Synthesis of Bis- and Tris(indolinylidenemethyl)benzenes by One-Pot Reactions of Polylithiated Nitriles with Bis(imidoyl)chlorides of Oxalic Acid

Peter Langer*[a] and Joachim T. Anders[a]

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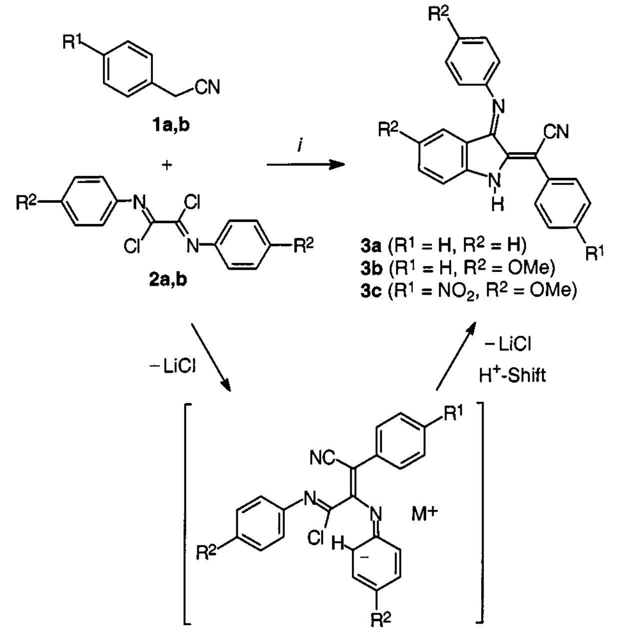
The reaction of polylithiated di- and tricyanomethylbenzenes with oxalic acid-bis(imidoyl)chlorides afforded novel oligo(indolinylidenemethyl)benzenes with the formation of up to six carbon-carbon bonds. The UV/Vis spectroscopic features of these and related compounds were studied. 1,4-Disubstituted benzenes containing a large π-system have been efficiently prepared by the reaction of dianions with 1,4-dicyanobenzene.

Introduction

Large heterocyclic π-systems, merocyanines and substituted benzenes[1] play an important role in the field of materials science due to their UV/Vis,[2] photochromic,[3] solvatochromic,[4] electron-transfer,[5] ferromagnetic,[6] and nonlinear optical properties.[7] In this context, *push-pull* substitution plays an important role. We have recently reported[8] a new and versatile synthesis of 2-alkylidene-3-iminoindoles, containing an aza-analogous indigo substructure, by cyclization of nitrile and sulfone dianions with oxalic acid-bis(imidoyl)chlorides.[9] A possible mechanism for this reaction is depicted in Scheme 1. Herein, we wish to report the extension of our methodology to the synthesis of *push-pull* substituted and extended π-systems. In this context, one-pot reactions of polylithiated di- and tricyanomethylbenzenes with oxalic acid-bis(imidoyl)chlorides are reported which involve the formation of up to six carbon-carbon bonds.



Scheme 1. Synthesis of *push-pull* substituted 2-alkylidene-3-iminoindole **3c**. *i*, for **3a,b**: 2.3 equiv. *n*BuLi, THF, −78 → 20 °C, 12 h; for **3c**: 3.3 equiv. NaH, THF, 12 h

Results and Discussion

The reactions of the dianion of phenylacetonitrile **1a** (generated by *n*BuLi or LDA) with oxalic acid-bis(phenylimidoyl)dichloride **2a** and oxalic acid-bis(*p*-methoxyphenylimidoyl)dichloride **2b** has been reported by us to give the indoles **3a** and **3b** respectively in high yields.[8] Our initial attempts to prepare the *push-pull* substituted 2-alkylidene-3-iminoindole **3c** by reaction of *p*-nitrophenylacetonitrile (**1b**) with **2b** were unsuccessful. Complex reaction mixtures were obtained when LDA or *n*BuLi was used, due to interaction of the highly reactive organolithium compounds with the nitro group. This problem was eventually solved by the use of sodium hydride and application of a stepwise deprotonation protocol. The reaction of **1b** with **2b** in the presence of NaH afforded the novel *push-pull* substituted indole **3c** (Scheme 1 and 2). As expected, the UV absorption of violet **3c** (λ_{max} = 519 nm) is shifted to significantly higher wavelengths than that of orange **3a** (λ_{max} = 469 nm). Some *push-pull* character can be anticipated for the red indole **3b**, due to the presence of the methoxy and the nitrile groups. Therefore the absorption of **3b** (λ_{max} = 501 nm) is shifted to significantly higher wavelengths than that of **3a**. The absorption of **3c** appears at lower energy than that of **3b** due to the presence of the nitro group.

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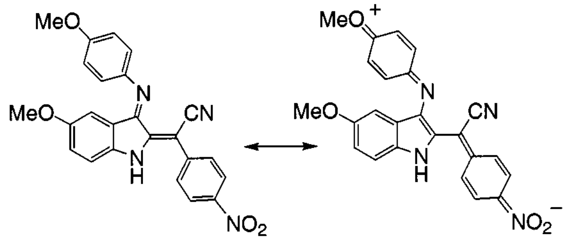
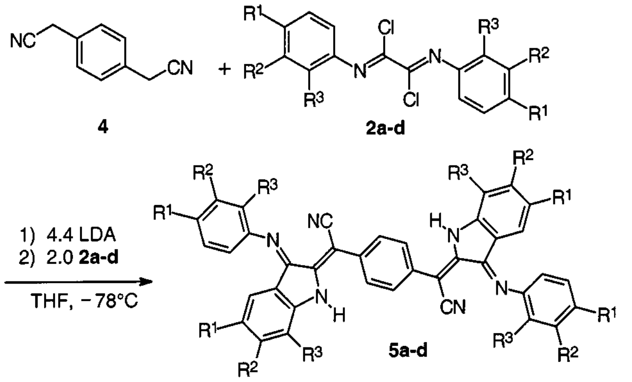
[a] Institut für Organische Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 2, 37077 Göttingen, Germany



Scheme 2. *Push-pull* substituted 2-alkylidene-3-iminoindole **3c**

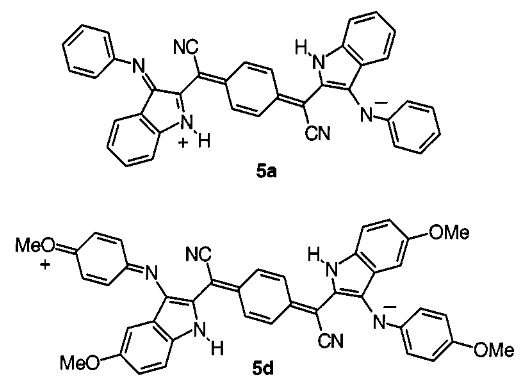
Treatment of 1,4-di(cyanomethyl)benzene (**4**) with four equivalents of LDA, and subsequent reaction with oxalic acid-bis(phenylimidoyl)chloride **2a**, afforded highly conjugated 1,4-bis(indolinylidenemethyl)benzene **5a** in 74% yield (Scheme 3). Similarly, the reaction of **4** oxalic acid-bis(2-tolylimidoyl)chloride (**2c**) or oxalic acid-bis(3-tolylimidoyl)chloride (**2d**) with oxalic acid-bis(4-methoxyphenylimidoyl)chloride (**2b**), afforded the 1,4-bis(indolinylidenemethyl)benzenes **5b**−**d** in good yields. The formation of **5a**−**d** can be explained by the formation of a tetraanion and subsequent twofold cyclization. Alternatively, generation of a dianion, double condensation, double lithiation and double cyclization is also a viable mechanism. Four carbon-carbon bonds were formed with very good regio- and *E*-diastereoselectivity.



Scheme 3. Cyclization of 1,4-di(cyanomethyl)benzene with oxalic acid-bis(imidoyl)chlorides

The colour of the bis-indoles **5** varies from deep red (**5a**−**c**) to violet (**5d**). The UV absorption of **5a** (λ_{max} = 495 nm) is shifted to higher wavelengths than in **3a**, due to delocalization of the electrons in a larger π-system (Scheme 4). Similar absorptions were observed for the alkyl-substituted derivatives **5b** and **5c** (Table 1). In contrast, a significant shift of the absorption was detected for **5d** (λ_{max} = 528 nm), due to the presence of the methoxy groups (Scheme 4).

The cyclization of 1,3-bis(cyanomethyl)benzene (**6**) with **2a**, **2c** and **2b** afforded the 1,3-bis(indolinylidenemethyl)benzenes **7a**, **7b** and **7c** in good yields, respectively (Scheme 5). In contrast to 1,4-disubstituted benzenes **5**, only very minor shifts were observed for the λ_{max} absorptions of 1,3-disubstituted benzenes **7a** (477 nm) and **7b** (476 nm) relative to **3a**. Due to the presence of methoxy groups, a significant shift of the absorption was detected for **7c** (λ_{max} = 510 nm) relative to **7a,b**. As expected, the λ_{max} absorption of **7c** appeared at lower wavelength than that of **5d** (Table 1).

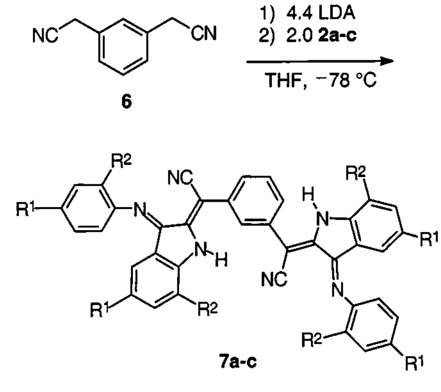


Scheme 4. Zwitterionic mesomeric structures of **5a** and **5d**

Table 1. Synthesis and UV/Vis properties of bis(indolinylidenemethyl)benzenes

	R^1	R^2	R^3	λ_{max} [a]	Yield (%)[b]
3a	H	H	–	469	75
3b	H	MeO	–	501	67
3c	NO_2	MeO	–	519	52
5a	H	H	H	495	74
5b	H	H	Me	498	72
5c	H	Me	H	496	52
5d	MeO	H	H	528	81
7a	H	H	–	477	78
7b	H	Me	–	476	52
7c	OMe	H	–	510	70
12	–	–	–	482	25

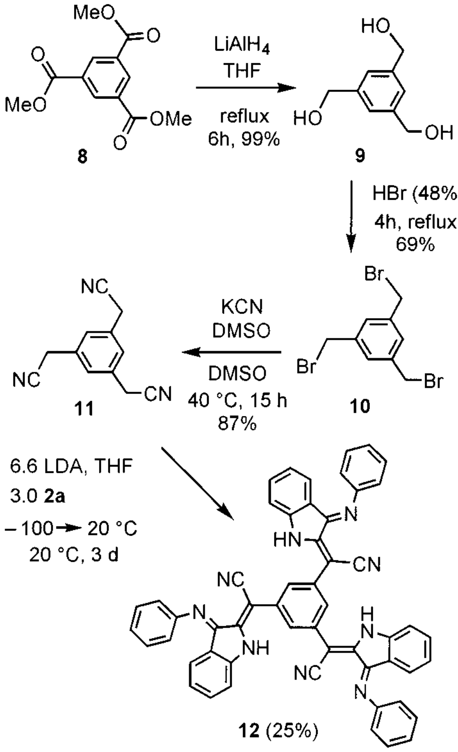
[a] [nm] (lg ε) (CH_3CN). [b] Isolated yield.



Scheme 5. Cyclization of 1,3-bis(cyanomethyl)benzene with oxalic acid-bis(imidoyl)chlorides

The synthesis of a C_3-symmetric benzene derivative was studied next (Scheme 6). The reaction of 1,3,5-benzenetricarboxylic acid with methanol afforded the triester **8**[10] which was reduced to the trialcohol **9** with $LiAlH_4$.[11] Subsequent treatment of **9** with HBr afforded the tribromide

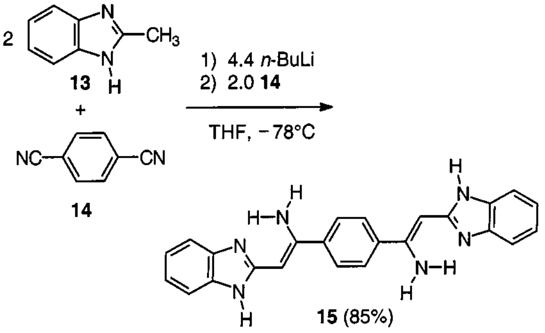
10[12] which was then transformed into 1,3,5-tri(cyanomethyl)benzene (**11**). Yamaguchi and co-workers have prepared **11** in 80% yield by reaction of 1,3,5-tris(chloromethyl)benzene with KCN in the presence of 18-crown-6 ether,[13] although the reaction time was rather long (6 days). We have improved the synthesis of the useful trivalent building block **11** by using tribromide **10** as the key intermediate. The reaction of **10** with NaCN in DMSO at 40 °C afforded **11** in 87% yield. The reaction time could be shortened considerably (15 h) and the use of rather expensive crown ethers was not required. The ^{13}C NMR and MS data of **11**, which have not yet been reported, have been recorded and are listed in the Exp. Sect.



Scheme 6. Cyclization of 1,3,5-tri(cyanomethyl)benzene with **2a**

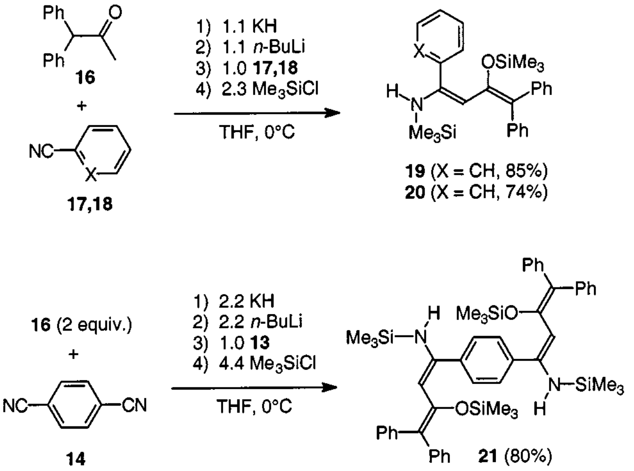
The LDA-mediated reaction of **11** with oxalic acid-bis(phenylimidoyl)chloride (**2a**) afforded tris(indolinylidenemethyl)benzene (**12**; Scheme 6). The yield was relatively low (25%). However, it has to be considered that six carbon-carbon bonds are formed in only one step, which corresponds to a yield of 80% per C−C bond formation. As expected, only a minor shift of the UV absorption was observed for **12** (λ_{max} = 482 nm) relative to **7a−c** and **3a** (Table 1).

A second approach to 1,4-disubstituted benzene derivatives containing a large π-system was developed based on reactions of dianions with 1,4-dicyanobenzene. Recently, the condensation of dilithiated 2-methylbenzimidazole (**13**) with benzonitrile has been reported.[14] Herein, we wish to report for the first time the reaction of this dianion with 1,4-dicyanobenzene (**14**) (Scheme 7). This reaction was remarkably efficient and afforded 1,4-bis(2-benzimidazolyl-2′-ethenyl)benzene (**15**) in 85% yield. The condensation proceeded by attack of the dianion (2 equiv.) onto **14** (1 equiv.) to give an open-chain tetraanionic intermediate, which was subsequently quenched with water.



Scheme 7. Condensation of dilithiated 2-methylbenzimidazole with 1,4-dicyanobenzene

The reaction of the dianion of 1,1-diphenylacetone (**16**) with nitriles was studied next. The reaction of the dianion of **16** with benzonitrile (**17**) or 2-cyanopyridine (**18**) and subsequent treatment with Me_3SiCl afforded the dienes **19** and **20**, respectively, in good yields and with very good regioselectivity (Scheme 8). The reaction of **16** with 1,4-dicyanobenzene (**14**) and Me_3SiCl afforded the 1,4-disubstituted benzene **21** in 80% yield. The reaction again proceeded by regioselective attack of the sterically less encumbered carbon of the dianion onto the dinitrile to give a tetraanionic intermediate. Addition of Me_3SiCl (4 equiv.) resulted in regioselective *O*/*N*-silylation.



Scheme 8. Condensation of the dianion of 1,1-diphenylacetone with 1,4-dicyanobenzene

In summary, we have reported the synthesis of novel oligo(indolinylidenemethyl)benzenes by one-pot reactions of polylithiated di- and tricyanomethylbenzenes with oxalic acid-bis(imidoyl)chlorides. In addition, 1,4-disubstituted benzenes containing a large π-system have been efficiently prepared by reaction of dianions with 1,4-dicyanobenzene. We are currently studying the influence of the oxidation state of the products prepared on their UV/Vis and other physical properties.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. The oxalic acid-bis(imidoyl)dichlorides **2** were prepared according to literature procedures.[9] For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR: 200, 300 and 400 MHz, ^{13}C NMR: 50, 75 and 100 MHz) tetramethysilane as internal standard and the deuterated solvents indicated were used. Mass spectroscopic data (MS) were obtained by electron ionization (70 eV), chemical ionization (CI, H_2O) or electrospray ionization techniques. For preparative scale chromatography silica gel (60−200 mesh) was used. Melting points are uncorrected. Elemental analyses were performed at the microanalytical laboratory of the University of Göttingen.

Synthesis of (*E*)-2-[1-Cyano-1-(4-nitrophenyl)methylidene]-5-methoxy-3-(4-methoxyphenyl)imino-2,3-dihydro-1*H*-indole (3c): 4-Nitrophenylacetonitrile (0.162 g, 1.00 mmol) and oxalic acid-bis(4-methoxyphenylimidoyl)chloride (0.337 g, 1.00 mmol) were added to a THF solution (40 mL) of sodium hydride (0.08 g, 3.3 mmol) and the mixture was stirred at 20 °C for 12 h. The solution was then poured into an aqueous solution of NH_4Cl (250 mL, 1 M) which was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, diethyl ether/petroleum ether, 1:1 → diethyl ether → acetone) to give **3c** as a violet solid (0.222 g, 0.521 mmol, 52%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 3.45$ (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 6.20 (s, 1 H, Ar), 6.90−7.08 (m, 7 H, Ar, NH), 7.87, 8.33 (2 × d, AA′XX′, 2 × 2 H, Ar). ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): $\delta = 55.15$ (OCH_3), 55.35 (OCH_3), 80.62 (*C*−CN), 110.36, 112.52, 114.67 (CH), 117.30, 119.03 (C), 119.57, 119.84, 124.03, 129.57 (CH), 130.62, 141.09, 142.64, 142.78, 145.88, 148.96, 153.53, 156.95 (C). MS (ESI): *m*/*z* (%) = 1301 (10) [3M + Na]$^+$, 875 (100) [2M + Na]$^+$, 589 (8), 449 (5) [M + Na]$^+$, 425 (100) [M − H]$^-$. IR (KBr): $\tilde{\nu} = 2922$ cm^{-1} (w), 2835 (w), 2187 (m, C≡N), 1653 (s), 1635 (m), 1600 (s), 1576 (m), 1516 (s), 1486 (s), 1339 (s), 1240 (m), 1220 (m), 1181 (m), 1107 (m), 1030 (m), 853 (w), 838 (m), 811 (w), 762 (w), 753 (w). UV/Vis (CH_3CN): λ_{max} (lg ε) = 518.9 nm (3.88), 356.7 (4.21), 272.2 (4.45).

General Procedure for the Cyclization of Bis(cyanomethyl)benzenes with Oxalic Acid-bis(imidoyl)chlorides: *n*-Butyllithium (13.0 mL, 1.54 M solution in *n*-hexane, 20 mmol) was added to a THF solution (30 mL) of diisopropylamine (2.024 g, 20 mmol) at 0 °C and the solution was stirred for 20 min. 1,4-Bis(cyanomethyl)benzene (0.625 g, 4.0 mmol) was then added at 0 °C and the solution was stirred for 60 min. It was then slowly transferred with a cannula to a THF solution (50 mL) of oxalic acid-bis(phenylimidoyl)chloride (2.217 g, 8.00 mmol) at −78 °C. The solution was warmed to 20 °C, stirred for 3 h and poured into an aqueous solution of NH_4Cl (250 mL, 1 M). The organic and the aqueous layers were separated and the latter was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, diethyl ether/petroleum ether, 3:1) to give **5a** as a deep red solid (1.67 g, 74%, $E/Z > 98:2$).

1,4-Bis{[(*E*)-(3-phenylimino)-2,3-dihydro-1*H*-indol-2-ylidene]-cyanomethyl}benzene (5a): ^{1}H NMR (300 MHz, [D$_6$]DMSO, 100 °C): $\delta = 6.55$ (d, 2 H, Ar), 6.63 (t, 2 H, Ar), 6.95−7.16 (m, 6 H, Ar), 7.21−7.35 (m, 8 H, Ar), 7.45 (t, 4 H, Ar), 7.80 (s, 2 H, NH). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 100 °C): $\delta = 84.00$ (*C*−CN), 111.68 (CH), 116.75 (C), 117.33 (CH), 118.60 (C), 119.83, 123.81, 125.04, 128.92, 128.93 (CH), 133.03 (C), 133.17 (CH), 147.04, 149.05, 150.06, 157.14 (C). MS (ESI): *m*/*z* (%) = 565 (55) [M + H]$^+$, 413 (16), 279 (35), 237 (30). IR (KBr): $\tilde{\nu} = 3058$ cm^{-1} (w, Ar-H), 3028 (w), 2197 (m, C≡N), 1640 (m), 1619 (s), 1589 (s), 1465 (s), 1341 (m), 1214 (s), 1148 (m), 1100 (m), 765 (w), 749 (m), 694 (m). UV/Vis (CH_3CN): λ_{max} (lg ε) = 495.0 nm (4.30), 261.5 (4.45), 224.5 (4.48).

1,4-Bis({(*E*)-7-methyl-[3-(2-tolyl)imino]-2,3-dihydro-1*H*-indol-2-ylidene}cyanomethyl)benzene (5b): The reaction was carried out according to the procedure given for the synthesis of **5a**. Starting with 1,4-bis(cyanomethyl)benzene (0.156 g, 1.00 mmol) and oxalic acid-bis(2-tolylimidoyl)dichloride (0.610 g, 2.00 mmol), **5b** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 3:1) as an orange solid (0.445 g, 0.718 mmol, 72%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, [D$_5$]pyridine): $\delta = 2.24$ (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 6.62 (t, *J* = 8.1 Hz, 2 H, Ar), 6.84 (d, *J* = 8.3 Hz, 2 H, Ar), 7.07−7.15 (m, 4 H, Ar), 7.23 (s, 2 H, Ar), 7.34 (2 × d, AA′XX′, 2 × 2 H, Ar), 7.78 (s, 4 H, Ar), 9.90 (br, 2 H, NH). ^{13}C NMR (75.5 MHz, [D$_5$]pyridine): $\delta = 16.50$ (CH_3), 18.03 (CH_3), 87.50 (*C*−CN), 117.86 (CH), 119.24, 119.78 (C), 121.82 (CH), 121.87, 123.19 (C), 124.11, 125.07, 127.28 (CH), 127.48 (C), 130.32, 131.50, 135.30 (CH), 148.62, 149.20, 149.70, 158.29 (C). MS (ESI): *m*/*z* (%) = 1884 (22) [3M + Na + 1]$^+$, 1574 (16), 1263 (100) [2M + Na]$^+$, 954 (8), 621 (30) [M + 1]$^+$, 620 (40) [M$^-$], 619 (100) [M − 1]$^-$. IR (KBr): $\tilde{\nu} = 3047$ cm^{-1} (m, Ar-H), 2925 (m), 2851 (w), 2201 (m, C≡N), 1642 (s), 1618 (s), 1585 (s), 1492 (m), 1483 (m), 1458 (m), 1426 (m), 1403 (s), 1338 (m), 1222 (s), 1183 (m), 1110 (m), 1076 (m), 932 (w), 850 (w), 792 (w), 786 (w), 773 (w), 745 (m). UV/Vis (CH_3CN): λ_{max} (lg ε) = 497.5 nm (4.27), 274.5 (4.43), 200.0 (5.01).

1,4-Bis({(*E*)-6-methyl-[3-(3-tolyl)imino]-2,3-dihydro-1*H*-indol-2-ylidene}cyanomethyl)benzene (5c): The reaction was carried out according to the procedure given for the synthesis of **5a**. Starting with 1,4-bis(cyanomethyl)benzene (0.156 g, 1.00 mmol) and oxalic acid-bis(3-tolylimidoyl)dichloride (0.610 g, 2.00 mmol), **5c** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 3:1) and subsequent recrystallization (acetone/diethyl ether, 1:1) as a deep red solid (0.323 g, 0.520 mmol, 52%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, [D$_5$]pyridine): $\delta = 2.11$ (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3), 6.43 (d, *J* = 8.1 Hz, 2 H, Ar), 6.84 (d, *J* = 8.3 Hz, 2 H, Ar), 6.93 (d, *J* = 7.5 Hz, 2 H, Ar), 7.07 (m, 6 H, Ar), 7.39 (t, *J* = 7.6 Hz, 2 H, Ar), 7.68 (d, s, *J* = 4.9 Hz, 4 H, Ar). ^{13}C NMR (75.5 MHz, [D$_5$]pyridine): $\delta = 21.44$ (CH_3), 21.92 (CH_3), 85.85 (*C*−CN), 112.45, 116.03, 116.65, 119.73, 122.36, 122.78, 125.56, 126.83, 129.82, 130.36, 139.80, 145.28, 149.41, 150.64, 151.93, 157.95. MS (ESI): *m*/*z* (%) = 1884 (22) [3M + Na + 1]$^+$, 1574 (16), 1263 (100) [2M + Na]$^+$, 1240 (20) [2M]$^-$, 954 (8), 621 (30) [M + H]$^+$, 620 (100) [M$^-$]. IR (KBr): $\tilde{\nu} = 3036$ cm^{-1} (w, Ar-H), 2951 (w), 2920 (w), 2858 (w), 2194 (m, C≡N), 1628 (s), 1579 (s), 1500 (w), 1479 (w), 1454 (m), 1342 (m), 1251 (m), 1221 (m), 1153 (m), 1114 (m), 1092 (m), 944 (w), 929 (w), 811 (w), 781 (w), 764 (w), 746 (w), 709 (w). UV/Vis (CH_3CN): λ_{max} (lg ε) = 496.0 nm (4.30), 283.5 (4.47), 202.5 (4.96). $C_{42}H_{32}N_6$ (620.76): calcd. C 81.27, H 5.20; found C 81.09, H 5.16.

1,4-Bis({(*E*)-5-methoxy-[3-(4-methoxyphenyl)imino]-2,3-dihydro-1*H*-indol-2-ylidene}cyanomethyl)benzene (5d): Starting with 1,4-bis(cyanomethyl)benzene (0.156 g, 1.00 mmol) and oxalic acid-bis(4-methoxyphenylimidoyl)dichloride (0.792 g, 2.10 mmol), **5d** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 3:1) and subsequent recrystallization (*n*-butyl alcohol) as a violet solid (0.554 g, 0.810 mmol, 81%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, [D$_5$]pyridine): δ = 3.54 (s, 6 H, OCH$_3$), 3.81 (s, 6 H, OCH$_3$), 6.79 (d, 2 H, Ar), 7.02 (m, 4 H, Ar), 7.16, 7.30 (2 × d, AA′XX′, 8 H, Ar), 7.80 (s, 4 H, Ar), 10.48 (br, 2 H, NH). ^{13}C NMR (75.5 MHz, [D$_5$]pyridine): δ = 55.96 (OCH$_3$), 56.01 (OCH$_3$), 85.33 (*C*-CN), 111.74, 112.66, 115.71 (CH), 119.33, 119.96 (C), 120.85, 121.33, 130.26 (CH), 144.50, 144.69, 149.46, 154.92, 158.35 (C). Three carbon signals are overlapped by the solvent signals. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 55.01 (OCH$_3$), 55.17 (OCH$_3$), 82.63 (*C*−CN), 110.08, 112.10, 114.56 (CH), 117.12, 118.75 (C), 119.75, 119.96, 128.85 (CH), 130.37, 133.08, 142.83, 142.92, 147.44, 153.10, 157.06. MS (ESI): *m*/*z* (%) = 1391 (100) [2M + Na]$^+$, 1106 (30), 707 (20) [M + Na]$^+$, 685 (15) [M + H]$^+$, 1367 (25) [2M − 1]$^-$, 683 (90) [M − H]$^-$. IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1} (m), 2851 (w), 2177 (m, C≡N), 1630 (m), 1575 (m), 1501 (s), 1486 (s), 1436 (s) 1334 (m), 1278 (m), 1241 (s), 1209 (s), 1123 (m), 1124 (m), 1092 (m), 1023 (m), 838 (w), 815 (w), 760 (m), 725 (w). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 527.5 nm (4.22), 261.0 (4.50), 230.0 (4.62).

1,3-Bis{[(*E*)-(3-phenylimino)-2,3-dihydro-1*H*-indol-2-ylidene]-cyanomethyl}benzene (7a): Starting with 1,3-Bis(cyano)methylbenzene (0.625 g, 4.00 mmol) and oxalic acid-bis(phenylimidoyl)dichloride (2.217 g, 8.00 mmol), **7a** was isolated as a deep red solid (1.76 g, 78%, *E*/*Z* > 98:2). The product was purified by chromatography (silica gel, diethyl ether/petroleum ether, 3:1). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.41 (d, 2 H, Ar), 6.64 (t, 2 H, Ar), 7.02 (td, 6 H, Ar), 7.20−7.36 (m, 4 H, Ar), 7.47 (t, 4 H, Ar), 7.63−7.75 (m, 4 H, Ar), 7.87 (br, 2 H, NH). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 50 °C): δ = 83.67 (*C*−CN), 111.75, 116.95, 117.52, 119.23, 120.21, 124.20, 125.44, 128.35, 129.13, 129.36, 129.99, 133.68, 134.54, 147.23, 149.14, 150.36, 157.42. MS (EI, 70 eV): *m*/*z* (%) = 564 (36) [M$^+$], 539 (16), 424 (20), 358 (16), 300 (30). IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} (w, Ar-H), 3027 (w), 2193 (m, C≡N), 1642 (s), 1619 (s), 1588 (s), 1465 (s), 1340 (m), 1220 (s), 1149 (m), 1101 (m), 773 (w), 749 (m), 694 (m). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 476.5 nm (4.31), 278.0 (4.54), 258.5 (4.53).

1,3-Bis({(*E*)-7-methyl-[3-(2-tolyl)imino]-2,3-dihydro-1*H*-indol-2-ylidene}cyanomethyl)benzene (7b): Starting with 1,3-bis(cyanomethyl)benzene (0.156 g, 1.00 mmol) and oxalic acid-bis(2-tolylimidoyl)dichloride (0.671 g, 2.20 mmol), **7b** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 1:1) as a deep-red solid (0.323 g, 0.520 mmol, 52%, *E*/*Z* > 98:2). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.12 (s, 6 H, CH$_3$), 2.23 (s, 6 H, CH$_3$), 6.30 (d, *J* = 7.2 Hz, 2 H, Ar), 6.58 (t, *J* = 7.2 Hz, 2 H, Ar), 6.84 (d, *J* = 7.2 Hz, 2 H, Ar), 7.14 (m, 4 H, Ar), 7.25 (d, *J* = 6.8 Hz, 2 H, Ar), 7.34 (d, *J* = 6.8 Hz, 2 H, Ar), 7.73 (s, 3 H, Ar), 8.01 (s, 1 H, Ar), 9.85 (br, 2 H, NH). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 35 °C): δ = 16.28 (CH$_3$), 17.39 (CH$_3$), 84.68 (*C*−CN), 116.74 (CH), 117.52, 119.57 (C), 121.04 (CH), 121.71 (C), 122.61, 124.43 (CH), 125.75 (C), 126.88, 128.59, 129.71, 130.14, 130.72 (CH), 134.71 (C), 134.99 (CH), 147.57, 147.87, 149.11, 157.48 (C). MS (ESI): *m*/*z* (%) = 1884 (24) [3M + Na + 1]$^+$, 1263 (100) [2M + Na]$^+$, 643 (14) [M + Na]$^+$, 622 (22) [M + H]$^+$, 621 (100) [M$^-$], 620 (70) [M − 1]$^-$. IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (w), 3020 (w), 2922 (m), 2850 (w), 2193 (m, C≡N), 1737 (m), 1721 (m), 1712 (m), 1698 (m), 1643 (s), 1619 (s), 1594 (s), 1573 (s), 1454 (m), 1378 (m), 1332 (m), 1218 (s), 1182 (m), 1109 (m), 1034 (w), 850 (w), 794 (w), 749 (m), 719 (w). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 475.5 nm (4.32), 280.0 (4.56), 227.5 (4.56).

1,3-Bis({(*E*)-5-methoxy-[3-(4-methoxyphenyl)imino]-2,3-dihydro-1*H*-indol-2-ylidene}cyanomethyl)benzene (7c): Starting with 1,3-bis(cyanomethyl)benzene (0.469 g, 3.00 mmol) and oxalic acid-bis(4-methoxyphenylimidoyl)dichloride (2.023 g, 6.00 mmol), **7c** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 1:1) as a violet solid (1.92 g, 2.80 mmol, 70%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 3.52 (s, 6 H, OCH$_3$), 3.86 (s, 6 H, OCH$_3$), 6.24 (d, 2 H, Ar), 6.80−7.15 (m, 16 H, Ar, NH), 7.60 (m, 2 H, Ar). ^{13}C NMR (62.9 MHz, [D$_6$]DMSO): δ = 54.87, 55.03 (OCH$_3$), 83.62 (*C*−CN), 110.80, 112.13, 114.59, 118.13, 119.38, 119.60, 119.70, 128.78, 129.38, 130.37, 135.70, 143.01, 143.86, 148.75, 153.82, 157.37, 157.63. MS (CI, 200 eV): *m*/*z* (%) = 685 (2) [M + H]$^+$, 660 (8), 631 (20). IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1} (w, Ar-H), 2998 (w), 2192 (m, C≡N), 1619 (m), 1601 (m), 1501 (s), 1485 (s), 1325 (m), 1219 (m), 1166 (w), 1105 (m), 763 (w), 726 (w). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 509.5 nm (4.13), 316.5 (4.37), 232.0 (4.63).

Tris(indolinylidenemethyl)benzene (12): Starting with 1,3,5-tris-(cyanomethyl)benzene (0.195 g, 1.00 mmol) and oxalic acid-bis-(phenylimidoyl)chloride (0.832 g, 3.00 mmol), **9** was isolated as an orange solid (202 mg, 25%, *E*/*Z* > 98:2). The reaction mixture was stirred for three days at 20 °C. The product was purified by sequential silica gel chromatography (diethyl ether/petroleum ether, 3:1) and Sephadex chromatography (CH$_2$Cl$_2$/MeOH, 3:2). A small amount of impurity could not be separated. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 6.42 (d, *J* = 7.6 Hz, 3 H, Ar), 6.64 (t, *J* = 7.6 Hz, 3 H, Ar), 7.01 (d, *J* = 7.7 Hz, 3 H, Ar), 7.15−7.95 (m, 12 H, Ar, NH), 7.48 (t, *J* = 7.6 Hz, 6 H, Ar), 7.85 (d, *J* = 8.4 Hz, 6 H, Ar). ^{13}C NMR (62.9 MHz, [D$_6$]DMSO): δ = 84.68 (*C*−CN), 111.88 (CH), 117.06 (CN), 117.67, 120.42, 124.47, 124.58, 128.61, 128.66, 129.56 (CH), 135.90, 137.53, 149.03, 150.50, 157.45, 158.54 (C). MS (ESI): *m*/*z* (%) = 807 (100) [M]$^+$. No other signals could be detected. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w, Ar-H), 3028 (w), 2953 (m), 2191 (m, C≡N), 1671 (s), 1644 (s), 1619 (s), 1588 (s), 1483 (s), 1465 (s), 1338 (m), 1220 (s), 1148 (m), 1100 (m), 775 (w), 750 (m), 718 (w), 694 (m). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 481.5 nm (4.05), 263.5 (4.50), 196.0 (4.98).

1,3,5 Tri(cyanomethyl)benzene (11): Sodium cyanide (5.453 g, 111.3 mmol) was dissolved in 150 mL of DMSO at 40 °C. A DMSO solution (50 mL) of 1,3,5-tri(bromomethyl)benzene (12.81 g, 35.89 mmol) was then slowly added during 1.5 h. The solution was stirred for 15 h at 40 °C. The reaction mixture was then poured into 200 mL of ice water and repeatedly extracted with diethyl ether and dichloromethane. The combined organic layers were washed with a saturated solution of brine (2 × 100 mL), dried (MgSO$_4$), filtered and the filtrate was concentrated in vacuo to give **11** as a slight yellow solid (6.127 g, 31.38 mmol, 87%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.80 (s, 6 H, C*H*$_2$CN), 7.30 (s, 3 H, Ar). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 23.21 (CH$_2$), 117.05 (CN), 127.25 (CH, Ar), 132.18 (C, Ar). MS (EI): *m*/*z* (%) = 195 (100) [M]$^+$.

(*Z*,*Z*)-α,α′-Bis[(1*H*-benzimidazol-2-yl)methylene]-1,4-benzenedimethanamine (15): *n*BuLi (16.5 mL, 2.2 equiv., 1.6 M solution in hexane) was added at 0 °C to a THF solution (40 mL) of 2-methylbenzimidazole (1.58 g, 12.0 mmol). After stirring for 60 min at 0 °C, 1,4-dicyanobenzene (6.0 mmol) was added. The colour of the suspension turned yellow. After stirring for 4 h at 20 °C the solution was poured into an aqueous solution of hydrochloric acid (0.1 M, 0 °C). After extraction of the mixture with a 1:1 mixture of THF and diethyl ether (1:1, 3 × 100 ml; 1:5, 3 × 100 mL) the combined organic layers were dried (MgSO$_4$) and filtered. The filtrate was concentrated in vacuo. Addition of diethyl ether to the crude product resulted in formation of a precipitate which was filtered off, washed with diethyl ether and dried in vacuo to give **15** as a yellow solid (2.00 g, 85%). ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 5.42 (s, 2

H, =C*H*−NH$_2$), 6.90−7.30 (m, 8 H, Ar), 7.45 (br, 4 H, NH), 7.75 (s, 4 H, Ar), 10.81 (br, 2 H, NH). ^{13}C NMR (50 MHz, [D$_8$]THF): δ = 83.67 (=CH−NH$_2$), 109.93, 117.98, 121.37, 121.39 (CH, Hetar), 126.73 (CH, Ph), 134.28 (C, Ph), 140.26, 145.45 (C, Hetar), 152.49 (=C−NH$_2$), 155.16 (C-2, Hetar). IR (KBr): $\tilde{\nu}$ = 3399 cm^{-1} (m, br, NH), 3056 (w), 1621 (s), 1581 (m), 1520 (s), 1452 (s), 1402 (m), 1363 (m), 1318 (w), 1274 (s), 1013 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 392 (100) [M]$^+$. $C_{24}H_{20}N_6$ (392.5): calcd. C 73.46, H 5.14, N 21.41; found C 73.08, H 5.52, N 20.96.

General Procedure for One-Pot Reactions with the Dianion of 1,1-Diphenylacetone: A THF solution (10 mL) of 1,1-diphenylacetone (2.62 g, 12.5 mmol) was added to a THF suspension (50 mL) of potassium hydride (0.5 g, 12.5 mmol). Evolution of hydrogen was observed. After stirring for 60 min at 20 °C, *n*BuLi (17.5 mL, 28 mmol, 1.6 M solution in hexane) was added by syringe at 0 °C. After stirring for 8 min, a red suspension was formed. A THF solution (30 mL) of benzonitrile, 2-cyanopyridine (12.5 mmol) or 1,4-dicyanobenzene (6.25 mmol) was added within 10 min at 0 °C. After stirring for 2 h at 20 °C a THF solution (20 mL) of Me$_3$SiCl (30 mmol) was added at 0 °C. After stirring for 12 h at 20 °C the solvent was removed in vacuo and the residue was extracted with three 50 mL portions of hexane. The extracts were filtered through a pad of Celite and the filtrate was concentrated in vacuo. In the case of **19** and **20** the residue was essentially pure. In the case of **21**, the pure product was precipitated by addition of hexane to a diethyl ether solution (2 mL) of the crude product. The precipitate was filtered off and dried in vacuo. The double bond configurations were not established experimentally.

(*Z*,*Z*)-[3,3-Diphenyl-2-(trimethylsilyloxy)-2-propenylidene]-*N*-(trimethylsilyl)benzenemethanamine (19): Starting with 2.62 g of 1,1-diphenylacetone (12.5 mmol), **19** was isolated as a yellow oil (4.56 g, 85%). ^{1}H NMR (200 MHz, CDCl$_3$): δ = −0.20, 0.10 (2 × s, 2 × 9 H, SiMe$_3$), 4.81 (s, 1 H, =CH−), 5.07 (s, 1 H, NH), 7.00−7.40 (m, 15 H, Ph). ^{13}C NMR (50 MHz, CDCl$_3$): δ = 0.70 (SiMe$_3$), 2.34 (SiMe$_3$), 100.18 (=CH−), 125.65 (Ph$_2$C=), 125.9, 126.2, 127.9, 128.1, 128.20, 128.45, 128.70, 131.20, 132.03 (CH, Ph), 141.86, 142.13, 142.61 (C, Ph), 147.76, 148.24 (=C−N, = C−O). $C_{28}H_{35}NOSi_2$ (457.8): calcd. C 73.47, H 7.71, N 3.06; found C 73.64, H 8.06, N 3.41.

(*Z*,*Z*)-[3,3-Diphenyl-2-(trimethylsilyloxy)-2-propenylidene]-*N*-(trimethylsilyl)-[(2-pyridine)methanamine] (20): Starting with 2.62 g of 1,1-diphenylacetone (12.5 mmol), **20** was isolated as a yellow solid (4.24 g, 74%). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.03, 0.12 (s, SiMe$_3$, 9 H), 5.58 (br, 1 H, NH), 5.62 (s, 1 H, =CH−), 7.00−7.50 (m, 12 H, Ar), 8.30−8.50 (m, 2 H, Ar). ^{13}C NMR (50 MHz, CDCl$_3$): δ = −0.55 (SiMe$_3$), 4.55 (SiMe$_3$), 97.45 (=CH−), 124.00 (Ph$_2$C=), 119.30, 122.24, 125.80, 127.50, 127.82, 128.00, 130.50, 131.00, 136.20 (CH, Ar), 145.50 (CH to N, Pyr), 141.03, 142.23 (C, Ph), 143.30 (=C−O), 148.11 (=C−N), 154.50 (C, Pyr).

(*Z*,*Z*)-α,α′-Bis[3,3-diphenyl-2-(trimethylsilyloxy)-2-propenylidene]-*N*,*N*′-bis(trimethylsilyl)-1,4-benzenedimethanamine (21): Starting with 2.62 g of 1,1-diphenylacetone (12.5 mmol), **21** was isolated as a yellow solid (4.18 g, 80%), m.p. 110 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ = −0.08, 0.18 (s, 36 H, SiMe$_3$), 4.90 (s, 2 H, =CH−), 5.09 (br. s, 2 H, NH), 7.20−7.40 (m, 24 H, Ph). ^{13}C NMR (50 MHz, CDCl$_3$): δ = 0.30 (SiMe$_3$), 1.47 (SiMe$_3$), 100.41 (= CH−), 122.91 (Ph$_2$C=), 125.58, 126.07, 127.48, 127.73, 128.01, 130.60, 130.79 (Ph), 141.10, 141.66, 142.13 (C, Ph), 147.18, 147.38 (=C−O, =C−N). IR (KBr): $\tilde{\nu}$ = 3354 cm^{-1} (s), 3054 (s), 2956 (m), 1592 (s), 1505 (s), 1493 (m), 1442 (s), 1382 (m), 1251 (s), 1190 (m), 1073 (m), 977 (s), 845 (s). MS (CI, H$_2$O): *m*/*z* = 837 [M + 1]$^+$, 257, 91. $C_{50}H_{64}N_2O_2Si_4$ (837.4): calcd. C 71.72, H 7.70, N 3.34; found C 71.22, H 8.14, N 3.86.

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[1] For *push-pull* substituted heterocycles and benzenes, see: R. Gompper, H.-U. Wagner, *Angew. Chem.* **1988**, *100*, 1492; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1437.

[2] J. Fabian, H. Nakazumi, M. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197.

[3] For recent examples of indole derived photochromic spirooxazines, see: [3a]V. Malatesta, R. Millini, L. Montanari, *J. Am. Chem. Soc.* **1995**, *117*, 6258. [3b] S. Delbaere, C. Bochu, N. Azaroual, G. Buntinx, G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1499.

[4] F. Effenberger, H. Schlosser, P. Bäuerle, S. Maier, H. Port, H. C. Wolf, *Angew. Chem.* **1988**, *100*, 274; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 281.

[5] [5a]C. Lambert, G. Nöll, *Angew. Chem.* **1998**, *110*, 2239; *Angew. Chem. Int. Ed.* **1998**, *37*, 2107. [5b] M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, P. Batail, *J. Am. Chem. Soc.* **1993**, *115*, 3752.

[6] [6a]R. Breslow, P. Maslak, J. S. Thomaides, *J. Am. Chem. Soc.* **1984**, *106*, 6453. [6b] M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* **1996**, *118*, 10626.

[7] J. J. Wolff, F. Sugler, R. Matschiner, R. Wortmann, *Angew. Chem.* **2000**, *112*, 1494; *Angew. Chem. Int. Ed.* **2000**, *39*, 1436 and cited references.

[8] P. Langer, J. Wuckelt, M. Döring, H. Görls, *J. Org. Chem.* **2000**, *65*, 3603.

[9] For the synthesis of oxalic acid-bis(imidoyl)chlorides, see: D. Lindauer, R. Beckert, M. Döring, P. Fehling, H. Görls, *J. Prakt. Chem.* **1995**, *337*, 143.

[10] R. O. Clinton, S. C. Laskowski, *J. Am. Chem. Soc.* **1948**, *70*, 3135.

[11] [11a]W. Storck, G. Manecke, *Makromol. Chem.* **1975**, *176*, 97.[11b] W. P. Cochrane, P. L. Pauson, T. S. Stevens, *J. Chem. Soc. (C)* **1968**, 630.

[12] M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, P. Batail, *J. Am. Chem. Soc.* **1993**, *115*, 3752.

[13] M. Kanashi, J.-i. Kunizaki, J. Inanaga, M. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3828.

[14] P. Langer, M. Döring, P. R. Schreiner, H. Görls, *Chem. Eur. J.* **2001**, *7*, 2617.

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