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Synthesis and properties of di- and trinitrobenzyl substituted pyridine derivates†

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A new method to obtain di- and trinitrobenzyl substituted pyridines is presented in this paper. By systematic variation of reaction parameters, the reaction conditions were optimized. The novel synthesis circumvents the commonly used nitration of benzyl pyridines, and thus avoids the nitration of the heterocycle which is a common side reaction. Furthermore, the starting materials for the synthesis of a variety of photochromic nitrobenzyl pyridines are easily accessible. The half-lives of the phototautomers of several new di- and trinitrobenzyl-substituted pyridines were determined. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: photochromic compound; photoswitchable acid; coupling reaction; nitrobenzyl pyridines

INTRODUCTION

In 1925 Tschitschibabin *et al.* observed the photochromic behavior of 2-(2,4-dinitrobenzyl)pyridine (DNBP) **1**.[1] The pale yellow crystals dye blue by exposure to sunlight and slowly fade back to yellow in the dark. The blue phototautomer was assigned to the enamine (**NH-1**), the corresponding yellow isomer is denoted by the 'CH' form (**CH-1**, Scheme 1.). The structure of **NH-1** was confirmed by NMR, IR, time resolved resonance Raman spectroscopy and finally in 2002 by a crystal structure analysis.[2–6] The initial photoproduct of **CH-1** is the *aci*-nitro tautomer (**OH-1**). This highly acidic form rapidly tautomerizes to **NH-1** in a thermal reaction.[7–11]

Such systems could be suited as proton pumps. The uphill transport of protons through membranes is an essential process in biology driving endergonic processes such as the synthesis of adenosine triphosphate.[12–17] Green plants use the photosynthetic transport of electrons and the coupled symport of protons as an energy source to build up proton gradients across membranes.[18] In most non-photosynthetic organisms, the energy source for the proton pump is the oxidation of glucose. Photoswitchable acids such as DNBP **1** could be eventually used as shuttles in artificial membranes to pump protons directly uphill across a membrane without linking it to a light driven electron transport (symport) (Scheme 2). In a recent study, we determined the pK_a values of all species in the photochemical and thermochemical equilibria using flash photolysis and by spectrophotometric titration.[19] Based on the pK_a values a hypothetical proton transport could be performed as follows.

Two aqueous phases are separated by a lipophilic membrane containing the photoswitchable acid. The CH form picks up a proton (forms CH—NH^+, top left) and diffuses to the opposite phase boundary (top right). Upon irradiation CH—NH^+ isomerizes to the highly acidic *O*-protonated (NH—OH^+) form, which in turn releases the proton to the aqueous acceptor phase forming the NH isomer. The NH form diffuses back to the aqueous donor phase and due to its metastable character tautomerizes to the CH form and the transport process starts over again. The life time of the metastable isomer and the reversibility of the photoreaction still have to be optimized to induce a light driven transport. To this end, several new photochromic DNBP derivatives have been synthesized and a novel synthetic method for their synthesis was developed.

RESULTS AND DISCUSSION

In principle there are two straightforward approaches to synthesize nitrobenzyl pyridines: (a) nitration of benzyl pyridine at the phenyl ring or (b) coupling of nitrobenzenes with 2-methylpyridine. The most frequently used method is nitration of benzyl pyridine. However, the introduction of more than one nitro group into the phenyl ring requires drastic conditions (high temperatures and concentrated acids).[20–22] Common side reactions are oxidation reactions and nitration of the heterocyclic compound. Trinitrobenzyl pyridines are not accessible by this method. Therefore the coupling of a 2-methyl pyridine (picoline) with a di- or trinitrobenzene would be the method of choice. Since nitrofluorbenzenes are susceptible to nucleophilic aromatic substitution and because 2-methyl pyridines are easily deprotonated and metallated at the methyl group a polar coupling reaction between both components seems obvious. However, only very little nucleophilic substitution reactions of nitrobenzenes with carbon nucleophiles are known. Organometallic compounds usually induce electron transfer processes instead.

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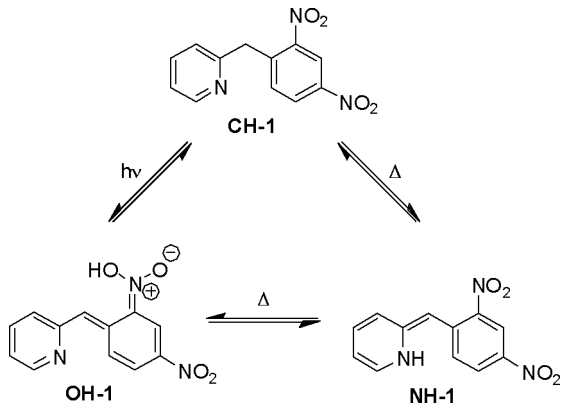
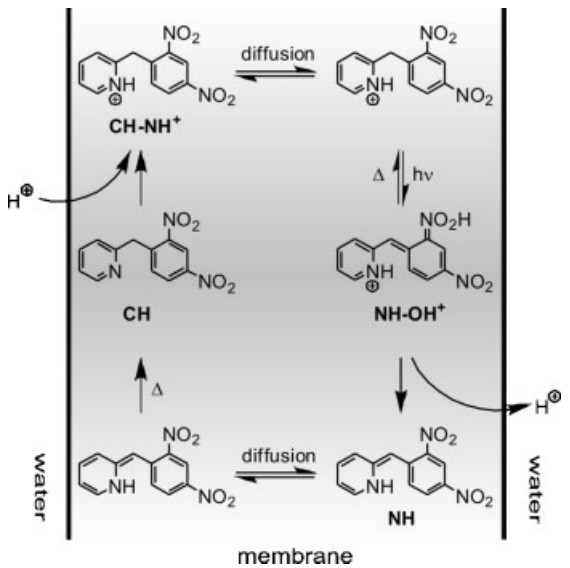


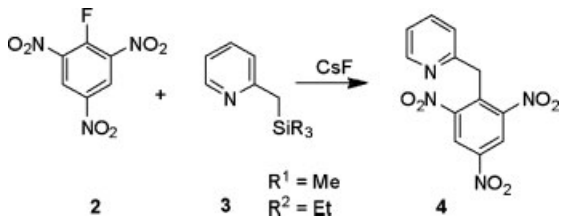
Scheme 1. Tautomers of DNBP **1**. The denotation alludes to the position of the transferred proton

Grignard reagents, in most cases reduce the nitro groups.[23–25] Dependent on the reaction conditions *N*,*N*-disubstituted hydroxylamines, secondary amines and nitrosyl compounds are formed.[26] Bartoli *et al*. investigated the Grignard reaction with nitrobenzene.[27] A conjugate addition leads to quinoid intermediates which upon oxidation give the corresponding *ortho* and *para* substituted products. However, the reaction is restricted to mono nitrated aromatic compounds and alkyl Grignard reagents. Alkyl lithium compounds react analogously.[28] In 1963, Severin and Schmitz performed a reaction between 2,4,6-trinitrobenzene and alkyl Grignard reagents that leads to a trinitro trialkylcyclohexane.[29] A Suzuki reaction was used to couple 2,4-dinitrobenzene with aromatic organoboron compounds.[30] Even though the method is compatible with nitro groups it is obviously not general. In our hands it failed in the synthesis of DNBP and several derivatives. We therefore developed a more general method to couple fluoronitrobenzenes with 2-methyl pyridines and several derivatives providing a convenient method for the preparation of nitrobenzyl pyridines.

To avoid the electron transfer reactions of benzyl Grignard and lithium compounds we use silylated 2-methyl pyridines (**3**) and cleave the silyl group *in situ* by applying fluoride ions. The



Scheme 2. Hypothetical light driven proton transport using **1** as a photoswitchable shuttle



Scheme 3. New method to obtain di- and trinitrobenzyl substituted pyridines

masked anion undergoes nucleophilic aromatic substitution with 2,4,6-trinitrofluorobenzene (**2**) (Scheme 3).

We systematically tested a number of fluoride sources and various reaction conditions to optimize the yields (Table 1.)

The highest yields are obtained when a mixture of 2,4,6-trinitrofluoro benzene **(2)** and cesium fluoride in tetrahydrofuran is heated to 65 °C and 2-(trimethylsilylmethyl)pyridine **(3)** is slowly added. Under these conditions, the stationary concentration of the carbanion is lowest. CsF, InF_3, tetra-*n*-butylammonium fluoride (TBAF) and KF/crown ether (18-crown-6) were used as fluoride sources. When the non-coordinating cations KF/crown ether and TBAF are used not even traces of the product are obtained. The yields also drop if less than one equivalent of the fluoride is used. Obviously, the counter ion of the fluoride is involved in the reaction. We therefore propose a six membered transition state as the mechanism (Scheme 4).

Table 1. Yields of the coupling reaction of **2** with **3** (Scheme 3) as a function of the fluoride source and the reaction conditions

	3	Reaction conditions	Yield (%)
(a)	R^2	CsF, THF, 10 min, rt	3
(b)	R^2	CsF, THF, 42 h, rt	10
(c)	R^2	CsF, THF, 6 h, 65°C	2
(d)	R^2	TBAF, THF, 25 min, rt	0
(e)	R^2	KF, 18-C-6, THF, 6 h, 65 °C	0
(f)	R^2	InF_3, THF, 10 min, rt	6
(g)	R^2	CsF, THF, 5d, rt	0
(h)	R^2	InF_3, THF, 5d, rt	3
(i)	R^2	InF_3, THF, 5 h, 65 °C	13
(j)	R^1	CsF, THF, 10 min, rt	8
(k)	R^1	CsF, THF, 5d, rt	0
(l)	R^1	InF_3, THF, 5 h, 65 °C	10
(m)	R^1	CsF, THF, 5 h, 65 °C	22
(n)	R^2	CsF, EtOH, 10 min, rt	0
(o)	R^2	CsF, DMF, 10 min, rt	0

Scheme 4. Proposed six membered transition state mechanism

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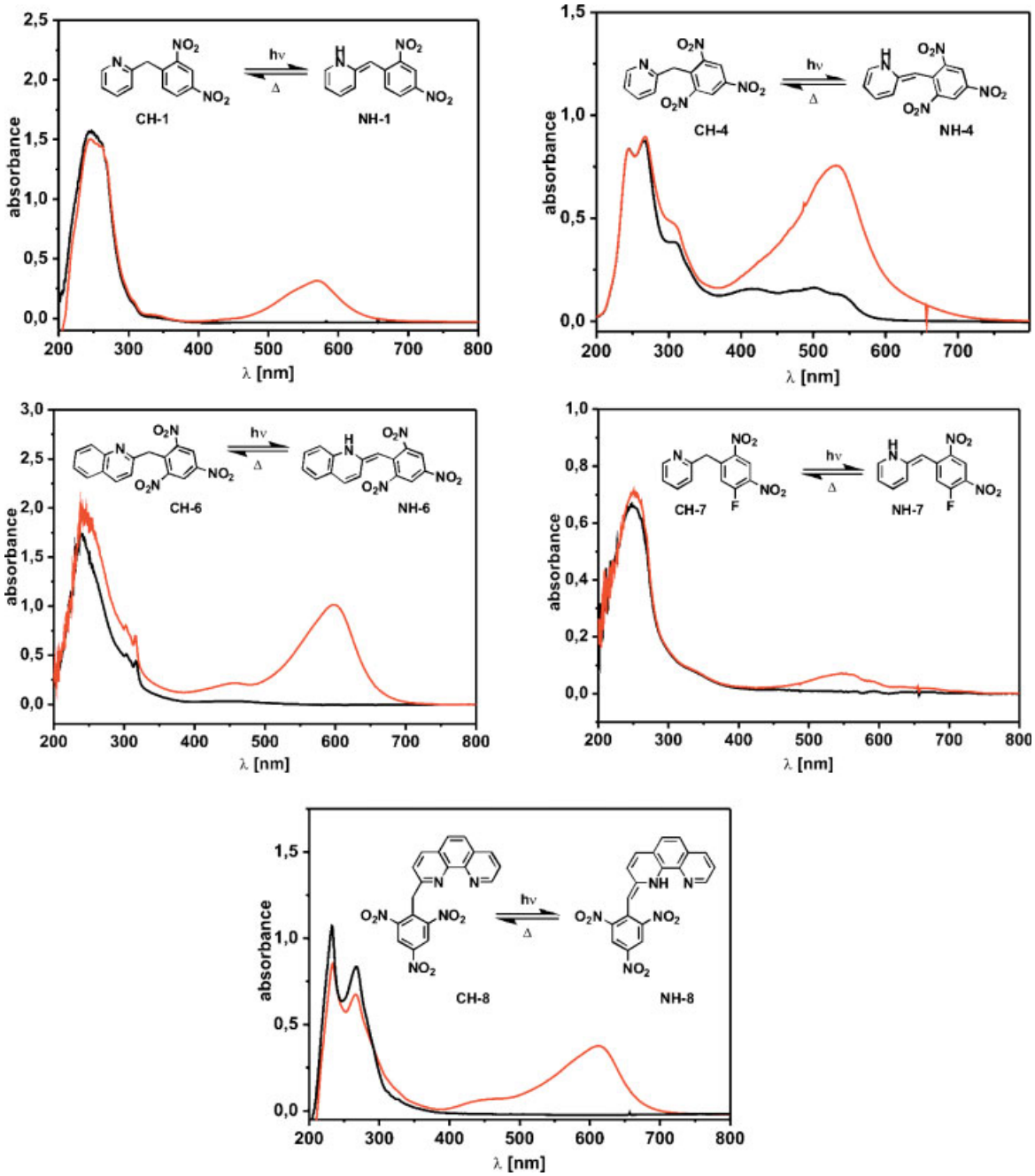
Table 2. Yield of several nitrobenzyl substituted heterocycles prepared by the fluoride mediated coupling of 2,4,6-trinitrofluorobenzene 2 and 1,5-difluoro-2,4-dinitrobenzene 5 with silylated methyl heterocycles

Product	Yield (%)
2-(2,4,6-trinitrobenzyl)pyridine (**4**)	22
2-(2,4,6-trinitrobenzyl)quinoline (**6**)	41
2-(5-fluoro-2,4-dinitrobenzyl)pyridine (**7**)	10
2-(2,4,6-trinitrobenzyl)phenanthroline (**8**)	66
2-(2,4,6-trinitrobenzyl)pyrazine (**9**)	0

Further indication for the cation participation is provided by the solvent dependence of the reaction. No product was obtained when protic or dipolar aprotic solvents were used, such as ethanol or DMF. THF seems to be the optimal solvent. Variation of the silyl protection group from trimethylsilyl to triethylsilyl does not change the yields but only increases reaction times.

After optimization of the reaction conditions other nitrogen heterocycles such as trimethylsilymethyl substituted quinoline **6**, phenanthroline **8**, and pyrazine **9** were used as nucleophiles. 2,4,6-trinitrofluorobenzene (**3**) and 1,5-difluoro-2,4-dinitrobenzene (**5**) were used as the electrophilic reagent (yields see Table 2).



Scheme 5. UV spectra of photoswitchable acids **1**, **4**, **6**, **7**, and **8** in ethanol in the CH form, before (black curve) and after irradiation (high pressure mercury lamp, 150 W, 60 s, −78 °C), (red curve, formation of the NH form).

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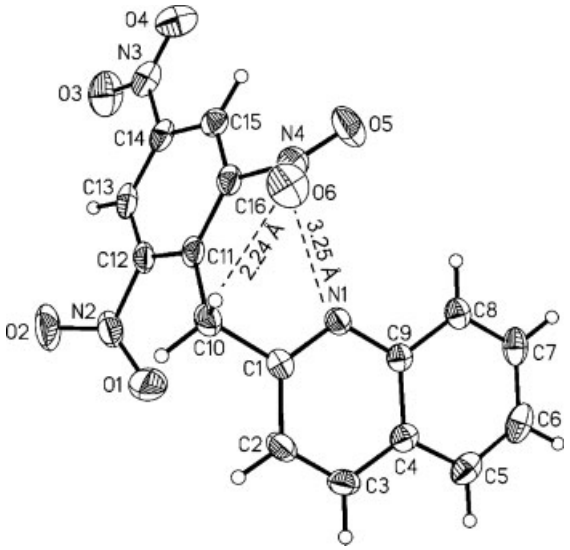

Scheme 6. Crystal structure of **6**

In general, the yield strongly depends on the electrophilicity and nucleophilicity of both components. Increasing electron density of the nucleophilic species leads to higher yields. The yield rises to 41 and 66% in case of the quinaldine derivate **6** and the phenanthroline derivate **8**. The electron deficient pyrazine derivative does not react. 1,5-difluoro-2,4-dinitrobenzene (**5**) which is less electrophilic than 2,4,6-trinitrofluorbenzene (**2**) gives only 10% yield.

To realize the above described proton transport in artificial liquid or solid supported membranes, it is necessary to stabilize the NH form of the photoswitchable acid to a half life which is close to the diffusion time through the membrane which is in the order of at least several seconds in liquid and solid support membranes. The half life of the blue NH form (**NH-1**, Scheme 1) of the parent photoswitchable acid DNBP **1** was determined as 0.02 s in toluene at 295 K and thus is too short for a transport experiment.[31–34]

Therefore, the half lives of the NH tautomers of our new photochromic acids with respect to reisomerization to the corresponding CH form were determined by UV spectroscopy (Scheme 5, Table 3).

The longest half life was determined for the NH form of 2-(2,4,6-trinitrobenzyl)pyridine (**4**) with 1217 min at −78 °C in ethanol (compared to 109 min for **1**). The stability of the NH form of **4** thus exceeds the one of DNBP (**1**) by a factor of about ten. This should be sufficient for transport applications in artificial membranes. The NH forms of **6** and **8** reisomerize at −78 °C with a half life of 241 and 336 min. Because of the weak absorption of 2-(5-fluoro-2,4-dinitrobenzyl)pyridine (**7**) the half life could not be measured.

Table 3. Half life ($t_{1/2}$) of the NH tautomers of new photochromic acids

Photoswitchable acid	$t_{1/2}$
2-(2,4-dinitrobenzyl)pyridine (**1**)	109 min
2-(2,4,6-trinitrobenzyl)pyridine (**4**)	1217 min
2-(2,4,6-trinitrobenzyl)quinoline (**6**)	241 min
2-(5-fluoro-2,4-dinitrobenzyl)pyridine (**7**)	—
2-(2,4,6-trinitrobenzyl)phenanthroline (**8**)	336 min

$t_{1/2}$ determined in ethanol at −78 °C.

A crystal structure of 2-(2,4,6-trinitrobenzyl)-quinoline (**6**) was obtained (Scheme 6). The structure supports theoretical calculations and spectroscopic measurements which predict that the proton is not directly shifted from carbon to nitrogen. The initial step is the proton transfer to one of the oxygen atoms of the nitro group (forming an *aci*-nitro group, OH form), which slightly rotates and hands over the proton to the pyridine nitrogen (CH → OH → NH).[19,35] According to our X-ray structure geometry, one of the protons of the CH_2 group points towards the nitro group. The H. . .O distance is only 2.242 Å. Moreover, one of the oxygen atoms of the nitro group is also very close to the pyridine nitrogen. So the *aci*-nitro group has to rotate only slightly to transfer the proton to the pyridine furnishing the NH tautomer. Hence, the geometry of 2-(2,4,6-trinitrobenzyl)-quinoline (**6**) in its crystal structure is ideally suited for the proton transfer process.

CONCLUSION

We conclude, that we (a) successfully developed a new method to synthesize nitrobenzylpyridine type photoswitchable acids which are not accessible by conventional methods. (b) The new photoswitchable acids exhibit extended life times in their phototautomeric N–H form which make them better candidates for the use as proton pumps in artificial membranes. Particularly compound **4** is promising in this aspect. (c) The X-ray structure of **6** reveals an ideal conformation for the intramolecular proton transfer in agreement with calculations and spectroscopy.

EXPERIMENTAL SECTION

The silylated heterocycles were prepared according to the following general procedure:[36,37]

General procedure for the preparation of silylated methylheterocycles

A solution of one equivalent of 2-methylheterocycle in dry tetrahydrofuran was mixed at 0 °C under nitrogen atmosphere with three equivalents of lithium di-isopropylamide. After warming up to room temperature, the solution was stirred for 1 h. One equivalent of trialkyl silylchloride was added and the mixture was stirred at room temperature for further 30 min. The reaction was stopped by adding water. The organic layer was separated with a saturated sodium chloride solution and the aqueous layer was washed twice with tetrahydrofuran. The combined organic layers were dried with sodium sulfate. The solvent was removed in vacuum and the crude product was purified by column chromatography. Yields are 60–65%.

General procedure for the synthesis of di- and trinitrobenzyl substituted pyridines

A solution of one equivalent of 2,4,6-trinitrofluorbenzene **(2)** and one equivalent of dry cesium fluoride in dry tetrahydrofuran was stirred under reflux. A mixture of one equivalent of a 2-(trimethylsilyl)-methylheterocycle in dry tetrahydrofuran was

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slowly added to the refluxing solution and the mixture was kept under reflux for 5 h. The reaction mixture was added to a saturated sodium chloride solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried with sodium sulfate. The solvent was removed in vacuum and the crude product was purified by column chromatography.

2-(2,4,6-Trinitrobenzyl)pyridine (4)

Following the general procedure a boiling mixture of 500 mg (2.16 mmol) of 2,4,6-trinitrofluorobenzene **(2)** and 330 mg (2.16 mmol) of cesium fluoride in 100 ml tetrahydrofuran was slowly mixed with 360 mg (2.16 mmol) of 2-(trimethylsilylmethyl)-pyridine (**3**). The crude product was purified on silica gel (deactivated with cyclohexane/triethylamine, 5:1, eluent: cyclohexane/dichloromethane/triethylamine, 20:10:1, $R_f = 0.29$). Yield: 145 mg (0.475 mmol, 22%); IR (film) 3093 (m), 2211 (w), 1588 (m), 1535 (s), 1470 (m), 1431 (m), 1341 (s), 1235 (m), 1149 (m), 1082 (m), 669 (m), 899 (m), 756 (m), 720 (s), 529 (m), 492 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.89$ (s, 2H), 8.31 (ddd, $J = 4.7$, 1.7, 0.9 Hz, 1H), 7.66 (ddd, $J = 7.7$, 7.7, 1.8 Hz, 1H), 7.27 (br. d, $J = 7.7$ Hz, 1H), 7.13 (ddd, $J = 7.6$, 4.8, 0.9 Hz, 1H), 4.8 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 154.9, 152.0, 149.2, 146.1, 137.0, 134.7, 123.0, 122.5, 122.2, 35.2; EI-MS (70 eV, *m/z*) $[M]^+$ 304.1; CI-MS (*m/z*) $[M + H]^+$ 305.0.

2-(2,4,6-Trinitrobenzyl)quinoline (6)

A mixture of 1.50 g (6.47 mmol) 2,4,6-trinitrofluorobenzene **(2)** and 980 mg (6.47 mmol) of cesium fluoride in 100 ml of tetrahydrofuran was heated to reflux and 1.39 g (6.47 mmol) of 2-(trimethylsilylmethyl)quinoline (**10**) was added. The crude product was purified on silica gel (deactivated with cyclohexane/triethylamine, 5:1, eluent: cyclohexane/dichloromethane/triethylamine, 20:10:1, $R_f = 0.41$). Yield: 940 mg (2.65 mmol, 41%); IR (film) 3104 (w), 2359 (s), 1601 (m), 1535 (s), 1499 (s), 1424 (m), 1338 (s), 1079 (m), 912 (m), 892 (m), 813 (m), 784 (m), 718 (s), 516 (m), 478 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.93$ (s, 2H), 8.31 (d, $J = 8.4$ Hz, 1H), 7.7–7.8 (m, 2H), 7.62 (ddd, $J = 8.4$, 6.9, 1.4 Hz, 1H), 7.48 (ddd, $J = 8.0$, 6.9, 1.0 Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 154.6, 152.2, 146.2, 137.3, 134.3, 129.8, 129.4, 128.9, 127.5, 126.9, 126.6, 122.4, 120.7, 35.8; EI-MS (70 eV, *m/z*) $[M]^+$ 354.0; CI-MS (*m/z*) $[M + H]^+$ 355.1. Anal. Calcd for $C_{16}H_{10}N_4O_6$: C, 54.24; H, 2.85; N, 18.81. Found: C, 55.08; H, 3.43; N, 15.10.

2-(5-Fluoro-2,4-dinitrobenzyl)pyridine (7)

Following the general procedure, a mixture of 1.43 g (7.02 mmol) of 1,5-difluoro-2,4-dinitrobenzene **(5)** and 1.07 g (7.02 mmol) of cesium fluoride in 100 ml of tetrahydrofuran was heated to reflux and 1.16 g (7.02 mmol) of 2-(trimethylsilylmethyl)-pyridine (**3**) was added. The crude product was purified on silica gel (deactivated with cyclohexane/triethylamine, 5:1, eluent: dichloromethane/ethyl acetate, 5:1, $R_f = 0.29$). Yield: 185 mg (0.667 mmol, 10%); IR (film) 3093 (m), 2211 (w), 1588 (m), 1535 (s), 1470 (m), 1431 (m), 1341 (s), 1235 (m), 1149 (m), 1082 (m), 969 (m), 899 (m), 756 (m), 720 (s), 529 (m), 492 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.76$ (d, $J_F = 6.9$ Hz, 1H), 8.42 (dd, $J = 4.8$, 0.8 Hz, 1H), 7.64 (ddd, $J = 7.7$, 7.7, 1.8 Hz, 1H), 7.40 (d, $J_F = 11.0$ Hz, 1H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.15 (br. dd, $J = 7.6$, 4.9 Hz, 1H), 4.55 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 155.7, 149.6, 143.7, 136.9, 135.2, 128.4, 123.6, 123.1, 122.9, 122.2 41.0; EI-MS (70 eV, *m/z*) $[M]^+$ 276.9; CI-MS (*m/z*) $[M + H]^+$ 278.0.

2-(2,4,6-Trinitrobenzyl)phenanthroline (8)

A solution of 1.43 g (7.02 mmol) of 2,4,6-trinitrofluorobenzene **(2)** and 1.07 g (7.02 mmol) of dry cesium fluoride in 100 ml of dry tetrahydrofuran was mixed and stirred under reflux. Then a mixture of 1.16 g (7.02 mmol) of 2-(triethylsilylmethyl)phenanthroline **(11)** in dry tetrahydrofuran was added to the hot solution and refluxed for 1 h. The reaction was stopped by adding water. The organic layer was separated with saturated sodium chloride solution. The aqueous layer was extracted with dichloromethane and the combined organic layer was dried with sodium sulfate. The solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel (deactivated with cyclohexane/triethylamine, 5:1, eluent: cyclohexane/dichloromethane/tri-ethylamine, 15:15:1, $R_f = 0.15$). Yield: 1.88 g (4.63 mmol, 66%); IR (film) 3049 (w), 1603 (w), 1535 (s), 1411 (w), 1342 (s), 1177 (w), 1140 (w), 1076 (w), 935 (w), 900 (m), 850 (s), 808 (w), 776 (w), 734 (s), 721 (s), 698 (w), 882 (w), 622 (w) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.14 (dd, $J = 4.3$, 1.8 Hz, 1H), 8.99 (s, 2H), 8.20 (m, 2H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 8.0$, 4.3 Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 1H), 5.15 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 155.3, 152.3, 150.5, 146.6, 145.9, 137.3, 135.8, 134.3, 129.1, 127.4, 126.8, 126.1, 123.1, 122.7, 121.8, 37.0; ESI-MS (*m/z*) $[M + H]^+$ calculated for $C_{19}H_{11}N_5O_6 + H$ 406.0782, found 406.0758.

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