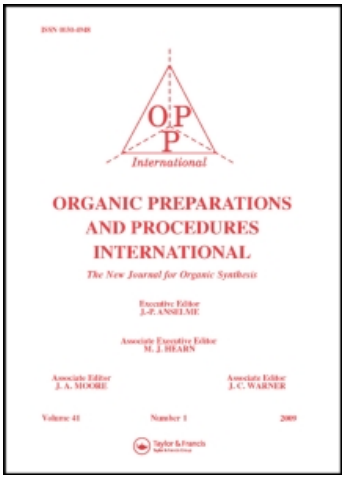

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

Regioselective Nucleophilic Aromatic Substitution of Benzo[*c*][2,7]naphthyridines

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Online publication date: 07 April 2010

To cite this Article Nutaitis, Charles F. , Przyuski, Katrin and Ross, Vincent(2010) 'Regioselective Nucleophilic Aromatic Substitution of Benzo[*c*][2,7]naphthyridines', Organic Preparations and Procedures International, 42: 2, 133 — 141
To link to this Article: DOI: 10.1080/00304941003676895
URL: http://dx.doi.org/10.1080/00304941003676895

Organic Preparations and Procedures International, 42:133–141, 2010

ISSN: 0030-4948 print
DOI: 10.1080/00304941003676895

Regioselective Nucleophilic Aromatic Substitution of Benzo[*c*][2,7]naphthyridines

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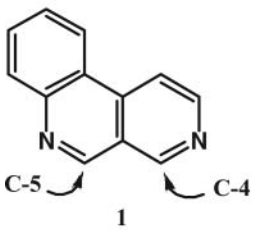
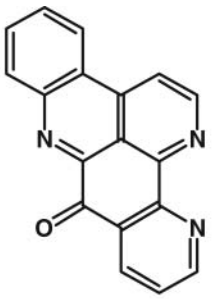
Over the past 25 years a number of biologically active natural products containing a benzo[*c*][2,7]naphthyridine subunit **1** have been reported.[1–3] Invariably, these natural products are C-4 and C-5 substituted, usually in the form of an additional fused ring system, as seen in ascididemine **2**.[4] It was envisioned that these natural products could be synthesized *via* two nucleophilic aromatic substitutions of **1**, at C-4 and C-5, accomplished through a series of sequential nucleophilic addition/dehydrogenation reactions utilizing appropriate dianion synthons such as **3**.



1



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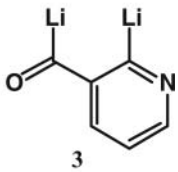

3

Due to the non-equivalency of C-4 and C-5, the correct order of anion generation in synthons such as **3** is crucial for a successful synthesis of the natural products as opposed to their non-natural regioisomers. However, studies pertaining to the regioselectivity of sequential nucleophilic additions of organolithiums to the parent benzo[*c*][2,7]naphthyridine system **1** have not been previously reported. We report herein the results of our studies on the regioselective nucleophilic substitution of **1**.

Perusal of the structures of the natural products in this class of compounds reveals that most of them possess an aromatic heterocyclic system directly linked to the naphthyridine system at either C-4 or C-5 (for example, the naphthyridine-pyridine bond in ascididemine **2**, shown above). Thus, lithiated aromatic heterocycles were chosen as the nucleophiles in this study. Moreover, mixed heteroarene oligomers, a class of compounds to which

Received October 16, 2009; in final form December 18, 2009.
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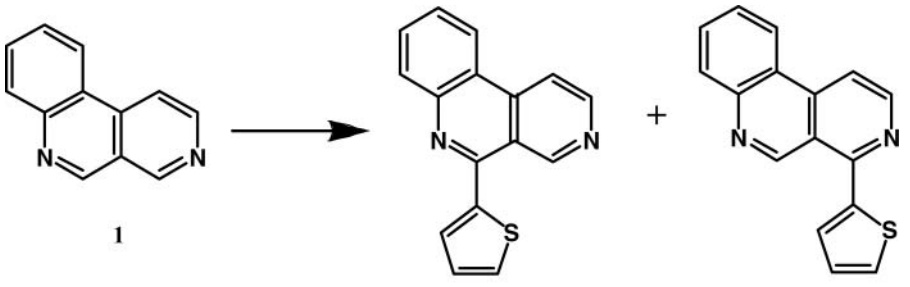
the expected products belong, have been shown to possess various biological, optical, and electronic properties.[4–13] However, very few derivatives of **1** that possess an aromatic heterocyclic substituent at C-4 or C-5 have been reported, and absolutely no derivatives of **1** containing aromatic heterocyclic substituents at *both* C-4 and C-5 have been reported.

In order to ease product identification, the first two nucleophiles chosen for study were 2-lithiothiophene and 2-lithiobenzo[b]furan; analogs of **1**, containing either a 2-thienyl or 2-benzo[b]furyl substituent at C-4, had been previously reported, having been synthesized by a different route.[14] A facile means to initially identify the regioisomeric products was critical, as routine NMR was not expected to be highly revealing. The largest structural change upon nucleophilic substitution of **1** is loss of a proton at C-4 or C-5, which appear as two extremely close singlets at 9.41 and 9.38 ppm. However, the chemical shift of the proton remaining after substitution would undoubtedly change due to electronic perturbation by the newly introduced heteroaromatic system, so monitoring the disappearance of the C-4 or C-5 proton signal would not be feasible. Although the chemical shifts of the remaining naphthyridine protons would also change slightly upon nucleophilic substitution, the overall characteristics of these resonances were expected to remain constant with respect to multiplicity and integration. As a result, easily predictable and identifiable features were not expected in the proton NMR to allow regioisomer identification.

Upon treatment of benzo[*c*][2,7]naphthyridine with one equivalent of 2-lithiothiophene in THF at −78°C and dehydrogenation with excess manganese dioxide in methylene chloride, two main products as well as unreacted starting material were apparent by both thin layer chromatography and proton NMR. In the proton NMR, the starting material C-4/C-5 protons were evident in the 9.4 ppm range while two additional singlets, corresponding to the remaining C-4 or C-5 proton in each of the regioisomeric products, appeared in the 9.9 ppm range. Thin layer chromatography (3:1 diethyl ether/hexane) exhibited two main overlapping product spots higher than starting material, with the higher one appearing fluorescent under UV-light. Separation of the products by flash chromatography and subsequent analysis revealed that both regioisomers had formed, in a 6:1 ratio, with the major isomer corresponding to substitution at C-5 (determined by comparison of melting points obtained for the two products to that previously reported for **5a**). It was thus determined that the minor C-4 substituted isomer **5a** corresponded to the higher Rf/fluorescent spot and the major C-5 substituted isomer **4a** corresponded to the lower Rf/non-fluorescent spot.

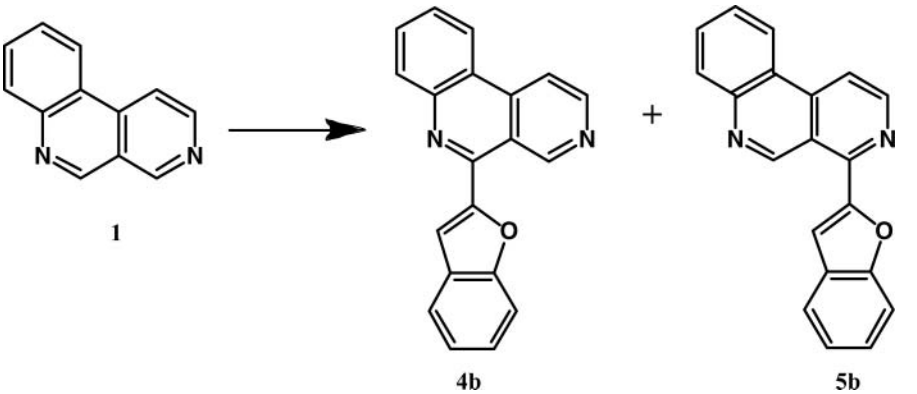


1 **4a** **5a**

This result was not unexpected as the C-5/N-6 double bond in **1** is comparable to the reactive 9,10 carbon-carbon double bond in phenanthrene.

Although the two regioisomeric products, **4a** and **5a**, were successfully separated and the nucleophilic substitution of **1** was demonstrated to be regioselective for C-5, the overall yield of the reaction was only 22%. In an effort to improve the yield, the reaction was repeated with the addition of one equivalent of N,N,N',N'-tetramethylethylenediamine (TMEDA). Once again, both **4a** and **5a** were formed in a 6:1 ratio, but the overall yield improved to 55% (47% isolated yield of **4a**). Employment of excess 2-lithiothiophene with TMEDA did not further improve the reaction yield and resulted in a more complex product mixture as evidenced by TLC.

Similarly, treatment of **1** with 2-lithiobenzo[b]furan in THF at −78°C in the presence of one equivalent of TMEDA afforded both regioisomers **4b** and **5b**, in a 5.5:1 ratio, and an overall yield of 39%. Comparison of the melting points of the products with that previously reported for **5b**, revealed that the C-5 substituted isomer **4b** was the major product. As before, the minor product **5b** exhibited a higher Rf value upon TLC and was fluorescent under UV-light.

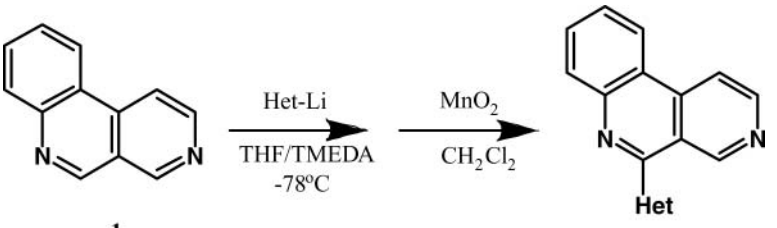


Complete separation of the regioisomers in both of the above reactions was extremely tedious, but necessary for isomer identification. However, it was noticed that it was always the minor isomers **5a** and **5b** that proved troublesome, often eluting as a mixture with a very small amount of **4a** and **4b**, respectively. In contrast, it was relatively easy to obtain the major isomers in pure form *via* less meticulous chromatography. Since the minor isomers were present in minute quantities, separation in all subsequent reactions targeted only the major isomers for complete purification and characterization. The results of these reactions are summarized in *Table 1*.

Attention was next focused on preparation of 4,5-diheteroaryl substituted derivatives of benzo[*c*][2,7]naphthyridine **1**, *via* a second nucleophilic addition/oxidation sequence, using the previously prepared 5-substituted derivatives **4** as substrates. In general, it was found that yields for the second nucleophilic substitution were much lower, and some reactions failed completely, resulting in recovery of unreacted starting material. The results are summarized in *Table 2*.

Although the relatively low yields obtained for the preparation of **6** can be attributed to steric hindrance, due to the peri substituent located at C-5, and to the inherent lower reactivity of C-4 toward nucleophilic attack, it is obvious that other factors are also important. As can be seen in *Table 2*, very low yields were obtained for products **6d** and **6e**, even though the substrate, **4a**, contains the smallest C-5 substituent of those studied. It was

Table 1
Preparation of 5-Heteroaryl Substituted Benzo[*c*][2,7]naphthyridines

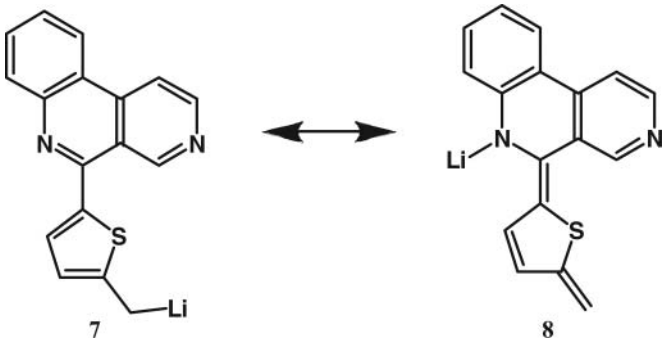


1 **4**

Product	Het	Yield (%)[a]
4a	2-Thienyl	47
4b	2-Benzo[b]furyl	33
4c	2-Benzo[b]thienyl	49
4d	2-Benzothiazolyl	31
4e	2-Thiazolyl	46
4f	2-Bithienyl	28
4g	2-(5-Methylthienyl)	35
4h	2-(5-Phenylthienyl)	31
4i	2-(1-Methylimidazolyl)	0
4j	2-Benzoxazolyl	0

[a]) Yields after flash chromatography.

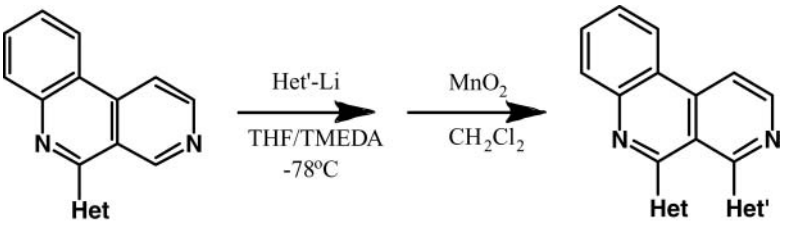
envisioned that the remaining α-proton on the thiophene substituent might be interfering with the reaction due to competing deprotonation. Thus, compound **4g**, which lacks a proton at this site, was prepared; however, **4g** also failed to undergo nucleophilic substitution. It is possible that **4g** undergoes lateral deprotonation due to the ability of N-6 to resonance stabilize the resulting anion (**7** $\longleftrightarrow$ **8**).



7 **8**

In order to test the hypothesis that deprotonation was interfering with nucleophilic substitution, substrates **4a** and **4g** were treated with 2-lithiothiophene followed by methyl

Table 2
Preparation of 4,5-Diheteroaryl Substituted Benzo[*c*][2,7]naphthyridines



4 6

Product	Het	Het'	Yield (%)[a]
6a	2-Benzothiazolyl	2-Thiazolyl	21
6b	2-Benzo[b]thienyl	2-Benzothiazolyl	35
6c	2-Benzo[b]thienyl	2-Bithienyl	19
6d	2-Thienyl	2-Thienyl	2[b]
6e	2-Thienyl	2-Benzo[b]furyl	6[b]
6f	2-(5-Methylthienyl)	2-Benzo[b]thienyl	0
6g	2-(5-Phenylthienyl)	2-Thienyl	0

[a]Yields after flash chromatography. [b]Identified by proton NMR; products were not fully characterized due to the extremely small quantities obtained.

iodide. However, in both cases starting material was recovered and no evidence of methylation was observed in the proton NMR spectra. Substrate **4h**, which lacks protons capable of deprotonation, also failed to undergo nucleophilic substitution, but this is likely due to steric hindrance.

Studies are currently underway to further determine the scope and limitations of nucleophilic addition to benzo[*c*][2,7]naphthyridine **1** and to explore the application of this methodology to the total synthesis of benzo[*c*][2,7]naphthyridine natural products.

Acknowledgements

We thank Lafayette College for supporting this work and the Kresge Foundation for the purchase of a 400 MHz FT-NMR spectrometer.

Experimental Section

All reactions were performed in oven-dried glassware (120°C), and all lithiation reactions were performed under nitrogen. Tetrahydrofuran was distilled from sodium/benzophenone. Thin layer chromatography was performed on precoated (0.25 mm) silica gel 60 F_{254} plastic sheets and was visualized with 254 nm ultraviolet light. Flash chromatography was performed with silica gel 60 (200–400 mesh). Proton and carbon NMR spectra were recorded on a Jeol Eclipse400 FT-NMR spectrometer; chemical shifts are reported in parts per million relative to internal-TMS (proton) or the solvent chloroform-d (carbon). Melting

points were determined in open capillary tubes with a Mel-Temp Laboratory Devices apparatus and are uncorrected. All starting materials were commercially available except for benzo[*c*][2,7]naphthyridine, which was prepared as previously described.[15]

Preparation of 5-(2-Thienyl)benzo[c][2,7]naphthyridine (4a) and 4-(2-Thienyl)-benzo[c][2,7]naphthyridine (5a)

To a magnetically stirred solution of thiophene (0.20 mL, 1.2 mmol) and TMEDA (0.20 mL, 1.3 mmol) in dry THF (5 mL) at −78°C under nitrogen, was added by means of a syringe n-butyllithium (0.50 mL, 2.36 M, 1.2 mmol) over a period of 1 min. The reaction mixture was allowed to warm over a period of 30 min then recooled to −78°C. A solution of benzo[*c*][2,7]naphthyridine (0.22 g, 1.2 mmol) in dry THF (5 mL) was added by means of a syringe over 3 min. The reaction mixture was allowed to slowly warm to room temperature and stirred for 24 h. The dark reaction mixture was diluted with water (25 mL) and extracted with chloroform (3 × 25 mL). The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The resulting brown oil was dissolved in methylene chloride (25 mL), manganese dioxide (0.60 g, 6.9 mmol) was added and the mixture was magnetically stirred for 24 h. The manganese dioxide was removed by filtering the reaction mixture through Celite and the Celite was washed with acetone until the filtrate eluting from the Celite was colorless. Silica gel was added to the filtrate and the mixture was concentrated *in vacuo* to a dry powder. Flash chromatography (2:1 hexanes/diethyl ether) gave 4-(2-thienyl)benzo[*c*][2,7]naphthyridine **(5a)** cleanly as a light yellow solid (0.025 g, 8%): mp. 154–156°C (*Lit.*[14] mp. 159°C) followed by 5-(2-thienyl)benzo[*c*][2,7]naphthyridine **(4a)** cleanly as a light yellow solid (0.153 g, 47%), which was recrystallized from hexanes/diethyl ether: mp. 98–100°C; ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 8.93 (d, 1H), 8.51 (dd, 1H), 8.38 (d, 1H), 8.21 (dd, 1H), 7.83 (td, 1H), 7.85–7.81 (m, 2H), 7.62 (dd, 1H), 7.26 (dd, 1H); ^{13}C NMR($CDCl_3$): δ 153.5, 151.8, 148.6, 145.2, 141.4, 138.6, 131.2, 130.5, 130.2, 129.1, 127.9, 127.6, 122.5, 121.4, 119.7, 115.5.

Anal. Calcd for $C_{16}H_{10}N_2S$: C, 73.26; H, 3.84; N, 10.68; S, 12.22. Found: C, 73.15; H, 3.84; N, 10.66; S, 12.09.

5-(2-Benzo[*b*]furyl)benzo[*c*][2,7]naphthyridine (4b) and 4-(2-Benzo[*b*]furyl)-benzo[*c*][2,7]naphthyridine (5b) were prepared analogously from benzo[*c*][2,7]-naphthyridine and 2-lithiobenzo[b]furan. Flash chromatography with 2:1 hexanes/diethyl ether gave 4-(2-benzo[b]furyl)benzo[*c*][2,7]naphthyridine **(5b)** as a yellow solid (6%): mp. 190–192°C (*Lit.*[14] mp. 193°C) followed by 5-(2-benzo[*b*]furyl)benzo[*c*][2,7]naphthyridine **(4b)** as a yellow solid (33%) which was recrystallized from hexanes/acetone: mp. 148–150°C: ^{1}H NMR ($CDCl_3$): δ 10.30 (s, 1H), 8.93 (d, 1H), 8.49 (dd, 1H), 8.36 (d, 1H), 8.23 (dd, 1H), 7.83 (ddd, 1H), 7.74–7.67 (m, 4H), 7.42 (td, 1H), 7.32 (td, 1H); ^{13}C NMR($CDCl_3$): δ 155.9, 154.4, 152.0, 149.0, 148.6, 145.2, 138.5, 131.2, 130.7, 128.1, 128.0, 126.1, 123.7, 122.6, 122.1, 121.9, 119.6, 115.4, 112.1, 110.5.

Anal. Calcd for $C_{20}H_{12}N_2O$: C, 81.07; H, 4.08; N, 9.45. Found: C, 80.77; H, 4.04; N, 9.33.

5-(2-Benzo[*b*]thienyl)benzo[*c*][2,7]naphthyridine (4c) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithiobenzo[b]thiophene as a yellow solid (49%) which was recrystallized from hexanes/acetone: mp. 161–163°C; ^{1}H NMR ($CDCl_3$): δ 9.99

(s, 1H), 8.97 (d, 1H), 8.56 (dd, 1H), 8.43 (d, 1H), 8.26 (dd, 1H), 7.97–7.90 (m, 3H), 7.87 (ddd, 1H), 7.73 (ddd, 1H), 7.46–7.43 (m, 2H); ^{13}C NMR($CDCl_3$): δ 153.5, 151.6, 148.7, 145.5, 141.5, 141.0, 140.1, 138.6, 131.3, 130.7, 128.0, 127.2, 125.8, 124.8, 124.7, 122.6, 122.4, 121.6, 119.8, 115.6.

Anal. Calcd for $C_{20}H_{12}N_2S$: C, 76.90; H, 3.87; N, 8.97; S, 10.26. Found: C, 76.80; H, 3.86; N, 8.97; S, 10.08.

5-(2-Benzothiazolyl)benzo[*c*][2,7]naphthyridine (4d) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithiobenzothiazole as a white solid (31%) which was recrystallized from diethyl ether/acetone: mp. 228–230°C; ^{1}H NMR ($CDCl_3$): δ 11.40 (s, 1H), 9.01 (d, 1H), 8.58 (dd, 1H), 8.42 (d, 1H), 8.29 (dd, 1H), 8.24 (d, 1H), 8.02 (dd, 1H), 7.89 (ddd, 1H), 7.79 (ddd, 1H), 7.56 (ddd, 1H), 7.49 (ddd, 1H); ^{13}C NMR($CDCl_3$): δ 169.6, 154.7, 153.4, 149.8, 148.7, 144.6, 138.4, 136.2, 131.2, 131.0, 130.8, 128.9, 126.5, 126.4, 124.6, 122.7, 121.7, 119.2, 115.1.

Anal. Calcd for $C_{19}H_{11}N_3S$: C, 72.82; H, 3.54; N, 13.41; S, 10.23. Found: C, 72.73; H, 3.64; N, 13.31; S, 10.02.

5-(2-Thiazolyl)benzo[*c*][2,7]naphthyridine (4e) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithiothiazole as a pale yellow solid (46%) which was recrystallized from diethyl ether/acetone: mp. 180–181°C; ^{1}H NMR ($CDCl_3$): δ 11.17 (s, 1H), 8.96 (d, 1H), 8.53 (dd, 1H), 8.37 (d, 1H), 8.21 (dd, 1H), 8.11 (d, 1H), 7.85 (ddd, 1H), 7.73 (ddd, 1H), 7.58 (d, 1H); ^{13}C NMR($CDCl_3$): δ 169.6, 153.4, 149.8, 148.7, 144.6, 144.5, 138.4, 131.1, 130.5, 128.4, 122.9, 122.7, 122.5, 118.9, 115.0.

Anal. Calcd for $C_{15}H_9N_3S$: C, 68.42; H, 3.45; N, 15.96; S, 12.18. Found: C, 68.41; H, 3.44; N, 15.97; S, 11.99.

5-(2-Bithienyl)benzo[*c*][2,7]naphthyridine (4f) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithiobithiophene as an orange solid (28%) which was recrystallized from diethyl ether/acetone: mp. 175–177°C; ^{1}H NMR ($CDCl_3$): δ 9.93 (s, 1H), 8.93 (d, 1H), 8.51 (d, 1H), 8.39 (d, 1H), 8.19 (d, 1H), 7.83 (td, 1H), 7.68 (td, 1H), 7.64 (d, 1H), 7.33 (dd, 1H), 7.31 (d, 1H), 7.29 (dd, 1H), 7.07 (dd, 1H); ^{13}C NMR($CDCl_3$): δ 152.8, 151.4, 148.7, 145.2, 141.1, 140.4, 138.7, 137.0, 131.3, 131.0, 130.4, 128.2, 127.6, 125.5, 124.8, 124.4, 122.5, 121.4, 119.5, 115.6.

Anal. Calcd for $C_{20}H_{12}N_2S_2$: C, 69.74; H, 3.51; N, 8.13; S, 18.62. Found: C, 69.66; H, 3.44; N, 8.01; S, 18.49.

5-(2-(5-Methylthienyl))benzo[*c*][2,7]naphthyridine (4g) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithio-5-methylthiophene as a tan solid (35%) which was recrystallized from hexanes/acetone: mp. 123–125°C; ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 8.89 (d, 1H), 8.45 (d, 1H), 8.33 (d, 1H), 8.15 (d, 1H), 7.79 (td, 1H), 7.63 (td, 1H), 7.49 (d, 1H), 6.91 (dd, 1H), 2.60 (s, 3H); ^{13}C NMR($CDCl_3$): δ 153.5, 151.7, 148.5, 145.2, 144.2, 139.2, 138.6, 131.1, 130.6, 130.3, 127.3, 126.4, 122.5, 121.2, 119.6, 115.5, 15.6.

Anal. Calcd for $C_{17}H_{12}N_2S$: C, 73.88; H, 4.38; N, 10.14; S, 11.60. Found: C, 73.87; H, 4.33; N, 10.11; S, 11.76.

5-(2-(5-Phenylthienyl))benzo[*c*][2,7]naphthyridine (4h) was prepared analogously from benzo[*c*][2,7]naphthyridine and 2-lithio-5-phenylthiophene as a yellow solid (31%) which was recrystallized from hexanes/acetone: mp. 143–145°C; ^{1}H NMR ($CDCl_3$): δ 9.94 (s, 1H), 8.93 (d, 1H), 8.50 (dd, 1H), 8.38 (d, 1H), 8.21 (dd, 1H), 7.83 (ddd, 1H), 7.74–7.66 (m, 4H), 7.45–7.41 (m, 3H), 7.34 (ddd, 1H); ^{13}C NMR($CDCl_3$): δ 153.1, 151.6, 148.6,

148.0, 145.2, 140.8, 138.7, 134.0, 131.3, 131.2, 130.4, 129.1, 128.3, 127.6, 126.2, 124.0, 122.5, 121.4, 119.6, 115.6.

Anal. Calcd for $C_{22}H_{14}N_2S$: C, 78.08; H, 4.17; N, 8.28; S, 9.47. Found: C, 78.05; H, 4.10; N, 8.23; S, 9.62.

5-(2-Benzothiazolyl)-4-(2-thiazolyl)benzo[*c*][2,7]naphthyridine (6a) was prepared analogously from 5-(2-benzothiazolyl)benzo[*c*][2,7]naphthyridine **(4d)** and 2-lithiothiazole as a yellow solid (21%) which was recrystallized from hexanes/acetone: mp. 195–197°C; ^{1}H NMR ($CDCl_3$): δ 8.99 (d, 1H), 8.58 (dd, 1H), 8.46 (d, 1H), 8.30 (dd, 1H), 7.94–7.89 (m, 2H), 7.78 (ddd, 1H), 7.67–7.65 (m, 1H), 7.39–7.32 (m, 2H), 7.22 (d, 1H), 7.06 (d, 1H); ^{13}C NMR($CDCl_3$): δ 169.7, 169.6, 153.4, 153.0, 152.3, 147.0, 144.3, 143.2, 140.8, 135.4, 131.5, 130.6, 128.8, 125.9, 125.7, 123.2, 122.8, 121.9, 121.7, 121.1, 115.9, 115.0.

Anal. Calcd for $C_{22}H_{12}N_4S_2$: C, 66.65; H, 3.05; N, 14.13; S, 16.17. Found: C, 66.43; H, 3.19; N, 13.87; S, 15.92.

5-(2-Benzo[b]thienyl)-4-(2-benzothiazolyl)benzo[*c*][2,7]naphthyridine (6b) was prepared analogously from 5-(2-benzo[b]thienyl)benzo[*c*][2,7]naphthyridine **(4c)** and 2-lithiobenzothiazole as a bright yellow solid (35%) which was recrystallized from hexanes/acetone: mp. 202–204°C; ^{1}H NMR ($CDCl_3$): δ 8.99 (d, 1H), 8.53 (d, 1H), 8.47 (d, 1H), 8.27 (dd, 1H), 7.87 (td, 1H), 7.73–7.64 (m, 3H), 7.59 (d, 1H), 7.31 (dd, 1H), 7.16–6.98 (m, 5H); ^{13}C NMR($CDCl_3$): δ 167.8, 153.4, 153.0, 146.7, 145.0, 144.8, 141.0, 140.1, 139.2, 135.4, 131.6, 130.4, 127.9, 125.9, 125.7, 125.6, 124.7, 123.9, 123.5, 123.4, 122.6, 121.8, 121.3, 120.9, 117.8, 115.8.

Anal. Calcd for $C_{27}H_{15}N_3S_2$: C, 72.78; H, 3.39; N, 9.43; S, 14.39. Found: C, 72.94; H, 3.43; N, 9.28; S, 14.30.

5-(2-Benzo[b]thienyl)-4-(2-bithienyl)benzo[*c*][2,7]naphthyridine (6c) was prepared analogously from 5-(2-benzo[b]thienyl)benzo[*c*][2,7]naphthyridine **(4c)** and 2-lithiobithiophene as an orange/brown solid (19%) which was recrystallized from hexanes/acetone: mp. 197–201°C (dec); ^{1}H NMR ($CDCl_3$): δ 8.93 (d, 1H), 8.54 (d, 1H), 8.31 (d, 1H), 8.25 (d, 1H), 7.88 (t, 1H), 7.81 (d, 1H), 7.72 (t, 1H), 7.51 (d, 1H), 7.28–7.16 (m, 4H), 7.05 (d, 1H), 6.97–6.95 (m, 1H), 6.79 (d, 1H), 6.61 (d, 1H); ^{13}C NMR($CDCl_3$): δ 153.4, 153.1, 146.9, 144.7, 143.7, 142.9, 141.1, 140.1, 139.9, 139.8, 136.9, 131.8, 131.3, 130.1, 127.9, 127.7, 125.2, 125.1, 124.4, 124.1, 122.8, 122.2, 121.2, 115.8, 113.0.

Anal. Calcd for $C_{28}H_{16}N_2S_3$: C, 70.56; H, 3.38; N, 5.88; S, 20.18. Found: C, 70.65; H, 3.33; N, 5.84; S, 20.09.

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