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Synthesis of Isoindoles by One-Electron Reductions of Dibenzo[1,4]diazocines

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A synthetic protocol to isoindoles is reported through one-electron reductions of dibenzo[1,4]diazocines. The utility of the approach has been demonstrated through the synthesis of six novel isoindole derivatives. Photophysical measurements revealed emissions between 440 and 460 nm. A reaction mechanism, supported by experimental results and quantum chemical calculations, is postulated.

Introduction

Isoindoles have been known since 1951 when Wittig et al. isolated the derivative *N*-methylisoindole.[1] The parent compound, however, was not isolated until 1972 due to its instability at room temperature.[2] Since then, the chemistry of isoindoles has expanded rapidly.[3] Derivatives of isoindole have applications in medicinal chemistry,[3b] namely as potential antitumor agents due to their antiproliferative activity,[4] and in materials science, due to their luminescent properties.[3b,5] In addition, the oxidized and reduced isoindole skeletons are found in many natural products.[6] Isoindoles are prone to oxidation due to their *o*-quinoid structure, and direct functionalization is generally only possible through electrophilic aromatic substitution,[3a] although some cases of functionalization have been achieved through nucleophilic substitution reactions.[7] Therefore synthetic methods are required to access differently substituted isoindoles from stable starting materials. Existing methods[3] include cycloaddition reactions, oxidative processes starting from isoindolines,[5b,8] reductive transformations of phthalimides, and condensation reactions of diketones with primary amines.

In this paper we describe a new synthetic pathway to isoindole derivatives **1** through one-electron reductions of dibenzo[1,4]diazocines **2** (Figure 1). The transformation, starting from stable and easily accessible diazocines **2**, yields aniline-substituted isoindoles **1** in good to excellent yields.

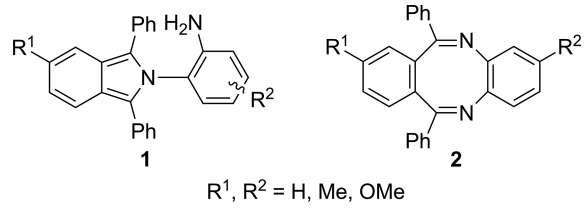
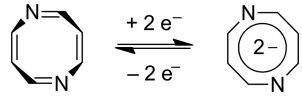


Figure 1. Isoindole derivatives **1** accessible through one-electron reductions of dibenzo[1,4]diazocines **2**.

Results and Discussion

We discovered this one-electron reaction during our investigations of organic redox-active polymers. It has been postulated that the diazocine core should show reversible reduction behavior due to the formation of a planar, aromatic dianion with 10π electrons upon two-electron reduction (Scheme 1),[9] making it a potential side-group for redox-active polymers.



Scheme 1. Predicted boat-to-planar conformational change of [1,5]diazocine through two-electron reduction.

Based on this prediction, dibenzo[1,5]diazocine was incorporated as a redox-active side-group into an aliphatic polymer (**P1**; Scheme 2). The synthesis of **P1** started from the brominated derivative **3**.[10] Reaction with 1 equiv. of *n*BuLi followed by quenching with MeOH led to the monobromo derivative **30**, which was subjected to Suzuki–Miyaura coupling with pinacol vinylboronate leading to **4**. Free-radical polymerization of **4** gave **P1** (M_w = 2.5 × 10^5 a.u., M_w/M_n = 2.05).[11]

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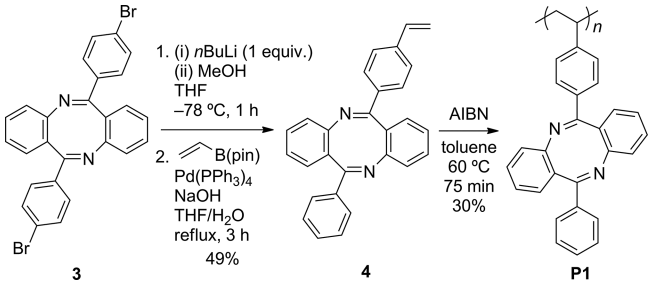
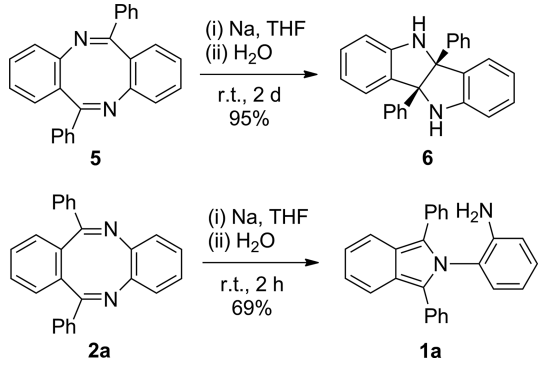


Scheme 2. Synthesis of **P1** as a potential redox-active polymer.

The cyclic voltammogram (CV) of **P1** in solution, however, showed irreversible redox processes, that is, two irreversible reductions at –2.5 and –3.1 V (vs. Fc/Fc^+, see Figure S2 in the Supporting Information). To gain a clearer picture of the redox processes that occur in **P1**, model compound **5** (Scheme 3), which was isolated as a byproduct in the synthesis of **4**, was studied by CV. Compound **5** shows a strong and electrochemically irreversible reduction wave at –2.5 V (vs. Fc/Fc^+; Figure 2). Similar irreversible behavior was observed by Koch and Dessy,[12] who described the formation of the tetrahydroindoloindole **6** (Scheme 3) from a transannular ring closure upon preparative-scale electrolysis of **5**. Eisch et al. recently demonstrated a chemical reduction of **5** to give **6** by using sodium metal.[13] Other reducing conditions, such as zinc/acetic acid or platinum/dihydrogen, can also induce transannular ring closure to **6**.[14]



Scheme 3. Products of the sodium reduction of dibenzo[1,5]diazocine **5**[13] and dibenzo[1,4]diazocine **2a**.

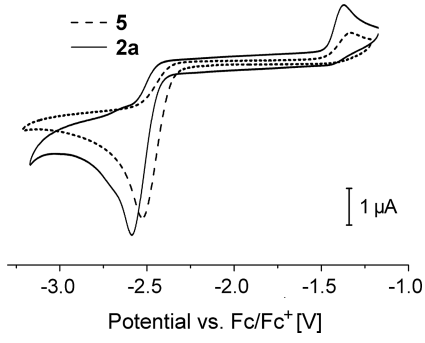


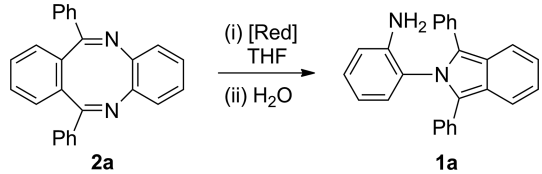
Figure 2. CVs of **5** and **2a** in THF (glassy carbon electrode, 1 mM solutions with 0.1 M nBu_4PF_6, scan rate = 0.2 V/s).

Due to the irreversibility of the redox processes of **5**, we turned our attention to the 1,4-derivative **2a** (for its synthesis, see Scheme 4). As shown in the CV in Figure 2, however, the electrochemical behavior of **2a** is similar to that of **5**, displaying one irreversible reduction wave at –2.6 V (vs. Fc/Fc^+).

Upon reduction of **2a** using sodium metal, in analogy to Eisch et al.,[13a] isoindole **1a** was isolated as the only product in good yield as an air-sensitive, yellow, fluorescent compound (Scheme 3).[15] Ollièro et al. reported the formation of **1a** through the reaction of **2a** with diborane, however, no yields were given for this transformation.[16] Transannular ring closure also occurred upon sodium reduction of the isomeric 6,7-diphenyldibenzo[*e*,*g*][1,4]diazocine to give a carbazole derivative.[17]

Considering the significance of isoindoles in medicinal chemistry as well as in materials science,[3] the conditions for the reduction of **2a** to **1a** were optimized (Table 1). All of the one-electron reduction agents tested (lithium naphthalenide, sodium naphthalenide, and magnesium anthracene[18]) yielded isoindole **1a** in good to excellent yields within 10 min. The best yield of **1a** (96%, Table 1, entry 4) was obtained by using an excess (8 equiv.) of sodium naphthalenide.

Table 1. Optimization of the reaction conditions for the one-electron reduction of dibenzo[1,4]diazocine **2a** to isoindole **1a**.

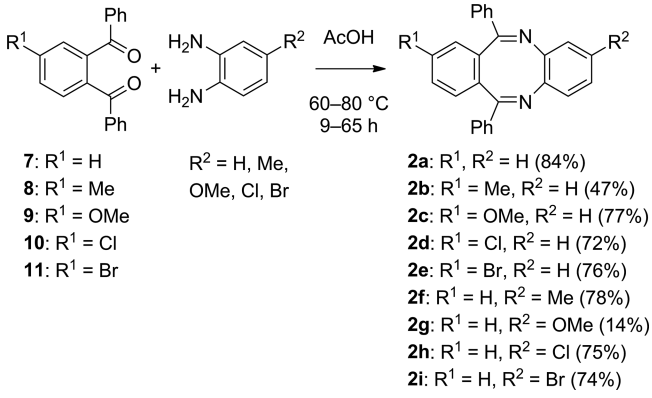


Entry	[Red]	*T* [°C]	Time [min]	Yield [%][a]
1	LiNaph[b] (8 equiv.)	40[e]	10	77
2	NaNaph[c] (2 equiv.)	40[e]	10	54
3	NaNaph[c] (4 equiv.)	r.t.[e]	10	77
4	NaNaph[c] (8 equiv.)	r.t.[e]	10	96
5	$[MgAnth(thf)_3]$[d] (4 equiv.)	r.t.[e]	10	85
6	Mg (8 equiv.), anthracene (10 mol-%), EtBr (10 mol-%)	70	30	<10

[a] Isolated yields. [b] Lithium naphthalenide. [c] Sodium naphthalenide. [d] Magnesium anthracene. [e] Ultrasound.

Substituted dibenzo[1,4]diazocines **2** were then synthesized to test the scope of the reduction to the corresponding isoindoles **1**. Me, OMe, Cl, and Br were chosen as substituents on either side of the diazocine core. The derivatives **2b**–**i** were synthesized by condensation of the corresponding 1,2-phenylenediamines with the respective diketones following a modified procedure of Ollièro and Solladié[19] (Scheme 4).

The substituted diketones **7**–**11** were accessed either through the oxidation of the corresponding isobenzofurans (diketones **7**, **8**, and **11** from **12**–**14**), nucleophilic replacement of carbothioates (diketone **10**), or oxidation of a

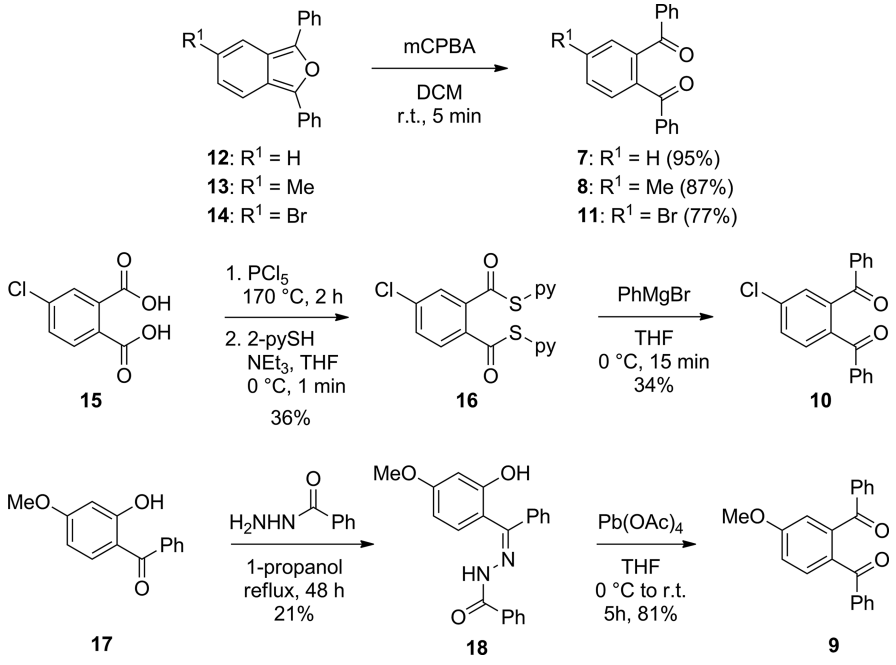


Scheme 4. Synthesis of dibenzo[1,4]diazocines **2a**–**i**.

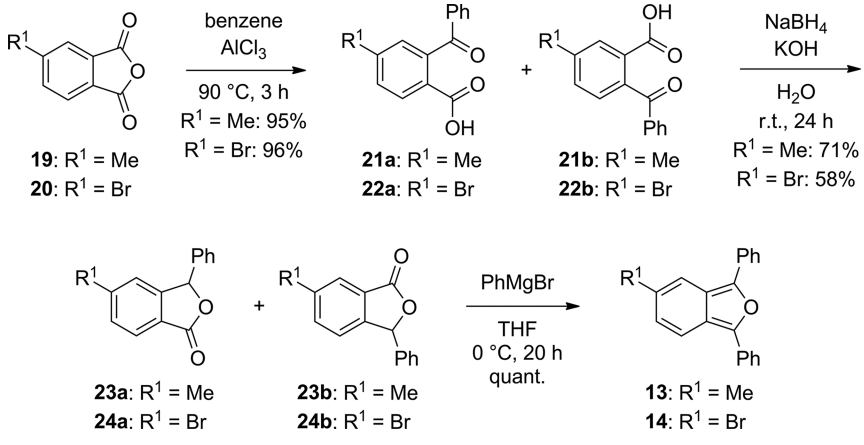
benzohydrazide (diketone **9**, Scheme 5). The substituted isobenzofurans **13** and **14** were synthesized as shown in Scheme 6.

Dibenzo[1,4]diazocines **2b**–**i** were then submitted to the previously optimized reduction conditions (Table 2). In those cases in which the substituent is on the diketone side of the dibenzodiazocine core (R^1), only one isomeric product can be formed (entries 2 and 3, products **1b**,**c**); however, if the diamine side is substituted (R^2), two regioisomeric products are possible (entries 6 and 7; products **1f**,**g** and **1j**,**k**).

By means of this simple protocol, six as yet unknown isoindole derivatives were synthesized with a methyl or methoxy substituent on the isoindole core (**1b**,**c**) or on the attached aniline moiety (**1f**,**g** and **1j**,**k**). The yields of the transformations were good in all cases; however, when R^2 was varied, one of the regioisomeric products (**1f**,**g**) was clearly preferred over the other (**1j**,**k**). This regioselectivity can be rationalized through the proposed mechanism (see below and Scheme 7). Halogen substituents did not withstand the reduction conditions and led to the unsubstituted

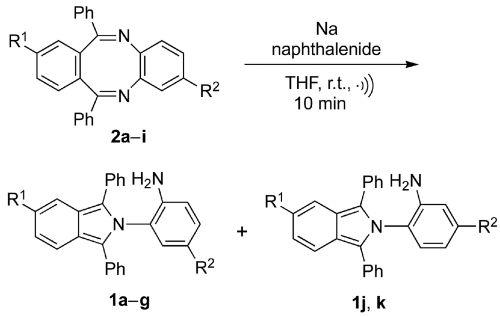


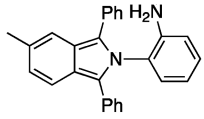
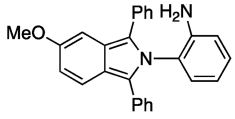
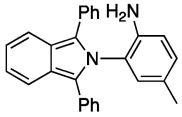
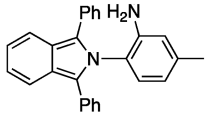
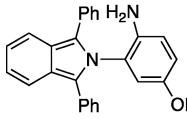
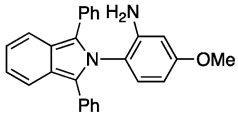
Scheme 5. Synthesis of diketones **7**–**11**.



Scheme 6. Synthesis of isobenzofurans **13** and **14**.

Table 2. Sodium naphthalenide reduction of dibenzo[1,4]diazocines **2a**–**i** to isoindoles **1a**–**k**.



Entry	R^1	R^2	Starting material	Product(s) (% yield)
1	H	H	**2a**	**1a** (96)
2	Me	H	**2b**	 **1b** (74)
3	OMe	H	**2c**	 **1c** (56)
4	Cl	H	**2d**	**1a**[a] (46)
5	Br	H	**2e**	**1a**[a] (70)
6	H	Me	**2f**	 **1f** (60)[b];  **1j** (17)[b,c]
7	H	OMe	**2g**	 **1g** (60)[b,c];  **1k** (2)[b,c]
8	H	Cl	**2h**	**1a**[a] (90)
9	H	Br	**2i**	**1a**[a] (71)

[a] Dehalogenation occurred. [b] Ratio determined by ^{1}H NMR spectroscopy. [c] Compound isolated as a mixture with the other isomer.

derivative **1a** (entries 4, 5, 8, and 9 in Table 2). When the bromo-substituted **2i** was reduced by using 1.9 equiv. of sodium naphthalenide, **2a** was isolated as the main product, which demonstrates that dehalogenation is faster than isoindole formation.

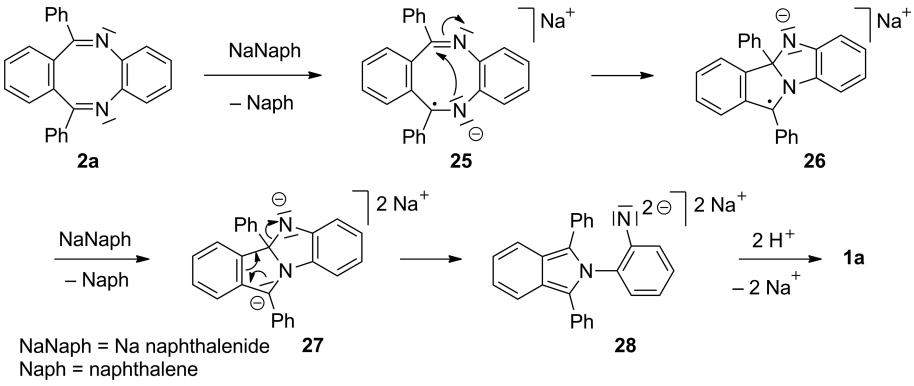
Several experiments were performed to elucidate the reaction mechanism for isoindole formation. A plausible mechanism is postulated in Scheme 7. An initial electron transfer to dibenzo[1,4]diazocine **2a** leads to radical anion **25**, which then undergoes transannular ring closure to **26** through attack of the negatively charged nitrogen center on the imine carbon. Transfer of a second electron to **26** leads to the tetracyclic dianion **27**, which can rearrange to form the isoindole core in **28**. Hydrolysis of **28** furnishes **1a**.

A one-electron transfer process is supported by two facts: When the reduction of **2a** was performed with 1 equiv. of sodium naphthalenide, no isoindole was formed, instead 99% of **2a** was recovered. This observation is in line with an initial quantitative formation of radical anion **25** by a one-electron transfer mechanism. Secondly, the observed regioselectivities in the reductions of **2f** and **2g** can be explained by assuming the corresponding derivatives of **25** as intermediates. The isomer in which the negatively charged nitrogen is located at the *meta* position with respect to the methyl or methoxy substituent is preferred over a *para* substitution.

Several NMR experiments were conducted to shed light on which dianionic intermediate **27** or **28** is present before the reaction is quenched with water. First, **2a** was reduced with sodium in [D_8]THF and the reaction was followed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the dark-red solution (see Figure S7 in the Supporting Information) indicates the presence of more than one species; however, the most pronounced signals show a pattern consistent with dianion **28**. The observed coupling patterns of four protons resemble that of the aniline ring in **1a**, but the resonances are shifted upfield by 0.7–0.8 ppm, as expected upon deprotonation of the amino group.

In a second experiment, ^{1}H NMR spectra were recorded after the addition of 1 equiv., 2 equiv., and an excess of *n*BuLi to a solution of **1a** in [D_8]THF (see Figures S6 and S7 in the Supporting Information). For comparison, **2a** was reduced with lithium in [D_8]THF and the reaction followed by ^{1}H NMR spectroscopy, as described above for sodium. The spectra after the addition of 2 or more equivalents of *n*BuLi appear similar to the in situ spectra recorded during lithium or sodium reduction, namely an upfield shift of the aniline ring protons of 0.3–0.8 ppm is observed. In addition, the resonance of the *ortho* protons of the phenyl substituents on the isoindole core experiences a downfield shift of 0.17 ppm and is found at the same chemical shift as in the ^{1}H NMR spectra recorded in situ during the reduction of **2a**. These observations support our postulated mechanism with **28** as an intermediate before quenching of the reaction.

To further elucidate the reaction mechanism, quantum chemical calculations were performed.[20] Of particular interest was the transformation of **27** into **28**; hence, these structures as well as transition state **29** were optimized[21] at the TPSS[22]-D3[23]/def2-TZVP[24] level of theory and including the COSMO[25] model to account for solvation. To find the transition state, constrained optimizations were performed with fixed lengths of the breaking C–N bond (Figure 3).



Scheme 7. Postulated mechanism for the formation of isoindole **1a** through the reduction of **2a** (NaNaph = sodium naphthalenide; Naph = naphthalene).

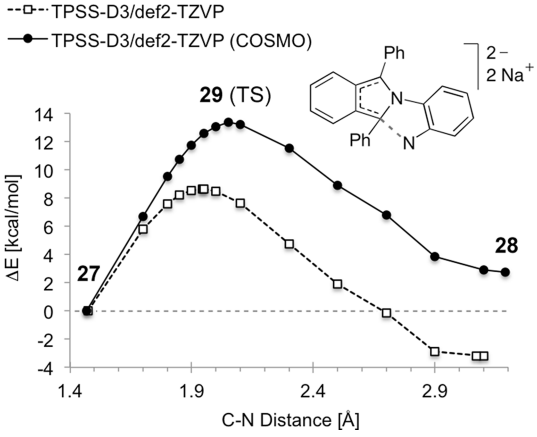


Figure 3. Energy profiles for the reaction of **27** to **28**.

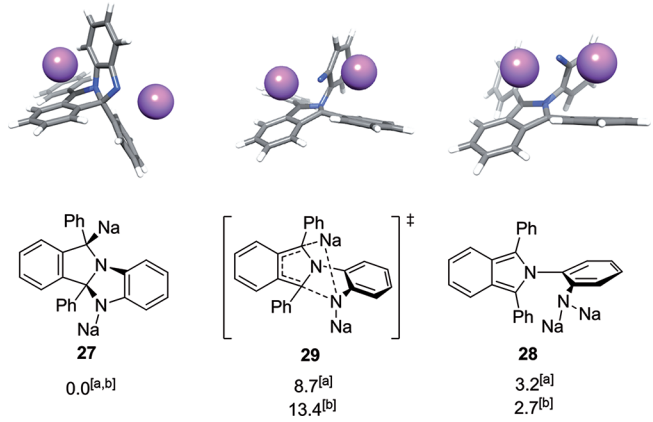


Figure 4. Optimized structures [TPSS-D3/def2-TZVP (COSMO)] and relative energies of the proposed intermediates **27** and **28** and transition state **29**. [a] TPSS-D3/def2-TZVP. [b] TPSS-D3/def2-TZVP (COSMO)).

At the TPSS-D3/def2-TZVP level of theory, the reaction from **27** to **28** is exothermic by 3.2 kcal/mol with an activation energy of 8.7 kcal/mol (Figure 3 and Figure 4). When the COSMO model is included to simulate the effect of bulk solvent, the reaction becomes endothermic by 2.7 kcal/mol with a higher barrier of 13.4 kcal/mol. These results show that the intermediates **27** and **28** have similar energies, and rearrangement of **27** to **28** is feasible.

Owing to their luminescent properties, isoindoles are attractive compounds for materials science. The synthesized isoindole derivatives **1a**–**c** and **1f**,**g** were characterized through their UV/Vis absorption and emission spectra (Figure 5). The UV/Vis spectra show several absorption maxima with the most intense peak below 200 nm and the longest wavelength absorption at 374 nm. All the derivatives show one emission maximum, which is found between 443 and 447 nm for **1a**,**b**,**f**,**g** and is slightly redshifted to 457 nm for the methoxy derivative **1c**. Thus, the emissions of isoindoles such as **1b** and **1c** can be shifted to longer wavelengths by substitution with electron-donating groups.

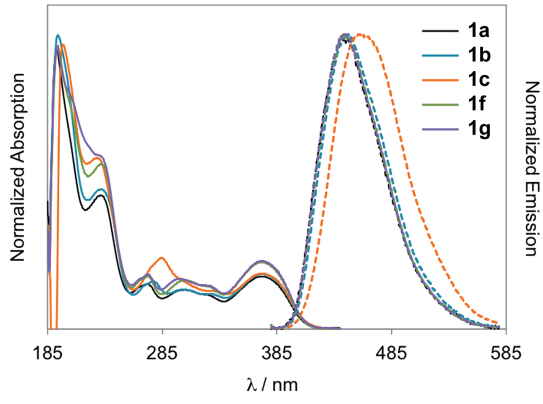


Figure 5. UV/Vis absorption (solid lines) and emission (dashed lines; excitation at 375 nm) spectra of isoindoles **1a**–**c** and **1f**–**g** in CH_3CN.

Conclusions

A unique and efficient route to 2-aniline-substituted isoindoles has been established through one-electron re-

ductions of dibenzo[1,4]diazocines using sodium naphthalenide. Six as yet unknown isoindole derivatives were synthesized by using this procedure, four of them in good yield, and further characterized through photophysical measurements. A mechanism for the formation of isoindoles has been proposed and underlined experimentally and through quantum chemical calculations.

Experimental Section

General: Commercially available chemicals were obtained from Sigma–Aldrich, Acros-Organics, TCI-Europe, and Alfa Aesar, and used without further purification. Experiments with water- or oxygen-sensitive substances were carried out under argon using glassware dried by heating under vacuum and standard Schlenk techniques. Anhydrous solvents were obtained from an M-Braun solvent purification system (MB-SPS), and stored under argon over molecular sieves (3 or 4 Å) for a minimum duration of 48 h. All other solvents were distilled prior to use. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded with Bruker Avance dpx 300 and 400 MHz spectrometers at room temperature unless stated otherwise and referenced to the residual proton or carbon resonance of the deuteriated solvent.[32] The NMR spectra were analyzed by using the MestReNova software.[33] Electrospray ionization mass spectra (ESI-MS) were recorded with a Bruker micrOTOF-Q time-of-flight spectrometer, and electron-impact ionization mass spectra(EI-MS) were recorded with a Thermo Finnigan (Bremen) MAT 90 or MAT 95 XL sector field device. The most abundant masses are reported. Silica gel layered alumina plates (Merck, Silica Gel 60 F_{254}) were used for TLC, and compounds were detected by using UV light (λ = 366 and 254 nm). For flash column chromatography silica gel (Merck 60, 40–63 μm) was used as the stationary phase. Eluents are described in the respective synthetic procedures. Polymer molecular weights were determined by using a GPC unit composed of an IsoPump G1310A, an ALS G1329A auto sampler, a VWD G1314B UV detector, and a RID G1362A RI detector by Agilent Technologies using a set of three columns (PSS Polymer Standard Service GmbH, polystyrene, 8 mm × 300 mm with a porosity of 10^2, 10^3, and 10^5 Å with an integrated precolumn). THF stabilized with 2.5 ppm BHT (p.a., Fisher) was used as eluent at a flow rate of 1 mL/min, and measurements were calibrated against polystyrene standards by PSS Polymer Standard Service GmbH. For thermal gravimetric analysis (TGA) a Mettler Toledo TGA/STAA851 instrument (SF 1100 °C, MT 1, N_2 atmosphere) was used with an Alox 40 μL melting pot. For differential scanning calorimetry (DSC) a Mettler Toledo DSC823^e instrument (HSS7, N_2 atmosphere, liquid N_2 cooling) was used with a standard aluminium 40 μL melting pot.

General Procedure for the Preparation of Isoindoles 1a–1c, 1f/1j, and 1g/1k: Na pieces were added to dry, degassed THF (4 mL), and the mixture sonicated for 20 min at room temp. Naphthalene was added, and the mixture sonicated for 20 min. Residual Na pieces were removed by using tweezers. The corresponding [1,4]diazocine **2** was added, and the mixture sonicated for 10 min. Water (1 mL) was added, and the solution was filtered through a pad of aluminium oxide. The mixture was purified by Kugelrohr distillation (100 °C, 10^{-2} mbar) and column chromatography (silica gel, cyclohexane/CH_2Cl_2/NEt_3) afforded isoindoles **1a**–**1c**, **1f/1j**, and **1g/1k** as slightly yellow, fluorescent solids.

2-(1,3-Diphenyl-2*H*-isoindol-2-yl)aniline (1a): The general procedure was followed by using Na (48.0 mg, 2.09 mmol), naphthalene (216 mg, 1.69 mmol), and (5*Z*,11*Z*)-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (**2a**; 75.0 mg, 209 μmol) and yielded 73 mg (96%) of **1a**. R_f = 0.81 (CH_2Cl_2/NEt_3, 100:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.60 (dd, J = 6.6, 3.0 Hz, 2 H), 7.37–7.34 (m, 4 H), 7.31–7.26 (m, 4 H), 7.22–7.17 (m, 2 H), 7.06–6.98 (m, 3 H), 6.91 (dd, J = 7.8, 1.6 Hz, 1 H), 6.66 (dd, J = 8.2, 1.4 Hz, 1 H), 6.47 (ddd, J = 7.6, 1.4 Hz, 1 H), 4.84 (s, 2 H) ppm. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.66 (dd, J = 6.7, 3.0 Hz, 2 H), 7.36 (d, J = 7.1 Hz, 4 H), 7.22 (dd, J = 7.2 Hz, 4 H), 7.12 (dd, J = 7.6 Hz, 2 H), 7.03–6.99 (m, 1 H), 6.95 (dd, J = 6.7, 3.0 Hz, 2 H), 6.87 (dd, J = 7.9, 1.6 Hz, 1 H), 6.59 (dd, J = 8.2, 1.4 Hz, 1 H), 6.47 (ddd, J = 7.5, 1.4 Hz, 1 H), 4.37 (s, 2 H) ppm. ^{13}C NMR (100 MHz [D$_6$]DMSO): δ = 145.1, 131.6, 129.9, 129.5, 129.3, 128.0, 126.3, 123.9, 122.8, 122.7, 122.1, 119.6, 115.8, 115.2 ppm. MS (EI$^+$): m/z = 360 [M]$^+$, 283 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{19}N_2$ 359.1543 [M – H]$^+$; found 359.1549. UV/Vis (MeCN): λ_{max} [log(ε/M^{-1} cm^{-1})] = 200, 233 [4.5], 272 [4.1], 305 [4.0], 372 nm [4.2]; emission (MeCN): λ = 445 nm.

2-(5-Methyl-1,3-diphenyl-2*H*-isoindol-2-yl)aniline (1b): The general procedure was followed by using Na (31.0 mg, 1.34 mmol), naphthalene (137 mg, 1.07 mmol), and (5*Z*,11*Z*)-8-methyl-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (**2b**; 50.0 mg, 134 μmol). Column chromatography (silica gel, cyclohexane/CH_2Cl_2/NEt_3, 2:1:0.01) yielded 37 mg (74%) of **1b**. R_f = 0.76 (cyclohexane/CH_2Cl_2/NEt_3, 1:1:0.01). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.52 (d, J = 8.7 Hz, 1 H), 7.36–7.32 (m, 5 H), 7.30–7.26 (m, 4 H), 7.20–7.16 (m, 2 H), 7.05–7.01 (m, 1 H), 6.91 (dd, J = 7.8, 1.5 Hz, 1 H), 6.86 (dd, J = 8.8, 1.4 Hz, 1 H), 6.65 (dd, J = 8.1, 1.3 Hz, 1 H), 6.46 (ddd, J = 7.5, 1.4 Hz, 1 H), 4.77 (s, 2 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz [D$_6$]DMSO): δ = 145.1, 131.8, 131.7, 130.8, 129.9, 129.4, 129.2, 129.1, 128.0, 128.0, 126.2, 126.1, 125.0, 123.8, 123.0, 123.0, 122.9, 121.5, 119.5, 117.4, 115.8, 115.2, 21.7 ppm. MS (EI$^+$): m/z = 374 [M]$^+$, 297 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{27}H_{22}N_2$ 374.1778 [M]$^+$; found 374.1779. UV/Vis (MeCN): λ_{max} [log(ε/M^{-1} cm^{-1})] = 200, 230 [4.4], 278 [3.9], 303 [3.8], 326 [3.8], 372 nm (4.0]; emission (MeCN): λ = 447 nm.

2-(5-Methoxy-1,3-diphenyl-2*H*-isoindol-2-yl)aniline (1c): The general procedure was followed by using Na (24.0 mg, 1.03 mmol), naphthalene (106 mg, 1.03 mmol), and (5*Z*,11*Z*)-8-methoxy-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (**2c**; 40.0 mg, 103 μmol). Column chromatography (silica gel cyclohexane/CH_2Cl_2/NEt_3, 2:1:0.01) yielded 27 mg (67%) of **1c**. R_f = 0.48 (CH_2Cl_2/NEt_3, 100:1). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.50 (dd, J = 9.2, 0.7 Hz, 1 H), 7.36–7.25 (m, 8 H), 7.22–7.14 (m, 2 H), 7.02 (ddd, J = 8.1, 7.3, 1.6 Hz, 1 H), 6.90 (dd, J = 7.8, 1.5 Hz, 1 H), 6.86 (m, 1 H), 6.70 (dd, J = 9.2, 2.2 Hz, 1 H), 6.64 (dd, J = 8.1, 1.3 Hz, 1 H), 6.45 (ddd, J = 7.5, 1.4 Hz, 1 H), 4.78 (s, 2 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 155.6, 145.2, 131.9, 131.5, 130.0, 129.4, 129.1, 129.0, 128.1, 128.0, 126.4, 126.0, 124.4, 123.0, 122.7, 122.5, 121.2, 119.3, 117.1, 115.8, 115.1, 95.5, 54.8 ppm. MS (EI$^+$): m/z = 390 [M]$^+$, 313 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{27}H_{22}N_2O$ 390.1727 [M]$^+$; found 390.1735. UV/Vis (MeCN): λ_{max} [log(ε/M^{-1} cm^{-1})] = 200, 228 [4.4], 285 [4.0], 372 nm (3.9]; emission (MeCN): λ = 457 nm.

2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-4-methylaniline (1f) and 2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-5-methylaniline (1j): The general procedure was followed by using Na (31.0 mg, 1.34 mmol), naphthalene (137 mg, 1.07 mmol), and (5*Z*,11*Z*)-2-methyl-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (**2f**; 75.0 mg, 201 μmol). Column chromatography (silica gel, cyclohexane/CH_2Cl_2/NEt_3, 2:1:0.01) afforded a mixture of **1f** and **1j** (58 mg, 77%) in a ratio of 78:22.

Analytical Data for 2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-4-methylaniline (1f): R_f = 0.56 (CH_2Cl_2/NEt_3, 100:1). ^{1}H NMR (400 MHz, [D$_6$]-

DMSO): δ = 7.58 (dd, J = 6.7, 3.0 Hz, 2 H), 7.39–7.34 (m, 4 H), 7.31–7.28 (m, 4 H), 7.22–7.18 (m, 2 H), 6.99 (dd, J = 6.7, 3.0 Hz, 2 H), 6.79 (d, J = 7.8 Hz, 1 H), 6.46 (br. s, 1 H), 6.28 (dd, J = 8.1, 1.9 Hz, 1 H), 4.74 (s, 2 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz [D$_6$]DMSO): δ = 144.7, 138.5, 131.7, 129.6, 129.3, 128.1, 126.3, 124.0, 122.6, 122.0, 120.6, 119.5, 116.8, 115.5, 21.0 ppm. MS (EI$^+$): m/z = 374 [M]$^+$, 297 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{27}H_{22}N_2$ 359.1699 [M – H]$^+$; found 359.1703. UV/Vis (MeCN): λ_{max} [log(ε/M^{-1} cm^{-1})] = 200, 232 [4.6], 272 [4.1], 305 [4.0], 372 nm [4.2]; emission (MeCN): λ = 443 nm.

In the purification process **1f** could be obtained in pure form; however, **1j** could only be obtained in a mixture with **1f**.

Analytical Data for 2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-5-methylaniline (1j): R_f = 0.54 (CH_2Cl_2/NEt_3, 100:1). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 7.60 (dd, J = 6.5, 3.0 Hz, 2 H), 7.38–7.35 (m, 4 H), 7.31–7.28 (m, 4 H), 7.22–7.18 (m, 2 H), 7.00 (dd, J = 6.5, 3.3 Hz, 2 H), 6.87 (dd, J = 8.4, 2.1 Hz, 1 H), 6.72 (d, J = 2.0 Hz, 1 H), 6.59 (d, J = 8.2 Hz, 1 H), 4.64 (s, 2 H), 2.02 (s, 3 H) ppm.

2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-4-methoxyaniline (1g) and 2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-5-methoxyaniline (1k): The general procedure was followed by using Na (29.0 mg, 1.28 mmol), naphthalene (130 mg, 1.02 mmol), and (5*Z*,11*Z*)-2-methoxy-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (**2g**; 40.0 mg, 102 µmol). Column chromatography (silica gel, cyclohexane/CH_2Cl_2/NEt_3, 2:1:0.01) afforded a mixture of **1g** and **1k** (24 mg, 62%) in a ratio of 96:4.

Analytical Data for 2-(1,3-Diphenyl-2*H*-isoindol-2-yl)-4-methoxyaniline (1g): R_f = 0.43 (CH_2Cl_2/NEt_3, 100:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.59 (dd, J = 6.7, 3.0 Hz, 2 H), 7.38–7.28 (m, 8 H), 7.23–7.18 (m, 2 H), 6.99 (dd, J = 6.6, 3.0 Hz, 2 H), 6.82 (d, J = 8.6 Hz, 1 H), 6.21 (d, J = 2.7 Hz, 1 H), 6.05 (dd, J = 8.6, 2.7 Hz, 1 H), 4.84 (s, 2 H), 3.64 (s, 3 H) ppm. ^{13}C NMR (75 MHz [D$_6$] DMSO): δ = 159.8, 146.1, 131.7, 130.7, 129.3, 128.1, 126.3, 124.1, 122.6, 122.0, 119.5, 116.4, 102.1, 99.3, 54.7 ppm. MS (EI$^+$): m/z = 390 [M]$^+$, 313 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{27}H_{22}N_2O$ 390.1727 [M]$^+$; found 390.1730. UV/Vis (MeCN): λ_{max} [log(ε/M^{-1} cm^{-1})] = 197, 231 [4.6], 272 [4.1], 300 [4.1], 372 nm [4.2]; emission (MeCN): λ = 445 nm.

General Procedure for the Preparation of [1,4]diazocines 2a–2i: According to a modified literature method,[19] the respective 1,2-dibenzoylbenzene was dissolved in AcOH. The respective *o*-phenylenediamine was added, and the reaction mixture was stirred at 60–80 °C for 5 h. A further 1–4 portions of the respective *o*-phenylenediamine were added, and the solution was stirred at 50–80 °C for 9–65 h. The mixture was neutralized with satd. aq. Na_2CO_3, extracted with CH_2Cl_2, washed with brine, and dried (Na_2SO_4). The solvent was then removed under reduced pressure. Column chromatography (silica gel, CH_2Cl_2 and/or cyclohexane/EtOAc) afforded [1,4]diazocines **2a**–**2i** as yellow solids.

(5*Z*,11*Z*)-6,11-Diphenyldibenzo[*b*,*f*][1,4]diazocine (2a): The general procedure was followed by using 1,2-dibenzoylbenzene (**7**; 2.67 g, 9.32 mmol), AcOH (120 mL), and *o*-phenylenediamine (portion 1: 1.01 g, 9.32 mmol; portion 2: 0.76 g, 6.99 mmol). Column chromatography (silica gel, cyclohexane/EtOAc, 15:1) yielded 2.83 g (84%) of **2a**. R_f = 0.27 (cyclohexane/EtOAc, 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 8.3, 1.5 Hz, 4 H), 7.44–7.34 (m, 8 H), 7.15 (dd, J = 5.7, 3.3 Hz, 2 H), 7.01–6.95 (m, 4 H) ppm. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.82–7.78 (m, 4 H), 7.41–7.36 (m, 4 H), 7.35–7.30 (m, 4 H), 7.14 (dd, J = 5.7, 3.3 Hz, 2 H), 6.93–6.84 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 142.1, 137.9, 136.6, 131.1, 129.1, 128.9, 128.4, 127.2, 124.2, 121.3 ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 170.3, 143.2, 139.1, 137.7, 131.8, 129.9, 129.7, 129.1, 128.1, 124.7, 122.0 ppm. MS (EI$^+$): m/z = 358 [M]$^+$, 281 [M – Ph]$^+$. Diazocine **2a** was further characterized by X-ray crystallography (see the Supporting Information).[26]

(5*Z*,11*Z*)-8-Methyl-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2b): The general procedure was followed by using 1,2-dibenzoyl-4-methylbenzene (**8**; 1.20 g, 4.00 mmol), AcOH (50 mL), and *o*-phenylenediamine (portion 1: 475 mg, 4.40 mmol; portion 2: 560 mg, 5.18 mmol). Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) yielded 694 mg (47%) of **2b**. R_f = 0.10 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.80 (m, 4 H), 7.44–7.33 (m, 6 H), 7.18 (ddd, J = 7.9, 1.7, 0.8 Hz, 1 H), 7.04 (d, J = 7.9 Hz, 1 H), 7.02–6.96 (m, 4 H), 6.95 (ddd, J = 1.5, 0.8 Hz, 1 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 170.0, 142.2, 139.0, 138.2, 136.6, 133.7, 131.0, 129.8, 129.1, 128.4, 128.3, 127.7, 127.2, 124.1, 124.1, 121.4, 21.5 ppm. MS (ESI$^+$): m/z = 767 [2M + Na]$^+$, 745 [2M + H]$^+$, 395 [M + Na]$^+$, 373 [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{27}H_{20}N_2Na$ 395.1519 [M + Na]$^+$; found 359.1521.

(5*Z*,11*Z*)-8-Methoxy-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2c): The general procedure was followed by using 1,2-dibenzoyl-4-methoxybenzene (**9**; 180 mg, 569 µmol), AcOH (9 mL), and *o*-phenylenediamine (portion 1: 61.5 mg, 569 µmol; portion 2: 61.5 mg, 569 µmol). Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) yielded 171 mg (77%) of **2c**. R_f = 0.33 (cyclohexane/EtOAc, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.79 (m, 4 H), 7.44–7.39 (m, 2 H), 7.38–7.33 (m, 4 H), 7.06 (d, J = 8.5 Hz, 1 H), 7.01–6.94 (m, 4 H), 6.90 (dd, J = 8.6, 2.6 Hz, 1 H), 6.63 (d, J = 2.5 Hz, 1 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 169.5, 159.7, 142.2, 142.1, 138.4, 138.1, 137.9, 131.1, 131.0, 129.2, 129.1, 128.8, 128.8, 128.4, 128.3, 124.2, 124.1, 121.4, 115.0, 112.1, 77.2, 55.5 ppm. MS (EI$^+$): m/z = 388 [M]$^+$, 373 [M – Me]$^+$ 311 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{27}H_{20}N_2O^+$ 388.1570 [M]$^+$; found 388.1573.

(5*Z*,11*Z*)-8-Chloro-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2d): The general procedure was followed by using 4-chloro-1,2-dibenzoylbenzene (**10**; 350 mg, 1.09 mmol), AcOH (15 mL), and *o*-phenylenediamine (portion 1: 130 mg, 1.20 mmol; portion 2: 130 mg, 1.20 mmol). Column chromatography (silica gel, cyclohexane/CH_2Cl_2, 1:1) yielded 304 mg (72%) of **2d**. R_f = 0.26 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.77 (m, 4 H), 7.46–7.41 (m, 2 H), 7.39–7.35 (m, 5 H), 7.15 (d, J = 2.1 Hz, 1 H), 7.09 (d, J = 8.3 Hz, 1 H), 7.04–6.95 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.4, 168.6, 141.4, 141.0, 138.1, 137.1, 137.1, 135.4, 134.7, 131.7, 131.7, 129.5, 129.3, 129.2, 128.8, 128.6, 128.6, 127.3, 124.8, 124.7, 121.6, 121.6 ppm. MS (EI$^+$): m/z = 392 [M]$^+$, 359 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}ClN_2$ 392.1075 [M]$^+$; found 392.1086.

(5*Z*,11*Z*)-8-Bromo-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2e): The general procedure was followed by using 4-bromo-1,2-dibenzoylbenzene (**11**; 198 mg, 542 µmol), AcOH (9 mL), and *o*-phenylenediamine (portion 1: 61.0 mg, 564 µmol; portion 2: 61.0 mg, 564 µmol; portion 3: 50.0 mg, 462 µmol; portion 4: 61.0 mg, 564 µmol). Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) yielded 181 mg (76%) of **2e**. R_f = 0.50 (cyclohexane/EtOAc, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.77 (m, 4 H), 7.52 (dd, J = 8.2, 2.0 Hz, 1 H), 7.46–7.41 (m, 2 H), 7.40–7.33 (m, 4 H), 7.30 (d, J = 2.0 Hz, 1 H), 7.07–6.95 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 168.3, 141.5, 141.4, 138.4, 137.4, 137.3, 135.4, 132.3, 131.5, 130.1, 129.1, 128.9, 128.6, 128.5, 124.6, 124.5, 123.3, 121.5, 121.5 ppm. MS (EI$^+$): m/z = 436 [M]$^+$, 359 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}BrN_2$ 436.0570 [M]$^+$; found 436.0573.

(5*Z*,11*Z*)-2-Methyl-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2f): The general procedure was followed by using 1,2-dibenzoylbenzene (**7**; 500 mg, 1.75 mmol), AcOH (25 mL), and 1,2-diamino-4-methylbenzene (portion 1: 214 mg, 1.75 mmol; portion 2: 214 mg, 1.75 mmol). Two consecutive column chromatography steps (silica gel, CH_2Cl_2 and cyclohexane/EtOAc, 20:1) yielded 507 mg of **2f** (78%). R_f = 0.15 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.78 (m, 4 H), 7.43–7.33 (m, 8 H), 7.17–7.12 (m, 2 H), 6.88–6.86 (m, 1 H), 6.81–6.79 (m, 2 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 169.6, 141.7, 139.3, 138.1, 138.0, 136.7, 136.6, 133.8, 131.1, 131.0, 129.1, 128.9, 128.8, 128.4, 128.4, 127.3, 127.3, 125.1, 121.8, 121.3, 21.0 ppm. MS (ESI$^+$): *m*/*z* = 395 [M + Na]$^+$, 373 [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{27}H_{21}N_2$ 373.1699 [M + H]$^+$; found 373.1698.

(5*Z*,11*Z*)-2-Methoxy-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2g): The general procedure was followed by using 1,2-dibenzoylbenzene (**7**; 500 mg, 1.75 mmol), AcOH (25 mL), and 1,2-diamino-4-methoxybenzene (portion 1: 242 mg, 1.75 mmol; portion 2: 214 mg, 1.75 mmol). Two consecutive column chromatography steps (silica gel, CH_2Cl_2 and cyclohexane/EtOAc, 20:1) yielded 92 mg (14%) of **2g**. R_f = 0.08 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 4 H), 7.44–7.32 (m, 8 H), 7.18–7.11 (m, 2 H), 6.90 (d, *J* = 8.7 Hz, 1 H), 6.59 (dd, *J* = 8.7, 2.8 Hz, 1 H), 6.53 (d, *J* = 2.7 Hz, 1 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8, 156.6, 142.9, 138.1, 137.8, 136.7, 136.5, 135.2, 131.2, 131.0, 129.1, 129.0, 128.9, 128.8, 128.4, 128.4, 127.4, 127.3, 122.6, 110.8, 106.0, 55.5 ppm. MS (ESI$^+$): *m*/*z* = 411 [M + Na]$^+$, 389 [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{27}H_{21}N_2O$ 389.1648 [M + H]$^+$; found 389.1635.

(5*Z*,11*Z*)-2-Chloro-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2h): The general procedure was followed by using 1,2-dibenzoylbenzene (**7**; 500 mg, 1.75 mmol), AcOH (25 mL), and 1,2-diamino-4-chlorobenzene (portion 1: 249 mg, 1.75 mmol; portion 2: 249 mg, 1.75 mmol). Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) yielded 517 mg (75%) of **2h**. R_f = 0.38 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 4 H), 7.45–7.39 (m, 4 H), 7.38–7.33 (m, 4 H), 7.19–7.12 (m, 2 H), 6.98 (d, *J* = 2.2 Hz, 1 H), 6.95 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.89 (d, *J* = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 170.5, 143.2, 140.7, 137.7, 137.6, 136.2, 136.2, 131.5, 131.4, 129.3, 129.2, 129.2, 129.1, 128.5, 128.5, 127.3, 127.3, 124.2, 122.6, 121.3 ppm. MS (ESI$^+$): *m*/*z* = 807 [2M + Na]$^+$, 415 [M + Na]$^+$, 393 [M + H]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}ClN_2Na$ 415.0972 [M + Na]$^+$; found 415.0986.

(5*Z*,11*Z*)-2-Bromo-6,11-diphenyldibenzo[*b*,*f*][1,4]diazocine (2i): The general procedure was followed by using 1,2-dibenzoylbenzene (**7**; 500 mg, 1.75 mmol), AcOH (25 mL), and 1,2-diamino-4-bromobenzene (portion 1: 325 mg, 1.75 mmol; portion 2: 195 mg, 1.05 mmol; portion 3: 260 mg, 1.40 mmol). Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) yielded 568 mg (74%) of **2i**. R_f = 0.56 (cyclohexane/EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.75 (m, 4 H), 7.46–7.32 (m, 8 H), 7.19–7.13 (m, 2 H), 7.12 (d, *J* = 2.0 Hz, 1 H), 7.09 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.84 (d, *J* = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.5, 143.5, 141.1, 137.6, 137.5, 136.2, 136.1, 131.5, 131.5, 129.2, 129.2, 129.2, 129.2, 128.5, 127.4, 127.3, 127.1, 124.2, 122.9, 117.0 ppm. MS (EI$^+$): *m*/*z* = 436 [M]$^+$, 359 [M – Ph]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}BrN_2$ 436.0570 [M]$^+$; found 436.0573.

(5*Z*,11*Z*)-6-Phenyl-12-(4-vinylphenyl)dibenzo[*b*,*f*][1,5]diazocine (4): (5*Z*,11*Z*)-6-(4-Bromophenyl)-12-phenyldibenzo[*b*,*f*][1,5]diazocine (**30**; 500 mg, 1.14 mmol) was dissolved in THF (30 mL). A solution of NaOH (140 mg, 3.5 mmol in 2 mL of water) was poured into the reaction flask, and the mixture was degassed with argon. Allylboronic acid pinacol ester (249 mg, 1.72 mmol) and [Pd(PPh$_3$)$_4$] (26 mg, 22.8 μmol, 2 mol-%) were added to the reaction mixture, which was stirred at 80 °C for 3 h. Water (5 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 40 mL). The organic layer was washed with brine (50 mL), dried with Na_2SO_4, and the solvent evaporated under reduced pressure resulting in a yellow foam. The crude product was purified by flash column chromatography (silica gel, cyclohexane/CH_2Cl_2, 1:1) to give 396 mg (90%) of **4** as a yellow solid. R_f = 0.74 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.44–7.30 (m, 7 H), 7.05–7.01 (m, 3 H), 7.00–6.96 (m, 2 H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.79 (dd, *J* = 17.6, 0.9 Hz, 1 H), 5.30 (dd, *J* = 10.9, 0.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 169.2, 152.1, 152.0, 140.3, 138.1, 137.5, 136.3, 131.2, 129.8, 129.8, 129.7, 129.5, 128.3, 127.7, 127.6, 127.1, 127.0, 126.1, 123.5, 123.5, 121.1, 121.0, 115.7 ppm. MS (EI$^+$): *m*/*z* = 384 [M]$^+$. HRMS (ESI$^+$): calcd. for $C_{28}H_{21}N_2$ 385.1699 [M + H]$^+$; found 385.1693.

1,2-Dibenzoylbenzene (7): Compound **7** was prepared according to a modified literature method.[27] 1,3-Diphenylisobenzofuran (**12**; 5.74 g, 21.2 mmol) was dissolved in CH_2Cl_2 (150 mL). mCPBA (70–75%, 5.50 g, 31.9 mmol) was added, and the reaction mixture was stirred at room temp. for 5 min. The solution was poured into satd. aq. $NaHCO_3$ (100 mL) and the mixture extracted with CH_2Cl_2 (3× 100 mL), washed with water and brine, and dried (Na_2SO_4). The solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/CH_2Cl_2, 1:2) afforded **7** (5.76 g, 95%) as a colorless solid. R_f = 0.61 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.69 (m, 4 H), 7.62 (s, 4 H), 7.54–7.49 (m, 2 H), 7.40–7.35 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.7, 140.2, 137.3, 133.1, 130.5, 130.0, 129.8, 128.5 ppm. MS (EI$^+$): *m*/*z* = 286 [M]$^+$, 209 [M – Ph]$^+$, 181 [M – Ph – CO]$^+$, 105 [M – 2Ph – CO]$^+$.

1,2-Dibenzoyl-4-methylbenzene (8): A mixture of lactones **23a** and **23b** (1.00 g, 4.46 mmol) was dissolved in dry THF (20 mL). PhMgBr (3 M in Et_2O, 1.78 mL, 5.35 mmol) was added dropwise at 0 °C during 15 min. The reaction mixture was warmed to room temp. and stirred for 20 h. The solution was cooled to 0 °C, acidified with 5.8 M aq. HCl (20 mL) and stirred for 30 min. The solution was warmed to room temp. and extracted with CH_2Cl_2 (3× 50 mL). The organic layer was washed with brine and 10% aq. Na_2CO_3 and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford 5-methyl-1,3-diphenylisobenzofuran (**13**; 1.30 g, quant.) as a yellow, fluorescent solid, which was used in the next step without further purification. Isobenzofuran **13** (1.30 g, 4.57 mmol) was dissolved in CH_2Cl_2 (20 mL), mCPBA (70–75%, 1.69 g, 6.86 mmol) was added, and the reaction mixture was stirred at room temp. for 5 min. The solution was poured into satd. aq. $NaHCO_3$ (100 mL) and the mixture extracted with CH_2Cl_2 (3× 50 mL), washed with water and brine, and dried (Na_2SO_4). The solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/EtOAc, 5:1) afforded **8** (1.20 g, 87%) as a colorless solid. R_f = 0.69 (cyclohexane/EtOAc, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.65 (m, 4 H), 7.55–7.53 (m, 1 H), 7.52–7.47 (m, 2 H), 7.41–7.34 (m, 6 H), 2.48 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 196.4, 141.6, 140.8, 137.6, 137.5, 136.9, 133.0, 132.9, 130.8, 130.3, 130.2, 129.9, 129.8, 128.4, 128.4, 21.6 ppm. MS (EI$^+$): *m*/*z* = 300 [M]$^+$, 223 [M – Ph]$^+$, 195 [M – Ph – CO]$^+$. HRMS (EI$^+$): calcd. for $C_{21}H_{16}O_2$ 300.1145 [M]$^+$; found 300.1148.

1,2-Dibenzoyl-4-methoxybenzene (9): Compound **9** was prepared in analogy to a published procedure.[30] $Pb(OAc)_4$ (399 mg, 900 μmol) was added to a suspension of (*Z*)-*N*′-[(2-hydroxy-4-methoxyphenyl)(phenyl)methylene]benzohydrazide (**18**; 295 mg, 852 μmol) in

THF (4 mL) at 0 °C. The mixture was warmed to room temp. and stirred for 5 h. The solvent was removed under reduced pressure and the resulting solid suspended in EtOAc and filtered through a pad of Celite. The filtrate was washed with satd. aq. $NaHCO_3$ and brine, the solution was dried (Na_2SO_4), and the solvent removed under reduced pressure. Column chromatography (silica gel, cyclohexane/EtOAc, 20:1) afforded **9** (218 mg, 81%) as a colorless solid. R_f = = 0.41 (cyclohexane/EtOAc, 4:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.69 (m, 2 H), 7.66–7.63 (m, 3 H), 7.52–7.47 (m, 2 H), 7.39–7.33 (m, 4 H), 7.08 (d, J = 2.5 Hz, 1 H), 7.05 (dd, J = 8.5, 2.6 Hz, 1 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.8, 195.3, 162.0, 143.5, 137.9, 137.3, 133.1, 132.8, 132.6, 131.2, 129.9, 129.6, 128.5, 128.4, 114.9, 114.9, 55.9 ppm.

4-Chloro-1,2-dibenzoylbenzene (10): Compound **10** was prepared in analogy to a published procedure.[28] PhMgBr (3 M, 2.38 mL, 7.14 mmol) was added dropwise to a solution of *S*,*S*′-dipyridin-2-yl 4-chlorobenzene-1,2-dicarbothioate (**16**; 1.25 g, 3.25 mmol) in THF (30 mL) at 0 °C. The solution was stirred for 15 min at 0 °C and quenched with 2 M HCl (65 mL). The solution was extracted with CH_2Cl_2 (3× 50 mL), and washed with 1 M aq. NaOH and satd. aq. $NaHCO_3$. The organic layer was dried (Na_2SO_4), and the solvent removed under reduced pressure. Column chromatography (silica gel, cyclohexane/CH_2Cl_2, 2:1) afforded **10** (360 mg, 34%) as a bright-yellow solid. R_f = 0.53 (CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.65 (m, 4 H), 7.59–7.58 (m, 3 H), 7.56–7.51 (m, 2 H), 7.41–7.36 (m, 4 H) ppm. ^{13}C NMR (75 MHz [D$_6$]DMSO): δ = 195.5, 195.3, 142.1, 138.1, 137.2, 137.0, 136.8, 133.5, 133.4, 131.3, 130.3, 129.9, 129.9, 129.6, 128.6, 128.6 ppm. MS (EI$^+$): m/z = 320 [M]$^+$, 285 [M – Cl]$^+$, 243 [M – Ph]$^+$, 215 [M – PhCO]$^+$.

4-Bromo-1,2-dibenzoylbenzene (11): A mixture of lactones **24a** and **24b** (399 mg, 1.38 mmol) was dissolved in dry THF (8 mL) and PhMgBr (3 M in Et_2O, 553 µL, 1.66 mmol) was added dropwise at 0 °C during 15 min. The reaction mixture was then warmed to room temp. and stirred for 20 h. The solution was cooled to 0 °C, acidified with 5.8 M aq. HCl (6 mL), and stirred for 30 min. The solution was again warmed to room temp., and extracted with CH_2Cl_2 (3× 20 mL). The organic layer was washed with brine and 10% aq. Na_2CO_3 and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford crude 5-bromo-1,3-diphenylisobenzofuran (**14**; 506 mg, quant.) as a yellow, fluorescent solid, which was used in the next step without further purification. Isobenzofuran **14** (468 mg, 1.34 mmol) was dissolved in CH_2Cl_2 (6 mL), mCPBA (70–75%, 347 mg, 2.01 mmol) was added, and the reaction mixture was stirred at room temp. for 5 min. The solution was poured into satd. aq. $NaHCO_3$ (25 mL), the mixture was extracted with CH_2Cl_2 (3× 10 mL), washed with water and brine, and dried (Na_2SO_4). The solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/EtOAc, 50:1) afforded **11** (376 mg, 77%) as a colorless solid. R_f = 0.20 (cyclohexane/EtOAc, 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.73 (m, 2 H), 7.69–7.65 (m, 4 H), 7.55–7.50 (m, 3 H), 7.41–7.36 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.6, 195.2, 142.1, 138.5, 137.0, 136.7, 133.5, 133.4, 133.3, 132.5, 131.4, 129.9, 129.9, 128.6, 128.6, 125.3 ppm.

***S*,*S*′-Dipyridin-2-yl 4-Chlorobenzene-1,2-dicarbothioate (16):** Compound **16** was prepared in analogy to a published procedure.[29] A mixture of 4-chlorophthalic acid (**15**; 3.50 g, 15.8 mmol) and PCl_5 (9.87 g, 47.4 mmol) was stirred at 170 °C for 2 h. The suspension was filtered. Distillation afforded 4-chlorophthaloyl dichloride (**31**; 2.65 g, 71%) as a colorless liquid. The product could not be obtained in pure form and was therefore used in the next step without further purification. 2-Mercaptopyridine (1.92 g, 17.24 mmol) was dissolved in a mixture of THF (30 mL) and NEt_3 (3 mL) at 0 °C and stirred at 0 °C for 15 min. Dichloride **31** (2.10 g, 8.84 mmol) in THF (30 mL) was then added in one portion. The mixture was stirred for 1 min and quenched with 1% aq. HCl (120 mL). The solution was extracted with CH_2Cl_2 (3× 5 mL) and washed with 10% aq. NaOH, 1 M aq. $NaHCO_3$, and water. The mixture was dried (Na_2SO_4), and the solvents removed under reduced pressure. The resulting oil was recrystallized from CH_2Cl_2/Et_2O to afford **16** (1.72 g, 50%) as a colorless solid. R_f = 0.32 (cyclohexane/EtOAc, 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31–8.30 (m, 1 H), 7.67 (dd, J = 1.8, 0.6 Hz, 1 H), 7.64 (dd, J = 8.2, 0.6 Hz, 1 H), 7.56 (dd, J = 8.0, 1.8 Hz, 1 H), 7.55–7.51 (m, 3 H), 7.40 (dd, J = 8.1, 1.7 Hz, 1 H), 7.09 (dd, J = 4.8, 2.0 Hz, 1 H), 7.08 (dd, J = 4.7, 2.0 Hz, 1 H) ppm. MS (ESI$^+$): m/z = 795 [2M + Na]$^+$, 716 [2M – Py + Na]$^+$, 562 [2M – 3Py + Na]$^+$, 409 [M + Na]$^+$, 387 [M + H]$^+$, 330 [M – Py + Na]$^+$.

(*Z*)-*N*′-[(2-Hydroxy-4-methoxyphenyl)(phenyl)methylene]benzohydrazide (18): Compound **18** was prepared in analogy to a published procedure.[30] 2-Hydroxy-4-methoxybenzophenone (**17**; 1.0 g, 4.38 mmol) and benzoylhydrazine (596 mg, 4.38 mmol) were dissolved in 1-propanol (25 mL) and heated at 110 °C for 48 h. The suspension was cooled to room temp., and the resulting colorless precipitate was filtered, washed with cold 1-propanol, and dried under high vacuum at 80 °C to afford **18** as a white solid (312 mg, 21%). ^1H NMR (400 MHz, $CDCl_3$): δ = 12.61 (s, 1 H), 8.82 (s, 1 H), 7.67–7.59 (m, 3 H), 7.55–7.47 (m, 3 H), 7.40–7.36 (m, 4 H), 6.69 (d, J = 8.8 Hz, 1 H), 6.61 (s, 1 H), 6.30 (dd, J = 8.8, 2.6 Hz, 1 H), 3.81 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 161.7, 132.3, 131.8, 130.6, 130.3, 130.1, 128.9, 128.1, 127.1, 112.5, 106.6, 101.9, 55.5 ppm.

2-Benzoyl-5-methylbenzoic Acid (21a) and 2-Benzoyl-4-methylbenzoic Acid (21b): 4-Methylphthalic anhydride (**19**; 1.29 g, 7.96 mmol) was added to benzene (10 mL). Anhydrous $AlCl_3$ (2.12 g, 15.9 mmol) was added, and the reaction mixture was stirred at 90 °C for 3 h. After cooling to room temp., ice was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3× 75 mL). The organic layer was extracted with 10% aq. Na_2CO_3, and the aqueous layer was acidified with HCl (conc.) and stored at 4 °C for 15 h. The resulting precipitate was filtered and dried to afford a mixture of **21a** and **21b** in a ratio of 38:62 (1.82 g, 95%) as a light-beige solid. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 13.07 (s, 1 H), 7.89 (d, J = 7.9 Hz, 0.62 H), 7.80 (d, J = 1.8 Hz, 0.38 H), 7.65–7.21 (m, 6 H), 7.29 (d, J = 7.7 Hz, 0.38 H), 7.21 (s, 0.62 H), 2.43 (s, 1.14 H), 2.40 (s, 1.86 H) ppm. MS (EI$^+$): m/z = 240 [M]$^+$, 196 [M – CO_2]$^+$, 163 [M – Ph]$^+$, 105 [PhCO]$^+$.

2-Benzoyl-5-bromobenzoic Acid (22a) and 2-Benzoyl-4-bromobenzoic Acid (22b): 4-Bromophthalic anhydride (**20**; 1.98 g, 8.72 mmol) was added to benzene (15 mL). Anhydrous $AlCl_3$ (2.34 mg, 17.6 mmol) was added, and the reaction mixture was stirred at 90 °C for 3 h. After cooling to room temp., ice was added to the reaction mixture, which was then acidified with HCl (conc.). The solution was extracted with CH_2Cl_2 (3× 30 mL), the organic layer was extracted with 10% aq. Na_2CO_3, and the aqueous layer was acidified with HCl (conc.) and stored at 4 °C for 15 h. The resulting precipitate was filtered and dried to afford **22a** and **22b** in a ratio of 35:65 (2.56 g, 96%, 2 isomers) as a light-beige solid. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 13.43 (s, 1 H), 8.10 (d, J = 2.0 Hz, 0.35 H), 7.94 (dd, J = 8.2, 2.1 Hz, 0.35 H), 7.92 (d, J = 8.3 Hz, 0.65 H), 7.87 (dd, J = 8.4, 2.0 Hz, 0.65 H), 7.69 (d, J = 1.9 Hz, 0.65 H), 7.65–7.61 (m, 3 H), 7.52–7.48 (m, 2 H), 7.41 (d, J = 8.1 Hz, 0.35 H) ppm. MS (EI$^+$): m/z = 304 [M]$^+$, 227 [M – Ph]$^+$, 181 [Ph – CO_2 – Br]$^+$, 105 [PhCO]$^+$.

5-Methyl-3-phenylisobenzofuran-1(3*H*)-one (23a) and 6-Methyl-3-phenylisobenzofuran-1(3*H*)-one (23b): Compounds **23a** and **23b** were prepared in analogy to a published procedure.[31] The mixture of **21a** and **21b** from the previous step (1.5 g, 6.24 mmol) was added to a solution of KOH (323 mg, 8.08 mmol) in water (6.20 mL). $NaBH_4$ (200 mg, 5.31 mmol) was then added within 15 min and the reaction mixture stirred at room temp. for 24 h. The solution was acidified to pH 0 with HCl (conc.) and extracted with CH_2Cl_2 (8 × 50 mL). The organic extracts were washed with 10% aq. Na_2CO_3 and brine. The solvent was removed under reduced pressure to afford a mixture of **23a** and **23b** (1.00 g, 71%) in a ratio of 38:62 as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.8 Hz, 0.62 H), 7.76 (ddd, J = 1.6, 0.8 Hz, 0.38 H), 7.46 (ddd, J = 7.9, 1.5, 0.8 Hz, 0.38 H), 7.41–7.34 (m, 3.62 H), 7.30–7.26 (m, 2 H), 7.22 (d, J = 7.8 Hz, 0.38 H), 7.12 (ddd, J = 1.5, 0.8 Hz, 0.62 H), 6.37 (s, 0.38 H), 6.35 (s, 0.62 H), 2.48 (s, 1.14 H), 2.44 (s, 1.86 H) ppm. MS (EI$^+$): m/z = 224 [M]$^+$.

5-Bromo-3-phenylisobenzofuran-1(3*H*)-one (24a) and 6-Bromo-3-phenylisobenzofuran-1(3*H*)-one (24b): Compounds **24a** and **24b** were prepared in analogy to a published procedure.[31] The mixture of **22a** and **22b** from the previous step (2.50 g, 8.20 mmol) was added to a solution of KOH (600 mg, 10.7 mmol) in water (8.20 mL). $NaBH_4$ (264 mg, 6.97 mmol) was added within 15 min and the reaction mixture was stirred at room temp. for 22 h. The solution was acidified to pH 0 with HCl (conc.) and extracted with CH_2Cl_2 (3× 50 mL). The organic extracts were washed with 10% aq. Na_2CO_3 and brine. The organic layer was dried with Na_2SO_4 and the solvent removed under reduced pressure to afford a mixture of **24a** and **24b** (1.42 g, 58%) in a ratio of 35:65 as a colorless solid. R_f = 0.84 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 1.7 Hz, 0.35 H), 7.82 (d, J = 8.1 Hz, 0.65 H), 7.76 (dd, J = 8.1, 1.8 Hz, 0.35 H), 7.69 (ddd, J = 8.1, 1.6, 0.7 Hz, 0.65 H), 7.49 (dt, J = 1.5, 0.7 Hz, 0.65 H), 7.43–7.37 (m, 3 H), 7.29–7.25 (m, 2 H), 7.22 (dt, J = 8.2, 0.8 Hz, 0.35 H), 6.37 (s, 1 H) ppm. MS (EI$^+$): m/z = 288 [M]$^+$, 211 [M – Ph]$^+$, 105 [PhCO]. HRMS (EI$^+$): calcd. for $C_{14}H_9BrO_2$ 287.9780 [M]$^+$; found 287.9787.

(5*Z*,11*Z*)-6-(4-Bromophenyl)-12-phenyldibenzo[*b*,*f*][1,5]diazocine (30) and (5*Z*,11*Z*)-6,12-Diphenyl-dibenzo[*b*,*f*][1,5]diazocine (5): (5*Z*,11*Z*)-6,12-Bis(4-bromophenyl)dibenzo[*b*,*f*][1,5]diazocine (**3**;[10] 1.95 g, 3.78 mmol) was dissolved in dry THF (45 mL), and *n*BuLi (2.6 mL, 4.16 mmol) was added during 10 min at –78 °C. After 1 h, MeOH (30 mL) and water (30 mL) were added to the reaction mixture, and the solution was extracted with CH_2Cl_2 (3× 50 mL). The organic layer was washed with brine (50 mL), dried with Na_2SO_4, and the solvent evaporated under reduced pressure resulting in a yellow foam. The crude product was purified by flash column chromatography (silica gel, cyclohexane/CH_2Cl_2, 5:2) to give 900 mg (54%) of **30** as a yellow solid as well as 200 mg (15%) of **5** as a yellow solid.

Analytical Data for (5*Z*,11*Z*)-6-(4-Bromophenyl)-12-phenyldibenzo[*b*,*f*]-[1,5]diazocine (30): R_f = 0.76 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 2 H), 7.64 (d, J = 8.6 Hz, 2 H), 7.47 (d, J = 8.6 Hz, 2 H), 7.45–7.41 (m, 1 H), 7.37–7.30 (m, 4 H), 7.05–6.93 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.7, 168.7, 152.1, 151.7, 138.0, 137.0, 131.5, 131.2, 131.0, 130.0, 129.8, 129.5, 128.4, 127.7, 127.4, 126.9, 126.4, 126.0, 123.7, 123.7, 123.6, 121.1, 120.9 ppm. MS (EI$^+$): m/z = 436 [M]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}BrN_2$ 436.0570 [M]$^+$; found 436.0575.

Analytical Data for (5*Z*,11*Z*)-6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5): R_f = 0.54 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.78 (m, 4 H), 7.45–7.41 (m, 2 H), 7.38–7.31 (m, 6 H), 7.06–6.97 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 151.8, 138.0, 131.3, 129.8, 129.6, 128.4, 127.7, 127.1, 123.6, 121.1 ppm. MS (EI$^+$): m/z = 358 [M]$^+$. HRMS (EI$^+$): calcd. for $C_{26}H_{17}N_2$ 357.1386 [M – H]$^+$; found 357.1390.

Polymer P1: (5*Z*,11*Z*)-6-Phenyl-12-(4-vinylphenyl)dibenzo[*b*,*f*]-[1,5]diazocine (**4**; 130 mg, 0.34 mmol) was dissolved in toluene (0.17 mL), and the solution was degassed with argon. AIBN (1.5 mg, 0.01 mmol) was added, and the flask was immersed in an oil bath preheated to 60 °C. After 75 min the reaction was quenched by the addition of MeOH (1 mL). The yellow precipitate was dissolved in $CHCl_3$ (50 mL), precipitated in MeOH, and isolated by centrifuge. These steps were repeated four times. 40 mg (30%) of **P1** as a yellow solid were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (vbr. s), 7.36 (vbr. s), 7.10 (vbr. s), 6.89 (vbr. s), 1.58 ppm (vbr. s). Anal. GPC (eluent: THF, polystyrene standard): M_n = 1.23 × 10^5 a.u., M_w/M_n = 2.05; DSC (10 °C/min, N_2): T_g = 260 °C; TGA (10 °C/min, N_2): $T_{d10\%}$ (temperature for 10% weight loss) = 397 °C.

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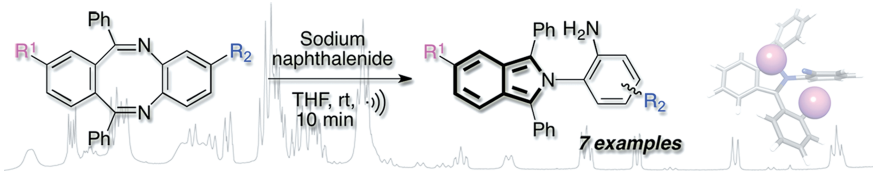
Isoindole Synthesis



A protocol for the synthesis of isoindoles through one-electron reductions of dibenzo[1,4]diazocines is reported. Six novel isoindole derivatives have been synthesized, and the reaction mechanism has been studied by ^{1}H NMR spectroscopy and quantum chemical calculations.

Keywords: Synthetic methods / Electrochemistry / Electron transfer / Reduction / Heterocycles

