Supporting information

Trimethylsilyl Halide-Promoted Michaelis-Arbuzov Rearrangement

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Experimental procedure:

Reagents were from Aldrich. All solvents were distilled before use, and reactions were performed under N_2 atmosphere. All chromatography (flash) was performed with Merck Silicagel 60 (0.02-0.04 mm). TLC was performed with fluorescent Merck F254 glass plates. NMR spectra were recorded on a Brucker AC-300 (300.15 MHz for ^{1}H, 75.4 MHz for ^{13}C and 121.5 MHz for ^{31}P) in $CDCl_3$ unless stated. Chemical shifts (are given in ppm and the coupling constant *J* is expressed in Hertz. MS were obtained with a Finnigan-Mat 4600 quadrupole system (chemical ionization with NH_3). Flash column chromatography was performed on Merck silicagel (60Å, 230-400 mesh). Elemental analyses were recorded at the *Institut de Chimie des Substances Naturelles*, Gif sur Yvette.

Phosphites were either purchased when commercially available (Aldrich or STREM) or directly prepared from the corresponding phosphorus (III) chloride using conventional methodologies (reaction performed in dried diethyl ether using 1.0 equivalent of alcohol and 1.5 equivalents of dried triethyl amine; careful triethylammonium chloride filtration under an N_2 atmosphere and excess

reactant removal yielded phosphites which were used without further purification).

A typical reaction process could be summarized as follows: In a flame-dried nitrogen-flushed pressure-resistant reaction vessel, 5 mol% trimethylsilyl halide was added to pure phosphinite (respectively phosphonite or phosphite). The reaction vessel was then made airtight with a Teflon stopper, and after stirring under the reaction conditions described in the manuscript, the crude reaction mixture was cooled to room temperature, and was either recrystallized or submitted to silicagel column chromatography (using a 1/9 acetone/dichloromethane mixture as the eluting solution), yielding pure phosphine oxide (respectively phosphinate or phosphonate).

Methyl diphenylphosphine oxide (**2**): The reaction was performed on 300 µL of O-Methyl diphenyl phosphinite (1.5 mmoles) without solvent at 80°C, with 20% catalyst (40 µL TMSBr and 43 µL TMSI). The crude reaction mixture was recrystallized in cyclohexane, affording respectively 288 mg (TMSBr, 96%) and 276 mg (TMSI, 92%) (**2**) as white crystals: ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.73-7.66 (m, 4H), 7.49-7.40 (m, 6H), 1.98 (d, *J(H,P)* = 13 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 134.1, 133.0 (d, J(C,P) = 98Hz),132.7 (d, *J(C,P)* = 5Hz, 2C), 131.4 (d *J(C,P)* = 12Hz, 2C), 16.2 (d, *J(C,P)* = 75Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 30.4; MS (CI, NH_3) *m/z:* 217 $[M+H]^+$, 234 $[M + NH_4]^+$; M.P.: 109-111°C; elemental analysis calcd (%) for $C_{13}H_{13}OP$: C 72.22, H 3.06; found C 72.28, H 6.27.

***O-O*-dimethyl methylphosphonate** (**5**):. ^{1}H NMR (300.15 MHz, $CDCl_3$) : 3.68 (d, *J(H,P)* = 11 Hz, 6H), 1.41 (d, *J(H,P)* = 17.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) :53.2 (d, *J(C,P)* = 5.5 Hz), 4.90 (d, *J(C,P)* = 143 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 33.30; MS (CI, NH_3) *m/z*:125$[M+H]^+$, 142 $[M + NH_4]^+$.

Diethyl Benzyl phosphine oxide (**8a**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.22-7.11 (m, 5H), 3.00 (d, *J(H,H)* = 14.5 Hz, 2H), 1.53 (d of q *J(H,H)* = 7.5 Hz, *J(H,P)* = 11.5 Hz, 4H), 1.03 (d of t, *J(H,H)* = 7.5 Hz, *J(H,P)* = 15 Hz, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) :132.2 (d, *J(C,P)* = 7.5 Hz), 129.5 (d, *J(C,P)* = 4 Hz,

2C), 128.8 (2C), 126.8, 35.2 (d, *J(C,P)* = 59 Hz), 29.3, 19.6 (d, *J(C,P)* = 66 Hz), 5.6 (d, *J(C,P)* = 4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 50.29. MS (CI, NH_3) *m/z*: 197 $[M+H]^+$, 214 $[M + NH_4]^+$.

Benzyl diphenylphosphine oxide (**8b**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.74-7.67 (m, 4H), 7.55-7.42 (m, 6H), 7.22-7.20 (m, 2H), 7.19-7.09 (m, 3H), 3.65 (d, *J(H,P)* = 14 Hz, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 29.7; MS (CI, NH_3) *m/z:* 293 $[M+H]^+$, 310 $[M + NH_4]^+$.

Ethyl diphenylphosphine oxide (**11**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.78-7.71 (m, 4H), 7.53-7.45 (m, 6H), 2.30 (d of q, *J(H,P)* = 11.5 Hz, *J(H,H)* = 7.5 Hz, 2H), 1.20 (d of t, *J(H,P)* = 17.5 Hz, *J(H,H)* = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 133.2 (d, J(C,P) = 102 Hz),131.8, 131.0 (d, *J(C,P)* = 5Hz, 2C), 128.8 (d *J(C,P)* = 11.5Hz, 2C), 22.7 (d, *J(C,P)* = 73Hz), 18.9; ^{31}P NMR (121.5 MHz, $CDCl_3$) : 34.6; MS (CI, NH_3) *m/z:* 231 $[M+H]^+$, 248 $[M + NH_4]^+$.

1-phenylethyl diphenylphosphine oxide (**13**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.95-7.88 (m, 4H), 7.56-7.53 (m, 2H), 7.49-7.43 (m, 4H), 7.28-7.17 (m, 5H), 3.61 (quint *J(H,P)* = *J(H,H)* = 7.5 Hz, 1H), 1.60 (dd, *J(H,P)* = 7.5 Hz, *J(H,P)* = 16 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 138.2, 132.0 (d, J(C,P) = 125 Hz), 131.8, 131.5, 131.4, 131.3, 131.2, 129.3, 129.2, 128.8, 128.7, 128.3, 128.2, 128.0, 127.0, 41.0 (d, *J(C,P)* = 43Hz), 15.55; ^{31}P NMR (121.5 MHz, $CDCl_3$) : 34.0; MS (CI, NH_3) *m/z:* 307 $[M+H]^+$.

2-methoxybenzyl diphenylphosphine oxide (**15**): In a nitrogen-flushed reaction vessel, 100 µL chloro diphenyl phosphinite (0.56mmole) were diluted in 5 mL dry THF. 100 µL triethyl amine (0.8mmole) and 81 µL 2-methoxybenzyl alcohol (0.6 mmole) were successively added dropwise. After overnight stirring at room temperature, triethyl ammonium salts were filtered off under nitrogen (glove box), and rinsed with dry Et_2O. Solvents and remaining starting material were removed under vacuum. The crude reaction mixture was transferred to a flame-dried, nitrogen-flushed pressure-resistant reaction vessel, and 7 µL TMSBr were added. The reaction vessel was then made airtight with a Teflon stopper, and after stirring for 2 hours at 80°C, the crude reaction mixture was submitted to silicagel column chromatography (using a 1/9

acetone/dichloromethane mixture as the eluting solution), yielding 139 mg (77%) pure phosphinate (**15**) as a white powder. ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.72-7.65 (m, 4H), 7.46-7.33 (m, 7H), 7.11 (t, *J(H,H)* = 7.5 Hz, 1H), 6.83 (t, *J(H,H)* = 7.5 Hz, 1H), 6.62 (d, *J(H,H)* = 7.5 Hz, 1H), 3.73 (d of d, *J(H,P)* = 35 Hz, *J(H,H)* = 14 Hz, 2H), 3.41 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 156.85, 132.9 (d, J(C,P) = 92Hz),131.8 (d, *J(C,P)* = 5Hz), 131.7, 1328.2(d *J(C,P)* = 12Hz), 128.1, 120.6, 119.9 (d, *J(C,P)* = 7.5 Hz), 110.3, 54.9, 31.2 (*J(C,P)* = 68 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 30.55. MS (CI, NH_3) *m/z*: 323 $[M+H]^{+;}$ elemental analysis calcd (%) for $C_{20}H_{19}O_2P$: C 74.52, H 5.94; found C 74.52, H 5.99. 2-hydroxybenzyl diphenylphosphine oxide (**16**) was also recovered as a secondary product (19 mg, 9%), ^{1}H NMR (300.15 MHz, $CDCl_3$) : 9.87 (s, 1H), 7.81-7.72 (m, 4H), 7.56-7.45 (m, 6H), 7.11 (t, *J(H,H)* = 8.0 Hz, 1H), 7.02 (d, *J(H,H)* = 8.0 Hz, 1H), 6.88 (d, *J(H,H)* = 8.0 Hz, 1H), 6.72 (t, *J(H,H)* = 8.0 Hz, 1H), 3.75 (d, *J(H,P)* = 15 Hz, 2H); elemental analysis calcd (%) for $C_{19}H_{17}O_2P$: C 74.01, H 5.56; found C 73.89, H 5.55.

***O*-Ethyl ethylphenylphosphinate** (**18**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.75-7.68 (m, 2H), 7.52-7.39 (m, 3H), 4.09-3.99 (m, 1H), 3.87-3.74 (m, 1H), 1.95-1.74 (m, 2H), 1.23 (t, *J(H,H)* = 7.5 Hz, 3H), 1.04 (d of t, *J(H,H)* = 7.5 Hz, *J(H,P)* = 19 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 133.0 (d, *J(C,P)* = 93 Hz), 132.2, 131.6 (d, *J(C,P)* = 16.0 Hz), 128.6 (d, *J(C,P)* = 12 Hz), 60.6 (d, *J(C,P)* = 5 Hz), 22.8 (d, *J(C,P)* = 102 Hz), 16.5 (*J(C,P)* = 7.0 Hz), 5.9; ^{31}P NMR (121.5 MHz, $CDCl_3$) : 46.85; MS (CI, NH_3) *m/z*: 199 $[M+H]^+$, 216 $[M + NH_4]^+$; elemental analysis calcd (%) for $C_{10}H_{15}O2P$: C 60.60, H 7.62; found C 60.48, H 7.69

***O-O*-diethyl benzylphosphonate** (**21**): ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.31-7.28 (m, 5H), 4.05-3.95 (m, 4H), 3.15 (d, *J(H,P)* = 22 Hz, 2H), 1.23 (t, *J(H,H)* = 7.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 131.3, 129.8, 128.6, 128.4, 127.9, 126.9, 62.1 (d, *J(C,P)* = 7 Hz), 33.8 (d, *J(C,P)* = 137 Hz), 16.4 (d, *J(C,P)* = 5.5 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) : 26.95.

2-Phenyl-[1,2]oxaphospholane 2-oxide (**26**): In a nitrogen-flushed reaction vessel 500 mg phosphonamidite **23** (1.98 mmole) were diluted in 20 mL dried toluene. 500 µL 1-*H* tetrazole (3.5% solution in acetonitrile) and 144 µL (2

mmoles) 1,3-propanediol were successively added and the reaction mixture was stirred overnight at room temperature. The crude reaction mixture was then diluted with 100 mL degassed CH_2Cl_2, and washed twice with a degassed 5% $NaHCO_3$ aqueous solution. The organic phase was then dried ($MgSO_4$), concentrated under vacuum, and placed in a nitrogen-flushed pressure-resistant glass vessel. 28 µL TMSI (0.2 mmole) were then added, the reaction vessel was made airtight with a Teflon stopper, and the reaction mixture was stirred at 60°C for three days. Black and tarry crude material was then submitted to silica gel column chromatography (using a 1/9 acetone/dichloromethane mixture as the eluting solution), yielding 173 mg (48%) pure phosphinate (**26**) as a pale yellow oil. ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.83-7.76 (m, 2H), 7.58-7.55 (m, 1H), 7.53-7.47 (m, 2H), 4.63-4.55 (m, 1H), 4.39-4.30 (m, 1H), 2.49-2.42 (m, 1H), 2.33-2.26 (m, 1H), 2.23-2.11 (m, 1H), 2.07-1.98 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 132.6, 131.9 (d, *J(C,P)* = 97 Hz), 131.5 (d, *J(C,P)* = 11 Hz, 2C), 128.7 (d, *J(C,P)* = 13 Hz, 2C), 70.7, 25.8 (d, *J(C,P)* = 81 Hz), 24.6; ^{31}P NMR (121.5 MHz, $CDCl_3$) : 59.36. MS (CI, NH_3) *m/z*: 183 $[M+H]^+$, 200 $[M + NH_4]^+$; elemental analysis calcd (%) for $C_9H_{11}O_2P$: C 59.34, H 6.09; found C 59.48, H 6.35.

4,4-dimethyl 2-Phenyl-[1,2]oxaphospholane 2-oxide (**27**): In a nitrogen-flushed reaction vessel 666 mg phosphonamidite **23** (2.6 mmole) were diluted in 15 mL dried toluene. 200 µL 1-*H* tetrazole (3.5% solution in acetonitrile) and 275 mg (2.64 mmoles) neopentylglycol were successively added and the reaction mixture was stirred overnight at room temperature. Crude reaction mixture was then filtered in a glove box, diluted with 100 mL degassed CH_2Cl_2, and washed twice with a degassed 5% $NaHCO_3$ aqueous solution. The organic phase was then dried ($MgSO_4$) and concentrated under vacuum. The phosphonite (^{31}P NMR (121.5 MHz, $CDCl_3$) : 145.86) was placed in a nitrogen-flushed pressure-resistant glass vessel with 1.0 mL dry benzene. 36 µL TMSI (0.26 mmole) were then added, the reaction vessel was made airtight with a Teflon stopper, and reaction mixture was stirred at 60°C for three days. Black and tarry crude material was then submitted to silica gel column chromatography (using a 1/9 acetone/dichloromethane mixture as the eluting

solution), yielding 229 mg (42%) pure phosphinate (**27**) as a pale brown oil. ^{1}H NMR (300.15 MHz, $CDCl_3$) : 7.82-7.73 (m, 2H), 7.57-7.46 (m, 3H), 4.27 (dd, *J(H,P)* = 13 Hz, *J(H,H)* = 9.5 Hz, 1H), 3.97 (t, *J(H,P)* = *J(H,H)* = 9.5 Hz, 1H), 2..13 (t, *J(H,P)* = *J(H,H)* = 14 Hz, 1H), 1.91 (dd *J(H,P)* = 6 Hz, *J(H,H)* = 14 Hz, 1H), 1.40 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) : 132.6, 132.4 (d, *J(C,P)* = 110 Hz), 131.0 (d, *J(C,P)* = 9 Hz, 2C), 128.4 (d, *J(C,P)* = 12.5 Hz, 2C), 81.7, 39.6 (d, *J(C,P)* = 70.5 Hz), 27.2, 26.9; ^{31}P NMR (121.5 MHz, $CDCl_3$) : 59.94. MS (CI, NH_3) *m/z*: 211 $[M+H]^+$.