Supporting information for

General Approach to Spiro Indole-3,1'-naphthalen Tetracyclic System: Stereoselective Pseudo Four-component Reaction of Isatins and Cyclic Carbonyl Compounds with two Molecules of Malononitrile

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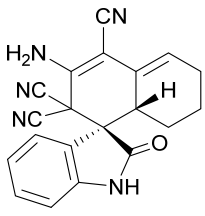
1. General Information

All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance II-300 spectrometer at ambient temperature in DMSO-d_6 solutions. Chemical shifts values are given in δ scale relative to Me_4Si. IR spectra were registered with a Bruker ALPHA-T FT-IR spectrometer in KBr pellets. Mass-spectra (EI = 70 eV) were obtained directly with a Finningan MAT INCOS 50 spectrometer. All starting materials were obtained from commercial sources and used without purification.

2. General Multicomponent Procedure

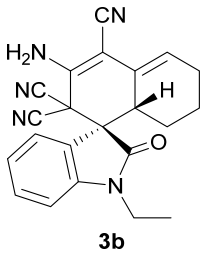
A mixture of isatin **1** (1 mmol), cyclic ketone **2** (1 mmol), malononitrile (0.132g, 2 mmol), Et_3N (0.02 g, 0.2 mmol) and ethanol (3 mL) was magnetically stirred at 20 °C for 1.5-2 h until deep red color of isatilydene malononitrile **4** was disappeared. Then the reaction mixture was filtered to isolate the solid products **3a-p**, which were then rinsed with ice-cold ethanol (2×2 mL) and dried under reduced pressure.



3a

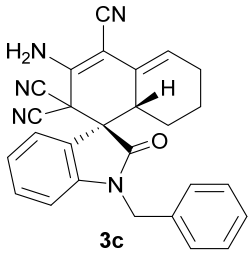
(3*R,8a′*R**)-3′-Amino-2-oxo-1,2,6′,8′,8a′-hexahydro-2′*H*-spiro[indole-3,1′-naphthalene]-2′,2′,4′-tricarbonitrile (3a)** (known compound, see: T. H. Babu, A. A. Joseph, D. Muralidharan and P. T. Perumal, *Tetrahedron Lett.,* 2010, **51**, 994): white solid; yield 0.29 g (85%); mp 271–273 °C (lit. mp 238–240 °C); ^{1}H NMR (300 MHz, DMSO-d_6): 0.46 (q, J = 11.7 Hz, 1H), 1.36–1.71 (m, 3H),

1.81–1.99 (m, 1H), 2.07–2.27 (m, 1H), 2.83–2.97 (m, 1H), 5.86–5.97 (m, 1H), 6.87 (d, J = 7.7 Hz, 1H, Ar), 7.00 (d, J = 7.7 Hz, 1H, Ar), 7.06 (t, J = 7.7 Hz, 1H, Ar), 7.37 (t, J = 7.7 Hz, 1H, Ar), 7.53 (s, 2H, NH_2), 11.36 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): 20.2, 23.4, 24.5, 37.0, 42.2, 54.6, 81.6, 110.2, 110.6, 110.7, 115.5, 122.5, 122.9, 123.7, 125.0, 125.4, 130.8, 142.3, 142.9, 173.3 ppm; IR (KBr): ν = 3416, 3328, 3223, 2944, 2221, 1749, 1728, 1656, 1596, 1471 cm^{-1}; MS (EI): *m/z* (%) = 341 ([M]$^+$, 100), 324 (25), 313 (21), 297 (15), 285 (13), 230 (11), 209 (10), 170 (10), 133 (28), 77 (13); Anal. calcd (%) for $C_{20}H_{15}N_5O$: C 70.37, H 4.43, N 20.52. Found (%): C 70.23, H 4.57, N 20.40.



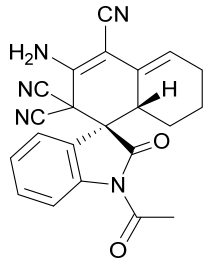
3b

(3*R,8a′*R**)-3'-Amino-1-ethyl-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro [indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3b):** white solid. Yield 0.32 g (86%); mp 268–269 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.40 (q, J = 12.1 Hz, 1H), 1.18 (t, J = 7.0 Hz, 3H, CH_3), 1.37–1.55 (m, 2H), 1.55–1.68 (m, 1H), 1.81–1.99 (m, 1H), 2.08–2.22 (m, 1H), 2.90–3.02 (m, 1H), 3.79–3.93 (m, 2H, CH_2), 5.89–5.98 (m, 1H), 6.94 (d, J = 7.7 Hz, 1H, Ar), 7.15 (t, J = 7.7 Hz, 1H, Ar), 7.29 (d, J = 7.7 Hz, 1H, Ar), 7.48 (t, J = 7.7 Hz, 1H, Ar), 7.55 (s, 2H, NH_2) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 12.2, 20.2, 23.3, 24.5, 34.8, 37.0, 42.2, 54.0, 81.6, 109.8, 110.0, 110.6, 115.5, 122.0, 123.5, 123.8, 124.9, 125.3, 131.0, 142.2, 143.2, 171.2 ppm; IR (KBr): ν = 3635, 3347, 3187, 2936, 2215, 1719, 1665, 1597, 1371 cm^{-1}; MS (EI): *m/z* (%) = 369 ([M]$^+$, 17), 326 (5), 287 (4), 161 (32), 130 (25), 77 (27), 29 (100). Anal. calcd (%) for $C_{22}H_{19}N_5O$: C 71.53, H 5.18, N 18.96. Found (%): C 71.27, H 5.25, N 18.78.



3c

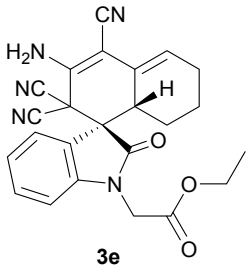
(3*R,8a′*R**)-3'-Amino-1-benzyl-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3c)**: white solid. Yield 0.39 g (90%); mp 243–245 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.38 (q, J = 12.1 Hz, 1H), 1.37–1.67 (m, 3H), 1.78–1.98 (m, 1H), 2.06–2.24 (m, 1H), 2.94–3.07 (m, 1H), 4.99–5.13 (m, 2H, CH_2), 5.89–5.99 (m, 1H), 6.95 (d, J = 7.3 Hz, 1H, Ar), 7.10–7.20 (m, 2H, Ar), 7.24– 7.47 (m, 6H, Ar), 7.58 (s, 2H, NH_2) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.2, 23.4, 24.5, 37.3, 42.2, 43.5, 54.2, 81.7, 110.2, 110.4, 110.6, 115.5, 121.8, 123.8, 124.0, 124.9, 125.2, 127.4 (2C), 127.8, 128.7 (2C), 131.0, 135.5, 142.2, 143.4, 171.9 ppm; IR (KBr): ν = 3353, 3216, 2944, 2217, 1716, 1664, 1600, 1378 cm^{-1}; MS (EI): *m/z* (%) = 431 ([M]$^+$, 13), 340 (5), 285 (4), 91 (100), 65 (18). Anal. calcd (%) for $C_{27}H_{21}N_5O$: C 75.16, H 4.91, N 16.23. Found (%): C 74.97, H 5.02, N 16.11.



3d

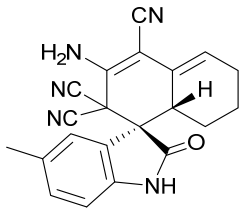
(3*R,8a′*R**)-1-Acetyl-3'-amino-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3d)**: white solid. Yield

0.25 g (65%); mp 251–253 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.45 (q, J = 12.1 Hz, 1H), 1.39–1.74 (m, 3H), 1.82–2.01 (m, 1H), 2.08–2.25 (m, 1H), 2.71 (s, 3H, CH_3), 2.99–3.12 (m, 1H), 5.95–6.05 (m, 1H), 7.03 (d, J = 7.3 Hz, 1H, Ar), 7.35 (t, J = 7.3 Hz, 1H, Ar), 7.56 (d, J = 7.7 Hz, 1H, Ar), 7.64 (s, 2H, NH_2), 8.24 (d, J = 8.0 Hz, 1H, Ar) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.1, 23.4, 24.5, 26.6, 38.1, 42.5, 55.3, 81.8, 109.8, 110.4, 115.3, 116.2, 121.3, 124.5, 124.7, 124.8, 126.3, 131.3, 140.6, 141.6, 170.1, 173.4 ppm; IR (KBr): ν = 3391, 3329, 3223, 2943, 2220, 1756, 1736, 1658, 1593, 1265 cm^{-1}; MS (EI): *m/z* (%) = 383 ([M]$^+$, 8), 341 (10), 285 (4), 133 (9), 43 (100). Anal. calcd (%) for $C_{22}H_{27}N_5O_2$: C 68.92, H 4.47, N 18.27. Found (%): C 68.79, H 4.58, N 18.01.



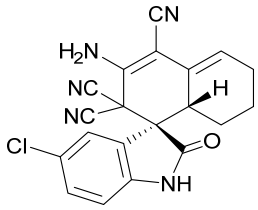
3e

(3*R,8a′*R**) Ethyl (3'-amino-2',2',4'-tricyano-2-oxo-6',7',8',8a'-tetrahydro-2'*H*-spiro[indole-3,1'-naphthalen]-1(2*H*)-yl)acetate (3e):** white solid. Yield 0.26 g (62%); mp 229–230 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.44 (q, J = 12.1 Hz, 1H), 1.19 (t, J = 7.0 Hz, 3H, CH_3), 1.38–1.55 (m, 1H), 1.55–1.70 (m, 2H), 1.82–2.01 (m, 1H), 2.07–2.25 (m, 1H), 2.89–3.03 (m, 1H), 4.16 (q, J = 7.0 Hz, 2H, CH_2), 4.67–4.83 (m, 2H, CH_2), 5.90–6.00 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H, Ar), 7.17 (t, J = 7.7 Hz, 1H, Ar), 7.24 (d, J = 7.7 Hz, 1H, Ar), 7.46 (t, J = 7.7 Hz, 1H, Ar), 7.56 (s, 2H, NH_2) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 14.0, 20.2, 23.4, 24.6, 37.3, 41.5, 42.1, 54.0, 61.4, 81.8, 109.8, 109.9, 110.5, 115.5, 121.7, 123.9, 124.0, 124.8, 125.3, 130.9, 142.1, 143.2, 167.0, 171.9 ppm; IR (KBr): ν = 3324, 3219, 2940, 2216, 1758, 1727, 1645, 1373, 1207 cm^{-1}; MS (EI): *m/z* (%) = 427 ([M]$^+$, 68), 353 (92), 336 (38), 243 (18), 208 (22), 117 (71), 29 (100). Anal. calcd (%) for $C_{24}H_{21}N_5O_3$: C 67.44, H 4.95, N 16.38. Found (%): C 67.21, H 5.07, N 16.19.



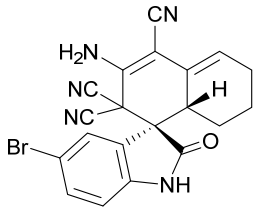
3f

(3*R,8a′*R**)-3'-Amino-5-methyl-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3f):** white solid. Yield 0.24 g (68%); mp 259–262 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.48 (q, J = 12.1 Hz, 1H), 1.37–1.71 (m, 3H), 1.83–2.03 (m, 1H), 2.08–2.21 (m, 1H), 2.31 (s, 3H, CH_3), 2.83–2.95 (m, 1H), 5.88–5.98 (m, 1H), 6.65 (s, 1H, Ar), 6.90 (d, J = 8.0 Hz, 1H, Ar), 7.19 (d, J = 8.0 Hz, 1H, Ar), 7.51 (s, 2H, NH_2), 11.26 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.2, 21.0, 23.4, 24.5, 37.0, 42.2, 54.6, 81.6, 110.3, 110.5, 110.7, 115.5, 122.6, 123.6, 125.3, 125.5, 131.2, 131.6, 140.5, 142.3, 173.2 ppm; IR (KBr): ν = 3337, 3224, 2928, 2214, 1723, 1644, 1598, 1490 cm^{-1}; MS (EI): *m/z* (%) = 355 ([M]$^+$, 100), 209 (15), 146 (52), 115 (23), 77 (51), 39 (78). Anal. calcd (%) for $C_{21}H_{17}N_5O$: C 70.97, H 4.82, N 19.71. Found (%): C 70.74, H 4.93, N 19.59.



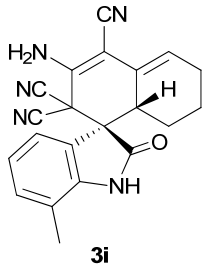
3g

(3*R,8a′*R**)-3'-Amino-5-chloro-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3g):** white solid. Yield 0.23 g (61%); mp 232–234 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.49 (q, J = 12.1 Hz, 1H), 1.37–1.77 (m, 3H), 1.88–2.07 (m, 1H), 2.07–2.32 (m, 1H), 2.86–3.01 (m, 1H), 5.92–6.03 (m, 1H), 6.78 (s, 1H, Ar), 7.06 (d, J = 8.4 Hz, 1H, Ar), 7.49 (d, J = 8.4 Hz, 1H, Ar), 7.64 (s, 2H, NH_2), 11.58 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.2, 23.4, 24.5, 37.0, 42.0, 54.8, 81.5, 110.1, 110.3, 112.4, 115.3, 124.3, 124.4, 124.7, 124.9, 126.7, 131.0, 142.0 (2C), 172.9 ppm; IR (KBr): ν = 3335, 3221, 2941, 2216, 1726, 1642, 1599, 1476 cm^{-1}; MS (EI): *m/z* (%) = 377 ([M]$^+$, 17), 375 (58) [M]$^+$, 169 (23), 167 (100), 102 (23), 77 (38), 41 (70). Anal. calcd (%) for $C_{20}H_{14}ClN_5O$: C 63.92, H 3.75, Cl 9.43, N 18.64. Found (%): C 63.78, H 3.91, Cl 9.31, N 18.47.



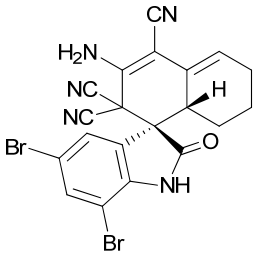
3h

(3*R,8a′*R**)-3'-Amino-5-bromo-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3h):** white solid. Yield 0.26 g (63%); mp 242–245 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.49 (q, J = 12.1 Hz, 1H), 1.38–1.76 (m, 3H), 1.88–2.06 (m, 1H), 2.09–2.31 (m, 1H), 2.87–3.00 (m, 1H), 5.92–6.03 (m, 1H), 6.90 (s, 1H, Ar), 7.01 (d, J = 8.4 Hz, 1H, Ar), 7.56–7.70 (m, 3H, Ar, NH_2), 11.58 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.2, 23.4, 24.5, 37.0, 42.0, 54.7, 81.4, 110.1, 110.3, 112.8, 114.3, 115.3, 124.3, 124.7, 124.9, 127.4, 133.9, 142.0, 142.4, 172.8 ppm; IR (KBr): ν = 3335, 3220, 2941, 2215, 1725, 1643, 1599, 1472 cm^{-1}; MS (EI): *m/z* (%) = 421 ([M]$^+$, 18), 419 ([M]$^+$, 17), 213 (21), 211 (19), 115 (28), 77 (61), 41 (90), 39 (100); Anal. calcd (%) for $C_{20}H_{14}BrN_5O$: C 57.16, H 3.36, Br 19.01, N 16.66. Found (%): C 56.97, H 3.48, Br 18.82, N 16.43.



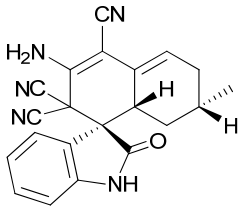
3i

(3*R,8a'*R**)-3'-Amino-7-methyl-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3i):** white solid. Yield 0.21 g (60%); mp 263-268 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.51 (q, J = 10.8 Hz, 1H), 1.47-1.64 (m, 3H), 1.87-1.92 (m, 1H), 2.13-2.20 (m, 1H), 2.90-2.93 (m, 1H), 2.26 (s, 3H, CH_3), 5.90-5.92 (m, 1H), 6.72 (d, J = 7.6 Hz, 1H, Ar), 6.99 (t, J = 7.7 Hz, 1H, Ar), 7.22 (d, J = 7.7 Hz, 1H, Ar), 7.54 (s, 2H, NH_2), 11.41 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): 16.5, 20.2, 23.5, 24.5, 37.1, 42.2, 54.7, 81.6, 110.2, 110.8, 115.5, 120.1, 122.2 (2C), 122.8, 123.6, 125.5, 132.1, 141.4, 142.3, 173.8 ppm; IR (KBr): ν = 3445, 3317, 3218, 2224, 1742, 1719, 1647, 1599, 1462, 1395 cm^{-1}; MS (EI): *m/z* (%) = 355 ([M]$^+$, 46), 297 (66), 254 (25), 184 (19), 151 (95), 128 (28), 115 (20), 91 (28), 65 (31), 15 (100); Anal. calcd (%) for $C_{21}H_{17}N_5O$: C 70.97, H 4.82, N 19.71. Found (%): C 70.85, H 4.93, N 19.60.



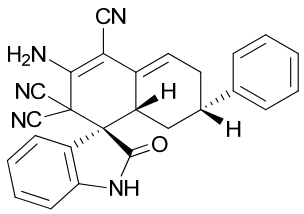
3j

(3*R,8a'*R**)-3'-Amino-5,7-dibromo-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3j):** white solid. Yield 0.40 g (81%); mp 304–309 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.54 (q, J = 11.4 Hz, 1H), 1.49-1.66 (m, 3H), 1.99-2.01 (m, 1H), 2.15-2.21 (m, 1H), 2.94-2.98 (m, 1H), 5.97-6.00 (m, 1H), 6.89 (s, 1H, Ar), 7.70 (s, 2H, NH_2), 7.96 (s, 1H, Ar), 11.99 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): 21.1, 24.5, 25.5, 38.1, 43.0, 56.6, 82.5, 105.3, 110.9, 111.0, 115.8, 116.2, 125.6, 125.7, 126.7, 127.6, 137.0, 142.7, 143.2, 173.8 ppm; IR (KBr): ν = 3443, 3347, 2221, 1747, 1633, 1622, 1457, 1392, 1296, 1163 cm^{-1}; MS (EI): *m/z* (%) = 501 ([M]$^+$, 9), 499 ([M]$^+$, 13), 391 (3), 291 (10), 209 (20), 184 (18), 128 (22), 114 (18), 77 (23), 27 (100); Anal. calcd (%) for $C_{20}H_{13}Br_2N_5O$: C 48.12, H 2.63, N, 14.03, Br 32.02. Found (%): C 48.03, H 2.71, N 13.95, Br 31.95.



3k

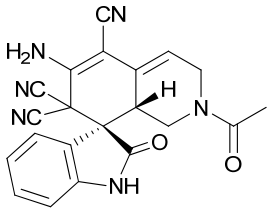
(3*R,7'*R**,8a'*R**)-3'-Amino-7'-methyl-2-oxo-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3k):** white solid. Yield 0.24 g (68%); mp 219–222 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.24 (q, J = 11.4 Hz, 1H), 0.79 (d, J = 6.3 Hz, 3H, CH_3), 1.40–1.60 (m, 2H), 1.63–1.80 (m, 1H), 2.16–2.30 (m, 1H), 2.92–3.04 (m, 1H), 5.85–5.94 (m, 1H), 6.86 (d, J = 7.3, 1H, Ar), 7.01 (d, J = 7.7 Hz, 1H, Ar), 7.06 (t, J = 7.7 Hz, 1H, Ar), 7.38 (t, J = 7.7 Hz, 1H, Ar), 7.54 (s, 2H, NH_2), 11.35 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 21.5, 27.2, 31.7, 33.4, 37.6, 42.3, 54.5, 81.5, 110.2, 110.6, 110.7, 115.6, 122.4, 123.0, 123.5, 125.0, 125.3, 130.9, 142.4, 142.9, 173.2 ppm; IR (KBr): ν = 3363, 3284, 2959, 2222, 1739, 1710, 1639, 1594, 1473 cm^{-1}; MS (EI): *m/z* (%) = 355 ([M]$^+$, 100), 313 (21), 285 (17), 133 (41), 115 (20), 77 (25), 46 (64), 31 (88). Anal. calcd (%) for $C_{21}H_{17}N_5O$: C 70.97, H 4.82, N 19.71. Found (%): C 70.78, H 4.98, N 19.57.



3l

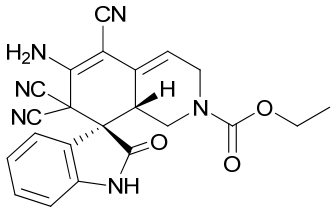
(3*R,7'*R**,8a'*R**)-3'-Amino-2-oxo-7'-phenyl-1,2,6',7',8',8a'-hexahydro-2'*H*-spiro[indole-3,1'-naphthalene]-2',2',4'-tricarbonitrile (3l):** white solid. Yield 0.30 g (72%); mp 284–286 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.74 (q, J = 12.4 Hz, 1H), 1.53–1.67 (m, 1H), 2.00–2.17 (m, 1H), 2.33–2.49 (m, 1H), 2.89–3.06 (m, 1H), 3.13–3.28 (m, 1H), 5.95–6.08 (m, 1H), 6.94 (d, J = 7.7, 1H, Ar), 6.97–7.30 (m, 7H, Ar), 7.40 (t, J = 7.3 Hz, 1H, Ar), 7.63 (s, 2H, NH_2), 11.32 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 31.2, 32.6, 37.8, 37.9, 42.2, 54.5, 81.2, 110.1, 110.6, 110.8, 115.5, 122.3, 123.1, 123.3, 125.0, 125.3, 126.4, 126.5 (2C), 128.5 (2C), 131.0, 142.6, 142.8, 142.9, 173.1 ppm; IR (KBr): ν = 3421, 3331, 3223, 2918, 2212, 1724, 1649, 1597, 1471 cm^{-1}; MS (EI): *m/z* (%) = 417 ([M]$^+$, 85), 313 (28), 285

(19), 115 (23), 104 (73), 91 (100), 77 (55), 44 (40). Anal. calcd (%) for $C_{26}H_{19}N_5O$: C 74.80, H 4.59, N 16.78. Found (%): C 74.61, H 4.72, N 16.59.



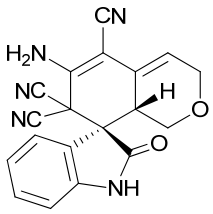
3m

(3*R,8a′*R**)-2'-Acetyl-6'-amino-2-oxo-1,1',2,2',3',8a'-hexahydro-7'*H*-spiro[indole-3,8'-isoquinoline]-5',7',7'-tricarbonitrile (3m)**: white solid. Yield 0.25 g (66%); mp 226–227 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.59 (t, J = 11.0 Hz, 1H), 1.96 (s, 3H, CH_3), 2.88–3.00 (m, 1H), 3.77–3.91 (m, 1H), 4.20–4.40 (m, 2H), 5.82–5.92 (m, 1H), 6.93 (d, J = 7.3 Hz, 1H, Ar), 7.01–7.16 (m, 2H, Ar), 7.41 (t, J = 7.7 Hz, 1H, Ar), 7.79 (s, 2H, NH_2), 11.51 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 21.5, 35.7, 37.7, 42.2, 44.9, 52.8, 80.0, 109.8, 110.3, 111.1, 115.2, 118.9, 121.4, 123.3, 124.6, 125.0, 131.3, 142.7, 143.3, 169.0, 172.5 ppm; IR (KBr): ν = 3624, 3498, 3328, 3149, 2210, 1729, 1648, 1600, 1472 cm^{-1}; MS (EI): *m/z* (%) = 384 ([M]$^+$, 5), 341 (6), 298 (8), 210 (10), 147 (12), 133 (13), 77 (5), 43 (100). Anal. calcd (%) for $C_{21}H_{16}N_6O_2$: C 65.62, H 4.20, N 21.86. Found (%): C 65.38, H 4.34, N 21.67.



3n

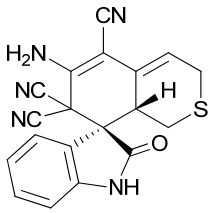
(3*R,8a′*R**)-Ethyl 6'-amino-5',7',7'-tricyano-2-oxo-1,1',2,3',7',8a'-hexahydro-2'*H*-spiro[indole-3,8'-isoquinoline]-2'-carboxylate (3n)**: white solid. Yield 0.25 g (60%); mp 240 ºC (dec); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.15 (t, J = 7.3 Hz, 3H, CH_3), 2.95–3.08 (m, 1H), 3.52–3.72 (m, 1H), 3.76–3.96 (m, 2H), 4.02 (q, J = 7.3 Hz, 2H, CH_2), 4.22–4.38 (m, 1H), 5.82–5.93 (m, 1H), 6.92 (d, J = 7.3 Hz, 1H, Ar), 7.05 (d, J = 7.7 Hz, 1H, Ar), 7.10 (t, J = 7.7 Hz, 1H, Ar), 7.41 (t, J = 7.3 Hz, 1H, Ar), 7.78 (s, 2H, NH_2), 11.53 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 14.5, 35.7, 40.3, 42.2, 43.2, 52.6, 61.2, 80.1, 109.7, 110.2, 111.1, 115.1, 119.0, 121.4, 123.3, 124.2, 125.0, 131.3, 142.6, 143.2, 154.5, 172.5 ppm; IR (KBr): ν = 3430, 3224, 2213, 1728, 1688, 1646, 1600, 1470 cm^{-1}; MS (EI): *m/z* (%) = 414 ([M]$^+$, 4), 341 (3), 313 (5), 259 (8), 210 (12), 133 (16), 77 (8), 29 (100). Anal. calcd (%) for $C_{22}H_{18}N_6O_3$: C 63.76, H 4.38, N 20.28. Found (%): C 63.52, H 4.51, N 20.03.



3o

(3*R,8a′*R**)-6′-Amino-2-oxo-3′,8a′-dihydrospiro[indoline-3,8′-isochromene]-5′,7′,7′(1′*H*)-tricarbonitrile (3o)**: white solid. Yield 0.25 g (73%); mp 258–260 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.44-2.51 (m, 1H, CH), 3.07-3.15 (m, 1H, CH), 3.67-3.72 (m, 1H, CH), 4.00 (d, J = 17.7 Hz, 1H, CH), 4.21 (d, J = 17.7 Hz, 1H, CH), 5.91 (s, 1H, CH), 6.93 (d, J = 7.7 Hz, 1H, Ar), 7.03 (d, J = 7.7 Hz, 1H, Ar), 7.10 (t, J = 7.7 Hz, 1H, Ar), 7.41 (t, J = 7.7 Hz, 1H, Ar), 7.79 (s, 2H, NH_2), 11.46 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 35.4, 42.3, 51.9, 63.4, 65.3,

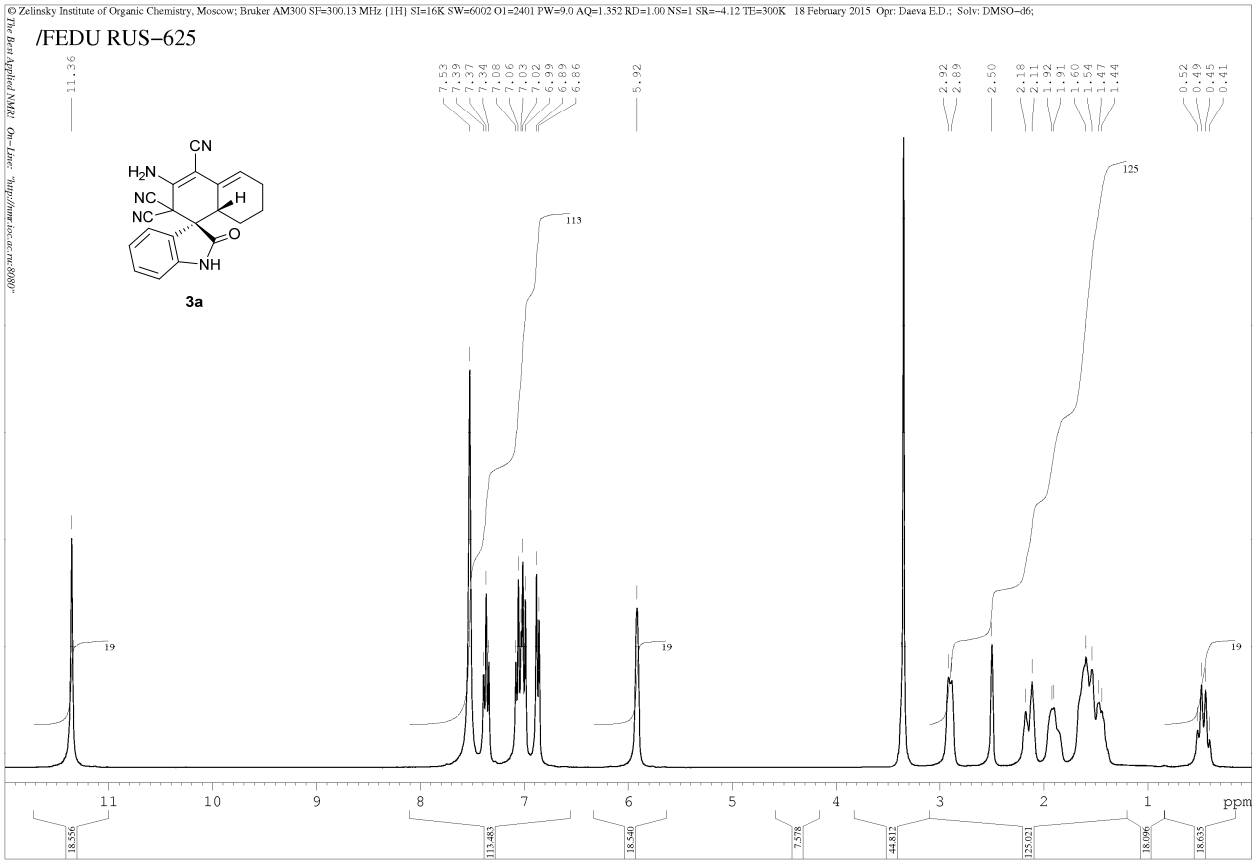
79.8, 109.7, 110.3, 111.0, 115.0, 120.4, 121.5, 123.2, 123.6, 124.9, 131.2, 142.5, 143.1, 172.3 ppm; MS (EI): *m/z* (%) = 343 ([M]$^+$, 100), 298 (38), 287 (35), 269 (24), 230 (19), 158 (43), 140 (85), 112 (65), 69 (36), 28 (58) ; IR (KBr): ν = 3339, 3196, 2825, 2224, 1736, 1666, 1598, 1472, 1390, 1127 cm^{-1}; Anal. calcd (%) for $C_{19}H_{13}N_5O_2$: C 66.47, H 3.82, N 20.40. Found (%): C 66.31, H 3.99, N 20.19.



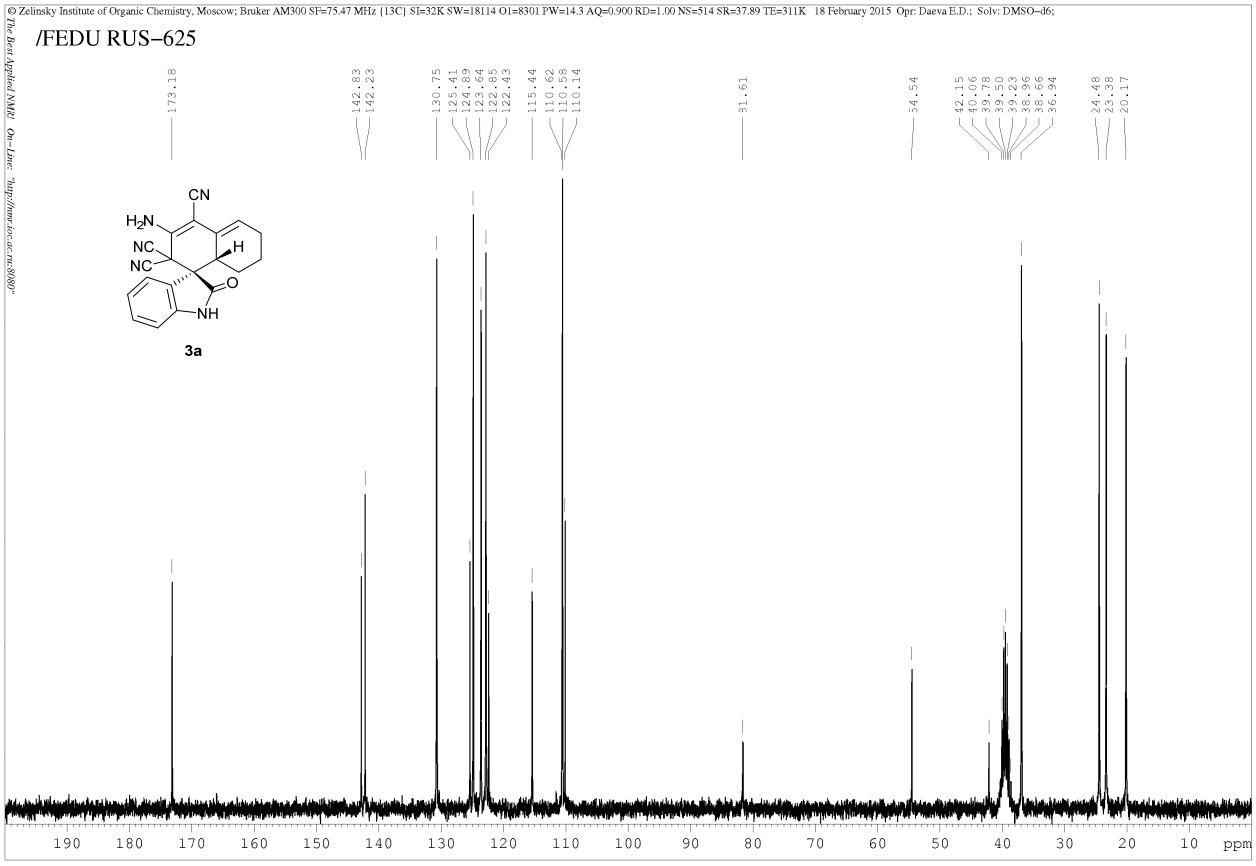
3p

(3*R,8a′*R**)-6′-Amino-2-oxo-3′,8a′-dihydrospiro[indoline-3,8′-isothiochromene]-5′,7′,7′(1′*H*)-tricarbonitrile (3p)** white solid. Yield 0.28 g (77%); mp 181–183 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.71-1.79 (m, 1H, CH), 2.44-2.48 (m, 1H, CH), 3.11-3.19 (m, 2H), 3.38-3.44 (m, 1H, CH), 6.14 (s, 1H, CH), 6.90 (d, J = 7.6 Hz, 1H, Ar), 7.02-7.11 (m, 2H, Ar), 7.41 (t, J = 7.7 Hz, 1H, Ar), 7.71 (s, 2H, NH_2), 11.50 (s, 1H, NH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 25.4, 25.5, 38.3, 42.9, 55.1, 82.2, 110.3, 111.0, 111.6, 115.9, 121.5, 122.0, 123.8, 125.6, 126.9, 131.8, 143.3, 143.4, 173.3; MS (EI): *m/z* (%) = 359 ([M]$^+$, 100), 326 (17), 258 (19), 298 (22), 230 (15), 195 (15), 164 (27), 133 (67), 77 (24), 45 (44); IR (KBr): ν = 3337, 3213, 2213, 1722, 1640, 1619, 1599, 1472, 1330, 1238 cm^{-1}; Anal. calcd (%) for $C_{19}H_{13}N_5OS$: C 63.49, H 3.65, N 19.49, S 8.92. Found (%): C 63.30, H 3.81, N 19.32, S 8.79.

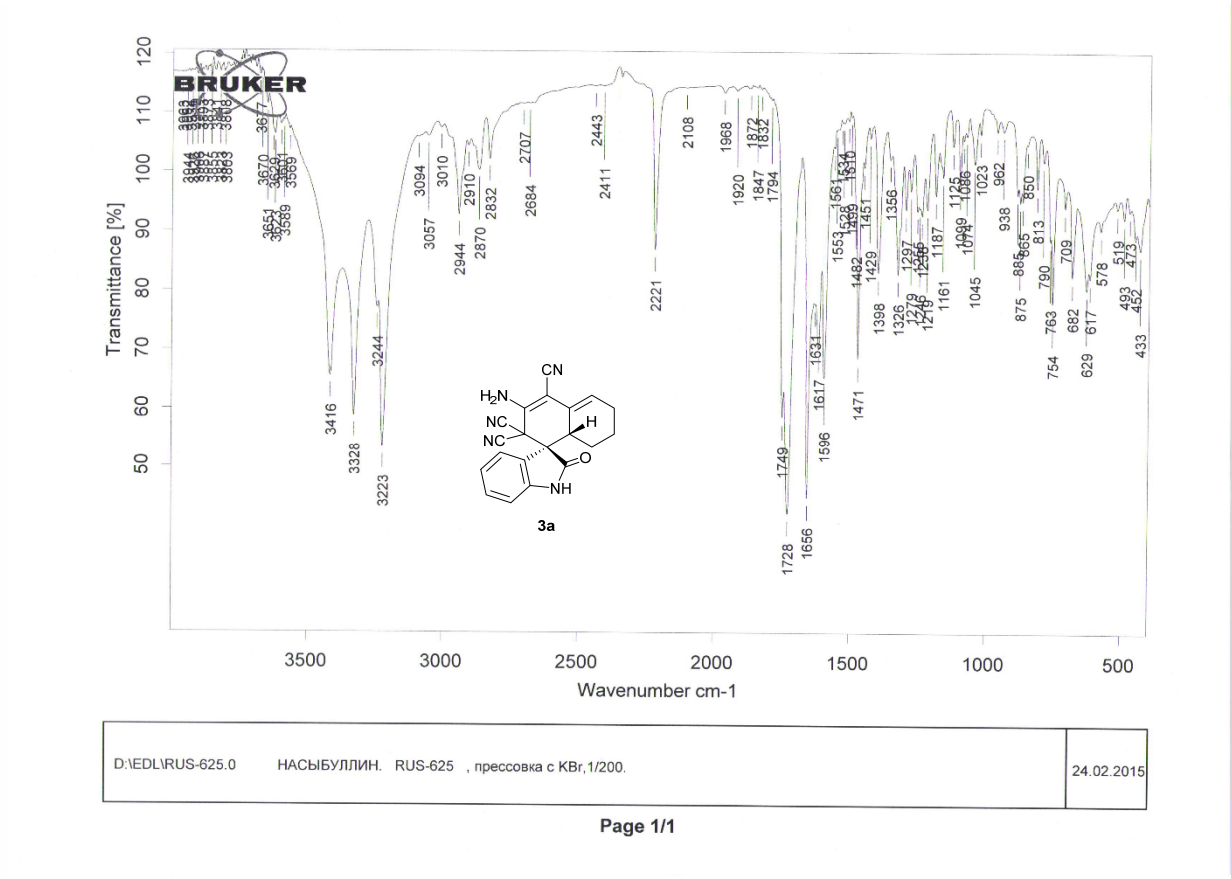
^{1}H-NMR for **3a**:



^{13}C-NMR for **3a**:



IR for **3a**:


BRUKER
Transmittance [%]
Wavenumber cm-1
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2000
1500
1000
500
3a
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24.02.2015
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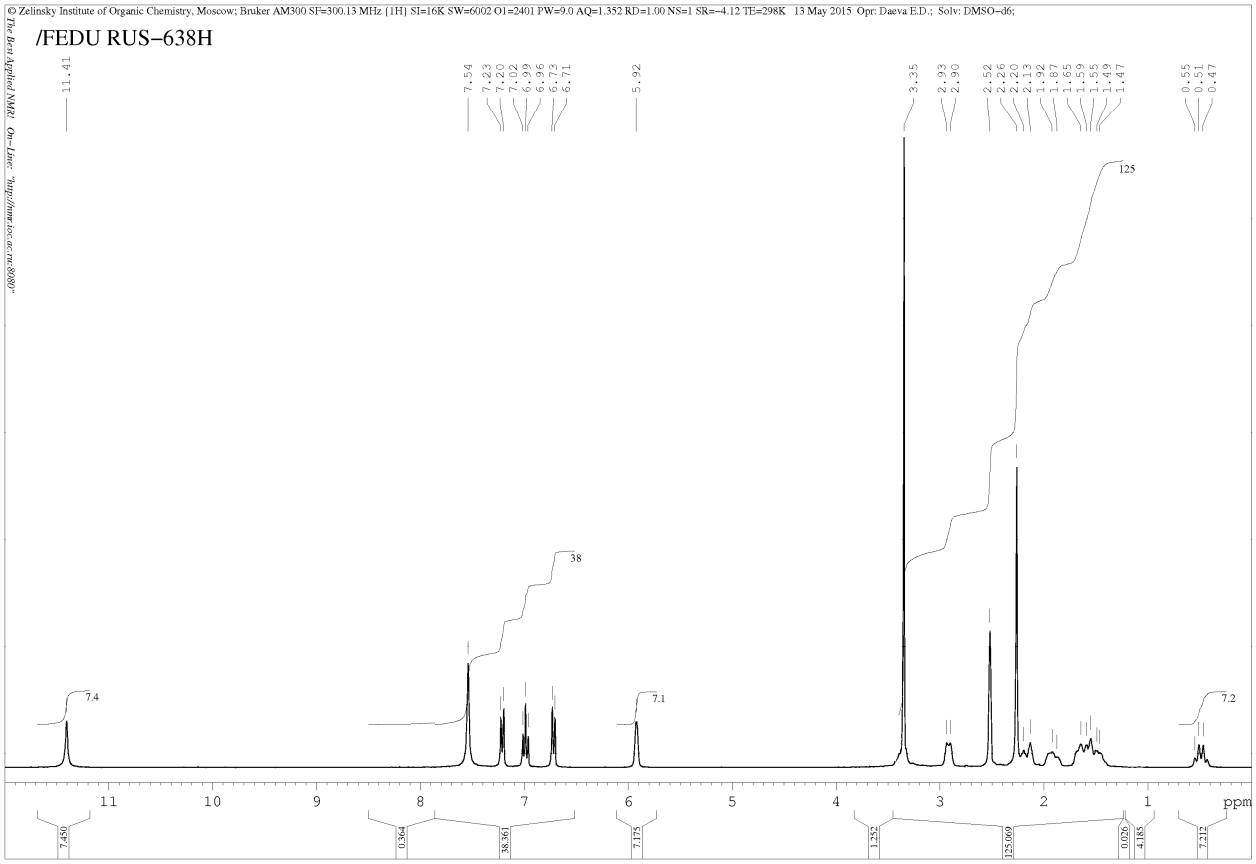
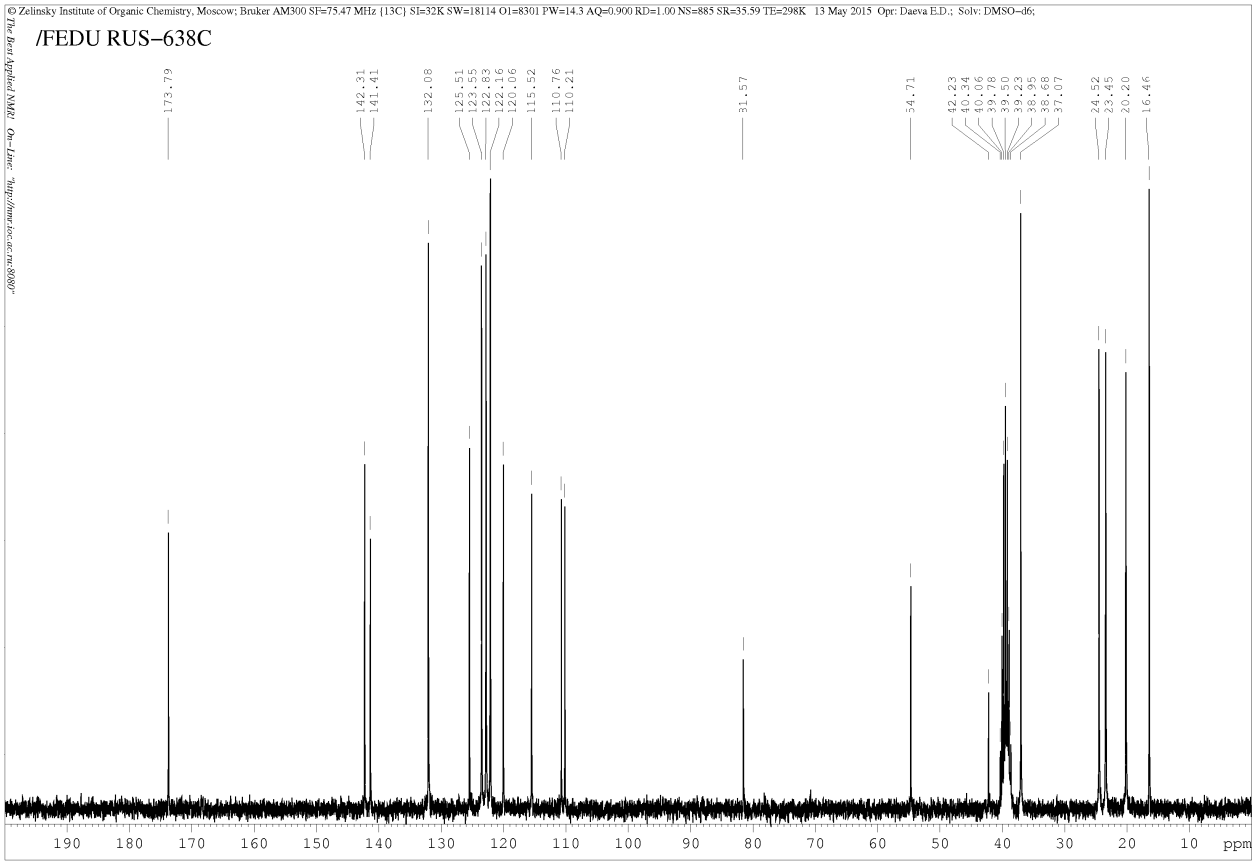
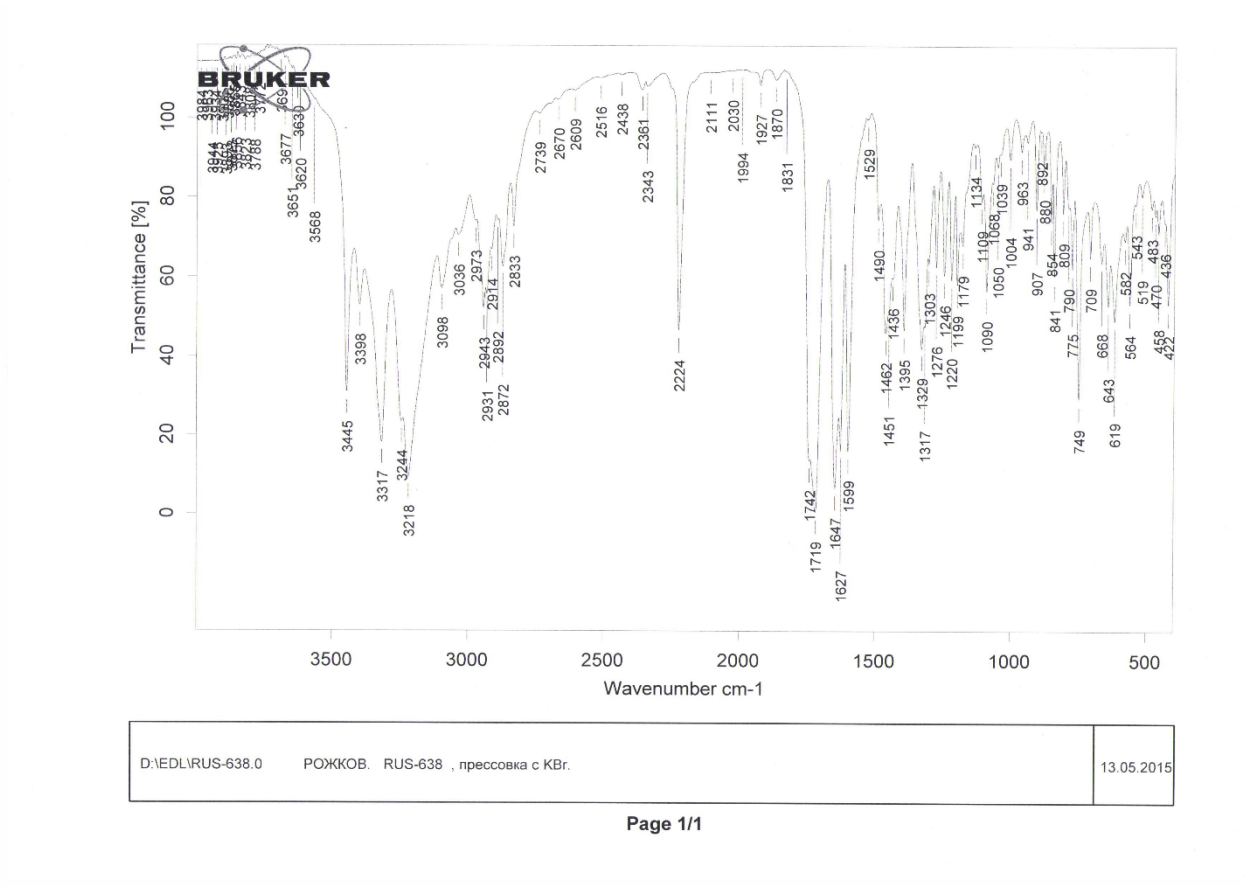
^{1}H-NMR for **3i**:



^{13}C-NMR for **3i**:



IR for **3i**:



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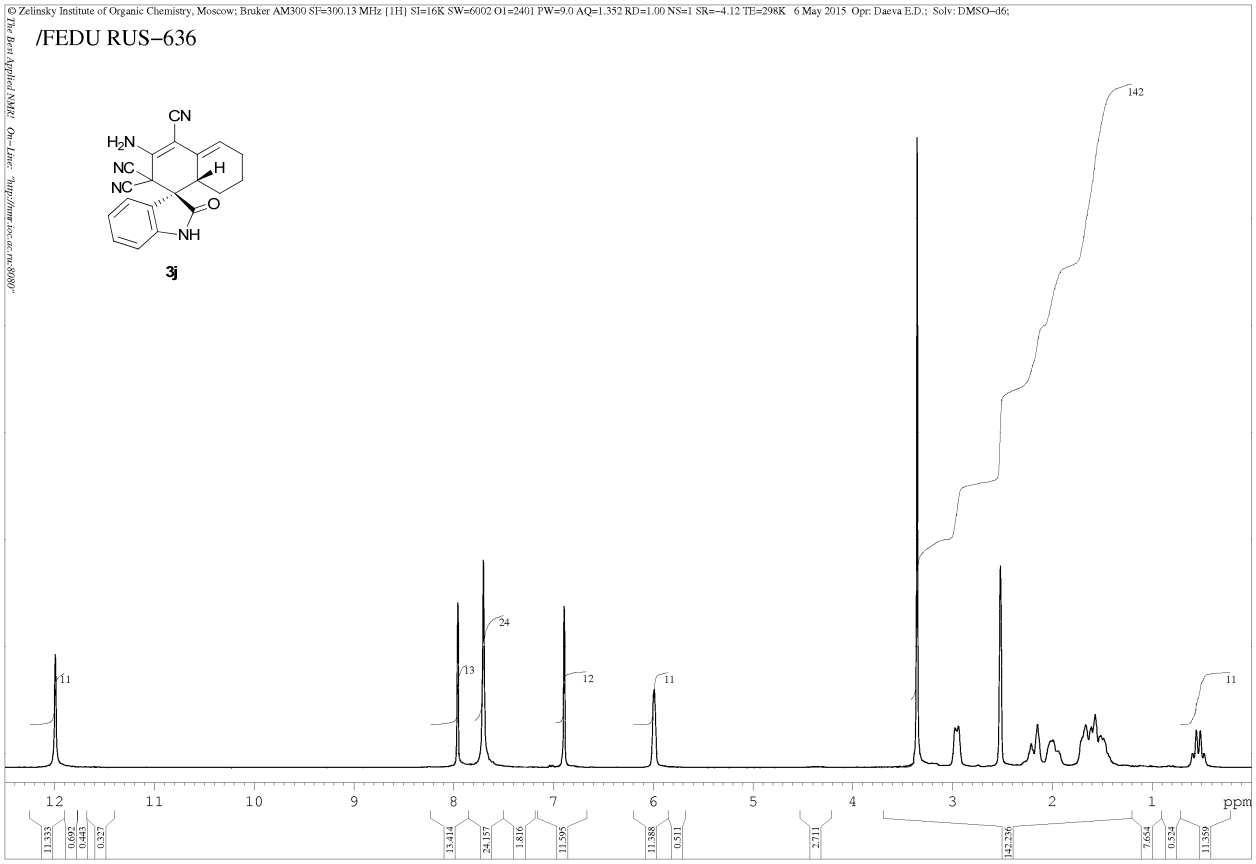
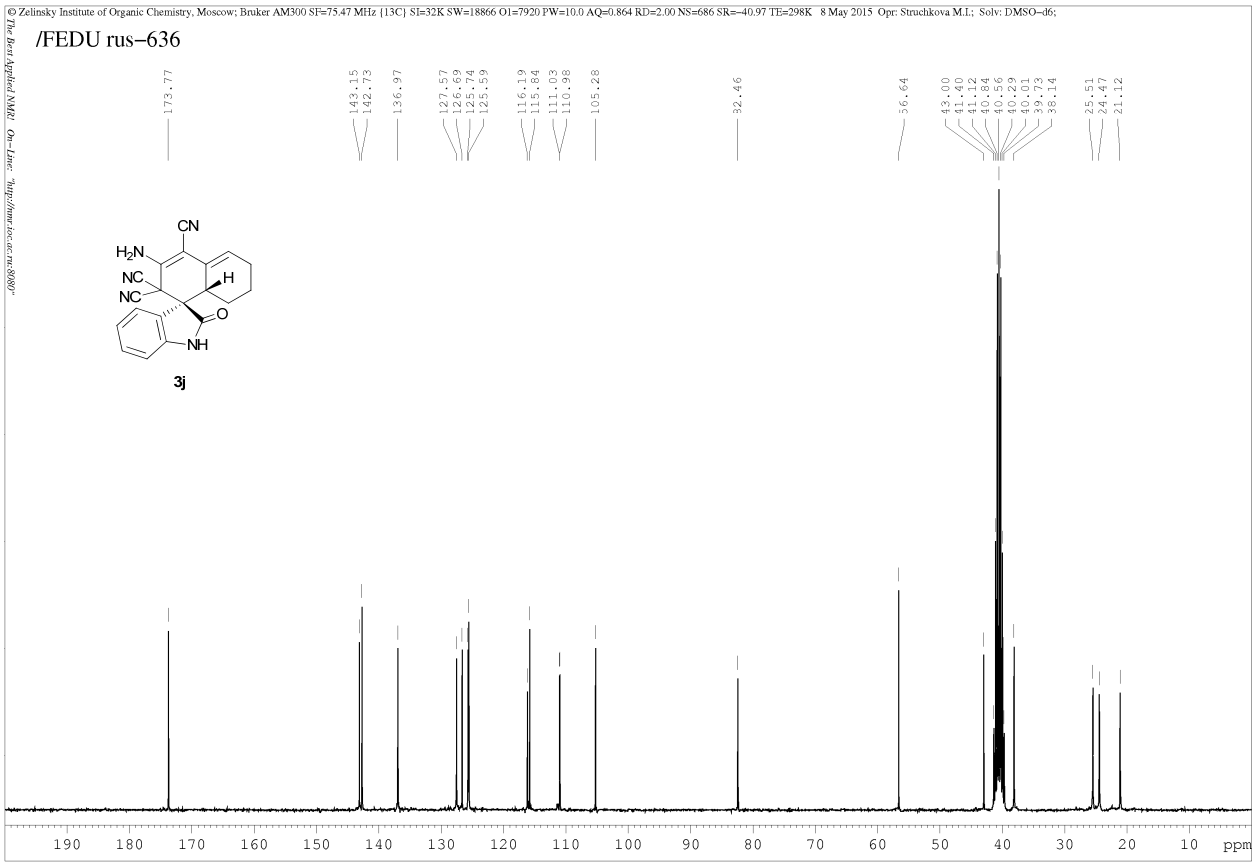
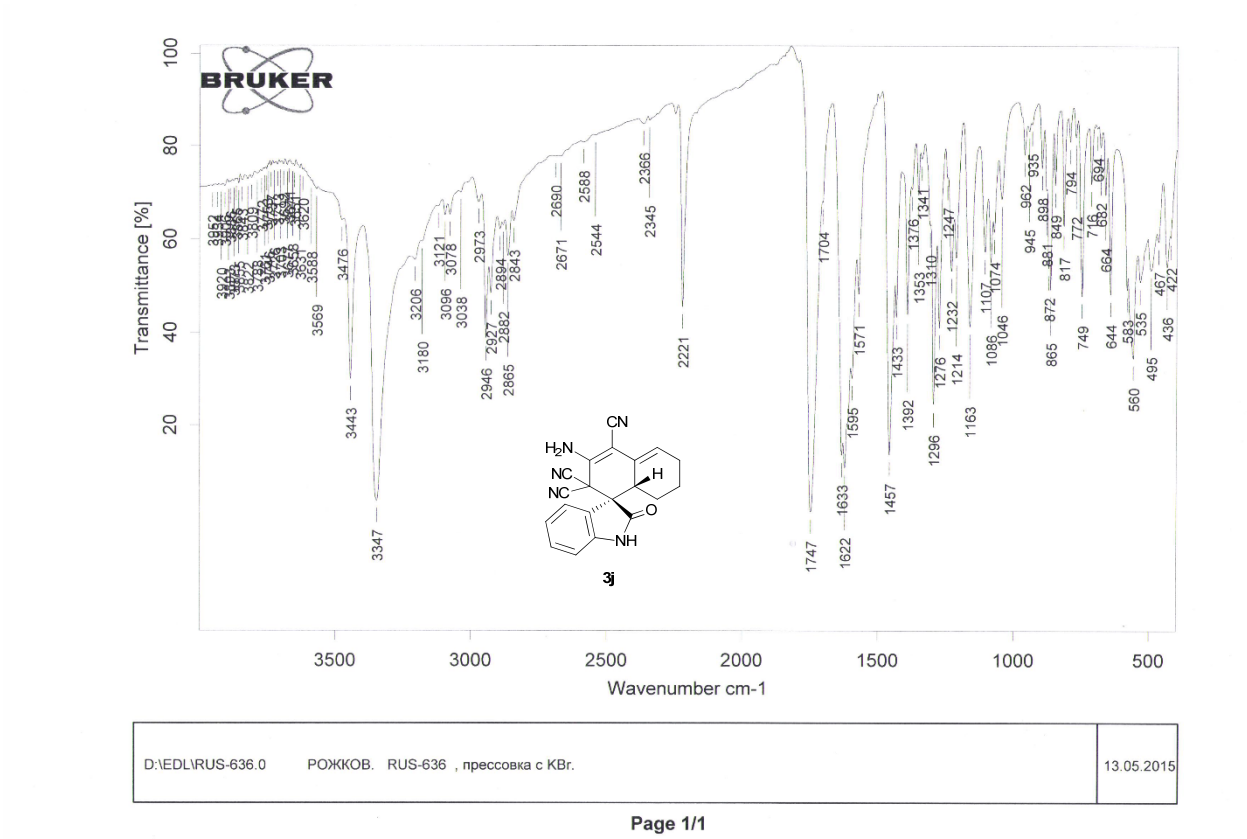
^{1}H-NMR for **3j**:



^{13}C-NMR for **3j**:



IR for **3j**:


BRUKER
Transmittance [%]
Wavenumber cm-1
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1000
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20
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60
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100
3476
3443
3347
3206
3180
3121
3096
3078
3038
2973
2946
2927
2894
2882
2865
2843
2690
2671
2588
2544
2366
2345
2221
1747
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1633
1622
1595
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1296
1276
1247
1232
1214
1163
1107
1086
1074
1046
962
945
935
898
881
872
865
849
817
784
772
749
716
694
682
664
644
583
560
535
495
467
436
422
3j
D:\EDL\RUS-636.0 РОЖКОВ. RUS-636 , прессовка с KBr.
13.05.2015
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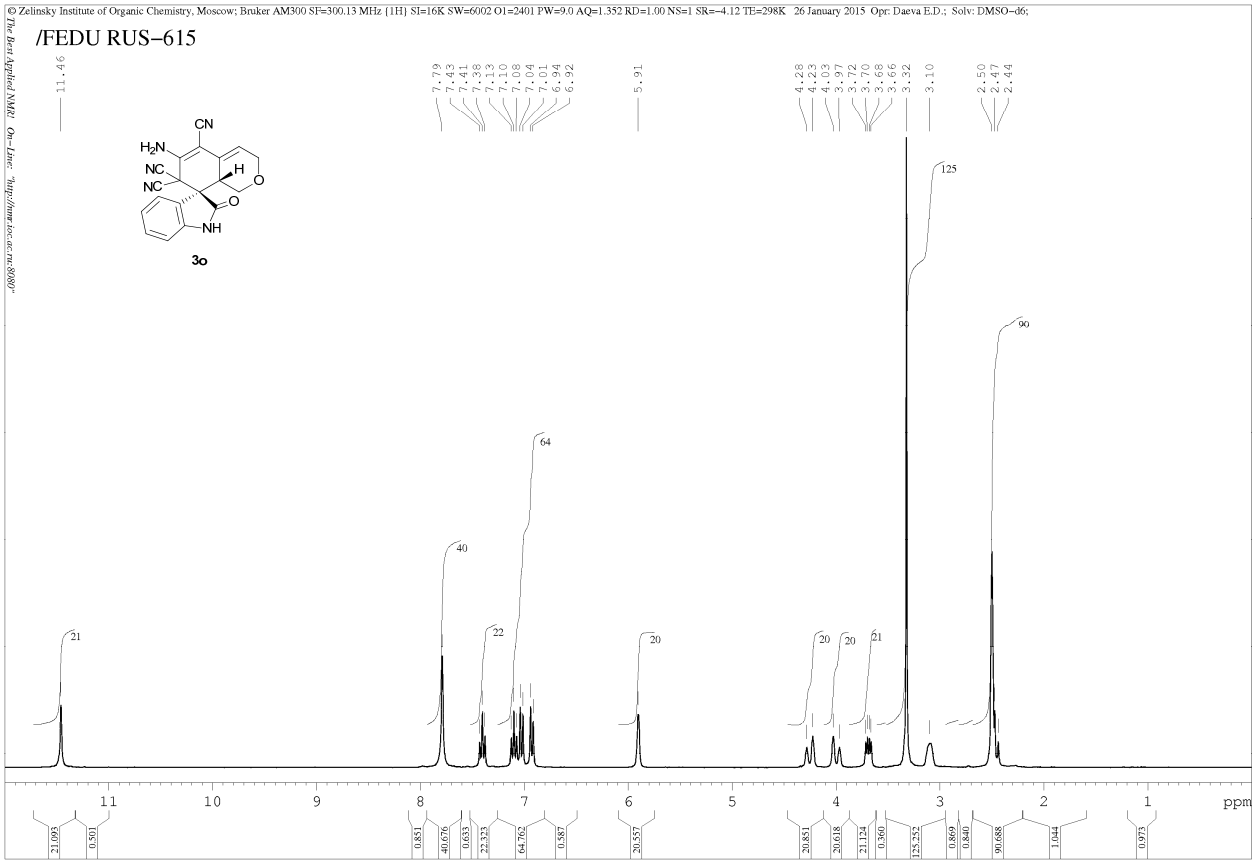
^{1}H-NMR for **3o**:



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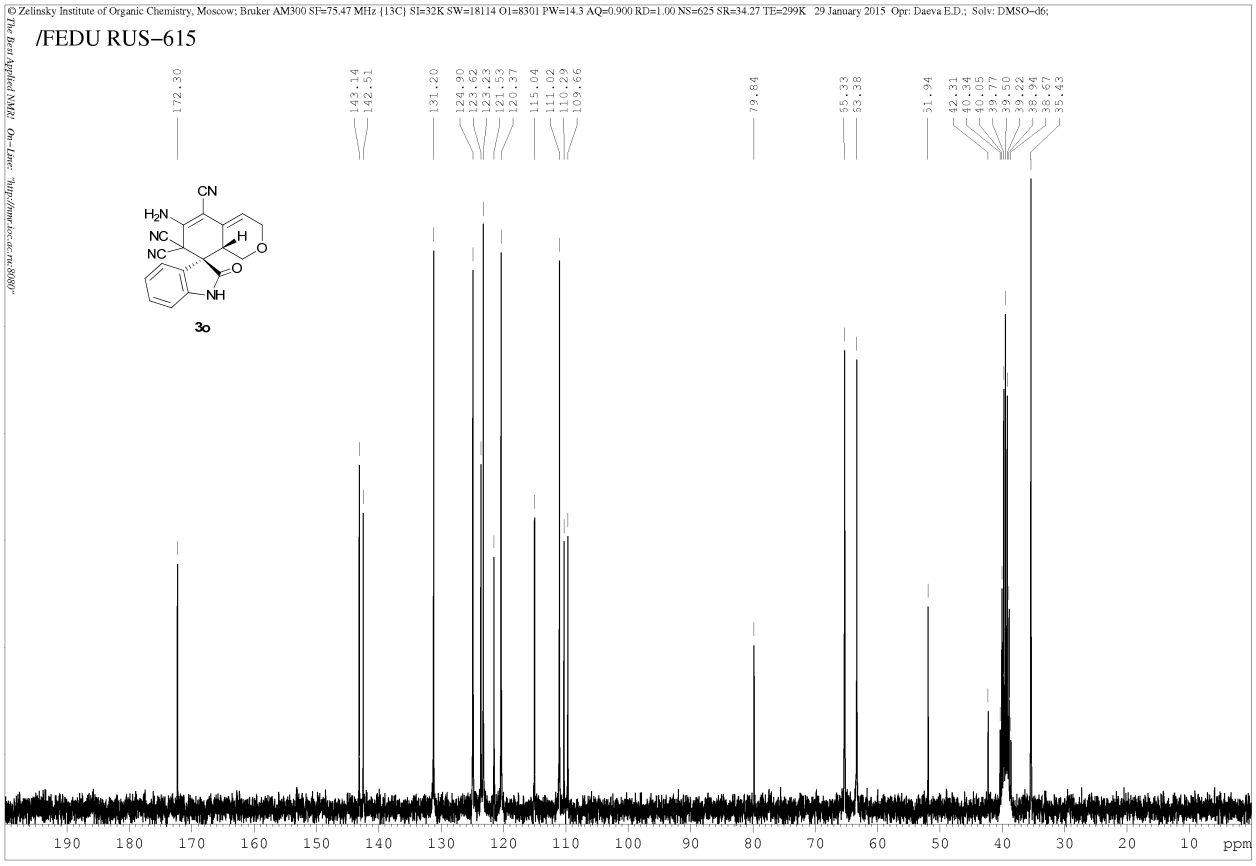
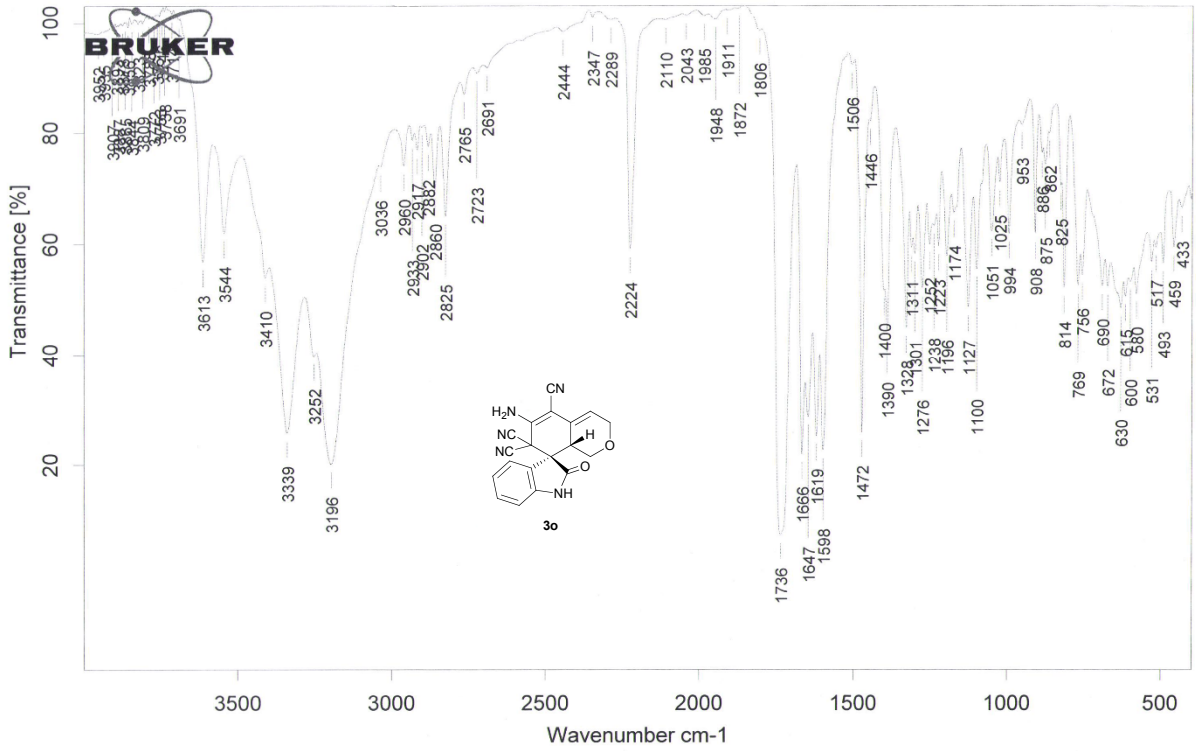
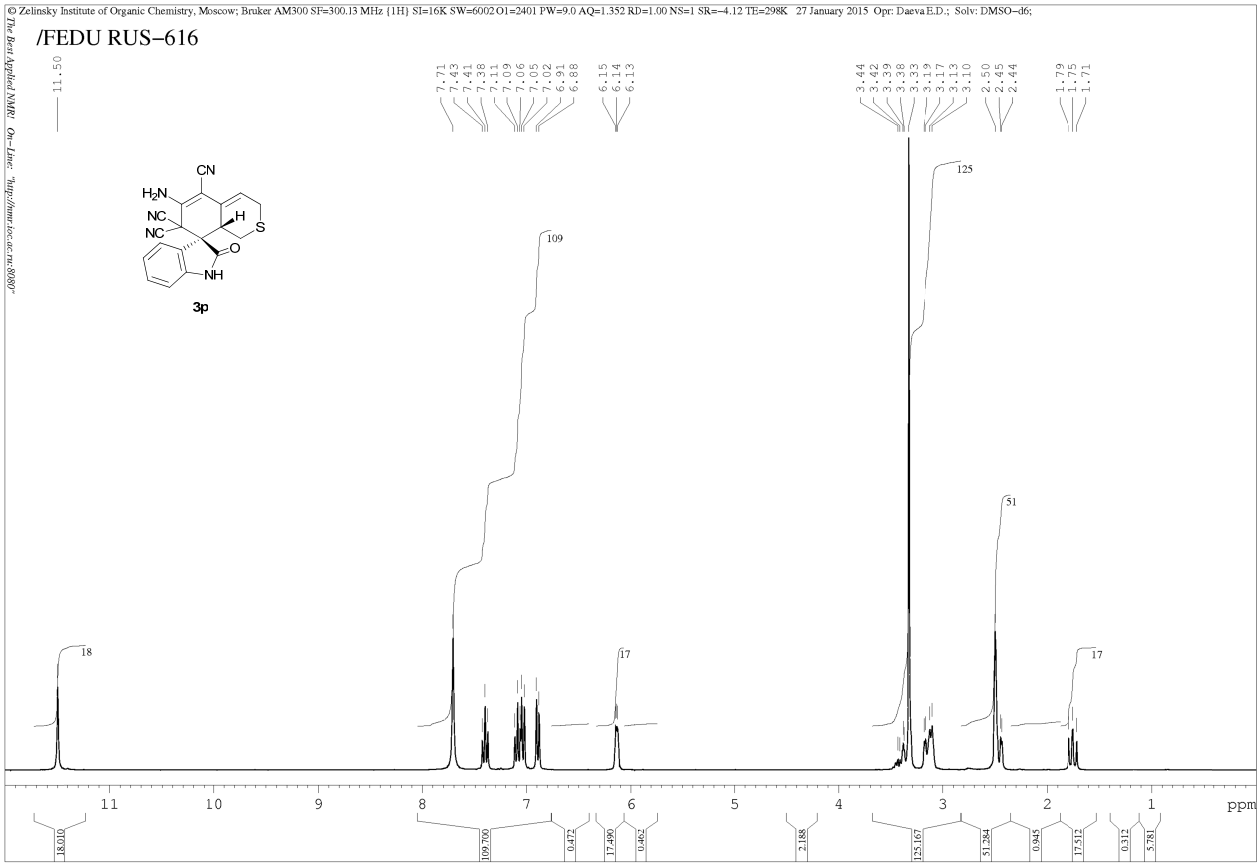


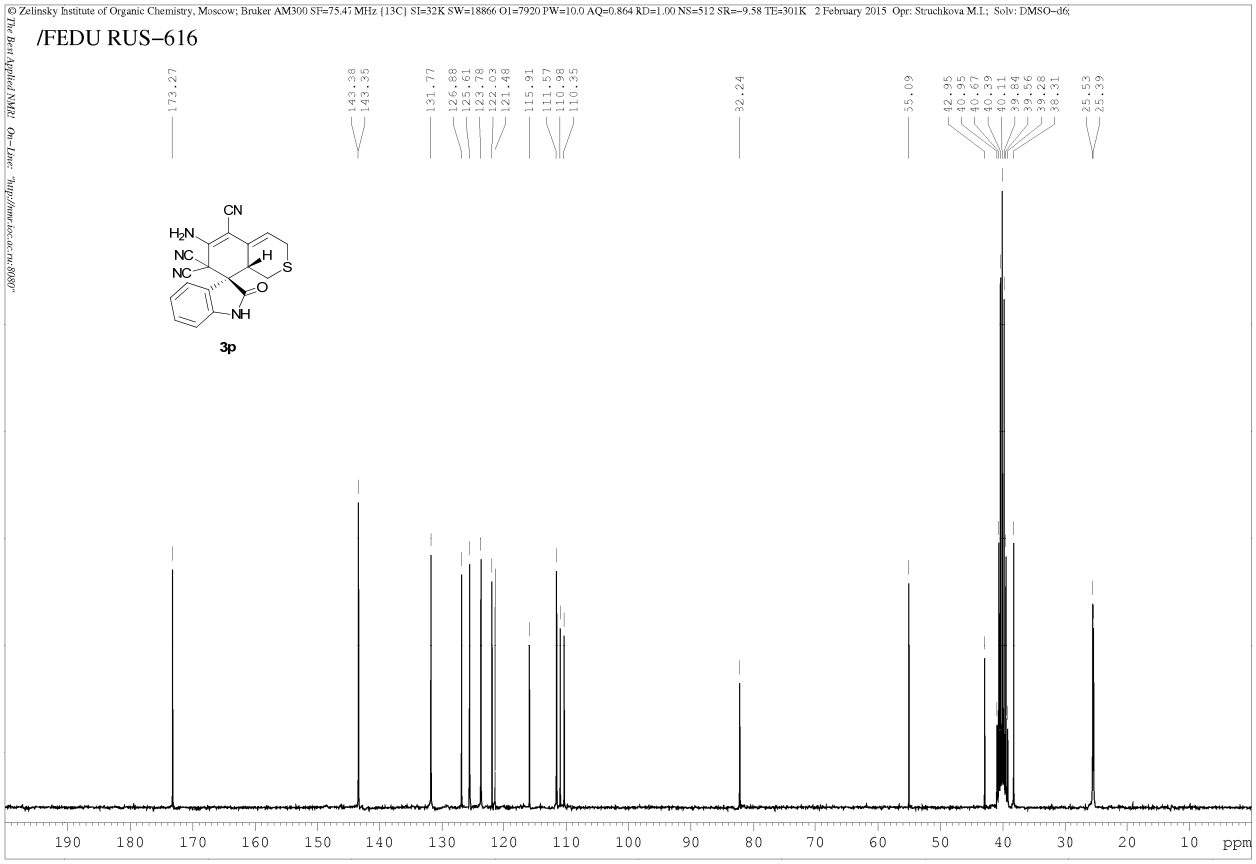
IR for **3o**:


BRUKER
Transmittance [%]
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
500
3o

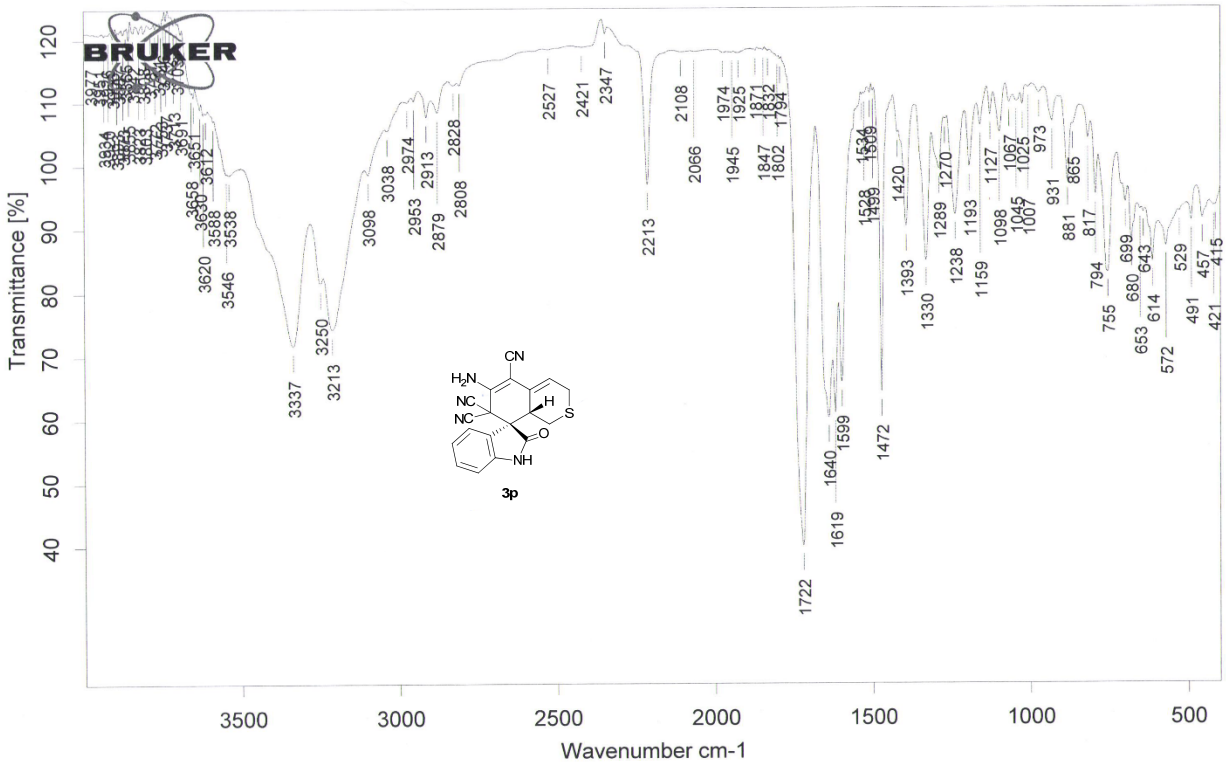
^{1}H-NMR for **3p**:



^{13}C-NMR for **3p**:



IR for **3p**:


BRUKER
Transmittance [%]
Wavenumber cm-1
3500
3000
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2000
1500
1000
500
3337
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3213
3098
3038
2974
2953
2913
2879
2828
2808
2527
2421
2347
2213
2108
2066
1974
1945
1925
1871
1847
1802
1794
1722
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1238
1193
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1098
1067
1045
1025
1007
973
931
881
865
817
794
755
699
680
643
614
572
529
491
457
421
415
3658
3630
3620
3612
3588
3546
3538
CN
H2N
NC
NC
H
S
O
NH
3p

3. Single-crystal X-ray diffraction

Single crystals of $C_{23}H_{24}N_5O_{2.5}$ (**3a**) were crystallized from EtOH. A suitable crystal was selected and mounted on a needle on a Bruker SMART 1000 diffractometer. The crystal was kept at 150 K during data collection. Using Olex2,[1] the structure was solved with the SHELXS[2] structure solution program using Direct Methods and refined with the SHELXL[2] refinement package using Least Squares minimization.

The crystal of **3a** contained two independent disordered EtOH moieties, one of them positioned around an inversion centre, resulting in a composition of $C_{20}H_{15}N_5O \cdot 1.5EtOH$. The disordered solvent molecules were refined using SAME and SIMU restraints as implemented in SHELXL 2014/7.

Crystal Data for $C_{23}H_{24}N_5O_{2.5}$ (M =410.47 g/mol): triclinic, space group P-1 (no. 2), a = 7.4809(18) Å, b = 11.265(3) Å, c = 13.576(3) Å, α = 77.760(6)°, β = 83.288(7)°, γ = 70.811(6)°, V = 1054.6(4) Å^3, Z = 2, T = 150 K, μ(MoKα) = 0.087 mm^{-1}, $Dcalc$ = 1.293 g/cm^3, 9729 reflections measured (3.074° ≤ 2Θ ≤ 52.742°), 4309 unique (R_{int} = 0.0359, R_{sigma} = 0.0575) which were used in all calculations. The final R_1 was 0.0631 (I > 2σ(I)) and wR_2 was 0.2092 (all data). The structure has been deposited with the CSD, deposition number CCDC 1050772.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

2. G. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112–122.