**Synthesis of 4,5-dihydro-1*H*-pyrazole derivatives based on**

**3-acetyl-5-nitropyridines**

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Experimental Procedures

Materials and Methods

IR spectra were recorded on an Infralum FT-801 spectrometer in KBr pellets. 1Н and 13C NMR spectra were acquired on a Bruker DRX400 instrument (400 and 100 MHz, respectively) using CDCl3 or DMSO-*d*6 the internal standard was TMS or residual solvent signals (7.25 and 77.0 ppm in the case of CDCl3 for 1Н and 13C nuclei, respectively; 2.49 and 39.9 ppm 1Н and for 13C nuclei in DMSO-*d*6). Elemental analysis was performed on a Carlo Erba EA 1106 automatic CHN-analyzer. The reaction progress and purity of the obtained compounds were controlled by TLC on Sorbfil AF-A-UV plates, visualization in iodine vapor and under UV light. Melting points were determined using a Koffler hot bench.

Starting Materials Preparation

**1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)ethan-1-one 4** and **1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-phenylprop-2-en-1-one 5** was synthesized according to a published procedure [25, 26].

General procedure for the synthesis of pyridylchalcones 6a-e, 7a–e

A solution of KOH (0.2 g (4 mmol) in H2O (3 ml) and EtOH (15 ml) was cooled in an ice bath (0-5 °C). Then 3-acetyl-5-nitro-6-phenylpyridine **4** or **5** (4 mmol) in CH­2Cl2 (1 ml) was added, and the constantly stirred mixture was treated by dropwise addition of the appropriate aromatic aldehyde (4 mmol). A precipitate of pyridylchalcone **6a-e**, **7a–e** formed after 10 min. The mixture was stirred at room temperature for additional 3 h. Then the precipitate is filtered, washed with a water-alcohol solution and dried in air. The crude product was purified by recrystallization from an appropriate solvent.

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|  | **1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-phenylprop-2-en-1-one (6a).** White crystals; m.p.: 138-140 °C (2*-*PrOH); yield: 1.13 g (92%); (KBr): = 1668 (C=O), 1530, 1334 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.63 (s, 3H, CH3), 6.43 (dd, *J* = 3.7 Hz, 1.9 Hz, 1H, H-4 furan), 6.73 (d, *J* = 3.7 Hz, 1H, H-3 furan), 6.82 (d, *J* = 16.0 Hz, 1H, 2-CH=), 7.30 (d, *J* = 16.0 Hz, 31H, -CH=), 7.36 – 7.43 (m, 3H, H-3',4',5' Ph), 7.45 – 7.52 (m, 6H, H-5 furan, H-3,4,5 Ph, H-2',6' Ph), 7.63 – 7.66 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 23.3 (CH3), 112.5, 114.8, 126.4, 128.0 (2C Ar), 128.6 (2C Ar), 128.87 (2C Ph), 128.97, 129.0 (2C Ph), 130.1, 131.3, 131.6, 133.7, 135.3, 142.2, 143.3, 145.5, 146.8, 150.7, 157.1, 194.8 (C=O) ppm; anal. calcd for C25H18N2O4: C 73.16, H 4.42, N 6.83, found C 73.47, H 4.71, N 6.63. |
|  | **1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-phenylprop-2-en-1-one (7a).** White crystals; m.p.: 155-156 °C (2*-*PrOH); yield: 992 mg (96%); IR (KBr): = 1665 (С=О), 1505, 1331 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.80 (s, 3H, CH3), 7.18 (d, *J* = 15.3, 1H, 2-CH=), 7.45 - 7.51 (m, 6H, 3-CH=, H-2',3',4',5',6' Ph), 7.59 - 7.64 (m, 5H, H-2,3,4,5,6 Ph), 8.29 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 24.0 (CH3), 124.8, 128.3 (2C Ph), 128.8 (4C Ph), 129.2 (2C Ph), 130.2, 131.6, 132.1, 132.7, 133.7, 135.9, 143.5, 147.9, 153.3, 160.7, 192.0 (C=O) ppm; anal. calcd for C21H16N2O3: C 73.24, H 4.68, N 8.13, found C 73.48, H 4.41, N 8.36. |
|  | **3-(furan-2-yl)-1-(4-(furan-2-yl)-2-methyl-5-nitro-phenylpyridin-3-yl)prop-2-en-1-one (6b).** Bright-beige crystals; m.p.: 150-152 °C (2-PrOH); yield: 1.10 g (94%); IR (KBr): = 1623 (C=O), 1543, 1375 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.62 (s, 3H, CH3), 6.44 (dd, *J* = 3.7 Hz, 1.8 Hz, 1H, H-4' furan), 6.50 (dd, *J* = 3.7 Hz, 1.8 Hz, 1H, H-4 furan), 6.66 – 6.75 (m, 3H, 2-CH=, H-3 furan, H-3' furan), 7.06 (d, *J* = 16.0 Hz, 1H, 3-CH=), 7.46 – 7.50 (m, 4H, H-3,4,5 Ph, H-5' furan), 7.52 (d, *J* = 1.3 Hz, 1H, H-5 furan), 7.60 – 7.64 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 23.2 (CH3), 112.4, 113.0, 114.9, 117.7, 123.7, 128.0 (3C Ph), 128.9 (3C Ph), 130.0, 131.6, 132.4, 135.4, 143.3, 145.5, 146.0, 150.3, 150.7, 157.0, 194.3 (C=O) ppm; anal. calcd for C23H16N2O5: C 69.00, H 4.03, N 7.00, found C 69.31, H 4.22, N 7.30. |
|  | **3-(furan-2-yl)-1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (7b).** Yellow crystals; m.p.: 160-161 °C (2*-*PrOH); yield: 712 mg (71%); IR (KBr): = 1657 (C=O), 1504, 1326 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.80 (s, 3H, CH3), 6.55 (br. s, 1H, H-4 furan), 6.80 (d, *J* = 3.0 Hz, 1H, H-3 furan), 7.07 (d, *J* = 15.2 Hz, 1H, 2-CH=), 7.41 (d, *J* = 15.2 Hz, 1H, 3-CH=), 7.46 - 7.50 (m, 3H, H-3,4,5 Ph), 7.58 (m, 3H, H-5 furan, H-2,6 Ph), 8.30 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 24.1 (CH3), 113.1, 118.2, 121.7, 128.3 (2C Ph), 128.8 (2C Ph), 130.1, 132.1, 132.8, 132.9, 135.9, 143.5, 146.1, 150.7, 153.3, 160.8, 191.0 (C=O) ppm; anal. calcd for C19H14N2O4: C 68.26, H 4.22, N 8.38, found C 68.10, H 4.01, N 8.19. |
|  | **1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one (6c).** Beige crystals; m.p.: 148-149 °C (2*-*PrOH); yield: 1.20 g (95%); IR (KBr): = 1643 (C=O), 1530, 1375 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.64 (s, 3H, CH3), 6.45 (br. s, 1H, H-4 furan), 6.62 (d, *J* = 16.8 Hz, 1H, 2-CH=), 6.75 (d, *J* = 3.1 Hz, 1H, H-3 furan), 7.08 (t, *J* = 4.6 Hz, 1H, H-4 thiophene), 7.30 (d, *J* = 3.1 Hz, 1H, Н-3 thiophene), 7.43 (d, *J* = 16.8 Hz, 1Н, 3-CH=), 7.41 – 7.52 (m, 6H, H-3,4,5 Ph, H-5 furan, H-5 thiophene), 7.62 – 7.68 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 23.3 (CH3), 112.4, 114.9, 125.0, 128.0 (2C Ph), 128.6, 128.9 (2C Ph), 128.9, 130.1, 130.4, 131.5, 132.9, 135.3, 139.0, 139.1, 142.2, 143.3, 145.5, 150.7, 157.1, 194.1 (C=O) ppm; anal. calcd for C23H16N2O4S: C 66.34, H 3.87, N 6.73, found C 66.14, H 4.05, N 6.55. |
|  | **1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one (7c).** Bright-yellow crystals; m.p.: 166-168 °C (2*-*PrOH); yield: 746 mg (71%); IR (KBr): = 1656 (C=O), 1503, 1323 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.79 (s, 3H, CH3), 6.95 (d, *J* = 16.8 Hz, 1H, 2-CH=), 7.14 (d, *J* = 4.6 Hz, 1H, H-4 thiophene), 7.40 (d, *J* = 3.0 Hz, 1H, H-3 thiophene), 7.47 - 7.55 (m, 4H, H-5 thiophene, H-3,4,5 Ph), 7.61 (d, *J* = 4.5 Hz, 2H, H-2,6 Ph), 7.75 (d, *J* = 15.3, 1H, 3-CH=), 8.28 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 24.0 (CH3), 123.3, 128.2 (2C Ph), 128.7, 128.8 (2C Ph), 130.2, 130.7, 132.0, 132.7, 133.4, 135.8, 139.2, 140.0, 143.4, 153.2, 160.6, 191.2 (C=O) ppm; anal. calcd for C19H14N2O3S: C 65.13, H 4.03, N 8.00, found C 65.41, H 4.29, N 7.81. |
|  | **1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(3-nitrophenyl)prop-2-en-1-one (6d).** Bright-beige crystals; m.p.: 146-148 °C (2*-*PrOH-CHCl3); yield: 1.30 g (98%); IR (KBr): = 1656 (C=O), 1530, 1353 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.64 (s, 3H, CH3), 6.45 (br. s, 1H, H-4 furan), 6.75 (d, *J* = 3.1 Hz, 1H, H-3 furan), 6.86 (d, *J* = 16.8 Hz, 1H, 2-CH=), 7.34 (d, *J* = 16.8 Hz, 1H, 3-CH=), 7.45 -7.52 (m, 4H, H-3,4,5 Ph, H-5 furan), 7.58 (t, *J* = 8.4 Hz, 1H, H-5 Ar), 7.63-7.65 (m, 2H, H-2,6 Ph), 7.76 (d, *J* = 7.6 Hz, 1H, H-6 Ar), 8.24 (d, *J* = 9.1 Hz, 1H, H-4 Ar), 8.30 (s, 1H, H-2 Ar) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 23.4 (CH3), 112.7, 115.0, 122.8, 125.3, 128.0 (2C Ph), 128.6, 128.9 (2C Ph), 129.0, 130.2, 130.3, 131.0, 133.9, 135.2, 135.5, 142.1, 142.9, 143.2, 145.7, 148.6, 151.1, 157.2, 193.9 (C=O) ppm; anal. calcd for C25H17N3O6: C 65.93, H 3.76, N 9.23, found C 65.69, H 3.98, N 9.00. |
|  | **1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(3-nitrophenyl)prop-2-en-1-one (7d).** White crystals; m.p.: 183-185 °C (2*-*PrOH-CHCl3); yield: 689 mg (59%); IR (KBr): = 1669 (С=О), 1605, 1366 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.85 (s, 3H, CH3), 7.33 (d, *J* = 15.2 Hz, 1H, 2-CH=), 7.50 - 7.54 (m, 3H, H-3,4,5 Ph), 7.62 - 7.65 (m, 2H, H-2,6 Ph), 7.67 - 7.73 (m, 2H, 3-CH=, H-5 Ar), 7.95 (d, *J* = 7.6 Hz, 1H, H-6 Ar), 8.33 (d, *J* = 7.6 Hz, 1H, H-4 Ar), 8.36 (s, 1H, H-2 Ar), 8.50 (s, 1H, H-4 pyridine). 13C (100 MHz, CDCl3, δ ppm): *δ* = 24.3 (CH3), 123.0, 125.6, 126.9, 128.3 (2C Ph), 128.9 (2C Ph), 130.3, 130.4, 131.9, 132.3, 134.2, 135.5, 135.7, 143.4, 144.3, 148.7, 153.8, 161.0, 190.8 (C=O) ppm; anal. calcd for C21H15N3O5: C 64.78, H 3.88, N 10.79, found C 64.91, H 3.63, N 10.58. |
|  | **3-(4-fluorophenyl)-1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (6e).** Bright-beige crystals; m.p.: 136-138 °C (2*-*PrOH); yield: 1.30 g (99%); IR (KBr): = 1670 (C=O), 1532, 1319 (NO2) cm-1; 1H (400 MHz, CDCl3): *δ* = 2.63 (s, 3H, CH3), 6.44 (br. s, 1H, H-4 furan), 6.72 - 6.76 (m, 2H, 2-CH=, H-3 furan), 7.08 (t, *J* = 8.4 Hz, 2H, H-3,5 Ar), 7.26 (d, *J* = 15.2 Hz, 1H, 3-CH=), 7.46 - 7.55 (m, 6H, H-5 furan, H-3,4,5 Ph, H-2,6 Ar), 7.62 - 7.68 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 23.3 (CH3), 112.5, 114.8, 116.3 (d, 2*J*C-F= 22.1 Hz, 2C Ar), 126.0, 128.0 (2C Ph), 128.9 (2C Ph), 128.95, 130.0, 130.1, 130.6 (d, 3*J*C-F= 8.6 Hz, 2C Ar), 131.5, 135.3, 142.1, 143.3, 145.4, 145.5, 150.8, 157.1, 164.4 (d, 1*J*C-F= 253.1 Hz), 194.6 (C=O) ppm; anal. calcd for C25H17FN2O4: C 70.09, H 4.00, N 6.54, found C 70.34, H 3.79, N 6.71. |
|  | **3-(4-fluorophenyl)-1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (7e).** White crystals; m.p.: 173-174 °C (2*-*PrOH); yield: 869 mg (80%); IR (KBr): = 1666 (C=O), 1510, 1345 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.79 (s, 3H, CH3), 7.07 - 7.15 (m, 3H, 2-CH=, H-3,5 Ar), 7.46 - 7.51 (m, 3H, 3-CH=, H-2,6 Ar), 7.54 - 7.63 (m, 5H, H-2,3,4,5,6 Ph), 8.28 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 24.0 (CH3), 116.5 (d, 2*J*C-F= 22.1 Hz, 2C Ar), 124.4, 128.3 (2C Ph), 128.8 (2C Ph), 130.1, 130.2, 130.8 (d, 3*J*C-F= 8.6 Hz, 2C Ar), 132.1, 132.6, 135.8, 143.5, 146.4, 153.3, 160.7, 164.6 (d, 1*J*C-F= 254.0 Hz), 191.6 (C=O) ppm; anal. calcd for C21H15FN2O3: C 69.61, H 4.17, N 7.73, found C 69.39, H 4.38, N 7.50. |

General procedure for the synthesis of 4,5-dihydro-1*H*-pyrazoles 8a-e, 9a-e

A solution of N2H4·H2O (0.3 ml, 5 mmol) in i-PrOH (4 ml) was constantly stirred and treated by dropwise addition of a solution of the appropriate pyridylchalcone **6a-e** or **7a-e** (0,5 mmol) in AcOH (10 ml). The mixture was refluxed for 20 h, then it was cooled and poured into ice–water mixture (50 ml). The formed precipitate of 4,5-dihydro-1*H*-pyrazole **8a-e**, **9a-e** was filtered off, washed with H2O and air-dried. The crude product was purified by recrystallization or by silica gel column chromatography (compound **8b**).

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|  | **1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8a).** Beige crystals; m.p.: 198-200 °C (2-PrOH); yield: 137 mg (59%); IR (KBr): = 1670 (C=O), 1536, 1350 (NO2) cm-1; 1H (400 MHz, CDCl3): *δ* = 2.40 (s, 3H, COCH3), 2.55 (dd, 2*J* = 16.8 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 2.74 (s, 3H, CH3), 3.29 (dd, 2*J* = 18.4 Hz, 3*J* = 12.3 Hz, 1H, 4-CH2 pyrazole), 5.62 (dd, 3*J* = 10.7 Hz, 3*J* = 4.6 Hz1H,, 5-CH pyrazole), 6.36 (br. s, 1H, H-4 furan), 6.64 (d, *J* = 3.1, 1H, H-3 furan), 7.17 (br. s, 3H, H-3',4',5' Ph), 7.27 – 7.32 (m, 1H, H-4 Ph), 7.33 - 7.39 (m, 2H, H-2',6' Ph), 7.48 (s, 3H, H-3,5 Ph, H-5 furan), 7.60 (d, *J* = 7.6 Hz, 2H, H-2',6' Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 21.9 (CH3), 24.2 (COCH3), 45.5 (4-CH2 pyrazole), 59.6 (5-CH pyrazole), 112.1, 114.4, 124.7, 125.3 (2C Ph), 127.7, 127.9 (3C Ph), 128.9 (4C Ph), 130.1, 131.0, 135.2, 140.9, 143.3, 145.3, 150.4, 152.1, 159.2, 169.0 (COCH3) ppm; anal. calcd for C27H22N4O4: C 69.52, H 4.75, N 12.01, found C 69.31, H 4.97, N 12.26. |
|  | **1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9a).** Yellow crystals; m.p.: 191-193 °C (2-PrOH); yield: 96 mg (48%); IR (KBr): = 1670 (C=O), 1536, 1350 (NO2) cm-1; 1H (400 MHz, CDCl3, δ ppm): *δ* = 2.45 (s, 3H, COCH3), 3.05 (s, 3H, CH3), 3.26 (dd, 2*J* = 16.8 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 3.87 (dd, 2*J* = 16.8 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.64 (dd, 3*J* = 12.2 Hz, 3*J* = 4.6 Hz, 1H, 5-CH pyrazole), 7.22 – 7.36 (m, 5H, H-2',3',4',5',6' Ph), 7.49 (m, 3H, H-3,4,5 Ph), 7.59 (d, *J* = 7.63 Hz, 2H, H-2,6 Ph), 8.10 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.1 (CH3), 27.2 (COCH3), 43.9 (4-CH2 pyrazole), 59.6 (5-CH pyrazole), 125.1, 125.4 (2C Ph), 128.0, 128.3 (2C Ph), 128.8 (2C Ph), 129.1 (2C Ph), 130.1, 131.9, 135.8, 141.0, 143.7, 150.2, 151.4, 161.1, 169.0 (COCH3) ppm; anal. calcd for C23H20N4O3: C 68.99, H 5.03, N 13.99, found C 68.78, H 5.2, N 14.20. |
|  | **1-[5-(furan-2-yl)-3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8b).** Beige crystals; m.p.: 176-178 °C (SiO2, EtOAc-hexane (1:3)); yield: 68 mg (30%); IR (KBr): = 1665 (C=O), 1542, 1358 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.32 (s, 3H, COCH3), 2.77 (s, 3H, CH3), 2.97 (dd, 2*J* = 18.3 Hz, 3*J* = 6.1 Hz, 1H, 4-CH2 pyrazole), 3.11 (dd, 2*J* = 18.3 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.66 (dd, 3*J* = 12.2 Hz, 3*J* = 4.6 Hz, 1H, 5-CH pyrazole), 6.33 (d, 3*J* = 4.6 Hz, 1H, H-4' furan), 6.36 (d, 3*J* = 3.1 Hz, 1H, H-3' furan), 6.50 (br. s, 1H, H-4 furan), 6.71 (d, *J* = 3.1 Hz, 1H, H-3 furan), 7.34 (br. s, 1H, H-5' furan), 7.45 – 7.54 (m, 4H, H-3,4,5 Ph, H-5 furan), 7.60 - 7.62 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.0 (CH3), 24.0 (COCH3), 41.2 (4-CH2 pyrazole), 53.3 (5-CH pyrazole), 107.9, 110.7, 112.3, 114.7, 124.5, 128.0 (2C Ph), 128.9 (2C Ph), 130.2, 130.9, 135.3, 142.0, 143.0, 143.5, 145.5, 150.7, 151.3, 152.4, 159.4, 169.2 (COCH3) ppm; anal. calcd for C25H20N4O5: C 65.78, H 4.42, N 12.27, found C 65.55, H 4.14, N 12.53. |
|  | **1-[5-(furan-2-yl)-3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9b).** Bright-yellow crystals; m.p.: 141-142 °C (CHCl3-hexane); yield: 59 mg (30%); IR (KBr): = 1667 (C=O), 1545, 1347 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.42 (s, 3H, -COCH3), 3.04 (s, 3H, CH3), 3.56 (dd, 2*J* = 16.7 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 3.70 (dd, 2*J* = 18.4 Hz, 3*J* = 10.6 Hz, 1H, 4-CH2 pyrazole), 5.74 (dd, 3*J* = 10.6 Hz, 3*J* = 4.6 Hz, 1H, 5-CH pyrazole), 6.36 (br. s, 1H, H-4 furan), 6.40 (br. s, 1H, H-3 furan), 7.33 (br. s, 1H, H-5 furan), 7.47-7.52 (m, 3H, H-3,4,5 Ph), 7.59-7.64 (m, 2H, H-2,6 Ph), 8.17 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.1 (CH3), 27.1 (COCH3), 39.6 (4-CH2 pyrazole), 53.0 (5-CH pyrazole), 108.3, 110.7, 125.0, 128.3 (2C Ph), 128.8 (2C Ph), 130.1, 132.0, 135.9,142.2, 143.7, 150.4, 151.1, 151.4, 161.2, 169.1 (COCH3) ppm; anal. calcd for C21H18N4O4: C 64.61, H 4.65, N 14.35, found C 64.90, H 4.39, N 14.07. |
|  | **1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8c).** Beige crystals; m.p.: 189-190 °C (2-PrOH); yield: 111 mg (47%); IR (KBr): = 1676 (C=O), 1534, 1349 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.35 (s, 3H, -COCH3), 2.75 (s, 3H, CH3), 2.81 (dd, 2*J* = 18.4 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 3.23 (dd, 2*J* = 18.4 Hz, 3*J* =12.2 Hz, 1H, 4-CH2 pyrazole), 5.87 (dd, 3*J* = 10.6 Hz, 3*J* = 4.6 Hz, 1H, 5-CH pyrazole), 6.44 (br. s, 1H, H-4 furan), 6.66 (d, *J* = 4.6 Hz, 1H, H-3 furan), 6.94-6.96 (m, 2H, H-3,4 thiophene), 7.23 (d, *J =* 4.5 Hz, 1H, H-5 thiophene), 7.33 (br. s, 1H, H-5 furan), 7.42-7.51 (m, 3H, H-3,4,5 Ph,), 7.57-7.65 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.0 (CH3), 24.2 (COCH3), 45.3 (4-CH2 pyrazole), 55.3 (5-CH pyrazole), 112.3, 114.6, 124.5, 124.66, 124.69, 126.9, 127.9 (2C Ph), 128.9 (2C Ph), 130.2, 131.0, 135.2, 143.1, 143.4, 143.9, 145.4, 150.6, 152.0, 159.2, 169.2 (COCH3) ppm; anal. calcd for C25H20N4O4S: C 63.55, H 4.27, N 11.86, found C 63.78, H 4.03, N 11.61. |
|  | **1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9c).** Beige crystals; m.p.: 174-175 °C (2-PrOH); yield: 169 mg (83%); IR (KBr): = 1676 (C=O), 1534, 1349 (NO2) cm-1; 1H NMR (400 MHz, CDCl3,): *δ* = 2.43 (s, 3H, COCH3), 3.04 (s, 3H, CH3), 3.43 (dd, 2*J* = 16.7 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 3.84 (dd, 2*J* = 16.8 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.96 (dd, 3*J* = 12.2 Hz, 3*J* = 3.1 Hz, 1H, 5-CH pyrazole), 6.96 (dd, *J* = 4.6 Hz, 3.1 Hz, 1H, H-4 thiophene), 7.06 (d, *J* = 3.1 Hz, 1H, H-3 thiophene), 7.23 (d, *J* = 4.6 Hz, 1H, H-5 thiophene), 7.44-7.54 (m, 3H, H-3,4,5 Ph), 7.56-7.65 (m, 2H, H-2,6 Ph), 8.14 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.1 (CH3), 27.0 (COCH3), 43.6 (4-CH2 pyrazole), 55.0 (5-CH pyrazole), 124.8, 125.0, 125.1, 127.0, 128.3 (2C Ph), 128.8 (2C Ph), 130.1, 131.9, 135.8, 143.4, 143.7, 150.2, 151.5, 161.1, 169.1 (COCH3) ppm; anal. calcd for C21H18N4O3S: C 62.06, H 4.46, N 13.78, found C 61.80, H 4.19, N 13.55. |
|  | **1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(3-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8d).** Beige crystals; m.p.: 165-168 °C (CH2Cl2-hexane); yield: 128 mg (50%); IR (KBr): = 1679 (C=O), 1534, 1345 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.41 (s, 3H, COCH3), 2.56 (dd, 2*J* = 18.3 Hz, 3*J* = 6.1 Hz, 1H, 4-CH2 pyrazole), 2.77 (s, 3H, CH3), 3.36 (dd, 2*J* = 18.3 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.64 (dd, 3*J* = 12.2 Hz, 3*J* = 6.1 Hz, 1H, 5-CH pyrazole), 6.43 (d, *J* = 3.0 Hz, 1H, H-4 furan), 6.69 (d, *J* = 3.1 Hz, 1H, H-3 furan), 7.35 (br. s, 1H, H-5 furan), 7.45-7.51 (m, 3H, H-3,4,5 Ph), 7.54-7.58 (m, 2H, H-5,6 Ar), 7.62 (d, *J* = 7.6 Hz, 2H, H-2,6 Ph), 8.06 (s, 1H, H-2 Ar), 8.18 (dd, *J* = 6.1 Hz, 3.1 Hz, 1H, H-4 Ar) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 21.9 (CH3), 24.2 (COCH3), 45.3 (4-CH2 pyrazole), 59.2 (5-CH pyrazole), 112.4, 114.5, 120.5, 122.9, 124.3, 127.9 (2C Ph), 128.9 (2C Ph), 130.0, 130.3, 131.1, 132.0, 135.1, 143.2, 143.3, 143.4, 145.3, 148.6, 150.7, 151.8, 159.1, 169.4 (COCH3) ppm; anal. calcd for C27H21N­5O6: C 63.40, H 4.14, N 13.69, found C 63.71, H 4.34, N 13.35. |
|  | **1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(3-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9d).** Beige crystals; m.p.: 181-182 °C (2-PrOH); yield: 171 mg (77%); IR (KBr): = 1679 (C=O), 1534, 1345 (NO2) cm-1. 1H NMR (400 MHz, CDCl3): *δ* = 2.48 (s, 3H, COCH3), 3.06 (s, 3H, CH3), 3.29 (dd, 2*J* = 16.8 Hz, 3*J* = 6.1 Hz, 1H, 4-CH2 pyrazole), 3.96 (dd, 2*J* = 18.3 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.71 (dd, 3*J* = 12.2 Hz, 3*J* = 6.1 Hz, 1H, 5-CH pyrazole), 7.47-7.54 (m, 3H, H-3,4,5 Ph), 7.54-7.64 (m, 4H, H-2,6 Ph, H-5,6 Ar), 8.10 (br. s, 2H, H-2 Ar, H-4 pyridine), 8.18 (d, *J* = 7.6 Hz, 1H, H-4 Ar) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.0 (CH3), 27.2 (COCH3), 43.6 (4-CH2 pyrazole), 59.0 (5-CH pyrazole), 120.6, 123.1, 124.5, 128.3 (2C Ph), 128.8 (2C Ph), 130.2 (2С Ar), 132.0 (2С Ar), 135.7, 143.0, 143.6, 148.7, 150.1, 151.7, 161.2, 169.3 (COCH3) ppm; anal. calcd for C23H19N­5O5: C 62.02, H 4.30, N 15.72, found C 61.83, H 4.59, N 15.97. |
|  | **1-[5-(4-fluorophenyl)-3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8e).** Beige crystals; m.p.: 181-183 °C (2-PrOH); yield: 157 mg (65%); IR (KBr): = 1667 (C=O), 1535, 1345 (NO2) cm-1; 1H NMR (400 MHz, CDCl3): *δ* = 2.38 (s, 3H, COCH3), 2.53 (dd, 2*J* = 18.3 Hz, 3*J* = 4.5 Hz, 1H, 4-CH2 pyrazole), 2.73 (s, 3H, CH3), 3.27 (dd, 2*J* = 18.3 Hz, 3*J* = 12.2 Hz, 1H, 4-CH2 pyrazole), 5.56 (dd, 3*J* = 12.2 Hz, 3*J* = 4.5 Hz, 1H, 5-CH pyrazole), 6.40 (br. s, 1H, H-4 furan), 6.64 (d, *J* = 4.5 Hz, 1H, H-3 furan), 7.04 (t, *J* = 9.1 Hz, 2H, H-3,5 Ar), 7.11-7.15 (m, 2H, H-2,6 Ar), 7.26 (br. s, 1H, H-5 furan), 7.43-7.48 (m, 3H, H-3,4,5 Ph), 7.58-7.63 (m, 2H, H-2,6 Ph) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 21.9 (CH3), 24.2 (COCH3), 45.5 (4-CH2 pyrazole), 59.0 (5-CH pyrazole), 112.2, 114.4, 115.8 (d, 2*J*C-F= 22.1 Hz, 2C Ar), 124.7, 127.1 (d, 3*J*C-F= 8.6 Hz, 2C Ar), 128.0 (2C Ph), 128.9 (2C Ph), 130.2, 131.0, 135.2, 136.8, 143.3, 143.4, 145.2, 150.5, 151.9, 159.1, 162.1 (d, 1*J*C-F= 246.3 Hz), 169.1 (COCH3) ppm; anal. calcd for C27H21FN­4O4: C 66.94, H 4.37, N 11.56, found C 66.70, H 4.65, N 11.91. |
|  | **1-[5-(4-fluorophenyl)-3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9e).** Yellow crystals; m.p.: 196-198 °C (2-PrOH); yield: 82 mg (39%); IR (KBr): = 1667 (C=O), 1511, 1409 (NO2) cm‑1; 1H NMR (400 MHz, CDCl3): *δ* = 2.42 (s, 3H, COCH3), 3.03 (s, 3H, CH3), 3.21 (dd, 2*J* = 17.9 Hz, 3*J* = 4.6 Hz, 1H, 4-CH2 pyrazole), 3.84 (dd, 2*J* = 17.9 Hz, 3*J* = 11.9 Hz, 1H, 4-CH2 pyrazole), 5.59 (dd, 3*J* = 11.9 Hz, 3*J* = 4.6 Hz, 1H, 5-CH pyrazole), 6.97-7.09 (m, 2H, H-3,5 Ar), 7.15-7.23 (m, 2H, H-2,6 Ar), 7.42-7.51 (m, 3H, H-3,4,5 Ph), 7.54-7.62 (m, 2H, H-2,6 Ph), 8.07 (s, 1H, H-4 pyridine) ppm; 13C NMR (100 MHz, CDCl3): *δ* = 22.1 (CH3), 27.1 (COCH3), 43.8 (4-CH2 pyrazole), 59.0 (5-CH pyrazole), 116.0 (d, 2*J*C-F= 22.0 Hz, 2C Ar), 124.9, 127.3 (d, 3*J*C-F= 7.6 Hz, 2C Ar), 128.3 (2C Ph), 128.8 (2C Ph), 130.1, 131.9, 135.8, 136.9, 143.7, 150.2, 151.5, 161.1, 162.3 (d, 1*J*C-F= 244.4 Hz), 169.1 (COCH3) ppm; anal. calcd for C23H19FN­4O3: C 66.02, H 4.58, N 13.39, found C 66.31, H 4.29, N 13.5. |

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Copies of NMR Spectra of Products

**1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-phenylprop-2-en-1-one (6a)**

**1H NMR (400 MHz, CDCl3)**

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**13C NMR (100 MHz, CDCl3)**



**1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-phenylprop-2-en-1-one (7a)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**3-(furan-2-yl)-1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (6b)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**3-(furan-2-yl)-1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (7b)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one (6c)**

**1H NMR (400 MHz, CDCl3)**



**13С NMR (100 MHz, CDCl3)**



**1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one (7c)**

**1H NMR (400 MHz, CDCl3)**



**13С NMR (100 MHz, CDCl3)**



**1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(3-nitrophenyl)prop-2-en-1-one (6d)**

**1H NMR (400 MHz, CDCl3)**



**13С NMR (100 MHz, CDCl3)**



**1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-3-(3-nitrophenyl)prop-2-en-1-one (7d)**

**1H NMR (400 MHz, CDCl3)**



**13С NMR (100 MHz, CDCl3)**



**3-(4-fluorophenyl)-1-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (6e)**

**1H NMR (400 MHz, CDCl3)**



**13С NMR (100 MHz, CDCl3)**



**3-(4-fluorophenyl)-1-(2-methyl-5-nitro-6-phenylpyridin-3-yl)prop-2-en-1-one (7e)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (8a)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (9a)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[5-(furan-2-yl)-3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (8b)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[5-(furan-2-yl)-3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (9b)**

**1H NMR (400 MHz, CDCl3)**



**1H NMR (400 MHz, CDCl3)**



**1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (8c)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (9c)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(3-nitrophenyl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (8d)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-5-(3-nitrophenyl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (9d)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[5-(4-fluorophenyl)-3-(4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (8e)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**



**1-[5-(4-fluorophenyl)-3-(2-methyl-5-nitro-6-phenylpyridin-3-yl)-4,5-dihydro-1*H-*pyrazol-1-yl]ethan-1-one (9e)**

**1H NMR (400 MHz, CDCl3)**



**13C NMR (100 MHz, CDCl3)**

