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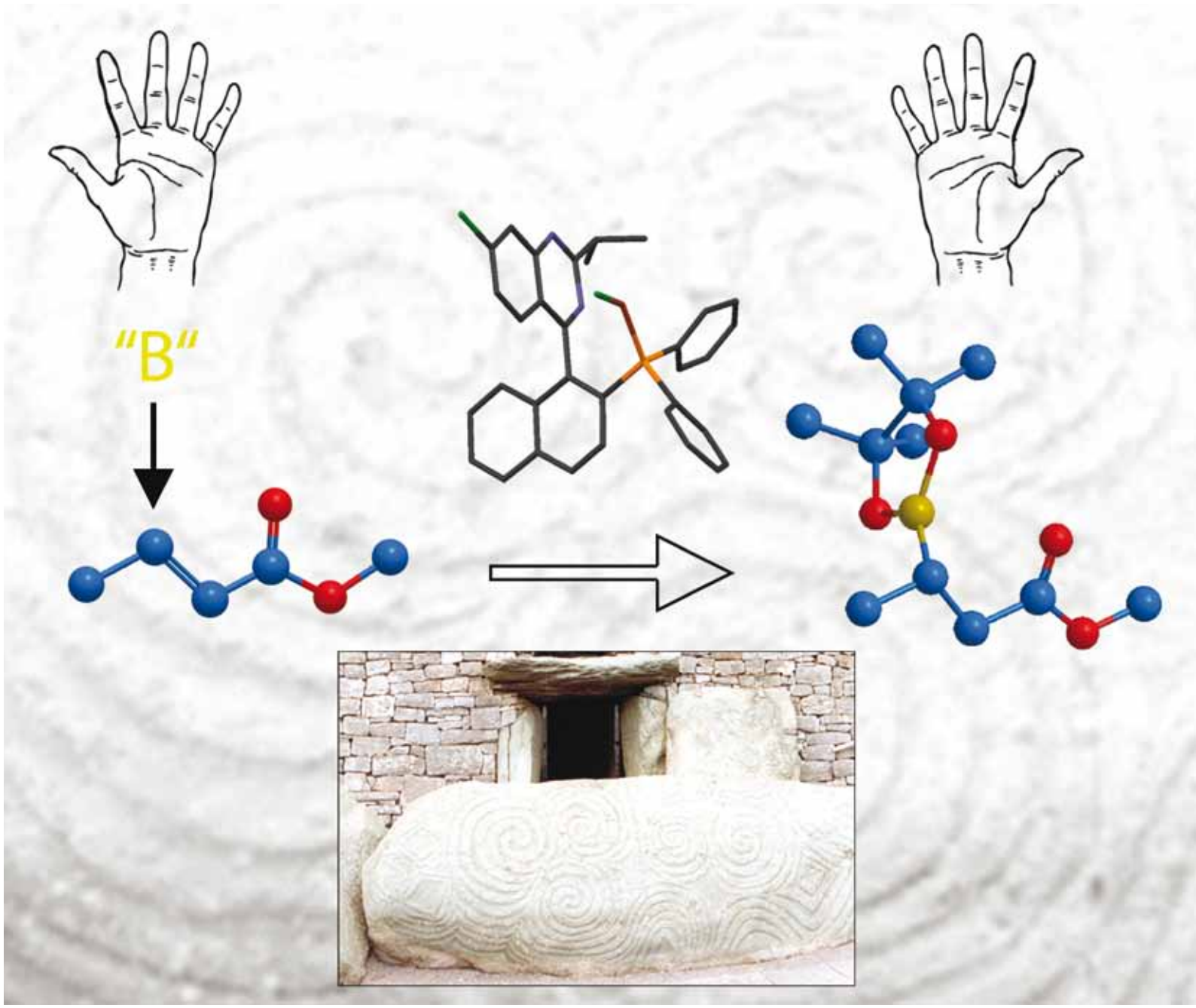

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Axially chiral P-N ligands for the copper catalyzed β-borylation of α,β-unsaturated esters†

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The synthesis and resolution of a new axially chiral Quinazolinap ligand are reported. The application of this and other related P-N ligands to the copper catalyzed β-borylation of α,β-unsaturated esters resulted in conversions of up to 100% and ee values of up to 79%. A diastereomerically pure palladacycle of the new ligand was characterised by X-ray crystallography.

Introduction

The synthetic challenges presented by structurally complex and diverse natural products provides the impetus for the development of new catalytic systems, which in turn offers an insight into the fundamental understanding of how new bonds can be formed.[1] Of particular interest is the challenge presented by issues of stereochemistry. Since the outstanding success of Noyori *et al*.'s BINAP ligand,[2] and its subsequent applications in asymmetric transition metal catalysis,[3] the development of new atropisomeric ligands has become an area of intense interest.[4] Of particular relevance to our work is the development of chiral heterobidentate systems due to their ability to induce asymmetry in a variety of reactions. Of these the phosphinamine ligand class has received the most interest due to the combination of steric and electronic effects exerted on substrates at the coordination sphere of the transition metal to which they are bound.[5]

The first successful axially chiral phosphinamine ligand, Quinap **1**, was developed by Brown *et al*. and incorporated a naphthalene–isoquinoline backbone with the necessary steric requirements to prevent free rotation about the biaryl linkage.[6] Stemming from this our group developed the Quinazolinap ligands (exemplified by **2a–e**, Fig. 1).[7] This allowed for studies on the effects of altering the basicity of the donor nitrogen, and for the facile introduction of steric bulk at the 2-position, which is believed to be important in the transfer of chiral information from catalyst to reaction product.

The quinazolinap ligands have proved efficacious in a variety of transition metal-catalyzed transformations, including rhodium-catalyzed hydroborations and palladium-catalyzed allylic alkylations.[7f–g,8] We wished to increase the scope of reactions to which Quinazolinap ligands can be applied and therefore initiated a study on the metal catalyzed β-borylation of α,β-unsaturated compounds, which is a promising transformation towards the stereoselective formation of a new C_β-B bond (Scheme 1).[9]

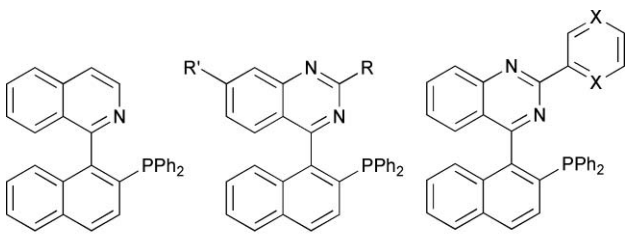
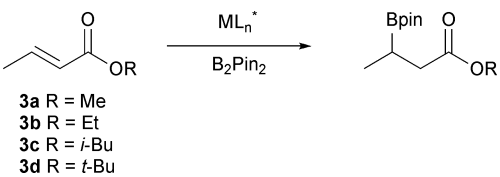


Fig. 1 Quinap and quinazolinap ligands.



Scheme 1

β-Borylation reactions have been catalyzed by a range of metals, most notably platinum and rhodium, yet the use of the inexpensive metal copper has recently been shown to be remarkably successful.[10] While bidentate P,P ligands[11] and N-heterocyclic ligands (NHC)[12] have recently demonstrated their efficiency in moderate to high asymmetric induction for the copper mediated reaction, only one bidentate P,N ligand has been tested to date.[11a] Herein we wish to report the application of Quinap **1** and Quinazolinaps **2a–e** to the asymmetric β-borylation of α,β-unsaturated esters **3a–d**, incorporating the synthesis and resolution of the new 7-substituted Quinazolinap **2c**. This is the first ligand in the Quinazolinap series that allows for the study of electronic variation at the 7-position. It was also envisaged that post-resolution modification at this position would provide an attractive route to a range of electronically diverse Quinazolinap ligands.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation data for **2c**, **4** and **6–11**, details of the resolution of **2c** and the general procedures employed for the asymmetric borylation. CCDC reference numbers 716086 and 716087. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900741e

‡ Correspondence concerning single-crystal X-ray data should be directed to this author (helge.muellerbunz@ucd.ie)

Results and discussion

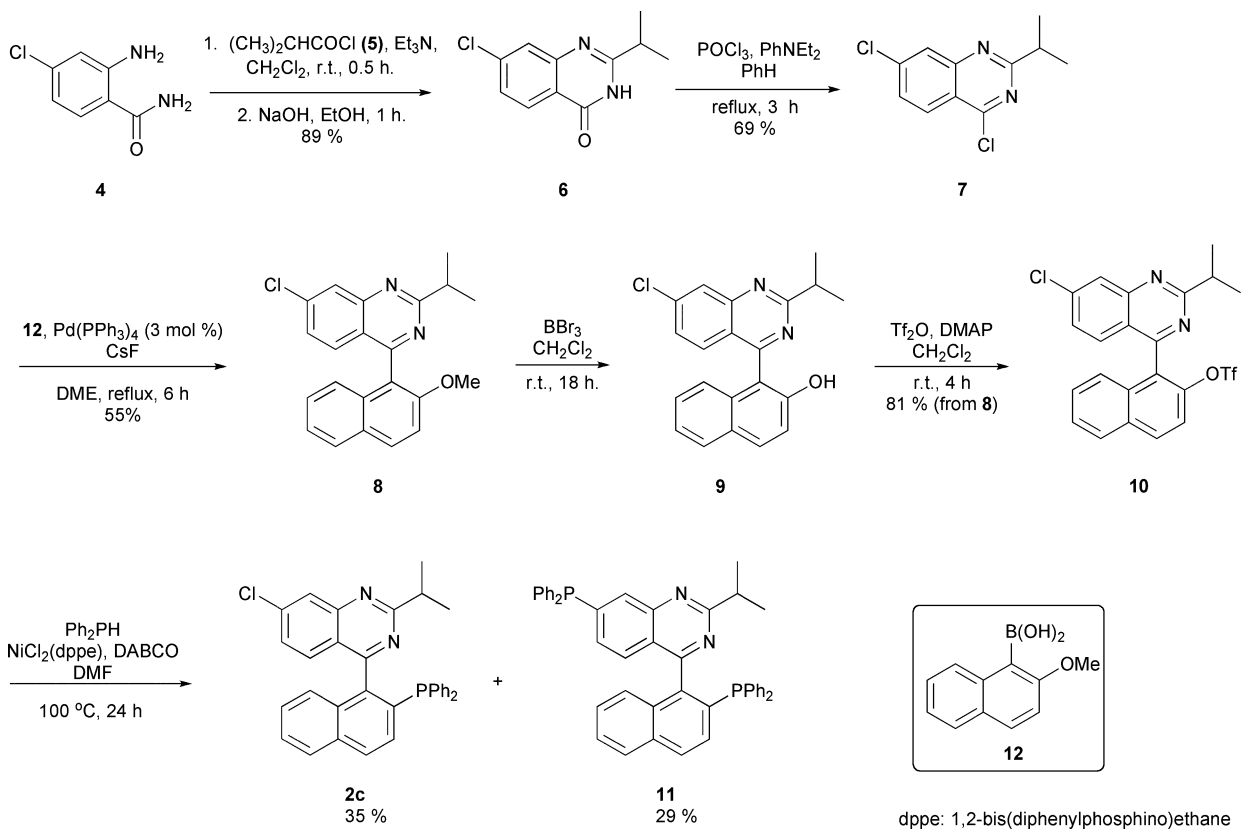
Synthesis and resolution of 2c

Racemic Quinazolinap **2c** was prepared using the synthetic route previously employed for the synthesis of other members of this class of ligand (Scheme 2).[7] The quinazolinone **6** was prepared by a 2 step acylation–cyclocondensation between commercially available 4-chloroanthranilamide **4** and isobutyryl chloride **5**, which proceeded in high overall yield (89% from **4**). Chlorination of **6** with $POCl_3$/$PhNEt_2$ in refluxing benzene gave the electrophilic partner **7** for the Suzuki–Miyaura cross-coupling, this proceeded with a yield of 69%. Using 3 mol% $Pd(PPh_3)_4$ as the catalyst and CsF as the base, the coupling of **7** and 2-methoxynaphthyl boronic acid **12** afforded the biaryl **8** in moderate yield (55%). The methyl ether of **8** was converted to the corresponding naphthol **9** by a BBr_3-mediated demethylation. Upon treatment of **9** with Tf_2O in the presence of DMAP the aryl triflate **10** was produced in good yield (81% from **8**). The final step in the ligand synthesis was the nickel-catalyzed cross-coupling between the triflate **10** and diphenylphosphine in the presence of $NiCl_2$(dppe)/DABCO following the protocol of Cai *et al*.[13] This afforded the desired triarylphosphane **2c** in low yield (35%), which can be accounted for by the unexpected formation of the di-coupled product **11** in 29% yield.[14] The formation of **11** shows an unusually high activity for an aryl–chloride bond which we intend to exploit for further diversification of the Quinazolinap ligand series.

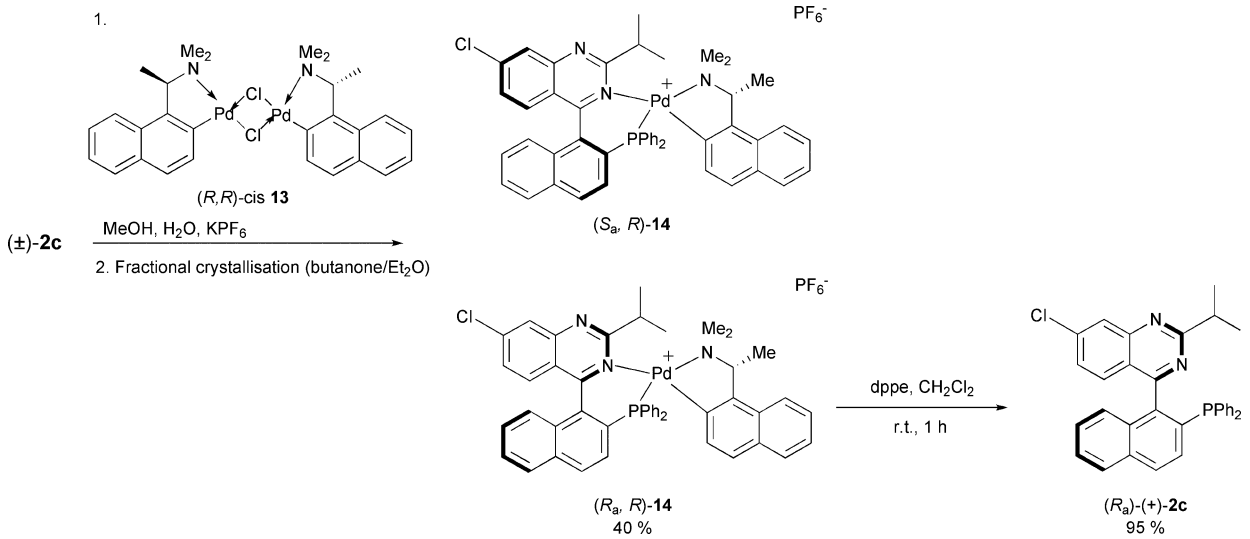
The resolution of atropisomeric P-N ligands is typically carried out by the formation of diastereomers using enantiopure palladacycles derived from palladium amine complexes, followed by fractional crystallisation to yield a diastereomerically pure complex. The palladium complex (*R,R*)-*cis*-**13** was used in the resolution of Quinap **1** and previously prepared members of the Quinazolinap family (Scheme 3). The racemic phosphane **2c** was resolved using this method *via* the formation of diastereomeric palladacycles (S_a,*R*)-**14** and (R_a, *R*)-**14**. These palladacycles were obtained by stirring the racemic phosphane **2c** in MeOH with the chloro-bridged resolving agent (*R,R*)-*cis*-**13** and subsequent addition of KPF_6 in water to form the corresponding diastereomers in a 1:1 ratio. Crystallisation from hot butanone/Et_2O precipitated (S_a,*R*)-**14** whose purity was determined to be >99% by ^1H and ^{31}P NMR spectroscopy. The mother liquor was subjected to two more crystallisations which afforded more (S_a,*R*)-**14**, with a total yield of 40%. Further crystallisations yielded only diastereomerically enriched crystals, although the remaining mother liquor was found to be diastereomerically pure (R_a,*R*)-**14**. Crystals of (S_a,*R*)-**14** suitable for X-ray crystallographic analysis were grown from $CDCl_3$ and pentane to confirm the stereochemistry (Fig. 2). Enantiomerically pure phosphinamine (R_a)-(+)-**2c** was obtained by decomplexation from the (R_a,*R*)-**14** complex with 1,2-bis(diphenylphosphino)ethane in dichloromethane (95%).

Copper(I) catalyzed β-borylation of α,β-unsaturated compounds

The copper-catalyzed enantioselective β-borylation of α,β-unsaturated olefins is a valuable synthetic transformation. The boron functionality can be readily converted into various



Scheme 2 Synthesis of racemic ligand **2c**.



Scheme 3 Optical resolution of **2c**.

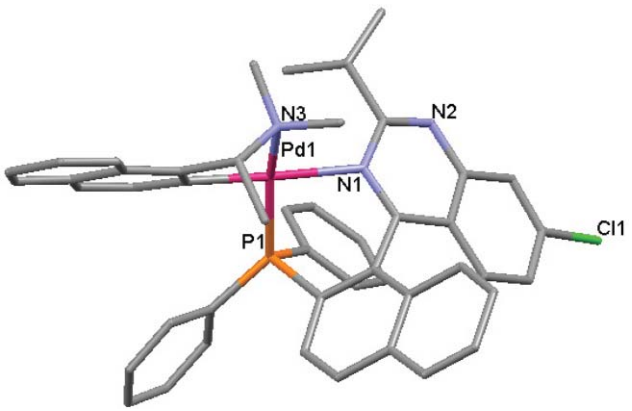


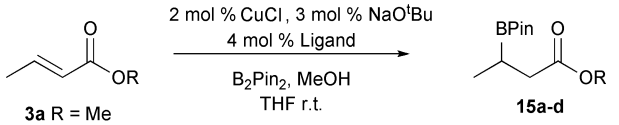
Fig. 2 Single-crystal X-ray structure of Pd^{II} complex (S_a,*R*)-**14**.[17] Hydrogen atoms and counter-ion omitted for clarity. The unit cell contains two independent cations, only one of which is shown. Bond lengths: Pd-P 2.274 Å, Pd-N1 2.215 Å, Pd-N3 2.135 Å and C-Cl 1.738 Å. Bond angles: N1-Pd-P 81.97°, N1-Pd-N2 39.33° and N3-Pd-P1 10.08°. Unit cell dimensions: a = 9.8195(9) Å, α= 90°; b = 29.059(3) Å, β= 95.039(2)°; c = 15.0113(14) Å. γ = 90°.

other functional groups.[15] This transformation typically employs a chiral catalyst and an achiral borane source such as bis(pinacolato)diboron. We now wish to report the application of Quinazolinap ligands to this copper mediated transformation.

For each catalytic reaction the catalyst system was generated by stirring copper(I) chloride with ligand (2 equiv.)[16] and NaO^{t}Bu in THF to form a putative bidentate complex, which is the active catalytic species. Bis(pinacolato)diboron was added followed by the α,β-unsaturated compound, and then MeOH (2 equiv. relative to substrate) to guarantee total conversion.[11b]

In the β-borylation of methyl crotonate **3a** (Table 1, entries 1–6) the conversions were optimised to give good to complete conversion, with the best ee values being obtained for the Quinazolinap ligand **2b** (51%, entry 3) and Quinap **1** (50%, entry 1). In the case of ethyl crotonate **3b** (Table 1, entries 7–12) the conversions again were good to excellent. The ee values for the

Table 1 Copper(I) catalyzed borylation of α,β-unsaturated compounds[a]



3a R = Me
3b R = Et
3c R = *i*-Bu
3d R = *t*-Bu

15a-d

Entry	R =	Ligand	Conversion (%)[b]	Ee (%)[c,d]
1	Me	(*S*)-**1**	100	50 (*S*)
2	Me	(*S*)-**2a**	95	20 (*S*)
3	Me	(*R*)-**2b**	65	51 (*R*)
4	Me	(*R*)-**2c**	100	40 (*R*)
5	Me	(*S*)-**2d**	100	25 (*S*)
6	Me	(*S*)-**2e**	71	13 (*S*)
7	Et	(*S*)-**1**	100	72 (*S*)
8	Et	(*S*)-**2a**	100	34 (*S*)
9	Et	(*R*)-**2b**	75	40 (*R*)
10	Et	(*R*)-**2c**	98	38 (*R*)
11	Et	(*S*)-**2d**	99	12 (*S*)
12	Et	(*S*)-**2e**	82	15 (*S*)
13	*i*-Bu	(*S*)-**1**	100	79 (*S*)
14	*i*-Bu	(*S*)-**2a**	100	35 (*S*)
15	*i*-Bu	(*R*)-**2b**	100	42 (*R*)
16	*i*-Bu	(*R*)-**2c**	23	48 (*R*)
17	*i*-Bu	(*S*)-**2d**	100	20 (*S*)
18	*i*-Bu	(*S*)-**2e**	26	20 (*S*)
19	*t*-Bu	(*S*)-**1**	100	72[e] (*S*)
20	*t*-Bu	(*S*)-**2a**	100	42[e] (*S*)
21	*t*-Bu	(*R*)-**2c**	100	43[e] (*R*)

[a] Standard conditions: 2% CuCl, 3% NaO^{t}Bu, 4% Ligand, 1.1 eq. B_2Pin_2, 2.0 eq. MeOH, THF, RT, 6 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral GC of product after oxidation and conversion to the corresponding acylated derivative. **15a** β-CD, 30 m, 80 °C, 11.4 psi, R_T = 17.4 min (*R*), 19.7 min (*S*). **15b** β-CD, 30 m, 80 °C, 27.1 psi, R_T = 13.8 min (*R*), 14.5 min (*S*). **15c** β-CD, 30 m, 100 °C, 14.5 psi, R_T = 17.9 min (*R*), 20.1 min (*S*). [d] Configuration of products was assigned by comparison to the known optical rotation values obtained for the oxidized derivatives of **15b** (see supporting information of reference 11a). [e] Determined by chiral HPLC of product after oxidation and conversion to the corresponding phenoxy derivative. **15d** Chiracel OD column, hexane:IPA (85:15), 1 mL/min. 220 nm. R_T = 20.7 min (*S*), 31.8 min (*R*).

ligands **2a–e** were similar to those obtained in the methyl crotonate case, although Quinap **1** showed an increase in ee to 72% (entry 7). A further increase in the size of the ester moiety of the substrate to *i*-Butyl **3c** (entries 13–18) did not alter the enantioselectivity by any appreciable amount for ligands **2a–e**. As for Quinap **1**, the general trend of an increased ee (79%, entry 13) with an increase in the bulk of the substrate ester continued. For the final set of reactions the size of the substrate ester was increased further to a *t*-butyl group **3d** (entries 19–21). In each of these reactions complete conversion was observed, although the enantioselectivity induced by Quinap **1** dropped slightly (72%) relative to the *i*-butyl containing substrate.

For the β-borylation of the various substrates **3a–d** the copper complex modified with the Quinazolinap ligands **2a–e** gave up to quantitative conversion along with ee values of up to 51% (entry 3). Of all the ligands tested, Quinap **1** gave the best and most consistent results, with 100% conversion in all cases and ee values ranging from 50–79%.

In an attempt to further understand the process under investigation, a crystal structure of a complex of ligand **2c** with copper was obtained. The complex was formed by stirring copper and **2c** in an equal volume mixture of IMS and Et_2O (IMS = 85% EtOH/15% MeOH). The complex formed under these conditions is a chlorine-bridged dimer lying about an inversion centre and is monodentate, Fig. 3. However, the high levels of enantioselectivity induced by these ligands suggests that the catalytic complex must have the ligands bound in a bidentate manner.

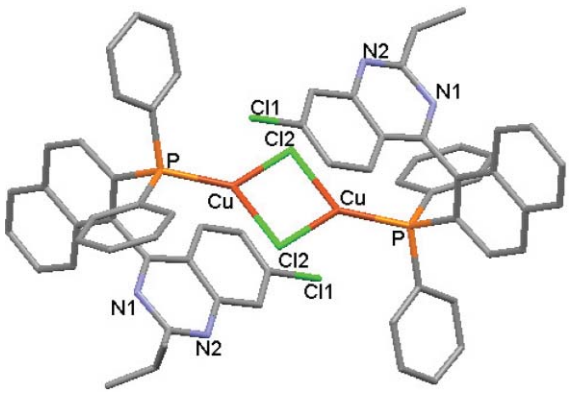


Fig. 3 Single-crystal X-ray structure Cu^{I} complex of **2c**.[18] Hydrogen atoms omitted for clarity. Duplicate atom labels are generated by the operation (1-x, 2-y, 2-z).

Conclusion

A new axially chiral 7-substituted Quinazolinap ligand has been synthesised and resolved. This ligand, along with other known Quinazolinap ligands and Quinap have been tested in the asymmetric β-borylation of α,β-unsaturated compounds.[19] Conversions of up to 100% and ee values of up to 79% were obtained. Work on further expanding the range of Quinazolinap ligands and on expanding the substrate scope in the β-borylation of α,β-unsaturated compounds is ongoing and will be reported in due course from these laboratories.

Experimental details

General experimental

All reactions were performed under anhydrous conditions and an inert atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials, unless otherwise indicated. Reagents were used as obtained from commercial sources or purified according to the guidelines of Perrin and Armarego.[20] Evaporation *in vacuo* refers to the removal of volatiles on a Büchi rotary evaporator with an integrated vacuum pump. Flash chromatography was carried out using Merck Kiesegel 60 F254 (230–400 mesh) silica gel following the method of Still *et al.*[21] Thin-layer chromatography (TLC) was performed on Merck DC-Alufolien plates pre-coated with silica gel 60 F254. They were visualized either by quenching of ultraviolet fluorescence, or by charring with an acidic vanillin soln. (vanillin, H_2SO_4 and acetic acid in MeOH). The Microanalytical Laboratory, University College Dublin, performed elemental analyses. Electrospray mass spectra were recorded on a Micromass Quattro with electrospray probe. Exact mass ESI mass spectra (HRMS) were measured on a micromass LCT orthogonal time of flight mass spectrometer with leucine enkephalin (Tyr-Gly-Phe-Leu) as an internal lock mass. ^{1}H NMR spectra were recorded on a 300 MHz Varian-Unity spectrometer, a 400 MHz Varian-Unity spectrometer or a 500 MHz Varian-Unity spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane and coupling constants (J) are quoted in Hz and are uncorrected. $CDCl_3$ was used as the solvent for all NMR spectra unless otherwise stated. 75.4 MHz ^{13}C spectra were recorded on a 300 MHz Varian-Unity spectrometer, 101 MHz ^{13}C spectra on a 400 MHz Varian-Unity spectrometer and 125 MHz ^{13}C spectra on a 500 MHz Varian-Unity spectrometer. Tetramethylsilane was used as the internal standard in all ^{13}C spectra recorded. 121.4 MHz ^{31}P spectra were recorded on a 300 MHz Varian-Unity spectrometer and 162 MHz ^{31}P spectra on a 400 MHz Varian-Unity spectrometer. ^{31}P Chemical shifts are reported relative to 85% aqueous phosphoric acid (0.0 ppm). All reaction solvents were distilled before use, unless otherwise indicated. Anhydrous solvents were obtained from a PureSolv-300-3-MD dry solvent dispenser and used without further purification unless otherwise stated. Melting points (mp) are quoted to the nearest 0.5 °C. GC and HPLC analysis was carried out using a Supelco 2–4304 beta-Dex® 120 (30 m × 0.25 mm, 0.25 mm film) and a Chiralcel OD column (0.46 cm I.D. × 25 cm) respectively. Optical rotation values were measured on a Perkin Elmer 241 Polarimeter. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

General procedure for the borylation of α,β-unsaturated esters

THF (3 mL) was added to CuCl (0.010 mmol, 1 mg), NaO^{t}Bu (0.015 mmol, 1.4 mg) and ligand (0.020 mmol) in a dry Schlenk tube under nitrogen. The mixture was stirred for 30 min at room temperature, at this point bis(pinacolato)diboron (0.550 mmol, 139.7 g) was added and stirred for a further 10 min. The α,β-unsaturated ester (0.500 mmol) was then added, followed by MeOH (1 mmol, 0.040 mL). Stirring was continued for 6 h and a sample removed for ^{1}H NMR analysis. Conversions were determined by ^{1}H NMR, ee values were determined by chiral GC

of the acylated products or chiral HPLC of the phenoxy derivative of the product (see ESI†).

Acknowledgements

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16 An excess of ligand is required to reduce the possibility of the formation of a catalytic species for the non-selective reaction. This is discussed further in reference 11a.
17 Crystal data and structure refinement for Pd^{II} complex (S_a,*R*)-**14**. Empirical formula: $C_{47}H_{42}N_3F_6P_2ClPd$. Formula weight 966.63. Temperature 100(2) K. Wavelength, 0.71073 Å. Crystal, system: Monoclinic. Space group P 21. Unit cell dimensions a = 9.8195(9) Å, α = 90°. b = 29.059(3) Å, β = 95.039(2)°. c = 15.0113(14) Å. γ = 90°. Volume 4266.8(7) $Å^3$. Z = 4. Reflections collected 34128. Independent reflections 19110 [R(int) = 0.0269]. Final R indices [I>2sigma(I)] R1 = 0.0408, wR2 = 0.1005.
18 Crystal data and structure refinement for Cu^I complex of **2c**. Empirical formula $C_{66}H_{52}N_4P_2Cl_4Cu_2$. Formula weight 1231.94. Temperature 293(2) K. Crystal, system: Triclinic. Space group P-1 (#2).Unit cell dimensions a = 10.7093(9) Å α = 114.885(2)°. b = 12.0684(11) Å β = 100.794(2)°. c = 13.4541(12) Å γ = 96.372(2)°. Volume 1514.0(2) $Å^3$. Z = 1. Reflections collected 9554. Independent reflections 3953 [R(int) = 0.0228]. Final R indices [I>2sigma(I)] R1 = 0.0535, wR2 = 0.1572 R indices (all data) R1 = 0.0666, wR2 = 0.1572.
19 After acceptance of this paper we became aware of a further important contribution to the enantioselective β-borylation of acyclic enones by Yun and co-workers: H.-S. Sim, X. Feng and J. Yun, *Eur. J. Org. Chem.*, 2009, **15**, 1939.
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