

Supporting Information

"A New One-pot Synthesis of Alkynyl Phosphonates"

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[(2R, 3S, 5R)-3-(*tert*-Butyl-diphenyl-silanyloxy)-5-(5-methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)-tetrahydro-furan-2ylethynyl]-phosphonic acid dimethyl ester (3). (Found (HRMS FAB) $M^+ + H$, 583.2047, $C_{29}H_{36}O_7N_2PSi$ requires 583.2029); ν_{max}/cm^{-1} 3391, 2955, 2933, 2205, 1694, 1463, 1394, 1365, 1309, 1294, 1278, 1105, 1053, 980, 955, 908, 843; δ_H (400 MHz, $CDCl_3$) 7.64 (4H, m), 7.44 (6H, m), 6.62 (1H, dd, J 8.4, 5.6), 4.64 (1H, d, J 3.2), 4.57 (1H, d, J 4.2), 3.74 (3H, d, J 12.2), 3.73 (3H, d, J 12.2), 2.46 (1H, m), 2.05 (1H, m), 1.92 (3H, s), 1.09 (9H, s); δ_C (67.5 MHz, $CDCl_3$) 163.6, 150.4, 135.6, 134.8, 132.3, 132.1, 130.3, 128.1, 111.8, 96.3, 95.6, 86.8, 78.1, 76.3, 53.4, 40.1, 26.7, 18.9; δ_P (161.98 MHz, $CDCl_3$) -3.83; m/z (FAB) 583 ($M^+ + H$, 33), 525 (21), 307 (20), 201 (45), 176 (32), 165 (27), 155 (28), 154 (94), 147 (22), 138 (32), 137 (68), 136 (100), 135 (30), 121 (23), 107 (39), 105 (27), 95 (23), 91 (47), 90 (34), 89 (36), 81 (33), 79 (25), 78 (20), 77 (47), 73 (66), 69 (39), 67 (25), 57 (46), 55 (48).

Cyclohexylethynyl-phosphonic acid dimethyl ester (5). (Found: C, 55.8; H 7.8. $C_{10}H_{17}O_3P$ requires C, 55.6; H, 7.9); (Found (HRMS FAB) $M^+ + H$, 217.1012, $C_{10}H_{18}O_3P$ requires 217.0994); ν_{max}/cm^{-1} 2937, 2857, 2201, 1450, 1272, 1048, 842; δ_H (400 MHz, $CDCl_3$) 3.78 (6H, d, J 12.3), 2.54 (1H, m), 1.83 (2H, m), 1.71 (2H, m),

1.52 (3H, m), 1.32 (3H, m); δ_{C} (67.5 MHz, CDCl_3) 108.2, 107.5, 53.5, 31.6, 29.7, 25.9, 24.8; δ_{P} (161.98 MHz, CDCl_3) -1.33 ; m/z (FAB) 218 ($\text{M}^+\text{+H}$, 11), 217 (100), 154 (8), 136 (10).

Acetic acid 4-(dimethoxy-phosphorylethynyl)-phenyl ester (7). (Found (HRMS ES) $\text{M}^+\text{+H}$, 269.0563, $\text{C}_{12}\text{H}_{14}\text{O}_5\text{P}$ requires 269.0579); $\nu_{\text{max}}/\text{cm}^{-1}$ 2955, 2854, 2190, 1766, 1600, 1504, 1371, 1275, 1165, 1046, 911, 871, 843; δ_{H} (400 MHz, CDCl_3) 7.59 (2H, d, J 8.6), 7.13 (2H, d, J 8.6), 3.85 (6H, d, J 12.3), 2.31 (3H, s); δ_{C} (67.5 MHz, CDCl_3) 168.7, 152.4, 134.0, 122.1, 116.7, 99.4, 98.6, 53.4, 21.0; δ_{P} (161.98 MHz, CDCl_3) -1.67 ; m/z (ES) 269 ($\text{M}^+\text{+H}$, 100), 254 (2).

(4-Methoxy-phenylethynyl)-phosphonic acid dimethyl ester (9). (Found (HRMS EI) M^+ , 240.0558, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}$ requires 240.0552); $\nu_{\text{max}}/\text{cm}^{-1}$ 2954, 2184, 1605, 1459, 1298, 1276, 1050, 872; δ_{H} (400 MHz, CDCl_3) 7.48 (2H, d, J 8.8), 6.85 (2H, d, J 8.8), 3.81 (6H, d, J 12.3), 3.80 (3H, s); δ_{C} (67.5 MHz, CDCl_3) 161.5, 134.9, 114.2, 110.9, 101.0, 100.3, 55.3, 53.2; δ_{P} (161.98 MHz, CDCl_3) -0.93 ; m/z (EI) 240 (M^+ , 9), 181 (13), 169 (9), 132 (59), 131 (52), 119 (23), 117 (13), 100 (11), 93 (14), 89 (21), 69 (100), 63 (10), 62 (10), 47 (13).

(4-Nitro-phenylethynyl)-phosphonic acid dimethyl ester (11). (Found: C, 47.2; H, 3.9; N, 5.4. $\text{C}_{10}\text{H}_{10}\text{NO}_5\text{P}$ requires C, 47.1; H 4.0; N 5.5); (Found (HRMS EI) $\text{M}^+\text{+H}$, 256.0385, $\text{C}_{10}\text{H}_{11}\text{O}_5\text{NP}$ requires 256.0375); $\nu_{\text{max}}/\text{cm}^{-1}$ 2955, 2195, 1596, 1528, 1488, 1458, 1348, 1277, 1047, 871, 857; δ_{H} (400 MHz, CDCl_3) 8.28 (2H, d, J 8.7), 7.76 (2H, d, J 8.7), 3.90 (6H, d, J 12.3); δ_{C} (100 MHz, CDCl_3) 171.6, 148.8, 133.7, 126.0, 53.8;

δ_{P} (161.98 MHz, CDCl_3) -2.95 ; m/z (EI) 256 ($\text{M}^+ + \text{H}$, 36), 154 (100), 138 (35), 137 (64), 136 (72), 107 (25), 89 (21).

Phenylethynyl-phosphonic acid dimethyl ester (13). (Found (HRMS EI) M^+ , 210.0452, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{P}$ requires 210.0446); $\nu_{\text{max}}/\text{cm}^{-1}$ 2995, 2955, 2854, 2189, 1490, 1459, 1273, 1047, 865, 842, 645; δ_{H} (400 MHz, CDCl_3) 7.57 (2H, m), 7.45 (1H, m), 7.37 (2H, m), 3.85 (6H, d, J 12.3); δ_{C} (67.5 MHz, CDCl_3) 132.9, 131.1, 128.8, 119.4, 100.5, 99.7, 53.6; δ_{P} (161.98 MHz, CDCl_3) -1.57 ; m/z (EI) 210 (M^+ , 13), 115 (47), 102 (100), 89 (27), 86 (20), 84 (31), 63 (19), 49 (92), 47 (25).

Furan-2-ylethynyl-phosphonic acid dimethyl ester (15). (Found (HRMS EI) M^+ , 200.0240, $\text{C}_8\text{H}_9\text{O}_4\text{P}$ requires 200.0239); $\nu_{\text{max}}/\text{cm}^{-1}$ 2955, 2854, 2192, 2177, 1613, 1458, 1277, 1048, 964, 942, 886, 842; δ_{H} (400 MHz, CDCl_3) 7.48 (1H, br d, J 1.8), 6.89 (1H, br d, J 3.5), 6.45 (1H, dd, J 3.5, 1.8), 3.83 (6H, d, J 12.3); δ_{C} (67.5 MHz, CDCl_3) 145.9, 134.2, 120.4, 111.3, 89.7, 88.9, 53.5; δ_{P} (161.98 MHz, CDCl_3) -2.21 ; m/z (EI) 200 (M^+ , 14), 92 (100), 77 (12), 64 (16), 63 (37), 62 (11), 51 (19), 47 (28).

Non-1-ynyl-phosphonic acid dimethyl ester (17). (Found (HRMS ES) $\text{M}^+ + \text{H}$, 233.1320, $\text{C}_{11}\text{H}_{22}\text{O}_3\text{P}$ requires 233.1307); $\nu_{\text{max}}/\text{cm}^{-1}$ 2954, 2930, 2856, 2207, 1459, 1273, 1048, 841; δ_{H} (400 MHz, CDCl_3) 3.76 (6H, d, J 12.2), 2.34 (2H, m), 1.58 (2H, m), 1.38 (2H, m), 1.26 (4H, m), 0.88 (3H, m); δ_{C} (67.5 MHz, CDCl_3) 105.9, 105.2, 54.4, 32.9, 30.0, 29.9, 28.7, 23.8, 20.5, 15.3; δ_{P} (161.98 MHz, CDCl_3) -1.70 .

((Z)-1-Bromo-2-cyclohexyl-vinyl)-phosphonic acid dimethyl ester (18). (Found (HRMS FAB) $M^+ + H$, 297.0264, $C_{10}H_{19}O_3PBr$ requires 297.0255); $\nu_{\max}/\text{cm}^{-1}$ 2932, 2854, 1614, 1450, 1278, 1042, 952, 881, 838; δ_H (400 MHz, $CDCl_3$) 6.99 (1H, dd, J 14.4, 9.0), 3.77 (6H, d, J 11.2), 2.61 (1H, m), 1.74 (5H, m), 1.35-1.20 (5H, m); δ_C (67.5 MHz, $CDCl_3$) 155.9, 108.5, 53.3, 41.2, 30.7, 25.6, 25.2; δ_P (161.98 MHz, $CDCl_3$) 4.00; m/z (FAB) 297 ($M^+ + H$, 100), 154 (52), 138 (21), 137 (49), 136 (40).

[(2R, 3S, 5R)-3-(*tert*-Butyl-diphenyl-silanyloxy)-5-(5-methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)-tetrahydro-furan-2ylethynyl]-phosphonic acid [(2R, 3S, 5R)-2-(*tert*-butyl-dimethyl-silanyloxy methyl)-5-(5-methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)-tetrahydro-furan-3-yl]-ester methyl ester (20).

Less polar diastereomer: (Found (HRMS ES) $M^+ + H$, 907.3546, $C_{44}H_{60}O_{11}N_4PSi_2$ requires 907.3535); $\nu_{\max}/\text{cm}^{-1}$ 3392, 2954, 2932, 2896, 2859, 2205, 1693, 1463, 1363, 1293, 1275, 1128, 1104, 1049, 1006, 979, 956, 908, 838, 611; δ_H (400 MHz, $CDCl_3$) 8.46 (1H, br s), 8.28 (1H, br s), 7.64 (4H, m), 7.46 (6H, m), 6.56 (1H, dd, J 8.5, 5.8), 6.32 (1H, dd, J 9.2, 5.1), 5.05 (1H, app t, J 6.9), 4.68 (1H, d, J 3.4), 4.61 (1H, d, J 4.6), 4.22 (1H, d, J 1.2), 3.88 (1H, dd, J 11.5, 2.1), 3.83 (1H, dd, J 11.5, 2.1), 3.74 (3H, d, J 12.5), 2.48 (2H, m), 2.16-2.01 (2H, m), 1.93 (6H, s), 1.10 (9H, s), 0.92 (9H, s), 0.12 (3H, s), 0.11 (3H, s); δ_C (100 MHz, $CDCl_3$) 163.4, 150.2, 135.8, 135.3, 135.1, 132.5, 132.3, 130.8, 128.5, 111.9, 111.4, 97.0, 96.5, 87.2, 86.0, 84.6, 79.4, 78.2, 76.4, 63.2, 53.7, 40.2, 39.2, 27.0, 26.0, 19.1, 18.4, 12.6, -5.3; δ_P (161.98 MHz, $CDCl_3$) -5.83; m/z (ES) 907 ($M^+ + H$, 43), 569 (8), 340 (8), 339 (100).

More polar diastereomer: (Found (HRMS ES) $M^+ + H$, 907.3521, $C_{44}H_{60}O_{11}N_4PSi_2$ requires 907.3535); $\nu_{\max}/\text{cm}^{-1}$ 3390, 2954, 2932, 2204, 1692, 1463, 1363, 1274, 1105,

1063, 979; δ_{H} (400 MHz, CDCl_3) 8.57 (1H, br s), 7.65 (4H, m), 7.45 (6H, m), 6.58 (1H, dd, J 8.6, 5.7), 6.36 (1H, dd, J 9.2, 5.2), 5.06 (1H, app t, J 7.1), 4.66 (1H, d, J 3.3), 4.60 (1H, d, J 4.5), 4.23 (1H, d, 1.3), 3.86 (1H, dd, J 11.5, 2.1), 3.80 (1H, dd, J 11.5, 2.1), 3.77 (3H, d, J 12.5), 2.48 (2H, m), 2.16-2.01 (2H, m), 1.93 (6H, s), 1.10 (9H, s), 0.91 (9H, s), 0.12 (3H, s), 0.11 (3H, s); δ_{C} (100 MHz, CDCl_3) 163.4, 150.3, 135.7, 132.4, 132.2, 130.5, 128.2, 112.0, 111.4, 96.8, 96.3, 87.0, 85.7, 84.7, 78.6, 78.1, 76.3, 63.2, 53.8, 40.1, 39.4, 26.8, 26.0, 19.1, 18.4, 12.6, -5.3; δ_{P} (161.98 MHz, CDCl_3) -5.75; m/z (ES) 907 ($\text{M}^+ + \text{H}$, 33), 709 (10), 576 (20), 339 (38).