DOI: 10.1002/cjoc.201400162

Special Chiral C_2-Symmetric *endo*-Biarylnorbornane: Synthesis and Structure Illustration

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A highly efficient and practical synthesis for strained special scaffold of chiral *endo*-biarylnorbornane starting from available norbornadione was achieved with direct stereoselective dehydroxylation of tertiary alcohol as the key step, and the structure was illustrated by X-ray structural analysis.

Keywords *endo*-biarylnorbornane, stereoselective dehydroxylation, synthesis design, X-ray diffraction, chiral auxiliaries

Introduction

Developing novel chiral auxiliaries with special structure is very important for drug discovery,[1] asymmetric catalysis[2] and valuable natural product synthesis.[3] In our pursuit in the synthesis of interesting chiral auxiliaries, norbornane(bicyclo[2,2,1]heptane) framework has aroused our attentions.[4] In fact, the special scaffold has received constant attention from researchers in a range of fields including medicinal chemistry,[5] peptidomimetics,[6] asymmetric synthesis[7] and organic synthesis,[8-14] functional material synthesis.[15]

It has been well documented that norbornene, norbornadiene, or norbornanone systems in general show high *exo*-facial selectivity in the electrophilic, nucleophilic, or cyclic additions, and the explanations to it include steric effects that the ethano bridge is larger than the methano bridge, torsional effect that is relieved by *exo* attack but increased by *endo* attack in the transition state, pyramidalization of the sp^2 carbons toward the *endo* directions leading to the favored attack on the convex face of the pyramidalized sp^2 carbons and so on. Since norbornene, norbornadiene, or norbornanone and their derivatives are versatile synthetic building blocks for further skeletal conversions, the high *exo* selectivity has been applied to development of a variety of useful stereospecific or stereoselective reactions in synthesis of *exo*-facial selective compounds,[8] while for the synthesis and structure illustration of *endo*-facial substituted strained norbornane, there are seldom reports about it.

In our previous work, we have synthesized the novel norbornane based bicyclo[2,2,1]heptane-*endo*,*endo*-2,5-diol[16] and in this work we will report the sythesis of more strained structure *endo*,*endo*-biarylbicyclo[2,2,1]-heptane.

Experimental

General methods

2,5-Norbornadione **1** is prepared by the methods reported.[17,18] All solvents and reagents were purified by standard techniques. Crude products were purified by column chromatography on silica gel of 200 meshes. Optical rotations were obtained on Jasco Dip 360 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker Avance 600. Chemical shifts are reported in parts per million with respect to internal TMS. HRMS spectra were recorded on Ser# microOTOF-QII10280 mass spectrometers. Mass spectra were recorded on Thermo Fannigan Polaris Q Mass spectrometers operating at a direct inlet system or GC/MS. X-ray crystallographic data were analyzed through Bruker AXS GMBH SMART APEX II X-ray diffractometer. A single crystal of **5** was obtained by the slow evaporation from solution of *n*-hexane.

Preparation of (1*R*,2*R*,4*R*,5*R*)-*exo*,*exo*-2,5-di(2-methoxy)phenylbicyclo[2,2,1]heptane-*endo*,*endo*-2,5-diol (**4**)

A 50 mL three-neck round-bottom flask under N_2 gas equipped with magnetic stirrer and thermometer was charged with dry THF (5 mL) and magnesium powder (1.4 g, 57.6 mmol). Under stirring, *ortho*-bromoanisole (9 g, 48 mmol) in THF (15 mL) was added carefully at a rate sufficient to maintain a gentle reflux, then the reaction was continued to reflux for 1 h and cooled to r.t. To the solution was added dione **1** (1.5 g, 12 mmol) in THF (5 mL) at r.t., then the reaction was refluxed at 60 ℃

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Received March 26, 2014; accepted June 17, 2014; published online July 3, 2014.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201400162 or from the author.

for 2 h. After cooling to r.t., cold sat. NH_4Cl (20 mL) was added carefully. The mixture was stirred for 10 min, the aqueous layer was extracted with Et_2O (15 mL×4). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica (hexanes∶EtOAc=1∶1, *V*∶*V*), bis-tertiary alcohol **4** was afforded. Yield 3.35 g (81%); white crystals; m.p. 140−142 ℃; $[\alpha]_D^{20}$ +36 (*c* 1.00, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 6.92−7.31 (m, 8H, ArH), 4.21 (s, 2H, 2 bridgehead), 3.93 (s, 6H, 2OCH_3), 2.76−2.78 (m, 2H, *endo*-CH_2), 2.73 (s, 2H, 2OH), 2.11−2.17 (m, 2H, *exo*-CH_2), 1.64 (s, 2H, bridge); ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 157.20 (Ar), 136.01 (Ar), 127.93 (Ar), 125.00 (Ar), 120.48 (Ar), 111.43 (Ar), 78.86 (Ar-C-OH), 55.33 (Ar-OCH_3), 45.99 (bridgehead), 39.27 (CH_2), 37.90 (bridge); EIMS *m*/*z*: 339 $[M-1]^+$; HRMS (TOF ESI) calcd for $C_{21}H_{24}O_4$ $[M+Na]^+$ 363.1567, found 363.1572.

Preparation of (1*R*,2*R*,4*R*,5*R*)-*endo*,*endo*-2,5-di(2-methoxy)phenylbicyclo[2,2,1]heptane (5)

To a stainless autoclave with polytef liner equipped with magnetic stirrer was added bis-tertiary alcohol **4** (1 g, 2.94 mmol), Pd-C (10%, 200 mg), dry ethanol (120 mL) and 8 drops of 70% aqueous $HClO_4$. The autoclave was purged three times with H_2 and the pressure was set to 2 atm, and dehydroxylation was performed at room temperature for 24 h. After carefully releasing the H_2, the reaction mixture was neutralized with solid Na_2CO_3 and filtrated. The solvent was removed under reduced pressure. The crude product thus acquired was purified by a short column chromatography on silica (hexane∶dichloromethane=3∶1, *V*∶*V*) to give biarylnorbornane as a mixture of two isomers, of which, 95.24% was *endo*-biarylnorbornane **5**. Through recrystallization from hexane, pure *endo*-biarylnorbornane **5** was afforded. Yield 0.6 g (67%); white crystals; m.p. 123−125 ℃; $[\alpha]_D^{20}$ +39 (*c* 1.00, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 6.83−7.24 (m, 8H, ArH), 3.80 (s, 6H, 2OCH_3), 3.37 (s, 2H, Ar-C-H), 2.72 (s, 2H, 2 bridgehead), 2.73 (s, 2H, 2OH), 1.80 (s, 2H, bridge), 1.65−1.70 (m, 2H, *endo*-CH_2), 1.50−1.55 (m, 2H, *exo*-CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 158.61 (Ar), 130.83 (Ar), 128.56 (Ar), 126.65 (Ar), 119.67 (Ar), 110.15 (Ar), 55.17 (Ar-OCH_3), 42.53 (bridge), 42.22 (Ar-CH), 41.11 (bridgehead), 26.07 (CH_2); EIMS *m*/*z*: 308 $[M]^+$; HRMS (TOF ESI) calcd for $C_{21}H_{24}O_2$ $[M+Na]^+$ 331.1669, found 331.1659.

Preparation of (1*R*,2*R*,4*R*,5*R*)-*endo*,*endo*-2,5-di(2-hydroxy)phenylbicyclo[2, 2, 1]heptane (6)

To a 50 mL round-bottom flask under N_2 gas equipped with magnetic stirrer was added *endo*-biarylnorbornane **5** (1 g, 3.25 mmol) and 18 mL dry dichloromethane, then BBr_3 (1.2 mL, 12 mmol) was added with stirring at −78 ℃. After the mixture was stirred for 30 min at −78 ℃, the cooling bath was removed and the stirring was continued for an additional 24 h. The reaction was quenched with cold water (18 mL), and dichloromethane was removed under reduced pressure. The aqueous solution was neutralized by addition of aqueous NaOH, and then extracted with dichloromethane (20 mL×4). The organic layer was washed with brine, and dried over Na_2SO_4. After removing the solvent, the residue was purified by a short column chromatography on silica (hexanes∶EtOAc=3∶1, *V*∶*V*) to give bisphenol **6**. Yield: 0.86 g (95%); white crystals; m.p. 152−155 ℃; $[\alpha]_D^{20}$ +32 (*c* 1.00, MeOH); ^{1}H NMR (600 MHz, MeOD) *δ*: 6.59−6.94 (m, 8H, Ph-H), 4.79 (s, 2H, 2Ar-OH), 3.25 (s, 2H, 2Ar-C-H), 2.66 (s, 2H, 2 bridgehead), 1.69 (s, 2H, bridge), 1.43−1.54 (m, 4H, 2CH_2); ^{13}C NMR (150 MHz, MeOD) *δ*: 156.06 (Ar), 128.40 (Ar), 128.28 (Ar), 126.18 (Ar), 118.20 (Ar), 114.39 (Ar), 41.94 (Ar-CH), 40.08 (bridgehead), 29.31 (bridge), 25.36 (CH_2); EIMS *m*/*z*: 280 $[M]^+$; HRMS (TOF ESI) calcd for $C_{19}H_{20}O_2$ $[M+Na]^+$ 303.1356, found 303.1361.

Preparation of (1*R*,2*R*,4*R*,5*R*)-*exo*,*exo*-2,5-methoxy)naphthylbicyclo[2,2,1]heptane-*endo*,*endo*-2,5-diol (10)

To a 250 mL round-bottom flask equipped with magnetic stirrer under N_2 gas was added 1-bromo-2-methoxynaphthalene (7.11 g, 30 mmol) and dry THF (70 mL), then 13.3 mL *n*-butyl lithium (2.27 mol/L in hexane) was added with stirring at −78 ℃. After the mixture was stirred for 30 min at −78 ℃, 2, 5-norbornadione **1** (1 g, 8 mmol) was added and the stirring was continued over night while the temperature was slowly raised to r.t. The reaction was poured into cold sat. NH_4Cl (70 mL), and then extracted with Et_2O (60 mL×4). The organic layer was washed with brine, and dried over Na_2SO_4. After removing the solvent, the residue was treated by column chromatography on silica (hexanes∶EtOAc=3∶1, *V*∶*V*), two chromatographic bands were acquired and GC-MS showed that each of the two bands probably contained two isomers, total four isomers were 1.65 g (yield 47%). EIMS *m*/*z*: 440 $[M]^+$ or 438 $[M-2H]^+$

Preparation of (1*R*,2*R*,4*R*,5*R*)-*exo*,*exo*-2,5-dinaphthylbicyclo[2,2,1]heptane-*endo*,*endo*-2,5-diol (12)

12 was prepared according to the procedure given for compound **10**. Yield 62%; white crystals; m.p. 154−56 ℃; $[\alpha]_D^{20}$ +42 (*c* 1.00, MeOH); ^{1}H NMR (600 MHz, THF-d_8) *δ*: 5.52−7.07 (m, 14H, napth-H), 1.37−1.40 (d, *J*=15 Hz, 2H, 2 bridgehead), 1.16−1.17 (s, 2H, bridge), 0.44−0.47 (m, 4H, 2CH_2); ^{13}C NMR (150 MHz, THF-d_8) *δ*: 142.88 (Ar), 133.60 (Ar), 130.13 (Ar), 126.80 (Ar), 126.48 (Ar), 125.60 (Ar), 122.97 (Ar), 122.58 (Ar), 122.32 (Ar), 119.34 (Ar), 77.37 (Ar-C-OH), 45.73 (bridgehead), 38.86 (CH_2), 36.44 (bridge); EIMS *m*/*z*: 380 $[M]^+$; HRMS (TOF ESI) calcd for $C_{27}H_{24}O_2$ $[M+Na]^+$ 403.1669, found 403.1674.

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Preparation of (1*R*,2*R*,4*R*,5*R*)-*endo*,*endo*-2,5-di(2-methoxy)naphthylbicyclo[2,2,1]heptane (11)

11 was prepared according to the procedure given for compound **5**. Starting material was bis-tertiary alcohol **10** (mixture of four isomers: 1 g, 2.27 mmol). Products were treated by column chromatography on silica (hexane∶dichloromethane＝3∶1, *V*∶*V*), two chromatographic bands were acquired and GC-MS showed that each of the two bands probably contained two isomers, total four isomers were 0.38 g (yield 41%). EIMS *m*/*z*: 408 $[M]^+$.

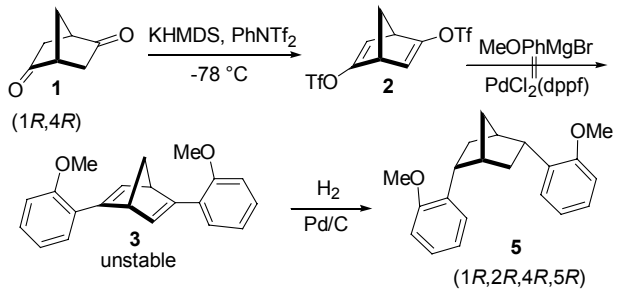
Preparation of (1*R*,2*R*,4*R*,5*R*)-*endo*,*endo*-2,5-dinaphthylbicyclo[2,2,1]heptane (13)

13 was prepared according to the procedure given for compound **5**. Yield 19%; white crystals; m.p. 134—136 ℃; $[\alpha]_D^{20}$ ＋41 (*c* 1.00, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.41—8.12 (m, 14H, ArH), 3.96—4.00 (s, 2H, Ar-CH), 2.95 (s, 2H, bridgehead), 2.11 (s, 2H, bridge), 1.80—1.90 (m, 4H, $2CH_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 137.60 (Ar), 134.17 (Ar), 133.18 (Ar), 128.89 (Ar), 126.81 (Ar), 125.50 (Ar), 125.26 (Ar), 124.98 (Ar), 124.68 (Ar), 124.45 (Ar), 44.54 (Ar-C), 43.03 (bridge), 42.86 (bridgehead), 26.62 (CH_2); EIMS *m*/*z*: 348 $[M]^+$; HRMS (TOF ESI) calcd for $C_{27}H_{24}$ [M＋Na]$^+$ 371.1770, found 371.1778.

Results and Discussion

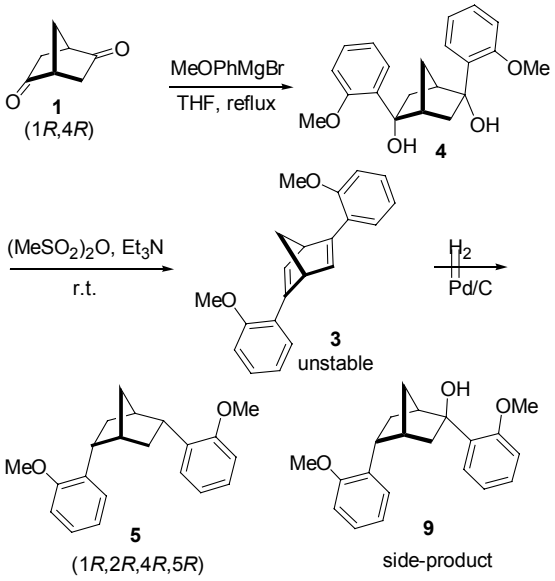
As scheme 1 showed, our initial synthetic approach designed toward diphenylbicyclo[2,2,1] **5** was started from the known chiral 2,5-norbornadione **1**.[17-20] But although the dienolization with KHMDS followed by treatment with $PhNTf_2$ gave a satisfactory yield of bis-triflate **2**, Pd(0)-catalyzed coupling of **2** with Grignard reagent[17,19] for diene **3** was unsuccessful.

Scheme 1 Synthesis of the chiral *endo*-biphenylnorbornane **5** through coupling reaction



As Scheme 2 showed, an alternative effort was made to synthesize biarylnorbornane **5** through the reaction of aryl Grignard reagents with dione **1**, then dehydration of bis-tertiary alcohol **4** with methanesulfonate anhydride and triethylamine at room temperature to afford diene **3**. In the dehydration reaction, we found diene **3** is a structure with high instability. After 30 min of dehydration reaction, we tested the product immediately by GC-MS, the result showed that the bis-tertiary alcohol **4** was completely converted to a pure product diene **3**. But only after 2 h of drying with anhydtate Na_2SO_4, GC-MS showed one side-product with *m*/*z* 324 $[M]^+$ appeared, we speculate that the structure of the side-product may be like **9**, but we failed to separate it out and characterize it.

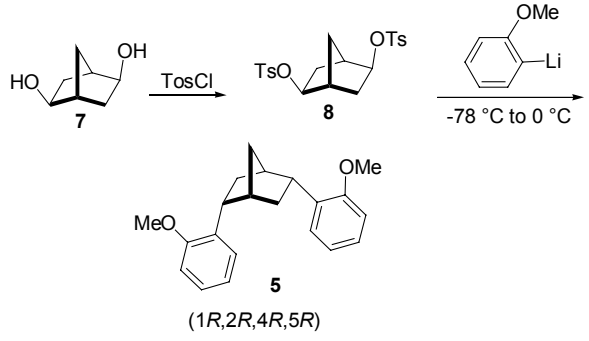
Scheme 2 Synthesis of the chiral *endo*-biphenylnorbornane **5** through dehydration reaction and hydrogenation



Since diene **3** is too sensitive to be present after chromatography over silica, we intended to carry on hydrogenation with Pd on charcoal at once when the immediate dehydration product which contained diene **3** was quickly washed by 10% aqueous HCl to remove residual triethylamine, the result was still only trace of *endo*-biarylnorbornane **5** afforded.

Efforts to synthesize the *endo*-biarylnorbornane **5** from diol **7**[16] through nucleophilic substitution to *p*-toluenesulfonate **8** with 2-methoxyphenyl lithium at different temperature within −78 ℃ to 0 ℃ was also unsuccessful (Scheme 3).

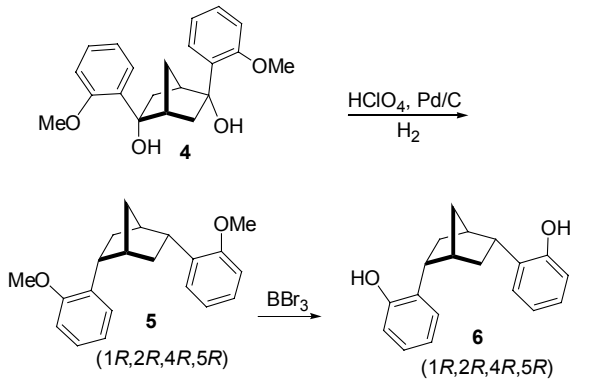
Scheme 3 Synthesis of the chiral *endo*-biphenylnorbornane **5** through nucleophilic substitution to *p*-toluenesulfonate



At last we try to reach *endo*-biarylnorbornane **5**

through direct dehydroxylation of the bis-tertiary alcohol **4** on the condition of hydrogenation with Pd on charcoal and $HClO_4$ as catalysis[21] and fortunately it was successful (Scheme 4), *endo*-biarylnorbornane **5** was afforded with a considerably high yield of 67%. At first it was not certain that biarylnorbornane **5** acquired by the methods was *endo*-conformation though we believe the product through hydrogenation of diene **3** with Pd on charcoal is.[19,20] So the product was mixed with that from hydrogenation of diene **3** and subjected to GC-MS. The test showed the two products had same conformation. Our explanation to the phenomenon is that tertiary alcohol reacts with $HClO_4$ to form carbocation intermediate that is plannar because of its sp^2 hydridization, which makes hydrogen attack the carbocation at C2 or C5 to give saturated norbornane with high *exo*-selectivity so that Ar-C5 or Ar-C2 will form a bond with *endo*-direction. The *endo*-biarylnorbornane **5** was subjected to X-ray structural analysis, and the result is shown in Figure 1 and Table 1.

Scheme 4 Synthesis of the chiral *endo*-biphenylnorbornane **5** through direct dehydroxylation of the bis-tertiary alcohol



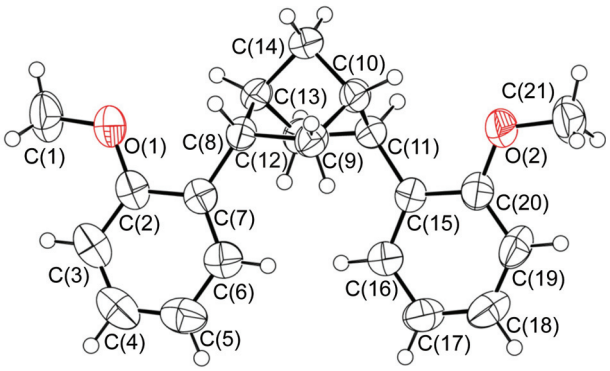


Figure 1 X-ray crystal structure of the chiral *endo*-biarylnorbornane **5**.

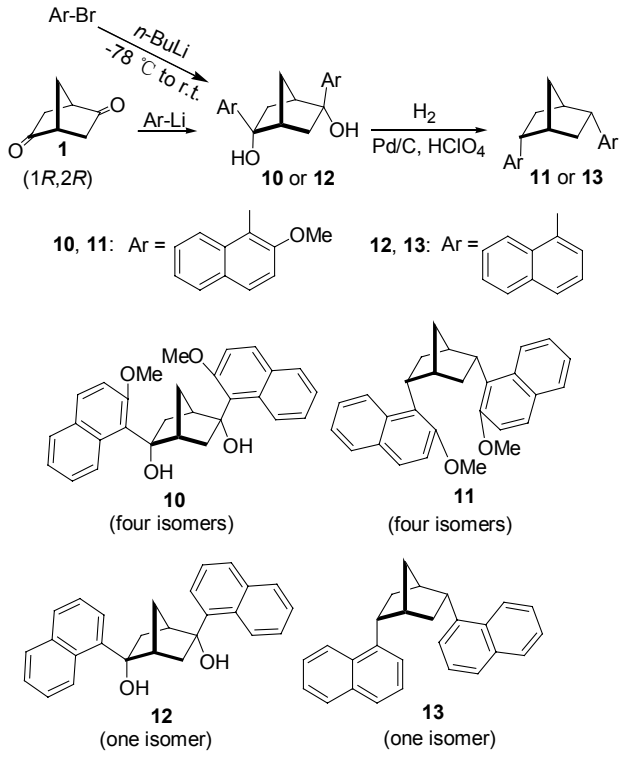
Demethylating *endo*-biarylnorbornane **5** by BBr_3, bisphenol **6** was afforded with a yield of 95%. The bisphenol **6** is a very stable structure, when it was dissolved in toluene and refluxed violently for 8 h, the resalt showed it have no loss in weight and no change in structure and specific rotation.

Table 1 X-ray crystallographic data of the chiral *endo*-biarylnorbornane **5**

Subject	Data
Formula	$C_{21}H_{24}O_2$
Crystal system	Monoclinic
Space group	*P*2(1)
Cell length/nm	*a* 1.0203(8), *b* 0.7485(6), *c* 1.1343(10)
Cell angle/(°)	α 90.00, β 106.886(13), γ 90.00
Cell volume/nm^3	0.82891
Z	2
μ/mm^{-1}	0.078
CCDC depository no.	993604

As Scheme 5 showed, we also synthesized bis-tertiary alcohols **10** and **12** with yields of 47% and 62% respectively through the reaction of aryllithium with dione **1**, and *endo*-biarylnorbornanes **11** and **13** were afforded with yields of 41% and 19% by direct dehydroxylation of bis-tertiary alcohols **10** and **12**. Both the bis-tertiary alcohol **10** and *endo*-biarylnorbornane **11** acquired were probably the mixture of four conformational isomers. Comparing with the bis-tertiary alcohols **4**, **12**, and *endo*-biarylnorbornanes **5**, **13** with only one conformation, we can infer that the steric effects of ethano bridge and methano bridge can not stop the free rotation of benzene ring which attaches to C2 and C5 of norbornane, but once the benzene ring is joined to

Scheme 5 Synthesis of the chiral binaphthylnorbornane skeleton



ortho-substituting group like methoxy group, the rotation will be stopped by ethano bridge and methano bridge. For instance, the methano bridge of bis-tertiary alcohol **10** may prevent the methoxy group and benzo group on the benzene ring from passing by so that each 2-methoxy-naphthyl group can be attached to C2 or C5 with two conformations and two 2-methoxy-naphthyl group will be sure to give four conformational isomers. Due to the same reasons, the *endo*-biarylnorbornane **11** also has four conformational isomers. While for compounds **4**, **12**, **5** and **13** with only one *ortho*-substituting group being joined to the benzene, the other side of the benzene ring still can rotate to pass by the ethano and methano bridge, so that these compounds have only one isomer.

Conclusions

In summary, we describe a highly efficient and practical synthesis for strained special scaffold of chiral *endo*-biarylnorbornane starting from available norbornadione. The structure of the product was illustrated by X-ray structural analysis. It is expected that these novel C_2-symmetric scaffold will find many applications in the fields such as asymmetric catalysis, medicinal chemistry and functional material synthesis. Also the stereoselective preparation of saturated alkane used in the paper by direct dehydroxation of tertiary alcohol may give a valuable reference for the synthesis of other chemicals.

Acknowledgement

This work was supported by National Natural Science Foundation of China (Nos. 30971934, 31272074).

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