Supporting Information for “A new bis(2,2,2-trifluoroethyl)phosphonate for the synthesis of Z-unsaturated N-Methoxy N-Methyl amides.”

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Infrared spectra (IR) were taken on a Perkin-Elmer 1600 FT-IR spectrometer. Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 instrument. The following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. Chemical shifts are reported in δ values relative to chloroform (7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR) as internal standard. The ^{13}C spectra experiment were recorded under decoupling conditions. Mass spectral (MS) assays were obtained on a VG Micromass ZAB-2F instrument with electronic ionization (70eV).

[(Methoxy-methyl-carbamoyl)-methyl]-phosphonic acid bis-(2,2,2-trifluoro-ethyl) ester (7).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 4.52-4.41 (4H, m), 3.73 (3H, s), 3.34 (2H, d, $J=20.9\text{Hz}$), 3.20 (3H, s).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 164.9, 122.6 (q, $J=277\text{Hz}$), 62.4 (q, $J=38\text{Hz}$), 61.5, 31.9, 31.6 (d, $J=147\text{Hz}$).

IR (film) ν (cm^{-1}) : 2977, 1667, 1422, 1297, 1266, 1172, 1073.

MS (m/e) : 347 (M^+)

HRMS : calcd. for $\text{C}_8\text{H}_{12}\text{O}_5\text{F}_6\text{PN}$: 347.0357; found: 347.0363 ± 0.0010 .

[1-(Methoxy-methyl-carbamoyl)-ethyl]-phosphonic acid bis-(2,2,2-trifluoro-ethyl) ester (8).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 4.53-4.33 (4H, m), 3.86-3.72 (1H, m), 3.77 (3H, m), 3.23 (3H, s), 1.54-1.44 (3H, dd, $J=19.7\text{Hz}$, 7.2Hz).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 169.2, 122.8 (qq, $J=277\text{Hz}$, $J=8\text{Hz}$), 63.2 (q, $J=38\text{Hz}$), 61.7, 35.8 (d, $J=143\text{Hz}$), 32.1, 12.5.

IR (film) ν (cm^{-1}) : 2976, 2950, 1661, 1458, 1421, 1391, 1263, 1170, 1074, 987, 963, 846.

MS (m/e) : 361 (M^+)

HRMS : calcd. for $\text{C}_9\text{H}_{14}\text{F}_6\text{NO}_5\text{P}$: 361.0514; found: 361.0508 ± 0.0011 .

[Bromo-(Methoxy-methyl-carbamoyl)-methyl]-phosphonic acid bis-(2,2,2-trifluoro-ethyl) ester (11).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 5.09-5.06 (1H, d, $J=10.7\text{Hz}$), 4.66-4.43 (4H, m), 3.84 (3H, s), 3.26 (3H, s).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 164.3, 122.3 (qq, $J=277\text{Hz}$, $J=8\text{Hz}$), 63.5 (q, $J=38\text{Hz}$), 61.7, 32.0, 29.7 (d, $J=163\text{Hz}$).

IR (film) ν (cm^{-1}) : 2978, 1666, 1420, 1392, 1295, 1266, 1174, 1071, 962, 846.

MS (m/e) : 425 (M^+)

HRMS : calcd. for $\text{C}_8\text{H}_{11}\text{O}_5\text{F}_6\text{BrPN}$: 424.9462; found: 424.9453 ± 0.0013 .

Z-Methyl-dec-2-enoic acid methoxy-methyl-amide (12).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 5.41 (1H, t, $J=7.4\text{Hz}$), 3.68 (3H, s), 3.24 (3H, s), 1.99 (2H, q, $J=8\text{Hz}$), 1.89 (3H, s), 1.25 (10H, m), 0.87 (3H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 177.0, 134.4, 130.7, 61.4, 31.8, 29.7, 29.4, 29.4, 29.3, 29.1, 22.6, 20.0, 14.1.

IR (film) ν (cm^{-1}) : 2927, 2856, 1651, 1456, 1381, 1177, 1118, 1074, 999.

MS (m/e) : 227 (M^+)

HRMS : calcd. for $\text{C}_{13}\text{H}_{26}\text{NO}_2$: 228.1963; found: 228.1957 $\pm$ 0.0007.

Z-2-Methyl-octa-2,4-dienoic acid methoxy-methyl-amide (13).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 6.04-5.91 (2H, m), 5.61 (1H, m), 3.61 (3H, s), 3.20 (3H, s), 1.98 (2H, m), 1.90 (3H, s), 1.33 (2H, m), 0.82 (3H, t, $J=7.04\text{Hz}$).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 171.4, 136.4, 129.6, 126.4, 61.4, 34.7, 22.3, 19.9, 19.4, 14.0, 13.6.

IR (film) ν (cm^{-1}) : 2961, 2933, 1660, 1455, 1384, 1172.

MS (m/e) : 197 (M^+)

HRMS : calcd. for $\text{C}_{11}\text{H}_{19}\text{NO}_2$: 197.1416; found: 197.1419 $\pm$ 0.0006.

Z-2-Methyl-6-(tetrahydro-pyran-2-yloxy)-hex-2-enoic acid methoxy-methyl-amide (14).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 5.44 (1H, t, $J=7.4\text{Hz}$), 4.55 (1H, t, $J=3.3\text{Hz}$), 3.88-3.68 (2H, m), 3.66 (3H, s), 3.60-3.36 (2H, m), 3.24 (3H, s), 2.14-2.06 (2H, m), 1.90 (3H, s), 1.87-1.43 (6H, m), 1.26 (2H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 180.0, 129.8, 98.9, 66.9, 62.4, 61.5, 30.7, 29.4, 26.4, 25.4, 20.1, 19.7.

IR (film) ν (cm^{-1}) : 2939, 2860, 1652, 1456, 1382, 1120, 1076, 1033.

MS (m/e) : 272 (MH^+)

HRMS : calcd. for $\text{C}_{14}\text{H}_{26}\text{NO}_4$: 272.1862; found: 272.1862 ± 0.0008 .

Z-2,2-Dimethyl-propionic acid 7-(methoxy-methyl-carbamoyl)-3-methyl-octa-2,6-dienyl ester (15).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 5.39 – 5.28 (2H, m), 4.53 (2H, d, $J= 6.9\text{Hz}$), 3.65 (3H, s), 3.22 (3H, s), 2.10 (4H, m), 1.87 (3H, s), 1.66 (3H, s), 1.17 (9H, s).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 178.3, 178.3, 140.6, 131.6, 129.3, 119.1, 61.3, 61.0, 38.8, 38.6, 27.6, 27.0, 19.9, 17.4, 16.2.

IR (film) ν (cm^{-1}) : 2972, 2934, 1728, 1652, 1456, 1283, 1154.

MS : 311 (M^+).

HRMS : calcd. for $\text{C}_{14}\text{H}_{29}\text{NO}_4$: 311.2096; found: 311.2090 ± 0.0009 .

Z-dec-2-enoic acid methoxy-methyl-amide (16).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 6.22 (1H, d), 6.11 (1H, m) , 3.68 (3H, s), 3.21 (3H, s), 2.61 (2H, m), 1.26 (10H, m), 0.87 (3H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 177.8, 147.8, 117.8, 61.3, 34.0, 31.7, 31.6, 29.2, 29.1, 29.0, 22.6, 14.0.

IR (film) ν (cm^{-1}) : 2957, 2856, 1661, 1459, 1343, 1177, 1097, 1002, 795.

MS (m/e) : 213 (M^+)

HRMS : calcd. for $\text{C}_{12}\text{H}_{23}\text{NO}_2$: 213.1729; found: 213.1724 $\pm$ 0.0006.

E-2-bromo-dec-2-enoic acid methoxy-methyl-amide (17).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 6.11 (1H, t, $J=8\text{Hz}$), 3.74 (3H, s), 3.27 (3H, s), 2.07 (2H, q, $J=8\text{Hz}$), 1.43-1.21 (10H, m), 0.87 (3H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 179.0, 136.8, 108.9, 61.7, 34.0, 31.7, 31.1, 29.0, 28.9, 28.6, 22.6, 14.0.

IR (film) ν (cm^{-1}) : 2928, 2856, 1661, 1461, 1384, 1180, 1107, 1005, 942.

MS (m/e) : 291 (M^+)

HRMS : calcd. for $\text{C}_{12}\text{H}_{22}\text{BrNO}_2$: 291.0837; found: 291.0837 $\pm$ 0.0008.

[1-(Methoxy-methyl-carbamoyl)-ethyl]-phosphonic acid diethylester (18).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 4.21-4.06 (4H, m), 3.76 (3H, m), 3.74-3.68 (1H, m), 3.21 (3H, m), 1.41 (3H, dd, $J=18.3\text{Hz}$, 7.2Hz), 1.24 (6H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 170.0, 62.8, 62.0, 61.4, 35.5, 33.6, 32.1, 16.3, 12.3.

IR (film) ν (cm^{-1}) : 2982, 2940, 1655, 1458, 1388, 1253, 1053, 1024, 964, 796.

MS (m/e) : 254 (MH^+)

HRMS : calcd. for $\text{C}_9\text{H}_{21}\text{NO}_5\text{P}$: 254.1157; found: 254.1153 ± 0.0007 .

E-Methyl-dec-2-enoic acid methoxy-methyl-amide (19).

NMR ^1H (300MHz, CDCl_3) δ (ppm) : 5.86 (1H, t, $J=7.3\text{Hz}$), 3.63 (3H, s), 3.22 (3H, s), 2.10 (2H, q, $J=8\text{Hz}$), 1.84 (3H, s), 1.27 (10H, m), 0.88 (3H, m).

NMR ^{13}C (75MHz, CDCl_3) δ (ppm) : 172.9, 134.3, 130.7, 60.9, 33.7, 31.8, 29.3, 29.1, 28.8, 27.7, 22.6, 20.0, 14.0.

IR (film) ν (cm^{-1}) : 2956, 2926, 2855, 1654, 1458, 1373, 1177, 1072, 1002.

MS (m/e) : 228 (MH^+)

HRMS : calcd. for $\text{C}_{13}\text{H}_{26}\text{NO}_2$: 228.1963; found: 228.1979 ± 0.0007 .

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