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Multicomponent assembling of salicylaldehydes, kojic acid and malonic acid derivatives

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Experimental section

All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 (300 and 75 MHz, respectively) at ambient temperature in DMSO-d_6 solutions. Chemical shift values are given in δ ppm 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.

Solvent-free grinding procedure

Salicylaldehyde (3 mmol, 0.37 g), malononitrile (3 mmol, 0.20 g), kojic acid (3 mmol, 0.43 g) and sodium acetate (0.3 mmol, 0.025 g) were mixed and ground in a mortar at room temperature by pestle for 18 min. When the reaction was completed, crude solid was analyzed by ^{1}H NMR spectroscopy.

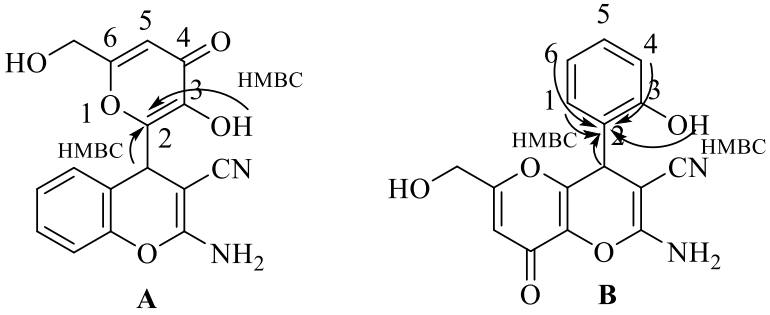
On-solvent procedure

A mixture of salicylaldehyde (3 mmol, 0.37 g), malononitrile (3 mmol, 0.20 g), kojic acid (3 mmol, 0.43 g) and sodium acetate (0.3 mmol, 0.025 g) in ethanol (5 ml) were stirred and refluxed for 1 h. Then the reaction mixture was cooled to 0–10° C. Solid was filtered off, washed by cold ethanol and if necessary purified by recrystallization from ethanol.

2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4a

Yield 0.90 g (96%), mp 254–255 °C. ^{1}H NMR (DMSO-d_6) δ: 4.08–4.22 (m, 2H, CH_2), 5.20 (s, 1H, CH), 5.58 (t, *J* 5.8 Hz, 1H, OH), 6.29 (s, 1H, CH), 7.06–7.32 (m, 6H, NH_2, Ar), 9.21 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.5, 51.0, 59.9, 109.4, 116.7, 119.9, 120.4, 125.4, 128.7, 129.5, 141.9, 149.4, 150.9, 162.0, 168.0, 174.2. MS, *m*/*z* (%): 312 (M^+, 52), 295 (4), 268 (12), 228 (100), 211 (22), 171 (17), 128 (16), 77 (12). IR (KBr, ν/cm^{-1}): 3658, 3362, 3310, 3086, 2193, 1654, 1490, 1459, 1279, 1075. Found (%): C, 61.39; H, 3.82; N, 8.78. Calc. for $C_{16}H_{12}N_2O_5$ (%): C, 61.54; H, 3.87; N, 8.97.

To confirm additionally the proposed structure **A** (2-amino-4*H*-chromene **4a**, Scheme 1**)**, a two-dimensional spectrum ^{1}H,^{13}C-HMBC was recorded. It was found that carbon C^2 interacted with the OH group at C^3, as well as with the proton of the chromene system. Further, the ^{13}C NMR spectrum was recorded without suppressing of the spin–spin interaction of carbon atoms with protons. In this spectrum, the C^2 signal was a doublet (*J* = 11 Hz) with the C–H proton of the 4*H*-pyran ring of chromene system (structure **A**). In the case of structure **B** (Scheme 1, 4,8-dihydropyrano[3,2-*b*]pyran **3**), in which the OH group is in the aromatic benzene ring, the C^2 signal should be a complex multiplet, as C^2 carbon interacts with the protons of the C^1, C^4, C^6 carbons of aromatic benzene ring (structure **B**).



Scheme 1

2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-6-methyl-4*H*-chromene-3-carbonitrile 4b

Yield 0.89 g (91%), mp 247–248 °C. ^{1}H NMR (DMSO-d_6) δ: 2.24 (s, 3H, Me), 4.07–4.30 (m, 2H, CH_2), 5.52 (t, *J* 5.8 Hz, 1H, OH), 5.63 (s, 1H, CH), 6.22 (s, 1H, CH), 6.94–6.98 (m, 2H, Ar), 7.06 (br s, 2H, NH_2), 7.12 (d, *J* 8.8 Hz, 1H, Ar), 9.24 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 20.2, 33.9, 50.5, 59.4, 108.9, 116.0, 119.1, 120.0, 128.1, 129.5, 134.0, 141.3, 147.0, 150.5, 161.6, 167.5, 173.7. MS, *m*/*z* (%): 326 (M^+, 75), 309 (14), 291 (13), 242 (21), 225 (33), 185

(100), 140 (26), 84 (8), 66 (15). IR (KBr, ν/cm^{-1}): 3568, 3368, 3325, 2192, 1650, 1499, 1458, 1411, 1184, 1079. Found (%): C, 62.41; H, 4.29; N, 8.38. Calc. for $C_{17}H_{14}N_2O_5$ (%): C, 62.57; H, 4.32; N, 8.59.

2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carbonitrile 4c

Yield 0.88 g (86%), mp 256–257 °C. ^{1}H NMR (DMSO-d_6) δ: 3.84 (s, 3H, OMe), 4.07–4.27 (m, 2H, CH_2), 5.19 (s, 1H, CH), 5.63 (t, J 5.8 Hz, 1H, OH), 6.30 (s, 1H, CH), 6.68 (d, J 7.3 Hz, 1H, Ar), 7.00–7.08 (m, 2H, Ar), 7.11 (s, 2H, NH_2), 9.25 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.1, 50.5, 55.7, 59.4, 108.9, 111.6, 119.1, 120.0, 120.2, 124.7, 138.5, 141.4, 147.2, 150.4, 161.5, 167.5, 173.8. MS, m/z (%): 342 (M^+, 100), 324 (78), 316 (3), 298 (26), 258 (49), 241 (63), 201(86), 186 (67), 158 (70), 131 (19), 103 (14). IR (KBr, ν/cm^{-1}): 3589, 3446, 3096, 3013, 2194, 1663, 1464, 1444, 1274, 1083. Found (%): C, 59.43; H, 4.09; N, 8.03. Calc. for $C_{17}H_{14}N_2O_6$ (%): C, 59.65; H, 4.12; N, 8.18.

2-Amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carbonitrile 4d

Yield 1.01 g (79%), mp 246–247 °C. ^{1}H NMR (DMSO-d_6) δ: 3.86 (s, 3H, OMe), 4.10–4.34 (m, 2H, CH_2), 5.18 (s, 1H, CH), 5.63 (t, J 5.8 Hz, 1H, OH), 6.31 (s, 1H, CH), 6.83 (s, 1H, Ar), 7.20 (br s, 3H, NH_2, Ar), 9.35 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.0, 50.3, 56.3, 59.4, 109.0, 114.8, 115.9, 119.6, 121.2, 122.1, 138.0, 141.5, 148.1, 149.9, 161.1, 167.6, 173.8. MS, m/z (%): 422 (M^+, 6, ^{81}Br), 420 (M^+, 7, ^{79}Br), 405 (4), 403 (4), 336 (4), 334 (3), 280 (26), 278 (28), 142 (33), 100 (42), 69 (74). IR (KBr, ν/cm^{-1}): 3568, 3481, 3464, 3072, 2191, 1650, 1412, 1200, 1089, 1038. Found (%): C, 48.35; H, 3.07; Br, 18.81; N, 6.53. Calc. for $C_{17}H_{13}BrN_2O_6$ (%): C, 48.48; H, 3.11; Br, 18,97; N, 6.65.

2-Amino-6-chloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4e

Yield 0.78 g (75%), mp 249–250 °C. ^{1}H NMR (DMSO-d_6) δ: 4.12–4.26 (m, 2H, CH_2), 5.21 (s, 1H, CH), 5.63 (t, J 5.8 Hz, 1H, OH), 6.31 (s, 1H, CH), 7.11 (m, 4H, Ar, NH_2), 7.38 (dd, J_1 1.7, J_2 8.1Hz, 1H, Ar), 9.34 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.1, 50.3, 59.4, 109.0, 117.4, 118.2, 119.7, 121.6, 127.5, 128.9, 141.5, 147.9, 149.9, 161.3, 167.6, 173.8. MS, m/z (%): 348 (M^+, 30, ^{37}Cl), 346 (M^+, 100, ^{35}Cl), 331 (6, ^{37}Cl), 329 (12, ^{35}Cl), 264 (7, ^{37}Cl), 262 (24, ^{35}Cl), 207 (35, ^{37}Cl), 205 (96, ^{35}Cl), 73 (12). IR (KBr, ν/cm^{-1}): 3569, 3362, 3324, 3089, 2197, 1651, 1509, 1414,

1120, 724. Found (%): C, 55.28; H, 3.07; Cl, 10.05; N, 8.12. Calc. for $C_{16}H_{11}ClN_2O_5$ (%): C, 55.43; H, 3.20; Cl, 10.23; N, 8.08.

2-Amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4f

Yield 0.93 g (79%), mp 225–226 °C. ^{1}H NMR (DMSO-d_6) δ: 4.10–4.26 (m, 2H, CH_2), 5.21 (s, 1H, CH), 5.61 (t, *J* 5.8 Hz, 1H, OH), 6.31 (s, 1H, CH), 7.06 (d, *J* 8.8 Hz,1H, Ar), 7.18 (s, 2H, NH_2), 7.28 (d, *J* 1.9 Hz, 1H, Ar), 7.49 (dd, J_1 1.9, J_2 8.8 Hz, 1H, Ar), 9.45 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 33.9, 50.3, 59.4, 109.0, 116.1, 118.5, 119.6, 122.0, 130.4, 131.8, 141.4, 148.3, 149.9, 161.2, 167.5, 173.7. MS, *m*/*z* (%): 392 (M^+, 100, ^{81}Br), 390 (M^+, 97, ^{79}Br), 374 (22, ^{81}Br), 372 (23, ^{79}Br), 346 (12, ^{81}Br), 344 (7, ^{79}Br) 308 (20, ^{81}Br), 306 (19, ^{79}Br), 250 (8, ^{81}Br), 248 (7, ^{79}Br), 141 (1), 71 (28). IR (KBr, ν/cm^{-1}): 3568, 3061, 2193, 1656, 1477, 1453, 1402, 1204, 1118, 571. Found (%): C, 48.95; H, 2.77; Br, 20.28; N, 7.11. Calc. for $C_{16}H_{11}BrN_2O_5$ (%): C, 49.13; H, 2.83; Br, 20.43; N, 7.16.

2-Amino-6,8-dichloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4g

Yield 0.89 g (78%), mp 245–246 °C. ^{1}H NMR (DMSO-d_6) δ: 4.15–4.25 (m, 2H, CH_2), 5.24 (s, 1H, CH), 5.62 (t, *J* 5.8 Hz, 1H, OH), 6.31 (s, 1H, CH), 7.15 (d, *J* 1.9 Hz, 1H, Ar), 7.34 (br s, 2H, NH_2), 7.67 (d, *J* 2.0 Hz, 1H, Ar), 9.37 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.5, 50.7, 59.4, 109.1, 119.2, 121.5, 123.1, 126.6, 128.2, 128.9, 141.7, 144.1, 149.5, 160.7, 167.6, 173.8. MS, *m*/*z* (%): 381 (M^+, 1, ^{37}Cl^{35}Cl), 379 (M^+, 1, ^{35}Cl^{35}Cl), 318 (1), 291 (2), 219 (1), 148 (4), 113 (4), 97 (8), 84 (11), 69 (59). IR (KBr, ν/cm^{-1}): 3568, 3366, 3075, 2192, 1650, 1569, 1450, 1241, 794, 662. Found (%): C, 50.37; H, 2.58; Cl, 18.58; N, 7.21. Calc. for $C_{16}H_{10}Cl_2N_2O_5$ (%): C, 50.42; H, 2.64; Cl, 18.60; N, 7.35.

2-Amino-6,8-dibromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4h

Yield 1.07 g (76%), mp 246–247 °C. ^{1}H NMR (DMSO-d_6) δ: 4.12–4.28 (m, 2H, CH_2), 5.24 (s, 1H, CH), 5.62 (t, *J* 5.8 Hz, 1H, OH), 6.31 (s, 1H, CH), 7.29 (d, *J* 1.8 Hz, 1H, Ar), 7.32 (br s, 2H, NH_2), 7.87 (d, *J* 1.8 Hz, 1H, Ar), 9.37 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.5, 50.8, 59.4, 109.1, 110.8, 116.2, 119.2, 123.4, 130.0, 134.3, 141.6, 145.5, 149.6, 160.9, 167.6, 173.8. MS, *m*/*z* (%): 472 (M^+, 30, ^{81}Br^{81}Br), 470 (M^+, 58, ^{81}Br^{79}Br), 468 (M^+, 28, ^{79}Br^{79}Br), 455 (14, ^{81}Br^{81}Br), 453 (9, ^{81}Br^{79}Br), 451 (12, ^{79}Br^{79}Br), 331 (17, ^{81}Br^{81}Br), 329 (25, ^{81}Br^{79}Br), 327 (20, ^{79}Br^{79}Br), 141 (14), 84 (13). IR (KBr, ν/cm^{-1}): 3499, 3475, 2189, 1649, 1534, 1499, 1407, 1158,

593, 553. Found (%): C, 40.73; H, 2.09; Br, 33.86; N, 5.73. Calc. for $C_{16}H_{10}Br_2N_2O_5$ (%): C, 40.88; H, 2.14; Br, 34.00; N, 5.96.

2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-6-nitro-4*H*-chromene-3-carbonitrile 4i

Yield 0.80 g (75%), mp 237–238 °C. ^{1}H NMR (DMSO-d_6) δ: 4.10–4.23 (m, 2H, CH_2), 5.34 (s, 1H, CH), 5.61 (t, *J* 5.8 Hz, 1H, OH), 6.32 (s, 1H, CH), 7.32 (d, *J* 9.5 Hz, 1H, Ar), 7.36 (s, 2H, NH_2), 8.00 (d, *J* 2.2 Hz, 1H, Ar), 8.18 (dd, J_1 2.2 Hz, J_2 9.5 Hz, 1H, Ar), 9.45 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 34.1, 50.5, 59.1, 109.1, 116.3, 119.3, 124.1, 125.8, 128.7, 141.7, 143.8, 149.7, 153.4, 160.8, 167.6, 173.8. MS, *m*/*z* (%): 357 (M^+, 63), 340 (98), 308 (100), 273 (7), 216 (16), 46 (6), 44 (14), 31 (22), 26 (4), 17 (2). IR (KBr, ν/cm^{-1}): 3569, 3325, 2959, 2198, 1656, 1530, 1487, 1449, 1342, 1088. Found (%): C, 53.71; H, 3.02; N, 11.61. Calc. for $C_{16}H_{11}N_3O_7$ (%): C, 53.79; H, 3.10; N, 11.76.

Methyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4j

Yield 0.88 g (85%), mp 208–210 °C. ^{1}H NMR (DMSO-d_6) δ: 3.53 (s, 3H, Me), 4.06–4.23 (m, 2H, CH_2), 5.32 (s, 1H, CH), 5.57 (t, *J* 5.8 Hz, 1H, OH), 6.20 (s, 1H, CH), 7.00–7.16 (m, 2H, Ar), 7.22–7.32 (m, 2H, Ar), 7.74 (s, 2H, NH_2), 8.86 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 33.6, 50.6, 59.5, 70.5, 108.8, 115.8, 122.2, 124.7, 128.5, 128.6, 140.3, 149.2, 153.3, 162.0, 166.9, 168.4, 173.9. MS, *m*/*z* (%): 345 (M^+, 33), 314 (4), 286 (100), 204 (19), 172 (51), 116 (20), 89 (24), 59 (31). IR (KBr, ν/cm^{-1}): 3414, 3305, 3089, 2948, 2837, 1586, 1439, 1301, 1229, 1071. Found (%): C, 58.97; H, 4.35; N, 3.97. Calc. for $C_{17}H_{15}NO_7$ (%): C, 59.13; H, 4.38; N, 4.06.

Ethyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4k

Yield 0.89 g (83%), mp 186–188 °C.^{1}H NMR (DMSO-d_6) δ: 1.07 (t, *J* 7.0 Hz, 3H, Me), 3.87–4.25 (m, 4H, $2CH_2$), 5.32 (s, 1H, CH), 5.58 (t, *J* 5.8 Hz, 1H, OH), 6.23 (s, 1H, CH), 7.03–7.16 (m, 2H, Ar), 7.24–7.34 (m, 2H, Ar), 7.74 (s, 2H, NH_2), 8.85 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 14.1, 33.6, 58.5, 59.4, 70.5, 108.6, 115.7, 121.9, 124.6, 128.5, 128.5, 140.4, 149.0, 153.4, 161.7, 166.7, 168.0, 173.8. MS, *m*/*z* (%): 359 (M^+, 40), 313 (13), 286 (100), 218 (10), 172 (39), 145 (13), 118 (17), 89 (33), 55 (10). IR (KBr, ν/cm^{-1}): 3407, 3087, 2985, 2944, 1690, 1586, 1408, 1301, 1225, 1064. Found (%): C, 60.03; H, 4.69; N, 3.78. Calc. for $C_{18}H_{17}NO_7$ (%): C, 60.17; H, 4.77; N, 3.90.

Ethyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carboxylate 4l

Yield 0.89 g (76%), mp 218–220 °C. ^{1}H NMR (DMSO-d_6) δ: 1.06 (t, *J* 7.3Hz, 3H, Me), 3.84 (s, 3H, Me), 3.89–4.25 (m, 4H, 2CH_2), 5.29 (s, 1H, CH), 5.59 (t, *J* 5.8 Hz, 1H, OH), 6.23 (s, 1H, CH), 6.83 (d, *J* 7.3 Hz, 1H, Ar), 6.95–7.08 (m, 2H, Ar), 7.79 (s, 2H, NH_2), 8.84 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 14.1, 33.6, 55.7, 58.6, 59.4, 70.4, 108.6, 111.2, 119.5, 122.6, 124.4, 138.4, 140.5, 146.9, 153.3, 161.6, 166.7, 168.1, 173.8. MS, *m*/*z* (%): 389 (M^+, 26), 344 (3), 317 (19), 316 (100), 286 (10), 248 (8), 202 (21), 187 (8), 159 (7), 89 (4). IR (KBr, ν/cm^{-1}): 3286, 3087, 2992, 2837, 1686, 1592, 1410, 1304, 1284, 1039. Found (%): C, 58.49; H, 4.89; N, 3.48. Calc. for $C_{19}H_{19}NO_8$ (%): C, 58.61; H, 4.92; N, 3.60.

Ethyl 2-amino-6-chloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4m

Yield 0.95 g (81%), mp 224–226 °C. ^{1}H NMR (DMSO-d_6) δ: 1.07 (t, *J* 7.4Hz, 3H, Me), 3.87–4.25 (m, 4H, 2CH_2), 5.30 (s, 1H, CH), 5.58 (br s, 1H, OH), 6.25 (s, 1H, CH), 7.12 (d, *J* 8.8Hz, 1H, Ar), 7.25–7.37 (m, 2H, Ar), 7.77 (s, 2H, NH_2), 8.96 (br s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 14.2, 33.8, 58.7, 59.5, 70.2, 108.9, 117.8, 124.0, 127.8, 128.1, 128.6, 140.7, 147.9, 153.0, 161.4, 166.9, 167.9, 173.9. MS, *m*/*z* (%): 395 (M^+, 11, ^{37}Cl), 393 (M^+, 31, ^{35}Cl), 349 (5, ^{37}Cl), 347 (13, ^{35}Cl), 322 (34, ^{37}Cl), 320 (100, ^{35}Cl), 266 (2, ^{37}Cl), 264 (5, ^{35}Cl), 208 (11, ^{37}Cl), 206 (29, ^{35}Cl), 152 (10), 89 (7). IR (KBr, ν/cm^{-1}): 3298, 3035, 2975, 1689, 1572, 1400, 1308, 1290, 1028, 738. Found (%): C, 54.68; H, 4.07; Cl, 8.87; N, 3.41. Calc. for $C_{18}H_{16}ClNO_7$ (%): C, 54.90; H, 4.10; Cl, 9.00; N, 3.56.

Methyl 2-amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4n

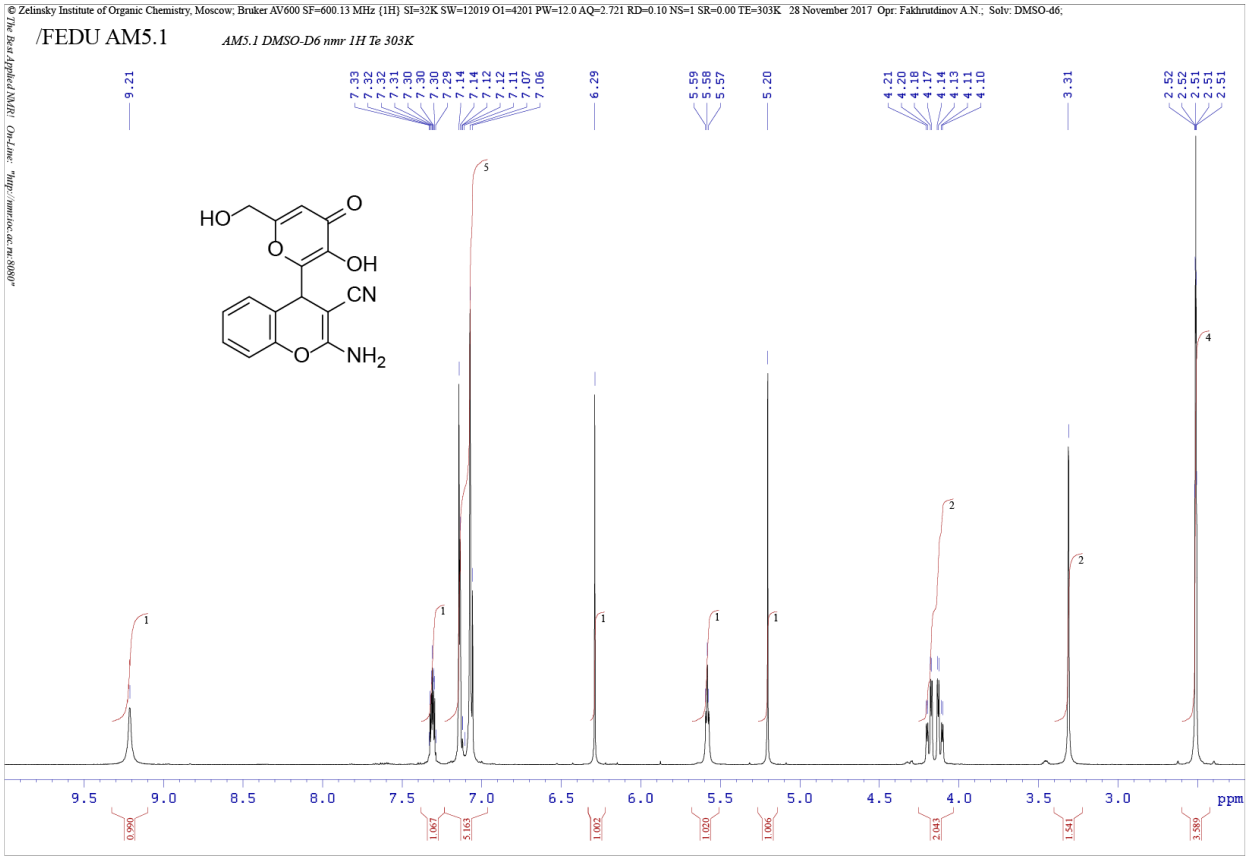
Yield 0.99 g (78%), mp 202–204 °C. ^{1}H NMR (DMSO-d_6) δ: 3.53 (s, 3H, Me), 4.12–4.20 (m, 2H, CH_2), 5.30 (s, 1H, CH), 5.56 (t, *J* 5.9 Hz, 1H, OH), 6.22 (s, 1H, CH), 7.03 (d, *J* 8.7Hz, 1H, Ar), 7.37–7.48 (m, 2H, Ar), 7.75 (s, 2H, NH_2), 8.93 (br s, 1H, OH). ^{13}CNMR (DMSO-d_6) δ: 33.5, 50.6, 59.5, 70.0, 108.9, 115.9, 118.1, 124.7, 130.6, 131.4, 140.4, 148.4, 152.7, 161.6, 166.9, 168.1, 173.8. MS, *m*/*z* (%): 425 (M^+, 40, ^{81}Br), 423 (M^+, 41, ^{79}Br), 394 (6, ^{81}Br), 392 (8, ^{79}Br), 366 (98, ^{81}Br) 364 (100, ^{79}Br), 324 (12, ^{81}Br), 322 (12, ^{79}Br), 284 (13, ^{81}Br), 282 (12, ^{79}Br), 250 (36, ^{81}Br), 252 (35, ^{79}Br), 143 (44), 59 (81). IR (KBr, ν/cm^{-1}): 3426, 3094, 2951, 2831, 1695, 1573, 1440, 1307, 1228, 601. Found (%): C, 48.02; H, 3.28; Br, 18.71; N, 3.17. Calc. for $C_{17}H_{14}BrNO_7$ (%): C, 48.13; H, 3.33; Br, 18.84; N, 3.30.

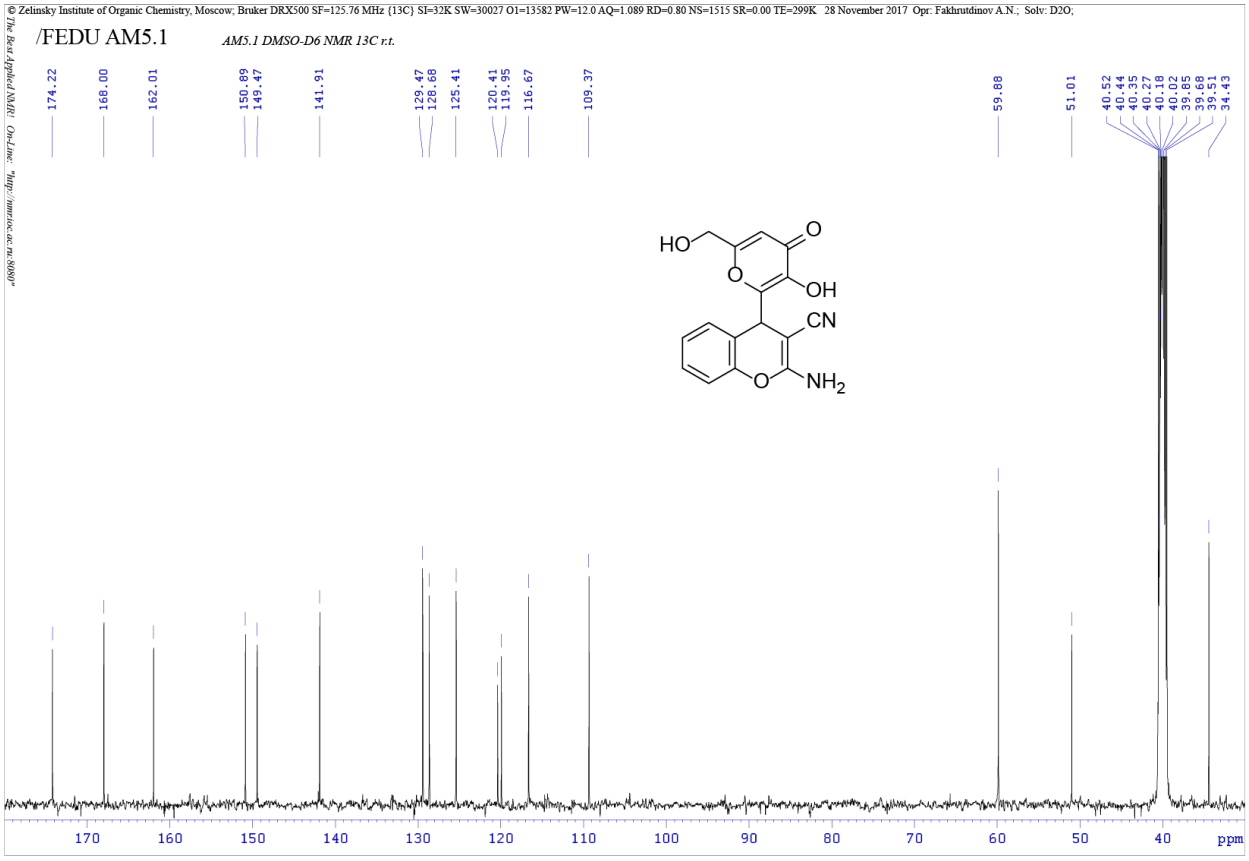
3-Amino-1-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-1*H*-benzo[*f*]chromene-2-carbonitrile 4o

Yield 0.77 g (71%), mp 283–284 °C. ^{1}H NMR (DMSO-d_6) δ: 3.98–4.11 (m, 2H, CH_2), 5.52 (t, *J* 5.9 Hz, 1H, OH), 5.63 (s, 1H, CH), 6.22 (s, 1H, CH), 7.22 (br s, 2H, NH_2),7.32 (d, *J* 8.8 Hz, 1H, Ar), 7.48–7.61 (m, 2H, Ar), 7.97 (m, 3H, Ar), 9.56 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 31.9, 51.5, 59.4, 108.9, 112.0, 116.9, 119.9, 122.3, 125.2, 127.6, 128.7, 129.9, 130.2, 130.5, 140.3, 147.6, 150.0, 161.6, 167.5, 173.6. MS, *m*/*z* (%): 362 (M^+, 28), 346 (1), 305 (2), 290 (2), 255 (4), 202 (36), 192 (100), 177 (2), 16 (8). IR (KBr, ν/cm^{-1}): 3568, 3071, 3055, 2189, 1656, 1510, 1491, 1414, 1194, 1085. Found (%): C, 66.17; H, 3.72; N, 7.58. Calc. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73.

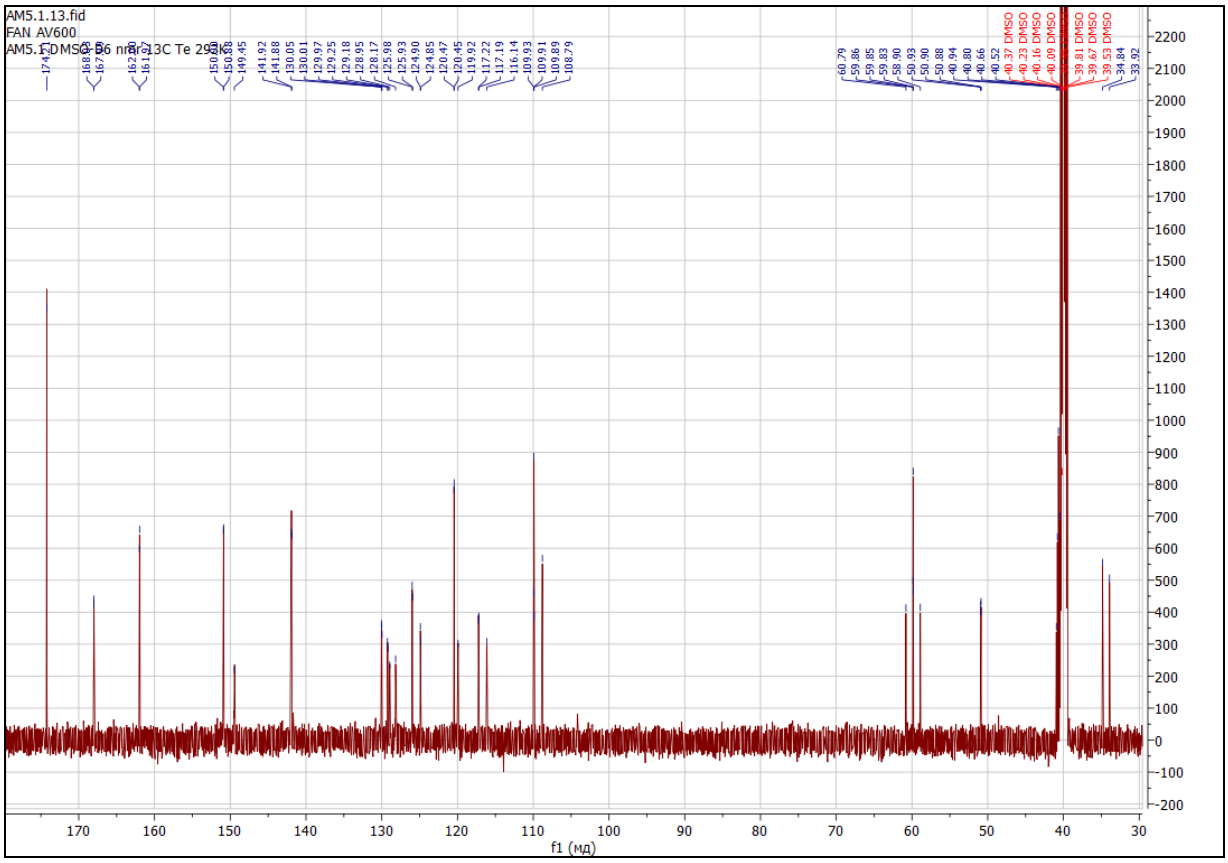
NMR spectra

2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4a

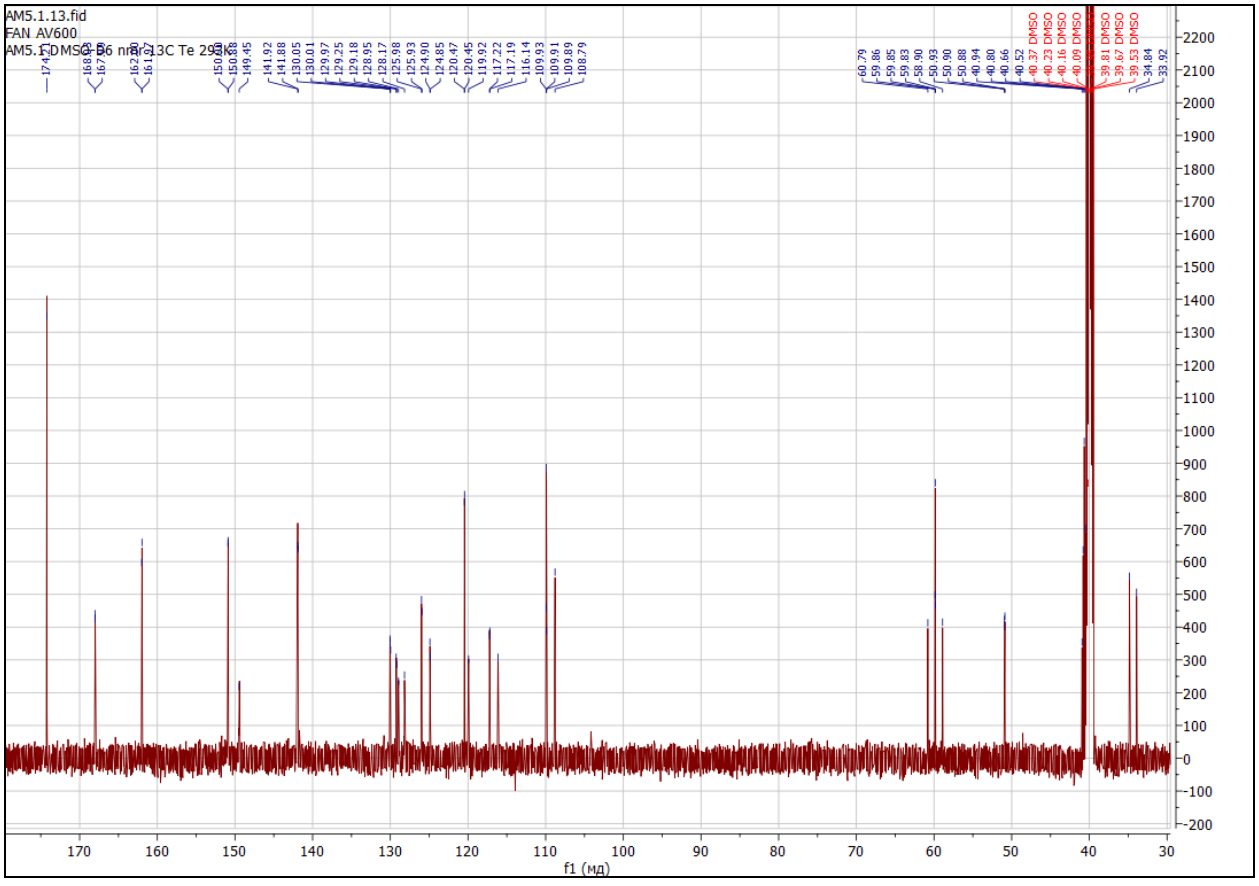




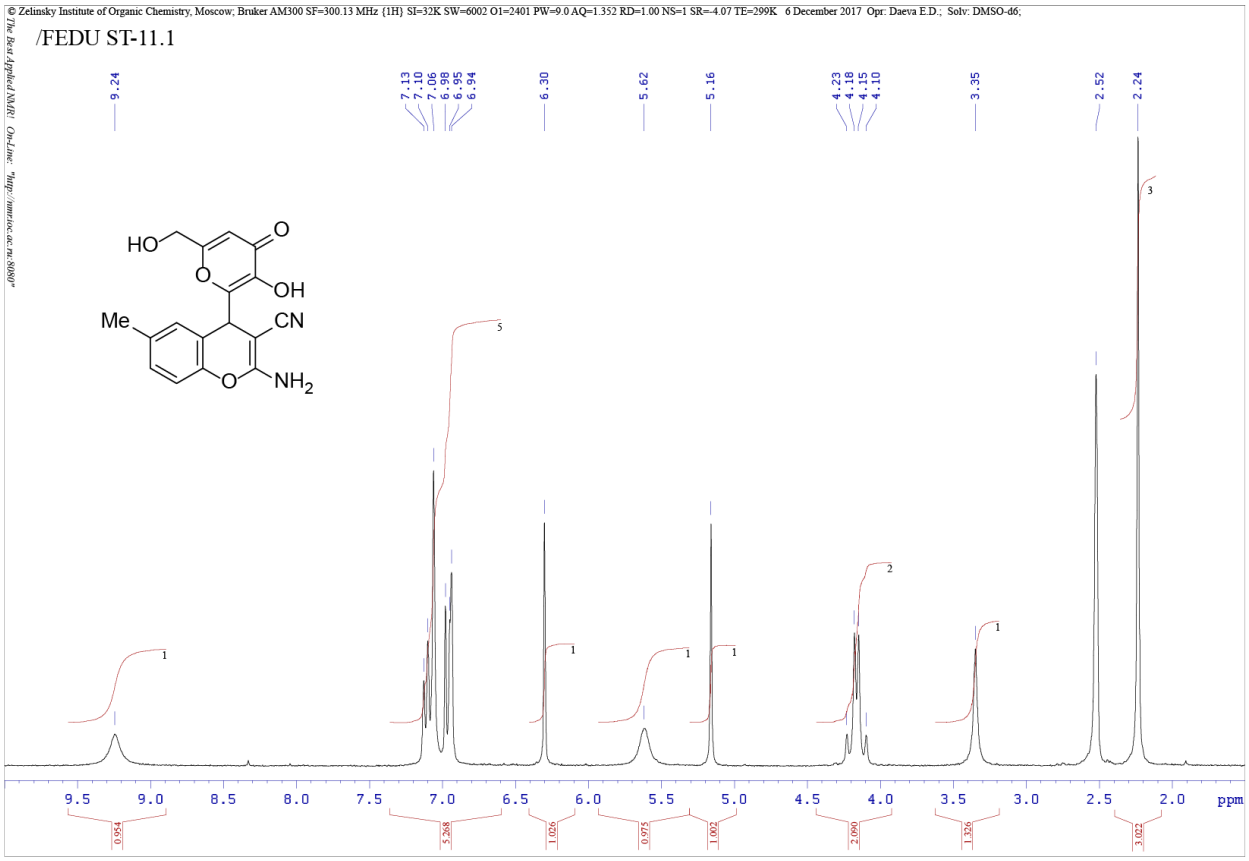
^{13}C spectrum of compound 4a without proton decoupling

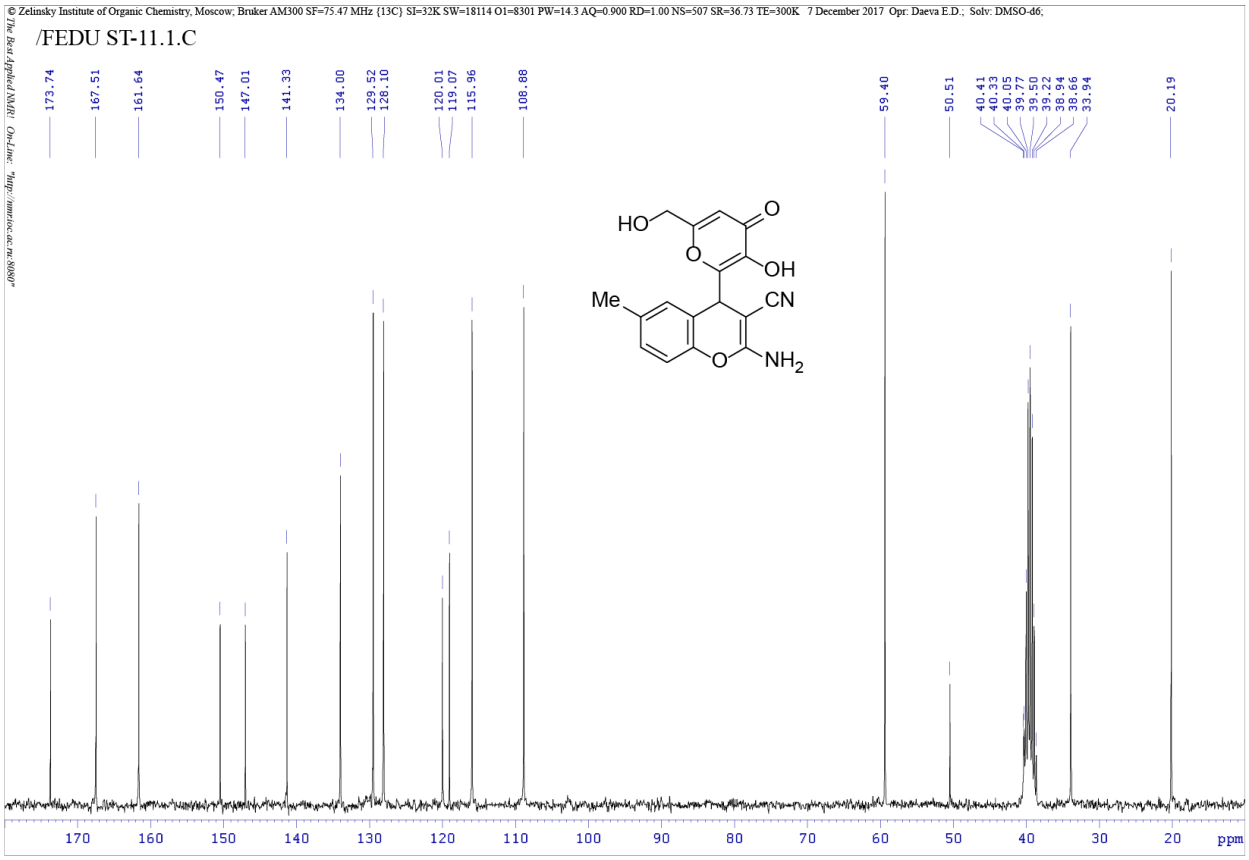


^{1}H,^{13}C-HMBC spectrum of compound 4a

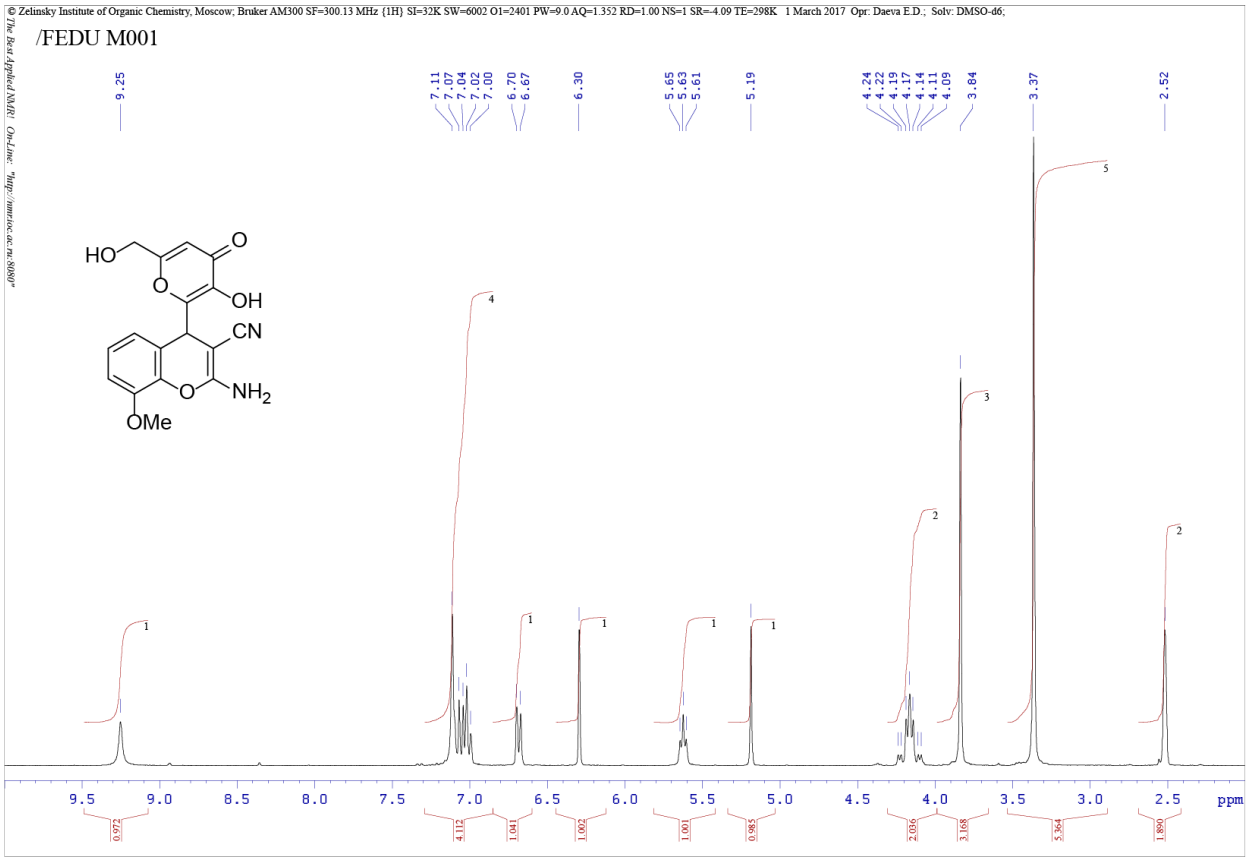


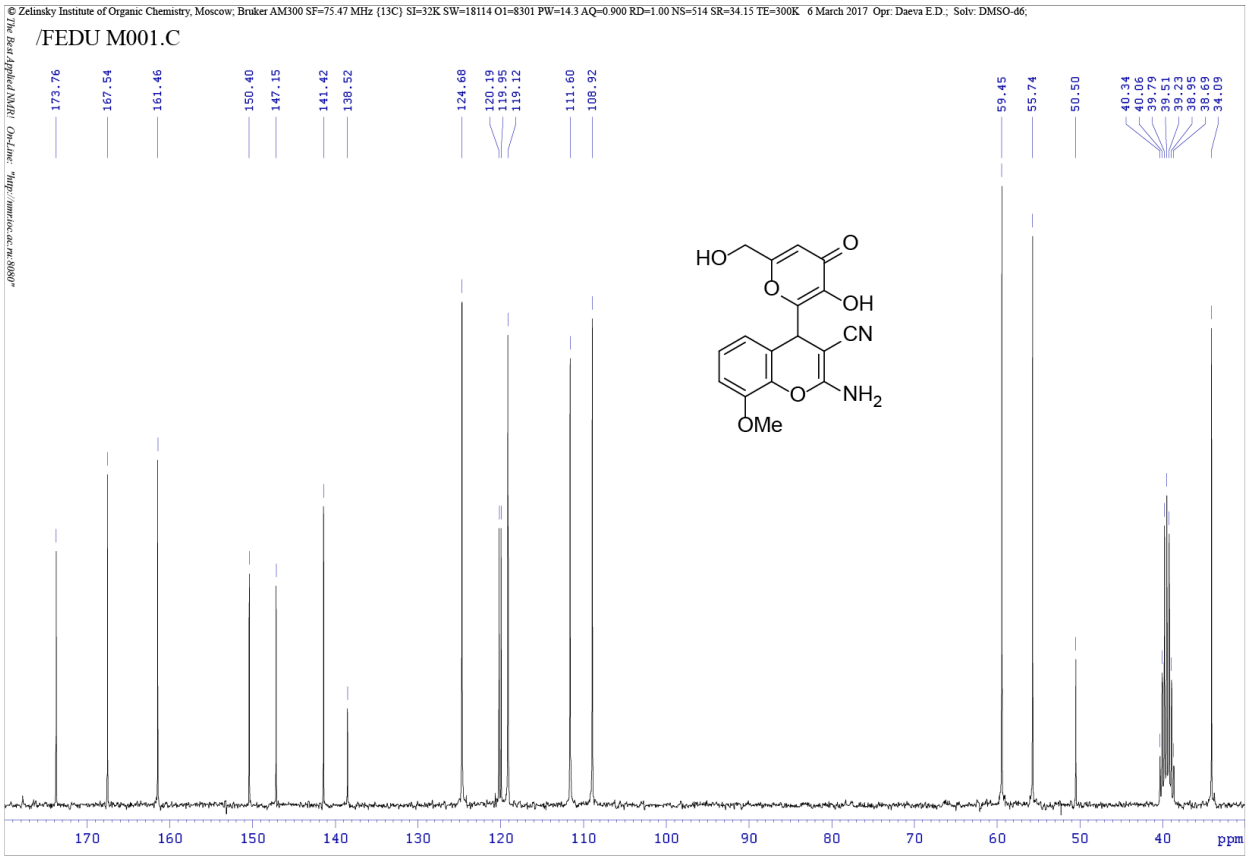
2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-6-methyl-4*H*-chromene-3-carbonitrile 4b



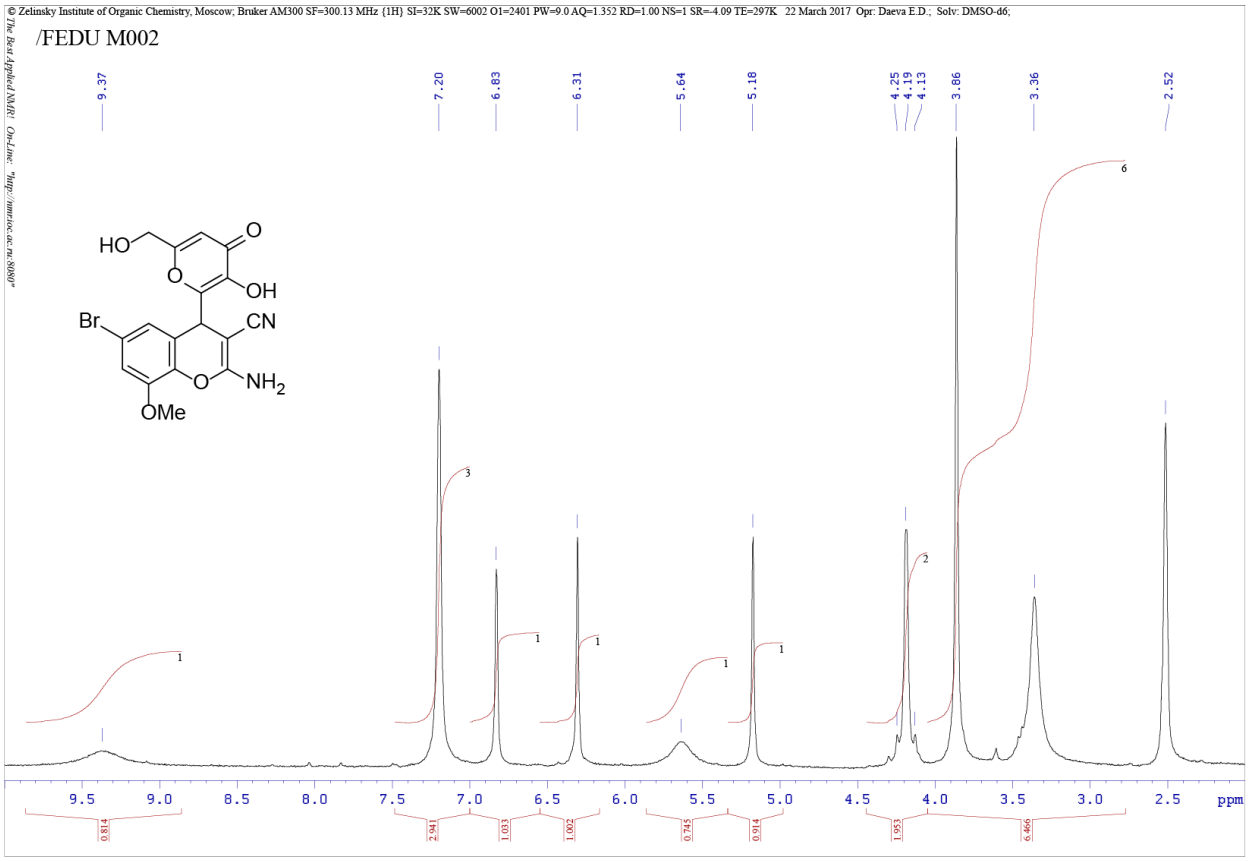


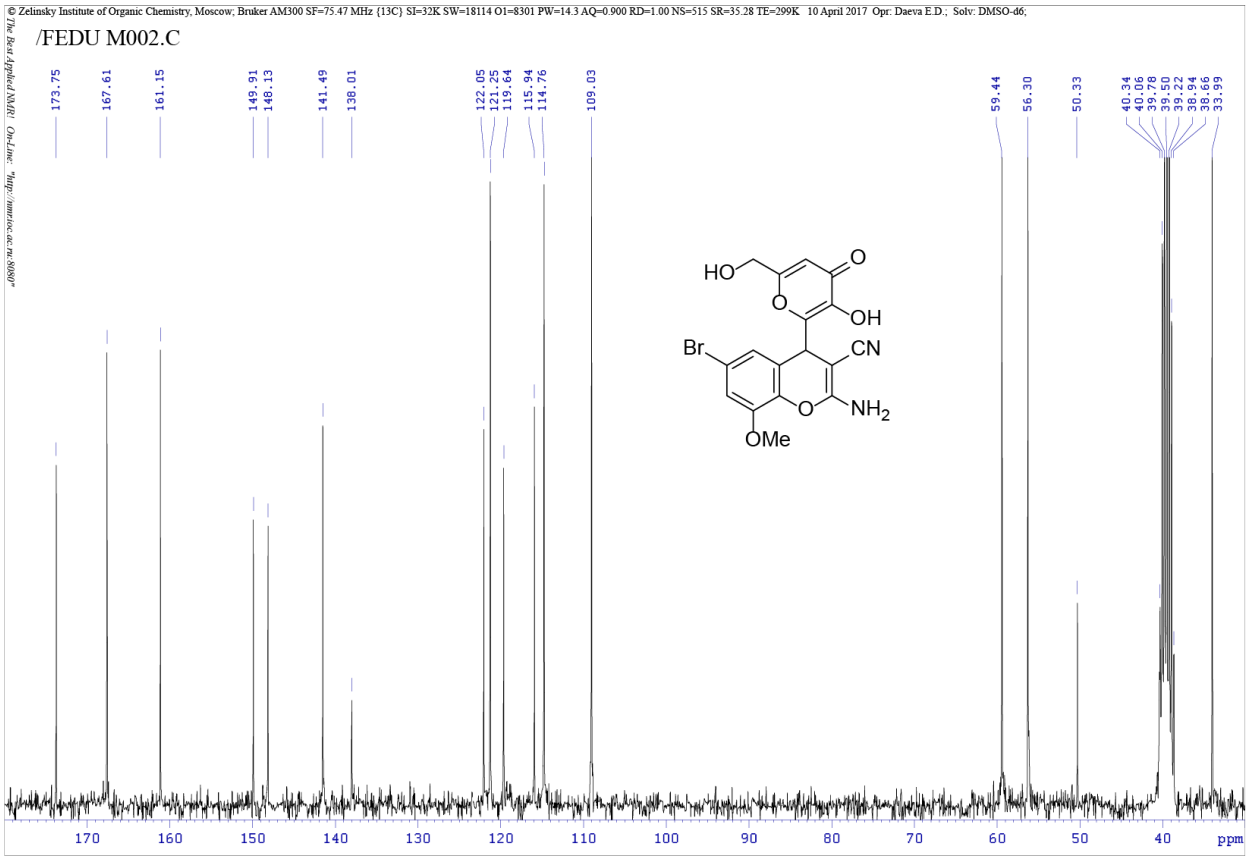
2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carbonitrile 4c



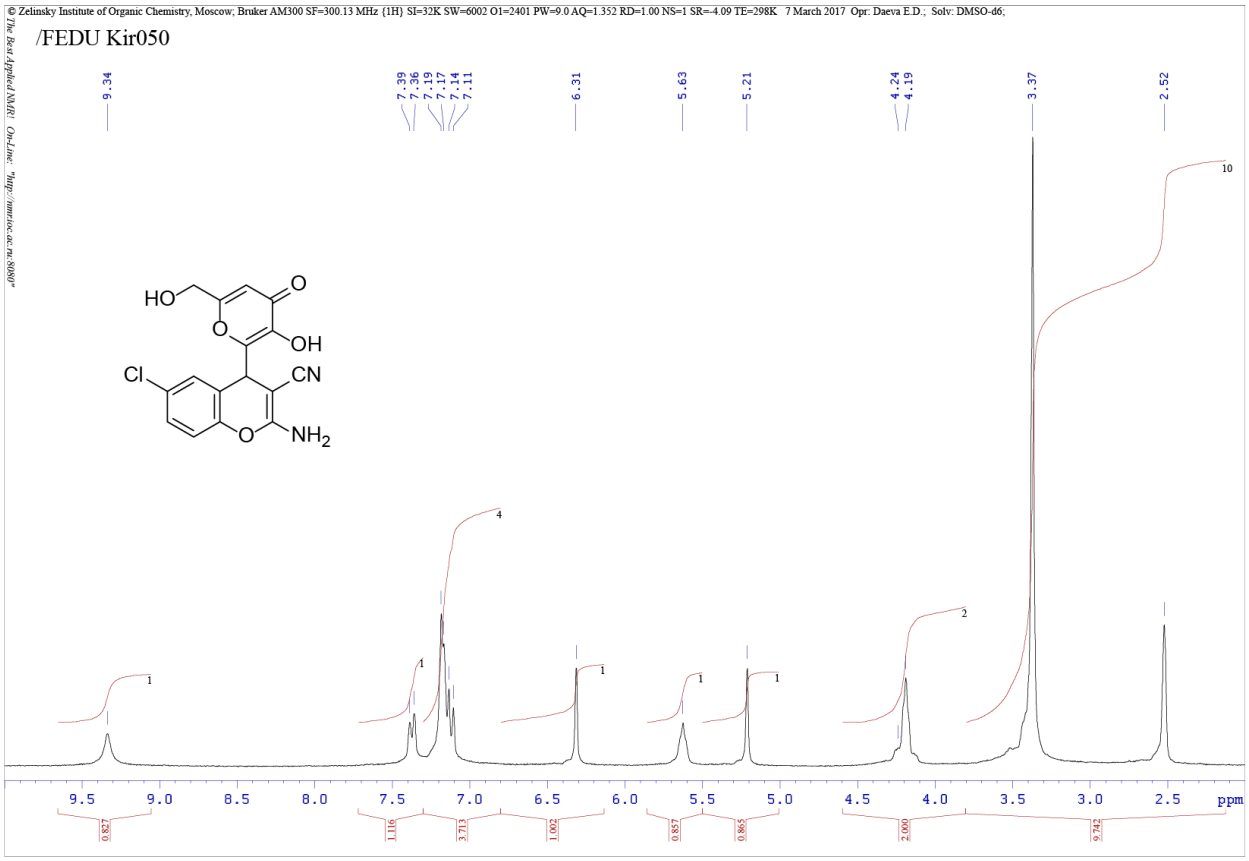


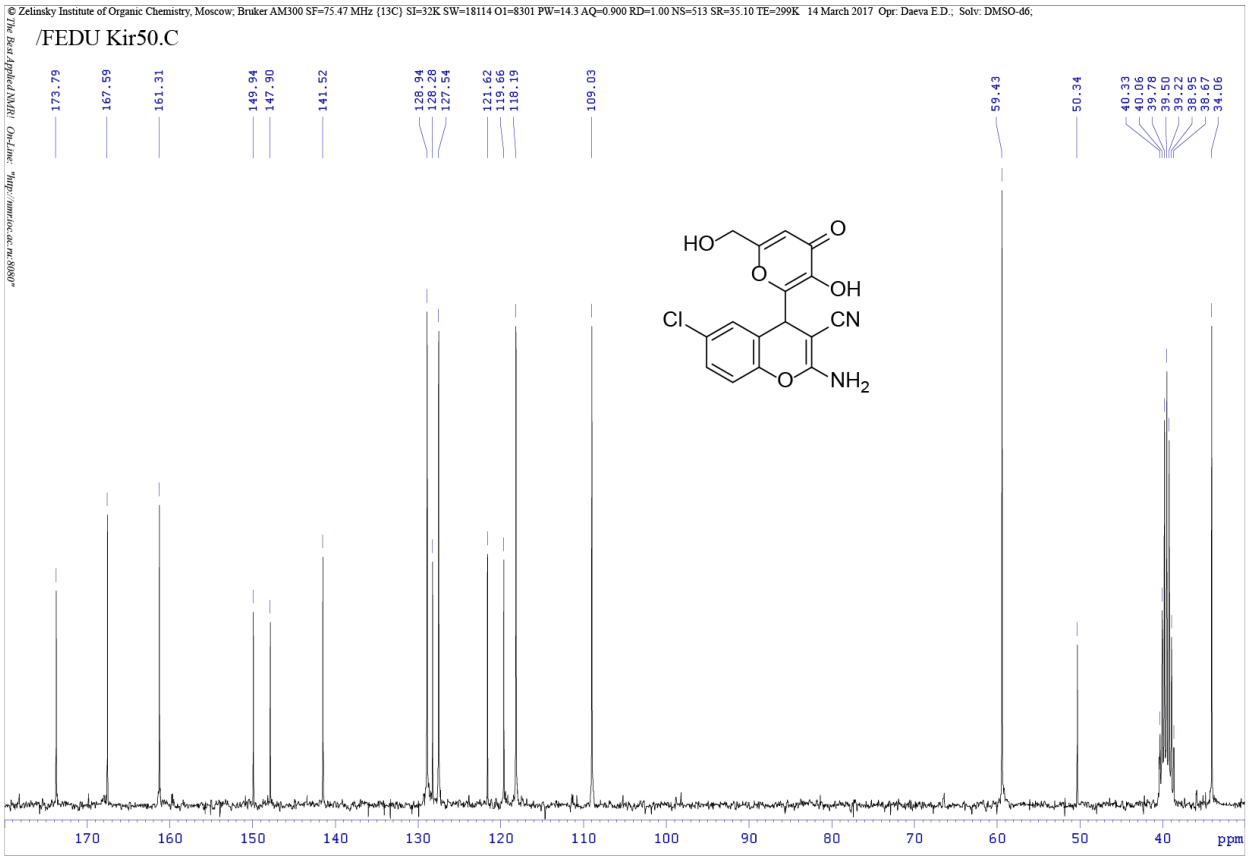
2-Amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carbonitrile 4d



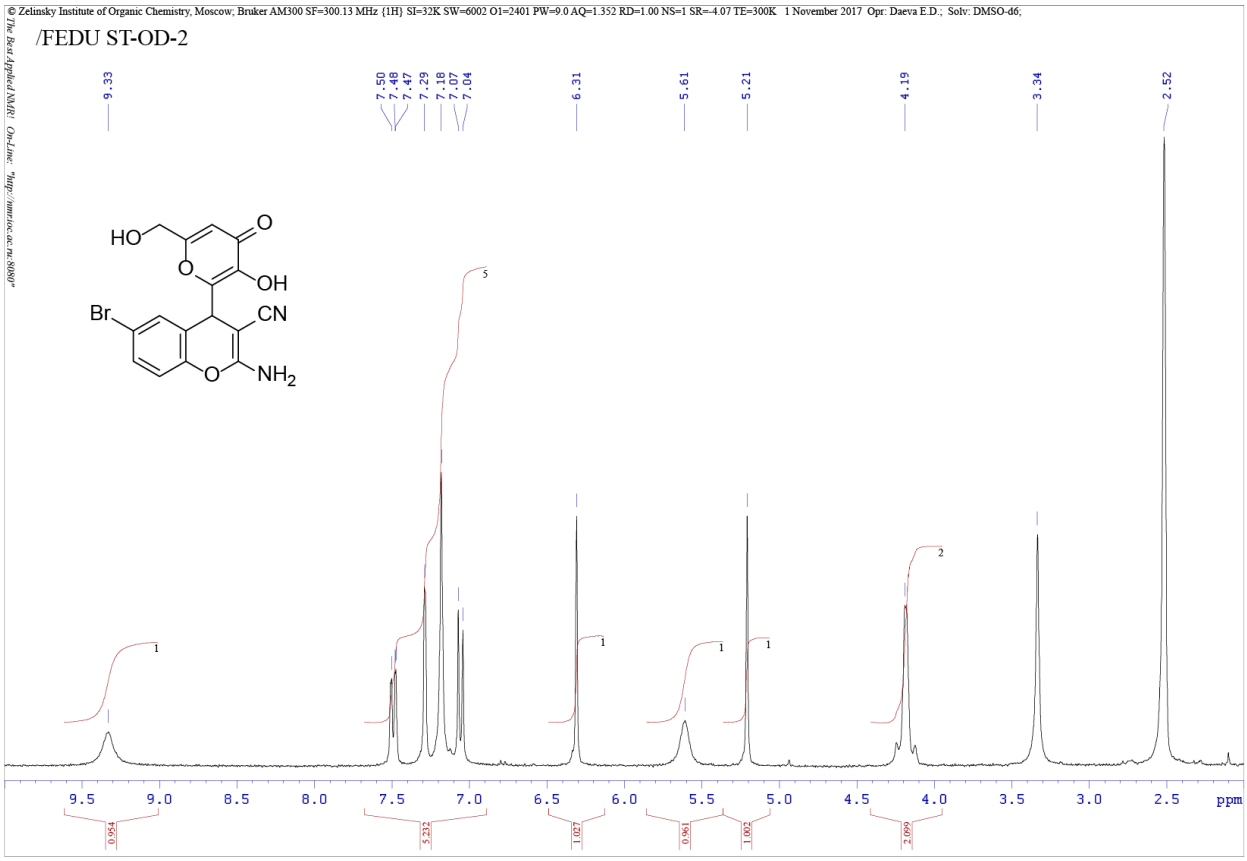


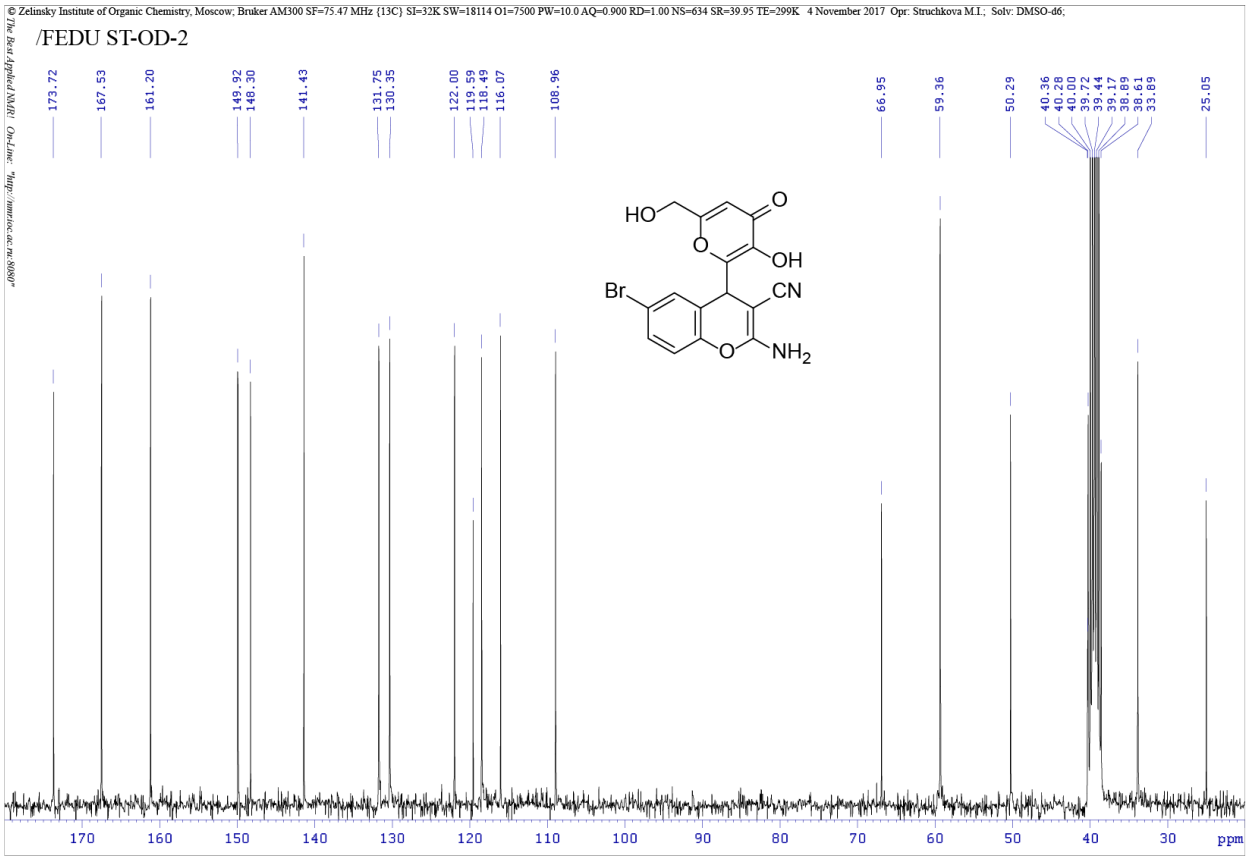
2-Amino-6-chloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4e



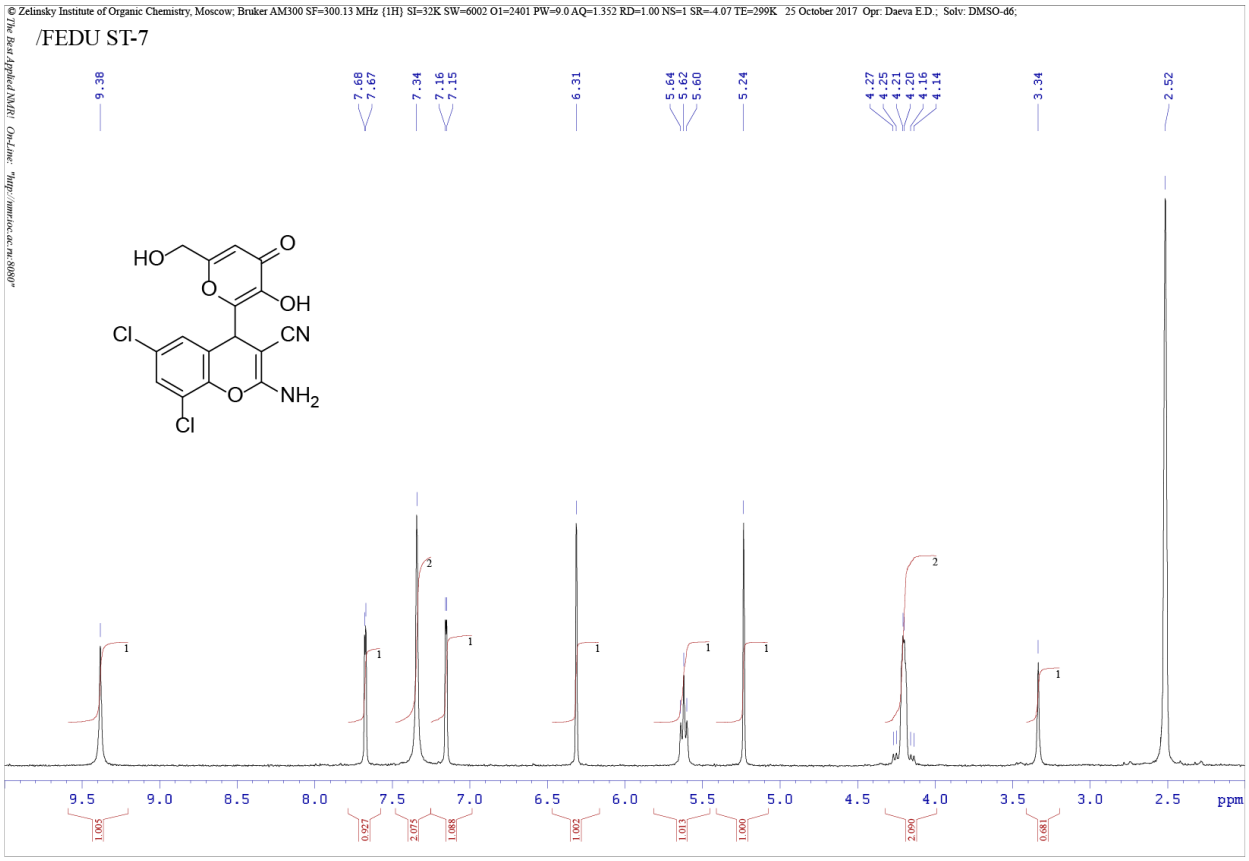


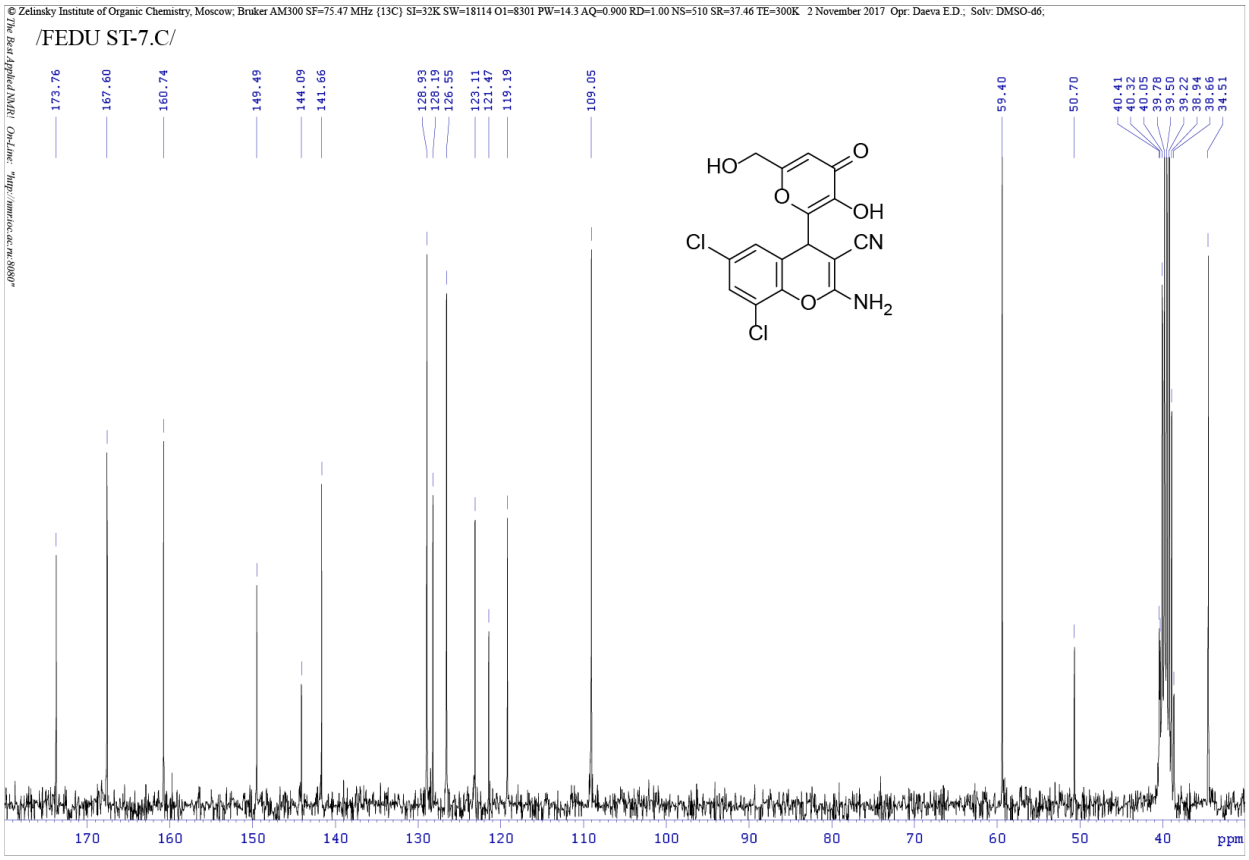
2-Amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4f



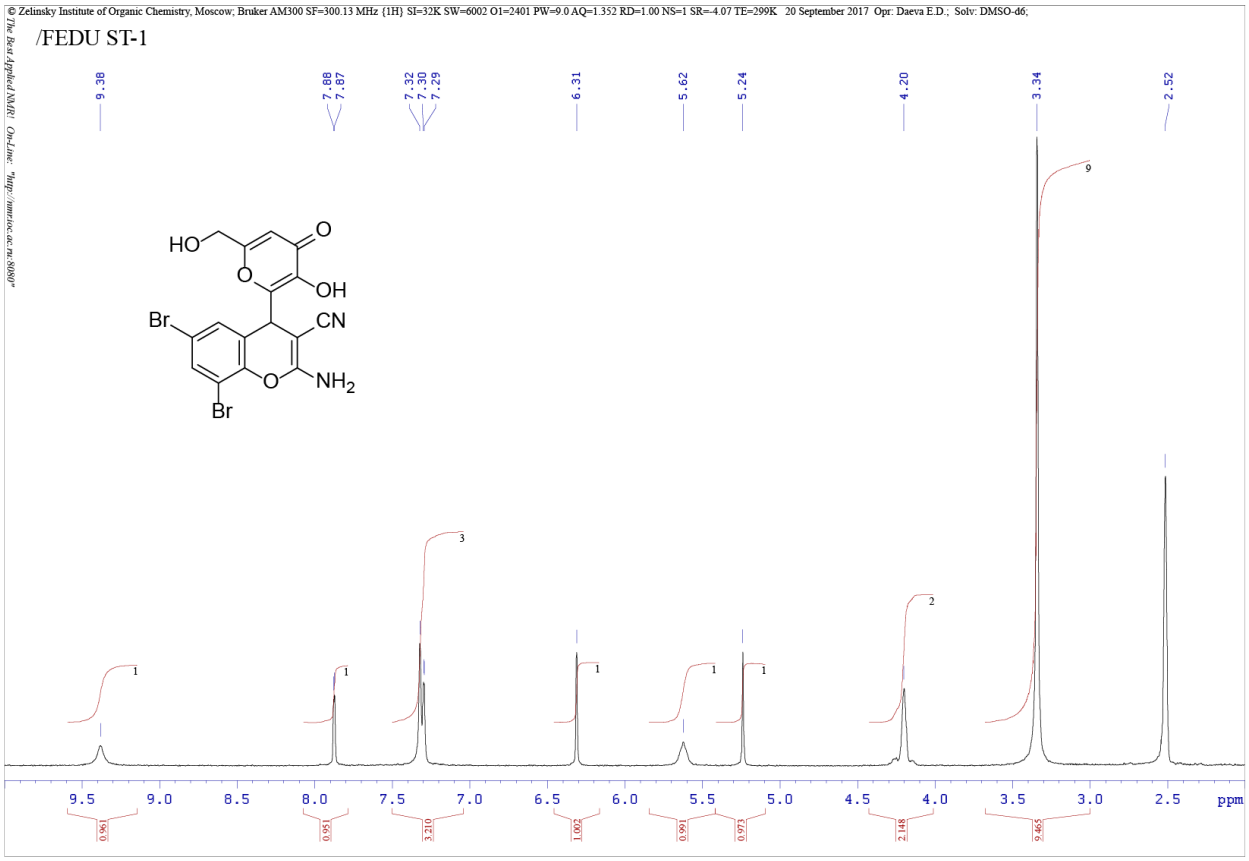


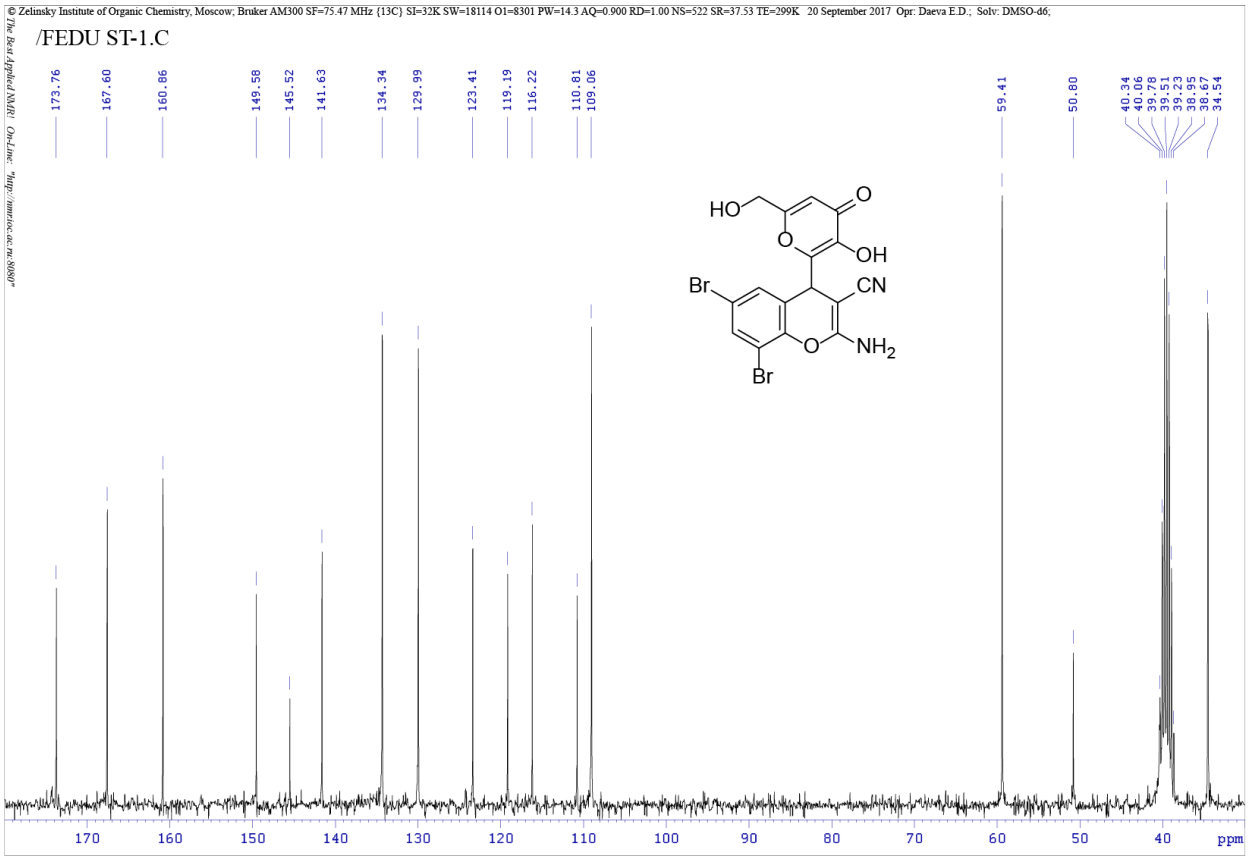
2-Amino-6,8-dichloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4g



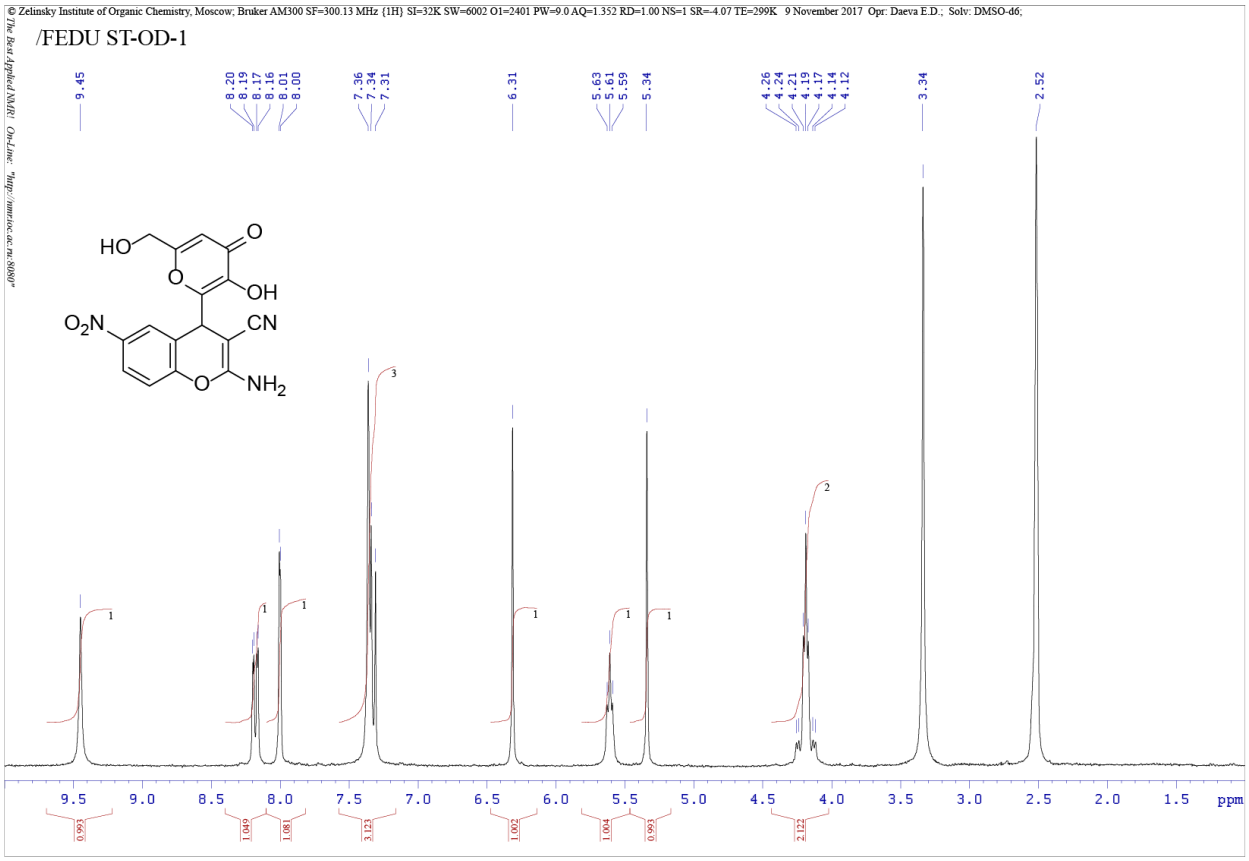


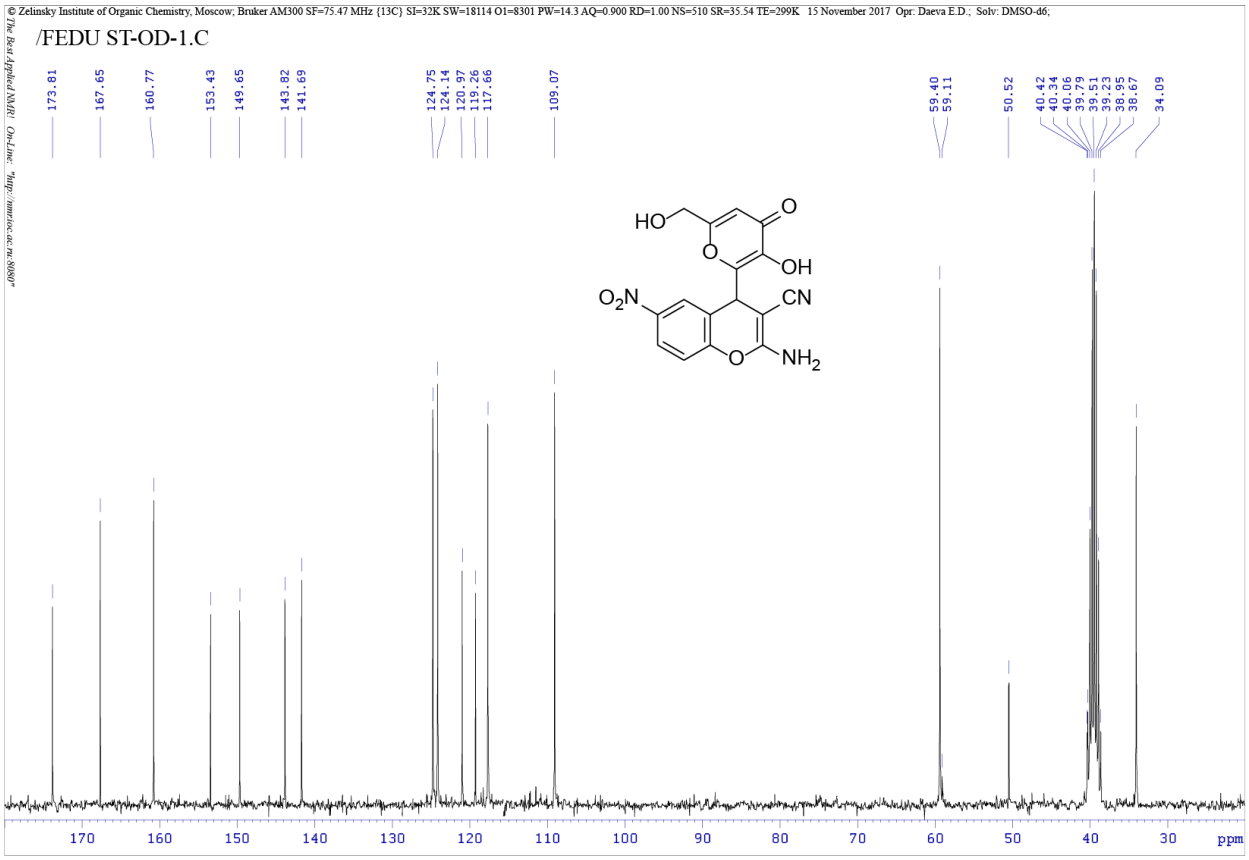
2-Amino-6,8-dibromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carbonitrile 4h



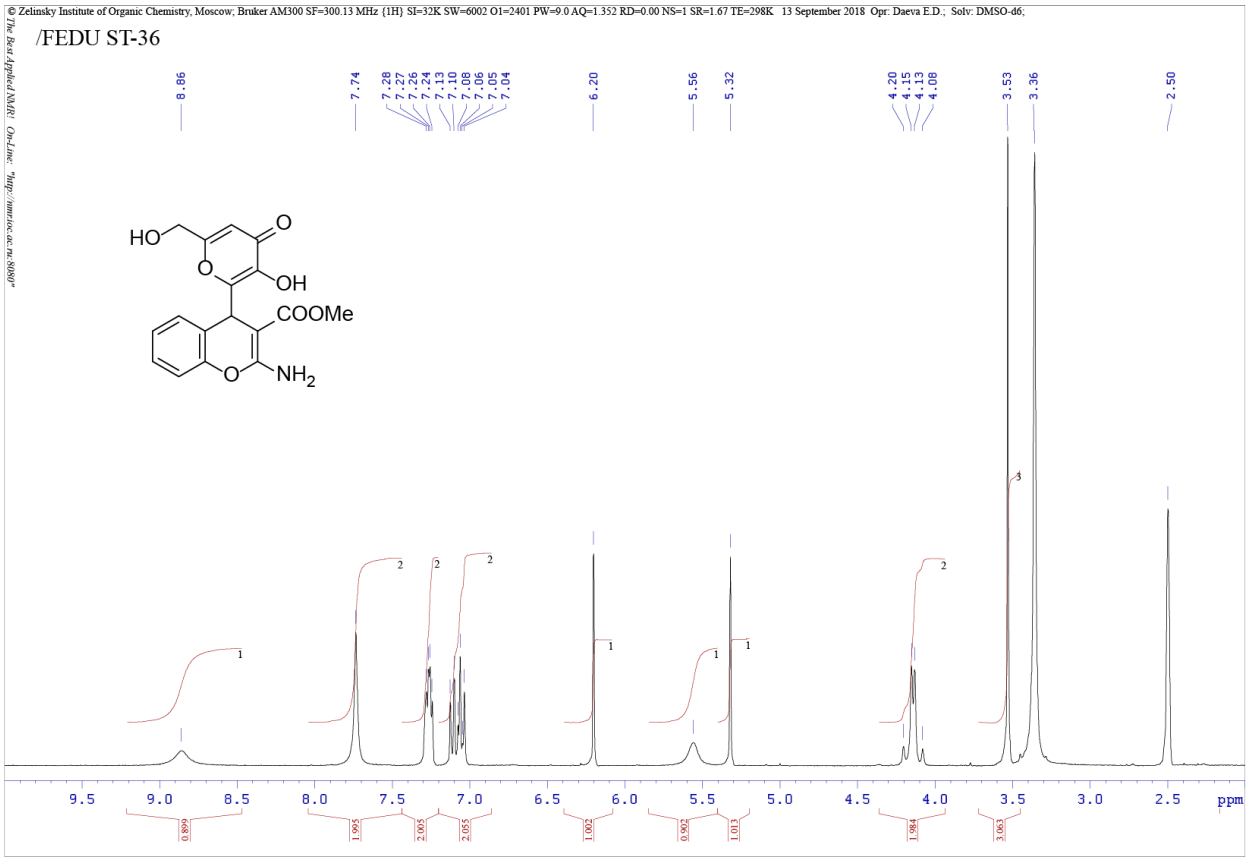


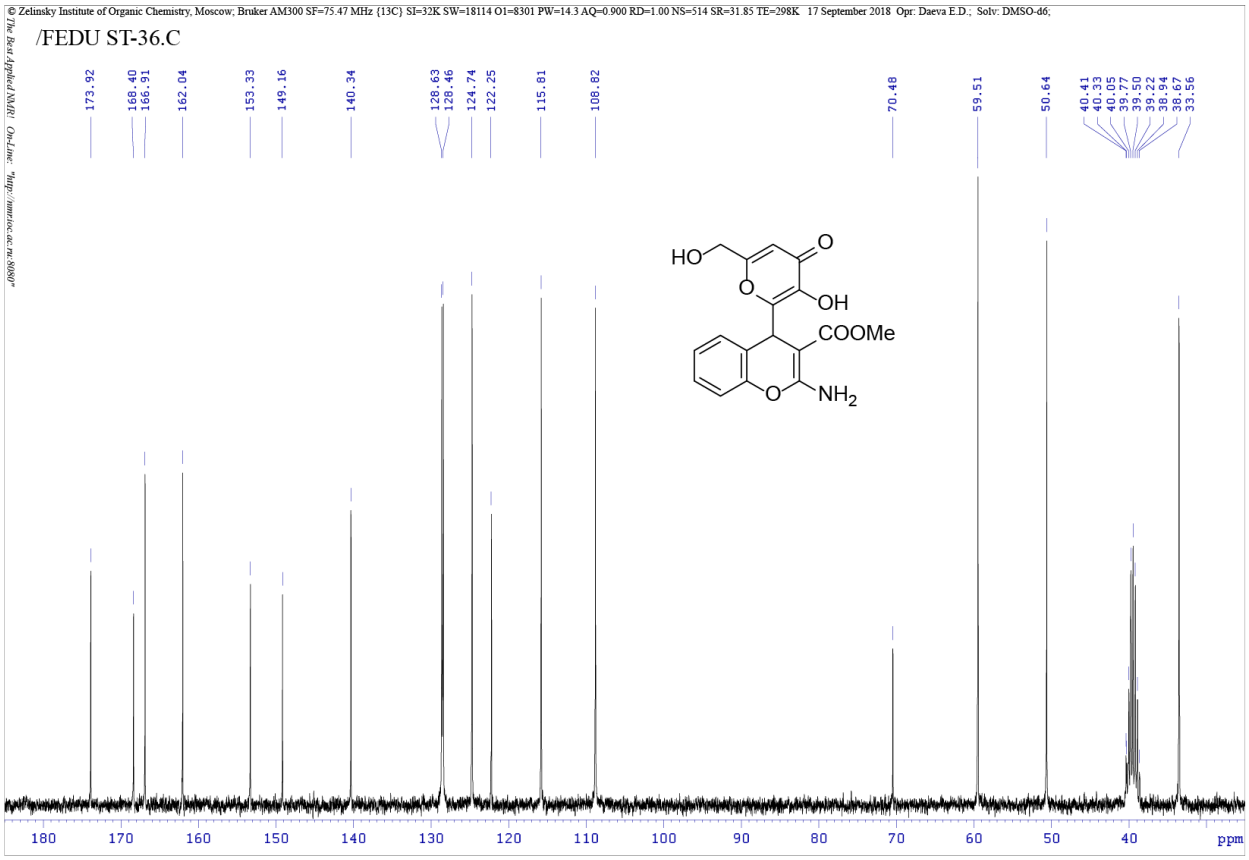
2-Amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-6-nitro-4*H*-chromene-3-carbonitrile 4i



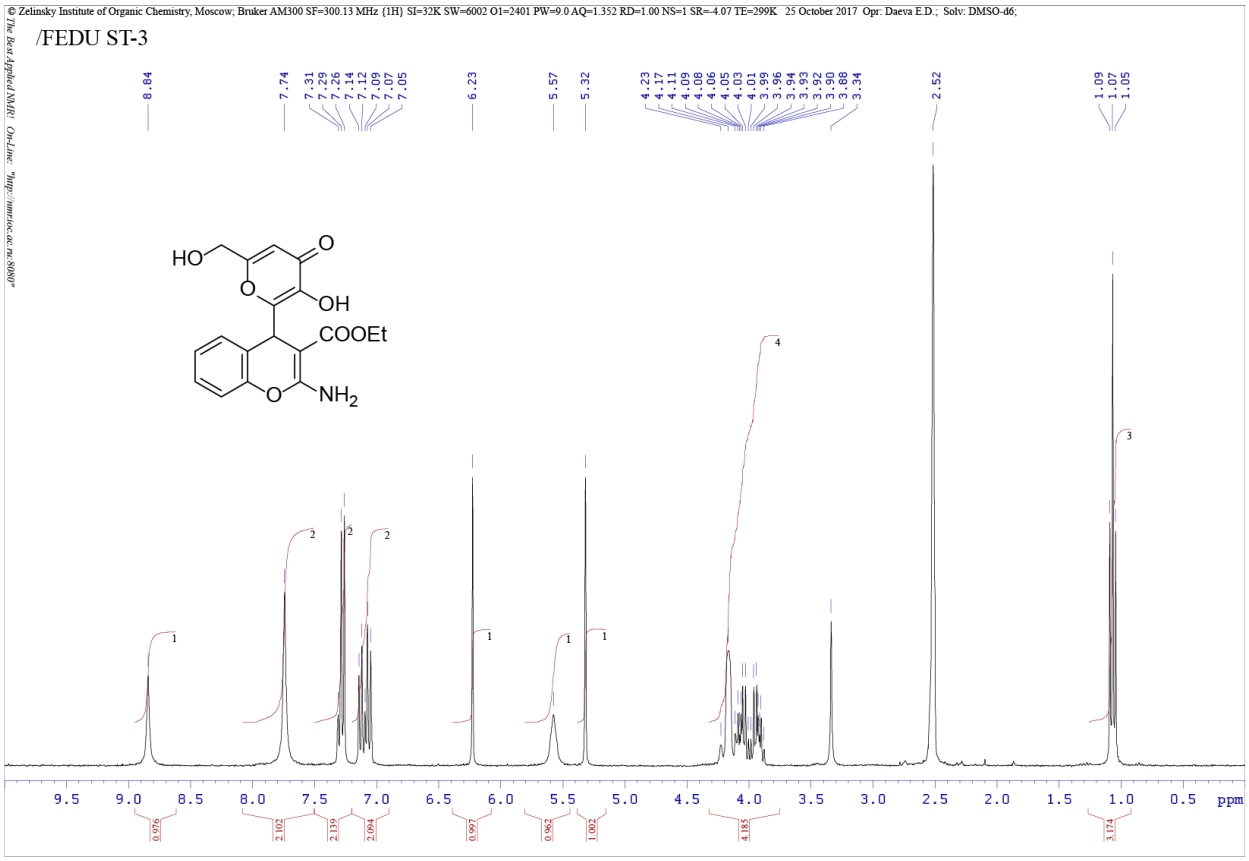


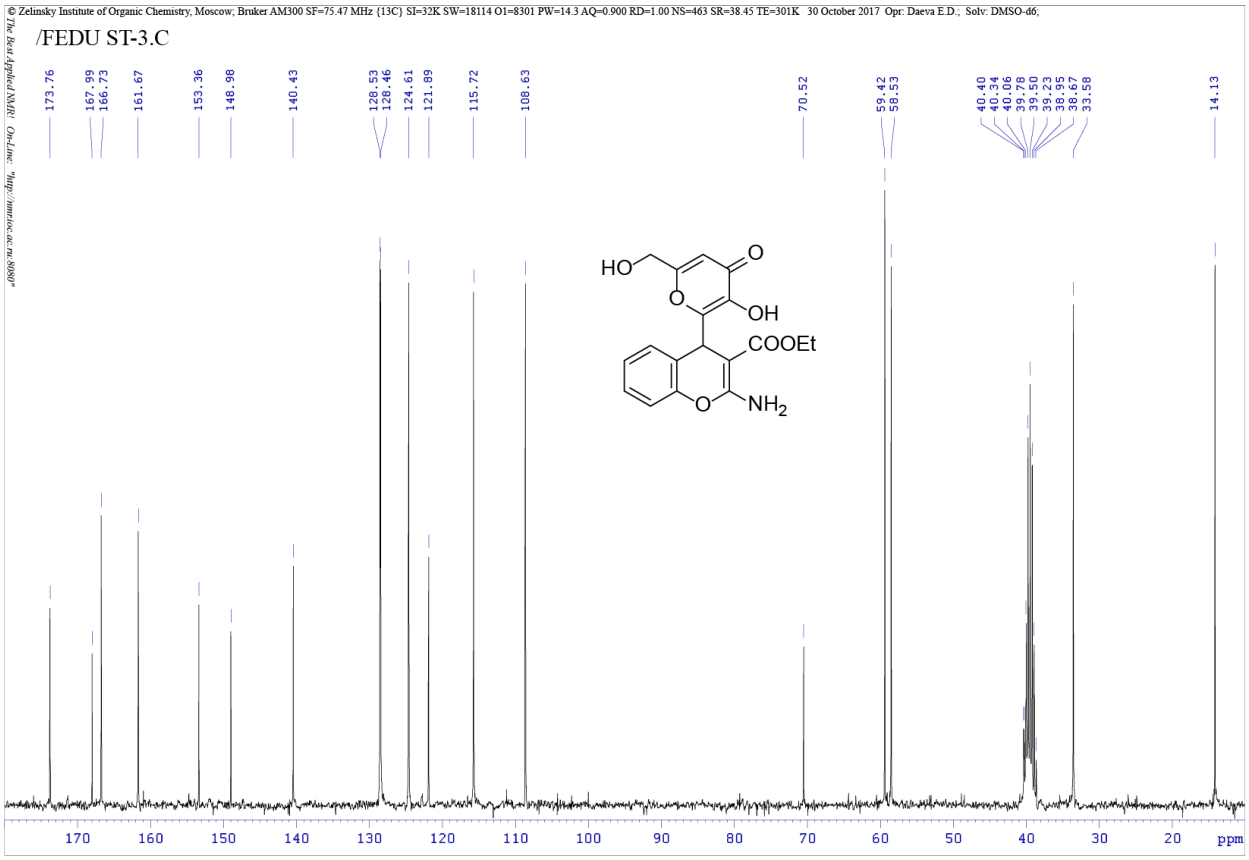
Methyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4j



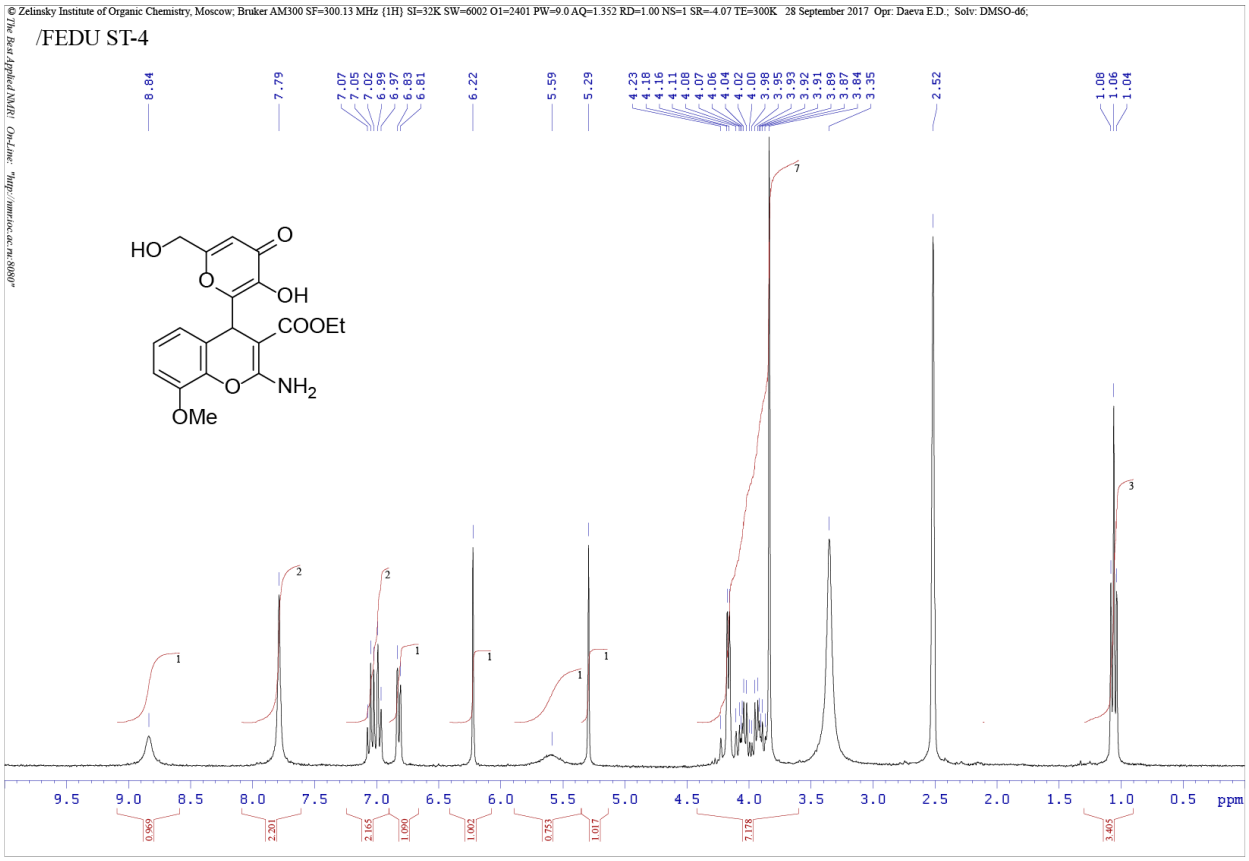


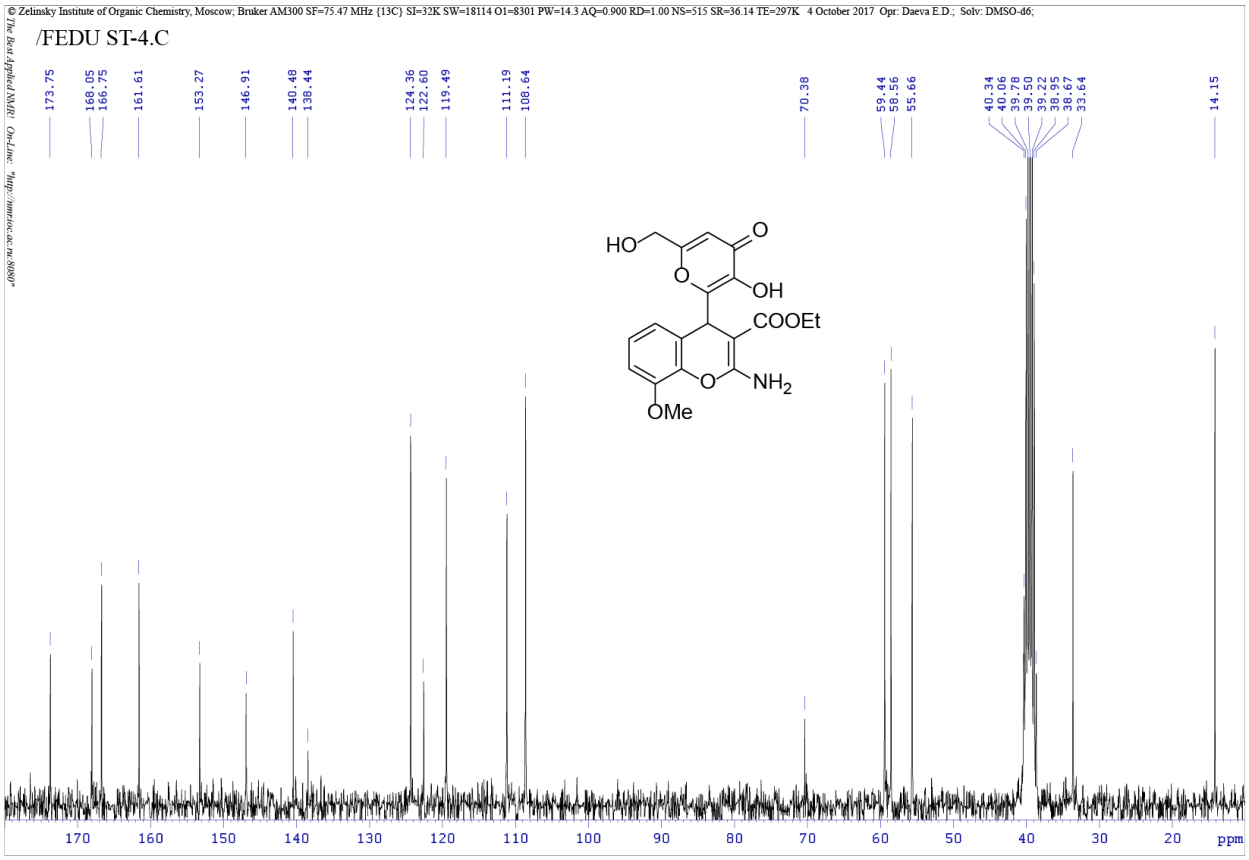
Ethyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4k



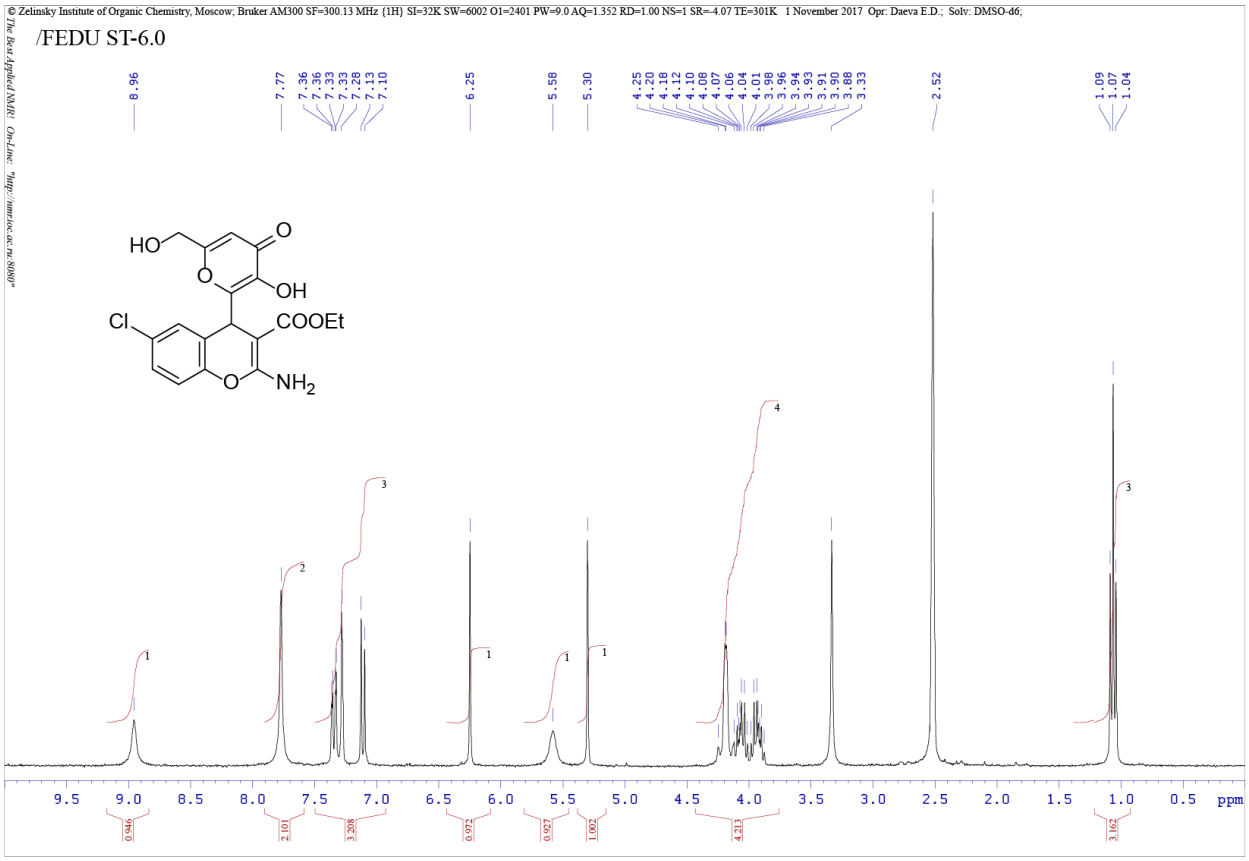


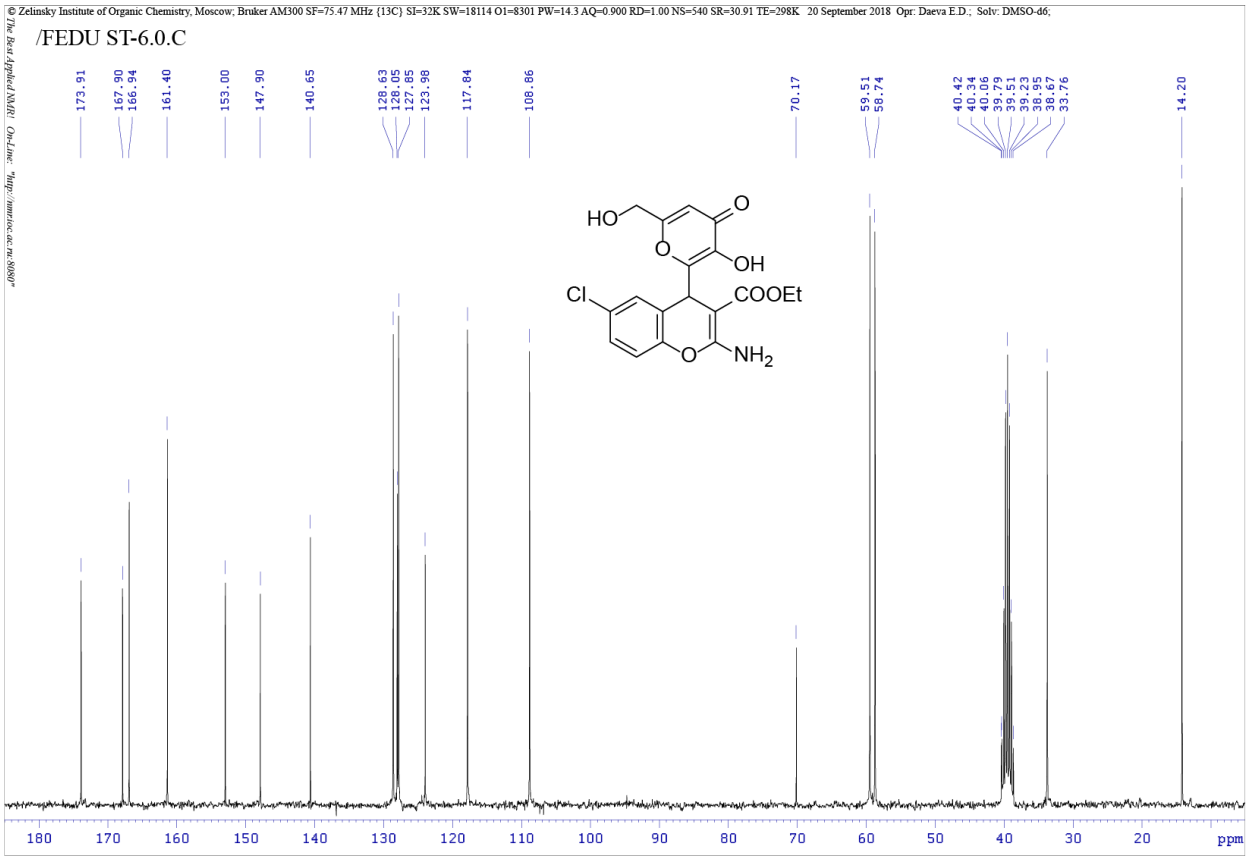
Ethyl 2-amino-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-8-methoxy-4*H*-chromene-3-carboxylate 4l



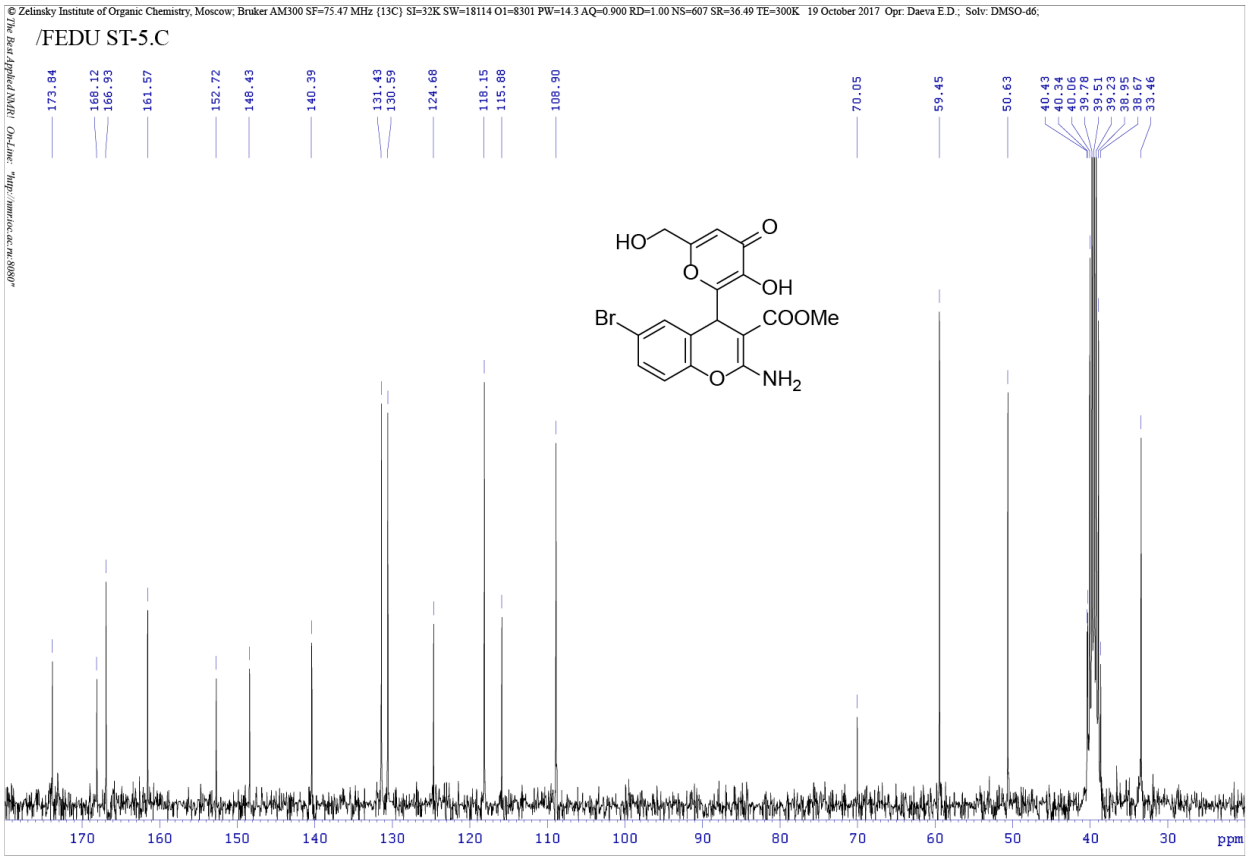


Ethyl 2-amino-6-chloro-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4m





Methyl 2-amino-6-bromo-4-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-4*H*-chromene-3-carboxylate 4n



3-Amino-1-[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]-1*H*-benzo[*f*]chromene-2-carbonitrile 4o