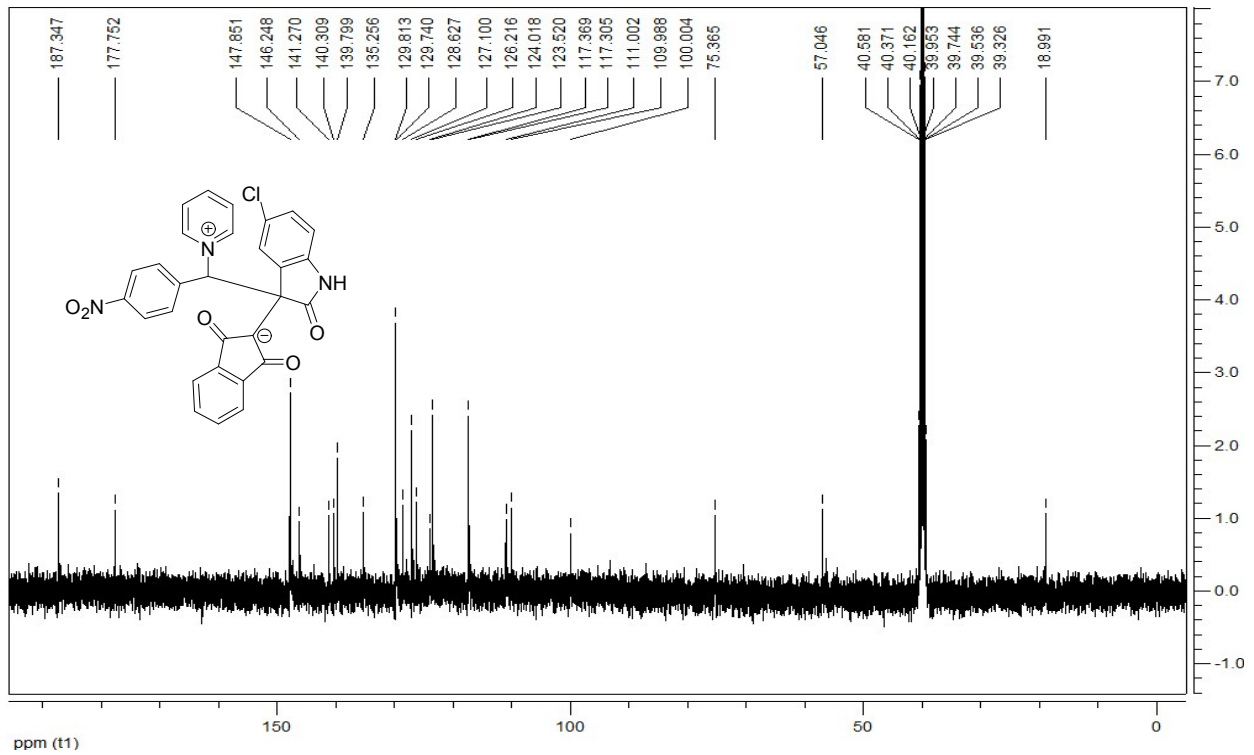
2-(5-Fluoro-3-((4-nitrophenyl)(pyridin-1-ium-1-yl)methyl)-2-oxoindolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (3c): yellow solid, 82%, m.p. 224 – 225 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.42 (br, 1H, NH), 10.06 (d, J = 6.0 Hz, 2H, ArH), 8.53 (t, J = 7.6 Hz, 1H, ArH), 8.10 (t, J = 6.8 Hz, 2H, ArH), 8.06 (d, J = 8.8 Hz, 2H, ArH), 7.84 (s, 1H, CH), 7.50 – 7.47 (m, 1H, ArH), 7.15 – 7.11 (m, 4H, ArH), 7.00 – 6.94 (m, 1H, ArH), 6.92 – 6.90 (m, 2H, ArH), 6.58 – 6.54 (m, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 186.9. 177.5, 158.0 (d, J = 235.8 Hz), 147.4, 147.3, 145.8, 140.9, 139.4, 137.2, 134.4 (d, J = 8.3 Hz), 129.4, 129.3, 126.7, 123.0, 116.9, 114.7 (d, J = 22.4 Hz), 110.1 (d, J = 25.0 Hz), 109.9 (d, J = 7.5 Hz), 99.6, 75.0, 56.8; IR (KBr) υ: 3144, 2923, 1715, 1629, 1608, 1487, 876, 810, 766 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{18}FN_3NaO_5$ ([M+Na]$^{+}$): 530.1123, Found: 530.1122.





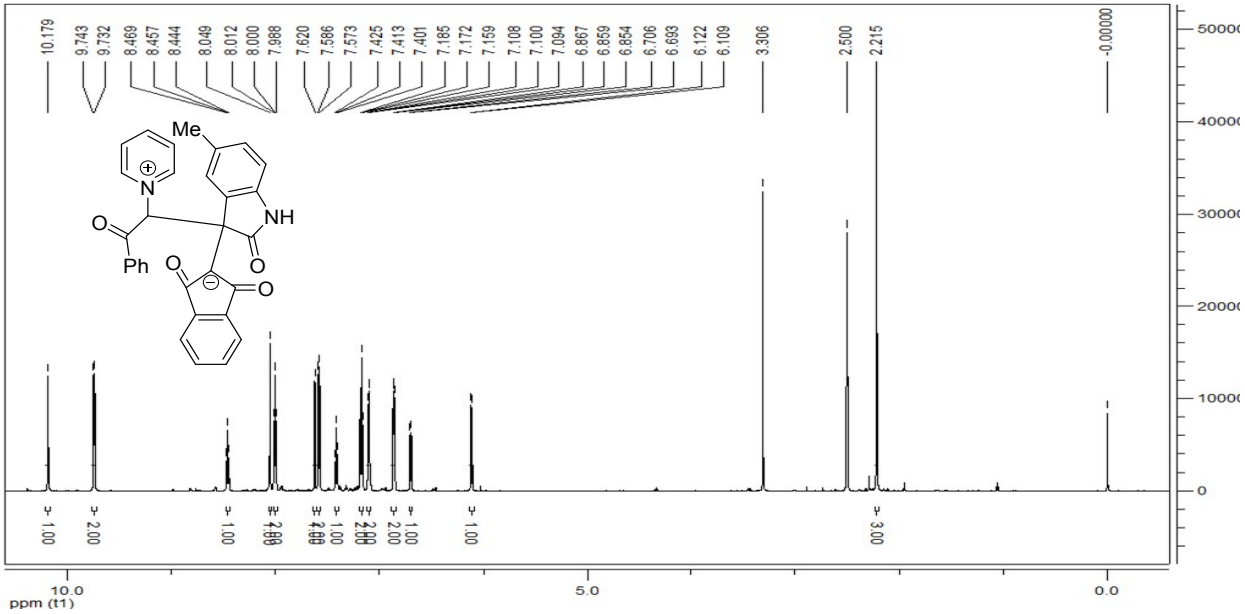
2-(5-Chloro-3-((4-nitrophenyl)(pyridin-1-ium-1-yl)methyl)-2-oxoindolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (3d): yellow solid, 70%, m.p. 220 – 221 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ : 10.50 (br, 1H, NH), 10.04 (d, J = 6.0 Hz, 2H, ArH), 8.53 (t, J = 8.0 Hz, 1H, ArH), 8.13 – 8.06 (m, 4H, ArH), 7.85 (s, 1H, CH), 7.70 – 7.69 (m, 1H, ArH), 7.20 – 7.14 (m, 3H, ArH), 7.11 (d, J = 4.4 Hz, 2H, ArH), 6.92 (m, 2H, ArH), 6.59 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 187.3, 177.8, 147.9, 146.2, 141.3, 140.3, 139.8, 135.3, 129.8, 128.6, 127.1, 126.2, 124.0, 123.5, 117.4, 117.3, 111.0, 110.0, 100.0, 75.4, 57.0; IR (KBr) υ: 3143, 3047, 2843, 1716, 1638, 1608, 1476, 876, 770 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{18}ClN_3NaO_5$ ([M+Na]$^+$): 546.0827, Found: 546.0827.

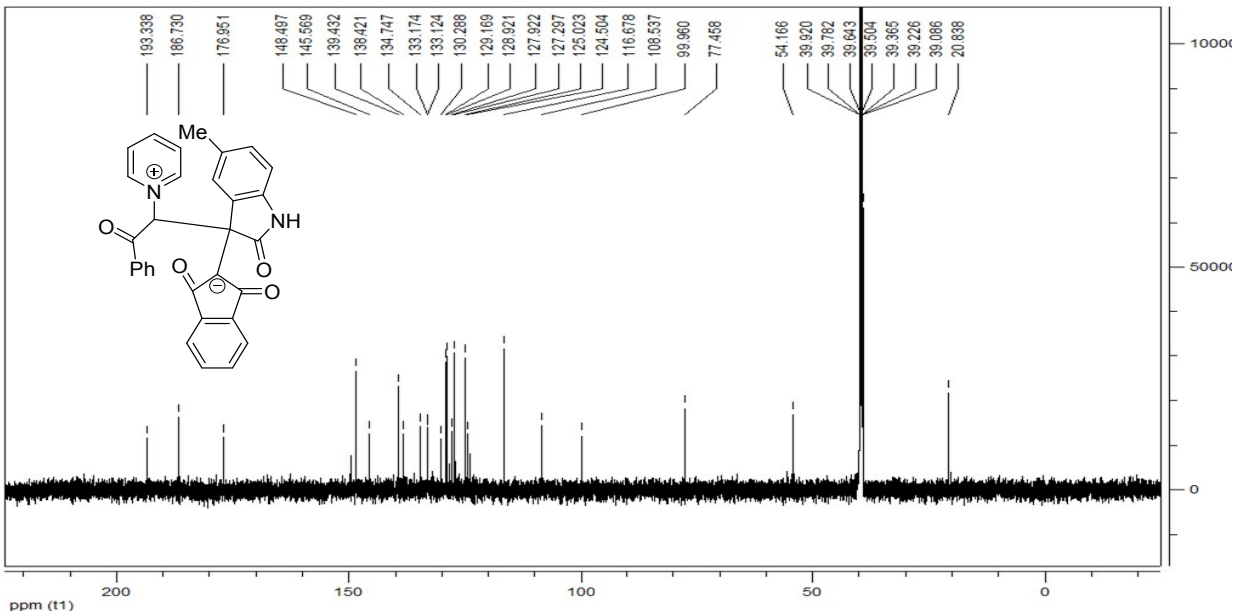




3. General procedure for synthesis of zwitterionic compounds 4a-4b from the reaction of pyridinium salts with isatins and indene-1,3-dione: A mixture of pyridinium salts (0.6 mmol), isatin (0.5 mmol), indene-1,3-dione (0.5 mmol) and triethylamine (0.5 mmol) in ethanol (20 mL) was stirred at room temperature overnight. The resulting precipitates were collected by filtration and washed with cold alcohol to give pure product for analysis.

2-(5-Methyl-2-oxo-3-(2-oxo-2-phenyl-1-(pyridin-1-ium-1-yl)ethyl)indolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (**4a**): Yellow Solid, 90%, m.p. 208 – 209 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.18 (br, 1H, NH), 9.74 (d, J = 7.2 Hz, 2H, ArH), 8.46 (d, J = 7.8 Hz, 1H, ArH), 8.05 (s, 1H, ArH), 8.00 (t, J = 7.2 Hz, 2H, ArH), 7.62 (s, 1H, CH), 7.58 (d, J = 9.0 Hz, 2H, ArH),7.41 (t, J = 7.2 Hz, 1H, ArH), 7.17 (t, J = 7.8 Hz, 2H, ArH), 7.11 – 7.09 (m, 2H, ArH), 6.87 – 6.85 (m, 2H, ArH), 6.70 (d, J = 7.8 Hz, 1H, ArH), 6.12 (d, J = 7.8 Hz, 1H, ArH), 2.22 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 193.3, 186.7, 177.0, 148.5, 145.6, 139.4, 138.4, 134.7, 133.2, 133.1, 130.3, 129.2, 128.9, 127.9, 127.3, 125.0, 124.5, 116.7, 108.5, 100.0, 77.5, 54.2, 20.8; IR (KBr) υ: 3064, 2970, 2805, 1692, 1613, 1534, 1416, 1314, 903, 804, 767 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{22}N_2O_4$ ([M+H]$^+$): 509.1472, Found: 509.1478.





2-(5-Chloro-3-(2-methoxy-2-oxo-1-(pyridin-1-ium-1-yl)ethyl)-2-oxoindolin-3-yl)-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (**4b**): Yellow Solid, 85%, m.p. 184 – 186 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.84 (br, 1H, NH), 9.64 (d, J = 6.0 Hz, 2H, ArH), 8.48 (t, J = 7.2 Hz, 1H, ArH), 8.03 (t, J = 7.2 Hz, 2H, ArH), 7.79 – 7.78 (m, 1H, ArH), 7.33 (s, 1H, CH), 7.15 (d, J = 8.4 Hz, 1H, ArH), 7.10 – 7.09 (m, 2H, ArH), 6.85 – 6.84 (m, 2H, ArH), 6.78 (d, J = 8.4 Hz, 1H, ArH), 3.52 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 186.4, 178.9, 167.2, 148.5, 146.2, 140.1, 139.0, 136.7, 129.3, 127.1, 125.6, 125.2, 122.5, 116.8, 110.4, 99.4, 74.5, 54.5, 53.2; IR (KBr) υ: 3042, 2839, 1719, 1613, 1535, 1479, 735, 686 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{18}ClN_2O_5$ ([M+H]$^+$): 461.0899, Found: 461.0893.