Supporting Information

for

A Simple and Efficient Method for One-Pot Three-Component Synthesis of Terminal Vinylphosphonates Using a Task-Specific Ionic Liquid

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General Information

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Avance DPX-400.
IR spectra were run on a Perkin–Elmer 780 instrument. Mass spectra were recorded on a Shimadzu GCMS-QP5050A. The
purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV_{254}
plates.

Synthesis and characterization data of 5-HPAA

5-HPAA was prepared according to the previously reported procedure for the synthesis of 2-hydroxyethylammonium
acetate.\(^1\) To a stirring solution of 5-amino-pentan-1-ol (50 mmol, 5.15 g) in EtOH (15 mL), a solution of acetic acid (0.5
mmol, 3 g) in EtOH (15 mL) was added dropwise at room temperature within 1 h. The resulting solution was stirred at
room temperature for another 20 h. EtOH was removed under reduced pressure and the oil in residue was dried under
reduced pressure at 50 °C for 48 h to give 5-HPAA as a light yellow viscous liquid. \(\delta_H\) 6.78 (s, 4H, OH and NH\(_3\)\(^+\)), 3.38
(t, 2H, \(J = 6.4\) Hz, CH\(_2\)), 2.67 (t, 2H, \(J = 7.6\) Hz, CH\(_2\)), 1.69 (s, 3H, CH\(_3\)), 1.48-1.54 (m, 2H, CH\(_2\)), 1.39-1.42 (m, 2 H,
CH\(_2\)), 1.32–1.37 (m, 2 H, CH\(_2\)) ppm. \(\delta_C\) 175.7, 60.8, 39.4, 32.4, 28.1, 25.0, 22.9 ppm. MS (EI, 70 eV): \(m/z\) (%)
146 (3 M\(^+-\)NH\(_3\)\(^+\) or M\(^+-\)OH), 104 (100 M\(^+-\)OAc), 59 (18 OAc).

Characterization data of vinylphosphonates

Vinylphosphonates 1a-m are known compounds.\(^2\) Diethyl 1-phenylethenylphosphonate (1a): Colorless oil. IR (neat): 1500, 1211, 1012, 781 cm\(^{-1}\). \(\delta_H\) 7.56 (d, \(J = 7.2\) Hz, 2H, Ar), 7.35-7.40 (m, 3H, Ar), 6.37 (d, \(J = 22.0\) Hz, 1H, =CH\(_2\)), 6.19 (d, \(J = 45.8\) Hz, 1H, =CH\(_2\)), 4.06-4.21 (m, 4H,
OCH\(_2\)CH\(_3\)), 1.31 (t, \(J = 7.2\) Hz, 6H, OCH\(_2\)CH\(_3\)) ppm. \(\delta_C\) 139.7 (d, \(J = 175.0\) Hz), 136.7 (d, \(J = 12.1\) Hz), 131.8 (d, \(J = 8.0\)
Hz), 128.5, 128.3, 127.4 (d, \(J = 5.0\) Hz), 62.2 (d, \(J = 5.0\) Hz), 16.2 (d, \(J = 7.0\) Hz) ppm.

Dimethyl 1-phenylethenylphosphonate (1b): Colorless oil. IR (neat): 1602, 1493, 1231, 1020, 834 cm\(^{-1}\). \(\delta_H\) 7.48-7.50 (m, 2H,
Ar), 7.38-7.41 (m, 3H, Ar), 6.56 (d, \(J = 22.8\) Hz, 1H, =CH\(_2\)), 6.34 (d, \(J = 49.2\) Hz, 1H, =CH\(_2\)), 3.90 (d, \(J = 10.4\) Hz,
6H, OCH\(_3\)) ppm.

Di-iso-propyl 1-phenylethenylphosphonate (1c): Colorless oil. IR (neat): 1584, 1491, 1225, 1019, 817 cm\(^{-1}\). \(\delta_H\) 7.57 (d, \(J =
6.8\) Hz, 2H, Ar), 7.31-7.37 (m, 3H, Ar), 6.38 (d, \(J = 22.0\) Hz, 1H, =CH\(_2\)), 6.17 (d, \(J = 46.0\) Hz, 1H, =CH\(_2\)), 4.72-4.76 (m, 2H,
CH\(_2\)(CH\(_3\))\(_2\)), 1.36 [d, \(J = 6.0\) Hz, 6H, OCH\(_2\)(CH\(_3\))\(_2\)], 1.22 [d, \(J = 6.4\) Hz, 6H, OCH\(_2\)(CH\(_3\))\(_2\)] ppm. \(\delta_C\) 140.8 (d, \(J = 179.0\)
Hz), 136.9 (d, \(J = 12.0\) Hz), 131.1, 128.3, 128.1, 127.5 (d, \(J = 6.0\) Hz), 71.2, 23.9 (dd, \(J = 42.7\) Hz, 4) ppm.

Diethyl 1-(4-methylphenyl)ethenylphosphonate (1d): Yellow oil. IR (neat): 1630, 1511, 1221, 1030, 817 cm\(^{-1}\). \(\delta_H\) 7.43
(d, \(J = 7.6\) Hz, 2H, Ar), 7.16 (d, \(J = 8.0\) Hz, 2H, Ar), 6.29 (d, \(J = 22.0\) Hz, 1H, =CH\(_2\)), 6.14 (d, \(J = 46.0\) Hz, 1H, =CH\(_2\)),
4.04-4.18 (m, 4H, OCH₂CH₃), 2.35 (s, 3H, CH₃), 1.28 (t, \( J = 6.8 \) Hz, 6H, OCH₂CH₃) ppm. \( \delta_C \) 139.3 (d, \( J = 174.0 \) Hz), 138.2, 133.6 (d, \( J = 12.0 \) Hz), 131.1 (d, \( J = 8.0 \) Hz), 129.1, 127.2 (d, \( J = 6.0 \) Hz), 62.2 (d, \( J = 5.0 \) Hz) 21.1, 16.2 (d, \( J = 6.0 \) Hz) ppm.

**Diethyl 1-(4-methoxyphenyl)ethenylphosphonate (1e):** Yellow oil. IR (neat): 1598, 1504, 1224, 1021, 823 cm⁻¹. \( \delta_H \) 7.44 (d, \( J = 8.4 \) Hz, 2H, Ar), 6.83 (d, \( J = 8.8 \) Hz, 2H, Ar), 6.19 (d, \( J = 22.0 \) Hz, 1H, \( =CH_2 \)), 6.05 (d, \( J = 46.0 \) Hz, 1H, \( =CH_2 \)), 3.92-4.03 (m, 4H, OCH₂CH₃), 3.75 (s, 3H, OCH₃), 1.23 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃) ppm.

**Diethyl 1-(3-methoxyphenyl)ethenylphosphonate (1f):** Yellow oil. IR (neat): 1621, 1510, 1235, 1011, 803 cm⁻¹. \( \delta_H \) 7.29 (t, \( J = 4.0 \) Hz, 1H, Ar), 7.12 (d, \( J = 8.8 \) Hz, 2H, Ar), 6.89 (d, \( J = 8.0 \) Hz, 1H, Ar), 6.35 (d, \( J = 21.6 \) Hz, 1H, \( =CH_2 \)), 6.18 (d, \( J = 45.6 \) Hz, 1H, \( =CH_2 \)), 4.04-4.20 (m, 4H, OCH₂CH₃), 3.83 (s, 3H, OCH₃), 1.30 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃) ppm.

**Diethyl 1-(2-methoxyphenyl)ethenylphosphonate (1g):** Yellow oil. IR (neat): 1604, 1501, 1241, 1015, 809 cm⁻¹. \( \delta_H \) 7.24-7.29 (m, 2H, Ar), 6.93 (d, \( J = 7.6 \) Hz, 1H, Ar), 6.89 (d, \( J = 8.0 \) Hz, 1H, Ar), 6.43 (d, \( J = 22.0 \) Hz, 1H, \( =CH_2 \)), 6.04 (d, \( J = 46.8 \) Hz, 1H, \( =CH_2 \)), 4.02-4.12 (m, 4H, OCH₂CH₃), 3.79 (s, 3H, OCH₃), 1.26 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃) ppm. \( \delta_C \) 156.6 (d, \( J = 5.0 \) Hz), 136.5 (d, \( J = 177.0 \) Hz), 134.2 (J = 7.0 Hz), 130.2, 129.3, 126.2 (d, \( J = 11.0 \) Hz), 120.3, 110.9, 62.0 (d, \( J = 6.0 \) Hz), 55.4, 16.2 (d, \( J = 6.0 \) Hz) ppm.

**Diethyl 1-(4-bromophenyl)ethenylphosphonate (1h):** Yellow oil. IR (neat): 1579, 1481, 1239, 1025, 801 cm⁻¹. \( \delta_H \) 7.48 (d, \( J = 8.8 \) Hz, 2H, Ar), 7.41 (d, \( J = 8.4 \) Hz, 2H, Ar), 6.34 (d, \( J = 22.0 \) Hz, 1H, \( =CH_2 \)), 6.15 (d, \( J = 45.6 \) Hz, 1H, \( =CH_2 \)), 4.01-4.13 (m, 4H, OCH₂CH₃), 1.29 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃) ppm. \( \delta_C \) 138.7 (d, \( J = 176.0 \) Hz) 132.1 (d, \( J = 8.0 \) Hz), 131.6, 130.9, 129.9 (d, \( J = 4.0 \) Hz), 129.1 (d, \( J = 6.0 \) Hz), 62.4 (d, \( J = 5.0 \) Hz), 16.2 (d, \( J = 6.0 \) Hz) ppm.

**Diethyl 1-(4-chlorophenyl)ethenylphosphonate (1i):** Yellow oil. IR (neat): 1593, 1499, 1227, 1011, 845 cm⁻¹. \( \delta_H \) 7.49 (d, \( J = 8.4 \) Hz, 2H, Ar), 7.34 (d, \( J = 8.0 \) Hz, 2H, Ar), 6.35 (d, \( J = 22.0 \) Hz, 1H, \( =CH_2 \)), 6.17 (d, \( J = 45.6 \) Hz, 1H, \( =CH_2 \)), 4.07-4.18 (m, 4H, OCH₂CH₃), 1.31 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃) ppm. \( \delta_C \) 138.7 (d, \( J = 175.0 \) Hz), 135.1 (d, \( J = 12.0 \) Hz), 134.3, 131.9 (d, \( J = 8.0 \) Hz), 128.8 (d, \( J = 6.0 \) Hz), 128.6, 62.4 (d, \( J = 5.0 \) Hz), 16.3 (d, \( J = 6.0 \) Hz) ppm.

**Diethyl 1-(1-propyl)ethenylphosphonate (1j):** colorless oil. IR (neat): 1587, 1483, 1229, 1018, 821 cm⁻¹. \( \delta_H \) 6.03 (d, \( J = 22.8 \) Hz, 1H, \( =CH_2 \)), 5.81 (d, \( J = 46.8 \) Hz, 1H, \( =CH_2 \)), 3.97-4.08 (m, 4H, OCH₂CH₃), 2.24 (t, \( J = 7.6 \) Hz, 2H, CH₂), 1.32-1.39 (m, 2H, CH₃), 1.25 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃), 0.89 (t, \( J = 7.2 \) Hz, 3H, CH₃) ppm.

**Diethyl 1-(1-ethyl)ethenylphosphonate (1k):** colorless oil. IR (neat): 1592, 1487, 1221, 1006, 800 cm⁻¹. \( \delta_H \) 6.45 (d, \( J = 21.2 \) Hz, 1H, \( =CH_2 \)), 6.27 (d, \( J = 46.0 \) Hz, 1H, \( =CH_2 \)), 4.04-4.10 (m, 4H, OCH₂CH₃), 2.03 (q, \( J = 8.0 \) Hz, 2H, CH₂), 1.27 (t, \( J = 7.2 \) Hz, 6H, OCH₂CH₃), 0.86 (t, \( J = 7.2 \) Hz, 3H, CH₃) ppm.
Diethyl 1-(1-naphthyl)ethenylphosphonate (1l): Yellow oil. IR (neat): 1598, 1503, 1229, 1009, 817 cm⁻¹. δH 8.03-8.05 (m, 1H, Ar), 7.84-7.89 (m, 2H, Ar), 7.44-7.52 (m, 4H, Ar), 6.70 (d, J = 22.4 Hz, 1H, =CH₂), 6.06 (d, J = 47.2 Hz, 1H, =CH₂), 4.03-4.14 (m, 4H, OCH₂CH₃), 1.22 (t, J = 7.2 Hz, 6H, OCH₂CH₃) ppm.

Diethyl 1-(1H-indol-3-yl)ethenylphosphonate (1m): yellow oil. IR (neat): 1601, 1499, 1222, 1001, 821 cm⁻¹. δH 8.91 (brs, 1H, NH), 8.86 (s, 1H, Ar), 7.62 (d, J = 7.6 Hz, 1H, Ar), 7.27 (d, J = 7.6 Hz, 1H, Ar), 7.09-7.13 (m, 2H, Ar), 6.35 (d, J = 48.0 Hz, 1H, =CH₂), 6.23 (d, J = 22.8 Hz, 1H, =CH₂), 3.99-4.09 (m, 4H, OCH₂CH₃), 0.96 (t, J = 7.2 Hz, 6H, CH₃) ppm.

Diethyl 1-(thiophene-2-yl)ethenylphosphonate (1n): yellow oil. IR (neat): 1617, 1510, 1235, 1015, 818 cm⁻¹. δH 7.39 (s, 1H, Ar), 7.27 (s, 1H, Ar), 7.04 (t, J = 4.4 Hz, 1H, Ar), 6.27 (d, J = 44.4 Hz, 1H, =CH₂), 6.22 (d, J = 21.6 Hz, 1H, =CH₂), 4.08-4.23 (m, 4H, OCH₂CH₃), 1.35 (t, J = 7.0 Hz, 6H, CH₃) ppm. δC 134.3 (d, J = 176 Hz), 129.2, 129.1, 127.8, 127.3 (d, J = 4.0 Hz), 125.6, 62.4 (d, J = 5.0 Hz), 16.2 (d, J = 7.0 Hz) ppm. MS (EI, 70 eV): m/z (%): 246 (2 M⁺), 138 (100), 109 (19 M⁺-OEt²).

References


$^{1}H$ NMR spectra of diethyl 1-phenylethenylphosphonate (1a)

Sample Code: J/R

$^{13}C$ NMR spectra of diethyl 1-phenylethenylphosphonate (1a)
$^1$H NMR spectra of dimethyl 1-phenylethenylphosphonate (1b)

$^1$H NMR spectra of di-iso-propyl 1-phenylethenylphosphonate (1c)
$^{13}$C NMR spectra of di-isopropyl 1-phenylethenylphosphonate (1c)

$^1$H NMR spectra of diethyl 1-(4-methylphenyl)ethenylphosphonate (1d)
$^{13}$C NMR spectra of diethyl 1-(4-methylphenyl)ethenylphosphonate (1d)

Sample code: 1/R

$^1$H NMR spectra of diethyl 1-(4-methoxyphenyl)ethenylphosphonate (1e)
$^1$H NMR spectra of diethyl 1-(3-methoxyphenyl)ethenylphosphonate (1f)

Sample code: 6f

$^1$H NMR spectra of diethyl 1-(2-methoxyphenyl)ethenylphosphonate (1g)

Sample code: 5f
$^{13}$C NMR spectra of diethyl 1-(2-methoxyphenyl)ethenylphosphonate (1g)

Sample code: 4/R.

$^1$H NMR spectra of diethyl 1-(4-bromophenyl)ethenylphosphonate (1h)
$^{13}$C NMR spectra of diethyl 1-(4-bromophenyl)ethenylphosphonate (1h)

Sample code: 322 (AI)

$^1$H NMR spectra of diethyl 1-(4-chlorophenyl)ethenylphosphonate (1i)

Sample code: 4/8
$^{13}$C NMR spectra of diethyl 1-(4-chlorophenyl)ethenylphosphonate (1i)

$^1$H NMR spectra of diethyl 1-(1-propyl)ethenylphosphonate (1j)
$^1$H NMR spectra of diethyl 1-(1-ethyl)ethenylphosphonate (1k)

Sample code: 2/k

$^1$H NMR spectra of diethyl 1-(1-naphthyl)ethenylphosphonate (1l)
$^1$H NMR spectra of diethyl 1-(1-indol-3-yl)ethenylphosphonate (1m)

$^1$H NMR spectra of diethyl 1-(thiophen-2-yl)ethenylphosphonate (1n)
$^{13}$C NMR spectra of diethyl 1-(thiophen-2-yl)ethenylphosphonate (1n)