Alkaloids, Diarylheptanoid and Naphthalene Carboxylic Acid Ester from *Rhoiptelea chiliantha*

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Two pyrrolidine alkaloids (1, 2) were isolated from the fruits of *Rhoiptelea chiliantha* DIEL *et* HAND.-MAZZ. (Rhoipteleaceae). A diphenyl ether-type diarylheptanoid (3), and a naphthalene carboxylic acid methyl ester (4) which is biogenetically-related to juglone were isolated from the branches of the same plant. Their chemical structures were elucidated on the basis of spectroscopic analysis and chemical evidence.

Key words *Rhoiptelea chiliantha*; Rhoipteleaceae; pyrrolidine alkaloid; diarylheptanoid; chemotaxonomy

In a series of papers on our chemical and chemotaxonomical studies of *Rhoiptelea chiliantha* DIEL *et* HAND.-MAZZ., the only species of the family Rhoipteleaceae, we have reported the structural elucidation of triterpenes,[1] triterpene esters[2] from the barks, diarylheptanoids,[3] ellagitannins,[4] euphane-type triterpene bisdesmosides and tridesmosides,[5] and dammmarane-type triterpene glycosides[6] from the fruits and leaves. In a continuation of this investigation, we chemically studied the branches whose constituents have not yet been examined, and also further separated the composition of the fruits. Herein, we describe the structural elucidation of two pyrrolidine alkaloids (**1** and **2**) from the fruits, a diphenyl ether-type diarylheptanoid (**3**) and a naphthalene carboxylic acid methyl ester (**4**) which is biogenetically-related to juglone from the branches.

Results and Discussion

The MeOH extracts of the air-dried fruits and branches of *Rhoiptelea chiliantha* were separately partitioned between H_2O and Et_2O, the remaining H_2O layers were further extracted with EtOAc. The H_2O layer of the fruits was subjected to column chromatography over MCI-gel CHP 20P, Bondapak ODS and silica gel to afford compounds **1** and **2**. The Et_2O layer of the branch was chromatographed over silica gel and MCI-gel CHP 20P to yield compound **3**. The H_2O layer of the branches was chromatographed over Sephadex LH-20 and silica gel to afford compound **4**.

Compound **1** was isolated from the fruits as colorless needles, mp 178—180 °C. It showed a pink spot on TLC when sprayed with ninhydrin reagent followed by heating, indicating the existence of nitrogen atom in its molecule. The molecular formula of **1** was established to be $C_{13}H_{17}NO_3$ on the basis of the molecular ion peak at *m/z*: 235 in EI-MS and the result of elemental analysis, suggesting that **1** is an alkaloid. Its ^{1}H-NMR spectrum displayed the signals due to a 1,2,3-trisubstituted benzene ring [δ_H 7.50 (1H, dd, J=2, 8 Hz), 7.36 (1H, dd, J=8, 9 Hz), 7.11 (1H, dd, J=2, 9 Hz)], an *N*-methyl [δ_H 2.62 (3H, s)] and a methoxyl group [δ_H 3.87(3H, s)]. Besides these, the signals arising from a carboxylic carbon, a methine [δ_C 62.4 (d, C-2)], and three methylenes [δ_C 54.8 (t, C-5), 31.0 (t, C-3), 22.6 (t, C-4)] were confirmed by the ^{13}C-NMR and DEPT spectra. The correlations (Fig. 1) of the methylenes and methine in the ^{1}H–^{1}H COSY spectrum and their chemical shifts suggested the presence of a 2-substituted pyrrolidine ring in compound **1**.[7] The HMBC correlations shown in Fig. 1 determined the positions of the carboxylic acid group and methoxyl group in C-2′ and C-6′, respectively, in the benzene ring. Furthermore, the HMBC correlations from H-2 signal to C-1′, C-2′ and C-6′ signals confirmed the linkage of 2-substituted pyrrolidine ring to the benzene ring at C-1′ position. Thus, the plain structure of **1** was concluded to be as shown in Fig. 1. The absolute configuration of C-2 of **1** was determined to be *R* on the basis of observation of a negative Cotton effect at 246 nm in the CD spectrum.[7]

Compound **2** was also isolated from the fruits as colorless crystals, mp 221—223 °C and showed a positive reaction to ninhydrin reagent on TLC by heating. Its molecular formula of $C_{12}H_{15}NO_2$ was deduced from the data of EI-MS spectrum (molecular ion peak at *m/z* 205 $[M]^+$) and elemental analysis. The ^{1}H- and ^{13}C-NMR data of **2** were very similar to those of **1**, exhibiting a 2-substituted pyrrolidine ring, a carboxylic acid group, an *N*-methyl group and a benzene ring. However, the presence of a 1,2-disubstituted benzene ring in **2** instead of a trisubstituted one in **1**, and the absence of methoxyl group in **2** indicated that there is no methoxyl group in C-6′ of the benzene ring. By comparing the NMR data of **2** with those of dihydroshihunine isolated from *Banisteriopsis cappi* (Malpighiaceae),[7] **2** was determined to possess a plain structure the same as dihydroshihunine. But the sign of the optical rotation of **2** (−257.4°) is opposite to that (+234.7°) of 2*S*-dihydroshihunine, suggesting **2** has a 2*R* configuration. Additionally, the appearance of a negative Cotton effect at 244 nm in the CD spectrum of **2** also confirmed this conclusion. From the above evidence, compound **2** was assigned to 2*R*-dihydroshihunine.

Compound **3** was isolated from the branches as a white amorphous powder which showed an $[M]^+$ ion peak at *m/z*

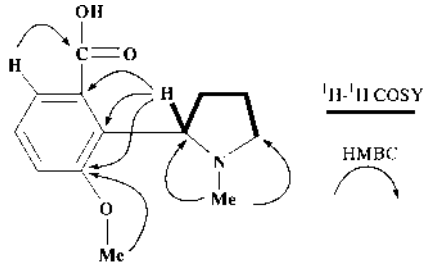

Fig. 1. Selected ^{1}H–^{1}H COSY and HMBC Correlations of Compound **1**

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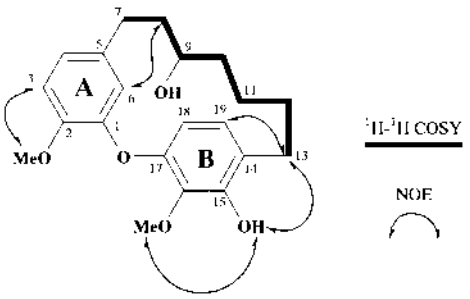


Fig. 2. ^{1}H–^{1}H COSY and NOE Correlations of Compound **3**

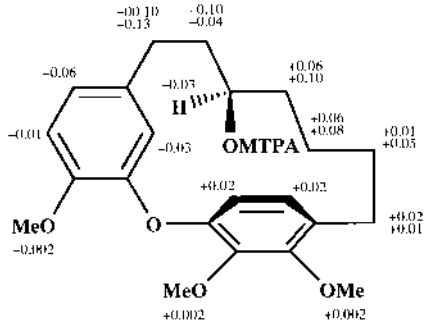


Fig. 3. $\Delta\delta$ ($\delta_S-\delta_R$) Values Obtained from MTPA Esters of Compound **3a**

358 in the EI-MS spectrum. Taking the ^{13}C-NMR data and the result of elemental analysis into account, the molecular formula of **3** was established to be $C_{21}H_{26}O_5$. In the ^{13}C-NMR spectrum, the signals due to two aromatic nuclei and seven aliphatic carbons along with two methoxyl groups were observed, indicating that **3** is a diarylheptanoid. Analysis of the aromatic signals in the ^{1}H-NMR spectra suggested the presence of a 1,2,3,4-tetrasubstituted [δ_H 6.89 (1H, d, J=8 Hz, H-19), 6.69 (1H, d, J=8 Hz, H-18)] and a 1,3,4-trisubstituted benzene ring [δ_H 6.84 (1H, d, J=8 Hz, H-3), 6.70 (1H, dd, J=2, 8 Hz, H-4), 5.72 (1H, d, J=2 Hz, H-6)]. In addition, a phenolic hydroxyl [δ_H 5.93 (1H, s, 15-OH)] and an alcoholic hydroxyl [δ_H 1.25 (1H, s, 9-OH)] which were exchangeable with D_2O, and two methoxyl groups [δ_H 4.00, 3.98 (each 3H, s)] were also confirmed in the ^{1}H-NMR spectrum. The ^{1}H- and ^{13}C-NMR spectral data mentioned above are very similar to those of platycarynol[8] (**5**) isolated from *Platycarya strobilacea* (Juglandaceae), suggesting that **3** is a diphenyl ether-type diarylheptanoid. The correlations of the aliphatic protons in the ^{1}H–^{1}H COSY spectrum displayed the connectivities from C-7 to C-13 (Fig. 2), revealing the location of a hydroxyl group at C-9 position. The NOE correlations between H-13 and H-19, between H-13 and phenolic hydroxyl, and between H-6 and H-8 which were observed in the NOE spectrum of **3** revealed the linkage of C-7 to C-5 of benzene ring A and C-13 to C-14 of benzene ring B (Fig. 2). Furthermore, the NOE correlations between H-3 and methoxyl (δ_H 3.98), between phenolic hydroxyl and methoxyl (δ_H 4.00) indicated the positions of methoxyls and hydroxyl in benzene rings. Hence, the linkage diphenyl ether is determined to be between C-1 and C-17. From the above evidence, the plain structure of **3** was determined to be as shown in Fig. 2.

To determine the absolute configuration of the secondary hydroxyl group at C-9, **3** was methylated with CH_2N_2 to give **3a** which was further esterified by (*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid (MTPA) and (*S*)-MTPA, respectively. By applying the modification of Mosher's method[9] to the MTPA esters (**3b**, **c**) of **3a**, the positive and negative $\Delta\delta$ ($\delta_S-\delta_R$) values shown in Fig. 3 unequivocally indicated a 9*R* configuration in compound **3**.

The negative Cotton effect at 241 nm and the positive one at 218 nm in the CD spectrum suggested the chiral plane of **3** is expressed as *S* configuration which is the same as that of (−)-galeon, a diarylheptanoid isolated from the Myrica plant.[10]

Compound **4** was isolated as a light yellow powder from the branches. Its molecular formula was determined to be

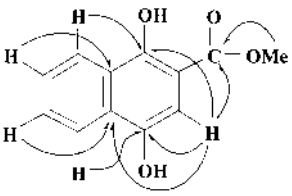
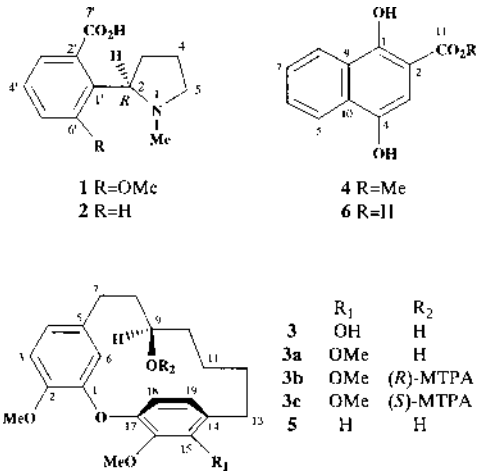


Fig. 4. HMBC Correlations of Compound **4**



	R_1	R_2
3	OH	H
3a	OMe	H
3b	OMe	(*R*)-MTPA
3c	OMe	(*S*)-MTPA
5	H	H

Chart 1

$C_{12}H_{10}O_4$ by high resolution EI-MS. The ^{1}H-NMR spectrum displayed the signals derived from a 1,2-disubstituted benzene ring [δ_H 8.32 (1H, dd, J=1, 8 Hz), 8.16 (1H, dd, J=1, 8 Hz), 7.61 (1H, dt, J=1, 8 Hz), 7.53 (1H, dt, J=1, 8 Hz)], a singlet aromatic signal (δ_H 7.11) and a methoxyl group (δ_H 3.98). The ^{13}C-NMR spectral data indicated the presence of an ester carbonyl (δ_C 172.2), a methoxyl group (δ_C 52.6) and 10 aromatic signals, suggesting **4** is a naphthalene carboxylic acid methyl ester. Therefore, the remaining residues of **4** are deduced to be two hydroxyl groups. The carbonyl and these two hydroxyl groups were determined to be located in C-2, C-1 and C-4, respectively, of the naphthalene ring by the HMBC correlations shown in Fig. 4. A glucoside of hydroxynaphthalene carboxylic acid methyl ester related to **4** was reported to be present in *Juglans mandshurica* (Juglandaceae).[11]

Compound **4**, a methyl ester of compound **6**, may be an artifact produced in the course of plant extraction or isolation. Compound **6** is a biogenetically important intermediate in the biosynthesis of juglone from *O*-succinoylbenzoic acid[12] (Chart 1).

In conclusion, we have isolated four new compounds (**1**—**4**) from the fruits and branches of *Rhoiptelea chiliantha* (Rhoipteleaceae). Compounds **1** and **2** belong to pyrrolidine-type alkaloids. Interestingly, compound **2** possesses an antipodal structure of 2*S*-dihydroshihunine which was isolated from *Banisteriopsis cappi* (Malpighiaceae).[7] Compound **3** has the same skeleton as **5** which was isolated from *Platycarya strobilacea* (Juglandaceae) in our previous paper.[8] Compound **4** is considered to be biogenetically-related to juglone which is widely distributed in Juglandaceous plants.

Chemotaxonomic studies on the Rhoipteleaceae based on our extensive and detailed investigations on the chemical constituents of *Rhoiptelea chiliantha* DIEL *et* HAND.-MAZZ.[1—6] have suggested the relationships of the order Rhoipteleales (comprising Rhoipteleaceae) to the Juglandales (comprising Juglandaceae), Fagales (comprising Betulaceae and Fagaceae) and Myricales (comprising Myriaceae).[3] The existence of **3** and **4** reported in the present paper further supported the affinity of a systematic position between the Rhoipteleales and Juglandales, and suggested the Juglandales is probably the most closely related order to the Rhoipteleales.

Experimental

General Melting points were determined on a micromelting point hot stage apparatus (Yanagimoto) and are uncorrected. Optical rotations were measured with a JASCO DIP-370 digital polarimeter. The CD spectra were measured with a JASCO J-725 apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded on Varian Unity *plus* 500, Varian Gemini 300 and Varian Gemini 200 spectrometers. Coupling constants (J) are expressed in Hz, and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. FAB-MS were recorded on a JEOL JMS DX-303 spectrometer with glycerol as a matrix. Column chromatographies were performed with Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia Fine Chemical Co., Ltd.) and MCI-gel CHP 20P (75—150 μm, Mitsubishi Chemical Co., Ltd.). Thin layer chromatography (TLC) was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm thick, Merck), and spots were detected by ultraviolet (UV) illumination and by spraying 10% sulfuric acid reagent or 2% ninhydrin in EtOH.

Plant Material The fruits and branches of *Rhoiptelea chiliantha* were collected in Guangxi, China in Oct., 1988. A voucher specimen has been deposited in the Laboratory of Plant Chemotaxonomy, China Pharmaceutical University, Nanjing, China.

Extraction and Isolation The MeOH extracts of the air-dried fruits (495 g) and branches (820 g) of *Rhoiptelea chiliantha* were separately suspended in H_2O, then successively extracted with Et_2O and EtOAc. The water layer of the fruits was chromatographed over MCI-gel CHP 20P (0—100% MeOH) to give fr.-1 (1.6 g), fr.-2 (0.9 g) and fr.-3 (13.7 g). Fraction-2 was subjected to Bondapak ODS (0—40% MeOH) and silica gel ($CHCl_3$: MeOH : H_2O, 9 : 1 : 0.1—8 : 2 : 0.2) column chromatographies to afford **1** (274 mg) and **2** (130 mg). The Et_2O layer (15.2 g) of branches was separated into fr.-1 (0.9 g), fr.-2 (4.7 g) and fr.-3 (5.8 g) by column chromatography on silica gel ($CHCl_3$: MeOH : H_2O, 10 : 0 : 0—7 : 3 : 0.5). Fraction-2 was chromatographed over MCI-gel CHP 20P (80—100% MeOH) and silica gel (hexane : EtOAc, 2 : 1—1 : 1) to afford **3** (276 mg). The H_2O layer of the branches was subjected to Sephadex LH-20 column chromatography to afford fr.-1 (17.3 g), fr.-2 (2.9 g) and fr.-3 (4.0 g). Fraction-2 was separated by silica gel chromatography ($CHCl_3$: MeOH : H_2O, 9 : 1 : 0.0—8 : 2 : 0.2) to yield **4** (162 mg).

Compound **1**: Colorless needles, mp 178—180 °C, $[\alpha]_D^{15}$ −189.4° (c=0.5, $CHCl_3$). *Anal.* Calcd for $C_{13}H_{17}NO_3 \cdot 3/4\ H_2O$: C, 62.76; H, 7.49; N, 5.63. Found: C, 62.80; H, 7.15; N, 5.54. EI-MS m/z: 235 (M^+), 220 (M^+-CH_3). ^{1}H-NMR (500 MHz, acetone-d_6): δ_H 7.50 (1H, dd, J=2, 8 Hz, H-3′), 7.36 (1H, dd, J=8, 9 Hz, H-4′), 7.11 (1H, dd, J=2, 9 Hz, H-5′), 4.96 (1H, dd, J=10, 11 Hz, H-2), 3.87 (3H, s, OMe), 3.83 (1H, ddd, J=4, 8, 11 Hz, H-5a), 3.16 (1H, dt, J=11, 10 Hz, H-5b), 2.62 (3H, s, NMe), 2.33 (1H, m, H-3a), 2.19 (2H, m, H_2-4), 2.11 (1H, m, H-3b). ^{13}C-NMR (125 MHz, acetone-d_6): δ_C 172.8 (s, C-7′), 158.7 (s, C-6′), 142.0 (s, C-2′), 130.3 (d, C-4′), 125.1 (d, C-3′), 120.8 (s, C-1′), 112.9 (d, C-5′), 62.4 (d, C-2), 56.7 (q, OMe), 54.8 (t, C-5), 37.4 (q, NMe), 31.0 (t, C-3), 22.6 (t, C-4). CD (c=0.011, MeOH) $[\theta]^{25}$ (nm): -1.9×10^4 (246).

Compound **2** (*R*-dihydroshihunine): Colorless needles, mp 221—223 °C, $[\alpha]_D^{25}$ −257.4° (c=0.2, $CHCl_3$). *Anal.* Calcd for $C_{12}H_{15}NO_2 \cdot 1/4\ H_2O$: C, 68.71; H, 7.45; N, 6.68. Found: C, 69.18; H, 7.31; N, 6.71. EI-MS m/z: 205 (M^+), 195 (M^+-CH_3). ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.19 (1H, dd, J=2, 7 Hz, H-3′), 7.44, 7.39 (each 1H, dt, J=2, 7 Hz, H-4′, 5′), 7.22 (1H, dd, J=2, 7 Hz, H-6′), 3.73 (1H, t, J=9 Hz, H-2), 3.61 (1H, m, H-5a), 2.83 (1H, dt, J=9, 10 Hz, H-5b), 2.49 (3H, s, NMe), 2.08—2.44 (4H, m, H_2-3, H_2-4); ^{1}H-NMR (300 MHz, acetone-d_6): δ_H 7.99 (1H, dd, J=2, 7 Hz, H-3′), 7.45 (3H, m, H-4′, 5′, 6′), 4.33 (1H, t, J=9 Hz, H-2), 3.91 (1H, dt, J=12, 5 Hz, H-5a), 3.24 (1H, dt, J=12, 9 Hz, H-5b), 2.72 (3H, s, NMe), 2.48 (1H, m, H-3a), 2.23 (3H, m, H-3b, H_2-4). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 171.3 (s, C-7′), 135.6 (s, C-1′), 134.2 (s, C-2′), 134.0 (d, C-5′), 131.0 (d, C-3′), 130.6 (d, C-4′), 129.2 (d, C-6′), 73.1 (d, C-2), 54.6 (t, C-5), 37.8 (q, NMe), 32.4 (t, C-3), 22.0 (t, C-4); ^{13}C-NMR (75 MHz, acetone-d_6): δ_C 173.4 (s, C-7′), 138.9 (s, C-1′), 133.3 (d, C-5′), 133.0 (s, C-2′), 132.6 (d, C-3′), 130.8 (d, C-4′), 130.0 (d, C-6′), 73.3 (d, C-2), 55.2 (t, C-5), 37.4 (q, NMe), 32.0 (t, C-3), 22.4 (t, C-4). CD (c=0.0032, MeOH) $[\theta]^{25}$ (nm): -2.4×10^4 (244).

Compound **3**: A white amorphous powder, $[\alpha]_D^{15}$ −58.5° (c=0.3, $CHCl_3$). *Anal.* Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 69.95; H, 7.25. EI-MS m/z: 358 (M^+). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 6.89 (1H, d, J=8 Hz, H-19), 6.84 (1H, d, J=8 Hz, H-3), 6.70 (1H, dd, J=2, 8 Hz, H-4), 6.69 (1H, d, J=8 Hz, H-18), 5.93 (1H, s, 15-OH), 5.72 (1H, d, J=2 Hz, H-6), 4.00 (3H, s, 16-OMe), 3.98 (3H, s, 2-OMe), 3.14 (1H, m, H-9), 3.11 (1H, m, H-13a), 2.64 (1H, ddd, J=4, 10, 17 Hz, H-7a), 2.55 (1H, ddd, J=4, 6, 17 Hz, H-7b), 2.38 (1H, ddd, J=4, 7, 13 Hz, H-13b), 1.83 (1H, m, H-12a), 1.50 (3H, m, H_2-8, H-12b), 1.25 (3H, m, H-10a, 11a, 9-OH), 1.15 (1H, m, H-11b), 1.04 (1H, m, H-10b). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 149.3 (s), 147.9 (s), 146.29 (s), 146.26 (s), 140.1 (s), 134.7 (s), 126.1 (s), 125.4 (d), 122.2 (d), 115.9 (d), 114.1 (d), 112.0 (d), 71.8 (d, C-9), 61.7, 56.2 (each q, 2, 16-OMe), 38.4 (t), 36.1 (t), 28.9 (t), 28.7 (t), 28.3 (t), 22.4 (t). CD (c=0.0016, MeOH) $[\theta]^{25}$ (nm): $+4.42\times10^4$ (218), -3.24×10^4 (241), -1.15×10^4 (283).

Methylation of 3 A solution of **3** (142 mg) in MeOH was treated with CH_2N_2 in Et_2O at room temperature. The reaction mixture was evaporated *in vacuo*, and the residue was separated with silica gel (hexane : EtOAc, 4 : 1—1 : 1) to give **3a** (28.2 mg): a white amorphous powder, $[\alpha]_D^{15}$ −4.5° (c=0.9, $CHCl_3$). EI-MS m/z: 372 (M^+). ^{1}H-NMR (200 MHz, $CDCl_3$): δ_H 6.95, 6.92 (each 1H, d, J=8 Hz, H-18, H-19), 6.69 (1H, dd, J=2, 8 Hz, H-4), 6.84 (1H, d, J=8 Hz, H-3), 5.74 (1H, d, J=2 Hz, H-6), 3.96, 3.83, 3.79 (each 3H, s, 4, 5, 19-OMe), 3.15 (1H, m, H-9), 3.10 (1H, m, H-13a), 2.51 (2H, m, H2-7), 2.40 (1H, m, H-13b).

Preparation of MTPA Esters of 3a A solution of **3a** (5 mg), dicyclohexylcarbodiimide (8 mg), 4-dimethylaminopyridine (6 mg) and (*R*)-(+)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid (8 mg) in CH_2Cl_2 was allowed to stand at room temperature for 18 h. The resulting mixture was purified over a micro-column (0.7×7 cm) of silica gel (hexane : EtOAc, 8 : 1—6 : 1) to afford (*R*)-MTPA ester **3b** (3 mg). The use of (*S*)-(−)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid gave the (*S*)-MTPA ester **3c** (3 mg).

Compound **4**: A light yellow amorphous powder. HR-EI-MS m/z: 218.0561 (M^+) (Calcd for $C_{12}H_{10}O_4$: 218.0579). ^{1}H-NMR (500 MHz, CD_3OD): δ_H 8.32 (1H, dd, J=1, 8 Hz, H-8), 8.16 (1H, dd, J=1, 8 Hz, H-5), 7.61 (1H, dt, J=1, 8 Hz, H-6), 7.53 (1H, dt, J=1, 8 Hz, H-7), 7.11 (1H, s, H-3), 3.98 (3H, s, OMe). ^{13}C-NMR (125 MHz, CD_3OD): δ_C 172.2 (s, C-11), 155.0 (s, C-1), 145.7 (s, C-4), 130.5 (s, C-10), 129.2 (d, C-6), 126.7 (d, C-7), 126.2 (s, C-9), 124.2 (d, C-8), 122.8 (d, C-5), 105.4 (s, C-2), 105.0 (d, C-3), 52.6 (q, OMe).

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