Heterocyclic β-Enamino Esters, 48[1]

Heterocondensed Pyridines by Cycloaddition-Extrusion Sequence of Bi- and Tricyclic 1,3-Oxazinones with *N,N*-Diethyl-1-propynylamine

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Received February 25, 1987

Dihalotriphenylphosphoranes convert the *N*-benzoylated ethyl 2-amino-4,5-dihydrofuran- (**5b**), -pyrrole- (**7b**), -isoxazole- (**9b**), and -oxazole-3- or -4-carboxylates (**11b**) into heterocondensed 1,3-oxazinones **6**, **8**, **10**, and **12**. Treatment with *N,N*-diethyl-1-propynylamine of these compounds as well as the already known 1,3-oxazinones **1a,b**, **2a,b**, and **3** results in a regiospecific cycloaddition-extrusion sequence to afford the corresponding heterocondensed pyridines **13a,b**, **14a,b**, **15a,b**, and **16–21**. Of these **15b** and the 4-oxonaphthyridines **16**, **17** represent examples of insertion of the acetylene reagent.

Heterocyclische β-Enaminoester, 48[1]. – Heterokondensierte Pyridine durch Cycloaddition-Extrusion-Sequenz bi- und tricyclischer 1,3-Oxazinone mit *N,N*-Diethyl-1-propinylamin

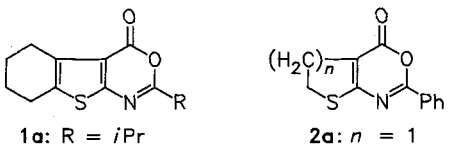
Dihalogentriphenylphosphorane überführen die *N*-benzoylierten 2-Amino-4,5-dihydrofuran- (**5b**), -pyrrol- (**7b**), -isoxazol- (**9b**) und -oxazol-3- oder -4-carbonsäure-ethylester (**11b**) in die heterokondensierten 1,3-Oxazinone **6**, **8**, **10** und **12**. Mit *N,N*-Diethyl-1-propinylamin ergeben diese und die bereits beschriebenen 1,3-Oxazinone **1a,b**, **2a,b** und **3** regiospezifisch in einer Cycloadditions-Extrusions-Sequenz die entsprechenden heterokondensierten Pyridine **13a,b**, **14a,b**, **15a,b**, **16–21**, von denen **15b** und die 4-Oxonaphthyridine **16**, **17** Beispiele für die Insertion des Acetylen-Reagens darstellen.

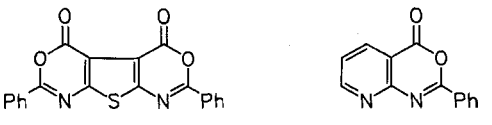
I. Heterocondensed 1,3-Oxazinones

1,3-Oxazin-6-ones are versatile intermediates in heterocyclic synthesis, and manifold methods exist for their preparation[4]. Recently, we have described a general and smooth access to heterocondensed 1,3-oxazin-6-ones by treatment of *N*-acylated heterocyclic β-enamino esters with dihalotriphenylphosphoranes[5], and this method has been also applied to the synthesis of monocyclic 1,3-oxazin-6-ones, e.g. from *tert*-butyl 3-(acylamino)acrylates[4,6].

The heterocondensed 1,3-oxazinones **1a,b**, **2a,b**[5], **3**[7], and **4**[8] are already known.

Scheme 1

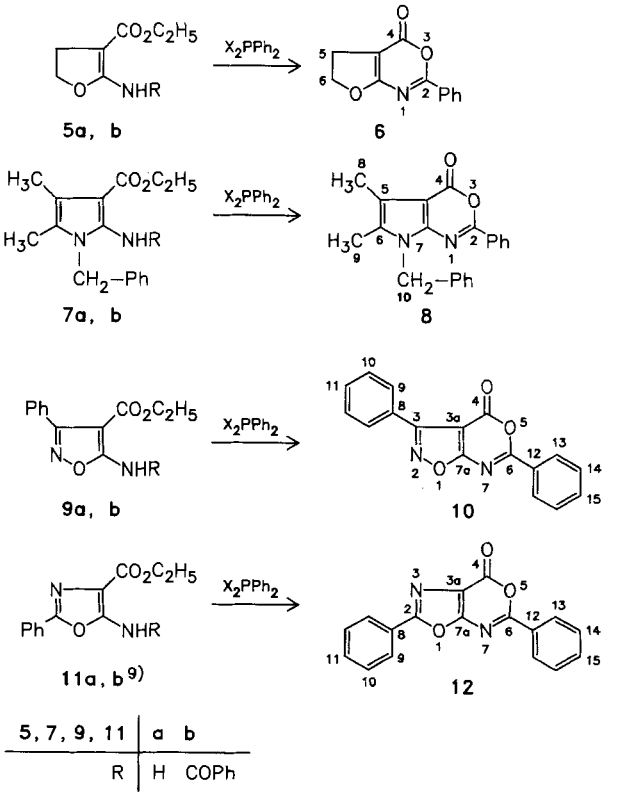




Additionally, the new heterocondensed 1,3-oxazinones **6**, **8**, **10**, **12** have been prepared on the same route by acylation of the 2-amino group of **5b**, **7b**, **9b**, **11b** and subsequent ring closure with the aid of dihalotriphenylphosphoranes.

The heterocyclic systems **3**[7], **6**, and **10** have not yet been described in the literature. For the oxazolo[5,4-*d*][1,3]oxazine system **12** cf. ref.[9,10] and for the pyrrolo[2,3-*d*][1,3]oxazine **8** cf. ref.[11].

Scheme 2



II. Cycloaddition-Extrusion Reaction with *N,N*-Diethyl-1-propynylamine

As Steglich et al.[4,12] have shown with monocyclic 1,3-oxazin-6-ones, alkynes add smoothly in a [4 + 2] manner

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with subsequent CO_2 expulsion to furnish pyridines, and employing ynamines this transformation reaction has been also observed with 4*H*-3,1-benzoxazinones[13].

As we have found this cycloaddition-extrusion reaction can be extended easily also to heterocondensed 1,3-oxazinones resulting in a smooth and simple annelation of a pyridine ring to an existing heterocyclic system. In the case of **1a,b, 2a,b, 3, 6, 8, 10, 12** this reaction proceeds completely regiospecifically to give the heterocondensed pyridines **13a,b, 14a,b, 15a, 18–21**.

Scheme 3

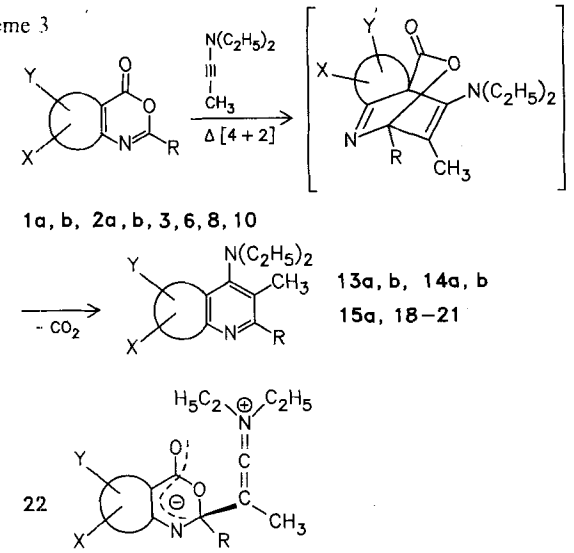
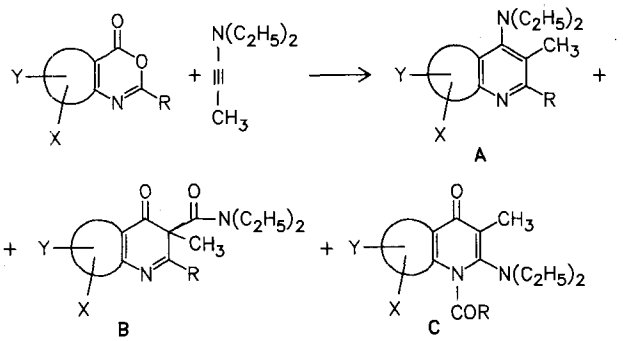
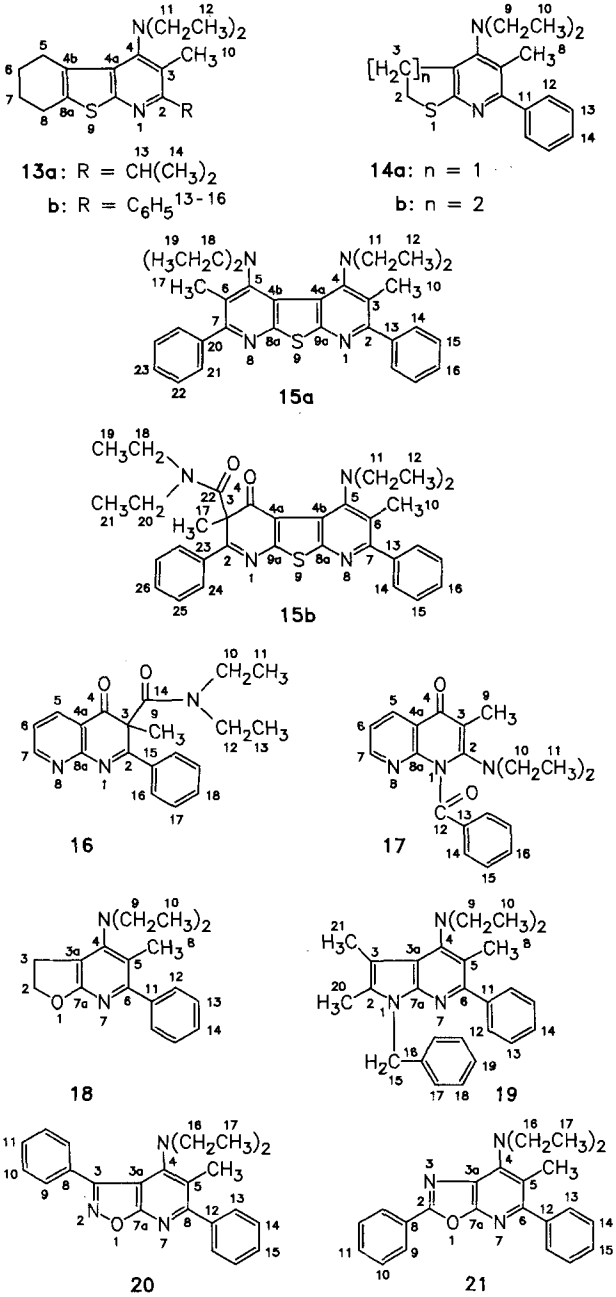


Table 1. Product distribution in the reaction of heterocondensed 1,3-oxazinones **1a,b, 2a,b, 3, 4, 6, 8, 10** with *N,N*-diethyl-1-propynylamine. Solvents toluene (T), acetonitrile (A), ether (E)



Starting compound	Solv.	Time	Temp. [°C]	Products	Product distribution [%] A	B	C
1a,b	T	60 min	110	**13a**	76		
	T	60 min	110	**13b**	71		
2a,b	T	20 min	110	**14a**	84		
	T	60 min	110	**14b**	80		
3	T	40 min	110	**15a,b**[a]	25	51	
4	T	40 min	110	**16**		58	
4	A	40 min	110	**17**			75
6	T	20 min	110	**18**	87		
8	A	48 h	81	**19**	10		
10	E	60 min	RT	**20**	35		
12	E	60 min	35	**21**	95		

[a] Separated and isolated by chromatography.



We have found, however, that the nature of the heterocycle condensed to the 1,3-oxazine system plays a certain role in the reactivity and the product distribution. Thus, from the reaction of the thieno-bis[1,3]oxazine **3** with *N,N*-diethyl-1-propynylamine the thieno[2,3-*b*:5,4-*b'*]dipyridine **15b** was isolated as side product; upon heating in toluene and acetonitrile, the pyrido[1,3]oxazine **4** results, however, solely in the formation of a 4-oxo-3,4-dihydro- (**16**) and 4-oxo-1,4-dihydronaphthyridine **17** (cf. Table 1), respectively, by insertion of the reagent. A similar behaviour has been reported for the treatment of 2-(trifluoromethyl)-4*H*-3,1-benzoxazinones with the same reagent[13], where a dipolar system, such as **22**, was discussed as primary adduct.

Monitoring the cycloaddition-extrusion sequence, the reaction is usually finished in 20–60 min; only the transformation **8** → **19** needs, as exemption, 48 h for completion.

This work was supported by the *Fonds der Chemischen Industrie*, the *Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen*, and the *Bayer AG*. – Y.-f. M. is very grateful to the *Max-Planck-Gesellschaft* for granting a research fellowship and N. H. thanks the *Land Nordrhein-Westfalen* for granting a Promotionsstipendium.

Experimental

IR spectra: Perkin-Elmer 157-G. – ^{1}H-NMR spectra: Bruker WH-90 and AC-200. – ^{13}C-NMR spectra: Bruker WH-90 and AC-200, TMS as internal standard. MS: MS-50 of Kratos (A.E.I.): – Melting points: uncorrected. – Elemental analyses: Analytical Laboratory of the Institute and Mikroanalytisches Laboratorium Dr. F. Pascher, D-5480 Remagen.

The synthesis of the heterocyclic and heteroaromatic β-enamino esters **5a**, **7a**, **9a**, and **11a** is described in ref.[14–17].

Ethyl 2-(Benzoylamino)-4,5-dihydro-3-furancarboxylate (**5b**) was prepared according to ref.[18] from 7.85 g (50 mmol) of **5a**[14] and 7.7 g (55 mmol) of benzoyl chloride in 15 ml of pyridine by warming to 40–50°C for 2 h. Working up like ref.[18]; yield 5.0 g (39%); m.p. 127–128°C. – IR (KBr): 3200 cm^{-1} (NH), 1705 (CO), 1670 (amide). – ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, CH_3, J = 7 Hz), 2.90 (t, CH_2-5, J = 9 Hz), 4.25 (q, CH_2, J = 7 Hz), 4.70 (t, CH_2-4), J = 9 Hz), 7.5–8.2 (m, $H_{ar.}$).

$C_{14}H_{15}NO_4$ (261.3) Calcd. C 64.37 H 5.78 N 5.36
Found C 64.37 H 5.83 N 5.93

Ethyl 2-(Benzoylamino)-1-benzyl-4,5-dimethyl-3-pyrrolecarboxylate (**7b**) was prepared like **5b** from 8.2 g (30 mmol) of **7a**[15] and 4.65 g (33 mmol) of benzoyl chloride in 15 ml of pyridine, yield 7.6 g (67%); m.p. 131–133°C. – IR (KBr): 3295 cm^{-1} (NH), 1690 (CO), 1660, 1585 (amide, C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, CH_3, J = 7 Hz), 2.05 (s, CH_3), 2.15 (s, CH_3), 4.25 (q, CH_2, J = 7 Hz), 5.15 (s, CH_2–Ph), 6.8–8.0 (m, $H_{ar.}$), 8.92 (s, NH).

$C_{23}H_{24}N_2O_3$ (376.5) Calcd. C 73.39 H 6.42 N 7.44
Found C 37.37 H 6.35 N 7.59

Ethyl 5-(Benzoylamino)-3-phenyl-4-isoxazolecarboxylate (**9b**) was prepared from 10.0 g (43 mmol) of **9a**[16] and 9 ml of 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) in 250 ml of dry benzene. To the refluxing solution slowly 7.0 g (50 mmol) of benzoyl chloride is added. After completion (TLC) and cooling to ambient temperature the solution is extracted two times with 100 ml of H_2O. The product is precipitated by acidification of the aqueous layer with acetic acid (to pH 5). An additional crop is obtained by evaporation of the benzene phase till dryness, extraction of the residue with ethanol, and evaporation of the solvent. From acetonitrile m.p. 106°C; yield 10.0 g (69%). – IR (KBr): 3280 cm^{-1} (NH), 1710, 1670 (CO). – ^{1}H NMR ([D$_6$]DMSO): δ = 1.07 (t, CH_3, J = 8 Hz), 4.19 (q, CH_2, J = 8 Hz), 7.4–8.1 (m, $H_{ar.}$), 11.64 (s, NH). – MS: m/z = 336 (M^+).

$C_{19}H_{16}N_2O_4$ (336.4) Calcd. C 67.85 H 4.79 N 8.33
Found C 67.18 H 4.94 N 8.34

Ethyl 5-(Benzoylamino)-3-phenyl-4-oxazolecarboxylate (**11b**)[9] is prepared like **9b** from 10.0 g (43 mmol) of **11a**[17] and 9 ml of DBN in 250 ml of benzene with 7.0 g (50 mmol) of benzoyl chloride. Yield 7.32 g (51%), m.p. 142–143°C. – IR (KBr): 3300 cm^{-1} (NH), 1700, 1675 (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.47 (t, CH_3, J = 7 Hz), 4.47 (q, CH_2, J = 7 Hz), 7.4–8.2 (m, $H_{ar.}$), 10.22 (s, NH). – MS: m/z = 336 (M^+).

$C_{19}H_{16}N_2O_4$ (336.4) Calcd. C 67.85 H 4.79 N 8.33
Found C 67.81 H 4.91 N 8.41

5,6-Dihydro-2-phenyl-4H-furo[2,3-d]-1,3-oxazin-4-one (**6**): To a solution of 1.31 g (5.0 mmol) of **5b** and 2.53 g (6.0 mmol) of dibromotriphenylphosphorane in 50 ml of absol. acetonitrile 0.9 ml (6 mmol) of triethylamine is added under argon. After working up as described in ref.[5] 0.30 g (20%) of **6** are obtained, m.p. 176–178°C. – IR (KBr): 1760 cm^{-1} (CO), 1585 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 3.10 (t, 5-H, J = 9 Hz), 5.04 (t, 6-H, J = 9 Hz), 7.5–8.4 (m, $H_{ar.}$). – MS: m/z = 215 (M^+).

$C_{12}H_9NO_3$ (215.3) Calcd. C 66.97 H 4.18 N 6.51
Found C 67.10 H 3.49 N 6.45

7-Benzyl-5,6-dimethyl-2-phenylpyrrolo[2,3-d]-1,3-oxazine-4(7H)-one (**8**): To a solution of 3.76 g (10 mmol) of **7b**, 3.2 g (12 mmol) of triphenylphosphane, and 2.9 g (12 mmol) of hexachloroethane in 100 ml of absol. acetonitrile 1.7 ml (12 mmol) of triethylamine is added under argon. Working up like ref.[5] affords 3.0 g (90%) of **8** as yellow crystals of m.p. 182–183°C. – IR (KBr): 1760 cm^{-1} (CO), 1560 (C=N, C=C). – ^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 8-H), 2.30 (s, 9-H), 5.45 (s, 10-H), 7.2–8.5 (m, $H_{ar.}$). – MS: m/z = 330 (M^+).

$C_{21}H_{18}N_2O_2$ (330.4) Calcd. C 76.36 H 5.45 N 8.48
Found C 76.41 H 5.60 N 8.54

3,6-Diphenyl-4H-isoxazolo[5,4-d][1,3]oxazin-4-one (**10**): To a mixture of 0.76 g (3.2 mmol) of hexachloroethane, 0.86 g (3.2 mmol) of triphenylphosphane and 1.0 g of **9b** in 20 ml of acetonitrile a solution of 1 ml of triethylamine in 5 ml of acetonitrile is added dropwise under inert gas. After 1 h stirring at room temp. the reaction mixture is refluxed for 1 h. After cooling the product precipitates together with triethylamine hydrochloride. The product is washed with ethanol and recrystallized from ethanol, yield 0.66 g (78%) of m.p. 214–215°C. – IR (KBr): 1790 cm^{-1} (CO). – ^{1}H NMR ([D$_6$]DMSO): δ = 7.5–8.4 (m, $H_{ar.}$). – ^{13}C NMR ([D$_6$]DMSO): δ = 94.88 (C-3a), 126.25 (C-8), 128.12 (C-10), 128.41 (C-12), 129.09 (C-9,-13), 129.42 (C-14), 131.59 (C-11), 134.79 (C-15), 154.21 (C-3), 159.33 (C-6), 166.16 (C-4), 176.29 (C-7a). – MS: m/z = 290 (M^+).

$C_{17}H_{10}N_2O_3$ (290.3) Calcd. C 70.34 H 3.47 N 9.65
Found C 71.02 H 3.59 N 9.54

2,6-Diphenyl-4H-oxazolo[5,4-d][1,3]oxazin-4-one (**12**) is obtained like **10** from 0.76 g (3.2 mmol) of hexachloroethane, 0.86 g (3.2 mmol) of triphenylphosphane, 1.0 g of **11b** in 20 ml of dry acetonitrile, and 1 ml of triethylamine solved in 5 ml of acetonitrile; yield 0.38 g (41%), yellow crystals of m.p. 224°C. – IR (KBr): 1780 cm^{-1}. – ^{1}H NMR ($CDCl_3$/[D$_6$]DMSO): δ = 7.5–8.3 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$/[D$_6$]DMSO): δ = 116.66 (C-3a), 125.03 (C-8), 126.66 (C-10), 128.12 (C-14), 128.59 (C-12), 128.75 (C-9), 128.84 (C-13), 131.79 (C-11), 133.47 (C-15), 153.12 (C-2), 159.51 (C-7a), 163.40 (C-6), 163.47 (C-4). – MS: m/z = 290 (M^+).

$C_{17}H_{10}N_2O_3$ (290.3) Calcd. C 70.34 H 3.47 N 9.65
Found C 70.64 H 3.71 N 9.51

Synthesis of the Heterocondensed Pyridines **13a,b**, **14a,b**, **15a,b**, **16–19**; *General Procedure:* To a solution of 10 mmol of **1a,b**, **2a,b**, **3**, **4**, **6**, and **8** in 15 ml of toluene or acetonitrile 1.7 ml (10 mmol) of *N,N*-diethyl-1-propynylamine is added. The mixture is heated under gentle reflux or kept at room temp. for 20 min to 48 h (cf. Table 1). After removal of the solvent, the resulting residue is crystallized from ether/petroleum ether. **15a,b** were separated by column chromatography on Al_2O_3 (eluents: petroleum ether (b.r. 60–90°C)/chloroform 1:1).

4-(Diethylamino)-5,6,7,8-tetrahydro-2-isopropyl-3-methylbenzo[4,5]thieno[2,3-b]pyridine (**13a**): Yield 2.4 g (76%), m.p. 98–99°C. – IR (KBr): 1560, 1510 cm^{-1} (C=C, C=N): – ^{1}H NMR ($CDCl_3$):

δ = 1.06 (t, 12H, *J* = 7 Hz), 1.76–2.02 (m, 6-, 7-H), 2.25 (s, 10-H), 2.66–3.10 (m, 5-, 8-H), 3.20 (q, 11-H, *J* = 7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 13.85 (C-12), 14.40 (C-10), 21.95 (C-14), 23.08 (C-6), 23.21 (C-7), 26.25 (C-5), 26.51 (C-8), 31.62 (C-17), 47.90 (C-11), 126.57 (C-4a), 128.14 (C-3), 131.35 (C-4b), 134.45 (C-8a), 150.96 (C-4), 159.57 (C-6), 162.94 (C-2). – MS: *m/z* = 316 (M^+).

$C_{19}H_{28}N_2S$ (316.5) Calcd. C 72.10 H 8.92 N 8.85
Found C 72.01 H 8.96 N 8.63

4-(Diethylamino)-5,6,7,8-tetrahydro-3-methyl-2-phenylbenzo[4,5]thieno[2,3-b]pyridine (**13b**): Yield 2.5 g (71%), m.p. 104–106°C. – IR (KBr): 1560, 1510 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 12-H, *J* = 7 Hz), 1.77–2.02 (m, 14–16-H), 2.20 (s, 10-H), 2.69–3.20 (m, 5,8-H), 3.30 (q, 11-H, *J* = 7 Hz), 7.2–7.6 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 13.79 (C-12), 17.19 (C-10), 22.98 (C-6), 23.11 (C-7), 26.31 (C-5); 26.38 (C-8), 47.58 (C-11), 126.33 (C-4a), 127.63 (C-3), 128.11 (C-15,16), 129.28 (C-14), 131.83 (C-4b), 136.04 (C-8a), 141.51 (C-13), 151.81 (C-4), 157.24 (C-9a), 159.80 ppm (C-2). – MS: *m/z* = 350 (M^+).

$C_{22}H_{26}N_2S$ (350.5) Calcd. C 75.39 H 7.48 N 7.99
Found C 75.26 H 7.64 N 7.99

4-(Diethylamino)-2,3-dihydro-5-methyl-6-phenylthieno[2,3-b]pyridine (**14a**): Yield 2.5 g (84%), m.p. 73–74°C. – IR (KBr): 1540 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, 10-H, *J* = 7 Hz), 2.12 (s, 8-H), 2.85–3.60 (m, 2,3-H), 3.10 (q, 9-H, *J* = 7 Hz), 7.2–7.5 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 13.85 (C-10), 16.15 (C-8), 30.85 (C-3), 33.44 (C-2), 45.83 (C-9), 124.87 (C-3a), 127.56 (C-14), 127.98 (C-13), 128.37 (C-5), 129.21 (C-12), 141.32 (C-11), 153.88 (C-4), 159.31 (C-7a), 163.75 (C-6). – MS: *m/z* = 298 (M^+).

$C_{18}H_{22}N_2S$ (298.5) Calcd. C 72.44 H 7.43 N 9.39
Found C 72.59 H 7.54 N 9.23

5-(Diethylamino)-3,4-dihydro-6-methyl-7-phenyl-2H-thiopyrano[2,3-b]pyridine (**14b**): Yield 2.55 g (80%), m.p. 99–100°C. – IR (KBr): 1530 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, 10-H, *J* = 7 Hz), 1.90–2.40 (m, 3-H), 2.10 (s, 8-H), 2.50–2.90 (m, 4-H), 2.90–3.28 (m, 2-H), 3.25 (q, 9-H, *J* = 7 Hz), 7.25–7.65 (m, $H_{ar.}$). – MS: *m/z* = 312 (M^+).

$C_{19}H_{24}N_2S$ (312.5) Calcd. C 73.03 H 7.44 N 8.96
Found C 73.07 H 7.79 N 8.69

4,5-Bis(diethylamino)-3,6-dimethyl-2,7-diphenylthieno[2,3-b:5,4-b']dipyridine (**15a**): Yield 1.28 g (25%), m.p. 250–252°C. – IR (KBr): 1550, 1530 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, 12,19-H, *J* = 7 Hz), 2.35 (s, 10,17-H), 3.34 (q, 11,18-H, *J* = 7 Hz), 7.25–7.85 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 14.95 (C-12,19), 19.19 (C-10,17), 46.35 (C-11,18), 120.63 (C-4a,4b), 122.93 (C-3,6), 128.18 (C-15,16,22,23), 129.96 (C-14,21), 141.06 (C-13,20), 152.94 (C-4,5), 158.21 (C-8a,9a), 159.22 (C-2,7). – MS: *m/z* = 508 (M^+).

$C_{32}H_{36}N_4S$ (508.7) Calcd. C 75.76 H 7.13 N 11.02
Found C 75.85 H 7.10 N 11.02

5-(Diethylamino)-N,N-diethyl-3,4-dihydro-3,6-dimethyl-4-oxo-2,7-diphenylthieno[2,3-b:5,4-b']dipyridine-3-carboxamide (**15b**): Yield 2.8 g (51%), m.p. 212–214°C. – IR (KBr): 1670 cm^{-1}, 1650 (CO, CO-amide), 1530 (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 0.65 (t, 20-H, *J* = 7 Hz), 0.90 (t, 19-H, *J* = 7 Hz), 1.04 (t, 12-H, *J* = 7 Hz), 1.98 (s, 17-H), 2.28 (s, 10-H), 2.53 (dq, 20-H, *J* = 12.6; 7 Hz), 3.30 (dq, 18-H, *J* = 12.6; 7 Hz), 3.42 (m, 11-H), 7.34–7.63 (m, $H_{ar.}$), 8.22–8.30 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 11.61 (C-19), 12.09 (C-21), 15.16 (C-12), 17.96 (C-10), 24.38 (C-17), 39.82 (C-18), 41.18 (C-20), 47.60 (C-11), 63.28 (C-3), 118.58 (C-4b), 124.25 (C-4a), 127.49 (C-6), 128.12 (C-25), 128.17 (C-16), 128.54 (C-24), 128.59 (C-15), 129.30 (C-14), 132.25 (C-26), 134.96 (C-23), 140.72 (C-13), 154.52 (C-5), 157.92 (C-7), 159.46 (C-2), 163.63 (C-8a), 168.59 (C-9a), 175.13 (C-22), 187.93 (C-4). – MS: *m/z* = 552 (M^+).

$C_{33}H_{36}N_4O_2S$ (552.7) Calcd. C 71.70 H 6.52 N 10.14
Found C 72.20 H 6.53 N 10.20

N,N-Diethyl-3,4-dihydro-3-methyl-4-oxo-2-phenyl-1,8-naphthyridine-3-carboxamide (**16**): Yield 1.94 g (58%), m.p. 162–164°C. – IR (KBr): 1702 cm^{-1}, 1645 (CO), 1585, 1565 (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 0.63 (t, 13-H, *J* = 7 Hz), 0.85 (t, 11-H, *J* = 7 Hz), 1.84 (s, 9-H), 2.48 (dq, 12-H, *J* = 13; 7 Hz), 3.25 (dq, 10-H, *J* = 13; 7 Hz), 7.32–7.52 (m, $H_{ar.}$), 8.40 (dd, 5-$H_{ar.}$, *J* = 7.5; 7 Hz), 8.93 (dd, 7-$H_{ar.}$, *J* = 4.5; 7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 11.40 (C-11), 12.04 (C-13), 25.54 (C-9), 39.88 (C-10), 41.01 (C-12), 60.50 (C-3), 116.20 (C-4a), 123.84 (C-6), 128.44 (C-17), 128.73 (C-16), 132.32 (C-18), 135.19 (C-15), 135.59 (C-5), 156.56 (C-7), 158.60 (C-2), 167.76 (C-8a), 175.66 (C-14), 194.40 (C-4). – MS: *m/z* = 335 (M^+).

$C_{20}H_{21}N_3O_2$ (335.4) Calcd. C 71.62 H 6.30 N 12.53
Found C 71.95 H 6.30 N 12.58

1-Benzoyl-2-(diethylamino)-3-methyl-4-oxo-1,8-naphthyridin-4(1H)-one (**17**): Yield 2.5 g (75%), m.p. 141°C. – IR (KBr): 1750 cm^{-1} (CO), 1616, 1590, 1545 (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 0.70 (t, 11-H, *J* = 7 Hz), 2.11 (s, 9-H), 3.07 (q, 10-H, *J* = 7 Hz), 7.24 (dd, 6-H, *J* = 8.0; 4.7 Hz), 7.25–7.71 (m, $H_{ar.}$), 8.50 (dd, 5-H, *J* = 4.7; 2 Hz), 8.67 ppm (dd, 7-H, *J* = 8; 2 Hz). – ^{13}C NMR ($CDCl_3$): δ = 10.68 (C-9), 12.27 (C-11), 46.42 (C-10), 115.39 (C-4a), 117.07 (C-3), 119.53 (C-6), 128.86 (C-14), 129.67 (C-15), 133.55 (C-13), 134.10 (C-16), 135.72 (C-5), 149.21 (C-2), 152.27 (C-7), 153.78 (C-8a), 169.87 (C-12), 179.90 (C-4). – MS: *m/z* = 335 (M^+).

$C_{20}H_{21}N_3O_2$ (335.4) Calcd. C 71.62 H 6.30 N 12.53
Found C 71.88 H 6.33 N 12.45

4-(Diethylamino)-2,3-dihydro-5-methyl-6-phenylfuro[2,3-b]pyridine (**18**): Yield 2.15 g (87%), m.p. 83–83°C. – IR (KBr): 1585, 1570 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, 10-H, *J* = 7 Hz), 2.13 (s, 8-H), 3.17 (q, 9-H, *J* = 7 Hz), 3.22 (t, 3-H, *J* = 8 Hz), 4.55 (t, 2-H, *J* = 8 Hz), 7.25–7.6 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 13.14 (C-10), 16.05 (C-8), 29.10 (C-3), 45.35 (C-9), 68.17 (C-2), 110.83 (C-3a), 120.51 (C-5), 127.30 (C-14), 127.66 (C-13), 129.34 (C-12), 141.41 (C-11), 155.98 (C-4), 156.60 (C-6), 167.34 (C-7a). – MS: *m/z* = 282 (M^+).

$C_{18}H_{22}N_2O$ (282.4) Calcd. C 76.56 H 7.86 N 9.92
Found C 76.69 H 7.84 N 10.02

1-Benzyl-4-(diethylamino)-2,3,5-trimethyl-6-phenylpyrrolo[2,3-b]pyridine (**19**): Yield 0.40 g (10%), m.p. 144–146°C. – IR (KBr): 1585, 1540 cm^{-1} (C=C, C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.08 (t, 10-H, *J* = 7 Hz), 2.19 (s, 21-H), 2.23 (s, 8-H), 2.35 (s, 15-H), 3.28 (q, 9-H, *J* = 7 Hz), 5.45 (s, 15-H), 7.2–7.8 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 10.42 (C-21), 10.88 (C-20), 14.37 (C-10), 17.32 (C-8), 44.90 (C-15), 47.68 (C-9), 104.52 (C-3a), 117.69 (C-5), 120.96 (C-3), 126.90 (C-19), 127.00 (C-14,17), 127.79 (C-13), 128.47 (C-18), 129.80 (C-12), 132.48 (C-2), 139.25 (C-11), 143.00 (C-16), 148.28 (C-4), 150.09 (C-6), 152.94 (C-7a). – MS: *m/z* = 397 (M^+).

$C_{27}H_{31}N_3$ (397.6) Calcd. C 81.57 H 7.86 N 10.57
Found C 81.39 H 7.85 N 10.50

4-(Diethylamino)-5-methyl-3,6-diphenylisoxazolo[5,4-b]pyridine (**20**) *and 4-(Diethylamino)-5-methyl-2,6-diphenyloxazolo[5,4-b]-pyridine* (**21**): To 0.50 g (1.5 mmol) of **10** or **12** in 50 ml of dry ether 0.19 g (1.7 mmol) of *N,N*-diethyl-1-propynylamine is added. While the oxazinones are slowly solved, stirring is continued for 1 h at the temp. listed in Table 1. Then, the solvent is removed *in vacuo*, and the residue is recrystallized several times from ethanol.

20: 0.21 g, m.p. 147°C. – IR (KBr): 1590 cm^{-1} (C=C, C=N). – ^1H NMR ($CDCl_3$): δ = 1.02 (t, 17-H, *J* = 6 Hz), 2.22 (s, 18-H), 3.04 (q, 16-H, *J* = 6 Hz), 7.4–7.8 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 13.69 (C-17), 18.93 (C-18), 47.09 (C-16), 106.20 (C-3a), 121.54 (C-5), 128.18, 128.40 (C-10, C-14)*, 128.66, 129.76 (C-11, C-15)*, 128.99, 129.54 (C-9, C-13)*, 129.15, 130.35 (C-8, C-12)*, 140.67 (C-4), 154.88 (C-3), 158.34 (C-6), 162.68 (C-7a). – MS: *m/z* = 357 (M^+).

$C_{23}H_{23}N_3O$ (357.5) Calcd. C 77.28 H 6.49 N 11.76
Found C 77.66 H 6.62 N 11.80

21: 0.58 g (95%), m.p. 99°C. – IR (KBr): 1615, 1575 cm^{-1} (C=C, C=N). – ^1H NMR ($CDCl_3$): δ = 1.20 (t, 17-H, *J* = 6 Hz), 2.33 (s, 18-H), 3.66 (q, 16-H, *J* = 6 Hz), 7.38–8.42 (m, $H_{ar.}$). – ^{13}C NMR ($CDCl_3$): δ = 13.56 (C-17), 18.03 (C-18), 46.56 (C-16), 122.06 (C-3a), 126.85 (C-5), 127.43 (C-10), 127.92 (C-14), 128.05 (C-11, C-15), 128.86 (C-9), 129.63 (C-13), 131.32 (C-8), 141.32 (C-12), 150.00 (C-2), 155.62 (C-4), 159.02 (C-6), 159.57 (C-7a). – MS: *m/z* = 357 (M^+).

$C_{23}H_{23}N_3O$ (357.5) Calcd. C 77.28 H 6.49 N 11.76
Found C 77.36 H 6.75 N 11.58

CAS Registry Numbers

1a: 79750-94-0 / **1b**: 73696-35-2 / **2a**: 79750-97-3 / **2b**: 79750-96-2 / **3**: 108561-19-9 / **4**: 23411-09-8 / **5a**: 29108-09-6 / **5b**: 108561-20-2 / **6**: 108561-21-3 / **7a**: 108561-22-4 / **7b**: 108561-23-5 / **8**: 108561-24-6 / **9a**: 29278-09-9 / **9b**: 108561-25-7 / **10**: 108561-26-8 / **11a**: 36231-81-9 / **11b**: 53589-28-9 / **12**: 108561-27-9 / **13a**: 108561-28-0 / **13b**: 108561-29-1 / **14a**: 108561-30-4 / **14b**: 108561-31-5 / **15a**: 108561-32-6 / **15b**: 108561-33-7 / **16**: 108561-34-8 / **17**: 108561-39-3 / **18**: 108561-35-9 / **19**: 108561-36-0 / **20**: 108561-37-1 / **21**: 108561-38-2 / *N,N*-diethyl-1-propynylamine: 4231-35-0

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