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First example of isatin used in four-component synthesis of ionic unsymmetrical scaffold with three different heterocyclic rings

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General information

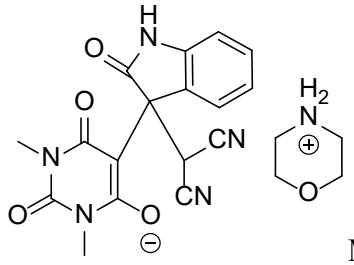
The solvents and reagents were purchased from commercial sources and used as received. Isatin **1i** was obtained from isatin **1a** and bromine in acetic acid according to literature data [B.B. Semenov *et al. Russ. Chem. Bull., Int. Ed.,* 2005, **54**, 988. https://doi.org/10.1007/s11172-005-0345-x].

All melting points were measured with a Gallenkamp melting-point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 with a Bruker AM300 spectrometer at ambient temperature. Two-dimensional (2D) NMR spectra were registered with a Bruker AV400 spectrometer at ambient temperature. Chemical shift values are relative to Me_4Si. In some cases, the cationic amino groups of salts were subjected to exchange processes in DMSO-d_6 and were absent from ^{1}H NMR spectra or had underestimated integral values. The IR spectrum was recorded with a Bruker ALPHA-T FT-IR spectrometer in a KBr pellet. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

Typical procedure

Isatin **1** (1 mmol), barbituric acid **2** (1 mmol), malononitrile (1 mmole) and morpholine (1 mmol) were stirred in 4 ml of ethanol for 1 h at ambient temperature. Then solvent was evaporated and the solid was crystallized from ethanol to isolate **3b-d,f.** In the case **3a,e,j-l** the reaction mixture was evaporated to the volume 1 ml, cooled to 0° for 2 h. After the formed solid was filtered, and rinsed with an ice-cold ethanol/water solution (1:1, 2 mL), and dried.

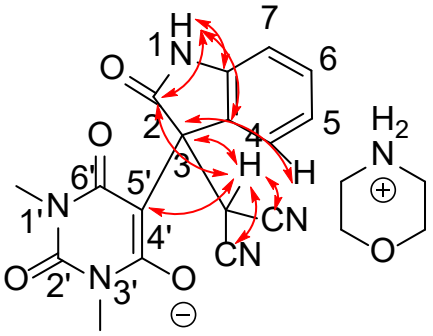
Characterization of synthesized compounds



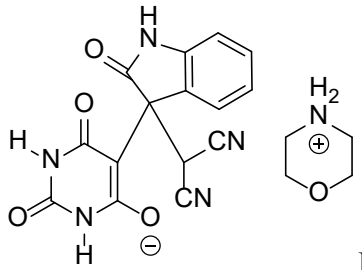
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3a).

Yield 0.40 g (91%), mp: 147-149 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.03 (s, 6H, 2 CH_3), 3.11 (t, ^{3}J = 4.8 Hz, 4H, 2 OCH_2), 3.77 (t, ^{3}J = 4.8 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 6.76 (d, ^{3}J = 7.7 Hz, 1H, CH Ar), 6.85 (t, ^{3}J = 7.6 Hz, 1H, CH Ar), 6.92 (s, 1H, CH), 7.15 (t, ^{3}J = 7.6 Hz, 1H, CH Ar), 7.32 (d, ^{3}J = 7.7 Hz, 1H, CH Ar), 7.90-9.42 (br s, 2H, NH_2^+ exch.), 10.33 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 26.9 (2C), 28.9, 43.0 (2C), 52.7, 63.4 (2C), 82.3, 108.9, 113.3, 113.4, 121.3 123.6, 128.4, 131.2, 142.6, 152.3, 161.7 (br, 2C), 176.9 ppm. IR (KBr) ν = 3175, 2976, 2868, 2507, 2256, 2201, 1713, 1577, 1433, 1106, 755 cm^{-1}. ESI-HRMS: found *m/z* 350.0900 $[M - C_4H_{10}NO]^+$; calculated for $C_{17}H_{12}N_5O_4$ 350.0895.

Complete assignment of signals to atoms for compound **3a**



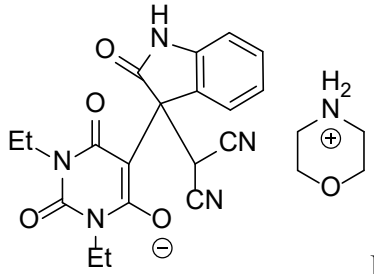
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H, H^1), 8.61 (br s, 2H, NH_2^+), 7.30 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, 1H, H^4), 7.13 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, 1H, H^6), 6.91 (s, 1H, 3-CH), 6.84 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, 1H, H^5), 6.75 (d, ^{3}J = 7.7 Hz, 1H, H^7), 3.80 – 3.70 (m, 4H, $CH_2NH_2^+$), 3.13 – 3.07 (m, 4H, OCH_2), 3.02 (s, 6H, 1'-CH_3, 3'-CH_3) ppm.
^{13}C NMR (101 MHz, DMSO-d_6) δ 176.9 (C^2), 161.7 (2C, $C^{4'}$, $C^{6'}$), 152.2 ($C^{2'}$), 142.6 (C^{7a}), 131.2 (C^{3a}), 128.4 (C^6), 123.6 (C^4), 121.2 (C^5), 113.4 (CN), 113.3 (CN), 108.9 (C^7), 82.3 ($C^{5'}$), 63.4 (2C, CH_2O), 52.6 (C^3), 43.0 (2C, $CH_2NH_2^+$), 28.9 (3-CH), 26.9 (2C, N-CH_3) ppm.



Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3b).

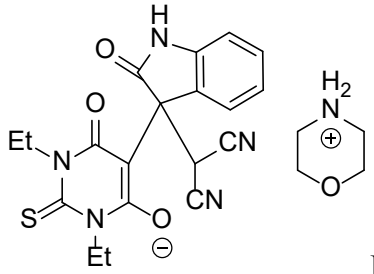
Yield 0.33 g (80%), mp: 234-236 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.00–3.18 (m, 4H, 2 OCH_2), 3.68–3.82 (m, 4H, 2 $C\underline{H_2}NH_2^+$), 6.76 (d, ^{3}J = 7.5 Hz, 1H, CH Ar), 6.88 (t, ^{3}J = 7.4 Hz, 1H, CH Ar), 6.97 (s, 1H, CH), 7.15 (t, ^{3}J = 7.5 Hz, 1H, CH Ar), 7.34 (d, ^{3}J = 7.4 Hz, 1H, CH

Ar), 9.31 (s, 2H, 2 NH $_{barb.}$), 10.38 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.7, 43.0 (2C), 52.0, 63.5 (2C), 81.9, 108.9, 113.2, 113.4, 121.3 123.6, 128.5, 131.3, 142.4, 151.5, 164.1 (br, 2C), 176.8 ppm. IR (KBr) v = 3305, 3234, 3178, 2974, 2194, 1714, 1645, 1617, 1474, 1311, 1111 cm^{-1}.ESI-HRMS: found *m/z* 322.0577 [M – $C_4H_{10}NO$]$^+$; calculated for $C_{15}H_8N_5O_4$ 322.0582.



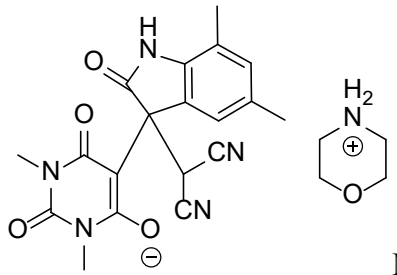
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-diethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3c).

Yield 0.41 g (87%), mp: 138-140 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.85-1.14 (m, 6H, 2 CH_3), 3.11 (t, ^3J = 4.7 Hz, 4H, 2 OCH_2), 3.52–3.90 (m, 8H, 2 CH_2 + 2 $C\underline{H_2}NH_2^+$), 6.77 (d, ^3J = 7.6 Hz, 1H, CH Ar), 6.86 (t, ^3J = 7.5 Hz, 1H, CH Ar), 6.94 (s, 1H, CH), 7.15 (t, ^3J = 7.5 Hz, 1H, CH Ar), 7.31 (d, ^3J = 7.5 Hz, 1H, CH Ar), 8.01-9.30 (br s, 2H, NH_2^+ exch.), 10.32 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.8 (2C), 29.0, 34.3 (2C), 43.0 (2C), 52.7, 63.4 (2C), 82.4, 108.9, 113.3, 113.4, 121.2 123.6, 128.4, 131.2, 142.6, 152.4, 161.6 (br, 2C), 176.9 ppm. IR (KBr) v = 3434, 2980, 2872, 2515, 2255, 2200, 1712, 1573, 1439, 1108, 754 cm^{-1}. ESI-HRMS: found *m/z* 378.1198 [M – $C_4H_{10}NO$]$^+$; calculated for $C_{19}H_{16}N_5O_4$ 378.1208.



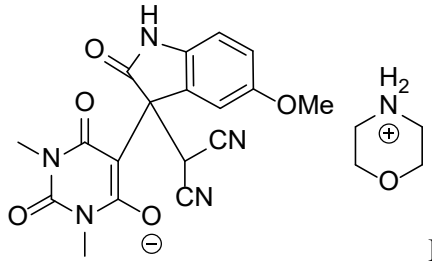
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-diethyl-6-oxo-2-thioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3d).

Yield 0.40 g (83%), mp: 193-194 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.01-1.22 (m, 6H, 2 CH_3), 3.11 (t, ^3J = 4.7 Hz, 4H, 2 OCH_2), 3.77 (t, ^3J = 4.7 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 4.20-4.51 (m, 4H, 2 CH_2), 6.77 (d, ^3J = 7.4 Hz, 1H, CH Ar), 6.81 (s, 1H, CH), 6.88 (t, ^3J = 7.4 Hz, 1H, CH Ar), 7.18 (t, ^3J = 7.4 Hz, 1H, CH Ar), 7.31 (d, ^3J = 7.4 Hz, 1H, CH Ar), 7.97-9.45 (br s, 2H, NH_2^+ exch.), 10.40 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.6 (2C), 29.0, 41.4 (2C), 42.9 (2C), 52.4, 63.3 (2C), 87.4, 109.0, 113.1, 113.2, 121.4 123.6, 128.7, 130.3, 142.8, 159.8 (br, 2C), 174.6, 176.4 ppm. IR (KBr) v = 3165, 2982, 2893, 2504, 2253, 1702, 1632, 1564, 1419, 1269, 1108 cm^{-1}.ESI-HRMS: found *m/z* 394.0976 [M – $C_4H_{10}NO$]$^+$; calculated for $C_{19}H_{16}N_5O_3S$ 394.0979.



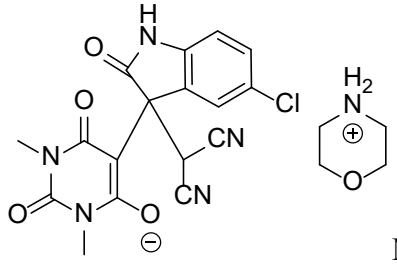
Morpholin-4-ium 5-(3-dicyanomethyl-5,7-dimethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3e).

Yield 0.44 g (98%), mp: 143-145 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.17 (s, 6H, 2 $CH_{3\ isatin}$), 3.04 (s, 6H, 2 CH_3), 3.11 (t, ^{3}J = 4.9 Hz, 4H, 2 OCH_2), 3.76 (t, ^{3}J = 4.9 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 6.78 (s, 1H, CH Ar), 6.89 (s, 1H, CH), 6.96 (s, 1H, CH Ar), 7.82-9.44 (br s, 2H, NH_2^+ exch.), 10.30 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 16.4, 20.6, 26.9 (2C), 29.1, 43.0 (2C), 53.0, 63.4 (2C), 82.5, 113.4, 113.5, 117.7, 121.3 129.9, 130.3, 130.9, 138.8, 152.3, 161.3 (br, 2C), 177.3 ppm. IR (KBr) v = 3465, 3186, 2970, 2863, 2502, 2255, 1716, 1589, 1430, 1107, 873 cm^{-1}. ESI-HRMS: found m/z 378.1198 [M – $C_4H_{10}NO$]$^+$; calculated for $C_{19}H_{16}N_5O_4$ 378.1208.



Morpholin-4-ium 5-(3-dicyanomethyl-5-methoxy-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3f).

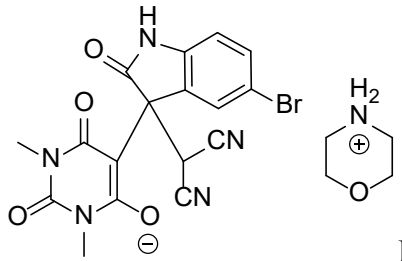
Yield 0.40 g (85%), mp: 193-194 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.04 (s, 6H, 2 CH_3), 3.12 (t, ^{3}J = 4.7 Hz, 4H, 2 OCH_2), 3.66 (s, 2H, OCH_3), 3.77 (t, ^{3}J = 4.7 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 6.63-6.79 (m, 2H, 2 CH Ar), 6.90 (s, 1H, CH), 6.94 (d, ^{4}J = 1.7 Hz, 1H, CH Ar), 8.81 (br s, 2H, NH_2^+), 10.17 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 26.9 (2C), 29.0, 43.0 (2C), 53.1, 55.3, 63.4 (2C), 82.3, 109.2, 110.6, 113.0, 113.3, 113.4, 132.4, 136.0, 152.3, 154.5, 161.9 (br, 2C), 176.8 ppm. IR (KBr) v = 3200, 2989, 2532, 2255, 2225, 1703, 1574, 1444, 1208, 1104, 872 cm^{-1}. ESI-HRMS: found m/z 380.1002 [M – $C_4H_{10}NO$]$^+$; calculated for $C_{18}H_{14}N_5O_5$ 380.1000.



Morpholin-4-ium 5-(5-chloro-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3g).

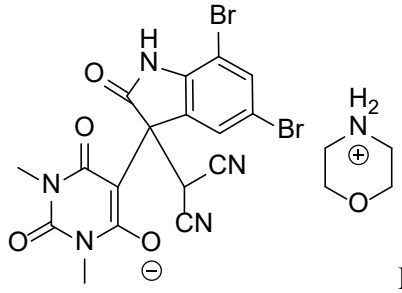
Yield 0.43 g (91%), mp: 142-144 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.04 (s, 6H, 2 CH_3), 3.11 (t, ^{3}J = 4.8 Hz, 4H, 2 OCH_2), 3.76 (t, ^{3}J = 4.8 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 6.79 (d, ^{3}J = 8.2 Hz, 1H, 1 CH Ar), 6.92 (s, 1H, CH), 7.21 (dd, ^{3}J = 8.2 Hz, ^{4}J = 2.0 Hz, 1H, CH Ar), 7.31 (d, ^{4}J = 2.0 Hz, 1H, 1 CH Ar), 8.03-9.47 (br s, 2H, NH_2^+), 10.51 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 26.9 (2C), 28.8, 43.0 (2C), 52.8, 63.4 (2C), 82.0, 110.4, 113.2 (2C), 123.5, 124.9, 128.4, 133.1, 141.6, 152.2, 161.8 (br, 2C), 176.6 ppm. IR (KBr) v = 3434, 2976, 2863, 2509, 2256, 2200, 1717, 1574, 1434, 1107, 774 cm^{-1}. ESI-HRMS: found m/z 384.0496 [^{35}Cl, M –

$C_4H_{10}NO]^+$, 386.0473 [^{37}Cl, M – $C_4H_{10}NO]^+$; calculated for $C_{17}H_{11}ClN_5O_4$ 384.0505 (^{35}Cl), 386.0477 (^{37}Cl).



Morpholin-4-ium 5-(5-bromo-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3h).

Yield 0.48 g (92%), mp: 160-162 °C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 3.04 (s, 6H, 2 CH_3), 3.00-3.20 (m, 4H, 2 OCH_2), 3.67-3.84 (m, 4H, 2 $C\underline{H_2}NH_2^+$), 6.75 (d, [c]1H, 1 CH Ar), 6.91 (s, 1H, CH), 7.34 (d, ^3J = 7.9 Hz, 1H, CH Ar), 7.42 (s, 1H, 1 CH Ar), 7.79-9.30 (br s, 2H, NH_2^+ exch.), 10.52 (s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 26.9 (2C), 28.8, 43.1 (2C), 52.8, 63.5 (2C), 82.0, 110.9, 112.5, 113.2 (2C), 126.2, 131.2, 133.5, 142.0, 152.2, 161.7 (br, 2C), 176.4 ppm. IR (KBr) ν = 3435, 2975, 2863, 2504, 2256, 2202, 1720, 1575, 1433, 1107, 773 cm^{-1}. ESI-HRMS: found *m/z* 427.9984 [^{79}Br, M – $C_4H_{10}NO]^+$, 429.9972 [^{81}Br, M – $C_4H_{10}NO]^+$; calculated for $C_{17}H_{11}BrN_5O_4$ 428.0000 (^{79}Br), 429.9980 (^{81}Br).

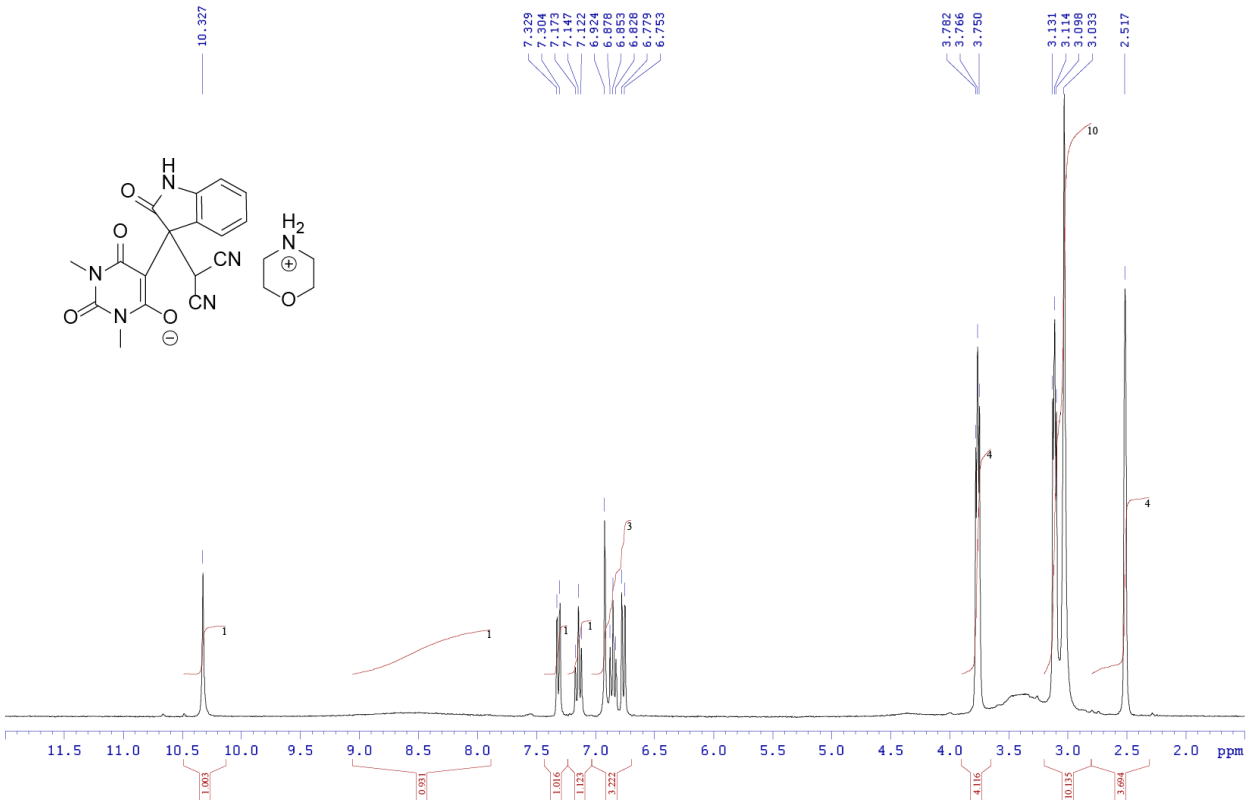


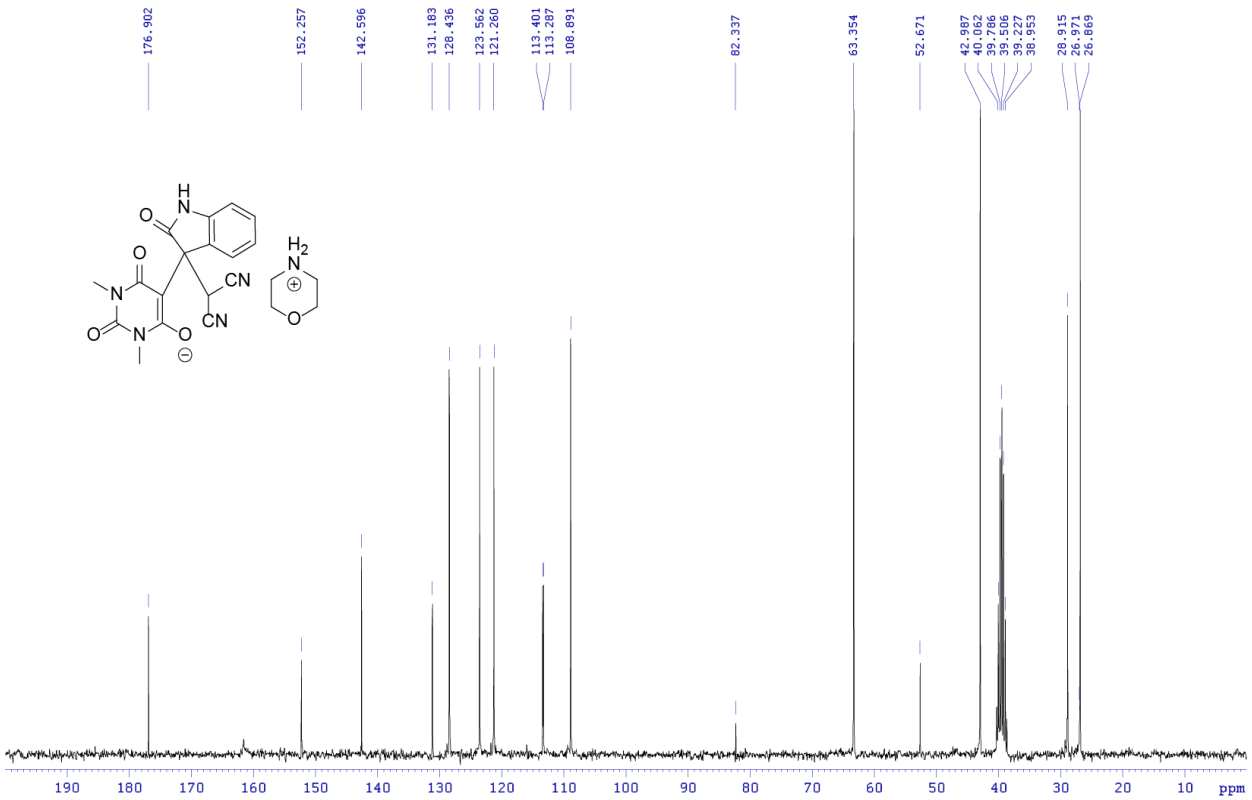
Morpholin-4-ium 5-(5,7-dibromo-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3i).

Yield 0.56 g (95%), mp: > 300°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 3.04 (s, 6H, 2 CH_3), 3.12 (t, ^3J = 4.8 Hz, 4H, 2 OCH_2), 3.77 (t, ^3J = 4.8 Hz, 4H, 2 $C\underline{H_2}NH_2^+$), 6.90 (s, 1H, CH), 7.42 (d, ^4J = 1.6 Hz, 1H, CH Ar), 7.62 (d, ^4J = 1.6 Hz, 1H, CH Ar), 8.20-9.18 (br s, 2H, NH_2^+), 10.55-11.29 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 26.9 (2C), 28.8, 43.0 (2C), 53.8, 63.4 (2C), 81.8, 102.1, 112.9, 113.0 (2C), 125.4, 133.2, 134.4, 141.7, 152.2, 161.4 (br, 2C), 176.2 ppm. IR (KBr) ν = 3435, 2970, 2863, 2501, 2256, 2200, 1728, 1572, 1436, 1107, 771 cm^{-1}. ESI-HRMS: found *m/z* 505.9093 [^{79}Br, ^{79}Br, M – $C_4H_{10}NO]^+$, 507.9075 [^{79}Br, ^{81}Br, M – $C_4H_{10}NO]^+$, 509.9060 [^{81}Br, ^{81}Br, M – $C_4H_{10}NO]^+$; calculated for $C_{17}H_{10}Br_2N_5O_4$ 505.9105 (^{79}Br, ^{79}Br), 507.9086 (^{79}Br, ^{81}Br), 509.9065 (^{81}Br, ^{81}Br).

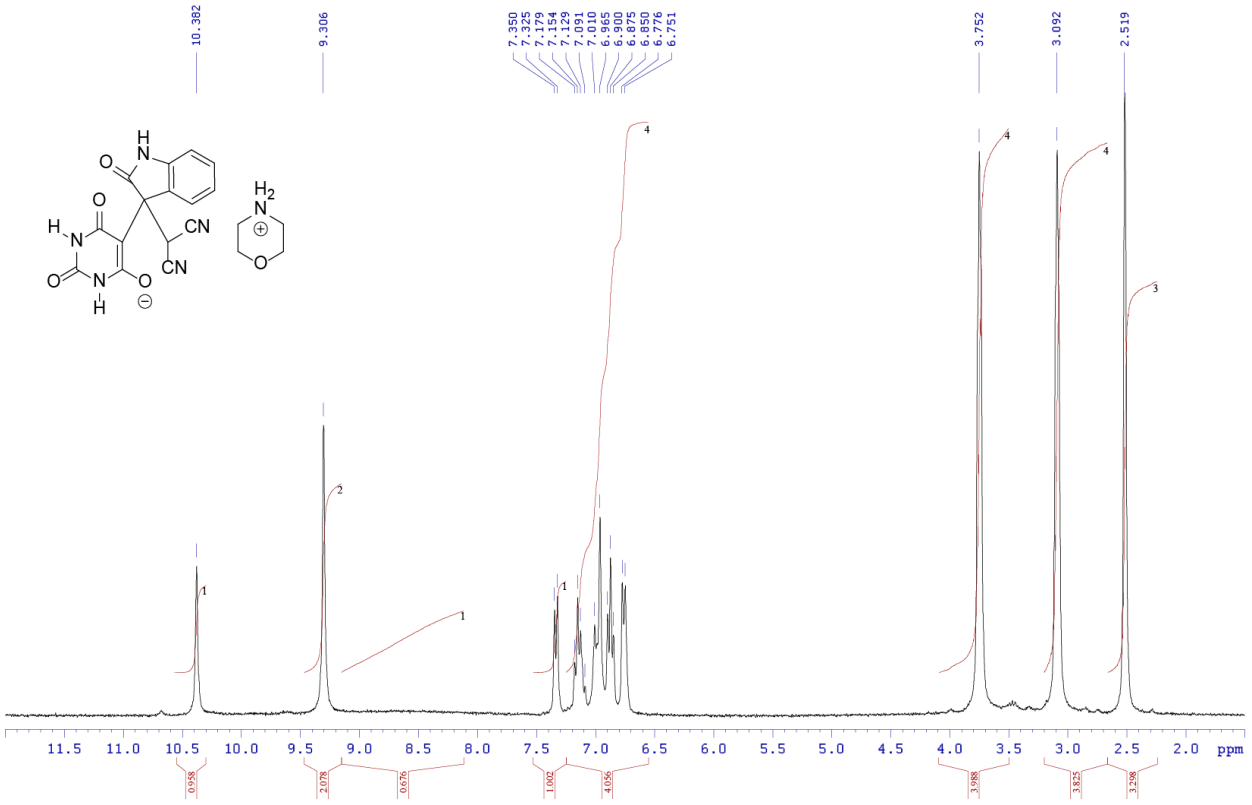
^{1}H and ^{13}C NMR spectra

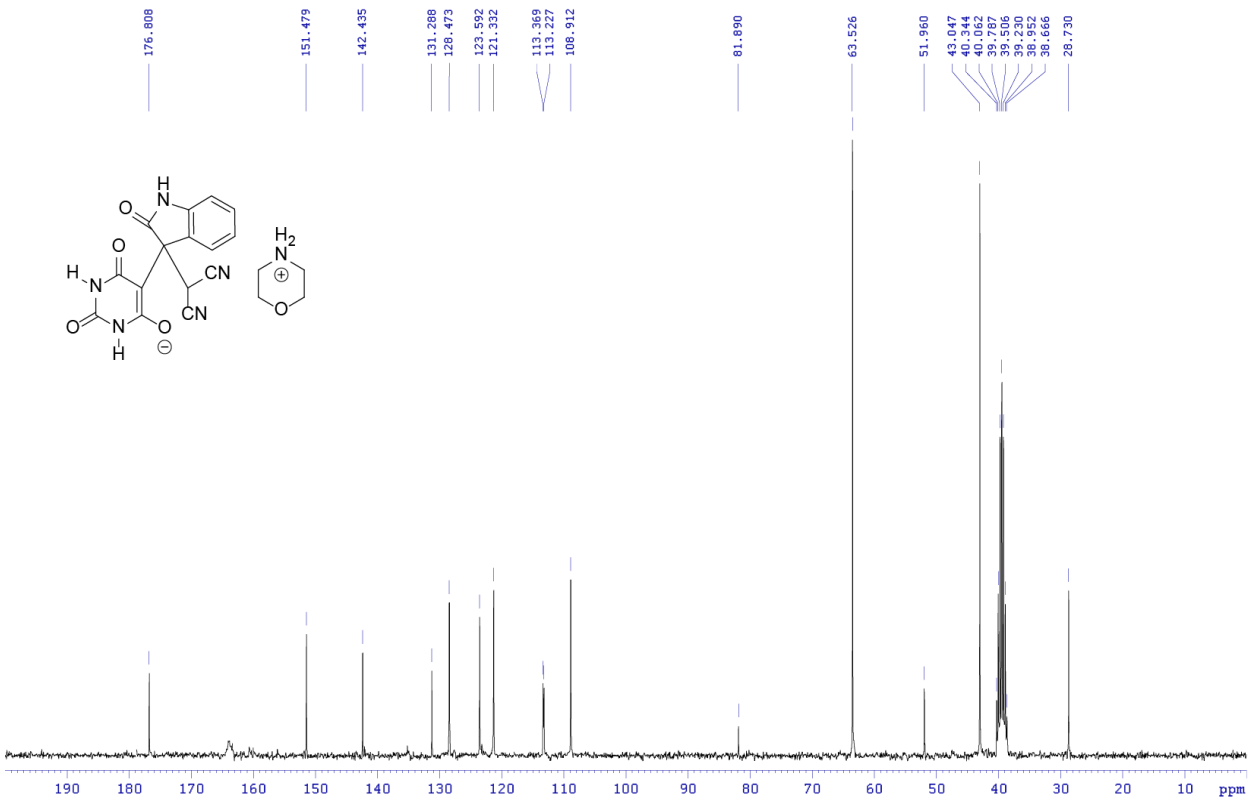
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3a).



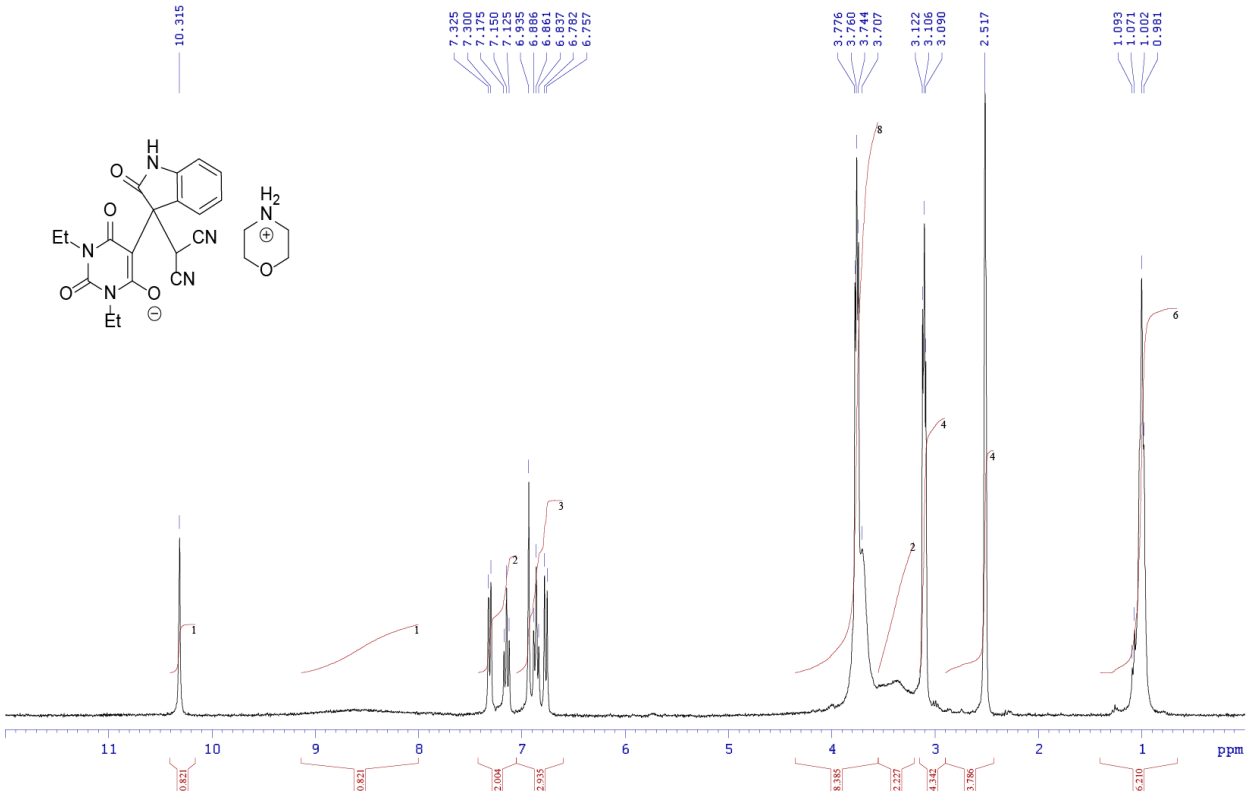


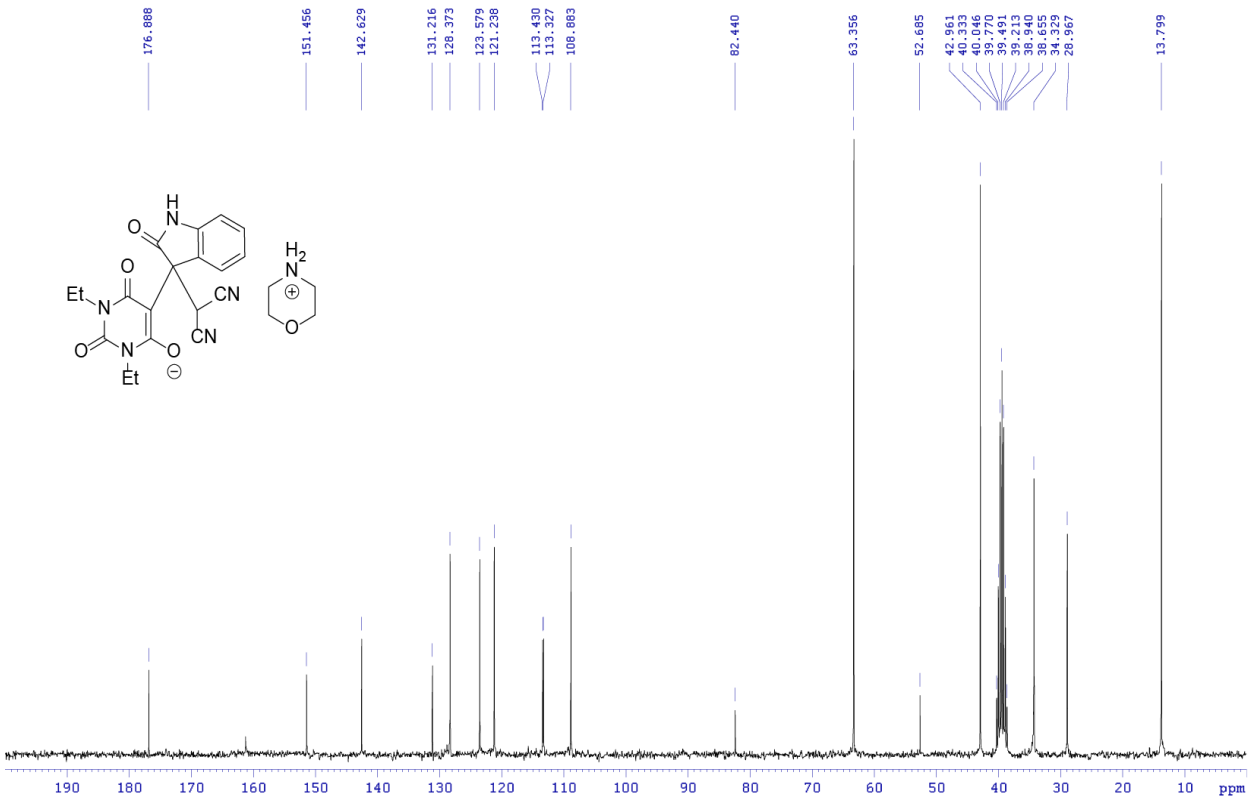
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3b).



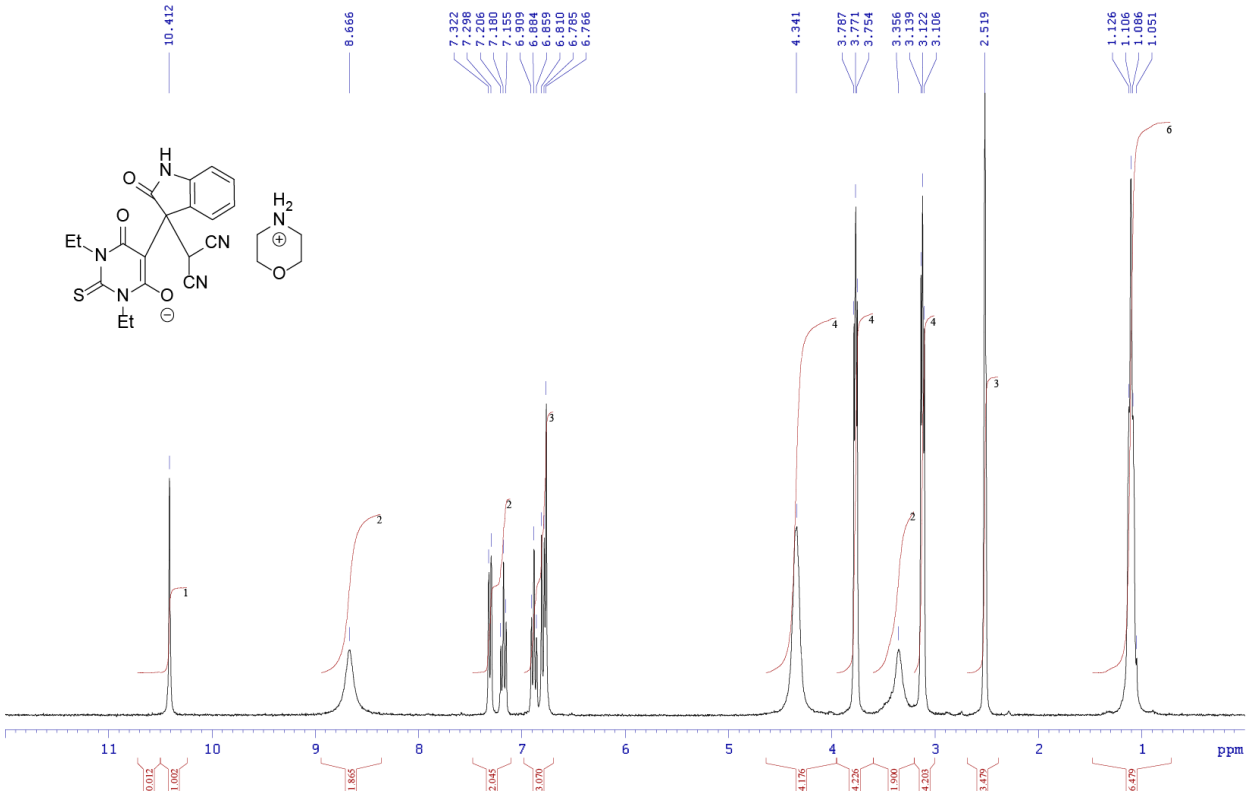


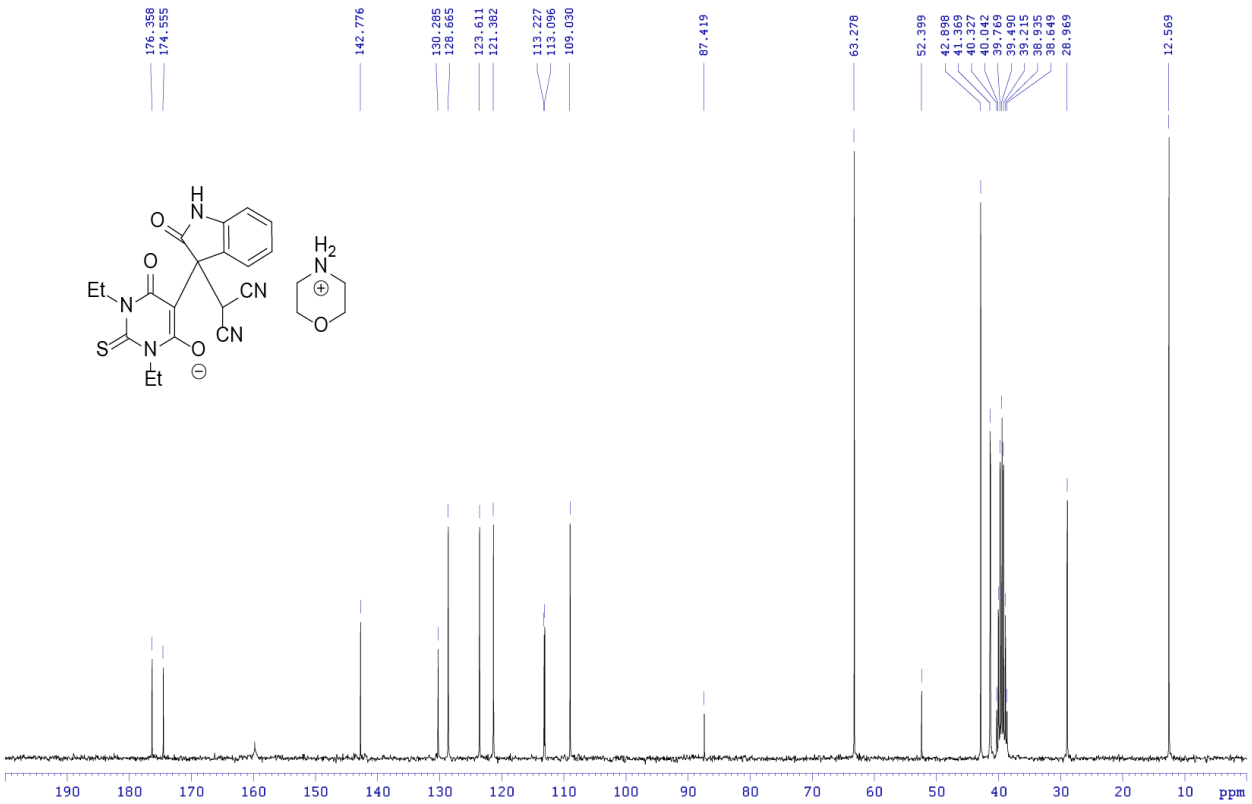
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-diethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3c).



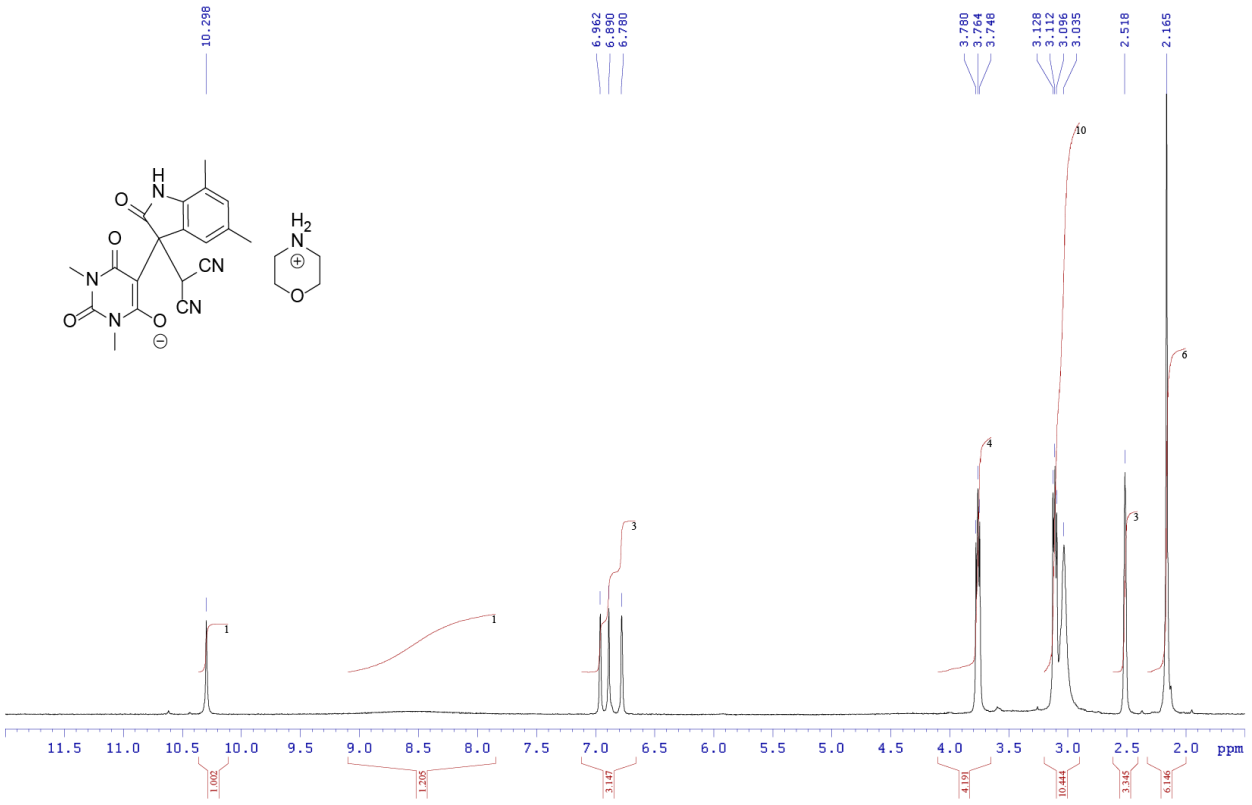


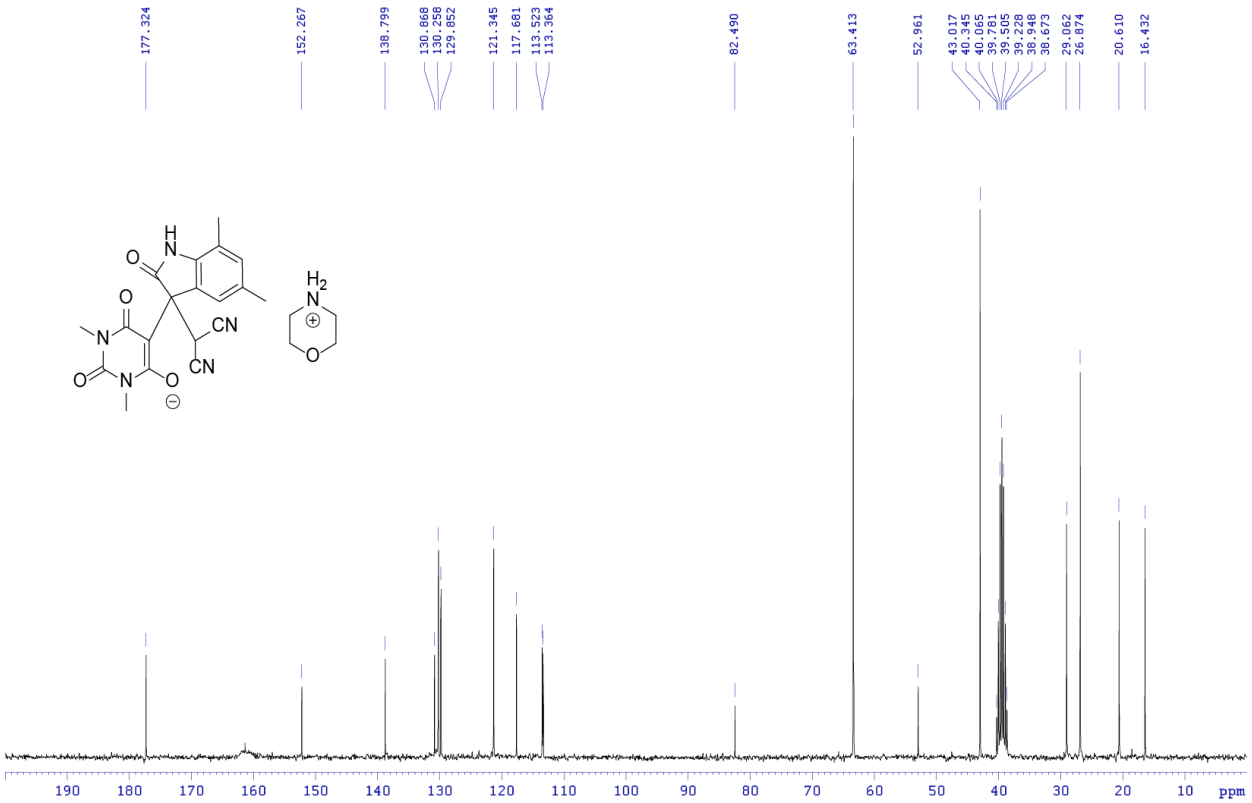
Morpholin-4-ium 5-(3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-diethyl-6-oxo-2-thioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3d).



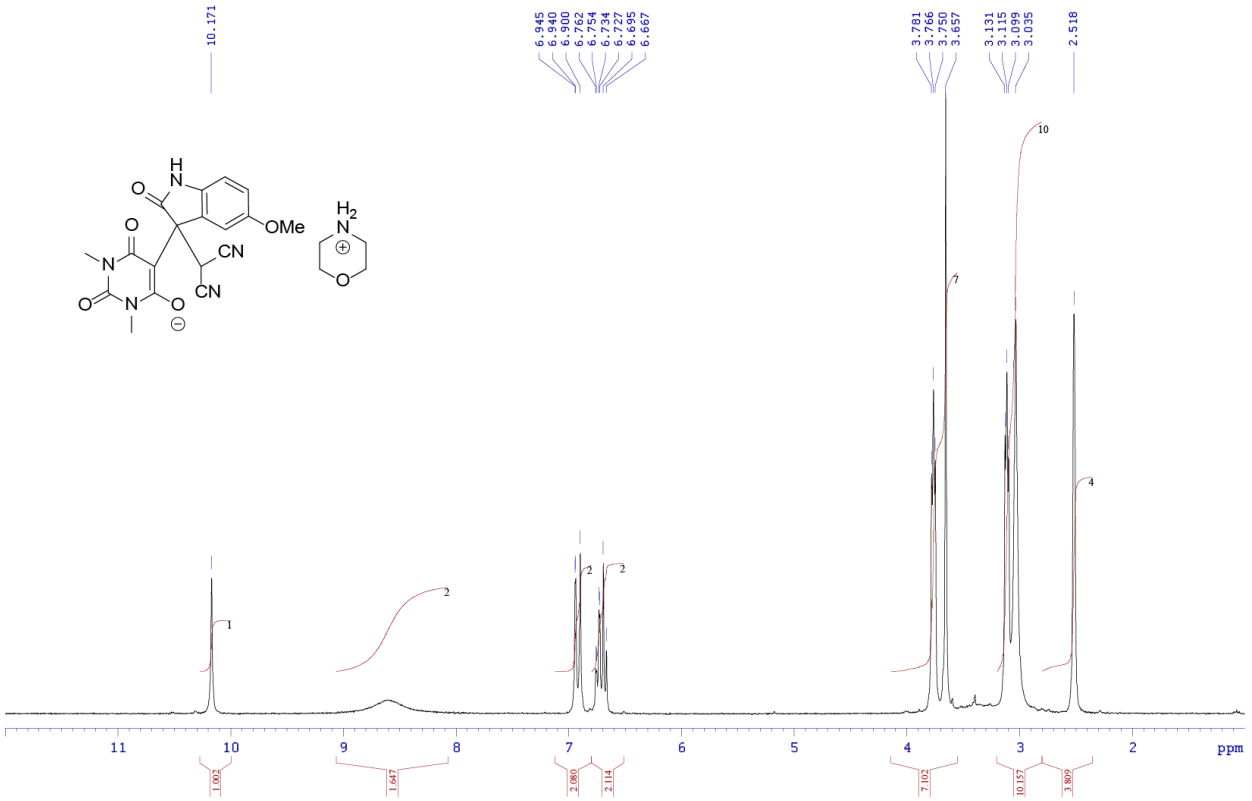


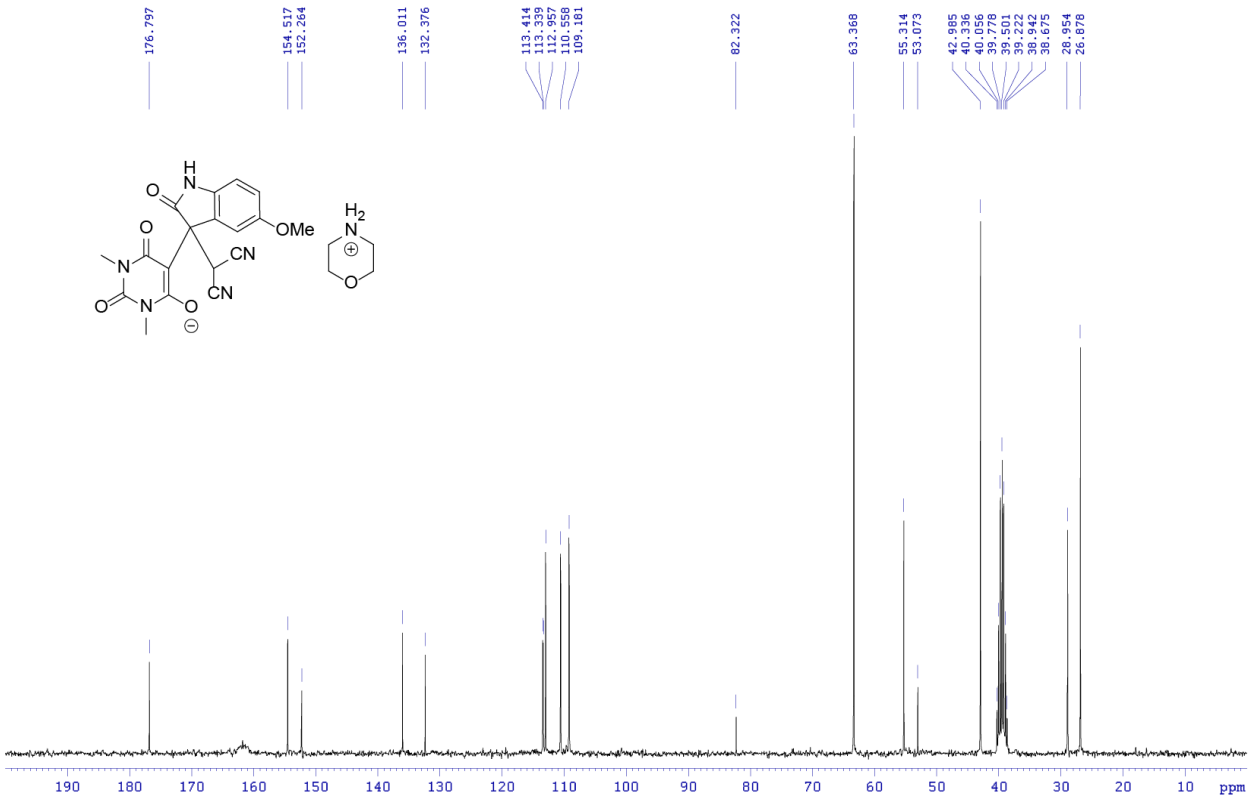
Morpholin-4-ium 5-(3-dicyanomethyl-5,7-dimethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3e).



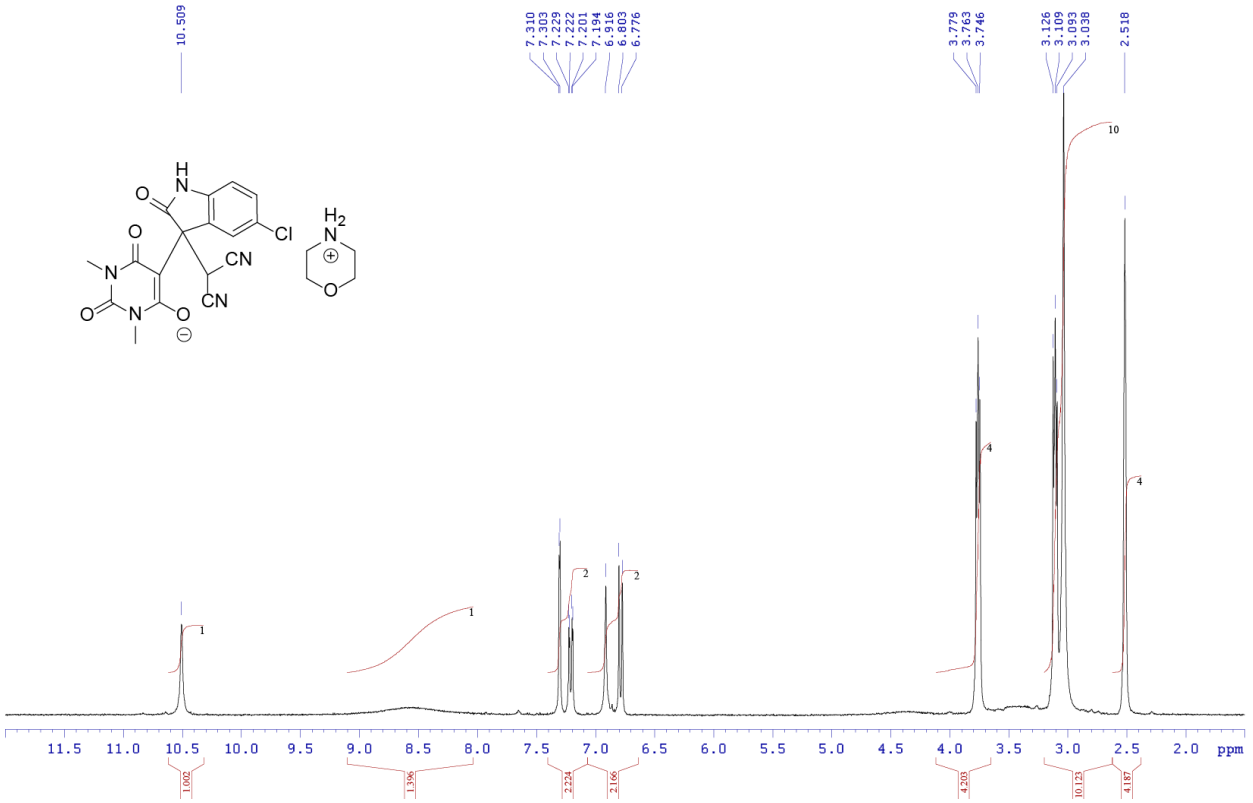


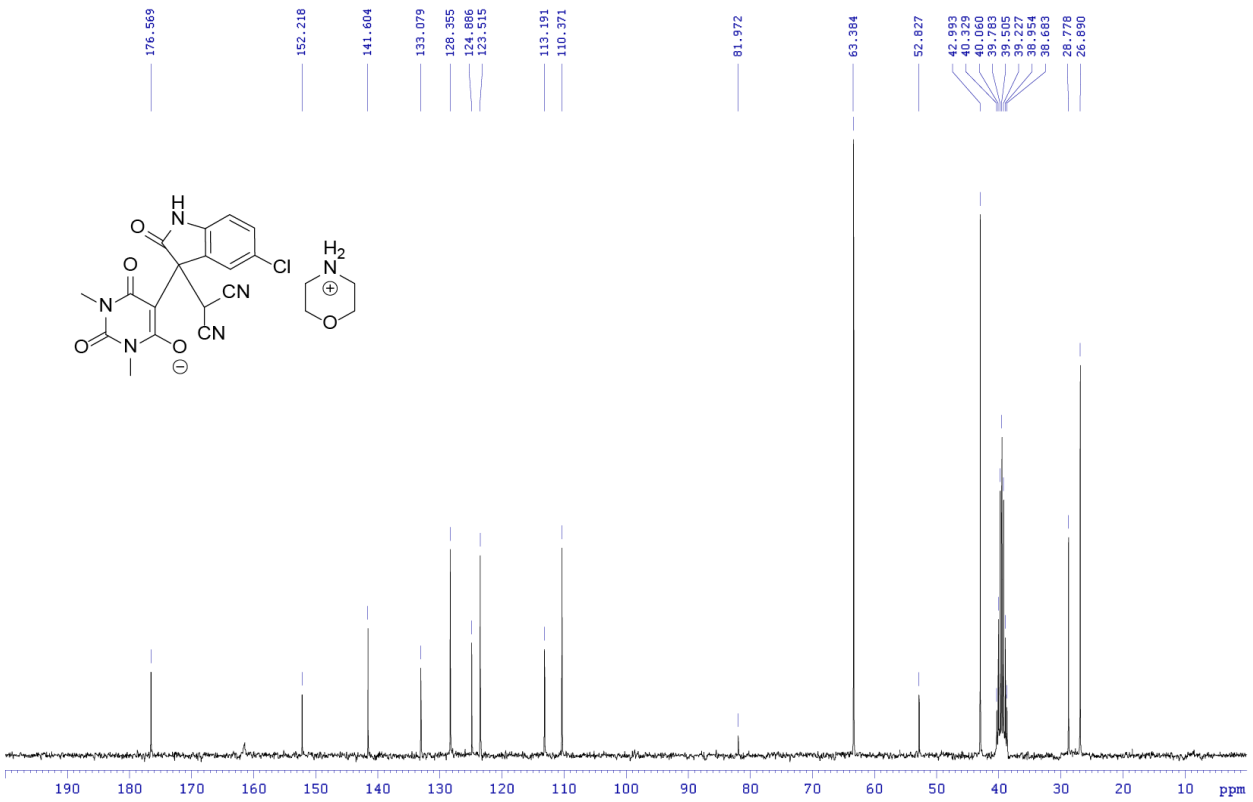
Morpholin-4-ium 5-(3-dicyanomethyl-5-methoxy-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3f).



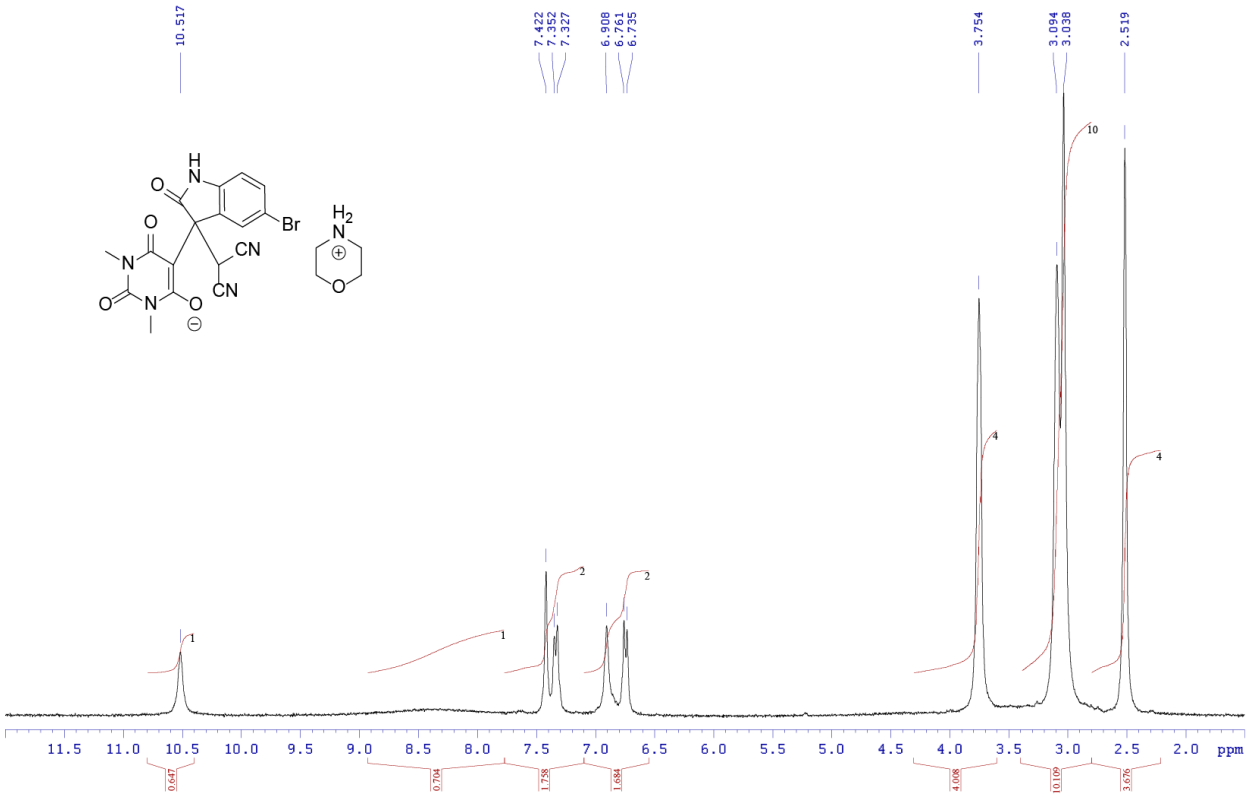


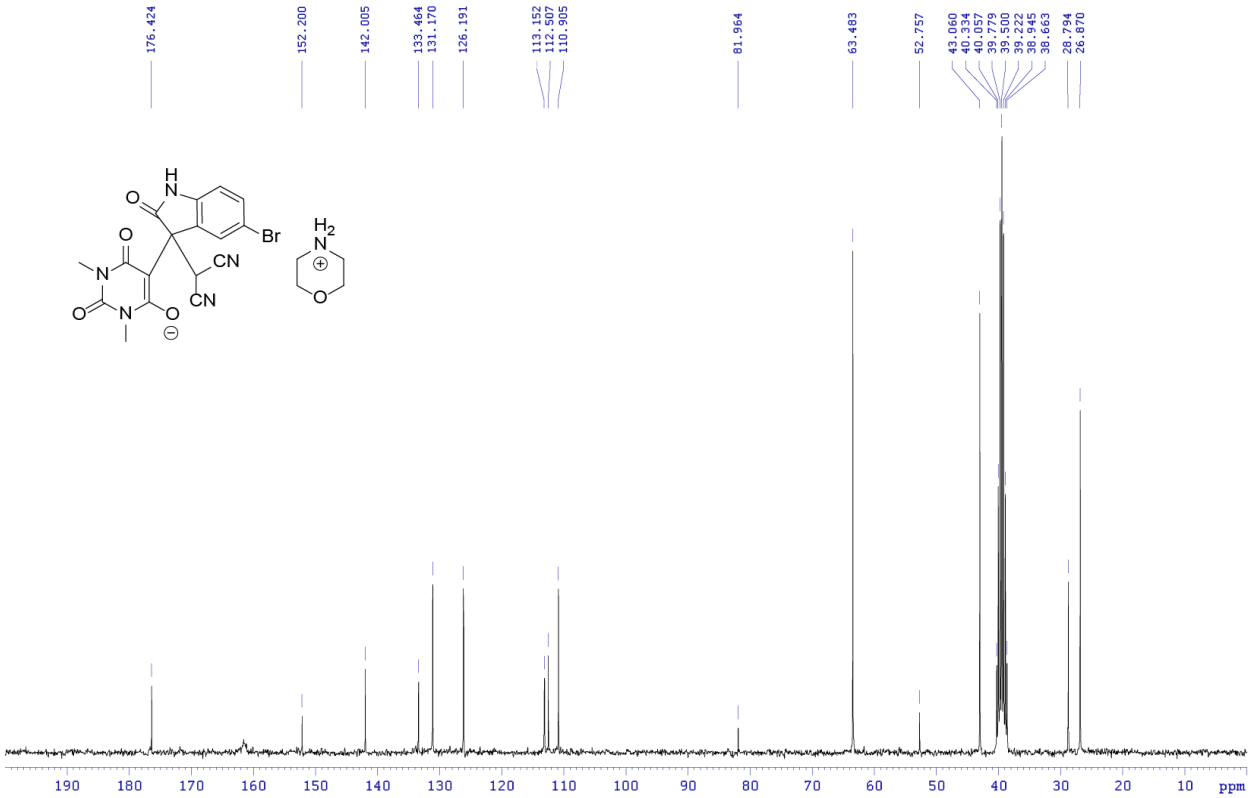
Morpholin-4-ium 5-(5-chloro-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3g).



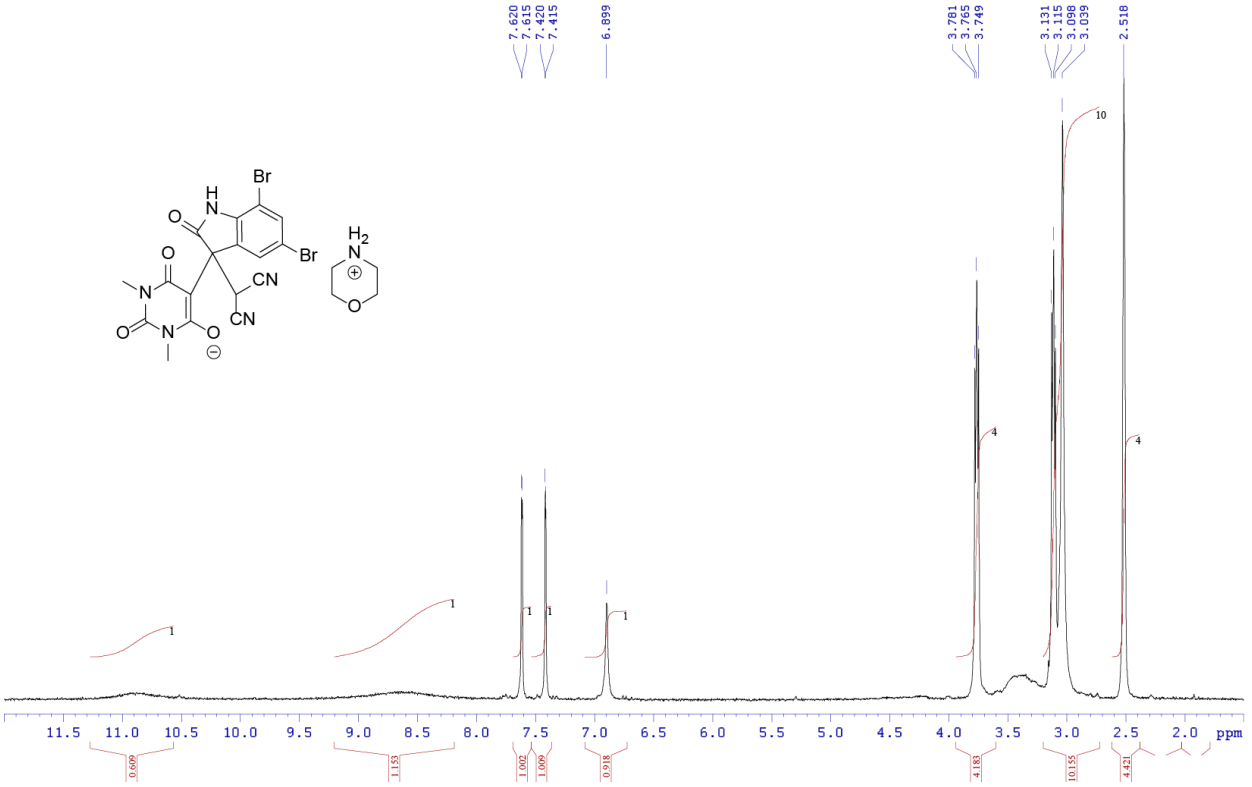


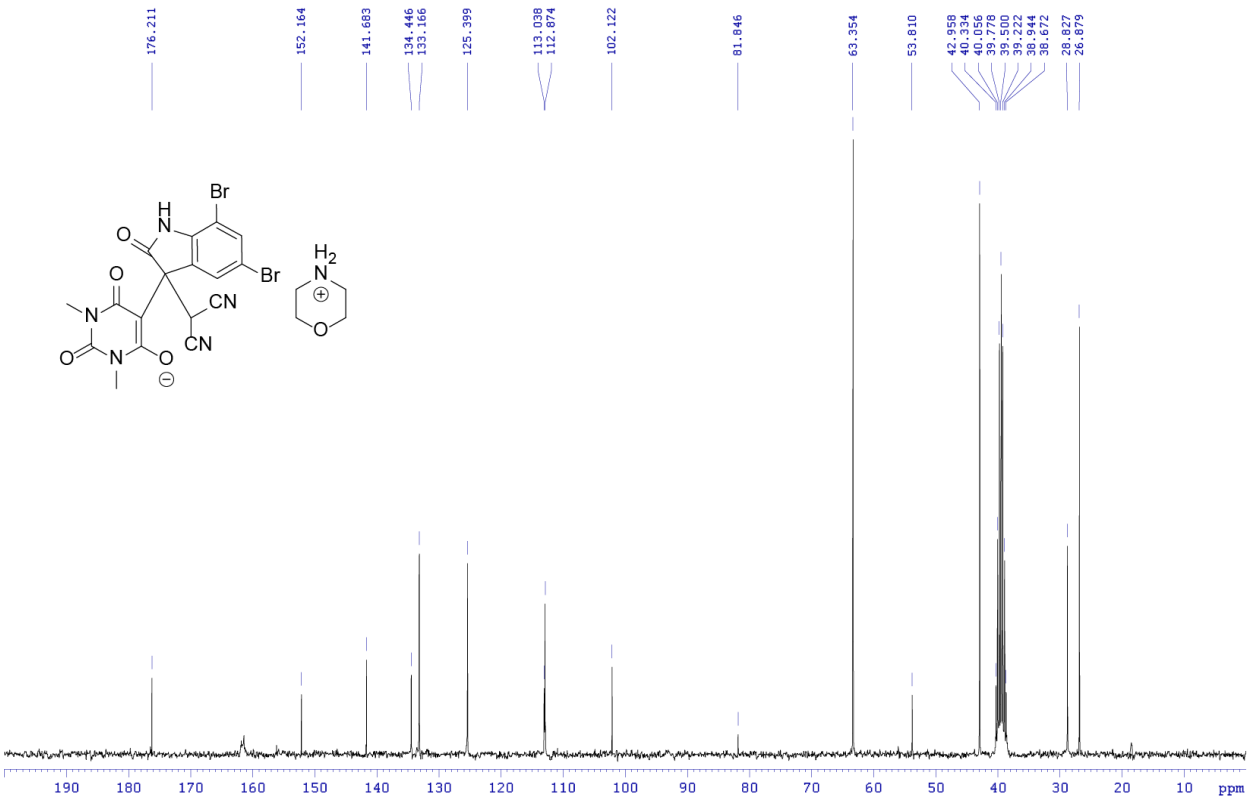
Morpholin-4-ium 5-(5-bromo-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3h).





Morpholin-4-ium 5-(5,7-dibromo-3-dicyanomethyl-2-oxoindolin-3-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (3i).





2D NMR spectra and description for compound 3a

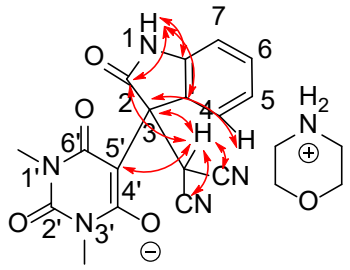
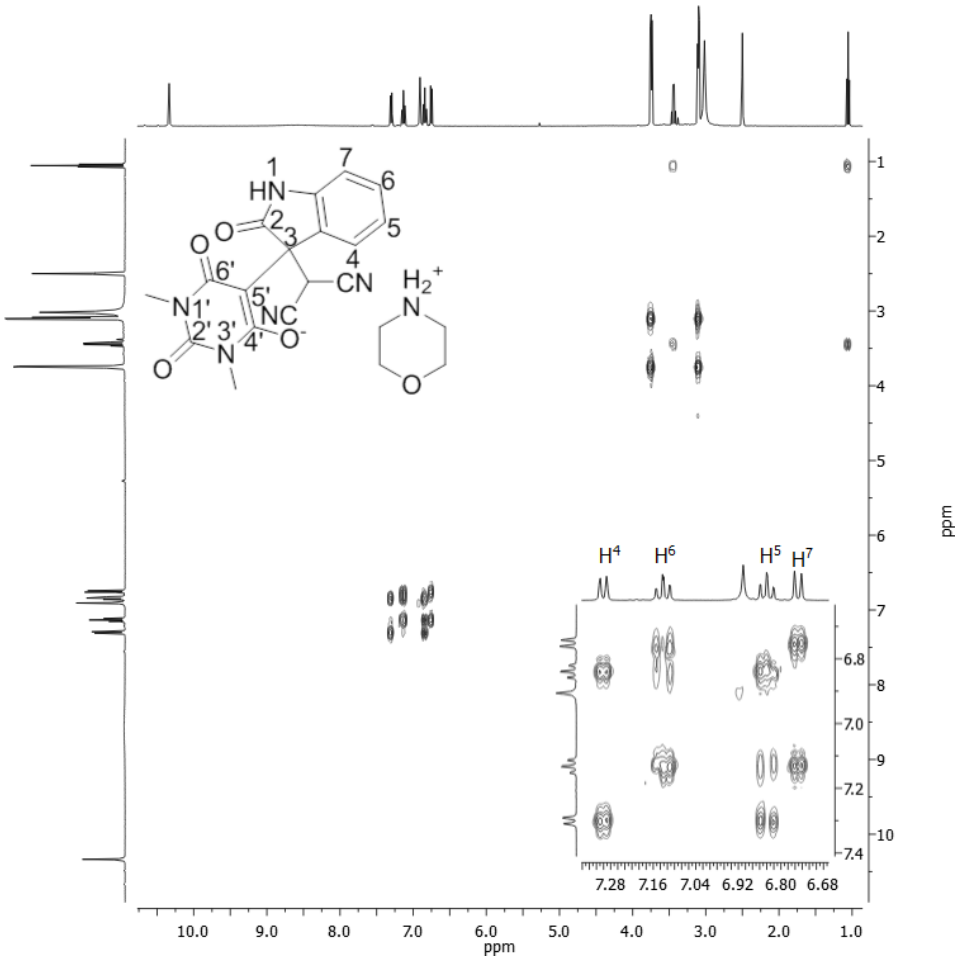


Figure S1. The structure and numbering of the compound **3a.** Key ^{1}H-^{13}C-HMBC spectrum correlations established by NMR are shown by arrows.

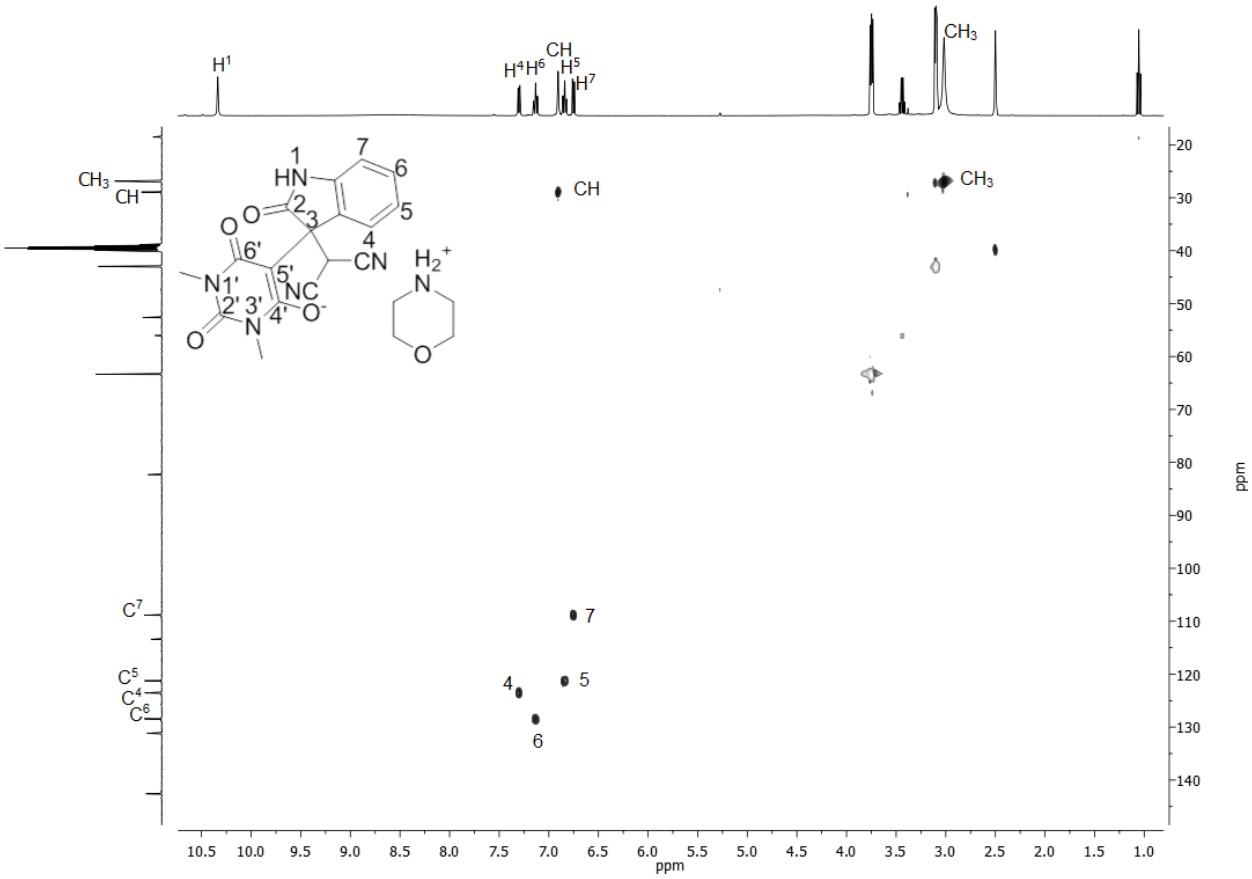
Complete assignment of signals to atoms for compound **3a**:
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H, H^{1}), 8.61 (br s, 2H, NH_2^+), 7.30 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, 1H, H^{4}), 7.13 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, 1H, H^{6}), 6.91 (s, 1H, 3-CH), 6.84 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, 1H, H^{5}), 6.75 (d, ^{3}J = 7.7 Hz, 1H, H^{7}), 3.80 – 3.70 (m, 4H, CH_2NH$_2^+$), 3.13 – 3.07 (m, 4H, OCH_2), 3.02 (s, 6H, 1'-CH_3, 3'-CH_3) ppm.
^{13}C NMR (101 MHz, DMSO-d_6) δ 176.9 (C^{2}), 161.7 (2C, C$^{4'}$, C$^{6'}$), 152.2 (C$^{2'}$), 142.6 (C^{7a}), 131.2 (C^{3a}), 128.4 (C^{6}), 123.6 (C^{4}), 121.2 (C^{5}), 113.4 (CN), 113.3 (CN), 108.9 (C^{7}), 82.3 (C$^{5'}$), 63.4 (2C, CH_2O), 52.6 (C^{3}), 43.0 (2C, CH_2NH$_2^+$), 28.9 (3-CH), 26.9 (2C, N-CH_3) ppm.

The structure of compound **3a** was confirmed by NMR spectroscopy. The full assignment was carried out using 2D NMR experiments such as ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC. The proton spectrum showed two broadened signals from the compound, which meant the presence of dynamics in the sample. Morpholinium NH_2 was in exchange with water, so both proton signals had a large width. Also, there was a broad singlet at 3.02 ppm from N-CH_3 groups due to keto-enol tautamerism. In the carbon NMR spectrum, C$^{4'}$ and C$^{6'}$ have the same chemical shifts and appear as a broad signal because of tautomrism too. It is noteworthy that the CH proton from the malononitrile moiety appeared at low field (6.91 ppm) and the assignment was made on the base of the HSQC cross-peak with the high field carbon signal (at 28.9 ppm).

^{1}H-^{1}H COSY NMR spectrum.



^{1}H-^{1}H COSY NMR spectrum.



^{1}H-^{13}C HMBC NMR spectrum.