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Synthesis of 3-Bromosubstituted 2-Arylbornylenes by Cross-Coupling

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Abstract—A catalyzed reaction of aryl group addition to bornene system is reported. This reaction is interesting for designing new chiral ligands based on camphor.

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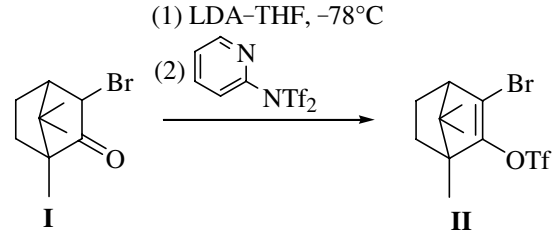
The principal stage of the synthesis of new chiral ligands based on camphor [1] is a catalytic addition of an aryl group to the bornene skeleton. The traditional way of aryl group introduction into the position *2* of bornen system is through Grignard reaction. Due to strong enolization of camphor the addition of arylmagnesium compounds occurred with a low yield [2]. The yield is enhanced by adding equimolar quantity of cerium chloride [3]. Yet even when the corresponding substituted borneol is obtained, its further transformation into arylbornylene is complicated by Wagner–Meerwein rearrangement resulting in the predominant formation of camphene [4]. The camphor functionalized in the position *3*, e.g., 3-bromocamphor, failed to be transformed into 2-substituted borneol even in the presence of cerium chloride. Therefore we planned to use the cross-coupling reaction to prepare 3-bromo-2-arylbornylene. The 2-trifluoromethylsulfoxybornylene is known to successfully participate in the cross-coupling [5, 6].

In the first stage proceeding from available bromocamphor (**I**) we prepared triflate **II** by deprotonation using LDA followed by reaction of the formed enol with pyridine triflimide (Scheme 1).

In [6] a synthesis was described of new P,N-ligands applying a cross-coupling of pyridine organozinc derivatives with triflate derivatives of terpenes. Our attempt to carry out an analogous cross-coupling of dimethylthiophene organozinc derivative with obtained triflate **II** was unsuccessful. Only the use of Grignard reagent **III** and traditional for such reactions nickel catalyst [7, 8] led to the formation of trace amounts of compound **IV** accompanied with prevailing homocoupling product **V** (Scheme 2).

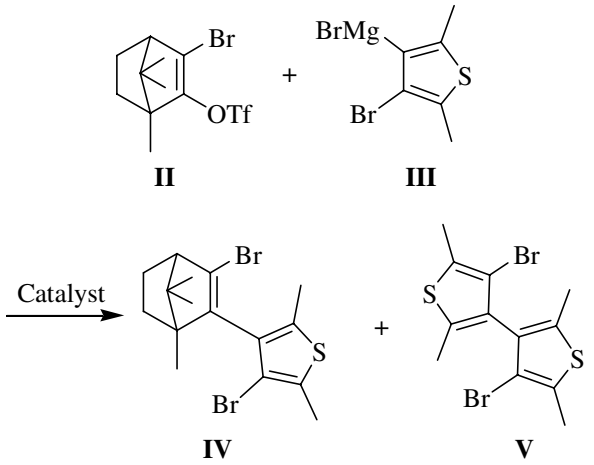
A selection of catalyst was performed to increase the yield of compound **IV**. The published data suggest that the cross-coupling of enol triflate with Grignard reagents

Scheme 1.



I **II**

Scheme 2.



II **III** **IV** **V**

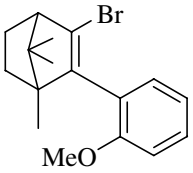
Yields of cross-coupling products obtained from compounds **II** and **III** depending on reaction conditions and catalyst applied (GLC data)

Catalyst[a]	Ligand	Salt added	Time, h	Temperature, °C	Yield, %			
					II	**III**	**IV**	**V**
$Ni(PPh3)_2Cl_2$			38	20	40.5	21.0	6.5	21.8
$Ni(PPh3)_2Cl_2$			7	70	41.7	20.8	2.1	25.4
$Ni(dppe)Cl_2$			38	20	36.9	54.3	0	0
$Ni(dppe)Cl_2$			7	70	35.9	55.4	0	0
$Ni(dppp)Cl_2$			38	20	35.4	48.6	0	0
$Ni(dppp)Cl_2$			7	70	31.9	47.6	0	0
$Pd(PPh_3)_4$			36	20	43.0	36.4	0	0
$Pd(PPh_3)_4$		LiCl	36	20	36.6	48.2	0	0
$Pd(PPh_3)_4$		$ZnBr_2$	36	20	40.6	32.9	5.3	4.9
$Pd(PPh_3)_4$			7	70	41.2	3.2	6.1	7.4
$Pd(OAc)_2$			25	40	41.7	36.3	0	9.6
$Pd(OAc)_2$	$PFur_3$		25	40	41.4	27.3	5.4	7.9
$Pd_2(dba)_3$	$PFur_3$	LiCl	48	20	34.5	55.9	0	0
$Pd_2(dba)_3$	$PFur_3$	LiCl	7	70	35.3	54.7	0	0
$Pd_2(dba)_3$	$PFur_3$	CuI	48	20	40.5	33.3	0	16.7
$Pd_2(dba)_3$	$PFur_3$	CuI	7	70	37.6	29.3	7.2	11.2
$Pd(OAc)_2$	$BuPAd_2$		25	40	58.4	8.7	0	19.9
$Pd(OAc)_2$	$BuPAd_2$	$ZnBr_2$	25	40	62.9	0	0	29.1
$Pd(PhCN)_2Cl_2$	$BuPAd_2$		4	20	33.9	36.4	0	17.8
$Pd(cod)Cl_2$	$BuPAd_2$		4	20	36.4	42.0	0	8.1
$Pd(PhCN)_2Cl_2$	PBu_3		4	20	31.9	52.8	0	10.2
$Pd(cod)Cl_2$	PBu_3		4	20	26.1	51.4	0	8.8
$Pd(PhCN)_2Cl_2$	PCy_3		4	20	30.9	54.5	0	9.8
$Pd(cod)Cl_2$	PCy_3		4	20	27.6	54.7	0	9.1
$Pd(PhCN)_2Cl_2$	$P(o\text{-}Tol)_3$		4	20	34.9	48.6	0	11.1
$Pd(cod)Cl_2$	$P(o\text{-}Tol)_3$		4	20	28.5	48.7	0	9.1
$Pd(OAc)_2$	PPh_3		25	40	44.3	39.9	0	8.4
$Pd(OAc)_2$	PPh_3	$ZnBr_2$	25	40	22.8	9.6	43.8	15.5
$Pd(PhCN)_2Cl_2$	PPh_3		25	20	17.4	28.1	38.2	6.6
$Pd(COD)Cl_2$	PPh_3		4	20	23.6	39.4	16.6	8.4
$Pd(PPh_3)_2Cl_2$			38	20	21.0	17.5	52.5	3.9
$Pd(PPh_3)_2Cl_2$			25	40	13.5	13.1	54.0	12.3
$Pd(PPh_3)_2Cl_2$		LiCl	48	20	41.7	39.7	7.6	0
$Pd(PPh_3)_2Cl_2$		$ZnBr_2$	25	40	21.0	11.8	41.5	16.6
$Pd(PhCN)_2Cl_2$	$AsPh_3$		4	20	24.8	44.9	10.7	8.7
$Pd(cod)Cl_2$	$AsPh_3$		4	20	26.7	37.2	13.4	8.7
$Pd(cod)Cl_2$	dppe		4	20	29.3	48.3	0	8.7
$Pd(cod)Cl_2$	dppb		4	20	32.1	47.4	0	10.8
$Pd(dcpf)Cl_2$			4	20	26.8	52.0	0	9.3
$Pd(dppf)Cl_2$			4	20	25.2	52.6	0	10.0
$Pd(d\text{-}o\text{-}tpf)Cl_2$			4	20	24.9	52.0	0	9.2

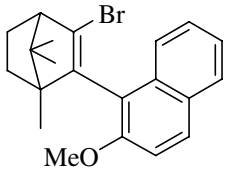
[a] dppe is 1,2-bis(diphenylphosphino)ethane; dppp is 1,3-bis(diphenylphosphino)propane; dppb is 1,3-bis(diphenylphosphino)butane; dba is dibenzylideneacetone; cod is 1,4-cyclooctadiene; dcpf is bis-1,1'-(dicyclohexylphosphino)ferrocene; dppf is bis-1,1'-(diphenylphosphino)-ferrocene; d-*o*-tpf is bis-1,1'-(di-*o*-tolylphosphino)ferrocene.

occurred successfully in the presence of nickel and palladium complexes [8–10].

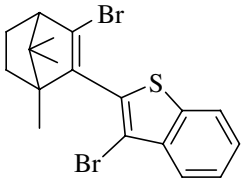
The data in the table show that the palladium complexes are more preferable than nickel ones. At the use in the palladium catalytic complexes of basic ligands ($PFur_3$, $BuPAd_2$, PBu_3, PCy_3) and of bulky $P(o\text{-Tol})_3$ the main reaction product is the unwanted compound **V** whereas the palladium complexes with ligands of low basicity PPh_3 and $AsPh_3$ catalyze the reaction in the desired direction. The bidentate ligands tested in this study led to the formation of exclusively compound **V**. The catalysis with the complex $Pd(PPh_3)_2Cl_2$ resulted in the maximum yield of compound **IV**. The higher temperature of reaction accelerated it and increased the fraction of homocoupling product **V**. The lithium chloride addition considerably decelerated the reaction, and the addition of zinc bromide affected it insignificantly. Further optimization of the process on a larger scale showed that the reaction was completed within 10 h at 50°C applying 5 mol% of the catalyst. We succided in isolating compound **IV** in an overall yield 78%.



VI



VII



VIII

Using the catalyst thus optimized we also prepared phenyl **VI**, naphthyl **VII**, and benzothienyl **VIII** derivatives. In the latter case a raise in temperature to 70°C was required, and compound **VIII** formed therewith in 51% yield.

Compounds **IV, VI–VIII** were obtained as mixtures of two atropoisomers. In the NMR spectra of compounds **VI** and **VIII** at the room temperature a characteristic peaks broadening is observed due to conformational isomerism with coalescence temperature around 60 and 40°C, respectively. This fact indicates a low barrier to racemization for the phenyl and benzothienyl fragments. Dimethylthienyl (**IV**) and naphthyl (**VII**) derivatives did not suffer racemization even at boiling in dimethyl sulfoxide. At the use of optimized catalyst dibromide **IV** formed with a prevalence of one of the atropoisomers in a ratio 9:1. The configuration of the main atopoisomer (R_a) was established by NMR spectroscopy. Compound **VII** was obtained as a mixture of two atropoisomers in a ratio 3:2, and from ethanol was crystallized a mixture of atropoisomers in a ratio 1:1.

Thus we optimized the catalytic cross-coupling of 3-bromocamphor enol triflate with Grignard reagents and prepared a series of new 3-bromosubstituted 2-arylbornylenes, important intermediate products in the synthesis of new chiral ligands.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker AMX at operating frequency 500 MHz. Electron-impact mass spectra with precision measurement of *m/z* value were obtained on MKh-1310 device coupled with a computer CM-4, ionizing electrons energy 70 eV, ion source temperature up to 200°C. All operations were carried out under an atmosphere of dry argon. The solvent before use were dryed by standard procedures. Palladium complexes and phosphine ligands were purchased from Aldrich. $BuPAd_2$, trade mark Cataxium® A, was provided by Degussa. 2-[*N,N*-Bis(trifluorosulfonyl)amino]pyridine [11], 3,4-dibromo-1,5-dimethylthiophene [12], 2,3-dibromo[*b*]benzothiophene [13], 1-bromo-2-methoxynaphthalene [14], $Pd(dcpf)Cl_2$, dichloro[bis-1,1'-(dicyclohexylphosphino)]ferrocenepalladium(II) [15], Pd(d-*O*-tpf)Cl_2, dichloro[bis-1,1'-(di-*o*-tolylphosphino)]ferrocenepalladium(II) [16] were prepared by known methods.

(1*R*)-3-Bromo-2-bornen-2-yl trifluoromethanesulfonate (II). To a solution of 120 g (0.52 mol) of (1*R*)-3-bromocamphor in 650 ml of anhydrous THF was added dropwise at–50 to –60°C 300 ml of 1.8 M solution of LDA in a mixture THF–heptane–ethylbenzene. After stirring for 30 min at–50 to –60°C was added dropwise a solution of 187 g (0.52 mol)of 2-[*N,N*-bis(trifluoromethanesulfonyl)amino]pyridine in 200 ml of THF. The reaction mixture was slowly (within 10 h) warmed at stirring to room temperature, then poured into ice water (500 ml). The reaction product was extracted into ethyl ether (8×50 ml), the combined extracts were washed with cooled 2 N solution of NaOH, then with saturated NaCl solution, dried with anhydrous magnesium sulfate, and evaporated in a water-jet pump vacuum. The residue was mixed with 200 ml of hexane, the heterogeneous mixture was filtered through a small bed of basic alumina, and

the filtrate was evaporated. The distillation of the residue yielded 173.7 g (92%) of compound **II**, bp 60–63°C (0.2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 s (3H, CH_3), 0.93 s (3H, CH_3), 1.03 s (3H, CH_3), 1.23 d.d.d (1H, *J* 12.6, 9.2, 3.7 Hz), 1.43 d.d.d (1H, *J* 12.4, 8.9, 3.4 Hz), 1.62 d.d.d (1H, *J* 12.4, 8.5 3.9 Hz), 1.87 d.d.t (1H, *J* 12.5, 8.6, 3.7 Hz), 2.46 d (1H, *J* 3.7 Hz). ^{13}C ($CDCl_3$), δ, ppm: 9.95, 18.71, 19.36, 24.96, 32.05, 56.16, 56.87, 58.72, 113.28, 118.43 q (*J* 320.3 Hz), 151.99. Mass spectrum, *m/z* (I_{rel}, %): 364 (100), 362 (98), 365 (13), 363 (13), 366 (4).

Screening of catalysts. Catalysts (0.1 mmol of complex and 0.12 mmol of ligand) were charged into Schlenk flasks in an argon flow, and into each flask was poured 2.4 ml of 0.5 M of Grignard reagent solution prepared from 3,4-dibromo-1,5-dimethylthiophene in anhydrous THF. Then 4 ml of 0.25 M solution of compound **II** in anhydrous THF was added, and the content of the flasks was stirred under an argon atmosphere at the temperature and for the time indicated in the table. The reaction was quenched by adding 1 ml of MeOH. The reaction mixture was filtered through alumina and analyzed by GLC. In the NMR spectra were observed weak signals from camphor, 3,4-dibromo-1,5-dimethylthiophene, and 3-bromocamphor; these compounds were not cited in the table.

(1*R*)-3-Bromo-2-(4-bromo-1,5-dimethyl-3-thienyl)bornylene (IV). A solution of Grignard reagent prepared from 116 g (0.43 mol) of 3,4-dibromo-1,5-dimethylthiophene and 12.2 g (0.5 mol) of magnesium activated with iodine vapor in 400 ml of anhydrous THF was charged under argon into a flask containing 11.6 g (16.5 mmol) of $Pd(PPh_3)_2Cl_2$ in 100 ml of anhydrous THF. After adding 120 g (0.33 mol) of compound **II** the reaction mixture was stirred at 50°C for 10 h. Excess Grignard reagent was decomposed by passing carbon dioxide through the reaction mixture cooled by ice bath, and the solution obtained was washed with half-saturated ammonium chloride solution. The reaction product was additionally extracted from the water layer by ethyl ether, the combined organic solvents were washed with a saturated NaCl solution, dried with anhydrous magnesium sulfate, and evaporated in a water-jet pump vacuum. The residue was dissolved in 50 ml of ethyl ether, and 150 ml of hexane was slowly added to the solution obtained. The resulting heterogeneous mixture was filtered through a thin bed of silica gel, and the filtrate was evaporated. The residue was distilled in a vacuum in a Kugelrohr type device to get 230 g of viscous oily substance, bp 130–140°C (0.001 mm Hg). According to ^{1}H NMR spectrum the reaction product is a mixture of two atropoisomers in a ratio 9:1. Major atropoisomer. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.61 s (H^{9}), 0.84 s (H^{10}), 1.01 s (H^{8}), 1.48 d.d.d ($H^{6\varepsilon}$, *J* 12.2, 8.5, 3.8 Hz), 1.55 d.d.d (H^{5a}, *J* 12.3, 8.9, 3.6 Hz), 1.76 d.d.t ($H^{5\varepsilon}$, *J* 12.0, 8.5, 3.6 Hz), 2.06 q ($H^{7'}$, *J* 0.6 Hz), 2.10 d.d.d (H^{6a}, *J* 9.0, 3.2, 3.2 Hz), 2.14 q ($H^{6'}$, *J* 0.6 Hz), 2.46 d (H^{4}, *J* 4.0 Hz). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 11.03 (C^{10}), 13.75 ($C^{7'}$), 13.87 ($C^{6'}$), 18.17 (C^{9}), 18.40 (C^{8}), 23.52 (C^{5}), 31.39 (C^{6}), 56.26 (C^{7}), 58.46 (C^{1}), 59.62 (C^{4}), 109.72 ($C^{5'}$), 126.93 (C^{3}), 129.58 ($C^{4'}$), 131.36 ($C^{3'}$), 133.43 ($C^{2'}$), 139.52 (C^{2}). Minor atropoisomer. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.64 s (H^{9}), 1.07 s (H^{10}), 1.30 s (H^{8}), 1.19 d.d (H^{6}, *J* 10.2, 2.0 Hz), 1.39 d.d.d (H^{6}, *J* 9.6, 9.6, 1.3 Hz), 1.69 d.d.d (H^{5}, *J* 7.2, 3.7, 1.4 Hz), 1.71–1.72 m (H^{5}), 2.02 q ($H^{7'}$, *J* 0.6 Hz), 2.06 q ($H^{6'}$, *J* 0.6 Hz), 2.33 d (H^{4}, *J* 3.7 Hz). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 11.27 (C^{10}), 13.43 ($C^{7'}$), 13.51 ($C^{6'}$), 17.96 (C^{9}), 19.13 (C^{8}), 23.93 (C^{5}), 31.82 (C^{6}), 55.36 (C^{7}), 58.97 (C^{1}), 60.72 (C^{4}), 110.32 ($C^{5'}$), 126.14 (C^{3}), 129.70 ($C^{4'}$), 130.97 ($C^{3'}$), 132.45 ($C^{2'}$), 139.90 (C^{2}).

Mass spectrum, *m/z* (I_{rel}, %): 404 (100), 406 (51.8), 402 (50.0), 405 (19.7), 407 (9.2), 408 (2.8).

(1*R*)-3-Bromo-2-(2-methoxyphenyl)bornylene (VI). Similarly from a solution of Grignard reagent prepared from 4.68 g (25 mmol) of 2-bromoanisole and 7.26 g (20 mmol) of compound **II** in the presence of 0.70 g (1 mmol) of $Pd(PPh_3)_2Cl_2$ was isolated by chromatography on silica gel (eluent hexane–ethyl acetate, 50:1) 3.12 g(49%) of crystalline compound **VI**. Analytically pure sample was obtained by recrystallization from methanol, mp 64.5–65°C. Conformer A. ^{1}H NMR spectrum (C_6D_6, 298 K), δ, ppm: 0.68 s (3H, CH_3), 0.87 s (3H, CH_3), 1.03 s (3H, CH_3), 1.52 d.d.d (1H, *J* 11.9, 9.0, 3.9 Hz), 1.58 d.d.d (1H, *J* 11.7, 8.7, 3.9 Hz), 1.83 d.d.d.d (H^{5}, *J* 11.9, 8.5, 3.8, 3.6 Hz), 2.11 d.d.d (H^{6}, *J* 11.6, 9.1, 3.6 Hz), 2.46 d (H^{4}, *J* 3.8 Hz), 3.23 s (OMe), 6.52 d.d (1H, *J* 8.3, 1.0 Hz), 6.89 t.d (1H, *J* 7.4, 1.1 Hz), 7.08 t.d (1H, *J* 8.0, 1.8 Hz), 7.28 d.d (1H, *J* 7.4, 1.7 Hz). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 12.77, 19.91, 20.09, 25.70, 32.45, 55.02, 58.32, 58.82, 61.17, 111.39, 121.25, 123.69, 126.21, 129,22, 131.84, 146.68, 157.34. Conformer B. ^{1}H NMR spectrum (C_6D_6, 298 K), δ, ppm: 0.69 s (3H, CH_3), 0.90 s (3H, CH_3), 1.25 s (3H, CH_3), 1.33–1.41 m (2H), 1.45–1.51 m (1H), 1.77 d.d.d (H^{5}, *J* 12.7, 8.4, 3.8 Hz), 2.51 d (H^{4}, *J* 3.7 Hz), 3.28 C (OMe), 6.55 d.d (1H, *J* 8.2, 0.7 Hz), 6.83 t.d (1H, *J* 7.4, 1.1 Hz), 6.92 d.d (1H, *J* 7.4, 1.9 Hz), 7.09 t.d (1H, *J* 8.0 1.7 Hz).

^{13}C NMR spectrum (C_6D_6), δ, ppm: 12.58, 20.00, 20.05, 25.75, 33.77, 55.26, 57.25, 59.53, 61.61, 111.58, 120.92, 123.72, 125.49, 129.45, 130.30, 145.27, 157.34.

Mass spectrum, *m/z* (I_{rel}, %): 320 (100), 322 (99.3), 321 (19.0), 323 (18.8), 324 (1.5).

(1*R*)-3-Bromo-2-(2-methoxy-1-naphthyl)bornylene (VII). Similarly from a solution of Grignard reagent prepared from 5.93 g (25 mmol) of 1-bromo-2-methoxynaphthalene and 7.26 g (20 mmol) of compound **II** in the presence of 0.70 g (1 mmol) of $Pd(PPh_3)_2Cl_2$ was isolated by chromatography on silica gel (eluent hexane–ethyl acetate, 50:1) 3.22 g (44%) of crystalline substance as a mixture of two atropoisomers in a ratio 3:2. By recrystallization from anhydrous ethanol we obtained compound **VII** as a mixture of atropoisomers in a ratio 1:1, mp 119–121°C. Prevailing atropoisomer. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.74 s (3H, CH_3), 0.88 s (3H, CH_3), 1.35 s (3H, CH_3), 1.47–1.71 m (3H), 1.87 d.d.d.d (H^5, *J* 11.5, 7.9, 3.8, 2.9 Hz), 2.59 d (H^4, *J* 3.6 Hz), 3.30 s (OMe), 6.86 d (1H, *J* 9.1 Hz), 7.18 d.d.d (1H, *J* 6.8, 4.1, 1.3 Hz), 7.36 d.d.d (1H, *J* 6.9, 1.4, 1.0 Hz), 7.58 d.d.d (1H, *J* 9.0, 1.5, 0.7 Hz), 7.65 d.d.d (1H, *J* 8.2, 1.4, 0.6 Hz), 7.77 d.d.d (1H, *J* 8.6, 2.0, 0.9 Hz). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 12.40, 19.99, 20.30, 25.87, 33.48, 55.87, 58,25, 60.79, 61.55, 113.77, 119.11, 124.20, 125.61, 126.08, 127.30, 129.09, 130.19, 130.27, 133.14, 143.23, 156.82. Minor atropoisomer. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.72 s (3H, CH_3), 0.85 s (3H, CH_3), 1.34 s (3H, CH_3), 1.47–1.71 m (2H), 1.91 d.d.d (1H, *J* 13.0, 8.0, 3.9 Hz), 2.13 d.d.d (1H, *J* 11.2, 8.8, 3.3 Hz), 2.63 d (H^4, *J* 3.7 Hz), 3.37 s (OMe), 6.89 d (1H, *J* 9.1), 7.20 d.d.d (1H, *J* 6.8, 4.1, 1.3 Hz), 7.38 d.d.d (1H, *J* 6.9, 1.3, 1.1 Hz), 7.58 d.d (1H, *J* 9.0, 1.4 Hz), 7.66 d.d.d (1H, *J* 8.2, 1.4, 0.7 Hz), 8.23 d.d.d (1H, *J* 8.6, 2.0, 0.8 Hz). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 13.10, 20.40, 20.79, 25.86, 33.03, 56.21, 57.15, 60.81, 61.79, 114.11, 119.41, 124.22, 126.38, 126.90, 127,29, 129.03, 130.17, 130.27, 135.06, 142.52, 155.04.

Mass spectrum, *m/z* (I_{rel}, %): 370 (100), 372 (99.5), 371 (24.0), 373 (23.8), 374 (2.4).

(1*R*)-3-Bromo-2-{3(2)-bromo-[*b*]benzothien-2(3)-yl}-bornylene (VIII). To a solution of 4.67 g (16 mmol) of 2,3-dibromo[*b*]benzothiophene in 30 ml of anhydrous THF was added dropwise at –78°C 11 ml of 1.6 M butyllithium solution in hexane. After stirring for 30 min at –78°C was added a solution in 20 ml of anhydrous ethyl ether of magnesium bromide prepared from 0.50 g (21 mmol) of magnesium and 1.7 ml (20 mmol) of 2-dibromoethane. The reaction mixture was warmed at stirring to room temperature, and the solution obtained was transferred under argon into a flask containing 0.5 g (0.7 mmol) of $Pd(PPh_3)_2Cl_2$. After adding 2.36 g (6.5 mmol) of compound **II** the reaction mixture was stirred at 70°C for 20 h. On cooling the excess Grignard reagent was decomposed with a half-saturated ammonium chloride solution, the water layer after separating the organic phase was additionally extracted with ether, the combined organic solutions were washed with a saturated NaCl solution, dried with anhydrous magnesium sulfate, and evaporated in a water-jet pump vacuum. The residue was dissolved in 5 ml of toluene, and 20 ml of hexane was slowly added to the solution obtained. The resulting heterogeneous mixture was filtered through a thin bed of silica gel, and the filtrate was evaporated. The residue was further purified by chromatography on silica gel (eluent hexane). On evaporating the solvent the oily substance obtained was crystallized from anhydrous ethanol at –20°C. Yield of compound **VIII** 1.4 g (51%), mp 64–65°C. Conformer A. ^{1}H NMR spectrum ($CDCl_3$, 273 K), δ, ppm: 0.85 s (3H, CH_3), 1.01 s (3H, CH_3), 1.19 s (3H, CH_3), 1.34 d.d.d (1H, *J* 12.4, 9.0, 3.6 Hz), 1.46 d.d.d (1H, *J* 12.3, 9.2, 3.3 Hz), 1.73 d.d.d (1H, *J* 12.1, 8.6, 3.7 Hz), 1.96 d.d.d (1H, *J* 12.4, 8.9, 3.5 Hz), 2.62 d (1H, *J* 3.6 Hz), 7.38 d.d.d (1H, *J* 7.9, 7.2, 0.7 Hz), 7.45 d.d.d (1H, *J* 8.9, 8.0, 1.0 Hz), 7.76 d.q (1H, *J* 8.4, 0.8 Hz), 7.81 d.q (1H, *J* 7.9, 0.7 Hz). ^{13}C NMR spectrum, δ, ppm: 12.14, 19.32, 19.63, 24.98, 32.65, 56.62, 59.35, 60.91, 108.13, 122.19, 123.07, 124.88, 125.28, 129.15, 131.98, 137.91, 137.93, 139.29. Conformer B. ^{1}H NMR spectrum ($CDCl_3$, 273 K), δ, ppm: 0.854 s (3H, CH_3), 1.02 s (3H, CH_3), 1.04 s (3H, CH_3), 1.47 d.d.d (1H, *J* 12.3, 9.1, 3.4 Hz), 1.68 d.d.d (1H, *J* 12.3, 8.7, 3.6 Hz), 1.82 d.d.d (1H, *J* 12.3, 9.1, 3.4 Hz), 1.99 d.d.d (1H, *J* 12.4, 9.4, 3.4 Hz), 2.58 d (1H, *J* 3.8 Hz), 7.38 d.d.d (1H, *J* 7.9, 7.3, 0.7 Hz), 7.44 d.d.d (1H, *J* 8.1, 8.0, 1.0 Hz), 7.78 d.q (1H, *J* 8.7, 0.9 Hz), 7.81 d.q (1H, *J* 8.2, 0.7 Hz). ^{13}C NMR spectrum, δ, ppm: 12.87, 19.23, 19.63, 24.72, 32.20, 58.03, 59.58, 60.79, 106.67, 122.11, 123.48, 124.88, 125.16, 129.62, 133.15, 137.99, 138.13, 138.68.

Mass spectrum, *m/z* (I_{rel}, %): 426 (100), 428 (50.1), 424 (46.1), 427 (21.9), 429 (10.9), 425 (10.4), 430 (2.1), 431 (1.2).

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