Supporting Information

Generation of Acyl Anion Equivalents from Acylphosphonates via Phosphonate-Phosphate Rearrangement: A Highly Practical Method for Cross Benzoin Reaction

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Table of Content

General Informations and general Procedures	S3-S4
Table 1. Products, Method and Yields of Cross-Benzoin reactions	S5-S6
Experimental Data for 3a	S6
Experimental Data for 3b, 3c	S7
Experimental Data for 3d, 3e, 3f	S8
Experimental Data for 3g, 3h	S9
Experimental Data for 3i, 3j	S10
Experimental Data for 3k, 3l, 3m	S11
Experimental Data for 3n, 3o	S12
Experimental Data for 3p, 3r	S13
Experimental Data for 3s, 3t, 3u	S14
Experimental Data for 5	S15
¹ H NMR spectra for 3a	S16
¹³ C NMR spectra for 3a	S17
¹ H NMR spectra for 3b	S18
¹³ C NMR spectra for 3b	S19
¹ H NMR spectra for 3c	S20
¹³ C NMR spectra for 3c	S21
¹ H NMR spectra for 3d	S22
¹³ C NMR spectra for 3d	S23
¹ H NMR spectra for 3e	S24
¹³ C NMR spectra for 3e	S25
¹ H NMR spectra for 3f	S26

¹³ C NMR spectra for 3f	S27
¹ H NMR spectra for 3g	S28
¹³ C NMR spectra for 3g	S29
¹ H NMR spectra for 3h	S30
¹³ C NMR spectra for 3h	S31
¹ H NMR spectra for 3i	S32
¹³ C NMR spectra for 3i	S33
¹ H NMR spectra for 3j	S34
¹³ C NMR spectra for 3j	S35
¹ H NMR spectra for 3k	S36
¹³ C NMR spectra for 3k	S37
¹ H NMR spectra for 3l	S38
¹³ C NMR spectra for 3l	S39
¹ H NMR spectra for 3m	S40
¹³ C NMR spectra for 3m	S41
¹ H NMR spectra for 3n	S42
¹³ C NMR spectra for 3n	S43
¹ H NMR spectra for 3o	S44
¹³ C NMR spectra for 3o	S45
¹ H NMR spectra for 3p	S46
¹³ C NMR spectra for 3p	S47
¹ H NMR spectra for 3r	S48
¹³ C NMR spectra for 3r	S49
¹ H NMR spectra for 3s	S50
¹³ C NMR spectra for 3s	S51
¹ H NMR spectra for 3t	S52
¹³ C NMR spectra for 3t	S53
¹ H NMR spectra for 3u	S54
¹³ C NMR spectra for 3u	S55
¹ H NMR spectra for 5	S56
¹³ C NMR spectra for 5	S57

General Information. DMF was purified by distillation under vacuum and stored over 4Å° Molecular Sieves. Toluene was freshly distilled from sodium-benzophenone. Purification of products was carried out by flash column chromatography using silica gel 60. Analytical thin layer chromatography was performed on aluminium sheets precoted with silica gel 60F₂₅₄. Visualization was accomplished with UV light and anisaldehyde or 2,4-dinitrophenylhydrazine followed by heating. ¹H-NMR spectra are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C-NMR spectra were recorded on a 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm). All aldehydes used in this study were commercially available and used without further purification. Acylphosphonates (**1**) were prepared according to well established procedures and purified by vacuum distillation.¹ All acylphosphonates were stored in flasks under nitrogen and they were stable at least for months. KCN was dried under vacuum at 100 °C. CsF was handled under nitrogen atmosphere and further dried under vacuum in the reaction flask prior to reaction. 18-crown-6 was recrystallized from acetonitrile and dried under vacuum at ambient temperature.

General Procedures for Cyanide Catalyzed Cross-Benzoin Reactions:

Reactions were carried out according to different procedures depending on the nature of substrates. All substrates and type of method used are summarized below in Table 1. Briefly reactions between aromatic acylphosphonates were carried out in DMF with 10% KCN catalysis (method A) and slight modifications in temperature (0 °C, method B) or catalyst load (30% KCN, method C) were made to optimize yields. Reactions between aromatic acylphosphonates and aliphatic aldehydes were carried out in DMF with CsF+TMSCN catalysis (method D) and reactions between aliphatic acylphosphonates and aromatic aldehydes were carried out in Toluene with 30% KCN and 30% 18-crown-6 as catalyst system (method E). Representative procedures are as follows:

Method A: To a solution of aromatic benzoylphosphonate (1 mmol) in 2 mL DMF under a positive nitrogen atmosphere was added aromatic aldehyde (1.1mmol, 1.1 equiv) and KCN (10%, 0.1 mmol)

1. (a) Maeda, H.; Takahashi, K.; Ohmori, H. *Tetrahedron* **1998**, *54*, 12233-12242. (b) Berlin, K. D.; Taylor, H. A. *J. Am. Chem. Soc.* **1964**, *86*, 3862-3866. (c) Kim, S.; Cho, C. H.; Lim, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9574.

successively and the resulting mixture was stirred at ambient temperature until the starting material was consumed (TLC analysis). To the reaction mixture was added 10 mL water and 10 mL Et₂O and organic phase was separated. The aqueous layer was washed with three 10 mL portions of Et₂O and combined organic extracts was washed with 20 mL of brine. The organic extract was dried (MgSO₄) and solvent was removed with a rotary evaporator. The product was purified by flash chromatography with a mixture of 1:3 petroleum ether/ether to obtain the product.

Method B: Method B is a slight modification of Method A. Reaction mixture was cooled to 0°C prior to addition of KCN (10%, 0.1 mmol) and stirred at this temperature until starting material was disappeared (TLC analysis). Then work-up and purification was carried out in the usual manner (Method A).

Method C: Method C is a slight modification of Method A. Reaction was carried out with 30% KCN at ambient temperature. Products were obtained following general procedure of method A.

Method D: CsF (20%, 0.2 mmol) was placed in a dry round bottom flask under a positive nitrogen atmosphere. DMF (1 mL) and TMSCN (30%, 0.3 mmol) were added successively via syringe and the mixture was stirred for 30 min at ambient temperature. Then a solution of aromatic acylphosphonate (1 mmol) and aliphatic aldehyde (1.1 mmol, 1.1 equiv) in 1 mL DMF was quickly added and the resulting mixture was stirred at ambient temperature until starting material was consumed (TLC monitoring, 5-10 min). Once starting material was consumed, crude mixture was worked-up following the procedure of Method A to obtain the products.

Method E: To a solution of KCN (30%, 0.03 mmol) and 18-crown-6 (30%, 0.03 mmol) in Toluene (5 mL) under a positive nitrogen atmosphere in a dry round bottom flask, aliphatic acylphosphonate (1 mmol) and aromatic aldehyde (2 mmol, 2 equiv) was successively added via syringe and mixture was heated to 100 °C until all starting material consumed (TLC monitoring, 4-6 h). To the reaction mixture was added 15 mL water and 15 mL Et₂O and layers were separated. The aqueous layer was washed with three 15 mL portions of Et₂O. The organic extracts were combined, dried (MgSO₄) and concentrated with a rotary evaporator. Crude product was purified by flash chromatography with a mixture of 1:1 to 1:3 petroleum ether/ether to afford the product.

Table 1. Products, Method and Yields of Cross-Benzoin reactions

entry	Acylphosphonate 1	Aldehyde 2	Product	Method	Yield (%) ^a
1				A	93
2				A	83
3				A	88
4				A	87
5				B	81 ^b
6				C	85
7				B	86
8				C	89
9				A	87
10				A	93
11				C	91
12				C	94

13				D	87
14				D	81
15				D	85
16				D	81
17				D	75
18				D	77
19				E	64
20				E	87

^a Isolated yields. ^b Impure product due to product decomposition during chromatographic purification.

Diethyl 1-(4-methoxyphenyl)-2-oxo-2-phenylethyl phosphate (3a): The title compound was prepared according to Method A using 242 mg (1 mmol) of acylphosphonate, 149.8 mg (1.1 mmol) of *p*-methoxybenzaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 15 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 350 (93%) mg of the product as a white solid (mp 58-60 °C); IR (CHCl₃) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.15 (3H, dt, *J*=0.8, 7.1 Hz), 1.25 (3H, dt, *J*=0.8, 7.1 Hz), 3.77 (3H, s), 3.85-4.0 (2H, m), 4.1-4.25 (2H, m), 6.6 (1H, d, *J*=7.9 Hz), 6.87 (2H, m), 7.3-7.4 (4H, m), 7.45-7.5 (1H, m), 7.9 (2H, d, *J*=7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 16.2 (d, *J*=7.1 Hz), 16.4 (d, *J*=6.9 Hz), 55.6, 64.2 (d, *J*=6.0 Hz), 64.6 (d, *J*=6.0), 80.0 (d, *J*=4.83 Hz), 114.9, 127.3 (d, *J*=5.1), 129.0, 129.3, 130.1, 133.8, 134.8, 160.8, 193.9 (d, *J*=4.9 Hz);

^{31}P NMR (161 MHz, CDCl_3) δ -1.19; Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_6\text{P}$: C, 60.31; H, 6.13. Found: C, 60.65; H, 6.11.

Diethyl 1-(4-fluorophenyl)-2-oxo-2-phenylethyl phosphate (3b): The title compound was prepared according to Method A using 242 mg (1 mmol) of acylphosphonate, 136.5mg (1.1 mmol) of *p*-fluorobenzaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 4 h at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 304 mg (83%) of the product as a colorless oil; IR (film) 2949, 2338, 1706, 1654, 1510, 1458, 1439, 1281, 1236, 1032, 943, 878cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (3H, dt, $J=0.8$, 7.1 Hz), 1.25 (3H, dt, $J=0.8$, 7.1 Hz), 3.80-3.90 (2H, m), 4.0-4.20 (2H, m), 6.54 (1H, d, $J=8.0$ Hz), 6.95-7.0 (2H, m), 7.32-7.47 (5H, m), 7-85 (2H,m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.8 (d, $J=6.7$ Hz), 16.0 (d, $J=6.9$ Hz), 64 (d, $J=6.2$ Hz), 64.3 (d, $J=6.0$ Hz), 75.1 (d, $J=4.7$ Hz), 116.1 (d, $J=22.0$ Hz), 128.7, 128.9, 139.0 (d, $J=8.6$ Hz), 163.2 (d, $J=249$ Hz), 193.5 (d, $J=5.0$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.33; Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{FO}_5\text{P}$: C, 59.02; H, 5.50. Found: C, 59.39; H, 5.52.

Diethyl 1-(3,5-dimethoxyphenyl)-2-oxo-2-phenylethyl phosphate (3c): The title compound was prepared according to Method A using 242 mg (1 mmol) of acylphosphonate, 182.8 mg (1.1 mmol) of 3,5-dimethoxybenzaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 15 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 359 mg (88%) of the product as a colorless oil; IR (film) 2965, 1691, 1507, 1443, 1435, 1283, 1229, 1036, 946, 875cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.18 (3H, dt, $J=0.9$, 7.0 Hz), 1.35 (3H, dt, $J=0.9$, 7.0 Hz), 3.75 (3H, s), 3.9-4.0 (2H, m), 4.14-4.20 (2H, m), 6.4 (1H, t, $J=2.2$ Hz), 6.50 (1H, d, $J=7.1$ Hz), 6.62(2H, d, $J=2.2$ Hz), 7.39 (2H, m), 7.51 (2H, m), 7.92 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 16.2 (d, $J=6.8$ Hz), 16.3 (d, $J=6.9$ Hz), 55.8, 64.4 (d, $J=6$ Hz), 64.6 (d, $J=6.0$ Hz), 80.5 (d, $J=4.7$ Hz), 101.5, 106.3, 129.0, 129.3, 133.9, 134.7, 137.2 (d, $J=5.6$ Hz), 161.6, 193.9 (d, $J=4.4$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -1.21; Anal. Calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_7\text{P}$: C, 58.82; H, 6.17. Found: C, 58.59; H, 6.32.

Diethyl 1-(naphthalen-1-yl)-2-oxo-2-phenylethyl phosphate (3d): The title compound was prepared according to Method A using 242 mg (1 mmol) of acylphosphonate, 172 mg (1.1 mmol) of 1-naphthaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 20 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 346 mg (87%) of the product as a colorless oil; IR (film) 2943, 1701, 1642, 1521, 1443, 1430, 1295, 1236, 1045, 940, 873 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.98 (3H, t, $J=7.1$ Hz), 1.37 (3H, t, $J=7.1$ Hz), 3.70-3.84 (2H, m), 4.20-4.34 (2H, m), 7.25-7.30 (2H, m), 7.31 (1H, d, $J=8.6$ Hz), 7.35-7.41 (2H, m), 7.49-7.53 (2H, m), 7.60-7.64 (1H, m), 7.71-7.79 (3H, m), 8.45 (1H, d, $J=8.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.6 (d, $J=6.9$ Hz), 16.0 (d, $J=7.3$ Hz), 63.9 (d, $J=6.2$ Hz), 64.4 (d, $J=6.1$ Hz), 78.2 (d, $J=5.5$ Hz), 123.5, 125.3, 126.3, 127.3, 128.2, 128.5, 128.6, 129.0, 130.5, 130.93, 130.98, 131.0, 133.4, 134.2, 134.6, 194.2 (d, $J=4.4$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.33; Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{O}_5\text{P}$: C, 66.33; H, 5.82. Found: C, 66.02; H, 5.55.

Diethyl 1-(furan-2-yl)-2-oxo-2-phenylethyl phosphate (3e): The title compound was prepared according to Method B using 242 mg (1 mmol) of acylphosphonate, 106 mg (1.1 mmol) of 2-furaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 25 min at 0 $^{\circ}\text{C}$, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 274 mg (81%, impure product due to product decomposition during chromatographic purification) of the product as a pale yellow oil; IR (film) 2965, 1685, 1503, 1454, 1436, 1289 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.17 (3H, dt, $J=0.8, 6.8$ Hz), 1.27 (3H, dt, $J=0.8, 7.2$ Hz), 3.89-3.99 (2H, m), 4.10-4.18 (2H, m), 6.30 (1H, m), 6.44 (1H, m), 6.65 (1H, d, $J=8.0$ Hz), 7.33-7.40 (3H, m), 7.45-7.52 (1H, m), 7.85-7.92 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9 (2C,m), 64.2 (2C,m), 73.2 (d, $J=4.4$ Hz), 111.1, 111.9, 128.7, 128.8, 133.6, 133.7, 144.2, 147.8 (d, $J=6.3$ Hz), 190.9 (d, $J=4.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.44.

Diethyl 2-(furan-2-yl)-2-oxo-1-phenylethyl phosphate (3f): The title compound was prepared according to Method C using 242 mg (1 mmol) of acylphosphonate, 106 mg (1.1 mmol) of 2-furaldehyde, 19.5 mg KCN (30 %, 0.3 mmol) and 2 mL of DMF. After 60 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 287 mg (85%) of the product as a pale yellow oil; IR (film)

2951, 1689, 1498, 1455, 1430, 1275 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (3H, t, $J=7.1$ Hz), 1.25 (3H, t, $J=7.1$ Hz), 3.82-3.91 (2H, m), 4.02-4.17 (2H, m), 6.35 (1H, d, $J=8.2$ Hz), 6.43 (1H, dd, $J=1.7$, 3.6 Hz), 7.22 (1H, d, $J=3.6$ Hz), 7.25-7.32 (3H, m), 7.40-7.50 (3H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 14.8 (d, $J=7.4$ Hz), 15.0 (d, $J=7.1$ Hz), 62.7 (d, $J=6.1$ Hz), 63.0 (d, $J=5.9$ Hz), 78.5 (d, $J=4.5$ Hz), 111.4, 118.1, 127.0, 127.7, 128.2, 133.7 (d, $J=4.9$ Hz), 145.7, 149.3, 181.0 (d, $J=4.6$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.45; Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_6\text{P}$: C, 56.81; H, 5.66. Found: C, 56.75; H, 5.54.

Diethyl 2-oxo-2-phenyl-1-(thiophen-2-yl)ethyl phosphate (3g): The title compound was prepared according to Method B using 242 mg (1 mmol) of acylphosphonate, 123 mg (1.1 mmol) of 2-thiophenecarboxaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 30 min at 0 °C, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 305 mg (86%) of the product as a pale yellow oil; IR (film) 2968, 1695, 1516, 1443, 1435, 1282 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.20 (3H, dt, $J=1$, 7 Hz), 1.31 (3H, dt, $J=1$, 7.9 Hz), 3.9-4.05 (2H, m), 4.1-4.25 (2H, m), 6.9 (1H, dj, $J=7.9$ Hz), 6.96 (1H, dd, $J=3.6$, 5.1 Hz), 7.17 (1H, dd, $J=1.1$, 3.6 Hz), 7.36 (1H, dd, $J=1.1$, 5.1 Hz), 7.4-7.44 (2H, m), 7.51-7.57 (1H, m), 7.95-7.9 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.73 (d, $J=7.3$ Hz), 15.85 (d, $J=6.8$ Hz), 63.9 (d, $J=6.3$ Hz), 64.3 (d, $J=5.9$ Hz), 74.7 (d, $J=4.2$ Hz), 127.2, 128.2, 128.6, 128.7, 128.9, 133.6, 134.0, 136.6 (d, $J=6.2$ Hz), 192.2 (d, $J=4.8$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.61; Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_5\text{PS}$: C, 54.23; H, 5.40. Found: C, 54.05; H, 5.26.

Diethyl 2-oxo-1-phenyl-2-(thiophen-2-yl)ethyl phosphate (3h): The title compound was prepared according to Method C using 242 mg (1 mmol) of acylphosphonate, 123 mg (1.1 mmol) of 2-thiophenecarboxaldehyde, 19.5 mg KCN (30 %, 0.3 mmol) and 2 mL of DMF. After 60 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 315 mg (89%) of the product as a white solid (mp 67.3-68.3 °C); IR (CHCl_3) 2969, 1685, 1516, 1456, 1435, 1278 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14 (3H, dt, $J=1.1$, 7.1 Hz), 1.29 (3H, dt, $J=1.0$, 7.0 Hz), 3.87-3.98 (2H, m), 4.10-4.21 (2H, m), 6.35 (1H, d, $J=8.2$ Hz), 7.055 (1H, dd, $J=3.9$, 4.9 Hz), 7.3-7.38 (3H, m), 7.51-7.54 (2H, m), 7.62 (1H, dd, $J=1.0$, 4.9 Hz), 7.79 (1H, dd, $J=1.0$, 3.9 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.7 (d, $J=7.0$ Hz), 15.92 (d, $J=7.3$ Hz), 64.0 (d, $J=6.1$ Hz), 64.28 (d, $J=5.9$ Hz), 80.8 (d,

$J=5.0$ Hz), 127.8, 128.2, 129.0, 129.3, 133.7, 134.6, 135.1 (d, $J=5.0$ Hz), 140.3, 186.6 (d, $J=4.9$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.52; Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_5\text{PS}$: C, 54.23; H, 5.40. Found: C, 54.12; H, 5.48.

Diethyl 2-(4-fluorophenyl)-2-oxo-1-phenylethyl phosphate (3i): The title

compound was prepared according to Method A using 260 mg (1 mmol) of acylphosphonate, 116.7 mg (1.1 mmol) of benzaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 15 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 319 mg (87%) of the product as a colorless oil; IR (film) 2947, 1698, 1651, 1515, 1449, 1432, 1278, 1230, 1035, 946, 881 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (3H, t, $J=7.1$ Hz), 1.27 (3H, t, $J=7.1$ Hz), 3.76-3.90 (2H, m), 4.03-4.17 (2H, m), 6.45 (1H, d, $J=8.1$ Hz), 6.93-7.00 (2H, m), 7.25-7.30 (3H, m), 7.35-7.41 (2H, m), 7.80-7.90 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9 (d, $J=7.3$ Hz), 16.1 (d, $J=6.6$ Hz), 63.8 (d, $J=6.1$ Hz), 64.2 (d, $J=5.9$ Hz), 80.1 (d, $J=4.8$ Hz), 115.8 (d, $J=21.6$ Hz), 128.0, 129.1, 129.3, 130.8 (d, $J=3.1$ Hz), 131.8 (d, $J=9.6$ Hz), 135.0 (d, $J=5.0$ Hz), 165.8 (d, $J=256$ Hz), 191.8 (d, $J=4.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.33; Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{FO}_5\text{P}$: C, 59.02; H, 5.50. Found: C, 59.15; H, 5.62.

Diethyl 2-(4-fluorophenyl)-1-(4-methoxyphenyl)-2-oxoethyl phosphate (3j):

The title compound was prepared according to Method A using 260 mg (1 mmol) of acylphosphonate, 149.8 mg (1.1 mmol) of *p*-methoxybenzaldehyde, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 25 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 368 mg (93%) of the product as a colorless oil; IR (film) 2986, 2839, 1698, 1601, 1512, 1461, 1443, 1257, 1177, 1159, 1044, 986 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.16 (3H, t, $J=7.0$ Hz), 1.33 (3H, t, $J=6.7$ Hz), 3.76 (3H, s), 3.88-3.96 (2H, m), 4.14-4.26 (2H, m), 6.58 (1H, d, $J=7.8$ Hz), 6.89 (2H, d, $J=8.7$ Hz), 7.05 (2H, m), 7.41 (2H, d, $J=8.7$ Hz), 7.94-7.98 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 16.2 (d, $J=6.9$ Hz), 16.3 (d, $J=6.9$ Hz), 55.6, 64.2 (d, $J=6.3$ Hz), 65.0 (d, $J=6.0$ Hz), 80.0 (d, $J=4.8$ Hz), 114.9, 116.1 (d, $J=22.0$ Hz), 127.1, 130.0, 131.1 (d, $J=2.9$ Hz), 132 (d, $J=9.2$ Hz), 160.8, 166.1 (d, $J=255$ Hz), 192.4 (d, $J=4.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -1.19; Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{FO}_6\text{P}$: C, 57.58; H, 5.59. Found: C, 57.31; H, 5.32.

Diethyl 2-(4-methoxyphenyl)-2-oxo-1-phenylethyl phosphate (3k): The title

compound was prepared according to Method C using 272 mg (1 mmol) of acylphosphonate, 116.7 mg (1.1 mmol) of benzaldehyde, 19.5 mg KCN (30 %, 0.3 mmol) and 2 mL of DMF. After 6 h at ambient temperature, the crude product was purified by flash chromatography with 1:4 petroleum ether/ether to afford 344 mg (91%) of the product as a colorless oil; IR (film) 2959, 1692, 1509, 1449, 1432, 1284, 1230, 1035, 940, 881 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14 (3H, t, $J=7.1$ Hz), 1.31 (3H, t, $J=7.1$ Hz), 3.82 (3H, s), 3.86-3.95 (2H, m), 4.13-4.22 (2H, m), 6.6 (1H, d, $J=8.1$ Hz), 6.86 (2H, d, $J=8.9$ Hz), 7.27-7.37 (3H, m), 7.45-7.55 (2H, m), 7.93 (2H, d, $J=8.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.7 (d, $J=7.0$ Hz), 15.9 (d, $J=7.0$ Hz), 55.4, 63.8 (d, $J=6.1$ Hz), 64.2 (d, $J=5.9$ Hz), 79.8 (d, $J=4.8$ Hz), 113.8, 127.1, 163.7, 191.9 (d, $J=4.8$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.33; Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_6\text{P}$: C, 60.31; H, 6.13. Found: C, 60.35; H, 6.09.

Diethyl 1-(4-fluorophenyl)-2-(4-methoxyphenyl)-2-oxoethyl phosphate (3l):

The title compound was prepared according to Method C using 272 mg (1 mmol) of acylphosphonate, 136.5 mg (1.1 mmol) of *p*-fluorobenzaldehyde, 19.5 mg KCN (30 %, 0.3 mmol) and 2 mL of DMF. After 6 h at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 372 mg (94%) of the product as a colorless oil; IR (film) 2993, 1693, 1601, 1511, 1261, 1173, 1037, 986 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.18 (3H, t, $J=7.1$ Hz), 1.33 (3H, t, $J=7.1$ Hz), 3.84 (3H, s), 3.89-3.98 (2H, m), 4.14-4.24 (2H, m), 6.60 (1H, d, $J=8.1$ Hz), 6.9 (2H, d, $J=8.8$ Hz), 7.06 (2H, m), 7.45-7.55 (2H, m), 7.93 (2H, d, $J=8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.8 (d, $J=7.1$ Hz), 16.0 (d, $J=7.0$ Hz), 55.4, 63.9 (d, $J=6.2$ Hz), 63.3 (d, $J=6$ Hz), 78.8 (d, $J=4.9$ Hz), 114, 116 (d, $J=22.1$ Hz), 130 (d, $J=8.2$ Hz), 131.3, 163.1 (d, $J=251$ Hz), 163.9, 191.7 (d, $J=4.9$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.30; Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{FO}_6\text{P}$: C, 57.58; H, 5.59. Found: C, 57.52; H, 5.61.

1-Cyclohexyl-2-oxo-2-phenylethyl diethyl phosphate (3m): The title compound

was prepared according to Method D using 242 mg (1 mmol) of acylphosphonate, 123.4 mg (1.1 mmol) of cyclohexanecarboxaldehyde, 30 mg CsF (20 %), 29.7 mg

TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 308 mg (87%) of the product as a colorless oil; IR (film) 2931, 1696, 1648, 1515, 1453, 1281, 1232, 1029 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.07-1.34 (11H (2CH₃ + 5H), m), 1.55-1.75 (5H, m), 1.91 (1H, m), 4.04-4.17 (4H, m), 5.38-5.41 (1H, m), 7.45-7.49 (2H, m), 7.56-7.60 (1H, m), 7.95 (2H, m); ^{13}C NMR (CDCl_3) δ 15.8 (d, $J=7.3$ Hz), 15.9 (d, $J=7.1$ Hz), 25.5, 25.7, 25.8, 27.0, 29.1, 41.0 (d, $J=7.0$ Hz), 63.8 (2C, m), 82.1 (d, $J=6.2$ Hz), 128.4, 128.6, 133.3, 135.3, 196.5; ^{31}P NMR (161 MHz, CDCl_3) δ -0.76; Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_5\text{P}$: C, 61.01; H, 7.68. Found: C, 61.14; H, 7.71.

1-Cyclohexyl-2-(4-fluorophenyl)-2-oxoethyl diethyl phosphate (3n): The title

compound was prepared according to Method D using 260 mg (1 mmol) of acylphosphonate, 123.4 mg (1.1 mmol) of cyclohexanecarboxaldehyde, 30 mg CsF (20 %), 29.7 mg TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:2 petroleum ether/ether to afford 302 mg (81%) of the product as a colorless oil; IR (film) 2936, 1706, 1652, 1511, 1462, 1293 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.05-1.25 (11H (2CH₃ + 5H), m), 1.50-1.70 (5H, m), 1.84 (1H, m), 3.98-4.10 (4H, m), 5.24-5.27 (1H, m), 7.06-7.10 (2H, m), 7.90-8.0 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.0 (2C, m), 24.7, 24.9, 26.5, 28.2, 29.9, 40.3 (d, $J=6.9$ Hz), 63.1 (2C, m), 81.5 (d, $J=6.1$ Hz), 114.9 (d, $J=21.7$ Hz), 130.4 (d, $J=9.2$ Hz), 130.9 (d, $J=3.1$ Hz), 164.9 (d, $J=254$ Hz), 194.3; ^{31}P NMR (161 MHz, CDCl_3) δ -1.85; Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{FO}_5\text{P}$: C, 58.06; H, 7.04. Found: C, 57.98; H, 7.15.

1-Cyclohexyl-2-(4-methoxyphenyl)-2-oxoethyl diethyl phosphate (3o): The

title compound was prepared according to Method D using 272 mg (1 mmol) of acylphosphonate, 123.4 mg (1.1 mmol) of cyclohexanecarboxaldehyde, 30 mg CsF (20 %), 29.7 mg TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 to 1:4 petroleum ether/ether to afford 327 mg (85%) of the product as a colorless oil; IR (film) 2981, 2852, 1688, 1648, 1596, 1511, 1263, 1237, 1029 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14-1.32 (11H (2CH₃ + 5H), m), 1.61-1.92 (6H, m), 3.87 (3H, s), 4.04-4.16 (4H, m), 5.31-5.35 (1H, m), 6.94 (2H, d, $J=8.9$ Hz), 8.0 (2H, d, $J=8.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9 (2C, m), 25.6, 25.9, 27.4, 29.2, 41.2, 41.3, 55.4, 63.9 (2C, m), 82.0 (d,

$J=6.0$ Hz), 114.0, 128.3, 131.0, 163.8, 195.0; ^{31}P NMR (161 MHz, CDCl_3) δ -1.95; Anal. Calcd. for $\text{C}_{19}\text{H}_{29}\text{O}_6\text{P}$: C, 59.37; H, 7.60. Found: C, 59.48; H, 7.48.

3-(Benzyloxy)-1-oxo-1-phenylpropan-2-yl diethyl phosphate (3p): The title compound was prepared according to Method D using 242 mg (1 mmol) of acylphosphonate, 165 mg (1.1 mmol) of benzyloxyacetaldehyde, 30 mg CsF (20 %), 29.7 mg TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 318 mg (81%) of the product as a colorless oil; IR (film) 2950, 2354, 1692, 1635, 1515, 1451 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.1-1.23 (6H, m), 3.8-3.83 (2H, m), 3.96-4.09 (4H, m), 4.43-4.52 (2H, m), 5.74-5.79 (1H, m), 7.14-7.23 (5H, m), 7.36-7.41 (2H, m), 7.49-7.53 (1H, m), 7.86-7.89 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9 (d, $J=2.76$ Hz), 16.0 (d, $J=2.79$ Hz), 64.12 (d, $J=6.0$ Hz), 64.2 (d, $J=6.0$ Hz), 70.4 (d, $J=6.1$ Hz), 73.4, 77.9 (d, $J=5.4$ Hz), 127.6, 127.8, 128.3, 128.8, (d, $J=3.0$ Hz), 133.6, 134.9, 137.3, 194.8 (d, $J=3.0$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.27; Anal. Calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_6\text{P}$: C, 61.22; H, 6.42. Found: C, 61.42; H, 6.64.

3-(Benzyloxy)-1-(4-fluorophenyl)-1-oxopropan-2-yl diethyl phosphate (3r): The title compound was prepared according to Method D using 260 mg (1 mmol) of acylphosphonate, 165 mg (1.1 mmol) of benzyloxyacetaldehyde, 30 mg CsF (20 %), 29.7 mg TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 308 mg (75%) of the product as a colorless oil; IR (film) 2946, 2347, 1696, 1647, 1507, 1452, 1280, 1231, 944, 877 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.15-1.25 (6H, m), 3.80-3.82 (2H, m), 3.95-4.08 (4H, m), 4.43-4.51 (2H, m), 5.64-5.68 (1H, m), 7.03-7.07 (2H, m), 7.14-7.25 (5H, m), 7.92-7.95 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.8 (d, $J=3.1$ Hz), 15.9 (d, $J=3.0$ Hz), 64.1 (d, $J=5.5$ Hz), 64.2 (d, $J=4.50$ Hz), 70.2 (d, $J=6.0$ Hz), 73.4, 77.8 (d, $J=5.3$ Hz), 115.8 (d, $J=21.9$ Hz), 127.6, 127.8, 128.3, 131.3 (d, $J=2.8$ Hz), 131.6 (d, $J=9.6$ Hz), 137.2, 166.0 (d, $J=256.3$), 193.5 (d, $J=3.3$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.24; Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{FO}_6\text{P}$: C, 58.54; H, 5.89. Found: C, 58.23; H, 5.77.

3-(Benzyloxy)-1-(4-methoxyphenyl)-1-oxopropan-2-yl diethyl phosphate

(3s): The title compound was prepared according to Method D using 272 mg (1 mmol) of acylphosphonate, 165 mg (1.1 mmol) of benzyloxyacetaldehyde, 30 mg CsF (20 %), 29.7 mg TMSCN (30%) and 2 mL of DMF. After 5-10 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 325 mg (77%) of the product as a colorless oil; IR (film) 2935, 2340, 1691, 1639, 1498, 1448 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.15-1.25 (6H, m), 3.75-3.81 (5H (OMe + 2H), m), 3.97-4.09 (4H, m), 4.45-4.52 (2H, m), 5.68-5.75 (1H, m), 6.85 (2H, d, $J=8.9$ Hz), 7.15-7.24 (5H, m), 7.87 (2H, d, $J=8.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9, 16.1, 55.5, 70.5, 70.6, 73.3, 77.5 (d, $J=5.9$ Hz), 113.9, 127.6, 127.7, 128.3, 131.2, 137.4, 164.0, 192.9 (d, $J=2.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ -2.24; Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{O}_7\text{P}$: C, 59.71; H, 6.44. Found: C, 59.51; H, 6.31.

2-Cyclohexyl-2-oxo-1-phenylethyl diethyl phosphate (3t): The title compound

was prepared according to Method E using 248 mg (1 mmol) of acylphosphonate, 212.2 mg (2 mmol) of benzaldehyde, 19.5 mg KCN (30 %, 0.3 mmol), 79 mg (30%, 0.3 mmol) 18-crown-6 and 5 mL of toluene. After 6 h at 100°C , the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 227 mg (64%) of the product as a colorless oil; IR (film) 2926, 1692, 1655, 1512, 1450, 1280, 1229, 1031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.16 (3H, dt, $J=0.9$, 7.2 Hz), 1.34 (3H, dt, $J=0.9$, 6.9 Hz), 1.10-1.45 (5H, m), 1.60-1.83 (5H, m), 2.50 (1H, m), 3.84-3.94 (2H, m), 4.11-4.21 (2H, m), 5.75 (1H, d, $J=8.1$ Hz), 7.30-7.40 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 15.9 (2C, m), 25.2, 25.6, 25.7, 28.0, 29.3, 29.7, 46.7, 64.1 (2C, m), 81.9 (d, $J=5.2$ Hz), 127.9, 128.9, 129.3, 134.5, 207.2; ^{31}P NMR (161 MHz, CDCl_3) δ -2.44; Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_5\text{P}$: C, 61.01; H, 7.68. Found: C, 61.24; H, 7.52.

Diethyl 3,3-dimethyl-2-oxo-1-phenylbutyl phosphate (3u): The title compound

was prepared according to Method E using 222 mg (1 mmol) of acylphosphonate, 272.3 mg (2 mmol) of p- methoxy benzaldehyde, 19.5 mg KCN (30 %, 0.3 mmol), 79 mg (30%, 0.3 mmol) 18-crown-6 and 5 mL of toluene. After 2.5 h at 100°C , the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 320 mg (87%) of the product as a colorless oil; IR (film) 2935, 1705, 1641, 1521, 1451, 1279, 1227, 1024 cm^{-1} ; ^1H NMR

(400 MHz, CDCl₃) δ 1.09 (9H,s), 1.13 (3H, t, $J=6.6$ Hz), 1.33 (3H, t, $J=6.7$ Hz), 3.81 (3H,s), 3.81-3.90 (2H,m), 4.11-4.17 (2H,m), 6.13 (1H, d, $J=7.4$ Hz), 6.89 (2H, d, $J=6.9$ Hz), 7.36 (2H, d, $J=7.0$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ 15.9 (2C,m), 26.9, 43.7, 55.3, 63.9 (2C,m), 77.9 (d, $J=5.1$ Hz), 114.3, 126.6 (d, $J=5.2$ Hz), 130.4, 160.5, 208.5; ³¹P NMR (161 MHz, CDCl₃) δ -2.66; Anal. Calcd. for C₁₆H₂₅O₅P: C, 58.53; H, 7.67. Found: C, 58.33; H, 7.44.

Diethyl 3,3,3-trifluoro-1-oxo-1,2-diphenylpropan-2-yl phosphate (5): The title

compound was prepared according to Method A using 242 mg (1 mmol) of acylphosphonate, 192 mg (1.1 mmol) of 2,2,2-Trifluoroacetophenone, 6.5 mg (10%, 0.1 mmol) KCN and 2 mL of DMF. After 30 min at ambient temperature, the crude product was purified by flash chromatography with 1:3 petroleum ether/ether to afford 362 (87%) mg of the product as a white solid (mp 94.9-95.3 °C); IR (CHCl₃) 2990, 2820, 1710, 1602, 1512 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.07 (3H, dt, $J=1.0, 7.1$ Hz), 1.20 (3H, dt, $J=1.0, 7.1$ Hz), 3.61-3.78 (2H, m), 3.93-4.09 (2H, m), 7.15-7.21 (2H, m), 7.32-7.37 (4H, m), 7.45-7.55 (2H, m), 7.60-7.63 (2H,m); ¹³C NMR (100 MHz, CDCl₃) δ 15.7 (d, $J=3.7$ Hz), 15.8 (d, $J=3.8$ Hz), 64.2 (d, $J=6.1$ Hz), 64.7 (d, $J=6.1$ Hz), 86.3 (d, $J=28$ Hz), 125.0 (q, $J=287$ Hz), 126.4, 128.0, 128.9, 130.0, 130.3, 132.1 (d, $J=10.4$ Hz), 133.0, 134.0, 189.6; ³¹P NMR (161 MHz, CDCl₃) δ -6.38; Anal. Calcd. for C₁₉H₂₀F₃O₅P: C, 54.81; H, 4.84. Found: C, 55.02; H, 4.90.