A Dehydrogenative Cross-Coupling Reaction Between Aromatic Aldehydes or Ketones with Dialkyl $H$-Phosphonates for Formyl or Acylphenylphosphonates

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Supporting Information

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1. General Information:

All aldehydes were distilled or purified via flash chromatography prior to use. Unless otherwise indicated, other reagents were purchased from commercial distributors and used without further purification. $^{13}P$ NMR, $^{1}H$ NMR and $^{13}C$ NMR were recorded at 162 MHz, 400 MHz and 100 MHz respectively, using tetramethylsilane as an internal standard. Mass spectra were obtained on an HRMS-EI instrument. Flash column chromatography was performed over silica gel 200-300 mesh.

2. Optimization of the Reaction Conditions

Table S1. Screening of reaction conditions.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M] (mol%)</th>
<th>[O] (equiv)</th>
<th>[S] (mL)</th>
<th>Yield (%)$^{[b]}$</th>
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<td>1</td>
<td>Cu(OTf)$_2$(10)</td>
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<td>CH$_3$CN:H$_2$O(2.5:2.5)</td>
<td>63</td>
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[a] Conditions: 1a 0.5mmol, 2a 1mmol, 100°C, 1.5h; [b] Isolated yields.
3. $^{31}$P NMR, $^1$H NMR, $^{13}$C NMR, and HR-MS Spectra of Products

$^{31}$P NMR Spectrum of diethyl formylphenylphosphonate 3aa
$^1$H NMR Spectrum of diethyl 4-formylphenylphosphonate 3aa
$^{13}$C NMR Spectrum of diethyl 4-formylphenylphosphonate 3aa
Tolerance = 1.0 mDa  /  DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
45 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hxn-13 401 (2.474)
TOP MS El+

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<td>5546943.0</td>
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$^{13}$P NMR Spectrum of dimethyl formylphenylphosphonate 3ab
$^{1}$H NMR Spectrum of dimethyl 4-formylphenylphosphonate 3ab
$^{13}$C NMR Spectrum of dimethyl 4-formylphenylphosphonate 3ab
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hxf-14 403 (2.482)
TOF MS El+

Minimum: 1.0 10.0 50.0
Maximum: -1.5

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  Formula
214.0394 214.0395 -0.1 -0.5 5.0 5546929.0 C9 H11 O4 P
$^{13}$P NMR Spectrum of diethyl formyl-3-methoxyphenylphosphonate 3da
$^1$H NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate 3da
$^{13}$C NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate 3da
HR-MS Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate 3da

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
50 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hxl-17 570 (3.094)
TOF MS El+

Minimum: 1.0 10.0 50.0
Maximum: -1.5

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  Formula
272.0816  272.0814  0.2  0.7  5.0  5545824.5  C12  H17  O5  P
\(^{13}\text{P NMR Spectrum of diethyl formyl-2-methoxyphenylphosphonate 3ea}\)
$^1$H NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate 3ea
$^{13}$C NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate 3ea
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
50 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hnl-16.570 (3.094)
TOF MS El+

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<td>5546443.0</td>
<td>C12 H17 O5 P</td>
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$^{13}$P NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate 3fa
$^1$H NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate 3fa
$^{13}$C NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate 3fa
HR-MS Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate 3fA

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(s) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1  F: 1-1

hxf-19 379 (2.394)
TOF MS EI+ 1.78e+003

Minimum:
Maximum:  
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$^{13}$P NMR Spectrum of diethyl 2-fluoroformylphenylphosphonate $3\text{ga}$
$^1$H NMR Spectrum of (diethyl 2-fluoro-4-formylphenylphosphonate 3ga
$^{13}$C NMR Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate 3ga
HR-MS Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate 3ga

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50   H: 0-200   O: 0-6   F: 1-1   P: 0-1

260.0608  260.0614  -0.6  -2.3  5.0  5546105.0  C11 H14 O4 F P
$^{13}$P NMR Spectrum of diethyl acetylphenylphosphonate 3ja
$^1$H NMR Spectrum of diethyl 4-acetylphenylphosphonate 3ja
$^{13}$C NMR Spectrum of diethyl 4-acetylphenylphosphonate 3ja
HR-MS Spectrum of diethyl 4-acetylphenylphosphonate 3j

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hxl-1 535 (2.666)
TOP MS El+

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<td>5546544.5</td>
<td>C12 H17 O4 P</td>
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$^{13}$P NMR Spectrum of dimethyl acetylphenylphosphonate 3jb
$^1$H NMR Spectrum of dimethyl 4-acetylphenylphosphonate \textbf{3jb}
$^{13}$C NMR Spectrum of dimethyl 4-acetylphenylphosphonate $3jb$
HR-MS Spectrum of dimethyl 4-acetylphenylphosphonate 3jb

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
m/z 11 495 (2.819)

TOF MS El+

Minimum: 1.0 10.0 -1.5
Maximum: 50.0

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$^{13}$P NMR Spectrum of diisopropyl acetylphenylphosphonate 3jc
$^1$H NMR Spectrum of diisopropyl 4-acetylphenylphosphonate 3je
$^{13}$C NMR Spectrum of diisopropyl 4-acetylphenylphosphonate 3je
S38 HR-MS Spectrum of diisopropyl 4-acetylphenylphosphonate

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
52 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-6  P: 0-1
hxf-12 502 (2.845)
TOF MS EI+

Minimum:
Mass    Calc. Mass mDa  PPM  DBE  i-FIT  Formula
284.1173  284.1177  -0.4  -1.4  5.0  5548386.0  C14 H21 O4 P
$^{31}$P NMR Spectrum of diethyl acetyl-2-methylphenylphosphonate 3ka
$^{1}H$ NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate 3ka
$^{13}$C NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate 3ka
HR-MS Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate 3ka
$^{13}$P NMR Spectrum of diethyl acetyl-3-fluorophenylphosphonate 3ma
$^{1}$H NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate \textbf{3ma}
$^{13}$C NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate 3ma
HR-MS Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate 3ma

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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hxf-5 602 (3.212)
TOF MS El+

Minimum: 10.00
Maximum: 100.00

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$^{13}$P NMR Spectrum of diethyl acetyl-2-fluorophenylphosphonate 3na
$^1$H NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate 3na
$^{13}$C NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate 3na
HR-MS Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate 3na

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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m/z 600 (3.204)
TOF MS El+

Minimum: 1.0  10.0  50.0
Maximum: -1.5

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$^{13}$P NMR Spectrum of diethyl acetyl-3-chlorophenylphosphonate 30a
$^1$H NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate 30a
$^{13}$C NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate 30a
HR-MS Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate 30a
HMBC Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate 3oa
$^{13}$P NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate $3pa$
$^1$H NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate 3pa
$^{13}$C NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate 3pa
HR-MS Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate
$^{13}$P NMR Spectrum of diethyl acetyl-3-bromophenylphosphonate 3qa
$^1$H NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate 3qa
$^{13}$C NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate 3qa
HR-MS Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
77 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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hxd-9 651 (3.391)
TOF MS El+

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$^{13}$P NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate 3sa
\(^1\)H NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate 3sa
$^{13}$C NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate 3sa
HR-MS Spectrum of diethyl 5,6,7,8-tetrahydro-5-oxo-2-naphthalenylphosphonate 3a
HMBC Spectrum of diethyl 5,6,7,8-tetrahydro-5-oxo-2-naphthalenylphosphonate 3sa
$^{13}$P NMR Spectrum of diethyl butanoylphenylphosphonate 3ua
$^1$H NMR Spectrum of diethyl 4-butoxoyphenylphosphonate 3ua
$^{13}$C NMR Spectrum of diethyl 4-butanoylphenylphosphonate 3ua
HR-MS Spectrum of diethyl 4-butanoylphenylphosphonate

Tolerance = 0.4 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50  H: 0-200  O: 0-5  P: 0-1

m/z 284.1178

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