Supporting Information

Regioselective Synthesis of Fluoroalkylated β -Aminophosphorus Derivatives and Aziridines from Phosphorylated Oximes and Nucleophilic Reagents.

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General Methods. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use: CH_2Cl_2 (P_2O_5); *n*-hexane, diethyl ether and THF (sodium, benzophenone ketyl); ethyl acetate (K_2CO_3); ethanol (EtMgI). All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. Analytical TLC was performed with silica gel 60 F_{254} plates. Visualization was accomplished by UV light and KMnO_4 solution. Flash chromatography was carried out using silica gel 60 (230–400 mesh). Melting points are uncorrected. ^1H (400, 300 MHz), ^{13}C (100, 75 MHz) and ^{31}P NMR (120 MHz) spectra were recorded using tetramethylsilane (TMS) (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in CDCl_3 solutions for ^1H NMR spectra or chloroform (77.0 ppm)

as an internal reference in CDCl_3 solutions for ^{13}C NMR, and phosphoric acid (85%) for ^{31}P NMR spectra. Chemical shifts (δ) are given in ppm; multiplicities are indicated by s (singlet), d (doublet), dd (double-doublet), t (triplet), q (quadruplet) or m (multiplet). Coupling constants (J) are reported in Hertz. Low-resolution mass spectra (MS) were obtained at 50–70 eV by electron impact (EI) or chemical ionization (CI). Data are reported in the form m/z (intensity relative to base = 100). Infrared spectra (IR) were taken on a IRFT spectrometer, and were obtained as solids in KBr or as neat oils in NaCl. Peaks are reported in cm^{-1} . Alkylphosphonates **6** were prepared according to literature procedures.¹

General Procedure for the Preparation of β -phosphorylated ketones 3/7, *gem*-diols 5/8 and enols 4. To a solution of LDA (6 mmol) in THF (25 mL) was added a solution of alkylphosphine oxide **1** or alkylphosphonate **6** (5 mmol) in THF (15 mL) cooled at -78°C under nitrogen atmosphere. The mixture was stirred for 1h at -78°C , next a solution of the corresponding ester was added (6 mmol) in THF (12 mL) at the same temperature and then was allowed to warm at room temperature (15 h). After the reaction was complete, the solvent was evaporated under vacuum. The crude residue was treated with HCl to 10% (5 mL) during 30min. The crude reaction was extracted three times with CH_2Cl_2 (3 x 15 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and the solvent was evaporated under vacuum. The crude product was purified by vacuum distillation or by chromatography using silica gel eluting with 2:1 hexane/ethyl acetate to afford according to the cases; β -phosphorylated ketones **3/7**, *gem*-diols **5/8** or enols **4**.

2,2-Difluoro-2-hydroxyprop-1-enyldiphenylphosphine oxide 4b. The general procedure was followed using diphenylmethylphosphine oxide **1a** (1.01 g, 5 mmol) and ethyl 2,2-difluoroacetate **2b** (0.75g, 6 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.10 g, (75 %) of compound **4b** as a yellow solid: *mp* $102\text{--}103^\circ\text{C}$; ^1H NMR (CDCl_3) δ 7.79–7.42 (m, 12H), 5.90(t, $^1J_{\text{FH}} = 55.2$ Hz, 1H) ppm; ^{13}C NMR (CDCl_3) δ 135.0–129.6(m), 114.6 (dt, $^1J_{\text{FC}} = 248.0$ Hz, $^3J_{\text{PC}} = 5.0$ Hz), 97.7 (t, $^2J_{\text{FC}} = 24.7$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 35.2 ppm; ^{19}F NMR (CDCl_3) δ -137.7

(d, $^1J_{\text{FH}} = 50.3$ Hz), -129.0 (d, $^1J_{\text{FH}} = 38.1$ Hz) ppm; IR (KBr) 3323, 3018, 2780, 2455, 1586, 1374, 1228 cm^{-1} ; MS (EI) m/z 294 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_2\text{O}_2\text{P}$: C, 61.23; H, 4.45;. Found: C, 61.38; H, 4.46.

2-Oxo-2-perfluoroheptylethyldiphenylphosphine oxide 3c and 2-perfluoroheptyl-2-hydroxyethenyldiphenylphosphine oxide 4c. The general procedure was followed using diphenylmethylphosphine oxide **1a** (1.01 g, 5 mmol) and ethyl perfluorooctanoate **2c** (2.65g, 6 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.77 g, (58 %) of a mixture of **3c** and **4c** derivatives as a yellow solid: *mp* 117-119°C; Spectroscopic data for **3c**: ^1H NMR (CDCl_3) δ 7.80-7.47 (m, 10H), 3.91(d, $^2J_{\text{PH}} = 14.2$ Hz, 2H) ppm; ^{13}C NMR (CDCl_3) δ 187 (m), 132.8-128.9(m), 119.5-106.6(m), 41.7 (d, $^1J_{\text{PC}} = 57.9$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 26.2 ppm; ^{19}F NMR (CDCl_3) δ -81.0, -119.0, -119.7, -122.0, -122.2, -123.0, -126.3 ppm. Spectroscopic data for **4c**: ^1H NMR (CDCl_3) δ 7.80-7.47 (m, 10H), 5.42(dd, $^2J_{\text{PH}} = 17.2$ Hz, $^4J_{\text{PH}} = 1.2$ Hz, 1H) ppm; ^{13}C NMR (CDCl_3) δ 160.7 (t, $^2J_{\text{FC}} = 26.2$ Hz), 132.8-128.9(m), 119.5-106.6(m), 88.1 (t, $^1J_{\text{PC}} = 101.2$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 37.2 ppm; ^{19}F NMR (CDCl_3) δ -81.1, -119.7, -122.0, -122.5, -123.0, -126.3 ppm.; IR (KBr) 3065, 2985, 2906, 1745, 1440, 1208, 1142 cm^{-1} ; MS (EI) m/z 612 (M^+ , 6), 243 ($\text{M}^+ - \text{C}_7\text{F}_{15}$, 100); Anal. Calcd. for $\text{C}_{21}\text{H}_{12}\text{F}_{15}\text{O}_2\text{P}$: C, 41.20; H, 1.98;. Found: C, 41.32; H, 1.98.

3,3,3-Trifluoro-1-methyl-2-oxopropylidiphenylphosphine oxide 3d and 3,3,3-trifluoro-2,2-dihydroxy-1-methylpropylidiphenylphosphine oxide 5d. The general procedure was followed using ethyldiphenylphosphine oxide **1b** (1.15 g, 5 mmol) and ethyl trifluoroacetate **2a** (0.86g, 6 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.22 g, (75 %) of a mixture of **3d** and **5d** derivatives as a pale yellow oil: *R_f* 0.82(ethyl acetate). Spectroscopic data for **3d**: ^1H NMR (CDCl_3) δ 7.88-7.26 (m, 10H), 4.17 (m, 1H), 1.51(dd, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{PH}} = 15.3$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3) δ 189 (q), 137.2-128.4(m), 119.5-106.6(m), 122.3 (dq, $^1J_{\text{FC}} = 288.1$ Hz, $^3J_{\text{PC}} = 13.6$ Hz), 44.3 (d, $^1J_{\text{PC}} = 58.4$ Hz), 12.7 (d, $^2J_{\text{PC}} = 3.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 30.0 ppm; ^{19}F NMR (CDCl_3) δ -82.4 ppm; IR (NaCl) 3061, 1730, 1154 cm^{-1} ; MS (EI) m/z 326 (M^+ , 28);. Spectroscopic data

for **5d**: ^1H NMR (CDCl_3) δ 7.88-7.26 (m, 10H), 5.60 (s, 2H), 3.13 (m, 1H), 1.19 (dd, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{PH}} = 18.0$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3) δ 137.2-128.4(m), 122.3 (dq, $^1J_{\text{FC}} = 288.1$ Hz, $^3J_{\text{PC}} = 13.6$ Hz), 96.6 (q, $^2J_{\text{FC}} = 30.0$ Hz), 35.7 (d, $^1J_{\text{PC}} = 68.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 44.1 ppm; ^{19}F NMR (CDCl_3) δ -78.4 ppm; IR (NaCl) 3183, 3058, 1730, 1154 cm^{-1} ; MS (EI) m/z 326 ($\text{M}^+ - 18$, 28); Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{O}_2\text{P}$: C, 58.90; H, 4.33;. Found: C, 59.08; H, 4.36.

Diethyl 3,3,3-trifluoro-2-oxopropylphosphonate 7a and diethyl 3,3,3-trifluoro-2,2-dihydroxypropylphosphonate 8a. The general procedure was followed using diethyl methylphosphonate **6a** (0.76 g, 5 mmol) and ethyl trifluoroacetate **2a** (0.86g, 6 mmol). The crude product was purified by vacuum distillation to afford 0.97 g, (78 %) of β -keto-phosphonate **7a** as a pale yellow oil: *bp* 55-56°C (10^{-1} Torr). Spectroscopic data for **8a**: ^1H NMR (CDCl_3) δ 6.36 (s, 2H), 4.12 (m, 4H), 2.24(d, $^2J_{\text{PH}} = 19.2$ Hz, 2H), 1.25 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 122.5 (dq, $^1J_{\text{FC}} = 286.5$ Hz, $^3J_{\text{PC}} = 20.6$ Hz), 62.8, 30.5 (d, $^1J_{\text{PC}} = 141.0$ Hz), 15.9 ppm; ^{31}P NMR (CDCl_3) δ 26.5 ppm; ^{19}F NMR (CDCl_3) δ -87.7 ppm; IR (NaCl) 3383, 1260, 1177 cm^{-1} ; MS (EI) m/z 248 ($\text{M}^+ - 18$, 6);. Spectroscopic data for **7a**: ^1H NMR (CDCl_3) δ 4.12 (m, 4H), 3.23 (d, $^2J_{\text{PH}} = 22.5$ Hz, 2H), 1.14 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 183.1 (q, $^2J_{\text{FC}} = 37.8$ Hz, $^2J_{\text{PC}} = 8.0$ Hz), 83.9 (dq, $^1J_{\text{FC}} = 182.2$ Hz, $^3J_{\text{PC}} = 17.1$ Hz), 62.8, 35.4 (d, $^1J_{\text{PC}} = 132.9$ Hz), 15.6 ppm; ^{31}P NMR (CDCl_3) δ 16.3 ppm; ^{19}F NMR (CDCl_3) δ -82.5 ppm; IR (NaCl) 1748, 1222, 1182 cm^{-1} ; MS (EI) m/z 248 (M^+ , 9); Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{F}_3\text{O}_4\text{P}$: C, 33.87; H, 4.83;. Found: C, 33.81; H, 4.89.

Diethyl 3,3,4,4-pentafluoro-2-oxobutylphosphonate 7b. The general procedure was followed using diethyl methylphosphonate **6a** (0.76 g, 5 mmol) and ethyl pentafluoropropionate **2c** (1.15g, 6 mmol). The crude product was purified by vacuum distillation to afford 1.12 g, (75 %) of β -keto-phosphonate **7b** as a pale yellow oil: *bp* 64-66°C (10^{-1} Torr); ^1H NMR (CDCl_3) δ 4.14 (m, 4H), 3.37 (d, $^2J_{\text{PH}} = 22.4$ Hz, 2H), 1.29 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 186.0 (dt, $^2J_{\text{FC}} = 28.8$ Hz, $^2J_{\text{PC}} = 8.1$ Hz), 123.2-105.9 (m), 63.0, 36.5 (d, $^1J_{\text{PC}} = 133.5$ Hz), 15.8 ppm; ^{31}P NMR (CDCl_3) δ 16.0 ppm; ^{19}F NMR (CDCl_3) δ -

82.5, -127.5 ppm; IR (NaCl) 1755, 1229, 1179 cm^{-1} ; MS (EI) m/z 298 (M^+ , 41); Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{F}_5\text{O}_4\text{P}$: C, 32.21; H, 4.03; Found: C, 32.13; H, 4.02.

Diethyl 3,3,3-trifluoro-1-methyl-2-oxopropylphosphonate 7c and diethyl 3,3,3-trifluoro-2,2-dihydroxypropylphosphonate 8c. The general procedure was followed using diethyl ethylphosphonate **6b** (0.83 g, 5 mmol) and ethyl trifluoroacetate **2a** (0.86g, 6 mmol). The crude product was purified by vacuum distillation to afford 0.96 g, (73 %) of β -keto-phosphonate **7c** as a pale yellow oil: bp 61-62°C (10^{-1} Torr). Spectroscopic data for **8c**: ^1H NMR (CDCl_3) δ 4.11 (m, 4H), 2.41(dq, $^2J_{\text{PH}} = 21.5$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 1.44(dd, $^3J_{\text{PH}} = 17.4$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 3H), 1.28 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H) ppm; ^{13}C NMR (CDCl_3) δ 114.8 (q, $^1J_{\text{FC}} = 291.6$ Hz), 62.9, 36.4 (d, $^1J_{\text{PC}} = 130.9$ Hz), 15.5, 11.0 ppm; ^{31}P NMR (CDCl_3) δ 26.0 ppm; ^{19}F NMR (CDCl_3) δ -88.0 ppm; IR (NaCl) 3200, 1260, 1050 cm^{-1} ; MS (EI) m/z 262 (M^+ -18, 18);. Spectroscopic data for **7c**: ^1H NMR (CDCl_3) δ 4.11 (m, 4H), 3.62 (dq, $^2J_{\text{PH}} = 24.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz 1H), 1.44 (dd, $^3J_{\text{PH}} = 17.4$ Hz, $^3J_{\text{HH}} = 7.0$ Hz 3H), 1.28 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H) ppm; ^{13}C NMR (CDCl_3) δ 188.1 (q, $^2J_{\text{FC}} = 30.2$ Hz), 114.8 (q, $^1J_{\text{FC}} = 291.6$ Hz), 62.9, 40.7 (d, $^1J_{\text{PC}} = 130.9$ Hz), 15.6, 11.1 ppm; ^{31}P NMR (CDCl_3) δ 19.9 ppm; ^{19}F NMR (CDCl_3) δ -78.4 ppm; IR (NaCl) 1638, 1177, 1025 cm^{-1} ; MS (EI) m/z 262 (M^+ , 18); Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{F}_3\text{O}_4\text{P}$: C, 36.65; H, 5.38; Found: C, 36.78; H, 5.40.

General Procedure for the Preparation of (Z) and (E) - β -phosphorylated ketoximes 9 and 10.

To a solution of the β -keto-phosphine oxides **3** or -phosphonate **7** (5 mmol) and hydroxylamine hydrochloride (0.42 g, 6 mmol) in ethanol (15 mL) was added pyridine (0.75 mL, 9.3 mmol) at 0 °C. The reaction mixture was kept at reflux for 6 h until the disappearance of the starting material. Solvent was removed under reduced pressure and the residue was diluted in CH_2Cl_2 and washed twice with HCl 2N (2 x 10 mL) and then with water (10 mL). The organic layer was dried with MgSO_4 anhydrous, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography using silica gel eluting with 1:1 hexane/ethyl acetate to afford β -ketoximes **9** or **10** as a variable mixture of *E* and *Z* isomers.

(Z)-3,3-Difluoro-2-N-hydroxyiminopropylidiphenylphosphine oxide 9b. The general procedure was followed using the enol **4b** (1.47 g, 5 mmol) Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.19 g, (77 %) of compound **9b** as a yellow solid: *mp* 143-144°C; ¹H NMR (CDCl₃) δ 7.81-7.39 (m, 11H), 6.06 (t, ²*J*_{FH}= 54.8 Hz, 2H), 3.61 (d, ²*J*_{PH}= 13.7 Hz, 2H) ppm; ¹³C NMR (CDCl₃) δ 143.5 (dt, ²*J*_{FC}= 29.1 Hz, ²*J*_{PC}= 10.3 Hz), 133.0-128.4 (m), 113.6 (t, ¹*J*_{FC}= 235.7 Hz), 26.3 (d, ¹*J*_{PC}= 65.0 Hz) ppm; ³¹P NMR (CDCl₃) δ 28.8 ppm; ¹⁹F NMR (CDCl₃) δ -177.8 ppm; IR (KBr) 3144, 3032, 2906, 1487, 1288, 1122 cm⁻¹; MS (EI) *m/z* 310 (*M*⁺+1, 100); Anal. Calcd. for C₁₅H₁₄F₂NO₂P: C, 58.26; H, 4.56; N: 4.53. Found: C, 58.40; H, 4.57; N: 4.52.

(Z)-2-Perfluoroheptyl-2-N- hydroxyiminoethylidiphenylphosphine oxide 9c. The general procedure was followed using β -keto-phosphine oxide **3c** (3.06 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 2.26 g, (84 %) of compound **9c** as a yellow solid: *mp* 131-132°C; ¹H NMR (CDCl₃) δ 13.2(s. 1H), 7.87-7.26 (m, 10H), 3.70 (d, ²*J*_{PH}= 13.4 Hz, 2H) ppm; ¹³C NMR (CDCl₃) δ 139.7 (dt, ²*J*_{FC}= 26.2 Hz, ²*J*_{PC}= 10.6 Hz), 132.7-128.6 (m), 119.5-110.2 (m), 28.6 (d, ¹*J*_{PC}= 64.0 Hz) ppm; ³¹P NMR (CDCl₃) δ 27.7 ppm; ¹⁹F NMR (CDCl₃) δ -81.0, -110.9, -121.0, -121.4, -122.2, -122.9, -126.4 ppm; IR (KBr) 3151, 3058, 2939, 1639, 1513, 1440, 1195, 1142 cm⁻¹; MS (EI) *m/z* 628 (*M*⁺+1, 100); Anal. Calcd. for C₂₁H₁₃F₁₅NO₂P: C, 40.21; H, 2.01; N: 2.23. Found: C, 40.08; H, 2.01; N: 2.24.

(Z)-and (E)-3,3,3-Trifluoro-2-N-hydroxyimino-1-methylpropylidiphenylphosphine oxide 9d. The general procedure was followed using β -keto-phosphine oxide **3d** (1.63g, 5mmol) Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.02 g, (60 %) of compound **9d** as a yellow solid: *mp* 54-56°C; ¹H NMR (CDCl₃) δ For *Z* and *E* isomers 7.80-7.24 (m, 11H), 3.51 (dd, ³*J*_{HH}= 7.3 Hz, ²*J*_{PH}= 8.2 Hz, 1H),), 1.43 (dd, ³*J*_{HH}= 7.7 Hz, ³*J*_{PH}= 15.4 Hz, 3H) ppm; ¹³C NMR (CDCl₃) δ 144.2 (q, ²*J*_{FC}= 33.2 Hz) for *Z* isomer, 142.0 (q, ²*J*_{FC}= 34.3 Hz) for *E* isomer, 133.1-128.2 (m) for *Z* and *E* isomers, 120.5 (q, ¹*J*_{FC}= 308.2 Hz) for *Z* and *E* isomers, 34.3 (d, ¹*J*_{PC}= 68.5 Hz) for *Z* and *E* isomers,

14.2 (d, $^2J_{\text{PC}} = 3.0$ Hz) for *Z* isomer, 10.4 (d, $^2J_{\text{PC}} = 4.5$ Hz) for *E* isomer ppm; ^{31}P NMR (CDCl_3) δ 34.2 for *E* isomer, 31.6 for *Z* isomer ppm; ^{19}F NMR (CDCl_3) δ -62.3 for *Z* isomer, -65.7 for *E* isomer ppm; IR (KBr) 3142, 3025, 1637, 1170 cm^{-1} ; MS (EI) m/z 342 ($\text{M}^+ + 1$, 45); Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NO}_2\text{P}$: C, 56.30; H, 4.43; N: 4.10. Found: C, 56.45; H, 4.45; N: 4.08.

Diethyl (Z)-3,3,3-trifluoro-2-N-hydroxyiminopropylphosphonate 10a. The general procedure was followed using the ketone **7a** (1.24 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.59 g, (45 %) of compound **10a** as a pale yellow oil: R_f 0.54(ethyl acetate); ^1H NMR (CDCl_3) δ 11.5 (s, 1H), 4.09 (m, 4H), 3.07 (d, $^2J_{\text{PH}} = 23.3$ Hz, 2H), 1.27 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 140.1 (dq, $^2J_{\text{FC}} = 33.7$ Hz, $^2J_{\text{PC}} = 11.6$ Hz), 120.5 (dq, $^1J_{\text{FC}} = 273.5$ Hz, $^3J_{\text{PC}} = 2.8$ Hz), 62.9 (d, $^2J_{\text{PC}} = 6.6$ Hz), 22.6 (d, $^1J_{\text{PC}} = 141.5$ Hz), 15.9 ppm; ^{31}P NMR (CDCl_3) δ 21.3 ppm; ^{19}F NMR (CDCl_3) δ -69.1 ppm; IR (KBr) 3176, 3075, 1641, 1193 cm^{-1} ; MS (EI) m/z 264 ($\text{M}^+ + 1$, 19); Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{F}_3\text{NO}_4\text{P}$: C, 31.95; H, 4.98; N: 5.32. Found: C, 32.10; H, 5.04; N: 5.28.

Diethyl (Z)-3,3,4,4,4-pentafluoro-2-N-hydroxyiminobutylphosphonate 10b. The general procedure was followed using the ketone **7b** (1.49 g, 5 mmol) Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.72 g, (46 %) of compound **10b** as a pale yellow oil: R_f 0.50(ethyl acetate); ^1H NMR (CDCl_3) δ 12.4 (s, 1H), 4.16 (m, 4H), 3.15 (d, $^2J_{\text{PH}} = 23.3$ Hz, 2H), 1.31 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 140.5 (dt, $^2J_{\text{FC}} = 27.7$ Hz, $^2J_{\text{PC}} = 11.1$ Hz), 124.6-106.1 (m), 63.2 ($^2J_{\text{PC}} = 7.1$ Hz), 23.2 (d, $^1J_{\text{PC}} = 142.5$ Hz), 16.3 (d, $^3J_{\text{PC}} = 6.6$ Hz), 16.2 (d, $^3J_{\text{PC}} = 6.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 21.7 ppm; ^{19}F NMR (CDCl_3) δ -82.1, -114.1 ppm; IR (KBr) 3217, 3076, 2885, 1720, 1202 cm^{-1} ; MS (EI) m/z 314 ($\text{M}^+ + 1$, 15); Anal. Calcd. for $\text{C}_8\text{H}_{13}\text{F}_5\text{NO}_4\text{P}$: C, 30.68; H, 4.18; N: 4.47. Found: C, 30.84; H, 4.17; N: 4.48.

Diethyl (E)-3,3,3-trifluoro-2-N-hydroxyimino-1-methylpropylphosphonate 10c. The general procedure was followed using the ketone **7c** (1.31 g, 5 mmol) Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.55 g, (40 %) of compound **10c** as a pale yellow oil: R_f

0.51(ethyl acetate); ^1H NMR (CDCl_3) δ 11.8 (s, 1H), 4.10 (m, 4H), 3.06 (dq, $^3J_{\text{HH}} = 7.2$ Hz, $^2J_{\text{PH}} = 23.0$ Hz, 1H), 1.39 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{PH}} = 18.2$ Hz, 3H), 1.27 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 142.9 (q, $^2J_{\text{FC}} = 29.2$ Hz), 118.0 (dq, $^1J_{\text{FC}} = 284.4$ Hz, $^3J_{\text{PC}} = 8.6$ Hz), 63.1 (d, $^2J_{\text{PC}} = 7.3$ Hz), 32.7 (d, $^1J_{\text{PC}} = 158.1$ Hz), 16.2, 13.7 (d, $^2J_{\text{PC}} = 5.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 27.4 ppm; ^{19}F NMR (CDCl_3) δ -65.5 ppm; IR (KBr) 3180, 3061, 1640, 1159 cm^{-1} ; MS (EI) m/z 278 ($\text{M}^+ + 1$, 24); Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{F}_3\text{NO}_4\text{P}$: C, 34.67; H, 5.45; N: 5.05. Found: C, 34.60; H, 5.42; N: 5.09.

General Procedure for the preparation of phosphorylated β -*p*-toluenesulfonyloximes **11 and **12**.** To a solution of NaH (5.5 mmol) in THF (15 mL) was added at 0 °C under nitrogen atmosphere, the oxime **9** or **10** and the mixture was allowed at room temperature during 30 min. Then, to the mixture was added in portions at 0 °C tosyl chloride (1.05 g, 5.5 mmol) freshly recrystallized from hexane. The mixture was allowed to warm at room temperature, and the reaction mixture was stirred for 2 h. The NaH remainder was neutralized with methanol, the solvent was evaporated under vacuum. The crude reaction was extracted with CH_2Cl_2 (15 mL) and washed with water (3 x 10 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and the solvent was evaporated under vacuum. The crude product was purified by chromatography using silica gel eluting with 2:1 hexane/ethyl acetate to yield the compounds **11** as a white solid and **12** like as a pale yellow oil.

(*Z*)-3,3-Difluoro-2-(*N-p*-toluenesulfonyloxyimino)propyldiphenylphosphine oxide **11b.** The general procedure was followed using the β -ketoxime-phosphine oxide **9b** (1.63 g, 5 mmol) Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.37 g, (59 %) of compound **11b** as a white solid: *mp* 135-136 °C; ^1H NMR (CDCl_3) δ 7.81-7.26 (m, 14H), 6.32 (t, $^2J_{\text{FH}} = 56.8$ Hz, 1H), 3.69 (d, $^2J_{\text{PH}} = 14.5$ Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 153.8 (dq, $^2J_{\text{FC}} = 26.2$ Hz, $^2J_{\text{PC}} = 8.1$ Hz), 146.1, 132.6-127.8 (m), 110.8 (t, $^1J_{\text{FC}} = 244.78$ Hz), 29.4 (d, $^1J_{\text{PC}} = 58.4$ Hz), 21.7 ppm; ^{31}P NMR (CDCl_3) δ 24.8 ppm; ^{19}F NMR (CDCl_3) δ -121.7 ppm; IR (KBr) 3065, 1616, 1593, 1367, 1195 cm^{-1} ; MS (EI) m/z 464 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{F}_2\text{NO}_4\text{PS}$: C, 57.02; H, 4.35; N: 3.02; S:6.92. Found: C, 57.16; H, 4.36; N: 3.01; S:6.93.

(Z)-2-Perfluoroheptyl-2-(N-*p*-toluenesulfonyloxyimino)ethyldiphenylphosphine oxide 11c. The general procedure was followed using the β -ketoxime-phosphine oxide **9c** (3.14 g, 5 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 2.50 g, (64 %) of compound **11c** as a white solid: *mp* 154-155°C; ^1H NMR (CDCl_3) δ 13.2(s, 1H), 7.87-7.26 (m, 14H), 3.71 (d, $^2J_{\text{PH}} = 14.8$ Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 151.2 (m), 146.1, 132.7-128.6 (m), 119.2-106.0 (m), 31.4 (d, $^1J_{\text{PC}} = 57.4$ Hz), 21.6 ppm; ^{31}P NMR (CDCl_3) δ 24.6 ppm; ^{19}F NMR (CDCl_3) δ -81.0, -110.4, -110.9, -121.0, -122.2, -123.0, -126.3 ppm; IR (KBr) 3065, 2906, 1600, 1440, 1202 cm^{-1} ; MS (EI) *m/z* 782 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_{28}\text{H}_{19}\text{F}_{15}\text{NO}_4\text{PS}$: C, 43.03; H, 2.45; N, 1.79; S, 4.10. Found: C, 42.91; H, 2.44; N, 1.80; S, 4.11.

Diethyl (Z)-3,3,3-trifluoro-2-(N-*p*-toluenesulfonyloxyimino)propylphosphonate 12a. The general procedure was followed using the β -ketoxime-phosphonate **10a** (1.26 g, 5 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.00 g, (48 %) of compound **12a** as a pale yellow oil: *R_f* 0.68(ethyl acetate); ^1H NMR (CDCl_3) δ 7.83 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 7.31 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 4.11 (m, 4H), 3.09 (d, $^2J_{\text{PH}} = 23.6$ Hz, 2H), 2.40 (s, 3H), 1.27 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 149.7 (dq, $^2J_{\text{FC}} = 35.2$ Hz, $^2J_{\text{PC}} = 10.6$ Hz), 146.2, 133.0-128.3 (m), 115.0 (q, $^1J_{\text{FC}} = 273.5$ Hz), 63.2 (d, $^2J_{\text{PC}} = 5.54$ Hz), 25.1 (d, $^1J_{\text{PC}} = 136.5$ Hz), 21.7, 16.1 ppm; ^{31}P NMR (CDCl_3) δ 16.5 ppm; ^{19}F NMR (CDCl_3) δ -70.2 ppm; IR (KBr) 2998, 1653, 1387, 1225, 1198 cm^{-1} ; MS (EI) *m/z* 418 ($\text{M}^+ + 1$, 18); Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{F}_3\text{NO}_6\text{PS}$: C, 40.29; H, 4.59; N, 3.36; S, 7.68. Found: , C, 40.35; H, 4.62; N, 3.33; S, 7.64.

Diethyl (Z)-3,3,4,4,4-pentafluoro-2-(N-*p*-toluenesulfonyloxyimino)butylphosphonate 12b. The general procedure was followed using the β -ketoxime-phosphonate **10b** (1.57 g, 5 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.00 g, (43 %) of compound **12a** as a pale yellow oil: *R_f* 0.72 (ethyl acetate); ^1H NMR (CDCl_3) δ 7.83 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 7.35 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 4.13 (m, 4H), 3.17 (d, $^2J_{\text{PH}} = 23.6$ Hz, 2H), 2.46 (s, 3H), 1.31 (q, $^3J_{\text{HH}} =$

7.1 Hz, 6H) ppm; ^{13}C NMR (CDCl_3) δ 149.7 (dt, $^2J_{\text{FC}} = 29.2$ Hz, $^2J_{\text{PC}} = 11.1$ Hz), 146.2, 129.0-131.2 (m), 118.1 (tq, $^1J_{\text{FC}} = 286.8$ Hz, $^2J_{\text{FC}} = 35.3$ Hz), 109.8 (tq, $^1J_{\text{FC}} = 258.9$ Hz, $^2J_{\text{FC}} = 38.3$ Hz), 63.3 (d, $^2J_{\text{PC}} = 6.6$ Hz), 25.3 (d, $^1J_{\text{PC}} = 137.0$ Hz), 21.9, 16.2 (d, $^3J_{\text{PC}} = 6.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 16.4 ppm; ^{19}F NMR (CDCl_3) δ -81.8, -113.7 ppm; IR (KBr) 2985, 2932, 1732, 1639, 1600, 1394 1202 cm^{-1} ; MS (EI) m/z 468 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO}_6\text{PS}$: C, 38.55; H, 4.10; N: 3.00; S: 6.86. Found: C, 38.65; H, 4.10; N: 3.01; S: 6.85.

Diethyl (*E*)-3,3,3-trifluoro-1-methyl -2-(*N*-*p*-toluenesulfonyloxyimino)propylphosphonate 12c.

The general procedure was followed using the β -ketoxime-phosphonate **10c** (1.33 g, 5 mmol) Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.97 g, (45 %) of compound **12c** as a pale yellow oil: R_f 0.56 (ethyl acetate); ^1H NMR (CDCl_3) δ 7.85 (m, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 7.34 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 4.09 (m, 4H), 3.21 (dq, $^3J_{\text{HH}} = 7.2$ Hz, $^2J_{\text{PH}} = 24.5$ Hz, 1H), 2.14 (s, 3H), 1.37 (m, 3H), 1.22 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 149.7 (dq, $^2J_{\text{FC}} = 34.0$ Hz, $^2J_{\text{PC}} = 9.2$ Hz), 146.7, 132.7-127.8 (m), 118.4 (q, $^1J_{\text{FC}} = 276.0$ Hz), 63.2 (d, $^2J_{\text{PC}} = 7.0$ Hz), 34.3 (d, $^1J_{\text{PC}} = 139.5$ Hz), 21.6, 16.1, 12.7 (d, $^2J_{\text{PC}} = 5.5$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 21.9 ppm; ^{19}F NMR (CDCl_3) δ -64.7 ppm; IR (KBr) 29989, 1605, 1455, 1387, 1198 cm^{-1} ; MS (EI) m/z 432 ($\text{M}^+ + 1$, 27); Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{F}_3\text{NO}_6\text{PS}$: C, 41.77; H, 4.91; N: 3.25; S: 7.43. Found: C, 41.89; H, 4.93; N: 3.24; S: 7.41.

General Procedure for the Preparation of Aziridines 14-17. To a solution of fluorinated *p*-toluenesulfonyl oximes **11** or **12** (5 mmol) in MeOH (15 mL) was added slowly at 0°C, under nitrogen atmosphere, the corresponding base (5.5 mmol). Then, the mixture was allowed to warm at room temperature until TLC indicated the disappearance of oxime. The solvent was evaporated under reduced pressure and the mixture was diluted in CH_2Cl_2 (15 mL) and washed with water. The organic phase was dried with anhydrous MgSO_4 , filtered and the solvent was evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (hexane/AcOEt 1/1) to yield the aziridines **14** or **15**.

***trans*-3-Difluoromethyl-3-methoxy-aziridin-2-yl**diphenylphosphine oxide **14b**. The general procedure was followed using (Z)-3,3-difluoro-2-(N-*p*-toluenesulfonyloxyimino) propyldiphenylphosphine oxide **11b** (2.31 g, 5 mmol) and triethylamine (0.76mL, 5.5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.20 g, (74 %) of compound **14b** as a white solid: *mp* 124-125°C; ¹H NMR (CDCl₃) δ 7.78-7.49 (m, 10H), 6.48 (t, ²*J*_{PH}= 20.9 Hz, 1H), 3.56 (s, 3H), 2.70 (dd, ²*J*_{PH}= 20.9 Hz, ³*J*_{HH}= 4.4 Hz, 1H), 1.71 (s, 1H) ppm; ¹³C NMR (CDCl₃) δ 132.8-128.3 (m), 114.2 (t, ¹*J*_{FC}= 243.0 Hz), 72.2 (t, ²*J*_{FC}= 26.0 Hz), 56.2, 38.4 (dd, ¹*J*_{PC}= 87.9 Hz, ³*J*_{FC}= 5.8 Hz) ppm; ³¹P NMR (CDCl₃) δ 25.6 ppm; ¹⁹F NMR (CDCl₃) δ -119.0 to -125.2 (m) ppm; IR (KBr) 3171, 3058, 1679, 1613, 1288, 1182 cm⁻¹; MS (EI) *m/z* 323 (*M*⁺+1, 100); Anal. Calcd. for C₁₆H₁₆F₂NO₂P: C, 59.45; H, 4.99; N: 4.33. Found: C, 59.59; H, 5.00; N: 4.33.

***trans*-3-Methoxy-3-perfluoroheptylaziridin-2-yl**diphenylphosphine oxide **14c**. The general procedure was followed using (Z)-2-perfluoroheptyl-2-(N-*p*-toluenesulfonyloxyimino) ethyldiphenylphosphine oxide **11c** (3.91 g, 5 mmol) and triethylamine (0.76mL, 5.5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 2.24 g, (70 %) of compound **14c** as a white solid: *mp* 161-162°C; ¹H NMR (CDCl₃) δ 7.87-7.44 (m, 10H), 3.46 (s, 3H), 2.73 (dd, ²*J*_{PH}= 17.0 Hz, ³*J*_{HH}= 11.2 Hz, 1H), 2.54 (dd, ³*J*_{PH}= 17.4 Hz, ³*J*_{HH}= 11.2 Hz, 1H) ppm; ¹³C NMR (CDCl₃) δ 134.1-128.3 (m), 119.7-107.4, 74.0 (t, ²*J*_{FC}= 30.2 Hz), 54.8, 40.1 (d, ¹*J*_{PC}= 83.6 Hz) ppm; ³¹P NMR (CDCl₃) δ 21.7 ppm; ¹⁹F NMR (CDCl₃) δ -81.0, -113.8, -120.8, -122.2, -123.0, -126.3 ppm; IR (KBr) 3217, 1440, 1374, 1261, 1149 cm⁻¹; MS (EI) *m/z* 642 (*M*⁺+1, 100); Anal. Calcd. for C₂₂H₁₅F₁₅NO₂P: C, 41.20; H, 2.36; N: 2.18. Found: C, 41.09; H, 2.35; N: 2.19.

Procedure for the Preparation of *trans*-2-methyl-3-methoxy-3-trifluoromethylaziridin-2-yldiphenylphosphine oxide **14d**. To a solution of NaH (11 mmol) in THF (15 mL) was added of ketoxime **9d** (2.40g, 5 mmol) at 0°C, the mixture was allowed at room temperature during 10 min. Then, to the mixture was added in portions at 0 °C tosyl chloride (1.05 g, 5.5 mmol) freshly recrystallized from hexane. The reaction mixture was allowed to warm room temperature and the

reaction mixture was stirred for 6 h, methanol was added (10 mL) and it continued stirred for 2 h. The solvent was evaporated under reduced pressure and the residue was diluted in CH₂Cl₂ (15 mL) and washed with water. The organic phase was dried with anhydrous MgSO₄, filtered and the solvent was evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (hexane/AcOEt 1/1) to afford 0.78g (44%) of compound **14d** as a white solid: *mp* 137-138°C; ¹H NMR (CDCl₃) δ 7.72-7.32 (m, 10H), 3.42 (s, 3H), 2.95 (d, ³*J*_{PH} = 17.1 Hz, 1H), 1.06 (d, ³*J*_{PH} = 11.0 Hz, 3H) ppm; ¹³C NMR (CDCl₃) δ 132.9-128.5 (m), 123.1 (q, ¹*J*_{FC} = 281.8 Hz), 74.3 (q, ²*J*_{FC} = 39.4 Hz), 55.2, 43.1 (d, ¹*J*_{PC} = 81.6 Hz), 18.6 (d, ¹*J*_{PC} = 11.1 Hz) ppm; ³¹P NMR (CDCl₃) δ 31.9 ppm; ¹⁹F NMR (CDCl₃) δ -68.7 ppm; IR (KBr) 3138, 1401, 1195 cm⁻¹; MS (EI) *m/z* 355 (M⁺, 8); Anal. Calcd. for C₁₇H₁₇F₃NO₂P: C, 57.47; H, 4.82; N: 3.94;. Found: C, 57.43; H, 4.79; N: 3.97.

Diethyl *trans*-3-methoxy-3-trifluoromethylaziridin-2-ylphosphonate 15a. The general procedure was followed using diethyl (Z)-3,3,3-trifluoro-2-(N-*p*-toluenesulfonyloxyimino)propylphosphonate **12a** (2.09 g, 5 mmol) and NaOMe (0.28g, 5.5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.00 g, (48 %) of compound **12a** as a pale yellow oil: *R_f* 0.65(ethyl acetate); ¹H NMR (CDCl₃) δ 4.16 (m, 4H), 3.52 (s, 3H), 2.36 (d, ²*J*_{PH} = 10.1 Hz, 1H), 2.03 (s, 3H), 1.36 (t, ³*J*_{HH} = 6.7 Hz, 6H) ppm; ¹³C NMR (CDCl₃) δ 122.6 (q, ¹*J*_{FC} = 280.5 Hz), 71.7 (q, ²*J*_{FC} = 39.3 Hz), 62.8 (d, ²*J*_{PC} = 7.1 Hz), 62.7 (d, ²*J*_{PC} = 6.0 Hz), 55.8, 16.0 (d, ³*J*_{PC} = 6.6 Hz), 15.9 (d, ³*J*_{PC} = 7.1 Hz) ppm; ³¹P NMR (CDCl₃) δ 16.4 ppm; ¹⁹F NMR (CDCl₃) δ -72.2 ppm; IR (KBr) 3197, 1653, 1454, 1387, 1235, 1189 cm⁻¹; MS (EI) *m/z* 278 (M⁺+1, 100); Anal. Calcd. for C₈H₁₅F₃NO₄P: C, 34.67; H, 5.45; N: 5.05. Found: , C, 34.74; H, 5.44; N: 5.06.

Procedure for the Preparation of *trans*-3-benzothio-3-trifluoromethylaziridin-2-yl diphenylphosphine oxide 17. To a solution of fluorinated *p*-toluenesulfonyl oximes **11a** (2.40g, 5 mmol) and benzenethiol (11 mmol) in CHCl₃ (15 mL) was added at 0°C, under nitrogen atmosphere, triethylamine (0.76mL, 5.5 mmol). Then, the mixture was allowed to warm at room temperature until TLC indicated the disappearance of oxime. The organic phase was washed with water and was dried

with anhydrous MgSO_4 , filtered and the solvent was evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (hexane/AcOEt 1/1) to afford 1.45g (69%) of compound **17** as a white solid: *mp* 158-159°C; ^1H NMR (CDCl_3) δ 7.92-7.37 (m, 15H), 3.26 (d, $^2J_{\text{PH}} = 20.3$ Hz, 1H) ppm; ^{13}C NMR (CDCl_3) δ 135.7-129.3 (m), 124.5 (q, $^1J_{\text{FC}} = 277.5$ Hz), 51.0, 43.4 (d, $^1J_{\text{PC}} = 98.2$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 26.0 ppm; ^{19}F NMR (CDCl_3) δ -67.1 ppm; IR (KBr) 3131, 3080, 3051, 1580, 1487, 1189 cm^{-1} ; MS (EI) *m/z* 420 ($\text{M}^+ + 1$, 35); Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NOPS}$: C, 60.14; H, 4.09; N, 3.34; S, 7.65. Found: C, 60.15; H, 4.10; N, 3.35; S, 7.63.

General Procedure for the Preparation of Aziridines 19-22. To a solution of fluorinated *p*-toluenesulfonyl oximes **11** or **12** (5 mmol) in THF (15 mL) cooled at -78°C , was added a solution of Grignard reagent **18** (15 mmol) in diethyl ether under nitrogen atmosphere. The mixture was stirred for 1h at -78°C and then was allowed to warm at room temperature (15 h). After the reaction was complete, the mixture was quenched with a saturated NH_4Cl solution (15 mL). The crude reaction was extracted three times with CH_2Cl_2 (3 x 15 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and the solvent was evaporated under vacuum. The crude residue was then purified by flash chromatography on silica gel (hexane/AcOEt 2/1) affording mixtures of *cis* and *trans* isomers, derivatives **19/20** as white solids and derivatives **21/22** as pale yellow oils.

3-Ethyl-3-trifluoromethylaziridin-2-yl-diphenylphosphine oxide 19/20b. The general procedure was followed using (*Z*)-3,3,3-trifluoro-2-(*N*-*p*-toluenesulfonyloxyimino) propyldiphenylphosphine oxide **11a** (2.40 g, 5 mmol) and ethyl magnesium bromide **18b** 3M (5 mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.14 g, (69 %) of a mixture (84/16) of *cis*-**19b** (major component) and *trans*-**20b** (minor component) as a white solid: *mp* 230-232°C; ^1H NMR (CDCl_3) δ 7.85-7.26 (m, 10H), 2.38 (dd, $^2J_{\text{PH}} = 18.1$ Hz, $^3J_{\text{HH}} = 9.7$ Hz 1H), 2.10 (m, 1H), 1.77 (s, 1H), 1.63 (m, 1H), 1.02 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3) δ 132.6-128.8, 125.1 (q, $^1J_{\text{FC}} = 278.5$ Hz), 47.0 (q, $^2J_{\text{FC}} = 35.0$ Hz), 39.3 (d, $^1J_{\text{PC}} = 91.2$ Hz), 26.8, 9.7 ppm; ^{31}P NMR (CDCl_3) δ 23.7 (*cis*- isomer), 23.4 (*trans* isomer) ppm; ^{19}F NMR (CDCl_3) δ -65.4 ppm; IR (KBr) 3224, 1427, 1301,

1202, 1129 cm^{-1} ; MS (EI) m/z 339 (M^+ , 10), 202 ($\text{P}(\text{O})\text{Ph}_2^+$, 100); Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NOP}$: C, 60.18; H, 5.05; N: 4.13. Found: : C, 60.07; H, 5.04; N: 4.14.

3-Allyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide 19/20c. The general procedure was followed using (Z)-3,3,3-trifluoro-2-(*N*-*p*-toluenesulfonyloxyimino) propyldiphenylphosphine oxide **11a** (2.40 g, 5 mmol) and allyl magnesium bromide **18c** 1M (15 mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.11 g, (63 %) of a mixture (66/34) of *cis*-**19c** (major component) and *trans*-**20c** (minor component) as a white solid: *mp* 157-159°C: ^1H NMR (CDCl_3) *cis* and *trans* isomer δ 7.81-7.19 (m, 20H), 5.68 (ddt, $^2J_{\text{HHtrans}} = 16.8$ Hz, $^3J_{\text{HHcis}} = 9.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 5.22 (dd, $^2J_{\text{HHgem}} = 12.8$ Hz, $^3J_{\text{HHcis}} = 9.3$ Hz, 2H), 5.09 (dd, $^3J_{\text{HHtrans}} = 15.7$ Hz, $^2J_{\text{HHgem}} = 11.3$ Hz, 2H), 2.75 (dd, $^2J_{\text{HHgem}} = 14.8$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 2.53 (dd, $^2J_{\text{HHgem}} = 15.7$ Hz, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 2.35 (d, $^2J_{\text{PH}} = 17.1$ Hz, 1H), 2.32 (d, $^2J_{\text{PH}} = 21.6$ Hz, 1H), 2.15 (m, 2H) ppm; ^{13}C NMR (CDCl_3) (*cis*- isomer), δ 134.4–130.7, 128.1 (q, $^1J_{\text{FC}} = 257.3$ Hz), 119.7, 45.7 (q, $^2J_{\text{FC}} = 35.3$ Hz), 38.5 (d, $^1J_{\text{PC}} = 85.1$ Hz), 36.9 ppm; ^{13}C NMR (CDCl_3) (*trans* isomer) δ 134.1–130.7, 128.1 (q, $^1J_{\text{FC}} = 257.3$ Hz), 122.8, 45.7 (q, $^2J_{\text{FC}} = 35.3$ Hz), 37.5 (d, $^1J_{\text{PC}} = 106.8$ Hz), 34.0 ppm; ^{31}P NMR (CDCl_3) δ 24.6 (*cis* isomer), 23.1 (*trans*- isomer) ppm; ^{19}F NMR (CDCl_3) δ -66.7 (*cis* isomer), -69.7 (*trans* isomer) ppm; IR (KBr) 3204, 3059, 1434, 1381, 1175 cm^{-1} ; MS (EI) m/z 352 (M^+ , 100); Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NOP}$: C, 61.54; H, 4.88; N: 3.99. Found: C, 61.62; H, 4.89; N: 3.98.

Procedure for the Preparation of 3-Allyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide 19/20c from ketoxime 9a. To a solution of fluorinated oxime **9a** (1.63g, 5 mmol) in toluene (15 mL) was added at 0°C a solution of allyl magnesium bromide **18c** 1M (15 mL, 15 mmol) in diethyl ether under nitrogen atmosphere. The mixture was kept at reflux for 3 h and then was allowed to warm at room temperature. After the reaction was complete, the mixture was quenched with a saturated NH_4Cl solution (15 mL). The crude reaction was extracted three times with CH_2Cl_2 (3 x 15 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and the solvent was evaporated under vacuum. The

crude residue was then purified by flash chromatography on silica gel (hexane/AcOEt 2/1) affording 0.78 g, (44 %) of a mixture (66/34) of *cis* and *trans* isomers **19/20c** as a white solid.

3-Phenyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide 19/20d. The general procedure was followed using (Z)-3,3,3-trifluoro-2-(*N*-*p*-toluenesulfonyloxyimino) propyldiphenylphosphine oxide **11a** (2.40 g, 5 mmol) and phenyl magnesium bromide **18d** 3M (5 mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.41 g, (73 %) of a mixture (95/5) of *cis*-**19d** (major component) and *trans*- **20d** (minor component) as a white solid: *mp* 175-177°C; ¹H NMR (CDCl₃) δ 7.96-7.02 (m, 30H), 3.30 (s, 1H, *trans*-), 2.84 (dd, ²*J*_{PH}= 20.6 Hz, ³*J*_{HH}= 9.0 Hz 1H, *cis*-), 2.58 (s, 2H) ppm; ¹³C NMR (CDCl₃) δ 134.8–128.1, 124.1 (q, ¹*J*_{FC}= 277.0 Hz), 47.1 (q, ²*J*_{FC}= 33.2 Hz), 42.4 (d, ¹*J*_{PC}= 75.0 Hz, *trans*-), 35.8 (d, ¹*J*_{PC}= 93.7 Hz, *cis*-), ppm; ³¹P NMR (CDCl₃) δ 23.0 (*cis* isomer), 22.8 (*trans* isomer) ppm; ¹⁹F NMR (CDCl₃) δ -74.6 (*cis* isomer), -65.1 (*trans* isomer) ppm; IR (KBr) 3204, 3059, 1487, 1282, 1169 cm⁻¹; MS (EI) *m/z* 387 (M⁺, 10), 201 (P(O)Ph₂⁺, 100); Anal. Calcd. for C₂₁H₁₇F₃NOP: C, 65.12; H, 4.42; N: 3.62. Found: : C, 65.05; H, 4.41; N: 3.63.

3-Difluoromethyl-3-phenylaziridin-2-ylidiphenylphosphine oxide 19/20e. The general procedure was followed using (Z)-3,3-difluoro-2-(*N*-*p*-toluenesulfonyloxyimino) propyldiphenylphosphine oxide **11b** (2.31 g, 5 mmol) and phenyl magnesium bromide **18d** 3M (5mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 1.02 g, (55 %) of a mixture (76/24) of *cis*-**19e** (major component) and *trans*- **20e** (minor component) as a white solid: *mp* 174-176°C; ¹H NMR (CDCl₃) δ 7.90-7.20 (m, 30H), 6.69 (t, ¹*J*_{FH}= 54.3 Hz, 2H), 2.80 (dd, ²*J*_{PH}= 22.1 Hz, ³*J*_{HH}= 11.1 Hz 1H, *trans*-), 2.57 (ddd, ²*J*_{PH}= 21.8 Hz, ³*J*_{HH}= 9.1 Hz, ⁴*J*_{FH}= 4.2 Hz 1H, *cis*-), 2.32 (dd, ³*J*_{PH}= 14.5 Hz, ³*J*_{HH}= 9.0 Hz, 2H), ppm; ¹³C NMR (CDCl₃) δ 134.1–128.2, 114.6 (q, ¹*J*_{FC}= 239.2 Hz), 48.2, 39.1 (d, ¹*J*_{PC}= 81.6 Hz) ppm; ³¹P NMR (CDCl₃) δ 27.0 (*cis* isomer), 24.6 (*trans* isomer) ppm; ¹⁹F NMR (CDCl₃) δ -108.4 to -117.8 (m) ppm; IR (KBr) 3171, 1633, 1182, 1109, 1043 cm⁻¹; MS (EI) *m/z* 370 (M⁺+1, 10),

201 (P(O)Ph₂⁺, 68); Anal. Calcd. for C₂₁H₁₈F₂NOP: C, 68.29; H, 4.91; N: 3.79. Found: C, 68.36; H, 4.92; N: 3.78.

Diethyl 3-ethyl-3-trifluoromethylaziridin-2-ylphosphonate 21/22a. The general procedure was followed using diethyl (Z)-3,3,3-trifluoro-2-(N-*p*-toluenesulfonyloxyimino)propylphosphonate **12a** (2.09 g, 5 mmol) and ethyl magnesium bromide **18b** 3M (5mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.78 g, (57 %) of a mixture (71/29) of *cis*-**21a** (major component) and *trans*-**22a** (minor component) as a pale yellow oil: *R_f* 0.30(ethyl acetate); ¹H NMR (CDCl₃) δ 4.17 (m, 4H), 2.08 (s, 1H), 1.72 (s, 1H), 1.63 (m, 2H), 1.35 (m, 6H), 1.03 (t, ³*J*_{HH}= 7.5 Hz, 3H) ppm; ¹³C NMR (CDCl₃) δ 123.6 (dq, ¹*J*_{FC}= 277.8 Hz, ³*J*_{PC}= 2.8 Hz, *cis*-), 123.6 (dq, ¹*J*_{FC}= 274.5 Hz, *trans*-), 66.7 (d, ²*J*_{PC}= 7.05 Hz), 62.6 (d, ²*J*_{PC}= 7.05 Hz), 45.5 (dq, ²*J*_{FC}= 34.8 Hz, ²*J*_{PC}= 4.8 Hz), 34.4 (d, ¹*J*_{PC}= 200.4 Hz, *cis*-), 28.5 (d, ¹*J*_{PC}= 211.0 Hz), 25.7, 16.2 (d, ³*J*_{PC}= 5.0 Hz), 16.1 (d, ³*J*_{PC}= 5.5 Hz), 9.0 ppm; ³¹P NMR (CDCl₃) δ 19.0 (*cis isomer*), 18.2 (*trans isomer*) ppm; ¹⁹F NMR (CDCl₃) δ -68.7 (*cis isomer*), -66.8 (*trans isomer*) ppm; IR (KBr) 3230, 1460, 1387, 1248, 1142 cm⁻¹; MS (EI) *m/z* 276 (M⁺+1, 100); Anal. Calcd. for C₉H₁₇F₃NO₃P: C, 39.28; H, 6.23; N: 5.09. Found: : C, 39.36; H, 6.24; N: 5.08.

Diethyl 3-benzyl-3-trifluoromethylaziridin-2-ylphosphonate 21/22b. The general procedure was followed using diethyl (Z)-3,3,3-trifluoro-2-(N-*p*-toluenesulfonyloxyimino)propylphosphonate **12a** (2.09 g, 5 mmol) and benzyl magnesium bromide **18e** 3M (5 mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.94 g, (56 %) of a mixture (55/45) of *cis*-**21b** (major component) and *trans*-**22b** (minor component) as a pale yellow oil: *R_f* 0.55 (ethyl acetate); ¹H NMR (CDCl₃) δ 7.51-7.12 (m, 10H), 4.20 (m, 8H), 2.49 (s, *cis isomer*, 2H), 2.4 (s, *trans isomer*, 2H), 2.17 (s, 2H), 1.97 (d, ²*J*_{PH}= 11.8 Hz, 2H), 1.32 (m, 12H) ppm; ¹³C NMR (CDCl₃) δ 131.1-125.7 (m), 124.0 (q, ¹*J*_{FC}= 288.6 Hz), 62.7 (d, ²*J*_{PC}= 6.5 Hz), 62.6 (d, ²*J*_{PC}= 5.0 Hz), 44.2 (m), 37.3 (d, *trans isomer* ¹*J*_{PC}= 214.0 Hz), 37.0 (*trans isomer*), 34.0 (*cis isomer*), 31.3 (d, *cis isomer* ¹*J*_{PC}= 213.0 Hz), 16.6 (d, ³*J*_{PC}= 6.0 Hz), 16.4 (d, ³*J*_{PC}= 6.0 Hz) ppm; ³¹P NMR (CDCl₃) δ 19.8 (*cis isomer*), 19.0 (*trans*

isomer) ppm; ^{19}F NMR (CDCl_3) δ -69.1 (*cis* isomer), -67.2 (*trans* isomer) ppm; IR (NaCl) 3410, 2979, 1625, 1440, 1239 cm^{-1} ; MS (EI) m/z 337 (M^+ , 6), 199 ($\text{M}^+ - \text{HP(O)(OEt)}_2$, 100); Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{FNO}_3\text{P}$: C, 49.86; H, 5.68; N, 4.15. Found: C, 49.97; H, 5.70; N, 4.14.

Diethyl cis-3-phenyl-3-trifluoromethylaziridin-2-ylphosphonate 21c. The general procedure was followed using diethyl (*Z*)-3,3,3-trifluoro-2-(*N-p*-toluenesulfonyloxyimino)propylphosphonate **12a** (2.09 g, 5 mmol) and phenyl magnesium bromide **18d** 3M (5mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.97 g, (60 %) of a mixture (100/0) of *cis*-**21c** (major component) and *trans*-**22a** (minor component) as a pale yellow oil: R_f 0.55(ethyl acetate); ^1H NMR (CDCl_3) δ 7.54-7.32 (m, 5H), 4.22 (m, 4H), 2.36 (d, $^2J_{\text{PH}} = 12.1$ Hz, 1H), 2.20 (s, 1H), 1.38 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 134.1-127.2 (m), 123.6 (q, $^1J_{\text{FC}} = 278.0$ Hz), 62.9 (d, $^2J_{\text{PC}} = 7.6$ Hz), 62.8 (d, $^2J_{\text{PC}} = 7.6$ Hz), 47.8 (dq, $^2J_{\text{FC}} = 31.7$ Hz, $^2J_{\text{PC}} = 4.5$ Hz), 36.8 (d, $^1J_{\text{PC}} = 197.4$ Hz), 16.3 (d, $^3J_{\text{PC}} = 3.0$ Hz), 16.2 (d, $^3J_{\text{PC}} = 3.5$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 18.4 ppm; ^{19}F NMR (CDCl_3) δ -68.1 ppm; IR (KBr) 3224, 1447, 1381, 1261, 1196 cm^{-1} ; MS (EI) m/z 323 (M^+ , 7), 185 ($\text{M}^+ - \text{HP(O)(OEt)}_2$, 100); Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{NO}_3\text{P}$: C, 48.30; H, 5.30; N: 4.33. Found: : C, 48.36; H, 5.29; N: 4.32.

Diethyl 3-allyl-3-trifluoromethyl-2-methylaziridin-2-ylphosphonate 21/22d. The general procedure was followed using diethyl (*E*)-3,3,3-trifluoro-1-methyl-2-(*N-p*-toluenesulfonyloxyimino)propylphosphonate **12c** (2.16 g, 5 mmol) and allyl magnesium bromide **18c** 1M (5mL, 15 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.92 g, (59 %) of a mixture (60/40) of *cis*-**21d** (major component) and *trans*-**22d** (minor component) as a pale yellow oil: R_f 0.55(ethyl acetate) *cis* isomer, 0.65(ethyl acetate) *trans* isomer; Spectroscopic data for *cis*-**21d**: ^1H NMR (CDCl_3) δ 5.81 (ddt, $^3J_{\text{HHtrans}} = 16.8$ Hz, $^3J_{\text{HHcis}} = 10.1$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 1H), 5.18 (ddd, $^3J_{\text{HHtrans}} = 16.6$ Hz, $^3J_{\text{HHcis}} = 10.1$ Hz, $^3J_{\text{HHgem}} = 1.3$ Hz, 2H), 4.16 (m, 4H), 2.85 (dd, $^3J_{\text{HHgem}} = 15.4$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 2.36 (d, $^2J_{\text{HHgem}} = 15.4$ Hz, 1H), 1.94 (s, 1H), 1.50 (d, $^3J_{\text{PH}} = 11.3$ Hz, 3H), 1.35 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 132.0, 125.1 (q, $^1J_{\text{FC}} = 276.0$ Hz), 118.9, 63.1, 62.9, 47.8 (q, $^2J_{\text{FC}} = 33.7$ Hz), 39.8 (d, $^1J_{\text{PC}} = 186.9$ Hz), 34.3, 18.5 (d, $^2J_{\text{PC}} = 9.6$ Hz), 16.5 (d, $^3J_{\text{PC}} = 5.5$ Hz), 16.4 (d, $^3J_{\text{PC}} =$

6.0 Hz) ppm; ^{31}P NMR (CDCl_3) δ 22.6 ppm; ^{19}F NMR (CDCl_3) δ -64.4 ppm; IR (KBr) 3217, 1719, 1633, 1454, 1381, 1228, 1175, 1023 cm^{-1} ; Spectroscopic data for *trans*-**22d**: ^1H NMR (CDCl_3) δ 5.89 (ddt, $^3J_{\text{HHtrans}} = 17.1$ Hz, $^3J_{\text{HHcis}} = 10.1$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 1H), 5.23 (d, $^3J_{\text{HHtrans}} = 17.1$ Hz, 1H), 5.15 (d, $^3J_{\text{HHcis}} = 10.1$ Hz, 1H), 4.18 (m, 4H), 2.97 (d, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 1.72 (s, 1H), 1.49 (d, $^3J_{\text{PH}} = 11.9$ Hz, 3H), 1.37 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 132.4, 125.3 (q, $^1J_{\text{FC}} = 280.5$ Hz, $^3J_{\text{PC}} = 3.0$ Hz), 119.2, 63.4 (d, $^2J_{\text{PC}} = 5.5$ Hz), 62.9 (d, $^2J_{\text{PC}} = 7.6$ Hz), 47.1 (q, $^2J_{\text{FC}} = 31.6$ Hz), 38.6 (d, $^1J_{\text{PC}} = 184.8$ Hz), 33.1, 16.6 (d, $^3J_{\text{PC}} = 5.0$ Hz), 16.5 (d, $^3J_{\text{PC}} = 6.0$ Hz), 15.4 (dd, $^2J_{\text{PC}} = 7.6$ Hz, $^4J_{\text{FC}} = 3.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 25.5 ppm; ^{19}F NMR (CDCl_3) δ -65.2 ppm; IR (KBr) 3273, 1723, 1644, 1453, 1397, 1239, 1177, 1025 cm^{-1} ; MS (EI) m/z 302 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{NO}_3\text{P}$: C, 48.30; H, 5.30; N, 4.33. Found: : C, 48.36; H, 5.29; N, 4.32.

General Procedure for Ring Opening of Aziridines. To a solution of aziridine-2-phosphine oxides **14** or **19/20** or aziridine-2-phosphonate **15** or **21/22** (5 mmol) in EtOH (15 mL) was added under nitrogen atmosphere, Pd/C (20 %), and then ammonium formate (4.74g, 75 mmol). The mixture was kept at reflux for 18 h, until TLC indicated the disappearance of azirine. The solvent was evaporated under reduced pressure and the mixture was diluted in water. Then, NH_4OH solution (25 %) was added until pH 8, and the aqueous layer was extracted three times with CH_2Cl_2 . The combined organic layers were dried over anhydrous MgSO_4 , and the solvent was evaporated. The crude mixture was purified by flash column chromatography on silica gel (hexane/AcOEt 1/1) to afford amino phosphorus derivatives **23** or **25-30** as white solids or colorless oils.

Diethyl 3,3,3-trifluoro-2-iminopropylphosphonate 25 and Diethyl 2-amino-3,3,3-trifluoropropen-1-ylphosphonate 26. The general procedure was followed using diethyl *trans*-3-methoxy-3-trifluoromethylaziridin-2-ylphosphonate **15a** (1.39 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.80 g, (65 %) of a mixture (50/50) of imine **25** and enamine **26** as a pale yellow oil: R_f 0.86 (ethyl acetate); Spectroscopic data for imine **25**: ^1H NMR (CDCl_3) δ 5.75 (s, 1H), 3.96 (m, 4H), 2.27 (d, $^2J_{\text{PH}} = 19.2$ Hz, 2H), 1.25 (m, 6H) ppm; ^{13}C NMR

(CDCl₃) δ 149.5 (dq, $^2J_{\text{FC}} = 33.2$ Hz, $^2J_{\text{PC}} = 7.6$ Hz), 122.1 (dq, $^2J_{\text{FC}} = 263.3$ Hz, $^3J_{\text{PC}} = 24.8$ Hz), 61.3, 30.4 (d, $^1J_{\text{PC}} = 139.9$ Hz), 16.1 ppm; ^{31}P NMR (CDCl₃) δ 26.6 ppm; ^{19}F NMR (CDCl₃) δ -105.4 ppm; Spectroscopic data for enamine **26**: ^1H NMR (CDCl₃) δ 5.83 (s, 2H), 4.34 (d, $^2J_{\text{PH}} = 8.7$ Hz, 1H), 3.96 (m, 4H), 1.25 (m, 6H) ppm; ^{13}C NMR (CDCl₃) δ 149.5 (dq, $^2J_{\text{FC}} = 33.2$ Hz, $^2J_{\text{PC}} = 7.6$ Hz), 120.0 (dq, $^1J_{\text{FC}} = 276.4$ Hz, $^3J_{\text{PC}} = 28.7$ Hz), 77.0 (dd, $^1J_{\text{PC}} = 192.6$ Hz), 61.6, 16.1 ppm; ^{31}P NMR (CDCl₃) δ 21.9 ppm; ^{19}F NMR (CDCl₃) δ -104.8 ppm; IR (KBr) 3348, 3206, 1217, 1042 cm⁻¹; MS (EI) m/z 247 (M⁺, 89); Anal. Calcd. for C₇H₁₃F₃NOP: C, 34.02; H, 5.30; N: 5.67. Found: : C, 34.16; H, 5.31; N: 5.69.

2-Amino-2-trifluoromethylbutyldiphenylphosphine oxide 27b. The general procedure was followed using 3-ethyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide **19/20b** (1.70 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.01 g, (59 %) of compound **27b** as a white solid: *mp* 104-106°C; ^1H NMR (CDCl₃) δ 7.82-7.45 (m, 10H), 2.71 (dd, $^2J_{\text{PH}} = 11.0$ Hz, $^2J_{\text{HHgem}} = 15.4$ Hz, 1H), 2.60 (dd, $^2J_{\text{PH}} = 12.1$ Hz, $^2J_{\text{HHgem}} = 15.4$ Hz, 1H), 1.99 (s, 2H), 1.87 (q, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 0.90 (dt, $^3J_{\text{HH}} = 7.5$ Hz, $^5J_{\text{PH}} = 1.4$ Hz, 3H) ppm; ^{13}C NMR (CDCl₃) δ 134.6-128.7 (m), 127.1 (dq, $^1J_{\text{FC}} = 286.6$ Hz, $^3J_{\text{PC}} = 12.1$ Hz), 59.4 (dq, $^2J_{\text{FC}} = 25.9$ Hz, $^2J_{\text{PC}} = 4.8$ Hz), 33.1 (d, $^1J_{\text{PC}} = 72.5$ Hz), 29.8 (d, $^3J_{\text{PC}} = 4.0$ Hz), 8.3 ppm; ^{31}P NMR (CDCl₃) δ 27.94 ppm; ^{19}F NMR (CDCl₃) δ -79.3 ppm; IR (KBr) 3403, 3323, 3058, 1613, 1430, 1162 cm⁻¹; MS (EI) m/z 341 (M⁺, 5), 201 (P(O)Ph₂⁺, 100); Anal. Calcd. for C₁₇H₁₉F₃NOP: C, 59.82; H, 5.61; N: 4.10. Found: C, 59.87; H, 5.62; N: 4.10.

2-Amino-2-trifluoromethylpentyldiphenylphosphine oxide 27c. The general procedure was followed using 3-allyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide **19/20c** (1.76 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.94 g, (53 %) of compound **27c** as a white solid: *mp* 72-74°C; ^1H NMR (CDCl₃) δ 7.81-7.27 (m, 10H), 2.71 (dd, $^2J_{\text{PH}} = 11.6$ Hz, $^2J_{\text{HHgem}} = 15.4$ Hz, 1H), 2.63 (dd, $^2J_{\text{PH}} = 11.6$ Hz, $^2J_{\text{HHgem}} = 15.4$ Hz, 1H), 2.09 (s, 2H), 1.72 (m, 2H), 1.52 (m, 2H), 0.71 (q, $^3J_{\text{HH}} = 7.2$ Hz, 3H) ppm; ^{13}C NMR (CDCl₃) δ 132.1-128.9 (m), 126.9 (dq,

$^1J_{\text{FC}} = 287.1$ Hz, $^3J_{\text{PC}} = 11.6$ Hz), 59.1(dq, $^2J_{\text{FC}} = 26.2$ Hz, $^2J_{\text{PC}} = 4.5$ Hz), 39.3 (d, $^3J_{\text{PC}} = 3.5$ Hz), 33.2 (d, $^1J_{\text{PC}} = 72.5$ Hz), 14.1 ppm; ^{31}P NMR (CDCl_3) δ 28.2 ppm; ^{19}F NMR (CDCl_3) δ -79.5 ppm; IR (KBr) 3356, 3295, 3051, 1593, 1434, 1241 cm^{-1} ; MS (EI) m/z 355 (M^+ , 6), 201 ($\text{P}(\text{O})\text{Ph}_2^+$, 100); Anal. Calcd. for $\text{C}_{18}\text{H}_{21}\text{F}_3\text{NOP}$: C, 60.84; H, 5.96; N: 3.94. Found: C, 60.94; H, 5.96; N: 3.95.

2-Amino-2-phenyl-2-trifluoromethylethyldiphenylphosphine oxide 27d. The general procedure was followed using 3-phenyl-3-trifluoromethylaziridin-2-ylidiphenylphosphine oxide **19/20d** (1.94 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 1.26 g, (65 %) of compound **27d** as a white solid: *mp* 131-133°C; ^1H NMR (CDCl_3) δ 8.38-7.01 (m, 15H), 3.12 (dd, $^2J_{\text{PH}} = 11.2$ Hz, $^2J_{\text{HH}_{\text{gem}}} = 3.5$ Hz, 2H), 1.68 (s, 2H) ppm; ^{13}C NMR (CDCl_3) δ 134.7-124.2 (m), 61.2 (dq, $^2J_{\text{FC}} = 26.7$ Hz, $^2J_{\text{PC}} = 4.0$ Hz), 36.2 (d, $^1J_{\text{PC}} = 72.0$ Hz) ppm; ^{31}P NMR (CDCl_3) δ 28.4 ppm; ^{19}F NMR (CDCl_3) δ -79.7 ppm; IR (KBr) 3423, 3211, 3058, 1593, 1440, 1241, 1162 cm^{-1} ; MS (EI) m/z 389 (M^+ , 8), 201 ($\text{P}(\text{O})\text{Ph}_2^+$, 100); Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{NOP}$: C, 64.78; H, 4.92; N: 3.60. Found: C, 64.85; H, 4.92; N: 3.61.

Diethyl 2-amino-2-trifluoromethylbutylphosphonate 28a. The general procedure was followed using diethyl 3-ethyl-3-trifluoromethylaziridin-2-ylphosphonate **21/22a** (1.38 g, 5 mmol). Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.89 g, (64 %) of compound **28a** as a pale yellow oil: *R_f* 0.30 (ethyl acetate); ^1H NMR (CDCl_3) δ 4.13 (m, 4H), 2.10 (d, $^2J_{\text{PH}} = 20.0$ Hz, 1H), 1.86 (m, 4H), 1.34 (m, 6H), 1.01 (m, 3H) ppm; ^{13}C NMR (CDCl_3) δ 127.4 (dq, $^1J_{\text{FC}} = 285.8$ Hz, $^3J_{\text{PC}} = 16.3$ Hz), 62.1 (d, $^2J_{\text{PC}} = 6.6$ Hz), 61.8 (d, $^2J_{\text{PC}} = 6.6$ Hz), 45.5 (dq, $^2J_{\text{FC}} = 26.2$ Hz, $^2J_{\text{PC}} = 3.0$ Hz), 30.3 (d, $^1J_{\text{PC}} = 104.0$ Hz), 29.4, 16.5, 16.4, 8.2 ppm; ^{31}P NMR (CDCl_3) δ 27.0 ppm; ^{19}F NMR (CDCl_3) δ -79.6 ppm; IR (KBr) 3403, 3310, 1633, 1467, 1394, 1162, 1056 cm^{-1} ; MS (EI) m/z 278 ($\text{M}^+ + 1$, 100); Anal. Calcd. for $\text{C}_9\text{H}_{19}\text{F}_3\text{NO}_3\text{P}$: C, 38.99; H, 6.91; N: 5.05. Found: C, 39.06; H, 6.92; N: 5.05.

Diethyl 2-amino-2-trifluoromethylpentylphosphonate 28b. The general procedure was followed using diethyl cis-3-allyl-2-methyl-3-trifluoromethylaziridin-2-ylphosphonate **21/22d** (1.52 g, 5 mmol).

Chromatographic purification eluting with 1:1 hexane/ethyl acetate to afford 0.87 g, (57 %) of compound **28b** as a pale yellow oil: R_f 0.58 (ethyl acetate); ^1H NMR (CDCl_3) δ 4.13 (m, 4H), 2.06 (dd, $^2J_{\text{HH}} = 16.9$ Hz, $^3J_{\text{HH}} = 8.8$ Hz, 1H), 1.90 (s, 4H), 1.46 (m, 7H), 1.32 (m, 6H), 0.95 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3) δ 125.3 (q, $^1J_{\text{FC}} = 279.5$ Hz), 63.4 (d, $^2J_{\text{PC}} = 7.0$ Hz), 63.0 (d, $^2J_{\text{PC}} = 7.0$ Hz), 48.7 (q, $^2J_{\text{FC}} = 36.4$ Hz), 42.0 (d, $^1J_{\text{PC}} = 159.1$ Hz), 32.2, 19.0, 16.6 (d, $^3J_{\text{PC}} = 6.0$ Hz), 16.5 (d, $^3J_{\text{PC}} = 6.0$ Hz), 15.3, 14.3 ppm; ^{31}P NMR (CDCl_3) δ 23.4, 22.8 ppm; ^{19}F NMR (CDCl_3) δ -64.3, -76.2 ppm; IR (KBr) 3462, 3204, 1460, 1394, 1215, 1176 cm^{-1} ; MS (EI) m/z 306 ($\text{M}^+ + 1$, 25); Anal. Calcd. for $\text{C}_{11}\text{H}_{23}\text{F}_3\text{NO}_3\text{P}$: C, 43.28; H, 7.59; N: 4.59. Found: C, 43.14; H, 7.57; N: 4.60.

Procedure for the Preparation of fluorine containing β -aminophosphine oxide **29 or β -aminophosphonate **30** from *p*-toluenesulfonyloxime **11** or **12**.** To a solution of fluorinated *p*-toluenesulfonyloxime phosphine oxide **11** (5 mmol) or *p*-toluenesulfonyloxime phosphate **12** (5 mmol) in THF (15 mL) was added NaBH_4 (15 mmol) at -30°C under nitrogen atmosphere. The mixture was stirred at -30°C until TLC indicated the disappearance of *p*-toluenesulfonyloxime. After the reaction was complete, the mixture was quenched with a saturated NH_4Cl solution (15 mL). The crude reaction was extracted three times with CH_2Cl_2 (3 x 15 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and the solvent was evaporated under vacuum. The crude residue was then purified by flash chromatography on silica gel (hexane/ AcOEt 2/1) to yield the compounds **29** and **30** like as a pale yellow oil.

Diethyl 2-amino-3,3,3-trifluoropropylphosphonate **30a.** The general procedure was followed using diethyl *Z*-3,3,3-trifluoro-2-(*N*-*p*-toluenesulfonyloxyimino)propylphosphonate **12a** (2.09 g, 5 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.90 g, (72 %) of compound **30a** as a pale yellow oil: R_f 0.15 (hexane/ethyl acetate, 3/7); ^1H NMR (CDCl_3) δ 4.10 (m, 4H), 3.61 (m, 1H), 2.08 (ddd, $^2J_{\text{PH}} = 20.9$ Hz, $^3J_{\text{HH}} = 2.4$ Hz, $^2J_{\text{HHgem}} = 15.3$ Hz, 1H), 1.83 (ddd, $^2J_{\text{PH}} = 17.4$ Hz, $^3J_{\text{HH}} = 11.4$ Hz, $^2J_{\text{HHgem}} = 15.3$ Hz, 1H), 1.66 (s, 2H), 1.29 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 125.6 (dq, $^1J_{\text{FC}} = 281.0$ Hz, $^3J_{\text{PC}} = 23.2$ Hz), 62.3, 49.8 (q, $^2J_{\text{FC}} = 30.2$ Hz), 27.0 (d, $^1J_{\text{PC}} = 146.6$ Hz), 16.3

ppm; ^{31}P NMR (CDCl_3) δ 27.2 ppm; ^{19}F NMR (CDCl_3) δ -80.6 ppm; IR (KBr) 3397, 3317, 1254, 1028 cm^{-1} ; MS (EI) m/z 250 ($\text{M}^+ + 1$, 7); Anal. Calcd. for $\text{C}_7\text{H}_{15}\text{F}_3\text{NO}_3\text{P}$: C, 33.74; H, 6.07; N: 5.62. Found: C, 33.63; H, 6.07; N: 5.61.

Diethyl 2-amino-3,3,4,4-pentafluorobutylphosphonate 30b. The general procedure was followed using diethyl 3,3,4,4-pentafluoro-2-(*N-p*-toluenesulfonyloxyimino)butylphosphonate **12b** (2.34 g, 5 mmol). Chromatographic purification eluting with 2:1 hexane/ethyl acetate to afford 0.90 g, (72 %) of compound **30b** as a pale yellow oil: R_f 0.11 (hexane/ethyl acetate, 3/7); ^1H NMR (CDCl_3) δ 4.10 (m, 4H), 3.71 (m, 1H), 2.18 (ddd, $^2J_{\text{PH}} = 21.0$ Hz, $^3J_{\text{HH}} = 2.1$ Hz, $^2J_{\text{HHgem}} = 15.3$ Hz, 1H), 1.89 (ddd, $^2J_{\text{PH}} = 17.4$ Hz, $^3J_{\text{HH}} = 11.4$ Hz, $^2J_{\text{HHgem}} = 15.3$ Hz, 1H), 1.63 (s, 2H), 1.28 (m, 6H) ppm; ^{13}C NMR (CDCl_3) δ 113.7(m), 48.8 (t, $^2J_{\text{FC}} = 22.7$ Hz), 26.9 (d, $^1J_{\text{PC}} = 146.0$ Hz), 16.4 ppm; ^{31}P NMR (CDCl_3) δ 27.6 ppm; ^{19}F NMR (CDCl_3) δ -81.3, -122.4 (d, $^2J_{\text{FF}} = 279.2$ Hz, 1F), -129.9 (d, $^2J_{\text{FF}} = 286.9$ Hz, 1F) ppm; IR (KBr) 3382, 1204, 1031 cm^{-1} ; MS (EI) m/z 300 ($\text{M}^+ + 1$, 35); Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{F}_5\text{NO}_3\text{P}$: C, 32.12; H, 5.05; N: 4.68. Found: C, 32.28; H, 5.06; N: 4.70.

References and Notes

(1) Lawrence, W. *Preparation of Alkenes. A Practical Approach*; Ed. Williams J. M.J.; Oxford. **1996**, 35–36.