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PASE synthesis of 1-azolyl-1*H*-1,2,4-triazoles by the reaction of diazoazoles with ethyl isocyanoacetate

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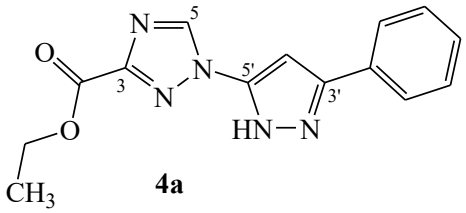
General information

Ethyl isocyanoacetate (**1**) was obtained as previously described.[S1] 5-Aryl-3-diazo-3*H*-pyrazoles[S2] (**2a–d**), ethyl 5-diazopyrazole-4-carboxylate[S3] (**2e**), ethyl 5-diazoimiazole-4-carboxylate[S4] (**3a**), 5-diazoimidazole-4-(*N*-substituted)carboxamides[S4] (**3b–d**,**6d**) were prepared according to a modified procedure by diazotization of the corresponding amines in dilute H_2SO_4 or HCl with $NaNO_2$ at -5°C. 5-Diazopyrazole-4-carboxamides (**6a,b**) and 5-diazoimidazole-4-carboxamide (**6c**) are commercially available.
IR spectra were recorded on a Bruker ALPHA FTIR spectrometer with a ZnSe ATR accessory for samples in the form of powders. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AVANCE II (400 and 100 MHz, respectively) spectrometer, using TMS as internal standard. Mass spectra were obtained on a Shimadzu GCMS-QP2010 instrument (EI ionization, 70 eV). Elemental analysis was performed on a PerkinElmer 2400 II CHNS-analyzer. Melting points were determined on a Stuart SMP-10 apparatus.

Synthesis of ethyl 1-azolyl-1*H*-1,2,4-triazole-3-carboxylates 4a–e and 5a–d (general procedure)

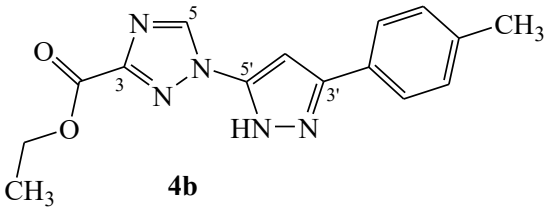
To a stirred mixture of ethyl isocyanoacetate **1** (60 μl, 0.55 mmol)[S1] and sodium acetate (45 mg, 0.55 mmol) in acetonitrile (3 ml) or acetone (3 ml), a cold solution of the corresponding 5-diazopyrazole **2a–e** (0.5 mmol)[S2,S3] in acetonitrile (3 ml) or 5-diazoimidazole **3a–d** (0.5 mmol)[S4,S5] in acetone (3 ml) was added at 0°C dropwise within 5 min. The temperature of the reaction mixture was raised to ambient, and the mixture was allowed to stand under these conditions until disappearing of the starting diazoazole (3–4 days, TLC control). Activated charcoal was added, and the reaction mixture was stirred for 15 min, and filtered. The filtrate was concentrated under reduced pressure at a temperature below 40 °C. The residue was treated with diethyl ether or hexane, the precipitate formed was collected by filtration and purified by flash column chromatography on silica gel by eluting with EtOAc – CH_2Cl_2.



4a

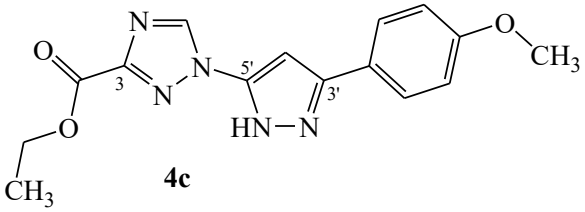
Ethyl 1-(3-phenyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4a**). Yield 105 mg (74 %), orange solid, mp 162–164 °C. IR spectrum, ν, cm^{-1}: 507, 560, 574, 598, 647, 670, 691, 727, 756, 797, 845, 924, 946, 960, 1024, 1057, 1075, 1094, 1115, 1192, 1227, 1280, 1299, 1341, 1370, 1416, 1445, 1469, 1487, 1535, 1572, 1727, 2901, 2969, 3140, 3196, 3218, 3262. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 7.1, $OCH_2C\mathbf{H}_3$); 4.40 (2H, q, *J* = 7.1, $OC\mathbf{H}_2CH_3$); 6.99 (1H, s, H-4'); 7.80 (2H, d, *J* = 7.4, 2H, 2",6"-H); 7.46–7.43 (2H, m, 3",5"-H); 7.38–7.34 (1H, m, 4"-H); 9.04 (1H, s, H-5); 13.57 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 13.9 ($OCH_2\mathbf{C}H_3$); 60.7 ($O\mathbf{C}H_2CH_3$); 93.4 (C-4'); 95.5 (C-1"); 125.2 (C-3",5"); 128.3 (C-4"); 128.5 (C-2",6"); 142.3 (C-5); 144.1 (C-3'); 146.4 (C-5'); 154.4 (C-3); 158.8 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 283 (100, M^+), 255 (15, M-28), 238 (57, M-45), 211 (86, M-72), 184 (9, M-99), 170 (26, M-113), 156 (7, M-127),

142 (15), 128 (31), 116 (22), 102 (40), 89 (9), 77 (34), 70 (5). Found, %: C 59.53; H 4.74; N 24.34. $C_{14}H_{13}N_5O_2$. Calculated, %: C 59.36; H 4.63; N 24.72.



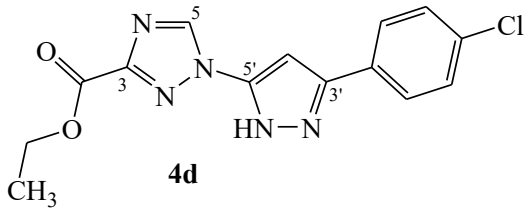
4b

Ethyl 1-[3-(*p*-tolyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4b**). Yield 120 mg (81 %), pale orange solid, mp 195–197 °C. IR spectrum, ν, cm^{-1}: 512, 621, 648, 669, 737, 780, 795, 821, 845, 891, 926, 946, 960, 1025, 1112, 1163, 1191, 1241, 1303, 1344, 1369, 1417, 1445, 1468, 1514, 1535, 1567, 1641, 1667, 1730, 2918, 2961, 3019, 3053, 3128, 3152, 3200. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 7.1, $OCH_2C\mathbf{H}_3$); 2.39 (3H, s, CH_3); 4.40 (2H, q, *J* = 7.1, $OC\mathbf{H}_2CH_3$); 6.91 (1H, s, H-4'); 7.25 (2H, d, *J* = 7.8, 3",5"-H); 7.67 (2H, d, *J* = 7.8, 2",6"-H); 9.04 (1H, s, H-5); 13.54 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 14.0 ($OCH_2\mathbf{C}H_3$); 20.8 (CH_3); 61.3 ($O\mathbf{C}H_2CH_3$); 93.7 (C-4'); 125.3 (C-3",5"); 125.6 (C-1"); 129.6 (C-2",6"); 138.5 (C-4"); 143.7 (C-5); 144.5 (C-3'); 146.3 (C-5'); 154.5 (C-3); 158.8 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 297 (100, M^+), 269 (8, M-28), 252 (40, M-45), 225 (68, M-72), 198 (7, M-99), 184 (13, M-113), 170 (5, M-127), 156 (13), 142 (14), 130 (13), 115 (32), 103 (6), 91 (13), 77 (5), 65 (7). Found, %: C 60.81; H 5.22; N 23.68. $C_{15}H_{15}N_5O_2$. Calculated, %: C 60.60; H 5.09; N 23.55.



4c

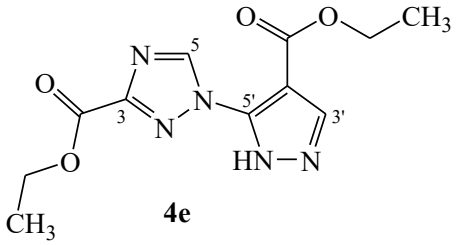
Ethyl 1-[3-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4c**). Yield 125 mg (80 %), pale yellow solid, mp 198–200 °C. IR spectrum, ν, cm^{-1}: 526, 551, 621, 649, 669, 739, 768, 795, 825, 895, 925, 949, 961, 1025, 1177, 1199, 1225, 1252, 1289, 1343, 1370, 1434, 1453, 1498, 1514, 1548, 1576, 1615, 1747, 2941, 2994, 3053, 3099, 3128, 3152, 3200. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 7.1, $OCH_2C\mathbf{H}_3$); 3.83 (3H, s, OCH_3); 4.40 (2H, q, *J* = 7.1, $OC\mathbf{H}_2CH_3$); 6.87 (1H, s, H-4'); 6.98 (2H, d, *J* = 8.8, 3",5"-H); 7.72 (2H, d, *J* = 8.8, 2",6"-H); 9.02 (1H, s, H-5); 13.55 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 15.1 ($OCH_2\mathbf{C}H_3$); 56.3 (OCH_3); 62.4 ($O\mathbf{C}H_2CH_3$); 94.3 (C-4'); 115.5 (C-3",5"); 122.0 (C-1"); 128.0 (C-2",6"); 144.7 (C-5); 145.5 (C-3'); 147.4 (C-5'); 155.5 (C-3); 160.3 (C=O); 160.8 (C-4"). Mass spectrum, *m*/*z* (I_{rel}, %): 313 (100, M^+), 258 (5, M-28), 268 (24, M-45), 241 (28, M-72), 214 (5, M-99), 200 (8, M-113), 186 (4, M-127), 172 (6), 158 (10), 146 (11), 134 (14), 117 (7), 103 (5), 89 (9), 77 (6). Found, %: C 57.71; H 4.96; N 22.54. $C_{15}H_{15}N_5O_3$. Calculated, %: C 57.50; H 4.83; N 22.35.



4d

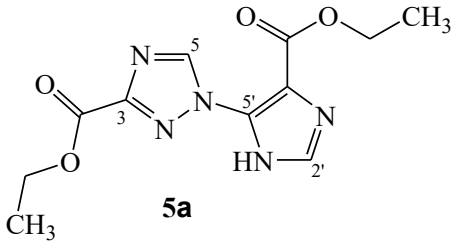
Ethyl 1-[3-(4-chlorophenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4d**). Yield 130 mg (82 %), pale gray solid, mp 230–232 °C. IR spectrum, ν, cm^{-1}: 517, 547, 619, 649, 700, 736, 784, 827, 844, 947, 962, 1023, 1060, 1091, 1113, 1165, 1193, 1330, 1248, 1300, 1310, 1336, 1402, 1433, 1451, 1473, 1490, 1544, 1567, 1607, 1650, 1733, 2897, 2972, 3002, 3115, 3144, 3202, 3220. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 7.0, $OCH_2C\mathbf{H}_3$); 4.40 (2H, q, *J* = 7.0, $OC\mathbf{H}_2CH_3$); 7.03 (1H, s, H-4'); 7.45 (2H, d, *J* = 8.1, 3",5"-H); 7.83 (2H, d, *J* = 8.1, 2",6"-H); 9.04 (1H, s, H-5);

13.53 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 15.1 ($OCH_2\mathbf{C}H_3$); 62.3 ($O\mathbf{C}H_2CH_3$); 95.2 (C-4'); 128.1 (C-2",6"); 129.0 (C-1"); 130.0 (C-3",5"); 134.1 (C-4"); 144.6 (C-5); 144.8 (C-3'); 147.3 (C-5'); 155.4 (C-3); 160.2 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 317 (100, M^+), 289 (16, M-28), 272 (56, M-45), 245 (97, M-72), 218 (9, M-99), 204 (21, M-113), 190 (3, M-127), 176 (7), 162 (15), 150 (15), 136 (40), 127 (14), 123 (6), 111 (8), 101 (10), 75 (12), 70 (6). Found, %: C 53.24; H 3.94; N 22.19. $C_{14}H_{12}ClN_5O_2$. Calculated, %: C 52.92; H 3.81; N 22.04.



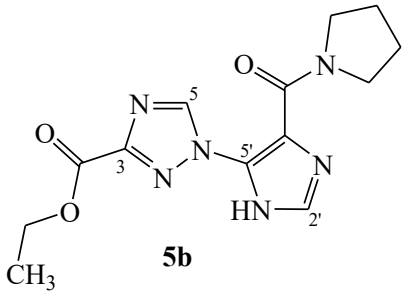
4e

Ethyl 1-(4-ethoxycarbonyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4e**). Yield 126 mg (90 %), white solid, mp 186–188 °C. IR spectrum, ν, cm^{-1}: 520, 558, 595, 622, 641, 668, 775, 800, 830, 872, 944, 981, 1030, 1064, 1091, 1143, 1167, 1202, 1242, 1273, 1314, 1342, 1391, 1453, 1485, 1532, 1556, 1705, 1735, 2725, 2792, 2830, 2971, 3149. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.21 (3H, t, *J* = 7.0, $OCH_2C\mathbf{H}_3$); 1.41 (3H, t, *J* = 7.0, $OCH_2C\mathbf{H}_3$); 4.14 (2H, q, *J* = 7.0, $OC\mathbf{H}_2CH_3$); 4.39 (2H, q, *J* = 7.0, $OC\mathbf{H}_2CH_3$); 8.25 (1H, s, H-3'); 8.85 (1H, s, H-5); 13.27 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 14.9 ($OCH_2\mathbf{C}H_3$); 15.0 ($OCH_2\mathbf{C}H_3$); 60.6 ($O\mathbf{C}H_2CH_3$); 62.2 ($O\mathbf{C}H_2CH_3$); 107.5 (C-4'); 137.7 (C-3'); 145.0 (C-5'); 148.6 (C-5); 155.1 (C-3); 160.4 (C=O); 162.4 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 279 (77, M^+), 251 (8, M-28), 234 (98, M-45), 207 (100, M-72), 188 (16, M-91), 178 (70, M-101), 166 (7, M-113), 161 (62, M-118), 138 (23), 136 (64), 135 (50), 134 (28), 124 (11), 120 (31), 108 (10), 94 (11), 81 (11), 68 (8), 60 (7), 54 (12), 53 (28), 52 (36), 45 (12), 43 (15). Found, %: C 47.37; H 4.72; N 25.02. $C_{11}H_{13}N_5O_4$. Calculated, %: C 47.31; H 4.69; N 25.08.



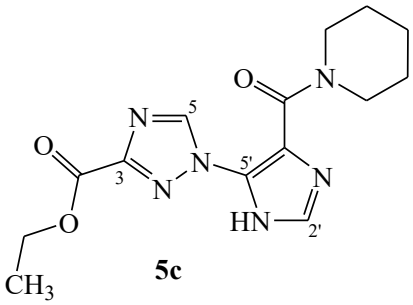
5a

Ethyl 1-(4-ethoxycarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5a**). Yield 116 mg (83 %), pale red solid, mp 180–183 °C. IR spectrum, ν, cm^{-1}: 518, 530, 562, 588, 628, 666, 775, 794, 835, 853, 873, 900, 941, 985, 1025, 1059, 1110, 1138, 1166, 1188, 1204, 1230, 1272, 1309, 1344, 1373, 1387, 1408, 1456, 1484, 1522, 1594, 1705, 1728, 2690, 2721, 2788, 2830, 2917, 2942, 2990, 3145. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.1, $OCH_2C\mathbf{H}_3$); 1.41 (3H, t, *J* = 7.1, $OCH_2C\mathbf{H}_3$); 4.14 (2H, q, *J* = 7.1, $OC\mathbf{H}_2CH_3$); 4.38 (2H, q, J = 7.1, $OC\mathbf{H}_2CH_3$); 7.49 (1H, s, H-2'); 8.71 (1H, s, H-5); 13.17 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 15.0 ($OCH_2\mathbf{C}H_3$); 15.1 ($OCH_2\mathbf{C}H_3$); 59.4 ($O\mathbf{C}H_2CH_3$); 61.9 ($O\mathbf{C}H_2CH_3$); 122.3 (C-4'); 139.6 (C-5'); 143.9 (C-2'); 148.1 (C-5); 154.2 (C-3); 160.9 (C=O); 163.8 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 279 (24, M^+), 234 (16, M-45), 207 (46, M-72), 188 (15, M-91), 179 (11, M-100), 161 (19, M-118), 138 (9), 136 (26), 135 (40), 134 (20), 120 (8), 112 (11), 108 (23), 95 (22), 94 (19), 81 (10), 68 (8), 60 (60), 54 (18), 53 (20), 45 (85), 43 (100). Found, %: C 47.43; H 4.74; N 24.92. $C_{11}H_{13}N_5O_4$. Calculated, %: C 47.31; H 4.69; N 25.08.



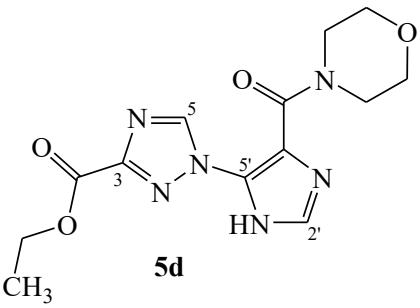
5b

Ethyl 1-(4-pyrrolidlinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5b**). Yield 114 mg (75 %), pale yellow solid, mp 127–129 °C. IR spectrum, ν, cm^{-1}: 652, 675, 750, 847, 876, 942, 988, 1018, 1063, 1097, 1131, 1159, 1180, 1224, 1272, 1341, 1365, 1382, 1444, 1459, 1515, 1602, 1738, 2852, 2964, 3031, 3055, 3077, 3104, 3123. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.45 (3H, t, *J* = 7.0, $OCH_2C\mathbf{H}_3$); 1.84–1.95 (4H, m, $2CH_2$); 3.48–3.59 (4H, m, $2NCH_2$); 4.44 (2H, q, *J* = 7.0, $OC\mathbf{H}_2CH_3$); 7.52 (1H, s, H-2'); 8.75 (1H, s, H-5); 12.33 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.0 ($OCH_2\mathbf{C}H_3$); 25.0 (CH_2); 25.5 (CH_2); 43.5 (NCH_2); 48.1 (NCH_2); 61.9 ($O\mathbf{C}H_2CH_3$); 114.4 (C-4'); 132.9 (C-5'); 135.0 (C-2'); 143.7 (C-5); 155.4 (C-3); 159.3 (C=O); 159.9 (C=O). Found, %: C 51.43; H 5.37; N 27.45. $C_{13}H_{16}N_6O_4$. Calculated, %: C 51.31; H 5.30; N 27.62.



5c

Ethyl 1-(4-piperidinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5c**). Yield 124 mg (78 %), pale yellow solid, mp 133–135 °C. IR spectrum, ν, cm^{-1}: 651, 673, 753, 843, 874, 942, 981, 1015, 1062, 1094, 1133, 1157, 1180, 1231, 1277, 1339, 1368, 1380, 1446, 1468, 1514, 1600, 1740, 2856, 2929, 2988, 3027, 3051, 3083, 3106, 3127. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.37–1.43 (2H, m, CH_2); 1.45 (3H, t, *J* = 7.0, $OCH_2\mathbf{C}H_3$); 1.56–1.69 (4H, m, $2CH_2$); 3.08–3.31 (2H, m, NCH_2); 3.61–3.80 (2H, m, NCH_2); 4.49 (2H, q, *J* = 7.0, $O\mathbf{C}H_2CH_3$); 7.58 (1H, s, H-2'); 8.81 (1H, s, H-5); 12.69 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.4 ($OCH_2\mathbf{C}H_3$); 24.4 (CH_2); 25.5 (CH_2); 25.9 (CH_2); 44.0 (NCH_2); 48.5 (NCH_2); 62.3 ($O\mathbf{C}H_2CH_3$); 114.6 (C-4'); 133.5 (C-5'); 135.4 (C-2'); 144.0 (C-5); 155.8 (C-3); 159.7 (C=O); 160.4 (C=O). Found, %: C 52.97; H 5.62; N 26.23. $C_{14}H_{18}N_6O_3$. Calculated, %: C 52.82; H 5.70; N 26.40.

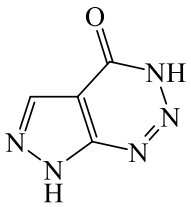


5d

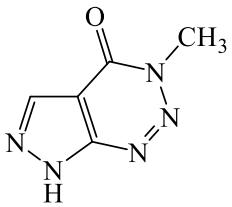
Ethyl 1-(4-morpholinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5d**). Yield 146 mg (91 %), pale yellow solid, mp 126–128 °C. IR spectrum, ν, cm^{-1}: 598, 651, 672, 735, 758, 797, 838, 863, 936, 983, 1023, 1067, 1111, 1185, 1235, 1275, 1302, 1338, 1364, 1391, 1442, 1515, 1623, 1732, 2676, 2758, 2812, 2852, 2955, 2974, 3030, 3056, 3097, 3126. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.46 (3H, t, *J* = 7.0, $O\mathbf{C}H_2CH_3$); 3.54–3.61 (4H, m, $2NCH_2$); 3.75–3.76 (4H, m,

2OCH_2); 4.45 (2H, q, *J* = 7.0, OCH_2CH_3); 7.60 (1H, s, H-2'); 8.91 (1H, s, H-5); 12.14 (1H, br.s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.4 ($OCH_2\mathbf{C}H_3$); 45.0 (NCH_2); 45.0 (NCH_2); 47.8 (NCH_2); 62.5 ($O\mathbf{C}H_2CH_3$); 64.4 (OCH_2); 66.3 (OCH_2); 114.6 (C-4'); 133.6 (C-5'); 135.5 (C-2'); 143.7 (C-5); 155.8 (C-3); 159.6 (C=O); 160.8 (C=O). Found, %: C 48.81; H 5.08; N 26.18. $C_{13}H_{16}N_6O_4$. Calculated, %: C 48.75; H 5.03; N 26.24.

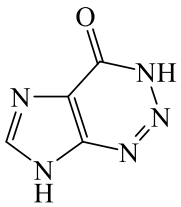
General procedure for the synthesis of 3-*R*-3,7-dihydroazolo[3,4-*d*][1,2,3]triazin-4-one (7a–d)



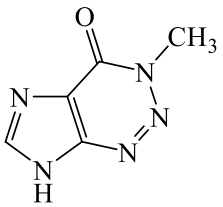
7a



7b



7c



7d

To a stirred mixture of ethyl isocyanoacetate **1** (60 μl, 0.55 mmol) and sodium acetate (45 mg, 0.55 mmol) in acetone (3 ml), a cold solution of the corresponding 5-diazopyrazole **6a,b** (0.5 mmol)[S3] or 5-diazoimidazole **6c,d** (0.5 mmol)[S4,S5] in acetone (3 ml) was added dropwise at 0°C for 5 min. The mixture was allowed to stand under these conditions until disappearing of the starting diazoazoles (TLC control). Activated charcoal was added, and the mixture was stirred for 15 min, and filtered. The filtrate was concentrated under reduced pressure at a temperature below 40 °C. The residue was crystallized from EtOH as white solid. Yield 60 mg (88 %) for **7a**[S6, S7], 64 mg (85 %) for **7b**[S7], 57 mg (83 %) for **7c**[S5,S8], 68 mg (90 %) for **7d**[S5]. Physical and spectral characteristics of these compounds are identical to those presented in the literature[S5–S8].

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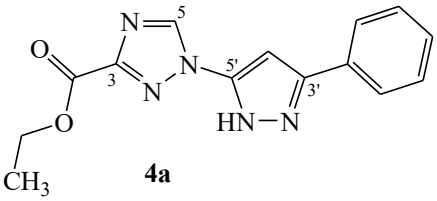


4a

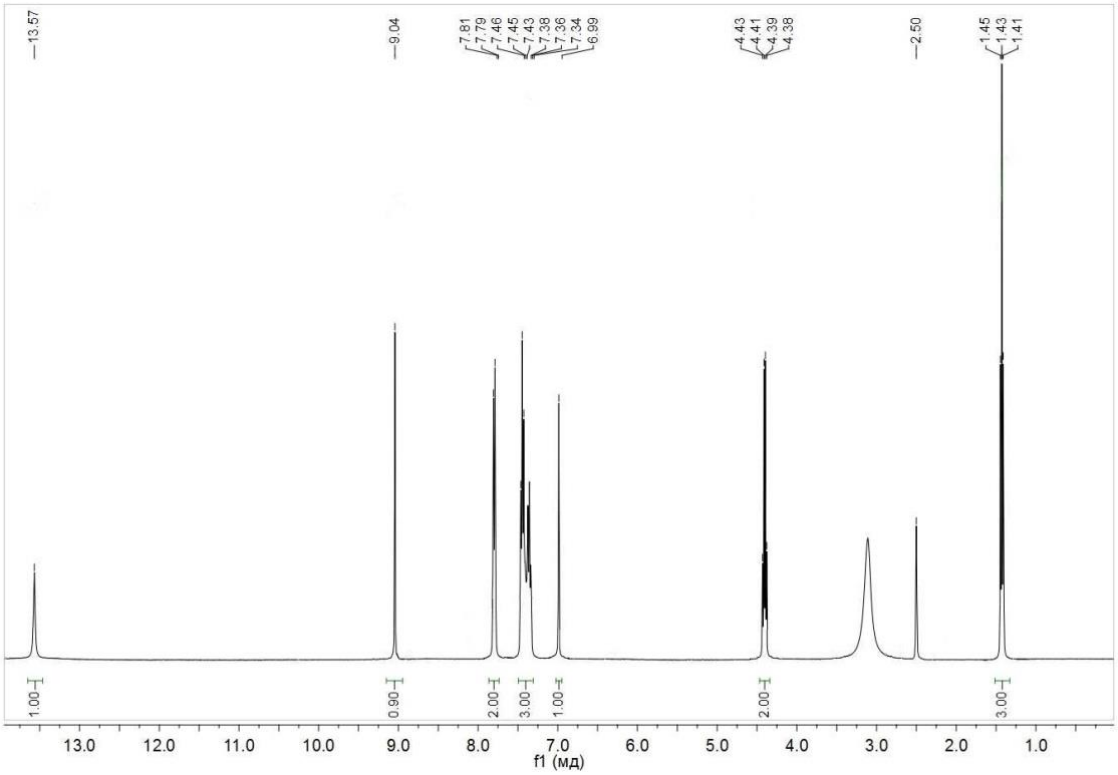


Figure S1. ^{1}H NMR for ethyl 1-(3-phenyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4a**)

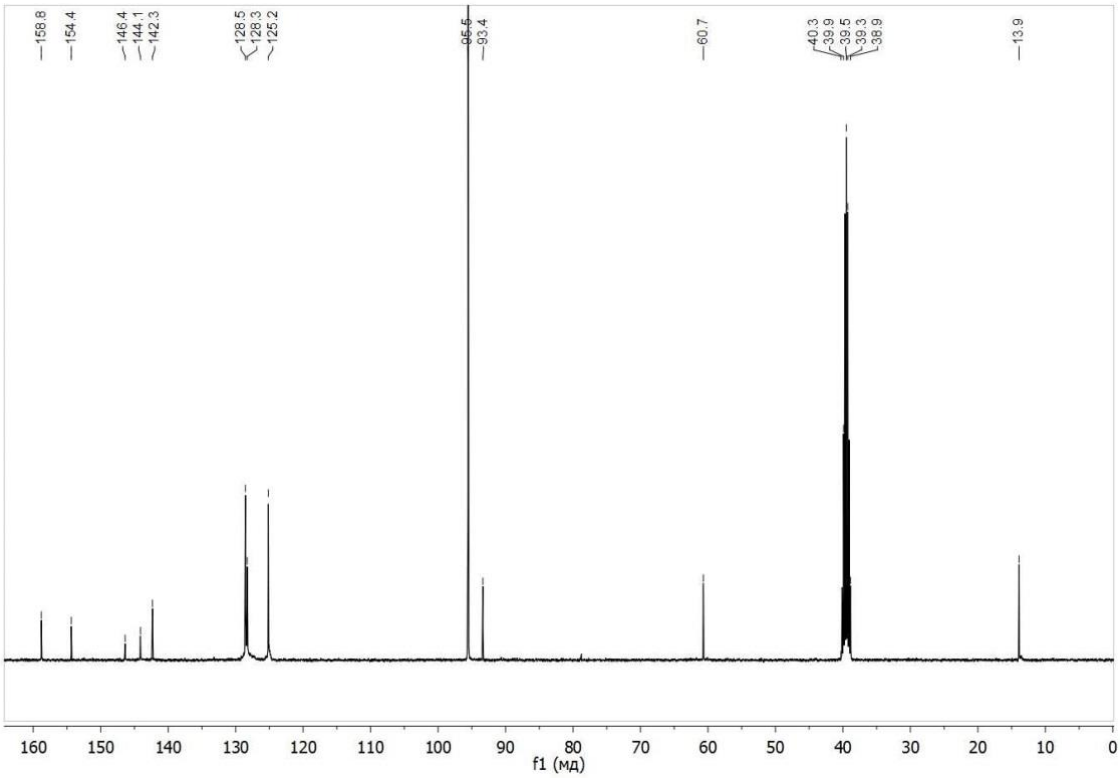
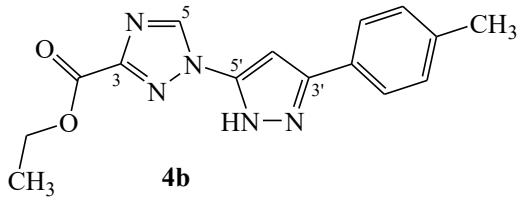


Figure S2. ^{13}C NMR for ethyl 1-(3-phenyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4a**)



4b

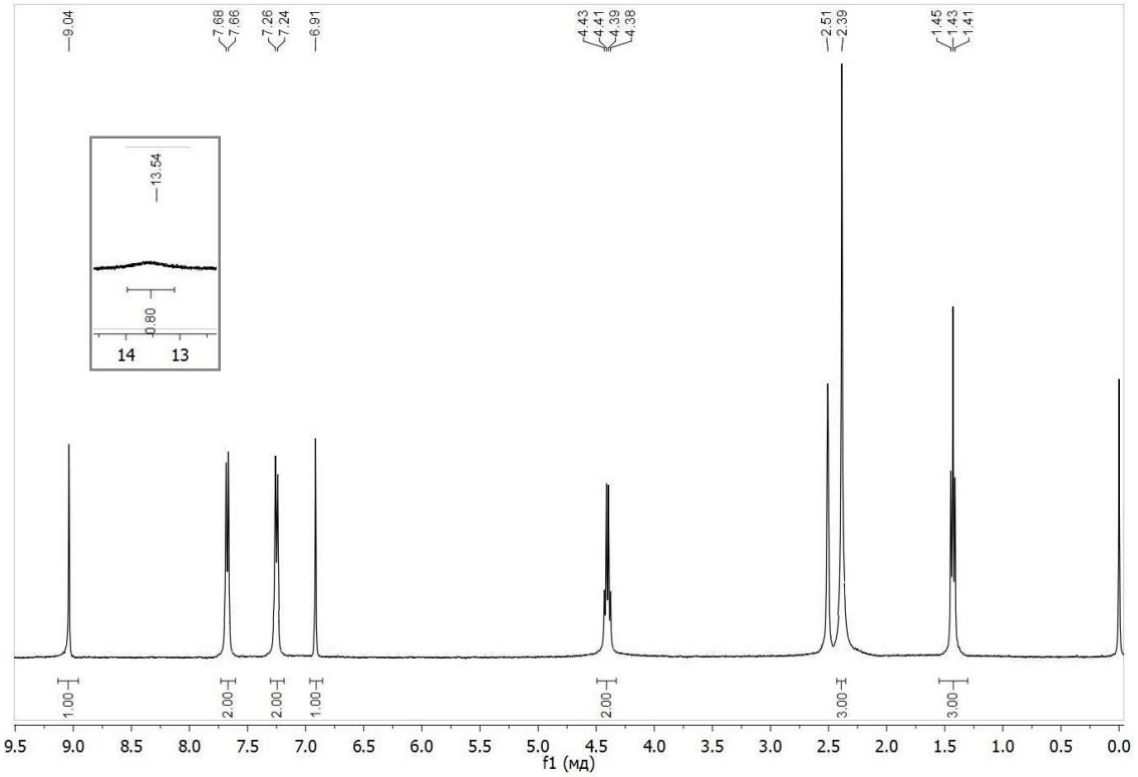


Figure S3. ^{1}H NMR for ethyl 1-[3-(*p*-tolyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4b**)

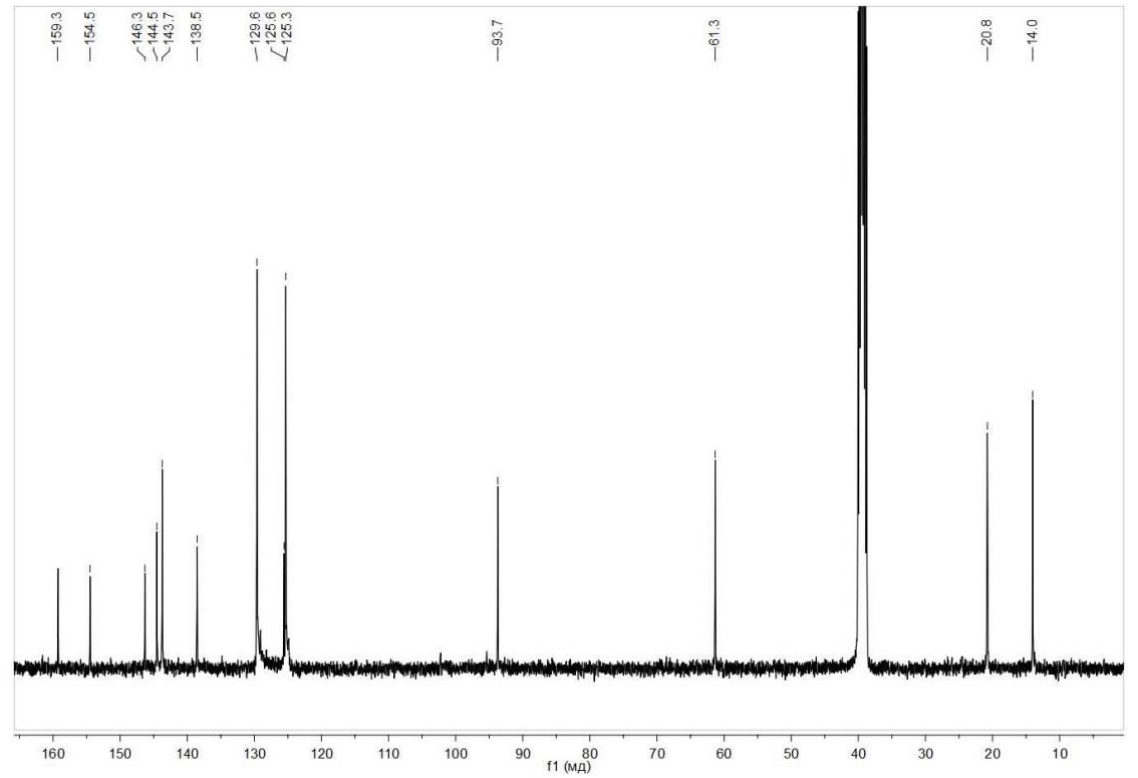


Figure S4. ^{13}C NMR for ethyl 1-[3-(*p*-tolyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4b**)

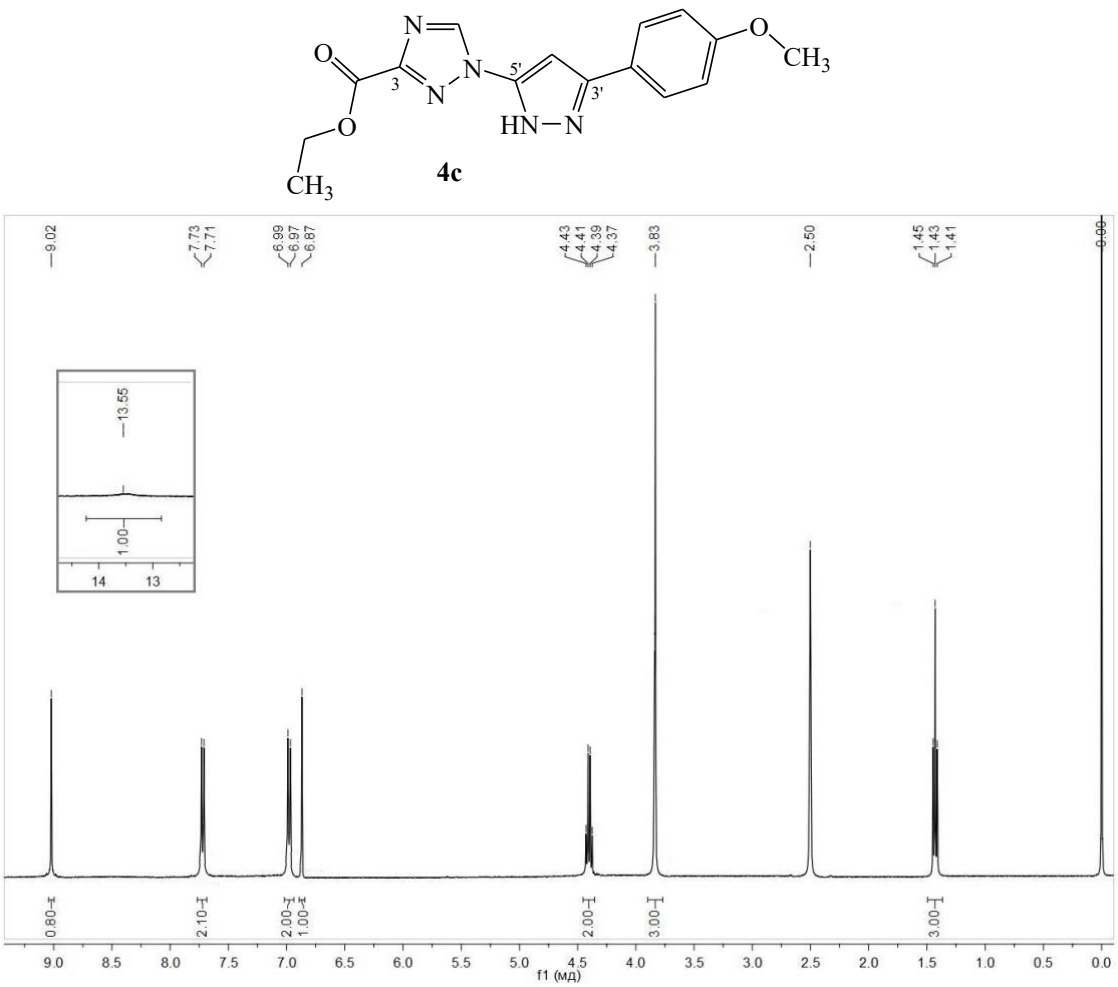


Figure S5. ^{1}H NMR for ethyl 1-[3-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4c)**

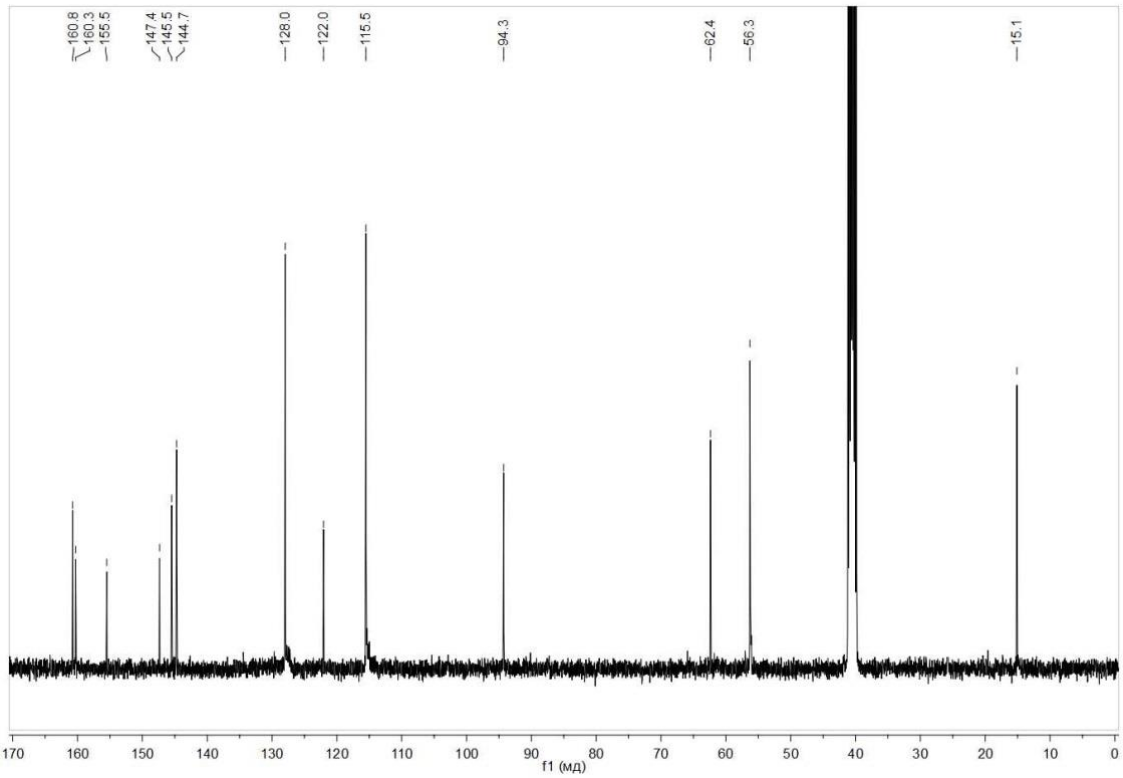


Figure S6. ^{13}C NMR for ethyl 1-[3-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4c**)

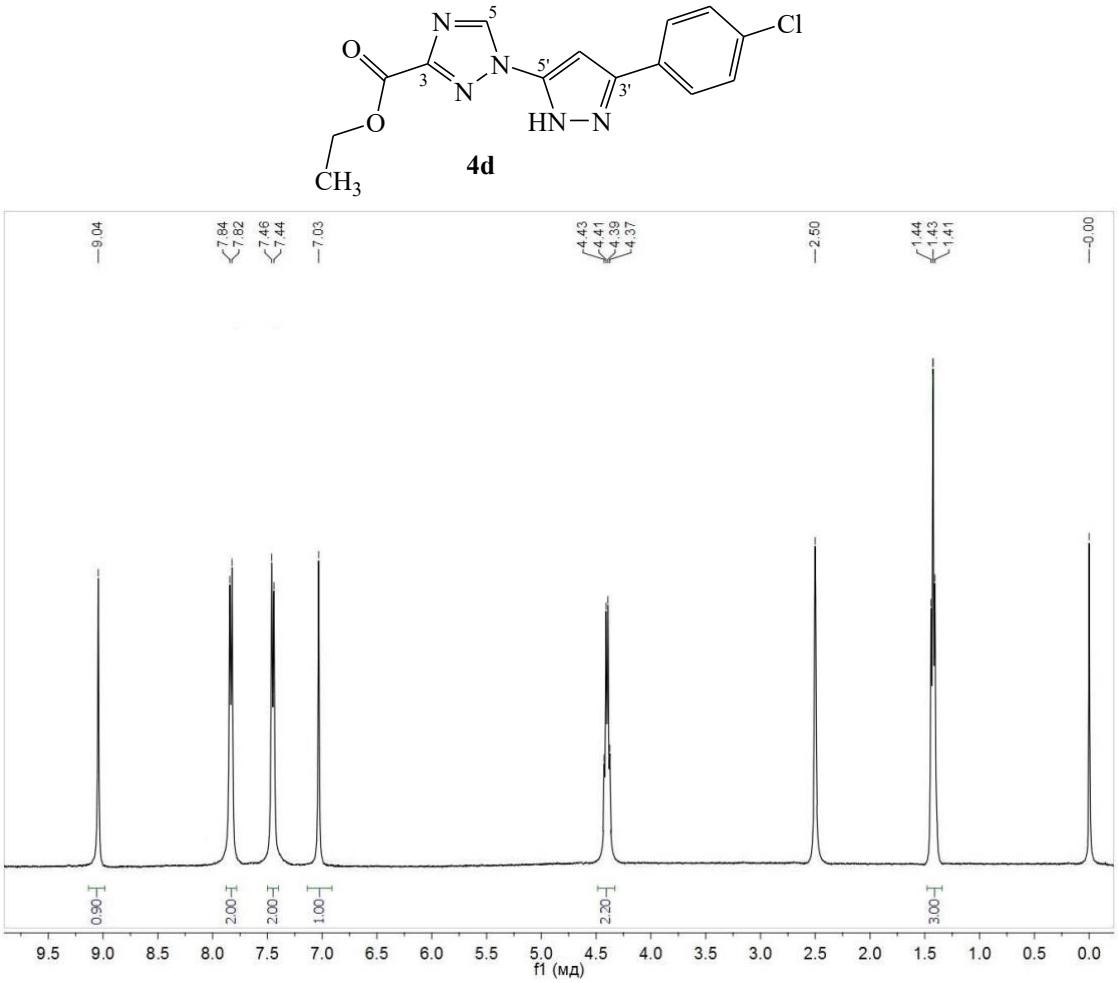


Figure S7. ^{1}H NMR for ethyl 1-[3-(4-chlorophenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4d**)

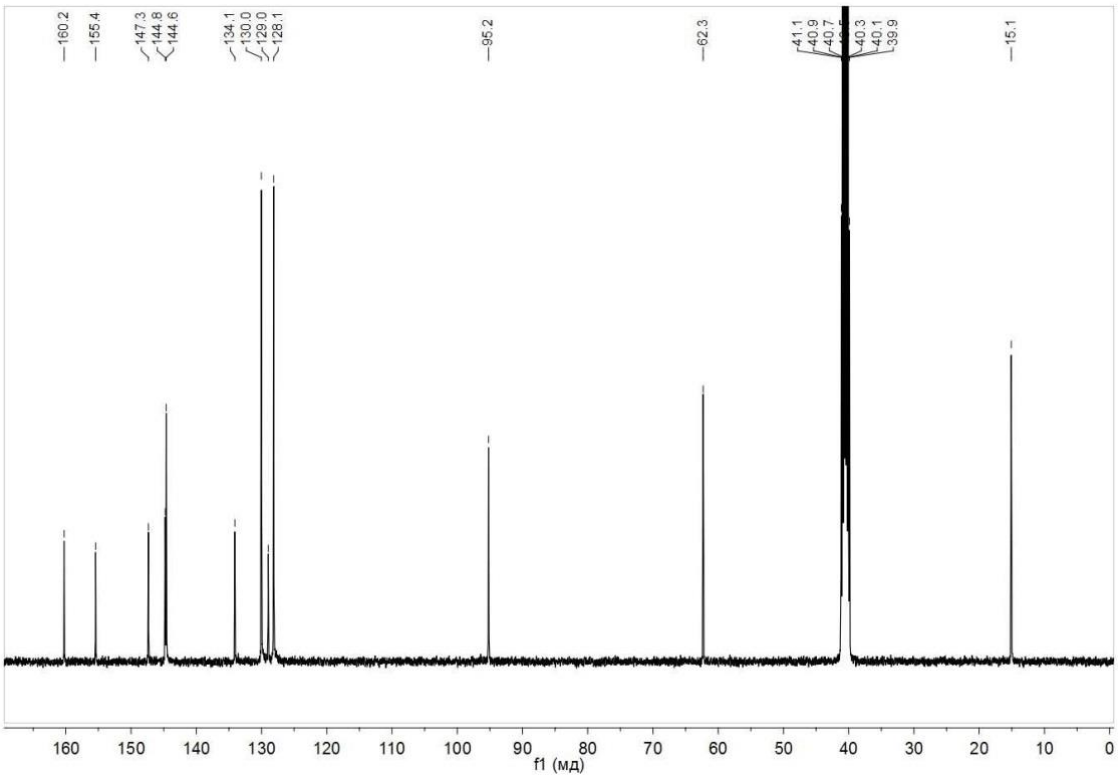
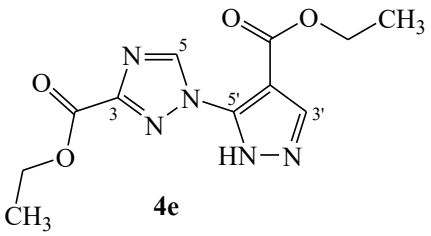


Figure S8. ^{13}C NMR for ethyl 1-[3-(4-chlorophenyl)-1*H*-pyrazol-5-yl]-1*H*-1,2,4-triazole-3-carboxylate (**4d**)



4e

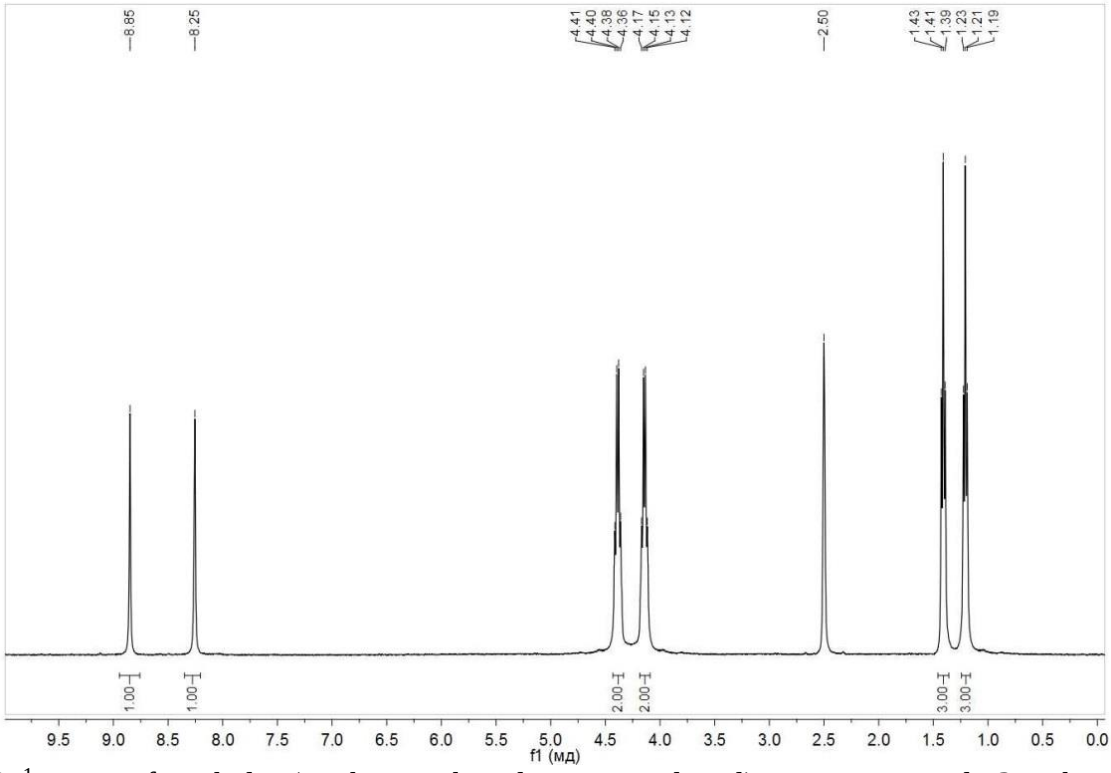


Figure S9. ^{1}H NMR for ethyl 1-(4-ethoxycarbonyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4e**)

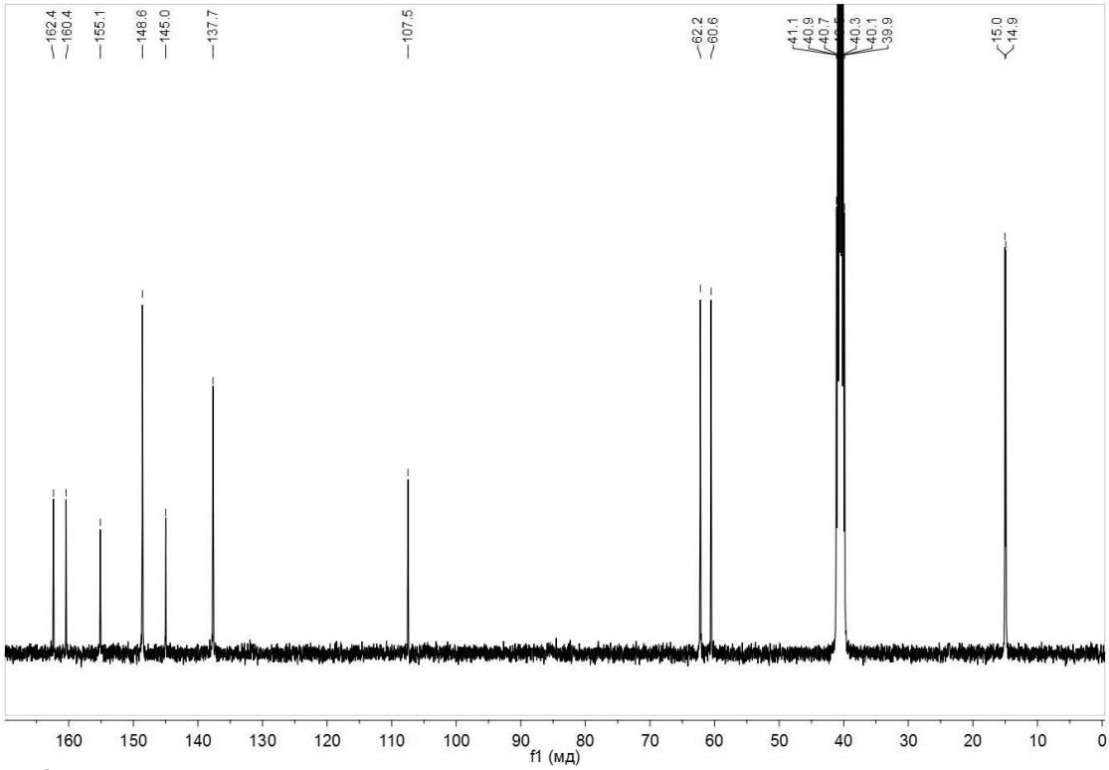
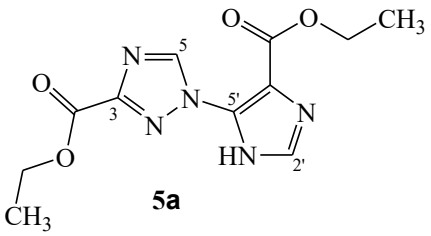


Figure S10. ^{13}C NMR for ethyl 1-(4-ethoxycarbonyl-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**4e**)



5a

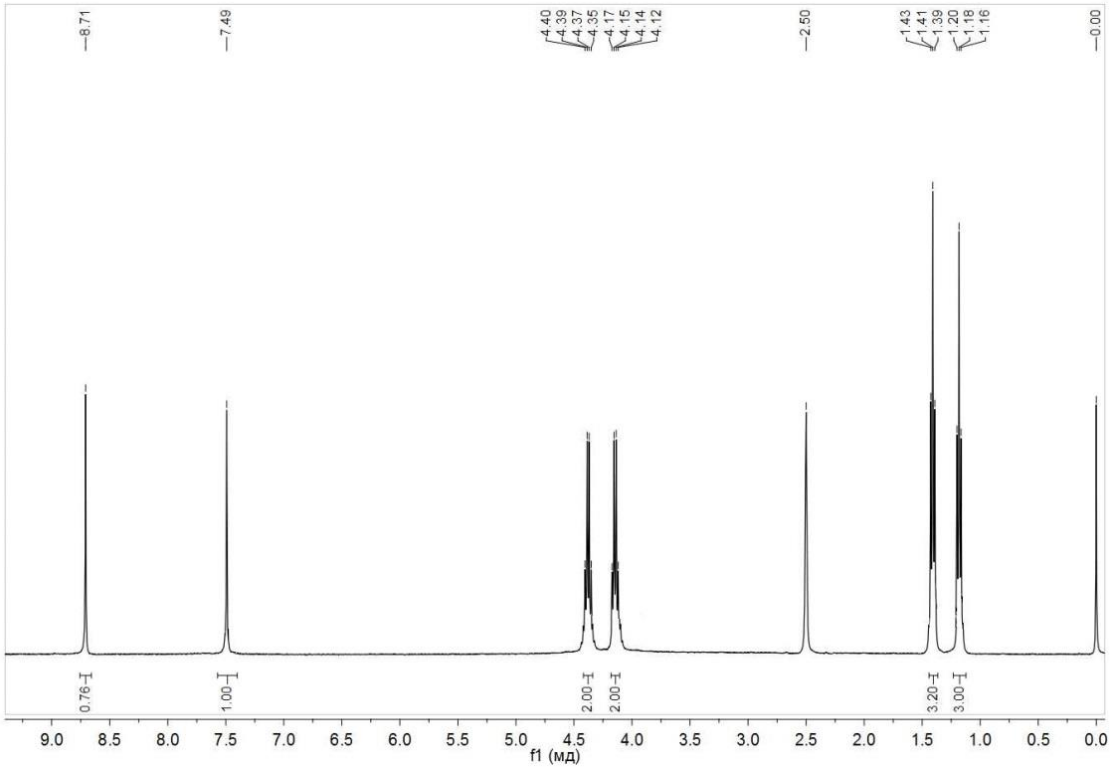


Figure S11. ^{1}H NMR for ethyl 1-(4-ethoxycarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5a**)

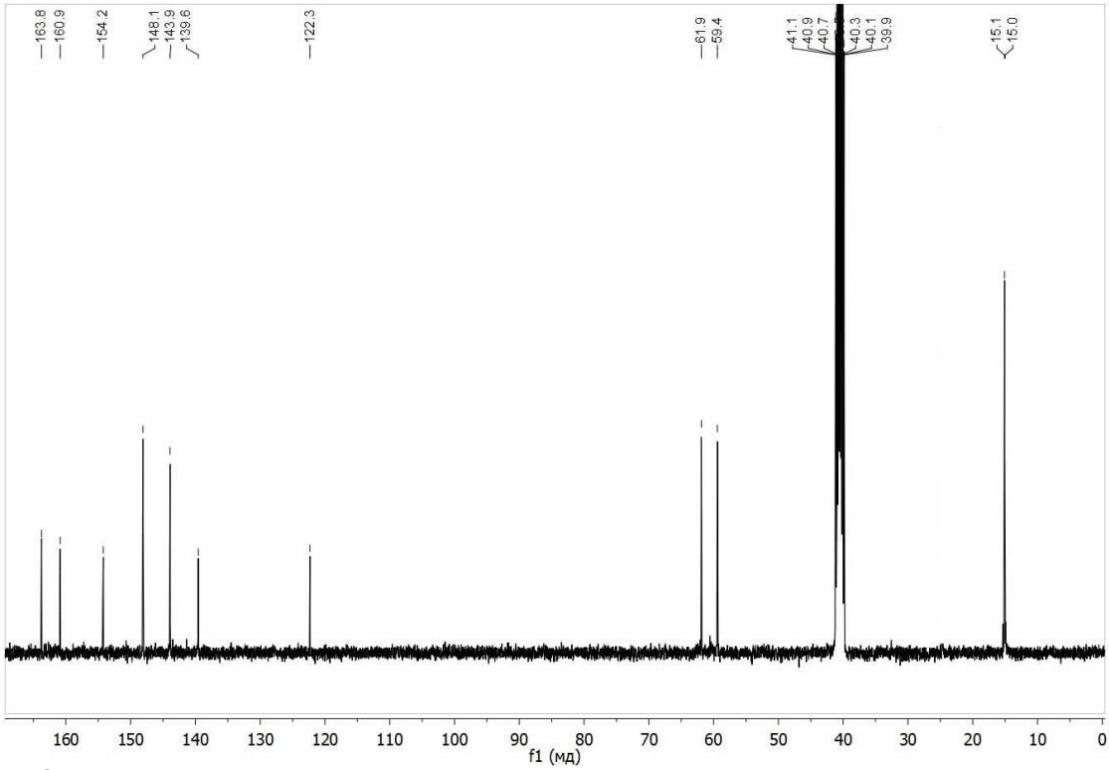
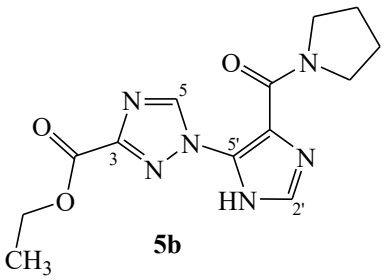


Figure S12. ^{13}C NMR for ethyl 1-(4-ethoxycarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5a**)



5b

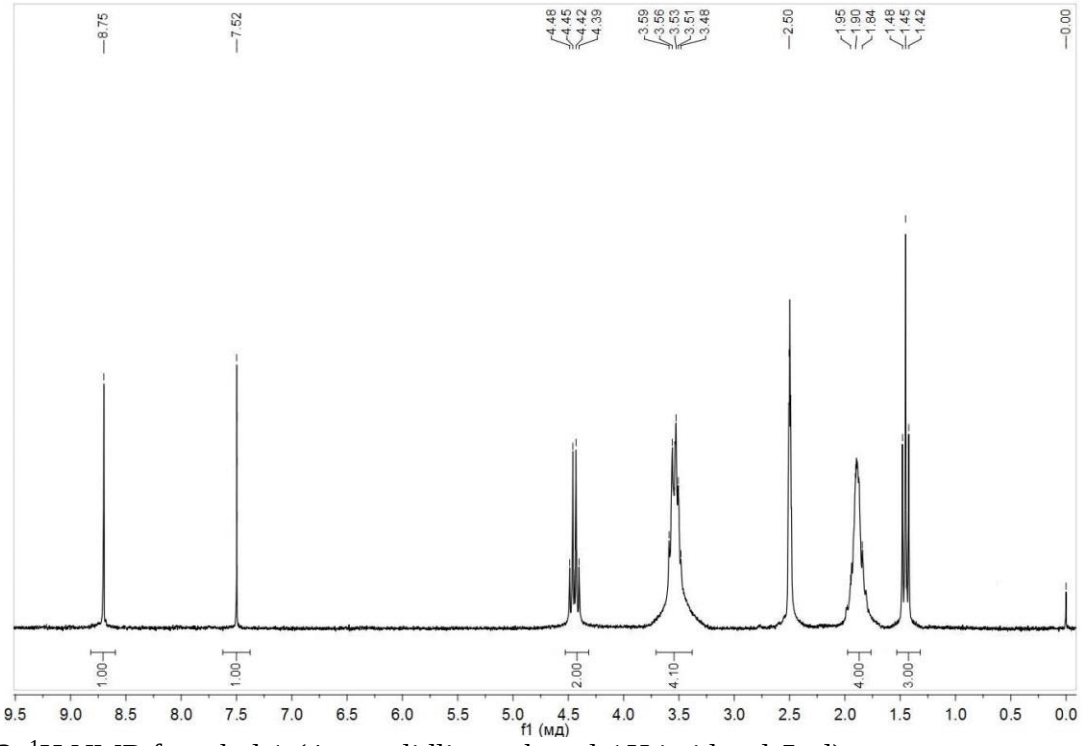


Figure S13. ^{1}H NMR for ethyl 1-(4-pyrrolidlinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5b**)

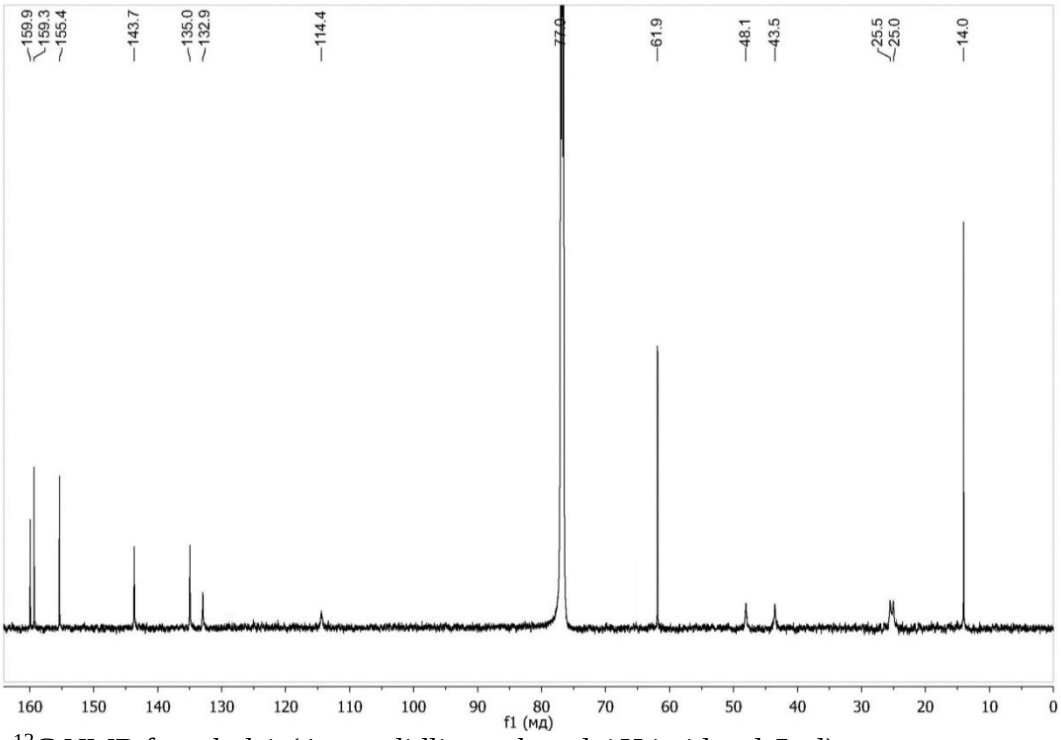
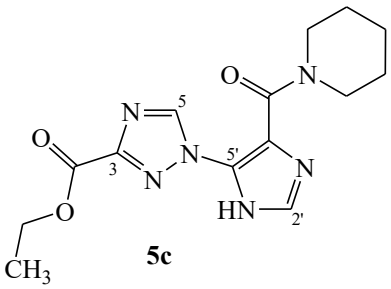


Figure S14. ^{13}C NMR for ethyl 1-(4-pyrrolidlinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5b**)



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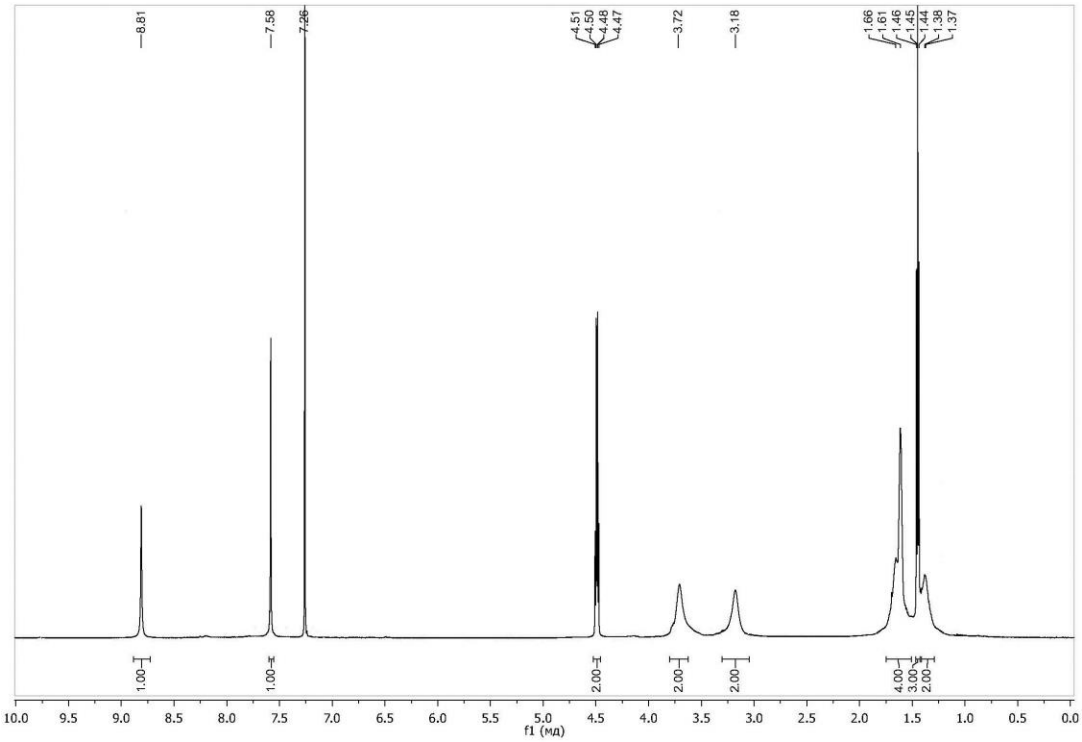


Figure S15. [1]H NMR for ethyl 1-(4-piperidinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5c**)

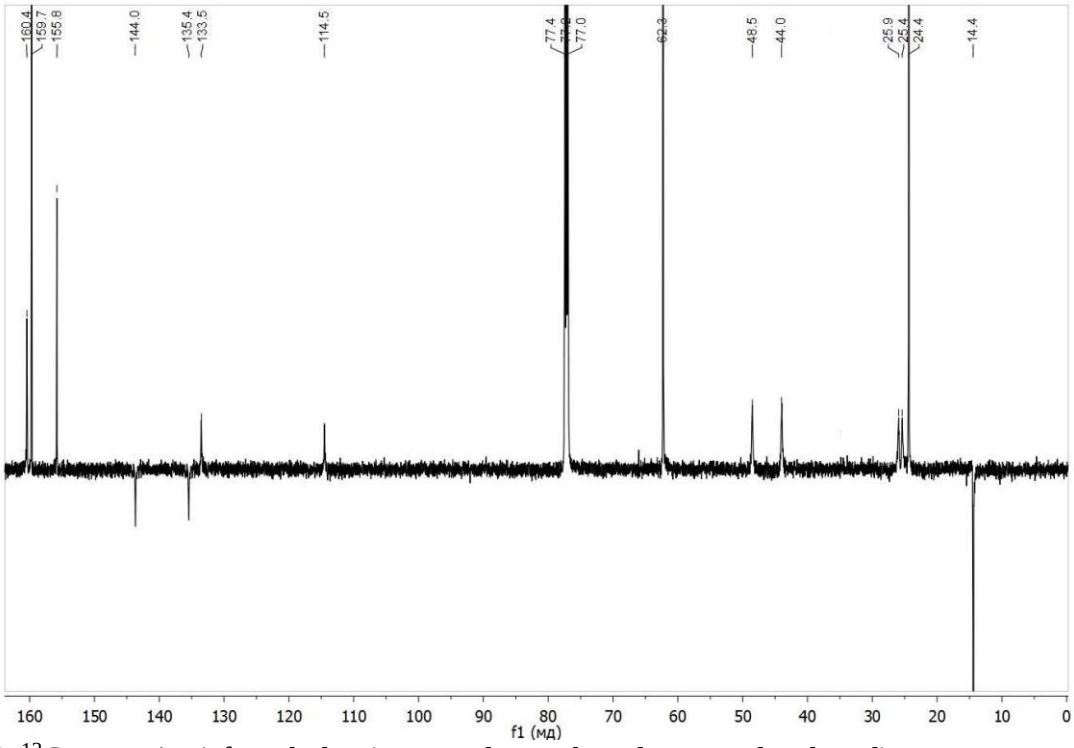
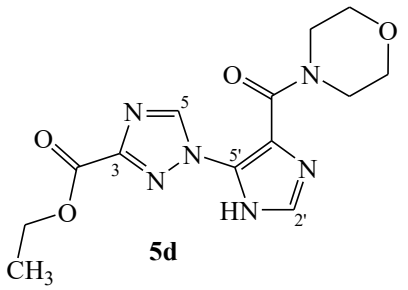


Figure S16. [13]C NMR (apt) for ethyl 1-(4-piperidinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5c**)



5d

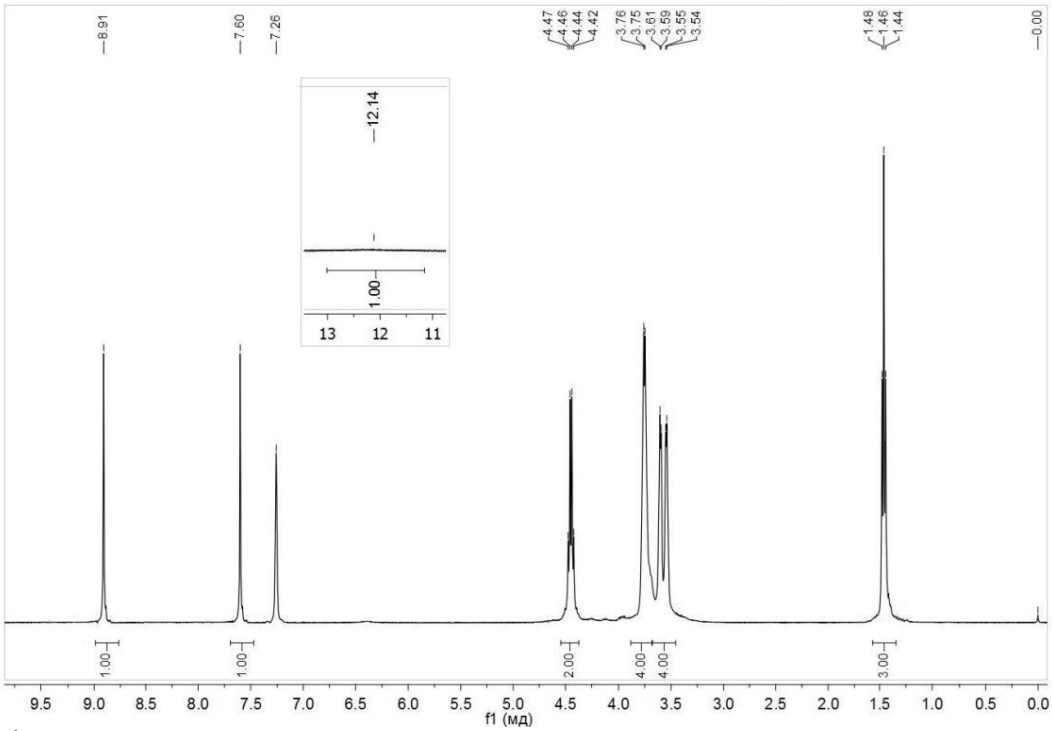


Figure S17. ^{1}H NMR for ethyl 1-(4-morpholinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5d**)

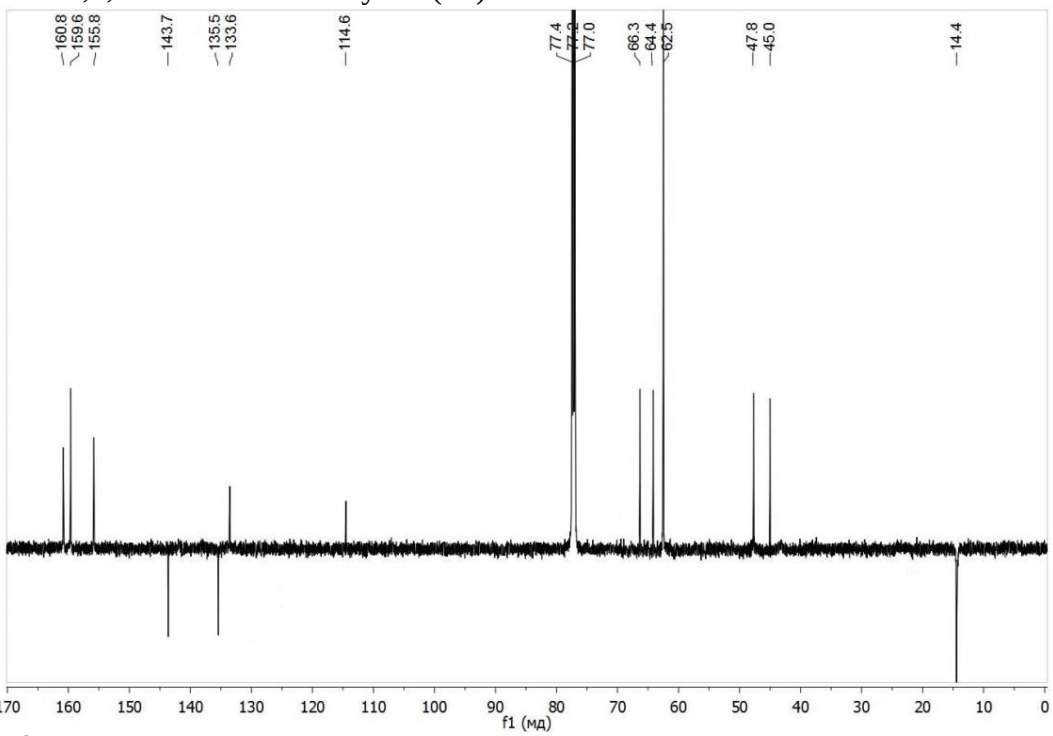


Figure S18. ^{13}C NMR (apt) for ethyl 1-(4-morpholinocarbonyl-1*H*-imidazol-5-yl)-1*H*-1,2,4-triazole-3-carboxylate (**5d**)