

Highly diastereoselective synthesis of a novel functionalized triepoxytrinaphthylene

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Dedicated to emeritus Professors Metin Balci (Middle East Technical University) and Ottorino De Lucchi (Ca Foscari University) for their valuable contribution to hydrocarbon chemistry.

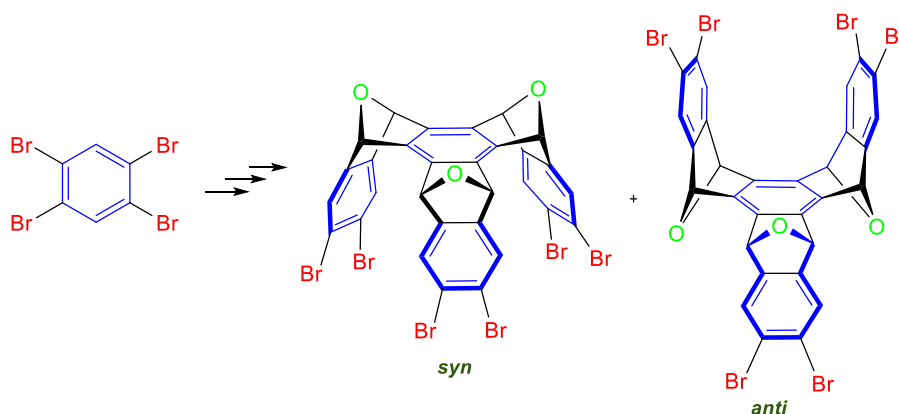
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Abstract

The high yielding synthesis of a novel benzocyclootrimer is herein presented. The *syn*-diastereomer is obtained as major product, presumably in virtue of the presence of an oxa-bridge of the bicyclic components. The three oxa-bridges can be used for further functionalization, as well as the six bromine atoms of the three aromatic rings, as demonstrated in the aromatization of a mixture of *anti*-**1** and *syn*-**1** (3:7) leading to trinaphthylene.



Keywords: Cyclotrimerization, copper, cup-shaped molecules, stereoselective reactions, aromatic compounds

Introduction

Benzocyclotrimers¹ are rigid molecules characterized by one or two cavities, which have been successfully employed in supramolecular chemistry.²⁻¹⁵ Amongst these, benzocyclotrimers bearing aromatic rings are characterized by large stiff cavities. The cavities are particularly deep and suitable for supramolecular applications in case of the more symmetrical *syn*-diastereomer, which is generally obtained in lower yields. In this report we describe the highly diastereoselective synthesis of the benzocyclotrimer *syn*-**1**, displaying one rigid and functionalized hemi-cavity in the bottom of the structure, concomitantly with three relatively reactive oxa-bridges (Figure 1). The reactivity of these moieties can be conveniently used for further functionalization of the less valuable diastereomer *anti*-**1**, which furnished the more symmetrical trinaphthylene **2** (Figure 1).

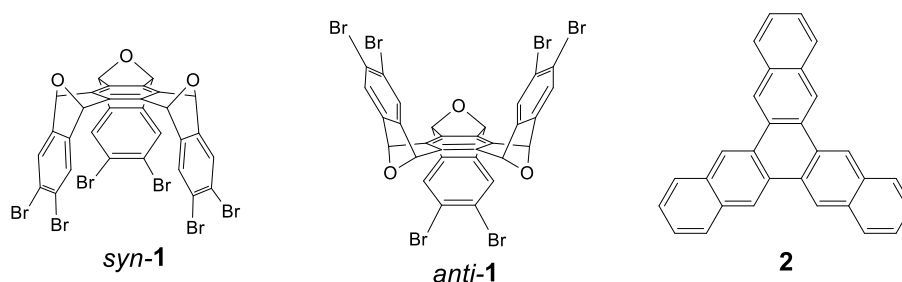
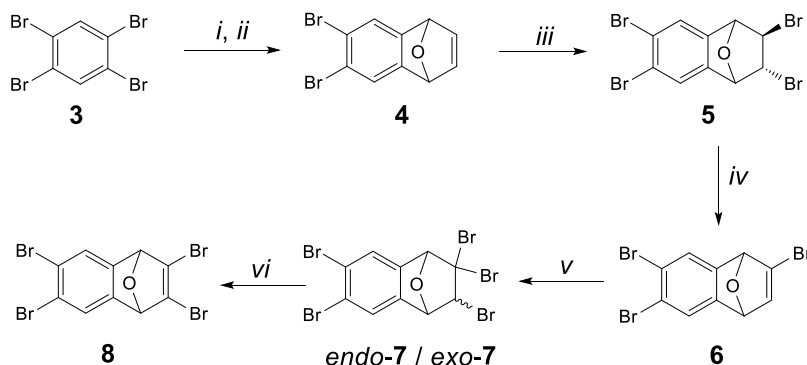


Figure 1. C_{3v} - and C_s -symmetric benzocyclotrimer *syn*-**1** and *anti*-**1**, and trinaphthylene **2**.

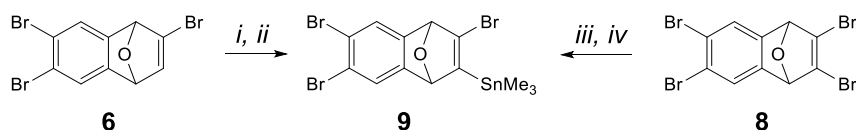
Results and Discussion

The starting material for the synthesis of the benzocyclotrimers *syn*-**1** and *anti*-**1** was 4,5-dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5,9-tetraene **4**, which can be obtained in 85% overall yield from commercially available 1,2,4,5-tetrabromobenzene **3**. The latter reacted with *n*-butyl lithium to afford 1-lithium-2,4,5-tribromobenzene, which decomposes to form the 4,5-dibromobenzyne. This reactive intermediate was captured by furan, acting as dienophile in a [4+2] cycloaddition (Scheme 1).¹⁶⁻²⁵ The resulting oxabicyclic **4** was brominated according to a well-established radical-driven procedure,¹⁴ which avoids Meerwein rearrangement with concomitant opening of the oxa-bridge (Scheme 1).²⁶ The radical bromination of **4** with 1,2-dibromotetrachloroethane (DBTCE) furnished the trans-dibromide diastereomer **5** in high yields (85%) (Scheme 1). In order to obtain the alkenyl bromide **6** the dehydrobromination reaction with potassium *tert*-butoxide in THF was used,²⁶ to afford the desired product **6** in good yield (90%) (Scheme 1). The latter was brominated under high temperature conditions, which ensures high yields of dibromination, with limited amounts of Meerwein rearrangement products,²⁶ to obtain alkenyl tribromides *exo*-**7** and *endo*-**7**, in a ratio of 2:1 and 96% overall yield (Scheme 1). The mixture of diastereomers was dehydrobrominated with potassium *tert*-butoxide in THF,²⁶ to afford the alkenyldibromide **8** in good yield (93%) (Scheme 1).



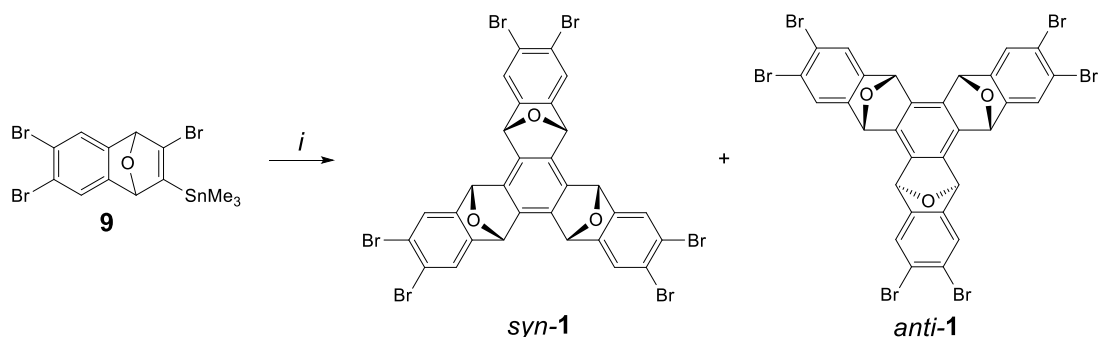
Scheme 1. Synthesis of the key intermediates for the precursor of the cyclotrimerization. (i) *n*-BuLi; (ii) furan in toluene, -78 °C to rt (85% for two steps) (iii) DBTCE, in CCl₄, hν, (85%), (iv) *t*-BuOK in THF, reflux. (90%) (v) Br₂ in CCl₄, reflux. (96%) (vi) *t*-BuOK in THF, reflux (93%).

The key reagent **9** for the cyclotrimerization was obtained either by proton abstraction of halide **6** with lithium diisopropylamide (LDA)^{11,13,27-33} or by removal of one of the bromine atoms of the dibromide **8** with *n*-butyl lithium^{30,31,34,35} followed by a trans-metalation reaction with trimethyltin chloride in 96% yield in both cases. The high chemoselectivity of removal of the bromine atom in **8** was surprisingly: indeed, the bromine atoms attached to the aromatic ring remained completely unaffected.



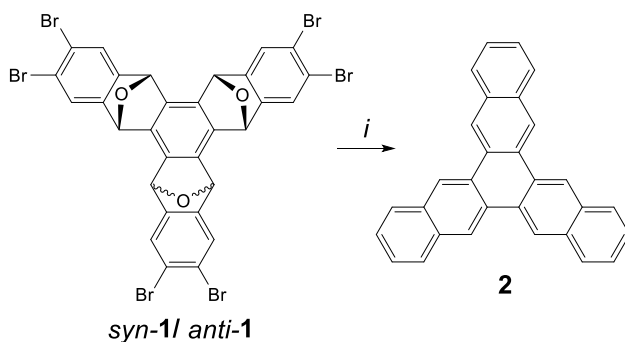
Scheme 2. Two feasible strategies the preparation of the precursor of cyclotrimerization **9**. (i) LDA; (ii) Me₃SnCl in THF, -78 °C to rt, (96% for two steps). (iii) *n*-BuLi; (iv) Me₃SnCl in THF, -78 °C to rt, (96% for two steps).

In order to accomplish the cyclotrimerization, the *vic*-bromostannane **9** was treated with copper(I) 2-thiophenecarboxylate (CuTC) in dry NMP (*N*-methyl-2-pyrrolidone) at low temperature.³⁶ The two isomeric benzocyclotrimers were formed in a highly favourable 7:3 *syn* to *anti* ratio and in a very good isolated yield (92%). The selectivity was opposite to the expected statistical distribution observed in the majority of cyclotrimerization reactions.¹ This behaviour has been previously observed when a ligating group is present in the monomer.^{37,38,11,32} It is likely that the oxa-bridge in the dihydronaphthalene is responsible for the high reverse selectivity, by means of coordination with copper. The separation of the two isomers was easily accomplished by chromatography on neutral alumina and the major *syn*-**1** isomer was available for further functionalization and supramolecular studies.



Scheme 3. Copper-mediated cyclotrimerization of **9**. (i) CuTC in NMP, -20 °C (25% for *anti*-**1** and 67% *syn*-**1** isolated yield).

The cyclotrimers *syn*-**1** and *anti*-**1** are a potential source for the synthesis of polyaromatic rings. In order to verify the potential of this strategy a mixture of *syn*-**1** and *anti*-**1** have been submitted to reductive oxygen elimination reactions.³⁹⁻⁴² The milder methodologies³⁹⁻⁴¹ based on the use of trimethylsilyl iodide or low valent titanium(III)chloride furnished complex mixtures of products, containing minor amounts of the expected 2,3,8,9,14,15-hexabromotrinaphthylene. When pure *syn*-**1** or *anti*-**1** (or mixture of *syn*-**1** and *anti*-**1**) is treated with titanium(III)chloride, generated *in situ* from TiCl₄, lithium aluminum hydride (LAH) and triethylamine (TEA) in refluxing THF,⁴² a quantitative yield of trinaphthylene **2**⁴³⁻⁵⁰ is obtained.



Scheme 4. Reductive aromatization of benzocyclotrimer *syn*-**1** and *anti*-**1**. (i) TiCl₄, LAH, TEA in THF, reflux (100% yield).

This approach opens up a new possible method for the preparation of polyaromatic systems, based on the highly chemo- and stereoselective cyclotrimerization reaction.⁵¹

Conclusions

In conclusion, a straightforward and high yielding synthesis of a new benzocyclotrimer was developed. The cyclotrimerization reaction afforded two possible diastereomers *syn* to *anti* in a very favourable 7:3 ratio. The more valuable *syn*-diastereomer will be considered for supramolecular applications. On the other hand, *anti* and *syn* diastereomers may be conveniently employed for the preparation of polyaromatic structures.

Experimental Section

General. All reactions were carried out under nitrogen and monitored by TLC and/or ^1H -NMR spectroscopy. All solvents were dried and distilled before use. Column chromatography was performed on silica gel (60 mesh, Merck) or on neutral alumina. TLC was carried out on silica gel 60 HF254 aluminum plates (Fluka). Melting points are uncorrected. The ^1H - and ^{13}C -NMR spectra were recorded on 400 MHz NMR spectrometers. Apparent splittings are given in all cases in ppm and coupling constants J in Hz. All new compounds gave satisfactory elemental analyses and/or HRMS (Q-TOF). All substances reported in this paper are in their racemic form.

4,5-Dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5,9-tetraene (4). To a mixture of 1,2,4,5-tetrabromobenzene **3** (5.00 g, 12.70 mmol) and furan (10 mL, 138.40 mmol) in toluene (100 mL) was added n -BuLi (2.5 M in n -hexane, 5.6 mL, 13.97 mmol) at $-78\text{ }^\circ\text{C}$. The resulting mixture was stirred for 1 h. The resulting reaction mixture was allowed to warm up to room temperature and stirred overnight. The mixture was diluted with saturated solution of ammonium chloride (10 mL) and extracted with EtOAc (3×25 mL). Combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified via column chromatography (silica-gel, 100 g; eluant 1:9 EtOAc/ n -hexane) to obtain 6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalene **4** (3.26 g, 85%) as colourless crystals from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:9), M.p. $125\text{--}126\text{ }^\circ\text{C}$ (lit.¹⁹ M.p. $125.2\text{--}126.6\text{ }^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3): 7.47 (s, 2 H), 6.99 (s, 2 H), 5.65 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): 150.2, 142.7, 125.5, 120.6, 81.8.

trans-4,5,9,10-Tetrabromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (5). In a 100-mL flask equipped with a reflux condenser, a solution of **4** (3.00 g, 9.93 mmol), 3.88 g (11.92 mmol) of DBTCE, and AIBN (10 mg) in CCl_4 (40 mL) was irradiated with a 500 W halogen lamp while refluxing for 24 h. Volatile materials were removed at reduced pressure and the residue was purified via column chromatography (silica-gel, 100 g; eluant n -hexane) to afford *trans*-2,3,6,7-tetrabromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalene **5** (3.90 g, 85%) as colorless crystals from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:9), M.p. $112\text{--}114\text{ }^\circ\text{C}$. IR (KBr): 3003, 1603, 1566, 1440, 1359, 1319, 1217, 1192, 1088, 983. ^1H NMR (400 MHz, CDCl_3): 7.64 (s, 1 H), 7.62 (s, 1 H), 5.39 (bs, 1 H), 5.38 (d, $J = 4.8$, 1 H), 4.49 (dd, $J = 4.8$ and 2.6 , 1 H), 3.77 (d, $J = 2.6$, 1 H). ^{13}C NMR (100 MHz, CDCl_3): 142.4 (2 overlapping C), 128.5, 125.3, 124.5, 124.1, 86.4, 82.7, 51.9, 49.8. Anal. calc. for $\text{C}_{10}\text{H}_6\text{Br}_4\text{O}$: C 26.01, H 1.31; found: C 26.07, H 1.33.

4,5,9-Tribromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5,9-tetraene (6). Under N_2 atmosphere, a solution of potassium *tert*-butoxide (0.58 g, 5.20 mmol) in dry THF (10 mL) was added to a stirred solution of **5** (2.00 g, 4.33 mmol) in dry THF (20 mL) in 15 min. The resulting mixture was heated at reflux temperature for 3 h. Volatile materials were evaporated and the residue was diluted with water and extracted with Et_2O (3×50 mL). Combined organic extracts were washed with water, dried over MgSO_4 , and concentrated at the reduced pressure. The residue was purified by column chromatography (silica-gel, 10 g; eluant EtOAc/ n -hexane (1:10)) to furnish 2,6,7-tribromo-1,4-dihydro-1,4-epoxynaphthalene **6** (1.50 g, 90%) as light brown crystals from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:3), M.p. $115\text{--}116\text{ }^\circ\text{C}$. IR (KBr): 3014, 1573, 1431, 1349, 1318, 1228, 1152, 1084, 992. ^1H NMR (400 MHz, CDCl_3): 7.60 (s, 1 H), 7.49 (s, 1 H), 6.92 (d, $J = 2.0$, 1 H), 5.69 (m, 1 H), 5.40 (bs, 1 H). ^{13}C NMR (100 MHz, CDCl_3): 148.6, 148.1, 139.3, 136.3, 126.1, 125.4, 121.8, 121.1, 86.4, 83.8.

exo/endo-4,5,9,9,10-Pentabromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (exo/endo-7). A hot solution of bromine (0.23 g, 1.44 mmol) in CCl_4 (5 mL) was added dropwise to a magnetically stirred refluxing solution of tribromide **6** (0.50 g, 1.31 mmol) in CCl_4 (25 mL). The solution was maintained under reflux for 20 min, after cooling to the room temperature the solvent was removed at the reduced pressure to afford a 2:1 mixture of pentabromides *exo*-**7** and *endo*-**7** (0.68 g, 96% yield), which was used in the following transformation

without further purification. ^1H NMR (400 MHz, CDCl_3) of *exo*-**7**: 7.76 (s, 1 H), 7.62 (s, 1 H), 5.67 (s, 1 H), 5.38 (s, 1 H), 4.36 (s, 1 H). ^1H NMR (400 MHz, CDCl_3) of *endo*-**7**: 7.69 (s, 1 H), 7.59 (s, 1 H), 5.67 (s, 1 H), 5.43 (d, $J = 4.7$, 1 H), 5.11 (d, $J = 4.7$, 1 H).

4,5,9,10-Tetrabromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5,9-tetraene (8). Under N_2 atmosphere, a solution of potassium *tert*-butoxide (0.18 g, 1.55 mmol) in dry THF (5 mL) was added to a stirred solution of *exo*-**7** and *endo*-**7** (0.70 g, 1.29 mmol) in dry THF (20 mL) in 15 min. The resulting mixture was maintained at room temperature overnight. Volatile materials were evaporated and the residue was diluted with water and extracted with Et_2O (3 \times 50 mL). Combined organic extracts were washed with water, dried over MgSO_4 and concentrated at reduced pressure. The residue was purified by column chromatography (silica-gel, 20 g; eluant EtOAc/n -hexane (1:9)) to furnish 2,3,6,7-tetrabromo-1,4-dihydro-1,4-epoxynaphthalene **8** (0.55 g, 93%) as colourless crystals from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:3), M.p. 197-199 °C. IR (KBr): 3014, 1587, 1429, 1345, 1317, 1222, 1155, 1082, 1053, 990. ^1H NMR (400 MHz, CDCl_3): 7.60 (s, 2 H), 5.52 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): 146.8, 133.3, 125.9, 122.2, 87.5. Anal. calc. for $\text{C}_{10}\text{H}_4\text{Br}_4\text{O}$: C 26.12, H 0.88; found: C 26.13, H 0.93.

4,5,9-Tribromo-10-(trimethylstannyl)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5,9-tetraene (9). Method A. Under N_2 , A solution of *n*-BuLi in *n*-hexane (2.5M, 0.05 mL, 1.25 mmol) was added dropwise to a solution of tetrabromide **8** (0.55 g, 1.19 mmol) in dry THF (20 mL) at -78 °C and the resulting mixture was stirred at the same temperature for 1 h. Trimethyltin chloride (0.22 g, 1.43 mmol) was added to the reaction mixture in one portion and the mixture was stirred 2 h at the same temperature. The resulting mixture was allowed to warm to room temperature overnight, it was diluted with water (50 mL) and extracted with Et_2O (3 \times 30 mL). Combined ethereal extracts were dried over MgSO_4 , and concentrated in *vacuo* to afford the bromo-stannyl olefin **9**, as a brown oil (0.68 g, 96%).

Method B. Under N_2 atmosphere, a solution of *n*-BuLi in hexane (2.5 M, 1.3 mL, 2.63 mmol) was added to a solution of dry diisopropylamine (0.40 mL, 2.88 mmol) in dry THF (5 mL) cooled at -78 °C. After 15 min, a solution of **6** (0.50 g, 1.31 mmol) in dry THF (15 mL) was added and the mixture was maintained at the same temperature for 1 h. A solution of trimethyltin chloride (0.31 g, 1.58 mmol) in dry THF (10 mL) was added dropwise and the temp. was left to rise to r.t. overnight. The final mixture was diluted with water (50 mL) and extracted with Et_2O (3 \times 50 mL). Combined ethereal extracts were dried over Na_2SO_4 , and concentrated in *vacuo* to afford the bromo-stannyl olefin **9**, as a brown oil (0.68 g, 96%). ^1H NMR (400 MHz, CDCl_3): 7.56 (s, 1 H), 7.38 (s, 1 H), 5.73 (s, 1 H), 5.36 (s, 1 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): 151.7, 149.2, 148.4, 146.3, 125.8, 124.7, 121.6, 120.8, 88.7, 86.8, -9.3. Compound **9** resulted pure enough for the following transformation and the purification was not attempted, because of the poor stability of the vinylstannane moiety on silica-gel.

syn- and anti-7,8,17,18,27,28-Hexabromo-31,32,33-trioxadecacyclo[22.6.1.1^{4,11}.1^{14,21}.0^{2,23}.0^{3,12}.0^{5,10}.0^{13,22}.0^{15,20}.0^{25,30}]tritriaconta-2,5,7,9,12,15,17,19,22,25,27,29-dodecaene (syn-1) and (anti-1). In a flame dried 50-ml two-necked round-bottomed flask fitted with a nitrogen inlet, copper(I) 2-thiophenecarboxylate (CuTC) (0.13 g, 0.69 mmol) was introduced, purging with nitrogen and capping with a rubber septum. The reactor was cooled to -20 °C and consecutively dry NMP (15 mL) and bromostannyl-olefin **9** (0.25 g, 0.46 mmol) were added via syringe. The reaction evolution was monitored by ^1H -NMR spectroscopy. After 30 min, an aqueous 10% NH_3 solution (20 mL) was added and the mixture was stirred until the brown solid disappeared. The mixture was extracted with diethyl ether (3 \times 20 mL) and the combined ethereal extracts were dried over MgSO_4 . Volatile materials were removed in *vacuo*, and the residue was purified by column chromatography on neutral aluminum oxide with EtOAc/n -hexane (3:7) as eluant.

First eluate: (anti-1) (34 mg, 25% yield), colorless crystals from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:3), M.p. > 350 °C (dec.). IR (KBr): 3008, 1725, 1566, 1435, 1352, 1308, 1264, 1230, 1188, 1158, 1085, 987, 936, 903, 837. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 7.87 (s, 2 H), 7.84 (s, 2 H), 7.82 (s, 2 H), 6.44 (s, 2 H), 6.42 (s, 2 H), 6.40 (s, 2 H). ^{13}C NMR (100 MHz,

DMSO-*d*₆): 149.4, 149.3, 149.3, 137.0, 136.7, 136.4, 126.9 (2 overlapping C), 126.6, 121.9, 121.9, 121.8, 79.9, 79.7, 79.6. Anal. calc. for C₃₀H₁₂Br₆O₃: C 40.04, H 1.34; found: C 40.09, H 1.36.

Second eluate: (*syn-1*) (92 mg 67% yield) colorless crystals from CH₂Cl₂/*n*-hexane (1:3), M.p. > 350 °C (dec.). IR (KBr): 3008, 1723, 1563, 1429, 1351, 1301, 1261, 1172, 1085, 982. ¹H NMR (400 MHz, CDCl₃): 7.44 (s, 6 H), 6.08 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃): 146.9, 135.5, 125.4, 122.7, 79.8. Anal. calc. for C₃₀H₁₂Br₆O₃: C 40.04, H 1.34; found: C 40.07, H 1.33.

Trinaphthylene (2). In a flame dried 50-ml two-necked round-bottomed flask fitted with argon inlet, titanium(IV) chloride (0.02 ml, 0.17 mmol) was added to dry THF (5 ml). Lithium aluminumhydride (2.4 mg, 0.06 mmol) and a solution of triethylamine (0.03 mL, 0.22 mmol) in dry THF (0.5 mL) were added consecutively and the resulting mixture was heated to reflux for 15 min. A solution of *anti-1*, or a 3:7 mixture of *anti-1* and *syn-1*, (15 mg, 0.02 mmol) in dry THF (2 mL) was added dropwise and the reaction mixture was refluxed for 12 h. The mixture was cooled and portioned between satd. aq. K₂CO₃ (10 mL) and CHCl₃ (3 × 10 mL). Combined organic extracts were dried over Na₂SO₄, concentrated under reduced pressure to afford a solid residue that was purified by column chromatography (silica-gel, 10 g; eluant EtOAc/*n*-hexane (1:10)) to furnish trinaphthylene **2** (6.2 mg, 98%) as colorless crystals from CH₂Cl₂/*n*-hexane (1:3), M.p. > 350 °C (lit.⁴⁴ > 320 °C). ¹H NMR (400 MHz, CDCl₃): 9.11 (s, 6 H), 8.11-8.07 (m, 6 H), 7.59-7.56 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): 133.1, 129.2, 128.3, 126.6, 122.9.

Acknowledgements

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Supplementary Material

¹H NMR Spectrum of *syn-1 anti-1*, **2**, **4**, **5**, **6**, *exo-7* and *endo-7*, **8**, **9**; ¹³C NMR Spectrum of *syn-1* and *anti-1*, **2**, **4**, **5**, **6**, **8**, **9**, Spectrum; and HRMS Spectra **5-6**, **8**, and **21-23**.

References

1. Fabris, F.; Zonta, C.; Borsato, G.; De Lucchi, O. *Acc. Chem. Res.* **2011**, *44*, 416-423.
<https://doi.org/10.1021/ar100128s>
2. Fabris, F.; De Lucchi, O.; Nardini, I.; Crisma, M.; Mazzanti, A.; Mason, S. A.; Cailleau-Lemée, M.-H.; Scaramuzzo, F. A.; Zonta, C. *Org. Biomol. Chem.* **2012**, *10*, 2464-2469.
<https://doi.org/10.1039/c2ob06774a>
3. Bao, X.; Rieth, S.; Stojanović, S.; Hadad, C. M.; Badjić, J. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 4816-4819.
<https://doi.org/10.1002/anie.201000656>
4. Rieth, S.; Bao, X.; Wang, B.-Y.; Hadad, C. M.; Badjić, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 773-776.
<https://doi.org/10.1021/ja908436c>
5. Tartaggia, S.; Scarso, A.; Padovan, P.; De Lucchi, O.; Fabris, F. *Org. Lett.* **2009**, *11*, 3926-3929.
<https://doi.org/10.1021/ol901621b>
6. Rieth, S.; Wang, B.-Y.; Bao, X.; Badjić, J. D. *Org. Lett.* **2009**, *11*, 2495-2498.
<https://doi.org/10.1021/ol9009392>

7. Gardlik, M.; Yan, Z.; Xia, S.; Rieth, S.; Gallucci, J.; Hadad, C. M.; Badjić, J. D. *Tetrahedron* **2009**, *65*, 7213-7219.
<https://doi.org/10.1016/j.tet.2008.11.098>
8. Wang, B.-Y.; Bao, X.; Yan, Z.; Maslak, V.; Hadad, C. M.; Badjić, J. D. *J. Am. Chem. Soc.* **2008**, *130*, 15127-15133.
<https://doi.org/10.1021/ja8041977>
9. Rieth, S.; Yan, Z.; Xia, S.; Gardlik, M.; Chow, A.; Fraenkel, G.; Hadad, C. M.; Badjić, J. D. *J. Org. Chem.* **2008**, *73*, 5100-5109.
<https://doi.org/10.1021/jo800748k>
10. Scarso, A.; Pellizzaro, L.; De Lucchi, O.; Linden, A.; Fabris, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 4972-4975.
<https://doi.org/10.1002/anie.200701123>
11. Fabris, F.; Pellizzaro, L.; Zonta, C.; De Lucchi, O. *Eur. J. Org. Chem.* **2007**, 283-291.
<https://doi.org/10.1002/ejoc.200600673>
12. Yan, Z.; Xia, S.; Gardlik, M.; Seo, W.; Maslak, V.; Gallucci, J.; Hadad, C. M.; Badjić, J. D. *Org. Lett.* **2007**, *9*, 2301-2304.
<https://doi.org/10.1021/ol0705595>
13. Maslak, V.; Yan, Z.; Xia, S.; Gallucci, J.; Hadad, C. M.; Badjić, J. D. *J. Am. Chem. Soc.* **2006**, *128*, 5887-5894.
<https://doi.org/10.1021/ja060534l>
14. Zonta, C.; Cossu, S.; De Lucchi, O. *Eur. J. Org. Chem.* **2000**, 1965-1971.
[https://doi.org/10.1002/\(SICI\)1099-0690\(200005\)2000:10<1965::AID-EJOC1965>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1099-0690(200005)2000:10<1965::AID-EJOC1965>3.0.CO;2-C)
15. Venugopalan, P.; Burgi, H.-B.; Frank, N. L.; Baldrige, K. K.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 2419-2422.
[https://doi.org/10.1016/0040-4039\(95\)00318-7](https://doi.org/10.1016/0040-4039(95)00318-7)
16. Gandeepan, P.; Rajamalli, P.; Cheng, C.-H. *Angew. Chem. Int. Ed.* **2016**, *55*, 4308-4311.
<https://doi.org/10.1002/anie.201512018>
17. Link, A.; Fischer, C.; Sparr, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 12163-12166.
<https://doi.org/10.1002/anie.201505414>
18. Akita, R.; Kawanishi, K.; Hamura, T. *Org. Lett.* **2015**, *17*, 3094-3097.
<https://doi.org/10.1021/acs.orglett.5b01364>
19. Haneda, H.; Eda, S.; Aratani, M.; Hamura, T. *Org. Lett.* **2014**, *16*, 286-289.
<https://doi.org/10.1021/ol4032792>
20. Luo, R.; Liao, J.; Xie, L.; Tang, W.; Chan, A. S. C. *Chem. Commun.* **2013**, *49*, 9959-9961.
<https://doi.org/10.1039/c3cc46009f>
21. Standera, M.; Häfliger, R.; Gershoni-Poranne, R.; Stanger, A.; Jeschke, van Beek, J. D.; Bertschi, L.; Schlueter, A. D. *Chem. Eur. J.* **2011**, *17*, 12163-12174.
<https://doi.org/10.1002/chem.201100443>
22. Davoust, M.; Kitching, J. A.; Fleming, M. J.; Lautens, M. *Chem. Eur. J.* **2010**, *16*, 50-54.
<https://doi.org/10.1002/chem.200902694>
23. Anthony, I. J.; Wege, D. *Austr. J. Chem.* **1996**, *49*, 1263-1272.
<https://doi.org/10.1071/CH9961263>
24. Hart, H.; Lai, C.; Nwokogu, G. C.; Shamouilian, S. *Tetrahedron* **1987**, *43*, 5203-5224.
[https://doi.org/10.1016/S0040-4020\(01\)87696-1](https://doi.org/10.1016/S0040-4020(01)87696-1)

25. Standera, M.; Haefliger, R.; Gershoni-Poranne, R.; Stanger, A.; Jeschke, G.; Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641-1654.
[https://doi.org/10.1016/S0040-4020\(01\)87581-5](https://doi.org/10.1016/S0040-4020(01)87581-5)
26. Altundas, A.; Dastan, A.; McKee, M. M.; Balci, M. *Tetrahedron*, **2000**, *56*, 6115-6120.
[https://doi.org/10.1016/S0040-4020\(00\)00561-5](https://doi.org/10.1016/S0040-4020(00)00561-5)
27. Giorgio, E.; Rosini, C.; Fabris, F.; Fregonese, E.; Toniolo, U.; De Lucchi, O. *Chirality* **2009**, *21*, S86-S97.
<https://doi.org/10.1002/chir.20780>
28. Borsato, G.; Brussolo, S.; Crisma, M.; De Lucchi, O.; Lucchini, V.; Zambon, A. *Synlett*, **2005**, 1125-1128.
<https://doi.org/10.1055/s-2005-865215>
29. Fabris, F.; Zambrini, L.; Rosso, E.; De Lucchi, O. *Eur. J. Org. Chem.* **2004**, 3313-3322.
<https://doi.org/10.1002/ejoc.200400120>
30. Dastan, A.; Uzundumlu, E.; Balci, M.; Fabris, F.; De Lucchi, O. *Eur. J. Org. Chem.* **2004**, 183-192.
<https://doi.org/10.1002/ejoc.200300478>
31. Sakurai, H.; Daiko, T.; Hirao, T. *Science*, **2003**, *301*, 1878.
<https://doi.org/10.1126/science.1088290>
32. Fabris, F.; Bellotto, L.; De Lucchi, O. *Tetrahedron Lett.* **2003**, *44*, 1211-1213.
[https://doi.org/10.1016/S0040-4039\(02\)02789-2](https://doi.org/10.1016/S0040-4039(02)02789-2)
33. Borsato, G.; De Lucchi, O.; Fabris, F.; Lucchini, V.; Pasqualotti, M.; Zambon, A. *Tetrahedron Lett.* **2003**, *44*, 561-563.
[https://doi.org/10.1016/S0040-4039\(02\)02533-9](https://doi.org/10.1016/S0040-4039(02)02533-9)
34. Bolzan, A.; Bortoluzzi, M.; Borsato, G.; Fabbro, C.; Dastan, A.; De Lucchi, O.; Fabris, F. *Helv. Chim. Acta* **2015**, *98*, 1067-1074.
<https://doi.org/10.1002/hlca.201500018>
35. Dastan, A.; Fabris, F.; De Lucchi, O.; Guney, M.; Balci, M. *Helv. Chim. Acta* **2003**, *86*, 3411-3416.
<https://doi.org/10.1002/hlca.200390285>
36. Borsato, G.; De Lucchi, O.; Fabris, F.; Groppo, L.; Lucchini, V.; Zambon, A. *J. Org. Chem.* **2002**, *67*, 7894-7897.
<https://doi.org/10.1021/jo020396s>
37. Yan, Z.; McCracken, T.; Xia, S.; Maslak, V.; Gallucci, J.; Hadad, C. M.; Badjić, J. D. *J. Org. Chem.* **2008**, *73*, 355-363.
<https://doi.org/10.1021/jo701538g>
38. De Lucchi, O.; Dastan, A.; Altundas, A.; Fabris, F.; Balci, M. *Helv. Chim. Acta* **2004**, *87*, 2364-2367.
<https://doi.org/10.1002/hlca.200490213>
39. Engelhart, J. U.; Tverskoy, O.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2014**, *136*, 15166-15169.
<https://doi.org/10.1021/ja509723q>
40. Haneda, H.; Eda, S.; Aratani, M.; Hamura, T. *Org. Lett.* **2014**, *16*, 286-289.
<https://doi.org/10.1021/ol4032792>
41. Dai, G.; Chang, J.; Zhang, W.; Bai, S.; Huang, K. W.; Xu, J.; Chi, C. *Chem. Commun.* **2015**, *51*, 503-506.
<https://doi.org/10.1039/C4CC07630C>
42. Niu, W. X.; Yang, E. Q.; Shi, Z. F.; Cao, X. P.; Kuck, D. *J. Org. Chem.* **2012**, *77*, 1422-1434.
<https://doi.org/10.1021/jo2022668>
43. Akin, E. T.; Erdogan, M.; Dastan, A.; Saracoglu, N. *Tetrahedron*, **2017**, *73*, 5537-5546.
<https://doi.org/10.1016/j.tet.2017.07.058>

44. Garcia-Lopez, J.-A.; Greaney, M. F. *Org. Lett.* **2014**, *16*, 2338-2341.
<https://doi.org/10.1021/ol5006246>
45. Brockmann, H.; Greve, H.; Waldmuller, W.; *Chem. Ber.* **1971**, *104*, 1436-1454.
<https://doi.org/10.1002/cber.19711040512>
46. Hausigk, D. *Chem. Ber.* **1970**, *103*, 659-662.
<https://doi.org/10.1002/cber.19701030302>
47. Bell, F.; Hunter, W. H. *J. Chem. Soc.* **1950**, 2903-2904.
48. Pummerer, R.; Pfaff, A.; Riegelbauer, G.; Rosenhauer, E. *Chem. Ber.* **1939**, *72*, 1623.
<https://doi.org/10.1002/cber.19390720829>
49. Pummerer, R.; Luttringhaus, A.; Fick, R.; Pfaff, A.; Riegelbauer, G.; Rosenhauer, E. *Chem. Ber.* **1938**, *71*, 2569-2572.
<https://doi.org/10.1002/cber.19380711224>
50. Rosenbauer, E.; Braun, F.; Pummerer, R.; Riegelbauer, G. *Chem. Ber.* **1937**, *70*, 2281-2287.
<https://doi.org/10.1002/cber.19370701117>