Double ring-closing approach for the synthesis of 2,3,6,7-substituted anthracene derivatives

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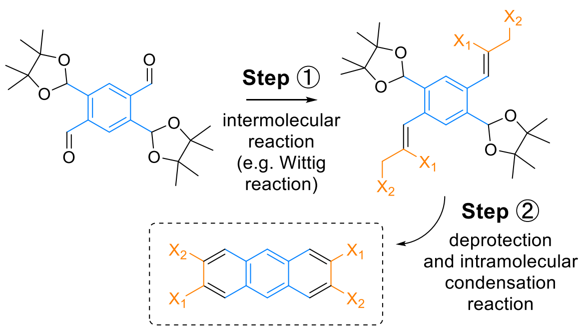


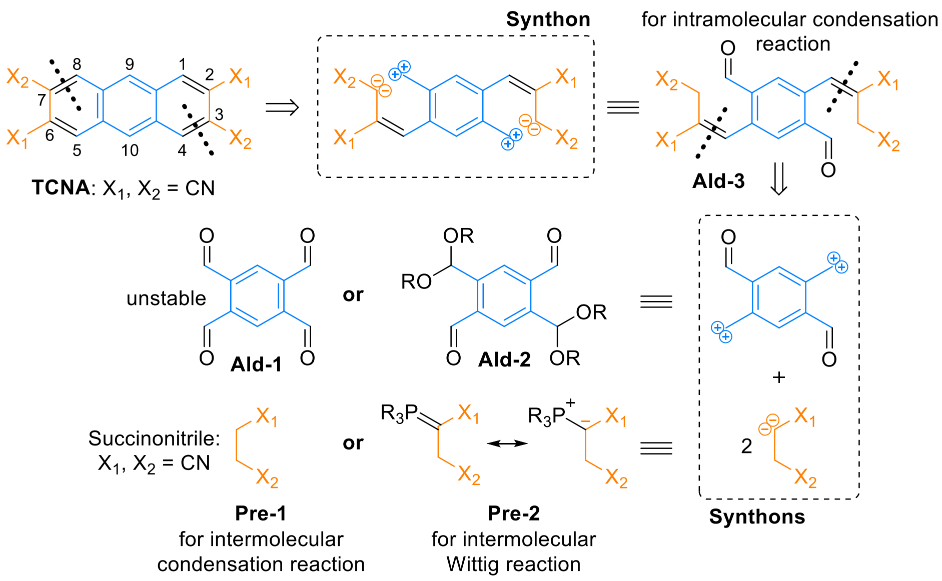
Abstract

A method for the synthesis of 2,3,6,7-substituted anthracene derivatives, one of the most challenging anthracene substitution patterns to obtain, is presented. The method is exemplified by the preparation of 2,3,6,7-anthracenetetracarbonitrile and employs a newly developed, stable protected 1,2,4,5-benzenetetracarbaldehyde as the precursor. The precursor can be obtained in two scalable synthetic steps from 2,5-dibromoterephthalaldehyde and is converted into the anthracene derivative by a double intermolecular Wittig reaction under very mild conditions followed by a deprotection and intramolecular double ring-closing condensation reaction.

Anthracene derivatives have been widely studied as materials for organic electronics and other applications and continue to be of immense interest in various fields of materials chemistry and beyond.[1-9] New synthetic methods keep being developed to facilitate the preparation of known anthracene derivatives and to enable the preparation and study of new derivatives, e.g. our recently developed method for the synthesis of substituted 9,10-anthracenedicarbonitriles (also known as 9,10-dicyanoanthracenes).[10-14] However, as with our method, most available synthetic methods yield anthracene derivatives with substituents in the central 9- and 10-positions. The preparation of anthracene derivatives without substituents in these positions is often more challenging.

Among the most challenging anthracene derivatives to synthesize are those with substituents in the terminal 2-, 3-, 6- and 7-positions (Scheme 1 top left). In 2008, the synthesis of 2,3,6,7-tetrabromo-anthracene, which can serve as a precursor for the introduction of substituents in the terminal positions, was achieved for the first time by a double Bergman cyclization reaction.[15] However, the cyclization precursor was reported to be explosive in the dry state and the cyclization itself had to be carried out in an autoclave, which may explain why the number of reported 2,3,6,7-substituted anthracene derivatives has remained low. In 2019, Bunz et al. published an alternative method for the synthesis of 2,3,6,7-halogenated anthracene derivatives via Vollhardt cyclization.[16] Their method enabled the synthesis of 2,3,6,7-tetrabromoanthracene under much milder conditions. Nevertheless, despite facilitating the synthesis, the preparation of the compound still required five synthetic steps, which all relied on column chromatography for purification. In order to further facilitate the preparation and to enable shorter, scalable synthetic routes to 2,3,6,7-substituted anthracene derivatives, we were looking for an alternative approach.

Retrosynthetic analysis (Scheme 1) suggested a double ring-closing condensation reaction as the final synthetic step towards 2,3,6,7-substituted anthracene derivatives. Initially, we planned to use 1,2,4,5-benzenetetracarbaldehyde (**Ald-1**) and **Pre-1** as the precursors for this approach, converting them into 2,3,6,7-substituted anthracene derivatives in two consecutive condensation steps: (i) intermolecular condensation reaction followed by (ii) the above-mentioned intramolecular ring-closing condensation reaction. In a similar approach, the monodirectional elongation of 1,2-benzene-dicarbaldehydes with succinonitrile gave substituted 2,3-napthalenedicarbonitriles in very good yields,[17] which explains our interest in the corresponding bidirectional elongation approach for the synthesis of anthracene derivatives. However, we soon realized that bidirectional elongation of **Ald-1** was considered previously for the synthesis of 2,3,6,7-anthracenetetracarbonitrile (**TCNA**) (X_1, X_2 = CN), but the reaction was dismissed due the instability of **Ald-1**.[18] Therefore, we decided to synthesize and investigate protected 1,2,4,5-benzenetetracarbaldehyde **Ald-2** as an alternative precursor for the bidirectional elongation reaction. Two of the four aldehyde groups of this precursor are protected as acetals, which was expected to improve its stability. In contrast to the conversion of **Ald-1**, the conversion of **Ald-2** into **TCNA** requires an additional deprotection step after the initial intermolecular reaction step. The deprotection yields intermediate **Ald-3**, which can then undergo the intramolecular double ring-closing condensation reaction as the final step of the synthesis.

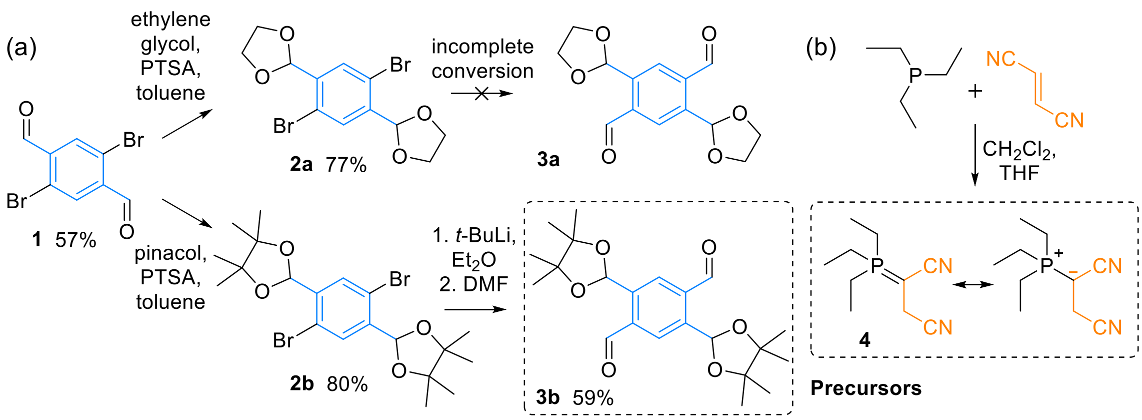


Scheme 1. Retrosynthetic analysis of 2,3,6,7-substituted anthracene derivatives and synthetic equivalents for the synthons.

For testing and demonstrating this approach, we selected **TCNA** as the target compound. This anthracene derivative was prepared previously by a related monodirectional elongation approach,[18] which we expected to facilitate the identification of the compound in our reactions and, hence, the evaluation of our double ring-closing approach. Exceptionally low solubility was reported for **TCNA** in the previous work, making it a particularly challenging target compound for any preparation method. Although the conversion of 2,3,6,7-tetrabromoanthracene (prepared by Bunz et al.) into **TCNA** by Rosenmund-von Braun reaction may in principle also be feasible, our double ring-closing approach has the advantage of not reducing the solubility until the final intramolecular ring-closing reaction step (which reduces the solubility by creating a large planar aromatic system). As an additional advantage of our approach, the substituents of the target compound are introduced as part of the stepwise elongation of the aldehyde precursor, which reduces the total number of required synthetic steps.

Using **Ald-2** as the precursor but replacing the intermolecular condensation reaction by a different reaction method, 2,3,6,7-substituted anthracene derivatives with $X_1 \neq X_2$ should become accessible. To demonstrate the feasibility of this approach, we planned to test a Wittig reaction instead of a condensation reaction for this first step, but we decided to keep **TCNA** as the target compound for these reactions in order to keep the identification of the intermediate and target compound as simple as possible and to ensure the comparability of results.[19]

Precursor synthesis and characterization. Our initial intention was to use ethylene glycol-protected benzenetetracarbaldehyde **3a** (Scheme 2a top) as the aldehyde precursor. For the synthesis of this compound, we prepared 2,5-dibromoterephthalaldehyde **1** by brominating terephthalaldehyde and protected the two aldehyde groups with ethylene glycol (using *p*-toluenesulfonic acid (PTSA) as the catalyst) to obtain compound **2a**. Unfortunately, the further conversion of **2a** into precursor **3a** by lithium-halogen exchange with *t*-butyllithium (*t*-BuLi) and subsequent addition of *N*,*N*-dimethylformamide (DMF) turned out not to be feasible. In diethyl ether (Et_2O), the lithium-halogen exchange remained incomplete, which we attributed to the poor solubility of **2a** in this solvent. Replacing Et_2O by tetrahydrofuran (THF) as the reaction solvent, a large range of by-products was obtained, which could not be assigned. Hence, we replaced ethylene glycol by pinacol for the protection of compound **1**, as we expected this to result in better solubility in Et_2O and to prevent possible side reactions. Indeed, using pinacol-protected 2,5-dibromoterephthalaldehyde **2b**, good yields and high selectivity were achieved for the synthesis of pinacol-protected benzenetetracarbaldehyde **3b** (Scheme 2a bottom). None of the steps towards precursor **3b** required column chromatography for purification; crystallization was found to afford all compounds in good yields and high purity, facilitating the synthesis of **3b** on a multigram scale. Alternative protection with ethanol instead of pinacol, which was reported previously for similar reactions,[20] did not give good results in our experiments. However, as an interesting alternative precursor, Lin et al. recently reported the synthesis of 1,3-propandiol-protected 1,2,4,5-benzenetetracarbaldehyde.[21] In contrast to our direct conversion of compound **2b** into precursor **3b**, they used a Heck coupling reaction followed by an ozonolysis step for the introduction of the aldehyde groups, presumably to circumvent similar synthetic issues as we observed in our attempted direct conversion of compound **2a**.

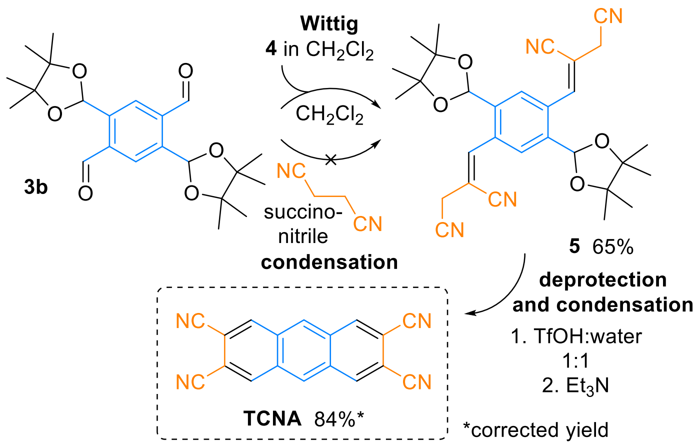


Scheme 2. (a) Attempted synthesis of ethylene glycol-protected 1,2,4,5-benzenetetracarbaldehyde **3a** (top) and successful synthesis of pinacol-protected 1,2,4,5-benzenetetracarbaldehyde **3b** (bottom). (b) Preparation of Wittig reagent **4**.

The structures of compounds **2b** and **3b** were confirmed by single crystal X-ray diffraction (crystallographic data available from The Cambridge Crystallographic Data Centre using CCDC numbers 1991590 and 1991591). As a surprising observation, we noticed that single crystals and powders of **3b** rapidly (and reversibly) turn from colorless to violet when irradiated with sunlight. A discussion of this photochromic effect as well as the crystallographic details of both compounds are provided in the Supporting Information.

Succinonitrile, the second precursor needed for the synthesis of **TCNA** by consecutive condensation reactions, is commercially available. For carrying out the first reaction step by a Wittig reaction instead of condensation reaction, Wittig reagent **4** (Scheme 2b) was prepared by adding triethylphosphine dissolved in THF to a solution of fumaronitrile in CH_2Cl_2 and stirring the reaction at r.t. for 2 h. The obtained yellow solution of reagent **4** was used directly (without work-up) for the Wittig reaction.

Wittig reaction and double ring-closing reaction. The intermolecular condensation reaction of precursor **3b** with succinonitrile (Scheme 3), which we attempted initially, did not yield any intermediate **5**. We attributed this to the fact that the intermediate can undergo further intermolecular condensation reactions, despite using an excess of succinonitrile. Luckily, the Wittig reaction gave more promising results. For this reaction, precursor **3b** was dissolved in CH_2Cl_2 and added to a freshly prepared solution of Wittig reagent **4**, after which the reaction was stirred at r.t. for 3 days. Subsequent evaporation of the solvent afforded intermediate **5** in relatively high purity. Nevertheless, the compound was further purified by recrystallization from ethanol in order to remove all impurities prior to the final deprotection and ring-closing condensation reaction step, as we expected the target compound **TCNA** to be more difficult to purify, due to the previously reported “abysmal solubility” of this anthracene derivative.[18] ^{1}H-^{1}H (NOESY) NMR measurements of the purified intermediate **5** confirmed the double bond configuration shown in Scheme 3 by indicating interactions of the vinylic and allylic protons.



Scheme 3. Synthesis of 2,3,6,7-anthracenetetracarbonitrile (**TCNA**) by intermolecular Wittig reaction to intermediate **5** and subsequent deprotection and intramolecular ring-closing condensation reaction to target compound **TCNA**.

Deprotection of the two aldehyde groups of intermediate **5** for the double ring-closing condensation reaction to **TCNA** was successful in a 1:1 mixture of triflic acid and water at 60 °C. The cyano groups were not affected by these conditions, which were inspired by a previously reported similar deprotection reaction.[22] Basic work-up of the deprotection reaction by addition of saturated aq. $NaHCO_3$ solution and extraction with CH_2Cl_2 resulted in an efficient double ring-closing condensation reaction on a small scale, but on a slightly larger scale (0.5 mmol) the ring-closing reaction was not complete after such work-up. To solve this issue, we added triethylamine to the combined organic layers of the extraction and stirred the mixture at r.t. for 45 min, resulting in complete formation of **TCNA** also on the larger scale. When evaporating the extraction solvent, pure **TCNA** crystallized first; the ^{1}H NMR spectrum of the solid was in accordance with the previously reported spectrum of the compound.[18] Full evaporation of the solvent and drying *in vacuo* afforded **TCNA** with some impurities of pinacol (approx. 3 m% based on ^{1}H NMR spectra), which could not be removed due to the difficult redissolution of **TCNA**. Deducting the small amounts of pinacol in the final product, a corrected yield of 84% was achieved for the deprotection and ring-closing reaction.

Conclusions

From the results, we can conclude that the synthesis of 2,3,6,7-substituted anthracene derivatives can indeed be achieved by the double ring-closing approach suggested in our retrosynthetic analysis. Pinacol-protected 1,2,4,5-benzenetetracarbaldehyde **3b**, which can be prepared on a multigram scale in just two steps from 2,5-dibromoterephthalaldehyde (**1**), is a suitable and stable precursor for this approach. For the first intermolecular reaction step to intermediate **5**, the Wittig reaction gave good results under very mild conditions; the alternative condensation reaction did not afford the product. Besides making 2,3,6,7-substituted anthracene derivatives with $X_1 \neq X_2$ accessible, using a Wittig reaction instead of a condensation reaction for the first reaction step is also expected to enable the introduction of substituents X_1 other than electron withdrawing groups. While the final intramolecular ring-closing condensation reaction to **TCNA** can also be carried out under very mild conditions, the intermediate deprotection reaction requires relatively strong acidic conditions. Here, the recently reported 1,3-propandiol-protected precursor of Lin et al.[21] can provide an easier to deprotect alternative.

The synthetic approach demonstrated in this work on the example of **TCNA** not only facilitates the synthesis of anthracene derivatives with substituents in the 2-, 3-, 6- and 7-positions but also enables the synthesis of anthracene derivatives with new substitution patterns and additional substituents in other positions. We expect that anthracene derivatives with additional substituents in the 9- and 10-positions can be synthesized by modifying the precursor with substituents on the benzene ring. Considering that substituents in the 1-, 4-, 5- and 8-positions can be introduced using ketone instead of aldehyde groups, even fully substituted anthracene derivatives may become accessible by this approach.

Experimental Section

Reagents and solvents for the reactions were purchased from commercial suppliers and used without further purification. NMR spectra were recorded at 600 MHz for ^{1}H and 151 MHz for ^{13}C on a Bruker Avance III HD spectrometer for all novel compounds and at 400 MHz for ^{1}H on a Bruker AV-400 spectrometer for previously reported compounds.

2,5-Dibromoterephthalaldehyde (1). Synthesis following a recently published protocol for the double bromination of terephthalaldehyde.[23] The crude product was purified by crystallization from chloroform to afford white needles of compound **1** in a yield of 57% (9.91 g, 33.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 2H), 8.16 (s, 2H) ppm; in accordance with the literature.

Ethylene glycol-protected 2,5-dibromoterephthalaldehyde 2a. Compound **1** (1.75 g, 6.0 mmol, 1.0 equiv.), *p*-toluenesulfonic acid monohydrate (23 mg, 0.12 mmol, 0.02 equiv.) and ethylene glycol (2.23 g, 2.01 mL, 36 mmol, 6.0 equiv.) were dissolved in toluene (60 mL) and heated to reflux in a flask equipped with a Dean-Stark apparatus for 1 day. The reaction solution was then concentrated to approx. 15 mL and allowed to slowly cool to r.t. for crystallization of compound **2a**. Filtration and washing with cold toluene and petroleum ether afforded **2a** as white solid in a yield of 77% (1.76 g, 4.6 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (s, 2H), 6.03 (s, 2H), 4.17 – 4.04 (m, 8H) ppm; $^{13}C\{1H\}$ NMR (150 MHz, $CDCl_3$): δ 139.3, 132.3, 121.9, 101.9, 65.7 ppm; HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{12}H_{12}Br_2O_4$, 378.9175; found, 378.9168 (APCI).

Pinacol-protected 2,5-dibromoterephthalaldehyde 2b. Compound **1** (9.78 g, 33.5 mmol, 1.0 equiv.), *p*-toluenesulfonic acid (127 mg, 0.67 mmol, 0.02 equiv.) and pinacol (23.8 g, 201 mmol, 6.0 equiv.) were dissolved in toluene (168 mL) and heated to reflux in a flask equipped with a Dean-Stark apparatus for 1 day. The reaction solution was then concentrated to approx. 50 mL and allowed to slowly cool to r.t. for crystallization of compound **2b**. Filtration and washing with petroleum ether afforded **2b** as pure white solid in a yield of 80% (13.2 g, 26.8 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (s, 2H), 6.09 (s, 2H), 1.33 (s, 12H), 1.27 (s, 12H) ppm; $^{13}C\{1H\}$ NMR (150 MHz, $CDCl_3$): δ 140.4, 132.2, 122.1, 98.3, 83.3, 24.4, 22.3 ppm; HRMS (*m/z*): $[M-H]^+$ calcd. for $C_{20}H_{28}Br_2O_4$, 489.0271; found, 489.0260 (APCI).

Pinacol-protected 1,2,4,5-benzenetetracarbaldehyde 3b. Compound **2b** (5.23 g, 10.6 mmol, 1.0 equiv.) was suspended in dry diethyl ether (106 mL, 0.1 M) under argon. The suspension was cooled to -80 °C with an acetone/liquid N_2 bath and *t*-BuLi, 1.7 M in pentane (25 mL, 42.5 mmol, 4.0 equiv.), was added dropwise by cannula transfer. The reaction mixture was then allowed to slowly warm to -40 °C over 2 h, cooled again to -70 °C for the slow addition of dry DMF (3.18 g, 3.4 mL, 43.5 mmol, 4.1 equiv.) and slowly warmed to r.t. overnight. The reaction was extracted with sat. aq. NH_4Cl solution (100 mL) and the aqueous phase was extracted three times with Et_2O (100 mL, 2 x 75 mL). The combined four organic phases were washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was recrystallized from approx. 15 mL ethyl acetate (and concentrated for further crystallization) to obtain compound **3b** as white needles in a yield of 59% (2.44 g, 6.25 mmol). ^{1}H NMR

(600 MHz, $CDCl_3$): δ 10.50 (s, 2H), 8.33 (s, 2H), 6.56 (s, 2H), 1.35 (s, 12H), 1.21 (s, 12H) ppm; $^{13}C\{1H\}$ NMR (150 MHz, $CDCl_3$): δ 191.4, 142.6, 136.9, 126.9, 96.2, 83.6, 24.1, 22.3 ppm; HRMS (*m/z*): $[M-H]^+$ calcd. for $C_{22}H_{30}O_6$, 389.1959; found, 389.1947 (APCI).

Wittig reagent 4. Triethylphosphine (11.6 mL, 11.6 mmol, 1.0 equiv., 1.0 M in THF) was slowly added to a stirred solution of fumaronitrile (906 mg, 11.6 mmol, 1.0 equiv.) in CH_2Cl_2 (29 mL, 0.4 M). After stirring at r.t. for 2 h, the resulting yellow solution of Wittig reagent **4** was used directly for the synthesis of compound **5** (no work-up or purification).

Wittig reaction product 5. A solution of compound **3b** (1.13 g, 2.90 mmol, 1.0 equiv.) in CH_2Cl_2 (58 mL, 0.05 M) was added to a solution of Wittig reagent **4** (11.6 mmol, 4.0 equiv.), which was freshly prepared as described above. The reaction flask was covered in aluminum foil as a precautionary measure and stirred at r.t. for 3 days. After evaporation of the reaction solvent, the dark residue was recrystallized from approx. 20 mL ethanol to give compound **5** as off-white solid in a yield of 65% (969 mg, 1.88 mmol). ^1H NMR (600 MHz, $CDCl_3$): δ 8.26 (s, 2H), 7.91 (t, J = 1.6 Hz, 2H), 6.06 (s, 2H), 3.57 (d, J = 1.6 Hz, 4H), 1.32 (s, 12H), 1.25 (s, 12H) ppm; $^{13}C\{1H\}$ NMR (150 MHz, $CDCl_3$): δ 145.1, 140.2, 132.7, 125.6, 116.3, 114.5, 103.1, 96.8, 83.6, 24.3, 24.1, 22.3 ppm; ^1H-^1H (NOESY) NMR confirmed the double bond configuration; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{30}H_{34}N_4O_4$, 537.2478; found, 537.2482 (ESI).

2,3,6,7-Anthracenetetracarbonitrile (TCNA). Triflic acid (2.5 mL) was carefully added to stirred deionized water (2.5 mL) in a 50 mL round-bottom flask. Following this exothermic addition, the mixture was cooled to r.t. and compound **5** (257 mg, 0.50 mmol, 1.0 equiv.) was added. The reaction was then heated to 60 °C under nitrogen for 5 h. After cooling to r.t., sat. aq. $NaHCO_3$ solution (25 mL) was added dropwise and the resulting suspension was stirred for 5 min at r.t. before being extracted four times with CH_2Cl_2 (1 x 100 mL, 3 x 50 mL). Triethylamine (202 mg, 0.28 mL, 2.0 mmol, 4.0 eq.) was added to the combined organic layers, which were then stirred for 45 min at r.t., extracted with water, dried over Na_2SO_4, and concentrated *in vacuo*. Final drying *in vacuo* afforded **TCNA** (120 mg) with small amounts of pinacol (approx. 3 m% according to ^1H NMR) as a light yellow solid. Considering the estimated amount of pinacol, a corrected yield of 84% (117 mg, 0.42 mmol) was achieved for the **TCNA** formation. ^1H NMR (400 MHz, DMSO-*d6*): δ 9.25 (s, 4H), 9.10 (s, 2H) ppm; in accordance with the literature.[18]

Supporting Information. ^1H NMR spectra of all isolated compounds. $^{13}C\{1H\}$ NMR spectra of all novel compounds. Crystallographic data and discussion for compounds **2b** and **3b**. Discussion of the photochromic effect of compound **3b**.

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