HETEROCYCLES, Vol. 83, No. 1, 2011, pp. 117 - 123. © The Japan Institute of Heterocyclic Chemistry
Received, 29th September, 2010, Accepted, 16th November, 2010, Published online, 24th November, 2010
DOI: 10.3987/COM-10-12074

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

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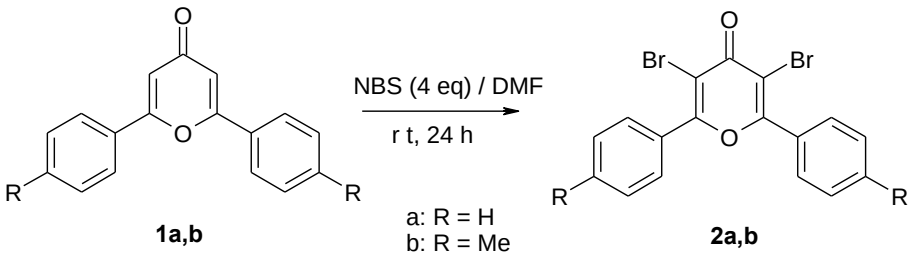
**Abstract** – Synthesis of two 2,6-diaryl-3,5-dibromo-4-pyrone derivatives is described, by using of NBS/DMF bromination of related 2,6-diaryl-4-pyrones. $PdCl_2$ catalyzed Heck coupling reactions of these dibromides, with emphasis on the use of *N*,*N*′-dibutylbenzimidazol-2-ylidene as ligand, resulted 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 carbens 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

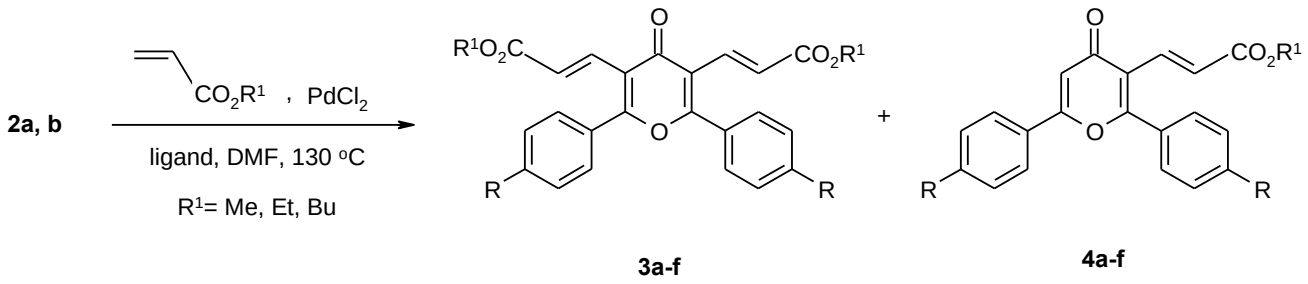
Heck vinylation reactions of these dibromides, catalyzed by *N,N′*-dibutylbenzimidazolium bromides (DBBIB)-$PdCl_2$ system.

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 evalution 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 $PdCl_2$ (1 eq%) as catalyst, triphenylphosphine (2 eq%) as ligand, and triethylamine as base at 130 $^oC$ 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 insted of $PPh_3$, consequently complete conversion of starting matarials 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 | *n*-Bu | **3c** (73) | **4c** (trace) |
| 4 | Me | Me | **3d** (64) | **4d** (22) |
| 5 | Me | Et | **3e** (60) | **4e** (15) |
| 6 | Me | *n*-Bu | **3f** (74) | **4f** (trace) |

Conditionds: 3,5-dibromo-4-pyrone (1 mmol), alkyl acrylate (4 mmol), $PdCl_2$ (1 mol%), DBBIB (2 mol%), $Et_3N$ (0.4 mL), 130 $^oC$, 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 $PdCl_2$-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 $^{13}C$ NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker Spectrospin Avance 400 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on a Shimadzo 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 $PF_{254+366}$) .

**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 $Et_2O$ (3 × 50 mL). The ether extracts were dried with $Na_2SO_4$, 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-4*H*-pyran-4-one (2a)**

White crystals, yield 61%, mp 169-170 °C. $\upsilon_{max}$ (KBr) 3060, 2924, 1645 (pyrone C=O), 1612, 1342, 1004, 755, 694 $cm^{-1}$. $^1H$ NMR ($CDCl_3$), δ 7.48-7.56 (6H, m, phenyl-H), 7.79-7.82 (4H, m, phenyl-H). $^{13}C$ NMR ($CDCl_3$), 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 $C_{17}H_{10}O_2Br_2$ (406.08): C, 50.28; H, 2.48. Found: C, 50.22; H, 2.55.

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

White crystals, yield 60%, mp 186-187 °C. $\upsilon_{max}$ (KBr) 3031, 2950, 1646 (pyrone C=O), 1611, 1505, 1340, 1006, 820, 756 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 2.43 (6H, s, $CH_3$), 7.30 (4H, d, *J*=8.1 Hz, aryl-H), 7.71 (4H, d, *J*=8.1 Hz, aryl-H). $^{13}C$ NMR ($CDCl_3$): 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 $C_{19}H_{14}O_2Br_2$ (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), $PdCl_2$ ( 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 $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by PLC on silicagel (hexane/$CH_2Cl_2$ 1:1) to give the mono- and di-vinylated products (**3, 4)**.

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

Yellow solid, yield 65%, mp 188-190 °C. $\upsilon_{max}$ (KBr) 3060, 2996, 1714 (ester C=O), 1648 (pyrone C=O), 1602, 1284, 1161 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 3.77 (6H, s, $CO_2CH_3$), 7.43 (2H, d, *J*=15.9 Hz, CH=C*H*-$CO_2$Me), 7.49-7.61 [8H, m, (6H, phenyl-H), (2H, C*H*=CH-$CO_2$Me)], 7.62-7.64 (4H, m, phenyl-H). $^{13}C$ NMR ($CDCl_3$): 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 $C_{25}H_{20}O_6$ (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-4*H*-pyran-4-one (3b)**

Yellow solid, yield 57%, mp 158-160 °C. $\upsilon_{max}$ (KBr) 3080, 2963, 1710 (ester C=O), 1647 (pyrone C=O), 1623, 1261, 1030 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 1.36 (6H, t, *J*=7.1 Hz, $CH_2CH_3$), 4.29 (4H, q, *J*=7.1 Hz,

C*H*$_2$CH$_3$), 7.49 (2H, d, *J*=15.8 Hz, CH=C*H*-CO$_2$Et), 7.57-7.64 [8H, m, (6H, phenyl-H), (2H, C*H*=CH-CO$_2$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 $C_{27}H_{24}O_6$ (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. υ$_{max}$ (KBr) 3070, 2929, 1712 (ester C=O), 1646 (pyrone C=O), 1625, 1274, 1025 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 0.93 (6H, t, *J*=7.3 Hz, (CH$_2$)$_3$-C*H*$_3$), 1.25-1.45 (4H, m, -(CH$_2$)$_2$-C*H*$_2$-CH$_3$), 1.59-1.67 (4H, m, CH$_2$C*H*$_2$CH$_2$CH$_3$), 4.15 (4H, t, *J*=6.5 Hz, CO$_2$C*H*$_2$), 7.42 (2H, d, *J*=15.8 Hz, CH=C*H*-CO$_2$Bu), 7.50-7.58 [8H, m, (6H, phenyl-H), (2H, C*H*=CH-CO$_2$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 $C_{31}H_{32}O_6$ (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, υ$_{max}$ (KBr) 3069, 2940, 1714 (ester C=O), 1648 (pyrone C=O), 1613, 1415, 1282, 1221 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 2.45 (6H, s, benzylic CH$_3$), 3.79 (6H, s, CO$_2$C*H*$_3$), 7.34 (4H, d, *J*=8.1 Hz, aryl-H), 7.43 (2H, d, *J*=15.9 Hz, CH=C*H*-CO$_2$Me), 7.50 (2H, d, *J*=15.9 Hz, C*H*=CH-CO$_2$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 $C_{27}H_{24}O_6$ (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. υ$_{max}$ (KBr) 3085, 2950, 1714 (ester C=O), 1646 (pyrone C=O), 1625, 1420, 1270 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 1.25 (6H, t, *J*=7.0 Hz, CH$_2$C*H*$_3$), 2.46 (6H, s, benzylic CH$_3$), 4.20 (4H, q, *J*=7.0 Hz, C*H*$_2$CH$_3$), 7.28 (4H, d, *J*=8.2 Hz, aryl-H), 7.35 (2H, d, *J*=15.9 Hz, CH=C*H*-CO$_2$Et), 7.51 (2H, d, *J*=15.9 Hz, C*H*=CH-CO$_2$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 $C_{29}H_{28}O_6$ (472.23): C, 73.75; H, 5.93. Found: C, 73.48; H, 5.88.

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

Yellow solid, yield 74%, mp 87-89 °C. υ$_{max}$ (KBr) 3084, 2950, 1714 (ester C=O), 1648 (pyrone C=O), 1613, 1415, 1282, 1221 cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 0.93 (6H, t, *J*=7.3 Hz, -(CH$_2$)$_3$-C*H*$_3$), 1.37-1.43 (4H, m, -(CH$_2$)$_2$C*H*$_2$CH$_3$), 1.62-1.65 (4H, m, -CH$_2$C*H*$_2$CH$_2$CH$_3$), 2.43 (6H, s, benzylic C*H*$_3$), 4.15 (4H, t, *J*=6.6 Hz, CO$_2$C*H*$_2$-), 7.31 (4H, d, *J*=8.0 Hz, aryl-H), 7.42 (2H, d, *J*=15.8 Hz, CH=C*H*-CO$_2$Bu), 7.49 (4H, d, *J*=8.0 Hz, aryl-H), 7.51 (2H, d, *J*=15.8 Hz, C*H*=CH-CO$_2$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 $C_{33}H_{36}O_6$ (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. $\upsilon_{max}$ (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, CH=C*H*-$CO_2$Me), 7.50-7.60 [7H, m, (1H, C*H*=CH-$CO_2$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 $C_{21}H_{16}O_4$ (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. $\upsilon_{max}$ (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, CH=C*H*-$CO_2$Et), 7.55-7.67 [7H, m, (1H, C*H*=CH-$CO_2$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 $C_{22}H_{18}O_4$ (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. $\upsilon_{max}$ (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, CH=C*H*-$CO_2$Me), 7.50 (1H, d, *J*=15.8 Hz, C*H*=CH-$CO_2$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 $C_{23}H_{20}O_4$ (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. $\upsilon_{max}$ (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, CH=C*H*-$CO_2$Et), 7.50 (1H, d, *J*=15.8 Hz, C*H*=CH-$CO_2$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 $C_{24}H_{22}O_4$ (374.20): C, 77.03; H, 5.88. Found: C, 76.86; H, 5.50.

## ACKNOWLEDGEMENTS

We thank research affair of University of Tabriz for financial support.

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