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# Efficient Synthesis of the *N*-(buta-2,3-dienyl)carboxamide of Isopimaric Acid and the Potential of This Compound towards Heterocyclic Derivatives of Diterpenoids

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The *N*-(2,3-butadienyl)carboxamide of isopimaric acid, that is, compound **3**, was prepared through a two-step synthetic procedure starting from the natural diterpene isopimaric acid. The Pd-catalyzed cross-coupling and subsequent cyclization of terpenoid allene **3** with several aryl iodides and aryl bromides gave access to optically active diterpenoid–oxazoline derivatives in good to excellent yields. The functional group tolerance in the aryl iodides was demonstrated by several examples, including substrates with additional *N*-*tert*-butoxycarbonyl-protected amino, hydroxy, and carboxy substituents in the *ortho* position. The cross-coupling–cyclization reaction of those compounds with allene **3** proceeded selectively with the formation of cyclization products on the substituent in the aromatic ring. This transformation opens a potential route to the synthesis of hybrid compounds containing a tricyclic diterpenoid and several heterocycles.

## 1. Introduction

Chemical substances derived from plants have been used to treat human diseases since the dawn of medicine. The use of natural compounds as "privileged structures" in terms of their ability to be useful templates for the synthesis of novel biologically active molecules and as a source of lead compounds for drug discovery has been defined.[1,2] Among the various classes of natural products, tricyclic diterpenes are interesting, structurally diverse secondary metabolites. Diterpenes are widely distributed in the plant kingdom and have long been considered to possess a broad spectrum of biological effects. For example, isopimaric acid (**1**) is a readily available and versatile tricyclic diterpenoid that is well represented in the resin of conifers of the genera *Pinus*, *Larix*, and *Picea*.[3,4] The attraction of compound **1** as a biorenewable compound and its interesting biological and pharmaceutical properties, which include antibacterial,[5–7] antiviral,[8] and anti-inflammatory[9] activities, has stimulated the development of a variety of chemistries for functionality, including oxidative[10–12] and isomeric[13] transformations, in addition to several modifications of the carboxyl group.[14,15] The number of examples in the literature detailing the functionalization of isopimaric acid is limited, and they do not result in the generation of evolvable libraries of compounds for structure–activity relationship studies. Very recently, our group realized a one-pot, two-step method involving metal catalysis for the synthesis of optically active halogenated oxazole derivatives from isopimaric acid.[15a] Accordingly, in light of new isopimaranes containing a heterocyclic substituent, we became interested in the targeted preparation of isopimaric acid derivatives through further transformation of its accessible derivatives—*N*-propargyl amide **2**. On the basis of the development of a straightforward method for the homologation of acetylenes to allenes,[16] herein we describe the synthesis of the *N*-(2,3-butadienyl)carboxamide of isopimaric acid, that is, compound **3**, and its Pd-catalyzed cross-coupling–cyclization reactions with (het)aryl iodides and aryl bromides. This consistent transformation is attractive due to the versatility of *N*-(2,3-butadienyl)carboxamides in synthesis,[17,18] and because it could enable the synthesis of a variety of chiral bioactive heterocyclic derivatives. During this study, we analyzed the scope of this reaction for the synthesis of several "hybrid" compounds by using several aryl iodides having a substituent in the *ortho* position in this coupling–cyclization reaction.

## 2. Results and Discussion

As the starting compound, we used the *N*-propargyl amide of isopimaric acid, that is, compound **2**, which was obtained on a gram scale in two steps from isopimaric acid.[10] The CuI-mediated reaction of terminal alkyne **2** with formaldehyde in the

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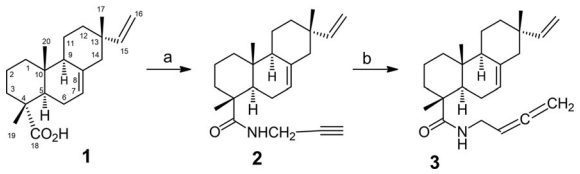
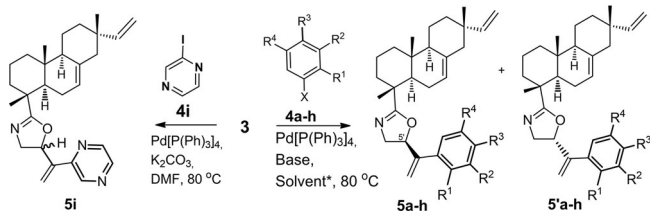


**Scheme 1.** Synthesis of the *N*-(2,3-butadienyl)carboxamide of isopimaric acid by the method of Grabbe et al. Reagents and conditions: a) 1) $(COCl)_2$, $CH_2Cl_2$, 0 °C; 2) propargyl amine hydrochloride, $CH_2Cl_2$, $Et_3N$, RT; b) CuI, $(HCHO)_n$, $iPr_2NH$, 1,4-dioxane, 100 °C, 10 h.

presence of diisopropylamine in dioxane gave isopimaric acid *N*-(2,3-butadienyl)carboxamide **3** (Scheme 1).

Several allenes have become extremely versatile building blocks in organic synthesis. They have notably been involved in transition-metal-mediated reactions, and good selectivity has been obtained by modifying the nature of the metal and the associated ligands.[19] Our attention was focused on the synthesis of terpenoid oxazolines. The 4,5-dihydrooxazole ring not only is present in many biologically active natural and unnatural compounds but also serves as a very versatile functionality in organic synthesis.[20,21] The coupling–cyclization reaction of *N*-(2,3-butadienyl)carboxamide **3** with 4-iodobenzonitrile (**4a**) and 1-iodobenzotrifluoride (**4b**) was performed in DMF at 80 °C in the presence of $Pd(PPh_3)_4$ (5 mol%) and $K_2CO_3$ (2 equiv.).[18a] Terpenoid-substituted 5-[1-(aryl)vinyl]-4,5-dihydrooxazoles **5a** and **5b** were isolated after column chromatography in yields of 87 and 60% as mixtures of diastereomers (dr = 50:50, the ratio was determined by analysis of the crude product by $^1H$ NMR spectroscopy) (Scheme 2, Table 1).



**Scheme 2.** Coupling–cyclization reaction of terpenoid allene **3**. [*] Solvent: DMF, entries 1–7; $CH_3CN$, entry 8; DMF/$CH_3CN$, entry 10 (Table 1).

Terpenoid-substituted 5-(*S*)- and 5-(*R*)-oxazolines **5a** and **5′a** were separated by column chromatography on silica gel. The reaction of allene **3** with unsubstituted iodobenzene (**4c**) in the presence of $K_2CO_3$ gave dihydrooxazole **5c** in a low yield (17%). A higher yield of compound **5c** was obtained by using $Cs_2CO_3$ (2 equiv.) as a base (Table 1, entry 3). The reaction of methoxy-substituted aryl iodides **4d–f** with **3** under these conditions led to target 5-(1-arylvinyl)-4,5-dihydrooxazoles **5d–f** in yields of 54–77% (Table 1, entries 4–6). The use of these conditions for the reaction of *N*-(2,3-butadienyl)carboxamide **3** with methyl 2-acetamido-5-bromobenzoate (**4g**) was unsuccessful; compound **5g** was isolated in 2% yield (Table 1, entry 7). However, upon conducting the same reaction in $CH_3CN$, target compound **5g** was delivered in 61% yield (Table 1, entry 8). By

**Table 1.** Coupling–cyclization reaction of terpenoid *N*-buta-2,3-dienyl)-amide **3** with aryl iodides **4a–f** and **4h**, aryl bromide **4g**, and 2-iodopyrazine (**4i**).

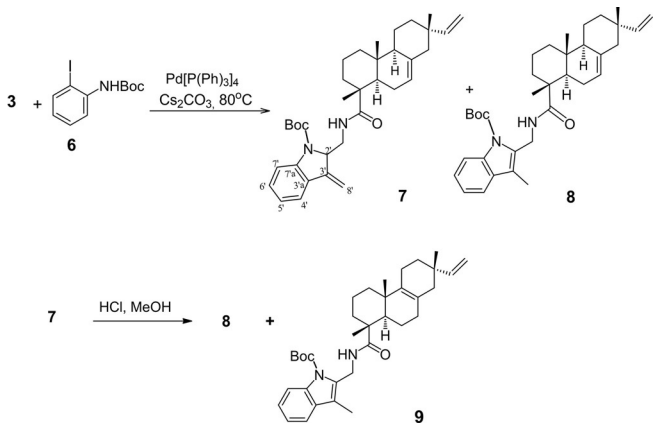
| Entry | Compound **4** $R^1$ | $R^2$ | $R^3$ | $R^4$ | X | Base | Compound **5** (yield[a] [%]) |
|---|---|---|---|---|---|---|---|
| 1 | H | H | CN | H | I | $K_2CO_3$ | **5a** (87) |
| 2 | H | $CF_3$ | H | H | I | $K_2CO_3$ | **5b** (60) |
| 3 | H | H | H | H | I | $Cs_2CO_3$ | **5c** (50) |
| 4 | $OCH_3$ | H | H | H | I | $Cs_2CO_3$ | **5d** (72) |
| 5 | H | $OCH_3$ | H | H | I | $Cs_2CO_3$ | **5e** (77) |
| 6 | H | H | $OCH_3$ | H | I | $Cs_2CO_3$ | **5f** (54) |
| 7 | H | $CO_2Me$ | NHAc | H | Br | $Cs_2CO_3$ | **5g** (2) |
| 8 | H | $CO_2Me$ | NHAc | H | Br | $Cs_2CO_3$ | **5g** (61) |
| 9 | H | CHO | OH | $OCH_3$ | I | $Cs_2CO_3$ | **5h** (18) |
| 10 | H | CHO | OH | $OCH_3$ | I | $Cs_2CO_3$ | **5h** (65) |

[a] Yield of isolated product. All 4,5-dihydrooxazoles were obtained as mixtures of diastereomers **5a–i**/ **5′a–i**, 50:50.

further fine-tuning the experimental parameters (Table 1, entries 9 and 10), we found that the yield of target diterpenoid dihydrooxazole **5g** could be improved to 65% by using a mixture of $CH_3CN$ and DMF in a ratio of 5:1. Additionally, 5-[1-(phenyl)vinyl]-4,5-dihydrooxazole (**5c**, 4% yield) was also isolated in this reaction. So, aryl iodides and aryl bromides with electron-donating and electron-withdrawing substituents in the *ortho*, *para*, or *meta* position of the aryl ring were all suitable for this transformation, and they gave the corresponding oxazoline derivatives in good yields. The reaction of heterocyclic 2-iodopyrazine (**4i**) also proceeded smoothly to afford corresponding cross-coupling product **5i** in excellent yield.

The main synthetic interest in allenes deals with the formation of carbo- and heterocycles. The Pd-catalyzed cross-coupling of allenes with aromatic iodides containing a nucleophile substituent (e.g., 2-iodoaniline, 2-iodophenol, 2-iodobensoic acid) in the *ortho* position gave the possibility for cyclization, which could occur through [α,β], [β,α], [β,γ], or [γ,β] attack on the allene function with the formation of an indole, isochromane, or benzofuran system.[22–25] The experimental results revealed the significant influence of the nature of the substituent in the functionalized allene on the direction of cyclization.[26] In light of the results obtained from the optimization of the reaction parameters (Table 1), we decided to explore the reaction of *N*-(2,3-butadienyl)carboxamide **3** further by using *ortho*-substituted aryl iodides.

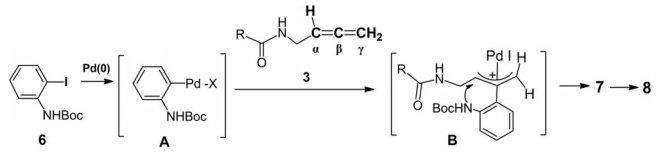
Compound **3** was submitted to the reaction with *N*-*tert*-butoxycarbonyl (*N*-Boc)-protected 2-iodoaniline (**6**) (Scheme 3). The reaction in acetonitrile proceeded with the formation of 3-methyleneindoline **7** as the only isolable product (55% yield after flash chromatography on silica gel). Upon performing the reaction in DMF, compound **7** (40% yield) and subsequent indole **8** (15% yield) were isolated. Treatment of compound **7** with HCl smoothly led to indole **8** (70% yield) within 1 h. Increasing the amount of HCl and the reaction time to 3 h led to isomerization of the double bonds in the heterocyclic ring and terpenic core. Compounds **8** (38% yield) and **9** (10% yield) were isolated. Interestingly, hydrolysis of the Boc protecting group under these conditions did not occur. As a result of the




**Scheme 3.** Synthesis of indole-substituted tricyclic diterpenoids.

above transformations, we obtained hybrid indole–diterpene compound **8** in a yield up to 70%.

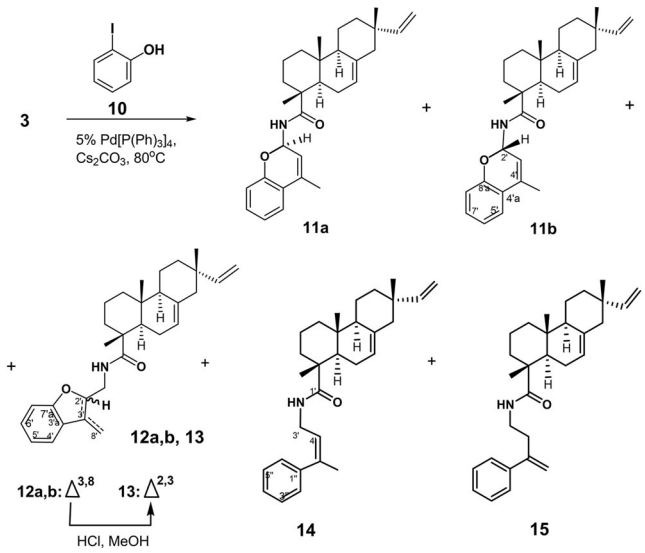
From a mechanistic viewpoint and by using the main principles of the palladium catalysis of this reaction,[27] the formation of compound **7** can be described as follows: the organic halide adds oxidatively to the palladium(0) catalyst, which forms palladium species **A**; species **A** then undergoes carbopalladation with allene **3** to generate regioselectively intermediate **B**. Finally, nucleophilic attack by the substituent leads to expected compound **7**. Indole **8** is the product of isomerization of 3-methyleneindoline **7** (Scheme 4).




**Scheme 4.** Pd-catalyzed reaction between *N*-protected *o*-iodoaniline **6** and isopimaric acid *N*-(2,3-butadienyl)carboxamide **3**.

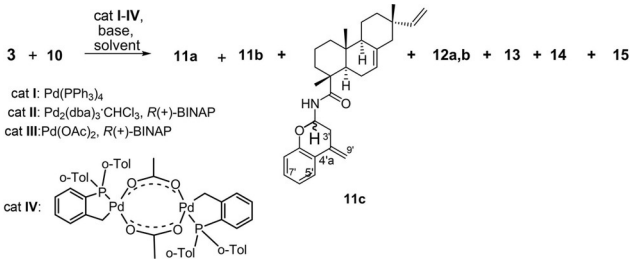
The reaction of allene **3** with *ortho*-hydroxy-substituted aryl iodide **10** under the found reaction conditions proceeded with the formation of a complex mixture of compounds (Scheme 5). So, by using $CH_3CN$ as the solvent, heterocyclic compounds **11a** (18% yield), **11b** (18% yield), **12a/12b** (29% yield), and **13** (4% yield) as well as styrenes **14** (4% yield) and **15** (6% yield) were isolated (Table 2, entry 1). Upon performing the reaction in DMF, 2*H*-1-benzopyranes **11a** (12% yield) and **11b** (12% yield), 3-methylene-2,3-dihydrobenzofurans **12a/12b** (30% yield), and *N*-(3-phenylbut-2-en-1-yl)amide **14** (10% yield) were obtained (Table 2, entry 2). Treatment of 3-methylene-2,3-dihydrobenzofurans **12a/12b** with HCl in methanol (35 equiv., 2 h) resulted in their transformation into 3-methylbenzofuran **13** (50% yield). So, diterpenoid 2*H*-chromenes **11a/11b** (isolated in 36% yield) and diterpenoid–benzofuran hybrid **13** (30% yield) were obtained in the reaction of allene **3** with aryl iodide **10** in the presence of $Pd(PPh_3)_4$.

The formation of benzofuran derivatives by the Pd-catalyzed reaction of 2-iodophenol (**10**) with several allenes (e.g., $CH_2$=C=CHPh, $CH_2$=C=$CHCO_2Et$, $CH_2$=C=$CHC_8H_{17}$) was established




**Scheme 5.** Pd-catalyzed reaction between 2-iodophenol (**10**) and terpenoid allene **3**.

**Table 2.** Coupling–cyclization reaction of terpenoid *N*-buta-2,3-dienyl)amide **3** with 2-iodophenol (**10**).

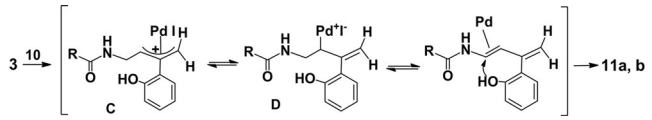



| Entry | Catalyst | Base | Solvent | Products (yield [%]) |
|---|---|---|---|---|
| 1 | **I** | $Cs_2CO_3$ | $CH_3CN$ | **11a** (18), **11b** (18), **12a/b** (29), **13** (5), **14** (4), **15** (8) |
| 2 | **I** | $Cs_2CO_3$ | DMF | **11a** (12), **11b** (12), **12a/b** (30), **14** (10) |
| 3 | **II** | $Cs_2CO_3$ | $CH_3CN$ | **11a** (24), **11b** (24), **12a/b** (5), **13** (3) |
| 4[a] | **III** | $K_2CO_3$ | $CH_3CN$/DMF/$H_2O$ | **11a** (12), **11b** (12), **12a/b** (25) |
| 5 | **IV** | $Cs_2CO_3$ | DMF | **11a** (13), **11b** (13), **12a/b** (22) |
| 6[a] | **IV** | $K_2CO_3$ | DMF/$H_2O$ | **11a** (9), **11b** (9), **11c** (8), **12a/b** (49) |
| 7[a] | **IV** | $K_2CO_3$ | $CH_3CN$/DMF/$H_2O$ | **11a** (9), **11b** (9), **11c** (28), **12a/12b** (37) |

[a] $Bu_4NBr$ was introduced as an additive.

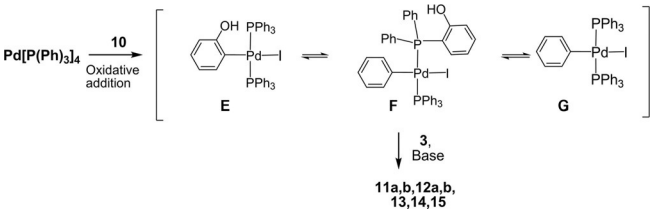
earlier;[26] the formation of 2*H*-chromene derivatives **11** in the reaction of allenes with 2-iodophenol (**10**) was not described. The proposed mechanism for the formation of isomeric compounds **11a/11b** includes the generation a $\eta^3$-allylpalladium intermediate **C**, which is in equilibrium with less stable σ-vinylpalladium species **D**, $\eta^1$-rearrangement, β-elimination, and finally attack on the activated double bond (Scheme 6).

Optically active styrene derivatives **14** and **15** were also isolated in the coupling reaction of allene **3** with compound **10** (also, compound **5c** in the reaction of terpenoid **3** with **4h**).



**Scheme 6.** Formation of compounds **11 a**/**11 b** in the reaction between 2-iodophenol (**10**) and terpenoid allene **3**.

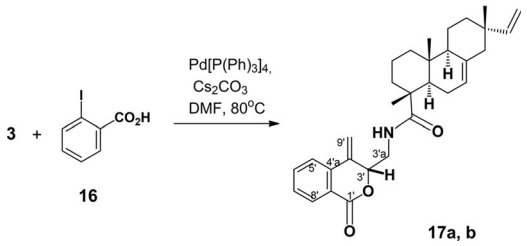
Presumably, these products were the result of aryl exchange between the arylpalladium and triphenylphosphine ligand.[28] The ease by which the aryl groups in the phosphine ligand can be exchanged with the phenolic residue of 2-iodophenol was previously shown.[26c] Scheme 7 shows the possible isomeric transformations of arylpalladium intermediate **E** into arylpalladium complexes **F** and **G** through aryl–aryl exchange between the $Pd^{II}$ center and the coordinated phosphine ligand. The possibility of the existence of arylpalladium intermediates **F** and **G** (as determined by their stability) governs the formation of side products **14** and **15**.



**Scheme 7.** Formation of compounds **14** and **15**.

To avoid the formation of compounds **14** and **15** and also to improve the selectivity, we studied the reaction between terpenoid allene **3** and 2-iodophenol (**10**) in more detail. First, we studied the effect of the palladium source in the catalytic system on the yield of the cyclization product (Table 2, entries 3–6). The reaction of allene **3** with **10** under the conditions[18b] of $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) as the palladium source and (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene [(*R*)-(+)-BINAP] as the ligand in acetonitrile with heating at 80 °C for 50 h led to a mixture of diterpenoid 2*H*-chromenes **11 a**/**11 b** (isolated in an overall yield of 48%) and benzofuran derivatives **12 a**/**12 b**/**13** (overall yield of 8%) (Table 2, entry 3). So, the selectively to 2*H*-chromene formation was increased without a change in the enantioselectivity. Upon performing the reaction in the presence of the $Pd(OAc)_2$/(*R*)-(+)-BINAP catalytic system with potassium carbonate as the base in the presence of tetrabutylammonium bromide as an additive in a mixture of $CH_3CN/DMF/H_2O$ (5:5:1, *v*/*v*/*v*) (Table 2, entry 4), desired 2*H*-chromenes **11 a**/**11 b** and 3-methylene-2,3-dihydrobenzofurans **12 a**/**12 b** were obtained in a ratio of about 1:1 (Table 2, entry 4). We also studied the possibility of using palladium catalyst **IV**, developed Herrmann and Beller,[29] in this coupling–cyclization reaction. Changing the catalyst (Table 2, entries 2 and 5) resulted in about the same yields of cyclization products **11** and **12** with a small increase in the selectivity to terpenoid 2*H*-chromenes **11 a**/**11 b**. Notably, the use of an organic solvent/water[30] combination, particularly DMF/$H_2O$, and also the addition of tetraalkylammonium salts to the reaction mixture, as proposed by Jeffery,[31] is common in the cross-coupling reactions. The reaction of allene **3** with 2-iodophenol (**10**) in the presence of potassium carbonate and tetrabutylammonium bromide as the additive in DMF/water (5:1, *v*/*v*) resulted in an improvement in the selectivity and also an increase in the overall yield of the cyclization products (Table 2, entries 6 and 7). Additionally, terpenoid 2*H*-chromanes **11 c** (two diastereomers) were also obtained by using a palladacycle in an organic solvent/water combination (compare with Table 2, entry 4). The addition of MeCN to the solvent system resulted in a decrease in the selectivity and an increase in the yield of tetrahydrobenzopyran **11 c** (Table 2, entry 7). So, the effectiveness of the palladacycle catalyst (Herrmann–Beller palladium catalyst) was demonstrated in the coupling–cyclization reactions of terpenoid allene **3** with 2-iodophenol (**10**).

The palladium-catalyzed reaction of allene **3** with 2-iodobenzoic acid (**16**) proceeded with the formation of 4-methylene-1-oxoisochromanes **17 a**/**17 b** (70% yield) as a mixture of diastereomers (1:1, determined by analysis of the reaction mixture by $^1H$ NMR spectroscopy) (Scheme 8). Mechanistically, the formation of compounds **17** proceeds according to the above Pd-catalyzed transformation. The π-allylpalladium species is generated as an intermediate. Previously, it was inferred that carboxylate displacement occurred at the more highly substituted terminus of π-allylpalladium compounds.[32] 4-Methylene-1-oxo-isochromanes **17 a**/**17 b** were the only products isolated from this reaction.



**Scheme 8.** Pd-catalyzed reaction between 2-iodobenzoic acid (**16**) and terpenoid allene **3**.

The structures of all new compounds were confirmed by IR, $^1H$ NMR, and $^{13}C$ NMR spectroscopy, in addition to mass spectrometry (MS) and X-ray analysis. The structures of compounds **2**, **3**, **8**, and **11 a** were unambiguously confirmed by single-crystal X-ray diffraction (Figure 1).[33]

The $^1H$ NMR and $^{13}C$ NMR spectra of all the synthesized compounds agreed with their structures and contained one set of characteristic signals for the tricyclic diterpenoid core and the corresponding substituent. The configurations of **5 a** and **5′ a** as *S* or *R* were confirmed by comparison with literature data for assignment of the related configuration by NMR spectroscopy:[34] the coupling constants of the H-4 with H-5 protons for the *S* diastereomers have values of $J = 7.5$ and 10.7 Hz, whereas those for the *R* diastereomers are $J = -8.2$ and 10.3 Hz. The X-ray data revealed that in the four studied structures, the cyclohexane rings have a "chair" conformation and that the cyclohexene rings have a "semichair" conformation.

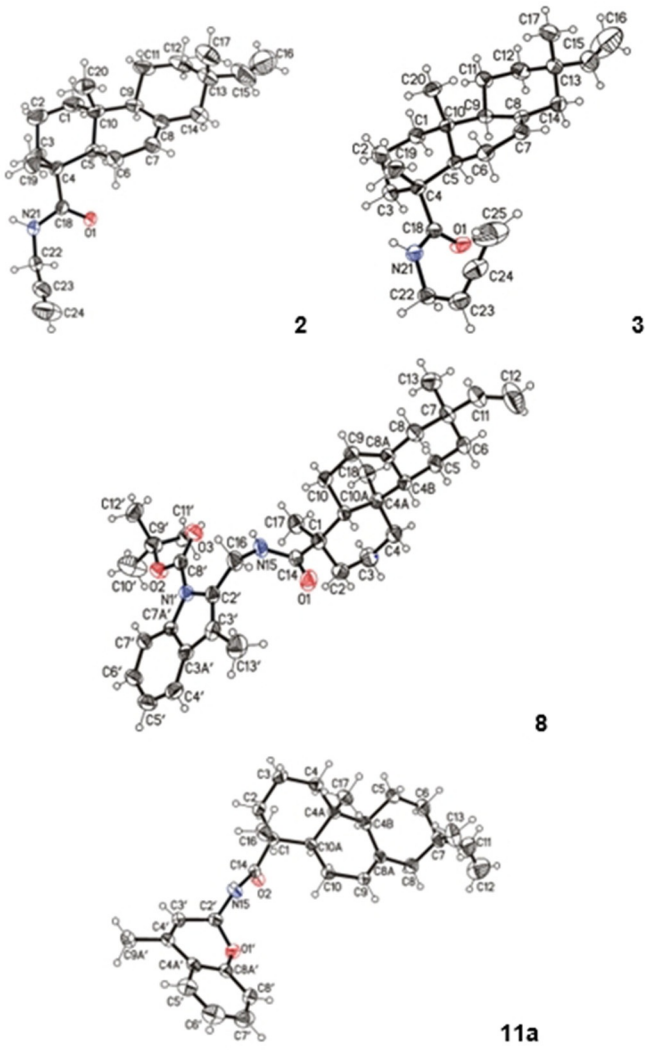



**Figure 1.** Structures of molecules **2**, **3**, **8**, and **11 a** in the crystals.

The bond lengths and bond angles are the same as the statistical values.[35] In the crystal packings of **2**, **3**, and **8**, intermolecular H-bonds are observed: N–H···O type for **2** and **3** and C–H··O for **8**. One-dimensional infinite chains of molecules are formed in the crystal through these H-bonds. It is interesting to note that in the crystal packing of **11 a**, intermolecular short contacts are not observed.

## 3. Conclusions

In summary, we presented a practical method for the synthesis of compound **3**, which is the *N*-(2,3-butadienyl)carboxamide of isopimaric acid. The Pd-catalyzed cross-coupling–cyclization of the new allene with several aryl halides was an effective method to prepare a new group of biologically interesting 5-[1-(aryl)vinyl]-4,5-dihydrooxazoles with a terpenoid substituent. The substrate scope was explored, and the tolerance of our conditions towards additional functionalities was examined. The reaction of the new terpenoid allene with N-protected 2-iodoaniline, 2-iodophenol, and 2-iodobensoic acid proceeded chemoselectively with the formation of hybrid compounds containing terpenoid and heterocyclic (indole, benzofuran, chromane, chromene, and isochromane) fragments. The effectiveness of a palladacycle catalyst was demonstrated in the coupling–cyclization reactions of allene **3** with 2-hydroxyaryl iodide **10**. The obtained results will be useful in our ongoing work on diterpenic acid transformations and, thus, present an opportunity for biological studies and deepened understanding of the underlying biology of this class of natural products. We are confident that by using this approach for the selective transformations of other natural compounds the field of complex biologically active chemicals will be enriched, thus opening up new avenues in the design and development of new and efficient pharmaceuticals.

## Experimental Section

### General Information

Melting points were determined by using a Stuart SMP30 melting point apparatus (Bibby Scientific, Staffordshire, UK). Specific rotation $[\alpha]_D$ values were measured at room temperature (23–25 °C) in $CHCl_3$ with a PolAAr 3005 polarimeter. $^1H$ NMR and $^{13}C$ NMR spectra were recorded by using a Bruker AV-300 [300.13 ($^1H$), 75.48 MHz ($^{13}C$)], AV-400 [400.13 ($^1H$), 100.78 MHz ($^{13}C$)], DRX-500 [500.13 ($^1H$), 125.77 MHz ($^{13}C$)] or AV-600 [600.30 ($^1H$), 150.95 MHz ($^{13}C$)] spectrometer. Chemical shifts were calibrated to tetramethylsilane ($Me_4Si$) as an internal reference. Chemical shifts are given in ppm and coupling constants (*J*) are given in Hz; the following abbreviations are used to indicate the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. In the description of the $^1H$ NMR and $^{13}C$ NMR spectra of compounds **3**, **5 a–i**, **7–9**, **11 a**/**11 b**, **12–15**, and **17 a**/**17 b**, the tricyclic diterpenoid core atom-numbering scheme given in structure **1** was used. NMR assignments were supported by using COSY, HMBC, and HMQC spectra if appropriate. IR absorption spectra were obtained for neat thin films by using a Bruker Vector-22 spectrometer. Mass spectra were recorded with a ThermoScientific DFS high-resolution mass spectrometer (evaporator temperature 200–250 °C, EI ionization at 70 V). X-ray crystallography study of the crystals of **2**, **3**, and **11 a** was performed with a Bruker Kappa Apex II CCD diffractometer by using φ,ω scans of narrow (0.5°) frames with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. A Bruker P4 diffractometer (monochromated MoKα radiation, $\theta/2\theta$ scans, $2\theta < 50°$) was used to measure the unit-cell dimensions and to collect data for compound **8**.

The reaction progress and the purity of the obtained compounds were monitored by TLC on Silufol UV−254 plates (Kavalier, Czech Republic, $CHCl_3$/EtOH, 100:1; detection under UV light or by spraying the plates with a 10% water solution of $H_2SO_4$ followed by heating at 100 °C). Preparative column chromatography was performed with 60H silica gel (0.063–0.200 mm, Merck KGaA, Darmstadt, Germany).

The starting materials 4-iodobenzonitrile (**4 a**), 1-iodo-3-(trifluoromethyl)benzene (**4 b**), iodobenzene (**4 c**), 1-iodo-2-methoxybenzene (**4 d**), 1-iodo-3-methoxybenzene (**4 e**), 1-iodo-4-methoxybenzene (**4 f**), methyl 2-acetamido-5-bromobenzoate (**4 g**), 2-hydroxy-5-iodo-3-methoxybenzaldehyde (**4 h**), 2-iodopyrazine (**4 i**), *tert*-butyl (2-iodophenyl)carbamate (**6**), 2-iodophenol (**10**), 2-iodobenzoic acid (**16**), paraformaldehyde (97%), CuI, $iPr_2NH$, $Cs_2CO_3$, *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), and $Pd(PPh_3)_4$ were purchased from Aldrich or Alfa Aesar. Isopimaric acid (**1**) was

isolated from *Pinus sibirica* R. Mayr sap by the reported method.[10] Solvents (1,4-dioxane, acetonitrile, DMF, and $CH_2Cl_2$) were purified by standard methods and were distilled in a stream of argon just before use. $CHCl_3$, ether, petroleum ether (refers to a light petroleum fraction, b.p. 60–75 °C) were used after distillation.

### Synthesis and Characterization of Coupling–Isomerization Products

(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-*N*-(Buta-2,3-dien-1-yl)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**3**): A mixture of paraformaldehyde (70 mg, 2.32 mmol) and CuI (30 mg, 0.15 mmol) in 1,4-dioxane (5 mL) was stirred at RT for 30 min. Then, $iPr_2NH$ (0.46 mL, 2.1 mmol) and compound **2** (500 mg, 1.51 mmol) were added, and mixture was stirred at 100 °C (external temperature) for 10 h. Then, the solvent was evaporated in vacuo, and the residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether). Crystallization of the third fraction from $CHCl_3$ gave compound **3** (0.35 g, 65%) as colorless prisms: $R_f$ = 0.36 ($CHCl_3$/EtOH, 10:1); m.p. 94–97 °C ($CHCl_3$); $[\alpha]_D^{25} = +10.64$ ($c$ = 0.47 in $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.81 (s, 3H, $C^{17}H_3$), 0.86 (s, 3H,$C^{20}H_3$), 1.09–1.14 (m, 1H, H-1), 1.23 (s, 3H, $C^{19}H_3$), 1.28–1.34 (m, 2H, H-11,12), 1.42–154 (m, 5H, H-12, 11, 2, 3, 2), 1.53–1.62 (m, 1H, H-6), 1.68–1.75 (m, 2H, H-6, 9), 1.79–1.97 (m, 5H, H-1, 14, 14, 3, 5), 3.80 (m, 2H, $NCH_2$), 4.80 (m, 3H, H-16, $C{=}CH_2$), 4.87 (dd, $J$ = 17.2, 1.1 Hz, 1H, H-16), 5.20 (q, $J$ = 6.5 Hz, 1H, $CH{=}C{=}CH_2$), 5.23 (d, $J$ = 5.8 Hz, 1H, H-7), 5.78 (dd, $J$ = 17.2, 10.7 Hz, 1H, H-15), 5.92 ppm (t, $J$ = 5.7 Hz, 1H, NH); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 15.2 (C-20), 17.2 (C-19), 18.0 (C-2), 19.8 (C-11), 21.3 (C-17), 24.7 (C-6), 34.9 (C-10), 35.9 (C-12), 36.6 (C-13), 37.1 (C-3), 37.2 (C-1), 38.6 (C-4), 45.5 (C-5), 45.9 (C-14), 46.2 ($CH_2$), 51.9 (C-9), 77.7 ($CH{=}C{=}CH_2$), 88.3 ($CH{=}C{=}CH_2$), 109.1 (C-16), 120.8 (C-7), 135.4 (C-8), 150.2 (C-15), 178.2 (C-18), 207.6 ppm ($CH{=}C{=}CH_2$); IR: $\tilde{\nu}$ = 3355, 2923, 2867, 1957, 1635, 1521, 1473, 1459, 1444, 1427, 1384, 1361, 1311, 1265, 1218, 1197, 1155, 1135, 998, 970, 910, 844, 850, 755, 651 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{24}H_{35}NO$ $[M+H]^+$: 353.2713; found: 353.2710.

### *General Procedure for the Synthesis of Terpenoid Oxazolines 5 a–i*

Compound **4** (1.71 mmol), $Cs_2CO_3$ (or $K_2CO_3$) (2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a solution of compound **3** (500 mg, 1.41 mmol) in DMF (2 mL) [$CH_3CN$ or DMF/$CH_3CN$ (1:5, 2 mL)] at RT under an argon atmosphere. The mixture was stirred at 80 °C for 4 h (TLC) and was then cooled and diluted with ethyl acetate (10 mL). The separated organic layer was washed with water (3×5 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ether, 4:1 to 1:1) to yield a mixture of **5 a** and **5′a** (560 mg, 87%). A second chromatography run of the fraction gave compounds **5 a** and **5′a**.

4-(1-{(*S*)-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a–dodecahydrophenanthren-1-yl]-4,5-dihydrooxazol-5-yl}vinyl)benzonitrile (**5 a**): Yellow oil; $R_f$ = 0.35 ($CHCl_3$/EtOH, 10:1); $[\alpha]_D^{25} = +34.4$ ($c$ = 0.40 in $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.84 (s, 3H, $C^{20}H_3$), 0.90 (s, 3H, $C^{17}H_3$), 1.09 (dt, 1H, $J$ = 12.6, 5.2, H-1), 1.31 (s, 3H, $C^{19}H_3$), 1.24–1.36 (m, 2H, H-11, 12), 1.44–1.48 (m, 1H, H-12), 1.50–1.66 (m, 5H, H-11, 2, 3, 2, 6), 1.69–1.75 (m, 2H, H-6, 9), 1.79–1.96 (m, 5H, H-1, 14, 14, 3, 5), 3.53 (dd, $J$ = 14.0, 7.5 Hz, 1H, H-4′), 4.04 (dd, $J$ = 14.0, 10.7 Hz, 1H, H-4′), 4.84 (dd, $J$ = 10.7, 1.6 Hz, 1H, H-16), 4.90 (dd, $J$ = 17.7, 1.6 Hz, 1H, H-16), 5.26–5.32 (m, 2H, H-7, 5′), 5.44 (s, 1H, $=CH_2$), 5.46 (s, 1H, $=CH_2$), 5.78 (dd, $J$ = 17.7, 10.7 Hz, 1H, H-15), 7.39 (d, $J$ = 8.2 Hz, 2H, H-2″, 6″), 7.60 ppm (d, $J$ = 8.2 Hz, 2H, H-3″, 5″); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 15.32 (C-20), 17.80 (C-2), 18.30 (C-19), 19.86 (C-11), 21.31 (C-17), 24.64 (C-6), 34.98 (C-10), 35.91 (C-12), 36.66 (C-13), 36.92 (C-3), 38.73 (C-1), 40.65 (C-4), 44.99 (C-5), 45.97 (C-14), 51.85 (C-9), 60.14 (C-4′), 79.15 (C-5′), 109.11 (C-16), 111.58 (C-4″), 115.23 (C-7′), 118.40 (CN), 120.96 (C-7), 127.17 (C-2″,6″), 132.17 (C-3″,5″), 135.52 (C-8), 142.50 (C-6′), 145.98 (C-1″), 150.13 (C-15), 173.97 ppm (C-2′); IR: $\tilde{\nu}$ = 2927, 2867,2846, 2825, 2229, 1650, 1606, 1502, 1457, 1444, 1384, 1234, 1182, 1139, 1126, 1103, 989, 912, 844, 755, 696 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{31}H_{38}N_2O$ $[M+H]^+$: 454.2979; found: 454.2971.

4-(1-{(*R*)-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazol-5-yl}vinyl)benzonitrile (**5′a**): Yellow oil; $R_f$ = 0.34 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 3H, $C^{20}H_3$), 0.90 (s, 3H, $C^{17}H_3$), 1.10 (dt, 1H, $J$ = 12.6, 4.8 Hz, H-1), 1.18–1.29 (m, 1H, H-12), 1.30 (s, 3H, $C^{19}H_3$), 1.30–1.38 (m, 1H, H-11), 1.45–1.50 (m, 1H, H-12), 1.52–1.68 (m, 5H, H-11, 2, 3, 2, 6), 1.70–1.74 (m, 2H, H-6, 9), 1.76–1.99 (m, 5H, H-1, 14, 14, 3, 5), 3.55 (dd, $J$ = 14.2, 8.2 Hz, 1H, H-4′), 4.04 (dd, $J$ = 14.2, 10.3 Hz, 1H, H-4′), 4.86 (dd, $J$ = 10.7, 1.3 Hz, 1H, H-16), 4.91 (dd, $J$ = 17.6, 1.3 Hz, 1H, H-16), 5.28–5.34 (m, 2H, H-7, 5′), 5.38 (s, 1H, $=CH_2$), 5.43 (s, 1H, $=CH_2$), 5.79 (dd, $J$ = 17.6, 10.7 Hz, 1H, H-15), 7.38 (d, $J$ = 8.4 Hz, 2H, H-2″, 6″), 7.60 ppm (d, $J$ = 8.4 Hz, 2H, H-3″, 5″); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 15.41 (C-20), 17.79 (C-2), 18.32 (C-19), 19.94 (C-11), 21.35 (C-17), 24.69 (C-6), 35.04 (C-10), 35.95 (C-12), 36.73 (C-13), 37.03 (C-3), 38.77 (C-1), 40.64 (C-4), 45.22 (C-5), 46.02 (C-14), 52.00 (C-9), 59.98 (C-4′), 79.33(C-5′), 109.11 (C-16), 111.55 (C-4″), 115.58 (C-7′), 118.47 (CN), 120.79 (C-7), 127.46 (C-2″,6″), 132.16 (C-3″,5″), 135.4 (C-8), 142.62 (C-6′), 145.99 (C-1″), 150.13 (C-15), 174.15 ppm (C-2′); IR: $\tilde{\nu}$ = 2927, 2869, 2850, 2825, 2230, 1650, 1606, 1506, 1457, 1446, 1367, 1263, 1234, 1218, 1182, 1139, 1126, 1105, 1056, 1033, 1016, 991, 914, 844, 752, 698 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{31}H_{38}N_2O$ $[M+H]^+$: 454.2979; found: 454.2980.

5-(*S*,*R*)-{1-[3-(Trifluoromethyl)phenyl]vinyl}-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazole (**5 b**): Yellow oil (420 mg, 60%); $R_f$ = 0.36 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 6H, 2$C^{20}H_3$), 0.91 (s, 6H, 2$C^{17}H_3$), 1.08–1.13 (m, 2H, 2H-1), 1.31 (s, 3H, $C^{19}H_3$), 1.32 (s, 3H, $C^{19}H_3$), 1.31–1.39 (m, 4H, 2H-11, 12), 1.44–1.49 (m, 2H, 2H-12), 1.53–1.68 (m, 10H, 2H-11, 2, 3, 2, 6), 1.68–1.78 (m, 4H, 2H-6, 9), 1.82–2.08 (m, 10H, 2H-1, 14, 14, 3, 5), 3.53 (dd, $J$ = 14.0, 7.5 Hz, 1H, H-4′), 3.55 (dd, $J$ = 14.0, 10.6 Hz, 1H, H-4′), 4.02 (dd, $J$ = 14.0, 10.6 Hz, 1H, H-4′), 4.04 (dd, $J$ = 14.0, 10.5 Hz, 1H, H-4′), 4.85 (dd, $J$ = 10.9, 1.6 Hz, 1H, H-16), 4.87 (dd, $J$ = 10.9, 1.6 Hz, 1H, H-16), 4.91 (dd, $J$ = 17.7, 1.6 Hz, 1H, H-16), 4.92 (dd, $J$ = 17.7, 1.6 Hz, 1H, H-16), 5.28–5.38 (m, 4H, 2-H-7, 5′), 5.40 (s, 2H, $=CH_2$), 5.42 (s, 1H, $=CH_2$), 5.41 (s, 2H, $=CH_2$), 5.44 (s, 1H, $=CH_2$), 5.78 (dd, $J$ = 17.7, 10.7 Hz, 1H, H-15), 5.80 (dd, $J$ = 17.7, 10.7 Hz, 1H, H-15), 7.18–7.28 (m, 2H, 2H-6″), 7.38–7.52 (m, 4H, 2-H-4″, 5″), 7.53–7.57 ppm (m, 2H, 2H-2″); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 15.01, 15.08 (2C-20), 17.51 (2C-2), 17.95, 17.99 (2C-19), 19.59 (2C-11), 21.03 (2C-17), 24.35 (2C-6), 34.74 (2C-10), 35.66 (2C-12), 36.37 (2C-13), 36.61, 36.85 (2C-3), 38.47 (2C-1), 40.28 (2C-4), 44.69, 45.02 (2C-5), 45.70 (2C-14), 51.58, 51.63 (2C-9), 59.80, 59.92 (2C-4′), 79.05, 79.39 (2C-5′), 109.11 (2C-16), 113.82, 114.16 (2C-7′), 120.55, 120.75 (2C-7), 123.19, 123.24 (2C-2″), 124.24, 124.30 (2C-4″), 127.64 (2C-5″), 128.53, 128.56 (2-$CF_3$), 129.64 (2C-6″), 134.09, 134.34 (2C-3″), 135.22 (2C-8), 138.51, 138.56 (2C-6′), 145.95 (2C-1″), 149.99 (2C-15), 173.61, 173.82 ppm (2C-2′); IR: $\tilde{\nu}$ = 2927, 2869,

1652, 1606, 1500, 1438, 1384, 1330, 1297, 1257, 1236, 1166, 1128, 1097, 1074, 1056, 991, 910, 806, 754, 696 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{31}H_{38}F_3NO$ $[M+H]^+$: 497.2900; found: 497.2893.

5-(1-Phenylvinyl)-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazole (**5c**): Yellow oil (300 mg, 50%); $R_f$ = 0.4 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 6H, 2C$^{20}$H$_3$), 0.92 (s, 6H, 2C$^{17}$H$_3$), 1.03–1.15 (m, 2H, 2H-1), 1.33 (s, 3H, C$^{19}$H$_3$), 1.34 (s, 3H, C$^{19}$H$_3$), 1.27–1.40 (m, 4H, 2H-11, 12), 1.42–1.49 (m, 2H, 2H-12), 1.51–1.78 (m, 12H, 2H-11, 2, 3, 2, 6, 9), 1.80–1.84 (m, 4H, 2H-14, 5), 1.86–2.01 (m, 8H, 2H-14, 6, 3, 1), 3.52 (dd, *J* = 14.0, 7.2 Hz, 1H, H-4′), 3.55 (dd, *J* = 14.0, 8.2 Hz, 1H, H-4′), 3.97–4.08 (m, 2H-4′), 4.85 (dd, *J* = 10.9, 1.6 Hz, 1H, H-16), 4.87 (dd, *J* = 10.9, 1.6 Hz, 1H, H-16), 4.91 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 4.92 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 5.28–5.40 (m, 4H, 2H-7, 5′), 5.30 (brs, 1H, =C*H*$_2$), 5.37 (brs, 2H, =C*H*$_2$), 5.37 (s, 1H, =C*H*$_2$), 5.72–5.83 (m, 2H, 2H-15), 7.25–7.36 ppm (m, 10H, 2Ph-H); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 15.32, 15.40 (2C-20), 17.81 (2C-2), 18.36, 18.29 (2C-19), 19.91 (2C-11), 21.30 (2C-17), 24.65 (2C-6), 34.98 (2C-10), 35.92 (2C-12), 36.68 (2C-13), 36.90, 37.02 (2C-3), 38.74 (2C-1), 40.57 (2C-4), 44.93, 45.16 (2C-5), 45.97 (2C-14), 51.81, 51.90 (2C-9), 60.25, 60.32 (2C-4′), 79.50, 79.61 (2C-5′), 109.08 (2C-16), 111.79, 112.11 (2C-7′), 120.91, 121.06 (2C-7), 126.36, 126.36 (4C-2″,6″), 127.84 (2C-4″), 128.32 (4C-3″,5″), 135.43 (2C-8), 137.81, 137.91 (2C-6′), 147.18 (2C-1″), 150.16 (2C-15), 173.97, 174.12 ppm (2C-2′); IR: $\tilde{\nu}$ = 2927, 2869, 2850, 1650, 1500, 1384, 1234, 1139, 1105, 1031, 991, 910, 859, 755, 701 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{30}H_{39}NO$ $[M+H]^+$: 429.3026; found: 429.3028.

5-(*S*,*R*)-[1-(2-Methoxyphenyl)vinyl]-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazole (**5d**): Yellow oil (470 mg, 72%); $R_f$ = 0.22 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 6H, 2-C$^{20}$H$_3$), 0.91 (s, 6H, 2-C$^{17}$H$_3$), 1.07–1.16 (m, 2H, 2H-1), 1.19–1.28 (m, 2H, 2H-11), 1.30 (s, 3H, C$^{19}$H$_3$), 1.32 (s, 3H, C$^{19}$H$_3$), 1.31–1.39 (m, 2H, 2H-3), 1.41–1.49 (m, 2H, 2H-12), 1.50–1.68 (m, 10H, 2H-11, 6, 2, 12, 2), 1.68–1.78 (m, 4H, 2H-6, 9),1.79–2.03 (m, 10H, 2H-1, 14, 14, 3, 5), 3.55 (dd, *J* = 14.0, 7.2 Hz, 1H, H-4′), 3.59 (1H, dd, *J* = 14.0, 8.6 Hz, H-4′), 3.79 (s, 6H, 2-OCH$_3$), 3.84 (dd, *J* = 14.0, 10.6 Hz, 1H, H-4′), 3.86 (dd, *J* = 14.0, 10.5 Hz, 2H, H-4′), 4.85 (dd, *J* = 10.9, 1.6 Hz, 2H, 2H-16), 4.91 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 4.92 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 5.31 (s, 2H, =C*H*$_2$), 5.30 (s, 1H, =C*H*$_2$), 5.37 (s, 1H, =C*H*$_2$), 5.40–5.46 (m, 4H, 2-H-7, 5′), 5.76 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 5.81 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 6.84 (d, *J* = 8.0 Hz, 2H, 2H-3″), 6.91 (dd, *J* = 8.6, 8.2 Hz, 2H, 2H-5″), 7.13 (dd, *J* = 8.6, 8.0 Hz, 2H, 2H-4″), 7.27 ppm (d, *J* = 8.2 Hz, 2H, 2H-6″); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 15.36 (2C-20), 17.89 (2C-2), 18.30, 18.35 (2C-19), 19.96 (2C-11), 21.37 (2C-17), 24.68 (2C-6), 35.02 (2C-10), 36.00 (2C-12), 36.45 (2C-13), 36.90, 37.06 (2C-3), 38.81 (2C-1), 40.57 (2C-4), 44.89, 45.11 (2C-5), 46.04 (2C-14), 51.96 (2C-9), 55.22 (OCH$_3$), 59.75, 59.97 (2C-4′), 79.23, 79.41 (2C-5′), 109.09 (2C-16), 110.44 (2C-3″), 113.10, 113.50 (2C-7′), 120.58 (2C-5″), 121.20 (2C-7), 128.11 (2C-6′), 129.16 (2C-4″), 130.67 (2C-6″), 135.31 (2C-8), 147.45, 147.73 (2C-1″), 150.30 (2C-15), 156.36 (2C-2″), 174.11 ppm (2C-2′); IR: $\tilde{\nu}$ = 2935, 2869, 2846, 1648, 1598, 1500, 1461, 1436, 1384, 1292, 1247, 1240, 1182, 1139, 1126, 1095, 1047, 1027, 985, 912, 870, 754 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{31}H_{41}NO_2$ $[M+H]^+$: 459.3132; found: 459.3131.

5-(*S*,*R*)-[1-(3-Methoxyphenyl)vinyl]-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazole (**5e**): Yellow oil (490 mg, 77%); $R_f$ = 0.22 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 6H, 2-C$^{20}$H$_3$), 0.92 (s, 6H, 2-C$^{17}$H$_3$), 1.07–1.15 (m, 2H, 2H-1), 1.19–1.29 (m, 2H, 2H-11), 1.32 (s, 3H, C$^{19}$H$_3$), 1.34 (s, 3H, C$^{19}$H$_3$), 1.31–1.39 (m, 2H, 2H-12), 1.44–1.49 (m, 2H, 2H-12), 1.52–1.68 (m, 10H, 2H-11, 2, 3, 2, 6), 1.70–1.78 (m, 4H, 2H-6, 9), 1.82–2.01 (m, 10H, 2H-1, 14, 14, 3, 5), 3.52 (dd, *J* = 14.0, 7.0 Hz, 1H, H-4′), 3.55 (dd, *J* = 14.0, 8.2 Hz, 1H, H-4′), 3.78 (s, 6H, 2-OCH$_3$), 4.00 (dd, *J* = 14.0, 10.2 Hz, 1H, H-4′), 4.03 (dd, *J* = 14.0, 10.6 Hz, 1H, H-4′), 4.85 (dd, *J* = 10.9, 1.6 Hz, 1H, H-16), 4.87 (dd, *J* = 10.9, 1.6 Hz, 1H, H-16), 4.91 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 4.92 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 5.28–5.38 (m, 4H, 2-H-7, 5′), 5.32 (s, 2H, =C*H*$_2$), 5.34 (s, 2H, =C*H*$_2$), 5.36 (s, 1H, =C*H*$_2$), 5.76 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 5.81 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 6.78–6.93 (m, 6H, 2H-2″, 4″, 6″), 7.19–7.22 ppm (m, 2H, 2H-5″); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 15.30, 15.37 (2C-20), 17.81 (2C-2), 18.26, 18.31 (2C-19), 19.90 (2C-11), 21.29 (2C-17), 24.66 (2C-6), 34.98 (2C-10), 35.93 (2C-12), 36.66 (2C-13), 36.91, 37.08 (2C-3), 38.74 (2C-1), 40.55, 40.60 (2C-4), 44.93, 45.21 (2C-5), 45.95 (2C-14), 51.81, 51.88 (2C-9), 55.02 (OCH$_3$), 60.41 (2C-4′), 79.27, 79.40 (2C-5′), 109.04 (2C-16), 111.74, 111.86 (2C-7′), 112.42, 112.49(2C-4″), 113.01 (2C-2″), 118.79 (2C-6″), 120.88, 121.07 (2C-7), 129.31 (2C-5″), 135.41 (2C-8), 139.42 (2C-6′), 147.19 (2C-1″), 150.17 (2C-15), 159.43 (2C-3″), 173.88, 174.03 ppm (2C-2′); IR: $\tilde{\nu}$ = 3301, 2935, 2867, 1652, 1598, 1500, 1488, 1459, 1384, 1288, 1226, 1182, 1139, 1126, 1105, 1309, 1317, 1365, 1074, 1051,1016, 989, 910, 881, 860, 833, 782, 755, 728, 696, 665 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{31}H_{41}NO_2$ $[M+H]^+$: 459.3132; found: 459.3140.

5-(*S*,*R*)-[1-(4-Methoxyphenyl)vinyl]-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazole (**5f**): Yellow oil (350 mg, 54%); $R_f$ = 0.22 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.85 (s, 6H, 2-C$^{20}$H$_3$), 0.92 (s, 6H, 2-C$^{17}$H$_3$), 1.08–1.15 (m, 2H, 2H-1), 1.19–1.29 (m, 2H, 2H-11), 1.32 (s, 6H, 2-C$^{19}$H$_3$), 1.34 (s, 3H, C$^{19}$H$_3$), 1.31–1.39 (m, 2H, 2H-12), 1.42–1.49 (m, 2H, 2H-12), 1.50–1.68 (m, 10H, 2H-11, 2, 3, 2, 6), 1.70–1.78 (m, 4H, 2H-6, 9), 1.83–2.01 (m, 10H, 2H-1, 14, 14, 3, 5), 3.50 (dd, *J* = 14.0, 7.6 Hz, 1H, H-4′), 3.54 (dd, *J* = 14.0, 8.4 Hz, 1H, H-4′), 3.79 (s, 6H, 2-OCH$_3$), 4.01 (dd, *J* = 14.0, 10.2 Hz, 1H, H-4′), 4.03 (dd, *J* = 14.0, 10.5 Hz, 1H, H-4′), 4.85 (dd, *J* = 10.9, 1.6 Hz, 2H, 2H-16), 4.91 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 4.92 (dd, *J* = 17.7, 1.6 Hz, 1H, H-16), 5.21 (s, 1H, =C*H*$_2$), 5.29 (s, 1H, =C*H*$_2$), 5.30 (s, 2H, =C*H*$_2$), 5.28–5.36 (m, 4H, 2-H-7, 5′), 5.77 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 5.81 (dd, *J* = 17.7, 10.7 Hz, 1H, H-15), 6.83 (d, *J* = 8.6 Hz, 2H, H-3″, 5″), 6.85 (d, *J* = 8.8 Hz, 2H, H-3″, 5″), 6.83 (d, *J* = 8.6 Hz, 2H, H-2″, 6″), 6.85 ppm (d, *J* = 8.8 Hz, 2H,H-2″, 6″); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 15.33, 15.37 (2C-20), 17.87 (2C-2), 18.34 (2C-19), 19.88 (2C-11), 21.31 (2C-17), 24.64 (2C-6), 34.99 (2C-10), 35.94 (2C-12), 36.71 (2C-13), 36.93, 37.06 (2C-3), 38.77 (2C-1), 40.59, 40.64 (2C-4), 44.96, 45.23 (2C-5), 45.99 (2C-14), 51.84, 51.92 (2C-9), 55.11 (OCH$_3$), 60.40, 60.44 (2C-4′), 79.62, 79.74 (2C-5′), 109.07 (2C-16), 110.28, 110.64 (2C-7′), 113.74, 112.49 (4C-3″,5″), 120.91, 121.10 (2C-7), 127.49 (4C-2″,6″), 130.28 (2C-8), 135.43, 135.48 (2C-6′), 146.54 (2C-1″), 150.21 (2C-15), 159.29 (2C-4″), 173.99, 174.13 ppm (2C-2′); IR: $\tilde{\nu}$ = 2995, 2950, 2867, 2848, 1652, 1608, 1573, 1511, 1459, 1432, 1384, 1365, 1294, 1268, 1249, 1180, 1139, 1126, 1103, 1076, 1054, 1033, 989, 910, 860, 833, 808, 755, 698 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{31}H_{41}NO_2$ $[M+H]^+$: 459.3132; found: 459.3130.

5-(*S*,*R*)-Methyl 2-acetamido-5-(1-{2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthren-1-yl]-4,5-dihydrooxazol-5-yl}vinyl)benzoate (**5g**): Yellowish solid (480 mg, 61%); $R_f$ = 0.13 ($CHCl_3$/EtOH, 10:1); m.p. 72–75 °C (petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.83 (s, 6H, 2-C$^{20}$H$_3$), 0.90 (s, 6H, 2-C$^{17}$H$_3$), 1.07–1.15 (m, 2H, 2H-1), 1.19–1.29 (m, 2H, 2H-11), 1.32 (s, 3H, C$^{19}$H$_3$), 1.34 (s, 3H, C$^{19}$H$_3$), 1.30–1.37 (m, 2H, 2H-12), 1.42–1.51 (m, 2H, 2H-12), 1.53–1.68 (m, 10H, 2H-11, 2, 3, 2, 6),

1.70–1.78 (m, 4H, 2H-6, 9), 1.81–1.98 (m, 10H, 2H-1, 14, 14, 3, 5), 2.21 (s, 6H, 2-$CH_3$), 3.50 (dd, $J$=14.2, 7.4, 1H, H-4′), 3.54 (dd, $J$=14.0, 8.2 Hz, 1H, H-4′), 3.90 (s, 6H, 2-$OCH_3$), 4.01 (dd, $J$=14.2, 10.7 Hz, 1H, H-4′), 4.03 (dd, $J$=14.0, 10.4 Hz, 1H, H-4′), 4.88 (dd, $J$=10.8, 1.6 Hz, 2H, 2H-16), 4.90 (dd, $J$=17.7, 1.6 Hz, 1H, H-16), 4.91 (dd, $J$=17.7, 1.6 Hz, 1H, H-16), 5.29 (s, 1H, =$CH_2$), 5.31 (s, 1H, =$CH_2$), 5.35 (s, 1H, =$CH_2$), 5.37 (s, 1H, =$CH_2$), 5.28–5.38 (m, 4H, 2H-7, 5′), 5.75 (dd, $J$=17.7, 10.7 Hz, 1H, H-15), 5.77 (dd, $J$=17.7, 10.7 Hz, 1H, H-15), 7.46 (d, $J$=8.6 Hz, 1H, H-5″), 7.49 (d, $J$=8.8 Hz, 1H, H-5″), 7.95 (d, $J$=2.0 Hz, 2H, 2H-2″), 8.65 (dd, $J$=8.8, 2.0 Hz, 2H, 2H-6″), 11.01 ppm (2H, s, 2NH); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=15.34, 15.37 (2C-20), 17.77 (2C-2), 18.19, 18.27 (2C-19), 19.82, 19.88 (2C-11), 21.26 (2C-17), 24.59, 24.65 (2C-6), 25.31 ($CH_3$), 34.95 (2C-10), 35.87 (2C-12), 36.63 (2C-13), 36.80, 37.08 (2C-3), 38.70 (2C-1), 40.57, 40.63 (2C-4), 44.93, 45.27 (2C-5), 45.88, 45.93 (2C-14), 51.79, 51.84 (2C-9), 52.27 ($OCH_3$), 59.92, 60.10 (2C-4′), 79.12, 79.64 (2C-5′), 109.05 (2C-16), 112.03, 112.71 (2C-7′), 114.52, 114.58 (2C-3″), 120.28 (2C-5″), 120.73, 120.98 (2C-7), 128.56 (2C-2″), 131.87 (2C-1″), 132.48, 132.66 (2C-6″), 135.43, 135.48 (2C-8), 141.04 (2C-4″), 145.63, 145.75 (2C-6′), 150.21 (2C-15), 168.27 (C=O), 168.91 (C=O), 174.10, 174.28 ppm (2C-2′); IR: $\tilde{\nu}$=3413, 3317, 2950, 2869, 2827, 1691, 1652, 1599, 1517, 1438, 1367, 1297, 1384, 1409, 1236, 1187, 1159, 1124, 1087, 1054, 1033, 991, 910, 846, 792, 754, 702 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{34}H_{44}N_2O_4$ $[M+H]^+$: 544.3296; found: 544.3302.

2-Hydroxy-3-methoxy-5-(*S*,*R*)-(1-{2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydro-phenanthren-1-yl]-4,5-dihydrooxazol-5-yl}vinyl)benzaldehyde (**5h**): Yellow oil (430 mg, 61%); $R_f$=0.10 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=0.82 (s, 6H, 2-C$^{20}$$H_3$), 0.89 (s, 6H, 2-C$^{17}$$H_3$), 1.06–1.13 (m, 2H, 2H-1), 1.19–1.29 (m, 2H, 2H-11), 1.30 (s, 3H, C$^{19}$$H_3$), 1.31 (s, 3H, C$^{19}$$H_3$), 1.30–1.37 (m, 2H, 2H-12), 1.42–1.49 (m, 2H, 2H-12), 1.51–1.64 (m, 10H, 2H-11, 2, 3, 2, 6), 1.68–1.75 (m, 4H, 2H-6, 9), 1.82–1.94 (m, 10H, 2H-1, 14, 14, 3, 5), 3.54 (dd, $J$=13.8, 7.4, 1H, H-4′), 3.57 (dd, $J$=14.0, 8.2, 1H, H-4′), 3.89 (s, 6H, 2-$OCH_3$), 4.01 (dd, $J$=14.0, 10.8, 1H, H-4′), 4.03 (dd, $J$=13.8, 10.6, 1H, H-4′), 4.82 (d, $J$=10.7 Hz, 2H, 2H-16), 4.88 (d, $J$=17.6 Hz, 2H, 2H-16), 5.25 (s, 1H, =$CH_2$), 5.31 (s, 2H, =$CH_2$), 5.33 (s, 1H, =$CH_2$), 5.25–5.35 (m, 4H, 2H-7, 5′), 5.73 (dd, $J$=17.7, 10.6 Hz, 1H, H-15), 5.78 (dd, $J$=17.7, 10.6 Hz, 1H, H-15), 7.06 (brs, 2H, 2H-2″), 7.23 (brs, 2H, 2H-6″), 9.86 (brs, 2H, 2C*H*O), 11.06 ppm (brs, 2H, 2-OH); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$=15.31 (2C-20), 17.79 (2C-2), 18.33 (2C-19), 19.85 (2C-11), 21.29 (2C-17), 24.64, 24.68 (2C-6), 34.97 (2C-10), 35.88 (2C-12), 36.64 (2C-13), 36.96, 37.11 (2C-3), 38.72 (2C-1), 40.61, 40.64 (2C-4), 45.03, 45.27 (2C-5), 45.95 (2C-14), 51.84 (2C-9), 56.19 ($OCH_3$), 59.99, 60.12 (2C-4′), 79.45, 79.79 (2C-5′), 109.10 (2C-16), 112.62, 112.86 (2C-7′), 116.36 (2C-6″), 120.11 (2C-1″), 120.81, 120.95 (2C-7), 122.10 (2C-2″), 129.74 (2C-3″), 135.51, 135.60 (2C-8), 145.73, 145.82 (2C-6′), 148.19 (2C-4″), 150.10 (2C-15), 151.42 (2C-5″), 174.10, 174.12(2C-2′), 196.22 ppm (2-*C*HO); IR: $\tilde{\nu}$=3330, 3079, 2925, 2867, 2850, 2820, 1656, 1602, 1496, 1463, 1427, 1413, 1386, 1344, 1268, 1218, 1139, 1184, 1097, 1078, 1056, 1031, 1018, 991, 966, 910, 871, 842, 802, 754, 710 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{32}H_{41}NO_4$ $[M+H]^+$: 503.3030; found: 503.3026.

5-(*S*,*R*)-[1-(Pyrazin-2-yl)vinyl]-2-[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydro-phenanthren-1-yl]-4,5-dihydrooxazole (**5i**): Yellow oil (550 mg, 91%); $R_f$=0.22 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=0.84 (s, 6H, 2-C$^{20}$$H_3$), 0.91 (s, 6H, 2-C$^{17}$$H_3$), 1.06–1.15 (m, 2H, 2H-1), 1.18–1.24 (m, 2H, 2H-11), 1.27–1.37 (m, 2H, 2H-12),1.33 (s, 3H, C$^{19}$$H_3$), 1.34 (s, 3H, C$^{19}$$H_3$), 1.42–1.49 (m, 2H, 2H-12), 1.51–1.60 (m, 10H, 2H-11, 2, 3, 2, 6), 1.62–1.78 (m, 4H, 2H-6, 9), 1.82–1.99 (m, 10H, 2H-1, 14, 14, 3, 5), 3.52 (dd, $J$=14.0, 7.3 Hz, 1H, H-4′), 3.55 (dd, $J$=14.0, 8.5 Hz, 1H, H-4′), 4.21 (dd, $J$=14.0, 10.8 Hz, 1H, H-4′), 4.23 (dd, $J$=14.0, 10.6 Hz, 1H, H-4′), 4.84 (d, $J$=10.7 Hz, 2H, 2H-16), 4.90 (d, $J$=17.6 Hz, 2H, 2H-16), 5.31 (m, 2H, 2H-7), 5.54 (s, 1H, =$CH_2$), 5.63 (s, 1H, =$CH_2$), 5.52 (d, $J$=7.3 Hz, 1H, H-5′), 5.60 (d, $J$=8.5 Hz, 1H, H-5′), 5.75 (dd, $J$=17.7, 10.6 Hz, 1H, H-15), 5.79 (dd, 1H, $J$=17.7, 10.6 Hz, H-15), 5.88 (s, 1H, =$CH_2$), 8.44 (d, $J$=9.6 Hz, 4H, 2H-3″, 4″), 8.82 ppm (s, 2H, 2H-6″); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$=15.36 (2C-20), 17.81 (2C-2), 18.27 (2C-19), 19.59 (2C-11), 21.26 (2C-17), 24.58, 24.64 (2C-6), 34.95 (2C-10), 35.86 (2C-12), 36.62 (2C-13), 36.93, 37.01 (2C-3), 38.74 (2C-1), 40.57, 40.62 (2C-4), 44.89, 45.26 (2C-5), 45.92 (2C-14), 51.82, 51.90 (2C-9), 61.17, 61.32 (2C-4′), 77.61, 79.79 (2C-5′), 109.03 (2C-16), 114.18, 114.38 (2C-7′), 120.72, 121.03 (2C-7), 131.83 (2C-4″), 135.35, 135.59 (2C-8), 142.02 (2C-6″), 142.82, 143.09 (2C-3″), 144.97 (2C-6′), 150.14 (2C-15), 151.26 (2C-1″), 173.65, 173.83 ppm (2C-2′); IR: $\tilde{\nu}$=3305, 2927, 2868, 1652, 1610, 1580, 1520, 1467, 1411, 1384, 1234, 1182, 1162, 1139, 1120, 1054, 1031, 1014, 989, 914, 860, 755, 715 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{28}H_{37}N_3O$ $[M+H]^+$: 431.2931; found: 431.2933.

### *Reaction of Terpenoid* N-*(2,3-Butadienyl)carboxamide 3 with* N-*Boc-(2-iodophenyl)aniline 6*

Conditions A: Compound **6** (550 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a stirred solution of **3** (500 mg, 1.41 mmol) in DMF (2 mL) at RT under an argon atmosphere. The mixture was heated at 80 °C for 3 h, cooled, diluted with ethyl acetate (10 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ether, 10:1→1:1) to give 3-methyleneindoline **7** (400 mg, 31%) and 3-methyl-1*H*-indole **8** (150 mg, 12%).

Conditions B: Compound **6** (550 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a stirred solution of **3** (500 mg, 1.41 mmol) in MeCN (2 mL) under an argon atmosphere. The mixture was heated at 80 °C for 3 h, cooled, diluted with ethyl acetate (20 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 1:1) to give 3-methyleneindoline **7** (420 mg, 55%) as a yellow oil.

2-(*S*,*R*)-*tert*-Butyl 3-methylene-2-{[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8, 10,10a-dodecahydrophenanthrene-1-carboxamido]methyl}indoline-1-carboxylate (**7**): $R_f$=0.12 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$=0.81 (s, 6H, 2-C$^{20}$$H_3$), 0.82 (s, 6H, 2C$^{17}$$H_3$), 0.81–0.90 (m, 1H, H-1), 0.94–1.05 (m, 1H, H-1), 1.16–1.26 (m, 2H, 2H-11), 1.30 (s, 3H, C$^{19}$$H_3$), 1.31 (s, 3H, C$^{19}$$H_3$), 1.28–1.41 (m, 4H, 2H-12, 3), 1.43–1.55 (m, 8H, 2H-12, 11, 2, 6), 1.57 (s, 9H, $(CH_3)_3$), 1.58 (s, 9H, $(CH_3)_3$), 1.60–1.79 (m, 12H, 2H-12, 2, 5, 3, 6, 9), 1.82–1.90 (m, 6H, 2H-1, 14, 14), 3.25–3.50 (m, 4H, 2-$CH_2$), 4.82–4.91 (m, 2H, 2H-2′), 4.83 (dd, $J$=10.7, 1.2 Hz, 1H, H-16), 4.84 (dd, $J$=10.7, 1.2 Hz, 1H, H-16), 4.89 (dd, $J$=17.6, 1.2 Hz, 1H, H-16), 4.90 (dd, $J$=17.6, 1.2 Hz, 1H, H-16), 5.07 (brs, 1H, NH), 5.08 (brs, 1H, NH), 5.19 (m, 1H, H-7), 5.22 (m, 1H, H-7), 5.55 (brs, 1H, H-3′a), 5.56 (brs, 1H, H-3′a), 5.76 (dd, $J$ 17.6, 10.7 Hz, 1H, H-15), 5.78 (dd, $J$ 17.6, 10.7 Hz, 1H, H-15), 6.95–7.01 (m, 4H, 2H-5′, 6′), 7.23 (m, 2H, 2H-4′), 7.38–7.41 ppm (m, 2H, 2H-7′); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=14.00 (2C-20), 15.11 (2C-11), 17.95 (2C-2), 19.70 (2C-19), 21.28 (2C-17), 24.57 (C-6), 28.25 (6C-2$(CH_3)_3$), 34.90 (2C-10), 35.95 (2C-12), 36.64 (2C-3), 37.08 (2C-1), 38.54 (2C-13), 41.72 (2C-4), 45.23 (2C-5), 46.84 (2C-14), 46.05 (2C-$(CH_2)$), 51.70 (2C-9), 60.18 (2*C*$(CH_3)_3$), 62.98 (2C-2′), 109.00 (2C-16), 109.88,

110.64 (2C-8′), 120.82 (2C-7′), 120.01, 120.22 (2C-3′a), 120.99 (2C-7), 122.73 (2C-5′), 128.14, 128.52 (2C-4′), 129.86 (2C-6′), 135.04 (2C-8), 135.17, 135.26 (2C-7′a), 145.96 (2C-3′), 150.17 (2C-15), 170.92 (2C-OC(=O)), 178.66 ppm (2C-C(=O)NH); IR: $\tilde{\nu}$ = 3463, 3374, 3079, 2971, 2925, 2869, 1710, 1681, 1644, 1604, 1513, 1473, 1384, 1348, 1321, 1294,1251, 1162, 1120, 1045, 1024, 1002, 971, 910, 879, 852, 754, 710, 665 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{35}H_{48}N_2O_3$ $[M+H]^+$: 544.3660; found: 544.3655.

*tert*-Butyl 3-methyl-2-{[(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamido]methyl}-1*H*-indole-1-carboxylate (**8**): Crystallization of the second fraction (conditions A) from EtOH gave compound **8** as colorless plates: $R_f$ = 0.32 ($CHCl_3$/EtOH, 10:1); m.p. 187–189 °C (EtOH); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 0.82 (s, 3H, $C^{20}H_3$), 0.86 (s, 3H, $C^{17}H_3$), 1.12–1.21 (m, 1H, H-1), 1.22 (s, 3H, $C^{19}H_3$), 1.21–1.33 (m, 2H, H-11, 12), 1.38–1.51 (m, 6H, H-12, 11, 2, 2, 3, 6), 1.65–1.72 (m, 3H, H-6, 14, 9), 1.70 (s, 9H, $C(CH_3)_3$), 1.72–1.88 (m, 4H, H-1, 14, 5, 3), 2.36 (s, 3H, $C^{8'}H_3$), 4.67 (d, *J* = 8.2 Hz, 1H, $CH_2$), 4.69 (d, *J* = 8.2 Hz, 1H, $CH_2$), 4.84 (dd, *J* = 10.7, 1.3 Hz, 1H, H-16), 4.91 (dd, *J* = 17.5, 1.3 Hz, 1H, H-16), 5.10–5.14 (m, 1H, H-7), 5.77 (dd, *J* = 17.5, 10.7 Hz, 1H, H-15), 7.01 (t, *J* = 6.2 Hz, 1H, NH), 7.21 (dd, *J* = 7.0, 7.2 Hz, 1H, H-5′), 7.29 (ddd, *J* = 7.2, 6.8, 1.8 Hz, 1H, H-6′), 7.46 (dd, *J* = 7.0, 1.8 Hz, 1H, H-4′), 7.95 ppm (d, 1H, *J* = 7.2 Hz, H-7′); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 8.5 (C-3′a), 15.1 (C-20), 17.1 (C-19), 18.0 (C-2), 19.8 (C-11), 20.3 (C-17), 24.5 (C-6), 28.1 (3C-$(CH_3)_3$), 34.8 ($CH_2$), 34.9 (C-10), 35.8 (C-12), 36.9 (C-13), 36.8 (C-3), 38.6 (C-1), 45.4 (C-5), 45.8 (C-14), 46.1 (C-4), 51.8 (C-9), 84.1 ($C(CH_3)_3$), 109.0 (C-16), 115.4 (C-7′), 117.2 (C-3′), 118.9 (C-4′), 120.9 (C-7), 122.5 (C-5′), 124.2 (C-6′), 130.4 (C-3′a), 132.7 (C-7′a), 135.0 (C-2′), 135.1 (C-8), 150.2 (C-15), 151.1 (C=O), 177.9 ppm (C=O); IR: $\tilde{\nu}$ = 3477, 2973, 2946, 2869, 1714, 1664, 1605, 1498, 1475, 1446, 1382, 1369, 1346, 1324, 1253, 1220, 1157, 1135, 1015, 975, 920, 866, 750, 710 $cm^{-1}$; HRMS (ESI+): *m/z* calcd for $C_{35}H_{48}N_2O_3$ $[M+H]^+$: 544.3660; found: 544.3665.

### *Isomerization of 3-Methyleneindoline 7*

Conditions A: A 36% aq solution of HCl (1.0 mL) was added to a stirred solution of **7** (200 mg, 0.37 mmol) in MeOH (5 mL). After stirring at RT for 1 h, the mixture was diluted with $CHCl_3$ (10 mL), washed with water (3×5 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the residue, which was purified by silica gel column chromatography (petroleum ether/ether, 2:1) to give compound **8** (140 mg, 70%).

Conditions B: An 36% aq solution of HCl (2.0 mL) was added to a stirred solution of **7** (200 mg, 0.37 mmol) in MeOH (5 mL). After stirring at RT for 1 h, the mixture was diluted with $CHCl_3$ (10 mL), washed with $H_2O$ (3×5 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ether) to give compounds **8** (80 mg, 38%) and **9** (20 mg, 10%) as a yellow oil.

*tert*-Butyl 3-methyl-2-{[(1*R*,4a*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,5,6,7,8,9,10,10a-dodecahydrophenanthrene-1-carboxamido]-methyl}-1*H*-indole-1-carboxylate (**9**): $R_f$ = 0.33 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.92 (s, 3H, $C^{20}H_3$), 0.93 (s, $C^{17}H_3$), 1.11–1.19 (m, 1H, H-1), 1.13 (s, 3H, $C^{19}H_3$), 1.19–1.29 (m, 2H, 3H, H−11, 12), 1.38–1.56 (m, 5H, H-12, 6, 11, 2, 3), 1.62–1.71 (m, 2H, H-2, 6), 1.70 (s, 9H, $C(CH_3)_3$), 1.72–1.89 (m, 7H, H-6, 14, 1, 14, 5, 3, 7), 2.36 (s, 3H, $C^{8'}H_3$), 4.67 (d, *J* = 8.2 Hz, 1H, $CH_2$), 4.71 (d, *J* = 8.2 Hz, 1H, $CH_2$), 4.83 (dd, *J* = 10.7, 1.3 Hz, 1H, H-16), 4.89 (dd, *J* = 17.5, 1.3 Hz, 1H, H-16), 5.71 (dd, *J* = 17.5, 10.7 Hz, 1H, H-15), 7.03 (t, *J* = 6.2 Hz, 1H, NH), 7.22 (dd, *J* = 7.0, 7.2 Hz, 1H, H-5′), 7.28 (ddd, *J* = 7.2, 6.8, 1.8 Hz, 1H, H-6′), 7.46 (dd, *J* = 7.0, 1.8 Hz, 1H, H-4′), 7.94 ppm (d, *J* = 7.2 Hz, 1H, H-7′); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 8.5 (C-3′a), 15.1 (C-20), 16.2 (C-19), 18.1 (C-2), 19.5 (C-17), 20.6 (C-11), 20.8 (C-6), 28.1 (3C-$(CH_3)_3$), 31.6 (C-7), 34.7 (C-10), 34.8 ($CH_2$), 35.4 (C-12), 36.6 (C-13), 36.8 (C-3), 38.6 (C-1), 41.8 (C-4), 46.7 (C-5), 47.1 (C-14), 84.0 ($C(CH_3)_3$), 110.7 (C-16), 115.3 (C-7′), 117.1 (C-3′), 118.9 (C-4′), 122.5 (C-5′), 124.2 (C-6′), 124.3 (C-8), 130.4 (C-3′a), 132.9 (C-7′a), 134.9 (C-2′), 136.3 (C-9), 145.9 (C-15), 151.1 (C=O), 177.9 ppm (C=O). HRMS (ESI+): *m/z* calcd for $C_{35}H_{48}N_2O_3$ $[M+H]^+$: 544.3660; found: 544.3667.

### *Reaction of Terpenoid* N-*(2,3-Butadienyl)carboxamide 3 with 2-Iodophenol (10) (Table 2)*

Entry 1: Compound **10** (380 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a stirred solution of **3** (500 mg, 1.41 mmol) in MeCN (2 mL) at RT under an argon atmosphere. The mixture was heated at 80 °C for 3 h, cooled, diluted with ethyl acetate (20 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (petroleum ether/ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11a** (110 mg, 18%), 4-methyl-2*H*-chromene **11b** (110 mg, 18%), 3-methylene-2,3-dihydrobenzofurans **12a**/**12b** (180 mg, 29%), 3-methylbenzofuran **13** (30 mg, 5%), compound **14** (20 mg, 4%), and compound **15** (40 mg, 8%).

Entry 2: Compound **10** (380 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a stirred solution of **3** (500 g, 1.41 mmol) in DMF (2 mL) at RT under an argon atmosphere. The mixture was heated at 80 °C for 3 h, cooled, diluted with ethyl acetate (10 mL), washed with water (3×5 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11a** (80 mg, 12%), 4-methyl-2*H*-chromene **11b** (80 mg, 12%), 3-methylene-2,3-dihydrobenzofurans **12a**/**12b** (210 mg, 30%), and compound **14** (60 mg, 12%).

Entry 3: Compound **10** (380 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), (*R*)-(+)-BINAP (70 mg, 0.10 mmol), and $Pd_2(dba)_3$·$CHCl_3$ (30 mg, 0.035 mmol) were added to a stirred solution of **3** (500 mg, 1.41 mmol) in anhydrous MeCN (2 mL) under a stream of argon, and the mixture was heated at 80 °C for 6 h. At that point, the conversion of the reaction was not complete (as determined by NMR spectroscopy), and the addition of (*R*)-(+)-BINAP (70 mg, 0.10 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (30 mg, 0.035 mmol) was repeated. After 50 h of heating at 80 °C, the mixture was cooled, diluted with ethyl acetate (10 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11a** (160 mg, 24%), 4-methyl-2*H*-chromene **11b** (160 mg, 24%), 3-methylene-2,3-dihydrobenzofurans **12a**/**12b** (30 mg, 5%), and 3-methylbenzofuran **13** (20 mg, 3%).

Entry 4: Compound **10** (380 mg, 1.71 mmol), $K_2CO_3$ (390 mg, 2.81 mmol), (*R*)-(+)-BINAP (130 mg, 0.21 mmol), and $Pd(OAc)_2$ (30 mg, 0.14 mmol) were added to a solution of **3** (500 mg, 1.41 mmol) in DMF/MeCN/$H_2O$ (5:5:1, 2 mL) under a stream of argon, and the mixture was heated at 80 °C for 6 h. The mixture was cooled, diluted with ethyl acetate (10 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum

ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11 a** (80 mg, 12%), 4-methyl-2*H*-chromene **11 b** (80 mg, 12%), and 3-methylene-2,3-dihydrobenzofurans **12 a**/**12 b** (160 mg, 25%).

Entry 5: Compound **11** (380 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (70 mg, 0.07 mmol) were added to a solution of **3** (500 mg, 1.41 mmol) in anhydrous DMF (2 mL), and the mixture was heated at 80 °C for 3 h. Then, the mixture was cooled, diluted with ethyl acetate (10 mL), washed with $H_2O$ (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11 a** (87 mg, 13%), 4-methyl-2*H*-chromene **11 b** (87 mg, 13%), and 3-methylene-2,3-dihydrobenzofurans **12 a**/**12 b** (140 mg, 22%).

Entry 6: Compound **11** (380 mg, 1.71 mmol), $K_2CO_3$ (390 mg, 2.81 mmol), $nBu_4NBr$ (450 mg, 1.41 mmol), and *trans*-bis(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (70mg, 0.07 mmol) were added to a solution of **3** (500 mg, 1.41 mmol) in DMF/$H_2O$ (5:1, 2 mL) under a stream of argon, and the mixture was heated at 80 °C for 3 h. Then, the mixture was cooled, diluted with ethyl acetate (10 mL), washed with $H_2O$ (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11 a** (62 mg, 9%), 4-methyl-2*H*-chromene **11 b** (61 mg, 9%), 4-methylene-2*H*-dihydrochromene **11 c** (52 mg, 8%), and 3-methylene-2,3-dihydrobenzofurans **12 a**/**12 b** (315 mg, 49%).

Entry 7: Compound **11** (380 mg, 1.71 mmol), $K_2CO_3$ (390 mg, 2.81 mmol), $nBu_4NBr$ (450 mg, 1.41 mmol), and *trans*-bis(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (70 mg, 0.07 mmol) were added to a solution of **3** (500 mg, 1.41 mmol) in DMF/MeCN/$H_2O$ (5:5:1, 2 mL) under a stream of argon, and the mixture was heated at 80 °C for 6 h. Then, the mixture was cooled, diluted with ethyl acetate (10 mL), washed with $H_2O$ (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/diethyl ether, 4:1→1:1) to give 4-methyl-2*H*-chromene **11 a** (60 mg, 9%), 4-methyl-2*H*-chromene **11 b** (62 mg, 9%), 4-methylene-2*H*-dihydrochromene **11 c** (190 mg, 28%), and 3-methylene-2,3-dihydrobenzofurans **12 a**/**12 b** (240 mg, 37%).

(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(*R*)-4-methyl-2*H*-chromen-2-yl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**11 a**): Yellowish needles; $R_f$ = 0.31 ($CHCl_3$/EtOH, 10:1); m.p. 168–170 °C (EtOH); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 0.82 (s, 3H, $C^{20}H_3$), 0.85 (s, 3H, $C^{17}H_3$), 1.11 (dt, 1H, *J* = 13.7, 6.8 Hz, H-1), 1.16 (s, 3H, $C^{19}H_3$), 1.26–1.35 (m, 2H, H-11,12), 1.43–1.54 (m, 5H, H-12, 3, 11, 2, 2), 1.55–1.61 (m, 1H, H-6), 1.64–1.70 (m, 2H, H-6, 9), 1.73–1.99 (m, 5H, H-1, 3, 14, 14, 5), 2.10 (s, 3H, $CH_3$), 4.85 (dd, *J* = 10.7, 1.2 Hz, 1H, H-16), 4.90 (dd, *J* = 17.5, 1.2 Hz, 1H, H-16), 5.21–5.26 (m, 1H, H-7), 5.54 (d, *J* = 4.2 Hz, 1H, H-3′), 5.77 (dd, 1H, *J* = 17.5, 10.7 Hz, H-15), 6.31 (br d, *J* = 8.8 Hz, 1H, NH), 6.47 (dd, *J* = 8.8, 4.2 Hz, 1H, H-2′), 6.88 (d, *J* = 8.1 Hz, 1H, H-8′), 6.94 (dd, *J* = 8.0, 7.8 Hz, 1H, H-6′), 7.16 (dd, *J* = 8.1, 8.0 Hz, 1H, H-7′), 7.23 ppm (d, *J* = 7.8 Hz, 1H, H-5′); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 14.9 (C-20), 16.8 (C-19), 17.5 (C-2), 17.6 ($CH_3$), 19.5 (C-11), 21.0 (C-17), 24.3 (C-6), 34.7 (C-10), 35.6 (C-12), 36.3 (C-13), 36.6 (C-3), 38.2 (C-1), 45.3 (C-5), 45.6 (C-14), 46.1 (C-4), 51.5 (C-9), 72.7 (C-2′), 108.8 (C-16), 115.0 (C-8′), 116.7 (C-6′), 120.3 (C-7), 120.8 (C-7′), 121.5 (C-4′a), 123.2 (C-5′), 129.1 (C-3′), 132.1 (C-4′), 135.1 (C-8), 149.9 (C-15), 151.0 (C-8′a), 177.9 ppm (C=O); IR: $\tilde{\nu}$ = 3438, 2971, 2941, 2915, 2904, 2863, 2844, 1664, 1608, 1490, 1473, 1448, 1380, 1363, 1322, 1243, 1274, 1209, 1149, 1122, 1081, 1037, 1000, 971,939, 923, 906, 889, 827, 752 cm$^{-1}$; HRMS (ESI+): *m*/*z* calcd for $C_{30}H_{39}NO_2$ [*M*+H]$^+$: 445.2975; found: 445.2969.

(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(*S*)-4-methyl-2*H*-chromen-2-yl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**11 b**): Yellow oil; $R_f$ = 0.30 ($CHCl_3$/EtOH, 10:1); $[\alpha]_D^{25}$ = +68.6 (*c* = 0.18 in $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.81 (s, 6H, $C^{20}H_3$ and $C^{17}H_3$), 1.16 (dt, *J* = 13.9, 6.2 Hz, 1H, H-1), 1.14 (s, 3H, $C^{19}H_3$), 1.28–1.35 (m, 2H, H-11, 12), 1.40–1.58 (m, 5H, H-12, 3, 11, 2, 2), 1.60–1.64 (m, 1H, H-6), 1.72–1.79 (m, 2H, H-6,9), 1.81–1.99 (m, 5H, H-1, 3, 14, 14, 5), 2.10 (s, 3H, $CH_3$), 4.89 (dd, *J* = 10.6, 1.2 Hz, 1H, H-16), 4.95 (dd, *J* = 17.5, 1.2 Hz, 1H, H-16), 5.21 (d, *J* = 4.4 Hz, 1H, H-7), 5.56 (d, *J* = 4.5 Hz, 1H, H-3′), 5.80 (dd, *J* = 17.5, 10.6 Hz, 1H, H-15), 6.33 (d, *J* = 8.5 Hz, 1H, NH), 6.51 (dd, *J* = 8.5, 4.5 Hz, 1H, H-2′), 6.95 (d, *J* = 8.0 Hz, 1H, H-8′), 7.01 (dd, *J* = 8.1, 7.8 Hz, 1H, H-6′), 7.24 (dd, *J* = 8.1, 8.0 Hz, 1H, H-7′), 7.29 ppm (d, *J* = 7.8 Hz, 1H, H-5′); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 15.1 (C-20), 17.0 (C-19), 17.8 (C-2), 17.9 ($CH_3$), 19.8 (C-11), 21.3 (C-17), 24.3 (C-6), 34.9 (C-10), 35.8 (C-12), 36.3 (C-13), 36.6 (C-3), 38.5 (C-1), 45.7 (C-5), 45.8 (C-14), 46.3 (C-4), 51.7 (C-9), 72.8 (C-2′), 109.1 (C-16), 116.8 (C-8′), 116.9 (C-6′), 120.6 (C-7), 121.1 (C-7′), 121.9 (C-4′a), 123.5 (C-5′), 129.4 (C-3′), 132.5 (C-4′), 135.3 (C-8), 150.1 (C-15), 151.3 C-8′a), 178.3 ppm (C=O); IR: $\tilde{\nu}$ = 3438, 2941, 2917, 2865, 2846, 1664, 1605, 1499, 1460, 1420, 1382, 1211, 1124, 1037, 1080, 1000, 911, 866, 752, 700 cm$^{-1}$; HRMS (ESI+): *m*/*z* calcd for $C_{30}H_{39}NO_2$ [*M*+H]$^+$: 445.2975; found: 445.2969.

(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(*R*,*S*)-4-methylene-chroman-2-yl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**11 c**): Yellowish solid; $R_f$ = 0.31 ($CHCl_3$/EtOH, 10:1); m.p. 142–145 °C ($CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 0.81 (s, 3H, $C^{20}H_3$), 0.83 (s, 3H, $C^{17}H_3$), 1.11 (dt, 1H, *J* = 12.6, 4.2 Hz, H-1), 1.16 (s, 3H, $C^{19}H_3$), 1.31 (t, 1H, *J* = 9.5 Hz, H-11), 1.45–1.54 (m, 6H, H-2, 2, 6, 12, 3, 12), 1.58 (br s, 1H, H-6), 1.70 (s, 1H, H-9), 1.79–1.84 (m, 5H, H-1, 12, 3, 14, 14), 1.82 (m, 1H, H-5), 2.52 (dd, 1H, *J* = 14.3, 4.8 Hz, H-3′), 2.88 (ddd, 1H, *J* = 14.3, 1.8, 1.5 Hz, H-3′), 4.85 (dd, 1H, *J* = 10.7, 1.1 Hz, H-16), 4.90 (dd, 1H, *J* = 17.5, 1.1 Hz, H-16), 5.01 (br s, 1H, H-9′), 5.13 (br d, 1H, *J* = 4.4 Hz, H-7), 5.64 (br s, 1H, H-9′), 5.77 (dd, 1H, *J* = 17.5, 10.7 Hz, H-15), 6.04 (dd, 1H, *J* 7.2, 4.8 Hz, H-2′), 6.45 (m, 1H, NH), 6.86 (dd, 1H, *J* = 8.1, 1.1 Hz, H-8′), 6.92 (td, 1H, *J* = 7.5, 1.1 Hz, H-6′), 7.19 (ddd, 1H, *J* = 8.1, 7.5, 1.5 Hz, H-7′), 7.53 ppm (dd, 1H, *J* = 7.5, 1.5 Hz, H-5′); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 15.2 (C-20), 16.9 (C-19), 17.9 (C-2), 19.8 (C-11), 21.3 (C-17), 24.3 (C-6), 34.9 (C-10), 35.5 (C-3′), 35.9 (C-12), 36.5 (C-13), 36.6 (C-3), 38.6 (C-1), 45.8 (C-5), 45.8 (C-14), 46.3 (C-4), 51.8 (C-9), 75.1 (C-2′), 109.1 (C-16), 110.4 (C-9′), 117.9 (C-8′), 120.7 (C-7), 120.7 (C-4a′), 121.0 (C-6′), 124.1 (C-5′), 130.1 (C-7′), 134.2 (C-4′), 135.3 (C-8), 150.2 (C-15), 151.9 (C-8′a), 178.4 ppm (C=O); IR: $\tilde{\nu}$ = 3386, 3079, 2923, 2850, 1727, 1654, 1639, 1610, 1573, 1519, 1479, 1456, 1349, 1319, 1299, 1278, 1255, 1218, 1201, 1162, 1155, 1126, 1081, 1039, 1000, 908, 883, 848, 833, 811, 804, 754, 728, 676, 667, 649 cm$^{-1}$; HRMS (ESI+): *m*/*z* calcd for $C_{30}H_{39}NO_2$ [*M*+H]$^+$: 445.2975; found: 445.2982.

(1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(*R*,*S*)-(3-methylene-2,3-dihydrobenzofuran-2-yl)methyl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamides (**12 a**/**12 b**): Yellow oil; $R_f$ = 0.12 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.82 (s, 3H, 2$C^{20}H_3$), 0.83 (s, 3H, 2$C^{20}H_3$), 0.85 (s, 3H, $C^{17}H_3$), 0.88 (s, 3H, $C^{17}H_3$), 1.09 (m, 2H, H-1), 1.14 (s, 3H, $C^{19}H_3$), 1.17 (s, 3H, $C^{19}H_3$), 1.31 (m, 4H, 2H-11, 12), 1.39–1.51 (m, 10H, 2H-12, 3, 11, 2, 2), 1.64–1.70 (m, 4H, 2H-6, 9), 1.73–1.96 (m, 12H, 2H-6, 1, 3, 14, 14, 5), 3.28–3.32 (m, 1H, $CH_2$), 3.36–3.42 (m, 1H, $CH_2$), 3.75–3.83 (m, 1H, $CH_2$), 3.96–4.04 (m, 1H, $CH_2$), 4.84 (dd, *J* = 10.7, 1.6 Hz, 2H, H-16), 4.89 (dd, *J* = 17.5, 1.6 Hz, 2H, H-16), 5.03 (d, *J* = 3.2 Hz, 1H, H-2′), 5.04 (br s, 1H,

H-2′), 5.18–5.26 (m, 4H, 2H-7, 2′a), 5.38 (s, 1H, H-8′), 5.45 (s, 1H, H-8′), 5.77 (dd, $J$=17.5, 10.7 Hz, 2H, H-15), 6.10 (m, 2H, 2-NH), 6.83 (d, $J$=7.2 Hz, 2H, H-7′), 6.89 (dd, $J$=7.6, 7.8 Hz, 2H, H-5′), 7.19 (dd, $J$=7.8, 7.2 Hz, 2H, H-6′), 7.30 ppm (d, $J$=7.6 Hz, 2H, H-4′); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=15.2 (2C-20), 17.1 (2C-19), 18.0, 18.2 (2C-2), 19.8 (2C-11), 21.4 (2C-17), 24.5, 24.7 (2C-6), 35.0, 35.0 (2C-10), 35.9 (2C-12), 37.0, 37.1 (2C-3), 38.6, 38.7 (2C-1), 36.66 (2C-13), 46.3 (2C-4), 44.1, 44.1 (2C-($CH_2$)), 45.3, 45.6 (2C-5), 45.9 (2C-14), 51.8, 51.9 (2C-9), 84.4, 84.4 (2C-2′), 109.1 (2C-16), 101.75, 101.7 (2C-8′), 110.4, (2C-7′), 125.6, 125.7 (2C-3′a), 120.9 (2C-7), 120.9 (2C-5′), 130.6 (2C-4′), 129.86 (2C-6′), 135.3, 135.4 (2C-8), 144.2, 144.3 (2C-3′), 150.2 (2C-15), 161.9 (2C-7′a), 178.7 ppm (2C-OC(=O); HRMS (ESI+): $m/z$ calcd for $C_{30}H_{39}NO_2$ $[M+H]^+$: 445.2975; found: 445.2966.

(1*R*,4a*R*,4bS,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(3-methylbenzofuran-2-yl)-methyl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**13**): Yellow oil; $R_f$=0.32 ($CHCl_3$/EtOH, 10:1); $[\alpha]_D^{25}$ = +21.9 ($c$=0.36 in $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=0.83 (s, 3H, $C^{20}H_3$), 0.89 (s, 3H, $C^{17}H_3$), 1.06–1.14 (m, 1H, H-1), 1.16–1.23 (m, 2H, H-11, 12), 1.26 (s, 3H, $C^{19}H_3$), 1.29–1.37 (m, 1H, H-2), 1.43–1.55 (m, 4H, H-12, 3, 11, 2, 2), 1.59–1.62 (m, 1H, H-6), 1.68–1.74 (m, 2H, H-6, 9), 1.80–1.96 (m, 5H, H-1, 3, 14, 14, 5), 2.07 (s, 3H, H-8′), 3.98–4.06 (m, 2H, $CH_2$), 4.84 (dd, $J$=10.7, 1.8 Hz, 1H, H-16), 4.89 (dd, $J$=17.5, 1.8 Hz, 1H, H-16), 5.20–5.28 (m, 1H, H-7), 5.74 (m, 1H, NH), 5.78 (dd, 1H, $J$=17.5, 10.7 Hz, H-15), 7.32 (dd, 1H, $J$=7.2, 7.0 Hz, H-5′), 7.38 (dd, $J$=7.2, 6.8 Hz, 1H, H-6′), 7.67 (d, 1H, $J$=6.8 Hz, H-7′), 7.85 ppm (d, 1H, $J$=7.0 Hz, H-4′); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=7.3 (C-8′), 15.2 (C-20), 17.9 (C-19), 17.9 (C-2), 19.8 (C-11), 21.3 (C-17), 24.6 (C-6), 34.9 (C-10), 35.2 (C-12), 35.8 (C-13), 36.6 (C-3), 37.0 (C-2a), 38.6 (C-1), 45.6 (C-5), 45.8 (C-14), 46.3 (C-4), 51.8 (C-9), 109.0 (C-16), 110.7 (C-7′), 112.4 (C-3′), 119.3 (C-4′), 120.7 (C-7), 122.2 (C-5′), 124.2 (C-6′), 129.6 (C-3′a), 135.3 (C-8), 148.9 (C-2′), 150.1 (C-15), 153.8 (C-7′a), 178.3 ppm (C=O); IR: $\tilde{\nu}$=3353, 2921, 2865, 2823, 1647, 1607, 1519, 1475, 1454, 1384, 1332, 1278, 1238, 1195, 1180, 1153, 1130, 1105, 1002, 986, 910, 868, 811, 746, 705 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{30}H_{39}NO_2$ $[M+H]^+$: 445.2975; found: 445.2971.

(1*R*,4a*R*,4bS,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-(3-phenylbut-2-en-1-yl)-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**14**): Yellow oil; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$=0.83 (s, 3H, $C^{20}H_3$), 0.89 (s, 3H, $C^{17}H_3$), 1.12–1.22 (m, 1H, H-1), 1.27 (s, 3H, $C^{19}H_3$), 1.26–1.37 (m, 2H, H-11, 12), 1.44–1.55 (m, 5H, H-12, 3, 11, 2, 2), 1.58–1.62 (m, 1H, H-6), 1.65–1.74 (m, 2H, H-6,9), 1.78–1.95 (m, 5H, H-1, 3, 14, 14, 5), 2.07 (s, 3H, $CH_3$), 3.99 (dd, $J$=13.9, 6.2 Hz, 1H, H-3′), 4.07 (dd, $J$=13.9, 6.2 Hz, 1H, H-3′), 4.84 (dd, $J$=10.7, 1.8 Hz, 1H, H-16), 4.90 (dd, $J$=17.6, 1.8 Hz, 1H, H-16), 5.22–5.30 (m, 1H, H-7), 5.72 (t, $J$=6.2 Hz, 1H, CH=), 5.75 (m, 1H, NH), 5.77 (dd, $J$=17.6, 10.7 Hz, 1H, H-15), 7.04 (m, 2H, H-2″, 6″), 7.26 (m, 2H, H-3″, 5″), 7.31 ppm (m, 2H, H-4″); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=15.2 (C-20), 16.0 ($CH_3$), 17.3 (C-19), 18.1 (C-2), 19.8 (C-11), 21.4 (C-17), 24.8 (C-6), 35.1 (C-10), 35.9 (C-12), 36.7 (C-13), 37.2 (C-3), 38.4 (C-4′), 38.7 (C-1), 45.7 (C-5), 45.9 (C-14), 46.3 (C-4), 51.9 (C-9), 109.1 (C-16), 120.8 (C-7), 123.5 (C-5′), 125.6 (C-2″,6″), 127.2 (C-4″), 128.2 (C-3″,5″), 135.5 (C-8), 138.4 (C-6′), 142.7 (C-1″), 150.2 (C-15), 178.4 ppm (C=O); IR: $\tilde{\nu}$=3398, 3079, 2865, 1727, 1646, 1600, 1521, 1496, 1452, 1380, 1315, 1261, 1240, 1135, 1101, 1072, 1027, 975, 912, 860, 768, 700 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{30}H_{41}NO$ $[M+H]^+$: 431.3175; found: 431.3165.

(1*R*,4a*R*,4bS,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-(3-phenylbut-3-en-1-yl)-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamide (**15**): Yellow oil; $R_f$=0.18 ($CHCl_3$/EtOH, 10:1); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$=0.83 (3H, s, $C^{20}H_3$), 0.86 (s, 3H, $C^{17}H_3$), 1.08–1.12 (m, 1H, H-1), 1.23 (s, 3H, $C^{17}H_3$), 1.28–1.35 (m, 2H, H-11, 12), 1.44–1.54 (m, 4H, H-12, 3, 11, 2), 1.54–1.61 (m, 2H, H-2, 6), 1.72–1.75 (m, 2H, H-6, 9), 1.77–1.98 (m, 5H, H-1, 3, 14, 14, 5), 2.70 (d, $J$=6.7 Hz, 1H, H-4′), 2.72 (d, $J$=6.7 Hz, 1H, H-4′), 3.29 (dd, $J$=6.5, 7.0 Hz, H, H-3′), 3.29 (dd, $J$=6.5, 7.0 Hz, 1H, H-3′), 4.84 (dd, $J$=10.7, 1.4 Hz, 1H, H-16), 4.90 (d, $J$=17.4, 1.4 Hz, 1H, H-16), 5.09 (d, $J$=1.2 Hz, 1H, H-6′), 5.20–5.26 (m, 1H, H-7), 5.35 (d, $J$=1.2 Hz, 1H, H-6′), 5.72 (t, 1H, $J$=6.5 Hz, NH), 5.77 (dd, 1H, $J$=17.7, 10.7 Hz, H-15), 7.04 (m, 1H, H-4″), 7.30 (m, 2H, H-3″, 5″), 7.38 ppm (m, 2H, H-2″, 6″); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=15.2 (C-20), 17.0 (C-19), 18.0 (C-2), 19.8 (C-11), 21.3 (C-17), 24.6 (C-6), 29.5, 34.8 (C-10), 34.9 (C-4′), 35.8 (C-12), 36.6 (C-13), 36.9 (C-3), 38.3 (C-3′), 38.6 (C-1), 45.4 (C-5), 45.8 (C-14), 46.2 (C-4), 51.8 (C-9), 109.0 (C-16), 114.3 (C-6′), 120.7 (C-7), 125.9 (C-2″,6″), 127.6 (C-4″), 128.4 (C-3″,5″), 135.4 (C-8), 142.5 (C-1″), 145.7 (C-5′), 150.2 (C-15), 178.3 ppm (C=O); IR: $\tilde{\nu}$=3355, 3079, 2923, 2863, 1367, 1259, 1384, 1448, 1523, 1631, 1203, 1102, 1056, 998, 906, 860, 777, 754, 701 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{30}H_{41}NO$ $[M+H]^+$: 431.3175; found: 431.3168.

### *Reaction of Terpenoid* N-*(2,3-Butadienyl)carboxamide 3 with 2-Iodobenzoic acid (16)*

Compound **16** (420 mg, 1.71 mmol), $Cs_2CO_3$ (920 mg, 2.81 mmol), and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) were added to a stirred solution of **3** (500 mg, 1.41 mmol) in anhydrous DMF (2 mL) under an argon atmosphere. The mixture was heated at 80 °C for 3 h, cooled, diluted with ethyl acetate (10 mL), washed with water (3×5 mL), dried with $K_2CO_3$, filtered, and concentrated. The residue was subjected to column chromatography on silica gel (petroleum ether/ether, 2:1), and crystallization (chloroform) of the solid from gave **17a**/**17b** (470 mg, 70%).

(1*R*,4a*R*,4bS,7*S*,10a*R*)-1,4a,7-Trimethyl-*N*-[(4-methylene-1-oxoisochroman-3-yl)methyl]-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxamides (**17a**/**17b**): Colorless solid; $R_f$=0.13 ($CHCl_3$/EtOH, 10:1); m.p. 176–180 °C ($CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=0.82 (s, 3H, $C^{20}H_3$), 0.87 (s, 3H, $C^{20}H_3$), 0.93 (s, 3H, $C^{17}H_3$), 0.95 (s, 3H, $C^{17}H_3$), 1.09–1.20 (m, 2H, 2H-1), 1.23 (s, 6H, 2$C^{19}H_3$), 1.26–1.36 (m, 4H, 2H-11, 12), 1.42–1.55 (m, 10H, 2H-12, 3, 11, 2, 6), 1.62–1.77 (m, 6H, 2H-2, 6, 9), 1.79–1.95 (m, 10H, 2H-1, 3, 14, 14, 5), 3.48–3.59 (m, 2H, 2-H-3′a), 3.76–3.87 (m, 2H, 2-H-3′a), 4.83 (dd, $J$=10.7, 1.6 Hz, 2H, 2H-16), 4.88 (dd, $J$=17.5, 1.6 Hz, 2H, 2H-16), 5.10–5.14 (m, 2H, 2H-3′), 5.18–5.27 (m, 2H, 2H-7), 5.43 (1H, s, H-9′), 5.44 (s, 1H, H-9′), 5.75 (dd, 2H, $J$=17.5, 10.7 Hz, 2H-15), 5.78 (s, 2H, 2H-9′), 6.24 (m, 2H, 2-NH), 7.45 (dd, $J$=7.3, 7.5 Hz, 2H, 2H-7′), 7.59 (d, $J$=7.0 Hz, 2H, 2H-5′), 7.61 (dd, $J$=7.5, 7.0 Hz, 2H, 2H-6′), 8.08 ppm (d, $J$=7.3, 2H, 2H-8′); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$=15.3 (C-20), 17.3 (C-19), 18.0, 18.1 (C-2), 19.9 (C-11), 21.4 (C-17), 24.9 (C-6), 35.1, 35.8 (C-10), 36.7, 37.2 (C-12), 37.3 (C-13), 38.7 (C-3), 41.3 (C-1), 45.5, 45.7 (C-3′a), 46.1 (C-14), 48.3 (C-5), 48.9 (C-4), 52.0 (C-9), 79.9, 80.1 (C-3′), 111.9 (C-16), 118.2, 118.3 (C-9′), 123.1 (C-7), 125.7 (C-8′a), 126.8 (C-5′), 130.2 (C-7′), 130.9 (C-8′), 135.8 (C-6′), 135.9 (C-4′), 138.7 (C-8), 138.8, 138.9 (C-4′a), 150.3 (C-15), 164.5 (C-1′), 179.2 ppm (C-18); IR: $\tilde{\nu}$=3400, 2925„ 2867, 1726, 1639, 1606, 1525, 1459, 1410, 1324, 1265, 1201, 1160, 1116, 1078, 1039, 1000, 920, 860, 816, 720 cm$^{-1}$; HRMS (ESI+): $m/z$ calcd for $C_{31}H_{39}NO_3$ $[M+H]^+$: 473.2925; found: 473.2919.

### X-ray Diffraction Analysis

The structures of **2**, **3**, **8**, and **11a** were solved by direct methods and were refined by the full-matrix least-squares method against all F2 in anisotropic approximation by using the SHELX-97 programs set.[36] The positions of the hydrogen atoms were calculated

with the riding model. Absorption corrections were applied by using the empirical multiscan method with the SADABS program[37] for **2**, **3**, and **11a**; absorption corrections was not applied for **9**. The terminal CH=$CH_2$ groups were disordered in all of the molecules of compounds **2**, **3**, **8**, and **11a**. The molecular structures of compounds **2**, **3**, **8**, and **11a** are illustrated in Figure 1. The obtained crystal structures were analyzed for short contacts between nonbonded atoms by using PLATON[38] and MERCURY programs.[39] The structure of **2** is formed by two crystallographically independent molecules, one of which is shown in Figure 1.

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