Chemistry of Heterocyclic Compounds, Vol. 50, No. 2, May, 2014 (Russian Original Vol. 50, No. 2, February, 2014)

AN IMPROVED SYNTHESIS OF β-CARBOLINE AND AZEPINO- AND AZOCINO[3,4-*b*]INDOLE DERIVATIVES FROM LACTAMS

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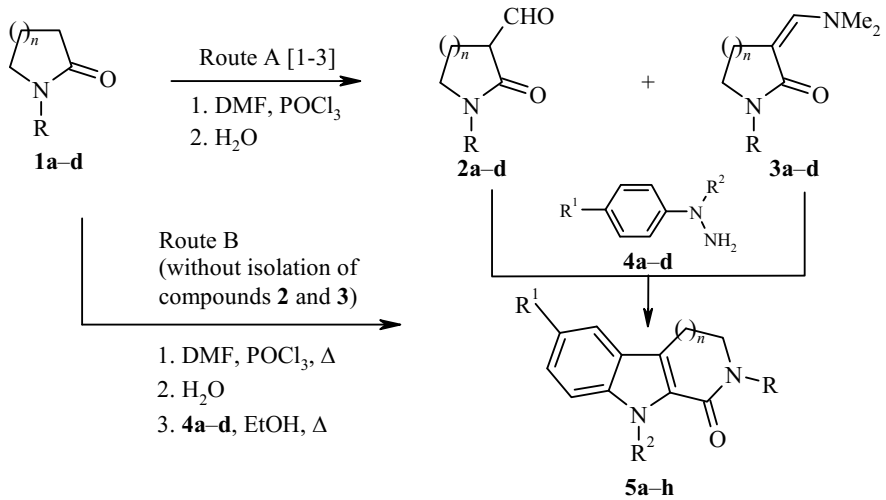
The Vilsmeier formylation of butyrolactam, N-methylbutyrolactam, N-methylvalerolactam, and N-methylcaprolactam followed by treatment with aryl hydrazines afforded the 2,3,4,9-tetrahydro-1H-β-carbolin-1-ones, 3,4,5,10-tetrahydroazepino[3,4-b]indol-1(2H)-ones, and 2,3,4,5,6,11-hexahydro-1H-azocino[3,4-b]indol-1-ones. The synthesis was performed as a one-pot process without isolating the intermediate α-formyl lactams.

Keywords: arylhydrazines, azepino[3,4-*b*]indoles, azocino[3,4-*b*]indoles, β-carbolines, lactams, Fischer reaction, rearrangements, Vilsmeier reaction.

In a series of previous publications [1-3] we described the Fischer reaction involving the α-formyl lactams **2** or their enamines **3**, obtained from the lactams **1**, as the carbonyl component. Depending on the ring size of the starting lactams **1**, the reaction gave 2,3,4,9-tetrahydro-1*H*-β-carbolin-1-ones **5** (*n* = 1), 3,4,5,10-tetrahydroazepino[3,4-*b*]indol-1(2*H*)-ones **5** (*n* = 2), or 2,3,4,5,6,11-hexahydro-1*H*-azocino[3,4-*b*]-indol-1-ones **5** (*n* = 3) in up to 80% yields (Scheme 1, route A).

Scheme 1



1a,**b**, **5a**–**c** *n* =1; **1c**, **5d**–**f** *n* = 2; **1d**, **5g**,**h** *n* = 3; **1a**, **5a** R = H; **1b**–**d**, **5b**–**h** R = Me; **4a**,**c**,**d**, **5a**–**d**,**f**–**h** R^1 = H; **4b**, **5e** R^1 = Me; **4a**,**b**, **5b**,**d**,**e**,**g** R^2 = H; **4c**, **5c** R^2 = Ph; **4d**, **5a**,**f**,**h** R^2 = CH_2Ph

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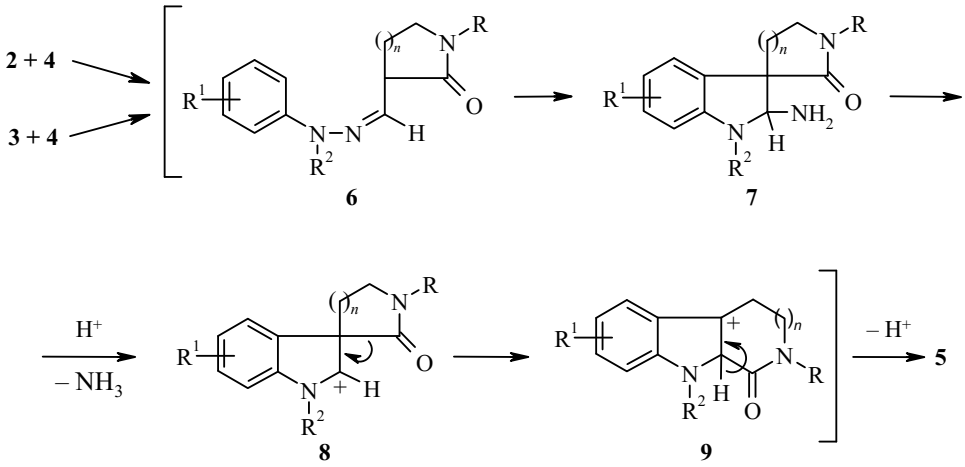
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 235-240, February, 2014. Original article submitted December 28, 2013; revision submitted February 21, 2014.

The proposed mechanism of this reaction [1] includes a sequence of two intramolecular rearrangements: the Fischer reaction and a rearrangement with lactam ring expansion. The first stage of the process involves interaction of the aldehyde **2** or enamine **3** with the arylhydrazine **4**, forming the hydrazone **6**, which undergoes Fischer cyclization in acidic medium, leading to the spiroindoline **7**. After the protonation of amino group in the spiroindoline **7**, a molecule of ammonia is eliminated, forming the cation **8**. The latter undergoes a rearrangement with lactam ring expansion, forming the cation **9**, which is stabilized by deprotonation and thus gives the tricyclic compound **5** (Scheme 2).

Scheme 2



The heterocycles **5**, and especially the β-carbolines attract a significant interest of researchers due to the broad range of biological activity [4-6] and the utility as starting materials for the further modification of indole molecules. Thus, the β-carbolines **5** (n = 1) are used for the preparation of tryptamines with various patterns of substitution [7], as well as the known medication incazane [8].

Quite a lot methods are known in the literature for the synthesis of β-carbolines **5** (n = 1). These methods are complicated and rely on starting materials that are costly or difficult to find. The better known of these methods is the Abramovich–Shapiro reaction [9] – the Fischer cyclization of piperidine-2,3-dione 3-aryl-hydrazones, obtained by the Japp–Klingemann reaction of aryldiazonium salts with 2-oxopiperidine-3-carboxylates. The azepinoindoles **5** (n = 2) were also obtained by the Fischer reaction from α-oxocaprolactam enamines [10]. The azocinoindoles **5** (n = 3) were unknown prior to our investigations.

Our goal was to simplify the synthesis of compounds **5** by avoiding the laborious isolation of the intermediate aldehydes **2** and enamines **3**. We applied a Vilsmeyer formylation reaction using DMF and $POCl_3$ to convert the starting lactams **1** to the aldehydes **2** and the respective enamines **3** [2, 11]. Several methods for the synthesis of α-formyl lactams have been described in the literature, based on Claisen condensation of *N*-substituted lactams with ethyl formate in the presence of potassium metal. These approaches are complicated and provide poor yields of the aldehydes: 3.6% [12], 15% [13] from *N*-methylbutyrolactam, and 23% [14] from *N*-methylvalerolactam. Our Vilsmeier formylation method gave formyl lactams in significantly higher yields (38-64%) and, in addition, provided the opportunity to obtain *N*-unsubstituted formyl lactams [2]. However, our experimental procedure was still quite complicated. The Vilsmeyer reaction with its aqueous work-up was followed by a laborious isolation of compounds **2** and **3** from water-containing phases. The good aqueous solubility of these compounds required salting out, multiple extractions, and finally, a vacuum distillation. An additional drawback of the method was the formation of the aldehydes **2** in mixtures with the enamines **3**.

We assumed that the isolation of compounds **2** and **3** was not necessary and aqueous solutions of the aldehydes **2** and/or the enamines **3** obtained after the aqueous work-up of formylation reactions of lactams **1** could be directly introduced into reactions with the arylhydrazines **4** (Scheme 1, route B). It was expected that the unreacted starting lactams **1** and DMF should not interfere with the formation of arylhydrazones and with the further rearrangements, and also with the isolation of the products. It was also assumed that the HCl and H_3PO_4 formed by aqueous work-up would catalyze the Fischer reaction.

The formylation reaction of the lactams **1** was concluded by a careful vacuum evaporation of the solvent (benzene) in order to obtain a homogeneous aqueous phase for the further transformations. The residue was worked up by adding cold water or ice. The obtained aqueous solution (or its aliquot) was used in reactions with the arylhydrazines **4**. The reactions successfully produced the heterocycles **5**, and the yields of these compounds from the lactams **1a**-**d** were comparable to the yields from pure andehydes **2** and enamines **3** [1-3]. Thus, the route B (without isolation of compounds **2** and **3**) was even more efficient than the route A.

It was further established that acidic aqueous solutions of the *N*-substituted α-formyl lactams **2b**-**d** were relatively stable when stored in a refrigerator and could be used at least for a week without a significant decrease in the yield of the heterocycles **5**. It should be noted that the adducts obtained in the Vilsmeier reaction from lactams, DMF, and $POCl_3$ were also quite stable. For instance, such an adduct of the lactam **1c** (after the removal of benzene) was stored in a refrigerator in an airtight vessel for more than a year. After dissolving it in water and reacting with the arylhydrazines **4a**,**d**, we obtained the azepinoindoles **5d**,**f** in nearly the same yields as from a freshly prepared adduct. Thus we consider these adducts to be convenient synthetic equivalents of the aldehydes **2**.

The structures of the obtained compounds **5a**-**h** were confirmed by ^1H and ^{13}C NMR data. The signals were assigned based on COSY, DEPT, and HMQC experiments. Compounds **5a**-**h** were also shown to be identical with previously obtained samples [1-3] by the lack of melting point depression of mixed samples, equivalent chromatographic properties, and matching IR spectra.

As was previously pointed out [3], the ^1H NMR spectrum of the 11-benzyl-substituted azocinoindole **5h** exhibited non-equivalent CH_2 group protons, unlike the other spectra. We should emphasize that this was not observed neither for the 11-unsubstituted azocinoindole **5g**, nor for the 10-benzyl-substituted azepinoindole **5f**. This can be explained by a steric hindrance between the benzyl group and the 8-membered lactam ring that inhibits the free rotation of the benzyl group and/or the conformational flux in the lactam ring. Such an interpretation was confirmed by the temperature-dependent coalescence of two benzyl proton doublets into a singlet [3].

Thus, we significantly streamlined the synthesis of β-carboline and azepino- and azocino[3,4-*b*]indole derivatives by eliminating the laborious isolation of α-formyl lactam intermediates generated by Vilsmeier formylation of lactams. Performing this sequence of reactions in one pot enabled us to use commercially available and affordable lactams, while the yield remained practically the same.

EXPERIMENTAL

IR spectra were recorded on a Perkin Elmer Spectrum 400 FTIR spectrometer in KBr pellets. ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance III 500 spectrometer (500 and 125 MHz, respectively) in $CDCl_3$, with residual solvent protons as internal standard (7.28 ppm for ^1H; 76.50 ppm for ^{13}C). Melting points were determined in glass capillaries on a electroheating block. TLC was performed on Silufol UV-254 plates with 6:1 benzene–acetone as an eluent, visualization under UV light or with iodine vapor.

N-Methylvalerolactam (**1c**) [15] and *N*-methylcaprolactam (**1d**) [16] were obtained according to literature methods. *p*-Tolylhydrazine hydrochloride (**4b**) (Reakhim), 1,1-diphenylhydrazine hydrochloride (**4c**) (Aldrich), 1-benzyl-1-phenylhydrazine hydrochloride (**4d**) (Kharkov chemical reagent plant), butyrolactam (**1a**)

(Merck), and $POCl_3$ (Fluka) were used without additional purification. *N*-Methylbutyrolactam (**1b**) (Ferak) was purified by vacuum distillation. Phenylhydrazine hydrochloride (**4a**) (Shostka chemical reagent plant) was purified according to the method [17].

Synthesis of Compounds 5a-h (General Method). A solution of $POCl_3$ (65 mmol) in anhydrous benzene (10 ml) was stirred and cooled on a water bath, while a solution of the lactam **1a** (15 mmol) or freshly distilled lactam **1b-d** (30 mmol) and anhydrous DMF (33 mmol) in anhydrous benzene (8 ml) was added dropwise over 10-15 min. The reaction mixture turned into a yellowish two-phase system, which was further stirred and refluxed for 5.5 h on a water bath in a flask equipped with a reflux condenser, while protecting from air moisture, and left overnight. The flask with the reaction mixture was transferred to a rotary evaporator, benzene and the excess of $POCl_3$ were removed by distillation over 1 h at 80°C. The residue was cooled and cautiously treated with cold water (15 ml) (lactams **1b-d**) or treated with ice (lactam **1a**), while avoiding overheating, stirred until dissolution and maintained for 1-1.5 h. The obtained solution was mixed together with a solution or suspension of the arylhydrazine hydrochloride **4a-d** (15 mmol for the lactam **1a** or 30 mmol for the lactams **1b-d**) in ethanol (50 ml), refluxed for 2 h in a flask with a reflux condenser, and cooled in a refrigerator. The precipitate of compounds **5a-g** was filtered off, washed with 50% ethanol and water, air-dried, and recrystallized from ethanol. The product **5h** was isolated by evaporation of the reaction mixture under vacuum, treating the residue with benzene and water, agitation of the two-phase system and separation of the benzene layer, washing with 10% HCl and water, drying over $MgSO_4$, and evaporation of benzene. The residue was treated with ether (30 ml), the undissolved debenzylated by-product **5g** was filtered off and washed with ether. The ether solution was evaporated, the residue was crystallized from a 1:1 mixture of hexane and cyclohexane.

9-Benzyl-2,3,4,9-tetrahydro-1*H*-β-carbolin-1-one (5a). Yield 38%, colorless plates, mp 182-184°C (yield 82%, mp 183-184°C (2-PrOH) [2]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.11 (2H, t, *J* = 6.9, 4-CH_2); 3.69 (2H, td, *J* = 6.9, *J* = 1.9, 3-CH_2); 5.70 (1H, br. s, NH); 5.93 (2H, s, $PhCH_2$); 7.16-7.23 (4H, m, H-6, H-2,4,6 Ph); 7.27 (2H, t, *J* = 7.2, H-3,5 Ph); 7.31 (1H, t, *J* = 7.9, H-7); 7.38 (1H, d, *J* = 7.9, H-8); 7.64 (1H, d, *J* = 8.0, H-5). ^{13}C NMR spectrum, δ, ppm: 20.7 (C-4); 41.3 (C-3); 47.3 ($PhCH_2$); 110.5 (C-8); 119.8, 119.9 (C-4a,5,6); 124.0 (C-4b(9a)); 124.6 (C-7); 124.9 (C-9a(4b)); 126.3 (C-2,6 Ph); 126.6 (C-4 Ph); 127.9 (C-3,5 Ph); 137.9, 138.2 (C-8a, C-1 Ph); 162.6 (C=O).

2-Methyl-2,3,4,9-tetrahydro-1*H*-β-carbolin-1-one (5b). Yield 61%, mp 233-235°C (yield 60%; mp 234°C (2-PrOH) [1]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.10 (2H, t, *J* = 7.1, 4-CH_2); 3.21 (3H, s, CH_3); 3.73 (2H, t, *J* = 7.1, 3-CH_2); 7.15 (1H, t, *J* = 7.9, H-6); 7.31 (1H, t, *J* = 7.9, H-7); 7.52 (1H, d, *J* = 7.9, H-8); 7.59 (1H, d, *J* = 7.9, H-5); 10.25 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.1 (C-4); 33.6 (CH_3); 49.7 (C-3); 112.1 (C-8); 117.3 (C-4a); 119.5 (C-5,6); 124.0 (C-7); 124.8, 126.6 (C-4b,9a); 137.1 (C-8a); 161.5 (C=O).

2-Methyl-9-phenyl-2,3,4,9-tetrahydro-1*H*-β-carbolin-1-one (5c). Yield 59%, colorless plates, mp 158-159°C (yield 62%, mp 160°C (MeOH) [1]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.10 (3H, s, CH_3); 3.17 (2H, t, *J* = 7.0, 4-CH_2); 3.76 (2H, t, *J* = 7.0, 3-CH_2); 7.21 (1H, d, *J* = 7.9, H-8); 7.23 (1H, t, *J* = 7.9, H-6); 7.30 (1H, t, *J* = 7.9, H-7); 7.43 (2H, d, *J* = 7.5, H-2,6 Ph); 7.47 (1H, t, *J* = 7.5, H-4 Ph); 7.54 (2H, t, *J* = 7.5, H-3,5 Ph); 7.67 (1H, d, *J* = 7.9, H-5). ^{13}C NMR spectrum, δ, ppm: 20.3 (C-4); 33.7 (CH_3); 49.1 (C-3); 111.1 (C-8); 119.5 (C-5); 119.6 (C-4a); 120.2 (C-6); 124.0 (C-4b(9a)); 124.6 (C-7); 126.9 (C-9a(4b)); 127.2 (C-4 Ph); 127.4 (C-2,6 Ph); 128.3 (C-3,5 Ph); 138.0, 139.6 (C-8a, C-1 Ph); 160.3 (C=O).

2-Methyl-3,4,5,10-tetrahydroazepino[3,4-*b*]indol-1(2*H*)-one (5d). Yield 56%, mp 237-239°C (yield 55%, mp 238°C (2-PrOH) [3]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22-2.26 (2H, m, 4-CH_2); 3.11 (2H, t, *J* = 6.6, 5-CH_2); 3.26 (3H, s, CH_3); 3.60-3.62 (2H, m, 3-CH_2); 7.14 (1H, t, *J* = 7.8, H-7); 7.32 (1H, t, *J* = 7.8, H-8); 7.42 (1H, d, *J* = 7.8, H-9); 7.61 (1H, d, *J* = 7.8, H-6); 9.19 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 24.7 (C-5); 25.9 (C-4); 36.7 (CH_3); 50.6 (C-3); 111.1 (C-9); 116.9 (C-5a); 119.1 (C-7); 119.6 (C-6); 124.2 (C-8); 127.0, 127.6 (C-5b,10a); 135.0 (C-9a); 163.0 (C=O).

2,7-Dimethyl-3,4,5,10-tetrahydroazepino[3,4-*b*]indol-1(2*H*)-one (5e). Yield 73%, mp 231-232°C (yield 76%, mp 232°C (2-PrOH) [3]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19-2.25 (2H, m, 4-CH_2); 2.48 (3H,

s, 7-CH_3); 3.07 (2H, t, J = 6.6, 5-CH_2); 3.25 (3H, s, NCH_3); 3.58-3.60 (2H, m, 3-CH_2); 7.15 (1H, d, J = 8.4, H-8); 7.32 (1H, d, J = 8.4, H-9); 7.38 (1H, s, H-6); 9.25 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.0 (7-CH_3); 24.7 (C-5); 25.9 (C-4); 36.7 (NCH_3); 50.6 (C-3); 110.8 (C-9); 116.4 (C-5a); 119.0 (C-6); 126.1 (C-8); 127.0, 127.8 (C-5b,10a); 128.3 (C-7); 133.3 (C-9a); 163.0 (C=O).

10-Benzyl-2-methyl-3,4,5,10-tetrahydroazepino[3,4-*b*]indol-1(2*H*)-one (5f). Yield 60%, mp 137-138°C (yield 57% and 70%; mp 139°C (2-PrOH) [3]). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.16-2.22 (2H, m, 4-CH_2); 3.06 (2H, t, J = 7.5, 5-CH_2); 3.17 (3H, s, NCH_3); 3.39-3.41 (2H, m, 3-CH_2); 5.74 (2H, s, PhCH_2); 7.08 (2H, d, J = 7.3, H-2,6 Ph); 7.16 (1H, t, J = 7.8, H-7); 7.19 (1H, t, J = 7.3, H-4 Ph); 7.24 (2H, t, J = 7.3, H-3,5 Ph); 7.27 (1H, t, J = 7.8, H-8); 7.33 (1H, d, J = 7.8, H-9); 7.65 (1H, d, J = 7.8, H-6). ^{13}C NMR spectrum, δ, ppm: 19.9 (C-5); 27.6 (C-4); 34.2 (CH_3); 47.2 (PhCH_2); 49.0 (C-3); 110.1 (C-9); 117.4 (C-5a); 119.0, 119.3 (C-6,7); 123.7 (C-8); 125.8 (C-5b(10a)); 126.0 (C-2,6 Ph); 126.4 (C-4 Ph); 127.9 (C-3,5 Ph); 128.8 (C-10a(5b)); 137.6, 138.3 (C-8a, C-1 Ph); 164.7 (C=O).

2-Methyl-2,3,4,5,6,11-hexahydro-1*H*-azocino[3,4-*b*]indol-1-one (5g). The reaction mixture was diluted to one half concentration with water and left overnight in refrigerator. Yield 11%, mp 208-210°C (yield 10%; mp 210°C (benzene) [3]). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.87-1.91 (2H, m, 4-CH_2); 2.01-2.05 (2H, m, 5-CH_2); 3.03-3.05 (2H, m, 6-CH_2); 3.16 (3H, s, CH_3); 3.70-3.72 (2H, m, 3-CH_2); 7.14 (1H, t, J = 7.8, H-8); 7.28 (1H, t, J = 7.8, H-9); 7.39 (1H, d, J = 7.8, H-10); 7.58 (1H, d, J = 7.8, H-7); 9.00 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.2 (C-5); 24.2 (C-6); 27.1 (C-4); 32.9 (CH_3); 48.6 (C-3); 110.9 (C-10); 117.9 (C-6a); 119.1, 119.2 (C-7,8); 123.7 (C-9); 125.7, 127.6 (C-6b,11a); 134.9 (C-10a); 164.7 (C=O).

11-Benzyl-2-methyl-2,3,4,5,6,11-hexahydro-1*H*-azocino[3,4-*b*]indol-1-one (5h). Yield 43%, colorless prisms, mp 78-79°C (yield 45%; mp 78°C (petroleum ether–cyclohexane) [3]). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.61-1.70 (1H, m, 4-C$\underline{H}_A$H$_B$); 1.70-1.82 (1H, m, 5-C$\underline{H}_A$H$_B$); 1.90-2.09 (2H, m, 4-CH$_A\underline{H}_B$, 5-CH$_A\underline{H}_B$); 2.92-3.05 (3H, m, 3-C$\underline{H}_A$H$_B$, 6-CH_2); 3.06 (3H, s, CH_3); 3.71-3.82 (1H, m, 3-CH$_A\underline{H}_B$); 5.47 (1H, d, J = 15.9) and 5.65 (1H, d, J = 15.9, PhCH_2); 7.10 (2H, d, J = 7.4, H-2,6 Ph); 7.17 (1H, t, J = 7.9, H-8); 7.19-7.27 (3H, m, H-3,4,5 Ph); 7.28 (1H, t, J = 7.9, H-9); 7.35 (1H, d, J = 7.9, H-10); 7.61 (1H, d, J = 7.9, H-7). ^{13}C NMR spectrum, δ, ppm: 21.5 (C-5); 23.7 (C-6); 26.8 (C-4); 32.4 (CH_3); 47.0 (PhCH_2); 48.9 (C-3); 109.7 (C-10); 117.5 (C-6a); 119.0, 119.1 (C-7,8); 123.2 (C-9); 126.3 (C-6b(11a)); 126.3 (C-2,6 Ph); 126.6 (C-4 Ph); 127.8 (C-3,5 Ph); 127.9 (C-11a(6b)); 137.2, 138.2 (C-10a, C-1 Ph); 164.2 (C=O).

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