Electronic Supplementary Information


Roberta Berrino, a Sandro Cacchi, a* Giancarlo Fabrizi, a Antonella Goggiamani, a Paolo Stabile b

a Dipartimento di Chimica e Tecnologie del Farmaco, La Sapienza, Università di Roma, P.le A. Moro 5, 00185 Rome, Italy.
b Chemical Development Department, GlaxoSmithKline, Via Fleming 4, I-37135 Verona, Italy
sandrocacchi@uniroma1.it

Contents

General information: S2
General procedures: S2
Characterization data: S4
References: S11
NMR Spectra: S12
GENERAL INFORMATION

Melting points are uncorrected. All of the reagents, catalysts, and solvents are commercially available and were used as purchased, without further purification. Reaction products were purified by flash column chromatography using SiO₂ 25-40 μm and eluting with n-hexane/EtOAc or n-hexane/EtOAc/methanol mixtures.

GENERAL PROCEDURES

Typical Procedure for the Preparation of (2): Diethyl 4-Methoxyphenylphosphonate (2a). To a stirred mixture of 1a (110.9 mg, 0.50 mmol) and KI (249.0 mg, 1.50 mmol) in 1.0 mL of anhydrous MeCN, Pd(OAc)₂ (0.025 mmol, 5.6 mg), P(OEt)₃ (0.75 mmol, 128 μL), and Cs₂CO₃ (1.0 mmol, 325.8 mg) were added at room temperature and under argon with 2.0 mL of MeCN (the reactor was protected from light with aluminium film). Then, the reaction mixture was stirred for 18 h at 80 °C under argon. After this time, the reaction mixture was cooled to room temperature, diluted with EtOAc, washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, n-hexane/EtOAc 15/85 v/v) to afford 102.8 mg (84% yield) of 2a: oil;¹ IR (neat) 2895, 2917, 1444, 1234, 1024, 966 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.74 (dd, J₁ = 12.7 Hz, J₂ = 8.7 Hz, 2 H), 6.96 (dd, J₁ = 8.7 Hz, J₂ = 3.3 Hz, 2 H), 4.16-3.95 (m, 4 H), 3.84 (s, 3 H), 1.31 (t, J = 7.0 Hz, 6 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 163.0 (d, J = 3.0 Hz), 133.7 (d, J = 11.1 Hz), 119.0 (d, J = 195.0 Hz), 114.0 (d, J = 16.2 Hz), 61.9 (d, J = 5.4 Hz), 55.3, 16.3 (d, J = 6.2 Hz); ³¹P NMR (161.9 MHz) δ -7.46. MS (m/z): 244 (29%) M⁺, 188 (95 %), 108 (100%), 77 (37%); Anal Calcd for C₁₁H₁₇O₄P C, 54.10; H, 7.02; found C, 54.21; H, 7.00.

Typical Procedure for the Preparation of (6): (4-Methoxyphenyl)diphenylphosphine oxide (6a). To a stirred solution of 1a (110.9 mg, 0.50 mmol) and KI (249.0 mg, 1.50 mmol) in 1.0 mL of anhydrous MeCN, Pd(OAc)₂ (0.025 mmol, 5.6 mg), H(O)PPPh₂ (0.75 mmol, 151.6 mg), and Cs₂CO₃ (1.00 mmol, 325.8 mg) were added at room temperature and under argon with 2.0 mL of MeCN (the reactor was protected from light with aluminium film). Then, the mixture was stirred for 4 h at 80 °C under argon. After this time, the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, n-hexane/EtOAc/methanol 10/85/5 v/v) to afford 138.9 mg (90% yield) of 6a: mp: 106-108 °C (lit.² mp: 113-115°C). IR (KBr) 1598, 1191, 1120 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.66-7.46 (m,
12 H), 6.93 (dd, J1 = 8.8 Hz, J2 = 2.0, 2 H), 3.76 (s, 3H); 13C NMR (100.6 MHz) (CDCl3) δ 162.5 (d, J = 2.8 Hz), 133.9 (d, J = 11.2 Hz), 132.8 (d, J = 103.6 Hz), 131.9 (d, J = 20.3 Hz), 131.8 (d, J = 52.7 Hz), 128.4 (d, J = 12.1 Hz), 123.4 (d, J = 111.1 Hz), 114.1 (d, J = 13.1 Hz), 55.3; 31P NMR (161.9 MHz) δ 1.98. MS (m/z): 308 (67%) M+, 307 (100%), 231 (23%), 215 (26%), 77 (30%). Anal Calcd for C19H17O2P, C, 74.02; H, 5.56; found C, 74.21; H, 5.54.

**Typical Procedure for the One-pot Preparation of (2) from Anilines: Diethyl 4-Methoxyphenylphosphonate (2a).** A solution of Et2O-BF3 (0.55 mmol, 56 µL) in 1.0 mL of anhydrous THF was cooled at -15°C and 4-methoxyaniline (61.5 mg, 0.50 mmol) was added. Then, tert-butyl nitrite (0.65 mmol, 77 µL) was added dropwise to the rapidly stirred reaction mixture. Following complete addition, the temperature was maintained at -15°C for 10 min and subsequently allowed to warm to 5 °C in an ice-water bath over a 20-min period. Then, the reaction mixture was warmed to room temperature and stirred at the same temperature till the starting aniline was converted into 4-methoxybenzenediazonium tetrafluoroborate 1a. The reaction mixture was then concentrated under reduced pressure. The residue was diluted with 3 mL of anhydrous MeCN, KI (249.0 mg, 1.50 mmol), Pd(OAc)2 (0.025 mmol, 5.6 mg), POEt3 (0.75 mmol, 128 µL), and Cs2CO3 (1.00 mmol, 325.8 mg) were added and the resultant reaction mixture was stirred at 80 °C for 4h (the reactor was protected from light with aluminium film). After this time, the usual workup afforded 69.0 mg (56% yield) of 2a.
CHARACTERIZATION DATA

Diethyl Tolylphosphonate (2b): oil. IR (neat) 2983, 1606, 1444, 1247, 1130, 968 cm\(^{-1}\). \(^1\)H NMR (400 MHz) (CDCl\(_3\)) \(\delta\) 7.62 (dd, \(J_1 = 12.8\) Hz, \(J_2 = 8.0\) Hz, 2 H), 7.19 (dd, \(J_1 = 7.6\) Hz, \(J_2 = 4.0\) Hz, 2 H), 4.07-3.95 (m, 4 H), 1.95 (s, 1 H), 1.28-1.18 (m, 6 H); \(^1^3\)C NMR (100.6 MHz) (CDCl\(_3\)) \(\delta\) 142.8 (d, \(J = 3.2\) Hz), 131.7 (d, \(J = 10.2\) Hz), 129.1 (d, \(J = 15.4\) Hz), 125.0 (d, \(J = 189.2\) Hz), 63.5 (d, \(J = 5.8\) Hz), 21.5, 15.9 (d, \(J = 6.5\) Hz); \(^{31}\)P NMR (161.9 MHz) \(\delta\) -7.64. MS (m/z): 228 (21%) M\(^+\), 172 (100%), 155 (48%), 91 (95%), 77 (6%). Anal Calcd for C\(_{11}\)H\(_{17}\)O\(_3\)P, C, 57.89; H, 7.51; found C, 57.93; H, 7.48.

Diethyl 3,5-Dimethylphenylphosphonate (2c): oil. IR (neat) 2981, 1444, 1245, 1054, 1024, 964, 586 cm\(^{-1}\). \(^1\)H NMR (400 MHz) (CDCl\(_3\)) \(\delta\) 7.42 (s, 1 H), 7.38 (s, 1 H), 7.15 (s, 1 H), 4.15-4.02 (m, 4 H), 2.33 (s, 6 H), 1.31 (t, \(J = 6.8\) Hz, 6 H); \(^1^3\)C NMR (100.6 MHz) (CDCl\(_3\)) \(\delta\) 138.1 (d, \(J = 15.7\) Hz), 133.9 (d, \(J = 3.0\) Hz), 129.3 (d, \(J = 9.7\) Hz), 128.0 (d, \(J = 186.3\) Hz), 61.9 (d, \(J = 5.4\) Hz), 21.1, 16.3 (d, \(J = 6.3\) Hz); \(^{31}\)P NMR (161.9 MHz) \(\delta\) -7.44. MS (m/z): 242 (36%) M\(^+\), 214 (26%), 186 (100%), 106 (95%), 77 (45%). Anal Calcd for C\(_{12}\)H\(_{19}\)O\(_3\)P, C, 59.50; H, 7.91; found C, 59.63; H, 7.90.

Diethyl 3,4,5-Trimethoxyphenylphosphonate (2d): oil. IR (neat) 2981, 1579, 1502, 1461, 1405, 1319, 1247, 1126, 1052, 1022, 966 cm\(^{-1}\). \(^1\)H NMR (400 MHz) (CDCl\(_3\)) \(\delta\) 7.01 (s, 1 H), 6.97 (s, 1 H), 4.14-4.02 (m, 4 H), 3.87 (s, 6 H), 3.86 (s, 3 H), 1.31 (t, \(J = 7.0\) Hz, 6 H); \(^1^3\)C NMR (100.6 MHz) (CDCl\(_3\)) \(\delta\) 153.3 (d, \(J = 22.0\) Hz), 141.6 (d, \(J = 3.7\) Hz), 122.8 (d, \(J = 191.5\) Hz), 108.8 (d, \(J = 11.3\) Hz), 62.2 (d, \(J = 5.3\) Hz), 60.7, 56.3 (d, \(J = 0.5\) Hz), 16.3 (d, \(J = 6.4\) Hz); \(^{31}\)P NMR (161.9 MHz) \(\delta\) -
7.84. MS (m/z): 304 (100%) M⁺, 232 (40%), 168 (59%), 93 (28%). Anal Calcd for C₁₃H₂₁O₆P, C, 51.31; H, 6.96; found C, 51.42; H, 6.95.

Diethyl 2-Methyl-4-Methoxyphenylphosphonate (2e): oil. IR (neat) 2981, 1600, 1444, 1243, 1087, 1024, 962 cm⁻¹. ^1H NMR (400 MHz) (CDCl₃) δ 7.85 (dd, J₁ = 13.6 Hz, J₂ = 8.4 Hz, 1 H), 6.79-6.75 (m, 2 H), 4.16-4.02 (m, 4 H), 3.82 (s, 3 H), 2.53 (s, 3 H), 1.31 (t, J = 6.8 Hz, 6 H); ^13C NMR (100.6 MHz) (CDCl₃) δ 162.8 (d, J = 3.3 Hz), 143.9 (d, J = 11.7 Hz), 136.1 (d, J = 11.9 Hz), 118.2 (d, J = 191.3 Hz), 117.1 (d, J = 15.6 Hz), 110.3 (d, J = 15.9 Hz), 61.7 (d, J = 4.5 Hz), 55.2, 21.3 (d, J = 3.2 Hz), 16.3 (d, J = 6.5 Hz); ^3¹P NMR (161.9 MHz) δ -6.87. MS (m/z): 258 (64%) M⁺, 230 (57%), 202 (100%), 186 (72%), 149 (70%), 121 (67%), 91 (55%), 77 (48%). Anal Calcd for C₁₂H₁₉O₄P, C, 55.81; H, 7.42; found C, 55.73; H, 7.45.

Diethyl Phenylphosphonate (2f): oil. ^1H NMR (400 MHz) (CDCl₃) δ 7.88-7.80 (m, 2 H), 7.60-7.53 (m, 1 H), 7.50-7.40 (m, 2 H), 4.25-3.99 (m, 4 H), 1.34 (t, J = 6.8 Hz, 6 H); ^13C NMR (100.6 MHz) (CDCl₃) δ 162.8 (d, J = 3.3 Hz), 143.9 (d, J = 11.7 Hz), 136.1 (d, J = 11.9 Hz), 118.2 (d, J = 191.3 Hz), 117.1 (d, J = 15.6 Hz), 110.3 (d, J = 15.9 Hz), 61.7 (d, J = 4.5 Hz), 55.2, 21.3 (d, J = 3.2 Hz), 16.3 (d, J = 6.5 Hz); ^3¹P NMR (161.9 MHz) δ -8.39. MS (m/z): 214 (22%) M⁺, 186 (12%), 158 (88%), 141 (84%), 77 (100%). Anal Calcd for C₁₀H₁₅O₃P, C, 56.07; H, 7.06; found C, 56.22; H, 7.04.

Diethyl 4-Acetylphenylphosphonate (2g): oil. ^1H NMR (400 MHz) (CDCl₃) δ 8.05-8.02 (m, 2 H), 7.98-7.91 (m, 2 H), 4.19-4.10 (m, 4 H), 2.66 (s, 3 H), 1.35 (t, J = 6.8 Hz, 6 H); ^13C NMR (100.6 MHz) (CDCl₃) δ 197.5, 139.8 (d, J = 3.5 Hz), 133.4 (d, J = 185.8 Hz), 132.1 (d, J = 10.1 Hz), 128.0 (d, J = 15 Hz), 62.4 (d, J = 5.6 Hz), 26.8, 16.3 (d, J = 6.3 Hz); ^3¹P NMR (161.9 MHz) δ -10.3 H MS (m/z): 256 (26%) M⁺, 241 (59%), 213 (100%).
Diethyl 4-Ethoxycarbonylphenylphosphonate (2h): oil.\textsuperscript{1} IR (neat) 2983, 2933, 2908, 1722, 1274, 1022, 970 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz) (CDCl\textsubscript{3}) $\delta$ 8.02-7.99 (m, 2 H), 7.82-7.74 (m, 2 H), 4.25 (q, $J$ = 7.2 Hz, 2H), 4.06-3.94 (m, 4 H), 1.29 (t, $J$ = 7.2 Hz, 3 H), 1.26-1.19 (m, 6 H); \textsuperscript{13}C NMR (100.6 MHz) (CDCl\textsubscript{3}) $\delta$ 165.6, 133.8 (d, $J$ = 3.3 Hz), 132.9 (d, $J$ = 186 Hz), 131.6 (d, $J$ = 10.1 Hz), 129.3 (d, $J$ = 15.1 Hz), 62.3 (d, $J$ = 5.5 Hz), 61.3, 16.3 (d, $J$ = 5.6 Hz), 14.1; \textsuperscript{31}P NMR (161.9 MHz) $\delta$ -10.2. MS (m/z): 286 (32%) M\textsuperscript{+}; 213 (100%); 202 (99%); 185 (72%), 177 (70%), 149 (42%), 77 (51%). Anal Calcd for C\textsubscript{13}H\textsubscript{19}O\textsubscript{5}P, C, 54.54; H, 5.44; found C, 54.63; H, 5.47.

Diethyl 4-Nitrophenylphosphonate (2i): oil.\textsuperscript{4} IR (neat) 2985, 1527, 1351, 1255, 1128, 1024, 973 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz) (CDCl\textsubscript{3}) $\delta$ 8.26 (dd, $J$_1 = 8.7 Hz, $J$_2 = 3.1 Hz, 2 H), 7.96 (dd, $J$_1 = 12.6 Hz, $J$_2 = 8.7 Hz, 2 H), 4.18-4.02 (m, 4 H), 1.28 (t, $J$ = 7.0 Hz, 6 H); \textsuperscript{13}C NMR (100.6 MHz) (CDCl\textsubscript{3}) $\delta$ 150.2 (d, $J$ = 4.2 Hz), 135.7 (d, $J$ = 186.3 Hz), 132.9 (d, $J$ = 10.5 Hz), 123.3 (d, $J$ = 15.2 Hz), 64.6 (d, $J$ = 5.6 Hz), 16.2 (d, $J$ = 6.2 Hz); \textsuperscript{31}P NMR (161.9 MHz) $\delta$ -12.3. MS (m/z): 258 (7%) M\textsuperscript{+}; 214 (17%), 204 (100%), 186 (37%), 123 (32%), 77 (39%). Anal Calcd for C\textsubscript{10}H\textsubscript{14}NO\textsubscript{5}P, C, 46.34; H, 5.44; found C, 46.25; H, 5.47.

Diethyl 4-Cyanophenylphosphonate (2j): oil. IR (neat) 2985, 2233, 1444, 1255, 1124, 1022, 971 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz) (CDCl\textsubscript{3}) $\delta$ 7.87 (dd, $J$_1 = 13.2 Hz, $J$_2 = 8.0 Hz, 2 H), 7.72-7.69 (m, 2 H), 4.15-4.01 (m, 4 H), 1.27 (t, $J$ = 7.2 Hz, 6 H); \textsuperscript{13}C NMR (100.6 MHz) (CDCl\textsubscript{3}) $\delta$ 133.9 (d, $J$ = 187.0 Hz), 132.2 (d, $J$ = 9.8 Hz), 131.9 (d, $J$ = 14.9 Hz), 117.8, 115.9 (d, $J$ = 3.4 Hz), 62.7 (d, $J$ = 5.6 Hz), 61.3 (d, $J$ = 5.6 Hz), 16.3 (d, $J$ = 5.6 Hz), 14.1; \textsuperscript{31}P NMR (161.9 MHz) $\delta$ -10.2. MS (m/z): 286 (32%) M\textsuperscript{+}; 213 (100%); 202 (99%); 185 (72%), 177 (70%), 149 (42%), 77 (51%). Anal Calcd for C\textsubscript{13}H\textsubscript{19}O\textsubscript{5}P, C, 54.54; H, 5.44; found C, 54.63; H, 5.47.
16.3 (d, J = 6.2 Hz); 31P NMR (161.9 MHz) δ -11.9. MS (m/z): 239 (7%) M⁺, 212 (22%), 184 (100%), 166 (90%), 130 (46%), 102 (64%), 75 (26%). Anal Calcd for C₁₁H₁₄NO₃P, C, 55.23; H, 5.90; found C, 55.32; H, 5.87.

**Diethyl 3-Trifluoromethylphenylphosphonate (2k):** oil. IR (neat) 2987, 1427, 1330, 1255, 1132, 1052, 1024, 970 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 8.06-7.94 (m, 2 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.58-7.57 (m, 1 H), 4.17-4.07 (m, 4 H), 1.30 (t, J = 7.6 Hz, 6 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 134.9 (d, J_C-P = 9.3 Hz), 131.15 (dq, J_C-P = 15.7 Hz, J_C-F = 32.0 Hz), 130.2 (d, J_C-P = 188.3 Hz), 129.0 (d, J_C-P = 14.9 Hz), 128.9 (q, J_C-F = 3.7 Hz), 128.6 (dq, J_C-P = 11.0 Hz, J_C-F = 3.8 Hz), 123.7 (dq, J_C-P = 11.0 Hz, J_C-F = 262.0 Hz), 62.5 (d, J_C-P = 5.9 Hz), 16.3 (d, J_C-P = 6.2 Hz); ³¹P NMR (161.9 MHz) δ -10.87; ¹⁹F NMR (376.5 MHz) δ -62.8. MS (m/z): 282 (8%) M⁺, 255 (24%), 227 (100%), 209 (43%), 145 (58%), 75 (16%). Anal Calcd for C₁₁H₁₄F₃O₃P, C, 46.82; H, 5.00; found C, 46.89; H, 5.01.

**Diethyl 4-Fluorophenylphosphonate (2l):** oil. IR (neat) 2985, 1594, 1502, 1130, 1024, 968 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.87-7.80 (m, 2 H), 7.19-7.14 (m, 2 H), 4.21-4.03 (m, 4 H), 1.33 (t, J = 7.2 Hz, 6 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 166.4 (d, J_C-P = 3.8 Hz, J_C-F = 251.5 Hz), 134.3 (dd, J₁ = 11.1 Hz, J₂ = 9.1 Hz), 125.5 (d, J_C-P = 194.3 Hz), 115.4 (dd, J_C-P = 16.4 Hz, J_C-F = 21.5 Hz), 62.1 (d, J_C-P = 5.4 Hz), 16.2 (d, J_C-P = 6.2 Hz); ³¹P NMR (161.9 MHz) δ -9.39; ¹⁹F NMR (376.5 MHz) δ -106.0. MS (m/z): 232 (17%) M⁺, 176 (100%), 159 (83%), 112 (40%), 95 (52%), 75 (33%). Anal Calcd for C₁₀H₁₄F₂O₃P, C, 51.73; H, 6.08; found C, 51.80; H, 6.04.

**Diethyl 4-Chlorophenylphosphonate (2m):** oil. IR (neat) 2983, 1444, 1251, 1024, 970, 775 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.73 (dd, J₁ = 12.9 Hz, J₂ = 8.4 Hz, 2 H), 7.43 (dd, J₁ = 8.4 Hz, J₂ =
3.2 Hz, 2 H), 4.19-4.01 (m, 4 H), 1.38-1.23 (m, 6 H); $^{13}$C NMR (100.6 MHz) (CDCl$_3$) δ 139.8 (d, $J$ = 4.0 Hz), 134.0 (d, $J$ = 10.7 Hz), 129.6 (d, $J$ = 15.7 Hz), 127.8 (d, $J$ = 191.9 Hz), 62.7 (d, $J$ = 5.5 Hz), 16.4 (d, $J$ = 6.4 Hz); $^{31}$P NMR (161.9 MHz) δ -9.62 . MS (m/z): 250 (6%) M$^{2+}$, 248 (18%) M$^+$, 192 (100%), 175 (52%), 139 (43%), 75 (42%). Anal Calcd for C$_{10}$H$_{14}$ClO$_3$P, C, 48.30; H, 5.68; found C, 48.45; H, 5.66.

Diethyl 2-Chlorophenylphosphonate (2n): oil. IR (neat) 2983, 1583, 1427, 1247, 1022, 971, 567 cm$^{-1}$. $^1$H NMR (400 MHz) (CDCl$_3$) δ 8.02 (dd, $J_1$ = 14.0 Hz, $J_2$ = 7.6 Hz, 2 H), 7.49-7.48 (m, 2 H), 7.39-7.35 (m, 1 H), 4.28-4.11 (m, 4 H), 1.37 (t, $J$ = 7.2 Hz, 6 H); $^{13}$C NMR (100.6 MHz) (CDCl$_3$) δ 136.8 (d, $J$ = 3.0 Hz), 135.9 (d, $J$ = 7.9 Hz), 133.7 (d, $J$ = 2.5 Hz), 130.8 (d, $J$ = 10.3 Hz), 127.2 (d, $J$ = 192.1 Hz), 126.5 (d, $J$ = 13.8 Hz), 62.7 (d, $J$ = 5.6 Hz), 16.2 (d, $J$ = 6.5 Hz); $^{31}$P NMR (161.9 MHz) δ -12.7. MS (m/z): 248 (9%) M$^{+}$, 213 (100%), 185 (93%), 139 (85%), 75 (68%). Anal Calcd for C$_{10}$H$_{14}$ClO$_3$P, C, 48.30; H, 5.68; found C, 48.25; H, 5.71.

Diethyl 4-Bromophenylphosphonate (2o): oil.$^3$ IR (neat) 2983, 1581, 1479, 1444, 1249, 1024, 968 cm$^{-1}$. $^1$H NMR (400 MHz) (CDCl$_3$) δ 7.65-7.55 (m, 4 H), 4.18-3.98 (m, 4 H), 1.27 (t, $J$ = 6.4 Hz, 6 H); $^{13}$C NMR (100.6 MHz) (CDCl$_3$) δ 133.3 (d, $J$ = 10.6 Hz), 131.7 (d, $J$ = 15.4 Hz), 127.4 (d, $J$ = 189.3 Hz), 127.5 (d, $J$ = 3.9 Hz), 62.3 (d, $J$ = 5.4 Hz), 16.3 (d, $J$ = 6.4 Hz); $^{31}$P NMR (161.9 MHz) δ -9.5 Hz. MS (m/z): 294 (18%) M$^{2+}$, 292 (19%) M$^+$, 236 (100%), 221 (38%), 185 (26%), 156 (25%), 76 (51%). Anal Calcd for C$_{10}$H$_{14}$BrO$_3$P, C, 40.98; H, 4.81; found C, 40.76; H, 4.83.

Diethyl 2-Bromophenylphosphonate (2p): oil.$^5$ IR (neat) 2983, 1452, 1247, 1022, 970 cm$^{-1}$. $^1$H NMR (400 MHz) (CDCl$_3$) δ 7.99-7.96 (m, 1 H), 7.95-7.61 (m, 1 H), 7.39-7.33 (m, 2 H), 4.22-4.05 (m, 4 H), 1.36-1.30 (m, 6 H); $^{13}$C NMR (100.6 MHz) (CDCl$_3$) δ 136.3 (d, $J$ = 8.2 Hz), 134.3 (d, $J$ =
11.1 Hz), 133.5 (d, J = 2.5 Hz), 129.3 (d, J = 191.4 Hz), 126.9 (d, J = 13.6 Hz), 125.2 (d, J = 3.9 Hz), 63.6 (d, J = 5.8 Hz), 16.2 (d, J = 6.5 Hz); 31P NMR (161.9 MHz) δ -12.5. MS (m/z): 294 (5%) M+2, 292 (5%) M+, 213 (51%), 185 (100%), 157 (86%), 141 (77%), 77 (54%). Anal Calcd for C10H14BrO3P, C, 40.98; H, 4.81; found C, 40.69; H, 4.78.

Triphenyl Phosphate oxide (6b): mp: 148-149°C (Lit.3 mp: 119-123°C). IR (KBr) 1436, 1118, 723 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.68-7.61 (m, 6 H), 7.52-7.38 (m, 9 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 132.5 (d, J = 105.0 Hz), 132.0 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 128.5 (d, J = 12.2 Hz); ³¹P NMR (161.9 MHz) δ 1.86. MS (m/z): 278 (42%) M⁺, 277 (100%), 201 (17%), 183 (19%), 77 (41%). Anal Calcd for C₁₈H₁₅OP, C, 77.69; H, 5.43; found C, 77.54; H, 5.46.

(4-Ethoxycarbonylphenyl)Diphenylphospine oxide (6c): oil. IR (neat) 3056, 2983, 1718, 1436, 1274, 1195, 1103, 728, 696 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 8.11 (dd, J₁ = 8.4 Hz, J₂ = 2.7 2 H), 7.75(dd, J₁ = 11.0 Hz, J₂ = 8.4, 2 H), 7.71-7.59 (m, 2 H), 7.57-7.50 (m, 4 H), 7.49-7.42 (m, 4 H), 4.40 (q, J = 7.3 Hz, 2 H), 1.36 (t, J = 7.0 Hz, 3H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 165.7, 137.5 (d, J = 100.8 Hz), 133.6 (d, J = 2.7 Hz), 132.2 (d, J = 2.7 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 104.8 Hz), 129.4 (d, J = 12.1 Hz), 128.6 (d, J = 12.1 Hz), 61.4, 14.2; ³¹P NMR (161.9 MHz) δ 1.27. MS (m/z): 350 (11%) M⁺, 349 (100%), 321 (25%), 305 (10%), 277 (8%), 201 (11%), 183 (23%), 77 (30%). Anal Calcd for C₂₁H₁₉O₃P, C, 71.99; H, 5.47; found C, 71.85; H, 5.49.

(4-Chlorophenyl)Diphenylphosphine oxide (6d): mp: 135-138 °C (Lit.3 mp: 143-145 °C). IR (KBr) 2921, 1597, 1438, 1191, 1116, 696 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.68-7.41 (m, 14 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 138.6 (d, J = 3.3 Hz), 133.5 (d, J = 10.7 Hz), 132.1 (d, J =
104.5 Hz), 132.2 (d, J = 2.6 Hz), 131.9 (d, J = 9.9 Hz), 131.2 (d, J = 105.1 Hz), 128.9 (d, J = 12.7 Hz), 128.6 (d, J = 12.2 Hz); ³¹P NMR (161.9 MHz) δ 1.13. MS (m/z): 314 (13%) M⁺, 312 (42%) M⁺, 311 (100%), 277 (8%), 201 (10%), 183 (20%), 152 (22%), 77 (50%). Anal Calcd for C₁₈H₁₄ClOP, C, 69.13; H, 4.51; found C, 69.26; H, 4.47.

(2-Chlorophenyl)diphenylphosphine oxide (6f): mp 99-102 °C. IR (KBr) 1434, 1187, 1120, 545 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.76-7.61 (m, 4 H), 7.60-7.47 (m, 9 H); 7.37-7.33 (m, 1 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 137.9 (d, J = 4.1 Hz), 135.6 (d, J = 9.5 Hz), 135.2, 133.4 (d, J = 1.7 Hz), 132.0 (d, J = 7.7 Hz), 131.8 (d, J = 106.8 Hz), 131.2 (d, J = 103.5 Hz), 131.1 (d, J = 6.8 Hz), 128.5 (d, J = 12.5 Hz), 126.6 (d, J = 10.9 Hz); ³¹P NMR (161.9 MHz) δ 1.52. MS (m/z): 312 (77%) M⁺, 282 (100%), 208 (97%), 152 (90%), 78 (67%). Anal Calcd for C₁₈H₁₄ClOP, C, 69.13; H, 4.51; found C, 69.21; H, 4.53.

(3,4,5-Trimethoxyphenyl)Diphenylphosphine oxide (6g): oil. IR (neat) 2938, 2221, 1577, 1502, 1436, 1403, 1313, 1122, 698 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.69-7.64 (m, 4 H), 7.56-7.52 (m, 2 H), 7.48-7.44 (m, 4 H), 6.87 (s, 1 H), 6.84 (s, 1 H), 3.88 (s, 3 H), 3.76 (s, 6 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 153.3 (d, J = 17.6 Hz), 141.2 (d, J = 5.4 Hz), 132.4 (d, J = 104.5 Hz), 132.5 (d, J = 9.8 Hz), 132.0 (d, J = 2.8 Hz), 128.5 (d, J = 12.2 Hz), 126.9 (d, J = 106.3 Hz), 60.8, 56.3(d, J = 0.9 Hz); ³¹P NMR (161.9 MHz) δ 2.78. MS (m/z): 368 (100%) M⁺, 367 (94%), 337 (13%), 199 (61%), 77 (26%). Anal Calcd for C₂₁H₂₁O₄P, C, 68.47; H, 5.75; found C, 68.53; H, 5.76.

(3,5-Dimethylphenyl)Diphenylphosphine oxide (6h): oil. IR (neat) 2217, 1598, 1436, 1187, 1118, 698 cm⁻¹. ¹H NMR (400 MHz) (CDCl₃) δ 7.70-7.65 (m, 4 H), 7.54-7.53 (m, 2 H), 7.48-7.45 (m, 4 H), 7.30 (s, 1 H), 7.27 (s, 1 H), 7.17 (s,1 H), 2.31 (s, 6 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 138.2
(d, J = 12.9 Hz), 133.8 (d, J = 2.7 Hz), 132.6 (d, J = 104.5 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 103.9 Hz), 131.8 (d, J = 2.6 Hz), 129.7 (d, J = 9.9 Hz), 128.5 (d, J = 12.2 Hz); \(^{31}\)P NMR (161.9 MHz) \(\delta 2.76\). MS (m/z): 306 (51%) M\(^{+}\), 305 (100%), 227 (9%), 199 (11%), 77 (24%). Anal Calcd for C\(_{20}\)H\(_{19}\)OP, C, 78.41; H, 6.25; found C, 78.57; H, 6.23.

REFERENCES

(1) Yong Luo, Jie Wu, Organometallics, **2009**, 28, 6823-6826.
NMR Spectra

2c: Diethyl 3,5-Dimethylphenylphosphonate
2c: Diethyl 3,5-Dimethylphenylphosphonate
2c: Diethyl 3,5-Dimethylphenylphosphonate
2d: Diethyl 3,4,5-Trimethoxyphenylphosphonate
2d: Diethyl 3,4,5-Trimethoxyphenylphosphonate
2d: Diethyl 3,4,5-Trimethoxyphenylphosphonate
2e: Diethyl 2-Methyl-4-Methoxyphenylphosphonate
2e: Diethyl 2-Methyl-4-Methoxyphenylphosphonate
2e: Diethyl 2-Methyl-4-Methoxyphenylphosphonate
2j: Diethyl 4-Cyanophenylphosphonate

![Diagram of Diethyl 4-Cyanophenylphosphonate](image)
2j: Diethyl 4-Cyanophenylphosphonate
2j: Diethyl 4-Cyanophenylphosphonate
2k: Diethyl 3-Trifluoromethylphenylphosphonate
2k: Diethyl 3-Trifluoromethylphenylphosphonate
2k: Diethyl 3-Trifluoromethylphenylphosphonate
2k: Diethyl 3-Trifluoromethylphenylphosphonate
2k: Diethyl 3-Trifluoromethylphenylphosphonate
2l: Diethyl 4-Fluorophenylphosphonate
2l: Diethyl 4-Fluorophenylphosphonate
2l: Diethyl 4-Fluorophenylphosphonate
2l: Diethyl 4-Fluorophenylphosphonate
2n: Diethyl 2-Chlorophenylphosphonate
2n: Diethyl 2-Chlorophenylphosphonate
2n: Diethyl 2-Chlorophenylphosphonate
6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide
6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide
6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide
6f: 2-Chlorophenyl Diphenylphosphine oxide
6f: 2-Chlorophenyl Diphenylphosphine oxide
6f: 2-Chlorophenyl Diphenylphosphine oxide
6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide
6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide
6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide
6h: 3,5-Dimethylphenyl Diphenylphosphine oxide

![Chemical Structure of 3,5-Dimethylphenyl Diphenylphosphine oxide]

- Chemical formula: $\text{MeO} \big| \text{Ph} \big| \text{Ph}$
6h: 3,5-Dimethylphenyl Diphenylphosphine oxide
6h: 3,5-Dimethylphenyl Diphenylphosphine oxide