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Variation of the Backbone Conjugation in NLO Model Compounds: Torsion-Angle-Restricted, Biphenyl-Based Push-Pull-Systems

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Terminal piperidinyl- and nitro-functionalized biphenyls, bridged between the 2 and 2′ positions by a variable number of methylene groups, are synthesized and fully characterized. These push-pull systems with defined and restricted torsion angles between their phenyl rings are ideal model compounds to investigate the influence of the chromophore's conjugation in nonlinear optic (NLO) responses. A general synthetic route that can be implemented to access these model compounds is reported, starting from dibromo or ditriflate biphenyls. Hartwig–Buchwald cross-coupling, a selective azacycloalkylation of diaminobiphenyls and a mild oxidation of primary amines to nitro groups in the presence of a tertiary amine summarizes the synthetic pathway towards the desired model compounds. NLO properties of the series of torsionally constrained push-pull biphenyls are collected by electric-field-induced second-harmonic generation (EFISH) experiments. The results agree qualitatively with semi-empirical simulations based on the AM1 Hamiltonian. A linear dependence of the quadratic response on the $\cos^2(\Phi)$ of the inter-aryl dihedral angle is observed, which points to oscillator strength loss as the dominant effect of increasing backbone twist.

Introduction

While the discovery of the Kerr effect,[1] which is the quadratic electric-field-induced change in the refraction index of a medium, is the earliest nonlinear response reported in the study of optics, it is the availability of strong electromagnetic fields, after the invention of the laser in 1960,[2] which made it possible to systematically investigate such effects. Given the ability to produce optical fields of sufficient strength, the observation of the phenomenon of second-harmonic generation (SHG) in quartz in 1961[3] marks the advent of nonlinear optical (NLO) studies. Since then, the search for NLO-active media has been extended to organic compounds where it has developed into an amazingly broad field because of numerous potential applications in photonic technologies, including all-optical switching, data processing,[4–7] or even scanning near-field microscopy.[8]

To design molecules for quadratic NLO responses, the first hyperpolarizability β must be optimized. Several models were developed for a quantitative analysis of the nonlinear optical response.[9–13] Oudar and Chemla established that the main contribution to β may be attributed to the lowest intramolecular charge-transfer (ICT) band characterized by a transition energy, an oscillator strength and a change in permanent dipole moment, thus defining their well known two-level model.[14] ICT is dependent on the backbone chromophore as well as on the substituents.[15] Therefore, the design of efficient organic materials for quadratic nonlinear optics is based on units containing highly delocalized π-electron moieties and additional electron-donor and electron-acceptor groups on opposite ends of the chromophore.

Donor-acceptor-substituted biphenyl derivatives are particularly interesting model compounds exhibiting intramolecular charge-transfer because the extent of "backbone"-conjugation and thus the extent of charge-transfer between both substituents depends on a controllable structural feature, namely the torsion angle between the two phenyl rings.[16–19] Correlations between intramolecular torsion angles and resulting NLO properties were already reported for quinopyrans by M. A. Ratner and co-workers.[20] Using numerical simulations for NLO properties and UV/Vis absorption spectra, the tuning of transition frequency and NLO amplitudes was achieved by effecting charge separation and by stabilizing the charge.[20] Also biphenyl-based chromophores have already been considered in theoretical studies. Ab initio calculations of fluorenyl-based push-pull systems suggested that the value of β corresponds to the energy difference between HOMO and LUMO.[21] By comparing the NLO properties of comparable substituted (-NH_2

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and -NO_2) biphenyl and fluorene derivatives a considerably increased response was observed for the planar fluorene compound, pointing at the importance of the π-conjugation in the central chromophore. Furthermore, correlations between backbone torsion angle and NLO properties have already been reported for zwitterionic compounds.[16]

The complexity of the nonlinear optical responses makes the design of new NLO materials very challenging. Especially on the molecular level, numerous publications document the very basic comprehension of structure-property relationships, in spite of the fact that great progress has been made in the last few years.[16,21–28] Indeed, large π-conjugated systems with donor and acceptor groups have been synthesized with a high potential for large nonlinear optical effects. Despite the advances in chromophore design, a deeper comprehension of structural features governing the NLO properties is required to enable reliable theoretical predictions and thus, allowing an improved design of tailor-made NLO materials. Improved theoretical models on the other hand can only be developed with suitable experimental data obtained from model compounds in which a particular structural feature is varied systematically.

Following this systematic approach, we would like to report here the synthesis of the entire series of neutral biphenyl push-pull systems with restricted torsion angles **1a**–**1g** as NLO model compounds varying mainly in the extent of backbone π-conjugation (cf. Figure 1). Furthermore, first optical studies like UV/Vis and EFISH (electric-field-induced second-harmonic generation) experiments were performed to investigate the consequences of the alteration in torsion angle on their optical properties. The observed correlations are further accompanied by semi-empirical simulations based on the AM1 Hamiltonian.

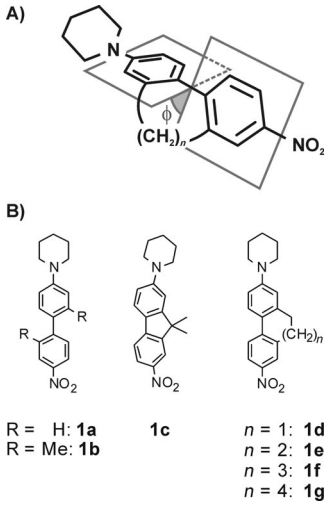


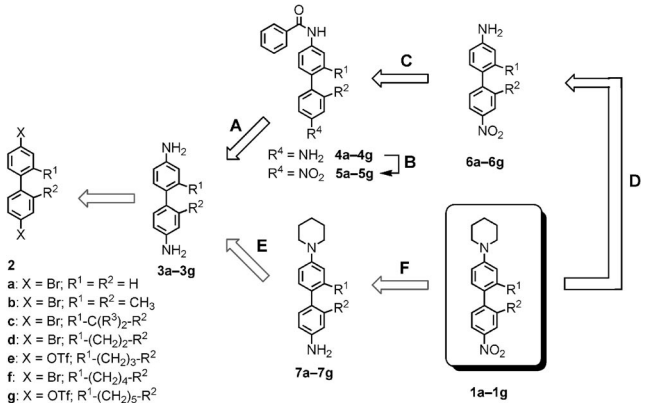
Figure 1. A) Illustration of the concept to fix the torsion angle *Φ* between the two phenyl rings by an additional interphenyl alkyl bridge of varying length. B) Target push-pull systems with increasing torsion angle from **1c** to **1g**; **1a** and **1b** were used as preliminary model compounds.

Results and Discussion

Molecular Design and Synthetic Strategy

For sizeable quadratic optical responses in linear push-pull systems a permanent dipole moment induced by electron-acceptor and -donor substituents and an intense intramolecular charge-transfer absorption band are required. While effects arising from the donor and acceptor substituents have been investigated extensively,[21,29–34] hardly any systematic study of the influence of the backbone's π-conjugation has been reported so far.[15,16] We recently developed a series of biphenyl building blocks terminally functionalized with leaving groups comprising alkyl chains of various lengths interlinking both phenyl rings to restrict the torsion angle of their biphenyl backbone.[18,35] These functional building blocks are ideally suited as starting materials of the here reported series of biphenyl-based push-pull systems as NLO model compounds with varying backbone conjugation. Nitrogen substituents in varied oxidation states have been chosen as push-pull substituents. While a terminal nitro group acts as electron acceptor, a piperidinyl substituent acts as electron donator on the opposed side. These substituents on a parent biphenyl core should provide a donor-acceptor system exhibiting a moderate hyperpolarizability, leaving investigation space for both, systems with stronger and weaker hyperpolarizabilities. To keep the model compounds as comparable as possible the terminal substituents were maintained throughout the series.

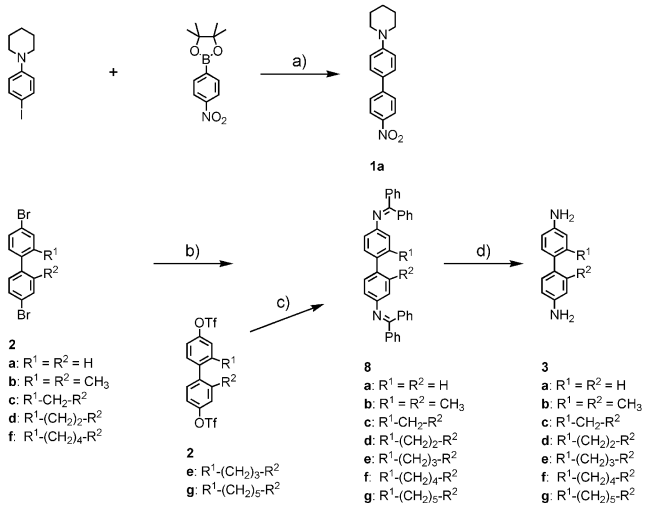
To preliminarily investigate the suitability of the push-pull system, the parent 4-nitro-4′-piperidinyl-biphenyl was straight forwardly synthesized by assembling the biphenyl backbone applying a Suzuki coupling protocol. However, the synthetic aim of this project was to develop a universal synthetic strategy for 4-nitro-4′-piperidinyl-substituted biphenyl systems based on available building blocks comprising terminal leaving groups such as bromines and triflates. The synthetic strategies considered are displayed in Scheme 1.



Scheme 1. Synthetic routes considered towards the desired biphenyl-based push-pull systems (R^3 = H for **2**, **3** and **7**; R^3 = CH_3 for **1**).

In the target compounds the oxidation state of both terminal nitrogen atoms differs by six units. Starting from symmetric diamino derivatives, which should be obtained either by palladium-catalyzed Hartwig–Buchwald-type chemistry[36,37] or by copper-catalyzed Ullmann-type reactions,[38,39] the synthetic challenge will be to oxidize exclusively one of the two nitrogen atoms. Furthermore, a suitable assembly sequence of the electron-donating piperidinyl unit and the electron-withdrawing nitro group had to be found. Two synthetic approaches were considered and are displayed as **A**–**D** and **E**–**F** in Scheme 1.

If the piperidinyl donor group is introduced first (**E**), oxidation of the remaining amino group (**F**) will be challenging, as tertiary amines are prone to the formation of *N*-oxides. However, a careful choice of the oxidation conditions might overcome this drawback of the **E**–**F** strategy. Alternatively, the oxidation step providing the electron-withdrawing nitro group could be considered prior to the assembly of the piperidinyl group (strategy **A**–**D**). Monoprotection of the diamine with a benzoyl group (**A**) should provide selectivity[40] and should reduce the electron density of the remaining amine providing an increased control over its oxidation (**B**), as electron rich anilines are prone to side reactions during oxidations due to their large reduction potentials. After deprotection (**C**), the assembly of the piperidinyl group was envisaged by an azacycloalkylation. However, the nucleophilicity of the remaining amino group is decreased due to the electron-withdrawing nitro group. Interestingly, the extent of this effect is expected to correlate with the backbone conjugation of the biphenyl core.



Scheme 2. Assembly of **1a** by Suzuki–Miyaura coupling. Synthesis of the 4,4′-diamino derivatives **3a**–**g** applying a Hartwig–Buchwald protocol. Reagents and conditions: a) $Pd(PPh_3)_4$, Cs_2CO_3, toluene/MeOH, 3:1, reflux, 18 h, 26%; b) benzophenone imine, $Pd_2(dba)_3 \cdot CHCl_3$, BINAP, NaO*t*Bu, toluene, 80 °C, 4 h, 85%-quant.; c) benzophenone imine, $Pd(OAc)_2$, BINAP, Cs_2CO_3, THF, 65 °C, 17 h, 98% for **8e**, 60% for **8g**; d) 3% aq. HCl, THF, room temp., 2 h, 80%-quant.

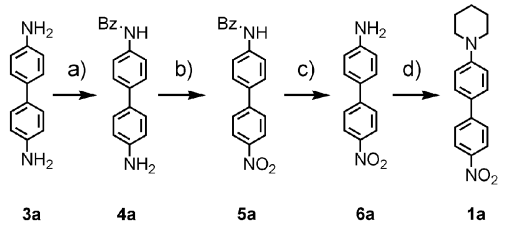
Synthesis

To investigate the suitability of these new types of biphenyl-based push-pull systems for EFISH experiments a straight forward assembly of the parent 4-nitro-4′-piperidinyl-biphenyl **1a** was considered. Particularly appealing is the synthesis of the biphenyl core by a Suzuki–Miyaura coupling as suitably functionalized phenyl precursors were already available.[41] As displayed in Scheme 2, 1-(4-iodophenyl)piperidine and 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane were treated with a palladium catalyst and a base in a refluxing toluene/methanol mixture to provide the desired NLO model compound **1a** in 26% yield after column chromatography (CC). Promising preliminary optical investigations of **1a** motivated the development of a general synthetic route to make the entire series of NLO model compounds available.

Both considered strategies (**A**–**D** and **E**–**F**) have the 4,4′-diaminobiphenyl synthon as a common precursor. Numerous catalyst-ligand systems for Hartwig–Buchwald cross-coupling reactions to substituted aryl halides, including 4-bromobiphenyl and 1,4-dibromobenzene[42] have been reported.[43] However, to the best of our knowledge, typical Hartwig–Buchwald conditions were neither applied to ditriflate- nor dibromobiphenyl systems. While 4,4′-dibromobiphenyl systems (**2a**–**2d**, **2f**) as precursors allowed rather harsh reaction conditions, this was less the case for 4,4′-ditriflatebiphenyl systems (**2e** and **2g**) which are prone to hydrolysis. To investigate the suitability of the synthetic strategy, the commercially available 4,4′-dibromobiphenyl (**2a**) was treated with benzophenone imine as an ammonia synthon[44] and sodium *tert*-butoxide as base in the presence of catalytic amounts of Pd_2dba_3 as Pd^0 source and BINAP as ligand in 80 °C toluene (condition b in Scheme 2). To protect the intermediate air-sensitive catalyst-ligand complex, the reaction was carried out under inert gas and dry conditions. After 4 h the starting material was consumed as observed by thin-layer chromatography (TLC). The diimine-biphenyl derivative **8a** was isolated by precipitation of the catalyst and recrystallization from methanol. In a first attempt, the diimine **8a** was cleaved using ammonium formate and catalytic amounts of palladium on charcoal.[44] As only 35% yield of the desired 4,4′-diaminobiphenyl (**3a**) was isolated, acidic hydrolysis was considered. Thus, **8a** was dissolved in tetrahydrofurane (THF) and hydrochloric acid was added. The desired diamine **3a** was isolated by column chromatography (CC) in 80% yield over both steps. Starting from the ditriflates **2e** and **2g**, the strong base sodium *tert*-butoxide was no longer considered. Instead caesium carbonate was used as base in THF together with a $Pd(OAc)_2$/BINAP catalyst system.[44] With these conditions, comparable yields were obtained for the ditriflates as for the dibromides providing good access to the 4,4′-diaminobiphenyl systems required for both strategies. It is noteworthy that all these biphenyl diamine derivatives **3a**–**3g** displayed limited stability due to immediate partial oxidation when exposed to air. Thus, elemental

analysis was obtained for the corresponding bis(trifluoroacetic acid) salts, which displayed considerably improved stabilities.

With the series of diamines **3a**–**3g** in hand, the strategy **A**–**D** (Scheme 3) was investigated first, again using the parent 4,4′-diaminobiphenyl **3a** as model compound to explore the potential of the envisaged synthetic route. To distinguish between both terminal amines protection with a benzoyl protection group was considered, which was reported to provide selectively only the monoprotected derivative of 1,4-diaminobenzene.[40] In analogy to the reported procedure, the diamine **3a** was dispersed in water by adding sodium dodecyl sulfate (SDS) and benzoic anhydride dissolved in acetonitrile was added at once. After work-up and recrystallization from hot toluene a yield of only 50% of the desired monoprotected diamine **4a** was obtained, pointing at its almost statistical formation. As the selectivity in the case of 1,4-diaminobenzene probably arises from the different solubilities of the unprotected and the monoprotected form, which precipitates the desired monoprotected product out of the reaction mixture, the fact that **3a** in water with SDS was a dispersion rather than a solution already raised questions whether this strategy towards monoprotected diamines will be generally applicable to the series of diamines **3a**–**3g**, for which differences in their solubility features had been expected.

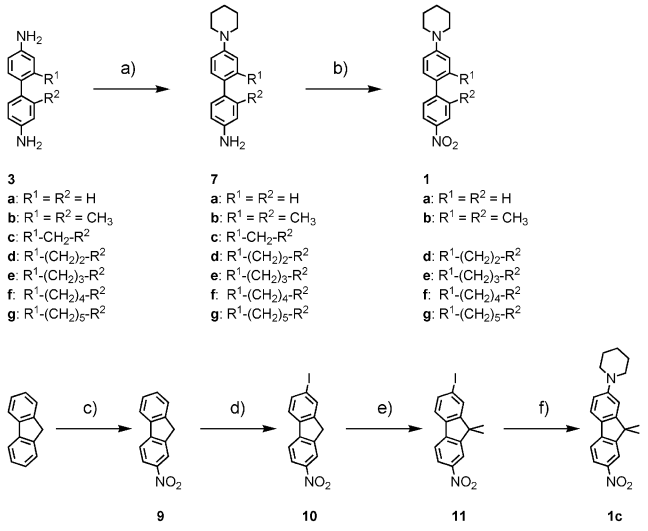


Scheme 3. Synthetic steps along the strategy **A**–**D**. Reagents and conditions: a) benzoic anhydride, MeCN, H_2O, SDS, room temp., 10 min, 50%; b) $NaBO_3{\cdot}4H_2O$, AcOH, 55–60 °C, 16 h, quant.; c) 10 M aq. KOH, DMSO, 80 °C, 60 h, 25%; d) 1,5-dibromopentane, K_2CO_3, toluene/EtOH, 1:1, MW, 150 °C, 40 min, 40%.

However, with reasonable quantities of **4a** in hand we further investigated the proposed strategy. Interestingly, the benzoyl protection group should also support the control over the oxidation of the remaining amine, as deactivated anilines containing electron-withdrawing groups are smoothly oxidized to the corresponding nitroarenes upon treatment with sodium perborate, whereas activated anilines containing electron-donating groups notoriously tend to overoxidation.[45] And indeed, treating the monoprotected **4a** with an excess of sodium perborate tetrahydrate in acetic acid at 60 °C provided the protected nitro derivative **5a** quantitatively without overoxidation. Strong basic conditions were considered to cleave the benzamide protection group of **5a**. By treatment with 10 M aqueous potassium hydroxide in dimethyl sulfoxide (DMSO)[46] the amine **6a** was obtained in a poor yield of 25% after CC as a red solid. As there was only a final step remaining the synthetic strategy **A**–**D** was accomplished in spite of the poor yield of this intermediate step. An azacycloalkylation was suggested to transform the remaining amine group of **6a** into a piperidinyl substituent. While piperidine subunits are usually introduced as nucleophiles substituting a halide in an Ullmann-type coupling reaction,[47–49] double alkylation of arylamines and hydrazines with alkyl dihalides based on a microwave-assisted approach was reported recently.[50,51] Thus, the amino biphenyl **6a** was treated with 1,5-dibromopentane and potassium carbonate as a base in a toluene/ethanol (1:1) mixture at 150 °C for 40 min in the microwave set-up. The desired 4-nitro-4′-piperidinyl-biphenyl (**1a**) was isolated in 40% yield as an orange solid by CC.

With the formation of the model compound **1a** the entire strategy **A**–**D** was accomplished, but several steps with moderate to poor yields considerably disfavour this approach. Initial attempts to apply the same strategy to the fluorene diamine starting compound **3c** provided even lower yields of the monoprotected intermediate **4c** than observed in the case of **4a**, further disqualifying the synthetic strategy.

The major drawback of the alternative strategy **E**–**F** was the statistical introduction of the piperidinyl substituent, even though the resulting mixture was expected to be easily separable into its components by CC. Furthermore, selective oxidation of primary amines in the presence of tertiary ones is synthetically challenging. However, as the yield of monoprotection of the strategy **A**–**D** did not exceed statistical values, the approach **E**–**F** with a reduced number of synthetic steps moved again into the focus of interest. The two synthetic steps are displayed in Scheme 4. To transform one



Scheme 4. Top: synthesis of the target structures **1a**–**b** and **1d**–**g** following the strategy **E**–**F**. Bottom: synthesis of the target structure **1c** based on an individual strategy. Reagents and conditions: a) 1,5-dibromopentane, K_2CO_3, toluene/EtOH, 1:1, MW, 150 °C, 40 min, 34–44%; b) $NaBO_3{\cdot}4H_2O$, $H_3PW_{12}O_{40}$, CTAB (hexadecyltrimethylammonium bromide) (10 cmc in water), 55–60 °C, 16 h, 45–64%; c) HNO_3/AcOH, –43 °C, 6 h, 15%; d) I_2, AcOH, room temp., 10 min, then concd. H_2SO_4, $NaNO_2$, reflux, 30 min, 76%; e) MeI, KI, KOH, DMSO, room temp., 2 h, 95%; f) piperidine, CsOAc, CuI, DMSO, 90 °C, 24 h, 15%.

Table 1. Screening results for the reaction of **3a** to **7a**.

	Solvent	Equiv. dihalide	Temperature [°C]	Reaction time [min]	Obtained ratio (mono/di)	Conversion[a] (mono+di)
1	water	1.10	120	20	50:50[b]	20%
2	water	1.10	150	40	45:55	47%
3	toluene/water 1:1	1.10	120	40	100:0	14%
4	toluene/water 1:1	1.10	120–150	40	mono > di[b]	40%
5	toluene/EtOH 1:1	1.10	150	40	84:16	50%
6	toluene/EtOH 1:1	1.50	145	40	77:23	53%
7	toluene/EtOH 10:1	1.10	80	40	100:0	2%
8	acetone	1.10	75	40	100:0	14%

[a] Conversion is related to the reisolated starting material. [b] Ratios determined qualitatively by TLC.

of the two terminal amino groups of the model compound **3a** into a piperidinyl substituent, a microwave-assisted double alkylation with 1,5-dibromopentane[50] was considered,[51] mainly due to its reported superior yields compared with thermally activated heterocyclization reactions of aniline derivatives. Following a reported protocol,[51] commercially available 4,4′-diaminobiphenyl (**3a**) was treated in the microwave reactor with 1,5-dibromopentane in water with potassium carbonate (K_2CO_3) as a base. The desired mono-piperidinyl derivative **7a** was isolated in a poor yield of only 10% and the formation of a black tar at the bottom of the reaction vessel, probably arising from the large amount of undissolved starting material was observed. In a second attempt toluene was added to increase the solubility of **3a**. The two-phase mixture was exposed for 20 min to microwave irradiation at 120 °C. To our surprise only the formation of the mono-piperidinyl derivative **7a** was observed by TLC with comparable low yields as obtained in pure water. Inspired by this unexpected chemoselectivity different solvent mixtures were screened, as summarized in Table 1. The yields of the reactions were determined by reverse phase HPLC (RP18) using acetonitrile as eluent.

In water almost equal quantities of mono- and dipiperidinyl (45:55) functionalized biphenyl were observed and large amounts of starting material was lost to side reactions (Entries 1 and 2). By addition of toluene both starting materials, the benzidine **3a** and the 1,5-dibromopentane, were dissolved in the organic phase while the microwave energy was absorbed by the aqueous phase. While the promising chemoselectivity of the system was corroborated (Entries 3 and 4), low yields disfavoured these reaction conditions. To bring the microwave absorbing species into the organic phase, ethanol (EtOH) was considered instead of water. In a 1:1 mixture of toluene and ethanol a conversion of 50% of the starting benzidine **3a** was observed with a chemoselectivity of 84:16 in favour of the desired mono-piperidinyl-substituted biphenyl system **7a** (Entry 5). A further increase in the dibromopentane concentration decreased the chemoselectivity by a comparable conversion (Entry 6), while a decrease in the EtOH fraction (Entry 7) or the use of acetone as neat solvent (Entry 8) increased the chemoselectivity by drastically reducing the conversion. We hypothesize that the activated secondary amine of the formed mono-piperidinyl-functionalized biphenyl system might be partially protonated during the reaction to explain its surprising stability towards a second cycloalkylation reaction. This hypothesis is further corroborated by the fact that K_2CO_3 is not dissolved in the most promising solvent mixture (toluene/EtOH, 1:1) suggesting the deprotonation at the phase boundary as the rate determining and reaction controlling step.

The best compromise between chemoselectivity and conversion was found empirically for entry 5 and similar reaction conditions were thus applied for the transformations of the diamines **3b**–**3g** to the piperidine derivatives **7b**–**7g**. The obtained yields and observed chemoselectivities are summarized in Table 2. For all diamines yields between 30% and 45% of the corresponding mono-piperidinyl-functionalized biphenyl system were obtained, pointing at the general applicability of the transformation procedure. With the exception of the fluorene derivative **7c**, very comparable chemoselectivities were observed. The slightly increased formation of the doubly piperidinyl-functionalized fluorene may point at an increased activation of the second amine by the first piperidinyl substituent due to the pronounced electronic coupling of both phenyl rings in the flat fluorene core.

Table 2. Azacycloalkylation of amines **3a**–**3g**.

Product	% Yield[a]	Selectivity (mono/di)
7a	41	42:8
7b	40	n.d.
7c	43	43:15
7d	44	44:7
7e	32	32:3
7f	41	41:5
7g	34	34:8

[a] Yields of the desired monoazacycloalkylated products **7** isolated by CC.

Finally, to accomplish the synthesis of the target structures **1a**–**1g**, the remaining amino group had to be oxidized to a nitro group. Unfortunately, most oxidants that are routinely used for the oxidation of primary amines to nitro groups are also able to oxidize tertiary amines. And indeed, immediate overoxidation to 1-(4′-nitrobiphenyl-4-yl)piperidine 1-oxide (isolated and characterized by ^{1}H NMR and IR spectroscopy) was observed by applying standard oxidation conditions such as in situ generated peracetic acid as an oxidizing agent and sulfuric acid as a catalyst, or sodium perborate in acetic acid.[45,52] Smooth oxidation conditions

for the conversion of anilines to nitrobenzene derivatives profiting from a water soluble tungstophosphoric acid ($H_3PW_{12}O_{40}$·nH_2O) as catalyst and phase-transfer oxidant and sodium perborate as an oxidant in micellar media have been reported.[53] According to the hypothesized mechanism, oxidation occurs in micelles of organic molecules where the concentration of the sterically demanding active species is low, providing very mild oxidation conditions.[54,55] By applying the described conditions to compound **7a** (Scheme 4), the target push-pull system **1a** was isolated in 55% yield after CC as a red solid without detectable formation of the *N*-oxide.

Similar reaction conditions applied to the diamines **3a**–**3g** provided the desired target structures **1b** and **1d**–**1g** in reasonable yields between 45% and 64%. However, in the case of the fluorene derivative **7c** the formation of the desired nitro derivative was not observed, probably different solubility properties of **7c** arising from the acidity of the hydrogen-atoms in C9 position avoided its oxidation. Nevertheless, besides the moderate yields it is noteworthy that, to the best of our knowledge, it is the first time that suitable oxidation conditions for oxidation of primary amines to nitro groups in the presence of alkylated amino groups were found. As displayed at the bottom of Scheme 4, the terminally nitro- and piperidinyl-substituted fluorene derivative **1c** comprising two methyl groups at the C9 position was synthesized based on previously reported synthetic steps.[47,56] In short, nitration and iodination of fluorene provided the terminally nitro- and iodo-functionalized fluorene **10**, which was methylated to remove the acidic hydrogen-atoms in the C9 position. Finally, the piperidine group was introduced by substituting the iodine atom in an Ullmann coupling-reaction to provide **1c** as a red solid in poor yields of about 2% over the four steps. However, the focus was set on the completion of the series of model compounds and thus this already reported procedure was not further optimized for the system under investigation.

All new compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and refraction index or melting points. The purity of the target structures is further documented by elemental analysis.

Summarizing the synthetic section, with the strategy **E**–**F** almost the entire series of push-pull model compounds was obtained in reasonable quantities enabling NLO investigations. Despite only moderate yields for both steps (**E**: 30–45%; **F**: 45–64%), the shortness and the general applicability clearly favours this strategy over the initially privileged approach **A**–**D**.

Optical Properties

The π-conjugation in the bridged target compounds **1c**–**1g** was investigated by UV/Vis measurements. The in 2 and 2′ position unsubstituted push-pull system **1a** showed absorption maxima at 268 (ε = 19840 L mol^{-1} cm^{-1}) and 398 nm (ε = 19646 L mol^{-1} cm^{-1}). The shorter wavelength absorption band can be assigned to a subfragment band of the biphenyl unit. The observed bathochromic shift compared to biphenyl (247 nm) probably arises from enlargement of the conjugated π-system due to substitution with lone pair containing nitrogen units.[57] The long wavelength absorption λ_{max} at 398 nm which levels off around 560 nm is assigned to a charge-transfer band.[58,59] Because a strong donor and a strong acceptor was used in the target push-pull systems **1c**–**1g**, the participation of the HOMO–LUMO transition decreases considerably for the long-wavelength absorption and the ICT-affected correction term reaches zero. Thus λ_{max} values of this charge-transfer band were used as indicator of the π-conjugation instead of its onset which reflects the HOMO–LUMO transition.[58] The subfragment absorption (λ_{max} ca. 268 nm) remains the same throughout the whole series, whereas a hypsochromic as well as a hypochromic shift was observed for the charge-transfer absorption with increasing torsion angle Φ (Figure 2). Values for Φ were obtained by semi-empirical calculations (MOPAC 2002 program[60] using the AM1 semi-empirical Hamiltonian[61]). The absorption data for the bridged compounds **1c**–**1g** are summarized in Table 3.

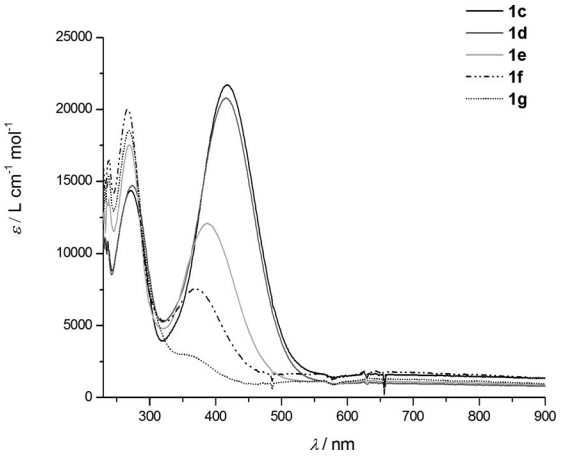


Figure 2. Cumulated absorption spectra of the push-pull systems **1c**–**1g**.

Table 3. λ_{max} of the CT-bands and the corresponding extinction coefficients ε of **1c**–**1g**.

	$\lambda_{max.}$(CT) [nm]	ε [L mol^{-1} cm^{-1}]
1c	418	21703
1d	416	20782
1e	388	12074
1f	371	7551
1g	351	3019

The hypochromic shift can be explained by an increase in the transition energy due to larger torsion angles when going from **1c** to **1g**. By increasing torsion angle Φ the conjugation is less pronounced leading to higher excitation energies and therefore to absorption at lower wavelengths. According to studies of similar compounds the hypsochromic shift can be related to $\cos^2(\Phi)$ (Figure 3).[58,59]

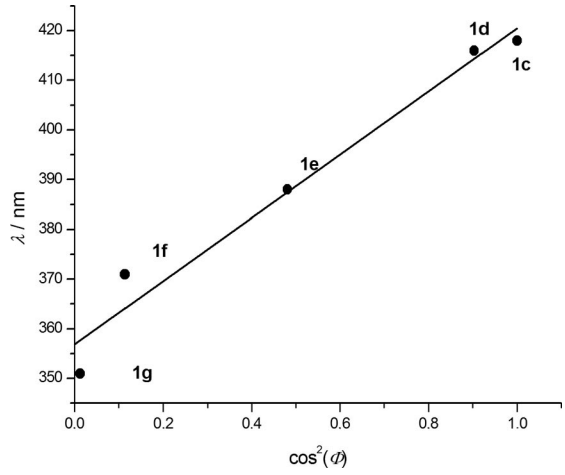


Figure 3. Correlation of λ_{max} to the calculated $\cos^2(\Phi)$.

This correlation beautifully illustrates the dependence of the conjugation to the torsion angle Φ in such biphenyl systems.

Quadratic Response

The molecular $\mu\beta$ values were measured using an EFISH setup.[62] Multiple measurements were performed for each molecule with different concentrations. The experimental results are shown in Table 4. The experimental uncertainties vary from 5% to 15% as the signal level intensities decrease except for **1b** for which the spread in repeated measurements was unusually large. The numerical simulations were performed with the MOPAC 2002 program[60] using the AM1 semi-empirical Hamiltonian.[61] The permanent ground-state dipole moments and the zero frequency hyperpolarizability tensor components obtained for the resulting equilibrium geometry have been combined to yield the theoretical $\mu\beta$ values listed in Table 4, together with the optimized inter-aryl torsion angle.

Table 4. Experimental EFISH results, two-level-system extrapolated zero-frequency values and MOPAC 2002 predictions with the AM1 Hamiltonian expressed in 10^{-48} esu.

	$\mu\beta$(1.907 μm)	$\mu\beta$(0) from TLS	$\mu\beta$(0) by AM1	Torsion angle[a]
1a	245 ± 15	190	136	38.4°
1b	70 ± 35	55	83	58.4°
1c	410 ± 40	300	192	0.1°
1d	400 ± 20	295	163	18.1°
1e	230 ± 10	180	132	46.1°
1f	130 ± 20	105	76	70.3°
1g	75 ± 10	60	62	83.5°

[a] Equilibrium position torsion angle.

The predicted response is consistently 30% below the experimental values extrapolated to zero frequency with the dispersion relation of the two-level model[14] using the CT-band frequencies deduced from the UV/Vis absorption spectra. This trend is not followed by the open dimethyl compound (**1b**) nor by the one containing the longest bridge (**1g**): the dynamical variations in torsion angles driven by solvent motion are the most likely explanations for these exceptions. Indeed, especially for compound **1b**, the equilibrium geometry corresponds to the lowest torsion angle, i.e. the best conjugation, compatible with the steric constrains. In this situation, the calculations will overestimate the actual response because less favourable geometries are not taken into account. It is noteworthy that the 2,2′-dimethyl biphenyl building block has already been integrated in molecular devices to tailor electronic transport properties.[35,63] In these compounds the interring torsion angle of the 2,2′-dimethyl biphenyl subunit was found to be close to 90°, at least in the solid state. Assuming a comparable torsion angle Φ for **1b**, the measured and calculated values would be shifted horizontally to $\cos^2(\Phi) = 0$ and would fit nicely with the linear progression calculated for the remaining members of the series.

The quadratic NLO responses have been plotted as a function of the $\cos^2(\Phi)$ of the equilibrium torsion angle in Figure 4. The finite-frequency, zero-frequency and finite-field results give rise to nearly linear progressions, if we overlook the values for compound **1b** as argued above.

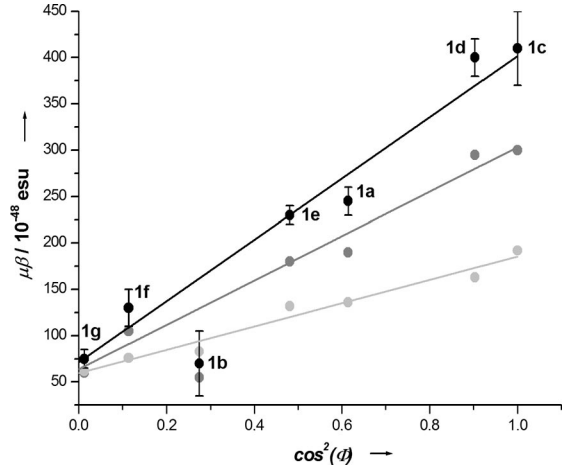


Figure 4. Quadratic nonlinear response as a function of the calculated equilibrium torsion angle Φ. Black curve: EFISH results; grey curve: scaled results; light grey curve: MOPAC 2002 predictions with the AM1 Hamiltonian. The values of compound **1b** were not considered for the least-squares fits displayed by the solid lines.

The finite-frequency measurements include the dispersion effect resulting from the shifts in transition energies of the absorption bands, but, because of the excitation wavelength used, it is hardly discernible in the plot. In any case, the fact that the dispersion corrected results follow the $\cos^2(\Phi)$ law almost as well as the calculated values is an indication that it is the overlap between the π_z orbitals of the central carbon atoms which is the relevant parameter. Because the absorption bands at short wavelengths show much less dependence on torsion angle than the CT bands, we may assume that the two-level model should be able to account for the observed trend. In this model, the quadratic response is proportional to the product of the oscillator strength, the change in dipole moment upon excitation and the ground-state dipole moment. We are thus led to the

conclusion that the dominant effect of increasing torsion angles lies in the resulting loss of oscillator strength while the permanent dipoles of the ground and the CT states are affected to a lesser degree.

Conclusions

To provide a series of push-pull systems that vary in the extent of π-conjugation of their central chromophores, a universal synthetic route towards terminal piperidinyl- and nitro-functionalized biphenyls comprising a restricted inter-ring torsion angle due to an interlinking chain of varying length between the 2 and 2′ position was developed. By following the most straightforward synthetic pathway **E**–**F**, target molecules **1a**–**1g** were synthesized, starting from the corresponding dibromo or ditriflate derivatives **2a**–**2g** in only three steps (Scheme 4). Conditions for a Hartwig–Buchwald hetero-cross-coupling reaction to exchange the bromide and triflate substituents to amino groups were developed with the biphenyl model compound **2a**, using benzophenone imine as an ammonia synthon. Similar reaction conditions were subsequently successfully applied to all biphenyl dihalides **2b**–**2d** and **2f** and ditriflates **2e** and **2g**, providing the corresponding diamines **3a**–**3g** in good yields. Furthermore, a microwave-assisted azacycloalkylation allowed the rather selective and inexpensive assembly of a piperidine ring at only one terminal amine group of the diaminobiphenyls **3a**–**3g**. By systematic solvent-screening encouraging selectivities and moderate conversions were reached with all diamines to provide the amino-piperidinyl derivatives **7a**–**7g**. Finally, a mild and selective oxidation of aminobiphenyls bearing a piperidinyl donor group was developed and applied successfully to the synthesis of model compounds **1a**, **1b** and **1d**–**1g**. The series was complemented by the dimethylfluorene derivative **1c**, which was assembled by an alternative route. The NLO properties of this series of torsion-angle-restricted, biphenyl-based push-pull systems have been successfully investigated by EFISH measurements. The results agree qualitatively with semi-empirical simulations based on the AM1 Hamiltonian. In particular, the linear dependence of the quadratic response on the $\cos^2(\Phi)$ of the inter-aryl dihedral angle points to oscillator strength loss as the dominant effect of increasing backbone twist, which would indicate that the change in permanent dipole moment upon CT transition is much less affected. To probe this aspect will require conducting experiments where the chromophores are excited at resonance, such as two-photon absorption cross-section measurements. It will then be of interest to see how more sophisticated electronic structure calculations will fare in describing the effect of the gradual twist of the conjugation path.

Experimental Section

General Remarks: All chemicals were directly used for the syntheses without purification where nothing else is remarked. Dry solvents were purchased from Fluka. The solvents for chromatography and extractions were distilled before use. When the Schlenk technique was used, the solvents were degassed with argon for several minutes. Characterizations were performed with the following instruments: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DPX NMR (400 MHz) or a Bruker BZH NMR (250 MHz) instrument, the *J* values are given in Hz (± 0.1 Hz). Mass spectra were recorded with a Bruker Esquire 3000 plus (for ESI), a Finnigan MAT 95Q (for EI) or a Voyager-De™ Pro (for MALDI-TOF) instrument. The elementary analyses were performed with an Analysator 240 instrument from Perkin–Elmer. The absorption spectra were recorded with an Agilent 8453 Diode Array Spectrophotometer using 1 cm cuvettes (1×10^{-5} M solutions in chloroform). The measurements were performed at room temperature. For column chromatography silica gel 60 (40–63 μm) from Fluka was used. TLC was carried out on silica gel 60 F_{254} glass plates with a thickness of 0.25 mm from Merck. Elementary analysis of the diamines **3f**–**3g** was performed on the TFA salts of these compounds. This was not possible for amines **7a**–**7g** because of the air sensitivity of these compounds.

EFISH Measurements: The excitation source was a Nd:YAG laser, actively Q-switched at 10 Hz, emitting 7 ns pulses at 1.064 μm wavelength. In order to avoid absorption of the fundamental and second harmonic beams, the pulses were Raman-shifted to 1.907 μm through a high-pressure hydrogen cell, bringing the second-harmonic signal to 953 nm, beyond the absorption band of the studied molecules. The nonlinear signal was selected by using an appropriate interferential filter placed before a photomultiplier.

In order to determine the absolute value of the second-harmonic generation, a quartz wedge was used as a reference,[14] taking its quadratic susceptibility $d_{11} = 1.2 \times 10^{-9}$ esu at 1.064 μm and extrapolating it to 1.1×10^{-9} esu at 1.907 μm. The molecules in chloroform were oriented by an electrical pulse of 2 kV/mm amplitude and of 5 μs duration synchronized to the laser excitation.

Representative Procedure A (Syntheses of Diamino Derivatives 3):[44] Toluene was degassed in an oven-dried Schlenk tube. In a Schlenk tube $Pd_2(dba)_3 \cdot CHCl_3$ (4 mol-%) and BINAP (12 mol-%) were dissolved in degassed toluene (0.16 M with respect to the dibromobiphenyl). The black solution was stirred for 15 min at room temp., while dibromobiphenyl (**2**) and NaO*t*Bu were added. To this dark-red solution benzophenone imine was added dropwise. The red reaction mixture was stirred at 80 °C until the starting material had been consumed as monitored by TLC. Afterwards, the mixture was cooled to room temp. and diluted with diethyl ether (4 × volume of toluene). The suspension was filtered through Celite and concentrated under reduced pressure. The crude was purified by recrystallization from methanol to afford *N*,*N*-bis(diphenylmethylene)biphenyldiamine (**8**) as a yellow solid. Diimine **8** was dissolved in THF (0.15 M) and 3 M aq. HCl (30% by volume of THF) was added. The pale yellow reaction mixture was stirred at room temp. until the starting material was consumed as monitored by TLC. Afterwards the solution was partitioned between 0.5 M aq. HCl and hexane/EtOAc (2:1). The organic layer was washed three times with 0.5 M aq. HCl and the combined aqueous layers made alkaline with 1 M aq. NaOH. The brown liquid was extracted with dichloromethane, dried with sodium sulfate, filtered, and concentrated in vacuo. The crude was purified by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3) to afford diamine **3**.

Benzidine (3a): From 4,4′-Dibromobiphenyl (200 mg, 1.00 equiv., 0.641 mmol) (**2a**), N^4,$N^{4\prime}$-bis(diphenylmethylene)biphenyl-4,4′-diamine (**8a**) (177.5 mg, 54%) was obtained as a yellow solid after purification by column chromatography (SiO_2, hexane/EtOAc, 5:1, 5% NEt_3) and recrystallization from methanol. Diimine **8a**

(73.0 mg, 1.00 equiv., 0.142 mmol) was cleaved following general procedure A to achieve benzidine (**3a**) (21.5 mg, 82%).

Analytical Data of 8a: M.p. 237–239 °C; R_f = 0.24 (hexane/EtOAc, 5:1, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H), 7.47 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H), 7.41 (m, 4 H), 7.34 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H), 7.30–7.24 (m, 6 H), 7.18–7.12 (m, 4 H), 6.75 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.6 (C_q, 2 C), 150.5 (C_q, 2 C), 140.2 (C_q, 2 C), 136.7 (C_q, 2 C), 135.9 (C_q, 2 C), 131.1 (C_t, 2 C), 130.0 (C_t, 4 C), 129.8 (C_t, 4 C), 129.1 (C_t, 2 C), 128.6 (C_t, 4 C), 128.5 (C_t, 4 C), 127.0 (C_t, 4 C), 121.9 (C_t, 4 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 514 (25), 513 (53), 512 (100). $C_{38}H_{28}N_2$ (512.65): calcd. C 89.03, H 5.50, N 5.46; found C 88.81, H 5.67, N 5.23.

Analytical Data of 3a: M.p. 118 °C; R_f = 0.26 (hexane/EtOAc, 1:1, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H), 6.72 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H), 3.65 (br. s, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.4 (C_q, 2 C), 132.2 (C_q, 2 C), 127.7 (C_t, 4 C), 115.9 (C_t, 4 C) ppm. IR: $\tilde{\nu}$ = 3402 (w), 3319 (w), 3171 (w), 3019 (w), 1602 (m), 1496 (s), 1263 (s), 1175 (m), 848 (s) cm^{-1}. MS (EI^+, 70 eV): *m*/*z* (%) = 185 (13), 184 (100), 183 (10), 156 (5), 92 (7).

9*H*-Fluorene-2,7-diamine (3c): General procedure A was followed using 1.00 g (1.00 equiv., 3.09 mmol) 2,7-dibromofluorene (**2c**) to afford 440 mg (81%) 2,7-diamino-9*H*-fluorene (**3c**) after purification by column chromatography (SiO_2, hexane/EtOAc, 1:3, 5% NEt_3).

Analytical Data of 8c: M.p. 219–220 °C; R_f = 0.27 (hexane/EtOAc, 1:3, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H), 7.46 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H), 7.42–7.38 (m, 6 H), 7.28–7.23 (m, 6 H), 7.17–7.13 (m, 4 H), 6.89–6.86 (m, 2 H), 6.66 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.9 Hz, 2 H), 3.62 (s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 167.8 (C_q, 2 C), 149.7 (C_q, 2 C), 143.7 (C_q, 2 C), 139.9 (C_q, 2 C), 137.1 (C_q, 2 C), 136.4 (C_q, 2 C), 130.6 (C_t, 2 C), 129.6 (C_t, 4 C), 129.3 (C_t, 4 C), 128.5 (C_t, 2 C), 128.2 (C_t, 4 C), 128.0 (C_t, 4 C), 119.9 (C_t, 2 C), 119.2 (C_t, 2 C), 118.0 (C_t, 2 C), 36.8 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 526 (6), 525 (11), 524 (100).

Analytical Data of 3c: M.p. 168–169 °C; R_f = 0.12 (hexane/EtOAc, 1:1, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.42 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.85–6.82 (m, 2 H), 6.67 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.2 Hz, 2 H), 3.72 (s, 2 H), 3.65 (br. s, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 144.3 (C_q, 2 C), 144.1 (C_q, 2 C), 133.5 (C_q, 2 C), 119.2 (C_t, 2 C), 113.8 (C_t, 2 C), 112.0 (C_t, 2 C), 36.7 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 197 (38), 196 (100).

9,10-Dihydrophenanthrene-2,7-diamine (3d): General procedure A was followed using 400 mg (1.00 equiv., 1.18 mmol) 2,7-dibromo-9,10-dihydrophenanthrene (**2d**) to afford 584 mg (92%) N^2,N^7-bis(diphenylmethylene)-9,10-dihydrophenanthrene-2,7-diamine (**8d**) as a pale yellow powder. The diimine **8d** (570 mg, 1.00 equiv., 1.08 mmol) was used without further purification to achieve diamine **3d** (185 mg, 83%) after purification by column chromatography (SiO_2, hexane/EtOAc, 1:5, 5% NEt_3) as a white solid.

Analytical Data of 8d: M.p. 230 °C; R_f = 0.47 (hexane/EtOAc, 5:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.74 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H), 7.46 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 7.42–7.37 (m, 6 H), 7.29–7.23 (m, 6 H), 7.17–7.13 (m, 4 H), 6.62 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.55 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.2 Hz, 2 H), 2.64 (s, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 167.8 (C_q, 2 C), 149.8 (C_q, 2 C), 139.8 (C_q, 2 C), 137.2 (C_q, 2 C), 136.4 (C_q, 2 C), 130.6 (C_t, 2 C), 129.7 (C_q, 2 C), 129.5 (C_t, 4 C), 129.3 (C_t, 4 C), 128.6 (C_t, 2 C), 128.2 (C_t, 4 C), 128.0 (C_t, 4 C), 123.3 (C_t, 2 C), 121.0 (C_t, 2 C), 119.5 (C_t, 2 C), 29.0 (C_s, 2 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 540 (98), 539 (100).

Analytical Data of 3d: M.p. 157–159 °C; R_f = 0.43 (hexane/EtOAc, 1:5, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.44 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 6.59 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.4 Hz, 2 H), 6.53 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H), 3.61 (br. s, 4 H), 2.74 (s, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 144.6 (C_q, 2 C), 137.6 (C_q, 2 C), 125.9 (C_q, 2 C), 123.7 (C_t, 2 C), 114.7 (C_t, 2 C), 113.7 (C_t, 2 C), 29.4 (C_s, 2 C) ppm. MS (EI^+, 70 eV): *m*/*z* (%) = 211 (16), 210 (100), 209 (27).

3,10-Diamino-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (3f): From dibromide **2f** (1.20 g, 1.00 equiv., 3.28 mmol), diimine **8f** (1.57 g, 85%) was obtained as a yellow powder. Diimine **8f** (1.56 g, 1.00 equiv., 2.76 mmol) was cleaved following general procedure A yielding in 605 mg (71%) of the diamine **3f** as a white solid after purification by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3). For analytical purpose a small amount of **3f** was dissolved in 2-propanol. While stirring at room temp., concd. TFA (1 mL) was added in one lot. The solution was stirred at room temp. for 15 min. Afterwards the TFA salt of **3f** was precipitated with ice cold Et_2O, filtered, washed with plenty of ether and dried.

Analytical Data of 8f: M.p. 121–122 °C; R_f = 0.34 (hexane/EtOAc, 5:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.77 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H), 7.47 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 7.44–7.38 (m, 4 H), 7.30–7.21 (m, 6 H), 7.16–7.10 (m, 4 H), 6.97 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.61 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.53 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H), 2.41 (dd, $^2J_{H,H}$ = 13.1, $^3J_{H,H}$ = 8.3 Hz, 2 H), 1.89–1.76 (m, 4 H), 1.15–1.05 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.3 (C_q, 2 C), 150.6 (C_q, 2 C), 142.8 (C_q, 2 C), 139.7 (C_q, 2 C), 136.4 (C_q, 2 C), 135.5 (C_t, 2 C), 130.6 (C_t, 2 C), 129.6 (C_q, 2 C), 129.3 (C_t, 4 C), 129.0 (C_t, 4 C), 128.4 (C_t, 2 C), 128.2 (C_t, 4 C), 127.8 (C_t, 4 C), 121.7 (C_t, 2 C), 118.5 (C_t, 2 C), 32.5 (C_s, 2 C), 29.5 (C_s, 2 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 568 (48), 567 (73), 566 (100).

Analytical Data of 3f: R_f = 0.22 (hexane/EtOAc, 1:1, 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.02 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H), 6.61–6.54 (m, 4 H), 3.62 (br. s, 4 H), 2.57 (dd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 8.5 Hz, 2 H), 2.16–2.06 (m, 2 H), 2.06–1.97 (m, 2 H), 1.51–1.42 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.5 (C_q, 2 C), 143.8 (C_q, 2 C), 131.5 (C_q, 2 C), 130.1 (C_t, 2 C), 115.7 (C_t, 2 C), 112.7 (C_t, 2 C), 32.9 (C_s, 2 C), 29.7 (C_s, 2 C) ppm. MS (EI^+, 70 eV): *m*/*z* (%) = 239 (18), 238 (100), 237 (5), 209 (21), 208 (9), 196 (6), 195 (20), 104 (6). Elemental analysis calcd. for $C_{16}H_{18}N_2$ (TFA salt): C 51.51, H 4.32, N 6.01; found C 51.55, H 4.33, N 5.97.

Representative Procedure B (Syntheses of Diamino Derivatives 3 Starting from the Triflate-Substituted Tricyclic Biphenyl Derivatives):[44] THF (absol.) was degassed by three freeze and thaw cycles. $Pd(OAc)_2$ (10 mol-%), BINAP (15 mol-%), ditriflate (1.00 equiv.) and caesium carbonate (2.80 equiv.) were given in a Schlenk tube and dissolved in degassed THF (0.07 M with respect to the ditriflate). To this yellow/orange suspension benzophenone imine (2.40 equiv.) was added dropwise and the resulting reaction mixture was stirred at 65 °C until the starting material had been consumed as monitored by TLC (overnight). Afterwards, the mixture was cooled to room temp. and diluted with diethyl ether (4 × volume of toluene). The suspension was filtered through Celite and concentrated under reduced pressure. The crude was purified by recrystallization from methanol to afford *N*,*N*-bis(diphenylmethylene)biphenyldiamine (**8**) as a yellow solid. Cleavage of the diimine **8** was performed according to procedure A.

3,9-Diamino-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (3e): According to representative procedure B, ditriflate **2e** (1.40 g, 1.00 equiv., 2.85 mmol) was reacted to diimine **8e** (1.54 g, 98%) which was isolated as a yellow powder. The diimine **8e** was cleaved without further purification. Diimine **8e** (1.51 g, 1.00 equiv., 2.73 mmol) was dissolved in THF (30 mL), adding 3 M aq. HCl (10 mL). Purification of the crude was performed by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3). Diamine **3e** (496 mg, 81%) was isolated as a colourless oil. The TFA salt of **3e** was obtained in the same manner as the TFA salt of **3f**.

Analytical Data of 8e: M.p. 212–213 °C; R_f = 0.41 (hexane/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.76 (d, $^3J_{H,H}$ = 7.2 Hz, 4 H), 7.46 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 7.44–7.38 (m, 4 H), 7.32–7.21 (m, 6 H), 7.18–7.11 (m, 4 H), 7.07 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.63 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.58 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H), 2.23 (t, $^3J_{H,H}$ = 6.9 Hz, 4 H), 1.91 (quint, $^3J_{H,H}$ = 6.9 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.1 (C_q, 2 C), 150.0 (C_q, 2 C), 139.8 (C_q, 2 C), 139.7 (C_q, 2 C), 136.4 (C_q, 2 C), 135.9 (C_t, 2 C), 130.6 (C_t, 2 C), 129.6 (C_q, 2 C), 129.6 (C_t, 4 C), 129.3 (C_t, 4 C), 128.5 (C_t, 2 C), 128.2 (C_t, 4 C), 127.8 (C_t, 4 C), 121.3 (C_t, 2 C), 119.0 (C_t, 2 C), 33.1 (C_s, 1 C), 31.3 (C_s, 2 C) ppm. MS (EI$^+$, 70 eV): *m*/*z* (%) = 554 (9), 553 (42), 552 (100), 475 (6), 276 (8), 237 (5), 199 (13).

Analytical Data of 3e: R_f = 0.34 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.13 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.64 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.4 Hz, 2 H), 6.58 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H), 3.62 (br. s, 4 H), 2.43 (t, $^3J_{H,H}$ = 7.0 Hz, 4 H), 2.12 (quint, $^3J_{H,H}$ = 7.0 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.1 (C_q, 2 C), 140.5 (C_q, 2 C), 131.8 (C_q, 2 C), 128.8 (C_t, 2 C), 115.3 (C_t, 2 C), 113.2 (C_t, 2 C), 32.8 (C_s, 1 C), 31.7 (C_s, 2 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 225 (36), 224 (100). Elemental analysis calcd. (%) for $C_{15}H_{16}N_2$ (TFA salt): C 50.45, H 4.01, N 6.19; found C 49.68, H 4.09, N 6.28.

3,11-Diamino-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (3g): By applying representative procedure B, ditriflate **2g** (1.40 g, 1.00 equiv., 2.70 mmol) was converted to diimine **8g** (930 mg, 60%), which was isolated as a yellow powder. The diimine **8g** was cleaved without further purification, to achieve diamine **3g** (391 mg, quant.) as a colourless oil. The TFA salt of **3g** was obtained in the same manner as the TFA salt of **3f**.

Analytical Data of 8g: M.p. 146–147 °C; R_f = 0.73 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.77 (d, $^3J_{H,H}$ = 7.1 Hz, 4 H), 7.47 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 7.45–7.38 (m, 4 H), 7.31–7.21 (m, 6 H), 7.18–7.11 (m, 4 H), 6.88 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.63 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.47 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H), 2.40–2.29 (m, 2 H), 1.85–1.74 (m, 2 H), 1.55–1.43 (m, 2 H), 1.17–0.97 (m, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.4 (C_q, 2 C), 150.4 (C_q, 2 C), 142.1 (C_q, 2 C), 139.7 (C_q, 2 C), 136.8 (C_q, 2 C), 136.5 (C_t, 2 C), 130.7 (C_t, 2 C), 129.6 (C_t, 4C), 129.3 (C_t, 4 C), 128.9 (C_t, 2 C), 128.4 (C_t, 2 C), 128.2 (C_t, 4 C), 127.8 (C_t, 4 C), 121.1 (C_t, 2 C), 118.4 (C_t, 2 C), 32.9 (C_s, 2 C), 29.0 (C_s, 2 C), 28.0 (C_s, 1 C) ppm. MS (EI$^+$, 70 eV): *m*/*z* (%) = 582 (10), 581 (45), 580 (100), 213 (9).

Analytical Data of 3g: R_f = 0.42 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.91 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H), 6.59–6.53 (m, 4 H), 3.62 (br. s, 4 H), 2.57–2.48 (m, 2 H), 2.14–2.10 (m, 2 H), 1.79–1.68 (m, 2 H), 1.55–1.35 (m, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.2 (C_q, 2 C), 143.3 (C_q, 2 C), 132.7 (C_q, 2 C), 130.1 (C_t, 2 C), 115.3 (C_t, 2 C), 112.5 (C_t, 2 C), 33.2 (C_s, 2 C), 29.0 (C_s, 2 C), 28.2 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 253 (28), 252 (100). Elemental analysis calcd. (%) for $C_{17}H_{20}N_2$ (TFA salt): C 52.50, H 4.62, N 5.83; found C 52.53, H 4.61, N 5.88.

***N*-(4′-Aminobiphenyl-4-yl)benzamide (4a):**[40] To a stirred heterogeneous suspension of diamine **3a** (461 mg, 1.00 equiv., 2.50 mmol) in water (15 mL) sodium dodecyl sulfate (SDS) (120 mg) was added. Then benzoic anhydride (566 mg, 1.00 equiv., 2.50 mmol) dissolved in acetonitrile (2.5 mL) was added at once to the still heterogeneous brown suspension. After stirring for 10 min at room temperature the grey suspension was diluted with acetonitrile (10 mL). After evaporation of the organic solvent solid sodium hydrogen carbonate was added in portions to adjust to pH 7. The remaining aqueous layer containing grey precipitate was filtered and the solid washed with water (100 mL). The solid, grey product **8a** was azeotroped with toluene and dried on high vacuum. The product was dissolved in toluene, and the precipitated byproduct was filtered. The remaining liquid was concentrated to afford product **4a** (363 mg, 50%); m.p. 228 °C; R_f = 0.12 (hexane/EtOAc, 3:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 10.25 (s, 1 H), 7.96 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H), 7.79 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.64–7.50 (m, 3 H), 7.53 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 7.36 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 6.63 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 5.20 (br. s, 2 H) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 25 °C): δ = 165.3 (C_q, 1 C), 147.9 (C_q, 1 C), 137.0 (C_q, 1 C), 136.0 (C_q, 1 C), 135.0 (C_q, 1 C), 131.4 (C_q, 1 C), 128.3 (C_t, 2 C), 127.5 (2 C, C_t), 127.1 (C_t, 1 C), 126.7 (C_t, 2 C), 125.2 (C_t, 2 C), 120.6 (C_t, 2 C), 114.2 (C_t, 2 C) ppm. IR: $\tilde{\nu}$ = 3340 (m), 3039 (w), 1650 (s), 1604 (m), 1512 (s), 1404 (w), 1319 (w), 1265 (w), 903 (w), 810 (s), 710 (m), 648 (s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 288 (100).

***N*-(4′-Nitrobiphenyl-4-yl)benzamide (5a):**[45] Sodium perborate tetrahydrate (544 mg, 5.00 equiv., 3.54 mmol) was dissolved in concd. acetic acid (9 mL) and heated to 60 °C. To this colourless solution a pale brown suspension of *N*-(4′-aminobiphenyl-4-yl)benzamide (**4a**) (204 mg, 1.00 equiv., 0.707 mmol) in concd. acetic acid (14 mL) was added dropwise over a period of 35 min. Afterwards the scarlet red suspension was stirred for 15 h at 60 °C. The pale red suspension containing sodiumborate was cooled down to room temp. and then the solvent was removed under reduced pressure. The brown residue was dissolved in H_2O and EtOAc. The red organic layer was separated, the aqueous layer reextracted with EtOAc (2 × 30 mL). Then the combined organic layers were washed with H_2O (1 × 20 mL) and brine (1 × 20 mL), dried with sodium sulfate, filtered and the solvents evaporated to dryness. Column chromatography with SiO_2 using hexane/EtOAc (1:1) as eluent afforded *N*-(4′-nitrobiphenyl-4-yl)benzamide (**5a**) as a red-brown solid. The crude was recrystallized from methanol and dried in high vacuum for 5 h to afford product **5a** (226 mg, quantitative) as a yellow solid; m.p. 257–258 °C; R_f = 0.25 (hexane/EtOAc, 3:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 10.46 (s, 1 H), 8.30 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 8.00–7.95 (m, 6 H), 7.84 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 7.62 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H), 7.56 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 25 °C): δ = 165.6 (C_q, 1 C), 146.1 (C_q, 1 C), 146.0 (C_q, 1 C), 140.1 (C_q, 1 C), 134.6 (C_q, 1 C), 132.4 (C_q, 1 C), 131.6 (C_t, 1 C), 128.3 (C_t, 2 C), 127.6 (C_t, 2 C), 127.5 (C_t, 2 C), 127.1 (C_t, 2 C), 124.0 (C_t, 2 C), 120.4 (C_t, 2 C) ppm. IR: $\tilde{\nu}$ = 3364 (w), 1659 (s), 1589 (m), 1504 (s), 1420 (w), 1350 (s), 1249 (w), 833 (s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 319 (100).

4′-Nitrobiphenyl-4-amine (6a):[46] *N*-(4′-nitrobiphenyl-4-yl)benzamide (**5a**) (260 mg, 1.00 equiv., 0.817 mmol) was dissolved in dimethyl sulfoxide (5 mL). To this yellow solution 10 M aq. KOH (10 mL) and EtOH (1 mL) was added. The reaction mixture was heated to 80 °C for 60 h, then neutralized with 1 M aq. HCl (until

solution is pale yellow) and extracted with *tert*-butyl methyl ether (3 × 70 mL), dried with sodium sulfate, filtered, and concentrated in vacuo. The resulting oil was purified by column chromatography (SiO_2, toluene/EtOAc, 1:1) to afford 4′-nitrobiphenyl-4-amine (**6a**) (43.3 mg, 25%) as a dark red solid; m.p. 202–203 °C; R_f = 0.53 (toluene/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.24 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.66 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.47 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 6.78 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 3.90 (br. s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 147.5 (C_q, 2 C), 147.5 (C_q, 1 C), 128.5 (C_q, 1 C), 128.4 (C_t, 2 C), 126.4 (C_t, 2 C), 124.1 (C_t, 2 C), 115.3 (C_t, 2 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 216 (17), 215 (64), 214 (60), 198 (100).

1-(4′-Nitrobiphenyl-4-yl)piperidine (1a):[50] 4′-Nitrobiphenyl-4-amine (**6a**) (20.0 mg, 1.00 equiv., 93.4 μmol) was dissolved in toluene (3.5 mL) and ethanol (3.5 mL). The orange solution was transferred to a pressure tube, and potassium carbonate (15.5 mg, 1.20 equiv., 0.112 mmol) and 1,5-dibromopentane (14.0 μL, 1.10 equiv., 0.103 mmol, 23.9 mg) were added. The reaction mixture was placed in a microwave synthesis system operating at 140 °C for 1 h (3 min ramp time). Afterwards the mixture was quenched with water (10 mL) and extracted with dichloromethane (3 × 15 mL). The extract was dried with sodium sulfate, filtered and concentrated under reduced pressure. Purification was performed by column chromatography (SiO_2, CH_2Cl_2). According to this procedure 1-(4′-nitrobiphenyl-4-yl)piperidine (**1a**) (10.5 mg, 40%) was obtained as an orange solid; m.p. 220 °C; R_f = 0.69 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.24 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.69 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.55 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.00 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 3.28 (t, $^3J_{H,H}$ = 5.8 Hz, 4 H), 1.76–1.67 (m, 4 H), 1.67–1.59 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.3 (C_q, 1 C), 147.4 (C_q, 1 C), 146.0 (C_q, 1 C), 128.1 (C_t, 2 C), 127.9 (C_q, 1 C), 126.4 (C_t, 2 C), 124.1 (C_t, 2 C), 115.8 (C_t, 2 C), 49.6 (C_s, 2 C), 25.5 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. IR: $\tilde{\nu}$ = 2949 (w), 2844 (w), 1589 (m), 1506 (s), 1337 (s), 1242 (s), 1224 (s), 1111 (m), 852 (s), 756 (s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 283 (55), 282 (100). $C_{17}H_{18}N_2O_2$ (282.34): calcd. C 72.32, H 6.43, N 9.92; found C 72.02, H 6.51, N 9.93. UV/Vis (chloroform): λ_{max} (ε) = 268 nm (19840 L mol^{-1} cm^{-1}), λ_{max} (ε) = 398 nm (19646 L mol^{-1} cm^{-1}).

Representative Procedure C [Syntheses of 4′-(Piperidin-1-yl)biphenyl-4-amine Derivatives 7]:[50] Diamine **3** (1.00 equiv.) and K_2CO_3 (1.20 equiv.) were weighed into a pressure tube. 1,5-Dibromopentane (1.10 equiv.) was added and the mixture was dissolved in the according solvent system (see Table 1) (0.1 M with respect to the diamine). The reaction tube was placed in a microwave-synthesis system, operated at 150 °C for 40 min. Afterwards 1 M aq. HCl was added and the mixture stirred for another 30 min at room temp. EtOAc was added and the aqueous layer was separated. The organic layer was reextracted twice with 1 M aq. HCl. The combined aqueous layers were made alkaline by 1 M aq. NaOH and extracted with dichloromethane. The pale yellow organic layer was dried with sodium sulfate, filtered and the solvent removed under reduced pressure. The pale brown solid was purified by column chromatography (SiO_2; hexane/EtOAc, 3:1, 5% NEt_3) to afford the product **7**.

4′-(Piperidin-1-yl)biphenyl-4-amine (7a): From benzidine **3a** (50.0 mg, 1.00 equiv., 0.271 mmol) colourless, solid product **7a** (29.5 mg, 43%) and 4,4′-bis(piperidin-1-yl)biphenyl (6.3 mg) were obtained by purification with column chromatography (SiO_2; hexane/EtOAc, 3:1, 5% NEt_3). A second column chromatography (SiO_2, CH_2Cl_2, 3% MeOH) provided pure, colourless, solid product **7a** (29.0 mg, 42%); m.p. 101–102 °C; R_f = 0.86 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.38 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 6.99 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 6.74 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H), 3.67 (s, 2 H), 3.19 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.74 (quint, $^3J_{H,H}$ = 5.6 Hz, 4 H), 1.60 (quint, $^3J_{H,H}$ = 5.6 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 150.7 (C_q, 1 C), 145.0 (C_q, 1 C), 132.1 (C_q, 1 C), 131.6 (C_q, 1 C), 127.3 (C_t, 2 C), 126.9 (C_t, 2 C), 116.7 (C_t, 2 C), 115.4 (C_t, 2 C), 50.7 (C_s, 2 C), 25.8 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. IR: $\tilde{\nu}$ = 3391 (w), 3316 (w), 3208 (w), 3019 (w), 2930 (w), 2809 (w), 1604 (m), 1499 (s), 1447 (m), 1385 (m), 1333 (m), 1264 (s), 1234 (s), 1124 (s), 1023 (m), 918 (m), 803 (s), 578 (s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 253 (26), 252 (100). Side product: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H), 7.00 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H), 3.20 (t, $^3J_{H,H}$ = 5.5 Hz, 8 H), 1.75 (quint, $^3J_{H,H}$ = 5.6 Hz, 8 H), 1.60 (quint, $^3J_{H,H}$ = 5.6 Hz, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 150.8 (C_q, 2 C), 131.8 (C_q, 2 C), 126.9 (C_t, 4 C), 116.7 (C_t, 4 C), 50.6 (C_s, 4 C), 25.8 (C_s, 4 C), 24.3 (C_s, 2 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 321 (17), 320 (100).

2,2′-Dimethyl-4′-(piperidin-1-yl)biphenyl-4-amine (7b): In accordance to general procedure C, 2,2′-dimethylbiphenyl-4,4′-diamine (**3b**) (150 mg, 1.00 equiv., 0.707 mmol) was converted into product **7b** (79.7 mg, 40%), which was isolated as a pale purple powder; m.p. 135–136 °C; R_f = 0.60 (hexane/EtOAc, 3:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.99 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 6.91 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 6.85 (d, $^4J_{H,H}$ = 2.6 Hz, 1 H), 6.80 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.6 Hz, 1 H), 6.61 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H), 6.55 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.5 Hz, 1 H), 3.61 (br. s, 2 H), 3.19 (t, $^3J_{H,H}$ = 5.6 Hz, 4 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.75 (quint, $^3J_{H,H}$ = 5.6 Hz, 4 H), 1.64–1.55 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.0 (C_q, 1 C), 137.3 (C_q, 1 C), 136.9 (C_q, 2 C), 132.2 (C_q, 2 C), 130.7 (C_t, 1 C), 130.5 (C_t, 1 C), 117.7 (C_q, 1 C), 116.3 (C_t, 1 C), 113.6 (C_t, 1 C), 112.3 (C_t, 1 C), 50.8 (C_s, 2 C), 26.0 (C_s, 2 C), 24.3 (C_s, 1 C), 20.3 (C_p, 1 C), 20.0 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 282 (4), 281 (36), 280 (100).

7-(Piperidin-1-yl)-9*H*-fluorene-2-amine (7c): By following the synthetic procedure C, from 2,7-diaminofluorene (**3c**) (250 mg, 1.00 equiv., 1.27 mmol) 7-(piperidin-1-yl)-9*H*-fluorene-2-amine (**7c**) (145 mg, 43%) was obtained. Purification was performed by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3); m.p. 186–187 °C; R_f = 0.36 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.49 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.44 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 7.10 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 6.93 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.1 Hz, 1 H), 6.84 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 6.67 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.1 Hz, 1 H), 3.75 (s, 2 H), 3.65 (br. s, 2 H), 3.16 (t, $^3J_{H,H}$ = 5.4 Hz, 4 H), 1.74 (quint, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.62–1.54 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 150.8 (C_q, 1 C), 144.5 (C_q, 1 C), 144.5 (C_q, 1 C), 143.5 (C_q, 1 C), 134.3 (C_q, 1 C), 133.4 (C_q, 1 C), 119.6 (C_t, 1 C), 118.9 (C_t, 1 C), 115.8 (C_t, 1 C), 113.8 (C_t, 2 C), 112.0 (C_t, 1 C), 51.7 (C_s, 2 C), 36.9 (C_s, 1 C), 26.0 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 266 (25), 265 (98), 264 (100). $C_{18}H_{20}N_2$ (264.37): calcd. C 81.78, H 7.62, N 10.60; found C 81.72, H 7.66, N 10.37.

7-(Piperidin-1-yl)-9,10-dihydrophenanthren-2-amine (7d): The general procedure C was followed using 174 mg (1.00 equiv., 0.829 mmol) 9,10-dihydrophenanthren-2,7-diamine (**3d**). Column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3) was performed to isolate product **7d** (101 mg, 44%) as a red oil. R_f = 0.43 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.52 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.47 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 6.85 (dd, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 2.6 Hz, 1 H), 6.78 (d, $^4J_{H,H}$ =

2.5 Hz, 1 H), 6.61 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.4 Hz, 1 H), 6.54 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H), 3.59 (br. s, 2 H), 3.17 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.83–2.73 (m, 4 H), 1.72 (quint, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.58 (quint, $^3J_{H,H}$ = 5.5 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 144.8 (C_q, 1 C), 137.8 (C_q, 1 C), 137.0 (C_q, 1 C), 123.9 (C_q, 1 C), 123.3 (C_t, 2 C), 116.1 (C_q, 1 C), 115.0 (C_q, 1 C), 114.7 (C_t, 2 C), 113.7 (C_t, 2 C), 50.8 (C_s, 2 C), 29.8 (C_s, 1 C), 29.5 (C_s, 1 C), 25.8 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 279 (100), 278 (95).

3-Amino-9-(piperidin-1-yl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (7e): By following the synthetic procedure C, using 439 mg (1.00 equiv., 1.96 mmol) diamine **3e** product **7e** (224 mg, 39%) was isolated as a colourless oil. Purification was performed by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3). R_f = 0.46 (hexane/EtOAc, 1:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.21 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.14 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 6.87 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 2.6 Hz, 1 H), 6.82 (d, $^4J_{H,H}$ = 2.6 Hz, 1 H), 6.64 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.5 Hz, 1 H), 6.58 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 3.64 (br. s, 2 H), 3.19 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.47 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 2.42 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 2.13 (quint, $^3J_{H,H}$ = 7.0 Hz, 2 H), 1.77–1.69 (m, 4 H), 1.62–1.54 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 145.1 (C_q, 1 C), 140.6 (C_q, 1 C), 140.1 (C_q, 2 C), 131.7 (C_q, 1 C), 128.8 (C_q, 1 C), 128.4 (C_q, 2 C), 116.7 (C_t, 1 C), 115.2 (C_t, 1 C), 114.3 (C_t, 1 C), 113.1 (C_t, 1 C), 50.9 (C_s, 2 C), 32.9 (C_s, 1 C), 32.1 (C_s, 1 C), 31.7 (C_s, 1 C), 25.9 (C_s, 2 C), 24.2 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 293 (62), 292 (100).

3-Amino-10-(piperidin-1-yl)-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (7f): By applying general procedure C, diamine **3f** (581 mg, 1.00 equiv., 2.44 mmol) was converted into product **7f** (308 mg, 41%), which was isolated as a colourless oil. Purification was performed by column chromatography (SiO_2, hexane/EtOAc, 1:1, 5% NEt_3). R_f = 0.31 (hexane/EtOAc, 3:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.10 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.03 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H), 6.86–6.79 (m, 2 H), 6.60 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H), 6.58 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 2.4 Hz, 1 H), 3.62 (br. s, 2 H), 3.19 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.68–2.52 (m, 2 H), 2.22–1.96 (m, 4 H), 1.73 (quint, $^3J_{H,H}$ = 5.5 Hz, 2 H), 1.63–1.54 (m, 2 H), 1.54–1.44 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 151.5 (C_q, 1 C), 145.5 (C_q, 1 C), 143.8 (C_q, 1 C), 143.3 (C_q, 1 C), 132.0 (C_q, 1 C), 131.5 (C_q, 1 C), 130.0 (C_t, 1 C), 129.7 (C_t, 1 C), 117.0 (C_t, 1 C), 115.7 (C_t, 1 C), 113.8 (C_t, 1 C), 112.7 (C_t, 1 C), 50.7 (C_s, 2 C), 33.4 (C_s, 1 C), 32.9 (C_s, 1 C), 29.8 (C_s, 1 C), 29.7 (C_s, 1 C), 26.0 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 308 (13), 307 (26), 306 (100).

3-Amino-11-(piperidin-1-yl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (7g): The general procedure C was followed using 363 mg (1.00 equiv., 1.44 mmol) diamine **3g**. Column chromatography (SiO_2, hexane/EtOAc, 3:1, 5% NEt_3) was performed to isolate product **7g** (154 mg, 34%) and diazacycloalkylated side product (43.2 mg, 8%). R_f = 0.30 (hexane/EtOAc, 3:1, 5% NEt_3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.99 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 6.92 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 6.83–6.77 (m, 2 H), 6.59–6.53 (m, 2 H), 3.48 (br. s, 2 H), 3.17 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.62–2.54 (m, 1 H), 2.54–2.46 (m, 1 H), 2.16–2.04 (m, 2 H), 1.81–1.64 (m, 6 H), 1.62–1.54 (m, 2 H), 1.54–1.43 (m, 2 H), 1.43–1.34 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 151.4 (C_q, 1 C), 145.3 (C_q, 1 C), 143.2 (C_q, 1 C), 142.9 (C_q, 1 C), 133.3 (C_q, 1 C), 132.9 (C_q, 1 C), 130.0 (C_t, 1 C), 129.8 (C_t, 1 C), 116.8 (C_t, 1 C), 115.3 (C_t, 1 C), 113.6 (C_t, 1 C), 112.5 (C_t, 1 C), 50.8 (C_s, 2 C), 33.8 (C_s, 1 C), 33.1 (C_s, 1 C), 29.1 (C_s, 2 C), 28.3 (C_s, 1 C), 26.0 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 322 (2), 321 (25), 320 (100).

Representative Procedure D (Mild Oxidation of Amines 7):[53] Phosphotungstic acid hydrate (0.45 mol-%) was dissolved in CTAB (10 cmc, 0.02 M in water) and stirred for 5 min at room temp. Afterwards, sodium perborate tetrahydrate (7.00 equiv.) was added and the resulting milky, colourless solution was heated to 60 °C. Then a warm solution of amine **7** (1.00 equiv.) in CTAB was added dropwise to the mixture. The cloudy, red-brown reaction mixture was stirred for 15 h at 60 °C and then cooled to room temp. The orange, organic layer was extracted with *t*BME, washed with H_2O, dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification was performed by column chromatography (SiO_2, CH_2Cl_2/hexane, 2:1).

1-(4′-Nitrobiphenyl-4-yl)piperidine (1a): The general procedure D was followed using 2.62 mg (0.45 mol-%, 0.91 μmol) phosphotungstic acid hydrate in CTAB (0.6 mL, 10 cmc, 0.02 M) and 320 mg (10.0 equiv., 2.08 mmol) sodium perborate tetrahydrate. Amine **7a** (52.0 mg, 1.00 equiv., 0.206 mmol) in CTAB (10 mL) was added dropwise to the mixture. The cloudy, brown reaction mixture was stirred for 15 h at 60 °C. Purification was performed by column chromatography (SiO_2, CH_2Cl_2). According to this procedure the red, solid target compound **1a** (32.0 mg, 55%) was isolated; m.p. 220 °C; R_f = 0.71 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.24 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.68 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.55 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.00 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 3.28 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.77–1.68 (m, 4 H), 1.67–1.60 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.3 (C_q, 1 C), 147.4 (C_q, 1 C), 146.0 (C_q, 1 C), 128.1 (C_t, 2 C), 127.9 (C_q, 1 C), 126.4 (C_t, 2 C), 124.1 (C_t, 2 C), 115.8 (C_t, 2 C), 49.6 (C_s, 2 C), 25.5 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. IR: $\tilde{\nu}$ = 2949 (w), 2844 (w), 1589 (m), 1506 (s), 1337 (s), 1242 (s), 1224 (s), 1111 (m), 852 (s), 756 (s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 283 (55), 282 (100). $C_{17}H_{18}N_2O_2$ (282.34): calcd. C 72.32, H 6.43, N 9.92; found C 72.02, H 6.51, N 9.93.

1-(2,2′-Dimethyl-4′-nitrobiphenyl-4-yl)piperidine (1b): By following the general procedure D 2,2′-dimethyl-4′-(piperidin-1-yl)biphenyl-4-amine (**7b**) (50.0 mg, 1.00 equiv., 0.178 mmol) in CTAB (15 mL) was added dropwise to a warmed mixture of phosphotungstic acid hydrate (1.57 mg, 0.45 mol-%, 0.545 μmol) in CTAB (0.4 mL, 10 cmc, 0.02 M) and sodium perborate tetrahydrate (192 mg, 7.00 equiv., 1.25 mmol). The pale yellow reaction mixture was stirred for 15 h at 60 °C. Column chromatography (SiO_2, CH_2Cl_2) provided the solid, yellow target compound **1b** (35.6 mg, 64%); m.p. 116–117 °C; R_f = 0.69 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.13 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 8.05 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 2.4 Hz, 1 H), 7.26 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 6.93 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 6.87–6.85 (m, 1 H), 6.85–6.80 (m, 1 H), 3.21 (t, $^3J_{H,H}$ = 5.6 Hz, 4 H), 2.17 (s, 3 H), 2.01 (s, 3 H), 1.78–1.69 (m, 4 H), 1.64–1.58 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 151.7 (C_q, 1 C), 149.0 (C_q, 1 C), 146.8 (C_q, 1 C), 138.5 (C_q, 2 C), 135.7 (C_q, 1 C), 130.8 (C_t, 1 C), 129.2 (C_t, 1 C), 124.5 (C_t, 1 C), 120.6 (C_t, 1 C), 117.5 (C_t, 1 C), 113.5 (C_t, 1 C), 50.3 (C_s, 2 C), 25.8 (C_s, 2 C), 24.3 (C_s, 1 C), 20.1 (C_p, 1 C), 20.0 (C_p, 1 C) ppm. MS (MALDI-TOF): *m*/*z* (%) = 310 (100). $C_{19}H_{22}N_2O_2$ (310.40): calcd. C 73.52, H 7.14, N 9.03; found C 73.41, H 7.20, N 8.77. UV/Vis (chloroform): λ_{max} (ε) = 270 nm (17598 L mol^{-1} cm^{-1}), λ_{max} (ε) = 354 nm (3003 L mol^{-1} cm^{-1}).

1-(7-Nitro-9,10-dihydrophenanthren-2-yl)piperidine (1d): Following the general procedure D using 2.94 mg (0.45 mol-%, 1.02 μmol) phosphotungstic acid hydrate in CTAB (0.7 mL, 10 cmc, 0.02 M). After adding sodium perborate tetrahydrate (360 mg, 7.00 equiv., 2.34 mmol) the temperature was raised to 60 °C. Amine **7d** (93.0 mg, 1.00 equiv., 0.334 mmol) in CTAB (20 mL) was added

dropwise to the mixture. The red reaction mixture was stirred for 17 h at 60 °C. Column chromatography (SiO_2, CH_2Cl_2) was used for purification. According to this procedure the solid, red target compound **1d** (57.4 mg, 56%) was isolated; m.p. 114–115 °C; R_f = 0.61 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 2.4 Hz, 1 H), 8.04 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H), 7.69 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.64 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.86 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 2.4 Hz, 1 H), 6.77 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 3.29 (t, $^3J_{H,H}$ = 5.7 Hz, 4 H), 2.96–2.82 (m, 4 H), 1.75–1.66 (m, 4 H), 1.66–1.59 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.4 (C_q, 1 C), 145.2 (C_q, 1 C), 141.6 (C_q, 1 C), 139.3 (C_q, 2 C), 136.9 (C_q, 1 C), 125.9 (C_t, 1 C), 123.1 (C_t, 1 C), 122.7 (C_t, 1 C), 122.4 (C_t, 1 C), 114.5 (C_t, 1 C), 114.1 (C_t, 1 C), 49.4 (C_s, 2 C), 29.2 (C_s, 1 C), 29.0 (C_s, 1 C), 25.5 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m/z* (%) = 309 (11), 308 (43), 307 (100). $C_{19}H_{20}N_2O_2$ (308.38): calcd. C 74.00, H 6.54, N 9.08; found C 73.63, H 6.61, N 9.03. UV/Vis (chloroform): λ_{max} (ε) = 274 nm (14713 L mol^{-1} cm^{-1}), λ_{max} (ε) = 416 nm (20782 L mol^{-1} cm^{-1}).

3-Nitro-9-(piperidin-1-yl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (1e): In accordance to the general procedure D 6.20 mg (0.45 mol-%, 7.15 μmol) phosphotungstic acid hydrate in CTAB (0.2 mL, 10 cmc, 0.02 M) and 771 mg (7.00 equiv., 5.01 mmol) sodium perborate tetrahydrate were used. Amine **7e** (209 mg, 1.00 equiv., 0.715 mmol) in CTAB (14 mL) was added dropwise to the mixture at 60 °C. The red reaction mixture was stirred for 15 h at 60 °C. By column chromatography (SiO_2, CH_2Cl_2) the crude was purified to achieve the push-pull system **1e** (135 mg, 59%) as a dark red solid; m.p. 109–110 °C; R_f = 0.58 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.16 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 2.4 Hz, 1 H), 8.09 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 7.45 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.27 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 6.92 (dd, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 2.5 Hz, 1 H), 6.84 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 3.27 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.59 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 2.46 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 2.23 (quint, $^3J_{H,H}$ = 7.0 Hz, 2 H), 1.77–1.69 (m, 4 H), 1.66–1.58 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.4 (C_q, 1 C), 148.6 (C_q, 1 C), 146.2 (C_q, 1 C), 140.8 (C_q, 1 C), 140.5 (C_q, 1 C), 129.3 (C_t, 1 C), 129.1 (C_q, 1 C), 128.4 (C_t, 1 C), 123.5 (C_t, 1 C), 121.8 (C_t, 1 C), 115.9 (C_t, 1 C), 113.8 (C_t, 1 C), 49.9 (C_s, 2 C), 32.9 (C_s, 1 C), 31.8 (C_s, 1 C), 31.7 (C_s, 1 C), 25.7 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (EI$^+$, 70 eV): *m/z* (%) = 323 (24), 322 (100), 321 (51), 275 (6), 191 (7). $C_{20}H_{22}N_2O_2$ (322.41): calcd. C 74.51, H 6.88, N 8.69; found C 74.41, H 6.90, N 8.43. UV/Vis (chloroform): λ_{max} (ε) = 269 nm (17538 L mol^{-1} cm^{-1}), λ_{max} (ε) = 388 nm (12074 L mol^{-1} cm^{-1}).

3-Nitro-10-(piperidin-1-yl)-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (1f): In accordance to the general procedure D 8.71 mg (0.45 mol-%, 9.89 μmol) phosphotungstic acid hydrate in CTAB (2.3 mL, 10 cmc, 0.02 M) and 1.07 g (7.00 equiv., 6.93 mmol) sodium perborate tetrahydrate were used. Amine **7f** (303 mg, 1.00 equiv., 0.989 mmol) in CTAB (80 mL) was added dropwise to the mixture at 60 °C. The orange reaction mixture was stirred for 15 h at 60 °C. By column chromatography (SiO_2, CH_2Cl_2/hexane, 2:1) the crude was purified to achieve the push-pull system **1f** (149 mg, 45%) as an orange solid; m.p. 124–125 °C; R_f = 0.34 (CH_2Cl_2/hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.14 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H), 8.06 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 2.4 Hz, 1 H), 7.37 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.10 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H), 6.86–6.83 (m, 2 H), 3.24 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 2.81 (dd, $^3J_{H,H}$ = 8.2, $^2J_{H,H}$ = 13.3 Hz, 1 H), 2.69 (dd, $^3J_{H,H}$ = 8.2, $^2J_{H,H}$ = 13.4 Hz, 1 H), 2.30–2.20 (m, 1 H), 2.19–1.94 (m, 3 H), 1.79–1.70 (m, 4 H), 1.66–1.49 (m, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.5 (C_q, 1 C), 147.8 (C_q, 1 C), 147.1 (C_q, 1 C), 144.3 (C_q, 1 C), 143.0 (C_q, 1 C), 130.0 (C_t, 1 C), 129.4 (C_t, 1 C), 129.2 (C_q, 1 C), 124.2 (C_t, 1 C), 120.7 (C_t, 1 C), 116.7 (C_t, 1 C), 113.6 (C_t, 1 C), 50.1 (C_s, 2 C), 33.1 (C_s, 1 C), 32.8 (C_s, 1 C), 29.5 (C_s, 1 C), 29.0 (C_s, 1 C), 25.8 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (EI$^+$, 70 eV): *m/z* (%) = 337 (24), 336 (100), 335 (42), 289 (5). $C_{21}H_{24}N_2O_2$ (336.43): calcd. C 74.97, H 7.19, N 8.33; found C 74.55, H 7.13, N 8.23. UV/Vis (chloroform): λ_{max} (ε) = 271 nm (20019 L mol^{-1}cm^{-1}), λ_{max} (ε) = 370 nm (7551 L mol^{-1} cm^{-1}).

3-Nitro-11-(piperidin-1-yl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (1g): In accordance to the general procedure D 3.76 mg (0.45 mol-%, 4.27 μmol) phosphotungstic acid hydrate in CTAB (1 mL, 10 cmc, 0.02 M) and 460 mg (7.00 equiv., 2.99 mmol) sodium perborate tetrahydrate were used. Amine **7g** (137 mg, 1.00 equiv., 0.427 mmol) in CTAB (33 mL) was added dropwise to the mixture at 60 °C. The orange-yellow reaction mixture was stirred for 15 h at 60 °C. By column chromatography (SiO_2, CH_2Cl_2/hexane, 2:1) the crude was purified to achieve the push-pull system **1g** (75 mg, 50%) as a yellow solid; m.p. 125–126 °C; R_f = 0.44 (CH_2Cl_2/hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.10 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.05 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.9 Hz, 1 H), 7.30 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 6.96 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H), 6.88–6.80 (m, 2 H), 3.22 (t, $^3J_{H,H}$ = 5.3 Hz, 4 H), 2.76–2.59 (m, 2 H), 2.30–2.20 (m, 1 H), 1.97–1.70 (m, 7 H), 1.66–1.28 (m, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.2 (C_q, 1 C), 149.6 (C_q, 1 C), 147.2 (C_q, 1 C), 144.3 (C_q, 1 C), 141.8 (C_q, 1 C), 130.7 (C_q, 1 C), 130.3 (C_t, 1 C), 128.8 (C_t, 1 C), 123.6 (C_t, 1 C), 120.6 (C_t, 1 C), 116.6 (C_t, 1 C), 113.7 (C_t, 1 C), 50.4 (C_s, 2 C), 33.7 (C_s, 1 C), 33.2 (C_s, 1 C), 28.9 (C_s, 1 C), 28.8 (C_s, 1 C), 28.2 (C_s, 1 C), 25.9 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m/z* (%) = 351 (10), 350 (18), 336 (26), 235 (43), 321 (86), 320 (45), 319 (100). $C_{22}H_{25}N_2O_2$ (349.45): calcd. C 75.40, H 7.48, N 7.99; found C 75.12, H 7.42, N 7.79. UV/Vis (chloroform): λ_{max} (ε) = 269 nm (18523 L mol^{-1} cm^{-1}), λ_{max} (ε) = 351 nm (3019 L mol^{-1} cm^{-1}).

2-Nitro-9*H*-fluorene (9): Compound **9** was synthesized according to a literature procedure.[64] Yield 15% (colourless solid); m.p. 162 °C; R_f = 0.39 [hexane/ethyl acetate (5:1)]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.40 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.30 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 2.0 Hz, 1 H), 7.89–7.86 (m, 2 H), 7.63–7.61 (m, 1 H), 7.48–7.41 (m, 2 H), 4.01 (s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 148.0 (C_q, 2 C), 144.8 (C_q, 1 C), 143.9 (C_q, 1 C), 139.4 (C_q, 1 C), 128.8 (C_t, 1 C), 127.4 (C_t, 1 C), 125.4 (C_t, 1 C), 123.1 (C_t, 1 C), 121.3 (C_t, 1 C), 120.5 (C_t, 1 C), 119.8 (C_t, 1 C), 37.0 (C_s, 1 C) ppm. MS (EI$^+$, 70 eV): *m/z* (%) = 212 (10), 211 (68), 194 (26), 166 (13), 165 (100), 164 (41), 163 (30).

7-Iodo-2-nitro-9*H*-fluorene (10): Compound **10** was synthesized according to a literature procedure.[65] Yield 76% (yellow powder). R_f = 0.56 (hexane/EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.40 (s, 1 H), 8.31 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.99 (s, 1 H), 7.85 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.61 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 3.99 (s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 147.1 (C_q, 2 C), 146.7 (C_q, 1 C), 143.4 (C_q, 1 C), 139.0 (C_q, 1 C), 136.5 (C_t, 1 C), 134.7 (C_t, 1 C), 123.3 (C_t, 1 C), 122.7 (C_t, 1 C), 120.5 (C_t, 1 C), 120.1 (C_t, 1 C), 94.8 (C_q, 1 C), 36.6 (C_s, 1 C) ppm. MS (MALDI-TOF): *m/z* (%) = 338 (11), 337 (100).

7-Iodo-9,9-dimethyl-2-nitro-9*H*-fluorene (11):[56] 7-Iodo-2-nitrofluorene (**10**) (200 mg, 1.00 equiv., 0.593 mmol), iodomethane (80.0 μL, 2.05 equiv., 1.22 mmol, 173 mg) and potassium iodide (10.8 mg, 0.110 equiv., 653 μmol) were dissolved in dimethyl sulfoxide (2 mL) under argon. Powdered potassium hydroxide (141 mg, 4.25 equiv., 2.52 mmol) was added in 15 portions to the solution. The green reaction mixture was stirred at room temp. for 1 h and quenched with water. After extraction with dichloromethane (3 × 50 mL), the

combined organic layers were dried with sodium sulfate, filtered and concentrated. The resulting solid was purified by column chromatography (SiO_2, hexane/EtOAc, 5:1) to afford 7-iodo-9,9-dimethyl-2-nitrofluorene (**11**) (205 mg, 95%) as a yellow solid; m.p. 215–216 °C; R_f = 0.62 (hexane/EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.29–8.24 (m, 2 H), 7.84 (d, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.79 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.75 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.54 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 1.53 (s, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 157.0 (C_q, 1 C), 154.0 (C_q, 1 C), 147.6 (C_q, 1 C), 144.7 (C_q, 1 C), 136.7 (C_t, 1 C), 136.4 (C_q, 1 C), 132.5 (C_t, 1 C), 123.5 (C_t, 1 C), 122.9 (C_t, 1 C), 120.3 (C_t, 1 C), 118.3 (C_t, 1 C), 95.5 (C_q, 1 C), 47.5 (C_q, 1 C), 26.6 (C_p, 2 C) ppm. MS (EI$^+$, 70 eV): *m/z* (%) = 366 (16), 265 (100), 350 (64), 304 (15), 177 (18), 176 (25).

1-(9,9-Dimethyl-7-nitro-9*H*-fluorene-2-yl)piperidine (1c):[47] To a pale yellow solution of 7-iodo-9,9-dimethyl-2-nitro-9*H*-fluorene (**11**) (140 mg, 1.00 equiv., 0.383 mmol) in dimethyl sulfoxide (2 mL), piperidine (0.170 mL, 4.40 equiv., 1.69 mmol, 144 mg), caesium acetate (174 mg, 2.37 equiv., 0.909 mmol) and copper iodide (3.65 mg, 5 mol-%, 19.2 μmol) were added. The red-brown reaction mixture was stirred for 23 h at 90 °C. After cooling to room temp. the crude was quenched with water (20 mL), extracted with EtOAc (3 × 30 mL) and washed with brine (2 × 20 mL). The organic layers were dried with sodium sulfate, filtered, and concentrated in vacuo. The reddish residue was purified by column chromatography (SiO_2, hexane/EtOAc, 5:1, 5% NEt_3) and by a second column (SiO_2, CH_2Cl_2). According to this procedure the desired product **1c** (18.5 mg, 15%) was isolated as a red solid; m.p. 163–164 °C; R_f = 0.55 (hexane/EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.22–8.19 (m, 2 H), 7.66–7.60 (m, 2 H), 6.98 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 6.94 (dd, $^3J_{HH}$ = 8.5, $^4J_{H,H}$ = 2.2 Hz, 1 H), 3.31 (t, $^3J_{H,H}$ = 5.6 Hz, 4 H), 1.75 (quint, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.67–1.60 (m, 2 H), 1.50 (s, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 156.9 (C_q, 1C), 153.8 (C_q, 1 C), 153.4 (C_q, 1 C), 146.5 (C_q, 1 C), 145.7 (C_q, 1 C), 127.4 (C_q, 1 C), 123.6 (C_t, 1 C), 122.3 (C_t, 1 C), 118.4 (C_t, 1 C), 118.0 (C_t, 1 C), 115.2 (C_t, 1 C), 109.6 (C_t, 1 C), 50.2 (C_s, 1 C), 47.1 (C_q, 1 C), 27.0 (C_p, 2 C), 25.7 (C_s, 1 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m/z* (%) = 323 (10), 322 (14), 321 (21), 307 (12), 293 (57), 292 (100). $C_{20}H_{22}N_2O_2$ (322.41): calcd. C 74.51, H 6.88, N 8.69; found C 74.25, H 6.78, N 8.52. UV/Vis (chloroform): λ_{max} (ε) = 271 nm (14362 L mol^{-1} cm^{-1}), λ_{max} (ε) = 418 nm (21703 L mol^{-1} cm^{-1}).

1-(4′-Nitrobiphenyl-4-yl)piperidine (1a) (by Suzuki–Miyaura Coupling): A solution of 1-(4-iodophenyl)piperidine (500 mg, 1.50 equiv., 1.74 mmol) in toluene (9 mL) and methanol (3 mL) was purged with argon for 15 min. Afterwards caesium carbonate (757 mg, 2.00 equiv., 2.32 mmol), 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (289 mg, 1.00 equiv., 1.16 mmol) and tetrakis(triphenylphosphane)palladium (134 mg, 10 mol-%, 0.116 mmol) were added to the stirred reaction at room temp. The dark-brown reaction mixture was heated at reflux for 18 h. After cooling to room temp. the mixture was filtered through Celite and concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, CH_2Cl_2) to yield the push-pull system **1a** as an orange solid (26%); m.p. 220 °C; R_f = 0.73 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.24 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.68 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H), 7.55 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.00 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 3.28 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H), 1.77–1.68 (m, 4 H), 1.67–1.60 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 152.3 (C_q, 1 C), 147.4 (C_q, 1 C), 146.0 (C_q, 1 C), 128.1 (C_t, 2 C), 127.9 (C_q, 1 C), 126.4 (C_t, 2 C), 124.1 (C_t, 2 C), 115.8 (C_t, 2 C), 49.6 (C_s, 2 C), 25.5 (C_s, 2 C), 24.3 (C_s, 1 C) ppm. MS (MALDI-TOF): *m/z* (%) = 283 (55), 282 (100).

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[1] B. Culshaw, *Optical Fibre Sensing and Signal Processing*, IET, London, **1984**.
[2] T. H. Maiman, *Nature* **1960**, *189*, 493.
[3] P. A. Franken, C. W. Peters, G. Weinreich, *Phys. Rev. Lett.* **1961**, *7*, 118.
[4] S. R. Marder, B. Kippelen, A. K. Y. Jen, N. Peyghammbarian, *Nature* **1997**, *388*, 845.
[5] S. R. Marder, J. W. Perry, *Adv. Mater.* **1993**, *5*, 804.
[6] W. H. Steier, A. Chen, S.-S. Lee, S. Garner, H. Zhang, V. Chuyanov, L. R. Dalton, F. Wang, A. S. Ren, C. Zhang, G. Todorova, A. Harper, H. R. Fetterman, D. Chen, A. Udupa, D. Bhattacharya, B. Tsap, *Chem. Phys.* **1999**, *245*, 487.
[7] D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195.
[8] Y. Nakayama, P. J. Pauzauskie, A. Radenovic, R. M. Onorato, R. J. Saykally, J. Liphardt, P. Yang, *Nature* **2007**, *447*, 1098.
[9] J. L. Oudar, H. Le Person, *Opt. Commun.* **1975**, *15*, 258.
[10] D. S. Chemla, J. L. Oudar, J. Jerphagnon, *Phys. Rev. B* **1975**, *12*, 4534.
[11] F. Kajzar, J. Messier, *Phys. Rev. A* **1985**, *32*, 2352.
[12] J. Zyss, *J. Chem. Phys.* **1979**, *70*, 3341.
[13] J. Zyss, *J. Chem. Phys.* **1979**, *71*, 909.
[14] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664.
[15] J. Y. Lee, K. S. Kim, B. J. Mhin, *J. Chem. Phys.* **2001**, *115*, 9484.
[16] A. Fort, A. Boeglin, L. Mager, C. Amyot, C. Combellas, A. Thiebault, V. Rodriguez, *Synth. Met.* **2001**, *124*, 209.
[17] L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nature* **2006**, *442*, 904.
[18] D. Vonlanthen, A. Mishchenko, M. Elbing, M. Neuburger, T. Wandlowski, M. Mayor, *Angew. Chem. Int. Ed.* **2009**, *48*, 8886.
[19] J. A. Malen, P. Doak, K. Baheti, T. D. Tilley, A. Majumdar, R. A. Segalman, *Nano Lett.* **2009**, *9*, 3406.
[20] I. D. L. Albert, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **1998**, *120*, 11174.
[21] K. S. Thanthiriwatte, K. M. Nalin de Silva, *THEOCHEM* **2002**, *617*, 169.
[22] P. Hrobarik, I. Sigmundova, P. Zahradnik, *Synthesis* **2005**, 600.
[23] E. M. Breitung, C.-F. Shu, R. J. McMahon, *J. Am. Chem. Soc.* **2000**, *122*, 1154.
[24] C. R. Moylan, S. Ermer, S. M. Lovejoy, I. H. McComb, D. S. Leung, R. Wortmann, P. Krdmer, R. J. Twieg, *J. Am. Chem. Soc.* **1996**, *118*, 12950.
[25] J. W. Perry, G. Bourhill, S. R. Marder, D. Lu, G. Chen, W. A. Goddard III, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1994**, *35*, 148.
[26] S. M. Risser, D. N. Beratan, S. R. Marder, *J. Am. Chem. Soc.* **1993**, *115*, 7719.
[27] C. Dehu, F. Meyers, J. L. Bredas, *J. Am. Chem. Soc.* **1993**, *115*, 6198.
[28] C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, G. Martin, F. Agullo-Lopez, I. Ledoux, J. Zyss, V. R. Ferro, J. M. Garcia de la Vega, *J. Phys. Chem. B* **2005**, *109*, 3800.
[29] A. K. Y. Jen, V. P. Rao, K. Y. Wong, K. J. Drost, *J. Chem. Soc., Chem. Commun.* **1993**, 90.
[30] V. P. Rao, A. K. Y. Jen, K. Y. Wong, K. J. Drost, *Tetrahedron Lett.* **1993**, *34*, 1747.

[31] L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631.
[32] S. R. Marder, D. N. Beratan, L. T. Cheng, *Science* **1991**, *252*, 103.
[33] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664.
[34] J. L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446.
[35] D. Vonlanthen, J. Rotzler, M. Neuburger, M. Mayor, *Eur. J. Org. Chem.* **2010**, 120.
[36] A. S. Guram, R. A. Rennels, S. L. Buchwald, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1348.
[37] J. Louie, J. F. Hartwig, *Tetrahedron Lett.* **1995**, *36*, 3609.
[38] A. Klapars, J. C. Antilla, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 7727.
[39] C.-Z. Tao, J. Li, Y. Fu, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2007**, *49*, 70.
[40] S. Naik, G. Bhattacharjya, B. Talukdar, B. K. Patel, *Eur. J. Org. Chem.* **2004**, 1254.
[41] D. J. Sinclair, M. S. Sherburn, *J. Org. Chem.* **2005**, *70*, 3730.
[42] S. Lee, M. Jorgensen, J. F. Hartwig, *Org. Lett.* **2001**, *3*, 2729.
[43] J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046.
[44] J. P. Wolfe, J. Ahman, J. P. Sadighi, R. A. Singer, S. L. Buchwald, *Tetrahedron Lett.* **1997**, *38*, 6367.
[45] A. McKillop, J. A. Tarbin, *Tetrahedron* **1987**, *43*, 1753.
[46] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, Oxford, **2001**.
[47] M. Sarkar, A. Samanta, *Synthesis* **2006**, 3425.
[48] B. de Lange, M. H. Lambers-Verstappen, L. Schmieder-van de Vondervoort, N. Sereinig, R. de Rijk, A. H. M. de Vries, J. G. de Vries, *Synlett* **2006**, 3105.
[49] A. S. Gajare, K. Toyota, M. Yoshifuji, F. Ozawa, *Chem. Commun.* **2004**, 1994.
[50] Y. Ju, S. Varma Rajender, *Org. Lett.* **2005**, *7*, 2409.
[51] Y. Ju, R. S. Varma, *J. Org. Chem.* **2006**, *71*, 135.
[52] W. D. Emmons, *J. Am. Chem. Soc.* **1957**, *79*, 5528.
[53] H. Firouzabadi, N. Iranpoor, K. Amani, *Green Chem.* **2001**, *3*, 131.
[54] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.
[55] S. Sakaue, T. Tsubakino, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* **1993**, *58*, 3633.
[56] K. D. Belfield, K. J. Schafer, W. Mourad, B. A. Reinhardt, *J. Org. Chem.* **2000**, *65*, 4475.
[57] A. Shaporenko, M. Elbing, A. Blaszczyk, C. Von Haenisch, M. Mayor, M. Zharnikov, *J. Phys. Chem. B* **2006**, *110*, 4307.
[58] H. Meier, *Angew. Chem. Int. Ed.* **2005**, *44*, 2482.
[59] L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, *J. Phys. Chem.* **1991**, *95*, 10643.
[60] J. J. P. Stewart, *Vol. Tokyo*, MOPAC **2002**, version 2.3.0, Fujitsu Ltd., Tokyo, **2002**.
[61] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
[62] T. Thami, P. Bassoul, M. A. Petit, J. Simon, A. Fort, M. Barzoukas, A. Villaeys, *J. Am. Chem. Soc.* **1992**, *114*, 915.
[63] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Haenisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8815.
[64] T. Ohwada, *J. Am. Chem. Soc.* **1992**, *114*, 8818.
[65] V. C. Marhevka, N. A. Ebner, R. D. Sehon, P. E. Hanna, *J. Med. Chem.* **1985**, *28*, 18.

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