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Cyclometalated N-Heterocyclic Carbene-Platinum Catalysts for the Enantioselective Cycloisomerization of Nitrogen-Tethered 1,6-Enynes

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Abstract: Platinum(II) complexes which combine six-membered N-heterocyclic carbene-containing metallacyclic units and monodentate chiral phosphines have been prepared. The key step of their synthesis is the intramolecular oxidative addition of *N*-2-iodobenzylimidazolylidene-platinum(0)-diene complexes in the presence of the chiral phosphorus ligands. The platinum(II) metallacycles have been used as well-defined pre-catalysts for the enantioselective cycloisomerization of nitrogen-tethered 1,6-enynes into 3-azabicyclo[4.1.0]hept-4-enes. High enantiomeric excesses have been obtained with either Monophos or phenyl-Binepine based catalysts (*ee*s = 82–96%), although phenyl-Binepine outperforms Monophos in these reactions. The absolute configuration of the final 3-azabicyclo[4.1.0.]heptenes has been established by X-ray diffraction studies. The method has been extended then to the cycloisomerization of dienynes with enantiotopic vinyl groups. An (*S*)-phenyl-Binepine-platinum(II) complex allows total diastereoselectivity and high enantioselectivity levels to be attained in these reactions (*ee*s up to 95%) which represent the first enantioselective desymetrizations achieved *via* enyne cycloisomerizations.

Keywords: chiral phosphines; enantioselective desymmetrization; enyne cycloisomerization; N-heterocyclic carbenes; platinacycles

Introduction

Enyne cycloisomerizations under transition metal catalysis have attracted considerable attention in recent years since they represent powerful synthetic tools for the construction of cyclic and heterocyclic moieties.[1] Except for palladium- or rhodium-promoted Alder-ene-type cyclizations,[2] asymmetric variants of these reactions are, however, comparatively underdeveloped.[3] This is the case also for the cycloisomerizations of 1,6-enynes into bicyclo[4.1.0]heptenes which are specifically targeted in this paper. They have been shown to proceed in the presence of various Pt(II),[4] Ir(I),[5] Rh(II)[6] and Au(I)[7] achiral pre-catalysts, while a very restricted range of enantioselective processes have been reported to date. Enantioselective variants make use of Ir/TolBinap,[5a] Au/MeO-BIPHEP[8] and Rh/chiral diene[9] complexes as the chiral catalysts. Altough high enantioselectivity is regularly attained, the restricted substrate scope and overall moderate efficiency fully motivate the search for new and efficient catalytic systems. In this context, we have disclosed recently Pt(II) complexes of the general formulae **I**[10] and **II**[11] as the first promising platinum-based chiral pre-catalysts for the cycloisomerization of 1,6-enynes bearing N-containing tethers (Figure 1).

Following on from our preliminary communication, we report here a more detailed account of the design and structural tuning of the platinacyclic complexes **II**, as well as a comparison of the catalytic properties of Binepine and Monophos containing pre-catalysts **II**. Finally, an extension of the cycloisomerization reactions to nitrogen-tethered dienynes is disclosed.

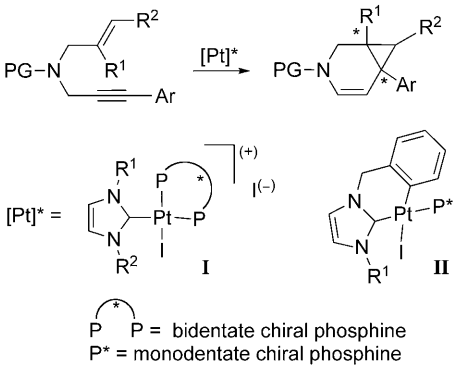


Figure 1. Platinum pre-catalysts for the enantioselective cycloisomerizations of N-tethered 1,6-enynes.

Results and Discussion

Catalysts Design and Optimization

Our design of the platinacyclic complexes **I** and **II** as potential pre-catalysts was based initially on a simple mechanistical hypothesis and a few literature data showing that platinum catalysts can operate as simple Lewis acids in some cycloisomerization processes.[1a,4c,12] It was anticipated, therefore, that 16-electron, tricoordinated platinum(II) complexes with a single free coordination site will promote cycloisomerization reactions of this class. The concept has been demonstrated initially by Gagné who carried out diene cycloisomerizations by means of cationic platinum complexes containing either a tridentate phosphorus ligand or a bidentate phosphine/monodentate phosphine pair.[13]

Shortly after, our group disclosed that the Pt(II) complexes **I** displaying a bidentate phosphine and an NHC ligand (NHC = N-heterocyclic carbene), together with a labile iodide ligand, afford suitable pre-catalysts for the cycloisomerization of nitrogen-tethered 1,6-enynes (Figure 1).[10] Enantioselective processes could be established by using (*S,S*)-Chiraphos as the chiral bidentate ligand, giving *ee*s up to 74% in a model cycloisomerization reaction.

These encouraging results led us to consider then an analogous series of tricoordinated Pt(II) complexes where the "bidentate phosphine/monodentate NHC" ligand pair of complexes **I** would be replaced by a "bidentate NHC/monodentate phosphine" pair. At this point, the specific design of the metallacyclic structures **II** was inspired by the synthetic approach used to access complexes **I**, that is a two-step sequence which involves oxidative addition of I_2 to a Pt(0)-NHC complex as the key step (Figure 2).[10]

We reasoned that the same oxidative addition/ligand exchange sequence might be easily adapted to the synthesis of platinacyclic derivatives by taking advantage of an intramolecular oxidative addition step. The metallacyclic unit will be combined then with a monodentate phosphorus ligand to complete the coordination sphere of platinum. With this in mind, we targeted Pt(0) complexes bearing *N*-2-iodobenzylimidazolylidene ligands (e.g., **2a** in Scheme 1) as suitable intermediates, prone to intramolecular oxidative addition through their aryl iodide function. In Scheme 1 hereafter, the preparation of complexes **3–5** typifies our synthetic strategy.

Complex **2a** has been prepared by reacting the *N*-(2-iodobenzyl)imidazolium salt **1a**[14] with a xylene solution of the so-called Karstedt's catalyst, $Pt_2(dvtms)_3$ (dvtms = divinyltetramethyldisiloxane), in the presence of *t*-BuOK as the deprotonating agent.[15] The Pt(0) complex **2a** was isolated in 68% yield after chromatography. The intramolecular oxidative addition reaction and the ligand exchange processes have been performed then in a single step by heating **2a** in the presence of the well known chiral monodentate phosphines (*R*)-MOP, (*S*)-Ph-Binepine[16] and (*R*)-Monophos.

These experiments led to isolation of the desired metallacyclic compounds **3–5** in moderate to good yields after purification by column chromatography. Crystals suitable for X-ray diffraction studies could be obtained for **4a** and **5a** by crystallization from toluene solutions. X-ray data for the Ph-Binepine complex **5a** have been reported in our previous communication, showing that the phosphorus ligand lies *trans* to the NHC unit. The solid state structure of the MonoPhos complex **4a** is shown in Figure 3 hereafter. Overall, it displays the same geometric features as **5a**: a square planar coordination of platinum, with the phosphorus ligand *trans* to the carbene moiety. The planar NHC

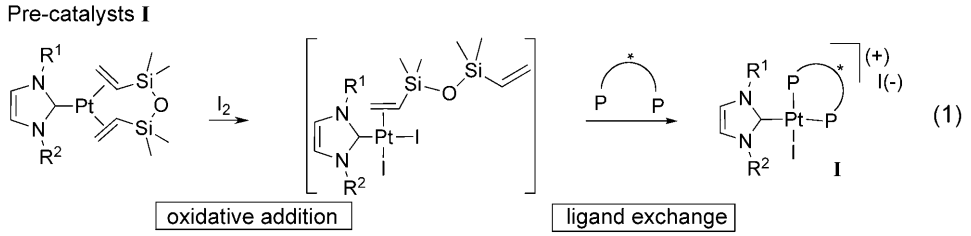
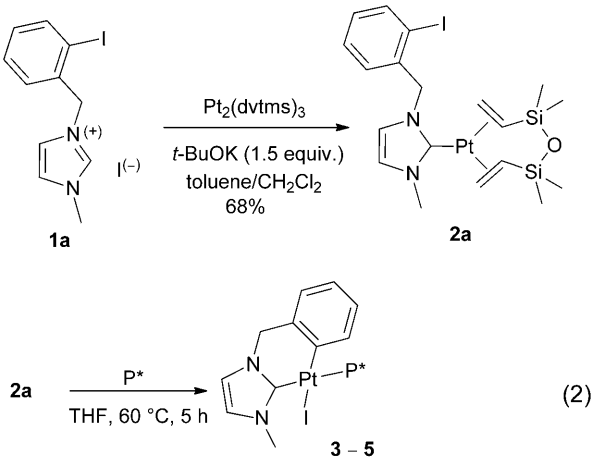
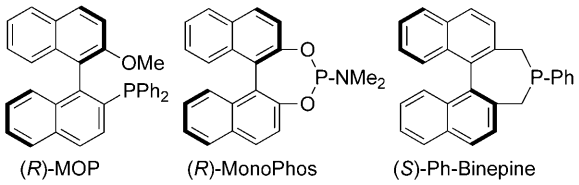


Figure 2. Synthetic approach to the 'first generation' 1,6-enynes cycloisomerization pre-catalysts, **I**.



Ligand	Yield	δ ^{31}P NMR (ppm)	^{1}J(P-Pt) (Hz)
3 (*R*)-MOP	20%	28.1	2836
		27.3	2834
4a (*R*)-Monophos	65%	130.6	4510
		130.2	4543
5a (*S*)-Ph-Binepine	63%	27.4	2750
		28.8	2777



Scheme 1. Synthesis and ^{31}P NMR data for the platinacyclic complexes **3**–**5**.

ligand forms a dihedral angle of 29.2° with the coordination plane of platinum.

The boat-shaped platinacyclic moiety differentiates the upper and bottom faces of the square planar complex which displays therefore a chiral core structure.[17,18] Axially chiral square planar NHC complexes have been shown to be usually configurationally stable.[19] Thus, complexes **3–5** which combine axial chirality and a chiral phosphorus ligand, are expected to form diastereomeric pairs. Complexes **3–5** were indeed obtained as mixtures of two isomers (isomers ratios: **3**, 55:45; **4a**, 75:25; **5a**, 80:20). The minor isomers have not been unambiguously characterized, nevertheless ^{31}P NMR data strongly support a *trans* relative coordination of the phosphorus and NHC ligands, since chemical shifts and P-Pt coupling constants are of the same order of magnitude as for the major isomer. Therefore the two observed isomers have been tentatively assigned as diastereomeric complexes with opposite axial configurations.

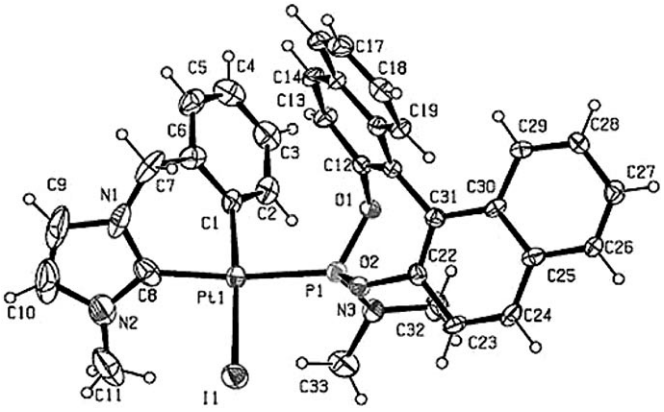


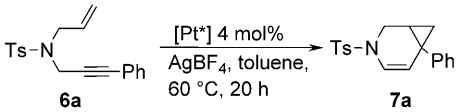
Figure 3. X-ray crystal structure for the (*R*)-MonoPhos complex (*R*,S_a)-**4a**. Selected bond distances (Å): Pt–I = 2.695(1), Pt–P = 2.261(2), Pt–C(1) = 2.012(8), Pt–C(8) = 2.00(1), C(8)–N(1) = 1.35(1), C(8)–N(2) = 1.38(2). Selected bond angles (deg): C(1)–Pt–C(8) = 84.0(4), C(8)–Pt–I = 92.8(3), I–Pt–P = 91.89(6), P–Pt–C(1) = 91.2(2), N1–C(8)–N(2) = 104.3(9).

According to our initial target, complexes **3–5** have been evaluated as pre-catalysts for the cycloisomerization of the *N*-allyl-*N*-3-phenylprop-2-ynylsulfonamide **6a** (Scheme 2). The reaction had been introduced by Fürstner et al. who demonstrated that the bicyclic sulfonamide **7a** is produced under $PtCl_2$ catalysis.[4b,c]

Starting from complexes **3–5**, the catalytically active species are formed by addition of $AgBF_4$ as the iodide trapping agent. Abstraction of the iodide ligand generates formally three-coordinated complexes which might adopt either a T-shaped[20] or a Y-shaped[21] arrangement. These three-coordinated complexes are anticipated to be either achiral (Y-shaped) or configurationally unstable (T-shaped) with respect to the above-mentioned axial chirality.[10b] Therefore, the diastereomeric mixtures of complexes **3–5** can be used as pre-catalysts, without foreseeable drawbacks in terms of chiral induction.

In standard conditions, complexes **3–5** displayed moderate to good catalytic activity, leading to the expected bicyclic sulfonamide **7a** in 40–93% isolated yields.

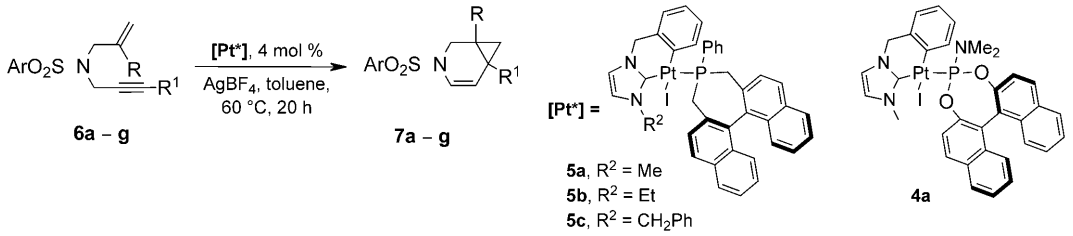
From this initial screening, the (*S*)-Ph-Binepine complex **5a** has emerged as the most efficient catalyst



[Pt*] = **3**: 40%, *ee* = 0%
4a: 93%, *ee* = 75%
5a: 88%, *ee* = 93%

Scheme 2. Screening of complexes **3–5** as pre-catalysts for a model cycloisomerization reaction.

Table 1. Platinum-promoted enantioselective cycloisomerizations of nitrogen-tethered 1,6-enynes.



Entry	Substrate	$ArSO_2$	R	R^1	Prod.	[Pt*]	Yield [%]	*ee*[b] [%]	[Pt*]	Yield [%]	*ee*[b] [%]
1	**6a**	Ts	H	Ph	**7a**	**5a**	88	93[a]	**4a**	93	75
2	**6a**	Ts	H	Ph	**7a**	**5c**	90	96[a]			
3	**6b**	Ts	H	3,5-$(Me_2)C_6H_3$	**7b**	**5a**	95	90[a]	**4a**	88	84
4	**6c**	Ts	H	4-MeO-C_6H_4	**7c**	**5b**	77	91[a]			
5	**6d**	Ts	H	4-NO_2-C_6H_4	**7d**	**5c**	51	97[a]			
6	**6e**	Ts	Me	Ph	**7e**	**5c**	98	88[a]	**4a**	77	25
7	**6f**	Ns	H	Ph	**7f**	**5c**	98	94			
8	**6g**	Ts	Me	Me	**7g**	**5a**	71	19			

[a] From ref.[11]
[b] Enantiomeric excesses have been measured by chiral HPLC.

giving a good conversion rate and high enantioselectivity level (93% enantiomeric excess). The MOP complex **3** gave a racemic product, while the Monophos complex **4a** gave a significant, 75% enantiomeric excess and a higher conversion rate than the Binepine complex **5a**.

To the best of our knowledge, these are the first known Pt-based catalysts for the enantioselective cycloisomerization of 1,6-enynes. Moreover, only a very few examples have been reported so far of analogous cycloisomerizations of N-tethered enynes by using other transition metal catalyts. These reactions have been carried out notably by means of Ir-TolBinap complexes, giving enantiomeric excesses in the range 35–78%.[5a] More recently, chiral gold-diphosphine[8] and rhodium-diene[9] complexes have been applied succesfully to these cycloisomerizations, on a rather restricted range of substrates (1 example, 98% *ee* and 7 examples, 68–95% *ee*, respectively).

The encouraging results obtained with **5a** (Scheme 2) led us to expand the family of Ph-Binepine-based catalysts to the platinacyclic complexes **5b** and **5c** which display an ethyl and a benzyl substituent on the carbene nitrogen atom, respectively. The nature of the nitrogen substituent was indeed expected to modulate the enantioselectivity levels by steric effects. With these three catalysts in hand, the scope of the enantioselective cycloisomerization reaction was established by considering various enyne substrates, as reported in our previous communication.[11] Selected results are recalled in Table 1. For comparison purposes, a few examples of cycloisomerization reactions promoted by the (*R*)-MonoPHOS based catalyst **4a** are also mentioned in this table.

Complexes **5a–c** efficiently promote the enantioselective cycloisomerization of allyl propargyl tosylamides, with various aryl groups on the alkyne moiety, into the corresponding bicyclo[4.1.0]heptenes. Enantiomeric excesses in the range 91–96% are obtained for the reactions in entries 1–5. As shown in entry 6, the presence of a methyl substituent on the allylic function is tolerated, since the cycloisomerization of **7e** (R = Me, R^1 = Ph) takes place with high yield and an enantiomeric excess of 88%. A dramatic decrease of the enantioselectivity was observed, however, in the cycloisomerization of substrate **6g** where the alkyne aryl group has been replaced by a methyl group (entry 8). The nitrogen tosyl substituent can be suitably replaced by a nosyl group (entry 7) while retaining high levels of chiral induction (94% *ee*, entry 7). Noteworthy, we have also ascertained that the nosyl group can be removed from the final bicyclic product. The nitrogen-deprotection procedure, which involves reaction of the *N*-nosyl substituted bicyclic derivative with $PhSH/K_2CO_3$ in MeCN,[22, 23] significantly expands the synthetic utility of the enantioselective cycloisomerizations mentioned above.

In addition to the high efficiency of the Ph-Binepine complexes **5**, the preliminary experiments in Table 1 (right columns) also highlight MonoPhos as a promising chiral ligand for cycloisomerization reactions of this class. The Monophos complex **4a** indeed combines significant enantioselectivity levels (*ee*s of 75% and 84% in the cycloisomerizations of the propargyl allyl amides **6a** and **6b** in entries 1 and 3, respec-

tively) and high catalytic activity. Moreover, the easy availability of the chiral auxiliary also represents a major practical advantage. This led us to investigate in more detail possible strategies for the optimization of the chiral induction from MonoPhos-based catalysts: (i) optimization of the reaction conditions; (ii) modulation of the carbene N and aryl substituents; (iii) addition of a stereogenic centre in the metallacyclic scaffold. The main results are reported hereafter.

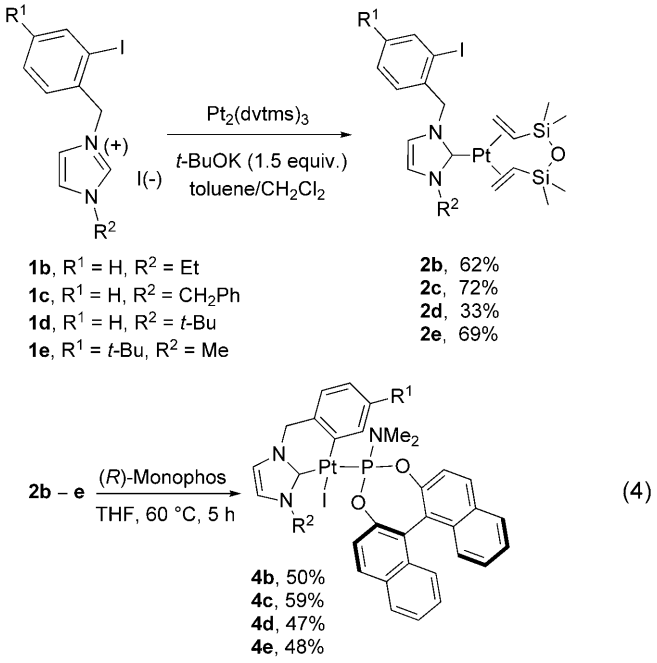
Firstly, the high catalytic efficiency of the Monophos complex **4a** allowed us to perform the cycloisomerization reaction of entry 1 (Table 1, right columns) in milder conditions. The reaction temperature was lowered, with respect to the initially applied 60 °C: conversion rates >95% and of ~50% were observed after 18 h at 40 °C and room temperature, respectively. Unexpectedly, however, lowering of the reaction temperature did not result in increased enantioselectivity. A slight decrease of the *ee* was observed for reactions run at room temperature (64% *ee*), while the *ee* is roughly constant at 75% for reaction temperatures between 50 °C and 90 °C. In this respect, the behaviour of the Pt-MonoPhos catalyst **4a** markedly contrasts with that of the Binepine complex **5a** which gives higher enantiomeric excesses at lower reaction temperature (82% *ee* at 90 °C *vs.* 93% *ee* at 60 °C).

Secondly, we thought that a major drawback of complex **4a**, when used in enantioselective catalysis, might be the unhindered rotation of the monodentate chiral phosphine around the Pt–P bond. We therefore considered the use of Monophos-platinacyclic complexes with increased steric constraints and consequently reduced conformational flexibility. Bulkier substituents have been introduced either on the carbene nitrogen atom (complexes **4b–d**) or on the aryl moiety of the platinacyclic unit (complex **4e**).

Complexes **4b–d** bearing ethyl, benzyl and *tert*-butyl substituents on the nitrogen atom have been prepared as shown in Eq. (4) (Scheme 3) from the corresponding Pt(0)-NHC complexes **2b–d**.

The *N*-Et, *N*-benzyl and *N*-*tert*-butyl substituted complexes **4b–d** were formed as 75:25, 80:20 and 77:23 mixtures of diastereomers, respectively. Crystals suitable for X-ray diffraction studies have been obtained for **4d**. An ORTEP drawing, selected bond angles and distances are given in Figure 4. The isolated crystalline complex **4d** displays an opposite axial configuration of the platinum core, with respect to complex **4a** above.[24]

As shown in Scheme 3 above, we have prepared also the Monophos complex **4e**, which displays an increased steric hindrance of the platinacyclic aryl moiety, due to the *t*-Bu group, *meta* to the Pt–C bond. The synthesis of **4e** starts from the 4-*tert*-butyl-2-iodobenzylimidazolium salt **1e** and involves generation of the N-heterocyclic carbene in the presence of $Pt_2(dvtms)_3$. The reaction affords **2e** in 69% yield. Then,



1b, R^1 = H, R^2 = Et
1c, R^1 = H, R^2 = CH_2Ph
1d, R^1 = H, R^2 = *t*-Bu
1e, R^1 = *t*-Bu, R^2 = Me

2b, 62%
2c, 72%
2d, 33%
2e, 69%

4b, 50%
4c, 59%
4d, 47%
4e, 48%

(4)

Scheme 3. Synthesis of the platinacyclic (*R*)-Monophos complexes **4b–e**.

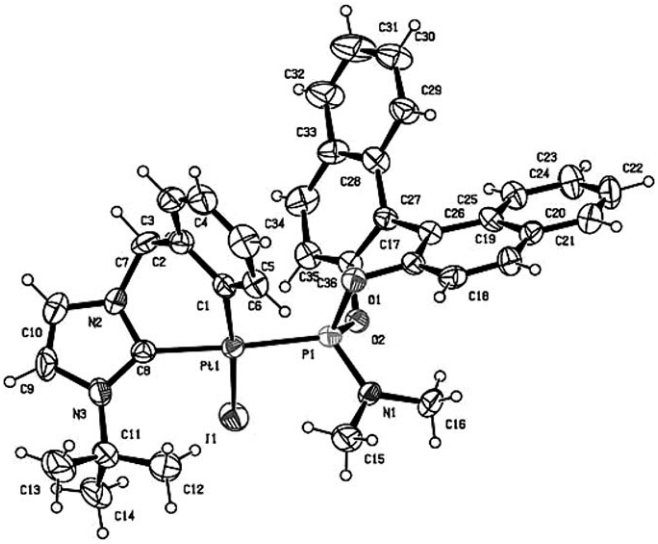
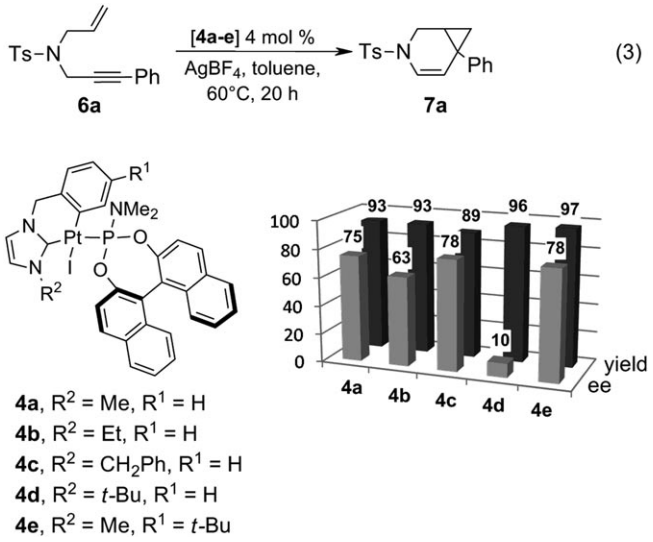


Figure 4. ORTEP drawing for the MonoPhos complex (R,S_a)-**4d**. Selected bond distances (Å): Pt–I = 2.7043(7), Pt–P = 2.233(2), Pt–C(1) = 2.002(8), Pt–C(8) = 2.047(7), C(8)–N(2) = 1.329(9), C(8)–N(2) = 1.368(9). Selected bond angles (deg): C(1)–Pt–C(8) = 83.7(3), C(8)–Pt–I = 91.8(2), I–Pt–P = 88.81(5), P–Pt–C(1) = 95.2(2), N1–C(8)–N(2) = 105.1(6).

heating of a 1:1 mixture of **2e** and (*R*)-Monophos in THF at 60 °C converts the Pt(0) complex **2e** into the platinacyclic derivative **4e** which was isolated as a >95:5 mixture of isomers (Scheme 3).

It should be mentioned here that the attempted synthesis of analogous *ortho*-substituted platinacycles



Scheme 4. Screening of the (*R*)-MonoPhos based cataysts **4** in the enantioselective cycloisomerization of the model allyl-propargylic amine **6a** (Scheme 2).

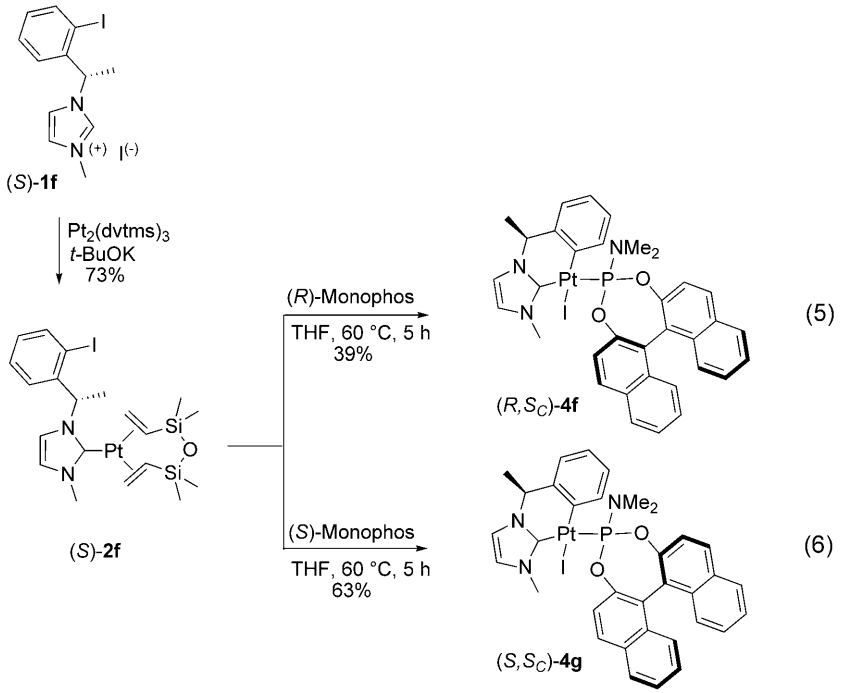
from a (3-methyl-2-iodobenzyl imidazolylidene)-platinum(0)(dvtms) complex failed, presumably due to the excessive steric hindrance which prevents the oxidative addition reaction to take place.

The new Monophos complexes **4** have been evaluated in the model cycloisomerization of enyne **6a**, in standard conditions (4 mol% pre-catalyst, excess $AgBF_4$, in toluene at 60 °C). Results are reported in Scheme 4.

From these experiments it appears that complexes **4** with nitrogen substituents of moderate steric hindrance afford significant levels of enantioselectivity, with *ee*s peaking at 78% for **4c** ($R^2 = CH_2Ph$). The pre-catalyst **4d** ($R^2 = t$-Bu), which displays high steric hindrance at the imidazole nitrogen, retains a high level of catalytic activity, it induces however a dramatic decrease of the enantiomeric excess (10% *ee vs.* 75% *ee* for **4a**, $R^2 = Me$). On the other hand, complex **4e**, which displays a *t*-Bu substituted aryl moiety, gives both a good yield (97%) and a slightly improved enantiomeric excess (78% *ee*), with respect to the reference catalyst **4a**. Although only moderate improvements of the enantioselectivity levels have been obtained so far, the above results demonstrate that modulation of both the aryl moiety and the nitrogen substituent have an effect on the catalytic properties of these Monophos complexes.

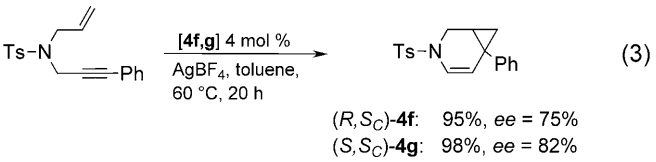
Thirdly and finally we envisioned the synthesis of the platinum complexes **4f** and **4g** (Scheme 5) displaying an additional stereogenic centre, with defined stereochemistry, at the platinacyclic units. Our aim was to highlight a cooperative effect between the chiral platinacyclic unit and the chiral Monophos ligand with appropriate relative configurations.

The Pt(0) complex (*S*)-**2f** was prepared from the corresponding chiral imidazolium salt (*S*)-**1f** and $Pt_2(dvtms)_3$, according to the general procedure. It was reacted then with Monophos ligands of opposite absolute configurations in the usual conditions (Scheme 5).



Scheme 5. Synthesis of the Monophos complexes **4f** and **4g** displaying a stereogenic carbon centre in the platinacyclic unit.

The (*R*)-Monophos complex (*R,S*$_C$)-**4f** was isolated as a 92:8 mixture of diastereomers [^{31}P NMR ($CDCl_3$): broad signal at $\delta = 131$ ($J_{P,Pt} = 4536$ Hz) for the major isomer], while a 7:3 mixture of the diastereomeric complexes (*S,S*$_C$)-**4g** was obtained from (*S*)-Monophos [Major isomer: ^{31}P NMR ($CDCl_3$): $\delta = 129$ ($J_{P,Pt} = 4600$ Hz); minor isomer: ^{31}P NMR ($CDCl_3$): $\delta = 131$, broad signal]. Complexes **4f** and **4g** have been evaluated as catalysts in the model cycloisomerization reaction of Eq. (3).



Scheme 6. Catalytic cycloisomerizations promoted by complexes **4f** and **4g**.

Both catalysts gave high conversion rates, 95% and 98% yields being obtained with **4f** and **4g**, respectively. The (*R,S*$_C$)-complex **4f** gave the same enantiomeric excess as the 'parent' complex **4a** (75% *ee*), while complex (*S,S*$_C$)-**4g** enabled the enantiomeric excess to be increased to 82%. The (*S*$_C$)-platinacycle/(*S*)-Monophos pair thus represents the matching pair for this cycloisomerization process. It provides so far the most efficient Monophos-based catalyst for the enantioselective cycloisomerization reaction of Eq. (3) (Scheme 6) (98% yield, 82% *ee*).

On the whole, the Monophos-based platinum catalysts **4a–g** do not attain so far the very high enantioselectivity levels afforded by the Binepine-platinum complexes **5**, nevertheless they often display higher catalytic activity and a proper design allows acceptable enantiomeric excesses, up to 82%, to be obtained. Moreover, the optimization study above highlights some trends in the structure-activity relationship and points out some simple structural units that can be modulated to improve the catalytic properties of the Monophos platinacyclic complexes. Therefore, we consider Monophos complexes as undoubtedly promising catalysts and their use in the cycloisomerization of other enynes is currently being investigated.

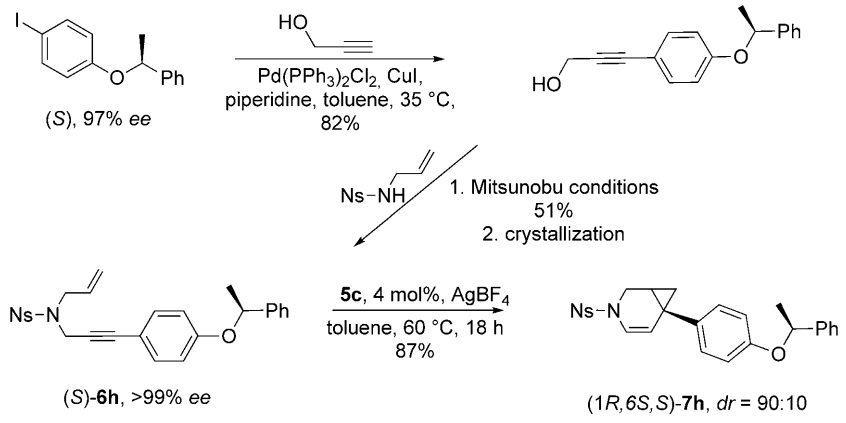
Assignment of the Absolute Configuration of the Cycloisomerization Products

To the best of our knowledge, the absolute configuration of the bicyclic *N*-tosylamines **7** is unknown so far. Therefore, in order to establish the sense of chiral induction from the chiral platinacyclic catalysts, we have considered using X-ray diffraction studies and vibrational circular dichroism (VCD) for their configurational assignment. The 6-azabicyclo[4.1.0]heptene **7h**, which contains a 1-phenylethoxy unit of known *S*-configuration, has been prepared by cycloisomerization of (*S*)-**6h** in the presence of the platinum catalyst **5c** (Scheme 7).

The reaction takes place with good yields and diastereoselectivity (90:10 isomers ratio) affording **7h** as a crystalline compound. The ORTEP drawing for the major diastereoisomer is depicted in Figure 5. Compound **7h** displays a (1*R*,6*S*) configuration of the bicyclic moiety.

As a further evidence for the sense of chiral induction from complexes **5**, the absolute configuration of the major enantiomer of **7a** (96% *ee*, from entry 2 in Table 1) has also been assigned by X-ray crystal studies and supported by VCD studies (see Supporting Information). These studies consistently demonstrate that (*S*)-Ph-Binepine complexes afford a (1*R*,6*S*) configured bicycloheptene units.

Bicyclic derivatives with the opposite (1*S*,6*R*) configurations are obtained by using (*R*)-Monophos as the chiral auxiliary.



Scheme 7. Synthesis of the 3-azabicyclo[4.1.0]heptene **7h** from enantiomerically enriched (*S*)-1-iodo-4-(1-phenylethoxy)benzene.

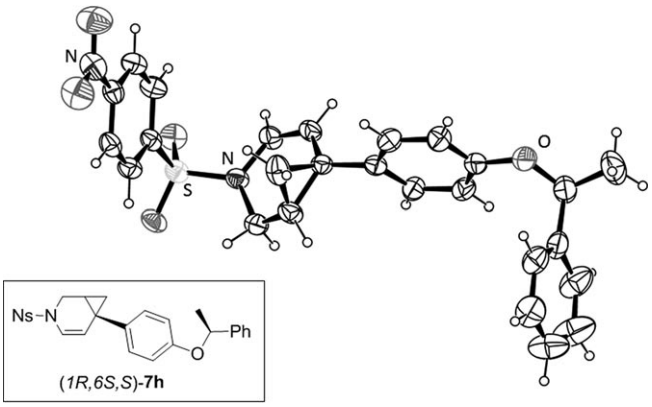
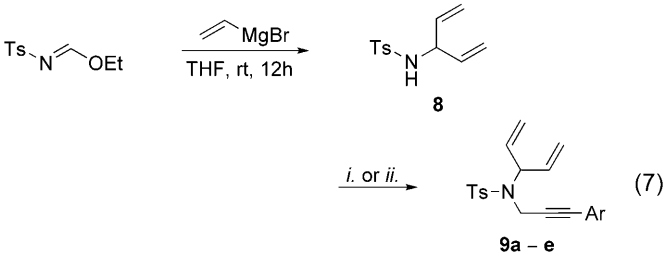


Figure 5. Crystal structure of (1*R*,6*S*,*S*)-**7h** allowing assignment of the absolute configuration of the bicyclic unit.

Enantioselective Cycloisomerizations of 1,6-Enynes with Enantiotopic Vinyl Moieties

As a further step in the development of enantioselective enyne cycloisomerizations, we next considered the dienyne derivatives **9** as potential new substrates. Substrates **9** display the same 1,6-enyne moiety as **6**, they have however two enantiotopic vinyl moieties. If the cycloisomerization reaction takes place according to the usual pathway, then the bicyclic scaffold **10** will be generated which contains an additional, vinyl-substituted stereogenic centre in position 2.[25] Our aim was to investigate these cyclization reactions and to evaluate the ability of chiral catalysts to induce both diastereo- and enantioselective tranformations of these substrates. As far as we know, the cycloisomerization of dienynes **9** has never been investigated before, while prochiral dienynes of this class have been used as substrates for enantioselective ring-closing enyne metathesis reactions,[26] as well as for asymmetric Pauson–Khand type reactions.[27]

The preferred synthetic approach to dienynes **9** involves addition of vinylmagnesium bromide to ethyl *N*-tosylformimidate[28] to produce the 1-vinylallylamide **8**,[27] and subsequent alkylation of the nitrogen atom with a propargylic bromide (Scheme 8).



i. $HOCH_2C{\equiv}C\text{-}Ar$, PPh_3, DIAD, r.t., 2.h
ii. $BrCH_2C{\equiv}C\text{-}Ar$, K_2CO_3, MeCN, 60 °C, 24 h

Scheme 8. Synthesis of the dienyne substrates **9**.

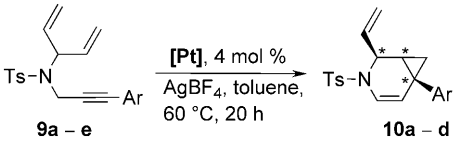
Dienynes **9** have been subjected to catalytic cycloisomerization in the presence of either platinum(II) chloride or the chiral (*S*)-Ph-Binepine complex **5a** (Table 2). The expected bicyclic products **10** were obtained as >95:5 diastereomeric mixtures,[29] irrespective of the catalyst used. This suggests that a highly diastereoselective, substrate controlled reaction pathway operates here.

In the cycloisomerizations of dienynes **9**, the chiral pre-catalyst **5a** displays a moderate catalytic activity, compared to that previously observed in the cycloisomerizations of the simple 1,6-enynes **6** (Table 1). This is likely due to the increased steric hindrance of the additional vinyl substituent. Gratifyingly, however catalyst **5a** affords very high diastereoselectivity, as well as high levels of enantioselectivity, with enantiomeric excesses of between 80% and 95% (entries 2–5 in Table 2).

The isolated yields given in Table 2, correspond to reactions run in standard conditions (60 °C, 24 h). Higher conversion rates can be attained at higher reaction temperatures, which induce however a significant decrease of the enantioselectivity levels (*ee* = 64% at 90 °C *vs.* 87% at 60 °C, for the cycloisomerization reaction in entry 2).

Crystals suitable for X-ray diffraction studies have been obtained from a CH_2Cl_2/heptane solution of **10d** (92% *ee*, from entry 5). The solid state structure of **10d** (Figure 6) displays a relatively flat tetrahydropyridine ring with a dihedral angle of 36° between the N–C12–C11 plane and the N–C8–C9 plane. The vinyl substituent is opposite to the cyclopropane unit, that is, *syn* to the aryl substituent. X-ray data display a torsion angle of 69.6° for the H–C8–C9–H moiety, which is overall consistent with the small ^3J coupling

Table 2. Catalytic cycloisomerization of dienynes **9** in the presence of Pt(II) catalysts.



Entry	Substrate	Ar	[Pt]	Product	Yield[a] [%]	*ee* [%]
1	**9a**	Ph	$PtCl_2$	**10a**	45[b]	–
2	**9a**	Ph	**5a**	**10a**	46	87
3	**9b**	3,5-$(Me_2)C_6H_3$	**5a**	**10b**	66	80
4	**9c**	4-MeO-C_6H_4	**5a**	**10c**	55	95
5	**9d**	3-MeO-C_6H_4	**5a**	**10d**	28	92
6	**9e**	4-NO_2-C_6H_4	**5a**	–	0	–

[a] Isolated yields. The isolated samples may contain some residual starting material. The yields of **10** are calculated then from ^{1}H NMR spectra.
[b] Reaction performed at 90 °C.

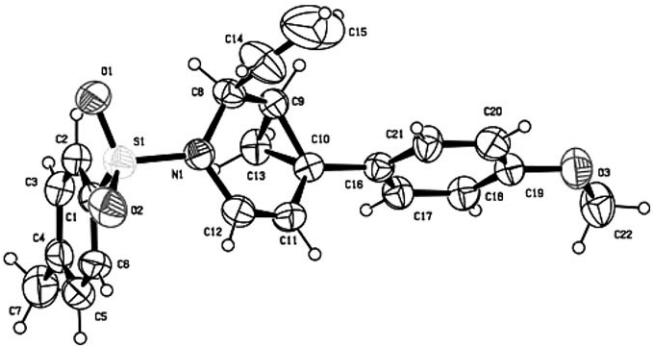


Figure 6. ORTEP drawing for the cycloisomerization product (1*R*,2*S*,6*S*)-**10d**.

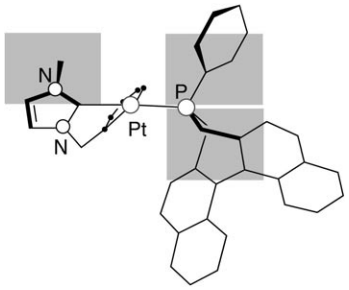


Figure 7. Geometrical features of the (*S*)-Ph-Binepine complex **5a** from X-ray crystal data (ref.[11]). Sterically hindered quadrants are displayed.

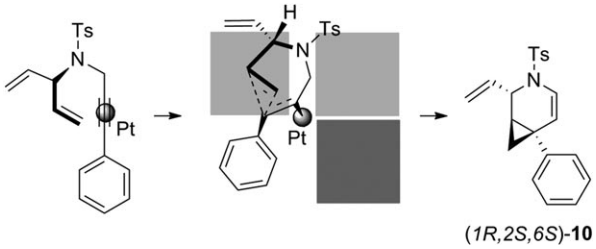


Figure 8. A plausible stereochemical pathway for the enantioselective cycloisomerizations promoted by **5a**.

constant (< 1 Hz) observed between the two adjacent CH groups in the ^{1}H NMR spectrum. The observed diastereomer was anticipated to be the most stable isomer, as far as it minimizes steric interactions between the vinyl substituent and the contiguous cyclopropane ring.

The major enantiomer of compound **10d** displays 1*R*,2*S*,6*S* configurations of the three stereogenic centres. Thus, cycloisomerizations of dienynes **9** take place with the same sense of chiral induction as observed for the simple enynes **6**. It can be reasonably assumed that, in both cases, the cyclopropane unit is constructed on the *Si*-face of the olefin (1*R*-configured products) under catalyst control. The configuration of the additional stereogenic centre in **10** might be dictated by the relative stabilities of the diastereomeric products, if the reaction involves a late, product-like transition state.

To date, building of simple models accounting for the observed stereochemical control is rather challenging, due to significant conformational freedom of both the Pt complex and the reaction intermediates. The chiral Pt(NHC)(phosphine) complexes themselves indeed display unlocked geometries, mainly due to free rotation of the chiral phosphorus ligand around the Pt–P bond. If we assume however that the active catalyst retains the solid state geometry of the corresponding pre-catalyst,[11] we can considered that the key Pt(II) complex shields three space quadrants, as shown in Figure 7.

Based on this hypothesis, the approach of the alkene moiety to the π-complexed alkyne might take place as shown in Figure 8 above. This model postulates that the highest steric constraints result from the alkyne aryl substituent, *cis* to the metal centre in the rigid transition state. This aryl group is expected therefore to occupy the less hindered quadrant, i.e., the bottom left quadrant in Figure 5. Obviously other hypothesis are plausible as well, which involve minimization of the steric interactions between the N-Ts group and the chiral complex.[9]

Anyhow, such foreseeable steric constraints and simplified models alone cannot afford a clear rational for the stereochemical control. Detailed mechanistic studies are still required.

Altogether, these experiments demonstrate that the prochiral dienynes **9** are suitable substrates in enantioselective cycloisomerizations. The platinum-promoted rearrangements produce the bicyclic, functionalized scaffolds **10** containing three stereogenic centres, with total control of their relative stereochemistry and high enantiomeric excess. The exocyclic vinyl groups of **10** open the way to further functionalizations for synthetic purposes.

Conclusions

In conclusion, this work highlights the (*S*)-Ph-Binepine-containing platinacycles **5** as excellent catalysts for the enantioselective cycloisomerization of nitrogen-tethered 1,6-enynes into the corresponding 3-azabicyclo[4.1.0]heptenes. The scope of the reaction has been successfully extended to the cycloisomerization of prochiral dienynes. As far as we know, these reactions represent the first examples of enantioselective desymmetrizations performed *via* cycloisomerization reactions. This work also demonstrates that the Monophos-containing platinacycles **4** are promising alternative chiral catalysts for enyne cycloisomerizations. Therefore, both Binepine and Monophos are

being considered as potentially suitable chiral ligands in our ongoing studies on various platinum promoted cycloisomerizations.

Experimental Section

The experimental procedures and spectral data given herein complement those reported in our preliminary communication.[11] X-ray data for compounds **4a**, **4d**, **7h**, **7a** and **10d** have been deposited at the Cambidge Data base, registry numbers CCDC 800935, CCDC 8000936, CCDC 8000937, CCDC 800938 and CCDC 800939. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the (NHC)Pt(0)(dvtms) Complexes 2a–e

The synthesis of complexes **2a–c** has been described in our previous report.

Synthesis of the (NHC)Pt(0)(dvtms) Complex 2d

Firstly, 1-*tert*-butylimidazole has been prepared in 33% yield from *tert*-butylamine, glyoxal and paraformaldehyde, according to the literature.[30]

Secondly, the imidazolium salt 1d was prepared as follows: 2-iodobenzyl methanesulfonate (312 mg, 1.8 mmol) was added to a solution of 1-*tert*-butylimidazole (152 mg, 1.2 mmol) in CH_3CN (1.8 mL). The mixture was stirred overnight at 80 °C. After concentration, the crude product was diluted in a minimun amount of DCM. Heptane was added until the solution became cloudy. After 2 h at −20 °C, the supernatant was removed and 1-(*tert*-butyl)-3-(2-iodobenzyl)imidazolium was obtained as an oil; yield: 485 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.74$ (s, 9H, CH_3), 2.85 (s, 3H, CH_3), 5.78 (s, 2H, CH_2), 7.12 (m, 1H), 7.25 (m, 1H), 7.47 (m, 2H), 7.81 (dd, $J = 6.9$ Hz, $J = 0.6$ Hz, 1H), 7.92 (dd, $J = 7.8$ Hz, $J = 1.2$ Hz, 2H), 10.13 (s, 1H, NCHN)

Thirdly, **2d** was synthesized as follows: An excess *t*-BuOK (96 mg, 0.86 mmol) was added at 0 °C to a suspension of the imidazolium salt **1d** (250 mg, 0.57 mmol) and Karstedt's catalyst [Pt_2(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)$_3$, 0.1 M in xylene, 5.7 mL] in a dichloromethane (2.5 mL)/toluene (9.5 mL) mixture. The reaction mixture was stirred overnight at room temperature and evaporated to dryness. The crude product was purified by column chromatography on silica gel with a heptane/ethyl acetate 9:1 mixture. Complex **2d** ($R_f = 0.3$) was obtained as an oil; yield: 231 mg (56%) (two rotamers in a 59/41 ratio). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ −0.55 (s, 6H, SiMe, major), −0.35 (s, 6H, SiMe, minor), 0.21 (s, 6H, SiMe, major), 0.25 (s, 6H, SiMe, minor), 1.56 (s, 9H, CMe_3, major), 1.59 (s, 9H, CMe_3, minor),1.8–1.9 (m, 4H), 2.1–2.2 (m, 2H), 5.12 (s, 2H, NCH_2, minor), 5.20 (s, 2H, NCH_2, major), 6.60 (d, $J = 7.2$ Hz, 1H, major), 6.8–7.3 (m, 5H), 7.74 (d, $J = 7.8$ Hz, 1H) ppm.

Synthesis of the (NHC)Pt(0)(dvtms) Complex 2e

Firstly, *N*-(4-*tert*-butyl-2-iodophenyl)methyl)imidazole has been prepared by reacting imidazole (102 mg, 1.5 mmol) with, successively, NaH (90 mg, 60% in mineral oil, 2.2 mmol) and 4-*tert*-butyl-2-iodobenzyl methanesulfonate (810 mg, 2.2 mmol, obtained from the corresponding alcohol,[31] mesyl chloride and Et_3N) in DMF (6 mL) at room temperature. The reaction mixture was stirred overnight at room temperature, diluted with water and extracted with dichloromethane. The *N*-substituted imidazole was purified by column chromatography with a CH_2Cl_2-MeOH 98:2 mixture as the eluent; yield: 330 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (s, 9H, CMe_3), 5.14 (s, CH_2), 6.82 (d, $^3J =$ 8.0 Hz, 1H, Ar), 6.95 (s, 1H, NCH), 7.12 (s, 1H, NCH), 7.34 (dd, $^3J = 8.0$ Hz, $^3J = 2.1$ Hz, 1H, Ar), 7.59 (s, 1H, NCHN), 7.87 (d, $^3J = 2.1$ Hz, 1H, Ar).

Secondly, the imidazolium salt **1e** was prepared as follows: *N*-(4-*tert*-butyl-2-iodophenyl)methyl)imidazole (210 mg, 0.62 mmol) has been reacted with MeI (46 μL, 0.74 mmol) in refluxing acetonitrile (3 mL) for 6 h in a sealed tube. After evaporation of the volatiles, the crude imidazolium salt **1e** was isolated and used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H, CMe_3), 3.89 (s, 3H, NMe), 5.42 (s, CH_2), 7.20 (d, $^3J = 8.0$ Hz, 1H, Ar), 7.51 (dd, $^3J = 8.0$ Hz, $^3J =$ 2.0 Hz, 1H, Ar), 7.77 (s, 1H, NCH), 7.78 (s, 1H, NCH), 7.92 (d, $^3J = 2.0$ Hz, 1H, Ar), 9.13 (s, 1H, NCHN).

Thirdly, **2e** was synthesized as follows: an excess of *t*-BuOK (47 mg, 0.39 mmol) was added at 0 °C to a suspension of the imidazolium iodide **1e** (125 mg, 0.26 mmol) and Karstedt's catalyst [Pt_2(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)$_3$, 0.1 M in xylene, 2.6 mL] in a dichloromethane (1 mL)/toluene (3 mL) mixture. The reaction mixture was stirred overnight at room temperature and evaporated to dryness. The crude product was purified by column chromatography on silica gel with a heptane/ethyl acetate 9:1 mixture. Complex **2e** ($R_f = 0.3$) was obtained as a white solid; yield: 132 mg (69%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.39$ (br, 6H, SiMe), 0.30 (s, 6H, SiMe), 1.27 (s, 9H, CMe_3), 1.8–1.9 (m, 4H), 2.1–2.2 (m, 2H), 3.58 (s, 3H, NMe), 5.12 (s, 2H, NCH_2), 6.97 (d, ^{3}J = 2.1 Hz, $^4J_{H,Pt} = 11$ Hz, 1H, NCH=), 7.04 (d, $^3J = 2.1$ Hz, $^4J_{H,Pt} = 12$ Hz, 1H, NCH=), 7.26 (br, 1H), 7.29 (d, $J = 2.1$ Hz, 1H), 7.79 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = -1.9$ (Me), 0.4 (Me), 1.5 (Me), 31.1 (CMe_3), 34.4 (CH_2=*C*HSi), 34.7 (=CHSi), 37.0 (NMe), 40.4 ($^1J_{C,Pt} = 157$ Hz, =CH_2), 57.6 (NCH_2), 120.7 ($^3J_{C,Pt} = 37$ Hz, NCH=), 122.3 ($^3J_{C,Pt} = 36$ Hz, NCH=), 125.5 (CH), 136.5 (CH).

Synthesis of the Cyclometalated (NHC)IPt(II)(phosphine) Complexes 3–5

Complexes **5a–c** have been described in our previous report.[11] The synthesis of the (*R*)-Monophos-Pt(II) complex **4a** is described hereafter as a representative procedure.

Typical Procedure: Synthesis of the (*R*)-Monophos-Pt(II) Complex 4a

A THF solution (5 mL) containing the Pt(0) complex **2a** (140 mg, 0.2 mmol) and (*R*)-Monophos (72 mg, 0.2 mmol) was heated at 60 °C for 5 h. After evaporation of the solvent, the final product was purified by column chromatography with a heptane/ethyl acetate gradient (from 8:2 to 7:3) as the eluent ($R_f = 0.2$ in heptane-ethyl acetate 7:3). Complex **4a** was obtained as a 75:25 mixture of isomers; yield:

110 mg (65%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 130.6$ (broad, $^1J_{P,Pt} = 4510$ Hz) (major), 130.2 ($^1J_{P,Pt} = 4543$ Hz) (minor); ^{1}H NMR (500 MHz, $CDCl_3$; major isomer): $\delta =$ 2.91 (d, $^3J_{H,P} = 10.0$ Hz, 6H, $PNMe_2$), 4.01 (s, 3H, NMe), 4.44 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 5.08 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 6.74 (s, 1H), 6.94 (s, 1H), 7.0–8.0 (aryls); (minor isomer): $\delta = 2.85$ (d, $^3J_{H,P} = 10.5$ Hz, 6H, $PNMe_2$), 3.98 (s, 3H, NMe), 4.23 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 4.90 (d, $^2J =$ 13.5 Hz, 1H, NCH_2); ^{13}C NMR ($CDCl_3$, 125 MHz, major isomer): $\delta = 38.5$ (d, $^2J_{C,P} = 10.9$ Hz, $PNMe_2$), 40.3 (NMe), 58.65 (NCH_2); HRMS (ESI): $m/z = 875.0690$, calcd. for $C_{33}H_{30}N_3IO_2P^{194}PtNa$: 875.0645.

(*R*)-MOP-Pt(II) Complex 3

Complex **3** was obtained from **2a** and (*R*)-MOP as a 55:45 mixture of isomers; yield: 38 mg (20%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 28.3$ ($^1J_{P,Pt} = 2836$ Hz) (major), 27.3 ($^1J_{P,Pt} = 2834$ Hz) (minor); ^{1}H NMR (500 MHz, $CDCl_3$; major isomer): $\delta = 3.36$ (s, 3H, OMe), 3.96 (s, NMe), 4.28 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 5.05 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 6.15 (t, $J = 6.5$ Hz, 1H), 6.4–7.9 (aryls); (minor isomer): $\delta = 3.66$ (s, 3H, OMe), 3.94 (s, NMe), 4.41 (d, $^2J =$ 13.5 Hz, 1H, NCH_2), 5.35 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 6.09 (t, $J = 6.5$ Hz, 1H), 6.4–7.9 (aryls); ^{13}C NMR ($CDCl_3$, 125 MHz; major isomer): $\delta = 40.3$ (NMe), 54.9 (OMe), 58.80 (NCH_2), 111.6 (CH); ^{13}C NMR ($CDCl_3$, 125 MHz; minor isomer): $\delta = 40.1$ (NMe), 55.3 (OMe), 58.9 (NCH_2), 112.1 (CH); HR-MS (ESI): $m/z = 834.2254$, calcd. for $C_{44}H_{37}N_2OP^{194}Pt$: 834.2270.

(*R*)-MonoPhos-Pt(II) Complex 4b (Scheme 3)

Complex **4b** was obtained from **2b** as a 75:25 mixture of isomers; yield: 87 mg (50%); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta =$ 130.5 (major), 129.9 ($^1J_{P,Pt} = 4550$ Hz) (minor); ^{1}H NMR (500 MHz, $CDCl_3$; major isomer): $\delta = 1.45$ (t, $^3J = 7.5$ Hz, 3H, Me), 2.90 (d, $^3J_{H,P} = 10.0$ Hz, 6H, $PNMe_2$), 4.43 (d, $^2J =$ 13.5 Hz, 1H, NCH_2), 4.48 (m, 1H, NCH_2CH_3), 4.63 (m, 1H, NCH_2CH_3), 5.08 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 6.80 (s, 1H, NCH=), 6.94 (s, 1H, NHC=), 7.0–8.0 (aryls); (minor isomer): $\delta = 1.47$ (t, $^3J = 7.5$ Hz, 3H, Me), 2.84 (d, $^3J_{H,P} =$ 10.5 Hz, 6H, $PNMe_2$), 4.23 (d, $^2J = 13.0$ Hz, 1H, NCH_2), 4.48 (m, 2H, NCH_2CH_3), 4.89 (d, $^2J = 13.0$ Hz, 1H, NCH_2); ^{13}C NMR ($CDCl_3$, 125 MHz, major isomer): $\delta = 15.9$ (Me), 38.4 (d, $J_{C,P} = 10.1$ Hz, NMe_2), 46.8 ($^3J_{C,Pt} = 26$ Hz, NCH_2CH_3), 58.7 (NCH_2), 119.4 (d, $^4J_{C,P} = 7.2$ Hz, CH=), 120.2 (d, $^4J_{C,P} = 5.4$ Hz, CH=); MS (ESI): 890 (M+Na, 19%), 771 (M−$C_5H_7N_2$, 100%), 740 (M−I, 100%); $[\alpha]_D$: −22 (*c*0.2, $CHCl_3$).

(*R*)-MonoPhos-Pt(II) Complex 4c (Scheme 3)

Complex **4c** was obtained from **2c** (157 mg, 0.2 mmol) and (*R*)-Monophos as a 80:20 mixture of isomers; yield: 110 mg (59%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 131$ (br, major), 129.5 ($^1J_{P,Pt} = 4552$ Hz, minor); ^{1}H NMR (500 MHz, $CDCl_3$; major isomer): $\delta = 2.86$ (d, $^3J_{H,P} = 10.5$ Hz, 6H, $PNMe_2$), 4.48 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 5.18 (br d, $^2J \approx 13$ Hz, 1H, NCH_2), 5.44 (d, $^2J = 14.8$ Hz, 1H, NCH_2), 6.20 (d, $^2J =$ 14.8 Hz, 1H, NCH_2), 6.61 (s, 1H, NCH=), 6.94 (s, 1H, NHC=), 7.0–8.0 (aryls); (minor isomer): $\delta = 2.77$ (d, $^3J_{H,P} =$ 10.5 Hz, 6H, $PNMe_2$), 4.30 (d, $^2J = 12.5$ Hz, 1H, NCH_2), 5.02 (br d, $^2J \approx 13$ Hz, 1H, NCH_2), 5.55 (d, $^2J = 14.8$ Hz, 1H, NCH_2), 6.00 (d, $^2J = 14.8$ Hz, 1H, NCH_2), 6.64 (s, 1H, NCH=), 6.8–8.3 (NCH, aryls); ^{13}C NMR ($CDCl_3$, 125 MHz; major isomer): $\delta = 38.4$ (d, $J_{C,P} = 10.1$ Hz, NMe_2), 55.5 (NCH_2Ph), 58.8 ($^3J_{C,Pt} = 104$ Hz, NCH_2); HR-MS (ESI): $m/z = 950.0914$, calcd. for $C_{39}H_{33}IN_3O_2P^{194}PtNa$: 950.0880; $[\alpha]_D$: −16 (*c* 0.5, $CHCl_3$).

(*R*)-MonoPhos-Pt(II) Complex 4d

Complex **4d** was obtained from **2d** (166 mg, 0.23 mmol) and (*R*)-Monophos (83 mg, 0.23 mmol) as a 77:23 mixture of isomers; yield: 96 mg (47%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta =$ 127.1 (major), 125.9 (minor); ^{1}H NMR (500 MHz, $CDCl_3$; major isomer): $\delta = 1.88$ (s, 9H, CMe_3), 2.87 (br, 6H, $PNMe_2$), 4.42 (d, $^2J = 13.5$ Hz, 1H, NCH_2), 5.32 (br, 1H, NCH_2), 6.73 (br, 1H, NCH=), 6.9–8.3 (aryls); (minor isomer): $\delta = 1.89$ (s, 9H, CMe_3), 2.8 (br, 6H, $PNMe_2$), 4.19 (br d, $^2J = 11$ Hz, 1H, NCH_2), 5.05 (br d, $^2J = 11$ Hz, 1H, NCH_2); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 32.0$ (CMe_3), 38.1 (d, $^2J_{C,P} = 8,6$ Hz, $PNMe_2$), 59.2 (NCH_2); HR-MS (ESI): $m/z = 768.2$ (M−I), calcd. for $C_{36}H_{36}IN_3O_2P^{195}Pt$: 909.1394.

(*R*)-MonoPhos-Pt(II) Complex 4e

Complex **4e** was obtained from **2e** (147 mg, 0.2 mmol) and (*R*)-Monophos as a >95:5 mixture of isomers; yield: 87 mg (48%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 130$ (broad signal, $^1J_{P,Pt} = 2765$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.2$ (br, 9H, CMe_3), 2.92 (br, 6H, $PNMe_2$), 4.02 (s, 3H, NMe), 4.43 (d, $^2J = 13.0$ Hz, 1H, NCH_2), 5.05 (br, 1H, NCH_2), 6.73 (s, 1H, NCH=), 6.92 (s, 1H, NCH=), 7.0–8.0 (aryls); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 31.3$ (CMe_3), 34.1 (CMe_3), 38.3 (d, $^2J_{C,P} = 10$ Hz, $PNMe_2$), 40.4 (NMe), 58.1 ($^3J_{C,Pt} = 97$ Hz, NCH_2), 171.4 (d, $^2J_{C,P} = 210$ Hz, C=Pt); $[\alpha]_D$: −3 (*c* 0.3, $CHCl_3$); HR-MS (ESI): $m/z = 909.1351$, calcd. for $C_{37}H_{38}IN_3O_2P^{195}Pt$: 909.1394.

Synthesis of the (NHC)Pt(0)(dvtms) Complex 2f

Firstly, (*S*)-*N*-[1-(2-iodophenyl)ethyl]imidazole was prepared from (*S*)-1-(2-iodophenyl)ethanamine,[32] glyoxal, parafomaldehyde and ammonium chloride according to the known procedure;[33] yield: 44%.^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.85 (d, $^3J = 7.0$ Hz, 3H, Me), 5.63 (q, $^3J = 7.0$ Hz, 1H, N-*CH*Me), 6.96 (s, 1H, NCH=), 6.98 (d, $^3J = 8.0$ Hz, 1H), 7.02 (t, $^3J = 8.0$ Hz, 1H), 7.11 (s, 1H, NCH=), 7.33 (t, $^3J = 8.0$ Hz, 1H), 7.65 (s, 1H, N=CH-N), 7.89 (d, $^3J = 8.0$ Hz, 1H); $[\alpha]_D$: +55 (*c* 1, $CHCl_3$).

Secondly, (*S*)-*N*-Me-*N*-[1-(2-iodophenyl)ethyl]imidazolium iodide (*S*)-**1f** was obtained by alkylation of (*S*)-*N*-[1-(2-iodophenyl)ethyl]imidazole with MeI (1.2 equiv.) in refluxing acetonitrile (5 h); yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.09$ (d, $^3J = 7.0$ Hz, 3H, Me), 4.17 (s, 3H, NMe), 5.88 (q, $^3J = 7.0$ Hz, 1H, N-*CH*Me), 7.08 (t, $^3J =$ 8.0 Hz, 1H), 7.14 (s, 1H, NCH=), 7.45 (t, $^3J = 8.0$ Hz, 1H), 7.47 (s, 1H, NCH=), 7.53 (d, $^3J = 8.0$ Hz, 1H), 7.88 (d, $J =$ 8.0 Hz, 1H),10.20 (s, 1H, N=CH-N); $[\alpha]_D$: +43 (*c* 1, $CHCl_3$).

Thirdly, an excess *t*-BuOK (40 mg, 0.35 mmol) was added at 0 °C to a suspension of the imidazolium iodide (*S*)-**1f** (100 mg, 0.23 mmol) and Karstedt's catalyst [Pt_2(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)$_3$, 0.1 M in xylene, 2.3 mL] in a

dichloromethane (1 mL)/toluene (3 mL) mixture. The reaction mixture was stirred overnight at room temperature and evaporated to dryness. The crude product was purified by column chromatography on silica gel with a heptane/ethyl acetate gradient (from 9:1 to 8:2 mixture). Complex **2f** was obtained as a white solid; yield: 121 mg (76%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.34$ (s, 3H, SiMe), −0.28 (s, 3H, SiMe), 0.27 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.78 (br, 1H, CH_2=CHSi), 1.49 (br, 2H, CH_2=CHSi), 1.69 (d, $^3J = 7.0$ Hz, 3H, CH*Me*), 1.88 (br, 2H, CH_2=CHSi), 2.30 (br, 1H, CH_2= CHSi), 3.53 (s, 3H, NMe), 5.71 (br, 1H, N*CH*Me), 6.90 (2H), 7.13 (s, 1H, NCH), 7.25 (1H), 7.38 (s,1H, NCH), 7.70 (d, $J = 8.0$ Hz,1H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta =$ −2.0 (Me), −2.1 (Me), 1.5 (Me), 20.7 (NCH*Me*), 34.4 ($^1J_{C,Pt} =$ 116 Hz, $CH_2 = CH$Si), 36.9 ($^3J_{C,Pt} = 54$ Hz, NMe), 39.6 (*CH*$_2$= CHSi), 39.9 (*CH*$_2$=CHSi), 62.8 (N*CH*Me), 118.5 (NCH=), 121.3 ($^3J_{C,Pt} = 37$ Hz, NCH=), 126.0, 128.4, 128.9, 139.5, 143.7 (C).

Synthesis of the Cyclometalated (NHC)IPt(II)(Monophos) Complexes 4f and 4g

The cyclometalated complexes **4f** and **g** were prepared according to the general procedure above.

Complex **4f** was obtained from the Pt(0) complex **2f** (145 mg, 0.2 mmol) and (*R*)-MonoPhos (72 mg, 0.2 mmol). Purification by column chromatography with heptane/ethyl acetate 7:3 mixture ($R_f = 0.2$) gave **4f** in an isomer ratio of 92:8; yield: 68 mg (0.08 mmol, 39%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 131$ (broad, $^1J_{P,Pt} \sim 4530$ Hz); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.91$ (br, 3H, Me), 2.94 (d, 6H, $^3J_{H,P} = 10.5$ Hz, $PNMe_2$), 4.05 (s, 3H, NMe), 5.00 (q, $J =$ 6.5 Hz, 1H, NCH), 6.77 (s, 1H, NCH=), 6.98 (s, 1H, NCH=), 7.5–8.0 (aryls); ^{13}C NMR ($CDCl_3$, 125 MHz)': $\delta = 26.7$ (CH*Me*), 38.5 (d, $^2J_{C,P} = 10.0$ Hz, $PNMe_2$), 40.9 (NMe), 66.8 ($^3J_{C,Pt} = 73$ Hz, N*C*HMe), 119.9 (d, $J = 6$ Hz, NCH=), 121.3 (d, $J = 6$ Hz, NCH=), 121.6–132 (Ar), 140.1 (d, $J = 13$ Hz, CH), 143.6, 147.9, 149.5 (d, $J = 13$ Hz, C), 171.5 (d, $J =$ 63 Hz, C); $[\alpha]_D$: −33 (*c* 0.4, $CHCl_3$); HR-MS (ESI): $m/z =$ 866.0886, calcd. for $C_{34}H_{32}N_3IO_2P^{194}Pt$: 866.0904.

Complex **4g** was obtained as a 6:4 mixture of isomers, from the Pt(0) complex **2f** (145 mg, 0.2 mmol) and (*S*)-MonoPhos (72 mg, 0.2 mmol); yield: 109 mg, (0.13 mmol, 63%). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 129.1$ ($^1J_{P,Pt} =$ 4604 Hz); ^{1}H NMR (300 MHz, $CDCl_3$; major isomer): $\delta =$ 1.58 (d, $^3J = 7.0$ Hz, 3H, CH*Me*), 2.89 (d, $^3J_{H,P} = 10.5$ Hz, 6H, $PNMe_2$), 4.03 (s, NMe),4.76 (q, ^{3}J = 7.0 Hz, *CH*Me), 6.7–8.4 (aryls); (minor isomer): $\delta = 1.94$ (d, $^3J = 7.0$ Hz, 3H, CH*Me*), 2.93 (d, $^3J_{H,P} = 10.0$ Hz, 6H, $PNMe_2$), 4.02 (s, NMe), 5.50 (br, *CH*Me), 6.7–8.0 (aryls); HR-MS (ESI): $m/z = 866.0946$, calcd. for $C_{34}H_{32}N_3IO_2P^{194}Pt$: 866.0904.

Preparation of 1,6-Enynes 6 (Table 1)

Enynes **6a–e** have been prepared according to the reported procedures (see ref.[11] and references therein).

N-Allyl-*N*-(3-phenyl-2-propynyl)-*p*-nitrophenylsulfonamide (**6f**) was prepared in two steps, as follows: Firstly, a solution of *p*-nitrobenzenesulfonyl chloride (2.0 g, 9.0 mmol) in CH_2Cl_2 (8 mL) was added to a solution of allylamine (0.60 mL, 8.0 mmol) and Et_3N (1.3 mL, 9 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was stirred at room temperature for 1 h and hydrolyzed then with aqueous NH_4Cl. After extraction with CH_2Cl_2 and evaporation of the solvent, the crude *N*-nosylallylamine was isolated and used for the next step; yield: 1.81 g (94%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 3.70 (tt, $^3J = 6$ Hz, $^4J = 1.5$ Hz, 2H, NCH_2), 5.00 (br t, $^3J =$ 6.0 Hz, 1H, NH), 5.1–5.2 (2H, CH_2=), 5.71 (m, 1H, $^3J =$ 17.1 Hz, $^3J = 10.2$ Hz, $^3J = 5.7$ Hz, CH=), 8.07 (2H, Ar), 8.37 (2H, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 45.8$ (NCH_2), 118.3 (CH_2=), 124.4 (Ns), 128.4 (Ns), 132.4 (CH), 146.1 (C), 150.1 (C).

Secondly, a solution of *N*-allyl-*p*-nitrobenzenesulfonamide (0.50 g, 2.0 mmol), 3-phenylpropargyl bromide (0.48 g, 2.4 mmol) and potassium carbonate (0.60 g, 4.3 mmol) in MeCN (5 mL) was heated at 60 °C overnight.The reaction mixture was filtered, the solid washed with CH_2Cl_2 and the solvents removed under vacuum. Enyne **6f** was purified by column chromatography with heptane-ethyl acetate 8:2 as the eluent and obtained as a yellow solid; yield: 0.63 g (89%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.95$ (d, $^3J = 6.5$ Hz, 2H, NCH_2), 4.37 (s, 2H, NCH_2), 5.33 (d, $J = 10.0$ Hz, 1H, = CH_2), 5.39 (d, $J = 17.0$ Hz, 1H, =CH_2), 5.84 (m, 1H, =CH), 7.0–7.2 (5H, Ph), 8.01 (2H, Ns), 8.28 (2H, Ns); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 36.9$ (NCH_2), 49.6 (NCH_2), 80.9 (C), 83.7 (C), 120.7 (CH_2=), 122.3 (C), 124.0, 128.4, 128.9, 129.0, 131.2, 144.8 (C), 150.1 (C); MS (ESI): $m/z = 379$ (M + Na, 100).

N-(2-Methylallyl)-*N*-(2-butynyl)-*p*-nitrophenylsulfonamide (**6g**) was prepared as follows: Firstly, a solution of *p*-toluenesulfonyl chloride (1.9 g, 10.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of 2-methylallylamine hydrochloride (1.0 g, 9.3 mmol) and Et_3N (1.4 mL, 10.2 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was stirred at room temperature overnight and hydrolyzed then with a saturated solution of NH_4Cl. After extraction with CH_2Cl_2, drying over $MgSO_4$ and evaporation of the solvent, the final product was purified by chromatography with a heptane/ethyl acetate gradient (from 9:1 to 1:1) to afford *N*-2-methylallyl-*p*-toluenesulfonamide;[34] yield: 1.1 g (51%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.67$ (s, 3H, Me), 2.42 (s, 3H, Me), 3.47 (d, $J = 6.6$ Hz, 2H, NCH_2), 4.69 (br, 1H, NH), 4.81 (s, 1H, CH=), 4.85 (s, 1H, CH=), 7.30 (d, $J = 8.4$ Hz, 2H, Ts), 7.75 (d, $J = 8.4$ Hz, 2H, Ts).

Secondly, a solution of *N*-2-methylallyl-*p*-toluenesulfonamide (0.61 g, 2.7 mmol), 1-bromo-2-butyne (260 μL, 3.0 mmol) and potassium carbonate (0.42 g, 3.0 mmol) in MeCN (5 mL) was heated at 60 °C overnight.The reaction mixture was filtered, the solid washed with CH_2Cl_2 and the solvents removed under vacuum. Enyne **6g**[35] was purified by column chromatography with heptane-ethyl acetate 9:1 as the eluent: yield: 0.63 g (2.27 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.49$ (t, $J = 2.3$ Hz, 3H, Me), 1.75 (s, 3H, Me), 2.42 (s, 3H, Me), 3.69 (s, 2H, NCH_2), 3.97 (q, $J =$ 2.3 Hz, 2H, NCH_2), 4.94 (2H, =CH_2), 7.28 (2H, Ts), 7.74 (2H, Ts); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 3.2$ (Me), 19.7 (Me), 21.5 (Me), 36.0 (NCH_2), 52.4 (NCH_2), 71.5 (C), 81.5 (C), 115.1 (=CH_2), 127.9 (CH, Ts), 129.2 (CH, Ts), 136.2 (C), 139.5 (C), 143.1 (C).

Synthesis of Dienynes 9 (Table 2)

Dienyne **9a** was prepared as described.[26] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.36$ (s, 3H, Me), 4.31 (s, 2H, NCH_2), 5.08 (m, 1H, NCH), 5.25 (d, $^3J = 17.0$ Hz, 2H, =

CH_2), 5.27 (d, ^3J = 10.5 Hz, 2H, =CH_2), 5.98 (ddd, ^3J = 17.0 Hz, ^3J = 10.5 Hz, ^3J = 6.0 Hz, H, CH=), 7.1–7.3 (7H, Ar), 7.81 (d, ^3J = 8.5 Hz, 2H, Ts).

Synthesis (3-Penta-1,4-dien-3-yl)tosylamide 8: Amide **8** was obtained by addition of vinylmagnesium bromide to ethyl *N*-tosylformimidate according to the reported method.[26] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H, Me), 4.39 (m, 1H, CH), 4.60 (br, 1H, NH), 5.1–5.2 (4H, CH_2=), 5.69 (ddd, J = 16.2 Hz, J = 10.2 Hz, J = 5.7 Hz, 2H, CH=), 7.3 (d, 2H, J = 8.1 Hz, Ts), 7.76 (d, 2H, J = 8.4 Hz, Ts).

Dienynes **9** were prepared from (3-penta-1,4-dien-3-yl)tosylamide **8** according to methods A or B.

Method A: Diisopropyl azodicarboxylate (DIAD) (375 mg, 1.9 mmol) was added dropwise at 0 °C to a THF solution (13 mL) containing (3-penta-1,4-dien-3-yl)tosylamide **8** (0.29 g, 1.2 mmol) and the desired 3-arylpropargyl alcohol (1.9 mmol). The mixture was stirred at room temperature for 2 h. After removal of the solvent, the final product was purified by column chromatography.

***Method B*:** Potassium carbonate (320 mg, 2.2 mmol) was added to a solution containing (3-penta-1,4-dien-3-yl)tosylamide **8** (0.27 g, 1.1 mmol) and 3-arylpropargyl bromide (1.4 mmol) in MeCN (4 mL). The mixture was heated overnight at 60 °C. After removal of the solvent, the final product was purified by column chromatography.

Enyne 9b: Prepared in 83% yield according to method B. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 6H, Me), 2.28 (s, 3H, Me), 4.99 (br t, 1H, NCH), 5.15 (d, J ~17 Hz, 2H, CH_2), 5.17 (d, J ~11 Hz, 2H, CH_2), 5.88 (ddd, J = 16.8 Hz, J = 10.8 Hz, J = 6.0 Hz, 2H, CH=), 6.71 (s, 2H), 6.85 (s, 1H), 7.14 (2H, ts), 7.75 (2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 21.1 (Me), 21.5 (Me), 34.4 (NCH_2), 62.2 (NCH), 84.3 (C≡), 84.9 (C≡), 118.8 (CH_2=), 122.3 (C), 127.8, 129.1, 129.3, 130.2, 134.7, 137.7 (C), 137.9 (C), 143.1 (C).

Enyne 9c: Prepared in 32% yield according to method A. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, Me), 3.82 (s, 3H, OMe), 4.28 (s, 2H, CH_2), 5.07 (br t, 1H, NCH), 5.23 (dm, J = 16 Hz, 2H, CH_2), 5.25 (dm, J = 10 Hz, 2H, CH_2), 5.97 (ddd, J = 16.5 Hz, J = 10.5 Hz, J = 5.7 Hz, 2H, CH=), 6.80 (2H, Ar), 7.12 (2H, Ar), 7.21 (2H, Ts), 7.83 (2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.4 (Me), 34.4 (NCH_2), 55.3 (OMe), 62.1 (NCH), 83.6 (C≡), 84.5 (C≡), 113.8 (CH), 114.7 (C), 118.7 (CH_2=), 127.8, 129.2, 132.8, 134.7, 137.8 (C), 143.1 (C), 159.6 (C).

Enyne 9d: Prepared in 40% yield according to method A. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, Me), 3.80 (s, 3H, OMe), 4.30 (s, 2H, CH_2), 5.08 (br t, 1H, NCH), 5.24 (dm, J = 16 Hz, 2H, CH_2), 5.26 (dm, J = 10 Hz, 2H, CH_2), 5.97 (ddd, J = 16.8 Hz, J = 10.5 Hz, J = 6.0 Hz, 2H, CH=), 6.71 (m, 1H, Ar), 6.78 (d, J = 7.5 Hz, 1H, Ar), 6.87 (ddd, J = 8.4 Hz, J = 2.7 Hz, J = 1.0 Hz, 1H, Ar), 7.19 (t, 2H, Ar), 7.23 (2H, Ts), 7.84 (2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.4 (Me), 34.3 (NCH_2), 55.2 (OMe), 62.1 (NCH), 84.5 (C≡), 84.9 (C≡), 114.4 (CH), 116.6 (CH), 118.8 (CH_2=), 123.6 (C), 123.9, 129.7, 134.6, 137.8 (C), 143.2 (C), 159.2 (C); HR-MS (ESI): m/z = 382.1494, calcd. for $C_{22}H_{24}NO_3S$: 382.1477.

Enyne 9e: Prepared in 16% yield according to method A. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H, Me), 4.32 (s, 2H, CH_2), 5.10 (br, 1H, NCH), 5.26 (dm, J = 17 Hz, 2H, CH_2), 5.29 (dm, J = 10 Hz, 2H, CH_2), 5.93 (ddd, J = 16.5 Hz, J = 10.2 Hz, J = 5.7 Hz, 2H, CH=), 7.24 (2H, Ar), 7.31 (2H, Ar), 7.82 (2H, Ts), 8.16 (2H, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.5 (Me), 34.2 (NCH_2), 62.0 (NCH), 82.7 (C≡), 90.8 (C≡), 119.2 (CH_2=), 123.4, 127.7, 129.3, 132.1, 134.3, 137.7 (C), 143.4 (C), 147.1 (C); HR-MS (ESI): m/z = 397.1236, calcd. for $C_{21}H_{21}N_2O_4S$: 397.1222.

General procedure for the Pt(II)-Promoted Cycloisomerizations

To a solution of the Pt(II) complex **5** ($6.4 \cdot 10^{-3}$ mmol, 4 mol%) in toluene (0.5 mL) under argon $AgBF_4$ (4 mg, 0.02 mmol) and the enyne substrate **6** (or **9**) (0.16 mmol, in 4.5 mL toluene) were added sequentially. The mixture was stirred at 60 °C for 18–24 h. The reaction was monitored by NMR. The solvent was removed under reduced pressure and the final product was purified by column chromatography. Enantiomeric excesses have been measured by chiral HPLC. Samples of racemic compounds have been obtained via $PtCl_2$ promoted cycloisomerizations.

NMR data for the bicyclic cycloisomerization products **7a–e** have been reported previously.[11]

6-Phenyl-3-(*p*-nitrophenysulfonyl)-3-azabicyclo[4.1.0]-hept-4-ene (7f): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (t, J = 5.3 Hz, 1H, CH_2), 1.42 (dd, J = 8.5 Hz, J = 5.3 Hz, 1H, CH_2), 1.79 (m, 1H, CH), 3.29 (dd, ^2J = 12.0 Hz, J = 2.5 Hz, 1H, NCH_2), 4.07 (d, ^2J = 12.0 Hz, 1H, NCH_2), 5.65 (d, ^3J = 8.0 Hz, 1H, =CH), 6.46 (d, ^3J = 8.0 Hz, 1H, NCH=), 7.1–7.3 (5H, Ph), 8.01 (2H, Ns), 8.42 (2H, Ns); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.0 (CH_2), 21.8 (C), 28.4 (CH), 41.1 (NCH_2), 117.1 (CH=), 119.9 (CH=), 124.5, 126.5, 126.9, 128.2, 128.5, 142.9 (C), 143.3 (C), 150.1 (C); HR-MS (ESI): m/z = 378.1139, calcd. for $C_{20}H_{21}NO_3SNa$: 378.1140; HPLC {[Chiralpak IA column; eluent heptane/2-propanol (98:2), 1 mL min^{-1}]: retention times 17.3 and 19.9 min (major).

1,6-Dimethyl-3-(*p*-nitrophenysulfonyl)-3-azabicyclo[4.1.0]-hept-4-ene (7g): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33 (d, J = 4.0 Hz, 1H, CH_2), 0.74 (d, J = 4.0 Hz, 1H, CH_2), 1.12 (s, 3H, Me), 1.13 (s, 3H, Me), 2.44 (s, 3H, Me), 2.68 (d, ^2J = 11.5 Hz, 1H, NCH_2), 3.79 (d, ^2J = 11.5 Hz, 1H, NCH_2), 5.19 (d, ^2J = 7.5 Hz, 1H, =CH), 6.26 (d, ^2J = 7.5 Hz, 1H, NCH=), 7.33 (2H, Ts), 7.66 (2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.5 (Me), 17.6 (C), 18.7 (Me), 21.5 (Me), 26.2 (CH_2), 29.4 (C), 46.6 (NCH_2), 118.2 (CH=), 120.0 (CH=), 127.0, 129.7, 135.0 (C), 143.6 (C); HR-MS (ESI): m/z = 300.1028, calcd. for $C_{15}H_{19}NO_2S.Na$: 300.1034; HPLC [Chiralpak AD-H column; eluent heptane/2-propanol (99:1), 1 mL min^{-1}]: retention times 11.0 and 12.0 min.

6-Phenyl-3-(*p*-toluenesulfonyl)-2-vinyl-3-azabicyclo[4.1.0]-hept-4-ene (10a): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.41 (t, J = 4.8 Hz, 1H, CH_2), 1.30 (dd, J = 9.0 Hz, J = 5.0 Hz, 1H, CH_2), 1.78 (br t, $J \approx 8$ Hz, 1H, CH), 2.46 (s, 3H, Me), 4.81 (d, ^3J = 6.0 Hz, 1H, NCH), 5.16 (d, ^3J = 10.5 Hz, 1H, =CH_2), 5.30 (d, ^3J = 17.5 Hz, 1H, =CH_2), 5.61 (d, ^3J = 8.0 Hz, 1H, = CH), 5.91 (ddd, ^3J = 17.5 Hz, ^3J = 10.5 Hz, ^3J = 6.0 Hz, H, CH=), 6.31 (d, ^3J = 8.0 Hz, 1H, NCH=), 7.1–7.4 (7H, ar), 7.72 (d, ^3J = 8.0 Hz, 2H, Ts); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.0 (CH_2), 21.6 (CH_3), 22.5 (C), 35.8 (CH), 52.7 (NCH), 116.4 (=CH_2), 117.7 (CH=), 118.5 (CH=), 126.3, 126.9, 127.2, 128.5, 129.7, 136.0, 136.4 (C); HR-MS (ESI): m/z = 352.1382, calcd. for $C_{21}H_{22}NO_2S$: 352.1371; HPLC [Chiralpak IC column; eluent heptane/ethanol (99:1), 1 mL min^{-1}]: retention times 29 and 32 min (major).

6-(3,5-Dimethylphenyl)-3-(*p*-toluenesulfonyl)-2-vinyl-3-azabicyclo[4.1.0]hept-4-ene (10b): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.37$ (t, $J = 4.8$ Hz, 1H, CH_2), 1.27 (dd, $J = 9.0$ Hz, $J = 4.8$ Hz, 1H, CH_2), 1.77 (br t, 1H, CH), 2.28 (s, 6H, Me), 2.46 (s, 3H, Me), 4.81 (d, $^3J = 6.3$ Hz, 1H, NCH), 5.18 (d, $^3J = 10.5$ Hz, 1H, $=CH_2$), 5.31 (d, $^3J = 17.1$ Hz, 1H, $=CH_2$), 5.61 (d, $^3J = 8.0$ Hz, 1H, =CH), 5.92 (ddd, $^3J = 17.1$ Hz, $^3J = 10.5$ Hz, $^3J = 6.3$ Hz, H, CH=), 6.30 (d, $^3J = 8.0$ Hz, 1H, NCH=), 6.81 (s, 2H), 6.86 (s, 1H), 7.35 (d, $^3J = 8.1$ Hz, 2H, Ts), 7.72 (d, $^3J = 8.1$ Hz, 2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.0$ (CH_2), 21.3 (Me), 21.6 (Me), 22.3 (C), 35.7 (CH), 52.8 (NCH), 116.4 (CH_2=), 118.1 (CH=), 118.3 (CH=), 125.0, 127.0, 128.0, 129.7, 136.1 (CH=), 136.4 (C), 138.0 (C), 143.5(C), 143.6 (C); HR-MS (ESI): $m/z =$ 402.1520, calcd. for $C_{23}H_{25}NO_2S.Na$: 402.1504; HPLC [Chiralpak IC column; eluent heptane/ethanol (99:1), 1 mL min^{-1}]: retention times 28 and 30 min (major).

6-(4-Methoxyphenyl)-3-(*p*-toluenesulfonyl)-2-vinyl-3-azabicyclo[4.1.0]hept-4-ene (10c): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.37$ (dd, $J = 6.0$ Hz, $J = 4.8$ Hz, 1H, CH_2), 1.22 (dd, $J = 9.0$ Hz, $J = 4.8$ Hz, 1H, CH_2), 1.74 (br t, 1H, CH), 2.46 (s, 3H, Me), 3.78 (s, 3H, OMe), 4.80 (d, $^3J = 6.3$ Hz, 1H, NCH), 5.17 (d, $^3J = 10.5$ Hz, 1H, $=CH_2$), 5.31 (dd, $^3J = 17.1$ Hz, $J = 1.2$ Hz, 1H, $=CH_2$), 5.56 (d, $^3J = 8.1$ Hz, 1H, =CH), 5.92 (ddd, $^3J = 17.1$ Hz, $^3J = 10.5$ Hz, $^3J = 6.3$ Hz, H, CH=), 6.29 (dd, $^3J = 8.1$ Hz, $J = 1.0$ Hz, 1H, NCH=), 6.82 (d, $^3J = 8.7$ Hz, 2H, Ar), 7.11 (d, $^3J = 8.7$ Hz, 2H, Ar), 7.35 (d, $^3J = 8.1$ Hz, 2H, Ts), 7.72 (d, $^3J = 8.1$ Hz, 2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.0$ (CH_2), 21.6 (Me), 22.0 (C), 35.6 (CH), 52.8 (NCH), 55.3 (OMe), 113.9 (CH), 116.3 (CH_2=), 118.3 (CH=), 118.3 (CH=), 127.0, 128.5, 129.7, 135.8 (C), 136.2 (CH=), 136.4 (C), 143.6 (C), 158.2 (C); HR-MS (ESI): $m/z = 382.1473$, calcd. for $C_{22}H_{24}NO_3S$: 382.1477; HPLC [Chiralpak IC column; eluent heptane/ethanol (98:2), 1 mL min^{-1}]: retention times 33 and 36 min. A sample of enantiomerically pure **10c** has been obtained by crystallization.

6-(3-Methoxyphenyl)-3-(*p*-toluenesulfonyl)-2-vinyl-3-azabicyclo[4.1.0]hept-4-ene (10d): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.41$ (dd, $J = 6.0$ Hz, $J = 4.8$ Hz, 1H, CH_2), 1.29 (dd, $J = 9.0$ Hz, $J = 4.8$ Hz, 1H, CH_2), 1.78 (br t, 1H, CH), 2.46 (s, 3H, Me), 3.79 (s, 3H, OMe), 4.80 (br d, $^3J = 6.4$ Hz, 1H, NCH), 5.16 (d, $^3J = 10.3$ Hz, 1H, $=CH_2$), 5.29 (d, $^3J = 17.0$ Hz, 1H, $=CH_2$), 5.60 (dd, $^3J = 8.0$ Hz, $J = 0.6$ Hz, 1H, =CH), 5.89 (ddd, $^3J = 17.0$ Hz, $^3J = 10.3$ Hz, $^3J = 6.3$ Hz, 1H, CH=), 6.31 (dd, $^3J = 8.0$ Hz, $J = 1.1$ Hz, 1H, NCH=), 6.76 (3H, Ar), 7.20 (m, 1H, Ar), 7.34 (d, $^3J = 8.3$ Hz, 2H, Ts), 7.72 (d, $^3J = 8.3$ Hz, 2H, Ts); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.2$ (CH_2), 21.6 (Me), 22.5 (C), 35.9 (CH), 52.7 (CH), 55.2 (OMe), 111.4 (CH), 113.4 (CH), 116.4 (CH_2=), 117.5 (CH),118,6 (CH), 119.5, 127.0 (Ts), 129.7 (Ts), 136.0 (CH), 136.3 (C), 143.6 (C), 145.2 (C), 159.7 (C); HR-MS (ESI): $m/z = 382.1462$, calcd. for $C_{22}H_{24}NO_3S$: 382.1477; HPLC [Chiralpak IC column; eluent heptane/2-propanol (98:2), 1 mL min^{-1}]: retention times 28 and 30 min.

(*S*)-*N*-Allyl-4-methyl-*N*-{3-[4-(1-phenylethoxy)-phenyl]-prop-2-yn-1-yl}-*p*-nitrophenylsulfonamide (6h) (Scheme 7)

Amide **6h** was prepared in three steps: (i) Diethyl azodicarboxylate (1.2 mL, 8.2 mmol) was added to a solution of *(R)*-phenylethanol (1 mL, 8.2 mmol), 4-iodophenol (1.8 g, 8.2 mmol) and triphenylphosphine (2.1 g, 8.2 mmol) in THF (30 mL) at 0 °C. After stirring overnight at room temperature, the solvents were removed under high vacuum. The crude mixture was taken up in hexane, filtered and the filtrate was evaporated. The residue was purified by flash chromatography with heptane/EtOAc (99:1) as eluent to give the desired product as a pale yellow solid; yield: 1.6 g (60%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.62$ (d, $J = 6.0$ Hz, 3H, Me), 5.25 (q, $J = 6.0$ Hz, 1H, CH), 6.63 (2H, Ar), 7.2–7.3 (m, 5H, Ph), 7.45 (2H, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 24.4$ (Me), 76.2 (CH), 82.7 (C–I), 118.3, 125.5, 127.6, 128.7, 138.1, 142.7 (C), 157.8 (O–C); MS (ESI): $m/z = 324.0$ [M], 219.0, 105.0; $[\alpha]_D$: −25 (*c* 0.9, $CHCl_3$; *ee* 97% by HPLC).

(ii) A solution of *(S)*-1-iodo-4-(1-phenylethoxy)benzene (0.35 g, 1.1 mmol), propargyl alcohol (67 μL, 1.14 mmol) in toluene (1.1 mL), bis(triphenylphosphine)palladium chloride (23 mg, 0.033 mmol, 3 mol%), copper iodide (12.5 mg, 0.066 mmol, 6 mol%) and piperidine (0.2 mL, 2.2 mmol) was heated at 35 °C for 4 h. The mixture was filtered and the solvents were removed under vacuum. The residue was purified by flash chromatography with DCM as eluent to give (*S*)-3-[4-(1-phenylethoxy)phenyl]-prop-2-yn-1-ol as an orange oil; yield: 0.23 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65 (d, $J = 6.0$ Hz, 3H, Me), 1.8 (br, 1H, OH), 4.46 (d, $J = 3.0$ Hz, 2H, CH_2OH), 5.32 (q, $J = 6.0$ Hz, 1H, CH), 6.80 (2H, Ar), 7.20 (2H, Ar), 7.2–7.3 (5H, Ph); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.4 (Me), 51.7 (CH_2OH) 76.1 (CH), 85.7 (C≡), 85.8 (C≡), 114.5 (C), 115.9, 125.5, 127.6, 128.7, 133.0, 142.7 (C), 158.2 (C); MS (ESI): $m/z = 251.1$ [M−H]; [α]: −28 (*c* 0.9, $CHCl_3$).

(ii) Di-*tert*-butyl azodicarboxylate (0.38 g, 1.6 mmol) was added to a solution of (*S*)-3-(4-(1-phenylethoxy)phenyl)-prop-2-yn-1-ol (0.41 g, 1.6 mmol), *N*-allyl-*p*-nitrobenzenesulfonamide (0.40 mg, 1.6 mmol) and triphenylphosphine (0.43 mg, 1.6 mmol) in THF (10 mL) at 0 °C. After stirring overnight at room temperature, solvents were removed under vacuum. The residue was purified by flash chromatography with a heptane/EtOAc gradient, from 95:5 to 90:10, as the eluent to give (*S*)-*N*-allyl-4-methyl-*N*-{3-[4-(1-phenylethoxy)phenyl]prop-2-ynyl}-*p*-nitrophenylsulfonamide **6h** as a yellow oil; yield: 0.40 g (51%); *ee* 97% by HPLC. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.65$ (d, $J = 6.0$ Hz, 3H, Me), 3.92 (d, $J = 7.0$ Hz, 2H, NCH_2), 4.34 (s, 2H, NCH_2), 5.3–5.4 (3H, $=CH_2$ + OCH), 5.78 (m, 1H, CH=), 6.73 (d, $J = 9.0$ Hz, 2H, Ar), 6.91 (d, $J = 9.0$ Hz, 2H, Ar), 7.2–7.4 (5H, Ph), 8.06 (d, $J = 9.0$ Hz, 2H, Ns), 8.70 (d, $J = 9.0$ Hz, 2H, Ns); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 24.4$ (Me), 37.0 (NCH_2), 49.5 (NCH_2), 76.2 (O*CH*Me), 79.5 (C≡), 86.4 (C≡), 113.4 (C), 115.9, 120.5 (CH_2=), 124.0, 125.5, 127.6, 128.7, 129.0, 131.4, 132.7, 142.6 (C), 144.9 (C), 150.0 (C), 158.4 (C); MS (ESI): $m/z = 499$ [M+Na]; HPLC [Chiralpak IA column, heptane/2-propanol (90:10), 1 mL min^{-1}]: retention times 14.8 (major) and 17.8 min; *ee* 97%.

6-{4-[(*S*)-1-Phenylethoxy]phenyl}-3-(*p*-nitrobenzenesulfonamide)-3-azabicyclo[4.1.0]hept-4-ene (7h) (Scheme 7): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.63$ (t, $J = 6.0$ Hz, 1H, CH_2), 1.26 (t, $J = 6.0$ Hz, 1H, CH_2), 1.60 (d, $J = 7.0$ Hz, 3H, Me), 1.65 (m, 1H, CH), 3.21 (d, $J = 12.0$ Hz, 1H, NCH_2), 4.00 (d, $J = 12.0$ Hz, 1H, NCH_2), 5.24 (q, $J = 7.0$ Hz, 1H, O*CH*Me), 5.53 (d, $J = 8.0$ Hz, 1H, CH=), 6.37 (d, $J = 8.0$ Hz,

1H, CH=), 6.74 (d, $J=9.0$ Hz, 2H, Ar), 6.96 (d, $J=9.0$ Hz, 2H, Ar), 7.2–7.3 (m, 5H, Ph), 7.97 (d, $J=9.0$ Hz, 2H, Ns), 8.39 (d, $J=9.0$ Hz, 2H, Ns); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=20.9$ (CH_2), 21.2 (C), 24.5 (CH*Me*), 28.0 (CH), 41.1 (NCH_2), 76.0 (O*CH*Me), 115.8, 117.7 (CH=), 119.5 (CH=), 124.5, 125.5, 127.4, 128.0, 128.2, 128.6; MS (ESI): $m/z=499$ [M+Na]; HPLC [Chiralpak IA column, eluent heptane-2-propanol (90:10), 1 mL min^{-1}]: retention times 24.6 (major) and 29.6 min.

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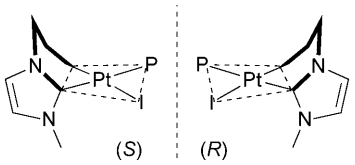

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