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Synthesis of non-racemic helicene-like molecules via diastereoselective [2+2+2] cycloisomerisation

Synopsis of Ph.D. Thesis

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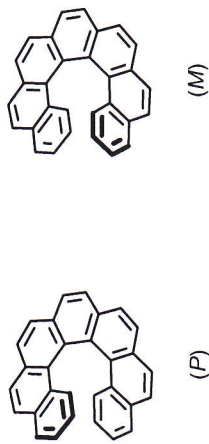


Academy of Sciences of the Czech Republic

Prague, 2006

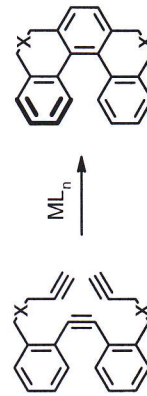
1 Introduction

Helicenes are non-planar polyaromatic hydrocarbons¹ containing a system of *ortho*-fused benzene rings. Their scaffold is inherently chiral and it can exist in two stable and isolable enantiomeric forms denoted (*P*) and (*M*) (Scheme 1).



Scheme 1: (*P*) and (*M*) enantiomer of hepta[helicene]

Various synthetic approaches have been proposed for the synthesis of helicenes, namely intramolecular photocyclisation of stilbene-type precursors², a double Diels-Alder reaction of benzoquinones and divinylaromatics³, a tandem radical cyclisation⁴ and several others⁵. An alternative, mild and general method has been developed at IOCB Prague⁶ that relies on transition metal catalysed [2+2+2] cycloisomerisation of aromatic triynes (Scheme 2).



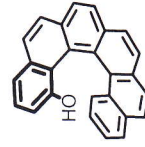
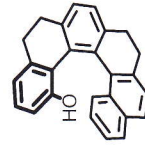
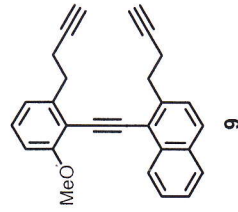
Scheme 2: [2+2+2] cycloisomerisation approach to helicene-like molecules

2 Goals

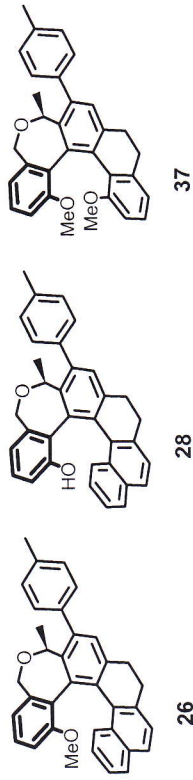
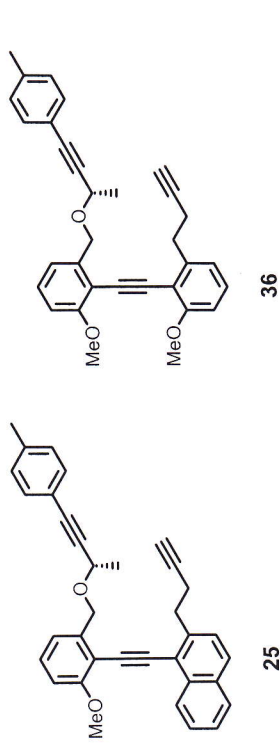
The aim of this project was to explore the generality and broaden the scope of the [2+2+2] cycloisomerisation methodology for the synthesis of small artificial helical molecules.

In particular, the goals were to:

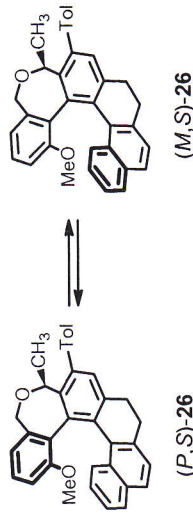
- Synthesise 1-hydroxy substituted hexahelicene derivatives **11** and **14** via [2+2+2] cycloisomerisation of triene **9** and investigate their ability to undergo further synthetic transformations in position 1 (Scheme 3).
- Synthesise functionalised helical compounds **26**, **28** and **37** with defined helicity via diastereoselective [2+2+2] cycloisomerisation of centrally chiral trienes **25** and **36**, respectively (Scheme 4).
- Investigate the kinetics of thermal epimerisation of compound **26** (Scheme 5).



Scheme 3

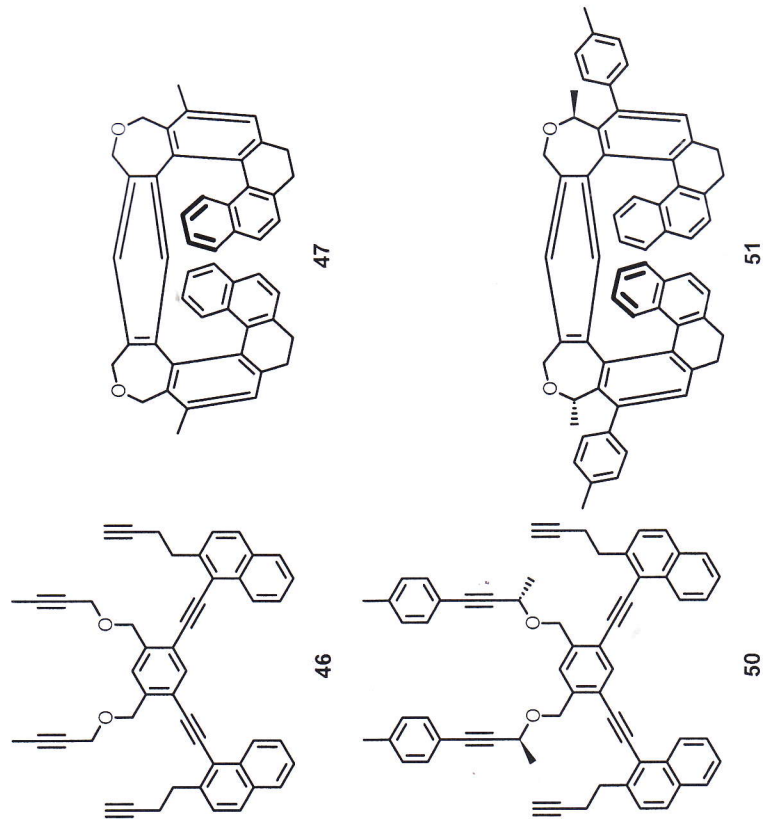


Scheme 4



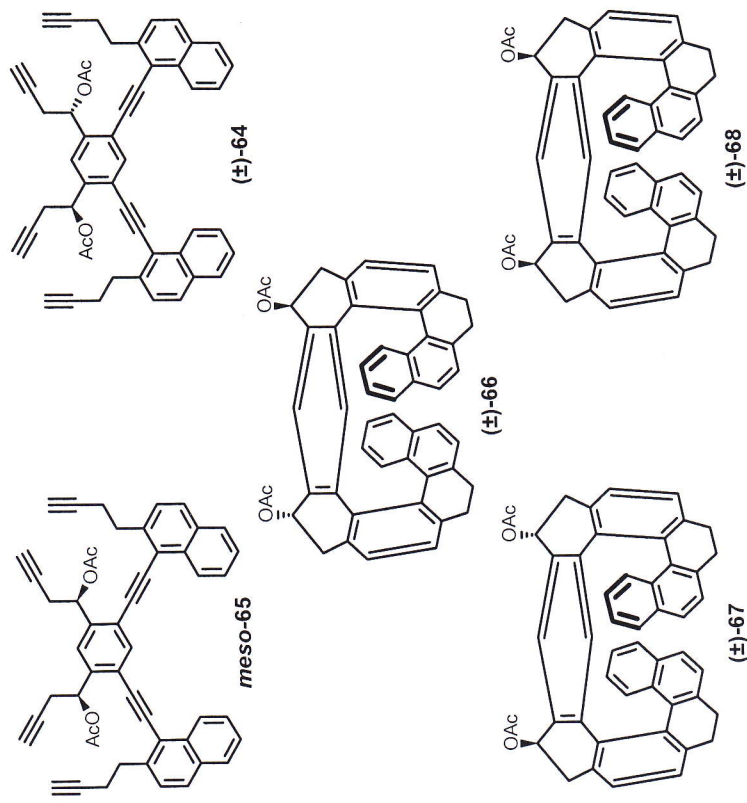
Scheme 5

- Synthesise higher extended helical molecule **47** via a double [2+2+2] cycloisomerisation of hexayne **46** (Scheme 6).
- Synthesise an extended [1¹]helicene-like molecule **51** with defined helicity via a diastereoselective double [2+2+2] cycloisomerisation of centrally chiral hexayne **50** (Scheme 6).



Scheme 6

- Synthesis diastereoisomeric hexaynes **64** and **65** and investigate their double [2+2+2] cycloisomerisation to extended functionalised [11]helicene-like molecules **66**, **67** and **68**, respectively (Scheme 7).

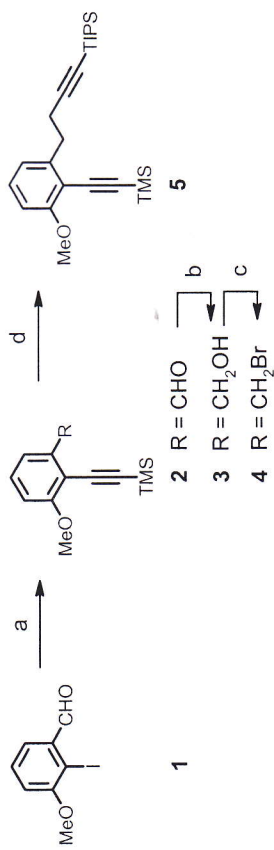


Scheme 7

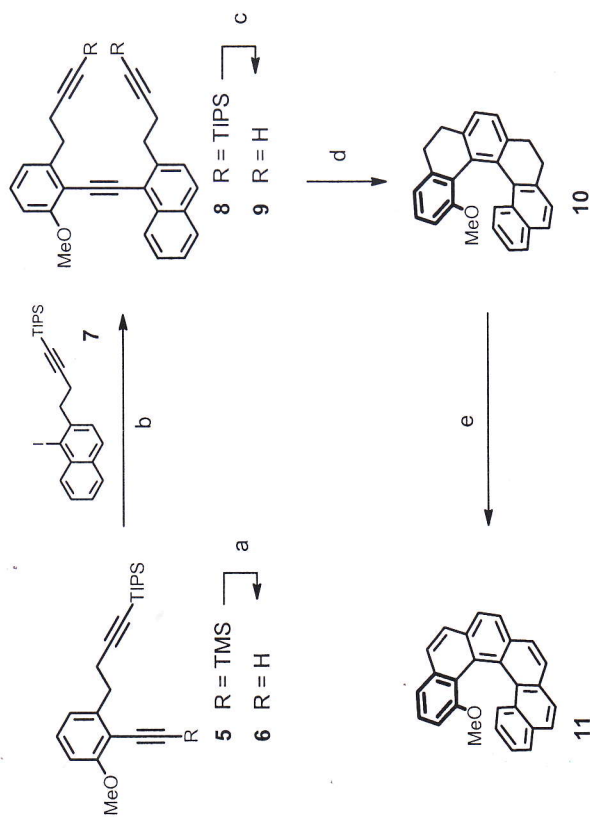
3 Synthesis of helical molecules

3.1 Synthesis of small helical molecules

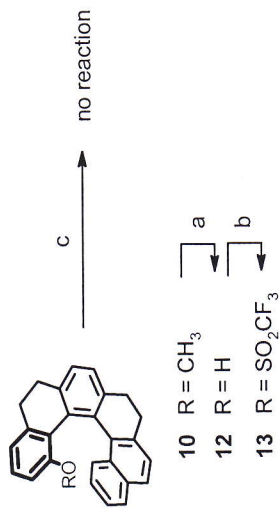
A convergent synthesis of 1-methoxyhexahelicene **11** starting from 3-methoxybenzaldehyde has been developed (10 steps, overall yield 23 %). (Schemes 8 and 9). **10** was further demethylated to alcohol **12** and triflate **13**. Attempts to introduce an alkyne moiety to position 1 via Sonogashira coupling were unsuccessful (Scheme 10). Nonafflate **15** was prepared from **11** via 1-hydroxyhelicene **14**, but it also proved unreactive under Sonogashira conditions (Scheme 11).



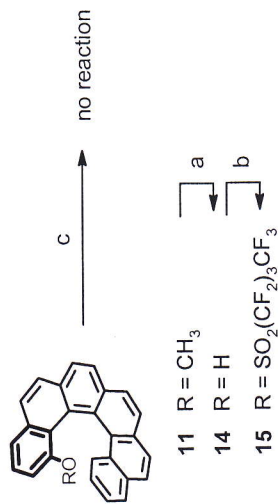
Scheme 8: (a) HC≡C-TMS, Pd(PPh₃)₄, CuI, *i*-Pr₂NH, 85 °C, 88 %; (b) DIBAL-H, toluene, -78 °C, 100 %; (c) CBr₄, PPh₃, MeCN, rt, 82 %; (d) Li-CH₂-C≡C-TIPS, THF, -78 °C, 85 %.



Scheme 9: (a) NaOMe, MeOH, rt, 97 %; (b) Pd(PPh₃)₄, CuI, *i*-Pr₂NH, rt, 92 %; (c) *n*-Bu₄NF, THF, rt, 99 %; (d) CpCo(CO)₂, PPh₃, decane, hv, 140 °C, 82 %; (e) Ph₃CBF₄, DCE, 80 °C, 87 %.



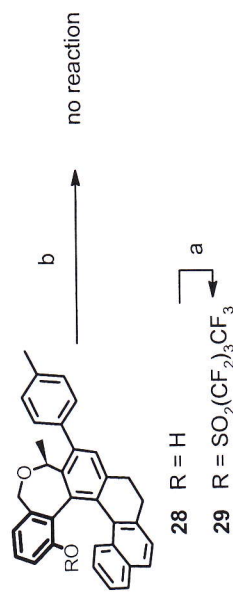
Scheme 10: (a) BBr₃, DCM, 0 °C, 100 %; (b) 1. *n*-BuLi, THF, -78 °C; 2. (CF₃SO₂)₂O, Et₃N, -78 °C, 16 %; (c) HC≡C-TMS, Pd(PPh₃)₄, CuI, *i*-Pr₂NH, 120 °C, no reaction.



Scheme 11: (a) BBr₃, DCM, 0 °C, 90 %; (b) 1. NaH, DMF, rt; 2. CF₃(CF₂)₃SO₂F, rt, 78 %; (c) HC≡C-TMS, Pd(PPh₃)₄, CuI, *i*-Pr₂NH, 120 °C, no reaction.

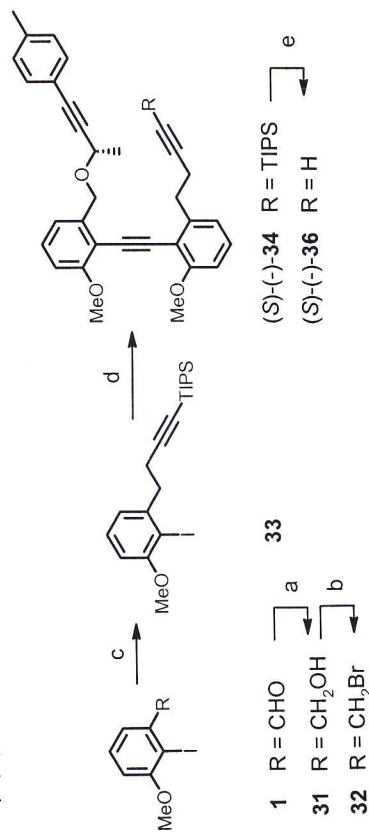
Based on an analogous procedure from our laboratory^{6b}, a modular synthesis of centrally chiral triyne (*S*)-(-)-**25** has been developed starting from 3-methoxy-2-hydroxybenzaldehyde and optically pure (*S*)-(-)-3-butyne-2-ol. Diastereoselective [2+2+2] cycloisomerisation of (*S*)-(-)-**25** with CpCo(CO)₂/PPh₃ at 140 °C gave (*P,S*)-**26** and (*M,S*)-**26** with 87:13 selectivity (Schemes 12 and 13). Demethylation of **26** followed by crystallisation gave optically pure (*P,S*)-(+)-**28**.

Attempts to introduce an alkyne substituent on the scaffold of **28** via conversion to nonaflate **29** and Sonogashira reaction have been unsuccessful (Scheme 14).

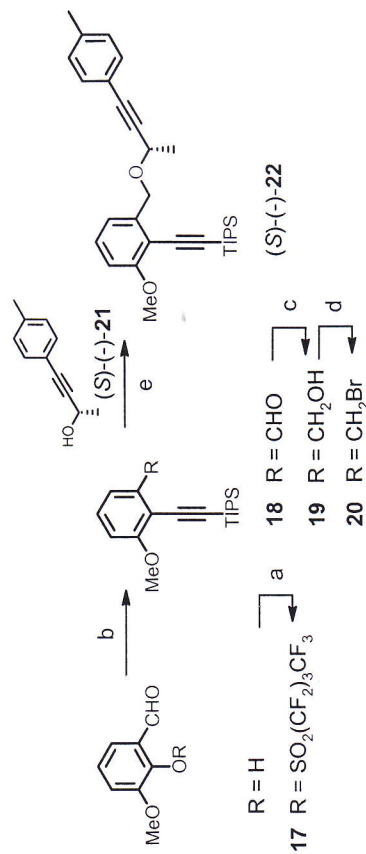


Scheme 14: (a) 1. NaH, DMF, rt; 2. CF₃(CF₂)₃SO₂F, rt, 87 %; (b) HC≡C-TMS, PdCl₂(PPh₃)₂, Et₃N, DMF, 110 °C, no reaction.

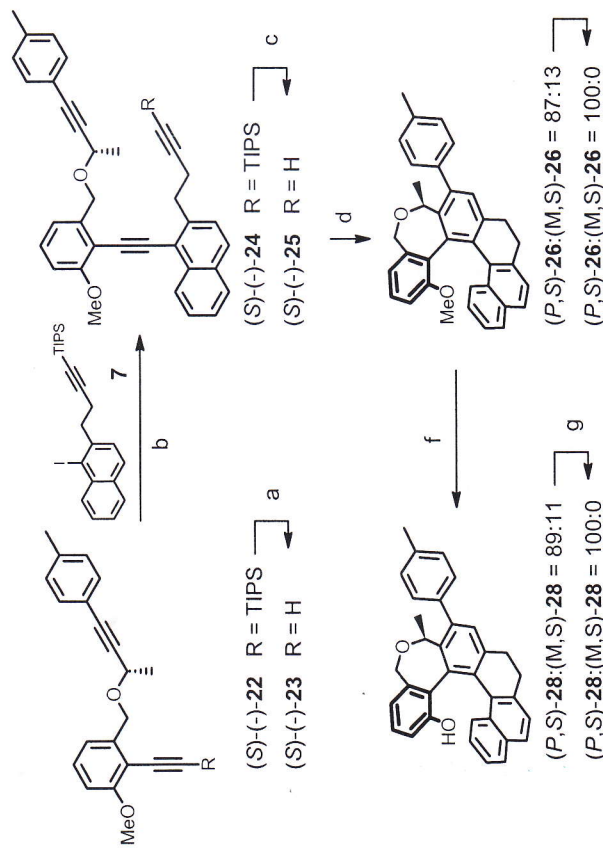
A bifunctional helical molecule **37** has been prepared via diastereoselective [2+2+2] cycloisomerisation of (S)-(-)-**36** (Schemes 15 and 16). The cyclisation of (S)-(-)-**36** with CpCo(CO)₂PPh₃ at 140 °C gave (P,S)-**37** and (M,S)-**37** with 91:9 selectivity. Optically pure (P,S)-(+)-**37** was obtained after one crystallisation.



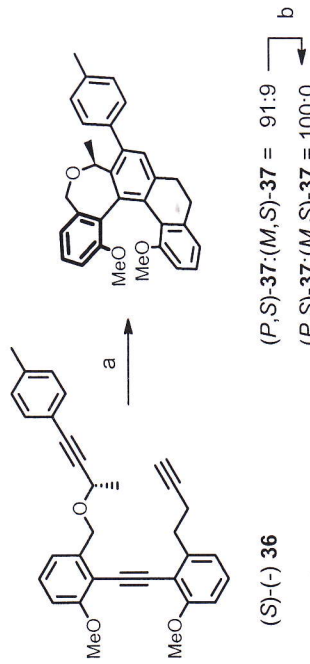
Scheme 15: (a) DIBAL-H, toluene, -78 °C, 72 %; (b) PBr₃, THF, 0 °C, 89 %; (c) Li-CH₂-C≡C-TIPS, THF, -78 °C, 80 %; (d) (S)-(-)-**23**, Pd(PPh₃)₄, CuI, *i*-Pr₂NH, 80 °C, 73 %; (e) *n*-Bu₄NF, THF, rt, 100 %.



Scheme 12: (a) 1. NaH, DMF, rt; 2. CF₃(CF₂)₃SO₂F, rt, 93 %; (b) HC≡C-TIPS, PdCl₂(PPh₃)₂, Et₃N, DMF, 90 °C, 91 %; (c) DIBAL-H, toluene, -78 °C, 100 %; (d) PBr₃, THF, 0 °C, 97 %; (e) NaH, THF, 0 to 40 °C, 74 %.



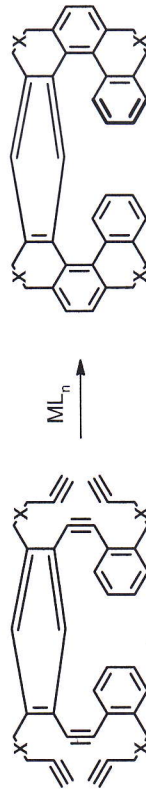
Scheme 13: (a) *n*-Bu₄NF, THF, rt, 100 %; (b) Pd(PPh₃)₄, CuI, *i*-Pr₂NH, rt, 82 %; (c) *n*-Bu₄NF, THF, rt, 86 %; (d) CpCo(CO)₂, PPh₃, decane, hv, 140 °C, 82 %; (e) crystallisation from heptane, 76 %; (f) crystallisation from heptane-toluene, 72 %; (g) crystallisation from heptane-toluene-ethanol, 72 %.



Scheme 16: (a) CpCo(CO)₂, PPh₃, decane, hv, 140 °C, 89 %; (b) crystallisation from pentane, 66 %.

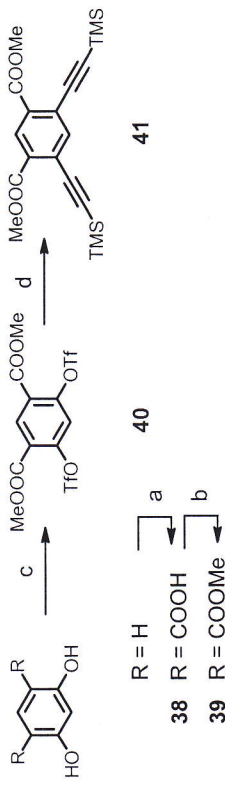
3.2 Synthesis of higher and extended helical molecules

The scope of the cycloisomerisation approach has been extended to molecules that could undergo two independent intramolecular [2+2+2] cycloisomerisations to provide higher extended helicene-like molecules (Scheme 17).

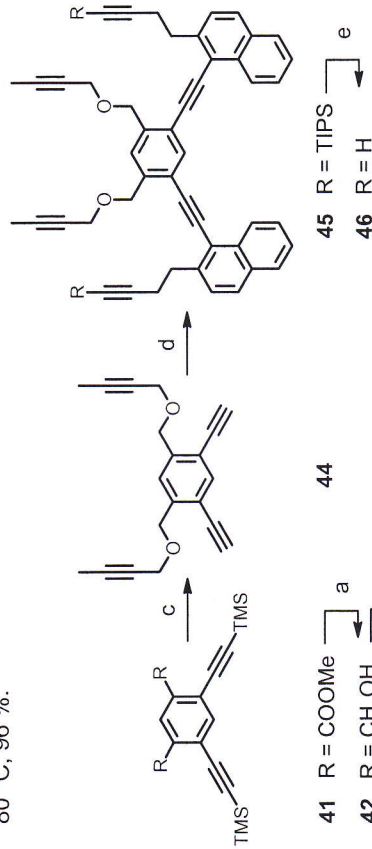


Scheme 17

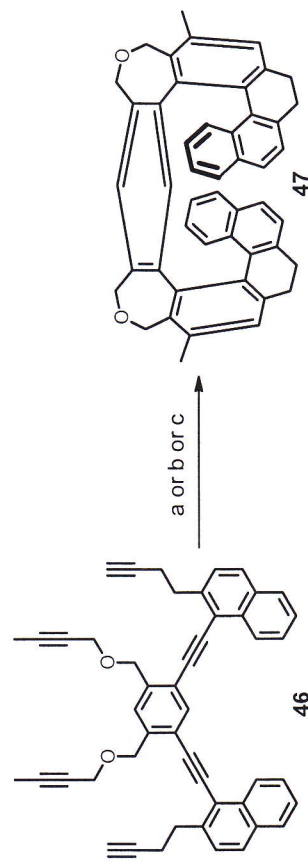
The feasibility of this approach was demonstrated by a successful synthesis of a higher extended helical molecule **47** via a double [2+2+2] cycloisomerisation of hexayne **46** (Schemes 18, 19 and 20).



Scheme 18: (a) KHCO₃, 210 °C, neat, 74 %; (b) MeOH, conc. H₂SO₄, reflux, 93 %; (c) Tf₂O, DCM, pyridine, 0 °C to rt, 89 %; (d) HC≡C-TMS, Pd(PPh₃)₄, Cul, *i*-Pr₂NH, 80 °C, 96 %.

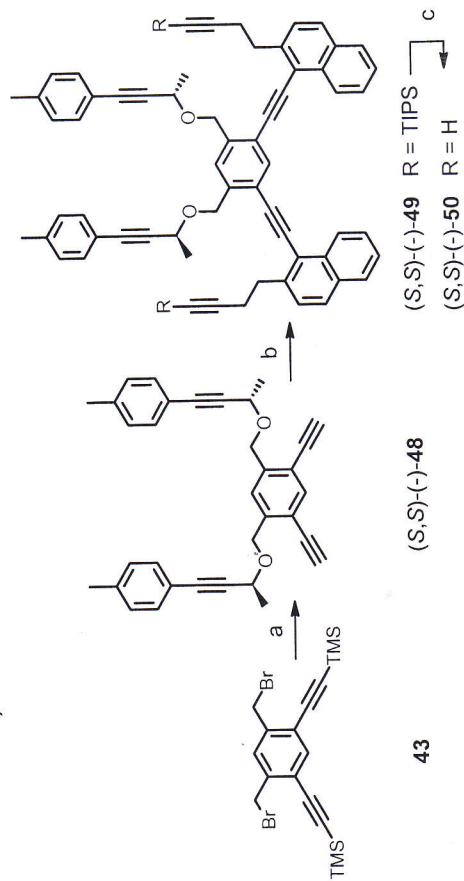


Scheme 19: (a) DIBAL-H, DCM, -78 °C, 91 %; (b) CBr₄, PPh₃, MeCN, rt, 61 %; (c) NaH, 2-butyn-1-ol, THF, 0 to 40 °C, 38 %; (d) iodide **7**, Pd(PPh₃)₄, Cul, *i*-Pr₂NH, 85 °C, 47 %; (e) *n*-Bu₄NF, THF, rt, 90 %.

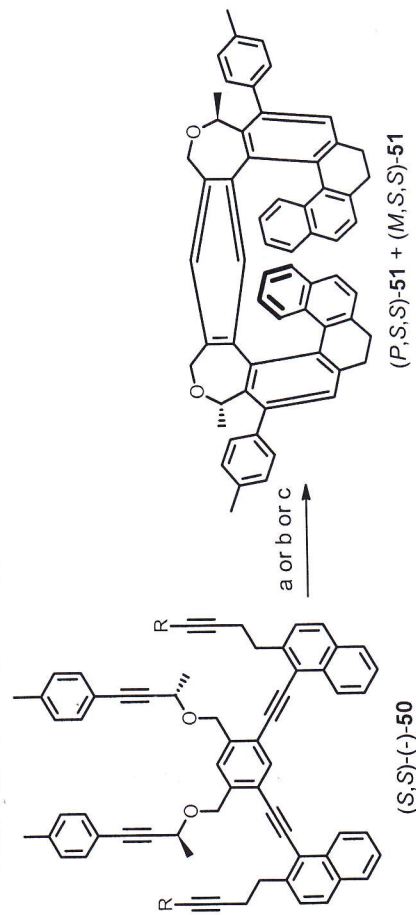


Scheme 20: (a) CpCo(CO)₂, PPh₃, decane, hv, 140 °C, 60 %; (b) CpCo(C₂H₄)₂, THF, rt, 45 %; (c) Ni(COD)₂, PPh₃, THF, rt, 24 %.

A model centrally chiral hexayne (*S,S*)-(-)-**50** was prepared and its diastereoselective cyclisation to [11]helicene-like molecule **51** was studied. (*S,S*)-(-)-**50** was prepared from a previously synthesised dibromide **43** and optically pure building block (*S*)-(-)-**21** (Schemes 21 and 22).

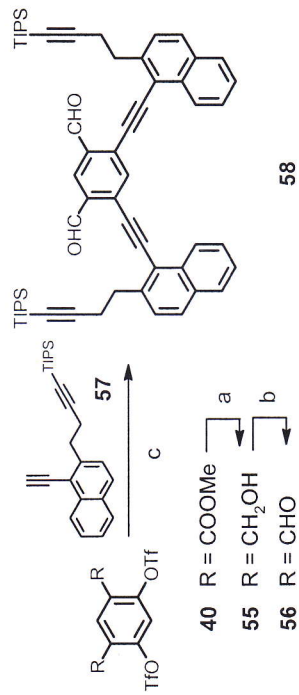


Scheme 21: (a) (*S*)-(-)-**21**, NaH, THF, 0 to 50 °C, 25 %; (b) iodide **7**, Pd(PPh₃)₄, CuI, *i*-Pr₂NH, 85 °C, 49 %; (c) *n*-Bu₄NF, THF, rt, 85 %.

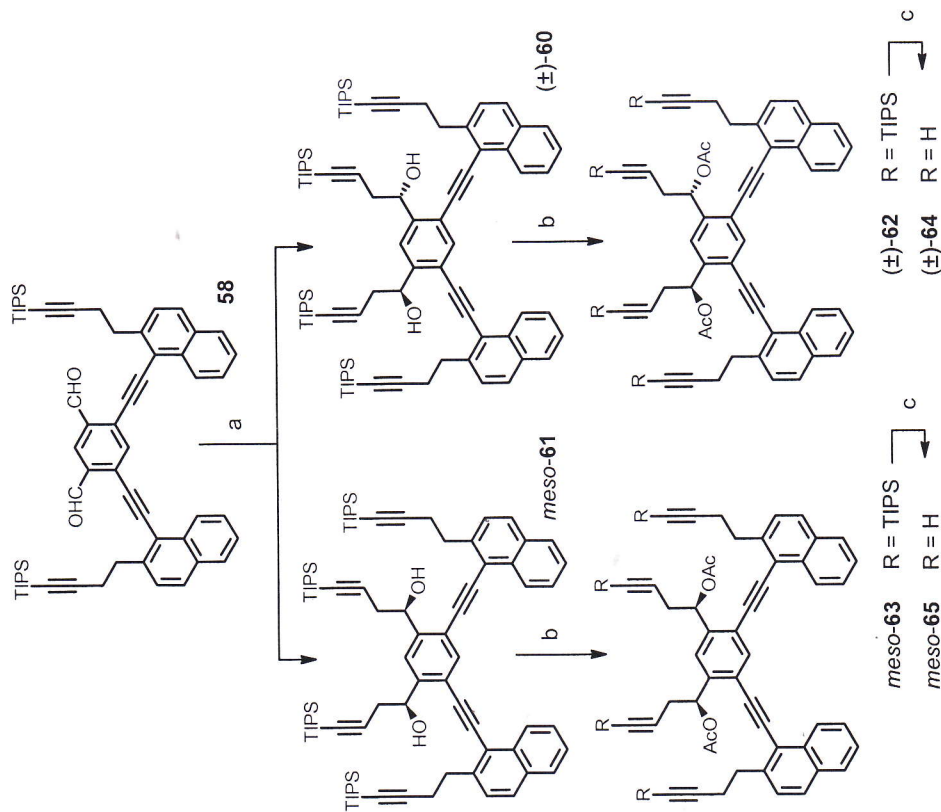


Scheme 22: (a) CpCo(CO)₂, PPh₃, decane, hv, 140 °C, 26 % ((*P,S,S*)-(*M,S,S*) = 90:10); (b) CpCo(CO)₂, PPh₃, THF, 200 °C, μW, 33 % ((*P,S,S*)-(*M,S,S*) = 90:10); (c) CpCo(C₂H₄)₂, THF, rt, 17 % ((*P,S,S*)-(*M,S,S*) = 75:25).

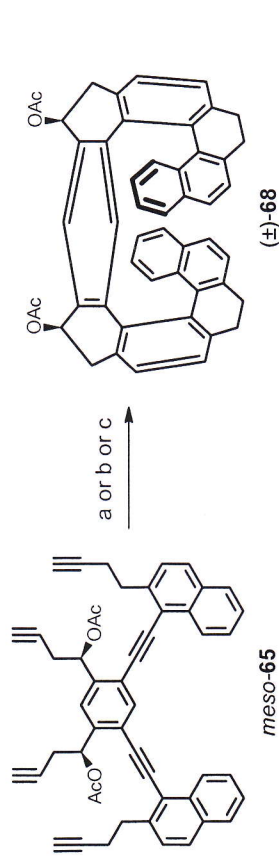
To demonstrate accessibility of functionalised higher helical molecules, diacetates **66**, **67** and **68** have been synthesised in a racemic form starting from the previously synthesised diester **40** (Schemes 23-26). The cyclisation of hexayne (\pm)-**64** produces a mixture of diastereomeric diacetates (\pm)-**66** and (\pm)-**67**. Using CpCo(CO)₂(PPh₃) at 140 °C, the (\pm)-**66**:(\pm)-**67** ratio was 83:17. By contrast, cyclisation reactions at room temperature provided different diastereoselectivity ranging from 43:57 to 17:83 in favour of (\pm)-**67** (see Appendix).



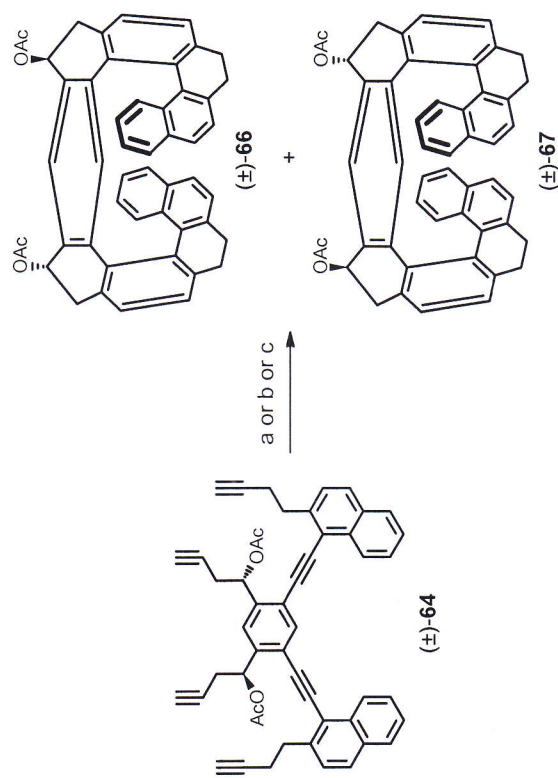
Scheme 23: (a) DIBAL-H, DCM, -78 °C, 75 %; (b) MnO₂, DCM, rt, 73 %; (c) Pd(PPh₃)₄, CuI, DMF, Et₃N, rt, 83 %.



Scheme 24: (a) $\text{Li-CH}_2\text{-C}\equiv\text{C-TIPS}$; THF, -78°C , 30 % (for **60**), 29 % (for **61**); (b) Ac_2O , DMAP, Et_3N , rt, 100 % (for **62**), 92 % (for **63**); (c) $n\text{-Bu}_4\text{NF}$, THF, rt, 68 % (for **64**), 66 % (for **65**).



Scheme 25: (a) CpCo(CO)_2 , PPh_3 , decane, hv, 140°C , 40 %; (b) $\text{CpCo(C}_2\text{H}_4)_2$, THF, rt, 30 %; (c) Ni(COD)_2 , PPh_3 , THF, rt, 17 %.



Scheme 26: (a) CpCo(CO)_2 , PPh_3 , decane, hv, 140°C , 25 % $(\pm)\text{-66}$; $(\pm)\text{-67} = 83:17$; (b) $\text{CpCo(C}_2\text{H}_4)_2$, THF, rt, 25 % $(\pm)\text{-66}$; $(\pm)\text{-67} = 43:57$; (c) Ni(COD)_2 , PPh_3 , THF, rt, 30 % $(\pm)\text{-66}$; $(\pm)\text{-67} = 28:72$. All yields are given for **66** and **67** combined.

4 Appendix

4.1 Thermal epimerisation of **26**

Kinetics of thermal equilibration of (*P,S*)-**26** and (*M,S*)-**26** was studied at temperatures 340 to 367 K. Dependence of the (*P,S*)-**26** : (*M,S*)-**26** ratio was monitored on HPLC. From the measured data, kinetic and thermodynamic parameters of the equilibration process have been calculated (Table 1).

temperature	340 K	350 K	360 K	367 K
solvent	heptane	heptane	heptane	decane
[<i>P,S</i>]eq.] (in %)	88.8	86.7	86.7	86.1
[<i>M,S</i>]eq.] (in %)	11.2	13.3	13.3	13.9
K	7.93	6.54	6.50	6.18
ΔG (in kJ/mol)	-5.86	-5.47	-5.60	-5.55
$\Delta G^{\ddagger}_{P \rightarrow M}$ (in kJ/mol)	116.8	116.2	116.1	116.1
$\Delta G^{\ddagger}_{M \rightarrow P}$ (in kJ/mol)	110.9	110.7	110.5	110.5
$t_{1/2}$ (in min)	157.2	43.8	14.4	7.0
$k_{P \rightarrow M}$ (in s ⁻¹)	8.23×10^{-5}	3.49×10^{-5}	1.07×10^{-4}	2.29×10^{-4}
$k_{M \rightarrow P}$ (in s ⁻¹)	6.53×10^{-5}	2.29×10^{-4}	6.96×10^{-4}	1.42×10^{-3}

Table 1

4.2 DFT diastereoselectivity calculations

As confirmed by DFT calculations (B3LYP/TZV+P, COSMO solvation model), the product ratios obtained in diastereoselective [2+2+2] cycloisomerisation reactions at 140 °C are determined by relative thermodynamic stabilities and the more stable diastereoisomer predominates in most cases. An overview of all diastereoselective cyclisation experiments is given in Table 2.

reactant	(S)-(-)- 25	(S)-(-)- 36	(S,S)-(-)- 50	(±)- 64
products	(<i>P,S</i>)- 26 (<i>M,S</i>)- 26	(<i>P,S</i>)- 37 (<i>M,S</i>)- 37	(<i>P,S,S</i>)- 51 (<i>M,S,S</i>)- 51	(±)- 66 (±)- 67
DFT method (B3LYP/TZV+P)	84 : 16	77 : 23	90 : 10	12 : 88
CpCo(CO) ₂ /PPh ₃ decane, hv, 140 °C	87 : 13	91 : 9	90 : 10	83 : 17
CpCo(C ₂ H ₄) ₂ THF, 20 °C	50 : 50	---	75 : 25	43 : 57
Ni(COD) ₂ /PPh ₃ THF, 20 °C	---	---	---	28 : 72
Ni(COD) ₂ THF, 20 °C	---	---	---	13 : 87

Table 2

5 List of publications of the author

1. 4,4'-Bipyridine-2,2',6,6'-tetracarboxamide. Synthesis and Self-assembly Properties of the Free Base and the 1 : 1 Silver(I) Triflate Complex
P. Sehnal, P. Holý, M. Tichý, J. Závada, I. Císařová
Collect. Czech. Chem. Commun. **2002**, *67* (8), 1236-1246.
2. Self-assembly of Chiral Hydrogen-bonded Grid Layers from Terephthalic Siamese Twins
P. Holý, P. Sehnal, M. Tichý, J. Závada, I. Císařová
Tetrahedron Asymmetry **2003**, *14* (2), 245-253.
3. Crystal Structure of 1,10-Biphenyl-2,2',3,3'-tetracarboxylic and 1,10-Biphenyl-2,2',3,3',5,5',6,6'-octacarboxylic Acids: Solid State Chiralisation and Dissociation
P. Holý, P. Sehnal, M. Tichý, J. Závada, I. Císařová
Tetrahedron Asymmetry **2004**, *15* (23), 3805-3810.
4. Synthetic Studies Toward Chiral Aromatic Triynes as Key Substrates for the Asymmetric Synthesis of Helicene-like Molecules
Z. Alexandrová, I. G. Stará, P. Sehnal, F. Teplý, I. Starý, D. Šaman, P. Fiedler
Collect. Czech. Chem. Commun. **2004**, *69* (12), 2193-2211.
5. Asymmetric Synthesis of [7]helicene-like Molecules
I. G. Stará, Z. Alexandrová, F. Teplý, P. Sehnal, I. Starý, D. Šaman, M. Buděšínský, J. Cvačka
Org. Lett. **2005**, *7* (13), 2547-2550.
6. Helicity Control in the Synthesis of Helicenes and Related Compounds
I. Starý, I. G. Stará, Z. Alexandrová, P. Sehnal, F. Teplý, D. Šaman, L. Rulišek
Pure Appl. Chem. **2006**, *78* (2), 495-499.
7. Modified Synthesis of [7]helicene and Its Resolution into Single Enantiomers
Z. Alexandrová, P. Sehnal, I. G. Stará, I. Starý, S. G. Urquhart
Collect. Czech. Chem. Commun. **2006**; manuscript in preparation

6 References and notes

1. C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448; for reviews on helicenes, see: (a) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, p. 321-330; (b) T. J. Katz, *Angew. Chem. Int. Ed.* **2000**, *39*, 1921; (c) H. Osuga, H. Suzuki, *J. Synth. Org. Chem., Jpn.* **1994**, *52*, 1020; (d) F. Vögtle, *Fascinating Molecules in Organic Chemistry*, Wiley, New York, **1992**, p. 156-180; (e) G. Oremek, U. Seiffert, A. Janecka, *Chem.-Ztg.* **1987**, *111*, 69; (f) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1; (g) W. H. Laarhoven, W. J. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63; (h) R. H. Martin, *Angew. Chem.* **1974**, *86*, 727; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649; (i) H. Wynberg, *Acc. Chem. Res.* **1971**, *4*, 65.
2. (a) L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769; (b) M. Flamming-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett.* **1967**, *743*; (c) C. S. Wood, F. B. Mallory, *J. Org. Chem.* **1964**, *29*, 3373.
3. (a) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899; (b) D. J. Weix, S. D. Dreher, T. J. Katz, *J. Am. Chem. Soc.* **2000**, *122*, 10027; (c) K. Paruch, L. Vyklický, T. J. Katz, C. D. Incarvito, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 8774; (d) K. Paruch, T. J. Katz, C. D. Incarvito, K. C. Lam, B. Rhatigan, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 7602; (e) T. Thongpanchang, K. Paruch, T. J. Katz, A. L. Rheingold, K. C. Lam, L. Liablesands, *J. Org. Chem.* **2000**, *65*, 1850; (f) S. D. Dreher, T. J. Katz, K. C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815; (g) S. D. Dreher, K. Paruch, T. J. Katz, *J. Org. Chem.* **2000**, *65*, 806; (h) J. M. Fox, T. J. Katz, S. Van Elshocht, T. Verbiest, M. Kauranen, A. Persoons, T. Thongpanchang, T. Krauss, L. Brus, *J. Am. Chem. Soc.* **1999**, *121*, 3453; (i) C. Nuckolls, T. J. Katz, G. Katz, P. J. Collings, L. Castellanos, *J. Am. Chem. Soc.* **1999**, *121*, 79; (j) S. D. Dreher, D. J. Weix, T. J. Katz, *J. Org. Chem.* **1999**, *64*, 3671; (k) J. M. Fox, T. J. Katz, *J. Org. Chem.* **1999**, *64*, 302; (l) C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 9541; (m) J. M. Fox, N. R. Goldberg, T. J. Katz, *J. Org. Chem.* **1998**, *63*, 7456; (n) T. J. Katz, L. Liu, N. D. Willmore, J. M. Fox, A. L. Rheingold, S. H. Shi, C. Nuckolls, B. H. Rickman, *J. Am. Chem. Soc.* **1997**, *119*, 10054; (o) Y. J. Dai, T. J.

- Katz, *J. Org. Chem.* **1997**, *62*, 1274; (p) C. Nuckolls, T. J. Katz, L. Castellanos, *J. Am. Chem. Soc.* **1996**, *118*, 3767; (q) Y. J. Dai, T. J. Katz, D. A. Nichols, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2109; (r) S. Shi, T. J. Katz, B. V. Yang, L. Liu, *J. Org. Chem.* **1995**, *60*, 1285; (s) N. D. Willmore, D. A. Hoic, T. J. Katz, *J. Org. Chem.* **1994**, *59*, 1889; (t) T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch, M. D. Ward, *J. Am. Chem. Soc.* **1993**, *115*, 3182; (u) N. D. Willmore, L. Liu, T. J. Katz, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093; (v) L. Liu, T. J. Katz, *Tetrahedron Lett.* **1990**, *31*, 3983.
4. (a) D. C. Harrowven, I. L. Guy, L. Nanson, *Angew. Chem. Int. Ed.* **2006**, *45*, 1; (b) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002**, *43*, 7345; (c) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002**, *43*, 3189.
 5. A. Urbano, *Angew. Chem. Int. Ed.* **2003**, *42*, 3986 and references therein.
 6. (a) I. Starý, I. G. Stará, Z. Alexandrová, P. Sehnal, F. Teplý, D. Šaman, L. Rulišek, *Pure Appl. Chem.* **2006**, *78* (2), 495-499; (b) I. G. Stará, Z. Alexandrová, F. Teplý, P. Sehnal, I. Starý, D. Šaman, M. Buděšínský, J. Cvačka, *Org. Lett.* **2005**, *7*, 2547; (c) Z. Alexandrová, I. G. Stará, P. Sehnal, F. Teplý, I. Starý, D. Šaman, P. Fiedler, *Collect. Czech. Commun.* **2004**, *69*, 2193; (d) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, P. Fiedler, *Collect. Czech. Commun.* **2003**, *68*, 917; (e) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, Š. Vyskočil, P. Fiedler, *J. Org. Chem.* **2003**, *68*, 5193; (f) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, L. Rulišek, P. Fiedler, *J. Am. Chem. Soc.* **2002**, *124*, 9175; (g) I. G. Stará, A. Kollárovič, F. Teplý, I. Starý, D. Šaman, P. Fiedler, *Collect. Czech. Commun.* **2000**, *65*, 577; (h) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, P. Fiedler, *Collect. Czech. Commun.* **1999**, *64*, 649; (i) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, Š. Vyskočil, D. Šaman, *Tetrahedron Lett.* **1999**, *40*, 1993; (j) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, P. Fiedler, *Tetrahedron* **1998**, *54*, 11209; (k) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, M. Tichý, *J. Org. Chem.* **1998**, *63*, 4046.