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# Heck reaction of β-substituted acrylates in ionic liquids catalyzed by a Pd-benzothiazole carbene complex

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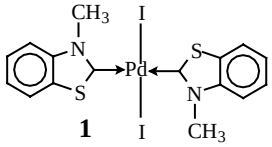
**Abstract**—A Pd-catalyst with benzothiazole carbene as ligands allows, in tetrabutylammonium bromide melt as solvent, very fast and efficient reactions of haloaromatics with β-substituted acrylates. 

The Heck reaction and related chemistry occupy a special place among basic types of palladium-catalyzed reactions.[1–3] In most of the papers dedicated to the Heck reaction, only a few examples of its use for the synthesis of trisubstituted olefins have been reported.[4–7] As some β,β-diaryl acrylates are useful intermediates for the synthesis of angiotensin II antagonist,[8] platelet activating factors antagonist,[9] and SRS-A antagonists (slow-reacting substance of anaphylaxis),[10] the development of an efficient process for the Heck arylation of β-substituted acrylates would be of significant utility. Arylation of β-substituted, α,β-unsaturated esters requires harsh reaction conditions, cyclopalladated phosphanes[5,6] or palladium acetate as catalysts, sterically hindered tertiary amines as bases and quaternary ammonium salts as phase-transfer agents in DMF or DMA as solvents[7] have been used.

Recently we reported the synthesis[11,12]of a Pd catalyst **1** with benzothiazole carbenes as ligands and its application to an efficient Heck synthesis[13] of trans-cinnamates in tetrabutylammonium bromide (TBAB) as solvent.




**1**

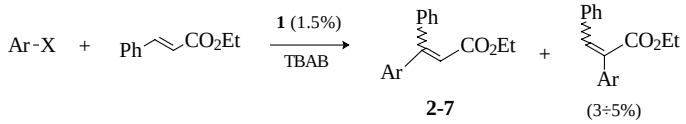
In these reactions, TBAB proved to be an excellent solvent for a fast and stereoselective synthesis of (*E*)-cinnamates. For example, bromobenzene reacted with butyl acrylate and sodium carbonate as base to give (*E*)-butyl cinnamate in only *ten minutes* and 94% yield.

In spite of the increasing interest in the use of ionic liquids[14] as environmentally benign solvents, different hypotheses on their role in catalysis have been reported.[2e] This paper reports our results on the synthesis of β-arylsubstituted cinnamates catalyzed by **1** in TBAB as solvent and the probable effects of this solvent in stabilizing the catalyst.

## 1. Results and discussion

Catalyst **1** efficiently allows the reaction of various *p*-substituted bromoaromatics with (*E*)-ethyl cinnamate in TBAB melt as solvent (Scheme 1).

As shown in Table 1, a procedure employing the catalyst **1** (1.5%), sodium formate (3%) as reducing agent and sodium bicarbonate as base in TBAB at 130°C, was very effective in coupling *trans*-cinnamates with both electron-rich and electron-poor aryl halides with 100% conversion. Even *p*-nitrochlorobenzene was coupled with ethyl cinnamate as the acceptor, albeit with a lower reaction rate, to give the




**2-7** (3÷5%)

**Scheme 1.** Ar=*p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CH_3COC_6H_4$, α-naphthyl, *p*-$O_2NC_6H_4$, *p*-$NCC_6H_4$; X=Cl, Br.

*Keywords*: β-aryl cinnamates; ionic liquids; carbenes; Heck reaction.

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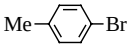
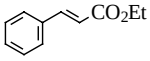
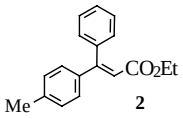
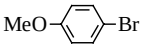
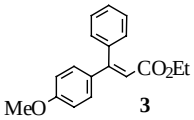
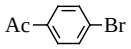
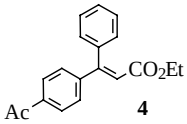
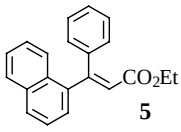
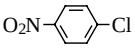
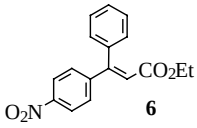
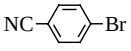
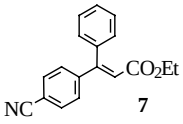
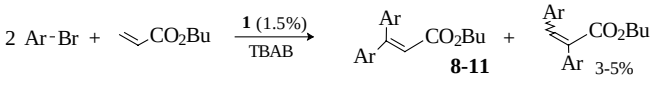
**Table 1.** Synthesis of β,β-diaryl acrylate in TBAB, catalyzed by Pd-benzothiazole carbene complex **1**

| Entry | Aryl halide | Olefin | Product | *E:Z* Ratio | Time [h] | Yield [%][a] |
|---|---|---|---|---|---|---|
| 1 |  |  |  **2** | 59:41 | 8 | 91 |
| 2 |  | " " |  **3** | 61:39 | 17 | 84 |
| 3 |  | " " |  **4** | 60:40 | 7 | 97 |
| 4 |  | " " |  **5** | 64:36 | 4 | 76 |
| 5 |  | " " |  **6** | 60:40 | 40 | 78 |
| 6 |  | " " |  **7** | 58:42 | 18 | 70 |

Conditions: 130°C, TBAB (3 g), $NaHCO_2$ 3 mol%; ratio haloarene/olefin/$NaHCO_3$ 1.5:1:2.5; 1.5 mol% of **1** with the exception of entry 5 (2.5 mol% of **1**).
[a] Yields refer to chromatographic isolated product.

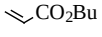
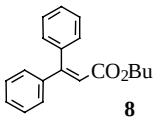
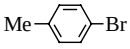
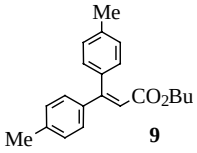
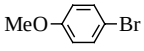
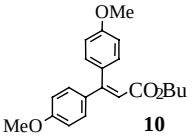
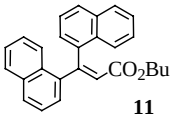
trisubstituted olefin (entry 5). On the other hand, by changing the olefin acceptor with *p*-nitrocinnamate, the reaction with bromobenzene did not afford the corresponding trisubstituted olefin. No palladium black deposition was observed and a phosphane ligand was not necessary. This result is important because a phosphane-free system is desirable particularly for industrial applications. In every case the coupling process was devoid of stereoselectivity. This finding is of considerable interest since the generally accepted mechanism for the Heck arylation of disubstituted alkenes predicts that the trisubstituted alkene should be formed in a stereospecific manner. The observed lack of stereoselectivity was probably due, as found by Buchwald et al.[7] to equilibration of cinnamate esters subsequent to the Heck arylation. Therefore, the stereochemistry of these reactions is likely to be defined by base-catalyzed isomerization of products leading to the accumulation of the more thermodynamically favourable isomer. This is not surprising as the olefins with such a substitution pattern must be susceptible to base-catalyzed *E*/*Z*-isomerization.

Due to the high catalytic activity of our system, we tried a one-pot synthesis of β,β-diarylacrylates by reaction of butyl acrylate with an excess of aryl bromides (Scheme 2). This procedure allows a fast and simple synthesis of trisubstituted olefins (Table 2, entries 1–4). Interestingly, besides the expected product, we observed, in all cases, the formation of very small quantities (3–5%) of 1,2-diaryl acrylates. To verify the observation[3,14–16] that ionic liquids bearing coordinating halide anions are necessary for a beneficial solvent effect, we tested a different ammonium salt, as butyl pyridinium tosylate (entry 5). Reaction in this solvent failed to give appreciable yield of coupling product. Recycling of TBAB and catalyst was also attempted but, after three cycles, the increase of NaBr rendered the reaction medium more viscous and prevented further addition of the reagents.




**Scheme 2.**

**Table 2.** Synthesis of β,β-diaryl acrylate in TBAB, catalyzed by Pd-benzothiazole carbene complex **1**

| Entry | Aryl halide | Olefin | Product | Time [h] | Yield [%][a] |
|---|---|---|---|---|---|
| 1 |  |  |  **8** | 3 | 82 |
| 2 |  | " " |  **9** | 8 | 85 |
| 3 |  | " " |  **10** | 12 | 86 |
| 4 |  | " " |  **11** | 7.5 | 89 |
| 5[b] | " " | " " | " " | 17 | 2 |

Conditions: 130°C, TBAB (3 g), $NaHCO_2$ 3 mol%; ratio haloarene/olefin/$NaHCO_3$ 2.3:1:2.5; 1.5 mol% of **1**.
[a] Yields refer to chromatographic isolated product.
[b] Butylpyridinium tosylate as solvent (3 g), 130°C.

## 2. Discussion

The results obtained in the TBAB melt were consistently higher than those obtained by us[11] with the same catalyst or by Herrmann et al.[15,16] in coupling styrene and unsubstituted acrylates with aryl bromides in DMA or DMF solvents. The catalyst **1** is very stable to high temperatures, air and moisture. This was due, as also found for Pd-complexes with imidazolidene carbene as ligands,[17] to the high binding energy of benzothiazolidene ligands to the Pd center which renders carbene decomplexation highly improbable. Furthermore, **1** is probably more stable and efficient, in ionic liquids,[18] than the Pd-complexes with imidazolidene ligands, with the latter requiring the addition of phosphanes to be efficient.[6,16,20] This stability in TBAB makes the recycling process feasible. Indeed, in only 3 g of TBAB, after three cycles, 8 g of bromobenzene were processed with a total TON of around 1720 thus making the whole process economically viable. Despite the observed beneficial effects exerted by quaternary ammonium salts on the Heck reaction, the exact nature of this influence cannot be ascribed to a single effect such as the high polarity or phase-transfer ability,[2e] but rather to a superposition of several factors. For example, Reetz et al.[21] found that reduction of a Pd salt in THF and in the presence of tetrabutylammonium acetate or formate gave Pd-nanoparticles stabilized by the large ammonium cation. Furthermore, Neghishi et al.[22] and Amatore and Jutand,[3] demonstrated that $Pd(0)(PPh_3)_2$, the proposed catalyst in the Heck reaction, was unstable in the absence of halide or acetate ions which transform this complex into a more stable and catalytically active 16-electron anionic complex as $[Pd(PPh_3)_2X]^{(-)}$. The stabilization of catalytic systems by halide salts was also demonstrated by extension of the lifetime of the Herrmann palladacycle.[23] To explain some ionic liquid effects, we propose some considerations that could explain our results. The addition of sodium formate does reduce[24] **1** to underligated $L_2Pd(0)$ complex, which, by reaction with TBAB, would afford an anionic and catalytically active 16-electron complex $[L_2Pd\ Br]^{(-)\,(+)}NR_4$. This would not be surprising, since in TBAB the bromide ion, being poorly solvated, should be a good nucleophile for palladium. On the contrary, ionic liquids bearing different anions such as tosylate or tetrafluoroborate should not stabilize, the 14-electron complex $L_2Pd(0)$ like halides can. Evidence for this was provided by the inefficacy of **1** in catalyzing the reaction in butylpyridinium tosylate. Furthermore, the same anion effect was observed[19] in other ionic liquids such as imidazolium tetrafluoborate. The stabilizing effect was exerted not only by the bromide ion, which is likely to enter the co-ordination shell of underligated $L_2Pd(0)$ to give the anionic complex, but also by the large tetrabutylammonium cation. Indeed, the formation of a large $[L_2Pd\ Br]^{(-)\,(+)}NR_4$ complex, by imposing a Coulombic barrier for collision, should impede the formation of clusters growing further into metal particles. Besides this effect, interaction of the tetrabutylammonium cation with the bromide or iodide ligated to the palladium center gives rise to the formation of ion pairs with a naked $L_2Pd(0)–Br^{(-)}–NR_4^{(+)}$ which does afford a more reactive palladium(0) complex.[3,22] Furthermore, the ammonium cation could electrostatically assist the polarization or decomplexation of the bromide ion

from the anionic Pd(II) pentacoordinated complex $[L_2PdArBr_2]^{(-)}NR_4^{(+)}$ deriving from oxidative addition with aryl bromides and this would render the Pd(II)-complex more electrophilic for a fast olefin insertion. This is conceivable since it was calculated, for analogous Pd-complexes with imidazolidene carbenes ligands, that the removal of bromide from the oxidative addition complex of aryl bromides was a strongly endothermic process.[17]

In conclusion, while some aspects of the catalytic cycle involving Pd-carbene complexes in ionic liquids are not well understood, our results show that ionic liquids cannot be considered as simple high polarity solvents but their efficacy is due to several factors which are studied by us.

## 3. Experimental

$^1$H- and $^{13}$C NMR were recorded in $CDCl_3$ on a Bruker AM 500 MHz spectrometer and chemical shifts were reported in ppm ($\delta$). IR and MS spectra were performed, respectively, on a Perkin–Elmer FT-1710 and on a Shimadzu QP5000 instruments. GC analyses were carried out on HP 5890A capillary gas-chromatograph (ZB-1, 30 m, 0.25 mm i.d.). Tetrabutylammonium bromide was purchased from Fluka and used as received. Palladium catalyst **1** was prepared as previous reported[11] and purified by flash cromatography on silica gel (eluent dichloromethane). The stereochemistry and the NMR signal assignment of all new compounds were secured by NOE experiments.

### 3.1. General procedure for the synthesis of bis-arylated acrylates

A pyrex reaction flask was charged with tetrabutylammonium bromide (3 g) and heated at 130°C. To the stirred molten salt were added in strict order the catalyst (0.11 mmol), sodium formate (0.22 mmol), haloarene (17.5 mmol), sodium bicarbonate (19 mmol) and butyl acrylate (7.6 mmol). The reaction was stirred at 130°C and monitored by GLC until the disappearance of the mono-arylated intermediate. When the ethyl cinnamate (5.7 mmol) was used as olefin, the amounts of reagents were: catalyst (0.09 mmol), sodium formate (0.18 mmol), sodium bicarbonate (14.3 mmol), haloarene (8.6 mmol). In this case, the reaction was stopped when ethyl cinnamate had completely disappeared. After completion of the reaction, the mixture was treated with aqueous HCl (30 ml) and extracted with 3×30 ml portions of diethyl ether. The organic layer was dried on $Na_2SO_4$ and the solvent evaporated under vacuum. The oily residue was chromatographed on silica gel (eluent petroleum ether/ethyl acetate) to give the following purified products:

**3.1.1. (*E*) and (*Z*) ethyl 3-phenyl-3-(*p*-tolyl)-propenoate (2).** This product was isolated as an oily mixture of the two *E*/*Z* stereoisomers. IR (liquid film) $\nu$ 3058, 3047, 2959, 2972, 1723, 1639, 1610, 1522, 1511, 1447, 1370, 1310, 1288, 1163, 1114, 1095, 1041, 988, 878, 822, 772, 699 cm$^{-1}$. The NMR signal assignment of the two isomers was made by comparison of the mixture spectral data with those reported in the literature.[25]

*(E)-Ethyl 3-phenyl-3-(p-tolyl)-propenoate.* $^1$H NMR $\delta$ 1.11 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 2.35 (s, 3H, $CH_3$ tolyl), 4.04 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.35 (s, 1H, vinyl proton), 7.11–7.14 (m, 2H, aromatic protons), 7.17–7.22 (m, 5H, aromatic protons), 7.36–7.39 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.76, 20.99, 59.66, 116.32, 127.57, 128.05, 128.36, 128.90, 129.03 137.74, 138.98, 140.95, 156.27, 165.91; MS (EI) *m*/*z* 267 ($M^+$+1, 18), 266 ($M^+$, 100), 265 (15), 237 (18), 222 (15), 221 (97), 195 (18), 194 (83), 193 (32), 191 (21), 179 (45), 178 (71), 165 (20), 152 (12), 120 (36), 115 (47), 105 (27), 95 (20), 91 (24), 89 (23), 82 (20), 77 (17), 55 (14), 51 (24).

*(Z)-Ethyl 3-phenyl-3-(p-tolyl)-propenoate.* $^1$H NMR $\delta$ 1.16 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 2.40 (s, 3H, $CH_3$ tolyl), 4.07 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.32 (s, 1H, vinyl proton), 7.09–7.12 (m, 2H, aromatic protons), 7.17–7.22 (m, 5H, aromatic protons), 7.29–7.32 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 14.11, 21.15, 60.21, 116.92, 127.81, 128.09, 128.36, 128.63, 129.12; 135.77, 139.36, 144.34, 156.54, 166.67; MS (EI) *m*/*z* 267 ($M^+$+1, 20), 266 ($M^+$, 98), 265 (12), 237 (20), 222 (12), 221 (100), 195 (15), 194 (79), 193 (35), 191 (20), 179 (42), 178 (74), 165 (17), 152 (12), 120 (38), 115 (47), 105 (26), 95 (15), 91 (29), 89 (21), 82 (21), 77 (15), 55 (17), 51 (23).

**3.1.2. (*E*) and (*Z*) ethyl 3-phenyl-3-(*p*-methoxyphenyl)-propenoate (3).** This product was isolated as an oily mixture of the two *E*/*Z* stereoisomers. IR (liquid film) $\nu$ 3050, 2980, 2935, 1719, 1604, 1574, 1511, 1484, 1464, 1445, 1421, 1373, 1354, 1252, 1151, 1096, 1035, 875, 834, 796, 775, 700 cm$^{-1}$. The NMR signal assignment of the two isomers was made by comparison of the mixture spectral data with those reported in the literature.[25]

*(E)-Ethyl 3-phenyl-3-(p-methoxyphenyl)-propenoate.* $^1$H NMR $\delta$ 1.12 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 3.79 (s, 3H, $OCH_3$), 4.05 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.34 (s, 1H, vinyl proton), 6.84 (d, $J$=8.9 Hz, 2H, aromatic protons), 7.20–7.24 (m, 1H, aromatic proton), 7.26 (d, $J$=8.9 Hz, 2H, aromatic protons), 7.30–7.33 (m, 2H, aromatic protons), 7.38–7.41 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.65, 55.12, 59.68, 113.61, 115.21, 127.66, 128.92, 129.15, 129.57, 130.77, 139.12, 156.08, 160.62, 166.07; MS (EI) *m*/*z* 283 ($M^+$+1, 18), 282 ($M^+$, 100), 253 (10), 238 (14), 237 (70), 211 (18), 210 (95), 209 (21), 195 (32), 194 (21), 178 (17), 166 (24), 165 (74), 152 (11), 139 (11), 135 (55), 119 (8), 105 (27), 91 (17), 89 (15), 82 (17), 77 (18), 63 (17), 51 (20).

*(Z)-Ethyl 3-phenyl-3-(p-methoxyphenyl)-propenoate.* $^1$H NMR $\delta$ 1.18 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 3.84 (s, 3H, $OCH_3$), 4.11 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.30 (s, 1H, vinyl proton), 6.92 (d, $J$=8.8 Hz, 2H, aromatic protons), 7.18 (d, $J$=8.8 Hz, 2H, aromatic protons), 7.30–7.33 (m, 2H, aromatic protons), 7.34–7.37 (m, 1H, aromatic proton), 7.38–7.41 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.97, 55.01, 59.80, 113.06, 116.73, 127.81, 128.14, 128.38, 130.97, 132.93, 141.38, 156.38, 159.59, 166.07; MS (EI) *m*/*z* 283 ($M^+$+1, 20), 282 ($M^+$, 100), 253 (11), 238 (11), 237 (73), 211 (17), 210 (94), 209 (20), 195 (29), 194 (21), 178 (15), 166 (21), 165 (74), 152 (11), 139 (11), 135 (50), 105 (33), 91 (15), 89 (17), 82 (10), 77 (17), 63 (18), 51 (21).

**3.1.3. (*E*) and (*Z*) ethyl 3-phenyl-3-(*p*-acetylphenyl)-propenoate (4).** This product was isolated as a yellow, oily mixture of the two *E*/*Z* stereoisomers.

*(E)-Ethyl 3-phenyl-3-(p-acetylphenyl)-propenoate.* $^1$H NMR $\delta$ 1.10 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 2.59 (s, 3H, $CH_3CO$), 4.05 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.40 (s, 1H, vinyl proton), 7.15–7.20 (m, 2H, aromatic protons), 7.35–7.40 (m, 5H, aromatic protons), 7.86–7.90 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.89, 26.63, 60.23, 119.26, 127.99, 128.30, 128.36, 128.41, 129.00, 137.30, 138.23, 146.21, 154.87, 165.71, 197.43; IR (liquid film) $\nu$ 3058, 2981, 2931, 2873, 1723, 1688, 1605, 1576, 1562, 1446, 1406, 1370, 1266, 1168, 1115, 1097, 1076, 1042, 958, 878, 839, 774, 701 cm$^{-1}$; MS (EI) *m*/*z* 294 ($M^+$, 27), 279 (24), 265 (2), 249 (15), 223 (6), 222 (5), 207 (22), 178 (10), 152 (5), 125 (5), 117 (2), 102 (2), 89 (5), 76 (7), 63 (2), 51 (5), 43 (100).

*(Z)-Ethyl 3-phenyl-3-(p-acetylphenyl)-propenoate.* $^1$H NMR $\delta$ 1.11 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 2.64 (s, 3H, $CH_3CO$), 4.06 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.42 (s, 1H, vinyl proton), 7.23–7.27 (m, 2H, aromatic protons), 7.29–7.38 (m, 5H, aromatic protons), 7.96–8.00 (m, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.97, 26.60, 60.20, 117.94, 127.95, 128.05, 128.50, 129.27, 129.68, 136.46, 139.81, 144.10, 155.48, 165.65, 197.65; IR (liquid film) $\nu$ 3070, 2981, 2925, 2870, 1723, 1688, 1612, 1570, 1562, 1446, 1370, 1263, 1168, 1115, 1089, 1076, 1042, 960, 878, 839, 770, 703 cm$^{-1}$; MS (EI) *m*/*z* 294 ($M^+$, 29), 279 (29), 265 (2), 249 (15), 223 (7), 222 (7), 207 (24), 178 (11), 152 (5), 125 (5), 117 (2), 102 (2), 89 (5), 76 (8), 63 (2), 51 (5), 43 (100).

**3.1.4. (*E*) and (*Z*) ethyl 3-phenyl-3-(1-naphthyl)-propenoate (5).** This product was isolated as an oily mixture of the two *E*/*Z* stereoisomers. IR (liquid film) $\nu$ 3057, 2979, 1723, 1615, 1592, 1576, 1506, 1463, 1445, 1368, 1271, 1254, 1197, 1164, 1065, 1046, 1027, 973, 957, 878, 797, 778 cm$^{-1}$.

*(E)-Ethyl 3-phenyl-3-(1-naphtyl)-propenoate.* $^1$H NMR $\delta$ 0.87 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 3.90 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.79 (s, 1H, vinyl proton), 7.26–8.02 (m, 12H, aromatic protons); $^{13}$C NMR $\delta$ 13.50, 59.73, 119.22, 125.02, 125.61, 125.87, 126.06, 127.35, 127.70, 128.15, 128.44, 128.83, 129.38, 131.47, 133.29, 136.81, 139.79, 154.42, 165.54; MS (EI) *m*/*z* 302 ($M^+$, 14), 273 (3), 257 (6), 255 (5), 239 (2), 230 (18), 229 (100), 228 (73), 227 (14), 226 (15), 215 (2), 202 (8), 189 (2), 167 (2), 152 (6), 151 (2), 127 (5), 114 (12), 113 (15), 101 (8), 88 (3), 77 (5), 63 (2), 51 (6).

*(Z)-Ethyl 3-phenyl-3-(1-naphtyl)-propenoate.* $^1$H NMR $\delta$ 1.23 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 4.20 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.27 (s, 1H, vinyl proton), 7.26–8.02 (m, 12H, aromatic protons); $^{13}$C NMR $\delta$ 13.91, 60.16, 121.31, 124.94, 125.32, 125.77, 126.27, 127.06, 127.92, 128.22, 128.38, 128.78, 129.38, 131.03, 133.70, 139.27, 139.74, 155.04, 166.15; MS (EI) *m*/*z* 302 ($M^+$, 12), 273 (3), 257 (6), 255 (5), 239 (2), 230 (17), 229 (100), 228 (76), 227 (12), 226 (17), 215 (2), 202 (9), 189 (2), 167 (2), 152 (8), 151 (8), 127 (3), 114 (12), 113 (12), 101 (9), 88 (2), 77 (5), 63 (2), 51 (6).

**3.1.5. (*E*) and (*Z*) ethyl 3-phenyl-3-(*p*-nitrophenyl)-propenoate (6).** This product was isolated as a yellow, oily mixture of the two *E*/*Z* stereoisomers.

*(E)-Ethyl 3-phenyl-3-(p-nitrophenyl)-propenoate.* $^1$H NMR $\delta$ 1.10 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 4.06 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.41 (s, 1H, vinyl proton), 7.15–7.20 (m, 2H, aromatic protons), 7.36–7.41 (m, 3H, aromatic protons), 7.44 (d, $J$=9.2 Hz, 2H, aromatic protons), 8.16 (d, $J$=9.2 Hz, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.85, 60.41, 120.61, 123.55, 123.77, 128.17, 128.68, 128.95, 137.63, 147.03, 148.03, 153.49, 165.35; IR (liquid film) $\nu$ 3110, 3065, 2989, 2935, 2968, 1719, 1630, 1590, 1530, 1475, 1440, 1411, 1342, 1263, 1174, 1110, 1077, 1032, 910, 855, 778, 760, 737, 698 cm$^{-1}$; MS (EI) *m*/*z* 298 ($M^+$+1, 12), 297 ($M^+$, 67), 296 (19), 280 (4), 269 (17), 268 (27), 253 (19), 252 (100), 236 (2), 225 (39), 224 (19), 207 (7), 206 (12), 179 (12), 178 (58), 177 (27), 176 (34), 165 (29), 152 (24), 151 (14), 115 (4), 105 (14), 102 (16), 88 (10), 76 (27), 63 (13), 51 (24).

*(Z)-Ethyl 3-phenyl-3-(p-nitrophenyl)-propenoate.* Yellow oil, $^1$H NMR $\delta$ 1.15 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 3.89 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.46 (s, 1H, vinyl proton), 7.24 (d, $J$=7.2, Hz, 2H, aromatic protons), 7.33–7.39 (m, 5H, aromatic protons), 8.24 (d, $J$=9.0 Hz, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.94, 60.37, 118.52, 123.16, 127.93, 128.65, 128.95, 129.96, 139.12, 145.97, 147.36, 154.31, 165.32; IR (liquid film) $\nu$ 3107, 3080, 2992, 2937, 2972, 1719, 1631, 1598, 1530, 1492, 1477, 1445, 1411, 1343, 1263, 1173, 1110, 1077, 1036, 912, 856, 777, 760, 737, 700 cm$^{-1}$; MS (EI) *m*/*z* 298 ($M^+$+1, 13), 297 ($M^+$, 67), 296 (22), 280 (2), 269 (14), 268 (25), 253 (18), 252 (100), 236 (4), 225 (39), 224 (22), 207 (7), 206 (12), 179 (14), 178 (63), 177 (27), 176 (34), 165 (27), 152 (23), 151 (17), 115 (5), 105 (12), 102 (17), 88 (10), 76 (24), 63 (12), 51 (24).

### 3.2. Ethyl 3-phenyl-3-(*p*-cyanophenyl)-propenoate (7)

This product was isolated as a yellow, oily mixture of the two *E*/*Z* stereoisomers.

*(E)-Ethyl 3-phenyl-3-(p-cyanophenyl)-propenoate.* Oil. $^1$H NMR $\delta$ 1.10 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 4.06 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.39 (s, 1H, vinyl proton), 7.15–719 (m, 2H, aromatic protons), 7.36–7.40 (m, 5H, aromatic protons), 7.59 (d, $J$=8.2 Hz, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.88, 60.38, 112.74, 118.39, 120.12, 128.15, 128.61, 128.77, 128.00, 132.14, 137.69, 145.18, 153.95, 165.46; IR (liquid film) $\nu$ 3058, 2980, 2934, 2873, 2228, 1719, 1621, 1575, 1556, 1504, 1492, 1465, 1446, 1409, 1392, 1370, 1266, 1170, 1117, 1096, 1075, 1035, 1001, 973, 925, 891, 840, 776, 701 cm$^{-1}$; MS (EI) *m*/*z* 278 ($M^+$+1, 12), 277 ($M^+$, 55), 276 (12), 248 (22), 233 (19), 232 (100), 218 (2), 205 (41), 204 (64), 203 (46), 190 (10), 177 (19), 176 (24), 151 (10), 125 (7), 110 (14), 105 (14), 88 (16), 77 (19), 63 (5), 51 (36).

*(Z)-Ethyl 3-phenyl-3-(p-cyanophenyl)-propenoate.* Oil. $^1$H NMR $\delta$ 1.13 (t, $J$=7.1 Hz, 3H, $CH_3$ ethyl), 4.04 (q, $J$=7.1 Hz, 2H, $CH_2$ ethyl), 6.43 (s, 1H, vinyl proton), 7.20–724 (m, 2H, aromatic protons), 7.29–7.38 (m, 5H, aromatic protons), 7.67 (d, $J$=8.1 Hz, 2H, aromatic

protons); $^{13}$C NMR $\delta$ 13.97, 60.33, 111.80, 118.40, 118.69, 128.00, 128.65, 129.82, 129.92, 131.70, 139.31, 143.99, 154.60, 165.40; IR (liquid film) $\nu$ 3060, 2981, 2936, 2873, 2228, 1719, 1619, 1575, 1556, 1503, 1492, 1465, 1448, 1409, 1392, 1370, 1266, 1173, 1118, 1096, 1076, 1032, 1003, 972, 926, 893, 841, 774, 702 cm$^{-1}$; MS (EI) *m/z* 278 ($M^+$+1, 13), 277 ($M^+$, 56), 276 (12), 248 (24), 233 (18), 232 (100), 218 (4), 205 (40), 204 (64), 203 (46), 190 (11), 177 (22), 176 (23), 151 (11), 125 (8), 110 (12), 105 (12), 88 (15), 77 (19), 63 (5), 51 (40).

**3.2.1. Butyl 3,3-diphenyl-propenoate (8).** Yellow oil. $^1$H NMR $\delta$ 0.85 (t, *J*=7.4 Hz, 3H, $CH_3$ butyl), 1.21 (sextet, *J*=7.4 Hz, 2H, $CH_2$ butyl), 1.40–1.48 (m, 2H, $CH_2$ butyl), 3.99 (t, *J*=6.6 Hz, 2H, $CH_2$ butyl), 6.36 (s, 1H, vinyl proton), 7.18–7.25 (m, 2H, aromatic protons), 7.26–7.39 (m, 8H, aromatic protons);$^{13}$C NMR $\delta$ 13.61, 19.01, 30.44, 63.99, 117.51, 127.80, 127.99, 128.19, 128.29, 129.05, 129.29, 131.47, 140.78, 156.22, 166.23; IR (liquid film) $\nu$ 3058, 3026, 2959, 2976, 1723, 1617, 1576, 1493, 1446, 1265, 1164, 1064, 1032, 772, 698 cm$^{-1}$; MS (EI) *m/z* 280 ($M^+$, 19), 224 (48), 223 (52), 207 (84), 180 (38), 179 (76), 178 (100), 167 (40), 152 (21), 105 (31), 89 (19), 77 (17), 51 (35), 41 (41). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.45; H, 7.22.

**3.2.2. Butyl 3,3-di-*p*-tolyl-propenoate (9).** Oil. $^1$H NMR $\delta$ 0.85 (t, *J*=7.3 Hz, 3H, $CH_3$ butyl), 1.18–1.27 (m, 2H, $CH_2$ butyl), 1.41–1.50 (m, 2H, $CH_2$ butyl), 2.34 (s, 3H, $CH_3$ tolyl), 2.38 (s, 3H, $CH_3$ tolyl), 3.99 (t, *J*=6.6 Hz, 2H, $CH_2$ butyl), 6.29 (s, 1H, vinyl proton), 7.06–7.38 (m, 8H, aromatic protons); $^{13}$C NMR $\delta$ 13.64, 19.04, 21.16, 21.28, 30.50, 63.87, 116.21, 128.22, 128.47, 128.96, 129.08, 130.71, 137.78, 138.24, 139.45, 156.59, 166.41; IR (liquid film) $\nu$ 3025, 2959, 2872, 1723, 1606, 1568, 1510, 1456, 1265, 1162, 1069, 1013, 821, 804, 730, cm$^{-1}$; MS (EI) *m/z* 308 ($M^+$, 65), 252 (73), 251 (48), 235 (100), 208 (87), 193 (48), 191 (46), 190 (43), 189 (43), 165 (16), 119 (63), 115 (40), 91 (24), 65 (14), 41 (43). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.82; H, 7.86.

**3.2.3. Butyl 3,3-di-(4-methoxyphenyl)-propenoate (10).** Yellow oil, $^1$H NMR $\delta$ 0.86 (t, *J*=7.4 Hz, 3H, $CH_3$ butyl), 1.20–1.29 (m, 2H, $CH_2$ butyl), 1.45–1.52 (m, 2H, $CH_2$ butyl), 3.79 (s, 3H, $OCH_3$), 3.82 (s, 3H, $OCH_3$), 4.00 (t, *J*=6.6 Hz, 2H, $CH_2$ butyl), 6.22 (s, 1H, vinyl proton), 6.82 (d, *J*=9.0 Hz, 2H, aromatic protons), 6.89 (d, *J*=8.8 Hz, 2H, aromatic protons), 7.13 (d, *J*=8.8 Hz, 2H, aromatic protons), 7.23 (d, *J*=9.0 Hz, 2H, aromatic protons); $^{13}$C NMR $\delta$ 13.64, 19.07, 30.56, 55.09, 55.25, 63.78, 113.15, 113.61, 114.94, 115.64, 129.90, 130.75, 131.26, 132.14, 156.10, 160.65, 166.54; IR (liquid film) $\nu$ 3037, 3001, 2958, 2873, 2837, 1718, 1600, 1510, 1490, 1462, 1420, 1248, 1149, 1034, 871, 833, 781, 749 cm$^{-1}$; MS (EI) *m/z* 340 ($M^+$, 37), 284 (19), 267 (32), 240 (65), 225 (33), 209 (16), 181 (9), 190 (43), 165 (13), 153 (14), 152 (21), 135 (100), 121 (9), 107 (7), 89 (7), 77 (8), 55 (7), 41 (40). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.16; H, 7.13.

**3.2.4. Butyl 3,3-di-(1-naphtyl)-propenoate (11).** Oil, $^1$H NMR $\delta$ 0.70 (t, *J*=7.3 Hz, 3H, $CH_3$ butyl), 0.86–0.96 (m, 2H, $CH_2$ butyl), 1.06–1.14 (m, 2H, $CH_2$ butyl), 3.82 (t, *J*=6.4 Hz, 2H, $CH_2$ butyl), 6.58 (s, 1H, vinyl proton), 7.29–7.55 (m, 8H, aromatic protons), 7.77–7.90 (m, 4H, aromatic protons), 8.04 (d, *J*=8.8 Hz, 1H, aromatic protons), 8.47 (d, *J*=8.8 Hz, 1H, aromatic protons); $^{13}$C NMR $\delta$ 13.52, 18.75, 30.11, 64.11, 125.01, 125.16, 125.23, 125.68, 125.89, 126.13, 126.40, 126.77, 127.04, 127.26, 127.80, 128.26, 128.41, 128.65, 128.96, 129.84, 130.69, 131.35, 134.11, 138.51, 139.48, 152.43, 165.99; IR (liquid film) $\nu$ 3056, 2959, 2872, 1724, 1613, 1591, 1562, 1507, 1464, 1379, 1278, 1217, 1187, 1163, 1061, 1023, 957, 866, 779, 738 cm$^{-1}$; MS (EI) *m/z* 380 ($M^+$, 15), 341 (9), 323 (8), 306 (9), 305 (29), 289 (11), 281 (11), 280 (18), 279 (85), 278 (89), 277 (62), 276 (45), 274 (9), 265 (8), 264 (11), 263 (12), 252 (15), 196 (15), 152 (15), 138 (24), 128 (33), 112 (3), 96 (5), 73 (39), 57 (18), 41 (100). Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 85.28; H, 6.35.

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