Dirhodium(II)-catalyzed carbonyl ylide generation. Stereoelectronic control in dioxolane formation

M. P. Doyle,[a,b]* *D. C. Forbes,*[a,b] *and K. R. Xavier*[b]

[a]*Department of Chemistry, Trinity University,*
San Antonio, Texas 78212, USA
[b]*Department of Chemistry, The University of Arizona,*
*P. O. Box 210041, Tucson, AZ 85721-0041, USA.**
Fax: +1 (520) 621 8407. E-mail: mdoyle@u.arizona.edu

The combination of ethyl diazoacetate with aryl aldehydes in the presence of copper(I) or rhodium(II) catalysts results in the formation of 1,3-dioxolane products in moderate to good yields. These reactions occur through a pathway that involves ylide intermediates. Catalyst-dependent diastereocontrol is observed and suggests that metal-associated ylides are involved in the product-determining step. The influence of aryl aldehyde substituents has been determined.

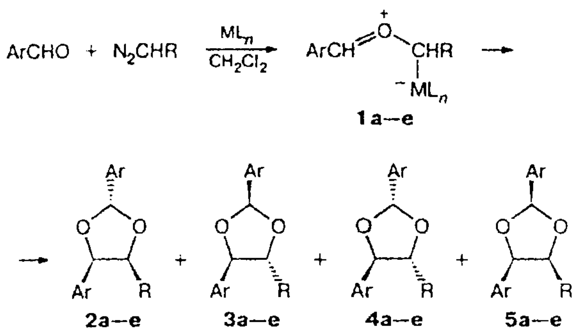
Key words: carbonyl ylides, metal-associated ylides; dipolar addition, rhodium(II) catalysts, copper(I) hexafluorophosphate; ethyl diazoacetate, metal carbenes.

The development of methodologies in which a catalyst controls the course and selectivity of a chemical process has been our goal for more than two decades.[1—3] During this time, focus has been placed on metal carbene transformations where the catalyst, generally copper(I) or rhodium(II), reacts with a diazo compound to produce a highly reactive metal carbene that transfers the carbene from the metal to an electron-rich substrate to form product and turn over the catalyst.[4,5] When the carbene transfer step is the product-determining step, electronic and steric influences from the metal can be employed to control the selectivity of the process.[6]

There is general belief that ylides formed from metal carbenes undergo metal dissociation prior to product formation.[8,9] In such transformations neither the metal nor its attendant ligands influence product selectivity. Recently, however, we have provided an example of carbonyl ylide formation and subsequent carbonyl addition in which both the nature of the metal and its ligands greatly influenced product selectivity (Scheme 1, Ar = p-$NO_2C_6H_4$).[9] Variation of the catalyst changed the product ratio from predominantly 2+3 to mainly 5, the thermodynamically least stable isomer. We now report our analysis of the electronic factors that influence this selectivity.

Results and Discussion

Scheme 1



R = COOEt; Ar = p-$NO_2C_6H_4$ (**a**), p-ClC_6H_4 (**b**), p-FC_6H_4 (**c**), p-$CF_3C_6H_4$ (**d**), p-$MeOC_6H_4$ (**e**)

When p-nitrobenzaldehyde is treated with ethyl diazoacetate in the presence of dirhodium(II) caprolactamate, $Rh_2(cap)_4$, a rapid two-step reaction involving ylide generation and subsequent dipolar addition takes place to yield mainly 1,3-dioxolanes **2a** and **3a**, and using $Cu(MeCN)_4PF_6$ as the catalyst, **5a** is the predominant product (Table 1). This variation in selectivity is consistent with a mechanism in which **2** and **3** result from dipolar addition of the free ylide **6** onto the aldehyde, and **4** and **5** arise from addition by the metal-associated ylide **7**, as described in Scheme 2 (R = COOEt). The stereochemical assignments of these products are based on ^1H NMR chemical shift values and coupling constants (Table 2), confirmed by NOE experiments.

The influence of arene substituents on product distributions from reactions of p-substituted benzalde-

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* Current address.

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Scheme 2

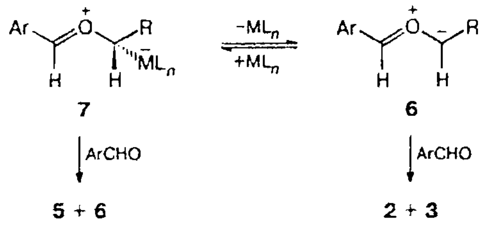


Table 1. Influence of catalyst on product steereochemistry for reactions of *p*-nitrobenzaldehyde with ethyl diazoacetate[a]

Catalyst	Product yield (%)[b]	Relative yield (%)			
		2a	**3a**	**4a**	**5a**
$Cu(MeCN)_4PF_6$	39	11	9	10	70
$Rh_2(OAc)_4$	37	21	22	3	54
$Rh_2(cap)_4$	35	43	41	—	16

[a] Reactions were performed with a 3-fold molar excess of *p*-nitrobenzaldehyde.

[b] Yield after chromatographic purification.

Table 2. Characteristic ^{1}H NMR chemical shifts and coupling constants for dioxolanes **2**—**5**

Compound	δ				$J_{H(4),H(5)}$ /Hz
	H(2)	H(4)	H(5)	OCH_2CH_3	
2a	6.83	5.51	5.05	0.88	7.2
2b	6.70	5.40	4.94	0.88	7.2
2c	6.72	5.43	4.94	0.88	7.2
2d	6.80	5.48	5.00	0.81	7.1
2e	6.69	5.42	4.92	0.88	7.2
3a	6.29	5.38	4.54	1.39	5.9
3b	6.14	5.19	4.47	1.34	6.1
3c	6.14	5.19	4.48	1.34	6.4
3d	6.24	5.31	4.52	1.37	6.4
3e	6.11	5.13	4.47	1.31	6.3
4a	6.39	5.39	4.62	1.31	6.0
4d	6.32	5.37	4.63	1.30	5.9
5a	6.19	5.61	5.02	0.86	7.9
5b	6.02	5.43	4.88	0.87	8.1
5c	6.03	5.44	4.88	0.87	8.0
5d	6.13	5.55	4.96	0.79	7.8

Table 3. Influence of aryl aldehyde on product stereochemistry for reactions of ethyl diazoacetate in the presence of $Cu(MeCN)_4PF_6$

Aldehyde	Product yield (%)	Relative yield (%)			
		2	**3**	**4**	**5**
p-$NO_2C_6H_4CHO$	39	11	9	10	70
p-ClC_6H_4CHO	57	24	34	—	42
p-FC_6H_4CHO	60	31	28	—	41
p-$CF_3C_6H_4CHO$	72	22	24	6	48
p-$MeOC_6H_4CHO$	38	37	40	4	19

Note. Reactions were performed with a 3-fold molar excess of aryl aldehyde.

hydes with ethyl diazoacetate in the presence of $Cu(MeCN)_4PF_6$ is reported in Table 3. Like the influence of catalyst ligands on product selectivity (see Table 1), in which the more electron withdrawing ligands favored the process leading to **4**+**5**, the greater the electron withdrawing properties of the *p*-substituent of the benzaldehyde, the greater is the proportion of product **4**+**5** relative to **2**+**3**. Note that the ratio **2** : **3** is nearly one whereas **4** : **5** is always greater than five. The nearly equal amounts of **2** and **3** implicate the absence of steric effects in dipolar addition to **6**, and this is consistent with what has been previously observed.[7–9] Preference for **5** rather than **4** is also a manifestation of the relative absence of steric effects in the formation of **5** relative to those in the formation of **4**. A Hammett correlation of log [(**4**+**5**)/(**2**+**3**)] with σ gives a ρ value of +1.0 (correlation coefficient (r) is 0.93);[10] a similar correlation with σ^+ provided a ρ value of +0.71 (r = 0.93).

Table 2 describes the ^{1}H NMR data that provided assignments for **2**—**5**. A distinct pattern emerges with chemical shift data for H(2), H(4), H(5), and the ethyl ester's methyl group. Furthermore, $J_{H(4),H(5)}$ is 7—8 Hz for 1,3-dioxolanes having the *cis* geometry and nearly 6 Hz for the *trans* disubstituted isomer. These data allow unambiguous assignment of stereochemistry, especially as they are correlated to assignments of the *p*-nitrophenyl derivatives for which NOE assignments were obtained. NOE experiments established the relative stereochemistry of 1,3-dioxolanes **2a**—**5a** and **2e**—**5e** through correlations with ^{1}H NMR absorptions at δ 6.19, 5.61, and 5.02. Characteristic ^{1}H NMR chemical shifts and coupling constants for **2b,c,d**—**5b,c,d**, (see Table 2) were used as comparative data for product stereochemistry assignments.

The influence of catalyst on product stereochemistry for reactions of *p*-chlorobenzaldehyde, *p*-fluorobenzaldehyde, and *p*-trifluoromethylbenzaldehyde with ethyl diazoacetate is reported in Tables 4—6, respectively. In all cases, catalysis by $Cu(MeCN)_4PF_6$ gives the highest relative yield of **5**. There is, however, no significant difference in the relative yield of **5** formed with either $Rh_2(OAc)_4$ or $Rh_2(cap)_4$ (contrast with results from reactions with *p*-nitrobenzaldehyde, see Table 1). With *p*-anisaldehyde **2a** and **2b** were the only dipolar addition products from reactions catalyzed by any of the catalysts examined. Overall, the composite results suggest a delicate balance in aldehyde and catalyst ligand for influence on the equilibrium between **6** and **7** (see Scheme 2).

Common reasoning and AM1 calculations have shown that free ylide **6** with Ar = p-$NO_2C_6H_4$ is more stable than **6** with Ar = p-$MeOC_6H_4$. This would argue for a greater percentage of reaction taking place through free ylide **6** in reactions with *p*-nitrobenzaldehyde than in

Table 4. Influence of catalyst on product stereochemistry for reactions of *p*-chlorobenzaldehyde with ethyl diazoacetate

Catalyst	Product yield (%)	Relative yield (%)			
		2b	**3b**	**4b**	**5b**
$Cu(MeCN)_4PF_6$	57	24	34	—	42
$Rh_2(OAc)_4$	48	45	43	—	12
$Rh_2(cap)_4$	18	38	47	—	15

Note. Reactions were performed with a 3-fold molar excess of *p*-chlorobenzaldehyde.

Table 5. Influence of catalyst on product stereochemistry for reactions of *p*-fluorobenzaldehyde with ethyl diazoacetate

Catalyst	Product yield (%)	Relative yield (%)			
		2c	3c	4c	5c
$Cu(MeCN)_4PF_6$	60	31	28	—	41
$Rh_2(OAc)_4$	68	44	52	—	4

Note. Reactions were performed with a 3-fold molar excess of *p*-fluorobenzaldehyde.

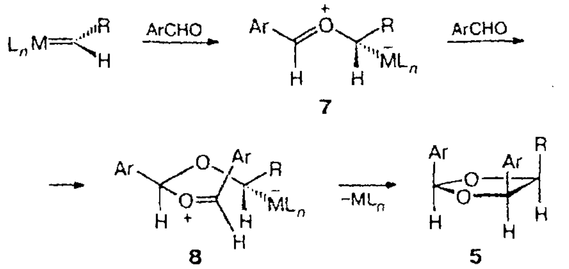
Table 6. Influence of catalyst on product stereochemistry for reactions of *p*-trifluoromethylbenzaldehyde with ethyl diazoacetate

Catalyst	Product yield (%)	Relative yield (%)			
		2d	**3d**	**4d**	**5d**
$Cu(MeCN)_4PF_6$	64	22	24	6	48
$Rh_2(OAc)_4$	93	28	43	5	24
$Rh_2(cap)_4$	50	33	38	3	26

Note. Reactions were performed with a 3-fold molar excess of *p*-trifluoromethylbenzaldehyde.

reactions with *p*-anisaldehyde. This is not observed and, instead, use of *p*-nitrobenzaldehyde leads to the highest percentage of metal-associated ylide-derived **5**, which is consistent with the extent to which the nucleophilic aldehyde controls subsequent reactions. The metal-associated ylide **7** undergoes stepwise addition of the reactant aldehyde **8** followed by subsequent ring closure that occurs with displacement of the ligated metal catalyst (Scheme 3, R = COOEt). Dipolar addition to **6** is concerted,[7,8] and *p*-anisaldehyde is the most reactive of the substrates that have been examined.

Scheme 3



Experimental

^1H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were obtained as solutions in $CDCl_3$, and chemical shifts (δ) are reported in parts per million downfield from internal Me_4Si. Mass spectra were obtained using electron ionization (70 eV) on a quadrupole instrument. Infrared spectra were recorded as a thin film on sodium chloride plates or in a KBr pellet, as indicated, and absorptions are reported in wavenumbers (cm^{-1}). Melting points are uncorrected. Anhydrous CH_2Cl_2 was dried over calcium hydride for 24 h and then distilled prior to use in catalytic reactions. Dirhodium(II) caprolactamate[11] and $Cu(MeCN)_4PF_6$ [12] were prepared by literature methods. Dirhodium(II) acetate was recrystallized[13] prior to use.

Reaction of *p*-nitrobenzaldehyde with ethyl diazoacetate (general procedure). A 25-mL oven-dried, two-neck, round-bottom flask was equipped with a reflux condenser, magnetic stir bar, septa, and drying tube. To a refluxing solution of *p*-nitrobenzaldehyde (0.45 g, 3.0 mmol) and copper(I) hexafluorophosphate (10 μmol, 1.0 mol.%) in dichloromethane (5 mL) was added *via* a syringe pump a solution of ethyl diazoacetate (0.114 g, 1.00 mmol) in dichloromethane (5 mL) at a rate of 0.5 mL h^{-1}. Upon completion of addition, the red-orange solution was cooled to room temperature and then filtered through a short plug of silica gel to remove the catalyst. The silica gel plug consisted of a 10 mL syringe without plunger fitted first with a cotton plug followed by the equivalent of 3 mL of silica gel. The plug was washed with dichloromethane (60 mL) and the combined washings were concentrated under reduced pressure to afford 0.50 g of a slightly yellow solid. GC and ^1H NMR analysis of the crude reaction mixture identified four distinct 1,3-dioxolanes in a ratio of 70 : 10 : 9 : 11 as well as excess *p*-nitrobenzaldehyde: GC (SPB-5, 100 °C (2 min), 10 °C per min, 275 °C): R_t(aldehyde), 9.39 min; R_t(**5a**), 39.67 min (70%); R_t(**4a**), 40.12 min (10%); R_t(**3a**), 40.49 min (9%); R_t(**2a**), 40.83 min (11%). Excess *p*-nitrobenzaldehyde was removed *via* bulb-to-bulb distillation (0.3 Torr/100 °C (air bath temp)). The resulting composite of 1,3-dioxolanes (0.18 g), which was of sufficient purity to require no further manipulation, was purified by column chromatography on silica gel (hexane—ethyl acetate, 1 : 2) to afford dioxolanes **2a—5a** in 39% overall yield (0.39 mmol). Selective crystallization from hexane—ethyl acetate, (1 : 1, 8 mL) provided a pure sample of the major product **5a** as a slightly yellow solid, m.p. 121—123 °C.

Ethyl 2,5-di(*p*-nitrophenyl)-1,3-dioxolane-4-carboxylate (mixture of isomers 2a—5a). ^1H NMR ($CDCl_3$), δ, isomer **2a**: 0.88 (t, 3 H, OCH_2CH_3, *J* = 7.2 Hz); 3.64—3.75 (comp, 1 H); 3.82—3.92 (comp, 1 H); 5.05 (d, 1 H, *J* = 7.2 Hz); 5.51 (d, 1 H, *J* = 7.2 Hz); 6.83 (s, 1 H); 7.59 (d, 2 H, *J* = 8.7 Hz); 7.74 (d, 2 H, *J* = 8.7 Hz); 8.24 (d, 2 H, *J* = 8.7 Hz); 8.29 (d, 2 H, *J* = 8.7 Hz); isomer **3a**: 1.39 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 4.17—4.33 (m, 2 H); 4.54 (d, 1 H, *J* = 5.9 Hz); 5.38 (d, 1 H, *J* = 5.9 Hz); 6.29 (s, 1 H); 7.62 (d, 2 H, *J* = 8.8 Hz); 7.79 (d, 2 H, *J* = 8.8 Hz); 8.27 (d, 2 H, *J* = 8.8 Hz); 8.32 (d, 2 H, *J* = 8.8 Hz); isomer **4a**: 1.31 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.2 Hz); 4.15—4.35 (m, 2 H); 4.62 (d, 1 H, *J* = 6.0 Hz); 5.39 (d, 1 H, *J* = 6.0 Hz); 6.39 (s, 1 H); isomer **5a**: 0.86 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.1 Hz); 3.65 (dq, 1 H, $C\underline{H}_aH_bCH_3$, *J* = 7.1, 10.9 Hz); 3.81 (dq, 1 H, $CH_a\underline{H}_bCH_3$, *J* = 7.1, 10.9 Hz); 5.02 (d, 1 H, *J* = 7.9 Hz);

5.61 (d, 1 H, J = 7.9 Hz); 6.19 (s, 1 H); 7.56 (d, 2 H, J = 8.7 Hz); 7.99 (d, 2 H, J = 8.7 Hz); 8.23 (d, 2 H, J = 8.7 Hz); 8.34 (d, 2 H, J = 8.7 Hz).

MS and elemental analyses data have been reported.[9]

Reaction of *p*-chlorobenzaldehyde with ethyl diazoacetate. From the combination of 0.42 g (3.0 mmol) *p*-chlorobenzaldehyde, 0.114 g (1.00 mmol) ethyl diazoacetate, and 4.0 mg (10 μmol) $Cu(MeCN)_4PF_6$, 0.21 g of 1,3-dioxolanes **2b—5b** was obtained (0.57 mmol, 57% yield). GC (SPB-5, 200 °C isotherm): R_t(**5b**), 84.59 min (42%); R_t(**2b**), 91.06 min (24%); R_t(**3b**), 93.00 min (34%).

Ethyl 2,5-di(*p*-chlorophenyl)-1,3-dioxolane-4-carboxylate (mixture of isomers 2b, 3b, and 5b). ^{1}H NMR ($CDCl_3$), δ: isomer **2b**: 0.88 (t, 2 H, $CH_2C\underline{H}_3$, J = 7.2 Hz); 3.64—3.91 (m, 2 H); 4.94 (d, 1 H, J = 7.2 Hz); 5.40 (d, 1 H, J = 7.2 Hz); 6.70 (s, 1 H); 7.26—7.55 (m, 8 H); isomer **3b**: 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 4.27—4.38 (m, 2 H); 4.47 (d, 1 H, J = 6.2 Hz); 5.19 (d, 1 H, J = 6.1 Hz); 6.14 (s, 1 H); 7.26—7.55 (m, 8 H); isomer **5b**: 0.87 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 4.88 (d, 1 H, J = 8.1 Hz); 5.43 (d, 1 H); 6.02 (s, 1 H). MS **5b**, *m/z*: 321 $[M-OEt]^+$, 319, 293, 264, 246, 226, 210, 182, 169, 139, 125, 111, 89, 77.

Reaction of *p*-fluorobenzaldehyde with ethyl diazoacetate. From the combination of 0.37 g (3.0 mmol) *p*-fluorobenzaldehyde, 0.114 g (1.00 mmol) ethyl diazoacetate, and 4.0 mg (10 μmol) $Cu(MeCN)_4PF_6$, 0.20 g of 1,3-dioxolanes **2c**, **3c**, and **5c** was obtained (0.60 mmol, 60% yield): GC (SPB-5, 100 °C (2 min), 10 °C per min, 275 °C): R_t(**5c**), 17.14 min (41%); R_t(**3c**), 19.4 min (28%); R_t(**2c**), 19.5 min (31%).

Ethyl 2,5-di(*p*-fluorophenyl)-1,3-dioxolane-4-carboxylate (mixture of isomers 2c, 3c, and 5c). ^{1}H NMR ($CDCl_3$), δ: isomer **2c**: 0.88 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.56—3.83 (m, 2 H); 4.94 (d, 1 H, J = 7.1 Hz); 5.43 (d, 1 H, J = 7.1 Hz); 6.72 (s, 1 H); 6.94—7.56 (m, 8 H); isomer **3c**: 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 4.09—4.29 (m, 2 H); 4.48 (d, 1 H, J = 6.2 Hz); 5.19 (d, 1 H, J = 6.2 Hz); 6.14 (s, 1 H); 6.94—7.56 (m, 8 H); isomer **5c**: 0.87 (t, 3 H); 4.88 (d, 1 H, J = 7.6 Hz); 5.44 (s, 1 H); 6.94—7.56 (m, 8 H). MS **2c**, *m/z*: 263 $[M-COOEt]^+$, 247, 235, 227, 211, 188, 183, 155, 153, 137, 123, 108, 95, 75.

Reaction of *p*-trifluoromethylbenzaldehyde with ethyl diazoacetate. From the combination of 0.52 g (3.0 mmol) *p*-trifluoromethylbenzaldehyde, 0.114 g (1.00 mmol) ethyl diazoacetate, and 4.0 mg (10 μmol) $Cu(MeCN)_4PF_6$, 0.28 g of 1,3-dioxolanes **2d—5d** was obtained (0.64 mmol, 64% yield).

Ethyl 2,5-di(*p*-trifluoromethyl)-1,3-dioxolane-4-carboxylate (mixture of isomers 2d—5d). ^{1}H NMR ($CDCl_3$), δ: isomer **2d**: 0.81 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.59—3.86 (m, 2 H); 5.00 (d, 1 H, J = 7.0 Hz); 5.48 (d, 1 H, J = 7.2 Hz); 6.80 (s, 1 H); 7.51—7.95 (m, 8 H); isomer **3d**: 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2); 4.17—4.42 (m, 2 H); 4.52 (d, 1 H, J = 6.0 Hz); 5.31 (d, 1 H, J = 6.7 Hz); 6.24 (s, 1 H); 7.51—7.95 (m, 8 H); isomer **4d**: 1.30 (t, 3 H); 4.63 (d, 1 H, J = 6.1 Hz); 5.37 (d, 1 H, J = 5.8 Hz); 6.32 (s, 1 H); isomer **5d**: 0.79 (t, 3 H, J = 7.2 Hz); 3.59—3.86 (m, 2 H); 4.96 (d, 1 H, J = 7.8 Hz); 5.55 (d, 1 H, J = 7.8 Hz); 6.13 (s, 1 H); 7.51—7.95 (m, 8 H). MS **2d**, *m/z*: 415 $[M-F]^+$, 387, 361, 332, 314, 303, 260, 203, 159, 145, 127.

Reaction of *p*-anisaldehyde with ethyl diazoacetate. From the combination of 0.41 g (3.0 mmol) *p*-anisaldehyde, 0.114 g (1.00 mmol) ethyl diazoacetate, and 4.0 mg (10 μmol) $Cu(MeCN)_4PF_6$, 0.14 g of 1,3-dioxolanes **2e—3e** was obtained (0.38 mmol, 38% yield).

Ethyl 2,5-di(*p*-methoxyphenyl)-1,3-dioxolane-4-carboxylate (mixture of isomers 2e and 3e). ^{1}H NMR ($CDCl_3$), δ: isomer **2e**: 0.88 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 3.36—3.90 (m, 2 H); 3.79 (s, 3 H, OCH_3); 3.81 (s, 3 H, OCH_3); 4.92 (d, 1 H, J = 7.2 Hz); 5.42 (d, 1 H, J = 7.2 Hz); 6.69 (s, 1 H); 6.86 (d, 2 H, J = 8.3 Hz); 6.92 (d, 2 H, J = 8.3 Hz); 7.30 (d, 2 H, J = 8.3 Hz); 7.47 (d, 2 H, J = 8.3 Hz); isomer **3e**: 1.31 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.80 (s, 3 H, OCH_3); 3.82 (s, 3 H, OCH_3); 4.23—4.37 (m, 2 H); 4.47 (d, 1 H, J = 6.3 Hz); 5.13 (d, 1 H, J = 6.3 Hz); 6.11 (d, 1 H); 6.92 (d, 2 H, J = 8.8 Hz); 6.94 (d, 2 H, J = 8.8 Hz); 7.40 (d, 2 H, J = 8.8 Hz); 7.53 (d, 2 H, J = 8.8 Hz).

MS and elemental analyses data have been reported.[9]

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This article was written in the memory of Mark E. Vol'pin, a friend whose extraordinary scientific and managerial capabilities were an inspiration to all who knew him.

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