# 4 Chemisch-experimenteller Teil

## 4.1 Allgemeine Angaben

**Schmelzpunkt-Bestimmung**

Die Schmelzpunkte wurden mit einem Lindström-Gerät bestimmt und sind unkorrigiert.

**Elementaranalyse**

Elementar Vario EL.

**IR-Spektren**

Perkin-Elmer 1420 Ratio Recording IR-Spectrophotometer

ATI Mattson Genesis Serie FTIR.

**$^{1}$HNMR Spektren**

Bruker AC 300 und Bruker Advance/DPX 400 in den angegebenen Lösungsmitteln. Die chemische Verschiebung wird in ppm nach der δ-TMS-Skala angegeben. Der Austausch azider Protonen erfolgte mittels $D_2O$.

**$^{13}$C NMR-Spektren**

Bruker Advance/DPX 400 in den angegebenen Lösungsmitteln**.**

**Massenspektren**

Die Massenspektren wurden mit der Ionenstoss-Ionisierungsmethode erhalten. Verwendet wurde entweder ein CH-7A-Varian-MAT (70 eV) oder Kratos MS 25 RF (80 eV). Es werden die intensitätsstärksten Peaks mit ihrem Verhältnis m/z und der relativen Intensität angegeben.

**Dünnschichtchromatographie**

Kieselgelfolien AluGram® SIL G/$UV_{254}$ der Firma Macherey-Nagel.

In Tabelle 53 sind die verwendeten Abkürzungen und Symbole erläutert**.**

**Tabelle 53:** Verwendete Abkürzungen und Symbole

| **Abkürzung/ Symbol** | **Bedeutung** |
|---|---|
| Ar | Aryl |
| Ausb. | Ausbeute |
| austauschb. | austauschbar |
| br | breit |
| Cyc | Cyclohexyl |
| dt | Doppeltriplett |
| Fur | Furyl |
| Furfur | Furfuryl |
| Lit | Literaturwert |
| Ph | Phenyl |
| Pipz | Piperazin |
| Py | Pyridin |
| Pyrim | Pyrimidin |
| q | Quartett |
| Thi | Thienyl |
| tt | Triplett eines Tripletts |

# 4.2 Synthesevorschriften und analytische Daten

## 4.2.1 Synthese der Vorstufen

### 4.2.1.1 2-Cyano-2-phenylhydrazonoacetamide (2)

Es werden 52 mmol des Anilins mit 30 ml 18%iger Salzsäure versetzt und auf 0 °C abgekühlt. Unter starkem Rühren läßt man 3.6 g (52 mmol) Natriumnitrit, in 20 mL Wasser gelöst, langsam zutropfen. Das entstandene Zwischenprodukt läßt man anschließend in eine Lösung von 4.4 g (52 mmol) 2-Cyanoacetamid und 12.5 g (150 mmol) Natriumacetat in 150 mL 50%igem Ethanol tropfen. Der sofort entstehende Niederschlag wird abgesaugt und mit wenig Ethanol gewaschen[61].

*2-Cyano-2-phenylhydrazonoacetamid* **(2a)**

Aus 4.9 g (52.7 mmol) Anilin (**1a**). Orangerote Kristalle, Schmp. 260 °C (Lit. 260-262 °C), Ausb. 9.7 g (98%). – $C_9H_8N_4O$ (188.2). – **IR** (KBr): ν = 3488 $cm^{-1}$; 3372; 2211 (Nitril); 1668 (Amid); 1602; 1542; 1492; 1416; 1273; 760.– **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.09 (dd, *J* = 7.4/ 7.4 Hz, 1H, Ph-4-H), 7.35 (dd, *J* = 8.4/ 7.5 Hz, 2H, Ph-3,5-H), 7.43 (s, 1H, $CONH_2$, austauschb.), 7.64 (d, *J* = 7.9 Hz, 2H, Ph-2,6-H), 7.76 (s, 1H, $CONH_2$, austauschb.), 11.67 (s, 1H, Ph-NH, austauschb.). – **MS** (70 eV): m/z (%) = 188 (100) [$M^{+\cdot}$], 143 (38) [$M^{+\cdot}$- $NH_3$, -CO], 105 (17) [$M^{+\cdot}$- C-(C≡N)-$CONH_2$ + H], 92 (14), 91 (31) [$C_6H_5N^+$], 77 (77) ($C_6H_5^+$), 65 (26), 51 (16), 44 (23) [$NH_2$=C=$O^+$], 39 (17), 28 (14).

*2-Cyano-2-[(4-hexylphenyl)hydrazono]acetamid* **(2b)**

Aus 7.6 g (40.4 mmol) 4-Hexylanilin. Orangerote Kristalle, Schmp. 162 °C, Ausb. 4.8 g (63%). – $C_{15}H_{20}N_4O$ (272.4). – **IR** (KBr): ν = 3405 $cm^{-1}$; 3228; 3171; 2948; 2923; 2857; 2216 (Nitril); 1655 (Amid); 1603; 1551; 1494; 1466; 1426; 1406; 1271; 824; 692. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.85 (t, *J* = 6.7 Hz, 3H, R-$CH_3$), 1.27 (m, schlecht. aufgelöst, 6H, $CH_3$-(C$H_2$)$_3$-$CH_2$-$CH_2$-Ph), 1.52 –1.56 (m, 2H, $CH_3$-$(CH_2)_3$-C$H_2$-$CH_2$-Ph), 2.54 (t, *J* = 7.7/ 7.5 Hz, 2H, $CH_3$-$(CH_2)_4$-C$H_2$-Ph), 7.15 (d, *J* = 8.5 Hz, 2H, Ph-2,6-H), 7.38 (s, 1H,

$CONH_2$, austauschb.), 7.54 (d, *J* = 8.5 Hz, 2H, Ph-3,5-H), 7.70 (s, 1H, $CONH_2$, austauschb.), 11.62 (s, 1H, Ph-NH, austauschb.). – **MS** (70 eV): m/z (%) = 272 (67) [$M^{+\cdot}$], 201 (100) [$M^{+\cdot}$-$C_5H_{11}$], 156 (25), 104 (21), 91 (19), 77 (10), 43 (11) [$NH{=}C{=}O^+$].

#### 4.2.1.2 4-Aminocinnolin-3-carboxamide (3)

Es werden 25 mmol des 2-Cyano-2-phenylhydrazonoacetamids mit 6.6 g (50 mmol) wasserfreiem $AlCl_3$ in 30 mL Chlorbenzol 1 h bei 135 °C (Siedehitze) umgesetzt. Nach dem Erkalten werden unter Eiskühlung vorsichtig 100 mL 18%iger HCl zugegeben und der Rückstand abfiltriert. Der Rückstand wird in 200 mL Wasser gelöst/ suspendiert und die freie Base mit 20%iger NaOH bei pH >12 ausgefällt[62]. Aus der wässrigen Phase des Filtrates erhält man durch Zugabe von NaOH (40%) unter Eiskühlung ebenfalls die freie Base[63]. Beide Niederschläge werden vereinigt und in DMF/$H_2O$ (1:1) umkristallisiert.

*4-Aminocinnolin-3-carboxamid* **(3a)**

Aus 4.7g (25 mmol) **2a**. Ockerfarbene Kristalle, Schmp. 287 °C (Lit 287 – 289 °C), Ausb. 3.7 g (79%). – $C_9H_8N_4O$ (188.2). – **IR** (KBr): ν = 3455 $cm^{-1}$; 3359; 3266; 3193; 1662 (Amid); 1614; 1610; 1606; 1487; 1453; 1395; 1322; 1276; 1245; 1208; 1129; 762; 748; 607. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.61 (s, 1H, $CONH_2$), 7.73 (dd, *J* = 7.7/ 7.6 Hz, 1H, Ar-7-H), 7.88 (dd, *J* = 7.7/ 7.1 Hz, 1H, Ar-6-H), 8.12 („s“, breit, 1H, Ar-$NH_2$, austauschb.), 8.21 (d, *J* = 8.4 Hz, 1H, Ar-5-H), 8.41 (d, *J* = 8.4 Hz, 1H, Ar-8-H), 8.46 (s, 1H, $CONH_2$), 9.16 (s, breit, 1H, Ar-$NH_2$, austauschb.). – **MS** (70 eV): m/z (%) = 188 (100) [$M^{+\cdot}$], 171 (11) [$M^{+\cdot}$- $NH_3$], 145 (23) [$M^{+\cdot}$- NH=C=O + H], 118 (16), 116 (14), 115 (28), 90 (13), 89 (15), 44 (13) [$NH_2{=}C{=}O^+$].

*4-Amino-6-hexyl-cinnolin-3-carboxamid* **(3b)**

Aus 5.4 g (20 mmol) **2b**. Ockerfarbene Kristalle, Schmp. 216 °C, Ausb. 4.5 g (83%). – $C_{15}H_{20}N_4O$ (272.4). – **IR** (KBr): ν = 3407 $cm^{-1}$; 3305; 3157; 2956; 2925; 2850; 2804; 1679; 1641 (Amid); 1599; 1413. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.0/ 6.9 Hz, 3H, R-$CH_3$), 1.28 – 1.31 (m, 6H, $CH_3$-($CH_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.68 –1.71 (m, 2H, $CH_3$-($CH_2$)$_3$-$CH_2$-$CH_2$-Ar), 2.82 (t, *J* = 7.8/ 7.5 Hz, 2H, $CH_3$-($CH_2$)$_4$-$CH_2$-Ar), 8.01 (d, *J* = 8.7 Hz, 1H, Ar-7-H), 8.09 (s, 1H, $CONH_2$, austauschb.), 8.17 (d, *J* = 8.7 Hz, 1H, Ar-8-H), 8.49 (s, 1H,

Ar-5-H), 8.62 (s, 1H, Ar-$NH_2$, austauschb.), 10.37 (s, 1H, $CONH_2$, austauschb.), 10.58 (s, 1H, Ar-$NH_2$, austauschb.). – **MS** (70 eV): m/z (%) = 272 (100) [$M^{+\cdot}$], 215 (11) [$M^{+\cdot}$- $C_4H_9$], 201 (15) [$M^{+\cdot}$- $C_5H_{11}$], 158 (24), 156 (21), 36 (19).

### 4.2.1.3 Pyrimido[5,4-c]cinnolin-4(3*H*)-one und Pyrimido[5,4-c]cinnolin-4-ole (4)

#### 4.2.1.3.1 In 2-Position unsubstituierte Pyrimido[5,4-c]cinnolin-4(3*H*)-one

Es werden 10 mmol des entsprechenden 4-Amino-cinnolin-3-carboxamids vom Typ **3** 2 h in einem Gemisch aus 30 mL Orthoameisensäure-triethylester und 20 mL Eisessig (*Methode A)* oder 1 h in 30 mL Formamid (*Methode B)* unter Rückfluß erhitzt [53]. Bei Raumtemperatur fällt nach einigen Stunden ein Niederschlag aus, der durch einen Büchnertrichter abgesaugt und mit Ethylacetat gewaschen wird.

*Pyrimido[5,4-c]cinnolin-4(3*H*)-on* **(4a)**

*Methode A*: Aus 1.9 g (10.0 mmol) **3a**. Dunkelgrüne Kristalle, Schmp. >360 °C (Lit: > 350 °C), Ausb. 1.2 g (61%). – $C_{10}H_6N_4O$ (198.2). – **IR** (KBr): ν = 3156 $cm^{-1}$; 3061; 2950; 2909; 2878; 2852; 1691 (C=O); 1596; 1560; 1479; 1432; 1357; 1308; 1268; 1215; 1031; 774; 730; 672; 630. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 8.09 (dd, *J* = 8.0/ 7.0 Hz, 1H, Ar-9-H), 8.21 (dd, *J* = 7.8/ 7.3 Hz, 1H, Ar-8-H), 8.55 (s, 1H, Ar-2-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.81 (d, *J* = 8.2 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 198 (100) [$M^{+\cdot}$], 170 (21), 115 (72), 114 (15), 88 (32), 62 (13), 45 (10), 43 (14).

*Methode B*: Aus 1.7 g (9 mmol) **3a**. Dunkelbraune Kristalle, Schmp. >360 °C (Lit: > 350 °C), Ausb. 0.9 g (50%). – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 8.09 (dd, *J* = 7.7/ 7.4 Hz, 1H, Ar-9-H), 8.18 (dd, *J* = 8.1/ 7.1 Hz, 1H, Ar-8-H), 8.58 (s, 1H, Ar-2-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.79 (d, *J* = 8.1 Hz, 1H, Ar-10-H), 13.21 (s, 1H, NH, austauschb.).

*9-Hexyl-pyrimido[5,4-c]cinnolin-4-on* **(4b)**

*Methode A* Aus 1.0 g (3.7 mmol) **3b**. Braune Kristalle, Schmp. >360 °C, Ausb. 0.7 g (67%). – $C_{16}H_{18}N_4O$ (282.3). – **IR** (KBr): ν = 3162 $cm^{-1}$; 3064; 2955; 2926; 2856; 1704 (C=O); 1598; 1562; 1495; 1442; 1218. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 0.87 (t, *J* = 7.0 Hz, 3H, R-$CH_3$), 1.25 – 1.34 (m, 6H, $CH_3$-(C*H*$_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.68 –1.76 (m, 2H, $CH_3$-($CH_2$)$_3$-C*H*$_2$-$CH_2$-Ar), 2.94 (t, *J* = 7.6 Hz, 2H, $CH_3$-($CH_2$)$_4$-C*H*$_2$-Ar), 8.04 (d, *J* = 8.6 Hz, 1H, Ar-8-H), 8.54 (m, 1H, Ar-7-H), 8.55 (s, 1H, Ar-10-H), 8.58 (s, 1H, Ar-2-H). – **MS** (70 eV): m/z (%) = 283 (20), 282 (100) [$M^{+\cdot}$], 226 (10), 225 (46) [$M^{+\cdot}$ - $C_4H_9$], 212 (82), 211 (26), 156 (29), 112 (28), 101 (10), 98 (16), 43 (21), 41 (18).
*Methode B*: Aus 2.4 g (9 mmol) **3b**. Braune Kristalle, Schmp. >360 °C, Ausb. 1.2 g (47%). – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 0.85 (t, *J* = 6.8 Hz, 3H, R-$CH_3$), 1.30 – 1.31 (m, 6H, $CH_3$-(C*H*$_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.70 – 1.73 (m, 2H, $CH_3$-($CH_2$)$_3$-C*H*$_2$-$CH_2$-Ar), 2.93 (t, *J* = 7.4 Hz, 2H, $CH_3$-($CH_2$)$_4$-C*H*$_2$-Ar), 8.03 (d, *J* = 9.0 Hz, 1H, Ar-8-H), 8.54 – 8.58 (m, 3H, Ar-2,7,10-H).

#### 4.2.1.3.2 In 2-Position substituierte Pyrimido[5,4-c]cinnolin-4-ole/ -one

Nach einer Vorschrift von *Rotella et. al.*[64]werden 5 mmol **3a** in 10 mL Pyridin suspendiert, mit einem 5–10-fachen Überschuß des Säurechlorids versetzt und bei der angegebenen Temperatur 1 – 2.5 h gerührt. Nach Ablauf der Reaktionszeit werden unter Eiskühlung 50 mL Wasser hinzugefügt und der kristalline Niederschlag abgesaugt. (Bei zähen öligen Rückständen wird der Überstand vorsichtig abpipettiert und das verbleibende Produkt mit wenig Ethanol ausgespült.) Der Rückstand wird mit 50 mL 50%igem Ethanol aufgenommen und mit 10 mL 20 % NaOH sowie 2 mL konzentriertem $H_2O_2$ versetzt und 1 h bei 90 °C gehalten. Es fällt meist noch in der Siedehitze ein voluminöser Niederschlag des Endproduktes, welches abgesaugt und mit Wasser und Ethanol gewaschen wird.

*2-Phenyl-pyrimido[5,4-c]cinnolin-4(3*H*)-on* **(4c)**

Aus 1.3 g (6.6 mmol) **3a** und 4.3 g (31 mmol) Benzoylchlorid. 80 °C, 2.5 h. Gelbe Kristalle, Schmp. >360 °C (EtOH/ $H_2O$/ DMF), Ausb. 1.0 g (61%). – $C_{16}H_{10}N_4O$ (274.3). – **IR** (KBr): ν = 3422 $cm^{-1}$ (NH), 1708 (C=O), 1552, 1499. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) =

7.47 – 7.51 (m, 3H, Ph-3,4,5-H), 7.85 (dd, *J* = 7.9/ 7.0 Hz, 1H, Ar-9-H), 7.94 (dd, *J* = 7.6/ 7.4 Hz, 1H, Ar-8-H), 8.53 – 8.59 (m, 3H, Ar-7-H, Ph-2,6-H) 8.90 (d, *J* = 8.0 Hz, 1H, Ar-10-H). – **$^{13}$C NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 122.44 (C-10a), 123.18 (C-10), 128.16 (Ph-C-3,5), 128.71 (Ph-2,6-C), 128.95 (Ph-C-4), 130.16 (C-8), 130.29 (C-9), 131.01 (C-7), 135.15 (Ph-C-1), 139.65 (C-10b), 143.49 (C-6a), 149.14 (C-4a), 165.48 (C-2), 171.30 (C-4). – **MS** (70 eV): m/z (%) = 274 (10) [$M^{+\cdot}$], 105 (100), 77 (35).

*2-(2-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4d)**

Aus 1.1 g (5.5 mmol) **3a** und 4.8 g (28 mmol) 2-Methoxybenzoylchlorid. 60 °C, 2.5 h. Gelbe Kristalle, Schmp. >360 °C , Ausb. 0.8 g (47%). – $C_{17}H_{12}N_4O_2$ (304.3). – **IR** (KBr): ν = 3430 $cm^{-1}$ (OH); 1592; 1561; 1508; 1491; 1478; 1378; 1286; 1247; 771. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.77 (s, 3H, $OCH_3$), 7.01 (dd, *J* = 7.6/ 7.3 Hz, 1H, Ph-5-H), 7.09 (d, *J* = 8.2 Hz, 1H, Ph-3-H), 7.38 (ddd, *J* = 8.0/ 7.6/ 1.8 Hz, 1H, Ph-4-H), 7.51 (dd, J = 7.4/ 1.7 Hz, Ph-6-H), 7.83 (ddd, *J* = 7.6/ 6.5/, 1.0 Hz, 1H, Ar-9-H), 7.95 (ddd, *J* = 7.7/ 7.6/ 1.2 Hz, Ar-8-H), 8.44 (d, *J* = 8.3 Hz, Ar-7-H), 8.69 (d, *J* = 7.7 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 318 (100), 317 (51), 304 (5) [$M^{+\cdot}$], 289 (11), 287 (33), 159 (11), 148 (37), 147 (11), 146 (20), 133 (29), 129 (11), 128 (10), 118 (13), 114 (16), 105 (16), 103 (11), 102 (11), 91 (11), 90 (12), 88 (11), 77 (14), 41 (12), 39 (13).

*2-(4-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4e)**

Aus 1.1 g (5.5 mmol) **3a** und 4.6 g (27 mmol) 4-Methoxybenzoylchlorid. 60 °C, 2.5 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.1 g (66%). – $C_{17}H_{12}N_4O_2$ (304.3). – **IR** (KBr): ν = 3574 $cm^{-1}$; 3389 (OH); 3073; 1580; 1559; 1531; 1507; 1482; 1444; 1424; 1403; 1376; 1283; 1250; 1164; 1028; 829; 770; 759. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.85 (s, 3H, $OCH_3$), 7.03 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 7.85 (ddd, *J* = 7.5/ 7.5/ 0.9 Hz, 1H, Ar-9-H), 7.94 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.40 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.54 (d, *J* = 8.8 Hz, 2H, Ph-2,6-H), 8.88 (d, *J* = 7.9 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 304 (100) [$M^{+\cdot}$], 303 (27), 276 (12), 275 (11), 143 (10), 134 (32), 133 (16), 119 (21), 115 (15), 103 (13), 91 (10), 90 (14), 63 (10), 44 (18), 41 (14), 39 (13), 31 (12).

*2-(4-Ethoxyphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4f)**

Aus 1.3 g (6.6 mmol) **3a** und 4.8 g (26 mmol) 4-Ethoxybenzoylchlorid. 60 °C, 2 h. Hellgelbe Kristalle, Schmp. >360 °C, Ausb. 0.9 g (43%). – $C_{18}H_{14}N_4O_2$ (318.3). – **IR** (KBr): ν = 3369 $cm^{-1}$ (OH); 2978; 1587; 1557; 1532; 1506; 1477; 1446; 1403; 1375; 1283; 1249; 1165; 1046; 772. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.38 (t, *J* = 6.9 Hz, 3H, O-$CH_2$-C*H*$_3$), 4.12 (q, *J* = 6.9 Hz, 2H, O-C*H*$_2$-$CH_3$), 7.02 (d, *J* = 8.7 Hz, 2H, Ph-3,5-H), 7.88 (dd, *J* = 7.8/ 7.1 Hz, 1H, Ar-9-H), 7.96 (dd, *J* = 7.8/ 7.3 Hz, 1H, Ar-8-H), 8.42 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.54 (d, *J* = 8.7 Hz, 2H, Ph-2,6-H), 8.90 (d, *J* = 8.0 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 318 (1) [$M^{+\cdot}$], 166 (11), 138 (18), 121 (32), 94 (16), 44 (100), 29 (13), 28 (49), 27 (17).

*2-(4-Propoxyphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4g)**

a) Synthese des 4-Propoxybenzoylchlorid:
5.0 g (28 mmol) 4-Propoxybenzoesäure und 10 mL Thionylchlorid werden in einer Destille unter Wasserstrahlvakuum auf 75 °C so lange erhitzt, bis die Gasentwicklung beendet ist und kein Destillat mehr übergeht. (Der im Kolben verbleibende Rückstand wurde keiner struktursichernden Analytik unterzogen, sondern sofort zur weiteren Umsetzung verwendet.) Orangerote, ölige Flüssigkeit, Ausbeute 4.9 g (95%). $C_{10}H_{11}ClO_2$ (198.6).
b) 1.3 g (6.6 mmol) **3a** werden mit 4.9 g (25 mmol) 4-Propoxybenzoylchlorid aus a) nach der allgemeinen Vorschrift umgesetzt. 60 °C, 2 h. Hellgelbe Kristalle, Schmp. >360 °C, Ausb. 1.2 g (55%). – $C_{19}H_{16}N_4O_2$ (332.4). – **IR** (KBr): ν = 3395 $cm^{-1}$ (OH); 2965; 1586; 1556; 1530; 1506; 1480; 1403; 1374; 1282; 1251; 1165; 771. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.02 (t, *J* = 7.4 Hz, 3H, O-$CH_2$-$CH_2$-C*H*$_3$), 1.73 – 1.82 (m, 2H, O-$CH_2$-C*H*$_2$-$CH_3$), 4.02 (t, *J* = 6.5 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_3$), 7.02 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 7.86 (dd, *J* = 7.7/ 7.2 Hz, 1H, Ar-9-H), 7.94 (dd, *J* = 7.5/ 7.3 Hz, 1H, Ar-8-H), 8.40 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.52 (d, *J* = 8.7 Hz, 2H, Ph-2,6-H), 8.88 (d, *J* = 8.0 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 333 (23), 332 (100) [$M^{+\cdot}$], 331 (12), 291 (16), 290 (83) [$M^{+\cdot}$ – $C_3H_6$], 289 (30), 262 (21), 261 (14), 254 (17),120 (30), 119 (23), 115 (17), 44 (18), 43 (23), 41 (26), 39 (13), 28 (20), 27 (21).

*2-(4-Butoxyphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4h)**

Aus 1.2 g (6.1 mmol) **3a** und 4.9 g (23 mmol) 4-Butoxybenzoylchlorid. 60 °C, 2.5 h. Hellgelbe Kristalle, Schmp. >360 °C, Ausb. 1.1 g (52%). – $C_{20}H_{18}N_4O_2$ (346.4). – **IR** (KBr): ν = 3367 $cm^{-1}$ (OH); 3073; 2957; 2934; 2871; 1586; 1557; 1530; 1506; 1479; 1444; 1424; 1403; 1374; 1283; 1249; 1165; 830; 771; 614. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.96 (t, *J* = 7.3 Hz, 3H, O-$CH_2$-$CH_2$-$CH_2$-C*H*$_3$), 1.43 – 1.52 (m, 2H, O-$CH_2$-$CH_2$-C*H*$_2$-$CH_3$), 1.71 – 1.78 (m, 2H, O-$CH_2$-C*H*$_2$-$CH_2$-$CH_3$), 4.06 (t, *J* = 6.5 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_2$-$CH_3$), 7.02 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 7.86 (ddd, *J* = 7.5/ 7.5/ 1.0 Hz, 1H, Ar-9-H), 7.94 (ddd, *J* = 7.7/ 7.5/ 1.4 Hz, 1H, Ar-8-H), 8.40 (d, *J* = 8.1 Hz, 1H, Ar-10-H), 8.52 (d, *J* = 8.8 Hz, 2H, Ph-2,6-H), 8.88 (dd, *J* = 8.0/ 0.9 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 402 (11); 350 (19); 346 (23) [$M^{+\cdot}$]; 290 (24); 182 (10); 175 (12); 120 (37); 119 (59); 57 (22); 56 (43), 55 (21); 44 (19); 43 (67); 42 (14); 41 (100); 39 (28); 29 (51); 28 (43); 27 (33).

*2-(2-Fluorphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4i)**

Aus 1.1 g (5.5 mmol) **3a** und 4.6 g (29 mmol) 2-Fluorbenzoylchlorid. 50 °C, 1 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.0 g (62%). – $C_{16}H_9FN_4O$ (292.3). – **IR** (KBr): ν = 3400 $cm^{-1}$ (OH); 1592; 1562; 1532; 1512; 1490; 1455; 1377; 1290; 769; 750. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.25 – 7.32 (m, 2H, Ph-3,5-H), 7.48 – 7.49 (m, 1H, Ph-4-H), 7.87 (dd, *J* = 7.6/ 7.1 Hz, 1H, Ar-9-H), 7.98 (dd, *J* = 7.7/ 7.1 Hz, 1H, Ar-8-H), 8.05 (dd, *J* = 7.5/ 7.4 Hz, 1H, Ph-6-H), 8.46 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.77 (d, *J* = 8.1 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 292 (55) [$M^{+\cdot}$], 291 (21), 135 (61), 122 (21), 121 (47), 118 (12), 115 (28), 102 (24), 94 (22), 88 (17), 77 (12), 76 (11), 75 (14), 50 (12), 44 (100), 43 (28), 39 (12), 28 (53), 27 (13), 23 (14).

*2-(4-Fluorphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4j)**

Aus 1.2 g (6.1 mmol) **3a** und 4.9 g (31 mmol) 4-Fluorbenzoylchlorid. 50 °C, 1.5 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.2 g (67%). – $C_{16}H_9FN_4O$ (292.3). – **IR** (KBr): ν = 3401 $cm^{-1}$ (OH); 1583; 1558; 1532; 1507; 1484; 1398; 1373; 1291; 1230; 1150; 770; 755. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.31 (dd, *J* = 8.9/ 8.9 Hz, 2H, Ph-3,5-H), 7.89 (dd, *J* = 7.5/ 7.4 Hz, 1H, Ar-9-H), 7.97 (dd, *J* = 8.2/ 6.9 Hz, 1H, Ar-8-H), 8.44 (d, *J* = 8.2 Hz, 1H,

Ar-10-H), 8.64 (dd, *J* = 7.3/ 7.3/ 2.5 Hz, 2H, Ph-2,6-H), 8.91 (d, *J* = 7.9 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 292 (16) [$M^{+\cdot}$], 291 (19), 122 (25), 121 (100), 115 (16), 95 (17), 94 (43), 88 (12), 75 (19), 50 (17), 44 (45), 43 (74), 42 (15), 29 (16), 28 (27), 27 (22), 23 (63), 20 (32).

*2-(4-Chlorphenyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4k)**

Aus 1.2 g (6.1 mmol) **3a** und 5.6 g (32 mmol) 4-Chlorbenzoylchlorid. 50 °C, 1.5 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.3 g (69%). – $C_{16}H_9ClN_4O$ (308.7). – **IR** (KBr): ν = 3403 $cm^{-1}$ (OH); 1587; 1561; 1533; 1509; 1481; 1392; 1373; 1283; 770. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.56 (dd, *J* = 7.0/ 1.6 Hz, 2H, Ph-3,5-H), 7.90 (ddd, *J* = 7.5/ 7.4/ 0.9 Hz, 1H, Ar-9-H), 7.99 (ddd, *J* = 8.3/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.46 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.59 (d, *J* = 8.6 Hz, 2H, Ph-2,6-H), 8.91 (d, *J* = 7.6 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 310 (33), 309 (26), 308 (100) [$M^{+\cdot}$], 307 (26), 280 (17), 143 (11), 138 (22), 137 (18), 115 (38), 114 (10), 102 (14), 88 (20), 75 (13), 44 (13), 36 (17), 28 (14).

*4-(4-Hydroxypyrimido[5,4-c]cinnolin-2-yl)benzonitril* **(4l)**

Aus 1.3 g (6.6 mmol) **3a** und 4.9 g (30 mmol) 4-Cyanobenzoylchlorid. 50 °C, 2 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 0.9 g (45%). – $C_{17}H_9N_5O$ (299.3). – **IR** (KBr): ν = 3371 $cm^{-1}$ (OH); 3192; 2228 (Nitril); 1679; 1587; 1560; 1508; 1480; 1420; 1373; 1284; 768; 611. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.88 – 7.92 (m, 1H, Ar-9-H), 7.96 – 8.01 (m, 3H, Ar-8-H, Ph-3,5-H), 8.45 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.64 (d, *J* = 8.4 Hz, 2H, Ph-2,6-H), 8.94 (d, *J* = 7.3 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 299 (4) [$M^{+\cdot}$], 298 (22), 146 (16), 130 (27), 129 (10), 128 (100), 102 (20), 101 (20), 75 (11), 50 (11), 44 (71), 28 (19).

*2-(2-Furyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4m)**

Aus 1.4 g (7.1 mmol) **3a** und 5.4 g (41 mmol) 2-Furoylchlorid. 60 °C, 2 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.5 g (80%). – $C_{14}H_8N_4O_2$ (264.2). – **IR** (KBr): ν = 3401 $cm^{-1}$ (OH); 1602; 1575; 1560; 1531; 1509; 1475; 1451; 1410; 1367; 1370; 1293; 769; 750. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 6.66 (dd, *J* = 3.3/ 1.6 Hz, 1H, Fur-4-H), 7.29 (d, *J* = 3.2 Hz, 1H, Fur-5-H), 7.84 – 7.88 (m, 2H, Fur-3-H, Ar-9-H), 7.95 (ddd, *J* = 7.7/ 7.6/ 1.3 Hz, 1H,

Ar-8-H), 8.41 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.79 (d, *J* = 7.9 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 264 (1) [$M^{+\cdot}$], 44 (100), 28 (33).

*2-(2-Thienyl)-pyrimido[5,4-c]cinnolin-4-ol* **(4n)**

Aus 1.1 g (5.5 mmol) **3a** und 4.4 g (30 mmol) 2-Thienylchlorid. 60 °C, 2.5 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.2 g (78%). – $C_{14}H_8N_4OS$ (280.3). – **IR** (KBr): ν = 3389 $cm^{-1}$ (OH); 1696; 1585; 1561; 1508; 1477; 1430; 1409; 1376; 1338; 1286; 771; 743; 710; 617. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) =7.19 (dd, *J* = 3.9/ 3.7 Hz, 1H, Thi-4-H), 7.67 (d, *J* = 4.5 Hz, 1H, Thi-5-H), 7.87 (dd, *J* = 7.3 Hz, 1H, Ar-9-H), 7.94 – 7.99 (m, 2H, Ar-8-H, Thi-3-H), 8.42 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 8.80 (d, *J* = 7.9 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) 280 (100) [$M^{+\cdot}$], 279 (13), 252 (11), 115 (11), 110 (16), 38 (10), 36 (28), 32 (51).

*2-[(E)-2-Phenylvinyl]pyrimido[5,4-c]cinnolin-4-ol* **(4p)**

Aus 1.1 g (5.5 mmol) **3a** und 6.1 g (37 mmol) trans-Zimtsäurechlorid. 60 °C, 1.5 h. Gelbe Kristalle, Schmp. >360 °C, Ausb. 1.3 g (78%). – $C_{19}H_{11}N_4O$ (300.3). – **IR** (KBr): ν = 3395 $cm^{-1}$ (OH); 1690; 1639 (Ar-HC=CH-Ph); 1582; 1558; 1506; 1481; 1449; 1414; 1378; 1289; 1251; 971; 771; 687. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.10 (d, *J* = 15.9 Hz, 1H, Ar-C*H*=CH-Ph), 7.36 (dd, *J* = 7.4/ 7.2 Hz, 1H, Ph-4-H), 7.45 (dd, *J* = 7.5/ 7.4 Hz, 2H, Ph-3,5-H), 7.73 (d, *J* = 7.5 Hz, 2H, Ph-2,6-H), 7.87 (dd, *J* = 7.8/ 7.2 Hz, 1H, Ar-9-H), 7.94 – 8.00 (m, 2H, Ar-8-H, Ar-CH=C*H*-Ph), 8.42 (d, *J* = 8.3 Hz, 1H, Ar-10-H), 8.83 (d, *J* = 8.1 Hz, 1H, Ar-7-H).

### 4.2.1.4 Synthese der 4-Chlorpyrimido[5,4-c]cinnoline (5)

*Methode A*[65]: Ein Gemisch aus 5 mmol des entsprechenden Pyrimido[5,4-c]cinnolin-4(3*H*)-ons wird mit einer äquimolaren Menge (0.8 g) Tetraethylammoniumchlorid, (24 h bei 80 °C getrocknet), 5 mL Acetonitril, 2 mL N,N-Diethylanilin sowie 5 mL Phosphoroxychlorid 20 – 45 min. zum Sieden erhitzt. Die entstehende Lösung wird unter vermindertem Druck auf die Hälfte eingeengt und anschließend vorsichtig auf 200 mL 5%ige Natriumhydrogencarbonat-Lösung (Eiswasser) gegeben. Die entstandenen Kristalle werden abgesaugt und mit Wasser gewaschen.

*Methode B*[66]: 5 mmol des entsprechenden Pyrimido[5,4-c]cinnolin-4(3*H*)-ons bzw. –4-ols werden mit 10 mL Phosphoroxychlorid unter Zusatz von 3 mL N,N-Diethylanilin für den jeweils angegebenen Zeitraum unter Rückfluß gehalten. Nach dem Erkalten wird die Lösung bzw. Suspension vorsichtig unter starkem Rühren auf 200 mL Eiswasser gegeben. Der entstehende Niederschlag wird abgesaugt, mit wenig 1N HCl und anschließend mit Ethanol gewaschen.

#### 4.2.1.4.1 In 2-Position unsubstituierte 4-Chlorpyrimido[5,4-c]cinnoline

*4-Chlorpyrimido[5,4-c]cinnolin* **(5a)**

*Methode A*. Aus 1.2 g (6.1 mmol) **4a**, 45 min. Dunkelgrüne Kristalle, Schmp. > 360 °C, Rohausb. 0.58 g (44%). – $C_{10}H_5ClN_4$ (216.6). – **IR** (KBr): ν = 3057 $cm^{-1}$; 1716; 1598; 1561; 1499; 1433; 1359; 775. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 8.28 (ddd, *J* = 7.9/ 7.1/ 1.0 Hz, 1H, Ar-9-H), 8.36 (ddd, *J* = 8.2/ 7.3/ 1.4 Hz, 1H, Ar-8-H), 8.92 (d, *J* = 7.9 Hz, 1H, Ar-7-H), 9.05 (d, *J* = 8.4 Hz, 1H, Ar-10-H), 9.51 (s, 1H, Ar-2-H) – **MS** (70 eV): m/z (%) = 218 (34), 217 (15), 216 (100) [$M^{+\cdot}$], 163 (21), 161 (71), 153 (51), 126 (25), 100 (12), 99 (11), 75 (11), 50 (13), 36 (15), 28 (15).
*Methode B*. Aus 0.8 g (4.0 mmol) **4a**, 45 min. Dunkelgrüne Kristalle, Schmp. > 360 °C, Rohausbeute 0.62 g (74%). – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 8.28 (ddd, *J* = 7.6/ 7.5/ 0.8 Hz, 1H, Ar-9-H), 8.35 (ddd, *J* = 7.7/ 7.7/ 1.3 Hz, 1H, Ar-8-H), 8.92 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 9.05 (d, *J* = 7.4 Hz, 1H, Ar-10-H), 9.54 (s, 1H, Ar-2-H).

*4-Chlor-9-hexyl-pyrimido[5,4-c]cinnolin* **(5b)**

*Methode B*. Aus 1.2 g (4.3 mmol) **4b,** 30 min. Dunkelgrüne Kristalle, Schmp. >360 °C, Ausb. 0.75 g (58%). – $C_{16}H_{17}ClN_4$ (300.8). – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 6.9 Hz, 3H, R-$CH_3$), 1.26 – 1.35 (m, 6H, $CH_3$-($CH_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.72 – 1.80 (m, 2H, $CH_3$-($CH_2$)$_3$-$CH_2$-$CH_2$-Ar), 3.02 (t, *J* = 7.6 Hz, 2H, $CH_3$-($CH_2$)$_4$-$CH_2$-Ar), 8.21 (dd, *J* = 8.5/ 1.6 Hz, Ar-8-H), 8.82 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.83 (s, 1H, Ar-10-H), 9.51 (s, 1H, Ar-2-H).

#### 4.2.1.4.2 In 2-Position substituierte 4-Chlorpyrimido[5,4-c]cinnoline

Die Verbindungen **5c – p** wurden alle nach *Methode B* dargestellt.

*4-Chlor-2-phenyl-pyrimido[5,4-c]cinnolin* **(5c)**

Aus 0.8 g (2.9 mmol) **4c**, 2.5 h. Hellbraune Kristalle, Schmp. 201 °C, Ausb. 0.6 g (69 %). – $C_{16}H_9ClN_4$ (292.7). – **IR** (KBr): ν = 1574 $cm^{-1}$; 1556; 1529; 1502; 1373; 845; 743; 691. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 7.63 – 7.73 (m, 3H, Ph-3,4,5-H), 8.26 (ddd, *J* = 7.6/ 7.4/ 0.9 Hz, 1H, Ar-9-H), 8.33 (ddd, *J* = 8.2/ 7.6/ 1.3 Hz, Ar-8-H), 8.68 – 8.71 (m, 2H, Ph-2,6-H), 8.87 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 9.20 (d, *J* = 7.7 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 294 (34), 293 (20), 292 (100) [$M^{+\cdot}$], 257 (19) [$M^{+\cdot}$– Cl], 229 (19), 163 (14), 161 (46), 126 (34), 77 (10).

*4-Chlor-2-(2-methoxyphenyl)-pyrimido[5,4-c]cinnolin* **(5d)**

Aus 0.8 g (2.6 mmol) **4d**, 1 h 45 min. Gelbe Kristalle, Schmp. 215 °C, Ausb. 0.56 g (65%). – $C_{17}H_{11}ClN_4O$ (322.8). – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) =3.92 (s, 3H, $OCH_3$), 7.19 (dd, *J* = 7.5/ 7.4 Hz, 1H, Ph-5-H), 7.29 (d, *J* = 8.3 Hz, 1H, Ph-3-H), 7.60 – 7.65 (m, 1H, Ph-4-H), 7.99 (dd, *J* = 7.6/ 1.4 Hz, Ph-6-H), 8.25 (dd, *J* = 7.4/ 7.2 Hz, 1H, Ar-9-H), 8.33 (dd, *J* = 7.2/ 7.0 Hz, Ar-8-H), 8.88 (d, *J* = 8.1 Hz, Ar-7-H), 9.05 (d, *J* = 7.8 Hz, 1H, Ar-10-H).

*4-Chlor-2-(4-methoxyphenyl)-pyrimido[5,4-c]cinnolin* **(5e)**

Aus 1.0 g (3.3 mmol) **4e**, 1 h 45 min. Braune Kristalle, Schmp. 194 °C (Zersetzung), Ausb. 0.65 g (61%). – $C_{17}H_{11}ClN_4O$ (322.8). – **IR** (KBr): ν = 1606 $cm^{-1}$; 1573; 1554; 1531; 1517; 1491; 1374; 1259; 1166; 845; 767. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 3.90 (s, 3H, $OCH_3$), 7.16 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.23 (m, 1H, Ar-9-H), 8.29 (ddd, *J* = 8.2/ 7.6/ 1.2 Hz, 1H, Ar-8-H), 8.60 (d, *J* = 8.9 Hz, Ph-2,6-H), 8.81 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.13 (d, *J* = 7.9 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 324 (39), 323 (21), 322 (100) [$M^{+\cdot}$], 287 (36), 216 (22), 161 (29), 134 (14), 133 (61), 127 (12), 126 (90), 103 (26), 100 (19), 99 (19), 90 (38), 77 (17), 76 (21), 75 (20), 64 (18), 63 (19), 51 (22), 50 (16), 39 (17), 38 (12), 36 ( 22).

*4-Chlor-2-(4-ethoxyphenyl)-pyrimido[5,4-c]cinnolin* **(5f)**

Aus 1.0 g (3.1 mmol) **4f**, 2 h. Dunkelgrüne Kristalle, Schmp. 213 °C, Ausb. 0.84 g (81%). – $C_{18}H_{13}ClN_4O$ (336.8). – **IR** (KBr): ν = 1606 $cm^{-1}$; 1573; 1553; 1528; 1492; 1413; 1374; 1339; 1305; 1258; 1075; 1046; 846; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO) (Spektrum schlecht aufgelöst): δ (ppm) = 1.40 („s“, 3H, O-$CH_2$-C*$H_3$*), 4.09 („m“, 2H, O-C*$H_2$*-$CH_3$), 7.18 (d, *J* = 6.8 Hz, 2H, Ph-3,5-H), 8.24 („m“, 1H, Ar-9-H), 8.31 („m“, 1H, Ar-8-H), 8.64 (d, *J* = 6.4 Hz, 2H, Ph-2,6-H), 8.83 („m“, 1H, Ar-7-H), 9.17 („m“, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 338 (36), 337 (22), 336 (100) [$M^{+\cdot}$], 311 (16), 310 (10), 309 (48) [$M^{+\cdot}$– $C_2H_3$], 283 (17), 273 (35), 245 (12), 163 (10), 161 (26), 126 (45), 119 (27), 29 (12).

*4-Chlor-2-(4-propoxyphenyl)-pyrimido[5,4-c]cinnolin* **(5g)**

Aus 1.3 g (3.9 mmol) **4f,** 1 h 45 min. Braune Kristalle, Schmp. 211 °C, Ausb. 1.0 g (74%). – $C_{19}H_{15}ClN_4O$ (350.8). – **IR** (KBr): ν = 1604 $cm^{-1}$; 1573; 1553; 1532; 1491; 1415; 1373; 1255; 1168; 1075; 846; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.03 (t, *J* = 7.4 Hz, 3H, O-$CH_2$-$CH_2$-C*$H_3$*), 1.83 – 1.76 (m, 2H, O-$CH_2$-C*$H_2$*-$CH_3$), 4.10 (t, *J* = 6.6 Hz, 2H, O-C*$H_2$*-$CH_2$-$CH_3$), 7.20 (d, *J* = 9.0 Hz, 2H, Ph-3,5-H), 8.24 (ddd, *J* = 7.6/ 7.5/ 1.0 Hz, 1H, Ar-9-H), 8.31 (ddd, *J* = 7.7/ 7.7/ 1.3 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.9 Hz, 2H, Ph-2,6-H), 8.84 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 9.19 (dd, *J* = 7.6/ 1.1 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 353 (22), 352 (14), 350 (62) [$M^{+\cdot}$], 310 (36), 309 (22), 308 (100) [$M^{+\cdot}$– $C_3H_6$], 273 (40), 245 (12), 242 (10), 161 (26), 126 (46), 119 (24), 43 (24), 41 (20), 28 (10), 27 (22).

*4-Chlor-2-(4-butoxyphenyl)-pyrimido[5,4-c]cinnolin* **(5h)**

Aus 1.1 g (3.2 mmol) **4h**, 1.5 h. Braune Kristalle, Schmp. 181 °C, Ausb. 0.76 g (66%). – $C_{20}H_{17}ClN_4O$ (364.8). – **IR** (KBr): ν = 2957 $cm^{-1}$; 2871; 1605; 1573; 1552; 1532; 1491; 1452; 1414; 1372; 1341; 1306; 1255; 1167; 1074; 1005; 845; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.97 (t, *J* = 7.3 Hz, 3H, O-$CH_2$-$CH_2$-$CH_2$-C*$H_3$*), 1.44 – 1.54 (m, 2H, O-$CH_2$-$CH_2$-C*$H_2$*-$CH_3$), 1.74 – 1.81 (m, 2H, O-$CH_2$-C*$H_2$*-$CH_2$-$CH_3$), 4.14 (t, *J* = 6.4 Hz, 2H, O-C*$H_2$*-$CH_2$-$CH_2$-$CH_3$), 7.20 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.24 (dd, *J* = 7.4/ 7.1 Hz, 1H, Ar-9-H), 8.32 (dd, *J* = 7.2/ 7.0 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.8 Hz, 2H, Ph-2,6-H), 8.84 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.19 (d, *J* = 7.7 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 366 (16),

365 (12), 364 (48) [$M^{+\cdot}$], 310 (35), 309 (22), 308 (100) [$M^{+\cdot}$– $C_4H_8$], 273 (32), 161 (16), 126 (32), 119 (14), 41 (17), 29 (32).

*4-Chlor-2-(2-fluorphenyl)-pyrimido[5,4-c]cinnolin* **(5i)**

Aus 1.1 g (3.8 mmol) **4i**, 2 h. Hellbraune Kristalle, Schmp. 174 °C (Zersetzung), Ausb. 0.90 g (76%). – $C_{16}H_8ClFN_4$ (310.7). – **IR** (KBr): ν = 3433 $cm^{-1}$; 1614; 1576; 1555; 1498; 1370; 756. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.43 – 7.49 (m, 2H, Ph-3,5-H), 7.71 – 7.76 (m, 1H, Ph-4-H), 8.27 (dd, *J* = 7.3/ 7.3 Hz, 1H, Ar-9-H), 8.34 (dd, *J* = 7.5/ 7.5 Hz, 1H, Ar-8-H), 8.42 (ddd, *J* = 7.8/ 7.3/ 1.2 Hz, 1H, Ph-6-H), 8.89 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.08 (d, *J* = 7.8 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 312 (37), 311 (20), 310 (100) [$M^{+\cdot}$], 275 (18) [$M^{+\cdot}$– Cl], 247 (34), 163 (25), 161 (75), 126 (64), 100 (20), 99 (18), 75 (20), 51 (12).

*4-Chlor-2-(4-fluorphenyl)-pyrimido[5,4-c]cinnolin* **(5j)**

Aus 1.6 g (5.5 mmol) **4j**, 1 h 45 min. Braune Kristalle, Schmp. 207 °C, Ausb. 1.3 g (76%). – $C_{16}H_8ClFN_4$ (310.7). – **IR** (KBr): ν = 1709 $cm^{-1}$; 1599; 1574; 1553; 1531; 1512; 1493; 1428; 1406; 1371; 1339; 1291; 1238; 1153; 1075; 915; 848; 819; 767; 749.– **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.49 (dd, *J* = 8.8/ 8.8 Hz, 2H, Ph-3,5-H), 8.25 (ddd, *J* = 7.5/ 7.5/ 0.8 Hz, 1H, Ar-9-H), 8.32 (ddd, *J* = 7.6/ 7.6/ 1.2 Hz, 1H, Ar-8-H), 8.71 – 8.74 (m, 1H, Ph-2,6-H), 8.85 (d, *J* = 8.1 Hz, Ar-7-H), 9.17 (d, *J* = 7.5 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 312 (32), 311 (17), 310 (100) [$M^{+\cdot}$], 275 (14), 247 (23), 163 (18), 161 (53), 149 (13), 134 (36), 127 (14), 126 (32), 106 (14), 99 (26), 95 (12), 77 (14), 75 (10), 69 (31), 57 (14), 51 (23), 50 (11), 44 (37), 44 (14), 43 (14), 38 (15), 36 (47), 28 (19).

*4-Chlor-2-(4-chlorphenyl)-pyrimido[5,4-c]cinnolin* **(5k)**

Aus 1.2 g (3.9 mmol) **4k**, 1.5 h. Gelbgrüne Kristalle, Schmp. 221 °C (Zersetzung), Ausb. 0.95 g (74%). – $C_{16}H_8Cl_2N_4$ (327.2). – **IR** (KBr): ν = 1573 $cm^{-1}$; 1554; 1532; 1400; 1371; 1075; 846; 763. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.73 (d, *J* = 8.6 Hz, 2H, Ph-3,5-H), 8.26 (ddd, *J* = 7.6/ 7.4/ 0.8 Hz, 1H, Ar-9-H), 8.33 (ddd, *J* = 7.7/ 7.6/ 1.3 Hz, 1H, Ar-8-H), 8.69 (d, *J* = 8.6 Hz, 2H, Ph-2,6-H), 8.87 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.20 (d, *J* = 7.8 Hz, 1H,

Ar-10-H). – **MS** (70 eV): m/z (%) = 329 (13), 328 (55), 327 (19), 326 (100) [$M^{+\cdot}$], 291 (13), 263 (15), 228 (11), 163 (21), 161 (61), 126 (44), 100 (13), 75 (15).

*4-(4-Chlorpyrimido[5,4-c]cinnolin-2-yl)-benzonitril* **(5l)**

Aus 0.9 g (3.0 mmol) **4l**, 15 min. Gelbgrüne Kristalle, Schmp. 197 °C, Ausb. 0.78 g (82%). – $C_{17}H_8ClN_5$ (317.7). – **IR** (KBr): ν = 2229 $cm^{-1}$ (C≡N); 1572; 1551; 1531; 1506; 1492; 1403; 1374; 1338; 1076; 849; 780; 767. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 8.09 – 8.16 (m, 2H, Ph-3,5-H), 8.29 (dd, *J* = 7.5/ 7.2 Hz, 1H, Ar-9-H), 8.36 (dd, *J* = 7.5/ 7.3 Hz, 1H, Ar-8-H), 8.85 (d, *J* = 8.6 Hz, 2H, Ph-2,6-H), 8.91 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 9.26 (d, *J* = 7.5 Hz, 1H, Ar-10-H).

*4-Chlor-2-(2-furyl)-pyrimido[5,4-c]cinnolin* **(5m)**

Aus 1.0 g (3.8 mmol) **4m**, 1 h. Dunkelgrüne Kristalle, Schmp. 216 °C, Ausb. 0.58 g (54%). – $C_{14}H_7ClN_4O$ (282.7). – **IR** (KBr): ν = 3433 $cm^{-1}$; 1572; 1552; 1530; 1498; 1471; 1366; 1075; 761. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 6.89 (dd, *J* = 3.5/ 1.7 Hz, 1H, Fur-4-H), 7.76 (d, *J* = 3.5 Hz, 1H, Fur-5-H), 8.19 – 8.24 (m, 2H, Fur-3-H, Ar-9-H), 8.31 (ddd, *J* = 7.7/ 7.7/ 1.2 Hz, 1H, Ar-8-H), 8.82 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.02 (d, *J* = 7.6 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 284 (33), 283 (15), 282 (100) [$M^{+\cdot}$], 219 (19), 164 (12), 163 (30), 161 (94), 126 (40), 100 (16), 99 (14), 93 (12), 75 (11), 51 (15), 50 (11), 39 (25), 28 (18).

*4-Chlor-2-(2-thienyl)-pyrimido[5,4-c]cinnolin* **(5n)**

Aus 0.8 g (2.9 mmol) **4n**, 1.5 h. Hellbraune Kristalle, Schmp. 193 °C, Ausb. 0.54 g (62%). – $C_{14}H_7ClN_4S$ (298.7). – **IR** (KBr): ν = 1575 $cm^{-1}$; 1554; 1536; 1491; 1434; 1406; 1378; 1357; 1075; 831; 780; 761; 729. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) =7.37 (dd, *J* = 4.9/ 3.9 Hz, 1H, Thi-4-H), 8.08 (dd, *J* = 5.0/ 1.0 Hz, 1H, Thi-5-H), 8.24 (ddd, *J* = 7.6/ 7.5/ 1.1 Hz, 1H, Ar-9-H), 8.29 – 8.33 (m, 2H, Ar-8-H, Thi-3-H), 8.83 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 9.04 (dd, *J* = 8.0/ 1.0 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 300 (38), 299 (16), 298 (100) [$M^{+\cdot}$], 263 (12) [$M^{+\cdot}$– Cl], 235 (16), 163 (14), 161 (42), 126 (21), 28 (10).

*4-Chlor-2-[(E)-2-phenylvinyl]pyrimido[5,4-c]cinnolin* **(5p)**

Aus 1.5 g (5.0 mmol) **4p**, 2.5 h. Dunkelgrüne Kristalle, Schmp. 192 °C, Ausb. 0.90 g (56%). – $C_{18}H_{11}ClN_4$ (318.8). – **IR** (KBr): ν = 1632 $cm^{-1}$; 1572; 1553; 1532; 1492; 1450; 1375; 1354; 1074; 767. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 7.45 – 7.51 (m, 3H, Ph-3,4,5-H), 7.55 (d, *J* = 15.9 Hz, 1H, Ar-C*H*=CH-Ph), 7.91 (d, *J* = 7.0 Hz, 2H, Ph-2,6-H), 8.23 (ddd, *J* = 7.6/ 7.5/ 1.2 Hz, 1H, Ar-9-H), 8.28 – 8.34 (m, 2H, Ar-8-H, Ar-CH=C*H*-Ph), 8.82 (d, *J* = 7.9 Hz, 1H, Ar-7-H), 9.05 (d, *J* = 7.9 Hz, 1H, Ar-10-H).

## 4.2.2 Synthese der Zielverbindungen

Zu einer auf 60 °C erwärmten Lösung von 1.0 mmol **5** in15 mL Ethanol wird unter Rühren langsam 10 mmol des Amins gegeben. Die Lösung wird 20 min in der Siedehitze gehalten, wobei die Produkte z. T. bereits als kristalline Niederschläge ausfallen. Bei den auch nach Abkühlen auf 4 °C nicht kristallisierenden Produkten wird das Reaktionsgemisch am Rotationsverdampfer auf ca. 5 mL eingeengt und anschließend zum Ausfällen des Produktes tropfenweise auf 100 mL Wasser gegeben. Der entstandene Niederschlag wird durch einen Büchnertrichter abgesaugt und mit jeweils ca. 20 mL Ethanol und Wasser gewaschen. Die zur Umkristallisierung verwendeten Lösungsmittel sind in Klammern hinter den Schmelzpunkten angegeben.

### 4.2.2.1 (Pyrimido[5,4-c]cinnolin-4-yl)alkohole mit basischem oder neutralem Zentrum in der Seitenkette

#### 4.2.2.1.1 2-[3-(Pyrimido[5,4-c]cinnolin-4-yl-amino)propylamino]ethanole (6)

*2-[(3-(9-Hexylpyrimido[5,4-c]-cinnolin-4-yl)aminopropyl)amino]ethanol* (**6a**)

Aus 0.20 g (0.66 mmol) **5b** und 1.6 g (13.5 mmol) [2-(3-Aminopropyl)amino]ethanol. Hellbraune Kristalle, Schmp. 116 °C, Ausb. 0.16 g (63%). – $C_{21}H_{30}N_6O$ (382.5) Ber. C 65.9 H 7.91 N 22.0 Gef. C 66.2 H 8.17 N 21.9. – **IR** (KBr): ν = 3337 $cm^{-1}$; 3295; 2925; 1608; 1572; 1549; 1301. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 6.9 Hz, 3H,

$CH_3$), 1.29 – 1.31 (m, 6H, $CH_3$-($CH_2$)$_3$-($CH_2$)$_2$-Ar), 1.69 –1.73 (m, 2H, $CH_3$-($CH_2$)$_3$-C$H_2$-$CH_2$-Ar), 1.85 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.60 (t, *J* = 5.7 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C$H_2$), 2.67 (t, *J* = 6.5 Hz, NH-C$H_2$-$CH_2$-OH), 2.93 (t, *J* = 7.5 Hz, 2H, $CH_3$-($CH_2$)$_4$-C$H_2$-Ar), 3.49 (t, *J* = 5.4 Hz, 2H, NH-$CH_2$-C$H_2$-OH), 3.71 („s“, 2H, Ar-NH-C$H_2$), 4.47 (s, 1H, OH, austauschb.), 7.98 (dd, *J* = 8.6/ 1.5 Hz, 1H, Ar-8-H), 8.57 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 8.59 (s, 1H, Ar-10-H), 8.76 (s, 1H, Ar-2-H), 9.82 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 382 (9) [$M^+$], 309 (21), 308 (23), 295 (17), 284 (19), 283 (100) [$M^{+\cdot}$– ($CH_2$)$_3$-NH-($CH_2$)$_2$-OH + 3H], 282 (36), 100 (39) [($CH_2$)$_3$-NH-($CH_2$)$_2$-$OH^+$ - 2H], 44 (10).

*2-[(3-[(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl]aminopropyl)amino]ethanol* (**6b**)

Aus 0.19 g (0.65 mmol) **5c** und 1.1 g (9.3 mmol) [2-(3-Aminopropyl)amino]ethanol. Hellgrüne Kristalle, Schmp. 198 °C (EtOH/ Ethylacetat/ DMF), Ausb. 0.14 g (57%). – $C_{21}H_{22}N_6O$ (374.5) Ber. C 67.4 H 5.92 N 22.4 Gef. C 67.3 H 5.93 N 22.2. – **IR** (KBr): ν = 3412 $cm^{-1}$; 3342; 1597; 1581; 1547; 1401; 1316. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.91 – 1.97 (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.62 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C$H_2$), 2.74 (t, *J* = 6.6 Hz, NH-C$H_2$-$CH_2$-OH), 3.49 – 3.50 (m, schlecht aufgel., 2H, NH-$CH_2$-C$H_2$-OH), 3.87 – 3.89 (m, 2H, Ar-NH-C$H_2$), 4.45 (s, 1H, OH, austauschb.), 7.56 – 7.62 (m, 3H, Ph-3,4,5-H), 8.08 (ddd, *J* = 8.0/ 7.0/ 1.1 Hz, 1H, Ar-9-H), 8.14 (ddd, *J* = 7.7/ 7.5/ 1.4 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.4 Hz, 1H, Ar-7-H), 8.67 – 8.71 (m, 2H, Ph-2,6-H), 9.02 (dd, *J* = 8.1/ 1.1 Hz, 1H, Ar-10-H), 9.85 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 374 (10) [$M^+$], 301 (18), 300 (20), 287 (23), 276 (23), 275 (100) [$M^{+\cdot}$– ($CH_2$)$_3$-NH-($CH_2$)$_2$-OH + 3H], 274 (37), 126 (13), 100 (27) [($CH_2$)$_3$-NH-($CH_2$)$_2$-$OH^+$ - 2H], 43 (11).

*2-[(3-[(2-(4-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]aminopropyl)amino]ethanol* (**6c**)

Aus 0.25 g (0.77 mmol) **5e** und 1.3 g (6.9 mmol) [2-(3-Aminopropyl)amino]ethanol. Gelbe Kristalle (EtOH/ EtAc), Schmp. 145 °C, Ausb. 0.21 g (68%). – $C_{22}H_{24}N_6O_2$ (404.5) Ber. C 65.3 H 5.98 N 20.8 Gef. C 65.1 H 5.88 N 20.6. – **IR** (KBr): ν = 3345 $cm^{-1}$; 1595; 1576; 1546; 1437; 1403; 1378; 1308; 1251; 1164; 767. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.94 (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.62 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C$H_2$), 2.73 (t, *J* = 6.5 Hz, NH-C$H_2$-$CH_2$-OH), 3.49 („m“, schlecht aufgel., 2H, NH-$CH_2$-C$H_2$-OH), 3.85 – 3.86 (m, 2H, Ar-NH-C$H_2$), 3.88 (s, 3H, $OCH_3$), 4.45 (s, 1H, OH, austauschb.),

7.12 (d, 2H, Ph-3,5-H), 8.06 (dd, *J* = 7.2/ 7.0 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 7.7/ 7.5/ 1.2 Hz, 1H, Ar-8-H), 8.61 – 8.65 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.4 Hz, 1H, Ar-10-H), 9.75 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 404 (14) [$M^{+\cdot}$], 331 (14), 330 (21), 319 (23), 318 (11), 309 (20), 307 (100), 306 (45), 127 (13), 126 (20), 100 (27) [$(CH_2)_3$-NH-$(CH_2)_2$-$OH^+$ - 2H], 56 (11), 45 (10), 44 (14), 31 (15), 30 (14).

*2-[(3-[2-(4-Ethoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]aminopropyl)amino]ethanol-semihydrat* (**6d**)

Aus 0.30 g (0.89 mmol) **5f** und 2.2 g (18.6 mmol) [2-(3-Aminopropyl)amino]ethanol. Hellgelbe Kristalle, Schmp. 158 °C (EtOH/ $H_2O$), Ausb. 0.22 g (60%). – $C_{23}H_{26}N_6O_2$ x 0.5 $H_2O$ (427.5) Ber. C 64.6 H 6.37 N 19.7 Gef. C 64.8 H 6.38 N 19.3. – **IR** (KBr): ν = 3283 $cm^{-1}$; 1593; 1577; 1546; 1436; 1404; 1378; 1308; 1251; 1166; 1048; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.39 (t, *J* = 6.9 Hz, 3H, O-$CH_2$-C*H*$_3$), 1.93 (tt, *J* = 6.6 Hz, 2H, NH-$CH_2$-C*H*$_2$-$CH_2$-NH), 2.62 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 2.73 (t, *J* = 6.6 Hz, 2H, NH-C*H*$_2$-$CH_2$-OH), 3.49 (dt, *J* = 5.4 Hz, 2H, NH-$CH_2$-C*H*$_2$-OH), 3.83 – 3.87 (m, 2H, Ar-NH-C*H*$_2$), 4.12 (q, *J* = 7.0 Hz, 2H, O-C*H*$_2$-$CH_3$), 4.47 (m, 1H, OH, austauschb.), 7.11 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.05 (ddd, *J* = 7.6/ 7.4/ 1.2 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.62 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (dd, *J* = 8.0/ 1.0 Hz, 1H, Ar-10-H), 9.76 (m, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 418 (16) [$M^{+\cdot}$], 387 (10), 345 (14), 344 (15), 320 (23), 319 (100) [$M^{+\cdot}$– $(CH_2)_3$-NH-$(CH_2)_2$-OH + 3H], 318 (41), 126 (11), 100 (20) [$(CH_2)_3$-NH-$(CH_2)_2$-$OH^+$ - 2H], 32 (10), 28 (44).

*2-[3-((2-(4-Propoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl)aminopropyl)amino]ethanol-semihydrat* (**6e**)

Aus 0.3 g (0.90 mmol) **5g** und 3.0 g (25.4 mmol) [2-(3-Aminopropyl)amino]ethanol. Hellgelbe Kristalle, Schmp. 97 °C (EtOH/ $H_2O$), Ausb. 0.21 g (53%). – $C_{23}H_{26}N_6O_2$ x $H_2O$ (441.5) Ber. C 65.3 H 6.62 N 19.0 Gef. C 65.4 H 6.99 N 19.2. – **IR** (KBr): ν = 3403 $cm^{-1}$; 1593; 1577; 1546; 1436; 1404; 1378; 1308; 1251; 1166; 1048; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.02 (t, *J* = 7.4 Hz, 3H, O-$CH_2$-$CH_2$-C*H*$_3$), 1.75 – 1.84 (m, 2H, O-$CH_2$-C*H*$_2$-$CH_3$), 1.93 (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.62 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 2.73 (t, *J* = 6.6 Hz, 2H, NH-C*H*$_2$-$CH_2$-OH), 3.49 (dt, *J* = 5.2 Hz, 2H,

NH-$CH_2$-C$H_2$-OH), 3.84 – 3.86 (m, 2H, Ar-NH-C$H_2$), 4.06 (t, *J* = 6.5 Hz, 2H, O-C$H_2$-$CH_2$-$CH_3$), 4.46 („m“, 1H, OH, austauschb.), 7.11 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.7/ 7.2 Hz, 1H, Ar-9-H), 8.10 – 8.14 (m, 1H, Ar-8-H), 8.62 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 8.1 Hz, 1H, Ar-10-H), 9.77 („m“, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 432 (14) [$M^{+\cdot}$], 401 (11), 359 (15), 358 (13), 345 (14), 334 (24), 333 (100) [$M^{+\cdot}$– $(CH_2)_3$-NH-$(CH_2)_2$-OH + 3H], 332 (38), 100 (15) [$(CH_2)_3$-NH-$(CH_2)_2$-$OH^+$ - 2H].

*2-[(3-[(2-(4-Butoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]aminopropyl)amino]ethanol-hydrat* (**6f**)

Aus 0.15 g (0.41 mmol) **5h** und 1.3 g (11.0 mmol) [2-(3-Aminopropyl)amino]ethanol. Gelbe Kristalle (EtOH), Schmp. 83 °C, Ausb. 0.10 g (54%). – $C_{25}H_{30}N_6O_2$ x $H_2O$ (464.6) Ber. C 64.6 H 6.94 N 18.1 Gef. C 64.3 H 6.76 N 17.7. – **IR** (KBr): ν = 3401 $cm^{-1}$; 3285; 2955; 1595; 1576; 1547; 1405; 1379; 1308; 1251; 1165; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.97 (t, *J* = 7.3 Hz, 3H, O-$CH_2$-$CH_2$-$CH_2$-C$H_3$), 1.44 – 1.53 (m, 2H, O-$CH_2$-$CH_2$-C$H_2$-$CH_3$), 1.75 (tt, *J* = 6.6 Hz, 2H, O-$CH_2$-C$H_2$-$CH_2$-$CH_3$), 1.93 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.62 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C$H_2$), 2.73 (t, *J* = 6.5 Hz, 2H, NH-C$H_2$-$CH_2$-OH), 3.49 – 3.50 (m, 2H, NH-$CH_2$-C$H_2$-OH), 3.84 – 3.86 (m, schlecht aufgel., 2H, Ar-NH-C$H_2$), 4.10 (t, *J* = 6.5 Hz, 2H, O-C$H_2$-$CH_2$-$CH_2$-$CH_3$), 4.45 (s, 1H, OH, austauschb.), 7.11 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.2/ 7.0 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 7.7/ 7.5/ 1.2 Hz, 1H, Ar-8-H), 8.61 – 8.63 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.5 Hz, 1H, Ar-10-H), 9.75 (m, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 446 (11) [$M^{+\cdot}$], 373 (12), 372 (12), 359 (15), 348 (23), 347 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-OH + 3H], 346 (45), 126 (11), 100 (17) [$(CH_2)_3$-NH-$(CH_2)_2$-$OH^+$ - 2H], 28 (11).

*2-[(3-[(2-Furyl)pyrimido[5,4-c]cinnolin-4-yl]aminopropyl)amino]ethanol* (**6g**)

Aus 0.30 g (1.06 mmol) **5m** und 1.7 g (14.4 mmol) [2-(3-Aminopropyl)amino]ethanol. Hellgrüne Kristalle, Schmp. 183°C (EtOH/ $H_2O$/ DMF), Ausb. 0.13 g (36%). – $C_{19}H_{20}N_6O_2$ (364.4) Ber. C 62.3 H 5.53 N 23.0 Gef. C 62.3 H 5.13 N 22.6. – **IR** (KBr): ν = 3343 $cm^{-1}$; 3311; 2830; 1603; 1574; 1544; 1496; 1476; 1434; 1405; 1367; 1315; 1241; 765. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.90 – (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.61 (t, *J* = 5.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C$H_2$), 2.70 (t, *J* = 6.5 Hz, 2H, NH-C$H_2$-$CH_2$-OH), 3.48 –

3.51 (m, schlecht aufgel., 2H, NH-$CH_2$-C$H_2$-OH), 3.79 (m, schlecht aufgel., 2H, Ar-NH-C$H_2$), 4.45 (s, 1H, OH, austauschb.), 6.76 - 6.78 (m, 1H, Fur-4-H), 7.54 (d, *J* = 3.5 Hz, 1H, Fur-5-H), 8.02 - 8.08 (m, 2H, Fur-3-H, Ar-9-H), 8.11 - 8.15 (m, 1H, Ar-8-H), 8.62 (d, *J* = 8.1, 1H, Ar-7-H), 8.87 (d, *J* = 7.7 Hz, 1H, Ar-10-H), 9.84 (s, 1H, Ar-NH, austauschb.). **MS** (EI, 70 °C): m/z (%) = 364 (11) [$M^{+\cdot}$], 291 (21), 290 (28), 277 (22), 276 (11), 266 (18), 265 (100) [$M^{+\cdot}$– $(CH_2)_3$-NH-$(CH_2)_2$-OH + 3H], 264 (47), 263 (11), 126 (13), 100 (30) [$(CH_2)_3$-NH-$(CH_2)_2$-$OH^+$ - 2H], 56 (11).

### 4.2.2.2 2-(4-Pyrimido[5,4-c]cinnolin-4-yl)piperazin-1-yl-ethanole (7)

*2-[4-(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl)]piperazin-1-yl-ethanol-semihydrat* (**7a**)

Aus 0.30 g (1.02 mmol) **5c** und 1.8 g (13.8 mmol) 2-Piperazin-1-yl-ethanol. Goldgelbe Kristalle, Schmp. 148 °C, Ausb. 0.24 g (61%). – $C_{22}H_{22}N_6O$ x 0.5 $H_2O$ (395.5) Ber. C 66.8 H 5.86 N 21.3 Gef. C 66.8 H 5.94 N 21.3. – **IR** (KBr): ν = 3432 $cm^{-1}$ (NH); 1575; 1542; 1303; 1258. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.50 – 2.52 (im DMSO-Peak, 2H, Pipz-C$H_2$-$CH_2$-OH), 2.74 (t, *J* = 4.9 Hz, 4H, Pipz-2,6-H), 3.59 (dt, *J* = 6.0 Hz, 2H, $CH_2$-C$H_2$-OH), 4.49 (t, *J* = 5.4 Hz, 1H, $CH_2$-$CH_2$-O*H*, austauschb.), 4.66 (s, br, 4H, Pipz-3,5-H), 7.57 – 7.61 (m, 3H, Ph-3,4,5-H), 8.06 (ddd, *J* = 7.9/ 7.1/ 1.0 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 8.3/ 7.0/ 1.4 Hz, 1H, Ar-8-H), 8.59 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.61 – 8.64 (m, 2H, Ph-2,6-H), 9.05 (dd, *J* = 8.0/ 1.0 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 387 (22), 386 (86) [$M^{+\cdot}$], 355 (15), 301 (10), 300 (27), 299 (24), 298 (27), 287 (43), 286 (78), 275 (27), 274 (27), 155 (13), 127 (18), 126 (16), 113 (21), 100 (100) [$(CH_2)_2(CH_2)$-N-$CH_2$-$CH_2$-$OH^+$ - H], 98 (12), 95 (16), 83 (10), 69 (11), 56 (15), 45 (12), 44 (13), 42 (17), 28 (41).

*2-[N-(2-(2-Furyl)pyrimido[5,4-c]cinnolin-4-yl)]piperazin-1-yl-ethanol* (**7b**)

Aus 0.30 g (1.06 mmol) **5m** und 1.4 g (10.8 mmol) 2-Piperazin-1-yl-ethanol. Ockerfarbene Kristalle, Schmp. 94 °C, Ausb. 0.31 g (77%). – $C_{20}H_{20}N_6O_2$ Ber. C 63.8 H 5.36 N 22.3 (376.4) Gef. C 63.5 H 5.41 N 22.4. – **IR** (KBr): 3420 $cm^{-1}$; 1576; 1541; 1523; 1493; 1476; 1364; 1305; 987; 764. – **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 2.49 – 2.52 (im DMSO-Peak, 2H, Pipz-C$H_2$-$CH_2$-OH), 2.72 (t, *J* = 4.6 Hz, 4H, Pipz-2,6-H), 3.59 (dt, *J* = 6.0 Hz, 2H, $CH_2$-C$H_2$-OH), 4.50 (t, *J* = 5.3 Hz, 1H, $CH_2$-$CH_2$-O*H*, austauschb.), 4.60 (s, br, 4H,

Pipz-3,5-H), 6.77 (dd, *J* = 3.3/ 1.7 Hz, 1H, Fur-4-H), 7.53 (d, *J* = 2.9 Hz, 1H, Fur-5-H), 8.00 – 8.04 (m, 2H, Fur-3-H, Ar-9-H), 8.10 – 8.14 (ddd, *J* = 8.2/ 7.1/ 1.2 Hz, 1H, Ar-8-H), 8.55 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.89 (d, *J* = 7.7 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 376 (32) [$M^{+\cdot}$], 295 (13), 294 (12), 293 (16), 285 (18), 284 (45), 127 (16),126 (13), 113 (25), 101 (10), 100 (100) [$(CH_2)_2(CH_2)$-N-$CH_2$-$CH_2$-$OH^+$ - H], 95 (19), 83 (12), 82 (10), 70 (11), 69 (18), 56 (26), 45 (10), 42 (34).

### 4.2.2.3 Sonstige Pyrimido[5,4-c]cinnolin-4-yl-alkohole (8 – 11)

*2-(Pyrimido[5,4-c]cinnolin-4-ylamino)ethanol (**8**)*

Aus 0.21 g (0.99 mmol) **5a** und 1.5 g (24.6 mmol) 2-Aminoethanol. Dunkelgrüne Kristalle, Schmp. 223 °C, Ausb. 0.16 g (66%). – $C_{12}H_{11}N_5O$ (241.3) Ber. C 59.8 H 4.60 N 29.0 Gef. C 59.6 H 4.76 N 28.8. – **IR** (KBr): ν = 3349 $cm^{-1}$; 3301; 1605; 1574; 1549; 1443; 1356; 1311; 1269; 1047; 782. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.71 – 3.77 (m, 4H, Ar-NH-($CH_2$)$_2$-OH), 4.89 (s, 1H, OH, austauschb.), 8.08 (dd, *J* = 7.6/ 7.4 Hz, 1H, Ar-9-H), 8.15 (dd, *J* = 8.0/ 7.2 Hz, 1H, Ar-8-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.84 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.46 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 241 (43) [$M^{+\cdot}$], 223 (25), 222 (41), 211 (45), 210 (100) [$M^{+\cdot}$– $CH_2$-OH], 198 (35), 197 (23), 183 (17), 156 (10), 128 (17), 127 (13), 126 (21), 30 (13).

*2-[(Pyrimido[5,4-c]cinnolin-4-yl)amino]-2-ethoxyethanol (**9**)*

Aus 0.26 g (1.23 mmol) **5a** und 1.4 g (13.3 mmol) 2-Amino-2-ethoxyethanol. Dunkelgrüne Kristalle, Schmp. 167 °C, Ausb. 0.13 g (38%). – $C_{14}H_{15}N_5O_2$ (285.3) Ber. C 58.9 H 5.30 N 24.6 Gef. C 58.5 H 5.45 N 24.3. – **IR** (KBr): ν = 3345 $cm^{-1}$; 1608; 1574; 1551; 1439; 1355; 1334; 1309; 1125; 1064; 781. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.51 (m, schlecht aufgel., 4H, O-($CH_2$)$_2$-OH)), 3.75 (t, *J* = 5.9 Hz, 2H, Ar-NH-$CH_2$-$CH_2$), 3.83 – 3.88 (m, 2H, Ar-NH-$CH_2$-$CH_2$), 4.61 (m, schlecht aufgel., 1H, OH), 8.08 (dd, *J* = 7.9/ 7.1 Hz, 1H, Ar-9-H), 8.16 (dd, *J* = 8.0/ 7.0 Hz, 1H, Ar-8-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.82 (s, 1H, Ar-2-H), 8.85 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.54 (s, 1H, Ar-NH). – **MS** (70 eV): m/z (%) =

285 (31) [$M^{+\cdot}$], 240 (17), 224 (14), 223 (21), 222 (22), 212 (16), 211 (100) [$M^{+\cdot}$– $CH_2$-O-$(CH_2)_2$-OH], 201 (16), 200 (50), 187 (14), 126 (12), 45 (11), 30 (11).

*2-[(3-[(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl]aminoethyl)amino]ethanol-hydrat (**10**)*

Aus 0.30 g (1.02 mmol) **5c** und 1.8 g (17.3 mmol) [2-(3-Aminoethyl)amino]ethanol. Hellgrüne Kristalle (Methanol), Schmp. 182 °C, Ausb. 0.20 g (52%). – $C_{20}H_{20}N_6O$ x $H_2O$ (378.4) Ber. C 63.5 H 5.86 N 22.2 Gef. C 63.8 H 5.46 N 22.4. – **IR** (KBr): ν = 3329 $cm^{-1}$; 3297; 1596; 1577; 1548; 1401; 1316; 1297. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.73 (t, *J* = 5.7 Hz, 2H, NH-C*H*$_2$-$CH_2$-OH,), 3.01 (t, *J* = 6.4 Hz, Ar-NH-$CH_2$-C*H*$_2$), 3.49 (t, *J* = 5.7 Hz, 2H, NH-$CH_2$-C*H*$_2$-OH), 3.89 – 3.93 (m, 2H, Ar-NH-C*H*$_2$), 7.57 – 7.61 (m, 3H, Ph-3,4,5-H), 8.09 (ddd, *J* = 7.5/ 7.4/ 1.2 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 8.3/ 7.0/ 1.4 Hz, 1H, Ar-8-H), 8.66 (d, *J* = 7.9 Hz, 1H, Ar-7-H), 8.68 – 8.70 (m, 2H, Ph-2,6-H), 9.03 (dd, *J* = 7.6/ 0.8 Hz, 1H, Ar-10-H), 9.52 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 360 (2) [$M^{+\cdot}$], 288 (21), 287 (100) [$M^{+\cdot}$ - $CH_2$-NH-$(CH_2)_2$-OH], 286 (23), 275 (18), 274 (83) [$M^{+\cdot}$– $(CH_2)_2$-NH-$(CH_2)_2$-OH +2H], 126 (11), 74 (38) [$CH_2$-NH-$(CH_2)_2$-$OH^+$], 56 (21), 44 (11), 30 (14).

*3-[(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl]-aminopropan-1,2-diol (**11**)*

Aus 0.28 g (0.96 mmol) **5c** und 1.4 g (15.4 mmol) 3-Aminopropan-1,2-diol. Hellgrüne Kristalle, Schmp. 196 °C, Ausb. 0.25 g (75%). – $C_{19}H_{17}N_5O_2$ x $H_2O$ (347.4) Ber. C 65.7 H 4.93 N 20.2 Gef. C 65.7 H 4.70 N 20.2. – **IR** (KBr): ν = 3391 $cm^{-1}$; 1597; 1578; 1548; 1402; 1375; 1317; 1299; 707. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.49 – 3.56 (m, 2H, NH-$CH_2$-CH(OH)-C*H*$_2$-OH), 3.72 – 3.79 (m, 1H, NH-$CH_2$-C*H*(OH)-$CH_2$-OH), 3.95 - 4.01 (m, 2H, Ar-NH-C*H*$_2$), 4.77 (t, *J* = 5.7 Hz, 1H, OH, austauschb.), 7.57 – 7.62 (m, 3H, Ph-3,4,5-H), 8.09 (ddd, *J* = 7.5/ 7.4/ 1.0 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 8.3/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 8.68 – 8.71 (m, 2H, Ph-2,6-H), 9.03 (dd, *J* = 8.0/ 0.8 Hz, 1H, Ar-10-H), 9.30 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 347 (32) [$M^{+\cdot}$], 317 (13), 316 (45), 298 (29), 287 (54), 286 (100) [$M^{+\cdot}$- CH(OH)-$CH_2$-OH], 274 (39), 273 (31), 127 (16), 126 (43).

### 4.2.2.4 (Pyrimido[5,4-c]cinnolin-4-yl)propan-1,3-diamine

#### 4.2.2.4.1 N-Alkyl-N´-(pyrimido[5,4-c]cinnolin-4-yl)propan-1,3-diamine (12)

*N-Methyl-N'-[(2-phenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**12a**)

Aus 0.30 g (1.02 mmol) **5c** und 1.2 g (16.6 mmol) N-Methylpropan-1,3-diamin. Hellbraune Kristalle, Schmp. 64 °C (EtOH/ Ethylacetat), Ausb. 0.24 g (69%). – $C_{20}H_{20}N_6$ (344.4) Ber. C 69.8 H 5.85 N 24.4 Gef. C 69.8 H 5.99 N 24.1. – **IR** (KBr): ν = 3401 $cm^{-1}$; 1596; 1577; 1547; 1401; 1376; 1316; 1298; 754; 706. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.94 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.34 (s, 3H, NH-C*H*$_3$), 2.65 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.86 (t, *J* = 6.6 Hz, 2H, Ar-NH-C*H*$_2$), 7.57 – 7.61 (m, 3H, Ph-3,4,5-H), 8.08 (ddd, *J* = 7.6/ 7.4/ 0.8 Hz, 1H, Ar-9-H), 8.14 (ddd, *J* = 7.7/ 7.5/ 1.2 Hz, 1H, Ar-8-H), 8.64 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.67 – 8.69 (m, 2H, Ph-2,6-H), 9.01 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.78 (s, 1H, Ar-NH, austauschb.).·– **MS** (70 eV): m/z (%) = 344 (11) [$M^{+\cdot}$], 301 (16), 287 (23), 276 (19), 275 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$CH_3$ + 3H], 274 (46), 126 (11), 70 (26) [$(CH_2)_3$-NH-$CH_3^+$ - 2H], 44 (28).

*N-[2-(2-Furyl)pyrimido[5,4-c]cinnolin-4-yl]-N'-methylpropan-1,3-diamin* (**12b**)

Aus 0.21 g (0.74 mmol) **5m** und 1.3 g (18.0 mmol) N-Methylpropan-1,3-diamin. Hellbraune Kristalle, Schmp. 119 °C (EtOH/ Ethylacetat), Ausb. 0.14 g (57%). – $C_{18}H_{18}N_6O$ (334.4) Ber.C 64.7 H 5.43 N 25.1 Gef. C 64.6 H 5.45 N 25.0. – **IR** (KBr): 3343 $cm^{-1}$; 3297; 1605; 1576; 1545; 1480; 1431; 1365; 1316; 767. **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 1.89 (tt, *J* = 6.7 Hz, 2H, NH-$CH_2$-C*H*$_2$-$CH_2$), 2.29 (s, 3H, NH-$CH_3$), 2.61 (t, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.79 (t, *J* = 6.6 Hz, 2H, Ar-NH-C*H*$_2$), 6.77 (dd, *J* = 3.2/ 1.6 Hz, 1H, Fur-4-H), 7.54 (d, *J* = 3.3 Hz, 1H, Fur-5-H), 8.03 – 8.08 (m, 2H, Fur-3-H, Ar-9-H), 8.13 (dd, *J* = 8.3/ 7.0 Hz, Ar-8-H), 8.62 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.88 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.75 (s, 1H, Ar-NH, austauschb.). – **MS** (EI, 70°C): m/z (%) = 334 (13) [$M^{+\cdot}$], 291 (16), 277 (22), 266 (19), 265 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$CH_3$ + 3H], 264 (47), 107 (35), 71 (20), 70 (39) [$(CH_2)_3$-NH-$CH_3^+$ - 2H], 69 (16), 57 (23), 55 (11), 44 (29), 43 (26), 42 (10), 41 (14).

*N-[(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl]-N'-propylpropan-1,3-diamin* (**12c**)

Aus 0.25 g (0.85 mmol) **5c** und 1.2 g (10.3 mmol) N-Propylpropan-1,3-diamin. Hellbraune Kristallnadeln, Schmp. 123 °C (EtOH), Ausb. 0.18 g (56%). – $C_{22}H_{24}N_6$ (372.5) Ber. C 70.9 H 6.49 N 22.6 Gef. C 71.3 H 6.29 N 22.2. – **IR** (KBr): ν = 3433 $cm^{-1}$; 1596; 1546; 1400; 1316; 707. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.3 Hz, 1H, NH-$CH_2$-$CH_2$-C*H*$_3$), 1.39 – 1.48 (m, 2H, NH-$CH_2$-C*H*$_2$-$CH_3$), 1.93 (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.46 – 2.48 (m, 2H, NH-C*H*$_2$-$CH_2$-$CH_3$), 2.69 (t, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.87 (t, *J* = 6.4 Hz, 2H, Ar-NH-C*H*$_2$), 7.56 – 7.63 (m, 3H, Ph-3,4,5-H), 8.08 (ddd, *J* = 7.6/ 7.4/ 1.2 Hz, 1H, Ar-9-H), 8.14 (ddd, *J* = 8.2/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.63 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.66 – 8.70 (m, 2H, Ph-2,6-H), 9.02 (dd, *J* = 8.0/ 0.8 Hz, 1H, Ar-10-H), 9.84 (s, 1H, Ar-NH, austauschb.).·– **MS** (70 eV): m/z (%) = 372 (11) [$M^{+\cdot}$], 301 (18), 300 (11), 287 (17), 276 (19), 275 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-$CH_3$ + 3H], 274 (32), 98 (39) [$(CH_2)_3$-NH-$(CH_2)_2$-$CH_3^+$ - 2H], 30 (16).

*N-[2-(4-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]-N'-propylpropan-1,3-diamin* (**12d**)

Aus 0.20 g (0.62 mmol) **5e** und 1.2 g (10.3 mmol) N-Propylpropan-1,3-diamin. Hellbraune Kristallnadeln, Schmp. 83 °C, Ausb. 0.22 g (87%). – $C_{23}H_{26}N_6O$ (402.5) Ber. C 68.6 H 6.51 N 20.9 Gef. C 68.6 H 6.23 N 20.7. – **IR** (KBr): ν = 1593 $cm^{-1}$; 1575; 1546; 1402; 1308; 1251; 1164; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.4 Hz, 3H, NH-$CH_2$-$CH_2$-C*H*$_3$), 1.39 – 1.48 (m, 2H, NH-$CH_2$-C*H*$_2$-$CH_3$), 1.92 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.47 (t, z.T. im DMSO, *J* = 7.1 Hz, 2H, NH-C*H*$_2$-$CH_2$-$CH_3$) 2.69 (t, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.86 – 3.88 (m, 4H, Ar-NH-C*H*$_2$, $OCH_3$), 7.12 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.06 (dd, *J* = 7.6/ 7.2 Hz, 1H, Ar-9-H), 8.12 (dd, *J* = 7.3/ 7.1 Hz, 1H, Ar-8-H), 8.61 - 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.76 (s, breit, 1H, Ar-NH, austauschb.). – **MS** (EI, 70°C): m/z (%) = 402 (14) [$M^{+\cdot}$], 331 (13), 317 (18), 306 (20), 305 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-$CH_3$ + 3H], 304 (38), 126 (11), 98 (30) [$(CH_2)_3$-NH-$(CH_2)_2$-$CH_3^+$ - 2H], 30 (17), 28 (16).

*N-[2-(4-Propoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]-N'-propylpropan-1,3-diamin* (**12e**)

Aus 0.12 g (0.34 mmol) **4g** und 1.1 g (9.5 mmol) N-Propylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 74 °C (EtOH/ Ethylacetat/ DMF), Ausb. 0.12 g (82%). – $C_{25}H_{30}N_6O$ (430.6) Ber. C 69.7 H 7.02 N 19.5 Gef. C 69.5 H 6.94 N 19.3. – **IR** (KBr): ν = 3351 $cm^{-1}$; 2961; 2933; 1595; 1576; 1546; 1436; 1402; 1377; 1309; 1250; 1164; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.3 Hz, 1H, NH-$CH_2$-$CH_2$-C*H*$_3$), 1.02 (t, *J* = 7.4 Hz, 3H, O-$CH_2$-$CH_2$-C*H*$_3$). 1.39 – 1.48 (m, 2H, NH-$CH_2$-C*H*$_2$-$CH_3$), 1.75 – 1.83 (m, 2H, O-$CH_2$-C*H*$_2$-$CH_3$), 1.92 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.46 – 2.48 (m, z.T. im DMSO, 2H, NH-C*H*$_2$-$CH_2$-$CH_3$), 2.69 (t, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.85 (s, breit, 2H, Ar-NH-C*H*$_2$), 4.05 (t, *J* = 6.5 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_3$), 7.10 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.3/ 7.0 Hz, 1H, Ar-9-H), 8.10 – 8.13 (m, 1H, Ar-8-H), 8.60 – 8.63 (m, 3H, Ar-10-H, Ph-2,6-H), 8.98 (d, *J* = 7.7 Hz, 1H, Ar-7-H), 9.74 (s, *J* = 5.4 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 431 (10), 430 (37) [$M^{+\cdot}$], 413 (10), 401 (20), 373 (14), 372 (11), 359 (26), 358 (21), 345 (25), 334 (22), 333 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-$CH_3$ + 3H], 332 (36), 126 (11), 98 (25) [$(CH_2)_3$-NH-$(CH_2)_2$-$CH_3^+$ - 2H], 44 (12), 28 (13).

*N-[2-(2-Furyl)pyrimido[5,4-c]cinnolin-4-yl]-N'-propylpropan-1,3-diamin* (**12f**)

Aus 0.25 g (0.88 mmol) **5m** und 1.4 g (12.1 mmol) N-Propylpropan-1,3,diamin. Goldgelbe Kristalle, Schmp. 118 °C (EtOH), Ausb. 0.15 g (47%). – $C_{20}H_{22}N_6O$ (362.4) Ber. C 66.3 H 6.12 N 23.2 Gef. C 66.4 H 6.04 N 22.9. – **IR** (KBr): 3351 $cm^{-1}$; 2954; 2931; 2872; 1602; 1574; 1544; 1480; 1432; 1403; 1365; 1318; 1239; 1009; 779; 766; 743. – **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 0.86 (t, *J* = 7.4 Hz, 3H, NH-$CH_2$-$CH_2$-C*H*$_3$), 1.39 – 1.48 (m, 2H, NH-$CH_2$-C*H*$_2$-$CH_3$), 1.89 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.47 (t, *J* = 7.1 Hz, 2H, NH-C*H*$_2$-$CH_2$-$CH_3$) 2.66 (t, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 (t, *J* = 6.4 Hz, 2H, Ar-NH-C*H*$_2$), 6.78 (dd, *J* = 3.2/ 1.6 Hz, 1H, Fur-4-H), 7.53 (d, *J* = 3.3 Hz, 1H, Fur-5-H), 8.03 – 8.07 (m, 2H, Fur-3-H, Ar-9-H), 8.11 – 8.14 (m, 1H, Ar-8-H), 8.62 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.88 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.81 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 362 (7) [$M^{+\cdot}$], 291 (13), 290 (10), 277 (17), 266 (16), 265 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-$CH_3$ + 3H], 126 (11), 98 (75) [$(CH_2)_3$-NH-$(CH_2)_2$-$CH_3^+$ - 2H], 72 (16), 70 (11), 56 (13), 44 (14), 43 (22), 42 (11), 41 (18), 39 (12), 20 (68), 28 (18), 27 (12).

*N-Propyl-N'-[2-(2-thienyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**12g**)

Aus 0.30 g (1.00 mmol) **5n** und 1.5 g (12.9 mmol) N-Propylpropan-1,3,diamin. Hellbraune Kristalle, Schmp. 134 °C (EtOH/ Ethylacetat), Ausb. 0.26 g (69%). – $C_{20}H_{22}N_6S$ (378.5). Ber. C 63.5 H 5.86 N 22.2 Gef.C 63.6 H 5.67 N 22.2. – **IR** (KBr): ν = 3351 $cm^{-1}$; 1595; 1575; 1537; 1524; 1433; 1311; 765. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.4 Hz, 3H, NH-$CH_2$-$CH_2$-C*H*$_3$), 1.39 – 1.48 (m, 2H, NH-$CH_2$-C*H*$_2$-$CH_3$), 1.90 (tt, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.47 (z.T. im DMSO-Peak, m, 2H, NH-C*H*$_2$-$CH_2$-$CH_3$), 2.68 (t, *J* = 6.5 Hz, 2H, Ar-$CH_2$-$CH_2$-C*H*$_2$), 3.80 (d, *J* = 6.5 Hz, 2H, Ar-NH-C*H*$_2$), 7.28 (dd, *J* = 4.8/ 3.9 Hz, 1H, Thi-4-H), 7.87 (dd, *J* = 5.0/ 0.8 Hz, 1H, Thi-5-H), 8.06 (dd, *J* = 7.1/ 7.0 Hz, 1H, Ar-9-H), 8.11 – 8.15 (m, 1H, Ar-8-H), 8.17 (dd, *J* = 3.5/ 0.9 Hz, 1H, Thi-3-H), 8.62 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.87 – 8.89 (m, 1H, Ar-10-H), 9.84 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 378 (11) [$M^{+\cdot}$], 361 (25), 360 (13), 322 (25), 321 (12), 320 (34), 319 (18), 307 (20), 306 (20), 293 (25), 292 (21), 282 (17), 281 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-$(CH_2)_2$-$CH_3$ + 3H], 155 (11), 135 (11), 127 (15), 126 (25), 110 (10), 98 (57) [$(CH_2)_3$-NH-$(CH_2)_2$-$CH_3^+$ - 2H], 72 (11), 43 (14), 41 (13), 30 (26), 28 (37).

#### 4.2.2.4.2 N-Cyclohexyl-N´-(pyrimido[5,4-c]cinnolin-4-yl)propan-1,3-diamine (13)

*N-Cyclohexyl-N'-[(2-Phenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**13a***)*

Aus 0.12 g (0.41 mmol) **5c** und 1.4 g (8.9 mmol) N-Cyclohexylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 131 °C, Ausb. 0.16 g (95%). – $C_{25}H_{28}N_6$ (412.5) Ber. C 72.8 H 6.84 N 20.4 Gef. C 72.7 H 6.89 N 20.5. – **IR** (KBr): ν = 3360 $cm^{-1}$; 2927; 2851; 1593; 1576; 1545; 1449; 1397; 1364; 1317; 1299; 707. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.96 – 1.04 (m, 2H, Cyc-3a,5a-H), 1.09 – 1.23 (m, 3H, Cyc-3e,4a,5e-H), 1.50 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.65 (m, 2H, Cyc-2a,6a-H), 1.81 – 1.84 (m, 2H, Cyc-2e,6e-H), 1.91 (tt, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 – 2.38 (m, 1H, Cyc-1-H), 2.73 (t, *J* = 6.1 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.88 (s, breit, 2H, Ar-NH-C*H*$_2$), 7.59 – 7.63 (m, 3H, Ph-3,4,5-H), 8.08 (dd, *J* = 7.6/ 7.4 Hz, 1H, Ar-9-H), 8.15 (dd, *J* = 8.2/ 6.9 Hz, 1H, Ar-8-H), 8.65 –8.70 (m, 3H, Ar-7-H, Ph-2,6-H), 9.03 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.93 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 412 (6) [$M^{+\cdot}$], 287 (12), 276 (16), 275 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 274 (19), 138 (57) [$(CH_2)_3$-NH-$Cyc^+$ - 2H], 56 (18), 30 (15).

*N-Cyclohexyl-N'-[2-(2-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin*

(**13b**)

Aus 0.20 g (0.62 mmol) **5d** und 1.9 g (12.1 mmol) N-Cyclohexylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 100 °C, Ausb. 0.18 g (66%). – $C_{26}H_{30}N_6O$ (442.6) Ber. C 70.6 H 6.83 N 19.0 Gef. C 70.6 H 6.90 N 18.6. – **IR** (KBr): ν = 3415 $cm^{-1}$; 3338; 2924; 1597; 1546; 1301. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.89 – 0.97 (m, 2H, Cyc-3a,5a-H), 1.04 – 1.18 (m, 3H, Cyc-3e,4a,5e-H), 1.49 – 1.52 (m, 1H, Cyc-4e-H), 1.59 – 1.62 (m, 2H, Cyc-2a,6a-H), 1.74 – 1.77 (m, 2H, Cyc-2e,6e-H), 1.87 (tt, J = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 2.28 – 2.33 (m, 1H, Cyc-1-H), 2.66 (t, *J* = 6.3 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 3.73 – 3.75 (m, 2H, Ar-NH-C*$H_2$*), 3.85 (s, 3H, $OCH_3$), 7.09 (dd, *J* = 7.5/ 7.2 Hz, 1H, Ph-4-H), 7.20 (d, *J* = 8.3 Hz, 1H, Ph-3-H), 7.50 (ddd, *J* = 7.9/ 7.6/ 1.8 Hz, 1H, Ph-5-H), 7.80 (dd, J = 7.6/ 1.8 Hz, 1H, Ph-6-H), 8.04 (dd, *J* = 8.0/ 7.1 Hz, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.6/ 7.6/ 1.3 Hz, 1H, Ar-8-H), 8.66 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.84 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.83 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 442 (3) [$M^{+\cdot}$], 317 (11), 306 (20), 305 (100) [$M^{+\cdot}$-$(CH_2)_3$-NH-Cyc + 3H], 304 (19), 138 (19) [$(CH_2)_3$-NH-$Cyc^+$ - 2H], 56 (12), 30 (11).

*N-Cyclohexyl-N'-[2-(4-Methoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin*

(**13c**)

Aus 0.40 g (1.24 mmol) **5e** und 2.5 g (15.9 mmol) N-Cyclohexylpropan-1,3-diamin. Hellgelbe, feinfaserige Kristalle, Schmp. 155 °C, Ausb. 0.31 g (56%). – $C_{26}H_{30}N_6O$ (442.6) Ber. C 70.6 H 6.83 N 19.0 Gef. C 70.3 H 6.63 N 18.7. – **IR** (KBr): ν = 2927 $cm^{-1}$; 1595; 1575; 1546; 1403; 1375; 1309; 1251; 1164; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.96 – 1.08 (m, 2H, Cyc-3a,5a-H), 1.09 - 1.22 (m, 3H, Cyc-3e,4a,5e-H), 1.51 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.65 (m, 2H, Cyc-2a,6a-H), 1.90 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 2.33 – 2.39 (m, 1H, Cyc-1-H), 2.73 (t, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 3.85 – 3.89 (m, 5H, Ar-NH-C*$H_2$*, $OCH_3$), 7.12 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.06 (ddd, *J* = 7.6/ 7.4/ 0.8 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.62 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (dd, *J* = 7.6/ 0.9 Hz, 1H, Ar-10-H), 9.82 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 442 (9) [$M^{+\cdot}$], 317 (13), 306 (21), 305 (100) [$M^{+\cdot}$-$(CH_2)_3$-NH-Cyc + 3H], 304 (25), 138 (37) [$(CH_2)_3$-NH-$Cyc^+$ - 2H], 56 (20), 30 (18), 28 (33).

*N-Cyclohexyl-N'-[2-(4-ethoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**13d**)

Aus 0.20 g (0.59 mmol) **5f** und 1.1 g (7.0 mmol) N-Cyclohexylpropan-1,3-diamin. Gelbe Kristalle, Schmp. 138 °C, Ausb. 0.12 g (44%). – $C_{27}H_{32}N_6O$ (456.6) Ber. C 71.0 H 7.06 N 18.4 Gef. C 70.6 H 7.09 N 18.6. – **IR** (KBr): ν = 3346 $cm^{-1}$; 2926; 2851; 1595; 1575; 1546; 1402; 1376; 1309; 1248; 1164; 768. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 0.96 – 1.21 (m, 5H, Cyc-3a,3e,4a,5a,5e-H), 1.39 (t, *J* = 6.9 Hz, 3H, O-$CH_2$-C*H*$_3$) 1.50 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.65 (m, 2H, 2 Cyc-2a,6a-H), 1.80 – 1.83 (m, 2H, Cyc-2e,6e-H), 1.90 (tt, J = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 – 2.38 (m, 1H, Cyc-1-H), 2.72 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.85 (m, 2H, Ar-NH-C*H*$_2$), 4.15 (q, *J* = 7.0 Hz, 2H, O-C*H*$_2$-$CH_3$), 7.10 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.8/ 7.2/ Hz, 1H, Ar-9-H), 8.12 (m, 1H, Ar-8-H), 8.62 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.4 Hz, 1H, Ar-10-H), 9.82 (m, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 456 (11) [$M^{+\cdot}$], 331 (12), 320 (22), 319 (100) [$M^{+\cdot}$-$(CH_2)_3$-NH-Cyc + 3H], 318 (22), 138 (34) [$(CH_2)_3$-NH-Cyc$^+$ - 2H].

*N-Cyclohexyl-N'-[2-(4-propoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin-hydrat* (**13e**)

Aus 0.25 g (0.71 mmol) **5g** und 1.4 g (8.9 mmol) N-Cyclohexylpropan-1,3-diamin. Gelbe Kristalle, Schmp. 109 °C, Ausb. 0.20 g (58%). – $C_{28}H_{34}N_6O$ (488.6) Ber. C 68.8 H 7.43 N 17.2 Gef. C 69.2 H 7.23 N 17.1. – **IR** (KBr): ν = 3347 $cm^{-1}$; 2926; 2852; 1593; 1578; 1547; 1463; 1436; 1401; 1376; 1309; 1250; 1164; 768. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 1.02 – 1.18 (m, 8H, O-$CH_2$-$CH_2$-C*H*$_3$, Cyc-3a,3e,4a,5a,5e-H), 1.50 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.65 (m, 2H, Cyc-2a,6a-H), 1.75 – 1.83 (m, 4H, O-$CH_2$-C*H*$_2$-$CH_3$, Cyc-2e,6e-H), 1.90 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 – 2.38 (m, 1H, Cyc-1-H), 2.72 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.85 (m, 2H, Ar-NH-C*H*$_2$), 4.05 (t, *J* = 6.5 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_3$), 7.10 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.05 (ddd, *J* = 7.5/ 7.5/ 1.0 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 8.4/ 7.5/ 1.4 Hz, 1H, Ar-8-H), 8.61 – 8.63 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.3 Hz, 1H, Ar-10-H), 9.81 (m, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 470 (8) [$M^{+\cdot}$], 334 (24), 333 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 332 (16), 138 (36) [$(CH_2)_3$-NH-Cyc$^+$ - 2H].

*N-[2-(4-Butoxyphenyl)-pyrimido[5,4-c]cinnolin-4-yl]-N'-cyclohexylpropan-1,3-diamin* (**13f**)

Aus 0.22 g (0.63 mmol) **5h** und 1.9 g (12.1 mmol) N-Cyclohexylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 126 °C, Ausb. 0.24 g (78%). – $C_{29}H_{36}N_6O$ (484.6) Ber. C 71.9 H 7.49 N 17.3 Gef. C 71.7 H 7.53 N 17.2. – **IR** (KBr): ν = 3449 $cm^{-1}$; 2928; 2852; 1595; 1575; 1546; 1435; 1402; 1376; 1309; 1248; 1164; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) (Spektrum schlecht aufgelöst) = 0.96 – 1.18 (m, 8H, O-$CH_2$-$CH_2$-$CH_2$-C*H*$_3$, Cyc-3a,3e,4a,5a,5e-H), 1.47 – 1.49 (m, 3H, O-$CH_2$-$CH_2$-C*H*$_2$-$CH_3$, Cyc-4e-H), 1.62 (m, 2H, 2 Cyc-2a,6a-H), 1.75 – 1.90 (m, 6H, O-$CH_2$-C*H*$_2$-$CH_2$-$CH_3$, Cyc-2e,6e-H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.36 (m, 1H, Cyc-1-H), 2.72 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.85 (m, 2H, Ar-NH-C*H*$_2$), 4.09 (m, 2H, O-C*H*$_2$-$CH_2$-$CH_2$-$CH_3$), 7.10 (d, *J* = 7.8 Hz, 2H, Ph-3,5-H), 8.05 – 8.07 (m, 1H, Ar-9-H), 8.10 – 8.12 (m, 1H, Ar-8-H), 8.61 – 8.63 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 6.9 Hz, 1H, Ar-10-H), 9.78 (m, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 484 (15) [$M^{+\cdot}$], 348 (21), 347 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 346 (20).

*4-[4-(N-Cyclohexylaminopropylamino)pyrimido[5,4-c]cinnolin-2-yl]benzonitril* (**13g**)

Aus 0.10 g (0.31 mmol) **5l** und 0.9 g (5.7 mmol) N-Cyclohexylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 183 °C, Ausb. 0.12 g (90%). – $C_{26}H_{27}N_7$ (437.6) Ber. C 71.4 H 6.22 N 22.4 Gef. C 71.1 H 6.48 N 22.1. – **IR** (KBr): 3371 $cm^{-1}$; 3340; 2928; 2850; 2227; 1591; 1573; 1543; 1434; 1398; 1364; 1317; 1269; 769. – **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 1.04 – 1.21 (m, 5H, Cyc-3a,3e,4a,5a,5e-H), 1.52 – 1.55 (m, 1H, Cyc-4e-H), 1.64 – 1.67 (m, 2H, Cyc-2a,6a-H), 1.84 – 1.87 (m, 2H, Cyc-2e,6e-H), 1.96 (tt, *J* = 6.5 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 (m, 1H, Cyc-1-H), 2.80 – 2.82 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.88 (d, *J* = 6.3 Hz, 2H, Ar-NH-C*H*$_2$), 8.07 (d, *J* = 8.4 Hz, 2H, Ph-2,6-H), 8.08 – 8.13 (m, 1H, Ar-9-H), 8.15 – 8.19 (ddd, *J* = 7.6/ 7.6/ 1.3 Hz, 1H, Ar-8-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.82 (d, *J* = 8.4 Hz, 2H, Ph-3,5-H), 9.04 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 10.04 (s, 1H, Ar-NH, austauschb.). **MS** (70 eV): m/z (%) = 437 (7) [$M^{+\cdot}$], 313 (10), 300 (25) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 138 (100) [$(CH_2)_3$-NH-Cyc$^+$ - 2H], 56 (15), 31 (21), 30 (12).

*N-Cyclohexyl-N'-[2-(2-furyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**13h**)

Aus 0.28 g (0.99 mmol) **5m** und 1.3 g (8.3 mmol) N-Cyclohexylpropan-1,3-diamin. Ockerfarbene, feine Kristalle, Schmp. 118 °C, Ausb. 0.38 g (95%). – $C_{23}H_{26}N_6O$ (402.5) Ber. C 68.6 H 6.51 N 20.4 Gef. C 68.4 H 6.36 N 20.6. – **IR** (KBr): 2926 $cm^{-1}$; 1605; 1575; 1545;

1480; 1366; 1315; 766. – **$^1$H NMR/** 400 MHz ([D6]DMSO): δ (ppm) = 0.96 – 1.22 (m, 5H, Cyc-3a,3e,4a,5a,5e-H), 1.51 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.65 (m, 2H, Cyc-2a,6a-H), 1.81 – 1.90 (m, 4H, Cyc-2e,6e-H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.32 – 2.37 (m, 1H, Cyc-1-H), 2.68 – 2.71 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 (s, breit, 2H, Ar-NH-C*H*$_2$), 6.77 (dd, *J* = 3.2/ 1.5 Hz, 1H, Fur-4-H), 7.53 (d, *J* = 3.2 Hz, 1H, Fur-5-H), 8.03 – 8.15 (m, 2H, Fur-3-H, Ar-9-H), 8.13 (dd, *J* = 7.9/ 7.2 Hz, 1H, Ar-8-H), 8.63 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.88 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.89 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 402 (5) [$M^{+\cdot}$], 277 (14), 266 (16), 265 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 138 (50) [$(CH_2)_3$-NH-Cyc$^+$ - 2H], 56 (21), 30 (14).

*N-Cyclohexyl-N'-[2-(2-thienyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**13i**)

Aus 0.30 g (1.00 mmol) **5n** und 1.3 g (8.3 mmol) N-Cyclohexylpropan-1,3-diamin. Gelbgrüne Kristalle, Schmp. 124 °C, Ausb. 0.22 g (52%). – $C_{23}H_{26}N_6S$ (418.6). Ber. C 66.0 H 6.26 N 20.1 Gef. C 66.0 H 6.31 N 19.9. – **IR** (KBr): ν = 3350 cm$^{-1}$; 2926; 2851; 1593; 1576; 1536; 1524; 1432; 1392; 1366; 1343; 1311; 464; 706. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.96 – 1.22 (m, 5H, Cyc-3a,3e,4a,5a,5e-H), 1.51 – 1.53 (m, 1H, Cyc-4e-H), 1.62 – 1.66 (m, 2H, Cyc-2a,6a-H), 1.81 – 1.85 (m, 2H, Cyc-2e,6e-H), 1.90 (tt, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 – 2.39 (m, 1H, Cyc-1-H), 2.70 – 2.73 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 (s, schlecht aufgelöst, 2H, Ar-NH-C*H*$_2$), 4.37 (s, 1H, Cyc-NH, teilw. ausgetauscht), 7.27 (dd, *J* = 4.9/ 3.7 Hz, 1H, Thi-4-H), 7.87 (dd, *J* = 5.0/ 0.9 Hz, 1H, Thi-5-H), 8.06 (dd, *J* = 7.1/ 6.8 Hz, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.16 – 8.17 (m, 1H, Thi-3-H), 8.62 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.68 (d, *J* = 7.5 Hz, 1H, Ar-10-H), 9.91 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 418 (7) [$M^{+\cdot}$], 307 (12), 293 (16), 282 (20), 281 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 280 (23), 138 (78) [$(CH_2)_3$-NH-Cyc$^+$ - 2H], 56 (21), 30 (15).

*N-Cyclohexyl-N'-[2-(E)-(2-Phenylvinyl)]pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**13j**)

Aus 0.30 g (0.94 mmol) **5p** und 1.1 g (7.0 mmol) N-Cyclohexylpropan-1,3-diamin. Grüne Kristalle, Schmp. 147 °C, Ausb. 0.23 g (56%). – $C_{27}H_{30}N_6$ (438.6) Ber. C 74.0 H 6.89 N 19.2 Gef. C 73.9 H 6.82 N 19.0. – **IR** (KBr): ν = 2926 cm$^{-1}$; 2851; 1591; 1573; 1544; 1449; 1402; 1375; 1322; 767. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.98 – 1.21 (m, 5H, Cyc-

3a,3e,4a,5a,5e-H), 1.61 – 1.65 (m, 2H Cyc-4e-H), 1.83 - 1.92 (m, 4H, Cyc-2e,6e-H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.33 – 2.39 (m, 1H, Cyc-1-H), 2.73 (t, *J* = 6.3 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.83 – 3.84 (m, 2H, Ar-NH-C*H*$_2$), 7.28 (d, *J* = 15.9 Hz, 1H, Ar-C*H*=CH-Ph), 7.40 – 7.49 (m, 3H, Ph-3,4,5-H), 7.81 (d, *J* = 7.2 Hz, 2H, Ph-2,6-H), 8.06 (ddd, *J* = 7.6/ 7.5/ 0.9 Hz, 1H, Ar-9-H), 8.11 – 8.13 (m, 1H, Ar-8-H), 8.17 (d, *J* = 15.8 Hz, 1H, Ar-CH=C*H*-Ph), 8.64 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.92 (d, *J* = 7.4 Hz, 1H, Ar-10-H), 9.82 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 438 (8) [$M^{+\cdot}$], 313 (11), 302 (23), 301 (100) [$M^{+\cdot}$- $(CH_2)_3$-NH-Cyc + 3H], 300 (23), 138 (51) [$(CH_2)_3$-NH-Cyc$^+$ - 2H], 56 (15), 30 (11).

#### 4.2.2.4.3 N,N-Dialkyl-N´-(pyrimido[5,4-c]cinnolin-4-yl)propan-1,3-diamine (14)

*N-[(2-(4-Methoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl]-N',N'-dimethylpropan-1,3-diamin* (**14a**)

Aus 0.20 g (0.62 mmol) **4e** und 1.5 g (14.7 mmol) N,N-Dimethylpropan-1,3-diamin. Hellgelbe, filzartige Kristalle (EtOH), Schmp. 172 °C, Ausb. 0.14 g (58%). – $C_{22}H_{24}N_6O$ (388.5) Ber. C 68.0 H 6.23 N 21.6 Gef. C 67.9 H 6.52 N 21.6. – **IR** (KBr): ν = 3476 cm$^{-1}$; 3423; 1595; 1576; 1547; 1404; 1309; 1253; 1165; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.91 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.22 (s, 6H, 2x $CH_3$), 2.45 (t, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 – 3.85 (m, 2H, Ar-NH-C*H*$_2$), 7.13 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.06 (dd, *J* = 8.0/ 7.0 Hz, 1H, Ar-9-H), 8.11 – 8.14 (m, 1H, Ar-8-H), 8.61 – 8.65 (m, 1H, Ph-2,6-H, Ar-7-H), 9.00 (d, *J* = 7.8 Hz, 1H, Ar-10-H), 9.67 (t, *J* = 5.7 Hz, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 388 (3) [$M^{+\cdot}$], 317 (19), 304 (28) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_3)_2$ - 3H], 85 (16), 84 (100) [$(CH_2)_3$-NH-$(CH_3)_2^+$ - 3H], 58 (61), 32 (34), 28 (99).

*N-[2-(2-Furyl)pyrimido[5,4-c]cinnolin-4-yl]-N',N'-dimethylpropan-1,3-diamin* (**14b**)

Aus 0.30 g (1.06 mmol) **5m** und 1.3 g (12.8 mmol) N,N-Dimethylpropan-1,3-diamin. Grüne Kristalle, Schmp. 119°C, Ausb. 0.22 g (57%). – $C_{19}H_{20}N_6O$ (348.4) Ber. C 65.5 H 5.78 N 24.1 Gef. C 65.4 H 5.83 N 23.7. – **IR** (KBr): 3341 cm$^{-1}$; 1606; 1574; 1544; 1495; 1479; 1436; 1367; 1316; 1265; 1241; 764. – **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 1.91 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.20 (s, 6H, 2x $CH_3$), 2.39 (t, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-

$CH_2$-C*H*$_2$), 3.74 – 3.79 (m, 2H, Ar-NH-C*H*$_2$), 6.77 (dd, *J* = 3.4/ 1.6 Hz, 1H, Fur-4-H), 7.52 (d, *J* = 3.5 Hz, 1H, Fur-5-H), 8.03 – 8.07 (m, 2H, Fur-3-H, Ar-9-H), 8.13 (ddd, *J* = 8.2/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.62 (d, *J* = 7.6 Hz, 1H, Ar-7-H), 8.87 – 8.90 (m, 1H, Ar-10-H), 9.71 (t, *J* = 5.7 Hz, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 348 (3) [$M^{+\cdot}$], 277 (21), 264 (22) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_3)_2$ + 3H], 85 (16), 84 (100) [$(CH_2)_3$-NH-$(CH_3)_2^+$ - 3H], 58 (61).

*N-[(2-Phenyl)pyrimido[5,4-c]cinnolin-4-yl]-N',N'-diethylpropan-1,3-diamin* (**14c**)

Aus 0.25 g (0.85 mmol) **5c** und 1.8 g (13.8 mmol) N,N-Diethylpropan-1,3-diamin. Goldgelbe Kristalle, Schmp. 88 °C, Ausb. 0.16 g (48%). – $C_{23}H_{26}N_6$ (386.5) Ber. C 71.5 H 6.78 N 21.7 Gef. C 71.4 H 6.50 N 21.7. – **IR** (KBr): ν = 3356 $cm^{-1}$; 2969; 1593; 1546; 1398; 1367; 1314; 705. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.01 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.95 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.55 – 2.56 (m, z.T. im DMSO, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 2.60 – 2.61 (m, schlecht aufgelöst, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.82 – 3.87 (m, 2H, Ar-NH-C*H*$_2$), 7.56 – 7.63 (m, 3H, Ph-3,4,5-H), 8.07 (ddd, *J* = 7.5/ 7.5/ 1.1 Hz, 1H, Ar-9-H), 8.14 (ddd, *J* = 7.6/ 7.5/ 1.4 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.67 – 8.69 (m, 2H, Ph-2,6-H), 9.01 (dd, *J* = 8.0/ 0.9 Hz, 1H, Ar-10-H), 9.87 (t, *J* = 5.6 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 386 (11) [$M^{+\cdot}$], 287 (12), 274 (6) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2$ + 3H], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (46).

*N,N-Diethyl-N'-[(2-(4-methoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin-semihydrat* (**14d**)

Aus 0.25 g (0.77 mmol) **5e** und 1.7 g (13.1 mmol) N,N-Diethylpropan-1,3-diamin.Gelbe, filzartige Kristalle, Schmp. 138 °C, Ausb. 0.19 g (59%). – $C_{24}H_{28}N_6O$ x 0.5 $H_2O$ (425.5) Ber. C 67.7 H 6.87 N 19.8 Gef. C 67.9 H 6.55 N 19.8. – **IR** (KBr): ν = 3438 $cm^{-1}$; 3339; 1599; 1576; 1547; 1403; 1308; 1257; 1166; – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.00 (t, *J* = 7.0 Hz, 6H, 2x $CH_3$), 1.92 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.53 – 2.55 (z. T. im DMSO-Peak, m, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 2.59 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.81 – 3.86 (m, 2H, Ar-NH-C*H*$_2$), 3.88 (s, 3H, $OCH_3$), 7.11 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.04 – 8.08 (m, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.3/ 7.1/ 1.2 Hz, 1H, Ar-8-H), 8.61 – 8.65 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.77 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). / ($CF_3COOD$): δ (ppm) = 1.49 (t, *J* = 7.3 Hz, 6H, 2x $CH_3$), 2.60 – 2.64 (m, 2H,

Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 3.41 – 3.52 (m, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 3.58 – 3.62 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 4.11 (s, 3H, $OCH_3$), 4.40 (t, *J* = 7.0 Hz, 2H, Ar-NH-C*H*$_2$), 7.32 (d, J = 9.1 Hz, 2H, Ph-3,5-H), 8.54 – 8.57 (m, 3H, Ar-9-H, Ph-2,6-H), 8.67 (dd, *J* = 8.2/ 7.7 Hz, 1H, Ar-8-H), 8.89 (d, *J* = 8.7 Hz, 1H, Ar-7-H,), 9.28 (d, *J* = 8.6 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 416 (15) [$M^{+\cdot}$], 317 (12), 304 (10) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2$ + 3H], 113 (10), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (41), 28 (13).

*N-[(2-(4-Ethoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl]-N′,N′-diethylpropan-1,3-diamin* (**14e**)

Aus 0.30 g (0.89 mmol) **5f** und 2.5 g (19.2 mmol) N,N-Diethylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 163 °C, Ausb. 0.30 g (79%). – $C_{25}H_{31}N_6O$ (431.6) Ber. C 69.6 H 7.24 N 19.5 Gef. C 69.5 H 7.03 N 19.4. – **IR** (KBr): ν = 3339 $cm^{-1}$; 2971; 2933; 1597; 1576; 1436; 1403; 1375; 1306; 1257; 1164; 1114; 1047; 768. – **$^1$H NMR** / 400 MHz ([$D_6$] DMSO): δ (ppm) = 1.00 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.39 (t, *J* = 6.9 Hz, 3H, O-$CH_2$-C*H*$_3$), 1.92 (tt, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.53 – 2.55 (z. T. im DMSO-Peak, m, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 2.59 (t, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.81 – 3.86 (m, 2H, Ar-NH-C*H*$_2$), 4.15 (q, *J* = 7.0 Hz, 2H, O-C*H*$_2$-$CH_3$), 7.10 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.8/ 7.2 Hz, 1H, Ar-9-H),8.10 - 8.14 (m, 1H, Ar-8-H), 8.61 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.6 Hz, 1H, Ar-10-H), 9.79 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 430 (18) [$M^{+\cdot}$], 336 (15), 324 (13), 113 (16), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (62), 30 (11).

*N,N-Diethyl-N′-[(2-(4-propoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl]-propan-1,3-diamin* (**14f**)

Aus 0.25 g (0.71 mmol) **5g** und 2.5 g (19.2 mmol) N,N-Diethylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 122 °C, Ausb. 0.21 g (66%). – $C_{26}H_{32}N_6O$ (444.6) Ber. C 70.2 H 7.26 N 18.9 Gef. C 70.2 H 7.31 N 19.0. – **IR** (KBr): ν = 3341 $cm^{-1}$; 2965; 2934; 1599; 1576; 1546; 1436; 1403; 1376; 1307; 1257; 1165; 767. – **$^1$H NMR** / 400 MHz ([$D_6$] DMSO): δ (ppm) = 0.98 – 1.07 (m, 9H, 3x $CH_3$), 1.75 – 1.83 (m, 2H, O-$CH_2$-$CH_2$-C*H*$_2$-$CH_3$), 1.92 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.53 – 2.55 (z. T. im DMSO-Peak, m, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 2.59 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.81 – 3.85 (m, 2H, Ar-NH-C*H*$_2$), 4.05 (t, *J* = 6.5 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_3$), 7.10 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.9/ 7.1 Hz, 1H, Ar-9-H), 8.12 (dd, *J* = 7.8/ 7.2 Hz, 1H, Ar-8-H), 8.61 – 8.63 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99

(d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.78 (t, *J* = 5.4 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 444 (11) [$M^{+\cdot}$], 332 (8) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2$ + 3H], 113 (10), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (42).

*N-[(2-(4Butoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl]-N′,N′-diethylpropan-1,3-diamin* (**14g**)

Aus 0.23 g (0.66 mmol) **5h** und 1.9 g (14.6 mmol) N,N-Diethylpropan-1,3-diamin. Hellgrüne Kristalle, Schmp. 84 °C, Ausb. 0.26 g (86%). – $C_{27}H_{34}N_6O$ (458.6) Ber. C 70.7 H 7.47 N 18.3 Gef. C 70.7 H 7.74 N 18.1. – **IR** (KBr): ν = 3342 $cm^{-1}$; 2960; 2934; 1584; 1566; 1435; 1400; 1377; 1308; 1248; 1162; 768. – **$^1$H NMR** / 400 MHz ([$D_6$] DMSO): δ (ppm) = 0.95 – 1.02 (m, 9H, 3x $CH_3$), 1.45 – 1.51 (m, 2H, O-$CH_2$-$CH_2$-C*H*$_2$-$CH_3$), 1.72 – 1.79 (m, 2H, O-$CH_2$-C*H*$_2$-$CH_2$-$CH_3$), 1.91 (tt, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.53 – 2.55 (z. T. im DMSO-Peak, m, 4H, N-(C*H*$_2$-$CH_3)_2$), 2.59 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 – 3.85 (m, 2H, Ar-NH-C*H*$_2$), 4.09 (t, *J* = 6.4 Hz, 2H, O-C*H*$_2$-$CH_2$-$CH_2$-$CH_3$), 7.10 (d, *J* = 8.8 Hz, 2H, Ph-3,5-H), 8.05 (dd, *J* = 7.4/ 7.1 Hz, 1H, Ar-9-H), 8.10 – 8.14 (m, 1H, Ar-8-H), 8.61 – 8.63 (m, 3H, Ar-7-H, Ph-2,6-H), 8.98 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.78 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 458 (11) [$M^{+\cdot}$], 113 (11), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (44).

*N,N-Diethyl-N′-[(2-(2-fluorphenyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**14h**)

Aus 0.20 g (0.64 mmol) **5i** und 2.1 g (16.1 mmol) N,N-Diethylpropan-1,3-diamin. Braune Kristalle, Schmp. 78 °C (EtOH/ $H_2O$), Ausb. 0.18 g (69%). – $C_{23}H_{25}FN_6$ (404.5) Ber. C 68.3 H 6.23 N 20.8 Gef. C 68.3 H 6.20 N 20.7. – **IR** (KBr): ν = 3432 $cm^{-1}$; 1597; 1575; 1306; 758. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.98 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.90 (tt, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.47 – 2.52 (im DMSO-Peak, 4H, N-(C*H*$_2$-$CH_3)_2$), 2.57 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.75 – 3.80 (m, 2H, Ar-NH-C*H*$_2$), 7.35 – 7.41 (m, 2H, Ph-4,5-H), 7.58 – 7.62 (m, 1H, Ph-3-H), 8.08 (dd, *J* = 7.9/ 7.1 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 7.7/ 7.5/ 1.2 Hz, 1H, Ar-8-H), 8.30 (ddd, *J* = 8.0/ 7.7/ 1.6 Hz, 1H, Ph-6-H), 8.67 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.90 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.93 (t, *J* = 5.4 Hz, 1H, Ar-NH, austauschb.)./ ($CF_3COOD$): δ (ppm) = 1.64 (t, *J* = 7.2 Hz, 6H, 2x $CH_3$), 2.77 (s, breit, 2H, NH-$CH_2$-C*H*$_2$-$CH_2$), 3.60 – 3.63 (m, 4H, N-(C*H*$_2$-$CH_3)_2$), 3.73 – 3.75 (m, 2H, NH-$CH_2$-$CH_2$-C*H*$_2$), 4.58 (t, *J* = 6.7 Hz, 2H, Ar-NH-C*H*$_2$), 7.67 – 7.72 (m, 1H, Ph-4-H), 7.79 (dd, *J* = 7.7/

7.6 Hz, 1H, Ph-5-H), 8.15 – 8.17 (m, 1H, Ph-3-H), 8.68 – 8.74 (m, 2H, Ph-6-H, Ar-9-H), 8.80 (dd, *J* = 7.8/ 7.5 Hz, 1H, Ar-8-H), 9.12 (d, *J* = 8.4 Hz, 1H, Ar-10-H), 9.17 (d, *J* = 8.5 Hz, 1H, Ar-7-H). – **MS** (70 eV): m/z (%) = 404 (9) [$M^{+\cdot}$], 305 (12), 292 (5) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2$ + 3H], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (44), 30 (10), 28 (25).

*N,N-Diethyl-N´-[(2-(4-fluorphenyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**14i**)

Aus 0.30 g (0.97 mmol) **5j** und 2.4 g (18.4 mmol) N,N-Diethylpropan-1,3-diamin. Ockergelbe Kristalle, Schmp. 114 °C, Ausb. 0.30 g (74%). – $C_{23}H_{25}FN_6$ (404.5) Ber. C 68.3 H 6.23 N 20.8 Gef. C 68.3 H 6.42 N 20.5. – **IR** (KBr): ν = 3358 $cm^{-1}$; 2968; 1602; 1589; 1571; 1546; 1401; 1305; 1233; 1147; 764. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.00 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.93 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 2.53 – 2.55 (z. T. im DMSO-Peak, m, 4H, N-(C*$H_2$*-$CH_3)_2$), 2.60 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 3.81 – 3.86 (m, 2H, Ar-NH-C*$H_2$*), 7.39 (dd, *J* = 8.8/ 8.8 Hz, 2H, Ph-3,5-H), 8.07 (ddd, *J* = 7.6/ 7.5/ 0.9 Hz, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.64 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 8.70 – 8.73 (m, 2H, Ph-2,6-H), 8.99 (dd, *J* = 7.7/ 0.9 Hz, 1H, Ar-10-H), 9.89 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). / ($CF_3COOD$): δ (ppm) = 1.49 (t, *J* = 7.3 Hz, 6H, 2x $CH_3$), 2.60 – 2.64 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.41 – 3.52 (m, 4H, N-(C*$H_2$*-$CH_3)_2$), 3.58 – 3.62 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 4.11 (s, 3H, $OCH_3$), 4.40 (t, *J* = 7.0 Hz, 2H, Ar-NH-C*$H_2$*), 7.32 (d, J = 9.1 Hz, 2H, Ph-3,5-H), 8.54 – 8.57 (m, 3H, Ar-9-H, Ph-2,6-H), 8.67 (dd, *J* = 8.2/ 7.7 Hz, 1H, Ar-8-H), 8.89 (d, *J* = 8.7 Hz, 1H, Ar-7-H,), 9.28 (d, *J* = 8.6 Hz, 1H, Ar-10-H)./ ($CF_3COOD$): δ (ppm) = 1.48 (t, *J* = 6.6 Hz, 6H, 2x $CH_3$), 2.58 – 2.63 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.41 – 3.52 (m, 4H, N-(C*$H_2$*-$CH_3)_2$), 3.59 (t, *J* = 7.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 4.42 (t, *J* = 6.6 Hz, 2H, Ar-NH-C*$H_2$*), 7.47 (dd, *J* = 7.6/ 7.4 Hz, 2H, Ph-3,5-H), 8.53 – 8.58 (m, 3H, Ar-9-H, Ph-2,6-H), 8.65 (dd, *J* = 7.7/ 7.5 Hz, 1H, Ar-8-H), 8.95 (d, *J* = 8.7 Hz, 1H, Ar-7-H), 9.27 (d, *J* = 8.5 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 404 (9) [$M^{+\cdot}$], 292 (4) [$M^{+\cdot}$- [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2$ + 3H], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (47), 58 (10), 30 (12).

*N-[(2-(4-Chlorphenyl)pyrimido[5,4-c]cinnolin-4-yl]-N´,N´-diethylpropan-1,3-diamin* (**14j**)

Aus 0.3 g (0.92 mmol) **5k** und 1.7 g (13.1 mmol) N,N-Diethylpropan-1,3-diamin. Gelbe, filzartige Kristalle, Schmp. 127 °C, Ausb. 0.24g (62%). – $C_{23}H_{25}ClN_6$ (420.9) Ber. C 65.6 H

5.99 N 20.0 Gef. C 65.7 H 5.74 N 19.7. – **IR** (KBr): ν = 3431 $cm^{-1}$; 1600; 1576; 1547; 1400; 1310. – **$^1$H NMR** / 400 MHz ($CF_3COOD$): δ (ppm) = 1.48 (t, *J* = 7.3 Hz, 6H, 2x $CH_3$), 2.58 – 2.66 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 3.39 – 3.53 (m, 4H, N-(C*H*$_2$-$CH_3$)$_2$), 3.58 – 3.62 (m, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 4.42 (t, *J* = 6.9 Hz, 2H, Ar-NH-C*H*$_2$), 7.78 (d, *J* = 8.6 Hz, 2H, Ph-3,5-H), 8.45 (d, *J* = 8.6 Hz, 2H, Ph-2,6-H), 8.55 (dd, *J* = 8.0/ 7.6 Hz, 1H, Ar-9-H), 8.65 (dd, *J* = 8.2/ 7.5 Hz, 1H, Ar-8-H), 8.95 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 9.27 (d, *J* = 8.6 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 420 (7) [$M^{+\cdot}$], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (53), 30 (10).

*4-[4-(N-Diethylaminopropylamino)pyrimido[5,4-c]cinnolin-2-yl]benzonitril* (**14k**)

Aus 0.30 g (0.94 mmol) **5l** und 1.8 g (13.8 mmol) N-Diethylpropan-1,3-diamin. Hellgelbe Kristalle, Schmp. 148 °C, Ausb. 0.26 g (70%). – $C_{24}H_{25}N_7$ (411.5) Ber. C 70.1 H 6.12 N 23.8 Gef. C 70.0 H 5.97 N 23.6. – **IR** (KBr): 2968 $cm^{-1}$; 2227; 1599; 1573; 1545; 1401; 1375; 1316; 767. – **$^1$H NMR**/ 400 MHz ([D6]DMSO): δ (ppm) = 0.99 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.91 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.52 – 2.55 (m, im DMSO-Peak, 4H, N-$(CH_2)_2$), 2.59 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.83 (m, 2H, Ar-NH-C*H*$_2$), 8.03 – 8.09 (m, 3H, Ph-3,5H, Ar-9-H), 8.15 (dd, *J* = 8.2/ 7.1 Hz, 1H, Ar-8-H), 8.65 (d, *J* = 8.2 Hz, Ar-7-H), 8.78 (d, *J* = 8.2 Hz, Ph-2,6-H), 8.99 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 10.02 (t, *J* = 5.4 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 411 (12) [$M^{+\cdot}$], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (52), 30 (10).

*N,N-Diethyl-N´-[2-(2-furyl)pyrimido[5,4-c]cinnolin-4-yl]-1,3-propandiamin* (**14l**)

Aus 0.30 g (1.06 mmol) **5m** und 1.7 g (13.1 mmol) N,N-Diethylpropan-1,3-diamin. Gelbgrüne Kristalle (Ethylacetat), Schmp. 93 °C, Ausb. 0.21 g (51%). – $C_{21}H_{24}N_6O$ (376.5) Ber. C 67.0 H 6.43 N 22.3 Gef. C 66.8 H 6.27 N 22.3. – **IR** (KBr): ν = 3340 $cm^{-1}$; 2969; 2796; 1603; 1575; 1545; 1497; 1480; 1433; 1368; 1318; 1241; 1012; 763. – **$^1$H NMR**/ 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.00 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.90 (tt, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.53 – 2.55 (im DMSO-Peak, m, 4H, N-($CH_2$-$CH_3$)$_2$), 2.59 (t, *J* = 6.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.78 (t, *J* = 6.4 Hz, 2H, Ar-NH-C*H*$_2$), 6.77 (dd, *J* = 3.3/ 1.7 Hz, 1H, Fur-4-H), 7.52 (d, *J* = 3.1 Hz, 1H, Fur-5-H), 8.02 – 8.07 (m, 2H, Fur-3-H, Ar-9-H), 8.11 – 8.15 (m, 1H, Ar-8-H), 8.63 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.88 (dd, *J* = 8.0/ 1.0 Hz, 1H, Ar-

10-H), 9.85 (t, *J* = 5.5 Hz, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 376 (13) [$M^{+\cdot}$], 277 (14), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (44).

*N',N'-Diethyl-N-[2-(2-thienyl)pyrimido[5,4-c]cinnolin-4-yl]propan-1,3-diamin* (**14m**)

Aus 0.30 g (1.00 mmol) **5n** und 1.3 g (10.0 mmol) N,N-Diethylpropan-1,3-diamin. Hellgrüne Kristalle, Schmp. 91 °C, Ausb. 0.35 g (89%). – $C_{21}H_{24}N_6S$ (392.5) Ber. C 64.3 H 6.16 N 21.4 Gef. C 64.2 H 6.12 N 21.1. – **IR** (KBr): ν = 3351 $cm^{-1}$; 2967; 1595; 1577; 1536; 1524; 1433; 1392; 1367; 1343; 1308; 763; 706. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.00 (t, *J* = 7.1 Hz, 6H, 2x $CH_3$), 1.90 (tt, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.52 (im DMSO-Peak, m, 4H, N-(C*H*$_2$-$CH_3)_2$), 2.59 (t, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.76 – 3.81 (m, 2H, Ar-NH-C*H*$_2$), 7.28 (dd, *J* = 4.9/ 3.8 Hz, 1H, Thi-4-H), 7.87 (dd, *J* = 4.9/ 1.1 Hz, 1H, Thi-5-H), 8.04 – 8.08 (m, 1H, Ar-9-H), 8.13 (ddd, *J* = 8.2/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.17 (dd, *J* = 3.7/ 1.1 Hz, Thi-3-H), 8.63 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.87 – 8.89 (m, 1H, Ar-10-H), 9.87 (t, *J* = 5.6 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 392 (9) [$M^{+\cdot}$], 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (86), 72 (18), 58 (48), 56 (31), 44 (17), 43 (16), 42 (38), 41 (14), 39 (12), 30 (80), 29 (45), 28 (28), 27 (11).

*N-[2-(E)-(2-Phenylvinyl)]pyrimido[5,4-c]cinnolin-4-yl]-N',N'-diethylpropan-1,3-diamin* (**14n**)

Aus 0.40 g (1.25 mmol) **4n** und 2.5 g (19.2 mmol) N,N-Diethylpropan-1,3-diamin. Dunkelgrüne Kristalle (Isopropanol/ $H_20$), Schmp. 122 °C, Ausb. 0.28 g (54%). – $C_{25}H_{28}N_6$ (412.5) Ber. C 72.8 H 6.84 N 20.4 Gef. C 73.1 H 6.70 N 20.0. – **IR** (KBr): ν = 2968 $cm^{-1}$; 1593; 1573; 1543; 1449; 1421; 1401; 1378; 1353; 1322; 1291; 767. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.01 (t, *J* = 7.0 Hz, 6H, 2x $CH_3$), 1.90 (tt, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.54 – 2.56 (m, z.T. im DMSO, 4H, N-(C*H*$_2$-$CH_3)_2$), 2.60 – 2.61 (t, *J* = 6.4 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*H*$_2$), 3.80 – 3.82 (m, 2H, Ar-NH-C*H*$_2$), 7.28 (d, *J* = 15.9 Hz, 1H, Ar-C*H*=CH-Ph) 7.40 – 7.49 (m, 3H, Ph-3,4,5-H), 7.79 (d, *J* = 7.4 Hz, 2H, Ph-2,6-H), 8.06 (dd, *J* = 7.5/ 7.3 Hz, 1H, Ar-9-H), 8.13 (dd, *J* = 8.1/ 8.0 Hz, 1H, Ar-8-H), 8.17 (d, *J* = 16.0 Hz, 1H, Ar-CH=C*H*-Ph), 8.63 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.91 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 9.79 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 412 (10) [$M^{+\cdot}$], 113 (11), 112 (100) [$(CH_2)_3$-NH-$(CH_2$-$CH_3)_2^+$ - 3H], 86 (56), 44 (15).

### 4.2.2.5 Pyrimido[5,4-c]cinnolin-4-amine mit basischem oder neutralem Heteroaromaten in der Seitenkette

#### 4.2.2.5.1 (N-Furylmethyl)pyrimido[5,4-c]cinnolin-4-amine (15)

*N-(2-Furylmethyl)pyrimido[5,4-c]cinnolin-4-amin* (**15a**)

Aus 0.19 g (0.90 mmol) **5a** und 1.1 g (11.3 mmol) 2-Furylmethylamin. Ockerfarbene Kristalle, Schmp. 191 °C, Ausb. 0.19 g (77%). – $C_{15}H_{11}N_5O$ (277.3) Ber. C 65.0 H 4.00 N 25.3 Gef. C 64.8 H 4.11 N 25.3. – **IR** (KBr): ν = 3341 $cm^{-1}$, 1589; 1569; 1546; 1332; 1310; 1270; 773; 750. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 4.88 (d, *J* = 6.1 Hz, 2H, Ar-NH-C*H*$_2$), 6.37 – 6.42 (m, 2H, Furfur-3,4-H), 7.59 (s, 1H, Furfur-5-H), 8.09 (ddd, *J* = 7.6/ 7.5/ 0.9 Hz, 1H, Ar-9-H), 8.17 (ddd, *J* = 8.3/ 7.0/ 1.4 Hz, 1H, Ar-8-H), 8.70 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.85 – 8.87 (m, 2H, Ar-2,10-H), 10.05 (t, *J* = 6.1 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 278 (17), 277 (89) [$M^{+\cdot}$], 249 (19), 248 (100) [$M^{+\cdot}$– CHO], 222 (12), 96 (11), 81 (23), 53 (17), 28 (15).

*N-(2-Furylmethyl)-(2-phenyl)-pyrimido[5,4-c]cinnolin-4-amin* (**15b**)

Aus 0.25 g (0.9 mmol) **5c** und 1.6 g (16.5 mmol) 2-Furylmethylamin. Gelbgrüne Kristalle, Schmp. 197 °C, Ausb. 0.23 g (72%). – $C_{21}H_{14}N_5O$ (353.4) Ber. C 71.3 H 4.28 N 19.8 Gef. C 71.3 H 4.41 N 19.8. – **IR** (KBr): ν = 3408 $cm^{-1}$; 1593; 1578; 1548; 1401; 1371; 1318; 1300; 755; 706. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 5.01 (d, *J* = 6.0 Hz, 2H, Ar-NH-C*H*$_2$), 6.43 (dd, *J* = 3.1/ 1.8 Hz, 1H, Furfur-4-H), 6.45 – 6.48 (m, 1H, Furfur-3-H), 7.57 – 7.65 (m, 4H, Ph-3,4,5-H, Furfur-5-H), 8.11 (ddd, *J* = 7.5/ 7.5/ 1.0 Hz, 1H, Ar-9-H), 8.17 (ddd, *J* = 8.2/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.66 – 8.73 (m, 3H, Ar-7-H, Ph-2,6-H), 9.04 (dd, *J* = 8.0/ 0.9 Hz, 1H, Ar-10-H), 10.06 (t, *J* = 6.0 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 354 (21), 353 (76) [$M^{+\cdot}$], 325 (26), 324 (100) [$M^{+\cdot}$– CHO].

*2-(2-Fluorphenyl)-N-(2-furylmethyl)-pyrimido[5,4-c]cinnolin-4-amin* (**15c**)

Aus 0.20 g (0.64 mmol) **5i** und 1.9 g (19.6 mmol) 2-Furylmethylamin. Ockergelbe Kristalle, Schmp. 203 °C, Ausb. 0.15 g (63%). – $C_{21}H_{14}FN_5O$ (371.4) Ber. C 67.9 H 3.80 N 18.9 Gef. C 67.9 H 3.80 N 18.7. – **IR** (KBr): ν = 3416 $cm^{-1}$ (NH); 3308; 1593; 1547; 1399; 1314; 755. – **$^1$H NMR** / 400 MHz ([D$_6$]DMSO): δ (ppm) = 4.94 (d, *J* = 5.9 Hz, 2H, Ar-NH-C*H*$_2$), 6.41 (s, 2H, Furfur-3,4-H), 7.37 – 7.42 (m, 2H, Ph-4,5-H), 7.60 – 7.65 (m, 2H, Ph-3-H, Furfur-5-H), 8.09 (dd, *J* = 7.5/ 7.3 Hz, 1H, Ar-9-H), 8.17 (dd, *J* = 8.1/ 7.0 Hz 1H, Ar-8-H), 8.33 (dd, *J* = 8.3/ 7.4 Hz, 1H, Ph-6-H), 8.69 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.92 (d, *J* = 8.2 Hz, 1H, Ar-10-H), 10.10 (t, *J* = 5.9 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 372 (17); 371 (65) [$M^{+\cdot}$], 343 (22), 342 (100) [$M^{+\cdot}$– CHO], 155 (10), 135 (14), 127 (25), 126 (15), 102 (11), 81 (27), 53 (27), 28 (33).

*2-(4-Fluorphenyl)-N-(2-furylmethyl)-pyrimido[5,4-c]cinnolin-4-amin* (**15d**)

Aus 0.40 g (1.29 mmol) **5j** und 1.9 g (19.6 mmol) 2-Furylmethylamin. Ockergelbe Kristalle, Schmp. 238 °C, Ausb. 0.27 g (57%). – $C_{21}H_{14}FN_5O$ (371.4) Ber. C 67.9 H 3.80 N 18.9 Gef. C 67.9 H 3.91 N 19.0. – **IR** (KBr): ν = 3314 $cm^{-1}$ (NH); 1602; 1579; 1547; 1433; 1403; 1369; 1316; 1148; 768. – **$^1$H NMR** / 400 MHz ($CF_3COOD$): δ (ppm) = 5.42 (s, 2H, Ar-NH-C*H*$_2$), 6.41 (dd, *J* = 3.1/ 2.9 Hz, 1H, Furfur-4-H), 6.62 (d, *J* = 3.3 Hz, 1H, Furfur-3-H), 7.47 – 7.51 (m, 3H, Ph-3,5-H, Furfur-5-H), 8.56 (dd, *J* = 7.9/ 7.5 Hz, 1H, Ar-9-H), 8.61 – 8.67 (m, 3H, Ar-8-H, Ph-2,6-H), 8.91 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 9.30 (d, *J* = 8.5 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 372 (17); 371 (70) [$M^{+\cdot}$], 343 (25), 342 (100) [$M^{+\cdot}$– CHO], 127 (18), 126 (13), 81 (24), 53 (22), 28 (11).

*2-(4-Chlorphenyl)-N-(2-furylmethyl)-pyrimido[5,4-c]cinnolin-4-amin* (**15e**)

Aus 0.30 g (0.92 mmol) **5k** und 1.7 g (17.5 mmol) 2-Furylmethylamin. Gelbe Kristalle (EtOH/ EtAc/ DMF), Schmp. 219 °C, Ausb. 0.31g (87%). – $C_{21}H_{14}ClN_5O$ (387.8) Ber. C 65.0 H 3.64 N 18.1 Gef. C 65.1 H 3.69 N 17.9. – **IR** (KBr): ν = 3341 $cm^{-1}$; 1591; 1575; 1547; 1401; 1317; 765. – **$^1$H NMR** / 400 MHz ($CF_3COOD$): δ (ppm) = 5.42 (s, 2H, Ar-NH-C*H*$_2$), 6.46 (d, *J* = 3.1 Hz, 1H, Furfur-4-H), 6.62 (d, *J* = 3.2 Hz, 1H, Furfur-3-H), 7.47 – 7.48 (m, 1H, Furfur-5-H), 7.80 (d, *J* = 8.7 H, 2H, Ph-3,5-H), 8.50 (d, *J* = 8.7 Hz, 2H, Ph-2,6-H), 8.55

(dd, *J* = 8.6/ 7.9 Hz, 1H, Ar-9-H), 8.64 (dd, *J* = 8.4/ 7.3 Hz, 1H, Ar-8-H), 8.92 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 9.29 (d, *J* = 8.6 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 389 (21), 388 (14), 387 (61) [$M^{+\cdot}$], 360 (29), 359 (24), 358 (85) [$M^{+\cdot}$– CHO], 179 (13), 161 (26), 160 (11), 155 (26), 140 (11), 138 (17), 128 (16), 127 (69), 126 (52), 115 (19), 114 (22), 111 (16), 102 (30), 101 (14), 100 (27), 99 (11), 96 (42), 88 (12), 81 (100) [Fur=$CH_2$], 76 (19), 75 (23), 53 (71), 52 (11), 51 (18), 39 (14).

*(4-Methoxyphenyl)-N-(5-(2-methyl)furylmethyl)-pyrimido[5,4-c]cinnolin-4-amin* (**15f**)

Aus 0.25 g (0.77 mmol) **5e** und 1.3 g (11.7 mmol) 2-(5-Metyl)furylmethylamin. Ockergelbe Kristalle, Schmp. 210 °C, Ausb. 0.24 g (78%). – $C_{23}H_{19}N_5O_2$ (397.4) Ber. C 69.5 H 4.82 N 17.6 Gef. C 69.5 H 4.65 N 17.8. – **IR** (KBr): ν = 3342 $cm^{-1}$ (NH); 1594; 1577; 1547; 1432; 1403; 1372; 1313; 1253; 1164; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.29 (s, 3H, Furfur-$CH_3$), 3.94 (s, 3H, $OCH_3$), 4.96 (d, *J* = 5.4 Hz, 2H, Ar-NH-C*$H_2$*), 6.06 (s, 1H, Furfur-4-H), 6.37 (s, 1H, Furfur-3-H), 7.18 (d, *J* = 8.6 Hz, 2H, Ph-3,5-H), 8.12 (dd, *J* = 7.7/ 7.1 Hz, 1H, Ar-9-H), 8.18 (dd, *J* = 7.6/ 7.2 Hz, 1H, Ar-8-H), 8.68 – 8.72 (m, 3H, Ar-7-H, Ph-2,6-H), 9.05 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.93 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 398 (14), 397 (50) [$M^{+\cdot}$], 355 (24), 354 (100) [$M^{+\cdot}$- $CH_3$-CO], 316 (14), 177 (15), 127 (14), 126 (17), 95 (50), 43 (30), 41 (16), 27 (27).

*2-(4-Fluorphenyl)-N-[2-(5-methyl)furylmethyl]pyrimido[5,4-c]cinnolin-4-amin* (**15g**)

Aus 0.30 g (0.97 mmol) **5j** und 1.7 g (15.3 mmol) 2-(5-Metyl)furylmethylamin. Ockergelbe Kristalle (Isopropanol), Schmp. 234 °C, Ausb. 0.26 g (69%). – $C_{22}H_{16}FN_5O$ (385.4) Ber. C 68.6 H 4.18 N 18.2 Gef. C 68.3 H 4.02 N 18.0. – **IR** (KBr): ν = 3340 $cm^{-1}$; 3276; 1603; 1578; 1548; 1509; 1433; 1401; 1372; 1345; 1315; 1272; 1221; 1149; 1019; 851; 768. – **$^1$H NMR** / 400 MHz ($CF_3COOD$): δ (ppm) = 2.30 (s, 3H, Furfur-$CH_3$), 5.36 (s, 2H, Ar-NH-C*$H_2$*), 6.05 (d, *J* = 2.4 Hz, 1H, Furfur-4-H), 6.50 (d, schlecht aufgelöst, 1H, Furfur-3-H), 7.50 (dd, 2H, *J* = 8.6/ 8.3 Hz, 2H, Ph-3,5-H), 8.56 (dd, *J* = 7.9/ 7.7 Hz, 1H, Ar-9-H), 8.63 – 8.67 (m, 3H, Ar-8-H, Ph-2,6-H), 8.90 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 9.30 (d, *J* = 8.5 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 386 (13), 385 (53) [$M^{+\cdot}$], 343 (23), 342 (100) [$M^{+\cdot}$- $CH_3$-CO], 95 (20).

*N-(2-(5-methyl)furylmethyl)-2-(2-furyl)pyrimido[5,4-c]cinnolin-4-amin* (**15h**)

Aus 0.28 g (1.00 mmol) **5m** und 3.2 g (28.8 mmol) 2-(5-Metyl)furylmethylamin. Ockergelbe feine Kristalle, Schmp. 199 °C, Ausb. 0.28 g (78%). – $C_{20}H_{15}N_5O_2$ (357.4) Ber. C 67.2 H 4.23 N 19.6 Gef. C 66.9 H 4.11 N 19.5. – **IR** (KBr): ν = 3260 $cm^{-1}$; 1604; 1574; 1546; 1495; 1479; 1431; 1367; 1317; 1243; 767. – **$^1$H NMR/** 400 MHz ([D6]DMSO): δ (ppm) = 2.34 (s, 1H, Furfur-$CH_3$), 4.86 (d, *J* = 5.9 Hz, Ar-NH-C*H*$_2$), 6.01 (m, 1H, Furfur-4-H), 6.34 (d, *J* = 3.0 Hz, 1H, Furfur-3-H), 6.78 (dd, *J* = 3.3/ 1.7 Hz, 1H, Fur-4-H), 7.59 (d, *J* = 3.4 Hz, 1H, Fur-5-H), 8.05 – 8.09 (m, 2H, Fur-3-H, Ar-9-H), 8.14 (ddd, *J* = 8.2/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.64 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.89 (d, *J* = 7.8 Hz, 1H, Ar-10-H), 9.93 (t, *J* = 5.9 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 358 (14), 357 (59) [$M^{+\cdot}$], 315 (24), 314 (100) [$M^{+\cdot}$- $CH_3$-CO], 95 (13).

*N-(2-(5-methyl)furylmethyl)-[2-(E)-(2-phenylvinyl)]pyrimido[5,4-c]cinnolin-4-amin* (**15i**)

Aus 0.28 g (0.89 mmol) **5p** und 1.1 g (9.9 mmol) 2-(5-Metyl)furylmethylamin. Grüne Kristalle (EtOH/ EtAc), Schmp. 200 °C, Ausb. 0.24 g (69%). – $C_{24}H_{19}N_5O$ (393.5) Ber. C 73.3 H 4.87 N 17.8 Gef. C 73.3 H 4.84 N 17.7. – **IR** (KBr): ν = 3403 $cm^{-1}$; 1588; 1574; 1546; 1401; 1324; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.24 (s, 3H, Furfur-$CH_3$), 4.89 (d, *J* = 5.8 Hz, 2H, Ar-NH-C*H*$_2$), 6.02 (d, *J* = 2.0 Hz, 1H, Furfur-4-H), 6.35 (d, *J* = 2.9 Hz, 1H, Furfur-3-H), 7.31 (d, *J* = 15.9 Hz, 1H, Ar-C*H*=CH-Ph), 7.40 – 7.53 (m, 3H, Ph-3,4,5-H), 7.83 (d, *J* = 7.3 Hz, 2H, Ph-2,6-H), 8.05 – 8.10 (m, 1H, Ar-9-H), 8.11 – 8.16 (m, 1H, Ar-8-H), 8.21 (d, *J* = 15.8 Hz, 1H, Ar-CH=C*H*-Ph), 8.64 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.92 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.83 (t, *J* = 5.9 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 394 (14), 393 (46) [$M^{+\cdot}$], 351 (26), 350 (100) [$M^{+\cdot}$- $CH_3$-CO], 312 (12), 174 (11), 95 (19), 43 (12).

#### 4.2.2.5.2 N-[3-(1*H*-imidazol-1-yl)propyl]pyrimido[5,4-c]cinnolin-4-amine (16)

*N-[3-(1H-imidazol-1-yl)propyl]-(2-phenyl)-pyrimido[5,4-c]cinnolin-4-amin* (**16a**)

Aus 0.30 g (1.02 mmol) **5c** und 1.8 g (14.4 mmol) 3-(1-Imidazolyl)propylamin. Hellbraune Kristalle, Schmp. 175 °C, Ausb. 0.26g (67%). – $C_{22}H_{19}N_7$ (381.4) Ber. C 69.3 H 5.02 N 25.7

Gef. C 69.2 H 5.13 N 25.4. – **IR** (KBr): ν = 3338 $cm^{-1}$ (NH); 1595; 1578; 1546; 1508; 1449; 1434; 1400; 1368; 1317; 1299; 774; 755; 708; 645. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.22 – 2.29 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.77 – 3.82 (m, 2H, Ar-NH-C*$H_2$*), 4.18 (t, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 6.94 (s, 1H, Im-5-H), 7.28 (s, 1H, Im-4-H), 7.56 – 7.62 (m, 3H, Ph-3,4,5-H), 7.71 (s, 1H, Im-2-H), 8.08 (ddd, *J* = 7.5/ 7.3/ 1.0 Hz, 1H, Ar-9-H), 8.14 (ddd, *J* = 8.3/ 7.0/ 1.3 Hz, 1H, Ar-8-H), 8.59 – 8.61 (m, 2H, Ph-2,6-H), 8.65 (d, *J* = 8.2 Hz, Ar-7-H), 9.01 (dd, *J* = 8.0/ 0.8 Hz, Ar-10-H), 9.75 (t, *J* = 5.8 Hz, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 382 (22), 381 (90) [$M^{+\cdot}$], 313 (75) [$M^{+\cdot}$- Im], 300 (50) [$M^{+\cdot}$- $CH_2$-Im + H], 298 (61), 287 (100) [$M^{+\cdot}$- $(CH_2)_2$-Im + H], 274 (61) [$M^{+\cdot}$- $(CH_2)_3$-Im + 2H], 257 (18), 190 (11), 155 (18), 127 (33), 126 (64), 108 (59) [$(CH_2)_3$-$Im^+$ - H], 104 (21), 95 (34), 81 (45), 77 (23), 68 (25), 41 (16).

*2-(4-Fluorphenyl)-N-[3-(1*H*-imidazol-1-yl)propyl]pyrimido[5,4-c]cinnolin-4-amin-hydrat*

(**16b**)

Aus 0.30 g (0.97 mmol) **5l** und 1.9 g (15.2 mmol) 3-(1-Imidazolyl)propylamin. Ockerfarbene Kristalle (Isopropanol), Schmp. 203 °C, Ausb. 0.21 g (52%). – $C_{22}H_{18}FN_7$ x $H_2O$ (417.5) Ber. C 63.3 H 4.82 N 23.5 Gef. C 62.9 H 5.11 N 23.5. – **IR** (KBr): ν = 3364 $cm^{-1}$; 1603; 1589; 1578; 1547; 1436; 1402; 1368; 1313; 1220; 1149; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.19 – 2.27 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.74 – 3.79 (m, 2H, Ar-NH-C*$H_2$*), 4.17 (t, *J* = 6.7 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 6.96 (s, 1H, Im-5-H), 7.28 (s, 1H, Im-4-H), 7.39 (dd, *J* = 8.8/ 8.8 Hz, 2H, Ph-3,5-H), 7.72 (s, 1H, Im-2-H), 8.04 – 8.09 (m, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.59 – 8.65 (m, 3H, Ph-2,6-H, Ar-7-H), 8.98 (d, *J* = 7.3 Hz, Ar-10-H), 9.79 (t, *J* = 5.8 Hz, Ar-NH, austauschb.)./ ($CF_3COOD$): δ (ppm) = 2.73 – 2.80 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 4.44 (t, *J* = 6.9 Hz, 2H, Ar-NH-C*$H_2$*), 4.66 (t, *J* = 7.6 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 7.47 (dd, *J* = 8.7/ 8.1 Hz, 2H, Ph-3,5-H), 7.55 (s, 1H, Im-5-H), 7.59 (d, *J* = 1.3 Hz, 1H, Im-4-H), 8.54 – 8.57 (m, 3H, Ar-9-H, Ph-2,6-H), 8.65 (dd, *J* = 8.4/ 7.5 Hz, 1H, Ar-8-H), 8.81 (s, 1H, Im-2-H), 8.95 (d, *J* = 8.6 Hz, 1H, Ar-7-H), 9.28 (d, *J* = 8.5 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 400 (23), 399 (100) [$M^{+\cdot}$], 332 (18), 331 (76) [$M^{+\cdot}$- Im], 330 (18), 321 (11), 320 (52), 319 (18), 318 (67) [$M^{+\cdot}$- $CH_2$-Im], 309 (15), 308 (87), 307 (28), 306 (19) [$M^{+\cdot}$- $(CH_2)_2$-Im + 2H], 296 (12), 295 (62), 294 (11), 277 (11), 155 (21), 128 (15), 127 (39), 126 (63), 122 (21), 115 (12),109 (11), 108 (80) [$(CH_2)_3$-$Im^+$ - H], 107

(13), 101 (11), 100 (13), 96 (15), 95 (53) [$(CH_2)_2$-$Im^+$], 82 (68) [$CH_2$-$Im^+$ + H], 81 (21), 69 (13), 68 (26), 54 (14), 41 (20).

*2-(2-Furyl)-N-[3-(1*H*-imidazol-1-yl)propyl]pyrimido[5,4-c]cinnolin-4-amin* (**16c**)

Aus 0.25 g (0.88 mmol) **5m** und 2.1 g (16.8 mmol) 3-(1-Imidazolyl)propylamin. Ockerfarbene Kristalle, Schmp. 195 °C, Ausb. 0.12 g (36%). – $C_{20}H_{17}N_7O$ (371.4) Ber. C 64.7 H 4.61 N 26.4 Gef. C 64.7 H 4.81 N 26.1. – **IR** (KBr): ν = 3328 $cm^{-1}$; 1603; 1575; 1543; 1499; 1477; 1433; 1405; 1369; 1317; 1282; 1266; 1239; 1015; 822; 781; 766. – **$^1$H NMR**/ 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.19 – 2.25 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.71 – 3.76 (m, 2H, Ar-NH-C*$H_2$*), 4.14 (t, *J* = 6.9 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 6.77 –6.78 (m, 1H, Fur-4-H), 6.91 (d, *J* = 0.6 Hz, 1H, Im-5-H), 7.28 (d, *J* = 0.7 Hz, 1H, Im-4-H), 7.49 (d, *J* = 3.4 Hz, Fur-5-H), 7.71 (s, 1H, Im-2-H), 8.03 (s, 1H, Fur-3-H), 8.06 (dd, *J* = 7.9/ 7.1 Hz, Ar-9-H), 8.14 (dd, *J* = 8.2/ 7.1 Hz, Ar-8-H), 8.63 (d, *J* = 8.2 Hz, Ar-7-H), 8.89 (d, *J* = 8.1 Hz, Ar-10-H), 9.71 (t, *J* = 5.8 Hz, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 372 (19), 371 (73) [$M^{+\cdot}$], 304 (13), 303 (67) [$M^{+\cdot}$- Im -H], 302 (11), 290 (45) [$M^{+\cdot}$- $CH_2$-Im], 289 (12), 288 (50), 278 (18), 277 (100) [$M^{+\cdot}$- $(CH_2)_2$-Im + H], 276 (23), 275 (21), 265 (11), 264 (69) [$M^{+\cdot}$- $(CH_2)_3$-Im + 2H], 248 (23), 242 (10), 155 (14), 127 (24), 126 (31), 108 (40), 96 (10), 95 (25) [$(CH_2)_2$-$Im^+$], 94 (11), 82 (35), 81 (13), 68 (18), 39 (13).

*N-[3-(1H-Imidazol-1-yl)propyl]-2-(2-thienyl)-pyrimido[5,4-c]cinnolin-4-amin* (**16d**)

Aus 0.25 g (0.83 mmol) **5n** und 2.2 g (17.6 mmol) 3-(1-Imidazolyl)propylamin. Hellbraune Kristalle, Schmp. 177 °C, Ausb. 0.11 g (34%). – $C_{20}H_{17}N_7S$ (387.5) Ber. C 62.0 H 4.42 N 25.3 Gef. C 61.6 H 4.50 N 25.1. – **IR** (KBr): ν = 3347 $cm^{-1}$ (NH); 1595; 1577; 1536; 1524; 1433; 1393; 1370; 1313; 764; 726. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.20 – 2.27 (m, 2H, Ar-NH-$CH_2$-C*$H_2$*-$CH_2$), 3.71 – 3.76 (m, 2H, Ar-NH-C*$H_2$*), 4.15 (t, *J* = 6.8 Hz, 2H, Ar-NH-$CH_2$-$CH_2$-C*$H_2$*), 6.91 (s, 1H, Im-5-H), 7.26 (s, 1H, Im-4-H), 7.28 (dd, *J* = 4.9/ 3.8 Hz, 1H, Thi-4-H), 7.70 (s, 1H, Im-2-H), 7.87 (dd, *J* = 4.8/ 0.9 Hz, 1H, Thi-5-H), 8.07 (m, 1H, Ar-9-H), 8.11 – 8.15 (m, 2H, Ar-8-H, Thi-3-H), 8.63 (d, *J* = 8.1 Hz, Ar-7-H), 8.88 (dd, *J* = 8.0/ 0.7 Hz, 1H, Ar-10-H), 9.74 (t, *J* = 5.8 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 387 (68) [$M^{+\cdot}$], 319 (36), 306 (48) [$M^{+\cdot}$- $CH_2$-Im], 304 (43), 293 (53) [$M^{+\cdot}$- $(CH_2)_2$-Im + H], 292 (22), 291 (17), 281 (12), 280 (58) [$M^{+\cdot}$- $(CH_2)_3$-Im + 2H], 264 (15), 155 (13), 127

(19), 126 (31), 110 (10), 108 (29), 95 (20) [$(CH_2)_2$-$Im^+$], 82 (75) [$CH_2$-$Im^+$ + H], 81 (23), 69 (18), 68 (23), 55 (27), 54 (12), 41 (19), 30 (100), 28 (63), 27 (29), 26 (13).

### 4.2.2.6 Sonstige Pyrimido[5,4-c]cinnolin-4-amine mit basischem Heterocyclus in der Seitenkette

#### 4.2.2.6.1 N-Morpholinoalkyl-pyrimido[5,4-c]cinnolin-4-amine (17)

*Morpholinoeth-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17a**)

Aus 0.20 g (0.93 mmol) **5a** und 1.5 g (11.5 mmol) 1-(2-Morpholino)ethylamin. Grüne Kristalle, Schmp. 120 °C, Ausb. 0.19 g (61%). – $C_{16}H_{18}N_6O$ (310.4) Ber. C 61.9 H 5.85 N 27.1 Gef C 61.8 H 6.05 N 26.9. – **IR** (KBr): ν = 3430 $cm^{-1}$ (w); 3353; 3335; 1601; 1573; 1547; 1307; 1115. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.30 – 2.38 (m, 2H, Morph-2a,6a-H), 2.68 (t, *J* = 6.6 Hz, 2H, C*H*$_2$-Morph), 3.56 – 3.60 (m, 6H, Morph-2e,6e-H, Morph-3,5-H), 3.80 (t, *J* = 6.5 Hz, 2H, Ar-NH-C*H*$_2$), 8.08 (dd, *J* = 7.7/ 7.3 Hz, 1H, Ar-9-H), 8.15 (dd, *J* =8.0/ 7.1 Hz, 1H, Ar-8-H), 8.67 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.80 (s, 1H, Ar-2-H), 8.83 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.47 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 310 (2) [$M^{+\cdot}$], 113 (30) [$(CH_2)_2$-$Morph^+$], 100 (100) [$CH_2$=$Morph^+$], 56 (15), 28 (17).

*9-Hexyl-N-(morpholinoeth-1-yl)-pyrimido[5,4-c]cinnolin-4-amin* (**17b**)

Aus 0.10 g (0.33 mmol) **5b** und 0.9 g (6.9 mmol) 1-(2-Morpholino)ethylamin. 4 x mit 20 mL $H_20$ gegen 20 mL $CH_2Cl_2$ ausgeschüttelt. Grüne Kristalle, Schmp. 130 °C, Ausb. 0.09 g (69%). – $C_{22}H_{30}N_6O$ (394.5) Ber. C 67.0 H 7.67 N 21.3 Gef. C 67.1 H 7.62 N 21.2 – **IR** (KBr): ν = 3436 $cm^{-1}$; 1599; 1308; 1117; 635. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 6.8 Hz, 3H, $CH_3$), 1.29 – 1.31 (m, 6H, $CH_3$-(C*H*$_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.68 –1.74 (m, 2H, C*H*$_2$-$CH_2$-Ar), 2.50 – 2.52 (im DMSO-Peak, 4H, Morph-2,6-H), 2.69 (s, breit, 2H, C*H*$_2$-Morph), 2.93 (t, *J* = 7.5 Hz, 2H, C*H*$_2$-Ar), 3.59 (t, *J* = 3.9 Hz, 4H, Morph-3,5-H), 3.77 – 3.82 (m, 2H, Ar-NH-C*H*$_2$), 7.99 (d, *J* = 8.5 Hz, 1H, Ar-8-H), 8.56 (d, 1H, *J* = 8.6 Hz, Ar-7-H), 8.60 (s 1H, Ar-10-H), 8.78 (s, 1H, Ar-2-H), 9.42 – 9.44 (m, 1H, Ar-NH, austauschb.). – **MS**

(70 eV): m/z (%) = 394 (4) [$M^{+\cdot}$], 113 (51) [$(CH_2)_2$-Morph$^+$], 100 (100) [$CH_2$=Morph$^+$], 56 (12).

*Morpholinoeth-1-yl-(2-phenyl)pyrimido[5,4-c]cinnolin-4-amin-sesquihydrat* (**17c**)

Aus 0.40 g (1.37 mmol) **5c** und 2.1 g (16.1 mmol) 1-(2-Morpholino)ethylamin. Hellbraune Kristalle, Schmp. 172 °C, Ausb. 0.38 g (61%). – $C_{22}H_{22}N_6O$ x 1.5 $H_2O$ (413.5) Ber. C 63.9 H 6.09 N 20.3 Gef. C 63.7 H 5.73 N 20.0. – **IR** (KBr): ν = 3399 $cm^{-1}$; 3339; 1595; 1577; 1547; 1399; 1372; 1318; 1299; 1117; 755; 708. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.53 – 2.61 (m, schlecht aufgelöst, 4H, Morph-2,6-H), 2.77 (t, *J* = 6.4 Hz, 2H, C*H*$_2$-Morph), 3.58 (t, *J* = 4.4 Hz, 4H, Morph-3,5-H), 3.92 – 3.96 (m, 2H, Ar-NH-C*H*$_2$), 7.57 – 7.61 (m, 3H, Ph-3,4,5-H), 8.09 (ddd, *J* = 7.4/ 7.2/ 1.3 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 8.1/ 7.0/ 1.4 Hz, 1H, Ar-8-H), 8.65 – 8.69 (m, 3H, Ar-7-H, Ph-2,6-H), 9.03 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.49 (t, *J* = 5.7 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 386 (3) [$M^{+\cdot}$], 275 (12), 274 (11), 113 (49) [$(CH_2)_2$-Morph$^+$], 100 (100) [$CH_2$=Morph$^+$].

*Morpholinoprop-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17d**)

Aus 0.25 g (1.16 mmol) **5a** und 1.5 g (10.4 mmol) 1-(3-Morpholino)propylamin. Gelbgrüne Kristalle, Schmp. 151 °C, Ausb. 0.12 g (41%). – $C_{17}H_{20}N_6O$ (324.4) Ber. C 63.0 H 6.21 N 25.9 Gef. C 62.8 H 6.15 N 25.9. – **IR** (KBr): ν = 3409 $cm^{-1}$; 2818; 1601; 1569; 1548; 1304; 1114. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.88 – 1.93 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.43 (s, br, 4H, Morph-2,6-H), 2.48 (im $D_2O$-Austausch: d, *J* = 6.6 Hz, 2H, C*H*$_2$-Morph), 3.62 - 3.64 (m, 4H, Morph-3,5-H), 3.71 – 3.76 (m, 2H, Ar-NH-C*H*$_2$), 8.07 (ddd, *J* = 7.5/ 6.7/ 0.9 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.68 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.78 (s, 1H, Ar-2-H), 8.82 (d, *J* = 8.1 Hz, 1H, Ar-10-H), 9.91 (t, *J* = 5.1 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 324 (25) [$M^{+\cdot}$], 239 (18), 211 (23), 198 (12) [$M^{+\cdot}$-$(CH_2)_3$-Morph + 2H], 127 (15), 126 (100) [$(CH_2)_3$-Morph – 2H], 100 (64) [$CH_2$=Morph$^+$], 56 (14), 28 (10).

*9-Hexyl-N-(morpholinoprop-1-yl)-pyrimido[5,4-c]cinnolin-4-amin* (**17e**)

Aus 0.25 g (0.83 mmol) **5b** und 1.4 g (9.7 mmol) 1-(3-Morpholino)propylamin. 3x mit 20 mL $CH_2Cl_2$ gegen $H_2O$ ausgeschüttelt Grüne Kristalle, Schmp. 73 °C (Aceton/ $H_2O$), Ausb. 0.10 g (29%). – $C_{23}H_{32}N_6O$ (408.6) Ber. C 67.6 H 7.90 N 20.6 Gef. C 67.5 H 7.62 N 20.5 – **IR** (KBr): ν = 3407 $cm^{-1}$; 2955; 2927; 2856; 2817; 1600; 1568; 1544; 1496; 1459; 1371; 1350; 1305; 1263; 1141; 1114. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 0.86 (t, *J* = 7.0 Hz, 3H, $CH_3$), 1.27 – 1.32 (m 6H, $CH_3$-(C*H*$_2$)$_3$-$CH_2$-$CH_2$-Ar), 1.69 –1.74 (m, 2H, $CH_3$-($CH_2$)$_3$-C*H*$_2$-$CH_2$-Ar), 1.89 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.41 (s, br, 4H, Morph-2,6-H), 2.48 – 2.50 (im DMSO-Peak, 2H, C*H*$_2$-Morph), 2.93 (t, *J* = 7.6 Hz, 2H, $CH_3$-($CH_2$)$_4$-C*H*$_2$-Ar), 3.63 (t, *J* = 4.5 Hz, 4H, Morph-3,5-H), 3.70 – 3.75 (m, 2H, Ar-NH-C*H*$_2$), 7.99 (dd, *J* = 8.5/ 1.8 Hz, 1H, Ar-8-H), 8.55 – 8.60 (m, 2H, Ar-7,10-H), 8.77 (s, 1H, Ar-2-H), 9.86 (s, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 408 (18) [$M^{+\cdot}$], 323 (19) [$M^{+\cdot}$- Morph + H], 295 (13), 282 (26) [$M^{+\cdot}$- ($CH_2$)$_3$-Morph + 2H], 224 (10), 127 (13), 126 (100) [($CH_2$)$_3$-Morph – 2H], 100 (59) [$CH_2$=Morph$^+$], 28 (29).

*2-(4-Methoxyphenyl)-morpholinoprop-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17f**)

Aus 0.20 g (0.62 mmol) **5e** und 1.9 g (13.2 mmol) 1-(3-Morpholino)propylamin. Ockergelbe Kristalle, Schmp. 173 °C, Ausb. 0.21 g (79%). – $C_{24}H_{26}N_6O_2$ (430.9) Ber. C 67.0 H 6.09 N 19.5 Gef. C 67.1 H 5.90 N 19.2. – **IR** (KBr): ν = 3432 $cm^{-1}$; 1594; 1576; 1546; 1403; 1376; 1309; 1251. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.93 – 1.97 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.43 (m, schlecht aufgelöst, 4H, Morph-2,6-H), 2.50 – 2.52 (im DMSO-Peak, 2H, C*H*$_2$-Morph), 3.64 (m, schlecht aufgelöst, 4H, Morph-3,5-H), 3.84 – 3.88 (m, 5H, Ar-NH-C*H*$_2$, $OCH_3$), 7.12 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.07 (ddd, *J* = 7.6/ 7.4/ 1.0 Hz, 1H, Ar-9-H), 8.12 (ddd, *J* = 8.3/ 7.0/ 1.4 Hz, 1H, Ar-8-H), 8.61 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (d, *J* = 7.9 Hz, 1H, Ar-10-H), 9.78 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 431 (12), 430 (46) [$M^{+\cdot}$], 317 (36), 316 (11), 305 (12), 304 (53) [$M^{+\cdot}$- ($CH_2$)$_3$-Morph + 2H], 127 (23), 126 (100) [($CH_2$)$_3$-Morph – 2H], 100 (61) [$CH_2$=Morph$^+$], 56 (17), 28 (14).

*2-(2-Fluorphenyl)-morpholinoprop-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17g**)

Aus 0.20 g (0.64 mmol) **5i** und 1.7 g (11.8 mmol) 1-(3-Morpholino)propylamin. Ockergelbe Kristalle, Schmp. 156 °C, Ausb. 0.21 g (78%). – $C_{23}H_{23}FN_6O$ (418.5) Ber. C 66.0 H 5.54 N 20.1 Gef. C 66.0 H 5.39 N 20.0. – **IR** (KBr): ν = 3432 $cm^{-1}$; 1597; 1575; 1546; 1308; 1114; 761. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.90 – 1.96 (m, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.41 (s, breit, 4H, Morph-2,6-H), 2.47 – 2.49 (z.T. im DMSO-Peak, 2H, C$H_2$-Morph), 3.61 (t, *J* = 4.4 Hz, 4H, Morph-3,5-H), 3.78 – 3.83 (m, 2H, Ar-NH-C$H_2$), 7.35 – 7.41 (m, 2H, Ph-4,5-H), 7.59 – 7.64 (m, 1H, Ph-3-H), 8.07 (dd, *J* = 7.6/ 7.2 Hz, 1H, Ar-9-H), 8.15 (dd, *J* = 7.3/ 7.1 Hz, 1H, Ar-8-H), 8.26 – 8.30 (m, 1H, Ph-6-H), 8.68 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.89 (d, *J* = 8.0 Hz, 1H, Ar-10-H), 9.93 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 418 (26) [$M^{+\cdot}$], 333 (12), 305 (27), 127 (16), 126 (100) [$(CH_2)_3$-Morph – 2H], 100 (48) [$CH_2$=Morph$^+$], 56 (11), 28 (19).

*2-(4-Fluorphenyl)-morpholinoprop-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17h**)

Aus 0.30 g (0.97 mmol) **4l** und 2.2 g (15.3 mmol) 1-(3-Morpholino)propylamin. Ockergelbe Kristalle, Schmp. 194 °C, Ausb. 0.30 g (74%). – $C_{23}H_{23}FN_6O$ (418.5) Ber. C 66.0 H 5.54 N 20.1 Gef. C 66.0 H 5.31 N 20.0. – **IR** (KBr): ν = 3401 $cm^{-1}$ (w), 2816; 1591; 1573; 1545; 1402; 1375; 1310; 1218; 1147; 1116; 770. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.92 – 1.98 (m, 2H, Ar-NH-$CH_2$-C$H_2$-$CH_2$), 2.43 (s, br, 4H, Morph-2,6-H), 2.50 – 2.52 (im DMSO-Peak, 2H, C$H_2$-Morph), 3.62 – 3.65 (m, 4H, Morph-3,5-H), 3.86 – 3.90 (m, 2H, Ar-NH-C$H_2$,), 7.41 (dd, *J* = 8.8/ 8.7 Hz, 2H, Ph-3,5-H), 8.08 (dd, *J* = 7.3/ 7.0 Hz, 1H, Ar-9-H), 8.13 – 8.16 (m, 1H, Ar-8-H), 8.67 (d, *J* = 8.0 Hz, 1H, Ar-7-H), 8.70 – 8.74 (m, 2H, Ph-2,6-H), 9.01 (d, *J* = 7.5 Hz, 1H, Ar-10-H), 9.91 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 418 (18) [$M^{+\cdot}$], 305 (17), 292 (16), 127 (19), 126 (100) [$(CH_2)_3$-Morph – 2H], 100 (55) [$CH_2$=Morph$^+$], 56 (15), 42 (10), 28 (13).

*2-(4-Chlorphenyl)-morpholinoprop-1-yl-pyrimido[5,4-c]cinnolin-4-amin* (**17i**)

Aus 0.30 g (0.92 mmol) **5k** und 1.9 g (13.2 mmol) 1-(3-Morpholino)propylamin. Hellgrüne Kristalle (EtOH), Schmp. 188 °C, Ausb. 0.23g (58%). – $C_{23}H_{23}ClN_6O$ (434.9) Ber. C 63.5 H 5.33 N 19.3 Gef. C 63.5 H 5.14 N 19.2. – **IR** (KBr): ν = 3432 $cm^{-1}$; 1597; 1574; 1546; 1400;

1374; 1310; 1116. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 1.92 – 1.98 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.42 (s, br, 4H, Morph-2,6-H), 2.50 – 2.52 (im DMSO-Peak, 2H, C*H*$_2$-Morph), 3.64 (d, *J* = 4.5 Hz, 4H, Morph-3,5-H), 3.86 – 3.91 (m, 2H, Ar-NH-C*H*$_2$,), 7.65 (dd, *J* = 6.9/ 1.7 Hz, 2H, Ph-3,5-H), 8.09 (ddd, *J* = 7.6/ 7.4/ 1.2 Hz, 1H, Ar-9-H), 8.15 (ddd, *J* = 7.6/ 7.5/ 1.4 Hz, 1H, Ar-8-H), 8.67 (m, 3H, Ar-7-H, Ph-2,6-H), 9.01 (d, *J* = 7.2 Hz, 1H, Ar-10-H), 9.94 (t, *J* = 5.6 Hz, 1H, Ar-NH, austauschb.). – **MS** (70 eV): m/z (%) = 434 (25) [$M^{+\cdot}$], 321 (15), 308 (13), 127 (18), 126 (100) [$(CH_2)_3$-Morph – 2H], 100 (57) [$CH_2$=Morph$^+$].

*Morpholinoprop-1-yl-[2-(E)-(2-phenylvinyl)]pyrimido[5,4-c]cinnolin-4-amin* (**17j**)

Aus 0.30 g (0.94 mmol) **5n** und 2.1 g (14.6 mmol) 1-(3-Morpholino)propylamin. Dunkelgrüne Kristalle, Schmp. 165 °C, Ausb. 0.28 g (70%). – $C_{25}H_{26}N_6O$ (426.5) Ber. C 70.4 H 6.14 N 19.7 Gef. C 70.3 H 6.20 N 19.6. – **IR** (KBr): ν = 3410 cm$^{-1}$; 1591; 1573; 1543; 1402; 1320; 1116; 768. – **$^1$H NMR** / 400 MHz ([$D_6$] DMSO): δ (ppm) = 1.90 – 1.97 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$-$CH_2$), 2.43 („s“, breit, 4H, Morph-2,6-H), 2.50 – 2.54 (m, z.T. im DMSO, 2H, C*H*$_2$-Morph), 3.64 (t, *J* = 4.5 Hz, 4H, Morph-3,5-H), 3.81 – 3.86 (m, 2H, Ar-NH-C*H*$_2$), 7.27 (d, *J* = 15.8 Hz, 1H, Ar-C*H*=CH-Ph), 7.40 – 7.49 (m, 3H, Ph-3,4,5-H), 7.80 (d, *J* = 7.2 Hz, 2H, Ph-2,6-H), 8.05 (ddd, *J* = 7.6/ 7.5/ 1.0 Hz, 1H, Ar-9-H), 8.10 – 8.13 (m, 2H, Ar-8-H, Ar-CH=C*H*-Ph), 8.64 (d, *J* = 8.1 Hz, 1H, Ar-7-H), 8.89 – 8.91 (m, 1H, Ar-10-H), 9.80 (t, *J* = 5.5 Hz, 1H, Ar-NH, austauschb.)./ – **MS** (70 eV): m/z (%) = 426 (40) [$M^{+\cdot}$], 341 (12), 313 (20), 312 (13), 300 (39), 127 (18), 126 (100) [$(CH_2)_3$-Morph – 2H], 100 (51) [$CH_2$=Morph$^+$], 56 (11).

#### 4.2.2.6.2 4-(Heteroaryl-piperazino)pyrimido[5,4-c]cinnoline (18)

*2-Phenyl-4-(4-(2-pyridinyl)piperazino)pyrimido[5,4-c]cinnolin* (**18a**)

Aus 0.25 g (0.85 mmol) **5c** und 2.1 g (12.9 mmol) 1-(2-Pyridinyl)piperazin. Hellgrüne Kristalle, Schmp. 204 °C, Ausb. 0.28 g (79%). – $C_{25}H_{21}N_7$ (419.5) Ber. C 71.6 H 5.05 N 23.4 Gef. C 71.5 H 5.04 N 23.4. – **IR** (KBr): ν = 1593 cm$^{-1}$; 1576; 1543; 1525; 1486; 1438; 1384; 1303; 1260; 1245; 1234; 981; 772; 752; 703. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.87 (t, *J* = 5.1 Hz, 4H, Pipz-3,5-H), 4.78 – 4.81 (s, br, 4H, Pipz-2,6-H), 6.70 (dd, *J* = 7.0/ 5.0 Hz, 1H, Py-4-H), 6.92 (d, *J* = 8.7 Hz, 1H, Py-6-H), 7.59 – 7.62 (m, 4H, Ph-3,4,5-H, Py-5-H),

8.09 (dd, *J* = 8.9/ 6.1 Hz, 1H, Ar-9-H), 8.15 – 8.19 (m, 2H, Ar-8-H, Py-3-H), 8.64 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.67 – 8.70 (m, 2H, Ph-2,6-H), 9.09 (d, *J* = 8.7 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 420 (31), 419 (100) [$M^{+\cdot}$], 312 (11), 300 (18), 299 (31), 298 (76), 287 (11), 286 (49) [$M^{+\cdot}$- Py-N(=$CH_2$)-$CH_2$-$CH_2$ + H], 145 (18), 133 (55) [Py-N(=$CH_2$)-$CH_2$-$CH_2^+$ - H], 127 (19), 126 (14), 121 (22), 119 (12), 107 (14), 79 (14), 78 (17).

*2-(4-Methoxyphenyl)-4-(4-(2-pyridinyl)piperazino)pyrimido[5,4c]cinnolin* (**18b**)

Aus 0.30 g (0.93 mmol) **5e** und 1.5 g (9.2 mmol) 1-(2-Pyridinyl)piperazin. Dunkelgrüne, feine Kristalle, Schmp. 169 °C (EtOH/ $H_2O$), Ausb. 0.25 g (60%). – $C_{26}H_{23}N_7O$ (449.5) Ber. C 69.5 H 5.16 N 21.8 Gef. C 69.6 H 5.34 N 21.9. – **IR** (KBr): ν = 3472 $cm^{-1}$; 3438; 1604, 1592; 1575; 1539; 1524; 1506; 1483; 1438; 1385; 1296; 1250; 1234; 1136; 980; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.86 (t, *J* = 5.2 Hz, 4H, Pipz-3,5-H), 3.89 (s, 3H, $OCH_3$), 4.75 (s, br, 4H, Pipz-2,6-H), 6.70 (dd, *J* = 5.0/ 1.9 Hz, 1H, Py-4-H), 6.92 (d, *J* = 8.6 Hz, 1H, Py-6-H), 7.14 (d, *J* = 8.6 Hz, 2H, Ph-3,5-H), 7.60 (ddd, *J* = 7.8/ 7.8/ 1.9 Hz, 1H, Py-5-H), 8.04 - 8.08 (m, 1H, Ar-9-H), 8.13 – 8.19 (m, 2H, Ar-8-H, Py-3-H), 8.59 – 8.64 (m, 3H, Ph-2,6-H, Ar-7-H), 9.06 (d, *J* = 7.6 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 450 (29), 449 (100) [$M^{+\cdot}$], 330 (16), 329 (26), 328 (60), 317 (11), 316 (48) [$M^{+\cdot}$- Pyrim-N(=$CH_2$)-$CH_2$-$CH_2$ + H], 224 (14), 146 (14), 145 (20), 134 (13), 133 (58) [Py-N(=$CH_2$)-$CH_2$-$CH_2^+$ - 1H], 127 (20), 126 (17), 121 (36), 119 (11), 107 (19), 79 (14), 78 (17), 28 (11).

*2-Phenyl-4-(4-(2-pyrimidinyl)piperazino)pyrimido[5,4-c]cinnolin* (**18c**)

Aus 0.18 g (0.61 mmol) **5c** und 1.7 g (10.4 mmol) 2-(1-Piperazinyl)pyrimidin. Gelbgrüne Kristalle, Schmp. 223 °C (EtOH/ Ethylacetat), Ausb. 0.15 g (59%). – $C_{24}H_{20}N_8$ (420.5) Ber. C 68.6 H 4.79 N 26.7 Gef. C 68.6 H 4.94 N 26.7. – **IR** (KBr): ν = 3435 $cm^{-1}$; 1585; 1545; 1524; 1446; 1386; 1358; 1305; 1254; 981; 704. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 4.09 (t, *J* = 5.0 Hz, 4H, Pipz-3,5-H), 4.68 – 4.83 (s, breit, 4H, Pipz-2,6-H), 6.71 (dd, *J* = 4.8/ 4.6 Hz, 1H, Pyrim-5-H), 7.59 – 7.62 (m, 3H, Ph-3,4,5-H), 8.09 (dd, *J* = 8.0/ 7.1 Hz, 1H, Ar-9-H), 8.18 (dd, *J* = 7.2/ 7.1 Hz, 1H, Ar-8-H), 8.45 (d, *J* = 4.7 Hz, 2H, Pyrim-4,6-H), 8.64 (d, *J* = 8.3 Hz, 1H, Ar-7-H), 8.68 – 8.70 (m, 2H, Ph-2,6-H), 9.09 (d, *J* = 7.9 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 421 (33), 420 (100) [$M^{+\cdot}$], 299 (24), 298 (59), 286 (42) [$M^{+\cdot}$- Pyrim-N(=$CH_2$)-

$CH_2$-$CH_2$ + H], 147 (21), 146 (22), 134 (68) [Pyrim-N(=$CH_2$)-$CH_2$-$CH_2^+$ - H], 127 (27), 126 (24), 80 (20), 28 (45).

*2-(2-Fluorphenyl)-4-(4-(2-pyrimidinyl)piperazino)pyrimido[5,4-c]-cinnolin-semihydrat* (**18d**)

Aus 0.26 g (0.84 mmol) **5i** und 1.6 g (9.7 mmol) 2-(1-Piperazinyl)pyrimidin. Ockergelbe Kristalle (EtOH/ EtAc), Schmp. 211 °C, Ausb. 0.36 g (96%). – $C_{24}H_{19}FN_8$ x 0.5 $H_2O$ (447.5) Ber. C 64.4 H 4.50 N 25.0 Gef. C 64.4 H 4.45 N 24.9. – **IR** (KBr): ν = 1585 $cm^{-1}$; 1543; 1525; 1495; 1446; 1390; 1357; 1304; 1293; 1250; 980; 758. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 4.07 (t, *J* = 5.1 Hz, 4H, Pipz-3,5-H), 4.73 (s, breit, 4H, Pipz-2,6-H), 6.71 (dd, *J* = 4.7/ 4.7 Hz, 1H, Pyrim-5-H), 7.38 – 7.44 (m, 2H, Ph-4,5-H), 7.61 – 7.67 (m, 1H, Ph-4-H), 8.08 (dd, *J* = 8.0/ 7.1 Hz, 1H, Ar-9-H), 8.18 (dd, *J* = 8.1/ 7.8 Hz, 1H, Ar-8-H), 8.36 (ddd, *J* = 7.9/ 7.7/ 1.7 Hz, 1H, Ph-6-H), 8.45 (d, *J* = 4.7 Hz, 2H, Pyrim-4,6-H), 8.65 (d, *J* = 8.2 Hz, 1H, Ar-7-H), 8.98 (d, *J* = 7.9 Hz, 1H, Ar-10-H). / ($CF_3COOD$): δ (ppm) = 4.56 – 4.61 (m, 4H, Pipz-3,5-H), 5.14 (s, 2H, Pipz-2,6-H), 5.41 (s, 2H, Pipz-3,5-H), 7.18 – 7.20 (m, 1H, Pyrim-5-H), 7.54 (m, 1H, Ph-4-H), 7.64 (dd, *J* = 7.1/ 6.7 Hz, 1H, Ph-5-H), 7.99 – 8.02 (m, 1H, Ph-3-H), 8.52 (dd, *J* = 7.7/ 7.6 Hz, 1H, Ar-9-H), 8.58 (dd, *J* = 7.3/ 7.1 Hz, 1H, Ph-6-H), 8.68 (dd, *J* = 8.6/ 7.5 Hz 1H, Ar-8-H), 8..73 – 8.74 (m, 2H, Pyrim-4,6-H), 8.96 (d, *J* = 7.5 Hz, 1H, Ar-7-H), 9.01 (d, *J* = 8.1 Hz, 1H, Ar-10-H). – **MS** (70 eV): m/z (%) = 439 (27), 438 (100) [$M^{+\cdot}$], 318 (12), 317 (20), 316 (45), 305 (11), 304 (47) [$M^{+\cdot}$- Pyrim-N(=$CH_2$)-$CH_2$-$CH_2$ + H], 219 (12), 147 (17), 146 (17), 134 (42) [Pyrim-N(=$CH_2$)-$CH_2$-$CH_2^+$ - H], 127 (19), 126 (15), 122 (14), 80 (12), 43 (10), 28 (13).

### 4.2.2.7 Sonstige in 4-Stellung substituierte Pyrimido[5,4-c]cinnoline (19, 20)

*N-Phenyl-N´-(4-Methoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl)ethan-1,2-diamin* (**19**)

Aus 0.30 g (0.93 mmol) **5e** und 1.4 g (10.3 mmol) N-Phenylethan-1,2-diamin. Hellgrüne Kristalle, Schmp. 178 °C, Ausb. 0.11 g (30%). – $C_{25}H_{22}N_6O$ (422.5) Ber. C 71.1 H 5.25 N 19.9 Gef. C 70.7 H 5.13 N 19.6. – **IR** (KBr): ν = 3360 $cm^{-1}$; 3339; 1592; 1576; 1546; 1509; 1400; 1311; 1252; 1163; 768. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 3.44 – 3.49 (m, 2H, Ar-NH-$CH_2$-C*H*$_2$), 3.89 (s, 3H, $OCH_3$), 3.96 – 4.01 (m, 2H, Ar-NH-C*H*$_2$), 5.94 („s“, 1H,

NH-Ph, austauschb.), 6.56 (dd, *J* = 7.3/ 7.2 Hz, 1H, NH-Ph-4-H), 6.69 (d, J = 7.8 Hz, 2H, NH-Ph-2,6-H), 7.08 - 7.13 (m, 4H, NH-Ph-3,5-H, Ph-3,5-H), 8.06 (ddd, *J* = 8.1/ 7.0/ 1.2 Hz, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.7/ 7.6/ 1.3 Hz, 1H, Ar-8-H), 8.61 – 8.64 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (dd, *J* = 7.9/ 1.1 Hz, 1H, Ar-10-H), 9.64 (t, *J* = 6.0 Hz, Ar-NH, austauschb.) – **MS** (70 eV): m/z (%) = 422 (5) [$M^{+\cdot}$], 317 (24), 316 (11), 305 (18), 304 (100) [M – $CH_2$-$CH_2$-NH-Ph + 2H], 119 (13), 106 (18).

*N-(2-(4-Methoxyphenyl)pyrimido[5,4-c]cinnolin-4-yl)4-amino-1-butansäure* (**20**)

Aus 0.30 g (0.93 mmol) **5e**. Rötlichbraune Kristalle, Schmp. 238 °C (EtOH/ $H_2O$), Ausb. 0.11 g (30%). – $C_{21}H_{19}N_5O_3$ (389.4) Ber. C 64.8 H 4.92 N 18.0 Gef. C 64.5 H 4.85 N 17.8. – **IR** (KBr): ν = 1712 $cm^{-1}$; 1593; 1576; 1547; 1403; 1310; 1252; 1164; 769. – **$^1$H NMR** / 400 MHz ([$D_6$]DMSO): δ (ppm) = 2.01 – 2.08 (m, 2H, C*H*$_2$-$CH_2$-COOH), 2.41 (t, *J* = 7.3 Hz, 2H, $CH_2$-C*H*$_2$-COOH), 3.80 – 3.85 (m, 2H, Ar-NH-C*H*$_2$), 3.88 (s, 3H, $OCH_3$), 7.12 (d, *J* = 8.9 Hz, 2H, Ph-3,5-H), 8.06 (ddd, *J* = 7.6/ 7.6/ 1.2 Hz, 1H, Ar-9-H), 8.13 (ddd, *J* = 7.7/ 7.5/ 1.3 Hz, 1H, Ar-8-H), 8.59 – 8.67 (m, 3H, Ar-7-H, Ph-2,6-H), 8.99 (dd, *J* = 8.0/ 0.8 Hz, 1H, Ar-10-H), 9.61 (t, *J* = 5.9 Hz, Ar-NH, austauschb.), 12.10 (s, 1H, COOH, austauschb.). – **MS** (70 eV): m/z (%) = 390 (27), 389 (100) [$M^{+\cdot}$], 331 (21), 330 (97) [M – $CH_2$-COOH], 317 (18), 316 (38), 315 (15), 304 (37), 303 (44), 171 (14), 155 (13), 134 (16), 127 (26), 126 (46).