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3-Hydroxypyridine and 3-(Hydroxymethyl)pyridine in the Synthesis of Salts of Aryldithiophosphonic Acids on the Basis of Monoterpenyl Alcohols

Supplementary Information

Salt (3a): FTIR: ν_{max} = 3318 m br (O–H), 3066 w (=C–H, Ar), 2955 st, 2924 st, 2870 m $\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, 2722 w (NH^+), 1596 m (C=N, Ar), 1557 m, 1498 m (C=C, Ar), 1455 m $\delta_{as}(CH_3)$, 1386 m, 1369 m $\delta_{sgem.}((CH_3)_2C)$, 1025 st ((P)O–C), 928 m δ(O–C, OC–C), 677 m (P=S), 547 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.82 (3H, d, H^8, $^3J_{HH}$ = 7.0 Hz), 0.84–0.92 (1H, m, H^7), 0.94 (6H, d, $H^{9,10}$, $^3J_{HH}$ = 6.9 Hz), 1.07–1.15 (1H, m, H^5), 1.37–1.49 (2H, m, H^3), 1.60–1.72 (2H, m, H^4), 1.91–1.98 (1H, m, H^7), 2.19–2.27 (2H, m, H^6), 3.31–3.37 (1H, m, H^1), 3.83 (3H, s, $H^{7"}$), 6.86 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.9 Hz), 6.87 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.8 Hz), 7.54–7.63 (1H, m, $H^{4'}$; 1H, $H^{5'}$), 8.02 (2H, dd, $H^{2",6"}$, $^3J_{HH}$ = 8.8 Hz, $^3J_{PH}$ = 13.5 Hz), 8.21 (1H, d, $H^{6'}$, $^3J_{HH}$ = 4.0 Hz), 8.27 (2H, s, $H^{2'}$).

Salt (3b): FTIR: ν_{max} = 3279 st br (O–H), 3062 w (=C–H, Ar), 2951 st, 2876 m $\nu_{as,s}$ (CH_3), $\nu_{as,s}$ (CH_2), 2715 w (NH^+), 1595 m (C=N, Ar), 1579 m, 1498 m, 1480 m (C=C, Ar), 1454 m $\delta_{as}(CH_3)$, 1388 m, 1367 m $\delta_{sgem.}$ ($(CH_3)_2C$), 1031 st ((P)O–C), 993 m, 979 m, 943 m δ(OC–C, C–C), 676 m (P=S), 555 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.86 (3H, s, H^8), 0.89 (6H, s , $H^{9,10}$), 1.24–1.29 (2H, m, H^5), 1.67–1.79 (2H, m, H^3), 1.92–2.00 (2H, m, H^6), 2.20–2.29 (1H, m, H^4), 3.84 (3H, s, $H^{7"}$), 3.93–3.98 (1H, m, H^2), 6.83 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.9 Hz), 6.87 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.9 Hz), 7.80–7.87 (1H, m, $H^{5'}$), 8.05 (2H, dd, $H^{2",6"}$, $^3J_{HH}$ = 8.8 Hz, $^3J_{PH}$ = 13.0 Hz), 8.10–8.15 (1H, m, $H^{4'}$; 1H, $H^{6'}$), 8.19 (1H, s, $H^{2'}$). ^{13}C (100.6 MHz, CD_3OD–CCl_4 1:1, δ, ppm, in parentheses is a view of signal in $^{13}C\{^1H\}$ NMR): 12.9 (q (s) $C^{9,10}$, $^1J_{CH}$ = 124.0 Hz), 17.5 (q (s) C^8, $^1J_{CH}$ = 127.4 Hz), 19.9 (q (s) $C^{9,10}$, $^1J_{CH}$ = 124.0 Hz), 25.9 (t (s) C^5, $^1J_{CH}$ = 136.5 Hz), 28.1 (t (s) C^5H_2, $^1J_{CH}$ = 129.1 Hz), 38.1 (t (s) C^3H_2, $^1J_{CH}$ = 128.4 Hz), 45.0 (d (s) C^4, $^1J_{CH}$ = 143.8 Hz), 57.1 (q (s) $C^{7"}$, $^1J_{CH}$ = 132.1 Hz), 76.4 (d, (s) C^2, $^1J_{CH}$ = 146.0 Hz), 104.8 (m (s) $C^{1"}$), 112.3 (d (s) $C^{3"}$, $C^{5"}$, $^1J_{CH}$ = 112.4 Hz), 112.5 (d (s) $C^{3"}$, $C^{5"}$, $^1J_{CH}$ = 112.4 Hz), 125.5 (d (s) $C^{4'}$, $^1J_{CH}$ = 166.5 Hz), 126.0 (d (s) $C^{5'}$, $^1J_{CH}$ = 166.5 Hz), 131.7 (d (s) $C^{2"}$, $C^{6"}$, $^1J_{CH}$ = 169.0 Hz), 131.9 (d (s) $C^{2"}$, $C^{6"}$, $^1J_{CH}$ = 169.0 Hz), 134.8 (d (s) $C^{2'}$, $^1J_{CH}$ = 178.3 Hz), 137.2 (d (s) $C^{2'}$, $^1J_{CH}$ = 178.3 Hz), 155.4 (s (s) $C^{3'}$), 163.0 (s (s) $C^{4"}$).

Salt (3c): FTIR: ν_{max} = 3326 st br (O–H), 3067 w (=C–H, Ar), 2951 st, 2878 m, 2838 m $\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, 2741 w (NH^+), 1596 st (C=N, Ar), 1568 m, 1557 m, 1498 m (C=C, Ar), 1455 m $\delta_{as}(CH_3)$, 1390 m, 1372 m $\delta_{sgem.}$ ($(CH_3)_2C$), 1031 st ((P)O–C), 971 m, 914 m δ(OC–C, C–C), 676 m, 664 m (P=S), 553 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.82 (6H, s, $H^{9,10}$), 0.84 (6H, s, $H^{9,10}$), 0.89 (6H, s, $H^{9,10}$), 0.90 (6H, s, $H^{9,10}$), 0.98 (3H, s, H^8), 0.90 (3H, s, H^8), 1.46–1.59 (2H, m, H^5), 1.61–1.74 (2H, m, H^3; 2H, H^6), 2.20–2.07 (1H, m, H^4), 3.80 (3H, s, $H^{7"}$), 3.81 (3H, s, $H^{7"}$), 4.45–4.52 (1H, m, H^2), 6.859 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.9 Hz), 6.865 (2H, d, $H^{3",5"}$, $^3J_{HH}$ = 8.9 Hz), 7.68–7.72 (1H, m, $H^{4'}$), 7.75–7.80 (1H, m, $H^{5'}$), 8.03 (2H, dd, $H^{2",6"}$, $^3J_{HH}$ = 8.8 Hz, $^3J_{PH}$ = 13.5 Hz), 8.245 (1H, d, $H^{6'}$, $^3J_{HH}$ = 4.7 Hz), 8.30 (1H, s, $H^{2'}$). ^{13}C (100.6 MHz, CD_3OD–CCl_4 1:1, δ, ppm, in parentheses is a view of signal in $^{13}C\{^1H\}$ NMR): 8.90 (q (s) C^8, $^1J_{CH}$ = 108.1 Hz), 9.98 (q (s) C^8, $^1J_{CH}$ = 109.3 Hz), 17.7 (q (s) C^9, C^{10}, $^1J_{CH}$ = 124.4 Hz], 17.8 (q (s) C^9, C^{10}, $^1J_{CH}$ = 124.4 Hz), 17.97 (q (s) C^9, C^{10}), $^1J_{CH}$ = 124.4 Hz), 18.0 (q (s) C^9, C^{10}, $^1J_{CH}$ = 124.4 Hz), 25.15 (t (s) C^5, $^1J_{CH}$ = 132.1 Hz), 25.20 (t (s) C^5, $^1J_{CH}$ = 132.1 Hz), 31.96 (t (s) C^6, $^1J_{CH}$ = 132.0 Hz), 32.14 (t (s) C^6, $^1J_{CH}$ = 132.0 Hz), 43.4 (d (s) C^4, $^1J_{CH}$ = 140.1 Hz), 43.8 (d (s) C^4, $^1J_{CH}$ = 140.1 Hz), 44.3 (s (s) C^7), 44.9 (s (s) C^1), 55.3 (q (s) $C^{7"}$, $^1J_{CH}$ = 142.0 Hz), 79.9 (d (d) C^2, $^1J_{CH}$ = 143.4 Hz), 110.5 (d (s) $C^{3"}$, $C^{5"}$, $^1J_{CH}$ = 159.9 Hz), 110.6 (d (s) $C^{3"}$, $C^{5"}$, $^1J_{CH}$ = 159.9 Hz), 110.9 (d (s) $C^{3"}$, $C^{5"}$, $^1J_{CH}$ = 160.3 Hz), 111.3–111.9 (m (s) $C^{1"}$), 125.5 (d (s) $C^{4'}$, $^1J_{CH}$ = 170.9 Hz), 128.3 (d (s) $C^{5'}$, $^1J_{CH}$ = 152.2 Hz), 129.7 (d (s) $C^{2"}$, $C^{6"}$, $^1J_{CH}$ = 161.8 Hz), 129.9 (s, $C^{2"}$, $C^{6"}$, $^1J_{CH}$ = 161.8 Hz), 132.7 (d (s) $C^{2'}$, $^1J_{CH}$ = 190.7 Hz), 154.8 (s (s) $C^{3'}$), 154.9 (s (s) $C^{3'}$), 159.24 (s (s) $C^{4"}$), 159.27 (s (s) $C^{4"}$).

Salt (3d): FTIR: ν_{max} = 3632 m (O–H, Ar), 3333 w br (O–H), 3068 w (=C–H, Ar), 2956 vw, 2958 vw, 2871 st $\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2$), 2721 w (NH^+), 1619 m (C=N, Ar), 1579 m, 1556 m (C=C, Ar), 1428 st $\delta_{as}(CH_3$ as), 1386 m, 1368 m $\delta_{sgem.}((CH_3)_2C)$, 1042 st ((P)O–C), 993 m, 929 m δ(OC–C, C–C), 660 st (P=S), 567 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.81 (3H, d, H^8, $^3J_{HH}$ = 7.1 Hz), 0.94 (6H, d, $H^{9,10}$, $^3J_{HH}$ = 7.1 Hz), 0.83–0.90 [1H, m, H^7], 0.95–1.04 (1H, m, H^5), 1.46 (18H, s, $H^{8"}$), 1.61–1.71 (2H, m, H^3), 1.92–1.96 (2H, m, H^4), 2.19–2.25 (2H, m, H^6), 7.66 (1H, d, H^4, $^3J_{HH}$ = 4.9 Hz), 7.67 (1H, d, H^4, $^3J_{HH}$ = 4.9 Hz), 7.70–7.73 (1H, m, H^5), 7.73–7.77 (1H, m, H^3), 7.96 (2H, d, $H^{2",6"}$, $^3J_{PH}$ =

14.8 Hz), 8.250 (1H, d, H^6, $^3J_{HH}$ = 4.9 Hz), 8.252 (1H, H^6, $^3J_{HH}$ = 4.9 Hz), 8.295 (1H, s, $H^{2'}$), 8.298 (1H, s, $H^{2'}$).

Salt (4a): FTIR: ν_{max} = 3313 m br (O–H), 3100 w, 3064 w (=C–H, Ar), 2954 vw, 2925 vw, 2869 st $\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$, 2700 w (NH^+), 1635 m (C=N, Ar), 1598 m, 1572 m, 1503 m (C=C, Ar), 1456 m $\delta_{as}(CH_3)$, 1386 m, 1369 m $\delta_{sgem.}((CH_3)_2C)$, 1043 vw ((P)O–C), 994 m δ(O–C, OC–C), 687 m (P=S), 540 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.82 (3H, d, H^8, $^3J_{HH}$ = 7.0 Hz), 0.936 (6H, d, $H^{9,10}$, $^3J_{HH}$ = 6.6 Hz), 0.942 (6H, d, $H^{9,10}$, $^3J_{HH}$ = 7.1 Hz), 0.84–0.91 (1H, m, H^7), 0.98–1.14 (1H, m, H^5), 1.69–1.72 (2H, m, H^3), 1.92–1.99 (2H, m, H^4), 2.17–2.28 (2H, m, H^6), 3.82 (3H, s, $H^{7''}$), 3.90–3.98 (1H, m, H^1), 4.77 (2H, s, $H^{7'}$), 6.86 (2H, d, $H^{3'',5''}$, $^3J_{HH}$ = 8.8 Hz), 6.87 (2H, d, $H^{3'',5''}$, $^3J_{HH}$ = 8.8 Hz), 7.74 (2H, dd, $H^{2'',6''}$, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 13.2 Hz), 8.01 (1H, d, $H^{5'}$, $^3J_{HH}$ = 8.7 Hz), 8.04 (1H, d, $H^{5'}$, $^3J_{HH}$ = 8.7 Hz), 8.20 (1H, d, $H^{4'}$, $^3J_{HH}$ = 7.9 Hz), 8.64 (1H, d, $H^{6'}$, $^3J_{HH}$ = 4.9 Hz), 8.72 (1H, s, $H^{2'}$). ^{13}C (100.6 MHz, CD_3OD–CCl_4 1:1, δ, ppm, in parentheses is a view of signal in $^{13}C\{^1H\}$ NMR): 15.0 (q (s) C^8, $^1J_{CH}$ = 127.4 Hz), 20.2 (q (s) C^9, $^1J_{CH}$ = 120.0 Hz), 21.4 (q (s) C^{10}, $^1J_{CH}$ = 124.0 Hz), 22.9 (t (s) C^3, $^1J_{CH}$ = 121.4 Hz), 25.4 (d (s) C^7, $^1J_{CH}$ = 128.8 Hz), 31.6 (d (s) C^5, $^1J_{CH}$ = 126.2 Hz), 34.4 (t (s) C^4, $^1J_{CH}$ = 128.7 Hz), 44.7 (t (s) C^6H_2, $^1J_{CH}$ = 127.7 Hz), 49.9 (d (s) C^2, $^1J_{CH}$ = 141.6 Hz), 54.4 (q (s) $C^{7''}$, $^1J_{CH}$ = 144.2 Hz), 60.5 (t (s) $C^{7'}$, $^1J_{CH}$ = 143.4 Hz), 70.7 (d (s) C^1, $^1J_{CH}$ = 139.0 Hz), 112.0 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 159.9 Hz), 112.1 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 159.9 Hz), 112.2 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 159.9 Hz), 112.3 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 159.9 Hz), 125.3 (d (s) $C^{5'}$, $^1J_{CH}$ = 169.5 Hz), 125.4 (d (s) $C^{5'}$, $^1J_{CH}$ = 169.5 Hz), 131.6 (s, $C^{2''}$, $C^{6''}$, $^1J_{CH}$ = 162.9 Hz), 131.7 (s, $C^{2''}$, $C^{6''}$, $^1J_{CH}$ = 162.9 Hz), 139.7 (d (s) $C^{4'}H$, $^1J_{CH}$ = 165.1 Hz), 140.3 (s (s) $C^{3'}$), 143.6 (d (s) $C^{6'}H$, $^1J_{CH}$ = 183.0 Hz), 143.8 (d (s) $C^{2'}H$, $^1J_{CH}$ = 188.2 Hz), 161.1 (s (s) $C^{4''}$).

Salt (4b): FTIR: ν_{max} = 3326 st br (O–H), 3063 w (=C–H, Ar), 2952 w, 2877 m, 2838 m $\nu_{as,s}$ (CH_3), $\nu_{as,s}$ (CH_2), 2694 w (NH^+), 1633 m (C=N, Ar), 1596 w, 1570 m, 1498 m (C=C, Ar), 1455 m $\delta_{as}(CH_3)$, 1389 m, 1373 m $\delta_{sgem.}$ ($(CH_3)_2C$), 1031 st ((P)O–C), 971 m, 914 m δ(OC–C, C–C), 665 m (P=S), 554 m (P–S) cm^{-1}. ^1H NMR (600 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 0.66 (6H, s, $H^{9,10}$), 0.68 [6H, s, $H^{9,10}$), 0.71 (6H, s, $H^{9,10}$), 0.73 (6H, s, $H^{9,10}$), 0.83 (3H, s, H^8), 0.85 (3H, s, H^8), 0.87 (3H, s, H^8), 0.88 (3H, s, H^8), 1.30–1.45 (2H, m, H^5), 1.47–1.68 (2H, m, H^3; 2H, H^6), 1.74–1.86 (1H, m, H^4), 3.26–3.43 (1H, m, H^2), 3.66 (3H, s, $H^{7''}$), 3.69 (3H, s, $H^{7''}$), 4.59 (2H, s, $H^{7'}$), 6.63–6.73 (2H, m, $H^{3'',5''}$), 6.75–6.84 (2H, m, $H^{3'',5''}$), 7.50–7.79 (1H, m, $H^{4'}$; 1H, $H^{5'}$), 7.83 (2H, dd, $H^{2'',6''}$, $^3J_{HH}$ = 8.5 Hz, $^3J_{PH}$ = 13.4 Hz), 8.07 (1H, d, $H^{6'}$, $^3J_{HH}$ = 7.7 Hz), 8.50 (1H, s, $H^{2'}$), 8.56 (1H, s, $H^{2'}$). $^{13}C\{^1H\}$ (100.6 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 11.1 (s , C^8), 12.1 (s, C^8), 20.1 (s, $C^{9,10}$), 27.1 (s, C^5), 27.2 (s, C^5), 33.9 (s, C^6), 34.0 (s, C^6), 40.0 (s, C^3), 40.6 (s, C^3), 45.0 (s, C^4), 45.4 (s, C^4), 54.6 (s, C^7), 54.7 (s, C^1), 57.1 (s, $C^{7''}$), 60.4 (s, $C^{7'}$), 81.7 (d, C^2), 112.2 (s, $C^{3''}$, $C^{5''}$), 112.4 (s, $C^{3''}$, $C^{5''}$), 112.5 (s, $C^{3''}$, $C^{5''}$), 113.3–137.7 (m, $C^{1''}$), 125.5 (s, $C^{5'}$), 131.6 (s, $C^{2''}$, $C^{6''}$), 131.7 (s, $C^{2''}$, $C^{6''}$), 131.8 (s, $C^{2''}$, $C^{6''}$), 131.9 (s, $C^{2''}$, $C^{6''}$), 132.4 (s, $C^{3'}$), 132.5 (s, $C^{3'}$), 140.6 (s, $C^{4'}$), 140.9 (s, $C^{4'}$), 142.5 (s, $C^{2'}$), 143.0 (s, $C^{2'}$), 163.0 (s (s) $C^{4''}$).

Salt (4c): FTIR: ν_{max} = 3329 st br (O–H), 3056 w, 3001 w (=C–H, Ar), 2959 st, 2928 m, 2872 m $\nu_{as,s}$ (CH_3)as,, $\nu_{as,s}(CH_2)$, 2722 w (NH^+), 1716 m (C=N, Ar), 1615 m, 1594 st, 1571 m, 1555 m (C=C, Ar), 1421 m $\delta_{as}(CH_3$), 1385 m, 1363 m $\delta_{sgem.}((CH_3)_2C)$, 1030 st ((P)O–C), 929 m δ(OC–C, C–C), 666 m (P=S), 558 m (P–S) cm^{-1}. ^1H NMR (400 MHz, CD_3OD–CCl_4 1:1, δ, ppm): 1.21 (6H, d, $H^{9,10}$, $^3J_{HH}$ = 6. Hz), 2.14 (3H, s, H^8), 2.77 (1H, sept., H^4, $^3J_{HH}$ = 6.6 Hz), 3.81 (3H, s, $H^{7''}$), 4.78 (2H, s, $H^{7'}$), 6.572 (1H, d, H^3; 1H, H^4, $^3J_{HH}$ = 7.1 Hz), 6.575 (1H, d, H^3; 1H, H^4, $^3J_{HH}$ = 7.9 Hz), 6.61–6.63 (1H, m, OH), 6.858 (2H, d, $H^{3'',5''}$, $^3J_{HH}$ = 8.8 Hz), 6.863 (2H, d, $H^{3'',5''}$, $^3J_{HH}$ = 8.8 Hz), 6.91 (1H, s, H^1), 6.93 (1H, s, H^1), 7.842 (1H, d, $H^{5'}$, $^3J_{HH}$ = 8.2 Hz), 7.847 (1H, d, $H^{5'}$, $^3J_{HH}$ = 8.2 Hz), 8.00 (2H, dd, $H^{2'',6''}$, $^3J_{HH}$ = 8.8 Hz, $^3J_{PH}$ = 13.7 Hz), 8.34 (1H, d, $H^{4'}$, $^3J_{HH}$ = 4.9 Hz), 8.68 (1H, d, $H^{6'}$, $^3J_{HH}$ = 4.9 Hz), 8.75 (1H, s, $H^{2'}$). ^{13}C (100.6 MHz, CD_3OD–CCl_4 1:1, δ, ppm, in parentheses is a view of signal in $^{13}C\{^1H\}$ NMR): 14.5 (q (s) C^8, $^1J_{CH}$ = 121.1 Hz), 23.2 (q (s) C^9, C^{10}, $^1J_{CH}$ = 103.4 Hz), 33.6 (d (s) C^7, $^1J_{CH}$ = 130.6 Hz), 60.3 (q (s) $C^{7''}$, $^1J_{CH}$ = 143.1 Hz), 63.0 (t (s) $C^{7'}$, $^1J_{CH}$ = 145.3 Hz), 112.3 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 154.8 Hz), 112.4–113.4 (m (m) $C^{1''}$), 117.1 (d (s) C^1, $^1J_{CH}$ = 155.5 Hz), 121.3 (d (s) C^3, $^1J_{CH}$ = 155.0), 125.7 (d (s) $C^{5'}$, $^1J_{CH}$ = 175.3 Hz), 132.2 (d (s) C^4, $^1J_{CH}$ = 154.8 Hz), 112.3 (d (s) $C^{3''}$, $C^{5''}$, $^1J_{CH}$ = 154.8 Hz), 131.6–133.0 (m (m) C^5), 141.1 (d (s) $C^{2''}$, $C^{6''}$, $^1J_{CH}$ = 146.0 Hz), 142.0 (d (s) $C^{6''}$, $^2J_{CP}$ = 39.6 Hz), 147.6 (d (s) $C^{2'}$, $^1J_{CH}$ = 146.0 Hz), 154.8 (d (s) $C^{2'}$, $^1J_{CH}$ = 178.0 Hz), 161.8 (s (s) $C^{4''}$).

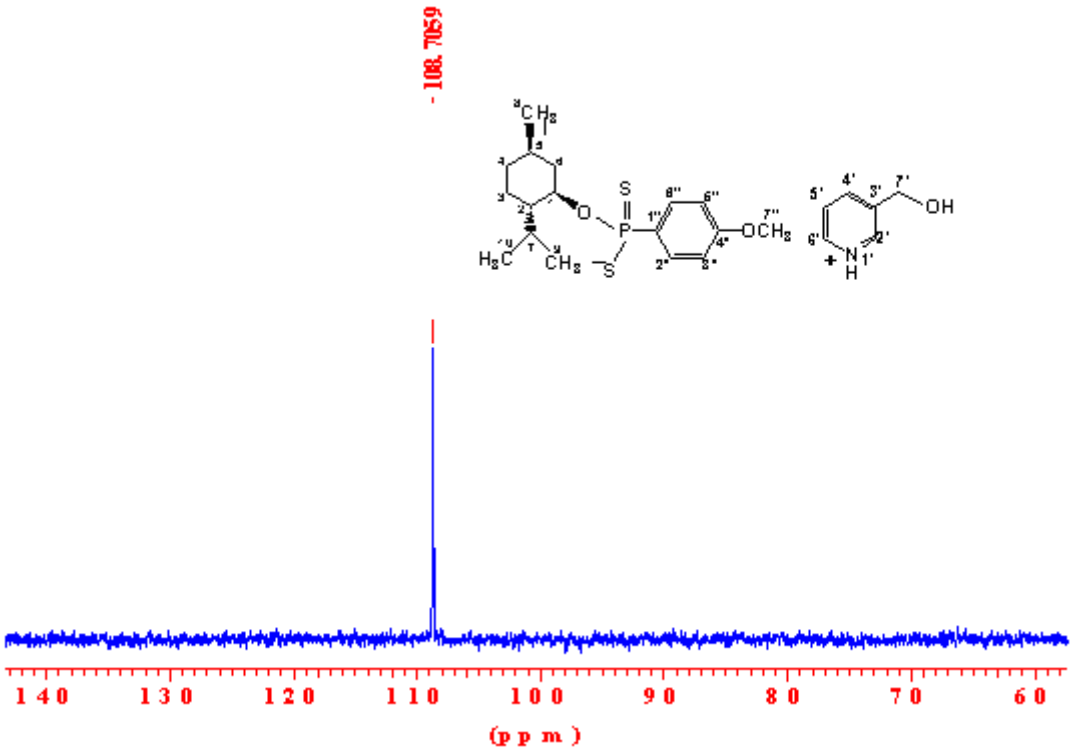

Figure $^{31}P\{^{1}H\}$ spectrum (161.98 MHz) of 3-hydroxypyridinium O-(1*R*,2*S*,5*R*)-(−)-2-isopropyl-5-methylcyclohex-yl 4-metoxyphenyldithiophosphonate (**3a**) in CD_3OD

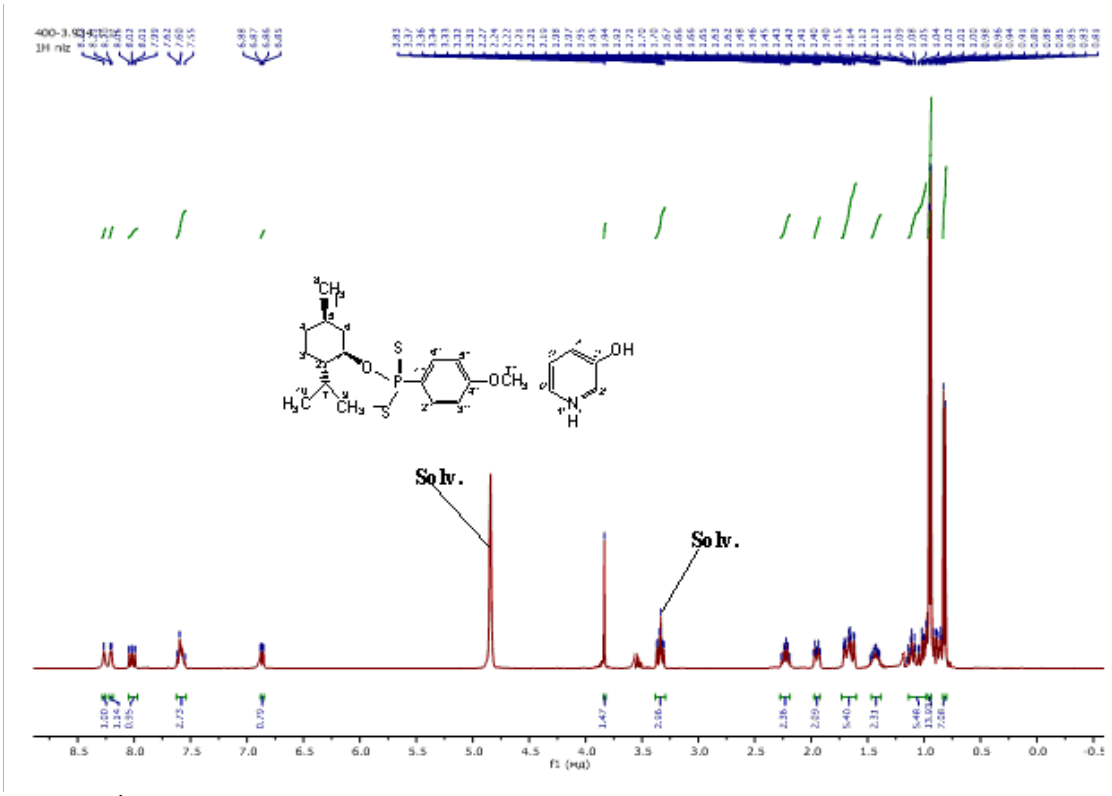

Figure S2: ^{1}H NMR spectrum (400 MHz) of 3-hydroxypyridinium O-(1*R*,2*S*,5*R*)-(−)-2-isopropyl-5-methylcyclohex-yl 4-metoxyphenyldithiophosphonate (**3a**) in CD_3OD–CCl_4 (1:1).

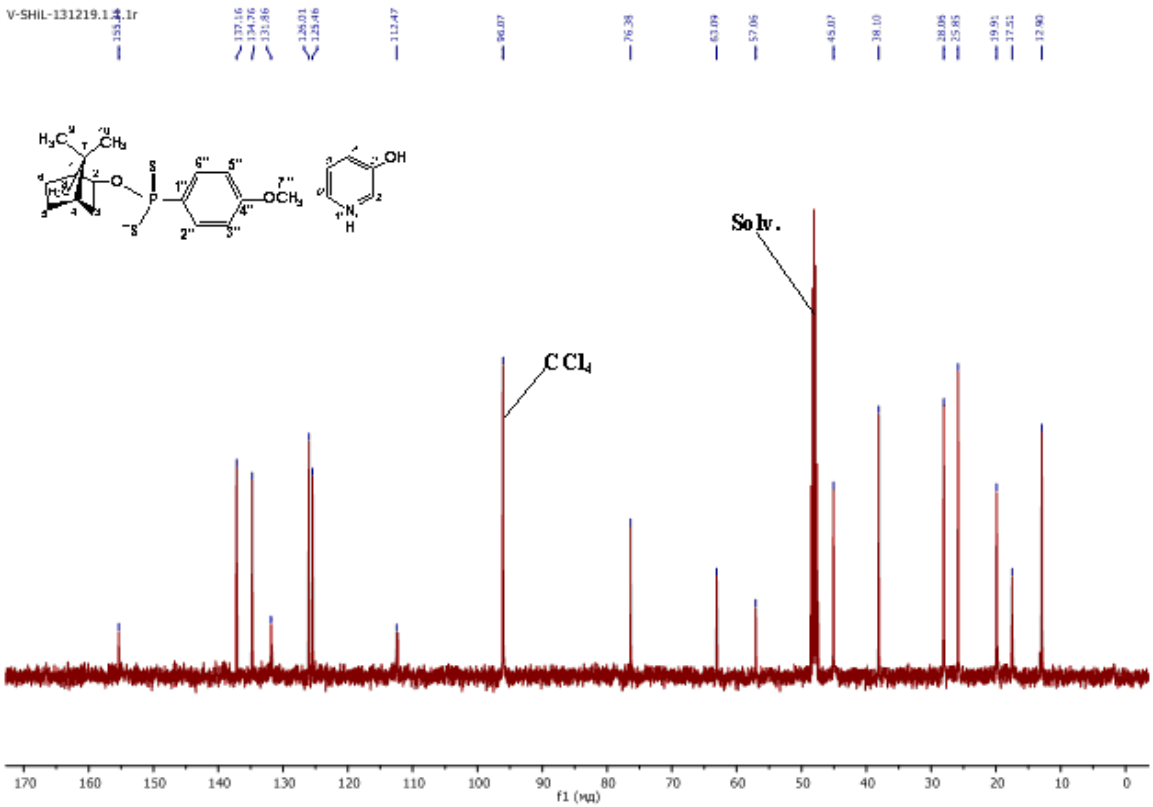

Figure S3: $^{13}C\{^{1}H\}$ spectrum (100.6 MHz) of 3-hydroxypyridinium O-*endo*-(1*S*)-(−)-trimethylbicyclo-[2.2.1]hept-2-yl 4-metoxyphenyldithiophosphonate (**3b**) in CD_3OD–CCl_4 (1:1).

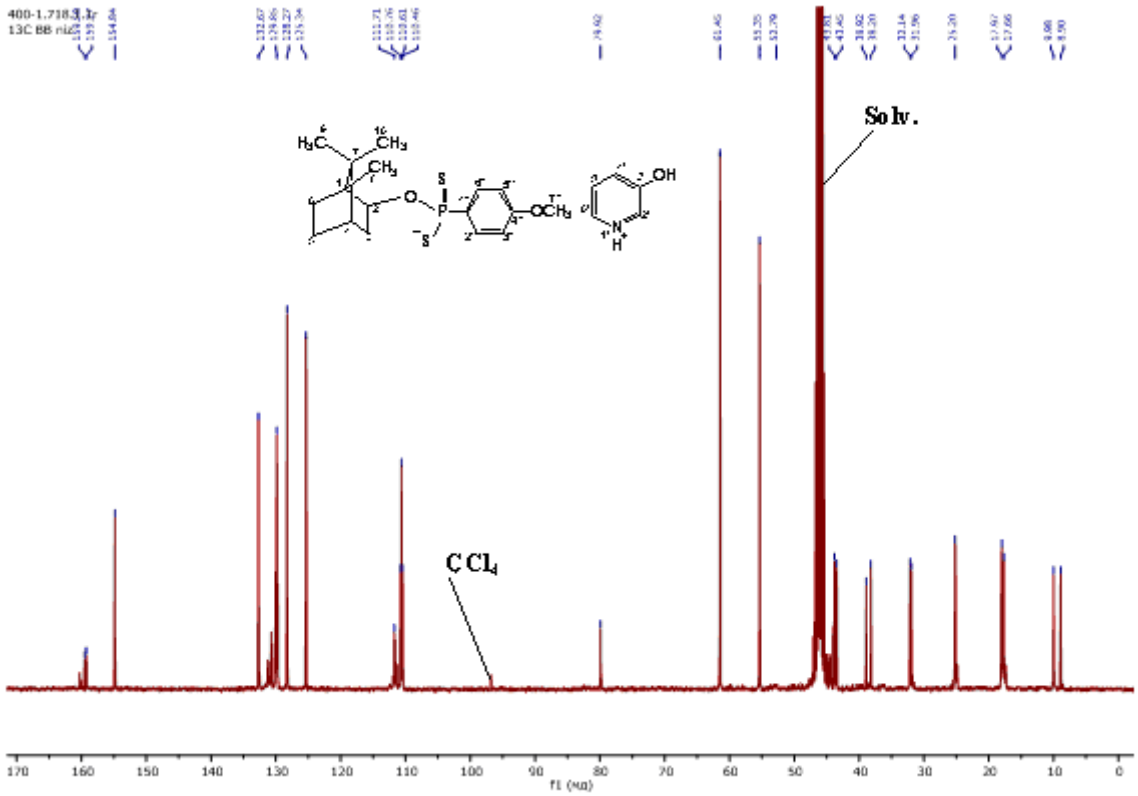

Figure S4: $^{13}C\{^{1}H\}$ spectrum (100.6 MHz) of 3-hydroxypyridinium O-(*R*,*S*)-(±)-trimethylbicyclo-[2.2.1]hept-2-yl 4-metoxyphenyldithiophosphonate (**3c**) in CD_3OD–CCl_4 (1:1).

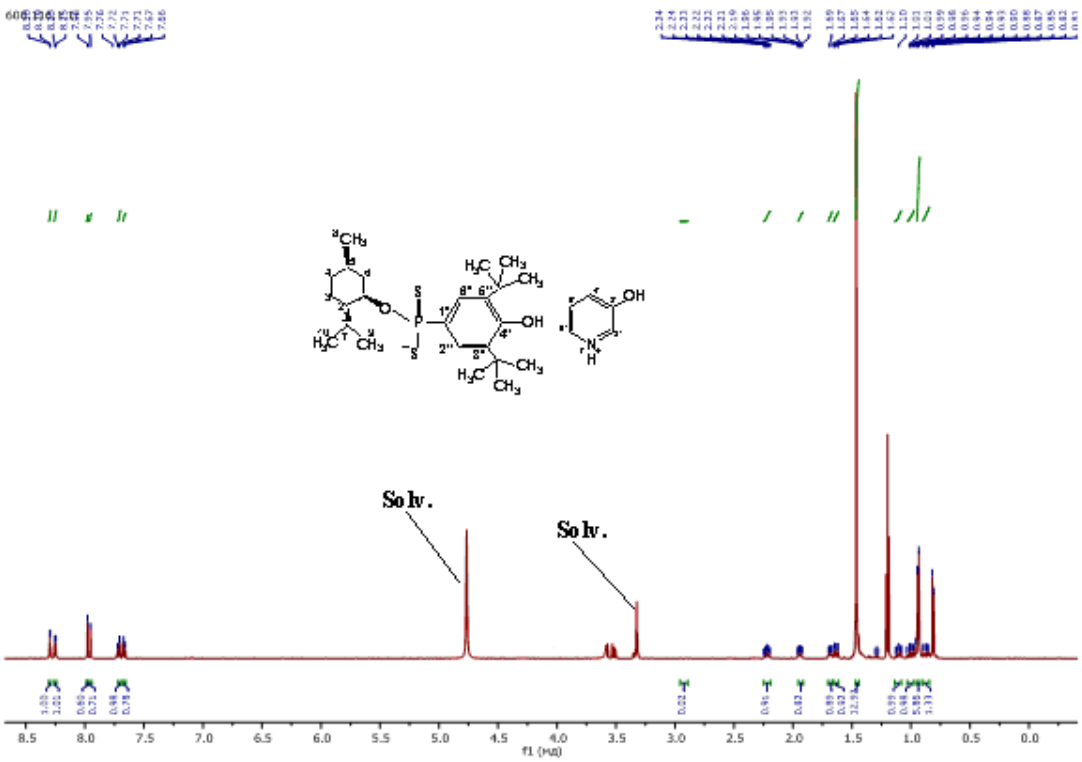

Figure S5: ^{1}H NMR spectrum (400 MHz) of 3-hydroxypyridinium O-(1*R*,2*S*,5*R*)-(−)-2-isopropyl-5-methylcyclohex-yl 3,5-di-*tert*-butylphenyldithiophosphonate (**3d**) in CD_3OD–CCl_4 (1:1).

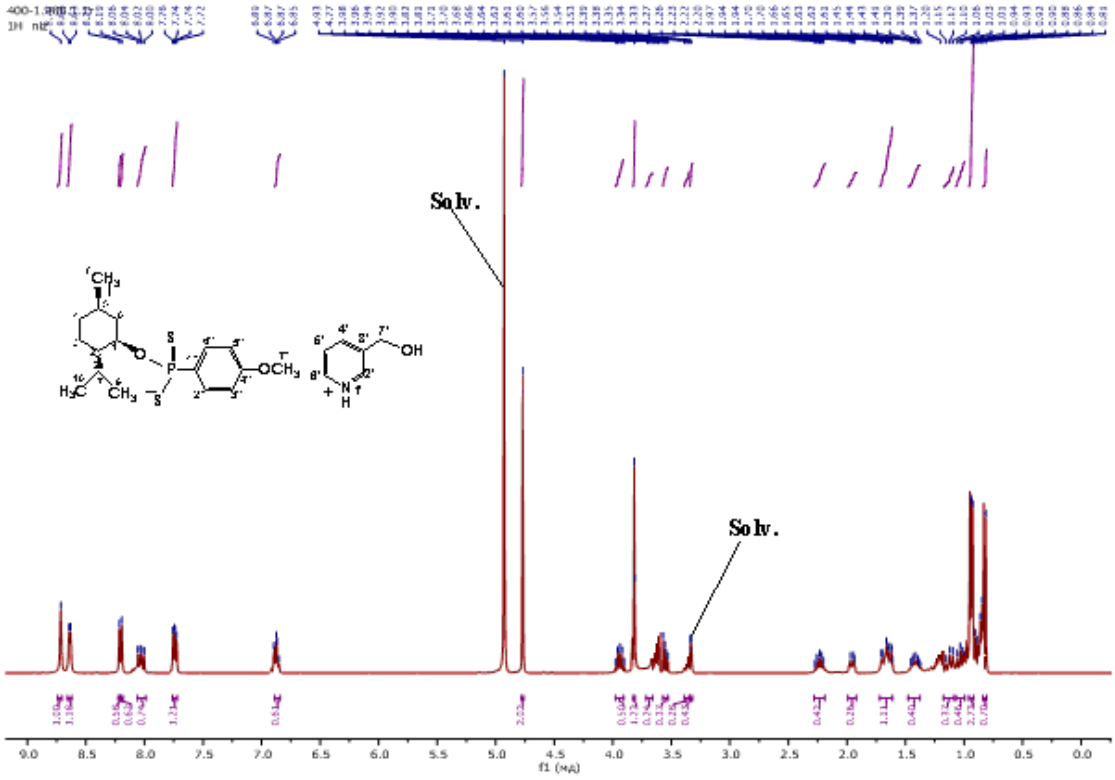

Figure S6: ^{1}H NMR spectrum (400 MHz) of 3-(hydroxymethyl)pyridinium O-(1*R*,2*S*,5*R*)-(−)-2-isopropyl-5-methylcyclohex-yl 4-metoxyphenyldithiophosphonate (**4a**) in CD_3OD–CCl_4 (1:1).

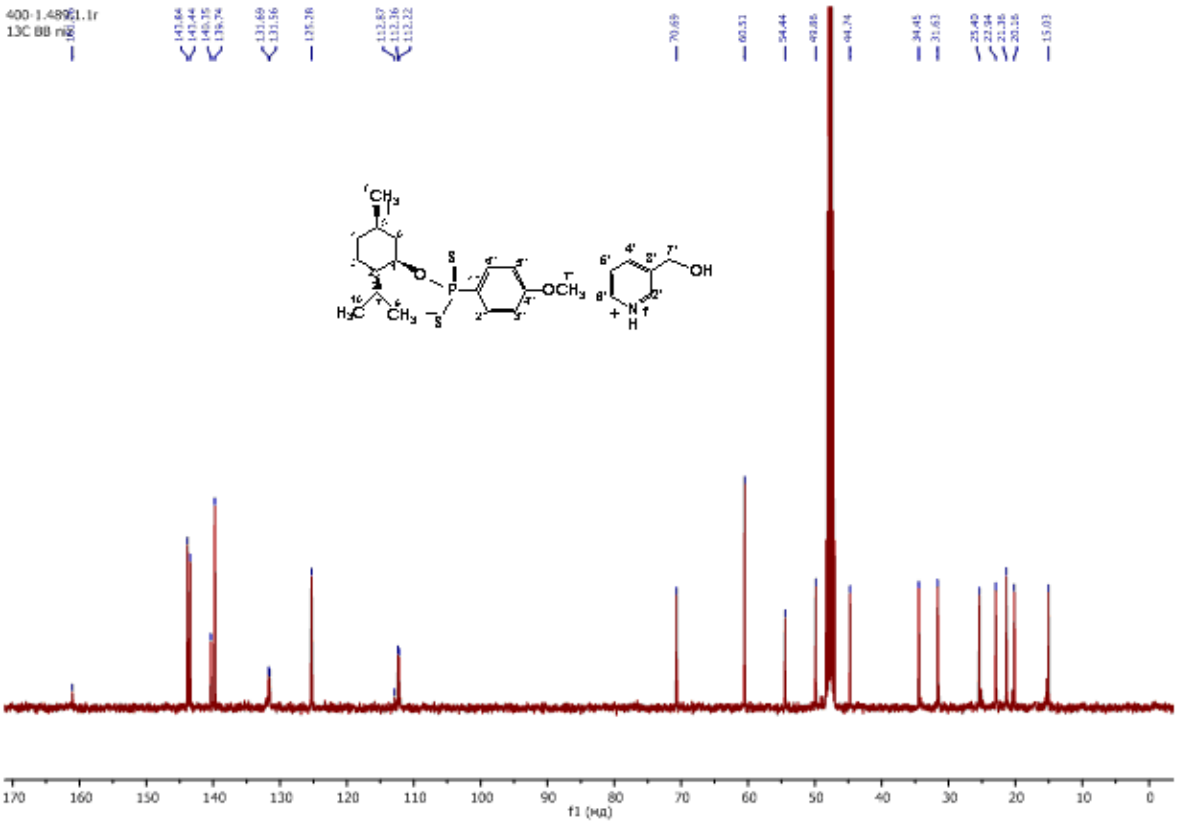

Figure S7: $^{13}C\{^{1}H\}$ spectrum (100.6 MHz) of 3-(hydroxymethyl)pyridinium O-(1*R*,2*S*,5*R*)-(−)-2-isopropyl-5-methylcyclohex-yl 4-metoxyphenyldithiophosphonate (**4a**) in CD_3OD–CCl_4 (1:1).

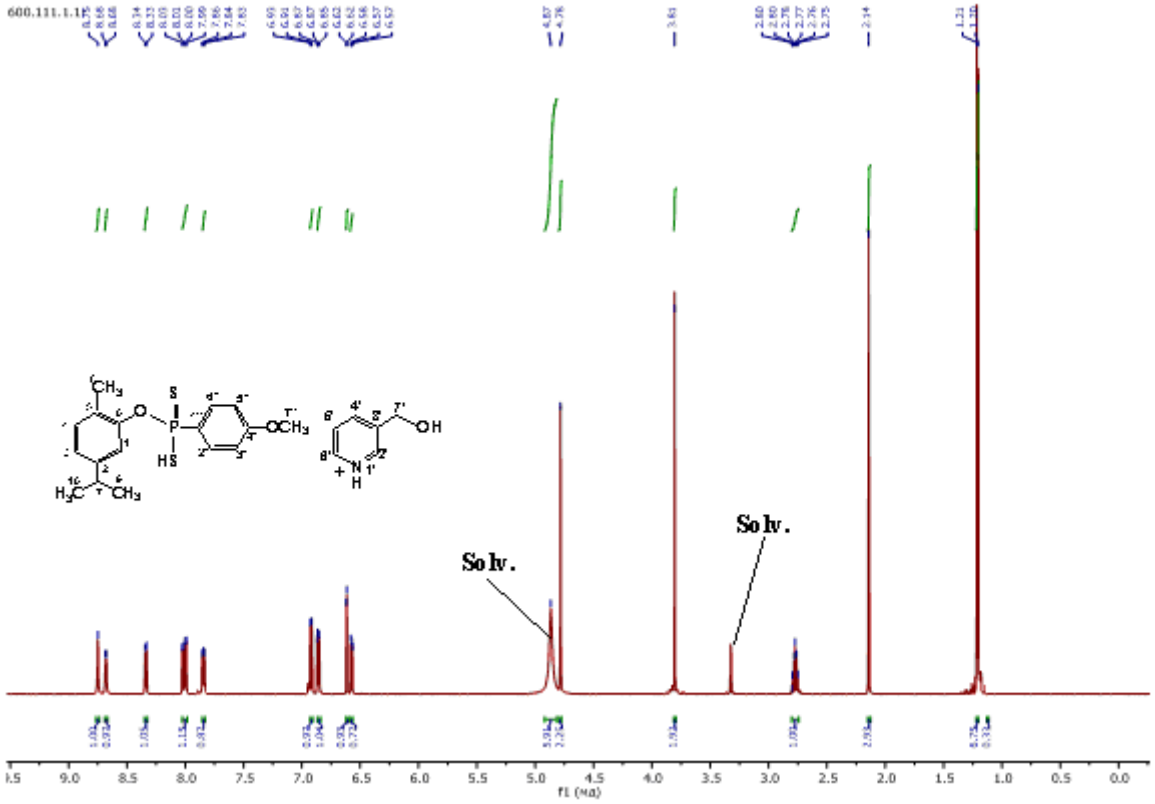

Figure S8: ^{1}H NMR spectrum (400 MHz) of 3-hydroxypyridinium O-(*R*,*S*)-(±)-trimethylbicyclo-[2.2.1]hept-2-yl 4-metoxyphenyldithiophosphonate (**3c**) in CD_3OD–CCl_4 (1:1).

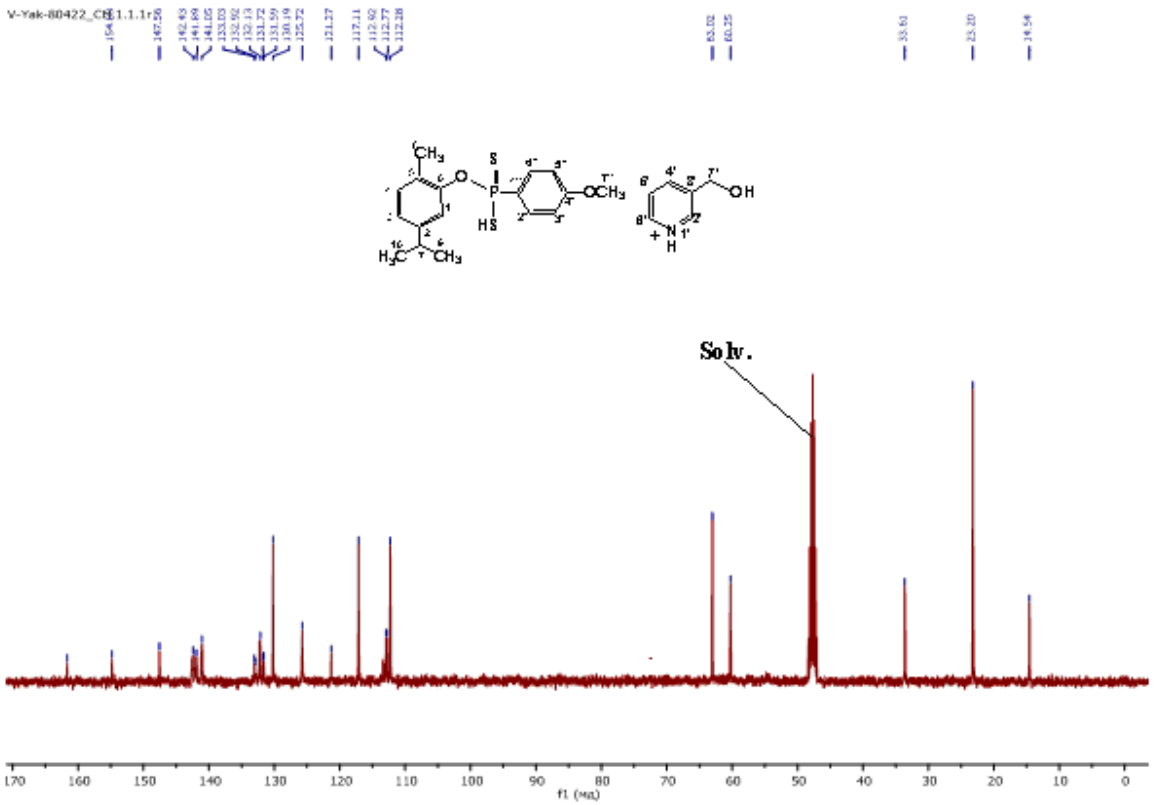

Figure S9: $^{13}C\{^{1}H\}$ spectrum (100.6 MHz) of 3-hydroxypyridinium O-(*R*,*S*)-(±)-trimethylbicyclo-[2.2.1]hept-2-yl 4-metoxyphenyldithiophosphonate (**3c**) in CD_3OD–CCl_4 (1:1).