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REARRANGEMENT REACTION IN 1-HYDROXYINDOLE CHEMISTRY: A SYNTHESIS OF NOVEL 7-SUBSTITUTED YOHIMBINE, AND 4a-SUBSTITUTED 1,2,3,4-TETRAHYDRO-β-CARBOLINE DERIVATIVES[1]

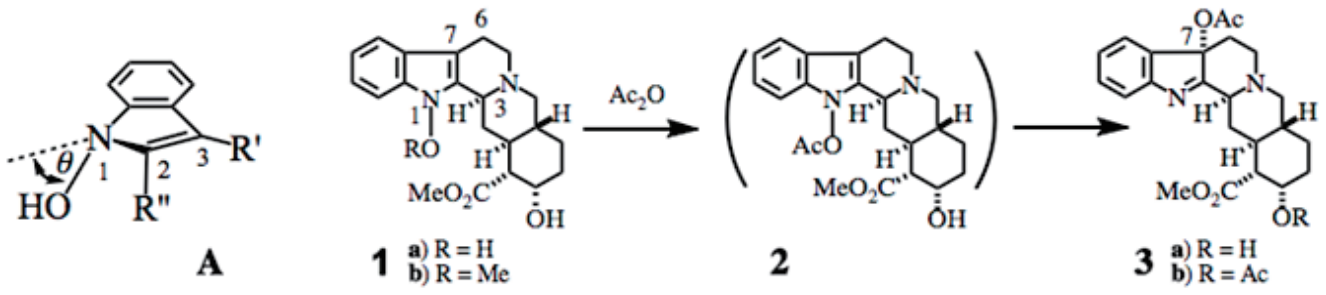
Katsumasa Yoshino,[a] Fumio Yamada,[b] Koichi Noguchi,[a] Kiyoka Kusuno,[a] and Masanori Somei[a,c]*

a Faculty of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan; b Sumika Technoservice Corporation, 2-1-4, Takatsukasa, Takarazuka, Hyogo, 665-0051, Japan; c Someiyakko Kenkyusho, 56-7 Matsuhidai, Matsudo, Chiba, 270-2214, Japan.
Corresponding author: e-mail address: somei.home@topaz.plala.or.jp

Abstract – X-Ray analyses of 1-hydroxyyohimbine derivatives definitely show the deviation of the N(1)—O bond from the indole molecular plane. This fact supports our working hypothesis "bishomoallylic conjugation". The deviation is responsible for the rearrangement reaction in 1-hydroxyindole chemistry. Effective synthetic method for novel 7α- and 7β-heteroarylyohimbine, and 4aα- and 4aβ-heteroaryl-1,2,3,4-tetrahydro-β-carboline derivatives are reported.

INTRODUCTION

Indole is a planar heteroaromatic molecule possessing sp^2 hybridized nitrogen.[2] In our 1-hydroxyindole hypothesis,[3] we expected that once a hydroxy group is introduced onto its nitrogen, especially in the cases



Scheme 1

of indoles having a C—C—N side chain at the 3-position, the nitrogen would become sp^3 like hybridized atom due to bishomoallylic conjugation[4] as reported in the previous communication.[4b] In fact the deviation of the N(1)—O bond from the indole molecular plane results and has an angle θ as shown in Scheme 1, **A**.[4]

We are confident the deviation is the reason for the unprecedented nucleophilic substitution[5] and rearrangement[6] reactions in simple 1-hydroxyindole derivatives. Now, we are interested to see if the same type of rearrangement reaction occurs in 1-hydroxyindole compounds with more complex structures, that may have biological activity.

RESULTS AND DISCUSSION

I. In the case of 1-hydroxyyohimbine (1a)

First, 1-hydroxy- (**1a**, Scheme 1) and 1-methoxyyohimbine[6] (**1b**) were prepared according to our synthetic procedures.[7] Then, we performed X-ray single crystal analysis of **1a** (**1a**$H^+ \cdot MeSO_3^-$) and **1b** and their ORTEP drawings are reported in the previous communication.[4b] Their positional parameters and *B* (eq) data are reported in the Experimental part of this report. They evidently demonstrate that the N(1)—O bond in **1a** and **1b** possess angle θ by 24.2° and 12.7°, respectively (Scheme 1, **A**). The values show that the rearrangement reaction is expected to take place judged from our hypothesis.[3] In fact, treatment of **1a** with Ac_2O afforded 66% yield of monoacetyl (**3a**)[6c,8] and 8% yield of di-acetyl product (**3b**). X-Ray analysis of **3b** exhibited that the desired rearrangement occurred and the presence of acetoxy group at the 7α-position of yohimbine skeleton as shown in Figure 1. The result proves that the initial formation of 1-acetoxyyohimbine (**2**) followed by the acetyl group rearrangement in the less hindered α-side.

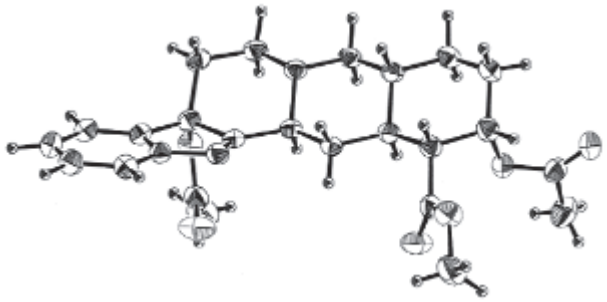
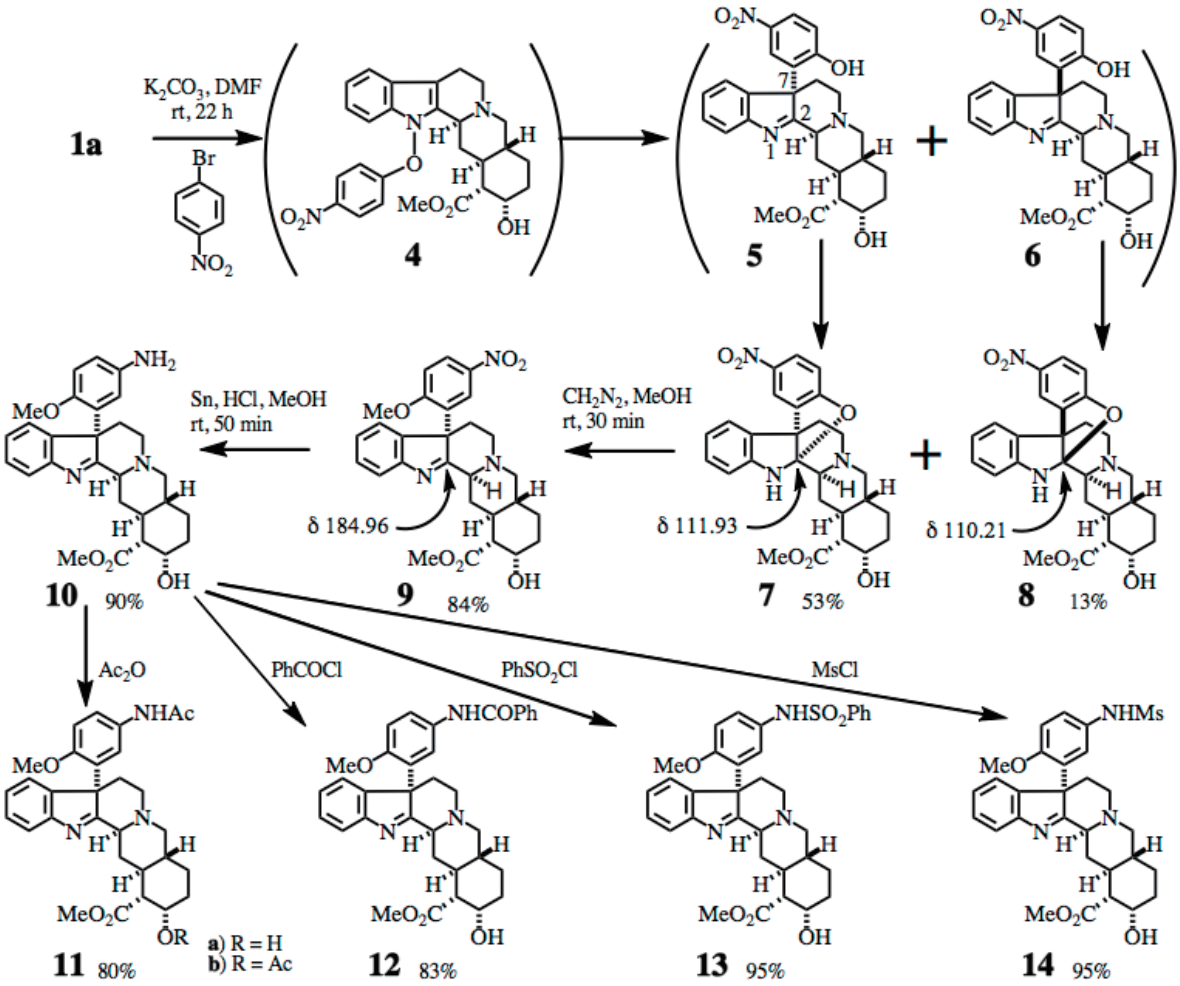


Figure 1

ORTEP drawing of **3b**, *R* =0.030 and *R*w=0.036

Employing larger substituent as a migrating group, the similar rearrangement took place. Thus, **1a** was treated with *p*-bromonitrobenzene in the presence of K_2CO_3 (Scheme 2). The reaction proceeded through the initial formation of 1-aryloxyyohimbine (**4**), followed by the rearrangement of *p*-nitrophenoxy group to the 7-position, giving **5** and **6**. Subsequent ring closure of the phenolic oxygen of the migrating group to the indolic imine carbon afforded **7** and **8**. Since the rearrangement occurs at the sterically less hindered α-side, **7** is the major (53%) 7α- and **8** is the minor 7β-product (13%). Their benzofuran fused structures are confirmed by the ^{13}C-NMR spectra of **7** and **8**, which showed signals at δ 111.93 and δ

110.21 ppm, respectively, showing newly born quaternal carbon at the 2 position.



Scheme 2

The reaction of **7** with CH_2N_2 in MeOH caused the opening of benzofuran ring with the formation of imine structure. The newly formed phenol part was methylated to give **9** in 84% yield, while its ^{13}C-NMR showed the presence of imine carbon signal at δ 184.96.

Reduction of **9** with Sn–HCl afforded **10** in 90% yield. The compound **10** is an useful compound for obtaining various novel derivatives having 7α-substituted yohimbine skeleton. For example, acetylation with Ac_2O at rt for 40 min produced **11a** in 80% yield, while at rt for 48 h afforded 94% yield of **11b**.

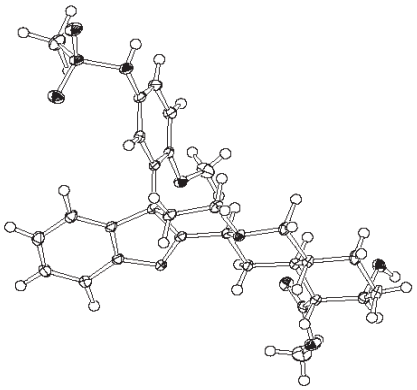


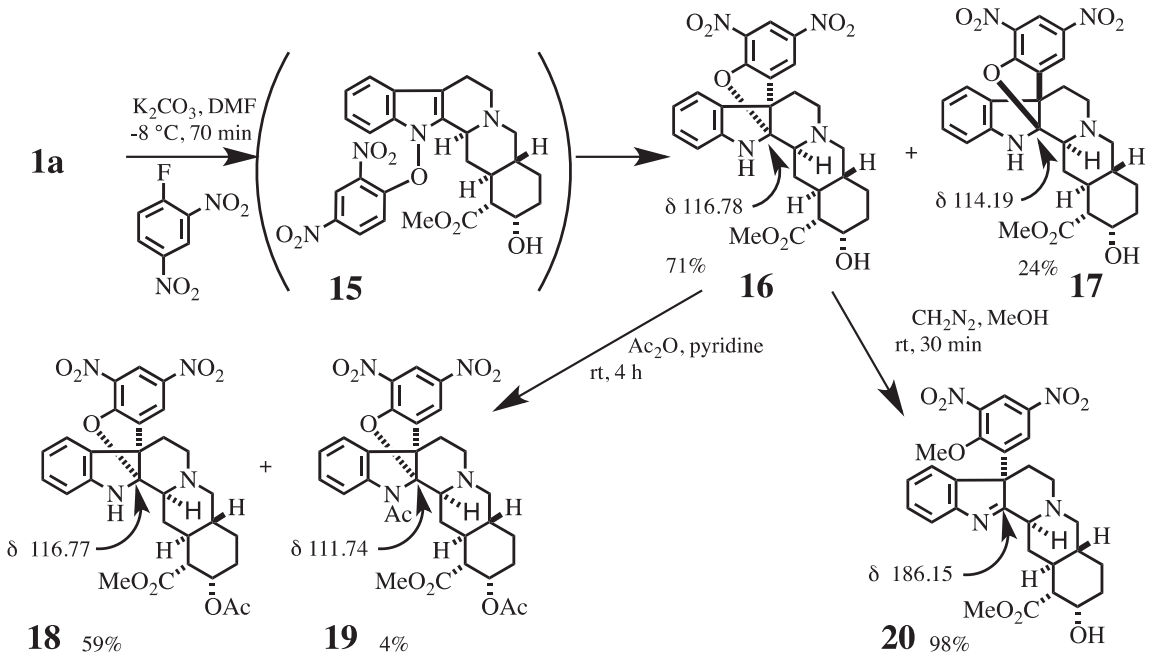
Figure 2

ORTEP drawing of **14**
R=0.038 and *R*w=0.049

Treatment of **10** with either benzoyl chloride, benzenesulfonyl chloride or mesyl chloride afforded the corresponding derivatives, **12**, **13,** and **14** in 83, 95, and 95% yields, respectively. The results of X-ray analysis of **14** are shown in

Figure 2, proving the structures of **9** through **14** including stereo-chemistries as depicted in Scheme 2.

The reaction of **1a** with 2,4-dinitrofluorobenzene in the presence of K_2CO_3 produced **16** and **17** in 71% and 24% yields, respectively (Scheme 3). These were produced through the intermediate **15**, followed by the rearrangement of 2,4-dinitrophenoxy group. The rearrangement proceeded mainly in the α-side similar to the reaction with *p*-fluoronitrobenzene and the major product **16** has the fused benzofuran moiety in the α-side. The presence of benzofuran fusion in **16** and **17** is proved by their ^{13}C-NMR spectrum exhibiting δ 116.78 and δ 114.19 ppm signals, respectively. Further treatment of **16** with Ac_2O-pyridine afforded 59% yield of monoacetyl (**18**) and 4% yield of diacetyl compound (**19**). On the other hand, treatment of **16** with diazomethane produced 98% yield of **20** whose ^{13}C-NMR showed newly formed imine carbon at δ 186.15 ppm proving the opening of benzofuran ring during methylation.



Scheme 3

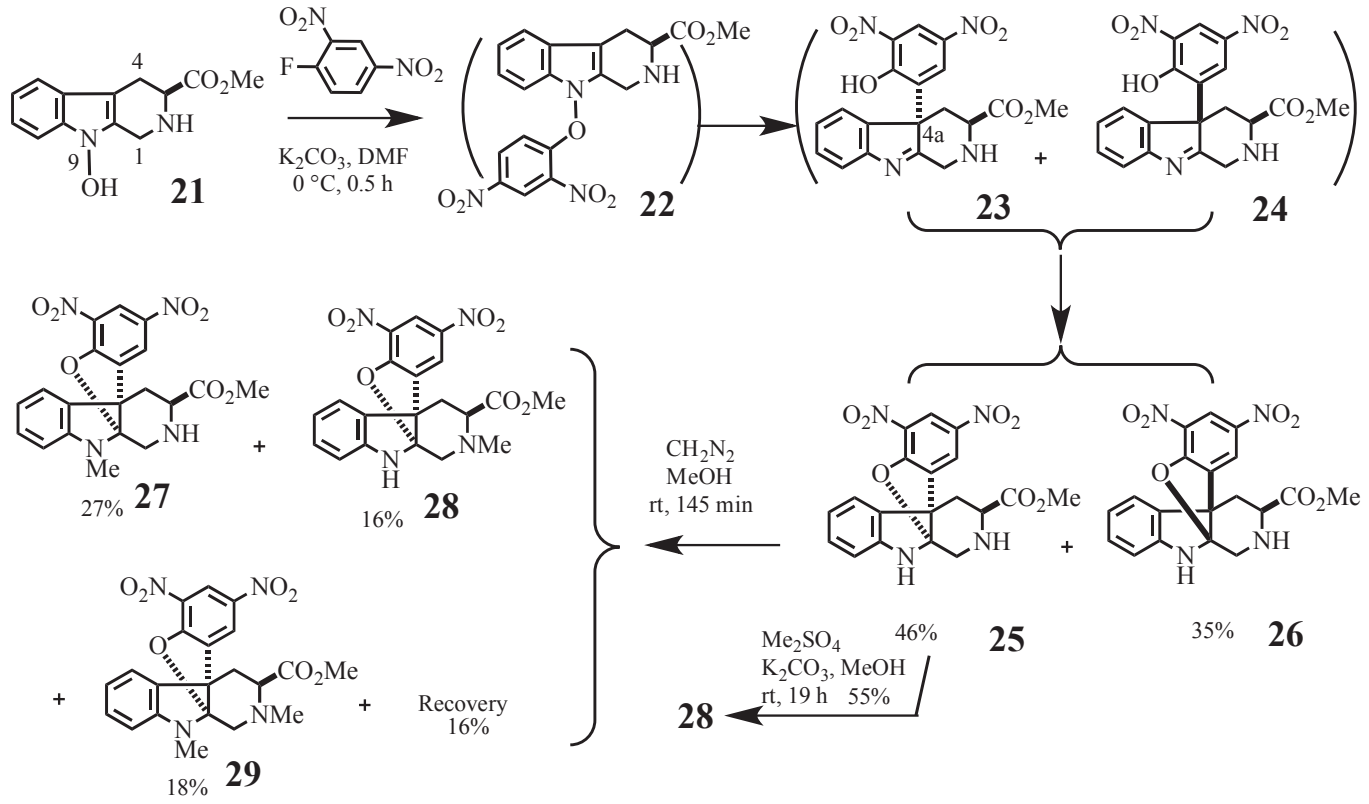
II. In the case of 9-hydroxy-1,2,3,4-tetrahydro-β-carboline derivatives

9-Hydroxy-3β-methoxycarbonyl-1,2,3,4-tetrahydro-β-carboline (**21**) was prepared according to our procedures.[9] In order to get novel 4a-heteroaromatic substituted derivatives, we tried the reaction of **21** with 2,4-dinitrofluorobenzene (Sanger reagent). In the presence of K_2CO_3, **21** afforded major product **25** and minor product **26** in 46 and 35% yields, respectively (Scheme 4).

The mechanism for their production might be explained as follows: initial formation of 1-aryloxy compound (**22**), and then rearrangement of aryloxy group to 4a position to give **23** and **24**, followed by the cyclization of phenolic oxygen to the newly formed imine carbon, culminating in the benzofuran-ring

formation of **25** and **26**. The rearrangement occurs at the less hindered α side and afford the benzofuran fused product from the α-side as the major product. Therefore, the minor product **26** is the corresponding β-isomer as for benzofuran ring.

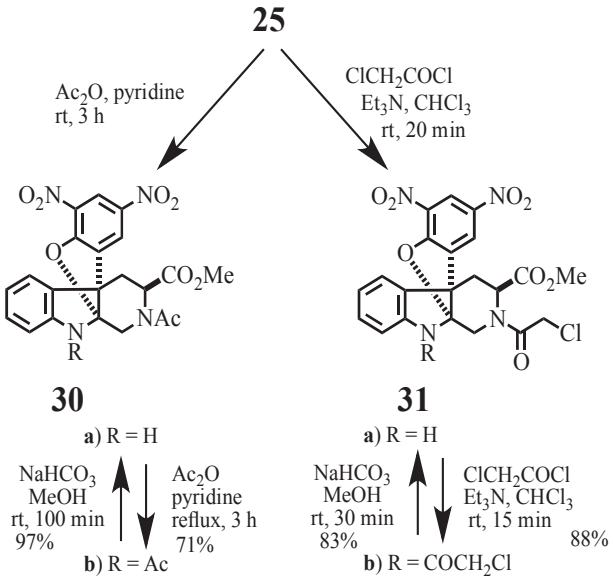
To determine their structures, various derivatizations were examined (Scheme 4). Thus, treatment of **25** with diazomethane gave **27**, **28**, and **29** in 27, 16, and 18% yields, respectively. Methylation of **25** with Me_2SO_4–K_2CO_3, afforded single isomer (**28**) in 55% yield with 17% yield of recovery. Further derivatization of **25** was carried out with Ac_2O–pyridine to yield **30a** and **30b** in 59% and 30% yields, respectively (Scheme 5). Further acetylation of **30a** afforded diacetylated **30b** in 71% yield, while mild hydrolysis of **30b** with $NaHCO_3$ provided **30a** in 97% yield. Treatment of **25** with chloroacetyl chloride–Et_3N formed **31a** and **31b** in 24 and 39% yields, respectively.



Scheme 4

Additional chloroacetylation of **31a** gave bis(chloroacetyl) compound **31b** in 88% yield. Partial hydrolysis of **31b** with $NaHCO_3$–MeOH afforded **31a** in 83% yield. Through extensive investigations of the spectroscopic data of the above many derivatives, we could not obtain any clues for their structures. However, **30a** formed a suitable prisms for X-ray single crystallographic analysis and the structure was finally determined unequivocally. The ORTEP drawing of **30a** is shown in Figure 3.

Since **30a** was proved to have benzofuran fused structure in the α side of β-carboline, the structures of **25** and **26—31** were determined as shown in Schemes 4 and 5. In combination with these results and ^{13}C-NMR data, the presence of benzofuran structure in yohimbine derivatives (**7** and **8**) are confirmed.



Scheme 5

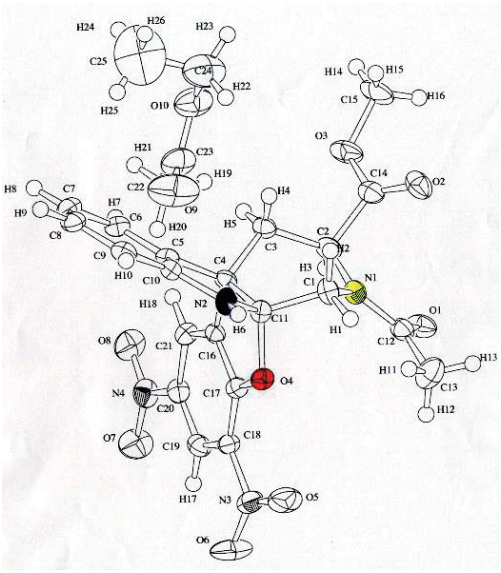


Figure 3

ORTEP drawing of **30a** *R*=0.060 and *R*w=0.091

In summary, we demonstrated further examples of rearrangement reactions based on 1-hydroxyindole chemistry and succeeded in the production of thus far unknown 7β- and 7α-heteroarylyohimbines, and 4aα- and 4aβ-heteroaryl-1,2,3,4-tetrahydro-β-carboline derivatives. We hope these novel compounds reported in this text would become a new member of our group of biologically active compounds that we have created so far.[10]

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra with a Shimadzu IR-420, a Shimadzu IR-460, and a Horiba FT-720 spectrophotometer and proton nuclear magnetic resonance (^{1}H-NMR) spectra with a JEOL JNM-GSX 500 spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL SX-102A spectrometer. Column chromatography was performed on silica gel (SiO_2, 100-200 mesh, from Kanto Chemical Co. Inc.) throughout the present study. The solution of diazomethane (CH_2N_2) in diethyl ether (Et_2O) was prepared as follows: a solution of potassium hydroxide (KOH) (5.50 g, 98.0 mmol) in H_2O (8.0 mL) was placed in a 500 mL round bottom flask and cooled in an ice bath. The 95%

EtOH (25 mL), Et_2O (60.0 mL), and *p*-tolylsulfonylmethylnitrosoamide (21.5 g, 100 mmol) were added and the whole was slowly distilled to give the Et_2O solution including about 3 g of CH_2N_2.

7α-Acetoxy- (3a) and 7α,17α-dacetoxy-7*H*-yohimbine (3b) from 1-hydroxyyohimbine (1a) — 98% NaOAc (93.6 mg, 1.1 mmol) was added to a solution of **1a** (207.1 mg, 0.56 mmol) in Ac_2O (10.0 mL) at rt and stirred at 65 °C for 1 h. After evaporation of the solvent and adding H_2O, the whole was made alkaline with 0.8% NaOH under ice cooling. The whole was extracted with $CHCl_3$ and the extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (97:3, v/v) to give **3a** (163.4 mg, 66%) and **3b** (21.4 mg, 8%). **3a**[8]: mp 120—122 °C (yellow powder, recrystallized from Et_2O–hexane). IR (KBr): 1747, 1726, 1597, 1203, 1146, 1111, 1078, 1018, 775, 758 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.36—1.63 (5H, m), 1.78—2.09 (4H, m), 2.06 (3H, s), 2.18 (1H, t, *J*=11.0 Hz), 2.37 (1H, dd, *J*=11.0, 2.0 Hz), 2.61—2.77 (3H, m), 2.91 (1H, dd, *J*=11.0, 3.4 Hz), 2.94 (1H, dd, *J*=11.0, 2.7 Hz), 3.15 (1H, s, disappeared on addition of D_2O), 3.76 (3H, s), 4.18 (1H, s), 7.20 (1H, dd, *J*=7.6, 7.3 Hz), 7.37 (1H, dd, *J*=7.6, 7.3 Hz), 7.38 (1H, d, *J*=7.6 Hz), 7.61 (1H, d, *J*=7.6 Hz). MS *m/z*: 412 (M^+). *Anal*. Calcd for $C_{23}H_{28}N_2O_5 \cdot 3/2H_2O$: C, 62.85; H, 7.11; N, 6.37. Found: C, 62.86; H, 7.28; N, 6.18. $[\alpha]^{23}_D$ +189° (c 0.221, $CHCl_3$). **3b**: mp 190—191 °C (pale yellow prisms, recrystallized from Et_2O–hexane). IR (KBr): 1736, 1597, 1369, 1254, 1147, 1024, 754 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.38—1.52 (4H, m), 1.59—1.68 (1H, m), 1.69 (1H. q, *J*=12.0 Hz), 1.90—2.03 (2H, m), 2.05 (3H, s), 2.06 (3H, s), 2.22 (1H, t, *J*=10.5 Hz), 2.30 (1H, dt, *J*=12.9, 3.0 Hz), 2.42 (1H, dd, *J*=11.5, 2.4 Hz), 2.64—2.78 (3H, m), 2.93 (1H, dd, *J*=11.0, 3.0 Hz), 3.06 (1H, dd, *J*=11.0, 2.4 Hz), 3.64 (3H, s), 5.41 (1H, dd, *J*=5.4, 2.4 Hz), 7.19 (1H, ddd, *J*=7.6, 7.3, 1.0 Hz), 7.36 (1H, ddd, *J*=7.8, 7.6. 1.0 Hz), 7.39 (1H, dd, *J*=7.3, 1.0 Hz), 7.59 (1H, dd, *J*=7.8, 1.0 Hz). *Anal*. Calcd for $C_{25}H_{30}N_2O_6$: C, 66.06; H, 6.65; N, 6.16. Found: C, 65.99; H, 6.78; N, 6.06. $[\alpha]^{30}_D$ +188° (c 0.201, $CHCl_3$).

(2α,7α)- (7) and (2β,7β)-26-Nitrobenzofurano[2,3-*n*]yohimbine (8) from 1a — A solution of K_2CO_3 (374.2 mg, 2.71 mmol) and *p*-bromonitrobenzene (329.2 mg, 1.63 mmol) in DMF (3.0 mL) was added to a solution of **1a** (500.5 mg, 1.35 mmol) in DMF (12.0 mL) and the whole was stirred at rt for 22 h. After addition of H_2O, the whole was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with EtOAc–hexane (1:1, v/v) to give **7** (358.0 mg, 53%) and **8** (89.6 mg, 13%). **7**: mp 275—276 °C (decomp., yellow powder, recrystallized from EtOAc–hexane). IR (film): 3545, 3392, 2360, 1596, 1506, 1387, 1327 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.30—1.77 (5H, m), 1.84—2.17 (6H, m), 2.20—2.32 (1H, m), 2.35 (1H, dd, *J*=12.5, 2.5 Hz), 2.60—2.97 (3H, m), 3.07 (1H, brs, disappeared on addition of D_2O), 3.83 (3H, s), 4.20 (1H, brs), 5.21 (1H, brs, disappeared on addition of D_2O), 6.77 (1H, d, *J*=9.2 Hz), 6.82 (1H,

dd, *J*=8.3, 1.7 Hz), 6.82 (1H, t, *J*=7.5 Hz), 7.01 (1H, dd, *J*=8.3, 1.7 Hz), 7.10 (1H, ddd, *J*=8.3, 8.3, 1.2 Hz), 8.12 (1H, dd, *J*=8.8, 2.5 Hz), 8.30 (1H, d, *J*=2.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 175.62 (C), 164.64 (C), 145.02 (C), 142.25 (C), 132.98 (C), 132.43 (C), 128.47 (CH), 126.02 (CH), 122.47 (CH), 121.04 (CH), 118.91 (CH), 111.93 (C), 110.68 (CH), 109.94 (CH), 66.52 (CH), 64.73 (CH), 61.42 (CH_2), 55.11 (C), 52.25 (CH_3), 52.03 (CH), 51.44 (CH_3), 40.09 (CH), 36.14 (CH), 31.73 (CH_2), 31.06 (CH_2), 29.74 (CH_2), 23.03 (CH_2). MS *m/z*: 491 (M^+). *Anal*. Calcd for $C_{27}H_{29}N_3O_6 \cdot 1/4H_2O$: C, 65.38; H, 5.99; N, 8.47. Found: C, 65.41; H, 5.89; N, 8.54. $[\alpha]^{23}_D$ +310° (c 0.221, MeOH). **8**: yellow viscous oil. IR (film): 3508, 3352, 1728, 1518, 1338 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23—1.62 (4H, m), 1.74—1.92 (4H, m), 1.92—2.00 (2H, m), 2.06 (1H, ddd, *J*=11.7, 11.7, 2.9 Hz), 2.33 (1H, dd, *J*=10.7, 2.4 Hz), 2.38 (1H, dd, *J*=10.9, 2.1 Hz), 2.59 (1H, dd, *J*=14.2, 3.4 Hz), 2.72 (1H, ddd, *J*=11.7, 4.2, 4.2 Hz), 2.81 (1H, brs, disappeared on addition of D_2O), 2.84 (1H, dd, *J*=11.2, 2.7 Hz), 3.83 (3H, s), 4.23 (1H, brs), 4.71 (1H, brs, disappeared on addition of D_2O), 6.63 (1H, d, *J*=7.8 Hz), 6.90 (1H, t, *J*=7.6 Hz), 6.95 (1H, d, *J*=8.8 Hz), 7.13 (1H, td, *J*=7.7, 1.2 Hz), 7.39 (1H, d, *J*=7.1 Hz), 7.94 (1H, d, *J*=2.4 Hz), 8.09 (1H, d, *J*=8.8, 2.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 175.62 (C), 162.15 (C), 147.60 (C), 142.87 (C), 136.19 (C), 129.03 (CH), 128.39 (C), 125.57 (CH), 122.57 (CH), 122.55 (CH), 120.44 (CH), 119.41 (CH), 110.92 (CH), 110.21 (C), 109.68 (CH), 66.82 (CH), 66.27 (CH), 61.63 (CH_2), 54.82 (C), 52.30 (CH), 52.04 (CH_3), 51.20 (CH_3), 39.95 (CH), 36.24 (CH), 31.78 (CH_2), 31.29 (CH_2), 29.40 (CH_2), 23.04 (CH_2). HR–MS *m/z*: Calcd for $C_{27}H_{29}N_3O_6$: 491.2057. Found: 491.2058. $[\alpha]^{23}_D$ +59.0° (c 0.370, MeOH).

7α-(2-Methoxy-5-nitrophenyl)-7*H*-yohimbine (9) from 7 — Excess CH_2N_2 in Et_2O was added to a solution of **7** (165.0 mg, 0.34 mmol) in MeOH (5 mL) and the whole was stirred at rt for 30 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **9** (142.8 mg, 84%) and unreacted **7** (26.7 mg, 16%). **9**: mp 171.5—172 °C (yellow prisms, recrystallized from $CHCl_3$–hexane). IR (KBr): 3392, 1734, 1589, 1344, 1269 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.33—1.85 (5H, m), 1.87—2.04 (2H, m), 2.05—2.32 (2H, m), 2.41—2.71 (3H, m, 1H disappeared on addition of D_2O), 2.87—3.24 (4H, m), 3.55 (3H, brs), 3.77 (3H, s), 4.67 (1H, brs), 6.86 (1H, d, *J*=10.0 Hz), 7.05 (1H, d, *J*=8.3 Hz), 7.15 (1H, t, *J*=8.3 Hz), 7.35 (1H, ddd, *J*=8.3, 8.3, 1.7 Hz), 7.73 (1H, d, *J*=8.3 Hz), 8.22 (1H, dd, *J*=10.0, 3.3 Hz), 8.51 (1H, brs). ^{13}C-NMR ($CDCl_3$) δ: 184.96 (C), 175.18 (C), 162.15 (C), 155.02 (C), 142.95 (C), 141.78 (C), 128.12 (CH), 125.54 (CH), 125.09 (CH), 123.85 (CH), 121.76 (CH), 120.95 (CH), 111.37 (CH), 67.06 (CH), 61.40 (C), 61.26 (CH_2), 59.09 (C), 55.85 (CH_3), 52.26 (CH_3), 51.80 (CH), 51.13 (CH_2), 50.66 (CH), 40.11 (CH), 36.59 (CH_2), 35.99 (CH), 31.45 (CH_2), 31.41 (CH_2), 23.06 (CH_2). HR–MS *m/z*: Calcd for $C_{28}H_{31}N_3O_6$: 505.2213. Found: 505.2206. $[\alpha]^{29}_D$ +289° (c 0.141, DMF).

7α-(5-Amino-2-methoxyphenyl)-7*H*-yohimbine (10) from 9 — Tin powder (75.6 mg, 0.64 mmol) was

added to a solution of **9** (30.9 mg, 0.06 mmol) in MeOH–8% HCl (3:1, v/v, 6.0 mL) and the whole was stirred at rt for 40 min. The resulting solution was made alkaline with 6% NaOH under ice cooling, and the whole was extracted with $CHCl_3$–MeOH–28% aq. NH_3 (46:3:0.3, v/v). The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH–28% aq. NH_3 (46:2:0.2, v/v) to give **10** (26.7 mg, 90%). **10**: mp 262—264 °C (decomp., yellow prisms, recrystallized from EtOAc–MeOH). IR (KBr): 3452, 3336, 3234, 2933, 1745, 1500, 1236, 1144, 1109, 1018 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.04 (1H, t, *J*=13.1 Hz), 1.61—1.43 (3H, m), 1.52—1.65 (2H, m), 1.70—1.79 (2H, m), 1.88 (1H, t, *J*=10.4 Hz), 2.15 (1H, brd, *J*=12.7 Hz), 2.25—2.33 (2H, m), 2.38—2.54 (1H, m), 2.65 (1H brd, *J*=11.5 Hz), 2.76 (1H, dd, *J*=10.9, 3.1 Hz), 2.83—3.11 [1H, m, on addition of D_2O, it changed to 2.89 (1H, brd, *J*=10.3 Hz)], 3.27 (3H, s), 3.64 (3H, s), 4.12 (1H, s), 4.20 (1H, brd, *J*=4.4 Hz, disappeared on addition of D_2O), 4.55 (2H, brs, disappeared on addition of D_2O), 6.48 (1H, dd, *J*=8.5, 2.7 Hz), 6.63 (1H, d, *J*=8.5 Hz), 6.84 (1H, brs), 7.06 (1H, t, *J*=7.4 Hz), 7.14 (1H, d, *J*=7.4 Hz), 7.23 (1H, t, *J*=7.4 Hz), 7.49 (1H, d, *J*=7.4 Hz). MS *m/z*: 475 (M^+). *Anal*. Calcd for $C_{28}H_{33}N_3O_4 \cdot 1/2H_2O$: C, 69.40; H, 7.07; N, 8.67. Found: C, 69.60; H, 7.10; N, 8.60. $[\alpha]^{30}_D$ +255° (c 0.210, MeOH).

17α-Acetoxy- (11b) and 7α-(5-acetylamino-2-methoxyphenyl)-7*H*-yohimbine (11a) from 10 — [**Entry 1]** Ac_2O (1.0 mL) was added to a solution of **10** (33.5 mg, 0.07 mmol) in pyridine (2.0 mL) and the whole was stirred at rt for 40 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH–30% aq. NH_3 (46:3:0.3, v/v) to give **11a** (30.3 mg, 80%) and **11b** (2.6 mg, 7%). [**Entry 2**] Ac_2O (1.0 mL) was added to a solution of **10** (28.4 mg, 0.06 mmol) in pyridine (2.0 mL) and the whole was stirred at rt for 2 days. The same work-up and purification as Entry 1 afforded **11b** (31.8 mg, 94%). **11a**: mp 180—182 °C (colorless powder, recrystallized from EtOAc–hexane). IR (KBr): 3434, 2927, 1731, 1668, 1608, 1548, 1500, 1244, 1146, 1024 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.09 (1H, td, *J*=3.3, 13.2 Hz), 1.17—1.41 (3H, m), 1.50—1.58 (1H, m), 1.62 (1H, q, *J*=11.9 Hz), 1.70—1.78 (2H, m), 1.84 (1H, t, *J*=10.8 Hz), 2.03 (3H, s), 2.14—2.19 (1H, m), 2.26—2.30 (2H, m), 2.43—2.53 (1H, m), 2.69—2.64 (1H, m), 2.76 (1H, dd, *J*=10.8, 3.5 Hz), 2.83 (1H, brd, *J*=10.8 Hz), 3.42 (3H, s), 3.64 (3H, s), 4.10—4.14 (1H, m), 4.21 (1H, d, *J*=4.6 Hz, disappeared on addition of D_2O), 6.84 (1H, d, *J*=8.8 Hz), 7.07 (1H, td, *J*=1.2, 7.5 Hz), 7.13 (1H, brd, *J*=7.5 Hz), 7.25 (1H, td, *J*=1.2, 7.5 Hz), 7.46 (1H, dd, *J*=7.8, 2.3 Hz), 7.51 (1H, brd, *J*=7.5 Hz), 7.72 (1H, brs), 9.56 (1H, s, disappeared on addition of D_2O). MS *m/z*: 517 (M^+). *Anal*. Calcd for $C_{30}H_{35}N_3O_5 \cdot H_2O$: C, 67.27; H, 6.96; N, 7.84. Found: C, 67.29; H, 6.92; N, 7.54. $[\alpha]^{28}_D$ +249° (c 0.411, MeOH). **11b**: mp 218—220 °C (orange prisms, recrystallized from EtOAc–hexane). IR (KBr): 3430, 2927, 1739, 1664, 1610, 1500, 1244, 1025 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.05—1.14 (1H, m), 1.19—1.45 (3H, m), 1.63—1.75 (3H, m), 1.79—1.86

(1H, m), 1.87—1.93 (1H, m), 1.94 (3H, s), 2.03 (3H, s), 2.06—2.12 (1H, m), 2.30 (1H, t, *J*=12.9 Hz), 2.38—2.55 (2H, m), 2.69 (1H, d, *J*=11.7 Hz), 2.80 (1H, d, *J*=8.3 Hz), 2.82—3.15 (1H, m), 3.40 (3H, s), 3.63 (3H, s), 5.28 (1H, brd, *J*=2.7 Hz), 6.84 (1H, d, *J*=8.8 Hz), 7.08 (1H, t, *J*=7.7 Hz), 7.13 (1H, brd, *J*=7.7 Hz), 7.25 (1H, t, *J*=7.7 Hz), 7.47 (1H, dd, *J*=8.8, 2.1 Hz), 7.52 (1H, d, *J*=7.7 Hz), 7.72 (1H, brs), 9.58 (1H, brs, disappeared on addition of D_2O). MS *m/z*: 559 (M^+). *Anal*. Calcd for $C_{32}H_{37}N_3O_6 \cdot 1/2H_2O$: C, 67.59; H, 6.74; N, 7.39. Found: C, 67.38; H, 6.57; N, 7.42. $[\alpha]^{24}_D$ +215° (c 0.204, $CHCl_3$).

7α-(5-Benzoylamino-2-methoxyphenyl)-7*H*-yohimbine (12) from 10 — Benzoyl chloride (0.02 mL, 0.16 mmol) was added to a solution of **10** (37.0 mg, 0.08 mmol) in pyridine (5.0 mL) and the mixture was stirred at rt for 1 h. After adding H_2O, the whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (95:5, v/v) to give **12** (38.8 mg, 83%). **12**: mp 191—193 °C (decomp., colorless prisms, recrystallized from $CHCl_3$–hexane). IR (KBr): 3435, 2927, 1732, 1649, 1500, 1111, 1026 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.13 (1H, td, *J*=13.2, 3.4 Hz), 1.19—1.59 (4H, m), 1.66 (1H, q, *J*=11.8 Hz), 1.73—1.92 (2H, m), 2.19 (1H, d, *J*=12.7 Hz), 2.25—2.37 (2H, m), 2.39—2.55 (1H, m), 2.70 (1H, brd, *J*=11.8 Hz), 2.78 (1H, dd, *J*=10.9, 3.1 Hz), 2.84—3.00 (1H, m), 3.14 (1H, brd, *J*=13.7 Hz), 3.44 (3H, brs), 3.65 (3H, s), 4.09 (1H, brs, disappeared on addition of D_2O), 4.13 (1H, brs), 6.90 (1H, d, *J*=8.8 Hz), 7.08 (1H, td, *J*=7.5, 1.1 Hz), 7.17 (1H, brd, *J*=7.5 Hz), 7.25 (1H, td, *J*=7.5, 1.1 Hz), 7.48—7.58 (4H, m), 7.68 (1H, dd, *J*=8.8, 2.4 Hz), 7.90—8.00 (3H, m), 9.86 (1H, brs, disappeared on addition of D_2O). MS *m/z*: 579 (M^+). *Anal*. Calcd for $C_{35}H_{37}N_3O_5 \cdot H_2O$: C, 70.33; H, 6.58; N, 7.03. Found: C, 70.30; H, 6.36; N, 7.16. $[\alpha]^{28}_D$ +239° (c 0.232, MeOH).

7α-(5-Benzenesulfonylamino-2-methoxyphenyl)-7*H*-yohimbine (13) from 10 — Benzenesulfonyl chloride (0.03 mL, 0.24 mmol) was added to a solution of **10** (54.8 mg, 0.12 mmol) in pyridine (6.0 mL) and the mixture was stirred at rt for 20 min. After adding H_2O, the whole was extracted with $CHCl_3$–MeOH (97:3, v/v). The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (95:5, v/v) to give **13** (68.0 mg, 95%). **13**: mp 277—279 °C (decomp., colorless prisms, recrystallized from MeOH). IR (KBr): 3388, 2924, 1738, 1500, 1460, 1441, 1163 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.03 (1H, td, *J*=13.4, 3.2 Hz), 1.18—1.32 (2H, m), 1.40 (1H, qd, *J*=12.5, 3.2 Hz), 1.50—1.64 (2H, m), 1.70—1.82 (2H, m), 2.01 (1H, t, *J*=11.8 Hz), 2.13 (1H, td, *J*=12.5, 3.2 Hz), 2.26 (1H, dd, *J*=11.8, 2.4 Hz), 2.45—2.52 (1H, m), 2.56 (1H, d, *J*=11.8 Hz), 2.67 (1H, d, *J*=11.0 Hz), 2.73 (1H, dd, *J*=11.0, 3.2 Hz), 2.80—3.00 (1H, m), 3.41 (3H, s), 3.65 (3H, s), 4.13 (2H, brs, disappeared 1H, on addition of D_2O), 6.80 (1H, d, *J*=8.5 Hz), 6.92 (1H, brd, *J*=7.6 Hz), 7.00 (1H, dd, *J*=8.5, 2.4 Hz), 7.04 (1H, t, *J*=7.6 Hz), 7.13 (1H, brs), 7.23 (1H, td, *J*=7.6, 1.2 Hz), 7.48 (1H, t, *J*=7.6 Hz), 7.53 (2H, t, *J*=7.6 Hz), 7.60 (1H, tt, *J*=7.6, 1.7 Hz), 7.73 (2H, dd,

J=7.6, 1.7 Hz), 9.55 (1H, brs, disappeared on addition of D_2O). MS *m/z*: 615 (M^+). *Anal*. Calcd for $C_{34}H_{37}N_3O_6S \cdot 1/2H_2O$: C, 65.84; H, 6.09; N, 6.77. Found: C, 65.91; H, 6.12; N, 6.75. $[\alpha]^{25}_D$ +223° (c 0.200, MeOH).

7α-(5-Mesylamino-2-methoxyphenyl)-7*H*-yohimbine (14) from 10 — MsCl (0.014 mL, 0.18 mmol) was added to a solution of **10** (42.3 mg, 0.09 mmol) in pyridine (5.0 mL) and the whole was stirred at rt for 40 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with EtOAc–MeOH (93:7, v/v) to give **14** (48.1 mg, 95%). **14**: mp 183.0—185.0 °C (colorless fine prisms, recrystallized from MeOH). IR (KBr): 3438, 1732, 1498, 1327, 1146 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 1.12 (1H, td, *J*=13.3, 3.4 Hz), 1.18—1.34 (2H, m), 1.37 (1H, qd, *J*=12.3, 3.4 Hz), 1.50—1.58 (1H, m), 1.65 (1H, q, *J*=11. 5 Hz), 1.71—1.80 (2H, m), 1.83—1.91 (1H, m), 2.16 (1H, d, *J*=12.3Hz), 2.28 (1H, dd, *J*=11.5, 2.0 Hz), 2.43—2.52 (1H, m), 2.65—2.71 (1H, m), 2.77 (1H, brd, *J*=11.5 Hz), 2.80—3.00 [1H, m, on addition of D_2O, it changed to 2.80—2.90 (1H, m)], 2.80—3.00 [3H, m, changed to 2.94 (3H, s) on addition of D_2O], 3.11 (1H, brd, *J*=13.3 Hz), 3.44 (3H, s), 3.65 (3H, s), 4.08 (1H, brs, disappeared on addition of D_2O), 4.13 (1H, brs), 6.89 (1H, d, *J*=8.9 Hz), 7.07 (1H, t, *J*=7.2 Hz), 7.13 (1H, d, *J*=7.2 Hz), 7.14 (1H, dd, *J*=8.9, 2.7 Hz), 7.25 (1H, td, *J*=7.2, 1.2 Hz), 7.42 (1H, brs), 7.52 (1H, d, *J*=7.2 Hz), 9.05 (1H, brs, disappeared on addition of D_2O). ^{13}C-NMR ($CDCl_3$) δ: 186.12 (C), 175.25 (C), 155.61 (C), 154.80 (C), 143.70 (C), 129.97 (C), 128.19 (C), 127.80 (CH), 125.36 (CH), 123.68 (CH), 123.10 (CH), 121.98 (CH), 120.74 (CH), 112.92 (CH), 67.15 (CH), 61.52 (CH), 61.35 (CH_2), 59.22 (C), 55.59 (CH_3), 52.27 (CH), 51.86 (CH_3), 51.34 (CH_2), 40.08 (CH), 39.00 (CH_3), 36.89 (CH_2), 36.04 (CH), 31.50 (CH_2), 31.40 (CH_2), 23.08 (CH_2). *Anal*. Calcd for $C_{29}H_{35}N_3O_6S \cdot 3/4H_2O$: C, 61.41; H, 6.49; N, 7.41. Found: C, 61.48; H, 6.39; N, 7.49. $[\alpha]^{25}_D$ +204° (c 0.250, $CHCl_3$).

(2α,7α)- (16) and (2β,7β)-24,26-Dinitrobenzofurano[2,3-*n*]yohimbine (17) from 1a — A solution of K_2CO_3 (76.7 mg, 0.55 mmol) and 2,4-dinitrofluorobenzene (62.8 mg, 0.34 mmol) in DMF (1.0 mL) was added to a solution of **1a** (102.8 mg, 0.28 mmol) in DMF (4.0 mL) and the whole was stirred at –8 °C for 70 min. After addition of H_2O, the whole was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (99:1, v/v) to give **16** (106.0 mg, 71%) and **17** (35.2 mg, 24%). **16**: yellow viscous oil. IR (film): 3481, 3286, 2934, 1701, 1622, 1606, 1535, 1523, 1473, 1437, 1375, 910 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.34—1.39 (1H, m), 1.44—1.54 (4H, m), 1.88—1.91 (5H, m), 2.15 (1H, dt, *J*=12.4, 2.4 Hz), 2.22 (1H, dd, *J*=11.5, 2.4 Hz), 2.33 (1H, dd, *J*=11.5, 1.7 Hz), 2.67—2.70 (1H, m), 2.75—2.78 (1H, m), 2.87 (1H, dd, *J*=11.5, 1.7 Hz), 3.11 (1H, disappeared on addition of D_2O), 3.84 (3H, s), 4.22 (1H, d, *J*=0.7 Hz), 5.41 (1H, s, disappeared on addition of D_2O), 6.84 (1H, dd, *J*=8.0, 0.7 Hz), 6.85 (1H, td, *J*=8.0, 0.7 Hz), 6.99 (1H, dd, *J*=8.0, 0.7 Hz), 7.15 (1H, dd, *J*=8.0, 0.7 Hz), 8.48 (1H,

d, *J*=2.2 Hz), 8.89 (1H, d, *J*=2.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 175.17 (C), 158.84 (C), 144.70 (C), 141.06 (C), 138.25 (C), 131.69 (C), 131.63 (C), 129.17 (CH), 122.59 (CH), 122.35 (CH), 121.76 (CH), 121.58 (CH), 116.78 (C), 115.15 (CH), 66.50 (CH), 64.76 (CH), 61.39 (CH_2), 54.86 (C), 52.34 (CH_3), 52.17 (CH), 51.44 (CH_2), 40.08 (CH), 36.07 (CH), 32.01 (CH_2), 31.06 (CH_2), 29.73 (CH_2), 22.97 (CH_2). HR–MS *m/z*: Calcd for $C_{27}H_{28}N_4O_8$: 536.1907. Found: 536.1903. $[\alpha]^{28}_D$ +258° (c 0.106, MeOH). **17**: yellow viscous oil. IR (film): 3556, 3381, 2935, 1716, 1619, 1608, 1535, 1336, 738 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25—1.60 (5H, m), 1.81—2.00 (5H, m), 2.16—2.22 (2H, m), 2.39—2.50 (2H, m), 2.64—2.67 (1H, m), 2.69 (1H, brs, disappeared on addition of D_2O), 2.77—2.81 (2H, m), 3.82 (3H, s), 5.14 (1H, s, disappeared on addition of D_2O), 6.67 (1H, d, *J*=7.8 Hz), 6.89 (1H, td, *J*=7.8, 1.0 Hz), 7.14 (1H, td, *J*=7.8, 1.0 Hz), 7.31 (1H, d, *J*=7.8 Hz), 8.21 (1H, dd, *J*=2.4, 1.5 Hz), 8.85 (1H, dd, *J*=2.4, 1.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 175.44 (C), 157.82 (C), 147.04 (C), 141.32 (C), 141.03 (C), 131.82 (C), 129.58 (CH), 128.37 (C), 122.78 (CH), 122.59 (CH), 121.30 (CH), 120.77 (CH), 114.19 (C), 109.92 (CH), 66.94 (CH), 64.13 (CH), 61.40 (CH_2), 54.80 (C), 52.06 (CH_3), 52.04 (CH), 50.00 (CH_2), 39.38 (CH), 35.70 (CH), 31.25 (CH_2), 30.22 (CH_2), 29.07 (CH_2), 22.89 (CH_2). HR–MS *m/z*: Calcd for $C_{27}H_{28}N_4O_8$: 536.1907. Found: 536.1902. $[\alpha]^{28}_D$ +121° (c 0.101, MeOH).

(2α,7α)-1-Acetyl- (19) and -17-acetoxy-24,26-dinitrobenzofurano[2,3-*n*]yohimbine (18) from 16 — Ac_2O (1.0 mL) was added to a solution of **16** (40.4 mg, 0.08 mmol) in pyridine (2.0 mL) and the whole was stirred at 60 °C for 4 h. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with EtOAc–hexane (2:1, v/v) to give **18** (26.1 mg, 59%) and **19** (2 mg, 4%). **18**: mp 200—201 °C (decomp., yellow powder, recrystallized from EtOAc–hexane). IR (KBr): 3423, 1749, 1728, 1599, 1572, 1543, 1373, 1355 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23—1.58 (5H, m), 1.63 (1H, m), 1.85—2.07 (4H, m), 2.02 (3H, s), 2.26—2.33 (1H, m), 2.36—2.45 (2H, m), 2.65—2.81 (2H, m), 2.90 (1H, dd, *J*=11.1, 3.1 Hz), 3.71 (3H, s), 5.42 (1H, brs, disappeared on addition of D_2O), 5.43 (1H, d, *J*=2.4 Hz), 6.83 (1H, d, *J*=7.6 Hz), 6.85 (1H, t, *J*=7.6 Hz), 6.99 (1H, d, *J*=7.6 Hz), 7.15 (1H, t, *J*=7.6 Hz), 8.49 (1H, d, *J*=2.3 Hz), 8.90 (1H, d, *J*=2.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.65 (C), 169.99 (C), 158.87 (C), 144.76 (C), 141.02 (C), 138.31 (C), 131.71 (C), 131.52 (C), 129.22 (CH), 122.51 (CH), 122.33 (CH), 121.68 (CH), 121.53 (CH), 116.77 (C), 111.14 (CH), 69.26 (CH), 64.79 (CH), 61.25 (CH_2), 54.83 (C), 52.01 (CH_3), 51.42 (CH_2), 51.36 (CH), 39.45 (CH), 36.16 (CH), 31.96 (CH_2), 29.70 (CH_2), 29.60 (CH_2), 23.68 (CH_2), 20.94 (CH_3). MS *m/z*: 578 (M^+). *Anal*. Calcd for $C_{29}H_{30}N_4O_9 \cdot 1/2H_2O$: C, 59.28; H, 5.32; N, 9.54. Found: C, 59.19; H, 5.33; N, 9.23. $[\alpha]^{24}_D$ +148° (c 0.220, $CHCl_3$). **19**: yellow viscous oil. IR (film): 1743, 1673, 1622, 1533, 1373, 1338 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.02 (1H, dd, *J*=24.7, 12.7 Hz), 1.20—1.36 (2H, m), 1.37—1.47 (1H, m), 1.49—1.66 (2H, m), 1.94—2.03 (2H, m), 2.06 (3H, s), 2.21—2.27 (2H, m), 2.56—2.69 (2H, m), 2.67 (3H, s), 2.74—2.89 (1H, m), 2.83—2.91 (2H, m), 3.63 (3H,

s), 4.25 (1H, dd, *J*=12.8, 2.1 Hz), 5.37 (1H, d, *J*=2.7 Hz), 7.19 (1H, t, *J*=7.6 Hz), 7.29 (1H, t, *J*=7.6 Hz), 7.42 (1H, d, *J*=7.8 Hz), 8.14 (1H, d, *J*=7.8 Hz), 8.18 (1H, d, *J*=2.3 Hz), 8.91 (1H, d, *J*=2.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.30 (C), 170.36 (C), 169.96 (C), 155.86 (C), 143.10 (C), 142.45 (C), 140.51 (C), 132.36 (C), 130.05 (CH), 129.00 (C), 125.00 (CH), 123.03 (CH), 121.57 (CH), 121.56 (CH), 117.45 (CH), 111.74 (C), 69.12 (CH), 62.77 (CH), 60.35 (CH_2), 54.33 (C), 51.90 (CH_3), 50.70 (CH), 41.10 (CH_2), 38.71 (CH), 33.30 (CH), 32.34 (CH_2), 29.74 (CH_2), 25.51 (CH_2), 24.52 (CH_3), 23.11 (CH_2), 21.02 (CH_3). HR–MS *m/z*: Calcd for $C_{31}H_{32}N_4O_{10}$: 620.2118. Found: 620.2124. $[\alpha]^{31}_D$ –38.2° (c 0.192, $CHCl_3$).

7α-(2-Methoxy-3,5-dinitrophenyl)-7*H*-yohimbine (20) from 16 — Excess CH_2N_2 in Et_2O was added to a solution of **16** (5.0 mg, 0.008 mmol) in MeOH (0.5 mL) and the whole was stirred at rt for 30 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (95:5, v/v) to give **20** (5.0 mg, 98%). **20**: yellow oil. IR (KBr): 2927, 1736, 1595, 1541, 1456, 1342, 1267, 1207 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.13—1.36 (5H, m), 1.51—1.63 (2H, m), 1.72—1.76 (2H, m), 1.91 (1H, d, *J*=10.5 Hz), 2.12 (1H, d, *J*=10.8 Hz), 2.30 (1H, dd, *J*=10.5, 2.4 Hz), 2.33 (1H, t, *J*=10.0 Hz), 2.76 (2H, dd, *J*=10.5, 2.4 Hz), 2.84 (1H, brd, *J*=10.0 Hz), 3.02 (3H, brs), 3.62 (3H, s), 4.10 (1H, brt, *J*=2.4 Hz), 4.55 (1H, d, *J*=2.8 Hz, disappeared on addition of D_2O), 7.18 (1H, t, *J*=7.6 Hz), 7.24 (1H, d, *J*=7.6 Hz), 7.36 (1H, t, *J*=7.6 Hz), 7.64 (1H, d, *J*=7.6 Hz), 8.75 (1H, d, *J*=2.4 Hz), 8.92 (1H, brs). ^{13}C-NMR (CD_3OD) δ: 186.15 C), 175.24 (C), 157.33 (C), 155.44 (C), 144.48 (C), 144.38 (C), 144.33 (C), 137.81 (C), 130.01 (CH), 128.51 (CH), 127.69 (CH), 123.72 (CH), 122.37 (CH), 121.82 (CH), 68.52 (CH), 62.92 (CH), 62.65 (CH_3), 62.04 (CH_2), 60.94 (C), 53.94 (CH), 52.09 (CH_3), 51.85 (CH_2), 41.22 (CH), 37.71 (CH_2), 36.54 (CH), 33.40 (CH_2), 32.56 (CH_2), 24.18 (CH_2). HR–MS *m/z*: Calcd for $C_{28}H_{30}N_4O_8$: 550.2063. Found: 550.2059. $[\alpha]^{26}_D$ +258° (c 0.101, MeOH).

(*S*)-(4aα,9aα)- (25) and (*S*)-(4aβ,9aβ)-3β-Methoxycarbonyl-11,13-dinitro-1,2,3,4-tetrahydro-9*H*-benzofurano[2,3-*m*]-β-carboline (26) from 21 — A solution of K_2CO_3 (168.5 mg, 1.2 mmol) and 2,4-dinitrofluorobenzene (84.6 mg, 0.45 mmol) in DMF (3.0 mL) was added to a solution of **21** (100.0 mg, 0.41 mmol) in DMF (7.0 mL) and the whole was stirred at 0 °C for 30 min. After addition of H_2O, the whole was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with EtOAc–hexane–Et_2O (1:1:1, v/v) to give **25** (77.5 mg, 46%), **26** (58.0 mg, 35%), and unreacted **21** (7.1 mg, 7%). **25**: mp 158.0—160.0 °C (yellow needles, recrystallized from Et_2O–hexane). IR (KBr): 3392, 1736, 1620, 1608, 1533, 1473, 1437, 1336 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.02 (1H, dd, *J*=14.4, 11.4 Hz), 2.04 (1H, brs, disappeared on addition of D_2O), 3.02 (1H, dd, *J*=14.4, 4.7 Hz), 3.23 (1H, d, *J*=14.2 Hz), 3.38 (1H, dd, *J*=11.4, 4.4 Hz), 3.69 (1H, d, *J*=14.2 Hz), 3.71 (3H, s), 5.41 (1H, brs, disappeared on addition of D_2O), 6.80 (1H, d, *J*=7.8 Hz), 6.84 (1H, t, *J*=7.8 Hz), 7.12 (1H, d, *J*=7.8 Hz), 7.16 (1H, t,

J=7.8 Hz), 8.51 (1H, dd, *J*=2.0, 1.0 Hz), 8.90 (1H, dd, *J*=2.0, 1.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 172.66 (C), 159.04 (C), 145.78 (C), 141.04 (C), 138.00 (C), 131.25 (C), 130.33 (C), 129.61 (CH), 122.78 (CH), 122.71 (CH), 121.88 (CH), 121.24 (CH), 113.33 (C), 110.54 (CH), 54.69 (C), 52.93 (CH), 52.47 (CH_3), 48.65 (CH_2), 34.50 (CH_2). *Anal.* Calcd for $C_{19}H_{16}N_4O_7 \cdot 1/8H_2O$: C, 55.03; H, 3.95; N, 13.41. Found: C, 55.13; H, 3.94; N, 13.19. $[\alpha]^{28}_D$ +206° (c 0.111, MeOH). **26**: yellow viscose oil. IR (film): 3402, 1732, 1618, 1608, 1533, 1473, 1433, 1333, 1255, 744 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.21 (1H, brs, disappeared on addition of D_2O), 2.55 (1H, dd, *J*=14.6, 6.6 Hz), 2.83 (1H, dd, *J*=14.6, 6.1 Hz), 3.39 (1H, d, *J*=14.4 Hz), 3.57 (1H, d, *J*=14.4 Hz), 3.60 (3H, s), 3.69 (1H, t, *J*=6.4 Hz), 5.17 (1H, s, disappeared on addition of D_2O), 6.75 (1H, d, *J*=8.1 Hz), 6.89 (1H, td, *J*=8.1, 0.7 Hz), 7.17 (1H, td, *J*=8.1, 0.7 Hz), 7.24 (1H, d, *J*=8.1 Hz), 8.36 (1H, d, *J*=2.2 Hz), 8.87 (1H, d, *J*=2.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 173.22 (C), 158.70 (C), 146.70 (C), 141.03 (C), 138.80 (C), 131.45 (C), 129.82 (CH), 129.24 (C), 123.57 (CH), 122.78 (CH), 121.82 (CH), 121.07 (CH), 113.09 (C), 110.14 (CH), 54.49 (C), 52.39 (CH_3), 51.51 (CH), 46.57 (CH_2), 32.30 (CH_2). HR–MS *m/z*: Calcd for $C_{19}H_{16}N_4O_7$: 412.1019. Found: 412.1024. $[\alpha]^{27}_D$ –171° (c 0.100, MeOH).

(*S*)-(4aα,9aα)-3β-Methoxycarbonyl-*N*b-methyl- (28), -*N*a-methyl- (27), and -*N*a,*N*b-dimethyl-11,13-dinitro-1,2,3,4-tetrahydro-9*H*-benzofurano[2,3-*m*]-β-carboline (29) from 25 — Excess CH_2N_2 in Et_2O was added to a solution of **25** (33.0 mg, 0.08 mmol) in MeOH (1.5 mL) and the whole was stirred at rt for 145 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **28** (5.4 mg, 16%), **27** (9.2 mg, 27%), **29** (6.4 mg, 18%), and unreacted **25** (5.4 mg, 16%). **28**: pale viscose oil. IR (film): 3380, 1743, 1621, 1610, 1373, 1336 cm^{-1}. ^{1}H-NMR (DMSO-d_6:D_2O=5:1, v/v) δ: 2.26 (1H, dd, *J*=15.0, 11.7 Hz), 2.37 (3H, s), 2.86 (1H, dd, *J*=15.0, 5.0 Hz), 3.02 (1H, d, *J*=14.2 Hz), 3.11 (1H, dd, *J*=11.7, 5.0 Hz), 3.70 (3H, s), 3.70 (1H, m), 4.52—4.81 (1H, brs, disappeared on addition of D_2O), 6.77 (1H, d, *J*=8.3 Hz), 6.85 (1H, t, *J*=8.3 Hz), 7.13 (1H, d, *J*=8.3 Hz), 7,16 (1H, t, *J*=8.3 Hz), 8.44 (1H, d, *J*=2.5 Hz), 8.89 (1H, d, *J*=2.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 172.30 (C), 159.35 (C), 146.16 (C), 140.95 (C), 138.36 (C), 130.91 (C), 129.68 (CH), 129.63 (C), 122.86 (CH), 122.36 (CH), 121.71 (CH), 121.07 (CH), 114.78 (C), 110.50 (CH), 59.85 (CH), 55.79 (CH_2), 54.19 (C), 52.04 (CH_3), 42.21 (CH_3), 33.77 (CH_2). HR–MS (FAB$^+$) *m/z*: Calcd for $C_{20}H_{18}N_4O_7$: 426.1175. Found: 427.1257. $[\alpha]^{31}_D$ +154° (c 0.234, $CHCl_3$). **27**: yellow oil. IR (film): 2952, 1736, 1620, 1606, 1489, 1435, 1338, 1246, 756 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.01 (1H, brs, disappeared on addition of D_2O), 2.02 (1H, dd, *J*=14.4, 11.2 Hz), 2.99 (1H, dd, *J*=14.4, 5.4 Hz), 3.14 (3H, s), 3.24 (1H, d, *J*=14.4 Hz), 3.42 (1H, dd, *J*=11.2, 5.4 Hz), 3.71 (3H, s), 3.75 (1H, d, *J*=14.4 Hz), 6.67 (1H, d, *J*=7.8 Hz), 6.83 (1H, d, *J*=7.8 Hz), 7.10 (1H, d, *J*=7.8 Hz), 7.21 (1H, t, *J*=7.8 Hz), 8.47 (1H, d, *J*=2.4 Hz), 8.87 (1H, d, *J*=2.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 172.98 (C), 159.40 (C), 148.41 (C), 140.81 (C), 138.45 (C), 131.17 (C),

129.85 (C), 129.71 (CH), 122.36 (CH), 122.35 (CH), 121.71 (CH), 120.35 (CH), 116.24 (C), 108.17 (CH), 54.26 (C), 52.60 (CH), 52.41 (CH_3), 46.12 (CH_2), 33.57 (CH_2), 28.55 (CH_3). HR–MS *m/z*: Calcd for $C_{20}H_{18}N_4O_7$: 426.1175. Found: 426.1165. $[\alpha]^{26}_D$ +42.9° (c 0.107, MeOH). **29**: yellow oil. IR (film): 2952, 1736, 1620, 1608, 1533, 1489, 1435, 1335, 1255, 1007, 744, 594 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.14 (1H, dd, *J*=14.7, 11.0 Hz), 2.36 (3H, s), 2.88 (1H, dd, *J*=14.7, 6.1 Hz), 3.10 (1H, d, *J*=14.0 Hz), 3.12 (3H, s), 3.21 (1H, dd, *J*=11.0, 6.1 Hz), 3.70 (3H, s), 3.77 (1H, d, *J*=14.0 Hz), 6.61 (1H, d, *J*=7.8 Hz), 6.79 (1H, t, *J*=7.8 Hz), 7.10 (1H, d, *J*=7.8 Hz), 7.19 (1H, t, *J*=7.8 Hz), 8.39 (1H, dd, *J*=2.2, 0.7 Hz), 8.85 (1H, dd, *J*=2.2, 0.7 Hz). ^{13}C-NMR ($CDCl_3$) δ: 172.50 (C), 159.95 (C), 148.56 (C), 140.60 (C), 138.88(C), 130.61(C), 129.68 (CH), 129.36 (C), 122.54 (CH), 121.75 (CH), 121.43 (CH), 119.95 (CH), 117.92 (C), 107.61 (CH), 58.98 (CH), 53.64 (C), 53.56 (CH_2), 51.83 (CH_3), 41.71 (CH_3), 33.04 (CH_2), 28.53 (CH_3). HR–MS *m/z*: Calcd for $C_{21}H_{20}N_4O_7$: 440.1332. Found: 440.1334. $[\alpha]^{27}_D$ +18.8° (c 0.110, MeOH).

28 from 25 — Me_2SO_4 (12.3 mg, 0.09 mmol) in MeOH (0.5 mL) was added to a solution of **25** (11.1 mg, 0.027 mmol) in MeOH (0.5 mL) and K_2CO_3 (13.4 mg, 13.0 mmol) at 0 °C and the mixture was stirred at rt for 19 h. After addition of H_2O, the whole was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (97:3, v/v) to give **28** (6.3 mg, 55%) and unreacted **25** (1.9 mg, 17%).

(*S*)-(4aα,9aα)-*N*b-Acetyl- (30a) and -*N*a,*N*b-diacetyl-3β-methoxycarbonyl-11,13-dinitro-1,2,3,4-tetrahydro-9*H*-benzofurano[2,3-*m*]-β-carboline (30b) from 25 — Ac_2O (1.0 mL) was added to a solution of **25** (40.0 mg, 0.09 mmol) in pyridine (2.0 mL) and the whole was stirred at rt for 3 h. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **30a** (30.8 mg, 59%) and **30b** (14.6 mg, 30%). **30a**: mp 198—200 °C (yellow prisms, recrystallized from EtOAc). IR (KBr): 3292, 1647, 1620, 1610, 1533, 1336 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.19 (3H, s), 2.24 (1H, dd, *J*=14.8, 12.7 Hz), 3.14 (1H, dd, *J*=12.6, 6.7 Hz), 3.72 (3H, s), 3.88 (1H, d, *J*=15.1 Hz), 4.42 (1H, dd, *J*=12.6, 6.7 Hz), 4.53 (1H, d, *J*=15.1 Hz), 5.27 (1H, s, disappeared on addition of D_2O), 6.74 (1H, d, *J*=8.1 Hz), 6.89 (1H, t, *J*=7.6 Hz), 7.18 (1H, t, *J*=7.8 Hz), 7.25 (1H, d, *J*=8.1 Hz), 8.46 (1H, d, *J*=2.2 Hz), 8.86 (1H, d, *J*=2.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.97 (C), 170.84 (C), 158.50 (C), 146.28 (C), 141.53 (C), 136.52 (C), 130.89 (C), 130.18 (CH), 128.16 (C), 123.36 (CH), 122.85 (CH), 122.17 (CH), 121.25 (CH), 113.31 (C), 110.26 (CH), 55.88 (C), 52.63 (CH_3), 50.98 (CH), 48.31 (CH_2), 31.74 (CH_2), 20.98 (CH_3). *Anal.* Calcd for $C_{21}H_{18}N_4O_8 \cdot 1/2EtOAc$: C, 55.42; H, 4.45; N, 11.24. Found: C,55.22; H, 4.45; N, 11.03. $[\alpha]^{31}_D$ +63.1° (c 0.194, MeOH). **30b**: yellow viscous oil. IR (film): 1747, 1685, 1655, 1614, 1541, 1340 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.27 (3H, s), 2.28 (1H, dd, *J*=14.9, 12.9 Hz), 2.68 (3H, s), 3.16 (1H, dd, *J*=15.0, 6.7 Hz), 3.72 (3H, s), 3.95 (1H, d, *J*=15.4 Hz), 4.40 (1H, dd,

J=12.9, 6.6 Hz), 5.26 (1H, brs), 7.19 (1H, t, *J*=7.6 Hz), 7.26 (1H, d, *J*=7.6 Hz), 7.35 (1H, t, *J*=7.9 Hz), 7.39 (1H, d, *J*=7.6 Hz), 8.49 (1H, d, *J*=2.2 Hz), 8.90(1H, d, *J*=2.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.89 (C), 170.66 (C), 169.04 (C), 157.24 (C), 142.52 (C), 141.49 (C), 135.21 (C), 131.63 (C), 130.43 (CH), 130.31 (C), 125.60 (CH), 123.17 (CH), 122.78 (CH), 122.56 (CH), 116.76 (CH), 110.67 (C), 56.16 (C), 52.59(CH_3), 50.69 (CH), 47.74 (CH_2), 32.66 (CH_2), 25.44 (CH_3), 20.83 (CH_3). HR–MS *m/z*: Calcd for $C_{23}H_{20}N_4O_9$: 496.1231. Found: 496.1232. $[\alpha]^{31}_D$ +89.3° (c 0.273, $CHCl_3$).

30b from 30a — Ac_2O (0.5 mL) was added to a solution of **30a** (10.0 mg, 0.02 mmol) in pyridine (1.0 mL) and the whole was refluxed for 3 h. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **30b** (7.7 mg, 71%).

30a from 30b — Sat. $NaHCO_3$ (1.0 mL) was added to a solution of **30b** (16.6 mg, 0.03 mmol) in MeOH (4.0 mL) and the whole was stirred at rt for 100 min. After addition of H_2O, the whole was extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **30a** (14.7 mg, 97%).

(*S*)-(4aα,9aα)-*N*b-Chloroacetyl- (31a) and -*N*a,*N*b-bis(chloroacetyl)-3β-methoxycarbonyl-11,13-dinitro-1,2,3,4-tetrahydro-9*H*-benzofurano[2,3-*m*]-β-carboline (31b) from 25 — Chloroacetyl chloride (0.012 mL, 0.18 mmol) and Et_3N (0.15 mL) was added to a solution of **25** (60.8 mg, 0.15 mmol) in $CHCl_3$ (1.5 mL) and the whole was stirred at rt for 20 min. The solvent was evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$ to give **31a** (17.2 mg, 24%), **31b** (32.8 mg, 39%), and unreacted **7** (4.3 mg, 7%). **31a**: mp 198—200 °C (yellow prisms, recrystallized from EtOAc). IR (KBr): 3382, 1749, 1729, 1668, 1654, 1619, 1610, 1373, 1336 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.31 (1H, dd, *J*=14.9, 12.6 Hz), 3.17 (1H, dd, *J*=14.9, 6.5 Hz), 3.73 (3H, s), 3.95 (1H, d, *J*=15.1 Hz), 4.11 (1H, d, *J*=12.7 Hz), 4.29 (1H, d, *J*=12.7 Hz), 4.42 (1H, dd, *J*=12.6, 6.5 Hz), 4.61 (1H, d, *J*=15.1 Hz), 5.40 (1H, brs, disappeared on addition of D_2O), 6.75 (1H, d, *J*=7.8 Hz), 6.89 (1H, t, *J*=7.8 Hz), 7.18 (1H, t, *J*=7.8 Hz), 7.24—7.28 (1H, m), 8.48 (1H, d, *J*=2.3 Hz), 8.85 (1H, d, *J*=2.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.21 (C), 166.82 (C), 158.16 (C), 146.09 (C), 141.75 (C), 136.20 (C), 131.17 (C), 130.33 (CH), 127.97 (C), 123.30 (CH), 122.85 (CH), 122.26 (CH), 121.50 (CH), 112.59 (C), 110.40 (CH), 55.88 (C), 52.81 (CH), 51.61 (CH_3), 48.13 (CH_2), 40.17 (CH_2), 31.60 (CH_2). HR–MS *m/z*: Calcd for $C_{21}H_{17}N_4O_8Cl$: 488.0734, 490.0705. Found: 488.0756, 490.0707. $[\alpha]^{28}_D$ +135° (c 0.141, DMF). **31b**: mp 223—224 °C (pale yellow prisms, recrystallized from EtOAc). IR (KBr): 1747, 1735, 1662, 1541, 1373, 1340 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.30 (1H, dd, *J*=15.3, 12.8 Hz), 3.13 (1H, dd, *J*=15.3, 6.1 Hz), 3.63 (3H, s), 3.98 (1H, d, *J*=15.9 Hz), 4.14 (1H, d, *J*=12.8 Hz), 4.23 (1H, d, *J*=13.1 Hz), 4.27 (1H, dd, *J*=12.8, 6.1 Hz), 4.42 (1H, d, *J*=12.8 Hz), 4.64 (1H, d, *J*=13.1 Hz), 5.26 (1H, d, *J*=15.9 Hz), 7.14—7.22 (1H, m), 7.31

(1H, t, *J*=7.8 Hz), 7.39 (1H, t, *J*=7.8 Hz), 7.76 1H, brd, *J*=7.8 Hz), 8.46 (1H, d, *J*=1.8 Hz), 8.81 (1H, d, *J*=1.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.90 (C), 167.15 (C), 165.56 (C), 156.52 (C), 142.97 (C), 140.39 (C), 134.65 (C), 132.04 (C), 130.77 (CH), 130.47 (C), 126.51 (CH), 123.47 (CH), 122.94 (CH), 122.74 (CH), 117.07 (CH), 109.90 (C), 56.20 (C), 52.79 (CH_3), 51.59 (CH), 47.01 (CH_2), 42.55 (CH_2), 40.23 (CH_2), 32.73 (CH_3). *Anal.* Calcd for $C_{23}H_{18}N_4O_9Cl_2$: C, 48.87; H, 3.21; N, 9.91. Found: C, 48.87; H, 3.29; N, 9.87. $[\alpha]^{30}_D$ +122° (c 0.200, DMF).

31b from 31a — Chloroacetyl chloride **(**54.8 mg, 0.49 mmol) and Et_3N (0.1 mL) was added to a solution of **31a** (11.7 mg, 0.02 mmol) in $CHCl_3$ (2.0 mL) and the whole was stirred at rt for 20 min. After addition of H_2O, the whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (99:1, v/v) to give **31b** (17.9 mg, 88%).

31a from 31b — Sat. $NaHCO_3$ (0.5 mL) was added to a solution of **31b** (10.4 mg, 0.02 mmol) in MeOH (2.0 mL) and the whole was stirred at rt for 30 min. After addition of H_2O, the whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO_2 with $CHCl_3$–MeOH (99:1, v/v) to give **31a** (7.5 mg, 83%).

X-Ray Analysis:

All measurements were made on a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069 Å). All calculations were performed using the teXsan package.[11] The structure was solved by a direct method (SIR).[12] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystal data for 1a: $C_{23}H_{36}N_2O_9S$, *M*=516.61; orthorhombic; space group, $P2_12_12_1$ (#19); *a*=8.738(3) Å, *b*=14.732(4) Å, *c*=19.428 (6) Å, *V*=2501 (1) Å^3, *Z*=4, D_{calc}= 1.372 g/cm^3. The final *R*- and *R*w-factors after full-matrix least-squares refinements were 0.038 and 0.049 for 3499 observed reflections [$I>3.00\sigma(I)$], respectively. Positional parameters and *B*(eq) for **1a** are shown in Table 1.

Crystal data for 1b: $C_{22}H_{28}N_2O_4$, *M*=384.47; monoclinic; space group, $P2_1$ (#4); *a*=8.200(3) Å, *b*=12.873(4) Å, *c*=9.296 (4) Å, β=97.769(4)°, *V*=972.2(6) Å^3, *Z*=2, D_{calc}= 1.313 g/cm^3. The final *R*- and *R*w-factors after full-matrix least-squares refinements were 0.035 and 0.050 for 4169 observed reflections [$I>3.00\sigma(I)$], respectively. Positional parameters and *B*(eq) for **1b** are shown in Table 2.

Crystal data for 3b: $C_{25}H_{30}N_2O_6$, *M*=454.52; monoclinic; space group, $P2_1$ (#4); *a*=8.1888(6) Å, *b*=10.7944(9) Å, *c*=13.8942(9) Å, β=97.262(1)°, *V*=1218.3(2) Å^3, *Z*=2, D_{calc}= 1.239 g/cm^3, F(000)=484 and μ(Cu–Kα)=6.92 cm^{-1}. The final *R*- and *R*w-factors after full-matrix least-squares refinements were 0.030 and 0.036 for 1632 observed reflections [$I>3.00\sigma(I)$], respectively. Positional parameters and *B*(eq)

for **3b** are shown in Table 3.

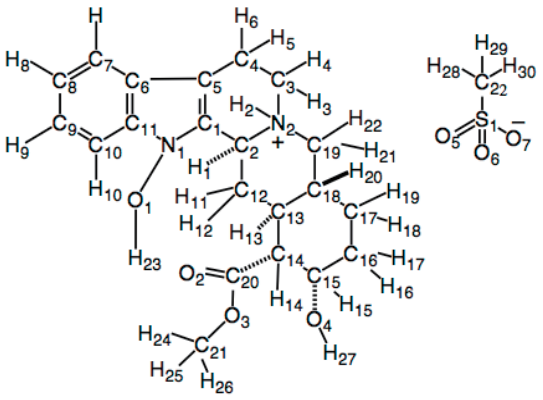


Figure 4. Numbering of **1a**. ORTEP drawing is reported in the previous communication.[4b]

Table 1. Positional Parameters and B (eq) for **1a**

atom	x	y	z	*B (eq)*	atom	x	y	z	*B (eq)*
O (1)	-0.2932 (4)	-0.0172 (2)	-0.6340 (2)	2.33 (7)	H (2)	-0.2354	-0.1598	-0.8515	7.2
O (2)	-0.2200 (4)	-0.2953 (2)	-0.5710 (2)	3.32 (8)	H (3)	-0.4422	-0.1518	-0.9123	7.2
O (3)	0.0083 (4)	-0.3656 (2)	-0.5695 (2)	2.67 (7)	H (4)	-0.5463	-0.1361	-0.8491	7.2
O (4)	-0.2571 (4)	-0.4902 (2)	-0.6525 (2)	2.63 (7)	H (5)	-0.293	-0.0337	-0.9101	7.2
N (1)	-0.2694 (4)	0.0086 (2)	-0.7022 (2)	1.41 (6)	H (6)	-0.4786	0.0112	-0.9007	7.2
N (2)	-0.3303 (4)	-0.1779 (2)	-0.8279 (2)	1.31 (6)	H (7)	-0.3312	0.1823	-0.8803	7.2
C (1)	-0.3184 (4)	-0.0444 (3)	-0.7568 (2)	1.22 (7)	H (8)	-0.2864	0.314	-0.8284	7.2
C (2)	-0.3341 (4)	-0.1463 (3)	-0.7542 (2)	1.22 (6)	H (9)	-0.1987	0.3156	-0.6957	7.2
C (3)	-0.4412 (5)	-0.1252 (3)	-0.8724 (2)	1.54 (8)	H (10)	-0.1944	0.1776	-0.6311	7.2
C (4)	-0.3888 (5)	-0.0275 (3)	-0.8812 (2)	1.48 (7)	H (11)	-0.1135	-0.1857	-0.7365	7.2
C (5)	-0.3410 (4)	0.0086 (3)	-0.8128 (2)	1.26 (6)	H (12)	-0.2074	-0.1749	-0.6666	7.2
C (6)	-0.3101 (4)	0.1003 (3)	-0.7923 (2)	1.45 (6)	H (13)	-0.3398	-0.3112	-0.6956	7.2
C (7)	-0.3122 (5)	0.1851 (3)	-0.8269 (2)	1.70 (8)	H (14)	-0.001	-0.3411	-0.6977	7.2
C (8)	-0.2720 (5)	0.2618 (3)	-0.7906 (2)	1.85 (7)	H (15)	-0.0314	-0.481	-0.6667	7.2
C (9)	-0.2290 (5)	0.2579 (3)	-0.7212 (2)	1.83 (7)	H (16)	-0.1554	-0.5498	-0.7693	7.2
C (10)	-0.2275 (5)	0.1764 (3)	-0.6851 (2)	1.66 (8)	H (17)	-0.0409	-0.4604	-0.785	7.2
C (11)	-0.2685 (5)	0.0983 (3)	-0.7222 (2)	1.49 (6)	H (18)	-0.2735	-0.4576	-0.8484	7.2
C (12)	-0.2087 (5)	-0.1968 (3)	-0.7136 (2)	1.50 (7)	H (19)	-0.372	-0.4443	-0.7696	7.2
C (13)	-0.2353 (5)	-0.2997 (3)	-0.7171 (2)	1.39 (7)	H (20)	-0.1303	-0.3163	-0.8168	7.2
C (14)	-0.1111 (4)	-0.3518 (3)	-0.6770 (2)	1.61 (7)	H (21)	-0.3518	-0.2909	-0.8865	7.2
C (15)	-0.1240 (5)	-0.4575 (3)	-0.6872 (3)	2.08 (8)	H (22)	-0.4574	-0.2925	-0.8143	7.2
C (16)	-0.1355 (5)	-0.4825 (3)	-0.7623 (3)	2.19 (9)	H (23)	-0.192	-0.0274	-0.6042	7.2
C (17)	-0.2674 (5)	-0.4333 (3)	-0.7980 (2)	1.85 (8)	H (24)	0.0258	-0.2982	-0.4787	7.2
C (18)	-0.2391 (4)	-0.3299 (3)	-0.7920 (2)	1.45 (6)	H (25)	0.1112	-0.3773	-0.4828	7.2
C (19)	-0.3581 (4)	-0.2781 (3)	-0.8327 (2)	1.61 (8)	H (26)	-0.0871	-0.3807	-0.4671	7.2
C (20)	-0.1182 (5)	-0.3329 (3)	-0.6010 (2)	2.21 (8)	H (27)	-0.2768	-0.4452	-0.619	7.2
C (21)	0.0116 (7)	-0.3574 (4)	-0.4959 (3)	3.6 (1)	H (28)	-0.068	-0.1196	-1.0625	7.2
S (1)	0.0329 (1)	-0.15252 (7)	-0.95496 (6)	1.72 (2)	H (29)	-0.1205	-0.0586	-0.9943	7.2
O (5)	0.1594 (4)	-0.0877 (3)	-0.9571 (2)	3.72 (8)	H (30)	-0.1955	-0.1555	-1.019	7.2
O (6)	-0.0451 (3)	-0.1524 (2)	-0.8889 (1)	2.00 (6)	H (31)	-0.4703	-0.3824	-0.4999	6
O (7)	0.0804 (4)	-0.2422 (2)	-0.9777 (2)	2.63 (7)	H (32)	-0.4937	-0.3379	-0.4283	6
O (8)	-0.5391 (6)	-0.4634 (3)	-0.4299 (3)	8.2 (2)	H (33)	-0.3526	-0.3994	-0.4416	6
O (9)	-0.1060 (4)	-0.3864 (2)	-0.9511 (2)	2.95 (8)	H (34)	-0.5314	-0.528	-0.4445	7.2
C (22)	-0.1026 (6)	-0.1149 (4)	-1.0161 (2)	2.9 (1)	H (35)	-0.047	-0.3273	-0.9689	7.2
C (23)	-0.4603 (9)	-0.3916 (4)	-0.4515 (4)	5.2 (2)	H (36)	-0.1896	-0.3922	-0.9846	7.2
H (1)	-0.4406	-0.1656	-0.7363	7.2					

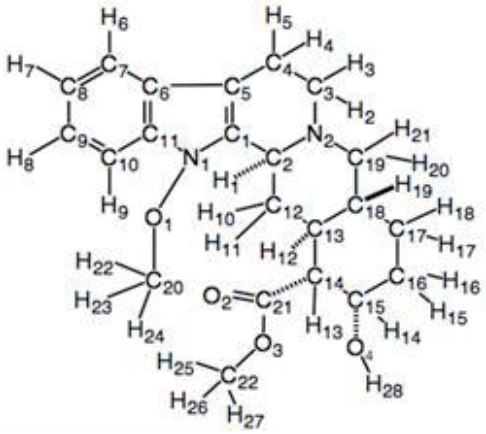


Figure 5. Numbering of **1b**. ORTEP drawing is reported in the previous communication.[4b]

Table 2. Positional Parameters and *B* (eq) for **1b**

atom	x	y	z	*B (eq)*	atom	x	y	z	*B (eq)*
O (1)	-0.9363 (1)	-0.0823 (4)	-0.6299 (1)	1.64 (2)	H (1)	-0.5326	-0.0432	-0.6698	2.6
O (2)	-0.8358 (2)	-0.1084 (4)	-0.9781 (1)	2.98 (3)	H (2)	-0.3058	-0.1322	-0.5415	2.6
O (3)	-0.9027 (2)	-0.0800 (4)	-1.2159 (1)	2.09 (2)	H (3)	-0.227	-0.2421	-0.5943	2.6
O (4)	-0.4877 (2)	0.1301 (4)	-1.1272 (1)	2.12 (2)	H (4)	-0.4325	-0.3455	-0.5238	2.6
N (1)	-0.8108 (2)	-0.1351 (4)	-0.5450 (1)	1.56 (2)	H (5)	-0.3602	-0.2924	-0.3935	2.6
N (2)	-0.4347 (2)	-0.1840 (4)	-0.7232 (1)	1.38 (2)	H (6)	-0.5807	-0.3369	-0.2063	2.6
C (1)	-0.6617 (2)	-0.1650 (4)	-0.5872 (2)	1.32 (3)	H (7)	-0.8163	-0.3358	-0.071	2.6
C (2)	-0.5788 (2)	-0.1174 (4)	-0.7053 (2)	1.35 (3)	H (8)	-1.0514	-0.2466	-0.1594	2.6
C (3)	-0.3308 (2)	-0.2016 (4)	-0.5836 (2)	1.85 (3)	H (9)	-1.0661	-0.1446	-0.3696	2.6
C (4)	-0.4168 (2)	-0.2710 (4)	-0.4852 (2)	1.82 (3)	H (10)	-0.7178	-0.1707	-0.8973	2.6
C (5)	-0.5891 (2)	-0.2331 (4)	-0.4851 (2)	1.53 (3)	H (11)	-0.7733	-0.0501	-0.8402	2.6
C (6)	-0.6978 (2)	-0.2486 (4)	-0.3793 (2)	1.47 (3)	H (12)	-0.541	-0.0265	-0.905	2.6
C (7)	-0.6860 (2)	-0.3031 (4)	-0.2479 (2)	1.83 (3)	H (13)	-0.7167	-0.0773	-1.1567	2.6
C (8)	-0.8152 (2)	-0.2986 (4)	-0.1674 (2)	1.96 (3)	H (14)	-0.6298	-0.0592	-1.3006	2.6
C (9)	-0.9567 (2)	-0.2398 (4)	-0.2142 (2)	1.84 (3)	H (15)	-0.4552	-0.0939	-1.262	2.6
C (10)	-0.9700 (2)	-0.1822 (4)	-0.3411 (2)	1.68 (3)	H (16)	-0.3509	-0.0098	-1.2744	2.6
C (11)	-0.8387 (2)	-0.1868 (4)	-0.4211 (2)	1.53 (3)	H (17)	-0.2698	-0.0043	-1.0285	2.6
C (12)	-0.6839 (2)	-0.1006 (4)	-0.8526 (2)	1.39 (3)	H (18)	-0.2225	-0.1166	-1.0814	2.6
C (13)	-0.5801 (2)	-0.0444 (4)	-0.9538 (2)	1.33 (3)	H (19)	-0.4713	-0.1759	-1.0122	2.6
C (14)	-0.6737 (2)	-0.0125 (4)	-1.1010 (2)	1.38 (3)	H (20)	-0.285	-0.07	-0.7776	2.6
C (15)	-0.5554 (2)	-0.0382 (4)	-1.1972 (2)	1.61 (3)	H (21)	-0.2303	-0.1794	-0.8295	2.6
C (16)	-0.4164 (2)	-0.0359 (4)	-1.2177 (2)	1.87 (3)	H (22)	-0.9514	-0.0469	-0.5074	2.6
C (17)	-0.3193 (2)	-0.0653 (4)	-1.0724 (2)	1.88 (3)	H (23)	-1.0333	-0.0504	-0.636	2.6
C (18)	-0.4319 (2)	-0.1132 (4)	-0.9724 (2)	1.46 (3)	H (24)	-0.8222	-0.0608	-0.67	2.6
C (19)	-0.3345 (2)	-0.1343 (4)	-0.8248 (2)	1.64 (3)	H (25)	-1.1206	-0.1228	-1.1635	2.6
C (20)	-0.9231 (2)	-0.0272 (4)	-0.5986 (2)	2.51 (4)	H (26)	-1.0208	-0.2084	-1.1645	2.6
C (21)	-0.8101 (2)	-0.0644 (4)	-1.0861 (2)	1.75 (3)	H (27)	-1.0862	-0.1756	-1.3158	2.6
C (22)	-1.0375 (2)	-0.1517 (4)	-1.2184 (2)	2.27 (3)	H (28)	-0.5165	-0.1929	-1.1736	2.6

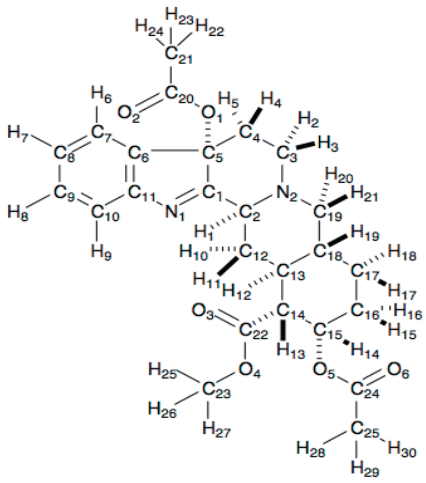


Figure 6. Numbering of **3b**

ORTEP drawing is reported in Figure 1.

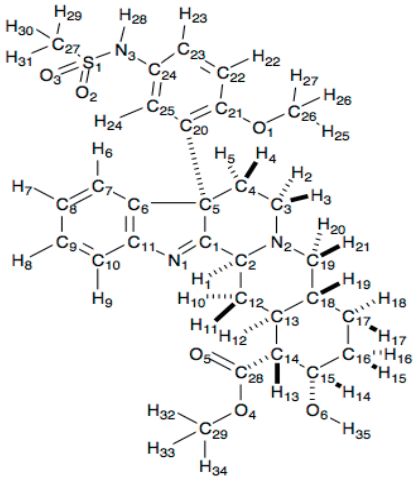


Figure 7. Numbering of **14**

ORTEP drawing is reported in Figure 2.

Table 3. Positional Parameters and *B* (eq) for **3b**

atom	x	y	z	*B(eq)*	atom	x	y	z	*B(eq)*
O (1)	0.5458 (3)	0.6394	0.3668 (2)	4.6 (1)	C (25)	-0.0867 (8)	0.9912 (7)	-0.1814 (4)	7.2 (3)
O (2)	0.7278 (4)	0.7041 (4)	0.2719 (2)	7.6 (2)	H (1)	0.368 (3)	0.816 (3)	0.242 (2)	3.70 (2)
O (3)	0.3777 (4)	1.0878 (3)	0.0136 (2)	6.7 (1)	H (2)	0.248 (4)	0.681 (4)	0.360 (3)	5.23 (2)
O (4)	0.3199 (3)	1.2847 (3)	0.0398 (2)	5.9 (1)	H (3)	0.148 (4)	0.750 (3)	0.439 (3)	5.03 (2)
O (5)	-0.0015 (3)	1.0630 (3)	-0.0253 (2)	4.8 (1)	H (4)	0.406 (5)	0.825 (4)	0.515 (3)	6.39 (3)
O (6)	-0.2163 (4)	1.1596 (4)	-0.1096 (2)	6.9 (2)	H (5)	0.411 (4)	0.676 (4)	0.509 (3)	5.45 (2)
N (1)	0.6297 (3)	0.9572 (4)	0.3774 (2)	4.1 (1)	H (6)	0.781 (5)	0.634 (4)	0.570 (3)	5.92 (3)
N (2)	0.2317 (3)	0.8688 (4)	0.3463 (2)	4.0 (1)	H (7)	1.035 (5)	0.746 (4)	0.638 (3)	6.77 (3)
C (1)	0.5249 (4)	0.8709 (4)	0.3550 (2)	3.7 (1)	H (8)	1.089 (4)	0.947 (4)	0.600 (3)	5.86 (2)
C (2)	0.3695 (4)	0.8832 (4)	0.2867 (2)	3.7 (1)	H (9)	0.907 (4)	1.053 (4)	0.482 (3)	5.32 (2)
C (3)	0.2444 (5)	0.7538 (4)	0.4037 (3)	4.7 (2)	H (10)	0.438 (4)	1.009 (3)	0.194 (2)	4.11 (2)
C (4)	0.4015 (5)	0.7506 (5)	0.4739 (3)	4.7 (2)	H (11)	0.368 (4)	1.072 (4)	0.283 (3)	4.98 (2)
C (5)	0.5508 (4)	0.7563 (4)	0.4183 (2)	4.0 (1)	H (12)	0.188 (3)	0.945 (3)	0.117 (2)	3.60 (1)
C (6)	0.7099 (4)	0.7874 (4)	0.4781 (2)	4.3 (2)	H (13)	0.167 (4)	1.205 (3)	0.162 (2)	4.28 (2)
C (7)	0.8094 (5)	0.7244 (5)	0.5494 (3)	5.0 (2)	H (14)	-0.014 (4)	1.233 (4)	0.022 (3)	5.31 (2)
C (8)	0.9489 (5)	0.7859 (5)	0.5941 (3)	5.5 (2)	H (15)	-0.141 (4)	1.192 (4)	0.162 (3)	6.23 (3)
C (9)	0.9851 (5)	0.9051 (5)	0.5680 (3)	5.4 (2)	H (16)	-0.242 (4)	1.115 (4)	0.068 (3)	5.55 (2)
C (10)	0.8847 (4)	0.9689 (5)	0.4964 (3)	4.7 (2)	H (17)	-0.211 (4)	0.967 (4)	0.208 (2)	5.56 (2)
C (11)	0.7478 (4)	0.9082 (4)	0.4521 (2)	3.9 (1)	H (18)	-0.125 (4)	0.932 (4)	0.119 (3)	4.73 (2)
C (12)	0.3543 (4)	1.0047 (4)	0.2322 (3)	3.9 (1)	H (19)	0.055 (4)	1.058 (4)	0.283 (3)	4.98 (2)
C (13)	0.1903 (4)	1.0127 (4)	0.1666 (2)	3.9 (1)	H (20)	0.068 (4)	0.787 (4)	0.230 (3)	5.21 (2)
C (14)	0.1661 (4)	1.1369 (4)	0.1144 (2)	4.2 (1)	H (21)	-0.015 (4)	0.862 (4)	0.322 (2)	4.87 (2)
C (15)	-0.0032 (5)	1.1495 (5)	0.0544 (3)	4.9 (2)	H (22)	0.666 (8)	0.491 (6)	0.212 (4)	9.81 (7)
C (16)	-0.1408 (5)	1.1200 (5)	0.1143 (3)	5.4 (2)	H (23)	0.522 (8)	0.501 (6)	0.209 (4)	10.11 (7)
C (17)	-0.1164 (5)	0.9961 (5)	0.1652 (3)	5.1 (2)	H (24)	0.60 (1)	0.426 (7)	0.291 (4)	17.8 (1)
C (18)	0.0498 (4)	0.9909 (4)	0.2275 (3)	4.1 (1)	H (25)	0.535 (6)	1.286 (5)	0.007 (4)	8.31 (3)
C (19)	0.0741 (4)	0.8699 (4)	0.2818 (3)	4.4 (2)	H (26)	0.437 (7)	1.417 (6)	-0.020 (4)	10.74 (5)
C (20)	0.6363 (4)	0.6267 (4)	0.2931 (3)	5.0 (2)	H (27)	0.396 (6)	1.285 (5)	-0.098 (4)	9.52 (4)
C (21)	0.603 (1)	0.5067 (6)	0.2431 (4)	7.3 (3)	H (28)	-0.16 (2)	0.95 (1)	-0.207 (6)	26.8 (3)
C (22)	0.2996 (4)	1.1637 (4)	0.0501 (2)	4.5 (2)	H (29)	-0.04 (2)	0.923 (7)	-0.155 (5)	23.0 (2)
C (23)	0.4419 (7)	1.3207 (7)	-0.0236 (5)	7.5 (3)	H (30)	-0.05 (2)	1.026 (7)	-0.231 (6)	27.0 (3)
C (24)	-0.1135 (5)	1.0808 (5)	-0.1035 (3)	5.1 (2)					

Table4. Positional Parameters and *B* (eq) for **14**

atom	x	y	z	*B (eq)*	atom	x	y	z	*B (eq)*
S (1)	0.59677 (3)	0.5665 (4)	0.52106 (2)	1.422 (7)	C (33)	-0.1390 (2)	0.3491 (5)	0.4030 (1)	3.47 (5)
O (1)	0.36261 (9)	0.5994 (4)	0.85257 (6)	1.28 (2)	H (1)	0.1423	0.5286	0.809	2
O (2)	0.6097 (1)	0.4108 (4)	0.54925 (7)	2.03 (2)	H (2)	0.1121	0.4561	0.6544	2
O (3)	0.5943 (1)	0.5963 (5)	0.43728 (7)	2.07 (2)	H (3)	0.0387	0.3099	0.6387	2
O (4)	-0.0736 (1)	0.4182 (4)	1.10452 (7)	1.83 (2)	H (4)	0.1984	0.1535	0.708	2
O (5)	0.05960 (9)	0.5702 (4)	1.05457 (6)	1.54 (2)	H (5)	0.2493	0.2509	0.6415	2
O (6)	-0.2252 (1)	0.6899 (4)	0.95992 (7)	1.53 (2)	H (6)	0.5419	0.1989	0.6974	2
N (1)	0.3009 (1)	0.2579 (5)	0.88820 (7)	1.18 (2)	H (7)	0.6924	0.0627	0.7905	2
N (2)	0.0421 (1)	0.3571 (5)	0.75195 (7)	1.19 (2)	H (8)	0.6586	-0.0258	0.9152	2
N (3)	0.4662 (1)	0.6333 (5)	0.54110 (8)	1.48 (2)	H (9)	0.4752	0.0785	0.9763	2
C (1)	0.2518 (1)	0.3420 (5)	0.82793 (8)	1.05 (2)	H (10)	0.1334	0.4466	0.9407	2
C (2)	0.1293 (1)	0.4226 (5)	0.82104 (8)	1.05 (2)	H (11)	0.0724	0.3004	0.9083	2
C (3)	0.0976 (1)	0.3582 (5)	0.67887 (8)	1.35 (3)	H (12)	-0.0452	0.6058	0.8823	2
C (4)	0.2156 (1)	0.2601 (5)	0.69009 (9)	1.31 (3)	H (13)	-0.1219	0.331	0.9647	2
C (5)	0.3181 (1)	0.3328 (5)	0.75519 (8)	1.09 (2)	H (14)	-0.2774	0.5172	1.0017	2
C (6)	0.4240 (1)	0.2268 (5)	0.78932 (9)	1.15 (2)	H (15)	-0.3555	0.3674	0.876	2
C (7)	0.5256 (1)	0.1714 (5)	0.75888 (9)	1.42 (3)	H (16)	-0.3985	0.5445	0.8715	2
C (8)	0.6124 (1)	0.0810 (5)	0.80817 (10)	1.62 (3)	H (17)	-0.2499	0.6205	0.7979	2
C (9)	0.5982 (1)	0.0458 (5)	0.88671 (10)	1.63 (3)	H (18)	-0.3086	0.4831	0.7568	2
C (10)	0.4958 (1)	0.0995 (5)	0.91764 (9)	1.49 (3)	H (19)	-0.1491	0.3044	0.8231	2
C (11)	0.4104 (1)	0.1905 (5)	0.86789 (9)	1.20 (3)	H (20)	-0.0652	0.5729	0.728	2
C (12)	0.0764 (1)	0.4079 (5)	0.89774 (8)	1.08 (2)	H (21)	-0.1263	0.4121	0.6938	2
C (13)	-0.0503 (1)	0.4853 (5)	0.89126 (8)	1.05 (2)	H (22)	0.4398	0.8468	0.7818	2
C (14)	-0.1116 (1)	0.4483 (5)	0.96409 (8)	1.10 (2)	H (23)	0.4813	0.8593	0.6605	2
C (15)	-0.2405 (1)	0.5279 (5)	0.95702 (9)	1.24 (3)	H (24)	0.3894	0.4074	0.6214	2
C (16)	-0.3241 (1)	0.4828 (5)	0.87863 (9)	1.51 (3)	H (25)	0.2996	0.8033	0.8654	2
C (17)	-0.2628 (1)	0.5123 (5)	0.80518 (9)	1.44 (3)	H (26)	0.4223	0.8043	0.9089	2
C (18)	-0.1375 (1)	0.4298 (5)	0.81468 (8)	1.20 (2)	H (27)	0.3045	0.703	0.9429	2
C (19)	-0.0745 (1)	0.4464 (5)	0.74138 (9)	1.28 (3)	H (28)	0.4647	0.7262	0.5185	2
C (20)	0.3659 (1)	0.4839 (5)	0.72673 (8)	1.04 (2)	H (29)	0.7169	0.7977	0.5529	2
C (21)	0.3852 (1)	0.6151 (5)	0.77582 (8)	1.11 (2)	H (30)	0.8127	0.6383	0.5601	2
C (22)	0.4276 (1)	0.7508 (5)	0.74767 (9)	1.41 (3)	H (31)	0.6903	0.6438	0.6421	2
C (23)	0.4567 (1)	0.7564 (5)	0.67050 (9)	1.46 (3)	H (32)	-0.008	0.5524	1.2034	2
C (24)	0.4414 (1)	0.6274 (5)	0.62239 (9)	1.29 (2)	H (33)	-0.0286	0.3776	1.2169	2
C (25)	0.3964 (1)	0.4928 (5)	0.65014 (9)	1.20 (2)	H (34)	0.087	0.4094	1.1848	2
C (26)	0.3476 (2)	0.7354 (5)	0.89664 (10)	2.07 (3)	H (35)	-0.2531	0.7191	1.0041	2
C (27)	0.7195 (2)	0.6722 (5)	0.5774 (1)	2.14 (3)	H (36)	0.259	0.4928	0.3464	2.9
C (28)	-0.0305 (1)	0.4887 (5)	1.04354 (9)	1.16 (2)	H (37)	0.1772	0.6313	0.3126	2.9
C (29)	-0.0026 (2)	0.4478 (5)	1.18359 (10)	2.42 (4)	H (38)	0.2964	0.6567	0.3766	2.9
O (7)	-0.0396 (1)	0.5321 (5)	0.49947 (9)	4.03 (4)	H (39)	0.2031	0.5302	0.4715	2.7
O (8)	0.0515 (1)	0.4687 (5)	0.39512 (8)	2.52 (3)	H (40)	0.1208	0.668	0.4374	2.7
C (30)	0.2283 (2)	0.5896 (5)	0.3590 (1)	2.44 (4)	H (41)	-0.1037	0.2504	0.4009	4.2
C (31)	0.1528 (2)	0.5716 (5)	0.4248 (1)	2.28 (3)	H (42)	-0.174	0.3815	0.3501	4.2
C (32)	-0.0398 (2)	0.4590 (5)	0.4389 (1)	2.71 (4)	H (43)	-0.2023	0.346	0.435	4.2

Crystal data for 14: $C_{23}H_{36}N_2O_9S$, M=516.61; orthorhombic; space group, $P2_12_12_1$ (#19); a=8.738(3) Å, b=14.732(4) Å, c=19.428(6) Å, V=2501(1) Å^3, Z=4, D_{calc}= 1.372 g/cm^3. The final R- and Rw-factors after

full-matrix least-squares refinements were 0.038 and 0.049 for 3499 observed reflections [$I>3.00\sigma(I)$], respectively. Positional parameters and B(eq) for **14** are shown in Table 4.

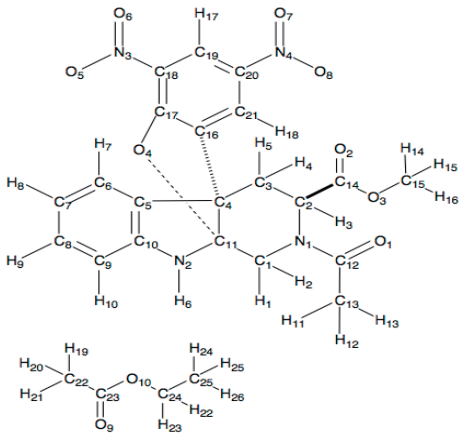


Figure 8. Numbering of **30a**

Table 5. Positional Parameters and B (eq) for **30a**

atom	x	y	z	B (eq)	atom	x	y	z	B (eq)
O (1)	0.4181 (1)	0.2519 (1)	0.1934 (7)	2.71(4)	C (20)	0.6196 (1)	-0.0749 (1)	0.1593 (7)	1.98 (4)
O (2)	0.5341 (3)	0.3880 (1)	0.3476 (7)	2.95(4)	C (21)	0.6635 (1)	-0.0026 (1)	0.2131 (7)	1.84 (4)
O (3)	0.5802 (1)	0.2768 (1)	0.4610 (7)	3.21(4)	C (22)	0.6387 (3)	-0.0692 (3)	0.5704 (7)	4.32 (7)
O (4)	0.6649 (1)	0.1730 (1)	0.0126 (7)	1.90(3)	C (23)	0.6895 (2)	0.0161 (2)	0.5450 (7)	3.70 (6)
O (5)	0.5627 (2)	0.0999 (2)	-0.1455 (7)	3.86(5)	C (24)	0.7542 (4)	0.1551 (3)	0.6189 (7)	5.65 (9)
O (6)	0.5446 (2)	-0.0476 (2)	-0.1508 (7)	4.37 (5)	C (25)	0.8573 (5)	0.1292 (4)	0.6180 (10)	9.5 (2)
O (7)	0.5747 (2)	-0.2286 (1)	0.1645 (7)	3.80 (5)	H (1)	0.6318	0.3395	0.0527	2.4
O (8)	0.6334 (1)	-0.1697 (1)	0.3057 (7)	3.42 (4)	H (2)	0.6825	0.3561	0.1593	2.4
O (9)	0.7188 (2)	0.0382 (2)	0.4592 (7)	5.91 (7)	H (3)	0.5486	0.1868	0.29	2.4
O(10)	0.7028 (2)	0.0690 (2)	0.6308 (7)	4.36 (5)	H (4)	0.7235	0.2646	0.3084	2.3
N (1)	0.5696 (1)	0.2781 (1)	0.1748 (7)	1.91 (3)	H (5)	0.6924	0.1683	0.3495	2.3
N (2)	0.8034 (1)	0.1547 (1)	0.0574 (7)	1.86 (3)	H (6)	0.8153	0.296	0.0004	2.2
N (3)	0.5665 (1)	0.0239 (2)	-0.1054 (7)	2.50 (4)	H (7)	0.8581	0.0669	0.3189	2.5
N (4)	0.6081 (2)	-0.1639 (1)	0.2142 (7)	2.68 (4)	H (8)	1.0203	0.0712	0.2999	2.9
C (1)	0.6506 (2)	0.3117 (1)	0.1174 (7)	2.00 (4)	H (9)	1.0866	0.1629	0.1684	2.6
C (2)	0.5867 (2)	0.2397 (2)	0.2803 (7)	1.98(4)	H (10)	0.9949	0.2505	0.0525	2.5
C (3)	0.6879 (2)	0.2111 (2)	0.2926 (7)	1.92 (4)	H (11)	0.5208	0.3422	0.0008	4.1
C (4)	0.7274 (1)	0.1657 (1)	0.1925 (7)	1.66 (3)	H (12)	0.4349	0.2790	-0.0140	4.1
C (5)	0.8317 (1)	0.1548 (1)	0.1963 (7)	1.64 (3)	H (13)	0.4241	0.3757	0.038	4.1
C (6)	0.8859 (2)	0.1035 (2)	0.2650 (7)	2.05 (4)	H (14)	0.5879	0.3117	0.6128	4.5
C (7)	0.9819 (2)	0.1064 (2)	0.0574 (7)	2.41 (4)	H (15)	0.6178	0.391	0.5372	4.5
C (8)	1.0211 (2)	0.1611 (2)	0.1752 (7)	2.20 (4)	H (16)	0.5137	0.3676	0.5512	5.5
C (9)	0.9672 (2)	0.2133 (1)	0.1059 (7)	2.06 (4)	H (17)	0.5576	-0.1172	0.0231	2.6
C (10)	0.8718 (1)	0.2093 (1)	0.1176 (7)	1.65 (4)	H (18)	0.6836	-0.0095	0.2843	2.2
C (11)	0.7141 (1)	0.2298 (1)	0.0947 (7)	1.65 (4)	H (19)	0.58	-0.0538	0.5995	5.2
C (12)	0.4806 (2)	0.2810 (2)	0.1388 (7)	2.22 (4)	H (20)	0.6302	-0.1046	0.5077	5.2
C (13)	0.4635 (2)	0.3234 (2)	0.0308 (7)	3.41 (6)	H (21)	0.673	-0.1045	0.6203	5.2
C (14)	0.5627 (2)	0.3116 (2)	0.3649 (7)	2.27 (4)	H (22)	0.7378	0.1846	0.5544	6.8
C (15)	0.5744 (2)	0.3425 (2)	0.5481 (7)	3.77 (6)	H (23)	0.7413	0.1954	0.6765	6.8
C (16)	0.6763 (1)	0.0790 (1)	0.1585 (7)	1.60 (3)	H (24)	0.8726	0.0983	0.6822	11.4
C (17)	0.6449 (1)	0.0904 (1)	0.0541 (7)	1.73 (4)	H (25)	0.8695	0.0894	0.5598	11.4
C (18)	0.6001 (1)	0.0166 (2)	0.0036 (7)	1.91 (4)	H (26)	0.8936	0.1837	0.6117	11.4
C (19)	0.5876 (2)	-0.0667 (2)	0.0568 (7)	2.13 (4)					

Crystal data for 30a: $C_{21}H_{18}N_4O_8$, M=542.50; tetragonal; space group, $P4_3$ (#78); a=14.441(2) Å, b=14.449(1) Å, c=12.626(2) Å, V=2633.2(7) Å^3, Z=4, D_{calc}=1.368 g/cm^3. The final R- and Rw-factors after full-matrix least-squares refinements were 0.060 and 0.091 for 5781 observed reflections [$I>3.00\sigma(I)$], respectively. Positional parameters and B(eq) for **30a** are shown in Table 5.

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