Electronic Supplementary Information for Copper/Iron-Catalyzed C–P Cross-Coupling of styrenes with H-Phosphine Oxides: A Facile and Selective Synthesis of Alkenylphosphine Oxides and β-Ketophosphonates

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1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by $^1$H NMR, $^{13}$C NMR, and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 202 MHz in CDCl$_3$, respectively, and chemical shifts are reported in ppm. High-resolution mass spectra data were obtained on Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. General Procedure

General Procedure for the Synthesis of alkenylphosphine oxides and β-Ketophosphonates from Alkenyls and H-Phosphonates: A mixture of alkenyls (0.5 mmol), H-phosphonates (2.0 mmol), CuCl (0.05 mmol), FeCl$_3$ (0.1 mmol), DTBP (1.0 mmol) and Et$_3$N (0.5 mmol) in DMSO (2.0 mL) under Ar was stirred at 110°C or 90°C for 15 h. After the completion of the reaction, the mixture was cooled to 25°C and then EtOAc and H$_2$O were added to it. The organic layer was separated and washed with brine, dried over Na$_2$SO$_4$. The volatiles were removed under vacuum to afford the crude product, and analyzed by GC. The crude product was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (25/75) to afford the desired pure product.

3. Characterization Data

(E)-diethyl styrylphosphonate 3aa$^{[1]}$, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.46 (m, 3H), 7.37 (dd, $J = 5.0$, 1.7 Hz, 3H), 6.25 (t, $J = 17.6$ Hz, 1H), 4.17 – 4.07 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.92 (s), 135.08 (s), 130.37 (s), 127.83 (s), 114.83 (s), 113.31 (s), 62.25 (s), 16.50 (s). MS (EI) m/z: 240 [M$^+$].

(E)-diethyl 4-methylstyrylphosphonate 3ba$^{[1]}$, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45 (dd, $J = 22.6$, 17.5 Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.17 (t, $J = 17.7$ Hz, 1H), 4.15 – 4.06 (m, 4H), 2.34 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.88
(E)-diethyl 2,4,6-trimethylstyrlylphosphonate 3ca\(^1\), yellow oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.65 (dd, \(J = 23.8, 17.9\) Hz, 1H), 6.94 (s, 2H), 5.91 (dd, \(J = 20.6, 17.9\) Hz, 1H), 4.25 – 4.17 (m, 4H), 2.34 (d, \(J = 16.4\) Hz, 9H), 1.42 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 147.71 (s), 138.28 (s), 136.03 (s), 129.21 (s), 120.91 (s), 119.44 (s), 70.64 (s), 61.95 (s), 21.01 (s), 16.58 (s).

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\begin{align*}
\text{3ca}
\end{align*}
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(E)-diethyl 4-methoxystyrlylphosphonate 3da\(^1\), yellow oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 (q, \(J = 15.9\) Hz, 3H), 6.93 (d, \(J = 8.6\) Hz, 2H), 6.12 (t, \(J = 17.6\) Hz, 1H), 4.20 – 4.11 (m, 4H), 3.86 (s, 3H), 1.38 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.43 (s), 148.60 (s), 129.45 (s), 127.67 (s), 114.36 (s), 111.71 (s), 110.18 (s), 61.86 (s), 55.49 (s), 16.50 (s).

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\begin{align*}
\text{3da}
\end{align*}
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(E)-diethyl 4-tert-butylstyrlylphosphonate 3ea, yellow oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.55 – 7.47 (m, 1H), 7.47 – 7.44 (m, 2H), 7.42 (d, \(J = 8.4\) Hz, 2H), 6.22 (t, \(J = 17.7\) Hz, 1H), 4.18 – 4.08 (m, 4H), 1.36 (t, \(J = 7.1\) Hz, 6H), 1.33 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 153.72 (s), 148.81 (s), 127.67 (s), 125.93 (s), 125.58 (s), 113.68 (s), 112.15 (s), 61.91 (s), 35.28 (s), 31.28 (s), 16.49 (s). \(^{31}\)P NMR (202 MHz, CDCl\(_3\)) \(\delta\) 20.21 (s). HRMS (ESI) Calcd. For 319.1439, \(C_{16}H_{25}O_{3}P\) [M-Na]\(^+\), found 319.1435.

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\begin{align*}
\text{3ea}
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(E)-4-(2-(diethoxyphosphoryl)vinyl)phenyl acetate 3fa, yellow oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 8.4\) Hz, 2H), 7.52 – 7.42 (m, 1H), 7.13 (d, \(J = 8.5\) Hz, 2H), 6.22 (t, \(J = 17.4\) Hz, 1H), 4.14 (tdt, \(J = 10.1, 6.8, 3.2\) Hz, 4H), 2.32 (s, 3H), 1.36 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 169.29 (s), 152.18 (s), 147.83 (s), 128.99 (s), 122.24 (s), 114.99 (s), 113.46 (s), 62.06 (s), 21.25 (s), 16.54 (s). \(^{31}\)P NMR (202 MHz, CDCl\(_3\)) \(\delta\) 19.40 (s). HRMS (ESI) Calcd. For 321.0868, \(C_{14}H_{19}O_{3}P\) [M-Na]\(^+\), found 321.0861.

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\begin{align*}
\text{3fa}
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(E)-diethyl 4-fluorostyrylphosphonate 3ga,[2] yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.58 – 7.46 (m, 3H), 7.12 (t, $J = 8.6$ Hz, 2H), 6.22 (t, $J = 17.4$ Hz, 1H), 4.23 – 4.13 (m, 4H), 1.40 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.99 (s), 162.99 (s), 147.84 (s), 129.74 (s), 116.19 (s), 114.64 (s), 113.11 (s), 62.00 (s), 16.51 (s).

(E)-diethyl 4-chlorostyrylphosphonate 3ha,[1], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (dt, $J = 14.3$, 11.7 Hz, 3H), 7.37 (d, $J = 8.5$ Hz, 2H), 6.24 (t, $J = 17.3$ Hz, 1H), 4.20 – 4.10 (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.37 (s), 136.29 (s), 129.25 (s), 129.02 (s), 115.63 (s), 114.10 (s), 62.10 (s), 16.51 (s).

(E)-diethyl 4-bromostyrylphosphonate 3ia,[1], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.4$ Hz, 2H), 7.43 (dd, $J = 22.5$, 17.5 Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.25 (t, $J = 17.3$ Hz, 1H), 4.20 – 4.05 (m, 4H), 1.36 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.46 (s), 132.22 (s), 129.24 (s), 124.62 (s), 115.77 (s), 114.10 (s), 112.83 (s), 16.48 (s).

(E)-diethyl 2-phenylprop-1-enylphosphonate 3ja,[3] yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J = 6.6$, 2.9 Hz, 2H), 7.39 – 7.34 (m, 3H), 5.91 (d, $J = 16.6$ Hz, 1H), 4.13 (p, $J = 7.3$ Hz, 4H), 2.51 (d, $J = 3.2$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.30 (s), 129.26 (s), 128.59 (s), 126.08 (s), 124.87 (s), 114.34 (s), 112.83 (s), 16.48 (s).

(E)-diethyl 2-(pyridin-2-yl)vinylphosphonate 3ka, white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J = 4.5$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.54 (dd, $J = 21.8$, 17.1 Hz, 1H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 4.9$ Hz, 1H), 6.95 – 6.84 (m, 1H), 4.20 – 4.12 (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR
(125 MHz, CDCl$_3$) δ 152.96 (s), 150.16 (s), 147.44 (s), 137.05 (s), 124.46 (s), 119.60 (s), 118.10 (s), 62.14 (s), 16.49 (s). $^{31}$P NMR (202 MHz, CDCl$_3$) δ 18.88 (s).

HRMS (ESI) Calcd. For C$_{11}$H$_{16}$NO$_3$P [M-Na]$^+$, found 264.0762.

(E)-diethyl 2-(thiophen-2-yl)vinylphosphonate 3la[3], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.55 (dd, $J = 21.9$, 17.2 Hz, 1H), 7.32 (d, $J = 5.0$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 7.00 (dd, $J = 4.8$, 3.8 Hz, 1H), 5.96 (t, $J = 17.0$ Hz, 1H), 4.12 – 4.04 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.38 (s), 140.96 (d, $J = 88.3$ Hz), 140.40 (s), 130.37 (s), 128.31 (s), 128.12 (s), 113.26 (s), 111.72 (s), 62.00 (s), 16.49 (s).

(E)-diisopropyl styrylphosphonate 3ab[1], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.48 (m, 3H), 7.38 (dd, $J = 5.1$, 2.0 Hz, 3H), 6.27 (t, $J = 17.5$ Hz, 1H), 4.72 (qd, $J = 12.4$, 6.2 Hz, 2H), 1.35 (dd, $J = 24.3$, 6.2 Hz, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.95 (s), 128.98 (t, $J = 150.2$ Hz), 115.78 (d, $J = 191.2$ Hz), 70.67 (s), 24.20 (s).

(E)-dibutyl styrylphosphonate 3ac[4], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.49 (m, 3H), 7.41 – 7.39 (m, 1H), 7.30 (d, $J = 4.5$ Hz, 1H), 6.23 (t, $J = 17.7$ Hz, 1H), 3.77 (t, $J = 10.1$, 6.7 Hz, 2H), 1.71 – 1.66 (m, 4H), 1.48 – 1.37 (m, 4H), 0.94 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.84 (s), 130.33 (s), 129.31 (s), 128.98 (s), 127.83 (s), 113.29 (s), 65.75 (s), 32.67 (s), 18.89 (s), 13.73 (s).

(E)-dimethyl styrylphosphonate 3ad[5], yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.56 – 7.49 (m, 3H), 7.41 – 7.39 (m, 2H), 7.30 (d, $J = 4.5$ Hz, 1H), 6.23 (t, $J = 17.7$ Hz, 1H), 3.77 (t, $J = 10.6$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 130.55 (s), 129.03 (s), 127.89 (s), 127.47 (s), 113.28 (s), 111.52 (s), 52.61 (s).
(E)-diphenyl styrylphosphonate 3af\textsuperscript{[1]}, yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.85 – 7.78 (m, 4H), 7.59 (dt, \(J = 6.0, 4.7\) Hz, 4H), 7.57 – 7.51 (m, 5H), 7.44 (dd, \(J = 5.1, 1.9\) Hz, 3H), 6.90 (dd, \(J = 22.3, 17.4\) Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 147.73 (s), 132.02 (s), 131.54 (d, \(J = 9.3\) Hz), 130.25 (s), 129.00 (s), 128.77 (d, \(J = 11.7\) Hz), 127.92 (s), 119.78 (s), 118.95 (s).

Diethyl 2-oxo-2-phenylethylphosphonate 4aa\textsuperscript{[6]}, light yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.01 (d, \(J = 7.2\) Hz, 2H), 7.58 (t, \(J = 7.4\) Hz, 1H), 7.47 (t, \(J = 7.7\) Hz, 2H), 4.17 – 4.10 (m, 4H), 3.63 (d, \(J = 22.7\) Hz, 2H), 1.27 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 192.11 (s), 133.80 (s), 128.96 (d, \(J = 55.1\) Hz), 62.84 (s), 39.12 (s), 38.09 (s), 16.38 (s). MS (EI) \(m/z\): 256 [M\textsuperscript{+}].

Diethyl 2-oxo-2-p-tolylethylphosphonate 4ba\textsuperscript{[6]}, light yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.84 (d, \(J = 8.2\) Hz, 2H), 7.20 (d, \(J = 7.9\) Hz, 2H), 4.10 – 4.03 (m, 4H), 3.53 (d, \(J = 22.7\) Hz, 2H), 2.35 (s, 3H), 1.21 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 191.63 (s), 144.80 (s), 134.21 (s), 129.38 (d, \(J = 11.6\) Hz), 62.73 (s), 39.02 (s), 37.99 (s), 21.64 (s), 16.37 (s).

Diethyl 2-mesityl-2-oxoethylphosphonate 4ca, yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 6.85 (s, 2H), 4.19 – 4.09 (m, 4H), 3.44 (d, \(J = 21.7\) Hz, 2H), 2.28 (s, 9H), 1.30 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 200.88 (s), 139.21 (s), 138.59 (s), 133.62 (s), 130.32 (s), 128.97 (s), 62.55 (s), 44.27 (s), 43.23 (s), 22.27 (s), 20.95 (d, \(J = 61.2\) Hz), 19.71 (s), 16.36 (s). \textsuperscript{31}P NMR (202 MHz, CDCl\textsubscript{3}) \(\delta\) 19.84 (s). HRMS (ESI) Calcd. For 321.1232, C\textsubscript{15}H\textsubscript{23}O\textsubscript{4}P [M-Na]\textsuperscript{+}, found 321.1229.

Diethyl 2-(4-methoxyphenyl)-2-oxoethylphosphonate 4da\textsuperscript{[6]}, light yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.94 (d, \(J = 7.0\) Hz, 2H), 6.88 (d, \(J = 8.9\) Hz, 2H), 4.07 (p, \(J = 7.1\) Hz, 4H), 3.81 (s, 3H), 3.51 (d, \(J = 22.7\) Hz, 2H), 1.22 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 190.21 (s), 164.18 (s), 131.54 (s), 129.82 – 129.66 (m), 113.67 (s), 62.80 (s), 55.56 (s), 16.31 (s).
diethyl 2-(4-tert-butylphenyl)-2-oxoethylphosphonate 4ea\[6\], yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.5\) Hz, 2H), 7.49 (d, \(J = 8.5\) Hz, 2H), 4.18 – 4.11 (m, 4H), 3.62 (d, \(J = 22.7\) Hz, 2H), 1.35 (s, 9H), 1.29 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 191.62 (s), 134.23 (s), 129.17 (s), 125.69 (s), 62.72 (s), 39.02 (s), 37.99 (s), 32.35 (s), 31.35 (d, \(J = 49.7\) Hz), 16.34 (s). \(^{31}\)P NMR (202 MHz, CDCl\(_3\)) \(\delta\) 20.38 (s). HRMS (ESI) Calcd. For C\(_{16}\)H\(_{25}\)O\(_4\)P \([M-\text{Na}]^+\), found 335.1385.

4-(2-(diethoxyphosphoryl)acetyl)phenyl acetate 4fa, yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 8.6\) Hz, 2H), 7.21 (d, \(J = 8.6\) Hz, 2H), 4.17 – 4.10 (m, 4H), 3.60 (d, \(J = 22.7\) Hz, 2H), 2.32 (s, 3H), 1.28 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 190.82 (s), 168.83 (s), 154.95 (s), 134.20 (s), 130.89 (s), 121.93 (s), 62.92 (s), 39.21 (s), 38.18 (s), 21.27 (s), 16.38 (s). \(^{31}\)P NMR (202 MHz, CDCl\(_3\)) \(\delta\) 19.59 (s). HRMS (ESI) Calcd. For C\(_{14}\)H\(_{19}\)O\(_6\)P \([M-\text{Na}]^+\), found 337.0813.

diethyl 2-(4-fluorophenyl)-2-oxoethylphosphonate 4ga\[6\], brown oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.99 (dd, \(J = 8.9, 5.4\) Hz, 2H), 7.08 (t, \(J = 8.6\) Hz, 2H), 4.11 – 4.03 (m, 4H), 3.53 (d, \(J = 22.8\) Hz, 2H), 1.22 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 190.46 (s), 133.09 (s), 132.01 (d, \(J = 9.0\) Hz), 115.99 (s), 115.81 (s), 62.89 (s), 39.28 (s), 38.25 (s), 16.41 (s).

Diethyl 2-(4-chlorophenyl)-2-oxoethylphosphonate 4ha\[6\], yellow green oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.6\) Hz, 2H), 7.39 (d, \(J = 8.6\) Hz, 2H), 4.12 – 4.02 (m, 4H), 3.53 (d, \(J = 22.8\) Hz, 2H), 1.22 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 190.84 (s), 133.09 (s), 132.01 (d, \(J = 9.0\) Hz), 115.99 (s), 115.81 (s), 62.89 (s), 39.18 (s), 38.17 (s), 16.31 (s).

Diethyl 2-(4-bromophenyl)-2-oxoethylphosphonate 4ia\[6\], yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.7\) Hz, 2H), 7.55 (d, \(J = 8.7\) Hz, 2H), 4.10 – 4.04 (m, 4H), 3.53 (d, \(J = 22.8\) Hz,
2H), 1.22 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 191.12 (s), 135.35 (s), 132.08 (s), 130.72 (s), 129.24 (s), 62.90 (s), 38.76 (d, J = 129.5 Hz), 16.40 (s).

**4la**

diethyl 2-oxo-2-(thiophen-2-yl)ethylphosphonate **4la**, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, J = 3.8 Hz, 1H), 7.68 (d, J = 4.9 Hz, 1H), 7.17 – 7.12 (m, 1H), 4.16 – 4.11 (m, 4H), 3.54 (d, J = 22.5 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 184.36 (s), 144.05 (s), 135.24 (s), 134.32 (s), 128.47 (s), 62.95 (s), 40.01 (s), 38.97 (s), 16.38 (s).

**4ma**
diethyl (1-oxo-1-phenylpropan-2-yl)phosphonate **4ma**, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.05 – 7.98 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 4.21 (q, J = 7.0 Hz, 1H), 4.16 – 4.04 (m, 4H), 1.54 (dd, J = 18.0, 7.0 Hz, 3H), 1.25 (dt, J = 42.3, 7.1 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 135.89 (s), 132.38 (s), 127.89 (s), 127.54 (s), 61.80 (s), 39.84 (s), 15.53 (s), 11.29 (s).

**4ab**
diisopropyl 2-oxo-2-phenylethylphosphonate **4ab**, light yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 4.73 (dq, J = 12.9, 6.3 Hz, 2H), 3.60 (d, J = 22.9 Hz, 2H), 1.77 (d, J = 6.0, 3.9 Hz, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 192.23 (s), 136.80 (s), 133.63 (s), 129.28 (s), 128.94 (d, J = 80.1 Hz), 71.60 (s), 40.36 (s), 39.32 (s), 24.08 (s).

**4ac**
dibutyl 2-oxo-2-phenylethylphosphonate **4ac**, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.02 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 4.13 – 4.02 (m, 4H), 3.64 (d, J = 22.8 Hz, 2H), 1.67 – 1.55 (m, 4H), 1.33 (dq, J = 14.8, 7.4 Hz, 4H), 0.89 (t, J = 7.4 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 192.08 (s), 133.74 (s), 129.70 – 129.32 (m), 128.95 (d, J = 59.4 Hz), 66.45 (s), 39.32 (s), 37.98 (s), 32.48 (s), 18.74 (s), 13.67 (s).

**4ad**
dimethyl 2-oxo-2-phenylethylphosphonate **4ad**, colorless and transparent oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 3.78 (d,
J = 11.2 Hz, 6H), 3.64 (d, J = 22.6 Hz, 2H). 13C NMR (125 MHz, CDCl₃) δ 191.90 (s), 136.54 (s), 133.94 (s), 128.98 (d, J = 33.7 Hz), 53.29 (s), 38.14 (s), 37.09 (s).


4. NMR Spectra of All Products

![NMR Spectra of All Products](image)

1H NMR 3aa
$^{13}$C NMR 3ba

$^1$H NMR 3ca
$^{13}$C NMR 3ca

$^1$H NMR 3da
$^{13}$C NMR 3ea

$^{31}$P NMR 3ea
$^1$H NMR 3fa

$^{13}$C NMR 3fa
$^{13}$C NMR 3ka

$^{31}$P NMR 3ka
$^1$H NMR 3ac

$^{13}$C NMR 3ac
$^1$H NMR 3ad

$^{13}$C NMR 3ad
$^{1}$$\text{H NMR 3af}$

$^{13}$$\text{C NMR 3af}$
$^1$H NMR 4ba

$^{13}$C NMR 4ba
$^{31}$P NMR $4ca$

$^1$H NMR $4da$
$^{13}$C NMR 4da

$^1$H NMR 4ca
$^1$H NMR 4fa

$^{13}$C NMR 4fa
$^{31}\text{P NMR 4fa}$

$^{1}\text{H NMR 4ga}$
$^{13}\text{C NMR 4ga}$

$^{1\text{H NMR 4ha}}$
$^{13}$C NMR 4ha

$^1$H NMR 4ia
$^{13}$C NMR 4ia

$^1$H NMR 4ia
$^{13}$C NMR 4ab

$^1$H NMR 4ac
$^{13}$C NMR 4ac

$^1$H NMR 4ad
$^{13}$C NMR 4ad