Phosphino Imidazoles and Imidazolium Salts for Suzuki *C*-*C* Coupling Reactions

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1 General synthesis procedure for phosphines 11a – f. To 0.5 g of **3a** (2.24 mmol), **3b** (1.68 mmol), **5** (1.52 mmol), **7** (1.42 mmol) or **9** (2.01 mmol) dissolved in in dry diethyl ether (**3a**, **5**, **7**, **9**, 40 mL) or tetrahydrofuran (**3b**, 40 mL) one eq of a 2.5 M solution of *n*-BuLi (**3a**, **5**, **7**, **9**) or a 2.0 M solution of lithium di-*i*-propylamide (**3b**) was added dropwise at -30 °C. After warming the solution to ambient temperature, it was again cooled to -30 °C and one eq of the chlorophosphines **10a** – **c** was added dropwise. The reaction mixture was stirred at ambient temperature for 2 h and the solvent was removed in vacuum. The crude product was purified by column chromatography on Silica or alumina and dried in vacuum.

1.1 Synthesis of 1-(4-bromophenyl))-2-(diphenylphosphino)-1*H*-imidazole (11a). Following the general procedure described above, **3a** (0.5 g, 2.24 mmol) was reacted with *n*-BuLi (0.90 mL, 2.25 mmol) and chlorodiphenylphosphine (**10a**, 0.40 mL, 2.23 mmol). The residue was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Phosphine **11a** was obtained as a colourless solid. Yield: 0.55 g (1.35 mmol, 60 % based on **3a**). Anal. Calcd. for $C_{21}H_{16}BrN_2P$ (407.24 g/mol): C, 61.93; H, 3.96; N, 6.88. Found: C, 61.85; H, 3.98; N, 6.87. Mp.: 170 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1432 (m, P-C), 1480 (s, N=C), 1582 (w, C=C), 3052/3138 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 7.09 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, H^o/C$_6H_4$), 7.23 (dd, $^3J_{HH}$ = 1.2 Hz, $^4J_{HP}$ = 2.0 Hz, 1 H, H^4/C$_3H_2N_2$), 7.32 – 7.35 (m, 6 H, H^{m,p}/C$_6H_5$), 7.38 (d, $^3J_{HH}$ = 1.2 Hz, H^5/C$_3H_2N_2$), 7.41 – 7.45 (m, 4 H, H^o/C$_6H_5$), 7.52 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.9 Hz, 2 H, H^m/C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 122.6 (s, C^p/C_6H$_4$), 123.7 (s, C^4/C_3H$_2$N$_2$), 128.0 (d, $^4J_{CP}$ = 3.7 Hz, C^o/C_6H$_4$), 128.6 (d, $^3J_{CP}$ = 7.5 Hz, C^m/C_6H$_5$), 129.3 (s, C^p/C_6H$_5$), 131.7 (d, $^3J_{CP}$ = 1.6 Hz, C^5/C_3H$_2$N$_2$), 132.4 (s, C^m/C_6H$_4$), 134.0 (d, $^2J_{CP}$ = 20.8 Hz, C^o/C_6H$_5$), 135.3 (d, $^1J_{CP}$ = 4.8 Hz, C^i/C_6H$_5$), 137.1 (d, $^3J_{CP}$ = 1.8 Hz, C^i/C_6H$_4$), 147.0 (d, $^1J_{CP}$ =

7.4 Hz, $C^2/C_3H_2N_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -29.4 (s). HRMS (ESI-TOF) $C_{21}H_{16}BrN_2P$ $[M+nH]^+$ *m/z*: calcd.: 407.0307, found: 407.0255.

1.2 Synthesis of 1-(4-bromophenyl))-2-(dicyclohexylphosphino)-1*H*-imidazole (11b). Using the general procedure described above, **3a** (0.5 g, 2.24 mmol) was reacted with *n*-BuLi (0.90 mL, 2.25 mmol) and chlorodicyclohexylphosphine (**10b**, 0.50 mL, 2.26 mmol). The residue was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Phosphine **11b** was obtained as a colourless solid. Yield: 0.46 g (1.10 mmol, 49 % based on **3a**). Anal. Calcd. for $C_{21}H_{28}BrN_2P$ (419.34 g/mol): C, 60.15; H, 6.73; N, 6.68. Found: C, 60.25; H, 6.62; N, 6.66. Mp.: 139 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1445 (m, P-C), 1481/1501 (m, N=C), 1586 (w, C=C), 2847/2922 (s, C-H), 3097/3150 (w, =C-H). ^1H NMR (500.30 MHz, $CDCl_3$, δ): 0.95 – 1.04 (m, 2 H, C_6H_{11}), 1.08 – 1.30 (m, 8 H, C_6H_{11}), 1.55 – 1.57 (m, 2 H, C_6H_{11}), 1.61 – 1.72 (m, 8 H, C_6H_{11}), 2.08 – 2.13 (m, 2 H, H^1/C_6H_{11}), 7.13 (dd, $^3J_{HH}$ = 1.1 Hz, $^4J_{HP}$ = 2.3 Hz, 1 H, $H^4/C_3H_2N_2$), 7.18 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, $^5J_{HP}$ = 1.0 Hz, 2 H, H^o/C_6H_4), 7.33 (d, $^3J_{HH}$ = 1.0 Hz, 1 H, $H^5/C_3H_2N_2$), 7.57 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz, H^m/C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 26.5 (s, C_6H_{11}), 26.9 (d, J_{CP} = 8.1 Hz, C_6H_{11}), 27.1 (d, J_{CP} = 12.7 Hz, C_6H_{11}), 29.3 (d, J_{CP} = 7.1 Hz, C_6H_{11}), 30.4 (d, J_{CP} = 16.1 Hz, C_6H_{11}), 34.4 (d, $^1J_{CP}$ = 7.7 Hz, C^1/C_6H_{11}), 122.3 (s, C^p/C_6H_4), 123.1 (s, $C^4/C_3H_2N_2$), 128.9 (d, $^4J_{CP}$ = 4.3 Hz, C^o/C_6H_4), 130.9 (s, $C^5/C_3H_2N_2$), 132.2 (s, C^m/C_6H_4), 137.6 (d, $^3J_{CP}$ = 1.4 Hz, C^i/C_6H_4), 147.4 (d, $^1J_{CP}$ = 19.9 Hz, $C^2/C_3H_2N_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -24.4 (s). HRMS (ESI-TOF) $C_{21}H_{28}BrN_2P$ $[M+nH]^+$ *m/z*: calcd.: 419.1246, found: 419.1224.

1.3 Synthesis of 1-(4-bromophenyl))-2-(di-2-furylphosphino)-1*H*-imidazole (11c). Based on the general procedure described above, **3a** (0.5 g, 2.24 mmol) was reacted with *n*-BuLi (0.90 mL, 2.25 mmol) and chlorodi-2-furylphosphine (**10c**, 0.45 g, 2.24 mmol). The residue was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using diethyl ether as eluent. Phosphine **11c** was obtained as colourless solid. Yield: 0.45 g (1.16 mmol, 52 % based on **3a**). Anal. Calcd. for $C_{17}H_{12}BrN_2O_2P$ (387.17 g/mol): C, 52.74; H, 3.12; N, 7.24. Found: C, 52.83; H, 3.09; N, 7.24. Mp.: 146 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1007 (s, C-O), 1449 (m, P-C), 1483/1498 (m, N=C), 1546 (w, C=C), 3073/3094/3112/3137 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 6.38 (dt $^4J_{HP}$ = 1.6 Hz, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 2 H, H^4/C$_4H_3$O), 6.77 (m, 2 H, H^3/C$_4H_3$O), 7.07 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, $^5J_{HP}$ = 1.1 Hz, 2 H, H^o/C$_6H_4$), 7.14 (pt, $^3J_{HH}$ = 1.4 Hz, H^4/C$_3H_2N_2$), 7.33 (d, $^3J_{HH}$ = 1.1 Hz, H^5/C$_3H_2N_2$), 7.51 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, H^m/C$_6H_4$), 7.65 (m, 2 H, H^5/C$_4H_3$O). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 111.0 (d, $^3J_{CP}$ = 6.6 Hz, C^4/C_4H$_3$O), 122.5 (d, $^2J_{CP}$ = 26.3 Hz, C^3/C_4H$_3$O), 122.7 (s, C^p/C_6H$_4$), 123.8 (s, C^4/C_3H$_2$N$_2$), 127.8 (d, $^4J_{CP}$ = 3.5 Hz, C^o/C_6H$_4$), 131.7 (d, $^3J_{CP}$ = 3.5 Hz, C^5/C_3H$_2$N$_2$), 132.4 (s, C^m/C_6H$_4$), 136.9 (m, C^i/C_6H$_4$), 143.7 (d, $^1J_{CP}$ = 7.8 Hz, C^2/C_4H$_3$O), 147.6 (m, C^2/C_3H$_2$N$_2$), 148.0 (d, $^4J_{CP}$ = 2.9 Hz, C^5/C_4H$_3$O). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -73.0 (s). HRMS (ESI-TOF) $C_{17}H_{12}BrN_2O_2P$ $[M+nH]^+$ *m/z*: calcd.: 386.9893, found: 386.9882; $[M+nNa]^+$ *m/z*: calcd.: 408.9712, found: 408.9698.

1.4 Synthesis of 1-(4-iodophenyl)-2-(diphenylphosphino)-4,5-dimethyl-1*H*-imidazole (11d). Compound **3b** (0.5 g, 1.68 mmol) was reacted with lithium di-*iso*-propylamide (0.84 mL, 1.68 mmol) and chlorodiphenylphosphine (**10a**, 0.31 mL, 1.73 mmol) as described earlier. The crude product was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Phosphine **11d** was obtained as a colourless solid. Yield: 0.53 g (1.10 mmol, 65 % based on **3b**). Anal. Calcd.

for $C_{23}H_{20}IN_2P$ (482.30 g/mol): C, 57.28; H, 4.18; N, 5.81. Found: C, 56.86; H, 4.36; N, 5.49. Mp.: 189 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1433 (m, P-C), 1479/1487 (s, N=C), 1581 (w, C=C), 2913 (w, C-H), 3048 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 1.96 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 6.77 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HP}$ = 0.9 Hz, 2 H, H^o/C$_6H_4$), 7.28 – 7.30 (m, 6 H, H^{m,p}/C$_6H_5$), 7.40 – 7.44 (m, 4 H, H^o/C$_6H_5$), 7.70 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, H^m/C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.7 (s, *C*H$_3$), 13.2 (s, *C*H$_3$), 94.5 (s, C^p/*C*$_6$H$_4$), 127.1 (s, C^4/*C*$_3$N$_2$), 128.5 (d, $^3J_{CP}$ = 7.6 Hz, C^m/*C*$_6$H$_5$), 128.9 (s, C^p/*C*$_6$H$_5$), 130.1 (d, $^4J_{CP}$ = 2.7 Hz, C^o/*C*$_6$H$_4$), 133.8 (d, $^2J_{CP}$ = 20.1 Hz, C^o/*C*$_6$H$_5$), 136.1 (d, $^1J_{CP}$ = 5.4 Hz, C^i/C$_6$H$_5$), 136.7 (d, $^3J_{CP}$ = 2.0 Hz, C^5/*C*$_3$N$_2$), 137.1 (d, $^3J_{CP}$ = 2.3 Hz, C^i/*C*$_6$H$_4$), 138.4 (s, C^m/*C*$_6$H$_4$), 143.9 (d, $^1J_{CP}$ = 2.6 Hz, C^2/(CH$_3$)$_2$*C*$_3$N$_2$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -29.1 (s). HRMS (ESI-TOF) $C_{23}H_{20}IN_2P$ $[M+nH]^+$ *m/z*: calcd.: 483.0482, found: 483.0479.

1.5 Synthesis of 1-(4-iodophenyl))-2-(dicyclohexylphosphino)-4,5-dimethyl-1*H*-imidazole (11e). Compound **3b** (0.5 g, 1.68 mmol) was reacted with lithium di-*iso*-propylamide (0.84 mL, 1.68 mmol) and chlorodicyclohexylphosphine (**10b**, 0.37 mL, 1.68 mmol) as described earlier. The residue was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Molecule **11e** was obtained as a colourless solid. Yield: 0.46 g (0.93 mmol, 55 % based on **3b**). Anal. Calcd. for $C_{23}H_{32}IN_2P$ (494.39 g/mol): C, 55.88; H, 6.52; N, 5.67. Found: C, 56.19; H, 6.62; N, 5.65. Mp.: 181 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1435 (m, P-C), 1459 (s, N=C), 1582 (w, C=C), 2855/2914/2936 (w, C-H), 3049/3070 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.97 – 1.06 (m, 2 H, C$_6H_{11}$), 1.09 – 1.30 (m, 8 H, C$_6H_{11}$), 1.56 – 1.58 (m, 2 H, C$_6H_{11}$), 1.61 – 1.72 (m, 8 H, C$_6H_{11}$), 1.93 (s, 3 H, CH_3), 2.07 – 2.12 (m, 2 H, H^1/C$_6H_{11}$), 2.25 (s, 3 H, CH_3), 6.85 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HP}$ = 0.7 Hz, 2 H, H^o/C$_6H_4$), 7.78 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, H^m/C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.8 (s, *C*H$_3$), 13.1

(s, CH_3), 26.5 (s, C_6H_{11}), 27.0 (d, J_{CP} = 8.7 Hz, C_6H_{11}), 27.1 (d, J_{CP} = 13.5 Hz, C_6H_{11}), 29.5 (d, J_{CP} = 7.7 Hz, C_6H_{11}), 30.6 (d, J_{CP} = 16.6 Hz, C_6H_{11}), 34.5 (d, $^1J_{CP}$ = 7.3 Hz, C^1/C_6H_{11}), 94.3 (s, C^p/C_6H_4), 125.8 (s, C^4/C_3N_2), 130.8 (d, $^4J_{CP}$ = 2.7 Hz, C^o/C_6H_4), 135.8 (s, C^5/C_3N_2), 137.7 (s, C^i/C_6H_4), 138.3 (s, C^m/C_6H_4), 144.9 (d, $^1J_{CP}$ = 13.4 Hz, C^2/C_3N_2). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -23.6 (s). HRMS (ESI-TOF) $C_{23}H_{32}IN_2P$ $[M+nH]^+$ *m/z*: calcd.: 495.1421, found: 495.1380.

1.6 Synthesis of 1-(4-iodophenyl))-2-(di-2-furylphosphino)-4,5-dimethyl-1*H*-imidazole (11f). Following the synthesis methodology described above, **3b** (0.5 g, 1.68 mmol) was reacted with lithium di-*i*-propylamide (0.84 mL, 1.68 mmol) and chlorodi-2-furylphosphine (**10c**, 0.37 mL, 1.68 mmol). The crude product was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using diethyl ether as eluent. Product **11f** was obtained as colourless solid. Yield: 0.52 g (1.13 mmol, 55 % based on **3b**). Anal. Calcd. for $C_{19}H_{16}IN_2O_2P$ (462.22 g/mol): C, 49.37; H, 3.49; N, 6.06. Found: C, 49.37; H, 3.65; N, 5.83. Mp.: 132 °C. IR (KBr, $\tilde{\nu}/cm^{-1}$): 1006 (s, C-O), 1454 (m, P-C), 1488 (s, N=C), 1550/1589 (w, C=C), 2914 (w, C-H), 3031/3045/3077 (w, =C-H). ^1H NMR (500.30 MHz, $CDCl_3$, δ): 1.92 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 6.35 (dt $^4J_{HP}$ = 1.6 Hz, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.7 Hz, 2 H, H^4/C_4H_3O), 6.71 (m, 2 H, H^3/C_4H_3O), 6.80 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, $^5J_{HP}$ = 0.9 Hz, 2 H, H^o/C_6H_4), 7.62 (m, 2 H, H^5/C_4H_3O), 7.72 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, H^m/C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 9.5 (s, CH_3), 13.2 (s, CH_3), 94.4 (s, C^p/C_6H_4), 111.0 (d, $^3J_{CP}$ = 6.9 Hz, C^4/C_4H_3O), 121.9 (d, $^2J_{CP}$ = 26.4 Hz, C^3/C_4H_3O), 127.4 (s, C^4/C_3N_2), 129.8 (d, $^4J_{CP}$ = 2.5 Hz, C^o/C_6H_4), 136.7 (d, $^3J_{CP}$ = 4.3 Hz, C^5/C_3N_2), 136.8 (d, $^3J_{CP}$ = 1.3 Hz, C^i/C_6H_4), 138.4 (s, C^m/C_6H_4), 140.4 (d, $^1J_{CP}$ = 12.1 Hz, C^2/C_3N_2), 147.7 (d, $^4J_{CP}$ = 2.7 Hz, C^5/C_4H_3O), 148.1 (d, $^1J_{CP}$ = 3.0 Hz, C^2/C_4H_3O). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -72.9 (s). HRMS (ESI-TOF) $C_{19}H_{16}IN_2O_2P$ $[M+nH]^+$ *m/z*: calcd.: 463.0066, found: 463.0067.

1.7 Synthesis of 1-(4-ferrocenylphenyl))-2-(diphenylphosphino)-1*H*-imidazole (11g). Molecule **5** (0.5 g, 1.52 mmol) was reacted with *n*-BuLi (0.61 mL, 1.53 mmol) and chlorodiphenylphosphine (**10a**, 0.28 mL, 1.56 mmol) as described above. The crude product was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 2:5, *v*:*v*) as eluent. The title compound **11g** was obtained as an orange solid. Yield: 0.49 g (0.96 mmol, 63 % based on **5**). Anal. Calcd. for $C_{31}H_{25}FeN_2P$ (512.36 g/mol): C, 72.67; H, 4.92; N, 5.47. Found: C, 72.24; H, 5.25; N, 5.39. Mp.: 171 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1431 (m, P-C), 1458/1475 (m, N=C), 1531/1537 (m, C=C), 2852/2923/2957 (w, C-H), 3043/3082 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 4.05 (s, 5 H, C_5H_5), 4.35 (pt, $^3J_{HH}$ = 1.8 Hz, C_5H_4), 4.64 (pt, $^3J_{HH}$ = 1.8 Hz, C_5H_4), 7.13 (dpt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.0 Hz, $^5J_{HP}$ = 1.3 Hz, 2 H, H^o/C_6H_4), 7.28 (dd, $^3J_{HH}$ = 1.2 Hz, $^4J_{HP}$ = 2.0 Hz, 1 H, H^5/$C_3H_2N_2$), 7.33 – 7.44 (m, 6 H, H^{m,p}/C_6H_5), 7.39 (d, $^3J_{HH}$ = 1.1 Hz, H^4/$C_3H_2N_2$), 7.42 – 7.47 (m, 6 H, H^o/C_6H_5 + H^m/C_6H_4). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 66.8 (s, C_5H_4), 69.5 (s, C_5H_4), 69.9 (s, C_5H_5), 84.0 (s, C^i/C_5H_4), 123.9 (s, C^4/$C_3H_2N_2$), 126.4 (d, $^4J_{CP}$ = 3.9 Hz, C^o/C_6H_4), 126.5 (s, C^p/C_6H_5), 128.6 (d, $^3J_{CP}$ = 7.4 Hz, C^m/C_6H_5), 129.2 (s, C^m/C_6H_4), 131.5 (d, $^3J_{CP}$ = 1.7 Hz, C^5/$C_3H_2N_2$), 134.1 (d, $^2J_{CP}$ = 20.8 Hz, C^o/C_6H_5), 135.6 (d, $^3J_{CP}$ = 1.7 Hz, C^i/C_6H_4), 135.7 (d, $^1J_{CP}$ = 5.5 Hz, C^i/C_6H_5), 140.2 (s, C^p/C_6H_4), 146.9 (d, $^1J_{CP}$ = 6.6 Hz, C^2/$C_3H_2N_2$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -28.0 (s). HRMS (ESI-TOF) $C_{31}H_{25}FeN_2P$ $[M+nH]^+$ *m/z*: calcd.: 513.1159, found: 513.1178.

1.8 Synthesis of 1-(4-(ethynylferrocenyl)phenyl))-2-(diphenylphosphino)-1*H*-imidazole (11h). **7** (0.5 g, 1.42 mmol) was reacted with *n*-BuLi (0.57 mL, 1.43 mmol) and chlorodiphenylphosphine (**10a**, 0.26 mL, 1.45 mmol) as described earlier. The residue was purified by column chromatography on Silica (column size: 12 × 3.5 cm) using diethyl ether as eluent. The product **11h** was obtained as orange solid. Yield: 0.34 g (0.63 mmol, 44 % based on **7**).

Anal. Calcd. for $C_{33}H_{25}FeN_2P$ (536.38 g/mol): C, 73.89; H, 4.70; N, 5.22. Found: C, 73.34; H, 4.85; N, 5.15. Mp.: 139 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1433 (m, P-C), 1477 (w, N=C), 1519 (m, C=C), 2204 (w, C≡C), 2852/2922 (w, C-H), 3050 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 4.25 (s, 5 H, C_5H_5), 4.27 (pt, $^3J_{HH}$ = 1.8 Hz, C_5H_4), 4.52 (pt, $^3J_{HH}$ = 1.8 Hz, C_5H_4), 7.18 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.8 Hz, $^5J_{HP}$ = 1.3 Hz, 2 H, H^o/C_6H_4), 7.26 (m, 1 H, H^5/$C_3H_2N_2$), 7.33 – 7.36 (m, 6 H,), 7.39 (d, $^3J_{HH}$ = 0.9 Hz, H^4/$C_3H_2N_2$), 7.43 – 7.46 (m, 6 H, H^{m,p}/C_6H_5), 7.49 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.8 Hz, 2 H, H^m/C_6H_4). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 64.8 (s, C^i/C_5H_4), 69.2 (s, C_5H_4), 70.2 (s, C_5H_5), 71.6 (s, C_5H_4), 84.8 (s, C≡C), 90.4 (s, C≡C), 123.7 (s, C^4/$C_3H_2N_2$), 124.6 (s, C^p/C_6H_4), 126.4 (d, $^4J_{CP}$ = 4.2 Hz, C^o/C_6H_4), 128.6 (d, $^3J_{CP}$ = 7.8 Hz, C^m/C_6H_5), 129.2 (s, C^p/C_6H_5), 131.7 (d, $^3J_{CP}$ = 1.3 Hz, C^5/$C_3H_2N_2$), 132.1 (s, C^m/C_6H_4), 134.0 (d, $^2J_{CP}$ = 20.9 Hz, C^o/C_6H_5), 135.6 (d, $^3J_{CP}$ = 5.1 Hz, C^i/C_6H_5), 137.1 (d, $^1J_{CP}$ = 1.7 Hz, C^i/C_6H_4), 146.9 (d, $^1J_{CP}$ = 7.8 Hz, C^2/$C_3H_2N_2$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -29.1 (s). HRMS (ESI-TOF) $C_{33}H_{25}FeN_2P$ $[M+nH]^+$ *m/z*: calcd.: 537.1109, found: 537.1178.

1.9 Synthesis of 1-(4-(1,1'-biphenyl))-2-(diphenylphosphino)-4,5-dimethyl-1*H*-imidazole (11i). Based on the general procedure described earlier, **9** (0.5 g, 2.01 mmol) was reacted with *n*-BuLi (0.80 mL, 2.00 mmol) and chlorodiphenylphosphine (**10a**, 0.36 mL, 2.01 mmol). The residue was purified by column chromatography on alumina (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Phosphine **11i** was obtained as a colourless solid. Yield: 0.58 g (1.34 mmol, 67 % based on **9**). Anal. Calcd. for $C_{29}H_{25}N_2P$ (432.50 g/mol): C, 80.53; H, 5.83; N, 6.48. Found: C, 80.35; H, 5.98; N, 6.48. Mp.: 151 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1432 (m, P-C), 1488 (s, N=C), 1587 (m, C=C), 2850/2916 (w, C-H), 3045/3062 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 2.02 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 7.12 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HP}$ = 0.8 Hz, 2 H, H^3/C_6H_5-C_6H_4), 7.28 –

7.31 (m, 6 H, $H^{m,p}/C_6H_5$), 7.39 (m, 1 H, $H^{4'}/C_6H_5$-C_6H_4), 7.45 – 7.49 (m, 6 H, $H^{3'}/C_6H_5$-C_6H_4+H^{o}/C_6H_5), 7.60 (dpt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, $H^{2'}/C_6H_5$-C_6H_4), 7.62 (dpt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, H^{2}/C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 9.8 (s, CH_3), 13.3 (s, CH_3), 127.3 (s, $C^{2'}/C_6H_5$-C_6H_4), 127.3 (s, C^{i}), 127.8 (s, C^{2}/C_6H_5-C_6H_4), 127.9 (s, $C^{4'}/C_6H_5$-C_6H_4), 128.4 (d, $^3J_{CP}$ = 7.6 Hz, C^{m}/C_6H_5), 128.6 (d, $^4J_{CP}$ = 2.7 Hz, C^{3}/C_6H_5-C_6H_4), 128.7 (s, $C^{3'}/C_6H_5$-C_6H_4), 129.0 (s, C^{p}/C_6H_5), 133.8 (d, $^2J_{CP}$ = 20.6 Hz, C^{o}/C_6H_5), 136.5 (s, C^{i}), 136.5 (d, $^3J_{CP}$ = 1.5 Hz, C^{4}/ C_6H_5-C_6H_4), 136.5 (d, $^1J_{CP}$ = 2.4 Hz, C^{i}/C_6H_5), 140.1 (s, C^{i}), 141.6 (s, C^{i}), 144.0 (d, $^1J_{CP}$ = 1.2 Hz, C^{2}/C_3N_2). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -28.9 (s). HRMS (ESI-TOF) $C_{29}H_{25}N_2P$ $[M\text{-}nH]^+$ *m/z*: calcd.: 433.1783, found: 433.1828.

1.10 Synthesis of 1-(4-(1,1'-biphenyl))-2-(dicyclohexylphosphino)-4,5-dimethyl-1*H*-imidazole (11j). Using the general synthesis methodology described above, **9** (0.5 g, 2.01 mmol) was reacted with *n*-BuLi (0.80 mL, 2.00 mmol) and chlorodicyclohexylphosphine (**10b**, 0.44 mL, 1.99 mmol). The residue was purified by column chromatography on alumina (column size: 12 × 3.5 cm) using a mixture of *n*-hexane-diethyl ether (ratio 2:1, *v*:*v*) as eluent. Phosphine **11j** was obtained as a colourless solid. Yield: 0.54 g (1.21 mmol, 61 % based on **9**). Anal. Calcd. for $C_{29}H_{37}N_2P$ (444.59 g/mol): C, 78.34; H, 8.39; N, 6.30. Found: C, 78.77; H, 8.61; N, 6.14. Mp.: 131 °C. IR (KBr, $\tilde{\upsilon}/cm^{-1}$): 1442 (m, P-C), 1488/1518 (m, N=C), 1591 (w, C=C), 2846/2922 (s, C-H), 3034 (w, =C-H). ^1H NMR (500.30 MHz, $CDCl_3$, δ): 1.06 – 1.31 (m, 10 H, C_6H_{11}), 1.62 – 1.75 (m, 10 H, C_6H_{11}), 1.97 (s, 3 H, CH_3), 2.10 – 2.16 (m, 2 H, H^{1}/C_6H_{11}), 2.28 (s, 3 H, CH_3), 7.18 (m, 2 H, H^{3}/C_6H_5-C_6H_4), 7.37 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, $H^{4'}/C_6H_5$-C_6H_4), 7.46 (m, 2 H, $H^{3'}$/ C_6H_5-C_6H_4), 7.64 (dpt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, $H^{2'}/C_6H_5$-C_6H_4), 7.68 (dpt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, H^{2}/C_6H_5-C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 9.8 (s, CH_3), 13.2 (s, CH_3), 26.6 (s, C_6H_{11}), 27.0 (d, J_{CP} = 8.4 Hz, C_6H_{11}), 27.1 (d, J_{CP} = 12.6 Hz, C_6H_{11}), 29.6 (d, J_{CP} = 8.0 Hz, C_6H_{11}), 30.5 (d,

J_{CP} = 16.9 Hz, C_6H_{11}), 34.6 (d, J_{CP} = 7.4 Hz, C^{1}/C_6H_{11}), 126.0 (s, C^{i}), 127.3 (s, $C^{2'}/C_6H_5$-C_6H_4), 127.7 (s, C^{2}/C_6H_5-C_6H_4), 127.8 (s, $C^{4'}/C_6H_5$-C_6H_4), 129.0 (s, $C^{3'}/C_6H_5$-C_6H_4), 129.2 (d, $^{4}J_{CP}$ = 2.7 Hz, C^{3}/C_6H_5-C_6H_4), 135.6 (s, C^{i}), 137.1 (d, $^{3}J_{CP}$ = 2.3 Hz, C^{4}/C_6H_5-C_6H_4), 140.2 (s, C^{i}), 141.3 (s, C^{i}), 144.9 (d, $^{1}J_{CP}$ = 12.1 Hz, C^{2}/C_3N_2). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -23.5 (s). HRMS (ESI-TOF) $C_{29}H_{37}N_2P$ $[M\text{-}nH]^+$ *m/z*: calcd.: 445.2725, found: 445.2767.

1.11 Synthesis of 1-(4-(1,1'-biphenyl))-2-(di-2-furyl-phosphino)-4,5-dimethyl-1*H*-imidazole (11k). Following the general synthesis methodology described above, **9** (0.5 g, 2.01 mmol) was reacted with *n*-BuLi (0.80 mL, 2.00 mmol) and chlorodi-2-furylphosphine (**10c**, 0.40 g, 1.99 mmol). The residue was purified by column chromatography on alumina (column size: 12 × 3.5 cm) using diethyl ether as eluent. Phosphine **11k** was obtained as a colourless solid. Yield: 0.59 g (1.43 mmol, 72 % based on **9**). Anal. Calcd. for $C_{25}H_{21}N_2O_2P$ (412.42 g/mol): C, 72.81; H, 5.13; N, 6.79. Found: C, 72.87; H, 5.27; N, 6.47. Mp.: 126 °C. IR (KBr, $\tilde{\upsilon}/cm^{-1}$): 1006 (s, C-O), 1449 (m, P-C), 1486/1518 (s, N=C), 1548/1584 (w, C=C), 2918 (w, C-H), 3029/3078/3100/3125 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 1.98 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 6.34 (dt $^{4}J_{HP}$ = 1.6 Hz, $^{3}J_{HH}$ = 3.4 Hz, $^{3}J_{HH}$ = 1.8 Hz, 2 H, H^{4}/C_4H_3O), 6.74 (m, 2 H, H^{3}/C_4H_3O), 7.14 (dpt, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.9 Hz, $^{5}J_{HP}$ = 0.8 Hz, 2 H, H^{3}/C_{65}-C_6H_4), 7.38 (tt, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.8 Hz, 2 H, $H^{4'}/C_6H_5$-C_6H_4), 7.47 (m, 2 H, $H^{3'}/C_6H_5$-C_6H_4), 7.60 – 7.63 (m, 6 H, H^{5}/C_4H_3O + H^{2}/C_6H_5-C_6H_4 + $H^{2'}/C_6H_5$-C_6H_4). $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 6.4 (s, CH_3), 13.2 (s, CH_3), 110.7 (d, $^{3}J_{CP}$ = 6.8 Hz, C^{4}/C_4H_3O), 121.6 (d, $^{1}J_{CP}$ = 25.9 Hz, C^{3}/C_4H_3O), 127.1 (s, C^{2}/C_6H_5-C_6H_4), 127.4 (s, C^{4}/C_3N_2), 127.6 (s, $C^{2'}/C_6H_5$-C_6H_4), 127.8 (s, $C^{4'}/C_6H_5$-C_6H_4), 128.1 (d, $^{4}J_{CP}$ = 2.5 Hz, C^{3}/C_6H_5-C_6H_4), 128.9 (s, $C^{3'}/C_6H_5$-C_6H_4), 136.0 (m, C^{5}/C_3N_2), 136.4 (d, $^{3}J_{CP}$ = 3.8 Hz, C^{4}/C_6H_5-C_6H_4), 139.9 (s, $C^{1,1'}/C_6H_5$-C_6H_4), 140.3 (d, $^{1}J_{CP}$ = 13.5 Hz, C^{2}/C_3N_2), 141.5 (s,

$C^{1,1'}/C_6H_5$-C_6H_4), 147.4 (d, $^4J_{CP}$ = 2.8 Hz, C^5/C_4H_3O), 148.3 (d, $^1J_{CP}$ = 3.1 Hz, C^1/C_4H_3O). HRMS (ESI-TOF) $C_{25}H_{21}N_2O_2P$ $[M+nH]^+$ *m/z*: calcd.: 413.1365, found: 413.1413.

2 General procedure for the synthesis of seleno phosphines 11a-Se – f-Se. To a toluene solution of **11a** – **f** (100 mg), 2 eq of elemental selenium was added in a single portion and stirred for 2 h at 100 °C. After cooling to ambient temperature, the solvent was removed in membrane-pump vacuum and the respective seleno phosphines were purified by column chromatography on Silica (column size: 2.5 × 8 cm) and dried in membrane-pump vacuum.

2.1 Synthesis of 1-(4-bromophenyl))-2-(diphenylphosphino selenide)-1*H*-imidazole (11a-Se). Using the general procedure described above, **11a** (100 mg, 0.25 mmol) was reacted with elemental selenium (40 mg, 0.51 mmol, 2 eq). The crude product was purified by column chromatography using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Compound **11a-Se** was obtained as a colourless solid. Yield: 0.10 g (0.21 mmol, 84 % based on **11a**). Anal. Calcd. for $C_{21}H_{16}BrN_2PSe$ (486.20 g/mol): C, 51.88; H, 3.32; N, 5.76. Found: C, 52.28; H, 3.31; N, 5.74. Mp.: 160 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 576 (s, P-Se), 1435 (m, P-C), 1484/1497 (m, N=C), 1560 (w, C=C), 3046/3069/3145 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 7.00 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^o/C_6H_4), 7.17 (dd, $^3J_{HH}$ = 1.2 Hz, $^4J_{HP}$ = 1.7 Hz, 1 H, $H^4/C_3H_2N_2$), 7.30 (dpt, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, H^m/C_6H_4), 7.33 (pt, $^3J_{HH}$ = 1.0 Hz, $H^5/C_3H_2N_2$), 7.40 – 7.44 (m, 4 H, H^m/C_6H_5), 7.47 – 7.51 (m, 2 H, H^p/C_6H_5), 7.82 – 7.87 (m, 4 H, H^o/C_6H_5). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 123.1 (s, C^p/C_6H_4), 126.8 (d, $^3J_{CP}$ = 1.8 Hz, $C^4/C_3H_2N_2$), 128.5 (d, $^3J_{CP}$ = 13.4 Hz, C^m/C_6H_5), 129.0 (s, C^o/C_6H_4), 130.3 (d, $^3J_{CP}$ = 43.1 Hz, $C^5/C_3H_2N_2$), 130.6 (d, $^1J_{CP}$ = 54.4 Hz, C^i/C_6H_5), 131.8 (s, C^m/C_6H_4), 132.0 (d, $^4J_{CP}$ = 3.3 Hz, C^p/C_6H_5), 132.9 (d, $^2J_{CP}$ = 11.3 Hz, C^o/C_6H_5), 136.4 (s,

C^{i}/C_6H_4), 139.7 (d, $^{1}J_{CP}$ = 120.8 Hz, $C^{2}/C_3H_2N_2$). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 19.1 ($^{1}J_{PSe}$ = 753.4 Hz). HRMS (ESI-TOF) $C_{21}H_{16}BrN_2PSe$ $[M+nH]^+$ *m/z*: calcd.: 486.9470, found: 486.9413; $[M+nNa]^+$ *m/z*: calcd.: 508.9290, found: 508.9222; $[2M+nNa]^+$ *m/z*: calcd.: 994.8681, found: 994.8595.

2.2 Synthesis of 1-(4-bromophenyl))-2-(dicyclohexylphosphino selenide)-1*H*-imidazole (11b-Se). Using the synthesis methodology described earlier, **11b** (100 mg, 0.24 mmol) was reacted with elemental selenium (38 mg, 0.48 mmol, 2 eq). The crude product was purified by column chromatography using mixture of *n*-hexane-diethyl ether (ratio 10:1, *v*:*v*) as eluent. Molecule **11b-Se** was obtained as colourless solid. Yield: 0.11 g (0.22 mmol, 92 % based on **11b**). Anal. Calcd. for $C_{21}H_{28}BrN_2PSe$ (498.30 g/mol): C, 50.62; H, 5.66; N, 5.62. Found: C, 50.60; H, 5.64; N, 5.52. Mp.: 170 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 558 (s, P-Se), 1445 (m, P-C), 1481/1497 (m, N=C), 1589 (w, C=C), 2928/2846 (s, C-H), 3133/3108 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 1.11 – 1.19 (m, 2 H, C_6H_{11}), 1.20 – 1.36 (m, 6 H, C_6H_{11}), 1.49 – 1.58 (m, 2 H, C_6H_{11}), 1.61 – 1.67 (m, 4 H, C_6H_{11}), 1.76 – 1.82 (m, 4 H, C_6H_{11}), 1.91 – 1.93 (m, 2 H, H^{1}/C_6H_{11}), 2.41 – 2.48 (m, 2 H, H^{1}/C_6H_{11}), 7.06 (pt, $^{3}J_{HH}$ = 1.2 Hz, 1 H, $H^{4}/C_3H_2N_2$), 7.19 (dpt, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2 H, H^{o}/C_6H_4), 7.33 (pt, $^{3}J_{HH}$ = 0.8 Hz, 1 H, $H^{5}/C_3H_2N_2$), 7.53 (dpt, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 2.0 Hz, H^{m}/C_6H_4). $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 26.9 (d, J_{CP} = 1.3 Hz, C_6H_{11}), 26.1 (s, C_6H_{11}), 26.2 (d, J_{CP} = 8.0 Hz, C_6H_{11}), 26.4 (d, J_{CP} = 7.0 Hz, C_6H_{11}), 26.7 (d, J_{CP} = 3.8 Hz, C_6H_{11}), 39.9 (d, $^{1}J_{CP}$ = 45.3 Hz, C^{1}/C_6H_{11}), 123.5 (s, C^{p}/C_6H_4), 126.9 (s, $C^{4}/C_3H_2N_2$), 129.4 (d, $^{3}J_{CP}$ = 12.6 Hz, $C^{5}/C_3H_2N_2$), 130.2 (s, C^{o}/C_6H_4), 131.6 (s, C^{m}/C_6H_4), 135.4 (d, $^{1}J_{CP}$ = 92.3 Hz, $C^{2}/C_3H_2N_2$), 136.8 (s, C^{i}/C_6H_4). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 41.6 ($^{1}J_{PSe}$ = 724.5 Hz). HRMS (ESI-TOF) $C_{21}H_{28}BrN_2PSe$ $[M+nH]^+$ *m/z*: calcd.: 499.0409, found: 499.0363; $[M+nNa]^+$ *m/z*: calcd.: 521.0229, found: 521.0195; $[2M]^+$ *m/z*: calcd.: 996.0662, found: 996.0560.

2.3 Synthesis of 1-(4-bromophenyl))-2-(di-2-furylphosphino selenide)-1*H*-imidazole (11c-Se). Reaction of **11c** (100 mg, 0.26 mmol) with elemental selenium (41 mg, 0.52 mmol, 2 eq) gave, after purification by column chromatography using diethyl ether as eluent, **11c-Se** as a colourless solid. Yield: 0.11 g (0.24 mmol, 92 % based on **11c**). Anal. Calcd. for $C_{17}H_{12}BrN_2O_2PSe$ (466.13 g/mol): C, 43.80; H, 2.59; N, 6.01. Found: C, 43.76; H, 2.59; N, 5.82. Mp.: 128 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 587 (s, P-Se), 1010 (s, C-O), 1455 (m, P-C), 1483/1494 (m, N=C), 1547 (w, C=C), 3090/3107/3128/3145 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 6.43 (dt $^4J_{HP}$ = 1.7 Hz, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.8 Hz, 2 H, H^4/C$_4H_3$O), 7.14 (dd, $^3J_{HH}$ = 1.0 Hz, $^4J_{HP}$ = 1.8 Hz, 1 H, H^4/C$_3H_2N_2$), 7.20 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^o/C$_6H_4$), 7.24 (m, 2 H, H^3/C$_4H_3$O), 7.32 (pt, $^3J_{HH}$ = 1.0 Hz, H^5/C$_3H_2N_2$), 7.39 (dpt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz, H^m/C$_6H_4$), 7.67 (m, 2 H, H^5/C$_4H_3$O). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 111.7 (d, $^3J_{CP}$ = 10.2 Hz, C^4/C_4H$_3$O), 123.2 (s, C^p/C_6H$_4$), 125.6 (d, $^2J_{CP}$ = 24.9 Hz, C^3/C_4H$_3$O), 126.5 (s, C^4/C_3H$_2$N$_2$), 128.4 (s, C^o/C_6H$_4$), 131.3 (d, $^3J_{CP}$ = 18.2 Hz, C^5/C_3H$_2$N$_2$), 131.9 (s, C^m/C_6H$_4$), 135.5 (s, C^i/C_6H$_4$), 138.6 (d, $^1J_{CP}$ = 139.9 Hz, C^2/C_3H$_2$N$_2$), 143.7 (d, $^1J_{CP}$ = 121.8 Hz, C^2/C_4H$_3$O), 149.3 (d, $^4J_{CP}$ = 7.3 Hz, C^5/C_4H$_3$O). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -20.7 ($^1J_{PSe}$ = 789.9 Hz). HRMS (ESI-TOF) $C_{17}H_{12}BrN_2O_2PSe$ $[M+nH]^+$ *m/z*: calcd.: 466.9055, found: 466.9056.

2.4 Synthesis of 1-(4-iodophenyl)-2-(diphenylphosphino selenide)-4,5-dimethyl-1*H*-imidazole (11d-Se). Compound **11d** (100 mg, 0.21 mmol) was reacted with elemental selenium (33 mg, 0.42 mmol, 2 eq) as described earlier. The residue was purified by column chromatography using a mixture of *n*-hexane-diethyl ether (ratio 1:2, *v*:*v*) as eluent. Seleno phosphine **11d-Se** was obtained as colourless solid. Yield: 0.10 g (0.18 mmol, 86 % based on **11d**). Anal. Calcd. for $C_{23}H_{20}IN_2PSe$ (561.26 g/mol): C, 49.22; H, 3.59; N, 4.99. Found: C,

48.91; H, 3.65; N, 4.91. Mp.: 86 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 557 (s, P-Se), 1435 (m, P-C), 1488 (m, N=C), 1580 (w, C=C), 2910/2965 (s, C-H), 3048 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 1.87 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 6.68 (dpt, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2 H, H^{o}/C$_6H_4$), 7.35 – 7.39 (m, 4 H, H^{m}/C$_6H_5$), 7.43 – 7.45 (m, 2 H, H^{p}/C$_6H_5$), 7.47 (dpt, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 2.0 Hz, H^{m}/C$_6H_4$), 7.81 – 7.86 (m, 4 H, H^{o}/C$_6H_5$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.5 (s, *C*H$_3$), 13.1 (s, *C*H$_3$), 94.8 (s, C^{p}/*C*$_6$H$_4$), 128.3 (d, $^{3}J_{CP}$ = 12.9 Hz, C^{m}/*C*$_6$H$_5$), 130.1 (s, C^{4}/*C*$_3$N$_2$), 130.7 (s, C*o*/*C*$_6$H$_4$), 130.9 (d, $^{1}J_{CP}$ = 81.6 Hz, C^{i}/*C*$_6$H$_5$), 131.6 (d, $^{4}J_{CP}$ = 2.8 Hz, C^{p}/C$_6$H$_5$), 133.0 (d, $^{2}J_{CP}$ = 11.4 Hz, C^{o}/*C*$_6$H$_5$), 135.8 (s, C^{i}/*C*$_6$H$_4$), 136.1 (d, $^{3}J_{CP}$ = 14.8 Hz, C^{5}/*C*$_3$N$_2$), 136.5 (d, $^{1}J_{CP}$ = 125.8 Hz, C^{2}/C$_3$N$_2$), 137.9 (s, C^{m}/*C*$_6$H$_4$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): 17.6 ($^{1}J_{PSe}$ = 745.4 Hz). HRMS (ESI-TOF) $C_{23}H_{20}IN_2PSe$ [M+nH]$^{+}$ *m/z*: calcd.: 562.9648, found: 562.9607; [M+nNa]$^{+}$ *m/z*: calcd.: 584.9467, found: 584.9415; [2M+nNa]$^{+}$ *m/z*: calcd.: 1146.9051, found: 1146.8976.

2.5 Synthesis of 1-(4-iodophenyl))-2-(dicyclohexylphosphino selenide)-4,5-dimethyl-1*H*-imidazole (11e-Se). Molecule **11e** (100 mg, 0.20 mmol) was reacted with elemental selenium (32 mg, 0.41 mmol, 2 eq) as described above. The crude product was purified by column chromatography using a mixture of *n*-hexane-diethyl ether (ratio 1:1, *v*:*v*) as eluent. Molecule **11e-Se** was obtained as colourless solid. Yield: 0.11 g (0.19 mmol, 95 % based on **11e**). Anal. Calcd. for $C_{23}H_{32}IN_2PSe$ (573.35 g/mol): C, 48.18; H, 5.63; N, 4.89. Found: C, 47.91; H, 5.79; N, 4.79. Mp.: 210 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 576 (m P-Se), 1444 (m, P-C), 1488 (m, N=C), 1590 (w, C=C), 2848/2926 (s, C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 1.12 –1.33 (m, 8 H, C$_6H_{11}$), 1.48 – 1.56 (m, 2 H, C$_6H_{11}$), 1.61 – 1.67 (m, 4 H, C$_6H_{11}$), 1.75 – 1.80 (m, 4 H, C$_6H_{11}$), 1.83 (s, 3 H, CH_3), 1.88 – 1.90 (m, 2 H, C$_6H_{11}$), 2.23 (s, 3 H, CH_3), 2.39 – 2.45 (m, 2 H, C$_6H_{11}$), 6.90 (dpt, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 2.6 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2 H, H^{o}/C$_6H_4$), 7.74 (dpt, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 2.6 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2 H, H^{m}/C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.6 (s, *C*H$_3$), 13.0 (s, *C*H$_3$), 26.0 (d, J_{CP} = 1.4 Hz, *C*$_6$H$_{11}$), 26.2 (d, J_{CP} = 6.8 Hz,

C_6H_{11}), 26.3 (d, J_{CP} = 8.4 Hz, C_6H_{11}), 26.4 (d, J_{CP} = 14.3 Hz, C_6H_{11}), 26.8 (d, J_{CP} = 3.7 Hz, C_6H_{11}), 39.9 (d, $^1J_{CP}$ = 45.7 Hz, C^1/C_6H_{11}), 95.0 (s, C^p/C_6H_4), 131.4 (s, C^o/C_6H_4), 129.3 (s, C^4/C_3N_2), 132.6 (d, $^1J_{CP}$ = 97.8 Hz, C^2/C_3N_2), 135.2 (d, $^3J_{CP}$ = 10.3 Hz, C^5/C_3N_2), 136.7 (s, C^i/C_6H_4), 137.9 (s, C^m/C_6H_4). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 41.2 ($^1J_{PSe}$ = 717.5 Hz). HRMS (ESI-TOF) $C_{23}H_{32}IN_2PSe$ $[M+nH]^+$ *m/z*: calcd.: 575.0587, found: 575.0521.

2.6 Synthesis of 1-(4-iodophenyl))-2-(di-2-furylphosphino selenide)-4,5-dimethyl-1*H*-imidazole (11f-Se). Phosphine **11f** (100 mg, 0.22 mmol) was reacted with elemental selenium (35 mg, 0.44 mmol, 2 eq) as described earlier. The crude product was purified by column chromatography using diethyl ether as eluent. Compound **11f-Se** was obtained as colourless solid. Yield: 0.11 g (0.20 mmol, 91 % based on **11f**). Anal. Calcd. for $C_{19}H_{16}IN_2O_2PSe$ (541.18 g/mol): C, 42.17; H, 2.98; N, 5.18. Found: C, 42.32; H, 3.10; N, 5.07. Mp.: 142 °C. IR (NaCl, $\tilde{\upsilon}/cm^{-1}$): 583 (s, P-Se), 1004 (s, C-O), 1456 (m, P-C), 1488 (s, N=C), 1550/1578 (w, C=C), 2918 (w, C-H), 3120 (w, =C-H). ^1H NMR (500.30 MHz, $CDCl_3$, δ): 1.90 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 6.41 (dt $^4J_{HP}$ = 1.7 Hz, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.8 Hz, 2 H, H^4/C_4H_3O), 6.90 (dpt, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^o/C_6H_4), 7.19 (m, 2 H, H^3/C_4H_3O), 7.58 (dpt, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 2.1 Hz, H^m/C_6H_4), 7.65 (m, 2 H, H^5/C_4H_3O). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 9.3 (s, CH_3), 13.1 (s, CH_3), 94.9 (s, C^p/C_6H_4), 111.6 (d, $^3J_{CP}$ = 10.1 Hz, C^4/C_4H_3O), 125.4 (d, $^2J_{CP}$ = 24.5 Hz, C^3/C_4H_3O), 129.9 (s, C^o/C_6H_4), 130.4 (s, C^4/C_3N_2), 135.4 (s, C^i/C_6H_4), 135.9 (s, C^5/C_3N_2), 137.1 (d, $^3J_{CP}$ = 17.2 Hz, $C^2/(CH_3)_2C_3N_2$), 138.1 (s, C^m/C_6H_4), 144.2 (d, $^1J_{CP}$ = 120.8 Hz, C^2/C_4H_3O), 149.0 (d, $^4J_{CP}$ = 7.3 Hz, C^5/C_4H_3O). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): -21.4 ($^1J_{PSe}$ = 781.0 Hz). HRMS (ESI-TOF) $C_{19}H_{16}IN_2O_2PSe$ $[M+nH]^+$ *m/z*: calcd.: 542.9233, found: 542.9206; $[M+nNa]^+$ *m/z*: calcd.: 564.9052, found: 564.9003.

3 General procedure for the synthesis of imidazolium salts 16a – 16d. To **3a** – **c** (0.5 g) dissolved in acetonitrile (50 mL) one eq of *n*-BuI (**12a**) or *n*-$C_8H_{17}I$ (**12b**) was added in a single portion and the reaction mixture was stirred at 70 °C for 5 (**12a**) or 14 (**12b**) days. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After completion of the reaction the solvent was removed in membrane-pump vacuum. The crude product was washed five times with diethyl ether (10 mL portions) and dried in membrane-pump vacuum.

3.1 Synthesis of 1-(4-bromophenyl)-3-^{n}butyl-1*H*-imidazolium iodide (16a). Following the synthesis methodology described above, **3a** (0.5 g, 2.24 mmol) was reacted with *n*-BuI (**12a**, 0.30 mL, 2.64 mmol, 1.2 eq). After appropriate work-up, the product was obtained as pale beige solid. Yield: 0.90 g (2.21 mmol, 99 % based on **3a**). Anal. Calcd. for $C_{13}H_{16}BrIN_2$ (407.09 g/mol): C, 38.36; H, 3.96; N, 6.88. Found: C, 38.40; H, 3.92; N, 6.64. Mp.: 120 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1496/1550 (s, N=C), 1590 (m, C=C), 2851/2872/2891/2932/2963/2995 (m – s, C-H), 3045/3073/3155 (w, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.93 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.39 (sext, $^3J_{HH}$ = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.95 (quint, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 4.50 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.63 (dpt, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.2 Hz, 2 H, $H^{o,m}/C_6H_4$), 7.76 (pt, $^3J_{HH}$ = 1.8 Hz, 1 H, $C_3H_3N_2$), 7.78 (dpt, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, $H^{o,m}$ /C_6H_4), 7.92 (pt, $^3J_{HH}$ = 1.9 Hz, 1 H, $C_3H_3N_2$), 10.54 (pt, $^4J_{HH}$ = 1.5 Hz, 1 H, $H^2/C_3H_3N_2$). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 13.5 (s, $CH_2CH_2CH_2CH_3$), 19.5 (s, $CH_2CH_2CH_2CH_3$), 32.1 (s, $CH_2CH_2CH_2CH_3$), 50.4 (s, $CH_2CH_2CH_2CH_3$), 121.3 (s, $C_3H_3N_2$), 123.6 (s, $C_3H_3N_2$), 123.8 (s, C^o/C_6H_4), 124.3 (s, C^p/C_6H_4), 133.3 (s, C^i/C_6H_4), 133.6 (s, C^m/C_6H_4), 135.0 (s, $C^2/C_3H_3N_2$). HRMS (ESI-TOF) $[C_{13}H_{16}BrN_2]^+$ $[M]^+$ *m/z*: calcd.: 279.0494, found: 279.0491.

3.2 Synthesis of 1-(4-bromophenyl)-3-^{n}octyl-1*H*-imidazolium hexafluorophosphate ([16b]PF$_6$). Compound **3a** (0.5 g, 2.24 mmol) was reacted with *n*-$C_8H_{17}I$ (**12b**, 0.41 mL, 2.27 mmol) as described earlier giving, after appropriate work-up, the imidazolium salt **16b** as yellow solid. Please, notice that due to the long reaction time, impurities were present which could not be removed, neither by chromatography nor precipitation. Therefore, the hexafluorophosphate salt was prepared by addition of a solution of potassium hexafluorophosphate (0.20 g, 1.09 mmol) in water (20 mL) to **16b** (0.5 g, 1.08 mmol) dissolved in acetone (20 mL). After stirring at ambient temperature for 1 h, the solvent was removed in membrane-pump vacuum and the crude product was purified by column chromatography on Silica (column size: 10 × 2 cm) using acetone as eluent. Compound **[16b]PF$_6$** was obtained as a pale yellow solid. Yield: 0.45 g (0.94 mmol, 87 % based on **3a**). Anal. Calcd. for $C_{17}H_{24}BrF_6N_2P$ (481.25 g/mol): C, 42.43; H, 5.03; N, 5.82. Found: C, 42.23; H, 4.95; N, 5.73. Mp.: 101 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1493 (m, N=C), 1549/1561 (m, C=C), 2851/2921/2950 (s, C-H), 3042/3060 (m, =C-H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.80 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.15 – 1.23 (m, 6 H, $CH_2(CH_2)_6CH_3$), 1.26 – 1.37 (m, 4 H, $CH_2(CH_2)_6CH_3$), 1.95 (pent, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 4.47 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 7.62 (m, 2 H, H^o/C_6H_4), 7.71 (m, 1 H, H^{4,5}/$C_3H_3N_2$), 7.78 (m, 2 H, H^m/C_6H_4), 7.94 (m, 1 H, H^{4,5}/$C_3H_3N_2$), 10.52 (s, 1 H, H^2/C_3H_3N2). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 14.0 (s, $CH_2(CH_2)_6CH_3$), 22.5 (s, $CH_2(CH_2)_6CH_3$), 26.2 (s, $CH_2(CH_2)_6CH_3$), 28.9 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 30.2 (s, $CH_2(CH_2)_6CH_3$), 31.6 (s, $CH_2(CH_2)_6CH_3$), 50.7 (s, $CH_2(CH_2)_6CH_3$), 121.3 (s, $C_3H_3N_2$), 123.5 (s, $C_3H_3N_2$), 123.8 (s, C^o/C_6H_4), 124.3 (s, C^p/C_6H_4), 133.3 (s, C^i/C_6H_4), 133.6 (s, C^m/C_6H_4), 134.9 (s, C^2/$C_3H_3N_2$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): -144.5 (sept, $^1J_{PF}$ = 712.6 Hz, PF_6). HRMS (ESI-TOF) $[C_{17}H_{24}BrN_2]^+$ $[M]^+$ *m/z*: calcd.: 335.1107, found: 335.1117.

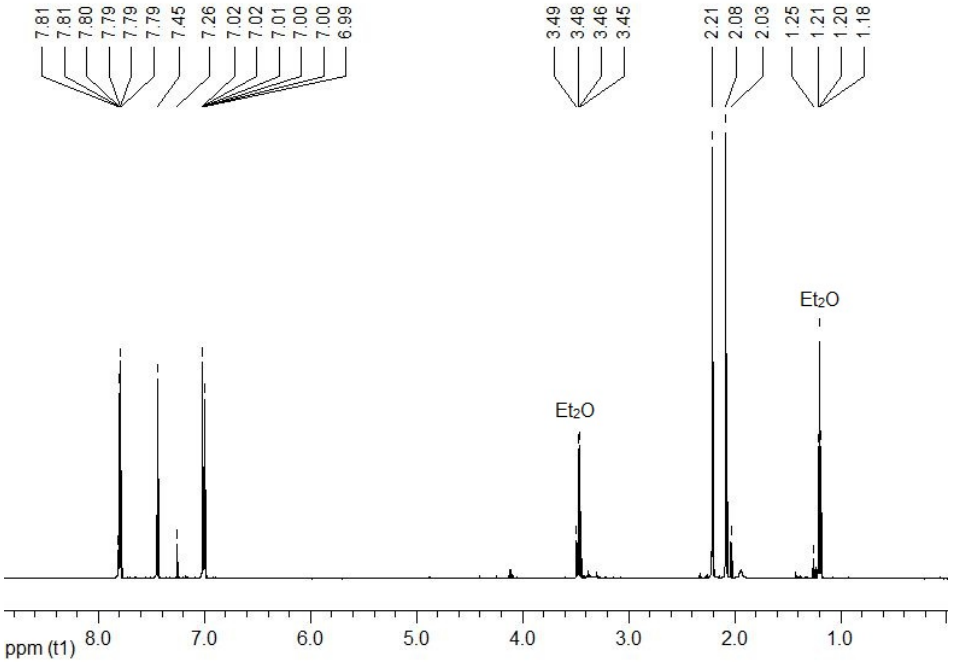
3.3 Synthesis of 1-(4-iodophenyl)-3-^{n}octyl-4,5-dimethyl-1*H*-imidazolium iodide (16c). Using the synthesis procedure described above, **3b** (0.5 g, 1.68 mmol) was reacted with *n*-$C_8H_{17}I$ (**12b**, 0.31 mL, 1.72 mmol). After appropriate work-up, **16c** was obtained as pale beige solid. Yield: 0.90 g (1.67 mmol, 99 % based on **3b**). Anal. Calcd. for $C_{19}H_{28}I_2N_2$ (538.25 g/mol): C, 42.40; H, 5.24; N, 5.20. Found: C, 42.19; H, 5.24; N, 4.93. Mp.: 175 °C. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1560 (s, N=C), 1636/1655 (m, C=C), 2855/2923/2974 (m, C-H), 3116 (w, =C-H).^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.87 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.26 – 1.41 (m, 10 H, $CH_2(CH_2)_6CH_3$), 1.93 (pent, $^3J_{HH}$ = 7.6 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 2.17 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.37 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 7.41 (dpt, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^o/C_6H_4), 7.92 (dpt, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^m/C_6H_4), 9.82 (s, 1 H, H^2/$(CH_3)_2C_3HN_2$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.1 (s, CH_3), 9.6 (s, CH_3), 14.1 (s, $CH_2(CH_2)_6CH_3$), 22.6 (s, $CH_2(CH_2)_6CH_3$), 26.4 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 29.9 (s, $CH_2(CH_2)_6CH_3$), 31.7 (s, $CH_2(CH_2)_6CH_3$), 47.9 (s, $CH_2(CH_2)_6CH_3$), 97.1 (s, C^p/C_6H_4), 127.2 (s, C_3HN_2), 127.4 (s, C_3HN_2), 127.9 (s, C^o/C_6H_4), 132.7 (s, C^i/C_6H_4), 134.7 (s, C^2/C_3HN_2), 139.4 (s, C^m/C_6H_4). HRMS (ESI-TOF) $[C_{19}H_{28}IN_2]I$ $[M]^+$ *m/z*: calcd.: 411.1250, found: 411.1292.

3.4 Synthesis of 1-phenyl-3-^{n}octyl-4,5-dimethyl-1*H*-imidazolium iodide (16d). Using the synthesis methodology described above, **3c** (0.5 g, 2.90 mmol) was reacted with *n*-$C_8H_{17}I$ (**12b**, 0.54 mL, 2.99 mmol). After appropriate work-up, **16d** could be isolated as yellow oil. Yield: 1.17 g (2.84 mmol, 98 % based on **3c**). Anal. Calcd. for $C_{19}H_{29}IN_2$ (412.35 g/mol): C, 55.34; H, 7.09; N, 6.79. Found: C, 55.04; H, 7.24; N, 6.21. IR (KBr, $\tilde{\upsilon}$/cm^{-1}): 1460 (m, P-C), 1498/1555 (s, N=C), 1596/1631 (m, C=C), 2854/2926/2954 (s, C-H), 3111 (w, =C-H).^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.77 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.14 – 1.35 (m, 10 H, $CH_2(CH_2)_6CH_3$), 1.84 (quint, $^3J_{HH}$ = 7.6 Hz, $CH_2(CH_2)_6CH_3$), 2.11 (s, 3 H, CH_3), 2.28

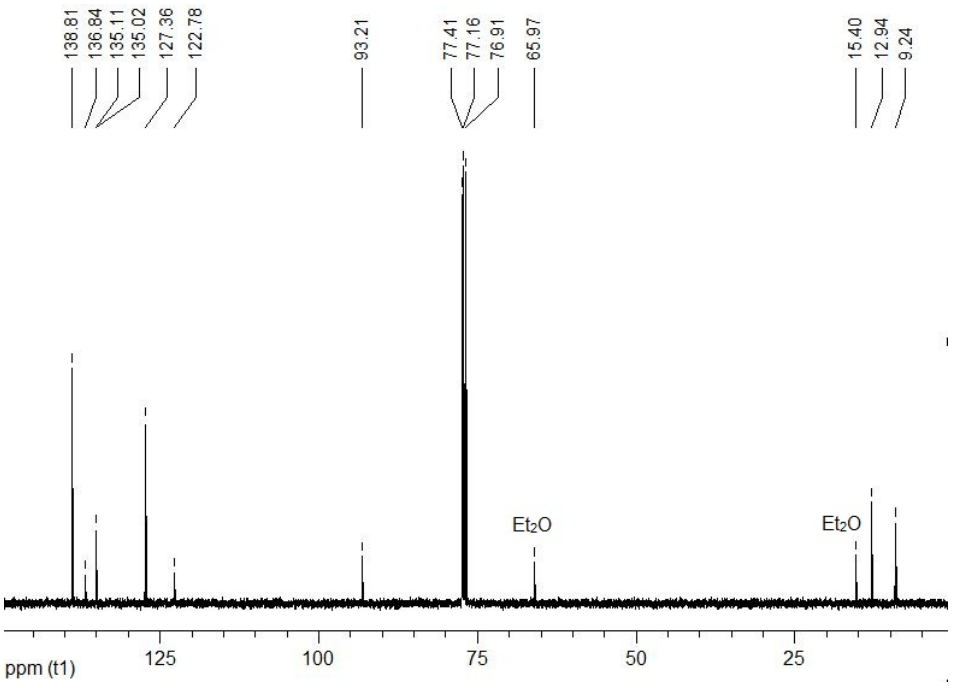
(s, 3 H, C*H*$_3$), 4.30 (t, $^3J_{HH}$ = 7.7 Hz, C*H*$_2$(CH$_2$)$_6$CH$_3$), 7.47 – 7.50 (m, 5 H, C$_6$*H*$_5$), 9.55 (s, 1 H, (CH$_3$)$_3$C$_3$*H*N$_2$). ^{13}C{^{1}H} NMR (125.81 MHz, CDCl$_3$, δ): 9.0 (s, *C*H$_3$), 9.4 (s, *C*H$_3$), 13.9 (s, CH$_2$(CH$_2$)$_6$*C*H$_3$), 22.4 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 26.2 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 28.9 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 28.9 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 29.8 (s, *C*H$_2$(CH$_2$)$_6$CH$_3$), 31.5 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 47.7 (s, CH$_2$(*C*H$_2$)$_6$CH$_3$), 125.9 (s, C^o/*C*$_6$H$_5$), 127.1 (s, *C*$_3$HN$_2$), 127.3 (s, *C*$_3$HN$_2$), 130.1 (s, C^m/*C*$_6$H$_5$), 130.6 (s, C^p/*C*$_6$H$_5$), 133.0 (s, C^i/*C*$_6$H$_5$), 134.4 (s, C^2/*C*$_3$HN$_2$). HRMS (ESI-TOF) [C$_{19}$H$_{29}$N$_2$]I [M]$^+$ *m/z*: calcd.: 285.2325, found: 285.2322.

NMR spectra of 3b

^{1}H NMR:

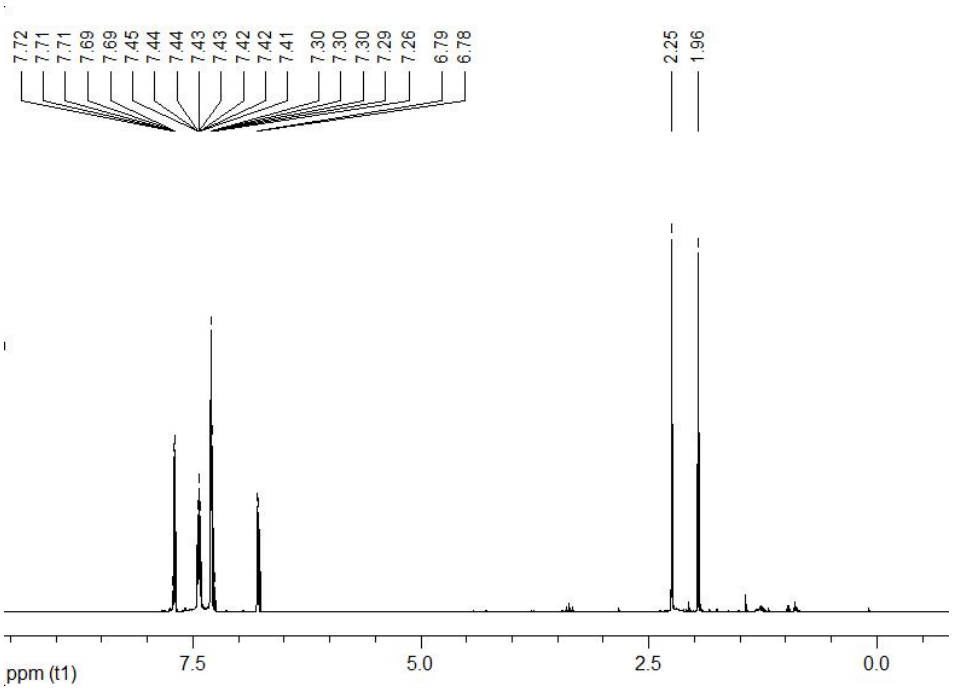


$^{13}C\{^{1}H\}$ NMR:

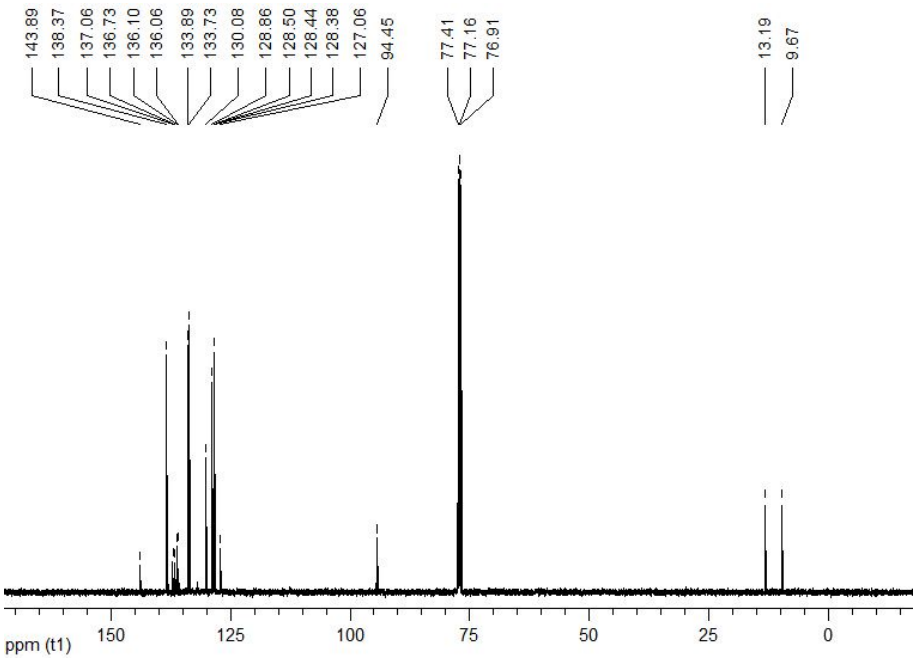


NMR spectra of 11d

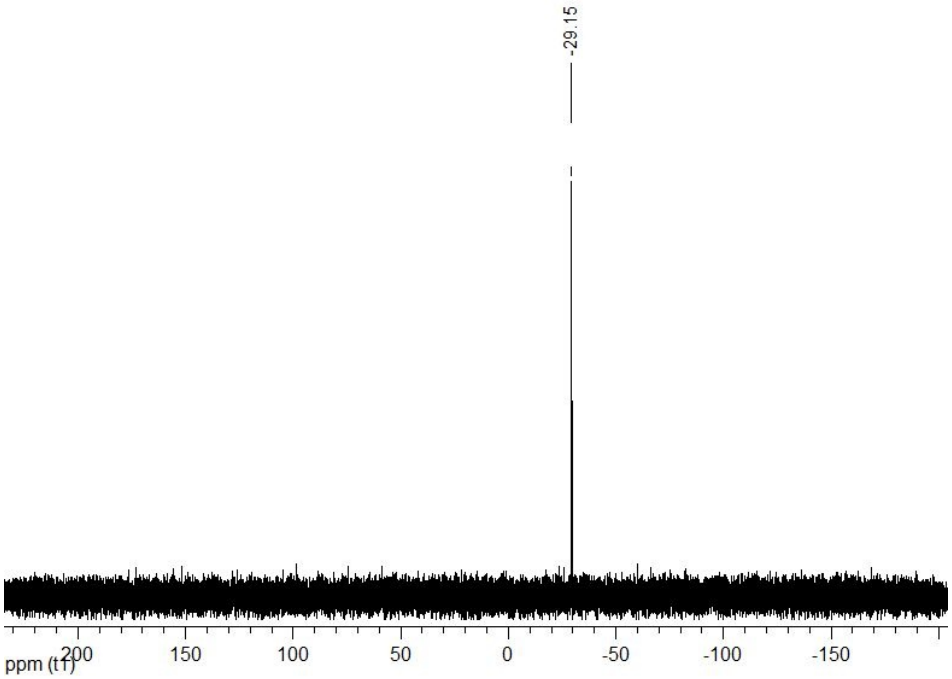
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:

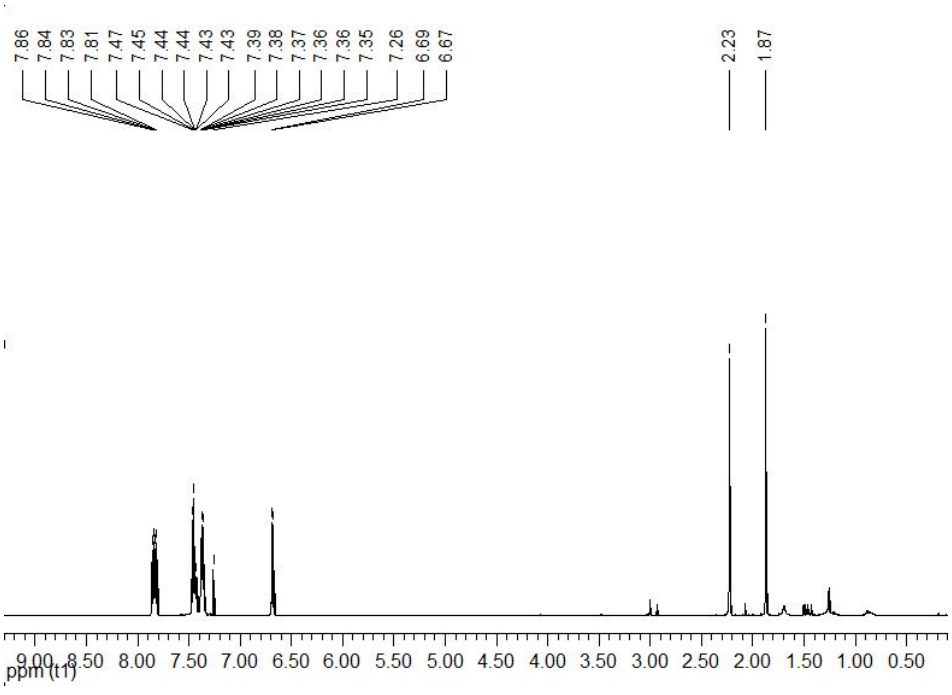


$^{31}P\{^{1}H\}$ NMR:

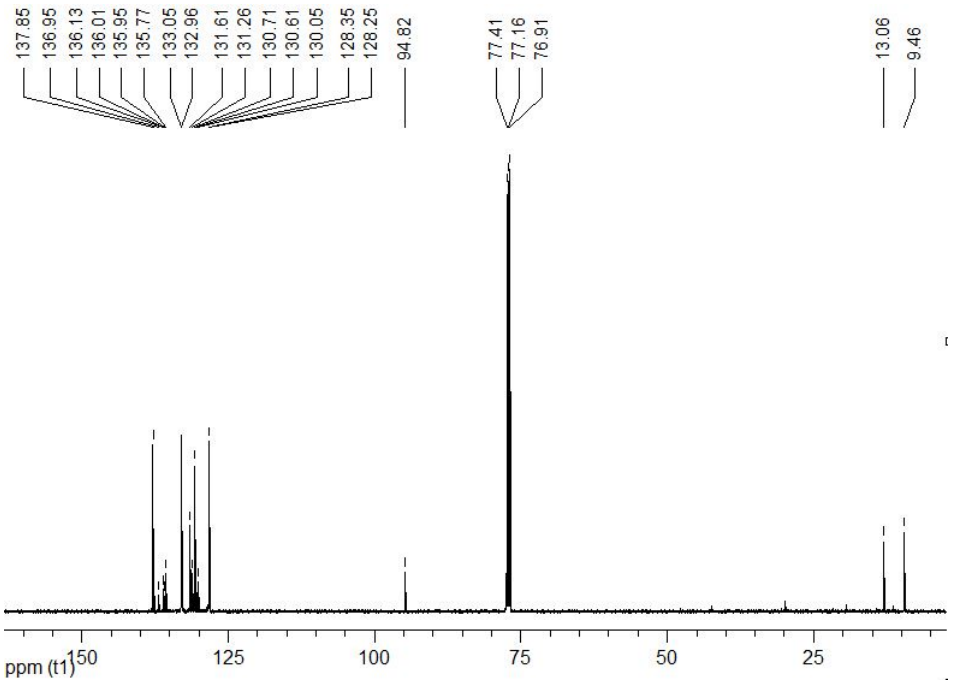


NMR spectra of 11d-Se

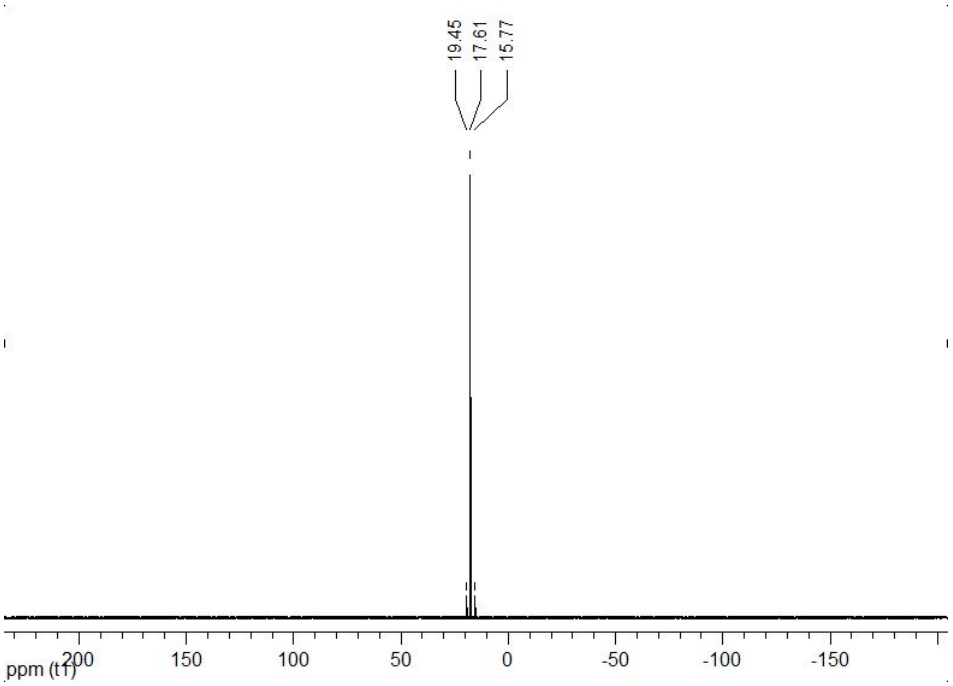
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:

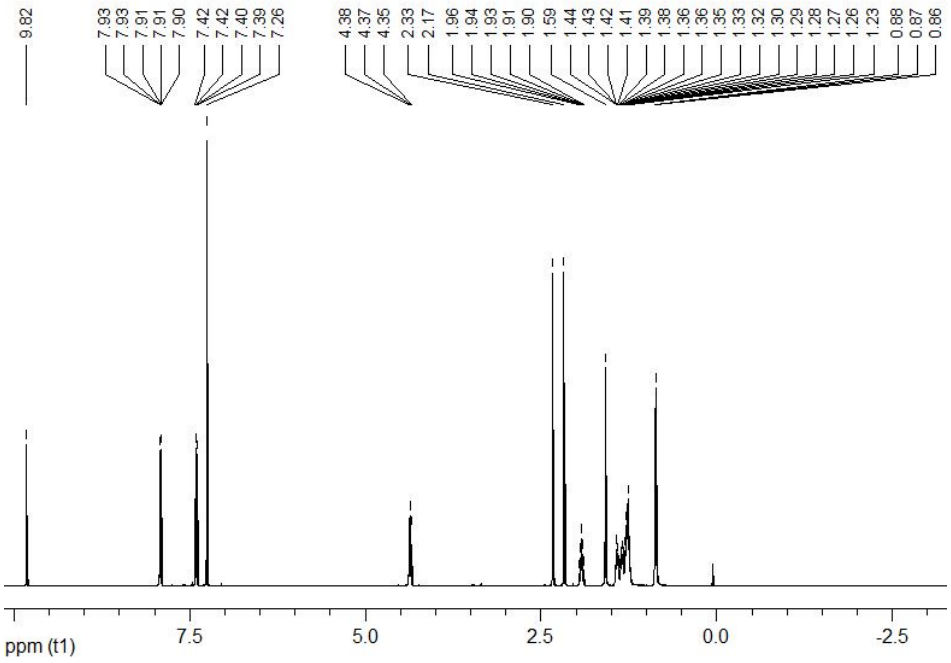


$^{31}P\{^{1}H\}$ NMR:

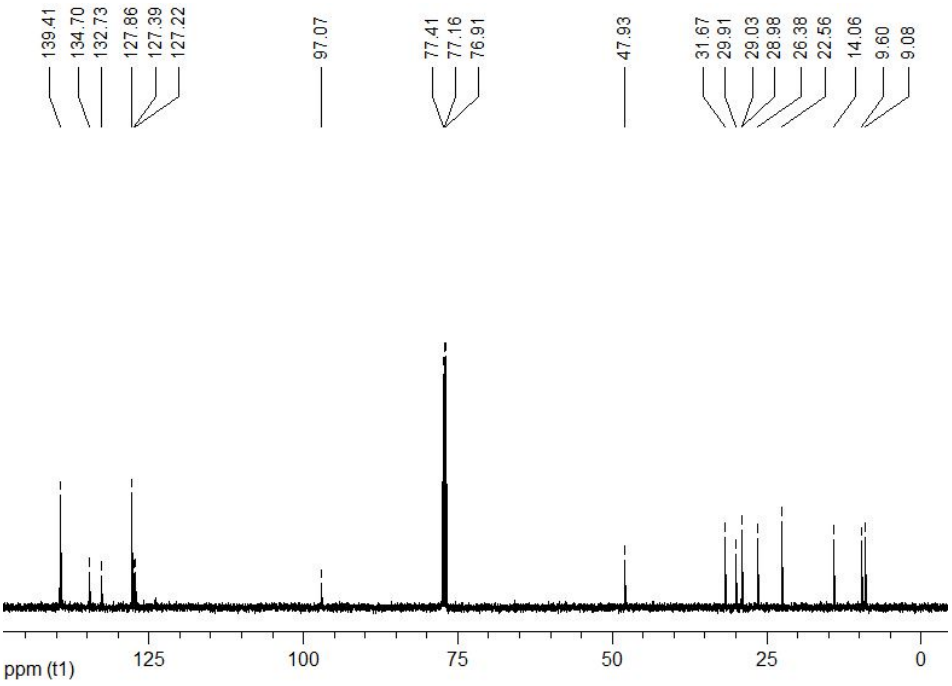


NMR spectra of 16c

^{1}H NMR:

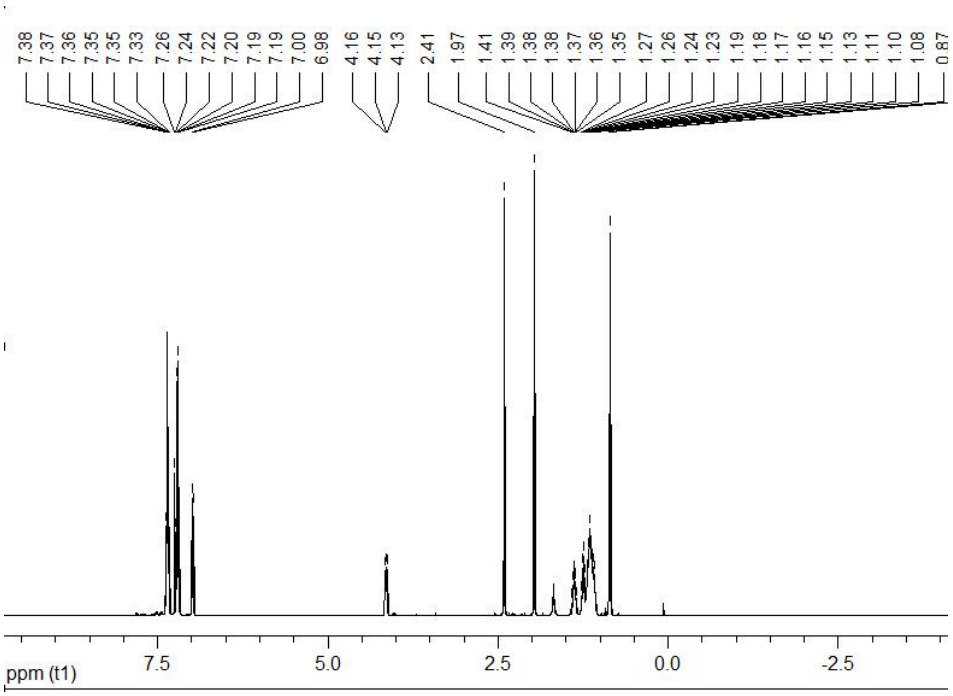


$^{13}C\{^{1}H\}$ NMR:

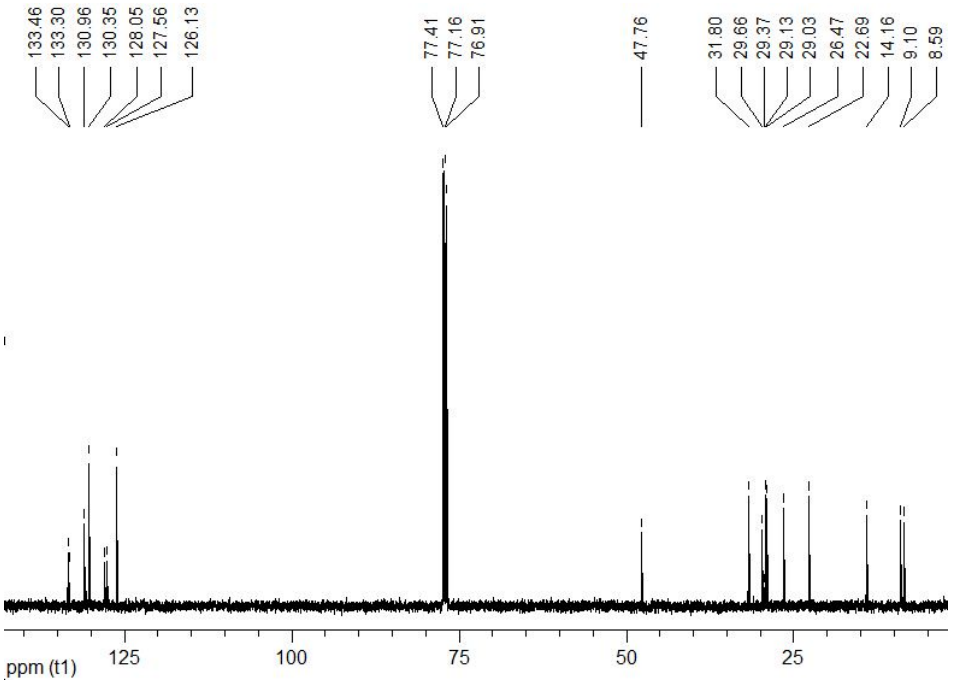


NMR spectra of 17a

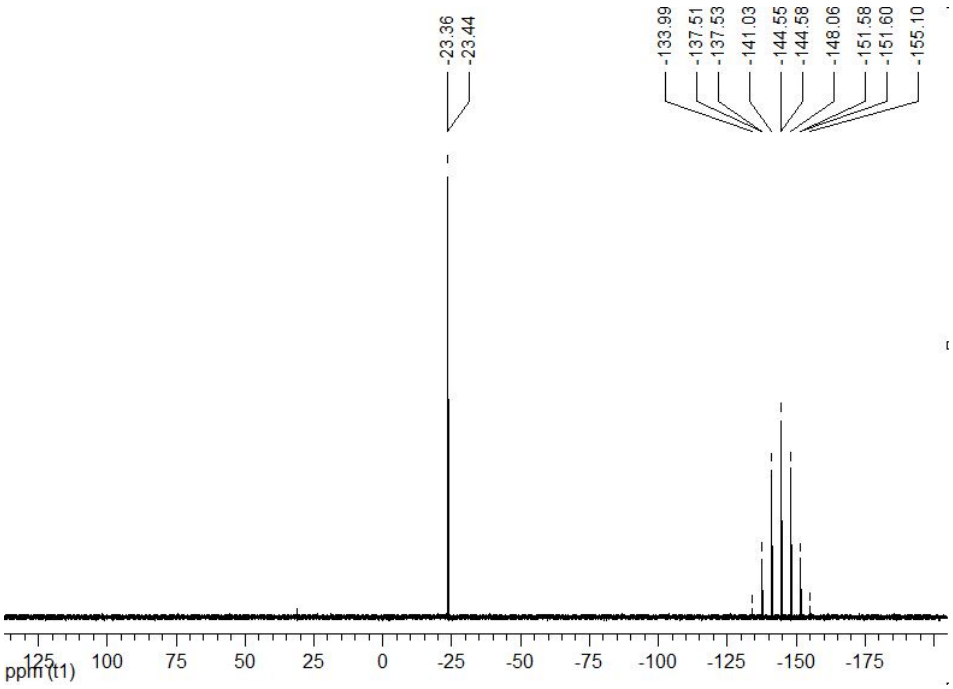
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:

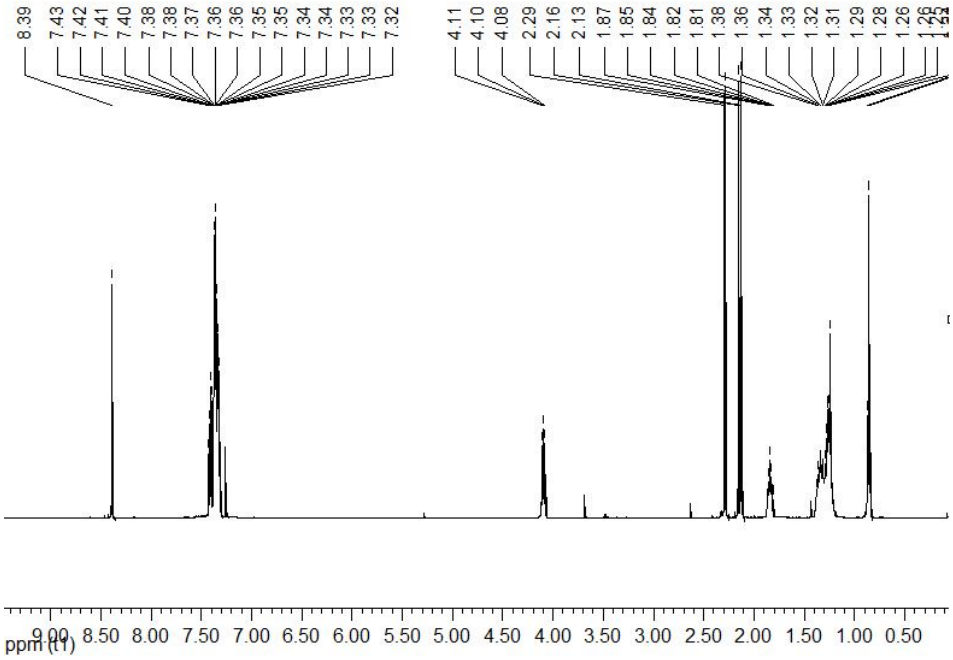


$^{31}P\{^{1}H\}$ NMR:

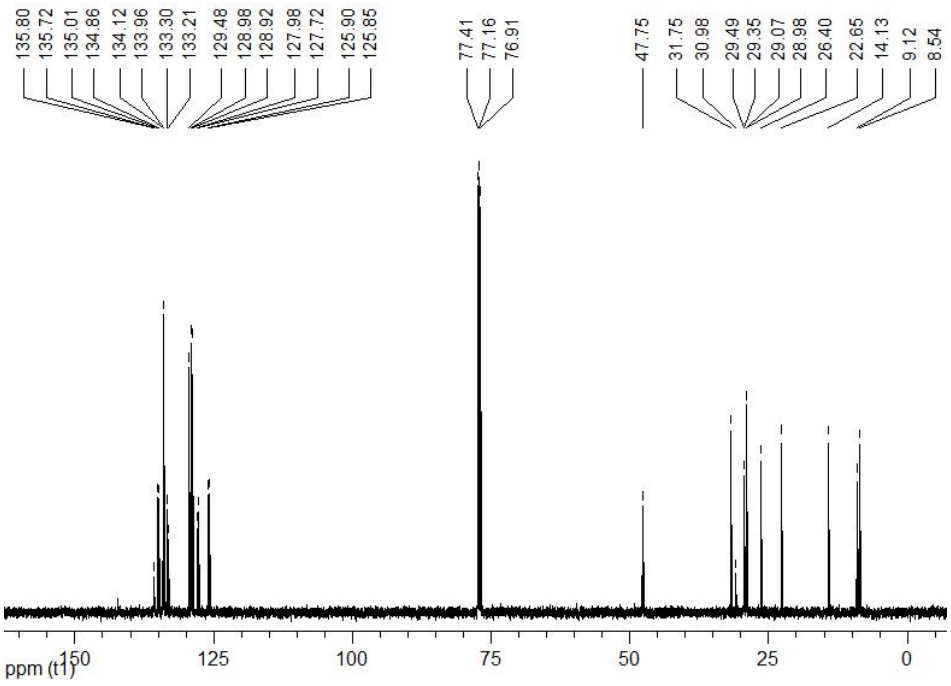


NMR spectra of 20

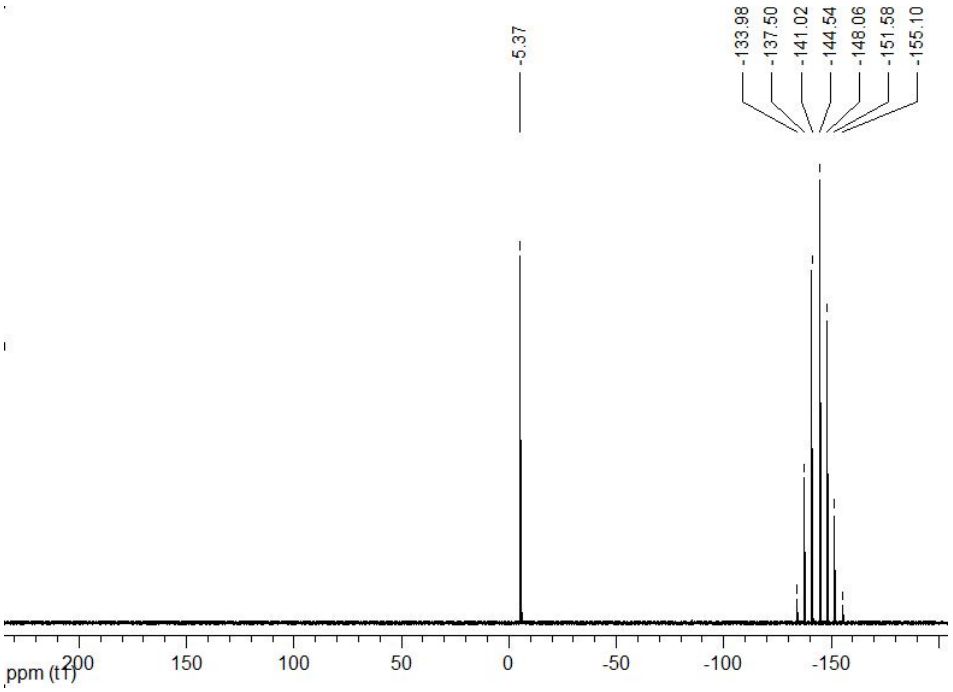
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:



$^{31}P\{^{1}H\}$ NMR:



Electronic Supplementary Material (ESI) for Dalton Transactions

Phosphino Imidazoles and Imidazolium Salts for Suzuki *C-C* Coupling Reactions

Bianca Milde, Dieter Schaarschmidt, Tobias Rüffer, and Heinrich Lang

Chemnitz University of Technology, Faculty of Science, Institute of Chemistry, Department of Inorganic Chemistry, Straße der Nationen 62, 09111 Chemnitz, Germany.

Electronic Supplementary Information

- General -

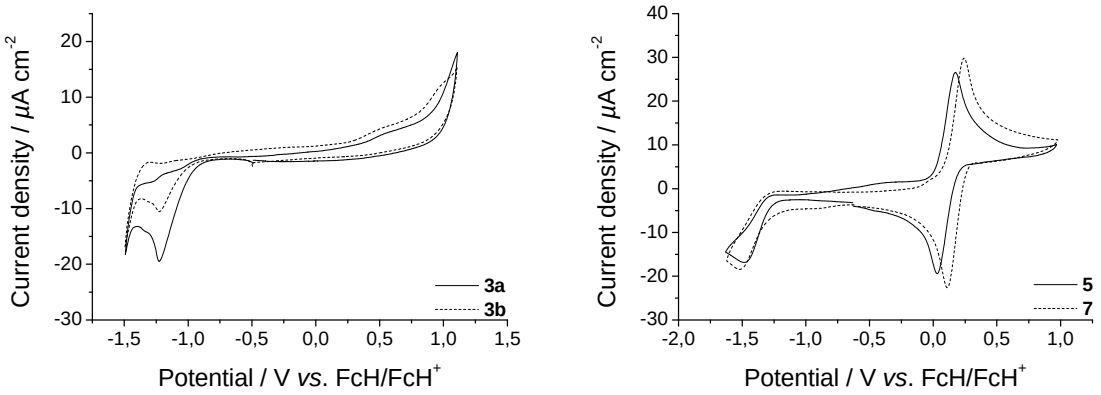


Figure S1. Cyclovoltammograms of **3a** and **3b** (left) and **5** and **7** (right) in dichloromethane solutions (1.0 mmol·dm^{-3}) at 25 °C, supporting electrolyte [(*n*-Bu)$_4$N][B(C$_6$F$_5$)$_4$] (0.1 mol·dm^{-3}) with a scan rate of 100 mV·s^{-1}.

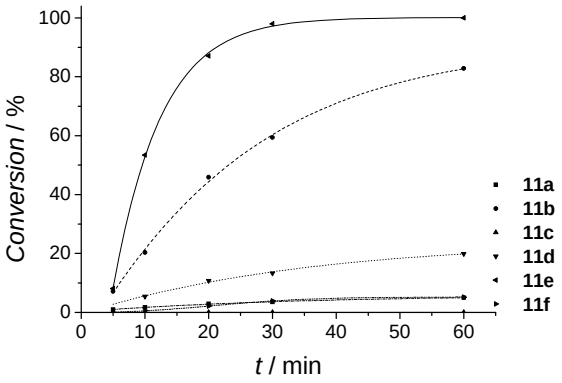


Figure S2 Reaction profile for the coupling of 2-bromo toluene (2.92 mmol) with phenyl boronic acid (3.85 mmol) to give 2-methyl biphenyl using [Pd(OAc)$_2$] / **11a** – **f** (0.25 mol% [Pd], 0.5 mol% **11a** – **f**) in the presence of K_2CO_3 (8.76 mmol) in a 1,4-dioxane-water mixture (ratio 2:1, *v*:*v*) at 100 °C.

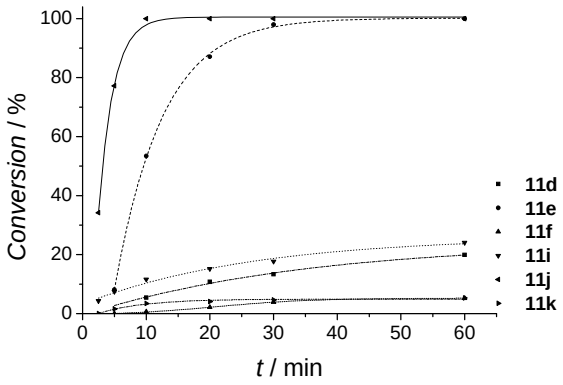


Figure S3 Reaction profile for the coupling of 2-bromo toluene (2.92 mmol) with phenyl boronic acid (3.85 mmol) to give 2-methyl biphenyl using [Pd(OAc)$_2$] / **11d** – **f**, **11i** – **k** (0.25 mol% [Pd], 0.5 mol% **11d** – **f**, **11i** – **k**) in the presence of K_2CO_3 (8.76 mmol) in a 1,4-dioxane-water mixture (ratio 2:1, *v*:*v*) at 100 °C.

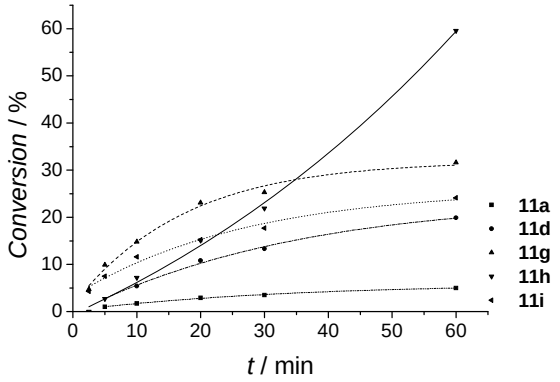


Figure S4 Reaction profile for the coupling of 2-bromo toluene (2.92 mmol) with phenyl boronic acid (3.85 mmol) to give 2-methyl biphenyl using [Pd(OAc)$_2$] / **11a** – **f** (0.25 mol% [Pd], 0.5 mol% **11a**, **11d**, **11g** – **i**) in the presence of K_2CO_3 (8.76 mmol) in a 1,4-dioxane-water mixture (ratio 2:1, *v*:*v*) at 100 °C.

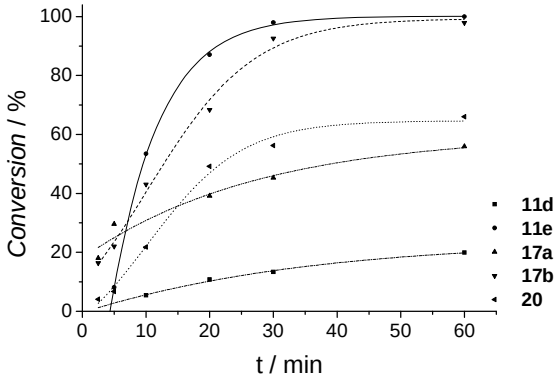


Figure S5 Reaction profile for the coupling of 2-bromo toluene (2.92 mmol) with phenyl boronic acid (3.85 mmol) to give 2-methyl biphenyl using [$Pd(OAc)_2$] / **11a** – **f** (0.25 mol% [Pd], 0.5 mol% **11d**, **11e**, **17a**, **17b**, **20**) in the presence of K_2CO_3 (8.76 mmol) in a 1,4-dioxane-water mixture (ratio 2:1, *v*:*v*) at 100 °C.

Electronic Supplementary Material (ESI) for Dalton Transactions

Phosphino Imidazoles and Imidazolium Salts for Suzuki *C,C* Coupling Reactions

Bianca Milde, Dieter Schaarschmidt, Tobias Rüffer, and Heinrich Lang

Chemnitz University of Technology, Faculty of Science, Institute of Chemistry, Department of Inorganic Chemistry, Straße der Nationen 62, 09111 Chemnitz, Germany.

Electronic Supplementary Information

- X-ray Crystallography -

For the refinement of *cis*-**19** the following restraints were applied:

DELU 0.010 0.010 C82 CL7 CL8 CL9

SIMU 0.040 0.080 1.700 C82 CL7 CL8 CL9

ISOR 0.100 C82 CL7 CL8 CL9

DELU 0.010 0.010 C81 CL4 CL5 CL6

SIMU 0.040 0.080 1.700 C81 CL4 CL5 CL6

ISOR 0.100 C81 CL4 CL5 CL6

DELU 0.010 0.010 C80 CL1 CL2 CL3

SIMU 0.040 0.080 1.700 C80 CL1 CL2 CL3

ISOR 0.100 C80 CL1 CL2 CL3

DFIX 1.500 0.020 C59 C60

BIND C59 C60

DANG 2.600 0.040 C58 C60

DFIX 1.500 0.020 C71 C72

DFIX 1.500 0.020 C72 C73

DANG 2.600 0.040 C71 C73

DFIX 1.500 0.020 C7 C8

DANG 2.600 0.040 C6 C8

DFIX 1.500 0.020 C45 C46

DFIX 1.500 0.020 C46 C47

DANG 2.600 0.040 C44 C46

DANG 2.600 0.040 C45 C47

DFIX 1.500 0.020 C58 C59

DFIX 1.500 0.020 C57 C58

DFIX 1.470 0.020 N9 C57

DFIX 1.500 0.020 C57 C58

DFIX 1.500 0.020 C58 C59

DFIX 1.500 0.020 C59 C60

DANG 2.500 0.040 N9 C58

DANG 2.500 0.040 C57 C59

DANG 2.500 0.040 C58 C60

DFIX 1.500 0.020 C58' C59'

DFIX 1.500 0.020 C57 C58'

DFIX 1.500 0.020 C59' C60'

DANG 2.500 0.040 N9 C58'

DANG 2.500 0.040 C57' C59'

DANG 2.500 0.040 C58' C60'

DFIX 1.460 0.020 N11 C70

DFIX 1.500 0.020 C70 C71

DFIX 1.500 0.020 C71 C72

DFIX 1.500 0.020 C72 C73

DANG 2.500 0.040 N11 C71

DANG 2.500 0.040 C70 C72

DANG 2.500 0.040 C71 C73

DFIX 1.500 0.020 C70 C71'

DFIX 1.500 0.020 C71' C72'

DFIX 1.500 0.020 C72' C73'

DANG 2.500 0.040 N11 C71'

DANG 2.500 0.040 C70 C72'

DANG 2.500 0.040 C71' C73'

DFIX 1.470 0.020 N7 C44

DFIX 1.500 0.020 C44 C45

DFIX 1.500 0.020 C45 C46

DFIX 1.500 0.020 C46 C47

DANG 2.500 0.040 N7 C45

DANG 2.510 0.040 C44 C46

DANG 2.520 0.040 C45 C47

DFIX 1.470 0.020 N5 C31

DFIX 1.500 0.020 C31 C32

DFIX 1.520 0.020 C32 C33

DFIX 1.500 0.020 C33 C34

DANG 2.500 0.040 N5 C32

DANG 2.520 0.040 C31 C33

DANG 2.520 0.040 C32 C34

DFIX 1.520 0.020 C32 C33'

DFIX 1.500 0.020 C33' C34'

DANG 2.520 0.040 C31 C33'

DANG 2.520 0.040 C32 C34'

DFIX 1.470 0.020 N3 C18

DFIX 1.520 0.020 C18 C19

DFIX 1.520 0.020 C19 C20

DFIX 1.520 0.020 C20 C21

DANG 2.500 0.040 N3 C19

DANG 2.520 0.040 C18 C20

DANG 2.520 0.040 C19 C21

DFIX 1.470 0.020 N1 C5

DFIX 1.520 0.020 C5 C6

DFIX 1.520 0.020 C6 C7

DFIX 1.500 0.020 C7 C8

DANG 2.520 0.040 N1 C6

DANG 2.520 0.040 C5 C7

DANG 2.520 0.040 C6 C8

DELU 0.010 0.010 C1 C2 C3 N1 N2

SIMU 0.040 0.080 1.700 C1 C2 C3 N1 N2

ISOR 0.100 C1 C2 C3 N1 N2

DELU 0.010 0.010 C6 C7 C8

SIMU 0.040 0.080 1.700 C6 C7 C8

ISOR 0.100 C6 C7 C8

DELU 0.010 0.010 C57 C58 C59 C60 N9

SIMU 0.040 0.080 1.700 C57 C58 C59 C60 N9

ISOR 0.100 C57 C58 C59 C60 N9

DELU 0.010 0.010 C57 C58' C59' C60' N9

SIMU 0.040 0.080 1.700 C57 C58' C59' C60' N9

ISOR 0.100 C57 C58' C59' C60' N9

EADP C59' C60'

DELU 0.010 0.010 C31 C32 C33' C34' N5

SIMU 0.040 0.080 1.700 C31 C32 C33' C34' N5

ISOR 0.100 C31 C32 C33' C34' N5

DELU 0.010 0.010 C31 C32 C33 C34

SIMU 0.040 0.080 1.700 C31 C32 C33 C34

ISOR 0.100 C31 C32 C33 C34

DELU 0.010 0.010 C70 C71 C72 C73 N11

SIMU 0.040 0.080 1.700 C70 C71 C72 C73 N11

ISOR 0.100 C70 C71 C72 C73 N11

DELU 0.010 0.010 C70 C71' C72' C73' N11

SIMU 0.040 0.080 1.700 C70 C71' C72' C73' N11

ISOR 0.100 C70 C71' C72' C73' N11

DFIX 2.600 0.020 PD3 I5

DFIX 2.600 0.020 PD3 I5'

DANG 3.800 0.040 I6 I5

DANG 3.800 0.040 I6 I5'

DANG 3.400 0.040 C62 I5

DFIX 3.700 0.020 I6 CL6

EADP C72 C73

EADP I6 I6'

The DELU, SIMU and ISOR restraints were used in order to refine respective atoms anisotropically. In case that selected atoms remained “not positive defined” EADP restraints were applied.

DFIX and DANG restraints were used in order to refine especially disordered fragments at reasonable bond distances and angles.