Supporting Information

Tertiary α,α-diarylmethylamines derived from diarylketimines and organomagnesium reagents

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General experimental information

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use, or distilled according to usual procedures.[1] Anhydrous 1,4-dioxane was purchased from Sigma Aldrich and used as received. Inert atmosphere experiments were performed with standard Schlenk techniques with dried (P_2O_5) nitrogen gas. Reactions were monitored by TLC (Merck silica gel 60 F254), and ^{1}H and ^{31}P NMR. Purification of the products, when necessary, was performed by column chromatography using Merck 60 Å 230-400 mesh silica gel, or preparative TLC (Merck silica gel 60 GF254, 1.0 mm).

NMR data was collected on Varian VXR400 and 200 spectrometers (^{1}H at 400.0 and 200.0 MHz, respectively; ^{13}C at 100.58 and 50.29 MHz resp.; ^{31}P at 161.94 and 80.97 MHz resp.; ^{19}F at 376.29 and 188.15 MHz resp.), equipped with a 5 mm *z*-gradient broadband probe. Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, 1H: 7.26 ppm; ^{13}C: 77.16 ppm; ^{31}P and ^{19}F are calibrated externally against H_3PO_4 and $CFCl_3$, respectively). ^{13}C was measured without decoupling from ^{31}P. Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations (s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublets, ddd: doublet of doublet of doublets, t: triplet, td: triplet of

[1]Armarego, W.L.F; Chai, C. *Purification of Laboratory Chemicals 7th ed.*, **2012** (Elsevier), ISBN 9780123821614

doublets, q: quadruplet, dq: doublet of quadruplets, m: multiplet). Exact mass spectra were recorded on a LTQ Orbitrap XL (ESI+) apparatus.

Representative procedure for the preparation of dialkylmagnesium reagents

In a flame-dried and nitrogen-flushed conical glass centrifuge vial, dry toluene (1 mL) and isobutylmagnesium bromide solution (2.0M in Et_2O, 1 mL, 2 mmol) are mixed together under vigorous magnetic stirring at room temperature. Dry 1,4-dioxane (190 µL, 2.2 mmol, 1.1 eq) is then added dropwise, slowly, so that the slurry formed does not interfere with efficient mixing. The resulting white milky suspension is then vigorously stirred overnight at room temperature. The vial is then centrifuged for 1 h at 5000 rpm. An aliquot of the pale yellow or colourless supernatant is then diluted in dry toluene and titrated with a 3.4 M *sec*-butanol solution in dry toluene, in the presence of 1,10-phenanthroline (a few crystals), until the dark purple solution turns bright yellow. Colour change appears at equimolarity of *s*BuOH and *i*Bu_2Mg (1:1 alcohol/magnesium ratio). Toluene also ensures bright colours for facile titration, as opposed to TBME. Typically the concentration was found to be 0.95-1.05 M (on 5 batches prepared). The supernatant of the centrifuged reaction mixture is used as such for the 1,2-addition reactions, and can be stored a few days in a sealed nitrogen-flushed vessel without erosion of concentration.

Note: This procedure can also be carried out in dry THF, Et_2O or TBME with the same outcome. However, THF proved deleterious (lower conversion) for our 1,2-addition procedure, and toluene gives the best results both in terms of solubility and conversion for the 1,2-addition reaction.

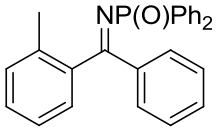
Representative procedure for the synthesis of the diphenylphosphoryl-protected diarylimines [2]

To a solution of hydroxylamine hydrochloride (1.390 g, 20 mmol, 2 eq) in pyridine (40 mL, 0.25 M) is added 2-methylbenzophenone (1.81 mL, 10 mmol, 1 eq), and the resulting mixture is refluxed overnight. Once cooled to room temperature, the crude is concentrated under reduced pressure, then poured in a beaker containing 100 mL of an ice/2N HCl 2:1 mixture. CH_2Cl_2 is added (ca. 40 mL) and the contents are stirred for 20 min. The biphasic solution is then extracted thrice with CH_2Cl_2, the organic layers washed with brine, dried over $MgSO_4$, filtered and dried under reduced pressure to afford the oxime as a *Z/E* mixture of isomers in usually

[2] S. Masumoto, H. Usuda, M. Suzuki, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.* 2003, **125**, 5634.

quantitative yield. The oxime is used as such without further purification, regardless of conversion, for the preparation of the corresponding *N*-DPP imine.

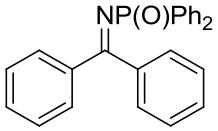
To a solution of 2-methylbenzophenone oxime (2.113 g, 10 mmol, 1 eq) in CH_2Cl_2 / pentane (1:1, 33 mL, 0.3M) under nitrogen atmosphere is added Et_3N (1.53 mL, 11 mmol, 1.1 eq). The resulting solution is then cooled to -40°C, and pure chlorodiphenylphosphine (2.02 mL, 11 mmol, 1.1 eq) is added dropwise while vigorously stirring the resulting slurry. The reaction mixture is kept at this temperature for 2h, then warmed to room temperature, and stirred for an additional 12 h. The crude mixture is then concentrated under reduced pressure without heating to remove pentane, redissolved with CH_2Cl_2, and washed with water. Following extraction with CH_2Cl_2, the organic layer is dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude residue is purified by careful column chromatography on silica gel (eluent Pentane / EtOAc 2:1 to 1.5:1) to yield the desired imine as a single diastereoisomer (3.45g, 87%). The off-yellow solid can be recrystallized from Et_2O to give white crystals.



***P,P*-diphenyl-*N*-(phenyl(o-tolyl)methylene)phosphinic amide (1e):**

Yield: 65%, off-white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 – 7.84 (m, 6H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.40 (tdd, *J* = 7.0, 5.4, 1.6 Hz, 8H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 1.87 (s, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 16.88; ^{13}C NMR ($CDCl_3$, 50 MHz): δ136.2, 134.6, 133.6, 133.0, 131.9, 131.7, 131.4, 131.4, 130.0, 129.7, 129.2, 128.8, 128.5, 128.3, 127.3, 127.3, 125.3, 19.9; HRMS: Calc. for $C_{26}H_{23}NOP$: 396.1512, found: 396.1496.

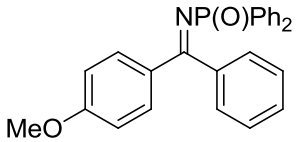


***N*-(diphenylmethylene)-*P,P*-diphenylphosphinic amide (1a):**

Prepared according to the general procedure from benzophenone, yield: 71%, white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (ddd, *J* = 11.8, 8.0, 1.4 Hz, 4H), 7.57 – 7.55 (m, 4H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.36 (m, 10H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 16.31;^{13}C NMR ($CDCl_3$,

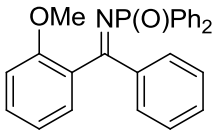
100.58 MHz): δ138.8, 138.7, 135.7, 134.4, 131.7, 131.6, 131.3, 131.2, 131.2, 129.5, 128.3, 128.2, 127.9; HRMS: Calc. for $C_{25}H_{21}NOP$: 382.1355, found: 382.1354.



***N*-((4-methoxyphenyl)(phenyl)methylene)-*P,P*-diphenylphosphinic amide (1b):**

Prepared according to the general procedure from 4-methoxybenwophenone, yield: 72%, off-white solid.

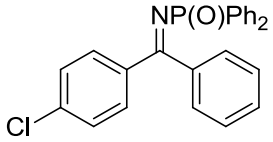
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (ddd, *J* = 11.8, 8.0, 1.4 Hz, 4H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.46 – 7.33 (m, 11H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H);^{31}P ($CDCl_3$, 161.94 MHz): δ 16.03; ^{13}C NMR ($CDCl_3$,50 MHz): δ 163.0, 139.1, 138.8, 136.8, 134.2, 132.5, 132.0, 131.9, 131.7, 131.6, 131.2, 131.2, 130.6, 129.3, 128.5, 128.2, 127.8, 113.5, 55.6;HRMS: Calc. for $C_{26}H_{23}NO_2P$: 412.1461, found: 412.1458.



***N*-((2-methoxyphenyl)(phenyl)methylene)-*P,P*-diphenylphosphinic amide (1l):**

Prepared according to the general procedure from 2-methoxybenzophenone, yield: 45%, white solid.

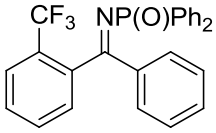
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 – 7.89 (m, 6H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 9H), 7.12 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.31 (s, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 16.51; ^{13}C NMR ($CDCl_3$, 100.58 MHz): 179.0, 179.0, 156.4, 139.5, 139.3, 135.8, 134.5, 132.7, 132.7, 132.6, 131.8, 131.7, 131.1, 131.1, 130.9, 130.9, 130.8, 129.9, 129.1, 129.1, 129.0, 128.4, 128.3, 128.1, 127.2, 127.1, 119.9, 110.4, 54.8; HRMS:Calc. for $C_{26}H_{23}NO_2P$: 412.1461, found: 412.1462



***N*-((4-chlorophenyl)(phenyl)methylene)-*P*,*P*-diphenylphosphinic amide (1m):**

Prepared according to the general procedure from 4-chlorobenzophenone, yield: 36%, white solid.

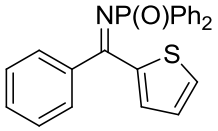
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 – 7.89 (m, 4H), 7.57 – 7.55 (m (app.d.), 2H), 7.53 – 7.34 (m, 13H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 16.56; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ180.6, 138.6, 138.4, 137.7, 137.2, 137.0, 135.5, 134.2, 131.8, 131.7, 131.5, 131.4, 131.0, 129.7, 128.5, 128.4, 128.3, 128.2; HRMS: Calc. for $C_{25}H_{20}ClNOP$: 416.0966, found: 416.0948



***N*-((4-chlorophenyl)(phenyl)methylene)-*P*,*P*-diphenylphosphinic amide (1n):**

Prepared according to the general procedure from 2-(trifluoromethyl)benzophenone, yield: ~10%, decomposes during column chromatography, yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 – 7.86 (m, 4H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.68 – 7.65 (m, 1H), 7.58 – 7.53 (m, 3H), 7.47 – 7.38 (m, 8H), 7.24 – 7.21 (m, 1H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 17.28; ^{19}F ($CDCl_3$, 376 MHz): δ -58.26; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 177.9, 177.8, 136.6, 135.9, 133.3, 133.1, 131.8, 131.6, 131.5, 131.4, 131.4, 129.7, 129.3, 128.7, 128.6, 128.6, 128.3, 126.5, 126.4, 126.3; HRMS: Calc. for $C_{26}H_{19}F_3NOPNa$: 472.1049, found: 472.1078

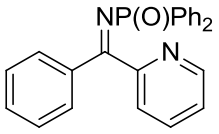


***P*,*P*-diphenyl-*N*-(phenyl(thiophen-2-yl)methylene)phosphinic amide (1o):**

Prepared according to the general procedure from 2-benzoylthiophene, yield: 66%, off-brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (ddd, *J* = 11.9, 8.0, 1.4 Hz, 4H), 7.68 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.45 – 7.32 (m, 11H), 7.23 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.08 (t, *J* = 4.2 Hz, 1H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 15.72; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 174.8, 174.7, 137.4, 137.2, 136.6, 135.6,

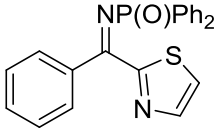
135.6, 134.3, 134.0, 131.8, 131.7, 131.3, 131.3, 130.4, 128.6, 128.5, 128.2, 127.7; HRMS: Calc. for $C_{23}H_{19}NOPS$: 388.0920, found: 388.0920.



***P,P*-diphenyl-*N*-(phenyl(pyridin-2-yl)methylene)phosphinic amide (1p):**

Prepared according to the general procedure from 2-benzoylpyridine, yield: 44%, off-yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.94 (ddd, *J* = 12.0, 7.9, 1.5 Hz, 4H), 7.81 – 7.74 (m, 3H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.38 (m, 8H), 7.36 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 17.91; ^{13}C NMR ($CDCl_3$, 50 MHz): δ179.1, 178.9, 156.2, 155.9, 149.0, 138.3, 137.9, 136.0, 135.9, 133.3, 132.6, 131.9, 131.7, 131.5, 131.4, 130.3, 128.6, 128.4, 128.3, 124.6, 124.2; HRMS: Calc. for $C_{24}H_{20}N_2OP$: 383.1308, found: 383.1312



P,P-diphenyl-N-(phenyl(thiazol-2-yl)methylene)phosphinic amide (1q):

Prepared from the parent ketone [3] according to the general procedure, yield: 62%, off- yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (dd, *J* = 3.1, 0.8 Hz, 1H), 7.97 – 7.91 (m, 4H), 7.66 (d, *J* = 3.1 Hz, 1H), 7.61 (bs, 1H), 7.59 (d, *J* = 1.4 Hz, 1H), 7.50 – 7.35 (m, 9H),^{31}P ($CDCl_3$, 161.94 MHz): δ 16.60; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 172.4, 172.3, 170.0, 169.7, 145.5, 135.0, 134.9, 134.8, 133.5, 131.7, 131.6, 131.3, 129.7, 128.5, 128.3, 127.5, 125.6, HRMS: Calc. for $C_{22}H_{18}N_2OPS$: 389.0868, found: 389.0872.

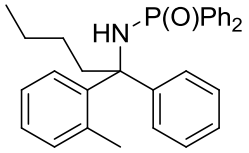
[3]Phenyl(thiazol-2-yl)methanone was prepared following a literature procedure: A.Dondoni, G.Fantin, M.Fogagnolo, A. Medici *J. Org. Chem.* 1988, **3** 1748–1761.

Representative procedure for the 1,2-addition of diorganomagnesium reagents to diarylimines

In a flame-dried, nitrogen flushed Schlenk tube, *P,P*-diphenyl-*N*-(phenyl(o-tolyl)methylene)phosphinic amide **1d** (40 mg, 0.1 mmol, 1 eq) is dissolved in dry toluene (1 mL, 0.1M) at room temperature. Dibutylmagnesium solution (1.0M in Et_2O/heptane, 120 µL, 1.2 eq) is then added in one portion. The reaction medium immediately becomes orange-brown, and quickly loses colour back to pale yellow. After stirring for 10-30 minutes at room temperature to ensure completion, the reaction is quenched with saturated aqueous NH_4Cl, extracted with EtOAc, the organic layers dried over $MgSO_4$, and concentrated *in vacuo*. Thorough reevaporation with chloroform followed by overnight drying under high vacuum yields the desired product as a colourless gum without further purification required.

For some entries, purification was performed by column chromatography on silica gel (eluent pentane/EtOAc 2:1 to 1:1), as indicated in their respective descriptions below.

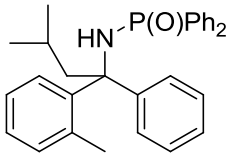
Important note: When performed with *aryl- or alkylmagnesium bromide reagents,* the following modifications were applied: 2 equivalents (0.2 mmol) of the Grignard reagent were used, and the reaction was stirred for 1h or the indicated time (1-16h).



***P,P*-diphenyl-*N*-(1-phenyl-1-(o-tolyl)pentyl)phosphinic amide (2e):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1e**, and purified by column chromatography. Yield: 93%, colourless gum.

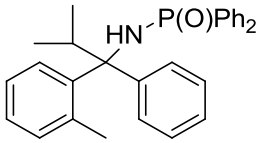
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (dd, *J* = 11.6, 7.3 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.37 – 7.31 (m, 3H), 7.24 – 7.18 (m, 4H), 7.16 – 7.08 (m, 5H), 6.89 (d, *J* = 6.9 Hz, 1H), 3.92 (d, *J* = 4.5 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.51 – 2.44 (m, 1H), 1.71 (s, 3H), 1.19 (dt, *J* = 14.5, 7.2 Hz, 2H), 1.01 – 0.93 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.41; ^{13}C NMR ($CDCl_3$, 50 MHz): δ145.7, 145.6, 143.3, 143.2, 136.8, 136.0, 135.1, 133.5, 132.7, 132.6, 131.9, 131.7, 131.6, 131.4, 131.4, 131.1, 131.0, 128.6, 128.3, 128.2, 128.0, 127.9, 127.4, 127.3, 127.0, 126.7, 125.4, 66.3, 66.28, 40.8, 27.1, 23.0, 22.3, 14.1; HRMS:Calc. for $C_{30}H_{32}NOPNa$: 476.2114, found: 476.2144.



***N*-(3-methyl-1-phenyl-1-(o-tolyl)butyl)-*P,P*-diphenylphosphinic amide (2f):**

Prepared according to the general procedure with iBu_2Mg (1.2eq), stirring overnight, from imine **1e**, and purified by column chromatography. Yield: 90%, colourless gum.

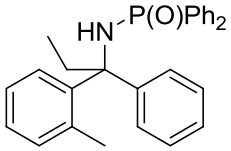
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (dd, *J* = 11.5, 7.4 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 11.8, 7.6 Hz, 2H), 7.37 (dd, *J* = 13.5, 6.4 Hz, 1H), 7.32 (d, *J* = 6.9 Hz, 3H), 7.25 – 7.19 (m, 4H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (bs, 3H), 6.89 (d, *J* = 7.2 Hz, 1H), 3.97 (d, *J* = 4.0 Hz, 1H), 2.62 (ddd, *J* = 18.0, 13.8, 4.8 Hz, 2H), 1.70 (s, 3H), 1.54 – 1.48 (m, 1H), 0.69 (d, *J* = 6.6 Hz, 3H), 0.51 (d, *J* = 6.6 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.06; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ144.8, 143.5, 143.4, 136.9, 134.9, 134.2, 134.1, 132.7, 131.7, 131.6, 131.5, 131.2, 131.2, 131.0, 130.95, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.4, 127.3, 126.9, 125.4, 66.4, 49.3, 29.8, 24.7, 24.2, 22.4; HRMS:Calc. for $C_{30}H_{33}NOP$: 454.2294, found: 454.2276.



***N*-(2-methyl-1-phenyl-1-(o-tolyl)propyl)-*P,P*-diphenylphosphinic amide (2g):**

Prepared according to the general procedure with iPr_2Mg (2.0 eq, 78% conversion) from imine **1e** and purified by column chromatography. Yield: 77%, colourless gum.

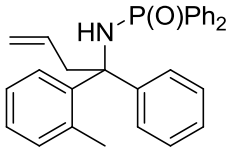
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, *J* = 11.0, 7.5 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.32 – 7.27 (m, 3H), 7.24 – 7.16 (m, 4H), 7.04 (t, *J* = 6.7 Hz, 4H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 4.03 (d, *J* = 4.0 Hz, 1H), 3.75 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.43 (s, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.86; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ142.2, 142.1, 139.5, 139.0, 136.1, 134.9, 133.4, 132.6, 132.1, 131.73, 131.7, 131.5, 131.4, 131.1, 131.1, 130.3, 130.3, 129.5, 128.8, 128.7, 127.6, 127.5, 127.4, 127.3, 126.5, 124.7, 68.9, 34.7, 23.3, 20.5, 18.0; HRMS:Calc. for $C_{29}H_{31}NOP$: 440.2138, found: 440.2110.



***P,P*-diphenyl-*N*-(1-phenyl-1-(o-tolyl)propyl)phosphinic amide (2h):**

Prepared according to the general procedure with Et_2Mg (1.2eq) from imine **1e**, without chromatographic purification. Yield: quantitative, colourless gum.

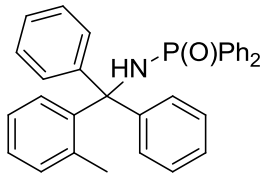
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 – 7.74 (m, 2H), 7.44 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.23-7.07 (m, 9H), 6.89 (d, *J* = 6.8 Hz, 1H), 3.93 (d, *J* = 4.8 Hz, 1H), 2.77 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.54 (dq, *J* = 14.0, 7.1 Hz, 1H), 1.71 (s, 3H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.73; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 145.4, 145.3, 142.9, 142.8, 137.0, 136.0, 134.98, 133.5, 132.7, 132.4, 131.9, 131.7, 131.5, 131.5, 131.4, 131.38, 131.3, 131.1, 131.00, 128.6, 128.3, 128.2, 128.0, 127.4, 127.41, 127.1, 126.7, 125.4, 66.6, 33.8, 22.4, 9.5; HRMS: Calc. for $C_{28}H_{28}NOPNa$: 448.1801, found: 448.1831.



***P,P*-diphenyl-*N*-(1-phenyl-1-(o-tolyl)but-3-en-1-yl)phosphinic amide (2i):**

Prepared according to the general procedure with AllylMgBr (2.0 eq) from imine **1e**, without chromatographic purification. Yield: quantitative, colourless gum.

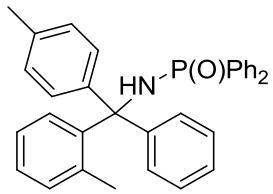
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 – 7.73 (m, 3H), 7.58 (dd, *J* = 12.1, 7.3 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.34 – 7.29 (m, 3H), 7.24 – 7.18 (m, 3H), 7.17 – 7.14 (m, 2H), 7.10 – 7.03 (m, 4H), 6.76 (d, *J*= 7.4 Hz, 1H), 5.35 – 5.20 (m, 2H), 5.02 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.00 (s, 1H), 3.65 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.33 (dd, *J* = 12.8, 6.3 Hz, 1H), 1.64 (s, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.65; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ143.4, 142.1, 137.1, 135.1, 134.5, 134.1, 133.9, 133.2, 132.5, 131.6, 131.5, 131.5, 131.4, 131.3, 131.2, 130.9, 130.86, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.66, 127.64, 126.9, 125.4, 120.6, 65.2, 46.4 (d, *J* = 1.5 Hz), 22.4; HRMS:Calc. for $C_{29}H_{29}NOP$: 438.1981, found: 438.1964.



***N*-(diphenyl(o-tolyl)methyl)-*P,P*-diphenylphosphinic amide (2j):**

Prepared according to the general procedure with PhMgBr (2.0 eq, overnight; 81% conversion) from imine **1e**, and purified by column chromatography. Yield: 79%, colourless gum.

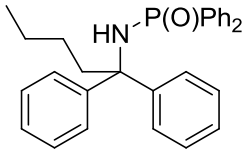
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 11.9, 7.2 Hz, 4H), 7.42 (dd, *J* = 7.0, 2.6 Hz, 4H), 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 4H), 7.21 (dd, *J* = 15.8, 8.5 Hz, 2H), 7.13 – 7.11 (m, 6H), 6.98 (d, *J* = 6.8 Hz, 1H), 4.16 (d, *J* = 6.0 Hz, 1H), 1.61 (s, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 17.69; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 143.9, 143.6, 143.5, 137.7, 135.5, 134.3, 132.5, 131.6, 131.6, 131.1, 131.08, 129.9, 129.3, 128.3, 128.2, 127.8, 127.2, 125.6, 71.8, 23.4; HRMS: Calc. for $C_{32}H_{29}NOP$: 474.1981, found: 474.1952.



***P,P*-diphenyl-*N*-(phenyl(o-tolyl)(p-tolyl)methyl)phosphinic amide (2k):**

Prepared according to the general procedure with *p*-TolMgBr (2.0 eq, overnight) from imine **1e**, without chromatographic purification. Yield: quantitative, pale yellow gum.

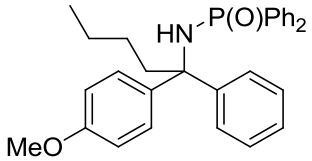
^{1}H NMR ($CDCl_3$, 400 MHz): 7.77 (d, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 11.7, 7.5 Hz, 4H), 7.42 – 7.38 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.30-7.24 (m, 7H), 7.21 – 7.13 (m, 1H), 7.11 – 7.07 (m, 3H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.88 (d, *J*=8.1 Hz, 2H), 4.13 (d, *J* = 6.2 Hz, 1H), 2.21 (s, 3H), 1.59 (s, 3H). ^{31}P ($CDCl_3$, 161.94 MHz): δ 17.54; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 13C NMR (101 MHz, cdcl3) δ = 144.10, 144.07, 143.74, 143.71, 140.55, 140.51, 137.71, 136.91, 135.64, 135.62, 134.35, 134.33, 132.55, 131.75, 131.70, 131.66, 131.61, 131.13, 131.11, 131.07, 131.04, 129.95, 129.61, 129.27, 128.50, 128.31, 128.19, 127.78, 127.72, 127.21, 126.98, 125.66, 115.65, 71.67, 23.49, 21.06. HRMS: Calc. for $C_{33}H_{31}NOP$: 488.21378, found: 488.21284.



***N*-(1,1-diphenylpentyl)-*P,P*-diphenylphosphinic amide (2c):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1a**, without chromatographic purification. Yield: 96%, colourless gum.

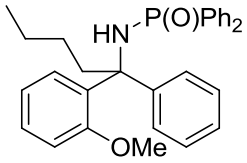
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 – 7.65 (m, 4H), 7.37 (dd, *J* = 10.9, 3.8 Hz, 2H), 7.32 – 7.27 (m, 8H), 7.18 – 7.10 (m, 6H), 3.72 (d, *J* = 5.3 Hz, 1H), 2.58 – 2.53 (m, 2H), 1.24 (dd, *J* = 13.1, 5.6 Hz, 2H), 1.07 – 0.99 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.43; ^{13}C NMR ($CDCl_3$, 50 MHz): δ145.8, 145.7, 135.8, 133.2, 131.8, 131.6, 131.2, 131.2, 128.6, 128.4, 128.2, 128.1, 127.8, 126.9, 66.3, 40.4, 27.0, 23.0, 14.1; HRMS:Calc. for $C_{29}H_{30}NOPNa$: 462.1957, found: 462.1988



***N*-(1-(4-methoxyphenyl)-1-phenylpentyl)-*P,P*-diphenylphosphinic amide (2d):**

Prepared according to the general procedure with Bu_2Mg (1.2eq, 94% conversion) from imine **1b**, and purified by column chromatography. Yield: 62% (unstable on silica gel), colourless gum.

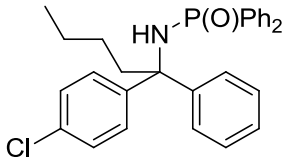
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (ddd, *J* = 24.2, 11.7, 7.4 Hz, 4H), 7.41 – 7.27 (m, 8H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.15 (dd, *J* = 7.7, 5.7 Hz, 3H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.70 (d, *J* = 4.7 Hz, 1H), 2.63 (td, *J* = 12.5, 4.7 Hz, 1H), 2.45 (td, *J* = 13.1, 4.2 Hz, 1H), 1.14-1.04 (m, 2H), 1.01-0.92 (m, 1H), 0.90-0.82 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.56; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 158.4, 146.4, 138.3, 137.1, 131.9, 131.8, 131.7, 131.6, 131.3, 131.2, 131.1, 130.0, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 126.8, 112.9, 65.9, 55.3, 41.0, 27.0, 23.0, 14.1; HRMS: Calc. for $C_{30}H_{33}NO_2P$: 470.2243, found: 470.2225



***N*-(1-(2-methoxyphenyl)-1-phenylpentyl)-*P,P*-diphenylphosphinic amide (2l):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1l**, and purified by column chromatography. Yield: 87%, colourless gum.

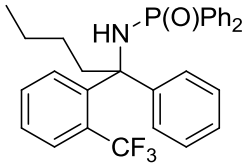
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 11.5, 7.0 Hz, 2H), 7.50 – 7.38 (m, 5H), 7.31 (dd, *J* = 17.5, 10.3 Hz, 5H), 7.25 – 7.15 (m, 7H), 7.14-7.10 (m, 1H), 6.86 (dd, *J* = 13.2, 7.7 Hz, 2H), 5.00 (d, *J* = 8.7 Hz, 1H), 3.34 (s, 3H), 2.48 (td, *J* = 12.9, 3.2 Hz, 1H), 2.19 – 2.10 (m, 1H), 1.07 (dd, *J* = 13.1, 6.1 Hz, 2H), 0.90 – 0.81 (m, 2H), 0.68 (t, *J* = 7.1 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.36; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 157.4, 147.9, 132.0, 131.9, 131.5, 131.5, 131.4, 130.9, 130.9, 128.54, 128.5, 128.4, 128.1, 128.0, 127.5, 127.1, 126.04, 126.0, 120.7, 113.1, 65.2, 55.6, 38.9, 38.89, 27.3, 23.0, 14.0; HRMS: Calc. for $C_{30}H_{33}NO_2P$: 470.2243, found: 470.2225



***N*-(1-(4-chlorophenyl)-1-phenylpentyl)-*P,P*-diphenylphosphinic amide (2m):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1m**, without chromatographic purification. Yield: 97%, colourless gum.

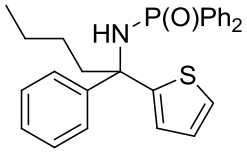
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dd, *J* = 11.9, 7.2 Hz, 2H), 7.62 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.43 – 7.28 (m, 7H), 7.24 – 7.14 (m, 6H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.69 (d, *J* = 4.8 Hz, 1H), 2.63 (td, *J* = 12.9, 4.3 Hz, 1H), 2.45 (td, *J* = 12.7, 4.3 Hz, 1H), 1.25 (dd, *J* = 13.5, 9.4 Hz, 2H), 1.10 – 1.04 (m, 1H), 0.99 – 0.91 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.57; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ145.6, 145.6, 143.7, 143.6, 135.1, 134.7, 133.9, 133.5, 132.9, 131.89, 131.7, 131.7, 131.6, 131.5, 131.4, 131.22, 131.2, 130.2, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.67, 127.1, 65.9, 40.7, 26.9, 23.0, 14.1; HRMS:Calc. for $C_{29}H_{30}ClNOP$: 474.1748, found: 474.1729



***P,P*-diphenyl-*N*-(1-phenyl-1-(2-(trifluoromethyl)phenyl)pentyl)phosphinic amide (2n):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **2n**, without chromatographic purification. Yield: quantitative, colourless gum.

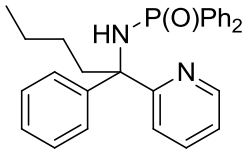
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (dd, *J* = 11.8, 7.3 Hz, 2H), 7.61 (dd, *J* = 6.8, 2.4 Hz, 2H), 7.50 (dd, *J* = 12.1, 7.5 Hz, 2H), 7.45 (d, *J* = 6.9 Hz, 1H), 7.41 (dd, *J* = 7.5, 2.9 Hz, 2H), 7.37 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32 (dd, *J* = 16.0, 7.1 Hz, 2H), 7.21-7.14 (m, 7H), 4.25 (d, *J* = 3.7 Hz, 1H), 2.72 (td, *J* = 12.9, 4.1 Hz, 1H), 2.49 – 2.41 (m, 1H), 1.14 (dt, *J* = 14.2, 7.2 Hz, 2H), 0.92 – 0.80 (m, 2H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.46; ^{19}F ($CDCl_3$, 376 MHz): δ -52.89; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 145.5, 144.5, 135.9, 135.0, 133.3, 132.4, 131.8, 131.7, 131.62, 131.6, 131.4, 131.29, 131.27, 131.2, 131.0, 129.7, 129.5, 129.4, 129.3, 129.2, 128.7, 128.6, 128.4, 128.3, 128.0, 127.6, 127.5, 127.3, 126.9, 126.6, 121.9, 66.1 (d, *J* = 2Hz), 42.3, 29.8, 27.5, 22.8, 14.1; HRMS:Calc. for $C_{30}H_{29}F_3NOPNa$: 530.1831, found: 530.1862



***P,P*-diphenyl-*N*-(1-phenyl-1-(thiophen-2-yl)pentyl)phosphinic amide (2o):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1o**, without chromatographic purification. Yield: 99%, colourless gum.

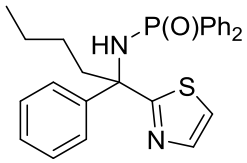
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (dt, *J* = 11.5, 8.0 Hz, 4H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.31 (td, *J* = 7.1, 1.8 Hz, 4H), 7.23 – 7.15 (m, 3H), 7.05 (d, *J* = 5.1 Hz, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.76 – 6.74 (m, 1H), 3.77 (d, *J* = 4.7 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.55 – 2.47 (m, 1H), 1.30 – 1.25 (m, 2H), 1.14 – 1.07 (m, 2H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.26; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 145.1, 134.7, 133.8, 133.77, 131.9, 131.8, 131.7, 131.6, 131.32, 131.3, 131.24, 131.2, 128.4, 128.3, 128.2, 127.9, 127.7, 127.5, 126.8, 126.5, 124.8, 64.5, 42.2, 27.0, 22.9, 14.1; HRMS: Calc. for $C_{27}H_{29}NOPS$: 446.1702, found: 446.1682



***P,P*-diphenyl-*N*-(1-phenyl-1-(pyridin-2-yl)pentyl)phosphinic amide (2p):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1p**, and purified by column chromatography. Yield: 38%, colourless gum.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, *J* = 4.7 Hz, 1H), 7.83 (dd, *J* = 11.9, 6.8 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.41 (td, *J* = 7.2, 3.1 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.16 (dd, *J* = 6.9, 5.1 Hz, 1H), 7.10 (ddd, *J* = 7.6, 5.6, 2.9 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 10.5 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.31 – 2.22 (m, 1H), 1.66 (bs, 1H), 1.60 (bs, 1H), 0.82 (t, *J* = 7.4 Hz, 2H); ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.42; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 163.6, 146.4, 137.2, 134.3, 133.0, 132.9, 132.4, 132.3, 132.2, 131.9, 131.7, 131.6, 131.4, 131.38, 130.5, 128.5, 128.4, 128.3, 127.8, 127.7, 127.65, 126.9, 122.2, 121.9, 65.0, 40.0, 26.1, 23.1, 14.2; HRMS: Calc. for $C_{28}H_{30}N_2OP$: 441.2090, found: 441.2071

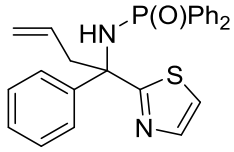


***P,P*-diphenyl-*N*-(1-phenyl-1-(thiazol-2-yl)pentyl)phosphinicamide (2q):**

Prepared according to the general procedure with Bu_2Mg (1.2eq) from imine **1q**, without chromatographic purification. Yield: quantitative, orange gum.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 – 7.75 (m, 2H), 7.65 (d, *J* = 3.3 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.44 (dd, *J* = 10.2, 4.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.06 – 7.03 (m, 3H), 5.25 (d, *J* = 8.5 Hz, 1H), 2.83 (td, *J* = 12.9, 4.2 Hz, 1H), 2.39 (td, *J* = 13.0, 4.1 Hz, 1H), 1.62 – 1.51 (m, 1H), 1.39 – 1.29 (m, 1H), 0.92 (ddd, J = 16.5, 12.7, 6.8 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.61; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 177.8, 177.76, 144.0, 143.97, 140.9, 135.3, 134.1, 134.0, 132.8, 132.1, 132.0, 131.6, 131.6, 131.56, 131.5, 131.0, 130.9, 128.5, 128.4, 128.0, 127.9,

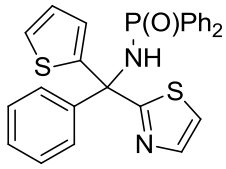
127.86, 127.8, 127.6, 120.3, 65.8, 41.2, 26.4, 22.9, 14.1. HRMS: Calc. for $C_{26}H_{28}N_2OPS$: 447.1655, found: 447.1642



***P,P*-diphenyl-*N*-(1-phenyl-1-(thiazol-2-yl)but-3-en-1-yl)phosphinic amide (2r):**

Prepared according to the general procedure with AllylMgBr (2.0 eq) from imine **1q**, without chromatographic purification. Yield: quantitative, orange gum.

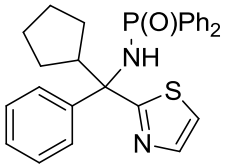
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 – 7.75 (m, 2H), 7.66 (d, *J* = 3.3 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.45 (dd, *J* = 10.4, 4.3 Hz, 1H), 7.38 (ddd, *J* = 7.0, 5.4, 2.5 Hz, 2H), 7.33 – 7.18 (m, 6H), 7.07 – 7.00 (m, 3H), 5.69 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.23 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.00 (d, *J* = 7.4 Hz, 1H), 3.72 (dd, *J* = 13.4, 7.3 Hz, 1H), 3.32 (dd, *J* = 13.5, 6.7 Hz, 1H), ^{31}P ($CDCl_3$, 161.94 MHz): δ 19.07; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 176.8, 142.1, 141.4, 135.1, 134.0, 133.9, 133.1, 132.7, 132.1, 132.0, 131.6, 131.57, 131.5, 131.4, 131.0, 130.9, 128.5, 128.4, 128.0, 127.9, 127.8, 127.76, 120.4, 120.3, 65.4, 46.5, HRMS: Calc. for $C_{25}H_{24}N_2OPS$: 431.1342, found: 431.1329



***P,P*-diphenyl-*N*-(phenyl(thiazol-2-yl)(thiophen-2-yl)methyl)phosphinic amide (2s):**

Prepared according to the general procedure with 2-thienylMgBr (2.0 eq, overnight) from imine **1q**, without chromatographic purification. Yield: quantitative, brown gum.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 – 7.69 (m, 5H), 7.39 – 7.26 (m, 10H), 7.23 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.11 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.82 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.51 (d, *J* = 7.5 Hz, 1H). ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.70; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 177.68, 177.61, 148.98, 148.96, 142.19, 142.16, 142.03, 131.87, 131.77, 131.76, 131.66, 131.34, 131.32, 131.24, 131.22, 129.60, 129.29, 128.53, 128.33, 128.28, 128.20, 128.15, 127.63, 126.97, 126.19, 120.91, 67.31. HRMS: Calc. for $C_{26}H_{22}N_2OPS_2$: 473.09057 found: 473.08985.



***N*-(cyclopentyl(phenyl)(thiazol-2-yl)methyl)-*P*,*P*-diphenylphosphinic amide (2t):**

Prepared according to the general procedure with $(cyclopentyl)_2Mg$ (2.0 eq, 3h) from imine **1q**, and purified by column chromatography. Yield: 60%, orange gum.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.77 – 7.73 (m, 1H), 7.72 (d, *J* = 3.3 Hz, 1H), 7.47 (dd, *J* = 12.5, 7.6 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.36 (td, *J* = 7.4, 7.3, 3.3 Hz, 3H), 7.30 (d, *J* = 3.3 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.17 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.12 (td, *J* = 7.5, 3.4 Hz, 2H), 6.95 – 6.88 (m, 3H), 5.34 (d, *J* = 9.0 Hz, 1H), 3.92 – 3.77 (m, 1H), 2.15 – 2.06 (m, 1H), 1.91 – 1.78 (m, 1H), 1.71 – 1.60 (m, 1H), 1.53 – 1.41 (m, 2H), 1.38 – 1.31 (m, 1H), 1.18 – 1.07 (m, 2H), 0. ^{31}P ($CDCl_3$, 161.94 MHz): δ 18.58; ^{13}C NMR ($CDCl_3$, 100.58 MHz): δ 175.18, 175.09, 141.15, 141.13, 140.79, 132.17, 132.08, 131.56, 131.53, 131.32, 131.23, 130.73, 130.70, 130.21, 128.60, 128.47, 127.92, 127.86, 127.74, 127.30, 120.16, 69.56, 48.60, 29.44, 28.49, 26.44, 26.07. HRMS: Calc. for $C_{27}H_{28}N_2OPS$: 459.16545, found: 459.16499.