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HECK REACTIONS IN 2,6-DIARYL-3,5-DIBROMO-4-PYRONES IN THE PRESENCE OF *N,N'*-DIBUTYLBENZIMIDAZOLIUM BROMIDE

Zarrin Ghasemi, Vahideh Nazari-Belvirdi, Maryam Allahvirdinasab, and Aziz Shahrissa*

Department of Organic and Bioorganic Chemistry, Faculty of Chemistry, University of Tabriz, 51664, Tabriz, Iran

*E-mail: ashahrissa@yahoo.com

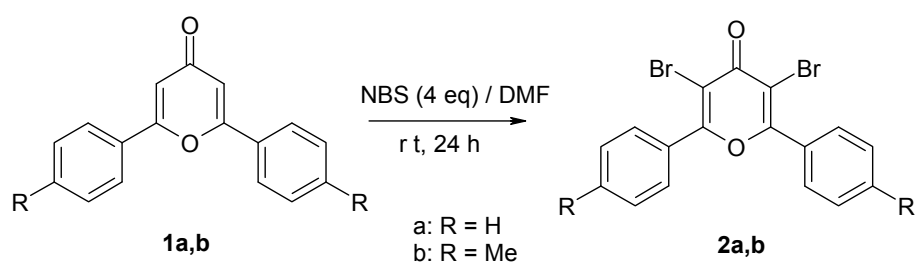
Abstract – Synthesis of two 2,6-diaryl-3,5-dibromo-4-pyrone derivatives is described, by using of NBS/DMF bromination of related 2,6-diaryl-4-pyrones. PdCl₂ catalyzed Heck coupling reactions of these dibromides, with emphasis on the use of *N,N'*-dibutylbenzimidazol-2-ylidene as ligand, resulted in the formation of two class of mono- and di-vinylated products.

Palladium-catalyzed cross-coupling Heck reaction of aryl and heteroaryl halides with various olefins is one of the most intensively studied reactions and an versatile C-C bond forming tool in synthesis of important functionalized compounds.¹ Phosphine-palladium complexes in homogeneous solutions or heterogeneous systems, palladacycles and *N*-heterocyclic carbene (NHC)-palladium complexes are the well established palladium species and generally employed as efficient catalysts for the Heck reactions. The use of *N*-heterocyclic carbenes as potential candidates for many palladium catalyzed coupling reactions is rapidly increased.² The electron richness of NHC ligands and strong palladium-carbon bond in such complexes provide the ancillary supporting and stabilization of metal center, and prevent the possible dissociation of the carbon-metal bond at different stages of these catalytic cycles, thereby making them thermally and oxidatively stable.³

4-Pyrone derivatives also, are of considerable pharmacological relevance and found in a whole spectrum of bioactive systems.⁴ Through our recently attempts for synthesis of cyclic and polyfunctional frameworks of 4-pyrones,⁵ we were interested in the coupling reactions in 4-pyrone backbone which have rarely been reported.⁶ We report here the 3,5-dibromination reactions of 2,6-diaryl-4-pyrones and the

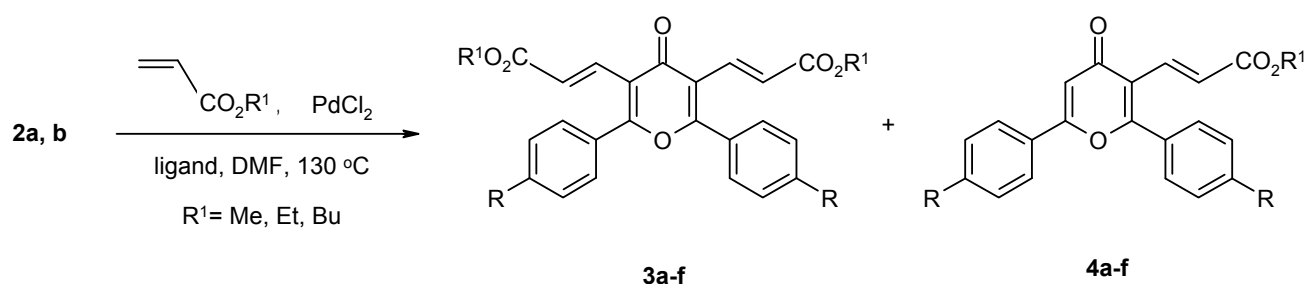
Heck vinylation reactions of these dibromides, catalyzed by *N,N'*-dibutylbenzimidazolium bromides (DBBIB)-PdCl₂ system.

The 2,6-diaryl-4-pyrones **1a** and **1b** used for bromination reactions, were prepared through cyclization of related 1,3,5-triketone derivatives under acidic conditions, which is a known route for the synthesis of a variety of 2,6-disubstituted-4-pyrone structures.⁷ We examined the bromination of compounds **1a** and **1b** by using of NBS in dry DMF at room temperature and achieved the brominated products **2a** and **2b** in good yields, respectively (Scheme 1). Although by the using of excess amount of brominating reagent (4 eq), the aryl rings of 2- and 6- positions were not affected. It should be noticed that treatment of **1b** with 2 eq. of NBS, gave a mixture of mono- and di- brominated products. The reagent NBS/DMF has been applied for electrophilic bromination at electron rich positions of various aryl and heterocyclic rings.⁸



Scheme 1. Electrophilic bromination of 2,6-diaryl-4-pyrones **1a,b**

For evaluation the reactivity of dibromides **2a-b** toward Pd(II) catalyzed Heck coupling reactions, we originally treated the compound **2a** with methyl acrylate (4 eq), in the presence of PdCl₂ (1 eq%) as catalyst, triphenylphosphine (2 eq%) as ligand, and triethylamine as base at 130 °C for 24 h. Under these conditions, products **3a** and **4a** were formed along with the large amounts of unreacted starting materials (Scheme 2). Formation of product **4a** can be explained by partial reduction of the in situ formed 3-bromo-5-alkenyl-4-pyrone intermediate. It is noteworthy that changes in the amounts of catalyst, ligand, alkene and base did not influence the situation of the results. Subsequently, we attempted these reactions under the same stoichiometric conditions by using *N,N'*-dibutylbenzimidazolium bromide instead of PPh₃, consequently complete conversion of starting materials as well as formation of two class products **3** and **4** were observed after 18 h. Yields of each of these products in the reactions of **2a,b** with alkyl acrylates have been monitored in Table 1. As the table shows, the reaction of dibromides **2a,b** with *n*-butyl acrylate, have exclusively resulted in the formation of only divinylated products (Entries 3, 6).



Scheme 2. Heck coupling reactions of 2,6-diaryl-3,5-dibromo-4-pyrones **2a,b**

Table 1. Heck reactions of compounds **2a-b** with alkyl acrylates

Entry	R	R ¹	Product 3 (yield %)	Product 4 (yield %)
1	H	Me	3a (65)	4a (19)
2	H	Et	3b (57)	4b (21)
3	H	<i>n</i> -Bu	3c (73)	4c (trace)
4	Me	Me	3d (64)	4d (22)
5	Me	Et	3e (60)	4e (15)
6	Me	<i>n</i> -Bu	3f (74)	4f (trace)

Conditions: 3,5-dibromo-4-pyrone (1 mmol), alkyl acrylate (4 mmol), PdCl₂ (1 mol%), DBBIB (2 mol%), Et₃N (0.4 mL), 130 °C, 18 h.

In conclusion We developed efficient electrophilic bromination of 2,6-diaryl-4-pyrone derivatives **1a,b** by using of NBS/DMF reagent, which in result, 2,6-diaryl-3,5-dibromo-4-pyrones were obtained by simple workup and good yields. Furthermore the Heck coupling reactions of these dibromides with methyl, ethyl and butyl acrylates in the presence of PdCl₂-DBBIB system gave the di- and mono- vinylated products. Photocyclization reactions of compounds **3a-f**, **4a,b** and **4d,e** are under investigation.

EXPERIMENTAL

Melting points were measured on a Electrothermal MEL-TEMP apparatus (model 1202D) and are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer. ¹H, and ¹³C NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker Spectrospin Avance 400 spectrometer with CDCl₃ as solvent and TMS as internal standard. Mass spectra were recorded on a Shimadzu spectrometer operating at an ionization potential of 70 eV. Elemental analyses for C and H were obtained using a Vario EL III apparatus (Elementar Co.). Preparative layer chromatography (PLC) was done using silica gel (Merk Kieselgel 60 PF₂₅₄₊₃₆₆).

General procedure for the electrophilic bromination of 2,6-diaryl-4-pyrones (**1a-b**)

To a 100 mL flask charged with 2,6-diaryl-4-pyrone (2 mmol) in dry DMF (10 mL) was added a solution of NBS (1.42 g, 8 mmol) in dry DMF (4 mL). The mixture was stirred at room temperature for 24 h and then poured into water (100 mL). Resulted white suspension was extracted with Et₂O (3 × 50 mL). The ether extracts were dried with Na₂SO₄, filtered, and concentrated *in vacuo* to dryness. Obtained solid was recrystallized with EtOH to give 2,6-diaryl-3,5-dibromo-4-pyrones (**2a-b**) as white crystals.

3,5-Dibromo-2,6-diphenyl-4H-pyran-4-one (**2a**)

White crystals, yield 61%, mp 169-170 °C. $\nu_{\max}$ (KBr) 3060, 2924, 1645 (pyrone C=O), 1612, 1342, 1004, 755, 694 cm⁻¹. ¹H NMR (CDCl₃), δ 7.48-7.56 (6H, m, phenyl-H), 7.79-7.82 (4H, m, phenyl-H). ¹³C NMR (CDCl₃), δ 109.9, 127.4, 128.1, 130.3, 130.4, 160.5, 168.8. MS, *m/z* (%) = 408 (M+4, 4), 406 (M+2, 12), 404 (M, 5), 377 (15), 113 (30), 105 (94), 77 (100). Anal. Calcd for C₁₇H₁₀O₂Br₂ (406.08): C, 50.28; H, 2.48. Found: C, 50.22; H, 2.55.

2,6-Bis(4-methylphenyl)-3,5-dibromo-4H-pyran-4-one (**2b**)

White crystals, yield 60%, mp 186-187 °C. $\nu_{\max}$ (KBr) 3031, 2950, 1646 (pyrone C=O), 1611, 1505, 1340, 1006, 820, 756 cm⁻¹. ¹H NMR (CDCl₃): δ 2.43 (6H, s, CH₃), 7.30 (4H, d, *J*=8.1 Hz, aryl-H), 7.71 (4H, d, *J*=8.1 Hz, aryl-H). ¹³C NMR (CDCl₃): δ 20.5, 109.4, 127.6, 128.0, 128.1, 140.9, 160.5, 168.9. MS, *m/z* (%) = 436 (M+4, 42), 434 (M+2, 58), 432 (M, 24), 405 (100), 403 (50), 353 (16), 194 (22). Anal. Calcd for C₁₉H₁₄O₂Br₂ (434.13): C, 52.57; H, 3.25. Found: C, 52.22; H, 3.55.

General procedure for the Heck coupling reactions of dibromides (**2a-b**) with alkyl acrylates

A mixture of 2,6-diaryl-3,5-dibromo-4-pyrone (1.0 mmol), alkyl acrylate (4.0 mmol), PdCl₂ (0.002 g, 1 mol%), *N,N'*-dibutylbenzimidazolium bromide (0.006 g, 2 mol%), triethylamine (0.4 mL, 4 mmol) in dry DMF (4 mL) was stirred at 130 °C for 18 h. Then, water (150 mL) was added, and after stirring (2 min), the mixture was extracted with EtOAc (3 × 50 mL). The organic layers were combined, dried with Na₂SO₄ and concentrated *in vacuo*. The residue was purified by PLC on silicagel (hexane/CH₂Cl₂ 1:1) to give the mono- and di-vinylated products (**3**, **4**).

3,5-Bis[*trans*-2-(methoxycarbonyl)ethenyl]-2,6-diphenyl-4H-pyran-4-one (**3a**)

Yellow solid, yield 65%, mp 188-190 °C. $\nu_{\max}$ (KBr) 3060, 2996, 1714 (ester C=O), 1648 (pyrone C=O), 1602, 1284, 1161 cm⁻¹. ¹H NMR (CDCl₃): δ 3.77 (6H, s, CO₂CH₃), 7.43 (2H, d, *J*=15.9 Hz, CH=CH-CO₂Me), 7.49-7.61 [8H, m, (6H, phenyl-H), (2H, CH=CH-CO₂Me)], 7.62-7.64 (4H, m, phenyl-H). ¹³C NMR (CDCl₃): δ 51.6, 118.5, 124.5, 128.8, 129.7, 131.2, 131.5, 135.2, 164.9, 168.0, 178.7. Anal. Calcd for C₂₅H₂₀O₆ (416.43): C, 72.11; H, 4.84. Found: C, 72.03; H, 4.93.

3,5-Bis[*trans*-2-(ethoxycarbonyl)ethenyl]-2,6-diphenyl-4H-pyran-4-one (**3b**)

Yellow solid, yield 57%, mp 158-160 °C. $\nu_{\max}$ (KBr) 3080, 2963, 1710 (ester C=O), 1647 (pyrone C=O), 1623, 1261, 1030 cm⁻¹. ¹H NMR (CDCl₃): δ 1.36 (6H, t, *J*=7.1 Hz, CH₂CH₃), 4.29 (4H, q, *J*=7.1 Hz,

CH_2CH_3), 7.49 (2H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.57-7.64 [8H, m, (6H, phenyl-H), (2H, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$)], 7.68-7.70 (4H, m, phenyl-H). ^{13}C NMR (CDCl_3): δ 13.2, 59.4, 117.5, 123.9, 127.8, 128.7, 130.2, 130.5, 133.9, 163.8, 166.6, 175.9. Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_6$ (444.21): C, 72.99; H, 5.40. Found: C, 72.62; H, 5.16.

3,5-Bis[*trans*-2-(butoxycarbonyl)ethenyl]-2,6-diphenyl-4*H*-pyran-4-one (3c)

Yellow solid, yield 73%, mp 85-87 °C. ν_{max} (KBr) 3070, 2929, 1712 (ester C=O), 1646 (pyrone C=O), 1625, 1274, 1025 cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (6H, t, $J=7.3$ Hz, $(\text{CH}_2)_3-\text{CH}_3$), 1.25-1.45 (4H, m, $-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_3$), 1.59-1.67 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.15 (4H, t, $J=6.5$ Hz, CO_2CH_2), 7.42 (2H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$), 7.50-7.58 [8H, m, (6H, phenyl-H), (2H, $\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$)], 7.60-7.62 (4H, m, phenyl-H). ^{13}C NMR (CDCl_3): δ 12.7, 18.2, 29.6, 63.3, 117.5, 123.9, 127.8, 128.7, 130.2, 130.5, 133.9, 163.8, 166.7 (ester C=O), 175.9 (pyrone C=O). Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_6$ (500.25): C, 74.42; H, 6.39. Found: C, 74.46; H, 6.66.

3,5-Bis[*trans*-2-(methoxycarbonyl)ethenyl]-2,6-bis (4-methylphenyl)-4*H*-pyran-4-one (3d)

Yellow solid, yield 64%, mp 201-202 °C, ν_{max} (KBr) 3069, 2940, 1714 (ester C=O), 1648 (pyrone C=O), 1613, 1415, 1282, 1221 cm^{-1} . ^1H NMR (CDCl_3): δ 2.45 (6H, s, benzylic CH_3), 3.79 (6H, s, CO_2CH_3), 7.34 (4H, d, $J=8.1$ Hz, aryl-H), 7.43 (2H, d, $J=15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), 7.50 (2H, d, $J=15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), 7.52 (4H, d, $J=8.1$ Hz, aryl-H). ^{13}C NMR (CDCl_3): δ 20.5, 50.6, 117.0, 122.9, 127.3, 128.5, 128.7, 134.6, 141.2, 164.1, 167.2, 175.9. Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_6$ (444.21): C, 72.99; H, 5.40. Found: C, 72.67; H, 5.45.

3,5-Bis[*trans*-2-(ethoxycarbonyl)ethenyl]-2,6-bis (4-methylphenyl)-4*H*-pyran-4-one (3e)

Yellow solid, yield 60%, mp 159-160 °C. ν_{max} (KBr) 3085, 2950, 1714 (ester C=O), 1646 (pyrone C=O), 1625, 1420, 1270 cm^{-1} . ^1H NMR (CDCl_3): δ 1.25 (6H, t, $J=7.0$ Hz, CH_2CH_3), 2.46 (6H, s, benzylic CH_3), 4.20 (4H, q, $J=7.0$ Hz, CH_2CH_3), 7.28 (4H, d, $J=8.2$ Hz, aryl-H), 7.35 (2H, d, $J=15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.51 (2H, d, $J=15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.69 (4H, d, $J=8.2$ Hz, aryl-H). ^{13}C NMR (CDCl_3): δ 13.2, 20.5, 59.3, 109.3, 123.1, 124.7, 128.2, 128.7, 128.8, 134.5, 163.7, 166.5, 175.8. Anal. Calcd for $\text{C}_{29}\text{H}_{28}\text{O}_6$ (472.23): C, 73.75; H, 5.93. Found: C, 73.48; H, 5.88.

3,5-Bis[*trans*-2-(butoxycarbonyl)ethenyl]-2,6-bis (4-methylphenyl)-4*H*-pyran-4-one (3f)

Yellow solid, yield 74%, mp 87-89 °C. ν_{max} (KBr) 3084, 2950, 1714 (ester C=O), 1648 (pyrone C=O), 1613, 1415, 1282, 1221 cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (6H, t, $J=7.3$ Hz, $-(\text{CH}_2)_3-\text{CH}_3$), 1.37-1.43 (4H, m, $-(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 1.62-1.65 (4H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.43 (6H, s, benzylic CH_3), 4.15 (4H, t, $J=6.6$ Hz, CO_2CH_2), 7.31 (4H, d, $J=8.0$ Hz, aryl-H), 7.42 (2H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$), 7.49 (4H, d, $J=8.0$ Hz, aryl-H), 7.51 (2H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$). ^{13}C NMR (CDCl_3): δ 12.7, 18.2, 20.5, 29.7, 63.2, 117.0, 123.4, 127.3, 128.5, 128.7, 134.4, 141.1, 164.1, 166.9, 176.1. Anal. Calcd for $\text{C}_{33}\text{H}_{36}\text{O}_6$ (528.27): C, 75.02; H, 6.81. Found: C, 74.64; H, 6.69.

2,6-Diphenyl-3-[*trans*-2-(methoxycarbonyl)ethenyl]-4*H*-pyran-4-one (4a)

Light yellow solid, yield 19%, mp 162-164 °C. $\nu_{\max}$ (KBr) 3070, 2993, 1712, 1648, 1607, 1403, 1286 cm^{-1} . ^1H NMR (CDCl_3): δ 3.76 (3H, s, CO_2CH_3), 6.90 (1H, s, pyrone-H), 7.42 (1H, d, $J=15.5$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), 7.50-7.60 [7H, m, (1H, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), (6H, phenyl-H)], 7.65-7.67 (2H, m, phenyl-H), 7.80-7.84 (2H, m, phenyl-H). ^{13}C NMR (CDCl_3): δ 51.6, 111.1, 118.9, 124.2, 125.8, 128.9, 129.1, 129.7, 130.5, 130.7, 131.4, 131.6, 135.4, 162.0, 166.4, 168.2, 178.5. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{O}_4$ (332.17): C, 75.93; H, 4.82. Found: C, 76.06; H, 4.63.

2,6-Diphenyl-3-[*trans*-2-(ethoxycarbonyl)ethenyl]-4*H*-pyran-4-one (4b)

Light yellow solid, yield 21%, mp 131-133 °C. $\nu_{\max}$ (KBr) 3066, 2928, 1707, 1646, 1611, 1261, 1096 cm^{-1} . ^1H NMR (CDCl_3): δ 1.36 (3H, t, $J=7.1$ Hz, CH_2CH_3), 4.29 (2H, q, $J=7.1$ Hz, CH_2CH_3), 6.97 (1H, s, pyrone-H), 7.48 (1H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.55-7.67 [7H, m, (1H, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), (6H, phenyl-H)], 7.72-7.74 (2H, m, phenyl-H), 7.87-7.89 (2H, m, phenyl-H). ^{13}C NMR (CDCl_3): δ 13.2, 59.3, 110.1, 117.9, 123.6, 124.8, 127.8, 128.1, 128.7, 129.7, 130.3, 130.5, 130.6, 134.1, 160.9, 165.0, 166.7, 177.6. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4$ (346.18): C, 76.32; H, 5.19. Found: C, 76.09; H, 5.11.

2,6-Bis(4-methylphenyl)-3-[*trans*-2-(methoxycarbonyl)ethenyl]-4*H*-pyran-4-one (4d)

Light yellow solid, yield 22%, mp 167-168 °C. $\nu_{\max}$ (KBr) 3080, 2994, 1713, 1645, 1607, 1405, 1290, 1034 cm^{-1} . ^1H NMR (CDCl_3): δ 2.43 (3H, s, benzylic CH_3), 2.45 (3H, s, benzylic CH_3), 3.77 (3H, s, CO_2CH_3), 6.92 (1H, s, pyrone-H), 7.27 (2H, d, $J=8.1$ Hz, aryl-H), 7.36 (2H, d, $J=8.0$ Hz, aryl-H), 7.43 (1H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), 7.50 (1H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Me}$), 7.54 (2H, d, $J=8.0$ Hz, aryl-H), 7.68 (2H, d, $J=8.1$ Hz, aryl-H). ^{13}C NMR (CDCl_3): δ 20.7, 20.9, 51.5, 111.3, 115.3, 123.6, 123.9, 127.2, 127.8, 128.1, 128.3, 128.5, 128.7, 134.2, 139.9, 158.9, 164.8, 166.6, 173.3. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4$ (360.19): C, 76.69; H, 5.55. Found: C, 76.38; H, 5.24.

2,6-Bis(4-methylphenyl)-3-[*trans*-2-(ethoxycarbonyl)ethenyl]-4*H*-pyran-4-one (4e)

Light yellow solid, yield 15%, mp 161-162 °C. $\nu_{\max}$ (KBr) 3060, 2965, 1709, 1645, 1611, 1507, 1453, 1414, 1283, 1033 cm^{-1} . ^1H NMR (CDCl_3): δ 1.32 (3H, t, $J=7.0$ Hz, CH_2CH_3), 4.20 (2H, q, $J=7.0$ Hz, CH_2CH_3), 2.42 (3H, s, benzylic CH_3), 2.46 (3H, s, benzylic CH_3), 6.84 (1H, s, pyrone-H), 7.28 (2H, d, $J=8.2$ Hz, aryl-H), 7.36 (2H, d, $J=8.0$ Hz, aryl-H), 7.41 (1H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.50 (1H, d, $J=15.8$ Hz, $\text{CH}=\text{CH}-\text{CO}_2\text{Et}$), 7.53 (2H, d, $J=8.0$ Hz, aryl-H), 7.69 (2H, d, $J=8.2$ Hz, aryl-H). ^{13}C NMR (CDCl_3): δ 13.3, 20.5, 20.6, 59.4, 112.3, 115.4, 123.8, 124.9, 127.1, 127.9, 128.1, 128.2, 128.5, 128.7, 134.1, 140.8, 159.6, 164.9, 166.8, 172.1. Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4$ (374.20): C, 77.03; H, 5.88. Found: C, 76.86; H, 5.50.

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