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Supporting Information

Efficient Thiabridged Triarylamine Heterohelicenes Synthesis, Resolution and Absolute Configuration Determination

Giuseppe Lamanna,[a] Cristina Faggi,[a] Francesco Gasparrini,[b] Alessia Ciogli,[b] Claudio Villani,[b] Philip J. Stephens,[c] Frank J. Devlin[c] and Stefano Menichetti*[a]

[a] Dipartimento di Chimica Organica e Laboratorio di Progettazione e Sintesi di Eterociclici Biologicamente Attivi (HeteroBioLab) Università di Firenze. Via della Lastruccia 13, 50019, Sesto Fiorentino, Firenze, Italy

[b] Dipartimento di Studi di Chimica e Tecnologia delle Sostanze
Biologicamente Attive Universita di Roma "La Sapienza"
P. le A. Moro 5, 00185 Roma, Italy

[c] Department of Chemistry, University of Southern California, Los Angeles, CA 90089

Experimental Section

GENERAL

Chloroform, dichloromethane and toluene, were dried following standard procedures. All reactions were monitored by tlc on commercially available precoated plates (silica gel 60 F254) and the products were visualized with acid vanillin solution. Silica gel 60, 230–400 mesh, was used for column chromatography. Petrol refers to light petroleum, bp 40–60 °C. Melting points were measured on a microscopic apparatus and are uncorrected. When not differently described, ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ solutions. Residual $CHCl_3$ was used as reference at 7.26 and 77.00 ppm, respectively. FT-IR spectra were recorded in KBr pellets or $CHCl_3$ solutions. Mass spectra were measured with a Shimadzu QP5050. Commercial available reagents, catalysts and ligands were used as obtained from freshly open container without further purifications. Phthalimidesulfenyl chloride **4** was prepared from the corresponding commercial available disulfide (purchased from Chemper snc) as reported elsewhere.[1-SI]

X-RAY DATA COLLECTION

Crystals were mounted on a glass fiber then compound **7a** was analyzed using a Goniometer Oxford Diffraction KM4 Xcalibur2 with a graphite-monochromated Cu/Kα radiation (40mA/-40KV) whereas compounds **7c** and **12** were analyzed with a graphite-monochromated Mo/Kα radiation (40mA/-40KV). All the measures were carried out at room temperature.

STRUCTURE REFINEMENT

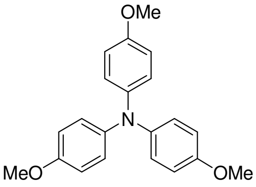
The integrated intensities, measured using the ω scan mode, were corrected for Lorentz and polarization effects.[2-SI] The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of symmetry-equivalent reflections. Structures were solved by direct methods of SIR2002[3-SI] and refined using the full-matrix least squares on F^2 provided by SHELXL97.[4-SI] The non-hydrogen atoms were refined anisotropically.

In all three cases methylic hydrogen atoms were assigned in calculated positions whereas the other hydrogens were found in the Fourier synthesis; all of them were refined as isotropic. Copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk; internet://www.ccdc.cam.ac.uk) with the deposition numbers reported below for each compound.

SYNTHESIS

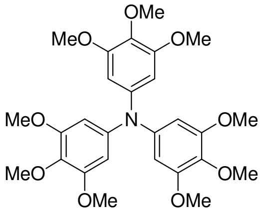
Tris(*p*-tolyl)amine **5a** is commercially available, amines **5b**, **5c** and **8** were prepared *via* Buchwald-Hartwig cross-coupling as it follows: An oven-dried Schlenk flask was charged with aniline (1.0 mmol), NaO*t*-Bu (2.5 mmol), P(*t*-Bu)$_2$-*o*-biphenyl (8 mol %), $Pd_2(dba)_3$ (2 mol %), dry toluene (5 mL) and aryl bromide (2.5 mmol), under a nitrogen atmosphere. The mixture was stirred at 100 °C for 15-48 h under nitrogen. Upon cooling, the reaction mixture was diluted with diethyl ether (20 mL), washed with brine (3x30 mL), and then dried over Na_2SO_4. Concentration in vacuum afforded the desired triarylamine that was purified by chromatography on silica gel.

Tris(4-methoxyphenyl)amine (5b)[5-SI]



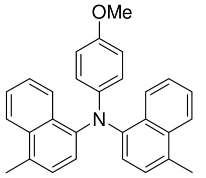
The product **5b** was obtained, after column chromatography (CH_2Cl_2/petroleum ether = 10/1), as a yellow solid (95% yield), m.p. 90-92 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.78 (s, 9H), 3.85 (s, 9H), 6.75-6.99 (m, 12H); MS: *m/z* (%) = 335 ($M^{\bullet+}$, 100), 320 (96), 168 (17); Anal. calcd. for $C_{21}H_{21}NO_3$: C 75.20, H 6.31, N 4.18; found: C 75.20, H 6.31, N 4.00.

Tris(3,4,5-trimethoxyphenyl)amine (5c)



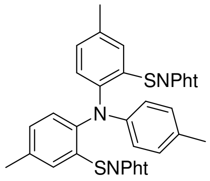
The product **5c** was obtained, after column chromatography (CH_2Cl_2/ethyl acetate = 10/1), as a brown solid (70% yield), m.p. 211-213 °C; ^{1}H NMR: δ = 3.72 (s, 18H), 3.85 (s, 9H), 6.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 56.23, 61.02, 101.75, 133.77, 143.37, 153.31; MS: *m/z* (%) = 515 ($M^{\bullet+}$, 96), 500 (100), 227 (11); Anal. calcd. for $C_{27}H_{33}NO_9$: C 62.90, H 6.45, N 2.72; found: C 63.00, H 6.63, N 2.20.

N-(4-methoxyphenyl)-4-methyl-*N*-(4-methylnaphthalen-1-yl)naphthalen-1-amine (8)



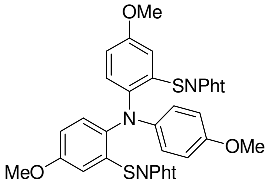
The product **8** was obtained, after column chromatography (petroleum ether/CH_2Cl_2 = 10/1), as a yellow solid (75% yield), m.p. 85-87 °C; ^{1}H NMR: δ = 2.67 (s, 6H), 3.74 (s, 3H), 6.67-6.75 (m, 4H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.30-7.35 (m, 2H), 7.46-7.51 (m, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.47, 55.56, 114.42, 122.66, 124.06, 124.76, 125.15, 125.80, 125.87, 126.88, 130.22, 131.22, 134.20, 144.38, 145.02, 154.24; MS: *m/z* (%) = 403 ($M^{\bullet+}$, 100), 388 (34), 115 (21); Anal. calcd. for $C_{29}H_{25}NO$: C 86.32, H 6.24, N 3.47; found: C 86.34, H 6.87, N 3.79.

Bis-*N*-thiophthalimide (6a)



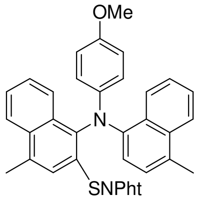
To a solution of tris(*p*-tolyl)amine (**5a**) (1.0 mmol) in dry $CHCl_3$ (15 mL) was added phthalimidesulfenyl chloride (**4**) (2.3 mmol) under a nitrogen atmosphere. After stirring at 60 °C for 24h, the reaction mixture was diluted with CH_2Cl_2 (5 mL), and washed with a saturated $NaHCO_3$ solution (2x30 mL) and water (2x30 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the crude material was purified by flash chromatography (CH_2Cl_2/petroleum ether = 4/1) to provide the product **6a** as a yellow solid (83% yield), m.p. 259-261 °C; IR (KBr): ν = 1787 + 1742 + 1709 (C=O stretching PhtN), 1278 cm^{-1}; ^{1}H NMR: δ = 2.22 (s, 6H), 2.26 (s, 3H), 6.68-6.71 (m, 2H), 6.86 (d, *J* = 1.2 Hz, 2H), 7.03-7.07 (m, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.76-7.81 (m, 4H), 7.91-7.96 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.92, 21.37, 118.42, 124.13, 127.10, 128.92, 129.83, 130.36, 130.56, 132.26, 133.75, 134.71, 136.35, 141.61, 146.31, 167.96; MS: *m/z* (%) = 641 ($M^{\bullet+}$, 3), 147 (43), 76 (100), 50 (88); Anal. calcd. for $C_{37}H_{27}N_3O_4S_2$: C, 69.25; H, 4.24; N 6.55. Found: C, 69.38; H, 4.10; N, 6.12.

Bis-*N*-thiophthalimide (6b)



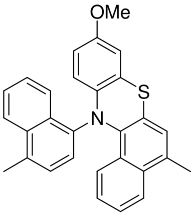
To a solution of triarylamine **5b** (1.0 mmol) in dry $CHCl_3$ (8 mL) was added phthalimidesulfenyl chloride (2.3 mmol) under a nitrogen atmosphere. After stirring at rt for 4h, the reaction mixture was diluted with CH_2Cl_2 (10 mL), and washed with a saturated $NaHCO_3$ solution (2x20 mL) and water (2x20 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the crude material was purified by flash chromatography (CH_2Cl_2) to provide the product **6b** as a yellow solid (83% yield), m.p. 195 °C dec.; IR (KBr): ν = 1787 + 1742 + 1709 (C=O stretching PhtN), 1485, 1275 cm^{-1}; ^1H NMR: δ = 3.68 (s, 6H), 3.76 (s, 3H), 6.56 (d, *J* = 2.8 Hz, 2H), 6.73-6.84 (m, 6H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.76-7.81 (m, 4H), 7.90-7.95 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 55.39, 55.50, 111.98, 113.01, 114.98, 119.48, 123.97, 129.75, 131.99, 134.63, 135.55, 137.05, 142.33, 153.89, 157.57, 167.62; MS: *m/z* (%) = 689 ($M^{\bullet+}$, 8), 542 (30), 365 (64), 147 (100), 104 (86), 76 (99); Anal. calcd. for $C_{37}H_{27}N_3O_7S_2$: C, 64.43; H, 3.95; N, 6.09. Found: C, 64.24; H, 3.93; N, 5.99.

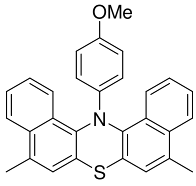
***N*-Thiophthalimide (9)**



To a solution of triarylamine **8** (1.0 mmol) in dry $CHCl_3$ (5 mL) a solution of phthalimidesulfenyl chloride (1.0 mmol) in dry $CHCl_3$ (8 mL) was added dropwise, at 0 °C under a nitrogen atmosphere. The mixture was stirred at rt for 3h then diluted with CH_2Cl_2 (10 mL), and washed with a saturated $NaHCO_3$ solution (2x20 mL) and water (2x20 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2), to give compound **9** as a yellow solid (87% yield), m.p. 145 °C dec.; IR (KBr): ν = 1784 + 1739 + 1711 (C=O stretching PhtN), 1504, 1275 cm^{-1}; ^1H NMR: δ = 2.58 (s, 3H), 2.67 (s, 3H), 3.74 (s, 3H), 6.66-6.76 (m, 3H), 6.88-6.94 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.28-7.36 (m, 2H), 7.38-7.44 (m, 2H), 7.49-7.53 (m, 1H), 7.75-7.81 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.94-8.02 (m, 3H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR: δ = 19.45, 19.84, 55.49, 114.42, 114.82, 119.95, 121.26, 122.55, 122.62, 124.18, 124.75, 124.89, 125.05, 125.07, 125.52, 125.85, 126.39, 127.13, 127.17, 128.41, 131.28, 132.21, 132.22, 132.69, 133.09, 134.17, 134.88, 134.91, 138.19, 140.08, 143.61, 153.91, 168.16; MS: *m/z* (%) = 580 ($M^{\bullet+}$, 17), 433 (100), 147 (51), 76 (79), 50 (67); Anal. calcd. for $C_{37}H_{28}N_2O_3S$: C, 76.53; H, 4.86; N, 4.82. Found: C, 76.49; H, 4.47; N, 4.22.

9-Methoxy-5-methyl-12-(4-methylnaphthalen-1-yl)-12*H*-benzo[*a*]phenothiazine (10) and 14-(4-Methoxyphenyl)-5,9-dimethyl-14*H*-dibenzo[*a,j*]phenothiazine (11)

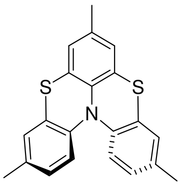




To a solution of amine **9** (1.0 mmol) in dry CH_2Cl_2 (10 mL) was added $BF_3{\cdot}Et_2O$ (40.0 mmol) under a nitrogen atmosphere. After 12h of stirring at rt, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with saturated Na_2CO_3 solution (2x20 mL) and saturated NaF solution (2x20 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent gave a 10:1 mixture of regioisomers **10** and **11**, that was purified by flash chromatography (petroleum ether/CH_2Cl_2 = 6/1). More mobile regioisomer **10** was obtained as a yellow solid (63% yield), m.p. 195 °C dec.; ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.20 (s, 3H), 2.27 (s, 3H), 3.13 (s, 3H), 6.37 (dd, J = 3.2, 9.2 Hz, 1H), 6.79 (d, J = 3.2 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 7.04-7.13 (m, 3H), 7.30-7.35 (m, 1H), 7.56-7.63 (m, 2H), 7.73 (d, J = 9.2 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H) 8.16 (d, J = 7.6 Hz, 1H), 8.83 (d, J = 9.2 Hz, 1H), 9.58 (d, J = 8.4 Hz, 1H); ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.07, 19.29, 54.99, 112.16, 113.44, 124.35, 124.85, 125.42, 125.47, 125.86, 125.91, 126.02, 126.28, 126.48, 127.33, 127.42, 127.84, 128.35, 131.19, 132.16, 132.27, 132.76, 133.36, 133.43, 134.61, 140.04, 141.44, 147.49, 157.34; MS: *m/z* (%) = 434 ($M^{\bullet+}$, 100), 418 (35), 292 (40); Anal. calcd. for $C_{29}H_{23}NOS$: C, 80.34; H, 5.35; N, 3.23. Found: C, 80.72; H, 5.41; N, 3.22.

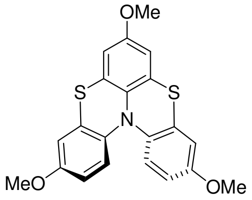
Less mobile regioisomer **11** was obtained as a white solid (7% yield), m.p. 210 °C dec.; ^{1}H NMR: δ = 2.72 (s, 6H), 3.64 (s, 3H), 6.25-6.29 (m, 2H), 6.52-6.56 (m, 2H), 7.45 (s, 2H), 7.54-7.58 (m, 2H), 7.60-7.65 (m, 2H), 8.03 (d, J = 8.4 Hz, 2H), 8.57 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 19.39, 55.46, 113.92, 115.76, 123.90, 124.67, 125.74, 126.47, 126.92, 132.15, 133.13, 134.28, 136.57, 141.25, 153.16; MS: *m/z* (%) = 434 ($M^{\bullet+}$, 100), 326 (57), 217 (23); Anal. calcd. for $C_{29}H_{23}NOS$: C, 80.34; H, 5.35; N, 3.23. Found: C, 80.41; H, 5.50; N, 3.67.

Heterohelicene 7a



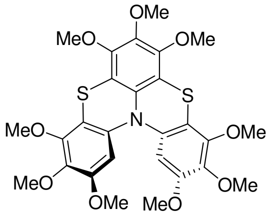
To a solution of bis-*N*-thiophthalimide **6a** (1.0 mmol) in dry CH_2Cl_2 (50 mL) was added $BF_3{\cdot}Et_2O$ (40.0 mmol) under a nitrogen atmosphere. After 3h of stirring at rt, the mixture was diluted with CH_2Cl_2 (15 mL) and washed with a saturated Na_2CO_3 solution (2x60 mL) and a saturated NaF solution (2x60 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent gave a crude that was purified by flash chromatography (petroleum ether/CH_2Cl_2 = 2/1) to afford the heterohelicene **7a** as a white solid (85% yield) further purified by recrystallization from $CHCl_3$, m.p. 162-164 °C; ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.80 (s, 3H), 1.96 (s, 6H), 6.55-6.59 (m, 4H), 6.87 (d, J = 1.2 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H); ^{13}C NMR (C_6D_6, 50 MHz): δ = 20.25, 20.56, 120.56, 125.98, 126.38, 127.31, 128.35, 134.07, 134.54, 137.78, 137.95, 140.90; MS: *m/z* (%) = 347 ($M^{\bullet+}$, 100), 315 (47), 158 (50); Anal. calcd. for $C_{21}H_{17}N_3NS_2$: C, 72.58; H, 4.93; N, 4.03. Found: C, 72.10; H, 4.98; N, 3.99. *Cristallographic data*: $C_{21}H_{17}NS_2$, M=347.47, Triclinic, space group P-1, a=7.739(1), b=14.834(1), c=15.147(1)Å, α=82.490(8), β=82.650(7), γ=89.300(7) V=1709.8(3)Å^3, Z=2 D_c=1.350, μ=2.810 mm^{-1}, F(000)=728. 18860 reflections were collected with a 4.49<θ<58.76 range with a completeness to theta 98,9%; 4850 were independent, the parameters were 497 and the final R index was 0.0431 for reflections having I>2σI, and 0.0887 for all data. There are two molecules (A and B of opposite helicity) in the asymmetric unit because they are not equivalent from a crystallographic point of view, that is due probably to the tiny difference in torsion angles between aromatic planes of molecule A and B respectively. Deposition number at the Cambridge Crystallographic Data Center: CCDC 673296.

Heterohelicene 7b



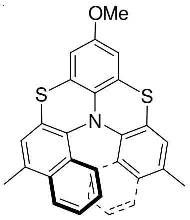
To a solution of bis-*N*-thiophthalimide **6b** (1.0 mmol) in dry CH_2Cl_2 (40 mL) was added $AlCl_3$ (4.0 mmol) under a nitrogen atmosphere. After 4h of stirring at rt, the mixture was diluted with CH_2Cl_2 (15 mL) and washed with a saturated Na_2CO_3 solution (2x50 mL) and water (2x50 mL). The organic layer was dried over Na_2SO_4. Evaporation of the solvent gave a crude that was purified by flash chromatography (CH_2Cl_2) to afford the heterohelicene **7b** as a dark yellow glassy solid (87% yield); ^1H NMR (C_6D_6, 400 MHz): δ = 3.11 (s, 3H), 3.22 (s, 6H), 6.49 (dd, J = 2.8, 8.8 Hz, 2H), 6.53 (s, 2H), 6.74 (d, J = 2.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H); ^{13}C NMR (C_6D_6, 100 MHz): δ = 55.17, 55.18, 111.37, 112.58, 114.23, 121.37, 127.13, 134.11, 136.77, 156.96, 157.36; MS: *m/z* (%) = 395 ($M^{\bullet+}$, 100), 380 (44), 160 (17); Anal. calcd. for $C_{21}H_{17}NO_3S_2$: C, 63.77; H, 4.33; N, 3.54. Found: C, 63.59; H, 4.29; N, 3.24.

Heterohelicene 7c



To a solution of triarylamine **5c** (1.0 mmol) in dry $CHCl_3$ (10 mL) was added phthalimidesulfenyl chloride (2.3 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 5h then diluted with CH_2Cl_2 (10 mL), and washed with a saturated $NaHCO_3$ solution (3x20 mL) and water (2x20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography (CH_2Cl_2) afforded the heterohelicene **7c** as a brown solid (63% yield) recrystallized from ethyl acetate, m.p. 150-152 °C; ^1H NMR (C_6D_6, 400 MHz): δ = 3.08 (s, 6H), 3.60 (s, 3H), 3.72 (s, 12H), 3.82 (s, 6H), 6.54 (s, 2H); ^{13}C NMR (C_6D_6, 100 MHz): δ = 55.83, 60.77, 60.90, 60.95, 101.81, 113.63, 116.26, 133.59, 138.46, 140.21, 144.27, 149.08, 150.70, 153.53; MS: *m/z* (%) = 575 ($M^{\bullet+}$, 100), 560 (20), 545 (13); Anal. calcd. for $C_{27}H_{29}NO_9S_2$: C, 56.33; H, 5.08; N, 2.43. Found: C, 56.36; H, 5.15; N, 2.41. *Cristallographic data*: $C_{27}H_{29}NO_9S_2$, M=575.63, Monoclinic, space group Pa, a=12.450(1), b=19.257(1), c=12.703(1)Å, β=119.265(4), V=2656.8(3)$Å^3$, Z=2 D_c=1.439, μ=0.257 mm^{-1}, F(000)=1208. 27045 reflections were collected with a 4.24<θ< 28.42 range with a completeness to theta 88.7%; the final R index was 0.0460 for reflections having I>2σI, and 0.0866 for all data. Also in this case there are two molecules (A and B of the same helicity), in the asymmetric unit. This is due to the small difference we can measure in the positions of the methoxy groups in molecule A and B respectively. Deposition number at the Cambridge Crystallographic Data Center: CCDC 673297.

Heterohelicene 12



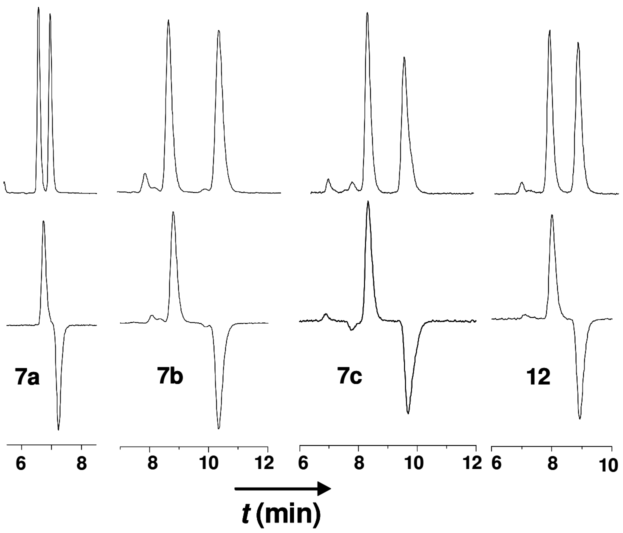
To a solution of thiazine **10** (1.0 mmol) in dry $CHCl_3$ (15 mL) was added phthalimidesulfenyl chloride (1.5 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 16h then diluted with CH_2Cl_2 (10 mL), and washed with a saturated $NaHCO_3$ solution (3x20 mL) and water (2x20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography (CH_2Cl_2/petroleum = ether 4/1) afforded the heterohelicene **12** as a yellow solid (75% yield) further purified by recrystallization from $CHCl_3$, m.p. 225-227 °C; ^{1}H NMR: δ = 2.66 (s, 6H), 3.76 (s, 3H), 6.73 (s, 2H), 6.98-7.04 (m, 2H), 7.22-7.27 (m, 2H), 7.31 (s, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C NMR: δ = 19.21, 55.85, 110.99, 122.63, 124.41, 125.41, 125.56, 125.95, 126.18, 127.64, 130.06, 131.71, 132.71, 136.99, 138.63, 157.30; MS: *m/z* (%) = 463 ($M^{\bullet+}$, 100), 433 (33), 201 (48), 57 (59); Anal. calcd. for $C_{29}H_{21}NOS_2$: C, 75.13; H, 4.57; N, 3.02. Found: C, 75.79; H, 4.67; N, 3.00. *Cristallographic data*: $C_{29}H_{21}NOS_2$, M=463.59, Monoclinic, space group P 21/c, a=8.750(1), b=13.973(2), c=18.329(2)Å, β=92.20(1), V=2239.3(5)Å^3, Z=4 D_c=1.375, μ=0.261 mm^{-1}, F(000)=968. 11153 reflections were collected with a 4.25<θ< 26.05 range with a completeness to theta 83.1%; the final R index was 0.0519 for reflections having I>2σI, and 0.1351 for all data. Deposition number at the Cambridge Crystallographic Data Center: CCDC 673298.

EXPERIMENTAL HPLC

Analytical (250*4.6 mm) and semipreparative (250*10 mm) columns packed with Chiralpak IA chiral stationary phase were obtained from Chiral Technologies Europe.

The HPLC resolution of **7a-c** and **12** was performed on a analytical chromatograph equipped with a Rheodyne model 7725i 20 μL loop injector, a PU-1580-CO_2 and PU-980 Jasco HPLC pumps, a spectrophotometer UV detector Jasco-975 and a circular dichroism detector Jasco 995-CD. Chromatographic data were collected and processed using Borwin software (Jasco Europe, Italy). Semi-preparative liquid chromatography was performed on a Waters chromatograph equipped with a Rheodyne model 7012 500 μL loop injector, a spectrophotometer UV SpectraMonitor 4100 and a refractive index Waters R401 detectors.

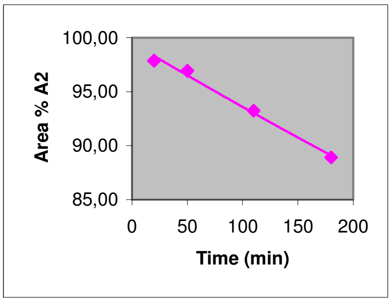
The mobile phase, delivered at a flow rate 1.00 mL/min, was optimized for each sample: hexane/dichloromethane 95/5 v/v for **7a**; hexane/dichloromethane 80/20 v/v for **7b**; hexane/dichloromethane 85/15 v/v + 0.1% MeOH for **7c**; hexane/dichloromethane 85/15 v/v for **12**.

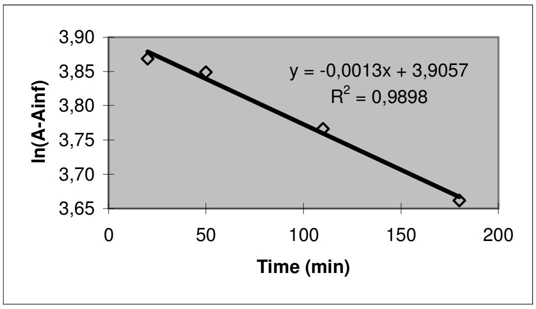


HPLC resolution of **7a-c** and **12** on a chiral stationary phase. UV (top) and CD (bottom) detections at 254 nm.

Kinetic of racemization of (-)-7a at 121 °C
temperature: 120,8 ± 0.2

Time(min)	Area **1** (%)	Area **2** (%)	A-Ainf	ln(A-Ainf)	%e.e,	ln (%ee)	Area **1** (µV*s)	Area **2** (µV*s)
20	2,12	97,88	47,88	3,87	95,75	4,56	84462	3893983
50	3,07	96,93	46,93	3,85	93,87	4,54	25865	817763
110	6,78	93,22	43,22	3,77	86,44	4,46	11717	161134
180	11,08	88,92	38,92	3,66	77,84	4,35	108129	867691



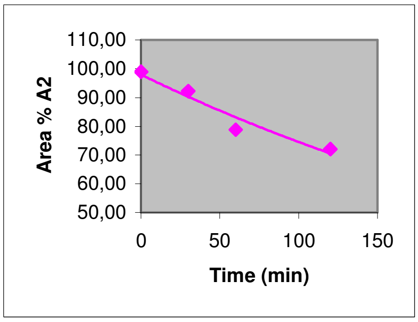


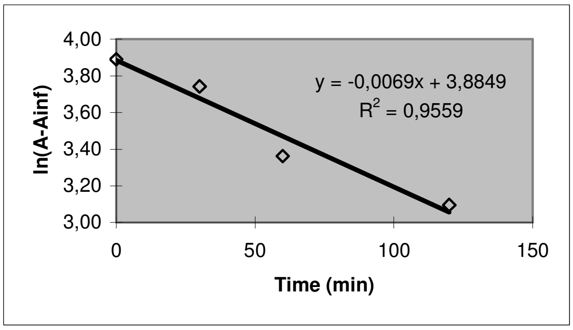
k (s-1)	**k (min-1)**	**T(°C)**	T(K)		DG#(Kcal/mol)		DG#(KJ/mol)
2,17E-05	0,0013	120,8	393,95		**31,68**		132,56

Kinetic of racemization of (-)-7a at 135℃

temperature: 135.3 ± 0.2

Time(min)	Area **1** (%)	Area **2** (%)	A-Ainf	ln(A-Ainf)	%e.e,	ln (%ee)	Area **1** (µV*s)	Area **2** (µV*s)
0	1,06	98,94	48,94	3,89	97,88	4,58	14749	1378594
30	7,81	92,19	42,19	3,74	84,38	4,44	87567	1033592
60	21,13	78,87	28,87	3,36	57,73	4,06	93281	348112
120	27,92	72,08	22,08	3,09	44,16	3,79	85318	220239



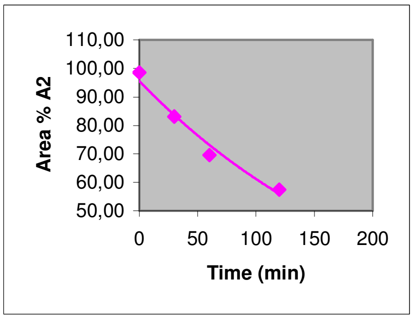


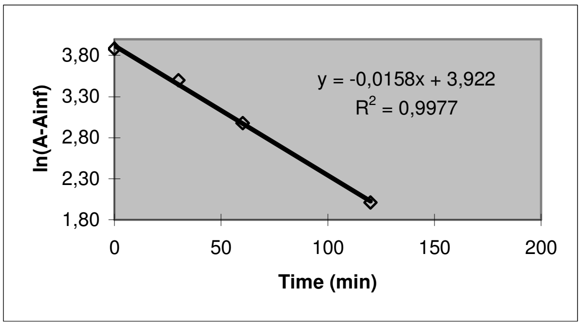
k (s-1)	**k (min-1)**	**T(℃)**	T(K)		DG#(Kcal/mol)		DG#(KJ/mol)
0,000115	0,0069	135,3	408,45		**31,52**		131,90

Kinetic of racemization of (-)-7a at 145℃

temperature 145.3 ± 0.2 ℃

Time(min)	Area **1** (%)	Area **2** (%)	A-Ainf	ln(A-Ainf)	%e.e,	ln (%ee)	Area **1** (µV*s)	Area **2** (µV*s)
0	1,49	98,51	48,51	3,88	97,02	4,57	30820	2037225
30	16,87	83,13	33,13	3,50	66,26	4,19	170213	838865
60	30,40	69,60	19,60	2,98	39,19	3,67	412774	944828
120	42,53	57,47	7,47	2,01	14,95	2,70	182605	246798



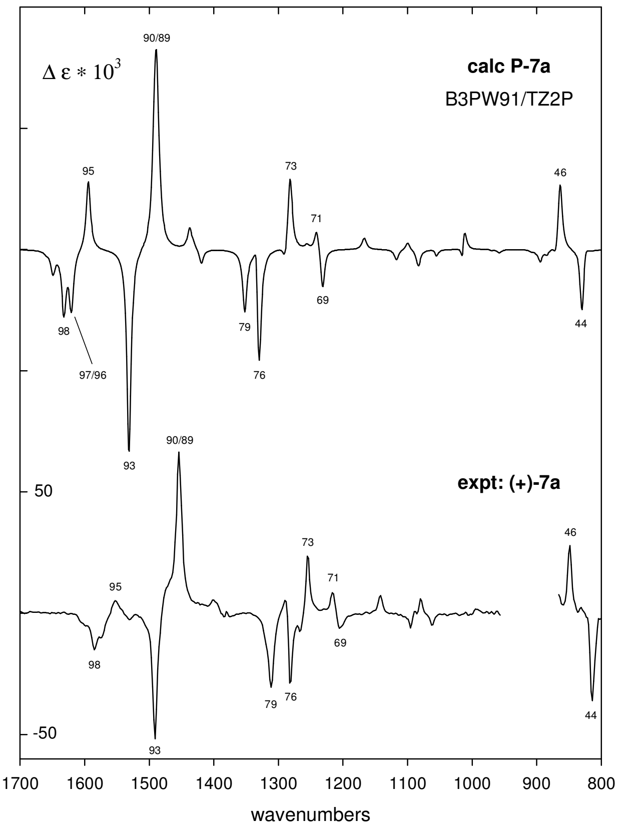


k (s-1)	**k (min-1)**	**T(℃)**	T(K)		DG#(Kcal/mol)		DG#(KJ/mol)
0,000263	0,0158	145,3	418,45		**31,63**		132,33

DETERMINATION OF ABSOLUTE CONFIGURATION

The VCD spectra of the (+) and (−) enantiomers of **7a**, ΔA(+) and ΔA(−), were measured using 0.05M $CDCl_3$ solutions, cell pathlengths of 236 and 546μ, and a Bomem/Biotools VCD instrument. The baselines were the VCD spectrum of *rac*-**7a**, ΔA(±). The spectra were converted to Δε units and normalised to 100%ee. The half-difference spectrum, ½[Δε(+)-Δε(−)] gives the VCD spectrum of (+)-**7a**, reported below.

The conformational analysis of **7a** was carried out using the MMFF94 molecular force field and the SPARTAN 02 program[6-SI]. DFT calculations of the equilibrium geometries and harmonic vibrational frequencies and rotational strengths of P and M **7a** were carried out using the GAUSSIAN 03 program[7-SI]. The resulting VCD spectra were predicted assuming Lorentzian band-shapes[8-SI].



Comparison of the B3PW91/TZ2P VCD spectrum of P-**7a** to the experimental VCD spectrum of (+)-**7a**. The numbers define the normal modes causing the bands.

SUPPLEMENTARY INFORMATION REFERENCES

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[4-SI] G. M. Sheldrick, *SHELXL97: Program for Crystal Structure Refinement*; Institut für Anorganische Chemie de Universitat Göttingen. Göttingen, Germany.

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[6-SI] SPARTAN, Wavefunction, Inc., www.wavefun.com.

[7-SI] GAUSSIAN, Gaussian Inc., www.gaussian.com.

[8-SI] a) R. W. Kawiecki, F. J. Devlin, P. J. Stephens, R. D. Amos, N. C. Handy, *Chem. Phys. Lett.* **1988**, *145*, 411-417; b) F. J. Devlin, P. J. Stephens, J. R. Cheeseman, M. J. Frisch, *J. Phys. Chem. A* **1997**, *101*, 6322-6333; c) F. J. Devlin, P. J. Stephens, J. R. Cheeseman, M. J. Frisch, *J. Phys. Chem. A* **1997**, *101*, 9912-9924.