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Heterogeneous photocatalysed Heck reaction over $PdCl_2/TiO_2$†

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The heterogeneous $PdCl_2/TiO_2$ efficiently catalyzes the C–C bond formation (Heck reaction) between aryliodides and olefins under photochemical and mild reaction conditions. This process gives good to excellent conversion under optimized reaction conditions. After completion of the reaction, Pd^{2+} is reduced to Pd^0. Further, Pd^0 can be easily converted into Pd^{2+} by heating with ammonium chloride at 400 °C for 30 min and the regenerated catalyst could be reused up to the third recycle with good catalytic activity. The catalysts (before and after reaction, as well as regenerated) were systematically characterized using Transmission Electron Microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, temperature programmed reduction and DRUV-visible spectroscopy techniques.

Introduction

The palladium-catalyzed Heck reaction[1] for the carbon–carbon (C–C) bond formation between aryl halides and olefins has become a widely used tool in organic synthesis.[2] It provides the simplest and most efficient way to synthesize various compounds useful in the pharmaceutical and agrochemical industries.[3] The Heck reaction is generally performed with 1–5 mol% palladium along with phosphine ligands for stabilization of active palladium intermediates in the presence of a suitable base under thermal conditions. Most of the efforts have been directed to enhance the catalytic activity of palladium by using homogeneous as well as heterogeneous reaction conditions.[4] Various phosphorous,[5,6] nitrogen,[7] sulfur[8] and carbene[9] based ligands have been tried successfully. However, due to their drawbacks, *viz.* air and moisture sensitive nature, toxicity, expense, non-recoverability and severe reaction conditions, a ligand-free Heck reaction has been developed. Also, the main problem associated with homogeneous reaction media is the recovery of the precious palladium metal and contamination of the product. To overcome this problem, many researchers have studied the Heck reaction over heterogeneous catalysts such as palladium supported on various metal oxides,[10a] silica,[10b] carbon,[10c,d] zeolite,[2d] graphene oxide,[10e] polyaniline,[11] polyacrylamide,[12] polyethylene glycol and non-cross-linked polystyrene,[13] Pd/TiO_2,[14] *etc.* Incorporation of palladium in ordered mesoporous materials enhances the catalytic activity and recyclability.[15] In the last decade, simple palladium salts such as $PdCl_2$ or $Pd(OAc)_2$ without any ligands are increasingly being used for the Heck reaction due to their low cost.[16] In order to increase the effectiveness of the catalyst, various methods such as ultrasonication,[17] microwaves[18] and electrochemistry[19] have been used. Fredricks *et al.* reported the acceleration of the Heck reaction using UV-visible irradiation over homogeneous $Pd(OAc)_2$ and heterogeneous (Pd/Al_2O_3 and Pd/TiO_2) catalysts.[20] Generally, the vast complexity of the Heck reaction at high temperatures (> 80 °C) is well known and it is carried out between 80–160 °C.[20] Even though Fredricks *et al.* reported the Heck reaction between 90–160 °C, there is a probability for domination of the thermal reaction as compared to photochemical reactions (same conversion observed with and without UV-visible light irradiation).[20] The recovery of precious Pd metal is important for a cost effective process. The development of the Heck reaction at ambient conditions and with catalyst recovery is also a challenging task for researchers. Recently, Chaudhary and Bedekar reported Mizoroki–Heck reaction over $Pd(OAc)_2$ under sunlight with a naphthalene derivative as a ligand.[20c] The time taken for this reaction is very long (9 days).

As a part of our research program aimed towards the development of new strategies for the C–C bond formation, we were encouraged to design a convenient and effective route to C–C bond formation under UV-visible light at mild reaction conditions.[21] In this context, herein a heterogeneous UV-visible light irradiated Heck reaction of various aryl iodides with olefins over $PdCl_2/TiO_2$ as a catalyst was carried out at ambient reaction conditions. The reusability of eco-friendly heterogeneous catalyst and the systematic study of the influence of different solvents, bases, catalyst concentrations and regeneration of the catalyst are successfully investigated.

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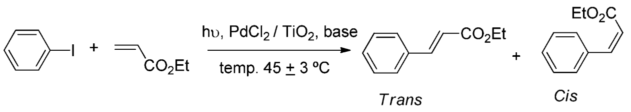
Results and discussion

At the outset of our study, iodobenzene and ethyl acrylate were chosen as model substrates to optimize the reaction conditions such as different palladium sources, various organic and inorganic bases, solvents, and catalyst concentrations (Scheme 1). Conversion of iodobenzene was obtained at 97% with ~9 : 1 selectivity for *trans* and *cis* isomers (ethyl cinnamate) in 5 h under UV-visible irradiation in the presence of $PdCl_2/TiO_2$ (0.5 mol% Pd) as catalyst (Table 1; entry 2). The observed *cis* isomer may be due to the UV-visible light-induced isomerization of alkenes (*trans–cis*).[20c,22] In order to confirm whether the reaction is photochemical or thermal, the reaction was carried without UV-visible light irradiation at 45 °C by keeping all other parameters constant. It gave only 2% conversion with 100% selectivity for the *trans* ethyl cinnamate (Table 1; entry 3). The reaction with TiO_2 with or without UV-visible light did not give conversion (entries 4 and 5). The reaction over $PdCl_2$ without UV-visible light did not give conversion, however under UV-visible light gave (homogeneous reaction conditions) 99% conversion with 88% selectivity (entries 6 and 7). These results show that the rate of reaction of C–C bond formation under UV-visible light has been remarkably increased. The physical mixture of $PdCl_2$–TiO_2 gave 75% conversion. The catalyst prepared by weight impregnation method is much more superior that the physical mixture. The screening of other sources of Pd loaded on TiO_2 gave conversion between 50–90% (entries 8–15). Among the studied heterogeneous catalyst $PdCl_2/TiO_2$ showed excellent catalytic activity under UV-visible light irradiation.

Among the various solvents studied, DMF and DMAc gave excellent conversion and selectivity for the *trans* ethyl cinnamate (Table 2; entries 1 and 2). The NMP showed 74% conversion (entry 3). The reaction in DMSO and ACN showed poor conversion (entries 4 and 5). Non-polar solvents do not show activity (entry 6). The order of activity is DMF ~ DMAc > NMP > DMSO > ACN > DPE > THF ~ diglyme > xylene. The catalytic activity of different palladium concentrations for the Heck coupling under photochemical conditions was studied and the results are summarized in Fig. 1. It was observed that percentage conversion increased with palladium concentration. At lower Pd concentration (0.12 mol%), 97% conversion was observed but it requires higher reaction time. The effect of organic as well as inorganic bases was studied for the reaction between iodobenzene and ethyl acrylate and results are shown in Table 3. TEA and TBA showed higher conversion compared to other inorganic bases. This was attributed to the solubility of bases in the solvent which directly affects the conversion of the reaction. The study of different bases shows that TEA was the best base among the bases in the presence of 0.5 mol% $PdCl_2/TiO_2$ as a catalyst. Using the



Scheme 1 Photochemical Heck reaction between iodobenzene and ethyl acrylate.

Table 1 Screening of the catalysts for Heck reaction[c]

Entry	Catalyst	UV-Vis light	Conversion (%)	Selectivity (% *trans*)
1	No	Yes	0	—
2	$PdCl_2/TiO_2$	Yes	97	89
3	$PdCl_2/TiO_2$	No	2	100
4	TiO_2	No	0	—
5	TiO_2	Yes	0	—
6	$PdCl_2$	No	12	100
7	$PdCl_2$[a]	Yes	99	88
8	$PdCl_2/TiO_2$[b]	Yes	75	95
9	$Pd(OAc)_2/TiO_2$	Yes	90	92
10	$Pd(NH_3)_4Cl_2{\cdot}H_2O/TiO_2$	Yes	51	91
11	$Pd(NH_3)_4(OAc)_2/TiO_2$	Yes	80	88
12	$Na_2PdCl_6{\cdot}4H_2O/TiO_2$	Yes	64	91
13	10% Pd/C	Yes	2	100
14	$[(C_6H_5)_3P]_4Pd/TiO_2$	Yes	40	89
15	$Pd(OAc)_2/TiO_2$	Yes	90	92
16	$Pd(NH_3)_4Cl_2{\cdot}H_2O/TiO_2$	Yes	51	91
17	PdO–TiO_2	Yes	0	—

[a] Reaction time 3 h. [b] Physical mixture. [c] Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (3 mmol), triethyl amine (3 mmol), 5 mL solvent, 0.5 mol% catalysts were stirred for 5 h under 400 W mercury vapour lamp at temperature 45 ± 3 °C.

Table 2 Reaction of iodobenzene with ethyl acrylate using different solvents[a]

Entry	Solvent	Conversion (%)	Selectivity (% *trans*)
1	DMF	97	89
1[b]	DMF	2	100
2	DMAc	97	86
3	NMP	74	84
4	DMSO	33	63
5	ACN	10	100
6	DPE	9	85
7	Xylene	1	100
8	THF	4	47
9	Diglyme	4	100
10	1,4-Dioxane	NR	—

[a] Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (3 mmol), triethyl amine (3 mmol), 5 mL solvent, 0.5 mol% $PdCl_2/TiO_2$ were stirred for 5 h under 400 W mercury vapour lamp at temperature 45 ± 3 °C. [b] Reaction was carried out without UV-visible irradiation at 45 °C for 5 h; light intensity. NR – no reaction.

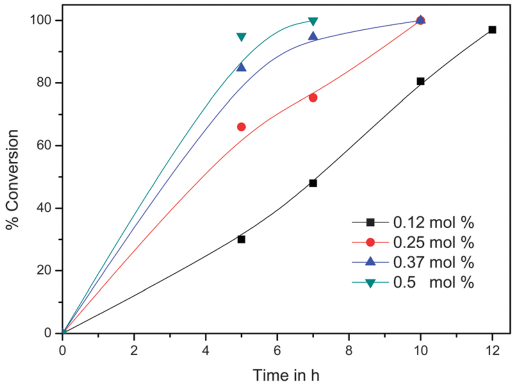


Fig. 1 Graph of percentage conversion *vs.* time using different amounts of catalyst concentration.

Table 3 Reaction of iodobenzene with ethyl acrylate using different bases[a]

Entry	Base	Conversion (%)	Selectivity (% *trans*)
1	TEA	97	89
2	TBA	93	93
3	NaOAc	12	86
4	K_2CO_3	12	53
5	Cs_2CO_3	NR	—
6	$Ca(OH)_2$	NR	—

[a] Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (3 mmol), base (3 mmol), 5 mL DMF, 0.5 mol% $PdCl_2/TiO_2$ were stirred for 5 h under 400 W mercury vapour lamp. NR – no reaction.

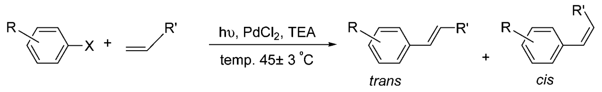
Table 4 Photocatalytic Heck coupling of aryl halides and olefins using $PdCl_2/TiO_2$[a]

Entry	R	X	R′	Conversion (%)	Selectivity (% *trans*)
1	H	I	CO_2Et	97	89
2	H	I	CO_2Me	90	95
3	H	I	CO_2nBu	94	89
4	H	I	Ph	11	90
5	H	I	COOH	29	100
6	H	I	CH_2CO_2nBu	7^{b}	100
7	H	I	CO_2NH_2	NR	—
8	H	I	CN	NR	—
9	2-OH	I	CO_2Et	49	100
10	2-OMe	I	CO_2Et	40	93
11	4-OMe	I	CO_2Et	85	80
12	2-NO_2	I	CO_2Et	NR	—
13	4-NO_2	I	CO_2Et	NR	—
14	2-NH_2	I	CO_2Et	NR	—
15	4-NH_2	I	CO_2Et	NR	—
16	2-NHCOMe	I	CO_2Et	48	100
17	2-CO_2Me	I	CO_2Et	72	82
18	3-CO_2Me	I	CO_2Et	55	93
19	4-CO_2Me	I	CO_2Et	89	95
20	4-CH_3	I	CO_2Et	94	86
21	4-Cl	I	CO_2Et	100	94
22	4-Br	I	CO_2Et	100	94^{b}
23	3-I	I	CO_2Et	99	27 72^{c}

[a] Reaction conditions: substrate (1 mmol), olefin (3 mmol), triethylamine (3 mmol), 5 mL DMF, 0.5 mol% $PdCl_2/TiO_2$ were stirred for 5 h under 400 W (mercury vapor lamp) UV-visible irradiation at temperature 45 ± 3 °C. [b] Reaction time = 7 h. [c] Di-substituted *trans* compound. NR – no reaction.

optimized reaction conditions, the C–C coupling reactions were studied with various substituted aryl iodides and olefins (Scheme 2) and the results are summarized in Table 4. Reaction of iodobenzene with ethyl, methyl and *n*-butyl acrylate gave excellent conversion and selectivity (Table 4; entries 1–3). Styrene, acryl acid and *n*-butyl methacrylate showed poor reactivity towards iodobenzene (entries 4–6) and acryl amide, while acrylonitrile did not react with iodobenzene under these reaction conditions (entries 7 and 8). *ortho*-Iodophenol gave 49% conversion with 100% selectivity for the *trans* product (entry 9). *ortho*- and *para*-iodoanisole gave 40% and 85% conversion with 93% and 80% selectivity for the corresponding *trans* products, respectively (entries 10 and 11). Under photochemical reaction conditions it is very likely that UV-visible light helps towards the formation of intermediate species between $PdCl_2$ and reaction mass, which accelerates the rate of reaction. We tried to trap and characterize these species, but it was not possible due to instrumental limitations.

Amino and nitro substituted substrates were not active under optimized reaction conditions. These functional groups might be retarding conversion of aryl iodides *via* competing efficiently for optical absorption. Under these reaction conditions *ortho*- and *para*-iodoaniline, and *ortho*- and *para*-iodonitrobenzene do not show any reaction (entries 12–15). The *ortho*-iodo acetanilide shows 48% conversion with 100% selectivity for the *trans* product. The effect of substitution at various positions in an aromatic ring on the activity of *ortho*-, *meta*- and *para*-iodomethylbenzoate was studied and the activity was found to be in the order *para* > *ortho* > *meta* (entries 17–19). The *para*-iodo toluene gave 94% conversion with 86% selectivity for the *trans* product (entry 20). We found that bromo and chloro substituted aryl iodides gave selectively the iodo coupled product (entries 21 and 22). *para*-Bromo and *para*-chloro iodobenzene gave 100% conversion with 94% selectivity for the *trans* isomer. Di-substituted products were observed for the reaction between 1,3 di-iodobenzene and ethyl acrylate with 99% conversion showing 72% selectivity for the di-substituted product (entry 23).



R- H, OH, OMe, NHCOMe, CO_2Me, NH_2, NO_2, CH_3, Cl, Br, I.
R'- Ph, CO_2Me, CO_2Et, CO_2nBu, CO_2NH_2, CN.

Scheme 2 Photochemical Heck reaction between substituted aryl halides and olefins.

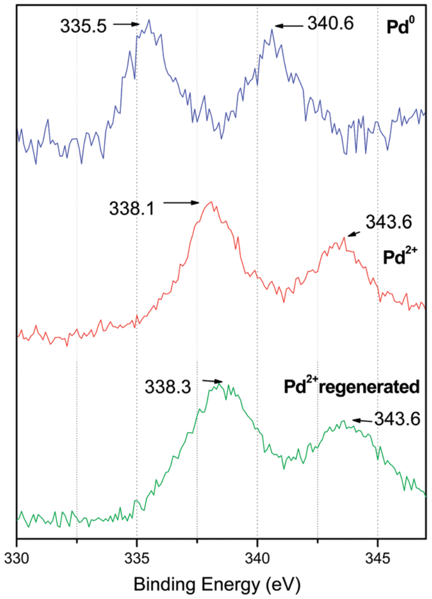


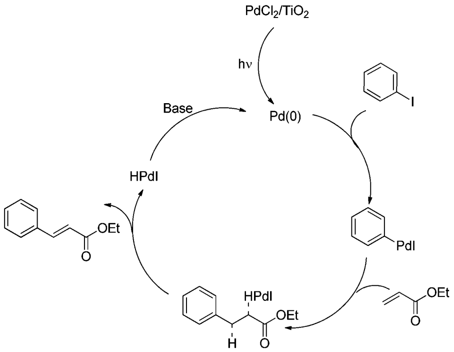
Fig. 2 XPS spectra of $PdCl_2/TiO_2$ before and after the reaction and after regeneration.

After completion of the reaction the spent catalyst was recovered as Pd^0 and does not show any conversion towards Heck reaction under photochemical reaction condition for

Table 5 Catalyst recycling study for Heck reaction[a]

Entry	Run	Conversion (%)	Selectivity (%)
1	First	96	90
2	Second	90	95
3	Third	87	93

[a] Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (3 mmol), triethyl amine (3 mmol), 5 mL solvent, 0.5 mol% $PdCl_2/TiO_2$ were stirred for 5 h under 400 W mercury vapour lamp at temperature 45 ± 3 °C.



Scheme 3 Proposed reaction mechanism for photochemical Heck reaction.

reuse (Fig. 2). To overcome this problem, Pd^0 was oxidized to Pd^{2+} by heating in presence of ammonium chloride at 400 °C for 30 min. It gave $PdCl_2/TiO_2$ catalyst and this regenerated catalyst was used for further study. The activity of the catalyst remains the same up to the third recycle (shown in Table 5).

The overall photochemical Heck reaction mechanism is believed to involve the migratory insertion pathway shown in Scheme 3. Palladium in $PdCl_2/TiO_2$ catalyst under UV-visible irradiation is reduced to Pd(0). Oxidative addition of Pd(0) to the aryl halide (C–X) bonds takes place. The olefin in the Heck reaction coordinates to the palladium, and then undergoes an insertion into the C–C π bond with concurrent migration of the aryl group to the adjacent carbon. The newly coupled aryl-olefin compound is then eliminated *via* a reductive β-hydride elimination (ethyl cinnamate) followed by a base deprotonation of the Pd(II) species and loss of halogen to form a salt.[23]

The XRD patterns and UV-visible absorption of the fresh and spent and regenerated catalyst are shown in the ESI† (Fig. S1 and S2). The structure of the support remains the same after regeneration of the catalyst.

The TEM technique was used to measure the size of the supported Pd particles, which were in the size range of 2–10 nm uniformly distributed over TiO_2 in fresh, spent and regenerated catalysts. The inter-planar *d*-spacing (inset of Fig. S3 in ESI†) is 0.22 nm support the (111) *hkl* plane of cubic palladium (Fig. S3 and S4 in ESI†).

The XPS spectra of the spent catalyst showed two peaks at 340.6 and 335.5 eV for zero valent palladium (metallic). XPS of fresh and regenerated catalyst showed two main peaks centered at 343.6 and 338.3 eV and related to Pd $3d^{3/2}$ and Pd $3d^{5/2}$. These signals were associated with $PdCl_2$ species, suggesting that the Pd salts kept chemical integrity within the TiO_2. The XPS spectra of fresh and regenerated catalysts show similar peaks for Pd $3d^{5/2}$ and Pd $3d^{3/2}$, which indicates that the Pd states of fresh and regenerated catalyst are same (Fig. 2) and Pd^{2+} (spent catalyst) is completely reduced to Pd^0 after a treatment of ammonium chloride. This catalyst is same as fresh catalyst. The activity of regenerated catalyst supports the integrity of the regenerated $PdCl_2/TiO_2$ catalyst also validates the regeneration of catalyst (Table 5).

Conclusion

In conclusion, we have developed a facile reusable simple $PdCl_2/TiO_2$ catalyzed under UV-visible light C–C coupling reaction for various substituted aryl iodides and olefins which affords good yield for the corresponding products at ambient reaction conditions under UV-visible light with light intensity (photon flux) of 2.1914×10^{12}. The present heterogeneous catalyst system is novel and provides many advantages over the homogenous catalyst, such as being recyclable. The oxidation of Pd^0 to Pd^{2+} can be done by heating the palladium with ammonium chloride at 400 °C, which gives smaller Pd nano particles (3–5 nm) than fresh catalyst (5–10 nm). The regenerated $PdCl_2/TiO_2$ shows good activity up to the third recycle. The TEM analysis confirms the formation of nano Pd particles on the TiO_2 surface.

Experimental section

(a) General procedure for the photochemical Heck reaction

To a 25 mL round bottom flask 1 mmol of aryl iodide, 3 mmol of olefin, 3 mmol of triethyl amine (TEA) in DMF (5 mL) were mixed, to this mixture 0.5 mol% $PdCl_2/TiO_2$ was added. The resulting reaction mixture was irradiated under 400 W mercury vapor lamp with continuous stirring in a closed box. The temperature of the reaction was controlled at 45 ± 3 °C with the help of fans. The mercury vapor lamp was kept vertically in a quartz tube provided with a water circulation arrangement in order to minimize the heating effect due to IR radiation. The progress of the reaction was monitored by gas chromatography (HP-5890) equipped with capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm). After completion, the reaction mixture was centrifuged at 4000 rpm for 20 min to separate the catalyst. The supernatant solution was diluted with water (10 mL) and the products were extracted using ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulphate and purified by using column chromatography over silica gel [hexane or hexane–ethyl acetate (9 : 1)]. The GC-MS spectra were recorded on Shimadzu QP-5050 equipped with TCD and capillary column (DB-5). FTIR spectra were recorded in Nujol mull and are expressed in cm^{-1}. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$.

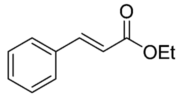
(b) Preparation of 1 wt% $PdCl_2/TiO_2$ catalyst

In 30 mL of distilled water, 10 mg of $PdCl_2$ and 1 g of TiO_2 were added and stirred for 2 h at room temperature and then refluxed for 3 h with constant stirring. The excess water was evaporated on a water bath and the solid powder was dried in an oven at 100 °C for 2 h. The dried $PdCl_2/TiO_2$ powder was mixed in a mortar and pestle for 30 min and used for further reactions.

Characterization data

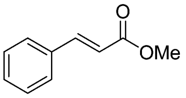
NMR and IR data of the final products (entries from Table 4).

(*E*)-Ethyl cinnamate [entry 1]



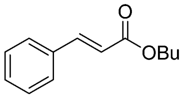
Colourless liquid, bp 271–272 °C, ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 1H, J = 15.9 Hz), 7.46 (m, 2H) 7.33 (t, 3H, J = 6.6 and 3.3 Hz), 6.38 (d, 1H, J = 15.9 Hz), 4.24 (q, 2H), 1.31 (t, 3H). ^{13}C NMR: δ 166.5, 144.2, 134.1, 129.9, 128.5, 127.7, 117.9, 60.2, 14.2. FTIR (KBr, cm^{-1}): 1040, 1164, 1260, 1310, 1648, 1734, 2983. MS (EI): *m*/*z* 176.17 (M$^+$).

(*E*)-Methyl cinnamate [entry 2]



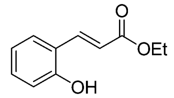
Colourless liquid, bp 263–264 °C, ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 1H, J = 15.9 Hz), 7.49 (m, 2H) 7.36 (t, 3H, J = 6.6 and 3.3 Hz), 6.42 (d, 1H, J = 15.9 Hz), 3.79 (s, 1H). ^{13}C NMR: δ 167.2, 144.7, 134.2, 130.1, 128.7, 127.9, 117.6, 51.7. FTIR (KBr, cm^{-1}): 1170, 1275, 1315, 1642, 1741, 2989. MS (EI): *m*/*z* 162.15 (M$^+$).

(*E*)-Butyl cinnamate [entry 3]



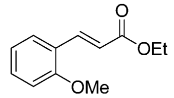
Colourless liquid, bp 290–295 °C, ^{1}H NMR ($CDCl_3$): δ 7.63 (d, 1H, J = 15.9 Hz), 7.46 (m, 2H) 7.32 (t, 3H, J = 6.6 and 3.3 Hz), 6.39 (d, 1H, J = 15.9 Hz), 4.17 (t, 2H), 1.68 (m, 2H), 1.45 (m, 2H), 0.94 (t, 3H). ^{13}C NMR: δ 166.8, 144.3, 134.2, 130.0, 128.6, 127.8, 118.0, 64.3, 30.7, 19.2, 13.7. FTIR (KBr, cm^{-1}): 1066, 1173, 1280, 1639, 1716, 2933. MS (EI): *m*/*z* 204.19 (M$^+$).

(*E*)-Ethyl 3-(2-hydroxyphenyl)acrylate [entry 9]



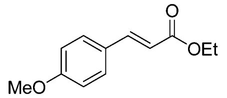
Colourless solid, mp 83–84 °C, ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 1H, J = 16.2 Hz), 7.42 (d, 1H, J = 6.8 Hz), 7.21 (m, 1H), 6.85 (m, 2H), 6.61 (d, 1H, J = 16.2 Hz), 4.26 (q, 3H), 1.32 (t, 3H). ^{13}C NMR: δ 168.7, 155.6, 140.9, 131.6, 129.0, 121.5, 120.3, 117.8, 116.3, 60.8, 14.3. FTIR (KBr, cm^{-1}): 1375, 1524, 1609, 1635, 1689, 3440. MS (EI): *m*/*z* 192.12 (M$^+$).

(*E*)-Ethyl 3-(2-methoxyphenyl)acrylate [entry 10]



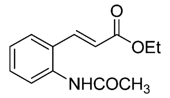
Colourless solid, mp 38–41 °C, ^{1}H NMR ($CDCl_3$): δ 7.96 (d, 1H, J = 16.2 Hz), 7.47 (d, 1H, J = 7.7 Hz), 7.30 (m, 1H), 6.87–6.96 (m, 2H), 6.52 (d, 1H, J = 16.2 Hz), 4.26 (q, 2H), 3.87 (s, 3H), 1.35 (t, 3H). ^{13}C NMR: δ 167.2, 158.0, 139.8, 131.2, 128.7, 123.2, 120.5, 118.6, 110.9, 60.2, 55.3, 14.4. FTIR (KBr, cm^{-1}): 1097, 1169, 1247, 1369, 1632, 1702, 2924. MS (EI): *m*/*z* 206.20 (M$^+$).

(*E*)-Ethyl 3-(4-methoxyphenyl)acrylate [entry 11]



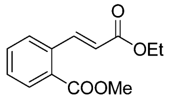
Colourless solid, mp 48–49 °C, ^{1}H NMR ($CDCl_3$): δ 7.58 (d, 1H, J = 15.9 Hz), 7.42 (d, 2H, J = 8.8 Hz), 6.88 (d, 2H, J = 8.8 Hz), 6.25 (d, 1H, J = 15.9 Hz), 4.23 (q, 2H), 3.80 (s, 3H), 1.32 (t, 3H). ^{13}C NMR: δ 167.0, 161.0, 144.0, 129.4, 126.9, 115.5, 114.1, 60.2, 55.2, 14.3. FTIR (KBr, cm^{-1}): 1033, 1170, 1250, 1365, 1632, 1714, 2942. MS (EI): *m*/*z* 206.19 (M$^+$).

(*E*)-Ethyl 3-(2-acetamidophenyl)acrylate [entry 16]



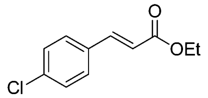
Colourless solid, mp 140–142 °C, ^{1}H NMR ($CDCl_3$): δ 7.74 (d, 1H, J = 15.6 Hz), 7.67 (d, 1H, J = 7.9 Hz), 7.46 (d, 1H, J = 7.7 Hz), 7.10–7.28 (m, 2H), 6.28 (d, 1H, J = 15.6 Hz), 4.16 (q, 2H), 2.16 (s, 3H), 1.26 (t, 3H). ^{13}C NMR: δ 168.6, 166.6, 139.0, 135.6, 130.6, 127.6, 126.9, 125.7, 125.0, 120.5, 60.7, 24.3, 14.3. FTIR (KBr, cm^{-1}): 948, 1069, 1236, 1275, 1360, 1456, 1536, 1579, 1663, 1705, 2963, 3269. MS (EI): *m*/*z* 233.27 (M$^+$).

(*E*)-Ethyl 3-(2-methoxyphenyl)acrylate [entry 17]



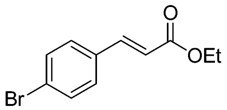
Colourless liquid, bp 154–156 °C, ^{1}H NMR ($CDCl_3$): δ 8.37 (d, 1H, J = 15.9 Hz), 7.91 (d, 1H, J = 7.7 Hz), 7.37–7.57 (m, 3H), 6.25 (d, 1H, J = 15.9 Hz), 4.23 (q, 2H), 3.91 (s, 3H), 1.35 (t, 3H). ^{13}C NMR: δ 166.9, 166.3, 143.4, 136.1, 132.1, 130.5, 129.5, 129.1, 127.7, 120.9, 60.5, 52.3, 14.3. FTIR (KBr, cm^{-1}): 765, 986, 1037, 1132, 1182, 1263, 1369, 1424, 1489, 1574, 1603, 1642, 1723, 2963. MS (EI): *m*/*z* 234.20 (M$^+$).

(*E*)-Ethyl 3-(4-chlorophenyl)acrylate [entry 21]



Colourless solid, mp 49–51 °C, ^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1H, J = 15.9 Hz), 7.38 (d, 2H, J = 8.2 Hz), 7.29 (d, 2H, J = 8.2 Hz), 6.34 (d, 1H, J = 15.9 Hz), 4.23 (q, 2H), 1.33 (t, 3H). ^{13}C NMR: δ 166.3, 142.6, 135.8, 132.6, 128.9, 128.8, 118.6, 60.5, 14.2. FTIR (KBr, cm^{-1}): 2926, 1710, 1637, 1491, 1313, 1180. MS (EI): *m*/*z* 210.34 (M$^+$).

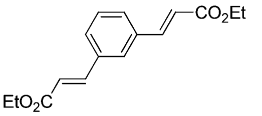
(*E*)-Ethyl 3-(4-bromophenyl)acrylate [entry 22]



Colourless liquid, bp 198–199 °C, ^{1}H NMR ($CDCl_3$): δ 7.65 (d, 1H, J = 15.9 Hz), 7.44 (d, 2H, J = 8.5 Hz), 7.33 (d, 2H, J = 8.5 Hz), 6.35 (d, 1H, J = 15.9 Hz), 4.12 (q, 2H), 1.32 (t, 3H).

^{13}C NMR: δ 166.2, 142.7, 133.0, 131.7, 130.8, 129.1, 118.6, 60.4, 14.2. FTIR (neat, cm^{-1}): 1182, 1320, 1463, 1635, 1711, 2983. MS (EI): *m*/*z* 254.04 (M$^+$).

Bis-ethyl (*E*)-3,3′-(1,3-phenylene)-2-propenoate [entry 23]



Colourless solid, mp 50–52 °C, ^{1}H NMR (CDCl$_3$): δ 7.62 (d, 3H, *J* = 15.6 Hz), 7.43 (d, 2H, *J* = 7.4 Hz), 7.32 (t, 1H, *J* = 7.1 and 7.9 Hz), 6.41 (d, 2H, 16.2 Hz), 4.24 (q, 4H), 1.32 (t, 6H). ^{13}C NMR: δ 165.7, 142.8, 134.4, 128.7, 127.0, 118.5, 59.9, 13.8. FTIR (KBr, cm^{-1}): 1197, 1496, 1643, 1719, 2746, 3056. MS (EI): *m*/*z* 274.25 (M$^+$).

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