



***Advanced***  
**Synthesis &  
Catalysis**

Supporting Information

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## Spectral and Analytical Data

$^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (101 MHz), and  $^{31}\text{P}$  NMR (162 MHz) spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts ( $\delta$ ) are denoted in ppm and are referenced to TMS as internal standard ( $\delta = 0$ ) ( $^1\text{H}$ ), to external  $\text{H}_3\text{PO}_4$  (85% solution in  $\text{D}_2\text{O}$ ,  $\delta = 0$ ) ( $^{31}\text{P}$ ), or to the solvent  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm) ( $^{13}\text{C}$ ). IR spectra were obtained using SPECORD 75 IR and Carl Zeiss UR-20 spectrophotometers. Mass spectra were recorded with Thermo Finnigan SSQ 7000 instrument (EI ionization, 70 eV). Elemental analysis was performed using autoanalyzer Carlo Erba.

***N*-(*p*-Anisyl)benzenecarboxyimidoyl chloride (1b).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.83$  (s, 3H,  $\text{CH}_3$ ), 6.95 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H), 7.07 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H), 7.46 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 2H), 7.52 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 1H), 8.16 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 55.4$  (? ?  $_3$ ), 114.0 (2? H), 122.4 (2CH), 126.9, 128.4 (2CH), 129.3 (2CH), 131.8 (CH), 135.8, 140.3, 157.3 (COMe).

***N*-(*p*-Anisyl)furan-2-carboxyimidoyl chloride (1e).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.82$  (s, 3H,  $\text{CH}_3$ ), 6.54 (dd,  $^3J_{? ?} = 3.5$  Hz,  $^3J_{? ?} = 1.8$  Hz, 1H), 6.93 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H), 7.13 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H), 7.17 (d,  $^3J_{\text{HH}} = 3.5$  Hz, 1H), 7.61 (d,  $^3J_{\text{HH}} = 1.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 55.3$  (? ?  $_3$ ), 112.1 (CH), 113.9 (2? H), 117.7 (CH), 123.0 (2CH), 130.3, 139.1, 146.4 (CH), 148.7, 157.6 (COMe).

***N*-(*p*-Anisyl)-2,2,2-trifluoroethanimidoyl chloride (1h).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.83$  (s, 3H,  $\text{CH}_3$ ), 6.95 (d,  $^3J_{\text{AB}} = 8.9$  Hz, 2H), 7.30 (d,  $^3J_{\text{AB}} = 8.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 55.5$  (? ?  $_3$ ), 114.3 (2? H), 117.0 (q,  $^1J_{\text{CF}} = 276.6$  Hz,  $\text{CF}_3$ ), 124.3 (2CH), 128.2 (q,  $^2J_{\text{CF}} = 42.5$  Hz, CCl), 135.5 (? -N), 159.6 (COMe).

**Diethyl *a*-(phenylimino)benzylphosphonate (2?).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.4$  and 6.5 (11:89).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for major isomer:  $\delta = 1.32$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H, 2 $\text{CH}_3$ ), 4.26 (m,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2 $\text{CH}_2$ ), 6.72 (d,  $^3J_{? ?} = 7.6$  Hz, 2H, 2 $\text{CH}_{\text{arom}}$ ), 6.99 (t,  $^3J_{? ?} = 7.6$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.16 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, 2 $\text{CH}_{\text{arom}}$ ), 7.20-7.35 (m, 5H, 5 $\text{CH}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) for major isomer: 16.2 (d,  $^3J_{\text{CP}} = 5.9$  Hz, 2 $\text{CH}_3$ ), 63.6 (d,  $^2J_{\text{CP}} = 6.8$  Hz, 2 $\text{CH}_2$ ), 120.5 (2CH), 124.7 (CH), 128.1 (2CH), 128.4 (2CH), 128.5 (2CH), 129.3 (CH), 133.7 (d,  $^2J_{\text{CP}} = 31.2$  Hz), 149.0 ( $^3J_{\text{CP}} = 32.9$  Hz, ? -N), 167.4 (d,  $^1J_{\text{CP}} = 216.7$  Hz, C-P). IR (film):  $\nu(\text{C}=\text{N}) = 1595$ ,  $\nu(\text{P}=\text{O}) = 1260$ ,  $\nu(\text{O}-\text{C}) = 1035$   $\text{cm}^{-1}$ .

**Diethyl *a*-(*p*-anisylimino)benzylphosphonate (2b).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.6$  and 7.0 (7:93).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for major isomer:  $\delta = 1.30$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H, 2 $\text{CH}_3$ ), 3.69 (s, 3H,  $\text{OCH}_3$ ), 4.23 (m,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2 $\text{CH}_2$ ), 6.68 (d,  $^3J_{\text{AB}} = 9.2$  Hz, 2H, 2 $\text{CH}_{p\text{-anisyl}}$ ), 6.72 (d,

$^3J_{AB} = 9.2$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 7.25-7.32 (m, 5H, 5CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) for major isomer: 16.1 (d,  $^3J_{CP} = 5.9$  Hz, 2CH<sub>3</sub>), 55.0 (OCH<sub>3</sub>), 63.3 (d,  $^2J_{CP} = 6.6$  Hz, 2CH<sub>2</sub>), 113.6 (2CH<sub>p-anisyl</sub>), 123.0 (2CH<sub>p-anisyl</sub>), 128.1 (d,  $^3J_{CP} = 4.4$  Hz, 2CH), 128.2 (2CH), 129.0 (CH), 134.2 (d,  $^2J_{CP} = 31.5$  Hz), 141.6 ( $^3J_{CP} = 33.7$  Hz, ? -N), 157.2 (COMe), 165.6 (d,  $^1J_{CP} = 219.6$  Hz). MS:  $m/z$  (I, %) = 347 (3.1, [M]<sup>+</sup>), 210 (100, [M-P(O)(OEt)<sub>2</sub>]<sup>+</sup>), 29 (15.4). IR (film):  $\nu(\text{C}=\text{N}) = 1595$ ,  $\nu(\text{P}=\text{O}) = 1245$ ,  $\nu(\text{O}-\text{C}) = 1015$  cm<sup>-1</sup>.

**Diethyl a-(p-anisylimino)-4-methylbenzylphosphonate (2c).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 2.9$  and 7.2 (7:93).  $^1\text{H}$  NMR (CDCl<sub>3</sub>) for major isomer:  $\delta = 1.32$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H, 2CH<sub>3</sub>), 2.30 (s, 3H, CCH<sub>3</sub>), 3.73 (s, 3H, OCH<sub>3</sub>), 4.23 (m,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2CH<sub>2</sub>), 6.70 (d,  $^3J_{AB} = 9.2$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.72 (d,  $^3J_{AB} = 9.2$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 7.07 (d,  $^3J_{AB} = 7.9$  Hz, 2H, 2CH<sub>arom</sub>), 7.20 (d,  $^3J_{AB} = 7.9$  Hz, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) for major isomer: 16.3 (d,  $^3J_{CP} = 5.8$  Hz, 2CH<sub>3</sub>), 21.3 (CCH<sub>3</sub>), 55.2 (OCH<sub>3</sub>), 63.5 (d,  $^2J_{CP} = 6.6$  Hz, 2CH<sub>2</sub>), 113.8 (2CH<sub>p-anisyl</sub>), 123.0 (2CH<sub>p-anisyl</sub>), 128.4 (d,  $^3J_{CP} = 4.4$  Hz, 2CH), 129.1 (2CH), 131.3 (d,  $^2J_{CP} = 31.5$  Hz), 139.3 (CMe), 142.1 ( $^3J_{CP} = 33.7$  Hz, ? -N), 157.3 (COMe), 165.9 (d,  $^1J_{CP} = 218.8$  Hz). MS:  $m/z$  (I, %) = 361 (15.2, [M]<sup>+</sup>), 224 (100, [M-P(O)(OEt)<sub>2</sub>]<sup>+</sup>), 29 (60.9). IR (film):  $\nu(\text{C}=\text{N}) = 1595$ ,  $\nu(\text{P}=\text{O}) = 1235$ ,  $\nu(\text{O}-\text{C}) = 1015$  cm<sup>-1</sup>.

**Diethyl a-(p-anisylimino)-4-fluorobenzylphosphonate (2d).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 2.5$  and 6.9 (9:91).  $^1\text{H}$  NMR (CDCl<sub>3</sub>) for major isomer:  $\delta = 1.33$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H, 2CH<sub>3</sub>), 3.73 (s, 3H, OCH<sub>3</sub>), 4.25 (m,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2CH<sub>2</sub>), 6.71 (s, 4H, 4CH<sub>p-anisyl</sub>), 6.97 (dd,  $^3J_{AB} = 8.1$  Hz,  $^3J_{\text{HF}} = 9.1$  Hz, 2H, 2CH<sub>arom</sub>), 7.33 (dd,  $^3J_{AB} = 8.1$  Hz,  $^4J_{\text{HF}} = 5.6$  Hz, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) for major isomer: 16.2 (d,  $^3J_{CP} = 5.1$  Hz, 2CH<sub>3</sub>), 55.2 (OCH<sub>3</sub>), 63.5 (d,  $^2J_{CP} = 6.6$  Hz, 2CH<sub>2</sub>), 113.8 (2CH<sub>p-anisyl</sub>), 115.5 (d,  $^2J_{\text{CF}} = 22.0$  Hz, 2CH), 122.9 (2CH<sub>p-anisyl</sub>), 130.2 (d,  $^2J_{CP} = 32.2$  Hz), 130.6 (d,  $^3J_{CP} = 3.7$  Hz,  $^3J_{\text{CF}} = 8.1$  Hz, 2CH), 141.6 ( $^3J_{CP} = 32.9$  Hz, ? -N), 157.4 (COMe), 162.8 (d,  $^1J_{\text{CF}} = 250.3$  Hz), 164.6 (d,  $^1J_{CP} = 221.8$  Hz). MS:  $m/z$  (I, %) = 365 (23.6, [M]<sup>+</sup>), 228 (100, [M-P(O)(OEt)<sub>2</sub>]<sup>+</sup>), 29 (46.4). IR (film):  $\nu(\text{C}=\text{N}) = 1590$ ,  $\nu(\text{P}=\text{O}) = 1230$ ,  $\nu(\text{O}-\text{C}) = 1015$  cm<sup>-1</sup>.

**Diethyl (p-anisylimino)(2-furyl)methylphosphonate (2e).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.6$  and 6.4 (14:86).  $^1\text{H}$  NMR (CDCl<sub>3</sub>) for major isomer:  $\delta = 1.38$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H, 2CH<sub>3</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 4.32 (m,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2CH<sub>2</sub>), 6.35 (dd,  $^3J_{\text{HH}} = 1.9$  Hz,  $^3J_{\text{HH}} = 3.5$  Hz, 1H), 6.68 (d,  $^3J_{\text{HH}} = 3.5$  Hz, 1H), 6.77 (d,  $^3J_{AB} = 8.8$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.87 (d,  $^3J_{AB} = 8.8$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 7.35 (br.d,  $^3J_{\text{HH}} = 1.9$  Hz, 1H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) for major isomer: 16.2 (d,  $^3J_{CP} = 5.9$  Hz, 2CH<sub>3</sub>), 55.2 (OCH<sub>3</sub>), 63.6 (d,  $^2J_{CP} = 6.6$  Hz, 2CH<sub>2</sub>), 111.4 (CH), 114.1 (2CH<sub>p-anisyl</sub>), 118.0 (d,  $^3J_{CP} = 2.9$  Hz, CH), 119.7 (2CH<sub>p-anisyl</sub>), 144.3 (CH), 144.3 (d,  $^3J_{CP} = 31.5$  Hz, ? -N), 146.8 (d,  $^2J_{CP} = 43.9$  Hz), 152.4 (d,  $^1J_{CP} = 226.2$  Hz), 156.9 (COMe). MS:  $m/z$  (I, %) = 337

(21.5,  $[M]^+$ ), 200 (100,  $[M-P(O)(OEt)_2]^+$ ), 29 (14.7). IR (film):  $\nu(C=N) = 1595$ ,  $\nu(P=O) = 1240$ ,  $\nu(O-C) = 1025\text{ cm}^{-1}$ .

**Diethyl (*p*-anisylimino)(2-thienyl)methylphosphonate (2f).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.8$  and 6.7 (22:78).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for major isomer:  $\delta = 1.38$  (t,  $^3J_{\text{HH}} = 7.0\text{ Hz}$ , 6H,  $2\text{CH}_3$ ), 3.81 (s, 3H,  $\text{OCH}_3$ ), 4.31 (m,  $^3J_{\text{HH}} = 7.0\text{ Hz}$ , 4H,  $2\text{CH}_2$ ), 6.73 (d,  $^3J_{\text{AB}} = 8.7\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ), 6.89 (d,  $^3J_{\text{AB}} = 8.7\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ), 6.96 (dd,  $^3J_{\text{HH}} = 3.8\text{ Hz}$ ,  $^3J_{\text{HH}} = 4.9\text{ Hz}$ , 1H), 7.35 (d,  $^3J_{\text{HH}} = 4.9\text{ Hz}$ , 1H), 7.91 (d,  $^3J_{\text{HH}} = 3.8\text{ Hz}$ , 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) for major isomer: 16.3 (d,  $^3J_{\text{CP}} = 5.9\text{ Hz}$ ,  $2\text{CH}_3$ ), 55.4 ( $\text{OCH}_3$ ), 63.7 (d,  $^2J_{\text{CP}} = 6.6\text{ Hz}$ ,  $2\text{CH}_2$ ), 114.8 ( $2\text{CH}_{p\text{-anisyl}}$ ), 120.1 ( $2\text{CH}_{p\text{-anisyl}}$ ), 126.4 (CH), 131.4 (CH), 133.5 (d,  $^2J_{\text{CP}} = 43.9\text{ Hz}$ ), 134.5 (CH), 144.3 ( $^3J_{\text{CP}} = 31.5\text{ Hz}$ , ? -N), 157.3 (COMe), 158.2 (d,  $^1J_{\text{CP}} = 222.5\text{ Hz}$ ). MS:  $m/z$  (I, %) = 353 (13.8,  $[M]^+$ ), 216 (100,  $[M-P(O)(OEt)_2]^+$ ), 29 (0.8). IR (Nujol):  $\nu(C=N) = 1580$  and 1605,  $\nu(P=O) = 1250$ ,  $\nu(O-C) = 1040\text{ cm}^{-1}$ .

**Diethyl 1-(*p*-anisylimino)-2,2-dimethylpropylphosphonate (2g).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.4$  and 6.9 (96:4).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for major isomer:  $\delta = 1.14$  (t,  $^3J_{\text{HH}} = 6.9\text{ Hz}$ , 6H,  $2\text{CH}_3$ ), 1.36 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 3.78 (s, 3H,  $\text{OCH}_3$ ), 3.89 (m, 4H,  $2\text{CH}_2$ ), 6.70 (d,  $^3J_{\text{AB}} = 8.5\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ), 6.82 (d,  $^3J_{\text{AB}} = 8.5\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) for major isomer: 16.0 (d,  $^3J_{\text{CP}} = 6.6\text{ Hz}$ ,  $2\text{CH}_3$ ), 27.9 ( $\text{C}(\text{CH}_3)_3$ ), 42.1 (d,  $^2J_{\text{CP}} = 34.4\text{ Hz}$ ,  $\text{C}(\text{CH}_3)_3$ ), 55.4 ( $\text{OCH}_3$ ), 61.3 (d,  $^2J_{\text{CP}} = 5.1\text{ Hz}$ ,  $2\text{CH}_2$ ), 113.5 ( $2\text{CH}_{p\text{-anisyl}}$ ), 118.6 ( $2\text{CH}_{p\text{-anisyl}}$ ), 144.2 ( $^3J_{\text{CP}} = 17.6\text{ Hz}$ , ? -N), 156.0 (COMe), 171.4 (d,  $^1J_{\text{CP}} = 120.0\text{ Hz}$ ). MS:  $m/z$  (I, %) = 327 (31.0,  $[M]^+$ ), 270 (12.1,  $[M-\text{C}_4\text{H}_9]^+$ ), 190 (100,  $[M-P(O)(OEt)_2]^+$ ), 134 (99.8,  $[M-P(O)(OEt)_2-\text{C}_4\text{H}_8]^+$ ), 29 (9.5). IR (film):  $\nu(C=N) = 1615$ ,  $\nu(P=O) = 1225$ ,  $\nu(O-C) = 1015\text{ cm}^{-1}$ .

**Diethyl 1-(*p*-anisylimino)-2,2,2-trifluoroethylphosphonate (2h).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -3.1$  and 1.9 (88:12).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for major isomer:  $\delta = 1.18$  (t,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ , 6H,  $2\text{CH}_3$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 4.00 (m,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ , 4H,  $2\text{CH}_2$ ), 6.92 (d,  $^3J_{\text{AB}} = 8.7\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ), 7.13 (d,  $^3J_{\text{AB}} = 8.7\text{ Hz}$ , 2H,  $2\text{CH}_{p\text{-anisyl}}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) for major isomer: 15.9 (d,  $^3J_{\text{CP}} = 5.9\text{ Hz}$ ,  $2\text{CH}_3$ ), 55.4 ( $\text{OCH}_3$ ), 63.5 (d,  $^2J_{\text{CP}} = 6.6\text{ Hz}$ ,  $2\text{CH}_2$ ), 113.8 ( $2\text{CH}_{p\text{-anisyl}}$ ), 119.4 (dd,  $^2J_{\text{CP}} = 47.9\text{ Hz}$ ,  $^1J_{\text{CF}} = 279.2\text{ Hz}$ ), 121.6 ( $2\text{CH}_{p\text{-anisyl}}$ ), 140.2 ( $^3J_{\text{CP}} = 13.9\text{ Hz}$ , ? -N), 150.7 (dd,  $^1J_{\text{CP}} = 158.8\text{ Hz}$ ,  $^2J_{\text{CF}} = 35.5\text{ Hz}$ ), 159.1 (COMe). MS:  $m/z$  (I, %) = 339 (100,  $[M]^+$ ), 270 (97.4,  $[M-\text{CF}_3]^+$ ), 214 (36.9), 202 (35.6,  $[M-P(O)(OEt)_2]^+$ ), 134 (52.8), 29 (26.9). IR (film):  $\nu(C=N) = 1585$ ,  $\nu(P=O) = 1255$ ,  $\nu(\text{CF}_3) = 1135$  and 1155,  $\nu(O-C) = 1015\text{ cm}^{-1}$ .

**Diethyl  $\alpha$ -(phenylamino)benzylphosphonate (3a).**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 22.8$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.11$  (dt,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ ,  $^4J_{\text{HP}} = 0.5\text{ Hz}$ , 3H,  $\text{CH}_3$ ), 1.28 (dt,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ ,  $^4J_{\text{HP}} = 0.5\text{ Hz}$ , 3H,  $\text{CH}_3$ ), 3.67 (m, 1H,  $\text{CH}_2$ ), 3.93 (m, 1H,  $\text{CH}_2$ ), 4.11 (m, 2H,  $\text{CH}_2$ ), 4.76 (d,  $^2J_{\text{HP}} = 24.3\text{ Hz}$ , 1H,  $\text{CHP}$ ), 4.79 (br.s, 1H,  $\text{NH}$ ), 6.59 (dd,  $^3J_{\text{HH}} = 8.6\text{ Hz}$ ,  $^4J_{\text{HH}} = 1.0\text{ Hz}$ , 2H,  $2\text{CH}_{\text{arom}}$ ),

6.69 (dt,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H, CH<sub>arom</sub>), 7.10 (dd,  $^3J_{\text{HH}} = 8.6$  Hz,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, 2CH<sub>arom</sub>), 7.26 (m, 1H, CH<sub>arom</sub>), 7.33 (m, 2H, 2CH<sub>arom</sub>), 7.47 (m,  $^4J_{\text{HP}} = 2.0$  Hz, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.2 (d,  $^3J_{\text{CP}} = 5.9$  Hz, CH<sub>3</sub>), 16.4 (d,  $^3J_{\text{CP}} = 5.9$  Hz, CH<sub>3</sub>), 56.0 (d,  $^1J_{\text{CP}} = 150.8$  Hz), 63.2 (d,  $^2J_{\text{CP}} = 5.9$  Hz, CH<sub>2</sub>), 63.3 (d,  $^2J_{\text{CP}} = 6.6$  Hz, CH<sub>2</sub>), 113.8 (2CH), 118.4 (CH), 127.8 ( $^3J_{\text{CP}} = 5.1$  Hz, 2? H), 127.9 ( $^5J_{\text{CP}} = 3.0$  Hz, ? H), 128.6 (2CH), 129.1 (2CH), 135.9, 146.3 ( $^3J_{\text{CP}} = 15.4$  Hz, ? -N).

**Diethyl a-(*p*-anisylamino)benzylphosphonate (3b).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 23.1$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.11$  (dt,  $^3J_{\text{HH}} = 7.1$  Hz,  $^4J_{\text{HP}} = 0.5$  Hz, 3H, CH<sub>3</sub>), 1.28 (dt,  $^3J_{\text{HH}} = 7.1$  Hz,  $^4J_{\text{HP}} = 0.5$  Hz, 3H, CH<sub>3</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.70 (m, 1H, CH<sub>2</sub>), 3.93 (m, 1H, CH<sub>2</sub>), 4.10 (m, 2H, CH<sub>2</sub>), 4.53 (br.s, 1H, NH), 4.69 (d,  $^2J_{\text{HP}} = 23.9$  Hz, 1H, CHP), 6.54 (d,  $^3J_{\text{AB}} = 9.1$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 6.68 (d,  $^3J_{\text{AB}} = 9.1$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 7.25 (m, 1H, CH<sub>arom</sub>), 7.31 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H, 2CH<sub>arom</sub>), 7.45 (m, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.1 (d,  $^3J_{\text{CP}} = 5.9$  Hz, CH<sub>3</sub>), 16.4 (d,  $^3J_{\text{CP}} = 5.1$  Hz, CH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 57.0 (d,  $^1J_{\text{CP}} = 150.8$  Hz), 63.1 (d,  $^2J_{\text{CP}} = 6.6$  Hz, CH<sub>2</sub>), 63.2 (d,  $^2J_{\text{CP}} = 7.3$  Hz, CH<sub>2</sub>), 114.7 (2CH<sub>*p*-anisyl</sub>), 115.2 (2CH<sub>*p*-anisyl</sub>), 127.8 ( $^5J_{\text{CP}} = 2.9$  Hz, ? H), 127.9 ( $^3J_{\text{CP}} = 5.1$  Hz, 2? H), 128.5 (2CH), 136.1, 140.4 ( $^3J_{\text{CP}} = 15.4$  Hz, ? -N), 152.7 (COMe). IR (Nujol):  $\nu(\text{N-H}) = 3303$ ,  $\nu(\text{P=O}) = 1245$ ,  $\nu(\text{O-C}) = 1030$  cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>24</sub>NO<sub>4</sub>P: ? 61.88, ? 6.92, N 4.01; found: ? 61.62, ? 6.82, N 4.12.

**Diethyl a-(*p*-anisylamino)-4-methylbenzylphosphonate (3c).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 23.2$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.13$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>3</sub>), 1.28 (t,  $^3J_{\text{HH}} = 7.0$  Hz, 3H, CH<sub>3</sub>), 2.30 (d,  $J = 1.9$  Hz, 3H, CCH<sub>3</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.71 (m, 1H, CH<sub>2</sub>), 3.95 (m, 1H, CH<sub>2</sub>), 4.11 (m, 2H, CH<sub>2</sub>), 4.49 (br.s, 1H, NH), 4.65 (d,  $^2J_{\text{HP}} = 23.8$  Hz, 1H, CHP), 6.54 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 6.68 (d,  $^3J_{\text{AB}} = 9.0$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 7.12 (d,  $^3J_{\text{AB}} = 8.1$  Hz, 2H, 2CH<sub>arom</sub>), 7.33 (dd,  $^3J_{\text{AB}} = 8.1$  Hz,  $^4J_{\text{HP}} = 2.1$  Hz, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.2 (d,  $^3J_{\text{CP}} = 5.9$  Hz, CH<sub>3</sub>), 16.4 (d,  $^3J_{\text{CP}} = 5.9$  Hz, CH<sub>3</sub>), 21.1 (CCH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 56.7 (d,  $^1J_{\text{CP}} = 151.5$  Hz), 63.1 (d,  $^2J_{\text{CP}} = 7.3$  Hz, CH<sub>2</sub>), 63.2 (d,  $^2J_{\text{CP}} = 6.6$  Hz, CH<sub>2</sub>), 114.7 (2CH<sub>*p*-anisyl</sub>), 115.2 (2CH<sub>*p*-anisyl</sub>), 127.7 (d,  $^3J_{\text{CP}} = 5.1$  Hz, 2? H), 129.2 (2CH), 132.9, 137.5 (d,  $^5J_{\text{CP}} = 2.9$  Hz, ? CH<sub>3</sub>), 140.5 (d,  $^3J_{\text{CP}} = 15.4$  Hz, ? -N), 152.7 (COMe). IR (Nujol):  $\nu(\text{N-H}) = 3340$ ,  $\nu(\text{P=O}) = 1240$ ,  $\nu(\text{O-C}) = 1060$  cm<sup>-1</sup>. Anal. Calcd. for C<sub>19</sub>H<sub>26</sub>NO<sub>4</sub>P: ? 62.80, ? 7.21, N 3.85; found: ? 63.16, ? 6.93, N 3.61.

**Diethyl a-(*p*-anisylamino)-4-fluorobenzylphosphonate (3d).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 22.7$  (d,  $^6J_{\text{PF}} = 6.0$  Hz).  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.14$  (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>3</sub>), 1.28 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>3</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.75 (br.s, 1H, NH), 3.77 (m, 1H, CH<sub>2</sub>), 3.97 (m, 1H, CH<sub>2</sub>), 4.11 (m, 2H, CH<sub>2</sub>), 4.68 (d,  $^2J_{\text{HP}} = 23.9$  Hz, 1H, CHP), 6.53 (d,  $^3J_{\text{AB}} = 8.9$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 6.69 (d,  $^3J_{\text{AB}} = 8.9$  Hz, 2H, 2CH<sub>*p*-anisyl</sub>), 7.01 (dd,  $^3J_{\text{AB}} = 8.6$  Hz,  $^3J_{\text{HF}} = 8.6$  Hz, 2H, 2CH<sub>arom</sub>),

7.43 (ddd,  $^3J_{AB} = 8.6$  Hz,  $^4J_{HF} = 5.3$  Hz,  $^4J_{HP} = 2.3$  Hz, 2H, 2CH<sub>arom</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.1 (d,  $^3J_{CP} = 5.9$  Hz, CH<sub>3</sub>), 16.34 (d,  $^3J_{CP} = 5.1$  Hz, CH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 56.3 (d,  $^1J_{CP} = 150.8$  Hz), 63.1 (d,  $^2J_{CP} = 6.6$  Hz, CH<sub>2</sub>), 63.3 (d,  $^2J_{CP} = 7.3$  Hz, CH<sub>2</sub>), 114.7 (2CH<sub>p-anisyl</sub>), 115.2 (2CH<sub>p-anisyl</sub>), 115.4 (d,  $^2J_{CF} = 22.7$  Hz, 2? H), 129.4 (dd,  $^3J_{CP} = 5.1$  Hz,  $^3J_{CF} = 8.1$  Hz, 2? H), 131.8, 140.1 (d,  $^3J_{CP} = 15.4$  Hz, ? -N), 152.8 (COMe), 162.4 (dd,  $^5J_{CP} = 2.9$  Hz,  $^1J_{CF} = 245.9$  Hz, CF). IR (Nujol):  $\nu(\text{N-H}) = 3310$ ,  $\nu(\text{P=O}) = 1240$ ,  $\nu(\text{O-C}) = 1050$  cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>FNO<sub>4</sub>P: ? 58.85, ? 6.31, N 3.81; found: ? 59.17, ? 6.23, N 3.90.

**Diethyl (p-anisylamino)(2-thienyl)methylphosphonate (3f).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 21.2$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.20$  (t,  $^3J_{HH} = 7.0$  Hz, 3H, CH<sub>3</sub>), 1.29 (t,  $^3J_{HH} = 7.1$  Hz, 3H, CH<sub>3</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 3.88 (m, 1H, CH<sub>2</sub>), 4.05 (m, 1H, CH<sub>2</sub>), 4.14 (m, 2H, CH<sub>2</sub>), 4.36 (br.s, 1H, NH), 4.95 (d,  $^2J_{HP} = 23.5$  Hz, 1H, CHP), 6.63 (d,  $^3J_{AB} = 8.7$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.73 (d,  $^3J_{AB} = 8.7$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.96 (dd,  $^3J_{HH} = 4.9$  Hz,  $^3J_{HH} = 3.7$  Hz, 1H), 7.13 (br.m, 1H, CH<sub>thienyl</sub>), 7.21 (d,  $^3J_{HH} = 4.9$  Hz, 1H, CH<sub>thienyl</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.2 (d,  $^3J_{CP} = 5.9$  Hz, CH<sub>3</sub>), 16.4 (d,  $^3J_{CP} = 5.1$  Hz, CH<sub>3</sub>), 53.1 (d,  $^1J_{CP} = 156.8$  Hz), 55.6 (OCH<sub>3</sub>), 63.3 (d,  $^2J_{CP} = 6.7$  Hz, CH<sub>2</sub>), 63.6 (d,  $^2J_{CP} = 6.7$  Hz, CH<sub>2</sub>), 114.7 (2CH<sub>p-anisyl</sub>), 115.5 (2CH<sub>p-anisyl</sub>), 125.2 (CH<sub>thienyl</sub>), 127.0 (CH<sub>thienyl</sub>), 127.7 (d,  $^3J_{CP} = 6.8$  Hz, CH<sub>thienyl</sub>), 140.1, 140.1 (d,  $^3J_{CP} = 13.5$  Hz, ? -N), 153.1 (COMe). MS:  $m/z$  (I, %) = 355 (2.1, [M]<sup>+</sup>), 354 (10.0, [M-H]<sup>+</sup>), 218 (100, [M-P(O)(OEt)<sub>2</sub>]<sup>+</sup>), 111 (27.3, [M-P(O)(OEt)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>OMe]<sup>+</sup>). IR (Nujol):  $\nu(\text{N-H}) = 3315$ ,  $\nu(\text{P=O}) = 1245$ ,  $\nu(\text{O-C}) = 1040$  cm<sup>-1</sup>.

**Diethyl (p-anisylamino)-2,2-dimethylpropylphosphonate (3g).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 25.2$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.12$  (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.15 (t,  $^3J_{HH} = 7.1$  Hz, 3H, CH<sub>3</sub>), 1.23 (t,  $^3J_{HH} = 7.1$  Hz, 3H, CH<sub>3</sub>), 3.38 (d,  $^2J_{HP} = 18.7$  Hz, 1H, CHP), 3.73 (s, 3H, OCH<sub>3</sub>), 3.73 (br.s, 1H, NH), 3.95 (m, 1H, CH<sub>2</sub>), 4.04 (m, 3H, CH<sub>2</sub>), 6.60 (d,  $^3J_{AB} = 9.0$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.76 (d,  $^3J_{AB} = 9.0$  Hz, 2H, 2CH<sub>p-anisyl</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.2 (d,  $^3J_{CP} = 5.9$  Hz, CH<sub>3</sub>), 16.4 (d,  $^3J_{CP} = 5.1$  Hz, CH<sub>3</sub>), 27.5 (d,  $^3J_{CP} = 6.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (d,  $^2J_{CP} = 8.1$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 61.2 (d,  $^1J_{CP} = 147.1$  Hz), 61.4 (d,  $^2J_{CP} = 7.3$  Hz, CH<sub>2</sub>), 62.4 (d,  $^2J_{CP} = 7.3$  Hz, CH<sub>2</sub>), 114.1 (2CH<sub>p-anisyl</sub>), 114.7 (2CH<sub>p-anisyl</sub>), 142.2 (d,  $^3J_{CP} = 3.7$  Hz, ? -N), 152.0 (COMe). IR (Nujol):  $\nu(\text{N-H}) = 3330$ ,  $\nu(\text{P=O}) = 1240$ ,  $\nu(\text{O-C}) = 1060$  cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>28</sub>NO<sub>4</sub>P: ? 58.34, ? 8.57, N 4.25; found: ? 58.22, ? 8.85, N 3.97.

**Diethyl 1-(p-anisylamino)-2,2,2-trifluoroethylphosphonate (3h).**  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta = 14.9$  (d,  $^3J_{PF} = 7.9$  Hz).  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 1.26$  (t,  $^3J_{HH} = 7.1$  Hz, 3H, CH<sub>3</sub>), 1.32 (t,  $^3J_{HH} = 7.1$  Hz, 3H, CH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 4.05-4.25 (m, 6H), 6.70 (d,  $^3J_{AB} = 8.8$  Hz, 2H, 2CH<sub>p-anisyl</sub>), 6.79 (d,  $^3J_{AB} = 8.8$  Hz, 2H, 2CH<sub>p-anisyl</sub>).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>): 16.2 (d,  $^3J_{CP} = 5.9$  Hz, CH<sub>3</sub>), 16.3 (d,  $^3J_{CP} = 5.1$  Hz, CH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 55.7 (dd,  $^1J_{CP} = 152.2$  Hz,  $^2J_{CF} = 31.5$  Hz),

63.6 (d,  $^2J_{\text{CP}} = 7.3$  Hz,  $\text{CH}_2$ ), 64.0 (d,  $^2J_{\text{CP}} = 7.3$  Hz,  $\text{CH}_2$ ), 114.9 ( $2\text{CH}_{p\text{-anisyl}}$ ), 115.4 ( $2\text{CH}_{p\text{-anisyl}}$ ), 124.0 (dd,  $^2J_{\text{CP}} = 11.7$  Hz,  $^1J_{\text{CF}} = 283.2$  Hz), 139.5 (d,  $^3J_{\text{CP}} = 6.6$  Hz, ? -N), 153.6 (COMe). IR (Nujol):  $\nu(\text{N-H}) = 3310$ ,  $\nu(\text{P=O}) = 1250$ ,  $\nu(\text{O-C}) = 1040$   $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{13}\text{H}_{19}\text{F}_3\text{NO}_4\text{P}$ : ? 45.75, ? 5.61, N 4.10 ; found: ? 45.94, ? 5.54, N 4.22.