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Functionalized 2,2′-Bipyridines and 2,2′:6′,2″-Terpyridines via Stille-Type Cross-Coupling Procedures

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Abstract: Stille-type cross-coupling procedures are utilized in order to prepare a variety of functionalized 2,2′-bipyridines and 2,2′:6′,2″-terpyridines. Such N-heterocyclic compounds are of great interest as chelating ligands for transition-metal ions in the field of supramolecular chemistry. Various mono- and disubstitued 2,2′-bipyridines were synthesized in high yields and multigram scales using a modular design principle. The terpyridines may be functionalized in one step with different substituents at the outer pyridine rings and at the 4′-position of the centered ring, leading to multifunctionalized compounds. The initially obtained methyl ester and ethyl ester groups can be simply converted into bromomethyl and hydroxymethyl groups which allow further functionalization reactions.

N-Heterocyclic compounds are of major importance in biological systems. In porphyrine derivatives, they act as ligands for transition metals and are responsible for energy conversion and substance transport in cells. In supramolecular chemistry, *oligo*pyridines are utilized as bi-, tri-, and multidentate ligands besides the well-known coronands, cryptands, and podands[1,2] and may form helical or grid-like superstructures.[3] Moreover, *oligo*pyridines allow the formation of supramolecular, metal containing polymers.[4] An efficient synthesis of *oligo*pyridines and the introduction of substituents in any ring position is required for the construction of versatile metallo-supramolecular architectures. Besides the coupling of organosulfur compounds[5] or of lithium pyridines with $CuCl_2$,[6] the most efficient way to well-directed functionalization of bi- and terpyridines is represented by modern palladium(0)-catalyzed cross-coupling procedures. Suzuki-,[7−9] Negishi-,[10,11] and Stille-type coupling reactions[12,13] are distinguished by excellent yields and the free choice of the substitution positions. Stille-type cross-coupling provides the possibility to introduce different functional groups into 2,2′-bipyridines and 2,2′:6′,2″-terpyridines in one step. A range of further functional group conversions described herein opens avenues to useful multifunctional chelating agents, which may form metal complexes with special photo- and electrochemical properties[14−17] or can be utilized as supramolecular initiators for different types of controlled polymerization procedures.[18−20]

Stille-type cross-coupling procedures enable the well-directed introduction of methyl substituents into any 2,2′-bipyridine ring position.[21] In particular, the unsymmetrically disubstituted methylbipyridines are not as common. The 4,6′- and the 4,5′-dimethyl-2,2′-bipyridines have been reported previously only as byproducts of the reaction of pyridine *N*-oxides with pyridine derivatives.[22,23] Starting from the cheap aminopicolines **1a**−**c**, the corresponding bromopicolines **2a**−**c** can be obtained in hundred gram quantities by a simple diazotation/bromination sequence (Scheme 1).[24,25] The bromopicolines can be utilized on one hand as one coupling agent for the Stille coupling and on the other hand for the further conversion to the 2-tributylstannylpyridines **3a**−**c**, which then act as the second coupling partner. The stannylation of the bromo compounds via *n*-butyllithium and the following transmetalation step can be performed nearly quantitative in the case of the 5- and 6-methyl-2-tributylstannylpyridine **3a** and **3b**.

The following Stille-type cross-coupling reaction is carried out in degassed toluene in the presence of tetrakis(triphenylphosphine)palladium(0) as catalyst. Depending on the position of the methyl groups in the starting materials, the corresponding monomethyl-substituted bipyridines **4**−**6** and symmetrically or unsymmetrically dimethyl-substituted bipyridines **7**−**12** are obtained in good yields (Scheme 1). For the synthesis of the monomethyl functionalized bipyridines **4**−**6**, the corresponding bromopicolines **2a**−**c** were coupled with 2-tributylstannylpyridine **3d**. However, it is also possible

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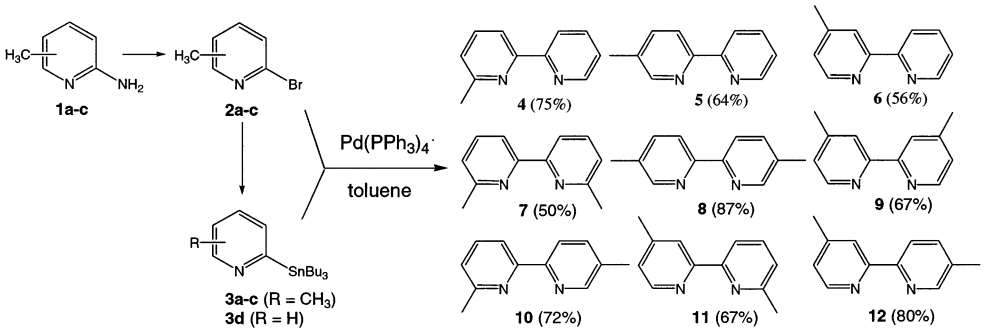
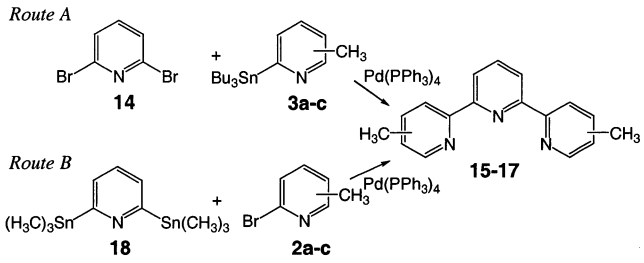
SCHEME 1. Preparation of Various 2,2′-Bipyridines with Methyl Substituents



SCHEME 2. Dimethyl-2,2′:6′,2″-terpyridines via Two "Orthogonal" Stille-Type Coupling Routes[a]



[a] Positions (and yields) of the methyl substituents: **15** = 6,6″ (A, 0%; B, 43%), **16** = 5,5″ (A, 90%; B, 69%), **17** = 4,4″ (A, 50%; B, 52%).

to prepare these bipyridines utilizing the 2-tributylstannylpicolines **3a**−**c** and 2-bromopyridine. Substituents at the 3-position are not considered closer due to the introduction of a twisting of the two pyridine rings, by which the chelating properties disappear. The monomethyl substituted bipyridines **4**−**6** could also be obtained via the more extensive Negishi coupling in excellent yields.[11]

The methyl groups of the bipyridines can be easily converted to the corresponding bromomethyl groups by use of *N*-bromosuccinimide (NBS) and azoisobutyronitrile (AIBN) as shown, e.g., in the case of the monomethylbipyridine **13** (see the Experimental Section). The bromomethyl group then acts as the key moiety for further functionalization reactions. In general, the disadvantage of the simple NBS bromination are the low yields. For that reason, Fraser et al. have developed another synthesis, where the bromofunction is introduced via substitution of a trimethylsilyl group in excellent yields.[11,26] To avoid the high synthetic and temporal expenditure of this method, we enhanced the classical NBS bromination of monomethyl bipyridines by a fast workup of the crude product, which otherwise rapidly decomposes.

The Stille-type cross-coupling procedures can be also used for the preparation of functionalized 2,2′:6′,2″-terpyridines (see also ref 27 for a first preliminary communication). The preparation of 2,2′:6′,2″-terpyridines requires the utilization of 2,6-bis-functionalized pyridines that act as central building blocks. After the Stille-coupling, they become the central pyridine unit of the terpyridine. By the use of 4-functionalized pyridine compounds, the introduction of functional groups into the interesting central 4′-position of terpyridines becomes straightforward. The coupling partners of the central compound continue to be the 2-bromo- or 2-tributylstannylpyridines **2a**−**c** or **3a**−**c**. 2,2′:6′,2″-Terpyridines without 4′-functions, bearing methyl substituents at different positions of the outer pyridine rings may be obtained via two "orthogonal" routes of preparation (Scheme 2).

In route A, 2,6-dibromopyridine **14** acts as the central unit and is coupled with 6-, 5-, or 4-methyl-2-tributylstannylpyridine (**3a**−**c**), respectively. The corresponding methyl-terpyridines **16** and **17** are obtained in good yields.[28−30] The attempt to synthesize 6,6″-dimethyl-2,2′:6′,2″-terpyridine leads to a mixture of different compounds, from whom the desired product may not be purely separated by common methods. As the main product, 6-bromo-6′-methyl-2,2′-bipyridine, was detected by GC−MS investigations. After the first coupling step, the reaction seems to stop due to the steric and/or electronic influence of the pyridine ring at the 6-position of this intermediate. Thereby, the reactivity of the bromo function is reduced.[31] The application of route B finally enables the synthesis of 6,6″-dimethyl-2,2′:6′,2″-terpyridine **15**. 2,6-Bis(trimethylstannyl)pyridine **18**[32] functions as central coupling agent and may be converted with the 2-bromopicolines **2a**−**c** to yield the terpyridines **15**−**17**. Therefore, compared to route 1, route 2 represents an inverse synthetic strategy.

The formation of the versatile multifunctional 2,2′:6′,2″-terpyridines can be achieved as mentioned above by the use of 2,6-dihalogenopyridines additionally functionalized in the 4-position. For this, 2,6-dichloroisonicotinic methyl or ethyl esters **19** or **20** are useful central building blocks. The Stille cross-coupling with 5-methyl-2-tributylstannylpyridine **3b** leads in high yields to the corresponding 5,5″-dimethyl-2,2′:6′,2″-terpyridine-4′-esters **21** and **22**. Both the central ester group and the outer methyl groups are available for different functionalization reactions which are outlined in Scheme 3. Therefore, such compounds function as basic agents for different functional group conversions toward multifunctional terpyridine ligands.

5,5″-Dimethyl-4′-(hydroxymethyl)-2,2′:6′,2″-terpyridine **23** can be obtained in very high yield by the

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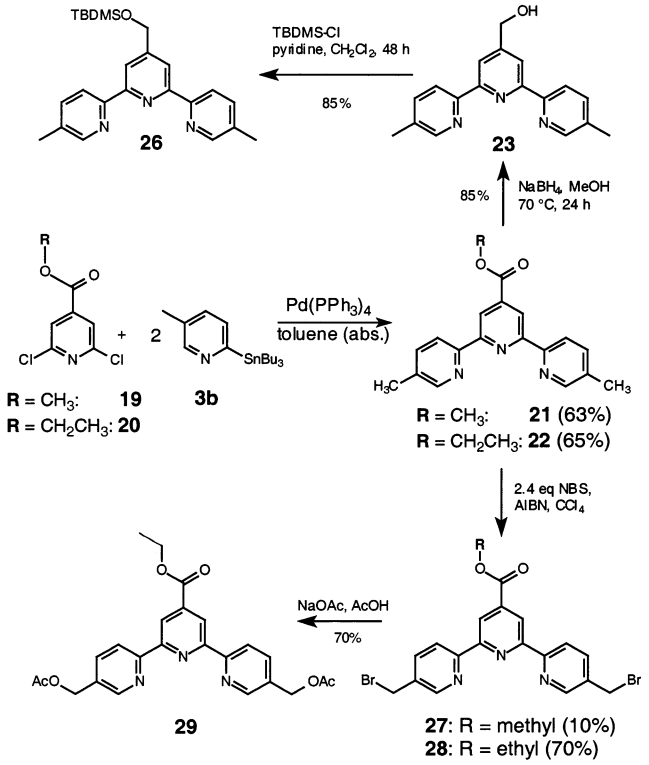
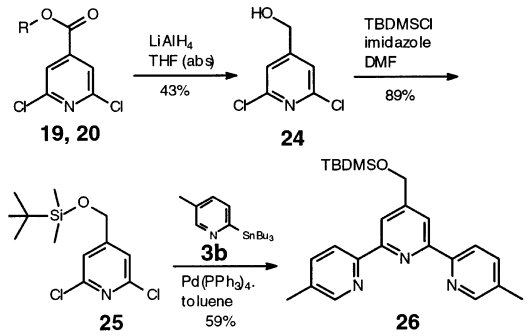
SCHEME 3. Introduction of an Ester Function into the 4′-Position and Functional Group Conversions



SCHEME 4. Alternative Route to 4′-TBDMSO-terpyridine 26 via Direct Stille Coupling



reduction of **21** with excess of $NaBH_4$ in methanol. The reaction of **23** with *tert*-butyldimethylsilyl chloride (TBDMSCl) in the presence of imidazole under basic conditions leads to **26**. Protection of the hydroxy function should enable the unaffected functionalization of the methyl groups.

Compound **26** is also accessible by direct Stille coupling with 2,6-dichloro-4-(*tert*-butyldimethylsilanyloxymethyl)-pyridine **25** (Scheme 4). Building block **25** is obtained starting from 2,6-dichloroisonicotinic ethyl ester **20** which at first can be reduced to the corresponding alcohol **24** with $LiAlH_4$ (for similar reaction see ref 33). Then, the protective group is introduced by the reaction with TBDMSCl to yield compound **25**. Stille-type cross-coupling of **25** and 5-methyl-2-tributylstannylpyridine **3b** leads to 5,5″-dimethyl-4′-(*tert*-butyl-dimethylsilanyl-oxymethyl)-2,2′:6′,2″-terpyridine **26**. The workup of **26** cannot be carried out as usual because HCl causes the deprotection of the hydroxy function. Instead, gel filtration and purification by column chromatography are applied.

Furthermore, the methyl groups of the 5,5″-dimethyl-2,2′:6′,2″-terpyridine-4′-carboxylic esters **21** and **22** may be brominated via NBS and AIBN in tetrachloromethane. Depending on the use of the methyl ester or ethyl ester derivative, the yields obtained differ considerably. Bromination of the methyl ester produces only 10% of the corresponding bis(bromomethyl)terpyridine **27**, whereas the 5,5″-bis(bromomethyl)-2,2′:6′,2″-terpyridine-4′-ethyl ester **28** can be isolated in approximately 70% yield. This result is most probably caused due to the purification method applied. Up to now recrystallization is the only way to recover the bis(bromomethyl) compounds because chromatographic separation could not yet be realized. Therefore, the influence of the solubility and the tending to crystallize are the most important factors for the different yields. However, in the case of the ethyl ester, it was not yet possible to avoid multiple bromination or to purify the resulting mixture, as it was also observed for similar terpyridine derivatives.[34]

Bromomethyl groups are suitable for almost any nucleophilic substitution reactions. As one example, the formation of 5,5″-bis(acetoxymethyl)-2,2′:6′,2″-terpyridine 4′-ethyl ester **29** is presented, which can be obtained by the reaction of **28** with pure acetic acid and sodium acetate in 70% yield. The acetate groups formally act as protective groups of the corresponding hydroxy functions and are therefore a potential starting point for a series of further derivatizations.

In this contribution, Stille-type cross-coupling procedure is shown to be an easy and universal way toward a large variety of substituted and functionalized bi- and terpyridines. The reactants can be seen as building blocks of a "unit construction system" by which the well-aimed introduction of functional groups into *oligo*pyridines is possible. The terpyridines can be functionalized in one step with different substituents at the outer pyridine rings as well as at the 4′-position of the centered ring. The obtained terpyridines with methyl ester and ethyl ester units can be simply converted into the corresponding bromomethyl and hydroxymethyl derivatives, which are common moieties for further reactions. Therefore, new functionalized terpyridines are accessible as valuable chelating ligands with additional potential applications besides their well-known photo- and electrochemical properties. Several experiments using such multifunctionalized terpyridines in the fields of supramolecular initiators and metallo-supramolecular assemblies are currently in progress.

Experimental Section

Bromopicolines **2a**−**c**, 2-tributylstannylpyridines **3a**−**c** and the methyl substituted 2,2′-bipyridines **4**−**12** were prepared as previously reported.[21] The synthesis of compound **23** we also described elsewhere.[35] The bromomethyl-2,2′-bipyridine **13** has been already reported,[11,36] although the procedure described herein is a considerably efficient modified NBS bromination and

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is therefore mentioned. 2,6-Bis-trimethylstannylpyridine **18** was synthesized according to ref 32.

General Procedures. Dimethyl-2,2′:6′,2″-terpyridines. Route A. The methyl-2-tributylstannylpyridine **3a**−**c** (3.00 g, 7.85 mmol), 2,6-dibromopyridine **14** (0.75 g, 3.17 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 6.0 mol %) were refluxed for 4 days in absolute toluene (50 mL). After removal of the solvent, the black residue was treated with aqueous HCl (3 × 20 mL, 6 M). The suspension was extracted with CH_2Cl_2, and the organic phase was washed again with HCl (20 mL, 6 M). The aqueous solution was added dropwise into cold aqueous ammonia (300 mL, 10%). The precipitate was filtered off, dissolved in CH_2Cl_2, and dried over Na_2SO_4, and the solvent was removed again. The residue was crystallized from ethyl acetate.

Dimethyl-2,2′:6′,2″-terpyridines. Route B. 2,6-Bis(trimethylstannyl)pyridine **18** (12.23 g, 7.66 mmol), the 2-bromomethylpyridine **2a**−**c** (3.29 g, 19.15 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.6 g, 6 mol %) were refluxed in dry toluene (70 mL) for 72 h at 110 °C. After removal of the solvent, the black residue was treated with aqueous HCl (3 × 20 mL, 6 M). The suspension was extracted with CH_2Cl_2, and the organic phase was washed again with HCl (20 mL, 6 M). The aqueous solution was added dropwise into cold aq ammonia (300 mL, 10%). The precipitate was filtered off, dissolved in CH_2Cl_2, and dried over Na_2SO_4, and the solvent was removed again. The residue was crystallized from ethyl acetate.

5-Bromomethyl-2,2′-bipyridine (13). 5-Methyl-2,2′-bipyridine **5** (3.0 g, 17.7 mmol), NBS (3.1 g, 18.0 mmol), and AIBN (40 mg) were refluxed for 2 h in dry CCl_4 (80 mL). Then, the suspension was filtrated. After removal of the solvent in vacuo, *n*-hexane (40 mL) was added immediately to the remaining oil. The mixture was stirred for 1 h, wherein a white solid precipitated. The crude product was filtered off, washed with *n*-hexane (40 mL), and dried over P_2O_5 in vacuo. Recrystallization was carried out in $CHCl_3$ yielding a white solid (2.2 g, 50%): mp 70 °C (ref[11] mp 71−73 °C).

5,5″-Dimethyl-2,2′:6′,2″-terpyridine 4′-Methyl or -Ethyl Ester (21/22). 2,6-Dichloroisonicotinic acid methyl or ethyl ester **19/20** (24.3 mmol), 5-methyl-2-tributylstannylpyridine **3b** (23 g, 60.7 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.7 g, 6 mol %) were dissolved in dry toluene (100 mL) and refluxed for 48 h at 110 °C. After removal of the solvent, the black residue was treated with aq HCl (70 mL, 6 m). The suspension was filtered and then extracted with CH_2Cl_2 (2 × 30 mL), and the organic phase was washed again with HCl (10 mL, 6 M). The aqueous solution was added dropwise into cold aq ammonia (300 mL, 10%). The precipitate was filtered off, dried in vacuo over P_2O_5, and crystallized from ethyl acetate to yield a white solid. **21**: 5.0 g, 63%; mp 157 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 6 H), 3.98 (s, 3 H), 7.63 (m, 2 H′), 8.47 (d, J = 8.2 Hz, 2 H), 8.53 (m, 2 H), 8.90 (s, 2 H). **22**: 5.9 g, 65% (ref[37] 37%); mp 245 °C (ref[37] mp 245−246 °C).

4′-Hydroxymethyl-5,5″-dimethyl-2,2′:6′,2″-terpyridine (23). To a suspension of 5,5″-dimethyl-2,2′:6′,2″-terpyridine 4′-methyl ester **21** (4.00 g, 12.5 mmol) in absolute methanol (200 mL) was added $NaBH_4$ (0.95 g, 25 mmol) in small portions. The mixture was refluxed for 24 h. Every 6 h, additional $NaBH_4$ (0.47 g, 12.5 mmol) was added. After removal of the solvent, aqueous Na_2CO_3 (30 mL, 10%) was added, and the mixture was extracted with chloroform (3 × 30 mL) under reflux. The combined organic phases were washed with water and brine and dried over Na_2SO_4, and the solvent was removed in vacuo. The crude product could be crystallized from CH_2Cl_2 or purified by column chromatography (silica, starting from CH_2Cl_2/CH_3OH 100:3 ending up with CH_2Cl_2/CH_3OH 1:2) to yield 2.8 g (75%) of a white powder: mp 249 °C; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 6 H), 3.63 (s, 1 H), 4.81 (s, 2 H), 7.60 (m, 2 H), 8.32 (s, 2 H), 8.42 (d, J = 7.98 Hz, 2 H), 8.46 (s, 2 H).

4′-(*tert*-Butyldimethylsilanyloxymethyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine (26). Route A. A mixture of 4′-hydroxymethyl-5,5″-dimethyl-2,2′:6′,2″-terpyridine **23** (1.0 g, 3.4 mmol), TBDMSCl (0.56 g, 3.7 mmol), imidazole (0.51 g, 7.4 mmol), and 4-(dimethylamino)pyridine (0.1 g) in absolute DMF (30 mL) was stirred for 24 h at 40 °C. After addition of aqueous $NaHSO_4$ solution (150 mL, 1 M) and diethyl ether (200 mL), the phases were separated and the aqueous phase was extracted with diethyl ether (2 × 40 mL). After washing with brine (30 mL), the solvent was removed in vacuo. The crude product was crystallized from hexane to yield colorless crystals: yield 1.1 g, 80%; mp 137 °C; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.96 (s, 9 H), 2.49 (s, 6 H), 4.82 (s, 1 H), 7.66 (dd, J = 8.01, 1.52 Hz, 2 H), 8.36 (s, 2 H), 8.49 (d, J = 8.01 Hz, 2 H), 8.52 (s, 2 H).

4′-(*tert*-Butyldimethylsilanyloxymethyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine (26). Route B. 2,6-Dichloro-4-(*tert*-butyldimethylsiloxy)methylpyridine **25** (1.0 g, 3.42 mmol), 2-tributylstannyl-5-methylpyridine **3b** (3.3 g, 8.6 mmol), and $Pd(PPh_3)_4$ (0.5 g) were dissolved in degassed dry toluene and refluxed for 48 h under argon. After cooling, the solvent was removed and the dark oil was dissolved in CH_2Cl_2 and filtrated on Al_2O_3 (A3, CH_2Cl_2/MeOH 95:5). The crude product was recrystallized from hexane to yield colorless crystals: yield 0.8 g, 59%.

5,5″-Bis(bromomethyl)-2,2′:6′,2″-terpyridine 4′-Methyl or -Ethyl Ester (27/28). 5,5″-Dimethyl-2,2′:6′,2″-terpyridine-4′-methyl or ethyl ester **21/22** NBS (1.1 eq) and AIBN were refluxed for 2 h in CCl_4. After filtration of the suspension, the solvent was removed in vacuo. The residue was crystallized twice from $CHCl_3$. A white solid was obtained. **27**: 50 mg, 10%; mp 132 °C; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 3 H), 4.57 (s, 4 H), 7.92 (m, 2 H), 8.60 (d, J = 8.2 Hz, 2 H), 8.75 (m, 2 H), 9.00 (s, 2 H). **28**: 3.2 g, 72%; mp 143 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (t, J = 6.06 Hz, 3 H), 4.47 (q, J = 7.06 Hz, 2 H), 4.55 (s, 4 H), 7.89 (dd, J = 8.20, 2.28 Hz, 2 H), 8.56 (d, J = 8.20 Hz, 2 H), 8.72 (s, 2 H), 9.00 (s, 2 H).

5,5″-Bis(acetoxymethyl)-2,2′:6′,2″-terpyridine 4′-Ethyl Ester (29). 5,5″-Bis(brommethyl)-2,2′:6′,2″-terpyridine 4′-ethyl ester **28** (0.5 g, 1.0 mmol) was dissolved in pure acetic acid (20 mL), and dry sodium acetate (82 mg, 1.0 mmol) was added. The mixture was heated under reflux for 1 h. After cooling, the solution was added dropwise to cold aqueous ammonia (150 mL, 10%). The oily product was extracted with CH_2Cl_2 (3 × 20 mL), washed with brine (30 mL), and dried over Na_2SO_4. After removal of the solvent, the crude product was crystallized from ethyl acetate to yield a white solid: yield 0.31 g, 71%; mp 231 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (t, J = 6.06 Hz, 3 H), 2.10 (s, 6 H), 4.45 (q, J = 7.06 Hz, 2 H), 5.17 (s, 4 H), 7.83 (dd, J = 8.01, 2.20 Hz, 2 H), 8.50 (d, J = 8.02 Hz, 2 H), 8.57 (s, 2 H), 8.90 (s, 2 H).

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Supporting Information Available: Characterization of all compounds by mp, ^{1}H and ^{13}C NMR, GC−MS, and EA. This material is available free of charge via the Internet at http://pubs.acs.org.

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