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β-Pinene and camphor based, pyrazole-tethered triarylphosphines as chiral P,N ligands for palladium

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This paper is dedicated to the memory of Professor Amitabha Sarkar

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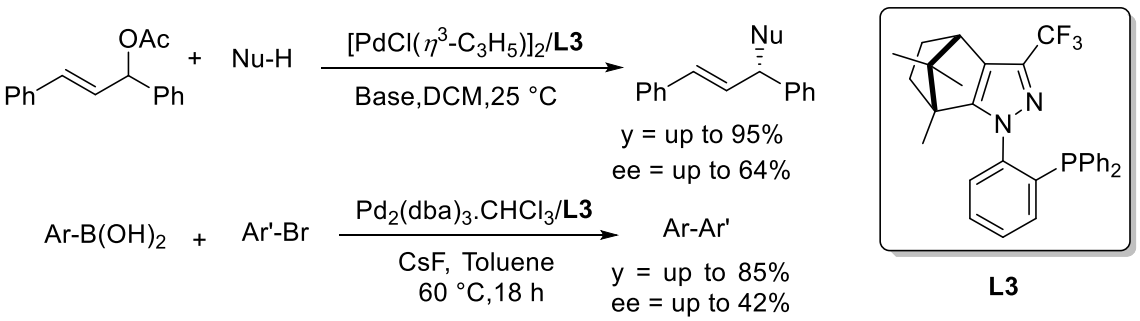
Abstract

New, optically active, β-pinene and camphor-based pyrazole tethered phosphorus-nitrogen bidentate ligands were synthesized and their utility in asymmetric catalysis was explored with respect to asymmetric allylic alkylation, amination and Suzuki-Miyaura cross coupling reactions.



Keywords: Pyrazolylphosphine, β-pinene, camphor, asymmetric allylation, asymmetric Suzuki-Miyaura cross-coupling

Introduction

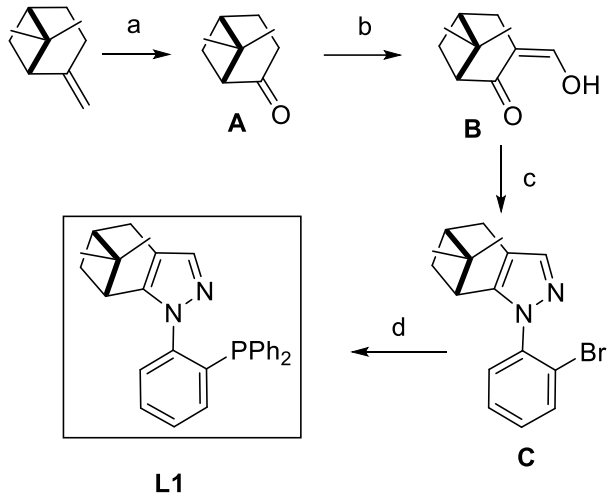
Asymmetric catalysis often requires design and synthesis of new chiral ligands to improve enantioselectivity in metal catalysed reactions. To date, a large number of P/N mixed donor ligands have been successfully used in asymmetric metal catalysed reactions[1-10]. These hemilabile ligands[11] are endowed with a soft phosphorus and a hard nitrogen donor atom. Phosphorus donor groups commonly include aryldialkyl or triarylphosphines, phosphites and heterophosphines where phosphorus is bound to nitrogen or any other hetero atom. Common nitrogen donors are pyridine, amine, imine, Schiff's base, azole etc.

Pyrazolate-bridged binuclear and polynuclear transition metal complexes have attracted special attention for many years[12-13]. Pyrazole being a π-excessive heterocycle is a poor π-acceptor. As a result, it has not been frequently used in catalysis with low-valent transition metals. However, pyrazole derivatives are relatively easy to synthesize, while substituents on the pyrazole nucleus permit electronic and steric control of the reactivity of metal centre[14]. We have used achiral chelating ligands derived from 1-arylpyrazoles to synthesize a variety of metal complexes, some of which has been successfully used in palladium catalysed coupling reactions[15-16]. It was considered worthwhile, therefore, to attach a chiral backbone to the pyrazole moiety so that enantiopure pyrazolyl ligands can be developed. There are a number of precedents where β-pinene[17-21] or camphor[22-29] moiety has been used as a chiral backbone to obtain optically pure ligands.

In this paper we describe (a) synthesis of bicyclo[3.1.1] and bicyclo[2.2.1] framework based 1-(2-diphenylphosphino)phenyl-1*H*-pyrazole ligands **L1**, **L2**, **L3** in enantiomerically pure form, (b) synthesis and characterization of a palladium complex with **L3** and (c) application of these ligands in asymmetric allylic alkylation, amination and Suzuki-Miyaura cross-coupling reactions.

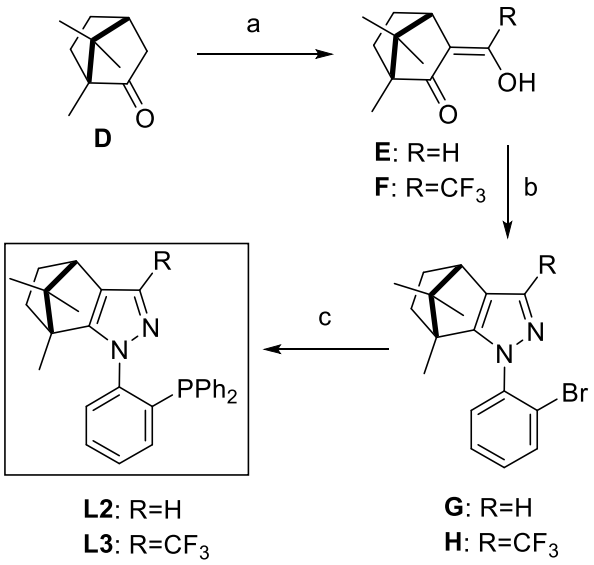
Results and Discussion

Synthesis of (-)-β-pinene based pyrazole ligand (**L1**) began with commercially available (-)-β-pinene of >98% optical purity. It was oxidised by $NaIO_4$-RuO_4 to afford (+)-nopinone **A**[30], which was formylated using a reported procedure[31] to obtain the product **B**. Condensation of the 1,3-dicarbonyl compound **B** with 2-bromophenylhydrazine afforded the pyrazole derivative **C**. Lithium-halogen exchange followed by quench with PPh_2Cl furnished the desired ligand **L1** in 31% overall yield from (-)-β-pinene (Scheme 1).



Scheme 1. (a) $RuCl_3$, H_2O, $NaIO_4$, CCl_4, CH_3CN, rt, 70%; (b) HCO_2Et, NaH, THF, rt, 85%; (c) 2-bromo phenylhydrazine hydrochloride, MeOH, reflux, 80%; (d) ^{n}BuLi,-78 °C, THF, PPh_2Cl, -78 °C to rt, 65%.

Camphor was similarly converted to acyl derivatives **E**[32] and **F** that were condensed with 2-bromophenyl hydrazine to afford the pyrazole nuclei **G** and **H**. Lithium-bromine exchange followed by treatment with PPh_2Cl yielded the desired optically active ligands **L2** and **L3**.



Scheme 2. (a) KH, HCO_2Et, THF (when R=H), 92%, NaH, DME, CF_3CO_2Et (when-R=CF3), 60%; (b) 2-bromophenylhydrazine hydrochloride, MeOH, reflux. 90%, (when R=H), 75% (when R=CF_3); (c) nBuLi, THF. -78°C, PPh_2Cl, -78°C, 85% (when R=H), 83% (when R=CF_3).

In order to have an impression of the structure of the ligand **L3** as well as a direct evidence of N, P coordination to the palladium centre, equimolar amount of ligand **L3** was mixed with the palladium dimer $[Pd(\eta^3\text{-}C_3H_5)Cl)]_2$ in DCM in presence of $AgSbF_6$. Unfortunately we were unable to grow X-ray grade crystals of the resulting complex. The ^{31}P NMR signal of the complex was shifted to 20.61 ppm from -15.48 ppm (in the ligand) indicating complex formation. The ^{1}H NMR spectrum was indeed very complex and ill-defined at room

temperature. Although the ligand **L3** has no signal in the region 2.5 to 6.0 ppm in the ^{1}H NMR spectrum, the spectrum of the complex featured seven peaks in this region, which may be attributed to π-C_3H_5 moiety[33-34].

When the ligand **L3** was treated with $Pd(CH_3CN)_2Cl_2$ in 1:1 ratio in $CHCl_3$, the resulting complex obtained, was crystallized from DCM/hexane. From the crystal structure depicted in Figure 1 it is evident that **L3** acts as a bidentate, P, N-donor ligand for palladium where phosphorus and pyrazole occupy *cis* coordination sites. The Pd-Cl bond length *trans* to P-Pd and N-Pd bonds are 2.347 Å and 2.280 Å respectively, as would be expected from a π-acceptor and a σ-donor ligand[35]. The pseudo equatorial Ph ring has an angle of 119.49° with the P-Pd bond and is oriented nearly orthogonal to the plane of the complex. Such an orientation would offer a steric hindrance to diminish the formation of the diastereomer **II** (*vide infra*).

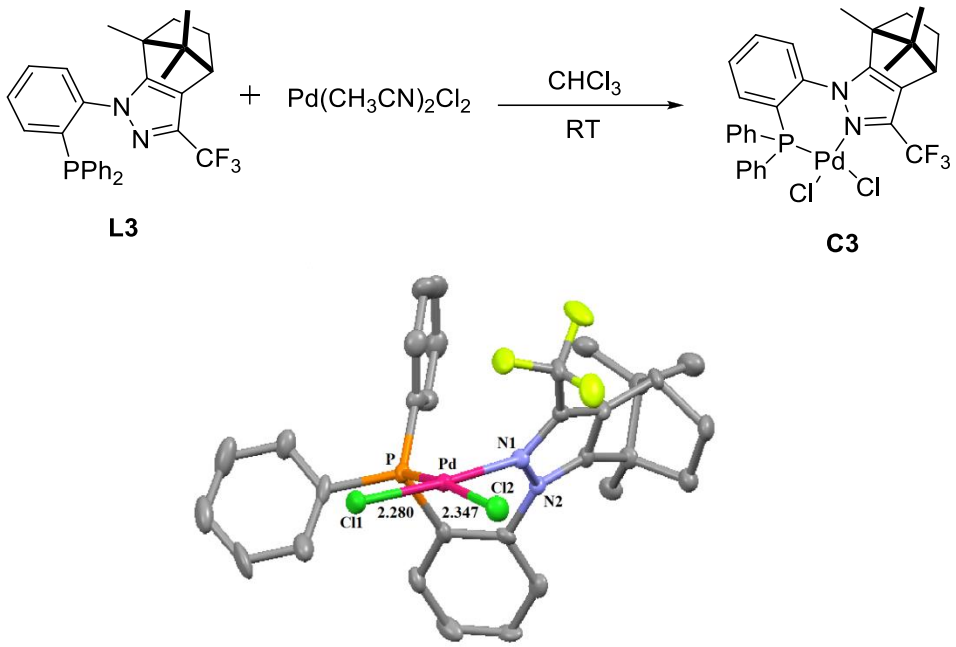
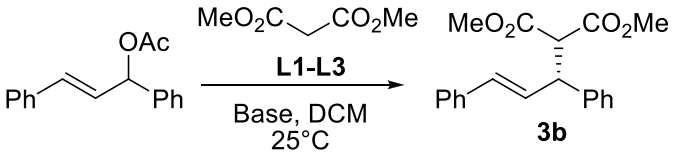


Figure 1. Synthesis and crystal structure of complex C3.

A large number of chiral, P,N-ligands are known to be effective in Pd catalysed asymmetric allylic alkylation reactions. With the ligands **L1**, **L2** and **L3** in hand, we undertook evaluation of these ligands in palladium catalysed alkylation of *rac*-(*E*)-1,3-diphenylprop-2-enyl acetate with dimethyl malonate, a benchmark reaction that has been traditionally used to assess the efficacy of new ligands[36]. For allylic substitution reactions, the active chiral palladium(II) catalyst was generated by the reaction of 2 mol% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and 4 mol% of chiral N,P ligand in DCM at room temperature. The results obtained for each ligand under same condition have been displayed in Table-1. From the data it is clear that the catalyst system was highly active and produced the substitution product in high chemical yield. The camphor derived ligands **L2** and **L3** displayed higher enantioselectivities than the one derived from (-)-β-pinene, *viz.* **L1**. Introduction of -CF_3 group at the 3 position of pyrazole ring in **L3** appears to have caused a slight decrease in the optical yield but afforded the product with a marginal increase in the chemical yield.

Table 1. Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate in presence of ligands **L1**-**L3**[a]



Entry	Ligand	Yield (%)[b]	ee[c] (%) (config[d])
1	**L1**	85	3 (*R*)
2	**L2**	79	58 (*R*)
3	**L3**	95	51 (*R*)

[a]Reaction condition: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2 mol%), Ligand (4 mol%),1,3-diphenylprop-2-enyl acetate (0.5mmol), Nu-H (1.5 mmol), M:L= 1:1, DCM (2 mL), KOAc (8 mol%), BSA (1.5 mmol), under Ar, [b]Isolated yield, [c]The ee values were determined by chiral HPLC, [d]The absolute configuration was determined by comparison of the sign of specific rotation with reported data.

The accepted mechanism for palladium catalysed allylic substitution postulates formation of a symmetrical Pd-allyl complex from the racemic substrate (Figure 2). The nucleophile can attack either of the two π-allyl termini of two alternative diastereomeric π-allyl palladium complexes (**I** and **II**). That is, there are four possible reaction pathways of which two pathways (a and d) would lead to product **3a** (with *S*-configuration) and the other two (b and c) would lead to product **3b (**with *R*-configuration).

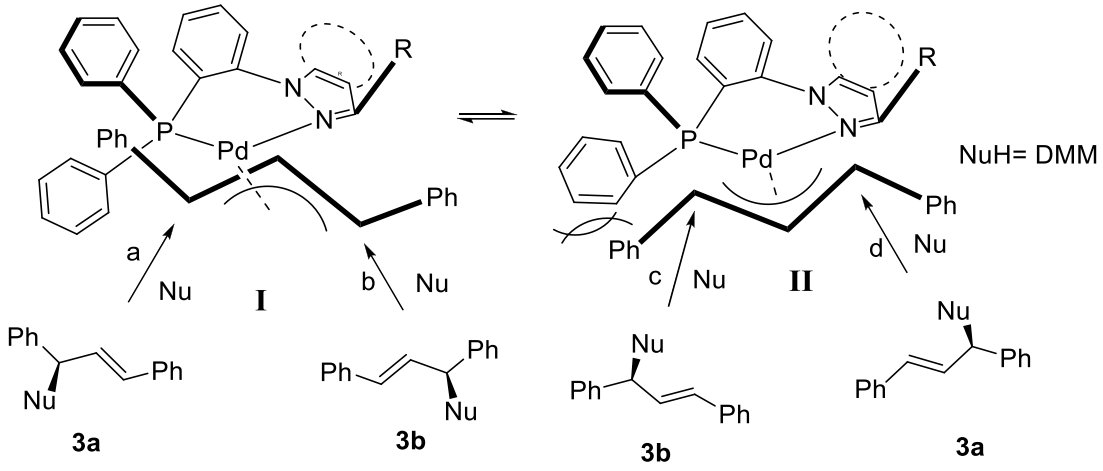


Figure 2. Symmetrical Pd-allyl complex from the racemic substrate (Figure 2 has been drawn maintaining a similarity with the crystal structure orientation).

With a ligand featuring two hetero-donor sites such as ours, overall stereochemistry of the ligand would determine the ratio of the two diastereomeric intermediates **I** and **II** at equilibrium[37] and the electronically different nature of the two donor centre would possibly direct the approach of the incoming nucleophiles.

It would be expected that the nucleophilic attack on these intermediates **I** and **II** could be regioselective since it is more likely to occur from a direction *trans* to phosphorus because phosphorus is a better π-acceptor than nitrogen. It can also be seen that the isomer **II** is more sterically encumbered than the corresponding **I** isomer: one of the terminal Ph ring of the allyl moiety can have unfavourable steric interaction with one Ph ring of the PPh_2 of the ligand. Therefore, in order to account for the observed *R*-configuration of the final major product **3b** we can assume that the product arises from the intermediate **I** by attack of the nucleophile on to the allyl carbon *trans* to phosphorus (path-b). The enantio-differentiation, however, remained inadequate for a practical utility, presumably because the bicyclic core of the terpene was far removed from the metal-binding site. The *gem*-dimethyl-substituted bridge in ligand **L1** is perhaps even farther removed for any effective chiral induction.

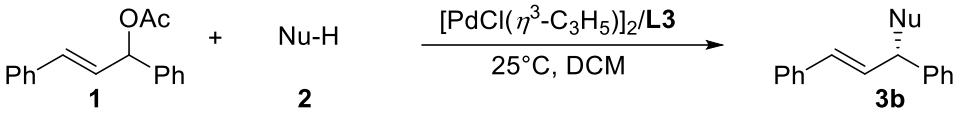
In ligand **L3** where a 3-CF_3 group is present on pyrazole, a slight decrease of *ee* was observed compared to **L2**. The electron withdrawing group probably makes nitrogen a weaker donor and ends up lowering the energy differences between nucleophilic attack *trans* to P and N. Nevertheless, using **L3**, we obtained the highest yield of product.

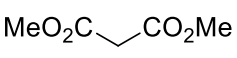
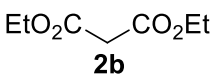
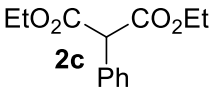
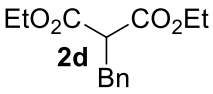
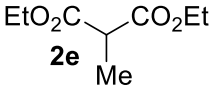
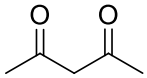
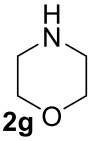
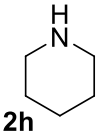
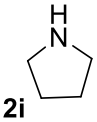
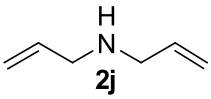
In view of the superior yield, a variety of carbon and nitrogen nucleophiles were tested using **L3** (Table 2). Though the yields are excellent with most of the nucleophiles, enatioselectivity was low to moderate. In terms of optical yield toluene was found to be a better solvent (entry-2, 4) than DCM though an increased amount of catalyst was required for high conversion. A primary amine like benzylamine however, gave poor yield[38]. The amination reaction required longer reaction time for completion and afforded products with inferior enantioselectivity.

Ligand **L3** was also utilized in asymmetric Suzuki-Miyaura cross-coupling reaction to synthesize axially chiral biaryls. Axially chiral biaryls are important units in numerous natural products and constitute an important class of ligands for asymmetric catalysis. Examples of asymmetric Suzuki-Miyaura reaction are not numerous as it is usually difficult to couple two sterically hindered arenes. To the best of our knowledge, pyrazole tethered phosphine ligands have never been used in the asymmetric version of the Suzuki-Miyaura reaction.

The reaction of aryl bromide and aryl boronic acid with Pd catalyst and ligand **L3** in presence of CsF in toluene afforded the coupling products in uniformly high yield (Table 3). A variety of 2-substituted aryl bromides were used. Enantioselectivity however, was far from satisfactory. When the methyl group is *ortho* to boronic acid instead of bromine (compare entry-4 with entry-5, Table 3), enantioselectivity was somewhat improved.

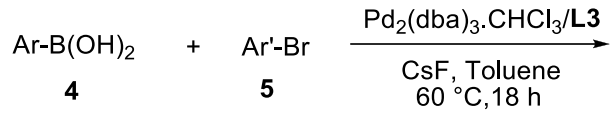
Table 2. Allylic substitution of 1,3-diphenylprop-2-enyl acetate with different carbon and nitrogen nucleophiles in presence of ligand **L3**[a]

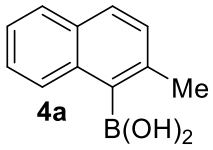
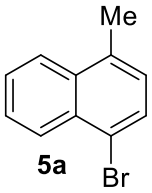
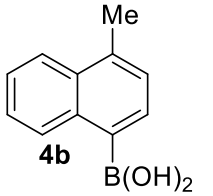
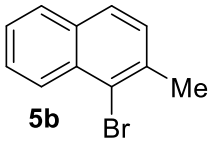
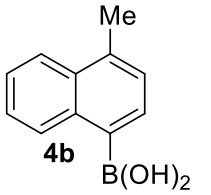
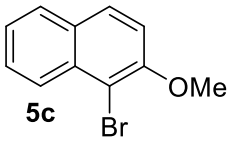
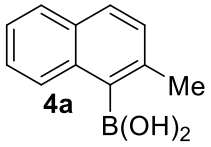
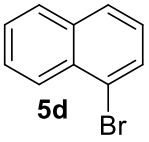


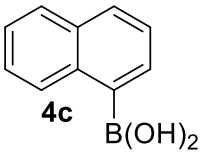
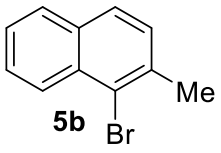
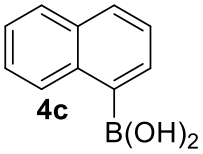
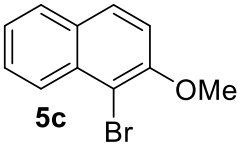
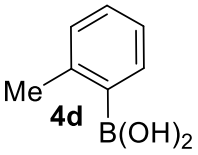
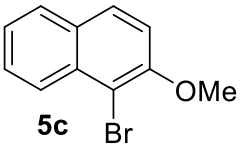
Entry	Nu-H	Pd Cat (mol %)	Time (h)	Product	Yield (%)[b]	ee[c] (%) (config[d])
1	 **2a**	2	2	**3b**	95	51 (*R*)
2[e]		4	5	**3b**	87	64 (*R*)
3	 **2b**	2	2	**3c**	89	37 (*R*)
4[e]		4	4	**3c**	90	58 (*R*)
5	 **2c**	2	4	**3d**	89	53 (*S*)
6	 **2d**	2	4	**3e**	91	53 (*S*)
7	 **2e**	2	5	**3f**	87	60 (*S*)
8	 **2f**	4	24	**3g**	88	51 (*R*)
9	 **2g**	2	24	**3h**	81	38 (*S*)
10	 **2h**	2	19	**3i**	95	31 (*S*)
11	 **2i**	4	20	**3j**	95	35 (*S*)
12	 **2j**	4	24	**3k**	84	34 (*S*)
13	 **2K**	2	24	**3l**	18	37 (*s*)

[a]Reaction condition: 1,3-diphenylprop-2-enyl acetate (0.5 mmol), Nu-H (1.5 mmol), M:L= 1:1, DCM (2 mL), KOAc (8 mol%), BSA (1.5 mmol), for amination base was not used, under Ar, [b]Isolated yield, [c]The ee values were determined by chiral HPLC, [d]The absolute configuration was determined by comparison of the sign of specific rotation with reported data, [e]Toluene used as solvent.

Table 3. Suzuki-Miyaura cross-coupling[a]



Entry	Ar-B(OH)$_2$	Ar'-Br	Product	Yield (%)[b]	ee (%)[c]
1			**6a**	80	33
2			**6a**	82	42
3			**6b**	83	20
4			**6c**	82	32

Entry	Ar-B(OH)$_2$	Ar'-Br	Product	Yield (%)[b]	ee (%)[c]
5			**6c**	85	8
6			**6d**	85	20
7			**6e**	80	10

[a]Reaction conditon: Ar'-Br (0.5 mmol), Ar-B(OH)$_2$ (0.75 mmol), CsF (1.5 mmol), Toluene (2 mL), $Pd_2(dba)_3.CHCl_3$ (4 mol%), **L3** (8 mol%), M:L=1:1, [b]Isolated yield, [c]The ee values were determined by chiral HPLC.

Conclusions

In summary, we synthesized chiral pyrazole tethered bidentate phosphorus-nitrogen ligands based on β-pinene and camphor scaffold. The crystal structure of a representative complex established the bidentate mode of P, N-coordination to palladium. These ligands provided excellent chemical yields in asymmetric allylic substitution (with carbon and nitrogen nucleophiles) and Suzuki-Miyaura cross-coupling reactions but optical yields remained modest. The structural motifs are being modified further in our laboratory to improve the enantio-discrimination of such chiral ligands in these and other reactions.

Experimental Section

General. Unless otherwise noted all starting materials were obtained from commercial suppliers. Organic solvents were dried and distilled as described elsewhere. All moisture and air sensitive reactions were carried out in a oven-dried flask under argon atmosphere. Column chromatography was performed with silica gel 230 ~ 400 and 100 ~ 200 meshes. All ^{1}H NMR (300 and 500 MHz), ^{13}C NMR (75 and 125 MHz), ^{31}P NMR (212 MHz) and ^{19}F NMR (470.5 MHz) spectra were recorded in $CDCl_3$ solution and reported in ppm (δ). X-ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation on a SMART APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX. The structure was solved by Patterson method and refined in a routine manner. Non hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically fixed.

Preparation of ligands L1, L2 and L3

(1R)-(+)-Nopinone (A) from (1S)-(-)-β-pinene.[30] ^{l}H NMR ($CDC1_3$, 500 MHz, ppm) δ 0.85 (s, 3 H), 1.33 (s, 3 H), 1.47 (d, *J* = 9.5 Hz, 1 H), 1.8-2.0 (m, 2H), 2.1-2.2 (m, 2 H), 2.4-2.5 (m, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 21.3, 22.0, 25.2, 25.8, 32.7, 40.3, 41.1, 57.9, 214.6.

Keto aldehyde (B) from (1R)-(+)-Nopinone (A).[31] ^{l}H NMR ($CDC1_3$, 500 MHz, ppm) δ 0.90 (s, 3H), 1.31 (s, 3H), 1.39 (d, *J* = 10.5 Hz, 1H), 2.23-2.24 (m, 1H), 2.43-2.55 (m, 4H), 7.18 (s,1H), 13.34 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 21.5, 25.3, 26.0, 27.5, 29.7, 39.4, 39.6, 53.5, 54.6, 107.2, 163.9, 209.4.

Preparation of bromo derivative (C) from keto aldehyde (B). A solution of keto aldehyde (B) (2.2 g, 13.05 mmol) and 2-bromophenylhydrazine hydrochloride (3.0 g, 13.33 mmol) in dry methanol (140 mL) was refluxed for 9 h. Solvent was removed under reduced pressure and the resulting liquid was purified by flash column chromatography (silica gel, 8% acetone/ petroleum ether) to afford the bromo derivative (C) as yellow liquid (3.31 g, 80%); $[\alpha]^{25}_{D}$ = +5.76 (c = 5.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, ppm). δ 0.53 (s, 3H), 1.12 (s, 3H), 1.25 (d, *J* = 8.5 Hz, 1H), 2.05-2.07 (m, 1H), 2.37 (t, *J* = 5 Hz, 1H), 2.43-2.46 (m, 1H), 2.49-2.59 (m, 2H), 7.03-7.06 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.26 (s, 1H), 7.44 (d, *J* = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 21.8, 24.5, 26.4, 29.4, 32.8, 40.7, 41.7, 112.4, 121.4, 128.2, 129.8, 130.2, 133.5, 138.1, 138.8, 150.5; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}BrN_2$ $[M+H]^+$ 317.0653, found 317.0646.

Preparation of L1 from bromo derivative (C). To a stirred solution of bromo derivative (C) (1.5 g, 4.73 mmol) in THF (18 mL) was added *n*-BuLi (2.3 mL, 5.68 mmol, 2.5 M in THF) dropwise at -78 °C. PPh_2Cl (1.1 mL, 5.68 mmol) was added dropwise at -78 °C and stirring was continued for 4 h. After usual work up, a pale yellow solid was obtained which was purified by flash column chromatography (silica gel, 7% acetone/ petroleum ether) to give the pure crystalline product L1 as yellow solid (1.44 g, 72%); mp 139-141 °C; $[\alpha]^{25}_{D}$ = -5.48 (c = 3.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 0.65 (s, 3H, $-CH_3$), 1.04 (d, *J* = 9.5 Hz, 1H, -CH), 1.25 (s, 3H, $-CH_3$),

2.15-2.17 (m, 1H, -CH), 2.34-2.39 (m, 1H, -CH), 2.49 (t, *J* = 5 Hz, 1H, -CH), 2.61-2.70 (m, 2H, $-CH_2$), 7.02-7.04 (m, 1H, Ar-H), 7.11-7.14 (m, 1H, Ar-H), 7.20-7.29 (m, 11H, Ar-H), 7.34-7.40 (m, 2H, Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 21.5, 24.4, 26.3, 29.4, 32.5, 40.6, 41.4, 112.2, 127.8, 127.8, 128.4, 128.4, 128.4, 128.5, 128.6, 128.7, 129.4, 133.8, 133.9, 134.9, 136.2, 136.4, 136.7, 136.8, 137.1, 137.2, 137.4, 143.2, 143.4, 149.9; ^{31}PNMR ($CDCl_3$, 202.44 MHz, ppm) δ -15.20 (PPh_3 used as standard); HRMS (ESI) *m/z* calcd for $C_{28}H_{28}N_2P$ $[M+H]^+$ 423.1990, found 423.1985.

Preparation of (1R)-3-hydroxymethylene-camphor (D) from (R)-(+)-camphor.[10] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.83 (s, 3H), 0.91 (s, 3H), 0.95 (s, 3H), 1.35- 1.44 (m, 2H), 1.66-1.71 (m, 1H), 1.98-2.03 (m, 1H), 2.42 (d, J = 4 Hz, 1H), 6.76 (s, 1H), 9.70-9.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.7, 9.2, 9.5, 18.6, 18.8, 19.0, 19.6, 20.5, 21.9, 22.2, 27.0, 27.9, 30.1, 30.2, 30.3, 44.2, 45.2, 46.8, 47.0, 49.9, 57.4, 58.7, 63.8, 67.0, 119.6, 151.8, 196.1, 212.9.

Preparation of bromo derivative (E) from 3-hydroxymethylene-camphor (D). To a solution of D (0.87 g, 4.8 mmol) in dry methanol (20 mL), 2-bromophenylhydrazine hydrochloride (0.89 g, 4 mmol) was added and heated under reflux for 6 h. Solvent was removed under reduced pressure and resulting solid was purified by column chromatography (silica gel, 3% ethyl acetate/petroleum ether) to give the desired product E as yellow solid (1.4 g, 90% yield); mp 88 - 90 °C , $[\alpha]^{25}_D$= -0.82 (c = 6.06, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.61 (s, 3H), 0.64 (s, 3H), 0.65 (s, 3H), 0.94 – 1.02 (m, 2H), 1.50 – 1.55 (m, 1H), 1.82 – 1.86 (m, 1H), 2.61 (d, *J* = 4 Hz, 1H), 7.04 – 7.15 (m, 4H), 7.45 (d, *J* = 8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.5, 19.7, 20.5, 27.8, 29.8, 33.6, 47.8, 52.6, 63.4, 122.3, 127.9, 128.7, 129.7, 130.5, 132.7, 133.3, 139.6, 155.6; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}N_2Br$ $[M+H]^+$ 331.0810, found 331.0805.

Preparation of L2 from bromo derivative (E). To a solution of N-(2-bromophenyl)-pyrazole E (0.44 g, 1.2 mmol) in dry THF (4 mL), *n*-BuLi (1.0 mL, 1.6 M in hexane, 1.5 mmol) was added drop wise at -78 °C. The colour of the solution changed to yellow. After stirring for 30 min, PPh_2Cl (0.12 mL, 1.5 mmol) was added dropwise at -78 °C and stirring was continued for 4 h. After usual work up, a pale yellow solid was obtained which was purified by flash column chromatography to give the pure crystalline product L2 (0.49 g, 85% yield) as yellow semi white solid; mp 136 - 139°C. $[\alpha]^{25}_D$ 5.37 (c = 4.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.64 (s, 3H, $-CH_3$), 0.84 (s, 3H, $-CH_3$), 0.88 (s, 3H, $-CH_3$), 1.09 – 1.19 (m, 2H, $-CH_2$), 1.64 - 1.68 (m, 1H, -CH), 2.02 (t, *J* = 11 Hz, 1H, -CH), 2.76 (d, *J* = 3.5 Hz, 1H, -CH), 7.08 – 7.10 (m, 1H, -CH), 7.24 – 7.33 (m, 13H, Ar-H), 7.40 (t, *J* = 7.5 Hz, 1H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.3, 19.7, 20.5, 27.8, 33.6, 47.5, 52.7, 53.5, 63.2, 127.7, 128.4, 128.5, 128.6, 128.7, 128.7, 129.0, 129.2, 131.9, 133.8, 133.9, 133.9, 134.0, 135.0, 136.6, 136.7, 136.9, 136.9, 137.0, 137.2, 144.0, 155.0; ^{31}PNMR ($CDCl_3$, 202.4 MHz, ppm) δ -16.12 (PPh_3 used as standard) HRMS *m/z* calcd for $C_{29}H_{30}N_2P$ $[M+H]^+$ 437.2147, found 437.2141.

Preparation of 3-trifluoromethylhydroxymethylene-camphor (F) from (R)-(+)-camphor.[39] To a slurry of NaH (1.85 g, 77.2 mmol, 60% oil suspention washed with dry pet ether) in DME, (R)-(+)-camphor (5 g, 32.8 mmol) was added in portions and was brought to reflux and stirred for 1 hour. Evolution of gas was observed shortly after reflux began. A solution of ethyl trifluoroacetate (5.1 g, 36.1 mmol) in DME (10 mL) was added to the refluxing reaction mixture dropwise. After the addition of the ester the gas evolution became more rapid and it slowed gradually after all the ester had been added. Reflux was continued for 2 hours after the addition of the ester was complete. The reaction mixture was cooled to room temperature and excess NaH was quenched with ice water and 95% ethanol (4 mL). The reaction mixture then poured to water (120 ml) and acidified with conc. HCl and extracted with pentane (3×30). The combined pentane mixture was washed subsequently with two portions of 5% $NaHCO_3$ solution and brine and dried over Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (silica gel, 2% ethyl acetate/petroleum ether) afforded F as red liquid (4.9 g, 60%); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.83 (s, 3H),

0.96-1.00 (m, 6H), 1.42-1.54 (m, 2H), 1.74-1.82 (m, 1H), 2.04-2.10 (m, 1H), 2.88 (d, *J* = 1.5 Hz,1H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 8.4, 18.2, 20.4, 26.6, 30.1, 47.1, 48.9, 58.0, 117.7, 121.2, 147.9, 148.4, 214.1.

Preparation of bromo derivative (G) from 3-trifluoromethylhydroxymethylene-camphor (F). To a solution of 3-trifluoromethylhydroxymethylene camphor F (1 g, 4 mmol) in dry methanol (20 mL), 2-bromophenylhydrazine hydrochloride (0.89 g, 4 mmol) was added and heated under reflux for 18 h. Solvent was removed under reduced pressure, and resulting yellow solid was purified by column chromatography (silica gel, 3% ethyl acetate/petroleum ether) to give the desired product G as pale yellow solid (1.21 g, 75% yield); mp 76- 78°C . $[\alpha]^{25}_D$ -0.2 (c = 7.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): *δ* 0.87-0.92 (m, 9H), 1.20-1.25 (m, 2H), 1.79-1.84 (m, 1H), 2.11-2.15 (m, 1H), 3.01(d, *J* = 3.5, 1H), 7.34-7.43 (m, 3H), 7.69-7.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 10.2, 19.5, 20.4, 27.3, 29.8, 47.5, 53.3, 63.9, 118.7, 120.8, 122.1, 123.0, 127.2, 128.1, 129.5, 131.2, 133.5, 135.9, 136.2, 138.8, 157.4; ^{19}F NMR (470.5 MHz, $CDCl_3$, ppm) *δ* -64.01(hexafluoro benzene as standard); HRMS (ESI) *m/z* calcd for $C_{18}H_{18}BrF_3N_2$ $[M+H]^+$: 398.0605, found: 399.0677.

Preparation of L3 from bromo derivative (G). To a solution of N-(2-bromophenyl)-pyrazole G (1 g, 2.5 mmol) in dry THF (8 ml), *n*-BuLi (1.9 mL, 1.6 M in hexane, 3.1 mmol) was added dropwise at -78 °C. The colour of the solution changed from yellow to dark brown. After stirring for 30 min, PPh_2Cl (0.68 g, 3.1 mmol) was added dropwise at -78 °C and stirring was continued for 4 h. After work up, a pale yellow solid was obtained which was purified by flash column chromatography to give the pure crystalline product **L3** (1.05 g, 83% yield) as pale yellow solid; mp 132-134 °C. $[\alpha]^{25}_D$ 5.4 (c = 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): *δ* 0.80 (s, 3H, -CH_3), 0.89(s, 3H, -CH_3), 0.95 (s, 3H, -CH_3), 1.16-1.20 (m, 1H, -CH), 1.37-1.42 (m, 1H, -CH), 1.73-1.78 (m, 1H, -CH), 2.06-2.11(m, 1H, -CH), 2.94 (d, *J* = 3.5 Hz, 1H, -CH), 7.13-7.15 (m, 1H, Ar-H), 7.21-7.32 (m, 11H, Ar-H), 7.35-7.41 (m, 2H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 11.0, 19.6, 20.5, 27.4, 33.6, 47.6, 53.3, 63.7, 120.8, 123.0, 127.3, 127.6, 128.5, 128.6, 128.9, 129.3, 129.5, 133.8, 133.9, 134.0, 134.1, 134.7, 134.8, 135.1, 136.2, 136.3, 136.4, 136.4, 137.4, 137.6, 143.2, 143.4, 156.75; ^{31} P NMR (202.44 MHz, $CDCl_3$, ppm) *δ* -16.30 (PPh_3 used as a standard); ^{19}F NMR (470.5 MHz, $CDCl_3$, ppm) *δ* -61.668 (hexafluoro benzene used as standard); HRMS (ESI) *m/z* calcd for $C_{30}H_{28}F_3N_2P$ $[M+H]^+$: 504.1942, found: 505.2013.

Preparation of Pd-L3 complex (C3). A solution of **L3** (100 mg, 0.21 mmol) and $Pd(CH_3CN)_2Cl_2$ (54.4 mg, 0.21 mmol) in in dry $CHCl_3$ (5 mL) was stirred for 4 h at RT. The solvent was removed under reduced pressure affording C3 as a deep yellow powder (114 mg, 83%) which was crystallized from DCM/hexane.

Crystal structure solution of complex C3. An x-ray grade colorless, block shaped crystal (0.28 X 0.19 X 0.08 mm) was grown from DCM/hexane for analysis: Empirical formula $C_{30}H_{28}Cl_2F_3N_2PPd$, *FW*= 681.81, monoclinic space group $P2_1$, *a* = 8.8797(7)Å, *b* = 15.9122(12)Å, *c* = 11.4502(9)Å, β = 102.348(2)°, *V* = 1580.4(2) Å^3, *T* = 150 K, *Z* = 2. ρ_{calcd} = 1.433 g cm^{-3}. *F* (000) = 688, *λ* (Mo–Kα) = 0.71073 Å, μ MoKα /mm^{-1} = 0.846, $2\theta_{max}$ = 50.0°, 15013 total reflections, 5237 unique reflections, 5001 observed (I>2σ (I)) 355 parameters; R_{int} = 0.0327, R_1 = 0.0322; wR_2 = 0.0762 (I>2σ (I)), R_1 = 0.0338; wR_2 = 0.0771 (all data) with GOF = 1.016. Crystallographic data (excluding structure factors) for the structure has been deposited with the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC No – 912500 for C3. Copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax : +44-(0)1223-336033 or e-mail : deposit@ccdc.cam.ac.uk).

Representative procedure for allylic alkylation. To the mixture of palladium allyl chloride dimer, ligand **L3** and KOAc (8 mol%) in 1 mL of DCM was added and stirred at 25 ºC for 30 minutes. Then to it a solution of 1,3-diphenyl 2-propenyl acetate (126.2 mg, 0.5 mmol) in 1 mL DCM was introduced and stirred at 25 ºC for 15 min. Then the alkylating agent (1.5 mmol), N,O-bis(trimethylsilyl)-acetamide (BSA) (0.37 mL, 1.5 mmol) were added subsequently. The reaction was monitored by TLC. The mixture was quenched by the addition of cold saturated aqueous NH_4Cl (2 mL) and extracted with EtOAc. The organic phase was dried over Na_2SO_4. After

filtration and concentration, the residue was purified by flash chromatography on silica gel to give the product. All known compounds were characterized by ^{1}H and ^{13}C NMR spectra by comparing with their reported data in the literature.

(*R*, *E*)-Dimethyl-2-(1,3-diphenylallyl)malonate (3b).[40] Colorless oil. $[\alpha]^{24}_{D}$ 5.4 (*c* 7.5, $CHCl_3$, 51% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H, MeOH/DEA = 100/0.1. flow rate: 1.0 mL/min, 27.6 min [(*S*)-isomer, minor] and *t*R 42.5 min [(*R*)-isomer, major] detection at 254 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 3.43 (s, 3H), 3.62 (s, 3H), 3.88 (d, *J* = 10.9 Hz, 1H), 4.19 (dd, *J* = 8.5 Hz, 10.8 Hz, 1H), 6.25 (dd, *J* = 8.4 Hz, 15.7 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 49.3, 52.6, 52.7, 57.8, 126.5, 127.3, 127.7, 127.9, 128,6, 128.8, 129.2, 132.0, 136.9, 140.3, 167.9, 168.3.

(*R*, *E*)-Diethyl 2-(1,3-diphenylallyl)malonate (3c).[40] Colorless oil. $[\alpha]^{24}_{D}$ 6.9 (*c* 5.7, $CHCl_3$, 37% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H , EtOH = 100, flow rate: 0.5 mL/min, *t*R 15.7 min [(*S*)-isomer, minor] and 30.7 min [(*R*)-isomer, major], detection at 254 nm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.02 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 3.92-4.02 (m, 3H), 4.15-4.32 (m, 3H), 6.36 (dd, *J* = 8.3 Hz, 15.7 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 7.20-7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 13.9, 14.2, 49.3, 57.9, 61.4, 61.7, 126.4, 127.2, 127.6, 128.1, 128.6, 128.7, 129.5, 131.8, 137.0, 140.4, 167.5, 168.0.

(*S*, *E*)-Diethyl 2-(1,3-diphenylallyl)-2-phenylmalonate (3d).[40] Colorless oil. $[\alpha]^{25}_{D}$ -8.6(*c* 2.1, $CHCl_3$, 53% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, EtOH/TFA = 100/0.1. flow rate: 0.5 mL/min, *t*R 9.1 min [(*S*)-isomer, major] and 10.1 min [(*R*)-isomer, minor], detection at 254 nm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.09-1.18 (m, 6H), 4.05-4.17 (m, 4H), 4.57 (d, *J* = 8.3 Hz, 1H), 6.31-6.46 (m, 2H), 6.90-6.93 (m, 2H), 7.05-7.14 (m, 4H), 7.17-7.25 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 14.0, 14.1, 55.4, 61.6, 61.7, 68.2, 126.4, 127.0, 127.4, 127.6, 127.7, 128.5, 129.2, 129.7, 130.3, 132.7, 135.6, 137.5, 139.6, 169.9, 169.7.

(*S*, *E*)-Diethyl-2-benzyl-2-(1,3-diphenylallyl)malonate (3e).[40] Colorless oil. $[\alpha]^{24}_{D}$ -27.4 (*c* 3.4, $CHCl_3$, 53% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H, IPA/hexane = 0.5/99.5. flow rate: 0.7 mL/min, *t*R 5.8 min [(*S*)-isomer, major] and 6.6 min [(*R*)-isomer, minor], detection at 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.04 (t, *J* = 7.1Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 3.12 (d, *J* = 13.8, 1H), 3.28 (d, *J* = 13.8, 1H), 3.95-4.04 (m, 2H), 4.13-4.27 (m, 2H), 4.32 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.80 (dd, *J* = 8.4 Hz, 15.8 Hz, 1H), 7.19-7.23 (m, 5H), 7.27-7.38 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 13.8, 14.1, 41.2, 54.9, 61.2, 61.3, 64.3, 126.5, 126.8, 127.3, 127.4, 128.0, 128.5, 128.5, 129.6, 130.1, 130.5, 132.3, 137.0, 137.6, 139.5, 170.3, 170.4.

(*S*, *E*)-Diethyl 2-(1,3-diphenylallyl)-2-methylmalonate (3f).[40] Colorless oil. $[\alpha]^{25}_{D}$ -9.2 (*c* 1.9, $CHCl_3$, 60% ee (S)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL AD-H, IPA/hexane = 0.5/99.5. flow rate: 0.7 mL/min, *t*R 17.6 min [(*S*)-isomer, major] and 20.8 min [(*R*)-isomer, minor], detection at 254 nm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.16-1.28 (m, 6H), 1.50 (s, 3H), 4.07-4.24 (m, 4H), 4.32 (d, *J* = 8.9 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.73 (dd, *J* = 15.7 Hz, 8.8 Hz, 1H), 7.21-7.37 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 14.1, 14.2, 19.0, 53.8, 54.0, 59.0, 61.5, 126.5, 127.2, 127.4, 128.3, 128.6, 129.0, 129.8, 132.7, 137.5, 139.6, 171.1, 171.3.

(*R*, *E*)-3-(1,3-Diphenylallyl)pentane-2,4-dione (3g).[41] $[\alpha]^{24}_{D}$ -2.6 (*c* 2.0, EtOH, 51% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL AD-H, ETOH/hexane = 1/99. flow rate: 1 mL/min, *t*R 14.1 min [(*S*)-isomer, minor] and 15.8 min [(*R*)-isomer, major], detection at 220 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.83 (s, 3H), 2.16 (s, 3H), 4.25-4.26 (m, 2H), 6.08-6.15 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.10-7.27 (m, 10H);); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 29.8, 30.1, 74.6, 126.4, 127.4, 127.8, 128.0, 128.6, 128.7, 128.8, 129.4, 131.8, 132.1, 136.6, 140.2, 202.7, 202.9.

Representative procedure for allylic amination

To the mixture of palladium allyl chloride dimer and ligand **L3**, 1 mL of DCM was added and stirred at 25 ºC for 30 minutes. Then to it a solution of 1,3-diphenyl 2-propenyl acetate (126.2 mg, 0.5 mmol) in 1 ml DCM was

introduced and stirred at rt for 15 min. Then amine (1.5 mmol) was added and the reaction mixture was stirred at 25 ºC. The reaction was monitored by TLC. The reaction mixture was dried under reduced pressure and the obtained residue was purified by flash column chromatography. All known compounds were characterized by ^{1}H and ^{13}C NMR spectra by comparing with their reported data in the literature.

(*S,E*)-4-(1,3-Diphenylallyl)morpholine (3h).[42] Pale solid. $[\alpha]^{25}_D$ 2.2 (*c* 5.8, $CHCl_3$, 38% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (OJ-H column , IPA /hexane = 5/95. flow rate: 0.5 mL/min, *t*R 9.3 min [(*S*)-isomer, major] and 12.4 min[(*R*)-isomer, minor], detection at 220 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.39-2.46 (m, 2H), 2.57-2.61 (m, 2H), 3.73-3.76 (m, 4H), 3.83 (d, *J* = 8.8 Hz, 1H), 6.33(dd, *J* = 8.9 Hz, 15.8 Hz, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 7.25-7.46 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 29.9, 52.4, 67.3, 75.0, 126.6, 127.5, 127.8, 128.2, 128.7, 128.9, 131.4, 131.8, 136.9, 141.6.

(*S,E*)-1-(1,3-Diphenylallyl)piperidine (3i).[42] Pale solid. $[\alpha]^{25}_D$ 2.2 (*c* 3.2, $CHCl_3$, 31% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK AD-H, 2-propanol/hexane = 5/95. flow rate: 0.5 mL/min, *t*R 4.9 min [(*R*)-isomer, minor] and 5.4 min [(*S*)-isomer, major], detection at 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.35-1.39 (m, 2H), 1.46-1.53 (m, 4H), 2.25-2.29 (m, 2H), 2.39 (br s, 2H), 3.74 (d, *J* = 8.6 Hz, 1H), 6.27 (dd, *J* = 8.6 Hz, 15.8 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 7.13-7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 24.8, 26.3, 52.8, 74.8, 126.5, 127.1, 127.5, 128.2, 128.6, 128.6, 131.1, 132.3, 137.2, 142.4.

(*S,E*)-1-(1,3-Diphenylallyl)pyrrolidine (3j).[42] Pale solid. $[\alpha]^{26}_D$ 1.1 (*c* 8.4, $CHCl_3$, 35% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK OD-H, IPA/hexane = 1/99. flow rate: 0.5 mL/min, *t*R 5.2 min [(*R*)-isomer, minor] and 5.7 min [(*S*)-isomer, major], detection at 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.80 (br s, 4H), 2.49-2.59 (m, 2H), 3.80 (d, *J* = 8.4Hz, 1H), 6.44 (dd, *J* = 8.4Hz, 18.0 Hz, 1H), 6.57 (d, *J* = 15.8Hz, 1H), 7.17-7.36 (m, 9H), 7.44 (d, *J* = 7.4Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 23.5, 53.2, 74.5, 126.5, 127.3, 127.5, 127.8, 128.6, 128.7, 130.1, 133.1, 137.2, 143.1.

(*S,E*)-*N,N*-Diallyl-1,3-diphenylprop-2-en-1-amine (3k).[43] Yellow oil. $[\alpha]^{24}_D$ 15.8 (*c* 5.7, $CHCl_3$, 34% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (AD column, 100% hexane. flow rate: 7.0 mL/min, *t*R 7.0 min [(*S*)-isome, majorr] and 7.7 min [(*R*)-isomer, minor], detection at 220 nm); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 3.01-3.16 (m, 4H), 4.35 (d, *J* = 8.6 Hz, 1H), 5.03-5.12 (m, 4H), 5.75-5.84 (m, 2H), 6.25 (dd, *J* = 8.6 Hz, 15.8 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 7.13-7.38 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 29.8, 52.8, 67.2, 117.2, 126.5, 127.1, 127.6, 128.1, 128.5, 128.7, 129.9, 132.6, 136.2, 136.5, 137.2, 142.3.

(*S,E*)-*N*-Benzyl-1,3-diphenylprop-2-en-1-amine (3l).[42] Yellow oil. $[\alpha]^{25}_D$ 8.5 (*c* 1.9, $CHCl_3$, 37% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, hexane/IPA/DEA = 85/15/0.1. flow rate: 0.4 mL/min, *t*R 19.3 min [(*S*)-isomer, major] and 23.0 min [(*R*)-isomer, minor], detection at 254 nm); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): *δ* 3.80 (d, *J* = 1.5 Hz, 2H), 4.41 (d, *J* = 7.5 Hz, 1H), 6.34 (dd, *J* = 7.5Hz, 15.9 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 7.18-7.46 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 51.4, 64.7, 126.6, 127.1, 127.5, 127.5, 127.6, 128.4, 128.6, 128.6, 128.8, 130.6, 132.5, 137.1, 140.3, 142.8.

Representative procedure for Suzuki-Miyaura cross-coupling

To the mixture of $Pd_2(dba)_3.CHCl_3$ (20.7 mg, 0.02 mmol), **L3** (20.2 mg, 0.04 mmol), CsF (227.8 mg, 1.5 mmol), phenylboronic acid (129 mg, 0.75 mmol) and aryl bromide (0.5 mmol) dry toluene (2 mL) was added and heated at 60 ˚C for 18 h. Reaction mixture was cooled at room temperature and filtered through celite. After removal of solvent crude product was obtained which was purified by flash column chromatography. All known compounds were characterized by ^{1}H and ^{13}C NMR spectra by comparing with their reported data in the literature.

2,4'-Dimethyl-1,1'-binaphthyl (6a).[44] White solid. $[\alpha]^{25}_D$ -10.1 (*c* 5.8, $CHCl_3$, 33% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ, IPA/hexane = 10/90. flow rate: 1.0 mL/min, *t*R 5.0 min [(*R*)-isomer, major] and 18.8 min[(*S*)-isomer, minor], detection at 225 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm):

δ 2.16 (s, 3H), 2.85 (s, 3H), 7.20-7.32 (m, 5H), 7.40-7.54 (m, 4H), 7.91 (dd, *J* = 2.9 Hz, 8.2 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 1H);); ^{13}CNMR (75 MHz, $CDCl_3$): *δ* 19.7, 20.7, 124.6, 124.9, 125.8, 125.9, 126.0, 126.5, 126.6, 126.8, 127.6, 127.8, 128.7, 132.1, 133.0, 133.8, 134.0, 134.6, 135.8, 136.5.

2-Methoxy-4'-methyl-1,1'-binaphthyl (6b).[44] White solid. $[\alpha]^{25}_D$ 3.7 (*c* 1.7, $CHCl_3$, 20% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK OJ, IPA/hexane = 10/90. flow rate: 1.0 mL/min, *t*R 4.4 min [(*R*)-isomer, minor] and 17.2 min [(*S*)-isomer, major], detection at 227 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.86 (s, 3H), 3.80 (s, 3H), 7.24-7.55 (m, 9H), 7.91 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 19.8, 29.8, 56.9, 114.0, 123.7, 124.5, 125.6, 125.8, 126.4, 126.6, 126.9, 127.9, 128.2, 129.2, 129.5, 132.9, 132.9, 133.1, 134.0, 134.6, 154.8.

2-Methyl-1,1'-binaphthyl (6c).[44] White solid. $[\alpha]^{25}_D$ -7.3 (*c* 5.1, $CHCl_3$, 8% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (CHIRALCEL OJ-H, IPA/hexane = 10/90. flow rate: 1.0 mL/min, *t*R 5.9 min [(*S*)-isomer, minor] and 8.8 min [(*R*)-isomer, major], detection at 220 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.14 (s, 3H), 7.16-7.32 (m, 4H), 7.39-7.55 (m, 4H), 7.61-7.66 (m, 1H), 7.90 (d, *J* = 8.4Hz, 2H), 7.98(d, *J* = 8.4Hz, 2H);; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 20.6, 125.0, 125.5, 125.8, 126.0, 126.0, 126.2, 126.3, 126.4, 127.7, 127.8, 127.9, 127.9, 128.1, 128.3, 128.4, 128.7, 132.2, 132.7, 133.6, 133.9, 134.5, 136.2, 137.6.

2-Methoxy-1-1'binaphthyl (6d).[44] White solid. $[\alpha]^{25}_D$ -2.8 (*c* 2.7, $CHCl_3$, 20% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK OJ-H, IPA/hexane = 5/95. flow rate: 1.0 mL/min, *t*R 6.3 min [(*R*)-isomer, minor] and 10.6 min[(*S*)-isomer, major], detection at 224 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 3.62 (s, 3H), 7.07-7.21 (m, 5H), 7.29-7.33 (m, 3H), 7.50 (t, *J* = 8.01 Hz, 1H), 7.73-7.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 56.8, 114.0, 123.7, 125.6, 125.7, 125.8, 126.0, 126.3, 126.5, 127.9, 127.9, 128.4, 128.7, 129.2, 129.6, 133.8, 134.4, 134.7, 154.8.

2-Methoxy-1-*o*-tolylnaphthalene(6e).[45] White solid. $[\alpha]^{25}_D$ 2.4 (*c* 7.0, $CHCl_3$, 10% ee). The enantiomeric excess was determined by HPLC analysis (CHIRALPAK OJ-H , IPA/hexane = 2/98. flow rate: 1.0 mL/min, *t*R 4.9 min [(*major*)-isomer] and 7.6 min[(*minor*)-isomer], detection at 254 nm).^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.01 (s, 3H), 3.84 (s, 3H), 7.17-7.20 (m, 1H), 7.26-7.40 (m,7H), 7.82-7.85 (m, 1H), 7.90 (d, *J* = 9.0 MHz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 19.9, 56.7, 113.8, 123.6, 124.7, 125.2, 125.8, 126.5, 127.6, 128.0, 129.1, 130.0, 131.0, 133.6, 136.3, 137.8, 153.8.

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Supplementary Material

The Supplementary Material file can be found in the online version. It contains the X-ray crystallographic data, NMR.

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