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Unprecedented Negishi Coupling at C−Br in the Presence of a Stannyl Group as a Convenient Approach to Pyridinylstannanes and Their Application in Liquid Crystal Synthesis

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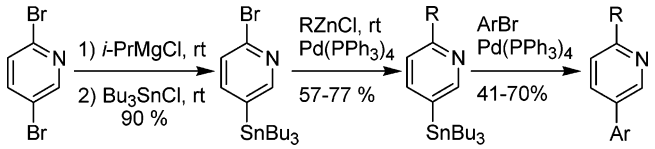


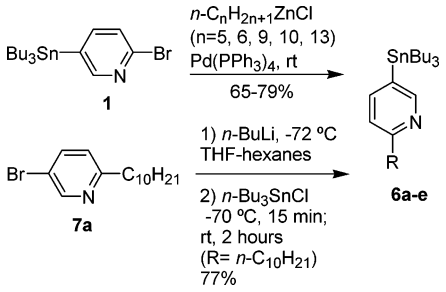
The 2-bromo-5(or 6)-tri-*n*-butylstannylpyridines, prepared from dibromopyridines and *i*-PrMgCl at room temperature, undergo Negishi coupling with either alkyl or arylzinc chlorides. The new alkyl- and aryl-substituted pyridylstannanes produced are shown to be suitable for further functionalization by Stille coupling. A group of new liquid crystalline materials with aromatic cores comprised of pyridine and thiophene rings were prepared utilizing these new pyridinylstannanes as key intermediates.

Introduction

A synthetic strategy wherein a substrate bearing both a halide and a group IV metal functionality selectively reacts at the halide site and leaves the metal group intact and available for subsequent transformations would be very useful. To our knowledge, the few examples of this strategy have been reported only for a combination of aryl halide and R_3Si functionalities.[1,2] For example, 2,5-dihexyl-1-bromo-4-trimethylsilylbenzene was converted into 2,5-dihexyl-1-aryl-4-trimethylsilylbenzene via initial transformation of the bromide into a boronic acid followed by Suzuki coupling with an aryl iodide. Here the TMS group must next be converted into an iodide suitable for a subsequent Pd-catalyzed Suzuki reaction to be performed.[1a] As another example, 1-bromo-4-trimethylsilylbenzene underwent Pd-catalyzed Kumada coupling with a Grignard reagent to obtain 1-(undec-10-enyl)-4-trimethylsilylbenzene. Here again, in an intervening step, the precursor TMS group had to be converted into an iodide, which is then the active site for a subsequent Pd-catalyzed Sonogashira coupling.[2]

A clear synthetic advantage should result from a comparable combination of halide and R_3Sn functionalities since aryl R_3Sn derivatives react directly in many organometallic couplings while most aryl R_3Si derivatives do not (although the recent improvements in Hiyama coupling of organosilicon reagents with aryl halides may make silicon derivatives an attractive alternative to toxic tin compounds[3]). Thus, the use of R_3Sn saves the additional step wherein the R_3Si group must otherwise be converted to a halogen prior to a second organometallic coupling.

SCHEME 1. The Successful Negishi Coupling of 2-Bromo-5-(tri-*n*-butylstannyl)pyridine (1) with Alkylzinc Chlorides and the Bromine−Metal Exchange Reaction as Practical Methods for the Preparation of 2-Alkylpyridin-5-yl Stannanes 6a−e



A pyridine ring bearing both a halogen and a tin moiety may serve as a valuable intermediate for the preparation of a variety of materials. As described in the literature, the trialkylstannyl group of halotrialkyltinpyridines has been exploited in Stille reactions with both vinyl and aryl halides. For example, the

* To whom correspondence should be addressed.

(1) (a) Hensel, V.; Schlüter, A.-D. *Liebigs Ann.* **1997**, 303. (b) Frahn, J.; Schlüter, A.-D. *Synthesis*, **1997**, 1301. (c) Manickam, G.; Schlüter, A.-D. *Eur. J. Org. Chem.* **2000**, 3475.

(2) Zhi, L.; Wu, J.; Mullen, K. *Org. Lett.* **2005**, *7*, 5761.

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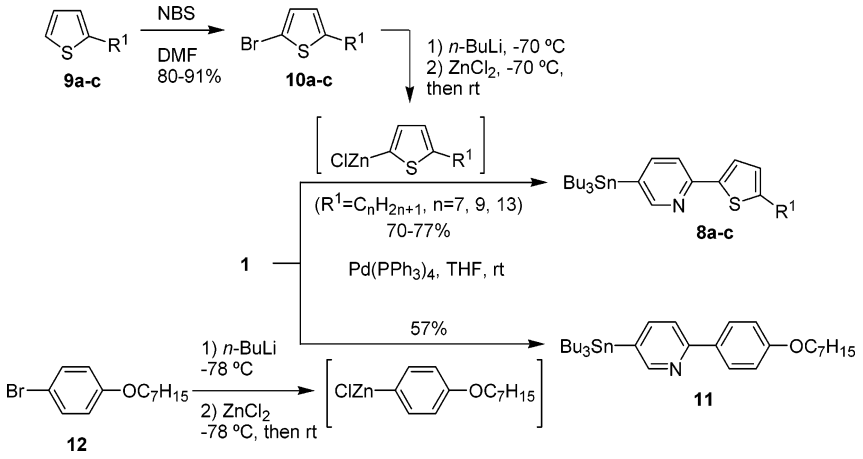
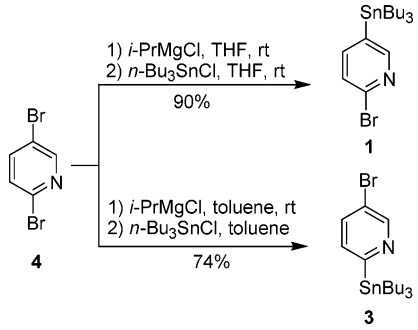
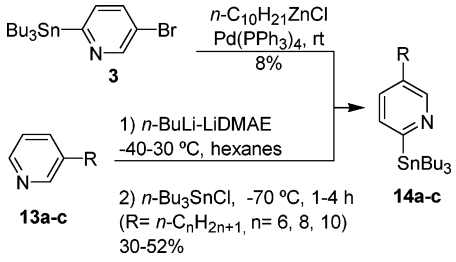
SCHEME 2. The Synthetic Route for Preparation of the Arylzinc Reagents and Their Successful Negishi Coupling with 2-Bromo-5-tri-*n*-butylstannylpyridine (1) Producing 8a−c and 11



SCHEME 3. The Preparation of the Isomeric Bromotri-*n*-butylstannylpyridines 1 and 3 from 2,5-Dibromopyridine (4) with a Coordinating or a Noncoordinating Solvent, Respectively



SCHEME 4. Preparation of 2-Tri-*n*-butylstannyl-5-alkylpyridines



Stille coupling of 2-tri-*n*-butylstannyl-5-halopyridines with an iodoalkene was used for the preparation of vinyl pyridine intermediates leading to epothilone B derivatives.[4] Likewise, 2-halo-5-trimethylstannylpyridines underwent Stille coupling with aryl iodides to produce 2-halo-5-arylpyridines,[5] and 2-bromo-6-tri-*n*-butylstannylpyridine (**2**) reacted with aryl bromides[6] as did 2-chloro-6-tri-*n*-butylstannylpyridine.[7] We recognized that both 2-bromo-5-tributylstannylpyridine **1** and 2-bromo-6-tributylstannylpyridine **2** contain a halide functionality, which is potentially selectively active in a coupling reaction with an organometallic reagent, and so we have tested the mild conditions of Negishi coupling with alkyl- and aryl-zinc chlorides on these substrates.

Here we report comprehensive methods for the convenient preparation of the isomeric precursors 2-bromo-5-tri-*n*-butylstannylpyridine (**1**) and 2-tri-*n*-butylstannyl-5-bromopyridine (**3**) from 2,5-dibromopyridine (**4**), as well as 6-bromo-2-tri-*n*-butylstannylpyridine (**2**) from 2,6-dibromopyridine (**5**), applying bromine−magnesium exchange. The halotributylstannylpyridines **1** and **2** synthesized in this fashion next underwent an unprecedented Negishi coupling at C−Br to produce new aryl stannanes with a Bu_3Sn-group left intact that was subsequently employed for the construction of a range of useful oligomeric intermediates and liquid crystals containing multiple heterocycles.

Results and Discussion

The Negishi coupling of 2-bromo-5-tri-*n*-butylstannylpyridine (**1**) with a series of alkylzinc reagents resulted in the clean formation of the 2-alkyl-5-(tri-*n*-butylstannyl)pyridines **6**. An alternative traditional method was also used for the preparation of 2-*n*-decyl-5-tri-*n*-butylstannylpyridine (**6d**) wherein 2-*n*-decyl-5-bromopyridine[8] (**7a**) was subjected to bromine−lithium exchange followed by trapping with tri-*n*-butyltin chloride to give **6d** in 77% yield (Scheme 1).

This Negishi coupling also worked well when 5-alkylthien-2-ylzinc chlorides derived from 2-bromo-5-alkylthiophenes **10a−c** were reacted with 2-bromo-5-tri-*n*-butylstannylpyridine (**1**). In this case 2-aryl-5-tri-*n*-butylstannylpyridines **8a−c** were isolated in 70−77% yield. The cross-coupling reaction of **1** with an arylzinc reagent obtained from 1-bromo-4-heptyloxybenzene (**12**) produced the aryl stannane **11** in a slightly lower isolated yield of 57% (Scheme 2).

An already established approach to 2-halo-5-trialkylstannylpyridines such as compound **1** involves the metalation of a

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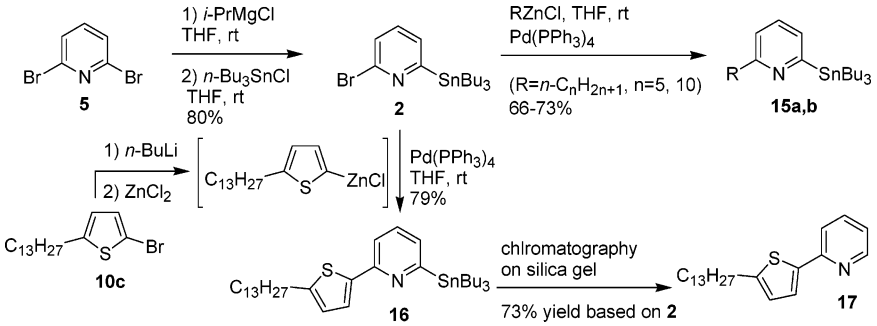
(6) Zoppellaro, G.; Ivanova, A.; Enkelmann, V.; Geies, A.; Baumgarten, M. *Polyhedron* **2003**, *22*, 2099.

(7) Choppin, S.; Gros, P.; Fort, Y. *Org. Lett.* **2000**, *2*, 803.

(8) Getmanenko, Y. A.; Twieg, R. J.; Ellman, B. D. *Liq. Cryst.* **2006**, *33*, 267.

SCHEME 5. Preparation of 2-Bromo-6-tri-*n*-butylstannylpyridine (2) and Its Negishi Reaction with Both Alkyl- and Aryl-Zinc Chlorides



2,5-dihalopyridine with *n*-BuLi at −78 °C followed by trapping of the lithiated species with a trialkyltin chloride.[5a,c] A synthesis of the isomeric 2-trialkylstannyl-5-bromopyridines such as **3** from 2,5-dibromopyridine[9] (**4**) and 2-iodo-5-bromopyridine[10] has been reported, and in both cases toluene was used as a solvent for halogen−lithium exchange with *n*-BuLi at −78 °C. A different approach involving a Pd-catalyzed reaction of the triflate derived from 2-hydroxy-5-chloropyridine with hexamethylditin has also been described.[11] Trecourt et al. have shown that 2,5-dibromopyridine (**4**) can be selectively metalated at the C-5 carbon by treatment with *i*-PrMgCl in THF at room temperature to produce 2-bromo-5-pyridinylmagnesium chloride, which can be trapped with a variety of electrophiles (D_2O, benzaldehyde, I_2, etc.) to form 2-bromo-5-substituted pyridines.[12]

We have now extended this latter method to the preparation of 2-bromo-5-*n*-tributylstannylpyridine (**1**), which was isolated in 90% yield (Scheme 3, 90% purity by ^{1}H NMR). Since this reaction with tri-*n*-butyltin chloride worked successfully at room temperature, it is a valuable alternative to the standard preparation, which is run under *n*-BuLi/−78 °C conditions.[5c] Wang et al.[13] reported that a change of solvent from coordinating (THF, Et_2O) to noncoordinating (toluene, CH_2Cl_2) led to a predominant formation of 2-lithio-5-bromopyridine when 2,5-dibromopyridine (**4**) was treated with *n*-BuLi at −78 °C and so this method was used for the preparation of the isomeric 2-trialkyltin-5-bromopyridines.[9] Toluene was evaluated as the solvent for the reaction of **4** with *i*-PrMgCl at room temperature (Scheme 3) and the trapping of the pyridyl Grignard with tri-*n*-butyltin chloride now successfully produced product **3**.

Our attempts to use a substrate with the trialkylstannyl group adjacent to the pyridine nitrogen, such as 2-tri-*n*-butylstannyl-5-bromopyridine (**3**), in a coupling reaction with alkylzinc chlorides met with little success. The reaction of **3** with *n*-pentylzinc chloride produced a complex mixture of products. In a similar reaction of **3** with *n*-decylzinc chloride, we were able to isolate 2-tri-*n*-butylstannyl-5-*n*-decylpyridine (**14c**) but in only 8% yield (Scheme 4). This inactivity at C-5 of 2-tri-*n*-butylstannyl-5-bromopyridine (**3**) in the Negishi coupling under selected conditions was anticipated, as low yields had been observed when we attempted to introduce a second aryl group to C-5 of 2,5-dibromopyridine (**4**) (vide infra). In fact, the low reactivity of the halide at C-5 of 2,5-dibromopyridine (**4**) under selected conditions allows selective coupling at C-2 to produce 2-substituted-5-bromopyridines.[14] A better approach to the 2-tri-*n*-butylstannyl-5-alkylpyridines (**14a**−**c**) involved the lithiation of 3-alkylpyridines (**13a**−**c**) with *n*-BuLi−$Me_2NCH_2CH_2$−OLi (LiDMAE) base (3 equiv)[15] under optimized temperature conditions[8] followed by trapping with an excess of Bu_3SnCl (3.5 equiv). In this case the desired materials were isolated in 30−52% yields. The column chromatography purification must be performed using silica gel treated with Et_3N to avoid protiodestannylation, which was otherwise observed on standard silica gel (vide infra).

The chemistry just described here for 2,5-dibromopyridine (**4**) has also been extended to the isomeric 2,6-dibromopyridine (**5**). The literature preparation of 2-bromo-6-tri-*n*-butylstannylpyridine (**2**) from 2,6-dibromopyridine (**5**) was achieved by using an excess of both *n*-BuLi (2.1 equiv) and tri-*n*-butyltin chloride (2.4 equiv) at −50 °C in diethyl ether.[6] A different approach to this type of intermediate was developed by Choppin et al.[7] wherein treatment of 2-chloropyridine with *n*-BuLi−$Me_2NCH_2CH_2OLi$ superbase at −78 °C followed by trapping with tributyltin chloride resulted in 6-chloro-2-tri-*n*-butylstannylpyridine in 84% yield. An obvious disadvantage of this latter method is the requirement for a large excess of both base (3 equiv) and electrophile (4 equiv).

The reaction of 2,6-dibromopyridine (**5**) with 1 equiv of *i*-PrMgCl resulted in a single bromine-magnesium exchange[12] and the reaction of the resulting monometalated pyridine with tri-*n*-butyltin chloride produced 2-bromo-6-tri-*n*-butylstannylpyridine (**2**) in 80% yield after purification by Kugelrohr distillation (Scheme 5). The Negishi reaction of **2** with *n*-alkylzinc chlorides successfully produced the desired 2-*n*-alkyl-6-tri-*n*-butylstannylpyridines **15a** and **15b** in 66−73% yield after purification by Kugelrohr distillation. Negishi coupling of **2** with an arylzinc chloride derived from 2-bromo-5-*n*-tridecylthiophene (**10c**) (Scheme 5) proceeded smoothly to produce 2-(5-*n*-tridecylthien-2-yl)-6-tri-*n*-butylstannylpyridine (**16**). An attempt to purify crude **16** on silica gel failed and the destannylated product **17** was the dominant product isolated in 73% yield. Mathieu et al. had observed such protiodestannylation during chromatography for 2-tri-*n*-butylstannyl-5-methylpyridine[15] and similar difficulties with purification of 2-trimethylstannyl-5-*n*-

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(12) Trecourt, F.; Breton, G.; Bonnet, V.; Mongin, F.; Marsais, F.; Quenguiner, G. *Tetrahedron* **2000**, *56*, 1349.
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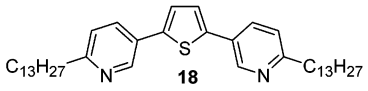
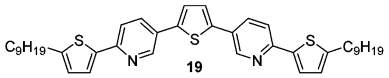
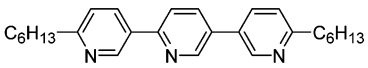
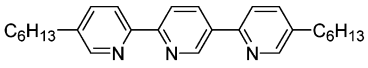
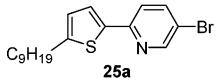
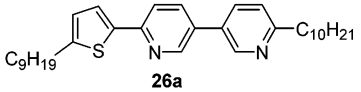
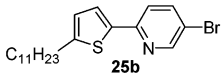
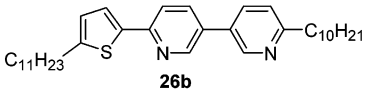
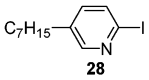
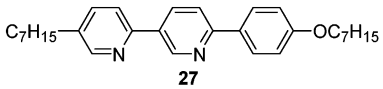
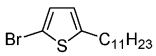
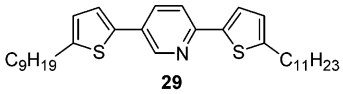
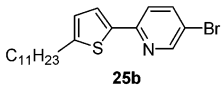
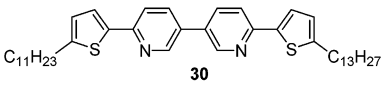
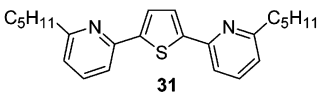
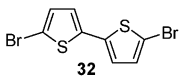
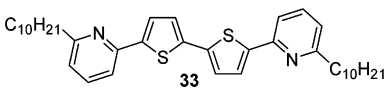
TABLE 1. New Mesogens Prepared by the Stille Coupling of Pyridinylstannanes with Aryl Halides

Entry	Stannane	Aryl halide	Product	Yield
1	**6e**	2,5-dibromothiophene	 **18**	57[a]
2	**8b**	2,5-dibromothiophene	 **19**	41[a]
3	**6b**	2,5-dibromopyridine (**4**)	 **20**	43[a]
4	**14a**	2,5-dibromopyridine (**4**)	 **23**	35[b]
5	**6d**	 **25a**	 **26a**	73[a]
6	**6d**	 **25b**	 **26b**	69[a]
7	**11**	 **28**	 **27**	44[a]
8	**8b**	 **10d**	 **29**	48[a]
9	**8c**	 **25b**	 **30**	59[a]
10	**15a**	2,5-dibromothiophene	 **31**	47[c]
11	**15b**	 **32**	 **33**	55[c]

[a] $Pd(PPh_3)_4$ (2−5 mol %), DMF, 130−140 °C. [b] $Pd(PPh_3)_4$ (1 mol %), CuI (2 mol %), DMF, 125−135 °C. [c] $Pd(PPh_3)_4$ (2 mol %), CuI (4 mol %), 100−112 °C.

alkylpyridine had been reported by Schwab et al.[16] Our present observations for **16** also indicate a lower stability of stannanes with trialkylstannyl moiety at C-2 of the pyridine ring in comparison with stannanes **1**, **6**, and **8** with the $SnBu_3$ group at C-3(5), all of which can be chromatographed using standard silica gel. To avoid protiodestannylation the silica gel was pretreated with Et_3N, and in this case 6-(5-*n*-tridecylthien-2-yl)-2-(tri-*n*-butylstannyl)pyridine (**16**) was successfully isolated in 79% yield (85% purity by ^1H NMR).

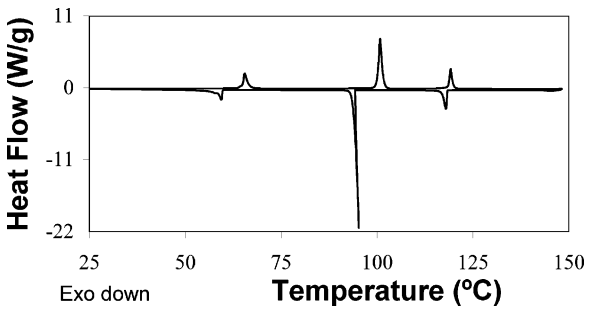


FIGURE 1. DSC thermogram of 2,5-bis(2-*n*-tridecylpyridin-5-yl)-thiophene **18**.

Thus far our attempts to extend this convenient method (wherein a substrate bearing both a halide and a group IV metal functionality on a pyridine ring selectively reacts at the halide site and leaves the metal group intact and available for subsequent transformations) to the preparation of new stannanes with thiophene and benzene rings instead of pyridine have not resulted in sufficiently clean coupling at the halide sites. Instead, for example, mixtures of products were produced when 2-halo-

(16) Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, *67*, 443.

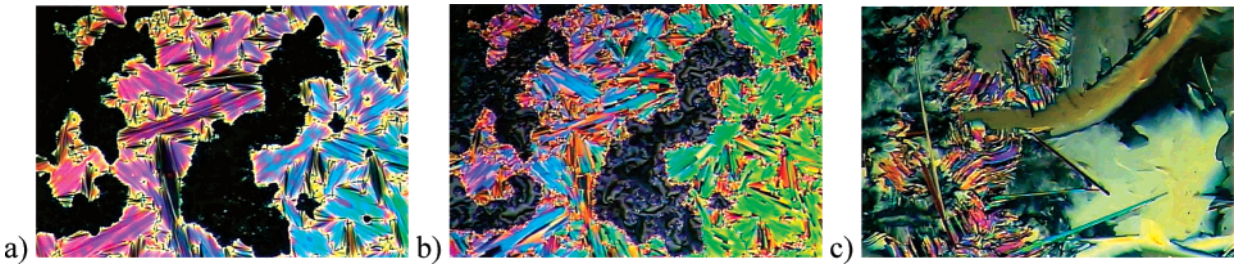


FIGURE 2. Textures of 2,5-bis(2-*n*-tridecylpyridin-5-yl)thiophene **18** observed by optical microscopy (a: SmA, 118.9 °C; b: SmC, 110.6 °C; c: Cr1, 96.6 °C; 200 × magnification).

TABLE 2. Results of DSC and Optical Microscopy Analysis of the New Liquid Crystals

entry	compd no.	DSC analysis (2nd heating−cooling cycle)	microscopy analysis
1	**18**	65.5, 100.8, 119.2 59.4, 95.25, 118.0	**Cr2** 60.5 **Cr1** 97.7 **SmC** 117.8 **SmA** 119.3 **Iso**
2	**19**	183.6, 289.6 177.8, 285.1	**Cr** 175.2 **SmC** 287.1 **Iso**
3	**20**	88.0, 136.5, 141.9, 158.5, 208.8 73.7, 135.5, *139.0**, 140.9, 158.0, 207.5	**Cr** 75.0 **SmG** 135.1 **SmF** 139.5 ***SmI***140.9 **SmC** 156.6 **SmA** 208.8 **Iso**
4	**23**	63.5, 82.8, 89.0, 92.5, 134.5, 165.5 53.2, 86.4, 88.2, 91.2, 133.3, 164.6	**Cr1/S2** 87.0 **S1** 88.0 **SmC** 133.8 **N** 164.0 **Iso**
5	**26a**	33.9*, 37.2, 43.0, 122.8, 147.7 20.2, 121.7, 146.3	**Cr** 20.2 **SmF** 121.9 **SmC** 147.3 **Iso**
6	**26b**	54.8*, 59.6, 66.0, 123.0, 143.7 40.7, 121.4, 141.7	**Cr** 40.6 **SmF** 123.4 **SmC** 143.8 **Iso**
7	**29**	67.7, 72.9, 122.0, 125.4 63.4, 69.1, 120.8, 123.8	**Cr** 71.9 **SmF** 122.2 **SmC** 125.1 **Iso**
8	**30**	68.9, 155.8, 217.3 56.0, 154.51, 215.7	**Cr** 50.3 **SmF** 151.9 **SmC** 215.2 **Iso**

[a] For **20** (entry 3): 139.0* − the transition appears as a shoulder of the peak at 140.9; for **26a** (entry 5): 33.9* − transition takes place at 62.9 °C during the first heating cooling cycle; for **26b** (entry 6): 54.8* − transition takes place at 68.5 °C during the first heating-cooling cycle; for the DSC analysis: the 1st row shows transition temperatures observed on heating, the 2nd row shows transition temperatures observed on cooling.

5-tri-*n*-butylstannylthiophenes and 1-halo-4-tri-*n*-butylstannylbenzenes underwent coupling with both alkylzinc chlorides and arylzinc chlorides in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ in THF at room temperature. A more detailed investigation/optimization of this reaction will be required in order to extend the method described here for 2-bromo-5(or 6)-tri-*n*-butystannylpyridines **1** and **2** to other aromatic systems with both halide and tin functionalities present.

Exemplary of their synthetic utility, we now demonstrate that the pyridinylstannanes described here are valuable intermediates for the preparation of a variety of new liquid crystalline materials (Table 1). For example, two of the 2-substituted-5-tri-*n*-butylstannylpyridines **6e** and **8b** already described here were used in a double Stille coupling reaction with 2,5-dibromothiophene, and in both cases the desired liquid crystalline materials were isolated in useful yields (Table 1, entries 1 and 2).

The 2-*n*-hexyl-5-tri-*n*-butylstannylpyridine (**6b**) was also tested in a double Stille coupling with 2,5-dibromopyridine (**4**),

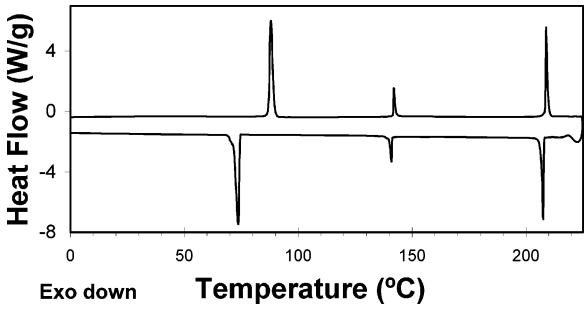


FIGURE 3. DSC thermogram of 2,5-di(2-*n*-hexylpyridin-5-yl)pyridine **20**.

and the desired liquid crystalline material **20** was isolated in 43% yield (Table 1, entry 3). This is the best method we have found so far for the preparation of this type of terpyridine. The Negishi coupling of 2 equiv of arylzinc chloride **21** (see the Supporting Information for the reaction scheme) derived from 2-*n*-hexyl-5-bromopyridine (**7b**) with 2,5-dibromopyridine (**4**) produced the same material in 17% yield, and the yield of the reaction was improved to 35% when 2-bromo-5-iodopyridine (**22**) was used instead. The double Stille coupling of 2-tri-*n*-butystannyl-5-*n*-hexylpyridine (**14a**) with 2,5-dibromopyridine (**4**) produced material with three contiguous pyridine rings (**23**) (Table 1, entry 4), but with different locations of the nitrogen atoms in the aromatic core relative to terpyridine **20** and the liquid crystal prepared earlier.[8]

The Stille coupling of 2-*n*-decyl-5-tri-*n*-butylstannylpyridine (**6d**) with aryl bromides **25a** and **25b** was used as a final step in the preparation of thiophene−bipyridine liquid crystals **26a**,**b** (Table 1, entries 5 and 6). The requisite aryl halides **25a**,**b** were prepared by Negishi coupling of arylzinc chlorides derived from 2-bromo-5-*n*-alkylthiophenes **10b**,**d** with 2,5-dibromopyridine (**4**) in 74−79% yield (see the Supporting Information for a reaction scheme). Their reactions with **6d** produced liquid crystal materials **26a**,**b** in good yields.

The liquid crystalline material **27** we reported earlier[8] has now been prepared in 44% yield by a convenient Stille coupling of 2-aryl-5-tri-*n*-butylstannylpyridine **11** with 2-iodo-5-*n*-heptylpyridine (**28**) (Table 1, entry 7). The 2-aryl-5-tri-*n*-butylstannylpyridine **8b** was also used for the preparation of liquid crystal **29** with a central pyridine ring and two thiophenes with different alkyl chains (Table 1, entry 8). The Stille coupling of 2-bromo-5-*n*-undecylthiophene (**10d**) with **8b** produced the requisite

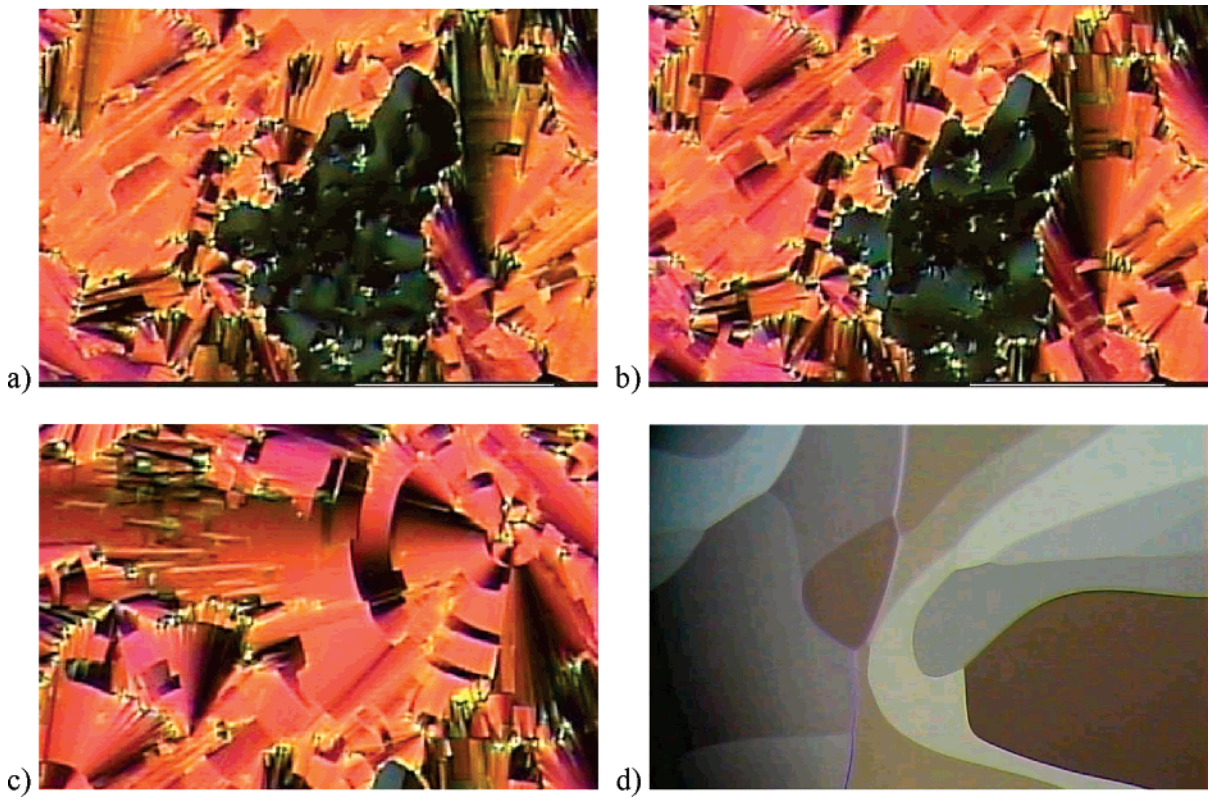


FIGURE 4. Textures of 2,5-di(2-*n*-hexylpyridin-5-yl)pyridine **20** observed by optical microscopy (a: 140.8 °C, ill defined *schlieren* and fan textures of SmI (slide); b: 139.2 °C, *schlieren*-mosaic and fan textures of SmF (slide); c: 139.2 °C, fan texture with "L"-shaped patterns; d: 130.0 °C, SmG (freely suspended film); 200 × magnification).

mesogen **29** (Table 1, entry 8), while the reaction of stannane **8c** with aryl bromide **25b** gave LC material **30** (Table 1, entry 9).

We found that the new stannanes such as **15** with the metal on the carbon adjacent to pyridine nitrogen gave poor results in coupling with arylhalides when $Pd(PPh_3)_4$ alone was used as a catalyst. For example, the Stille coupling of **15a** with 2,5-dibromothiophene produced **31** in only 15% yield. However, addition of CuI cocatalyst[17] resulted in a cleaner reaction and an improved yield of **31** (Table 1, entry 10). These same cocatalyst reaction conditions were also successfully extended to the preparation of **33** from 5,5′-dibromo-2,2′-bithiophene (**32**) and stannane **15b** (Table 1, entry 11).

Liquid Crystalline Behavior of the New Mesogens. The liquid crystalline behavior of the mesogens prepared here using the new haloaryltrialkyltin intermediates was studied by DSC and optical microscopy and the pertinent data are summarized in Table 2.

The DSC trace of **18** showed three reversible peaks (Figure 1), while analysis of the textures observed by polarized optical microscopy suggests one more phase transition. The isotropic liquid was converted to a SmA phase on cooling for a short temperature range. A homeotropic texture of SmA was clearly observed as black areas surrounded by a fan texture in Figure 2a. This texture gave rise to the *schlieren* texture of SmC, while the fan texture became broken (Figure 2b). The crystallization event was rather unusual with an initial formation of highly colored tiny mosaics that quickly transformed into large colored platelets (as in the right corner of Figure 2c).

(17) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359.

The DSC of liquid crystal **20** showed five reversible peaks (Figure 3; second heating−cooling cycle, 2 deg/min rate; see the Supporting Information for the enlarged region with weakly first-order/second-order transitions). The single peak at 140.9 °C with a shoulder at 139.0 °C was detected by DSC analysis on cooling, but two close transitions were detected by optical microscopy. The ill-defined *schlieren* texture typical for SmI phase (Figure 4a) was observed along with subtle changes in the fan texture after transition from the SmC phase at 140.9 °C (this transition was clearly detected by the DSC analysis). Another transition occurred on further cooling, and a *schlieren*-mosaic texture (Figure 4b) characteristic for SmF formed from the *schlieren* of SmI at 139.5 °C. The fan texture became more defined with the appearance of "L"-shaped patterns. These observations suggest the formation of a SmI phase for a very short temperature range. A freely suspended film of **20** can be prepared readily, and the mosaic texture of the SmG phase was observed (Figure 4d).

Liquid crystals of type **26** form a SmC phase from the isotropic liquid on cooling (Figure 5a, freely suspended film) followed by formation of SmF, which exhibits fan texture with L-shapes (Figure 5b) and a *schlieren*-mosaic texture (Figure 5c, freely suspended film).

The liquid crystals described here (except for mesogen **19** with 5 conjugated aromatic rings) exhibit quite low melting points (20−75 °C) and clearing points (<210 °C) and a tendency to form tilted smectic phases. Comparison of the liquid crystalline behavior of isomeric liquid crystals **20** and **23** demonstrates that the position of the nitrogen atoms in the aromatic core is an important factor for both transition temperatures and mesomorphic behavior. Interestingly, increase of the

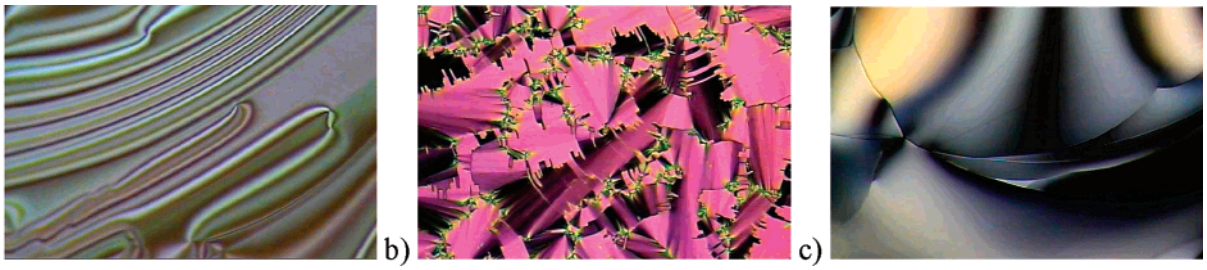


FIGURE 5. Textures of 6′-*n*-decyl-6-(5-*n*-undecylthiophen-2-yl)[3,3′]bipyridinyl **26b** observed by optical microscopy (a: 138.4 °C, SmC (freely suspended film); b: 122.9 °C, SmF (slide); c: 125.4 °C, SmF (freely suspended film).

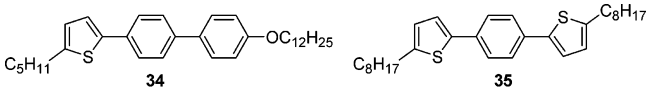


FIGURE 6. The structure and mesomorphic behavior of two known benzene-based mesogens **34** and **35** closely related to the new pyridine-containing mesogens **26** and **29**.

alkyl chain from C9 to C11 in mesogens **26** led to a significant change in melting point (20 °C) with only a slight effect on other transitions. Insertion of one more pyridine ring into the aromatic core of **26** resulted in a considerable increase of clearing point in **30** with preserved phase sequence and only a slight change in melting point.

Comparison of the mesomorphic behavior of liquid crystals **26a**,**b** with an alkyl thiophene ring and two pyridines in the aromatic core with the closely related mesogen[18] with benzene instead of pyridine rings shows a substantial decrease of both the clearing point (147.3 °C (**26a**) and 143.3 °C (**26b**) vs 178.7 °C for the known thienylbiphenyl **34**) in pyridine-containing mesogens and the melting points (20.2 °C (**26a**) and 40.6 °C (**26b**) vs 92.3 °C (**34**)). Introduction of two nitrogens into the aromatic core also resulted in the formation of tilted phases SmC and SmF in **26a**,**b** while only an orthogonal SmA phase was observed for the analogous benzene-containing mesogen **34**.

The decrease of the clearing point by the substitution of the pyridine for benzene in the aromatic core of the smectic mesogens was also observed for 2,5-dithienyl-pyridine LC **29** (125.4 °C for **29** vs 145 °C for 1,4-dithienylbenzene **35**[19]). Interestingly, in this case the pyridine-containing mesogen exhibits a simpler mesomorphic behavior with the formation of two titled phases (SmC and SmF) while the closely related benzene mesogen **35** showed the formation of three unidentified phases.[19]

Conclusions

Three isomeric bromo-tri-*n*-butylstannylpyridines were prepared from the corresponding dibromopyridines using convenient reaction conditions (*i*-PrMgCl at room temperature). Depending on the solvent utilized, 2,5-dibromopyridine (**4**) was converted to 2-bromo-5-tri-*n*-butylstannylpyridine (**1**) (THF) or 2-tri-*n*-butylstannyl-5-bromopyridine (**3**) (toluene) with very high selectivity and in good yields. The halogen site in the 2-bromo-5-(or 6)-tri-*n*-butylstannylpyridines **1** and **2** reacted smoothly with alkyl/aryl-zinc chlorides under Negishi coupling conditions to give new arylstannanes. These arylstannanes are themselves valuable intermediates for the preparation of new materials and here we have demonstrated their utility for the preparation of a variety of new series of liquid crystalline thiophene−pyridine oligomers. It is still an open question if the methodology described here is unique for dibromopyridines with halogen at C-2 activated toward Pd-catalyzed reaction under mild conditions or if it represents a more general concept and therefore can be extended to the preparation of organotin reagents from other halide−Ar−$SnBu_3$ substrates by selective coupling at the halide site.

Experimental Section

Solvents. THF was distilled from sodium benzophenone ketyl and toluene was distilled under nitrogen and stored over sodium. The $ZnCl_2$ solution used for the transmetalation reactions was prepared as follows: solid $ZnCl_2$ was dried by melting and cooling under vacuum, freshly distilled THF (an amount to prepare ∼1 M solution of $ZnCl_2$) was added, and the mixture was stirred under nitrogen until a homogeneous solution was obtained. 2,5-Dibromopyridine (**4**) (98%), 2,5-dibromothiophene (98%), 2,6-dibromopyridine (**5**) (98%), *i*-PrMgCl (2.0M in ether), *n*-BuLi (2.5M in hexanes), anhydrous DMF, and tributyltin chloride were used as received. The catalyst tetrakis(triphenylphosphine)palladium(0) was prepared from $PdCl_2$ by reduction with hydrazine hydrate in DMSO.[20] Literature procedures were adapted for the preparation of 2-alkylthiophenes **9a**−**d**,[21] 2-bromo-5-alkylthiophenes **10a**−**d**,[22] 2-*n*-alkyl-5-bromopyridine **7a**,**b**, 2-iodo-5-*n*-heptylpyridine (**28**),[8] 3-*n*-alkylpyridines **13a**−**c**,[23] 2-bromo-5-iodopyridine (**22**),[12] and 5,5′-dibromo-2,2′-bithiophene (**32**).[24]

Both ^1H and ^{13}C NMR spectra were recorded with 300 and 400 MHz spectrometers (TMS as internal standard), a FT-IR spectrometer was used to record IR spectra, a diode array spectrophotometer was used to record UV−vis spectra, and an ion trap mass spectrometer was used for the analysis of the synthesized materials (APCI source, drying gas temperature 300−350 °C, APCI heater temperature 250−300 °C). A differential scanning calorimeter (scanning rate of 2 or 5 deg min^{-1}) and a polarizing microscope equipped with a hot stage (0.2−0.5 deg min^{-1} cooling rate at transition temperatures determined by DSC) were used to determine the phase transitions. Phase assignments were made based on microscopic observations and images were obtained with a CCD camera.

2-Bromo-5-(tri-*n*-butylstannyl)pyridine (1). An oven-dried three-necked flask equipped with magnetic stir bar, nitrogen inlet,

(18) Kiryanov, A.; Sampson, P.; Seed, A. J. *J. Mater. Chem.* **2001**, *11*, 3068.
(19) Oikawa, O.; Monobe, H.; Takahashi, J.; Tsuchiya, K.; Heinrich, B.; Guillon, D.; Shimizu, Y. *Chem. Commun.* **2005**, 5337.
(20) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121.
(21) Ponomarenko, S.; Kirchmeyer, S. *J. Mater. Chem.* **2003**, *13*, 197.
(22) Bäuerle, P.; Würthner, F.; Götz, G.; Effenberger, F. *Synthesis* **1993**, *11*, 1099.
(23) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.
(24) Chaloner, P.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin 2* **1997**, 1597.

septum, and bubbler was charged with 2,5-dibromopyridine (**4**) (0.05 mol, 11.84 g), and anhydrous THF (50 mL) was added under a nitrogen atmosphere. *i*-PrMgCl (2.0 M in diethyl ether, 0.05 mol, 25 mL) was added dropwise (a water bath was used to control the temperature). The reaction mixture turned yellow, then orange, and precipitation took place after addition of 10 mL of *i*-PrMgCl. The orange reaction mixture with a white precipitate was stirred at room temperature for an hour, and tri-*n*-butyltin chloride (96% purity, 0.0525 mol, 17.8 g) was added (an ice water bath was used to control the temperature). The reaction mixture was stirred for 18 h at room temperature, and then the thick orange-brown mixture was treated with 10 mL of water. The resulting mixture was transferred to a 250-mL round-bottomed flask and the organic solvents were removed by rotary evaporation. Water (20 mL) and hexanes (75 mL) were added, and the resulting mixture was vacuum filtered to remove a small amount of insoluble matter. The deep orange organic phase was separated, and the aqueous phase was extracted with hexanes (50 mL, then 3 × 25 mL). The orange organic phases were combined, washed with brine, and then dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The orange oil was Kugelrohr distilled (128−142 °C/0.11 mmHg) to give a slightly cloudy yellow oil (20 g, 89.5% yield, 90% purity by NMR). MS (APCI): 448.0 (with satellites at 446.2, 447.1, 449.9) (calcd FW 447.0584). FT-IR (cm^{-1}): 3052 (weak), 2967, 2923, 2847, 1556, 1537, 1462, 1410, 1365, 1164, 1119, 1097, 977, 874, 778, 731. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85−0.92 (t, J = 7.25 Hz, 9H), 1.05−1.14 (m, 6H), 1.25−1.38 (m, 6H), 1.47−1.60 (m, 6H), 7.38−7.46 (dd, J = 7.72 Hz, 0.77 Hz, 1H), 7.56−7.62 (dd, J = 7.72 Hz, 1.86 Hz, 1H), 8.32−8.38 (dd, J = 1.71 Hz, 0.75 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.71, 13.62, 27.26, 28.94, 128.16 (CH), 135.76 (quaternary C), 142.69 (quaternary C), 146.17 (CH), 156.17 (CH).

2-Bromo-6-(tri-*n*-butylstannyl)-pyridine (2). An oven-dried three-necked flask equipped with magnetic stir bar, nitrogen inlet, septum, and bubbler was charged with 2,6-dibromopyridine (**5**) (0.025 mol, 5.92 g) and anhydrous THF (25 mL) was added under a nitrogen atmosphere. *i*-PrMgCl (2.0 M in diethyl ether, 0.025 mol, 12.5 mL) was added dropwise to the gray solution of 2,6-dibromopyridine (**5**). The reaction mixture turned yellow, and precipitation took place after stirring for 50 min. The mixture was stirred for an additional hour (2 h total), and tri-*n*-butyltin chloride (96% purity, 0.025 mol, 8.48 g) was added via syringe. The reaction mixture became warm to the touch and additional precipitate formed to produce a thick gray suspension. The mixture was left to stir overnight at room temperature (18 h) then transferred to a round-bottomed flask, and the organic solvents were removed by rotary evaporation. The residue was treated with 50 mL of water and 50 mL of hexanes, and the resulting mixture was vacuum filtered to remove a small amount of insoluble solid. The organic phase was separated and the aqueous phase was extracted with hexanes (3 × 25 mL). The combined organic phases were washed with brine and then dried over $MgSO_4$, and the solvent was removed by rotary evaporation to give a yellow oil. The crude material was Kugelrohr distilled (140−145 °C/0.08 mmHg), and the purified material was isolated as yellow oil in 80.5% yield (9.00 g). MS analysis (APCI): 448.0 (with satellites at 446.3, 447.3, 449.8) (calcd FW 447.0584). FT-IR (cm^{-1}): 3039 (weak), 2956, 2928, 2871, 2859, 1555, 1537, 1462, 1410, 1164, 1120, 1098, 1071, 976, 960, 863, 778, 731, 692. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89−0.94 (t, J = 5.11 Hz, 9H), 1.13−1.18 (m, 6H), 1.30−1.40 (m, 6H), 1.54−1.63 (m, 6H), 7.30−7.33 (m, 1H), 7.34−7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.11, 13.69, 27.28, 28.97, 126.26 (CH), 131.20 (CH), 135.62 (CH), 143.65 (quaternary C), 176.93 (quaternary C).

2-(Tri-*n*-butylstannyl)-5-bromopyridine (3). An oven-dried three-necked flask equipped with magnetic stir bar, nitrogen inlet, septum, and bubbler was charged with 2,5-dibromopyridine (**4**) (0.025 mol, 5.92 g) and anhydrous toluene (50 mL) was added under a nitrogen atmosphere. *i*-PrMgCl (2.0 M in diethyl ether, 0.025 mol, 12.5 mL) was added dropwise to the colorless solution of 2,5-dibromopyridine (**4**) (0.5M) at room temperature. During this addition the reaction mixture became yellow, and then yellow orange, and then dark red, but no heating was observed. The reaction mixture was stirred for 30 min, then tri-*n*-butyltin chloride (96% purity, 1.05 equiv, 0.02625 mol, 8.90 g) was added dropwise and the reaction mixture became lighter in color. After 20 h of stirring the reaction became cloudy and yellow in color. The mixture was subjected to vacuum distillation (water aspirator) to remove toluene. The residue was treated with 25 mL of water and 50 mL of hexanes and vacuum filtered to remove a small amount of insoluble solid. The organic phase was separated and the aqueous phase was extracted with hexanes (4 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed by rotary evaporation to give the crude product, which was purified by Kugelrohr distillation at 120−125 °C/0.12−0.13 mmHg (yellow oil, 8.35 g, 74.7% yield) (some solid separated during distillation at 85−100 °C/0.12 mmHg). MS (APCI): 448.0 (with satellites at 446.2, 447.2, 449.9) (calcd FW 447.0584). FT-IR (cm^{-1}): 3048 (weak), 2956, 2922, 2851, 1461, 1439, 1377, 1343, 1110, 1074, 1000, 960, 874, 819, 722, 662. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87−0.93 (t, J = 7.31 Hz, 9H), 1.11−1.17 (m, 6H), 1.29−1.40 (m, 6H), 1.52−1.62 (m, 6H), 7.30−7.34 (dd, J = 7.93 Hz, 0.76 Hz, 1H), 7.65−7.68 (dd, J = 7.95 Hz, 2.46 Hz, 1H), 8.82−8.85 (dd, J = 2.42 Hz, 0.70 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.94, 13.67, 27.31, 29.01, 120.42 (quaternary C), 133.01 (CH), 135.84 (CH), 151.41 (CH), 172.21 (quaternary C).

Representative Procedure for the Preparation of Compounds 6: 2-*n*-Pentyl-5-(tri-*n*-butylstannyl)pyridine (6a). An alkyl Grignard reagent was prepared from 1-bromopentane (2 equiv, 0.014 mol, 2.11 g) and Mg turnings (0.0168 mol, 0.41 g) in 14 mL of anhydrous THF. This freshly prepared Grignard was added dropwise to a solution of $ZnCl_2$ (0.0168 mol, 2.29 g) in 17 mL of anhydrous THF (ice−water bath). A white precipitate formed after several minutes of stirring, and the reaction mixture was stirred for an additional hour at room temperature. Next, 2-bromo-5-(tri-*n*-butylstannyl)pyridine (**1**) (0.007 mol, 3.13 g), $Pd(PPh_3)_4$ (0.5 mol %, 0.035 mmol, 0.04 g), and 7 mL of anhydrous THF were mixed in an oven-dried three-necked flask under a nitrogen atmosphere (clear yellow solution formed), and the freshly prepared *n*-pentylzinc chloride solution (∼1.5 equiv, ∼23 mL) was added dropwise via syringe to the yellow reaction mixture (the flask became warm to the touch). The reaction mixture was stirred for 3 h at room temperature then transferred to another round-bottomed flask, and the solvent was removed by rotary evaporation. The residue was treated with 25 mL of water and 50 mL of petroleum ether, and the resulting mixture was vacuum filtered to remove insoluble matter. The organic phase was separated and the aqueous phase was extracted with petroleum ether (4 × 10 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed by rotary evaporation to give the crude product as a cloudy yellow oil (3.69 g). The product was purified by Kugelrohr distillation (135−152 °C/0.17 mmHg), and the desired material was isolated as yellow oil in 70.0% yield (2.15 g). FT-IR (cm^{-1}): 3066 (weak), 2957, 2927, 2862, 2852, 1572, 1542, 1462, 1377, 1344, 1073, 1015, 960, 841, 692. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.84−0.92 (m, 12H), 1.03−1.11 (m, 6H), 1.25−1.40 (m, 10H), 1.50−1.58 (m, 6H), 1.63−1.78 (m, 2H), 2.71−2.78 (m, 2H), 7.07−7.12 (dd, J = 7.48 Hz, 0.83 Hz, 1H), 7.63−7.67 (dd, J = 7.51 Hz, 1.64 Hz, 1H), 8.48−8.55 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.55, 13.64, 14.03, 22.56, 27.32, 29.03, 29.57, 31.70, 38.38, 122.87 (CH), 132.88 (quaternary C), 144.31 (CH), 155.48 (CH), 161.82 (quaternary C).

A Representative Procedure for the Preparation of Compounds 8: 2-(5-*n*-Heptylthien-2-yl)-5-(tri-*n*-butylstannyl)pyridine (8a). An oven-dried three-necked flask equipped with magnetic stir bar, bubbler, and nitrogen inlet was charged with 2-bromo-5-*n*-heptylthiophene (**10a**) (0.033 mol, 8.62 g) and anhydrous THF (76 mL). The colorless solution was cooled (acetone/CO_2 bath), *n*-BuLi (2.5 M in hexanes, 0.033 mol, 13.2 mL) was added

dropwise, and the light yellow reaction mixture was stirred for half an hour. A solution of $ZnCl_2$ (0.0396 mol, 5.40 g) in anhydrous THF (40 mL) was added to the reaction mixture, the cooling bath was removed, and the mixture was stirred for an hour. Half of the freshly prepared arylzinc chloride (~65 mL, 0.0165 mol) was added in portions to the flask charged with 2-bromo-5-tri-*n*-butylstannylpyridine (**1**) (0.015 mol, 6.71 g), $Pd(PPh_3)_4$ (0.5 mol %, 0.075 mmol, 0.087 g), and 30 mL of anhydrous THF. The reaction mixture became warm during addition of the arylzinc chloride. After 2 h of stirring the yellow solution was transferred to a 250-mL round-bottomed flask, and the solvents were removed by rotary evaporation. The residue was treated with hexanes (75 mL) and water (50 mL), and the resulting mixture was vacuum filtered to remove insoluble matter. The organic phase was removed, and the aqueous layer was extracted with hexanes (100 mL, then 50 mL, then 2 × 25 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The product was purified by column chromatography (120 g of silica gel, hexanes:EtOAc = 20:1 as eluant). The purified material was isolated as light yellow oil in 71.8% yield (5.90 g). MS (APCI): 548.1, (with satellites at 546.2, 547.2, 549.1, 550.9) (calcd FW 458.4659). FT-IR (cm^{-1}): 3066 (weak), 2956, 2927, 2870, 2853, 1566, 1485, 1460, 1379, 1348, 1290, 1081, 1045, 1005, 965, 798, 753, 731, 691. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.86−0.90 (m, 12H), 1.06−1.11 (m, 6H), 1.24−1.40 (m, 14H), 1.50−1.60 (m, 6H), 1.67−1.75 (m, 2H), 2.80−2.83 (t, J = 7.53 Hz, 2H), 6.75−6.80 (d, J = 3.64 Hz, 1H), 7.37−7.41 (d, J = 3.63 Hz, 1H), 7.52−7.56 (dd, J = 7.75 Hz, 0.91 Hz, 1H), 7.70−7.75 (dd, J = 7.76 Hz, 1.56 Hz, 1H), 8.50−8.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.66, 13.67, 14.11, 22.67, 27.34, 28.94, 29.05, 29.15, 30.43, 31.57, 31.78, 118.23 (CH), 124.07 (CH), 125.14 (CH), 134.38 (quaternary C), 142.40 (quaternary C), 144.51 (CH), 148.35 (quaternary C), 152.20 (quaternary C), 155.72 (CH).

2-(4-*n*-Heptyloxyphenyl)-5-(tri-*n*-butylstannyl)pyridine (11). An oven-dried three-necked flask was charged with 4-*n*-heptyloxy-1-bromobenzene (**12**) (18 mmol, 4.88 g), anhydrous THF (36 mL) was added, and the resulting mixture was cooled in an acetone/CO_2 bath under nitrogen atmosphere. *n*-BuLi (2.5 M in hexanes, 18 mmol, 7.2 mL) was added dropwise to a clear colorless solution. The light yellow reaction mixture was stirred for half an hour, analyzed by TLC, and a solution of $ZnCl_2$ (21.6 mmol, 2.94 g) in 22 mL of anhydrous THF was added dropwise. After completion of addition of $ZnCl_2$ solution the cooling bath was removed, and the light yellow clear reaction mixture was stirred for half an hour. This freshly prepared arylzinc chloride solution was added in portions to the flask charged with 2-bromo-5-(tri-*n*-butylstannyl)-pyridine (**1**) (15 mmol, 6.70 g) and $Pd(PPh_3)_4$ (1 mol %, 0.15 mmol, 0.17 g). After stirring for several minutes the solution became warm to the touch. The reaction mixture was stirred for 2 h, the yellow solution was transferred to a round-bottomed flask, and the organic solvents were removed by rotary evaporation. The residue was treated with 30 mL of water and 50 mL of hexanes, and the resulting mixture was vacuum filtered to remove insoluble matter. The organic phase was separated; the aqueous phase was extracted with hexanes (50 mL, then 4 × 25 mL). The combined organic phases were dried with $MgSO_4$, and crude material was obtained as a yellow cloudy oil after the removal of solvent by rotary evaporation. The crude product was purified by chromatography (150 g of silica gel, CH_2Cl_2:hexanes = 4:1 as eluant). The purified product was isolated as a light yellow oil in 56.8% (4.75 g). MS (APCI): 558.1, 560.0 (1:1 intensity ratio, calcd FW 559.2836). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.82−0.90 (m, 12H), 1.03−1.13 (m, 6H), 1.25−1.40 (m, 14H), 1.50−1.65 (m, 6H), 1.75−1.82 (m, 2H), 3.95−4.02 (t, J = 6.57 Hz, 2H), 6.97−7.02 (d, J = 8.83 Hz, 2H), 7.60−7.65 (d, J = 7.74 Hz, 1H), 7.75−7.80 (dd, J = 7.73 Hz, 1.50 Hz, 1H), 7.92−8.00 (d, J = 7.79 Hz, 2H), 8.62−8.70 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 9.78, 13.82, 14.25, 22.79, 26.20, 27.69, 29.23, 29.26, 31.97, 69.19, 114.79 (two CH), 119.86 (CH), 128.09 (two CH), 131.90 (quaternary C), 134.07 (quaternary C), 144.87 (CH), 155.97 (CH), 156.21 (quaternary C), 160.19 (quaternary C).

A Representative Procedure for the Preparation of Compounds 14: 2-Tri-*n*-butylstannyl-5-*n*-octylpyridine (14b). *N*,*N*-Dimethylaminoethanol (0.0159 mol, 1.40 g) and 30 mL of hexanes were placed into an oven-dried three-necked round-bottomed flask. *n*-BuLi (2.5 M in hexanes, 0.0314 mol, 12.50 mL) was added slowly (acetone/CO_2 bath), then the reaction mixture was stirred for half an hour (~0 °C) and cooled down to −50 °C. The solution of 3-octylpyridine (**13b**) (0.0052 mol, 1.00 g) in 5 mL of hexanes was added dropwise (−50 to −40 °C internal temperature). The bright yellow reaction mixture was allowed to warm up to −30 °C, stirred for 45 min, then cooled down to −70 °C, and a solution of tri-*n*-butyltin chloride (3.5 equiv, 0.0183 mol, 5.95 g) in anhydrous THF (40 mL) was added dropwise (−70 to −40 °C internal temperature during addition) and the color of the mixture faded away during the addition, and the mixture became yellowish cloudy after completion of addition of *n*-Bu_3SnCl solution. The reaction mixture was stirred for 1 h, the cooling bath was removed, and the mixture was allowed to warm up to room temperature. The contents of the reaction flask were transferred to a round-bottomed flask and the solvents were removed by rotary evaporation. The residue (yellow cloudy oil) was treated with 25 mL of water and 25 mL of hexanes. The organic phase was removed; the aqueous phase was extracted with hexanes (4 × 15 mL) and the combined organic extracts were dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude light yellow oil (7.63 g) was subjected to Kugelrohr distillation. Some byproduct was collected at 127−132 °C/0.15 mmHg, and the product was collected as a slightly cloudy oil at 180−190 °C/0.16 mmHg (1.03 g, 44.6% yield, 90% purity by ^1H NMR). This product can be used without further purification. Column chromatography with silica gel (10 g) treated with Et_3N (0.75 g in 50 mL of hexanes) was attempted for the purification of ~0.25 g of the product, followed by Kugelrohr distillation, but no significant improvement in the purity was observed. Probably, the column chromatography even for the treated with Et_3N silica gel results in slight protio-destannylation of the product. MS (APCI): 478.3, 480.2, 482.1 (calcd FW 481.2730). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.84−0.91 (m, 12H), 1.08−1.14 (m, 6H), 1.22−1.38 (m, 16H), 1.50−1.62 (m, 8H), 2.50−2.57 (m, 2H), 7.28−7.33 (d, J = 1.59 Hz, 2H), 8.57−8.60 (*appears as t*, J = 1.40 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.74, 13.68, 14.09, 22.66, 27.64, 29.10, 29.40, 29.72, 31.12, 31.86, 33.12, 131.90 (CH), 133.26 (CH), 136.09 (quaternary C), 151.00 (CH), 169.95 (quaternary C).

Representative Procedure for the Stille Coupling of Pyridinyl Stannanes with Aryl Bromides: 6′-Decyl-6-(5-undecylthiophen-2-yl)[3,3′]bipyridinyl (26b). An oven-dried flask was charged with 2-(5-*n*-undecylthien-2-yl)-5-bromopyridine (**25b**) (2.75 mmol, 1.01 g) and 2-*n*-decyl-5-(tri-*n*-butylstannyl)pyridine (**6d**) (2.75 mmol, 1.40 g, colorless oil). Anhydrous DMF (10 mL) was added under nitrogen atmosphere, and the resulting mixture was heated for 2 h (130−140 °C). After an hour of stirring the mixture became darker in color (green-gray), and no starting stannane **6d** was observed by TLC after 2 h of heating. The dark green-gray mixture was cooled, the solution with precipitate was applied to the top of the column (75 g of silica gel), and the organic materials were eluted with hexanes:CH_2Cl_2 = 1:1. The solvents were removed from combined fractions by rotary evaporation, the product was dissolved in ~10 mL of hexanes, the solution was cooled in a freezer, and the product was isolated as off-white solid (1.01 g, 68.7% yield) after vacuum filtration. The material was dissolved in several milliliters of dichloromethane and filtered through basic Al_2O_3 column (50 g, CH_2Cl_2 as eluant). The white solid isolated after the evaporation of the solvent from combined fractions was recrystallized from ~20 mL of 1-PrOH (0.74 g, 73.3% recovery). MS (APCI): 533.6 (calcd FW 532.3851). FT-IR (cm^{-1}): 3081, 2955, 2915, 2848, 1595, 1547, 1484, 1468, 1429, 1403, 1376, 1355, 1064, 1025, 994, 967, 929, 825, 798, 756, 720, 648. ^1H NMR ($CDCl_3$,

400 MHz): δ 0.84−0.92 (t, J = 6.84 Hz, 6H), 1.20−1.45 (m, 30H), 1.68−1.81 (m, 4H), 2.80−2.88 (m, 4H), 6.80−6.83 (d, J = 3.68 Hz, 1H), 7.21−7.28 (d, *overlaps with $CHCl_3$ signal*, 1H), 7.42−7.46 (d, J = 3.63 Hz, 1H), 7.64−7.70 (dd, J = 8.30 Hz, 0.70 Hz, 1H), 7.77−7.82 (dd, J = 8.04 Hz, 2.43 Hz, 1H), 7.82−7.88 (dd, J = 8.28 Hz, 2.35 Hz, 1H), 8.73−8.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.14, 22.70, 29.09, 29.35, 29.39, 29.44, 29.53, 29.56, 29.58, 29.63, 29.66, 29.92, 30.46, 31.56, 31.92, 38.18, 118.32 (CH), 122.83 (CH), 124.74 (CH), 125.37 (CH), 130.52 (quaternary C), 131.08 (quaternary C), 134.26 (CH), 134.64 (CH), 141.43 (quaternary C), 147.25 (CH), 147.59 (CH), 149.23 (quaternary C), 152.24 (quaternary C), 162.24 (quaternary C).

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Supporting Information Available: Detailed synthetic procedures and characterization data for the synthesized compounds, reaction schemes for the preparation of LC **20**, aryl bromides **25a**,**b**, and mesogens **26a**,**b**, and DSC analysis for the compounds **20** and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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