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Communication

Azahelicenes

Synthesis of 5,9-Diaza[5]helicenes

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Abstract: A new method for the synthesis of 5,9-diaza[5]helicenes is presented using 2,3-bis(acylamino)-substituted *ortho*-terphenyls as precursors. Activation of the amide groups and electrophilic substitution at the *ortho* positions of the adjacent phenyl groups leads to the 5,9-diaza[5]helicenes. A stepwise reaction including protection of the first amino group, amide formation at the second amino group with subsequent cyclization, followed by deprotection, amide formation and cyclization at the first amino group ensures that both electrophilic substitutions take place at sufficiently activated arenes and allows for the different substituents at the diaza[5]helicenes brought in with the amide groups. The terphenyl precursors are synthesized by two Suzuki couplings of suitably substituted building blocks. Three different 5,9-diaza[5]helicenes with aliphatic, alkenyl and methoxycarbonylalkyl substituents were prepared; the latter would allow to attach further functionalities by ester or amide linkage.

Helicenes, i.e. polycyclic aromatic compounds with *ortho*-fused benzenes, have special optical and electronic properties, which are similarly present in derivatives bearing heteroatoms or being constructed from other aromatic or heteroaromatic moieties.[1–3] According to the IUPAC definition,[4] the helicenes consist of at least five rings (pentahelicene, [5]helicene). [5]Helicenes are non-planar and thus chiral, albeit with a very low racemization barrier (Figure 1).[5,6]

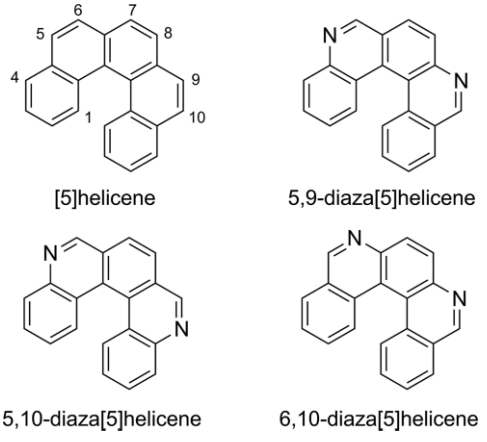

Figure 1. Aza- and diaza[5]helicenes.

Seven aza[5]helicenes and 91 diaza[5]helicenes can be constructed, where a small fraction of these compounds have been realized in prior syntheses.[1,7,8] These and other azahelicenes have been used as chiral organocatalysts in asymmetric synthesis[9–12] and in kinetic resolutions,[13] as proton sponges,[14–16] and for the synthesis of helicene-based transition metal complexes.[17] The quite related, positively charges azoniahelicenes turned out to have a high binding selectivity for triple helix DNA[18] or show a high thin film conductivity making them possibly useful for the field of optoelectronics.[19]

The most common syntheses of helicenes and azahelicenes include the construction of *Z*-configured stilbene-type compounds (typically by Wittig olefination) and their subsequent electrocyclization (with concomitant oxidation).[1–3,7,8] Further occasionally applied methods for the synthesis of aza- and diazahelicenes are the transition metal-catalyzed coupling of *ortho,ortho'*-dihalobiaryls,[9,20,21] the [2+2+2] cyclization of suitable aromatic triynes,[22] or the $PtCl_4$/$InCl_3$-catalyzed cyclization of *ortho*-alkynylbiaryls.[23] Herein we present a novel approach to 5,9-diaza[5]helicenes starting with *ortho*-terphenyls.

A first considered retrosynthetic approach would cleave the 5,9-diaza[5]helicenes **A** in two concomitant retro-Friedel-Crafts-type substitutions into a 2,3′-bis(acylamino)terphenyl **B**, which could be traced back in a retro-cross coupling to a suitably metalated building block **D** and a 2-halo-3-nitrobiphenyl **E**. The latter should again be accessible by cross coupling (Scheme 1).

In the here reported first investigations within this strategy we considered it useful to aim at first for 3,12-dimethoxy-substituted diaza[5]helicenes to facilitate the synthetic approach (including the final electrophilic acylations), to furthermore improve the solubility of the final products, and to allow for a later attachment of further functionalities at possibly liberated hydroxy groups.

An electrophilic coupling partner suitable for a Suzuki coupling towards terphenyl derivative **11**, the *ortho*-iodinated biphenyl derivative **7**, was on its part prepared by cross coupling (Scheme 2): 2-Iodo-3-nitroaniline **3**, obtained from purchasable 2,6-dinitroaniline (**1**) by Sandmeyer reaction (→ **2**)[24] and re-

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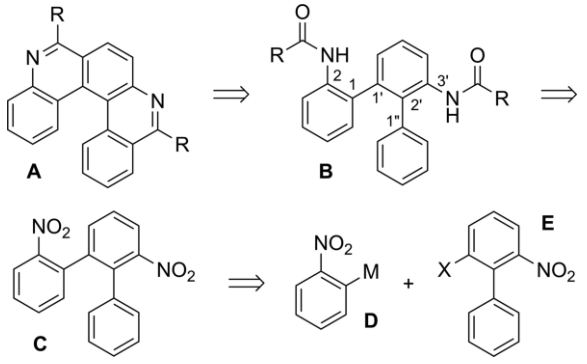


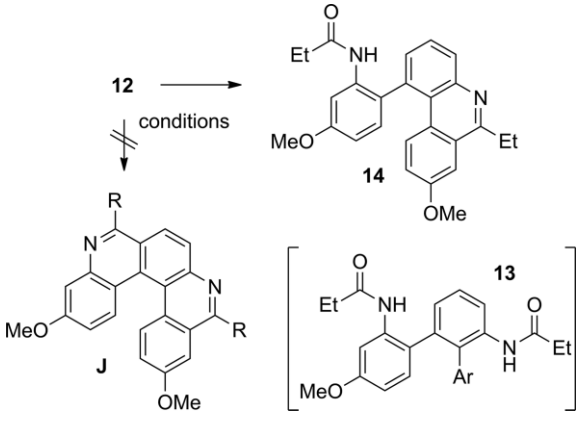
Scheme 1. Retrosynthetic analysis for the synthesis of 5,9-diaza[5]helicenes.

duction of one nitro group,[8] was treated with a borylated anisole **5**, prepared from the respective commercially available bromide **4** by halogen-lithium exchange and subsequent transmetalation.[25]

Suzuki coupling using tetrakis(triphenylphosphine)palladium(0)[26] as catalyst furnished 2-aminobiphenyl **6**, which was again subjected to a Sandmeyer reaction[27] and a subsequent reduction of the nitro group,[28] yielding the iodinated substrate **7** in an overall yield of 21 % over four consecutive steps.

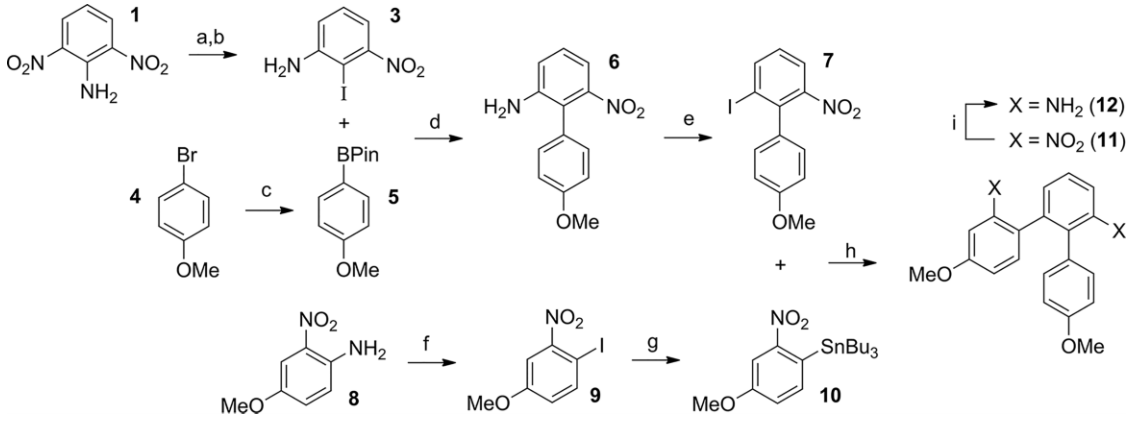
The nucleophilic coupling partner for the cross coupling to terphenyl **11** was prepared from commercially available 4-methoxy-2-nitroaniline (**8**), which was converted into an iodo derivative **9**. It turned out that this could not be transferred to a boronate (possibly due to the *ortho*-nitro group), preventing the planned Suzuki coupling. We alternatively considered a Stille coupling and prepared aryl stannane **10** by reaction with bis(tributyltin) in the presence of bis(triphenylphosphine)palladium(II) dichloride as catalyst (57 % over two steps). Stille cross coupling of building blocks **7** and **10** was achieved with tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide as catalysts and yielded terphenyl derivative **11** (88 %). Reduction to diamine **12** was successfully performed with potassium borohydride/copper(I) chloride.[29]

Nevertheless, all tested protocols for an amide formation with concomitant cyclization towards **J** failed (Scheme 3). Reaction with *tert*-butyl isocyanide in the presence of cobalt(II) acetylacetonate and oxygen (as recently reported by Tobisu et al. for the synthesis of phenanthridines[30]) did not lead to any well-defined product. Amide coupling with propionic acid in the presence of propylphosphonic anhydride (T3P®) to bis(amide) **13** was successful, but a subsequent cyclization with Eaton's reagent (P_2O_5 in $MeSO_3H$)[31] did only lead to the formation of phenanthridine derivative **14** (albeit with poor yields). Obviously, the fastest aromatic substitution is that of the eastern amide group at the activated (i.e., OMe-substituted) benzene. The acylamino-substituted benzene seems to be less reactive; its substitution proceeds with lower rates. Once the phenanthridine **14** is formed, the second substitution at this electron-deficient arene is obviously too sluggish – even at elevated temperatures.



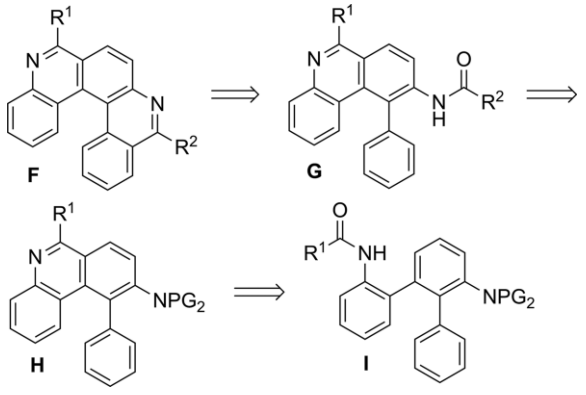
Scheme 3. Attempted acylation towards diaza[5]helicenes.

Consequently we changed our strategy and decided to pursue a stepwise strategy (Scheme 4). This would allow to perform both electrophilic aromatic substitutions with activated arenes and would furthermore give access to products **F** with different substituents R^1 and R^2 introduced with the amide moieties. We planned to build the western amide function, where the other amino group is still suitably protected (**I**); electrophilic acylation towards phenanthridine **H** would now proceed at an



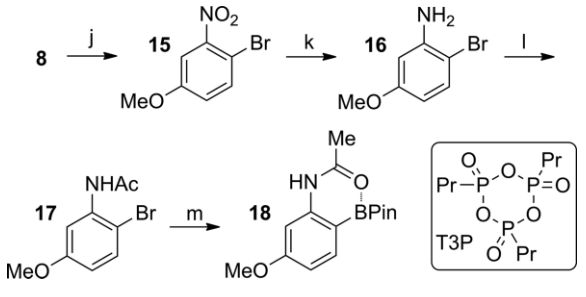
Scheme 2. Synthesis of a terphenyl derivative. Conditions: (a) $NaNO_2$, H_2SO_4, AcOH, 40 °C, 30 min; then KI, H_2O, 0–70 °C, 15 min (79 %); (b) Fe, AcOH, reflux, 2.5 h (44 %); (c) BuLi, –78 °C, 1.5 h; then *i*PrOB(pin), –78 °C to r.t., 16 h (95 %); (d) cat. $Pd(PPh_3)_4$, K_2CO_3, dioxane/H_2O (4:1), 95 °C, 2 d (86 %); (e) $NaNO_2$, conc. HCl/MeCN (5:3), 0 °C to r.t., 30 min; then KI, H_2O, 0–80 °C, 15 min (69 %); (f) $NaNO_2$, H_2SO_4, H_2O, –5 °C, 10 min; then KI, 0 °C, 30 min (78 %); (g) Sn_2Bu_6, cat. $Pd(PPh_3)_2Cl_2$, PPh_3, xylene, 100 °C, 66 h (73 %); (h) cat. $Pd(Ph_3)_4$, cat CuI, CsF, DMF, 45 °C, 18 h (88 %); (i) KBH_4, CuCl, MeOH, r.t., 20 min, 88 %.

activated substrate. Deprotection and amide formation at the eastern amino group would furnish a substrate **G**, which again should be sufficiently reactive towards a substitution.



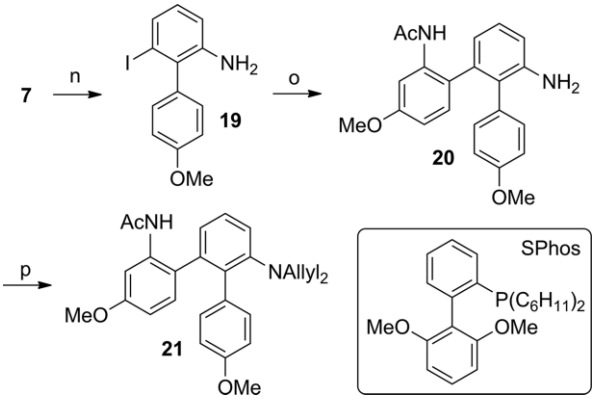
Scheme 4. Revised retrosynthetic scheme.

For this approach we again started with 4-methoxy-2-nitroaniline (**8**), which was subjected to a Sandmeyer reaction (now furnishing the respective bromo compound **15**[32]) and reduced to aniline **16**.[33] Acylation furnishing acetanilide **17** was here performed with acetic acid in the presence of propylphosphonic anhydride (T3P®) as coupling agent.[34] This transformation yielded amides with excellent yields (further derivatives have been prepared but are not part of this publication), but could in principle be similarly performed with simpler protocols (e.g. by coupling with the respective acid chlorides). Borylation to a suitable nucleophile **18** for a pursued Suzuki coupling was achieved by reaction with bis(pinacolato)diboron in the presence of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) as catalyst (Scheme 5).[35] The rather low yield of 59 % for this step was due to the poor solubility of the boronate, which led to losses during the work-up and purification process. Nevertheless, boronate **18** was thus obtained in four consecutive steps with a total yield of 41 %. A stannylated substrate which could have been used in a Stille coupling was similarly synthesized, but since a non-identified side product could not be separated by conventional methods, this variation was thus no longer pursued.



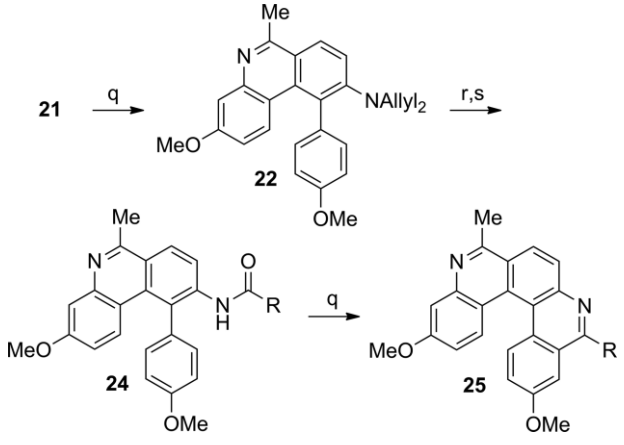
Scheme 5. Synthesis of the nucleophilic coupling partner for a Suzuki coupling. Conditions: (j) $NaNO_2$, HBr, MeCN, 0 °C to r.t., 2 h; then CuBr, HBr, 80 °C, 10 min (80 %); (k) Fe, NH_4Cl, EtOH/H_2O (3:2), reflux, 2 h (95 %); (l) AcOH, T3P, EtOAc/pyridine (2:1), 0 °C to r.t., 18 h (92 %); (m) B_2Pin_2, cat. Pd(dppf)Cl_2·CH_2Cl_2, KOAc, 1,4-dioxane, reflux, 3 h (59 %).

The nitrobiphenyl **7** (Scheme 2) was reduced to amine **19** by a standard protocol.[28] Cross coupling with boronate **18** to terphenylamine **20** was achieved in 87 % yield using a proven method with palladium(II) acetate as precatalyst and SPhos (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) as ligand (Scheme 6).[36] We considered allyl groups suitable as protecting groups for the amino group,[37] which can be introduced with standard protocols.[38] They should not deactivate the arene in the electrophilic substitution, and they can be cleaved with rhodium catalysis not affecting any of the other functional groups in the substrates. A double allylation of terphenylamine **20** towards **21** was achieved with 61 % yield.



Scheme 6. Synthesis of terphenyl derivative **21**. Conditions: (n) Fe, HCl, EtOH, reflux, 3 h (93 %); (o) **18**, cat. $Pd(OAc)_2$, SPhos, Cs_2CO_3, dioxane/H_2O (7:1), 70 °C, 18 h (87 %); (p) allyl bromide, Na_2CO_3, DMF, reflux, 8 h (61 %).

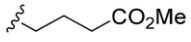
Dehydrating ring closure to phenanthridine **21** and (in the further course of the synthesis similarly to the diaza[5]helicene **25**) was performed with triphenylphosphine oxide and trifluoromethanesulfonic anhydride [Hendrickson reagent, $(Ph_3P^+)_2O{\cdot}2F_3CSO_3^-$],[39] which proved to be superior to a more conventional protocol using phosphoryl chloride (Scheme 7). Phenanthridine derivative **22** was thus obtained in 81 % yield. The second cyclization towards diaza[5]helicenes **25** was achieved after cleavage of the allyl groups (→ **23**)[40] and amide



Scheme 7. Synthesis of 5,9-diaza[5]helicenes. Conditions: (q) Ph_3PO/Tf_2O (2:1), CH_2Cl_2, 0 °C, 15 min; then **21**, CH_2Cl_2, 0 °C to r.t., 15 h (**22**: 81 %); (r) cat. $(PPh_3)_3RhCl$, MeCN/H_2O (4:1), 100 °C, 16 h (→ **23**: 80 %); (s) RCO_2H, T3P, EtOAc/pyridine (2:1), 0 °C to r.t. (see Table 1).

formation (→ **24**) with T3P® (vide supra). The obtained substrates together with yields for the last two steps are summarized in Table 1.

Table 1. Synthesis of 5,9-diaza[5]helicenes.

R	Amides **24**	Yield (%)	Helicenes **25**	Yield (%)
Et	**24a**	59	**25a**	[a]
isopentyl	**24b**	72	**25b**	81
	**24c**	50	**25c**	65
	**24d**	67	**25d**	68

[a] Helicene formation yielded product with a non-separable side product.

This strategy was applied to three 5,9-diaza[5]helicenes (Table 1) with different substituents at positions C-6 and C-10. To reduce the synthetic effort, we used only one common terphenyl precursor **21** bearing a methyl substituent at the position later being C-6 in the diazahelicenes. Different substituents were introduced with the second amide moiety, an isopropyl, an (*E*)-2-propenyl, and a 3-(methoxycarbonyl)propyl group. The propenyl group would allow for the introduction of further functionalities, while the latter could be especially useful for the attachment of structures via an ester or an amide linkage. Introduction of a 4-heptanyl group was not successful: The respective amide **24** was only isolated with a poor 20 % yield, possibly due to steric reasons; it was not used in a 5,9-diaza[5]helicene synthesis. No amide was obtained, when amine **23** was treated with 4-bromobutanoic acid. Cyclization of amide **24a** (R = Et) led to the formation of helicene **25a**, but the presence of unidentified side products and problems during the purification process prevented an isolation of the product. Its synthesis was thus not included in Table 1. The 5,9-aza[5]helicenes **25** were additionally characterized by their UV/Vis spectra; they show distinct absorptions around 237 and 310 nm. Detailed data and spectra are given in the Supporting Information.

5,9-Aza[5]helicenes **25** were thus obtained in total yields of 2–4 % over 11 linear steps (total 15 steps) starting with commercially available 2,6-dinitroaniline and 4-methoxy-2-nitroaniline. The herein presented method allows for variable substituents at positions C-6 and C-10, but could be applicable with further substituted starting materials (compounds **25** bear methoxy groups at positions C-3 and C-12). Slight modifications of this protocol should furthermore give access to the related 5,10- and 6,10-diaza[5]helicenes (Figure 1); their synthesis is now investigated in our laboratories, as is the extension of these methods to the synthesis of higher helicene-type compounds.

Experimental Section

Methyl 5-{[3-Methoxy-10-(4-methoxyphenyl)-6-methylphenanthridin-9-yl]amino}-5-oxopentanoate (24d): T3P solution (≥ 50 % in MeCN, 625 mg, corresponds to ≥ 313 mg of T3P, 984 μmol) was added at 0 °C to a solution of amine **23** (73.8 mg, 213 μmol) and monomethyl glutarate (58.9 mg, 403 μmol) in EtOAc/pyridine (2:1, 4 mL) placed in a 10 mL flask, the cooling bath was removed, and the mixture was stirred for 25 h at r.t. 1 M HCl (10 mL) was added and the phases were separated. The aqueous phase was brought to pH > 7 by addition of NaOH and extracted with Et_2O (3 × 5 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure and purified by MPLC (silica gel, EtOAc/hexanes, 3:1) to yield the product as a colourless solid (67.1 mg, 142 μmol, 67 %): R_f = 0.58 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.87 (quint, ^3J = 7.2 Hz, 2H, 3-H_2), 2.22 (t, ^3J = 7.3 Hz, 2H, 4-H_2), 2.33 (t, ^3J = 7.2 Hz, 2H, 2-H_2), 3.03 (s, 3H, 6′-Me), 3.66 (s, 3H, CO_2Me), 3.88 (s, 3H, 3′-OMe or 4″-OMe), 3.96 (s, 3H, 4″-OMe or 3′-OMe), 6.68 (dd, ^3J = 9.4 Hz, ^4J = 2.8 Hz, 1H, 2′-H), 7.05 (d, ^3J = 9.4 Hz, 1H, 1′-H), 7.15 (bs, 1H, NH), 7.16–7.20 (m, 2H, 2″-H, 6″-H or 3″-H, 5″-H), 7.20–7.25 (m, 2H, 3″-H, 5″-H or 2″-H, 6″-H), 7.44 (d, ^4J = 2.4 Hz, 1H, 4′-H), 8.25 (d, ^3J = 9.1 Hz, 2H, 1′-H, 7′-H), 8.67 ppm (d, ^3J = 9.0 Hz, 1H, 8′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_2), 23.9 (CH_3), 33.0 (CH_2), 36.8 (CH_2), 51.8 (CH_3), 55.5 (CH_3), 55.6 (CH_3), 106.7 (CH), 115.7 (CH), 116.3 (2 × CH), 118.3 (C), 119.6 (CH), 122.9 (C), 126.2 (C), 127.6 (CH), 127.7 (CH), 130.0 (C), 131.2 (2 × CH), 132.3 (C), 138.9 (C), 147.2 (C), 159.2 (C), 159.3 (C), 160.1 (C), 170.4 (C), 173.4 ppm (C); IR (ATR): $\tilde{\nu}$ = 3401 (w), 2998 (w), 2950 (w), 1732 (m), 1691 (m), 1588 (m), 1499 (m), 1026 (m), 829 (m) cm^{-1}; MS (FAB): *m/z* (%): 474 (35) [M^+ + 1], 473 (100) [M^+], 472 (24), 345 (19); HRMS (FAB): *m/z* calcd. for $C_{28}H_{29}N_2O_5^+$: 473.2076, found 473.2077.

Methyl 4-(3,12-Dimethoxy-6-methyl-5,9-diaza[5]helicene-10-yl)butanoate (25d): Tf_2O (0.07 mL, 117 mg, 416 μmol) was added slowly at 0 °C to a solution of Ph_3PO (184 mg, 661 μmol) in anhydrous CH_2Cl_2 (4 mL) placed in a 25 mL Schlenk flask and the mixture was stirred at 0 °C for 10 min. A solution of amide **24d** (51.1 mg, 108 μmol) in anhydrous CH_2Cl_2 (2 mL) was added slowly and the solution was stirred for 1 h at r.t. Saturated aqueous $NaHCO_3$ solution (15 mL) was added, the mixture was stirred vigorously, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by MPLC (silica gel, cyclohexane/EtOAc, 1:1) to yield the product as a yellow solid (33.5 mg, 73.7 μmol, 68 %): R_f = 0.41 (cyclohexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25–2.46 (m, 2H, 3-H_2), 2.56–2.66 (m, 2H, 2-H_2), 3.12 (s, 3H, 6-Me), 3.38–3.55 (m, 2H, 4-H_2), 3.71 (s, 3H, CO_2Me), 3.98 (s, 3H, 3′-OMe), 4.04 (s, 3H, 12′-OMe), 6.92 (dd, ^3J = 9.2 Hz, ^4J = 2.7 Hz, 1H, 2′-H), 7.15 (dd, ^3J = 9.2 Hz, ^4J = 2.6 Hz, 1H, 13′-H), 7.52 (d, ^4J = 2.7 Hz, 1H, 4′-H), 7.69 (d, ^4J = 2.6 Hz, 1H, 11′-H), 8.03 (d, ^3J = 8.7 Hz, 1H, 7′-H), 8.19 (d, ^3J = 8.7 Hz, 1H, 8′-H), 8.25 (d, ^3J = 9.2 Hz, 1H, 1′-H), 8.46 ppm (d, ^3J = 9.3 Hz, 1H, 14′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8 (CH_3), 23.8 (CH_2), 33.7 (CH_2), 35.4 (CH_2), 51.1 (CH_3), 55.7 (CH_3), 55.8 (CH_3), 104.9 (CH), 107.9 (CH), 115.9 (CH), 118.9 (C), 119.0 (C), 119.7 (CH), 124.5 (C), 124.9 (CH), 126.9 (C), 128.1 (CH), 128.3 (C), 128.5 (CH), 129.4 (CH), 130.6 (C), 144.8 (C), 146.5 (C), 158.6 (C), 158.8 (C), 160.1 (C), 161.8 (C), 174.1 ppm (C); IR (ATR): $\tilde{\nu}$ = 2920 (w), 1729 (m), 1612 (w), 1224 (w), 1166 (m), 1028 (w), 825 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ (log ε) = 236 (4.7), 262 (4.4), 305 (4.4), 315 (4.4), 338 (4.2), 389 (3.4), 410 (3.5) nm (dm^3 mol^{-1} cm^{-1}); MS (FAB): *m/z* (%): 455 (15), 133 (100), 91 (15), 89 (21); HRMS (FAB): *m/z* calcd. for $C_{28}H_{27}N_2O_4^+$: 455.1971, found 455.1972.

Acknowledgments

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Keywords: Helicenes · *ortho*-Biphenyls · Suzuki coupling · Phenanthridines · Electrophilic aromatic substitution

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