The Synthesis and Anti-geotropic Activity of *o*-Arylethenylbenzoic Acids

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Fourteen new and three known *o*-arylethenylbenzoic acids (**10~18**), required for testing as potential plant growth regulators, have been synthesized by the Wittig reaction. The *cis*- and *trans*-isomers were separated by fractional crystallization and identified by NMR spectroscopy. The preliminary assay results on cress seedlings are reported and show that both geometric isomers appear to have nearly identical anti-geotropic activity in this test system.

Recent investigations in our laboratories¹⁾ have shown that a wide range of *o*-substituted benzoic acid (**1**, X, Y, and Z=O, S, N, CH) related to 1-(2-carboxyphenyl)-3-phenylpropan-1,3-dione (**2**)²⁾ abolish the normal positive geotropic response of seedling roots. One of the most common structural features of these compounds, apart from having a 2-carboxyphenyl group, is that the two aryl groups are placed on the heterocyclic ring in a 1,3-relationship as in (**1**), so that the three aromatic rings are capable of assuming coplanarity. It is suggested that at least some degree of conjugation between the two ends of the molecule, perhaps enabling it to

cannot be coplanar. As expected they are found to be inactive on the cress seedlings assay (Table II). However, in view of the difficulty we experienced in making more of these 1,2-diarylheterocyclic compounds we decided to make the 1,2-diarylethylenes, which could provide the *cis*- (nonplanar) and the *trans*- (planar) compounds,⁴⁾ instead. It is well known that, while *cis*-cinnamic acid is active as an auxin, the *trans*-isomer is inactive,⁵⁾ and therefore it was expected that there would be significant differences in the activities of the *cis*- and *trans*-diarylethylenes. This paper reports the synthesis of the *o*-arylethenylbenzoic acids (**10~18**) and the anti-geotropic activity of these compounds.

achieve planarity, is a necessary requirement for high activity.^{1a)} It was of interest to know how important planarity is for activity, and in this context we synthesized several 1,2-diarylthiazoles (**3**)³⁾ in which the two aryl groups

Synthesis of *o*-arylethenylbenzoic acids

The Wittig reaction has been used for this purpose. Thus, the phosphonium salt of the ethyl ester of 2-bromomethylbenzoic acid (**4**)⁶⁾ and sodium hydride were treated in dry dimethylformamide to yield the phosphorane (**5**) *in situ*. To this mixture an appropriate aromatic aldehyde was added and stirred overnight at room temperature. After work-up the reaction mixture was extracted with benzene and chromatographed on a silica gel column. The fore-run with benzene/light petroleum generally gave a mixture of unreacted starting materials, ethyl *o*-toluate (**6**) and in one case

trans-1,2-bis-(2-ethoxycarbonylphenyl)-ethylene (7). These compounds may be formed due to moisture and oxygen present in the reaction conditions used according to the following mechanism.⁷⁾

The esters (8) were obtained in 60~80% yield after elution with benzene. They were usually a 1:1 mixture of *cis*- and *trans*-isomers and were difficult to separate. However, only

the *trans* isomers of the 3-indolyl (8, Ar=3-indolyl) and 9-anthracenyl derivatives (8, Ar=9-anthracenyl) were crystallized out because the former is the only product and the latter is the major product, respectively. The 4-nitrophenyl derivatives (8, Ar=4-nitrophenyl) gave crystalline *cis*- and *trans*-esters which were separated by fractional crystallization.

Hydrolysis of the mixture of isomeric esters was carried out either in 10% sodium hydroxide with some ethanol or in concentrated hydrochloric acid at 100°C to give a mixture of *cis*- and *trans*-benzoic acid (9) almost quantitatively. These mixtures could be separated by fractional crystallization and the purity of an isomer checked by its NMR spectrum. In the *cis*-isomer, the ethylenic protons appear as a pair of doublets with a coupling constant of 10~13 Hz whereas in the *trans*-isomers they appear as a pair of doublets with a coupling constant of 15~18 Hz. The compounds synthesized in this way are listed in Table I.

It is of interest to note here that the hydrolysis of the indole-ester (8, Ar=3-indolyl) gave the indolenine derivative (19) when neutralized with acetic acid.

The compound (19) crystallized out from methanol as yellow fluorescent needles, mp

TABLE I.

 (Z = <i>cis</i>)		 (E = <i>trans</i>)	
Compound	Ar	Compound	Ar
10Z 10E		15Z 15E	
11Z 11E		16Z 16E	
12Z 12E		17Z 17E	
13Z 13E		18E	
14Z 14E

145~147° and was found to be quite stable in air. In the NMR spectrum, signals for an ABX system appear at 3.16~3.5 δ (multiplet) and 5.8 δ (quartet), and for the acid hydrogen at 8.35 δ (broad singlet) which disappeared on addition of D₂O. The infrared spectrum in Nujol showed a strong absorption at 1680 cm⁻¹ for a conjugated carboxylic acid. When neutralized with concentrated hydrochloric acid, however, the normal indole derivative (18E) was obtained. The indolenine (19) was converted to the indole (18E) by dissolving it in aqueous sodium carbonate and acidifying with concentrated hydrochloric acid. However, it was not possible to convert the indole (18E) back to the indolenine (19) through neutralization of its alkali solution with acetic acid, indicating that unlike 2-aminoindole⁸⁾ and 3-nitrosoindole⁹⁾ which both exist predominantly in their indolenine forms, these compounds are not simple indole-indolenine tautomers. More detailed study on this subject will be published elsewhere.

Attempts to synthesize the 4-pyridine derivative (20) failed. The product obtained after the hydrolysis was found to be 3-[(pyridine-4-yl)methyl]isobenzofuran-1(3H)-one (21) exclusively, indicating that the acid (20), formed after hydrolysis, prefers to exist in the cyclic form (21) in this case. This could be due to the strong electron withdrawing effect of the 4-pyridyl group. However, the 4-nitrophenyl derivative mentioned above with a similar activated double bond, did not give any cyclized product.

Effects on root geotropism

The methods used for determining effects on

TABLE II. EFFECTS ON ROOT GEOTROPISM ON CRESS SEEDLINGS

Compound	Molar concentration		
	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷
2	++	++	++
3	+	-	-
10Z	++	+	-
10E	++	+	-
11Z	++	++	+
11E	++	++	+
12Z	++	+	-
12E	++	+	+
13Z	++	++	+
13E	++	(++)	-
14Z	-	-	-
14E	(+)	-	-
15Z	-	-	-
15E	-	-	-
16Z	-	-	-
16E	-	-	-
17Z	+	-	-
17E	(+)	-	-
18E	(+)	-	-
19	++	+	(+)

++ Complete loss of geotropism; (++) *ca.* 75% loss; + 50% loss; (+) 25% loss; - no effects.

root geotropism were based on that used by Jones *et al.*,¹⁰⁾ and have been fully described previously.^{1a,2)} The preliminary results are recorded in Table II. Contrary to expectations, the *cis*- and *trans*-isomers show nearly identical results in this assay system. This can be explained in two ways: a) the *cis*- and *trans*-forms are active in their own right; or b) biologically inactive *cis*-isomers are converted to the active *trans*-forms. Since an energy-rich *cis*-form is convertible into a more stable *trans*-form, it is possible that the sterically crowded *cis*-isomers are converted to the planar *trans*-isomers in the plant under the test conditions. The reported isomerization of the biologically inactive *cis*-isomer of diethylstilbestrol to the active *trans*-isomer *in vivo*¹¹⁾ seems to support the above possibility. However, it is unlikely that the *cis*-isomers are converted into the *trans*-forms in the plant in the present case, because, unlike *cis*-diethylstilbestrol, these *cis*-isomers are chemically quite stable and the bioassays used in this

work are carried out under relatively mild conditions. The fact that in a similar auxin type assay, biologically active *cis*-cinnamic acid does not change to the inactive *trans*-form⁵ suggests that the *cis*-isomers in the present work are active in their own right. In fact this is supported by data for compounds (13Z), (13E), (18E), and (19) which suggest that non-planar compounds are more active than their planar analogues. This implies that molecular planarity may not be all that critical for activity.

EXPERIMENTAL

Melting points are uncorrected and were taken on an Electrothermal melting point apparatus. NMR spectra were recorded on a Varian A60-D instrument with tetramethylsilane as internal reference, and infra-red spectra were determined with a Perkin-Elmer 457 spectrophotometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and mass spectra were recorded by the Mass Spectrometry Unit, Division of Entomology, CSIRO.

General procedure for the Wittig olefine synthesis. To a suspension of the triphenylphosphonium salt to the ethyl ester of 2-bromomethylbenzoic acid⁶ (10.1 g; 0.02 mol) in dry DMF (100 ml) NaH (0.84 g; 56% dispersion in oil) is added. The mixture is stirred at room temperature until a clear orange solution has resulted. An aldehyde (0.02 mol) in DMF (10 ml) is added slowly to the solution with stirring. The solution is stirred overnight at room temperature. After removing the solvent under reduced pressure, the residue is extracted with benzene and the extract washed with water and dried (Na₂SO₄). Concentration and cooling of the extract deposited some triphenylphosphine oxide, which is filtered off. The filtrate is applied to a silica gel column and eluted firstly with benzene/light petroleum (60–80) (1:1). Secondly, elution with benzene gives a roughly 1:1 mixture of *cis*- and *trans*-isomers of the ethyl esters. The esters are heated either in 10% NaOH/EtOH or in conc. Hydrochloric acid at 100°C to give the acids, which are fractionally recrystallized to separate the *cis*- and *trans*-isomers.

cis- and *trans*-2-(2-Phenylethenyl)benzoic acid (10Z) and (10E). These compounds were prepared according to the literature.⁶

2-[2-(1-Naphthyl)ethenyl]benzoic acids (11). 1-Naphthaldehyde (3.12 g; 0.02 mol) was treated as above to give the acid mixture (3.9 g, 75%). Fractional recrystallization from EtOH gave first *cis*-2-[2-(1-naphthyl)ethenyl]benzoic acid (11Z), mp 195~196°. *Anal.* Found:

C, 82.6; H, 5.1. Calcd. for C₁₉H₁₄O₂: C, 83.2; H, 5.1. NMR δ (CDCl₃/DMSO-*d*₆): 7.16 and 7.47 (2H, a pair of doublets, *J*=13.0 Hz), 9.7 (1H, broad singlet), MS *m/z*: 274 (M⁺, 100) and *trans*-2-[2-(1-naphthyl)ethenyl]benzoic acid (11E), mp 160~161° (lit.¹²) mp 160~161°. NMR δ (CDCl₃/DMSO-*d*₆): 7.14 and 7.9 (2H, a pair of doublets, *J*=15.0 Hz), 11.6 (1H, broad singlet). MS *m/z*: 274 (M⁺, 100).

2-[2-(2-Naphthyl)ethenyl]benzoic acids (12). 2-Naphthaldehyde (3.1 g; 0.02 mol) gave an oil (4.0 g), which was hydrolyzed in 10% NaOH (20 ml) to give the acids (2.8 g). Recrystallization of the sample from ethyl acetate gave *trans*-2-[2-(2-naphthyl)ethenyl]benzoic acid (12E), mp 216~218°. *Anal.* Found: C, 83.1; H, 5.15. Calcd. for C₁₉H₁₄O₂: C, 83.2; H, 5.1%. NMR δ (CDCl₃/DMSO-*d*₆): 7.27 and 8.28 (2H, a pair of doublets, *J*=17.0 Hz). MS *m/z*: 274 (M⁺, 100) and from the mother liquor *cis*-2-[2-(2-naphthyl)ethenyl]benzoic acid (12Z) was isolated. It has mp 172~175° (acetone/light petroleum (60~80)), *Anal.* Found: C, 83.3; H, 5.2%. NMR δ (CDCl₃/DMSO-*d*₆): 7.09 and 7.67 (2H, a pair of doublets, *J*=12.0 Hz), 10.2 (1H, broad singlet). MS *m/z*: 274 (M⁺, 100).

2-[2-(9-Anthracenyl)ethenyl]benzoic acids (13). 9-Anthraldehyde (4.1 g; 0.02 mol) gave an oil (7.1 g). Crystallization of the oil from EtOH gave ethyl *trans*-2-[2-(9-anthracenyl)ethenyl]benzoate (4.5 g), mp 114~116°. *Anal.* Found: C, 84.9; H, 5.6. Calcd. for C₂₅H₂₀O₂: C, 85.2; H, 5.7%. NMR δ (CDCl₃): 1.26 (3H, triplet), 4.29 (2H, quartet), 7.3~7.6 (6H, multiplet), 7.76 (1H, doublet, *J*=16.0 Hz), 7.8~8.1 (4H, multiplet), 8.4 (1H, singlet), 8.5 (2H, multiplet). MS *m/z*: 352 (M⁺, 22). The mother liquor was evaporated to dryness. The residue was heated in 10% NaOH for 3 hr and neutralized with dil. HCl. The resulting yellow solid was recrystallized from ethanol to give *trans*-2-[2-(9-anthracenyl)ethenyl]benzoic acid (13E), mp 253~255°, orange red plates. *Anal.* Found: C, 84.9; H, 5.1. Calcd. for C₂₃H₁₆O₂: C, 85.2; H, 5.0%. NMR δ (CDCl₃/DMSO-*d*₆): 7.3~7.7 (6H, multiplet), 7.9 (1H, doublet, *J*=16.0 Hz), 7.95~8.1 (4H, multiplet), 8.5 (1H, singlet), 8.55 (2H, multiplet). MS *m/z*: 324 (M⁺, 100) and then *cis*-2-[2-(9-anthracenyl)ethenyl]benzoic acid (13Z), yellow needles, mp 246~248°. *Anal.* Found: C, 85.2; H, 5.1%. NMR δ (CDCl₃/DMSO-*d*₆): 6.5~7.1 (3H, multiplet), 7.45 and 7.82 (2H, a pair of doublets, *J*=10.0 Hz), 7.35~7.6 (4H, multiplet), 7.7~8.2 (3H, multiplet), 8.4 (2H, multiplet), 8.4 (1H, singlet) MS *m/z*: 324 (M⁺, 100).

2-[2-(Pyridin-3-yl)ethenyl]benzoic acids (14). 3-Pyridinecarbaldehyde (2.14 g; 0.02 mol) was treated as above and gave the crude esters (4.8 g), which were hydrolysed in conc. HCl at 100°C for 4 hr. Neutralization of the solutions with aq. Na₂CO₃ deposited the benzoic acids (3.0 g). Crystallization from ethanol gave first *trans*-2-[2-(pyridin-3-yl)ethenyl]benzoic acid (14E), mp 190~192°. *Anal.* Found: C, 74.4; H, 5.2; N, 6.4. Calcd. for

$C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2%. NMR δ ($CDCl_3$ /DMSO- d_6): 7.07 and 8.4 (2H, a pair of doublets, $J=16.0$ Hz), MS m/z : 225 (M^+ , 100) and then *cis*-2-[2-(pyridin-3-yl)ethenyl]benzoic acid (**14Z**), mp 168~169°. Anal. Found: C, 74.9; H, 5.05; N, 6.5%. NMR δ ($CDCl_3$ /DMSO- d_6): 6.6 and 7.24 (2H, a pair of doublets, $J=12.0$ Hz). MS m/z : 225 (M^+ , 100).

2-[2-(4-Nitrophenyl)ethenyl]benzoic acids (**15**). From 4-nitrobenzaldehyde (3.1 g; 0.02 mol) the crude ester (**5**, 1 g) was obtained. Crystallization from EtOH precipitated yellow needles, ethyl *trans*-2-[2-(4-nitrophenyl)ethenyl]benzoate (1.3 g), mp 77~79°. Anal. Found: C, 68.8; H, 5.3; N, 4.9. Calcd. for $C_{17}H_{15}NO_4$: C, 68.7; H, 5.1; N, 4.7%. NMR δ ($CDCl_3$ /DMSO- d_6): 7.02 and 8.17 (2H, a pair of doublets, $J=16.0$ Hz). MS m/z : 297 (M^+ , 100). Concentration of the mother liquor deposited yellow plates of ethyl *cis*-2-[2-(4-nitrophenyl)ethenyl]benzoate (1.8 g), mp 86~88°. Anal. Found: C, 68.7; H, 5.2; N, 4.8%. NMR δ ($CDCl_3$ /DMSO- d_6): 6.71 and 7.3 (2H, a pair of doublets, $J=12.0$ Hz), MS m/z : 297 (M^+ , 100). Hydrolysis of the ester in 10% NaOH gave the acid, respectively; *trans*-2-[2-(4-nitrophenyl)ethenyl]benzoic acid (**15E**), mp 204~207°. Anal. Found: C, 67.4; H, 4.2; N, 5.3. Calcd. for $C_{15}H_{11}NO_4$: C, 66.9; H, 4.1; N, 5.2%. NMR δ ($CDCl_3$ /DMSO- d_6): 7.04 and 8.23 (2H, a pair of doublets, $J=16.0$ Hz), 9.8 (1H, broad singlet); MS m/z : 269 (M^+ , 100) *cis*-2-[2-(4-nitrophenyl)ethenyl]benzoic acid (**15Z**), mp 193~195°. Anal. Found: C, 66.55; H, 4.3; N, 5.2%. NMR δ ($CDCl_3$ /DMSO- d_6): 6.74 and 7.28 (2H, a pair of doublets, $J=12.0$ Hz), 10.9 (1H, broad singlet). MS m/z : 269 (M^+ , 100).

2-[2-(2-Furyl)ethenyl]benzoic acids (**16**). 2-Furaldehyde (1.92 g; 0.02 mol) gave an oil (4.4 g) after chromatography. Hydrolysis with 10% NaOH and recrystallization of the product from light-petroleum (80~100°) gave first *cis*-2-[2-(2-furyl)ethenyl]benzoic acid (**16Z**), mp 102~105°. Anal. Found: C, 72.5; H, 4.6; O, 22.6. Calcd. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.7; O, 22.4%. NMR δ ($CDCl_3$): 5.97 (1H, doublet, $J=4.0$ Hz), 6.22 (1H, multiplet), 7.21, (1H, broad singlet), 6.5 and 6.98 (2H, a pair of doublets, $J=12.0$ Hz), 7.5 (3H, multiplet), 8.2 (1H, multiplet), 11.1 (1H, broad singlet), MS m/z : 214 (M^+ , 100), and *trans*-2-[2-(2-furyl)ethenyl]benzoic acid (**16E**), mp 126~127°. Anal. Found: C, 73.0; H, 5.0; O, 22.3%. NMR δ ($CDCl_3$): 6.47 (2H, broad singlet), 6.88 and 8.0 (2H, a pair of doublets, $J=16.0$ Hz), 7.1~7.8 (4H, multiplet), 8.1 (1H, multiplet), 10.6 (1H, broad singlet). MS m/z : 214 (M^+ , 100).

2-[2-(2-Thienyl)ethenyl]benzoic acids (**17**). 2-Thiophenecarbaldehyde (2.24 g; 0.02 mol) gave the crude esters (4.9 g). Hydrolysis with 10% NaOH and crystallization of the product from light petroleum (80~100°) gave yellow needles, mp 133~135.5°, which was found to

be a 1:1 mixture of the *cis*-*trans*-isomers. (lit.¹³) mp 133~135°. Recrystallization from MeOH precipitated first *cis*-2-[2-(2-thienyl)ethenyl]benzoic acid (**17Z**), mp 142~144°. Anal. Found: C, 67.7; H, 4.5; S, 13.8. Calcd. for $C_{13}H_{10}O_2S$: C, 67.8; H, 4.4; S, 13.9%. NMR δ ($CDCl_3$ /DMSO- d_6): 6.82 and 6.95 (2H, a pair of doublet, $J=12.0$ Hz), 9.4 (1H, broad singlet), MS m/z : 230 (M^+ , 93) and *trans*-2-[2-(2-thienyl)ethenyl]benzoic acid (**17E**), mp 132~133°. Anal. Found: C, 67.8; H, 4.7; S, 13.4%. NMR δ ($CDCl_3$): 7.2 and 7.88 (2H, a pair of doublets, $J=16.0$ Hz), 10.2 (1H, broad singlet). MS m/z : 230 (M^+ , 100).

2-[2-(3-Indolyl)ethenyl]benzoic acid (**18**). 3-Indolecarbaldehyde (3.4 g; 0.025 mol) was treated as above except that the mixture was heated at ca. 70°C overnight. Chromatography with light petroleum (60~80) separated ethyl *o*-toluate (**6**) (1.4 g) and then *trans*-1,2-bis-(2-ethoxycarbonylphenyl)ethylene (**7**) (0.3 g), mp 81~83° (light-petroleum (60~80°)). Anal. Found: C, 74.2; H, 6.3. Calcd. for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2%. NMR δ ($CDCl_3$): 1.4(6H, triplet), 4.42 (4H, quartet), 7.98 (2H, singlet), 6.9~8.1 (8H, multiplet). MS m/z : 324 (M^+ , 54). Elution with benzene separated a yellow band from which ethyl *trans*-2-[2-(3-indolyl)ethenyl]benzoate (3.2 g), mp 113~115° crystallized out. Anal. Found: C, 78.1; H, 6.1; N, 5.1. Calcd. for $C_{19}H_{17}NO_2$: C, 78.35; H, 5.9; N, 4.8%. NMR δ ($CDCl_3$): 7.21 and 8.03 (2H, a pair of doublet, $J=17.0$ Hz). MS m/z : 291 (M^+ , 100). The ester (1.0 g) in 10% NaOH (15 ml) and EtOH (5 ml) was refluxed for 1 hr. The solution was neutralized with acetic acid. The product was extracted with ethyl acetate, washed with water and dried (Na_2SO_4). After removing the solvent the residue was recrystallized from MeOH to give 2-[2-(3H-indol-3-ylidene)ethyl]benzoic acid (**19**) (0.6 g), mp 145~147°. Anal. C, 77.3; H, 5.2; N, 5.25. Calcd. for $C_{17}H_{13}NO_2$: C, 77.5; H, 5.0; N, 5.38. NMR δ ($CDCl_3$): 3.16~3.5 (2H, multiplet, CH_2), 5.8 (1H, quartet, $-CH=$), 7.0~7.76 (8H, multiplet, ArH), 8.0~8.2 (1H, multiplet), 8.35 (1H, broad singlet, COOH). IR ν_{max} (Nujol): 1680 cm^{-1} (COOH). MS m/z : 263 (M^+ , 59), 228 (25), 118 (100), 90 (25). The ester (0.5 g) was treated as above and acidified with conc. HCl. After work-up the product was recrystallized from EtOH to give *trans*-2-[2-(3-indolyl)ethenyl]benzoic acid (0.1 g) (**18E**), mp 238 (dec.). Anal. Found: C, 77.25; H, 5.1; N, 5.1. Calcd. for $C_{17}H_{13}NO_2$: C, 77.5; H, 5.0; N, 5.3%. NMR δ ($CDCl_3$): 10.0 (1H, broad singlet). MS m/z : 263 (M^+ , 50). This was also obtained from the indolenine (**19**) by dissolving in alkali and acidifying with conc. HCl.

3-[(Pyridin-4-yl)methyl]isobenzofuran-1(3H)-one (**21**). 4-Pyridinecarbaldehyde (2.14 g; 0.02 mol) gave a 1:1 mixture of the crude esters (3.9 g). After treatment with 48% HBr/AcOH the hydrobromide of ethyl *trans*-2-[2-(pyridin-4-yl)ethenyl]benzoate, mp 178~180° crystallized out. Anal. Found: C, 57.5; H, 5.15; N, 4.4. Calcd. for

$C_{16}H_{16}BrNO_2$: C, 57.5; H, 4.8; N, 4.2%. NMR δ ($D_2O/DMSO-d_6$): 1.42 (3H, triplet), 4.42 (2H, quartet), 7.15 and 8.36 (2H, a pair of doublet, $J=16.0$ Hz), 7.4~7.9 (4H, multiplet), 8.1 (2H, doublet, $J=6.0$ Hz), 8.77 (2H, doublet, $J=6.0$ Hz). MS m/z : 253 ($M^+ -80$, 100). Attempts to crystallize the *cis*-isomer failed. The hydrolysis of the esters either in conc. HCl or 10% NaOH gave only one product in 90% yield and found to be 3-[(pyridin-4-yl)methyl]isobenzofuran-1(3H)-one (**21**), mp 119~121° (EtOH). Anal. Found: C, 74.5; H, 5.1; N, 6.2. Calcd. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2%. NMR δ ($CDCl_3$): 3.1 (2H, quartet), 5.77 (1H, triplet), 7.2 (2H, quartet), 7.3~7.98 (4H, multiplet), 8.51, (2H, quartet). IR ν_{max} (Nujol) cm^{-1} . 1745 (5-membered ring lactone). MS m/z : 225 (M^+ , 42).

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