C_3 Symmetric oxazolinyl ligand as catalyst in the enantioselective addition of diethylzinc to aldehydes

T.H. Chan and G.Z. Zheng

Abstract: The C_3 symmetric oxazolinyl ligand **1** has been synthesized. Compound **1** catalyzed the addition of diethylzinc to aromatic aldehydes to give secondary alcohols with high enantiomeric excesses (up to 90%).

Key words: diethylzinc, enantioselective synthesis, C_3 symmetric ligands, enantioselective addition reactions, oxazolinyl ligands.

Résumé : On a synthétisé le coordinat oxazolinyle **1**, de symétrie C_3. Le composé **1** catalyse l'addition du diéthylzinc sur les aldéhydes aromatiques qui conduit à des alcools secondaires avec des excès énantiomériques élevés (jusqu'à 90%).

Mots clés : diéthylzinc, synthèse énantiosélective, coordinats de symétrie C_3, réactions d'addition énantiosélective, coordinats oxazolinyles.

[Traduit par la rédaction]

Introduction

The success of many C_2 symmetric ligands as catalyst in a number of highly enantioselective chemical transformations (1) has underscored the important role that symmetry could play in the stereocontrol of these reactions. It has been suggested that the C_2 ligand enhances the optical yield of the reaction by reducing the number of competing diastereomeric pathways due to the homotopic nature of the remaining coordination sites of the complexes formed by the ligand (1). As a consequence, considerable efforts have been directed to prepare higher order symmetrical compounds (2), such as C_3 symmetric ligands, to see if they can be useful reagents to induce high enantioselectivity in chemical reactions. Although C_3 symmetric phosphine ligands (2*a*), pyrazolyl compounds (2*c*,*d*,*e*), pyridinyl compounds (2*f*), and tris-alkoxides (2*b*) have been made previously, there have been few reports on the use of these ligands in asymmetric synthesis. One example (2*a*) is the asymmetric hydrogenation of dimethyl itaconate using a C_3 phospine ligand giving high ee (95%). On the other hand, for carbon–carbon bond formation, the single report on the use of a chiral C_3 copper complex that catalyzed the cyclopropanation of styrene with diazoacetates gave maximum ee's of only 60% (2*d*). We report here the synthesis of a C_3 symmetric tris(oxazolinyl) compound **1** and its application in asymmetric synthesis.

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This paper is dedicated to Professor William A. Ayer on the occasion of his 65th birthday.

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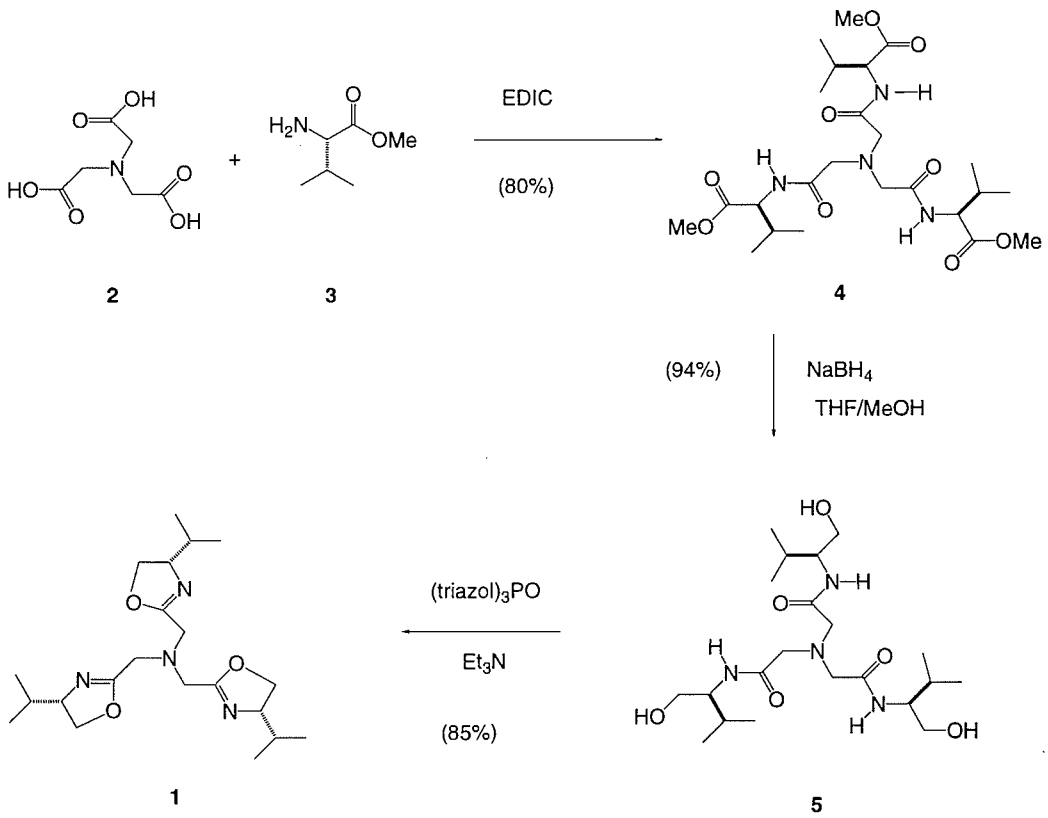
Synthesis

Compound **1** was prepared via the coupling of the triacid **2** with (*S*)-valine methyl ester (**3**) mediated by the coupling agent *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI) (3) (80% yield, Scheme 1). As three chiral centers have been implanted into compound **4**, any racemization during the coupling step should be easily detected by ^{1}H NMR spectroscopy of **4**. The results showed that there was no significant racemization at any of the chiral centres, with or without the presence of 1-hydroxybenzotriazole (HOBT), a reagent reported to prevent racemization during such coupling reactions (4). Selective reduction of the ester functions of **4** to the alcohol **5** was achieved using sodium borohydride (5). The reaction had to be carried out in a mixed solvent system (MeOH:THF = 50:50), and a large excess (5–10 equiv.) of sodium borohydride was used to drive the reduction to completion (94%). The alcohol **5** was subsequently cyclized with the assistance of tris(triazole)phosphine oxide (6) to give the final C_3 product **1** with high yield (85%; Scheme 1). Other cyclization reagents, such as thionyl chloride (7), $(CF_3CO)_2O$–Et_3N (8), *N,N*-dimethylchloromethyleneammonium chloride (9), and $(CF_3SO_2)_2O$–Ph_3PO (10) gave a mixture of products with no significant amount of **1**. Compound **1** could be obtained pure using gel (Sephadex LH-20) filtration (11). It was reasonably stable when stored as a solution of benzene at low temperature. Since the completion of our work, another synthesis of **1** has been reported in the literature (12), using a somewhat different synthetic scheme with lower overall yield.

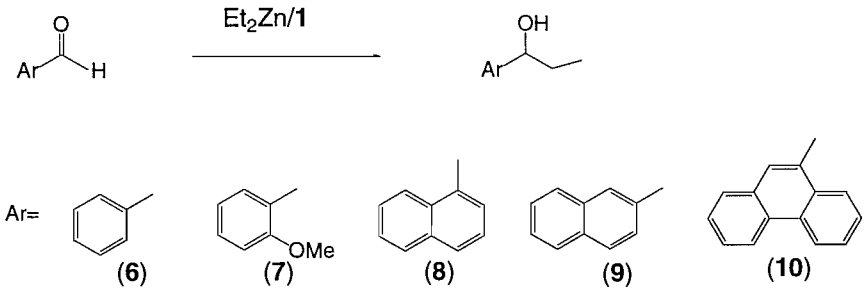
Enantioselective addition of diethylzinc to aldehydes

The C_3 symmetric ligand **1** was used as catalyst in the addition of diethylzinc to aromatic aldehydes **6**–**10** (Scheme 2). The results were encouraging in that the enantiomeric excesses of the alcohols obtained were quite high (up to 90% ee), even

Scheme 1.



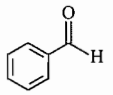
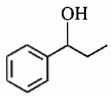
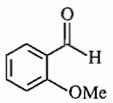
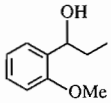
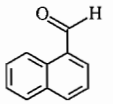
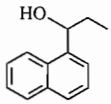
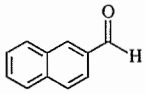
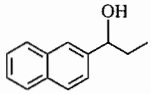
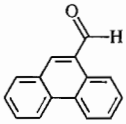
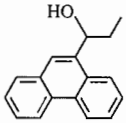
Scheme 2.



though slightly lower than the best results reported for the same reaction using other types of chiral ligands (13). The results are summarized in Table 1. The optical purity and the absolute configuration of the product were determined by conversion to the corresponding Mosher ester and analysed by NMR. The reaction was carried out in toluene as solvent and gave excellent chemical yield in general, with good to high optical yield (72–90% ee). Similar chemical yields were obtained in hexane as solvent, but with somewhat lower enantiomeric excesses for the products. Even in toluene, the amounts of compound **1** in the reaction mixture were crucial for good stereochemical outcome. Relatively large amounts of **1** (>2% mol) were required to produce high ee. However, over 20% mol concentration of catalyst **1** in the reaction mixture did not enhance the enantiomeric excess significantly. When using 26% mol of the catalyst in the reaction, similar enantiomeric excess was obtained (82% ee (*R*); 90% yield) when the substrate was benzaldehyde (**6**). Reducing the amounts of diethylzinc from 6 equivalents (substrate/Et_2Zn = 1 mmol: 3 mmol) to 4 equivalents (substrate/Et_2Zn = 1 mmol:2 mmol) reduced the enantiomeric excess of the product (to 68% ee (*R*) (82% yield) for **6**). Upon further reduction of the relative amount of diethylzinc to 2 equivalents, the enantiomeric excess decreased even further (to 54% (*R*) (70% yield) for **6**). Such concentration dependence is in agreement with the proposed mechanism in which a dinuclear zinc species involving a second molecule of diethylzinc has been postulated as the reactive intermediate in the critical alkyl transfer step (13).

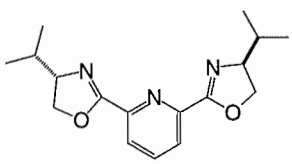
It is interesting to note that under identical reaction conditions, the use of a similar C_2 symmetric ligand **11**, prepared according to literature procedures (14), as the catalyst gave much lower ee's (<20%) for the reaction of diethylzinc with benzaldehyde. We conclude therefore that the C_3 symmetric ligand **1** is an effective catalyst in promoting high enantioselective addition of diethylzinc to aromatic aldehydes. The results justify the search for other C_3 symmetric ligands, as

Table 1. Addition of diethylzinc to aldehydes catalyzed by **1**.

Entry	Substrate	Product	Yield[a] (%)	%ee[b]
1	 **(6)**		92	82 (*R*)
2	 **(7)**		95	72 (*R*)
3	 **(8)**		95	84 (*R*)
4	 **(9)**		90	78 (*R*)
5	 **(10)**		81	90 (*R*)

[a]Purified yield.

[b]The absolute configurations were assigned by NMR analysis of the corresponding Mosher esters.



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well as further exploration of these ligands in asymmetric synthesis.

Experimental section

General

THF was distilled over sodium – benzophenone ketyl radical prior to use. Hexanes, ethyl acetate, dichloromethane, triethylamine, pyridine, DMF, and acetonitrile were distilled over calcium hydride. 1,2,4-Triazole was recrystallized from CH_2Cl_2–*n*-pentane. Thionyl chloride, phosphoryl chloride, and oxalyl chloride were distilled prior to use. Nuclear magnetic resonance spectra were recorded on Varian Gemini 200 (^{1}H 200 MHz, ^{13}C 50 MHz), XL-200 (^{1}H 200 MHz, ^{13}C 50 MHz), XL-300 (^{1}H 300 MHz, ^{13}C 75 MHz), and Unity 500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm) and the references are the residual proton signals of $CDCl_3$ (δ = 7.24 ppm for ^{1}H, δ = 77.00 ppm for ^{13}C NMR). The following abbreviations were used for NMR spectra: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. IR spectra were recorded on an Analet FT A25-18 spectrometer between NaCl plates (neat liquids), a film on a NaCl plate, or as a KBr disk. Mass spectra were recorded on a Kratos MS25RFA mass spectrometer.

All the solvents, liquid reagents, and substrates used in asymmetric hydrosilation were degassed via a freeze–thaw cycle under argon prior to use. All asymmetric addition reactions were carried out under an inert atmosphere (argon). The glassware, syringes, needles, and magnetic stirring bars (Teflon coated) were dried at 120°C overnight or longer and were then allowed to cool over Drierite in a glass desiccator. Enantiomeric excess was determined via the (*S*) Mosher's esters of the products using ^{1}H NMR. The corresponding (*R*)-α-methoxy-α-trifluoromethylphenylacetyl chloride was prepared from (*S*)-α-methoxy-α-trifluoromethylphenylacetic acid and thionyl chloride.

Flash column chromatographic separations were performed with Merck Kieselgel 60 (230–400 mesh ASTM) under air pressure. All thin-layer chromatography (TLC) was carried out using precoated cellular plates with Silica Gel 60 F254. The spots were detected by using UV light, or phosphomolybdic acid – Ce_2SO_4 solution followed by charring with a hot-air gun. Gel filtration was performed using Sephadex LH-20.

Low-temperature reactions were carried out in a Dry Ice – acetone bath (−78°C), and in methanol baths cooled by Neslab Cryocool CC-100 II (−20°C to −100°C) and Cryocool PBC-75 II (20°C to −20°C).

N,N,N-Tris[1-((*S*)-1-methoxycarbonyl-2-methylpropyl)]-nitrilotriacetamide (4)

L-Valine methyl ester hydrochloride (7.50 g, 44.7 mmol), nitrilotriacetic acid (2.48 g, 13.0 mmol), 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (7.5 g, 39.1 mmol), and DMAP (0.12 g, 0.1 mmol) were dissolved in CH_2Cl_2 (250 mL) in a 500 mL flask under argon. 4-Methylmorpholine (6 mL, 5.52 g, 55 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 2 days. To the clear, light-yellow solution, saturated aqueous ammonium chloride solution was added. The organic layer was washed with water (2 × 30 mL) and dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (5.51 g, 80%). IR (film): 1116, 1154, 1210, 1530, 1535, 1543, 1649, 1656, 1742, 2938, 2964, 3263 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.9 Hz, 3H), 4.53 (dd, J = 8.9, 5.2 Hz, 3H), 3.72 (s, 9H), 3.44 (d, J = 15.2 Hz, 3H), 3.28 (d, J = 15.2 Hz, 3H), 2.20 (m, 3H), 0.96 (d, J = 6.3 Hz, 9H), 0.92 (d, J = 6.6 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 172.1, 169.4, 58.3, 57.6, 52.4, 30.6, 19.7, 18.5; MS *m/z* calcd. for $C_{24}H_{42}O_9N_4$: 530.2952; found: 530.2959; $[\alpha]_D^{20}$ +9.1 (c = 0.0527 g/mL, MeOH).

N,N,N-Tris[2-((*S*)-1-hydroxy-3-methylbutyl)]-nitrilotriacetamide (5)

In a 500 mL, three-neck flask equipped with a condenser, *N,N,N*-tris[1-((*S*)-1-methoxycarbonyl-2-methylpropyl)]nitrilotriacetamide (**4**, 5.40 g, 10.2 mmol) was dissolved in methanol

(50 mL) and THF (50 mL) under argon. $NaBH_4$ (3.0 g, 78.9 mmol) was added in small portions to the solution at room temperature. Another portion of $NaBH_4$ (3.0 g, 78.9 mmol) was added to the reaction mixture 2 h later at room temperature. The reaction mixture was stirred at room temperature for 3 h before being quenched with saturated aqueous ammonium chloride solution at 0°C. A clear solution was obtained after HCl (2 N, 30 mL) was added at 0°C. The latter was then neutralized by saturated aqueous K_2CO_3 solution. The organic solvents were removed via rotary evaporator, and the aqueous residue was extracted with ethyl acetate (10 × 40 mL). The combined organic layers were washed with saturated aqueous K_2CO_3 solution (2 mL), water (3 × 10 mL), and then dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (4.33 g, 96%). The product can be purified by flash chromatography on silica gel (ethyl acetate:methanol = 10:1). IR (film): 1076, 1371, 1389, 1466, 1558, 1657, 2934, 2963, 3280, 3294, 3318 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.69 (d, 3H), 4.21 (br, 3H), 3.73 (m, 6H), 3.52 (dd, J = 10.1, 8.3 Hz, 3H), 3.39 (d, J = 5.9 Hz, 6H), 1.77 (m, 3H), 0.91 (d, J = 5.1 Hz, 9H), 0.88 (d, J = 5.1 Hz, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 170.5, 62.9, 59.9, 57.3, 29.9, 20.1, 19.6; MS *m/z* calcd. for $C_{21}H_{40}O_5N_4-(M-H_2O)$: 428.2999; found: 428.3003; $[\alpha]_D^{20}$ −13.7 (c = 0.0648 g/mL, MeOH).

N,N,N-Tris[((4*S*)-isopropyl-2-oxazolin-2-yl)methyl]-amine (1)

1,2,4-Triazole (21.9 g, 317 mmol) was dissolved in acetonitrile (425 mL) in an 1 L flask furnished with a Drierite drying tube. Phosphorus oxychloride (9.7 mL, 15.96 g, 104 mmol) was added at 0°C, followed by triethylamine (50 mL, 36.3 g, 359 mmol) dropwise. The reaction mixture was then stirred at 0°C for 2 h. The mixture was siphonated through a cannula to a sealed sintered glass filter, which was placed in the neck of a 2 L flask, so that the clear filtrate could be added directly to the solution of N,N,N-tris[2-((*S*)-1-hydroxy-3-methylbutyl)]nitrilotriacetamide (**5**, 4.07 g, 9.1 mmol) in triethylamine (900 mL) and acetonitrile (100 mL). After the addition was finished, the reaction mixture was stirred another 20 min before saturated aqueous $NaHCO_3$ solution (100 mL) was introduced to the reaction flask. The organic solvents were removed via a rotary evaporator, and the remaining mixture was extracted with CH_2Cl_2 (10 × 50 mL). The combined organic layers were washed with water (3 × 40 mL) and then dried over Na_2SO_4. Removal of solvent gave a reasonably pure product (3.04 g, 85%). The product could be further purified using a gel filtration method (Sephadex LH-20, ethyl acetate). IR (film): 983, 1145, 1194, 1386, 1468, 1672, 2873, 2963, 33.52 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 4.21 (m, 3H), 3.89 (m, 6H), 3.59 (s, 6H), 1.69 (m, 3H), 0.91 (d, J = 6.7 Hz, 9H), 0.83 (d, J = 6.8 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.9, 72.0, 67.0, 50.3, 32.4, 18.7, 18.1; MS *m/z* calcd. for $C_{21}H_{36}N_4O_3$: 392.2787; found: 392.2785; $[\alpha]_D^{20}$ −73.7 (c = 0.1191 g/mL, CH_2Cl_2).

General procedure for addition of diethylzinc to aldehydes

Benzaldehyde (106 mg, 1.0 mmol) was placed in a 25 mL round-bottom flask furnished with a magnetic stir bar and sealed with a rubber septum under argon. Diethylzinc (2.7 mL, 1.1 M in toluene, 3.0 mmol) was added to this flask at 0°C followed by compound **1** (80 mg, 0.20 mmol) in toluene (1 mL). The reaction mixture was maintained at 0°C for 2 days before quenching with saturated ammonium chloride in aqueous solution.

The reaction mixture was then acidified with HCl (2 N), followed by sodium carbonate (saturated aqueous solution). The mixture was extracted with dichloromethane (3 × 5 mL), and the combined organic layers were dried over Na_2SO_4. After removal of solvent, the crude product was purified via a Kugelröhr apparatus (80°C/5 Torr (1 Torr = 133.3 Pa); 125 mg, 92%). IR (neat): 3400, 3000, 2950, 1500, 1100, 1000, 800 cm^{-1}; ^1H NMR (500 MHz) δ: 7.34 (m, 3H), 7.26 (m, 2H), 4.58 (t, J = 7.0 Hz, 1H), 1.84 (br, 1H), 1.75–1.80 (m, 2H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C (125 MHz) δ: 144.6, 128.4, 127.5, 126.0, 76.0, 31.9, 10.1; MS (*m/z*): 77 (16.5), 79 (35.2), 92 (13.1), 107 (100.0), 108 (9.1), 136 (14.5, M), 137 (3.0).

1-(2′-Methoxyphenyl)-1-propanol: IR (neat): 753, 1029, 1046, 1089, 1237, 1458, 1464, 1491, 1494, 1588, 1601, 2838, 2936, 2968, 3386 cm^{-1}; ^1H NMR (500 MHz) δ: 7.27 (dd, J = 8.0, 2.0 Hz, 1H), 7.22 (td, J = 7.5, 2.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 4.76 (t, J = 6.5 Hz, 1H), 3.83 (s, 3H), 1.80 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); ^{13}C (125 MHz): 156.6, 132.3, 128.2, 127.1, 120.7, 110.5, 72.5, 55.2, 30.1, 10.5; MS (*m/z*): 77 (19.5), 94 (10.0), 107 (58.7), 109 (14.0), 121 (14.0), 137 (100.0), 138 (13.6), 166 (8.9, M).

1-(1′-Naphthyl)-1-propanol: IR (neat): 777, 800, 1029, 1168, 1259, 1458, 1511, 1598, 2875, 2965, 2280 cm^{-1}; ^1H (500 MHz) δ: 7.81 (m, 3H), 7.77 (s, 1H), 7.45 (m, 3H), 4.76 (t, J = 5.0 Hz, 1H), 1.87 (m, 2H), 0.93 (t, J = 8.0 Hz, 3H); ^{13}C (125 MHz) δ: 141.9, 133.2, 132.9, 128.2, 127.9, 127.6, 126.1, 125.7, 124.7, 124.1, 76.1, 31.7, 10.1; MS (*m/z*): 127 (25.6), 128 (39.5), 129 (76.3), 157 (100.0), 158 (15.2), 186 (37.8, M), 187 (5.4).

1-(2′-Naphthyl)-1-propanol: IR (neat): 748, 819, 856, 1018, 1126, 1455, 1463, 2875, 2931, 2965, 3378 cm^{-1}; ^1H (500 MHz) δ: 8.11 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.0 Hz, 1H), 7.48 (m, 3H), 5.39 (dd, J = 7.5, 5.0 Hz, 1H), 2.02 (m, 1H), 1.92 (m, 1H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C (125 MHz) δ: 140.1, 133.7, 130.3, 128.7, 127.7, 125.8, 125.3, 125.2, 123.1, 122.7, 72.5, 30.9, 10.4; MS (*m/z*): 127 (36.2), 128 (49.2), 129 (100.0), 130 (12.8), 157 (97.5), 158 (14.2), 186 (32.2, M), 187 (4.7).

1-(9′-Phenanthrenyl)-1-propanol: IR (neat): 763, 807, 970, 1046, 1450, 1496, 1654, 2875, 2963, 3301 cm^{-1}; ^1H (500 MHz) δ: 8.74 (dd, J = 8.0, 1.5 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.15 (dd, J = 7.5, 1.5 Hz, 1H), 7.89 (s, 1H), 7.88, dd, J = 8.5, 1.5 Hz, 1H), 7.62 (m, 4H), 5.42 (dd, J = 8.0, 5.0 Hz, 1H), 1.96–2.11 (m, 2H), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C (125 MHz): 138.3, 131.4, 130.8, 130.0, 129.7, 128.8, 126.7, 126.6, 126.5, 126.3, 123.9, 123.7, 123.4, 122.4, 72.8, 30.8, 10.5; MS (*m/z*): 177 (21.9), 178 (59.5), 179 (94.2), 180 (13.9), 207 (100.0), 208 (16.7), 236 (32.1, M), 237 (6.1).

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