A Novel One-pot Method for the Preparation of Pyrazoles by 1,3-Dipolar Cycloadditions of Diazo Compounds Generated *In Situ*

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1. General Methods

Flash chromatography was performed on silica gel (Merck Kieselgel 60 F₂₅₄ 230-400 mesh). TLC was carried out on aluminium backed silica plates (0.2 mm, 60 F₂₅₄) which were developed using standard visualising agents: UV fluorescence (254 and 366 nm), ninhydrin/ Δ , phosphomolybdic acid/ Δ , anisaldehyde/ Δ , permanganate/ Δ . Melting points (m.p.) were determined on a Khöfler hot stage. Infrared spectras were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using an ATR sample accessory unless otherwise specified. Only selected absorbencies ($\epsilon_{\text{max}}/\text{cm}^{-1}$) are reported. Optical rotations were measured using a Perkin-Elmer 241MC polarimeter. $[\alpha]_{\text{D}}^{20}$ values are given in $10^{-1} \text{ deg mL mg}^{-1}$. ^1H NMR spectras were recorded at 270, 300 or 400 MHz on Delta GX/270, Eclipse-300 or Delta GX/400 instruments at rt unless otherwise specified. Chemical shifts (δ_{H}) are quoted in parts per million (ppm) and referenced to TMS. ^{13}C NMR spectras were recorded at 68, 75 or 100 MHz on Delta GX/270, Eclipse-300 or Delta GX/400 instruments at rt unless otherwise specified. Chemical shifts (δ_{C}) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak and are assigned as s, d, t, q for C, CH, CH₂ and CH₃. Degenerate peaks were prefixed by the number of carbons. DEPT ^{13}C NMR spectras are reported instead of simple ^{13}C NMR spectras in those cases when quaternary carbons were not recorded in ^{13}C NMR spectras, most probably due to longer relaxation times which is a consequence of the neighboring nitrogen atoms present in highly conjugated systems.¹ Low resolution mass spectras (m/z) were recorded on a Micromass Analytical Autospec spectrometer with only molecular ions (M^+ or $[\text{M}+\text{H}]^+$), and major peaks being reported with intensities quoted as percentages of the base peak. High-resolution mass spectras were recorded on a Micromass Analytical Autospec spectrometer. Microanalyses were performed using a Carlo Erba EA1108. GC-MS analysis were performed using an Agilent 6890 apparatus equipped with a capillary column HP-5MS (HP190915-433, 5% Phenyl Methyl Siloxane, 30 m $\times$ 250 μm $\times$ 0.25 μm nominal) under the following conditions: helium 1 mL/min (constant flow mode), injector 250°C (splitless

mode), detector EI (agilent MSD 5973), oven 70°C (3 min), 15°C/min (15.3 min), 300°C (8 min). All chemicals were purchased from common chemical suppliers and used as delivered.

2. Synthesis of 3,5-Disubstituted Pyrazoles

Representative Procedure for the Preparation of 3-Phenyl-5-substituted Pyrazoles (table 1)

Benzaldehyde was added to a solution of *p*-toluenesulphonylhydrazide (279 mg, 1.5 mmol). After stirring for 3 h at RT, a solution of 5N NaOH (300 μ L, 1.5 mmol) was added and the mixture was stirred for a further 20 min. Phenylacetylene (823 μ L, 7.5 mmol) was added and the mixture was stirred at 50°C for 48 h. The volatiles were evaporated under reduced pressure and the residue was dissolved in a 1:1 mixture of water-ethyl acetate (70 mL). The organic layer was separated and dried over MgSO₄. After filtration and removal of the solvent under reduced pressure, the crude material was purified by flash chromatography (eluent petroleum ether/ethyl acetate 3:1) to afford 292 (202 mg, 61%) as an off white solid.

3,5-Diphenyl-1H-pyrazole (table 1, entry 1)²

White solid (61% yield); eluent petroleum ether/ethyl acetate 3:1, R_f = 0.35; m.p. 201-203°C (petroleum ether/ethyl acetate) (lit.,² 201°C); ¹H NMR (270 MHz, CDCl₃) • 6.85 (1H, s, Pz H-4), 7.28-7.42 (6H, m, Ph), 7.74 (4H, dd, J = 6.6 and 1.6 Hz, Ph); ¹³C NMR (68 MHz, CDCl₃) • 100.1 (d), 125.7 (4d), 128.2 (2d), 128.9 (4d), 134.4 (2s), 148.7; IR • /cm⁻¹_{max} 2829, 1460, 1272, 1180, 1074, 974, 974, 750, 685; MS m/z (EI) 220 (M⁺, 100), 191 (28), 165 (8), 104 (8), 77 (13).

4-(5-Phenyl-1H-3-pyrazolyl)benzonitrile (table 1, entry 2)

Yellow needles (61% yield); eluent DCM/MeOH 9:1, $R_f = 0.45$; m.p. 250-252°C (methanol); ^1H NMR (300 MHz, 105°C, d_6 -DMSO) • 7.18 (1H, s, Pz H-4), 7.34 (1H, t, $J = 7.3$ Hz, H_p -Ph), 7.45 (2H, t, $J = 7.3$ Hz, H_m -Ph), 7.80 (4H, m), 8.01 (2H, d, $J = 8.3$ Hz, H_o -ArCN), 11.98 (1H, br .s, NH); ^{13}C NMR (DEPT, 75 MHz, 105°C, d_6 -DMSO) • 101.4 (d), 125.9 (2d), 126.4 (2d), 128.6 (d), 129.3 (2d), 133.1 (2d); IR • cm^{-1} 2862, 2223, 1608, 1456, 1268, 1179, 1058, 974, 838, 755, 678; MS m/z (EI) 245 (M^+ , 100), 218 (38), 190 (12), 123 (12), 89 (10), 77 (16), 63 (6); HRMS: found 245.0955, $\text{C}_{16}\text{H}_{11}\text{N}_3$ requires 245.0953. Anal. Calc'd for $\text{C}_{16}\text{H}_{11}\text{N}_3$: C, 78.35; H, 4.52; N, 17.13. Found: C, 78.20; H, 4.18; N, 17.10.

3-(4-Methoxyphenyl)-5-phenyl-1H-pyrazole (table 1, entry 3)³

Colourless cubic solid (51% yield); eluent petroleum ether/ethyl acetate 3:1, $R_f = 0.20$; m.p. 160-162°C (methanol) (lit.,³ 166-168°C); ^1H NMR (400 MHz, CDCl_3) • 3.84 (3H, s, CH_3), 6.76 (1H, s, Pz H-4), 6.94 (2H, d, $J = 8.8$ Hz, ArOCH_3), 7.34 (1H, tt, $J = 7.1$ and 2.9 Hz, p -Ph), 7.42 (1H, tt, $J = 7.5$ and 2.8 Hz, m -Ph), 7.66 (2H, d, $J = 8.8$ Hz, ArOCH_3), 7.73 (2H, dt, $J = 7.5$ and 2.8 Hz, o -Ph); ^{13}C NMR (100 MHz, CDCl_3) • 55.4 (q), 99.5 (d), 114.3 (2d), 123.8 (s), 125.6 (2d), 126.9 (2d), 128.0 (d), 128.7 (2d), 131.4 (s), 148.3 (s), 148.9 (s), 159.7 (s); IR • cm^{-1} 2833, 1613, 1508, 1458, 1251, 1174, 1028, 974, 831, 760, 688; GC-MS retention time 18.14 min., m/z (EI) 250 (M^+ , 100), 235 (43), 207 (32), 178 (50), 152 (21), 77 (21).

3-(5-Phenyl-1H-3-pyrazolyl)pyridine (table 1, entry 4)⁴

White solid (33% yield); eluent petroleum ether/ethyl acetate 1:3, $R_f = 0.25$; m.p. 187-189°C (methanol) (lit.,⁴ 187-188°C ethanol); ^1H NMR (270 MHz, CDCl_3) • 6.76 (1H, s, Pz H-4), 7.18-7.34 (4H, m), 7.57 (2H, dt, $J = 7.0$ and 1.6 Hz, H_o -Ph), 8.01 (1H, dt, $J = 8.0$ and 1.9 Hz, H-4 Py), 8.34 (1H,

d, $J = 3.9$ Hz, H-6 Py), 8.82 (1H, d, $J = 1.9$ Hz, H-1 Py); ^{13}C NMR (DEPT, 68 MHz, CDCl_3) • 100.2 (d), 124.0 (d), 125.5 (2d), 128.4 (d), 128.8 (2d), 133.5 (d), 146.3 (d), 148.0 (d); IR • $_{\text{max}}/\text{cm}^{-1}$ 3114, 2827, 1572, 1435, 960, 799, 759, 681, 662; GC-MS retention time 17.09 min., m/z (EI) 221 (M^+ , 100), 192 (23), 207 (32), 178 (50), 152 (21), 77 (21).

Representative Procedure for the Preparation of 3-(3-Pyridinyl)-5-substituted-Pyrazoles (table 1)

Benzaldehyde was added to a solution of *p*-toluenesulphonylhydrazide (279 mg, 1.5 mmol). After stirring for 3 h at RT, a solution of 5N NaOH (300 •L, 1.5 mmol) was added and the mixture was stirred for a further 20 min. 3-Ethynylpyridine (773 mg, 7.5 mmol) was added and the mixture was stirred at 50°C for 48 h. The solvent was evaporated under reduced pressure and the residue was dissolved in a 1:1 mixture of water-ethyl acetate (70 mL). The organic layer was separated and dried over MgSO_4 . After filtration and removal of the solvent under reduced pressure, the crude material was purified by flash chromatography (eluent petroleum ether/ethyl acetate 1:3) to afford 295 (120 mg, 36%) as an off white solid.

4-[5-(3-Pyridyl)-1H-3-pyrazolyl]benzonitrile (table 1, entry 6)

White solid (19% yield); eluent DCM/MeOH 9:1, $R_f = 0.5$; m.p. 250-252•C (DCM/MeOH); ^1H NMR (300 MHz, 60•C, d_6 -DMSO) • 7.36 (1H, s, Pz H-4), 7.46 (1H, dd, $J = 7.9$ and 4.8 Hz, H-5 Py), 7.86 (2H, d, $J = 8.2$, H_m -ArCN), 8.00 (2H, d, $J = 8.2$ Hz, H_o -ArCN), 8.15 (1H, d, $J = 7.9$ Hz, H-4 Py), 8.54 (1H, dd, $J = 4.8$ and 1.3 Hz, H-6 Py), 9.05 (1H, d, $J = 1.3$ Hz, H-1 Py), 12.29 (1H, br .s, NH); ^{13}C NMR (DEPT, 75 MHz, 60•C, d_6 -DMSO) • 102.1 (d), 124.3 (d), 126.5 (2d), 133.0 (2d), 133.2 (d), 147.2 (d), 149.5 (d); IR • $_{\text{max}}/\text{cm}^{-1}$ 2853, 2223, 1739, 1612, 1570, 1504, 1458, 1411, 1380, 963, 840, 799, 705; MS m/z (EI) 246 (M^+ , 100), 217 (16), 190 (12), 164 (10); HRMS: found 246.0904, $\text{C}_{15}\text{H}_{10}\text{N}_4$ requires 246.0905. Anal. Calc'd for $\text{C}_{15}\text{H}_{10}\text{N}_4$: C, 73.16; H, 4.09; N, 22.75. Found: C, 73.01; H, 3.70; N, 22.51.

3-[3-(4-Methoxyphenyl)-1H-5-pyrazolyl]pyridine (table 1, entry 7)

White solid (54% yield); eluent DCM/MeOH 9:1, $R_f = 0.28$; m.p. 203-205°C (methanol); ^1H NMR (300 MHz, 110°C, d_6 -DMSO) • 3.77 (3H, s, OCH_3), 6.99 (2H, d, $J = 8.6$ Hz, $\text{H}_o\text{-ArOCH}_3$), 7.01 (1H, s, Pz H-4), 7.37 (1H, dd, $J = 7.7$ and 4.8 Hz, H-5 Py), 7.72 (2H, d, $J = 8.2$, $\text{H}_m\text{-ArOCH}_3$), 8.12 (1H, dt, $J = 7.9$ and 1.9 Hz, H-4 Py), 8.50 (1H, dd, $J = 4.8$ and 1.3 Hz, H-6 Py), 9.03 (1H, d, $J = 1.3$ Hz, H-1 Py), 11.74 (1H, br .s, NH); ^{13}C NMR (DEPT, 75 MHz, 105°C, d_6 -DMSO) • 55.8 (q), 99.9 (d), 115.0 (d), 124.1 (d), 127.3 (2d), 132.9 (2d), 147.1 (d), 149.0 (d); IR • $_{\text{max}}/\text{cm}^{-1}$ 3129, 3029, 2835, 1619, 1514, 1504, 1432, 1303, 1256, 1184, 1169, 1074, 1025, 973, 839, 795, 697; GC-MS retention time 18.26 min., m/z (EI) 251 (M^+ , 100), 236 (35), 208 (22), 152 (20); HRMS: found 251.1059, $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$ requires 251.1059. Anal. Calc'd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.30; H, 5.19; N, 16.76.

3-[5-(3-Pyridyl)-1H-3-pyrazolyl]pyridine (table 1, entry 8)⁵

White solid (24% yield); eluent DCM/MeOH 19:1, $R_f = 0.30$; m.p. 223-225°C (DCM/MeOH) (lit.,⁵ 230.5-232°C isopropanol); ^1H NMR (400 MHz, CDCl_3) • 6.95 (1H, s, Pz H-4), 7.38 (2H, dd, $J = 7.7$ and 4.8 Hz, H-5 Py), 8.12 (2H, d, $J = 7.7$ Hz, H-4 Py), 8.46 (2H, m, H-6 Py), 8.90 (2H, m, H-1 Py); ^{13}C NMR (DEPT, 100 MHz, CDCl_3) • 100.8 (d), 124.1 (2d), 133.6 (2d), 146.2 (2d), 148.4 (2d); IR • $_{\text{max}}/\text{cm}^{-1}$ 3113, 2820, 1414, 1025, 960, 798, 704, 693; GC-MS retention time 17.80 min., m/z (EI) 222 (M^+ , 100), 193 (13), 166 (11), 140 (15), 118 (15), 78 (20), 63 (26), 51 (28).

3. Preparation of 3-Substituted Pyrazoles

Representative Procedure for the Preparation of 3-Substituted Pyrazoles (table 2)

Benzaldehyde was added to a solution of *p*-toluenesulphonylhydrazide (279 mg, 1.5 mmol). After stirring for 3 h at RT, a solution 5N NaOH (300 μ L, 1.5 mmol) was added and the mixture was stirred for a further 20 min. 1-Vinylimidazole (679 μ L, 7.5 mmol) was added and the mixture was stirred at 50°C for 48 h. The volatiles were evaporated under reduced pressure and the residue was dissolved in a 1:1 mixture of water-ethyl acetate (70 mL). The organic layer was separated and dried over MgSO₄. After filtration and removal of the solvent under reduced pressure, the crude material was purified by flash chromatography (eluent petroleum ether/ethyl acetate 3:1) to afford 3-(Phenyl)-1*H*-pyrazole (121 mg, 56%) as a white solid.

3-(Phenyl)-1*H*-pyrazole (table 2, entry 1)⁶

White solid (56% yield); eluent petroleum ether/ethyl acetate 3:1, R_f = 0.40; m.p. 102-104°C (petroleum ether/ethyl acetate) (lit.,⁶ 99°C); ¹H NMR (400 MHz, CDCl₃) • 6.63 (1H, d, J = 2.2 Hz, Pz H-4), 7.34 (1H, tt, J = 7.4 and 2.6 Hz, *p*-Ph), 7.42 (1H, tt, J = 8.8 and 2.0 Hz, *m*-Ph), 7.63 (1H, d, J = 2.2 Hz, Pz H-5), 7.75 (1H, d, J = 8.8 Hz, *o*-Ph), 10.24 (1H, br. s, NH); ¹³C NMR (68 MHz, CDCl₃) • 102.7 (d), 125.9 (2d), 128.1 (d), 128.8 (2d), 132.2 (s), 133.4 (d), 149.8 (s); IR •_{max}/cm⁻¹ 3160, 2917, 1455, 1353, 1071, 1047, 952, 917, 825, 749, 693; GC-MS retention time 11.35 min., m/z (EI) 144 (M⁺, 100), 115 (42), 89 (22), 77 (22), 63 (14), 51 (14).

3-(2-Methylphenyl)-1*H*-pyrazole (table 2, entry 2)

Off white solid (47% yield); eluent petroleum ether/ethyl acetate 3:1, R_f = 0.2; m.p. 46-48°C (petroleum ether/ethyl acetate); ¹H NMR (270 MHz, CDCl₃) • 2.41 (3H, s, CH₃), 6.39 (1H, d, J = 2.3 Hz, Pz H-4), 7.16-7.29 (3H, m, Ar), 7.46 (1H, d, J = 7.2 Hz, *o*-Ar), 7.49 (1H, d, J = 2.3 Hz, Pz H-5), 11.23 (1H, br. s, NH); ¹³C NMR (68 MHz, CDCl₃) • 20.9 (q), 105.5 (d), 126.0 (d), 128.3 (d), 129.3 (d),

130.9 (d), 131.6 (s), 134.2 (d), 136.2 (s), 147.2 (s); IR $\bullet_{\text{max}}/\text{cm}^{-1}$ 3163, 2921, 1449, 1038, 953, 932, 752, 722; GC-MS retention time 11.72 min., m/z (EI) 158 (M^+ , 100), 130 (88), 103 (15), 77 (15), 63 (13), 51 (12); HRMS: found 158.0841, $\text{C}_{10}\text{H}_{10}\text{N}_2$ requires 158.0844. Anal. Calc'd for $\text{C}_{10}\text{H}_{10}\text{N}_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.99; H, 6.25; N, 18.08.

3-(4-Chlorophenyl)-1H-pyrazole (table 2, entry 5)⁶

White solid (71% yield); eluent petroleum ether/ethyl acetate 3:1, $R_f = 0.2$; m.p. 184-186°C (petroleum ether/ethyl acetate) (lit.,⁷ 195-197°C); ^1H NMR (270 MHz, CDCl_3) $\bullet$ 6.55 (1H, d, $J = 2.0$ Hz, Pz H-4), 7.31 (2H, d, $J = 8.8$ Hz, *o*-Ar), 7.55 (1H, d, $J = 2.0$ Hz, Pz H-5), 7.64 (2H, d, $J = 8.8$ Hz, *m*-Ar), 11.81 (1H, br. s, NH); ^{13}C NMR (68 MHz, CDCl_3) $\bullet$ 102.8 (d), 127.2 (2d), 129.0 (2d), 130.9 (d), 132.7 (s), 133.9 (s), 148.8 (s); IR $\bullet_{\text{max}}/\text{cm}^{-1}$ 3162, 2919, 1510, 1447, 1090, 1047, 1012, 953, 832, 757, 734; GC-MS retention time 13.05 min., m/z (EI) 178 (M^+ , 100), 151 (13), 115 (34), 89 (17), 75 (15), 63 (13).

4-(1H-3-Pyrazolyl)benzonitrile (table 2, entry 4)

White solid (79% yield); eluent petroleum ether/ethyl acetate 2:1, $R_f = 0.25$; m.p. 141-143°C (methanol); ^1H NMR (400 MHz, CDCl_3) $\bullet$ 6.71 (1H, d, $J = 2.3$ Hz, Pz H-4), 7.65 (1H, d, $J = 2.3$ Hz, Pz H-5), 7.68 (2H, d, $J = 8.6$ Hz, *o*-Ar), 7.90 (2H, d, $J = 8.6$ Hz, *m*-Ar), 8.90 (1H, br. s, NH); ^{13}C NMR (68 MHz, CDCl_3) $\bullet$ 103.6 (d), 111.3 (s), 119.0 (s), 126.2 (2d), 131.3 (d), 132.7 (2d), 137.3 (s), 149.2 (s); IR $\bullet_{\text{max}}/\text{cm}^{-1}$ 3281, 2222, 1608, 1174, 1044, 947, 843, 774; GC-MS retention time 14.26 min., m/z (EI) 169 (M^+ , 100), 140 (19), 115 (14), 89 (10), 75 (11), 63 (10), 51 (8); HRMS: found 169.0644, $\text{C}_{10}\text{H}_7\text{N}_3$ requires 169.0639.

3-(4-Methoxyphenyl)-1H-pyrazole (table 2, entry 3)⁸

White solid (62% yield); eluent petroleum ether/ethyl acetate 2:1, $R_f = 0.40$; m.p. 128-130°C (methanol) (lit.,⁸ 129-131°C); ^1H NMR (270 MHz, CDCl_3) • 3.82 (3H, s, OCH_3), 6.52 (1H, d, $J = 1.9$ Hz, Pz H-4), 6.92 (2H, d, $J = 8.8$ Hz, *o*-Ph), 7.58 (1H, d, $J = 1.9$ Hz, Pz H-5), 7.66 (2H, d, $J = 8.8$ Hz, *m*-Ph), 9.40 (1H, br .s, NH); ^{13}C NMR (68 MHz, CDCl_3) • 55.4 (q), 102.1 (d), 114.3 (2d), 124.8 (s), 127.2 (2d), 133.7 (d), 148.5 (s), 159.6 (s); IR •_{max}/cm⁻¹ 3113, 2838, 1610, 1508, 1453, 1438, 1248, 1180, 1096, 1026, 831, 772; GC-MS retention time 13.41 min., m/z (EI) 174 (M^+ , 100), 159 (64), 131 (61), 102 (12), 77 (26), 63 (10), 51 (11).

3-(1H-3-Pyrazolyl)pyridine (table 2, entry 8)⁹

White gum (32% yield); eluent ethyl acetate, $R_f = 0.28$; ^1H NMR (270 MHz, CDCl_3) • 6.68 (1H, d, $J = 1.2$ Hz, Pz H-4), 7.33 (1H, dd, $J = 7.6$ and 5.3 Hz, Py H-5), 7.64 (1H, d, $J = 1.2$ Hz, Pz H-5), 8.09 (1H, d, $J = 7.6$ Hz, Py H-4), 8.56 (1H, d, $J = 5.3$ Hz, Py H-6), 9.06 (1H, s, Py H-2); ^{13}C NMR (68 MHz, CDCl_3) • 102.9 (d), 123.8 (d), 129.0 (s), 131.8 (d), 133.3 (d), 147.1 (d), 147.5 (s), 148.7 (d); IR •_{max}/cm⁻¹ 3138, 2907, 1418, 1028, 924, 758, 703; GC-MS retention time 12.38 min., m/z (EI) 145 (M^+ , 100), 118 (10), 91 (8), 63 (15).

3-(3-Furyl)-1H-pyrazole (table 2, entry 6)

Orange solid (33% yield); eluent petroleum ether/ethyl acetate 2:1, $R_f = 0.25$; m.p. 93-95°C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, CDCl_3) • 6.40 (1H, d, $J = 2.2$ Hz, Pz H-4), 6.70

(1H, m, Fur H-4), 7.45 (1H, t, $J = 1.6$ Hz, Fur H-5), 7.57 (1H, d, $J = 2.2$ Hz, Pz H-5), 7.76 (1H, m, Fur H-2), 10.41 (1H, br .s, NH); ^{13}C NMR (100 MHz, CDCl_3) • 102.9 (d), 109.2 (d), 118.6 (s), 132.7 (d), 139.3 (d), 142.2 (s), 143.6 (d); IR •_{max}/cm⁻¹ 3139, 1614, 1520, 1348, 1192, 1153, 1047, 985, 895, 872, 796, 757; GC-MS retention time 9.80 min., m/z (EI) 134 (M^+ , 100), 105 (34), 79 (17), 51 (31); HRMS: found 134.0482, $\text{C}_7\text{H}_6\text{N}_2\text{O}$ requires 134.0480.

3-(2-Thienyl)-1H-pyrazole (table 2, entry 7)¹⁰

Off white solid (32% yield); eluent petroleum ether/ethyl acetate 3:1, $R_f = 0.17$; m.p. 90-92°C (petroleum ether/ethyl acetate) (lit.,¹⁰ 96.5-98 °C); ^1H NMR (270 MHz, CDCl_3) • 6.52 (1H, d, $J = 2.3$ Hz, Pz H-4), 7.05 (1H, dd, $J = 5.0$ and 3.7 Hz, Th H-4), 7.25 (1H, dd, $J = 5.0$ and 1.0 Hz, Th H-5), 7.33 (1H, dd, $J = 3.7$ and 1.0 Hz, Th H-3), 10.76 (1H, br .s, NH); ^{13}C NMR (68 MHz, CDCl_3) • 102.7 (d), 124.2 (d), 124.7 (d), 127.7 (d), 131.5 (d), 135.9 (s), 145.7 (s); IR •_{max}/cm⁻¹ 3161, 2918, 1563, 1473, 1408, 1048, 909, 845, 690; GC-MS retention time 11.59 min., m/z (EI) 150 (M^+ , 100), 121 (28), 96 (16), 78 (12).

4. NMR Spectras

5. References

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