Supporting Information

Fluoride Catalyzed P-Aryl-Coupling –

a Mild Approach to Functionalized Triarylphosphines

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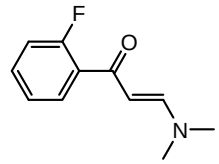
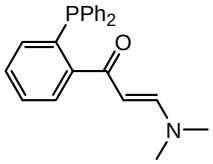
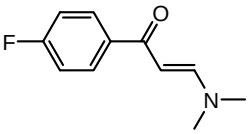
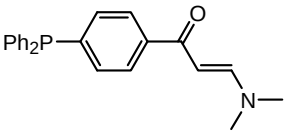
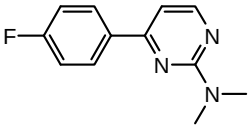
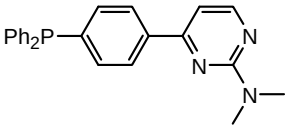
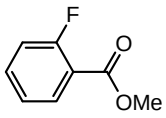
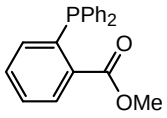
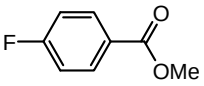
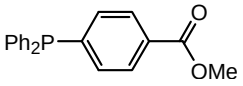
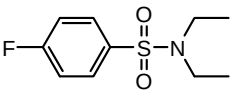
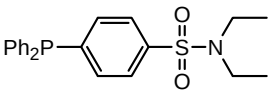
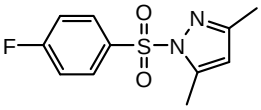
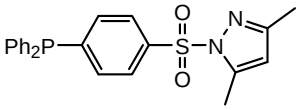
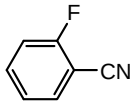
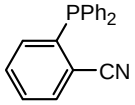
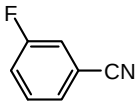
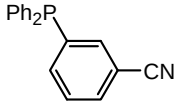
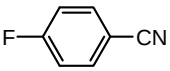
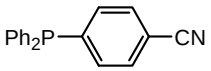
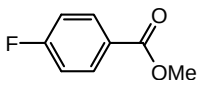
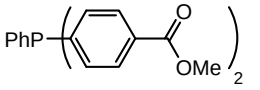
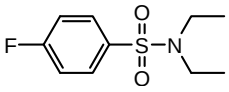
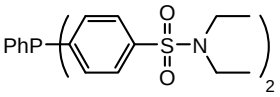
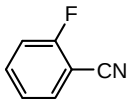
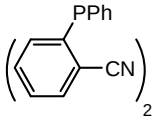
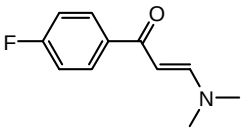
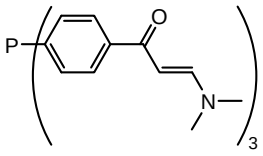
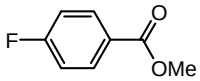
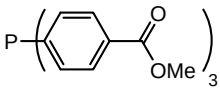
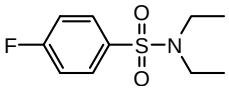
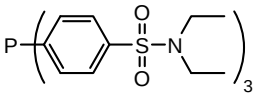
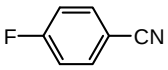
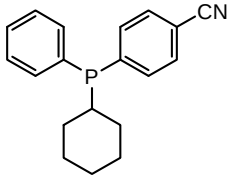
Table 1. Fluoride catalyzed coupling of diphenyl(trimethylsilyl)phosphine (**1a**) with aryl fluorides.

aryl fluoride		CsF [mol%]	T [°C]	t [min]	product		yield [%]
2a		126	RT	2880	**3a**		95[a]
2b		20	80	60	**3b**		94[b]
2c		10	RT	1440	**3c**		74[b]
2d		50	RT	60	**3d**		81[b]
2e		20	RT	50	**3e**		92[b]
2f		50	RT	5	**3f**		99[b]
2g		32	-12	75	**3g**		90[b]
2h		50	RT	10	**3h**		94[b]
2i		21	RT	20	**3i**		97[b]
2j		17	RT	10	**3j**		80[b]

[a] yield determined by ^{31}P and/or ^{1}H NMR. [b] isolated yield.

Table 2. Fluoride catalyzed coupling of phenylbis(trimethylsilyl)phosphine (**1b**), tris(trimethylsilyl)phosphine (**1c**) and cyclohexylphenyl(trimethylsilyl)phosphine (**1d**) with different aryl fluorides.

phosphine	aryl fluoride	CsF [mol%]	*T* [°C]	*t* [min]	product	yield [%]
1b	**2e** 	50	RT	10	**3k** 	81[b]
1b	**2f** 	100	RT	10	**3l** 	93[b]
1b	**2h** 	47	RT	10	**3m** 	80[b]
1c	**2b** 	44	100	240	**3n** 	97[b]
1c	**2e** 	50	RT	360	**3o** 	94[b]
1c	**2f** 	297	RT	360	**3p** 	94[b]
1d	**2j** 	30	60	1200	**3q** 	72

[a] yield determined by ^{31}P and/or ^{1}H NMR. [b] isolated yield.

1. General remarks

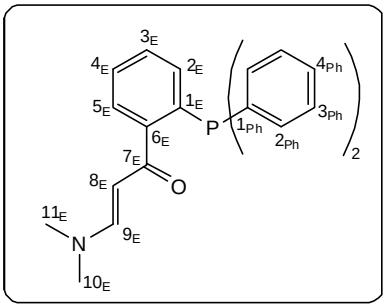
Reactions were performed under nitrogen atmosphere in flame-dried glassware using standard Schlenk technique. Unless otherwise stated, chemicals and solvents are commercially available and were used without further purification. Solvents had to be degassed prior to use. CsF was activated by dissolving in water, removing the solvent and drying at 150 °C. Diphenyl(trimethylsilyl)phosphine,[1] phenylbis(trimethylsilyl)phosphine[1b,2] and tris(trimethylsilyl)phosphine[3] were synthesized following literature procedures. NMR spectra were obtained on Bruker DPX 200, DPX-400 or Bruker Avance 600 systems using $CDCl_3$ as solvent, with proton (200 MHz, 400 MHz or 600 MHz), carbon (50 MHz, 101 MHz or 151 MHz) and phosphorous resonances (81 MHz, 162 MHz or 243 MHz).

2. Experimental procedures and analytical data

a) Reactions with diphenyl(trimethylsilyl)phosphine (1a)

Synthesis of (*E*)-[2-((3'-*N*,*N*-dimethylamino)prop-2'-en-1'-onyl)phenyl]diphenylphosphine (3a)

In a flame-dried, nitrogen flushed three-necked flask CsF (176 g, 1.16 mol) was suspended in dry DMF (700 mL) and (*E*)-3-(*N*,*N*-dimethylamino)-1-(2'-fluorophenyl)prop-2-en-1-one (**2a**) (178 g, 921.23 mmol) was added. After dropwise addition of diphenyl(trimethylsilyl)phosphine (**1a**) (238 mL, 929.45 mmol), the reaction mixture was stirred for 48 h at room temperature. The mixture was diluted with H_2O (800 mL) and CH_2Cl_2 (800 mL), the layers were seperated and the aqueous layer was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic layers were washed with H_2O (3 x 400 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product **3a** was obtained as a yellow solid (314 g, 95 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 2.69 + 2.94 (2 s, 6 H, H-10_E, H-11_E), 5.40 (d, $^3J_{HH}$ = 12.6 Hz, 1 H, H-8_E), 7.04 (dd, $^3J_{HP}$ = 3.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1 H, H-2_E), 7.26−7.34 (m, 12 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}, H-3_E, H-4_E), 7.38 (ddd, $^4J_{HP}$ = 1.2 Hz, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.5, 1 H, H-5_E), 7.64 (m, 1 H, H-9_E) ppm. ^{13}C-NMR ($CDCl_3$, 100.62 MHz): δ = 36.51 + 44.38 (s, 6 C, C-10_E, C-11_E), 95.89 (s, 1 C, C-8_E), 127.10 (d, $^3J_{CP}$ = 5.5 Hz, 1 C, C-5_E), 127.76 (s, 2 C, C-4_{Ph}), 127.82 (d, $^3J_{CP}$ = 6.5 Hz, 4 C, C-3_{Ph}), 128.03 (s, 1C, C-4_E), 128.83 (s, 1C, C-3_E), 133.15 (d, $^2J_{CP}$ = 19.4 Hz, 4 C, C-2_{Ph}), 134.17 (s, 1 C, C-1_E), 135.55 (d, $^2J_{CP}$ = 19.4 Hz, 1 C, C-2_E), 138.40 (d, $^1J_{CP}$ = 11.1 Hz, 2 C, C-1_{Ph}), 146.94 (d, $^2J_{CP}$ = 25.9 Hz, 4 C, C-6_E), 154.28 (s, 1 C, C-9_E), 190.91 (s, 1 C, C-7_E) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -8.8 (s) ppm.



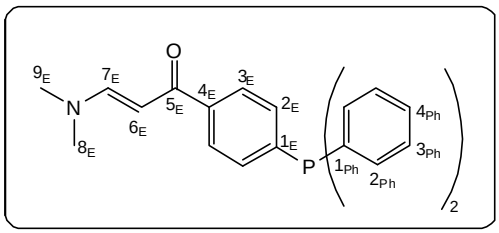
1 (a) S. E. Tunney, J. K. Stille, *J. Org. Chem.* **1987**, *52*, 748−753. (b) R. Appel, K. Geisler, *J. Organometal. Chem.* **1976**, *112*,61-64. (c) A. M. Aguiar, J. Beisler, A. Mills, *J. Org. Chem.* **1962**, *27*, 1001-1005.

2 (a) K. Issleib, H. Schmidt, H. Meyer, *J. Organomet. Chem.* **1980,** *192*, 33−39. (b) S. Hietkamp, H. Sommer, O. Stelzer, *Chem. Ber.* **1984**, *117*, 3400−3413.

3 (a) E. Niecke, H. Westermann, *Synthesis* **1988**, 330-330. (b) G. W., Luther III, G. Beyerle, *Inorg. Synth.* **1977**, *17*, 186-188. (c) M. Baudler, A. Zarkadas, *Chem. Ber.* **1973**, *106*, 3970-3971. (d) J. Holz, O. Zayas, H. Jiao, W. Baumann, A. Spannenberg, A. Monsees, T. H. Riermeier, J. Almena, R. Kadyrov, A. Börner, *Chem. Eur. J.* **2006**, *12*, 5001-5013. (e) G. Becker, *Inor. Synth.* **1990**, *27*, 243-249.

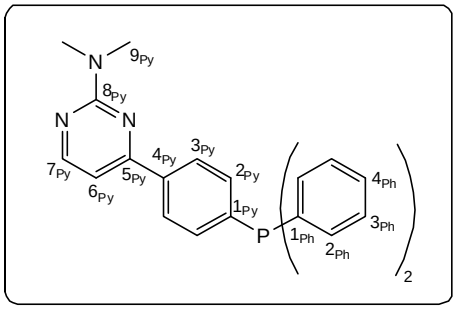
Synthesis of (*E*)-[4-((3'-*N*,*N*-dimethylamino)prop-2'-en-1'-onyl)phenyl]diphenylphosphine (3b)

In an analogous procedure to **3a,** phosphine **3b** was synthesized from (*E*)-3-(*N*,*N*-dimethylamino)-1-(4'-fluorophenyl)prop-2-en-1-one (**2b**) (593 g, 3.07 mol), diphenyl(trimethylsilyl)phosphine (**1a**) (789 mL, 3.08 mol) and CsF (94.80 g, 624.09 mmol) in dry DMF (600 mL). The reaction mixture was stirred for 60 min at 80 °C. The work-up corresponds to procedure **3a**. The product **3b** was obtained as a yellow solid (1036 g, 94 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 2.90 + 3.13 (s, 3 H, H-8_E, H-9_E), 5.69 (d, $^{3}J_{HH}$ = 12.3 Hz, 1 H, H-6_E), 7.31−7.40 (m, 12 H, H-2_E, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}), 7.81 (d, $^{3}J_{HH}$ = 12.4 Hz, 1 H, H-7_E), 7.84 (dd, $^{4}J_{HP}$ = 1.3 Hz, $^{3}J_{HH}$ = 8.2 Hz, 2 H, H-3_E) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 37.3 + 45.0 (s, 6 C, C-8_E, C-9_E), 92.3 (s, 1 C, C-6_E), 127.3 (d, $^{3}J_{CP}$ = 6.7 Hz, 2 C, C-3_E), 128.5 (d, $^{3}J_{CP}$ = 6.9 Hz, 4 C, C-3_{Ph}), 128.8 (d, $^{4}J_{CP}$ = 6.7 Hz, 2 C, C-4_{Ph}), 133.3 (d, $^{2}J_{CP}$ = 19.0 Hz, 2 C, C-2_E), 133.8 (d, $^{2}J_{CP}$ = 19.7 Hz, 4 C, C-2_{Ph}), 136.8 (d, $^{1}J_{CP}$ = 10.9 Hz, 2 C, C-1_{Ph}), 140.7 (s, 1 C, C-4_E), 140.8 (d, $^{1}J_{CP}$ = 12.5 Hz, 1 C, C-1_E), 154.3 (s, 1 C, C-7_E), 188.2 (s, 1 C, C-5_E) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -3.9 (s) ppm.



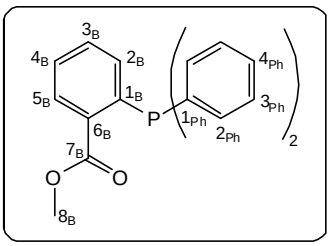
Synthesis of [4-((2'-(*N*,*N*-dimethylamino)pyrimid-4-yl)phenyl]diphenylphosphine (3c)

In an analogous procedure to **3a,** phosphine **3c** was synthesized from 2-(*N*,*N*-dimethylamino)-4-(4'-fluorophenyl)pyrimidine (**2c**) (0.81 g, 3.73 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (1.00 mL, 3.91 mmol) and CsF (0.06 g, 0.39 mmol) in dry DMF (0.80 mL). The reaction mixture was stirred for 24 h at room temperature . The work-up corresponds to procedure **3a.** The product **3c** was obtained as a yellow solid (1.06 g, 74 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 3.26 (s, 6 H, H-9_{Py}), 6.89 (d, $^{3}J_{HH}$ = 5.2 Hz, 1 H, H-6_{Py}), 7.34−7.37 (m, 10 H, H-2_{Ph}, H-3_{Ph},H-4_{Ph}), 7.40 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HP}$ = 9.4 Hz, 2 H, H-2_{Py}), 8.04 (dd, $^{4}J_{HP}$ = 0.9 Hz, $^{3}J_{HH}$ = 8.0 Hz, 2 H, H-3_{Py}), 8.37 (d, $^{3}J_{HH}$ = 5.2 Hz, 1 H, H-7_{Py}) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 37.0 (s, 6 C, C-9_{Py}), 104.8 (s, 1 C, C-6_{Py}), 126.9 (d, $^{3}J_{CP}$ = 6.7 Hz, 2 C, C-3_{Py}), 128.5 (d, $^{3}J_{CP}$ = 6.9 Hz, 4 C, C-3_{Ph}), 128.8 (s, 2 C, C-4_{Ph}), 133.7 (d, $^{2}J_{CP}$ = 19.2 Hz, 2 C, C-2_{Py}), 133.8 (d, $^{2}J_{CP}$ = 19.6 Hz, 4 C, C-2_{Ph}), 136.8 (d, $^{1}J_{CP}$ = 11.0 Hz, 2 C, C-1_{Ph}), 138.1 (s, 1 C, C-4_{Py}), 140.2 (d, $^{1}J_{CP}$ = 12.3 Hz, 1 C, C-1_{Py}), 158.2 (s, 1 C, C-5_{Py}), 162.5 (s, 1 C, C-7_{Py}), 163.5 (s, 1 C, C-8_{Py}) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -4.2 (s) ppm.



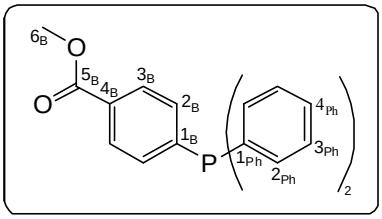
Synthesis of [2-(methoxycarbonyl)phenyl]diphenylphosphine (3d)

In an analogous procedure to **3a,** phosphine **3d** was synthesized from 2-fluorobenzoic acid methyl ester (**2d**) (1.07 mL, 8.40 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (2.25 mL, 8.79 mmol) and CsF (0.64 g, 4.21 mmol) in dry DMF (5.00 mL). The reaction mixture was stirred for 60 min at room temperature. The work-up corresponds to procedure **3a.** The product **3d** was obtained as a yellow solid (2.19 g, 81 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 3.74 (s, 3 H, H-8_B), 6.95−7.00 (m, 1 H, H-2_B), 7.26−7.35 (m, 10 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}), 7.36−7.40 (m, 2 H, H-4_B, H-3_B), 8.04−8.09 (m, 1 H, H-5_B) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 51.9 (s, 1 C, C-8_B), 128.1 (s, 1 C, C-4_B), 128.3 (s, 2 C, C-4_{Ph}), 128.5 (d, $^{3}J_{CP}$ = 4.7 Hz, 4 C, C-3_{Ph}), 130.5 (s, 1 C, C-3_B), 131.8 (s, 1 C, C-5_B), 132.2 (d, $^{3}J_{CP}$ = 21.4 Hz, 1 C, C-6_B), 133.8 (d, $^{3}J_{CP}$ = 20.8 Hz, 4 C, C-2_{Ph}), 134.1 (d, $^{3}J_{CP}$ = 7.9 Hz, 1 C, C-2_B), 137.8 (d, $^{3}J_{CP}$ = 11.0 Hz, 2 C, C-1_{Ph}), 140.4 (d, $^{3}J_{CP}$ = 26.6 Hz, 1 C, C-1_B), 167.2 (s, 1 C, C-7_B) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -2.9 (s) ppm.



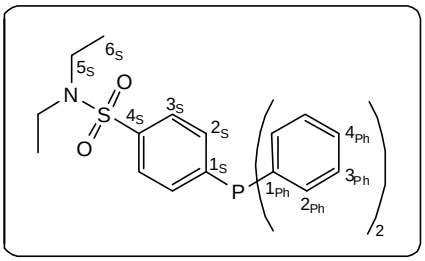
Synthesis of [4-(methoxycarbonyl)phenyl]diphenylphosphine (3e)

In an analogous procedure to **3a,** phosphine **3e** was synthesized from 4-fluorobenzoic acid methyl ester (**2e**) (6.50 mL, 50.18 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (13.40 mL, 52.33 mmol) and CsF (1.54 g, 10.14 mmol) in dry DMF (24.00 mL). The reaction mixture was stirred for 50 min at room temperature. The work-up corresponds to procedure **3a.** The product **3e** was obtained as a colorless solid (14.83 g, 92 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 3.91 (s, 3 H, H-6_B), 7.30−7.39 (m, 12 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}, H-2_B), 7.98 (dd, $^{4}J_{HP}$ = 1.4 Hz, $^{3}J_{HH}$ = 8.3 Hz, 2 H, H-3_B) ppm. ^{13}C-NMR ($CDCl_3$, 50.33 MHz): δ = 52.1 (s, 1 C, C-6_B), 128.6 (d, $^{3}J_{CP}$ = 7.2 Hz, 4 C, C-3_{Ph}), 129.1 (s, 2 C, C-4_{Ph}) 129.2 (d, $^{3}J_{CP}$ = 6.4 Hz, 2 C, C-3_B), 130.0 (s, 1 C, C-4_B), 133.1 (d, $^{2}J_{CP}$ = 18.8 Hz, 2 C, C-2_B), 133.9 (d, $^{2}J_{CP}$ = 20.0 Hz, 4 C, C-2_{Ph}), 136.11 (d, $^{1}J_{CP}$ = 0.6 Hz, 2 C, C-1_{Ph}), 144.0 (d, $^{1}J_{CP}$ = 14.4 Hz, 1 C, C-1_B), 166.8 (s, 1 C, C-5_B) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -3.6 (s) ppm.



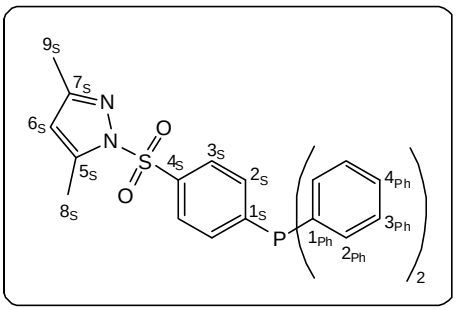
Synthesis of [4-(*N*,*N*-diethylsulfonamido)phenyl]diphenylphosphine (3f)

In an analogous procedure to **3a,** phosphine **3f** was synthesized from *N*,*N*-diethyl-4-fluorobenzenesulfonamide (**3f**) (6.51 g, 28.15 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (7.50 mL, 29.29 mmol) and CsF (2.13 g, 14.02 mmol) in dry DMF (25.00 mL). The reaction mixture was stirred for 5 min at room temperature. The work-up corresponds to procedure **3a.** The product **3f** was obtained as a colorless solid (11.03 g, 99 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 1.13 (t, $^{3}J_{HH}$ = 7.2 Hz, 6 H, H-6_S), 3.24 (q, $^{3}J_{HH}$ = 7.2 Hz, 4 H, H-5_S), 7.30−7.40 (m, 10 H, H-3_S, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}), 7.74 (dd, $^{3}J_{HP}$ = 1.2 Hz, $^{3}J_{HH}$ = 8.4 Hz, 2 H, H-3_S) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 14.2 (s, 2 C, C-6_S), 42.1 (s, 2 C, C-5_S), 126.7 (d, $^{3}J_{CP}$ = 6.2 Hz, 2 C,C-3_S), 128.7 (d, $^{3}J_{CP}$ = 7.3 Hz, 4 C, C-3_{Ph}), 129.3 (s, 2 C, C-4_{Ph}), 133.5 (d, $^{2}J_{CP}$ = 19.3 Hz, 2 C, C-2_S), 133.9 (d, $^{2}J_{CP}$ = 20.3 Hz, 4 C, C-2_{Ph}), 135.7 (d, $^{1}J_{CP}$ = 10.5 Hz, 2 C, C-1_{Ph}), 140.3 (s, 1 C, C-4_S), 143.7 (d, $^{1}J_{CP}$ = 15.3 Hz, 1 C, C-1_S) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -3.8 (s) ppm.



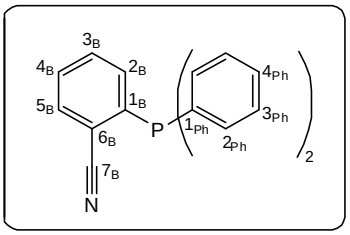
Synthesis of 1-[4'-(diphenylphosphino)benzenesulfonic acid]-3,5-dimethylpyrazolide (3g)

In an analogous procedure to **3a,** phosphine **3g** was synthesized from 1-(4'-fluorobenzenesulfonic acid)-3,5-dimethylpyrazolide (**2g**) (0.94 g, 3.70 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (1.00 mL, 3.91 mmol) and CsF (0.18 g, 1.18 mmol) in dry DMF (5.00 mL). The reaction mixture was stirred for 75 min at -12 °C. The work-up corresponds to procedure **3a.** The product **3g** was obtained as a colorless oil (1.40 g, 90 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 2.20 (s, 3 H, H-9_S), 2.48 (s, 3 H, H-8_S), 5.91 (s, 1 H, H-6_S), 7.26−7.39 (m, 10 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}), 7.55−7.67 (m, 2 H, H-3_S), 7.80−7.86 (m, 2 H, H-2_S) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 12.9 (s, 1 C, C-9_S), 13.6 (s, 1 C, C-8_S), 110.8 (s, 1 C, C-6_S), 126.9 (d, ^{3}J = 6.0 Hz, 1 C, C-3_S), 128.9 (d, ^{3}J = 7.6 Hz, 4 C, C-3_{Ph}), 129.4 (s, 2 C, C-4_{Ph}), 133.3 (d, ^{2}J = 18.5 Hz, 2 C, C-2_S), 133.9 (d, ^{2}J = 20.5 Hz, 4 C, C-2_{Ph}), 136.5 (d, ^{1}J = 130.5 Hz, 1 C, C-1_{Ph}), 135.0 (s, 1 C, C-7_S), 145.5 (d, ^{1}J = 114.6 Hz, 1 C, C-1_S), 153.5 (s, 1 C, C-5_S) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -3.0 (s) ppm.



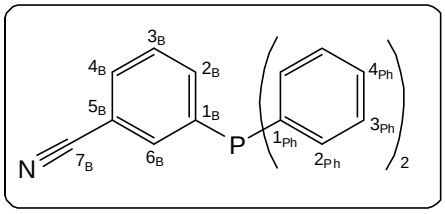
Synthesis of (2-cyanophenyl)diphenylphosphine (3h)

In an analogous procedure to **3a,** phosphine **3h** was synthesized from 2-fluorobenzonitrile (**2h**) (1.94 mL, 17.78 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (4.75 mL, 18.55 mmol) and CsF (1.35 g, 8.89 mmol) in dry DMF (8.00 mL). The reaction mixture was stirred for 10 min at room temperature. The work-up corresponds to procedure **3a.** The product **3h** was obtained as a colorless solid (4.80 g, 94 %). ^{1}H-NMR ($CDCl_3$, 600.13 MHz): δ = 7.04 (dd, $^{3}J_{HP}$ = 3.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1 H, H-2_B), 7.31 (ddd, $^{4}J_{HP}$ = 1.5 Hz, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 9.4 Hz, 4 H, H-3_{Ph}), 7.36−7.40 (m, 6 H, H-2_{Ph}, H-4_{Ph}), 7.42 (ddd, $^{4}J_{HP}$ = 1.0 Hz, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 8.6 Hz, 1 H, H-3_B), 7.48 (ddd, $^{4}J_{HH}$ = 1.1 Hz, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HH}$ = 8.8 Hz, 1 H, H-4_B), 7.70−7.73 (m, 1 H, H-5_B) ppm. ^{13}C-NMR ($CDCl_3$, 150.90 MHz): δ = 117.6 (d, $^{2}J_{CP}$ = 3.5 Hz, 1 C, C-6_B), 117.8(d, $^{3}J_{CP}$ = 33.0 Hz, 1 C, C-7_B), 128.8 (s, 2 C, C-4_{Ph}), 128.8 (s, 1 C, C-3_B), 129.4 (s, 4 C, C-3_{Ph}), 132.4 (s, 1 C, C-4_B), 133.4 (s, 1 C, C-5_B), 133.7 (d, $^{2}J_{CP}$ = 4.5 Hz, 1 C, C-2_B), 134.0 (d, $^{2}J_{CP}$ = 20.6 Hz, 4 C, C-2_{Ph}), 134.6 (d, $^{1}J_{CP}$ = 10.5 Hz, 2 C, C-1_{Ph}), 143.0 (d, $^{1}J_{CP}$ = 19.6 Hz, 1 C, C-1_B) ppm. ^{31}P-NMR ($CDCl_3$, 242.94 MHz): δ = -8.5 (s) ppm.



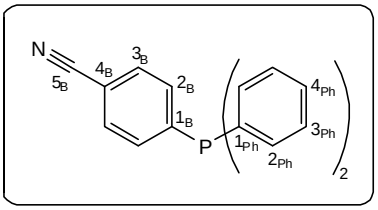
Synthesis of (3-cyanophenyl)diphenylphosphine (3i)

In an analogous procedure to **3a,** phosphine **3i** was synthesized from 3-fluorobenzonitrile (**2i**) (0.80 mL, 7.46 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (2.00 mL, 7.81 mmol) and CsF (0.24 g, 1.58 mmol) in dry DMF (1.50 mL). The reaction mixture was stirred for 20 min at room temperature. The work-up corresponds to procedure **3a.** The product **3i** was obtained as a colorless solid (2.07 g, 97 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.28−7.34 (m, 4 H, H-2_{Ph}), 7.35−7.40 (m, 6 H, H-3_{Ph}, H-4_{Ph}), 7.43 (ddd, $^{4}J_{HP}$ = 0.9 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1 H, H-3_B), 7.49−7.56 (m, 2 H, H-2_B, H-4_B), 7.61 (ddd, $^{4}J_{HH}$ = 1.4 Hz, $^{4}J_{HH}$ = 1.3 Hz, $^{3}J_{HP}$ = 6.2 Hz, 1 H, H-6_B) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 112.9 (d, $^{3}J_{CP}$ = 6.1 Hz, 1 C, C-5_B), 118.6 (s, 1 C, C-7_B), 128.9 (d, $^{3}J_{CP}$ = 7.3 Hz, 4 C, C-3_{Ph}), 129.0 (d, $^{3}J_{CP}$ = 6.1 Hz, 1 C, C-3_B), 129.4 (s, 2 C, C-4_{Ph}), 131.9 (s, 1 C, C-4_B), 133.8 (d, $^{1}J_{CP}$ = 20.2 Hz, 2 C, C-1_{Ph}), 135.5 (d, $^{2}J_{CP}$ = 10.6 Hz, 1 C, C-6_B), 136.4 (d, $^{2}J_{CP}$ = 18.1 Hz, 4 C, C-2_{Ph}), 137.5 (d, $^{2}J_{CP}$ = 20.4 Hz, 1 C, C-2_B), 140.4 (d, $^{1}J_{CP}$ = 16.5 Hz, 1 C, C-1_B) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -4.1 (s) ppm.



Synthesis of (4-cyanophenyl)diphenylphosphine (3j)

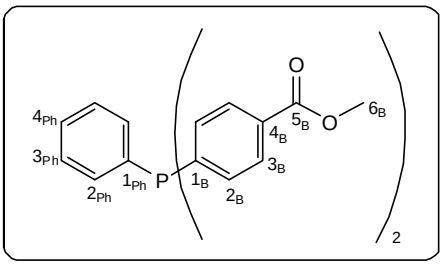
In an analogous procedure to **3a,** phosphine **3j** was synthesized from 4-fluorobenzonitrile (**2j**) (0.91 g, 7.51 mmol), diphenyl(trimethylsilyl)phosphine (**1a**) (2.00 mL, 7.81 mmol) and CsF (0.19 g, 1.25 mmol) in dry DMF (2.00 mL). The reaction mixture was stirred for 10 min at room temperature. The work-up corresponds to procedure **3a.** The product **3j** was obtained as a colorless solid (1.72 g, 80 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.29−7.41 (m 12 H, H-2_B, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}), 7.58 (dd, $^{4}J_{HP}$ = 1.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 2 H, H-3_B) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 111.9 (s, 1 C, C-4_B), 118.5 (s, 1 C, C-5_B), 128.7 (d, $^{3}J_{CP}$ = 7.4 Hz, 4 C, C-3_{Ph}), 129.4 (s, 2 C, C-4_{Ph}), 131.6 (d, $^{3}J_{CP}$ = 6.0 Hz, 2 C, C-3_B), 133.4 (d, $^{2}J_{CP}$ = 18.6 Hz, 2 C, C-2_B), 133.9 (d, $^{2}J_{CP}$ = 20.3 Hz, 4 C, C-2_{Ph}), 134.5 (d, $^{1}J_{CP}$ = 9.3 Hz, 1 C, C-1_B), 135.3 (d, $^{1}J_{CP}$ = 10.8 Hz, 2 C, C-1_{Ph}) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -2.9 (s) ppm.



b) Reactions with phenylbis(trimethylsilyl)phosphine (1b)

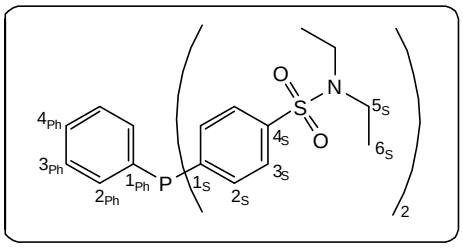
Synthesis of bis[4,4'-(methoxycarbonyl)phenyl]phenylphosphine (3k)

In an analogous procedure to **3a,** phosphine **3k** was synthesized from 4-fluorobenzoic acid methyl ester (**2e**) (22.20 mL, 17.14 mmol), phenylbis(trimethylsilyl)phosphine (**1b**) (2.50 mL, 8.48 mmol) and CsF (0.64 g, 4.21 mmol) in DMF (1.70 mL). The reaction mixture was stirred for 10 min at room temperature. The mixture was diluted with aqueous HCl (20 %) (10 mL) and CH_2Cl_2 (10 mL), the layers were seperated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with aqueous HCl (20 %) (3 x 20 mL) and H_2O (2 x 50 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product **3k** was obtained as a yellow oil (2.61 g, 81 %). ^{1}H-NMR ($CDCl_3$, 200.13 MHz): δ = 3.95 (s, 3 H, H-6_B), 7.30−7.45 (m, 9 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}, H-2_B, H-3_B), 8.02 (d, $^{3}J_{HH}$ = 8.12 Hz, 4 H, H-3_B) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 52.2 (s, 2 C, C-6_B), 128.8 (d, $^{3}J_{CP}$ = 7.5 Hz, 2 C, C-3_{Ph}), 129.4 (d, $^{3}J_{CP}$ = 6.8 Hz, 4 C, C-3_B) , 130.4 (s, 2 C, C-4_B), 132.1 (d, $^{4}J_{CP}$ = 8.6 Hz, 1 C, C-4_{Ph}), 133.3 (d, $^{2}J_{CP}$ = 19.3 Hz, 4 C, C-2_B), 134.1 (d, $^{2}J_{CP}$ = 20.4 Hz, 2 C, C-2_{Ph}), 135.2 (d, $^{1}J_{CP}$ = 9.8 Hz, 1 C, C-1_{Ph}), 142.8 (d, $^{1}J_{CP}$ = 14.1 Hz, 2 C, C-1_B), 166.7 (s, 2 C, C-5_B) ppm. ^{31}P-NMR ($CDCl_3$, 81.01 MHz): δ = -3.7 (s) ppm.



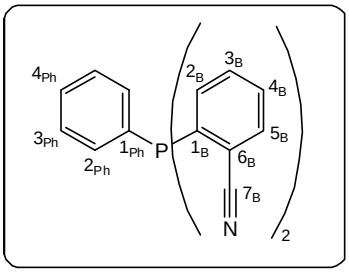
Synthesis of bis[4,4'-(*N*,*N*-diethylbenzenesulfonamido)phenyl]phenylphosphine (3l)

In an analogous procedure to **3a,** phosphine **3l** was synthesized from *N*,*N*-diethyl-4-fluorobenzenesulfonamide (**2f**) (1.25 g, 5.40 mmol), phenylbis(trimethylsilyl)phosphine (**1b**) (0.80 mL, 2.70 mmol) and CsF (0.41 g, 2.70 mmol) in dry DMF (1.50 mL). The reaction mixture was stirred for 10 min at room temperature. The product **3l** was obtained as a colorless oil (1.34 g, 93 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 1.13 (t, $^{3}J_{HH}$ = 7.2 Hz, 12 H, H-6_S), 3.24 (q, $^{3}J_{HH}$ = 7.1 Hz, 8 H, H-5_S), 7.29 (ddd, $^{4}J_{HH}$ = 1.4 Hz, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HP}$ = 9.5 Hz, 2 H, H-2_{Ph}), 7.36 (dd, $^{3}J_{HP}$ = 6.9 Hz, $^{3}J_{HH}$ = 8.3 Hz, 4 H,H-2_S), 7.41 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 8.0 Hz, 2 H, H-3_{Ph}), 7.38 (m, 1 H, H-4_{Ph}), 7.76 (dd, $^{4}J_{HP}$ = 1.2 Hz, $^{3}J_{HH}$ = 8.3 Hz, 4 H, H-3_S) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 14.0 (s, 2 C, C-6_S), 42.0 (s, 2 C, C-5_S), 126.7 (d, ^{3}J = 6.7 Hz, 4 C, C-3_S), 128.9 (d, ^{3}J = 7.7 Hz, 2 C, C-3_{Ph}), 129.7 (s, 1 C, C-4_{Ph}), 133.7 (d, ^{3}J = 19.5 Hz, 4 C, C-2_S), 134.0 (d, ^{2}J = 20.7 Hz, 2 C, C-2_{Ph}), 134.2 (d, ^{3}J = 10.3 Hz, 1 C, C-1_{Ph}), 140.8 (s, 2 C, C-4_S), 141.9 (d, ^{3}J = 15.3 Hz, 2 C, C-1_S) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -4.2 (s) ppm.



Synthesis of bis(2,2'-cyanophenyl)phenylphosphine (3m)

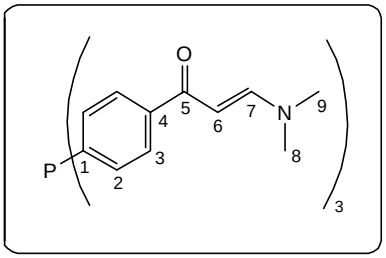
In an analogous procedure to **3a,** phosphine **3m** was synthesized from 2-fluorobenzonitrile (**2h**) (1.32 mL, 12.10 mmol), phenylbis(trimethylsilyl)phosphine (**1b**) (1.80 mL, 6.08 mmol) and CsF (0.43 g, 2.83 mmol) in dry DMF (7.00 mL). The reaction mixture was stirred for 10 min at room temperature. The product **3m** was obtained as a colorless oil (1.52 g, 80 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.01 (ddd, $^{4}J_{HH}$ = 1.3 Hz, $^{3}J_{HP}$ = 3.8 Hz, $^{3}J_{HH}$ = 8.7 Hz, 2 H, H-2_B), 7.34 (ddd, $^{4}J_{HH}$ = 1.4 Hz, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 8.3 Hz, 2 H, H-4_B), 7.39–7.55 (m, 7 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}, H-3_B), 7.75 (ddd, $^{4}J_{HH}$ = 2.0 Hz, $^{4}J_{HP}$ = 3.0 Hz, $^{3}J_{HH}$ = 7.3 Hz, 2 H, H-5_B) ppm. ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ = 117.1 (d, ^{3}J = 3.8 Hz, 2 C, C-6_B), 117.9 (d, ^{3}J = 32.2 Hz, 2 C, C-7_B), 129.1 (d, ^{3}J = 7.9 Hz, 2 C, C-3_{Ph}), 129.5 (s, 2 C, C-4_B), 130.2 (s, 1 C, C-4_{Ph}), 131.9 (d, ^{3}J = 9.8 Hz, 2 C, C-2_B), 133.6 (s, 2 C, C-5_B), 133.5 (d, ^{3}J = 1.0 Hz, 2 C, C-3_B), 134.0 (d, ^{3}J = 4.7 Hz, 2 C, C-2_{Ph}), 134.4 (d, ^{3}J = 21.6 Hz, 2 C, C-1_B), 140.2 (d, ^{3}J = 18.7 Hz, 1 C, C-1_{Ph}) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -8.5 (s) ppm.



c) Reactions with tris(trimethylsilyl)phosphine (1c)

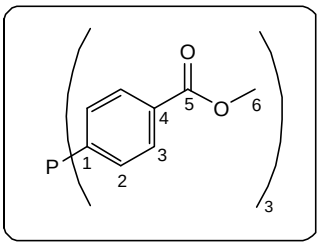
Synthesis of (*E*)-tris[4-((3'-*N*,*N*-dimethylamino)prop-2'-en-1'-onyl)phenyl]phosphine (3n)

In an analogous procedure to **3a,** phosphine **3n** was synthesized from (*E*)-3-(*N*,*N*-dimethylamino)-1-(4'-fluorophenyl)prop-2-en-1-one (**2b**) (2.51 g, 12.99 mmol), tris(trimethylsilyl)phosphine (**1c**) (1.29 mL, 4.34 mmol) and CsF (0.29 g, 1.91 mmol) in dry DMF (12.00 mL). The reaction mixture was stirred for 4 h at 100 °C. The work-up corresponds to procedure **3a,** removing most of the solvent *in vacuo* before starting the work-up. The product **3n** was obtained as a red oil (2.34 g, 97 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 2.88 + 3.11 (s, 6 H, H-8, H-9), 5.65 (d, $^{3}J_{HH}$ = 12.3 Hz, 3 H, H-6), 7.32 (dd, $^{3}J_{HP}$ = 8.7 Hz, $^{3}J_{HH}$ = 8.7 Hz, 6 H,H-2), 7.79 (d, $^{3}J_{HH}$ = 12.3 Hz, 3 H, H-7), 7.82 (dd, $^{4}J_{HP}$ = 5.6 Hz, $^{3}J_{HH}$ = 8.7 Hz, 6 H, H-3) ppm. ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ = 33.7 + 45.2 (s, 6 C, C-8, C-9), 91.2 (s, 3 C, C-6), 129.6 (d, $^{3}J_{CP}$ = 8.8 Hz, 3 C, C-3), 136.6 (d, $^{2}J_{CP}$ = 3.0 Hz, 3 C, C-2), 139.7 (d, $^{1}J_{CP}$ = 12.2 Hz, 3 C, C-1), 141.0 (s, 3 C, C-4), 154.2 (s, 3 C, C-7), 188.0 (s, 3 C, C-5) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -4.4 (s) ppm.



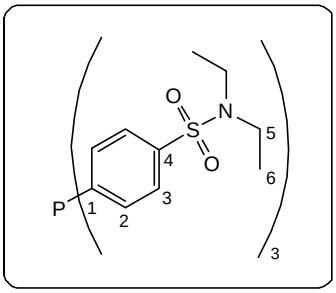
Synthesis of tris[4,4',4''-(methoxycarbonyl)phenyl]phosphine (3o)

In an analogous procedure to **3a,** phosphine **3o** was synthesized from 4-fluorobenzoic acid methyl ester (**2e**) (1.49 mL, 11.50 mmol), tris(trimethylsilyl)phosphine (**1c**) (1.14 mL, 3.82 mmol) and CsF (0.29 g, 1.91 mol) in dry DMF (3.00 mL). The reaction mixture was stirred for 6 h at room temperature. The product **3o** was obtained as a yellow oil (1.57 g, 94 %). ^{1}H-NMR ($CDCl_3$, 200.13 MHz): δ = 3.90 (s, 9 H, H-6), 7.10−7.42 (m, 6 H, H-2), 7.90−8.16 (m, 6 H, H-3) ppm. ^{13}C-NMR ($CDCl_3$, 50.33 MHz): δ = 52.2 (s, 3 C, C-6), 115.4 (d, $^{3}J_{CP}$ = 22.0 Hz, 6 C, C-3), 129.6 (d, $^{4}J_{CP}$ = 6.9 Hz, 3 C, C-4), 132.1 (d, $^{2}J_{CP}$ = 9.4 Hz, 6 C, C-2), 133.6 (d, $^{1}J_{CP}$ = 19.9 Hz, 3 C, C-1), 166.6 (s, 3 C, C-5) ppm. ^{31}P-NMR ($CDCl_3$, 81.01 MHz): δ = -4.0 (s) ppm.



Synthesis of tris[4,4',4''-(*N*,*N*-diethylbenzenesulfonamido)phenyl]phosphine (3p)

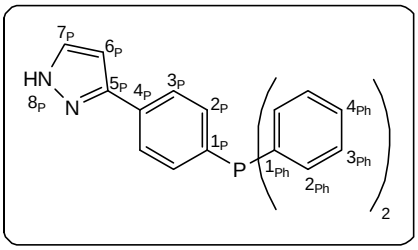
In an analogous procedure to **3a,** phosphine **3p** was synthesized from *N*,*N*-diethyl-4-fluorobenzenesulfonamide (**2f**) (1.00 g, 4.32 mmol), tris(trimethylsilyl)phosphine (**1c**) (0.43 mL, 1.44 mmol) and CsF (0.65 g, 4.28 mmol) in dry DMF (2.00 mL). The reaction mixture was stirred for 6 h at room temperature. The product **3p** was obtained as a colorless solid (0.90 g, 94 %). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 1.14 (t, $^{3}J_{HH}$ = 7.1 Hz, 18 H, H-6), 3.25 (q, $^{3}J_{HH}$ = 7.1 Hz, 12 H, H-5), 7.36 (dd, $^{3}J_{HP}$ = 7.4 Hz, $^{3}J_{HH}$ = 8.1 Hz, 6 H, H-2), 7.79 (dd, $^{4}J_{HP}$ = 1.1 Hz, $^{3}J_{HH}$ = 8.3 Hz, 6 H, H-3) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 14.2 (s, 6 C, C-6), 42.1 (s, 6 C, C-5), 127.2 (d, $^{3}J_{CP}$ = 6.9 Hz, 6 C, C-3), 134.1 (d, $^{2}J_{CP}$ = 20.2 Hz, 6 C, C-2), 140.5 (d, $^{1}J_{CP}$ = 14.9 Hz, 3 C, C-1), 141.9 (s, 3 C, C-4) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -4.8 (s) ppm.



d) One-pot P-C-coupling with follow-up functionalization reaction

Synthesis of [4-(pyrazol-3'-yl)phenyl]diphenylphosphine (4)

In a flame-dried, nitrogen flushed Schlenk tube CsF (0.36 g, 2.37 mmol) was suspended in dry DMF (4.70 mL) and (*E*)-3-(*N*,*N*-dimethylamino)-1-(4'-fluorophenyl)prop-2-en-1-one (**2b**) (4.61 g, 23.86 mmol) was added. After dropwise addition of diphenyl(trimethylsilyl)phosphine (**1a**) (7.10 mL, 23.80 mmol), the reaction mixture was stirred for 10 min at 100 °C. Following hydrazine monohydrate (3.50 mL, 72.01 mmol) and ethanol (10.00 mL) were added and the reaction mixture was refluxed for 15 h. The work-up corresponds to procedure **3a**. The product **4** was obtained as a yellow solid (6.33 g, 81 %). ^{1}H-NMR ($CDCl_3$, 200.13 MHz): δ = 6.65 (d, $^{3}J_{HH}$ = 2.3 Hz, 1 H, H-6_P), 7.34−7.46 (m, 12 H, H-2_{Ph}, H-3_{Ph}, H-4_{Ph}, H-2_P,), 7.63 (d, $^{3}J_{HH}$ = 2.2 Hz, 1 H, H-7_P), 7.78 (d, $^{3}J_{HH}$ = 7.1 Hz, 2 H, H-3_P) ppm. ^{13}C- NMR ($CDCl_3$, 100.61 MHz): δ = 102.8 (s, 1 C, C-6_P), 125.7 (d, $^{3}J_{CP}$ = 6.9 Hz, 2 C, C-3_P), 128.5 (d, $^{3}J_{CP}$ = 7.0 Hz, 4 C, C-3_{Ph}), 128.7 (s, 2 C, C-4_{Ph}), 132.1 (s, 1 C, C-7_P), 132.6 (s, 4 C, C-4_P), 133.7 (d, $^{3}J_{CP}$ = 19.5 Hz, 1 C, C-2_{Ph}), 134.1 (d, $^{3}J_{CP}$ = 19.5 Hz, 2 C, C-2_P), 137.0 (d, $^{3}J_{CP}$ = 11.9 Hz, 2 C, C-1_{Ph}), 137.10 (d, $^{3}J_{CP}$ = 11.2 Hz, 1 C, C-1_P), 148.9 (s, 1 C, C-5_P) ppm. ^{31}P-NMR ($CDCl_3$, 91.01 MHz): δ = -4.4 (s) ppm.



e) Reaction with cyclohexylphenyl(trimethylsilyl)phosphine (1d)

Synthesis of (4-cyanophenyl)cyclohexylphenylphosphine (3q)

In a flame-dried, nitrogen flushed three-necked flask CsF (497 mg, 3.27 mmol) was suspended in dry DMF (15 mL) and stirred for 30 min at room temperature. 4-Fluorobenzonitrile (**2j**) (1.31 g, 10.81 mmol) was added and the reaction mixture was stirred for further 10 min at room temperature. After addition of cyclohexylphenyl(trimethylsilyl)phosphine (**1d**) (2.83 g, 10.70 mmol), the reaction mixture was stirred for 20 h at 60 °C and the solvent was removed *in vacuo*. The residue was diluted with aqueous NH_4Cl (50 mL) and CH_2Cl_2 (50 mL), the layers were seperated and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with H_2O (3 x 20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product **3q** was obtained as a yellow-brown oil (2.25 g, 72 %). ^{1}H-NMR ($CDCl_3$, 600.13 MHz): δ = 1.14−1.34 (m, 5 H, H_{cy}), 1.65−1.79 (m, 5 H, H_{cy}), 2.17−2.23 (m, 1 H, H_{cy}), 7.36−7.37 (m, 3 H, H_{ar}), 7.43−7.46 (m, 2 H, H_{ar}), 7.50−7.53 (m, 2 H, H_{ar}), 7.57−7.58 (m, 2 H, H_{ar}) ppm. ^{13}C-NMR ($CDCl_3$, 150.92 MHz): δ = 26.3 (s, C-8_{Cy}), 26.9 (d, $^{3}J_{CP}$ = 12.5 Hz, 2 C, C-7_{Cy}), 29.4 (d, $^{2}J_{CP}$ = 12.5 Hz, C-6_{Cy}), 29.8 (d, $^{2}J_{CP}$ = 16.6 Hz, C-6_{Cy}), 35.4 (d, $^{1}J_{CP}$ = 11.1 Hz, C-5_{Cy}), 111.9 (s, C-12_{Ph}), 118.9 (s, C-13_{Ph}), 128.7 (d, $^{3}J_{CP}$ = 6.9 Hz, 2 C, C-3_{Ph}), 129.5 (s, C-4_{Ph}), 131.7 (d, $^{3}J_{CP}$ = 5.6 Hz, 2 C, C-11_{Ph}), 133.7 (d, $^{2}J_{CP}$ = 18.0 Hz, 2 C, C-10_{Ph}), 134.2 (d, $^{2}J_{CP}$ = 20.8 Hz, 2 C, C-2_{Ph}), 135.3 (d, $^{1}J_{CP}$ = 13.9 Hz, C-1_{Ph}), 145.2 (d, $^{1}J_{CP}$ = 20.8 Hz, C-9_{Ph}) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = -2.1 (s) ppm.