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Supporting Information

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A Highly Configurationally Stable [4]Heterohelicenium Cation

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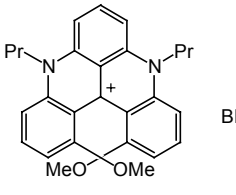
General Remarks: All reactions were carried out under dry N_2 or Ar by means of an inert gas/vacuum double manifold line and standard Schlenk techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use: CH_2Cl_2 from CaH_2. $CDCl_3$ (SDS) was filtered on basic alumina. Known cation **3** was prepared according to the reported procedure.[1] $[Me_2NH_2][(\Delta,S)$-**5**] or $[Me_2NH_2][(\Lambda,R)$-**5**] salts were prepared from enantiopure (*S*)- and (*R*)-BINOL (Kankyo Kagaku Center Co.), *o*-chloranil (Fluka) and $P(NMe_2)_3$ (Freshly distilled, Fluka) and tetrachlorocatechol (anhydrous, recrystallized, Lancaster).[2] NMR spectra were recorded on Bruker AMX-400 at room temperature unless otherwise stated. ^{1}H-NMR: chemical shifts are given in ppm relative to Me_4Si with the solvent resonance used as the internal standard. ^{31}P-NMR (162 MHz): chemical shifts were reported in ppm relative to H_3PO_4. ^{13}C-NMR (100 MHz): chemical shifts were given in ppm relative to Me_4Si, with the solvent resonance used as the internal standard ($CDCl_3$ δ 77.0 ppm, CD_3CN δ 117.8 ppm). Assignments may have been achieved using COSY, HETCOR and/or NOESY experiments. IR spectra were recorded with a Perkin-Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (M.p.) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and were uncorrected. Electron-spray mass spectra (ES-MS) were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva. UV spectra were recorded on a CARY-1E spectrometer in a 1.0 cm quartz cell; λ_{max} are given in nm and molar adsorption coefficient ε in $cm^{-1}\cdot dm^3\cdot mol^{-1}$. Circular dichroism spectra were recorded on a JASCO J-715 polarimeter in a 1.0 cm quartz cell; λ are given in nm and molar circular dichroic absorptions ($\Delta\varepsilon$ in $cm^2\cdot mmol^{-1}$). Optical rotations were measured on a Perkin-Elmer 241 or a JASCO P-1030 polarimeter in a thermostated (20 °C) 10.0 cm long microcell with high pressure lamps of sodium or mercury and are reported as follows: $[\alpha]_\lambda^{20}$ (c (g/100 ml), solvent). HPLC analyses were performed on an Agilent LC-1100 apparatus (binary pump, autosampler, column thermostat and diode array detector).

VCD spectra were measured on a Bruker PMA 37 accessory coupled to a IFS/33 Fourier transform infrared spectrometer. The infrared beam is first linearly polarized using a wire grid polarizer. The linearly polarized light is then alternately switched at 50 kHz between left- and right-handed circular polarization by a photoelastic modulator (Hinds PEM 90) set at l/4 retardation. The beam transmits the variable path-lengths cell (SPECAC 7100) equipped with KBr windows containing the chiral sample and is focused by a broadband-coated ZnSe lens onto a MCT detector. The detected signal is divided into two channels. The first signal is low-pass filtered and contains the normal single beam spectrum. The signal from the second channel is high-pass filtered and demodulated at 50 kHz using a lock-in amplifier (SR830 DSP). This signal corresponds to the differential absorption of left- and right-handed circular polarized light. Both signals are collected and stored simultaneously. An optical low-pass filter (< 1800 cm-1) was put before the photoelastic modulator. A VCD spectrum of the neat solvent was subtracted from the VCD spectrum of the dissolved molecules. For VCD measurements a solution of 12 mg (+)-$[(P)$-**4**$][PF_6]$ in 2 ml CH_2Cl_2 was prepared and the path lengths of the transmission cell was set to 400 μm. A total of 7000 scans at a resolution of 4 cm^{-1} were averaged for both sample and solvent.



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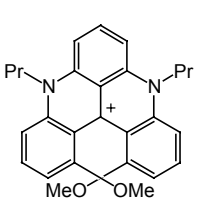
Racemic 5,9-dipropyl-1,13-dimethoxy-quinacridinium tetrafluoroborate or (±)-[4][BF_4]: *n*-Propylamine (30 ml, 0.36 mol) was added to a solution of tris(2,6 dimethoxyphenyl)carbenium tetrafluoroborate (7.00 g, 13.7 mmol) in anhydrous NMP (80 ml). The reaction mixture was heated at 110 °C for 3 hours and then allowed to cool to room temperature. The crude product precipitated upon addition of water (~80 ml). The precipitate was filtered and washed several times with water and collected. Selective precipitation by addition of diethyl ether to a solution of crude product in

[1] B. W. Laursen, F. C. Krebs, *Angew. Chem. Int. Ed.* **2000**, *39*, 3432-3434 and references therein.
[2] J. Lacour, A. Londez, C. Goujon-Ginglinger, V. Buß, G. Bernardinelli, *Org. Lett.* **2000**, *2*, 4185-4188.

CH_2Cl_2 afforded the titled compound (5.80 g, 85%): **^{1}H NMR** (400 MHz, CD_3CN) δ 8.20 (t, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 9.1 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.66 (m, 2H), 4.42 (m, 2H), 3.76 (s, 6H), 2.10 (m, 4H), 1.23 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.0, 159.5, 142.4, 141.9, 138.8, 136.8, 136.3, 119.2, 112.8, 107.4, 104.8, 55.4, 51.1, 19.3, 10.1. **MS** (ES, m/z) + 413. **IR** 2969 , 2940 , 1605 , 1582 , 1502 , 1343 , 1265 , 1176 , 1091 , 1049 , 768 cm^{-1}. **M.p.** 344.9-346 °C



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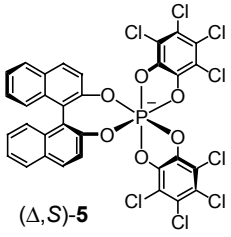
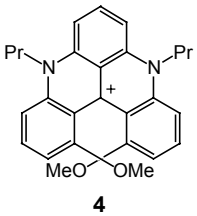


(Δ,*S*)-**5**

[*rac*-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][(Δ)-bis(tetrachlorobenzenediolato)mono((S)-1,1'-dinaphthyl-2, 2'-diolato)phosphate(V)] or [*rac*-4][(Δ,*S*)-5]: To a solution of (±)-[**4**][BF_4] (1.50 g, 2.90 mmol) in CH_2Cl_2:acetone (1:1, 50 ml) was added a solution of [Me_2NH_2][(Δ,*S*)-**5**] (3.32 g, 3.90 mmol) in acetone (50 ml). The reaction mixture was stirred for 5 minutes at room temperature and the solvent was removed under reduced pressure. Chromatography over basic alumina (100g, CH_2Cl_2) afforded a single eluted fraction which was concentrated in vacuo to give the title compound as a blue-green solid (3.50 g, 97%): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 8.6 Hz, 1H), 7.91 (t, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 4H), 7.67 (t, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 4H), 7.29 (d, *J* = Hz, 2H), 7.25-7.22 (m, 10H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.05-6.99 (m, 6H), 6.68 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 4H), 4.46-4.38 (m, 2H), 4.29-4.07 (m, 6H), 3.50 (s, 12H), 1.11 (t, *J* = 7.3 Hz, 6H), 1.05 (t, *J* = 7.3 Hz, 6H). **^{13} C NMR** (100 MHz, $CDCl_3$) δ 159.5, 159.2, 152.6, 143.2, 142.7, 142.4, 141.8, 141.7, 138.4, 138.3, 137.1, 136.4, 132.4, 130.1, 128.4, 127.8, 127.2, 124.8, 123.4, 123.1, 123.0, 120.2, 119.0, 118.9, 113.6, 113.4, 113.2, 113.0, 112.9, 107.0, 106.8, 104.8, 104.5, 102.9, 102.4, 55.4, 55.2, 51.3, 19.7, 19.5, 11.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ - 81.6. **IR** 2926, 1606, 1584, 1502, 1455, 1340, 1265, 1250, 1232, 1170, 1134, 1092, 993, 954, 822, 753, 671 cm^{-1}. **UV/Vis** (CH_2Cl_2, 1.10^{-5} M) λ_{max} (ε) 617.0 ($1.6 \cdot 10^5$), 435.0 ($8.0 \cdot 10^3$), 311.0 ($5.9 \cdot 10^4$), 284.0 ($3.8 \cdot 10^5$), 228.0 ($1.4 \cdot 10^6$). **MS** (ES, m/z) +413, -807.1. **M.p.** 267-268 °C. **Anal**. Calcd. for $C_{59}H_{41}Cl_8N_2O_8P$: C, 58.06 ; H, 3.39 ; N, 2.30. Found: C, 57.94 ; H, 3.60 ; N, 2.12.



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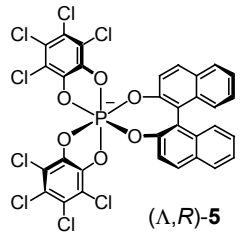
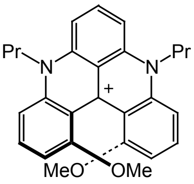
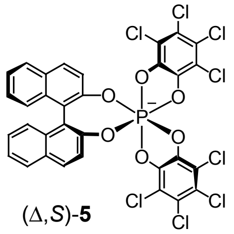


(Λ,*R*)-**5**

[*rac*-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][(Λ)-bis(tetrachlorobenzenediolato)mono((*R*)-1,1'-dinaphthyl-2, 2'-diolato)phosphate(V)] or [*rac*-4][(Λ,*R*)-5]: As described for [*rac*-**4**][(Δ,*S*)-**5**] with (±)-[**4**][BF_4] (0.20 g, 0.39 mmol) and [Me_2NH_2][(Λ,*R*)-**5**] (0.41 g, 0.48 mmol) affording the titled compound as a blue solid (0.46 g, 96%).

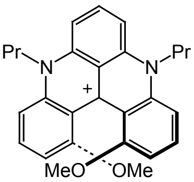
Typical procedure for the resolution of carbenium ion 4: To a solution at room temperature of salt [*rac*-**4**][(Δ,*S*)-**5**] (3.4 g) in THF (42.5 ml) was added three times (3x) the amount of benzene (*vs.* THF). The resulting solution was placed in a fridge at –25°C for 24 hours. The frozen reaction crude was allowed to slowly warm-up to room temperature and left standing at 20 °C for 24 hours. A blue-green solid was observed, filtered over a Büchner funnel and collected (0.75 g). The mother-liquor was placed (again) in a fridge at –25°C for 24 hours, allowed to slowly warm-up and left standing for 24 hours. The solid was filtered (0.25 g) and collected with the first fraction (total 1.0 g, 30%, d.r. >49:1); the configuration of which was determined to be [(*P*)-**4**][(Δ,*S*)-**5**] in the course of the study (see below). From the mother-liquor, a blue-green solid (2.4 g, 70%, d.r. 2.45:1) was obtained after concentration in vacuo; the configuration of which was determined to be predominantly [(*M*)-**4**][(Δ,*S*)-**5**]. Using [*rac*-**4**][(Λ,*R*)-**5**], the same procedure was used and analogous results were obtained.

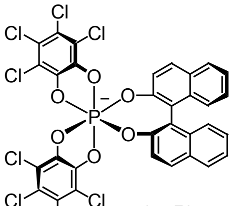

(*P*)-**4**


(Δ,*S*)-**5**

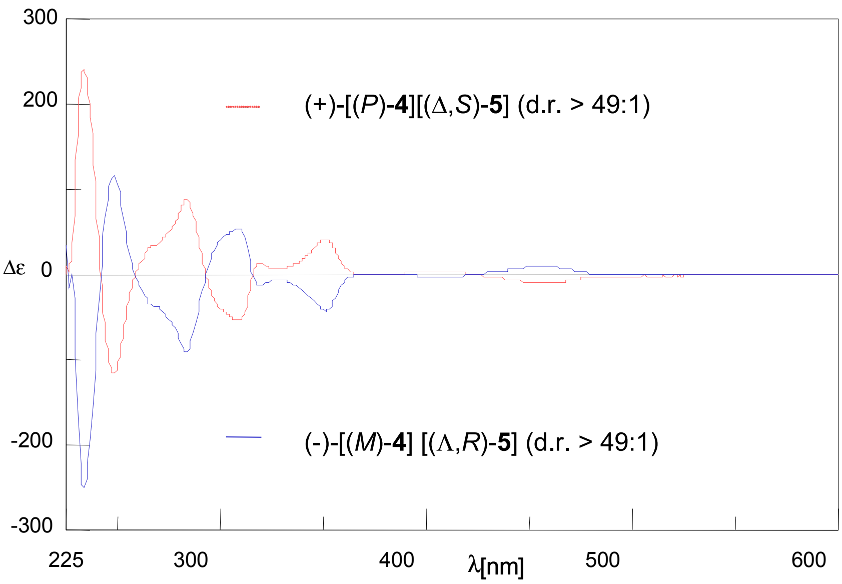
[(*P*)-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][(Δ)-bis(tetrachlorobenzenediolato)mono((*S*)-1,1'-dinaphthyl-2, 2'-diolato)phosphate(V)] or [(*P*)-4][(Δ,*S*)-5]: Diastereomer obtained in the solid from the resolution of [*rac*-**4**][(Δ,*S*)-**5**]. Diastereomeric purity >49:1 as indicated by the ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (t, *J* = 8.6 Hz, H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.62 (t, J = 8.6 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.26-7.21 (m, 4H), 7.03-6.98 (m, 4H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 8.6 Hz, 2H), 4.12-3.97 (m, 4H), 3.41 (s, 6H), 1.96-1.72 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) 159.1, 152.6, 142.3, 142.7, 142.3, 141.6, 138.3, 137.1, 136.5, 132.4, 130.1, 128.5, 127.8, 127.2, 124.8, 123.4, 123.1, 123.0, 121.8, 120.3, 118.9, 113.4, 113.2, 112.8, 106.9, 104.7, 102.4, 55.2, 51.2, 19.5, 11.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -81.8. **M.p.** >230 °C (decomposition).
CD (CH_2Cl_2, 1.10^{-5} M, 20 °C) λ (Δε) 234 (256.8), 248.5 (-118.9), 284 (90.8), 309 (-54.5), 319.5 (13.4), 351 (42.2), 456 (-10.3). **$[\alpha]_{436}$** = +3200, $[\alpha]_{365}$ = +6600 (c = 0.0012, CH_2Cl_2).[3]


(*M*)-**4**

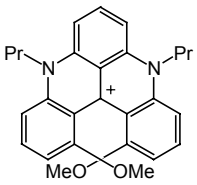

(Λ,*R*)-**5**

[(*M*)-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][(Λ)-bis(tetrachlorobenzenediolato)mono((*R*)-1,1'-dinaphthyl-2, 2'-diolato)phosphate(V)] or [(*M*)-4][(Λ,*R*)-5]: As described for [(*P*)-**4**][(Δ,*S*)-**5**]. Diastereomer obtained in the solid from the resolution of [*rac*-**4**][(Λ,*R*)-**5**]. Diastereomeric purity >49:1 as indicated by the ^{1}H NMR analysis. ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data are identical to those of [(*P*)-**4**][(Δ,*S*)-**5**] .
CD (CH_2Cl_2, 1.10^{-5} M, 20 °C) λ (Δε) 234 (-249.8), 248.5 (116.3), 284 (-91.3), 309 (53.8), 319.5 (-14.1), 351 (-43.0), 456 (9.2). **$[\alpha]_{435}$** = -2500, $[\alpha]_{365}$ = -5900 (c = 0.0012, CH_2Cl_2).[3]



CD spectra of (+)-[(*P*)-**4**][(Δ,*S*)-**5**](red line, CH_2Cl_2, 1.10^{-5} M, 20 °C) and (-)-[(*M*)-**4**][(Δ,*S*)-**5**] (blue line, CH_2Cl_2, 1.10^{-5} M, 20 °C).

[3] Cation **4** is an effective dye absorbing light efficiently in most of the visible region (B. W. Laursen, F. C. Krebs, *Angew. Chem. Int. Ed.* **2000**, *39*, 3432-3434; B. W. Laursen, F. C. Krebs, *Chem. Eur. J.* **2001**, *7*, 1773-1783.). Very dilute solutions and restricted wavelengths were required to measure the specific optical rotations. Although the sign of the optical rotation is ascertained, the precision of the measurement of the amplitude is very low. Strong variations were observed for highly enantiomerically enriched samples (checked by CSP-HPLC, see below).



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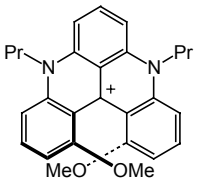
PF_6^-

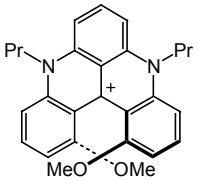
General procedure for the formation of [5,9-Dipropyl-1,13-dimethoxy-quinacridinium][hexafluorophosphate] salts or [4][PF_6]: To a solution of [**4**][**5**] (100 mg, 0.082 mmol)[4] in dichloromethane (200 ml) was added a solution of KPF_6 (5.0 g, 27 mmol) in water (200 ml). The biphasic mixture was stirred vigorously for 48 hours at room temperature. The phases were separated and the organic layer was washed with water (3x100 ml), dried over $CaCl_2$, filtered and concentrated under reduced pressure. Purification by chromatography (basic Al_2O_3, CH_2Cl_2 then CH_2Cl_2:MeOH 96:4) afforded the titled compound as a blue-green solid (44.3 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (t, *J* = 8.6 Hz, 1H), 7.88 (t, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 9.1 Hz, 2H), 6.85 (d, *J* = 8.1Hz, 2H), 4.66-4.58 (m, 2H), 4.44-4.37 (m, 2H), 3.76 (s, 3H), 2.18-2.08 (m, 4H), 1.25 (t, *J* = 7.1Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.0, 159.5, 142.4, 141.9, 138.8, 136.8, 136.3, 119.2, 112.8, 107.4, 104.8, 55.4, 51.1, 19.3, 10.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -144.1. **IR** 2941, 2881, 1605, 1580, 1522, 1495, 1468, 1342, 1263, 1249, 1170, 1035, 1094, 831, 757 cm^{-1}. **MS** (ES, m/z) + 413. **UV/Vis** (CH_2Cl_2, 1.10^{-5} M) λ_{max} (ε) 617 ($1.6 \cdot 10^4$), 441 ($5.8 \cdot 10^3$), 312 ($4.9 \cdot 10^4$), 284 ($2.3 \cdot 10^4$), 261 ($2.4 \cdot 10^4$), 241 ($2.5 \cdot 10^4$). **M.p.** > 303.6°C.



(*P*)-**4**
PF_6^-

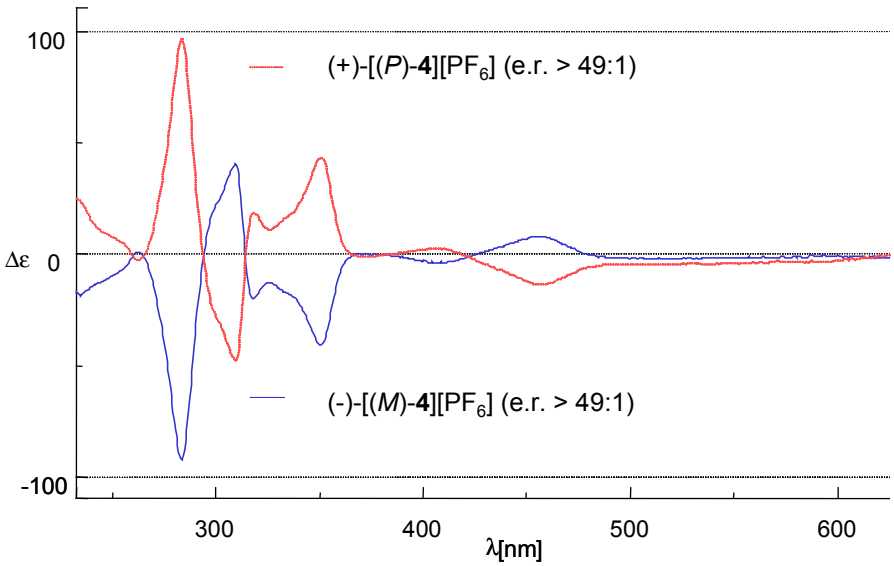
(+)-[(*P*)-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][hexafluorophosphate] salt or (+)-[(*P*)-4][PF_6]: as described following the general procedure starting from [(*P*)-**4**][(Δ,*S*)-**5**] (e.r.>49:1, ^{1}H NMR): **M.p.** 264.9-265.5°C.
ee > 98%. **CD** (CH_2Cl_2, 1.10^{-5} M, 20°C) λ (Δε) 456.5 (-14.2), 351 (42.8), 309.5 (-47.8), 284 (96.1), 263.5 (-3.2), 233 (24.3) ; $[\alpha]_{435}$ = + 9400, $[\alpha]_{365}$ = + 18500 (c = $5.7 \cdot 10^{-4}$, CH_2Cl_2).[3]



(*M*)-**4**
PF_6^-

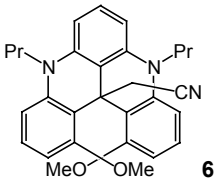
(-)-[(*M*)-5,9-Dipropyl-1,13-dimethoxy-quinacridinium][hexafluorophosphate] salt or (-)-[(*M*)-4][PF_6]: as described following the general procedure starting from [(*M*)-**4**][(Λ,*R*)-**5**] (e.r.>49:1, ^{1}H NMR): ee > 96%: **CD** (CH_2Cl_2, 1.10^{-5} M, 20°C) λ (Δε) 456 (7.5), 351 (-41.4), 318.5 (-20.4), 310 (39.8), 284 (-92.8), 235 (-18.8) ; $[\alpha]_{435}$ = -7700, $[\alpha]_{365}$ = -17700 (c = $5.4 \cdot 10^{-4}$, CH_2Cl_2).[3]

CD spectra



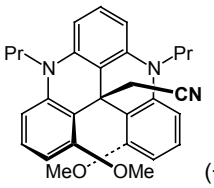
CD spectra of (+)-[(*P*)-**4**][PF_6](red line, CH_2Cl_2, 1.10^{-5} M, 20 °C) and (-)-[(*M*)-**4**]PF_6](blue line, CH_2Cl_2, 1.10^{-5} M, 20 °C).

[4] The absolute configuration and diastereomeric purity of the [**4**][**5**] salts do not change the outcome of the metathesis.



6

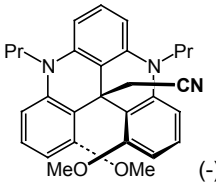
General procedure for the formation of (1,13-Dimethoxy-5,9-dipropyl-5*H*,9*H*-5,9-diaza-naphto[3,2,1-*de*]anthracen-13b-yl)-acetonitrile or 6: To an argon purged solution of **[4]**[PF_6] (0.100 g, 0.179 mmol) in acetonitrile (50 ml) was added NaH (0.225 g, 60 % in mineral oil) as a solid. The reaction mixture was stirred at room temperature until a complete disappearance of the blue-green colour occurred (~2 hours). The crude was poured into cold water (400 ml). The reaction mixture was extracted with Et_2O (3x100ml). The organic phases were collected, washed with brine, dried over $CaCl_2$, filtered and concentrated under reduced pressure. Purification by chromatography (SiO_2, Et_2O:*c*-Hex 70:30) afforded the titled compound as a white solid (45mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.3 Hz, 1H), 7.16-7.10 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.63 (t, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 2H), 4.03-3.90 (m, 2H), 3.84-3.66 (m, 2H), 3.77 (s, 3H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.34 (s, 3H), 3.29 (d, *J* = 16.4 Hz, 1H), 2.02-1.94 (m, 2H), 1.85-1.77 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H) ; **IR** 2950, 2932, 2871, 2237, 1612, 1584, 1467, 1430, 1383, 1312, 1223, 1130, 1066, 743 cm^{-1}. **M.p.** 175.2-177.6 °C; **UV/Vis** (CH_2Cl_2, 6.10^{-5} M) λ_{max} (ε) 326 ($1.5 \cdot 10^4$), 273 ($1.2 \cdot 10^4$), 228 ($2.9 \cdot 10^4$).[5]



(+)-**6**

of supposed *P* configution

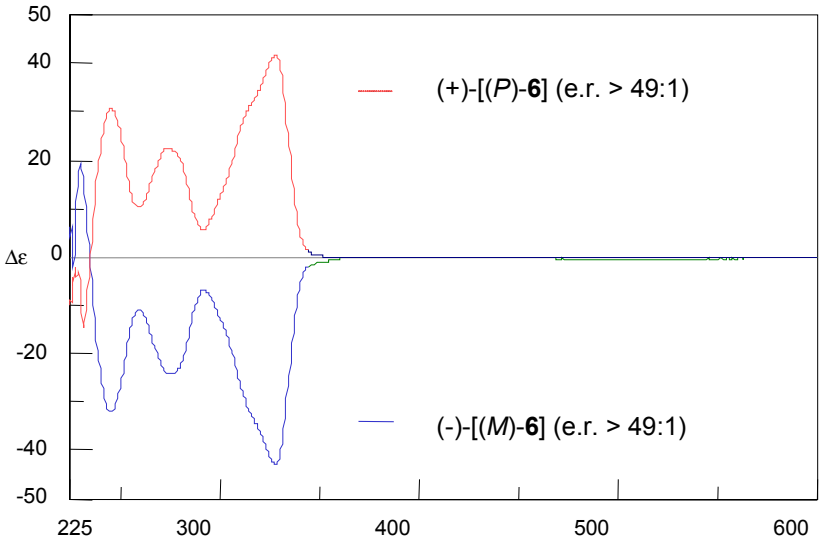
(+)-(1,13-Dimethoxy-5,9-dipropyl-5*H*,9*H*-5,9-diaza-naphto[3,2,1-*de*]anthracen-13b-yl)-acetonitrile or (+)-6: Made from **(+)-**[(*P*)-**4**][PF_6]: ee > 98% as determined by CSP-HPLC.[6] **CD** (CH_2Cl_2, 6.10^{-5} M, 20 °C) λ (Δε) 328 (41.6), 274.5 (22.5), 246 (30.7) ; $[\alpha]_{589}$ = + 850, $[\alpha]_{578}$ = + 900, $[\alpha]_{546}$ = + 1100, $[\alpha]_{436}$ = + 2500, $[\alpha]_{365}$ = + 7700 (c = 0.0273, CH_2Cl_2).



(-)-**6**

of supposed (*M*) configuration

(-)-(1,13-Dimethoxy-5,9-dipropyl-5*H*,9*H*-5,9-diaza-naphto[3,2,1-*de*]anthracen-13b-yl)-acetonitrile or (-)-6: Made from **(-)-**[(*M*)-**4**][PF_6]:ee > 96% as determined by CSP-HPLC.[6] **CD** (CH_2Cl_2, 6.10^{-5} M, 20 °C) λ (Δε) 328.5 (-42.8), 275 (-24.3), 245.5 (-32.1) ; $[\alpha]_{589}$ = - 910, $[\alpha]_{578}$ = - 980, $[\alpha]_{546}$ = - 1130, $[\alpha]_{436}$ = - 2900, $[\alpha]_{365}$ = -8700 (c = 0.0134, CH_2Cl_2).



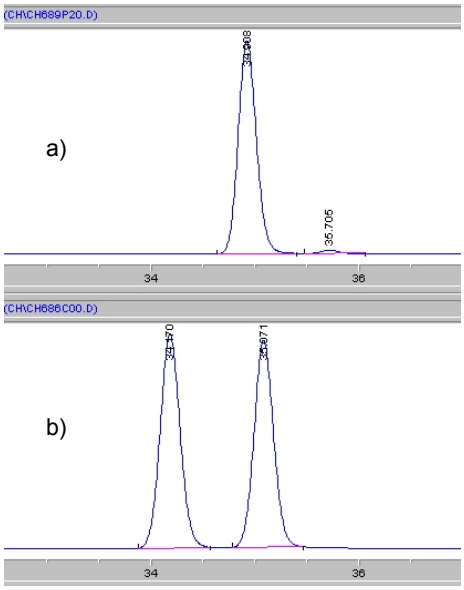
CD spectra of (+)-**6** (red line, CH_2Cl_2, 6.10^{-5} M, 20 °C) and (-)-**6** (blue line, CH_2Cl_2, 6.10^{-5} M, 20 °C).

[5] Efficient decomposition of **6** into **4** was observed in mass spectrometry (EI).
[6] HPLC (Chiracel AD-H, *n*-hexane / *i*-PrOH 99:1 for 20 minutes, gradient to 85:15 in 15 min, then gradient to 99:1 in 15 min, 0.5 mL/min, 23 °C, λ 325 nm). Retention times 34.9 and 35.7 min.

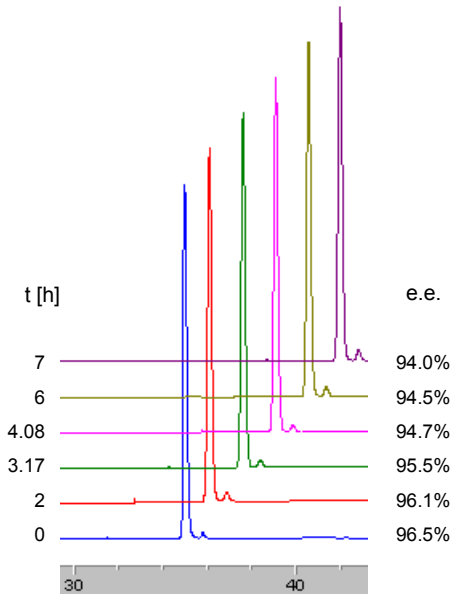
General procedure for the racemization of (-)-[(*M*)-4][PF_6]: In a molten metal bath (temperature controlled by two independent probes), samples (1.0 mg) of salt (-)-[(*M*)-**4**][PF_6] were heated together in separated (1 ml) vials at the desired temperature (200-230 °C). At given times, a vial was removed and allowed to cool to room temperature. After dissolution of the [**4**][PF_6] salt in CH_3CN, addition of NaH led to colourless solutions in about 1 hour, which were analysed by CSP-HPLC.[6]

CSP-HPLC analysis of salts [4][PF_6]:[6]

a) (-)-[(*M*)-**4**][PF_6] e.r. 55.8:1
b) (±)-[**4**][PF_6] e.r. 1:1



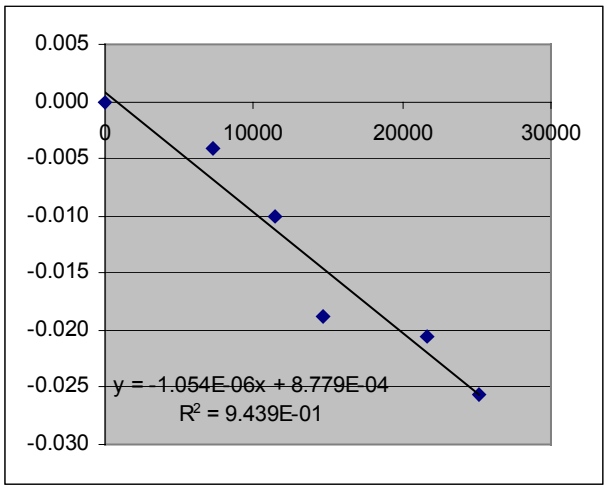
Kinetics of racemization of (-)-(*M*)-[**4**][PF_6] at 200 °C



t [s]	Maj	Min	e.e.	[a]/[a0]	ln ([a]/[ao])
0	98.24	1.76	96.5%	1.00	0.000
7200	98.04	1.96	96.1%	1.00	-0.004
11412	97.76	2.24	95.5%	0.99	-0.010
14688	97.34	2.66	94.7%	0.98	-0.019
21600	97.26	2.74	94.5%	0.98	-0.021
25200	97.02	2.98	94.0%	0.97	-0.026

$Ln(e.e./e.e._0)=f(t)$

slope = -1.054E-06



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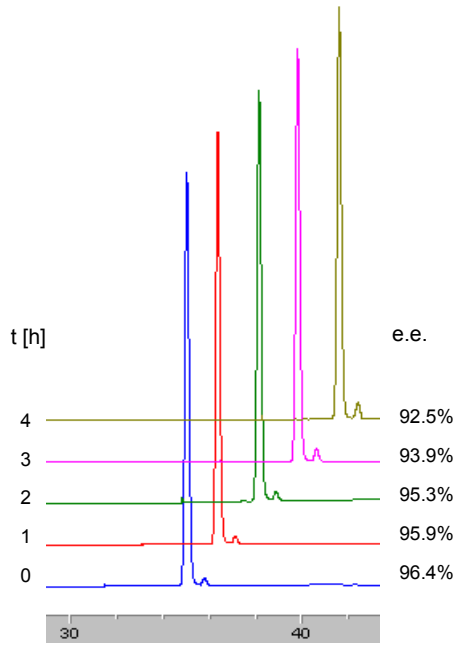
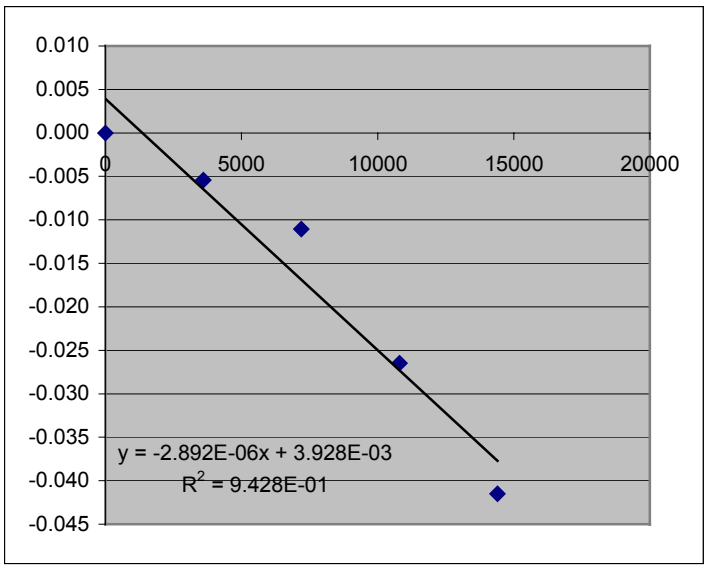
Kinetics of racemization of (-)-(*M*)-[**4**][PF_6] at 210 °C



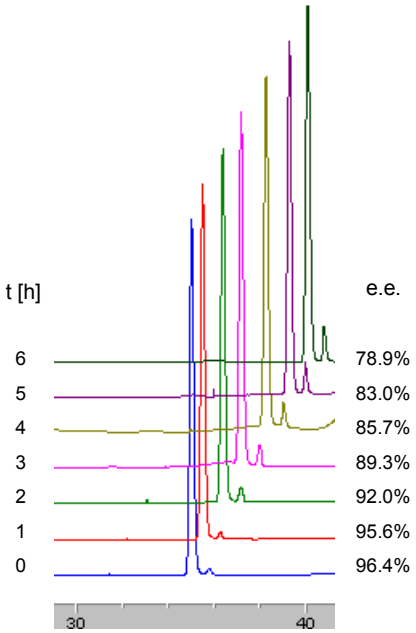
t [s]	Maj	Min	e.e.	[a]/[a0]	ln ([a]/[ao])
0	98.20	1.80	96.4%	1.00	0.000
3600	97.94	2.06	95.9%	0.99	-0.005
7200	97.67	2.33	95.3%	0.99	-0.011
10800	96.94	3.06	93.9%	0.97	-0.026
14400	96.24	3.76	92.5%	0.96	-0.042

$Ln(e.e./e.e._0)=f(t)$

slope = -2.892E-06



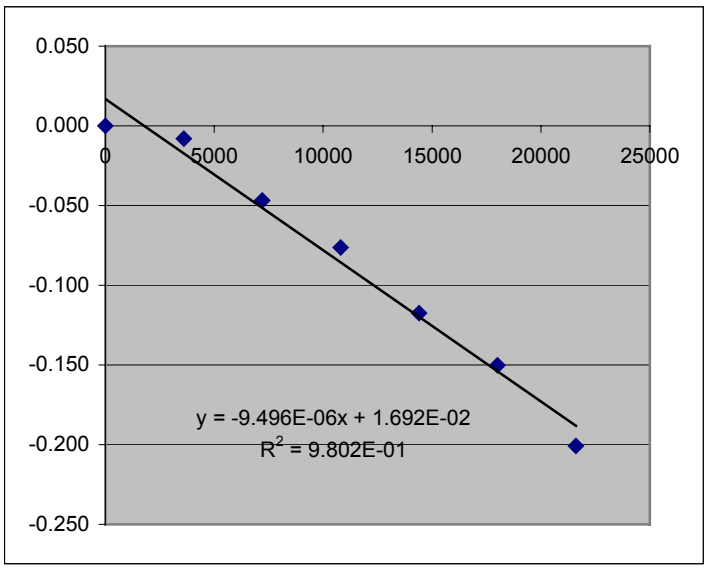
Kinetics of racemization of (-)-(*M*)-[**4**][PF_6] at 220 °C



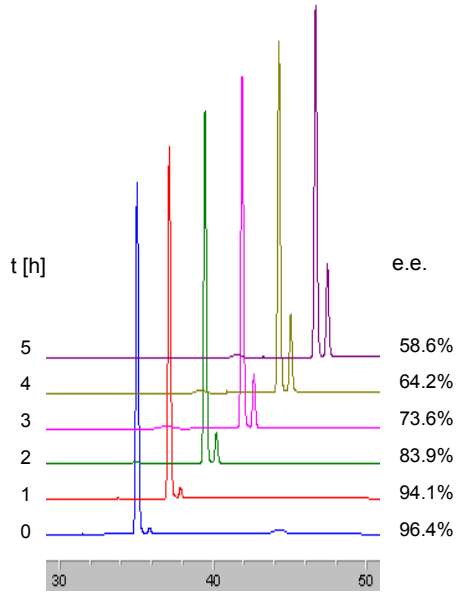
t [s]	Maj	Min	e.e.	[a]/[a0]	ln ([a]/[ao])
0	98.20	1.80	96.4%	1.00	0.000
3600	97.81	2.19	95.6%	0.99	-0.008
7200	96.00	4.00	92.0%	0.95	-0.047
10800	94.66	5.34	89.3%	0.93	-0.076
14400	92.86	7.14	85.7%	0.89	-0.117
18000	91.48	8.52	83.0%	0.86	-0.150
21600	89.43	10.57	78.9%	0.82	-0.201

Ln(e.e./e.e.$_0$)=f(t)

slope = -9.496E-06



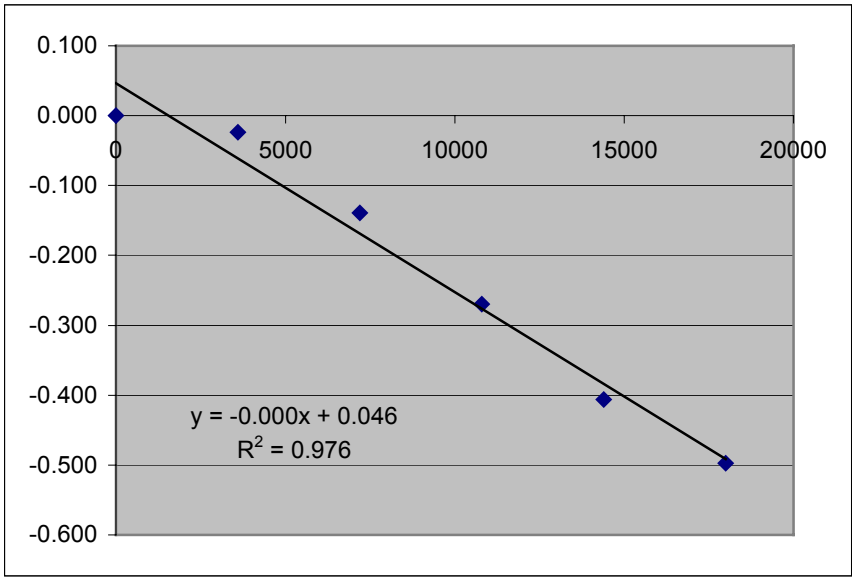
Kinetics of racemization of (-)-(*M*)-[**4**][PF_6] at 230 °C



t [s]	Maj	Min	e.e.	[a]/[a0]	ln ([a]/[ao])
0	98.20	1.80	96.4%	1.00	0.000
3600	97.07	2.93	94.1%	0.98	-0.024
7200	91.94	8.06	83.9%	0.87	-0.139
10800	86.82	13.18	73.6%	0.76	-0.269
14400	82.12	17.88	64.2%	0.67	-0.406
18000	79.31	20.69	58.6%	0.61	-0.497

Ln(e.e./e.e.$_0$)=f(t)

slope = -2.987E-05



Combined kinetic data

T [°C]	T [K]	1000/T	k [s^{-1}]	ln(k)	$\Delta G^{\ddagger}$ [kJ/mol]	t1/2 [h]
200	473.15	2.1135	1.054E-06	-13.763	171.839	182.74
210	483.15	2.0698	2.892E-06	-12.754	171.499	66.58
220	493.15	2.0278	9.496E-06	-11.565	170.257	20.27
230	503.15	1.9875	2.987E-05	-10.419	169.000	6.45

Ln(k)=f(1000/T)

slope=	-26.698	i.e. - Ea/R
intercept=	42.596	i.e. Ln(A)

T	210	°C
Ea	222.66	kJ/mol
A	3.16E+18	s^{-1}

Ea: Activation energy, A: pre-exponential factor.

$\Delta H^{\ddagger} = Ea - RT$
$\Delta S^{\ddagger} = R\,[\ln((h*A)/(k*T))-1]$
$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$