EurJOC European Journal of Organic Chemistry

SHORT COMMUNICATION

DOI: 10.1002/ejoc.201201043

# Modular Synthesis of Planar-Chiral *para*-Substituted Paracyclophanes by Double Suzuki Coupling

Murat Cakici[a,b] and Stefan Bräse*[a,c]

**Keywords:** Cyclophanes / Cross-coupling / Chirality / Boron / Hydrocarbons

The first synthesis of enantiomerically pure 4,7-paracyclophane ditriflate starting from a quinone was reported. Using this molecule, mono- or dicoupling with boronic acids delivered enantiomerically pure arylparacyclophanes.

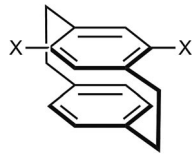
## Introduction

[2.2]Paracyclophanes belong to a unique class of strained hydrocarbons with an increasing number of applications[1] in disciplines such as material science[2] or catalysis.[3] Therefore, the synthesis of chiral paracyclophanes is still a field of interest. There are a variety of methods for the synthesis of chiral, non-racemic *ortho*- (i.e., 4,5-) or monosubstituted paracyclophanes.[4] For an application in material science, we needed a modular synthesis of *para*-substituted paracyclophanes (i.e., 4,7-).[5–8] However, there are only a few known examples of 4,7-diarylcyclophanes that give access to racemic material.[9,10] The methods used were mostly bottom-up syntheses from the two layers.

## Results and Discussion

Retrosynthetically, *para*-substituted paracyclophanes can be obtained from difunctionalized paracyclophanes **1**-X (Figure 1), which in turn can undergo cross-coupling reactions. To our surprise, this was not investigated before, although a number of 4,7-dihydroxylated paracyclophanes (X = OH) are known.[11]

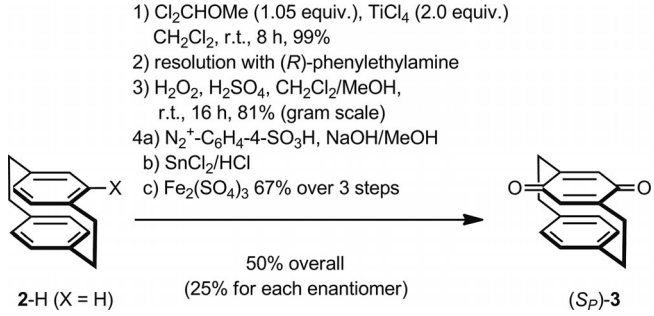
Although 4,7-dihaloparacyclophanes **1**-Hal (Hal = Br) are known,[12] an asymmetric synthesis might be tedious. Therefore, we turned our attention to (so far unknown) *para*-ditriflate **1**-OTf.[13] The latter might be accessible from a hydroquinone, the reduction product of a known quinone.[14] An asymmetric synthesis of this quinone is reported.[15]




**1**-X

Figure 1. *para*-Substituted paracyclophanes **1**-X. X = Hal, OH, OTf (this work).

The synthesis of non-racemic quinone **3** was therefore envisaged. Our synthesis started with the preparation of enantiopure hydroxyparacyclophane ($S_P$)-**2**-OH, which is accessible on gram scale in three steps from parent paracyclophane **2**-H by using our optimized protocol (Scheme 1, steps 1–3).[4a] Conversion to quinone ($S_P$)-**3** proceeded smoothly in 67% yield by addition of a diazonium salt at the *para* position and subsequent reduction of the azo compound followed by oxidation with iron(III) sulfate according to a literature procedure.[16] The absolute configuration of quinone ($S_P$)-**3** can be traced back to the configuration of phenol ($S_P$)-**2**-OH and/or aldehyde ($S_P$)-**2**-CHO.




**2**-H (X = H) ($S_P$)-**3**

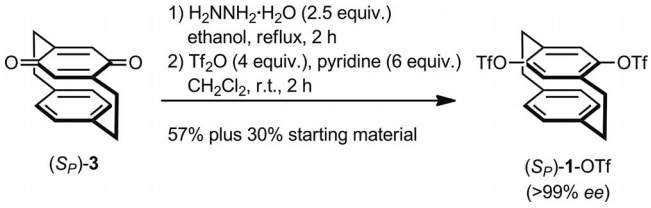
Scheme 1. Asymmetric synthesis of quinone **3**.

[a] Soft Matter Synthesis Lab, Institute for Biological Interfaces I, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany
[b] Faculty of Sciences, Department of Chemistry, Ataturk University, 25240 Erzurum, Turkey
[c] Karlsruhe Institute of Technology, Campus South, Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
Fax: +49-721-6088581
E-mail: braese@kit.edu
Homepage: http://www.ioc.kit.edu/braese

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201043.

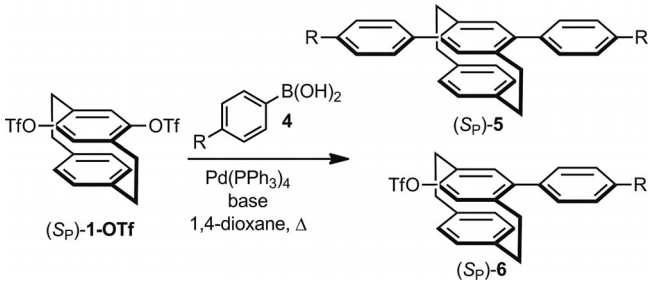
After some experimentation, we were able to convert quinone ($S_P$)-**3** via hydroquinone ($S_P$)-**1**-OH into triflate ($S_P$)-**1**-OTf in the presence of triflate anhydride and a base (Scheme 2). It was crucial to exclude air under these conditions, as re-oxidation of novel hydroquinone ($S_P$)-**1**-OH proceeds fast with oxygen. However, triflate ($S_P$)-**1**-OTf is a stable molecule. The enantiomeric excess (determined by HPLC on chiral column) was identical to that of starting quinone ($S_P$)-**3**.




Scheme 2. Synthesis of non-racemic triflate ($S_P$)-**1**-OTf.

Gratifyingly, double Suzuki coupling of racemic or enantiopure ditriflate **1**-OTf with aryl boronic acids **4** proceeded smoothly to yield diarylparacyclophanes **5** in good yields (Table 1, entries 3 & 4). The enantiomeric excess was over 99%*ee* for **5b** (determined by HPLC). Under different conditions (fewer equivalents of the boronic acid, lower temperature, different base), monoarylated paracyclophanes **6** were isolated in good yields (Table 1, entries 1 & 2).

Table 1. Suzuki coupling of racemic and enantiopure ditriflate **1**-OTf with aryl boronic acids **4**.




| Entry | R | Base | Temp. [°C] | Product | Conv. [%] | Yield [%] |
|---|---|---|---|---|---|---|
| 1[a] | H | $K_2CO_3$ | 80 | *rac*-**6a** | 64 | 52 (81)[c] |
| 2[a] | $CO_2Me$ | $K_2CO_3$ | 80 | *rac*-**6b** | 80 | 71 (89)[c] |
| 3[b] | H | $K_3PO_4$ | 100 | *rac*-**5a** | quant. | 77 |
| 4[b] | $CO_2Me$ | $K_3PO_4$ | 100 | ($S_P$)-**5b**[d] | quant. | 88 |

[a] Reaction conditions: *rac*-**1**-OTf (1.0 equiv.), boronic acid (3.0 equiv.), $Pd(PPh_3)_4$ (5.0 mol-%), $K_2CO_3$ (3.0 equiv.), 24 h, under argon atmosphere. [b] Reaction conditions: *rac*- or ($S_P$)-**1**-OTf (1.0 equiv.), boronic acid (4.0 equiv.), $Pd(PPh_3)_4$ (6.0 mol-%), $K_3PO_4$ (3.0 equiv.), 48 h, under argon atmosphere. [c] Calculated with respect to consumed **1**-OTf. [d] >99%*ee* (determined by HPLC).

## Conclusions

We have demonstrated that a chiral, non-racemic ditriflate is a suitable starting material for aryl-substituted paracyclophanes. This triflate should also be a suitable precursor for other cross-coupling and/or polymerization reactions.

## Experimental Section

**[2.2]Paracyclophane-4,7-quinone (3):** Racemic and optically active **3** were synthesized from *rac*- and (*S*)-4-hydroxy[2.2]paracyclophane[4a] by the procedure reported in the literature.[16] M.p. >200 °C (dec.); $R_f$ ($CH_2Cl_2$) = 0.37. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.85 (d, $J$ = 7.9 Hz, 2 H), 6.73 (d, $J$ = 7.9 Hz, 2 H), 5.82 (s, 2 H), 3.28–3.20 (m, 2 H), 3.17–3.01 (m, 4 H), 2.36–2.26 (m, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 187.4, 149.2, 139.0, 134.8, 133.5, 131.5, 33.5, 28.9 ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1649, 1597, 1413, 1351, 1233, 1115, 1093 cm$^{-1}$. $[\alpha]^{20}$ = +224.0 ($c$ = 0.185, benzene) {ref.[15b] $[\alpha]^{20}$ = +211($c$ = 0.185, benzene)}. HPLC (Chiralcel AS-H column, *n*-hexane/*i*PrOH = 90:10, flow rate = 1 mL min$^{-1}$, $\lambda$ = 254 nm): $t_R$ = 17.4 (*S*), 18.6 min (*R*); >99%*ee*.

**($S_P$)-[2.2]Paracyclophane-4,7-bistriflate [($S_P$)-1-OTf]:** Hydrazine hydrate (0.051 mL, 1.050 mmol) was added to a solution of ($S_P$)-[2.2]-paracyclophane-4,7-quinone [($S_P$)-**3**; 100 mg, 0.420 mmol] in anhydrous EtOH (15 mL). The reaction mixture was heated at reflux for 2 h, the solvent and the excess amount of hydrazine hydrate were distilled off in vacuo, and the flask was filled with argon. The crude [2.2]paracyclophane-4,7-hydroquinone was dissolved in dry dichloromethane (10 mL) under an atmosphere of nitrogen at room temperature followed by the addition of dry pyridine (0.204 mL, 2.520 mmol). Trifluoromethanesulfonic anhydride (triflic anhydride; 0.282 mL, 1.680 mmol) in dry dichloromethane (2 mL) was then added dropwise. The color of the solution changed from yellow to orange and white fumes evolved. The reaction mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was then added, and the reaction mixture was extracted with dichloromethane (3 × 15 mL). The combined organic phase was washed with brine and dried with $MgSO_4$. The residue after rotary evaporation was purified by column chromatography (silica gel; hexane/ethyl acetate, 90:10). Unconsumed quinone was re-isolated (30 mg, 0.126 mmol, 30%). Triflate ($S_P$)-**1**-OTf (85 mg, 0.169 mmol, 57% with respect to consumed quinone) was obtained and recrystallized (hexane) to give colorless crystals. M.p. 99–100 °C; $R_f$ (hexane/EtOAc = 90:10) = 0.79. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.93 (dd, $J$ = 8.0, 1.6 Hz, 2 H), 6.50 (dd, $J$ = 8.0, 1.6 Hz, 2 H), 6.32 (s, 2 H), 3.42–3.36 (m, 2 H), 3.24–3.13 (m, 4 H), 2.83–2.75 (m, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 147.4, 139.1, 135.5, 133.1, 130.6, 130.3, 118.8 (q, $J$ = 320.8 Hz, 1 C), 34.0, 31.3 ppm. IR (ATR): $\tilde{\nu}$ = 2931, 2857, 1489, 1412, 1202, 1135, 1106, 1094, 1033 cm$^{-1}$. HRMS: calcd. for $C_{18}H_{14}F_6O_6S_2$ 504.0136; found 504.0138. $[\alpha]^{20}$ = +17.5 ($c$ = 1, DCM). HPLC (Chiralcel OD-H column, *n*-hexane/*i*PrOH = 90:10, flow rate = 1 mL min$^{-1}$, $\lambda$ = 220 nm): $t_R$ = 6.7 (*R*), 8.8 min (*S*); >99%*ee*.

**General Procedure for the Suzuki Coupling:** [2.2]Paracyclophane-4,7-bistriflate [*rac*- or ($S_P$)-**1**-OTf; 150 mg 0.300 mmol), powdered $K_3PO_4$ (191 mg, 0.900 mmol), and boronic acid **4** (1.20 mmol) were added to a 10-mL, two-necked flask that had been purged with argon. A solution of $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) in dry dioxane (6 mL) was added, and the reaction mixture was stirred under an atmosphere of argon at 100 °C for 2 d. The reaction mixture was cooled and filtered through a short pad of Celite. The filtrate was

concentrated under reduced pressure to remove the solvents. The crude product was purified by column chromatography [silica gel; hexane/EtOAc = 98:02 (for **5a**), hexane/EtOAc = 90:10 (for **5b**)] to give diaryl paracyclophanes **5**.

***rac*-5a:** Recrystallization (hexane) gave colorless crystals. Yield 77%; m.p. 157–159 °C; $R_f$ (hexane/EtOAc = 98:02) = 0.57. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.57 (d, $J$ = 7.5 Hz, 4 H), 7.50 (t, $J$ = 7.6 Hz, 4 H), 7.38 (t, $J$ = 7.3 Hz, 2 H), 6.77 (d, $J$ = 7.8 Hz, 2 H), 6.70 (s, 2 H), 6.67 (d, $J$ = 7.8 Hz, 2 H), 3.59 (ddd, $J$ = 12.2, 10.0, 2.5 Hz, 2 H), 3.00–2.84 (m, 4 H), 2.65 (ddd, $J$ = 12.2, 10.0, 5.4 Hz, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 141.0, 141.0, 139.7, 137.2, 135.2, 132.1, 129.9, 129.9, 128.7, 127.0, 34.7, 34.3 ppm. IR (ATR): $\tilde{\nu}$ = 2968, 2925, 2853, 1598, 1502, 1472, 1444, 1210, 1074, 1023 cm$^{-1}$. HRMS: calcd. for $C_{28}H_{24}$ 360.1878; found 360.1876.

**($S_P$)-5b:** Recrystallization (hexane) gave colorless crystals. Yield 88%; m.p. 219–220 °C; $R_f$ (hexane/EtOAc = 90:10) = 0.39. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.17 (d, $J$ = 8.1 Hz, 4 H), 7.62 (d, $J$ = 8.1 Hz, 4 H), 6.73 (s, 2 H), 6.70 (d, $J$ = 7.9 Hz, 2 H), 6.66 (d, $J$ = 7.9 Hz, 2 H), 3.98 (s, 6 H), 3.57–3.52 (m, 2 H), 3.05–2.83 (m, 4 H), 2.64–2.58 (m, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 167.0, 145.1, 140.5, 139.4, 137.5, 135.2, 131.9, 129.9, 129.7, 129.5, 128.7, 52.1, 34.5, 34.1 ppm. IR (ATR): $\tilde{\nu}$ = 2945, 1705, 1602, 1431, 1276, 1262, 1180, 1101, 1014 cm$^{-1}$. HRMS: calcd. for $C_{32}H_{28}O_4$ 476.1988; found 476.1989. $[a]^{20}$ = +403.0 ($c$ = 1, DCM). HPLC (Chiralcel OD-H column, *n*-hexane/*i*PrOH = 90:10, flow rate = 1 mL min$^{-1}$, $\lambda$ = 365 nm): $t_R$ = 14.5 (*S*), 25.5 min (*R*); >99% *ee*.

***rac*-6a:** Recrystallization (hexane) gave colorless crystals. Yield 81%; m.p. 90–92 °C; $R_f$ (hexane/EtOAc = 98:02) = 0.51. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.51–7.39 (m, 5 H), 7.02 (dd, $J$ = 7.9, 1.9 Hz, 1 H), 6.68 (dd, $J$ = 7.9, 1.9 Hz, 1 H), 6.65 (s, 1 H), 6.59–6.54 (m, 2 H), 6.27 (s, 1 H), 3.48–3.36 (m, 2 H), 3.21 (dd, $J$ = 8.4, 6.0 Hz, 2 H), 2.93–2.67 (m, 4 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 147.2, 142.6, 139.8, 139.4, 139.3, 139.0, 135.0, 132.6, 132.3, 131.9, 130.2, 130.0, 129.5, 129.4, 128.7, 127.5, 120.3, 34.3, 33.9, 33.5, 31.3 ppm. IR (KBr): $\tilde{\nu}$ = 2932, 2857, 1597, 1477, 1420, 1247, 1211, 1141, 1071, 1029 cm$^{-1}$. $C_{23}H_{19}F_3O_3S$ (432.46): calcd. C 63.88, H 4.43, S 7.41; found C 63.56, H 4.58, S 7.49.

***rac*-6b:** Recrystallization (hexane) gave colorless crystals. Yield 89%; m.p. 122–125 °C; $R_f$ (hexane/EtOAc = 90:10) = 0.53. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.16 (d, $J$ = 8.1 Hz, 2 H), 7.53 (d, $J$ = 8.1 Hz, 2 H), 7.02 (dd, $J$ = 8.0, 1.6 Hz, 1 H), 6.67 (s, 1 H), 6.63 (dd, $J$ = 8.0, 1.6 Hz, 1 H), 6.59–6.54 (m, 2 H), 6.29 (s, 1 H), 3.97 (s, 3 H), 3.48–3.42 (m, 1 H), 3.39–3.30 (m, 1 H), 3.23–3.20 (m, 2 H), 2.95–2.78 (m, 3 H), 2.68–2.60 (m, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 167.0, 147.8, 144.1, 141.7, 140.2, 139.4, 135.3, 132.8, 132.6, 132.4, 130.5, 130.3, 130.2, 129.8, 129.7, 129.5, 120.5, 52.4, 34.6, 34.1, 33.7, 31.6 ppm. IR (KBr): $\tilde{\nu}$ = 2949, 2858, 1722, 1609, 1421, 1281, 1247, 1213, 1141, 1070, 1019 cm$^{-1}$. $C_{25}H_{21}F_3O_5S$ (490.49): calcd. C 61.22, H 4.32, S 6.54; found C 60.95, H 4.41, S 6.62.

**Supporting Information** (see footnote on the first page of this article): All preparation procedures as well as $^1$H NMR and $^{13}$C NMR spectra for all compounds and HPLC chromatograms.

**Note Added in Proof** (September 19, 2012): The stereochemistry of one product has been proven by a molecular structure determined by X-ray diffraction.[17]

## Acknowledgments

M. C. acknowledges the Ataturk University for the financial support.

[1] a) J. Paradies, *Synthesis* **2011**, 3749–3766; b) S. E. Gibson, J. D. Knight, *Org. Biomol. Chem.* **2003**, *1*, 1256–1269; c) R. Gleiter, H. Hopf, *Modern Cyclophane Chemistry*, Wiley-VCH, Weinheim, **2004**; d) F. Vögtle, *Cyclophane Chemistry*, Wiley, New York, **1993**.

[2] a) J. Lahann, M. Balcells, T. Rodon, J. Lee, I. S. Choi, K. F. Jensen, R. Langer, *Langmuir* **2002**, *18*, 3632–3638; b) J. Lahann, H. Höcker, R. Langer, *Angew. Chem.* **2001**, *113*, 746; *Angew. Chem. Int. Ed.* **2001**, *40*, 726–728; c) J. Lahann, R. Langer, *Macromolecules* **2002**, *35*, 4380–4386; d) A. Marrocchi, I. Tomasi, L. Vaccaro, *Isr. J. Chem.* **2012**, *52*, 41–52; e) E. Elacqua, L. R. MacGillivray, *Eur. J. Org. Chem.* **2010**, 6883–6894; f) H. Hopf, *Angew. Chem.* **2008**, *120*, 9954; *Angew. Chem. Int. Ed.* **2008**, *47*, 9808–9812; g) G. C. Bazan, *J. Org. Chem.* **2007**, *72*, 8615–8635.

[3] a) S. Dahmen, S. Bräse, *Org. Lett.* **2001**, *3*, 4119–4122; b) S. Ay, R. E. Ziegert, H. Zhang, M. Nieger, K. Rissanen, R. M. Gschwind, S. Bräse, *J. Am. Chem. Soc.* **2010**, *132*, 12899–12905; c) review: S. Bräse, S. Dahmen, S. Höfener, F. Lauterwasser, M. Kreis, R. E. Ziegert, *Synlett* **2004**, 2647–2669; d) S. Dahmen, S. Bräse, *J. Am. Chem. Soc.* **2002**, *124*, 5940–5941.

[4] a) C. J. Friedmann, S. Ay, S. Bräse, *J. Org. Chem.* **2010**, *75*, 4612–4614; b) V. I. Rozenberg, D. Y. Antonov, E. V. Sergeeva, E. V. Vorontsov, Z. A. Starikova, I. V. Fedyanin, C. Schulz, H. Hopf, *Eur. J. Org. Chem.* **2003**, 2056–2061; c) V. Rozenberg, T. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, A. Korlyukov, H. Hopf, *Eur. J. Org. Chem.* **2002**, 468–477; d) V. Rozenberg, T. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, K. Lysenko, Y. Belokon, *Eur. J. Org. Chem.* **2000**, 3295–3303.

[5] *para*-Dicarboxylic acid: R. Gray, V. Boekelheide, *J. Am. Chem. Soc.* **1979**, *101*, 2128–2136.

[6] *para*-Esters: V. I. Rozenberg, E. L. Popova, H. Hopf, *Helv. Chim. Acta* **2002**, *85*, 431–441.

[7] *para*-Styryl: a) D. Bléger, D. Kreher, F. Mathevet, A.-J. Attias, I. Arfaoui, G. Metgé, L. Douillard, C. Fiorini-Debuisschert, F. Charra, *Angew. Chem.* **2008**, *120*, 8540; *Angew. Chem. Int. Ed.* **2008**, *47*, 8412–8415; b) G. P. Bartholomew, G. C. Bazan, *J. Am. Chem. Soc.* **2002**, *124*, 5183–5196.

[8] *para*-Bromo: a) K. P. Butin, A. A. Moiseeva, T. V. Magdesieva, E. V. Sergeeva, V. I. Rozenberg, V. G. Kharitonov, *Russ. Chem. Bull.* **1994**, *43*, 783–789; b) N. V. Vorontsova, V. I. Rozenberg, E. V. Sergeeva, E. V. Vorontsov, Z. A. Starikova, K. A. Lyssenko, H. Hopf, *Chem. Eur. J.* **2008**, *14*, 4600–4617.

[9] A. C. Garcia Espino, Dissertation, University of Göttingen, **1989**.

[10] a) B. König, B. Knieriem, A. Meijere, *Chem. Ber.* **1993**, *126*, 1643–1650; b) L. Czuchajowski, A. Zemanek, *Pol. J. Chem.* **1990**, *64*, 499–504; c) A. K. Wisor, L. Czuchajowski, *Monatsh. Chem.* **1983**, *114*, 1023–1034.

[11] a) M. Montanari, A. Bugana, A. K. Sharma, D. Pasini, *Org. Biomol. Chem.* **2011**, *9*, 5018–5020; b) C.-Y. Yu, M. Helliwell, J. Raftery, M. L. Turner, *Chem. Eur. J.* **2011**, *17*, 6991–6997; c) A. R. Forrester, R. Ramasseul, *J. Chem. Soc. B* **1971**, 1638–1644; d) W. Rebafka, H. A. Staab, *Angew. Chem.* **1973**, *85*, 831–832; e) A. Davatz, W. Jenny, *Chimia* **1974**, *28*, 183–185; f) R. C. Helgeson, J. M. Timko, D. J. Cram, *J. Am. Chem. Soc.* **1974**, *96*, 7380–7382.

[12] a) K. Y. Kay, Y. G. Baek, D. W. Han, S. Y. Yeu, *Synthesis* **1997**, 35–37; b) H. J. Reich, D. J. Cram, *J. Am. Chem. Soc.* **1969**, *91*, 3527–3533.

[13] Monotriflate **2**-OTf is known: a) B. Ortner, H. Hubner, P. Gmeiner, *Tetrahedron: Asymmetry* **2001**, *12*, 3205–3208; b) M. Kreis, S. Bräse, *Adv. Synth. Catal.* **2005**, *347*, 313–319; c) M. Kreis, C. J. Friedmann, S. Bräse, *Chem. Eur. J.* **2005**, *11*, 7387–7394; for the nonaflate: d) M. Kreis, M. Nieger, S. Bräse, *J. Organomet. Chem.* **2006**, *691*, 2171–2181.

[14] I. V. Fedyanin, K. A. Lyssenko, N. V. Vorontsova, V. I. Rozenberg, M. Y. Antipin, *Mendeleev Commun.* **2003**, 15–16.

[15] a) N. V. Vorontsova, D. Antonov, L. Rozenberg, E. V. Vorontosv, Z. A. Starikova, Y. N. Bubnov, *Modern Trends in Organometallic Catalytic Chemistry, Mark Vol'pin, Memorial International Symposium*, Moscow, Russia, **2003**, May 16–23, p. 95; b) N. Vorontsova, V. Rozenberg, E. Vorontsov, D. Antonov, Z. Starikova, *Eur. J. Org. Chem.* **2003**, 761–770.

[16] a) D. J. Cram, A. C. Day, *J. Org. Chem.* **1966**, *31*, 1227–1232; b) N. V. Vorontsova, V. I. Rozenberg, E. V. Vorontsov, D. Y. Antonov, Z. A. Starikova, Y. N. Bubnov, *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 1483–1490.

[17] M. Nieger, M. Cakici, S. Bräse, unpublished results.

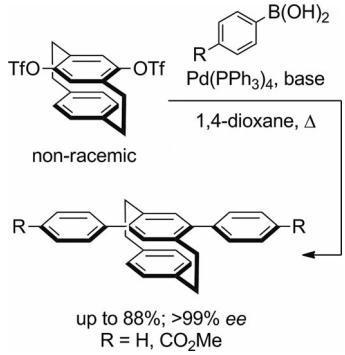
Received: August 2, 2012
Published Online: ■

EurJOC European Journal of Organic Chemistry



The reaction of a chiral, non-racemic paracyclophane ditriflate under Suzuki conditions gave – depending on the reaction conditions – the mono- or diarylated (pictured) enantiopure paracyclophane.






**Keywords:** Cyclophanes / Cross-coupling / Chirality / Boron / Hydrocarbons