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Electrocatalytic one-pot multicomponent assembly of aldehydes, 2,4-dihydro-3*H*-pyrazol-3-ones and kojic acid

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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 with a Bruker AM-300 (300 and 75 MHz, respectively) at ambient temperature in DMSO-d_6 solutions. Chemical shift 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. A suitable crystal was selected and kept on a 'Bruker APEX-II CCD' diffractometer.

General procedure

A solution of aldehyde **1** (5 mmol), 2,4-dihydro-3*H*-pyrazol-3-ones **2** (5 mmol), kojic acid (5 mmol) and sodium bromide (0.1 g, 1 mmol) in ethanol (20 mL) was electrolyzed in an undivided cell equipped with a magnetic stirrer, a graphite anode and an iron cathode at 78 ºC under a constant current density of 5 mA/cm^2 (I = 25 mA, electrodes square 5 cm^2) until the catalytic quantity of 0.3 F/mol of electricity was passed. After the electrolysis was finished, the reaction mixture was concentrated to one fifth of its initial volume (*ca.* 4 mL) and cold to 0° C to crystallize the solid product **3**, which was then filtered, twice rinsed with an ice-cold ethanol/water solution (8:2, 4 mL), and dried under reduced pressure.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](phenyl)methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3a)

Yield 1.43 g (87%), mp: 226-227 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (s, 3H, CH_3), 4.22 (s, 2H, CH_2), 5.49-5.72 (m, 2H, CH+OH), 6.33 (s, 1H, CH), 7.12 (d, ^{3}J = 7.3 Hz, 2H, 2 CH Ar),

7.20 (t, ^{3}J = 7.3 Hz, 1H, CH Ar), 7.29 (t, ^{3}J = 7.3 Hz, 2H, 2 CH Ar), 8.98 (br s, 1H, OH), 9.68-11.76 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.1, 36.9, 59.6, 99.4, 109.1, 126.4, 127.7 (2C), 128.4 (2C), 138.2, 140.2, 141.5, 150.8, 159.8, 167.3, 173.7 ppm. MS (m/z, relative intensity %): 328 [M^+] (100), 251 (8), 231 (55), 227 (87), 185 (67), 157 (22), 128 (68), 109 (31), 77 (55), 29 (67). IR (KBr): 3383, 3225, 3032, 2903, 1621, 1583, 1500, 1446, 1206, 702 cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53%. Found: C, 62.05; H, 4.86; N, 8.45%.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](phenyl)methyl}-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3b)

Yield 1.92 g (95%), mp: 248-249 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.91 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 5.61 (br s, 1H, OH), 5.72 (br s, 1H, CH), 6.35 (s, 1H, CH), 7.11-7.28 (m, 4H, 4 CH Ar), 7.32 (t, ^{3}J = 7.4 Hz, 2H, 2 CH Ar), 7.43 (t, ^{3}J = 7.9 Hz, 2H, 2 CH Ar), 7.43 (d, ^{3}J = 7.9 Hz, 2H, 2 CH Ar), 9.10 (br s, 1H, OH), 11.09 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.1 (br s), 37.1, 59.6, 109.2, 118.4 (br s), 124.7 (br s), 126.5, 127.5 (4C), 128.4 (2C), 128.8 (4C), 139.5, 141.9, 146.0 (br s), 149.8, 167.1, 173.5 ppm. MS (m/z relative intensity %): 404 [M^+] (11), 329 (1), 303 (2), 262 (23), 231 (32), 174 (30), 142 (7), 77 (100), 39 (34). IR (KBr) ν = 3344, 3227, 2767, 1620, 1573, 1496, 1452, 1226, 1198, 708 cm^{-1}. Anal. calcd for $C_{23}H_{20}N_2O_5$: C, 68.31; H, 4.98; N, 6.93%. Found: C, 68.17; H, 4.95; N, 6.84%.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](p-tolyl)methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3c)

Yield 1.34 g (78%), mp: 174-175 °C; ^{1}H NMR (300 MHz, DMSO-d_6): 1.85 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 5.54-5.63 (m, 2H, CH+OH), 6.30 (s, 1H, CH), 6.98 (d, ^{3}J = 8.0 Hz, 2H, 2 CH Ar), 7.07 (d, ^{3}J = 8.0 Hz, 2H, 2 CH Ar), 8.94 (br s, 1H, OH), 9.64-11.71 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.5, 21.0, 36.9, 60.0, 99.8, 109.4, 128.0 (2C), 129.3 (2C), 135.8, 137.6, 138.5, 141.8, 151.4, 160.2, 167.6, 174.1 ppm. MS (m/z, relative intensity %): 342 [M^+] (77), 283 (7), 246 (28), 241 (100), 185 (85), 171 (17), 115 (68), 91 (45), 69 (43), 29 (67). IR (KBr): 3401, 3165, 3049, 2866, 1621, 1578, 1516, 1450, 1208, 790 cm^{-1}. Anal. calcd for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18%. Found: C, 62.97; H, 5.26; N, 8.03%.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](4-methoxyphenyl)methyl}-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3d)

Yield 1.85 g (85%), mp: 177-178 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.93 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 4.25 (s, 2H, CH_2), 5.50-5.73 (m, 2H, OH+CH), 6.34 (br s, 1H, CH), 6.88 (d, ^{3}J =

8.6 Hz, 2H, 2 CH Ar), 7.08 (d, ^{3}J = 8.6 Hz, 2H, 2 CH Ar), 7.20 (t, ^{3}J = 7.6 Hz, 1H, CH Ar), 7.43 (t, ^{3}J = 7.6 Hz, 2H, 2 CH Ar), 7.73 (d, ^{3}J = 7.6 Hz, 2H, 2 CH Ar), 9.03 (br s, 1H, OH), 11.09 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.1 (br s), 36.5, 55.1, 59.6, 109.2, 113.9, 118.3 (br s), 121.0 (br s), 124.5 (br s), 128.7 (4C), 128.9 (4C), 131.4, 137.2 (br s), 141.8, 150.3, 157.9, 167.1, 173.6 ppm. MS (m/z relative intensity %): 434 [M^+] (25), 333 (2), 292 (15), 261 (100), 185 (6), 174 (44), 142 (2), 105 (12), 77 (61), 39 (22). IR (KBr) ν = 3515, 3068, 2914, 1623, 1568, 1507, 1456, 1367, 1247, 754 cm^{-1}. Anal. calcd for $C_{24}H_{22}N_2O_6$: C, 66.35; H, 5.10; N, 6.45%. Found: C, 66.18; H, 5.06; N, 6.31%.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](3-methoxyphenyl)methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3e)

Yield 1.43 g (80%), mp: 158-159 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (s, 3H, CH_3), 3.67 (s, 3H, OCH_3), 4.20 (s, 2H, CH_2), 5.57 (s, 1H, CH), 5.59 (br s, 1H, OH), 6.31 (s, 1H, CH), 6.63 (d, ^{4}J = 2.3 Hz, 1H, CH Ar), 6.68 (d, ^{3}J = 7.9 Hz, 1H, CH Ar), 6.77 (dd, ^{3}J = 7.9 Hz, ^{4}J = 2.3 Hz, 1H, CH Ar), 7.19 (t, ^{3}J = 7.9 Hz, 1H, CH Ar), 8.98 (br s, 1H, OH), 9.81-11.65 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.5, 37.3, 55.4, 60.0, 99.6, 109.5, 111.8, 114.2, 120.5, 129.8, 138.6, 141.9, 142.2, 151.1, 159.7, 160.1, 167.6, 174.1 ppm. MS (m/z, relative intensity %): 358 [M^+] (53), 262 (24), 257 (43), 229 (26), 215 (58), 185 (29), 142 (22), 115 (47), 69 (45), 29 (100). IR (KBr) ν = 3355, 3228, 2837, 1642, 1601, 1570, 1491, 1440, 1200, 792 cm^{-1}. Anal. calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82%. Found: C, 60.18; H, 5.02; N, 7.69%.

4-{(3-Chlorophenyl)[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]methyl}-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3f)

Yield 1.80 g (82%), mp: 261-262 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.96 (br s, 3H, CH_3), 4.25 (s, 2H, CH_2), 5.47-5.91 (m, 2H, OH+CH), 6.36 (br s, 1H, CH), 7.10-7.28 (m, 3H, 3 CH Ar), 7.28-7.50 (m, 4H, 4 CH Ar), 7.73 (d, ^{3}J = 8.1 Hz, 2H, 2 CH Ar), 9.19 (br s, 1H, OH), 11.27 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.0 (br s), 37.0, 59.5, 109.2, 118.5 (br s), 121.1 (br s), 124.8 (br s), 126.4 (2C), 126.6, 127.3 (2C), 128.9 (4C), 130.3 (2C), 133.1, 141.9, 148.9, 167.2, 173.5 ppm. MS (m/z relative intensity %): 440 [M^+] (11, ^{37}Cl), 438 [M^+] (32, ^{35}Cl), 379 (1, ^{37}Cl), 377 (2, ^{35}Cl), 339 (9, ^{37}Cl), 337 (27, ^{35}Cl), 298 (9, ^{37}Cl), 296 (22, ^{35}Cl), 267 (38 ^{37}Cl), 265 (100, ^{35}Cl), 191 (7), 174 (15), 128 (9), 77 (46), 39 (7). IR (KBr) ν = 3353, 3069, 2915, 1650, 1620, 1566, 1499, 1461, 1212, 727 cm^{-1}. Anal. calcd for $C_{23}H_{19}ClN_2O_5$: C, 62.95; H, 4.36; Cl, 8.08; N, 6.38%. Found: C, 62.82; H, 4.32; Cl, 7.95; N, 6.27%.

4-{(4-Bromophenyl)[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3g)

Yield 1.49 g (73%), mp: 190-191 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 5.56 (s, 1H, CH), 5.59 (br s, 1H, OH), 6.30 (s, 1H, CH), 7.06 (d, ^{3}J = 8.3 Hz, 2H, 2 CH Ar), 7.46 (d, ^{3}J = 8.3 Hz, 2H, 2 CH Ar), 9.05 (br s, 1H, OH), 9.59-11.78 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.4, 37.0, 60.0, 99.3, 109.5, 119.9, 130.4 (2C), 131.6 (2C), 138.5, 140.1, 142.0, 150.5, 160.1, 167.7, 174.1 ppm. MS (m/z relative intensity %): 408 [M^+] (35, ^{81}Br), 406 [M^+] (37, ^{79}Br), 309 (35, ^{81}Br), 307 (48, ^{79}Br), 267 (19, ^{81}Br), 265 (35, ^{79}Br), 251 (13), 185 (33), 142 (21), 128 (59), 98 (29), 69 (52), 29 (100). IR (KBr): 3423, 3243, 3100, 2924, 1628, 1591, 1534, 1453, 1208, 758 cm^{-1}. Anal. calcd for $C_{17}H_{15}BrN_2O_5$: C, 50.14; H, 3.71; Br, 19.62; N, 6.88%. Found: C, 50.01; H, 3.55; Br, 19.48; N, 6.75%.

4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](3-nitrophenyl)methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3h)

Yield 1.59 g (85%), mp: 161-162 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.93 (s, 3H, CH_3), 4.21 (s, 2H, CH_2), 5.59 (br s, 1H, OH), 5.72 (s, 1H, CH), 6.34 (s, 1H, CH), 7.61 (d, ^{3}J = 6.3 Hz, 2H, 2 CH Ar), 7.95 (s, 1H, CH Ar), 8.10 (t, ^{3}J = 6.3 Hz, Hz, 1H, CH Ar), 8.70-11.64 (br s, 3H, OH + 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.8, 36.9, 59.4, 98.3, 109.1, 121.6, 122.2, 129.9, 134.5, 138.0, 141.6, 142.4, 147.9, 149.9, 159.6, 167.3, 173.6 ppm. MS (m/z relative intensity %): 373 [M^+] (10), 276 (6), 231 (27), 214 (5), 185 (20), 142 (13), 128 (39), 109 (48), 77 (41), 29 (100). IR (KBr) ν = 3334, 3248, 2975, 1643, 1606, 1579, 1531, 1448, 1347, 1204 cm^{-1}. Anal. calcd for $C_{17}H_{15}N_3O_7$: C, 54.69; H, 4.05; N, 11.26%. Found: C, 54.60; H, 3.98; N, 11.13%.

Methyl 4-{[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)methyl}benzoate (3i)

Yield 1.84 g (95%), mp: 161-162 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.86 (s, 3H, CH_3), 3.83 (s, 3H, $COOCH_3$), 4.21 (s, 2H, CH_2), 5.61 (br s, 1H, OH), 5.67 (s, 1H, CH), 6.33 (s, 1H, CH), 7.26 (d, ^{3}J = 8.1 Hz, 2H, 2 CH Ar), 7.89 (d, ^{3}J = 8.1 Hz, 2H, 2 CH Ar), 9.12 (br s, 1H, OH), 9.62-11.82 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.9, 37.0, 52.0, 59.5, 98.7, 109.0, 127.8, 128.0 (2C), 129.2 (2C), 138.0, 141.6, 145.8, 149.8, 159.6, 166.1, 167.2, 173.6 ppm. MS (m/z relative intensity %): 386 [M^+] (24), 290 (38), 244 (29), 229 (18), 185 (37), 142 (23), 128 (32), 109 (32), 69 (37), 29 (100). IR (KBr) ν = 3350, 3218, 2955, 1715, 1617, 1447, 1367, 1287, 1208, 1114 cm^{-1}. Anal. calcd for $C_{19}H_{18}N_2O_7$: C, 59.07; H, 4.70; N, 7.25%. Found: C, 58.92; H, 4.67; N, 7.13%.

Methyl 4-{[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](5-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)methyl}benzoate (3j)

Yield 2.08 g (90%), mp: 178-179 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.91(br s, 3H, CH_3), 3.84 (s, 3H, $COOCH_3$), 4.25 (s, 2H, CH_2), 5.61 (br s, 1H, CH), 5.77 (br s, 1H, OH), 6.37 (br s, 1H, CH), 7.21 (t, ^{3}J = 7.6 Hz, 1H, CH Ar), 7.32 (d, ^{3}J = 7.6 Hz, 2H, 2 CH Ar), 7.44 (t, ^{3}J = 7.6 Hz, 2H, 2 CH Ar), 7.74 (d, ^{3}J = 8.1 Hz, 2H, 2 CH Ar), 7.93 (d, ^{3}J = 8.1 Hz, 2H, 2 CH Ar), 9.22 (br s, 1H, OH), 11.25 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.9 (br s), 37.3, 52.1, 59.6, 109.3, 118.4 (br s), 121.1 (br s), 124.6 (br s), 124.8 (br s), 128.0, 128.1 (4C), 129.0 (3C), 129.5 (2C), 142.1, 145.2, 149.0 (br s), 166.1, 167.3, 173.6 ppm. MS (m/z relative intensity %): 462 [M^+] (11), 361 (5), 289 (64), 274 (5), 230 (29), 174 (33), 128 (16), 77 (100), 39 (16). IR (KBr) ν = 3507, 3071, 2954, 1713, 1624, 1569, 1500, 1454, 1290, 1220 cm^{-1}. Anal. calcd for $C_{25}H_{22}N_2O_7$: C, 64.93; H, 4.80; N, 6.06%. Found: C, 64.79; H, 4.72; N, 5.93%.

4-{(Furan-2-yl)[3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl]methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3k)

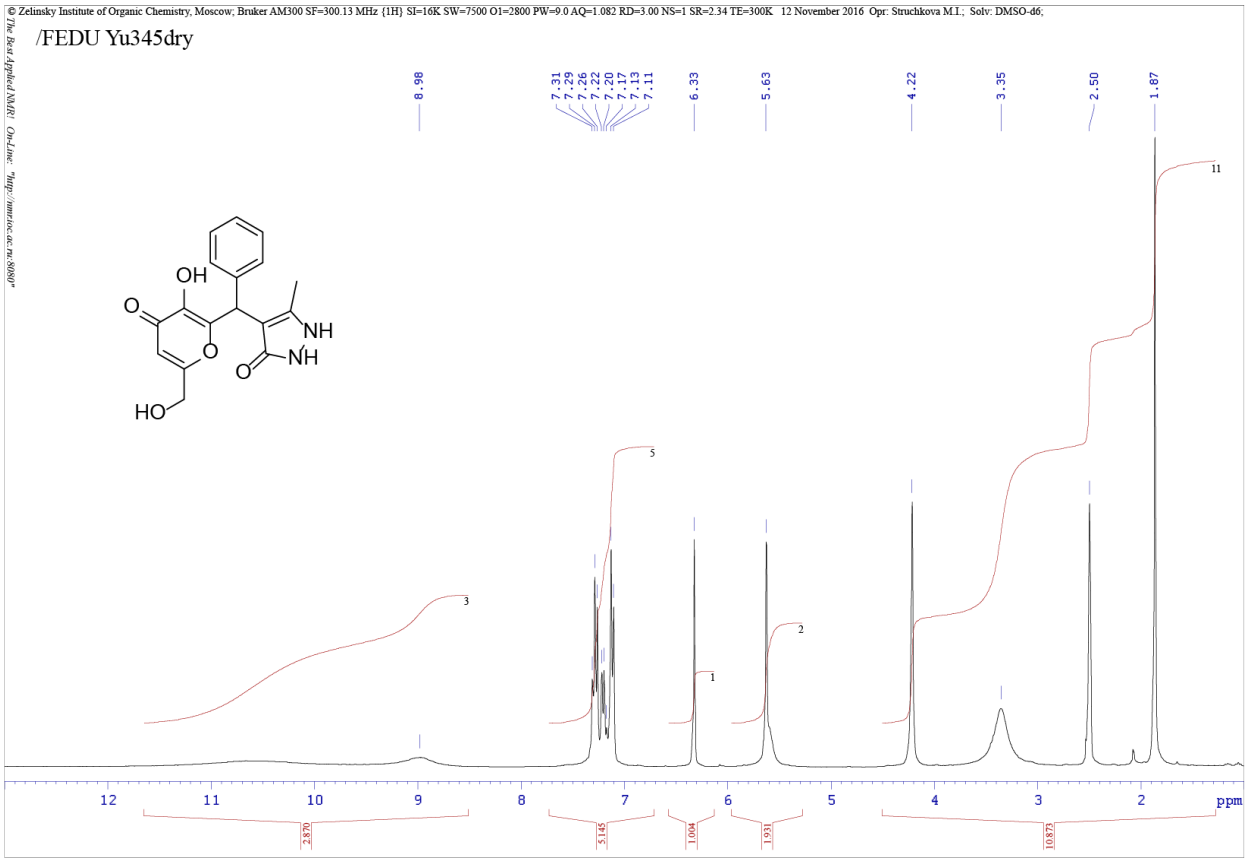
Yield 1.30 g (82%), mp: 207-207 (decomp.) °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.96 (s, 3H, CH_3), 4.23 (s, 2H, CH_2), 5.38-5.79 (m, 2H, OH+CH), 6.05 (d, ^{3}J = 2.9 Hz, 1H, CH Ar), 6.31 (s, 1H, CH), 6.37 (t, ^{3}J = 2.9 Hz, 1H, CH Ar), 7.54 (d, ^{3}J = 2.9 Hz, 1H, CH Ar), 8.72-11.60 (br s, 3H, OH+2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.7, 31.8, 59.6, 97.4, 107.0, 109.1, 110.5, 138.4, 141.1, 142.1, 149.0, 152.5, 159.5, 167.2, 173.8 ppm. MS (m/z relative intensity %): 318 [M^+] (36), 259 (2), 233 (2), 221 (53), 176 (35), 142 (33), 119 (21), 98 (24), 69 (35), 29 (100). IR (KBr) ν = 3288, 2867, 1652, 1610, 1560, 1454, 1354, 1223, 1016, 745 cm^{-1}. Anal. calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.43; N, 8.80%. Found: C, 56.48; H, 4.39; N, 8.64%.

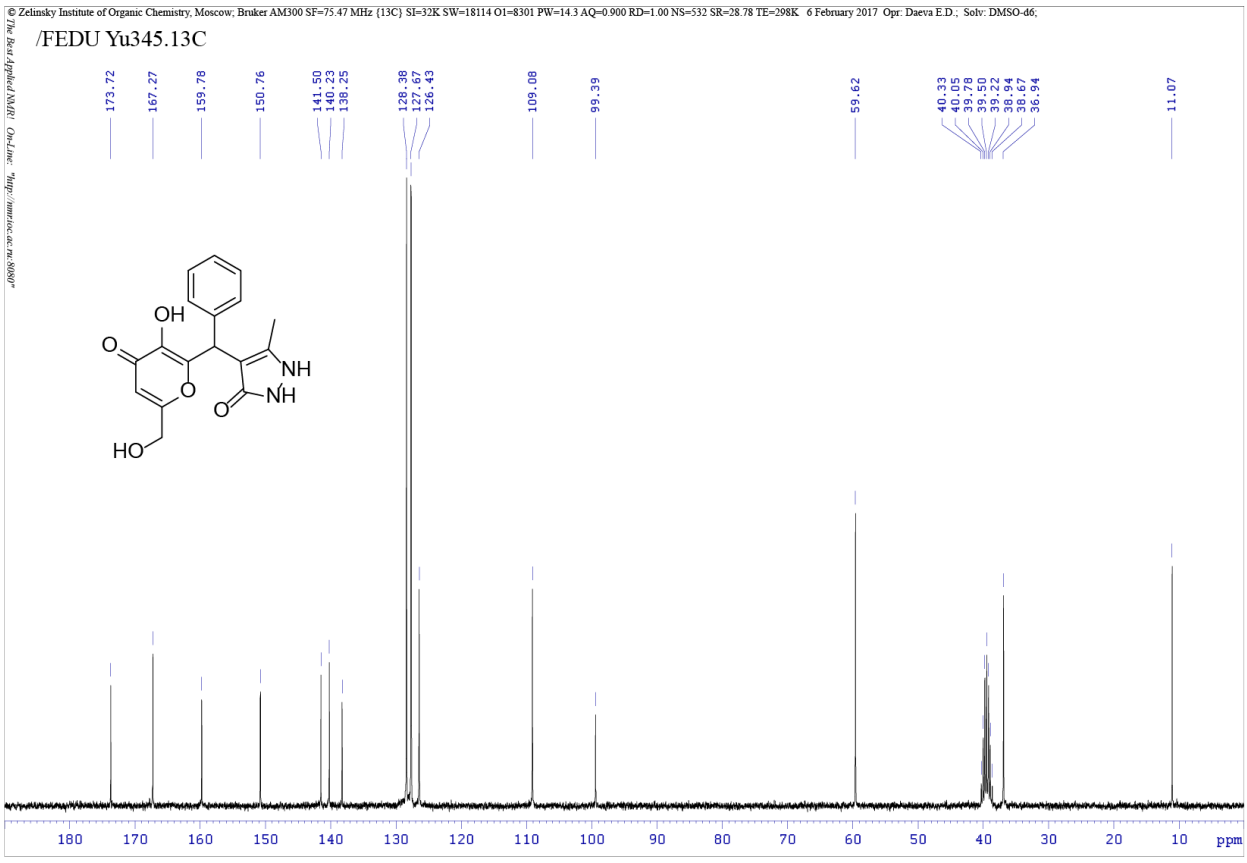
4-{[3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl](naphthalen-1-yl)methyl}-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3l)

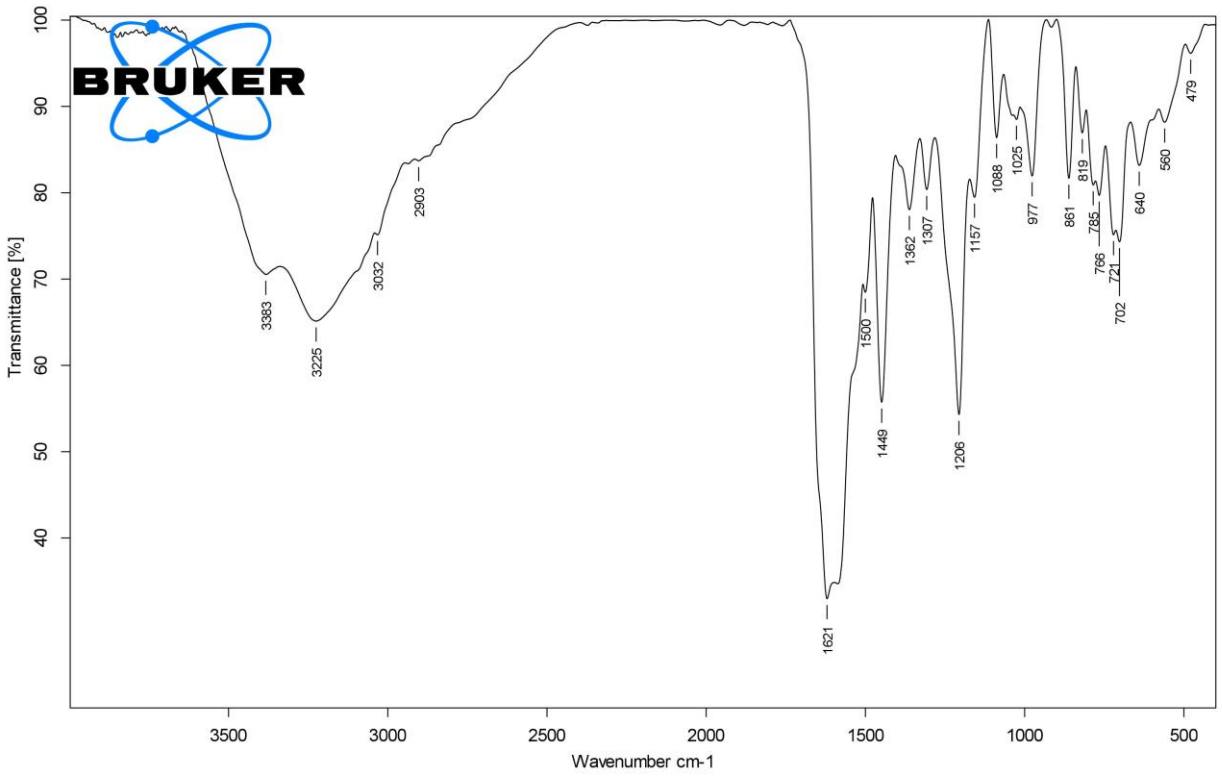
Yield 1.48 g (78%), mp: 190-191 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.78 (s, 3H, CH_3), 4.22 (s, 2H, CH_2), 5.59 (br s, 1H, OH), 6.24 (s, 1H, CH), 6.35 (s, 1H, CH), 7.26 (d, ^{3}J = 7.1 Hz, 1H, CH Ar), 7.38-7.55 (m, 3H, 3 CH Ar), 7.81 (d, ^{3}J = 8.2 Hz, 1H, CH Ar), 7.87-7.96 (m, 1H, CH Ar), 8.00-8.10 (m, 1H, CH Ar), 9.03 (br s, 1H, OH), 9.62-11.61 (br s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.9, 34.5, 59.7, 99.0, 109.4, 123.3, 125.2, 125.3, 125.8, 126.4, 127.5, 128.9, 131.1, 133.6, 136.3, 138.7, 141.3, 151.1, 159.4, 167.3, 173.8 ppm. MS (m/z relative intensity %): 378 [M^+] (95), 277 (36), 249 (45), 235 (100), 178 (62), 152 (80), 141 (30), 98 (35), 69 (27), 29 (62). IR (KBr) ν = 3367, 3205, 2713, 1644, 1600, 1564, 1440, 1224, 1199, 795 cm^{-1}. Anal. calcd for $C_{21}H_{18}N_2O_5$: C, 66.66; H, 4.80; N, 7.40%. Found: C, 66.51; H, 4.77; N, 7.27%.

^{1}H and ^{13}C NMR, IR, MS spectra for compounds 3a-l

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3a)







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14 Nov 2019

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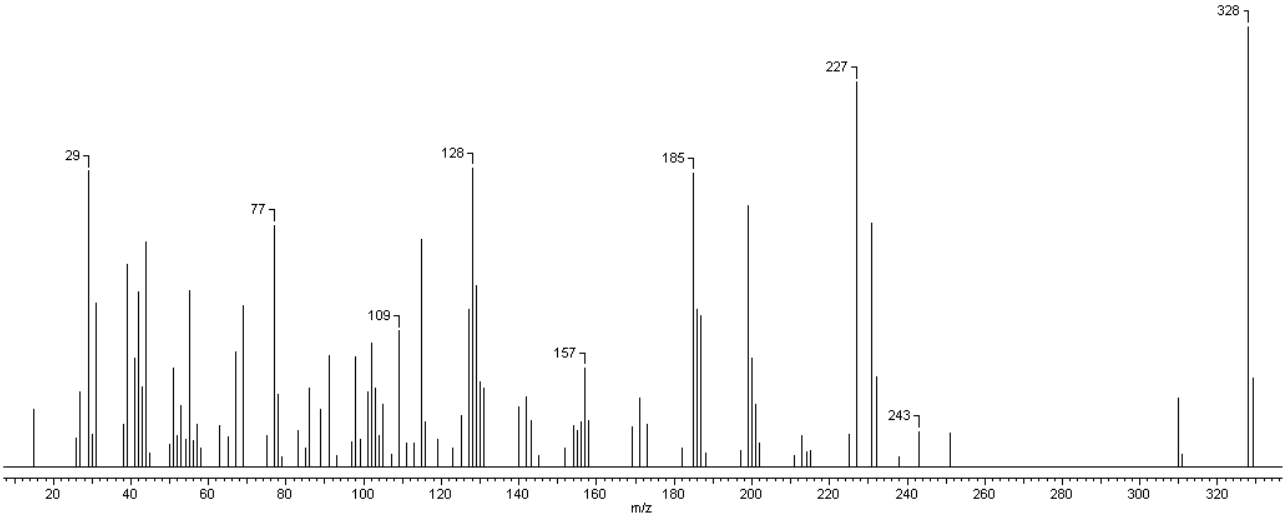
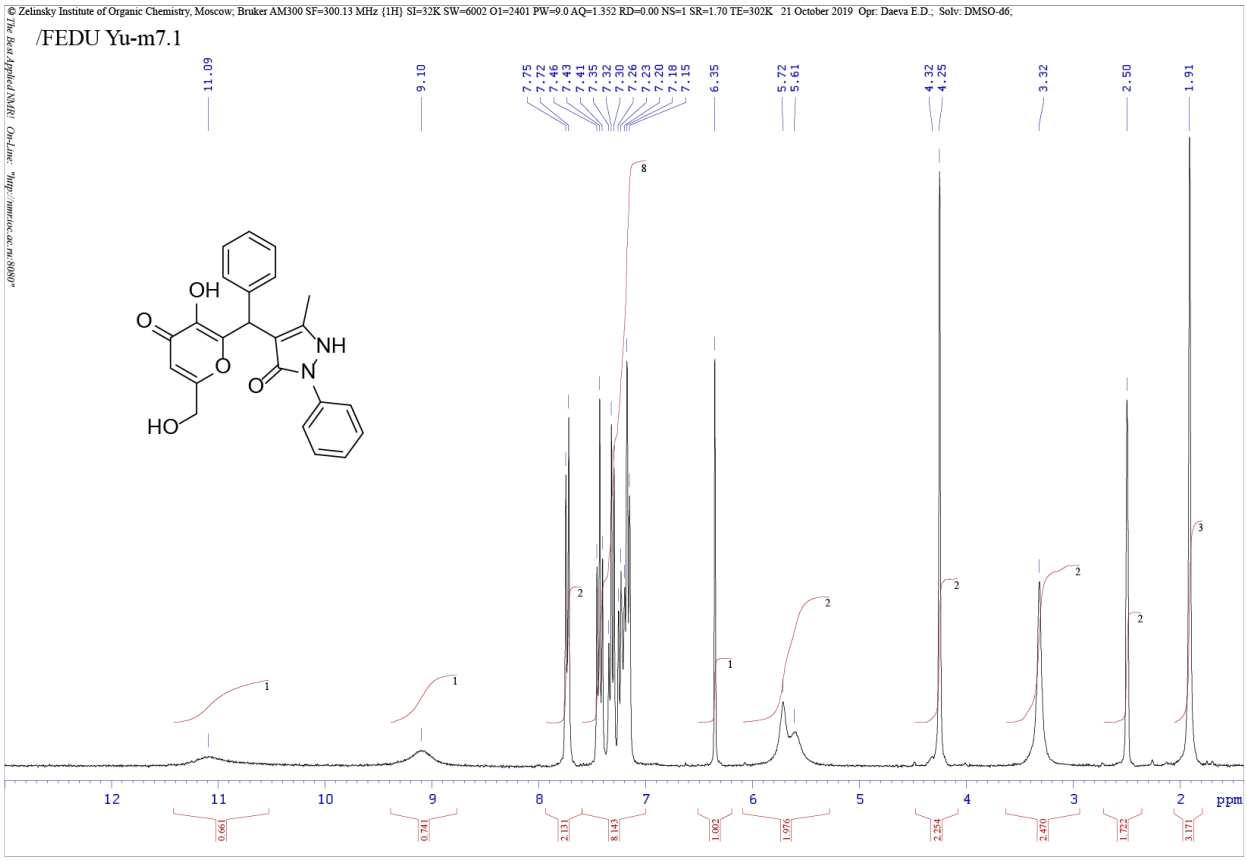
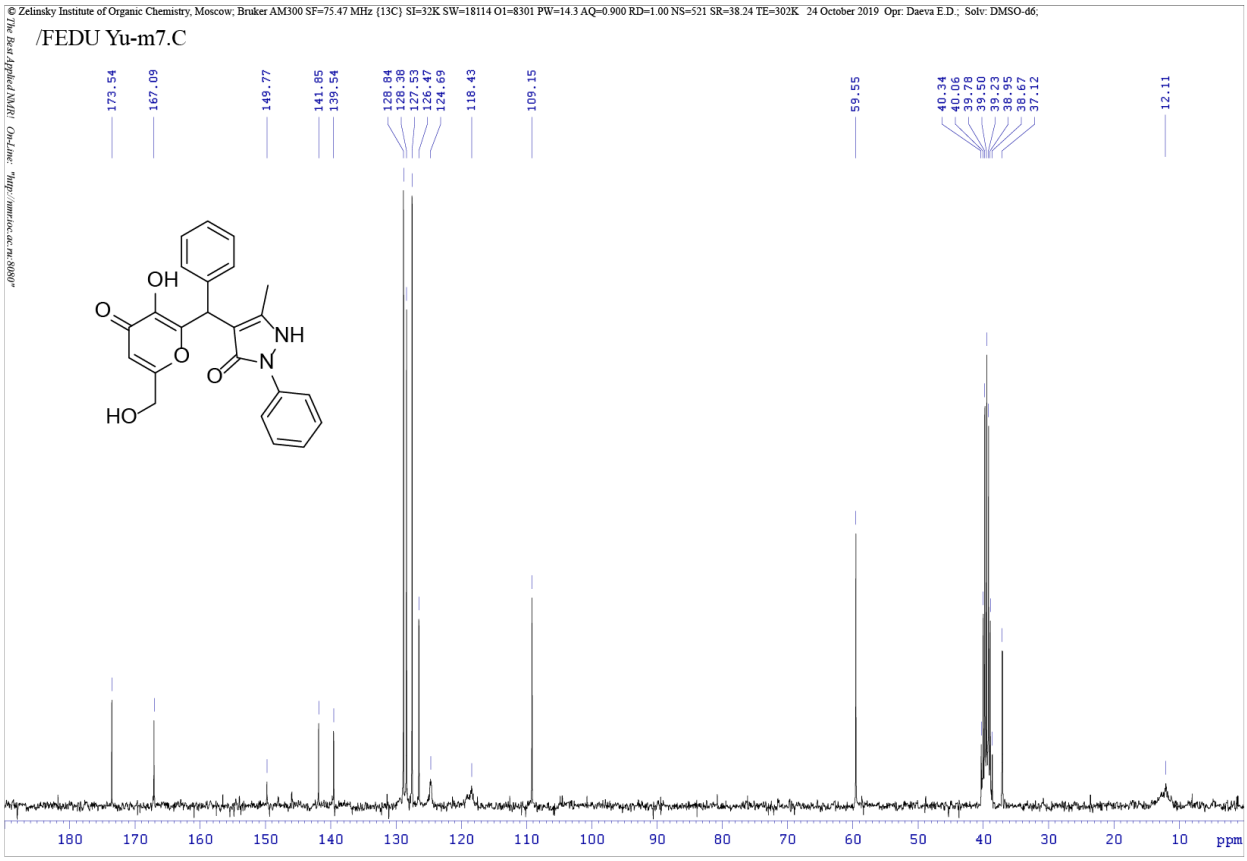


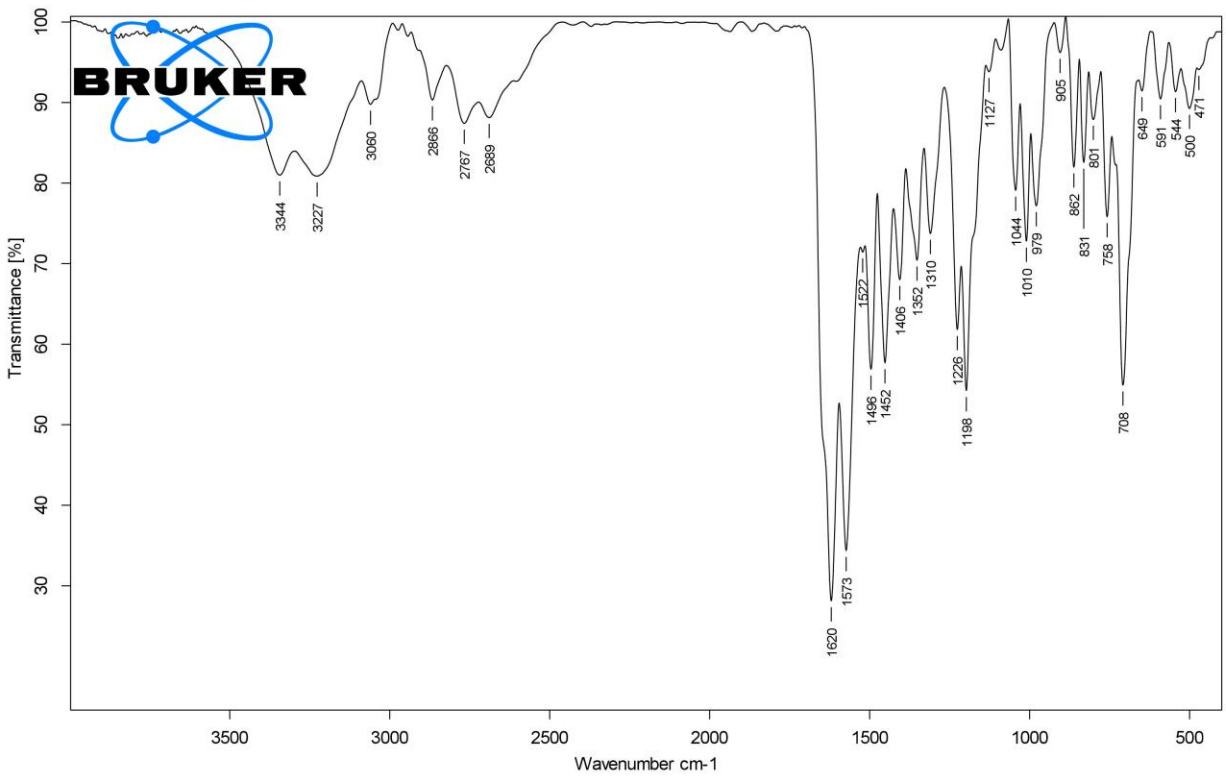
No.	m/z	RI(%)	DI
1	29.000	67.077	67.077
2	77.000	54.825	54.825
3	109.000	30.763	30.763
4	128.000	67.877	67.877
5	157.000	22.482	22.482
6	185.000	66.637	66.637
7	227.000	87.239	87.239
8	243.000	8.031	8.031
9	328.000	100.000	100.000

No.	m/z	TIC(%)
1	29.000	3.625
2	77.000	2.963
3	109.000	1.662
4	128.000	3.668
5	157.000	1.215
6	185.000	3.601
7	227.000	4.714
8	243.000	0.434
9	328.000	5.404

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(phenyl)methyl)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3b)







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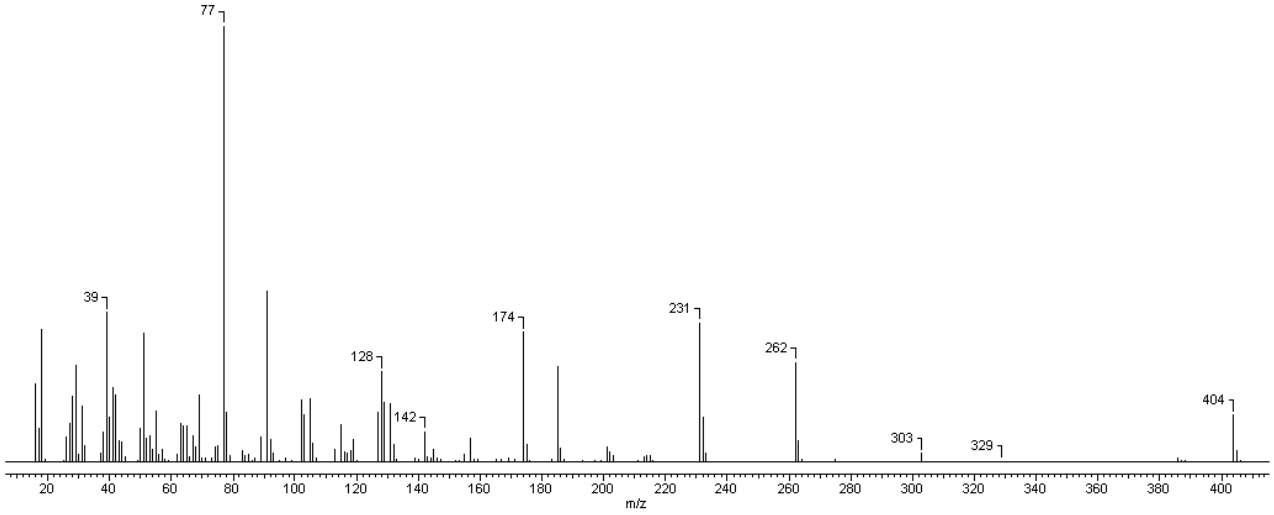
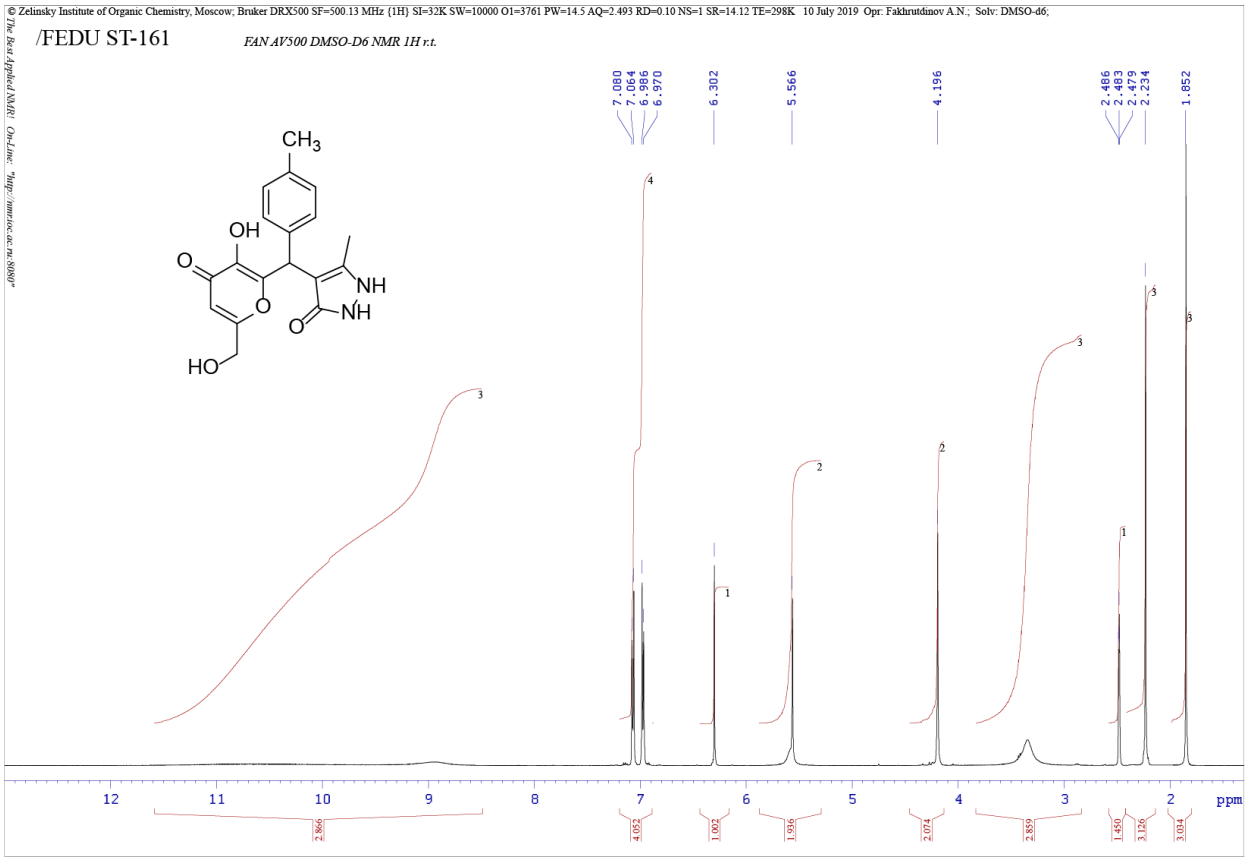
Count	140	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	Yu-m7
Spectrum Title	MASS SPECTRUM	***TIC***	858.90	***Owner***	Copyright(C) by Victor (2019)

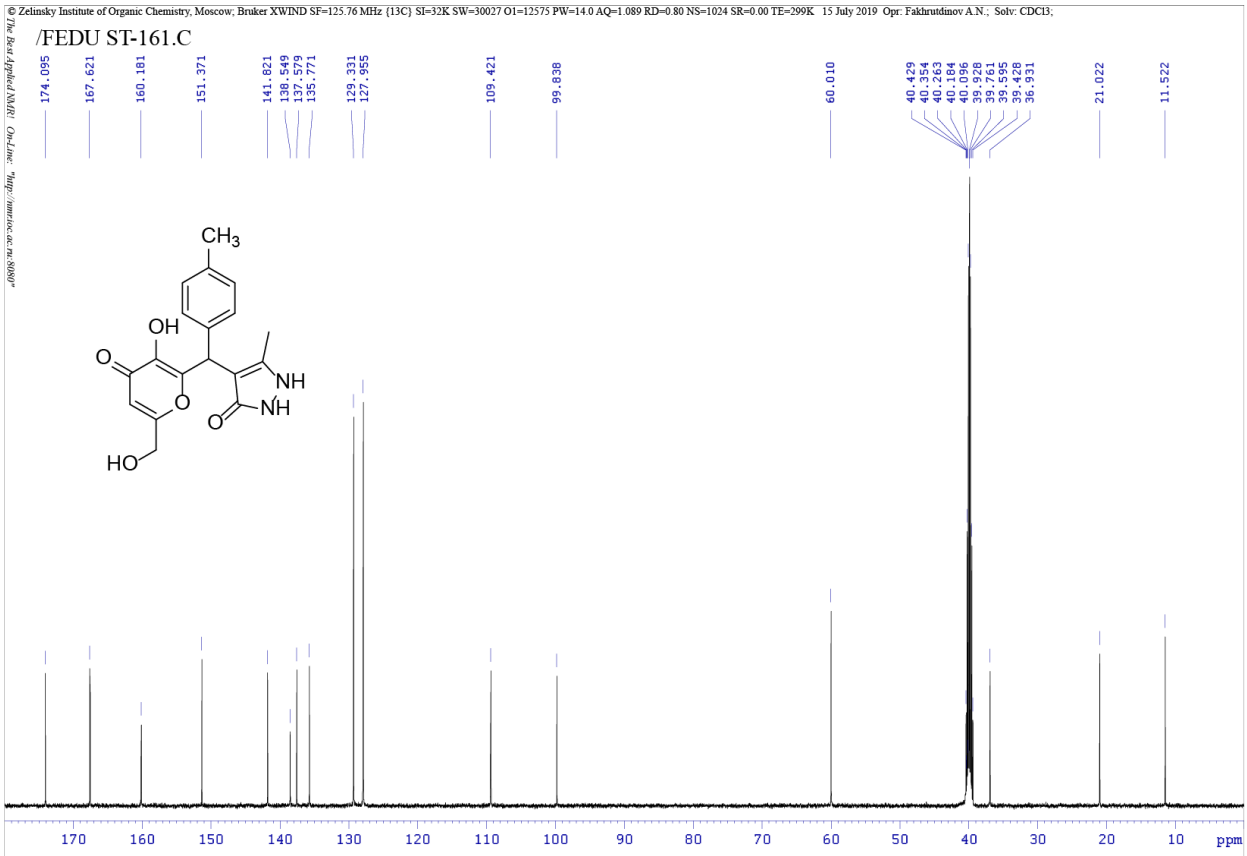


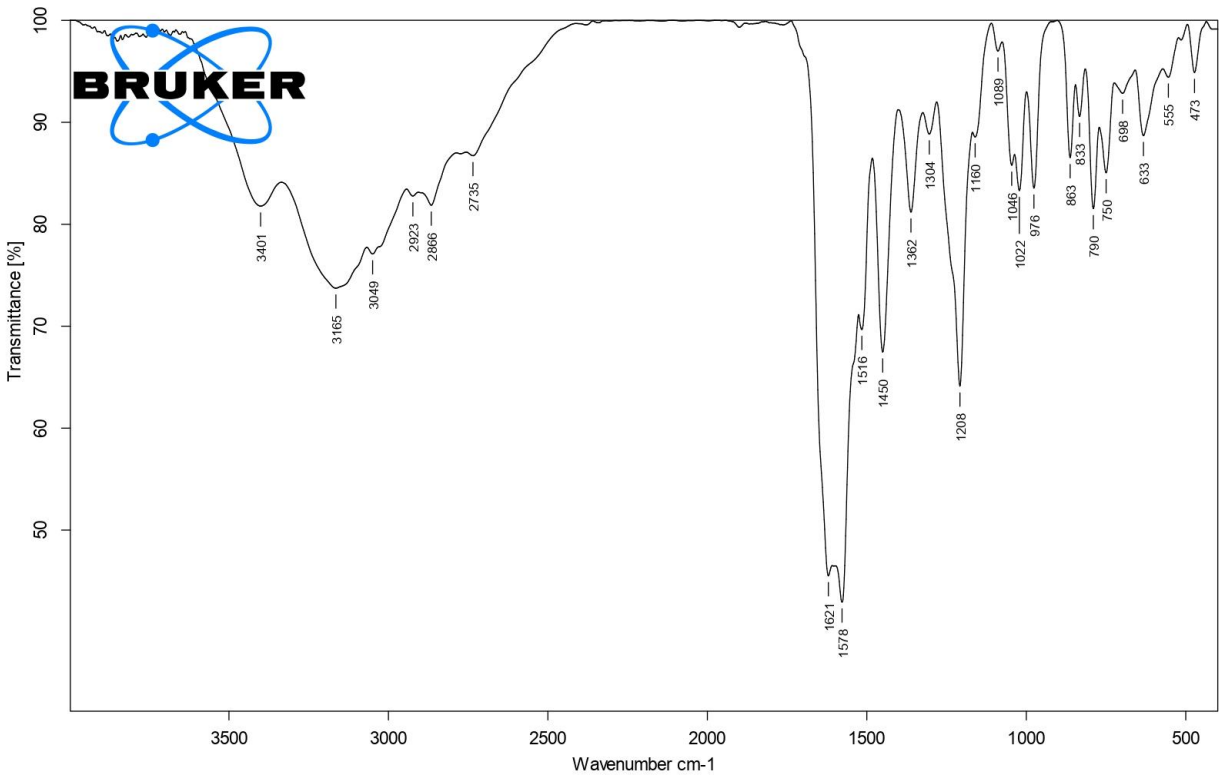
No.	m/z	RI(%)	DI
1	39.000	34.383	34.383
2	77.000	100.000	100.000
3	128.000	20.692	20.692
4	142.000	6.971	6.971
5	174.000	29.783	29.783
6	231.000	31.923	31.923
7	262.000	22.782	22.782
8	303.000	1.910	1.910
9	329.000	0.260	0.260
10	404.000	10.741	10.741

No.	m/z	TIC(%)
1	39.000	4.003
2	77.000	11.643
3	128.000	2.409
4	142.000	0.812
5	174.000	3.468
6	231.000	3.717
7	262.000	2.653
8	303.000	0.222
9	329.000	0.030
10	404.000	1.251

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(p-tolyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3c)







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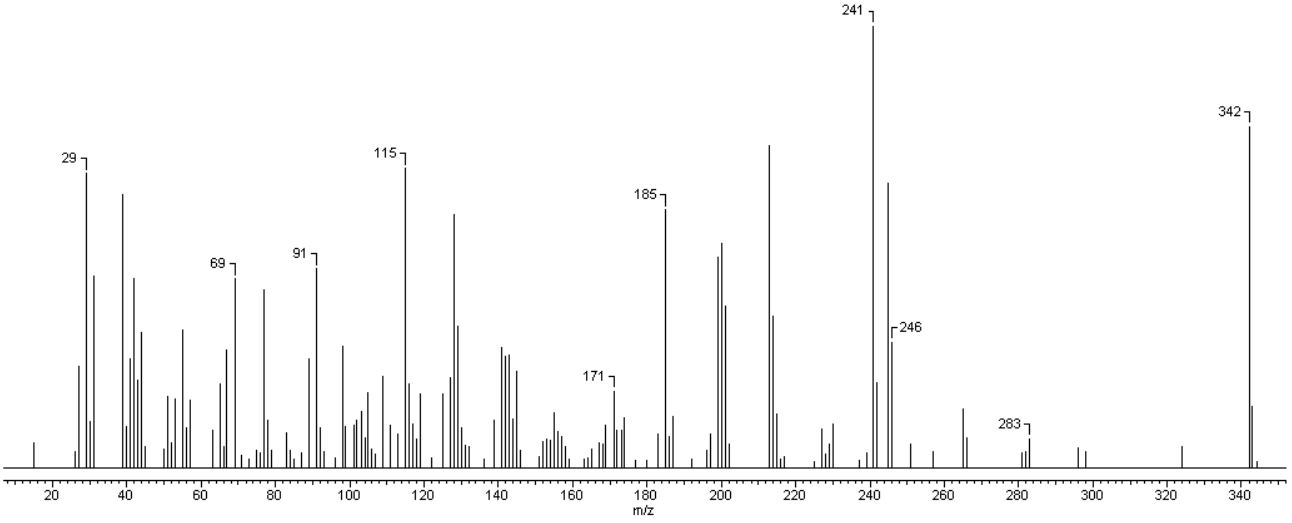
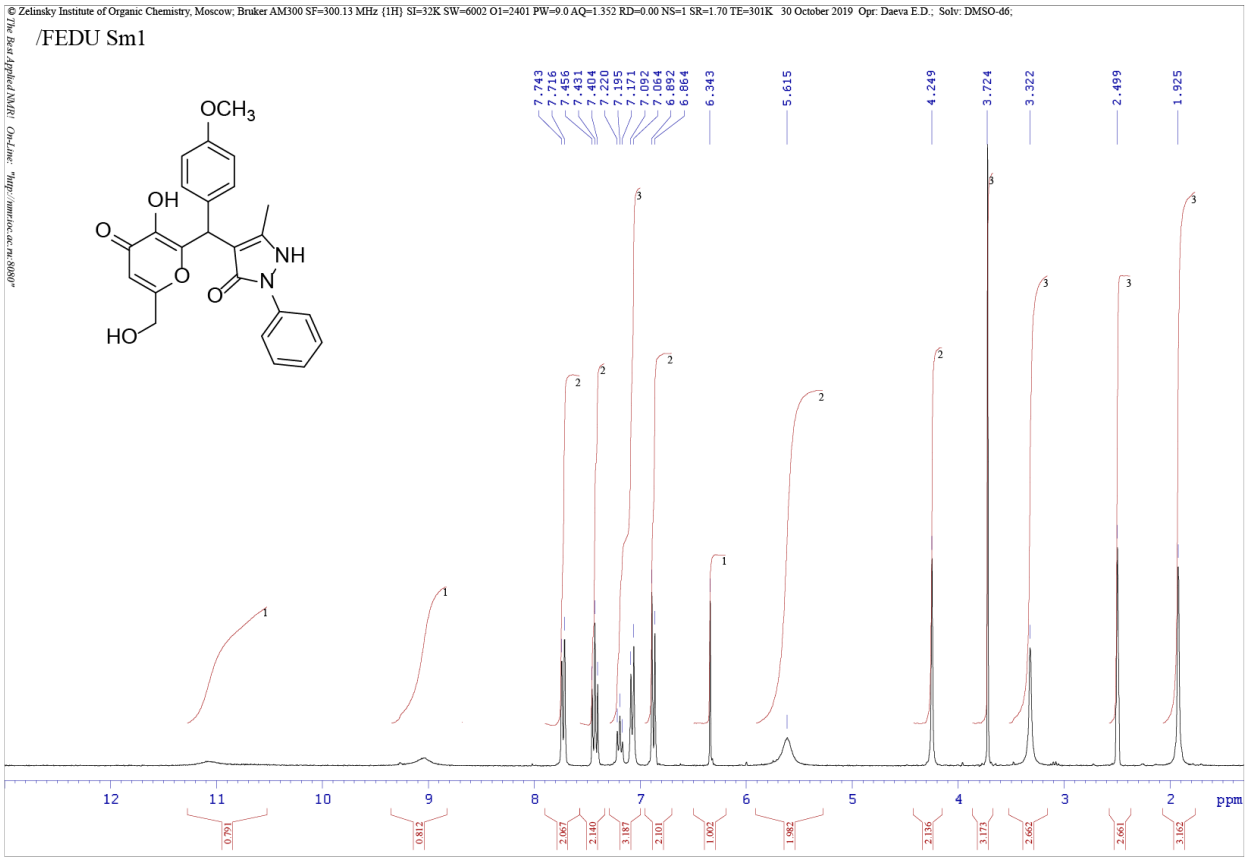
Count	135	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-161	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	2152.77				

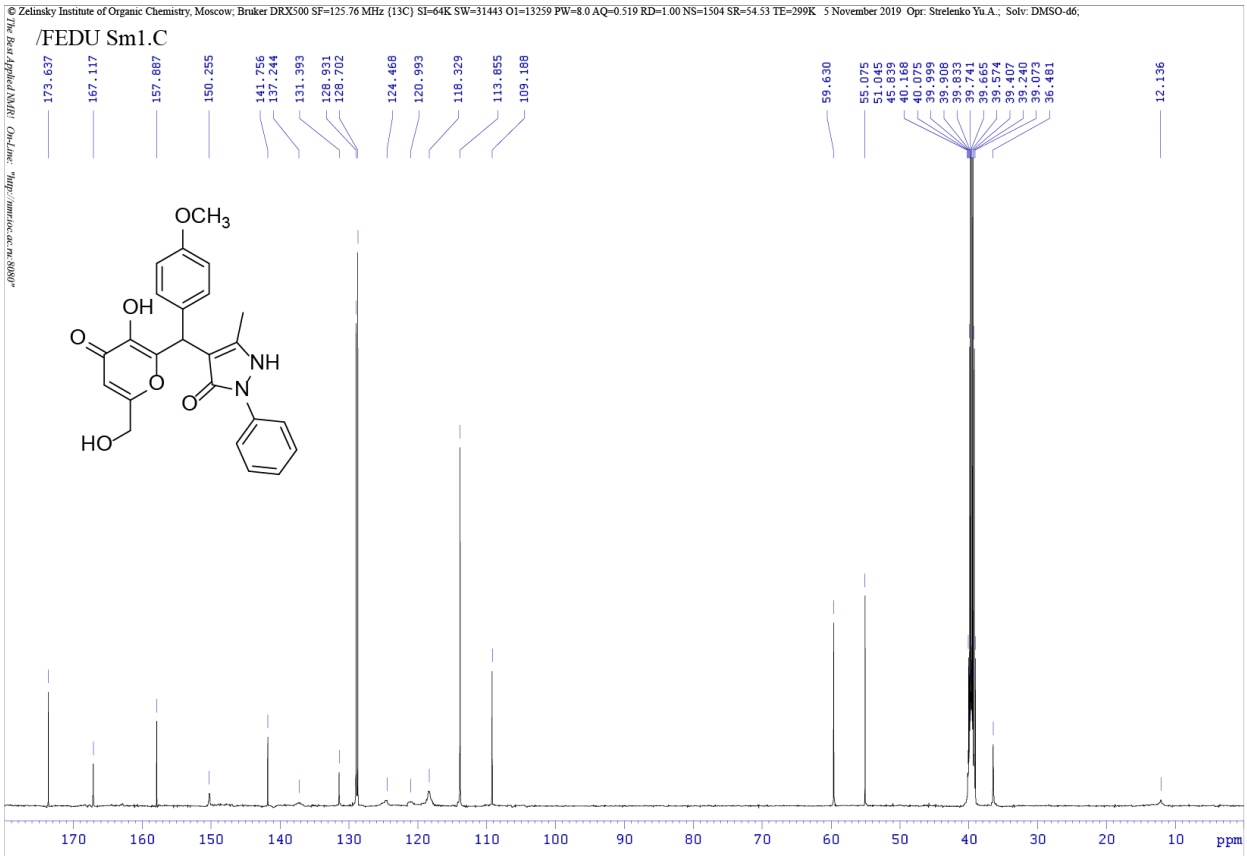


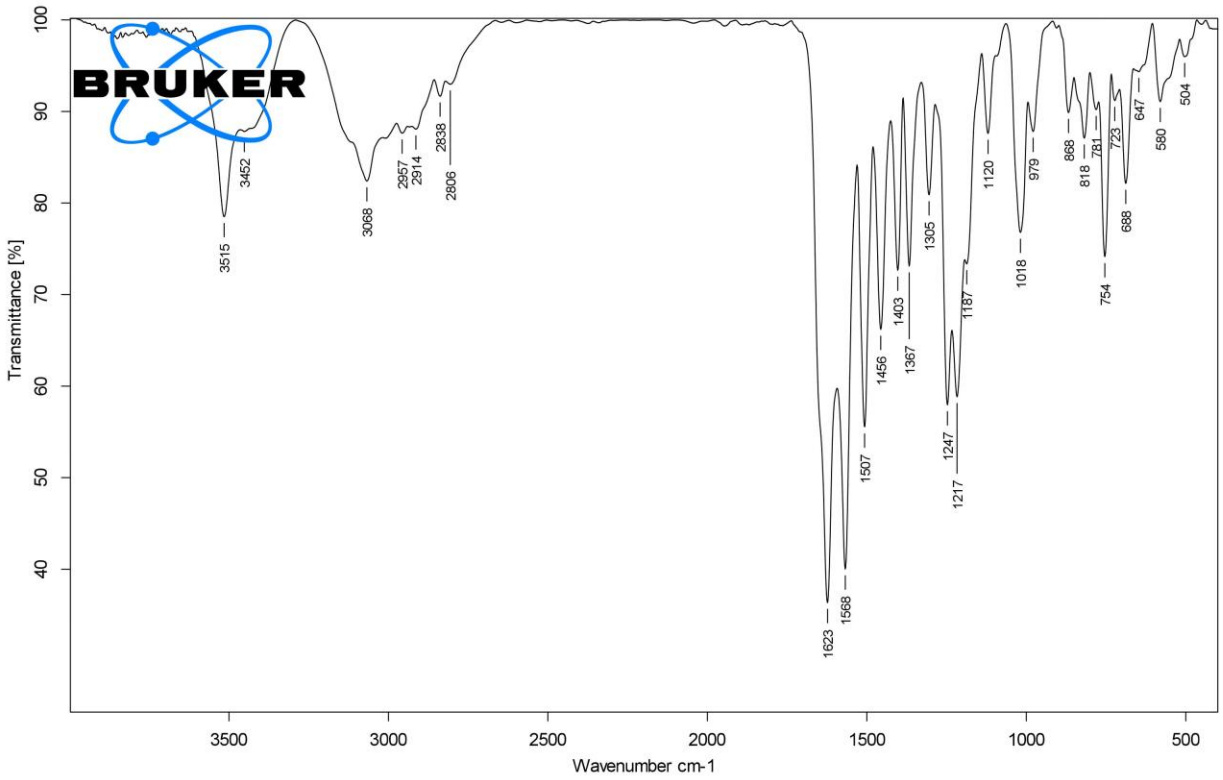
No.	*m/z*	RI(%)	DI
1	29.000	66.647	66.647
2	69.000	42.824	42.824
3	91.000	45.155	45.155
4	115.000	67.867	67.867
5	171.000	17.492	17.492
6	185.000	58.446	58.446
7	241.000	100.000	100.000
8	246.000	28.463	28.463
9	283.000	6.661	6.661
10	342.000	77.268	77.268

No.	*m/z*	TIC(%)
1	29.000	3.096
2	69.000	1.989
3	91.000	2.098
4	115.000	3.153
5	171.000	0.813
6	185.000	2.715
7	241.000	4.645
8	246.000	1.322
9	283.000	0.309
10	342.000	3.589

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(4-methoxyphenyl)methyl)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3d)







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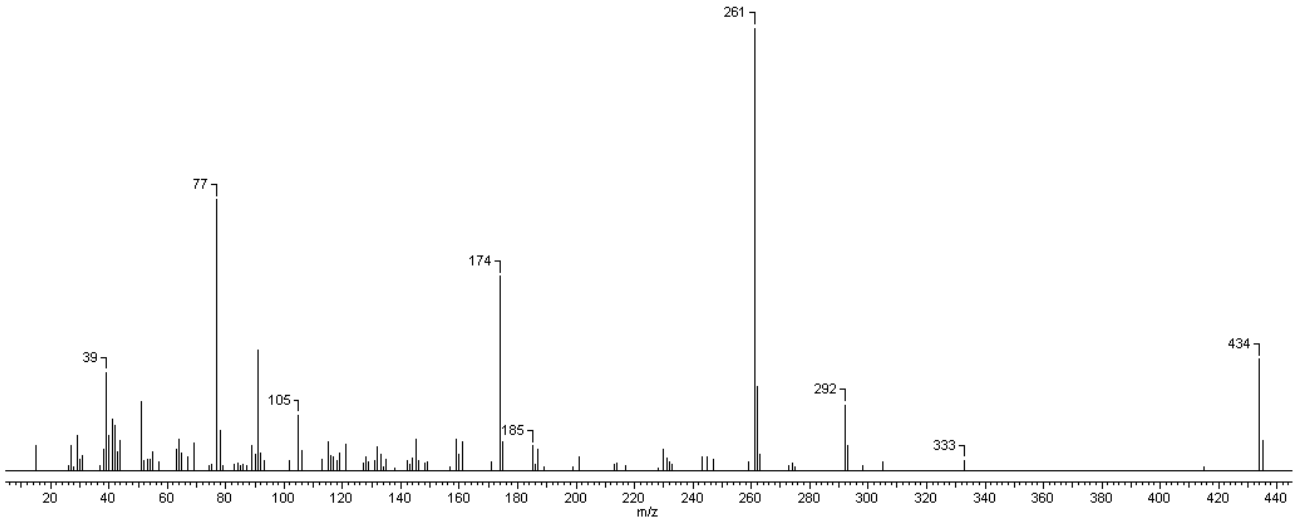
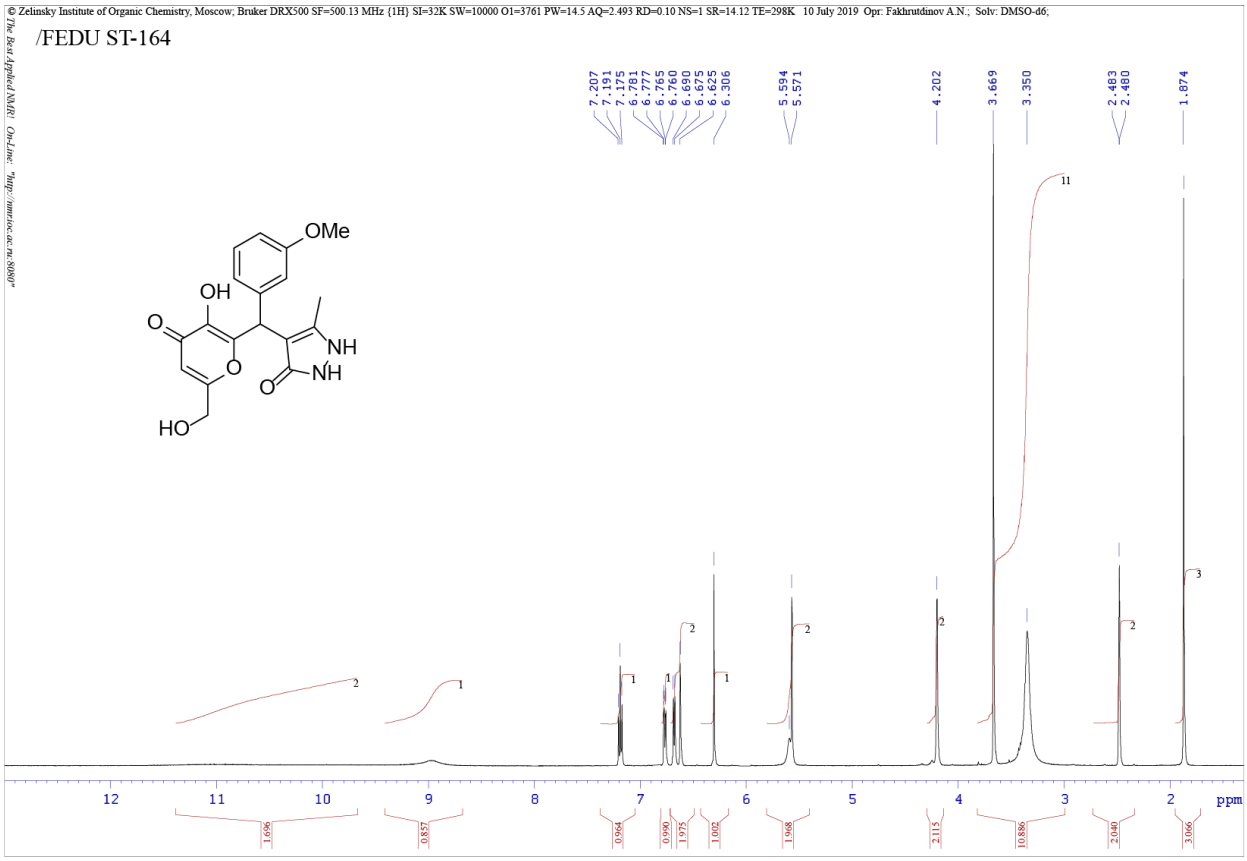
Count	106	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	SM-1	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	658.02				

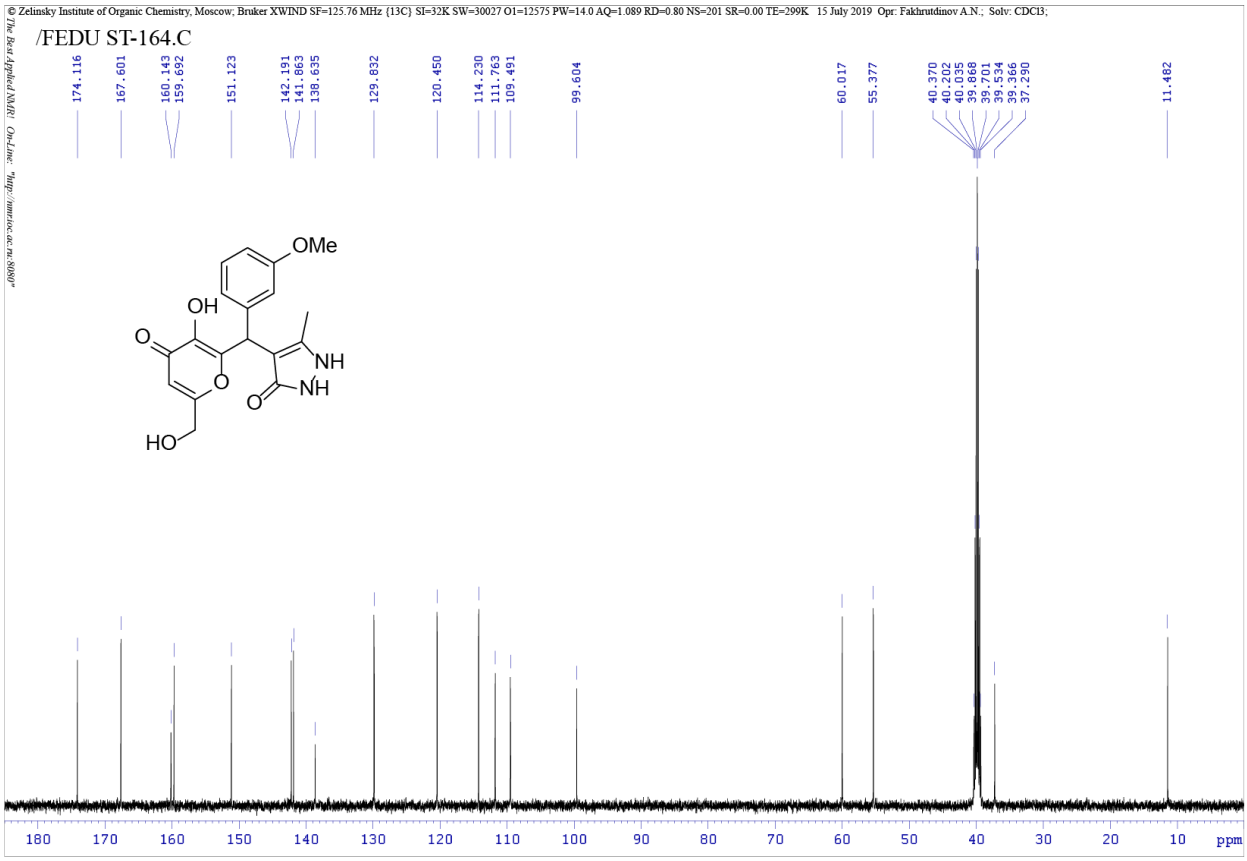


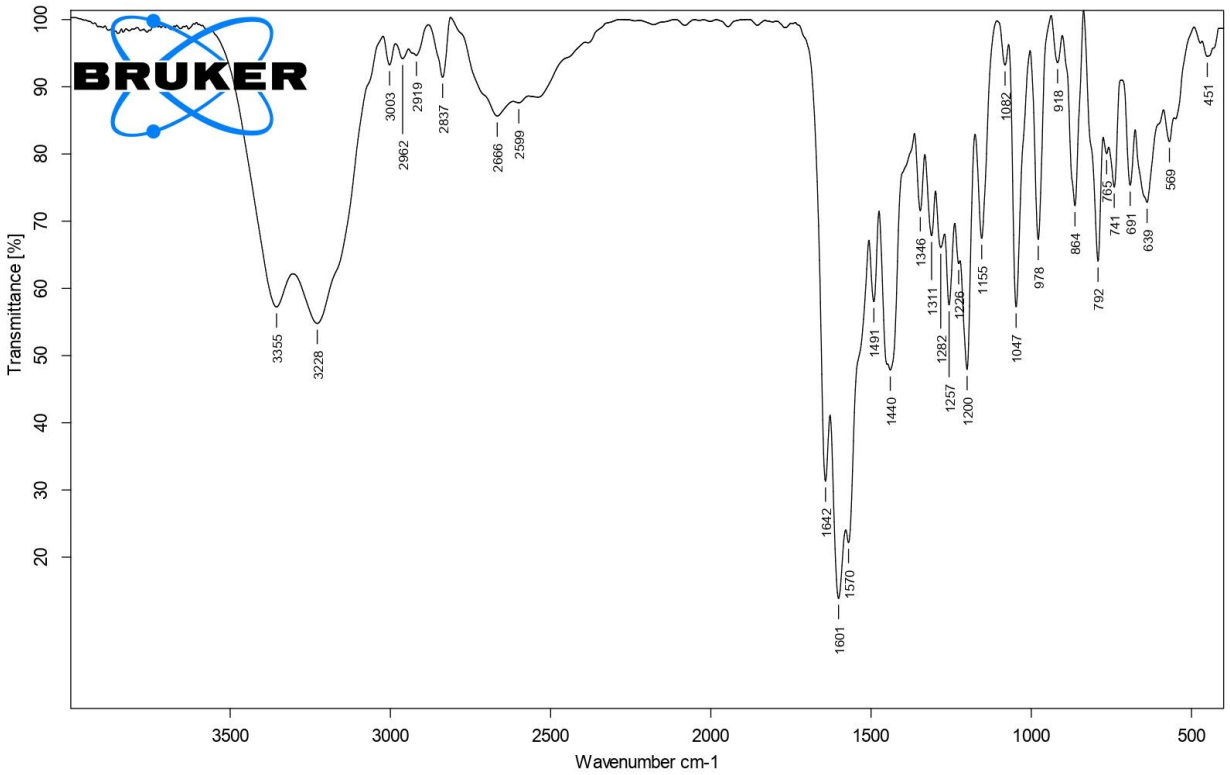
No.	m/z	RI(%)	DI
1	39.000	22.082	22.082
2	77.000	61.236	61.236
3	105.000	12.481	12.481
4	174.000	43.884	43.884
5	185.000	5.601	5.601
6	261.000	100.000	100.000
7	292.000	14.871	14.871
8	333.000	2.310	2.310
9	434.000	25.093	25.093

No.	m/z	TIC(%)
1	39.000	3.356
2	77.000	9.306
3	105.000	1.897
4	174.000	6.669
5	185.000	0.851
6	261.000	15.197
7	292.000	2.260
8	333.000	0.351
9	434.000	3.813

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(3-methoxyphenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3e)







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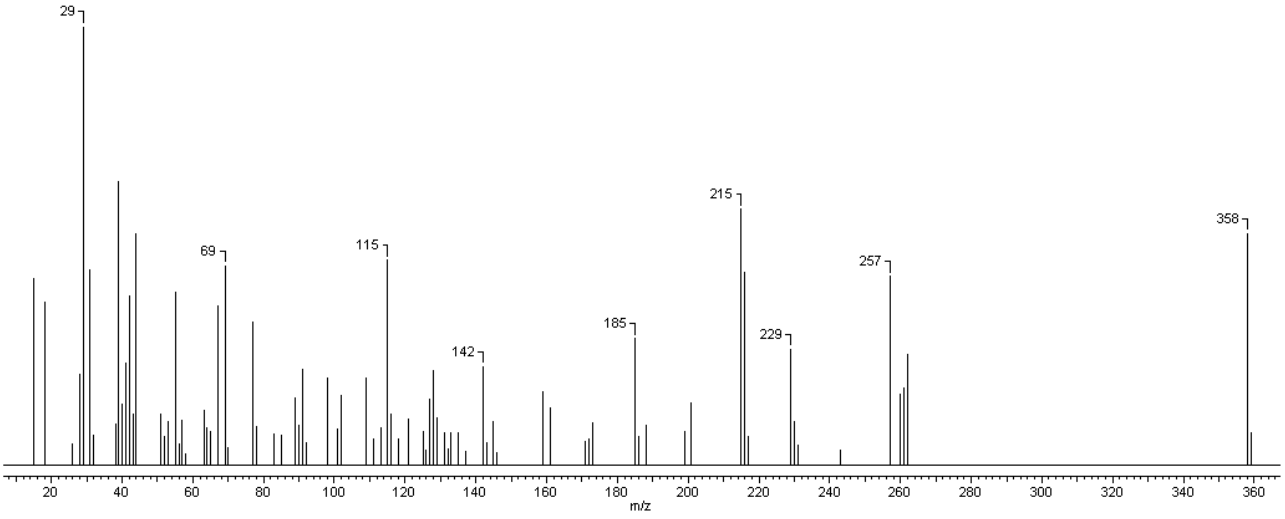
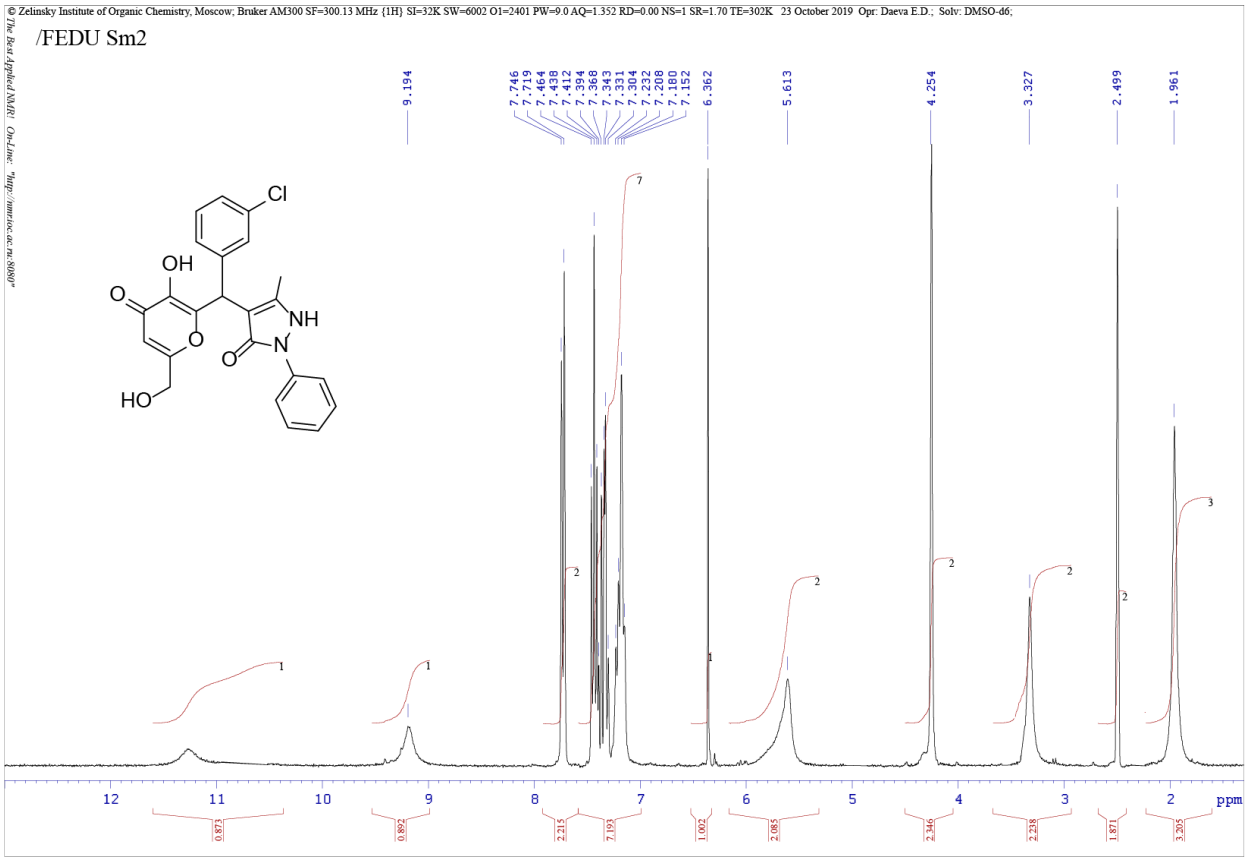
Count	82	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-164	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	1488.12				

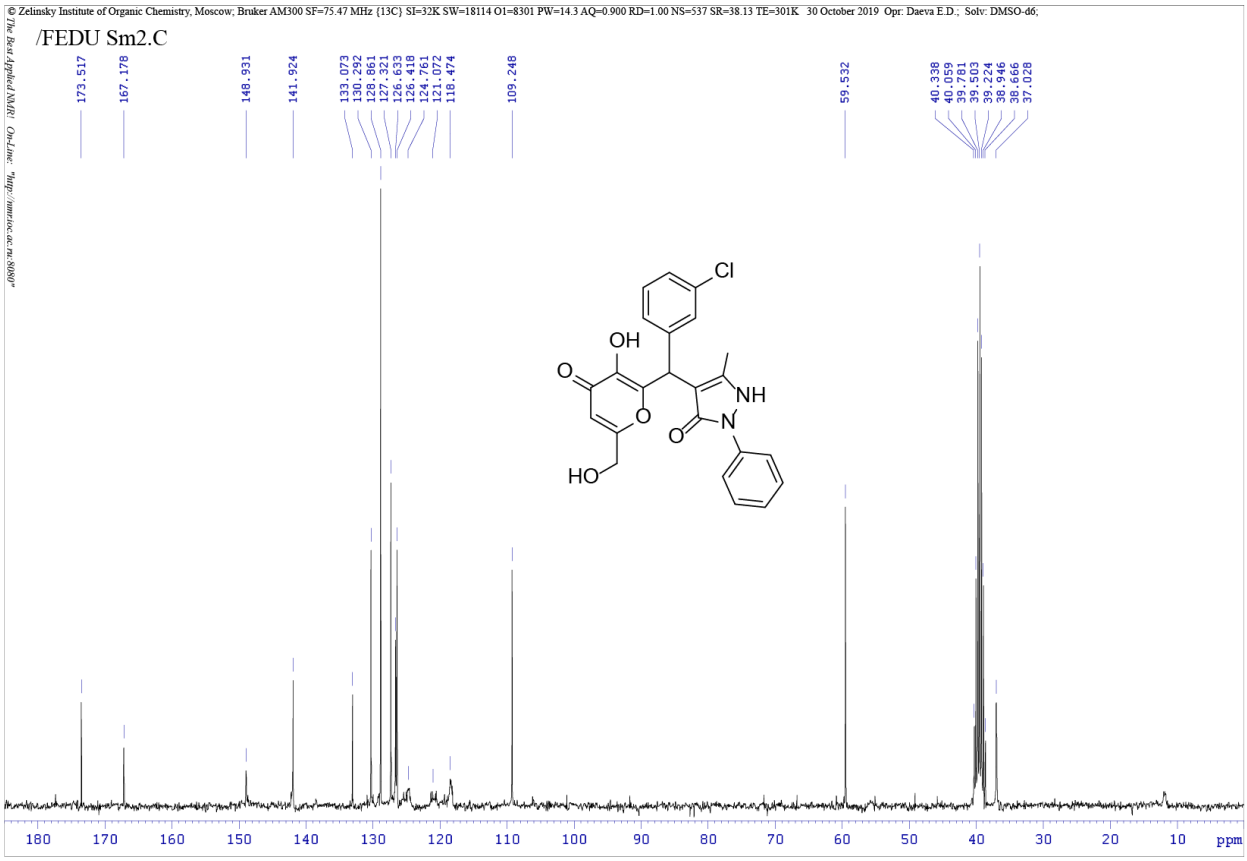


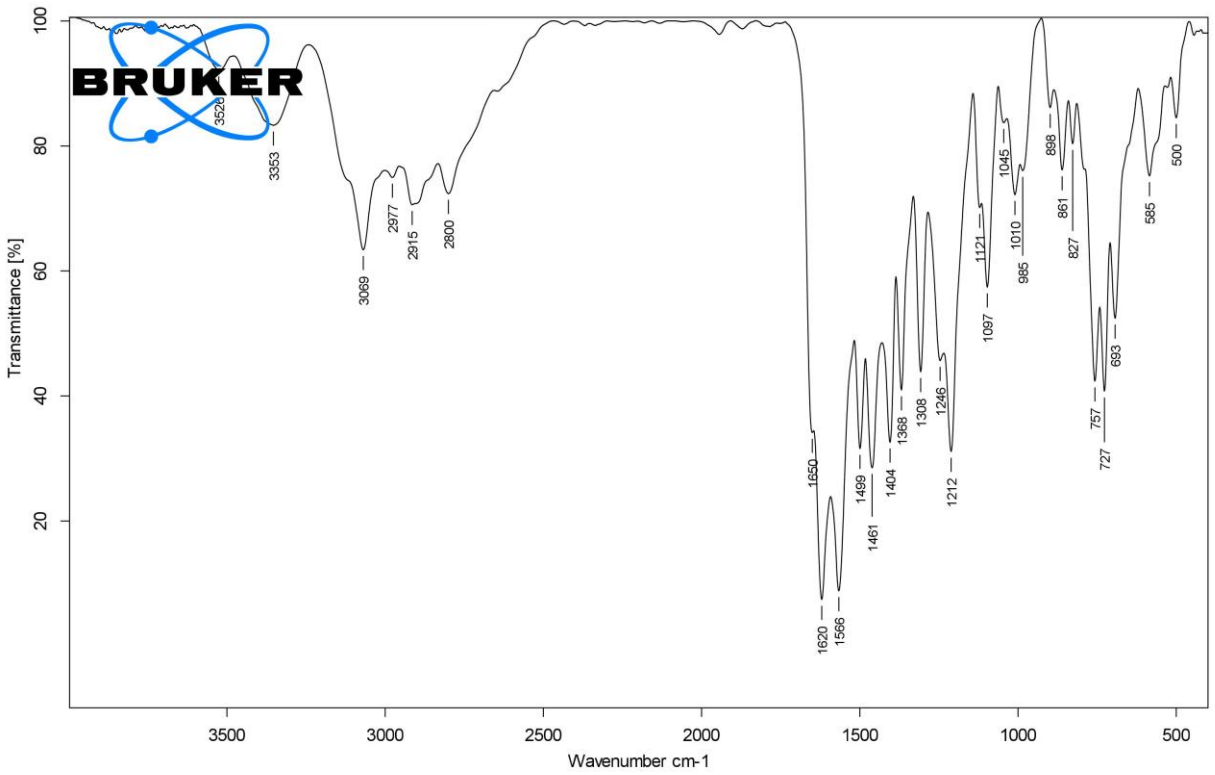
No.	m/z	RI(%)	DI
1	29.000	100.000	100.000
2	69.000	45.415	45.415
3	115.000	46.655	46.655
4	142.000	22.462	22.462
5	185.000	28.883	28.883
6	215.000	58.336	58.336
7	229.000	26.403	26.403
8	257.000	42.984	42.984
9	358.000	52.765	52.765

No.	m/z	TIC(%)
1	29.000	6.720
2	69.000	3.052
3	115.000	3.135
4	142.000	1.509
5	185.000	1.941
6	215.000	3.920
7	229.000	1.774
8	257.000	2.888
9	358.000	3.546

4-((3-Chlorophenyl)(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)methyl)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (3f)







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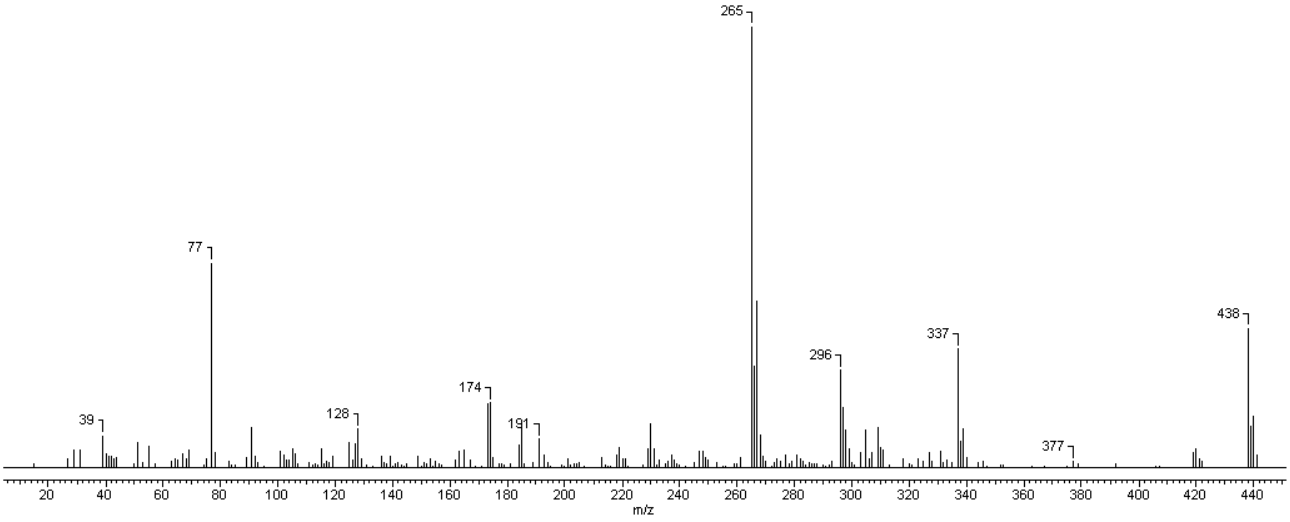
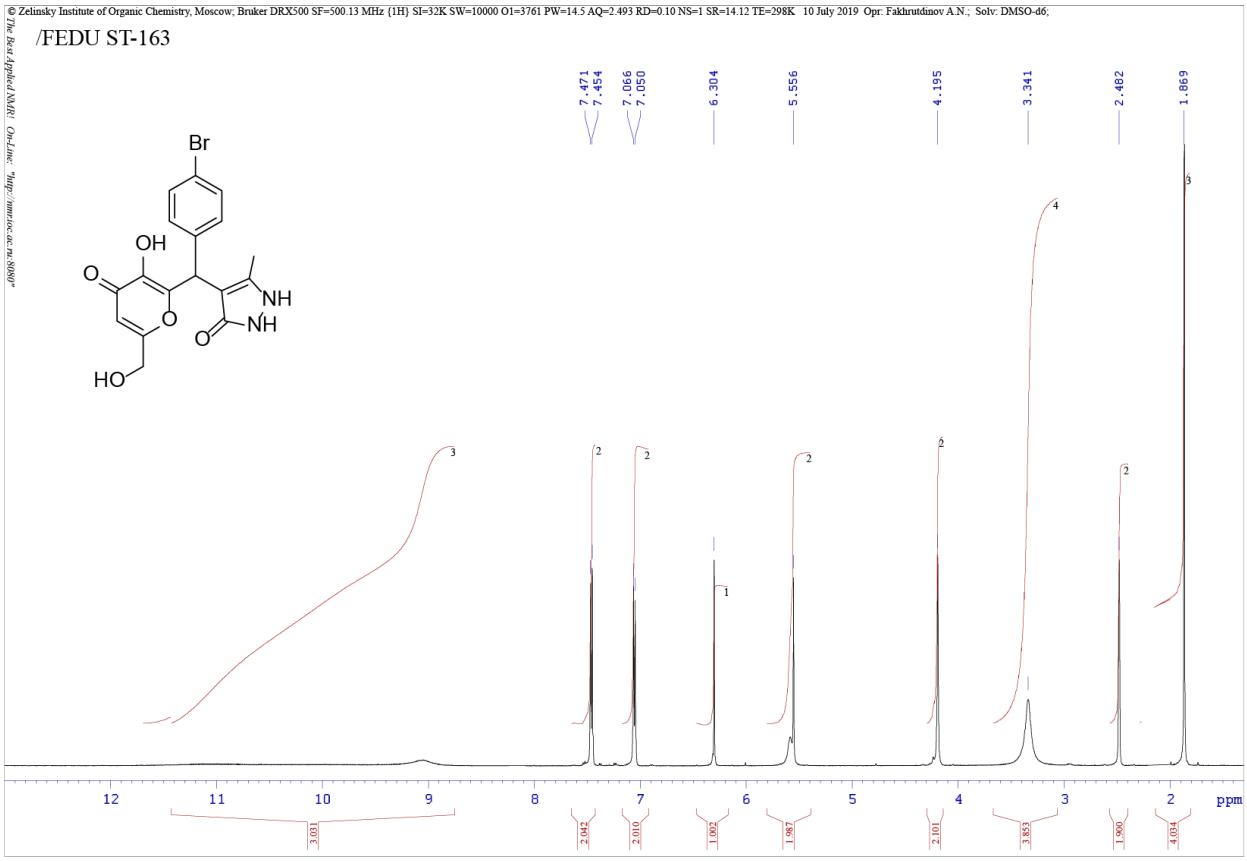
Count	212	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	SM-2	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	787.14				

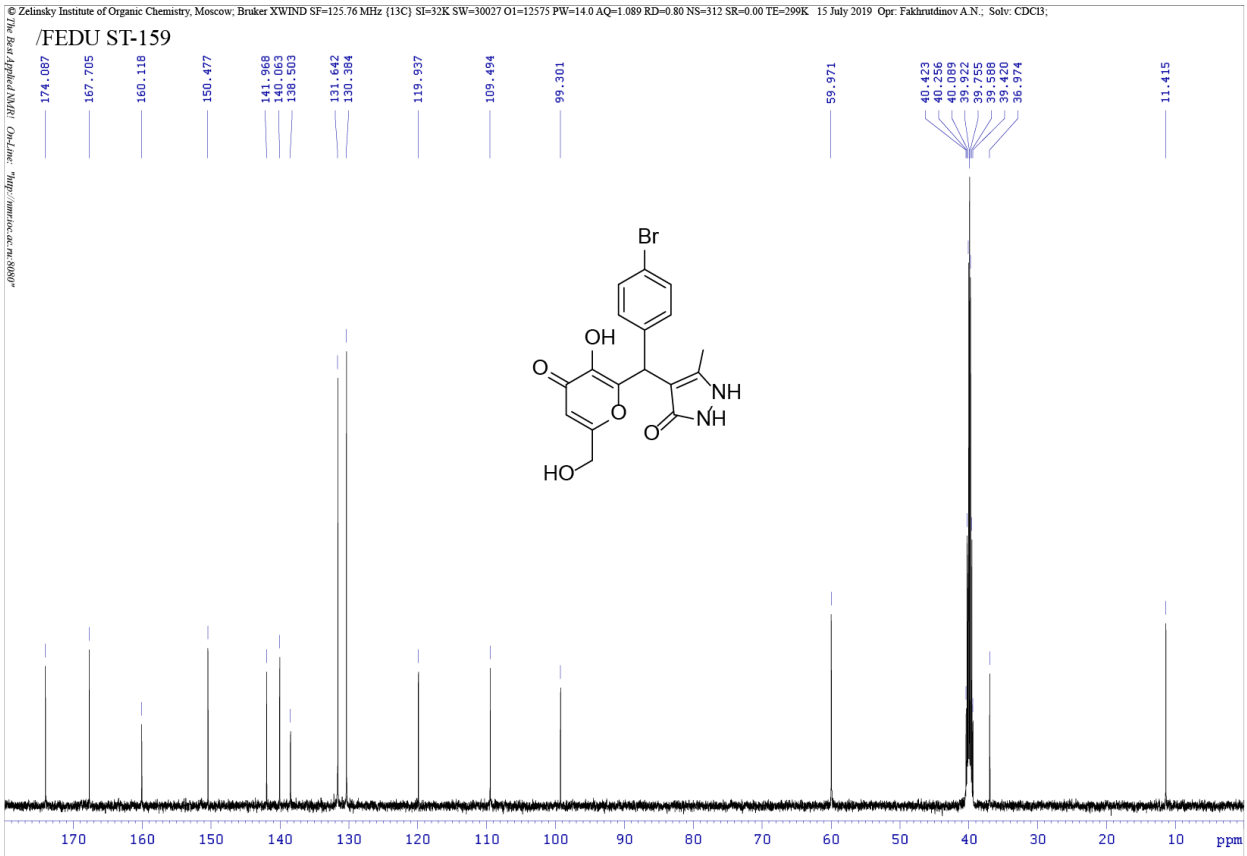


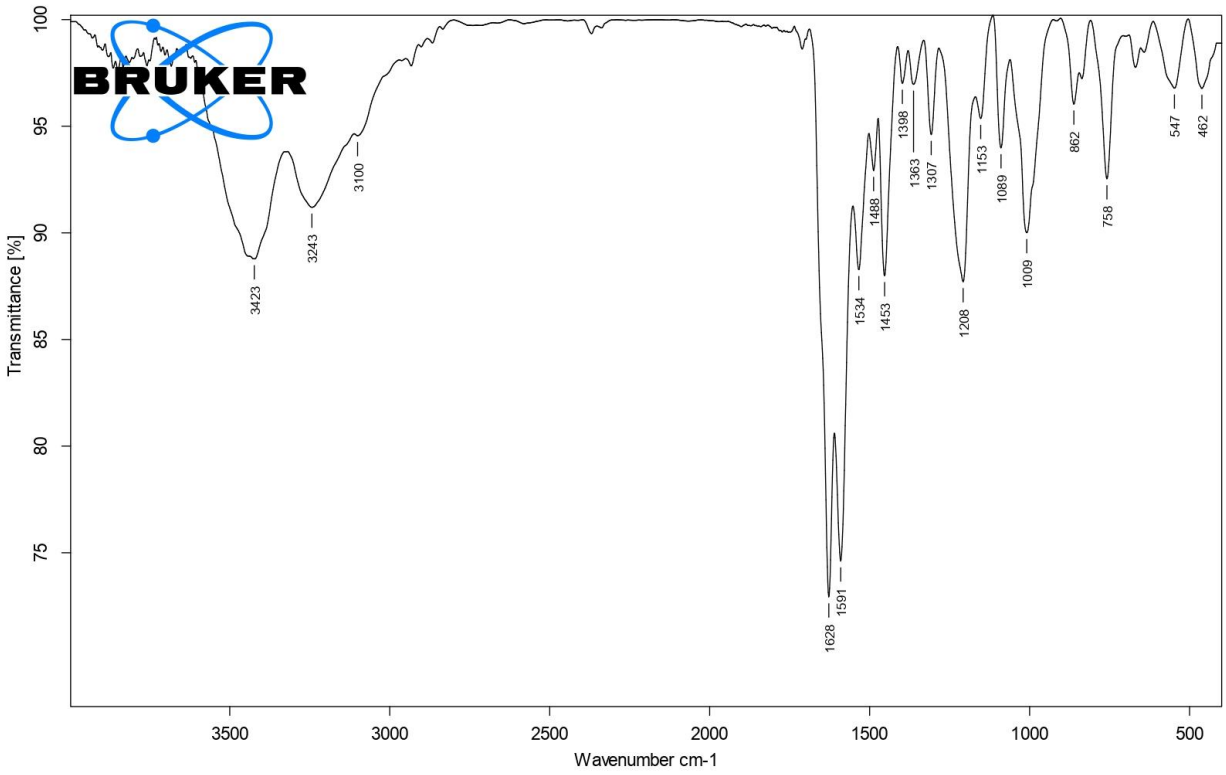
No.	m/z	RI(%)	DI
1	39.000	7.271	7.271
2	77.000	46.455	46.455
3	128.000	8.711	8.711
4	174.000	14.861	14.861
5	191.000	6.571	6.571
6	265.000	100.000	100.000
7	296.000	22.122	22.122
8	337.000	26.963	26.963
9	377.000	1.400	1.400
10	438.000	31.613	31.613

No.	m/z	TIC(%)
1	39.000	0.924
2	77.000	5.902
3	128.000	1.107
4	174.000	1.888
5	191.000	0.835
6	265.000	12.704
7	296.000	2.810
8	337.000	3.425
9	377.000	0.178
10	438.000	4.016

4-((4-Bromophenyl)(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3g)







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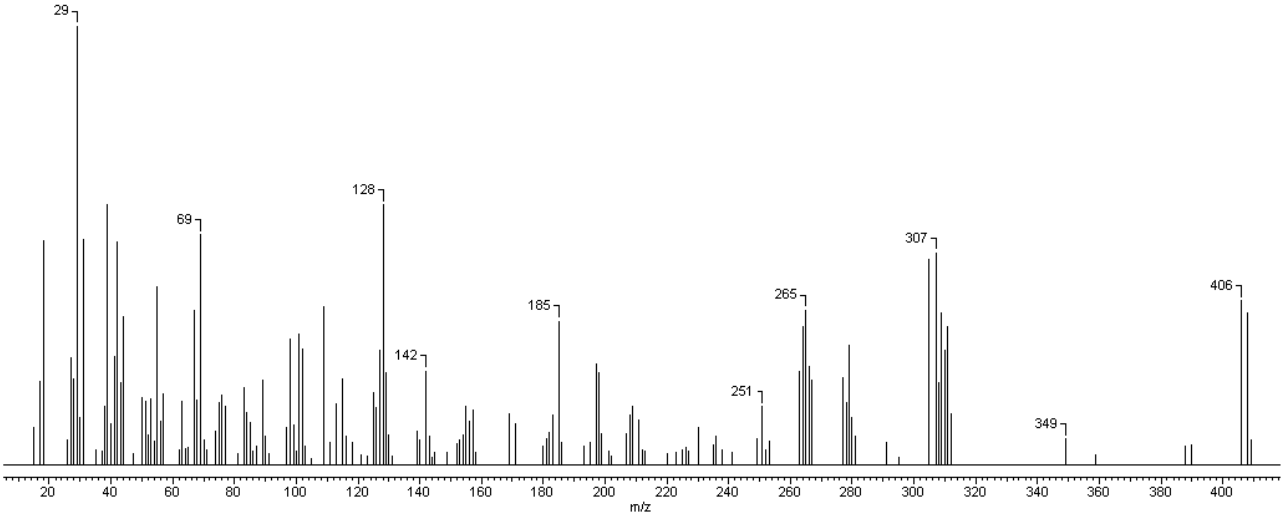
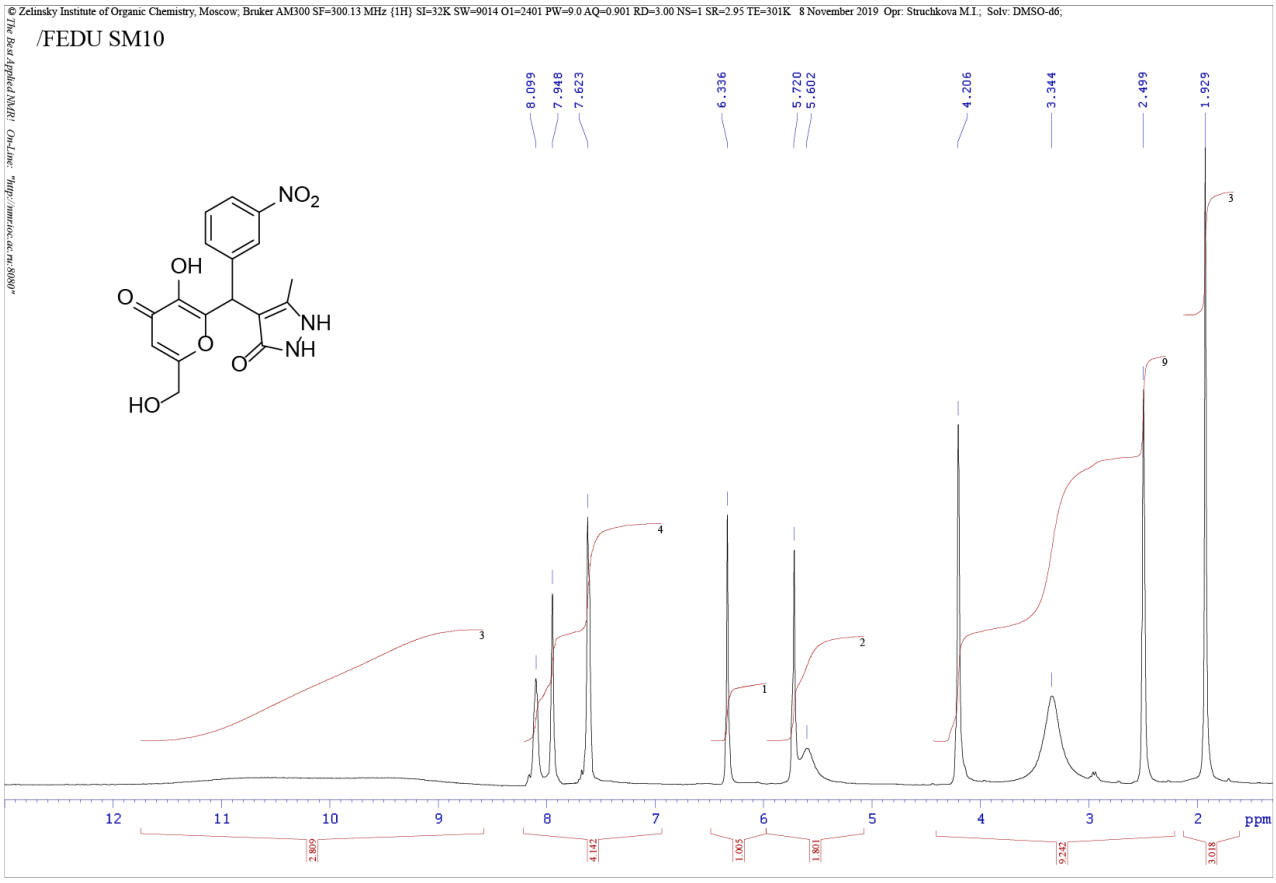
Count	147	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC
Inlet Mode	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-163
Spectrum Title	MASS SPECTRUM	***TIC***	2163.36	***Owner***	Copyright(C) by Victor (2019)

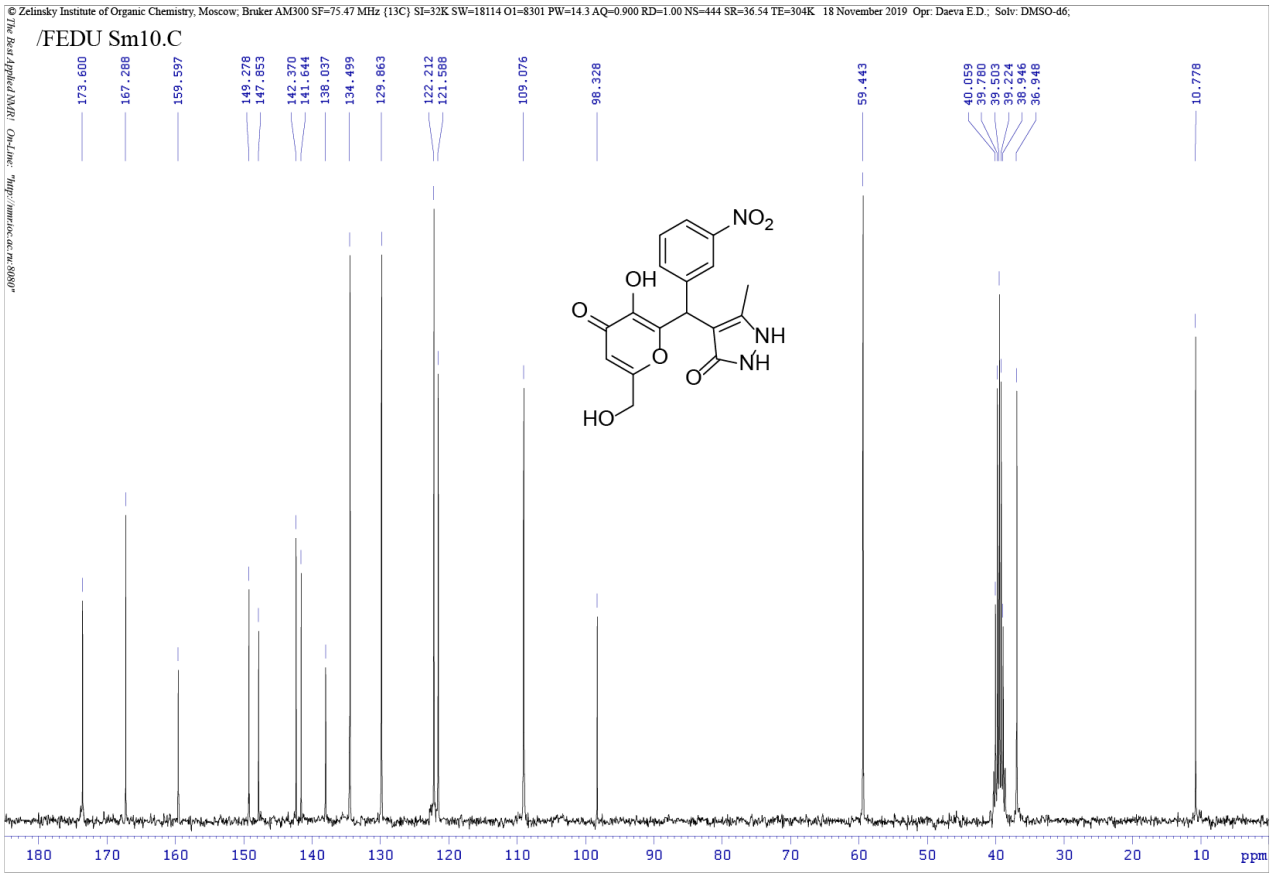


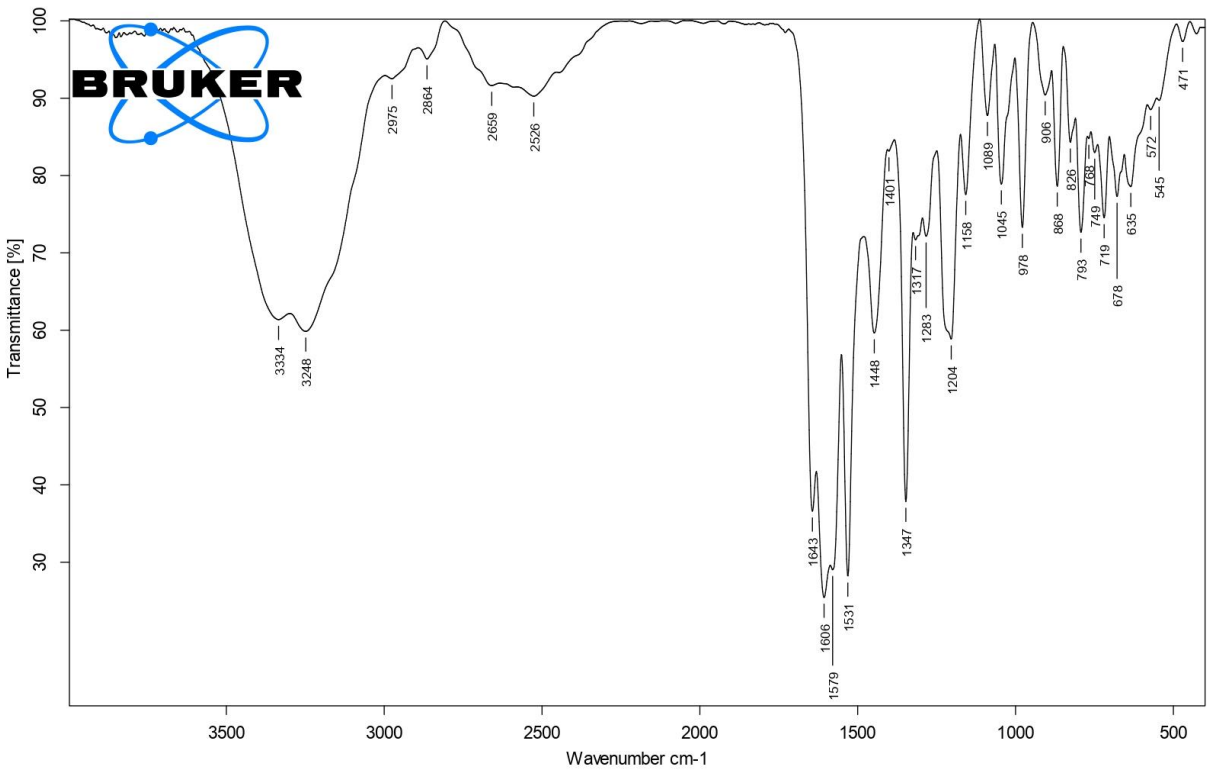
No.	m/z	RI(%)	DI
1	29.000	100.000	100.000
2	69.000	52.375	52.375
3	128.000	59.296	59.296
4	142.000	21.422	21.422
5	185.000	32.833	32.833
6	251.000	13.341	13.341
7	265.000	35.304	35.304
8	307.000	48.345	48.345
9	349.000	6.021	6.021
10	406.000	37.454	37.454

No.	m/z	TIC(%)
1	29.000	4.622
2	69.000	2.421
3	128.000	2.741
4	142.000	0.990
5	185.000	1.518
6	251.000	0.617
7	265.000	1.632
8	307.000	2.235
9	349.000	0.278
10	406.000	1.731

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(3-nitrophenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3h)







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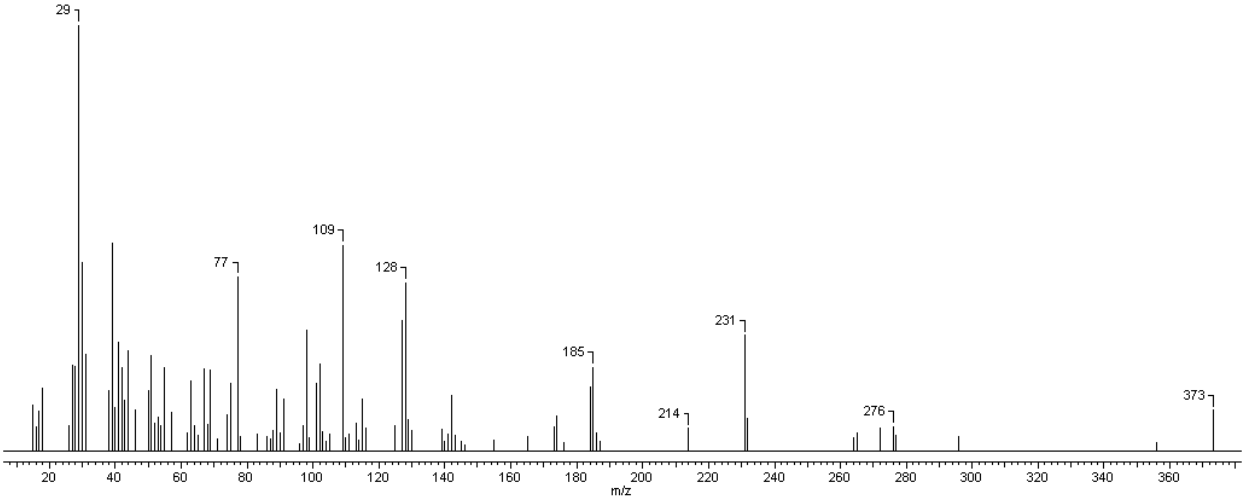
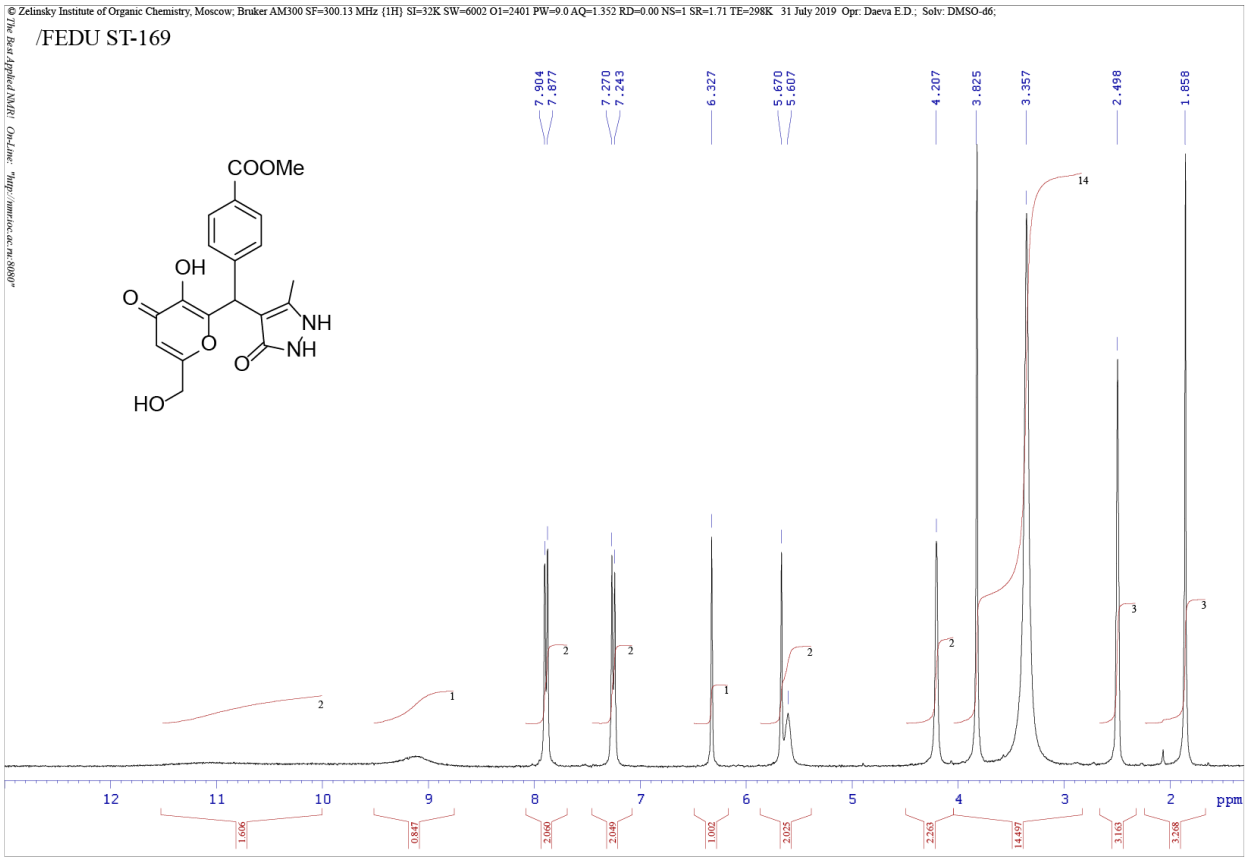
Count	92	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	SM-10
Spectrum Title	MASS SPECTRUM	***TIC***	1121.63		

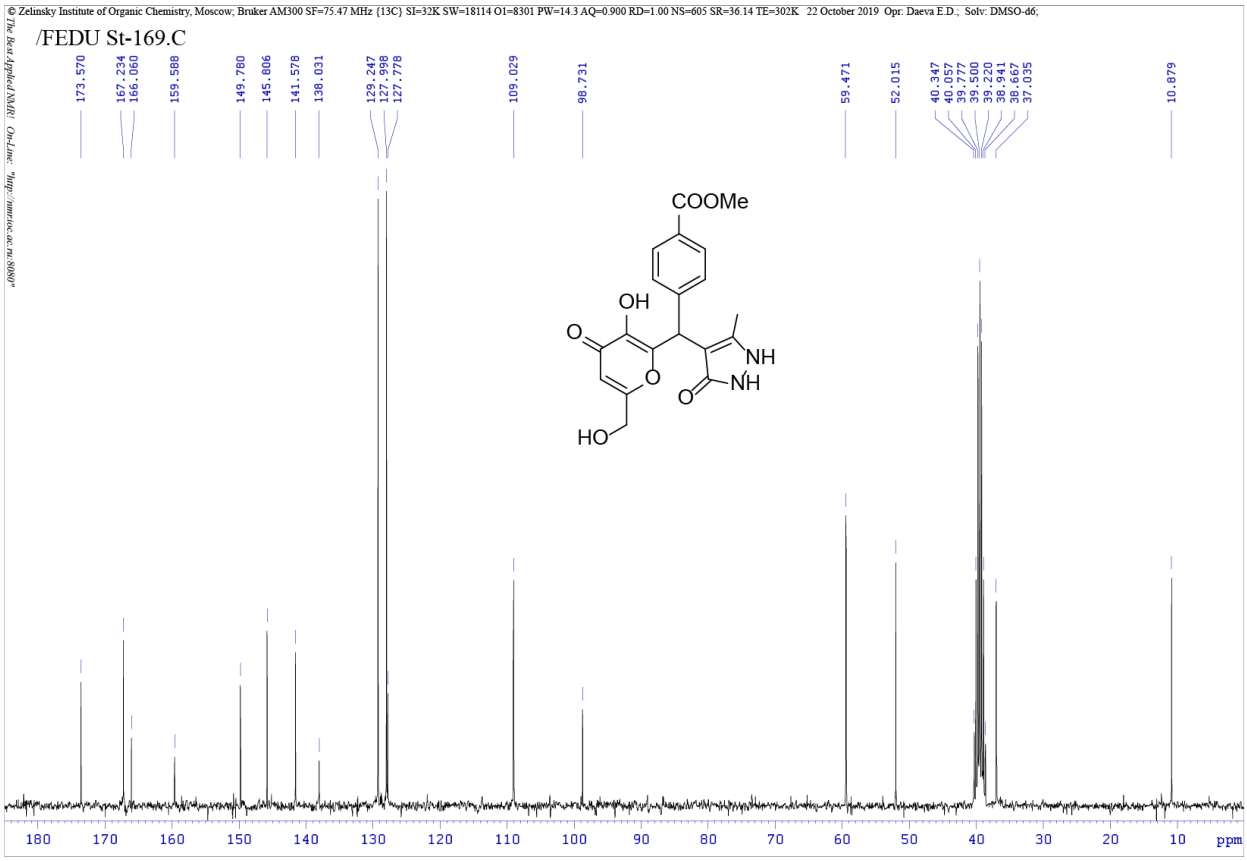


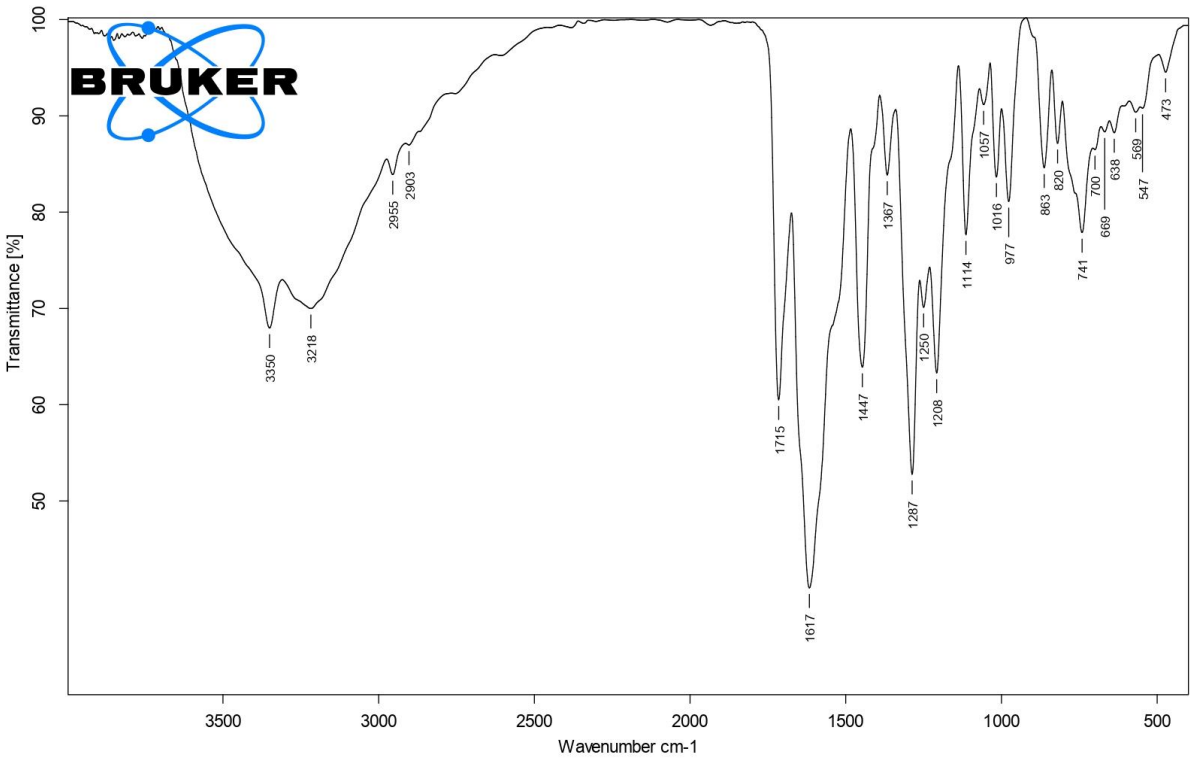
No.	m/z	RI(%)	DI
1	29.000	100.000	100.000
2	77.000	40.894	40.894
3	109.000	48.285	48.285
4	128.000	39.494	39.494
5	185.000	19.612	19.612
6	214.000	5.321	5.321
7	231.000	27.143	27.143
8	276.000	5.801	5.801
9	373.000	9.501	9.501

No.	m/z	TIC(%)
1	29.000	8.916
2	77.000	3.646
3	109.000	4.305
4	128.000	3.521
5	185.000	1.749
6	214.000	0.474
7	231.000	2.420
8	276.000	0.517
9	373.000	0.847

Methyl 4-((3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)methyl)benzoate (3i)







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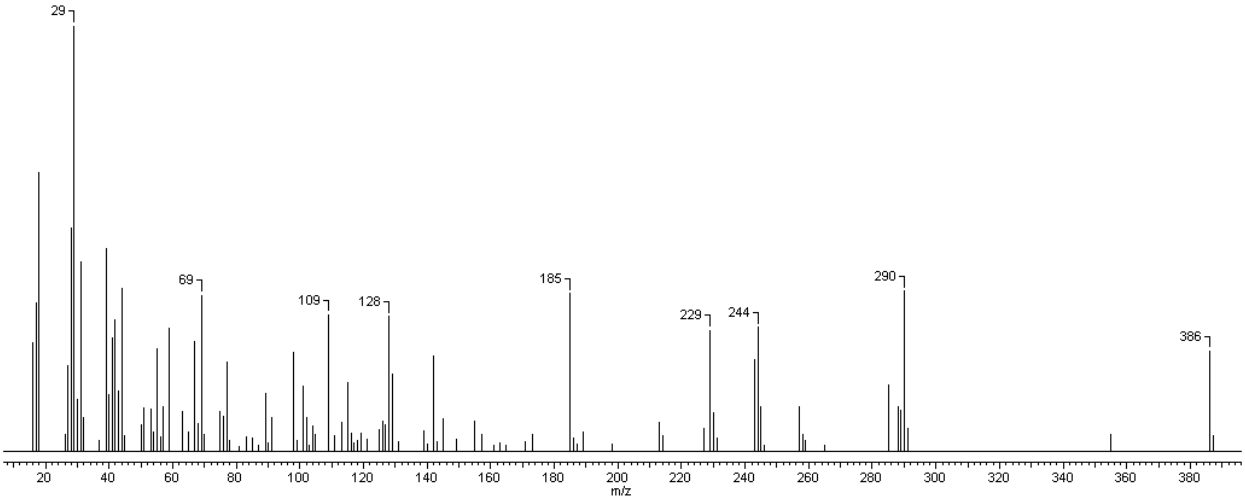
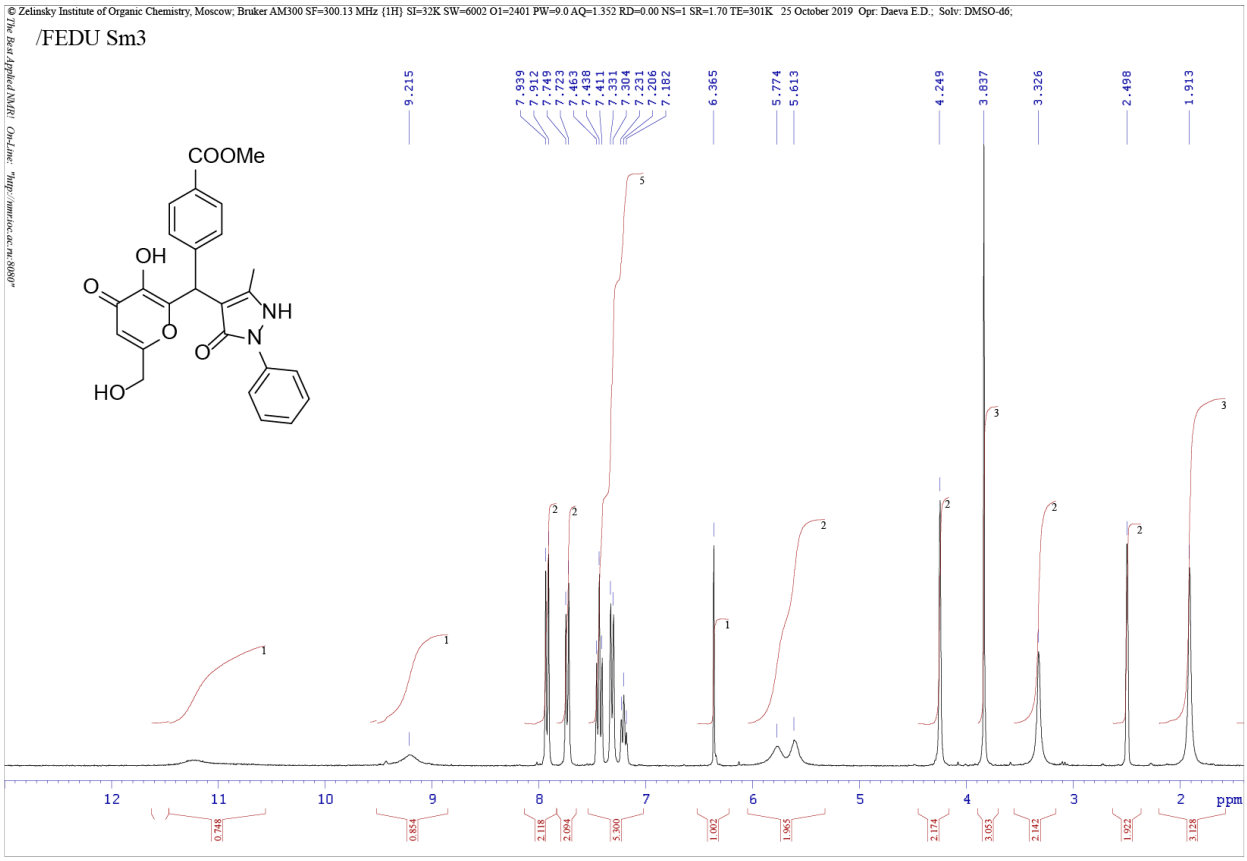
Count	105	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-169	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	1365.06				

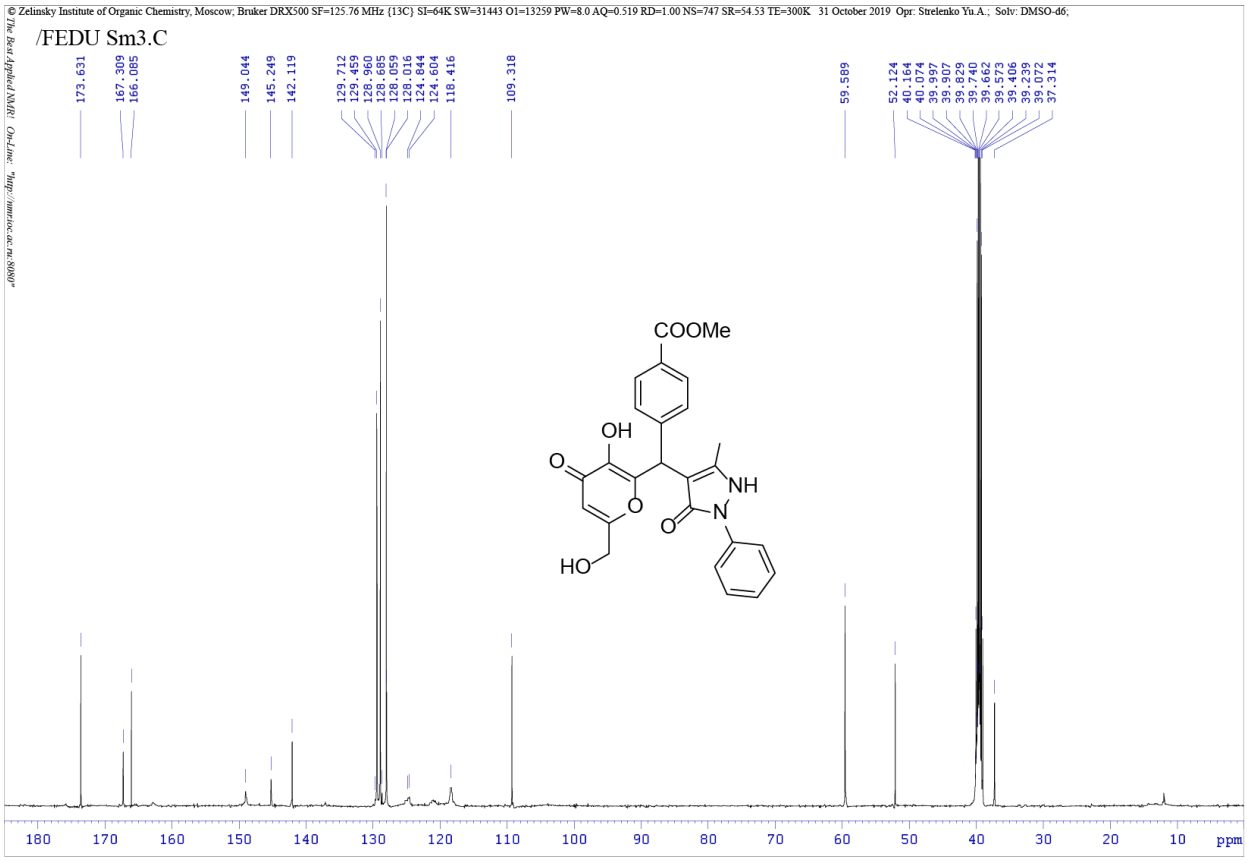


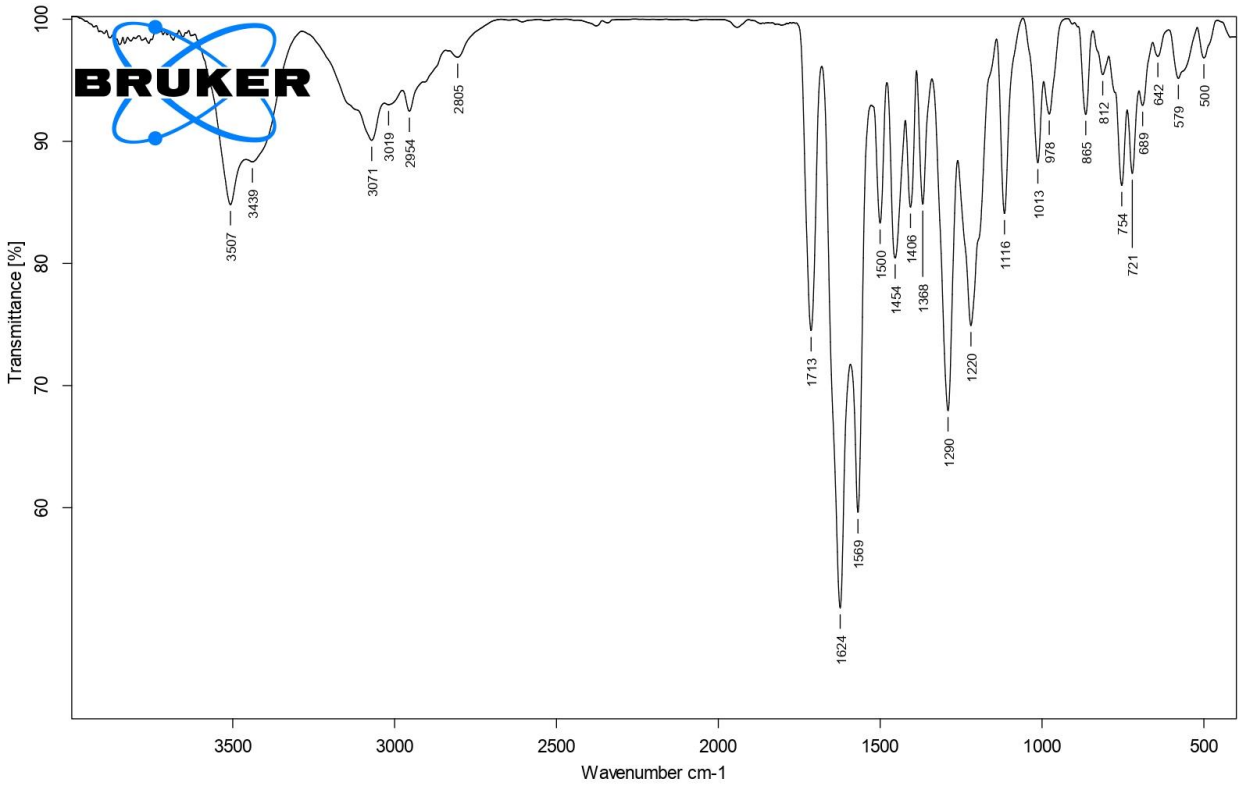
No.	m/z	RI(%)	DI
1	29.000	100.000	100.000
2	69.000	36.694	36.694
3	109.000	32.093	32.093
4	128.000	31.733	31.733
5	185.000	37.094	37.094
6	229.000	28.443	28.443
7	244.000	29.123	29.123
8	290.000	37.644	37.644
9	386.000	23.572	23.572

No.	m/z	TIC(%)
1	29.000	7.326
2	69.000	2.688
3	109.000	2.351
4	128.000	2.325
5	185.000	2.717
6	229.000	2.084
7	244.000	2.133
8	290.000	2.758
9	386.000	1.727

Methyl 4-((3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(5-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)methyl)benzoate (3j)



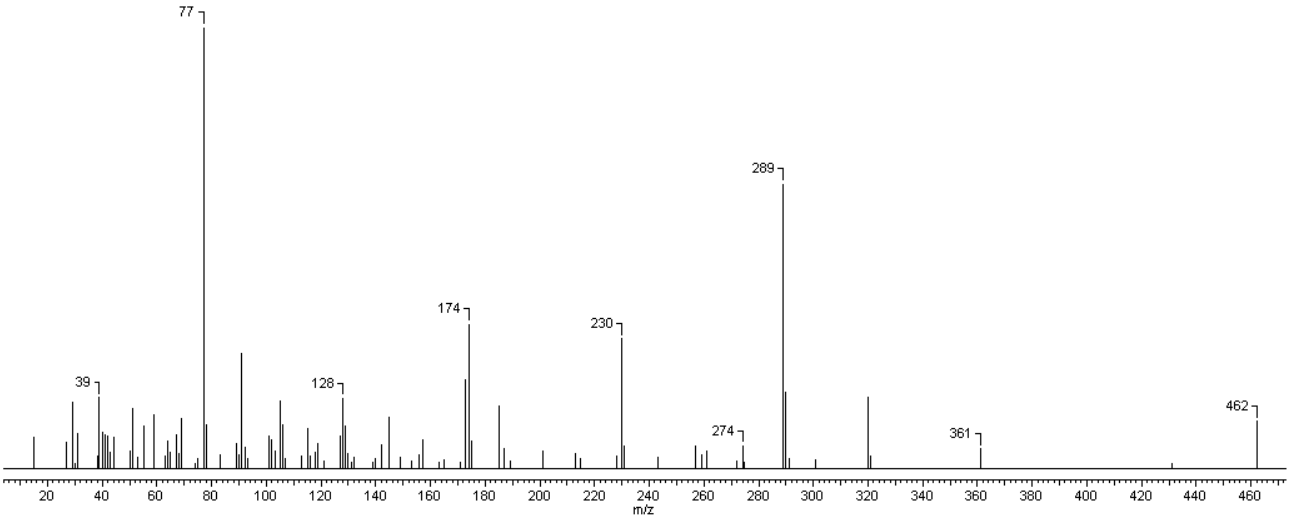




D:\IrB\Рыжкова Sm3.0 Рыжкова Sm3 KBr прессовка		13.11.2019

14 Nov 2019

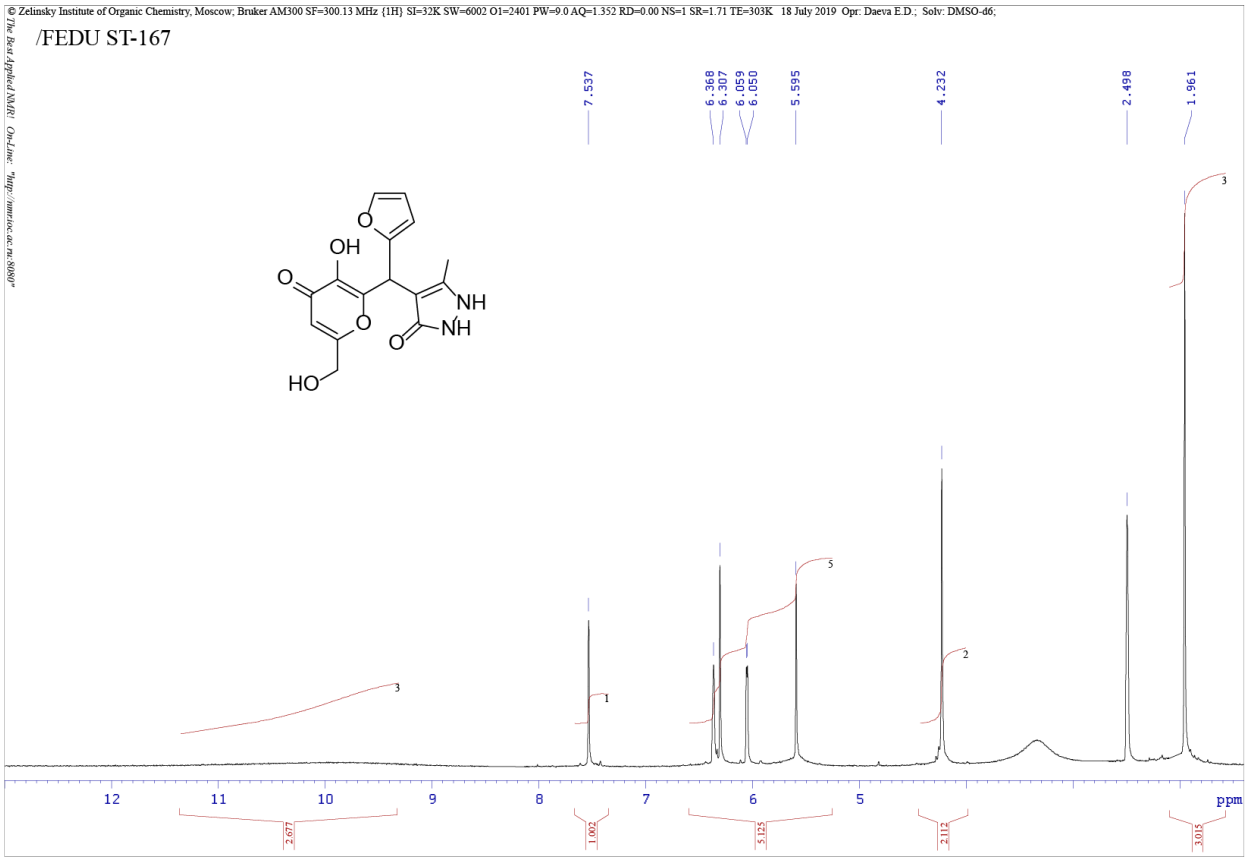
Count	90	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	SM-3	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	745.77				

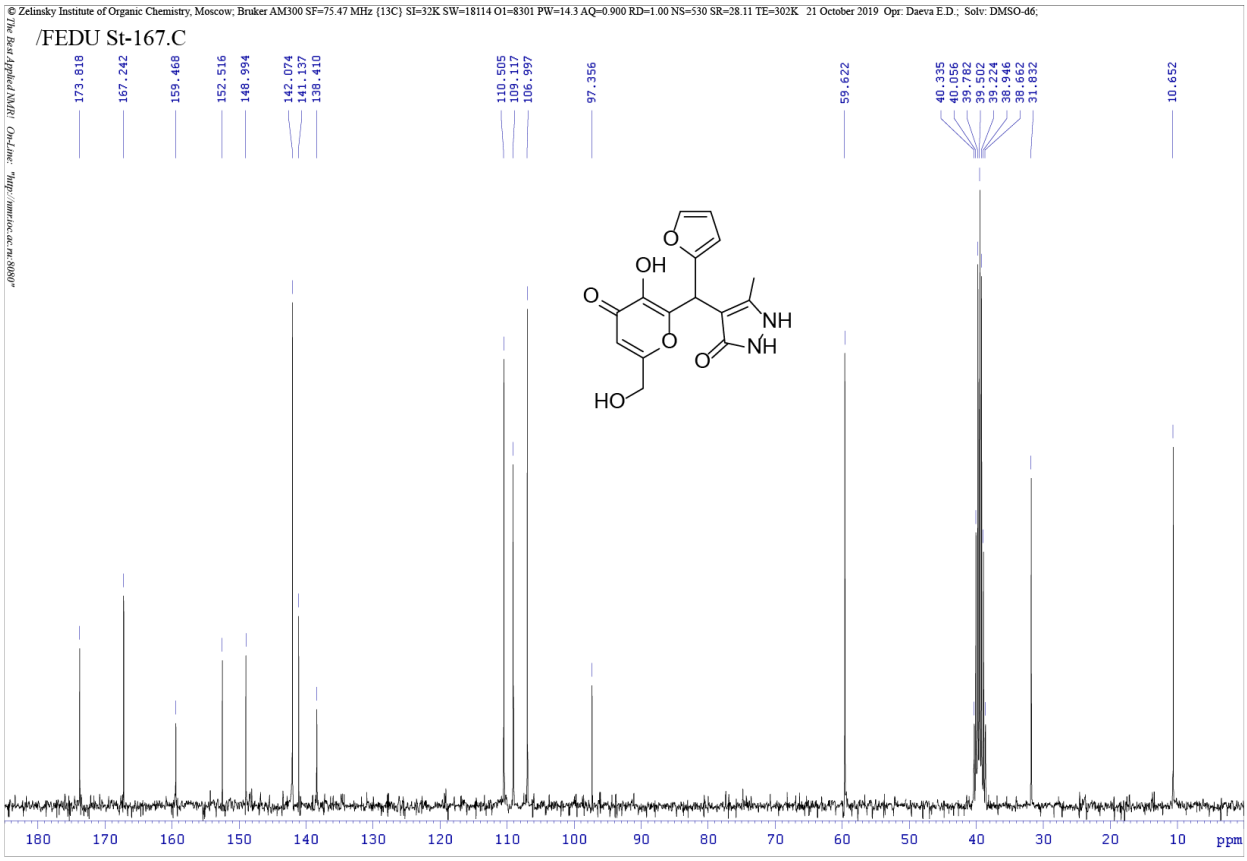


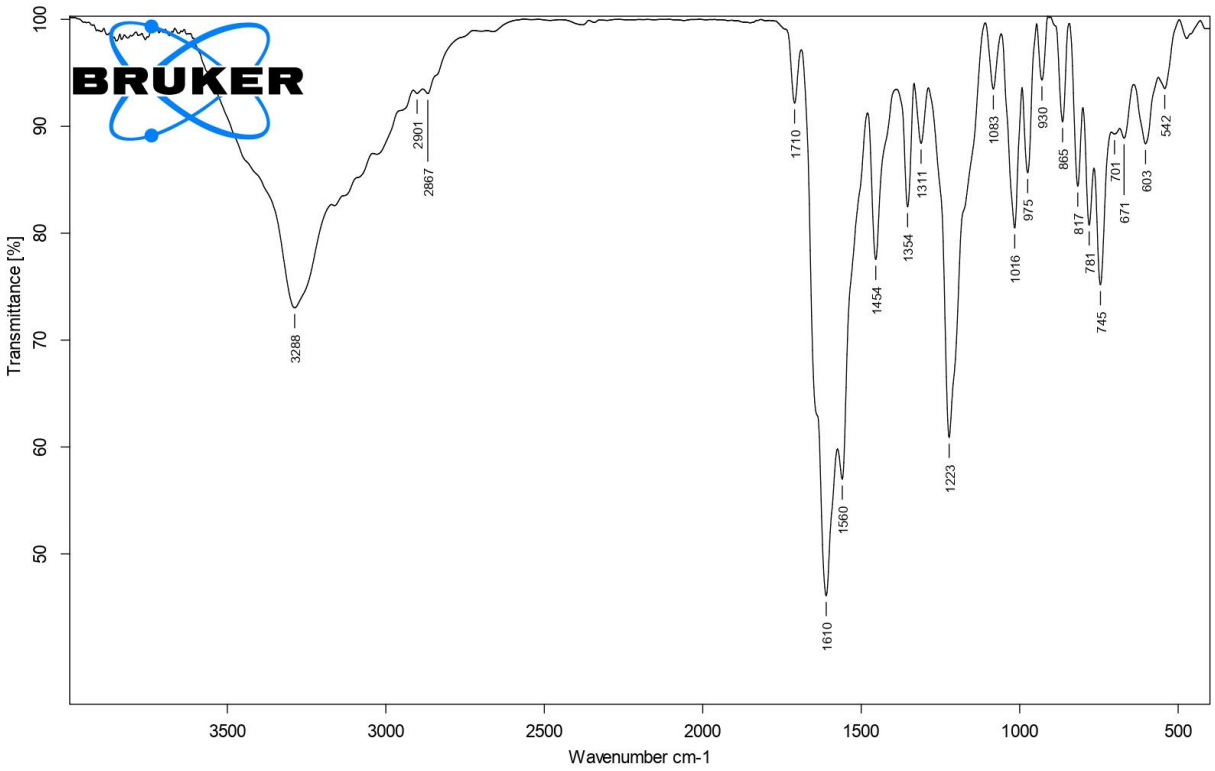
No.	*m/z*	RI(%)	DI
1	39.000	16.072	16.072
2	77.000	100.000	100.000
3	128.000	15.882	15.882
4	174.000	32.683	32.683
5	230.000	29.363	29.363
6	274.000	5.141	5.141
7	289.000	64.466	64.466
8	361.000	4.500	4.500
9	462.000	10.681	10.681

No.	*m/z*	TIC(%)
1	39.000	2.155
2	77.000	13.409
3	128.000	2.130
4	174.000	4.382
5	230.000	3.937
6	274.000	0.689
7	289.000	8.644
8	361.000	0.603
9	462.000	1.432

4-(Furan-2-yl(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3k)







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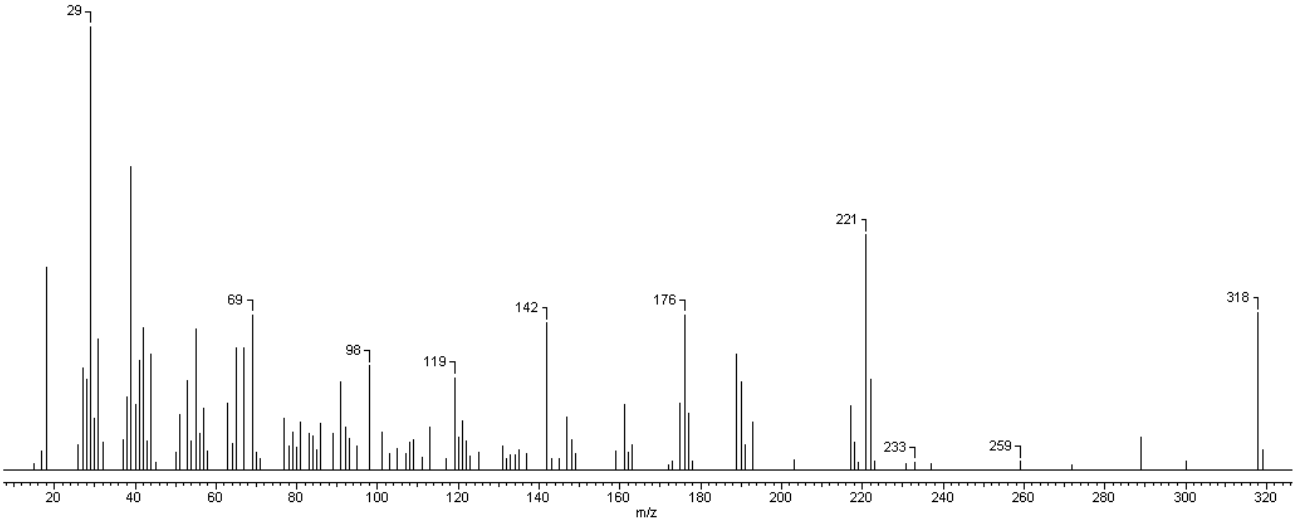
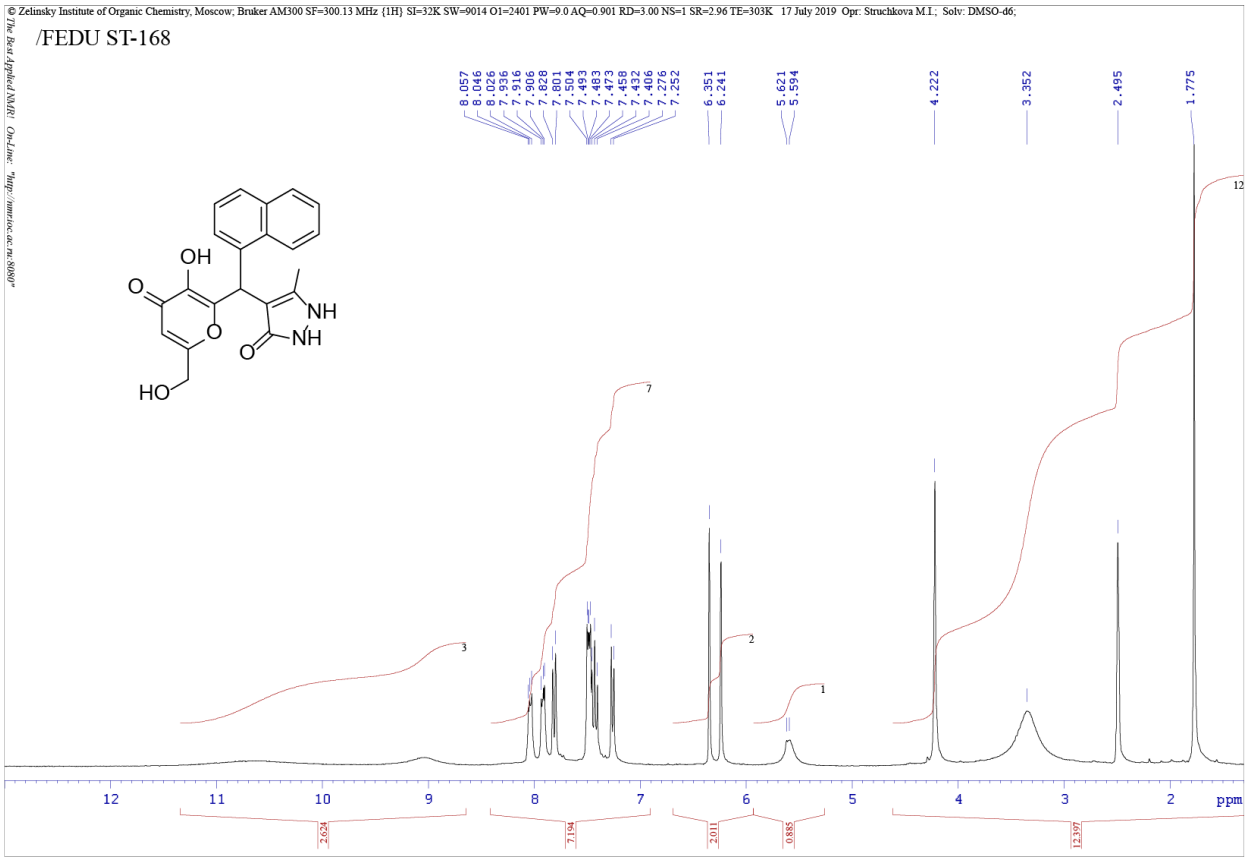
Count	106	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38		
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC		
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-167	***Owner***	Copyright(C) by Victor (2019)
Spectrum Title	MASS SPECTRUM	***TIC***	1320.95				

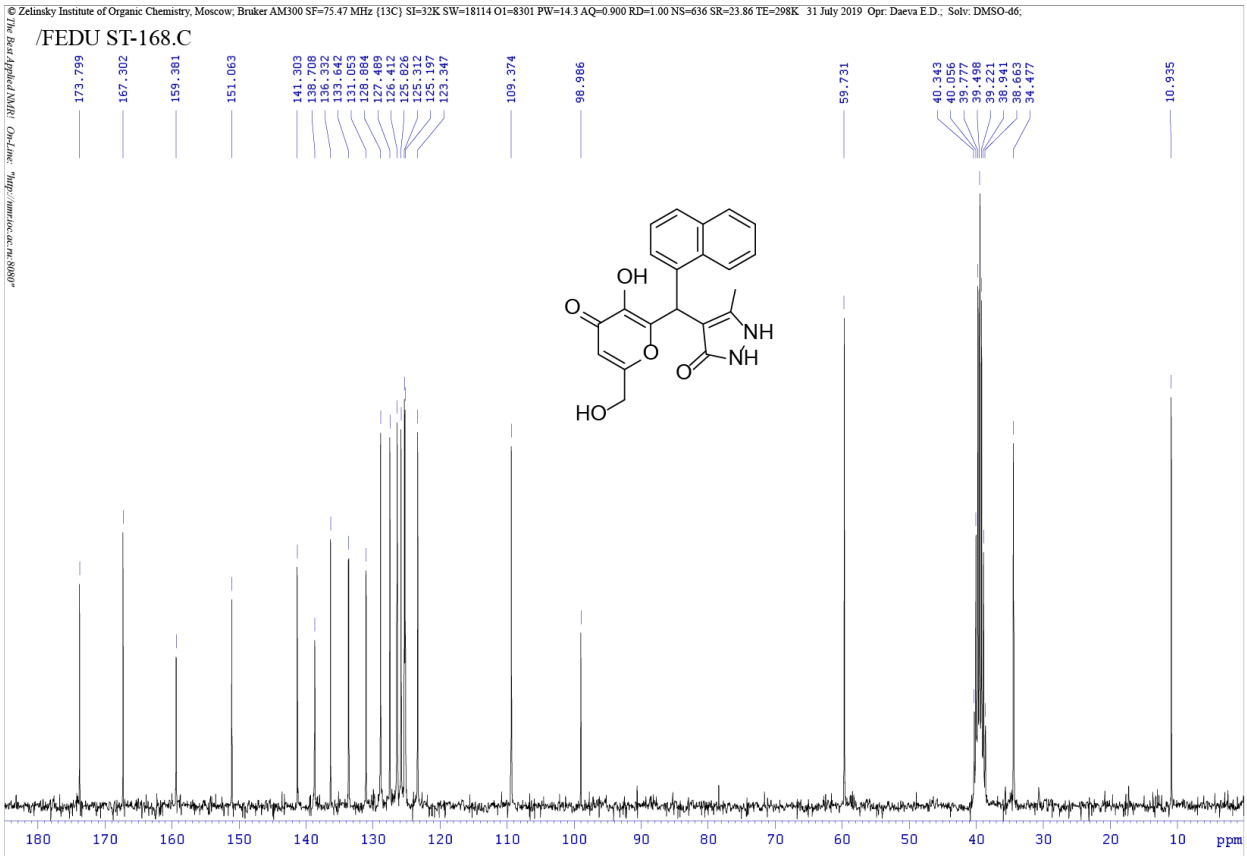


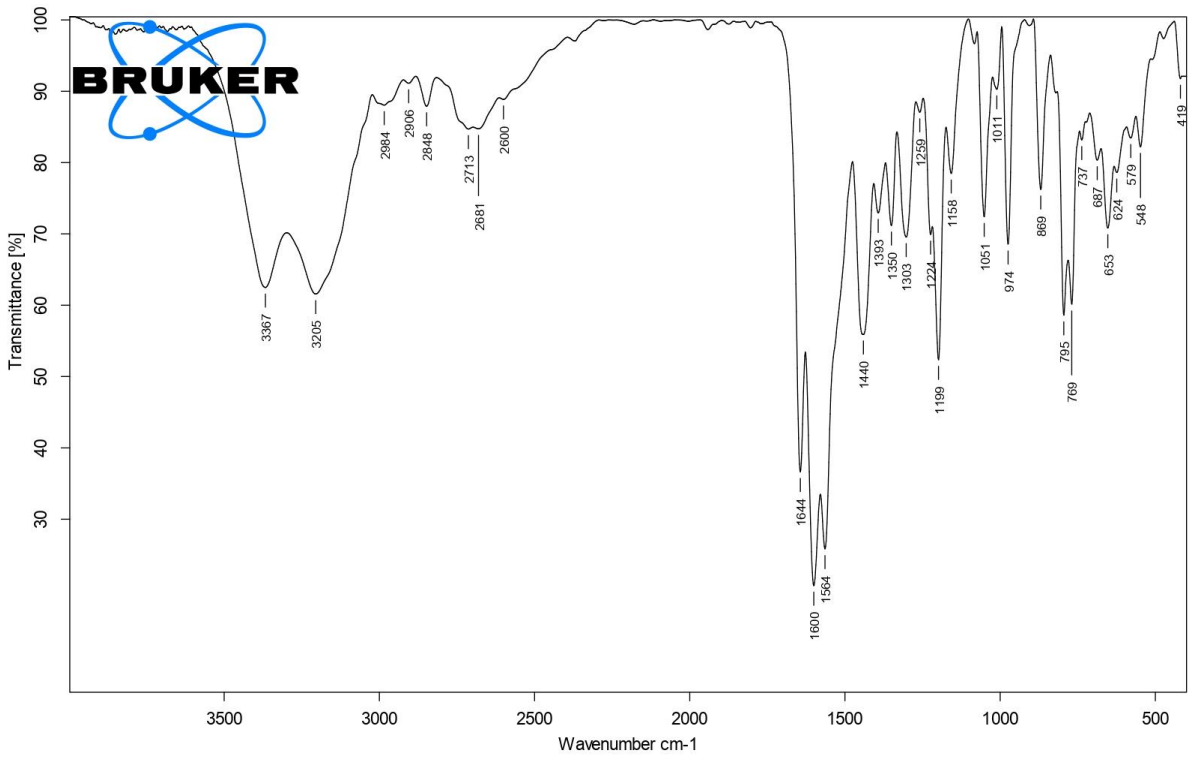
No.	*m/z*	RI(%)	DI
1	29.000	100.000	100.000
2	69.000	35.004	35.004
3	98.000	23.522	23.522
4	119.000	20.892	20.892
5	142.000	33.243	33.243
6	176.000	34.983	34.983
7	221.000	53.065	53.065
8	233.000	1.820	1.820
9	259.000	2.060	2.060
10	318.000	35.514	35.514

No.	*m/z*	TIC(%)
1	29.000	7.570
2	69.000	2.650
3	98.000	1.781
4	119.000	1.582
5	142.000	2.517
6	176.000	2.648
7	221.000	4.017
8	233.000	0.138
9	259.000	0.156
10	318.000	2.688

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(naphthalen-1-yl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (3l)







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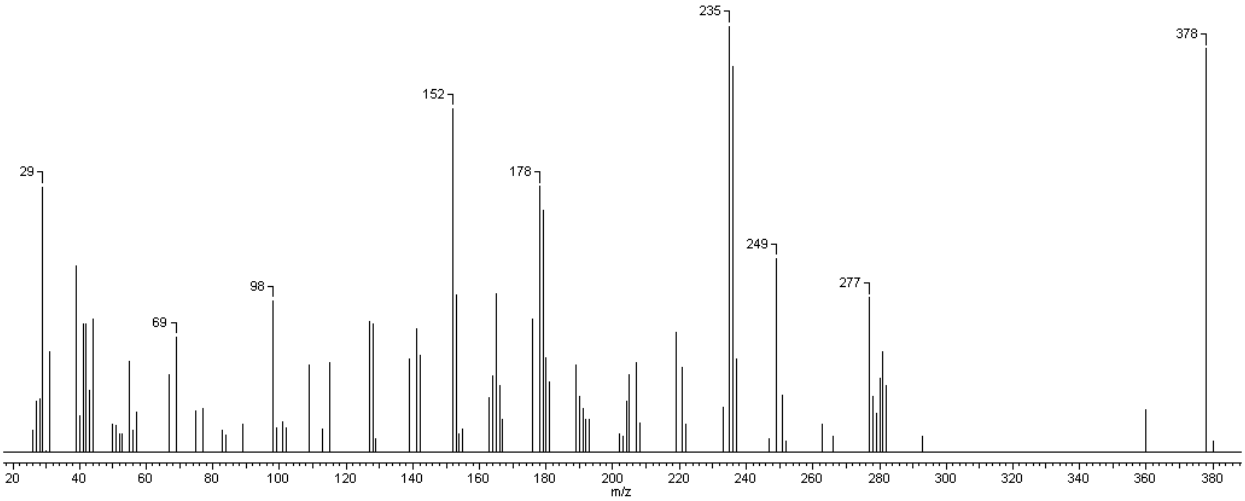
Count	87	***Data Type***	MASS SPECTRUM	***Date***	11 Nov 2019 12:57:38
Date Stamp	11 Nov 1919 13:31:07			***File Name***	C:\Users\Yuliya\Downloads\ms13.JC
Inlet Model	DIRECT	***Instrumental Parameters***	LOW RESOLUTION	***Origin***	ST-168
Spectrum Title	MASS SPECTRUM	***TIC***	1756.91		



No.	m/z	RI(%)	DI
1	29.000	62.196	62.196
2	69.000	27.023	27.023
3	98.000	35.474	35.474
4	152.000	80.498	80.498
5	178.000	62.266	62.266
6	235.000	100.000	100.000
7	249.000	45.455	45.455
8	277.000	36.134	36.134
9	378.000	94.629	94.629

No.	m/z	TIC(%)
1	29.000	3.540
2	69.000	1.538
3	98.000	2.019
4	152.000	4.582
5	178.000	3.544
6	235.000	5.692
7	249.000	2.587
8	277.000	2.057
9	378.000	5.386

X-Ray data for 3a

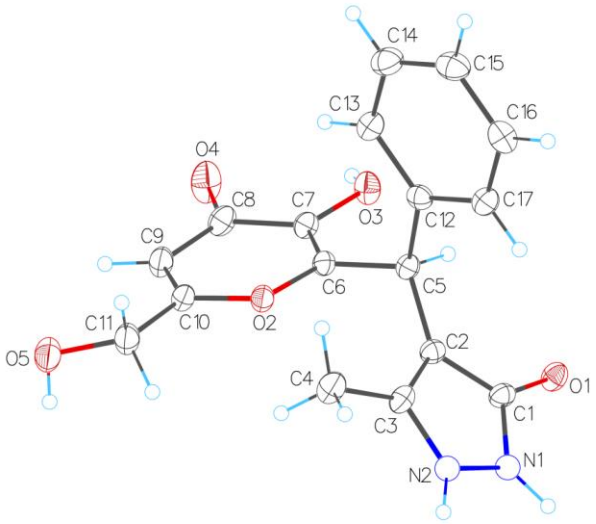


Fig. 1. Molecular structure of **3a** in crystal. Atoms are represented by spheres indicating their isotropic thermal displacements (p = 50%).

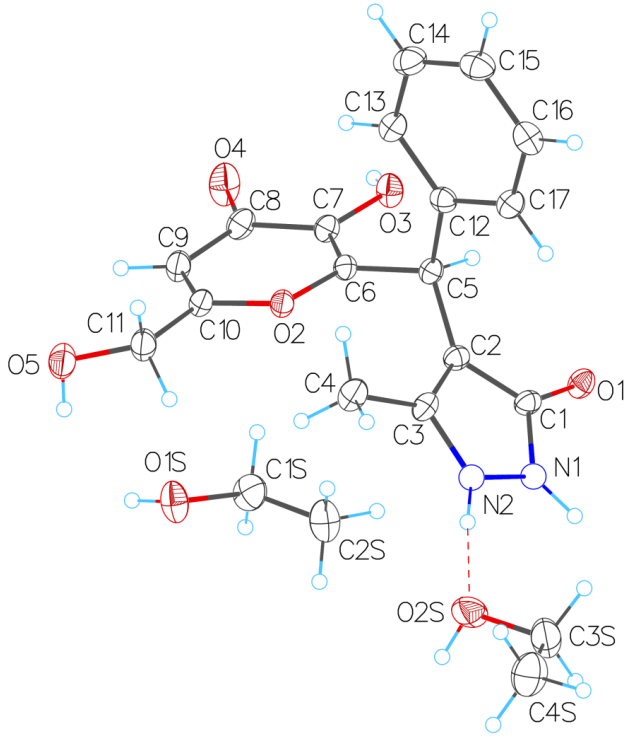


Fig. 2. The independent part of the unit cell of **3a***2EtOH in crystal. Atoms are represented by spheres indicating their isotropic thermal displacements (p = 50%).

Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{21}H_{28}N_2O_7$
Formula weight	420.45
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	7.4689(19)
b/Å	8.235(2)
c/Å	17.198(4)
α/°	79.683(6)
β/°	89.451(6)
γ/°	83.594(6)
Volume/Å^3	1034.2(5)
Z	2
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	0.102
F(000)	448.0
Crystal size/mm^3	0.35 × 0.26 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.82 to 56.56
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-22 \leq l \leq 22$
Reflections collected	12152
Independent reflections	5103 [R_{int} = 0.0852, R_{sigma} = 0.1188]
Data/restraints/parameters	5103/6/292
Goodness-of-fit on F^2	0.936
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1013
Final R indexes [all data]	R_1 = 0.1230, wR_2 = 0.1270
Largest diff. peak/hole / e Å^{-3}	0.26/-0.31

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	4436(2)	3334(2)	1535.8(9)	18.5(4)
O1	6743(2)	524.2(19)	4205.4(9)	20.3(4)
O3	9090(2)	1701(2)	1741.8(10)	22.4(4)
O2S	-829(2)	2375(3)	4544.3(11)	33.9(5)
O5	1577(3)	3344(2)	-122.1(10)	30.5(5)
N2	2378(3)	2350(3)	3914.0(12)	22.0(5)
O4	8344(2)	1390(2)	221.3(10)	33.3(5)
C7	7426(3)	2139(3)	1423.5(13)	17.8(5)
C5	6351(3)	3159(3)	2670.4(12)	16.1(5)
N1	3685(3)	1231(3)	4314.7(11)	20.4(5)
C6	6119(3)	2808(3)	1854.0(13)	16.4(5)
C11	2140(3)	3829(3)	575.2(13)	23.7(6)
C13	7362(3)	5932(3)	1983.9(14)	21.4(6)
C1	5269(3)	1377(3)	3930.9(13)	18.0(5)
C9	5281(3)	2462(3)	337.8(14)	21.7(6)
C12	6736(3)	4959(3)	2657.5(13)	17.6(5)
C16	7068(3)	7167(3)	3379.9(15)	24.8(6)
C3	3092(3)	3183(3)	3269.6(13)	19.8(5)
C8	7095(3)	1948(3)	622.5(14)	22.0(6)
C15	7704(3)	8119(3)	2705.0(15)	26.2(6)
C10	4050(3)	3140(3)	794.1(13)	19.1(5)
C4	1888(3)	4478(3)	2734.7(14)	24.9(6)
C17	6595(3)	5604(3)	3349.3(14)	20.9(5)
C3S	-1023(4)	2514(4)	5356.6(15)	35.6(7)
C2	4899(3)	2608(3)	3240.7(13)	16.8(5)
C14	7838(3)	7493(3)	2010.8(15)	26.3(6)
C4S	-2751(4)	3498(4)	5504.9(16)	39.8(8)
O1S	1655(2)	-91(2)	1118.2(10)	28.8(5)
C1S	3073(4)	-984(3)	1627.1(15)	30.8(7)
C2S	2715(4)	-725(4)	2452.9(15)	36.7(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	16.4(9)	23.9(9)	14.4(8)	-2.2(7)	-0.5(7)	-0.8(7)
O1	20.1(10)	20.2(9)	18.2(9)	0.3(7)	0.5(7)	2.1(7)
O3	17.6(10)	28.8(11)	19.9(9)	-6.7(8)	-1.1(7)	5.5(8)
O2S	22.7(11)	51.5(14)	31.6(11)	-14.4(9)	8.1(9)	-11.7(9)
O5	28.6(11)	40.9(13)	20.3(10)	-1.4(9)	-3.8(8)	-3.3(9)
N2	15.6(12)	25.8(12)	21.8(11)	2.3(9)	2.3(9)	-0.2(9)
O4	24.4(11)	51.3(13)	23.6(10)	-14.5(9)	1.4(8)	11.1(9)
C7	19.1(13)	17.1(13)	16.5(12)	-1.5(10)	-0.5(10)	-0.5(10)
C5	17.0(13)	16.3(12)	14.7(11)	-2.6(9)	0.7(9)	-0.3(10)
N1	18.1(11)	21.9(12)	18.1(10)	3.1(9)	2.8(9)	-0.3(9)
C6	15.3(13)	17.4(12)	15.3(12)	-0.3(9)	-1.6(9)	-1.1(10)
C11	22.6(15)	31.1(15)	17.0(13)	-4.6(11)	-1.5(10)	-1.1(11)
C13	23.0(14)	22.2(14)	18.4(12)	-2.2(10)	1.3(10)	-1.2(11)
C1	19.3(14)	19.4(13)	16.1(12)	-4.1(10)	4.2(10)	-3.8(10)
C9	22.7(14)	26.4(14)	15.5(12)	-3.3(10)	-1.4(10)	-0.9(11)
C12	13.4(13)	18.2(13)	20.7(12)	-2.9(10)	-0.6(10)	-0.6(10)
C16	22.0(15)	25.9(15)	27.5(14)	-8.6(11)	-3.1(11)	-0.8(11)
C3	24.6(15)	17.8(13)	15.7(12)	0.2(10)	0.9(10)	-1.6(10)
C8	24.7(15)	23.9(14)	17.0(12)	-5(1)	4.5(11)	0.3(11)
C15	23.3(15)	18.8(14)	35.7(15)	-2.5(11)	-0.9(12)	-2.6(11)
C10	22.1(14)	20.2(13)	14.3(12)	-0.6(10)	-1.2(10)	-3.3(10)
C4	21.2(14)	29.3(15)	20.8(13)	-0.1(11)	2.4(10)	3.9(11)
C17	21.8(14)	21.7(14)	18.7(12)	-3.3(10)	1.8(10)	-1.9(11)
C3S	28.7(17)	52(2)	26.9(15)	-10.5(14)	-3.8(12)	-1.9(14)
C2	17.3(13)	17.3(13)	16.1(12)	-3.5(9)	2.3(10)	-2.2(10)
C14	25.9(15)	22.5(14)	28.4(14)	2.1(11)	1.2(11)	-3.9(11)
C4S	46(2)	44.9(19)	30.2(16)	-14.0(14)	4.1(14)	1.3(15)
O1S	24.7(11)	36.8(11)	25(1)	-13.4(9)	-5.6(8)	9.1(8)
C1S	25.5(16)	29.5(16)	32.8(15)	1.3(12)	-2.6(12)	5.3(12)
C2S	36.4(18)	42.5(18)	30.2(16)	-6.6(13)	-9.3(13)	1.0(14)

Table 4 Bond Lengths for a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C6	1.369(3)	C11	C10	1.501(3)
O2	C10	1.351(3)	C13	C12	1.394(3)
O1	C1	1.283(3)	C13	C14	1.381(3)
O3	C7	1.348(3)	C1	C2	1.423(3)
O2S	C3S	1.427(3)	C9	C8	1.437(3)
O5	C11	1.411(3)	C9	C10	1.342(3)
N2	N1	1.364(3)	C12	C17	1.386(3)
N2	C3	1.334(3)	C16	C15	1.391(3)
O4	C8	1.250(3)	C16	C17	1.382(3)
C7	C6	1.347(3)	C3	C4	1.498(3)
C7	C8	1.441(3)	C3	C2	1.383(3)
C5	C6	1.499(3)	C15	C14	1.381(4)
C5	C12	1.537(3)	C3S	C4S	1.490(4)
C5	C2	1.508(3)	O1S	C1S	1.429(3)
N1	C1	1.356(3)	C1S	C2S	1.491(4)

Table 5 Bond Angles for a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	C6	120.31(18)	C17	C12	C13	118.3(2)
C3	N2	N1	109.1(2)	C17	C16	C15	119.7(2)
O3	C7	C8	119.6(2)	N2	C3	C4	118.3(2)
C6	C7	O3	119.0(2)	N2	C3	C2	108.9(2)
C6	C7	C8	121.3(2)	C2	C3	C4	132.8(2)
C6	C5	C12	111.94(18)	O4	C8	C7	120.4(2)
C6	C5	C2	114.53(19)	O4	C8	C9	124.4(2)
C2	C5	C12	113.77(19)	C9	C8	C7	115.2(2)
C1	N1	N2	109.11(18)	C14	C15	C16	119.4(2)
O2	C6	C5	113.85(19)	O2	C10	C11	110.4(2)
C7	C6	O2	120.5(2)	C9	C10	O2	122.2(2)
C7	C6	C5	125.6(2)	C9	C10	C11	127.3(2)
O5	C11	C10	111.7(2)	C16	C17	C12	121.4(2)
C14	C13	C12	120.6(2)	O2S	C3S	C4S	112.0(2)
O1	C1	N1	121.9(2)	C1	C2	C5	122.4(2)
O1	C1	C2	131.5(2)	C3	C2	C5	131.2(2)
N1	C1	C2	106.6(2)	C3	C2	C1	106.2(2)
C10	C9	C8	120.4(2)	C13	C14	C15	120.6(2)
C13	C12	C5	122.0(2)	O1S	C1S	C2S	109.4(2)
C17	C12	C5	119.5(2)				

Table 6 Torsion Angles for a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C2	C5	-0.5(4)	C12	C5	C6	O2	-81.3(2)
O1	C1	C2	C3	-176.2(3)	C12	C5	C6	C7	94.5(3)
O3	C7	C6	O2	177.1(2)	C12	C5	C2	C1	-112.3(2)
O3	C7	C6	C5	1.5(4)	C12	C5	C2	C3	62.3(3)
O3	C7	C8	O4	-0.5(4)	C12	C13	C14	C15	0.0(4)
O3	C7	C8	C9	-179.5(2)	C16	C15	C14	C13	-0.5(4)
O5	C11	C10	O2	−167.70(18)	C3	N2	N1	C1	1.5(3)
O5	C11	C10	C9	14.3(4)	C8	C7	C6	O2	-0.3(3)
N2	N1	C1	O1	176.4(2)	C8	C7	C6	C5	-175.9(2)
N2	N1	C1	C2	-2.3(3)	C8	C9	C10	O2	-1.5(4)
N2	C3	C2	C5	-176.7(2)	C8	C9	C10	C11	176.3(2)
N2	C3	C2	C1	-1.5(3)	C15	C16	C17	C12	-0.1(4)
C5	C12	C17	C16	174.7(2)	C10	O2	C6	C7	2.1(3)
N1	N2	C3	C4	179.6(2)	C10	O2	C6	C5	178.16(19)
N1	N2	C3	C2	0.1(3)	C10	C9	C8	O4	-176.0(2)
N1	C1	C2	C5	178.1(2)	C10	C9	C8	C7	3.0(3)
N1	C1	C2	C3	2.3(3)	C4	C3	C2	C5	3.9(5)
C6	O2	C10	C11	−179.26(19)	C4	C3	C2	C1	179.1(3)
C6	O2	C10	C9	-1.1(3)	C17	C16	C15	C14	0.5(4)
C6	C7	C8	O4	176.9(2)	C2	C5	C6	O2	50.1(3)
C6	C7	C8	C9	-2.1(3)	C2	C5	C6	C7	-134.1(2)
C6	C5	C12	C13	-19.2(3)	C2	C5	C12	C13	-151.0(2)
C6	C5	C12	C17	165.9(2)	C2	C5	C12	C17	34.1(3)
C6	C5	C2	C1	117.2(2)	C14	C13	C12	C5	-174.5(2)
C6	C5	C2	C3	-68.3(3)	C14	C13	C12	C17	0.4(4)
C13	C12	C17	C16	-0.4(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for a.

Atom	*x*	*y*	*z*	U(eq)
H5A	7480	2457	2882	19
H11A	1338	3434	1014	28
H11B	2034	5056	498	28
H13	7461	5517	1502	26
H9	4952	2322	-176	26
H16	6960	7588	3860	30
H15	8042	9191	2721	31
H4A	1322	3961	2344	37
H4B	2602	5334	2463	37
H4C	953	4986	3048	37
H17	6164	4959	3812	25
H3SA	-5	3053	5521	43
H3SB	-975	1389	5682	43
H14	8263	8143	1547	32
H4SA	-2802	4614	5186	60
H4SB	-2824	3578	6066	60
H4SC	-3764	2947	5360	60
H1SA	4239	-589	1450	37
H1SB	3144	-2183	1605	37
H2SA	2579	467	2466	55
H2SB	3725	-1277	2796	55
H2SC	1606	-1194	2639	55
H2	1270(30)	2390(30)	4097(15)	44
H3	9730(40)	1110(30)	1470(15)	44
H1	3470(40)	660(30)	4797(11)	44
H1S	1660(40)	-430(30)	695(12)	44
H2S	-1590(30)	1750(30)	4439(17)	44
H5	1100(40)	2500(30)	22(17)	44

Experimental

Single crystals of $C_{21}H_{28}N_2O_7$ **[3a]** were grown from ethanol. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the XS [2] structure solution program using Direct Methods and refined with the XL [2] refinement package using Least Squares minimisation.

Crystal structure determination of 3a

Crystal Data for $C_{21}H_{28}N_2O_7$ (M =420.45 g/mol): triclinic, space group P-1 (no. 2), a = 7.4689(19) Å, b = 8.235(2) Å, c = 17.198(4) Å, α = 79.683(6)°, β = 89.451(6)°, γ = 83.594(6)°, V = 1034.2(5) Å^3, Z = 2, T = 120 K, μ(MoKα) = 0.102 mm^{-1}, *Dcalc* = 1.350 g/cm^3, 12152 reflections measured (4.82° ≤ 2Θ ≤ 56.56°), 5103 unique (R_{int} = 0.0852, R_{sigma} = 0.1188) which were used in all calculations. The final R_1 was 0.0572 (>2sigma(I)) and wR_2 was 0.1270 (all data). CCDC 1965816 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

References

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