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1,3-Diethynylallenes (DEAs): Enantioselective Synthesis, Absolute Configuration, and Chiral Induction in 1,1,4,4-Tetracyanobuta-1,3-dienes (TCBDs)

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Index

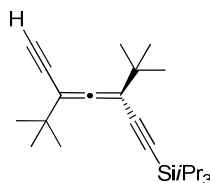
Experimental section.....	S3
Materials and general methods	S3
Preparation and characterization of (<i>M</i>)- 4a	S4
Derivatization of (<i>M</i>)- 4a with (<i>R</i>)-Mosher acid chloride	S4
Preparation and characterization of (<i>M</i>)- 4b	S6
Optical resolution of (\pm)- 4b by HPLC on a CSP	S6
Preparation and characterization of (<i>M,M</i>)- 5	S8
Preparation and characterization of (<i>M</i>)- 6	S9
Confirmation of the CT absorptions of (\pm)- 6 by acidification/reneutralization.....	S11
Optical resolution of (\pm)- 6 by HPLC on a CSP	S12
Preparation and characterization of (<i>M</i>)- 7	S13
Preparation and characterization of (<i>M</i>)- 8	S14
Preparation and characterization of (<i>M</i>)- 9 and (<i>M,M</i>)- 10	S15
Photoisomerization of (<i>P,P</i>)- 10 followed by CD spectroscopy.....	S16
Preparation and characterization of (<i>M,M</i>)- 11	S17
Optical resolution of 11 by HPLC on a CSP.....	S19
References:.....	S20

Experimental section:

Materials and general methods:

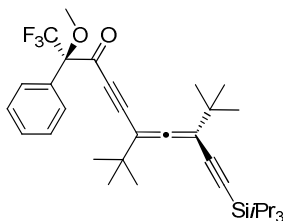
Reagents and solvents were purchased at reagent grade from Acros, Aldrich, and Fluka, and used as received. THF was freshly distilled from Na/benzophenone under N₂. Toluene was freshly distilled from Na under N₂. Flash chromatography (FC) was carried out with SiO₂ 60 (particle size 0.040–0.063 mm, 230-400 mesh; Fluka) and distilled technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO₂ 60 F254 obtained from Macherey-Nagel; visualization with a UV lamp (254 or 366 nm) and with a 10% solution of phosphomolybdic acid in ethanol. ¹H NMR and ¹³C NMR spectra were measured with a Varian Gemini 300, a Varian Mercury 300, or a Bruker ARX300 at 300 and 75 MHz, respectively. Chemical shifts are reported in ppm relative to the signal of Me₄Si. Residual solvent signals in the ¹H and ¹³C NMR spectra were used as an internal reference. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet) or d (doublet). UV/Vis spectra were recorded with a Varian Cary-500 Scan spectrophotometer. The absorption wavelengths are reported in nm with the molar extinction coefficient ϵ (M⁻¹cm⁻¹) in brackets. High-resolution (HR) EI-MS spectra were measured with a Hitachi–Perkin–Elmer VG-Tribrid spectrometer. HR FT-MALDI spectra were measured with an IonSpec Ultima Fourier transform (FT) instrument with 3-hydroxypicolinic acid (3-HPA) as matrix. The most important signals are reported in *m/z* units with M⁺ as the molecular ion. Elemental analyses were performed at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument.

Preparation and characterization of (*M*)-3,5-di-*tert*-butyl-1-(triisopropylsilyl)hepta-3,4-diene-1,6-diyne ((*M*)-4a)



To a solution of (*M*)-**1a** (73 mg, 0.17 mmol; e.r. 95:5) in THF (1.5 mL) and MeOH (1.5 mL), K₂CO₃ (26 mg, 0.19 mmol) was added and the mixture was stirred at 25°C for 2 h. The mixture was partitioned between saturated aq. NH₄Cl solution and hexane. The aqueous phase was extracted with hexane, and the combined organic phases were dried (MgSO₄), followed by removal of the solvent under reduce pressure. (*M*)-**4a** (48 mg, 0.13 mmol, 79%; e.r. 95:5) was obtained as a pale yellow oil. [α]_D: -125° (*c* = 1, CHCl₃). The spectroscopic data were identical to the reported ones.^[1]

Derivatization of (*P*)-4a with (*R*)-Mosher acid chloride: (2*R*,*P*)-6,8-di-*tert*-butyl-1,1,1-trifluoro-10-triisopropylsilyl-2-methoxy-2-phenyldeca-6,7-dien-4,9-diyne-3-one



Allene (*P*)-**4a** (44 mg, 0.12 mmol, 1.0 equiv., [α]_D = +125°; e.r. 95:5) was dissolved in dry THF (1.5 mL) and hexane (1.5 mL) and cooled to -60 °C. *n*-BuLi (81 μ L of a 1.6 M solution in hexane, 0.13 mmol, 1.05 equiv.) was added, followed by (*R*)-Mosher acid

chloride (44 μL , 0.24 mmol, 1.9 equiv.) after a few minutes. The solution was slowly warmed to 0 $^{\circ}\text{C}$ then to 20 $^{\circ}\text{C}$. Cyclohexane was added and the solution washed twice with H_2O . The organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The resulting oil was purified by flash-chromatography (SiO_2 ; cyclohexane/10% CH_2Cl_2). The ketone was obtained as colorless oil (22 mg, 37 μmol , 31%; d.r. = 95:5). The ^1H NMR spectrum in C_6D_6 showed two distinct signals for the methoxy-groups of the 2 diastereoisomers.^[2]

^1H NMR spectrum for determination of the e.r.

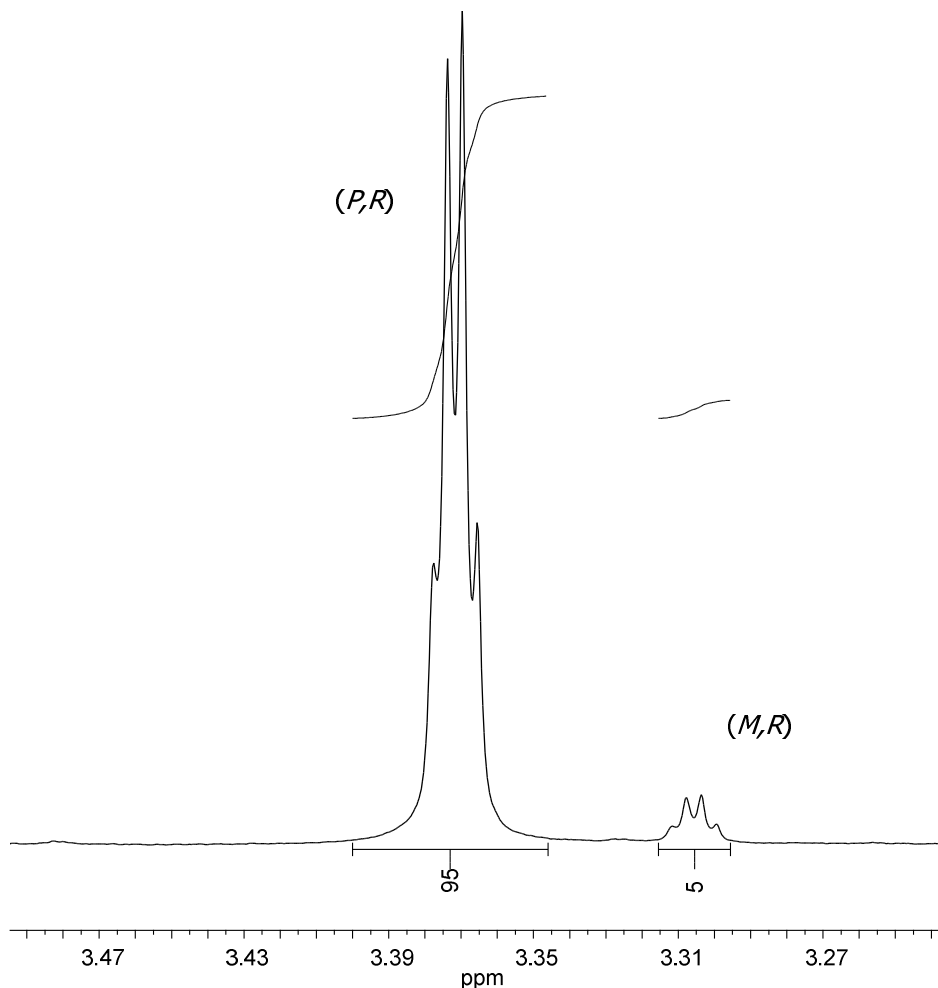
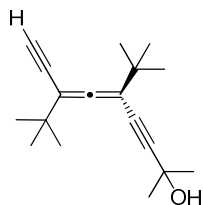


Figure S1: ^1H NMR spectrum of Mosher ketone in C_6D_6 from entry 6, Table 1. E.r. 95:5.

Preparation and characterization of (*M*)-5,7-di-*tert*-butyl-2-methylnona-5,6-diene-3,8-diyne-2-ol ((*M*)-4b)



To a solution of (*M*)-**1b** (62 mg, 0.15 mmol; e.r. 96:4) in THF (2 mL), *n*-Bu₄NF (150 μL, 1M, 0.15 mmol) was added and the mixture was stirred at 25°C for 2 h. Removal of the solvent under reduced pressure and purification by FC on SiO₂ (hexane/10% AcOEt) gave (*M*)-**4b** (31 mg, 0.12 mmol, 79%; e.r. 96:4) as a pale yellow oil. [α]_D = -98° (*c* = 1, CHCl₃). HPLC on the chiral stationary phase (CSP) WHELK-O1 (hexane/0.25% *i*PrOH) showed an e.r. of 96:4. The spectroscopic data were identical to the reported ones.^[3]

Optical resolution of (±)-4b by HPLC on a CSP

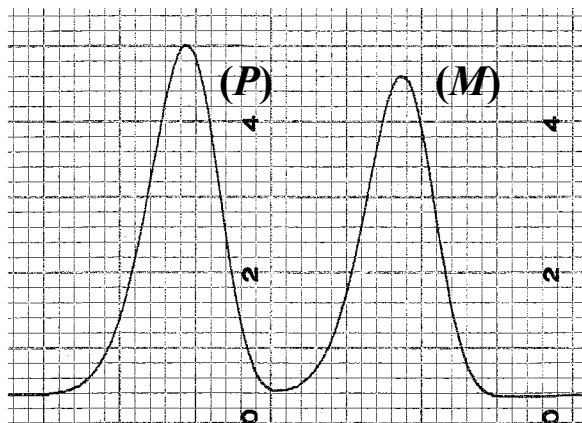


Figure S2. Recycling HPLC of (±)-**4b** on the CSP WHELK-O1 (hexane/0.25% *i*PrOH).

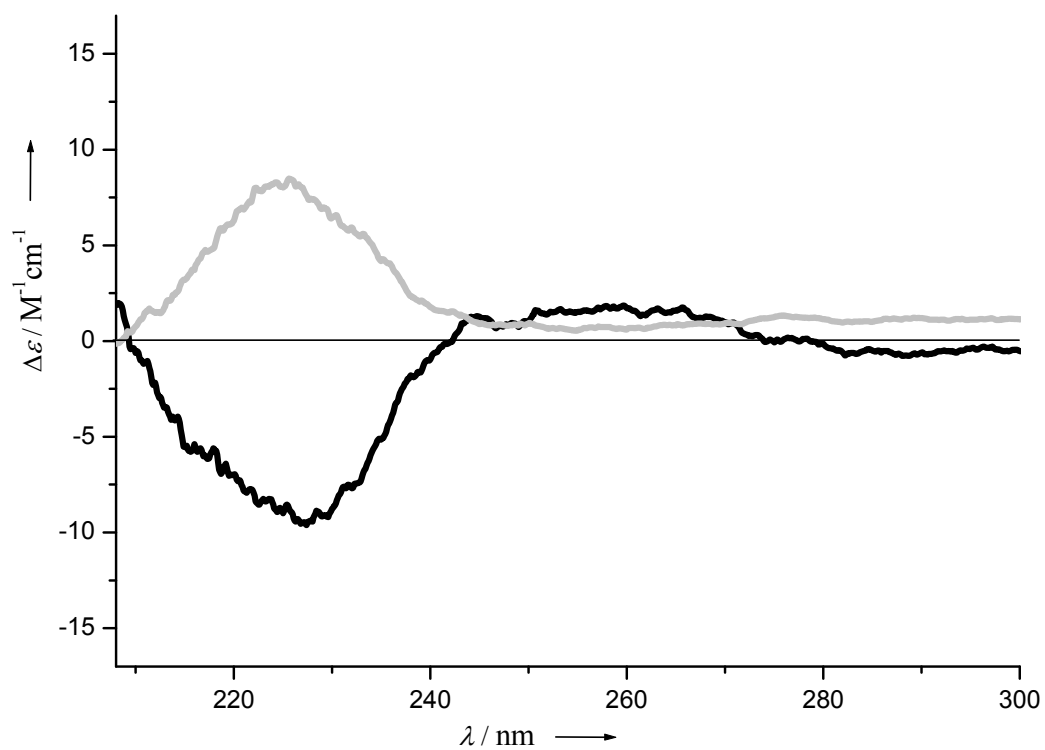


Figure S3. CD spectrum of (*P*)-**4b** (e.r. 100:0, gray line) and (*M*)-**4b** (e.r. 100:0, black line) in hexane.

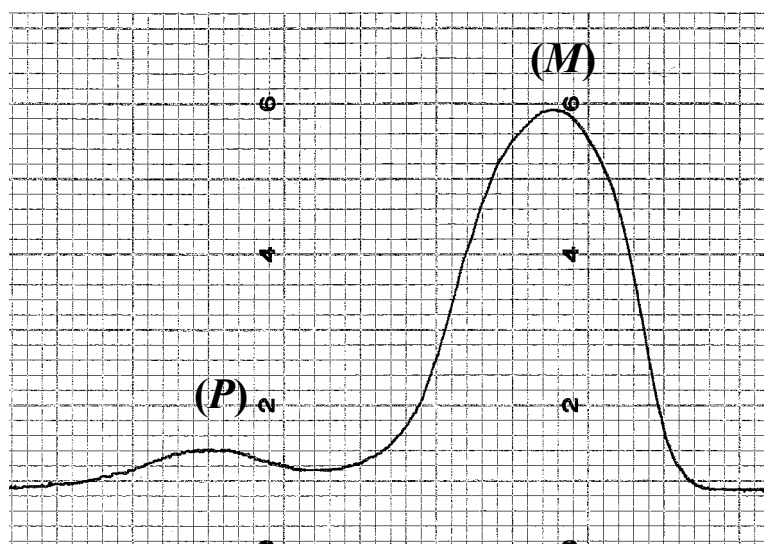
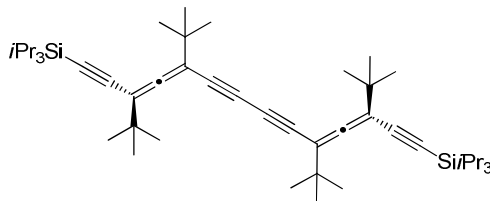


Figure S4. Recycling HPLC of (*M*)-**4b** on the CSP WHELK-O1 (hexane/0.25% *i*PrOH) from entry 3, Table 1.

Preparation and characterization of (*M,M*)-3,5,10,12-tetra-*tert*-butyl-1,14-bis(triisopropylsilyl)tetradeca-3,4,10,11-tetraene-1,6,8,13-tetrayne ((*M,M*)-5)



The compound was prepared from (*M*)-4a ($[\alpha]_D = -125^\circ$ ($c = 1$, CHCl_3); e.r. 95:5) as reported in the literature.^[2] (*M,M*)-5: M.p. 124°C , $[\alpha]_D = -234^\circ$, ($c = 1$, CHCl_3), d.r. = 90.25 ((*M,M*)-5) : 9.5 ((*M,P*)-5) : 0.25 ((*P,P*)-5) is expected for an unselective homocoupling reaction. X-ray analysis of (*M,M*)-5: the structure was solved by direct methods (SIR-97)^[4] and refined by full-matrix least-squares analysis (SHELXL-97),^[5] using an isotropic extinction correction. All heavy atoms were refined anisotropically; H atoms were refined isotropically, whereby H-positions are based on stereochemical considerations. Crystal data at 160(2) K for $\text{C}_{48}\text{H}_{78}\text{Si}_2$, $M_r = 711.28$ monoclinic, space group $P2_1$ (no. 4), $\rho_{\text{calcd}} = 0.963 \text{ g cm}^{-3}$, $Z = 2$, $a = 9.1043(14)$, $b = 10.8512(15)$, $c = 24.843(2) \text{ \AA}$, $V = 2453.5(5) \text{ \AA}^3$. Bruker-Nonius Kappa-CCD diffractometer, $\text{MoK}\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$, $\mu = 0.100 \text{ mm}^{-1}$. A colourless crystal (linear dimensions ca. 0.31 x 0.28 x 0.02 mm) was obtained by slow diffusion of MeOH into a solution of (*M,M*)-5 in hexane at 20°C . Number of measured and unique reflections are 6167. Final $R(F) = 0.062$, $wR(F^2) = 0.148$ for 476 parameters, 1 restraint and 5277 reflections with $I > 2\sigma(I)$ and $2.24 < \theta < 23.52^\circ$ (corresponding R values based on all 6167 reflections are 0.077 and 0.157, respectively). CCDC-691335 contains the supplementary crystallographic data of (*M,M*)-5. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data/cif.

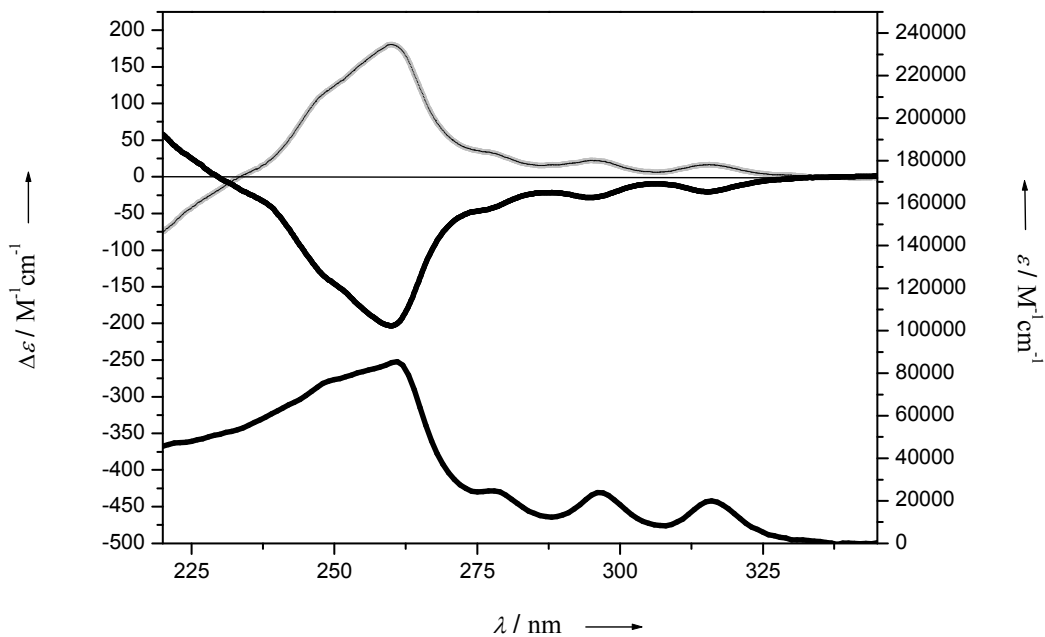
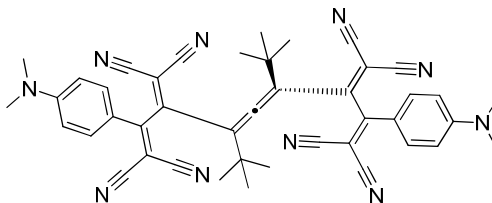


Figure S5. CD spectrum of *(M,M)*-5, d.r. = 90.25 *((M,M)*-5) : 9.5 *((M,P)*-5) : 0.25 *((P,P)*-5) is expected for an unselective homocoupling reaction, (black line) and *(P,P)*-5, d.r. = 90.25 *((P,P)*-5) : 9.5 *((M,P)*-5) : 0.25 *((M,M)*-5) is expected for an unselective homocoupling reaction, (gray line) top and UV/Vis spectra (bottom) recorded in hexane, T = 298 K.

Preparation and characterization of 3,3'-*((M)*-2,2,6,6-tetramethylhepta-3,4-diene-3,5-diyl)bis{2-[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} (*(M)*-6)



To a solution of *(M)*-9 (18 mg, 0.04 mmol) in CDCl_3 (2 mL), TCNE (15 mg, 0.12 mmol) was added and the mixture stirred at 25°C for 48 h. Removal of the solvent under reduced pressure and purification by FC on SiO_2 (CH_2Cl_2) gave *(M)*-6 (24 mg, 0.034 mmol, 86%) as a red solid. E.r. 91:9, determined by HPLC on the CSP WHELK-O1

(hexane/EtOH/MeOH 65:30:5). M.p. >290°C (decomp); ¹H NMR (300 MHz, CDCl₃): δ = 7.44 (d, *J* = 9.1, 4H), 6.70 (d, *J* = 9.1, 4H), 3.04 (s, 12H), 0.81 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ = 195.9, 166.4, 161.3, 154.0, 131.4, 116.8, 115.1, 113.2, 112.6, 112.2, 112.1, 109.6, 97.7, 83.6, 40.1, 38.3, 28.2; IR (neat): ν = 2924, 2219, 1600, 1495, 1438, 1379, 1328, 1295, 1187 cm⁻¹; UV/Vis (CH₂Cl₂): λ (ε) = 260 (35300), 305 (16100), 392 (29100), 520 nm (15800); HR-MALDI-MS: *m/z* calcd. for C₄₃H₃₈N₁₀Na⁺: 717.3173; found: 717.3186 [M+Na]⁺; X-Ray analysis of (±)-**6**: the structure was solved by direct methods (SIR-97)^[4] and refined by full-matrix least-squares analysis (SHELXL-97),^[5] using an isotropic extinction correction. All heavy atoms were refined anisotropically; H atoms were refined isotropically, whereby H-positions are based on stereochemical considerations. Crystal data at 170(2) K for C₄₃H₃₈N₁₀ · 0.5 (C₆H₁₂), Mr = 736.91 monoclinic, space group *P2/c* (no. 13), ρ_{calcd} = 1.197 g cm⁻³, *Z* = 4, *a* = 19.0008(16), *b* = 11.5256(14), *c* = 19.2715(17) Å, *V* = 4088.7(7) Å³. Bruker-Nonius Kappa-CCD diffractometer, MoK_α radiation, λ = 0.7107 Å, μ = 0.074 mm⁻¹. A red crystal (linear dimensions ca. 0.23 x 0.11 x 0.09 mm) was obtained by diffusion of cyclohexane into a solution of (±)-**6** in CH₂Cl₂ at 20°C. Number of measured and unique reflections are 13597 and 7310, respectively (*R*_{int} = 0.045). Final *R*(*F*) = 0.064, *wR*(*F*²) = 0.162 for 516 parameters and 5618 reflections with *I* > 2σ(*I*) and 3.22 < θ < 25.68° (corresponding *R* values based on all 7310 reflections are 0.086 and 0.180, respectively). CCDC-691333 contains the supplementary crystallographic data of (±)-**6**. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data/cif.

Confirmation of the CT absorptions of (\pm)-6** by acidification/re-neutralization.**

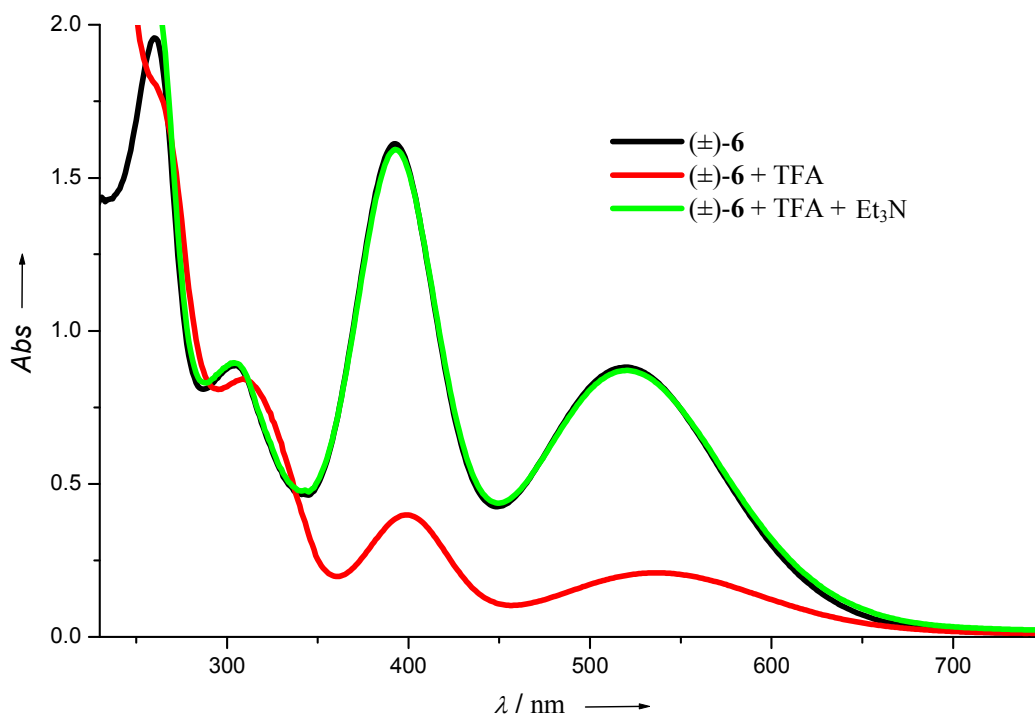


Figure S6. UV/Vis spectra of (\pm)-**6** in CH_2Cl_2 (black line). Disappearance to a large extent of the CT absorption was observed when trifluoroacetic acid (TFA) was added to the solution (red line) and the original bands were completely recovered after neutralization with Et_3N (green line).

Resolution of (\pm)-6 by HPLC on a CSP

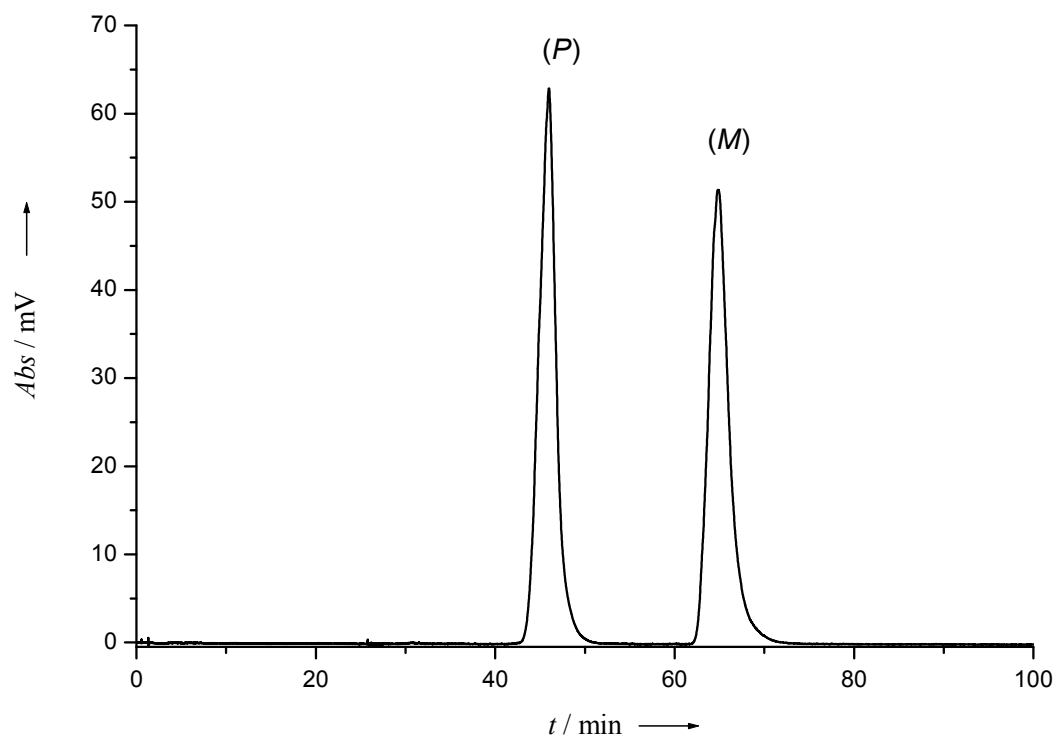
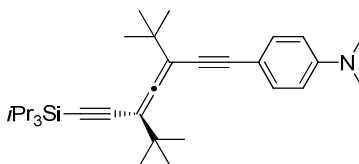


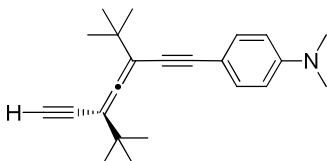
Figure S7. HPL chromatogram of (\pm)-6 on a preparative WHELK-O1 CSP (hexane/EtOH/MeOH 65:30:5).

Preparation and characterization of (*M*)-4-[3,5-di-*tert*-butyl-7-(triisopropylsilyl)hepta-3,4-dien-1,6-diynyl]-*N,N*-dimethylaniline ((*M*)-7)



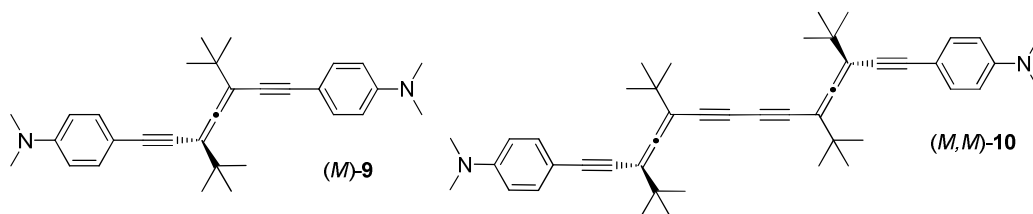
A degassed solution of (*M*)-4a (650 mg, 1.82 mmol; e.r. 95:5), 4-iododimethylaniline (450 mg, 1.82 mmol), [PdCl₂(PPh₃)₂] (38 mg, 0.055 mmol), and CuI (21 mg, 0.11 mmol) in *i*Pr₂NH (10.0 mL) and THF (20.0 mL) was stirred at 40°C under N₂ for 5 h. Removal of the solvent under reduced pressure and purification by FC on SiO₂ (hexane/CH₂Cl₂ 10% → 25%) gave (*M*)-7 (615 mg, 1.29 mmol, 71%, e.r. ≥91:9) as a yellow oil. [α]_D = -468°, (*c* = 1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ = 7.35 (d, *J* = 7.0, 2H), 6.63 (d, *J* = 7.0, 2H), 2.99 (s, 6H), 1.22 (s, 9H), 1.21 (s, 9H), 1.13 (s, 21H); ¹³C NMR (75 MHz, CDCl₃) δ = 211.5, 149.7, 132.4, 111.7, 110.7, 103.4, 103.3, 100.8, 93.6, 93.3, 80.8, 40.3, 35.9, 35.4, 29.2, 29.1, 18.8, 11.5; IR (neat): ν =; 2944, 2865, 2199, 2141, 1609, 1523, 1461, 1361, 1235 cm⁻¹; UV/Vis (hexane): λ (ϵ) = 232 (19800), 242 (16600), 305 (24500), 320 nm (23600); HR-MALDI-MS: *m/z* calcd. for C₃₂H₅₀NSi⁺: 476.3707, found 476.3699 [M+H]⁺.

Preparation and characterization of (*M*)-4-(3,5-di-*tert*-butylhepta-3,4-dien-1,6-diynyl)-*N,N*-dimethylaniline (*(M)*-8)



To a solution of (*M*)-7 (308 mg, 0.65 mmol) in THF (13 mL), *n*-BuLi (650 μ L, 1M, 0.65 mmol) was added and the mixture stirred at 25 °C for 2 h. Removal of the solvent under reduced pressure and purification by FC on SiO₂ (hexane/25% CH₂Cl₂) gave (*M*)-8 (170 mg, 0.53 mmol, 82%) as a yellow solid. M.p. 55°C; [α]_D = -253°, (*c* = 1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ = 7.34 (d, *J* = 7.0, 2H), 6.64 (d, *J* = 7.0, 2H), 3.00 (s, 1H), 2.98 (s, 6H), 1.22 (s, 9H), 1.19 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ = 211.6, 149.9, 132.5, 111.7, 110.6, 104.4, 101.8, 94.1, 80.4, 79.9, 78.0, 40.2, 35.7, 35.2, 29.0, 28.8; IR (neat): ν = 2964, 2901, 2866, 2806, 2569, 2198, 1769, 1618, 1522, 1475, 1448, 1360, 12226, 1190, 1060 cm⁻¹; UV/Vis (hexane): λ (ϵ) = 222 (20300), 230 (16200), 306 (25600), 319 nm (25000); HR-EI-MS: *m/z* calcd. for C₂₃H₃₀N⁺: 320.2373; found: 320.2381 [M+H]⁺.

Preparation and characterization of (*M*)-4,4'-(3,5-di-*tert*-butylhepta-3,4-dien-1,6-diyne-1,7-diyl)bis(*N,N*-dimethylaniline) ((*M*)-9) and 4,4'-((*M,M*)-3,5,10,12-tetra-*tert*-butyltetradeca-3,4,10,11-tetraen-1,6,8,13-tetrayne-1,14-diyl)bis(*N,N*-dimethylaniline) ((*M,M*)-10)



A degassed solution of (*M*)-8 (150 mg, 0.47 mmol), 4-iododimethylaniline (116 mg, 0.47 mmol), [PdCl₂(PPh₃)₂] (10 mg, 0.014 mmol), and CuI (5 mg, 0.028 mmol) in *i*Pr₂NH (3.0 mL) and THF (6.0 mL) was stirred at 50 °C under N₂ for 1 h. Removal of the solvent under reduced pressure and purification by FC on SiO₂ (hexane/CH₂Cl₂ 10% → 35%) gave (*M*)-9 (141 mg, 0.32 mmol, 69 %) and (*M,M*)-10 (28 mg, 0.044 mmol, 19 %) as colourless oils. Experimental data for (*M*)-9: [α]_D = -1121°, (*c* = 1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ = 7.35 (d, *J* = 7.0, 4H), 6.64 (d, *J* = 7.0, 4H), 2.97 (s, 12H), 1.24 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ = 210.9, 149.9, 132.5, 111.8, 111.0, 103.5, 93.3, 81.2, 40.2, 35.7, 29.1; IR (neat): ν = 2960, 2924, 2854, 2360, 2340, 1770, 1760, 1463, 1377, 1244, 1057; UV/Vis (hexane): λ (ϵ) = 218 (26000), 308 (42900), 327 nm (49700); HR-MALDI-MS: *m/z* calcd. for C₃₁H₃₉N₂: 439.3108; found: 439.3106 [M+H]⁺; elemental analysis calc. (%) for C₃₁H₃₈N₂ (438.6): C 84.88, H 8.73, N 6.39; found: C 84.72, H 8.72, N 6.27. Experimental data for (*M,M*)-10: [α]_D = -616°, (*c* = 1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ = 7.33 (d, *J* = 7.0, 4H), 6.62 (d, *J* = 7.0, 4H), 2.97 (s, 12H), 1.20 (s, 18H), 1.18 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ = 213.4, 150.0, 132.5, 111.8, 110.7, 104.8, 102.5, 94.5, 80.2, 76.8, 75.6, 40.2, 35.8, 35.8, 29.1, 29.0; IR (neat): ν = 2962, 2926, 2855, 2360, 2340, 1770, 1760, 1467, 1378, 1244, 1057; UV/Vis (hexane): λ

(ε) = 220 (31800), 247 (29300), 307 (42500), 327 nm (49700); HR-MALDI-MS: m/z calcd. for $C_{46}H_{57}N_2$: 637.4516; found: 637.4525 $[M+H]^+$.

Photoisomerization of 4,4'-((*P,P*)-3,5,10,12-tetra-*tert*-butyltetradeca-3,4,10,11-tetraen-1,6,8,13-tetrayne-1,14-diyl)bis(*N,N*-dimethylaniline) ((*P,P*)-10) followed by CD spectroscopy

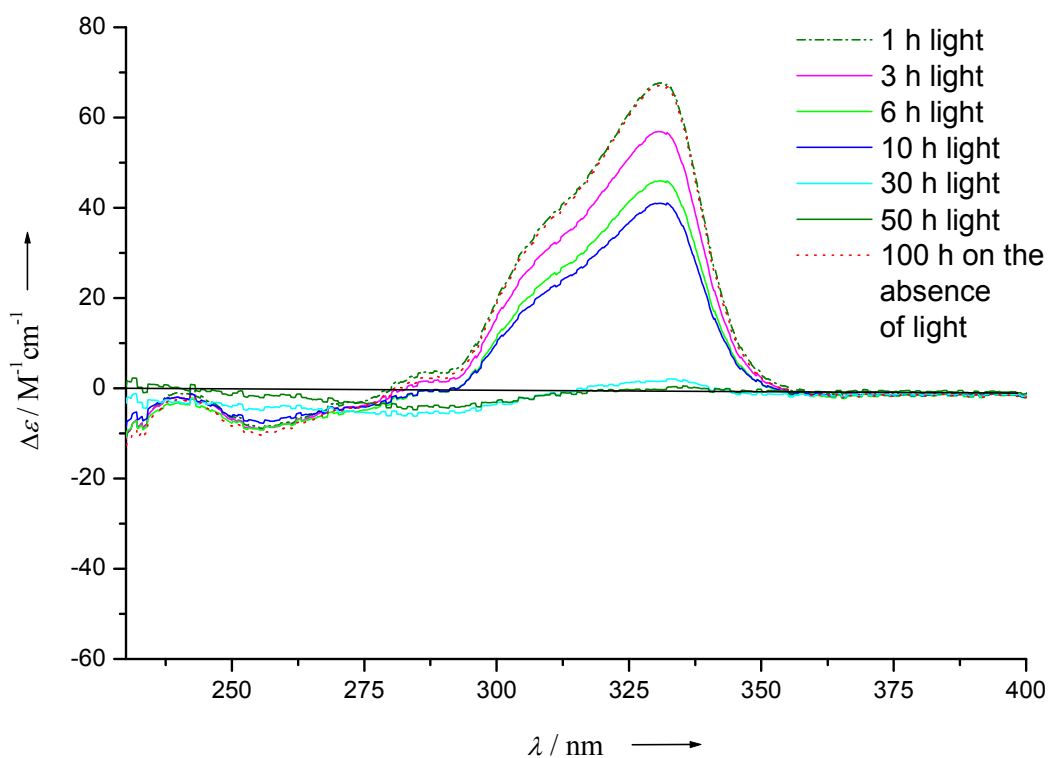
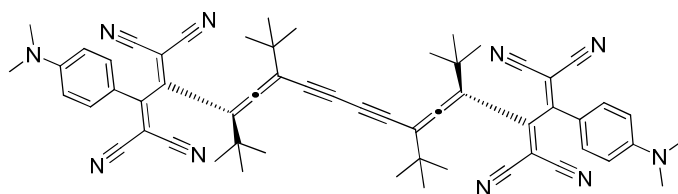


Figure S8. Photoracemization of (*P,P*)-10 upon exposure to daylight over various periods of time, monitored by CD spectroscopy in hexane.

Preparation and characterization of 3,3'-((*M,M*)-5,10-di-*tert*-butyl-2,2,13,13-tetramethyltetradeca-3,4,10,11-tetraen-6,8-diyne-3,12-diyl)bis{2-[4-(dimethylamino)phenyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile} ((*M,M*)-11)



To a solution of (*M*)-**10** (28 mg, 0.044 mmol) in CDCl₃ (1 mL), TCNE (17 mg, 0.132 mmol) was added and the mixture stirred at 25°C for 12 h. Removal of the solvent under reduced pressure and purification by FC on SiO₂ (CH₂Cl₂) gave (*M,M*)-**11** (34 mg, 0.038 mmol, 86%, d.r. 78 ((*M,M*)-**11**) : 20 ((*M,P*)-**11**) : 2 ((*P,P*)-**11**) determined by recycling HPLC on the CSP WHELK-O1 (hexane/55% CH₂Cl₂) as a red solid. M.p. 128°C; ¹H NMR (300 MHz, CDCl₃) δ = 7.43 (d, *J* = 7.0, 4H), 6.70 (d, *J* = 7.0, 4H), 3.13 (s, 12H), 1.20 (s, 18H), 1.06 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ = 210.5, 165.4, 165.2, 154.1, 154.1, 131.8, 116.6, 115.1, 113.5, 111.9, 111.3, 110.9, 107.0, 94.1, 80.7, 77.2, 74.2, 40.1, 38.1, 36.5, 29.9, 28.7; IR (neat): ν = 2969, 2883, 1960, 1603, 1468, 1379, 1240, 1057; UV/Vis (CH₂Cl₂): λ (ε) = 231 (46400), 250 (43800), 294 (26600), 390 (27200), 486 nm (18500); HR-ESI-MS: *m/z* calcd. for C₅₈H₅₆N₁₀Na: 915.4582; found: 915.4586 [M+Na]⁺; X-Ray analysis of (*M,M*)-**11**: the structure was solved by direct methods (SIR-97)^[4] and refined by full-matrix least-squares analysis (SHELXL-97),^[5] using an isotropic extinction correction. All heavy atoms were refined anisotropically; H atoms were refined isotropically, whereby H-positions are based on stereochemical considerations. Crystal data at 220(2) K for C₅₈H₅₆N₁₀ Mr = 893.13 orthorhombic, space group *P*2₁2₁2₁ (no. 19), ρ_{calcd} = 1.117 g cm⁻³, *Z* = 4, *a* = 16.1159(11), *b* = 16.9569(11), *c* = 19.4347(13) Å, *V* = 5311.0(6) Å³. Bruker-Nonius Kappa-CCD diffractometer, MoKα radiation, λ = 0.7107 Å, μ = 0.068 mm⁻¹. A red crystal (linear dimensions *ca.* 0.10 x 0.05 x 0.02 mm)

was obtained by slow diffusion of MeOH into a solution of (*M,M*)-**11** in CH₂Cl₂ at 20°C. Numbers of measured and unique reflections are 6405 and 3586, respectively ($R_{\text{int}} = 0.083$). Final $R(F) = 0.068$, $wR(F^2) = 0.162$ for 630 parameters and 2128 reflections with $I > 2\sigma(I)$ and $1.59 < \theta < 21.95^\circ$ (corresponding R values based on all 3586 reflections are 0.126 and 0.205, respectively). Note that a pseudo inversion-symmetric structure could also be solved in the space group $P b c a$ (no. 61) and refined to $R(F) = 0.15$. CCDC-691334 contains the supplementary crystallographic data of (*M,M*)-**11**. The ORTEP plot deposited is the mirror image of (*M,M*)-**11**. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data/cif.

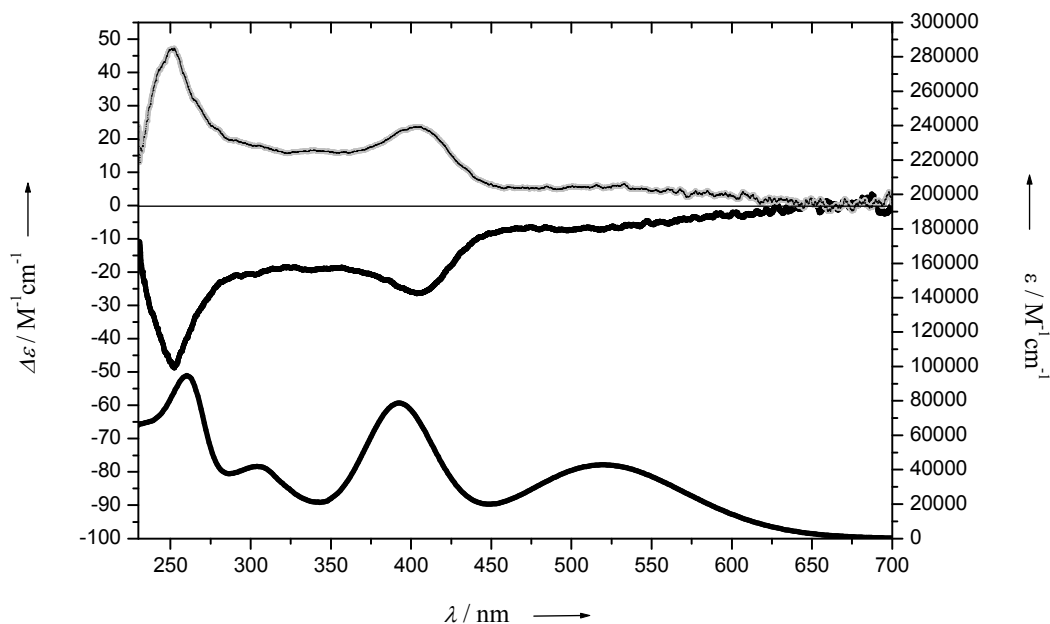


Figure S9. CD spectrum of (*M,M*)-**11** (e.r. 100:0, black line) and (*P,P*)-**11** (e.r. 100:0, gray line) top and UV/Vis spectra (bottom) recorded in CH₂Cl₂, T = 298 K.

Optical resolution of **11** by HPLC on a CSP

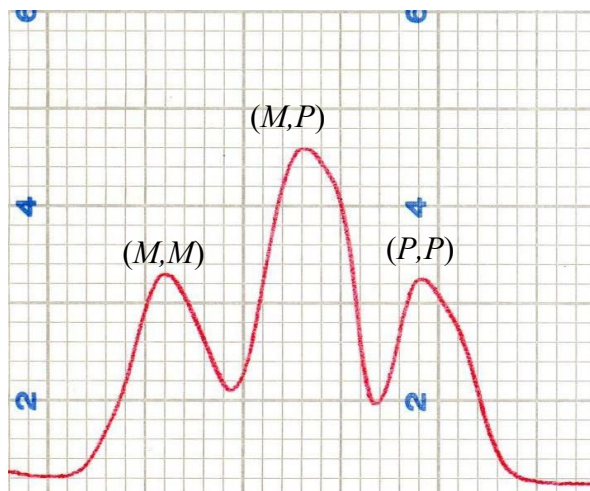


Figure S10. Chromatogram of **11** on a preparative WHELK-O1 CSP (hexane/55% CH₂Cl₂).

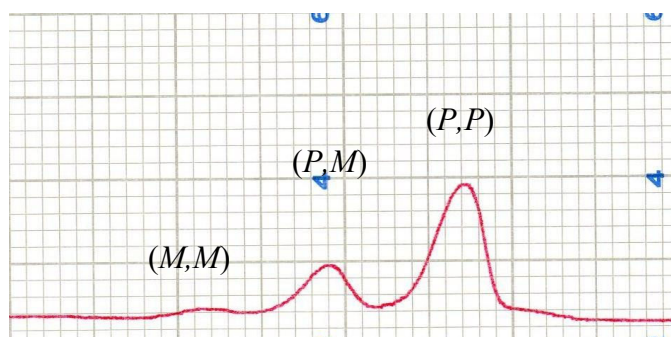


Figure S11. Chromatogram of (*P,P*)-**11** (d.r. 78 ((*P,P*)-**11**) : 20 ((*P,M*)-**11**) : 2 ((*M,M*)-**11**)) on the CSP WHELK-O1 (hexane/55% CH₂Cl₂).

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