DOI: 10.1002/ejoc.200701023

Syntheses of Sterically Hindered Zwitterionic Pyridinium Phenolates as Model Compounds in Nonlinear Optics[‡]

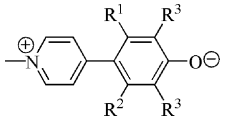
Vincent Diemer,[a] Hélène Chaumeil,*[a] Albert Defoin,[a] Alain Fort,[b] Alex Boeglin,[b] and Christiane Carré[c]

Keywords: Donor–acceptor systems / Zwitterions / Nonlinear optics / Cross-coupling / Chromophores / N heterocycles

Pyridinium phenolates possess a dissymmetric delocalised π-electron system providing a huge quadratic nonlinearity. They are a promising class of molecules for applications in photoelectronics and photonics. Semiempirical calculations indicate that the interplanar angle between the two aromatic rings leads to enhancement in the NLO properties of these compounds. The confirmation of this feature may be provided by the study of a new series of sterically hindered pyridinium phenolates **2a**–**e** bearing two *tert*-butyl substituents at the *ortho* position(s) of the phenolate functionality. Such bulky groups would enhance the solubility of zwitterions in organic solvents and would limit the formation of aggregates. Their efficient preparations by using Suzuki cross-coupling reactions involving 3,5-dialkylated 4-bromopyridine *N*-oxides are described herein.

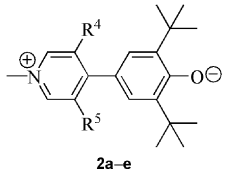
Introduction

Polymers doped with nonlinear molecules have shown great potential in the elaboration of organic nonlinear optic (NLO) devices for optoelectronic applications.[1] A large dissymmetric delocalised π system is known to provide a large quadratic nonlinearity. Thus, push–pull molecules possessing a donor and an acceptor end group connected through a π-conjugated system are promising molecules.[2] Semiempirical calculations indicate that the NLO properties of such molecules can be enhanced by increasing the interplanar angle existing between the two aromatic rings.[3] In order to experimentally confirm this features, we have already published the synthesis of a first series of sterically hindered pyridinium phenolates **1a**–**g** (Figure 1).[4] Alkyl groups of increasing size (methyl, ethyl, isopropyl) were anchored at *meta* positions of the phenolate functionality. Unfortunately, these zwitterions were far too insoluble to allow conventional EFISHG (electronic field-induced second harmonic generation) measurements. Moreover, they present an unexpected behaviour in dilute solutions: as the concentration decreased, the Beer–Lambert law no longer applied. As an explanation, different assumptions may be given forward. Among them, the more likely were either the protonation of the phenolate functionality with traces of water or the formation of aggregates, a consequence of the high dipole moments of these derivatives.[5] These characteristics were not observed with the zwitterions, synthesized by Combellas et al.,[6] bearing bulky lipophilic groups anchored at the *ortho* positions of the phenolate functional group. This steric hindrance induced in the neighbouring group to the phenolate functionality would certainly minimize the interactions between the oxygen atom and the surrounding medium and would also limit the formation of aggregates. These zwitterions have been obtained by an electrochemical $S_{RN}1$ reaction between 2,6-di-*tert*-butyl- or 2,6-dipentylphenols and 4-chloropyridine. Owing to steric hindrance, this synthetic method unfortunately prevents the introduction of aliphatic groups at the *ortho* position of the intercyclic bond.



1a–g

	1a	1b	1c	1d	1e	1f	1g
R^1	H	H	Me	Et	*i*Pr	H	Me
R^2	H	Me	Me	Et	*i*Pr	H	Me
R^3	H	H	H	H	H	Me	Me



2a–e

	2a	2b	2c	2d	2e
R^4	H	H	Me	Et	*i*Pr
R^5	H	Me	Me	Et	*i*Pr

Figure 1. Zwitterions synthesized (first[4] and second series).

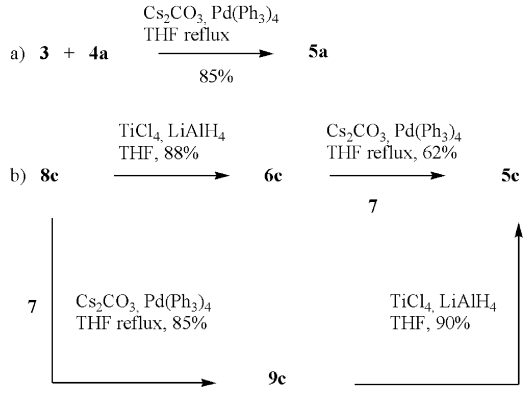
[‡] Part 2. Part 1: Ref.[4]

[a] Laboratoire de Chimie Organique, Bioorganique et Macromoléculaire, CNRS UMR 7015, Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace,
3 rue Alfred Werner, 68093 Mulhouse Cedex, France
E-mail: helene.chaumeil@uha.fr
[b] Institut de Physique et Chimie des Matériaux de Strasbourg – GONLO, CNRS UMR 7504,
23 rue du Lœss, B.P. 43, 67034 Strasbourg Cedex 2, France
[c] FOTON, CNRS UMR 6082, GET-ENST Bretagne, Département Optique, Technopôle Brest Iroise,
CS 83818, 29238 Brest Cedex, France

Nevertheless, in order to achieve physical studies, the requirement for the synthesis of a new series of hindered pyridinium phenolate compounds became obvious. This time, as for the derivatives of Combellas, two *tert*-butyl groups were anchored at the *ortho* positions of the phenolate functionality (Figure 1, compounds **2a**–**e**). Their synthesis can be achieved by using a Suzuki–Miyaura reaction as the key step.[7] This reaction is one of the most valuable reactions for the synthesis of dissymmetric biaryls, and it was already the key step of the preparation of our first series of zwitterions.[4] To avoid the protonolysis of the C–B bond, which occurs especially with sterically hindered coupling partners, the best and cheaper alternative was the use, under anhydrous conditions, of aryl boronic esters in place of boronic acids. Moreover, the presence of base in the Suzuki reaction led to the necessity of phenol protection, that is, in our case, the use of anisole derivatives. An interplanar angle between the two aromatic rings of zwitterions must be induced by introducing alkyl groups (methyl, ethyl, isopropyl) at the *ortho* position(s) of the intercyclic bond. However, in order to avoid the tricky syntheses of extremely substituted anisoles, the alkyl groups were introduced at the *meta* positions of the pyridine moiety.

Discussion

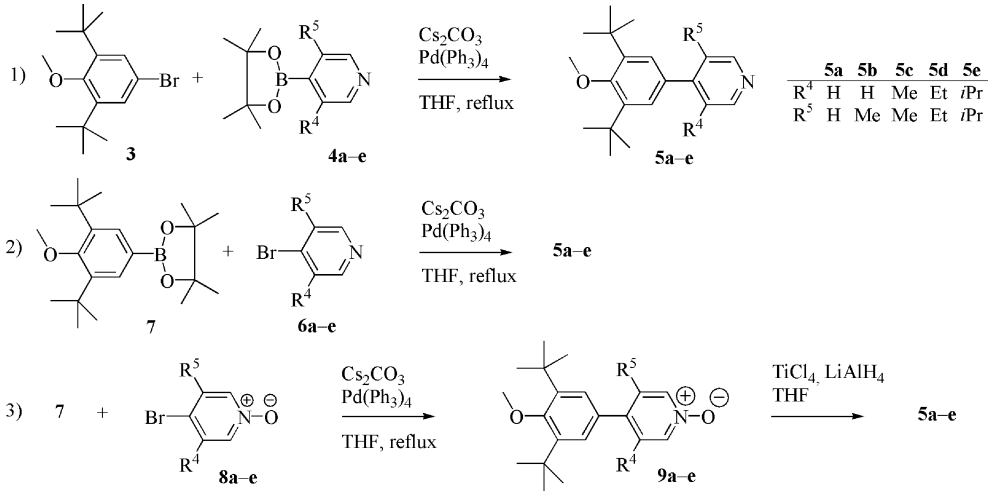
In a first approach, the coupling reactions between 2,6-disubstituted-4-bromoanisole **3** and pyridin-4-ylboronic esters **4a**–**e** were considered (Scheme 1). The reaction between unsubstituted pyridin-4-ylboronate **4a** and 4-bromoanisole **3** certainly provided, under our standard conditions,[4] corresponding biaryl **5a** in 85% yield (Scheme 2). Nevertheless, because of steric hindrance induced by the R^4 and R^5 alkyl groups, a moderate yield may be expected for the preparation of pyridin-4-ylboronates **4b**–**e** by borylation of the other 3,5-dialkylated bromopyridines. As a consequence, this synthetic pathway was rapidly given up. Two other synthetic alternatives involving a cross-coupling reaction between boronic ester **7** and either bromopyridines **6a**–**e** or pyridine *N*-oxides **8a**–**e** were conceivable (Scheme 1). For example, the reaction between 4-bromo-3,5-dimethylpyridine (**6c**) and **7** afforded desired biaryl **5c** in 62% yield (Scheme 2). It is worth noting that **6c** was obtained by reduction of 3,5-dimethylpyridine *N*-oxide **8c** in 88% yield. This synthetic pathway starting from **8c** gave readily **5c** in a 54% global yield. On the other hand, the cross-coupling reaction between pyridine *N*-oxide **8c** with boronic ester **7**, followed by the reduction of anisole pyridine *N*-oxide led to **5c** in 64% yield (Scheme 2). These two procedures for the preparation of **5c** seemed to be quite equivalent. However, knowing the instability of unsubstituted 4-bromopyridine at room temperature and intending to prepare biaryls **5a**–**e** by using the same synthetic method, only the cross-coupling reactions between **7** and pyridine *N*-oxides **8a**–**e** were used in the following.



Scheme 2.

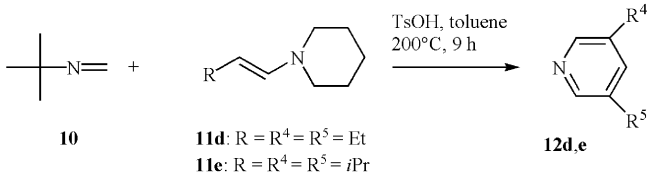
Synthesis of 4-Bromopyridine *N*-Oxides

Pyridines **12a**–**c** are commercially available. However, 3,5-diethyl- and 3,5-diisopropylpyridines **12d**,**e** required synthesis. This can be achieved according to the literature.

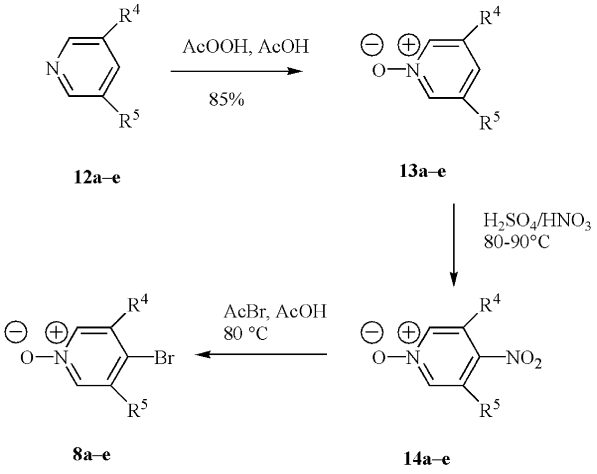


Scheme 1. Synthetic alternatives to obtain **5a**–**e**.

Imine **10** was obtained by condensation of *tert*-butylamine with paraformaldehyde[8] and enamines **11d**,**e** were obtained by condensation of piperidine with the corresponding aldehydes in the presence of potassium carbonate.[9] Compounds **10** and **11d**,**e** were then allowed to react, in toluene, in a sealed tube at 200 °C to furnish desired 3,5-disubstituted pyridines **12d**,**e**[8] (Scheme 3). The pyridines **12a**–**e** were first oxidized to pyridine *N*-oxides **13a**–**e** with peracetic acid (Scheme 4).[11] This change in oxidation degree favoured the selective *para* substitution of the heteroaromatic ring.[12] The next step was the *para* bromination of pyridine *N*-oxides **13a**–**e**. To the best of our knowledge, only the synthetic method published by Hamana et al. afforded a direct *para* bromination of pyridine *N*-oxides.[13] These authors used bromine in acetic acid in the presence of thallium acetate. Unfortunately, these conditions were incompatible with a large-scale reaction because of the toxicity of both reagents. Therefore, pyridine *N*-oxides **13a**–**e** were thus readily converted into their 4-nitro derivatives **14a**–**e** by classical aromatic electrophilic nitration.[14] As a consequence of the deactivation of the 2,6-positions of the *N*-oxide, only 4-substituted derivatives **14a**–**e** were obtained free from 2,6-disubstituted compounds. From **12a**–**e**, the yields ranged from 30 to 65% (Table 1). These low-to-moderate yields were unexpected, as all starting pyridine *N*-oxide was consumed during the reaction. Finally, the reaction with acetyl bromide, in acetic acid at 80 °C, led to the substitution of nitro derivatives **14a**–**e**. The different 4-bromopyridine *N*-oxides **8a**–**e** were obtained in moderate-to-good yields (Table 1).



Scheme 3. Synthesis of 3,5-disubstituted pyridines **12d**,**e**.



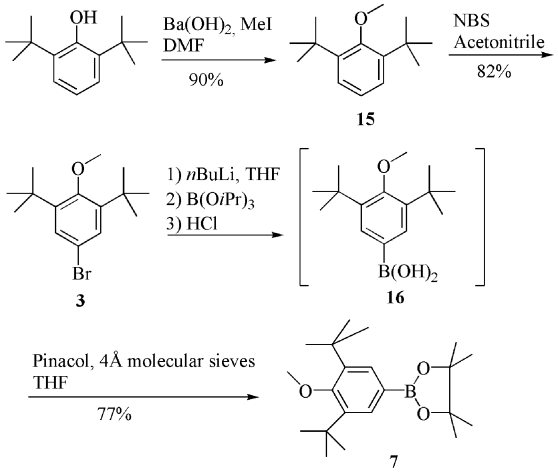
Scheme 4. Synthesis of 4-bromopyridine *N*-oxides **8a**–**e**.

Table 1. Conversion of pyridines **12a**–**e** into biphenyls **9a**–**e**.

Oxidation and nitration	Yield [%]	Substitution	Yield [%]	Suzuki cross-coupling	Yield [%]
14a	64	**8a**	66	**9a**	84
14b	53	**8b**	73	**9b**	89
14c	65	**8c**	86	**9c**	71
14d	36	**8d**	94	**9d**	85
14e	30	**8e**	95	**9e**	85

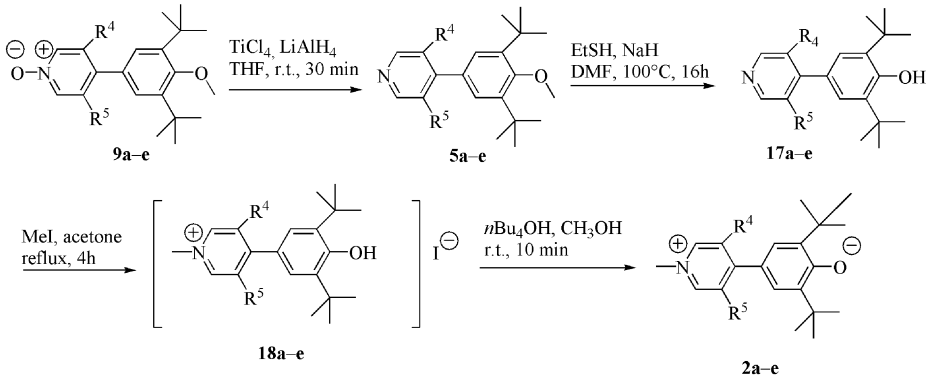
Synthesis of Boronic Ester 7

The first step of the synthesis of boronic ester **7** (Scheme 5) was the *O*-protection of 2,6-di-*tert*-butylphenol. By taking into account the steric hindrance of the *tert*-butyl groups, a small protecting group was required. The most judicious was the use of a methoxy group. Treatment of 2,6-di-*tert*-butylphenol with iodomethane in the presence of barium hydroxide as a base readily gave desired anisole **15**.[15] This was then brominated into bromoanisole **3** with NBS (82%).[16] Apart from the starting material, only bromoanisole **3** was recovered. The bromination may also be performed in acetonitrile by using a selectfluor/NaBr mixture.[17] Unfortunately, in spite of the 81% yield, selectfluor is too expensive of a reagent to be compatible with a large-scale reaction and hence was not further used. On the other hand, tetra-*n*-butylammonium tribromide, known to easily brominate phenols at the *ortho* position, failed to give **3** efficiently.[18] The rate of reaction was too low. After 4 d, at room temperature, only 65% of bromoanisole **3** was formed according to NMR spectroscopic analysis of the reaction mixture.



Scheme 5. Synthesis of boronic ester **7**.

Boronic acid **16** was then synthesized according to the method published by Liao et al. by lithium–halogen exchange in THF, followed by reaction with triisopropylborate at –78 °C.[19] Finally, boronic acid **16** was converted into ester **7** at room temperature in THF by reaction with pinacol in the presence of molecular sieves.[20] Eventually, the synthesis of boronic ester **7** was performed in 57% overall yield from bromoanisole **3** and in a 77% yield from 2,6-di-*tert*-butylphenol.



Scheme 6. Modification of biphenyls **9a**–**e** to obtain zwitterions **2a**–**e**.

Suzuki Cross–Coupling Reaction

The Suzuki cross-coupling reactions of **7** with 4-bromopyridine *N*-oxides **8a**–**e** were performed in accordance with the condition of our previous work, that is, in THF by using Cs_2CO_3 as the base and $[Pd(PPh_3)_4]$ as the catalyst (Scheme 1, reaction 3).[4] Biaryls **9a**–**e** were recovered in good-to-excellent yield (from 71 to 89%) (Table 1), in spite of the steric hindrance involved by the alkyl groups at the *meta* position of the *N*-oxide.

Reduction of the *N*-Oxide Functionality

The procedure, developed by Malinowsky, was retained to reduce the *N*-oxide functionalities of **9a**–**e** into **5a**–**e** (Scheme 6, Table 2).[21] The reducing agent is a Ti^0 complex generated in situ in THF at room temperature by reaction of $TiCl_4$ with $LiAlH_4$.

Table 2. Modifications of biphenyls **9a**–**e**.

Reduction of *N*-oxide		Deprotection		Quaternisation		Deprotonation	
	Yield [%]		Yield [%]		Yield [%]		Yield [%]
5a	84	**17a**	65	**18a**	100	**2a**	83
5b	87	**17b**	94	**18b**	97	**2b**	85
5c	90	**17c**	96	**18c**	97	**2c**	56
5d	90	**17d**	89	**18d**	96	**2d**	88
5e	94	**17e**	97	**18e**	97	**2e**	78

Deprotection, Quaternization and Deprotonation

The oxygen deprotection of the biaryls **5a**–**e** occurred, in DMF at 100 °C, with sodium ethanethiolate,[22] synthesized in situ by deprotonation of the corresponding thiol with sodium hydride (Scheme 6). All free phenols **17a**–**e** were obtained in good yields. The next step was the quaternization of pyridine in acetone with methyl iodide to give the corresponding biaryl iodide salts **18a**–**e**.[23] Finally, the derivatives had to be deprotonated and carefully purified to obtain pyridinium phenolates **2a**–**e** free from traces of inorganic salts. Deprotonation occurred in methanol by using *n*-Bu_4NOH as the base, in small excess, in accordance with our previous work.[4] After evaporation of the solvent, the crystallized residue consisted of circa, an equal amount of pyridinium phenolates **2a**–**e** and crystallized *n*Bu_4NI. The crude mixture was treated with an excess amount of a mixture of cyclohexane/CH_2Cl_2 (6:4), in which zwitterions **2a**–**e** are weakly soluble and *n*Bu_4NI is totally soluble, as well as the excess amount of *n*Bu_4NOH. After centrifugation, final zwitterions **2a**–**e** were easily recovered free from any trace amounts of organic iodide.

Conclusion

Five new zwitterionic pyridinium phenolates **2a**–**e** bearing methyl, ethyl or isopropyl substituents were readily synthesized. The presence of two *tert*-butyl substituents at the 2,6-positions of the phenolate dramatically enhances their solubilities in organic solvents and a lesser tendency to form aggregates was observed. Their quadratic optical properties have already been measured by EFISHG and Hyper-Rayleigh techniques and were interpreted by semiempirical calculations.[24] We also intend to study other physical properties of these powerful molecules as for example the photoinduced intramolecular charge-transfer gathering the fluorescence spectra.[25] The solvatochromism of each derivative is presently under investigation and will be further published. The measured transition energies will be correlated with those of compound $E_T(30)$.[26] Compound $E_T(30)$ has a structure related to those of pyridinium phenolates **2a**–**e** but with a different localisation of N^+ and five phenyl substituents.

Experimental Section

General Remarks: Reagents were purchased from commercial suppliers and used without further purification. THF was freshly distilled from sodium/benzophenone and CH_3CN from CaH_2. A freshly opened DMF bottle was used, and DMF was dried with 3 Å molecular sieves. All melting points were recorded with a Kofler bench. IR spectra were recorded with a Nicolet 205 FTIR spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were measured with a Bruker Avance serie 400 instrument. Chemical shifts are reported in ppm relative to $SiMe_4$. Microanalyses were performed by the analytical service of microanalyses of

the Service de Microanalyse du CNRS in Vernaison and high-resolution MS were measured with a Waters Micromass Q-Tof Ultima API spectrometer in the firm Basilea Pharmaceuticals in Basel (Switzerland). Previously reported procedures were used to prepare 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)pyridine (**4a**)[27] and *tert*-butylmethylamine (**10**).[8] The published procedure to synthesize 1-(pent-1-enyl)piperidine (**11d**) and 1-(4-methyl-pent-1-enyl)-piperidine (**11e**)[9] was slightly adapted, as toluene was used as the solvent instead of benzene. $Pd(PPh_3)_4$ was prepared according to ref.[28] and used immediately or within 3 months while stored under an atmosphere of N_2 at –30 °C.

General Procedures

Procedure A. Synthesis of Pyridines: Enamines **11d**–**e** (2 equiv.), *tert*-butylmethylamine (**10**; 2 equiv.) and *para*-toluenesulfonic acid (0.03 equiv.) dissolved in toluene (2 to 3 mL per mmol of imine) were heated at 200 °C in a sealed tube for 9 h. The reaction mixture was allowed to reach room temperature, diluted with Et_2O and then washed with aqueous NaOH (1 M). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo. Pyridines **12d**–**e** were purified by column chromatography.

Procedure B. Synthesis of Pyridine *N*-Oxides: Under an atmosphere of Ar at 0 °C, peracetic acid (39% in acetic acid, 0.2 mL per mmol of pyridine) was added dropwise to pyridine **12a**–**e**. After stirring 2 h at 85 °C, the reaction mixture was allowed to reach 0 °C. Aqueous NaOH (4 M) was then added until neutralisation. The aqueous layer was then extracted with CH_2Cl_2. The combined extract was dried with $MgSO_4$ and concentrated in vacuo. Pyridine *N*-oxides **13a**–**e** were used without further purification.

Procedure C. Nitration of Pyridine *N*-Oxides: To unpurified pyridine *N*-oxides **13a**–**e** was added concentrated H_2SO_4 (0.32 mL per mmol of pyridine **12a**–**e**) and fuming HNO_3 (0.17 mL per mmol of pyridine **12a**–**e**). The temperature was gradually raised to 85–90 °C. The reaction mixture was stirred 6 h at this temperature and then allowed to reach room temperature. Crushed ice was added. The aqueous layer was neutralised with solid K_2CO_3. The precipitate was filtered and first washed with water and then with CH_2Cl_2. The organic filtrate was concentrated in vacuo to obtain a first fraction of compound **13a**–**e**, which was purified by chromatography or recrystallization. The aqueous filtrate was extracted four times with CH_2Cl_2. The combined extract was dried with $MgSO_4$ and concentrated in vacuo to obtain a fraction of pure compound **14a**–**e**.

Procedure D. Bromination of 4-Nitropyridine *N*-Oxides: Under an atmosphere of Ar, to 4-nitropyridine *N*-oxides in acetic acid (2 mL per mmol of compounds **14a**–**e**) was added dropwise acetyl bromide (1.2 mL per mmol of **14a**–**e**). After stirring 3 h at 80 °C, the reaction mixture was allowed to reach room temperature. The crude product was poured onto crushed ice and then neutralised by the addition of aqueous NaOH (10 M) and then Na_2CO_3. The aqueous layer was extracted four times with CH_2Cl_2. The combined extract was dried with $MgSO_4$ and concentrated in vacuo. Derivatives **8a**–**e** were used without further purification.

Procedure E. Suzuki Cross-Coupling Reactions: Under an atmosphere of Ar, to **8a**–**e** (1 equiv.) in anhydrous THF (10 mL per mmol of **8a**–**e**) was successively added Cs_2CO_3 (1.2 equiv.), **7** (1.2 equiv.) and $[Pd(Ph_3)_4]$ (0.08 equiv.). The reaction mixture was heated at reflux and monitored by NMR spectroscopy. On completion of the reaction, the suspension was filtered through Celite with CH_2Cl_2. The solvent was concentrated in vacuo, and the residue was purified by chromatography (AcOEt/EtOH, 95:5) to obtain pure **9a**–**c**.

Procedure F. Reduction of the Pyridine *N*-Oxides: Under an atmosphere of Ar, to $TiCl_4$ (0.99 equiv.) suspended in anhydrous THF was gradually added $LiAlH_4$ (0.72 equiv.). The reaction mixture was stirred 15 min at room temperature. Then, at 0 °C, **9a**–**e** or 3,5-dimethylpyridine-1-oxide **8c** (1 equiv.) was gradually added. The mixture was then stirred 30 min at room temperature. Hydrolysis was carried out by adjunction of H_2O (2.5 mL per mmol of **9a**–**e** or **8c**) and then NH_4OH (33% in water, 2.5 mL per mmol of **9a**–**e**). After dilution, the aqueous layer was extracted three times with Et_2O. The combined extract was dried with $MgSO_4$ and concentrated in vacuo. Derivatives **5a**–**e** or **6c** were purified by chromatography (cyclohexane/AcOEt, 8:2 or 7:3).

Procedure G. Deprotection of Phenols: Under an atmosphere of Ar, to NaH (8 equiv.) suspended in DMF (14 mL per mmol of **5a**–**e**) was dropwise added EtSH (7 equiv.). As the emission of H_2 stopped, **5a**–**e** (1 equiv.) was introduced into the reaction mixture. After stirring overnight at 100 °C, H_2O (2.5 mL per mmol of **5a**–**e**), HCl (1 M, 8 mL per mmol of **5a**–**e**) and phosphate buffer (0.5 M, pH = 7.2) was successively added. The aqueous layer was extracted three times with Et_2O. The combined organic layer was then extracted twice with H_2O, then dried with $MgSO_4$ and concentrated in vacuo. Crude **17a**–**e** were purified by chromatography.

Procedure H. Alkylation Reaction: Under an atmosphere of Ar, a suspension of deprotected biaryl **17a**–**e** (1 equiv.) in acetone (16 mL per mmol of **17a**–**e**) was treated with iodomethane (4 equiv.). The reaction mixture was heated at reflux for 4 h, and the solvent was then removed in vacuo. The residue was washed with Et_2O and then AcOEt. Iodine salts **18a**–**e** were not further purified and only characterized by NMR spectroscopy.

Procedure I. Deprotonation: A solution of nBu$_4$OH (0.1 M in *i*PrOH/MeOH, 9:1; 1.05 equiv.) was added to a stirred solution of **18a**–**e** (1 equiv.) in MeOH (11 mL per mmol of **18a**–**e**). After 15 min of reaction, the solvent was removed in vacuo. Cyclohexane/CH_2Cl_2 (6:4, 16 mL per mol of **18a**–**e**) was added to the crushed crystalline residue dried under high vacuum. The precipitate was filtered off, washed twice with CH_2Cl_2/cyclohexane (3:7; 5.3 mL per mol of **18a**–**e**) and dried.

3,5-Diethylpyridine (12d): Compound **12d** (3.79 g, 52%) was obtained as a colourless oil from **10** and **11d** (7.5 g, 54 mmol) by using procedure A. ^{1}H NMR (400 MHz, $CDCl_3$)[29]: δ = 1.24 (t, J = 7.5 Hz, 6 H), 2.62 (q, J = 7.5 Hz, 4 H), 7.32 (br. s, 1 H), 8.27 (br. s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.4, 26.0, 134.7, 138.8, 147.0 ppm.

3,5-Diisopropylpyridine (12e): Compound **12e** (2.99 g, 46%) was obtained as an oil from **9** and **10e** (6.12 g, 40 mmol) by using procedure A. ^{1}H NMR (400 MHz, $CDCl_3$):[10] δ = 1.27 (d, J = 7.0 Hz, 12 H), 2.91 (hept, J = 7.0 Hz, 2 H), 7.35 (t, J = 2.0 Hz, 1 H), 8.31 (d, J = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.8, 31.9, 131.7, 143.4, 146.3 ppm.

Pyridine-1-oxide (13a): Compound **13a** was obtained as very hygroscopic colourless crystals from **11a** by using procedure B. ^{1}H NMR (400 MHz, $CDCl_3$):[30] δ = 2.27 (m, 3 H), 8.20 (m, 2 H) ppm.

3-Methylpyridine-1-oxide (13b): Compound **13b** was obtained as hygroscopic colourless crystals from **12b** by using procedure B. ^{1}H NMR (400 MHz, $CDCl_3$):[31] δ = 2.32 (s, 3 H), 7.09 (d, J = 7.6 Hz, 1 H), 7.17 (t, J = 7.6 Hz, 1 H), 8.06 (d, J = 7.6 Hz, 1 H), 8.08 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$):[31] δ = 18.4, 125.5, 127.5, 136.7, 137.0, 139.4 ppm.

3,5-Dimethylpyridine-1-oxide (13c): Compound **13c** was obtained as hygroscopic colourless crystals from **12c** by using procedure B. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 6 H), 6.86 (s, 1 H), 7.84 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$):[32] δ = 18.2, 128.5, 136.0, 136.6 ppm.

3,5-Diethylpyridine-1-oxide (13d): Compound **13d** was obtained as hygroscopic colourless crystals from **12d** by using procedure B. Compound **13d** was not further purified and only characterized by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.6 Hz, 6 H), 2.57 (q, J = 7.6 Hz, 4 H), 6.94 (s, 1 H), 7.93 (s, 2 H) ppm.

3,5-Diisopropylpyridine-1-oxide (13e): Compound **13e** was obtained as very hygroscopic colourless crystals from **12e** by using procedure B. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, J = 7.1 Hz, 12 H), 2.95 (hept, J = 7.1 Hz, 2 H), 7.45 (s, 1 H), 8.33 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.0, 31.6, 123.6, 135.1, 146.8 ppm.

4-Nitropyridine-1-oxide (14a): Compound **14a** (8.96 g, 64%) was obtained as yellow crystals from **12a** (7.9 g, 100 mmol) by using procedure C. M.p. 163 °C (ref.[33] 163 °C). ^{1}H NMR (400 MHz, $CDCl_3$):[34] δ = 8.11 (d, J = 7.6 Hz, 2 H), 8.25 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 121.3, 140.6, 142.6 ppm.

3-Methyl-4-nitropyridine-1-oxide (14b): Compound **14b** (8.2 g, 53%) was obtained as yellow crystals from **12b** (9.3 g, 100 mmol) after recrystallisation in acetone by using procedure C. M.p. 136–138 °C (ref.[35] 136–138 °C). ^{1}H NMR (400 MHz, $CDCl_3$):[14a] δ = 2.61 (s, 3 H), 8.01 (d, J = 7.0 Hz, 1 H), 8.10 (d, J = 7.0 Hz, 1 H), 8.13 (1, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.2, 122.0, 133.0, 137.9, 141.7, 143.1 ppm.

3,5-Dimethyl-4-nitropyridine-1-oxide (14c): Compound **14c** (9.5 g, 65%) was obtained as beige crystals from **12c** (10.7 g, 100 mmol) by using procedure C. M.p. 177 °C (ref.[14b] 174–175 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 6 H), 7.99 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.5, 129.4, 138.8, 146.5 ppm.

3,5-Diethyl-4-nitropyridine-1-oxide (14d): Compound **14d** (1.46 g, 36%) was obtained as beige crystals from **12d** (2.79 g, 20.7 mmol) after recrystallisation from butan-2-ol by using procedure C. Sublimation was also possible (100 °C, 0.05 Torr). M.p. 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.6 Hz, 6 H), 2.60 (q, J = 7.6 Hz, 4 H), 8.02 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.8, 22.4, 134.4, 137.9, 146.2 ppm. IR (KBr): $\tilde{\nu}$ = 632, 646, 1064, 1087, 1110, 1183, 1309, 1341, 1362, 1456, 1465, 1520, 1533, 1538, 1598, 2982, 3071, 3452 cm^{-1}. $C_9H_{12}N_2O_3$ (196.21): calcd. C 55.09, H 6.16, N 14.28; found C 55.07, H 6.17, N 14.17.

3,5-Diisopropyl-4-nitropyridine-1-oxide (14e): Compound **14e** (952 mg, 30%) was obtained as beige crystals from **12e** (2.31 g, 14 mmol) after chromatography (AcOEt/EtOH, 9:1 to 8:2) by using procedure C. Sublimation was also possible (110 °C, 0.05 Torr). M.p. 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, J = 6.8 Hz, 12 H), 2.86 (hept, J = 6.8 Hz, 2 H), 8.07 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.8, 27.9, 136.3, 138.1, 145.5, 147.3 ppm. IR (KBr): $\tilde{\nu}$ = 461, 643, 846, 861, 1023, 1088, 1154, 1174, 1196, 1253, 1304, 1344, 1372, 1469, 1532, 1537, 1598, 2342, 2361, 2970 cm^{-1}. $C_{11}H_{16}N_2O_3$ (224.26): calcd. C 58.91, H 7.19, N 12.49; found C 58.97, H 7.16, N 12.44.

4-Bromopyridine-1-oxide (8a):[36] Compound **8a** (7.22 g, 66%) was obtained as colourless crystals from **14a** (7.05 g, 50 mmol) by using procedure D. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 7.3 Hz, 2 H), 8.05 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 119.0, 129.5, 140.3 ppm.

4-Bromo-3-methylpyridine-1-oxide (8b):[37] Compound **8b** (6.31 g, 73%) was obtained as colourless crystals from **14b** (5.72 g, 37.1 mmol) by using procedure D. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 7.40 (d, J = 6.8 Hz, 1 H), 7.90 (d, J = 6.8 Hz, 2 H), 8.07 (d, J = 2 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4, 122.4, 129.6, 137.5, 138.0, 140.3 ppm.

4-Bromo-3,5-dimethylpyridine-1-oxide (8c):[12] Compound **8c** (10.62 g, 86%) was obtained as colourless crystals from **14b** (8.4 g, 50 mmol) by using procedure D. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 6 H), 7.94 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.6, 125.5, 136.8, 137.4 ppm.

4-Bromo-3,5-diethylpyridine-1-oxide (8d): Compound **8d** (1.58 g, 94%) was obtained as colourless crystals from **14d** (1.2 g, 6.12 mmol) by using procedure D. M.p. 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.6 Hz, 6 H), 2.71 (q, J = 7.6 Hz, 4 H), 7.95 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2, 27.5, 124.4, 136.8, 142.1 ppm. IR (KBr): $\tilde{\nu}$ = 605, 636, 855, 897, 1087, 1172, 1286, 1337, 1419, 1432, 1448, 1459, 1581, 2342, 2361, 2941, 2976, 3065, 3446 cm^{-1}. $C_9H_{12}BrNO$ (230.10): calcd. C 46.98, H 5.26, Br 34.72, N 6.09; found C 46.90, H 5.19, Br 34.42, N 5.91.

4-Bromo-3,5-diisopropylpyridine-1-oxide (8e): Compound **8e** (1.70 g, 95%) was obtained as colourless crystals from **14e** (1.34 g, 5.98 mmol) by using procedure D. M.p. 102 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 6.8 Hz, 12 H), 3.36 (hept, J = 6.8 Hz, 2 H), 7.98 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.2, 32.4, 124.6, 135.7, 146.4 ppm. IR (KBr): $\tilde{\nu}$ = 454, 462, 506, 518, 562, 573, 584, 596, 614, 637, 726, 1143, 1186, 1281, 1332, 1418, 1452, 1467, 1590, 2960, 3068, 3433 cm^{-1}. $C_{11}H_{16}BrNO$ (258.16): calcd. C 51.18, H 6.25, Br 30.95, N 5.43; found C 51.04, H 6.25, Br 30.66, N 5.25.

4-Bromo-3,5-dimethylpyridine (6c): Compound **6c** (153 mg, 53%) was obtained as a colourless oil from **8c** (202 mg, 1 mmol) after crystallisation at –20 °C by using procedure F. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 6 H), 8.23 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3, 134.0, 137.7, 148.3 ppm.

1,3-Di-*tert*-Butyl-2-methoxybenzene (15): Under an atmosphere of Ar, to 2,6-di-*tert*-butylphenol (10.0 g, 48.5 mmol) in degassed DMF (150 mL) was successively added barite (20 g, 63.7 mmol) and CH_3I (10 mL, 160 mmol). The reaction mixture was stirred overnight. Et_2O (300 mL) was then added. The organic layer was extracted with H_2O (200 mL), aqueous NaOH (1 M, 150 mL) and H_2O (2 × 250 mL). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo. The crude residue was purified by distillation (102 °C, 10 Torr) to obtain pure **15** (9.6 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 18 H), 3.69 (s, 3 H), 6.97 (t, J = 7.8 Hz, 1 H), 7.24 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$):[38] δ = 32.5, 36.1, 64.6, 123.3, 126.9, 144.1, 159.9 ppm.

5-Bromo-1,3-di-*tert*-butyl-2-methoxybenzene (3): Under an atmosphere of Ar, NBS (4.0 g, 22.4 mmol) was added to a stirred solution of **15** (3.53 g, 16 mmol) in CH_3CN (80 mL). After 48 h, the solvent was removed in vacuo. The crude product was brought into cyclohexane. The precipitate was filtered off and rinsed with cyclohexane. The solvents were evaporated, and the residue was purified by distillation (120 °C, 1 Torr) to obtain the desired product (3.96 g, 82%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 18 H), 3.67 (s, 3 H), 7.33 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$):[39] δ = 32.0, 36.1, 64.5, 116.5, 129.7, 146.2, 158.9 ppm.

2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)boronic Acid (16) and 2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (7): Under an atmosphere of Ar, to a stirred solution of **3** (6 g, 20 mmol) in anhydrous THF (40 mL) was added dropwise at –78 °C a solution of *t*BuLi (1.5 M in heptane, 26.6 mL, 40 mmol). After 2 h, $B(OiPr)_3$ (4.6 mL, 20 mmol) was added dropwise. The

reaction mixture was warmed to room temperature and aqueous HCl (1 M) was added until acidification of the solution. The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined extract was dried with $MgSO_4$ and concentrated in vacuo to give the colourless solid containing boronic acid **16**. Compound **16** was only characterized by ^1H NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 18 H), 3.76 (s, 3 H), 8.16 (s, 2 H) ppm.

Under an atmosphere of Ar, to a stirred solution of **16** (20 mmol) in anhydrous THF (47 mL) was added pinacol (2.36 g, 20 mmol) and activated 4 Å molecular sieves (20 g). After stirring overnight, the reaction mixture was filtered through Celite and rinsed with THF. The solvent was then removed in vacuo. Recrystallisation in CH_3CN gave **7** as colourless crystals (4.24 g, 61% from **3**). M.p. 172 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 12 H), 1.44 (s, 18 H), 3.68 (s, 3 H), 7.70 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.0, 32.3, 35.8, 64.4, 83.6, 133.5, 143.1, 162.7 ppm. IR (KBr): $\tilde{\nu}$ = 693, 855, 967, 1015, 1119, 1129, 1146, 1167, 1223, 1254, 1258, 1307, 1352, 1364, 1372, 1379, 1471, 1480, 1596, 2967, 2979, 2992 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{21}H_{35}BO_3$ $[M]^{+}$ 347.2752; found 347.2755.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)pyridine-1-oxide (9a): Crude **9a** was obtained as colourless crystals from **8a** (2.18 g, 12.5 mmol) after 72 h at reflux by using procedure E. After chromatography, pure **9a** (3.40 g, 85%) was obtained. Sublimation was possible (185 °C, 0.05 Torr). M.p. 194 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 18 H), 3.73 (s, 3 H), 7.44 (s, 2 H), 7.46 (d, J = 7.3 Hz, 2 H), 8.23 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 32.1, 36.1, 64.6, 123.7, 124.9, 130.5, 139.3, 139.8, 145.1, 161.0 ppm. IR (KBr): $\tilde{\nu}$ = 533, 585, 841, 886, 1012, 1029, 1083, 1115, 1176, 1224, 1252, 1262, 1361, 1396, 1415, 1447, 1459, 1489, 2867, 2912, 2961, 3420 cm^{-1}. $C_{20}H_{27}NO_2 \cdot 0.4H_2O$ (320.65): calcd. C 74.92, H 8.74, N 4.37; found C 75.08, H 8.78, N 4.08.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3-methylpyridine-1-oxide (9b): Crude **9b** was obtained as colourless crystals from **8b** (2.53 g, 12.5 mmol) after 72 h at reflux by using procedure E. After chromatography, pure **9b** (3.27 g, 80%) was obtained. Sublimation was possible (170 °C, 0.05 Torr). M.p. 144 °C.^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 18 H), 2.27 (s, 3 H), 3.74 (s, 3 H), 7.16 (s, 2 H), 7.16 (d, J = 6.5 Hz, 1 H), 8.09 (d, J = 6.5 Hz, 1 H), 8.14 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.1, 32.2, 36.0, 64.5, 126.6, 127.1, 131.5, 134.2, 136.5, 139.7, 141.4, 144.2, 159.8 ppm. IR (KBr): $\tilde{\nu}$ = 589, 748, 865, 1007, 1074, 1116, 1166, 1220, 1238, 1262, 1282, 1361, 1397, 1411, 1444, 1455, 1488, 2870, 2913, 2962, 3380 cm^{-1}. $C_{21}H_{29}NO_2 \cdot 0.75H_2O$ (340.99): calcd. C 73.97, H 9.02, N 4.11; found C 74.05, H 8.83, N 3.87.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-dimethylpyridine-1-oxide (9c): Crude **9c** was obtained as colourless crystals from **8c** (101 mg, 0.5 mmol) after 72 h at reflux by using procedure E. After chromatography, pure **9c** (121 mg, 71%) was obtained. Sublimation was possible (160 °C, 0.05 Torr). M.p. 141–143 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 18 H), 2.01 (s, 6 H), 3.73 (s, 3 H), 6.94 (s, 2 H), 8.01 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.0, 32.3, 36.0, 64.5, 126.8, 130.5, 135.0, 137.0, 142.2, 144.3, 159.2 ppm. IR (KBr): $\tilde{\nu}$ = 883, 1017, 1052, 1079, 1117, 1164, 1222, 1257, 1314, 1408, 1459, 1687, 2920, 2962 cm^{-1}. $C_{22}H_{31}NO_2 \cdot 0.6H_2O$ (352.31): calcd. C 75.00, H 9.21, N 3.98; found C 75.22, H 9.02, N 3.65.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-diethylpyridine-1-oxide (9d): Crude **9d** was obtained as colourless crystals from **8d** (873 mg, 3.79 mmol) after 7 d at reflux by using procedure E. After chromatography, pure **9d** (1.19 g, 85%) was obtained. Sublimation was possible (170 °C, 0.05 Torr). M.p. 148 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.6 Hz, 6 H), 1.42 (s, 18 H), 2.30 (q, J = 7.6 Hz, 4 H), 3.72 (s, 3 H), 6.94 (s, 2 H), 8.04 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.7, 24.5, 32.3, 36.0, 64.5, 127.1, 130.0, 136.1, 141.1, 141.7, 144.1, 159.2 ppm. IR (KBr): $\tilde{\nu}$ = 859, 1015, 1078, 1119, 1165, 1223, 1263, 1296, 1341, 1362, 1341, 1396, 1412, 1448, 1456, 2872, 2968 cm^{-1}. $C_{24}H_{35}NO_2 \cdot 0.5H_2O$ (373.16): calcd. C 77.25, H 9.56, N 3.75; found C 77.32, H 9.38, O 3.45.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-diisopropylpyridine-1-oxide (9e): Crude **9e** was obtained as colourless crystals from **8e** (1.47 mg, 5.71 mmol) after 7 d at reflux by using procedure E. After chromatography, pure **9e** (1.9 mg, 85%) was obtained. Sublimation was possible (170 °C, 0.05 Torr). M.p. 213 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, J = 6.8 Hz, 6 H), 1.43 (s, 18 H), 2.62 (sept, J = 6.8 Hz, 2 H), 3.74 (s, 3 H), 6.93 (s, 2 H), 8.07 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.6, 29.1, 32.3, 36.0, 64.5, 127.3, 130.1, 134.7, 140.1, 144.0, 145.8, 159.1 ppm. IR (KBr): $\tilde{\nu}$ = 587, 886, 994, 1010, 1072, 1116, 1181, 1210, 1223, 1258, 1310, 1343, 1363, 1388, 1396, 1409, 1437, 1465, 1607, 2869, 2958, 2967, 3007, 3027, 3424 cm^{-1}. $C_{26}H_{39}NO_2$ (397.61): calcd. C 78.54, H 9.89, O 8.05, N 3.52; found C 78.56, H 9.85, N 3.22.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)pyridine (5a): Compound **5a** (1.75 g, 84%) was obtained as colourless crystals from **9a** (2.19 g, 7.0 mmol) after chromatography by using procedure F. Sublimation was possible (130 °C, 1 Torr). M.p. 112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 18 H), 3.74 (s, 3 H), 7.46 (d, J = 6.3 Hz, 2 H), 7.5 (s, 2 H), 8.62 (d, J = 6.3 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 32.2, 36.1, 64.5, 121.7, 125.5, 132.5, 144.7, 149.1, 150.2, 160.8 ppm. IR (KBr): $\tilde{\nu}$ = 546, 612, 821, 888, 992, 1010, 1085, 1116, 1219, 1264, 1361, 1396, 1415, 1445, 1460, 1463, 1541, 1592, 2870, 2912, 2959, 2997, 3400 cm^{-1}. $C_{20}H_{27}NO$ (297.44): calcd. C 80.76, H 9.15, N 4.71; found C 80.85, H 9.14, N 4.51.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3-methylpyridine (5b): Compound **5b** (2.3 g, 87%) was obtained as colourless crystals from **9b** (2.78 g, 8.51 mmol) after chromatography by using procedure F. Sublimation was possible (140 °C, 1 Torr). M.p. 92 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 18 H), 2.31 (s, 3 H), 3.75 (s, 3 H), 7.16 (d, J = 5.0 Hz, 1 H), 7.20 (s, 2 H), 8.44 (d, J = 5.0 Hz, 2 H), 8.48 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.7, 32.2, 36.0, 64.4, 124.2, 127.2, 130.7, 133.3, 143.8, 147.4, 149.8, 151.5, 159.4 ppm. IR (KBr): $\tilde{\nu}$ = 626, 835, 1010, 1116, 1173, 1222, 1263, 1362, 1397, 1417, 1449, 1458, 1478, 2868, 2962, 3010, 3461 cm^{-1}. $C_{21}H_{29}NO$ (311.47): calcd. C 80.98, H 9.38, N 4.50; found C 81.16, H 9.41, N 4.31.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-dimethylpyridine (5c): Compound **5c** (851 mg, 90%) was obtained as colourless crystals from **9c** (1 g, 2.91 mmol) after chromatography by using procedure F. Sublimation was possible (130 °C, 1 Torr). M.p. 116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 18 H), 2.05 (s, 6 H), 3.73 (s, 3 H), 6.96 (s, 2 H), 8.32 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.6, 32.3, 36.0, 64.4, 126.6,131.2, 132.2, 143.9, 148.5, 150.2, 158.7 ppm. IR (KBr): $\tilde{\nu}$ = 525, 670, 877, 887, 997, 1012, 1119, 1167, 1223, 1265, 1361, 1378, 1395, 1411, 1453, 1480, 1584, 2868, 2920, 2960, 3010 cm^{-1}. $C_{22}H_{31}NO$ (325.50): calcd. C 81.18, H 9.60, N 4.30; found C 81.32, H 9.52, N 4.18.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-diethylpyridine (5d): Compound **5d** (896 mg, 90%) was obtained as colourless crystals from **9d** (1.04 g, 2.82 mmol) after chromatography by using procedure F. Sublimation was possible (150 °C, 1 Torr). M.p. 89 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, J = 7.5 Hz, 6 H), 1.43 (s, 18 H), 2.36 (q, J = 7.5 Hz, 4 H), 3.73 (s, 3 H), 6.97 (s, 2 H), 8.35 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.8, 24.4, 32.3, 35.9, 64.5, 126.9, 131.5, 137.4, 143.5, 147.4, 149.5, 158.7 ppm.

IR (KBr): $\tilde{\nu}$ = 879, 889, 1017, 1058, 1075, 1084, 1119, 1168, 1210, 1224, 1263, 1361, 1370, 1394, 1413, 1459, 1480, 1582, 2871, 2935, 2966, 3016 cm^{-1}. $C_{24}H_{35}NO$ (353.55): calcd. C 81.53, H 9.98, N 3.96; found C 81.68, H 9.91, N 4.04.

4-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3,5-diisopropylpyridine (5e): Compound **5e** (1.69 g, 94%) was obtained as colourless crystals from **9e** (1.85 g, 4.72 mmol) after chromatography by using procedure F. Sublimation was possible (160 °C, 1 Torr). M.p. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.0 Hz, 12 H), 1.43 (s, 18 H), 2.68 (hept, J = 7.0 Hz, 2 H), 3.75 (s, 3 H), 6.94 (s, 2 H), 8.44 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.0, 28.9, 32.3, 35.9, 64.4, 126.9, 131.7, 141.4, 143.4, 145.1, 148.1, 158.6 ppm. IR (KBr): $\tilde{\nu}$ = 884, 1015, 1063, 1118, 1208, 1223, 1257, 1361, 1411, 1445, 1462, 2866, 2924, 2962 cm^{-1}. $C_{26}H_{38}NO$ (381.61): calcd. C 81.84, H 10.30, N 3.67; found C 81.74, H 10.27, N 3.83.

2,6-Di-*tert*-butyl-4-(pyridin-4-yl)phenol (17a): Compound **17a** (774 mg, 65%) was obtained as colourless crystals from **5a** (1.25 g, 4.21 mmol) after chromatography (cyclohexane/AcOEt, 7:3) by using procedure G. M.p. 242 °C (ref.[40] 244 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 18 H), 5.42 (s, 1 H), 7.45 (s, 2 H), 7.45 (d, J = 6 Hz, 2 H), 8.60 (d, J = 6 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.4, 34.6, 121.5, 124.0, 129.4, 136.8, 149.3, 150.2, 155.1 ppm.

2,6-Di-*tert*-butyl-4-(3-methylpyridin-4-yl)phenol (17b): Compound **17b** (1.53 g, 94%) was obtained as colourless crystals from **5b** (1.7 g, 5.47 mmol) after chromatography (cyclohexane/AcOEt, 7:3) by using procedure G. Sublimation was possible (150 °C, 1 Torr). M.p. 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 18 H), 2.32 (s, 3 H), 5.41 (s, 1 H), 7.15 (s, 2 H), 7.17 (d, J = 5.0 Hz, 1 H), 8.44 (d, J = 5.0 Hz, 1 H), 8.47 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.6, 30.4, 34.6, 124.3, 125.6, 130.1, 130.7, 136.0, 147.4, 150.1, 151.4, 153.9 ppm. IR (KBr): $\tilde{\nu}$ = 633, 842, 887, 1021, 1060, 1103, 1193, 1233, 1257, 1261, 1281, 1402, 1434, 1597, 2871, 2913, 2960, 2995, 3242 cm^{-1}. $C_{20}H_{27}NO$ (297.44): calcd. C 80.76, H 9.15, N 4.71; found C 80.86, H 9.17, N 4.56.

2,6-Di-*tert*-butyl-4-(3,5-dimethylpyridin-4-yl)phenol (17c): Compound **17c** (8.15 g, 96%) was obtained as colourless crystals from **5c** (1.7 g, 5.23 mmol) after chromatography (cyclohexane/AcOEt, 7:3) by using procedure G. M.p. 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 18 H), 2.06 (s, 6 H), 5.26 (s, 1 H), 6.88 (s; 2 H), 8.32 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.8, 30.6, 34.6, 124.9, 129.0, 131.4, 136.1, 148.5, 150.4, 153.1 ppm. IR (KBr): $\tilde{\nu}$ = 880, 1070, 1105, 1130, 1236, 1249, 1283, 1423, 1432, 1443, 1592, 1737, 2918, 2953, 3320 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{21}H_{29}NO$ $[M]^{\cdot+}$ 312.2322; found 312.2316.

2,6-Di-*tert*-butyl-4-(3,5-diethylpyridin-4-yl)phenol (17d): Compound **17d** (610 mg, 89%) was obtained as colourless crystals from **5d** (714 mg, 2.02 mmol) after chromatography (cyclohexane/AcOEt, 7:3) by using procedure G. M.p. 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.6 Hz, 6 H), 1.44 (s, 18 H), 2.36 (q, J = Hz 7.6 H, 4 H), 5.30 (s, 1 H), 6.89 (s, 2 H), 8.34 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.8, 24.4, 30.6, 34.5, 125.1, 128.4, 135.8, 137.5, 147.5, 149.6, 153.1 ppm. IR (KBr): $\tilde{\nu}$ = 645, 665, 684, 749, 780, 788, 873, 890, 1021, 1060, 1110, 1130, 1174, 1198, 1237, 1257, 1283, 1358, 1366, 1373, 1388, 1399, 1430, 1452, 1573, 1591, 1600, 2873, 2915, 2936, 2962, 2997, 3290 cm^{-1}. $C_{23}H_{33}NO$ (339.53): calcd. C 81.37, H 9.80, N 4.13; found C 81.53, H 9.86, N 4.23.

2,6-Di-*tert*-butyl-4-(3,5-diisopropylpyridin-4-yl)phenol (17e): Compound **17e** (1.25 g, 97%) was obtained as colourless crystals from **5e** (1.3 g, 3.5 mmol) after chromatography (cyclohexane/AcOEt, 7:3) by using procedure G. Sublimation was possible (170 °C, 1 Torr). M.p. 238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.0 Hz, 12 H), 1.45 (s, 18 H), 2.69 (hept, J = 7.0 Hz, 2 H), 5.31 (s, 1 H), 6.86 (s, 2 H), 8.43 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.1, 28.9, 30.6, 34.5, 125.2, 128.3, 135.8, 141.9, 144.8, 148.7, 153.1 ppm. IR (KBr): $\tilde{\nu}$ = 885, 890, 1044, 1058, 1117, 1133, 1238, 1256, 1283, 1361, 1387, 1431, 1442, 1458, 2864, 2923, 2954, 2964, 3247 cm^{-1}. $C_{25}H_{37}NO$ (367.58): calcd. C 81.69, H 10.15, N 3.81; found C 81.46, H 10.16, N 3.98.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-methylpyridinium Iodide (18a): Compound **18a** (425 mg, 100%) was obtained as colourless crystals from biaryl **17a** (287 mg, 1 mmol) by using procedure H. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.52 (s, 18 H), 4.35 (s, 3 H), 7.78 (s, 2 H), 8.28 (d, J = 7.0 Hz, 2 H), 8.73 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 30.4, 35.8, 47.7, 124.6, 125.8, 126.3, 140.3, 146.0, 158.2, 160.1 ppm.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,3-dimethylpyridinium Iodide (18b): Compound **18b** (1.29 g, 98%) was obtained as colourless crystals from biaryl **17b** (891 mg, 3 mmol) by using procedure H. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.49 (s, 18 H), 2.55 (s, 3 H), 4.36 (s, 3 H), 7.26 (s, 2 H), 7.90 (d, J = 6.5 Hz, 1 H), 8.65 (d, J = 6.5 Hz, 1 H), 8.77 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 18.6, 30.6, 35.8, 48.0, 127.1, 127.7, 128.6, 137.2, 139.8, 143.3, 146.9, 157.6, 160.1 ppm.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,3,5-trimethylpyridinium Iodide (18c): Compound **18c** (1.32 g, 97%) was obtained as colourless crystals from biaryl **17b** (933 mg, 3 mmol) by using procedure H. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.46 (s, 18 H), 2.26 (s, 6 H), 4.33 (s, 3 H), 7.02 (s, 2 H), 8.64 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 18.3, 30.7, 35.8, 48.0, 125.2, 126.7, 138.7, 140.3, 143.9, 156.3, 161.0 ppm.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3,5-diethyl-1-methylpyridinium Iodide (18d): Compound **18d** (231 mg, 96%) was obtained as colourless crystals from biaryl **17b** (170 mg, 0.5 mmol) by using procedure H. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.15 (t, J = 7.6 Hz, 6 H), 1.47 (s, 18 H), 2.59 (q, J = 6.5 Hz, 4 H), 4.40 (s, 3 H), 7.01 (s, 2 H), 8.70 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 15.0, 25.6, 30.7, 35.8, 125.3, 126.3, 140.2, 143.4, 144.6, 156.1, 160.3 ppm.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3,5-diisopropyl-1-methylpyridinium Iodide (18e): Compound **18e** (296 mg, 97%) was obtained as colourless crystals from biaryl **17e** (230 mg, 0.6 mmol) by using procedure H. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.22 (d, J = 6.8 Hz, 12 H), 1.45 (s, 18 H), 2.89 (hept, J = 6.8 Hz, 2 H), 4.42 (s, 3 H), 6.98 (s, 2 H), 8.74 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 23.4, 30.7, 30.9, 35.8, 49.0, 125.3, 126.3, 140.3, 142.1, 149.3, 156.2, 158.9 ppm.

2,4-Di-*tert*-butyl-4-(1-methylpyridinium-4-yl)phenolate (2a): Compound **2a** (247 mg, 83%) was obtained as red crystals from **18a** (283 mg, 1 mmol) by using procedure I. M.p. 240–260 °C (dec.). ^{1}H NMR (400 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2a**] = 10^{-2} M): δ = 1.41 (s, 18 H), 3.88 (s, 3 H), 7.57 (s, 2 H), 7.57 (d, J = 7.6 Hz, 2 H), 7.85 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2a**] = 10^{-2} M): δ = 30.6, 36.2, 44.9, 111.7, 117.5, 126.0, 142.2, 142.3, 154.6, 180.8 ppm. IR (KBr): $\tilde{\nu}$ = 882, 1056, 1100, 1161, 1192, 1198, 1256, 1307, 1315, 1320, 1348, 1393, 1444, 1457, 1476, 1481, 1499, 1498, 1539, 1578, 1581, 1585, 1649, 2948 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{20}H_{27}NO$ $[M]^{\cdot+}$ 298.2165; found 298.2175.

2,4-Di-*tert*-butyl-4-(1,3-dimethylpyridinium-4-yl)phenolate (2b): Compound **2b** (777 mg, 85%) was obtained as brown crystals from

18b (1.288 g, 2.93 mmol) after recrystallisation from CH_3CN by using procedure I. M.p. >260 °C. ^{1}H NMR (400 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2b**] = 10^{-2} M): δ = 1.42 (s, 18 H), 2.55 (s, 3 H), 4.06 (s, 3 H), 7.33 (s, 2 H), 7.60 (d, J = 6.5 Hz, 1 H), 8.10 (d, J = 6.5 Hz, 1 H), 8.18 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2b**] = 10^{-2} M): δ = 20.6, 30.8, 36.2, 45.8, 114.9, 124.0, 128.1, 132.3, 140.6, 141.2, 144.7, 159.1, 177.1 ppm. IR (KBr): $\tilde{\nu}$ = 848, 1060, 1153, 1180, 1202, 1217, 1257, 1303, 1344, 1381, 1421, 1428, 1475, 1576, 1582, 1638, 2944, 2950 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{21}H_{29}NO$ $[M]^{\cdot+}$ 312.2322; found 312.2289.

2,4-Di-*tert*-butyl-4-(1,3,5-trimethylpyridinum-4-yl)phenolate (2c): Compound **2c** (533 mg, 56%) was obtained as maroon crystals from **18c** (1.325 g, 2.92 mmol) after recrystallisation from CH_3CN by using procedure I. M.p. >260 °C. ^{1}H NMR (400 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2c**] = 10^{-2} M): δ = 1.42 (s, 18 H), 2.37 (s, 6 H), 4.19 (s, 3 H), 6.89 (s, 2 H), 8.37 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2c**] = 10^{-2} M): δ = 19.3, 31.2, 36.2, 46.8, 114.3, 126.7, 136.9, 140.2, 142.9, 162.8, 172.7 ppm. IR (KBr): $\tilde{\nu}$ = 1197, 1251, 1304, 1327, 1374, 1410, 1425, 1434, 1466, 1587, 1643, 2892, 2917, 2944 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{22}H_{31}NO$ $[M]^{\cdot+}$ 326.2478; found 326.2451.

2,4-Di-*tert*-butyl-4-(3,5-diethyl-1-methylpyridinium-4-yl)phenolate (2d): Compound **2d** (146 mg, 93%) was obtained as red crystals from **18d** (231 mg, 0.47 mmol) by using procedure I. M.p. >260 °C. ^{1}H NMR (400 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2d**] = 10^{-2} M): δ = 1.13 (t, J = 7.6 Hz, 6 H), 1.43 (s, 18 H), 2.73 (q, J = 7.6 Hz, 4 H), 4.27 (s, 3 H), 6.79 (s, 2 H), 8.45 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2d**] = 10^{-2} M): δ = 15.1, 25.8, 31.3, 36.1, 47.4, 114.7, 125.4, 140.5, 142.5, 144.0, 162.9, 171.5 ppm. IR (KBr): $\tilde{\nu}$ = 1197, 1250, 1283, 1299, 1320, 1375, 1418, 1425, 1464, 1589, 1637, 2875, 2920, 2941, 2950, 2969 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{24}H_{35}NO$ $[M]^{\cdot+}$ 354.2791; found 354.2814.

2,4-Di-*tert*-butyl-4-(3,5-diisopropyl-1-methylpyridinium-4-yl)phenolate (2e): Compound **2e** (173 mg, 78%) was obtained as red crystals from **18e** (300 mg, 0.58 mmol) after recrystallisation from CH_3CN by using procedure I. M.p. >260 °C. ^{1}H NMR (400 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2e**] = 10^{-2} M): δ = 1.21 (d, J = 6.8 Hz, 12 H), 1.43 (s, 18 H), 3.28 (hept, J = 6.8 Hz, 2 H), 4.32 (s, 3 H), 6.74 (s, 2 H), 8.53 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, [KOH] = 10^{-1} M, [**2e**] = 10^{-2} M): δ = 23.9, 30.4, 31.3, 36.1, 47.8, 114.7, 125.3, 140.4, 141.3, 149.2, 161.7, 170.9 ppm. IR (KBr): $\tilde{\nu}$ = 748, 889, 1201, 1257, 1299, 1311, 1339, 1415, 1428, 1454, 1464, 1585, 1634, 2872, 2908, 2952, 3416 cm^{-1}. HRMS (ESI-Q-Tof): calcd. for $C_{26}H_{39}NO$ $[M]^{\cdot+}$ 382.3104; found 382.3098.

Acknowledgments

The authors are indebted to The Région Alsace, the Programme Interreg III A *Rhenaphotonics*, for their financial support. We gratefully acknowledge Dr. Mathias Wind for the mass determinations. The authors also thank the undergraduate students Julien Fiault and Thomas Sbarrato for their dedicated help in the syntheses.

[1] H. S. Nalva, S. Miyata (Eds.), *Nonlinear Optics of Organics Molecules and Polymers*, CRC Press, Boca Raton, **1997**.
[2] a) S. R. Marder, B. Kippelen, A. K. Y. Jen, N. Peyghambarian, *Nature* **1997**, *388*, 845–851; b) M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus, R. Wortman, *Chem. Eur. J.* **1997**, *3*, 1091–1104; c) L. R. Dalton, *Pure Appl. Chem.* **2004**, *76*, 1421–1433.
[3] a) S. Keinan, E. Zojer, J.-L. Brédas, M. A. Ratner, T. J. Marks, *Theochem* **2003**, 227–235; H. Kang, A. Frachetti, P. Zu, H. Jiang, Y. Yang, E. Cariati, S. Righetto, R. Ugo, C. Zuccaccia, A. Macchioni, C. Stern, Z. Liu, S.-T. Ho, T. J. Marks, *Angew. Chem. Int. Ed.* **2005**, *44*, 7922–7925.
[4] V. Diemer, H. Chaumeil, A. Defoin, A. Fort, A. Boeglin, C. Carré, *Eur. J. Org. Chem.* **2006**, 2727–2738.
[5] V. Diemer, H. Chaumeil, A. Defoin, A. Boeglin, A. Barsella, A. Fort, P. Jacques, C. Carré, *Proc. Spie – Org. Optoelectron. Photonics II* **2006**, *6192*, 559–565.
[6] a) C. Combellas, C. Suba, A. Thiébault, *Tetrahedron Lett.* **1992**, *33*, 4923–4926; b) C. Combellas, C. Suba, A. Thiébault, *Tetrahedron Lett.* **1992**, *33*, 5741–5744; c) N. Alam, C. Combellas, C. Amatore, A. Thiébault, J. N. Verpeaux, *J. Org. Chem.* **1990**, *55*, 6347–6356.
[7] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263; c) A. J. Suzuki, *Organomet. Chem.* **1999**, *28*, 147; d) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633; e) F. Bellina, A. Carpita, R. Rossi, *Synthesis* **2004**, 2419.
[8] R. J. Vinj, H. J. Arts, R. Gren, A. M. Castelijns, *Synthesis* **1994**, 573–578.
[9] D. H. Wadsworth, M. R. Detty, B. J. Murray, C. H. Weidner, N. F. Haley, *J. Org. Chem.* **1984**, *49*, 2676–2681.
[10] M. Komatsu, H. Ohgishi, S. Takamatsu, Y. Ohshiro, T. Agawa, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 214–240.
[11] P. Klan, *Monatsh. Chem.* **1993**, *124*, 327–330.
[12] E. Ochiai, *J. Org. Chem.* **1953**, *18*, 534–551.
[13] H. Saito, M. Hamana, *Heterocycles* **1979**, *12*, 475–479.
[14] a) Z.-L. Zhou, J. M. Navratil, S. X. Cai, E. R. Whittemore, S. A. Espitia, J. E. Hawkinson, M. Tran, R. M. Woodward, E. Weber, J. F. W. Keana, *Bioorg. Med. Chem.* **2001**, *9*, 2061–2071; b) J. M. Esserey, K. Schofield, *J. Chem. Soc.* **1960**, 4953–4959.
[15] F. A. Neugebauer, H. Fischer, H. Weger, *Chem. Ber.* **1977**, *110*, 2802–2808.
[16] M. C. Carreno, J. L. G. Ruano, G. Sanz, M. A. Toledo, A. Urbano, *J. Org. Chem.* **1995**, *60*, 5328–5331.
[17] R. G. Syvret, K. M. Butt, T. P. Nguyen, V. L. Bulleck, R. D. Rieth, *J. Org. Chem.* **2002**, *67*, 4487–4493.
[18] J. Berthelot, C. Guette, P.-L. Desbène, J. Basselier, *Can. J. Chem.* **1989**, *67*, 2061–2066.
[19] Y. Liao, C. Xie, P. M. Lahti, R. T. Weber, J. J. Jiang, D. P. Barr, *J. Org. Chem.* **1999**, *64*, 5176–5182.
[20] R. Holland, J. Spenser, J. J. Deadman, *Synthesis* **2002**, *16*, 2379–2382.
[21] a) M. Malinowski, L. Kaczmarek, *Synthesis* **1987**, 1013–1015; b) M. Malinowski, L. Kaczmarek, *J. Prakt. Chem./Chem.-Ztg.* **1988**, *330*, 154–158.
[22] K. K. Anderson, D. A. Shultz, D. A. Dougherty, *J. Org. Chem.* **1997**, *62*, 7575–7584.
[23] C. Combellas, C. Suba, A. Thiébault, *Tetrahedron Lett.* **1992**, *33*, 4923–4926, and references therein.
[24] A. Boeglin, A. Barsella, A. Fort, F. Mançois, V. Rodriguez, V. Diemer, H. Chaumeil, A. Defoin, P. Jacques, C. Carré, *Chem. Phys. Lett.* **2007**, *442*, 289–301.
[25] J.-P. Malval, V. Diemer, F. Morlet Savary, P. Jacques, X. Allonas, H. Chaumeil, A. Defoin, C. Carré, *Chem. Phys. Lett.* Accepted.
[26] C. Reichardt, P. Milart, G. Schäfer, *Liebigs Ann. Chem.* **1990**, 441–447.
[27] C. Coudret, *Synth. Commun.* **1996**, *26*, 3543–3547.
[28] F. A. Cotton, *Inorg. Synth.* **1972**, *13*, 121–124.
[29] J. I. Grayson, R. Dinkel, *Helv. Chim. Acta* **1984**, *67*, 2100–2110.
[30] N. K. Jana, J. G. Verkade, *Org. Lett.* **2003**, *21*, 3787–3790.
[31] P. M. Hatton, S. Sternhell, *J. Heterocycl. Chem.* **1992**, *29*, 935–946.
[32] Y. Nakashima, M. Fukunaga, K. Suzuki, K. Takahashi, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2143–2148.

[33] T. Kubota, H. Miyazaki, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2057–2062.
[34] G. Panke, T. Schwalbe, W. Stirner, S. Taghavi-Moghadam, G. Wille, *Synthesis* **2003**, 2827–2830.
[35] W. Herz, L. Tsai, *J. Am. Chem. Soc.* **1954**, *76*, 4184–4185.
[36] M. R. Kidd, W. H. Watson, *Inorg. Chem.* **1969**, *8*, 1886–1891.
[37] R. A. Abramovitch, M. Saha, *Can. J. Chem.* **1966**, *44*, 1765–1771.
[38] P. W. Jardon, E. H. Vickery, L. P. Pahler, N. Pourahmady, G. J. Mains, E. J. Eisenbraun, *J. Org. Chem.* **1984**, *49*, 2130–2135.
[39] K. S. Dhami, J. B. Stothers, *Can. J. Chem.* **1966**, *44*, 2855–2866.
[40] N. Alam, C. Combellas, C. Amatore, A. Thiébault, J. N. Verpeaux, *J. Org. Chem.* **1990**, *55*, 6347–6356.

Received: October 29, 2007
Published Online: February 12, 2008

