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The First Domino Reduction / Imine Formation / Intramolecular Aza-Diels–Alder Reaction for the Diastereoselective Preparation of Tetrahydrochromano[4,3-*b*]quinolines

Hans-Georg Imrich,[a] Jürgen Conrad,[a] and Uwe Beifuss*[a]

Dedicated to Professor Junjappa Hiriyakkanavar on the occasion of his 80th birthday

The first domino reduction / imine formation / intramolecular aza-Diels–Alder reaction is reported. Tetrahydrochromano[4,3-*b*]quinolines are formed with high *exo*-*E*-*anti* selectivity and with yields up to 87% when a nitrobenzene and a 2-(cinnamyloxy)-benzaldehyde are reacted in aqueous citric acid using iron as a reductant and montmorillonite K10 as a catalyst. The domino process starts with the in situ reduction of the nitrobenzene to the corresponding aniline, is followed by imine formation and terminated by an intramolecular aza-Diels–Alder reaction.

Introduction

N-Heterocycles are structural motifs of a great number of natural as well as unnatural biologically active compounds.[1] This is the reason for the continuing interest in the development of new and efficient methods for their selective synthesis.[2] Among others, *N*-heterocycles can be constructed by reductive cyclization of nitro compounds.[3–16] Initially, reduction of the nitro group occurs and forms a nitroso group and/or a nitrene, an *N*-hydroxylamino or an amino group as an intermediate. This is followed by the actual ring closure. Using nitro compounds as substrates, numerous five membered *N*-heterocycles such as pyrroles,[3] pyrrolidin-2-ones,[4] pyrrolin-*N*-oxides,[5] indoles,[6] indeno[1,2-*b*]indoles,[7] carbazoles,[8] hexahydrocarbazoles,[9] 2*H*-indazoles,[10] and isoxazolidines,[11] can be synthesized. Among the best known methods for the synthesis of indoles, for example, are the indole syntheses according to Leimburger-Batcho,[6d] Bartoli and Reissert,[6a] the transition metal catalysed reductive *N*-heteroannulation of *o*-nitrostyrenes[6b,c] and the Cadogan cyclization.[6e] Six membered *N*-heterocycles such as dihydropyridin-4-ones,[12] quinolines,[13] tetrahydroquinolines,[14] tetrahydroquinoxalines[15] and dihydrobenzoxazines[16] can also be obtained by reductive cyclizations of nitroaromatics.

The preparation of tetrahydroquinolines and related ring systems is particularly relevant, because many compounds with this skeleton display pronounced biological activities.[17] In addition, tetrahydroquinolines are also of interest for several industrial applications.[18]

A number of tetrahydroquinoline derivatives, namely the tetrahydrochromano[4,3-*b*]quinolines, show antiproliferative activity against MDA-MB-231 and MCF-7 breast cancer cell lines.[19]

The synthesis of tetrahydroquinolines can be achieved by numerous methods, including the domino reduction / intramolecular reductive amination of 2-nitroarylketones,[20c] the domino reduction / intramolecular Michael addition of *ω*-(2-nitroaryl) substituted *α*,*β*-unsaturated esters[20b,d] and the reductive cyclization of 2-nitrochalcones.[20a] Another important method for the construction of tetrahydroquinolines is the aza-Diels–Alder reaction of electron poor 2-azabutadienes with electron rich dienophiles. This transformation which is also known as the Povarov reaction allows for the efficient and selective preparation of tetrahydroquinolines and related skeletons.[21,22] Since the required 2-azabutadienes are rather sensitive to moisture,[23] it is advantageous when they are prepared in situ. This can be achieved for example by reacting an aniline with a carbonyl compound in the presence of the dienophile under the conditions of the Povarov reaction.[21,22] This three component reaction can be catalysed / promoted by numerous Brønsted[22a–c] and Lewis acids[22d–g] to deliver the resulting tetrahydroquinolines. Since anilines are usually obtained from the corresponding nitrobenzenes by reduction[24] and many anilines are known to be sensitive towards oxidation[25] it is highly attractive to combine the reduction of the nitrobenzenes to the anilines, their condensation with carbonyls to imines and their intermolecular Povarov reaction with dienophiles to a one-pot reaction.

Recently, we have reported that this type of three-component reaction between a nitrobenzene, a benzaldehyde and cyclopentadiene can be achieved (Scheme 1a).[26] The reactions were performed in aqueous citric acid under mild reaction conditions using iron as a reductant and montmorillonite K10 as a catalyst and delivered the products of a domino reduction / imine formation / intermolecular aza-Diels–Alder reaction with high *endo*-selectivities and high yields.

We wondered whether it is also possible to combine the in situ reduction of a nitrobenzene to an aniline with the reaction of an *ω*-unsaturated aldehyde to an imine and its subsequent intramolecular aza-Diels–Alder reaction. Here, we present the first examples of the domino reduction / imine formation / intramolecular aza-Diels–Alder reaction (Scheme 1b).

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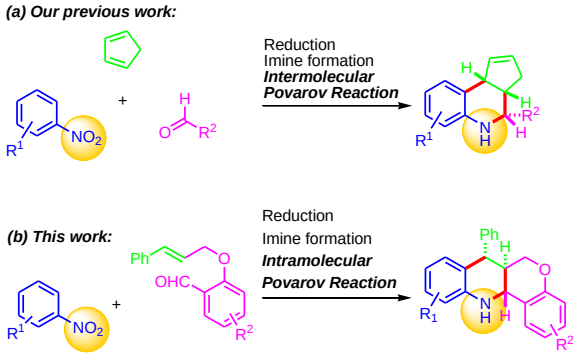


Scheme 1. Intermolecular and intramolecular versions of the Povarov reaction using nitrobenzenes as substrates.

Results and Discussion

The reaction between nitrobenzene (**1a**) and 2-(cinnamyloxy)benzaldehyde (**2a**) to the tetrahydrochromano[4,3-*b*]quinoline **3a** was used to demonstrate the feasibility of this transformation. The reason was that the corresponding transformation between aniline (**4a**) and 2-(cinnamyloxy)-benzaldehyde (**2a**) in the presence of an excess of a strong Brønsted acid (10 equiv. trifluoroacetic acid) in an organic solvent (acetonitrile) is known to deliver **3a**.[27a] In order to establish that the imine formation / aza-Diels–Alder reaction between aniline (**4a**) and **2a** to the tetrahydrochromano[4,3-*b*]quinoline **3a** can also be catalysed by montmorillonite K10, equimolar amounts of **4a** and **2a** were reacted with montmorillonite K10 (10 wt-%) in aqueous citric acid for 4 h at 40 °C. The cycloadduct **3a** was formed; its yield, however, amounted to only 3%. Despite of the disappointingly low yield of the experiment with aniline (**4a**), the reaction between equimolar amounts of nitrobenzene (**1a**) and the aldehyde **2a** in the presence of Fe (4 equiv.) as reductant and montmorillonite K10 (10 wt-%) as catalyst in aqueous citric acid for 4 h at 40 °C was performed. The positive result of this experiment was that the desired cycloadduct **3a** was formed at all. However, the yield of **3a** was only 2% (Table 1, entry 1). After some experimentation, we found that the yield of **3a** could be improved dramatically by simply raising the reaction temperature. Already at 60 °C the yield of **3a** amounted to 73% (Table 1, entry 2). A further improvement of the yield to 82% and 87% could be achieved by increasing the reaction temperature to 70 °C and 80 °C (Table 1, entries 3 and 6). However, a further increase of the reaction temperature to 100 °C had no positive effect on the outcome of the transformation (Table 1, entry 7). Next, the reaction time was shortened. While a reduction of the reaction time from 4 h to 3 h had no significant effect on the yield, it decreased to 78% upon halving the reaction time (Table 1, entries 4 and 5). Further experiments addressed the reduction of the amount of montmorillonite K10 to 7 wt-% (Table 1, entry 8) and that of citric acid to 3 equiv. (Table 1, entry 9). Under both conditions, the yields were higher than 80%, but the yield of Table 1, entry 6 could not be exceeded.

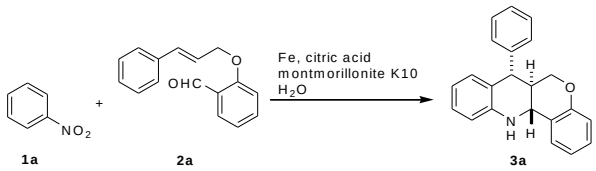


Table 1. Optimization of the reaction conditions of the montmorillonite K10-catalyzed reaction between nitrobenzene (**1a**) and 2-(cinnamyloxy)benzaldehyde (**2a**).[a]

Entry	Fe [equiv.]	Citric acid [equiv.]	Clay [wt-%]	*T* [°C]	Time [h]	Yield of **3a** [%]
1	4	4	10	40	4	2
2	4	4	10	60	4	73
3	4	4	10	70	4	82
4	4	4	10	80	2	78
5	4	4	10	80	3	86
6	4	4	10	80	4	87
7	4	4	10	100	4	85
8	4	4	7	80	4	81
9	3	3	13	80	4	84
10	-	4	13	80	4	-
11	4	-	20	80	4	-
12	4	4	-	80	4	-

[a] Reactions were performed using 2 mmol of nitrobenzene (**1a**) and 2 mmol of **2a** in 15 mL aqueous citric acid in a sealed flask (25 mL).

Finally, three control experiments established that the cycloadduct was not formed at all in the absence of a) Fe, b) montmorillonite K10 and c) citric acid (Table 1, entries 10–12). The results from the control experiments support the assumption that the reduction of nitrobenzene (**1a**) to aniline (**4a**) is achieved using Fe as reducing reagent in combination with citric acid as chelating agent under aqueous conditions. Aniline then reacts with the unsaturated aldehyde **2a** to the corresponding imine, which undergoes a montmorillonite K10-catalyzed Povarov reaction to the cycloadduct **3a**. In summary, the tetrahydrochromano[4,3-*b*]quinoline **3a** could be obtained in diastereomerically pure form in 87% yield by reacting nitrobenzene (**1a**) and 2-(cinnamyloxy)benzaldehyde (**2a**) under the conditions of Table 1, entry 6. The optimization experiments clearly demonstrated that the reduction of nitrobenzene (**1a**) to aniline (**4a**), the imine formation between **4a** and aldehyde **2a**, and the intramolecular aza-Diels–Alder reaction can be combined to a one-pot process. The efficiency of the method reported here can be seen from the fact that the yield of cycloadduct **3a** from the reaction between equimolar amounts of aniline (**4a**) and 2-(cinnamyloxy)benzaldehyde (**2a**) in the

presence of 10 wt-% montmorillonite K10 as catalyst in aqueous citric acid for 4 h at 80 °C amounts to 84%. This means that it is in the same range as the yield of the reaction between nitrobenzene (**1a**) and aldehyde **2a** under the conditions of Table 1, entry 6.

With optimized reaction conditions at hand the influence of the substrate structures on yield and diastereoselectivity of the domino reaction was studied (Table 2). First, the structure of the nitrobenzene was addressed. For this purpose, 2-(cinnamyloxy)-benzaldehyde (**2a**) was reacted with a number of *o*- and *p*-substituted nitrobenzenes **1b–i** under optimized reaction conditions. Irrespective of the substitution pattern of the nitrobenzenes, the products of the domino reduction / imine formation / aza-Diels–Alder reaction were isolated exclusively. The yields of the diastereomerically pure cycloadducts were ranging between 69% and 83% (Table 2, **3b–i**). These experiments demonstrated that the transformation tolerates a number of substituents, including alkyl, methoxy, fluoro, chloro, bromo, and nitrile groups in the *o*- and *p*-position of nitrobenzenes.

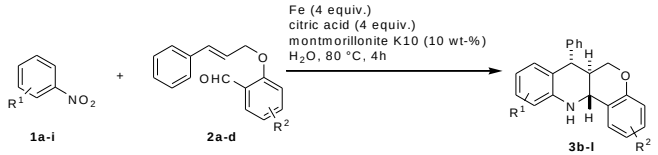
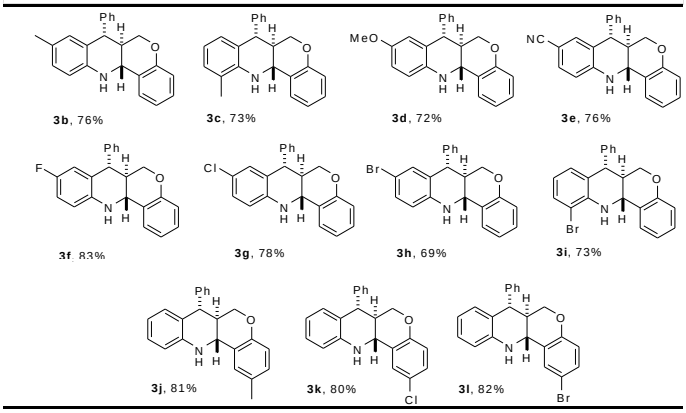
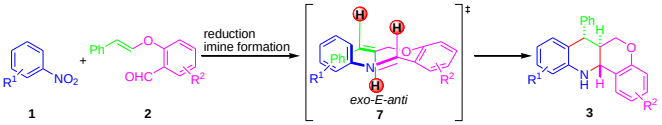


Table 2. Reaction of nitrobenzenes **1a-i** with 2-(cinnamyloxy)benzaldehydes **2a-d**.[a]



[a] Reactions were performed using 2 mmol of the nitrobenzene **1**, 2 mmol of the 2-cinnamyloxybenzaldehyde **2** and 15 mL aqueous citric acid in a sealed flask (25 mL).

In a second set of experiments the reactions between nitrobenzene (**1a**) and a number of 2-(cinnamyloxy)benz-aldehydes **2a-d** carrying different substituents on the benz-aldehyde moiety were studied. The required 2-(cinnamyloxy)-benzaldehydes **2b-d** were obtained by Williamson ether synthesis of the substituted salicylic aldehydes **5b-d** with cinnamyl chloride (**6**) under basic conditions in high yields (see Experimental Section). The reactions between **1a** and **2b-d** were performed under the optimized reaction conditions. Again, the products of the domino reduction / imine formation / aza-Diels–Alder reaction, were formed exclusively in a highly diastereoselective manner with yields between 80 and 82% (Table 2, **3j–l**). It should be noticed that all reactions can be run in an aqueous solvent system under mild conditions and that the crude products are almost free of any side products. The cycloadducts were obtained in high purity (~95%) after workup and column filtration on silica gel. Analytically pure samples were obtained by crystallization or flash chromatography.



Scheme 2. Proposed reaction mechanism for the formation of tetrahydrochromano[4,3-b]quinolines **3**.

It is assumed that the transformations can be classified as a domino reduction / imine formation / intramolecular aza-Diels–Alder reaction with inverse electron demand (Scheme 2). After selective reduction of the nitrobenzene **1**, the resulting aniline **4** undergoes condensation with the aldehyde **2** to the corresponding imine or iminium ion. It can be assumed that they adopt the *E*-configuration, since *E*-imines and *E*-iminium salts are known to be more stable than the corresponding *Z*-isomers.[28] The formation of the C=N double bond is followed by the intramolecular aza-Diels–Alder reaction that yields the *trans*-*trans* diastereomer with an equatorial phenyl group at C-7 exclusively. The high degree of diastereoselectivity – only one out of four diastereomers is formed – is attributed to the fact that the cyclization proceeds via the *exo-E-anti* transition state structure **7** with an *E*-configuration of both the C=N bond of the diene and the C=C bond of the dienophile.

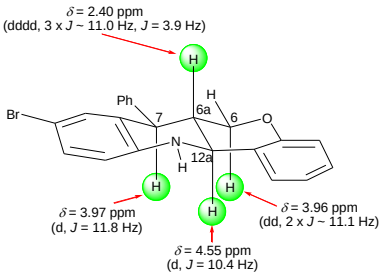


Figure 1. Relative configuration of **3h**.

The cyclization products **3** were isolated in diastereomerically pure form by column filtration on silica gel of the crude products followed by crystallization. In no case, an additional diastereomer could be detected. The structures of all Povarov products were unambiguously established by mass spectrometry and NMR spectroscopy. The full assignment of the ^{1}H and ^{13}C chemical shifts was achieved by evaluating their gCOSY, gHSQC and gHMBC spectra (Figures 1, 2). Compound

3h is particularly suitable for the determination of the relative configuration of the cycloadducts since all 16 proton signals in the ^{1}H NMR are well separated. Analysis of the gCOSY spectrum revealed four spin systems. In addition to three aromatic spin systems there is one spin system consisting of the four aliphatic protons 6-H(ax), 6-H(eq), 6a-H, 7-H and 12a-H. The proton 6a-H resonates at δ = 2.40 ppm as dddd with coupling constants of J = 3.9 ($^{3}J_{\text{6a-H, 6-Heq}}$), ~ 11 ($^{3}J_{\text{6a-H, 6-Hax}}$), ~ 11 ($^{3}J_{\text{6a-H, 7-H}}$) and ~ 11 ($^{3}J_{\text{6a-H, 12-H}}$) Hz. The large vicinal coupling constants $^{3}J_{\text{6a-H, 7-H}}$ ~ 11 Hz and $^{3}J_{\text{6a-H, 12-H}}$ ~ 11 Hz indicate the positions of 6a-H, 7-H and 12-H as axial. This proves the *trans* arrangement of both rings as well as the equatorial position of the phenyl group at C-7 unequivocally.

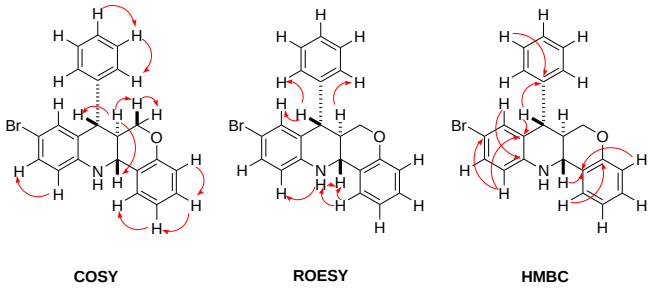


Figure 2. Selected COSY, ROESY and HMBC correlations of **3h**.

HMBC- and ROESY spectra allowed for the unequivocal assignment of all ^{13}C NMR signals as well as the connectivities (Figure 2). In this regard, the HMBC correlations of 11-H to C-7a, 8-H to C-11a, 7-H to C-11a, 12a-H to C-12b, 1-H to C-4a and 4-H to C-12b were particularly significant. The structural assignment is well supported by the ROESY correlations of NH to 11-H, 12a-H to 1-H, 7-H to 8-H and 7a-H to 2'-H.

Conclusions

In conclusion, the domino reduction / imine formation / intramolecular aza-Diels–Alder reaction is reported for the first time. The reaction between nitrobenzenes and *ω*-unsaturated aldehydes, i.e. 2-(cinnamyloxy)benzaldehydes, in the presence of iron as reductant and catalytic amounts of montmorillonite K10 in aqueous citric acid at 80 °C produces *trans*-fused tetrahydrochromano[4,3-*b*]quinolines exclusively and with yields between 69% and 87%. It is assumed that the sequence of reactions starts with the iron-mediated reduction of the nitrobenzene. The resulting aniline reacts with the *ω*-unsaturated aldehyde to the corresponding imine which in turn undergoes an intramolecular aza-Diels–Alder reaction. This Povarov type reaction is catalysed by montmorillonite K10, proceeds via an *exo-E-anti* transition state structure and delivers the *trans*-fused tetrahydrochromano[4,3-*b*]quinolines in diastereomerically pure form. The new method allows the replacement of anilines with nitrobenzenes as substrates for intramolecular aza-Diels–Alder reactions. The domino reaction can be performed with numerous functionalized nitrobenzenes and a number of 2-(cinnamyloxy)benzaldehydes.

Experimental Section

General Remarks: Nitrobenzene (**1a**) and solvents used for extraction and purification were distilled prior to use. Iron powder was treated with diluted aqueous HCl, washed with water and acetone and dried in vacuo. All other reagents were used without further purification. Reaction temperatures are reported as bath temperatures. Thin-layer chromatography (TLC) was performed on TLC silica gel 60 F_{254}. Compounds were visualized with UV light (λ = 254 nm) and by immersion in a $KMnO_4$ solution followed by heating. Products were purified by flash chromatography on silica gel, 0.04-0.053 mm mesh (Macherey–Nagel & Co), or by crystallization. Melting points were recorded with a Büchi B-545 melting point apparatus with open capillary tubes and are uncorrected. IR spectra were measured with a Bruker Alfa FTIR spectrometer. UV/Vis spectra were recorded with a Varian Cary 50 instrument. ^{1}H and ^{13}C NMR spectra were recorded at 500/125 or 300/75 MHz using Varian Unity Inova spectrometers, with $CDCl_3$ or CD_3COCD_3 as the solvents. The ^{1}H and ^{13}C chemical shifts were referenced to residual signals at $\delta_{H/C}$ = 7.26/77.00 ppm ($CDCl_3$) and $\delta_{H/C}$ = 2.05/29.9 (CD_3COCD_3). HSQC-, HMBC- and COSY-spectra were recorded with Varian Unity Inova spectrometers at 300 and 500 MHz. Coupling constants J [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), app d (apparent dublett), app t (apparent triplett) and br (broad). 1D and 2D homonuclear NMR spectra were measured with standard pulse sequences. Copies of the NMR spectra were prepared using SpinWorks.[29] Low-resolution electron impact mass spectra (MS) and exact mass electron impact mass spectra (HRMS) were obtained at 70 eV using a double focusing sector field mass spectrometer (Finnigan MAT 95). Intensities are reported as percentages relative to the base peak (I = 100%).

General Procedure I for the Preparation of 2-(Cinnamyloxy)benzaldehydes 2 from 2-Hydroxybenzaldehydes 5 and Cinnamyl Chloride (6): 2-Hydroxybenzaldehyde **5** (100 mmol), cinnamyl chloride (**6**) (110 mmol), K_2CO_3 (150 mmol), KI (15 mmol) and *N*,*N*-dimethylformamide (75 mL) were stirred at room temperature for 3d. Then, water (100 mL) was added. The mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (3 × 50 mL) and water (50 mL). The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and filtered over silica gel. Crystallization of the crude product from *i*-propanol gave analytically pure 2-(cinnamyloxy)benzaldehyde **2**.

2-(Cinnamyloxy)benzaldehyde (2a):[30a] K_2CO_3 (20.9 g, 151.2 mmol), KI (253 mg, 1.5 mmol), 2-hydroxybenzaldehyde (**5a**) (12.3 g, 101 mmol) and cinnamyl chloride (**6**) (16.8 g, 110 mmol) were used according to general procedure I. After workup, 2-(cinnamyloxy)benzaldehyde (**2a**) was obtained (21.9 g, 91.9 mmol, 92 %) as a colourless solid. R_f = 0.29 (petroleum ether/dichloromethane, 1:1), m.p. 54–55 °C (ref.[30a] m.p. 51–52 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.83 (dd, J = 5.7, J = 1.4 Hz, 2 H), 6.43 (dt, J = 16.0, J = 5.7 Hz, 1 H), 6.77 (dt, J = 16.0, J = 1.4 Hz, 1 H), 7.01–7.08 (m, 2 H), 7.25–7.38 (m, 3 H), 7.43 (app d, J = 8.0 Hz, 2 H), 7.55 (ddd, 2 × J ≈ 7.4, J = 1.9 Hz, 1 H), 7.87 (dd, J = 7.9, J = 1.9 Hz, 1 H), 10.58 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.1, 112.9, 120.9,

123.4, 125.1, 126.6, 128.1, 128.5, 128.7, 133.5, 135.8, 136.1, 161.0, 189.8 ppm. MS (EI): *m/z* (%) = 238 (8) $[M]^+$, 209 (11), 115 (100), 91 (18).

2-(Cinnamyloxy)-5-methylbenzaldehyde (2b):[30b] K_2CO_3 (2.07 g, 15.0 mmol), KI (28 mg, 0.15 mmol), 2-hydroxy-5-methylbenzaldehyde (**5b**) (1.37 g, 10.1 mmol) and cinnamyl chloride (**6**) (1.69 g, 11.0 mmol) were used according to general procedure I. Crystallization of the crude product from *i*-propanol gave 2-(cinnamyloxy)-5-methylbenzaldehyde (**2b**) (1.88 g, 7.47 mmol, 74%) as a colourless solid. R_f = 0.35 (petroleum ether/dichloromethane, 1:1), m.p. 58–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 4.82 (dd, *J* = 5.7, *J* = 1.4 Hz, 2 H), 6.42 (dt, *J* = 16.0, *J* = 5.7 Hz, 1 H), 6.75 (dt, *J* = 16.0, *J* = 1.5 Hz, 1 H), 6.94 (d, *J* = 8.5 Hz, 1 H), 7.28 (app t, *J* = 7.3 Hz, 1 H), 7.32–7.36 (m, 3 H), 7.42 (app d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 2.6 Hz, 1 H), 10.54 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 69.2, 113.0, 123.6, 124.8, 126.6, 128.1, 128.5, 128.6, 130.3, 133.4, 136.1, 136.5, 159.1, 189.9 ppm. MS (EI): *m/z* (%) = 252 (36) $[M]^+$, 234 (29), 224 (31), 209 (27), 191 (14), 161 (26), 133 (21), 115 (100), 105 (24), 91 (32), 77 (19).

5-Chloro-2-(cinnamyloxy)benzaldehyde (2c):[30b] K_2CO_3 (3.14 g, 22.7 mmol), KI (42 mg, 0.25 mmol), 5-chloro-2-hydroxybenzaldehyde (**5c**) (2.35 g, 15.0 mmol) and cinnamyl chloride (**6**) (2.53 g, 16.6 mmol) were used according to general procedure I. Crystallization of the crude product from *i*-propanol gave 5-chloro-2-(cinnamyloxy)benzaldehyde (**2c**) (3.52 g, 12.9 mmol, 86%) as a colourless solid. R_f = 0.39 (petroleum ether/dichloromethane, 1:1), m.p. 94–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.82 (dd, *J* = 5.8, *J* = 1.3 Hz, 2 H), 6.40 (dt, *J* = 15.9, *J* = 5.8 Hz, 1 H), 6.76 (dt, *J* = 16.0, *J* = 1.5 Hz, 1 H), 7.00 (d, *J* = 8.9 Hz, 1 H), 7.25–7.45 (m, 5 H), 7.48 (dd, *J* = 8.9, *J* = 2.8 Hz, 1 H), 7.81 (d, *J* = 2.8 Hz, 1 H), 10.49 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.6, 114.6, 122.9, 126.0, 126.6, 128.0, 128.3, 128.7, 134.0, 135.3, 135.9, 159.4, 188.4 ppm. MS (EI): *m/z* (%) = 272 (23) $[M]^+$, 237 (31), 209 (61), 181 (32), 153 (21), 125 (21), 115 (100), 91 (34).

5-Bromo-2-(cinnamyloxy)benzaldehyde (2d):[30a] K_2CO_3 (6.36 g, 46 mmol), KI (78 mg, 0.47 mmol), 5-bromo-2-hydroxybenzaldehyde (**5d**) (6.15 g, 30.6 mmol) and cinnamyl chloride (**6**) (5.13 g, 33.6 mmol) were used according to general procedure I. Crystallization of the crude product from *i*-propanol gave 5-bromo-2-(cinnamyloxy)benzaldehyde (**2d**) (8.72 g, 27.5 mmol, 90%) as a colourless solid. R_f = 0.31 (petroleum ether/dichloromethane, 7:3), m.p. 101–104 °C (ref.[30a] m.p. 69–71 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.81 (dd, *J* = 5.8, *J* = 1.4 Hz, 2 H), 6.40 (dt, *J* = 16.0, *J* = 5.8 Hz, 1 H), 6.76 (dt, *J* = 16.0, *J* = 1.5 Hz, 1 H), 6.95 (d, *J* = 8.9 Hz, 1 H), 7.25–7.44 (m, 6 H), 7.62 (dd, *J* = 8.9, *J* = 2.7 Hz, 1 H), 7.95 (d, *J* = 2.6 Hz, 1 H), 10.47 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.5, 113.7, 115.0, 122.8, 126.4, 126.6, 128.3, 128.7, 131.0, 134.0, 135.9, 138.2, 159.8, 188.3 ppm. MS (EI): *m/z* (%) = 316 (73) $[M]^+$, 287 (14), 237 (75), 208 (65), 191 (29), 178 (18), 165 (16), 131 (19), 115 (100), 91 (25), 77 (12).

General Procedure II for the Domino Reactions between Nitroarenes 1 and 2-(Cinnamyloxy)benzaldehydes 2: A 25 mL screw-capped round bottom flask was equipped with a magnetic stirring bar and charged with iron powder (447 mg, 8 mmol), citric acid monohydrate (1.682 g, 8 mmol), montmorillonite K10 (300 mg), water (15 mL), the nitroarene **1** (2 mmol), and the 2-(cinnamyloxy)benzaldehyde **2** (2 mmol). The sealed reaction flask was stirred at 80 °C for 4 h. Each hour the reaction flask was shaken and sonicated for a few seconds using an ultrasonic bath. The reaction mixture was filtered with suction; the filter cake was washed with water (3 × 50 mL) and then extracted with hot acetone (3 × 50 mL). The combined organic extracts were evaporated under reduced pressure. The residue thus obtained was dissolved in dichloromethane (100 mL) and filtered over silica gel. Analytically pure compounds were obtained by crystallization or flash chromatography on silica gel.

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3a):[27a] Iron powder (447 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (305 mg), nitrobenzene (**1a**) (247 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (476 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3a**) was obtained (545 mg, 1.74 mmol, 87%). Crystallization from methanol gave **3a** in analytically pure form as a colourless solid. R_f = 0.29 (petroleum ether/dichloromethane, 1:1), m.p. 168–170 °C. IR: $\tilde{\nu}$ = 3363, 3026, 2974, 2892, 2858, 1599, 1577, 1486, 1451, 1421, 1354, 1306, 1232, 1204, 1141, 1126, 1075, 1040, 1017, 897, 856, 818, 776, 746, 724, 705, 675, 640, 625, 551, 506 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.49 (dddd, $^3J_{6a\text{-}H,7\text{-}H}$ ≈ 11.2, $^3J_{6a\text{-}H,6\text{-}H(ax)}$ ≈ 11.2, $^3J_{6a\text{-}H,12a\text{-}H}$ ≈ 11.2, $^3J_{6a\text{-}H,6\text{-}H(eq)}$ = 3.8 Hz, 1 H, 6a-H), 3.85 (d, $^3J_{7\text{-}H,6a\text{-}H}$ = 11.6 Hz, 1 H, 7-H), 3.87 (dd, $^2J_{6\text{-}H(ax),6\text{-}H(eq)}$ ≈ 11.1, $^3J_{6\text{-}H(ax),6a\text{-}H}$ ≈ 11.1 Hz, 1 H, 6-H(ax)), 4.05 (dd, $^3J_{6\text{-}H(eq),6\text{-}H(ax)}$ ≈ 11.0, $^3J_{6\text{-}H(eq),6a\text{-}H}$ = 3.6 Hz, 1 H, 6-H(eq)), 4.38 (brs, 1 H, N-H), 4.50 (d, $^3J_{12a\text{-}H,6a\text{-}H}$ = 10.3 Hz, 1 H, 12a-H), 6.62–6.66 (m, 2 H, 8-H and 9-H), 6.76 (d, $^3J_{11\text{-}H,10\text{-}H}$ = 8.0 Hz, 1 H, 11-H), 6.83 (d, $^3J_{4\text{-}H,3\text{-}H}$ = 8.0 Hz, 1 H, 4-H), 7.00 (dd, $^3J_{2\text{-}H,1\text{-}H}$ ≈ 7.6, $^3J_{2\text{-}H,3\text{-}H}$ ≈ 7.6 Hz, 1 H, 2-H), 7.04–7.08 (m, 1 H, 10-H), 7.16–7.22 (m, 3 H, 3-H, 2'-H and 6'-H), 7.29 (app t, *J* = 7.3 Hz, 1 H, 4'-H), 7.31–7.36 (m, 3 H, 1-H, 3'-H and 5'-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.1 (C-6a), 47.0 (C-7), 52.1 (C-12a), 67.6 (C-6), 116.0 (C-11), 117.0 (C-4), 118.9 (C-9), 120.7 (C-2), 122.6 (C-12b), 124.7 (C-1), 125.4 (C-7a), 127.1 (C-4'), 127.3 (C-10), 128.67 (C-3 or C-3' and C-5'), 128.73 (C-3 or C-3' and C-5'), 129.1 (C-2' and C-6'), 130.4 (C-8), 142.9 (C-1'), 144.4 (C-11a), 154.1 (C-4a) ppm. MS (EI) *m/z* (%) = 313 (100), $[M]^+$, 280 (14), 254 (6), 232 (37), 206 (15), 180 (12), 154 (18), 139 (12).

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3b): Iron powder (447 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (301 mg), 4-nitrotoluene (**1b**) (275 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (477 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3b**) was obtained (498 mg, 1.52 mmol, 76%). Crystallization from methanol gave **3b** in analytically pure form as a colourless solid. R_f = 0.25 (petroleum ether/dichloromethane, 1:1), m.p. 207–209 °C. IR: $\tilde{\nu}$ = 2897, 1611, 1580, 1493, 1447, 1350, 1314, 1288, 1227, 1204, 1156, 1135, 1079, 1064, 1041, 1015, 943, 898, 881, 828, 806, 786, 755, 725, 705, 674, 648, 624, 551, 522, cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 305 (3.37), 283 (3.59), 262 (3.97) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, CH_3), 2.46 (dddd, $^3J_{6a\text{-}H,7\text{-}H}$ ≈ 11.6, $^3J_{6a\text{-}H,6\text{-}H(ax)}$ ≈ 11.6, $^3J_{6a\text{-}H,12a\text{-}H}$ ≈ 11.6, $^3J_{6a\text{-}H,6\text{-}H(eq)}$ = 3.7 Hz, 1 H, 6a-H), 3.81 (d, $^3J_{7\text{-}H,6a\text{-}H}$ = 11.5 Hz, 1 H, 7-H), 3.87 (dd, $^2J_{6\text{-}H(ax),6\text{-}H(eq)}$ ≈ 11.2, $^3J_{6\text{-}H(ax),6a\text{-}H}$ ≈ 11.2 Hz, 1 H, 6-H(ax), 4.04 (dd, $^2J_{6\text{-}H(eq),6\text{-}H(ax)}$ = 11.0, $^3J_{6\text{-}H(eq),6a\text{-}H}$ = 3.6 Hz, 1 H, 6-H(eq)), 4.25 (brs, 1 H, N-H), 4.45 (d, $^3J_{12a\text{-}H,6a\text{-}H}$ = 10.3 Hz, 1 H, 12a-H), 6.46 (s, 1 H, 8-H), 6.71 (d, $^3J_{11\text{-}H,10\text{-}H}$ = 8.1 Hz, 1 H, 11-H), 6.83 (dd, $^3J_{4\text{-}H,3\text{-}H}$ = 8.2, $^4J_{4\text{-}H,2\text{-}H}$ = 1.1 Hz, 1 H, 4-H), 6.89 (dd, $^3J_{10\text{-}H,11\text{-}H}$ = 8.2, $^4J_{10\text{-}H,8\text{-}H}$ = 1.9 Hz, 1 H, 10-H), 7.00 (ddd, $^3J_{2\text{-}H,1\text{-}H}$ ≈ 7.6, $^3J_{2\text{-}H,3\text{-}H}$ ≈ 7.6, $^4J_{2\text{-}H,4\text{-}H}$ = 1.2 Hz, 1 H, 2-H), 7.16–7.23 (m, 3 H, 3'-H, 2'-H and 6'-H), 7.29 (app t, *J* = 7.2 Hz, 1 H, 4'-H), 7.32–7.39 (m, 3 H, 1-H, 3'-H and 5'-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5 (CH_3), 41.4 (C-6a), 47.0 (C-7), 52.3 (C-12a), 67.6 (C-6), 116.3 (C-11), 116.9 (C-4), 120.7 (C-2), 122.8 (C-12b), 124.8 (C-1), 125.5 (C-7a), 127.0 (C-4'), 128.1 (C-10), 128.3 (C-9), 128.6 (C-3 or C-3' and C-5'), 128.7 (C-3 or C-3' and C-5'), 129.1 (C-2' and C-6'), 130.9 (C-8), 142.1 (C-11a), 143.0 (C-1') ppm. MS (EI): *m/z* (%) = 327 (100) $[M]^+$, 308 (4), 246 (7), 220 (18), 194 (9), 153 (3), 131 (7). HRMS (EI): calcd. for $C_{23}H_{21}NO$ $[M]^+$ 327.1618; found 327.1623.

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-11-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3c): Iron powder (449 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (300 mg), 2-nitrotoluene (**1c**) (274 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (476 mg, 2.0 mmol) were used according to general procedure II. After workup and column chromatography on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-11-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3c**) (478 mg, 1.46 mmol, 73%) was obtained. Crystallization from *i*-propanol gave **3c** in analytically pure form as a colourless solid. R_f = 0.53 (petroleum ether/dichloromethane, 1:1), m.p. 169–170 °C. IR: $\tilde{\nu}$ = 3029, 2898, 1595, 1579, 1486, 1464, 1447, 1356, 1314, 1244, 1226, 1141, 1094, 1078, 1041, 1020, 1009, 946, 919, 883, 842, 797, 776, 761, 746, 701, 673, 626, 554, 517 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 283 (3.69), 276 (3.68), 249 (3.97) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 2.47 (dddd, $^3J_{6a\text{-}H,7\text{-}H} \approx 11.3$, $^3J_{6a\text{-}H,6\text{-}H(ax)} \approx 11.3$, $^3J_{6a\text{-}H,12a\text{-}H} \approx 11.3$, $^3J_{6a\text{-}H,6\text{-}H(eq)} = 3.6$ Hz, 1 H, 6a-H), 3.87 (d, $^3J_{7\text{-}H,6a\text{-}H} = 11.6$ Hz, 1 H, 7-H), 3.88 (dd, $^2J_{6\text{-}H(ax),6\text{-}H(eq)} \approx 11.2$, $^3J_{6\text{-}H(ax),6a\text{-}H} \approx 11.2$ Hz, 1 H, 6-H(ax)), 4.05 (dd, $^2J_{6\text{-}H(eq),6\text{-}H(ax)} = 11.0$, $^3J_{6\text{-}H(eq),6a\text{-}H} = 3.6$ Hz, 1 H, 6-H(eq)), 4.50 (d, $^3J_{12a\text{-}H,6a\text{-}H} = 10.4$ Hz, 1 H, 12a-H), 6.54 (d, $^3J_{8\text{-}H,9\text{-}H} = 7.8$ Hz, 1 H, 8-H), 6.59 (dd, $^3J_{9\text{-}H,8\text{-}H} \approx 7.3$, $^3J_{9\text{-}H,10\text{-}H} \approx 7.3$ Hz, 1 H, 9-H), 6.85 (dd, $^3J_{4\text{-}H,3\text{-}H} = 8.3$, $^4J_{4\text{-}H,2\text{-}H} = 1.2$ Hz, 1 H, 4-H), 6.98 (ddd, $^3J_{10\text{-}H,9\text{-}H} = 7.2$, $2 \times J \approx 0.8$ Hz, 1 H, 10-H), 7.03 (ddd, $^3J_{2\text{-}H,1\text{-}H} \approx 7.5$, $^3J_{2\text{-}H,3\text{-}H} \approx 7.5$, $^4J_{2\text{-}H,4\text{-}H} = 1.2$ Hz, 1 H, 2-H), 7.17 (app d, J = 7.9 Hz, 2 H, 2'-H and 6'-H), 7.22 (ddd, $^3J_{3\text{-}H,2\text{-}H} \approx 7.8$, $^3J_{3\text{-}H,4\text{-}H} \approx 7.8$, $^4J_{3\text{-}H,1\text{-}H} = 1.6$ Hz, 1 H, 3-H), 7.28 (app t, J = 7.3 Hz, 1 H, 4'-H), 7.34 (app t, J = 7.5 Hz, 2 H, 3'-H and 5'-H), 7.42 (ddd, $^3J_{1\text{-}H,2\text{-}H} = 7.7$, $2 \times J \approx 1.3$ Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.4 (CH_3), 40.9 (C-6a), 47.3 (C-7), 52.1 (C-12a), 67.7 (C-6), 117.1 (C-4), 118.4 (C-9), 120.8 (C-2), 122.9 (C-12b), 123.3 (C-11), 124.7 (C-1), 125.3 (C-7a), 127.0 (C-4'), 128.3 (C-8 or C-10), 128.4 (C-8 or C-10), 128.71 (C-3 or C-3' and C-5'), 128.72 (C-3 or C-3' and C-5'), 129.1 (C-2' and C-6'), 142.3 (C-11a), 143.1 (C-1'), 154.2 (C-4a) ppm. MS (EI): *m/z* (%) = 327 (100) $[M]^+$, 248 (11), 220 (25), 194 (14), 165 (9), 131 (10), 115 (6), 91 (9), 77 (7). HRMS (EI): calcd. for $C_{23}H_{21}NO$ $[M]^+$ 327.1618; found 327.1607.

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-9-methoxy-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3d): Iron powder (446 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (303 mg), 4-methoxynitrobenzene (**1d**) (307 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (475 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-9-methoxy-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3d**) was obtained (494 mg, 1.44 mmol, 72%). Crystallization from *i*-propanol gave **3d** in analytically pure form as a colourless solid. R_f = 0.11 (petroleum ether/dichloromethane, 1:1), m.p. 185–186 °C. IR: $\tilde{\nu}$ = 3024, 2892, 1607, 1580, 1493, 1437, 1313, 1266, 1226, 1151, 1138, 1083, 1063, 1036, 1013, 943, 921, 900, 849, 826, 805, 785, 755, 746, 726, 705, 675, 648, 625, 569, 557, 531 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 358 (3.04), 317 (3.54), 249 (3.98) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (dddd, $^3J_{6a\text{-}H,\ 6\text{-}H(ax)} \approx 11.3$, $^3J_{6a\text{-}H,7\text{-}H} \approx 11.3$, $^3J_{6a\text{-}H,12a\text{-}H} \approx 11.3$, $^3J_{6a\text{-}H,6\text{-}H(eq)} = 3.7$ Hz, 1 H, 6a-H), 3.59 (s, 3 H, OCH_3), 3.80 (d, $^3J_{7\text{-}H,6a\text{-}H} = 11.5$ Hz, 1 H, 7-H), 3.87 (dd, $^2J_{6\text{-}H(ax),6\text{-}H(eq)} \approx 11.2$, $^3J_{6\text{-}H(ax),6a\text{-}H} \approx 11.2$ Hz, 1 H, 6-H(ax)), 4.06 (dd, $^2J_{6\text{-}H(eq),6\text{-}H(ax)} = 11.0$, $^3J_{6\text{-}H(eq),6a\text{-}H} = 3.7$ Hz, 1 H, 6-H(eq)), 4.07 (brs, 1 H, N-H), 4.41 (d, $^3J_{12a\text{-}H,6a\text{-}H} = 10.4$ Hz, 1 H, 12a-H), 6.23 (d, $^4J_{8\text{-}H,10\text{-}H} = 2.6$ Hz, 1 H, 8-H), 6.70 (dd, $^3J_{10\text{-}H,11\text{-}H} = 8.6$, $^4J_{10\text{-}H,8\text{-}H} = 2.7$ Hz, 1 H, 10-H), 6.76 (d, $^3J_{11\text{-}H,10\text{-}H} = 8.7$ Hz, 1 H, 11-H), 6.83 (dd, $^3J_{4\text{-}H,3\text{-}H} = 8.2$, $^4J_{4\text{-}H,2\text{-}H} = 1.0$ Hz, 1 H, 4-H), 7.00 (ddd, $^3J_{2\text{-}H,1\text{-}H} \approx 7.5$, $^3J_{2\text{-}H,3\text{-}H} \approx 7.5$, $^4J_{2\text{-}H,4\text{-}H} = 1.1$ Hz, 1 H, 2-H), 7.16–7.22 (m, 3 H, 3-H, 2'-H and 5'-H), 7.28 (app t, 1 H, 4'-H), 7.34 (app t, 2 H, 3'-H and 5'-H), 7.38 (d, $^3J_{1\text{-}H,2\text{-}H} = 7.7$ Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.2 (C-6a), 47.2 (C-7), 52.5 (C-12a), 55.5 (OCH_3), 67.6 (C-6), 113.4 (C-10), 115.7 (C-8), 116.9 (C-4), 117.7 (C-11), 120.7 (C-2), 122.9 (C-12b), 125.0 (C-1), 127.1 (C-4' and C-7a), 128.6 (C-3 or C-3' and C-5'), 128.7 (C-3 or C-3' and C-5'), 129.1 (C-2' and C-6'), 142.7 (C-1'), 138.2 (C-11a), 153.0 (C-9), 154.1 (C-4a) ppm. MS (EI): *m/z* (%) = 343 (100) $[M]^+$, 326 (4), 264 (8), 236 (6), 210 (5), 131 (3), 69 (4), 55 (7). HRMS (EI): calcd. for $C_{23}H_{21}NO_2$ $[M]^+$ 343.1567; found 343.1563.

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline-9-carbonitrile (3e): Iron powder (449 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (300 mg), 4-nitrobenzonitrile (**1e**) (297 mg, 2 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (476 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline-9-carbonitrile (**3e**) was obtained (514 mg, 1.52 mmol, 76%). Crystallization from *i*-propanol gave **3e** in analytically pure form as a colourless solid. R_f = 0.10 (petroleum ether/dichloromethane, 1:1), m.p. 241–243 °C. IR: $\tilde{\nu}$ = 3362, 3031, 2212, 1607, 1582, 1504, 1480, 1464, 1446, 1342, 1320, 1251, 1225, 1194, 1137, 1066, 1045, 1017, 943, 888, 827, 816, 779, 746, 700, 677, 653, 626, 588, 567, 541, 509 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 357 (2.91), 303 (4.01), 272 (4.02) nm. ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 2.46 (dddd, $^3J_{6a\text{-}H,7\text{-}H} \approx 11.5$, $^3J_{6a\text{-}H,12a\text{-}H} \approx 11.5$, $^3J_{6a\text{-}H,6\text{-}H(ax)} \approx 11.5$, $^3J_{6a\text{-}H,6\text{-}H(eq)} = 3.7$ Hz, 1 H, 6a-H), 3.91 (dd, $^2J_{6\text{-}H(eq),6\text{-}H(ax)} = 11.1$, $^3J_{6\text{-}H(eq),6a\text{-}H} = 3.7$ Hz, 1 H, 6-H(eq)), 3.99 (dd, $^2J_{6\text{-}H(ax),6\text{-}H(eq)} \approx 11.2$, $^3J_{6\text{-}H(ax),6a\text{-}H} \approx 11.2$ Hz, 1 H, 6-H(ax)), 4.02 (d, $^3J_{7\text{-}H,6a\text{-}H} = 11.4$ Hz, 1 H, 7-H), 4.71 (d, $^3J_{12a\text{-}H,6a\text{-}H} = 10.2$ Hz, 1 H, 12a-H), 6.65 (brs, 1 H, N-H) 6.75 (s, 1 H; 8-H), 6.78 (dd, $^3J_{4\text{-}H,3\text{-}H} = 8.3$, $^4J_{4\text{-}H,2\text{-}H} = 0.8$ Hz, 1 H, 4-H), 6.97 (ddd, overlapped, $^3J_{2\text{-}H,1\text{-}H} \approx 7.6$, $^3J_{2\text{-}H,3\text{-}H} \approx 7.6$ Hz, $^4J_{2\text{-}H,4\text{-}H} \approx 0.9$ Hz, 1 H, 2-H), 6.97 (d, overlapped, $^3J_{11\text{-}H,10\text{-}H} = 8.4$ Hz, 1 H, 11-H), 7.19 (dd, $^3J_{3\text{-}H,2\text{-}H} \approx 7.7$, $^3J_{3\text{-}H,4\text{-}H} \approx 7.7$ Hz, 1 H, 3-H), 7.31 (d, overlapped, $^3J_{10\text{-}H,11\text{-}H} = 8.3$ Hz, 1 H, 10-H), 7.31 (app d, overlapped, 2 H, 2'-H and 6'-H), 7.36 (app t, J = 7.4 Hz, 1 H, 4'-H), 7.44 (app t, J = 7.6 Hz, 2 H, 3'-H and 5'-H), 7.59 (d, $^3J_{1\text{-}H,2\text{-}H} = 7.8$ Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 40.7 (C-6a), 46.8 (C-12a), 52.5 (C-7), 68.1 (C-6), 99.8 (C-9), 116.3 (C-11), 117.6 (C-4), 121.4 (C-2), 123.2 (C-12b), 126.2 (C-7a), 126.5 (C-1), 128.4 (C-4'), 129.5 (C-3), 130.0 (C-2', C-3', C-5' and C-6'), 131.9 (C-10), 134.7 (C-8), 142.8 (C-1'), 150.2 (C-11a), 155.0 (C-4a) ppm. MS (EI): *m/z* (%) = 338 (100) $[M]^+$, 259 (13), 231 (26), 205 (12), 190 (9), 131 (29), 91 (8), 77 (8). HRMS (EI): calcd. for $C_{23}H_{18}N_2O$ $[M]^+$ 338.1414; found 338.1410.

(6a*RS*,7*SR*,12a*RS*)-9-Fluoro-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3f): Iron powder (448 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (300 mg), 4-fluoronitrobenzene (**1f**) (283 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (477 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-9-fluoro-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3f**) was obtained (550 mg, 1.66 mmol, 83%). Crystallization from *i*-propanol gave **3f** in analytically pure form as a colourless solid. R_f = 0.62 (petroleum ether/dichloromethane, 7:3), m.p. 170–172 °C; IR: $\tilde{\nu}$ = 3025, 2983, 2862, 1605, 1580, 1493, 1475, 1463, 1451, 1356, 1312, 1259, 1230, 1205, 1189, 1135, 1079, 1056, 1042, 1015, 958, 932, 920, 871, 829, 811, 762, 743, 711, 699, 645, 615, 548, 516 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 250 (4.01) nm. ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 2.39 (dddd, $^3J_{6a\text{-}H,7a\text{-}H} \approx 10.5$, $^3J_{6a\text{-}H,6\text{-}H(ax)} \approx 10.5$, $^3J_{6a\text{-}H,12a\text{-}H} \approx 10.5$, $^3J_{6a\text{-}H,6\text{-}H(eq)} = 4.3$ Hz, 1 H, 6a-H), 3.93 (dd, $^2J_{6\text{-}H(eq),6\text{-}H(ax)} = 11.0$, $^3J_{6\text{-}H(eq),6a\text{-}H} = 4.4$ Hz, 1 H, 6-H(eq)), 3.97 (d, $^3J_{7\text{-}H,6a\text{-}H} = 11.7$ Hz, 1 H, 7-H), 3.97 (dd, ^{2}J6-H(ax),6-H(eq) ≈ 10.9, $^3J_{6\text{-}H(ax),6a\text{-}H} \approx 10.9$ Hz, 1 H, 6-H(ax)), 4.51 (d, $^3J_{12a\text{-}H,6a\text{-}H} = 10.9$ Hz, 1 H, 12a-H), 5.67 (brs, 1 H, N-H), 6.24 (dd, $^3J_{8\text{-}H,9\text{-}F} = 10.1$, $^4J_{8\text{-}H,10\text{-}H} = 2.9$ Hz, 1 H, 8-H), 6.76 (dd, $^3J_{4\text{-}H,3\text{-}H} = 8.1$, $^4J_{4\text{-}H,2\text{-}H} = 1.2$ Hz, 1 H, 4-H), 6.78 (ddd, $^3J_{10\text{-}H,9\text{-}F} = 8.3$, $^3J_{10\text{-}H,11\text{-}H} = 8.3$, $^4J_{10\text{-}H,8\text{-}H} = 3.0$ Hz, 1 H, 10-H), 6.87 (dd, $^3J_{11\text{-}H,10H} = 8.9$, $^4J_{11\text{-}H,9\text{-}F} = 5.1$ Hz, 1 H, 11-H), 6.95 (ddd, $^3J_{2\text{-}H,1\text{-}H} \approx 7.6$, $^3J_{2\text{-}H,3\text{-}H} \approx 7.6$, $^4J_{2\text{-}H,4\text{-}H} = 1.3$ Hz, 1 H, 2-H), 7.16 (ddd, $^3J_{3\text{-}H,2\text{-}H} \approx 7.3$, $^3J_{3\text{-}H,4\text{-}H} \approx 7.3$, $^4J_{3\text{-}H,1\text{-}H} = 1.7$ Hz, 1 H, 3-H), 7.33 (app t, J = 7.4 Hz,

1 H, 4'-H), 7.41 (app t, *J* = 7.1 Hz, 2 H, 3'-H and 5'-H), 7.27 (app d, *J* = 8.2 Hz, 2 H, 2'-H and 6'-H), 7.59 (ddd, $^3J_{1\text{-H},2\text{-H}}$ = 7.7, 2 × *J* ≈ 1.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): *δ* = 41.8 (C-6a), 47.4 (C-7), 52.9 (C-12a), 68.1 (C-6), 114.6 (d, $^2J_{CF}$ = 22.6 Hz, C-10), 116.5 (d, $^2J_{CF}$ = 22.6 Hz, C-8), 117.4 (C-4), 117.9 (d, $^3J_{CF}$ = 7.5 Hz, C-11), 121.3 (C-2), 124.2 (C-12b), 126.8 (C-1), 127.4 (d, $^3J_{CF}$ = 6.2 Hz, C-7a), 128.1 (C-4'), 129.3 (C-3), 129.8 (C-3' and C-5'), 130.0 (C-2' and C-6'), 143.0 (d, $^4J_{CF}$ = 1.9 Hz, C-11a), 143.9 (C-1'), 156.9 (d, J_{CF} = 233.6 Hz, C-9), 157.6 (C-4a) ppm. MS (EI): *m/z* (%) = 331 (100) $[M]^+$, 252 (12), 224 (21), 198 (10), 183 (6), 131 (9). HRMS (EI): calcd. for $C_{22}H_{18}NOF$ $[M]^+$ 331.1367; found 331.1381.

(6a*RS*,7*SR*,12a*RS*)-9-Chloro-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3g): Iron powder (449 mg, 8.0 mmol), citric acid monohydrate (1.69 g, 8.0 mmol), montmorillonite K10 (304 mg), 4-chloronitrobenzene (**1g**) (315 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (476 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), 9-chloro-(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3g**) was obtained (543 mg, 1.56 mmol, 78%). Crystallization from dichloromethane/petroleum ether gave **3g** in analytically pure form as a colourless solid. R_f = 0.38 (petroleum ether/dichloromethane, 1:1), m.p. 173–174 °C. IR: $\tilde{\nu}$ = 2897, 1598, 1581, 1478, 1449, 1349, 1313, 1288, 1260, 1227, 1156, 1126, 1095, 1080, 1061, 1042, 1017, 944, 921, 901, 874, 827, 804, 779, 753, 727, 706, 663, 644, 621, 550, 512 cm^{-1}. UV (CH_3CN): λ_{max} (log *ε*): 310 (3.39), 260 (4.10) nm. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 2.45 (dddd, $^3J_{6a\text{-H},6\text{-H(ax)}}$ ≈ 11.4, $^3J_{6a\text{-H},7\text{-H}}$ ≈ 11.4, $^3J_{6a\text{-H},12a\text{-H}}$ ≈ 11.4, $^3J_{6a\text{-H},6\text{-H(eq)}}$ = 3.5 Hz, 1 H, 6a-H), 3.79 (d, $^3J_{7\text{-H},6a\text{-H}}$ = 11.5 Hz, 1 H, 7-H), 3.85 (dd, $^2J_{6\text{-H(ax)},6\text{-H(eq)}}$ ≈ 11.2, $^3J_{6\text{-H(ax)},6a\text{-H}}$ ≈ 11.2 Hz, 1 H, 6-H(ax)), 4.02 (dd, $^2J_{6\text{-H(eq)},6\text{-H(ax)}}$ = 11.0, $^3J_{6\text{-H(eq)},6a\text{-H}}$ = 3.5 Hz, 1 H, 6-H(eq)), 4.38 (brs, 1 H, N-H), 4.47 (d, $^3J_{2a\text{-H},6a\text{-H}}$ = 10.4 Hz, 1 H, 12a-H), 6.60 (d, $^4J_{8\text{-H},10\text{-H}}$ = 2.2 Hz, 1 H, 8-H), 6.68 (d, $^3J_{11\text{-H},10\text{-H}}$ = 8.6 Hz, 1 H, 11-H), 6.83 (dd, $^3J_{4\text{-H},3\text{-H}}$ = 8.2, $^4J_{4\text{-H},2\text{-H}}$ = 1.1 Hz, 1 H, 4-H), 6.98–7.03 (m, 2 H, 2-H and 10-H), 7.16 (app d, *J* = 6.9 Hz, 2 H, 2'-H and 6'-H), 7.20 (dd, $^3J_{3\text{-H},2\text{-H}}$ ≈ 7.7, $^3J_{3\text{-H},4\text{-H}}$ ≈ 7.7 Hz, 1 H, 3-H), 7.31 (app t, *J* = 7.6 Hz, 1 H, 4'-H), 7.32 (d, overlapped, $^3J_{1\text{-H},2\text{-H}}$ = 7.1 Hz, 1 H, 1-H), 7.36 (app t, *J* = 7.6 Hz, 2 H, 3'-H and 5'-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 40.7 (C-6a), 46.9 (C-7), 52.1 (C-12a), 67.4 (C-6), 117.08 (C-4 or C-11), 117.13 (C-4 or C-11), 120.8 (C-2), 122.2 (C-12b), 123.5 (C-9), 124.6 (C-1), 127.0 (C-7a), 127.38 (C-10), 127.40 (C-4'), 128.8 (C-3), 129.0 (overlapped, C-2', C-3', C-5' and C-6'), 129.9 (C-8), 141.9 (C-1'), 143.0 (C-11a), 154.0 (C-4a) ppm. MS (EI): *m/z* (%) = 347 (100) $[M]^+$, 308 (9), 268 (14), 240 (14), 214 (9), 154 (12). HRMS (EI): calcd. for $C_{22}H_{18}ClNO$ $[M]^+$ 347.1071; found 347.1065.

(6a*RS*,7*SR*,12a*RS*)-9-Bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3h): Iron powder (447 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (301 mg), 4-bromonitrobenzene (**1h**) (405 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (475 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-9-bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3h**) was obtained (542 mg, 1.38 mmol, 69%). Crystallization from *i*-propanol gave **3h** in analytically pure form as a colourless solid. R_f = 0.37 (petroleum ether/dichloromethane, 1:1), m.p. 167–168 °C. IR: $\tilde{\nu}$ = 3026, 2897, 1582, 1477, 1449, 1379, 1350, 1313, 1288, 1256, 1288, 1256, 1228, 1204, 1156, 1127, 1077, 1059, 1043, 1018, 943, 920, 900, 886, 871, 853, 826, 804, 777, 705, 652, 619, 551, 509 cm^{-1}. UV (CH_3CN): λ_{max} (log) = 310 (3.36), 261 (4.13) nm. ^{1}H NMR (500 MHz, CD_3COCD_3): *δ* = 2.40 (dddd, $^3J_{6a\text{-H},7a\text{-H}}$ ≈ 11.1, $^3J_{6a\text{-H},6\text{-H(ax)}}$ ≈ 11.1, $^3J_{6a\text{-H},12a\text{-H}}$ ≈ 11.1, $^3J_{6a\text{-H},6\text{-H(eq)}}$ = 3.9 Hz, 1 H, 6a-H), 3.90 (dd, $^2J_{6\text{-H(eq)},(6\text{-H(ax)}}$ = 11.0, $^3J_{6\text{-H(eq)},6a\text{-H}}$ = 3.9 Hz, 1 H, 6-H(eq)), 3.96 (dd, $^2J_{6\text{-H(ax)},6\text{-H(eq)}}$ ≈ 11.1, $^3J_{6\text{-H(ax)},6a\text{-H}}$ ≈ 11.1 Hz, 1 H, 6-H(ax), 3.97 (d, $^3J_{7\text{-H},6a\text{-H}}$ = 11.8 Hz, 1 H, 7-H), 4.55 (d, $^3J_{12a\text{-H},6a\text{-H}}$ = 10.4 Hz, 1 H, 12a-H), 5.93 (brs, 1 H, N-H), 6.60 (s, 1 H, 8-H), 6.76 (dd, $^3J_{4\text{-H},3\text{-H}}$ = 8.2, $^4J_{4\text{-H},2\text{-H}}$ = 0.8 Hz, 1 H, 4-H), 6.83 (d, $^3J_{11\text{-H},10\text{-H}}$ = 8.6 Hz, 1 H, 11-H), 6.95 (ddd, $^3J_{2\text{-H},1\text{-H}}$ ≈ 7.5 Hz, $^3J_{2\text{-H},3\text{-H}}$ ≈ 7.5, $^4J_{2\text{-H},4\text{-H}}$ = 1.0 Hz, 1 H, 2-H), 7.10 (dd, $^3J_{10\text{-H},11\text{-H}}$ = 8.6, $^4J_{10\text{-H},8\text{-H}}$ = 2.3 Hz, 1 H, 10-H), 7.17 (dd, $^3J_{3\text{-H},2\text{-H}}$ ≈ 7.7, $^3J_{3\text{-H},4\text{-H}}$ ≈ 7.7 Hz, 1 H, 3-H), 7.28 (app d, *J* = 7.2 Hz, 2 H, 2'-H and 6'-H), 7.34 (app t, *J* = 7.4 Hz, 1 H, 4'-H), 7.41 (app t, *J* = 7.4 Hz, 2 H, 3'-H and 5'-H), 7.58 (d, $^3J_{1\text{-H},2\text{-H}}$ = 7.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 41.6 (C-6a), 47.2 (C-7), 52.6 (C-12a), 68.1 (C-6), 109.6 (C-9), 117.4 (C-4), 118.4 (C-11), 121.3 (C-2), 123.9 (C-12b), 126.7 (C-1), 128.2 (C-7a), 128.8 (C-4'), 129.3 (C-3), 129.8 (C-3' and C-5'), 130.0 (C-2' and C-6'), 130.6 (C-10), 133.0 (C-8), 143.6 (C-1'), 145.8 (C-11a), 155.0 (C-4a) ppm. MS (EI): *m/z* (%) = 391 (100) $[M]^+$, 312 (8), 284 (13), 260 (6), 204 (6), 165 (7), 131 (15). HRMS (EI): calcd. for $C_{22}H_{18}BrNO$ $[M]^+$ 391.0566; found 391.0545.

(6a*RS*,7*SR*,12a*RS*)-11-Bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3i): Iron powder (449 mg, 8.0 mmol), citric acid monohydrate (1.70 g, 8.1 mmol), montmorillonite K10 (303 mg), 2-bromonitrobenzene (**1i**) (404 mg, 2.0 mmol) and 2-(cinnamyloxy)benzaldehyde (**2a**) (477 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-11-bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3i**) was obtained (573 mg, 1.46 mmol, 73%). Crystallization from petroleum ether gave **3i** in analytically pure form as a colourless solid. R_f = 0.46 (petroleum ether/dichloromethane, 1:1), m.p. 202–204 °C. IR: $\tilde{\nu}$ = 3024, 2892, 1607, 1580, 1493, 1437, 1313, 1266, 1227, 1151, 1138, 1083, 1063, 1036, 1013, 943, 921, 900, 849, 826, 805, 784, 755, 746, 725, 705, 675, 624, 569, 556, 531, 453 cm^{-1}. UV (CH_3CN): λ_{max} (log *ε*) = 302 (3.48), 284 (3.62), 275 (3.63), 251 (3.94) nm. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 2.50 (dddd, $^3J_{6a\text{-H},7\text{-H}}$ ≈ 11.4, $^3J_{6a\text{-H},6\text{-H(ax)}}$ ≈ 11.4, $^3J_{6a\text{-H},12a\text{-H}}$ ≈ 11.4, $^3J_{6a\text{-H},6\text{-H(eq)}}$ = 3.6 Hz, 1 H, 6a-H), 3.86 (d, $^3J_{7\text{-H},6a\text{-H}}$ = 11.7 Hz, 1 H, 7-H), 3.87 (dd, $^2J_{6\text{-H(ax)},6\text{-H(eq)}}$ ≈ 11.2, $^3J_{6\text{-H(ax)},6a\text{-H}}$ ≈ 11.2 Hz, 1 H, 6-H(ax), 4.04 (dd, $^2J_{6\text{-H(eq)},6\text{-H(ax)}}$ = 11.0, $^3J_{6\text{-H(eq)},6a\text{-H}}$ = 3.7 Hz, 1 H, 6-H(eq), 4.54 (d, $^3J_{12a\text{-H},6a\text{-H}}$ = 10.3 Hz, 1 H, 12a-H), 5.07 (brs, 1 H, N-H), 6.48 (dd, $^3J_{9\text{-H},8\text{-H}}$ ≈ 7.8, $^3J_{9\text{-H},10\text{-H}}$ ≈ 7.8 Hz, 1 H, 9-H), 6.59 (ddd, $^3J_{8\text{-H},9\text{-H}}$ = 7.7, 2 × *J* ≈ 1.2 Hz, 1 H, 8-H), 6.85 (dd, $^3J_{4\text{-H},3\text{-H}}$ = 8.2, $^4J_{4\text{-H},2\text{-H}}$ = 1.2 Hz, 1 H, 4-H), 7.04 (ddd, $^3J_{2\text{-H},1\text{-H}}$ ≈ 7.6, $^3J_{2\text{-H},3\text{-H}}$ ≈ 7.6, $^4J_{2\text{-H},4\text{-H}}$ = 1.3 Hz, 1 H, 2-H), 7.17 (app d, *J* = 8.2 Hz, 2 H, 2'-H, 6'-H), 7.22 (ddd, $^3J_{3\text{-H},2\text{-H}}$ ≈ 7.7, $^3J_{3\text{-H},4\text{-H}}$ ≈ 7.7, $^4J_{3\text{-H},1\text{-H}}$ = 1.6 Hz, 1 H, 3-H), 7.30 (app t, *J* = 7.3 Hz, 1 H, 4'-H), 7.33 (d overlapped, 1 H, 10-H), 7.35 (app t, *J* = 7.3 Hz, 2 H, 3'-H and 5'-H), 7.40 (ddd $^3J_{1\text{-H},2\text{-H}}$ = 7.7, 2 × *J* ≈ 1.3 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 40.7 (C-6a), 47.3 (C-7), 52.1 (C-12a), 67.5 (C-6), 110.3 (C-11), 117.0 (C-4), 118.7 (C-9), 120.9 (C-2), 122.0 (C-12b), 124.5 (C-1), 126.7 (C-7a), 127.3 (C-4'), 128.85 (C-3 or C-3' and C-5'), 128.87 (C-3 or C-3' and C-5'), 129.0 (C-2' and C-6'), 129.6 (C-8), 130.6 (C-10), 141.6 (C-11a), 142.3 (C-1'), 153.9 (C-4a) ppm. MS (EI): *m/z* (%) = 391 (100) $[M]^+$, 312 (9), 284 (15), 260 (4), 234 (4), 204 (7), 180 (13), 165 (7), 131 (10). HRMS (EI): calcd. for $C_{22}H_{18}BrNO$ $[M]^+$ 391.0566; found 391.0557.

(6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-Tetrahydro-2-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3j): Iron powder (447 mg, 8.0 mmol), citric acid monohydrate (1.69 g, 8.0 mmol), montmorillonite K10 (300 mg), nitrobenzene (**1a**) (247 mg, 2.0 mmol) and 2-cinnamyloxy-5-methylbenzaldehyde (**2b**) (505 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-6a,7,12,12a-tetrahydro-2-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3j**) was obtained (530 mg, 1.62 mmol, 81%). Crystallization from *i*-propanol gave **3j** in analytically pure form as a colourless solid. R_f = 0.45 (petroleum ether/dichloromethane, 1:1), m.p. 205–206 °C. IR: $\tilde{\nu}$ = 3392, 3025, 1598, 1515, 1492, 1439, 1320, 1269, 1249, 1222, 1203, 1152, 1126, 1087, 1072, 1029, 991, 967, 883, 866, 806, 744, 704, 688, 620,

573, 532, 509 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 291 (3.76), 251 (4.02) nm. ^1H NMR (500 MHz, CD_3COCD_3): δ = 2.27 (s, 3 H, CH_3), 2.33–2.41 (m, 1 H, 6a-H), 3.88–3.93 (m, 2 H, 6-H(ax) and 6-H(eq)), 3.93 (d, $^3J_{7\text{-H,6a-H}}$ = 11.8 Hz, 1 H, 7-H), 4.49 (d, $^3J_{12\text{a-H,6a-H}}$ = 10.3 Hz, 1 H, 12a-H), 5.67 (brs, 1 H, N-H), 6.48–6.54 (m, 2 H, 8-H and 9-H), 6.64 (d, $^3J_{4\text{-H,3-H}}$ = 8.3 Hz, 1 H, 4-H), 6.84 (d, $^3J_{11\text{-H,10-H}}$ = 8.2 Hz, 1 H, 11-H), 6.94–6.99 (m, 2 H, 3-H and 10-H), 7.24 (app d, *J* = 7.2 Hz, 2 H, 2'-H and 6'-H), 7.29 (app t, *J* = 7.3 Hz, 1 H, 4'-H), 7.41 (s, 1 H, 1-H), 7.37 (app t, *J* = 7.4 Hz, 2 H, 3'-H and 5'-H) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 20.8 (CH_3), 42.4 (C-6a), 47.5 (C-7), 53.0 (C-12a), 68.8 (C-6), 116.6 (C-11), 117.1 (C-4), 118.6 (C-9), 123.9 (C-12b), 125.8 (C-7a), 127.1 (C-1), 127.78 (C-4' or C-10), 127.80 (C-4' or C-10), 129.6 (C-3' and C-5'), 129.7 (C-3), 130.0 (C-2' and C-6'), 130.2 (C-2), 130.8 (C-8), 144.7 (C-1'), 146.6 (C-11a), 152.9 (C-4a) ppm. MS (EI): *m/z* (%) = 327 (100) $[M]^+$, 312 (7), 248 (14), 220 (18), 180 (15), 145 (15), 115 (9), 91 (9). HRMS (EI): calcd. for $C_{23}H_{21}NO$ $[M]^+$ 327.1618; found 327.1607.

(6a*RS*,7*SR*,12a*RS*)-2-Chloro-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3k): Iron powder (448 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (300 mg), nitrobenzene (**1a**) (248 mg, 2.0 mmol) and 5-chloro-2-(cinnamyloxy)benzaldehyde (**2c**) (547 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 7:3), (6a*RS*,7*SR*,12a*RS*)-2-chloro-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3k**) was obtained (556 mg, 1.60 mmol, 80%). Crystallization from *i*-propanol gave **3k** in analytically pure form as a colourless solid. R_f = 0.50 (petroleum ether/dichloromethane, 7:3), m.p. 160–161 °C. IR: $\tilde{\nu}$ = 3391, 3025, 2978, 2854, 1603, 1581, 1477, 1407, 1350, 1310, 1268, 1236, 1220, 1204, 1146, 1101, 1058, 1021, 934, 896, 874, 856, 817, 777, 749, 729, 702, 645, 605, 559, 544, 529 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 294 (3.67), 232 (4.11) nm. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.46 (dddd, $^3J_{6\text{a-H,7-H}}$ ≈ 11.2, $^3J_{6\text{a-H,6-H(ax)}}$ ≈ 11.2, $^3J_{6\text{a-H,12a-H}}$ ≈ 11.2, $^3J_{6\text{a-H,6-H(eq)}}$ = 3.5 Hz, 1 H, 6a-H), 3.83 (d, $^3J_{7\text{-H,6a-H}}$ = 11.7 Hz, 1 H, 7-H), 3.85 (dd, $^2J_{6\text{-H(ax),6-H(eq)}}$ ≈ 11.2, $^3J_{6\text{-H(ax),6a-H}}$ ≈ 11.2 Hz, 1 H, 6-H(ax)), 4.05 (dd, $^2J_{6\text{-H(eq),6-H(ax)}}$ = 11.0, $^3J_{6\text{-H(eq),6a-H}}$ = 3.7 Hz, 1 H, 6-H(eq)), 4.32 (brs, 1 H, N-H), 4.45 (d, $^3J_{12\text{a-H,6a-H}}$ = 10.4 Hz, 1 H, 12a-H), 6.63 (d, $^3J_{8\text{-H,9-H}}$ = 7.4 Hz, 1 H, 8-H), 6.66 (ddd, $^3J_{9\text{-H,8-H}}$ ≈ 7.5, $^3J_{9\text{-H,10-H}}$ ≈ 7.5, $^4J_{9\text{-H,11-H}}$ = 1.1 Hz, 1 H, 9-H), 6.76 (d, $^3J_{4\text{-H,3-H}}$ = 8.4 Hz, 1 H, 4-H), 6.80 (d, $^3J_{11\text{-H,10-H}}$ = 7.9 Hz, 1 H, 11-H), 7.08 (ddd, $^3J_{10\text{-H,9-H}}$ ≈ 7.4, $^3J_{10\text{-H,11-H}}$ ~ 7.4, $^4J_{10\text{-H,8-H}}$ = 1.5 Hz, 1 H, 10-H), 7.14 (dd, $^3J_{3\text{-H,4-H}}$ = 8.7, $^4J_{3\text{-H,1-H}}$ = 2.4 Hz, 1 H, 3-H), 7.17 (app d, *J* = 7.1 Hz, 2 H, 2'-H and 6'-H), 7.29 (app t, *J* = 7.3 Hz, 1 H, 4'-H), 7.33 (s, 1 H, 1-H), 7.35 (app t, *J* = 7.1 Hz, 2 H, 3'-H and 5'-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.8 (C-6a), 46.9 (C-7), 52.0 (C-12a), 67.8 (C-6), 116.3 (C-11), 118.4 (C-4), 119.3 (C-9), 124.2 (C-12b), 124.8 (C-1), 125.4 (C-7a), 125.6 (C-2), 127.2 (C-4'), 127.4 (C-10), 128.6 (C-3), 128.8 (C-3' and C-5'), 129.1 (C-2' and C-6'), 130.4 (C-8), 142.6 (C-1'), 144.0 (C-11a), 152.7 (C-4a) ppm. MS (EI): *m/z* (%) = 347 (100) $[M]^+$, 268 (15), 240 (13), 206 (20), 180 (24), 165 (27), 152 (9), 115 (9), 77 (12); HRMS (EI): calcd. for $C_{22}H_{18}NOCl$ $[M]^+$ 347.1071; found 347.1073.

(6a*RS*,7*SR*,12a*RS*)-2-Bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3l): Iron powder (447 mg, 8.0 mmol), citric acid monohydrate (1.68 g, 8.0 mmol), montmorillonite K10 (301 mg), nitrobenzene (**1a**) (247 mg, 2.01 mmol) and 5-bromo-2-(cinnamyloxy)benzaldehyde (**2d**) (634 mg, 2.0 mmol) were used according to general procedure II. After workup and column filtration on silica gel (petroleum ether/dichloromethane = 1:1), (6a*RS*,7*SR*,12a*RS*)-2-bromo-6a,7,12,12a-tetrahydro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (**3l**) was obtained (643 mg, 1.64 mmol, 82%). Crystallization from *i*-propanol gave **3l** in analytically pure form as a colorless solid. R_f = 0.40 (petroleum ether/dichloromethane, 1:1), m.p. 172–173 °C. IR: $\tilde{\nu}$ = 3386, 3023, 2977, 2853, 1603, 1582, 1477, 1403, 1350, 1310, 1270, 1235, 1204, 1134, 1092, 1058, 1021, 931, 856, 816, 777, 749, 726, 702, 644, 630, 597, 558, 540, 524 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 294 (3.68), 232 (4.16) nm. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.45 (dddd, $^3J_{6\text{a-H,7-H}}$ ≈ 11.2, $^3J_{6\text{a-H,6-H(ax)}}$ ≈ 11.2, $^3J_{6\text{a-H,12a-H}}$ ≈ 11.2, $^3J_{6\text{a-H,6-H(eq)}}$ = 3.6 Hz, 1 H, 6a-H), 3.83 (d, $^3J_{7\text{-H,6a-H}}$ = 11.9 Hz, 1 H, 7-H), 3.84 (dd, $^2J_{6\text{-H(ax),6-H(eq)}}$ ≈ 11.4, $^3J_{6\text{-H(ax), 6a-H}}$ ≈ 11.4 Hz, 1 H, 6-H(ax)), 4.05 (dd, $^2J_{6\text{-H(eq),6-H(ax)}}$ = 11.1, $^3J_{6\text{-H(eq),6a-H}}$ = 3.6 Hz, 1 H, 6-H(eq)), 4.30 (brs, 1 H, N-H), 4.45 (d, $^3J_{12\text{a-H,6a-H}}$ = 10.4 Hz, 1 H, 12a-H), 6.63 (d, $^3J_{8\text{-H,9-H}}$ = 7.2 Hz, 1 H, 8-H), 6.66 (dd, $^3J_{9\text{-H,8-H}}$ ≈ 7.5, $^3J_{9\text{-H,10-H}}$ ≈ 7.5 Hz, 1 H, 9-H), 6.71 (d, $^3J_{4\text{-H,3-H}}$ = 8.8 Hz, 1 H, 4-H), 6.80 (d, $^3J_{11\text{-H,10-H}}$ = 7.9 Hz, 1 H, 11-H), 7.08 (ddd, $^3J_{10\text{-H,9-H}}$ ≈ 7.5, $^3J_{10\text{-H,11-H}}$ ≈ 7.5, $^4J_{10\text{-H,8-H}}$ = 1.5 Hz, 1 H, 10-H), 7.17 (app d, *J* = 7.1 Hz, 2 H, 2'-H and 6'-H), 7.26–7.31 (m, 2 H, 3-H and 4'-H), 7.35 (app t, *J* = 7.2 Hz, 2 H, 3'-H and 5'-H), 7.35 (s, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.7 (C-6a), 46.9 (C-7), 51.9 (C-12a), 67.8 (C-6), 112.8 (C-2), 116.3 (C-11), 118.8 (C-4), 119.3 (C-9), 124.8 (C-12b), 125.4 (C-7a), 127.2 (C-4'), 127.5 (C-10), 127.8 (C-1), 128.8 (C-3' and C-5'), 129.1 (C-2' and C-6'), 130.4 (C-8), 131.5 (C-3), 142.6 (C-1'), 144.0 (C-11a), 153.3 (C-4a) ppm. MS (EI): *m/z* (%) = 391 (100) $[M]^+$, 312 (28), 284 (11), 234 (13), 206 (34), 180 (30), 165 (18), 139 (16), 91 (13), 77 (14). HRMS (EI) calcd. for $C_{22}H_{18}NOBr$ $[M]^+$ 391.0566; found 391.0537.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for compounds **2a–d** and **3a–l**.

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Keywords: Domino reactions • Nitrogen heterocycles • Oxygen heterocycles • Reduction

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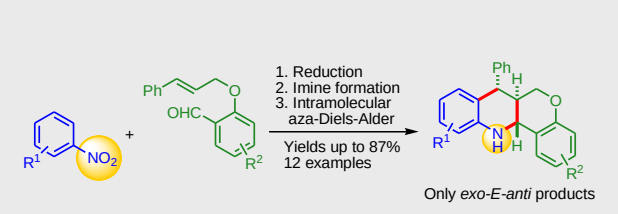

Domino reduction / imine formation / intramolecular aza-Diels–Alder reaction delivers tetrahydrochromano[4,3-*b*]quinolines with high *exo-E-anti* selectivity and with yields up to 87% by reacting nitrobenzenes and a 2-(cinnamyloxy)-benzaldehyde in aqueous citric acid using iron as a reductant and montmorillonite K10 as a catalyst.

One-Pot Reactions

*Hans-Georg Imrich, Jürgen Conrad, Uwe Beifuss**

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