Supplementary Material (ESI) for Chemical Communicationsl

Direct synthesis of 1,1-diaryl alkenes from alkenyl phosphates via nickel(0)-catalysed Suzuki-Miyaura coupling

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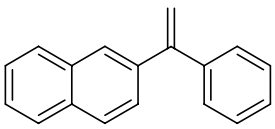
General Methods. Solvents were dried according to standard procedures, reactions were monitored by thin-layer chromatography (TLC) analysis and flash chromatography was carried out on silica gel 60 (230-400 mesh). The chemical shifts are reported in ppm relative to solvent residual peak.[1] MS spectra were recorded on a LC TOF (ES) apparatus. All Suzuki-Miyaura couplings were carried out in 8.0 mL sample vials with a teflon sealed screwcap in a glovebox under an argon atmosphere. All purchased chemicals were used as received without further purification.

All 1-arylethenyl diphenyl phosphates were synthesized according to methods previously reported.[2]

General Procedure for the Suzuki-Miyaura Coupling. The 1-Arylethenyl diphenyl phosphate (1 equiv.), boronic acid or boronic ester (1.5 equiv), K_3PO_4 (3 equiv.) and HBF_4PCy_3 (0.08 equiv.) were dissolved in THF (3 mL). $Ni(COD)_2$ (0.04 equiv.) was then added and the sample vial was fitted with a teflon sealed screwcap and removed from the glovebox. The reaction mixture was heated for the time stated for each product at 65°C. Ensure prober stirring as reaction mixture thickens during the first hours of reaction. The reaction was monitored by TLC. After completed reaction the crude reaction mixture was filtered through celite washing with CH_2Cl_2. After concentration *in vacuo* the crude product were purified by column chromatography.

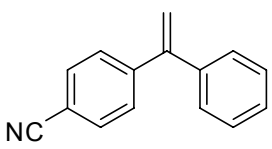
2-(1-Phenylvinyl)naphthalene (4).[3]



1-(Naphthalen-2-yl)vinyl diphenyl phosphate (100 mg, 0.249 mmol), phenylboronic acid (45.5 mg, 0.373 mmol), K_3PO_4 (159 mg, 0.747 mmol), HBF_4PCy_3 (7.3 mg, 0.020 mmol) and $Ni(COD)_2$ (2.7 mg, 0.010 mmol) were reacted for 16 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (9:1) as eluent. This afforded 52.9 mg of the title compound (92% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89-7.82 (m, 4H), 7.54-7.49 (m, 3H), 7.42-7.39 (m, 5H), 5.64 (d, 1H, J = 1.2 Hz), 5.60 (d, 1H, J = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.2, 141.7, 139.0, 133.4, 133.1, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 126.5, 126.3, 126.2, 115.0. Mass confirmed by GCMS analysis.

Table 1

4-(1-Phenylvinyl)benzonitrile (Entry 1).[4]

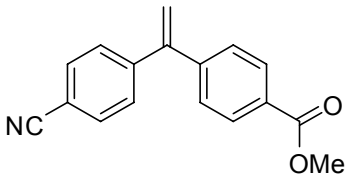


1-(4-Cyanophenyl)vinyl diphenyl phosphate (88.0 mg, 0.233 mmol), phenylboronic acid (55 mg, 0.45 mg), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 17 h.

[1] H. E. Gottlieb, , V. Kotlyar, A. Nudelman, *J. Org. Chem.*, 1997, ***62***, 7512.
[2] A. L. Hansen, J-P. Ebran, M. Ahlquist, P-O. Norrby, T. Skrydstrup., *Angew Chem.*, 2006, **45**, 3349.
[3] U. Nuechter, G. Zimmermann, V. Francke and H. Hopf, *Liebigs Ann. Recl.*, 1997, **7**, 1505
[4] C. A. Walree, V. E. M. Kaats-Richters, S. J. Veen, B. Wieczorek, H. Johanna and B. C. Wiel, *Eur. J. Org. Chem.*, 2004, **14**, 3046.

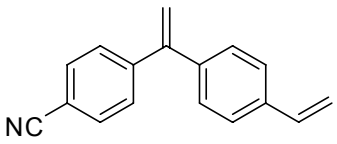
The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (9:1) -> (1:1) as eluent. This afforded 48.2 mg of the title compound (99% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54-7.51 (m, 2H), 7.36-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.21-7.18 (m, 2H) 5.50 (d, 1H, J = 0.8 Hz), 5.45 (d, 1H, J = 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.9, 146.3, 140.4, 132.3, 129.1, 128.7, 128.5, 128.4, 119.1, 117.0, 111.6. Mass confirmed by GCMS analysis.

Methyl 4-(1-(4-cyanophenyl)vinyl)benzoate (Entry 2).



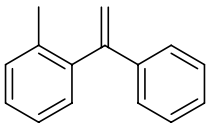
1-(4-Cyanophenyl)vinyl diphenyl phosphate (110.6mg, 0.29 mmol), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (112 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 17 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (3:1) -> (1:1) as eluent. This afforded 61.7 mg of the title compound (80% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, 2H, J = 8.4 Hz), 7.63 (d, 2H, J = 8.8 Hz), 7.40 (d, 2H, J = 8.8 Hz), 7.34 (d, 2H, J = 8.4 Hz), 5.66 (s, 1H), 5.63 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.7, 148.0, 145.4, 144.7, 132.3, 130.0, 129.9, 128.9, 128.2, 118.8, 118.3, 111.8, 52.3. HRMS $C_{17}H_{13}O_2N$ [M^++Na]; calculate: 286.0844 found: 286.0843.

4-(1-(4-Vinylphenyl)vinyl)benzonitrile (Entry 3).



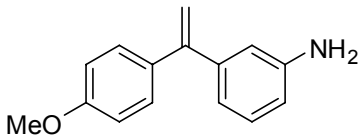
1-(4-Cyanophenyl)vinyl diphenyl phosphate (113.0mg, 0.30 mmol), 4-vinylphenylboronic acid (66.6 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 17 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent. This afforded 66.5 mg of the title compound (96% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 (d, 2H, J = 8.8 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.25 (d, 2H, J = 8.8 Hz), 6.74 (dd, 1H, J = 17.6, 10.8 Hz), 5.79 (dd, 1H, J = 17.6, 0.8 Hz), 5.61 (d, 1H, J = 0.8 Hz), 5.52 (d, 1H, J = 0.8 Hz) 5.29 (dd, 1H, J = 10.8, 0.8 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.4, 146.1, 139.6, 137.7, 136.3, 132.1, 129.0, 128.4, 126.4, 118.9, 116.6, 114.5, 111.5. Mass confirmed by GCMS analysis.

1-Methyl-2-(1-phenylvinyl)benzene (Entry 4).[5]



Diphenyl 1-*o*-tolylvinyl phosphate (110 mg, 0.3 mmol), phenylboronic acid (55.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 44 h (75% conversion). The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (10:1) as eluent. This afforded 40.2 mg of the title compound (69% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30-7.19 (m, 9H), 5.78 (d, 1H, J = 1.2 Hz), 5.21 (d, 1H, J = 1.2 Hz), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.6, 141.8, 140.7, 136.3, 130.22, 130.16, 128.5, 127.70, 127.67, 126.6, 125.8, 115.0, 20.3. Mass confirmed by GCMS analysis.

3-[1-(4-Methoxyphenyl)vinyl]aniline (Entry 5).

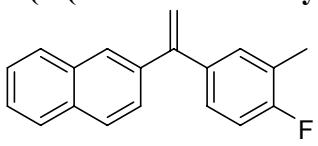


1-(4-Methoxyphenyl)vinyl diphenyl phosphate (115 mg, 0.3 mmol), 3-aminophenylboronic acid (70.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 18 h (74% conversion). The crude product was purified by flash chromatography on silica gel using Et_2O/pentane/CH_2Cl_2 (1:5:4) as eluent. This afforded 40.5 mg of the title compound (60% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.27 (m, 2H), 7.13 (t, 1H, J = 7.2 Hz), 6.86 (m, 2H), 6.76 (dt, 1H, J = 8.0, 1.2 Hz), 6.66-6-63 (m,

[5] F. Berthiol, H. Doucet and M. Santelli, *Eur. J. Org. Chem.*, 2003, **6**, 1091.

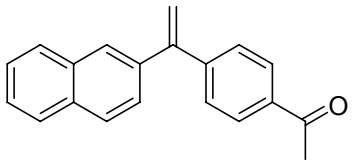
2H), 5.36 (d, 1H, *J* = 1.6 Hz), 5.34 (d, 1H, *J* = 1.6 Hz), 3.83 (s, 3H), 3.65 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.5, 149.8, 146.3, 143.2, 134.3, 129.7, 129.3, 119.2, 115.4, 114.8, 113.7, 112.9, 55.5. HRMS $C_{15}H_{15}ON$ [M^++H]; calculate: 226.1232 found: 226.1238.

2-(1-(4-Fluoro-3-methylphenyl)vinyl)naphthalene (Entry 6)



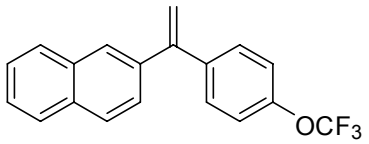
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (100.0 mg, 0.249 mmol), 4-fluoro-3-methylphenylboronic acid (69.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 19 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (20:1) as eluent. This afforded 47.8 mg of the title compound (73% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88-7-80 (m, 4H), 7.52-7.48 (m, 3H), 7.24-7.18 (m, 2H), 7.01 (t, 1H, *J* = 8.4 Hz), 5.57 (d, 1H, *J* = 1.2 Hz), 5.52 (d, 1H, *J* = 1.2 Hz), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.2 (d, 1C, *J* = 210 Hz), 149.6, 139.0, 133.4. 131.6, 131.5, 128.3, 127.9, 127.7, 127.5, 127.42, 127.37, 126.5, 126.4, 126.2, 124.7 (d, 1C, *J* = 17.6 Hz), 114.9 (d, 1C, *J* = 17.6 Hz), 114.7, 14.7 (d, 1C, *J* = 3.1 Hz). Mass confirmed by GCMS analysis.

1-(4-(1-(Naphthalen-2-yl)vinyl)phenyl)ethanone (Entry 7).



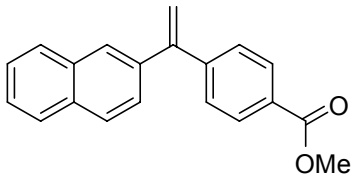
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (100.0 mg, 0.249 mmol), 4-acetylphenylboronic acid (74.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 19 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) -> CH_2Cl_2 as eluent. This afforded 44.5 mg of the title compound (66% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97-7.94 (m, 2H), 7.87-7.79 (m, 3H), 7.76 (d, 1H, *J* = 1.6 Hz), 7.50-7.46 (m, 5H), 5.70 (d, 1H, *J* = 0.8 Hz), 5.64 (d, 1H, *J* = 0.8 Hz), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 149.3, 146.4, 138.2, 136.6, 133.4, 133.2, 128.7, 128.5, 128.3, 128.1, 127.8, 127.5, 126.5, 126.4, 126.3, 116.6, 26.8. Mass confirmed by GCMS analysis.

2-(1-(4-(Trifluoromethoxy)phenyl)vinyl)naphthalene (Entry 8).



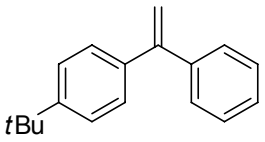
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (100.0 mg, 0.249 mmol), 4-(trifluoromethoxy)phenylboronic acid (93.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 19 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) -> CH_2Cl_2 as eluent. This afforded 45.0 mg of the title compound (58% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88-7.82 (m, 3H), 7.79 (s, 1H), 7.52-7.47 (m, 3H), 7.44-7.42 (m, 2H), 7.23 (d, 2H, *J* = 7.6 Hz), 5.64 (d, 1H, *J* = 0.8 Hz), 5.57 (d, 1H, *J* = 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.02, 148.96, 140.3, 138.5, 133.4, 133.2, 129.6, 128.3, 128.0, 127.8, 127.4, 126.5, 126.4, 126.3, 120.8, 120,7 (q, 1C, *J* = 255 Hz), 115.6. Mass confirmed by GCMS analysis.

Methyl 4-(1-(naphthalen-2-yl)vinyl)benzoate (Entry 9).



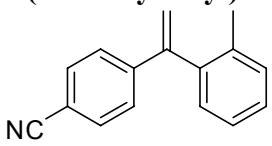
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (121.0 mg, 0.30 mmol), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (112 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 19 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (3:1) -> (1:1) as eluent. This afforded 51.5 mg of the title compound (60% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96-7.93 (m, 2H), 7.77-7.69 (m, 3H), 7.67 (d, 1H, *J* = 1.6 Hz), 7.42-7.34 (m, 5H), 5.59 (d, 1H, *J* = 0.8 Hz), 5.54 (d, 1H, *J* = 0.8 Hz), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0, 149.4, 146.2, 138.3, 133.4, 133.2, 129.7, 129.6, 128.5, 128.3, 128.0, 127.7, 127.5, 126.44, 126.35, 126.26, 116.5, 52.2. HRMS $C_{20}H_{16}O_2$ [M^++Na]; calculate: 311.1048 found: 311.1039.

1-*tert*-Butyl-4-(1-phenylvinyl)benzene (Entry 10).[6]



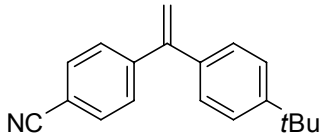
1-(4-*tert*-Butylphenyl)vinyl diphenyl phosphate (123.0 mg, 0.30 mmol), phenylboronic acid (55 mg, 0.45 mg), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 18 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (15:1) as eluent. This afforded 65.6 mg of the title compound (93% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.31 (m, 9H), 5.49 (d, 1H, J = 1.6 Hz), 5.44 (d, 1H, J = 1.6 Hz) 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.9, 150.0, 141.8, 138.6, 128.5, 128.2, 128.0, 127.7, 125.2, 113.8, 34.7, 31.5. Mass confirmed by GCMS analysis.

4-(1-*o*-Tolylvinyl)benzonitrile (Entry 11).



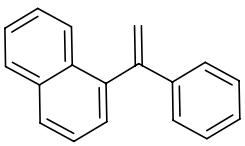
1-(4-Cyanophenyl)vinyl diphenyl phosphate (113.0 mg, 0.30 mmol), 5,5-dimethyl-2-*o*-tolyl-1,3,2-dioxaborinane (91.8 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 18 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (2:1) -> (1:1) as eluent. This afforded 48.9 mg of the title compound (74% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (d, 2H, J = 8.8 Hz), 7.37 (d, 2H, J = 8.8 Hz), 7.31-7.19 (m, 4H), 5.88 (d, 1H, J = 0.8 Hz), 5.38 (d, 1H, J = 0.8 Hz), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.4, 145.3, 140.4, 136.1, 132.5, 130.6, 130.2, 128.4, 127.3, 126.3, 119.1, 118.2, 111.3, 20.3. Mass confirmed by GCMS analysis.

4-(1-(4-*tert*-Butylphenyl)vinyl)benzonitrile (Entry 12).



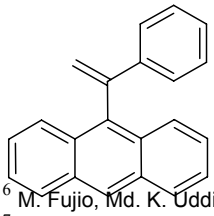
1-(4-Cyanophenyl)vinyl diphenyl phosphate (113.0 mg, 0.30 mmol), 4-tert-butylphenylboronic acid (80.1 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 22 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (10:1) as eluent. This afforded 71.5 mg of the title compound (91% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (dt, 2H, J = 8.4, 2.0 Hz), 7.50 (dt, 2H, J = 8.4, 2.0 Hz), 7.42 (dt, 2H, J = 8.8, 2.2 Hz), 7.27 (dt, 2H, J = 8.8, 2.2 Hz), 6.63 (d, 1H, J = 0.4 Hz), 5.54 (d, 1H, J = 0.4 Hz), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 151.5, 148.6, 146.4, 137.2, 132.1, 129.0, 127.9, 125.4, 119.0, 116.2, 111.3, 34.7, 31.4. Mass confirmed by GCMS analysis.

1-(1-Phenylvinyl)naphthalene (Entry 13).[7]



1-(Naphthalen-1-yl)vinyl diphenyl phosphate (121.0 mg, 0.30 mmol), phenylboronic acid (55.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 18 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (9:1) as eluent. This afforded 66.5 mg of the title compound (96% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89-7.86 (m, 2H), 7.80 (d, 1H, J = 8.4 Hz), 7.52 (t, 1H, J = 6.8 Hz), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 3H), 7.30-7.27 (m, 3H), 6.01 (d, 1H, J = 1.2 Hz), 5.42 (d, 1H, J = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.4, 141.2, 139.9, 133.8, 132.0, 128.5, 128.3, 128.1, 127.8, 127.4, 126.8, 126.6, 126.0, 125.8, 125.6, 116.4. Mass confirmed by GCMS analysis.

9-(1-Phenylvinyl)anthracene (Entry 15).[8]



1-(Anthracen-9-yl)vinyl diphenyl phosphate (136.0 mg, 0.30 mmol),), phenylboronic acid (55.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 44 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (9:1) as

[6] M. Fujio, Md. K. Uddin, H-J. Kim and Y. Tsuno, *J. Phys. Org. Chem.*, 2002, **15**, 544.

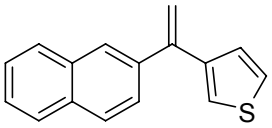
[7] G. B. Bajracharya, I. Nakamura and Y. Yamamoto, *J. Org. Chem.*, 2005, **3**, 892.

[8] M. S. Passafaro and B. A. Keay, *Tetrahedron lett.*, 1996, **37**, 429.

eluent. This afforded 28.9 mg of the title compound (34% yield) as a pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.48 (s, 1H), 8.08-8.02 (m, 4H), 7.46 (t, 2H, J = 7.2 Hz), 7.38 (t, 2H, J = 8.4 Hz), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 3H), 6.43 (s, 1H), 5.43 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 140.7, 136.4, 131.7, 130.1, 128.7, 128.6, 128.0, 126.8, 126.7, 126.4, 125.7, 125.3, 118.0. Mass confirmed by GCMS analysis.

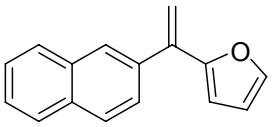
Table 2

3-(1-(Naphthalen-2-yl)vinyl)thiophene (Entry 1).



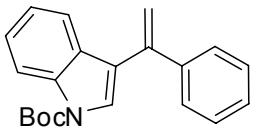
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (121.0 mg, 0.30 mmol), thiophen-3-ylboronic acid (57.6 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 22 h. The crude product was purified by flash chromatography on silica gel using pentane as eluent. This afforded 66.0 mg of the title compound (93% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91-7.86 (m, 4H), 7.60 (dd, 1H, J = 8.0, 1.6 Hz), 7.55-7.51 (m, 2H), 7.37 (dd, 1H, J = 5.2, 2.8 Hz), 7.27 (dd, 1H, J = 5.2, 1.2 Hz), 7.22 (dd, 1H, J = 2.8, 1.2 Hz), 5.68 (d, 1H, J = 0.8 Hz), 5.53 (d, 1H, J = 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.7, 142.7, 139.0, 133.4, 133.1, 128.3, 127.8, 127.7, 127.4, 127.1, 126.5, 126.3, 126.2, 125.6, 123.6, 114.1. Mass confirmed by GCMS analysis.

2-(1-(Naphthalen-2-yl)vinyl)furan (Entry 2).



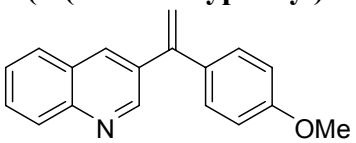
1-(Naphthalen-2-yl)vinyl diphenyl phosphate (121.0 mg, 0.30 mmol), furan-2-ylboronic acid (57.6 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 22 h. The crude product was purified by flash chromatography on silica gel using pentane as eluent. This afforded 66.0 mg of the title compound (93% yield) as a colorless solid. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 7.97 (d, 1H, J = 1.2 Hz), 7.90-7.94 (m, 3H), 7.53-7.59 (m, 4H), 6.50 (dd, 1H, J = 3.6, 2.0 Hz), 6.32 (d, 1H J = 3.2 Hz), 5.82 (d, 1H, J = 1.2 Hz), 5.40 (d, 1H, J = 1.2 Hz). ^{13}C NMR (100 MHz, CD_3CN) δ (ppm) 154.7, 143.9, 140.3, 137.7, 134.2, 134.1, 129.0, 128.8, 128.5, 128.0, 127.4, 127.3, 113.3, 112.4, 110.4. Mass confirmed by MS analysis.

***tert*-Butyl 3-(1- -butyl 3 phenylvinyl)-1H-indole-1-carboxylate (Entry 3).**



tert -(1-(Diphenoxyphosphoryloxy)vinyl)-1H-indole-1-carboxylate (147.0 mg, 0.30 mmol), phenylboronic acid (55.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 26 h. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (7:3) as eluent. This afforded 81.8 mg of the title compound (92% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, 1H, J = 8.4 Hz), 7.61 (s, 1H), 7.47-7.40 (m, 2H), 7.37-7.31 (m, 5H), 7.16 (t, 1H, J = 7.2 Hz), 5.61 (s, 2H), 1.70 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.9, 142.1, 141.1, 135.9, 129.6, 128.4, 128.1, 127.9, 125.0, 124.6, 122.8, 122.2, 121.0, 115.4, 114.8, 84.0, 28.4. HRMS $C_{21}H_{21}O_2N$ [M^++Na]; calculate: 342.1470 found: 342.1455.

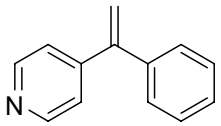
3-(1-(4-Methoxyphenyl)vinyl)quinoline (Entry 4).



1-(4-Methoxyphenyl)vinyl diphenyl phosphate (55.0 mg, 0.145 mmol), 3-quinolinyl boronic acid (30.0 mg, 0.173 mmol (1.2 equiv.)), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 21 h. The crude product was purified by flash chromatography on silica gel using pentane/EtOAc (4:1) as eluent. This afforded 37.4 mg of the title compound (99% yield) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.95 (d, 1H, J = 1.6 Hz), 8.12 (d, 1H, J = 8.4 Hz), 8.04 (d, 1H, J = 2.0 Hz), 7.77 (d, 1H, J = 8.0 Hz), 7.71 (t, 1H, J = 8.4 Hz), 7.54 (t, 1H, J = 8.0 Hz), 7.32-7.29 (m, 2H), 6.90 (d, 2H, J = 8.8 Hz), 5.59 (s, 1H), 5.53 (s, 1H), 3.84 (s, 9H).

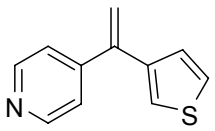
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.8, 150.9, 147.7, 146.6, 134.8, 134.7, 133.1, 129.6, 129.4, 129.3, 128.1, 127.8, 127.0, 114.9, 114.0, 55.4. HRMS $C_{18}H_{16}ON$ [M^++H]; calculate: 262.1232 found: 262.1235.

4-(1-Phenylvinyl)pyridine (Entry 5).[9]



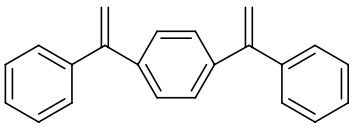
Diphenyl 1-(pyridin-4-yl)vinyl phosphate (106.0 mg, 0.30 mmol), phenylboronic acid (55.0 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 18 h. The crude product was purified by flash chromatography on silica gel using EtOAc/CH_2Cl_2 (1:1) as eluent. This afforded 28.0 mg of the title compound (52% yield) as an pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57 (dd, 2H, J = 6.0, 1.6 Hz), 7.37-7-34 (m, 3H), 7.31-7.28 (m, 2H), 7.25-7-23 (m, 2H), 5.61 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)149.9, 149.0, 148.0, 139.9, 128.6, 128.4, 128.3, 122.9, 117.1. Mass confirmed by GCMS analysis.

4-(1-(Thiophen-3-yl)vinyl)pyridine (Entry 6).



Diphenyl 1-(pyridin-4-yl)vinyl phosphate (106.0 mg, 0.30 mmol), thiophen-3-ylboronic acid (57.6 mg, 0.45 mmol), K_3PO_4 (191 mg, 0.90 mmol), HBF_4PCy_3 (8.8 mg, 0.024 mmol) and $Ni(COD)_2$ (3.3 mg, 0.012 mmol) were reacted for 17 h. The crude product was purified by flash chromatography on silica gel using Et_2O/CH_2Cl_2 (1:4) as eluent. This afforded 48.3 mg of the title compound (86% yield) as an pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.59 (d, 2H, J = 6.0 Hz), 7.32 (dd, 1H, J = 5.2, 3.2 Hz), 7.29-7-27 (m, 2H), 7.13 (dd, 1H, J = 5.2, 1.2 Hz), 7.11 (dd, 1H, J = 3.2, 1.2 Hz), 5.63 (d, 1H, J = 1.2 Hz), 5.45 (d, 1H, J = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.0, 149.0, 142.6, 140.8, 127.0, 126.1, 123.7, 122.8, 115.8. HRMS $C_{11}H_9SN$ [M^++H]; calculate: 188.0535 found: 188.0464.

1,4-*bis*(1-Thenylvinyl)benzene (6).[10]



1,1'-(1,4-phenylene)bis(ethene-1,1-diyl) tetraphenyl diphosphate (188.0 mg, 0.30 mmol), phenylboronic acid (110.0 mg, 0.90 mmol), K_3PO_4 (255 mg, 1.20 mmol), HBF_4PCy_3 (17.6 mg, 0.048 mmol) and $Ni(COD)_2$ (6.6 mg, 0.024 mmol) were reacted for 20 h in 6 ml of THF. The crude product was purified by flash chromatography on silica gel using Pentane/CH_2Cl_2 (9:1) as eluent. This afforded 79.4 mg of the title compound (94% yield) as colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.34 (m, 14H), 5.53 (d, 1H, J = 0.8 Hz), 5.49 (d, 1H, J = 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.8, 141.6, 141.0, 128.5, 128.3, 128.2, 127.9, 114.5. Mass confirmed by GCMS analysis.

[9] V. J. Traynelis, K. Yamauchi and J. P. Kimball, *J. Am. Chem. Soc.*, 1974, **96**, 7289.

[10] M. Klokkenburg, M. Lutz, A. L. Spek, J. H. Maas and C. A. Walree., *Chem. Eur. J.*, 2003, **9**, 3544.