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From Nitrobenzenes to Substituted Tetrahydroquinolines in a Single Step by a Domino Reduction/Imine Formation/Aza-Diels–Alder Reaction

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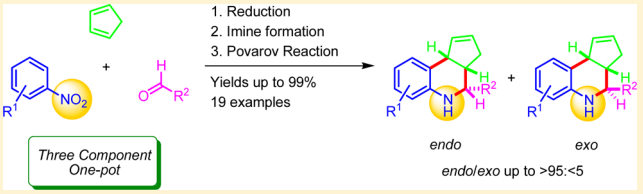
Supporting Information

ABSTRACT: The three-component reaction between a nitrobenzene, an aldehyde, and a dienophile in the presence of iron powder as a reductant and montmorillonite K10 as a catalyst in aqueous citric acid delivers the products of an aza-Diels–Alder (Povarov) reaction with high *endo*-selectivity and yields up to 99%.



INTRODUCTION

The Povarov reaction is an aza-Diels–Alder reaction with inverse electron demand between an electron-poor 2-azabutadiene as diene and an electron-rich dienophile.[1,2] It allows the efficient assembly of substituted tetrahydroquinolines and related ring systems.[3] Such *N*-heterocycles exhibit a remarkably broad range of biological activities[4] and also find applications as ligands for transition-metal-catalyzed reactions,[5] such as Rh-catalyzed asymmetric hydrogenations,[5a] asymmetric Friedel–Crafts reactions,[5b] as dyes,[5c–f] as antioxidants,[5g] and as corrosion inhibitors.[5h] This justifies the great interest in the further development of efficient and selective variants of the Povarov reaction.[1,2] The required 2-azabutadiene can be prepared by reaction of an aromatic or heteroaromatic amine with a carbonyl component and subsequently reacted with a dienophile.[6] It is also possible to generate the imine *in situ* and to react it directly with the dienophile.[7] The advantage of the three-component approach is that the imines, which tend to be instable and are prone to hydrolysis,[8] need not to be isolated. The Povarov reaction can be catalyzed by a wide range of Brønsted and Lewis acids; typical catalysts are lanthanide reagents,[9a] BF_3 OEt_2,[9b] $FeCl_3$,[9c] $Mg(ClO_4)_2$,[9d] and $BiCl_3$.[9e] The three-component reaction between anilines, aldehydes, and dienophiles can also be catalyzed by clay minerals, such as montmorillonite KSF, in solvents like water, dichloroethane, dichloromethane, and acetonitrile.[6a,10] Since many of the required anilines (a) tend to undergo oxidation[11] and (b) are usually derived by reduction of the readily available nitrobenzenes, it was considered to combine the nitrobenzene reduction with the three-component Povarov reaction to a new domino process. Numerous methods are available for the transformation of nitrobenzenes into anilines,[12] and it is also known that anilines that are formed *in situ* by reduction of the corresponding nitrobenzenes can undergo further transformations. Examples include the *in situ* formation of anilines and their reaction with carbonyl compounds to imines[13] and secondary anilines, respectively.[14] The transition-metal-catalyzed reaction between nitrobenzene and alcohols to imines[15] and anilines, respectively,[16] is another example. However, only little is known about multicomponent reactions involving the reduction of nitroaromatic compounds. Among the few examples reported are the reaction between a nitrobenzene, a benzaldehyde, and an allylstannane to the corresponding homoallylamine[17] and the reaction of a nitrobenzene, a carbonyl compound, and a phosphite to an α-aminophosphonate.[18] The reduction of a nitrobenzene to an aniline using indium as reductant, followed by addition of an aldehyde and Danishefsky's diene, delivers the corresponding dihydropyridin-4-one.[19] The use of nitroaromatics as substrates for Povarov reactions remains largely unexplored. It is known that the reaction of a nitrobenzene with an excess of dihydrofuran in the presence of indium under acidic conditions delivers the corresponding Povarov products as diastereomeric mixtures with yields between 43% and 87%.[20] However, it seems that the method is restricted to enol ethers as substrates since the dihydrofuran serves as precursor for both the carbonyl component and the dienophile. Another example is the reaction between *m*-nitrotoluene and ethanol.[21] Irradiation with UV light (350 nm) in the presence of TiO_2 delivers a mixture of 2,7-dimethyl-4-ethoxy-1,2,3,4-tetrahydroquinoline and *m*-toluidine. Here, ethanol serves four functions: as solvent, as reductant, and as the precursor of both the carbonyl compound and the dienophile. To the best of our knowledge, the reduction of a nitrobenzene in the presence of a carbonyl compound and a dienophile has not been explored so far. Here, we report on the combination of the reduction of nitrobenzenes to anilines with the three-component Povarov reaction.

RESULTS AND DISCUSSION

The reaction between nitrobenzene (**1a**), benzaldehyde (**2a**), and cyclopentadiene (**3**) was selected as a model transformation, since it is known that the corresponding three-component

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Scheme 1. Montmorillonite-Catalyzed Povarov Reaction between Aniline (4), Benzaldehyde (2a), and Cyclopentadiene (3)

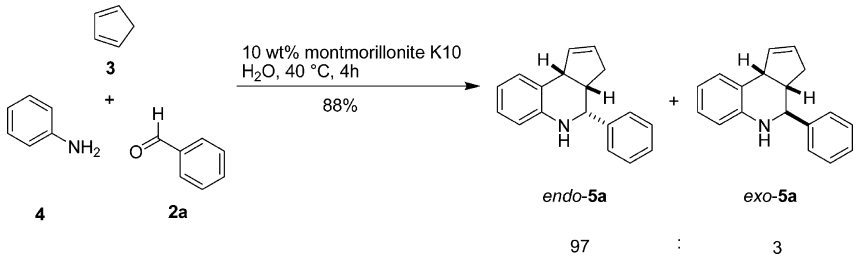
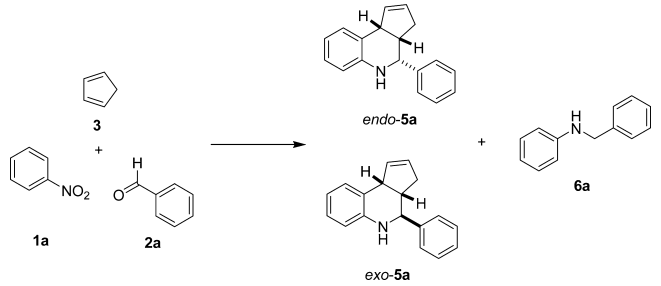


Table 1. Initial Experiments for the Povarov Reaction between Nitrobenzene (1a), Benzaldehyde (2a), and Cyclopentadiene (3)



entry	1a:2a:3 (equiv)	reductant (equiv)	clay (wt %)[a]	T (°C)	time (h)	yield 5a (%)[b]	endo/exo[c]	yield 6a (%)[d]
1[e]	1:1.3:7	H_2, Pd/C	6	30	22			
2[f]	1:1.3:4	In (3), HCl, NH_4Cl		50	5			
3[g]	1.2:1:5	Zn (6), AcOH (6)	10	40	4			22
4[h]	1:1:2	Fe (10), HCl (10)	5	65	5	21	91:9	5
5[h]	1:1:5	Fe (10), HCl (10)	5	65	5	42	89:11	4
6[h]	1:1:5	Fe (10), HCl (10)	30	65	5	43	93:7	3
7[i]	1.2:1:5	Fe (10), AcOH (10)	6	40	4	69	95:5	4
8[i]	1.5:1:5	Fe (10), citric acid (10)	6	40	4	96	95:5	

[a]Montmorillonite K10 was used as a catalyst. [b]Yields refer to the mixture of *endo*-**5a** and *exo*-**5a** after flash chromatography. [c]Ratio was determined from ^{1}H NMR of the crude product. [d]Yield was assessed from the ^{1}H NMR of the crude product. [e]**1a** (10 mmol), **2a**, and **3** in MeOH (50 mL) were reacted with H_2 in the presence of 1 mol % Pd/C as catalyst using a hydrogenation apparatus (30 °C, 2 atm). [f]**1a** (2 mmol), **2a**, and **3** were reacted in a mixture of 0.1 N HCl (6 mL) and sat. aqueous NH_4Cl solution (2 mL). [g]**1a** (2 mmol), **2a**, and **3** were reacted in H_2O (5 mL). [h]**1a** (2 mmol), **2a**, and **3** were reacted in a mixture of H_2O (8 mL) and EtOH (12 mL). [i]**1a** (2 mmol), **2a**, and **3** were reacted in water (10 mL).

reaction between aniline (**4**), benzaldehyde (**2a**), and cyclopentadiene (**3**) delivers the cyclopenta[*c*]quinolines *endo*-**5a** and *exo*-**5a** under different conditions in high chemical yields.[10e,22−25] Depending on the reaction conditions, the *endo*/*exo* ratio varies between 69:31[23] to 95:5.[22] Preliminary experiments have demonstrated that the reaction between aniline (**4**), **2a**, and **3** in the presence of 10 wt % montmorillonite K10 in water yields 88% of the Povarov products *endo*-**5a** and *exo*-**5a** in a 97:3 ratio (Scheme 1).[6a,10b,26]

To combine the reduction of nitrobenzene (**1a**) to aniline (**4**) and the Povarov reaction between aniline (**4**), benzaldehyde (**2a**), and cyclopentadiene (**3**) to a one-pot process, **1a**, **2a**, and **3** were reacted in the presence of both a reductant and montmorillonite under acidic conditions. Initial experiments with H_2, 1 mol % Pd/C, and 6 wt % montmorillonite K10 in methanol as solvent were disappointing since not even a trace of **5a** was formed (Table 1, entry 1). Also, the experiment employing 3 equiv of In as the reductant under acidic conditions, but in the absence of montmorillonite K10, did not deliver the Povarov products **5a** (Table 1, entry 2). The reaction of **1a**, **2a**, and **3** with 3 equiv of Zn in acetic acid resulted in reduction of **1a**; however, the aniline (**4**) formed reacted with **2a** by means of a reductive amination and yielded *N*-benzylaniline (**6a**) in 22% yield (Table 1, entry 3). The first positive results were obtained when Fe was employed as the reductant. The reaction of 1 equiv of nitrobenzene (**1a**), 1 equiv of benzaldehyde (**2a**), and 2 equiv of cyclopentadiene (**3**) with 10 equiv of Fe and 5 wt % montmorillonite K10 in aqueous ethanolic HCl delivered a mixture of 21% of the Povarov products *endo*- and *exo*-**5a** in a 91:9 ratio and 5% **6a** (Table 1, entry 4). By increasing the amount of the dienophile from 2 to 5 equiv, the yield of **5a** could be raised to 42% (Table 1, entry 5). An increase of the amount of montmorillonite K10 from 5 to 30 wt % did not pay off (Table 1, entry 6). A clear improvement with respect to chemical yield and *endo*/*exo*-selectivity was achieved by replacing HCl with less acidic acetic acid: the reaction with 10 equiv of Fe in 2 N aqueous acetic acid and 6 wt % montmorillonite K10 delivered 69% *endo*- and *exo*-**5a** in a 95:5 ratio (Table 1, entry 7). A further enhancement was observed when the acetic acid was substituted for citric acid. Under these conditions, the Povarov products *endo*- and *exo*-**5a** (*endo*/*exo* = 95:5 ratio) were isolated with 96% (Table 1, entry 8). Possibly, the efficient reduction of nitrobenzene (**1a**) to aniline (**4**) and the high yields of the cycloadducts can be ascribed to the chelating effect of citric acid.[27] It is also remarkable that, under these conditions, the formation of *N*-benzylaniline (**6a**) is completely suppressed (NMR).

The next goal was the optimization of the reaction conditions, i.e., minimization of the amounts of substrates, Fe, citric acid, and montmorillonite required (Table 2). In the light of

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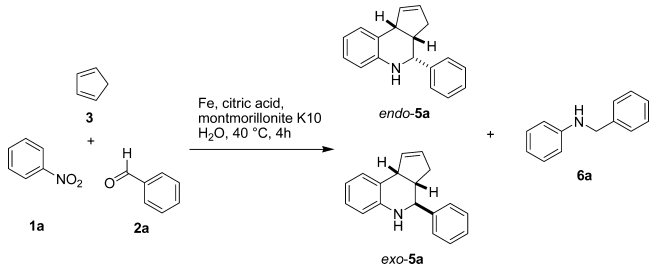
Table 2. Optimization of the Reaction Conditions[a]



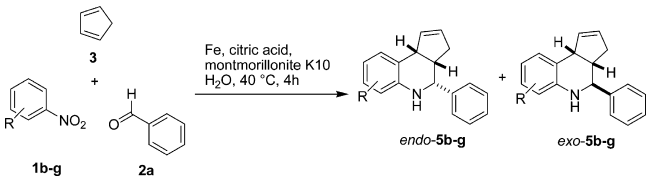
entry	1a:2a:3 (equiv)	Fe (equiv)	citric acid (equiv)	clay (wt %)	yield 5a (%)	*endo*/*exo*	yield 6a (%)
1	1.4:1:5.3	4	2	6	87	>95:5	
2	1.1:1:2	4	4	5	65	94:6	4
3	1.1:1:3	4	4	5	92	>95:5	
4	1.2:1:4	4	4	5	73	93:7	5
5	1:1:4	3	3	6	96	96:4	
6	1:1:3	3.1	2.8	6	92	94:6	
7	1:1:3	3	2	7	84	95:5	
8	1.1:1:5	4	4				
9	1.2:1:4	4		11			
10	1:1:4	0.1	4	5			

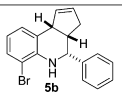
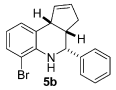
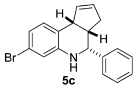
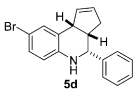
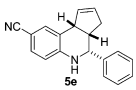
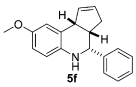
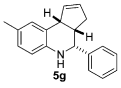
[a]All reactions were performed using 2 mmol of benzaldehyde (**2a**) and 10 mL H_2O in a sealed flask (25 mL).

the results shown in Table 1, entry 8, the amounts of the substrates and the reagents were decreased either simultaneously or consecutively. It was found that the equivalents of nitrobenzene (**1a**) and cyclopentadiene (**3**) as well as the load of Fe and citric acid could be reduced without affecting yield and selectivity of the model reaction. The best results were obtained when **1a**, **2a**, and **3** in a ratio of 1:1:4 were reacted with 3 equiv of Fe and 6 wt % montmorillonite K10 in 3 equiv of aqueous citric acid for 4 h at 40 °C. Under these conditions, 96% of *endo*-**5a** and *exo*-**5a** in a 96:4 ratio were isolated (Table 2, entry 5). Control experiments established that the three-component reaction cannot be performed in the absence of citric acid and montmorillonite K10, respectively (Table 2, entries 8 and 9). It was also demonstrated that the formation of **5a** cannot be achieved by using a combination of 10 mol % Fe, 5 wt % montmorillonite K10, and 4 equiv of aqueous citric acid (Table 2, entry 10).

After optimization of the reaction conditions (Table 2, entry 5), the scope of the new method was evaluated. In a first set of experiments, the structure of the nitroaromatic compound was varied. Toward this end, benzaldehyde (**2a**) and cyclopentadiene (**3**) were reacted with a number of *o*-, *m*-, and *p*-substituted nitrobenzenes **1b**–**g** (Table 3). In all cases, the nitroaromatic compound was selected as the limiting reactant, since, in the model reaction, **1a** had been fully consumed. When *o*-bromonitrobenzene (**1b**) was reacted with **2a** and **3** under the conditions of Table 3, entry 1, only 63% of a 93:7 mixture of *endo*-**5b** and *exo*-**5b** could be isolated. In order to improve the yield, the transformation was repeated with 4 equiv of Fe and 4.3 equiv of citric acid. Under these conditions, the yield of **5b** could be raised to 74% (Table 3, entry 2). The reactions with the remaining nitrobenzenes **1c**–**g** were run under similar conditions (Table 3, entries 3–7). In all cases, the products of the domino reduction/imine formation/Povarov reaction were isolated exclusively and with yields in the range between 70% and 98%. The *endo*/*exo* ratio of the cyclopenta[*c*]quinolines varied between 92:8 and >95:<5. In none of the reactions, the formation of the corresponding *N*-benzylanilines **6** could be detected.

Table 3. Variation of the Nitrobenzene[a,b,c,d,e]



entry	1b–g:2a:3 (equiv)	Fe (equiv)	citric acid (equiv)	product[b]	yield 5b–g (%)[c]	*endo*/*exo*[d]
1	1:1:4	3	3.1	 5b	63	93:7
2	1:1.1:4.5	4	4.3	 5b	74	92:8
3	1:1.2:4.5	4.2	4.2	 5c	98	95:5
4	1:1.1:4.8	4	4.2	 5d	88	94:6
5	1:1.2:4	3.7	4.1	 5e	70	95:5
6	1:1.1:4.3	4	4.2	 5f	87	94:6
7	1:1.2:4.9	4	4.3	 5g	98	>95:5[e]

[a]All reactions were performed using 2 mmol of the nitrobenzene **1**, 5 wt % montmorillonite K10, and 10 mL of H_2O in a sealed flask (25 mL). [b]Only the structure of the major *endo*-diastereomer is given. [c]The corresponding *N*-benzylanilines **6b**–**g** could not be detected. [d]The *endo*/*exo* ratios were obtained from the ^{1}H NMR spectra of **5b**–**g**. [e]Only the *endo*-isomer *endo*-**5g** could be detected.

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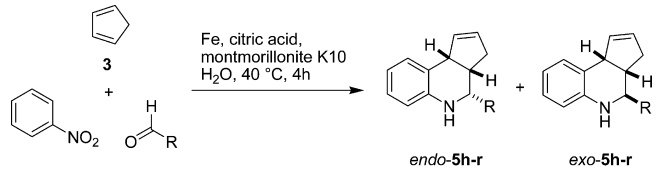
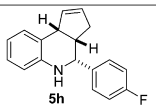
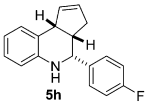
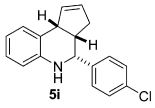
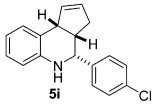
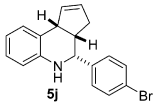
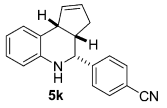
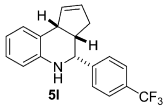
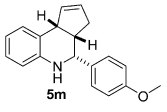
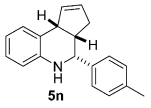
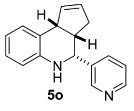
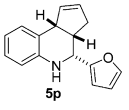
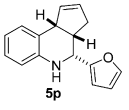
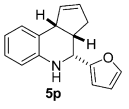
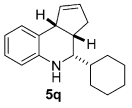
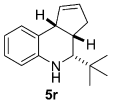
Table 4. Variation of the Aldehyde[a,b,c]



entry	1a:2b–l:3 (equiv)	Fe (equiv)	citric acid (equiv)	product[b]	yield 5h–r (%)	*endo*/*exo*[c]
1	1:1.1:4.1	4.1	4.2	 **5h**	95	96:4
2	1:1.1:4	3.2	3.7	 **5h**	94	96:4
3	1:1.1:4.2	4.1	4.2	 **5i**	78	95:5
4	1:1.3:4.4	3.1	3.3	 **5i**	77	96:4
5	1:1.1:4.5	4	4.2	 **5j**	95	96:4
6	1:1.1:4.3	3.8	4.2	 **5k**	70	96:4
7	1:1.1:4.7	4	4.3	 **5l**	89	95:5
8	1:1.2:5	4	4.5	 **5m**	57	87:13
9	1:1.3:5	4.1	4.3	 **5n**	99	95:5
10	1:1.2:5.9	4.1	4.4	 **5o**	53	95:5
11	1:1.1:4.5	4.1	4.2	 **5p**	28	95:5
12	1:3.2:4.5	4.1	4.2	 **5p**	58	95:5
13	1:3.3:4.6	3.2	4.4	 **5p**	60	94:6
14	1:1.2:4.5	4.2	4.1	 **5q**	92	95:5
15	1:1.2:4.8	3.9	3.9	 **5r**	88	100:0

[a]In all reactions, 2 mmol of nitrobenzene (**1a**) and 5 wt % montmorillonite K10 were reacted in a sealed flask (25 mL) in water (10 mL). [b]Only the structure of the major diastereomer is given. [c]Ratio determined from ^{1}H NMR spectra of the products *endo*/*exo*-**5h**–**r**.

Subsequently, the carbonyl scope of the three-component reaction was evaluated. For this purpose, nitrobenzene (**1a**) and cyclopentadiene (**3**) were reacted with different types of aldehydes. First, it was established that electron-poor as well as electron-rich benzaldehydes can be used as substrates. The reactions with the *p*-substituted benzaldehydes **2b**–**h** delivered the Povarov products **5h**–**n** exclusively with yields ranging from 57% to 99% (Table 4, entries 1–9). In all cases, the *endo*-isomer was formed predominantly. Then, it was demonstrated that the reaction is not limited to benzaldehydes, but can also be performed with heteroaromatic aldehydes like pyridine-3-carbaldehyde (**2i**) and 2-furancarbaldehyde (**2j**) (Table 4, entries 10–13). In a first attempt with 1.1 equiv of 2-furancarbaldehyde (**2j**), the yield of **5p** was only 28% (Table 4, entry 11). However, by increasing the amount of the heteroaromatic aldehyde **2j** to 3.3 equiv, the yield of the cycloadduct could be improved to 60% (Table 4, entry 13). Finally, it was studied whether the three-component reaction can be extended to aliphatic aldehydes. The reactions with cyclohexanecarbaldehyde (**2k**) and pivaldehyde (**2l**) were successful and delivered the Povarov products **5q** and **5r** in excellent yields of 92% and 99%, respectively. In conclusion, the three-component reaction can be performed with aromatic, heteroaromatic, and aliphatic aldehydes.

Finally, the transformation between 1 equiv of **1a**, 1.1 equiv of **2a**, and 3 equiv of **7** as the dienophile was studied.[2a,e,28] When the reaction was performed at 40 °C, only the imine *N*-benzylidenebenzenamine (**9**) was formed. To facilitate the cycloaddition, the reaction temperature was increased. When the reaction was run at 80 °C, the *endo*-isomer (2*SR*,4*RS*)-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (**8**) was formed exclusively in 99% yield (Scheme 2). Obviously, the domino reduction/imine formation/Povarov reaction is not restricted to cyclopentadiene (**3**) as the dienophile.

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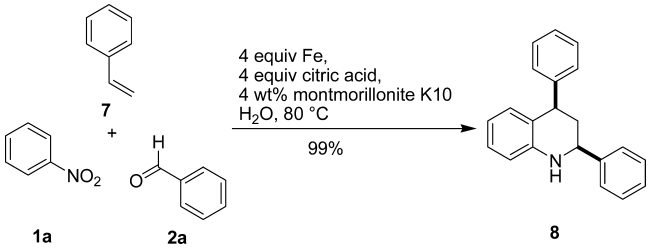
Scheme 2. Montmorillonite-Catalyzed Povarov Reaction between Nitrobenzene (1a), Benzaldehyde (2a), and Styrene (7)



It should be emphasized that all transformations presented here are three-component domino reactions in a strict sense; i.e., all substrates, reagents, the catalyst, and the solvent were present in the reaction flask right from the start and reacted under identical reaction conditions.[29] The reactions can be run in aqueous citric acid under mild conditions, and most of them are exceptionally clean and free of any side products. This allowed a simple and efficient work-up procedure and easy separation of the products. The products were obtained in high purity (~95%) after simple extraction and column filtration over silica gel. Analytically pure samples were obtained by crystallization or column chromatography.

The structures of all Povarov products were unambiguously established by mass spectrometry and NMR spectroscopy. To elucidate the relative configuration, both the *endo*- and *exo*-products were required in diastereomerically pure form. All *endo*-isomers (**5a**–**r** and **8**), i.e., the major diastereomers, could be obtained in diastereomerically pure form by filtration of the crude products over silica gel, followed by crystallization or column chromatography. Moreover, a few of the minor *exo*-isomers (*exo*-**5a** and *exo*-**5d**) could be isolated by Kugelrohr distillation, followed by column chromatography in diastereomerically pure form. The full assignment of the ^{1}H and ^{13}C chemical shifts of the *endo*- as well as the *exo*-isomers was achieved by evaluating their gCOSY, gHSQC, and gHMBC spectra (Figure 1). The relative configuration of the diastereomeric

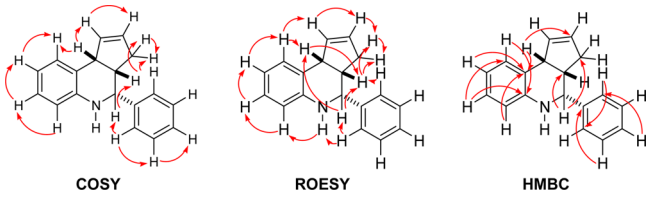


Figure 1. Important COSY, ROESY, and HMBC correlations of *endo*-**5a**.

cycloadducts could be established on the basis of the coupling constants of protons 3a-H and 4-H as well as the ROESY spectra. As an example, in *endo*-**5a**, the vicinal coupling constant ^{3}J (3a-H, 4-H) amounts to only 3.3 Hz, which—according to the Karplus equation—corresponds to a dihedral torsion angle of around 60° (Table 5). This, in turn, proves the *cis*-arrangement of protons 3a-H and 4-H and thus the *endo*-stereochemistry of *endo*-**5a**. The value of ^{3}J (3a-H, 4-H) in *endo*-**5a** is significantly smaller than the corresponding coupling constant in *exo*-**5a**, which amounts to 10.5 Hz and proves the *trans*-arrangement of 3a-H and 4-H as well as the *exo*-stereochemistry of *exo*-**5a**. Using this approach, the relative configuration of all *endo*- and *exo*-isomers was determined.

Unequivocal evidence for the structures of **5b,d,h** was provided by X-ray crystal structure analysis.[30]

CONCLUSIONS

In summary, it has been established that the reduction of nitrobenzenes to anilines and the three-component Povarov reaction of an aniline, an aldehyde, and a dienophile can be combined to an easy to perform and efficient one-pot process. The newly developed method, which can be regarded as a domino reduction/imine formation/intermolecular Povarov reaction, allows the replacement of anilines with nitrobenzenes as substrates for Povarov reactions. Iron was employed as reductant for the reduction of the nitrobenzenes to the anilines, and catalytic amounts of montmorillonite were used to catalyze the Povarov reaction. The three-component reaction between nitrobenzenes, aldehydes, and cyclopentadiene was performed in aqueous citric acid at 40 °C and delivered the cyclopenta[*c*]quinolines with very high levels of *endo*-selectivity and with yields ranging from 53% to 99%. The domino reaction can be performed with numerous nitrobenzenes and aromatic, heteroaromatic, and aliphatic aldehydes and is characterized by a high functional group tolerance.

EXPERIMENTAL SECTION

General Remarks. Nitrobenzene (**1a**), benzaldehyde (**2a**) and furfural (**2j**), styrene (**7**), and solvents used for extraction and purification were distilled prior to use. Cyclopentadiene (**3**) was obtained by heating of dicyclopentadiene. 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 temperature. 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, 0.04–0.063 mm or by crystallization. Melting points were recorded on a melting point apparatus with open capillary tubes and are uncorrected. IR spectra were measured on an FT-IR spectrometer. UV/vis spectra were recorded with a spectrophotometer. ^{1}H (^{13}C) NMR spectra were recorded at (500/125 and 300/75 MHz) using $CDCl_3$ as the solvent. The ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals at δ H/C 7.26/77.00 ($CDCl_3$) relative to TMS as internal standard. HSQC, HMBC, and COSY spectra were recorded on an NMR spectrometer 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) and br (broad). 1D and 2D homonuclear NMR spectra were measured with standard pulse sequences. Copies of the NMR spectra were prepared using SpinWorks.[31] 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. Intensities are reported as percentages relative to the base peak (I = 100%).

General Procedure for the Domino Reaction between Nitroarenes (1a–g), Aldehydes (2a–l), and Dienophiles (3, 7). 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 (1.537 g, 8 mmol), montmorillonite K10 (150 mg), water (10 mL), a nitroarene **1** (2 mmol), an aldehyde **2** (2 mmol), and a dienophile (**3** or **7**) (8 mmol). The sealed reaction flask was stirred at 40 °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 *in vacuo*. Then, water (200 mL) was added and the resulting suspension was again evaporated to dryness *in vacuo*. The residue thus obtained was dissolved in dichloromethane (100 mL) and

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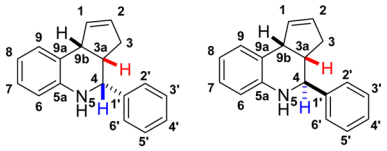
Table 5. ^{1}H NMR Data of *endo*-5a and *exo*-5a

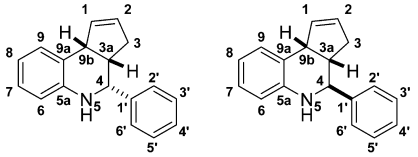


endo-**5a** *exo*-**5a**

	endo-**5a**			*exo*-**5a**		
proton	δ_H (ppm)	multiplicity	J (Hz)	δ_H (ppm)	multiplicity	J (Hz)
1-H	5.84−5.87	m		5.93−5.96	m	
2-H	5.65−5.68	m		5.68−5.72	m	
3-H(a)	1.83	dddd	16.3, 8.7, 2.6, 1.5	2.11	bd	16.8
3-H(b)	2.66	dddd	16.4, 8.7, 2.6, 1.5	2.42−2.49	dm	16.8
3a-H	3.03	dddd	9.0, 9.0, 9.0, **3.3**	2.75	bddd	**10.5**, 7.2, 7.2
4-H	4.66	d	**3.1**	3.73	d	**10.5**
5-H	3.76	s		3.9	s	
6-H	6.64	d	7.4	6.58	dd	8.0, 1.2
7-H	7.0	ddd	7.7, 7.7, 1.8	7.02	dddd	8.1, 7.3, 1.6, 0.8
8-H	6.77	ddd	7.3, 7.3, 1.4	6.79	ddd	7.4, 7.4, 1.2
9-H	7.08	ddd	7.6, 1.6, 1.0	7.26	bd	7.5
9b-H	4.13	bd	8.6	4.02	bd	7.5
2′-H, 6′-H	7.45	d	7.4	7.43	m	
3′-H, 5′-H	7.39	t	7.4	7.38	m	
4′-H	7.29	t	7.4	7.32	m	

filtered over silica gel. Using this procedure, the Povarov products were obtained with ∼95% purity (^{1}H NMR). The major *endo*-diastereomers were obtained in analytically pure form by crystallization or flash chromatography on silica gel.

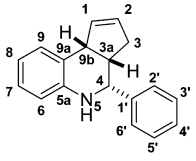
*(3aSR,4RS,9bRS)-4-Phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5a**) and (3aSR,4SR,9bRS)-4-Phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (exo-**5a**).*



endo-**5a** *exo*-**5a**

According to the general procedure, iron powder (335 mg, 6 mmol), citric acid (1.18 g, 6.14 mmol), montmorillonite K10 (150 mg), nitrobenzene (**1a**) (255 mg, 2.07 mmol), benzaldehyde (**2a**) (215 mg, 2.03 mmol), and cyclopentadiene (**3**) (530 mg, 8.02 mmol) were reacted for 4 h at 40 °C. After work up, a 94:6 mixture of *endo*-**5a** and *exo*-**5a** (^{1}H NMR) was isolated in 96% yield (479 mg, 1.94 mmol). Crystallization from dichloromethane/methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5a**) as colorless crystals.

*(3aSR,4RS,9bRS)-4-Phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5a**).*[22]

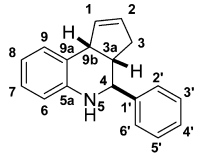


endo-**5a**

mp 123−125 °C (lit.[22] mp 123−125 °C); R_f = 0.34 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3355 (NH), 3025 (C-H), 1605, 1587 (C═C), 1498, 1474, 1449 (CH_2), 1361, 1286, 1260, 1137, 1110, 1026, 1005, 929, 844, 778, 745, 700 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 209 (4.57), 251 (3.85), 298 (3.38) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.7 Hz, J = 2.6 Hz, J = 1.5 Hz, 1H, 3-H(a)), 2.66 (dddd, ^2J (3-H(b), 3-H(a)) = 16.4 Hz, ^3J (3-H(b), 3a-H) = 9.2 Hz, J ∼ 2.4 Hz, J ∼ 2.4 Hz, 1H, 3-H(b)), 3.03 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.0 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.0 Hz, ^3J (3a-H, 9a-H) ∼ 9.0 Hz, ^3J (3a-H, 9b-H) = 3.3 Hz, 1H, 3a-H), 3.76 (s, 1H, N-H), 4.13 (bd, ^3J (9b-H, 3a-H) = 8.6 Hz, 1H, 9b-H), 4.66 (d, ^3J (4-H, 3a-H) = 3.1 Hz, 1H, 4-H), 5.65−5.68 (m, 1H, 2-H), 5.84−5.87 (m, 1H, 1-H), 6.64 (d, ^3J (6-H, 7-H) = 7.4 Hz, 1H, 6-H), 6.77 (ddd, ^3J (8-H, 7-H) ∼ 7.3 Hz, ^3J (8-H, 9-H) ∼ 7.3 Hz, ^4J (8-H, 6-H) = 1.4 Hz, 1H, 8-H), 7.00 (ddd, ^3J (7-H, 6-H) ∼ 7.7 Hz, ^3J (7-H, 8-H) ∼ 7.7 Hz, ^4J (7-H, 9-H) = 1.8 Hz, 1H, 7-H), 7.08 (ddd, ^3J (9-H, 8-H) = 7.6 Hz, ^4J (9-H, 7-H) = 1.6 Hz, ^5J (9-H, 6-H) = 1.0 Hz, 1H, 9-H), 7.29 (t like, J = 7.4 Hz, 1H, 4′-H), 7.39 (t like, J = 7.4 Hz, 2H, 3′-H and 5′-H), 7.45 (d like, J = 7.4 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5 (C-3), 46.0 (C-3a), 46.4 (C-9b), 58.1 (C-4), 115.9 (C-6), 119.2 (C-8), 126.1 (C-9a), 126.3 (C-7), 126.5 (C-2′ and C-6′), 127.2 (C-4′), 128.5 (C-3′ and C-5′), 129.0 (C-9), 130.4 (C-2), 134.0 (C-1), 142.8 (C-1′), 145.6 (C-5a); MS (EI, 70 eV) m/z (%) 247 (100) [M]$^+$, 218 (10), 206 (15), 193 (7), 170 (21), 156 (36), 129 (10), 115 (7), 91 (4), 77 (5), 44 (8).

After crystallization of the *endo*-isomer (*endo*-**5a**) from methanol, the filtrate was evaporated *in vacuo*. *N*-benzylaniline (**6a**) and the *exo*-isomer (*exo*-**5a**) were volatile enough to be removed via Kugelrohr distillation. The *exo*-isomer was obtained in pure form by flash chromatography (silica gel; petroleum ether/AcOEt 19:1) of the distillate.

*(3aSR,4SR,9bRS)-4-Phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (exo-**5a**).*[22]



exo-**5a**

R_f = 0.24 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3368 (NH), 3052 (C-H), 2929 (CH_2), 2847, 1608, 1588 (C═C), 1495, 1474, 1454 (CH_2), 1421, 1346, 1315, 1296, 1264, 1252, 1173, 1109, 1064, 1029, 923, 871, 807, 747, 717, 701, 669 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 209 (4.50), 251 (3.92), 299 (3.41) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11 (bd, ^2J (3-H(a), 3-H(b)) = 16.8 Hz, 1H, 3-H(a)), 2.42−2.49 (dm, ^2J (3-H(b), 3-H(a)) = 16.8 Hz, 1H, 3-H(b)), 2.75 (bddd, ^3J (3a-H, 4-H) = 10.5 Hz, ^3J (3a-H, 9b-H) ∼ 7.2 Hz, ^3J (3a-H, 3-H) ∼ 7.2 Hz, 1H, 3a-H), 3.73 (d, ^3J (4-H, 3a-H) = 10.5 Hz, 1H, 4-H), 3.90 (bs, 1H, N-H), 4.02 (bd, ^3J (9b-H, 3a-H) = 7.5 Hz, 1H,

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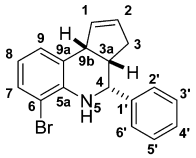
9b-H), 5.68−5.72 (m, 1H, 2-H), 5.93−5.96 (m, 1H, 1-H), 6.58 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H, 6-H), 6.79 (ddd, ^3J (8-H, 7-H) ∼ 7.4 Hz, ^3J (8-H, 9-H) ∼ 7.4 Hz, ^4J (8-H, 6-H) = 1.2 Hz, 1H, 8-H), 7.02 (dddd, ^3J (7-H, 6-H) = 8.1 Hz, ^3J (7-H, 8-H) = 7.3 Hz, ^4J (7-H, 9-H) = 1.6 Hz, J = 0.8 Hz, 1H, 7-H), 7.26 (bd, ^3J (9-H, 8-H) = 7.5 Hz, 1H, 9-H), 7.31−7.33 (m, 1H, 4′-H) 7.36−7.40 (m, 2H, 3′-H and 5′-H), 7.41−7.44 (m, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.8 (C-3), 43.1 (C-3a), 46.8 (C-9b), 58.4 (C-4), 114.8 (C-6), 118.4 (C-8), 124.1 (C-9a), 126.5 (C-7), 127.8 (C-4′), 128.1 (C-1), 128.5 (C-2′, C-6′, C-3′ and C-5′) 129.4 (C-9), 136.1 (C-2), 142.9 (C-1′), 145.7 (C-5a); MS (EI, 70 eV) m/z (%) 247 (100) $[M]^+$, 218 (25), 206 (28), 193 (15), 170 (24), 156 (41), 129 (37), 115 (15), 91 (5), 77 (8).

*(3aSR,4RS,9bRS)-6-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5b**).*

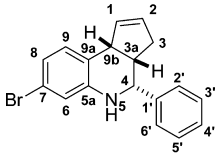


endo-**5b**

According to the general procedure, iron powder (458 mg, 8.2 mmol), citric acid (1.66 g, 8.6 mmol), montmorillonite K10 (155 mg), 2-bromonitrobenzene (**1b**) (406 mg, 2.02 mmol), benzaldehyde (**2a**) (243 mg, 2.29 mmol), and cyclopentadiene (**3**) (600 mg, 9.08 mmol) were reacted for 4 h at 40 °C. After work up, a 92:8 mixture (^{1}H NMR) was isolated in 84% yield (550 mg, 1.69 mmol). Column chromatography over silica gel (petroleum ether/dichloromethane = 7:3) afforded the *endo*-isomer (3a*SR*,4*RS*,9b*RS*)-6-bromo-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5b**) as colorless crystals in 74% yield (490 mg, 1.50 mmol).

mp 90−92 °C; R_f = 0.67 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3360 (NH), 3042 (C-H), 2928 (CH_2), 2869, 1594 (C═C), 1568, 1476, 1451 (CH_2), 1436, 1414, 1361, 1331, 1302, 1290, 1266, 1220, 1177, 1153, 1126, 1108, 1075, 1056, 1028, 1007, 986, 959, 928, 901, 884, 866, 802, 760, 748, 733, 702, 664 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 301 (3.59), 251 (3.92), 213 (4.61), 194 (4.57) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (dddd, ^2J (3-H(a), 3-H(b)) = 16.5 Hz, ^3J (3-H(a), 3a-H) = 8.7 Hz, J = 2.6 Hz, J = 1.5 Hz, 1H, 3-H(a)), 2.63 (ddddd, ^2J (3-H(a), 3-H(b)) = 16.5 Hz, ^3J (3-H(b), 3a-H) = 9.4 Hz, J = 2.6 Hz, J ∼ 2.5 Hz, J ∼ 2.5 Hz, 1H, 3-H(b)), 3.05 (ddddd, ^3J (3a-H, 3-H(a)) ∼ 9.0 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.0 Hz, ^3J (3a-H, 9b-H) ∼ 9.0 Hz, ^3J (3a-H, 4-H) = 3.3 Hz, J = 1.9 Hz, 1H, 3a-H), 4.16 (d, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H), 4.48 (bs, 1H, N-H), 4.67 (d, ^3J (4-H, 3a-H) = 2.8 Hz, 1H, 4-H), 5.65−5.69 (m, 1H, 2-H), 5.81−5.84 (m, 1H, 1-H), 6.63 (dd, ^3J (8-H, 7-H) ∼ 7.7 Hz, ^3J (8-H, 9-H) ∼ 7.7 Hz, 1H, 8-H), 7.02 (d, ^3J (9-H, 8-H) = 7.7 Hz, 1H, 9-H), 7.27 (dd, ^3J (7-H, 8-H) = 7.7 Hz, ^4J (7-H, 9-H) = 1.1 Hz, 1H, 7-H), 7.33 (t like, J = 7.2 Hz, 1H, 4′-H), 7.42 (t like, J = 7.2 Hz, 2H, 3′-H and 5′-H), 7.48 (d like, J = 7.2 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5 (C-3), 46.1 (C-3a), 46.7 (C-9b), 57.8 (C-4), 110.4 (C-6), 119.4 (C-8), 126.4 (C-2′ and C-6′), 127.4 (C-4′), 127.7 (C-9a), 128.0 (C-9), 128.6 (C-3′ and C-5′), 129.6 (C-7), 130.7 (C-2), 133.7 (C-1), 142.2 (C-1′), 142.9 (C-5a); MS (EI, 70 eV) m/z 327 (96) $[M]^+$, 286 (15), 250 (18) $[M - C_6H_5]^+$, 236 (20), 155 (25); HRMS (EI, M^+) calcd for $C_{18}H_{16}NBr$ (325.0461), found 325.0464.

*(3aSR,4RS,9bRS)-7-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5c**).*

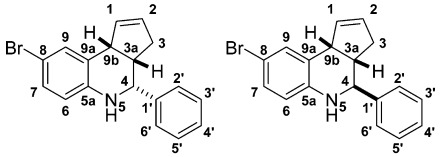


endo-**5c**

According to the general procedure, iron powder (470 mg, 8.41 mmol), citric acid monohydrate (1.77 g, 8.4 mmol), montmorillonite K10 (160 mg), 3-bromonitrobenzene (**1c**) (410 mg, 2.02 mmol), benzaldehyde (**2a**) (258 mg, 2.43 mmol), and cyclopentadiene (**3**) (600 mg, 9.08 mmol) were reacted for 4 h at 40 °C. After work up, *endo*-**5c** was obtained with ∼95% purity (^{1}H NMR) as an orange liquid in 98% yield (651 mg, 1.99 mmol). Crystallization from dichloromethane/methanol afforded (3a*SR*,4*RS*,9b*RS*)-7-bromo-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5c**) as a colorless solid.

mp 102−104 °C; R_f = 0.35 (petroleum ether/dichloromethane = 9:1); IR (ATR) $\tilde{\nu}$ 3365 (C-H), 1590, 1490, 1454 (CH_2), 1358, 1291, 1259, 1239, 1132, 1119, 1081, 1056, 1032, 1004, 971, 935, 896, 869, 835, 813, 783, 756, 705 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 305 (6.56), 257 (6.89), 215 (6.89) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.5 Hz, J = 2.3 Hz, J = 1.5 Hz, 1H, 3-H(a)), 2.60 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.2 Hz, ^3J (3-H(b), 3a-H) = 9.2 Hz, 3 × J ∼ 2.4 Hz, 1H, 3-H(b)), 3.00 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.9 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.9 Hz, ^3J (3a-H, 9b-H) ∼ 8.9 Hz, ^3J (3a-H, 4-H) = 3.3 Hz, 1H, 3a-H), 3.81 (bs, 1H, N-H) 4.05 (bd, ^3J (9b-H, 3a-H) = 8.9 Hz, 1H, 9b-H), 4.63 (d, ^3J (4-H, 3a-H) = 3.2 Hz, 1H, 4-H), 5.64−5.69 (m, 1H, 2-H), 5.79−5.84 (m, 1H, 1-H), 6.78 (d, ^4J (6-H, 8-H) = 1.8 Hz, 1H, 6-H), 6.85 (dd, ^3J (8-H, 9-H) = 8.2 Hz, ^4J (8-H, 6-H) = 1.8 Hz, 1H, 8-H) 6.91 (d, ^3J (9-H, 8-H) = 8.3 Hz, 1H, 9-H), 7.29−7.33 (m, 1H, 4′-H), 7.36−7.40 (m, 2H, 3′-H and 5′-H), 7.40−7.43 (m, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.8 (C-3a), 45.9 (C-9b), 57.8 (C-4), 118.3 (C-6), 119.6 (C-7), 121.9 (C-8), 125.0 (C-9a), 126.4 (C-2′ and C-6′), 127.4 (C-4′), 128.6 (C-3′ and C-5′), 130.4 (C-9), 130.7 (C-2), 133.5 (C-1), 142.2 (C-1′), 147.0 (C-5a); MS (EI, 70 eV) m/z (%) 325 (100) $[M]^+$, 298 (10), 284 (16), 271 (8), 248 (27) $[M-C_6H_5]^+$, 234 (33), 217 (11), 167 (19), 155 (56), 115 (20), 91 (19) $[C_7H_6]^+$, 77 (13) $[C_6H_5]^+$; HRMS (EI, M^+) calcd for $C_{18}H_{16}NBr$ (325.0461), found 325.0444.

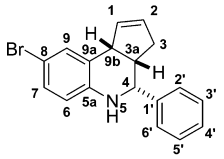
*(3aSR,4RS,9bRS)-8-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5d**) and (3aSR,4SR,9bRS)-8-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (exo-**5d**).*



endo-**5d** *exo*-**5d**

According to the general procedure, iron powder (454 mg, 8.12 mmol), citric acid (1.69 g, 8.82 mmol), montmorillonite K10 (150 mg), 4-bromonitrobenzene (**2d**) (420 mg, 2.08 mmol), benzaldehyde (**2a**) (249 mg, 2.39 mmol), and cyclopentadiene (**3**) (670 mg, 10.1 mmol) were reacted for 4 h at 40 °C. After work up, a 94:6 mixture of *endo*-**5d** and *exo*-**5d** (^{1}H NMR) was isolated in 88% yield (593 mg, 1.82 mmol). Crystallization from dichloromethane/methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-8-bromo-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline as colorless crystals.

*(3aSR,4RS,9bRS)-8-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5d**).*



endo-**5d**

mp 134−136 °C; R_f = 0.56 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3367 (NH), 3052 (C-H), 2909 (CH_2), 1594 (C═C), 1483, 1448 (CH_2), 1360, 1299, 1284, 1260, 1232, 1154, 1127, 1124, 1011, 866, 806, 776, 746, 718, 697 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 204 (4.24), 216 (4.33), 309 (3.39) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.6 Hz, J = 2.6 Hz, J = 1.6 Hz, 1H, 3-H(a)), 2.62 (ddq, ^2J (3-H(b), 3-H(a)) = 16.4 Hz, ^3J (3-H(b), 3a-H) = 9.4 Hz, J = 2.4 Hz, 1H, 3-H(b)), 3.01 (dddd, ^3J (3a-H, 3-H) ∼ 9.0 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.0 Hz, ^3J (3a-H, 9b-H) ∼ 9.0 Hz, ^3J (3a-H, 4-H) = 3.4 Hz, 1H, 3a-H), 3.78 (bs, 1H, N-H), 4.08 (bd, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H),

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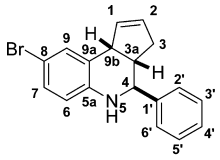
4.61 (d, ^3J (4-H, 3a-H) = 3.4 Hz, 1H, 4-H), 5.67−5.70 (m, 1H, 2-H), 5.81−5.84 (m, 1H, 1-H), 6.51 (d, ^3J (6-H, 7-H) = 8.2 Hz, 1H, 6-H), 7.07 (dd, ^3J (7-H, 6-H) = 8.7 Hz, ^4J (7-H, 9-H) = 2.3 Hz, 1H, 7-H), 7.18 (d, ^4J (9-H, 7-H) = 2.0 Hz, 1H, 9-H), 7.31 (t like, J = 6.8 Hz, 1H, 4′-H), 7.39 (t like, J = 7.8 Hz, 2H, 3′-H and 5′-H), 7.43 (d like, J = 7.8 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.7 (C-3a), 46.2 (C-9b), 57.9 (C-4), 110.7 (C-8), 117.4 (C-6), 126.4 (C-2′ and C-6′), 127.4 (C-4′), 128.2 (C-9a), 128.5 (C-3′ and C-5′), 129.0 (C-7), 130.9 (C-2), 131.5 (C-9), 133.4 (C-1), 142.3 (C-1′), 144.7 (C-5a); MS (EI, 70 eV) m/z (%) 325 (75) $[M]^+$, 296 (12), 284 (19), 271 (7), 248 (21) $[M - C_6H_5]^+$, 245 (24) 234 (32), 217 (13), 204 (12), 167 (27), 155 (100), 139 (8), 129 (12), 115 (15), 91 (9) $[C_7H_6]^+$, HRMS (EI, M^+) calcd for $C_{18}H_{16}BrN$ (325.0461), found 325.0460.

After the major diastereomer (3a*SR*,4*RS*,9b*RS*)-8-bromo-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5d**) was crystallized from methanol, the filtrate was evaporated *in vacuo*. Column chromatography of the residue over silica gel (petroleum ether/NEt_3 = 19:1) and subsequent column chromatography over silica gel (petroleum ether/dichloromethane = 8:2) afforded the *exo*-diastereomer (3a*SR*,4*SR*,9b*RS*)-8-bromo-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*exo*-**5d**) as a pale yellow solid.

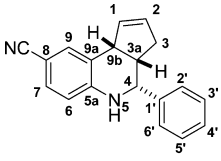
*(3aSR,4SR,9bRS)-8-Bromo-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (exo-**5d**).*



exo-**5d**

mp 91−93 °C; R_f = 0.38 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3351 (NH), 3066, 3046 (C-H), 2950, 2925 (CH_2), 2832 (C-H), 1805, 1594 (C═C), 1578 (C═C), 1485, 1458, 1443 (CH_2), 1391, 1341, 1296, 1268, 1254, 1229, 1203, 1176, 1130, 1106, 1072, 1063, 1031, 1019, 1002, 949, 938, 929, 921, 882, 861, 841, 802, 781, 763, 712, 701, 671 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 309 (3.39), 260 (4.05), 215 (4.36) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08−2.14 (dm, ^2J (3-H(a), 3-H(b)) = 17.0 Hz, 1H, 3-H(a)), 2.41−2.49 (dm, ^2J (3-H(b), 3-H(a)) = 16.9 Hz, 1H, 3-H(b)), 2.70 (dddd, ^3J (3a-H, 4-H) = 10.4 Hz, ^3J (3a-H, 3-H) ∼ 7.5 Hz, ^3J (3a-H, 9b-H) ∼ 7.5 Hz, J = 1.2 Hz, 1H, 3a-H), 3.69 (d, ^3J (4-H, 3a-H) = 10.5 Hz, 1H, 4-H), 3.91 (bs, 1H, N-H), 3.97 (bd, ^3J (3a-H, 9b-H) = 7.2 Hz, 1H, 9b-H), 5.70−5.73 (m, 1H, 2-H), 5.88−5.91 (m, 1H, 1-H), 6.45 (d, ^3J (6-H, 7-H) = 8.3 Hz, 1H, 6-H), 7.09 (dd, ^3J (6-H, 7-H) = 8.3 Hz, ^4J (7-H, 9-H) = 2.0 Hz, 1H, 7-H), 7.32−7.41 (m, 6H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H and 9-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.7 (C-3), 42.8 (C-3a), 46.7 (C-9b), 58.2 (C-4), 109.9 (C-8), 116.3 (C-6), 126.3 (C-9a), 128.0 (C-4′), 128.4 (C-2′ and C-6′), 128.55 (C-3′ and C-5′), 128.57 (C-2), 129.2 (C-7), 131.9 (C-9), 135.4 (C-1), 142.4 (C-1′), 144.7 (C-5a); MS (EI, 70 eV) m/z (%) 327 (100) $[M]^+$, 250 (18) $[M - C_6H_5]^+$, 155 (45); HRMS (EI, M^+) calcd for $C_{18}H_{16}NBr$ (325.0461), found 325.0450.

*(3aSR,4RS,9bRS)-4-Phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta-[c]quinoline-8-carbonitrile (endo-**5e**).*

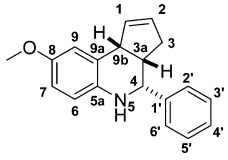


endo-**5e**

According to the general procedure, iron powder (460 mg, 8.23 mmol), citric acid (1.73 g, 9 mmol), montmorillonite K10 (153 mg), 4-nitrobenzonitrile (**1e**) (330 mg, 2.23 mmol), benzaldehyde (**2a**) (269 mg, 2.54 mmol), and cyclopentadiene (**3**) (580 mg, 8.77 mmol) were reacted for 4 h at 40 °C. After work up, a 95:5 mixture of *endo*-**5e** and *exo*-**5e** (^{1}H NMR) was isolated in 70% yield (425 mg, 1.56 mmol). Crystallization from dichloromethane/petroleum ether gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline-8-carbonitrile (*endo*-**5e**) as colorless crystals.

mp 167−168 °C; R_f = 0.51 (petroleum ether/EtOAc = 8:2); IR (ATR) $\tilde{\nu}$ 3354 (NH), 3048 (C-H), 2932 (CH_2), 2850 (CH_2), 2216 (CN), 1602, 1500, 1465, 1452 (CH_2), 1362, 1284, 1270, 1232, 1216, 1176, 1161, 1124, 1028, 1010, 985, 960, 922, 905, 845, 821, 801, 775, 756, 745, 725, 699 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 286 (7.30), 211 (7.39) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (dddd, ^2J (3-H(a), 3-H(b)) = 16.4 Hz, ^3J (3-H(a), 3a-H) = 8.5 Hz, J = 2.6 Hz, J = 1.5 Hz, 1H, 3-H(a)), 2.56 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.3 Hz, ^3J (3-H(b), 3a-H) = 9.8 Hz, 3 × J ∼ 2.4 Hz, 1H, 3-H), 3.03 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.8 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.8 Hz, ^3J (3a-H, 9b-H) ∼ 8.8 Hz, ^3J (3a-H, 4-H) = 3.5 Hz, 1H, 3a-H), 4.08 (bd, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H), 4.27 (bs, 1H, N-H), 4.72 (d, ^3J (4-H, 3a-H) = 3.5 Hz, 1H, 4-H), 5.67−5.71 (m, 1H, 2-H), 5.83−5.86 (m, 1H, 1-H), 6.61 (d, ^3J (6-H, 7-H) = 8.3 Hz, 1H, 6-H), 7.23 (dd, ^3J (7-H, 6-H) = 8.4 Hz, ^4J (7-H, 9-H) = 1.2 Hz, 1H, 7-H), 7.30 (bs, 1H, 9-H), 7.31−7.41 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.4 (C-9b), 45.7 (C-3a), 57.2 (C-4), 100.7 (C-8), 115.7 (C-6), 120.2 (CN), 126.1 (C-9a), 126.3 (C-2′ and C-6′), 127.6 (C-4′), 128.7 (C-3′ and C-5′), 130.4 (C-7), 131.0 (C-2), 133.1 (C-1), 133.3 (C-9), 141.4 (C-1′), 149.4 (C-5a); MS (EI, 70 eV) m/z (%) 272 (100) $[M]^+$, 243 (17), 231 (26), 218 (9), 195 (36) $[M - C_6H_5]^+$, 181 (6), 155 (13), 91 (28); HRMS (EI, M^+) calcd for $C_{19}H_{16}N_2$ (272.1308), found 272.1312.

*(3aSR,4RS,9bRS)-8-Methoxy-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5f**).*[23]



endo-**5f**

According to the general procedure, iron powder (452 mg, 8.09 mmol), citric acid (1.62 g, 8.45 mmol), montmorillonite K10 (154 mg), 4-methoxynitrobenzene (**1f**) (305 mg, 1.99 mmol), benzaldehyde (**2a**) (238 mg, 2.24 mmol), and cyclopentadiene (**3**) (570 mg, 8.6 mmol) were reacted for 4 h at 40 °C. After work up, a 94:6 mixture of *endo*-**5f** and *exo*-**5f** (^{1}H NMR) was isolated in 87% yield (482 mg, 1.74 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,-9b*RS*)-8-methoxy-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]-quinoline (*endo*-**5f**) as colorless crystals.

mp 103−105 °C; R_f = 0.45 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3356 (NH), 3063 (C-H), 2942 (CH_2), 1610, 1500 (C═C), 1461, 1440 (CH_2), 1358, 1326, 1291, 1260, 1241, 1224, 1186, 1161, 1147, 1133, 1099, 1032, 1010, 958, 912, 858, 818, 794, 776, 760, 745, 699 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 315 (3.49), 251 (3.87), 208 (4.49) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (dddd, ^2J (3-H(a), 3-H(b)) = 16.5 Hz, ^3J (3-H(a), 3a-H) = 8.8 Hz, J = 2.6 Hz, J = 1.8 Hz, 1H, 3-H(a)), 2.66 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.4 Hz, ^3J (3-H(b), 3a-H) = 9.3 Hz, 3 × J ∼ 2.7 Hz, 1H, 3-H(b)), 3.02 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.8 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.8 Hz, ^3J (3a-H, 9b-H) ∼ 8.8 Hz, ^3J (3a-H, 4-H) = 3.3 Hz, 1H, 3a-H), 3.58 (bs, 1H, N-H), 3.77 (s, 3H, OCH_3), 4.11 (d, ^3J (9b-H, 3a-H) = 8.6 Hz, 1H, 9b-H), 4.59 (d, ^3J (4-H, 3a-H) = 3.5 Hz, 1H, 4-H), 5.67−5.71 (m, 1H, 2-H), 5.83−5.87 (m, 1H, 1-H), 6.59 (d, ^3J (6-H, 7-H) = 8.7 Hz, 1H, 6-H), 6.66 (dd, ^3J (7-H, 6-H) = 8.6 Hz, ^4J (7-H, 9-H) = 2.8 Hz, 1H, 7-H), 6.68 (d, ^4J (9-H, 7-H) = 2.9 Hz, 1H, 9-H), 7.30 (t like, J = 7.5 Hz, 1H, 4′-H), 7.38 (t like, J = 7.5 Hz, 2H, 3′-H and 5′-H), 7.46 (d like, J = 7.6 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.8 (C-3a), 46.9 (C-9b), 55.7 (OCH_3), 58.5 (C-4), 112.4 (C-7), 114.1 (C-9), 116.7 (C-6), 126.5 (C-2′ and C-6′), 127.1 (C-4′), 127.2 (C-9a), 128.4 (C-3′ and C-5′), 130.6 (C-2), 133.7 (C-1), 139.5 (C-5a), 143.0 (C-1′), 153.0 (C-8); MS (EI, 70 eV) m/z (%) 277 (100) $[M]^+$, 273 (45), 262 (17) $[M - CH_3]^+$, 230 (23), 200 (17) $[M - C_6H_5]^+$, 186 (24) 155 (14) 115 (9), 91 (9), 77 (6) $[C_6H_5]^+$; HRMS (EI, M^+) calcd for $C_{19}H_{19}NO$ (277.1461), found 277.1469.

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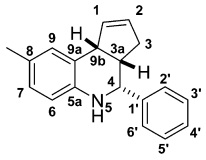
*(3aSR,4RS,9bRS)-8-Methyl-4-phenyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5g**).*[10d]

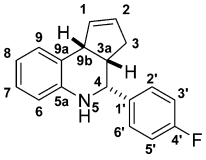


endo-**5g**

According to the general procedure, iron powder (457 mg, 8.18 mmol), citric acid (1.73 g, 9.0 mmol), montmorillonite K10 (154 mg), 4-methylnitrobenzene (**1g**) (287 mg, 2.09 mmol), benzaldehyde (**2a**) (269 mg, 2.54 mmol), and cyclopentadiene (**3**) (670 mg, 10.1 mmol) were reacted for 4 h at 40 °C. After work up, the *endo*-diastereomer (^{1}H NMR) was isolated in 98% yield (546 mg, 2.1 mmol) as a colorless solid. Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-8-methyl-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5g**) as colorless crystals.

mp 107−109 °C (lit.[10d] mp 108−110 °C); R_f = 0.38 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3362 (NH), 3044 (C-H), 2931, 1614, 1506 (C═C), 1450 (CH_2), 1359, 1288, 1260, 1157, 1132, 1027, 999, 957, 931, 881, 815, 797, 780, 746, 719, 698, 687, 662 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 303 (3.42), 252 (3.90), 215 (4.31) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 9.2 Hz, J = 2.4 Hz, J = 1.7 Hz, 1H, 3-H(a)), 2.26 (s, 3H, 8-CH_3), 2.66 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.3 Hz, ^3J (3-H(b), 3a-H) = 9.5 Hz, 3 × J ∼ 2.5 Hz, 1H, 3-H(b)), 3.01 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.1 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.1 Hz, ^3J (3a-H, 9b-H) ∼ 9.1 Hz, ^3J (3a-H, 4-H) = 3.4 Hz, 1H, 3a-H), 3.66 (bs, 1H, N-H), 4.09 (bd, ^3J (9b-H, 3a-H) = 9.2 Hz, 1H, 9b-H), 4.62 (d, ^3J (4-H, 3a-H) = 3.5 Hz, 1H, 4-H), 5.65−5.69 (m, 1H, 2-H), 5.85−5.88 (m, 1H, 1-H), 6.57 (d, ^3J (6-H, 7-H) = 8.2 Hz, 1H, 6-H), 6.83 (dd, ^3J (7-H, 6-H) = 8.2 Hz, ^4J (7-H, 9-H) = 2.1 Hz, 1H, 7-H), 6.90 (s, 1H, 9-H), 7.30 (t like, J = 7.5 Hz, 1H, 4′-H), 7.38 (t like, J = 7.7 Hz, 2H, 3′-H and 5′-H), 7.46 (d like, J = 7.8 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6 (8-CH_3), 31.4 (C-3), 46.0 (C-3a), 46.4 (C-9b), 58.3 (C-4), 115.9 (C-6), 126.0 (C-9a), 126.5 (C-2′ and C-6′), 127.0 (C-7), 127.2 (C-4′), 128.3 (C-8), 128.4 (C-3′ and C-5′), 129.4 (C-9), 130.4 (C-2), 134.0 (C-1), 143.0 (C-1′), 143.2 (C-5a); MS (EI, 70 eV) m/z (%) 261 (100) [M]$^+$, 257 (72), 232 (11) 220 (18), 207 (8), 184 (30) [M − C_6H_5]$^+$, 170 (50), 155 (17), 128 (10), 115 (15), 91 (11), 77 (8) [C_6H_5]$^+$; HRMS (EI, M$^+$) calcd for $C_{19}H_{19}N$ (261.1512) found 261.1494.

*(3aSR,4RS,9bRS)-4-(4-Fluorophenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5h**).*[24]

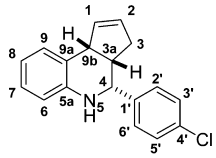


endo-**5h**

According to the general procedure, iron powder (358 mg, 6.4 mmol), citric acid (1.4 g, 7.3 mmol), montmorillonite K10 (150 mg), nitrobenzene (**1a**) (247 mg, 2.01 mmol), 4-fluorobenzaldehyde (**2b**) (281 mg, 2.26 mmol), and cyclopentadiene (**3**) (530 mg, 8 mmol) were reacted for 4 h at 40 °C. After work up, a 96:4 mixture of *endo*-**5h** and *exo*-**5h** (^{1}H NMR) was isolated in 94% yield (502 mg, 1.89 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(4-fluorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5h**) as colorless crystals.

mp 121−123 °C (lit.[24] mp 146 °C); R_f = 0.38 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3366 (NH), 1604, 1504 (C═C), 1474 (CH_2), 1359, 1314, 1289, 1261, 1218, 1156, 1093, 1034, 1006, 932, 851, 820, 800, 787, 762, 747, 714, 685 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 297 (3.38), 251 (3.85), 209 (4.51) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (dddd, ^2J (3-H(a); 3-H(b)) = 16.2 Hz, ^3J (3-H(a), 3a-H) = 8.7 Hz, J = 2.6 Hz, J = 1.7 Hz, 1H, 3-H(a)), 2.62 (ddd, ^2J (3-H(b), 3-H(a)) = 16.3 Hz, ^3J (3-H(b), 3a-H) = 9.6 Hz, J = 2.5 Hz, 1H, 3-H(b)), 2.98 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.9 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.9 Hz, ^3J (3a-H, 9b-H) ∼ 8.9 Hz, ^3J (3a-H, 4-H) = 3.3 Hz, 1H, 3a-H), 3.71 (bs, 1H, N-H), 4.12 (d, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H), 4.64 (d, ^3J (4-H, 3a-H) = 2.9 Hz, 1H, 4-H), 5.65−5.68 (m, 1H, 2-H), 5.84−5.88 (m, 1H, 1-H), 6.64 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H, 6-H), 6.78 (ddd, ^3J (8-H, 7-H) ∼ 7.5 Hz, ^3J (8-H, 9-H) ∼ 7.5 Hz, ^4J (8-H, 6-H) = 1.3 Hz, 1H, 8-H), 7.01 (bddd, ^3J (7-H, 6-H) ∼ 7.9 Hz, ^3J (7-H, 8-H) ∼ 7.9 Hz, ^4J (7-H, 9-H) = 1.6 Hz, 1H, 7-H), 7.05−7.10 (m, 3H, 9-H, 2′-H and 6′-H), 7.42 (dd, ^3J (3′-H and 5′-H, 2′-H and 6′-H) = 8.5 Hz, ^4J (3′-H and 5′-H, 4′-F) = 5.6 Hz, 2H, 3′-H and 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 46.0 (C-3a), 46.3 (C-9b), 57.4 (C-4), 115.3 (d, $^2J_{CF}$ = 21.1 Hz, C-3′ and C-5′), 115.9 (C-6), 119.3 (C-8), 126.0 (C-9a), 126.4 (C-7), 128.0 (d, $^3J_{CF}$ = 7.7 Hz, C-2′ and C-6′), 129.0 (C-9), 130.3 (C-2), 134.0 (C-1), 138.6 (d, $^4J_{CF}$ = 3.4 Hz, C-1′), 145.4 (C-5a), 162.0 (d, $^1J_{CF}$ = 245.2 Hz, C-4′); MS (EI, 70 eV) m/z (%) 265 (100) [M]$^+$, 236 (14), 224 (21), 170 (25) [M − C_6H_4F]$^+$, 156 (73), 129 (20), 115 (9), 93 (9), 77 (6) [C_6H_5]$^+$; HRMS calcd for $C_{18}H_{16}NF$ (265.1261), found 265.1269.

*(3aSR,4RS,9bRS)-4-(4-Chlorophenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5i**).*[32]

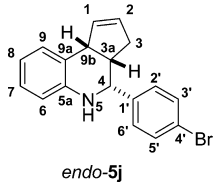


endo-**5i**

According to the general procedure, iron powder (343 mg, 6.14 mmol), citric acid (1.26 g, 6.56 mmol), montmorillonite K10 (155 mg), nitrobenzene (**1a**) (249 mg, 2.02 mmol), 4-chlorobenzaldehyde (**2c**) (369 mg, 2.62 mmol), and cyclopentadiene (**3**) (580 mg, 8.77 mmol) were reacted for 4 h at 40 °C. After work up, a 96:4 mixture of *endo*-**5i** and *exo*-**5i** (^{1}H NMR) was isolated in 77% yield (440 mg, 1.56 mmol). Crystallization from dichloromethane/petroleum ether gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(4-chlorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5i**) as colorless crystals.

mp 143−144 °C (lit.[32] mp 141−142 °C); R_f = 0.51 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3361 (NH), 3043 (C-H), 2929 (CH_2), 1590 (C═C), 1489, 1470 (CH_2), 1419, 1408, 1353, 1318, 1288, 1265, 1130, 1113, 1086, 1033, 1014, 1001, 938, 890, 866, 843, 810, 794, 752, 724, 697, 680 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 294 (3.50), 250 (2.93), 224 (4.13) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (dddd, ^2J (3-H(a), 3-H(b)) = 16.4 Hz, ^3J (3-H(a), 3a-H) = 8.5 Hz, J = 2.4 Hz, J = 1.4 Hz, 1H, 3-H(a)), 2.61 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.2 Hz, ^3J (3-H(b), 3a-H) = 9.5 Hz, 3 × J ∼ 2.4 Hz, 1H, 3-H(b)), 2.99 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.9 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.9 Hz, ^3J (3a-H, 9b-H) ∼ 8.9 Hz, ^3J (3a-H, 4-H) = 3.2 Hz, 1H, 3a-H), 3.70 (bs, 1H, N-H), 4.13 (d, ^3J (9b-H, 3a-H) = 8.6 Hz, 1H, 9b-H), 4.63 (d, ^3J (4-H, 3a-H) = 2.5 Hz, 1H, 4-H), 5.64−5.69 (m, 1H, 2-H), 5.85−5.90 (m, 1H, 1-H), 6.65 (bd, ^3J (6-H, 7-H) = 7.4 Hz, 1H, 6-H), 6.79 (t, ^3J (8-H, 7-H and 9-H) = 7.4 Hz, 1H, 8-H), 7.02 (t, ^3J (7-H, 6-H and 8-H) = 7.4 Hz, 1H, 7-H), 7.08 (d, ^3J (9-H, 8-H) = 7.4 Hz, 1H, 9-H), 7.36−7.41 (m, 4H, 2′-H, 3′-H, 5′-H, and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.9 (C-3a), 46.2 (C-9b), 57.5 (C-4), 116.0 (C-6), 119.4 (C-8), 125.9 (C-9a), 126.4 (C-7), 127.8 (C-2′ and C-6′), 128.6 (C-3′ and C-5′), 129.0 (C-9), 130.2 (C-2), 132.8 (C-4′), 134.0 (C-1), 141.3 (C-1′), 145.2 (C-5a); MS (EI, 70 eV) m/z (%) 281 (100) [M]$^+$, 240 (16), 227 (7), 170 (25) [M − C_6H_4Cl]$^+$, 156 (71), 129 (13), 93 (7), 77 (6).

*(3aSR,4RS,9bRS)-4-(4-Bromophenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5j**).*



endo-**5j**

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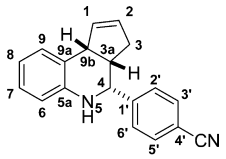
According to the general procedure, iron powder (461 mg, 8.25 mmol), citric acid (1.66 g, 8.66 mmol), montmorillonite K10 (152 mg), nitrobenzene (**1a**) (253 mg, 2.06 mmol), 4-bromobenzaldehyde (**2d**) (425 mg, 2.3 mmol), and cyclopentadiene (**3**) (610 mg, 9.23 mmol) were reacted for 4 h at 40 °C. After work up, a 96:4 mixture of *endo*-**5j** and *exo*-**5j** (^{1}H NMR) was isolated in 95% yield (637 mg, 1.95 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,-9b*RS*)-4-(4-bromophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]-quinoline (*endo*-**5j**) as colorless crystals.

mp 152−153 °C; R_f = 0.61 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3361 (NH), 3039 (C-H), 2928 (CH_2), 1604, 1589 (C═C), 1473 (CH_2), 1419, 1405, 1353, 1288, 1265, 1131, 1113, 1069, 1033, 1011, 1001, 938, 889, 866, 842, 809, 753, 724, 692, 669 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 295 (3.44), 247 (3.91), 199 (4.59) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (dddd, ^2J (3-H(a), 3-H(b)) = 16.2 Hz, ^3J (3-H(a), 3a-H) = 8.6 Hz, J = 2.6 Hz, J = 1.8 Hz, 1H, 3-H(a)), 2.61 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.4 Hz, ^3J (3-H(b), 3a-H) = 9.5 Hz, 3 × J ∼ 2.5 Hz, 1H, 3-H(b)), 2.98 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.2 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.2 Hz, ^3J (3a-H, 9b-H) ∼ 9.2 Hz, ^3J (3a-H, 4-H) = 3.5 Hz, 1H, 3a-H), 3.69 (bs, 1H, N-H), 4.12 (bd, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H), 4.62 (d, ^3J (4-H, 3a-H) = 3.3 Hz, 1H, 4-H), 5.64−5.68 (m, 1H, 2-H), 5.85−5.89 (m, 1H, 1-H), 6.64 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 0.9 Hz, 1H, 6-H), 6.79 (ddd, ^3J (8-H, 7-H) ∼ 7.6 Hz, ^3J (8-H, 9-H) ∼ 7.6 Hz, ^4J (8-H, 6-H) = 1.3 Hz, 1H, 8-H), 7.01 (ddd, ^3J (7-H, 6-H) ∼ 7.6 Hz, ^3J (7-H, 8-H) ∼ 7.6 Hz, ^4J (7-H, 9-H) = 1.3 Hz, 1H, 7-H), 7.08 (bd, ^3J (9-H, 8-H) = 7.6 Hz, 1H, 9-H), 7.34 (d like, J = 8.8 Hz, 2H, 2′-H and 6′-H), 7.52 (d like, J = 8.8 Hz, 2H, 3′-H and 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.8 (C-3a), 46.2 (C-9b), 57.5 (C-4), 116.0 (C-6), 119.4 (C-8), 120.9 (C-4′), 125.9 (C-9a), 126.4 (C-7), 128.2 (C-2′ and C-6), 129.0 (C-9), 130.2 (C-2), 131.6 (C-3′ and C-5′), 133.9 (C-1), 141.9 (C-1′), 145.2 (C-5a); MS (EI, 70 eV) m/z (%) 327 (100) [M]$^+$, 286 (10), 246 (7) [M − Br]$^+$, 170 (15) [M−C_6H_4Br]$^+$, 156 (36); HRMS (EI, M$^+$) calcd for $C_{18}H_{16}$NBr (325.0461), found 325.0435.

*4-((3aSR,4RS,9bRS)-3a,4,5,9b-Tetrahydro-3H-cyclopenta[c]-quinolin-4-yl)benzonitrile (endo-**5k**).*

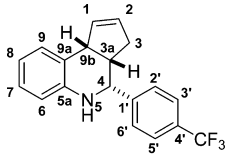


endo-**5k**

According to the general procedure, iron powder (447 mg, 8 mmol), citric acid (1.71 g, 8.9 mmol), montmorillonite K10 (154 mg), nitrobenzene (**1a**) (262 mg, 2.13 mmol), 4-cyanobenzaldehyde (**2e**) (295 mg, 2.25 mmol), and cyclopentadiene (**3**) (600 mg, 9.08 mmol) were reacted for 4 h at 40 °C. After work up, a 96:4 mixture of *endo*-**5k** and *exo*-**5k** (^{1}H NMR) was isolated in 70% yield (400 mg, 1.47 mmol). Crystallization from methanol gave the *endo*-diastereomer 4-((3a*SR*,4*RS*,9b*RS*)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinolin-4-yl)benzonitrile (*endo*-**5k**) as colorless crystals.

mp 186−189 °C; R_f = 0.31 (petroleum ether/dichloromethane = 1:1); IR (ATR) $\tilde{\nu}$ 3352 (NH), 3053 (C-H), 2937 (CH_2), 2223 (CN), 1606, 1586 (C═C), 1488, 1411 (CH_2), 1360, 1345, 1314, 1292, 1264, 1231, 1156, 1108, 1033, 1012, 932, 853, 824, 804, 765, 747, 717, 693, 675 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 294 (3.52), 279 (3.50), 240 (4.39), 234 (4.40), 212 (4.49), 210 (4.81), 203 (7.52) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.75 (dddd, ^2J (3-H(a), 3-H(b)) = 16.2 Hz, ^3J (3-H(a), 3a-H) = 8.6 Hz, J = 2.3 Hz, J = 1.3 Hz, 1H, 3-H(a)), 2.57 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.2 Hz, ^3J (3-H(b), 3a-H) = 9.6 Hz, 3 × J ∼ 2.6 Hz, 1H, 3-H(b)), 3.00 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.9 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.9 Hz, ^3J (3a-H, 9b-H) ∼ 8.9 Hz, ^3J (3a-H, 4-H) = 2.4 Hz, 1H, 3a-H), 3.74 (bs, 1H, N-H), 4.15 (bd, ^3J (9b-H, 3a-H) = 9.1 Hz, 1H, 9b-H), 4.70 (d, ^3J (4-H, 3a-H) = 3.4 Hz, 1H, 4-H), 5.63−5.67 (m, 1H, 2-H), 5.85−5.89 (m, 1H, 1-H), 6.66 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.0 Hz, 1H, 6-H), 6.79 (ddd, ^3J (8-H, 7-H) ∼ 7.5 Hz, ^3J (8-H, 9-H) ∼ 7.5 Hz, ^4J (8-H, 6-H) = 1.1 Hz, 1H, 8-H), 7.02 (bddd, ^3J (7-H, 6-H) ∼ 7.6 Hz, ^3J (7-H, 8-H) ∼ 7.6 Hz, ^4J (7-H, 9-H) = 1.4 Hz, 1H, 7-H), 7.08 (bd, ^3J (9-H, 8-H) = 7.5 Hz, 1H, 9-H), 7.57 (d like, J = 8.4 Hz, 2H, 2′-H and 6′-H), 7.67 (d like, J = 8.4 Hz, 2H, 3′-H and 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.3 (C-3), 45.6 (C-3a), 46.2 (C-9b), 57.8 (C-4), 111.1 (C-4′), 116.1 (C-6), 118.8 (CN), 119.7 (C-8), 125.8 (C-9a), 126.5 (C-7), 127.2 (C-2′ and C-6′), 129.0 (C-9), 130.0 (C-2), 132.3 (C-3′ and C-5′), 133.9 (C-1), 144.7 (C-5a), 148.3 (C-1′); MS (EI, 70 eV) m/z (%) 272 (100) [M]$^+$, 268 (12), 231 (17), 218 (11), 170 (22) [M − C_6H_4CN]$^+$, 156 (62), 129 (15), 115 (7); HRMS (EI, M$^+$) calcd for $C_{19}H_{16}N_2$ (272.1308), found 272.1296.

*(3aSR,4RS,9bRS)-4-(4-(Trifluoromethyl)phenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5l**).*[24]

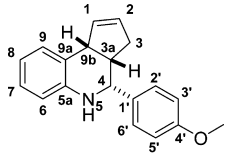


endo-**5l**

According to the general procedure, iron powder (454 mg, 8.12 mmol), citric acid (1.72 g, 8.9 mmol), montmorillonite K10 (155 mg), nitrobenzene (**1a**) (252 mg, 2.05 mmol), 4-trifluoromethylbenzaldehyde (**2f**) (395 mg, 2.27 mmol), and cyclopentadiene (**3**) (640 mg, 9.68 mmol) were reacted for 4 h at 40 °C. After work up, a 95:5 mixture of *endo*-**5l** and *exo*-**5l** (^{1}H NMR) was isolated in 89% yield (574 mg, 1.82 mmol). Crystallization from petroleum ether gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(4-(trifluoromethyl)phenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5l**) as colorless crystals.

mp 113−114 °C; R_f = 0.55 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 1606, 1586 (C═C), 1499, 1477, 1426 (CH_2), 1321, 1297, 1261, 1185, 1164, 1127, 1103, 1064, 1035, 1017, 1007, 935, 856, 823, 802, 748, 717, 687, 658 cm^{-1}; UV (CH_3CN): λ_{max} (log ε) 295 (3.49), 247 (3.91), 199 (4.59) nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (dddd, ^2J (3-H(a), 3-H(b)) = 16.0 Hz, ^3J (3-H(a), 3a-H) = 8.6 Hz, J = 2.5 Hz, J = 1.2 Hz, 1H, 3-H(a)), 2.62 (ddddd, ^2J (3-H(a), 3-H(b)) = 16.1 Hz, ^3J (3-H(a), 3a-H) = 9.4 Hz, 3 × J ∼ 2.4 Hz, 1H, 3-H(b)), 3.03 (dddd ^3J (3a-H, 3-H(a)) ∼ 9.2 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.2 Hz, ^3J (3a-H, 9b-H) ∼ 9.2 Hz, ^3J (3a-H, 4-H) = 3.1 Hz, 1H, 3a-H), 3.74 (bs, 1H, N-H), 4.16 (d, ^3J (9b-H, 3a-H) = 9.0 Hz, 1H, 9b-H), 4.72 (d, ^3J (4-H, 3a-H) = 3.3 Hz, 1H, 4-H), 5.64−5.68 (m, 1H, 2-H), 5.85−5.89 (m, 1H, 1-H), 6.66 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 0.8 Hz, 1H, 6-H), 6.80 (bddd, ^3J (8-H, 7-H) ∼ 7.6 Hz, ^3J (8-H, 9-H) ∼ 7.6 Hz, ^4J (8-H, 6-H) = 0.9 Hz, 1H, 8-H), 7.02 (bddd, ^3J (7-H, 6-H) ∼ 7.7 Hz, ^3J (7-H, 8-H) ∼ 7.7 Hz, ^4J (7-H, 9-H) = 1.3 Hz, 1H, 7-H), 7.08 (bd, ^3J (9-H, 8-H) = 7.7 Hz, 1H, 9-H), 7.58 (d like, J = 8.1 Hz, 2H, 2′-H and 6′-H), 7.65 (d like, J = 8.1 Hz, 2H, 3′-H and 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (C-3), 45.8 (C-3a), 46.3 (C-9b), 57.8 (C-4), 116.1 (C-6), 119.6 (C-8), 123.1 (q, $^1J_{CF}$ = 260 Hz, CF_3), 125.5 (q, $^3J_{CF}$ = 3.8 Hz, C-3′ and C-5′), 125.9 (C-9a), 126.5 (C-7), 126.8 (C-2′ and C-6′), 129.0 (C-9), 129.6 (q, $^2J_{CF}$ = 32.2 Hz, C-4′), 130.2 (C-2′), 133.9 (C-1′), 145.0 (C-5a), 146.9 (C-1′); MS (EI, 70 eV) m/z (%) 315 (100) [M]$^+$, 311 (37), 274 (30), 261 (17), 170 (45) [M − $C_6H_4CF_3$]$^+$, 156 (81); HRMS (EI, M$^+$) calcd for $C_{19}H_{16}NF_3$ (315.1229), found 315.1221.

*(3aSR,4RS,9bRS)-4-(Methoxyphenyl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5m**).*[24]



endo-**5m**

According to the general procedure, iron powder (455 mg, 8.14 mmol), citric acid (1.76 g, 9.14 mmol), montmorillonite K10 (157 mg), nitrobenzene (**1a**) (251 mg, 2.04 mmol), 4-methoxybenzaldehyde (**2g**) (329 mg, 2.42 mmol), and cyclopentadiene (**3**) (670 mg, 10.1 mmol) were reacted for 4 h at 40 °C. After work up, a 87:13 mixture of *endo*-**5m** and *exo*-**5m** (^{1}H NMR) was isolated in 57% yield (324 mg,

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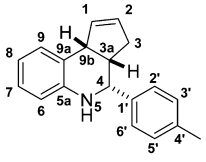
1.17 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(methoxyphenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline *endo*-**5m** as gray crystals.

mp 117−118 °C; R_f = 0.37 (petroleum ether/dichloromethane = 6:4); IR (ATR) $\tilde{\nu}$ 3364 (NH), 3051 (C-H), 2936, 2907, 2809 (OCH_3), 2162, 1739, 1608, 1586 (C═C), 1511, 1474, 1446 (CH_2), 1423, 1359, 1314, 1302, 1284, 1242, 1176, 1162, 1135, 1106, 1029, 1004, 955, 927, 887, 868, 848, 815, 801, 781, 749, 727, 719, 697, 685 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 296 (3.47), 252 (3.94), 248 (3.55), 216 (4.31) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 1.86 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.6 Hz, J = 2.3 Hz, J = 1.5 Hz, 1H, 3-H(a)), 2.67 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.3 Hz, ^3J (3-H(b), 3a-H) = 9.3 Hz, 3 × J ∼ 2.4 Hz, 1H, 3-H(b)), 2.99 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.1 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.1 Hz, ^3J (3a-H, 9b-H) ∼ 9.1 Hz, ^3J (3a-H, 4-H) = 3.0 Hz, 1H, 3a-H), 3.72 (bs, 1H, N-H), 3.84 (s, 3H, OCH_3), 4.12 (d, ^3J (9b-H, 3a-H) = 8.8 Hz, 1H, 9b-H), 4.61 (d, ^3J (4-H, 3a-H) = 3.1 Hz, 1H, 4-H), 5.66−5.70 (m, 1H, 2-H), 5.85−5.89 (m, 1H, 1-H), 6.63 (dd, ^3J (6-H, 7-H) = 7.9 Hz, ^4J (6-H, 8-H) = 1.0 Hz, 1H, 6-H), 6.77 (ddd, ^3J (8-H, 7-H) ∼ 7.5 Hz, ^3J (8-H, 9-H) ∼ 7.5 Hz, ^4J (8-H, 6-H) = 1.1 Hz, 1H, 8-H), 6.94 (d like, J = 9.3 Hz, 2H, 3′-H and 5′-H), 7.01 (ddd, ^3J (7-H, 6-H) ∼ 7.9 Hz, ^3J (7-H, 8-H) ∼ 7.9 Hz, ^4J (7-H, 9-H) = 1.4 Hz, 1H, 7-H), 7.09 (bd, ^3J (9-H, 8-H) = 7.5 Hz, 1H, 9-H), 7.38 (d like, J = 9.3 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5 (C-3), 46.1 (C-3a), 46.4 (C-9b), 55.3 (OCH_3), 57.5 (C-4), 113.8 (C-3′ and C-5′), 115.8 (C-6), 119.1 (C-8), 126.1 (C-9a), 126.3 (C-7), 127.5 (C-2′ and C-6′), 129.0 (C-9), 130.4 (C-2), 134.0 (C-1), 135.0 (C-1′), 145.7 (C-5a), 158.8 (C-4′); MS (EI, 70 eV) m/z (%) 277 (100) $[M]^+$, 273 (14), 236 (10), 168 (14), 121 (28); HRMS (EI, M^+) calcd for $C_{19}H_{19}NO$ (277.1461), found 277.1471.

*(3aSR,4RS,9bRS)-4-p-Tolyl-3a,4,5,9b-tetrahydro-3H-cyclopenta-[c]quinoline (endo-**5n**).*[24]

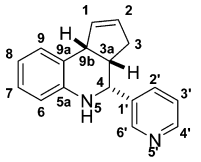


endo-**5n**

According to the general procedure, iron powder (460 mg, 8.23 mmol), citric acid (1.68 g, 8.76 mmol), montmorillonite K10 (152 mg), nitrobenzene (**1a**) (250 mg, 2.03 mmol), 4-methylbenzaldehyde (**2h**) (325 mg, 2.7 mmol), and cyclopentadiene (**3**) (670 mg, 10.1 mmol) were reacted for 4 h at 40 °C. After work up, a 95:5 mixture of *endo*-**5n** and *exo*-**5n** (^1H NMR) was isolated in 99% yield (537 mg, 2.01 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-*p*-tolyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]-quinoline (*endo*-**5n**) as colorless crystals.

mp 77−79 °C; R_f = 0.46 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3366 (NH), 3041 (C-H), 2923, 1604, 1590 (C═C), 1513, 1497, 1470 (CH_2), 1418, 1352, 1311, 1283, 1264, 1225, 1155, 1130, 1111, 1035, 1002, 967, 937, 889, 865, 844, 809, 796, 748, 725, 687 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 297 (3.41), 251 (3.89), 218 (4.23) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 1.84 (dddd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.7 Hz, J = 2.5 Hz, J = 1.7 Hz, 1H, 3-H(a)), 2.37 (s, 3H; 4′-CH_3), 2.65 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.3 Hz, ^3J (3-H(b), 3a-H) = 9.4 Hz, 3 × J ∼ 2.6 Hz, 1H, 3-H(b)), 3.01 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.2 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.2 Hz, ^3J (3a-H, 9b-H) ∼ 9.2 Hz, ^3J (3a-H, 4-H) = 3.4 Hz, 1H, 3a-H), 3.73 (bs, 1H, N-H), 4.12 (bd, ^3J (9b-H, 3a-H) = 8.9 Hz, 1H, 9b-H), 4.62 (d, ^3J (4-H, 3a-H) = 3.2 Hz, 1H, 4-H), 5.63−5.69 (m, 1H, 2-H), 5.82−5.87 (m, 1H, 1-H), 6.62 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H, 6-H), 6.75 (ddd, ^3J (8-H, 7-H) ∼ 7.4 Hz, ^3J (8-H, 9-H) ∼ 7.4 Hz, ^4J (8-H, 6-H) = 1.2 Hz, 1H, 8-H), 6.99 (dddd, ^3J (7-H, 6-H) ∼ 7.5 Hz, ^3J (7-H, 8-H) ∼ 7.5 Hz, ^4J (7-H, 9-H) = 1.6 Hz, J = 0.6 Hz, 1H, 7-H), 7.07 (bd, ^3J (9-H, 8-H) = 7.7 Hz, 1H, 9-H), 7.19 (d like, J = 8.2 Hz, 2H, 3′-H and 5′-H), 7.34 (d like, J = 8.2 Hz, 2H, 2′-H and 6′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (4′-CH_3), 31.5 (C-3), 46.1 (C-3a), 46.4 (C-9b), 57.9 (C-4), 115.9 (C-6), 119.1 (C-8), 126.1 (C-9a), 126.3 (C-7), 126.4 (C-2′ and C-6′), 129.0 (C-9), 129.1 (C-3′ and C-5′), 130.4 (C-2), 134.0 (C-1), 136.8 (C-4′), 139.8 (C-1′), 145.7 (C-5a); MS (EI, 70 eV) m/z (%) 261 (100) $[M]^+$, 246 (17) $[M - CH_3]^+$, 232 (9), 220 (17), 170 (21) $[M - C_6H_5CH_3]^+$, 156 (48), 129 (11), 105 (13), 91 (6) $[C_7H_7]^+$; HRMS (EI, M^+) calcd for $C_{19}H_{19}N$ (261.1512), found 261.1520.

*(3aSR,4RS,9bRS)-4-(Pyridin-3-yl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5o**).*

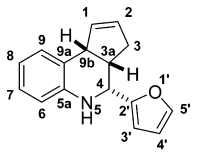


endo-**5o**

According to the general procedure, iron powder (472 mg, 8.44 mmol), citric acid (1.75 g, 9.1 mmol), montmorillonite K10 (155 mg), nitrobenzene (**1a**) (254 mg, 2.06 mmol), pyridine-3-carbaldehyde (**2i**) (271 mg, 2.53 mmol), and cyclopentadiene (**3**) (800 mg, 12.1 mmol) were reacted for 4 h at 40 °C. After work up, a 95:5 mixture of *endo*-**5o** and *exo*-**5o** (^1H NMR) was isolated in 53% yield (270 mg, 1.09 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(pyridin-3-yl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta-[*c*]quinoline (*endo*-**5o**) as colorless crystals.

mp 182−184 °C; R_f = 0.19 (dichloromethane/methanol = 99:1); IR (ATR) $\tilde{\nu}$ 3249 (NH), 3048 (C-H), 2931 (CH_2), 1607, 1589 (C═C), 1576, 1486, 1425 (CH_2), 1359, 1334, 1309, 1288, 1265, 1230, 1183, 1156, 1141, 1105, 1035, 1026, 1009, 987, 971, 956, 938, 909, 842, 805, 788, 774, 746, 713, 698, 671, 659 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 295 (3.44), 251 (3.93), 217 (4.09) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 1.83 (bdd, ^2J (3-H(a), 3-H(b)) = 16.4 Hz, ^3J (3-H(a), 3a-H) = 8.7 Hz, 1H, 3-H(a)), 2.61−2.75 (m, 1H, 3-H(b)), 3.01 (bdddd, ^3J (3a-H, 3-H(a)) ∼ 9.0 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.0 Hz, ^3J (3a-H, 9b-H) ∼ 9.0 Hz, ^3J (3a-H, 4-H) = 3.2 Hz, 1H, 3a-H), 3.72 (bs, 1H, N-H), 4.13 (bd, ^3J (9b-H, 3a-H) = 8.6 Hz, 1H, 9a-H), 4.69 (d, ^3J (4-H, 3a-H) = 2.3 Hz, 1H, 4-H), 5.62−5.69 (m, 1H, 2-H), 5.82−5.91 (m, 1H, 1-H), 6.65 (bd, ^3J (6-H, 7-H) = 7.9 Hz, 1H, 6-H), 6.78 (bdd, ^3J (8-H, 7-H) ∼ 7.4 Hz, ^3J (8-H, 9-H) ∼ 7.4 Hz, 1H, 8-H), 7.01 (bdd, ^3J (7-H, 6-H) ∼ 7.5 Hz, ^3J (7-H, 8-H) ∼ 7.5 Hz, 1H, 7-H), 7.07 (bd, ^3J (9-H, 8-H) = 7.6 Hz, 1H, 9-H), 7.31 (dd, ^3J (5′-H, 4′-H) = 7.5 Hz, ^3J (5′-H, 6′-H) = 4.5 Hz, 1H, 5′-H), 7.78 (bd, ^3J (4′-H, 5′-H) = 7.6 Hz, 1H, 4′-H), 8.56 (bd, ^3J (6′-H, 5′-H) = 4.0 Hz, 1H, 6′-H), 8.69 (s, 1H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.4 (C-3), 45.8 (C-3a), 46.1 (C-9b), 56.0 (C-4), 116.1 (C-6), 119.6 (C-8), 123.4 (C-5′), 125.9 (C-9a), 126.4 (C-7), 129.0 (C-9), 130.1 (C-2), 134.0 (C-1), 134.1 (C-4′), 138.2 (C-3′), 145.0 (C-5a), 148.6 (C-2′), 148.8 (C-6′); MS (EI, 70 eV) m/z (%) 248 (100) $[M]^+$, 219 (12), 207 (15), 194 (8), 170 (29) $[M - C_5H_4N]^+$, 156 (44), 129 (15), 115 (9); HRMS (EI, M^+) calcd for $C_{17}H_{16}N_2$ (248.1308), found 248.1300.

*(3aSR,4RS,9bRS)-4-(Furan-2-yl)-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5p**).*[24]



endo-**5p**

According to the general procedure, iron powder (353 mg, 6.3 mmol), citric acid (1.68 g, 8.8 mmol), montmorillonite K10 (153 mg), nitrobenzene (**1a**) (255 mg, 2.07 mmol), furfural (**2j**) (624 mg, 6.5 mmol), and cyclopentadiene (**3**) (600 mg, 9.1 mmol) were reacted for 4 h at 40 °C. After work up, a 94:6 mixture of *endo*-**5p** and *exo*-**5p** (^1H NMR) was isolated in 60% yield (295 mg, 1.24 mmol). Crystallization from petroleum ether gave the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-(furan-2-yl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5p**) as colorless crystals.

mp 115−116 °C (lit.[24] mp 104 °C); R_f = 0.51 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3369 (NH), 3145, 3050 (C-H),

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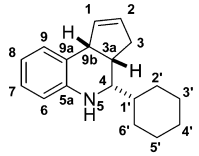
2940 (CH_2), 2787, 1601, 1584 (C═C), 1476, 1429 (CH_2), 1345, 1308, 1287, 1263, 1226, 1187, 1159, 1135, 1112, 1077, 1033, 1007, 958, 929, 883, 865, 849, 807, 794, 754, 744, 722, 705, 684 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 296 (6.38), 250 (3.78), 226 (3.80) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 2.18 (dddd, ^2J (3-H(a), 3-H(b)) = 16.5 Hz, ^3J (3-H(a), 3a-H) = 8.9 Hz, J = 2.1 Hz, J = 1.9 Hz, 1H, 3-H(a)), 2.66 (ddddd, ^2J (3-H(b), 3-H(a)) = 16.5 Hz, ^3J (3-H(b), 3a-H) = 8.8 Hz, 3 × J ∼ 2.5 Hz, 1H, 3-H(b)), 3.20 (dddd, ^3J (3a-H, 3-H(a)) ∼ 8.9 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.9 Hz, ^3J (3a-H, 9b-H) ∼ 8.9 Hz, ^3J (3a-H, 4-H) = 3.3 Hz, 1H, 3a-H), 3.86 (bs, 1H, N-H), 4.10 (bd, ^3J (9b-H, 3a-H) = 9.4 Hz, 1H, 9b-H), 4.64 (d, ^3J (4-H, 3a-H) = 3.5 Hz, 1H, 4-H), 5.66−5.70 (m, 1H, 2-H), 5.79−5.83 (m, 1H, 1-H), 6.26 (ddd, ^3J (3′-H, 4′-H) = 3.6 Hz, J = 2 × ∼ 0.9 Hz, 1H, 3′-H), 6.38 (dd, ^3J (4′-H, 3′-H) = 3.3 Hz, ^3J (4′-H, 5′-H) = 1.9 Hz, 1H, 4′-H), 6.64 (dd, ^3J (6-H, 7-H) = 7.9 Hz, ^4J (6′-H, 8′-H) =1.2 Hz, 1H, 6-H), 6.77 (ddd, ^3J (8-H, 7-H) ∼ 7.5 Hz, ^3J (8-H, 9-H) ∼ 7.5 Hz, ^4J (8-H, 6-H) = 1.2 Hz, 1H, 8-H), 7.00 (ddd ^3J (7-H, 6-H) ∼ 7.3 Hz, ^3J (7-H, 8-H) ∼ 7.3 Hz, ^4J (7-H, 9-H) = 1.6 Hz, 1H, 7-H), 7.06 (bd, ^3J (9-H, 8-H) = 7.7 Hz, 1H, 9-H), 7.40 (dd, ^3J (5′-H, 4′-H) = 1.9 Hz, ^4J (5′-H, 3′-H) = 0.9 Hz, 1H, 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.5 (C-3), 42.5 (C-3a), 46.1 (C-9b), 52.7 (C-4), 105.3 (C-3′), 110.2 (C-4′), 115.9 (C-6), 119.5 (C-8), 126.3 (C-9), 126.3 (C-7), 129.0 (C-9), 130.3 (C-2), 134.0 (C-1), 141.5 (C-5′), 144.9 (C-5a), 155.7 (C-2′); MS (EI, 70 eV) m/z (%) 237 (92) $[M]^+$, 220 (9), 204 (14), 196 (17), 180 (18), 168 (22), 156 (38), 130 (21), 115 (12), 72 (56), 59 (100); HRMS (EI, M^+) calcd for $C_{16}H_{15}NO$ (237.1148), found 237.1153.

*(3aSR,4RS,9bRS)-4-Cyclohexyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5q**).*

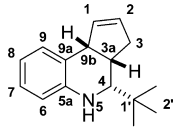


endo-**5q**

According to the general procedure, iron powder (487 mg, 8.71 mmol), citric acid (1.64 g, 8.55 mmol), montmorillonite K10 (150 mg), nitrobenzene (**1a**) (258 mg, 2.09 mmol), cyclohexanecarbaldehyde (**2k**) (281 mg, 2.5 mmol), and cyclopentadiene (**3**) (620 mg, 9.38 mmol) were reacted for 4 h at 40 °C. After work up, a 95:5 mixture of *endo*-**5q** and *exo*-**5q** (^1H NMR) was isolated in 92% yield (490 mg, 1.93 mmol). Crystallization from methanol gave the *endo*-diastereomer (3a*SR*,4*RS*,-9b*RS*)-4-cyclohexyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5q**) as colorless crystals.

mp 84−85 °C; R_f = 0.49 (petroleum ether/methanol = 7:3); IR (ATR) $\tilde{\nu}$ 3408 (NH), 2921, 2841, 2349, 1588 (C═C), 1478, 1442 (CH_2), 1354, 1295, 1268, 1133, 1112, 1033, 936, 853, 804, 747, 723, 699, 664 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 303 (3.42), 252 (3.90), 215 (4.31) nm; ^1H NMR (MHz, $CDCl_3$) δ 1.02 (ddd, ^2J (6′-H(ax), 6′-H(eq)) ∼ 12.0 Hz, ^3J (6′-H(ax), 1′-H) ∼ 12.0 Hz, ^3J (6′-H(ax), 5′-H(ax)) ∼ 12.0 Hz, 1H, 6′-H(ax)), 1.03 (ddd, ^2J (2′-H(ax), 2′-H(eq)) ∼ 12.0 Hz, ^3J (2′-H(ax), 1′-H) ∼ 12.0 Hz, ^3J (2′-H(ax), 3′-H(ax)) ∼ 12.0 Hz, 1H, 2′-H(ax)), 1.20 (ddddd, ^2J (4′-H(ax), 4′-H(eq)) ∼ 12.6 Hz, ^3J (4′-H(ax), 3′-H(ax)) ∼ 12.6 Hz, ^3J (4′-H(ax), 5′-H(ax)) ∼ 12.6 Hz, ^3J (4′-H(ax), 3′-H(eq)) ∼ 3.7 Hz, ^3J (4′-H(ax), 5′-H(eq)) ∼ 3.7 Hz, 1H, 4′-H(ax)), 1.29 (ddd, ^2J (3′-H(ax), 3′-H(eq)) ∼ 13.0 Hz, ^3J (3′-H(ax), 2′-H(ax)) ∼ 13.0 Hz, ^3J (3′-H(ax), 4′-H(ax)) ∼ 13.0 Hz, 1H, 3′-H(ax)), 1.31 (ddd, ^2J (5′-H(ax), 5′-H(eq)) ∼ 13.0 Hz, ^3J (5′-H(ax), 4′-H(ax)) ∼ 13.0 Hz, ^3J (5′-H(ax), 6′-H(ax)) ∼ 13.0 Hz, 1H, 5′-H(ax)), 1.34−1.43 (m, 1H, 1′-H), 1.71 (bd, ^2J (4′-H(eq), 4′-H(ax)) = 12.4 Hz, 1H, 4′-H(eq)), 1.83 (bd, ^2J (5′-H(eq), 5′-H(ax)) = 13.3 Hz, 1H, 5′-H(eq)), 1.91 (bd, ^2J (2′-H(eq), 2′-H(ax)) = 12.4 Hz, 1H, 2′-H(eq)), 1.97 (bd, ^2J (6′-H(eq), 6′-H(ax)) = 12.4 Hz, 1H, 6′-H(eq)), 2.24 (bdd, ^2J (3-H(a), 3-H(b)) = 16.3 Hz, ^3J (3-H(a), 3a-H) = 8.9 Hz, 1H, 3-H(a)), 2.53 (bdd, ^2J (3-H(b), 3-H(a)) = 16.1 Hz, ^3J (3-H(b), 3a-H) = 9.2 Hz, 1H, 3-H(b)), 2.96 (dddd, ^3J (3a-H, 3-H(a)) ∼ 9.1 Hz, ^3J (3a-H, 3-H(b)) ∼ 9.1 Hz, ^3J (3a-H, 9b-H) ∼ 9.1 Hz, ^3J (3a-H, 4-H) = 3.1 Hz, 1H, 3a-H), 3.03 (dd, ^3J (4-H, 1′-H) = 9.2 Hz, ^3J (4-H, 3a-H) = 2.5 Hz, 1H, 4-H), 3.66 (bs, 1H, N-H), 3.96 (bd, ^3J (9b-H, 3a-H) = 8.9 Hz, 1H, 9b-H), 5.69−5.73 (m, 1H, 2-H), 5.81−5.85 (m, 1H, 1-H), 6.56 (bd, ^3J (6-H, 7-H) = 7.9 Hz, 1H, 6-H), 6.69 (bdd, ^3J (8-H, 7-H) ∼ 7.9 Hz, ^3J (8-H, 9-H) ∼ 7.9 Hz, 1H, 8-H), 6.95 (bdd, ^3J (7-H, 6-H) ∼ 7.8 Hz, ^3J (7-H, 8-H) ∼ 7.8 Hz, 1H, 7-H), 7.00 (bd, ^3J (9-H, 8-H) = 7.8 Hz, 1H, 9-H); ^{13}C NMR (MHz, $CDCl_3$) δ 25.9 (C-5′), 26.1 (C-3′), 26.3 (C-4′), 29.0 (C-2′), 30.2 (C-6′), 31.0 (C-3), 39.8 (C-1′), 40.6 (C-3a), 46.4 (C-9b), 58.7 (C-4), 115.5 (C-6), 118.6 (C-8), 126.1 (C-7), 126.4 (C-9a), 128.8 (C-9), 130.2 (C-2), 134.5 (C-1), 145.8 (C-5a); MS (EI, 70 eV) m/z (%) 253 (8) $[M]^+$, 170 (100) $[M - C_6H_{11}]^+$; HRMS (EI, M^+) calcd for $C_{18}H_{23}N$ (253.1825), found 253.1812.

*(3aSR,4RS,9bRS)-4-tert-Butyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (endo-**5r**).*

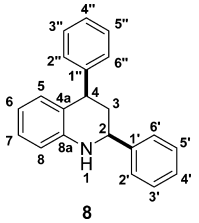


endo-**5r**

According to the general procedure, iron powder (478 mg, 8.55 mmol), citric acid (1.63 g, 8.48 mmol), montmorillonite K10 (152 mg), nitrobenzene (**1a**) (267 mg, 2.17 mmol), pivaldehyde (**2l**) (229 mg, 2.66 mmol), and cyclopentadiene (**3**) (690 mg, 10.4 mmol) were reacted for 4 h at 40 °C. After work up, followed by column chromatography on silica gel (petroleum ether/dichloromethane = 7:3), the *endo*-diastereomer (3a*SR*,4*RS*,9b*RS*)-4-*tert*-butyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (*endo*-**5r**) was isolated in 88% yield (430 mg, 1.89 mmol) as a pale yellow liquid.

R_f = 0.57 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3400 (NH), 3050 (C-H), 2952, 2870, 1606, 1587 (C═C), 1479, 1465 (CH_2), 1421, 1397, 1365, 1300, 1286, 1258, 1239, 1224, 1203, 1184, 1156, 1140, 1112, 1037, 1026, 981, 958, 931, 876, 847, 801, 782, 740, 719, 683 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 301 (3.40), 255 (3.56), 223 (3.55) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H, 2′-H), 2.22 (dddd, ^2J (3-H(a), 3-H(b)) = 15.9 Hz, ^3J (3-H(a), 3a-H) = 8.5 Hz, J = 2.7 Hz, J = 1.4 Hz, 1H, 3-H(a)), 2.42 (ddddd, ^2J (3-H(b), 3-H(a)) = 15.8 Hz, ^3J (3-H(b), 3a-H) = 9.6 Hz, 3 × J ∼ 2.3 Hz, 1H, 3-H(b)), 2.92 (dddd, ^3J (3a-H, 3-H(a)) = 9.8 Hz, ^3J (3a-H, 3-H(b)) ∼ 8.5 Hz, ^3J (3a-H, 9b-H) ∼ 8.5 Hz, ^3J (3a-H, 4-H) = 2.3 Hz, 1H, 3a-H), 3.16 (d, ^3J (4-H, 3a-H) = 1.8 Hz, 1H, 4-H), 3.52 (bs, 1H, N-H), 3.98 (d, ^3J (9b-H, 3a-H) = 8.6 Hz, 1H, 9a-H), 5.72−5.75 (m, 1H, 2-H), 5.88−5.92 (m, 1H, 1-H), 6.58 (dd, ^3J (6-H, 7-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H, 6-H), 6.68 (ddd, ^3J (8-H, 7-H) ∼ 7.5 Hz, ^3J (8-H, 9-H) ∼ 7.5 Hz, ^4J (8-H, 6-H) = 1.2 Hz, 1H, 8-H), 6.95 (dddd, ^3J (7-H, 6-H) = 7.9 Hz, ^3J (7-H, 8-H) = 7.3 Hz, ^4J (7-H, 9-H) = 1.6 Hz, J = 0.7 Hz, 1H, 7-H), 6.99 (ddd, ^3J (9-H, 8-H) = 7.6 Hz, J = 2 × ∼ 1.2 Hz, 1H, 9-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.4 (C-2′), 32.0 (C-3), 33.6 (C-1′), 41.4 (C-3a), 48.1 (C-9b), 62.6 (C-4), 115.4 (C-6), 118.4 (C-8), 126.0 (C-9a), 126.1 (C-7), 129.0 (C-9), 131.2 (C-2), 133.6 (C-1), 146.2 (C-5a); MS (EI, 70 eV) m/z (%) 227 (10) $[M]^+$, 170 (100), 57 (3) $[C_4H_9]^+$; HRMS (EI, M^+) calcd for $C_{16}H_{21}N$ (227.1669), found 227.1674.

*(2SR,4RS)-2,4-Diphenyl-1,2,3,4-tetrahydroquinoline (**8**).*[28c]



8

According to the general procedure, iron powder (452 mg, 8.09 mmol), citric acid (1.66 g, 8.64 mmol), montmorillonite K10 (150 mg), nitrobenzene (**1a**) (260 mg, 2.11 mmol), benzaldehyde (**2a**) (250 mg, 2.36 mmol), and styrene (**7**) (644 mg, 6.19 mmol) were reacted for 5 h at 80 °C. After work up, (2*SR*,4*RS*)-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (**8**) was isolated in 99% yield (596 mg, 2.09 mmol).

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Crystallization from methanol gave the diastereomer (2*SR*,4*RS*)-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (**8**) as colorless crystals.

mp 92−94 °C (lit.[28c] mp 99−101 °C); R_f = 0.39 (petroleum ether/dichloromethane = 7:3); IR (ATR) $\tilde{\nu}$ 3025 (C-H), 2308, 1600, 1491, 1472, 1454 (CH_2), 1333, 1304, 1249, 1154, 1107, 1079, 1029, 940, 855, 779, 747, 700, 663 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 303 (3.45), 253 (4.02), 211 (4.60) nm; ^1H NMR (MHz, $CDCl_3$) δ 2.24 (bddd, ^2J (3-H(ax), 3-H(eq)) ∼ 12.0 Hz, ^3J (3-H(ax), 2-H) ∼ 12.0 Hz, ^3J (3H(ax), 4-H) ∼ 12.0 Hz, 1H, 3-H(ax)), 2.31 (bddd, ^2J (3-H(eq), 3-H(ax)) = 12.8 Hz, ^3J (3-H(eq), 4-H) = 4.3 Hz, J = 2.1 Hz, 1H, 3-H(eq)), 4.08 (bs, 1H, N-H), 4.33 (bdd, ^3J (4-H, 3-H(ax)) = 10.8 Hz, ^3J (4-H, 3-H(eq)) = 4.3 Hz, 1H, 4-H), 4.63 (bd, ^3J (2-H, 3-H(ax)) = 10.9 Hz, 1H, 2-H), 6.62 (d, ^3J (8-H, 7-H) = 8.3 Hz, 1H, 8-H), 6.62 (t, ^3J (6-H, 5-H and 7-H) = 7.4 Hz, 1H, 6-H), 6.67 (d, ^3J (5-H, 6-H) = 7.4 Hz, 1H, 5-H), 7.03 (t, ^3J (7-H, 6-H and 8-H) = 7.9 Hz, 1H, 7-H), 7.28 (t like, J = 7.8 Hz, 1H, 4″-H), 7.30 (d like, J = 8.1 Hz, 2H, 2″-H and 6″-H), 7.34 (d like, J = 7.6 Hz, 1H, 4′-H), 7.36 (t like, J = 7.9 Hz, 2H, 3″-H and 5″-H), 7.37 (t like, J = 7.3 Hz, 2H, 3′-H and 5′-H), 7.47 (d like, J = 7.3 Hz, 2H, 2′-H and 6′-H);[33] ^{13}C NMR (MHz, $CDCl_3$) δ 42.1 (C-3), 44.9 (4-H), 57.3 (C-2), 114.2 (C-8), 117.6 (C-6), 124.7 (C-4a), 126.5 (C-4″), 126.6 (C-2′ and C-6′), 127.2 (C-7), 127.7 (C-4′), 128.5 (C-3″ and C-5″), 128.6 (C-3′ and C-5′), 128.7 (C-2″ and C-6″), 129.6 (C-5), 143.9 (C-1′), 145.28 (C-1″), 145.32 (C-8a); MS (EI, 70 eV) m/z (%) 285 (100) $[M]^+$, 280 (41), 270 (11), 206 (70), 194 (84), 180 (25), 165 (17), 130 (33), 91 (46), 77 (31) $[C_6H_5]^+$; HRMS (EI, M^+) calcd for $C_{21}H_{19}N$ (285.1512), found 285.1498.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for compounds **5a−r** and **8**; X-ray crystal structures of **5b**, **5d**, and **5h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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