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Synthesis of pyrrolo[1,2-*a*]naphthyridines by Lewis acid mediated cycloisomerization

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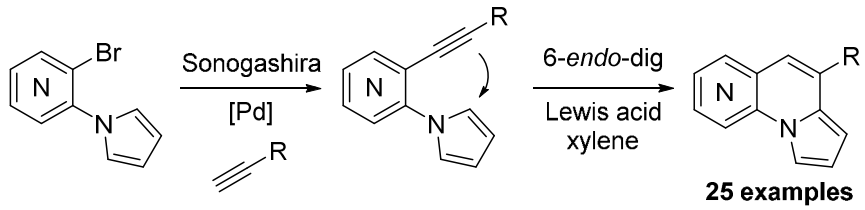
Abstract: Pyrrolo[1,2-*a*]naphthyridines were synthesized from 3-alkynyl-2-([1*H*]-pyrrol-1-yl)pyridines and 3-alkynyl-4-([1*H*]-pyrrol-1-yl)pyridines by cycloisomerization. The reactions are performed by application of the Lewis acids $PtCl_2$ or $Bi(OTf)_3$ without the need of further additives. With the described methods a number of derivatives containing a variety of functional groups have been synthesized in up to 78% yield.

Graphical abstract:



Keywords: pyrrolonaphthyridine, naphthyridine, indolizine, nitrogen heterocycle, annulation, cycloisomerization, Lewis acid, Sonogashira reaction

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Introduction

Nitrogen heterocycles are found in many natural products and exhibit not only biological activity, but also interesting properties in the field of material science. For instance, naphthyridines are fused heterocycles which belong to the group of diazanaphthalines and contain one nitrogen atom in each aromatic ring (Figure 1). Their derivatives show antibacterial, antitumor, antiviral and analgesic activity as well as anticancer potential.[1] Furthermore, naphthyridines have been applied as ligands in transition metal complexes[2], they have been investigated for their corrosion inhibition[3] and they were used as fluorescent dyes[4]. Likewise, indolizines, which consist of a fused pyrrole and pyridine system, have been proven to be interesting core structures. They have been examined for their vast biological activity[5] and, more recently, because of their fluorescence properties[6].

The synthesis of functionalized, annulated heterocycles can be achieved through intramolecular or intermolecular cyclization of dienyl alkynes. Accordingly, arylations have been realized under transition-metal catalysis or by employing acids.[7] The group of Fürstner reported the synthesis of phenanthrenes by 6-*endo*-dig cyclization of *ortho*-alkynylated biphenyls in the presence of catalytic amounts of transition metals. Later, the same group extended their substrates to *ortho*-alkynylated *N*-pyrrolylbenzenes and other heteroarenes.[8] Moreover, Fürstner utilized his strategy repeatedly for the synthesis of natural products.[9] Grätzel, on the other hand, introduced in 2013 the synthesis of ullazines applying $InCl_3$ as a Lewis acid and performing a twofold cyclization on 1-(2,6-bisalkynylphenyl)-[1*H*]pyrroles.[10] Recently, Das *et al.* developed a photocatalyzed method for the synthesis of pyrrolo[1,2-*a*]quinolines and ullazines. Therein, the formation of 6-phenylpyrrolo[1,2-*a*]-[1,8]naphthyridine and 6-(*para*-tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine has been described in the presence of the organic dye rhodamine 6G under visible light irradiation.[11] Recent approaches for the synthesis of pyrrolo[1,2-*a*]naphthyridines are summarized in Figure 1. These strategies often require complex starting materials, harsh reaction conditions or ineconomic catalyst systems.[12]

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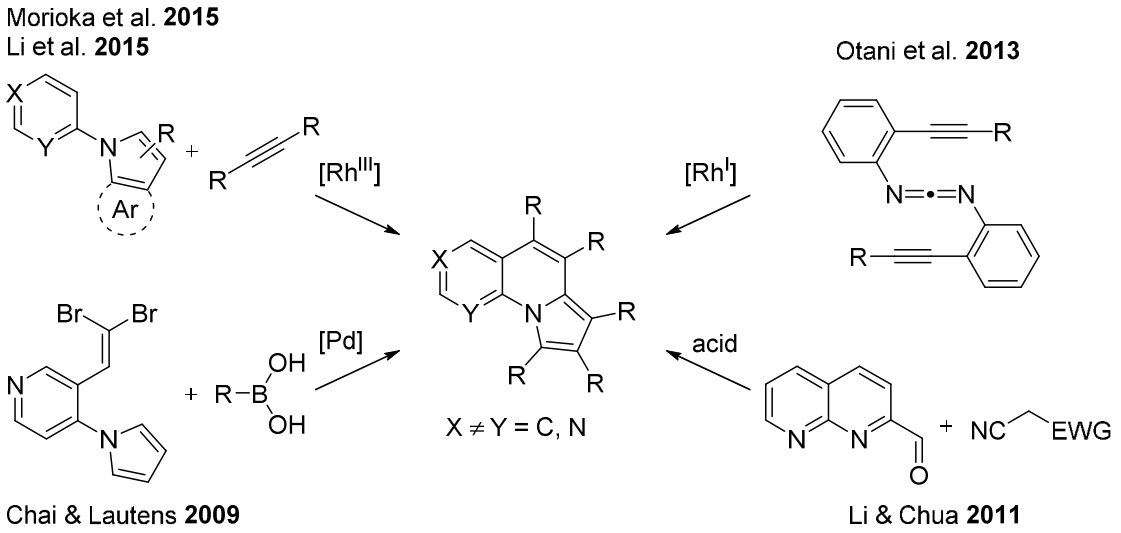
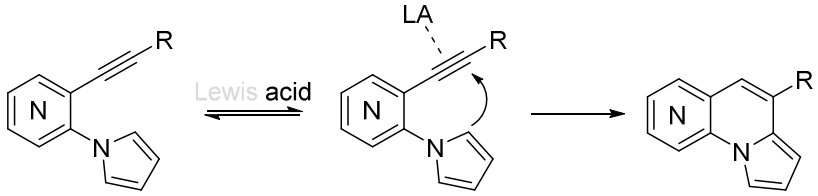


Figure 1. Overview of recently published results synthesizing pyrrolo[1,2-*a*]naphthyridines

Based on the importance of fused heterocycles, we herein report the synthesis of [1,6]- and [1,8]naphthyridine derivatives by Lewis acid-mediated cycloisomerization of *ortho*-alkynyl-*N*-pyrrolylpyridines (Scheme 1). This methodology is highly efficient, versatile and operationally simple and allows the introduction of various functional groups without the need of specific ligands, metal catalysts or other additives.



Scheme 1. Strategy for the synthesis of pyrrolo[1,2-*a*]naphthyridines

Results & discussion

The starting material **1a** was prepared by Clauson-Kaas reaction[13] of 2-amino-3-bromopyridine (Scheme 2). Subsequently, the Sonogashira coupling[14] of **1a** with phenyl acetylene was thoroughly optimized under both standard Sonogashira conditions[14] as well as by using different catalyst/ligand-systems and different solvents (Table 1). Under the best

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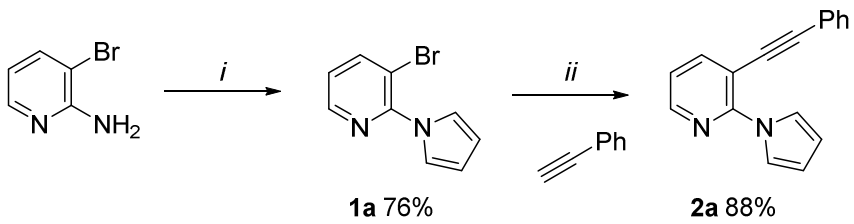
conditions, the use of $PdCl_2(PPh_3)_2$ (0.03 eq.) as catalyst and triethylamine (3 eq.) as the base in acetonitrile at 50 °C (16 h), allowed the preparation of the desired product **2a** in 88% yield. Especially the solvent proved to be of great importance in this coupling reaction.



Scheme 2. Synthesis of **1a** and **2a**; reagents and conditions: *(i)* 2,5-dimethoxytetrahydrofuran (1.05 eq.), H_2O/HOAc (2:1), DCE, 80 °C, 12 h; *(ii)* $PdCl_2(PPh_3)_2$ (0.03 eq.), CuI (0.02 eq.), Et_3N (3 eq.), MeCN, 50 °C, 16 h.

Table 1. Optimization of Sonogashira reaction of 2-bromo([1*H*]-pyrrol-1-yl)pyridine (**1a**)[a]

entry	catalyst (0.03 eq.)	ligand (0.06 eq.)	base	eq.	solvent	temp. [°C]	time [h]	yield [%][c]
1	$PdCl_2(PPh_3)_2$	–	NEt_3	3	DMF	100	24	20
2	$PdCl_2(PPh_3)_2$	P(*t*Bu)$_3$	NEt_3	3	DMF	100	24	–
3	$PdCl_2(PPh_3)_2$	–	–	–	Et_2NH	r.t.	48	63
4	$PdCl_2(PPh_3)_2$	–	–	–	NEt_3	r.t.	48	–
5[b]	$PdCl_2(PPh_3)_2$	–	NEt_3	3	DMF	80	3	–[d]
6	$Pd(OAc)_2$	PCy_3	NEt_3	1.5	THF	50	48	–
7	$Pd(OAc)_2$	XPhos	NEt_3	1.5	THF	50	48	–[d]
8	$PdCl_2(PPh_3)_2$	–	NEt_3	3	dioxane	50	4	45
9	$P(PPh_3)_4$	–	NEt_3	3	dioxane	50	4	–
10	$PdCl_2(PPh_3)_2$	–	NEt_3	3	MeCN	50	16	88
11	$Pd(OAc)_2$	CataCXium A	NEt_3	3	MeCN	50	16	92

[a] Reaction conditions: **1a** (0.5 mmol, 111.5 mg) and phenyl acetylene (1.5 eq., 0.75 mmol, 82 µl) react with CuI (0.02 eq., 0.01 mmol, 1.9 mg) in 2 ml of solvent in a glass tube under argon. [b] Reaction with phenyl acetylene (3 eq.). [c] Isolated yields. [d] Occurrence of inseparable mixtures.

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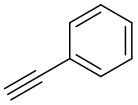
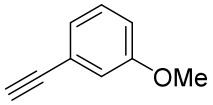
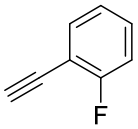
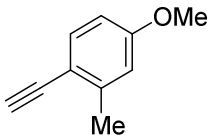
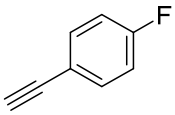
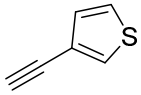
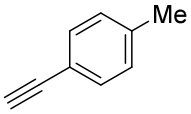
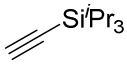
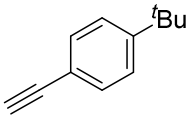
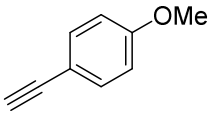
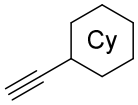
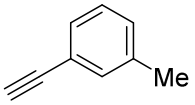
In the following, the optimized conditions for the Sonogashira coupling were applied to the synthesis of **2a-m** (Table 2). All products were obtained in good to very good yields. With regard to the aryl-substituted alkynes, both electron withdrawing and donating functional groups were successfully employed. Alkynes with aliphatic substituents were also successfully employed.

Table 2. Synthesis of starting material **2-m**

product	alkyne	yield [%][a]	product	alkyne	yield [%][a]
2a		88	**2h**		98
2b		81	**2i**		98
2c		86	**2j**		94
2d		78	**2k**		94
2e		98	**2l**		87
2f		89	**2m**		86
2g		95			

[a] Isolated yield.

The cyclization was studied next. In an initial attempt, 3-phenylethynyl-2-([1*H*]-pyrrol-1-yl) pyridine **2a** was cyclized in the presence of $InCl_3$ (1.5 eq.) under argon in toluene at 80 °C for 24 h (entry 1 in Table 3) to give the desired [1,8]naphthyridine **3a**, albeit, in only 13% yield. The same conditions were previously employed by Grätzel and gave ullazines in an overall yield of 55%.[10] To improve the reaction conditions different Lewis acids[8a, 15] (entries 1 to 6 in Table 3) and Brønsted acids[16] (entries 7 to 12 in Table 3) were employed. In addition, the reaction time was prolonged. The use of $PtCl_2$ (entry 5 & 6 in Table 3) proved to be the most

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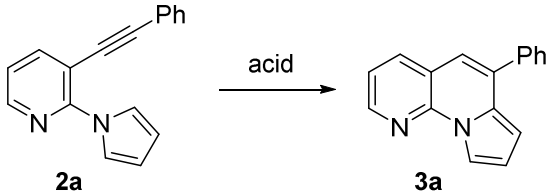
efficient catalyst and **3a** could be isolated in up to 50% when the temperature was increased to 120 °C using xylene as the solvent.

Table 3. Synthesis of 6-phenylpyrrolo[1,2-*a*][1,8]naphthyridine (**2a**)[a]



2a **3a**

entry	acid	eq.	solvent	temp. [°C]	time [h]	yield [%][b]
1	$InCl_3$	1.5	toluene	80	24	13
2	$Cu(OTf)_2$	1.5	toluene	80	24	–
3	$In(OTf)_3$	1.5	toluene	80	20	20
4	$Bi(OTf)_3$	1.5	toluene	80	20	28
5	$PtCl_2$	0.05	toluene	80	12	33
6	$PtCl_2$	0.05	xylene	120	24	50
7	Tf_2NH	0.1	DCM	−20	2	–
8	TFA	18	DCM	r.t.	24	–
9	TFA	6.5	DCE	90	24	15
10	*p*TSA	14	DCE	80	12	28
11	*p*TSA	65	xylene	120	24	28
12	*p*TSA	65	xylene	140	24	18

[a] Reaction conditions: **2a** (0.205 mmol) with acid under argon in 2 ml solvent. [b] Isolated yield.

With these optimized conditions in hand, the scope of the reaction was examined by employment of various substituted alkynes. Both electron poor and electron rich arylalkynes were tested as well as alkyl-substituted alkyne moieties (Table 4). Products **3a-m** were obtained in 40–66% yield. Disparity in yields for the cyclized products can be explained due to varying capability of substituents to stabilize cationic transition states of Lewis acid-adduct-complexes.[7, 8] Therefore, the cyclization afforded generally higher yields for arylalkynes in comparison to alkylalkynes. With regard to the aromatic substituents of **3a-i**, both electron poor and electron rich systems gave equally good results. Slightly deviating results may appear because of the poor solubility and consequently difficulties during purification of some products. Product **3j**, containing a thiophene moiety, was also prepared (41% yield). The synthesis of **3k**, containing a triisopropylsilyl protecting group, failed probably due to steric hindrance. The alkyl substituted derivatives **3l** and **3m** were successfully prepared in 37% and 62% yields, respectively.

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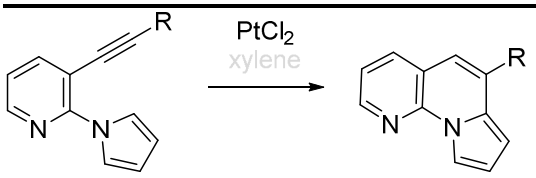
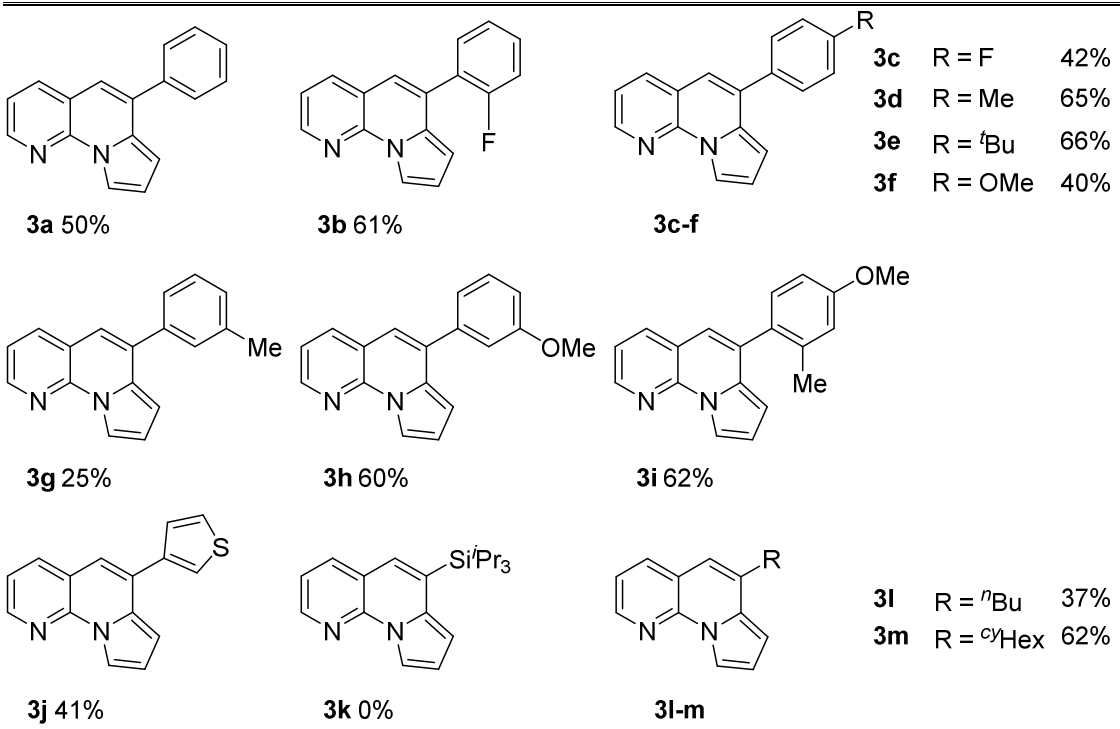
Table 4. Cyclization of 3-alkynyl-2-([1*H*]-pyrrol-1-yl)pyridines[a]



2a-m **3a-m**



3a 50% **3b** 61% **3c-f**

3c	R = F	42%
3d	R = Me	65%
3e	R = ^{t}Bu	66%
3f	R = OMe	40%

3g 25% **3h** 60% **3i** 62%

3j 41% **3k** 0% **3l-m**

3l	R = ^{n}Bu	37%
3m	R = ^{cy}Hex	62%

[a] Reaction conditions: **3a-m** (0.6 mmol) and $PtCl_2$ (0.03 mmol) under argon in xylene (2 ml) at 120 °C for 24 h.

The synthesis of [1,6]naphthyridines was studied next. The reaction of 4-amino-3-bromopyridine with 2,5-dimethoxytetrahydrofuran afforded 3-bromo-4-([1*H*]-pyrrol-1-yl)pyridine **1c** (Scheme 3). The conditions of the Sonogashira coupling of **1c** with phenyl acetylene were thoroughly optimized (Table 5). The best yield of the desired product **4a** (81%) was obtained using 1.5 eq. of the acetylene, $Pd(MeCN)_2Cl_2$ (0.05 eq.) as the catalyst, XPhos (0.1 eq.) as ligand, CuI (0.05 eq.) as co-catalyst and triethylamine (3 eq.) as base in dioxane under inert atmosphere at room temperature for 24 h (entry 7 in Table 5).

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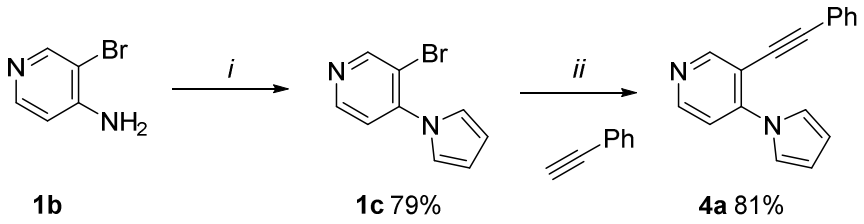

1b **1c** 79% **4a** 81%

Scheme 3. Synthesis of **1c** and **4a**; reagents and conditions: *(i)* 2,5-dimethoxytetrahydrofuran (2.5 eq.), HOAc, 120 °C, 1 h; *(ii)* $Pd(MeCN)_2Cl_2$ (0.05 eq.), CuI (0.05 eq.), XPhos (0.1 eq.), Et_3N (3 eq.), dioxane, r.t., 24 h.

Table 5. Optimization of Sonogashira reaction of 2-bromo([1*H*]-pyrrol-1-yl)pyridine (**1c**)[a]

entry	catalyst (0.05 eq.)	ligand (0.1 eq.)	base	eq.	solvent	temp. [°C]	yield [%][b]
1	$Pd(PPh_3)_2Cl_2$	–	Et_3N	3	DMF	140	59
2	$Pd(PPh_3)_2Cl_2$	–	Et_3N	3	dioxane	50	56
3	$Pd(PPh_3)_2Cl_2$	$P(tBu)_3 \cdot HBF_4$	Et_3N	3	dioxane	50	65
4	$Pd(PPh_3)_2Cl_2$	$P(tBu)_3 \cdot HBF_4$	$HNiPr_2$	3	dioxane	50	65
5	$Pd(MeCN)_2Cl_2$	$P(tBu)_3 \cdot HBF_4$	Et_3N	3	dioxane	50	69
6	$Pd(MeCN)_2Cl_2$	XPhos	Et_3N	3	dioxane	50	73
7	$Pd(MeCN)_2Cl_2$	XPhos	Et_3N	3	dioxane	r.t.	81

[a] Reaction conditions: **1a** (0.45 mmol, 100 mg) and phenyl acetylene (1.5 eq., 0.68 mmol, 73 µl) react with CuI (0.05 eq., 0.01 mmol, 4.3 mg) in 2 ml of solvent in a glass tube under argon for 24 h. [b] Isolated yields.

Subsequently, products **4a-n** were prepared under the optimized conditions (Table 6). Different aromatic alkynes bearing electron donating substituents gave the corresponding products in good to very good yields. Moderate yields were observed for the strongly electron withdrawing trifluoromethyl group of **4e** (55%) and the aliphatic moieties of **4m** (56%) and **4n** (56%).

Table 6. Synthesis of starting material **4a-n**

product	alkyne	yield [%][a]	product	alkyne	yield [%][a]

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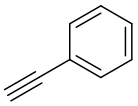
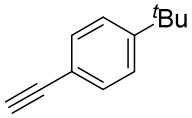
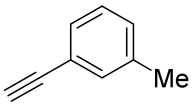
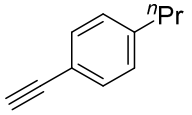
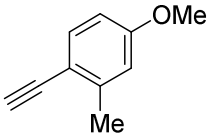
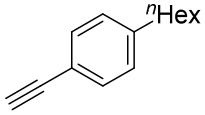
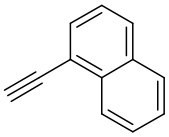
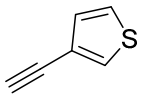
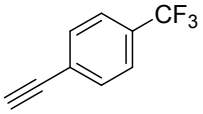
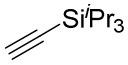
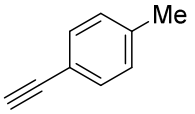
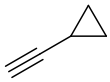
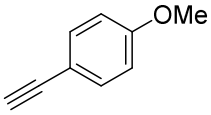
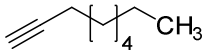
4a		81	**4h**		98
4b		88	**4i**		86
4c		91	**4j**		83
4d		99	**4k**		76
4e		55	**4l**		78
4f		88	**4m**		56
4g		95	**4n**		56

[a] Isolated yield.

Subsequently, the synthesis of [1,6]naphthyridines by cyclization was studied. The conditions were optimized for derivate **4a** (Table 7). The first test reaction using $In(OTf)_3$ (1 eq.) in toluene at 100 °C (24 h) afforded the desired cyclized product **5a**, albeit, in only 20% yield. The yield was improved by employing $Bi(OTf)_3$. An increase of the temperature to 120 °C and the use of xylene as solvent resulted in the formation of **5a** in 55% yield (entry 10 in Table 7). The application of the Brønsted acids trifluoroacetic acid (TFA) or *para*-toluenesulfonic acid (*p*TSA) (entry 11 & 12 in Table 7) yielded the desired product only in trace amounts.

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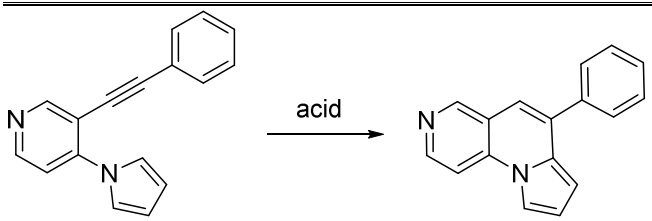
Table 7. Synthesis of 6-phenylpyrrolo[1,2-*a*][1,6]naphthyridine (**5a**)[a]



4a **5a**

entry	acid	eq.	solvent	temp. [°C]	yield [%][b]
1	$In(OTf)_3$	1	toluene	100	20
2	$Zn(OTf)_2$	1	toluene	100	22
3	$AuCl_3$	1	toluene	100	8
4	Ag(OAc)	1	toluene	100	15
5	$PtCl_2$	1	toluene	100	–
6	$Bi(OTf)_3$	0.5	toluene	100	7
7	$Bi(OTf)_3$	1	toluene	100	50
8	$Bi(OTf)_3$	2	toluene	100	30
9	$Bi(OTf)_3$	1	toluene	110	55
10	$Bi(OTf)_3$	1	xylene	120	55
11	TFA	20	toluene	100	traces
12	*p*TSA	25	toluene	100	mixtures

[a] Reaction conditions: **4a** (0.41 mmol) with acid in 3 ml solvent for 24 h. [b] Isolated yield.

The scope of the reaction was studied next. The cyclization of **4a–n** afforded the desired products **5a–n** in 25–78% yield (Table 8). With regards to the aromatic alkynes, electron donating substituents gave higher yields than electron withdrawing groups, due to a better stabilization of cationic transition states. Therefore, products **5a–d** and **5f–k** were obtained in moderate to good yields. The presence of the electron withdrawing trifluoromethyl group in **5e** resulted in only 25% yield, possibly caused by the less stabilizing effect of electron acceptors during charged transition states.[8] Furthermore, aliphatic alkynes gave the cyclized products **5m** and **5n** only in traces, while the sterically demanding triisopropylsilyl fragment **5l** could not be synthesized, again. Overall, the latter 3-alkynyl-4-pyrrolopyrodines appear to be less active for this type of cycloisomerization requiring electron rich substituents at the alkyne moiety. Hence, it can be considered that the pyridine moiety and specifically the position of the *N*-atom can similarly promote the reaction.

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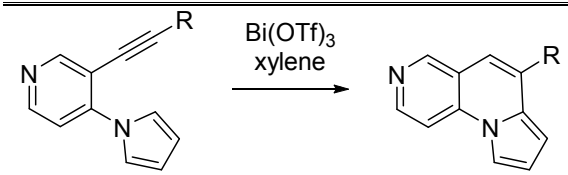
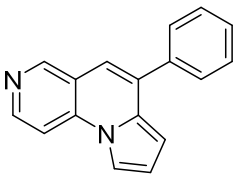
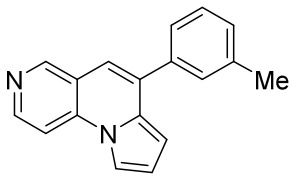
Table 8. Cyclization of 3-alykynl-4-([1*H*]-pyrrol-1-yl)pyridines[a]



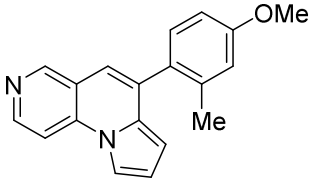
4a-n **5a-n**



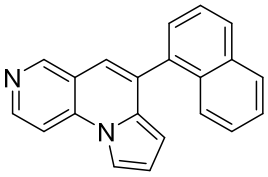
5a 55%



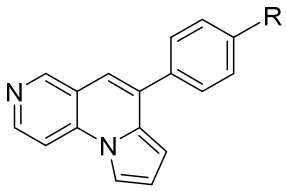
5b 51%



5c 73%

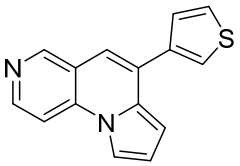


5d 51%

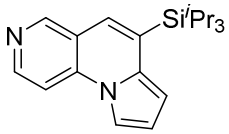


5e-j

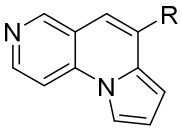
5e	R = CF_3	25%
5f	R = Me	50%
5g	R = OMe	78%
5h	R = ^{t}Bu	41%
5i	R = ^{n}Pr	53%
5j	R = ^{n}Hex	45%



5k 72%



5l 0%



5m	R = ^{cy}Pr	traces
5n	R = ^{n}Oct	traces

[a] Reaction conditions: **3a-o** (0.4–0.7 mmol) and $Bi(OTf)_3$ (1 eq.) under argon in xylene (2 ml) at 120 °C for 24 h.

Conclusion

To conclude, we prepared a variety of pyrrolo[1,2-*a*][1,8]naphthyridines and pyrrolo[1,2-*a*][1,6]naphthyridines. The reactivity of alkynes **4** was lower than the reactivity of **2**. Therefore, the yields of [1,6]naphthyridines were, in most cases, lower than the yields of the isomeric [1,8]naphthyridines. Our strategy required no special catalyst/ligand-systems and was realized by the application of $PtCl_2$ and $Bi(OTf)_3$ as simple Lewis acids.

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Experimental Section

General

For NMR spectra the substrates were dissolved in $CDCl_3$, DMSO-d_6 or C_6D_6 and the spectra recorded on a Bruker AVANCE 300 III, 250 II or 500. The IR spectra were measured as ATR experiments with a Nicolet 6700 FT-IR spectrometer and a Nicolet 550 FT-IR spectrometer. MS and HRMS were measured by an Agilent 6890 N/5973 GC-MS and an Agilent 1200/6210 Time-of-Flight LC-MS. Melting points were determined by a Micro-Hot-Stage GalenTM III Cambridge Instruments.

Synthesis of starting materials

3-Bromo-2-([1*H*]-pyrrol-1-yl)pyridine[11] **1a.** To a solution of 2-amino-3-bromopyridine (5.8 mmol, 1.0 g) in 1.5 ml DCE at 80 °C 2,5-dimethoxytetrahydrofuran (1.05 eq., 6.1 mmol, 0.79 ml) was added. A mixture of H_2O/HOAc (2:1, 2 ml) was poured into the solution. The reaction was stirred at 80 °C for 12 h. Thereafter, the crude product was washed with distilled water and extracted with DCM. Following the evaporation of the organic solvent the product **1a** was obtained after column chromatography (heptane/DCM, 5:1) as a white solid (76% yield, 978.1 mg); mp 36–39 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.45 (dd, ^3J = 4.6 Hz, ^4J = 1.6 Hz, 1H, $CH_{pyridine}$), 8.03 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, $CH_{pyridine}$), 7.41–7.32 (m, 2H, $CH_{pyrrole}$), 7.11 (dd, ^3J = 7.9 Hz, ^3J = 4.6 Hz, 1H, $CH_{pyridine}$), 6.39–6.32 (m, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 150.1 ($C_{pyridine}$), 147.6, 143.7, 122.7 ($CH_{pyridine}$), 121.5 ($CH_{pyrrole}$), 112.5 ($C_{pyridine}$), 110.2 ($CH_{pyrrole}$) ppm. **MS (EI, 70 eV):** *m/z* (%) = 224 ($[C_9H_7{}^{81}BrN_2]^+$, 98), 222 ($[C_9H_7{}^{79}BrN_2]^+$, 100), 198 (16), 197 (42), 196 (17), 195 (41), 158 (12), 156 (12), 143 (20), 142 (18), 117 (12), 116 (60), 89 (20), 78 (12), 76 (25), 63 (12), 51 (18), 50 (17), 39 (18). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_9H_7{}^{79}BrN_2$ ($[M+H]^+$) 222.98654, found 222.98668. Calcd. for $C_9H_7{}^{81}BrN_2$ ($[M+H]^+$) 224.98453, found 224.98458.

4-Amino-3-bromopyridine 1b. *N*-Bromosuccinimide (1.1 eq., 29.2 mmol, 5.2 g) was added slowly to a stirred solution of 4-aminopyridine (26.6 mmol, 2.5 g) in 140 ml acetonitrile. The mixture was stirred for 48 h at room temperature. Afterwards the solvent was removed under reduced pressure and the product was purified by column chromatography (heptane/ethyl acetate, 2:1 → 1:2) to yield 4-amino-3-bromopyridine **1b** as a white solid (86% yield, 3.95 g). **^{1}H NMR (300 MHz, DMSO):** δ = 11.11 (bs, 2H, NH_2), 8.23 (s, 1H, $CH_{pyridine}$), 7.96 (d,

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^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 6.68 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$) ppm. **^{13}C NMR (75 MHz, DMSO):** δ = 151.4 (C-NH_2), 150.8, 148.2, 109.9 (CH_{Ar}), 105.5 (C-Br) ppm. **IR (ATR):** $\tilde{\nu}$ = 3440 (w), 3342 (w), 3217 (w), 2946 (w), 2545 (br, w), 1700 (s), 1632 (s), 1501 (m), 1199 (s), 1074 (w), 1014 (m), 815 (s), 633 (s), 562 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 174 ($[C_9H_7{}^{81}BrN_2]^+$, 100), 172 ($[C_9H_7{}^{79}BrN_2]^+$, 99), 145 (2), 119 (8), 117 (6), 93 (53). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_5H_5N_2{}^{79}Br$ (M^+) 171.96306, found 171.96313; calcd. for $C_5H_5N_2{}^{81}Br$ (M^+) 173.96102, found 173.96131.

3-Bromo-4-([1*H*]-pyrrol-1-yl)pyridine 1c. 2,5-dimethoxytetrahydrofuran (2.5 eq., 28.9 mmol, 3.75 ml) was added to a stirred solution of **1b** (17.3 mmol, 3.0 g) in 12 ml HOAc. The mixture was then refluxed (120 °C) for 1 h. Afterwards, the reaction mixture was diluted with DCM and washed with distilled water and $NaHCO_3$ solution subsequently. The aqueous phase was extracted with DCM. The organic fractions were combined and the solvent removed under vacuum. Finally, the crude product was purified from reagent residues through column chromatography (heptane/ethyl acetate, 4:1) to obtain **1c** as a white solid (79% yield, 2.03 g). **^{1}H NMR (300 MHz, DMSO-*d*$_6$):** δ = 8.87 (s, 1H, $CH_{pyridine}$), 8.60 (d, ^3J = 5.2 Hz, 1H, $CH_{pyridine}$), 7.48 (d, ^3J = 5.2 Hz, 1H, $CH_{pyridine}$), 7.19 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.33 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, DMSO-*d*$_6$):** δ = 153.4, 149.8 ($CH_{pyridine}$), 145.7 ($Cq_{pyridine}$), 121.8 ($CH_{pyridine}$), 121.6 ($CH_{pyrrole}$), 114.5 (C-Br), 110.5 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3118 (br, w), 1737 (w), 1574 (s), 1497 (s), 1339 (s), 1180 (w), 1069 (s), 1017 (s), 834 (s), 726 (s), 667 (s), 619 (s), 570 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 222 ($[M]^+$, 100), 196 (7), 183 (3), 156 (4), 143 (27), 142 (18), 116 (67). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_9H_7N_2{}^{79}Br$ (M^+) 221.97871, found 221.97828. Calcd. for $C_9H_7N_2{}^{81}Br$ (M^+) 223.97667, found 223.97663.

General procedure for Sonogashira reaction to synthesize 3-alykynl-2-([1*H*]-pyrrol-1-yl)pyridines 2.

1a was dissolved in 3 ml MeCN under an argon atmosphere. After the addition of $PdCl_2(PPh_3)_2$ (0.03 eq.), CuI (0.02 eq.) and Et_3N (3 eq.) in advance of the corresponding acetylene (1.2 eq.) the reaction is stirred at 50 °C for 24 h. The reaction mixture was subsequently cooled to room temperature and washed with distilled water and extracted with DCM. The organic layers were collected and the solvent evaporated. The crude product was thereafter purified by column chromatography (heptane/DCM, 5:1) to give the alkynylated

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products **2a-m**. Thereby, 1–2 ml Et_3N were added to 250 ml eluent mixture to deactivate the acidic silica.

3-(Phenylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2a. The reaction of **1a** (0.9 mmol, 200 mg) with phenylacetylene (1.08 mmol, 118.3 µl) gave **2a** as a pale brown solid (382 mg, 88%); mp 82–84 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.43 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.96 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.85–7.80 (m, 2H, $CH_{pyrrole}$), 7.57–7.50 (m, 2H, CH_{Ph}), 7.42–7.34 (m, 3H, CH_{Ph}), 7.16 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.39–6.35 (m, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 151.3 ($C_{pyridine}$), 147.9, 143.4 ($CH_{pyridine}$), 131.6, 129.1, 128.6 (CH_{Ph}), 122.6 (C_{Ph}), 120.8 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 110.5 ($CH_{pyrrole}$), 110.4 ($C_{pyridine}$), 96.1, 85.7 (C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3052 (w), 1562 (w), 1469 (w), 1437 (m), 1336 (w), 1060 (w), 800 (w), 728 (m), 687 (m), 624 (w), 553 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 244 ($[M]^+$, 100), 243 (77), 242 (43), 241 (5), 218 (11), 216 (8), 215 (5), 214 (6), 190 (6), 189 (5), 177 (6), 151 (6), 150 (9), 121 (11), 109 (6), 77 (5), 75 (5), 51 (5), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{12}N_2$ (M^+) 244.09950, found 244.09919.

3-((2-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2b. 2-ethynyl-1-fluorobenzene (0.6 mmol, 78 µl) reacted with **1a** (0.5 mmol, 111.5 mg) to **2b** as a pale brown oil (106 mg, 81%); R_f 0.39 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.44 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.97 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.88–7.83 (m, 2H, $CH_{pyrrole}$), 7.50 (ddd, ^3J = 7.7 Hz, ^3J = 7.1 Hz, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.39–7.33 (m, 1H, CH_{Ar}), 7.15 (dd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 7.21–7.11 (m, 2H, CH_{Ar}), 6.40–6.35 (m, 2H, $CH_{pyrrole}$) ppm. **^{19}F NMR (235 MHz, $CDCl_3$):** δ = −109.1 ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 162.92 (d, $^1J_{C,F}$ = 252.7 Hz, C-F), 151.2 ($C_{pyridine}$), 148.4, 143.6 ($CH_{pyridine}$), 133.32 (d, $^4J_{C,F}$ = 1.3 Hz, CH_{Ar}), 130.87 (d, $^3J_{C,F}$ = 8.0 Hz, CH_{Ar}), 124.24 (d, $^3J_{C,F}$ = 3.7 Hz, CH_{Ar}), 120.7 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 115.80 (d, $^2J_{C,F}$ = 20.6 Hz, CH_{Ar}), 111.31 (d, $^2J_{C,F}$ = 15.6 Hz, C_{Ar}), 110.5 ($CH_{pyrrole}$), 110.2 ($C_{pyridine}$), 90.54 (d, $^3J_{C,F}$ = 3.2 Hz, C_{alkyne}), 89.6 (C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3065 (br, w), 2921 (w), 1708 (br, w), 1560 (m), 1472 (m), 1434 (m), 1224 (m), 1095 (m), 1058 (m), 797 (m), 754 (s), 728 (s), 544 (m), 470 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 262 ($[M]^+$, 100), 261 (61), 260 (33), 243 (6), 242 (8), 236 (10), 234 (5), 168 (5), 130 (5), 118 (5). **HRMS (ESI-TOF):** *m/z* = calculated for $C_{17}H_{11}FN_2$ ($[M+H]^+$) 263.09790, found 263.09786.

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3-((4-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2c. 1a (0.5 mmol, 111.5 mg) and 4-ethynyl-1-fluorobenzene (0.6 mmol, 68.8 µl) achieved **2c** as a yellow solid (113 mg, 86%); mp 78–82 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.43 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.93 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.83–7.72 (m, 2H, $CH_{pyrrole}$), 7.56–7.46 (m, 2H, CH_{Ar}), 7.15 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyrrole}$), 7.12–7.02 (m, 2H, CH_{Ar}), 6.38 (dt, ^3J = 3.8 Hz, ^4J = 2.3 Hz, 2H, $CH_{pyrrole}$) ppm. **^{19}F NMR (235 MHz, $CDCl_3$):** δ = −109.4 ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 162.98 (d, $^1J_{C,F}$ = 250.9 Hz, C-F), 151.3 ($C_{pyridine}$), 148.0, 143.1 ($CH_{pyridine}$), 133.50 (d, $^3J_{C,F}$ = 8.5 Hz, CH_{Ar}), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 118.67 (d, $^4J_{C,F}$ = 3.5 Hz, C_{Ar}), 115.97 (d, $^2J_{C,F}$ = 22.2 Hz, CH_{Ar}), 110.4 ($CH_{pyrrole}$), 110.1 ($C_{pyridine}$), 94.9 (C_{alkyne}), 85.40 (d, $^5J_{C,F}$ = 1.6 Hz, C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3049 (w), 1600 (w), 1562 (w), 1505 (w), 1472 (w), 1439 (w), 1216 (w), 1056 (w), 833 (w), 806 (w), 728 (m), 640 (w), 620 (w), 532 (w), 522 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 262 ([M]+, 100), 261 (75), 260 (39), 236 (12), 234 (7), 232 (5), 208 (5), 195 (5), 169 (5), 168 (7), 130 (5), 118 (5), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ (M^+) 262.09008, found 262.08955.

3-((4-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2d. 4-Ethynyltoluene (0.6 mmol, 76 µl) and **1a** (0.5 mmol, 111.5 mg) gave **2d** as a yellow solid (101 mg,78%); mp 71–75 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.42 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.89–7.79 (m, 2H, $CH_{pyrrole}$), 7.43 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.18 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.14 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{pyridine}$), 6.43–6.33 (m, 2H, $CH_{pyrrole}$), 2.39 (s, 3H, Me) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 151.2 ($C_{pyridine}$), 147.7, 143.2 ($CH_{pyridine}$), 139.4 (C-Me), 131.4, 129.4 (CH_{Ar}), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 119.5 (C_{Ar}), 110.5 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 96.3, 85.1 (C_{alkyne}), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3030 (w), 2916 (w), 1703 (br, w), 1565 (w), 1474 (w), 1439 (w), 1339 (w), 1311 (w), 1099 (w), 1060 (w), 1017 (w), 818 (w), 733 (m), 529 (w) cm^{-1}.**MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (47), 256 (12), 255 (17), 243 (15), 242 (36), 232 (7), 231 (6), 128 (6), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12281.

3-((4-*tert*-Butylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2e. The reaction of **1a** (0.5 mmol, 111.5 mg) with 4-*tert*-butylphenylacetylene (0.6 mmol, 108 µl) resulted in the product **2e** as a pale brown oil (155 mg, 98%); R_f 0.45 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.42 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.86–7.79 (m, 2H, $CH_{pyrrole}$), 7.48 (d, ^3J = 8.6 Hz, 2H,

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CH_{Ar}), 7.40 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.15 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.43–6.35 (m, 2H, $CH_{pyrrole}$), 1.34 (s, 9H, CH_{3tBu}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 152.5 ($C_{pyridine}$), 147.8, 143.2 ($CH_{pyridine}$), 131.3, 125.7 (CH_{Ar}), 120.7($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 119.6 (C_{Ar}), 110.5 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.2 (C-*t*Bu), 96.3, 85.1 (C_{alkyne}), 35.0 (C_{tBu}), 31.3 (CH_{3tBu}) ppm. **IR (ATR):** $\tilde{\nu}$ = 2953 (w), 1562 (w), 1469 (w), 1437 (w), 1338 (w), 1059 (w), 926 (w), 833 (w), 724 (m), 625 (w), 561 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 300 ($[M]^+$, 67), 286 (23), 285 (100), 284 (8), 283 (8), 270 (23), 269 (18), 268 (10), 267 (5), 258 (6), 257 (27), 255 (18), 244 (13), 243 (20), 242 (21), 241 (5), 128 (26), 121 (6), 115 (6), 41 (7), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{21}H_{20}N_2$ (M^+) 300.16210, found 300.16165.

3-((4-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2f. 1a (0.25 mmol, 56 mg) and 4-ethynylanisole (0.3 mmol, 40 µl) gave **2f** as a solid (61 mg, 89%); mp 61–64 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.40 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.92 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.85–7.79 (m, 2H, $CH_{pyrrole}$), 7.48–7.45 (m, 2H, CH_{Ar}), 7.14 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.94–6.86 (m, 2H, CH_{Ar}), 6.42–6.31 (m, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 160.3 (C-OMe), 151.1 ($C_{pyridine}$), 147.6, 143.0 ($CH_{pyridine}$), 133.1 (CH_{Ar}), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 114.7 (C_{Ar}), 114.3 (CH_{Ar}), 110.7 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 96.2, 84.5 (C_{alkyne}), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 3011 (br, w), 2215 (w), 1604 (w), 1508 (m), 1435 (w), 1245 (m), 1173 (w), 1028 (w), 833 (w), 725 (m), 699 (w), 536 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M]^+$, 100), 260 (6), 259 (33), 258 (7), 242 (5), 232 (7), 231 (41), 230 (25), 229 (29), 205 (13), 203 (11), 177 (5), 176 (5), 164 (7), 137 (6), 115 (7), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11784.

3-((3-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2g. 3-ethynyltoluene (0.6 mmol, 77 µl) and **1a** (0.5 mmol, 111.5 mg) gave **2g** as a yellow oil (123 mg, 95%); R_f 0.44 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.43 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.90–7.86 (m, 2H, $CH_{pyrrole}$), 7.40–7.35 (m, 2H, CH_{Ar}), 7.29 (t, ^3J = 7.7 Hz, 1H, CH_{Ar}), 7.24–7.18 (m, 1H, CH_{Ar}), 7.14 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.45–6.41 (m, 2H, $CH_{pyrrole}$), 2.39 (s, 3H, Me) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 151.2 ($C_{pyridine}$), 147.8, 143.1 ($CH_{pyridine}$), 138.2 (C-Me), 132.0, 129.9, 128.6, 128.4 (CH_{Ar}), 122.3 (C_{Ar}), 120.6 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.2 ($C_{pyridine}$), 96.2, 85.3 (C_{alkyne}), 21.3 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2915 (w), 1705 (br, w), 1558 (w), 1474 (w), 1433 (w), 1308 (w), 1165 (w), 1057 (w), 782

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(w), 728 (w), 687 (w), 442 (w), 406 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (42), 256 (11), 255 (17), 243 (16), 242 (36), 231 (8), 128 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12289.

3-((3-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2h. Substrate **1a** (0.5 mmol, 111.5 mg) reacted with 3-ethynylanisole (0.6 mmol, 78 µl) to give **2h** as a brown oil (152 mg, 98%); R_f 0.38 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.43 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, $CH_{pyridine}$), 7.95 (dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, $CH_{pyridine}$), 7.86–7.78 (m, 2H, $CH_{pyrrole}$), 7.30 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.15 (dd, ^3J = 7.8 Hz, ^4J = 4.8 Hz, 1H, $CH_{pyridine}$), 7.15–7.11 (m, 1H, CH_{Ar}), 7.05 (dd, ^4J = 2.5 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 6.94 (ddd, ^3J = 8.4 Hz, ^4J = 2.7 Hz, ^3J = 1.1 Hz, 1H, CH_{Ar}), 6.41–6.29 (m, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 159.5 (C_{Ar}), 151.3 ($C_{pyridine}$), 148.0, 143.3 ($CH_{pyridine}$), 129.7, 124.1 (CH_{Ar}), 123.6 (C_{Ar}), 120.8 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 116.4, 115.7 (CH_{Ar}), 110.5 ($CH_{pyrrole}$), 110.3 ($C_{pyridine}$), 96.0, 85.5 (C_{alkyne}), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2936 (br, w), 2833 (w), 1710 (br, w), 1573 (m), 1475 (m), 1434 (m), 1235 (m), 1038 (m), 868 (m), 708 (m), 730 (m), 684 (m), 551 (m), 461 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) =274 ($[M]^+$, 100), 273 (23), 244 (12), 243 (17), 242 (19), 241 (7), 231 (24), 230 (18), 229 (23), 205 (8), 204 (7), 203 (10), 164 (8), 115 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11807.

3-((4-Methoxy-2-methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)-pyridine 2i. The reaction of **1a** (0.5 mmol, 111.5 mg) and 1-ethynyl-4-methoxy-2-methylbenzene (0.6 mmol, 87.7 mg) gave **2i** as a yellow oil (141 mg, 98%); R_f 0.50 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.40 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.93 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.82–7.77 (m, 2H, $CH_{pyrrole}$), 7.42 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.15 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.77 (d, ^4J = 2.6 Hz, 1H, CH_{Ar}), 6.73 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1H, CH_{Ar}), 6.38–6.31 (m, 2H, $CH_{pyrrole}$)), 3.82 (s, 3H, OMe), 2.45 (s, 3H, Me) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 160.3 (C-OMe), 151.0 ($C_{pyridine}$), 147.6, 143.2 ($CH_{pyridine}$), 142.4 (C-Me), 133.6 (CH_{Ar}), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 115.4 (CH_{Ar}), 114.7 (C_{Ar}), 111.6 (CH_{Ar}), 111.1 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 95.5, 88.0 (C_{alkyne}), 55.4 (OMe), 21.2 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2916 (br, w), 2205 (w), 1706 (br, w), 1602 (m), 1560 (m), 1472 (m), 1433 (m), 1294 (m), 1236 (s), 1036 (m), 797 (m), 727 (m), 561 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 288 ($[M]^+$, 58), 287 (100), 273 (19), 272 (17), 271 (8), 261 (8), 256 (7), 255 (10), 245 (14), 244 (21), 243 (42), 242 (18), 230 (7), 229 (8), 218 (10), 205 (9),

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151 (6), 128 (6), 122 (7), 39 (7). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{19}H_{16}N_2O$ ($[M+H]^+$) 289.13354, found 289.13364.

2-([1*H*]-pyrrol-1-yl)-3-(thiophen-3-ylethynyl)pyridine 2j. The starting material **1a** (0.5 mmol, 111.5 mg) and 1-ethynyl-4-methoxy-2-methylbenzene (0.6 mmol, 59 µl) delivered **2j** as a yellow oil (117 mg, 94%); R_f 0.48 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.42 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.92 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.87–7.81 (m, 2H, $CH_{pyrrole}$), 7.57 (dd, ^4J = 3.0 Hz, ^4J = 1.2 Hz, 1H,$CH_{thioph.}$), 7.32 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, $CH_{thioph.}$), 7.21 (dd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 1H, $CH_{thioph.}$), 7.12 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.44–6.38 (m, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 151.1 ($C_{pyridine}$), 147.8, 143.0 ($CH_{pyridine}$), 129.5, 129.4, 125.8 ($CH_{thioph.}$), 121.5 ($C_{thioph.}$), 120.6 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.0 ($C_{pyridine}$), 91.4, 85.2 (C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3107 (w), 3050 (w), 1561 (w), 1473 (w), 1438 (w), 1335 (w), 1058 (w), 1017 (w), 869 (w), 781 (w), 726 (m), 625 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$,100), 249 (62), 248 (24), 224 (11), 223 (5), 222 (6), 205 (18), 140 (5), 113 (5), 45 (5), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{10}N_2S$ ($[M+H]^+$) 251.06375, found 251.06395.

2-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 2k. The reaction of **1a** (1 mmol, 223 mg) with ethynyltriisopropylsilane (1.2 mmol, 269 µl) achieved product **2k** as a pale yellow oil (295 mg, 94%); R_f 0.60 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.40 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.90 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.88–7.85 (m, 2H, $CH_{pyrrole}$), 7.09 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{pyridine}$), 6.33–6.27 (m, 2H, $CH_{pyrrole}$), 1.16–1.09 (m, 21H, iPr$_3$) ppm. **^{29}Si INEPT NMR (60 MHz, $CDCl_3$):** δ = −1.4 ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 151.2 ($C_{pyridine}$), 148.0, 144.5 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 119.9 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.0 ($C_{pyridine}$), 102.8, 99.7 (C_{alkyne}), 18.8 ($CH_{3i\text{Pr}}$), 11.5 ($CH_{i\text{Pr}}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2942 (w), 2864 (m), 2153 (w), 1720 (br, w), 1531 (m), 1476 (m), 1436 (s), 1070 (m), 881 (m), 727 (m), 674 (m), 629 (m), 557 (w), 412 (w) cm^{-1}.**MS (EI, 70 eV):** *m/z* (%) = 324 ($[M]^+$, 12), 282 (32), 281 (100), 253 (23), 240 (12), 239 (30), 225 (14), 223 (10), 211 (18), 209 (11), 195 (35), 181 (15), 169 (12), 168 (12), 43 (10). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{20}H_{28}N_2Si$ ($[M+H]^+$) 325.20945, found 325.20938.

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3-(*n*-Hex-1-yn-1-yl)-2-([1*H*]-pyrrol-1-yl)pyridine 2l. 1-Hexyne (0.6 mmol, 69 µl) and **1a** (0.5 mmol, 111.5 mg) gave the desired product **2l** as a yellow oil (98 mg,87%); R_f 0.43 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.36 (dd, ^3J = 4.8 Hz, ^3J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81 (dd, ^3J = 7.7 Hz, ^3J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.79–7.74 (m, 2H, $CH_{pyrrole}$), 7.08 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{pyridine}$), 6.36–6.32 (m, 2H, $CH_{pyrrole}$), 2.45 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.70–1.53 (m, 2H, CH_2), 1.54–1.40 (m, 2H, CH_2), 0.96 (t, ^3J = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 151.3 ($C_{pyridine}$), 147.2, 143.6 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 120.0 ($CH_{pyridine}$), 110.9 ($C_{pyridine}$), 110.0 ($CH_{pyrrole}$), 98.0, 76.9 (C_{alkyne}), 30.4, 22.2, 19.5 (CH_2), 13.7 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2930 (w), 2870 (w), 2230 (w), 1530 (m), 1474 (m), 1434 (s), 1336 (m), 1073 (m), 1068 (m), 925 (m), 797 (m), 725 (s), 517 (m), 545 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 224 ($[M]^+$, 5), 223 (8), 209 (5), 196 (5), 195 (22), 194 (6), 193 (7), 183 (13), 182 (100), 181 (67), 179 (14), 169 (5), 168 (14), 155 (12), 154 (9), 153 (6), 128 (5), 127 (7), 63 (5), 51 (5), 43 (7), 41 (14), 39 (12), 29 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{16}N_2$ ($[M+H]^+$) 225.13862, found 225.13859. Calcd. for $C_{15}H_{16}N_2$ ($[M+Na]^+$) 247.12057, found 247.12030.

3-(Cyclohexylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2m. The reaction of **1a** (1 mmol, 223 mg) with ethynylcyclohexane (1.2 mmol, 157 µl) provided **2m** as a yellow oil (214 mg, 86%); R_f 0.56 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.35 (dd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81–7.77 (m, 2H, $CH_{pyrrole}$), 7.07 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 1H, $CH_{pyridine}$), 6.36–6.29 (m, 2H, $CH_{pyrrole}$), 2.64 (tt, $^3J_{a,a}$ = 9.2 Hz, $^3J_{a,e}$ = 3.8 Hz, 1H, CH_a), 1.96–1.84 (m, 2H, CH_2), 1.81–1.67 (m,2H, CH_2), 1.63–1.48 (m, 3H, CH_2), 1.45–1.30 (m, 3H, CH_2) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 151.2 ($C_{pyridine}$), 147.2, 143.6 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 120.0 ($CH_{pyridine}$), 110.9 ($C_{pyridine}$), 109.9 ($CH_{pyrrole}$), 101.7, 76.9 (C_{alkyne}), 32.2 (CH_2), 30.1 (CH), 25.9, 25.0 (CH_2) ppm. **IR (ATR):** $\tilde{\nu}$ = 2926 (m), 2852 (w), 2223 (w), 1717 (br, w), 1451 (m), 1434 (s), 1336 (m), 1074 (m), 926 (m), 796 (m), 726 (s), 617 (w) cm^{-1}.**MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$, 28), 249 (20), 221 (18), 209 (13), 207 (23), 206 (13), 205 (17), 196 (17), 195 (100), 193 (20), 192 (12), 182 (24), 181 (16), 169 (17), 168 (22), 155 (14). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{18}N_2$ ($[M+H]^+$) 251.15428, found 251.15414

General method for cycloisomerization to achieve 6-substituted pyrrolo[1,2-*a*][1,8]naphthyridines 3.

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In a pressure tube the Sonogashira products **2** were dissolved in xylene (3 ml, isomeric mixture) under an argon atmosphere. The catalyst $PtCl_2$ (0.05 eq.) was added to the mixture. The solution was stirred at 120 °C for 24 h.

After cooling to room temperature the crude product was treated with water and extracted with DCM. For further purification the organic solvent was evaporated and column chromatography (heptane/DCM, 5:1 → 3:1) was performed. Thereby, 1–2 ml Et_3N were added to 250 ml eluent mixture to deactivate the acidic silica.

6-Phenylpyrrolo[1,2-*a*][1,8]naphthyridine 3a. 2a (0.2 mmol, 50 mg) cyclized in the presence of $PtCl_2$ (0.01 mmol, 2.7 mg) to give **3a** as a pale yellow solid (25 mg, 50%); mp 102–105 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.54 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.46 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.97 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.72 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H, CH_{Ph}), 7.55–7.44 (m, 3H, CH_{Ph}), 7.30 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.91 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 138.5 (C_{Ph}), 136.3 ($CH_{naphtyr.}$), 134.2 ($C_{naphtyr.}$), 131.5 ($C_{pyrrole}$), 128.8, 128.5, 128.5 (CH_{Ph}), 120.1 ($CH_{naphtyr.}$), 119.2 ($C_{naphtyr.}$), 116.2 ($CH_{naphtyr.}$), 114.5 ($CH_{naphtyr.}$), 113.3, 105.3 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3119 (w), 3094 (w), 2921 (w), 2851 (w), 1726 (w), 1595 (w), 1531 (w), 1493 (w), 1442 (w), 1370 (w), 1297 (w), 1143 (w), 1074 (w), 958 (w), 848 (w), 761 (m), 740 (m), 701 (m), 663 (w), 583 (w), 446 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 244 ($[M]^+$, 100), 243 (81), 242 (43), 218 (13), 216 (8), 214 (7), 190 (7), 151 (7), 150 (10), 122 (5), 121 (7), 77 (6), 51 (7), 39 (8). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_{17}H_{12}N_2$ 244.09950, found 244.09919.

6-(2-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3b. 2b (0.36 mmol, 95 mg) gave **3b** under the influence of $PtCl_2$ (0.02 mmol, 5.3 mg) as a pale green solid (58 mg, 61%); mp 96–99 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.56 (dd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 8.43 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.62 (td, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H, CH_{Ar}), 7.43 (dddd, ^3J = 9.2 Hz, ^3J = 8.1 Hz, $^4J_{H,F}$ = 5.1 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.31 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.29–7.23 (m, 1H, CH_{Ar}), 7.23–7.20 (m, 1H, CH_{Ar}) 6.95 (d, $^5J_{H,F}$ = 1.2 Hz, 1H, $CH_{naphtyr.}$), 6.82 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.47 (dt, ^3J = 3.8 Hz, ^3J = 1.4 Hz, $^5J_{H,F}$ = 1.4 Hz 1H, $CH_{pyrrole}$) ppm. **^{19}F NMR (235 MHz, $CDCl_3$):** δ = −114.3 ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 160.14 (d, $^1J_{C,F}$ = 248.5 Hz, C-F), 147.1

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($CH_{naphtyr.}$), 144.1 ($C_{naphtyr.}$), 136.4 ($CH_{naphtyr.}$), 131.4 (C_{Ar}), 131.22 (d, $^4J_{C,F}$ = 3.3 Hz, CH_{Ar}), 130.12 (d, $^3J_{C,F}$ = 8.2 Hz, CH_{Ar}), 128.0 ($C_{pyrrole}$), 125.76 (d, $^2J_{C,F}$ = 14.9 Hz, C_{Ar}), 124.27 (d, $^3J_{C,F}$ = 3.7 Hz, CH_{Ar}), 120.1 ($CH_{naphtyr.}$), 118.8 ($C_{naphtyr.}$), 117.96 (d, $^4J_{C,F}$ = 2.1 Hz, $CH_{naphtyr.}$), 116.30 (d, $^2J_{C,F}$ = 22.3 Hz, CH_{Ar}), 114.3, 113.3 ($CH_{pyrrole}$), 105.07 (d, $^5J_{C,F}$ = 1.8 Hz, $CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3033 (w), 2921 (w), 2851 (w), 1724 (br, w), 1571 (m), 1433 (m), 1370 (m), 1259 (m), 1216 (m), 1087 (m), 1037 (m), 863 (m), 781 (m), 757 (m), 720 (s), 651 (m), 525 (m), 434 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 262 ($[M]^+$, 100), 261 (26), 260 (14), 242 (5), 118 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ ($[M+H]^+$) 263.09790, found 263.09795.

6-(4-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3c. 2c (0.2 mmol, 45 mg) reacted with $PtCl_2$ (0.01 mmol, 2.3 mg) to give **3c** as a pale green solid (19 mg, 42%); mp 128–131 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.55 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.43 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.95 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.73–7.64 (m, 2H, CH_{Ar}), 7.30 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.24–7.12 (m, 2H, CH_{Ar}), 6.87 (s, 1H, $CH_{naphtyr.}$), 6.83 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.62 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **^{19}F NMR (235 MHz, $CDCl_3$):** δ = −113.4 ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 162.95 (d, $^1J_{C,F}$ = 247.6 Hz, C-F), 147.0 ($CH_{naphtyr.}$), 144.1 ($C_{naphtyr.}$), 136.1 ($CH_{naphtyr.}$), 134.60 (d, $^4J_{C,F}$ = 3.4 Hz, C_{Ar}), 133.1 ($C_{naphtyr.}$), 131.4 ($C_{pyrrole}$), 130.13 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 120.2 ($CH_{naphtyr.}$), 119.1 ($C_{naphtyr.}$), 116.3 ($CH_{pyrrole}$), 115.73 (d, $^2J_{C,F}$ = 21.4 Hz, CH_{Ar}), 114.5 ($CH_{naphtyr.}$), 113.3, 105.0 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3041 (w), 2921 (w), 1724 (w), 1601 (w), 1508 (m), 1454 (m), 1438 (m), 1368 (w), 1298 (w), 1223 (m), 1160 (m), 1092 (m), 1036 (w), 857 (m), 831 (m), 794 (m), 725 (m), 623 (m), 556 (m), 510 (m), 497 (m), 448 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 262 ($[M]^+$, 100), 261 (36), 260 (19), 118 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ ($[M+H]^+$) 263.09790, found 263.09759.

6-(4-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3d. The reaction of **2d** (0.3 mmol, 78 mg) with $PtCl_2$ (0.015 mmol, 4 mg) gave **3d** as a yellow solid (34 mg, 68%); mp 86–91 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.53 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.64–7.57 (m, 2H, CH_{Ar}), 7.35–7.25 (m, 3H, $CH_{naphtyr./Ar}$), 6.89 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.45 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 146.3 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 138.4

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(C-Me), 136.3 ($CH_{naphtyr.}$), 135.6 (C_{Ar}), 134.2 ($C_{naphtyr.}$), 131.6 ($C_{pyrrole}$), 129.5, 128.3 (CH_{Ar}), 120.0 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$), 115.8, 114.5 ($CH_{naphtyr.}$), 113.4, 105.3 ($CH_{pyrrole}$), 21.5 (Me) ppm. **IR(ATR):** $\tilde{\nu}$ = 3120 (m), 2917 (m), 2851 (m), 1723 (m), 1665 (w), 1604 (m), 1571 (m), 1510 (m), 1436 (s), 1369 (m), 1299 (m), 1282 (m), 1180 (m), 1145 (m), 1095 (m), 1060 (m), 1033 (m), 927 (m), 850 (m), 816 (s), 761 (s), 735 (vs), 722 (vs), 624 (m), 557 (m), 496 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (21), 256 (6), 255 (10), 243 (6), 242 (14), 128 (8). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12293.

6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3e. Starting material **2e** (0.3 mmol, 90.1 mg) reacted with $PtCl_2$ (0.015 mmol, 4 mg) giving **3e** as a brown oil (59 mg, 66%); R_f 0.58 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.53 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.94 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.70–7.65 (m, 2H, CH_{Ar}), 7.55–7.50 (m, 2H, CH_{Ar}), 7.29 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.90 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.73 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 1.41 (s, 9H, CH_{3tBu}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 151.6 (C-*t*Bu), 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 136.0 ($CH_{naphtyr.}$), 135.6 (C_{Ar}), 134.1 ($C_{naphtyr.}$), 131.6 ($C_{pyrrole}$), 128.1, 125.7 (CH_{Ar}), 120.0 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 116.0 ($CH_{pyrrole}$), 114.3 ($CH_{naphtyr.}$), 113.2, 105.3 ($CH_{pyrrole}$), 34.9 (C_{tBu}), 31.5 (CH_{3tBu}) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (w), 1721 (w), 1589 (w), 1512 (w), 1434 (m), 1362 (m), 1268 (m), 1146 (w), 1092 (m), 1018 (w), 831 (m), 787 (m), 768 (m), 722 (m), 610 (m), 542 (m), 448 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 300 ($[M]^+$, 100), 286 (13), 285 (64), 270 (12), 269 (8), 268 (7), 257 (13), 255 (9), 244 (7), 243 (9), 242 (12), 128 (15). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{21}H_{20}N_2$ ($[M+H]^+$) 301.16993, found 301.16950.

6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3f. 2f (0.15 mmol, 42 mg) cyclized under influence of $PtCl_2$ (0.01 mmol, 2 mg) giving **3f** as a pale yellow solid (17 mg, 40%); mp 123–128 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.53 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.44 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.69–7.62 (m, 2H, CH_{Ar}), 7.30 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.06–7.00 (m, 2H, CH_{Ar}), 6.87 (s, 1H, $CH_{naphtyr.}$), 6.83 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 3.89 (s, 3H, OMe) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 160.0 (C-OMe), 146.3 ($CH_{naphtyr.}$), 143.7 ($C_{naphtyr.}$), 136.1 ($CH_{naphtyr.}$), 133.9 (C_{Ar}), 131.7 ($C_{naphtyr.}$), 131.0 ($C_{pyrrole}$), 129.6 (CH_{Ar}), 120.1 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$),

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115.6 ($CH_{pyrrole}$), 114.4 ($CH_{naphtyr.}$), 114.2 (CH_{Ar}), 113.3, 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2919 (w), 2849 (w), 1720 (w), 1601 (w), 1509 (w), 1436 (w), 1367 (w), 1280 (w), 1239 (w), 1175 (w), 1111 (w), 1032 (w), 834 (w), 782 (w), 768 (w), 732 (w), 621 (w), 563 (w), 523 (w), 445 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M]^+$, 100), 259 (18), 242 (5), 231 (21), 230 (13), 229 (19), 205 (15), 204 (7), 203 (6), 115 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11788. Calcd. for $C_{18}H_{14}N_2O$ ($[M+Na]^+$) 297.09983, found 297.10014.

6-(3-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3g. 2g (0.32 mmol, 82 mg) and $PtCl_2$ (0.016 mmol, 4 mg) gave the product **3g** as a yellow oil (21 mg, 25%); mp 86–89 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.54 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, ^3J = 3.0 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.98 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.57–7.47 (m, 2H, CH_{Ar}), 7.42–7.36 (m, 1H, CH_{Ar}), 7.32 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, $CH_{naphtyr.}$), 7.29–7.27 (m, 1H, CH_{Ar}), 6.90 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.45 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 146.4 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 138.5 (C-Me), 136.4 ($CH_{naphtyr.}$), 134.5 (C_{Ar}), 131.6 ($C_{naphtyr.}$), 129.3, 129.1, 128.7, 125.6 (CH_{Ar}), 120.1 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$), 116.0 ($CH_{pyrrole}$), 114.6 ($CH_{naphtyr.}$), 113.4, 105.4 ($CH_{pyrrole}$), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3142 (w), 2917 (w), 1722 (w), 1603 (w), 1571 (w), 1531 (w), 1436 (m), 1366 (w), 1304 (w), 1283 (w), 1091 (w), 1038 (w), 1019 (w), 860 (m), 782 (m), 728 (m), 708 (m), 665 (w), 589 (w), 447 (w), 436 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (20), 256 (5), 255 (11), 243 (6), 242 (16), 128 (8). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12314.

6-(3-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3h. Substrate **2h** (0.6 mmol, 166 mg) and $PtCl_2$ (0.03 mmol, 8 mg) reacted to **3h** as a pale brown oil (99 mg, 60%); R_f 0.36 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.54 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.41 (dd, ^3J = 8.1 Hz, ^3J = 7.5 Hz, 1H, CH_{Ar}), 7.34–7.26 (m, 3H, $CH_{naphtyr./Ar}$), 7.00 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 6.92 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, ^3J = 3.8 Hz, ^4J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.71 (dd, ^3J = 3.8 Hz, ^3J = 1.5 Hz, 1H, $CH_{pyrrole}$), 3.88 (s, 3H, OMe) ppm. **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 159.9 (C-OMe), 146.8 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 139.9 (C_{Ar}), 136.2 ($CH_{naphtyr.}$), 134.0 ($C_{naphtyr.}$), 131.4 ($C_{pyrrole}$), 129.8, 120.9 (CH_{Ar}), 120.1 ($CH_{naphtyr.}$), 119.1 ($C_{naphtyr.}$), 116.2 ($CH_{pyrrole}$), 114.4

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($CH_{naphtyr.}$), 114.1, 114.0 (CH_{Ar}), 113.3, 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2933 (w), 2832 (w), 1574 (m), 1434 (m), 1239 (m), 1169 (m), 1038 (m), 851 (m), 785 (m), 725 (m), 694 (m), 555 (m), 447 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M]^+$, 100), 259 (9), 258 (9), 242 (6), 231 (9), 230 (7), 229 (13), 205 (5), 203 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11795.

6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3i. 2i (0.5 mmol, 149 mg) and $PtCl_2$ (0.03 mmol, 7 mg) achieved **3i** as a pale brown oil (92 mg, 62%); R_f 0.40 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.57 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.93 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.33 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.30 (dd, ^3J = 7.8 Hz, ^4J = 4.8 Hz, 1H, $CH_{naphtyr.}$), 6.93 (d, ^4J = 2.6 Hz, 1H, CH_{Ar}), 6.87 (dd, ^3J = 8.4 Hz, ^4J = 2.7 Hz, 1H, CH_{Ar}), 6.82 (dd, ^3J = 3.7 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.78 (s, 1H, $CH_{naphtyr.}$), 6.29 (dd, ^3J = 3.9 Hz, ^4J = 1.6 Hz, 1H, $CH_{pyrrole}$), 3.90 (s, 3H, OMe), 2.29 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 159.4 (C-OMe), 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 137.9 (C-Me), 135.8 ($CH_{naphtyr.}$), 133.6 (C_{Ar}), 132.5 ($C_{naphtyr.}$), 130.7 (CH_{Ar}), 130.2 ($C_{pyrrole}$), 119.9 ($CH_{naphtyr.}$), 119.0 ($C_{naphtyr.}$), 117.0 (CH_{Ar}), 115.8 ($CH_{pyrrole}$), 113.9 ($CH_{naphtyr.}$), 113.1 ($CH_{pyrrole}$), 111.1 (CH_{Ar}), 105.1 ($CH_{pyrrole}$), 55.3 (OMe), 20.2 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2919 (w), 2833 (w), 1722 (w), 1604 (w), 1560 (w), 1499 (w), 1455 (m), 1434 (m), 1368 (w), 1291 (m), 1237 (m), 1161 (w), 1042 (m), 940 (w), 856 (w), 788 (m), 725 (m), 626 (w), 557 (w), 446 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 288 ($[M]^+$, 86), 287 (100), 273 (10), 272 (10), 271 (5), 256 (5), 255 (8), 245 (8), 244 (13), 243 (30), 242 (15), 229 (7), 218 (5), 205 (5), 128 (6), 122 (7), 109 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{19}H_{16}N_2O$ ($[M+H]^+$) 289.13354, found 289.13338.

6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,8]naphthyridine 3j. 2j (0.3 mmol, 86 mg) reacted with $PtCl_2$ (0.015 mmol, 4 mg) giving **3j** as a yellow solid (35 mg, 41%); R_f 0.55 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.54 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.97 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.70 (dd, ^4J = 2.9 Hz, ^4J = 1.4 Hz, 1H, $CH_{thioph.}$), 7.50 (dd, ^3J = 5.0 Hz, ^4J = 1.4 Hz, 1H, $CH_{thioph.}$), 7.46 (dd, ^3J = 5.0 Hz, ^4J = 2.9 Hz, 1H, $CH_{thioph.}$), 7.31 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, $CH_{naphtyr.}$), 7.00 (s, 1H. $CH_{naphtyr.}$), 6.85 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.81 (dd, ^3J = 3.8 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 146.3 ($CH_{naphtyr.}$), 143.7 ($C_{naphtyr.}$), 138.9 ($C_{thioph.}$), 136.4 ($CH_{naphtyr.}$), 131.2 ($C_{naphtyr.}$), 128.9 ($C_{pyrrole}$), 127.8, 126.1, 123.5 ($CH_{thioph.}$), 120.1 ($CH_{naphtyr.}$), 119.2

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($C_{naphtyr.}$), 115.6 ($CH_{pyrrole}$), 114.7 ($CH_{naphtyr.}$), 113.5, 105.3 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3091 (w), 2921 (w), 1717 (br, w), 1570 (m), 1469 (m), 1435 (s), 1136 (m), 1080 (m), 859 (m), 836 (m), 777 (m), 715 (s), 633 (m), 448 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$, 100), 249 (22), 248 (9), 205 (10). **HRMS (EI):** *m/z* = calcd. for $C_{15}H_{10}N_2S$ ($[M]^+$) 250.05592, found 250.05591.

6-(*n*-Butyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3l. Substrate **2l** (0.2 mmol, 50 mg) and $PtCl_2$ (0.01 mmol, 2.6 mg) resulted in product **3l** as an oil (19 mg, 37%); R_f 0.63 (heptane/ethyl acetate 5:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.48 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.33 (dd, ^3J = 2.9 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.87 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.25 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.80 (dd, ^3J = 3.7 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.73 (s, 1H, $CH_{naphtyr.}$), 6.62 (dd, ^3J = 3.7 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.79 (t, ^3J = 7.7 Hz, 2H, CH_2), 1.78 (p, ^3J = 7.5 Hz, 2H, CH_2), 1.45 (hept, ^3J = 7.4 Hz, 2H, CH_2), 0.98 (t, ^3J = 7.3 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 146.1 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 135.4 ($CH_{naphtyr.}$), 134.0 ($C_{naphtyr.}$), 132.6 ($C_{pyrrole}$), 119.8 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 114.7 ($CH_{pyrrole}$), 113.8 ($CH_{naphtyr.}$), 112.7, 102.7 ($CH_{pyrrole}$), 32.2, 31.1, 22.9 (CH_2), 14.1 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2855 (w), 2927 (w), 2858 (w), 1723 (w), 1612 (w), 1592 (w), 1559 (w), 1537 (w), 1459 (w), 1436 (w), 1377 (w), 1289 (w), 1171 (w), 1090 (w), 1033 (w), 849 (w), 783 (w), 726 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 224 ($[M]^+$, 40), 195 (12), 194 (5), 193 (7), 183 (13), 182 (100), 181 (42), 179 (5), 168 (7), 154 (5), 127 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{16}N_2$ ($[M+H]^+$) 225.13862, found 225.13887.

6-(Cyclohexyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3m. Starting material **2m** (0.8 mmol, 204 mg) and $PtCl_2$ (0.04 mmol, 10.6 mg) gave **3m** as an oil (127 mg, 62%); R_f 0.58 (heptane/ethyl acetate 5:1). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.47 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.37 (dd, ^3J = 3.0 Hz, ^4J = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.86 (dd, ^3J = 7.8 Hz, ^3J = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.23 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.82 (dd, ^3J = 3.7 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.74 (s, 1H, $CH_{naphtyr.}$), 6.67 (dd, ^3J = 3.8 Hz, ^3J = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.86 (tt, $^3J_{a,a}$ = 8.2 Hz, $^3J_{a,e}$ = 3.2 Hz, 1H, CH_a), 2.22–2.05 (m, 2H, CH_2), 1.98–1.79 (m, 3H, CH_2), 1.62–1.44 (m, 3H, CH_2), 1.47–1.24 (m, 2H, CH_2) ppm. **^{13}C NMR (63 MHz, $CDCl_3$):** δ = 146.1 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 139.2 ($C_{naphtyr.}$), 135.5 ($CH_{naphtyr.}$), 132.3 ($C_{pyrrole}$), 119.8 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 113.7 ($CH_{pyrrole}$), 112.6 ($CH_{naphtyr.}$), 112.2, 102.4 ($CH_{pyrrole}$), 40.4 (CH), 33.1, 27.0, 26.5 (CH_2) ppm. **IR (ATR):** $\tilde{\nu}$ = 2924 (m), 2850 (m), 1720 (br, w), 1560 (w), 1434 (s), 1336 (m), 1289 (m), 1073 (m),

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1059 (m), 845 (m), 783 (m), 721 (s), 615 (m), 554 (m), 448 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$, 100), 249 (23), 235 (6), 221 (18), 219 (6), 209 (12), 207 (23), 206 (13), 205 (22), 196 (13), 195 (70), 194 (19), 193 (27), 192 (11), 182 (26), 181 (17), 169 (6), 168 (22), 140 (6), 56 (6), 41 (13), 39 (8). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{18}N_2$ ($[M]^+$) 250.14645, found 250.14577.

General procedure for the Sonogashira reaction to synthesize 3-alykynl-4-([1*H*]-pyrrol-1-yl)pyridines 4.

1c was dissolved in 2 ml dioxane under an argon atmosphere. After the addition of $Pd(MeCN)_2Cl_2$ (0.05 eq.), CuI (0.05 eq.), XPhos (0.1 eq.) and Et_3N (3 eq.) in advance of the corresponding acetylene (1.5 eq.) the reaction was stirred at room temperature for 24 h. The reaction mixture was subsequently cooled to room temperature and washed with distilled water and ethyl acetate. The organic layers were collected and the solvent evaporated. The crude product was thereafter purified by column chromatography (heptane/ethyl acetate, 10:1 → 2:1) to give the alkynylated products **4a–n**[1].

3-(Phenylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4a. Reaction of **1c** (0.45 mmol, 100 mg) and phenylacetylene (0.07 mmol, 73 µl gave **4a** as a white solid (88 mg, 81%); mp 68–69 ˚C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.77 (bs, 1H, $CH_{pyridine}$), 8.51 (bs, 1H, $CH_{pyridine}$), 7.43–7.39 (m, 2H, Ph), 7.31 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.27–7.25 (m, 3H, Ph), 7.18–7.13 (m, 1H, $CH_{pyridine}$), 6.32 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR[2] (62.9 MHz, $CDCl_3$):** δ = 155.0, 149.5 ($CH_{pyridine}$), 147.2 ($C_{pyridine}$), 131.6, 129.1, 128.6 (CH_{Ph}), 122.4 (C_{Ph}), 120.8 ($CH_{pyrrole}$), 111.3 ($CH_{pyrrole}$), 96.8, 84.2 (C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3130 (w), 3055 (w), 2220 (w), 1562 (m), 1589 (m), 1393 (m), 1344 (m), 1185 (w), 1062 (m), 1018 (m), 920 (w), 836 (s), 749 (s), 722 (s), 685 (s), 621 (m), 562 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 244 ($[M^+]$, 100), 243 (69), 242 (36), 218 (8), 216 (7), 215 (5), 214 (5), 189 (6), 150 (8), 122 (5). **HRMS (EI, 70 eV):** calcd. for $C_{17}H_{12}N_2$ ($[M]^+$) 244.09950, found 244.09904.

3-((3-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4b. Reaction of **1c** (1.35 mmol, 300 mg) and tolylacetylene (2.02 mmol, 234.3 mg) gave **4b** as a white solid (304 mg, 88%); mp 99–100 ˚C. **^{1}H NMR (250 MHz, C_6D_6):** δ = 8.91 (s, 1H, $CH_{pyridine}$), 8.21 (d, ^3J = 5.5 Hz,

[1] The pyridine fragment provides very broad signals in ^{1}H and ^{13}C NMR spectra. Therefore, it was not possible to detect all pyridine signals of some substrates. Known effects that can lead to broad or undetecTable NMR signals are exchange broadening due to changes in the spin and rotational states of the observed atom or aggregation with the solvent. However, all signals reappear in the cyclized products **5a–n**.
[2] *meta*-$C_{pyridine}$ and *meta*-$CH_{pyridine}$ are undetectable.

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1H, $CH_{pyridine}$), 7.27 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 7.22 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.23 (s, 1H, CH_{Ar}), 6.94 (t, ^3J = 7.6 Hz, 1H, CH_{Ar}), 6.82 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 6.52 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 6.36 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.96 (s, 3H, Me) ppm. **^{13}C NMR (62.9 MHz, C_6D_6):** δ = 155.5, 150.1 ($CH_{pyridine}$), 147.1 ($C_{pyridine}$), 138.4 (C_{Ar}), 132.4, 130.1, 129.1, 128.6 (CH_{Ar}), 122.8 (C_{Ar}), 121.0 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 113.0 ($C_{pyridine}$), 111.5 ($CH_{pyrrole}$), 97.2, 84.6 (C_{alkyne}), 21.0 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3034 (w), 2919 (w), 2207 (w), 1720 (w), 1577 (w), 1558 (m), 1498 (s), 1392 (w), 1339 (s), 1180 (w), 1062 (m), 1018 (m), 827 (w), 782 (m), 722 (s), 687 (m), 569 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M^+], 100), 257 (38), 256 (12), 255 (16), 243 (22), 242 (32), 241 (4), 231 (6), 229 (4), 214 (4), 202 (3), 164 (3), 163 (6). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([$M]^+$) 258.11515, found 258.11562.

3-((4-Methoxy-2-methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4c. Reaction of **1c** (1.35 mmol, 300 mg) and 4-methoxy-2-methylphenylacetylene (294.9 mg, 2.017 mmol) gave **4c** as a yellow solid (356 mg, 91%); mp 77–78 °C. **^{1}H NMR (250 MHz, C_6D_6):** δ = 8.90 (bs, 1H, $CH_{pyridine}$), 8.20 (bs, 1H, $CH_{pyridine}$), 7.35–7.15 (m, 3H, CH_{Ar}), 6.54–6.31 (m, 5H, CH_{Ar}), 3.20 (s, 3H, OMe), 2.23 (s, 3H, Me) ppm. **^{13}C NMR (62.9 MHz, C_6D_6):** δ = 160.7 (C_{Ar}), 155.5, 149.7 ($CH_{pyridine}$), 146.6 ($C_{pyridine}$), 142.6 (C_{Ar}), 133.9 (CH_{Ar}), 121.0 ($CH_{pyrrole}$), 117.3 ($CH_{pyridine}$), 115.7 (CH_{Ar}), 115.0 (C_{Ar}), 113.8 ($C_{pyridine}$), 111.8 (CH_{Ar}), 111.3 ($CH_{pyrrole}$), 96.4, 87.2 (C_{alkyne}), 54.8 (OMe), 21.0 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (w), 2202 (w), 1725 (w), 1602 (w), 1560 (m), 1491 (m), 1341 (w), 1276 (w), 1237 (s), 1022 (w), 846 (w), 815 (s), 726 (s), 688 (m), 576 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 288 ([M^+], 100), 287 (77), 273 (9), 272 (15), 271 (8), 257 (6), 256 (9), 255 (10), 246 (7), 245 (40), 244 (23), 243 (39), 242 (15), 230 (10), 229 (10), 218 (7), 217 (6), 216 (5), 205 (5), 151 (6). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{16}ON_2$ ([$M]^+$) 288.12571, found 288.12528.

3-(Naphtalen-1-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4d. Reaction of **1c** (1.57 mmol, 350 mg) and 1-naphthylacetylene (2.35 mmol, 364 µl) gave **4d** as a white solid (458 mg, 99%); mp 121–122 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 9.00 (bs, 2H, $CH_{pyridine}$), 8.27–8.23 (m, 1H, $CH_{naphthyl.}$), 7.90–7.85 (m, 2H, $CH_{naphthyl.}$), 7.78–7.74 (m, 1H, $CH_{naphthyl.}$), 7.58–7.50 (m, 2H, $CH_{naphthyl.}$), 7.47–7.44 (m, 1H, $CH_{naphthyl.}$), 7.45 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.18–7.05 (m, 1H, $CH_{pyridine}$), 6.46 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR[3] (62.9 MHz, $CDCl_3$):** δ = 133.2, 133.2 ($C_{naphthyl.}$), 131.1, 129.8, 128.5, 127.2, 126.8, 126.2, 125.3 ($CH_{naphthyl.}$), 121.0 ($CH_{pyrrole}$), 120.0 ($C_{naphthyl.}$), 111.6 ($CH_{pyrrole}$), 95.6, 88.7 (C_{alkyne}) ppm. **IR**

[3] All carbon signals of the pyridine moiety were undetectable.

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(ATR): $\tilde{\nu}$ = 3043 (w), 2206 (w), 1556 (w), 1494 (m), 1388 (w), 1340 (m), 1179 (w), 1063 (m), 1019 (w), 832 (m), 803 (s), 777 (s), 728 (s), 672 (m), 620 (m), 560 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 293 ([M^+], 100), 292 (50), 291 (11), 266 (6), 265 (8), 264 (7), 238 (3), 200 (6), 174 (2), 146 (6), 132 (5). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{13}N_2$ ([$M]^+$) 293.10732, found 293.10668.

3-((4-Trifluoromethylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4e. Reaction of **1c** (2.02 mmol, 450 mg,) and 4-(trifluoromethyl)-phenylacetylene (2.80 mmol, 494 µl) gave **4e** as a yellow solid (343 mg, 55%); mp 75–76 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.92 (bs, 1H, $CH_{pyridine}$), 8.32 (bs, 1H, $CH_{pyridine}$), 7.22–7.13 (m, 6H, CH_{Ar}), 6.58 (bs, 1H, $CH_{pyridine}$), 6.40 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 155.5, 150.7 ($CH_{pyridine}$), 147.3 ($C_{pyridine}$), 131.9 (CH_{Ar}), 130.5 (q, $^2J_{C,F}$ = 32.6 Hz, C_{Ar}), 126.3 (q, $^4J_{C,F}$ = 1.4 Hz, C_{Ar}), 125.5 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.4 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 120.9 ($CH_{pyrrole}$), 117.3 ($CH_{pyridine}$), 111.6 ($CH_{pyrrole}$), 105.2($C_{pyridine}$), 95.1, 87.0 (C_{alkyne}) ppm. ^{19}F NMR (282 MHz, C_6D_6) δ = −62.59 ppm. **IR (ATR):** $\tilde{\nu}$ = 2929 (w), 1724 (w), 1613 (w), 1583 (w), 1557 (w), 1496 (m), 1407 (w), 1324 (s), 1163 (m), 1101 (s), 1062 (s), 1016 (m), 834 (s), 729 (s), 675 (m), 577 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 312 ([M^+], 100), 311 (37), 310 (8), 293 (5), 291 (5), 286 (7), 243 (9), 242 (20), 214 (4), 199 (4). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{11}F_3N_2$ ([$M]^+$) 312.28855, found 312.28849.

3-((4-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4f. Reaction of **1c** (1.57 mmol, 350 mg) and 4-methylphenylacetylene (2.35 mmol, 274 mg) gave **4f** as a white solid (355 mg, 88%); mp 97–98 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.91 (bs, 2H, $CH_{pyridine}$), 7.42 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.40 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.18 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.19–7.10 (m, 1H, $CH_{pyridine}$), 6.42 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 2,38 (s, 3H, Me) ppm. **^{13}C NMR[4] (62.9 MHz, $CDCl_3$):** δ = 139.6 (C-Me), 131.6, 129.4 (CH_{Ar}), 120.8 ($CH_{pyrrole}$), 119.2 (C_{Ar}), 111.4 ($CH_{pyrrole}$), 97.6, 83.7 (C_{alkyne}), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3128 (w), 2658 (w), 2217 (m), 1560 (m), 1494 (s), 1389 (s), 1313 (w), 1179 (m), 1115 (w), 1068 (s), 1016 (s), 821 (m), 808 (s), 732 (s), 685 (m), 623 (w), 577 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M^+], 100), 257 (40), 256 (12), 255 (14), 243 (17), 242 (30), 231 (5), 163 (6), 139 (3), 128 (4). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([$M]^+$) 258.11515, found 258.11472.

[4] All carbon signals of the pyridine moiety were undetectable.

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3-((4-Methoxyphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4g. Reaction of **1c** (1.57 mmol, 350 mg) and 4-methoxyphenylacetylene (2.35 mmol, 311 mg) gave **4g** as a yellow solid (408 mg, 95%); mp 89–90 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.72 (bs, 2H, $CH_{pyridine}$), 7.45 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.45 (t, ^3J = 2.0 Hz, 2H, $CH_{pyrrole}$), 7.31 (bs, 1H, $CH_{pyridine}$), 6.89 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.41 (t, ^3J = 2.0 Hz, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **^{13}C NMR[5] (62.9 MHz, $CDCl_3$):** δ = 160.5 (C-OMe), 133.3 (CH_{Ar}), 120.9 ($CH_{pyrrole}$), 114.5 (C_{Ar}), 114.4 (CH_{Ar}), 111.5 ($CH_{pyrrole}$), 97.5, 82.9 (C_{alkyne}), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 3035 (w), 2933 (w), 2218 (m), 1559 (m), 1504 (s), 1338 (m), 1290 (m), 1247 (s), 1174 (m), 1067 (m), 1020 (s), 826 (s), 732 (s), 686 (s), 326 (m), 542 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 274 ([M^+], 100), 273 (8), 259 (36), 232 (8), 231 (46), 230 (38), 229 (34), 205 (10), 204 (9), 203 (12), 151 (7), 137 (12). **HRMS (EI, 70 eV)**: calcd. for $C_{18}H_{14}N_2O$ ([$M]^+$) 274.11006, found 274.10990.

3-((4-*tert*-Butylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4h. Reaction of **1c** (1.57 mmol, 350 mg) and 4-*tert*-butylphenylacetylene (2.35 mmol, 425 µl) gave **4h** as a brown oil (463 mg, 98%). **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.99 (bs, 2H, $CH_{pyridine}$), 7.46 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.42 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.39 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.20–7.09 (m, 1H, $CH_{pyridine}$), 6.41 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.33 (s, 9H, CH_{3tBu}) ppm. **^{13}C[6] NMR (62.9 MHz, $CDCl_3$):** δ = 152.6 (C-*t*Bu), 131.4, 125.6 (CH_{Ar}), 120.8 ($CH_{pyrrole}$), 119.3 (C_{Ar}), 111.3 ($CH_{pyrrole}$), 97.3, 83.7 (C_{alkyne}), 35.0 (C_{tBu}), 31.2 (CH_{3tBu}) ppm. **IR (ATR):** $\tilde{\nu}$ = 2960 (m), 2866 (w), 2217 (w), 1724 (w), 1559 (m), 1494 (s), 1394 (m), 1340 (s), 1266 (w), 1180 (w), 1063 (m), 1018 (m), 926 (w), 831 (s), 724 (s), 677 (m), 617 (w), 562 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 300 ([M^+], 64), 286 (22), 285 (100), 270 (11), 269 (17), 257 (22), 256 (7), 255 (16), 244 (10), 243 (17), 242 (13), 128 (12). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{20}N_2$ ([$M]^+$) 300.16210, found 300.16172.

3-((4-*n*-Propylphenly)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4i. Reaction of **1c** (1.35 mmol, 300 mg,) and 4-*n*-propylphenylacetylene (2.02 mmol, 291 mg) gave **4i** as a white solid (332 mg, 86%), mp 74–75 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.93 (bs, 1H, $CH_{pyridine}$), 8.22 (bs, 1H, $CH_{pyridine}$), 7.38 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}) 7.23 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.85 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 6.52 (d, ^3J = 5.0 Hz, 1H, $CH_{pyridine}$), 6.37 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 2.29 (t, ^3J = 7.6 Hz, 2H, CH_2), 1.40 (tq, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 2H, CH_2), 0.77 (t,

[5] All carbon signals of the pyridine moiety were undetectable.
[6] All carbon signals of the pyridine moiety were undetectable.

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^3J = 7.3 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 155.5, 150.0 ($CH_{pyridine}$), 147.0 ($C_{pyridine}$), 144.0 (C_{Ar}), 131.9, 129.0 (CH_{Ar}), 121.0 ($CH_{pyrrole}$), 120.3 (C_{Ar}), 117.2 ($CH_{pyridine}$), 111.4 ($CH_{pyrrole}$), 105.0 ($C_{pyridine}$), 97.3, 84.4 (C_{alkyne}), 38.1 (CH_2), 24.5 (CH_2), 13.8 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2954 (w), 2926 (w), 2220 (w), 1715 (w), 1560 (m), 1497 (m), 1343 (m), 1182 (w), 1119 (w), 1062 (m), 1018 (m), 835 (s), 812 (s), 727 (s), 672 (m), 622 (w), 563 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 286 ([M^+], 68), 258 (20), 257 (100), 256 (19), 255 (37), 243 (12), 242 (16), 230 (4), 229 (6), 163 (9). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{18}N_2$ ([M]$^+$) 286.14645, found 286.14637.

3-((4-*n*-Hexylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4j. Reaction of **1c** (1.35 mmol, 300 mg) and 4-*n*-hexylphenylacetylene (2.02 mmol, 424 µl) gave **4j** as a yellow oil (367 mg, 83%). **^{1}H NMR (300 M Hz, C_6D_6):** δ = 8.66 (s, 1H, $CH_{pyridine}$), 8.08 (d, ^3J = 5.3 Hz, 1H, $CH_{pyridine}$), 7.40 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.23 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.90 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 6.70 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.51 (d, ^3J = 5.3 Hz, 1H, $CH_{pyridine}$), 2.36 (t, ^3J = 7.3 Hz, 2H, CH_2), 1.47–1.40 (m, 2H, CH_2), 1.27–1.15 (m, 6H, CH_2), 0.87 (t, ^3J = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 154.3, 149.7 ($CH_{pyridine}$), 147.1 ($C_{pyridine}$), 144.3 (C_{Ar}), 131.9, 128.9 (CH_{Ar}), 121.0 ($CH_{pyrrole}$), 120.3 (C_{Ar}), 117.2 ($CH_{pyridine}$), 111.4 ($CH_{pyrrole}$), 105.0 ($C_{pyridine}$), 97.3, 84.4 (C_{alkyne}), 36.2, 32.0, 31.4, 29.2, 23.0 (CH_2), 14.3 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2925 (w), 2854 (w), 2217 (w), 1722 (w), 1575 (m), 1495 (s), 1395 (w), 1339 (m), 1180 (w), 1063 (m), 1016 (m), 827 (m), 721 (s), 667 (w), 618 (w), 569 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 328 ([M^+], 59), 285 (6), 272 (6), 271 (15), 258 (29), 257 (100), 256 (23), 255 (43), 244 (5), 243 (20), 242 (18), 229 (6), 228 (9), 227 (6), 202 (5). **HRMS (EI, 70 eV):** calcd. for $C_{23}H_{24}N_2$ ([M]$^+$) 328.19340, found 328.19342.

3-(Thiophen-3-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4k. Reaction of **1c** (1.35 mmol, 300 mg,) and thiophen-3-ylacetylene (2.02 mmol, 199 µl) gave **4k** as a white solid (254 mg, 76%), mp 80–81 ˚C. **^{1}H NMR (250 MHz, C_6D_6):** δ = 8.84 (s, 1H, $CH_{pyridine}$), 8.21 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 7.20 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.14 (dd, ^3J = 1.2 Hz, ^3J = 3.0 Hz, 1H, $CH_{thioph.}$), 6.93 (dd, ^3J = 1.2 Hz, ^3J = 5.0 Hz, 1H, $CH_{thioph.}$), 6.71 (dd, ^3J = 5.0 Hz, ^3J = 3.0 Hz, 1H, $CH_{thioph.}$), 6.56 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 6.34 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **^{13}C NMR (62.9 MHz, C_6D_6):** δ = 155.3, 150.1 ($CH_{pyridine}$), 147.0 ($C_{pyridine}$), 129.9, 129.7, 125.9 ($CH_{thioph.}$), 121.9 ($C_{thioph.}$), 120.9 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 112.8 ($C_{pyridine}$), 111.5 ($CH_{pyrrole}$), 92.4, 84.4 (C_{alkyne}) ppm. **IR (ATR):** $\tilde{\nu}$ = 3100 (w), 2928 (w), 2216 (w), 1721 (w), 1558 (m), 1493 (m), 1386 (w), 1335 (m), 1116 (w), 1061

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(m), 1013 (w), 827 (m), 791 (m), 731 (s), 676 (s), 621 (s), 571 (s), 483 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 250 ([M^+], 100), 249 (55), 248 (22), 224 (5), 223 (6), 222 (5), 216 (3), 205 (16), 179 (3). **HRMS (EI, 70 eV):** calcd. for $C_{15}H_{10}N_2S$ ([M]$^+$) 250.05592., found 250.05594.

4-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 4l. Reaction of **1c** (1.35 mmol, 300 mg) and ethynyltriisopropylsilane (2.02 mmol, 449 µl) gave **4l** as a yellow oil (339 mg, 78%). **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.99 (s, 1H, $CH_{pyridine}$), 8.27 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 7.30 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.55 (d, ^3J = 5.5 Hz, 1H, $CH_{pyridine}$), 6.45 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.21 (s, 3H, $CH_{i\mathrm{Pr}}$), 1.20 (s, 18H, $CH_{3i\mathrm{Pr}}$) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 156.6, 150.3 ($CH_{pyridine}$), 147.3 ($C_{pyridine}$), 120.9 ($CH_{pyrrole}$), 116.9 ($CH_{pyridine}$), 112.9 ($C_{pyridine}$), 111.3 ($CH_{pyridine}$), 102.2, 99.7 (C_{alkyne}), 18.8 ($CH_{3i\mathrm{Pr}}$), 11.7 ($CH_{i\mathrm{Pr}}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2941 (m), 2863 (m), 2154 (w), 1724 (w), 1579 (w), 1559 (w), 1497 (s), 1462 (w), 1341 (m), 1063 (m), 1018 (m), 881 (m), 831 (s), 722 (s), 667 (s), 562 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 324 ([M^+], 5), 283 (6), 282 (26), 281 (100), 253 (19), 239 (16), 225 (12), 211 (17), 195 (19), 181 (6), 169 (8), 168 (7), 149 (12), 113 (9). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{28}N_2Si$ ([M]$^+$) 324.20163, found 324.20133.

3-(Cyclopropylethynyl)-4-(1*H*-pyrrol-1-yl)pyridine 4m. Reaction of **1c** (1.35 mmol, 300 mg) and ethynylcyclopropane (2.02 mmol, 171 µl) gave **4m** as a white solid (155 mg, 56%); mp 120–121 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.82 (bs, 1H, $CH_{pyridine}$), 8.19–8.17 (m, 1H, $CH_{pyridine}$), 7.66–7.62 (m, 1H, $CH_{pyridine}$), 7.16–7.14 (m, 2H, $CH_{pyrrole}$), 7.35–7.33 (m, 2H, $CH_{pyrrole}$), 1.30–1.18 (m, 1H, CH), 0.57–0.53 (m, 2H, CH_2), 0.37–0.34 (m, 2H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 155.8, 149.5 ($CH_{pyridine}$), 147.2 ($C_{pyridine}$), 120.8 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 113.6 ($C_{pyridine}$), 111.1 ($CH_{pyrrole}$), 101.4, 71.1 (C_{alkyne}), 8.6 (CH_2), 0.8 (CH) ppm. **IR (ATR):** $\tilde{\nu}$ = 2926 (w), 2857 (w), 2228 (w), 1721 (m), 1581 (w), 1558 (w), 1498 (s), 1340 (m), 1271 (s), 1121 (m), 1064 (m), 1019 (w), 952 (w), 829 (w), 724 (s), 675 (w), 579 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 208 ([M^+], 68), 207 (100), 206 (16), 205 (17), 193 (8), 192 (6), 181 (11), 180 (38), 179 (20), 168 (3), 155 (21), 152 (4), 89 (4). **HRMS (ESI-TOF):** calcd. for $C_{14}H_{11}N_2$ ([M+H]$^+$) 207.09167, found 207.09121.

3-(Dec-1-yn-1-yl)-4-(1*H*-pyrrol-1-yl)pyridine 4n. Reaction of **1c** (1.57 mmol, 350 mg) and 1-decyne (2.35 mmol, 424 µl,) gave **4n** as a brown solid (244 mg, 56%), mp 76–77 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.77 (bs, 2H, $CH_{pyridine}$), 7.36–7.23 (m, 1H, $CH_{pyridine}$), 6.97 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.31 (t, ^3J = 2.2 Hz, 2H, $CH_{pyrrole}$), 2.45 (t, ^3J = 7.0 Hz, 2H,

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CH_2), 1.65–1.57 (m, 2H, CH_2), 1.47–1.22 (m, 10H, CH_2), 0.89 (t, ^3J = 6.6 Hz, 3H, CH_3) ppm. **^{13}C NMR[7] (62.9 MHz, $CDCl_3$):** δ = 154.0, 146.4 ($CH_{pyridine}$), 121.5, 111.0 ($CH_{pyrrole}$), 31.9, 29.3, 29.2, 29.1, 28.3, 22.7, 19.8 (CH_2), 14.2 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2923 (m), 2853 (w), 2230 (w), 1720 (w), 1575 (s), 1496 (s), 1396 (w), 1339 (m), 1180 (w), 1122 (w), 1063 (s), 1016 (s), 925 (w), 828 (m), 720 (s), 667 (m), 617 (m), 570 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 280 ([M^+], 7), 279 (8), 209 (8), 195 (27), 193 (9), 183 (16), 182 (100), 181 (48), 169 (14), 168 (11), 167 (4), 155 (11), 154 (5). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{24}N_2$ ([M]$^+$) 280.19340, found 280.19281.

General method for cycloisomerization to achieve 6-substetuted pyrrolo[1,2-*a*][1,6]naphthyridines 5.

In a glas tube the Sonogashira product **4a-n** was dissolved in xylene (3 ml, isomeric mixture) under an argon atmosphere. The catalyst $Bi(OTf)_3$ (1 eq.) was added to the mixture. The solution was stirred at 120 °C for 24 h. After cooling to room temperature the crude product was diluted with water and extracted with ethyl acetate. For further purification the organic solvent was evaporated and column chromatography (heptane/acetone, 2:1 → 1:1) was performed.

6-(Phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5a. Reaction of **4a** (0.41 mmol, 100 mg) with $Bi(OTf)_3$ (0.41 mmol, 268 mg) gave **5a** as a white solid (55 mg, 55%); mp 217–218 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.99–8.97 (bs, 1H, $CH_{naphthyr.}$), 8.62 (d, ^3J = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.95–7.94 (m, 1H, $CH_{naphthyr.}$), 7.79 (d, ^3J = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.71–7.68 (m, 2H, CH_{Ph}), 7.53–7.47 (m, 3H, CH_{Ph}), 7.05–7.03 (m, 1H, $CH_{pyrrole}$), 6.93–6.91 (m, 1H, $CH_{pyrrole}$), 6.75–6.72 (m, 1H, $CH_{pyrrole}$) ppm. **^{13}C NMR (62.9 MHz, $CDCl_3$):** δ = 149.2, 145.4 ($CH_{naphthyr.}$), 138.2, 138.1, 135.5, 131.6 (C_{Ar}), 129.0 (CH_{Ph}), 129.0 (CH_{Ph}), 128.5 (CH_{Ph}), 120.6 ($C_{naphthyr.}$), 115.2, 114.8, 114.0, 109.1 (CH_{Ar}), 105.9 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 1673 (w), 1602 (m), 1492 (w), 1258 (s), 1231 (s), 1169 (s), 1035 (s), 816 (w), 766 (m), 697 (m), 631 (s), 573 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 244 ([M^+], 100), 243 (33), 242 (17), 216 (5), 215 (4), 189 (4), 163 (2). **HRMS (EI, 70 eV):** calcd. for $C_{17}H_{12}N_2$ ([M]$^+$) 244.09950, found 244.09913.

[7] Carbon signals for the *meta*- and *para*-position of the pyridine moiety were undetecTable as well as the alkyne signals.

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6-(3-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5b. Reaction of **4b** (0.58 mmol, 150 mg) with $Bi(OTf)_3$ (0.58 mmol, 381 mg) gave **5b** as a white solid (76 mg, 51%); mp 125–126 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.80 (s, 1H, $CH_{naphthyr.}$), 8.45 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.41 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 7.38–7.36 (m, 2H, $CH_{pyrrole/Ar}$), 7.20 (dd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, 1H, CH_{Ar}), 7.05 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 6.91 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.71–6.67 (m, 2H, $CH_{pyrrole}$), 6.58 (s, 1H, $CH_{naphthyr.}$), 2.19 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 151.1, 147.5 ($CH_{naphthyr.}$), 139.0, 138.4, 137.1, 134.5, 131.6 (C_{Ar}), 129.4, 129.3, 128.8, 125.9 (CH_{Ar}), 120.3 (C_{Ar}), 115.3, 114.3, 113.5, 108.3, 105.1 (CH_{Ar}), 21.4 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 3029 (w), 2919 (w), 1732 (w), 1597 (m), 1484 (m), 1414 (w), 1363 (w), 1302 (w), 1202 (w), 1131 (w), 1037 (w), 851 (w), 810 (m), 787 (s), 709 (s), 645 (w), 569 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M^+], 100), 257 (16), 256 (5), 255 (9), 243 (6), 242 (13), 229 (2), 214 (2), 202 (2). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([M]$^+$) 258.11515, found 258.11553.

6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5c. Reaction of **4c** (0.52 mmol, 150 mg) with $Bi(OTf)_3$ (0.52 mmol, 338 mg) gave **5c** as a yellow solid (109 mg, 73%); mp 92–93 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.80 (s, 1H, $CH_{naphthyr.}$), 8.47 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.42 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.22 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.01 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.87 (d, ^4J = 2.6 Hz, 1H, CH_{Ar}), 6.75 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1H, CH_{Ar}), 6.67 (dd, ^3J = 3.8 Hz, ^3J = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.49 (s, 1H, $CH_{naphthyr.}$), 6.32 (dd, ^3J = 3.8 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 3.44 (s, 3H, OMe), 2.10 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 160.1 (C), 150.9, 147.4 (CH), 138.1, 137.3, 134.1, 132.5, 131.1 (C), 130.6 (CH), 120.1 (C), 116.3, 116.3, 114.4, 113.4, 111.5, 108.4, 105.2 (CH), 54.9 (OMe), 20.1 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2951 (w), 2921 (w), 1601 (m), 1491 (m), 1421 (w), 1364 (w), 1250 (s), 1232 (s), 1167 (s), 1113 (w), 1033 (s), 811 (m), 718 (w), 701 (m), 632 (s), 571 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 288 ([M^+], 99), 287 (100), 273 (6), 272 (8), 256 (5), 255 (7), 245 (8), 244 (12), 243 (25), 242 (13), 229 (7), 205 (3). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{16}ON_2$ ([M]$^+$) 288.12511, found 288.12571.

6-(Naphth-1-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5d. Reaction of **4d** (0.68 mmol, 200 mg) with $Bi(OTf)_3$ (0.68 mmol, 446 mg) gave **5d** as a white solid (100 mg, 51%); mp 103–104 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.96 (s, 1H, $CH_{naphthyr.}$), 8.64–8.66 (m, 1H, $CH_{naphthyr.}$), 7.97–7.90 (m, 3H, $CH_{Ar/pyrrole}$), 7.84 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.74 (d, ^3J = 5.7 Hz, 1H, CH_{Ar}), 7.62–7.47 (m, 3H, CH_{Ar}), 7.41–7.34 (m, 1H, $CH_{naphthyl.}$), 7.08 (s, 1H, $CH_{naphthyr.}$), 6.79

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(dd, ^3J = 3.8 Hz, ^3J = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.20 (dd, ^3J = 3.8 Hz, ^4J = 1.2 Hz, 1H, $CH_{pyrrole}$) ppm. **^{13}C NMR (62.9 MHz, $CDCl_3$):** δ = 150.7, 147.2 (CH), 137.6, 135.8, 133.9, 133.2, 132.5, 131.8 (C), 128.8, 128.5, 127.1, 126.3, 126.2, 125.9, 125.5 (CH), 120.0 (C), 116.9, 114.6, 113.3, 108.6, 105.5 (CH) ppm. **IR (ATR):** $\tilde{\nu}$ = 3042 (w), 1598 (w), 1489 (w), 1416 (w), 1364 (w), 1299 (w), 1197 (w), 1030 (m), 906 (m), 854 (w), 800 (m), 774 (s), 712 (s), 664 (m), 569 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 294 ([M$^+$], 100), 293 (93), 292 (54), 291 (12), 290 (6), 265 (6), 264 (6), 238 (4). **HRMS (ESI-TOF):** calcd. for $C_{21}H_{15}N_2$ ([M+H]$^+$) 295.12352, found 295.12336.

6-(4-[Trifluoromethyl]phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5e. Reaction of **4e** (0.64 mmol, 200 mg) with $Bi(OTf)_3$ (0.64 mmol, 420 mg) gave **5e** as a white solid (49 mg, 35%); mp 110–111 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.46 (d, ^3J = 5.8 Hz, 1H, $CH_{naphthyr.}$), 7.44 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.35–7.33 (m, 1H, $CH_{pyrrole}$), 7.32 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 6.88 (d, ^3J = 5.8 Hz, 1H, $CH_{naphthyr.}$), 6.67 (dd, ^3J = 3.8 Hz, ^3J = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.46 (dd, ^3J = 3.8 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 6.39 (s, 1H, $CH_{naphthyr.}$) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 151.3, 148.0 ($CH_{naphthyr.}$), 142.3, 137.3, 132.7, 130.7 (C_{Ar}), 130.5 (q, $^2J_{C,F}$ = 32.4 Hz, C_{Ar}), 128.9 (CH), 125.8 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 125.0 (q, $^1J_{C,F}$ = 272.1 Hz, CF_3), 119.8 ($C_{naphthyr.}$), 116.0, 114.4, 113.8, 108.3, 104.9 (CH) ppm. **^{19}F NMR (282 MHz, C_6D_6):** δ = −62.06 ppm. **IR (ATR):** $\tilde{\nu}$ = 3106 (w), 3026 (w), 1616 (w), 1600 (m), 1500 (w), 1625 (w), 1370 (w), 1322 (s), 1165 (m), 1096 (s), 1066 (s), 1015 (m), 830 (s), 712 (s), 689 (s), 614 (m), 567 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 312 ([M$^+$], 100), 311 (20), 293 (4), 243 (7), 242 (10), 214 (3). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{11}N_2F_3$ ([M]$^+$) 312.08688, found 312.08676.

6-(4-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5f. Reaction of **4f** (0.58 mmol, 150 mg) with $Bi(OTf)_3$ (0.58 mmol, 381 mg) gave **5f** as a white solid (74 mg, 50%); mp 130–131 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.93 (s, 1H, $CH_{naphthyr.}$), 8.57 (d, ^3J = 6.0 Hz, 1H, $CH_{naphthyr.}$) 7.90 (s, 1H, $CH_{naphtyr.}$), 7.83 (d, ^3J = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.52 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 7.26 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 6.97–6.95 (m, 1H, $CH_{pyrrole}$), 6.90–6.88 (m, 1H, $CH_{pyrrole}$), 6.71–6.70 (m, 1H, $CH_{pyrrole}$), 2.38 (s, 3H, Me) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 147.3, 143.3 ($CH_{naphthyr.}$), 139.2, 138.9, 136.3, 134.9, 131.8 (C_{Ar}), 129.8, 128.3 (CH_{Ar}), 121.0 ($C_{naphthyr.}$), 115.9, 114.4, 114.1, 109.6, 106.6 (CH_{Ar}), 21.6 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 1600 (m), 1496 (m), 1424 (w), 1367 (w), 1254 (s), 1161 (s), 1133 (m), 1028 (s), 808 (s), 712 (m), 635 (s), 559 (w) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M$^+$],

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100), 257 (12), 243 (4), 242 (9), 202 (2), 129 (2), 128 (9). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{15}N_2$ ($[M+H]^+$) 259.12352, found 259.12432.

6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5g. Reaction of **4g** (0.64 mmol, 175 mg) with $Bi(OTf)_3$ (0.64 mmol, 419 mg) gave **5g** as a white solid (136 mg, 78%); mp 137–138 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.97 (s, 1H, $CH_{naphthyr.}$), 8.62 (d, ^3J = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.95 (dd, ^3J = 3.1 Hz, ^4J = 1.2 Hz, 1H, $CH_{pyrrole}$), 7.83 (d, ^3J = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.64 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.04 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.00 (s, 1H, $CH_{naphthyr.}$), 6.93 (dd, ^3J = 3.1 Hz, ^3J = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.74 (dd, ^3J = 3.8 Hz, ^4J = 1.2 Hz, 1H, $CH_{pyrrole}$), 3.90 (s, 3H, OMe) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 160.1 (C_{Ar}), 150.4, 146.6 ($CH_{naphthyr.}$), 137.4, 134.4, 131.7 (C_{Ar}), 130.8 (CH_{Ar}), 129.6 (CH_{Ar}), 120.4 ($C_{naphthyr.}$), 114.6, 114.5 (CH_{Ar}), 114.3 (CH_{Ar}), 113.6 ($CH_{naphthyr.}$), 108.6 ($C_{naphthyr.}$), 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 1599 (w), 1493 (w), 1366 (w), 1249 (s), 1232 (s), 1170 (s), 1109 (w), 1036 (s), 1019 (s), 829 (m), 806 (m), 714 (w), 681 (s), 636 (s), 568 (s) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M^+]$, 100), 259 (19), 231 (21), 230 (17), 29 (20), 205 (9), 203 (7), 176 (5). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{15}ON_2$ ($[M+H]^+$) 275.11844, found 275.12061.

6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5h. Reaction of **4h** (0.67 mmol, 200 mg,) with $Bi(OTf)_3$ (0.67 mmol, 437 mg) gave **5h** as a white solid (82 mg, 41%); mp 70–71 °C. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 8.94 (s, 1H, $CH_{naphthyr.}$), 8.59 (d, ^3J = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.89 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.89 (d, ^3J = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.66–7.62 (m, 2H, CH_{Ar}), 7.55–7.50 (m, 2H, CH_{Ar}), 7.00 (s, 1H, $CH_{naphthyr.}$), 6.87 (dd, ^3J = 3.0 Hz, ^3J = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.73 (dd, ^3J = 3.8 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 1.40 (s, 9H, CH_{3tBu}) ppm. **^{13}C NMR (62.9 MHz, $CDCl_3$):** δ = 151.8 (C_{Ar}), 150.5, 146.7 ($CH_{naphthyr.}$), 137.4, 135.4, 134.6, 131.5 (C_{Ar}), 128.1, 125.8 (CH_{Ar}), 120.4 ($C_{naphthyr.}$), 114.9, 114.6, 113.5, 108.6, 105.3 (CH), 34.9 (C), 31.5 (CH_{3tBu}) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (m), 2865 (w), 1597 (m), 1491 (m), 1421 (w), 1361 (m), 1267 (w), 1178 (w), 1108 (w), 1037 (w), 908 (w), 830 (s), 809 (m), 714 (s), 701 (s), 621 (w), 542 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 300 ($[M^+]$, 100), 286 (18), 285 (81), 284 (5), 270 (11), 269 (10), 268 (7), 257 (21), 256 (6), 255 (15), 243 (12), 242 (14), 214 (3), 143 (6), 128 (28). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{20}N_2$ ($[M]^+$) 300.39690, found 300.39686.

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6-(4-*n*-Propylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5i. Reaction of **4i** (0.45 mmol, 130 mg) with $Bi(OTf)_3$ (0.45 mmol, 298 mg) gave **5i** as a yellow solid (68 mg, 53%); mp 90–91 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.44 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.53 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.37 (dd, ^3J = 2.9 Hz, ^4J = 1.4 Hz, 1H, $CH_{pyrrole}$), 7.13 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 6.92 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.72 (dd, ^3J = 3.8 Hz, ^4J = 1.4 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, ^3J = 3.8 Hz, ^3J = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.60 (s, 1H, $CH_{naphthyr.}$), 2.50 (t, ^3J = 7.6 Hz, 2H, CH_2), 1.59 (tq, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 2H, CH_2), 0.90 (t, ^3J = 7.3 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 151.1, 147.4 ($CH_{naphthyr.}$), 143.1, 137.1, 136.4, 134.4, 131.6 (C), 129.0, 128.6 (CH_{Ar}), 120.3 ($C_{naphthyr.}$), 115.2, 114.3, 113.5, 108.2, 105.1 (CH_{Ar}), 38.1, 24.9 (CH_2), 14.0 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2955 (w), 2926 (w), 2868 (w), 1596 (m), 1489 (m), 1422 (m), 1364 (w), 1302 (w), 1177 (w), 829 (m), 808 (s), 713 (s), 700 (s), 568 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 286 ([M^+], 100), 258 (13), 257 (66), 256 (11), 255 (25), 243 (6), 242 (8), 229 (3), 228 (3), 202 (2). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{18}N_2$ ([M]$^+$) 286.14645, found 286.14708.

6-(4-*n*-Hexylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5j. Reaction of **4j** (0.46 mmol, 150 mg,) with $Bi(OTf)_3$ (0.46 mmol, 299 mg) gave **5j** as a yellow oil (67 mg, 45%). **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.44 (d, ^3J = 5.8 Hz, 1H, $CH_{naphthyr.}$), 7.55 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.37 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.17 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 6.91 (d, ^3J = 5.8 Hz, 1H, $CH_{naphthyr.}$), 6.73 (dd, ^3J = 3.8 Hz, ^4J = 1.3 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, ^3J = 3.8 Hz, ^3J = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.61 (s, 1H, $CH_{naphthyr.}$), 2.57 (t, ^3J = 7.7 Hz, 2H, CH_2), 1.62–1.58 (m, 2H, CH_2), 1.34–1.24 (m, 6H, CH_2), 0.90 (t, ^3J = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 151.1, 147.4 ($CH_{naphthyr.}$), 143.4, 137.1, 136.4, 134.4, 131.6 (C), 129.0, 128.7 (CH_{Ar}), 120.3 (C), 115.2, 114.3, 113.5, 108.3, 105.1 (CH), 36.2, 32.2, 31.9, 29.4, 23.1 (CH_2), 14.4 (CH_3) ppm. **IR (ATR):** $\tilde{\nu}$ = 2923 (s), 2853 (m), 1597 (m), 1491 (m), 1422 (m), 1365 (w), 1303 (w), 1176 (w), 1037 (w), 828 (s), 810 (s), 714 (s), 702 (s), 569 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 328 ([M^+], 100), 271 (5), 270 (3), 258 (13), 257 (53), 256 (10), 255 (22), 243 (4), 242 (7), 229 (3), 228 (3). **HRMS (EI, 70 eV):** calcd. for $C_{23}H_{24}N_2$ ([M]$^+$) 328.19340, found 328.19321.

6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5k. Reaction of **4k** (0.46 mmol, 115 mg,) with $Bi(OTf)_3$ (0.46 mmol, 301 mg) gave **5k** as a white solid (82 mg, 72%); mp 234–235 °C. **^{1}H NMR (300 MHz, C_6D_6):** δ = 8.76 (s, 1H, $CH_{naphthyr.}$), 8.43 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.34 (dd, ^3J = 2.8 Hz, ^4J = 1.6 Hz, 1H, $CH_{pyrrole}$), 7.26 (dd, ^3J = 5.0 Hz,

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^4J = 1.3 Hz, 1H, $CH_{thioph.}$), 7.19 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, $CH_{thioph.}$), 6.97 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, $CH_{thioph.}$), 6.88 (d, ^3J = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.70–6.66 (m, 2H, $CH_{pyrrole}$), 6.59 (s, 1H, $CH_{naphtyr.}$) ppm. **^{13}C NMR (75 MHz, C_6D_6):** δ = 151.0, 147.5 ($CH_{naphthyr.}$), 139.3, 137.0, 131.1, 128.9 (C), 127.9, 126.0, 123.6 (CH), 120.0 ($C_{naphthyr.}$), 114.9, 114.2, 113.5, 108.2, 105.0 ($CH_{naphthyr.}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2922 (w), 1599 (w), 1495 (w), 1422 (w), 1357 (w), 1258 (s), 1230 (s), 1171 (s), 1034 (s), 838 (w), 785 (m), 706 (s), 636 (s), 570 (m), 540 (m) cm^{-1}. **MS (EI, 70 eV):** *m/z* (%) = 250 ([M^+], 100), 249 (18), 248 (9), 223 (3), 222 (2), 205 (10), 204 (2), 203 (3), 178 (3), 151 (2). **HRMS (EI, 70 eV):** calcd. for $C_{15}H_{10}N_2S$ ([$M]^+$) 250.05592, found 250.05610.

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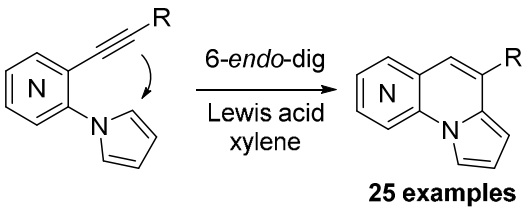
Table of contents entry

"Synthesis of pyrrolo[1,2-*a*]naphthyridines by Lewis acid mediated cycloisomerization"

Authors: Anika Flader,[a,b] Silvio Parpart,[a] Peter Ehlers,[a,b] and Peter Langer*[a,b]

Graphic (max. 8 cm x 4 cm):



Entry: Functionalized pyrrolo[1,2-*a*]naphthyridines were synthesized by application of $PtCl_2$ and $Bi(OTf)_3$ as simple Lewis acids in a cycloisomerization reaction.