

Product identification and distribution from the oscillatory *versus* non-oscillatory palladium(II) iodide-catalysed oxidative carbonylation of phenylacetylene

Christophe Grosjean^a, Katarina Novakovic^b, Stephen K. Scott^c,
Andrew Whiting^{a,*}, Mark J. Willis^b, Allen R. Wright^b

^a Department of Chemistry, Durham University, Science Laboratories,
South Road, Durham DH1 3LE, United Kingdom

^b School of Chemical Engineering and Advanced Materials, Merz Court, University of Newcastle upon Tyne,
Newcastle upon Tyne NE1 7RU, United Kingdom

^c University of Leeds, School of Chemistry, Leeds LS2 9JT, United Kingdom

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Abstract

The oxidative carbonylation of phenylacetylene was studied in order to determine the production distribution and reaction conditions which result in oscillatory *versus* non-oscillatory behaviour. Unambiguous identification of the products and their distribution was undertaken, after which, it was found that reaction conditions which result in oscillatory behaviour produce high conversions, and more selective product distribution.

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1. Introduction

The transition metal-catalysed carbonylation of alkenes and alkynes is an addition process which has been known since the 1930s [1]. It was recognised over 40 years ago [2] that in the presence of palladium catalysts, mild reaction conditions result in the rapid formation of a wide-variety of products. Carbonylation reactions of terminal alkynes are of particular interest as they lead to the formation of useful building blocks for synthetic chemistry, such as cyclic anhydrides, 2-alkynoates and α,β -unsaturated esters, *i.e.* both mono- and di-carbonylated products [3–5]. Oxidative carbonylation reactions of terminal alkynes are of particular interest since they potentially lead to the formation of several different products from the same starting materials, as those outlined in Fig. 1. The selectivity towards the various products is mainly dependent on the conditions used and more specifically the nature of the gas mixture and/or catalyst.

The first report of a palladium-catalysed oxidative carbonylation of an alkyne [2] was in the presence of an iodine-containing catalyst in 1962. Further early studies [6] on the palladium-catalysed carbonylation of alkynes highlighted the occurrence of concomitant mono- and di-carbonylation processes leading to acrylate, fumarate and/or maleate, and muconyl derivatives. Interestingly, the formation of an unsaturated lactone, α,β -diphenyl- γ -crotonolactone **1**, was reported as a product in the case of the oxidative carbonylation of diphenylacetylene [7] clearly showing the potential for both oxidative and reductive addition of carbon monoxide to the acetylene. In both those studies, palladium(II) chloride was used as a catalyst where it facilitated three competing reactions: mono-carbonylation; dicarbonylation; and dimerization, followed by dicarbonylation [6b]. The above findings were subsequently supported [8] by results which showed that following the carbonylation reaction of phenylacetylene in the presence of a palladium(II) chloride-thiourea catalyst, *trans*- and *cis*-dimethyl 2-phenylbut-2-ene-1,4-dioate **2** and **3**, respectively, methyl *trans*-3-phenylacrylate **4**, methyl 2-phenylacrylate **5**, and 3-phenyl-5*H*-furan-2-one **6** were isolated. It is again noteworthy

* Corresponding author. Tel.: +44 191 334 2081; fax: +44 191 384 4737.
E-mail address: andy.whiting@durham.ac.uk (A. Whiting).

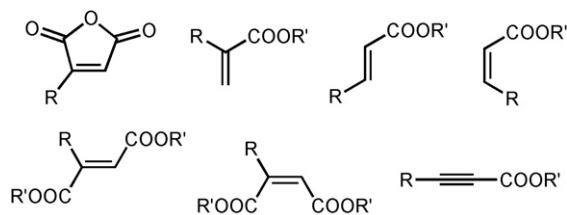
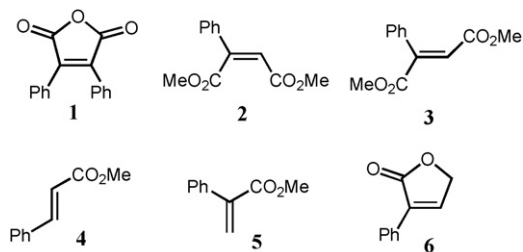
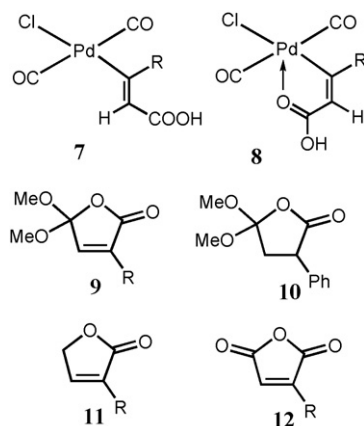


Fig. 1. Common products from the oxidative carbonylation of a general terminal alkyne RCCH in alcohol solvents.

that both oxidative and reductive carbonylation reactions occur simultaneously in the absence of oxygen.



In the early 1990s, the hydrocarboxylation of various alkynes was described [4], providing further mechanistic insights into palladium-catalysed carbonylation of alkynes. Based on Heck's model [5], it was argued that the carbonylation insertion step led to two possible intermediates, *i.e.* **7** and **8**, depending upon the stereochemistry of the process (*trans* or *cis*, respectively). Subsequent nucleophilic attack by water followed by reductive elimination (or CO migratory insertion, followed by nucleophilic attack by water) on these two intermediates account for the formation of fumaric and maleic acid and their derivatives. Nickel or palladium-catalysed carbonylations can result in the formation of anhydride derivatives [9] which proceed through oxidative addition of the palladium-carboxylic complex **8** to carbon monoxide [4].



It has also been reported [8] that the use of the palladium(II) iodide–potassium iodide [10] in methanol yields the corresponding methyl fumarate **3** and maleate **2**, along with the corresponding α,β -unsaturated diacids and the anhydride dimethylacetal **9**. Similar to previous mechanistic interpretations of the reaction [4], the products formed are thought to

be the result of the competing oxidative, reductive and additive carbonylations [11]. The formation of acetal **9** was attributed to the likely presence of palladium(II) alkoxide species, which are known to catalyse ring-chain tautomerism [12]. Optimisation of these reactions has therefore been possible to improve product selectivity, hence, the reductive carbonylation pathway to the formation of *5H*-furan-2-ones such as **11** is facilitated by water, with palladium(II) iodide–potassium iodide being the best catalytic system [13]. Conversely, addition of carbon dioxide (40 atmospheres) in the gas mixture led mainly to the formation of anhydride derivatives such as **12** [14]. In these systems, an excess of carbon dioxide (*i.e.* not generated as a by-product) was thought to be necessary in order to lower the concentration of the intermediate palladium-hydride species involved in the furanone formation. This route occurs in favour of the formation of palladium-CO insertion intermediates: Pd-CO₂H and Pd-O(CO)H. However, it is interesting to note that NMR-based ¹³C-incorporation studies showed that carbon dioxide acted as a promoter, rather than as a reagent in these cases [15]. A further alternative product in the carbonylation terminal alkynes is the formation of 2-alkynoates in the presence of a base [2]. Since the first reported case, other groups have reproduced these results [16,5], and commented that the alkynoate might result from *trans*-elimination of H-Pd-Cl from an intermediate monocarboalkoxylated-vinylpalladium species.

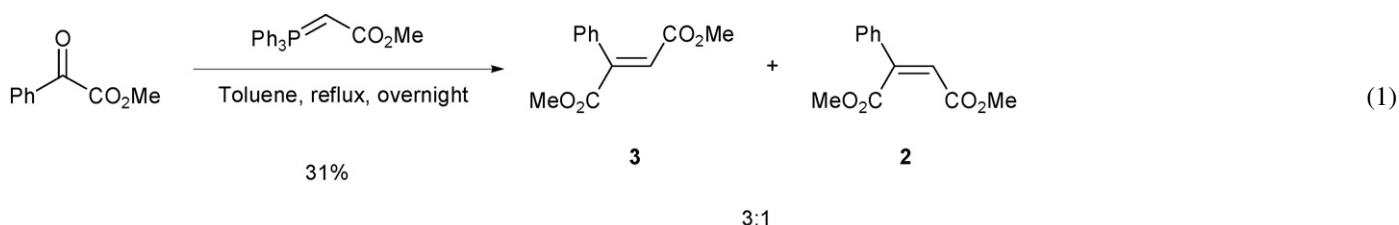
Thus, the carbonylation reaction of terminal alkynes can lead to a variety of products under different conditions (*i.e.* oxidative, reductive, presence/absence of carbon dioxide or water *etc.*). Several intermediates have been suggested to account for the formation of the products and although no definite overall mechanistic explanation has been formulated, there appears to be a general agreement over the broad processes operating. However, a series of studies by Temkin and co-workers [17] has cast uncertainty over any broad understanding of the mechanistic processes which might be operating in these types of reactions, by reporting both unexpected products and, more importantly, highly unexpected oscillatory reaction behaviour. In their attempts to delve more deeply into the mechanistic pathways operating in oxidative carbonylations of alkynes, a series of oscillating patterns were observed when using phenylacetylene with palladium(II) iodide–potassium iodide catalysis. This led to the formation of phenyl fumarate **3**, phenyl maleate **2** and the previously unreported dimethyl lactone derivative **10** [17a].

We were intrigued by both the unusual oscillatory behaviour observed in this reaction, since such processes are infrequently reported and little understood [18], and additionally, the appearance of a novel chiral product **10** attracted our attention with the prospect of developing new asymmetric catalytic methods. Recently we have published details of an experimental methodology to achieve reproducible oscillations [19] and most importantly, the work demonstrated oscillatory activity in both pH and reaction heat evolution rate, Q_r. In this paper we report details of structures of products and their distribution in oxidative carbonylation reactions of phenylacetylene and investigations into the experimental conditions required to achieve oscillations.

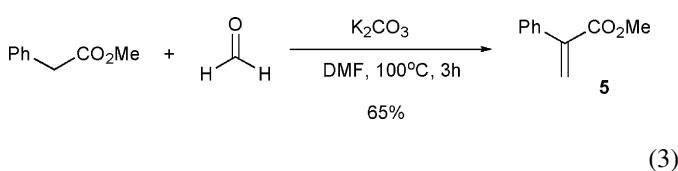
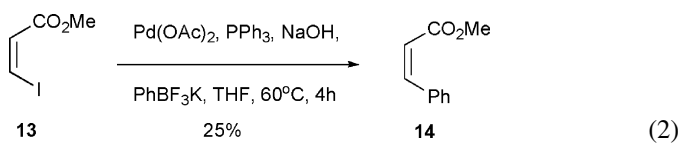
2. Results and discussion

2.1. Synthesis of standards

A series of standard compounds (**2–6**) were either prepared according to literature methods or sourced commercially (*vide infra*) for GC analytical purposes. Esters **2** and **3** were prepared as a 3:1 mixture of diastereoisomers by ¹H NMR as outlined in Eq. (1), from which their respective GC retention times were readily determined.



Methyl Z-3-phenylacrylate **14** was prepared using a Suzuki–Miyaura coupling according to Eq. (2), and methyl phenylacrylate **5** was prepared using a Knoevenagel condensation, as outlined in Eq. (3).



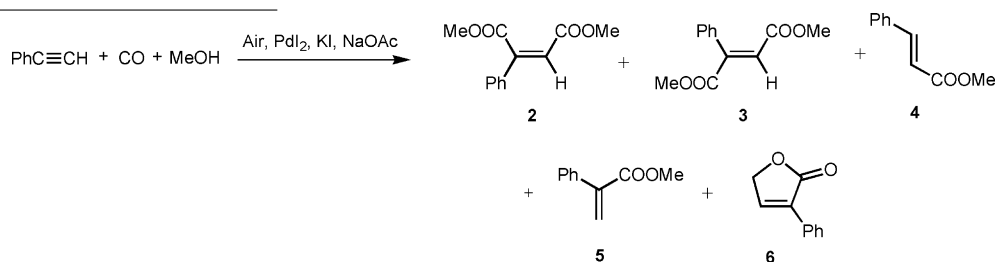
2.2. Oxidative carbonylation of phenylacetylene

The report [20] of parallel oxidation of CO to CO₂ and the associated oscillations of pH, redox potential and rate of gaseous CO–CO₂ mixture consumption has been observed for up to 3.5 h during palladium-mediated oxidative carbonylations. It was suggested that the water formed during the reaction catalyses

[20] and that replacement of PdI₂ by K₂Pd₂I₄ produces sustained oscillations, together with highlighting the importance of hydrogen peroxide-iodine as oxidising agents for the conversion of an intermediate palladium hydride complex back to the Pd(II) species [17c]. The oscillating pattern was suggested as being associated with the autocatalytic formation of the Pd(I) species and ended by the oxidation of palladium hydride and Pd(I). Four equally probable mechanisms have been proposed; each of them including four essential steps, *i.e.* (1) formation of

palladium hydride; (2) formation of the active catalyst species [Pd(I) complex]; (3) synthesis of the alkyne carbonylation products; and (4) oxidation of the palladium hydride.

Our attempts to reproduce similar oscillations in the PdI₂-KI catalysed carbonylation of phenylacetylene proved unsuccessful until reaction conditions were carefully controlled. In particular, this involved control of gas flow rates, which was accomplished using a calorimeter-based system [19]. Our initial studies focussed on the oxidative carbonylation of phenylacetylene performed using small-scale reactions of ca. 10 mL. The gas mixture used on these small-scale reactions consisted of carbon monoxide and air (1:1 by volume), which was introduced directly into the system at atmospheric pressure. The products resulting from this reaction (Eq. (4)) were isolated and purified by flash chromatography. ¹H NMR spectroscopy was used to compare the standards prepared above with the isolated products to allow accurate, unambiguous identification of all the reaction products. From these types of initial, small-scale reactions, three major fractions were obtained (alkene stereoisomers were inseparable by silica gel chromatography), as summarised by two such experiments (Table 1) carried out according to Eq. (4).



(4)

the oxidation of CO to CO₂ and that the catalytic species is a Pd(I)-based species. It was reported that the active Pd(I) species had the form Pd₂X₄(CO)₂²⁻ in alkyne carbonylations

Under these initial reaction conditions, the overall conversion and associated product yields were unremarkable (Table 1), however, there was consistency of product ratios, as determined

Table 1
Carbonylation of phenylacetylene in the presence of catalytic PdI₂; **A** and **B**: [phenylacetylene]=0.1 M in 10 mL

Products	Conditions A		Conditions B	
	Yield (%) ^a	Ratio ^b	Yield (%) ^a	Ratio ^b
4:5	27	1:1	31	1:1
2:3^c	17	9:1 ^c	11	1:0
6	4	/	3	/

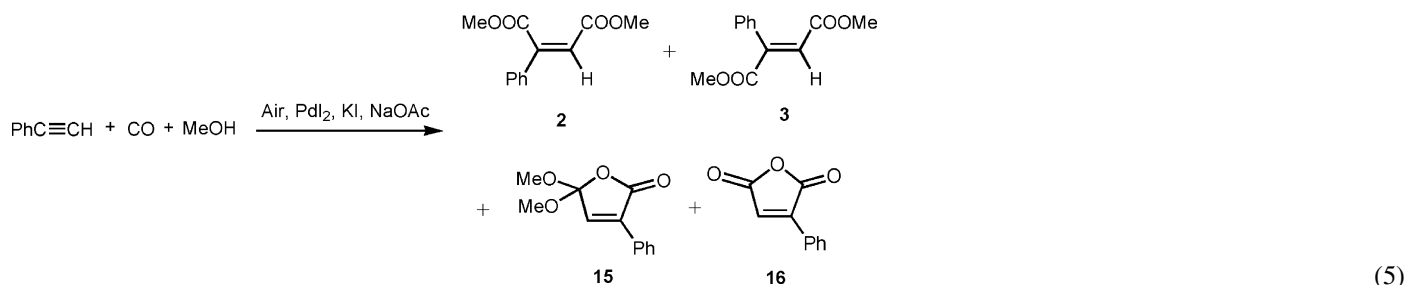
^a All yields as isolated yields.

^b All ratios calculated using ¹H NMR spectroscopy.

^c Assignment of the stereochemistry of the stereoisomers determined using ¹³C NMR spectroscopy.

by ¹H NMR. This shows that the reactions were reproducible under these particular conditions. The main products of the reactions were the monocarbonylated compounds **4** and **5** resulting from the additive pathway, and a smaller quantity of the isomeric dicarbonylated compounds **2** and **3**. The other major fraction was the cyclic product, 3-phenyl-5*H*-furan-2-one **6**, which has been reported [13] to result from a competing reductive pathway. The fact that products from both an oxidative and reductive pathway were recovered demonstrates a lack of control of the CO–air gas ratio which not only accounts for poor yields, but also accounts for the observed products. In addition, following the pH of the reaction over time (Fig. 2) produced an immediate sharp drop to a value of 0.2 with only subsequent minor fluctuations. Importantly, no clear oscillatory behaviour was observed in these small-scale reactions.

Therefore, the transfer of these reactions to a system which could exert control over the reaction conditions, and especially the CO–air ratio was essential. There was also the additional capability of being able to monitor both pH and heat output with respect to time *in situ*. Hence, larger scale, calorimeter [19]-based reactions were carried out on approximately 0.45 L. The results are summarised in Eq. (5), Table 2 and Fig. 3.



The initial results from several runs of this reaction (Table 2, conditions B), confirmed both the rate and extent of the pH drop during the early course of the reaction. In addition, the products that were identified by GC-MS (Table 2) broadly matched those observed on the small-scale studies. Hence comparing the small-scale reaction (Table 2, conditions A) with the larger scale reaction (Table 2, conditions B), shows that under conditions B, the main reaction product becomes dimethyl *cis*-2-phenylbut-2-enedioate **2**. The amount of the corresponding *trans*-isomer **3** formed was found to be marginal (<2%). The acrylate deriva-

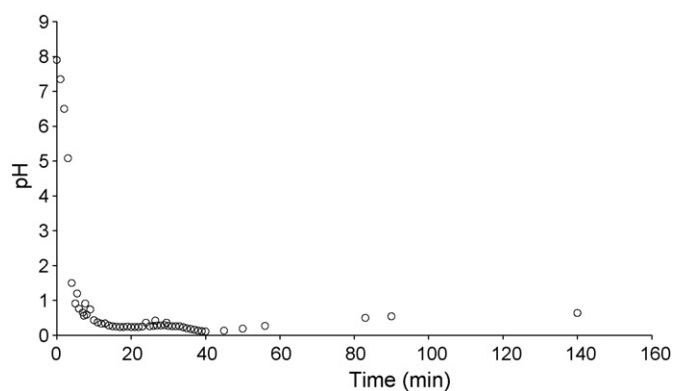


Fig. 2. pH profile for the carbonylation of phenylacetylene (0.1 M in 10 mL) in the presence of catalytic PdI₂ (10 mol%).

Table 2
Carbonylation of phenylacetylene in the presence of catalytic PdI₂; **A**: [phenylacetylene]=0.1 M in 10 mL; **B**: [phenylacetylene]=0.1 M in 450 mL (non-oscillatory); **C**: [phenylacetylene]=0.125 M in 450 mL (oscillatory)

Products	Yields		
	Conditions A ^a (%)	Conditions B ^b (%)	Conditions C ^b (%)
5	15	9	0.5
4	15	4.5	0
2	14	17	67
3	0	1	5
6	4	0	0
15	0	0	14 ^c
16	0	0.5	2

^a All yields as isolated yields.

^b Yields calculated from GC/MS data.

^c Estimated from conversion of phenylacetylene = 88.5% by GC-MS.

tives **4** and **5** was also observed under conditions B (Table 2), although in lower proportions than under the smaller scale reaction conditions A. It is notable that there was no evidence

for the formation of the chiral, reduction carbonylation product **10**. In addition, it appears that control over the gas supply (conditions B, Table 2) in the system prevents the formation of the lactone **6** by effectively shutting off the reductive carbonylation pathway, presumably due to the supply of sufficient air (oxygen) to prevent the competing reductive pathway.

Oscillatory behaviour, as shown by Fig. 3, was achieved only after considerable experimentation. This was achieved by increasing the substrate concentration by ca. 25%, with the ratio of the catalyst and other additives, relative to phenylacetylene,

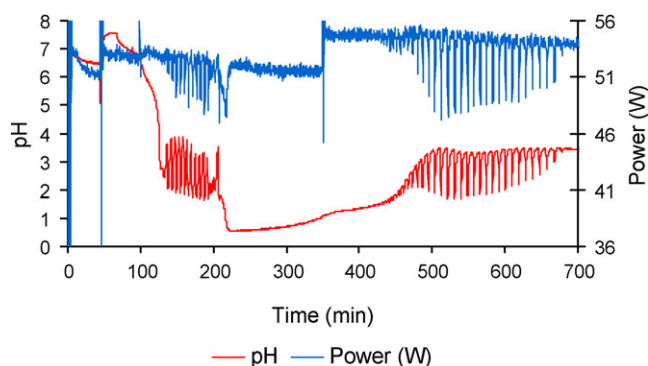


Fig. 3. pH and heater power (W) recorded for the carbonylation of phenylacetylene (0.125 M) in the HEL calorimeter.

remaining constant. It was discovered that the granularity of palladium(II) iodide catalyst, which differs from batch to batch (even from the same supplier) has a profound effect. Firstly on the initial pH fall, and secondly, on the subsequent oscillatory behaviour. Careful regulation of the amount of PdI₂ was required, ensuring that the initial pH did not fall lower than 1. Under these conditions, prolonged and regular oscillations were readily achieved. A typical reaction product profile carried out in this way which showed oscillatory behaviour is shown in Table 2, conditions C. Interesting results were obtained when reaction samples were taken before, in between and after the oscillatory activity, which showed that one major, one minor and three very minor products were consistently forming over the reaction time period. The products obtained, also as summarised by Eq. (5), were entirely as expected for the oxidative carbonylation pathway alone. While these results (conditions C) broadly match those reported for the non-oscillatory reactions (conditions A and B, Table 2), the overall conversion was substantially improved and in addition to obtaining the diesters **2** (major, 67%) and **3** (minor), the anhydride acetal **15** was also observed (14%) [10]. It was also found that reasonably rapid analysis of the crude reaction mixture was required to ensure obtaining accurate product ratios. Acetal **15** gradually decomposes, presumably by reaction with methanol to form *cis*-diester **2**, whereas reaction with small amounts of water is likely to result in the formation of anhydride **16**. From these observations, it is likely, therefore, that the formation of acetal **15** is the result of the reaction mechanism itself, rather than reaction of the anhydride **16** with methanol. Further work is required to confirm this.

3. Summary and conclusions

The particular oxidative carbonylation studied in this work involving conversion of phenylacetylene to the various reaction products is highly dependent upon the reaction conditions. Both efficient conversion of phenylacetylene and selective oxidative carbonylation product formation are highly dependent upon gas flow control, concentration, stirrer speed and palladium(II)

iodide grain size and loading, as is the production of reproducible reaction oscillations. When oscillations do occur, this appears to be related to high conversion and changes in products and product distribution with particular improvements in selectivity for the formation of *cis*-diester **2**. Additionally anhydride acetal **15** is observed. Although these results cannot be directly linked to the oscillatory behaviour of the reaction itself at this point, further work is ongoing to examine the detailed relationship between oscillatory behaviour and product formation, and on the mechanistic origin of the oscillations. The results of these studies and a detailed insight into the origin of this type oscillatory behaviour will be published shortly.

4. Experimental

4.1. General experimental

All ¹H NMR were recorded on Varian Unity-300, Varian Mercury-400, Bruker Avance-400 or Varian Inova-500 spectrometers. ¹³C NMR spectra were recorded on Varian Mercury-400, Bruker Avance-400 and Varian Inova-500 instruments at frequencies of 100 or 126 MHz. Chemical shifts are expressed as parts per million downfield from the internal standard TMS for ¹H and ¹³C. EI mass spectrometry was performed on a Micromass Autospec, Finnigan MAT 900XLT or Finnigan MAT 95XP with electrospray methods, both +ve and -ve, conducted on a VG platform. GC-MS was performed on either a Thermoquest Trace or VG Trio. Column chromatography was performed on Davisil silica gel, 60 mesh. TLC was performed on Polygram SIL G/UV₂₅₄ plastic backed silica gel plates with visualization achieved using a UV lamp, or by staining with KMnO₄ or vanillin. All glassware was oven dried (130 °C) before use and cooled under a positive pressure of argon. All reactions were performed at room temperature unless otherwise stated. All evaporations were carried out on a Büchi rotary evaporator, followed by drying *in vacuo*. Crude reactions products were dried over anhydrous magnesium sulfate. GC/MS analysis was performed on a GC-MS Saturn 2000 using a Varian VF5 column. The method was as follows: injector temp: 150 °C; oven initial temp: 100 °C followed by 5 successive ramps (1 min at 20 °C/min then hold for 5 min) up to 195 °C (final temperature) held for 8 min. Methyl *trans*-3-phenylacrylate **4** and phenylmaleic anhydride **16** as purchased commercially from Aldrich, dimethyl *cis*-2-phenylbut-2-enedioate **2** was prepared according to a literature method [21], as were 3-phenyl-5*H*-furan-2-one **6** [22], and dimethyl 2-benzylidenemaleate [22], and methyl *cis*-3-iodoacrylate [23]. All other materials were purchased from either Aldrich or Lancaster and used without further purification, unless stated otherwise.

4.1.1. Methyl 2-phenylacrylate (5)

To a stirred solution of methyl phenylacetate (3.3 mmol, 500 mg) and potassium carbonate (3.3 mmol, 456 mg) in dimethylformamide (50 mL) was added *para*-formaldehyde (4.95 mmol, 149 mg). The solution was heated at 100 °C for 3 h. Water (100 mL) was added and the mixture extracted using diethyl ether (5 × 25 mL). The combined organic extracts were

Table 3
¹H NMR data used to identify the reaction product distribution

Compound	Retention times (min) ^a	¹ H NMR (400 MHz, CDCl ₃)
Naphthalene	6.97	n/a
Phenylacetylene	2.62	δ 3.03 (s, 1H, HCC), 7.30–7.33 (m, 3H, Ph), 7.44–7.47 (m, 2H, Ph) [28]
2	21.37	δ 3.80 (s, 3H, HCCOOCH ₃), 3.96 (s, 3H, PhCCOOCH ₃), 6.33 (s, 1H, CH), 7.42–7.51 (m, 5H, Ph) [21]
3	17.81	δ 3.60 (s, 3H, HCCOOCH ₃), 3.80 (s, 3H, PhCCOOCH ₃), 7.02 (s, 1H, CH), 7.42–7.51 (m, 5H, Ph) [26]
4	12.29	δ 3.82 (s, 3H, CH ₃), 6.46 (d, 1H, J 16 Hz, C(Ph)H), 7.36–7.42 (m, 5H, Ph), 7.72 (d, 1H, J 16 Hz, PhC=CH) [29]
5	9.09	δ 3.83 (s, 3H, CH ₃), 5.90 (d, 1H, J 1.2 Hz, CHH), 6.37 (d, 1H, J 1.2 Hz, CHH), 7.35–7.43 (m, 5H, Ph) [24]
6	19.80	δ 4.95 (d, 2H, J 2 Hz, CH ₂), 7.41–7.44 (m, 3H, Ph) 7.66 (t, 1H, J 2 Hz, CH), 7.85–7.88 (m, 2H, Ph) [22]
16	17.15	δ 7.00 (s, 1H, CH), 7.47–7.60 (m, 5H, Ph) [15]
15	21.54	δ 3.48 (s, 6H, CH ₃), 7.10 (s, 1H, CH), 7.32–7.45 (m, 2H, Ph), 7.84–7.86 (m, 3H, Ph) [10]
14	10.01	δ 3.72 (s, 3H, CH ₃), 5.96 (d, 1H, J 12.4 Hz, C=C(Ph)H), 6.96 (d, 1H, J 12.4 Hz, PhC=CH), 7.34–7.37 (m, 3H, Ph), 7.58–7.60 (m, 2H, Ph) [27]
Dimethyl 2-benzylidenemaleate	21.17	δ 3.85 (s, 6H, 2 × CH ₃), 7.36–7.43 (m, 3H, Ph), 7.77 (s, 1H, CH), 7.85–7.88 (m, 2H, Ph) [22]

^a Run under the conditions reported in Section 4.1.

washed with water (2 × 20 mL), brine (2 × 20 mL), dried and evaporated to afford essentially pure methyl 2-phenylacrylate **5** as a pale yellow oil (0.345 g, 65%) whose spectroscopic and analytical data were identical to those reported in the literature [24].

4.1.2. Dimethyl *trans*-2-phenylbut-2-enedioate (**3**)

To a stirred solution of [(methoxycarbonyl)methylene]triphenylphosphorane [25] (0.75 mmol, 250 mg) in toluene (50 mL) was added methyl benzoylformate (0.75 mmol, 0.79 mL). The mixture was heated at reflux overnight. After cooling and evaporation, the crude product was extracted using petroleum ether:ether (1:1) (25 mL), the precipitate was removed by filtration and the filtrate evaporated to give a residue which was purified by silica gel chromatography (hexane:ethyl acetate as eluent, 1:1) to afford a mixture of dimethyl *trans*-2-phenylbut-2-enedioate **3** [26] and dimethyl *cis*-2-phenylbut-2-enedioate **2** [21] as a pale yellow oil (165 mg, 31%, *trans*:*cis* 74:26); both compounds had spectroscopic and analytical properties identical to those reported in the literature [26,21].

4.1.3. Methyl *cis*-3-phenylacrylate (**14**)

To a dried Schlenk tube under argon was added Pd(OAc)₂ (9 mg, 0.04 mmol), PPh₃ (22 mg, 0.084 mmol) and THF (1 mL). The mixture was stirred for 2 min. Before the addition of NaOH (170 mg, 4.25 mmol), THF (8 mL), water (1 mL), potassium phenyltrifluoroborate (200 mg, 1.09 mmol) and methyl *cis*-3-iodoacrylate **13** (0.100 mL, 0.90 mmol) were added. The mixture was degassed using the freeze-pump-thaw method (3 ×) and heated at 60 °C for 4 h. After cooling, dilution with EtOAc (60 mL) and water (5 mL), filtration through Celite, washing with 5% HCl (10 mL) and brine (10 mL), drying and evaporation, a crude brown solid was obtained. Purification by silica gel chromatography (ethyl acetate: petroleum ether as eluent, 2:98) gave methyl *cis*-3-phenylacrylate **14** (37 mg, 25%) as a clear oil whose analytical and spectroscopic and analyti-

cal properties were identical to those reported in the literature [27].

4.1.4. General carbonylation procedure (small scale)

In a three-necked round bottom flask, PdI₂ (36.0 mg, 0.1 mmol), KI (0.664 g, 4 mmol) and sodium acetate (1.97 mg, 0.024 mmol) were dissolved in 8 mL of methanol with vigorous stirring for 15 min. Carbon monoxide and air were then supplied to the system using side necks and the reaction flask purged. Phenylacetylene (0.102 g, 1 mmol) dissolved in 2 mL of methanol was added to the solution. The reaction was stirred at 40 °C for 3 h under atmospheric pressure of carbon monoxide and air. At the end of the 3 h the solution was filtered over silica. The solvent was removed under reduced pressure and the products separated by flash chromatography using a concentration gradient of hexane:ethyl acetate from 100:0 to 50:50 yielding a mixture of methyl *trans*-3-phenylacrylate **4** and methyl 2-phenylacrylate **5**, dimethyl *cis*-2-phenylbut-2-enedioate **2**, dimethyl *trans*-2-phenylbut-2-enedioate **3** and 3-phenyl-5*H*-furan-2-one **6**. The products were compared (GC and ¹H NMR, see Table 3) to those synthesised using the methods reported above or as purchased.

4.1.5. General carbonylation procedure (large scale)

Methanol (400 mL) and PdI₂ (2.03 g, 5.60 mmol) (note: it is essential to control the granularity of the PdI₂, see Ref. [30] for a detailed study) were stirred at 550 rpm and the temperature maintained at 40 °C. After 45 min, KI (37.39 g, 225 mmol) and NaOAc (114 mg, 1.40 mmol) in 50 mL of methanol were added. After a further 20 min, purging of the system commenced using a mixture of CO and air by simultaneous introduction through dip tubes and controlled flow rates of 50 mL/min. After 30 mins phenylacetylene (6.2 mL, 56.5 mmol) was added. A sample of the solution was filtered over silica, diluted and analysed by GC-MS as outlined above. Standard: naphthalene (C = 0.001 M).

Acknowledgments

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