Synthesis of $\alpha,\beta$-alkynyl esters and unsymmetrical maleate esters catalysed by Pd/C; an efficient phosphine free catalytic system for oxidative alkoxy carbonylation of terminal alkynes.

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1) Material and Methods:

All chemicals were purchased from Lancaster (Alfa-Aesar), Sigma-Aldrich, S. D. fine chemical and commercial suppliers. The Pd/C purchased from Sigma-Aldrich (extent of labelling: 10 wt. % loading, matrix: activated carbon support, Product Number: 205699, Brand: Aldrich). The progress of reaction was monitored by gas chromatography Perkin Elmer Clarus 400 GC equipped with capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). Product was purified by column chromatography on silica gel (100-200) mesh. All yields reported in table 2 are referred to isolated yields and pure as determined by 1H NMR while yields reported in Table 1 and fig. 1 are GC yields. The product was visualized with a 254 nm UV lamp. The 1H NMR and 13C NMR spectra were recorded with JEOL FT-NMR, Model-AL300 (300 MHz) and Varian-400 MHz FT-NMR spectrometer in CDCl3. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. J (coupling constant) were reported in Hz, splitting patterns of proton are described as s (singlet), d (doublet), t (triplet), m (multiplet). Mass spectra were obtained on Shimadzu GCMS-QP 2010 instrument (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80°C to 240°C at 10°/min. rise.). The HR-MS were recorded on a Thermo Scientific Q Exactive mass spectrometer. The IR spectra were recorded with FT-IR (Perkin Elmer). All known compounds were confirmed by comparison with authentic samples on GC and GC-MS. However new compounds were confirmed by GC-MS, FT-IR, 1H NMR, 13C NMR and HR-MS techniques.

2) General experimental procedure for oxidative alkoxy carbonylation of terminal alkyne:

To a 100 ml stainless steel autoclave, 1-alkyne (1 mmol), alcohol (0.5 ml), 10% Pd/C (10 mol%), TBAI (0.6 mmol), 1,4-dioxane (10 ml) were added. The autoclave was closed, pressurized with oxygen (1 atm) and CO (5 atm) without flushing. Reaction mixture stirred with mechanical stirred (550 rpm), heated at 80°C for 8 hour. The reactor was then cooled to room temperature, the pressure was then released. The reactor vessel was washed with ethyl acetate (3×4 ml) to remove traces of catalyst and product if present. The reaction mixture was filtered and filtrates washed with saturated solution of sodium thiosulphate (3×4 ml), dried over Na2SO4. The crude product was purified by column chromatography (Silica gel 100-200 mesh, petroleum ether/ethyl acetate) to afford the corresponding product in good to excellent yield.

The purity of compounds was confirmed 1H NMR, GC-MS analysis. The structure of product was confirmed by GC-MS, HR-MS, FT-IR, 1H NMR and 13C NMR spectroscopic techniques.
3) Experimental procedure for recycling of Pd/C catalyst:
The catalyst was filtered and washed first with distilled water (3 x 4 mL) and then with methanol (3 x 4 mL) to remove any traces of organic material if present, and dried under reduced pressure. The dried catalyst was then used for catalyst recyclability experiment.

4) Table 1. Effect of catalyst screening and loading on the oxidative alkoxy carbonylation of terminal alkyne:

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst loading (mol%)</th>
<th>Yield[b] (%)</th>
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<tr>
<td></td>
<td>Catalyst Screening</td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td>PS-Pd-NHC</td>
<td>10</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>Pd/C (10%)</td>
<td>10</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Catalyst Loading</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PS-Pd-NHC</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Pd/C (10%)</td>
<td>8</td>
<td>85</td>
</tr>
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</table>

Reaction conditions: phenylacetylene (1 mmol), ethanol (0.5 mL), CO/O2 pressure (5/1 atm), TBAI (0.6 mmol), 1,4-dioxane (10 mL), temperature 80°C, time 8 h. b GC yield

5) 1H, 13C, DEPT, GC-MS, and HR-MS spectrs of the compounds:

(3a) ethyl-3-phenylpropiolate
Yield- 95%; Yellowish liquid.
IR (Neat): 2210, 1708 cm–1; GCMS (EI, 70 eV): m/z (%): 174 (16, M⁺), 129 (100), 102 (83), 75 (24); 1H NMR (400 MHz, CDCl3): δ 7.60-7.57 (m, 2H, CH, Ar), δ 7.46-7.35 (m, 3H, CH, Ar), δ 4.30 (q, 2H, CH₂CH₃), δ 1.36 (t, 3H, CH₂CH₃).

(3b) ethyl 3-(p-tolyl)propiolate
Yield- 88%; Yellowish liquid.
IR (Neat): 2203, 1789 cm–1; GCMS (EI, 70 eV): m/z (%): 188 (20, M⁺), 143 (83), 116 (100), 89 (14); 1H NMR (400 MHz, CDCl3): δ 7.48 (d, 2H, CH, Ar), δ 7.18 (d, 2H, CH, Ar), δ 4.29 (q, 2H, CH₂CH₃), δ 2.38 (s, 3H, CH₃Ph), δ 1.35 (t, 3H, CH₂CH₃).

(3c) ethyl 3-(4(trifluoromethyl)phenyl)propiolate
Yield- 83%; Colourless liquid.
IR (Neat): 2253, 1711 cm–1; GCMS (EI, 70 eV): m/z (%): 242 (7, M⁺), 223 (3), 197 (100), 170 (67), 147 (7); 1H NMR (300 MHz, CDCl3): δ 7.71-7.59 (m, 4H, CH, Ar), δ 4.32 (q, 2H, CH₂CH₃), δ 1.34 (t, 3H, CH₂CH₃).

(3d) ethyl 3-(4(dimethylamino)phenyl)propiolate
Yield- 90%; Yellowish liquid.
IR (Neat): 2198, 1704 cm–1; GCMS (EI, 70 eV): m/z (%): 217 (54, M⁺), 188 (9), 172 (41), 145 (100), 128 (10), 86 (12); 1H NMR (400 MHz, CDCl3): δ 7.46 (d, 2H, CH, Ar), δ 6.62 (d, 2H, CH, Ar), δ 4.27 (q, 2H, CH₂CH₃), δ 3.01 (s, 6H, CH₂NCH₃), δ 1.34 (t, 3H, CH₂CH₃).

(3e) ethyl 3-(pyrene-2-yl)propiolate
Yield- 85%; Yellowish solid.
IR (KBr): 2205, 1704 cm–1; 1H NMR (400 MHz, CDCl3): δ 8.57 (d, 1H, CH, Ar), δ 8.27-8.04 (m, 8H, CH, Ar), δ 4.40 (q, 2H, CH₂CH₃), δ 1.44. (t, 3H, CH₃CH₂); 13C NMR (75 MHz, CDCl₃): δ 154.30, 132.63, 132.63, 130.69, 130.63, 130.48, 129.14, 129.02, 126.74, 126.23, 126.13, 125.99, 124.53, 124.11, 123.76, 123.53, 113.08, 85.94, 85.59, 62.05, 14.17; HRMS (ESI): m/z = 321.0886 Calculated for [(C₂₁H₁₆O₂) Na]⁺, Observed 321.0879
(4e) diethyl 2-(p-tolyl)maleate
Yield- 90%; (Yellowish liquid).
IR (Neat): 1724, 1629 cm–1; 1H NMR (300 MHz, CDCl3): δ 7.40-7.37 (m, 2H, CH, Ar), δ 7.20 (d, J= 8 Hz, 2H, CH, Ar), δ 6.27 (s, 1H, COCH=CCO), δ 4.42 (q, J=7 Hz, 2H, CH2CH2O), δ 4.26 (q, J=7.5 Hz, 2H, CH2CH2O), δ 2.37 (s, 3H, CH3Ph), δ 1.38 (t, J=7.2 Hz, 3H, CH3CH2O), δ 1.31 (t, J=7.2 Hz, 3H, CH3CH2O); 13C NMR (75 MHz, CDCl3): δ 168.18, 165.17, 148.88, 141.07, 130.66, 129.82, 126.76, 116.34, 61.87, 60.94, 29.80, 14.29, 14.14; GCMS (EI, 70 eV): m/z (%): 262 (70, M +), 247 (11), 234 (11), 217 (27), 189 (61), 161 (64), 146 (19), 115 (100), 91 (21), 69 (55); HRMS (ESI): m/z =285.1097 Calculated for [(C13H18O4) Na]+, Observed 285.1092

(4f) diethyl 2-(4-(trifluoromethyl)phenyl)maleate
Yield- 93%; (Yellowish liquid).
IR (Neat): 1724, 1629 cm–1; 1H NMR (300 MHz, CDCl3): δ 7.72-7.59 (m, 4H, CH, Ar), δ 6.34 (s, 1H, COCH=CCO), δ 4.42 (q, J=7.2 Hz, 2H, CH2CH2O), δ 4.26 (q, J=7.2 Hz, 2H, CH2CH2O), δ 1.38 (t, J=7.2 Hz, 3H, CH3CH2O), δ 1.33 (t, J=7.2 Hz, 3H, CH3CH2O); 13C NMR (75 MHz, CDCl3): δ 167.29, 164.58, 147.17, 137.15, 129.39, 127.23, 126.08, 126.04, 120.08, 62.23, 61.34, 14.23, 14.07; GCMS (EI, 70 eV): m/z (%): 316 (29, M+), 271 (26), 243 (100), 215 (70), 199 (25), 170 (28), 151 (36), 120 (10), 69 (26); HRMS (ESI): m/z =339.0815 Calculated for [(C15H15O4F3) Na]+, Observed 339.0809.

(4g) diethyl 2-(pyridine-3-yl)maleate
Yield- 89%; (Yellowish liquid).
IR (Neat): 1724, 1629 cm–1; 1H NMR (300 MHz, CDCl3): δ 8.76 (d, J=1.8Hz, 1H, CH, Ar), δ 8.67-8.65 (m, 1H, CH, Ar), δ 7.86-7.82 (m, 1H, CH, Ar), δ 7.41-7.37 (m, 1H, CH, Ar), δ 6.35 (s, 1H, COCH=CCO), δ 4.43 (q, J=6.9 Hz, 2H, CH2CH2O), δ 4.26 (q, J=6.9 Hz, 2H, CH2CH2O), δ 1.38 (t, J=6.9 Hz, 3H, CH3CH2O), δ 1.33 (t, J=6.9 Hz, 3H, CH3CH2O); 13C NMR (75 MHz, CDCl3): δ 166.92, 164.44, 150.60, 147.40, 145.12, 134.60, 130.11, 123.92, 120.14, 62.32, 61.38, 14.22, 14.06; GCMS (EI, 70 eV): m/z (%): 249 (13, M+), 220 (78), 204 (55), 192 (16), 176 (91), 148 (100), 132 (25), 120 (18), 104 (56), 76 (33), 50 (24); HRMS (ESI): m/z =250.1074 Calculated for [(C13H15O4N) H]+, Observed 250.1070

(3a) 1H NMR
3a) MS

(3i) $^1$H NMR
(3i) MS

(3j) $^1$H NMR
(3j) MS

(3k) $^1$H NMR
(3k) MS

(3l) $^1$H NMR
(3I) $^{13}$C NMR

(3I) DEPT
(3l) HRMS

(4e) $^1$H NMR
(4e) $^{13}$C NMR

(4e) MS
(4e) HRMS

\[ \text{C}_{15} \text{H}_{10} \text{O}_4 \text{Na} = 285.1097 \]

-1.8882 ppm

(4f) ^1H NMR
(4f) $^{13}$C NMR

(4f) MS
(4f) HRMS

C_{15}H_{16}O_4F_3 \text{ Na} = 339.0815
-1.5693 \text{ ppm}

339.0609
R=61807

(4g) $^1$H NMR
(4g) $^{13}$C NMR

(4g) MS
6) References