Pergamon

Tetrahedron 54 (1998) 2365–2370

TETRAHEDRON

A New Approach to Symmetric 2,2':6',2''-Terpyridines

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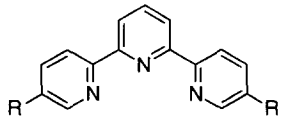
Received 2 September 1997; revised 17 December 1997; accepted 21 December 1997

Abstract: A novel four step process for the preparation of symmetric terpyridines is presented. The title compound, 2,2':6',2''-terpyridine (**1a**) and a substituted derivative, 5,5''-dimethyl-2,2':6',2''-terpyridine (**1b**) are prepared. Both **1a** and **1b** share a common precursor, 2,6-diacetylpyridine (**2**) and are prepared in overall yields of 73 and 93% respectively. The purities of the *crude* terpyridine products are in the 90-95% range.

The tridentate ligand 2,2':6',2''-terpyridine **1a** forms very stable hexacoordinate complexes of predictable geometry with a wide range of transition metals. As such, it has seen a recent increase in its application as a dependable well defined architectural component in supramolecular chemistry.[1] Despite the increased interest in taking advantage of this family of molecule's tenacious ability to form stable metal complexes few new methods to prepare terpyridines have been reported. According to Thompson's recent comprehensive review of the synthesis of these ligands[2] the two most common approaches to terpyridines are, (1) methods by which the central ring is constructed usually via the ammonia condensation of a 1,5-enedione (most often generated in situ)[3] and (2) the direct coupling of pyridine rings.[4] The first method is by far the most common and has proven successful in producing a wide variety of terpyridine products.[2] Although this method has the advantage of directness (usually two steps) the crude products of the final condensation step are often described as "black tars," requiring a determined effort to isolate and purify the desired terpyridine. I contrast, when it can be applied, the direct coupling of pyridine rings affords clean products in good yields. In this paper we wish to present a novel approach to the preparation of symmetric terpyridines which combines both high overall yields and excellent *crude* product purities.



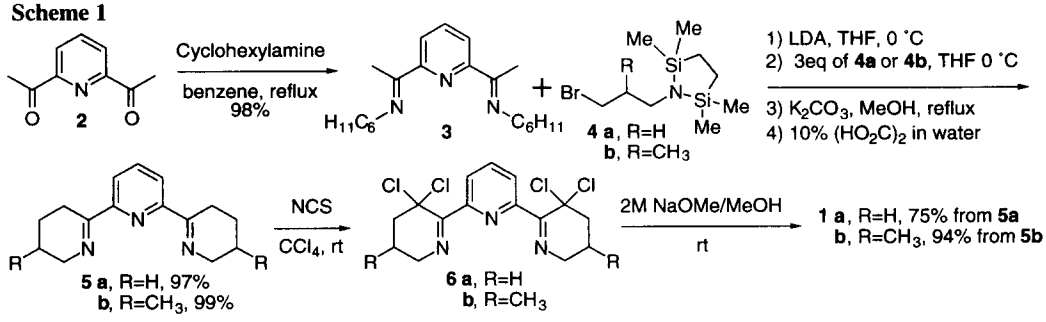
1 a, R=H
b, R=CH_3

Recently, a highly efficient route to pyridines via 2,3,4,5-tetrahydropyridines was reported.[5] This strategy, outlined in Scheme 1, could be used in a tandem approach to prepare symmetric terpyridines. The target terpyridines, **1a** and **1b**,[6] were prepared form the commercially available 2,6-diacetylpyridine[7] (**2**), which

0040-4020/98/$19.00
PII: S0040-4020(98)00005-2

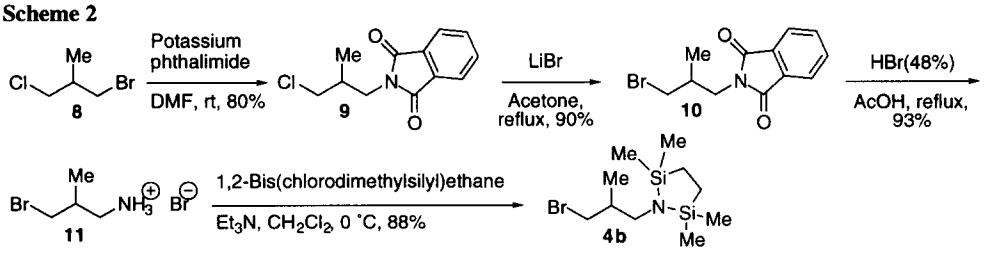
is quantitatively converted to 2,6-bis(*N*-cyclohexylacetimidoyl)pyridine (**3**) by reaction with cyclohexylamine in refluxing benzene with a Dean-Stark trap. The tetrahydropyridines **5a** and **5b** are obtained by cyclization of the bis-imine **3** with the ethylenetetramethyldisilyl-protected 3-bromopropylamines **4a**[8] or **4b**, in 97 and 98% yield, respectively, via α-alkylation, *N*-deprotection and transimination. The tetrachlorination of either **5a** or **5b** is accomplished by reaction with *N*-chlorosuccinimide (NCS) in carbon tetrachloride at room temperature. The tetrachloro adducts **6a** or **6b** are not isolated but are converted by the action of sodium methoxide in methanol at room temperature directly to the desired terpyridines, **1a** or **1b**. The overall yields for the title terpyridines, starting from the bis-imine **3** are 73 and 93%, respectively. The yields are not optimized.

Scheme 1



For substitution on the terminal rings the present method requires the preparation of a 3-bromo-(or iodo)-propylamine derivative. This is in contrast to current methods which require either the manipulation of the terminal pyridine rings prior to construction of the terpyridine[1b,e] or selective modification of the terpyridine product.[3b] Scheme 2 illustrates the preparation of the ethylenetetramethyldisilyl-protected 3-bromo-2-methylpropylamine, **4b**, required for the synthesis of **1b**. It has to be stressed that this is a very high-yielding procedure for the synthesis of γ-bromoamine derivative **4b**, which is otherwise difficultly accessible. Given the relative ease of manipulating malonate or acetoacetate, many synthons of the required propane derivatives can be envisioned.

Scheme 2



A novel synthetic approach to the preparation of symmetric terpyridines which affords the target in high purity and good to excellent yields, is presented. Since the target terpyridine is likely to be only a component in a multi-step synthesis or otherwise intended for further study, researchers may well not be interested in spending a great deal of time optimizing reaction conditions. With this in mind, we report here the "first time" efficiency of this process. It is interesting to note, that **1b** was prepared after **1a**. The resulting excellent yield of **1b** is due

simply to practicing the reaction sequence. This process poses little problem for scale-up, as demonstrated by the multigram synthesis of **1b**. Finally, this tandem approach is not limited to the title compounds but could be used to prepare other terpyridine and polypyridine products. Efforts to modify this method for the preparation of unsymmetric 2,2':6',2"-terpyridines are currently on-going and will be reported in due course.

EXPERIMENTAL

General. Melting points were determined on a Mel-Temp II® capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs of Norcross, Georgia. Low and high resolution mass spectra were performed by the Mass Spectrometry Service of the University of Illinois. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were determined at 200 MHz, and ^{13}C NMR spectra were determined at 50 MHz and were obtained on a Varian Gemini 200 MHz spectrometer.

2,6-Bis(*N*-cyclohexylacetimidoyl)pyridine (3) A stirred solution of 5.02 g (30.8 mmol) of 2,6-diacetylpyridine (**2**) and 13.00 g (131.1 mmol) of cyclohexylamine in 100 mL of benzene was heated at reflux with a Dean-Stark trap. After 24 h the reaction mixture was concentrated *in vacuo* to afford ≈15 g of wet crystals. The wet crystals were then recrystallized from 100 mL of MeOH affording 9.79 g of **3** as colorless plates (98%); mp 137-138 °C; Rf = 0.41 (SiO_2, 4% EtOAc/hexane); IR (Thin film) 2923, 2851, 1636, 1569, 1451, 1354, 1313, 1262, 1097, 1077, 985, 887, 821, 744 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 8.06 (d, 2H, J = 8.0 Hz), 7.66 (t, 1H, J = 8.0 Hz), 3.56 (m, 2H), 2.46 (s, 6H), 1.90-0.70 (m, 20H); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 164.0, 156.7, 136.5, 121.1, 60.3, 33.5, 25.9, 24.9, 13.5; HRMS (EI), *m/z* calcd for $C_{21}H_{31}N_3$ (M^+) 325.2518, measured 325.2516. Anal. calcd for $C_{21}H_{31}N_3$: C, 77.49; H, 9.60. Found: C, 77.73; H, 9.51.

3,3",4,4",5,5",6,6"-Octahydro-2,2':6',2"-terpyridine (5a) To a stirred solution of 6.4 mmol of LDA (generated in situ) in 6 mL THF at 0 °C was added, in a dropwise fashion, a solution of 0.65 g (2.0 mmol) of **3** in 6 mL of THF. After 2 h the ice bath was removed and a solution of 1.71 g (6.1 mmol) of the silyl-protected 3-bromopropylamine, **4a**, in 6 mL of THF was added dropwise. After 15 h the reaction mixture was poured into 5 mL of a 0.5 M NaOH solution and extracted with 3x25 mL portions of ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford a viscous brown residue. The residue was dissolved in 8 mL of absolute MeOH. To this stirred solution was added 1.65 g (12 mmol) of K_2CO_3 and heated to reflux. After 3 h the reaction mixture was poured into 100 mL of water and extracted with 3x25 mL portions of CH_2Cl_2. The combined organic phases were concentrated *in vacuo* and the resulting residue was dissolved in 10 mL of ether. The ether solution was then poured into 8 mL of a 10% oxalic acid solution and this mixture was shaken and separated. The aqueous layer was washed with 2x25 mL portions of ether and then made alkaline by addition of NaOH pellets. The alkaline aqueous phase was extracted with 3x25 mL portions of CH_2Cl_2, dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford 0.47 g (97%) of **5a** as a viscous brown oil which solidified on standing. The crude **5a** was used in the next step; Rf = 0.31 (Alumina, 1% MeOH/CH_2Cl_2); IR (Thin film) 2933, 2851, 1641, 1569, 1446, 1364, 1067, 810, 744 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 8.00 (d, 2H, J = 8.0 Hz), 7.72 (t, 1H, J = 8.0 Hz), 3.85 (m, 4H), 2.88 (m, 4H), 1.83 (m,

4H) 1.69 (m, 4H); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 167.7, 155.7, 138.5, 120.5, 50.1, 25.8, 22.1, 18.5; HRMS (EI), *m/z* calcd for $C_{15}H_{19}N_3$ (M^+) 241.1579, measured 241.1578.

5,5"-Dimethyl-3,3",4,4",5,5",6,6"-octahydro-2,2':6',2"-terpyridine (5b) The preparation was analogous to **5a** (yield of **5b**; 3.22 g, 99%), starting with **3** (3.93 g, 12.1 mmol) and **4b** (10.67 g, 36.2 mmol) and was used in the next step without further purification; mp 109-111 °C; Rf = .37 (Alumina, 1% MeOH/CH_2Cl_2); IR (Thin film) 2954, 2923, 2872, 1672, 1533, 1456, 1380, 1169, 1077, 995, 923, 728 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 8.00 (d, 2H, J=8.0 Hz), 7.72 (t, 1H, J = 8.0 Hz), 4.00 (ddd, 2H, J = 2 Hz, J = 3 Hz, J = 18 Hz), 3.26 (m, 4H), 2.65 (m, 2H), 1.94 (m, 2H), 1.72 (m, 2H), 1.38 (m, 2H), 1.01 (d, 6H, J = 7 Hz); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 165.8, 154.1, 134.9, 119.0, 56.1, 26.2, 25.8, 24.7, 17.6; HRMS (EI), *m/z* calcd for $C_{17}H_{23}N_3$ (M^+) 269.1892, measured 269.1887.

4,4",5,5",6,6"-Hexahydro-3,3,3",3"-tetrachloro-2,2':6',2"-terpyridine (6a) To a stirred solution of 0.28 g (1.2 mmol) of **5a** in 3 mL of CCl_4 at room temperature was added 0.77 g (5.8 mmol) of NCS. After 15 h the reaction mixture was cooled to 0 °C and the succinamide removed by filtration. The filtrate was then evaporated to afford 0.40 g of **6a**, which was used, as is, in the next step. **Caution:** Care must be taken not to heat the reaction mixture above room temperature or significant decomposition occurs; IR (Thin film) 3354, 2933, 1708, 1579, 1446, 1390, 1067, 1036, 790, 733 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 7.72 (m, 3H), 3.98 (t, 4H, J=6.0 Hz), 2.77 (m, 4H), 2.06 (m, 4H); HRMS (EI), *m/z* calcd for $C_{15}H_{15}Cl_4N_3$ (M^+) 377.0020, measured 377.0020.

5,5"-Dimethyl-4,4",5,5",6,6"-hexahydro-3,3,3",3"-tetrachloro-2,2':6',2"-terpyridine (6b) The preparation was analogous to **6a**, starting with **5b** (2.96 g, 11.0 mmol); IR (Thin film) 2955, 2927, 2871, 1715, 1631, 1575, 1454, 1380, 1161, 1031, 901, 877, 826, 790 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 7.82 (m, 3H), 4.18 (ddd, 2H, J = 3 Hz, J = 5 Hz, J = 19 Hz), 3.29 (dd, 2H, J = 10.0 Hz, J = 19 Hz), 2.83 (ddd, 2H, J = 1 Hz, J = 3 Hz, J = 12 Hz), 2.33 (m, 4H), 1.05 (d, 6H, J = 6.0 Hz); HRMS (EI), *m/z* calcd for $C_{17}H_{19}Cl_4N_3$ (M^+) 405.0333, measured 405.0329.

2,2':6',2"-terpyridine (1a) A solution of 0.40 g of **6a** in 6.0 mL of 2M NaOMe in MeOH was stirred at room temperature. **Caution:** Care must be taken not to heat the reaction mixture above room temperature or significant decomposition occurs. After 20 h the reaction mixture was poured into ≈20 mL of water and extracted with 3x20 mL portions of CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford 0.21 g (75% from **5a**) of **1a** as a light tan solid. The purity was estimated by ^{1}H-NMR to be ≥ 95%. Crystalline material can be obtained if the crude product is passed through a short column (50mm x 15mm) of neutral alumina and eluted with 2% Et_2O/CH_2Cl_2; crude mp 84-86 °C (Lit mp 84-87 °C[2d]); Rf = 0.55 (alumina, 1% MeOH/CH_2Cl_2); IR (Thin film) 3056, 3015, 1580, 1564, 1472, 1456, 1421, 1262, 1149, 1103, 1077, 1041, 990, 769, 738, 656, 631 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 8.71 (ddd, 2H, J = 1.0 Hz, J = 2.0 Hz, J = 5.0 Hz), 8.64 (dt, 2H, J = 1.0 Hz, J = 1.0 Hz, J = 8.0 Hz), 8.71 (d, 2H, J = 8.0 Hz), 7.97 (t, 1H, J = 8.0 Hz), 7.87 (td, 2H, J = 2.0 Hz, J = 8.0 Hz), 7.35 (ddd, 2H, J = 1.0 Hz, J = 5.0 Hz, J = 8.0 Hz); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 156.2, 155.3, 149.2, 137.8, 136.8, 123.8, 121.1, 121.0; LRMS, *m/z* calcd for $C_{15}H_{11}N_3$ (M^+) 233.1, measured 233.1; Anal. calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.18; H, 4.75; N, 18.02.

5,5"-dimethyl-2,2':6',2"-terpyridine (1b) The preparation was analogous to **1a** starting with **6b** (yield of **1b**; 2.70 g, 94% from **5b**); mp 169-171 °C (Lit mp 171 °C[1e,4c]); Rf = 0.55 (alumina, 1%

MeOH/CH_2Cl_2); IR (Thin film) 2995, 2964, 2913, 1590, 1559, 1487, 1446, 1374, 1256, 1133, 1076, 1026, 867, 815, 754 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 8.53 (bs, 2H), 8.51 (d, 2H, J = 8.0 Hz), 8.38 (d, 2H, J = 8.0 Hz), 7.92 (t, 1H, J = 8.0 Hz), 7.65 (dd, 2H, J = 2.0 Hz, J = 8.0 Hz), 2.41 (s, 6H); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 155.4, 153.8, 149.6, 137.7, 137.3, 133.3, 120.6, 120.3, 18.2; HRMS (EI), *m/z* calcd for $C_{17}H_{15}N_3$ (M^+) 261.1265, measured 261.1267.

***N*-(3-Chloro-2-methylpropyl)phthalimide (9).** To a stirred solution of 11.2 g (65.4 mmol) of **8** in 65 mL of DMF at room temperature was added 14.9 g (5.8 mmol) of potassium phthalimide. After 48 h the reaction mixture was poured into 300 mL of water. The resulting oil was separated and the aqueous phase was extracted with 3x50 mL portions of CH_2Cl_2 which are combined with the initial oil. The combined organic phases were washed sequentially with 3x100 mL portions of water, 50 mL of 10% NaOH, and 50 mL of sat. NaCl, dried ($MgSO_4$), filtered and concentrated *in-vacuo* to afford 12.4 g (80%) of a clear colorless oil which crystallizes on standing, affording a white microcrystalline solid. The crude product was used in the next step without further purification. An analytical sample was recrystallized from 10% water/EtOH; mp 60-62 °C; IR (Thin film) 2970, 1774, 1714, 1614, 1465, 1435, 1395, 1361, 1311, 1266, 1191, 1047, 913, 718 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 7.86 (dd, 2H, J = 3.0 Hz, J = 6.0 Hz), 7.72 (dd, 2H, J = 3.0 Hz, J = 6.0 Hz), 3.72 (dd, 1H, J = 7.0 Hz, J = 14.0 Hz), 3.67 (dd, 1H, J = 6.0 Hz, J = 14.0 Hz), 3.50 (m, 2H), 2.41 (m, 1H), 1.07 (d, 3H, J = 7.0 Hz); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 167.0, 132.6, 130.4, 121.9, 46.8, 39.9, 33.5, 14.2; HRMS (EI), *m/z* calcd for $C_{12}H_{12}ClNO_2$ (M^+) 237.0556, measured 237.0557; Anal. calcd for $C_{12}H_{12}ClNO_2$: C, 60.64; H, 5.09; N, 5.89. Found: C, 60.74; H, 5.13; N, 5.82.

***N*-(3-Bromo-2-methylpropyl)phthalimide (10).** A stirred solution of 10.4 g (43.9 mmol) of **9** and 20.5 g (236 mmol) of LiBr in 50 mL of acetone was heated at reflux. After 24 h a precipitate is observed. After a total of 48 h the reaction mixture was poured into 200 mL of water. The resulting yellow oil was separated and the aqueous phase was extracted with 3x50 mL portions of CH_2Cl_2 which were combined with the initial oil. The combined organic phases were washed sequentially with 3x50 mL portions of water and 50 mL of sat. NaCl, dried ($MgSO_4$), filtered and concentrated *in-vacuo* to afford 11.1 g (90%) of a clear yellow oil which crystallizes on standing, affording a white microcrystalline solid. The crude product was used in the next step without further purification. An analytical sample was recrystallized from methanol; mp 70-71 °C; IR (Thin film) 2964, 2927, 1770, 1715, 1435, 1398, 1361, 1040, 915, 719 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 7.86 (dd, 2H, J = 3.0 Hz, J = 5.0 Hz), 7.73 (dd, 2H, J = 3.0 Hz, J = 5.0 Hz), 3.69 (m, 2H), 3.41 (dd, 1H, J = 5.0 Hz, J = 10.0 Hz), 3.35 (dd, 1H, J = 7.0 Hz, J = 10.0 Hz), 2.40 (m, 1H), 1.08 (d, 3H, J = 7.0 Hz); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 166.8, 132.6, 130.3, 121.7, 40.5, 36.1, 33.2, 15.2; HRMS (EI), *m/z* calcd for $C_{12}H_{12}BrNO_2$ (M^+) 281.0051, measured 281.0051; Anal. calcd for $C_{12}H_{12}BrNO_2$•0.2($C_{12}H_{12}ClNO_2$): C, 52.46; H, 4.40; N, 5.10. Found: C, 52.57; H, 4.42; N, 5.04.

3-Bromo-2-methylpropylamine Hydrobromide (11). A stirred suspension of 15.4 g (54.4 mmol) of **10** in 50 mL of a 48% HBr/Glacial AcOH (2:1, v:v) solution was heated at reflux. After 15 h the reaction mixture was a homogeneous amber solution which was poured directly onto ice. The phthalic acid precipitate was removed by filtration and washed sequentially with 10 mL 10% HBr and 20 mL of water. The filtrate was concentrated by vacuum distillation (25 mm Hg) almost to dryness. The resulting wet solid was dissolved in 25

mL of hot EtOH and concentrated *in vacuo* ; this process was repeated twice. The resulting solid was then crushed with Et_2O and isolated by filtration, affording 11.75 g (93%) of **11** as a gray solid. No further purification was done; mp 156-160 °C; 200 MHz ^{1}H-NMR (D_2O) δ 3.34 (m, 2H), 2.99 (dd, 1H, J = 6.0 Hz, J = 13.0 Hz), 2.75 (dd, 1H, J = 8.0 Hz, J = 13.0 Hz), 2.06 (m, 1H), 0.92 (d, 3H, J = 7.0 Hz); 50 MHz ^{13}C-NMR (D_2O) δ 41.6, 35.5, 14.6, 13.6; HRMS (FAB), *m/z* calcd for $C_4H_{11}Br_2N$ (M – Br^+) 152.0075, measured 152.0074; Anal. calcd for $C_4H_{11}Br_2N$: C, 20.62; H, 4.76; N, 6.02. Found: C, 20.73; H, 4.60; N, 6.41.

1-(3-Bromo-2-methylpropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (4b). To a stirred suspension of 10.5 g (45.2 mmol) of **11** in 50 mL of CH_2Cl_2 was added 20.0 mL (144 mmol) of dry Et_3N. After 5 min the reaction mixture was cooled to 0 °C and a solution of 9.90 g (46.0 mmol) of 1,2-bis(chlorodimethylsilyl)ethane in 25 mL of CH_2Cl_2 was added dropwise. After the addition was complete the ice bath was removed. After 2 h the solvent was removed *in vacuo* from the resulting suspension and the residue was taken up in 100 mL of pentane. The triethylamine hydrobromide and hydrochloride salts were removed by filtration and the filtrate was concentrated *in vacuo* affording 11.76 g (88%) of **4b** as a pale yellow oil. No further purification was done; IR (neat) 2954, 2913, 1456, 1421, 1380, 1251, 1128, 1031, 949, 846, 780 cm^{-1}; 200 MHz ^{1}H-NMR ($CDCl_3$) δ 3.48 (dd, 1H, J = 4.0 Hz, J = 10.0 Hz), 3.29 (dd, 1H, J = 6.0 Hz, J = 10.0 Hz), 2.72 (m, 2H), 1.83 (m, 1H), 0.97 (d, 3H, J = 7.0 Hz), 0.70 (s, 4H), 0.52 (s, 12H); 50 MHz ^{13}C-NMR ($CDCl_3$) δ 47.1, 39.3, 38.3, 17.0, 7.9, -0.2, -0.5.

Acknowledgment: This work was supported by a grant from the Research Corporation, Cottrell College Science Award # CC1465. Facilities support from Union College is gratefully acknowleged.

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6. The 5,5"-dimethylterpyridine, **1b**, was recently reported by Hasenknopf and Lehn (ref. 1e) and by Cárdenas and Sauvage (ref. 3c). Hasenknopf and Lehn prepared **1b** by the method of Jameson (ref. 3d), a 1,5-enedione condensation, in a 35% yield for the final condensation step. Cárdenas and Sauvage prepared **1b** via a Stille cross-coupling reaction in a 64% overall yield.

7. R.-A. Fallahpour and E. C. Constable have recently reported a preparation of symmetric terpyridines starting from chelidamic acid which is converted the 2,6-diactylpyridine derivative. The termninal rings, with substituents at the C(4), C(5) and/or C(6) positions are then constructed via a Kröhnke synthesis in 45-60% yields from the diactylpyridines. *J. Chem. Soc., Perkin Trans. 1* **1997,** 2263-2264.

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