Supporting Information

for

A New Entry to A Three Component Pyrimidine Synthesis by TMS-Ynones via Sonogashira-Coupling

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Experimental section

General Considerations. All reactions involving water sensitive compounds were carried out in oven dried Schlenk glassware under a nitrogen atmosphere. The solvents were dried according to standard procedures¹ and were distilled prior to use. Column chromatography: silica gel 60 M (Macherey-Nagel), mesh 230–400, aluminum oxide 5016 A basic Fluka. Thin layer chromatography (TLC): aluminum oxide layered aluminium foil (60 F₂₅₄ Merck, Darmstadt). Melting points (uncorrected): SMP3 from Bibby Sterling, UK. Phenylacetylene, 1-hexyne, trimethylsilylacetylene, (Ph₃P)₂PdCl₂, CuI, acyl chlorides, and the applied amines were purchased from ACROS or Merck and used without further purification. ¹H and ¹³C NMR spectra: Bruker ARX250, Bruker DRX300, CDCl₃ or [D₆]DMSO as solvents. The assignments of quaternary C, CH, CH₂ and CH₃ was made on the basis of DEPT spectra. IR: Bruker Vector 22 FT-IR. MS: Jeol JMS-700 and Finnigan TSQ-700. – Elemental analysis were carried out in the Microanalytical Laboratory of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg.

General Procedure for the synthesis of (trimethylsilyl)ethynyl ketones 3

The stirred mixture of 14 mg (0.02 mmol) of Pd(PPh₃)₂Cl₂, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed. Then 0.14 mL (1 mmol) of triethylamine, 1 mmol of acid chloride and 0.14 mL (1 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h at room temperature until the complete consumption of alkyne (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (pentane/diethylether 9:1), R_f ≅ 0.3.

1-(4-Methoxy-phenyl)-3-trimethylsilanyl-propynone (3a)

According to the GP from the reaction of 171 mg (1.00 mmol) of **1a** 191 mg (82 %) of **3a** were isolated after chromatography on silica gel as a colorless oil. ^1H NMR (CDCl_3 , 250 MHz): δ 0.32 (s, 9 H), 3.89 (s, 3 H), 6.96 (d, $J = 8.9$ Hz, 2 H), 8.12 (d, $J = 8.9$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -0.7 (CH_3), 55.5 (CH_3), 99.4 ($\text{C}_{\text{quat.}}$), 101.0 ($\text{C}_{\text{quat.}}$), 113.8 (CH), 129.9 ($\text{C}_{\text{quat.}}$), 132.0 (CH), 164.5 ($\text{C}_{\text{quat.}}$), 176.2 ($\text{C}_{\text{quat.}}$). EI +Q1MS (m/z (%)): 232 (M^+ , 55), 217 ($\text{M}^+ - \text{CH}_3$, 100), 135 ((MeOPhCO) $^+$, 56).

1-(4-Nitro-phenyl)-3-trimethylsilanyl-propynone (3b)

According to the GP from the reaction of 186 mg (1.00 mmol) of **1b** 162 mg (65 %) of **3b** were isolated after chromatography on silica gel as white crystals, Mp. 107-108 °C. ^1H NMR (CDCl_3 , 250 MHz): δ 0.12 (s, 9 H), 8.04-8.15 (m, 4 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -0.8 (CH_3), 100.1 ($\text{C}_{\text{quat.}}$), 103.5 ($\text{C}_{\text{quat.}}$), 123.8 (CH), 130.6 (CH), 140.6 ($\text{C}_{\text{quat.}}$), 150.9 ($\text{C}_{\text{quat.}}$), 175.6 ($\text{C}_{\text{quat.}}$). EI +Q1MS (m/z (%)): 247 (M^+ , 5), 232 ($\text{M}^+ - \text{CH}_3$, 100). Anal. calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_3\text{Si}$ (247.3): C, 58.28; H, 5.30; N, 5.66. Found: C, 58.51; H, 5.47; N, 5.81

1-(2-Bromo-phenyl)-3-trimethylsilanyl-propynone (3c)

According to the GP from the reaction of 185 mg (1.00 mmol) of **1c** 169 mg (61 %) of **3c** were isolated after chromatography on silica gel as a yellow oil. ^1H NMR (CDCl_3 , 250 MHz): δ 0.32 (s, 9 H), 7.35-7.50 (m, 2 H), 7.67-7.73 (m, 1 H), 8.04-8.09 (m, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -0.8 (CH_3), 101.5 ($\text{C}_{\text{quat.}}$), 101.6 ($\text{C}_{\text{quat.}}$), 121.3 ($\text{C}_{\text{quat.}}$), 127.3 (CH), 133.1 (CH), 133.4 (CH), 135.0 (CH), 136.9 ($\text{C}_{\text{quat.}}$), 176.9 ($\text{C}_{\text{quat.}}$).

Acetic acid 2-(3-trimethylsilanyl-propynoyl)-phenyl ester (3d)

According to the GP from the reaction of 199 mg (1.00 mmol) of **1d** 190 mg (73 %) of **3d** were isolated after chromatography on silica gel as a yellow oil. ^1H NMR (CDCl_3 , 250 MHz): δ 0.30 (s, 9 H), 2.36 (s, 3 H), 7.11 (d, $J = 7.9$ Hz, 1 H), 7.38 (t, $J = 7.9$ Hz, 1 H), 7.60 (t, $J = 7.9$ Hz, 1 H), 8.22 (d, $J = 7.9$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -0.9 (CH_3), 20.8 (CH_3), 99.9 ($\text{C}_{\text{quat.}}$), 101.2 ($\text{C}_{\text{quat.}}$), 123.9 (CH), 126.0 (CH), 128.7 ($\text{C}_{\text{quat.}}$), 133.4 (CH), 135.7 (CH), 150.0 ($\text{C}_{\text{quat.}}$), 169.2 ($\text{C}_{\text{quat.}}$), 175.4 ($\text{C}_{\text{quat.}}$). EI +Q1MS (m/z (%)): 260 (M^+ , 2), 245 ($\text{M}^+ - \text{CH}_3$, 42), 217 ($\text{M}^+ - \text{CH}_3\text{CO}$, 37), 203 ($\text{M}^+ - \text{CH}_3 - \text{CH}_2\text{CO}$, 100), 73 (Me_3Si^+ , 9). IR (neat): $\tilde{\nu}$ 2962 cm^{-1} , 2902, 2153, 2095, 1772, 1646, 1604, 1481, 1368, 1239, 1019, 849, 764. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 248 nm (8800), 266 (11700). HRMS calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Si}$: 260.0864. Found: 260.0881.

1-Thiophen-2-yl-3-trimethylsilanyl-propynone (3e)

According to the GP from the reaction of 147 mg (1.00 mmol) of **1e** 170 mg (82 %) of **3d** were isolated after chromatography on silica gel as a colorless oil. ^1H NMR (CDCl_3 , 250 MHz): δ 0.07 (s, 9 H), 6.93 (dd, $J = 4.9$ Hz, $J = 3.7$ Hz, 1 H), 7.48 (dd, $J = 4.9$ Hz, $J = 1.2$ Hz, 1 H), 7.69 (dd, $J = 3.7$ Hz, $J = 1.2$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -1.0 (CH_3), 98.8 ($\text{C}_{\text{quat.}}$), 100.2 ($\text{C}_{\text{quat.}}$), 128.6 (CH), 135.3 (CH), 135.4 (CH), 144.4 ($\text{C}_{\text{quat.}}$), 169.1 ($\text{C}_{\text{quat.}}$).

(E)-3-Diethylamino-1-phenyl-propenone (4)

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 141 mg (1.00 mmol) of benzoylchloride (**1f**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene

were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then 0.21 mL (2.00 mmol) of diethylamine in 5 mL of methanol were added. The reaction mixture was heated to reflux temp for 3 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on neutral alumina (hexane/ethylacetate 4:1) to give **4** as a light yellow oil. ^1H NMR (CDCl_3 , 300 MHz): δ 1.19 (t, $J = 7.2$ Hz, 6 H), 3.30 (q, $J = 7.2$ Hz, 4 H), 5.74 (d, $J = 12.5$ Hz, 1 H), 7.37-7.42 (m, 3 H), 7.79 (d, $J = 12.5$ Hz, 1 H), 7.84-7.88 (m, 2 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 11.6 (CH_3), 14.7 (CH_3), 42.7 (CH_2), 50.4 (CH_2), 91.6 (CH), 127.4 (CH), 128.3 (CH), 130.6 (CH), 140.7 (C_{quat}), 152.3 (CH), 188.6 (C_{quat}). EI +Q1MS (m/z (%)): 203 (M^+ , 46), 186 ($\text{M}^+ - \text{OH}$, 30), 105 (PhCO, 100). IR (neat): $\tilde{\nu}$ 2975 cm^{-1} , 2934, 1639, 1582, 1365, 1219, 1051, 707. UV/Vis (CHCl_3): λ_{max} (ϵ) 246 nm (11200), 340 (19400). HRMS calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}$: 203.1306. Found: 203.1314.

3-Oxo-3-thiophen-2-yl-propionaldehyde oxime (**5**)

$E/Z = 1:6$

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 140 mg (2.00 mmol) of hydroxylamine hydrochloride and 687 mg (2.4 mmol) of sodium carbonate decahydrate in 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 2 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (hexane/ethylacetate 4:1) to give 135 mg (80%) of **5** as a 6:1 mixture (determined by ^1H NMR) of geometrical isomers as yellow crystals, Mp. 113-114°C. ^1H NMR ($[\text{D}_6]$ DMSO, 300 MHz): δ 4.00 (d, $J = 5.3$ Hz, 2 H), 6.98 (t, $J = 5.3$ Hz, 1 H), 7.21-7.28 (m, 1 H), 7.98-8.04 (m, 2 H), 11.20 (s, 1 H, disappears upon addition of D_2O). Additional signals for the minor isomer: δ 3.90 (d, $J = 6.0$ Hz, 2 H), 7.21-7.28 (m, 1 H), 7.45 (t, $J = 6.0$ Hz, 1 H), 7.98-8.04 (m, 2 H), 10.80 (s, 1 H, disappears upon addition of D_2O). In the 2D-NOESY a cross-peak between protons of OH and CH groups for minor isomer appears. Therefore, the minor isomer is *E*-configured. ^{13}C NMR ($[\text{D}_6]$ DMSO, 75 MHz): δ 35.4 (CH_2), 128.8 (CH), 133.9 (CH), 135.3 (CH), 142.9 (CH), 143.2 (C_{quat}),

188.7 (C_{quat}). Additional signals for the minor isomer: δ 39.5 (CH₂), 128.8 (CH), 134.2 (CH), 135.3 (CH), 144.4 (CH), 189.6 (C_{quat}). EI +Q1MS (m/z (%)): 169 (M⁺, 4), 111 (2-ThCO⁺, 100). IR (KBr): $\tilde{\nu}$ 3206 cm⁻¹, 3102, 2861, 1654, 1515, 1414, 1213, 1083, 911, 827, 741. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) 264 nm (8400), 286 (6900). Anal. calcd. for C₇H₇NO₂S (169.2): C, 49.69; H, 4.17; N, 8.28. Found: C, 49.44; H, 4.13; N, 8.28.

3-(2-Hydroxyphenyl-1-amino)-1-(2-thienyl)-propenone (6)

A stirred mixture of 14 mg (0.02 mmol) of Pd(PPh₃)₂Cl₂, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 131 mg (1.20 mmol) of 2-hydroxyaniline in 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 2 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (hexane/ethylacetate 2:1) to give 150 mg (61%) of **6** as yellow crystals, Mp. 217-218°C. ¹H NMR ([D₆] DMSO, 300 MHz): δ 6.00 (d, J = 7.7 Hz, 1 H), 6.80-6.96 (m, 3 H), 7.18 (dd, J = 4.8 Hz, J = 3.7 Hz, 1 H), 7.38 (d, J = 7.7 Hz, 1 H), 7.78-7.88 (m, 3 H), 10.04 (s, 1 H, disappears upon addition of D₂O), 11.80 (d, J = 13.2 Hz, 1 H, disappears upon addition of D₂O). ¹³C NMR ([D₆] DMSO, 75 MHz): δ 93.1 (CH), 113.6 (CH), 115.3 (CH), 119.7 (CH), 123.4 (CH), 128.4 (CH), 128.9 (C_{quat}), 129.4 (CH), 132.3 (CH), 144.1 (CH), 145.7 (C_{quat}), 146.3 (C_{quat}), 182.3 (C_{quat}). EI +Q1MS (m/z (%)): 246 (M⁺ + 1, 18), 245 (M⁺, 100), 244 (M⁺ - 1, 64), 111 (2-ThCO⁺, 33). IR (KBr): $\tilde{\nu}$ 1631 cm⁻¹, 1300, 1255, 780, 743. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) 264 nm (9800), 288 (6700), 388 (24300). Anal. calcd. for C₁₃H₁₁NO₂S (245.3): C, 63.65; H, 4.52; N, 5.71. Found: C, 63.68; H, 4.60; N, 5.72.

3-(2-Aminophenyl-1-amino)-1-(2-thienyl)-propenone (7)

2 : 1

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 130 mg (1.2 mmol) of 1,2-diaminobenzene in 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 2 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (hexane/ethylacetate 2:1) to give 105 mg (43%) of **7** as a 2:1 mixture (determined by ^1H NMR) of tautomers as red crystals, Mp. 174-175°C. ^1H NMR ($[\text{D}_6]$ DMSO, 300 MHz): δ 4.84 (s, 2 H, disappears upon addition of D_2O), 6.01 (d, $J = 7.9$ Hz, 1 H), 6.80-6.90 (m, 3 H), 7.14-7.22 (m, 3 H), 7.75 (dd, $J = 12.4$ Hz, $J = 7.9$ Hz, 1 H), 7.80-7.82 (m, 1 H), 11.62 (d, $J = 12.4$ Hz, 1 H, disappears upon addition of D_2O). Additional signals for the minor isomer: δ 5.02 (s, 2 H, disappears upon addition of D_2O), 6.24 and 9.17 (2 br s, together 1 H, disappear upon addition of D_2O), 6.57-6.64 (m, 1 H), 7.02 (d, $J = 7.5$ Hz, 1 H), 7.61-7.64 (m, 1 H), 7.82-7.95 (m, 6 H). ^{13}C NMR ($[\text{D}_6]$ DMSO, 75 MHz): δ 93.0 (CH), 116.2 (CH), 117.3 (CH), 118.4 (CH), 124.4 (CH), 128.1 (C_{quat}), 128.5 (CH), 129.2 (CH), 132.3 (CH), 138.2 (C_{quat}), 146.5 (CH), 147.1 (C_{quat}), 182.2 (C_{quat}). Additional signals for the minor isomer: δ 115.8 (CH), 128.3 (CH), 128.9 (CH), 131.7 (CH), 132.2 (CH), 179.9 (C_{quat}). EI +Q1MS (m/z (%)): 246 ($\text{M}^+ + 2$, 5), 245 ($\text{M}^+ + 1$, 17), 244 (M^+ , 100), 243 ($\text{M}^+ - 1$, 54), 111 (2-ThCO $^+$, 17). IR (KBr): $\tilde{\nu}$ 3390 cm^{-1} , 3339, 1622, 1517, 1478, 1296, 1257, 1060, 982, 859, 772, 747. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 262 nm (10800), 284 (8800), 393 (20200). Anal. calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{OS}$ (244.3): C, 63.91; H, 4.95; N, 11.47. Found: C, 63.76; H, 4.97; N, 11.38.

4-Thiophen-2-yl-pyrimidin-2-ylamine (**8a**)

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of CH_3CN was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1.00 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 1.0 g (3.5 mmol) of $\text{Na}_2\text{CO}_3 \times 10 \text{ H}_2\text{O}$, 240 mg (2.50 mmol) of guanidinium hydrochloride and 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 14 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (ethylacetate) to give 90 mg (51 %) of **8a** as white crystals, Mp. 189-190 $^\circ\text{C}$ (methanol). ^1H NMR ($[\text{D}_6]$ DMSO, 250 MHz): δ 6.67 (s, 2 H), 7.07 (d, $J = 5.2$ Hz, 1 H), 7.19 (dd, $J = 4.9$ Hz, $J = 3.7$ Hz, 1 H), 7.73 (dd, $J = 5.2$ Hz, $J = 1.2$ Hz, 1 H), 7.89 (dd, $J = 3.7$ Hz, $J = 1.2$ Hz, 1 H), 8.25 (d, $J = 5.2$ Hz, 1 H). ^{13}C NMR ($[\text{D}_6]$ DMSO, 75 MHz): δ 104.3 (CH), 127.5 (CH), 128.4 (CH), 129.8 (CH), 142.8 (C_{quat}), 158.7 (CH), 158.9 (C_{quat}), 163.5 (C_{quat}). EI MS (m/z (%)): 177 (M, 100), 176 ($\text{M}^+ - \text{H}$, 44), 135 ($\text{M}^+ - \text{H}_2\text{NCN}$, 24). IR (KBr): $\tilde{\nu}$ 3186 cm^{-1} , 1643, 1557, 1461. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 248 (14379). Anal. calcd. for $\text{C}_8\text{H}_7\text{N}_3\text{S}$ (177.2): C, 54.22; H, 3.98; N, 23.71. Found: C, 54.03; H, 4.02; N, 23.58.

4-(4-Methoxyphenyl)-2-yl-pyrimidin-2-ylamin (**8b**)

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of CH_3CN was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 171 mg (1.00 mmol) of *p*-anisoyl chloride and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 1.0 g (3.5 mmol) of $\text{Na}_2\text{CO}_3 \times 10 \text{ H}_2\text{O}$, 240 mg (2.50 mmol) of guanidinium hydrochloride and 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 14 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (ethylacetate) to give 98 mg (49 %) of **8b** as white crystals, Mp. 191-192 $^\circ\text{C}$ (methanol). ^1H NMR ($[\text{D}_6]$ DMSO, 250 MHz): δ 3.83 (s, 3 H), 6.58 (s, 2 H), 7.02-7.08 (m, 3 H), 8.05 (d, $J = 9.1$ Hz, 2 H), 8.25 (d, $J =$

5.4 Hz, 1 H). ^{13}C NMR ($[\text{D}_6]$ DMSO, 75 MHz): δ 55.3 (CH_3), 105.0 (CH), 114.0 (CH), 128.2 (CH), 129.3 (C_{quat}), 158.7 (CH), 161.2 (C_{quat}), 163.1 (C_{quat}), 169.7 (C_{quat}). EI MS (m/z (%)): 201 (M^+ , 100), 200 ($\text{M}^+ - \text{H}$, 66), 186 ($\text{M}^+ - \text{CH}_3$, 9). Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$ (201.2): C, 65.66; H, 5.51; N, 20.88. Found: C, 65.47; H, 5.55; N, 20.60.

2-(4-Nitro-phenyl)-4-thiophen-2-yl-pyrimidine (**8c**)

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 1.0 g (3.5 mmol) of $\text{Na}_2\text{CO}_3 \times 10 \text{ H}_2\text{O}$, 243 mg (1.20 mmol) of *p*-nitrophenyl amidinium hydrochloride in 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 14 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (hexane/ethylacetate 2:1) to give 85 mg (30 %) of **8c** as brown crystals, Mp. 195 °C. ^1H NMR (CDCl_3 , 250 MHz): δ 7.24 (dd, $J = 5.1, 3.7$ Hz, 1H), 7.56 (d, $J = 5.2$ Hz, 1 H), 7.63 (dd, $J = 5.1, 1.2$ Hz, 1 H), 7.89 (dd, $J = 3.8, 1.2$ Hz, 1 H), 8.38 (d, $J = 9.1$ Hz, 2 H), 8.74 (d, $J = 9.1$ Hz, 2 H), 8.83 (d, $J = 5.2$ Hz, 1 H). ^{13}C NMR, 75 MHz): δ 113.8 (CH), 123.7 (CH), 128.1 (CH), 128.6 (CH), 129.2 (CH), 130.9 (CH), 142.1 (C_{quat}), 143.0 (C_{quat}), 149.4 (C_{quat}), 157.6 (CH), 159.5 (C_{quat}), 162.3 (C_{quat}). FAB^+ MS (m/z (%)): 283 (M^+ , 100). IR (KBr): $\tilde{\nu}$ 1574 cm^{-1} , 1562, 1521, 1444, 1345. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 274 nm (17000). Anal. calcd. for $\text{C}_{14}\text{H}_9\text{N}_3\text{O}_2\text{S}$ (283.3): C, 59.35; H, 3.20; N, 14.83. Found: C, 58.88; H, 3.31; N, 14.42.

2-(4-Methoxyphenyl)-4-(2-thienyl)pyrimidine (**8d**)

A stirred mixture of 14 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 7 mg (0.04 mmol) of CuI in 5 mL of THF was degassed for 5 min. Then 0.14 mL (1.00 mmol) of triethylamine, 147 mg (1 mmol) of 2-thienylacid chloride (**1e**) and 0.14 mL (1.00 mmol) of trimethylsilyl acetylene were added. The reaction mixture was stirred for 1 h under nitrogen at room temp until the alkyne was completely consumed (monitored by TLC). Then a solution of 1.0 g (3.5 mmol) of $\text{Na}_2\text{CO}_3 \times 10 \text{ H}_2\text{O}$, 224 mg (1.20 mmol) of *p*-methoxyphenyl amidinium hydrochloride in 5 mL of methanol was added. The reaction mixture was heated to reflux temp for 14 h until the conversion was complete (monitored by TLC). The solvents were evaporated and the residue was chromatographed on silica gel (hexane/ethylacetate 4:1) to give 217 mg (81 %) of **8d** as white crystals, Mp. 82 °C (pentane/ CH_2Cl_2).

^1H NMR (CDCl_3 , 250 MHz): δ 3.80 (s, 3 H), 6.93 (d, $J = 9.1$ Hz, 2 H), 7.08 (dd, $J = 5.1, 3.8$ Hz, 1 H), 7.28 (d, $J = 5.3$ Hz, 1 H), 7.45 (dd, $J = 5.1, 1.2$ Hz, 1 H), 7.71 (dd, $J = 3.8, 1.2$ Hz, 1 H), 8.41 (d, $J = 9.1$ Hz, 2 H), 8.62 (d, $J = 5.3$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 55.3 (CH_3), 112.0 (CH), 113.9 (CH), 127.4 (CH), 128.3 (CH), 129.9 (CH), 130.1 (CH), 143.0 (C_{quat}), 156.3 (C_{quat}), 157.1 (CH), 159.0 (C_{quat}), 162.0 (C_{quat}), 164.1 (C_{quat}). FAB^+ MS (m/z (%)): 269 (M^+ , 100). IR (KBr): $\tilde{\nu}$ 1562 cm^{-1} , 1416, 1252. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) 296 nm (34500). Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{OS}$ (268.3): C, 67.14; H, 4.51; N, 10.44. Found: C, 66.78; H, 4.51; N, 10.29.

¹ *Organikum*, 20th ed.; Becker, H. G. O.; Berger, W.; Domschke, G.; Fanghänel, E.; Faust, J.; Fischer, M.; Gentz, F.; Gewald, K.; Gluch, R.; Mayer, R.; Müller, K.; Pavel, D.; Schmidt, H.; Schollberg, K.; Schwetlick, K.; Seiler, E.; Zeppenfeld, G.; Johann Ambrosius Barth Verlag: Heidelberg, Leipzig, **1996**.