Supporting Information (1/3) for:

Synthesis and reactivity of imide derived bis-vinylphosphates.

Reactivity of 2,6-disubstituted-1,4-dihydropyridines

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Experimental details

THF and benzene were distilled from sodium/benzophenone ketyl immediately prior use. Dichloromethane was distilled over CaH_2 and methanol from magnesium turnings. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F_{254}) plates. Compounds were visualized by UV irradiation and/or spraying with a solution of potassium permanganate, followed by charring at 150 °C. Column chromatography was performed on silica gel 60 (230-400 mesh, 0.040-0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. The infrared spectra of compounds were recorded on an Infrared Fourier Transform spectrophotometer using NaCl plates or KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 250 MHz (^{13}C, 62.9 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) as internal standard. Ionspray or electronic impact methodology were used to record mass spectra. Nomenclature of the obtained compounds follows the rules of IUPAC and was checked with AutoNom.[i] Petroleum ether (P.E.) had a boiling point range 40–60 °C.

2,6-bis{(phenyloxy)-[bis-phosphoryl]oxy}-1-(*tert*-butoxycarbonyl)-1,4-dihydropyridine (1). To a solution of 1-(*tert*-butoxycarbonyl)-2,6-dioxopiperidine[8] (4.69 mmol, 1.0 g) in THF (9 mL) at –78°C under argon, LDA (12.19 mmol, 2 M in hexane, 6.1 mL) was added dropwise. After stirring for 2h at –78°C, diphenyl chlorophosphate (11,25 mmol, 2.33 mL) was added and the mixture was allowed to warm up to room temperature over 15h. The reaction was quenched by slow addition of H_2O. Ethyl acetate was then added, the organic layer was separated and dried ($MgSO_4$) and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc 6:4) to afford the bis-vinyl phosphate **1** (64% yield) as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.41 (s, 9H); 2.75-2.78 (m, 2H); 5.36-5.40 (m, 2H); 7.14-7.33 (m,

20H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 21.5, 27.9, 83.9, 101.7, 101.8, 120.2, 120.3, 125.6, 129.9, 141.4, 141.5, 150.4, 150.6, 151.3. IR ν_{max} (NaCl film) 3071, 2980, 2934, 1743, 1590, 1493, 1457, 1345. MS (IS) m/z 678.50 $[M+H]^+$.

7,9-bis{(phenyloxy)-[bis-phosphoryl]oxy}-8-(*tert*-butoxycarbonyl)-8-aza-spiro[4.5]deca-6,9-diene (2). The reaction was carried out as described for compound **1** using 8-(*tert*-butoxycarbonyl)-7,9-dioxo-8-aza-spiro[4.5]decane 13[8] as starting material. After final purification, the desired vinyl phosphate **2** was obtained in 70% yield as a brown oil. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.40 (s, 9H); 1.56-1.64 (m, 2H); 5.27 (d, 2H, *J* = 2 Hz) ; 7,14-7,33 (m, 20H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 23.6, 27.6, 27.9, 40.5, 44.1, 83.8, 110.7, 110.8, 120.2, 120.3, 125.6, 129.9, 140.2, 140.3, 150.5, 150.7. IR ν_{max} (NaCl film) 3012, 2959, 2874, 1743, 1591, 1489, 1456, 1301. MS (IS) m/z 732.50 $[M+H]^+$.

(*E,E*)-1-(*tert*-butoxycarbonyl)-2,6-diethenyl-1,4-dihydropyridine (3). The Stille coupling reaction was carried out as described in the general procedure (**A**) by using tributyl(vinyl)tin. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), the desired compound **3** was obtained in 88% yield.

The Suzuki coupling reaction was carried out as described in the general procedure (**B**) by using dibutyl vinylboronate. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), in this case, the desired compound **3** was obtained in 54% yield.

Orange solid. Mp 134-135 °C. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.44 (s, 9H); 2.74 (m, 2H); 5.08 (d, 2H, J_{cis} = 10 Hz); 5.35 (d, 2H, J_{trans} = 17 Hz); 5.70 (t, 2H, *J* = 5 Hz); 6.35 (dd, 2H, J_{cis} = 10 Hz and J_{trans} = 17 Hz). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.6, 28.2, 81.4, 112.8, 119.3, 133.1, 141.8, 152.8. IR ν_{max} (KBr) 2979, 2930, 1715, 1596. MS (IE) m/z 234 $[M+H]^+$. HRMS (IE) m/z $[M-^{\bullet}CHCH_2-C_4H_8]^+$ calcd for $C_8H_8NO_2$: 150.0555; found 150.0552.

(*E*,*E*)-1-(*tert*-butoxycarbonyl)-2,6-dihex-1-en-1-yl-1,4-dihydropyridine (5). The Stille coupling reaction was carried out as described in the general procedure (**A**) by using trans-1-hexen-1-yltrimethyltin. In this case, the reaction was completed in 30 minutes. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), the desired compound **5** was isolated as a yellow oil (54% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.80-0.88 (m, 6H); 1.26-1.41 (m, 17H); 2.02-2.10 (m, 4H); 2.60 (m, 2H); 5.51 (m, 2H); 5.68-5.80 (m, 2H); 5.99 (s, 1H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 14.0, 22.4, 28.2, 31.2, 31.6, 32.3, 32.6, 80.7, 117.6, 126.1, 129.9, 141.9, 152.8. IR ν_{max} (KBr) 2960, 2930, 2872, 2864, 1715, 1160, 1633, 1578. MS (IE) m/z 346.50 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}HCO_2tBu]^{+\bullet}$ calcd for $C_{17}H_{25}N$: 243.1987; found 232.1970.

1-(*tert*-butoxycarbonyl)-2,6-dibenzofuran-2-yl-1,4-dihydropyridine (8). The Suzuki coupling reaction was carried out as described in the general procedure (**B**) by using 2-benzofuranboronic acid. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), the desired compound **8** was isolated as an orange solid (25% yield). Mp 159-160°C ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.22 (s, 9H); 3.03 (t, 2H, *J* = 5 Hz); 6.33 (t, 2H, *J* = 5 Hz); 6.80 (s, 2H); 7.17-7.29 (m, 4H); 7.46-7.49 (m, 2H); 7.55-7.58 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.7, 27.8, 82.1, 102.8, 111.1, 119.3, 121.1, 122.9, 124.3, 128.9, 134.0, 152.5, 153.0, 154.5. IR ν_{max} (KBr) 2977, 2933, 2813, 1719, 1596, 1540, 1478. MS (IE) m/z 414.50 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}^{\bullet}CO_2tBu]^+$ calcd for $C_{21}H_{14}NO_2$: 312.1024; found 312.1005.

1-(*tert*-butoxycarbonyl)-2,6-dithien-2-yl-1,4-dihydropyridine (9). The Suzuki coupling reaction was carried out as described in the general procedure (**B**) by using 2-thienylboronic

acid. The reaction was completed in 3 hours. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), the desired compound **9** was isolated as a white solid (60% yield). Mp 117-118°C ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.19 (s, 9H); 2.88 (t, 2H, *J* = 5 Hz); 5.90 (t, 2H, *J* = 5 Hz); 6.97-7.00 (m, 2H); 7.16-7.20 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.7, 27.7, 81.7, 117.1, 123.1, 123.9, 127.1, 137.3, 142.2, 152.5. IR ν_{max} (KBr) 3024, 2979, 2932, 1712, 1566, 1524, 1461. MS (IE) m/z 346.50 $[M+H]^+$. HRMS (IE) m/z $[M]^{\bullet+}$ calcd for $C_{18}H_{19}NO_2S_2$: 345.0857; found 345.0856.

1-(*tert*-butoxycarbonyl)-2,6-difuran-2-yl-1,4-dihydropyridine (10). The Suzuki coupling reaction was carried out as described in the general procedure (**B**) by using 2-furanboronic acid. The reaction was completed in 3 hours. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1), the desired compound **10** was isolated as an orange oil (61% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.26 (s, 9H); 2.88 (t, 2H, *J* = 5 Hz); 5.98 (t, 2H, *J* = 5 Hz); 6.37-6.41 (m, 4H); 7.36 (s, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.1, 27.7, 81.4, 106.1, 111.1, 116.1, 133.9, 141.1, 151.2, 152.2. IR ν_{max} (NaCl film) 2979, 2933, 2818, 1719, 1613, 1573, 1496, 1163. MS (IE) m/z 213 $[M-{}^{\bullet}CO_2tBu]^+$. HRMS (IE) m/z $[M-HCO_2tBu]^{+\bullet}$ calcd for $C_{13}H_9NO_2$: 211.0633; found 211.0622.

8-(*tert*-butoxycarbonyl)-9-phenyl-7-(thien-2-yl)-8-aza-spiro[4.5]deca-6,9-diene (17b). The Suzuki coupling reaction was carried out as described in the general procedure (**C**) by using 2-thienylboronic acid. The reaction was completed in 3 hours. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 8:2), the desired compound **17b** was isolated as a colorless solid (100% yield). Mp 116-117°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.10 (s, 9H); 1.74-1.78 (m, 8H); 5.71 (s, 1H); 5.79 (s, 1H); 6.98-7.01 (m, 1H); 7.17-7.37 (m, 5H); 7.52-7.55 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.1, 27.7, 40.5,

45.9, 81.3, 122.9, 123.8, 125.5, 126.5, 126.8, 127.0, 127.3, 128.2; 135.3, 138.6, 140.9, 142.7, 152.4. IR ν_{max} (KBr) 3002, 2960, 2878, 1713, 1453. MS (IS) m/z 394.50 $[M+H]^+$. HRMS (IE) m/z $[M-^{\bullet}CO_2tBu]^+$ calcd for $C_{19}H_{18}NS$: 292.1160; found 292.1149.

8-(*tert*-butoxycarbonyl)-7-furan-9-phenyl-8-aza-spiro[4.5]deca-6,9-diene (17c). The Suzuki coupling reaction was carried out as described in the general procedure (**C**) by using 2-furaneboronic acid. The reaction was completed in 3 hours. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 8:2), the desired compound **17c** was isolated as a colorless solid (79% yield). Mp 116-117°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.13 (s, 9H); 1.74-1.79 (m, 8H); 5.67 (d, 1H, *J* = 2 Hz); 5.90 (s, 1H); 7.22-7.40 (m, 5H); 7.48-7.54 (m, 3H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.1, 27.8, 40.5, 45.7, 81.2, 105.9, 111.2, 125.5, 125.8, 126.6, 127.3, 128.1, 132.1, 132.5, 133.6, 138.7, 140.7, 140.9, 141.1, 152.3. IR ν_{max} (KBr) 2946, 2872, 1727, 1600, 1579, 1122. MS (IS) m/z 378.50 $[M+H]^+$.

7-(benzofuran-2-yl)-8-(*tert*-butoxycarbonyl)-9-phenyl-8-aza-spiro[4.5]deca-6,9-diene (17d). The Suzuki coupling reaction was carried out as described in the general procedure (**C**) by using 2-benzofuraneboronic acid. The reaction was completed in 3 hours. After purification by flash column chromatography (silica gel, P.E. then P.E./EtOAc 8:2), the desired compound **17d** was isolated as a colorless solid (48% yield). Mp 116-117°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.11 (s, 9H); 1.79-1.83 (m, 8H); 5.71 (d, 1H, *J* = 2 Hz); 6.20 (s, 1H); 6.8 (s, 1H); 7.20-7.58 (m, 9H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.2, 27.7, 40.5, 45.9, 81.5, 102.6, 111.0, 120.9, 122.8, 124.1, 125.5, 126.5, 127.4, 128.2, 128.9, 129.0, 132.2, 138.6, 140.9, 152.4, 153.4, 154.5. IR ν_{max} (KBr) 2946, 2872, 1727, 1600, 1579, 1122. MS (IS) m/z 428.5 $[M+H]^+$.

8-(*tert*-butoxycarbonyl)-7-(hex-1-en-1-yl)-9-phenyl-8-aza-spiro[4.5]deca-6,9-diene (17e).

To a solution of mono-vinyl phosphate **16** (0.18 mmol, 100 mg) in THF (1.5 mL) under argon, 2-trans-1-hexen-1-trimethyltin (0.36 mmol), anhydrous lithium (0.27 mmol, 12 mg) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg) were added. The flask was evacuated and backfilled with argon three times, and the mixture was refluxed for 3 hours. After cooling, the reaction mixture was diluted with water, ethyl acetate was added, the organic layer was separated and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1) to afford **17e** (50% yield) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.92 (t, 3H, *J* = 7 Hz); 1.16 (s, 9H); 1.38-1.46 (m, 4H); 1.66-1.75 (m, 8H); 2.17-2.21 (m, 2H); 5.53 (s, 1H); 5.63 (d, 1H, *J* = 1 Hz); 5.94 (dt, 1H, *J* = 16 Hz and 7 Hz); 6.05 (d, 1H, *J* = 16Hz); 7.22-7.41 (m, 3H); 7.43-7.44 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 14.1, 22.5, 24.1, 27.9, 31.6, 32.4, 40.4, 45.5, 80.8, 125.4, 126.2, 126.5, 127.06, 128.1, 130.0, 139.2, 139.5, 141.1, 152.6. IR ν_{max} (NaCl film) 2946, 2872, 1716, 1612, 1579, 1166. MS (IS) m/z 394.5 $[M+H]^+$.

7-(1,4-benzodioxin-2-yl)-8-(*tert*-butoxycarbonyl)-9-phenyl-8-aza-spiro[4.5]deca-6,9-diene (17f).

To a solution of mono-vinyl phosphate **16** (0.18 mmol, 100 mg) in THF (1.5 mL) under argon, trimethyl(benzodioxin)tin (0.36 mmol), anhydrous lithium (0.27 mmol, 12 mg) and $Pd(PPh_3)_4$ (0.01 mmol, 10 mg) were added. The flask was evacuated and backfilled with argon three times, and the mixture was refluxed for 3 hours. After cooling, the reaction mixture was diluted with water, ethyl acetate was added, the organic layer was separated and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, P.E. then P.E./EtOAc 9:1) to afford **17f** (52% yield) as a colorless

oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.20 (s, 9H); 1.70-1.78 (m, 8H); 5.65 (s, 1H); 5.82 (s, 1H); 6.32 (s, 1H); 6.82-6.86 (m, 4H); 7.26-7.40 (m, 5H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.1, 27.8, 40.3, 45.6, 81.6, 116.1, 116.4, 123.9, 124.0, 124.2, 125.4, 126.2, 126.8, 127.3, 128.2, 132.3, 135.2, 140.8, 142.5, 143.0, 156.7. IR ν_{max} (NaCl film) 2946, 2872, 1716, 1612, 1579, 1166. MS (IS) m/z 444.5 $[M+H]^+$. HRMS (IE) m/z $[M-^{\bullet}CO_2tBu]^+$ calcd for $C_{23}H_{20}NO_2$: 342.1494; found 342.1519.

1-(*tert*-butoxycarbonyl)-4-(hydroxybenzyl)-2,6-diphenyl-1,4-dihydropyridine (18c). The functionalisation reaction was carried out as described in the general procedure (**D**) by using benzaldehyde. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **18c** was isolated as a yellow oil (75% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.05 (s, 9H); 3.38-3.45 (m, 1H); 4.71-4.75 (m, 1H); 5.45 (d, 1H, *J* = 5 Hz); 5.82 (d, 1H, *J* = 5 Hz); 7.27-7.50 (m, 15H); 7.55-7.59 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.6, 44.2, 81.6, 117.4, 125.6, 125.7, 126.5, 127.7, 128.0, 128.3, 128.5, 138.7, 138.8, 142.4, 143.4, 143.5, 152.2. IR ν_{max} (KBr) 3421, 3062, 3025, 2976, 1705, 1596, 1556, 1494. MS (IS) m/z 440.30 $[M+H]^+$. HRMS (IE) m/z $[M-2H-HCO_2tBu]^{+\bullet}$ calcd for $C_{24}H_{17}NO$: 335.1310; found 335.1337.

1-(*tert*-butoxycarbonyl)-4-(2-hydroxypropan-2-yl)-2,6-diphenyl-1,4-dihydropyridine (18d). The functionalisation reaction was carried out as described in the general procedure (**D**) by using acetone. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **18d** was isolated as a yellow solid (100% yield). Mp 133-134 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.99 (s, 9H); 1.33 (s, 6H); 3.17 (t, 1H, *J* = 6 Hz); 5.74 (d, 2H, *J* = 6 Hz); 7.25-7.41 (m, 6H); 7.55-7.59 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.0, 27.5, 48.0, 74.6, 81.4, 117.4, 125.6, 127.6, 128.3, 139.0, 143.4, 152.1.

IR ν_{max} (KBr) 3528, 2975, 2944, 2898, 1709, 1599, 1577. MS (IS) m/z 392.30 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}HCO_2tBu]^{+\bullet}$ calcd for $C_{20}H_{19}NO$: 289.1466; found 289.1483.

1-(*tert*-butoxycarbonyl)-4-(hydroxy-4-methoxybenzyl)-2,6-diphenyl-1,4-dihydropyridine (18e). The functionalisation reaction was carried out as described in the general procedure (**D**) by using 4-methoxybenzaldehyde. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **18e** was isolated as a yellow oil (65% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.03 (s, 9H); 3.83 (s, 3H); 4.58 (s, 1H); 4.64 (d, 1H, *J* = 7.5 Hz); 5.42 (d, 1H, *J* = 5 Hz); 6.86-6.95 (m, 4H); 7.24-7.49 (m, 10H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.6, 44.2, 55.3, 76.4, 81.5, 113.8, 114.0,117.5, 117.8, 125.5, 125.6, 127.2, 127.6, 127.7, 127.8, 128.2, 128.7, 128.9, 133.2, 138.7, 143.1, 143.2, 152.2, 159.3. IR ν_{max} (KBr) 3444, 3008, 2982, 2938, 1707, 1610, 1513, 1504. MS (IS) m/z 470.50 $[M+H]^+$.

1-(*tert*-butoxycarbonyl)-4-(1-hydroxycyclohexyl)-2,6-diphenyl-1,4-dihydropyridine (18f). The functionalisation reaction was carried out as described in the general procedure (**D**) by using cyclohexanone. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **18f** was isolated as a white solid (80% yield). Mp 154-155 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.00 (s, 9H); 1.57-1.66 (m, 11H); 3.15 (t, 1H, *J* = 6 Hz); 5.74 (d, 2H, *J* = 6 Hz); 7.24-7.40 (m, 6H); 7.56-7.59 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 21.8, 25.8, 27.6, 34.4, 47.9, 75.7, 81.2, 117.1, 125.6, 125.9, 127.5, 128.2, 139.0, 143.5, 152.2. IR ν_{max} (KBr) 3549, 2976, 2930, 2853, 1711, 1629, 1593. MS (IS) m/z 432.50 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}HCO_2tBu]^{+\bullet}$ calcd for $C_{23}H_{23}NO$: 329.1779; found 329.1786.

1-(*tert*-butoxycarbonyl)-4-(1-hydroxy-1-methylallyl)-2,6-diphenyl-1,4-dihydropyridine (18g). The functionalisation reaction was carried out as described in the general procedure (**D**) by using methyl vinyl ketone. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **18g** was isolated as a white oil (41% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.01 (s, 9H); 1,40 (s, 3H); 3.23 (t, 1H, *J* = 6 Hz); 5.16 (d, 1H, *J* = 11Hz); 5.31 (d, 1H, *J* = 18Hz); 5.68 (m, 2H); 6.05 (dd, 1H, *J* = 11 and 18 Hz); 7.27-7.41 (m, 6H); 7.54-7.58 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.9, 27.6, 46.8, 81.4, 113.4, 116.6, 116.7, 125.6, 125.7, 127.6, 128.2, 128.3, 139.0, 139.1, 142.9, 143.7, 143.8, 151.8. IR ν_{max} (KBr) 3411, 2981, 2930, 2848, 1701, 1598, 1578, 1557. MS (IS) m/z 302.50 $[M+H]^+$. MS (IS) m/z 302.50 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}HCO_2tBu]^{+\bullet}$ calcd for $C_{21}H_{19}NO$: 301.1466; found 301.1458.

1-(*tert*-butoxycarbonyl)-4-methyl-4-(2-hydroxypropan-2-yl)-2,6-diphenyl-1,4-dihydropyridine (19c). Starting from the compound **18a**, the second functionalisation reaction was carried out as described in the general procedure (**E**) by using acetone. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **19c** was isolated as a beige solid (10% yield). Mp 124-125°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.99 (s, 9H); 1.27 (s, 3H); 1.33 (s, 6H); 5.49 (s, 2H); 7.30-7.41 (m, 6H); 7.57 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.2, 25.5, 27.5, 46.2, 81.4, 123.0, 125.6, 127.5, 128.3, 139.2, 141.5, 152.2. IR ν_{max} (KBr) 3530, 2977, 2938, 2868, 1713, 1493, 1474, 1450. MS (IS) m/z 406.50 $[M+H]^+$. HRMS (IE) m/z $[M\text{-}^{\bullet}C(CH_3)_2OH]^+$ calcd for $C_{23}H_{24}NO_2$: 346.1807; found 346.1793.

1-(*tert*-butoxycarbonyl)-4,4-diallyl-2,6-diphenyl-1,4-dihydropyridine (19d). Starting from the compound **18b**, the second functionalisation reaction was carried out as described in the general procedure (**E**) by using allyl bromide. After purification by flash column

chromatography (silica gel, P.E./EtOAc 9.5:0.5), the desired compound **19d** was isolated as a beige oil (100% yield).

One step procedure: To a solution of the 1-(*tert*-butoxycarbonyl)-2,6-diphenyl-1,4-dihydropyridine (**6**) (0.28 mmol, 100 mg) in THF (3 mL) at –78°C under argon, n-BuLi (0.31 mmol, 1.6 M in hexane, 197 µl) was added dropwise. After stirring for 5min at –78°C, allyl bromide (0.84 mmol, 73 µL) was added, and the mixture was stirred for 2h at –78°C. Then, at the same temperature, *t*-BuLi (0.31 mmol, 1.7 M in hexane, 196 µL) was added dropwise. After stirring for 5min at –78°C, allyl bromide (0.84 mmol, 73 µL) was added, and the mixture was stirred for additional 2h at –78°C. The reaction was quenched by slow addition of H_2O. Ethyl acetate was then added, the organic layer was separated and dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by flash column chromatography (silica gel, P.E./EtOAc 8:2) to afford **19d** (100% yield) as a beige oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.00 (s, 9H); 2.30 (d, 4H, *J* = 7 Hz); 5.03-5.11 (m, 4H); 5.49 (s, 2H); 5.73-5.90 (m, 2H); 7.29-7.40 (m, 6H); 7.52-7.56 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.6, 41.1, 44.7, 81.1, 118.2, 123.4, 125.7, 127.4, 128.2, 134.1, 139.1, 141.8, 152.0. IR ν_{max} (NaCl film) 3018, 2976, 2944, 1712, 1507, 1475, 1443. MS (IS) m/z 414.50 $[M+H]^+$.HRMS (IE) m/z $[M-{}^{\bullet}C_3H_5-{}^{\bullet}C_4H_8]^+$ calcd for $C_{26}H_{22}NO_4$: 412.1548; found 412.1539.

1-(*tert*-butoxycarbonyl)-4-allyl-4-(hydroxy-4-methoxybenzyl)-2,6-diphenyl-1,4-dihydropyridine (19e). Starting from the compound **18b**, the second functionalisation reaction was carried out as described in the general procedure (**E**) by using 4-methoxybenzaldehyde. After purification by flash column chromatography (silica gel, P.E./EtOAc 9.5:0.5), the desired compound **19e** was isolated as a white solid (88% yield). Mp 161-162°C ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.03 (s, 9H); 2.17-2.48 (m, 2H); 2.31 (s, 1H); 3.84 (s, 3H); 4.68 (s, 1H); 4.91-5.03 (m, 2H); 5.44 (d, 2H, *J* = 11 Hz); 5.57-5.74 (m,

1H); 6.92 (d, 2H, *J* = 8 Hz); 7.32-7.42 (m, 8H); 7.58 (d, 4H, *J* = 7 Hz). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 27.6, 40.1, 47.3, 55.4, 81.6, 113.3, 118.0, 121.3, 121.4, 125.6, 125.8, 127.6, 127.7, 128.3, 128.4, 129.0, 132.5, 134.6, 138.8, 138.9, 142.5, 143.2, 152.3, 159.3. IR ν_{max} (KBr) 3020, 2970, 2938, 1716, 1608, 1520, 1424. MS (IS) m/z 510.50 $[M+H]^+$. HRMS (IE) m/z $[M-^{\bullet}C_3H_5-^{\bullet}C_4H_8-CO_2]^+$ calcd for $C_{20}H_{18}N$: 272.1439; found 272.1432.

1,5-dithiophen-2-yl-pentane-1,5-dione (21b).[19] The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **9**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9:1), the desired compound **21b** was isolated as a brown solid (100% yield). Mp 84-85°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.14-2.25 (quint, 2H, *J* = 7 Hz); 3.05 (t, 4H, *J* = 7 Hz); 7.10-7.14 (m, 2H); 7.61-7.63 (m, 2H); 7.73-7.75 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 19.4, 38.2, 128.2, 132.1, 133.6, 144.2, 192.8. IR ν_{max} (KBr) 2915, 2895, 2850, 1661, 1516, 1494, 1413. MS (IS) m/z 265.00 $[M+H]^+$.

1,5-dibenzothiophen-2-yl-pentane-1,5-dione (21c). The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **7**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9:1), the desired compound **21c** was isolated as a yellow oil (95% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.24-2.35 (m, 2H); 3.17 (t, 4H, *J* = 7 Hz); 7.39-7.54 (m, 4H); 7.85-7.88 (d, 2H, *J* = 7.5 Hz); 8.39 (s, $2H_r$); 8.78-8.81 (dd, 2H, *J* = 1 Hz and 7 Hz). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 19.7, 39.3, 122.4, 125.5, 125.8, 125.9, 135.1, 136.7, 137.1, 195.3. IR ν_{max} (KBr) 3028, 2982, 2938, 1674, 1502, 1466, 1436. MS (IS) m/z 382.00 $[M+H_2O]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{21}H_{16}O_2S_2$: 364.0591; found 364.0617.

3-cyclopentyl-1,5-diphenylpentane-1,5-dione (21d). The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **11**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9,5:0,5), the desired compound **21d** was isolated as a beige solid (94% yield). Mp 78-79°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.67-1.80 (m, 8H); 3.42 (s, 4H); 7.37-7.53 (m, 6H); 7.90-7.94 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.3, 43.3, 45.4, 128.0, 128.5, 132.8, 138.1, 200.7. IR ν_{max} (KBr) 3018, 2963, 2867, 1685, 1564, 1513, 1450. MS (IS) m/z 307.00 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{21}H_{22}O_2$: 306.1619; found 306.1632.

3-Cyclopentyl-1,5-dibenzothiophen-2-ylpentane-1,5-dione (21e). The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **12**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9,5:0,5), the desired compound **21e** was isolated as a brown solid (82% yield). Mp 128-129°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.72-1.83 (m, 8H); 3.38 (s, 4H); 7.29-7.41 (m, 4H); 7.80 (t, 4H, *J* = 7 Hz); 7.92 (s, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 24.1, 38.9, 44.3, 45.7, 122.9, 124.9, 126.0, 127.3, 129.3, 139.2, 142.4, 144.9, 195.0. IR ν_{max} (KBr) 3020, 2944, 2874, 1648, 1596, 1564, 1513. MS (IS) m/z 419.50 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{25}H_{22}O_2S_2$: 418.1061; found 418.1036.

3-Allyl-1,5-diphenyl-pentane-1,5-dione (21f). The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **18b**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9,5:0,5), the desired compound **21f** was isolated as a colorless oil (77% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.25 (t, 2H, *J* = 7 Hz); 2.80-2.91 (m, 1H); 2.99-3.17 (m, 4H); 5.04-5.09 (m, 2H); 5.72-5.83 (m, 1H); 7.43-7.56 (m, 6H); 7.97-8.00 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 30.7, 38.5, 42.4, 117.7,

128.3, 128.7, 133.2, 136.1, 137.1, 199.8. IR ν_{max} (KBr) 3026, 2976, 2918, 1684, 1602, 1584, 1570. MS (IS) m/z 293.00 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{20}H_{20}O_2$: 292.1463; found 292.1469.

3,3-Dimethyl-1,5-diphenylpentane-1,5-dione (21g). The hydrolysis reaction was carried out as described in the general procedure (**F**) starting from compound **19a**. After purification by flash column chromatography (silica gel, P.E./EtOAc 9,5:0,5), the desired compound **21g** was isolated as a colorless oil (100% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.23 (s, 6H; 3.28 (s, 4H); 7.40-7.56 (m, 6H); 7.93-7.96 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 29.0, 33.4, 47.2, 128.1, 128.6, 132.9, 138.3, 200.4. IR ν_{max} (NaCl film) 3018, 2958, 2931, 1685, 1597, 1580, 1570. MS (IS) m/z 281.50 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{19}H_{20}O_2$: 280.1463; found 280.1448.

2,6-dibenzothiophen-2-yl-pyridine (22b). The aromatization reaction was carried out as described in the general procedure (**G**) starting from compound **7**. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **22b** was isolated as a yellow oil (100% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.37-7.42 (m, 4H); 7.69 (d, 2H, *J* = 7.5 Hz); 7.85-7.96 (m, 5H); 8.62-8.66 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 120.7, 122.8, 124.7, 124.9, 126.7, 136.8, 137.3, 137.4, 141.0, 154.4. IR ν_{max} (NaCl film) 3054, 2964, 2928, 1586, 1567, 1512. MS (IS) m/z 344.50 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{21}H_{13}NS_2$: 343.0489; found 343.0513.

2,6-dithiophen-2-yl-pyridine (22c).[21] The aromatisation reaction was carried out as described in the general procedure (**G**) starting from compound **9**. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **22c** was isolated as a brown oil (55% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.10-7.13 (m, 2H); 7.40 (d,

2H, *J* = 5 Hz); 7.47-7.51 (d, 2H, 8 Hz); 7.64-7.67 (m, 3H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 116.8, 124.8, 127.9, 128.0, 137.4, 143.3, 152.9. IR ν_{max} (NaCl film) 2987, 2952, 2883, 1598, 1563, 1511. MS (IS) m/z 244.00 $[M+H]^+$.

2,6-difuran-2-yl-pyridine (22d).[22] The aromatisation reaction was carried out as described in the general procedure (**G**) starting from compound **10**. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **22c** was isolated as a yellow oil (50% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 6.53-6.55 (m, 2H); 7.13 (d, 2H, *J* = 3 Hz); 7.53-7.56 (m, 4H); 7.70-7.76 (m, 1H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 109.0, 112.1, 116.8, 137.3, 143.4, 149.3, 153.8. IR ν_{max} (NaCl film) 3022, 2925, 2853, 1609, 1578, 1501, 1158. MS (IS) m/z 212.00 $[M+H]^+$.

4-(2-hydroxypropan-2-yl)-2,6-diphenyl-pyridine (22e). The aromatisation reaction was carried out as described in the general procedure (**G**) starting from compound **18d**. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **22e** was isolated as an orange oil (80% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.67 (s, 6H); 7.39-7.53 (m, 8H); 7.80 (s, 2H); 8.14-8.18 (m, 2H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 31.6, 72.5, 114.9, 127.2, 128.7, 129.0, 139.8, 157.3, 159.5. IR ν_{max} (NaCl film) 3424, 3028, 2982, 2930, 1608, 1562, 1532. MS (IS) m/z 290.30 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{20}H_{19}NO$: 289.1466 ; found 289.1455.

4-cyclohexan-1-ol-2,6-diphenyl-pyridine (22f). The aromatisation reaction was carried out as described in the general procedure (**G**) starting from compound **18f**. After purification by flash column chromatography (silica gel, P.E./EtOAc 8:2), the desired compound **22f** was isolated as a beige oil (85% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.25 (s, 10H); 7.38-

7.53 (m, 6H); 7.82 (s, 2H); 8.14-8.18 (m, 4H). ^{13}C NMR (250 MHz ; $CDCl_3$) δ (ppm) 21.9, 38.5, 73.3, 115.1, 127.2, 128.7, 129.0, 139.9, 157.2, 159.8. IR ν_{max} (NaCl film) 3408, 3017, 2931, 2848, 1597, 1558, 1583. MS (IS) m/z 330.00 $[M+H]^+$. MS (IS) m/z 330.00 $[M+H]^+$. HRMS (IE) m/z $[M]^{+\bullet}$ calcd for $C_{23}H_{23}NO$: 329.1779; found 329.1786.

[i] ACD-Chem Sketch; http://www.acdlabs.com