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# Flow-Based, Cerium Oxide Enhanced, Low-Level Palladium Sonogashira and Heck Coupling Reactions by Perovskite Catalysts

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**Abstract**: A flow chemistry procedure for Sonogashira and Heck cross-coupling reactions using a low-level palladium perovskite catalyst (LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub>) deposited on cerium oxide is reported. The catalyst was generated in situ at high temperature using a flow platform. The system could be applied to a wide range of functionalised substrates, allowing clean and fast delivery of the products within a few minutes (10–30 min), after scavenging with thiourea polymer (QP-

TU) and sulfonic acid resin (QP-SA). The use of an in-line evaporator/solvent switching device allowed us to recover the solvent and transport the material into the following stage. The catalyst could be continuously used for at least 24 h, without any noticeable decrease in the catalytic efficiency. In one example the system was scaled to deliver 10 mmol of product.

Keywords: cerium oxide • cross-coupling • flow chemistry • heterogeneous catalysis • perovskite phases

#### Introduction

Cleaner and environmentally benign protocols are in great demand for all chemical processes.<sup>[1]</sup> In particular, metal-catalysed cross-coupling reactions are important in many synthesis programs.<sup>[2]</sup>

In our own work,<sup>[3]</sup> we have been focusing efforts on developing improved tools for organic synthesis.<sup>[4]</sup> Recently, we have demonstrated that the use of monolithic reactors, solid-phase reagents and inorganic metal oxides can provide efficient heterogeneous systems for flow-based applications.<sup>[5]</sup> These combinations facilitate recycling and promote minimum downstream processing.

Perovskite-type catalysts are mixed-metal oxides that present a typical formulation structure of ABO<sub>3</sub>, where the elements A and B are represented mainly by rare earth, alkaline earth, alkali and other large atomic metal cations.<sup>[6]</sup> Doping of these systems can be used to modify the oxygen mobility within the lattice of the perovskite structure, altering the valance state of the heterogeneous matrix and creating oxygen vacancies, which represent important catalytic sites.<sup>[7]</sup> This is usually achieved by incorporating noble metals into the perovskite lattice to exchange the B sites and create mixed-valance states.<sup>[7,8]</sup>

In the past, we reported studies on several ABO<sub>3</sub> perovskites and found that perovskites with B sites doped by palladium were particularly effective in catalytic crosscoupling processes.<sup>[7–11]</sup>

The most attractive features of these catalysts are the low levels of palladium and their potential to be reused



Figure 1. General matrix structure of ABO<sub>3</sub> perovskites.

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without loss of catalytic turnover.<sup>[9]</sup> We have also demonstrated that partial desorption of palladium catalyst from the "heterogeneous" lattice can occur. This results in a conventional homogeneous-phase catalytic cycle, followed by redeposition of palladium on the modified solid phase after the reaction is complete.<sup>[10]</sup> However, partial desorption of palladium catalyst from the "heterogeneous" matrix can be considered a potential issue, since it implies leaching of palladium.<sup>[9]</sup> This, therefore, reduces the advantage of utilising a heterogeneous system, namely, that the catalyst should be easily recovered by filtration.

Ceria or cerium oxide (CeO<sub>2</sub>) has found widespread use in several industrial applications due to its unique properties, ranging from optical to mechanical, thermal and chemical stability.<sup>[12]</sup> Depending on temperature and oxygen pressure, different final stoichiometries can arise, for example intermediate oxides whose composition is in the range between Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. The property of these oxides, acting as oxygen reservoirs, is controlled by the valence change of its cations from 4<sup>+</sup> to 3<sup>+</sup>. It is well known, however, that reduction of the cerium ions is a reversible process, leading to easy oxidation of Ce<sup>3+</sup> species.<sup>[13]</sup>

Recently, the role of ceria in the water gas shift (WGS) reaction, in which hydrogen and carbon dioxide are obtained from water and carbon monoxide, has been explored.<sup>[14]</sup> Indeed, CeO<sub>2</sub> nanoparticles on gold (normally not active in this reaction) have been observed to facilitate the metal's oxidation of CO.<sup>[14,15]</sup> Fornasiero et al. demonstrated that the CeO<sub>2</sub>-coated palladium unit was endowed with an enhanced rate of methane oxidation at lower temperatures (below 700 K) than those previously reported and displayed outstanding thermal stability.<sup>[16]</sup> CeO<sub>2</sub>-supported metal nanoparticles (NPs) present higher turnover and better stability, which can be attributed to the CeO<sub>2</sub> support. Attractive features of these systems are the fine dispersion of the supported particles and the prevention of agglomeration of the catalytic species due to the interaction between the CeO<sub>2</sub> surface and metal atoms.<sup>[17]</sup>

Given these previously mentioned features of palladium-containing perovskite-type oxides and of CeO<sub>2</sub>, we have studied their synergetic properties for the Sonogashira<sup>[18]</sup> and Heck<sup>[19]</sup> cross-coupling reactions. In particular, we aimed to generate an in situ deposition of the catalytic metal onto the surface of CeO<sub>2</sub> and use their positive interactions in the heterogeneous flow cross-coupling of various substrates. In our case, we have used flow chemistry methods not only to contain the heterogeneous catalyst, but also for the deposition of the catalyst itself on the surface of the support within our flow device. The method does not require any multistep procedures or particular handling of materials and simplifies greatly the mixing procedure, hence, representing an advantage over other procedures.

#### **Results and Discussion**

We began by investigating the use of different perovskite/ metal oxide binary systems under microwave conditions to establish the best catalyst for the Sonogashira crosscoupling reaction. Notably, only palladium-containing perovskites were active and the addition of  $CeO_2$ (10 mol%) increased the catalytic turnover of the system (Table 1).

**Table 1.** Screening of different catalysts for the Sonogashira crosscoupling reaction in the presence or absence of  $CeO_2$ .

Entry	Catalyst <sup>[a]</sup>	Conversion <sup>[b]</sup>		
		No additive [%]	CeO <sub>2</sub> <sup>[c]</sup> [%]	
1	La <sub>1.02</sub> Fe <sub>0.58</sub> Cu <sub>0.37</sub> Pd <sub>0.05</sub> O <sub>3</sub>	4	10	
2	La <sub>0.96</sub> Fe <sub>0.96</sub> Au <sub>0.04</sub> Pd <sub>0.04</sub> O <sub>3</sub>	2	5	
3	La₂CuO₄	0	0	
4	LaSrFeNbO₅	0	0	
5	LaFe <sub>0.95</sub> Pd <sub>0.05</sub> O <sub>3</sub>	5	13	
6	La <sub>2</sub> CoNbO <sub>6</sub>	0	0	
7	La <sub>3</sub> CoRuO <sub>9</sub>	0	0	
8	LaFe <sub>0.54</sub> Co <sub>0.36</sub> Pd <sub>0.1</sub> O <sub>3</sub>	5	15	
9	YBaCu <sub>3</sub> O <sub>7</sub>	0	0	
10	LaFe <sub>0.56</sub> Co <sub>0.38</sub> Pd <sub>0.05</sub> O <sub>3</sub>	2	10	
11	Pd/C	5	13	
12	Pd(AcO) <sub>2</sub>	0	0	

[a] 5 mol% of catalyst was used in the reaction between 2,5-dimethylphenylacetylene (1.1 mmol), 4-iodoacetophenone (1 mmol) and tetramethylguanidine (TMG, 2 mmol) for 20 min. [b] Conversion of compounds was based on the <sup>1</sup>H NMR spectrum of the crude material. [c] 50 mol%.

Running the reaction for 140 min (Figure 2) with La- $Fe_{0.95}Pd_{0.05}O_3$  (5 mol%) in the presence of  $CeO_2$  (10 mol%) and TMG (2 equiv) gave a 70% conversion. Completion was reached after 200 min without any by-products being detected.

In the absence of CeO<sub>2</sub>, the reaction took approximately 6 h to reach completion. Additionally, the use of aluminium oxide, zirconium oxide or silica gel did not give comparable reaction rates compared to CeO<sub>2</sub> as an additive. To assess the catalytic activity of CeO<sub>2</sub>, we measured the conversion in the presence of different amounts of the metal oxide at a given time and in the presence of a standard reaction mixture. We were pleased to find that increasing the amount of CeO<sub>2</sub> enhanced the catalytic turnover of the system, resulting in higher conversions (Figure 3).

Additionally, we investigated the importance of using wet DMF (5%  $H_2O$  in DMF) for the reaction and we found that in the absence of water the reaction was defined by a slower turnover and reduced yield. Ethyl acetate or toluene gave a slower coupling turnover, whereas there was no cooperation between CeO<sub>2</sub> and perovskites when ethanol was employed as a solvent. Interestingly, we observed the formation of ethyl acetate when using

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20 min 40 min 60 min 120 min 140 min 200 min





Figure 3. Catalytic activity of different amounts of  $CeO_2$  in the presence of LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub> (5 mol%; microwave 130 °C, 20 min).

ethanol, which was thought to arise from partial oxidation of ethanol with the  $CeO_2$  surface in the presence of perovskite catalysts.<sup>[20]</sup>

The heterogeneous catalyst for the flow experiments was prepared simply by mixing  $CeO_2$  and  $LaFe_{0.95}Pd_{0.05}O_3$  within a shaker, before packing it into an Omnifit<sup>®</sup> glass column.<sup>[21]</sup> The catalyst was then activated by passing DMF through the column at 130 °C (Figure 4).

The X-ray diffraction analysis pattern of the catalyst (Figure 5) confirmed that there was a difference between  $CeO_2$ ,  $LaFe_{0.95}Pd_{0.05}O_3$  and the catalyst formed "in situ" through deposition on the ceria surface. We speculate this to be the result of interactions of ceria with the lattice of the perovskite material, inducing a transformation within the oxygen mobility, hence, a change in the structure of the catalyst itself. In particular, we believe that the poly-



Figure 4. Generation of the catalyst through deposition onto the surface of ceria.



Figure 5. XRD spectra of perovskite  $LaFe_{0.95}Pd_{0.05}O_3$  (red spectrum) and  $LaFe_{0.95}Pd_{0.05}O_3$  on  $CeO_2$  (blue spectrum).

valent Pd species are transformed into the catalytically active species  $Pd^0$  and these are deposited as clusters or aggregates onto the surface of cerium oxide. Although we believe the catalytic activity of the Pd species produced by deposition on the surface of ceria is key to the efficiency of the system, we cannot exclude any proper role of the ceria surface in the catalytic cycle and these speculations are still under scrutiny in our research group.

Having developed this interesting heterogeneous catalyst, we established the flow parameters for the Sonogashira elaboration of a range of commercially available substituted aryl iodides and phenylacetylenes. Under the optimised conditions, a solution of acetylene (1 mmol), aryl iodide (1 mmol) and TMG (2 mmol) in wet DMF (5% H<sub>2</sub>O in DMF, 4 mL) was passed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) packed with the catalyst (0.4 g) and heated at 130 °C. The solution was then flowed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) packed with polymer-supported base and metal-scavenging resins,<sup>[22]</sup> namely, Quadrapure–sulfonic acid<sup>®</sup> (QP-SA) and Quadrapure–thiourea<sup>®</sup> (QP-TU), respectively (Scheme 1).

One of the main advantages of this system was the fast delivery of the products with residence times ranging from 15 to 30 min. Under these conditions, we were able to process a useful number of substrates with both electron-withdrawing and -donating substituents (Table 2).



Scheme 1. General flow scheme for the Sonogashira cross-coupling reaction.

We were also pleased to observe that the low level of palladium present (*just 1.6 mg wt in total, corresponding to 15 µmol of palladium*) in the column was able to continuously process 10 mmol of substrate (entry 6, Table 2) without noticeable alteration of the catalytic efficiency. When we changed the solvent to ethyl acetate, we found that the same conversion could be obtained over longer times (25–45 min). However, the presence of by-products discouraged us from using this solvent.

Using a recently designed solvent evaporator system, we have demonstrated an in-line solvent switch from high-boiling solvent to low-boiling solvents and vice versa.<sup>[23]</sup> We then opted to apply this technology for the purpose of reducing the environmental impact of using harmful solvents such as DMF by allowing their simple removal and recycling.

Under the optimised conditions, the reaction mixture (entry 3, Table 2) was passed through the catalyst at 130 °C. After exiting the column, the mixture was scavenged by passage through QP-SA, QP-TU and MgSO<sub>4</sub> packed in an Omnifit<sup>®</sup> glass column. Feeding the bespoke evaporating system with this solution, we were able to concentrate the output and switch from DMF to a more acceptable solvent (isopropanol (IPA)), with 92% of the product recovered (Scheme 2). Additionally, we were able to recover and recycle part of the DMF used for the reaction (around 60%).

While we had prior knowledge of perovskite catalysis for the Sonogashira cross-coupling reaction, the same was not true for Heck cross-couplings. We therefore investigated the opportunity to elaborate Heck reactions with these new catalytic systems using microwave irradiation. The results are reported in Table 3. Again it was observed that palladium inclusion in the perovskites was critical for the reaction. Gratifyingly, excellent conversions could be obtained after just 20 min reaction time.

A similar cooperation between  $\text{CeO}_2$  and the catalyst was observed for the Heck reaction as that found for the Sonogashira process. However, this cooperation was found to be dependent on the solvent because we did not observe any cooperation when exchanging DMF for any other solvent. We believe that, at high temperature, DMF can play an active role in the reduction of Pd species within the heterogeneous lattice; hence, enhancing the cooperation between Pd and CeO<sub>2</sub>.

We selected  $LaFe_{0.95}Pd_{0.05}O_3$  as the catalyst of choice, since it proved to have the best catalytic properties in



Scheme 2. Solvent switching from DMF to IPA using our bespoke system.

combination with CeO<sub>2</sub>. The heterogeneous catalyst system was "assembled" using the same conditions as those for the Sonogashira reaction and applied to the processing of different aryl iodides with *tert*-butyl acrylate by Heck cross-coupling (Table 4). Under the optimised conditions, a solution of *tert*-butyl acrylate (1 mmol), aryl iodide (1 mmol) and TEA (1 mmol) in DMF (4 mL) was passed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.× 100.0 mm length) containing the catalyst (0.4 g), and heated at 130 °C. The solution was then flowed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) packed with polymer-supported acid and metal-scavenging resin, namely QP-SA (2 g) and QP-TU (1 g), respectively (Scheme 3).

We were pleased to observe that the low level of palladium present (just 1.6 mg wt in total, corresponding to 15  $\mu$ mol of palladium) in the column was able to continuously process different substrates without any apparent decrease of the catalytic activity (over 24 h).



Scheme 3. General flow scheme for the Heck cross-coupling reaction.

#### Conclusion

We have developed an efficient and facile system for the rapid delivery of Sonogashira and Heck cross-coupling products with an extremely low level of palladium cata-

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#### Enhanced Coupling Reactions by Perovskite Catalysts

Table 2. Sonogashira cross-coupling in flow using  $La_{1.02}Fe_{0.57}Pd_{0.05}O_3$  deposited on  $CeO_2$ .

Entry <sup>[a]</sup>	Alkyne	Iodide	Product (yield [%]) <sup>[b]</sup>
1			
2			
3		I	93 <sup>[d]</sup>
4		· \$	$\bigcirc - \overset{\circ}{\Longrightarrow}$
5	n-Bu	IMe	86 n-Bu-
6	n-Bu-		n-Bu
7	n-Bu		n-Bu
8	F	I-	F 98
9	Me Me	I-	Me Me 95
10			
11	HO	IF	HO 49 <sup>[d]</sup>
12	Me	IF	OH Me 52 <sup>[d]</sup>
13	F		

[a] A solution of acetylene (1 mmol), aromatic iodide (1 mmol) and TMG (2 mmol) in wet DMF (5 %  $H_2O$  in DMF, 4 mL) was pumped (flow rate 30–100  $\mu$ Lmin<sup>-1</sup>) through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) containing the catalyst (0.4 g) and heated at 130 °C. The solution was then passed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) packed with polymer supported base and metal scavenging resin, namely, QP-SA (2 g) and QP-TU (1 g), respectively. [b] Yield was calculated after extraction and concentration in vacuo. [c] 10 mmol scale. [d] The QP-SA scavenging process was avoided. [e] After column chromatography.

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**Table 3.** Screening of different catalysts for the Heck cross-coupling reaction in the presence or absence of  $CeO_2$ .

Entry	Catalyst <sup>[a]</sup>	Conversion <sup>[b]</sup>		
		No additive [%]	CeO <sub>2</sub> <sup>[c]</sup> [%]	
1	La <sub>0.96</sub> FeAu <sub>0.04</sub> O <sub>3</sub>	0	_	
2	La <sub>0.96</sub> Fe <sub>0.96</sub> Au <sub>0.04</sub> Pd <sub>0.04</sub> O <sub>3</sub>	14	_	
3	LaFe <sub>0.95</sub> Pd <sub>0.05</sub> O <sub>3</sub>	83	92 <sup>[d]</sup>	
4	La₂CuO₄	0	_	
5	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0	_	
6	La₄PdO <sub>7</sub>	39	56 <sup>[d]</sup>	
7	$La_{1.02}Fe_{0.58}Cu_{0.37}Pd_{0.05}O_{3}$	13	63 <sup>[d]</sup>	

[a] 5 mol% of catalyst was used in the reaction between *tert*-butyl acrylate (1.0 mmol), 4-iodoacetophenone (1 mmol) and triethylamine (TEA, 1 mmol) in DMF (4 mL) for 20 min at 130  $^{\circ}$ C. [b] Conversions of compounds are based on the H-NMR spectrum of the crude material. [c] 50 mol%. [d] Heated at 130  $^{\circ}$ C for 10 min.

lyst. In particular, we were able to contain a catalyst generated in situ by favourable interactions between palladium-containing perovskites and cerium oxide. This system was uniquely achieved using a flow-chemistry platform. Under the optimised conditions, we were able to scale one of the reactions to deliver 10 mmol of product. The use of our bespoke solvent evaporator allowed us to recover the solvent (60%) and recycle it for further use, hence, reducing the environmental impact of these chemistries. We strongly believe that the application of this system can be useful for a wide range of functionalities. However, we noticed that the elaboration of Sonogashira and Heck couplings using aryl bromide derivatives was characterised by a very slow reaction time profile and formation of by-products. We are still working on these transformations to access catalysts whose application would be universal to all aryl halides.

#### **Experimental Section**

General: <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer with the residual solvent signal as the internal reference  $(CDCl_3 = 7.26 \text{ ppm},$  $[D_6]DMSO = 2.50 \text{ ppm}$ ). <sup>1</sup>H resonances are reported to the nearest 0.01 ppm. <sup>13</sup>C NMR spectra were recorded on the same spectrometers with the central resonance of the solvent signal as the internal reference (CDCl<sub>3</sub>= 77.16 ppm,  $[D_6]DMSO = 39.52$  ppm). All <sup>13</sup>C resonances are reported to the nearest 0.1 ppm. DEPT 135, COSY, HMQC and HMBC experiments were used to aid structural determination and spectral assignment. The multiplicity of <sup>1</sup>H signals are indicated as follows: s=singlet, d = doublet, t = triplet, sext = sextet, m = multiplet, br =broad, or combinations of thereof. Coupling constants (J)are quoted in Hz and reported to the nearest 0.1 Hz. Where appropriate, averages of the signals from signals displaying multiplicity were used to calculate the value of the coupling constant. IR spectra were recorded neat on

Table 4. Heck cross-coupling in flow using  $La_{1.02}Fe_{0.57}Pd_{0.05}O_3$  deposited on CeO<sub>2</sub>.



[a] A solution of *tert*-butyl acrylate (1 mmol), aromatic iodide (1 mmol) and TEA (1 mmol) in DMF (4 mL) was pumped (flow rate 50–100  $\mu$ L/min) through an Omnifit® glass column (6.6 mm i.d.× 100.0 mm length) containing the catalyst (0.4 g) and heated at 130 °C. The solution was then passed through an Omnifit® glass column (6.6 mm i.d.×100.0 mm length) packed with polymer-supported base and metal-scavenging resin, namely, QP-SA (2 g) and QP-TU (1 g), respectively. [b] Yield was calculated after extraction and concentration in vacuo. [c] The QP-SA scavenging process was avoided. [d] After column chromatography.

a PerkinElmer Spectrum One FTIR spectrometer using Universal ATR sampling accessories. Unless stated otherwise, reagents were obtained from commercial sources and used without purification. Laboratory reagent grade EtOAc, petroleum ether 40-60, and DCM were obtained from Fischer Scientific and distilled before use. Unless stated otherwise, heating was conducted using standard laboratory apparatus. The removal of solvent under reduced pressure was carried out on a standard rotary evaporator. Melting points were performed on either a Stanford Research Systems MPA100 (OptiMelt) automated melting point system and are uncorrected. High-resolution mass spectrometry (HRMS) was performed using a Waters Micromass LCT Premier<sup>TM</sup> spectrometer using time of flight with positive ESI, or conducted by Paul Skelton on a Bruker BioApex 47e FTICR spectrometer using positive ESI or EI at 70 eV to within a tolerance of 5 ppm of the theoretically calculated value. LC-MS analysis was performed on an Agilent HP 1100 series chroma-

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tography (Mercury Luna 3u C18 (2) column) attached to a Waters ZQ2000 mass spectrometer with ESCi ionisation source in ESI mode. Elution was carried out at a flow rate of 0.6 mLmin<sup>-1</sup> using a reverse-phase gradient of acetonitrile and water containing 0.1% formic acid. Retention time is given in min to the nearest 0.1 min and the m/z value is reported to the nearest mass unit (m.u.). Elemental analyses within a tolerance of  $\pm 0.3\%$  of the theoretical values were determined by Alan Dickerson and Patricia Irele in the microanalytical laboratories at the Department of Chemistry, University of Cambridge. X-ray powder diffraction analyses were performed using a Panalytical Empyrean High throughput, high resolution X-ray powder diffractometer. Unless otherwise specified, all flow reactions were performed with a Vapourtec R2/ R4 + flow platform.<sup>[24]</sup>

General flow procedure for the Sonogashira cross-coupling: A solution of acetylene (1 mmol), aromatic iodide (1 mmol) and TMG (2 mmol) in wet DMF (5 % H<sub>2</sub>O in DMF, 4 mL) was pumped (flow rate 30–100  $\mu$ L/min) through an Omnifit<sup>®</sup> glass column (6.6 mm i.d. × 100.0 mm length) containing the catalyst and heated at 130 °C. The solution was then passed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d. × 100.0 mm length) packed with polymer-supported base and metal-scavenging resin, namely, QP-SA (2 g) and QP-TU (1 g), respectively. Ethyl acetate (10 mL) was added to the organic solution containing the product. The organic fraction was washed with water (4 × 10 mL), brine (20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and concentration in vacuo of the organic solution gave the desired product. Unless otherwise stated, no chromatographic purification was carried out.

**Solvent-switching procedure**: The solution output was collected and directed  $(0.15 \text{ mLmin}^{-1})$  to a T-piece, where it was combined with a flowing stream of IPA  $(0.75 \text{ mLmin}^{-1})$ . The resulting mixture was directed into the device and the flow rate of the nitrogen desolvation gas was maintained at 10 Lmin<sup>-1</sup>. The evaporation chamber<sup>[23]</sup> (an Omnifit<sup>®</sup> column) was heated at 60 °C using a Vapourtec R2/R4 + column heater. The output of unvapourised solvent was controlled by a WPI Peristar-Pro peristaltic pump (0.2 mLmin<sup>-1</sup>).

General flow procedure for the Heck cross-coupling reaction: A solution of *tert*-butyl acrylate (1 mmol), aromatic iodide (1 mmol) and TEA (1 mmol) in DMF (4 mL) was pumped (flow rate 50- $-100 \,\mu L \,min^{-1}$ ) through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) containing the catalyst and heated at 130 °C. The solution was then passed through an Omnifit<sup>®</sup> glass column (6.6 mm i.d.×100.0 mm length) packed with polymer-supported base and metal-scavenging resin, namely, QP-SA (2 g) and QP-TU (1 g), respectively. Ethyl acetate (10 mL) was added to the organic solution containing the product. The organic fraction was washed with water (4× 10 mL), brine (20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and concentration in vacuo of the organic solution gave the desired product. Unless otherwise stated, no chromatography purification was carried out.

**1-Chloro-2-(phenylethynyl)benzene (1)**: Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.70 (s, 1H), 7.60 (d, 1H, *J* = 8.6 Hz), 7.37–7.26 (m, 5H), 7.01 ppm (t, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 137.13 (CH), 135.67 (CH), 135.07 (CH), 131.68 (CH), 131.44 (C), 130.96 (CH), 128.48 (CH), 128.40 (CH), 125.02 (C), 122.76 ppm (C); FTIR (neat):  $\tilde{\nu}$  = 3000, 2990, 1601, 1581, 1470, 1414, 1358, 1282, 1149, 1107, 781, 759, 735 cm<sup>-1</sup>; LC-MS: retention time 4.39 min, *m/z*: 213.13 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>10</sub>Cl<sup>+</sup>: 213.0944; found: 213.0946; elemental analysis calcd (%) for C<sub>14</sub>H<sub>9</sub>Cl: C 79.07, H 4.27, Cl 16.67; found: C 79.00, H 4.18, Cl 16.55.

**2-(Phenylethynyl)pyrazine (2)**: Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.73$  (s, 1H), 8.57 (d, 1H, J = 7.5 Hz), 8.50 (d, 1H, J = 7.5 Hz), 7.61 (d, 2H, J = 8.6 Hz), 7.41–7.30 ppm (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 147.74$  (CH), 144.43 (CH), 142.77 (CH), 140.40 (C), 132.15 (CH), 129.57 (CH), 128.51 (CH), 121.49 (C), 93.30 (C), 85.78 ppm (C); FTIR (neat):  $\tilde{\nu} = 3060$ , 1598, 1515, 1490, 1461, 1394, 1140, 1052, 1010, 846, 752, 688 cm<sup>-1</sup>; LC-MS: retention time 4.48 min, *m/z*: 181.13 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>N<sub>2</sub><sup>+</sup>: 181.0766; found: 181.0773; elemental analysis calcd (%) for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>: C 79.98, H 4.47, N 15.55; found: C 79.82, H 4.33, N 15.19.

**1-[4-(Phenylethynyl)phenyl]ethan-1-one (3)**: Yellowish solid; m.p. 94–96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.92 (d, 2H, *J*=8.6 Hz), 7.61 (d, 2H, *J*=8.6 Hz), 7.55 (m, 2H), 7.32 (m, 3H), 2.61 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =197.29 (C), 135.45 (C), 131.73 (CH), 131.69 (CH), 128.80 (CH), 128.43 (CH), 128.26 (CH), 122.65 (C), 92.70 (C), 87.54 (C), 26.60 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$ =2950, 2920, 2853, 1692, 1592, 1400, 1343, 1243, 1156, 983, 831 cm<sup>-1</sup>; LC-MS: retention time 5.09 min, *m/z*: 221.19 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>13</sub>O<sup>+</sup>: 221.0961; found: 221.0958.

**1-[2-(Phenylethynyl)phenyl]ethan-1-one** (**4**): Orange oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.76 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 8.0 Hz), 7.57–7.55 (m, 2H), 7.48 (t, 1H, J = 8 Hz), 7.42–7.36 (m, 4H), 2.80 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 200.35 (C), 140.77 (C), 133.88 (CH), 131.52 (CH), 131.30 (CH), 128.77 (CH), 128.70 (CH), 128.47 (CH), 128.28 (CH), 122.89 (C), 121.70 (C), 95.03 (C), 88.49 (C), 30.00 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$  = 3061, 1680, 1591, 1561, 1492, 1473, 1442, 1356, 1276, 1245, 1233, 1163, 1109, 1069, 1025, 954, 915, 849 cm<sup>-1</sup>; HRMS (ESI): *m*/*z* calcd for C<sub>14</sub>H<sub>10</sub>Cl<sup>+</sup> : 220.0888; found: 220.0895.

**1-{4-[(4-Butylphenyl)ethynyl]phenyl}ethan-1-one** (5): Yellowish solid; m.p. 66–68 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.93 (d, 2H, J=8.6 Hz), 7.61 (d, 2H, J=8.6 Hz), 7.43 (d, 2H, J=8.6 Hz), 7.18 (d, 2H, J= 8.6 Hz), 2.62 (m, 5H), 1.62 (sext, 2H, J=7.5 Hz), 1.37 (sext, 2H, J=7.5 Hz), 0.92 ppm (t, 3H, J=7.5 Hz); <sup>13</sup>C

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NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 197.31$  (C), 144.07 (C), 136.02 (C), 132.02 (C), 131.65 (CH), 131.60 CH), 128.56 (CH), 128.48 (CH), 119.75 (C), 93.07 (C), 87.54 (C), 35.62 (CH<sub>2</sub>), 33.34 (CH<sub>2</sub>), 26.59 (CH<sub>2</sub>), 22.29 (CH<sub>3</sub>), 13.91 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu} = 2956$ , 2925, 2858, 1681, 1596, 1403, 1355, 1261, 1175, 956, 820 cm<sup>-1</sup>; LC-MS: retention time 5.70 min, *m*/*z*: 277.16 [*M*+H]; HRMS (ESI): *m*/*z* calcd for C<sub>20</sub>H<sub>21</sub>O<sup>+</sup>: 277.1587; found: 277.1580.

**2-[(4-Butylphenyl)ethynyl]pyridine (6)**: Yellowish oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$ =8.61 (d, 1H, *J*= 4.3 Hz), 7.66–7.60 (m, 1H), 7.60–7.41 (m, 3H), 7.25–7.07 (m, 3H), 2.62 (t, 2H, *J*=7.5 Hz), 1.60 (q, 2H, *J*=7.5 Hz), 1.37 (sext, 2H, *J*=7.5 Hz), 0.92 ppm (t, 3H, *J*=7.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$ =149.98 (CH), 144.20 (C), 143.66 (C), 136.08 (CH), 131.95 (CH), 128.49 (CH), 127.04 (CH), 119.34 (CH), 115.46 (C), 89.60 (C), 88.06 (C), 35.63 (CH<sub>2</sub>), 33.30 (CH<sub>2</sub>), 22.29 (CH<sub>3</sub>), 13.90 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$ =3004, 2955, 2929, 2858, 1718, 1580, 1560, 1506, 1460, 1426, 1365, 1229, 1154, 829, 775 cm<sup>-1</sup>; LC-MS: retention time 5.28 min, *m/z*: 236.22 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>17</sub>H<sub>18</sub>N<sup>+</sup>: 236.1434; found: 236.1430.

**1-Butyl-4-(phenylethynyl)benzene (7)**: Yellowish oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.62 (m, 2H), 7.51–7.32 (m, 5H), 7.20 (d, 2H, *J* = 8.4 Hz), 2.63 (t, 2H, *J* = 7.5 Hz), 1.61 (q, 2H, *J* = 7.5 Hz), 1.38 (sext, 2H, *J* = 7.5 Hz), 0.92 ppm (t, 3H, *J* = 7.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 143.66 (C), 136.20 (CH), 131.95 (CH), 128.55 (CH), 128.13 (CH), 127.19 (CH), 120.14 (CH), 119.30 (C), 89.22 (C), 88.06 (C), 35.62 (CH<sub>2</sub>), 33.31 (CH<sub>2</sub>), 22.28 (CH<sub>3</sub>), 13.90 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$  = 3010, 2955, 2929, 2858, 1520, 1511, 1432, 1200, 1154, 829, 733 cm<sup>-1</sup>; LC-MS: retention time 6.24 min, *m*/ *z*: 235.17 [*M*+H]; HRMS (ESI): *m*/*z* calcd for C<sub>18</sub>H<sub>19</sub><sup>+</sup>: 236.1808; found: 236.1809.

**1-{4-[(3-Fluorophenyl)ethynyl]phenyl}ethan-1-one (8):** Yellowish solid; m.p. 90–93 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.91 (d, 2H, *J*=8.4 Hz), 7.60 (d, 2H, *J*=8.4 Hz), 7.32 (m, 2H), 7.25 (m, 1H), 7.08 (m, 1H), 2.63 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ = 197.24 (C), 163.61 (C), 136.48 (C), 131.78 (CH), 130.08 (CH), 129.99 (CH), 127.63 (CH), 118.60 (CH), 116.04 (CH), 89.45 (C), 88.22 (C), 26.61 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$ =2922, 1725, 1676, 1600, 1310, 1264, 829, 782 cm<sup>-1</sup>; LC-MS: retention time 5.14 min, *m/z*: 239.12 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>12</sub>FO<sup>+</sup>: 239.1400; found: 239.1403.

**1-{4-[(2,5-Dimethylphenyl)ethynyl]phenyl}ethan-1-one** (9): Yellowish solid; m.p. 89–92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.96 (d, 2H, *J*=8.4 Hz), 7.66 (d, 2H, *J*=8.4 Hz), 7.35 (m, 1H), 7.13 (m, 1H), 7.09 (m, 1H), 2.64 (s, 3H), 2.45 (s, 3H), 2.30 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =197.4 (C), 137.4 (C), 132.5 (C), 131.6 (CH), 130.10 (CH), 129.8 (C), 128.6 (CH), 127.3 (CH), 122.2 (CH), 118.9 (CH), 117.8 (CH), 89.7 (C), 88.1 (C), 26.7 (CH<sub>3</sub>),20.8 (CH<sub>3</sub>), 20.2 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$ =2926, 1726, 1670, 1602, 1310, 1264, 829, 798 cm<sup>-1</sup>; LC-MS: retention time 5.18 min, *m*/*z*: 249.13 [*M*+H]; HRMS (ESI): *m*/*z* calcd for C<sub>18</sub>H<sub>17</sub>O<sup>+</sup>: 249.5767; found: 249.5757.

**2-[(4-Phenoxyphenyl)ethynyl]pyridine (10)**: Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.62$  (d, 1H, J =3.6 Hz), 7.67 (td, 1H, J = 1.8, Hz, J = 7.7 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.51 (d, 1H, J = 8.1 Hz), 7.38 (m, 2H), 7.23 (m, 1H), 7.16 (m, 1H), 7.05 (d, 2H, J = 8.1 Hz), 6.97 ppm (d, 2H, J = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta =$ 156.12 (C), 150.03 (C), 146.13 (C), 136.08 (CH), 133.69 (CH), 129.92 (CH), 129.89 (CH), 126.98 (CH), 124.03 (C), 89.95 (C), 88.09 ppm (C); FTIR (neat):  $\tilde{\nu} = 3040$ , 2988, 2926, 1706, 1655, 1600, 1509, 1300, 1288, 1264, 829, 798 cm<sup>-1</sup>; LC-MS: retention time 5.07 min, m/z: 272.05 [M+H]; HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>15</sub>NO<sup>+</sup>: 272.2234; found: 272.2237.

**5-(6-Fluoropyridin-3-yl)pent-4-yn-1-ol (11)**: Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =8.21 (s, 1H), 7.83 (m, 1H), 6.89 (m, 1H) 3.82 (t, 2H, *J*=7.2 Hz), 2.57 (q, 2H, *J*=7.2 Hz), 1.87 (q, 2H, *J*=7.2 Hz), 1.76 ppm (br s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =164.22 (C), 147.89 (CH), 139.08 (CH), 118.17 (CH), 114.99 (C), 89.05 (C), 65.20 (CH), 32.33 (CH<sub>2</sub>), 30.50 ppm (CH<sub>2</sub>); FTIR (neat):  $\tilde{\nu}$ =3359, 2928, 1634, 1593, 1567, 1490, 1455, 1406, 1374, 1342, 1258, 1063, 1037, 836, 687 cm<sup>-1</sup>; LC-MS: retention time 4.04 min, *m*/*z*: 180.15 [*M*+H]; HRMS (ESI): *m*/*z* calcd for C<sub>10</sub>H<sub>11</sub>NFO<sup>+</sup>: 180.0825; found: 180.0831.

**1-(6-Fluoropyridin-3-yl)pent-1-yn-3-ol (12)**: Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.30$  (m, 1H), 7.83 (m, 1H), 6.90 (m, 1H) 4.56 (t, 2H, J = 7.2 Hz), 3.10 (s, 3H), 2.57 (q, 2H, J = 7.2 Hz), 1.93 ppm (t, 3H, J = 7.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 164.22$  (C), 147.89 (CH), 139.08 (CH), 118.17 (CH), 114.99 (C), 89.05 (C),  $\delta = 20$  (CH), 32.33 (CH<sub>2</sub>), 30.50 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu} = 3353$ , 2964, 2933, 1653, 1603, 1515, 1482, 1392, 1255, 1121, 1008, 962, 833, 668 cm<sup>-1</sup>; LC-MS: retention time 4.00 min, m/z: 180.14 [M+H]; HRMS (ESI): m/z calcd for C<sub>10</sub>H<sub>11</sub>NFO<sup>+</sup>: 180.0825; found: 180.0833.

**1-Fluoro-3-[(3-methoxyphenyl)ethynyl]benzene** (13): Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.66 (s, 1H), 7.40–7.20 (m, 5H), 7.11 (m, 1H), 6.93 (m, 1H), 3.84 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 163.61 (C), 136.48 (C), 131.78 (CH), 130.08 (CH), 129.99 (CH), 128.75 (CH), 128. 55 (CH), 128.15 (CH), 128.01 (CH), 127.63 (CH), 118.60 (C), 116.04 (C), 89.45 (C), 88.22 (C), 26.61 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$  = 3072, 3005, 2938, 1607, 1577, 1491, 1433, 1323, 1282, 1238, 1194, 1175, 1155, 1040, 961, 870, 778, 746, 680 cm<sup>-1</sup>; LC-MS: retention time 6.08 min, *m/z*: 227.17 [*M*+H]; HRMS (ESI): *m/z* calcd for C<sub>15</sub>H<sub>12</sub>FO<sup>+</sup>: 227.0867; found: 227.0860.

*tert*-Butyl (*E*)-3-(4-acetylphenyl)acrylate (14): Yellow solid; m.p. 98–100 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.84 (d, 2H, *J*=8.0 Hz), 7.47 (m, 3H), 6.34 (d, 1H, *J*=16.0 Hz), 2.49 (s, 3H), 1.43 ppm (s, 9H); <sup>13</sup>C NMR

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(100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =197.11 (C), 165.56 (C), 141.82 (CH), 138.89 (C), 137.65 (C), 128.68 (CH), 127.89 (CH), 122.63 (CH), 80.71 (C), 28.03 (CH<sub>3</sub>), 26.53 ppm (CH<sub>3</sub>) LC-MS: retention time 4.98 min, *m*/*z*: 191.16 [*M*-*t*-Butyl]; HRMS (ESI): *m*/*z* calcd for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub><sup>+</sup>: 247.1334; found: 247.1330.

*tert*-Butyl (*E*)-3-(1*H*-indol-5-yl)acrylate (15): Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.68$  (br s, 1H), 7.78–7.75 (m, 2H), 7.38 (m, 2H), 7.19 (m, 1H), 6.57 (m, 1H), 6.37 (d, 1H, *J*=16.1 Hz), 1.59 ppm (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 167.23$  (C), 145.54 (CH), 136.95 (C), 128.12 (CH), 126.58 (C), 125.34 (CH), 122.14 (CH), 121.42 (CH), 116.90 (CH), 111.59 (CH), 103.24 (CH), 80.17 (C), 28.07 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu} = 3415$ , 3101, 2972, 1724, 1681, 1609, 1442, 1408, 1366, 1337, 1311, 1282, 1219, 1145, 1128, 1089, 1064, 981, 856, 797, 731 cm<sup>-1</sup>; LC-MS: retention time 5.00 min, *m/z*: 170.18 [*M*-O-C(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup>: 230.2936; found: 230.2939.

*tert*-Butyl (*E*)-3-(6-fluoropyridin-3-yl)acrylate (16): Yellowish solid; m.p. 89–91 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.33$  (d, 2H, J = 2.2 Hz), 7.93 (m, 1H), 7.54 (d, 1H, J = 16.1 Hz), 6.95 (dd, 1H, J = 8.4 Hz, J = 2.9 Hz), 6.38 (d, 1H, J = 16.1 Hz), 1.55 ppm (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 165.38$  (C), 164.30 (C), 147.89 (CH), 139.08 (CH), 138.17 (CH), 128.67 (C), 122.20 (CH), 110.16 (CH), 81.06 (C), 28.12 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu} = 2999$ , 2975, 2932, 1737, 1697, 1644, 1594, 1487, 1391, 1366, 1300, 1243, 1216, 1148, 993, 883, 832 cm<sup>-1</sup>; LC-MS: retention time 4.80 min, *m/z*: 168.12 [*M*-C(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>15</sub>FNO<sub>2</sub><sup>+</sup>: 224.1081; found: 224.1076. elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>FNO<sub>2</sub>: C 64.56, H 6.32, N 6.27; found: C 64.50, H 6.22, N 6.10.

*tert*-Butyl (*E*)-3-(4-methoxyphenyl)acrylate (17): Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =7.55 (d, 1H, *J*=16.1 Hz), 7.42 (d, 2H, *J*=8.5 Hz), 6.88 (d, 2H, *J*=8.5 Hz), 6.24 (d, 1H, *J*=16.1 Hz), 3.81 (s, 3H), 1.53 ppm (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ = 166.64 (C), 161.11 (C), 143.17 (CH), 129.52 (CH), 127.37 (C), 117.83 (CH), 114.23 (CH), 80.17 (C), 55.29 (CH<sub>3</sub>), 28.21 ppm (CH<sub>3</sub>); FTIR (neat):  $\tilde{\nu}$ =2971, 2933, 2893, 1738, 1701, 1633, 1603, 1575, 1511, 1391, 1366, 1248, 1140, 1030, 979, 874, 825 cm<sup>-1</sup>; LC-MS: retention time 5.11 min, *m/z*: 161.11 [*M*-C(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>17</sub>O<sub>3</sub>Na<sup>+</sup>: 257.1148; found: 257.1144.

*tert*-Butyl (*E*)-3-(2-acetylphenyl)acrylate (18): Brownish oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =8.02 (d, 1H, *J*=8.0 Hz), 7.69 (d, 1H, *J*=7.5 Hz), 7.46 (d, 1H, *J*= 7.5 Hz), 7.40 (d, 1H, *J*=7.5 Hz), 6.19 (d, 1H, *J*=8.0 Hz), 2.57 (s, 3H), 1.50 ppm (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =200.89 (C), 165.76 (C), 142.67 (CH), 138.26 (C), 134.82 (C), 131.81 (CH), 129.17 (CH), 129.09 (CH), 128.26 (CH), 122.85 (CH), 80.49 (C), 29.35 (CH<sub>3</sub>), 28.15 ppm (CH<sub>3</sub>); LC-MS: retention time 4.96 min, *m/z*: 191.12 [*M*-*t*-Butyl]; HRMS (ESI): m/z calcd for  $C_{15}H_{19}O_3^+$ : 247.1334; found: 247.1330.

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