Supporting Information
For

Substituent controlled reactivity switch: selective synthesis of α-diazoalkylphosphonates or vinylphosphonates via nucleophilic substitution of alkyl bromides with Bestmann-Ohira reagent

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Experimental Section

General

All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100-200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer’s RX I FTIR spectrophotometer. NMR spectra were recorded on a Brucker Avance spectrometer at 400 MHz (1H), 100 MHz (13C), and 162 MHz (31P). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for 1H and 13C and phosphoric acid as the external standard for 31P. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used. The coupling constants (J) are given in Hz. The ESI-HRMS spectra were recorded on Agilent 6520- Q-TofLC/MS system.

All reactions were conducted in oven-dried glasswares under Nitrogen. Dimethyl oxopropyl phosphonate was purchased from Sigma Aldrich and used as received for the synthesis of the Bestmann-Ohira reagent 2.1,2 All other reagents were purchased from local suppliers and used without purification. Alkyl bromides were either commercially available or prepared from respective aldehydes via sodium borohydride reduction followed by bromination with PBr3.3 The brominated Morita-Baylis-Hillman product 1v was synthesized following literature procedure.4

General procedure for the reaction of alkyl bromides 1 with BOR 2

To a stirred solution of alkyl bromide 1 (1 mmol) in dry MeOH (5 mL) was added Bestmann-Ohira reagent 2 (1.2 mmol, 230 mg) followed by KOH (1.2 mmol, 67 mg) and the reaction mixture was stirred at room temperature until the completion of the reaction (TLC monitoring). Methanol was distilled off under reduced pressure and crude residue was directly subjected to column chromatography on silica gel using 0-60% (0-80% in case of 5) hexane/ethyl acetate as eluent to afford the products 3/4 or 5. (Amount of BOR and KOH was doubled in case of 1q-r & 1v).
Table S1. Various conditions screened for the conversion of diazomethyl benzylphosphonate 3a into dimethyl styrylphosphonate 4a/4a’

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<td>DCC, BF3.OEt, DCM, 0 °C – 5 °C</td>
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<td>3</td>
<td>Cu powder, MeOH, reflux, 4h</td>
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<td>4</td>
<td>Cu powder, 1,4-dioxan, reflux, 1h</td>
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*a*ratio of isomers assigned on the basis of crude 1H NMR, *b*Intractable mixture.

**Condition 1: NaOMe mediated reaction**

To a stirred solution of diazomethyl benzylphosphonate 3a (240 mg, 1 mmol) in anhydrous THF (5 mL) was added NaOMe (81 mg, 1.5 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. However, no product could be isolated as 3a underwent decomposition resulting into an intractable mixture.

**Condition 2: BF3.OEt/DCC mediated reaction**

To a stirred solution of diazomethyl benzylphosphonate 3a (240 mg, 1 mmol) and DCC (247 mg, 1.2 mmol) in DCM (5 mL) was added BF3.OEt (0.15 mL, 1.2 mmol in 2 mL DCM) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. After the completion of reaction, the reaction mixture was diluted with DCM and washed with NaHCO3 and water. The solvent was distilled off under reduced pressure and crude residue was submitted for proton NMR. The crude product was purified by column chromatography on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product 4a.

**Condition 3: Cu powder mediated reaction**

To a stirred solution of diazomethyl benzylphosphonate 3a (240 mg, 1 mmol) in solvent (5 mL) was added Cu powder (6.3 mg, 10 mol %) and the reaction mixture was refluxed until the completion of the reaction (TLC monitoring). Solvent was distilled off under reduced pressure and crude residue was directly subjected to column chromatography on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product 4a.
General procedure for the conversion of dimethyl diazoethyl phosphonates 3 into corresponding vinylphosphonates 4

To a stirred solution of dimethyl diazoethylphosphonate 3 (1 mmol) in toluene (5 mL) was added Cu powder (6.3 mg, 10 mol %) and the reaction mixture was refluxed until the completion of the reaction (TLC monitoring). Toluene was distilled off under reduced pressure and crude residue was directly subjected to column chromatography on silica gel using 0-60% hexane/ethyl acetate as eluent to afford the product 4.

**Dimethyl 1-diazo-2-phenylethylphosphonate (3a)**

![3a](image)

Yellow oil; isolated yield 87% (209 mg). $R_f$ 0.50 (70% EtOAc/hexane); IR (Film, cm$^{-1}$): 2358, 2081, 1496, 1249, 1030; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 – 7.28 (m, 2H), 7.17 – 7.21 (m, 3H), 3.63 (d, $J_{H-P}$ = 11.6 Hz, 6H), 3.36 (d, $J_{H-P}$ = 10.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.2 (d, $J_{C-P}$ = 3.1 Hz, C$_{Ar}$), 128.8 (C$_{Ar}$H x 2), 128.3 (C$_{Ar}$H x 2), 127.2 (C$_{Ar}$H), 52.8 (d, $J_{C-P}$ = 5.5 Hz, {PO}$OCH_3$ x 2), 30.0 (d, $J_{C-P}$ = 8.6 Hz, CH$_2$); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 24.19; HRMS for C$_{10}$H$_{13}$N$_2$O$_3$P: calcd. (MH$^+$): 241.0742, found: 241.0729

**Dimethyl 1-diazo-2-(3-nitrophenyl)ethylphosphonate (3d)**

![3d](image)

Yellow oil; isolated yield 80% (231 mg). $R_f$ 0.30 (70% EtOAc/hexane); IR (Film, cm$^{-1}$): 2373, 2081, 1531, 1455, 1257, 1028; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 8.06 (m, 2H), 7.53 – 7.55 (m, 1H), 7.42 – 7.46 (m, 1H), 3.65 (d, $J_{H-P}$ = 11.6 Hz, 6H), 3.48 (d, $J_{H-P}$ = 10.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.5 (C$_{Ar}$), 139.6 (C$_{Ar}$, $J_{C-P}$ = 2.1 Hz), 134.4 (C$_{Ar}$H), 129.8 (C$_{Ar}$H), 123.1 (C$_{Ar}$H), 122.3 (C$_{Ar}$H), 53.1 (d, $J_{C-P}$ = 5.4 Hz, {PO}$OCH_3$ x 2), 30.0 (d, $J_{C-P}$ = 8.7 Hz, CH$_2$); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 23.12; HRMS for C$_{10}$H$_{12}$N$_3$O$_5$P: calcd. (MH$^+$): 286.0593, found: 286.0578.
Dimethyl 1-diazo-2-p-tolylethylphosphonate (3e)

Yellow oil; isolated yield 78% (198 mg). $R_f$ 0.50 (70% EtOAc/hexane); IR (Film, cm$^{-1}$): 2371, 2081, 1525, 1254, 1031; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (s, 4H), 3.64 (d, $J_{H-P}$ = 11.6 Hz, 6H), 3.32 (d, $J_{H-P}$ = 9.8 Hz, 2H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.9 (C$_{Ar}$), 134.1 (d, $J_{C-P}$ = 2.3 Hz, C$_{Ar}$), 129.5 (C$_{Ar}$H x 2), 128.3 (C$_{Ar}$H x 2), 52.9 (d, $J_{C-P}$ = 5.2 Hz, $\{PO\}OCH$_3 x 2), 29.6 (d, $J_{C-P}$ = 8.9 Hz, CH$_2$), 21.1 (CH$_3$); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 24.41; HRMS for C$_{11}$H$_{15}$N$_2$O$_3$P: calcd. (MH$^+$): 255.0899, found: 255.0891.

Dimethyl 1-diazo-2-(3-methoxyphenyl)ethylphosphonate (3f)

Yellow oil; isolated yield 79% (213 mg). $R_f$ 0.50 (70% EtOAc/hexane); IR (Film, cm$^{-1}$): 2081, 1599, 1489, 1257, 1036; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 – 7.20 (m, 1H), 6.73 – 6.77 (m, 3H), 3.73 (s, 3H), 3.64 (d, $J_{H-P}$ = 11.6 Hz, 6H), 3.33 (d, $J_{H-P}$ = 10.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.5 (CO), 159.9 (C$_{Ar}$), 138.8 (d, $J_{C-P}$ = 3.4 Hz, C$_{Ar}$), 129.9 (C$_{Ar}$H), 120.6 (C$_{Ar}$H), 114.1 (C$_{Ar}$H), 112.6 (C$_{Ar}$H), 55.2 (OCH$_3$), 52.9 (d, $J_{C-P}$ = 5.3 Hz, $\{PO\}OCH$_3 x 2), 30.1 (d, $J_{C-P}$ = 8.5 Hz, CH$_2$); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 24.29; HRMS for C$_{11}$H$_{15}$N$_2$O$_4$P: calcd. (MH$^+$): 271.0848, found: 271.0839.

Dimethyl 2-(2-bromophenyl)-1-diazoethylphosphonate (3g)

Yellow oil; isolated yield 76% (241 mg). $R_f$ 0.50 (70% EtOAc/hexane); IR (Film, cm$^{-1}$): 2373, 1603, 1248, 1034; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (dd, $J$ = 8.0, 1.0 Hz, 1H), 7.20 – 7.26 (m, 2H), 7.04 – 7.08 (m, 1H), 3.59 (d, $J_{H-P}$ = 11.6 Hz, 6H), 3.52 (d, $J_{H-P}$ = 10.1 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.6 (d, $J_{C-P}$ = 2.8 Hz, C$_{Ar}$), 133.1 (C$_{Ar}$H), 130.9 (C$_{Ar}$H), 128.9 (C$_{Ar}$H), 127.7 (C$_{Ar}$H), 124.4 (C$_{Ar}$), 52.9 (d, $J_{C-P}$ = 5.2 Hz, $\{PO\}OCH$_3 x 2), 30.7 (d, $J_{C-P}$ = 8.9 Hz, CH$_2$); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 23.88; HRMS for C$_{10}$H$_{12}$BrN$_2$O$_3$P: calcd. (MH$^+$): 318.9847, found: 318.9836.
Dimethyl 2-(3-bromophenyl)-1-diazoethylphosphonate (3h)

\[
\text{Br} \quad \text{N}_2 \quad \text{PO(OMe)}_2
\]

Yellow oil; isolated yield 75% (238 mg). \(R_f\) 0.50 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)):
2371, 1617, 1455, 1250, 1032; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.34 (m, 2H), 7.10 – 7.16 (m, 2H), 3.64 (d, \(J_{H-P} = 11.6\) Hz, 6H), 3.33 (d, \(J_{H-P} = 10.3\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 175.4 (C=\(\text{N}_2\)), 139.5 (d, \(J_{C-P} = 2.0\) Hz, C\(_{Ar}\)), 131.3 (C\(_{Ar}\)), 130.3 (C\(_{Ar}\)), 126.9 (C\(_{Ar}\)), 122.7 (C\(_{Ar}\)), 53.0 (d, \(J_{C-P} = 5.2\) Hz, \{PO\}OCH\(_3\) x 2), 29.6 (d, \(J_{C-P} = 8.7\) Hz, CH\(_2\)); \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\)) \(\delta\) 23.68; HRMS for C\(_{10}\)H\(_{12}\)BrN\(_2\)O\(_3\)P: calcd. (MH\(^+\)): 318.9847, found: 318.9853.

Dimethyl 1-diazo-2-(4-fluorophenyl)ethylphosphonate (3i)

\[
\text{F} \quad \text{N}_2 \quad \text{PO(OMe)}_2
\]

Yellow oil; isolated yield 78% (201 mg). \(R_f\) 0.50 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)):
2369, 1602, 1230, 1035; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.12 – 7.16 (m, 2H), 6.91 – 6.96 (m, 2H), 3.62 (d, \(J_{H-P} = 11.6\) Hz, 6H), 3.33 (d, \(J_{H-P} = 10.1\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.9 (d, \(J_{C-F} = 244.1\) Hz, C\(_{Ar}\)), 132.9 (dd appearing as t, \(J_{J_{C-P}} = 3.3\) Hz, \(J_{C-F} = 3.2\) Hz, C\(_{Ar}\)), 129.9 (C\(_{Ar}\)), 129.8 (C\(_{Ar}\)), 115.7 (C\(_{Ar}\)), 115.5 (C\(_{Ar}\)), 52.8 (d, \(J_{C-P} = 5.3\) Hz, \{PO\}OCH\(_3\) x 2), 29.3 (d, \(J_{C-P} = 8.5\) Hz, CH\(_2\)); \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\)) \(\delta\) 23.89; HRMS for C\(_{10}\)H\(_{12}\)FN\(_2\)O\(_3\)P: calcd. (MH\(^+\)): 259.0648, found: 259.0643.

Dimethyl 1-diazo-3-alkylphosphonate (3o)

\[
\text{N}_2 \quad \text{PO(OMe)}_2
\]

Yellow oil; isolated yield 76% (144 mg). \(R_f\) 0.50 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)):
2084, 1252, 1035; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.67 – 5.77 (m, 1H), 5.05 – 5.10 (m, 2H), 3.65 (d, \(J_{H-P} = 11.6\) Hz, 6H), 2.73 – 2.77 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 132.5 (d, \(J_{C-P} = 3.1\) Hz, CH), 117.8 (\(\delta\)-CH\(_2\)), 52.9 (d, \(J_{C-P} = 5.6\) Hz, \{PO\}OCH\(_3\) x 2), 28.0 (d, \(J_{C-P} = 8.3\) Hz, \(\beta\)-CH\(_2\)); \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\)) \(\delta\) 21.46; HRMS for C\(_6\)H\(_{11}\)N\(_2\)O\(_3\)P: calcd. (MH\(^+\)): 191.0586, found: 191.0580.
Dimethyl 1-diazo-2-(thiophen-3-yl)ethylphosphonate (3p)

![Structure](image)

Yellow oil; isolated yield 78% (192 mg). R<sub>f</sub> 0.50 (70% EtOAc/hexane); IR (Film, cm<sup>-1</sup>): 2374, 1458, 1247, 1034; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (dd, J = 4.9 Hz, J = 3.0 Hz, 1H), 7.02 (t, J = 0.8 Hz, 1H), 3.63 (d, J<sub>H-P</sub> = 11.6 Hz, 6H), 3.38 (d, J<sub>H-P</sub> = 9.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.5 (d, J<sub>C-P</sub> = 3.4 Hz, C<sub>Ar</sub>), 127.6 (C<sub>Ar</sub>H), 126.6 (C<sub>Ar</sub>H), 122.2 (C<sub>Ar</sub>H), 52.9 (d, J<sub>C-P</sub> = 5.5 Hz, PO<sub>OMe</sub>x 2), 24.8 (d, J<sub>C-P</sub> = 8.8 Hz, CH<sub>2</sub>); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>) δ 24.06; HRMS for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub>PS: calcd. (MH<sup>+</sup>): 247.0306, found: 247.0301.

Dimethyl 1-diazo-2-(2-(methoxymethyl)phenyl)ethylphosphonate (3q)

![Structure](image)

Yellow oil; isolated yield 86% (244 mg). R<sub>f</sub> 0.50 (70% EtOAc/hexane); IR (Film, cm<sup>-1</sup>): 2370, 1617, 1249, 1032; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 – 7.26 (m, 4H), 4.41 (s, 2H), 3.63 (d, J<sub>H-P</sub> = 11.6 Hz, 6H), 3.46 (d, J<sub>H-P</sub> = 9.3 Hz, 2H), 3.30 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.1 (C<sub>Ar</sub>), 135.8 (d, J<sub>C-P</sub> = 3.4 Hz, C<sub>Ar</sub>), 129.9 (C<sub>Ar</sub>H), 129.8 (C<sub>Ar</sub>H), 128.5 (C<sub>Ar</sub>H), 127.4 (C<sub>Ar</sub>H), 72.9 (CH<sub>2</sub>), 58.1(OCH<sub>3</sub>), 52.9 (d, J<sub>C-P</sub> = 5.3 Hz, PO<sub>OMe</sub>x 2), 26.5 (CH<sub>2</sub>, J<sub>C-P</sub> = 8.8 Hz); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>) δ 24.44; HRMS for C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>P: calcd. (MH<sup>+</sup>): 285.1004, found: 285.0995.

Dimethyl 1-diazo-2-(4-(methoxymethyl)phenyl)ethylphosphonate (3r)

![Structure](image)

Yellow oil; isolated yield 88% (250 mg). R<sub>f</sub> 0.50 (70% EtOAc/hexane); IR (Film, cm<sup>-1</sup>): 2370, 1654, 1247, 1036; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.36 (s, 2H), 3.63 (d, J<sub>H-P</sub> = 11.6 Hz, 6H), 3.35 (d, J<sub>H-P</sub> = 10.0 Hz, 2H), 3.30 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.3 (C<sub>Ar</sub>), 136.6 (d, J<sub>C-P</sub> = 3.1 Hz, C<sub>Ar</sub>), 128.4 (C<sub>Ar</sub>H x 2), 128.2 (C<sub>Ar</sub>H x 2), 74.3 (CH<sub>2</sub>), 58.1(OCH<sub>3</sub>), 52.9 (d, J<sub>C-P</sub> = 5.3 Hz, PO<sub>OMe</sub>x 2), 29.7 (CH<sub>2</sub>, J<sub>C-P</sub> = 8.6 Hz); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>) δ 24.28; HRMS for C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>P: calcd. (MH<sup>+</sup>): 285.1004, found: 285.0998.
(E)-Dimethyl 1-diazo-4-phenylbut-3-enylphosphonate (3s)

Yellow oil; isolated yield 79% (210 mg). Rf 0.50 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2369, 1456, 1250, 1035; ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.28 (m, 4H), 7.13 – 7.17 (m, 1H), 6.42 (d, Jₜ-H-P = 15.7 Hz, 1H), 6.05 – 6.13 (m, 1H), 3.68 (d, Jₜ-H-P = 11.6 Hz, 6H), 2.91 – 2.95 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 136.6 (C Ar), 132.9 (C ali H), 128.6 (C Ar H x 2), 127.8 (C Ar H), 126.3 (C Ar H x 2), 124.1 (d, Jₜ-C-P = 3.1 Hz, C ali H), 53.0 (d, Jₜ-C-P = 5.2 Hz, {PO}OCH₃ x 2), 27.6 (d, Jₜ-C-P = 8.6 Hz, CH₂); ³¹P NMR (161.9 MHz, CDCl₃) δ 24.24; HRMS for C₁₂H₁₅N₂O₃P: calcd. (MH⁺): 267.0899, found: 267.0879.

Dimethyl 1-diazo-2-(naphthalene-2-yl)ethylphosphonate (3t)

Yellow oil; isolated yield 87% (252 mg). Rf 0.50 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2373, 1687, 1339, 1238, 1037; ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.76 (m, 3H), 7.60 (br s, 1H), 7.36 – 7.42 (m, 2H), 7.31 (dd, J = 8.4 Hz, J = 1.8 Hz, 1H), 3.63 (d, Jₜ-H-P = 11.6 Hz, 6H), 3.52 (d, Jₜ-H-P = 10.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 134.7 (d, Jₜ-C-P = 3.2 Hz, C Ar), 133.5 (C Ar), 132.6 (C Ar), 128.8 (C Ar H), 127.7 (C Ar H), 127.6 (C Ar H), 126.9 (C Ar H), 126.5 (C Ar H), 126.4 (C Ar H), 125.9 (C Ar H), 53.0 (d, Jₜ-C-P = 4.9 Hz, {PO}OCH₃ x 2), 30.3 (d, Jₜ-C-P = 8.6 Hz, CH₂); ³¹P NMR (161.9 MHz, CDCl₃) δ 24.15; HRMS for C₁₄H₁₅N₂O₃P: calcd. (MH⁺): 291.0899, found: 291.0893.

(E)-Dimethyl styrylphosphonate (4a)

Colorless oil; isolated yield 98% (208 mg). Rf 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2402, 1525, 1216, 1036, 927; ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.50 (m, 3H), 7.30 – 7.31 (m, 3H), 6.14 (t, Jₜ-H-P = 17.8 Hz, 1H), 3.69 (d, Jₜ-H-P = 11.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7 (d, Jₜ-C-P = 6.7 Hz, β-CH), 134.7 (d, Jₜ-C-P = 23.3 Hz, C Ar), 130.4 (C Ar H), 128.9 (C Ar H x 2), 127.8 (C Ar H x 2), 112.3 (d, Jₜ-C-P = 191.5 Hz, α-CH), 52.5 (d, Jₜ-C-P = 5.5 Hz,
(PO)OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 22.41; HRMS for C₁₀H₁₃O₃P, calcd (MH⁺): 213.0681, found: 213.0689.

**(E)-Dimethyl 4-nitrostyrylphosphonate (4b)**

![Image of (E)-Dimethyl 4-nitrostyrylphosphonate (4b)](image)

Yellow solid; isolated yield 85% (218 mg). Rᵣ 0.30 (70% EtOAc/hexane); Mp 97-100 °C; IR (Film, cm⁻¹): 1526, 1217, 1038; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.46 (dd, Jₙₐₚ = 22.2 Hz, J = 17.7 Hz, 1H), 6.31 (dd appearing as t, Jₙₐₚ = 17.0 Hz, J = 17.0 Hz, 1H), 3.71 (d, Jₙₐₚ = 11.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 148.6 (Cₐ), 146.4 (d, Jₘₜ = 6.0 Hz, β-CH), 140.6 (d, Jₙₐₚ = 21.5 Hz, Cₐ), 128.4 (CₐH x 2), 124.2 (CₐH x 2), 117.9 (d, Jₙₐₚ = 190.1 Hz, α-CH), 52.6 (d, Jₙₐₚ = 5.1 Hz, {PO}OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 20.01; HRMS for C₁₀H₁₂NO₅P, calcd (MH⁺): 258.0531, found: 258.0526.

**(E)-Dimethyl 2-nitrostyrylphosphonate (4c)**

![Image of (E)-Dimethyl 2-nitrostyrylphosphonate (4c)](image)

Colorless oil; isolated yield 88% (226 mg). Rᵣ 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2371, 1525, 1347, 1252, 1030; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.47 – 7.59 (m, 3H), 6.11 (dd appearing as t, Jₙₐₚ = 17.7 Hz, J = 17.4 Hz, 1H), 3.75 (d, Jₙₐₚ = 10.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9 (Cₐ), 144.6 (d, Jₘₜ = 7.8 Hz, β-CH), 133.7 (Cₐ), 131.5 (d, Jₙₐₚ = 24.6 Hz, Cₐ), 130.4 (CₐH), 129.2 (CₐH), 124.9 (CₐH), 118.7 (d, Jₙₐₚ = 188.8 Hz, α-CH), 52.8 (d, Jₙₐₚ = 5.6 Hz, {PO}OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 19.20; HRMS for C₁₀H₁₂NO₅P, calcd (MH⁺): 258.0531, found: 258.0534.

**(E)-Dimethyl 3-nitrostyrylphosphonate (4d)**

![Image of (E)-Dimethyl 3-nitrostyrylphosphonate (4d)](image)

Colorless oil; isolated yield 88% (226 mg). Rᵣ 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2402, 1532, 1035, 909; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (t, Jₙₐₚ = 1.7 Hz, 1H), 8.16 (dd, J
= 8.2 Hz, \( J = 1.3 \) Hz, 1H\); 7.72 (d, \( J = 7.6 \) Hz, 1H\); 7.44 – 7.54 (m, 2H\), 6.32 (dd, \( J_{\text{H-P}} = 16.4 \) Hz, \( J = 17.5 \) Hz, 1H\); 3.73 (d, \( J_{\text{H-P}} = 11.1 \) Hz, 6H\); 13C NMR (100 MHz, CDCl\( _3 \)) \( \delta \) 146.5 (d, \( J_{\text{C-P}} = 6.7 \) Hz, \( \beta \)-CH), 146.4 (C\( _{\text{Ar}} \)), 136.4 (d, \( J_{\text{C-P}} = 23.8 \) Hz, C\( _{\text{Ar}} \)), 133.5 (C\( _{\text{Ar}} \)), 130.0 (C\( _{\text{Ar}} \)), 124.7 (C\( _{\text{Ar}} \)), 122.0 (C\( _{\text{Ar}} \)), 116.6 (d, \( J_{\text{C-P}} = 190.5 \) Hz, \( \alpha \)-CH), 52.7 (d, \( J_{\text{C-P}} = 5.7 \) Hz, \{PO\}OCH\( _3 \) x 2); 31P NMR (161.9 MHz, CDCl\( _3 \)) \( \delta \) 20.3; HRMS for C\( _{10} \)H\( _{12} \)NO\( _5 \)P, calcd (MH\(^+\)): 258.0531, found: 258.0530.

\((E)\)-Dimethyl 4-methylstyrylphosphonate (4e)

\[ \text{Colorless oil; isolated yield 98\% (221 mg).} \]
\[ \text{IR (Film, cm}^{-1}\text{): 1216, 1156, 1035, 867;} \]
\[ \text{1H NMR (400 MHz, CDCl\( _3 \)) \( \delta \) 7.42 (dd, \( J_{\text{H-P}} = 22.6 \) Hz, \( J = 17.6 \) Hz, 1H\); 7.32 (d, \( J = 8.0 \) Hz, 2H\); 7.12 (d, \( J = 8.0 \) Hz, 2H\); 6.08 (t, \( J_{\text{H-P}} = 17.8 \) Hz, 1H\); 3.69 (d, \( J_{\text{H-P}} = 11.1 \) Hz, 6H\); 2.30 (s, 3H); 13C NMR (100 MHz, CDCl\( _3 \)) \( \delta \) 149.7 (d, \( J_{\text{C-P}} = 6.7 \) Hz, \( \beta \)-CH), 140.9 (C\( _{\text{Ar}} \)), 132.0 (d, \( J_{\text{C-P}} = 23.5 \) Hz, C\( _{\text{Ar}} \)), 129.6 (C\( _{\text{Ar}} \) x 2), 127.8 (C\( _{\text{Ar}} \) x 2), 110.9 (d, \( J_{\text{C-P}} = 192.1 \) Hz, \( \alpha \)-CH), 52.4 (d, \( J_{\text{C-P}} = 5.4 \) Hz, \{PO\}OCH\( _3 \) x 2), 21.4 (CH\( _3 \)); 31P NMR (161.9 MHz, CDCl\( _3 \)) \( \delta \) 22.92; HRMS for C\( _{11} \)H\( _{15} \)O\( _3 \)P, calcd (MH\(^+\)): 228.0837, found: 228.0830.

\((E)\)-Dimethyl 3-methoxystyrylphosphonate (4f)

\[ \text{Colorless oil; isolated yield 96\% (232 mg).} \]
\[ \text{IR (Film, cm}^{-1}\text{): 1216, 1156, 1034, 836;} \]
\[ \text{1H NMR (400 MHz, CDCl\( _3 \)) \( \delta \) 7.41 (dd, \( J_{\text{H-P}} = 22.5 \) Hz, \( J = 17.5 \) Hz, 1H\); 7.21 (t, \( J = 7.9 \) Hz, 1H\); 7.01 (d, \( J = 7.6 \) Hz, 1H\); 6.94 (t, \( J = 2.1 \) Hz, 1H\); 6.85 (dd, \( J = 8.2 \) Hz, \( J = 2.4 \) Hz, 1H\); 6.12 (t, \( J_{\text{H-P}} = 17.6 \) Hz, 1H\); 3.74 (s, 3H\); 3.69 (d, \( J_{\text{H-P}} = 11.1 \) Hz, 6H\); 13C NMR (100 MHz, CDCl\( _3 \)) \( \delta \) 159.9 (C\( _{\text{Ar}} \)), 149.5 (d, \( J_{\text{C-P}} = 6.6 \) Hz, \( \beta \)-CH), 136.1 (d, \( J_{\text{C-P}} = 23.3 \) Hz, C\( _{\text{Ar}} \)), 129.9 (C\( _{\text{Ar}} \)), 120.4 (C\( _{\text{Ar}} \)), 116.2 (C\( _{\text{Ar}} \)), 112.7 (C\( _{\text{Ar}} \)), 112.7 (d, \( J_{\text{C-P}} = 190.9 \) Hz, \( \alpha \)-CH), 55.3 (OCH\( _3 \)), 52.5 (d, \( J_{\text{C-P}} = 5.4 \) Hz, \{PO\}OCH\( _3 \) x 2); 31P NMR (161.9 MHz, CDCl\( _3 \)) \( \delta \) 22.22; HRMS for C\( _{11} \)H\( _{15} \)O\( _4 \)P, calcd (MH\(^+\)): 243.0786, found: 243.0780.
(E)-Dimethyl 2-bromostyrylphosphonate (4g)^9

\[
\begin{align*}
\text{Br} & \quad \text{PO} \quad \text{OMe}_2 \\
4g
\end{align*}
\]

Colorless oil; isolated yield 95% (276 mg). \( R_f \) 0.30 (70% EtOAc/hexane); \( \text{IR} \) (Film, cm\(^{-1}\)): 2402, 1463, 1247, 1036; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.75 (dd, \( J_{H-P} = 22.5 \) Hz, \( J = 17.5 \) Hz, 1H), 7.48 – 7.54 (m, 2H), 7.23 – 7.27 (m, 1H), 7.13 – 7.17 (m, 1H), 6.13 (t, \( J_{H-P} = 17.8 \) Hz, 1H), 3.72 (d, \( J_{H-P} = 11.1 \) Hz, 6H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 147.5 (d, \( J_{C-P} = 7.9 \) Hz, \( \beta \)-CH), 136.8 (d, \( J_{C-P} = 23.6 \) Hz, \( C_{Ar} \)), 133.2 (\( C_{Ar} \)H), 130.3 (\( C_{Ar} \)H), 126.5 (\( C_{Ar} \)H), 123.1 (\( C_{Ar} \)), 114.4 (d, \( J_{C-P} = 190.7 \) Hz, \( \alpha \)-CH), 52.7 (d, \( J_{C-P} = 5.7 \) Hz, \{PO\}OCH\(_3\) x 2); \( ^{31}\text{P NMR} \) (161.9 MHz, CDCl\(_3\)) \( \delta \) 20.74; \( \text{HRMS} \) for C\(_{10}\)H\(_{12}\)BrO\(_3\)P, calcd (MH\(^+\)): 290.9786, found: 290.9785.

(\( \text{E} \))-Dimethyl 3-bromostyrylphosphonate (4h)

\[
\begin{align*}
\text{Br} & \quad \text{PO} \quad \text{OMe}_2 \\
4h
\end{align*}
\]

Colorless oil; isolated yield 91% (264 mg). \( R_f \) 0.30 (70% EtOAc/hexane); \( \text{IR} \) (Film, cm\(^{-1}\)): 1620, 1216, 1155, 856; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (t, \( J = 1.6 \) Hz, 1H), 7.41 – 7.43 (br m, 1H), 7.31 – 7.37 (m, 2H), 7.16 – 7.23 (m, 1H), 6.15 (t, \( J_{H-P} = 17.3 \) Hz, 1H), 3.69 (d, \( J_{H-P} = 11.1 \) Hz, 6H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 147.8 (d, \( J_{C-P} = 6.8 \) Hz, \( \beta \)-CH), 136.8 (d, \( J_{C-P} = 23.6 \) Hz, \( C_{Ar} \)), 133.2 (\( C_{Ar} \)H), 130.4 (\( C_{Ar} \)H), 126.5 (\( C_{Ar} \)H), 123.1 (\( C_{Ar} \)), 114.4 (d, \( J_{C-P} = 190.7 \) Hz, \( \alpha \)-CH), 52.7 (d, \( J_{C-P} = 5.7 \) Hz, \{PO\}OCH\(_3\) x 2); \( ^{31}\text{P NMR} \) (161.9 MHz, CDCl\(_3\)) \( \delta \) 21.30; \( \text{HRMS} \) for C\(_{10}\)H\(_{12}\)BrO\(_3\)P, calcd (MH\(^+\)): 290.9786, found: 290.9785.

(\( \text{E} \))-Dimethyl 4-fluorostyrylphosphonate (4i)

\[
\begin{align*}
\text{F} & \quad \text{PO} \quad \text{OMe}_2 \\
4i
\end{align*}
\]

Colorless oil; isolated yield 98% (225 mg). \( R_f \) 0.30 (70% EtOAc/hexane); \( \text{IR} \) (Film, cm\(^{-1}\)): 3411 (br m), 3021 (m), 1657 (m), 1428 (w), 1216 (s), 1039 (m), 932 (s); \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.34 – 7.44 (m, 3H), 6.98 (t, \( J = 8.7 \) Hz, 2H), 6.04 (t, \( J_{H-P} = 17.5 \) Hz, 1H), 3.68 (d, \( J_{H-P} = 11.1 \) Hz, 6H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 163.9 (d, \( J_{C-F} = 249.9 \) Hz, \( C_{Ar} \)F), 148.3 (d, \( J_{C-P} = 6.8 \) Hz, \( \beta \)-CH), 130.9 (dd, \( J_{C-P} = 23.9 \) Hz, \( J_{C-F} = 3.5 \) Hz, \( C_{Ar} \)), 129.7 (\( C_{Ar} \)H), 129.6 (\( C_{Ar} \)H), 116.1 (\( C_{Ar} \)H), 115.9 (\( C_{Ar} \)H), 112.2 (dd, \( J_{C-P} = 192.0 \) Hz, \( J_{C-F} = 2.2 \) Hz, \( \alpha \)-CH), 52.5...
(d, \( J_{\text{C-P}} = 5.7 \text{ Hz} \), \{PO\}OCH\(_3\) x 2); \(^{31}\text{P NMR}\) (161.9 MHz, CDCl\(_3\)) \( \delta \) 22.15; \(^{1}\text{HRMS}\) for C\(_{10}\)H\(_{12}\)FO\(_3\)P, calcd (MH\(^+\)): 231.0586, found: 231.0582.

\( (E)\)-Dimethyl 2-cyanostyrylphosphonate (4j)

![4j]

Colorless oil; isolated yield 86% (204 mg). \( R_f \) 0.30 (70% EtOAc/hexane); \(^{1}\text{IR}\) (Film, cm\(^{-1}\)): 2226, 1622, 1254, 1032; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 7.61 – 7.70 (m, 3H), 7.54 – 7.58 (m, 1H), 7.39 – 7.43 (m, 1H), 6.43 (dd, \( J_{\text{H-P}} = 17.5 \text{ Hz} \), \( J = 16.8 \text{ Hz} \), 1H), 3.75 (d, \( J_{\text{H-P}} = 11.1 \text{ Hz} \), 6H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 143.7 (d, \( J_{\text{C-P}} = 6.7 \text{ Hz} \), \( \beta\)-CH), 137.6 (d, \( J_{\text{C-P}} = 23.7 \text{ Hz} \), C\(_{\text{Ar}}\)), 133.5 (C\(_{\text{Ar}}\)H), 133.0 (C\(_{\text{Ar}}\)H), 130.1 (C\(_{\text{Ar}}\)H), 127.1 (C\(_{\text{Ar}}\)H), 118.8 (d, \( J_{\text{C-P}} = 189.7 \text{ Hz} \), \( \alpha\)-CH), 117.0 (CN), 112.2 (C\(_{\text{Ar}}\)), 52.8 (d, \( J_{\text{C-P}} = 5.7 \text{ Hz} \), \{PO\}OCH\(_3\) x 2); \(^{31}\text{P NMR}\) (161.9 MHz, CDCl\(_3\)) \( \delta \) 19.46; \(^{1}\text{HRMS}\) for C\(_{11}\)H\(_{12}\)NO\(_3\)P: calcd. (MH\(^+\)): 238.0633, found: 238.0626.

\( (E)\)-Dimethyl 4-cyanostyrylphosphonate (4k)

![4k]

Colorless oil; isolated yield 83% (197 mg). \( R_f \) 0.30 (70% EtOAc/hexane); \(^{1}\text{IR}\) (Film, cm\(^{-1}\)): 2370, 1596, 1347, 1247, 1032; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 7.58 (d, \( J = 8.4 \text{ Hz} \), 2H), 7.49 (d, \( J = 8.4 \text{ Hz} \), 2H), 7.41 (dd, \( J_{\text{H-P}} = 22.4 \text{ Hz}, \ J = 17.6 \text{ Hz} \), 1H), 6.25 (dd, \( J_{\text{H-P}} = 17.5 \text{ Hz} \), \( J = 16.6 \text{ Hz} \), 1H), 3.69 (d, \( J_{\text{H-P}} = 11.1 \text{ Hz} \), 6H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 147.0 (d, \( J_{\text{C-P}} = 6.7 \text{ Hz} \), \( \beta\)-CH), 138.8 (d, \( J_{\text{C-P}} = 23.5 \text{ Hz} \), C\(_{\text{Ar}}\)), 132.7 (C\(_{\text{Ar}}\)H x 2), 128.1 (C\(_{\text{Ar}}\)H x 2), 118.3 (CN), 116.9 (d, \( J_{\text{C-P}} = 190.3 \text{ Hz} \), \( \alpha\)-CH), 113.5 (C\(_{\text{Ar}}\)), 52.8 (d, \( J_{\text{C-P}} = 5.6 \text{ Hz} \), \{PO\}OCH\(_3\) x 2); \(^{31}\text{P NMR}\) (161.9 MHz, CDCl\(_3\)) \( \delta \) 19.46; \(^{1}\text{HRMS}\) for C\(_{11}\)H\(_{12}\)NO\(_3\)P: calcd. (MH\(^+\)): 238.0633, found: 238.0626.

\( (E)\)-Dimethyl 2-(6-nitrobenzo[d][1,3]dioxol-5-yl)vinylphosphonate (4l)

![4l]

Yellow solid; isolated yield 78% (235 mg). \( R_f \) 0.30 (70% EtOAc/hexane); Mp 116-118 °C; \(^{1}\text{IR}\) (KBr, cm\(^{-1}\)): 2375, 1516, 1261, 1032; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 (dd, \( J_{\text{H-P}} = 21.8 \text{ Hz}, \ J = 17.3 \text{ Hz} \), 1H), 7.46 (s, 1H), 6.87 (s, 1H), 6.08 (s, 2H), 5.98 (dd appearing as t, \( J_{\text{H-P}} = \) 23.5 Hz, 1H), 3.69 (d, \( J_{\text{H-P}} = 11.1 \text{ Hz} \), 6H).
35.0 Hz, J = 17.5 Hz, 1H), 3.73 (d, JH-P = 11.1 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 152.2 (CAr), 148.9 (CAr), 144.9 (d, JC-P = 8.3 Hz, β-CH), 142.5 (CAr), 128.1 (d, JC-P = 25.2 Hz, CAr), 117.4 (d, JC-P = 189.4 Hz, α-CH), 107.4 (CArH), 105.5 (CArH), 103.4 (CH2), 52.7 (d, JC-P = 5.7 Hz, {PO}OCH3 x 2); 31P NMR (161.9 MHz, CDCl3) δ 19.50; HRMS for C11H12NO7P, calcd (MH+): 302.0430, found: 302.0430.

(E)-Dimethyl 5-chloro-2-nitrostyrylphosphonate (4m)

Colorless oil; isolated yield 80% (233mg). Rf 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2358, 1496, 1247, 1029; 1H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 8.8 Hz, 1H), 7.78 (dd, JH-P = 21.8 Hz, J = 17.4 Hz, 1H), 7.48 (d, J = 2.2 Hz, 1H), 7.43 (dd, J = 8.8 Hz, J = 2.2 Hz, 1H), 6.11 (dd appearing as t, JH-P = 17.3 Hz, 1H), 3.74 (d, JH-P = 11.1 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 145.8 (CAr), 143.5 (d, JC-P = 8.2 Hz, β-CH), 140.3 (CAr), 133.3 (d, JC-P = 29.9 Hz, CAr), 130.2 (CArH), 129.1 (CArH), 126.4 (CArH), 119.9 (d, JC-P = 188.6 Hz, α-CH), 52.8 (d, JC-P = 5.7 Hz, {PO}OCH3 x 2); 31P NMR (161.9 MHz, CDCl3) δ 18.53; HRMS for C10H11ClNO5P, calcd (MH+): 292.0142, found: 292.0136.

(E)-Dimethyl 3-methoxy-2-nitrostyrylphosphonate (4n)

Colorless oil; isolated yield 79% (227 mg). Rf 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 1536, 1386, 1217, 1058; 1H NMR (400 MHz, CDCl3) δ 7.34 (t, J = 8.2 Hz, 1H), 7.21 (dd, JH-P = 22.2 Hz, J = 17.4 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.21 (dd appearing as t, JH-P = 17.2 Hz, 1H), 3.83 (s, 3H), 3.69 (d, JH-P = 11.1 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 151.1 (CAr), 143.5 (d, JC-P = 8.2 Hz, β-CH), 140.3 (CAr), 133.3 (d, JC-P = 29.9 Hz, CAr), 130.2 (CArH), 129.1 (CArH), 126.4 (CArH), 119.9 (d, JC-P = 188.6 Hz, α-CH), 52.8 (d, JC-P = 5.7 Hz, {PO}OCH3 x 2); 31P NMR (161.9 MHz, CDCl3) δ 18.93; HRMS for C10H14NO6P, calcd (MH+): 288.0637, found: 288.0631.
(E)-Dimethyl buta-1,3-dienylphosphonate (4o)

\[
\begin{array}{c}
\text{O} \\
\text{P(OMe)$_2$}
\end{array}
\]

Colorless oil; isolated yield 85% (138 mg). \( R_f \) 0.30 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)): 2241, 1585, 1245, 1035; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.88 – 7.01 (m, 1H), 6.23 – 6.30 (m, 1H), 5.50 – 5.59 (m, 1H), 5.42 (d, \( J_{H-P} = 16.9 \) Hz, 1H), 5.31 – 5.35 (m, 1H), 3.58 (d, \( J_{H-P} = 11.1 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.6 (d, \( J_{C-P} = 5.8 \) Hz, \( \gamma \)-CH), 135.4 (d, \( J_{C-P} = 26.9 \) Hz, \( \beta \)-CH), 125.2 (CH\(_2\)), 116.3 (d, \( J_{C-P} = 190.0 \) Hz, \( \alpha \)-CH), 52.2 (d, \( J_{C-P} = 5.6 \) Hz, {PO}OCH\(_3\) x 2); \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\)) \( \delta \) 21.46; HRMS for C\(_6\)H\(_{11}\)O\(_3\)P, calcd (MH\(^+\)): 163.0524, found: 163.0522.

(E)-Dimethyl 2-(thiophen-3-yl)vinylphosphonate (4p)

\[
\begin{array}{c}
\text{S} \\
\text{O} \\
\text{P(OMe)$_2$}
\end{array}
\]

Colorless oil; isolated yield 95% (207 mg). \( R_f \) 0.30 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)): 1534, 1217, 1061; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 – 7.48 (m, 2H), 7.24 – 7.27 (m, 1H), 7.20 (t, dd, \( J = 5.1 \) Hz, \( J = 1.1 \) Hz, 1H), 5.93 (t, \( J_{H-P} = 17.8 \) Hz, 1H), 3.69 (d, \( J_{H-P} = 11.1 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 143.2 (d, \( J_{C-P} = 6.7 \) Hz, \( \beta \)-CH), 138.2 (d, \( J_{C-P} = 25.8 \) Hz, C\(_{Ar}\)), 127.9 (C\(_{Ar}\)), 127.0 (C\(_{Ar}\)), 124.9 (C\(_{Ar}\)), 111.7 (d, \( J_{C-P} = 191.9 \) Hz, \( \alpha \)-CH), 52.4 (d, \( J_{C-P} = 5.4 \) Hz, {PO}OCH\(_3\) x 2); \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\)) \( \delta \) 22.68; HRMS for C\(_8\)H\(_{11}\)O\(_3\)PS, calcd (MH\(^+\)): 219.0245, found: 219.0239.

(E)-Dimethyl 2-(methoxymethyl)styrylphosphonate (4q)

\[
\begin{array}{c}
\text{OMe} \\
\text{O} \\
\text{P(OMe)$_2$}
\end{array}
\]

Colorless oil; isolated yield 96% (256 mg). \( R_f \) 0.30 (70% EtOAc/hexane); IR (Film, cm\(^{-1}\)): 2226, 1622, 1254, 1032; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.73 (dd, \( J_{H-P} = 22.8 \) Hz, \( J = 17.5 \) Hz, 1H), 7.49 – 7.52 (m, 1H), 7.25 – 7.34 (m, 3H), 6.12 (dd, \( J_{H-P} = 18.8 \) Hz, \( J = 17.5 \) Hz, 1H), 4.49 (s, 2H), 3.72 (d, \( J_{H-P} = 11.1 \) Hz, 6H), 3.35 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 146.6 (d, \( J_{C-P} = 6.8 \) Hz, \( \beta \)-CH), 136.7 (C\(_{Ar}\)), 134.1 (d, \( J_{C-P} = 22.8 \) Hz, C\(_{Ar}\)), 129.9 (C\(_{Ar}\)), 129.5 (C\(_{Ar}\)), 128.4 (C\(_{Ar}\)), 126.5 (C\(_{Ar}\)), 114.7 (d, \( J_{C-P} = 189.8 \) Hz, \( \alpha \)-CH), 72.4 (CH\(_2\)), 72.4 (CH\(_2\)).
58.3 (OCH₃), 52.5 (d, J₃-P = 5.4 Hz, {PO}OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 21.88; HRMS for C₁₂H₁₇O₄P: calcd. (MH⁺): 257.0943, found: 257.0937.

*(E)-Dimethyl 4-(methoxymethyl)styrylphosphonate (4r)*

![4r]

Colorless oil; isolated yield 96% (256 mg). Rₚ 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2226, 1622, 1254, 1032; ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.48 (m, 3H), 7.27 (d, J = 8.1 Hz, 2H), 6.13 (t, Jₜ-P = 17.7 Hz, 1H), 4.39 (s, 2H), 3.69 (d, Jₜ-P = 11.1 Hz, 6H), 3.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3 (d, J₃-P = 6.6 Hz, β-CH), 140.8 (Cₐr), 134.0 (d, J₃-P = 23.3 Hz, Cₐ), 127.9 (CₐH x 2), 127.8 (CₐH x 2), 112.2 (d, J₃-P = 191.5 Hz, α-CH), 74.1 (CH₂), 58.3 (OCH₃), 52.5 (d, J₃-P = 5.6 Hz, {PO}OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 22.40; HRMS for C₁₁H₁₇O₄P: calcd. (MH⁺): 257.0943, found: 257.0937.

*(E)-Dimethyl 2-(naphthalene-2-yl)vinylphosphonate (4t)*

![4t]

Colorless oil; isolated yield 96% (251 mg). Rₚ 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 2925, 1216, 1156, 1061; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.74 – 7.79 (m, 3H), 7.55 – 7.66 (m, 2H), 7.42 – 7.45 (m, 2H), 6.25 (t, Jₜ-P = 17.6 Hz, 1H), 3.73 (d, Jₜ-P = 11.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7 (d, J₃-P = 6.9 Hz, β-CH), 140.8 (Cₐr), 134.3 (Cₐ), 132.1 (d, J₃-P = 23.3 Hz, Cₐ), 129.6 (CₐH), 128.7 (CₐH), 128.6 (CₐH), 127.8 (CₐH), 127.3 (CₐH), 126.8 (CₐH), 123.1 (CₐH), 112.4 (d, J₃-P = 191.4 Hz, α-CH), 52.5 (d, J₃-P = 5.5 Hz, {PO}OCH₃ x 2); ³¹P NMR (161.9 MHz, CDCl₃) δ 22.49; HRMS for C₁₄H₁₆O₃P, calcd. (MH⁺): 263.0837, found: 263.0830.

**Dimethyl (9H-fluoren-9-ylidene)methylphosphonate (4u)**

![4u]

Colorless oil; isolated yield 85% (243 mg). Rₚ 0.30 (70% EtOAc/hexane); IR (Film, cm⁻¹): 1537, 1216, 1156, 1033, 929; ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 7.8 Hz, 1H), 7.52 –
7.57 (m, 3H), 7.30 – 7.35 (m, 2H), 7.20 – 7.26 (m, 2H), 6.41 (d, $J_{H-P} = 11.6$ Hz, 1H), 3.74 (d, $J_{H-P} = 11.4$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.0 (d, $J_{C-P} = 6.4$ Hz, $\beta$-CH), 142.4 (C$_{Ar}$), 140.7 (C$_{Ar}$), 138.1 (C$_{Ar}$), 135.2 (C$_{Ar}$), 130.9 (C$_{Ar}$H), 130.8 (C$_{Ar}$H), 128.1 (C$_{Ar}$H), 127.6 (C$_{Ar}$H), 127.5 (C$_{Ar}$H), 121.4 (C$_{Ar}$H), 119.8 (C$_{Ar}$H), 119.7 (C$_{Ar}$H), 107.4 (d, $J_{C-P} = 192.1$ Hz, $\alpha$-CH), 52.6 (d, $J_{C-P} = 5.5$ Hz, {PO}OCH$_3$ x 2); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 19.34; HRMS for C$_{16}$H$_{15}$O$_3$P: calcd. (MH$^+$): 287.0837, found: 287.0838.

**Dimethyl 3-(methoxymethyl)-4-(4-methoxyphenyl)-1H-pyrazol-5-ylphosphonate (5)**

![Image of compound 5]

Colorless gummy solid; isolated yield 65% (243 mg). $R_f$ 0.40 (90% EtOAc/hexane); IR (Film, cm$^{-1}$): 1219, 1252, 1035, 932; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 4.38 (s, 2H), 3.77 (s, 3H), 3.59 (d, $J_{H-P} = 11.5$ Hz, 6H), 3.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2 (C$_{Ar}$), 130.9 (C$_{Ar}$H x 2), 128.4 (C$_{Ar}$), 123.1 (C$_{Ar}$), 113.7 (C$_{Ar}$H x 2), 65.4 (CH$_2$), 58.3 (OCH$_3$), 55.2 (OCH$_3$), 53.1 (d, $J_{C-P} = 5.4$ Hz, {PO}OCH$_3$ x 2); $^{31}$P NMR (161.9 MHz, CDCl$_3$) $\delta$ 10.99; HRMS for C$_{14}$H$_{19}$N$_2$O$_5$P: calcd. (MH$^+$): 327.1110, found: 327.1104.
Figure 1: $^1$H NMR spectrum of 3a

Figure 2: $^{13}$C NMR spectrum of 3a
Figure 3: $^{31}$P NMR spectrum of 3a

Figure 4: $^1$H NMR spectrum of 3d
Figure 5: $^{13}$C NMR spectrum of 3d

Figure 6: $^{31}$P NMR spectrum of 3d
Figure 7: $^1$H NMR spectrum of 3e

Figure 8: $^{13}$C NMR spectrum of 3e
Figure 9: $^{31}$P NMR spectrum of 3e

Figure 10: $^1$H NMR spectrum of 3f
Figure 11: $^{13}$C NMR spectrum of 3f

Figure 12: $^{31}$P NMR spectrum of 3f
Figure 13: $^1$H NMR spectrum of 3g

Figure 14: $^{13}$C NMR spectrum of 3g
Figure 15: $^{31}$P NMR spectrum of 3g

Figure 16: $^1$H NMR spectrum of 3h
Figure 17: $^{13}$C NMR spectrum of 3h

Figure 18: $^{31}$P NMR spectrum of 3h
Figure 19: $^1$H NMR spectrum of 3i

Figure 20: $^{13}$C NMR spectrum of 3i
Figure 21: $^{31}$P NMR spectrum of 3i

Figure 22: $^1$H NMR spectrum of 3o
Figure 23: $^{13}$C NMR spectrum of 3o

Figure 24: $^{31}$P NMR spectrum of 3o
Figure 25: $^1$H NMR spectrum of 3p

Figure 26: $^{13}$C NMR spectrum of 3p
Figure 27: $^{31}$P NMR spectrum of 3p

Figure 28: $^1$H NMR spectrum of 3q
Figure 29: $^{13}$C NMR spectrum of 3q

Figure 30: $^{31}$P NMR spectrum of 3q
Figure 31: $^1$H NMR spectrum of 3r

Figure 32: $^{13}$C NMR spectrum of 3r
Figure 33: $^{31}$P NMR spectrum of 3r

Figure 34: $^1$H NMR spectrum of 3s
Figure 35: $^{13}$C NMR spectrum of 3s

Figure 36: $^{31}$P NMR spectrum of 3s
Figure 37: $^1$H NMR spectrum of 3t

Figure 38: $^{13}$C NMR spectrum of 3t
Figure 39: $^{31}$P NMR spectrum of 3t

Figure 40: $^1$H NMR spectrum of 4a
Figure 41: $^{13}$C NMR spectrum of 4a

Figure 42: $^{31}$P NMR spectrum of 4a
Figure 43: $^1$H NMR spectrum of 4b

Figure 44: $^{13}$C NMR spectrum of 4b
Figure 45: $^{31}P$ NMR spectrum of 4b

Figure 46: $^1H$ NMR spectrum of 4c
Figure 47: $^{13}$C NMR spectrum of 4c

Figure 48: $^{31}$P NMR spectrum of 4c
Figure 49: $^1$H NMR spectrum of 4d

Figure 50: $^{13}$C NMR spectrum of 4d
Figure 51: $^{31}$P NMR spectrum of 4d

Figure 52: $^1$H NMR spectrum of 4e
Figure 53: $^{13}$C NMR spectrum of 4e

Figure 54: $^{31}$P NMR spectrum of 4e
Figure 55: $^1$H NMR spectrum of 4f

Figure 56: $^{13}$CNMR spectrum of 4f
Figure 57: $^{31}$P NMR spectrum of 4f

Figure 58: $^1$H NMR spectrum of 4g
Figure 59: $^{13}$C NMR spectrum of 4g

Figure 60: $^{31}$P NMR spectrum of 4g
Figure 61: $^1$H NMR spectrum of 4h

Figure 62: $^{13}$C NMR spectrum of 4h
Figure 63: $^{31}$P NMR spectrum of 4h

Figure 64: $^1$H NMR spectrum of 4i
Figure 65: $^{13}$C NMR spectrum of 4i

Figure 66: $^{31}$P NMR spectrum of 4i
Figure 67: $^1$H NMR spectrum of 4j

Figure 68: $^{13}$C NMR spectrum of 4j
Figure 69: $^{31}$P NMR spectrum of 4j

Figure 70: $^1$H NMR spectrum of 4k
Figure 71: $^{13}$C NMR spectrum of 4k

Figure 72: $^{31}$P NMR spectrum of 4k
Figure 73: $^1$H NMR spectrum of 4l

Figure 74: $^{13}$C NMR spectrum of 4l
Figure 75: $^{31}$P NMR spectrum of 4l

Figure 76: $^1$H NMR spectrum of 4m
Figure 77: $^{13}$C NMR spectrum of 4m

Figure 78: $^{31}$P NMR spectrum of 4m
Figure 79: $^1$H NMR spectrum of 4n

Figure 80: $^{13}$C NMR spectrum of 4n
Figure 81: $^{31}$P NMR spectrum of 4n

Figure 82: $^1$H NMR spectrum of 4o
Figure 83: $^{13}$C NMR spectrum of 4o

Figure 84: $^{31}$P NMR spectrum of 4o
Figure 85: $^1$H NMR spectrum of 4p

Figure 86: $^{13}$C NMR spectrum of 4p
Figure 87: $^{31}$P NMR spectrum of 4p

Figure 88: $^1$H NMR spectrum of 4q
Figure 89: $^{13}$C NMR spectrum of 4q

Figure 90: $^{31}$P NMR spectrum of 4q
Figure 91: $^1$H NMR spectrum of 4r

Figure 92: $^{13}$C NMR spectrum of 4r
Figure 93: $^{31}$P NMR spectrum of 4r

Figure 94: $^1$H NMR spectrum of 4t
Figure 95: $^{13}$C NMR spectrum of 4t

Figure 96: $^{31}$P NMR spectrum of 4t
Figure 97: $^1$H NMR spectrum of 4u

Figure 98: $^{13}$C NMR spectrum of 4u
Figure 99: $^{31}$P NMR spectrum of 4u

Figure 100: $^1$H NMR spectrum of 5
Figure 101: $^{13}$C NMR spectrum of 5

Figure 102: $^{31}$P NMR spectrum of 5
References