Supporting Information

Ionic Liquid Promoted Phospha-Michael Reaction: A Convenient Access to β -Nitrophosphonates

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Spectral Data of Compounds 4a-l

Diphenyl (2-nitro-1-phenylethyl)phosphonate (4a)

White solid, Isolated yield = 89 %; mp 152-153 °C; IR: ν = 3056, 2915, 1635, 1588, 1326, 1194 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.47-6.75 (m, 15H), 5.25-5.06 (m, 2H, CH_2), 4.50-4.37 (m, 1H, CH); ^{13}C NMR (75 MHz, CDCl_3): δ 149.8, 129.9, 129.7, 129.3, 129.2, 128.9, 125.7, 125.4, 120.4, 120.1, 74.9, 44.3; ^{31}P NMR (120 MHz, CDCl_3): δ 16.8; MS (ESI): m/z 384 $[\text{M}+\text{H}]^+$; Anal.Calc'd.for $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{P}$: C, 62.66; H, 4.73; O, 20.87; Found: C, 62.49; H, 4.58; O, 20.63.

Diethyl (2-nitro-1-phenylethyl)phosphonate (4b)

White solid, Isolated yield = 83 %, mp 76-77 °C; IR: ν = 3028, 2912, 1642, 1576, 1318, 1136 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.37-6.99 (m, 5H, Ar), 4.92-4.87 (m, 2H, CH_2), 4.11-4.04 (m, 2H, OCH_2), 3.98-3.87 (m, 2H, OCH_2), 3.74-3.69 (m, 1H, CH), 1.36 (t, $J=7.1$ Hz, 3H, CH_3), 1.17 t, $J=7.1$ Hz, 3H, OCH_3); ^{13}C NMR (75 MHz, CDCl_3): δ 137.5, 129.4, 128.2, 126.7, 68.4, 62.7, 61.8, 41.6, 18.3, 17.5; ^{31}P NMR (120 MHz, CDCl_3): δ 21.6; MS (ESI): m/z 288 $[\text{M}+\text{H}]^+$; Anal.Calc'd.for $\text{C}_{12}\text{H}_{18}\text{NO}_5\text{P}$: C, 50.18; H, 6.32; O, 27.85; Found: C, 49.88; H, 6.16; O, 27.64.

Dimethyl (2-nitro-1-phenylethyl)phosphonate (4c)

White solid, Isolated yield = 81 %, mp 68-69 °C; IR: ν = 3044, 2898, 1629, 1581, 1332, 1165 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.34-7.02 (m, 5H, Ar), 4.94-4.86 (m, 2H, CH_2), 3.99-3.91 (m, 1H, CH), 3.71-3.69 (d, $J=10.8$ Hz, 3H, OCH_3), 3.52-3.50 (d, $J=10.7$ Hz, 3H, OCH_3); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 138.4, 131.3, 126.5, 123.9, 69.8, 56.3, 55.2, 42.4; ^{31}P NMR (120 MHz, CDCl_3): δ 22.3; MS (ESI): m/z 260 $[\text{M}+\text{H}]^+$; Anal.Calc'd.for $\text{C}_{10}\text{H}_{14}\text{NO}_5\text{P}$: C, 46.34; H, 5.44; O, 30.86; Found: C, 46.24; H, 5.26; O, 30.69.

Diethyl (1-(4-(diethylamino)phenyl)-2-nitroethyl)phosphonate (4d)

Pale yellowish liquid, Isolated yield = 89 %; IR: ν = 3059, 2921, 1632, 1577, 1312, 1138 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.44-6.62 (m, 4H, Ar), 4.92-4.87 (m, 2H, CH_2), 4.15-4.04 (m, 4H, 2OCH_2), 3.75-3.71 (m, 1H, CH), 3.38-3.24 (q, J = 7.0 Hz, 4H, 2CH_2), 1.29 (t, J = 7.0 Hz, 6H, $2\text{O}-\text{CH}_2-\text{CH}_3$), 1.16 (t, J = 7.1 Hz, 6H, $2\text{N}-\text{CH}_2-\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3): δ 146.9, 129.6, 125.4, 116.7, 68.3, 64.3, 63.1, 47.2, 46.3, 38.8, 16.7, 15.8, 13.7, 13.1; ^{31}P NMR (120 MHz, CDCl_3): δ 21.6; MS (ESI): m/z 359 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_5\text{P}$: C, 53.62; H, 7.59; O, 22.32; Found: C, 53.35; H, 7.29; O, 22.16.

Diphenyl (2-nitro-1-(p-tolyl)ethyl)phosphonate (4f)

White semi solid, Isolated yield = 91 %; IR: ν = 3052, 2914, 1628, 1576, 1321, 1186 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.33-6.78 (m, 14H, Ar), 5.18-5.09 (m, 2H, CH_2), 4.39-4.36 (m, 1H, CH), 2.33 (s, 3H; CH_3); ^{13}C NMR (75 MHz, CDCl_3): δ 150.0, 149.9, 138.7, 129.9, 129.6, 129.0, 129.02, 127.4, 125.6, 125.4, 120.3, 120.1, 75.0, 43.0, 21.0; ^{31}P NMR (120 MHz, CDCl_3): δ 17.1; MS (ESI): m/z 398 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{21}\text{H}_{20}\text{NO}_5\text{P}$: C, 63.47; H, 5.07; O, 20.13; Found: C, 63.15; H, 4.88; O, 20.02.

Diphenyl (1-(4-methoxyphenyl)-2-nitroethyl)phosphonate (4g)

white solid, Isolated yield = 86 %, mp 126-127 $^{\circ}\text{C}$; IR: ν = 3032, 2888, 1637, 1569, 1329, 1193 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.37-6.78 (m, 14H, Ar), 5.18-5.07 (m, 2H, CH_2), 4.39-4.37 (m, 1H, CH), 3.80 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, CDCl_3): δ 157.6, 150.4, 150.3, 130.2, 130.0, 129.8, 129.4, 125.6, 125.4, 121.3, 120.5, 120.2, 119.4, 111.6, 74.8, 56.1, 36.5; ^{31}P NMR (120 MHz): δ 16.6; MS (ESI): m/z 414 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{21}\text{H}_{20}\text{NO}_6\text{P}$: C, 61.02; H, 4.88; O, 23.22; Found: C, 60.84; H, 4.62; O, 23.08.

Diethyl (1-(4-methoxyphenyl)-2-nitroethyl)phosphonate (4h)

Yellowish solid, Isolated yield = 83 %, mp 74-75 °C; IR: ν = 3041, 2932, 1629, 1572, 1331, 1132 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.29-6.88 (m, 4H, Ar), 4.94-4.89 (m, 2H, CH_2), 4.13-4.06 (m, 2H, OCH_2), 4.02-3.92 (m, 2H, OCH_2), 3.80 (s, 3H), 3.78-3.73 (m, 1H, CH), 1.33 (t, J = 7.0 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H), ^{13}C NMR (75 MHz, CDCl_3): δ 157.4, 129.6, 123.2, 115.3, 69.2, 63.4, 62.7, 54.9, 41.8, 16.3, 16.1; ^{31}P NMR (120 MHz, CDCl_3): δ 21.3; MS (ESI): m/z 318 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{13}\text{H}_{20}\text{NO}_6\text{P}$: C, 49.21; H, 6.35; O, 30.26; Found: C, 48.92; H, 6.24; O, 30.16.

Dimethyl (1-(4-methoxyphenyl)-2-nitroethyl)phosphonate (4i)

Yellowish solid, Isolated yield = 82 %, mp 63-64 °C; IR: ν = 3019, 2916, 1632, 1581, 1328, 1167 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.30-6.88 (m, 4H, Ar), 4.92-4.84 (m, 2H, CH_2), 4.03-3.95 (m, 1H, CH), 3.78 (s, 3H, OCH_3), 3.74-3.72 (d, J =10.9 Hz, 3H, OCH_3), 3.53-3.51 (d, J =10.6 Hz, 3H, OCH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 159.6, 129.8, 122.7, 114.4, 75.1, 55.1, 54.0, 53.0, 40.8; ^{31}P NMR (120 MHz, CDCl_3): δ 22.4; MS (ESI): m/z 290 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{11}\text{H}_{16}\text{NO}_6\text{P}$: C, 45.68; H, 5.58; O, 33.19; Found: C, 45.31; H, 5.25; O, 32.83.

Diphenyl (1-(3-bromophenyl)-2-nitroethyl)phosphonate (4j)

White solid, Isolated yield = 86 %, mp 114-115 °C; IR: ν = 3062, 2891, 1643, 1574, 1319, 1189 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.58-6.80 (m, 14H, Ar), 5.19-5.08 (m, 2H, CH_2), 4.38-4.40 (m, 1H, CH); ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 149.9, 134.0, 130.9, 130.4, 130.2, 129.9, 129.3, 128.4, 126.6, 125.9, 125.6, 120.6, 120.1, 74.9, 42.0; ^{31}P NMR (120 MHz, CDCl_3): δ 17.3; MS (ESI): m/z 462 $[\text{M}+\text{H}]^+$; Anal.Calcd.for $\text{C}_{20}\text{H}_{17}\text{BrNO}_5\text{P}$: C, 51.97; H, 3.71; O, 17.31; Found: C, 51.57; H, 3.43; O, 17.11.

Diethyl (1-(3-bromophenyl)-2-nitroethyl)phosphonate (4k)

Yellowish brown liquid, Isolated yield = 78 %; IR: ν = 3027, 2911, 1637, 1586, 1332, 1138 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.48-6.81 (m, 4H, Ar), 4.91-4.86 (m, 2H, CH_2), 4.11-4.04 (m, 1H,

CH), 4.01-3.92 (m, 2H, OCH₂), 3.76-3.71 (m, 2H, OCH₂), 1.37 (t, $J = 7.1$ Hz, 3H, CH₃), 1.18 (t, $J = 7.1$ Hz, 3H, CH₃), ¹³C NMR (75 MHz, CDCl₃): δ 137.4, 134.8, 131.6, 128.3, 126.4, 123.7, 68.6, 64.3, 61.8, 41.4, 17.3, 16.7; ³¹P NMR (120 MHz, CDCl₃): δ 21.6; MS (ESI): m/z 366 [M+H]⁺; Anal.Calcd.for C₁₂H₁₇BrNO₅P: C, 39.36; H, 4.68; O, 21.85; Found: C, 39.12; H, 4.35; O, 21.38.

Dimethyl (1-(3-bromophenyl)-2-nitroethyl)phosphonate (4l)

Brownish liquid, Isolated yield = 76 %; IR: $\nu = 3039, 2908, 1628, 1579, 1326, 1173$ cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.32-6.89 (m, 4H, Ar), 4.88-4.91 (m, 2H, CH₂), 4.04-3.93 (m, 1H, CH), 3.71-3.69 (d, $J=10.8$ Hz, 3H, OCH₃), 3.54-3.49 (d, $J=10.7$ Hz, 3H, OCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 136.7, 133.4, 131.2, 127.5, 126.7, 122.4, 69.2, 56.2, 55.8, 39.6; ³¹P NMR (120 MHz, CDCl₃): δ 22.0; MS (ESI): m/z 337 [M+H]⁺; Anal.Calcd.for C₁₀H₁₃BrNO₅P: C, 35.52; H, 3.88; O, 23.66; Found: C, 35.47; H, 3.63; O, 23.36.

¹H NMR Spectrum of compound 4e

^{13}C NMR Spectrum of compound 4e

Mass Spectrum of compound 4e

^1H NMR Spectrum of compound 4i

^{13}C NMR Spectrum of compound 4i

SAMLE-6

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TLV-II 19071108 2544 (25.739) Cm (2542:2567-2519:2527)

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Mass Spectrum of compound 4i