Synthesis of Enantiomerically Pure Bis-Sulfinyl Substituted Phenylene Ethynylenes

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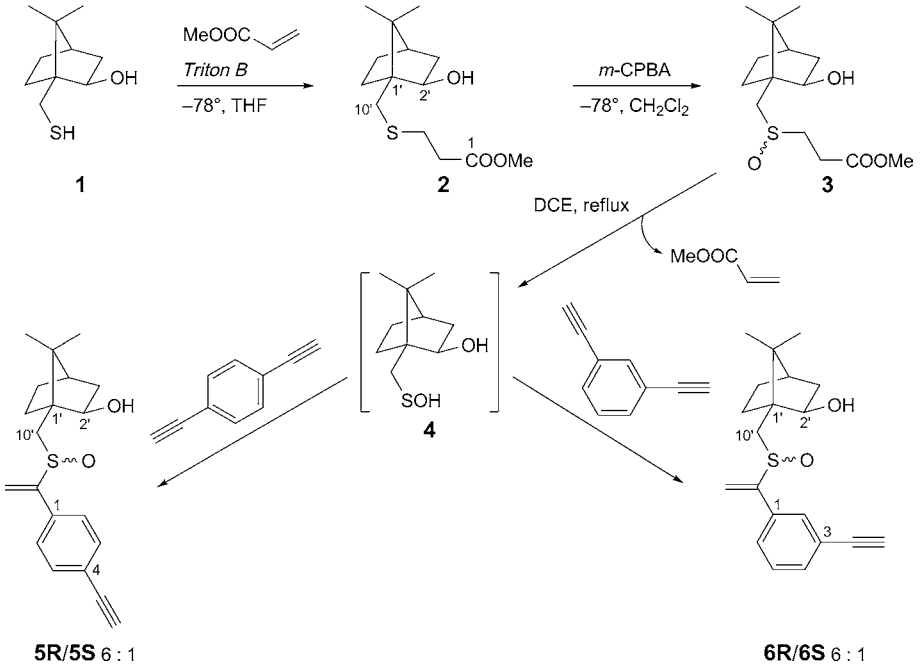
The stereoselective and efficient monoaddition of transient [(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl]methanesulfenic (=(1*S*)-isoborneol-10-sulfenic) acid to isomeric diethynylbenzenes affords {1-[(1*S*)-isoborneol-10-sulfinyl]ethenyl}ethynylbenzenes. Their enantiomerically pure (R_S)-epimers are involved in a Cu-free *Sonogashira* coupling with 1,4-diiodo-2,5-dimethoxybenzene to give C_2-symmetric bis-sulfinyl phenylene ethynylenes, stimulating prototypes of new sulfurated chiral architectures that can find application as chelating agents.

Introduction. – Phenylene ethynylenes with extended conjugated aromatic systems are rigid, rod-like molecules whose functional properties can be tuned by changing the conjugation length, the electronic characteristics of the aryl substituents, or the nature of the terminal substituents [1]. This class of molecules has displayed intriguing luminescent properties and high quantum yields, and has been employed in materials chemistry and molecular electronics. Furthermore, cationic oligo(*p*-phenylene ethynylene)s (OPEs) have been shown to be very effective against both *Gram*-positive and *Gram*-negative strains of bacteria, particularly when irradiated with UV light [2].

In continuing our studies on sulfoxides involved in coordination chemistry [3], we envisaged the possibility of using phenylene ethylene units in the construction of C_2-symmetric molecular architectures containing enantiomerically pure sulfinyl functions as potential chelating agents. In particular, the isoborneol sulfinyl moiety appeared to be a significant chiral controller and an interesting 'structurally privileged' residue [4]. For this purpose, we decided to combine the classical synthetic procedure of OPE preparation, which involves the *Sonogashira* cross-coupling, with the well-known sulfenic acid/alkyne *syn*-addition [5] to obtain sulfinyl derivatives in a stereocontrolled manner. Herein, the results of this synthetic strategy, where enantiomerically pure sulfoxides are involved in a *Sonogashira* Cu-free reaction, to prepare bis-sulfinyl-substituted phenylene ethynylenes are reported. To the best of our knowledge, there are only few reports describing the sulfoxide participation in this kind of reactions, namely a few examples of *Negishi*- and *Suzuki*-type coupling with sulfinyl compounds [6] and one example of *Sonogashira* reaction involving racemic sulfoxides [7].

Results and Discussion. – The synthethic strategy is outlined in *Scheme 1*. Treatment of thiol **1** with *Triton B* (benzyl(trimethyl)ammonium hydroxide) gave a reactive thiolate that immediately added, at −78° and in anhydrous THF, to the conjugated C=C bond of methyl acrylate to afford quantitavely sulfide **2**, which was stereoselectively oxidized by *m*-CPBA (*m*-chloroperoxybenzoic acid) to a mixture of sulfoxide epimers **3**, new precursors of transient sulfenic acid **4**. The diastereoisomeric mixture, where one epimer was predominant (30:1), was not separated, because, at the moment of the subsequent thermolysis, the stereogenic center at the S-atom was lost.

Scheme 1. *Synthetic Route to Diastereoisomeric Sulfoxides* **5** *and* **6**



As reported by *Jones* and co-workers [8], the harshness of the high-temperature conditions in the thermolytic step can affect the yields of the addition products. We had previously used a different precursor of **4**, derived by acrylonitrile [4], able to thermolize above the reflux temperature of xylene mixture (140°). However, our new results on the preparation of other sulfenic acid precursors [3] demonstrated that, together with a comparable stability, methyl 3-[(alkyl)sulfinyl]propanoates such as **3** could be thermolized at lower temperatures, without affecting the final yields. To test the best thermolysis conditions, **3** was heated in different solvents (toluene, 1,4-dioxane, 1,2-dichloroethane (DCE), THF) at their respective reflux temperature, in the presence of an excess (1:6) of two different dialkynes, 1,3- or 1,4-diethynylbenzene. While only decomposition products were obtained above 100° (toluene and dioxane as solvents), **4** was efficiently generated *in situ* in DCE at reflux (83°) and trapped by 1,3- or 1,4-diethynylbenzene to give **5** and **6** in excellent yields (> 70%). Furthermore, even if the reaction times are longer than one day, only traces of sulfenic acid by-products

were detected. Excesses of the dialkynes were recovered from the heads of the chromatographic columns and reutilized. Thermolysis at reflux temperature of THF was too slow to be significant.

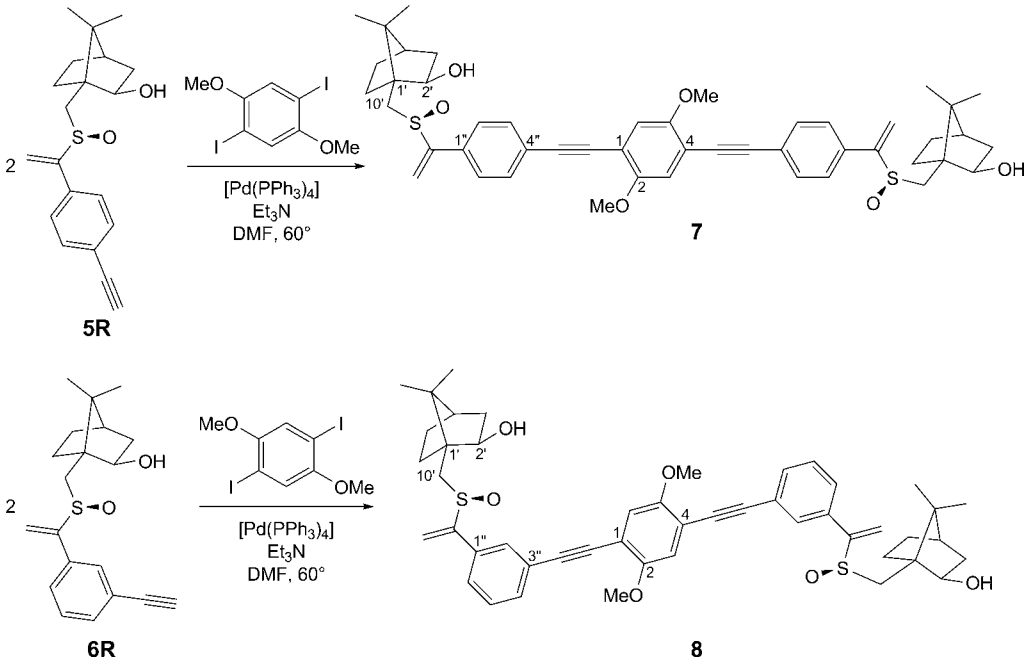
The high diastereoselectivity of both additions (see *Scheme 1*) is ascribable to the preferred conformation adopted by **4**, due to a strong intramolecular H-bond between the sulfenic and the OH functions. This rigid and highly populated conformation forces the diethynylbenzene approach predominantly on the *Re*-face of **4** [4c]. The two couples of epimers **5R**/**5S** and **6R**/**6S** were easily separated by column chromatography and the four compounds were obtained in enantiomerically pure form. The correct configuration at the new stereogenic S-atom was attributed on the basis of previously reported crystallographic data [4d] that assigned the (R_S)-configuration at the chromatographically more mobile epimers. Reactions of both dialkynes with an excess of sulfenic acid precursor **3**, in DCE at 83°, gave only **5** or **6**, together with sulfenic acid self-coupling products. All attempts to add a second molecule of **4** to the residual C≡C bond of the major epimers **5R** and **6R** did not give any result. Reaction of both alkynes **5R** or **6R** in the presence of an excess (1 : 4) of **3**, in DCE at 83°, led only to the isolation of unreacted **5R** or **6R**, together with self-coupling products of **4**. Furthermore, an attempt of simultaneous addition of two molecules of **4** on both C≡C bonds of the dialkynes failed, too. These negative results can be explained by the high sterical requirements of the first addition products that obstruct a second productive sulfenic acid approach.

Aiming at the construction of new C_2-symmetric molecular architectures containing 'privileged structures' like the isobornyl one, together with two enantiomerically pure sulfinyl functions, we tried to exploit the reactivity of the residual terminal C≡C bond of **5R** and **6R** in cross-coupling reactions, in particular in the Cu-free *Sonogashira* reaction, not previously applied to sulfoxides. The results of cross-coupling reactions of **5R** or **6R** with 1,4-diiodo-2,5-dimethoxybenzene at 60° in DMF solution, and in the presence of a large excess of Et_3N and a catalytic amount of $Pd(PPh_3)_4$ are outlined in *Scheme 2*. Despite the large excess of base, no racemization at the S-atom occured, and enantiomerically pure C_2-symmetric bis-sulfoxides **7** and **8** were obtained as sole products in high yields.

An inspection of the ^{1}H-NMR spectra of **5R**, **5S**, and **7**, as for **6R**, **6S**, and **8**, was useful to confirm the configurations at the S-atom. As shown in the *Figure*, the chemical shifts of the lower-field signals of the *AB* pattern related to the diastereotopic isoborneol $CH_2(10')$ H-atoms have significant difference (δ(H) 0.3) for (R_S)- or (S_S)-epimers. This feature is maintained in the final cross-coupling products **7** and **8**, where the only *AB* system present is strictly related to the (R_S) configuration. Altogether the simplicity of the ^{1}H-NMR spectra of **7** and **8** confirms their C_2 symmetry.

Conclusions. – Finding an efficient sulfenic-acid precursor, joined with the suitable cross-coupling conditions, opens access to C_2-symmetric enantiomerically pure bis-sulfoxides. It is the first time that Cu-free *Sonogashira* reaction is reported for enantiomerically pure sulfoxides, and its occurrence with retention of configuration of the sulfoxide has been verified. This result can open the way to the construction of new S-containing chiral molecular architectures that can find application in many fields, from the biology to the organocatalysis.

Scheme 2. *Synthesis to* **7** *and* **8**



Experimental Part

General. Solvents were purified according to standard procedures. All reactions were monitored by TLC on commercially available precoated silica gel plates (SiO_2; *60 F_{254}*; *Aldrich*), and the products were visualized with vanillin (1 g dissolved in MeOH (60 ml) and conc. H_2SO_4 (0.6 ml)). Column chromatography (CC): SiO_2 *60* (*Aldrich*). ^{1}H- and ^{13}C-NMR spectra: *Varian 500* spectrometer (at 500 and 125 MHz resp.); δ in ppm rel. to Me_4Si as internal standard, J in Hz, assignments supported by HSQC and COSY experiments. Elemental analysis: *FISONS EA1108*; in %.

Methyl 3-({[(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl]methyl}sulfanyl)propanoate (**2**). To a soln. of **1** (1.90 g, 10.20 mmol) in anh. THF (43 ml), under Ar at $-78°$, *Triton B* soln. (40 wt-% in MeOH, 0.51 ml, 1.33 mmol) was added. After 5 min stirring at $-78°$, methyl acrylate (1.03 ml, 11.44 mmol) was added, and the mixture was allowed to stirred at r.t., until the reaction was complete (overnight, AcOEt/hexane 4:6). The mixture was concentrated *in vacuo*, and the crude residue was purified by flash CC (AcOEt/hexane 1:9) to provide **2** (2.63 g, 9.65 mmol, 95%). Transparent oil. R_f (AcOEt/hexane 3:7) 0.65. $[\alpha]_D^{25} = -48$ ($c = 0.007$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.82, 1.05 (2 *s*, Me(8′), Me(9′)); 1.00–1.76 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.63–2.84 (*m*, CH_2(2), CH_2(3), CH_2(10′), OH); 3.70 (*s*, MeO); 3.85 (*dd*, J(2′,3′) = 8.3, 3.9, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 19.9, 20.6 (C(8′), C(9′)); 27.1, 31.0 (C(5′), C(6′)); 28.4 (C(3)); 31.9 (C(10′)); 34.2 (C(2)); 39.1 (C(3′)); 45.1 (C(4′)); 47.6 (C(7′)); 51.9 (MeO); 52.1 (C(1′)); 76.7 (C(2′)); 172.5 (C(1)). Anal. calc. for $C_{14}H_{24}O_3S$ (272.40): C 61.73, H 8.88; found: C 61.71, H 8.89.

Methyl 3-({[(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl]methyl}sulfinyl)propanoate (**3**; mixture of epimers). A soln. of **2** (2.61 g, 9.58 mmol) in CH_2Cl_2 (40 ml) was stirred at $-78°$, and a soln. of *m*-CPBA (77%, 2.15 g, 9.58 mmol) in CH_2Cl_2 (40 ml) was slowly added. The reaction was monitored by TLC and appeared complete by the end of the oxidant addition. The reaction was quenched by adding aq. $Na_2S_2O_3$ (10 wt-%), and the combined org. extracts were washed twice with a sat. $NaHCO_3$ soln. and twice with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to afford **3**

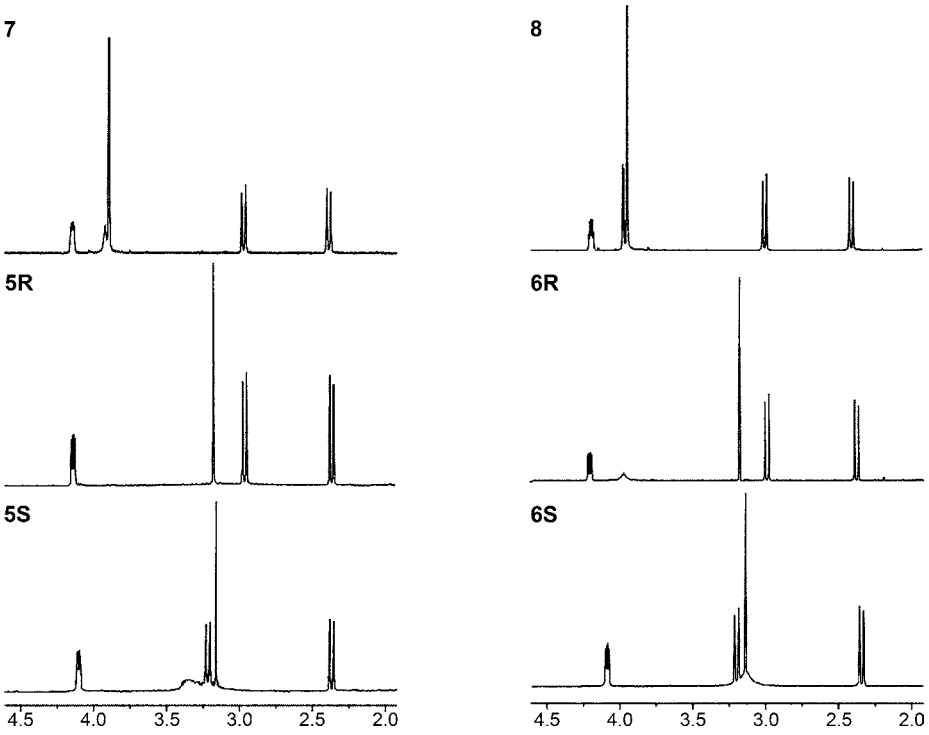


Fig. 1. *Significant parts of* ^{1}*H-NMR spectra of [1-[(1*S*)-isoborneol-10-sulfinyl]ethenyl]ethynylbenzenes* **5** *and* **6**, *and phenylene ethynylenes* **7** *and* **8**

(2.62 g, 9.08 mmol, 95%). Transparent oil. Major epimer: R_f (AcOEt/hexane 3:7) 0.10. ^{1}H-NMR ($CDCl_3$): 0.63, 1.00 (2 *s*, Me(8′), Me(9′)); 1.05–1.85 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.38, 3.25 (*AB*, J_{AB} = 13.2, CH_2(10′)); 2.79–3.11 (*m*, CH_2(2), CH_2(3), OH); 3.71 (*s*, MeO); 4.02 (*dd*, *J*(2′,3′) = 8.3, 3.9, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 19.8; 20.4 (C(8′), (C(9′)); 26.7 (C(2)); 27.0; 30.8 (C(5′), C(6′)); 38.4 (C(3′)); 44.9 (C(4′)); 48.0 (C(3)); 48.1 (C(7′)); 49.2 (C(1′)); 52.2 (MeO); 53.1 (C(10′)); 76.8 (C(2′)); 171.6 (C(1)). Anal. calc. for $C_{14}H_{24}O_4S$ (288.40): C 58.30, H 8.39; found: C 58.28, H 8.40.

Thermolysis of Sulfoxides **3** *in the Presence of Diethynylbenzenes. General Procedure.* A soln. of sulfoxides **3** (0.70 g, 2.43 mmol) and commercial diethynyl acceptor (1.84 g, 14.59 mmol) in DCE (10 ml) was heated at reflux (83°) and maintained under stirring until the disappearance of starting sulfoxides (TLC; overnight). The solvent was removed under reduced pressure, and the crude material was purified by CC (SiO_2; AcOEt/hexane, gradient from 1:9 to 3:7) to give the unreacted alkyne and **5** (70% total yield of epimeric mixture) or **6** (75% total yield of epimeric mixture). Epimers are reported in order of retention time.

*(1*S*,2*R*,4*R*,*R*$_S$*)-1-([[1-(4-Ethynylphenyl)ethenyl]sulfinyl]methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol* (**5R**; major, more mobile). White crystals. Yield: 60%. M.p. 164–166°. R_f (AcOEt/hexane 3:7) 0.75. $[\alpha]_D^{25} = -10$ (*c* = 0.007, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.63, 1.00 (2 *s*, Me(8′), Me(9′)); 1.05–1.85 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.35 and 2.95 (*AB*, J_{AB} = 13.7, CH_2(10′)); 3.17 (*s*, H–C≡); 4.16 (*dd*, *J*(2′,3′) = 7.9, 4.4, H–C(2′)); 6.07, 6.14 (2 *s*, =CH_2); 7.35 and 7.53 (*AA'BB'*, J_{ortho} = 8.3, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR ($CDCl_3$): 19.8, 20.3 (C(8′), C(9′)); 27.1, 30.8 (C(5′), C(6′)); 38.4 (C(3′)); 45.1 (C(4′)); 48.1 (C(7′)); 51.5 (C(1′)); 55.2 (C(10′)); 76.9 (C(2′)); 79.1 (≡CH); 82.7 (C≡); 117.5 (=CH_2); 123.4 (C(4)); 126.2, 132.9 (C(2), C(3), C(5), C(6)); 134.0 (C(1)); 152.3 (C=). Anal. calc. for $C_{20}H_{24}O_2S$ (328.47): C 73.13, H 7.36; found: C 73.16, H 7.37.

(1S,2R,4R,S$_S$)-1-({[1-(4-Ethynylphenyl)ethenyl]sulfinyl}methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (**5S**; minor, less mobile). Pale-yellow oil. Yield: 10%. R_f (AcOEt/hexane 3:7) 0.45. $[\alpha]_D^{25} = -8$ (c = 0.021, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.65, 0.99 (2 *s*, Me(8′), Me(9′)); 1.05–1.80 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.37 and 3.21 (*AB*, J_{AB} = 14.1, CH_2(10′)); 3.16 (*s*, H–C≡); 3.38 (br. *s*, OH); 4.10 (*dd*, *J*(2′,3′) = 7.8, 3.9, H–C(2′)); 6.09, 6.16 (2 *s*, =CH_2); 7.39 and 7.50 (*AA'BB'*, J_{ortho} = 8.3, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR ($CDCl_3$): 20.1, 20.3 (C(8′), C(9′)); 29.6, 31.3 (C(5′), C(6′)); 40.0 (C(3′)); 44.5 (C(4′)); 48.9 (C(7′)); 52.3, 52.4 (C(1′), C(10′)); 76.2 (C(2′)); 79.0 (≡CH); 82.7 (C≡); 118.2 (=CH_2); 123.2 (C(4)); 126.3, 132.7 (C(2), C(3), C(5), C(6)); 134.1 (C(1)); 151.9 (C=). Anal. calc. for $C_{20}H_{24}O_2S$ (328.47): C 73.13, H 7.36; found: C 73.11, H 7.35.

(1S,2R,4R,R$_S$)-1-({[1-(3-Ethynylphenyl)ethenyl]sulfinyl}methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (**6R**; major, more mobile). Yellow crystals. Yield: 64%. M.p. 108–110°. R_f (AcOEt/hexane 3:7) 0.78. $[\alpha]_D^{25} = +2$ (c = 0.082, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.64, 1.02 (2*s*, Me(8′), Me(9′)); 1.10–1.93 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.36 and 2.96 (*AB*, J_{AB} = 13.2, CH_2(10′)); 3.15 (*s*, H–C≡); 3.94 (br. *s*, OH); 4.17 (*dd*, *J*(2′,3′) = 8.3, 3.9, H–C(2′)); 6.07, 6.14 (2 *s*, =CH_2); 7.36–7.54 (*m*, H–C(2), H–C(4), H–C(5), H–C(6)). ^{13}C-NMR ($CDCl_3$): 19.8, 20.2 (C(8′), C(9′)); 26.9, 30.6 (C(5′), C(6′)); 38.2 (C(3′)); 44.9 (C(4′)); 47.9 (C(7′)); 51.3 (C(1′)); 54.9 (C(10′)); 76.7 (C(2′)); 78.5 (≡CH); 82.3 (C≡); 117.4 (=CH_2); 123.2 (C(3)); 126.4, 129.1, 129.7, 132.8 (C(2), C(4), C(5), C(6)); 133.7 (C(1)); 152.0 (C=). Anal. calc. for $C_{20}H_{24}O_2S$ (328.47): C 73.13, H 7.36; found: C 73.15, H 7.36.

(1S,2R,4R,S$_S$)-1-({[1-(3-Ethynylphenyl)ethenyl]sulfinyl}methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (**6S**; minor, less mobile). Pale-yellow oil. Yield: 11%. R_f (AcOEt/hexane 3:7) 0.50. $[\alpha]_D^{25} = -4$ (c = 0.039, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.62, 0.96 (2*s*, Me(8′), Me(9′)); 1.00–1.83 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.33 and 3.17 (*AB*, J_{AB} = 14.2, CH_2(10′)); 3.11 (br. *s*, OH); 3.12 (*s*, H–C≡); 4.07 (*dd*, *J*(2′,3′) = 7.5, 3.5, H–C(2′)); 6.05, 6.12 (2 *s*, =CH_2); 7.32–7.53 (*m*, H–C(2), H–C(4), H–C(5), H–C(6)). ^{13}C-NMR ($CDCl_3$): 20.0, 20.2 (C(8′), C(9′)); 27.3, 31.2 (C(5′), C(6′)); 40.1 (C(3′)); 44.5 (C(4′)); 48.7 (C(7′)); 52.2, 52.5 (C(1′), C(10′)); 76.1 (C(2′)); 78.4 (≡CH); 82.6 (C≡); 118.0 (=CH_2); 123.0 (C(3)); 126.7, 129.0, 129.8, 132.7 (C(2), C(4), C(5), C(6)); 134.1 (C(1)); 151.5 (C=). Anal. calc. for $C_{20}H_{24}O_2S$ (328.47): C 73.13, H 7.36; found: C 73.14, H 7.35.

General Procedure for the Preparation of **7** *and* **8** *by Coupling Reaction in the Presence of [Pd(PPh$_3$)$_4$] and Et$_3$N.* [$Pd(PPh_3)_4$] (0.07 g, 0.06 mmol), 1,4-diiodo-2,5-dimethoxybenzene (0.20 g, 0.51 mmol), and the alkyne **5R** or **6R** (0.39 g, 1.19 mmol) were dissolved in dry DMF (8 ml). To this mixture Et_3N (8 ml) was added. The mixture was heated at 60° and maintained under continuous stirring under Ar until the disappearance of the alkyne was verified by TLC. Solvents were removed under reduced pressure. The crude product was subjected to CC (SiO_2; AcOEt/hexane 3:7).

p-*Diisoborneolsulfinylethenyl OPE* (=*(1S,2R,4R,R$_S$)-1,1′-[(2,5-Dimethoxybenzene-1,4-diyl)bis-(ethyne-2,1-diylbenzene-4,1-diylethene-1,1-diylsulfinylmethanediyl)]bis(7,7-dimethylbicyclo[2.2.1]heptan-2-ol)*; **7**). Reaction time: 3 h. Yellow crystals. Yield: 85%. M.p. 200–202°. R_f (AcOEt/hexane 4:6) 0.55. $[\alpha]_D^{25} = +9$ (c = 0.011, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.64, 1.02 (2 *s*, Me(8′), Me(9′)); 1.11–1.88 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.38 and 2.97 (*AB*, J_{AB} = 13.4, CH_2(10′)); 3.92 (*s*, MeO); 3.94 (br. *s*, OH); 4.17 (*dd*, *J*(2′,3′) = 8.3, 4.4, H–C(2′)); 6.10, 6.15 (2 *s*, =CH_2); 7.04 (*s*, H–C(3), H–C(6)); 7.40 and 7.62 (*AA'BB'*, J_{ortho} = 8.3, H–C(2″), H–C(3″), H–C(5″), H–C(6″)). ^{13}C-NMR ($CDCl_3$): 19.7, 20.3 (C(8′), C(9′)); 27.0, 30.8 (C(5′), C(6′)); 38.4 (C(3′)); 45.0 (C(4′)); 48.0 (C(7′)); 51.4 (C(1′)); 55.2 (C(10′)); 56.4 (MeO); 76.9 (C(2′)); 87.4, 92.2 (C≡C); 113.2 (C(1), C(4)); 115.5 (C(3), C(6)); 117.2 (=CH_2); 124.4 (C(4″)); 126.2, 132.4 (C(2″), C(3″), C(5″), C(6″)); 132.0 (C(1″)); 152.3 (C=); 153.9 (C(2), C(5)). Anal. calc. for $C_{48}H_{54}O_6S_2$ (791.07): C 72.88, H 6.88; found: C 72.90, H 6.90.

m-*Diisoborneolsulfinylethenyl OPE* (=*(1S,2R,4R,R$_S$)-1,1′-[(2,5-Dimethoxybenzene-1,4-diyl)bis-(ethyne-2,1-diylbenzene-3,1-diylethene-1,1-diylsulfinylmethanediyl)]bis(7,7-dimethylbicyclo[2.2.1]heptan-2-ol)*; **8**). Reaction time: 20 h. Yellow crystals. Yield: 80%. M.p. 102–104°. R_f (AcOEt/hexane 4:6) 0.47. $[\alpha]_D^{25} = +10$ (c = 0.016, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.62, 1.02 (2 *s*, Me(8′), Me(9′)); 1.12–1.83 (*m*, CH_2(3′), H–C(4′), CH_2(5′), CH_2(6′)); 2.39 and 2.98 (*AB*, J_{AB} = 13.2, CH_2(10′)); 3.93 (*s*, MeO); 3.95 (*d*, OH); 4.17 (*ddd*, *J*(2′,3′) = 7.8, 3.9, *J*(2′,OH) = 2.9, H–C(2′)); 6.09, 6.16 (2 *s*, =CH_2); 7.06 (*s*, H–C(3), H–C(6)); 7.34–7.61 (*m*, H–C(2″), H–C(4″), H–C(6″)). ^{13}C-NMR ($CDCl_3$): 19.7, 20.3 (C(8′), C(9′)); 27.0, 30.7 (C(5′), C(6′)); 38.4 (C(3′)); 45.1 (C(4′)); 48.1 (C(7′)); 51.4 (C(1′)); 55.1 (C(10′)); 56.4 (MeO); 76.9 (C(2′)); 86.7, 94.0 (C≡C); 113.2 (C(1), C(4)); 115.5 (C(3), C(6)); 117.6 (=CH_2); 124.4 (C(3″)); 126.1,

129.2, 129.6, 132.5 (C(2″), C(4″), C(5″), C(6″)); 134.0 (C(1″)); 152.3 (C=); 153.9 (C(2), C(5)). Anal. calc. for $C_{48}H_{54}O_6S_2$ (791.07): C 72.88, H 6.88; found: C 72.91, H 6.87.

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