Basicity and bulkiness effects of 1,8-diaminonaphthalene, 8-aminoquinoline and their alkylated derivatives on the different efficiencies of η^5-C_5H_5 and η^5-C_5Me_5 ruthenium precatalysts in allylic etherification reactions†

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The different behaviours of Ru(η^5-C_5H_5) and Ru(η^5-C_5Me_5) precatalysts, [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me), in the allylic etherification reaction of cinnamyl chloride using the phenoxide anion as a nucleophile was considered. The *N*,*N* ligands are the commercial products 1,8-diaminonaphthalene and 8-aminoquinoline, and their derivatives obtained by alkylation of the amino nitrogen atoms: alkyl substituents that are also bulky chiral C_2-symmetric frameworks allow modulation of the basicity and steric demand of the ligands. Some of the precatalysts, [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me), were also synthesized and characterized. The cinnamyl phenyl ether isomers were obtained with very high B/L regioselectivity values, either with Ru(η^5-C_5H_5) or Ru(η^5-C_5Me_5) precatalysts. The highest B/L regioselectivity values achieved with Ru(η^5-C_5Me_5) precatalysts were found with the *N*,*N* ligand 1,8-diaminonaphthalene and its derivatives; with Ru(η^5-C_5H_5) precatalysts best B/L values were obtained with ligands derived from 8-aminoquinoline. A correlation between the B/L regioselectivity, and the σ-donor power and bulkiness of the substituents at the nitrogen atoms of the *N*,*N* coordinated ligand was established, but the Ru(η^5-C_5H_5) or Ru(η^5-C_5Me_5) precatalysts followed an opposite trend. It was also found that the low ee values did not depend on the diastereomeric composition of the chiral-at-metal precatalyst [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6.

Introduction

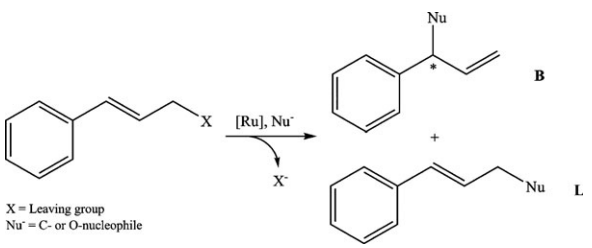
Transition metal-catalyzed allylic substitution reactions are still a topic that continues to attract interest.[1] Recently, attention has turned to obtain chiral branched isomers from asymmetric prochiral allylic precursors, such as cinnamyl derivatives, with high regioselectivity and enantioselectivity, by nucleophilic substitution at the more substituted allylic carbon.[2] Enantio-enriched chiral allyl alkyl compounds and allylic aryl ethers are useful precursors for asymmetric synthesis.

Trost,[3] Bruneau[4] and other research groups[5] have found that the [Ru(η^5-C_5Me_5)(NCMe)$_3$]PF_6 complex and some of its derivatives containing mono- or bidentate ligands are efficient precatalysts, and induce very high values of regio-selectivity in favour of the branched product, both in alkyl-ation and etherification reactions of cinnamyl derivatives, leading to the formation of C–C and C–O bonds, respectively (Scheme 1).

In contrast, Ru(η^5-C_5H_5) precatalysts have been considered poorly efficient and stereoselective in the same reactions. Concerning the enantioselectivity in the formation of the branched product, only a few examples of high ee values are reported in the literature.[5b,6a]

Recently, we reported on the efficiency of the precatalysts [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me) in the catalyzed alkylation and etherification reactions of cinnamyl derivatives, where dimethylmalonate and phenoxide anions were used as nucleophiles.[7]

The above-mentioned *N*,*N* bulky chiral ligands are characterized by either a flexible or a rigid backbone. Surprisingly, using [Ru(η^5-C_5H_5)(NCMe)(*N*,*N*)]PF_6 precatalysts, values of B/L regioselectivity (94/6) higher than those obtained using the corresponding [Ru(η^5-C_5H_5)(NCMe)$_3$]PF_6 precursor were reached in the etherification reactions of cinnamyl chloride with phenoxide anions. Such results led us to carry out further



Scheme 1 Scheme for the ruthenium-catalyzed allylic alkylation and etherification of cinnamyl derivatives.

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investigations aiming to clarify the effect of basicity and steric hindrance of the cyclopentadienyl rings η^5-C_5H_5 or η^5-C_5Me_5 or even of the coordinated ligands, on the precatalyst features during each step of the catalytic process. Herein, we report the results obtained by using the complexes $[Ru(\eta^5\text{-}C_5R_5)(NCMe)(N,N)]PF_6$ (R = H, Me) as precatalysts in the etherification reaction of cinnamyl chloride by phenoxide anions; the *N*,*N* ligands are 1,8-diaminonaphthalene, 8-aminoquinoline and their alkylated derivatives. Some of the ligands presented in this paper have been reported in work directed towards the study of 1,8-bis(dimethylamino)naphthalene derivatives as atropoisomeric proton sponges.[8]

Results and discussion

Synthesis of the ligands

The herein-reported ligands are derived from 1,8-diaminonaphthalene and 8-aminoquinoline; their structures are characterized by coplanarity between the donor atoms and the ligand skeleton. The basicity of the donor atoms and the steric hindrance around them have been modulated by their functionalization with suitable substituents. It has to be considered that, while the ligands synthesized from 1,8-diaminonaphthalene give a six-membered ring by coordination to a metal centre, those derived from 8-aminoquinoline form a five-membered ring; consequently the 1,8-diaminonaphthalene derived ligands exhibit a reduced bite angle with respect to those derived from 8-aminoquinoline. Moreover, the latter induce a lower electronic density at the ruthenium centre with respect to the 1,8-diaminonaphthalene derived ligands (Fig. 1).

(a) Ligands **2–4** and **6–8** were obtained by substitution of the NH_2 hydrogen atoms in starting compounds **1** and **5** (used also as ligands) by alkyl groups so that the σ-donor properties of the ligands were tuned (Fig. 1a); they are not chiral (ligand **8** is in racemic form) and have a low steric hindrance. Only ligand **9** has an aryl substituent at the nitrogen atom of 8-aminoquinoline; in this ligand, the amino nitrogen basicity is lower than that of its precursor.

(b) Ligands **10–15** derived from 1,8-diaminonaphthalene are bulky chiral ligands containing the C_2-symmetric (*S*)-(+)-2,2′-(2-azapropane-1,3-diyl)-1,1′-binaphthalene or *trans*-(*R*,*R*)-2,5-dimethylpyrrolidinyl framework (Fig. 1b). Ligands **10–15** were synthesized with the aim of increasing the steric demand and evaluating the asymmetric induction on the branched isomer formed in the enantioselective allylic etherification (see Catalytic experiments). The chiral ligands **16** and **17**, derived from 8-aminoquinoline and containing the same chiral moieties as ligands **10–15**, have been previously reported by our research group and already used in the same catalytic process, but in different experimental conditions.[7]

The synthesis and the NMR spectroscopic data for all the prepared ligands are reported in a detailed way in the Experimental section. All ligands were characterized by elemental analysis, GC-MS and NMR spectroscopy.

Synthesis of the precatalysts $[Ru(\eta^5\text{-}C_5R_5)(NCMe)(N,N)]PF_6$

Preliminarily to the catalytic study, some of the complexes $[Ru(\eta^5\text{-}C_5R_5)(NCMe)(N,N)]PF_6$ used as precatalysts were

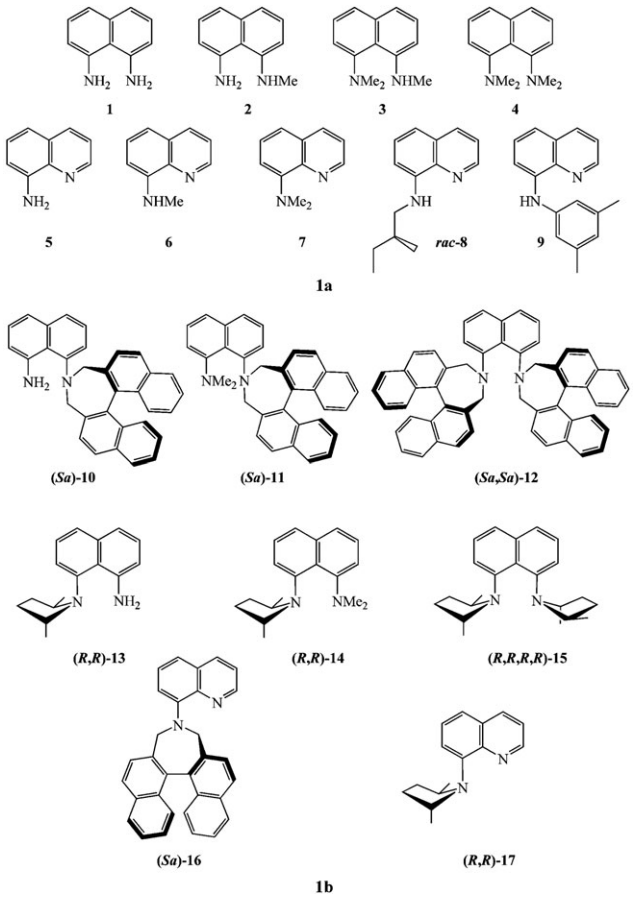

Fig. 1 The used *N*,*N* ligands: (a) the 8-aminoquinoline and (b) the 1,8-diaminonaphthalene derivatives.

synthesized and characterized with the aim of comparing their catalytic performance with that of the precatalysts made *in situ*. The $[Ru(\eta^5\text{-}C_5R_5)(NCMe)(N,N)]PF_6$ complexes (*N*,*N* = **1**, R = Me, **18**; *N*,*N* = (*R*,*R*)-**13**, R = Me, **19**; *N*,*N* = (*R*,*R*)-**14**, R = H, **20**; *N*,*N* = **7**, R = H, **21**; *N*,*N* = **7**, R = Me, **22**; *N*,*N* = **9**, R = Me, **23**) were synthesized by reacting the cationic complex $[Ru(\eta^5\text{-}C_5R_5)(NCMe)_3]PF_6$, in acetonitrile, with an equimolar amount of the *N*,*N* ligand dissolved in toluene. Compounds **18–23** are solids each of various colour; some of them are relatively stable towards air and moisture, and were characterized by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectra showed the splitting of some peculiar signals of the ligand derived from 1,8-diaminonaphthalene or 8-aminoquinoline due to the coordination to the ruthenium centre.

Particularly, in the ^{1}H NMR spectra of complexes **18** (*N*,*N* = **1**, R = Me), **19** (*N*,*N* = (*R*,*R*)-**13**, R = Me) and **20** (*N*,*N* = (*R*,*R*)-**14**, R = H), containing ligands derived from 1,8-diaminonaphthalene, some of the aromatic protons in the naphthalene ring are shifted upfield owing to ligand coordination to the metal centre. In the ^{1}H NMR spectrum in acetone-d_6 of **18**, the aromatic protons show three signals at 6.20, 5.95, 5.71 ppm, whereas the aminic hydrogens are shifted downfield at 5.72 and 5.40 ppm, compared with the free ligand signals. The methyl groups of the coordinated η^5-C_5Me_5 give a singlet at 1.68 ppm. Given that the ruthenium itself is a stereogenic

centre, in principle, a mixture of diastereomers, (S_a,R_{Ru}) and (S_a,S_{Ru}), differing in the absolute configuration at the metal centre, can be obtained in the synthesis of the [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 precatalysts **19** and **20** containing the *N*,*N* chiral ligands (*R*,*R*)-**13** and (*R*,*R*)-**14**. In their ^{1}H NMR spectra, **19** and **20** show the CH and CH_2 proton signals of the pyrrolidinyl chiral fragment slightly shifted at high field in comparison with the free ligands; moreover, compound **20** shows the splitting of the broad signal of the $(CH_3)_2N$ methyl groups. In the ^{1}H NMR spectrum of **19** in acetone-d_6, the presence of two signals for the η^5-C_5Me_5 methyl protons in an 86 : 14 ratio at 1.64 ppm for the major isomer, and at 1.72 ppm for the minor isomer supports the formation of two diastereoisomers. Acetone-d_6 solutions of **19** are not air and moisture stable; in solution, under an argon atmosphere, the ratio between the diastereomers is unchanged. We were not able to separate and obtain the diastereomers in pure form. In contrast, in the ^{1}H NMR spectrum of **20** in acetone-d_6, the η^5-C_5H_5 protons give only one signal as a singlet at 5.16 ppm, indicating that compound **20** is formed as a single diastereomer. Because we were not able to obtain crystals of **20** suitable for X-ray diffractometry, we have no information about the absolute configuration at the ruthenium centre of the single diastereomer obtained. However, the acquaintance of these data does not seem to be indispensable in obtaining useful information about the induction of enantioselectivity when **20** is used as the precatalyst. Since the catalytic runs were carried out in CH_3CN, we confirmed that in CD_3CN the diastereomeric ratios are equal and do not change with time.

In complexes **21** (*N*,*N* = **7**, R = H), **22** (*N*,*N* = **7**, R = Me) and **23** (*N*,*N* = **9**, R = Me), the coordinated *N*,*N* ligands are derived from 8-aminoquinoline (**5**) by methylation or, in only one case, arylation of the amino nitrogen atom. Ligand coordination to metal centre causes a downfield shift of the α-quinolinyl hydrogen atom signal. Compounds **21** and **22** differ from each other in their coordination to the ruthenium centre of the η^5-C_5H_5 and η^5-C_5Me_5 ions, respectively. They were obtained as dark orange solids that are moderately stable to air and moisture. In both the ^{1}H NMR spectra of **21** and **22**, diastereotopic methyl groups bound to nitrogen atoms appear as singlets at 3.54 and 3.48 ppm, and at 3.32 and 3.22 ppm, respectively. In free ligand **7**, these methyl protons give one singlet at 3.09 ppm. η^5-C_5H_5 protons in **21** and η^5-C_5Me_5 methyl protons in **22** exhibit singlets at 4.32 and 1.58 ppm, respectively. Precatalyst **23** contains *N*-(3,5-dimethylphenyl)-quinolin-8-amine ligand **9**; it was obtained as a dark green powder. The ^{1}H NMR spectrum in CD_3CN shows a singlet at 2.40 ppm for the methyl groups of the 3,5-dimethylphenyl moiety and a singlet at 6.99 ppm for the aminic hydrogen; methyl protons of the η^5-C_5Me_5 ligand show a singlet at 1.40 ppm. In the ^{1}H NMR spectrum of compounds **19–23**, the methyl signal of the acetonitrile ligand was found in the 2.01–2.84 ppm range.

Catalytic experiments

The [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me; *N*,*N* = **1–15**) precatalysts were tested in the etherification reaction of cinnamyl chloride with phenoxide anions. The reaction, leading to a new carbon–oxygen bond, affords linear and branched cinnamyl phenyl ether isomers; the branched isomer contains a stereogenic carbon atom (Scheme 1).

The reactions were carried out in CH_3CN at room temperature, and the precatalyst was formed *in situ* by adding the *N*,*N* ligand to [Ru(η^5-C_5R_5)$(NCMe)_3$]PF_6 (R = H, Me). After 1 h, to the solution containing the precatalyst (3 mol%) were sequentially added cinnamyl chloride and a slight excess of phenol in the presence of K_2CO_3. We verified that the same results were obtained by using the synthesized precatalyst as by forming it *in situ*. The results are reported in Table 1.

A comparison with data reported in the literature[4b] indicates that the catalytic systems are very active in the experimental conditions used; in fact, the conversion of cinnamyl chloride was quantitative or close to 100% after 20 h in almost all experiments, both with Ru(η^5-C_5Me_5) and Ru(η^5-C_5H_5) precatalysts. In some cases, the full conversion was reached in a few hours as indicated by monitoring the reaction *via* TLC.

The results highlight that Ru(η^5-C_5Me_5) precatalysts give the highest B/L values with 1,8-diaminonaphthalene derivatives, while the Ru(η^5-C_5H_5) precatalysts are more regioselective when 8-aminoquinoline derivatives are the coordinating ligands. This trend can be correlated to the different bite angle of ligands derived from 1,8-diaminonaphthalene and 8-aminoquinoline; for a better counterbalance of steric interactions, the more crowded C_5Me_5 ring prefers the coordination of 1,8-diaminonaphthalene derived ligands, featuring a smaller bite angle than the 8-aminoquinoline derivatives.

In all cases, it appears clear that the coplanarity of the *N*-donor and the skeleton ligand atoms in the chelating agent

Table 1 Allylic etherification of cinnamyl chloride with phenol catalyzed by [Ru(η^5-C_5R_5)(*N*,*N*)(NCMe)]PF_6 (R = H, Me) complexes[a]

		Ru(η^5-C_5H_5)		Ru(η^5-C_5Me_5)	
Entry	*N*,*N*	Conversion[b]	B/L[b]	Conversion (%)[b]	B/L (%)[b]
1	**1**	100	71/29	100	95/5
2	**2**	100	75/25	100	93/7
3	**3**	100	68/32	100	87/13
4	**4**	97	76/24	95	81/19
5	**5**	100	72/28	100	81/19
6	**6**	100	84/16	100	68/32
7	**7**	100	90/10	75	87/13
8	*rac*-**8**	100	86/14	100	81/19
9	**9**	100	57/43	100	70/30
10[c]	(S_a)-**10**	90	68/32	100	84/16
11[c]	(S_a)-**11**	97	67/33	100	86/14
12[c]	(S_a,S_a)-**12**	97	70/30	100	93/7
13[c]	(*R*,*R*)-**13**	99	69/31	100	86/14
14[c]	(*R*,*R*)-**14**	97	72/28	100	86/14
15[c]	(*R*,*R*,*R*,*R*)-**15**	89	79/21	97	91/9
16[d]	(S_a)-**16**	100	83/17	—	—
17[d]	(*R*,*R*)-**17**	100	84/16	—	—

[a] Experimental conditions: catalyst (3 mol%), phenol (1.5 equiv.), K_2CO_3 (1 equiv.), CH_3CN as solvent, room temperature, 24 h. [b] Determined by ^{1}H NMR and GC-MS. [c] A complete table of ee values of the branched isomer is reported in the ESI. [d] Ligands already used in previous work. The corresponding Ru(η^5-C_5Me_5) derivatives were not stable enough to be used in the catalytic experiments.[7]

is a requirement of primary importance to achieve high regioselectivity values.[4a,c,d]

The influence of the *N*,*N* ligand on the efficiency of the catalyst is also evidenced by the correlation between the B/L regioselectivity and the σ-donor power of the amino nitrogen atoms in the coordinated ligand. Looking at the 1,8-diaminonaphthalene derived ligands, it appears that, using [Ru(η^5-C_5Me_5)(NCMe)(*N*,*N*)]PF_6 complexes, the B/L regioselectivity reaches the highest value of 95 : 5 with 1,8-diaminonaphthalene ligand **1**, whose donor nitrogen atoms possesses the lowest basicity. The B/L regioselectivity decreases for [Ru(η^5-C_5Me_5)(NCMe)(*N*,*N*)]PF_6 precatalysts (*N*,*N* from **1** to **4**) as the nitrogen atom basicity grows. An opposite trend is observed with the corresponding [Ru(η^5-C_5H_5)(NCMe)(*N*,*N*)]PF_6 precatalysts; in this case, the B/L regioselectivity increases, although in a limited way, from **1** to **4** as the nitrogen atom basicity grows, and the highest value (90 : 10) is found with the most basic ligand derived from 8-aminoquinoline. Summarizing, when the catalytic precursor contains the η^5-C_5Me_5 ligand, which offers the metal centre more electronic density than the η^5-C_5H_5 ligand, the highest B/L regioselectivity values are found with ligands having the lowest σ-donor power. A stronger σ-donor power of the *N*,*N* ligand is required in the Ru(η^5-C_5H_5) precatalysts in order to counterbalance the low charge density at the ruthenium centre and to obtain the highest B/L regioselectivity values.

It is noteworthy that the B/L values found with precatalysts [Ru(η^5-C_5Me_5)(NCMe)(**1**)]PF_6 and [Ru(η^5-C_5H_5)(NCMe)(**7**)]PF_6 are higher compared to those reported for the corresponding precursors [Ru(η^5-C_5R_5)$(NCMe)_3$]PF_6 (R = H, Me), respectively 75 : 25 and 90 : 10.

This assumption also explains the results achieved with the [Ru(η^5-C_5Me_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me) precatalysts, having *N*,*N* ligands with comparable electronic properties but very different steric demands. In fact, the increase of ligand bulkiness modifies in an opposite way the B/L regioselectivity induced by Ru(η^5-C_5Me_5) and Ru(η^5-C_5H_5) precatalysts (see and compare entry 4 with entries 11, 12, 14 and 15 in the Ru(η^5-C_5Me_5) series or entry 7 with entries 16 and 17 in the Ru(η^5-C_5H_5) series). Indeed, it was established that in similar pentamethylcyclopentadienyl ruthenium and rhodium complexes containing diamine ligands with substituents of different steric demand on nitrogen donor atoms, the bulky groups cause a lengthening of the M–N bond distance, with a consequent lowering of the electronic density contribution to the metal centre.[9] Therefore, in accordance with the verified effect induced by the increase of donor atom basicity on the regioselectivity of the process, the increase of steric demand of the coordinated ligands raises the B/L regioselectivity ratio in Ru(η^5-C_5Me_5) systems and produces the opposite effect in Ru(η^5-C_5H_5) systems.

To the best of our knowledge, even if the allylic substitution process catalyzed by chiral ruthenium(II) complexes leads to the formation of the branched isomer with excellent regioselectivity, it induces poor or modest ee values, except for only a few examples reported by the Bruneau,[6a] Onitsuka[6b] and Lacour[6c–f] research groups.

The results herein reported highlight very low enantioselectivity values (in the range 4–7%) by the use of [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, CH_3; *N*,*N* = enantiopure nitrogen ligand) precatalysts. It was also very surprising for us to observe that the product 1-phenoxy-1-phenyl-2-propene was obtained nearly in a racemic form using the Ru(η^5-C_5Me_5) precatalyst containing the *N*,*N* chiral ligand (*R*,*R*)-**13** as diastereomeric mixture (86 : 14), or even the Ru(η^5-C_5H_5) precatalyst containing the ligand (*R*,*R*)-**14**) as a single diastereomer (see above, Synthesis of the precatalysts). It is noteworthy that ligands (*R*,*R*)-**13** and (*R*,*R*)-**14** are structurally very similar, possessing the same chiral moiety in an enantiopure form; moreover, they give a similar regioselectivity. Preliminarily, the ^{1}H NMR spectra of **19** and **20** in acetone-d_6 and their invariability with time led us to exclude changes in the precatalyst due to breaking processes of the Ru–N bond induced by the solvent. Therefore, the very similar enantioselectivity values indicate that, at least in this case, there is no correlation between the diastereomeric composition of the precatalyst and the ee, which should then be determined by the diastereomeric ratio of the catalytic intermediate [Ru(η^3-PhCHCHCH$_2$)(η^5-C_5Me_5)(*N*,*N*)]$^{2+}$, produced by the oxidative addition of cinnamyl chloride to the precatalyst; further investigations are in progress in order to confirm this point of view.

Conclusions

The [Ru(η^5-C_5R_5)(NCMe)(*N*,*N*)]PF_6 (R = H, Me) complexes are active and effective precatalysts in the allylic etherification of cinnamyl chloride with phenoxide anions. The branched isomer cinnamyl phenyl ether was obtained with very good regioselectivity, either with Ru(η^5-C_5Me_5) (up to 95 : 5) or with Ru(η^5-C_5H_5) (up to 90 : 10) precatalysts. These values are very close to the highest reported for the classic catalytic test of allylic etherification with PhOH/K_2CO_3.[4b] It is noteworthy that these regioselectivity values have been obtained with precatalysts containing the commercial and low-cost 1,8-diaminonaphthalene and the 8-dimethylaminoquinoline, readily synthesized from commercial 8-aminoquinoline. Nevertheless, the work emphasizes and explains for the first time the opposite effect of the σ-donor power of the *N*,*N* coordinated ligand on the B/L regioselectivity values for Ru(η^5-C_5Me_5) and Ru(η^5-C_5H_5) precatalysts. In fact, the results demonstrate that a counterbalance between the electronic density induced by the η^5-cyclopentadienyl ligand at the ruthenium centre and the σ-donor power of the *N*,*N* coordinated ligand plays a determining role in the regioselectivity.

It was also noted that the presence of highly bulky groups in the coordinated ligand influences in the opposite way the B/L regioselectivity values by the use of Ru(η^5-C_5Me_5) and Ru(η^5-C_5H_5) precatalysts, depending on the charge density required by the metal center in the catalytic process.

Experimental

General methods

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Freshly distilled solvents were used throughout and dried by standard

procedures. Published methods were used to prepare the following precursors: (S_a)-(+)-2,2′-dibromomethyl-1,1′-binaphthalene[10] and (2*S*,5*S*)-2,5-hexandiol cyclic sulfate.[11] Cinnamyl methyl carbonate[12] and the ligand *N*-(3,5-dimethylphenyl)quinolin-8-amine (**9**)[13] were prepared according to published procedures. 1,8-Diaminonaphthalene (**1**), *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine (**4**) and 8-aminoquinoline (**5**) were purchased from Sigma-Aldrich and Strem, and used as supplied. The ligands **16** and **17** were prepared as previously reported by our research group.[7] For column chromatography, silica gel 60 (220 ± 440 mesh) purchased from Fluka and basic alumina (70–290 mesh) purchased from Sigma-Aldrich were used. GC-MS analysis were carried out with a Shimadzu GCMS-QP5000 spectrometer. NMR experiments were carried out using a Varian 300 spectrometer and referenced to internal tetramethylsilane. Enantiomeric excesses were determined by a HPLC Shimadzu LC-8A. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milan, Italy.

Synthesis of ligands

Synthesis of *N*′-methylnaphthalene-1,8-diamine (2) and *N*′,*N*′,*N*-trimethylnaphthalene-1,8-diamine (3). To a solution of sodium hydride (152 mg, 6.33 mmol) in 5 mL of THF, 1,8-diaminonaphthalene (500 mg, 3.16 mmol) was added. After stirring for 3 h, methyl iodide (0.098 mL, 1.58 mmol) was added dropwise and the mixture was left to react overnight; the progress of the reaction was monitored by GC-MS. The reaction mixture was cautiously quenched with water (5 mL) and then extracted with ethyl acetate (3–5 mL). The combined organic phases were dried ($MgSO_4$) and the solvent was removed *in vacuo* to obtain an oil purified by column chromatography on neutral alumina. Elution with a gradient from 1 to 10% with ethyl acetate in hexane gave in different fractions the ligand **3**, dimethyl substituted naphthalene and ligand **2**, respectively.

***N*′-methylnaphthalene-1,8-diamine (2).** Yield: 40% (218 mg, 1.26 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H, ArH), 7.18–7.11 (m, 2H, ArH), 6.62 (dd, 1H, ArH, ^3J = 7 Hz, ^4J = 1 Hz), 6.49 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 5.79 (b, 1H, CH_3–NH), 4.39 (b, 2H, NH_2), 2.88 (s, 3H, CH_3–NH). ^{13}C NMR: δ 147.89, 143.81, 136.82, 126.64, 126.27, 125.87, 120.49, 117.90, 112.66, 104.77, 31.47. Anal. calc. for $C_{11}H_{12}N_2$ (172.2): C, 76.71; H, 7.02; N, 16.27. Found: C, 76.41; H, 7.09; N, 16.08.

***N*′,*N*′,*N*-trimethylnaphthalene-1,8-diamine (3).** Yield: 30% (218 mg, 1.26 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (b, 1H, N*H*), 7.50 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 7.33–7.27 (m, 2H, ArH), 7.14 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 7.04 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 6.41 (d, 1H, ArH, ^3J = 7 Hz), 2.96 (d, 3H, C*H*$_3$-N ^3J = 5 Hz), 2.74 (s, 6H, C*H*$_3$–N–C*H*$_3$). ^{13}C NMR: δ 151.93, 148.10, 136.86, 126.98, 125.52, 125.24, 115.01, 114.84, 102.37, 46.05, 30.43. Anal. calc. for $C_{13}H_{16}N_2$ (200.3): C, 77.96; H, 8.05; N, 13.99. Found: C, 77.71; H, 8.18; N, 13.81.

Synthesis of *N*-methylquinolin-8-amine (6) and *N*,*N*-dimethylquinolin-8-amine (7). To a solution of NaH (0.8 g, 37 mmol) in anhydrous THF (10 mL) was added a solution of 8-aminoquinoline (0.25g, 1.68 mmol) in THF (40 mL) followed by $(CH_3)_2SO_4$ (1.6 mL, 16.8 mmol). The reaction mixture was stirred at 75 °C for 24 h, then allowed to cool to room temperature. A solution of NaOH pellets (12 g) in H_2O (30 mL) was added and the mixture was stirred at room temperature overnight. The resulting solution was transferred to a separating funnel and extracted with CH_2Cl_2 (2 × 150 mL). The CH_2Cl_2 solution was washed with H_2O (2 × 500 mL), dried over $MgSO_4$, filtered and evaporated *in vacuo*. The resulting yellow oil was purified by chromatographic column (silica gel; hexane–ethyl acetate 3 : 1) giving in two different fractions the desired products **6** and **7**.

***N*-methylquinolin-8-amine (6).** Yield: 8% (21.3 mg, 0.134 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (dd, 1H, H *a*-quinoline, ^3J = 4 Hz, ^4J = 2 Hz), 8.06 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 2 Hz), 7.34–7.43 (m, 2H, ArH), 7.05 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 2 Hz), 6.65 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 6.11 (bs, 1H, N*H*), 3.04 (d, 3H, NHC*H*$_3$, ^3J = 6 Hz). ^{13}C NMR: δ 146.81, 145.82, 138.23, 136.00, 128.55, 127.85, 121.38, 113.68, 104.12, 30.07. Anal. calc. for $C_{10}H_{10}N_2$ (158.2): C, 75.92; H, 6.37; N, 17.71. Found: C, 76.01; H, 6.31; N, 17.59.

***N*,*N*-dimethylquinolin-8-amine (7).** Yield: 82% (237.3 mg, 1.38 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (dd, 1H, H *a*-quinoline, ^3J = 4 Hz, ^4J = 2 Hz), 8.10 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 2 Hz), 7.34–7.46 (m, 3 H, ArH), 7.12 (dd, 1H, ArH, ^3J = 7 Hz, ^4J = 2 Hz), 3.09 (s, 6H, N(C*H*$_3$)$_2$). ^{13}C NMR: δ 150.59, 147.84, 142.77, 136.36, 129.57, 126.62, 120.85, 120.83, 115.68, 44.52. Anal. calc. for $C_{11}H_{12}N_2$ (172.2): C, 76.71; H, 7.02; N, 16.27. Found: C, 76.55; H, 7.21; N, 16.89.

Synthesis of (*rac*)-*N*-(2-methylbutyl)quinolin-8-amine (8). To a mixture of 8-aminoquinoline (0.145 g, 1 mmol), K_2CO_3 (0.27 g, 1.96 mmol) in anhydrous DMF (5 mL) at 120 °C, 1-bromo-2-methyl butane (0.49 mL, 3.94 mmol) was added. The solution was stirred under reflux for 24 h, then extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The resulting brown oil was purified by chromatographic column (silica gel; hexane–ethyl acetate 3 : 1) to give the product as a yellow oil.

Yield: 72% (154.3 mg, 0.72 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (dd, 1H, H *a*-quinoline, ^3J = 4 Hz, ^4J = 2 Hz), 8.04 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 2 Hz), 7.32–7.40 (m, 2H, ArH), 7.00 (d, 1H, ArH, ^3J = 8 Hz), 6.65 (d, 1H, ArH, ^3J = 8 Hz), 6.23 (b, 1H, N*H*), 3.20–3.29 (m, 1H, C*H*$_2$NH), 3.05–3.15 (m, 1H, C*H*$_2$NH), 1.80–1.92 (m, 1H, C*H*), 1.53–1.67 (m, 1H, CH$_3$C*H*$_2$), 1.22–1.34 (m, 1H, CH$_3$C*H*$_2$), 1.05 (d, 3H, C*H*$_3$CH, ^3J = 7 Hz), 0.97 (t, 3H, CH$_2$C*H*$_3$, ^3J = 7 Hz). ^{13}C NMR: δ 146.65, 136.05, 136.02, 127.83, 121.30, 113.23, 104.34, 49.47, 34.37, 34.17, 27.46, 18.29, 17.77, 11.43. Anal. calc. for $C_{14}H_{18}N_2$ (214.3): C, 78.46; H, 8.47; N, 13.07. Found: C, 78.11; H, 8.61; N, 13.29.

Synthesis of (*S*)-8-(3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl)-naphthalen-1-amine (10). In a Schlenk flask, to a solution of (S_a)-2,2′-bis(bromomethyl)-1,1′-binaphthalene (600 mg, 1.36 mmol) in 10 mL of toluene, Et_3N (0.57 mL, 4.08 mmol)

and 1,8-diaminonaphthalene (1.29 g, 8.18 mmol) were added. The mixture was stirred at 100 °C overnight. The reaction mixture was quenched with water (5 mL) and then extracted with diethyl ether (3–5 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Purification by chromatographic column (basic alumina, hexane–diethyl ether 2 : 1) gave the product as a white solid.

Yield: 50% (154.3 mg, 0.72 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93–8.03 (m, 4H, ArH), 7.74 (d, 1H, ArH, ^3J = 8 Hz), 7.46–7.56 (m, 5H, ArH), 7.13–7.34 (m, 6H, ArH), 6.93 (d, 1H, ArH, ^3J = 7 Hz), 6.60 (d, 1H, ArH, ^3J = 7), 6.25 (b, 2H, NH_2), 4.15, (d, 1H, CH_2N, ^3J = 14 Hz), 4.08 (d, 1H, CH_2N, ^3J = 11 Hz), 4.05 (d, 1H, CH_2N, ^3J = 14 Hz), 3.88 (d, 1H, CH_2N, ^3J = 11 Hz). ^{13}C NMR: δ 149.81, 146.01, 137.32, 135.55, 134.78, 134.03, 133.30, 133.20, 132.21, 131.48, 129.13, 128.65, 128.35, 128.17, 127.58, 127.52, 127.48, 126.68, 125.99, 125.73, 125.69, 125.16, 119.15, 116.99, 109.73, 57.77, 55.14. Anal. calc. for C_{32} $H_{24}N_2$ (436.6): C, 88.04; H, 5.54; N, 6.42. Found: C, 88.31; H, 5.71; N, 6.29.

Synthesis of (*S*)-8-(3*H*-dinaphtho[2,1-*c* : 1′,2′-*e*]azepin-4(5*H*)-yl)-*N*,*N*-dimethylnaphthalen-1-amine (11). To a solution of sodium hydride (123 mg, 5.13 mmol) in 3 mL of THF, a solution of ligand **10** (100 mg, 0.229 mmol) in 4 mL of THF and CH_3I (0.214 mL, 3.43 mmol) were sequentially added. The mixture was refluxed for 48 h, then allowed to cool to room temperature. A solution of NaOH pellets (1.67 g) in H_2O (4 mL) was added and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with water (5 mL) and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was dissolved in acetone and boiled. After slow cooling the product was obtained as white solid.

Yield: 40% (42.6 mg, 0.09 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (dd, 2H, ArH, ^3J = 8 Hz), 7.87 (d, 1H, ArH, ^3J = 8 Hz), 7.71 (d, 2H, ArH, ^3J = 8 Hz), 7.59–7.16 (m, 10H, ArH), 6.95 (d, 1H, ArH, ^3J = 6 Hz), 6.88 (d, 1H, ArH, ^3J = 8 Hz), 6.78 (d, 1H, ArH, ^3J = 8 Hz), 4.10 (d, 1H, N–C*H*H, ^3J = 10 Hz), 4.03 (s, 2H, CH*H*–*N*–CH*H*), 3.92 (d, 1H, N–C*H*H, ^3J = 10 Hz), 2.69 (bs, 3H, CH_3-NCH_3), 2.61 (bs, 3H, CH_3–N–CH_3). ^{13}C NMR: δ 155.16, 147.57, 145.18, 137.11, 134.75, 131.34, 131.30, 128.58, 128.37, 128.28, 128.15, 127.69, 127.45, 125.78, 125.51, 125.27, 121.91, 114.04, 58.27, 52.89, 29.71. Anal. calc. for $C_{34}H_{28}N_2$ (464.6): C, 87.90; H, 6.07; N, 6.03. Found: C, 88.05; H, 5.96; N, 6.18.

Synthesis of 1,8-bis((*S*)-3*H*-dinaphtho[2,1-*c* : 1′,2′-*e*]azepin-4(5*H*)-yl)naphthalene (12). To a solution of 1,8-diaminonaphthalene (79.1 mg, 0.5 mmol) in 5 mL of toluene and Et_3N (0.42 mL, 3 mmol), a 10 mL solution of (S_a)-2,2′-bis-(bromomethyl)-1,1′-binaphthalene in toluene (440 mg, 1 mmol) was added dropwise. The mixture was stirred under reflux at 110 °C for 72 h. After this time, the solvent was removed and the residue was dissolved in dichloromethane, washed sequentially with water and brine. The combined organic phases were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Chromatographic purification over basic alumina (hexane–diethyl ether 2 : 1 as eluent) gave the product as a white solid.

Yield: 45% (160.8 mg, 0.225 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, 2H, ArH, ^3J = 8 Hz), 7.73 (d, 2H, ArH, ^3J = 8 Hz), 7.58 (t, 4H, ArH), 7.38–7.48 (m, 12H, ArH), 7.22–7.28 (m, 2H, ArH), 6.90 (d, 2H, ArH, ^3J = 8 Hz), 6.88 (d, 2H, ArH, ^3J = 8 Hz), 6.75 (d, 2H, ArH, ^3J = 7 Hz), 6.53 (d, 2H, ArH, ^3J = 8 Hz), 3.95 (s, 4H, CH_2N), 3.89 (d, 2H, CH_2N, ^3J = 10 Hz), 3.80 (d, 2H, CH_2N, ^3J = 10 Hz). ^{13}C NMR: δ 152.45, 147.93, 134.79, 134.18, 133.73, 133.67, 133.41, 132.93, 132.57, 131.28, 130.88, 129.46, 128.67, 128.27, 128.25, 127.66, 127.47, 127.23, 127.19, 127.07, 125.96, 125.69, 125.51, 125.29, 125.25, 124.65, 121.94, 113.91, 58.15, 52.03. Anal. calc. for $C_{54}H_{38}N_2$ (714.9): C, 90.72; H, 5.36; N, 3.92. Found: C, 90.59; H, 5.22; N, 4.01.

Synthesis of 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine (13) and 1,8-bis((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)-naphthalene (15). Ligands **13** and **15** were synthesized following the same procedure but changing the *ratio* of the starting reagents. 1,8-diaminonaphthalene and (2*S*,5*S*)-2,5-hexandiol cyclic sulfate were refluxed in dry THF (20–25 mL) for 24–48 h. The resulting precipitate indicated the presence of the zwitterionic amine–sulfate species. The Schlenk flask was cooled to −78 °C and 1.1 equivalents of n-butyllithium 1.6 M were added. The mixture was warmed to room temperature and then refluxed for 72 h. Diethyl ether was added to the solution which was then washed with 10% ammonium chloride, water and brine and extracted into diethyl ether. The extract was dried ($MgSO_4$) and concentrated to yield the crude material. Purification using column chromatography, (basic alumina, hexane–diethyl ether 2 : 1) gave the product.

Ligand **13**: 1,8-diaminonaphthalene (3.95 g, 25 mmol) and (2*S*,5*S*)-2,5-hexandiol cyclic sulfate (0.9 g, 5 mmol), 5/1 *ratio* respectively. N-butyl lithium (1.6 M, 3.5 mL, 5.5 mmol). The mixture of reaction was refluxed for 48 h. The ligand was obtained as a red oil. Yield: 65% (0.78 g, 3.25 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, 1H, ArH, ^3J = 8 Hz), 7.26 (t, 1H, ArH, ^3J = 7 Hz), 7.17 (t, 1H, ArH, ^3J = 8 Hz), 7.10 (d, 1H, ArH, ^3J = 8 Hz), 7.01 (d, 1H, ArH, ^3J = 7), 6.52 (d, 1H, ArH, ^3J = 8 Hz), 6.15 (b, 2H, NH_2), 3. 90 (m, 1H, C*H*), 3.77 (m, 1H, C*H*), 2.22 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.17 (d, 3H, CH_3, ^3J = 7 Hz), 0.64 (d, 3H, CH_3, ^3J = 7 Hz). ^{13}C NMR: δ 146.11, 143.52, 137.16, 126.36, 124.79, 124.64, 120.69, 119.13, 116.99, 109.23, 59.56, 52.23, 32.05, 30.77, 20.05, 16.64. Anal. calc. for $C_{16}H_{20}N_2$ (240.3): C, 79.96; H, 8.39; N, 11.66. Found: C, 80.08; H, 8.26; N, 11.51.

Ligand **15**: 1,8-diaminonaphthalene (1.07 g, 6.8 mmol) and (2*S*,5*S*)-2,5-hexandiol cyclic sulfate (2.45 g, 13.6 mmol), 1/2 *ratio* respectively. N-butyl lithium (1.6 M, 4.7 mL, 7.5 mmol). The mixture of reaction was refluxed for 24 h. The ligand was obtained as a yellow powder. Yield: 10% (219 mg, 0.68 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (dd, 2H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 7.28 (t, 2H, ArH), 6.88 (dd, 2H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 4.39 (sextet, 2H, C*H*, ^3J = 6 Hz), 3.76 (sextet, 2H, C*H*, ^3J = 6 Hz), 2.08–2.29 (m, 4H, CH_2), 1.63-1.71 (m, 2H, CH_2), 1.30–1.40 (m, 2H, CH_2), 1.34 (d, 6H, CH_3, ^3J = 6 Hz), 0.31(d, 6H, CH_3, ^3J = 6 Hz). ^{13}C NMR: δ 144.86, 124.92, 124.55, 121.87, 121.46, 115.87, 115.56, 60.31, 60.08, 50.22, 49.94, 32.32, 32.06, 30.47, 30.07, 19.49, 19.05, 16.92, 16.64.

Anal. calc. for $C_{22}H_{30}N_2$ (322.5): C, 81.94; H, 9.38; N, 8.69. Found: C, 82.09; H, 9.25; N, 8.57.

Synthesis of 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)-*N*,*N*-dimethylnaphthalen-1-amine (14). This ligand was synthesized following the same procedure used for ligand **11**, starting from ligand **13**(300 mg, 1.25 mmol) but refluxing the reaction mixture for 24 h. After chromatographic purification of the crude product (basic Al_2O_3, hexane–diethyl ether 2 : 1) the ligand was obtained as a yellow oil.

Yield: 55% (184.5 mg, 0.69 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (m, 5H, ArH), 6.90 (m, 1H, ArH), 6.87 (m, 1H, ArH), 4.23 (sextet, 1H, C*H*, ^3J = 6 Hz), 3.80 (sextet, 1H, C*H*, ^3J = 6 Hz), 2.90–2.60 (two bs, 6H, CH_3–N–CH_3), 2.15 (m, 3H, CH_2), 1.68 (m, 1H, CH_2), 1.32 (d, 3H, CH–CH_3, ^3J = 6 Hz), 0.34 (d, 3H, CH–CH_3, ^3J = 6 Hz). ^{13}C NMR: δ 151.14, 144.18, 137.78, 125.13, 125.11, 122.13, 121.45, 116.16, 112.79, 59.90, 50.67, 32.39, 31.03, 19.09, 17.42. Anal. calc. for $C_{18}H_{24}N_2$ (268.4): C, 80.55; H, 9.01; N, 10.44. Found: C, 80.41; H, 9.01; N, 10.58.

General procedure for the synthesis of [Ru(η^5-C_5R_5)(NCMe)-(*N*,*N*)]PF_6 (18–23) (R = H or Me). The [Ru(η^5-C_5R_5)(*N*,*N*)-CH_3CN]PF_6 complexes with *N*,*N* = **1**, (R = Me, **18**), **13** (R = Me, **19**), **14** (R = H, **20**), **7**, (R = H, **21**, R = Me, **22**), **9** (R = Me, **23**) were synthesized in the same way with the following procedure.

A solution of the *N*,*N* ligand (0.1 mmol) in toluene (2 mL) was added to a solution of [Ru(η^5-C_5H_5)(NCMe)$_3$]PF_6 (45 mg, 0.1 mmol) or [Ru(η^5-C_5Me_5)(NCMe)$_3$]PF_6 (50.4 mg, 0.1 mmol) in acetonitrile (1 mL). The mixture was stirred for about 1 h while the starting colour of the solution changed depending on the ligand. After this time the solvent was removed under inert atmosphere and the residue was washed with diethyl ether still under inert atmosphere. The complexes were obtained as powders of different colour.

[Ru(η^5-C_5Me_5)(NCMe)(1)]PF_6 (18). Purple powder. Yield: 90% (52.2 mg, 0.09 mmol). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.37 (t, 1H, ArH, ^3J = 7 Hz), 6.91 (m, 2H, ArH), 6.20 (d, 1H, ArH, ^3J = 6 Hz), 5.95 (m, 1H, ArH), 5.72 (b, 2H, NH_2), 5.71 (d, 1H, ArH, ^3J = 6 Hz), 5.40 (b, 2H, NH_2), 2.80, (s, 3H, CH_3CN), 1.68 (s, 15H, C_5Me_5). Anal. calc. for $C_{22}H_{28}F_6N_3PRu$ (580.5): C, 45.52; H, 4.86; N, 7.24. Found: C, 45.38; H, 4.81; N, 7.22.

[Ru(η^5-C_5Me_5)(NCMe)(*R*,*R*-13)]PF_6 (19). Green powder. Yield: 88% (58.3 mg, 0.088 mmol). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.57 (t, 1H, ArH, ^3J = 9 Hz), 7.34 (d, 1H, ArH, ^3J = 8 Hz), 7.26 (d, 1H, ArH, ^3J = 7 Hz), 6.65 (b, 2H, NH_2), 6.20 (d, 1H, ArH, ^3J = 6 Hz), 5.90 (t, 1H, ArH, ^3J = 6 Hz), 5.74 (d, 1H, ArH, ^3J = 6 Hz), 3.95 (m, 1H, C*H*), 3.85 (m, 1H, C*H*), 2.80 (s, 3H, CH_3CN), 2.25 (m, 2H, CH_2), 1.54 (s, 15H, C_5Me_5), 1.70–1.50 (m, 2H, CH_2), 1.30 (d, 3H, CH_3, ^3J = 6 Hz), 0.60 (d, 3H, CH_3, ^3J = 6 Hz). Anal. calc. for $C_{28}H_{38}F_6N_3PRu$ (662.7): C, 50.75; H, 5.78; N, 6.34. Found: C, 50.82; H, 5.65; N, 6.32.

[Ru(η^5-C_5H_5)(NCMe)(*R*,*R*-14)]PF_6 (20). Yellow powder. Yield: 92% (57.1 mg, 0.092 mmol). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.40 (d, 2H, ArH, ^3J = 6 Hz), 7.10 (d, 1H, ArH, ^3J = 6 Hz), 6.84 (d, 1H, ArH, ^3J = 5.86 Hz), 6.66 (d, 1H, ArH, ^3J = 6 Hz), 6.20 (t, 1H, ArH, ^3J = 6 Hz), 5.16 (s, 5H, C_5H_5), 4.19 (m, 1H, C*H*), 3.85 (m, 1H, C*H*), 3.05 (s, 3H, CH_3-N), 2.91 (s, 3H, CH_3-N), 2.84 (s, 3H, CH_3CN), 2.30–2.10 (m, 2H, CH_2) 1.70 (m, 1H, CH_2), 1.43–1.23 (m, 1H, CH_2), 1.32 (d, 3H, CH_3, ^3J = 6 Hz), 0.35 (d, 3H, CH_3, ^3J = 6 Hz). Anal. calc. for $C_{25}H_{32}F_6N_3PRu$ (620.6): C, 48.39; H, 5.20; N, 6.77. Found: C, 48.28; H, 5.09; N, 6.71.

[Ru(η^5-C_5H_5)(NCMe)(7)]PF_6 (21). Brown powder. Yield: 78.5% (41 mg, 0.0785 mmol). ^{1}H NMR (300 MHz, CD_3CN): δ 9.62 (dd, 1H, H *a*-quinoline, ^3J = 5 Hz, ^4J = 1 Hz), 8.40 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 1 Hz), 7.88–7.93 (m, 2H, ArH), 7.68 (t, 1H, ArH, ^3J = 8 Hz), 7.55 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 5 Hz), 4.32 (s, 5H, C_5H_5), 3.54 (s, 3H, N(CH_3)$_2$), 3.48 (s, 3H, N(CH_3)$_2$), 2.19 (s, 3H, CH_3CN). Anal. calc. for $C_{18}H_{20}F_6N_3PRu$ (524.4): C, 41.23; H, 3.84; N, 8.01. Found: C, 41.02; H, 3.57; N, 7.92.

[Ru(η^5-C_5Me_5)(NCMe)(7)]PF_6 (22). Dark orange powder. Yield: 72% (42.8 mg, 0.072 mmol). ^{1}H NMR (300 MHz, CD_3CN): δ 9.10 (dd, 1H, H *a*-quinoline, ^3J = 5 Hz, ^4J = 1 Hz), 8.31 (dd, 1H, ArH, ^3J = 8 Hz, ^3J = 1 Hz), 7.81 (t, 2H, ArH, ^3J = 8 Hz), 7.65 (dt, 2H, ArH, ^3J = 8 Hz, ^4J = 5 Hz), 3.32 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 2.01 (s, 3H, CH_3CN), 1.58 (s, 15H, C_5Me_5). Anal. calc. for $C_{23}H_{30}F_6N_3PRu$ (594.5): C, 46.26; H, 5.09; N, 7.07. Found: C, 46.11; H, 5.22; N, 7.01.

[Ru(η^5-C_5Me_5)(NCMe)(9)]PF_6 (23). Dark green powder. Yield: 80% (53.6 mg, 0.08 mmol). ^{1}H NMR (300 MHz, CD_3CN): δ 9.07 (dd, 1H, H *a*-quinoline, ^3J = 6 Hz, ^3J = 2 Hz), 8.53 (dd, 1H, ArH, ^3J = 8 Hz, ^4J = 2 Hz), 7.98 (dd, 2H, ArH, ^3J = 8 Hz, ^4J = 6 Hz), 7.43 (d, 1H, ArH, ^3J = 10 Hz), 7.12 (s, 1H, ArH), 6.99 (bs, 2H, ArH), 6.87 (bs, N*H*), 6.69 (d, 1H, ^3J = 10 Hz, ArH), 2.40 (s, 6H, 2 CH_3Ph), 2.07 (s, 3H, CH_3CN), 1.40 (s, 15H, C_5Me_5). Anal. calc. for $C_{29}H_{34}F_6N_3PRu$ (670.6): C, 51.94; H, 5.11; N, 6.27. Found: C, 52.08; H, 5.23; N, 6.33.

Allylic etherification reaction

After stirring 0.015 mmol of [Ru(η^5-C_5R_5)(NCMe)$_3$]PF_6 and 0.015 mmol of *N*,*N* ligand in acetonitrile at room temperature for 1 h, 0.75 mmol of potassium carbonate and 0.5 mmol of cinnamyl chloride were added and after 15 min, 0.75 mmol of phenol were added. The mixture was stirred for 24 h and monitored by TLC (hexane/1% Et_2O). After this time, the solution was filtered on silica and concentrated under *vacuo*. The resulting oil was analyzed by ^{1}H NMR spectroscopy (determined by integration of allylic proton) and GC-MS to determine the conversion; the enantiomeric excess was determined by HPLC (Daicel OJ-H column, hexane/iPrOH = 99/1, 220 nm, t_R = 42.7 min (*R* enantiomer), t_R = 46.3 min (*S* enantiomer)).

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