

## ENANTIOSELECTIVE [2+2+2] CYCLOISOMERISATION OF ALKYNES IN THE SYNTHESIS OF HELICENES: THE SEARCH FOR EFFECTIVE CHIRAL LIGANDS

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Dedicated to Professor Pavel Kočovský on the occasion of his 60th birthday.

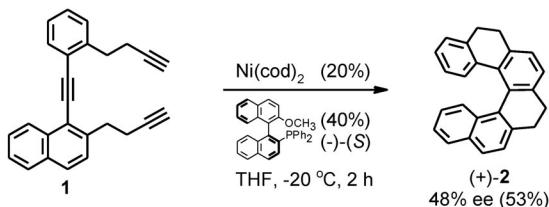
The enantioselective [2+2+2] cycloisomerisation of the aromatic triynes under nickel(0) catalysis to afford nonracemic [6]- and [7]helicene derivatives has been systematically studied. A collection of mono- and bidentate phosphines, phosphites, phosphinites and phosphinous amides possessing stereogenic units such as chiral centre, axis or plane (or their combinations) has been tested and axially chiral binaphthyl-derived monodentate MOP-type phosphine ligands were the optimal class of ligands. Nickel complexes of these ligands afforded nonracemic tetrahydro[6]helicene in up to 64% ee in a model reaction.

**Keywords:** Helicenes; Alkynes; Cycloisomerisation; Nickel catalysis; Phosphorus ligands; Enantioselectivity; Chirality; Asymmetric catalysis.

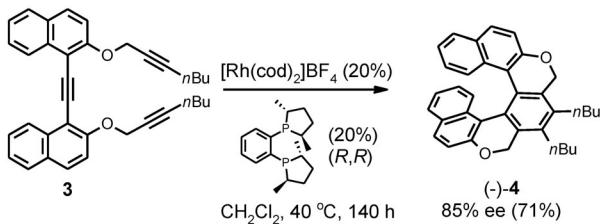
Helicenes represent unique nonplanar aromatic systems, which are inherently chiral<sup>1</sup>. By and large they are sufficiently configurationally stable at elevated temperature<sup>2</sup> to be attractive chiral auxiliaries for asymmetric

synthesis and in other branches of science dealing with aspects of chirality. Although a general methodology for the preparation of optically pure helicenes or their analogues has not yet been developed, significant achievements in this regard have already been presented. Along with recent advances in stoichiometric asymmetric synthesis of helicenes<sup>3</sup> and racemate resolutions<sup>4</sup>, enantioselective catalysis applied to the helicity-forming step is particularly attractive but very challenging. The [2+2+2] cycloisomerisation of alkynes under transition metal catalysis warrants an enantioselective variant since the versatility of this methodology for the synthesis of helicenes has already been proved by a number of laboratories<sup>5,6</sup>. The aforementioned enantioselective reaction has been pioneered by Stará, Starý et al.<sup>7</sup> in the carbohelicene series and Tanaka et al.<sup>6d,6e</sup> within the helicene-like compounds (Scheme 1). While the nickel(0)-catalysed

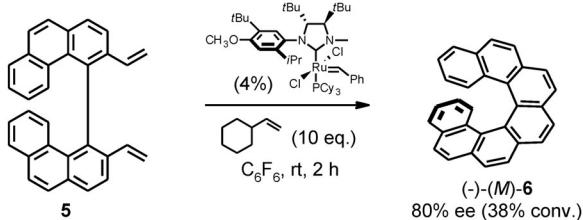
Stará, Starý et al. 1999



Tanaka et al. 2007



Collins et al. 2008



SCHEME 1

Enantioselective catalysis used in the formation of helicene skeletons

cycloisomerisation (**1**→**2**) in the presence of axially chiral monodentate phosphine ligands led in the former case to moderate enantiomeric excesses of 40–48% ee<sup>7</sup>, in the latter case (**3**→**4**) rhodium(I) catalysts possessing chiral bidentate phosphines improved the enantioselectivity up to 60–85% ee<sup>6d,6e</sup>. Interestingly, Collins et al.<sup>8</sup> have developed an alternative approach to nonracemic helicenes based on kinetic resolution of axially chiral biaryls by means of asymmetric olefin metathesis (**5**→**6**) reaching enantiomeric excesses of up to 80% (Scheme 1). To the best of our knowledge, no other attempts at synthesising nonracemic helicenes and their analogues by employing enantioselective catalysis in the helicity-forming step have been published. Herein, we provide a detailed account of our efforts to identify promising chiral ligands for the enantioselective [2+2+2] cycloisomerisation of alkynes to obtain nonracemic helicenes.

## RESULTS AND DISCUSSION

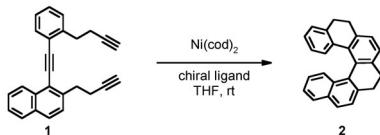
### *Screening Chiral Ligands in Enantioselective Ni(0)-Catalysed Cycloisomerisation*

The first attempts at developing enantioselective intramolecular [2+2+2] cycloisomerisation of triynes to obtain nonracemic helicenes<sup>7</sup> indicated the feasibility of this concept. However, we screened a small collection of chiral ligands and attained a promising enantiomeric excess (48% ee) in the tetrahydro[6]helicene **2**. In order to identify a more effective chiral ligand or a group of them, we needed to understand the basic structural requirements for such chiral inductors. Accordingly, we decided first to screen a representative collection of chiral ligands of different types in enantioselective cycloisomerisation of **1**, which served as a model substrate.

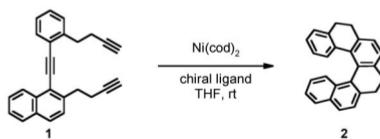
We started with phosphorus ligands<sup>9</sup> since phosphines, phosphites, phosphinites and aminophosphines are generally good ligands for zero-valent nickel and, moreover, many of them are commercially available. First, we screened bidentate phosphorus ligands **L1**–**L9** possessing different types of stereogenic units (Table I). We examined  $C_2$  symmetric centrally or axially chiral bisphosphines **L1**, **L2** and **L4** (entries 1, 2 and 4), bisphosphine **L3** with a broken  $C_2$  symmetry (entry 3), ferrocene-derived bisphosphine **L5** comprising a chiral plane (entry 5), bisphosphinite **L6** and bisphosphine **L7** employing a chiral pool of natural products (entries 6 and 7) and, finally, phosphinous amide-phosphinite **L8**<sup>10</sup> and phosphine-phosphinite **L9**<sup>11</sup> containing the centrally chiral phosphorus atom in the phosphine part (entries 8 and 9). Although the series covered prototypal

TABLE I

Ni(0)-mediated enantioselective cycloisomerisation of the triyne **1** affording tetrahydro-[6]helicene **2**



Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Time	% ee of <b>2</b> <sup>a</sup>	Yield of <b>2</b> , % (Conversion of <b>1</b> , %) <sup>b</sup>
1		100	100	-3	70 (92)
2		100	100	+9	51 (66)
3		100	100	-36	2 (33)
4		40	20	+2	98 (100)
5		100	100	+12	38 (100)
6		100	100	+4	47 (100)

TABLE I  
(Continued)

Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Time	% ee of 2 <sup>a</sup>	Yield of 2, % (Conversion of 1, %) <sup>b</sup>
7		100	100	-6	45 (100)
8		30	30	-30	21 (51) <sup>c</sup>
9		20	20	+1	68 (100) <sup>c</sup>

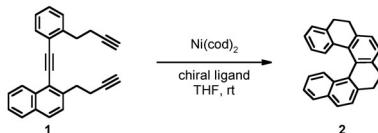
<sup>a</sup> Determined by HPLC on a (R,R)-Whelk 01 column, the +/- sign indicates the sense of optical rotation of 2 measured at the sodium D line (589 nm). <sup>b</sup> Isolated, the conversion based on the starting material recovered. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

representatives of important classes of bidentate phosphorus ligands, we observed either a reasonable reactivity of 1 but low enantioselectivity ( $\leq 12\%$  ee) of cyclisation as for L1, L4, L5, L6, L7 and L9 or promising enantiomeric excess of 2 (up to 36% ee) but low reactivity of 1 as for L3 and L8. The privileged ligand<sup>12</sup> BINAP L2, which is otherwise highly successful in numerous catalytic enantioselective processes<sup>13</sup>, provided a low ee (9% ee) and moderate conversion.

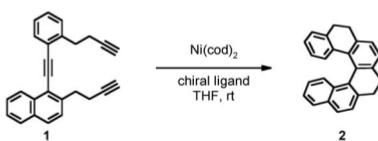
From the introductory series of cycloisomerisation experiments with 1 utilising the diverse chiral ligands L1–L9 we inferred that the mixed aminophosphine-phosphinite ligand L8 represented a compromise be-

tween enantioselectivity and reactivity. Accordingly, we decided to explore its structural analogues **L10–L18**<sup>10a,14</sup> with the aim of achieving better stereocontrol and higher levels of conversion (Table II). First, we varied substituents at the phenyl group attached to the stereogenic phosphorus atom in the ligands **L10–L14** (entries 1–6). Except for the ligand **L11**, we achieved better conversion than with **L8** but, to our discouragement, the

TABLE II  
Ni(0)-catalysed enantioselective cycloisomerisation of **1** in the presence of the aminophosphine-phosphinite ligands **L8**, **L10–L18**



Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Time	% ee of <b>2</b> <sup>a</sup>	Yield of <b>2</b> , % (Conversion of <b>1</b> , %) <sup>b</sup>
1		30	20	12 h	-30 24 (51) <sup>c</sup>
2	R = BnO, (1S,2R,R <sub>p</sub> )- <b>L10</b>	40	20	1 h	-24 (90) <sup>c</sup>
3	R = <i>i</i> -PrO, (1S,2R,R <sub>p</sub> )- <b>L11</b>	40	20	12 h	+16 (<5) <sup>c</sup>
4	R = Ph, (1S,2R,R <sub>p</sub> )- <b>L12</b>	40	20	1 h	-2 (60) <sup>c</sup>
5		20	20	5 min	-14 (100) <sup>c</sup>
	(1S,2R,R <sub>p</sub> )- <b>L13</b>				
6		40	20	5 min	-21 (100) <sup>c</sup>
	(1S,2R,R <sub>p</sub> )- <b>L14</b>				
7		40	20	5 min	-12 (100) <sup>c</sup>
	(1S,2R,R <sub>p</sub> )- <b>L15</b>				

TABLE II  
(Continued)

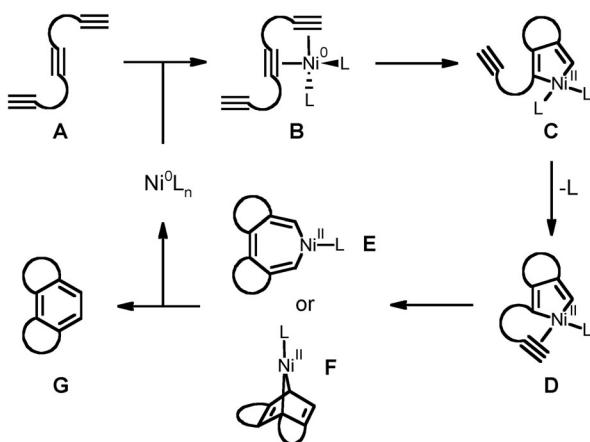
Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Time	% ee of 2 <sup>a</sup>	Yield of 2, % (Conversion of 1, %) <sup>b</sup>
8		30	20	+3	(95) <sup>c</sup>
9		30	20	-	no reaction
10		20	20	0	(20) <sup>c</sup>

<sup>a</sup> Determined by HPLC on a (R,R)-Whelk 01 column, the +/- sign indicates the sense of optical rotation of 2 measured at the sodium D line (589 nm). <sup>b</sup> Isolated, the conversion based on the starting material recovered. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

levels of enantioselectivity were generally lower ( $\leq 24\%$  ee). Then, we continued in the modification of the structure of L8 by introducing the 2-pyridyl, cyclohexyl or ferrocenyl moieties as exemplified by the ligands L15–L18 (the ligand L18 possessing the free hydroxyl group instead of the diphenylphosphinite moiety; entries 7–10). However, the enantiomeric excesses observed were negligible ( $\leq 12\%$  ee) and the conversion of 1 in the presence of the ferrocenyl-based ligands L17 and L18 was below the detection limit or very low, respectively.

The experimental results obtained prompted us to re-consider the mechanism of alkyne cycloisomerisation under nickel(0) catalysis in order to identify more promising chiral ligands within the rich portfolio of commercially available phosphorus ligands, or those described in the literature

and, moreover, to reduce the number of ligands to be scrutinised. Although aspects of the mechanism remain ambiguous, it is generally accepted that a metallacyclopentadiene complex **D** (formed from two alkynes) with  $\pi$ -coordinated alkyne (the third alkyne component) is a common intermediate for the two alternative mechanistic pathways to involve either metallacycloheptatriene **E** or the [4+2] cycloaddition product **F** (Scheme 2)<sup>15</sup>. Apparently, the proposed sixteen-electron nickel(II) complex **D** adopting the square planar geometry bears only one *L* ligand. Then, strongly chelating ligands might be incompatible with this mechanism if they dissociate too slowly and occupy only one coordination site of nickel(II) in **D**<sup>16</sup>. Based on these general assumptions, we proposed exploring further chiral monodentate phosphorus ligands rather than bidentate ones even though some of them could be effective in Ni(0)-catalysed enantioselective alkyne cycloisomerisation<sup>17</sup>.

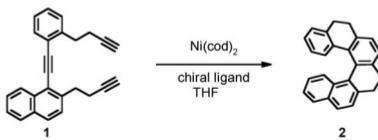


SCHEME 2  
The mechanism of [2+2+2] cycloisomerisation of alkynes

In the literature, there have only been a few successful chiral monodentate phosphines described and a prominent position among them has been occupied by the axially chiral MOP ligand and its analogues developed and utilised by Hayashi et al.<sup>16</sup>. Hence, we pinned our hopes on this class of ligand to control effectively chirality transfer in enantioselective cycloisomerisation of **1** to give the nonracemic helical product **2**. Indeed, this concept was supported by the experimental results with the ligands **L19–L23**<sup>18</sup> supported this concept (Table III). The use of the MOP ligand **L19** at room temperature led indeed to **2** being produced in a reasonable

TABLE III

Ni(0)-catalysed enantioselective cycloisomerisation of **1** in the presence of the axially chiral monophosphines **L19–L23**



Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Conditions	% ee of <b>2</b> <sup>a</sup>	Yield of <b>2</b> , % (Conversion of <b>1</b> , %) <sup>b</sup>
1	 R = CH <sub>3</sub> O, (−)-(S)-MOP	L19 40	20 5 min THF, r.t.	+39	49 (100)
2		L19 40	20 4.5 h THF, −20 °C	+48	53 (100) <sup>7c</sup>
3	R = BnO, (−)-(S)-BOP	L20 40	20 20 h THF, r.t.	+48	30 (72)
4		L20 40	20 15 min EtOAc, r.t.	+31	88 (100)
5		L20 40	20 1 h dioxane, r.t.	+39	56 (94)
6		L20 40	20 5 min toluene, r.t.	+53	59 (100)
7		L20 40	20 3 h THF, −20 °C	+50	81 (100)
8		L20 80	20 3 h THF, −20 °C	+54	61 (100) <sup>c</sup>
9		L20 40	20 1.5 h THF, −40 °C	−	no reaction
10	R = iPrO, (−)-(S)	L21 40	20 5 min THF, r.t.	+34	66 (100)
11		L21 40	20 5 min THF, −20 °C	+42	70 (82)
12	R = OH, (−)-(S)	L22 40	20 20 h THF, r.t.	+14	22 (71)
13	R = Et, (−)-(R)	L23 40	20 5 min THF, r.t.	+26	67 (100)

<sup>a</sup> Determined by HPLC on a (R,R)-Whelk 01 column, the +/− sign indicates the sense of optical rotation of **2** measured at the sodium D line (589 nm). <sup>b</sup> Isolated, the conversion based on the starting material recovered. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

yield and the highest enantiomeric excess (39% ee) obtained up to this point in the study (entry 1)<sup>7c</sup>. By lowering the temperature to -20 °C, enantioselectivity of the cyclisation further increased to 48% ee (entry 2)<sup>7c</sup>. We reasoned that a bulkier substituent than methyl in MOP **L19** might result in a more congested transition state and, accordingly, to better chirality transfer from the ligand to the substrate. Hence, we displaced the methyl group in MOP **L19** by a benzyl one as in BOP **L20** and thus achieved a further improvement in enantiomeric excess performing the reaction at room temperature (48% ee, entry 3). Encouraged by this result, we screened other solvents in order to determine whether enantioselectivity of the cyclisation might be positively influenced by the reaction medium. While the use of ethyl acetate (entry 4) or dioxane (entry 5) noticeably lowered enantiomeric excess ( $\leq 39\%$  ee), toluene as a solvent was slightly superior to tetrahydrofuran (53% ee, entry 6 vs 48% ee, entry 3). However, because of the better solubility of the reaction components, we used tetrahydrofuran as the solvent throughout the remainder of the present study. The combination of the BOP ligand **L20** and lower temperature (-20 °C) did not appreciably increase enantioselectivity of the reaction (50% ee, entry 7) and neither did it in the presence of a four-fold excess of the ligand to the nickel catalyst (54% ee, entry 8). At -40 °C, we reached the reactivity limit and the cyclisation did not proceed (entry 9). Thus, we returned to the idea of increasing the steric demand of the alkoxy substituent of the MOP-type ligand and, therefore, we focused on the isopropyl analogue **L21** (entries 10 and 11). However, the steric bulk of the isopropyl group did not suit the delicate demands of the transition state to favour one enantiodiscriminating channel over the other and the cyclisation exhibited lower enantioselectivity ( $\leq 42\%$  ee) than with MOP **L19** or BOP **L20** at room temperature or -20 °C. The use of the dealkylated analogue **L22** as well as the ethyl derivative **L23** led to a significant decrease in enantioselectivity of cycloisomerisation ( $\leq 26\%$  ee, entries 12 and 13).

#### *Screening Diverse Triynes in Enantioselective Ni(0)-Catalysed Cycloisomerisation*

With having promising results with the MOP **L19** and BOP **L20** ligands, we embarked on investigating the effect of the substrate structure on enantioselectivity of [2+2+2] cycloisomerisation by studying other aromatic triynes **7–16** (Table IV). First, we examined the influence of the substituents at the tethered alkyne units. The introduction of the terminal methyl groups as in **7** resulted in a slightly diminished enantiomeric excess of **17** when using

TABLE IV

Ni(0)-catalysed enantioselective cycloisomerisation of **1**, **7–16** in the presence of the axially chiral monophosphines **L19** and **L20**

Entry	Tryine	Conditions <sup>a</sup>	Product	% ee <sup>b</sup>	Yield, % (Conversion, %) <sup>c</sup>
1		A r.t., 5 min		+39	49 (100)
2		A r.t., 12 h		+35	30 (45)
3		A r.t., 12 h		–	no reaction
4		B r.t., 5 min		+28	69 (100)
5		B r.t., 10 min		+42	74 (100)
6		B r.t., 2 h		+24	31 (43)
7		B r.t., 15 min		–10	66 (100) <sup>d</sup>

TABLE IV  
(Continued)

Entry	Tryine	Conditions <sup>a</sup>	Product	% ee <sup>b</sup>	Yield, % (Conversion, %) <sup>c</sup>
8		C r.t., 5 min		-2	44 (96)
9		A r.t., 2 h		+41	41 (51)
10		A r.t., 5 min		+37	87 (100)
11		A 60 °C, 24 h		-	no reaction

<sup>a</sup> A: Ni(cod)<sub>2</sub> (20 mole %), (−)-(S)-MOP L19 (40 mole %), THF; B: Ni(cod)<sub>2</sub> (20 mole %), (−)-(S)-BOP L20 (40 mole %), THF; C: Ni(cod)<sub>2</sub> (50 mole %), (−)-(S)-BOP L20 (100 mole %), THF. <sup>b</sup> Determined by HPLC on a (R,R)-Whelk O1 or Chiracel OD-H column, the +/− sign indicates the sense of optical rotation of the helical product measured at the sodium D line (589 nm). <sup>c</sup> Isolated, the conversion based on the starting material recovered. <sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy.

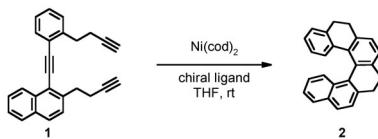
the MOP ligand **L19** (35% ee, entry 2 vs 39% ee, entry 1). The presence of more bulky trimethylsilyl groups made triyne **8** unreactive (entry 3). Since transition metal-catalysed alkyne [2+2+2] cycloisomerisation is tolerant to various functional groups, we decided to extend the portfolio of the triynes studied to the substrates **9–11** affording functionalised tetrahydro-[6]helicenes **19–21**. We found in all cases that enantioselectivity controlled by BOP ligand **L20** dropped either significantly like for the 1-methoxy substituted **19** (28% ee, entry 4) and the pyrido analogue **21** (24% ee, entry 6) or slightly as for the 3-methoxy substituted **20** (42% ee, entry 5). Disappointingly, *cis,cis*-dienetriynes **12** and **13**, which allow for the synthesis of fully aromatic [6]helicenes<sup>5e</sup> **22** and **23**, respectively, were not suitable substrates for enantioselective cycloisomerisation since enantiomeric excesses achieved with the BOP ligand **L20** were in both cases very low ( $\leq 10$ % ee, entries 7 and 8). In contrast, the unfunctionalised triyne **14** and 2-methoxy substituted triyne **15**, which are precursors of tetrahydro[7]helicenes **24** and **25**, respectively, provided in the presence of the ligand **L19** products with practically the same enantiomeric excesses as the model triyne **1** regardless of the presence of an additional annulated benzene ring or the 2-methoxy substituent (41% and 37% ee, entries 9 and 10, respectively, vs 39% ee, entry 1). The substrate **16** with its ether tethers bearing the methyl-substituted alkyne units did not react in the presence of the MOP ligand **L19** and the nickel catalyst even at elevated temperature and the expected [7]helicene derivative **26** with the incorporated 2,7-dihydrooxepine units was not formed (entry 11).

#### *Screening Axially Chiral Monodentate Phosphines in Enantioselective Ni(0)-Catalysed Cycloisomerisation*

While screening diverse chiral ligands in order to optimise enantiomeric excess in enantioselective [2+2+2] cycloisomerisation performed with the various triynes **1** and **7–16**, we identified the axially chiral monophosphines MOP **L19** and BOP **L20** as the most promising ligands inducing up to 54% ee for **1**–**2** (Table III, entry 8). Furthermore, triyne **1** was found to be a suitable model substrate. Since additional axially chiral monophosphines emerged in the course of this study, we decided to examine their ability to control the stereochemical outcome of enantioselective [2+2+2] cycloisomerisation of **1** (Table V). While the PINAP ligands **L24** and **L25**, developed by Carreira<sup>19</sup>, performed less effectively in the chirality transfer to **2** ( $\leq 22$ % ee, entries 1 and 2), the quinazoline-containing ligand **L26**, one of a class of axially chiral P,N ligands studied by Guiry<sup>20</sup>, was as good as

TABLE V

Ni(0)-catalysed enantioselective cycloisomerisation of **1** in the presence of the monophosphine ligands **L24–L27**



Entry	Ligand, mole %	Ni(cod) <sub>2</sub> , mole %	Conditions	% ee of <b>2</b> <sup>a</sup>	Yield of <b>2</b> , % (Conversion of <b>1</b> , %) <sup>b</sup>
1		<b>L24</b> 40	20	12 h	+9 33 (33) <sup>c</sup>
2		<b>L25</b> 40	20	12 h	+22 26 (26) <sup>c</sup>
3		<b>L26</b> 40	20	15 min	+40 75 (83)
4		<b>L27</b> 40	20	5 min	-64 53 (100)
5		<b>L27</b> 40	20	20 min -20 °C	-64 (100) <sup>c</sup>

<sup>a</sup> Determined by HPLC on an (R,R)-Whelk 01 column, the +/- sign indicates the sense of optical rotation of **2** measured at the sodium D line (589 nm). <sup>b</sup> Isolated, the conversion based on the starting material recovered. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

MOP **L19** (40% ee, entry 3 vs 39% ee, Table III, entry 1). Most importantly, the use of the modified BOP ligand **L27**<sup>22</sup> bearing the trifluoromethane-sulfonyl group ortho to the benzyloxy unit led to the highest enantiomeric excess of **2** monitored within this study (64% ee, entry 4). Applying the same ligand and going from room temperature to -20 °C, the stereochemical outcome of the reaction was surprisingly not changed (64% ee, entry 5).

## CONCLUSION

We tested a large and diverse collection of the phosphorus ligands **L1–L27** aimed at developing the enantioselective [2+2+2] cycloisomerisation of aromatic triynes **1** and **7–16** under Ni(0) catalysis to construct helicene backbones in a nonracemic form. Among mono- and bidentate phosphines, phosphites, phosphinites and aminophosphines possessing stereogenic units such as chiral centre, axis or plane (or their combinations) we identified a class of privileged ligands that are axially chiral binaphthyl-derived monodentate phosphines such as MOP **L19**, BOP **L20** and its triflate-modified analogue **L27**. For the reaction of the model triyne **1** affording nonracemic tetrahydro[6]helicene **2**, we achieved up to 64% ee. Furthermore, we found that Ni(0)-catalysed enantioselective [2+2+2] cycloisomerisation of the aromatic triynes is significantly sensitive to the structure of the triyne substrates as well as chiral ligands in terms of both reactivity and enantioselectivity. However, our results indicate that the higher enantiocontrol in the helicity forming step might be achieved by additional structural modification of the MOP-type ligands.

## EXPERIMENTAL

The chiral ligands **L1–L7**, **L24** and **L25** were commercially available, the ligands **L19–L23**<sup>18</sup> were prepared according to the literature procedures, and the synthesis of the ligands **L8**<sup>10</sup>, **L9**<sup>11</sup>, **L10**<sup>21</sup>, **L11**<sup>21</sup>, **L12**<sup>10a</sup>, **L13**<sup>14</sup>, **L14**<sup>21</sup>, **L15**<sup>21</sup>, **L16**<sup>10a</sup>, **L17**<sup>10a</sup>, **L18**<sup>21</sup>, **L26**<sup>20</sup> and **L27**<sup>22</sup> we developed earlier. We had already prepared and characterised the starting aromatic triynes **1**<sup>7c,23</sup>, **7**<sup>23</sup>, **8**<sup>23</sup>, **9**<sup>24</sup>, **10**<sup>7b</sup>, **11**<sup>5c</sup>, **12**<sup>5e</sup>, **13**<sup>5e</sup>, **14**<sup>7a</sup>, **15**<sup>5a</sup> and **16**<sup>25</sup> and the corresponding cyclised products **2**<sup>7c,26</sup>, **17**<sup>26</sup>, **19**<sup>24</sup>, **20**<sup>7b</sup>, **21**<sup>5c</sup>, **22**<sup>5e</sup>, **23**<sup>5e</sup>, **24**<sup>7a</sup>, **25**<sup>5a</sup> and **26**<sup>27</sup>. Enantiomeric excesses were determined by HPLC on an (R,R)-Whelk 01 or Chiracel OD-H column using heptane or heptane-isopropanol mobile phases. The resolved enantiomers were monitored by UV and polarimetric detectors coupled in a series.

Typical experiment with the MOP ligand **L19**: A Schlenk flask was charged with Ni(cod)<sub>2</sub> (3.3 mg, 0.012 mmol, 20 mole %) in a glove box under the nitrogen atmosphere. Subsequently, the Schlenk flask was removed from the glove box, attached to the argon line and THF (1 ml) was added. A solution of chiral monodentate phosphine (0.024 mmol, 40 mole %) in THF (1 ml) under argon was added and the formed solution was stirred at

room temperature for 5 min. Then a solution of triyne **1** (20 mg, 0.060 mmol) in THF (1 ml) was added dropwise. The reaction mixture was stirred at room temperature until the starting material disappeared or the reaction stopped (usually 5 min to 1 h; the reaction progress was checked by TLC). Subsequently, the excess of methyl iodide was added in order to eliminate the phosphine ligand that might interfere during a chiral HPLC analysis on the (*R,R*)-Whelk 01 column. The mixture was stirred at room temperature for an additional 30 min, volatiles were evaporated in *vacuo* and the residue was chromatographed on silica gel (petroleum ether-diethyl ether 100:0 to 96:4) to afford tetrahydro[6]helicene **2**<sup>28</sup>.

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28. Tetrahydro[6]helicene **2** is configurationally stable at room temperature for >1 month (its barrier to racemisation was preliminary estimated to be ca. 30 kcal/mol).