Supporting Information to Accompany:

Generation of Phosphoranes Derived from Phosphites. A New Class of Phosphorus Ylides Leading to High *E* Selectivity with Semi-Stabilizing Groups in Wittig Olefinations

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General Methods: Reactions requiring anhydrous conditions were performed in vacuum flame-dried glassware under a nitrogen atmosphere. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe or cannula into the reaction vessels through rubber septa. The ^1H and ^{13}C NMR spectra were recorded at the specified field strength using a Jeol JNM-GX 270 or 400 FT spectrometer. The ^{31}P NMR spectra were obtained on an Eclipse 300 FT spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm), referenced to TMS or to the residual solvent resonance. Coupling constants are quoted in Hertz (Hz). Chemical shifts in the ^{13}C NMR spectra are assigned as s, d, t, q for C, CH, CH_2 , and CH_3 . Degenerate peaks are prefixed by the number of carbons. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrometer. GC-MS analysis was performed using an Agilent 6890 apparatus equipped with a capillary column HP-5MS (HP190915-433, 5% Phenyl Methyl Siloxane, 30 m x 250 μm x 0.25 μm nominal) under the following conditions: helium 1 mL/min (constant flow mode), injector 250 $^\circ\text{C}$ (splitless mode), detector EI (Agilent MSD 5973), oven 70 $^\circ\text{C}$ (3 min), 15 $^\circ\text{C}/\text{min}$ (15.3 min), 300 $^\circ\text{C}$ (8 min) unless otherwise specified. Low resolution mass spectra (m/z) were recorded on either VG platform or VG Prospec spectrometers, with only molecular ions (M^+ or MH^+) and major peaks being reported with relative intensities quoted. High-resolution mass spectra were recorded on a VG Prospec spectrometer. Analytical TLC was performed on Merck Kieselgel 60F₂₅₄ aluminium plates which were visualised using standard visualising agents: phosphomolybdic acid/ Δ , potassium permanganate/ Δ , *para*-anisaldehyde/ Δ . Flash chromatography was performed using Kieselgel 60F₂₅₄, 40-63 micron silica gel. Anhydrous THF, toluene and acetonitrile were obtained from a purification column composed of activated alumina (A-2); see Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518. 1,4-Dioxane was distilled over sodium wire. Liquid aldehydes were dried and purified by standard procedures, as specified in 'Purification of Laboratory Chemicals'. D. D. Perrin and W. L. F. Armarego, Pergamon Press, **1988**, 3rd Ed. ClFeTPP was purchased from Aldrich. All other chemicals were purchased from Aldrich, Fluka or Lancaster.

Table 1. Effect of Different Phosphorus Reagents on Yield and Diastereoselectivity

Reagents and conditions: (a) ClFeTPP (0.01 eq), BnEt₃NCl (0.05 eq), PR₃ (1 eq), toluene, 40°C, 48 h.

Entry	PR ₃	Yield (%) ^a	<i>E/Z</i> ^a
1	P(<i>n</i> -Bu) ₃	30	96:4
2	P(Cy) ₃	14	89:11
3	P(OMe) ₃	74	82:18
4	P(OEt) ₃	78	73:27
5	P(<i>Oi</i> -Pr) ₃	51	80:20
6	P(OAr-3,5- <i>t</i> -Bu) ₃	16	57:43
7	(BnO) ₂ PN(Et) ₂	67	82:18
8	(BnO) ₂ PN(Me) ₂	76	76:24
9	PhP(OMe) ₂	73	68:32
10	Ph ₂ P(OMe)	70	82:18
11	Ph ₂ P(OEt)	51	93:7
12	PhP(OEt) ₂	85	79:21

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

Table 2. Solvent and Counterion Salt Effect on the Olefination Reactions

Reagents and conditions: (a) ClFeTPP (0.01 eq), BnEt₃NCl (0.05 eq), PR₃ (1 eq), solvent, 40°C, 48 h.

Entry	Salt	PR ₃	Solvent	Yield (%) ^a	E/Z ^a
1	Na	P(OMe) ₃	acetonitrile	66	83:17
2	Na	P(OMe) ₃	1,2-dichloroethane	49	70:30
3	Na	P(OMe) ₃	THF	50	85:15
4	Li ^b	P(OMe) ₃	1,4-dioxane	74	63:37
5	Li ^b	P(OMe) ₃	toluene	62	72:28
6	Li ^b	PPh ₃	toluene	91	55:45
7	Na	P(OMe) ₃	1,4-dioxane	73	87:13
8	Na	P(OMe) ₃	toluene	74	82:18
9	Na	PPh ₃	toluene	92	60:40
10	K ^c	P(OMe) ₃	1,4-dioxane	81	92:8
11	K ^c	P(OMe) ₃	toluene	74	94:6
12	K ^c	PPh ₃	toluene	90	62:38

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard. ^b *In situ* salt formation from benzaldehyde tosylhydrazone using LiHMDS as the base. ^c *In situ* salt formation from benzaldehyde tosylhydrazone using KHMDS as the base.

Investigation of alternative metal counterions of the hydrazone salt revealed that high *E* selectivity could be achieved when using the K⁺ salt. This is generally in accord with what is known in the literature regarding the effects of metal ions in Wittig reactions. In Wittig reactions Ward and EcEwen¹ showed that in most cases, the presence of lithium ions resulted in alkene formation favouring *Z* alkenes but increasing amounts of the *E* isomer were formed when sodium or potassium ions were present instead. Our results with phosphites also follow the same trends.

¹ Ward, W. J., Jr.; McEwen, W. E. *J. Org. Chem.* **1990**, *55*, 493-500.

Table 3. Counterion Salt Effect in the Olefination Reactions Using Different Phosphites

Entry	Salt	Solvent	Phosphite	Yield (%) ^a	E/Z ^a
1	K ^b	toluene	P(OMe) ₃	74	94:6
2	K ^b	toluene	P(OEt) ₃	88	81:19
3	K ^b	toluene	P(Oi-Pr) ₃	81	83:17

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard. ^b *In situ* salt formation from benzaldehyde tosylhydrazone using KHMDS as the base.

Table 4. Optimisation of Reaction Conditions

Reagents and conditions: (a) (i) 0.15M *t*-BuOK (1-1.5 eq) in toluene, 0°C to RT, 1 h. (ii) ClFeTPP, (0.01 eq), BnEt₃NCl (0-0.05 eq), P(OMe)₃ (1-1.2 eq), 40°C, 48 h.

Entry	PTC (mol%)	Hyd. (eq)	P(OMe) ₃ (eq)	Yield ^a (%)	E/Z ^a
1	5	1.0	1.0	64	94:6
2	5	1.0	1.2	70	93:7
3	5	1.2	1.0	88	94:6
4	5	1.2	1.2	87	95:5
5	5	1.2	1.5	80	87:13
6	5	1.5	1.2	68	95:5
7	5	1.5	1.5	95	96:4
8	-	1.5	1.5	65	80:20
9	-	1.2	1.2	61	81:19
10	2	1.2	1.2	99	87:13

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

In many cases it was difficult to reproduce exactly the same yields and ratios of olefin isomers. This was traced to the incomplete solubility of the PTC in toluene. Changing to Aliquat[®] 336 (tri-*n*-octylmethylammonium chloride) solved this problem.

Table 5. Olefination of a Range of Aldehydes with Benzaldehyde Tosylhydrazone

Reagents and conditions: (a) (i) 0.15M *t*-BuOK (1.2 eq) in toluene, 0°C to RT, 1 h. (ii) RCHO (1 eq), ClFeTPP (0.01 eq), Aliquat[®] 336 (0.1 eq), P(OMe)₃ (1.2 eq), 40°C, 48 h.

Entry	R	R'	Yield (%) ^a	E:Z ^b
1	4-ClC ₆ H ₄	Ph	92	97:3
2	4-MeOC ₆ H ₄	Ph	95	97:3
3	2,6-Me ₂ C ₆ H ₃	Ph	86	97:3
4	(<i>E</i>)-PhCH=CH	Ph	88	86:14
5	<i>c</i> -C ₆ H ₁₁	Ph	91	93:7
6	Ph	4-ClC ₆ H ₄	88	96:4
7	Ph	4-MeOC ₆ H ₄	84	98:2
8	Ph	4-CNC ₆ H ₄	79	84:16

^a Isolated yield after column chromatography. ^b Determined by GC-MS.

General Procedure for the Optimisation of the Olefination of Aldehydes Using Diazo Compounds Generated *in Situ* (Table 1, Table 2, Table 3 and Table 4)

A mixture of benzaldehyde tosylhydrazone sodium (lithium or potassium, 1 mmol) salt, PTC (benzyltriethylammonium chloride) (12 mg, 0.05 mmol), *p*-chlorobenzaldehyde (140 mg, 1 mmol), benzyltriethylammonium chloride, ClFeTPP (7 mg, 0.01 mmol) and the selected phosphorus reagent in the anhydrous solvent (4 mL) chosen was vigorously stirred for 48 h at 40°C. Benzyl ether (or 1-methyl naphthalene) was added to the resultant mixture, which was analysed by GC-MS.

Representative Procedure for the Olefination of Aldehydes Using Phenylhydrazomethane Generated *in Situ* (Table 5, entries 1-5).

A 0.15 M solution of potassium *tert*-butoxide in anhydrous toluene (8.0 mL, 1.20 mmol) was added to benzaldehyde tosylhydrazone (329 mg, 1.2 mmol) under an atmosphere of nitrogen at 0°C. The mixture was allowed to warm to RT and stirred for 1 h. Aliquat 336[®] (0.62 M solution in toluene, 162 μ L, 0.1 mmol), ClFeTPP (7 mg, 0.01 mmol), *p*-chlorobenzaldehyde (140 mg, 1.0 mmol), trimethylphosphite (142 μ L, 1.2 mmol), and anhydrous toluene (5.0 mL) were then added and the reaction vigorously stirred for 48 h at 40°C. Water (7.0 mL) was added to the mixture, which was then extracted with diethyl ether (3 $\times$ 15 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and evaporated under reduced pressure to give a dark brown residue. The crude material was purified by flash chromatography (petroleum ether) to afford the corresponding (*E*)-isomer (191 mg, 89%) and (*Z*)-isomer (6 mg, 3%).

Table 5, entry 1: **1-Chloro-4-[(*E*) and (*Z*)-2-phenyl-1-ethenyl]benzene.¹**

(*E*)-isomer; White solid; eluent petroleum ether, R_f = 0.30; m.p. 128-129°C (petroleum ether) (lit.,¹ 128°C); ¹H NMR (400 MHz, CDCl₃) δ 7.02 (1H, d, J = 16.6 Hz, CH=CH), 7.06 (1H, d, J = 16.6 Hz, CH=CH), 7.20-7.60 (9H, m, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 126.5 (2d), 127.3 (d), 127.6 (2d), 127.8 (2d), 128.7 (2d), 128.8 (2d), 129.3 (d), 133.1 (s), 135.8 (s), 137.0 (s); GC-MS retention time 13.95 min., m/z (EI) 214 (M^+ , 78), 178 (100), 152 (14), 89 (28), 76 (26).

(*Z*)-isomer; Colourless oil; eluent petroleum ether, R_f = 0.50; ¹H NMR (400 MHz, CDCl₃) δ 6.52 (1H, d, J = 12.2 Hz, CH=CH), 6.61 (1H, d, J = 12.2 Hz, CH=CH), 7.14-7.26 (9H, m, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 127.3 (d), 128.3 (2d), 128.4 (2d), 128.8 (2d), 128.9 (d), 130.2 (2d), 130.9 (d), 132.7 (s), 135.6 (s), 136.9 (s); GC-

¹ Ward, W. J., Jr.; McEwen, W. E. *J. Org. Chem.* **1990**, 55, 493-500.

MS retention time 12.39 min., m/z (EI) 214 (M^+ , 55), 178 (100), 152 (15), 89 (15), 76 (26).

Table 5, entry 2: **1-Methoxy-4-[(E) and (Z)-2-phenyl-1-ethenyl]benzene.**¹

(E)-isomer; White solid (92% yield); eluent petroleum ether/ethyl acetate 4:1, R_f = 0.53; m.p. 134-136°C (petroleum ether/ethyl acetate) (lit.,¹ 135°C); ¹H NMR (400 MHz, CDCl₃) δ 3.81 (3H, s, CH₃O), 6.90 (2H, d, J = 8.8 Hz, Ar), 6.98 (1H, d, J = 16.5 Hz, CH=CH), 7.07 (1H, d, J = 16.5 Hz, CH=CH), 7.21-7.26 (1H, m, Ar), 7.35 (2H, t, J = 7.3 Hz, Ar), 7.44-7.52 (4H, m, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 55.4 (q), 114.2 (2d), 126.3 (2d), 126.7 (d), 127.3 (d), 127.8 (2d), 128.3 (d), 128.7 (2d), 130.3 (s), 137.8 (s), 159.4 (s); GC-MS retention time 14.36 min., m/z (EI) 210 (M^+ , 100), 195 (17), 179 (13), 165 (46), 152 (31).

(Z)-isomer; (3% yield); GC-MS retention time 12.96 min., m/z (EI) 210 (M^+ , 100), 195 (17), 179 (15), 165 (77), 152 (52).

Table 5, entry 3: **1,3-Dimethyl-2-[(E) and (Z)-2-phenyl-1-ethenyl]benzene.**²

(E)-isomer; Colourless oil (83% yield); eluent petroleum ether, R_f = 0.35; ¹H NMR (400 MHz, CDCl₃) δ 2.37 (6H, s, 2 $\times$ CH₃), 6.61 (1H, d, J = 16.8 Hz, CH=CH), 7.08 (3H, m, Ar), 7.12 (1H, d, J = 16.8 Hz, CH=CH), 7.25-7.31 (1H, m, Ar), 7.38 (2H, t, J = 7.3 Hz, Ar), 7.49-7.54 (2H, m, Ar); ¹³C NMR (100 MHz, CDCl₃) δ 21.0 (2q), 126.3 (2d), 126.7 (d), 126.9 (d), 127.5 (d), 127.8 (2d), 128.7 (2d), 134.0 (d), 136.2 (2s), 136.9 (s), 137.6 (s); GC-MS retention time 13.13 min., m/z (EI) 208 (M^+ , 95), 193 (100), 178 (77), 165 (16), 130 (28), 115 (36).

¹ Ward, W. J., Jr.; McEwen, W. E. *J. Org. Chem.* **1990**, 55, 493-500.

² Derong, C.; Schollmeyer, D.; Meier, H. *Eur. J. Org. Chem.* **1999**, 4, 791-796.

(Z)-isomer; (3% yield); GC-MS retention time 11.85 min., m/z (EI) 208 (M^+ , 85), 193 (100), 178 (82), 130 (34), 115 (53).

Table 5, entry 4: **1-[(1E,3E) and (1E,3Z)-4-Phenyl-1,3-butadienyl]benzene**.³

(E)-isomer; Yellow solid (76% yield); eluent petroleum ether, R_f = 0.23; m.p. 148-150°C (petroleum ether) (lit.,³ 152-153°C); ^1H NMR (400 MHz, CDCl_3) δ 6.67 (2H, dd, J = 12.2 and 2.9 Hz, $\text{CH}=\text{CH}$), 6.96 (2H, dd, J = 12.2 and 2.9 Hz, $\text{CH}=\text{CH}$), 7.18-7.27 (2H, m, Ar), 7.28-7.48 (8H, m, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 126.4 (4d), 127.5 (2d), 128.6 (4d), 129.2 (2d), 132.8 (2d), 137.4 (2s); GC-MS retention time 14.53 min., m/z (EI) 206 (M^+ , 100), 191 (34), 128 (53), 91 (70).

(Z)-isomer; (12% yield); GC-MS retention time 13.70 min., m/z (EI) 206 (M^+ , 100), 191 (42), 128 (68), 91 (75).

Table 5, entry 5: **1-[(E) and (Z)-2-Cyclohexyl-1-ethenyl]benzene**.⁴

(E)-isomer; Colourless oil (85% yield); eluent petroleum ether, R_f = 0.61; ^1H NMR (400 MHz, CDCl_3) δ 1.10-1.43 (5H, m, $5 \times \text{CH}$), 1.64-1.88 (5H, m, $5 \times \text{CH}$), 2.07-2.18 (1H, m, $\text{CHCH}=\text{CH}$), 6.17 (1H, dd, J = 15.8 and 7.0 Hz, $\text{CHCH}=\text{CH}$), 6.34 (1H, d, J = 15.8 Hz, $\text{CHCH}=\text{CHPh}$), 7.14-7.21 (1H, m, Ar), 7.22-7.38 (4H, m, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 26.1 (t), 26.3 (2t), 33.1 (2t), 41.2 (d), 126.0 (2d), 126.8 (d), 127.3 (d), 128.5 (2d), 136.9 (d), 138.2 (s); GC-MS retention time 11.47 min., m/z (EI) 186 (M^+ , 28), 143 (13), 129 (30), 115 (25), 104 (100).

(Z)-isomer; (6% yield); GC-MS retention time 10.34 min., m/z (EI) 186 (M^+ , 10), 104 (86), 91 (100).

General Procedure for the Olefination of Aldehydes Using Substituted Diazo Compounds Generated *in Situ* (Table 5, entries 6-8 and anti-cancer compound).

A 0.15 M solution of potassium *tert*-butoxide in anhydrous toluene (8.0 mL, 1.20 mmol) was added to the tosylhydrazones (1.2 mmol) under an atmosphere of nitrogen at 0°C. The mixture was allowed to warm to RT and stirred for 1 h. Aliquat 336[®] (0.62 M solution in toluene, 162 μ L, 0.1 mmol), ClFeTPP (7 mg, 0.01 mmol), the aldehyde (1.0 mmol), trimethylphosphite (142 μ L, 1.2 mmol), and anhydrous toluene (5.0 mL) were then added and the reaction vigorously stirred for 48 h at 40°C. Water (7.0 mL) was added to the mixture, which was then extracted with diethyl ether (3 $\times$ 15 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and evaporated under reduced pressure to give a dark brown residue. The crude material was purified by flash chromatography to afford to give the pure products.

Table 5, entry 6: **1-Chloro-4-[(*E*) and (*Z*)-2-phenyl-1-ethenyl]benzene.**

(*E*)-isomer; White solid (85% yield). **(*Z*)-isomer**; Colourless oil (3% yield).

Compound characterisation data as earlier.

Table 5, entry 7: **1-Methoxy-4-[(*E*) and (*Z*)-2-phenyl-1-ethenyl]benzene.**

(*E*)-isomer; White Solid (82% yield). **(*Z*)-isomer**; (2% yield).

Compound characterisation data as earlier.

³ Sukakira, O. *J. Org. Chem.* **1976**, *41*, 2049-2052.

⁴ Wang, Z.; Zhang, I. G.; Verkade, J. G. *J. Org. Chem.* **2001**, *66*, 3521-3524.

Table 5, entry 8: **1-Cyano-4-[(E) and (Z)-2-phenyl-1-ethenyl]benzene.**⁵

(E)-Isomer; Yellow solid (66% yield); eluent petroleum ether/ethyl acetate 5:1, R_f = 0.40; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (1H, d, J = 16.6 Hz, $\text{CH}=\text{CH}$), 7.22 (1H, d, J = 16.6 Hz, $\text{CH}=\text{CH}$), 7.29-7.67 (9H, m, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 110.7 (s), 119.0 (s), 126.8 (d), 126.9 (2d), 127.0 (3d), 128.7 (d), 128.9 (2d), 132.5 (2d), 136.4 (s), 141.9 (s); GC-MS retention time 14.89 min., m/z (EI) 205 (M^+ , 100), 190 (33).

(Z)-Isomer; (13% yield); GC-MS retention time 13.52 min., m/z (EI) 205 (M^+ , 100), 204 (100), 190 (40), 156 (35), 109 (30) 89, (20).

3,5,4'-Trimethoxy-(E)-Stilbene.⁶

(E)-Isomer; White solid (79% yield); eluent DCM/petroleum ether 1:1, R_f = 0.17; m.p. 55-57°C (Dichloromethane) (lit.,⁶ 55-57°C); ^1H NMR (400 MHz, CDCl_3) δ 3.81 (3H, s, CH_3O), 3.82 (6H, s, 2 x CH_3O), 6.37 (1H, t, J = 2.2 Hz, Ar), 6.64 (2H, d, J = 2.2 Hz, Ar), 6.88 (2H, d, J = 8.8 Hz, Ar), 6.90 (1H, d, J = 16.2 Hz, $\text{CH}=\text{CH}$), 7.03 (1H, d, J = 16.2 Hz, $\text{CH}=\text{CH}$), 7.43 (2H, d, J = 8.8 Hz, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 55.3 (q), 55.4 (2q), 99.8 (d), 104.5 (2d), 114.3 (2d), 126.7 (d), 127.9 (2d), 128.9 (d), 130.1 (s), 139.8 (s), 159.5 (s), 161.1 (2s); GC-MS retention time 17.77 min., m/z (EI) 270 (M^+ , 100).

(Z)-Isomer; (2% yield); GC-MS retention time 16.04 min., m/z (EI) 270 (M^+ , 100).

⁵ Singh, A. K.; Kanvah, S. *J. Chem. Soc., Perkin Trans. 2*, **2001**, 395-401.

⁶ Kim, S.; Ko, H.; Park, J. E.; Jung, S.; Lee, S. K.; Chun, Y.-J.; *J. Med. Chem.* **2002**, 45, 160.

Table 6. Effect of Different Phosphorus Reagents on the Yield and Diastereoselectivity

Reagents and conditions: (a) ClFeTPP (0.01 eq), PR_3 (1 eq), toluene, 50°C, 48 h.

Entry	PR_3	Yield (%) ^a	E/Z ^a
1	PPh_3	44	96:4
2	P(OMe)_3	57	69:31
3	P(OEt)_3	36	73:27
4	P(Oi-Pr)_3	35	88:12
5	$(\text{BnO})_2\text{PN(Et)}_2$	22	86:14
6	$(\text{BnO})_2\text{PN(Me)}_2$	35	89:11
7	$\text{Ph}_2\text{P(OMe)}$	23	86:14
8	$\text{Ph}_2\text{P(OEt)}$	10	84:16
9	PhP(OEt)_2	11	82:18

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

Table 7. Salt Effect on the Olefination of Benzaldehyde with Trimethylphosphite

Reagents and conditions: (a) ClFeTPP (0.01 eq), salt (0-1 eq), P(OMe)_3 (1 eq), solvent, 50°C, 48 h.

Entry	Salt (eq)	Solvent	Yield (%) ^a	E/Z ^a
1	-	toluene	58	69:31
2	-	1,4-dioxane	46	64:36
3	KBr (1)	1,4-dioxane	36	81:19
4	NaBr (1)	1,4-dioxane	49	90:10
5	LiBr (1)	1,4-dioxane	54	97:3
6	LiBr (0.1)	1,4-dioxane	29	72:28
7	LiBr (0.5)	1,4-dioxane	22	95:5
8	LiBr (0.5)	THF	30	89:11
9	LiBr (0.5)	MeCN	28	87:13
10	LiBr (0.5)	toluene	27	89:11
11	LiBr (1) ^b	1,4-dioxane	65	97:3

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

^b EDA was added in one portion.

Table 8. Effect of Different Phosphorus Reagents and Temperature on the Yield and Diastereoselectivity

Reagents and conditions: (a) ClFeTPP (0.01 eq), LiBr (1 eq), PR₃ (1 eq), 1,4-dioxane, 48 h.

Entry	PR ₃	Temp. (°C)	Yield (%) ^a	E/Z ^a
1	P(OMe) ₃	50	65	97:3
2	P(OEt) ₃	50	37	88:12
3	P(Oi-Pr) ₃	50	39	88:12
4	PPh ₃	50	75	97:3
5	P(OMe) ₃	85	69	97:3

6	P(OEt) ₃	85	66	90:10
7	P(Oi-Pr) ₃	85	27	89:11

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

Table 9. Optimisation of Reaction Conditions

Reagents and conditions: (a) ClFeTPP (0.01 eq), LiBr (1 eq), P(OMe)₃ (1 eq), 1,4-dioxane, 85°C, 48 h.

Entry	EDA (eq)	P(OMe) ₃ (eq)	Yield (%) ^a	E/Z ^a
1	1.0	1.0	74	97:3
2	1.2	1.2	77	97:3
3	1.2	1.5	81	97:3
4	1.5	1.2	94	97:3

^a Calculated by GC-MS using 1-methylnaphthalene as an internal standard.

Table 10. Olefination of a Range of Aldehydes with EDA

Reagents and conditions: (a) ClFeTPP (0.01 eq), LiBr (1 eq), P(OMe)₃ (1.2 eq), EDA (1.5 eq), 1,4-dioxane, 85°C, 18 h.

Entry	R	Yield (%) ^a	E/Z ^b
1	Ph	86	96:4
2	4-MeOC ₆ H ₄	59	98:2
3	2,6-Me ₂ C ₆ H ₃	45	94:6
4	(E)-PhCH=CH	90	89:11

5	CH ₃ COC ₆ H ₄	75	95:5
6	4-ClC ₆ H ₄	90	96:4
7	PhCH ₂	92	90:10
8	<i>c</i> -C ₆ H ₁₁	82	94:6

^a Isolated yields. ^b Determined by GC-MS.

Table 11. Additive Effect on the Olefination of Benzaldehyde with Trimethylphosphite under Optimized Reaction Conditions.

Reagents and conditions: (a) ClFeTPP (0.01 eq), additive (1 eq), P(OMe)₃ (1.2 eq), 1,4-dioxane, 85°C, 48 h.

Entry	Additive	Yield (%) ^a	E/Z ^a
1	No salt	90	69:31
2	LiBr	94	97:3
3	LiBPh ₄	87	62:38
4	LiOTf	84	67:33
5	LiTs	95	73:27
6	LiI	90	95:5
7	NaI	88	94:6

^a Calculated by GC-MS using benzylether as an internal standard.

Table 12. Salt Effect on the Olefination of Benzaldehyde with Triethylphosphite

Reagents and conditions: (a) ClFeTPP (0.01 eq), salt (1 eq), P(OEt)₃ (1 eq), solvent, 85°C, 48 h.

Entry	Salt (eq)	Solvent	Yield (%) ^a	E/Z ^a
1	-	1,4-dioxane	26	80:20
2	LiBr	1,4-dioxane	62	83:17

^a Calculated by GC-MS using benzylether an internal standard.

General Procedure for the Optimization of the Olefination of Aldehydes Using Ethyl Diazoacetate.

Ethyl diazoacetate (114 μ L, 1 mmol) was added to a mixture of ClFeTPP (7 mg, 0.01 mmol), benzaldehyde (102 μ L, 1.0 mmol), the selected phosphorus reagent (1 mmol) and the corresponding additive in the anhydrous solvent (4 mL) chosen. The mixture was vigorously stirred for 48 h. Benzyl ether (or 1-methyl naphthalene) was added to the resultant mixture, which was analyzed by GC-MS.

Representative Procedure for the Olefination of Aldehydes Using Ethyl Diazoacetate (Table 10, entries 1-8).

Ethyl diazoacetate (173 μ L, 1.5 mmol) was added dropwise to a mixture of ClFeTPP (7 mg, 0.01 mmol), benzaldehyde (102 μ L, 1.0 mmol), trimethylphosphite (141 μ L, 1.2 mmol) and lithium bromide (86 mg, 1.0 mmol) in anhydrous 1,4-dioxane (3.0 mL) under an atmosphere of nitrogen at 85°C. After stirring for 18 h at 85°C, water (7.0 mL) was added to the mixture, which was then extracted with diethyl ether (3 $\times$ 15 mL). The combined organic extracts were dried over Na₂SO₄, filtered and evaporated under reduced pressure to give a dark brown residue. The crude material was purified by flash chromatography to afford the corresponding(*E*)-isomer (145 mg, 83%) and (*Z*)-isomer (3 mg, 4%).

Table 10, entry 1: **Ethyl (*E*) and (*Z*)-3-phenyl-2-propenoate.**⁷

⁷ Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, 67, 3096-3103.

(E)-Isomer; Colourless oil; eluent petroleum ether/ethyl acetate 19:1, $R_f = 0.45$; ^1H NMR (400 MHz, CDCl_3) δ 1.33 (3H, t, $J = 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 4.26 (2H, q, $J = 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 6.44 (1H, d, $J = 16.1$ Hz, $\text{CH}=\text{CHCO}$), 7.34-7.42 (3H, m, Ar), 7.49-7.56 (2H, m, Ar), 7.69 (1H, d, $J = 16.1$ Hz, $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.4 (q), 60.5 (t), 118.4 (d), 128.1 (2d), 128.9 (2d), 130.3 (d), 134.6 (s), 144.6 (d), 167.0 (s); GC-MS retention time 10.32 min., m/z (EI) 176 (M^+ , 28), 147 (17), 131 (100), 103 (50), 77 (33).

(Z)-Isomer; GC-MS retention time 9.55 min., m/z (EI) 176 (M^+ , 19), 147 (16), 131 (100), 103 (60), 77 (37).

Table 10, entry 2: **Ethyl (E) and (Z)-3-(4-methoxyphenyl)-2-propenoate.**⁷

(E)-Isomer; Colourless oil (58% yield); eluent petroleum ether/ethyl acetate 10:1, $R_f = 0.35$; ^1H NMR (400 MHz, CDCl_3) δ 1.33 (3H, t, $J = 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 3.83 (3H, s, CH_3O), 4.25 (2H, q, $J = 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 6.31 (1H, d, $J = 16.1$ Hz, $\text{CH}=\text{CHCO}$), 6.90 (2H, d, $J = 8.8$ Hz, Ar), 7.47 (2H, d, $J = 8.8$ Hz, Ar), 7.64 (1H, d, $J = 16.1$ Hz, $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.4 (q), 55.4 (q), 60.4 (t), 114.4 (2d), 115.8 (d), 127.3 (s), 129.7 (2d), 144.3 (d), 161.4 (s), 167.4 (s); GC-MS retention time 12.61 min., m/z (EI) 206 (M^+ , 50), 178 (13), 161 (100), 134 (56), 89 (17).

(Z)-Isomer; (1% yield); GC-MS retention time 11.94 min., m/z (EI) 206 (M^+ , 45), 178 (12), 161 (100), 134 (59), 89 (20).

Table 10, entry 3: **Ethyl (E) and (Z)-3-(2,6-dimethylphenyl)-2-propenoate.**⁸

⁷ Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, 67, 3096-3103.

⁸ Xiang, L.; Wu, H.; Hruby, V. J. *Tetrahedron: Asymmetry.* **1995**, 6, 83-86.

(E)-Isomer; Colourless oil (42% yield); eluent petroleum ether/ethyl acetate 10:1, R_f = 0.50; ^1H NMR (400 MHz, CDCl_3) δ 1.35 (3H, t, J = 7.1 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 2.34 (6H, s, $2 \times \text{CH}_3\text{Ar}$), 4.28 (2H, q, J = 7.1 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 6.06 (1H, d, J = 16.3 Hz, $\text{CH}=\text{CHCO}$), 7.03-7.16 (3H, m, Ar), 7.84 (1H, d, J = 16.3 Hz, $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.4 (q), 20.1 (2q), 60.6 (t), 124.1 (d), 128.3 (2d), 128.3 (d), 134.1 (s), 136.7 (2s), 143.3 (d), 166.8 (s); GC-MS retention time 11.40 min., m/z (EI) 204 (M^+ , 14), 189 (13), 159 (94), 130 (100), 115 (75), 91 (33). HRMS: found $[\text{M}+\text{H}]^+$ 205.1227, $\text{C}_{13}\text{H}_{17}\text{O}_2$ requires 205.1229.

(Z)-Isomer; (3% yield); GC-MS retention time 10.89 min., m/z (EI) 159 (M^+ - 45, 77), 130 (100), 115 (77), 91 (30).

Table 10, entry 4: **Ethyl (E,E) and (E,Z)-5-phenylpenta-2,4-dienoate**.⁹

(E)-Isomer; Orange oil (80% yield); eluent petroleum ether/ethyl acetate 4:1, R_f = 0.38; ^1H NMR (400 MHz, CDCl_3) δ 1.31 (3H, t, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 4.23 (2H, q, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 6.44 (1H, d, J = 16.1 Hz, $\text{CH}=\text{CHCO}$), 6.82-6.93 (2H, m), 7.28-7.54 (6H, m, Ar and $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.4 (q), 60.4 (t), 121.4 (d), 126.4 (d), 127.2 (2d), 128.9 (2d), 129.1 (d), 136.1 (s), 140.4 (d), 144.6 (d), 167.1 (s); GC-MS retention time 12.68 min., m/z (EI) 202 (M^+ , 18), 157 (23), 129 (100).

(Z)-Isomer; (10% yield); GC-MS retention time 12.18 min., m/z (EI) 202 (M^+ , 13), 157 (18), 129 (100).

Table 10, entry 5: **Ethyl (E) and (Z)-3-(4-acetylphenyl)-2-propenoate (334)**.¹⁰

(E)-Isomer; Off white solid (71% yield); eluent petroleum ether/ethyl acetate 10:1, R_f = 0.15; m.p. 44-46°C (petroleum ether/ethyl acetate) (lit.,¹⁰ 40-42°C); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (3H, t, J = 7.1 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 2.62 (3H, s, CH_3CO), 4.29 (2H, q, J = 7.1 Hz $\text{CH}_3\text{CH}_2\text{O}$), 6.52 (1H, d, J = 16.1 Hz, $\text{CH}=\text{CHCO}$); 7.61 (2H, d, J = 8.4 Hz, Ar), 7.69 (1H, d, J = 16.1 Hz, $\text{CH}=\text{CHCO}$), 7.97 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3 (q), 26.7 (q), 60.8 (t), 120.9 (d), 128.1 (2d), 128.9 (2d), 138.0 (s), 138.8 (s), 143.0 (d), 166.5 (s), 197.2 (s); GC-MS retention time 13.54 min., m/z (EI) 218 (M^+ , 33), 175 (28), 131 (24), 102 (30).

(Z)-Isomer; (4% yield); GC-MS retention time 12.91 min., m/z (EI) 218 (M^+ , 30), 203 (100), 175 (28), 131 (23), 102 (30).

Table 10, entry 6: **Ethyl (E) and (Z)-3-(4-chlorophenyl)-2-propenoate.**⁷

(E)-Isomer; Clear orange oil (86% yield); eluent petroleum ether/ethyl acetate 4:1, R_f = 0.44; ^1H NMR (400 MHz, CDCl_3) δ 1.34 (3H, t, J = 7.1 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 4.27 (2H, q, J = 7.1 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 6.41 (1H, d, J = 16.1 Hz, $\text{CH}=\text{CHCO}$), 7.36 (2H, d, J = 8.5 Hz, Ar), 7.46 (2H, d, J = 8.5 Hz, Ar), 7.63 (1H, d, J = 16.1 Hz, $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3 (q), 60.7 (t), 119.0 (d), 129.2 (2d), 129.2 (2d), 133.0 (s), 136.2 (s), 143.1 (d), 166.7 (s); GC-MS retention time 11.87 min., m/z (EI) 210 (M^+ , 33), 182 (25), 165 (100), 137 (32), 102 (44).

(Z)-Isomer; (4% yield); GC-MS retention time 11.20 min., m/z (EI) 210 (M^+ , 20), 182 (18), 165 (100), 137 (34), 102 (45).

Table 10, entry 7: **Ethyl (E) and (Z)-4-phenyl-2-butenate.**¹¹

⁹ Rathke, M. W.; Nowak, M. *J. Org. Chem.* **1985**, 50, 2624-2626.

¹⁰ Moreno-Mañas, M.; Perez, M.; Pleixats, R. *Tetrahedron Lett.* **1996**, 41, 7449-7452.

⁷ Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, 67, 3096-3103.

¹¹ Yi, P.; Zhuanggu, Z.; Hongwen, H. *Syn. Commun.* **1992**, 22, 2019-2029.

(E)-Isomer; Orange oil (83% yield); eluent petroleum ether/ethyl acetate 4:1, R_f = 0.40; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (3H, t, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 3.52 (2H, dd, J = 7.1 Hz and 1.6 Hz $\text{CH}_2\text{CH}=\text{CH}$), 4.17 (2H, q, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 5.81 (1H, dt, J = 15.8 and 1.6 Hz, $\text{CH}=\text{CHCO}$), 7.10 (1H, dt, J = 15.8 and 7.1 Hz, $\text{CH}=\text{CHCO}$), 7.15-7.36 (5H, m, Ar); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3 (q), 38.5 (t), 60.3 (t), 122.5 (d), 126.7 (d), 128.7 (2d), 128.9 (2d), 137.8 (s), 147.3 (d), 166.5 (s); GC-MS retention time 10.71 min., m/z (EI) 190 (M^+ , 32), 145 (36), 117 (100), 91 (83).

(Z)-Isomer; (9% yield); GC-MS retention time 10.27 min., m/z (EI) 190 (M^+ , 34), 144 (37), 115 (100), 91 (30).

Table 10, entry 8: **Ethyl (E) and (Z)-3-cyclohexyl-2-propenoate.**⁷

(E)-Isomer; Pale orange oil (77% yield); eluent petroleum ether/ethyl acetate 4:1, R_f = 0.55; ^1H NMR (400 MHz, CDCl_3) δ 1.08-1.36 (5H, m, $2 \times \text{CH Cy}$), 1.29 (3H, t, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.63-1.71 (1H, m, CH Cy), 1.72-1.83 (4H, m, $4 \times \text{CH Cy}$), 2.07-2.21 (1H, m, $\text{CHCH}=\text{CHCO}$), 4.18 (2H, q, J = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 5.76 (1H, dd, J = 15.8 Hz and 1.4 Hz, $\text{CH}=\text{CHCO}$), 6.92 (1H, dd, J = 15.8 and 6.6 Hz, $\text{CH}=\text{CHCO}$); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3 (q), 25.8 (t), 26.0 (2t), 31.8 (2t), 40.4 (d), 60.2 (t), 119.0 (d), 154.3 (d), 167.2 (s); GC-MS retention time 9.72 min., m/z (EI) 182 (M^+ , 62), 154 (17), 137 (75), 107 (54), 94 (53), 79 (53), 67 (100), 55 (100).

(Z)-Isomer; (5% yield); GC-MS retention time 12.18 min., m/z (EI) 182 (M^+ , 79), 154 (35), 137 (59), 107 (87), 79 (75), 67 (89), 55 (100).

Synthesis of Tosylhydrazones

Representative Procedure for the Preparation of Tosylhydrazones

Benzaldehyde (2.36 mL, 23.30 mmol) was added dropwise to a rapidly stirred suspension of *p*-toluenesulphonyl hydrazide (5.0 g, 26.79 mmol) in anhydrous methanol (10 mL) under nitrogen at RT. A mildly exothermic reaction ensued and the

⁷ Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, 67, 3096-3103.

hydrazide dissolved. Within 5-10 minutes the tosylhydrazone began to precipitate. After approximately 30 min, the mixture was cooled to 0°C and the product removed by filtration, washed with a small quantity of cold methanol and then crystallized from hot methanol to afford the hydrazone as fine white needles (5.81 g, 91%).

Benzaldehyde tosylhydrazone.¹²

White needles (91% yield); m.p. 127-128°C (methanol) (lit.,¹² 128-129°C); ¹H NMR (400 MHz, CDCl₃) δ 2.39 (3H, s, CH₃), 7.29-7.36 (5H, m, Aryl H), 7.52-7.57 (2H, m, Aryl H), 7.78 (1H, s, CHN), 7.89 (2H, d, *J* = 8.3 Hz, Aryl H), 8.29 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 21.6 (q), 127.3 (2d), 127.9 (2d), 128.6 (2d), 129.7 (2d), 130.4 (d), 133.1 (s), 135.2 (s), 144.3 (s), 147.9 (d).

p-Chlorobenzaldehyde Tosylhydrazone.¹³

Colourless needles (6.74 g, 91 %), m.p. 146-148 °C (lit.,¹³ 148-151°C); (Found C, 54.3; H, 4.1; N, 9.2. C₁₄H₁₃N₂SO₂Cl requires C, 54.5; H, 4.4; N, 9.1 %); ν_{max} (KBr disc) / cm⁻¹ 3187, 1332; ¹H NMR (250 MHz, CDCl₃) 2.41 (3H, s, CH₃), 7.30-7.35 (4H, m, ArH), 7.49 (2H, d, *J* = 7.8 Hz, ArH), 7.75 (1H, s, CH), 7.87 (2H, d, *J* = 7.8 Hz, ArH), 8.42 (1H, br s, NH); ¹³C NMR (63 MHz, CDCl₃) 21.6, 127.9, 128.4, 128.9, 129.8, 131.7, 135.1, 136.3, 144.5, 146.5; *m/z* (EI) 308 (*M*⁺, 49 %), 152 (38), 124 (100), 89, (100), 63 (32).

p-Methoxybenzaldehyde Tosylhydrazone.¹³

¹² McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456-2469.

¹³ Sayer, J. M.; Peskin, M.; Jencks, P. *J. Am. Chem. Soc.* **1973**, *95*, 4277-4287.

White needles (6.10 g, 83 %), m.p. 103-105 °C (lit.,¹³ 110-112 °C); (Found C, 59.2; H, 5.2; N, 9.2. C₁₅H₁₆N₂O₃S requires C, 59.2; H, 5.3; N, 9.2%); $\nu_{\max}$ (KBr disc) / cm⁻¹ 3222, 1161; ¹H NMR (250 MHz, CDCl₃) 2.35 (3H, s, CH₃), 3.75 (3H, s, OCH₃), 6.81 (2H, d, *J* = 10.8 Hz, ArH), 7.25 (2H, d, *J* = 8.1 Hz, ArH), 7.48 (2H, d, *J* = 10.8 Hz, ArH), 7.74 (1H, s, CH), 7.88 (2H, d, *J* = 8.2 Hz, ArH), 8.55 (1H, br s, NH); ¹³C NMR (63 MHz, CDCl₃) 21.6, 55.4, 114.1, 126.0, 127.9, 128.9, 129.7, 135.3, 144.2, 148.4, 161.4; *m/z* (EI) 304 (*M*⁺, 57 %), 149 (94), 139 (43), 135 (60), 121 (100), 91 (90), 77 (48).

***p*-Cyanobenzaldehyde Tosylhydrazone.¹⁴**

Pale yellow needles (5.95 g, 83 %), m.p. 161-164 °C; (Found C, 60.2; H, 4.3; N, 14.1. C₁₅H₁₃N₃O₂S requires C, 60.2; H, 4.3; N, 14.0 %); $\nu_{\max}$ (KBr disc) / cm⁻¹ 3170, 2230, 1171; ¹H NMR (250 MHz, CDCl₃) 2.40 (3H, s, CH₃), 7.32 (2H, d, *J* = 8.0 Hz, ArH), 7.64 (4H, m, ArH), 7.80 (1H, s, CH), 7.88 (2H, d, *J* = 8.0 Hz, ArH), 8.87 (1H, br s, NH); ¹³C NMR (63 MHz, CDCl₃) 21.7, 113.4, 118.4, 127.6, 127.9, 129.9, 132.4, 134.9, 137.4, 144.8, 144.9; *m/z* (EI) 299 (*M*⁺, 6 %), 156 (27), 143 (28), 115 (100), 91 (57), 65 (36).

Synthesis of Benzaldehyde Tosylhydrazone Salts

Procedure for the Preparation of Benzaldehyde Tosylhydrazone Sodium Salt

¹⁴ Aggarwal, V. K.; Alonso, E.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Porcelloni, M.; Studley, J. R. *Angew. Chem. Int. Ed.*, **2001**, *41*, 1430.

A 1M sodium methoxide solution was prepared by adding sodium (423 mg, 18.39 mmol) to anhydrous methanol (19 mL) at 10°C under nitrogen. Once all of the metal was dissolved, benzaldehyde tosylhydrazone (4.80 g, 17.51 mmol) was added and the mixture stirred until the entire solid dissolved. After stirring for a further 15 minutes, the methanol was removed under reduced pressure (without external heating). The last traces of methanol were removed under high vacuum (0.1 mmHg). The resultant salt was then ground using a mortar and pestle to afford the product as a fine white powder (5.21 g, 99%). The product was stored in a cool dry place in absence of direct light.

Benzaldehyde Tosylhydrazone Sodium Salt.¹⁵

White powder; ¹H NMR (400 MHz, D₂O) δ 2.17 (3H, s, CH₃), 7.15-7.23 (5H, m, Aryl H), 7.35-7.40 (2H, m, Aryl H), 7.60 (2H, d, *J* = 8.4 Hz, Aryl H), 7.83 (1H, s, CHN); ¹³C NMR (100 MHz, D₂O) δ 20.7 (q), 126.6 (2d), 126.7 (2d), 128.8 (2d), 129.5 (2d), 129.6 (d), 135.8 (s), 139.2 (s), 142.8 (s), 145.9 (d).

Procedure for the Preparation of Benzaldehyde Tosylhydrazone Potassium Salt

Benzaldehyde tosylhydrazone (4.00 g, 14.6 mmol) was added to a vigorously stirred Potassium methoxide solution (145.6 mL, 14.6 mmol, 0.1 N in toluene/methanol) under an atmosphere of nitrogen. The hydrazone dissolved after 1 minute and then the product precipitated immediately. After stirring for a further 30 minutes the methanol was removed under reduced pressure (without external heating). The last traces of methanol were removed under high vacuum (0.1 mmHg) to give the resultant salt as a fine white powder (4.56 g, 100%). The product was stored in a cool dry place in absence of direct light.

Benzaldehyde Tosylhydrazone Potassium Salt.

¹⁵ Creary, X. Org. Synth. **1986**, 64, 207-216.

White powder; ^1H NMR (400 MHz, D_2O) δ 2.17 (3H, s, CH_3), 7.15-7.23 (5H, m, Aryl H), 7.35-7.40 (2H, m, Aryl H), 7.60 (2H, d, $J = 8.4$ Hz, Aryl H), 7.83 (1H, s, CHN); ^{13}C NMR (100 MHz, D_2O) δ 20.7 (q), 126.6 (2d), 126.7 (2d), 128.8 (2d), 129.5 (2d), 129.6 (d), 135.8 (s), 139.2 (s), 142.8 (s), 145.9 (d).

Mechanistic Study of the Olefination Reactions of *p*-Chlorobenzaldehyde Using Phenyldiazomethane

General Procedure for Obtaining Aliquots

Standard air-sensitive techniques were employed in all aliquot transfers. Aliquots were transferred via gas-tight syringes into a dry NMR tube containing a sealed capillary tube of PPh_3 in d_8 -toluene (δ -5.6 against 85% H_3PO_4) as an internal reference. The tubes were then sealed with a teflon cap.

Procedure for Monitoring Olefination Reaction of Benzaldehyde Using Phenyldiazomethane

Under N_2 , phenyldiazomethane (0.45M in toluene, 1.0 mL, 0.45 mmol) was added at a rate of 0.5 mL/h to a toluene (6 mL) solution of $\text{P}(\text{OMe})_3$ (60 μL , 0.51 mmol) and ClFeTPP (7 mg, 0.01 mmol) in toluene (6 mL) at 40 $^\circ\text{C}$. After addition, aliquot 1 was obtained. To the stirring solution, a toluene (0.25 mL) solution of *p*-chlorobenzaldehyde (70 mg, 0.50 mmol) was added. After 12 h, aliquot 2 was obtained. The ^{31}P -NMR (121 MHz) spectrum of aliquot 1 revealed resonances corresponding to unreacted $\text{P}(\text{OMe})_3$, a resonance at δ 55.2, and small amounts of $\text{OP}(\text{OMe})_3$ at δ 2.7 and hydrolysis product **6b** at δ 25.5. The ^{31}P -NMR (121 MHz) spectrum of aliquot 1 revealed resonances corresponding to $\text{P}(\text{OMe})_3$, $\text{OP}(\text{OMe})_3$ and small amounts of hydrolysis product **6b**.

Generation of Hydrolysis Product **6b**.¹⁶

The same experiment was repeated but water (500 μ L, 28 mmol) was added instead of *p*-chlorobenzaldehyde, provoking the formation of phosphonate **6b** (25.5 ppm). Colourless oil; eluent ethyl acetate, R_f = 0.5; ¹H NMR (400 MHz, CDCl₃) δ 3.14 (2H, dd, J = 21.5 and 2.4 Hz, PCH₂Ph), 3.65 (6H, d, J = 10.8 Hz, 2 $\times$ CH₃O), 7.30 (5H, m, Ar); ¹³C NMR (100 MHz, *d*₈-tol) δ 32.8 (t, J_{C-P} = 136 Hz), 60.5 (2q, J_{C-P} = 6.9 Hz), 126.8 (d), 128.3 (2d), 129.9 (2d), 132.1 (s); IR ν_{max}/cm^{-1} 3474, 2955, 1603, 1496, 1455, 1246, 1019, 830, 697; ³¹P NMR (121 MHz, *d*₈-tol) δ 25.5; GC-MS retention time 10.75 min., *m/z* (EI) 200 (*M*⁺, 30), 104 (32), 91 (100); HRMS: found 200.0613, C₉H₁₃O₃P requires 200.0602.

Procedure for Monitoring Olefination Reactions of Benzaldehyde Using EDA, Salt Free

Under N₂, EDA (350 μ L, 3.0 mmol) was slowly added to a 85 °C dioxane solution (6mL) of P(OMe)₃ (280 μ L, 2.4 mmol), ClFeTPP (7 mg, 0.01 mmol). After addition, aliquot 1 was obtained. Benzaldehyde (205 μ L) was then added to the reaction flask. After 10 minutes, aliquot 2 was obtained. The ³¹P-NMR (121 MHz) spectrum of aliquot 1 revealed resonances corresponding to unreacted P(OMe)₃, a major resonance at δ 63.2, and small amounts of OP(OMe)₃ at δ 2.7 and hydrolysis product **6a** at δ 22.8. The ³¹P-NMR (121 MHz) spectrum of aliquot 2 revealed resonances corresponding to P(OMe)₃, OP(OMe)₃ and small amounts of hydrolysis product **6a**.

Generation of Hydrolysis Product **6a**

The same experiment was repeated but water (500 μ L, 28 mmol) was added instead of benzaldehyde, provoking the formation of ethyl dimethylphosphonoacetate **6a**; Colourless oil; ¹H NMR (400 MHz, *d*₈-tol) δ 0.95 (3H, t, J = 7.1 Hz, CH₃CH₂), 2.67 (2H, J = 21.6 Hz, PCH₂C), 3.44 (6H, d, J = 10.4 Hz, 2 $\times$ CH₃O); ³¹P NMR (121 MHz, *d*₈-tol) δ 22.8 (compared with an authentic sample from Aldrich).

Procedure for Monitoring Olefination Reaction of Benzaldehyde Using EDA, added LiBr

¹⁶ Ganapathy, S.; Sekhar, B. B.; Akutagawa, K.; Bentrude, W. G.; *J. Am. Chem. Soc.*, **1999**, *121*, 2085-2096.

Under N₂, EDA (350 μ L, 3.0 mmol) was slowly added to a 85 °C dioxane solution (6mL) of P(OMe)₃ (280 μ L, 2.4 mmol), ClFeTPP (7 mg, 0.01 mmol) and LiBr (203mg, 2.33 mmol). After addition, aliquot 1 was obtained. Benzaldehyde (205 μ L) was then added to the reaction flask. After 10 m, aliquot 2 was obtained. The ³¹P-NMR (121 MHz) spectrum of aliquot 1 revealed resonances corresponding to unreacted P(OMe)₃, a major resonance at δ 42.8, and small amounts of OP(OMe)₃ at δ 2.7, hydrolysis product **6a** at δ 22.8 and multiple other small resonances. The ³¹P-NMR (121 MHz) spectrum of aliquot 2 revealed the disappearance of the resonance at δ 42.8; no other change in the NMR spectrum was observed. The precipitate was filtered and dissolved into *d*₄-MeOH. The ³¹P-NMR spectrum revealed resonance at δ 3.5 corresponding to (MeO)₂(O)P(OLi) (versus identical sample prepared according to the procedure by Poulter).¹⁷

Deprotonation of Ethyl Dimethylphosphonoacetate.

n-BuLi (1.6M in toluene, 625 μ L, 1 mmol) was added under nitrogen to a solution of ethyl dimethylphosphonoacetate (196 mg, 1 mmol) in anhydrous THF (500 μ L) contained in a dry NMR tube at RT. Decoupled ³¹P-NMR spectroscopy analysis showed the formation of lithium enolate **3a** (δ 42.8).

Competition Study Between (OMe)₃PCHCO₂Et and Ph₃PCHCO₂Me

Under nitrogen, a flask was charged with ClFeTPP (7 mg, 0.01 mmol), 6 mL freshly distilled 1,4-dioxane, and P(OMe)₃ (118 μ L, 1.0 mmol). The solution was heated to 85 °C and EDA (105 μ L, 1.0 mmol) was slowly added. To this was added a 2.0 mL solution of Ph₃PCHCO₂Me (334 mg, 1.0 mmol) followed by benzaldehyde (20.3 μ L, 0.1 mmol). An aliquot (A) for GC-MS was obtained after 3 h, and additional benzaldehyde was added (300 μ L, 2.95 mmol). The reaction was stopped after an additional 12 h. GC-MS of aliquot A revealed >99 % of alkene present to be PhCHCHCO₂Me. GC-MS of final reaction mixture revealed a 62:38 mixture of PhCHCHCO₂Me and PhCHCHCO₂Et.

¹⁷ Poulter, C. D.; Phan, R. M. *J. Org. Chem.* **2001**, *66*, 6705-6510