Supporting Information for:

Horner–Wadsworth–Emmons (HWE) reactions in THF: effect of hydroperoxide species

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1. General information

NMR spectra were obtained in the solvent indicated, using a JEOL ECX400 or JEOL ECS400 spectrometer (400MHz for $^1$H, 100 MHz for $^{13}$C and 162 MHz for $^{31}$P). Chemical shifts are reported in parts per million and were referenced to the residual undeuterated solvent of the deuterated solvent used (CHCl$_3$ $\delta$ = 7.26 and 77.16, CDHCl$_2$ $\delta$ = 5.31 and 53.80, (CHD)$_2$SO(CD$_3$)$_2$ $\delta$ 2.50 and 39.52, $^1$H and $^{13}$C respectively). All $^{13}$C NMR spectra were obtained with $^1$H decoupling. $^{31}$P NMR were externally referenced to H$_3$PO$_4$, and obtained with $^1$H decoupling. NMR spectra were processed using MestrNova software. For $^{13}$C NMR spectra the coupling constants are quoted to $\pm 1$ Hz. For the $^1$H NMR spectra the resolution varies from $\pm 0.15$ to $\pm 0.5$ Hz; the coupling constants have been quoted to $\pm 0.5$ Hz in all cases for consistency.

Melting points were recorded using a Stuart digital SMP3 machine. IR spectroscopy was undertaken using a Jasco/MIRacle FT/IR-4100typeA spectrometer using an ATR attachment on solid and liquid compounds; KBr IR spectra were obtained on a Nicolet Avatar 370 FT IR spectrometer. The relative intensities of the peaks are denoted by (s) = strong, (m) = medium and (w) = weak, whilst (br) is used to describe broad peaks. MS spectra were measured using a Bruker Daltronics microTOF MS, Agilent series 1200LC with electrospray ionisation (ESI) or on a Thermo LCQ using electrospray ionisation, with <5 ppm error recorded for all HRMS samples. Mass spectral data is quoted as the $m/z$ ratio along with the relative peak height in brackets (base peak = 100).

TLC analysis was carried out on Merck TLC aluminium sheets (silica gel 60 F254) and visualised with UV light (254 nm), iodine vapour or an aqueous solution of potassium permanganate. All column chromatography was run on silica gel 60 using the solvent systems specified in the text. The fraction of petroleum ether used was 40-60.

Dry and degassed solvents were used were indicated in the text. Dry and degassed CH$_2$Cl$_2$ was obtained from a Pure Solv MD-7 solvent purification system. THF was either obtained from a Pure Solv MD-7 solvent purification system and degassed by
the freeze-pump-thaw method or purged with N\textsubscript{2} under sonication, or dried over sodium-benzophenone ketyl and collected by distillation. All air sensitive procedures were carried out using Schlenk techniques. Nitrogen gas was oxygen free and was dried immediately prior to use by passage through a column containing sodium hydroxide pellets and silica. Room temperature was between 13-25 °C. Commercial chemicals were purchased from Sigma-Aldrich and Alfa Aesar and used directly unless stated in the text. Brine refers to a saturated aqueous solution of NaCl. Compounds 2,\textsuperscript{i} 3,\textsuperscript{i} 6\textsuperscript{ii} and tetrahydrofuran-1-ol\textsuperscript{iii} were prepared according to literature procedures. The tetrahydrofuran-1-ol was obtained as a 90% pure product (by \textsuperscript{1}H NMR) and used without further purification.

Microwave reactions were carried out using a CEM Discover S-class instrument (maximum limits set for Power = 150 W and Pressure = 250 psi).
Closed system preparation of dbaTHIOPHOS previously described in A. G. Jarvis, A.

**Microwave method**

1,3-Bis(phosphonato)acetone (2) (128 mg, 1 eq., 0.39 mmol) was added to a stirring
solution of compound 3 (250 mg, 2 eq., 0.78 mmol) in THF (2 mL). To this NaOH
(62 mg, 4 eq., 1.56 mmol) dissolved in H₂O (0.25 mL) was added dropwise. The
mixture was heated in a microwave for 1.5 h at 110 °C. After cooling, the solution
was washed with saturated NH₄Cl(aq) (3 mL) and extracted with EtOAc (4x 5 mL).
The organic phases were combined and then dried over Na₂SO₃ and filtered. After
removing the solvent *in vacuo* the product was purified by column chromatography
on silica gel eluting with EtOAc:toluene (5:95 v/v) to afford dbaTHIOPHOS, **1** (172
mg, 67%).

A repeat of the reaction using 1.2 eq. of 1,3-bis(phosphonato)acetone, **2** (154 mg, 0.47
mmol) and only heating for 1h gave an 80% yield of dbaTHIOPHOS (206 mg).

Characterisation matches the literature.' 1H NMR (400 MHz, CD₂Cl₂) δ 8.17 (d,
3JHH = 16.0 Hz, 2H, He), 7.84-7.69 (m, 10H, He and o-Ar), 7.64-7.57 (m, 2H, Hf),
7.56-7.49 (m, 4H, p-Ar), 7.49-7.41 (m, 8H, m-Ar), 7.34 (tdd, J = 7.5, 2.5, 1.5 Hz, 2H,
Hg), 7.09 (ddd, 3JHP = 14.5 Hz, JHH = 8.0, 1.0 Hz, 2H, Hh), 6.48 (d, 3JHH = 16.0
Hz, 2H, Hb); 13C NMR (100 MHz, CD₂Cl₂) δ 188.6 (C=O), 141.5 (d, 3JCP = 8 Hz,
Cc), 138.9 (d, 2JCP = 7 Hz, Cd), 133.9 (d, 1JCP = 83 Hz, ipso-C), 133.4 (d, 2JCP =
11 Hz, Ch), 132.7 (d, 2JCP = 11 Hz, o-Ar), 132.5 (d, 1JCP = 85 Hz, ipso-C), 132.4 (d,
$4\text{J}_{\text{CP}} = 3 \text{ Hz, Cf}$, 132.2 (d, $4\text{J}_{\text{CP}} = 3 \text{ Hz, p-Ar}$), 129.6 (d, $3\text{J}_{\text{CP}} = 12 \text{ Hz, Cg}$), 129.0 (d, $3\text{J}_{\text{CP}} = 13 \text{ Hz, m-Ar}$), 128.8 (d, $3\text{J}_{\text{CP}} = 10 \text{ Hz, Ce}$), 126.8 (Cb); $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) $\delta$ 42.07 (s); HRMS (ESI) m/z [$\text{MNa}$]$^+$ 689.1266 (calculated for C$_{41}$H$_{32}$NaOP$_2$S$_2$: 689.1262); LRMS (ESI) m/z (rel.%) 689.1 [$\text{MNa}$]$^+$ (100), 667.1 [$\text{MH}$]$^+$ (3).
2. Microwave studies

General microwave method.

The relevant phosphonate ester (0.65 mmol) was added to a stirring solution of the benzaldehyde, if using, in THF (3 mL). (Triethylphosphite was added at this point when used.) To this was added dropwise NaOH dissolved in H₂O (2.174 mmol in 0.35 mL to give a 6M solution). The mixture was heated in a microwave for 1 h at 110 °C in a 10 mL microwave tube. After cooling to ambient temperature the solution was washed with saturated NH₄Cl(aq) (5 mL) and extracted with EtOAc (5 x 5 mL). The combined organic phases were dried over Na₂SO₃ and filtered. Purification was carried out by column chromatography on silica gel to give the organic product(s).

\[(E)-4-(2-(diphenylphosphorothioyl)phenyl)-1-(tetrahydrofuran-2-yl)but-3-en-2-one, 4\]

1,3-Bis(phosphonato)acetone (2) (215 mg, 1.2 eq., 0.65 mmol) was added to a stirring solution of compound 3 (350 mg, 2 eq., 1.09 mmol) in THF (3 mL). To this NaOH (87 mg, 4 eq., 2.17 mmol) dissolved in H₂O (0.35 mL) was added dropwise. The mixture was heated in a microwave for 1.5 h at 110 °C. After cooling, the solution was washed with saturated NH₄Cl(aq) (5 mL) and extracted with EtOAc (5x 5 mL). The organic phases were combined and then dried over Na₂SO₃ and filtered. After removing the solvent in vacuo the product was purified by column chromatography on silica gel eluting with EtOAc:toluene (5:95 v/v) to afford dbaTHIOPHOS, 1 (88 mg, 25%) and the title compound as an off-white solid (71 mg, 25%). M.p. 152-154 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, 3JHH = 16.5 Hz, 1H, H₉), 7.87-7.78 (m, 4H, Ar), 7.73-7.68 (m, 1H, H₁), 7.57-7.43 (m, 7H, Hₖ, p-H and Ar), 7.29 (apparent tdd, 3JHH = 7.5, 2.5, 1.5 Hz, 1H, H₈), 7.03 (ddd, 3JHP = 14.5 Hz, JHH = 8.0, 1.5 Hz, 1H, H₉), 6.34 (d, 3JHH = 16.5 Hz, 1H, H₉), 4.09 (apparent quintet, 3JHH = 6.5 Hz, 1H, Ha),
3.80 (ddd, $J_{HH} = 8.0, 7.0, 6.5$ Hz, 1H, Hₐ), 3.70-3.64 (m, 1H, Hₐ), 2.60 (dd, $^2J_{HH} = 15.5$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, Hₗ), 2.46 (dd, $^2J_{HH} = 15.5$ Hz, $^3J_{HH} = 6.0$ Hz, 1H, Hₗ), 2.04-1.94 (m, 1H, Hₗ), 1.91-1.77 (m, 2H, Hₜ), 1.42-1.31 (m, 1H, Hₜ); $^{31}$P NMR (162 MHz, CDCl₃) δ 42.23 (s); $^{13}$C NMR (100 MHz, CDCl₃) δ 199.5 (Cf), 143.3 (d, $^3J_{CP} = 8$ Hz, Hₖ), 138.5 (d, $^2J_{CP} = 8$ Hz, Cᵣ), 133.6 (d, $^1J_{CP} = 83$ Hz, ipso-C), 133.1 (d, $^2J_{CP} = 11$ Hz, Cₗ), 132.60 (d, $^3J_{CP} = 11$ Hz, Ar), 132.56 (d, $^3J_{CP} = 11$ Hz, Ar), 132.2 (d, $^4J_{CP} = 3$ Hz, Cₗ), 132.2 (d, $^1J_{CP} = 84$ Hz, ipso-C), 132.1 (d, $^1J_{CP} = 85$ Hz, ipso-C), 132.1 (d, $^4J_{CP} = 3$ Hz, p-Ar), 132.0 (d, $^4J_{CP} = 3$ Hz, p-Ar), 131.7 (d, $^2J_{CP} = 10$ Hz, Cᵣ), 129.6 (Cᵣ), 129.4 (d, $^3J_{CP} = 12$ Hz), 128.9 (d, $^3J_{CP} = 13$ Hz, Ar), 128.8 (d, $^3J_{CP} = 13$ Hz, Ar), 128.6 (d, $^3J_{CP} = 9$ Hz, Cᵣ), 75.3 (Cd), 67.9 (Ca), 44.4 (Cₖ), 31.6 (Cb), 25.7 (Cc); HRMS (ESI) m/z 433.1380 [MH]$^+$ (calculated for C₂₆H₂₆OPS = 433.1386); LRMS (ESI) m/z (rel.%) 455 [MNa]$^+$ (80), 433 [MH]+$^+$ (100), 401 (4), 301 (4), 236 (7); IR (ATR, ν cm⁻¹): 2966 (w), 2861 (w), 1658 (br, m), 1583 (w), 1478(w), 1457 (w), 1435 (m), 1387 (w), 1311 (w), 1260 (w), 1184 (w), 1162 (m), 1120 (w), 1097 (m), 1059 (m), 1027 (m), 998 (m), 970 (m), 798 (br, m), 755 (m), 709 (s), 690 (s).

Crystals suitable for X-ray diffraction were grown by slow evaporation from 1,4-dioxane.

(E)-4-phenyl-1-(tetrahydrofuran-2-yl)but-3-en-2-one, 7

![Chemical structure](image)

The reaction was carried out following the general procedure. Purification by column chromatography on silica-gel eluting with EtOAc:petroleum ether (20:80 v/v) gave the title compound as a yellow oil (26 mg, 19%). $^1$H NMR (400 MHz, CDCl₃) δ 7.59-7.52 (m with underlying d, $^3J_{HH} = 16.0$ Hz, 3H, Hₖ and Ar), 7.43-7.32 (m, 3H, Hᵣ and Ar), 6.77 (d, $^3J_{HH} = 16.0$ Hz, 1H, Hₗ), 4.33 (apparent dq, $^1J_{HH} = 13.0, 6.5$ Hz, 1H, Hₗ), 3.89 (apparent dt, $^1J_{HH} = 8.5, 7.0$ Hz, 1H, Hₗ), 3.80-3.70 (m, 1H, Hₗ), 3.05 (dd, $^2J_{HH} = 15.5$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, Hₗ), 2.78 (dd, $^2J_{HH} = 15.5$ Hz, $^3J_{HH} = 6.0$ Hz, 1H, Hₗ), 2.21-2.09 (m, 1H, Hₗ), 1.98-1.88 (m, 2H, Hₕ), 1.61-1.47 (m, 1H, Hₗ), 1.31 (m, 1H, Hₗ); $^{13}$C NMR (100 MHz, CDCl₃) δ 198.6 (Cᵣ), 143.2 (Cᵣ), 134.6 (Cᵣ), 130.6 (Cᵣ), 129.1 (Ar), 128.5 (Ar),
126.6 (C_g), 75.6 (C_d), 68.0 (C_a), 46.9 (C_e), 31.7 (CH_2), 25.7 (CH_2); HRMS (ESI) m/z 239.1035 \ [MNa]^+ \) (calculated for C_{14}H_{16}NaO_2 = 239.1043), 217.1213 \ [MH]^+ \) (calculated for C_{14}H_{17}O_2 = 217.1223); IR (ATR, \ nu \ cm^{-1}): 2929 (w), 2865 (w), 1685 (m), 1653 (m), 1576 (w), 1495 (w), 1448 (m), 1380 (w), 1332 (w), 1180 (br, m), 1128 (w), 1046 (br, s), 977 (m), 918 (w), 748 (s), 690 (s).

1,3-Bis(tetrahydrofuran-2-yl)propan-2-one, 5

The reaction was carried out following the general procedure described. Purification by column chromatography on silica-gel eluting with EtOAc gave the title compound as a clear oil (11 mg, 8%, 1:1 mixture of diastereoisomers). \ ^1H \ NMR (400 MHz, CDCl_3) \ \delta \ 4.22 \) (apparent tdd, \ J_{HH} = 10.5, 7.0, 3.5 Hz, 2H, H_d), 3.88-3.81 (m, 2H, H_a), 3.76-3.63 (m, 2H, H_a), 2.77 (ddd, \ J_{HH} = 16.0 Hz, J_{HH} = 7.0, 2.5 Hz, 2H, H_e), 2.58 (ddd, \ J_{HH} = 16.0 Hz, J_{HH} = 5.5, 1.0 Hz, 2H, H_e), 2.15-2.04 (m, 2H, H_c), 1.93-1.82 (m, 4H, H_b), 1.46 (ddd, \ J_{HH} = 16.0, 12.0, 8.0 Hz, 2H, H_c). \ ^13C \ NMR (100 MHz, CDCl_3) \ \delta \ 207.9 (C_i), 207.8 (C_i), 75.04 (C_d), 75.02 (C_d), 67.95 (C_a), 67.95 (C_a), 49.5 (C_e), 49.4 (C_e), 31.6 (CH_2), 25.7 (CH_2); HRMS (ESI) m/z 221.1148 (calculated C_{11}H_{18}NaO_3 = 221.1148); IR (ATR, \ nu \ cm^{-1}): 2952 (br, w), 2877 (br, w), 1709 (br, m), 1458 (br, w), 1383 (br, w), 1240 (br, w), 1163 (br, w), 1029 (br, s), 982 (br, m), 855 (br, w).

\((E)-2\text{-oxo-4-phenylbut-3-enyl} \text{phosphonic acid}, 8\)

To a solution of 6 (300 mg, 1 eq., 1.06 mmol) in dry and degassed CH_2Cl_2 (10 mL) at 0 °C was added trimethylsilyliodide, TMSI (0.3 mL, 2 eq., 2.12 mmol). The solution was stirred overnight at r.t. MeOH (10 mL) was added and the solution stirred, before removal of the solvents in vacuo. This was repeated two further times. The resultant oily solid was stirred with CHCl_3; filtration afforded a pale brown solid, which was
dried in vacuo (234 mg, 98%). M.p. 139-145 °C; 1H NMR (400 MHz, DMSO-d6) δ 7.68 (dd, \( J_{HH} = 6.5, 3.0 \) Hz, 2H, Hf), 7.60 (d, \( J_{HH} = 16.0 \) Hz, 1H, Hb), 7.47-7.41 (m, 3H, Hg and Hh), 6.94 (d, \( J_{HH} = 16.0 \) Hz, 1H, Hc), 6.59 (br s, OH), 3.21 (d, \( J_{HP} = 22.5 \) Hz, 2H, Ha); \(^{13}\)C NMR (100 MHz, DMSO-d6) δ 192.8 (d, \( J_{CP} = 5 \) Hz, Cb), 142.92, 134.40, 130.57, 129.03, 128.45, 126.69, 43.4 (d, \( J_{CP} = 122 \) Hz, Ca); \(^{31}\)P NMR (162 MHz, DMSO-d6) δ 15.6 (s); HRMS (ESI) m/z 227.0463 \([\text{MH}]^+\) (calculated for C\(_{10}\)H\(_{12}\)O\(_{4}\)P = 227.0468); IR (KBr, \( \nu \text{ cm}^{-1}\)): 3300-3000 (br, s), 2942 (s), 2905 (s), 2500 (br, m), 2256 (br, m), 1700 (w), 1621 (s, br), 1599 (s), 1576 (s), 1494 (w), 1450 (m), 1370 (w), 1344 (br, s), 1305 (w), 1265 (m), 1200 (br, s), 1153 (br, s), 976 (br, s), 949 (br, s), 885 (m), 866 (m), 822 (m), 750 (s), 686 (s), 655 (m), 525 (s).

Alkene additions

The following reactions were carried out following the general procedure described in section 2.7.3.1, using between 0.54 and 0.59 mmol of benzaldehyde (1 eq.), with the addition of alkenes (5 eq.). Analysis of the crude reactions mixtures was carried out using \(^{1}\)H NMR spectroscopy and mass spectrometry (ESI).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzaldehyde</th>
<th>Phosphonate</th>
<th>Eq.</th>
<th>NaOH, Eq.</th>
<th>Alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>Cyclohexene</td>
</tr>
<tr>
<td>2</td>
<td>Benzaldehyde</td>
<td>2</td>
<td>1.1</td>
<td>4</td>
<td>Cyclohexene</td>
</tr>
<tr>
<td>3(^a)</td>
<td>Benzaldehyde</td>
<td>2</td>
<td>1.1</td>
<td>4</td>
<td>Cyclohexene</td>
</tr>
<tr>
<td>4</td>
<td>Benzaldehyde</td>
<td>2</td>
<td>1.1</td>
<td>4</td>
<td>Norbornene</td>
</tr>
<tr>
<td>5</td>
<td>None</td>
<td>2</td>
<td>1 (0.652 mmol)</td>
<td>3.3</td>
<td>2,3-dimethylbut-2-ene</td>
</tr>
<tr>
<td>6(^b)</td>
<td>None</td>
<td>6</td>
<td>1 (0.652 mmol)</td>
<td>3.3</td>
<td>Cis-cyclooctene</td>
</tr>
</tbody>
</table>

\(^a\) Solvent: dioxane, \(^b\) alkene used as the solvent.
Alteration of the base

The following reactions were carried out following the general procedure, using the phosphonate esters stated in the table below (1 eq., 0.65 mmol). Purification of the products was carried out by column chromatography on silica-gel eluting with EtOAc for 2, and EtOAc:petroleum ether (20:80 v/v) for 6.

<table>
<thead>
<tr>
<th>Phosphonate ester</th>
<th>Base</th>
<th>Base, Eq</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>NaOH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>1.7</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>3.3</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>NEt₃</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NaOMeᵃ</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NaOEtᵇ</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NaOH</td>
<td>3.3</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>NaOMe</td>
<td>3.3</td>
<td>21</td>
</tr>
</tbody>
</table>

ᵃ anhydrous conditions using dry and N₂ purged THF.

Triethyl phosphite reactions

Triethyl phosphite and NaOH (6M) in dioxane was subject to microwave irradiation at 110 °C. After 1 h, ³¹P NMR spectroscopic analysis of the crude mixture revealed that none of the triethyl phosphite had been oxidised under the reaction conditions. ³¹P NMR (Dioxane, 400 MHz) δ 137.88.

The following reactions were carried out following the general procedure, using 2-(diphenylthiophosphino)benzaldehyde, 3 (1.67 eq., 0.37 mmol) and 1,3-bis(diethoxyphosphonato)-acetone, 2 (1.0 eq.) in THF (1.5 mL).

<table>
<thead>
<tr>
<th>Entry</th>
<th>P(OEt)₃, Eq.</th>
<th>P(OEt)₃:PO(OEt)₃ ratio by ³¹P NMR</th>
<th>Yield 4 (1), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1:0.2</td>
<td>19 (33)</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1:0.5</td>
<td>17 (22)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-</td>
<td>14 (17)ᵃ</td>
</tr>
</tbody>
</table>

ᵃ conventionally heated reaction, reflux, 48 h, using 0.65 mmol 2.
Formation of 1,3-Bis(tetrahydrofuran-2-yl)propan-2-one, 5 using 2-hydroxytetrahydrofuran.

1,3-Bis(phosphonato)acetone (2) (215 mg, 1.2 eq., 0.652 mmol) was added to a stirring solution of tetrahydrofuran-2-ol (96 mg, 2 eq., 1.09 mmol) in THF (3 mL). To this was added dropwise NaOH (87 mg, 4 eq., 2.17 mmol) dissolved in H2O (0.35 mL). The mixture was heated in a microwave for 1 h at 110 °C. After cooling, the solution was washed with saturated NH4Cl(aq) (5 mL), extracted with EtOAc (5 x 5 mL), dried over Na2SO3 and filtered. After removal of the solvent in vacuo the product was purified by column chromatography on silica gel eluting with EtOAc to afford 5 as a clear oil (60 mg, 56%). The product exhibited identical characterisation data as that given above.

Competition reaction between 2-(diphenylthiophosphino)benzaldehyde, 3 and tetrahydrofuran-2-ol.

Tetrahydrofuran-2-ol (22 mg, 90% pure, 1 eq., 0.224 mmol) and 2-(diphenylthiophosphino)benzaldehyde, 3 (72 mg, 1 eq., 0.244 mmol) were added to a solution of 1,3-bis(ethoxyphophonato)acetone, 2 (74 mg, 1 eq., 0.224 mmol) in THF (1.5 mL). A NaOH solution (30 mg in 0.12 mL H2O, 6M) was added dropwise. The mixture was then heated in a microwave for 1 h at 110 °C. After cooling, the solution was washed with saturated NH4Cl(aq) (5 mL), extracted with EtOAc (5 x 5 mL), dried over Na2SO3 and filtered. After removal of the solvent in vacuo the crude product was analysed by 1H NMR spectroscopy and mass spectrometry (ESI). No dbaTHIOPHOS or phophonate ester was observed. 1,3-Bis(tetrahydrofuran-2-yl)propan-2-one, 5, (E)-4-(2-(diphenylphosphorothioyl)phenyl)-1-(tetrahydrofuran-2-yl)but-3-en-2-one, 4 and the 2-(diphenylthiophosphino)benzaldehyde, 3 were observed in a 0.18:0.30:0.53 ratio respectively.
3. NMR spectra

DbaTHIOPHOS, (1)

Figure 1: $^1H$ NMR spectrum of dbaTHIOPHOS (1) (400 MHz, CD$_2$Cl$_2$, 298 K).

Figure 2: $^{31}P$ NMR spectrum of dbaTHIOPHOS (1) (162 MHz, CD$_2$Cl$_2$, 298 K).
Figure 3: $^{13}$C NMR spectrum of dbaTHIOPHOS (1) (100 MHz, CD$_2$Cl$_2$, 298 K).

Phosphine sulfide THF addition product, 4

Figure 4: $^1$H NMR spectrum of 4 (400 MHz, CDCl$_3$, 298 K).
Figure 5: $^{31}$P NMR spectrum of 4 (162 MHz, 298 K, CDCl$_3$).

Figure 6: $^{13}$C NMR spectrum of 4 (CDCl$_3$, 100 MHz, 298 K).
Figure 7: $^{13}$C DEPT NMR spectrum of 4 (CDCl$_3$, 100 MHz, 298 K).

Figure 8: $^1$H COSY NMR spectrum of 4 (400 MHz, CDCl$_3$, 298 K).
Figure 9: $^1$H NOESY NMR spectrum of 4 (400 MHz, CDCl$_3$, 298 K).

Benzaldehyde THF addition product, 7

Figure 10: $^1$H NMR spectrum of 7 (400 MHz, CDCl$_3$, 298 K).
Figure 11: $^{13}$C NMR spectrum of 7 (CDCl$_3$, 100 MHz, 298 K).

Bis-THF addition product, 5

Figure 12: $^1$H NMR spectrum of 5 (400 MHz, CDCl$_3$, 298 K).
Figure 13: $^{13}$C NMR spectrum of 5 (CDCl$_3$, 100 MHz, 298 K).

Figure 14: $^{13}$C DEPT NMR spectrum of 5 (CDCl$_3$, 100 MHz, 298 K).
Figure 15: $^1$H COSY NMR spectrum of 5 (400 MHz, CDCl$_3$, 298 K).
Figure 16: $^1$H-$^{13}$C HSQC NMR spectrum of 5 (400 MHz, CDCl$_3$, 298 K).

Phosphonic acid, 8

Figure 17: $^1$H NMR spectrum of 8 (400 MHz, DMSO, 298 K).
Figure 18: $^{31}$P NMR spectrum of 8 (162 MHz, 298 K, DMSO).

Figure 19: $^{13}$C NMR spectrum of 8 (DMSO, 100 MHz, 298 K).
4. References

