Preparation and Characterisation of Iodo-functionalised Azobenzene Derivatives of the Type I–*p*-C_6H_4–N=N–*p*-C_6H_4–X

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A broad range of azobenzene derivates of the general type I–*p*-C_6H_4–N=N–*p*-C_6H_4–X (**1**) have been prepared. In the case of X = Ph (**b**), C≡C–Fc (**e**, Fc = ferrocenyl), OMe (**g**), O*i*-Pr (**i**), and NMe_2 (**m**), these compounds have been characterised by single-crystal X-ray structure analysis. In addition, the closely related 4-dimethylamino-1-(4-iodophenylazo)naphthalene **2** and 8-(4-iodophenylazo)quinoline **3** have also been prepared. Furthermore, the ferrocene derivative Fc–C≡C–*p*-C_6H_4–NH_2 (**4**), which served as a starting material for the synthesis of I–*p*-C_6H_4–N=N–*p*-C_6H_4–*p*-C_6H_4–C≡C–Fc (**1e**), was prepared and structurally characterised by X-ray diffraction.

Key words: Azobenzene, Azo-coupling, Crystal Structure, Ferrocene, Nitroso-Amine Condensation

Introduction

Self-assembled monolayers (SAMs) [1] which contain azobenzene-based tailgroups are of great current interest, since these SAMs can exhibit photoswitchable properties [2], which are due to the photochromic behaviour of azobenzene derivatives [3]. The synthesis of azobenzene derivatives suitable for chemisorption on solid substrates is a prerequisite for the fabrication of such 'smart' surfaces. Gold and silicon have been used most extensively as substrate materials in this context. In the case of gold, reactive sulfur-containing headgroups (thiols, disulfides, thioacetates) are most popular for chemisorption [1b – e]. In the case of hydrogen-terminated silicon surfaces, hydrosilylative chemisorption of terminal alkene or alkyne groups is the standard approach [4], while with hydroxylated silicon surfaces the use of reactive silyl groups, usually $SiCl_3$ or $Si(OR)_3$, is preferred [1a]. The synthesis of azobenzene derivatives containing reactive headgroups suitable for anchoring on gold or silicon is flourishing [2, 5]. We recently reported very promising switchability results for SAMs fabricated by chemisorption of Cl_3Si–*p*-C_6H_4–N=N–Ph on hydroxylated silicon [2m]. Saliently, this system exhibited an exceptionally large reversible water contact angle change upon irradiation. The trichlorosilyl derivative is prepared from 4-iodoazobenzene in a one-pot procedure, which involves metal-halide exchange with *n*-BuLi and subsequent reaction with $SiCl_4$. By applying an optimised protocol, we have almost doubled the yield originally reported [6]. In order to be able to fabricate SAMs with enhanced optically switchable properties such as, for example, the binding and release of metal ions or Lewis acidic target molecules, tailgroups containing a terminal functional group X are essential. Iodo-substituted azobenzene derivatives of the type I–*p*-C_6H_4–N=N–*p*-C_6H_4–X (**1**) are therefore key compounds in this context. We here report on the preparation and characterisation of a wide range of such compounds.

Results and Discussion

The iodo-substituted azobenzene derivatives of type **1** prepared in our study are collected in Scheme 1. The nature of the substituent X varies considerably, ranging from simple hydrocarbyl (X = *t*-Bu, Ph,) to extended rigid-rod type units (X = C≡C–Ph, C≡C–*p*-C_6H_4–C≡C–Ph), including also the redox-active organometallic C≡C–Fc unit. Polar groups relevant to the binding and release of Lewis acidic moieties have also been included, *viz.* OR and NMe_2 [7].

The OR substituted derivatives were obtained in high yields by the alkylation of I–*p*-C_6H_4–N=N–*p*-C_6H_4–OH [8] with the respective alkyl halide RY (Y = Br, I) in DMF in the presence of a base (K_2CO_3/Cs_2CO_3). All other derivatives were pre-

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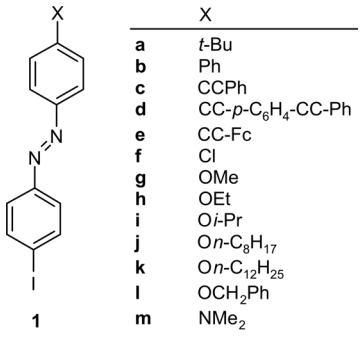

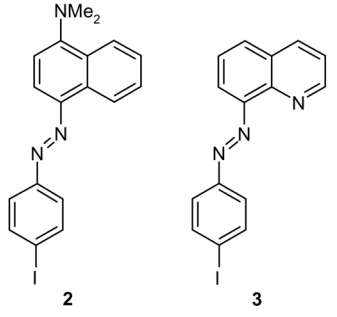

Scheme 1. Azobenzene derivatives and related compounds prepared in this investigation.

pared by the condensation [9] of the readily available 4-iodonitrosobenzene [10] with the respective aniline derivative H_2N–*p*-C_6H_4–X in acetic acid. Isolated yields were generally good to excellent. In addition, the dimethylamino-functionalised 1-(4-iodophenylazo)naphthalene **2** and 8-(4-iodophenylazo)quinoline **3** were also prepared. The heterocyclic compound **3** was obtained from the condensation of 4-iodonitrosobenzene with 8-aminoquinoline. Compound **2** was conveniently synthesised by azo-coupling from 1-(dimethylamino)naphthalene and the diazonium species I–*p*-C_6H_4–N_2^+ (generated *in situ* from the corresponding aniline derivative by diazotisation). Such azo-coupling reactions, although restricted to rather electron-rich, nucleophilic arenes, represent the most frequently used method for the preparation of aromatic azo compounds [11].

Single crystal X-ray structure analyses were performed for the azobenzene derivatives **1b**, **1e**, **1g**, **1i** and **1m**. In addition, the crystal structure of Fc–C≡C–*p*-C_6H_4–NH_2 (**4**), which served as a starting material for the preparation of **1e**, was also determined. The molecular structures of these compounds are shown in Figs. 1 – 6.

Bond parameters are unexceptional in all cases. The N–N double bond lengths are *ca.* 1.26 Å and are indistinguishable within experimental error. This compares well with the value of *ca.* 1.25 Å reported for pristine azobenzene [12]. Essentially the same holds true for the azobenzene nitrogen bond angles, which are *ca.* 114° in each case. The azobenzene cores are almost planar. The amino nitrogen atoms of compounds **1m** and **4** are in an essentially trigonal pla-

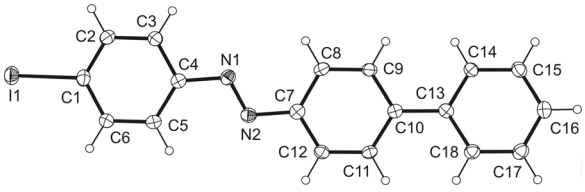

Fig. 1. Molecular structure of compound **1b** in the crystal.

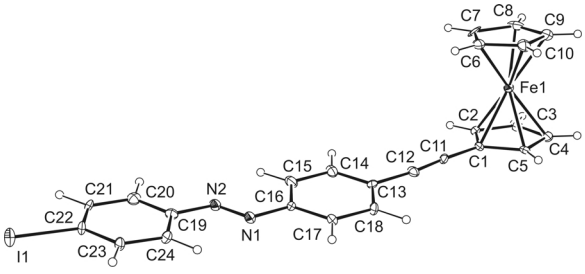

Fig. 2. Molecular structure of compound **1e** in the crystal.

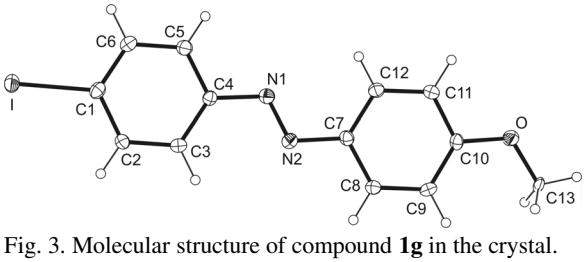

Fig. 3. Molecular structure of compound **1g** in the crystal.

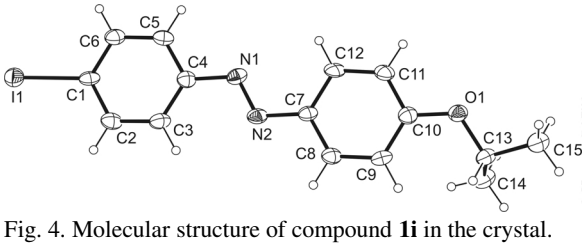

Fig. 4. Molecular structure of compound **1i** in the crystal.

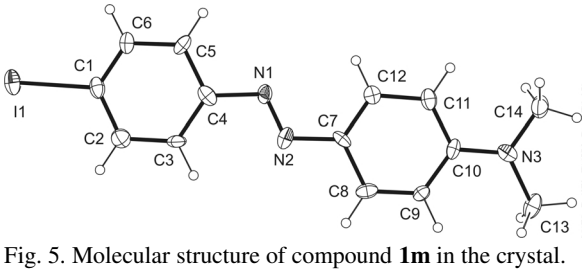

Fig. 5. Molecular structure of compound **1m** in the crystal.

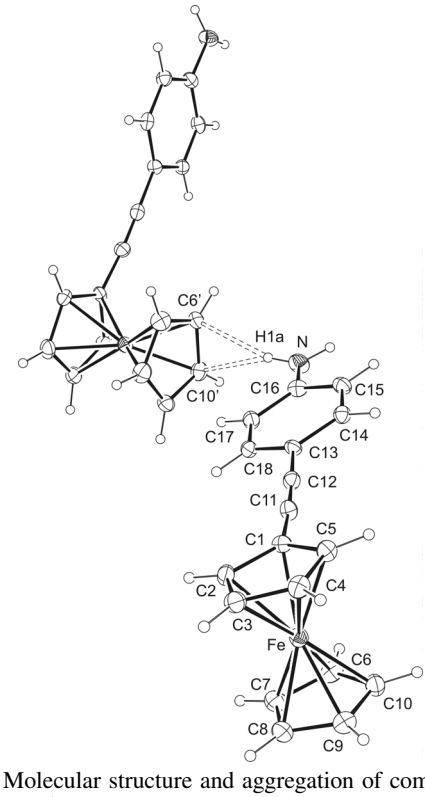

Fig. 6. Molecular structure and aggregation of compound **4** in the crystal.

nar bonding environment, which indicates an efficient conjugation of the *p*-type nitrogen lone pair with the respective aromatic π system. In the case of **4**, one of the NH_2 hydrogen atoms (H1A) exhibits a contact to the two adjacent carbon atoms C6′ and C10′ of a cyclopentadienyl ring of a neighbouring molecule in the crystal. H1A has an almost perpendicular orientation with respect to the C6′–C10′ bond axis of the cyclopentadienyl ring. The corresponding C···H distances are below the sum of the estimated van der Waals radii of 2.9 Å for carbon and hydrogen. These C···H distances are probably systematically overestimated in view of the fact that the experimentally determined N–H bond lengths of 0.88(2) and 0.90(2) Å are shorter than the sum of the covalent radii (1.02 Å) [13]. The closest C···H distance of this type is *ca.* 2.54 Å and occurs with C6′, the corresponding carbon-nitrogen distance is *ca.* 3.63 Å and the NHC angle is *ca.* 165°. The second such interaction, which occurs with C10′, exhibits a C···H distance of *ca.* 2.67 Å, a carbon−nitrogen distance of *ca.* 3.51 Å and an NHC angle of *ca.* 155°. These data are in agreement with the presence of a weak N–H π-hydrogen bond [14]. Such interactions are well documented for organometallic crystals [15].

Experimental Section

The following starting materials were prepared according to, or by slight modification of, published procedures: I–*p*-C_6H_4–NO [10], I–*p*-C_6H_4–N=N–*p*-C_6H_4–OH [16], Fc–C≡C–H [17], Ph–C≡C–*p*-C_6H_4–NH_2 [18], Ph–C≡C–*p*-C_6H_4–C≡C–*p*-C_6H_4–NH_2 [19]. All other starting materials were commercially available.

NMR spectra: Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ^{1}H. Mass spectra: Thermoquest Finnigan LCQ Deca mass spectrometer and Bruker Daltonics micrOTOF mass spectrometer (HRMS). Melting points (uncorrected): Stuart Electric SMP 3 melting point apparatus. Elemental analyses: microanalytical laboratory of the University of Halle, Halle (Germany). X-Ray crystal structure analyses: For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using MoK_α radiation (λ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-RED [20]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by Direct Methods (SHELXS-97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97) [21]. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. Pertinent crystallographic data are collected in Table 1.

CCDC 705442 – 705447 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the preparation of the azobenzene derivatives of type I–p-C_6H_4–N=N–p-C_6H_4–X by condensation of 4-iodonitrosobenzene with H_2N–p-C_6H_4–X

The aniline derivative (1.0 mmol) and 4-iodonitrosobenzene (233 mg, 1.0 mmol) were dissolved in a 1 : 1 mixture of acetic acid and ethyl acetate (*ca.* 5 mL; in the case of less soluble aniline derivatives: a minimal amount). The reaction mixture was stirred at 40 °C. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction (*ca.* 4 – 6 h), water (*ca.* 20 mL) was added and the mixture subsequently extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with water (20 mL)

Table 1. Crystal structure data for **1b**, **1e**, **1g**, **1i**, **1m** and **4**.

Compound	**1b**	**1e**	**1g**	**1i**	**1m**	**4**
Empirical formula	$C_{18}H_{13}IN_2$	$C_{24}H_{17}FeIN_2$	$C_{13}H_{11}IN_2O$	$C_{15}H_{15}IN_2O$	$C_{14}H_{14}IN_3$	$C_{18}H_{15}Fe_1N_1$
Formula weight	384.20	516.15	338.14	366.19	351.18	301.16
Temperature, K	153(2)	133(2)	153(2)	153(2)	153(2)	153(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$Pna2_1$	$P2_1/c$	$Pca2_1$	$P2_1/c$	$P2_1$	$Pna2_1$
Lattice parameters						
a, Å	6.0270(4)	5.9809(5)	6.1320(5)	5.1734(9)	10.7154(10)	10.4844(15)
b, Å	7.5646(8)	31.005(3)	7.1513(6)	9.5706(12)	21.1749(15)	22.066(2)
c, Å	33.773(4)	10.6385(11)	27.897(3)	29.529(6)	6.1548(6)	5.8689(6)
β, deg	90	94.668(8)	90	93.078(15)	102.941(8)	90
Cell volume, Å^3	1482.7(2)	1966.2(3)	1223.34(19)	1459.9(4)	1361.0(2)	1357.8(3)
Z	4	4	4	4	4	4
$d_{calcd.}$, g cm^{-3}	1.721	1.744	1.836	1.666	1.714	1.473
μ, mm^{-1}	2.154	2.349	2.602	2.187	2.339	1.098
$F(000)$	752	1016	656	720	688	624
θ range, deg	2.41 to 25.00	2.03 to 25.00	1.46 to 25.00	1.38 to 25.00	1.92 to 25.00	1.85 to 25.00
Index ranges	$-7 \rightarrow h \rightarrow 6$	$-7 \rightarrow h \rightarrow 6$	$-6 \rightarrow h \rightarrow 7$	$-5 \rightarrow h \rightarrow 6$	$-12 \rightarrow h \rightarrow 12$	$-12 \rightarrow h \rightarrow 12$
	$-8 \rightarrow k \rightarrow 8$	$-36 \rightarrow k \rightarrow 36$	$-8 \rightarrow k \rightarrow 8$	$-11 \rightarrow k \rightarrow 10$	$-24 \rightarrow k \rightarrow 25$	$-26 \rightarrow k \rightarrow 26$
	$-40 \rightarrow l \rightarrow 40$	$-12 \rightarrow l \rightarrow 12$	$-32 \rightarrow l \rightarrow 32$	$-34 \rightarrow l \rightarrow 34$	$-7 \rightarrow l \rightarrow 7$	$-6 \rightarrow l \rightarrow 6$
Refls. collected	7565	12035	7150	8587	8851	8453
Independent refls.	2528	3443	2152	2530	2465	2338
	[$R_{int} = 0.0354$]	[$R_{int} = 0.0774$]	[$R_{int} = 0.0407$]	[$R_{int} = 0.1279$]	[$R_{int} = 0.0378$]	[$R_{int} = 0.1184$]
Refls. observed	2333	2452	2058	1861	2364	1638
T_{min} / T_{max}	0.65 / 0.78	0.76 / 0.93	0.35 / 0.95	0.49 / 0.90	0.49 / 0.79	0.73 / 0.98
Data / restraints / parameters	2528 / 1 / 190	3443 / 0 / 253	2152 / 1 / 155	2530 / 0 / 174	2465 / 1 / 329	2338 / 3 / 188
GOF on F^2	1.048	0.826	1.040	1.144	0.949	0.859
$R1/wR2$ [$I \geq 2\sigma(I)$]	0.0237/0.0628	0.0294/0.0507	0.0247/0.0638	0.0748/0.1631	0.0199/0.0464	0.0444/0.0881
$R1/wR2$ (all data)	0.0252/0.0631	0.0519/0.0540	0.0258/0.0642	0.0980/0.1738	0.0214/0.0468	0.0677/0.0937
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.38/−0.53	0.62/−0.73	0.36/−0.41	0.53/−1.35	0.43/−0.67	0.39/−0.29

and dried with anhydrous sodium sulfate. Volatile components were removed *in vacuo*. The crude product was purified by recrystallisation or column chromatography (silica gel).

1a (X = *t*-Bu): eluent *n*-hexane-toluene 1 : 1, yield 350 mg (96 %), m. p. 124 – 125 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 9 H, *t*-Bu), 7.54 (m, 2 H, arom. CH), 7.64 (m, 2 H, arom. CH), 7.86 (m, 4 H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 31.3, 35.1, 97.2, 122.7, 124.4, 126.1, 138.3, 150.4, 152.1, 155.0. – HRMS (ESI): *m/z* = 365.0518 (calcd. 365.0509 for $C_{16}H_{18}IN_2^+$, $[M+H]^+$).

1b (X = Ph): eluent toluene, yield 374 mg (97 %), m. p. 211 – 213 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.40 (m, 1 H), 7.48 (m, 2 H), 7.68 (m, 4 H), 7.76 (m, 2 H), 7.88 (m, 2 H), 8.00 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 97.6, 123.5, 124.5, 127.2, 127.8, 128.0, 128.9, 138.4, 140.1, 144.1, 151.6, 152.0. – Anal. for $C_{18}H_{13}N_2I$ (384.2): calcd. C 56.27, H 3.41, N 7.29; found C 56.15, H 3.76, N 7.11.

1c (X = C≡C–Ph): recrystallisation from THF by layering with *n*-hexane, yield 252 mg (62 %), m. p. 209 – 210 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.37 (m, 3 H), 7.57 (m, 2 H), 7.67 (m, 4 H), 7.88 (m, 2 H), 7.92 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 89.1, 92.2, 98.0, 122.9, 123.1, 124.5, 126.4, 128.4, 128.7, 131.7, 132.4, 138.4, 151.6, 151.9. – Anal. for $C_{20}H_{13}N_2I$ (408.2): calcd. C 58.84, H 3.21, N 6.86; found C 58.81, H 3.29, N 6.89.

1d (X = C≡C–*p*-C_6H_4–C≡C–Ph): recrystallisation from hot toluene, yield 391 mg (77 %), m. p. 287 – 288 °C. – MS (APCI): *m/z* = 509.13 (100 %, $[M+H]^+$). – Anal. for $C_{28}H_{17}N_2I$ (508.4): calcd. C 66.16, H 3.37, N 5.51; found C 66.61, H 3.49; N 5.52.

1e (X = C≡C–Fc): eluent *n*-hexane-toluene 1 : 1, recrystallisation from trichloromethane, yield 165 mg (32 %), dec. > *ca.* 200 °C. – ^{1}H NMR ($CDCl_3$): δ = 4.27 (s, 5 H, C_5H_5), 4.29 (m, 2 H, C_5H_4), 4.54 (m, 2 H, C_5H_4), 7.61 (m, 2 H, arene CH), 7.66 (m, 2 H, arene CH), 7.88 (m, 4 H, arene CH). – ^{13}C NMR ($CDCl_3$): δ = 64.7, 69.2, 70.1, 71.6, 85.7, 91.9, 97.8, 123.1, 123.9, 124.5, 132.1, 138.4, 151.1, 152.0. – HRMS (ESI): *m/z* = 515.9767 (calcd. 515.9780 for $C_{24}H_{18}FeIN_2^+$, $[M+H]^+$).

1f (X = Cl): eluent toluene, yield 311 mg (91 %), m. p. 182 – 183 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.49 (m, 2 H), 7.64 (m, 2 H), 7.87 (m, 4 H).). – ^{13}C NMR ($CDCl_3$): δ = 98.0, 124.2, 124.5, 129.4, 137.3, 138.4, 150.8, 151.7. – Anal. for $C_{12}H_8N_2I$ (342.6): calcd. C 42.07, H 2.35, N 8.18; found C 42.11, H 2.43, N 8.31.

General procedure for the preparation of the alkoxy-substituted azobenzene derivatives of type I–p-C_6H_4–N=N–p-C_6H_4–OR by alkylation of 4-hydroxyazobenzene with RY

4-Hydroxyazobenzene (324 mg, 1.0 mmol) was added to a stirred suspension of finely ground K_2CO_3 (276 mg, 2.0 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in DMF (5 mL). After 10 min the alkyl halide (2.0 mmol) was added. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction (*ca*. 3 – 6 h), water (*ca*. 20 mL) was added and the mixture subsequently extracted with ethyl acetate (5 × 10 mL). The combined organic layers were washed with water (2 × 20 mL) and dried with anhydrous sodium sulfate. Volatile components were removed *in vacuo*. The crude product was purified by column chromatography (*n*-hexane, silica gel).

1g (R = Me): Y = I, yield 324 mg (96 %), m. p. 179 – 181 °(175 °C) [7]. – ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3 H, Me), 7.01 ("d", 2 H, apparent J = 8.9 Hz, CH), 7.61 ("d", 2 H, apparent J = 8.5 Hz, CH), 7.84 ("d", 2 H, apparent J = 8.5 Hz, CH), 7.92 ("d", 2 H, apparent J = 8.9 Hz, CH). – ^{13}C NMR ($CDCl_3$): δ = 55.6, 96.7, 114.3, 124.2, 124.9, 138.2, 146.8, 152.0, 162.3. – Anal. for $C_{13}H_{11}N_2IO$ (338.1): calcd. C 46.18, H 3.28, N 8.28; found C 46.24, H 3.37, N 8.39.

1h (R = Et): Y = I, yield 331 mg (94 %), m. p. 156 – 158 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.46 (t, 3 H, J = 7.0 Hz, Me), 4.12 (q, 2 H, J = 7.0 Hz, CH_2), 7.00 ("d", 2 H, apparent J = 9.0 Hz, CH), 7.61 ("d", 2 H, apparent J = 8.6 Hz, CH), 7.83 ("d", 2 H, apparent J = 8.6 Hz, CH), 7.90 ("d", 2 H, apparent J = 9.0 Hz, CH). – ^{13}C NMR ($CDCl_3$): δ = 14.8, 63.9, 96.6, 114.7, 124.2, 124.9, 138.2, 146.7, 152.1, 161.8. – Anal. for $C_{14}H_{13}N_2IO$ (352.2): calcd. C 47.75, H 3.72, N 7.95; found C 47.46, H 3.79, N 7.88.

1i (R = *i*-Pr): Y = Br, yield 322 mg (88 %), m. p. 109 – 110 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.39 (d, 6 H, J = 6.1 Hz, Me), 4.66 (sept, 1 H, J = 6.1 Hz, C*H*Me_2), 6.98 ("d", 2 H, apparent J = 9.0 Hz, CH), 7.61 ("d", 2 H, apparent J = 8.6 Hz, CH), 7.83 ("d", 2 H, apparent J = 8.6 Hz, CH), 7.89 ("d", 2 H, apparent J = 9.0 Hz, CH). – ^{13}C NMR ($CDCl_3$): δ = 22.0, 70.2, 96.6, 115.8, 124.2, 124.9, 138.2, 146.5, 152.1, 160.8. – Anal. for $C_{15}H_{15}N_2IO$ (366.2): calcd. C 49.20, H 4.13, N 7.65; found C 49.18, H 4.14, N 7.72.

1j (R = *n*-C_8H_{17}): Y = Br, yield 314 mg (77 %), m. p. 111 – 113 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, 3 H, J = 7.0 Hz, Me), 1.33 (br. s, 8 H, CH_2), 1.48 (m, 2 H, CH_2), 1.82 (m, 2 H, CH_2), 4.03 (t, 2 H, J = 6.6 Hz, OCH_2), 6.99 (m, 2 H, CH), 7.61 (m, 2 H, CH), 7.83 (m, 2 H, CH), 7.90 (m, 2 H, CH). – ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 26.0, 29.1, 29.2, 29.4, 31.8, 68.4, 96.6, 114.7, 124.2, 124.9, 138.2, 146.6, 152.0, 162.0. – Anal. for $C_{20}H_{25}N_2IO$ (436.3): calcd. C 55.05, H 5.78, N 6.42; found C 55.05, H 5.73, N 6.45.

1k (R = *n*-$C_{12}H_{25}$): Y = Br, yield 340 mg (69 %), m. p. 108 – 110 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3 H, J = 7.2 Hz, Me), 1.30 (br. m, 16 H, CH_2), 1.46 (m, 2 H, CH_2), 1.82 (m, 2 H, CH_2), 4.05 (t, 2 H, J = 6.4 Hz, OCH_2), 7.00 ("d", 2 H, apparent J = 9.0 Hz, CH), 7.61 ("d", 2 H, apparent J = 8.7 Hz, CH), 7.83 ("d", 2 H, apparent J = 8.7 Hz, CH), 7.90 ("d", 2 H, apparent J = 9.0 Hz, CH). – ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.5, 29.6, 29.65, 29.7, 31.9, 68.4, 96.6, 114.7, 124.2, 124.9, 138.2, 146.6, 152.1, 162.0. – Anal. for $C_{24}H_{33}N_2IO$ (492.4): calcd. C 58.54, H 6.75, N 5.69; found C 58.58, H 6.74, N 5.61.

1l (R = CH_2Ph): Y = Cl, yield 393 mg (95 %), m. p. 168 – 170 °C. – ^{1}H NMR ($CDCl_3$): δ = 5.16 (s, 2 H, CH_2), 7.09 (m, 2 H, CH), 7.36 (m, 1 H, CH), 7.44 (m, 4 H, CH), 7.62 (m, 2 H, CH), 7.84 (m, 2 H, CH), 7.92 (m, 2 H, CH). – ^{13}C NMR ($CDCl_3$): δ = 70.3, 96.7, 115.2, 124.2, 124.9, 127.5, 128.2, 128.7, 136.3, 138.2, 146.9, 152.0, 161.5. – Anal. for $C_{19}H_{15}N_2IO$ (414.2): calcd. C 55.09, H 3.65, N 6.76; found C 55.06, H 3.66, N 6.77.

*Preparation of **1m** (X = NMe_2)*

4-Iodoaniline (2.20 g, 10.0 mmol) was dissolved in warm 3.5 M hydrochloric acid (20 mL). The solution was cooled rapidly to 0 °C to precipitate the anilinium hydrochloride as a microcrystalline solid. One drop of a concentrated aqueous solution of $NaHSO_3$ was added. An ice-cold solution of $NaNO_2$ (0.69 g, 10.0 mmol) in water (10 mL) was added dropwise to the stirred suspension. After 15 min the resulting yellow solution of the diazonium species was added dropwise to a stirred solution of *N*,*N*-dimethylaniline (1.21 g, 10.0 mmol) in 1 M hydrochloric acid (11 mL). The mixture was stirred for 30 min. The reaction temperature was kept between 0 and 5 °C during the whole procedure. A saturated aqueous sodium carbonate solution was added until CO_2 evolution stopped. Brine (50 mL) was added and the brown solid isolated by filtration. The crude product was purified by column chromatography (trichloromethane, silica gel), affording the product as orange crystals.

Yield 2.55 g (73 %), m. p. 159 – 160 °C (162 °C) [7]. – ^{1}H NMR ($CDCl_3$): δ = 3.09 (s, 6 H, Me), 6.75 (m, 2 H, CH), 7.58 (m, 2 H, CH), 7.80 (m, 2 H, CH), 7.87 (m, 2 H, CH). – ^{13}C NMR ($CDCl_3$): δ = 40.3, 95.2, 11.4, 123.9, 125.2, 138.0, 143.4, 152.5, 152.6. – MS (ACPI): m/z = 352.13 (100 %, $[M+H]^+$).

*Preparation of **2***

4-Iodoaniline (1.10 g, 5.0 mmol) was diazotised in the way described for the preparation of **1m**. The ice-cold yellow solution of the diazonium species was added dropwise to a stirred solution of 1-*N*,*N*-dimethylaminonaphthalene (862 mg, 5.0 mmol) in ethanol-water 9 : 1 (10 mL) at 30 °C. Sodium acetate (1.00 g, 12.2 mmol) was added after 5 min.

The mixture was cooled to 0 °C. The dark precipitate was filtered off and dissolved in dichloromethane (350 mL). The solution was extracted with a saturated aqueous solution of $NaHCO_3$ (2 × 100 mL) and subsequently dried with sodium sulfate. Volatile components were removed *in vacuo*. The crude product was purified by column chromatography (silica gel, *n*-hexane-THF 95 : 5), affording a dark red, viscous oil, which slowly solidified upon prolonged standing at 4 °C.

Yield 1.65 g (82 %), m. p. 79 – 80 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.03 (s, 6 H, Me), 7.08 (d, 1 H, J = 8.4 Hz, CH), 7.61 (m, 1 H, CH), 7.68 (m, 1 H, CH), 7.77 (m, 2 H, CH), 7.89 (m, 2 H, CH), 7.92 (d, 1 H, J = 8.4 Hz), 8.27 (m, 1 H, CH), 9.04 (m, 1 H, CH). – ^{13}C NMR ($CDCl_3$): δ = 44.8, 96.5, 112.6, 113.0, 123.7, 124.4, 124.5, 125.3, 126.7, 128.0, 133.1, 138.1, 142.4, 152.6, 154.6. – Anal. for $C_{18}H_{16}N_3I$ (401.2): calcd. C 53.88, H 4.02, N 10.47; found C 54.08, H 4.09, N 10.47.

Preparation of ***3***

8-Aminoquinoline (432 mg, 3.0 mmol) was added to a stirred solution of 4-iodonitrosobenzene (696 mg, 3.0 mmol) in acetic acid (30 mL). After 24 h the solution was poured on ice (200 g). The mixture was allowed to warm to r. t. and was subsequently extracted with dichloromethane (3 × 50 mL). The combined extracts were dried with sodium sulfate. Volatile components were removed *in vacuo*, affording the product as a brown, microcrystalline solid.

Yield 972 mg (90 %), m. p. 209 °C. – ^{1}H NMR ($CDCl_3$): δ = 6.94 (m, 1 H), 7.16 (d, 1 H, J = 1.6 Hz), 7.33 (d, 1 H, J = 1.6 Hz), 7.37 (m, 1 H), 7.84 (m, 1 H), 7.92 (m, 1 H), 8.02 (m, 1 H), 8.77 (m, 1 H), 8.08 (m, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 98.7, 110.2, 116.0, 121.3, 123.9, 125.0, 127.2, 127.4, 128.8, 136.2, 137.9, 138.0, 138.1, 143.8, 147.3. – HRMS (ESI): m/z = 359.9998 (calcd. 359.9992 for $C_{15}H_{11}N_3I^+$, $[M+H]^+$).

Preparation of ***4***

CuI (6 mg, 0.03 mmol) and $[PdCl_2(PPh_3)_2]$ (21 mg, 0.03 mmol) were added to a stirred solution of ethynylferrocene (525 mg, 2.5 mmol) and 4-iodoaniline (548 mg, 2.5 mmol) in diisopropylamine (25 mL). After 20 h volatile components were removed *in vacuo*. The residue was taken up in toulene-*n*-hexane 3 : 1 (20 mL) and subjected to column chromatography (silica gel), which afforded the product as a red, microcrystalline solid.

Yield 498 mg (66 %), dec. > *ca.* 188 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.77 (br. s, 2 H, NH_2), 4.20 ("t", 2 H, apparent J = 1.8 Hz, C_5H_4), 4.23 (s, 5 H, C_5H_5), 4.46 ("t", 2 H, apparent J = 1.8 Hz, C_5H_4), 6.62 (m, 2 H, arene CH), 7.30 (m, 2 H, arene CH). – ^{13}C NMR ($CDCl_3$): δ = 66.1, 68.5, 69.9, 71.2, 85.5, 86.1, 113.4, 114.7, 132.7, 146.1.

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