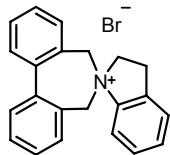


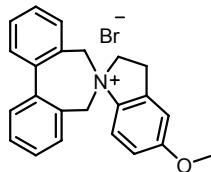
Enantioselective [1,2]-Stevens Rearrangement of Quaternary Ammonium Salts. A Mechanistic Evaluation

Supporting Information



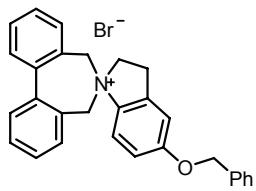
5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [3a][Br].

To a suspension of indoline (150 mg, 1.253 mmol, 1.0 equiv.) in CH₃CN (21 mL) was added K₂CO₃ (780 mg, 5.637 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (511 mg, 1.504 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in CH₂Cl₂ and the inorganic salts filtered. The mother liquor was concentrated in vaccuo. The compound was purified by column chromatography over silica gel using CH₂Cl₂ as eluent and then CH₂Cl₂:MeOH from 99:01 to 95:05. After evaporation of the solvent, the product was dissolved in a minimum amount of CH₂Cl₂, and dropwise addition of Et₂O provided a white precipitate, which was collected by filtration and washed with Et₂O to afford the desired compound as a white solid (390 mg, 83%). **M.p.** 250 °C (decomposition); **IR** (neat): 2999, 2940, 1606, 1485, 1455, 1380, 1201, 1090, 1013, 917, 789, 775, 731, 711 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K) δ 8.28 (d, 1H, *J* = 7.5 Hz), 7.75-7.68 (m, 4H), 7.63-7.54 (m, 4H), 7.47 (d, 1H, *J* = 7.5 Hz), 7.41-7.37 (m, 1H), 7.30 (d, 1H, *J* = 8.4 Hz), 5.00 (d, 1H, *J* = 13.0 Hz), 4.92-4.88 (m, 1H), 4.64 (d, 1H, *J* = 13.3 Hz), 4.32 (d, 1H, *J* = 13.3 Hz), 4.20-4.03 (m, 3H), 3.55-3.49 (m, 1H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 233 K) δ 145.4 (C^{IV}), 140.8 (C^{IV}), 140.3 (C^{IV}), 134.4 (C^{IV}), 132.4 (CH), 131.7 (CH), 131.6 (2CH), 131.5 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 127.3 (CH), 127.2 (C^{IV}), 127.0 (C^{IV}), 118.2 (CH), 67.3 (CH₂), 64.5 (CH₂), 64.2 (CH₂), 27.2 (CH₂); **MS-ES** (+) *m/z* (rel intensity) 338.3 (23%) 323.3 (36%), 299.5 (30%), 298.5 (100%[M]⁺); **HRMS**: Calculated for C₂₂H₂₀N 298.1590, found 298.1597.



5'-methoxy-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [3b][Br].

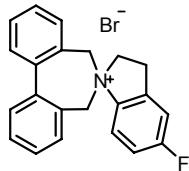
To a suspension of 5-methoxyindolinium chloride salt (250 mg, 1.351 mmol, 1.0 equiv.) in CH₃CN (22 mL) was added K₂CO₃ (840 mg, 6.079 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (551 mg, 1.621 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in CH₂Cl₂:MeOH 1:1 and the inorganic salts filtered. To the mother liquor was added an excess of KBr (20 equiv.) and the mixture was stirred for 30 min. The resulting KCl salts were filtered and the mother liquor was concentrated in vaccuo. The compound was purified by column chromatography over silica gel using CH₂Cl₂ as eluent and then CH₂Cl₂:MeOH from 99:01 to 95:05. After evaporation of the solvent, the product was dissolved in a minimum amount of CH₂Cl₂:MeOH 1:1, and dropwise addition of Et₂O provided a white precipitate, which was collected by filtration and washed with Et₂O to afford the desired compound as a white solid (404 mg, 71%). **M.p.** 258 °C (decomposition); **IR** (neat): 3001, 2957, 1602, 1481, 1447, 1259, 1169, 1147, 1026, 876, 858, 796, 771 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K) δ 8.27 (d, 1H, *J* = 7.5 Hz), 7.74-7.67 (m, 4H), 7.63-7.56 (m, 2H), 7.46 (d, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 8.8 Hz), 7.00 (d, 1H, *J* = 2.5 Hz), 6.84 (dd, 1H, *J* = 8.8 Hz, *J* = 2.5 Hz), 4.99 (d, 1H, *J* = 13.0 Hz), 4.92-4.87 (m, 1H), 4.57 (d, 1H, *J* = 13.2 Hz), 4.29 (d, 1H, *J* = 13.2 Hz), 4.15-4.02 (m, 3H), 3.82 (s, 3H), 3.50-3.44 (m, 1H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 233 K) δ 161.5 (C^{IV}), 140.8 (C^{IV}), 140.3 (C^{IV}), 138.2 (C^{IV}), 136.3 (C^{IV}), 132.3 (CH), 131.6 (2CH), 131.4 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 127.3 (C^{IV}), 127.2 (C^{IV}), 119.0 (CH), 115.0 (CH), 110.0 (CH), 67.6 (CH₂), 64.9 (CH₂), 64.6 (CH₂), 55.9 (CH₃), 27.4 (CH₂); **MS-ES** (+) *m/z* (rel intensity) 391.5 (25%), 329.5 (29%), 328.5 (100%[M]⁺), 323.3 (21%); **HRMS**: Calculated for C₂₃H₂₂NO 328.1695, found 328.1685.



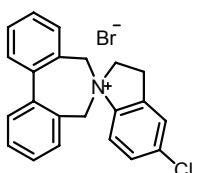
5'-(benzyloxy)-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [3c][Br].

To a suspension of 5-benzyloxyindolinium chloride salt (125 mg, 0.479 mmol, 1.0 equiv.) in CH₃CN (8 mL) was added K₂CO₃ (298 mg, 2.154 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (195 mg, 0.574 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in CH₂Cl₂:MeOH 1:1 and the inorganic salts filtered. To the mother liquor was added an excess of KBr (20 equiv.) and the mixture was stirred for 30 min. The resulting KCl salts were filtered and the mother liquor was concentrated in vaccuo. The compound was purified by column chromatography over silica gel using CH₂Cl₂ as eluent and then CH₂Cl₂:MeOH from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of CH₂Cl₂:MeOH 1:1, and dropwise addition of Et₂O provided a white precipitate, which was collected by filtration and washed with Et₂O to afford the desired compound as a white solid (170 mg, 73%). **M.p.** 180 °C; **IR** (neat): 3376, 2924, 1599, 1485, 1454, 1266, 1166, 1013, 758 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K) δ 8.26 (d, 1H, *J* = 7.6 Hz), 7.74-7.66 (m, 4H), 7.62-7.56 (m,

2H), 7.48-7.33 (m, 6H), 7.19 (d, 1H, $J = 8.8$ Hz), 7.07 (d, 1H, $J = 2.5$ Hz), 6.90 (dd, 1H, $J = 8.8$ Hz, $J = 2.5$ Hz), 5.07 (s, 2H), 5.00 (d, 1H, $J = 13.0$ Hz), 4.90-4.86 (m, 1H), 4.59 (d, 1H, $J = 13.2$ Hz), 4.28 (d, 1H, $J = 13.2$ Hz), 4.14-4.02 (m, 3H), 3.49-3.44 (m, 1H); $^{13}\text{C-NMR}$ (126 MHz, CD_2Cl_2 , 233 K) δ 160.6 (C^{IV}), 140.8 (C^{IV}), 140.4 (C^{IV}), 138.4 (C^{IV}), 136.4 (C^{IV}), 135.7 (C^{IV}), 132.4 (CH), 131.7 (CH), 131.6 (CH), 131.4 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.6 (2CH), 128.3 (CH), 127.7 (2 CH), 127.3 (C^{IV}), 127.2 (C^{IV}), 119.1 (CH), 115.6 (CH), 111.5 (CH), 70.2 (CH₂), 67.6 (CH₂), 64.9 (CH₂), 64.6 (CH₂), 27.4 (CH₂); **MS-ES** (+) m/z (rel intensity) 405.5 (38%), 404.6 (100%[M]⁺), 323.5 (28%); **HRMS**: Calculated for $\text{C}_{29}\text{H}_{26}\text{NO}$ 404.2008, found 404.2007.



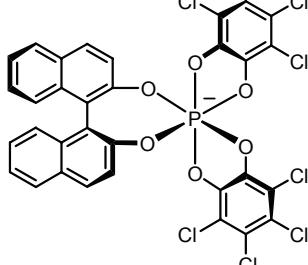
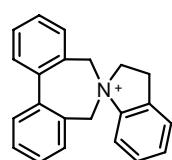
5'-fluoro-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [3d][Br]. To a suspension of 5-fluoroindolinium chloride salt (59 mg, 0.341 mmol, 1.0 equiv.) in MeOH (6 mL) was added NaHCO_3 (58 mg, 0.682 mmol, 2.0 equiv.) and 2,2'-bis(bromomethyl)biphenyl (140 mg, 0.409 mmol, 1.2 equiv.). The mixture was heated at 65 °C for 6h and let cool down. After adding an excess of KBr (20 equiv.), the mixture was stirred for 30 min. The resulting KCl salts filtered and the mother liquor was concentrated in vaccuo. The compound was purified by column chromatography over silica gel using CH_2Cl_2 as eluent and then $\text{CH}_2\text{Cl}_2:\text{MeOH}$ from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 1:1, and dropwise addition of Et₂O provided a pale grey precipitate, which was collected by filtration and washed with Et₂O to afford the desired compound as a pale grey solid (121 mg, 90%). **M.p.** 260 °C (decomposition); **IR** (neat): 3000, 2956, 2924, 1728, 1601, 1480, 1447, 1367, 1259, 1202, 1146, 1121, 1013, 929, 874, 863, 816, 798, 768, 749 cm⁻¹; **$^1\text{H-NMR}$** (500 MHz, CD_2Cl_2 , 233 K) δ 8.33 (d, 1H, $J = 7.5$ Hz), 7.75-7.67 (m, 4H), 7.61-7.57 (m, 2H), 7.46 (d, 1H, $J = 7.5$ Hz), 7.28-7.24 (m, 2H), 7.08 (td, 1H, $J = 8.8$ Hz, $J = 2.5$ Hz), 5.13 (d, 1H, $J = 13.0$ Hz), 5.00-4.96 (m, 1H), 4.67 (d, 1H, $J = 13.2$ Hz), 4.30 (d, 1H, $J = 13.2$ Hz), 4.24-4.12 (m, 3H), 3.55-3.50 (m, 1H); **$^{13}\text{C-NMR}$** (126 MHz, CD_2Cl_2 , 233 K) δ 164.7-162.7 (d, C^{IV} , $J_{\text{C}-\text{F}} = 251.8$ Hz), 141.4 (C^{IV}), 140.9 (C^{IV}), 140.4 (C^{IV}), 137.6 (d, C^{IV} , $J_{\text{C}-\text{F}} = 9.7$ Hz), 132.5 (CH), 131.7 (CH), 131.6 (CH), 131.5 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 129.0 (CH), 127.1 (C^{IV}), 127.0 (C^{IV}), 120.0 (d, CH, $J_{\text{C}-\text{F}} = 9.7$ Hz), 116.2 (d, CH, $J_{\text{C}-\text{F}} = 24.3$ Hz), 114.3 (d, CH, $J_{\text{C}-\text{F}} = 24.3$ Hz), 67.7 (CH₂), 65.1 (CH₂), 64.7 (CH₂), 27.5 (CH₂); **$^{19}\text{F-NMR}$** (352 MHz, CD_2Cl_2 , 233 K) δ -108.06; **MS-ES** (+) m/z (rel intensity) 323.3 (39%), 317.5 (28%), 316.1 (100%[M]⁺), 122.2 (33%); **HRMS**: Calculated for $\text{C}_{22}\text{H}_{19}\text{NF}$ 316.1496, found 316.1504.



5'-chloro-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [3e][Br]. To a suspension of 5-chloroindolinium chloride salt (61 mg, 0.323 mmol, 1.0 equiv.) in CH_3CN (6 mL) was added K_2CO_3 (200 mg, 1.452 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (132 mg, 0.387 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 1:1 and the inorganic salts filtered. To the mother liquor was added an excess of KBr (20 equiv.) and the mixture was stirred for 30 min. The resulting KCl salts filtered and the mother liquor was concentrated in vaccuo. The compound was purified by column chromatography over silica gel using CH_2Cl_2 as eluent and then $\text{CH}_2\text{Cl}_2:\text{MeOH}$ from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of $\text{CH}_2\text{Cl}_2:\text{MeOH}$ 1:1, and dropwise addition of Et₂O provided a pale grey precipitate, which was collected by filtration and washed with Et₂O to afford the desired compound as a pale grey solid (111 mg, 84%). **M.p.** 269 °C (decomposition); **IR** (neat): 3412, 2962, 2923, 1732, 1602, 1533, 1470, 1451, 1426, 1350, 1144, 1100, 1066, 1011, 899, 885, 796, 775, 723 cm⁻¹; **$^1\text{H-NMR}$** (500 MHz, $\text{CD}_2\text{Cl}_2+\text{MeOH}-d_4$, 233 K) δ 8.0 (d, 1H, $J = 7.5$ Hz), 7.77-7.69 (m, 4H), 7.63-7.57 (m, 3H), 7.47 (d, 1H, $J = 7.5$ Hz), 7.38 (dd, 1H, $J = 8.8$ Hz, $J = 2.2$ Hz), 7.26 (d, 1H, $J = 8.8$ Hz), 4.76-4.65 (m, 3H), 4.32 (d, 1H, $J = 13.2$ Hz), 4.22-4.14 (m, 2H), 3.87-3.81 (m, 1H), 3.56-3.50 (m, 1H); **$^{13}\text{C-NMR}$** (126 MHz, $\text{CD}_2\text{Cl}_2+\text{MeOH}-d_4$, 233 K) δ 144.0 (C^{IV}), 140.8 (C^{IV}), 140.4 (C^{IV}), 137.3 (C^{IV}), 136.5 (C^{IV}), 132.0 (CH), 131.8 (CH), 131.7 (CH), 131.6 (CH), 129.6 (CH), 129.3 (2CH), 129.2 (CH), 129.1 (CH), 127.4 (CH), 127.0 (C^{IV}), 126.5 (C^{IV}), 119.4 (CH), 67.2 (CH₂), 64.8 (CH₂), 64.7 (CH₂), 27.0 (CH₂); **MS-ES** (+) m/z (rel intensity) 335.5 (10%), 334.4 (37%), 333.5 (27%), 332.5 (100%[M]⁺), 323.5 (57%), 279.5 (39%), 122.3 (37%); **HRMS**: Calculated for $\text{C}_{22}\text{H}_{19}\text{NCl}$ 332.1200, found 332.1207.

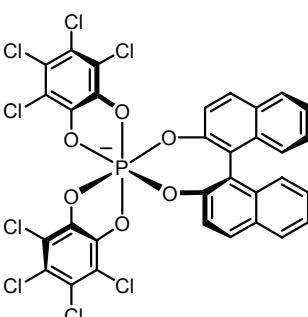
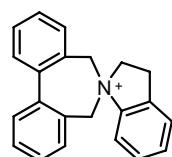
General Procedure for the synthesis of the diphenylazepinium BINPHAT salts [3a][Δ -5] to [3e][Δ -5] and [3a][Λ -5]

To a solution of diphenylazepinium (1.0 equiv.) in CH₂Cl₂ or in CH₂Cl₂:MeOH 1:1 (3.4 mL per 0.1 mmol of substrate) was added a solution of salt [Me₂NH₂][(Δ)-5] (or its enantiomer, 1.2 equiv.) in acetone (5.1 mL per 0.1 mmol of substrate). After stirring for 10 min, the mixture was concentrated under reduced pressure. The resulting salt was purified by column chromatography over basic alumina using CH₂Cl₂ as eluent.



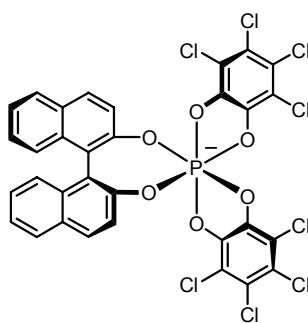
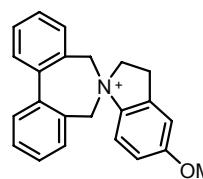
5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium [Δ -bis(tetrachloro-benzenediolato)mono((S)-1,1'-dinaphthyl-2,2'-diolato)phosphate] - [3a][Δ -5]

Starting from 80 mg (0.212 mmol) of [3a][Br], salt [3a][Δ -5] was obtained as a white solid after purification by column chromatography (226 mg, 97%). **M.p.** 243 °C (decomposition); $[\alpha]_D^{20} -123.4$ (*c* 0.1, CH₂Cl₂); **IR** (neat): 1593, 1453, 1389, 1236, 993, 953, 820, 783, 752, 730, 698, 671 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K, Major (*Maj*) or minor (*min*) enantiomers of the cation) δ 7.83 (d, 2H, BT, *J* = 8.2 Hz), 7.58 (d, 2H, BT, *J* = 8.8 Hz), 7.50-7.03 (m, 6H, BT + 10H, *Maj* + 10H, *min*), 6.85 (d, 1H, *Maj*, *J* = 8.2 Hz), 6.75 (d, 1H, *min*, *J* = 8.2 Hz), 6.54 (d, 1H, *min*, *J* = 7.2 Hz), 6.47 (d, 1H, *Maj*, *J* = 7.2 Hz), 6.14 (d, 2H, BT, *J* = 8.8 Hz), 4.53-4.49 (m, 1H, *min*), 4.39 (d, 1H, *Maj*, *J* = 14.0 Hz), 4.11-4.07 (m, 1H, *Maj* + 1H, *min*), 3.85-3.69 (m, 4H, *Maj* + 5H, *min*), 3.20-3.15 (m, 1H, *min*), 2.65-2.59 (m, 1H, *Maj*), 2.51-2.44 (m, 1H, *Maj*); **³¹P-NMR** (203 MHz, CD₂Cl₂, 233 K) δ -83.3; **MS-ES** (+) *m/z* (rel intensity) 338.5 (38%), 299.5 (67%), 298.4 (100%[M]⁺), 181.4 (34%), 122.3 (31%), **MS-ES** (-) *m/z* (rel intensity) 807.3 (100%[M+5]⁺, BINPHAT); **HRMS**: Calculated for C₂₂H₂₀N 298.1590, found 298.1589 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7901.



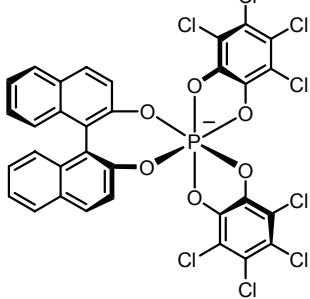
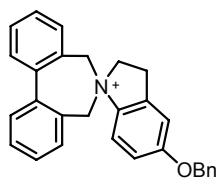
5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium [Δ -bis(tetrachloro-benzenediolato)mono((R)-1,1'-dinaphthyl-2,2'-diolato)phosphate] - [3a][Λ -5]

Starting from 40 mg (0.0106 mmol) of [3a][Br], salt [3a][Λ -5] was obtained as a white solid after purification by column chromatography (136 mg, 87%). $[\alpha]_D^{20} +123.6$ (*c* 0.1, CH₂Cl₂).

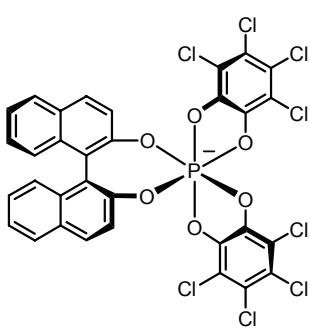
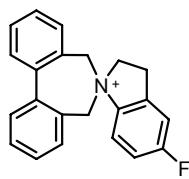


5'-methoxy-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium [Δ -bis(tetrachlorobenzenediolato)mono((S)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [3b][Δ -5]

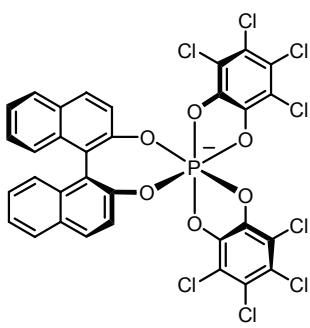
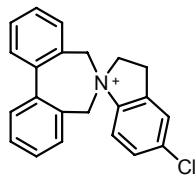
Starting from 80 mg (0.196 mmol) of [3b][Br], salt [3b][Δ -5] was obtained as a white solid after purification by column chromatography (218 mg, 98%). **M.p.** 218 °C (decomposition); $[\alpha]_D^{20} -128.7$ (*c* 0.1, CH₂Cl₂); **IR** (neat): 2926, 1723, 1594, 1488, 1451, 1388, 1269, 1230, 992, 953, 817, 781, 752, 731 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K, Major (*Maj*) or minor (*min*) enantiomers of the cation) δ 7.84 (d, 2H, BT, *J* = 8.2 Hz), 7.63-7.06 (m, 8H, BT + 8H, *Maj* + 8H, *min*), 6.80 (m, 1H, *Maj* + 1H, *min*), 6.72-6.67 (m, 2H, *min*), 6.60 (m, 1H, *Maj* + 1H, *min*), 6.44 (dd, 1H, *Maj*, *J* = 9.1 Hz, *J* = 2.5 Hz), 6.28-6.25 (m, 2H, BT + 1H, *Maj*), 4.52-4.44 (m, 1H, *Maj* + 1H, *min*), 4.15-4.10 (m, 1H, *Maj* + 1H, *min*), 3.92-3.75 (m, 4H, *Maj* + 5H, *min*), 3.69 (s, 3H, *min*), 3.56 (s, 3H, *Maj*), 3.20-3.14 (m, 1H, *min*), 2.84-2.78 (m, 1H, *Maj*), 2.66-2.62 (m, 1H, *Maj*); **³¹P-NMR** (203 MHz, CD₂Cl₂, 233 K) δ -83.4; **MS-ES** (+) *m/z* (rel intensity) 329.5 (38%), 328.5 (100%[M]⁺), 338.5 (31%), 122.2 (28%), **MS-ES** (-) *m/z* (rel intensity) 807.3 (100%[M+5]⁺, BINPHAT); **HRMS**: Calculated for C₂₃H₂₂NO 328.1695, found 328.1680 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7918.



7.28 (m, 8H, BT + 8H, *Maj* + 8H, *min*), 7.22 (d, 1H, *Maj*, *J* = 7.2 Hz), 7.15-7.12 (m, 3H, *Maj* + 4H, *min*), 6.89 (sd, 1H, *min*, *J* = 1.9 Hz), 6.77 (d, 1H, *Maj*, *J* = 8.8 Hz), 6.72-6.69 (m, 1H, *min*), 6.65-6.63 (m, 1H, *Maj* + 1H, *min*), 6.49 (dd, 1H, *Maj*, *J* = 8.8 Hz, *J* = 2.2 Hz), 6.46 (d, 1H, *min*, *J* = 7.7 Hz), 6.27 (d, 1H, *Maj*, *J* = 7.5 Hz), 6.17 (d, 2H, BT, *J* = 8.8 Hz), 4.97 (d, 1H, *min*, *J* = 11.3 Hz), 4.81-4.77 (m, 1H, *Maj* + 1H, *min*), 4.70 (d, 1H, *Maj*, *J* = 11.0 Hz), 4.54-4.49 (m, 1H, *min*), 4.40 (d, 1H, *Maj*, *J* = 13.9 Hz), 4.14-4.08 (m, 1H, *Maj* + 1H, *min*), 3.94-3.82 (m, 4H, *Maj* + 2H, *min*), 3.76 (d, 1H, *min*, *J* = 12.9 Hz), 3.71-3.66 (m, 1H, *min*), 3.46 (d, 1H *min*, *J* = 12.9 Hz), 3.2-3.14 (m, 1H, *min*), 2.82-2.72 (m, 1H, *Maj*), 2.67-2.60 (m, 1H, *Maj*); ³¹P-NMR (203 MHz, CD₂Cl₂, 233 K) δ -83.2; MS-ES (+) *m/z* (rel intensity) 405.5 (42%), 404.6 (100%[M]⁺), 122.3 (22%), MS-ES (-) *m/z* (rel intensity) 807.3 (100%[M+5]⁺, BINPHAT), 769.1 (20%); HRMS: Calculated for C₂₉H₂₆NO 404.2008, found 404.2010 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7884.



6.76 (dd, 1H, *min*, *J* = 9.1 Hz, *J* = 4.1 Hz), 6.71 (td, 1H, *Maj*, *J* = 8.5 Hz, *J* = 2.5 Hz), 6.65 (d, 1H, *min*, *J* = 7.2 Hz), 6.30 (d, 1H, *Maj*, *J* = 7.6 Hz), 6.21 (d, 2H, BT, *J* = 8.8 Hz), 4.54-4.49 (m, 1H, *min*), 4.42 (d, 1H, *Maj*, *J* = 14.0 Hz), 4.15 (d, 1H, *Maj*, *J* = 14.0 Hz), 4.08 (d, 1H, *min*, *J* = 12.9 Hz), 3.94-3.76 (m, 4H, *Maj* + 3H, *min*), 3.71-3.65 (m, 1H, *min*), 3.61 (d, 1H, *min*, *J* = 12.9 Hz), 3.19-3.13 (m, 1H, *min*), 2.78-2.71 (m, 1H, *Maj*), 2.60-2.56 (m, 1H, *Maj*); ³¹P-NMR (203 MHz, CD₂Cl₂, 233 K) δ -83.8; ¹⁹F-NMR (352 MHz, CD₂Cl₂, 233 K) δ -107.41 (s, *min*), -107.79 (s, *Maj*); MS-ES (+) *m/z* (rel intensity) 338.3 (23%), 317.5 (31%), 316.4 (100%[M]⁺), MS-ES (-) *m/z* (rel intensity) 807.3 (100%[M+5]⁺, BINPHAT); HRMS: Calculated for C₂₂H₁₉NF 316.1496, found 316.1500 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7909.



6.93 (dd, 1H, *Maj*, *J* = 8.5 Hz, *J* = 1.9 Hz), 6.78 (d, 1H, *Maj*, *J* = 8.8 Hz), 6.72 (d, 1H, *min*, *J* = 8.8 Hz), 6.62 (d, 1H, *min*, *J* = 7.6 Hz), 6.21 (d, 2H, BT, *J* = 8.8 Hz), 6.00 (d, 1H, *Maj*, *J* = 7.6 Hz), 4.47-4.45 (m, 1H, *Maj* + 1H, *min*), 4.15 (d, 1H, *Maj*, *J* = 14.1 Hz), 4.10-3.67 (m, 4H, *Maj* + 5H, *min*), 3.57 (d, 1H, *min*, *J* = 12.6 Hz),

5'-(benzyloxy)-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium|[Δ-bis(tetrachlorobenzenediolato)mono((S)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [3c][Δ-5]

Starting from 90 mg (0.186 mmol) of [3c][Br], salt [3c][Δ-5] was obtained as a white solid after purification by column chromatography (195 mg, 87%). **M.p.** 202 °C (decomposition); [α]_D²⁰ -105.9 (*c* 0.1, CH₂Cl₂); **IR** (neat): 2925, 1739, 1594, 1485, 1451, 1388, 1236, 992, 953, 819, 782, 752, 732 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K, Major (*Maj*) or minor (*min*) enantiomers of the cation) δ 7.78 (d, 2H, BT, *J* = 8.2 Hz), 7.61-

5'-fluoro-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium|[Δ-bis(tetrachlorobenzenediolato)mono((S)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [3d][Δ-5]

Starting from 80 mg (0.202 mmol) of [3d][Br], salt [3d][Δ-5] was obtained as a pale brown solid after purification by column chromatography (157 mg, 70%). **M.p.** 196 °C (decomposition); [α]_D²⁰ -122.7 (*c* 0.1, CH₂Cl₂); **IR** (neat): 2925, 1738, 1593, 1483, 1452, 1389, 1236, 992, 953, 818, 782, 751, 731 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K, Major (*Maj*) or minor (*min*) enantiomers of the cation) δ 7.86 (d, 2H, BT, *J* = 8.5 Hz), 7.63 (d, 2H, BT, *J* = 8.8 Hz), 7.60-6.83 (m, 6H, BT + 9H, *Maj* + 9H, *min*),

3.71-3.65 (m, 1H, *min*), 3.61 (d, 1H, *min*, *J* = 12.9 Hz), 3.19-3.13 (m, 1H, *min*), 2.78-2.71 (m, 1H, *Maj*), 2.60-2.56 (m, 1H, *Maj*); ³¹P-NMR (203 MHz, CD₂Cl₂, 233 K) δ -83.8; ¹⁹F-NMR (352 MHz, CD₂Cl₂, 233 K) δ -107.41 (s, *min*), -107.79 (s, *Maj*); MS-ES (+) *m/z* (rel intensity) 338.3 (23%), 317.5 (31%), 316.4 (100%[M]⁺), MS-ES (-) *m/z* (rel intensity) 807.3 (100%[M+5]⁺, BINPHAT); HRMS: Calculated for C₂₂H₁₉NF 316.1496, found 316.1500 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7909.

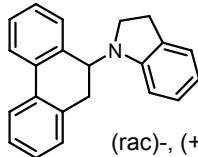
5'-chloro-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium|[Δ-bis(tetrachlorobenzenediolato)mono((S)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [3e][Δ-5]

Starting from 100 mg (0.243 mmol) of [3e][Br], salt [3e][Δ-5] was obtained as a pale brown solid after purification by column chromatography (214 mg, 77%). **M.p.** 208 °C (decomposition); [α]_D²⁰ -144.0 (*c* 0.1, CH₂Cl₂); **IR** (neat): 3052, 1591, 1450, 1388, 1236, 992, 952, 817, 781, 751, 726 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 233 K, Major (*Maj*) or minor (*min*) enantiomers of the cation) δ 7.88 (d, 2H, BT, *J* = 8.2 Hz), 7.63-7.02 (m, 8H, BT + 8H, *Maj* + 9H, *min*), 6.93 (dd, 1H, *Maj*, *J* = 8.5 Hz, *J* = 1.9 Hz), 6.78 (d, 1H, *Maj*, *J* = 8.8 Hz), 6.72 (d, 1H, *min*, *J* = 8.8 Hz), 6.62 (d, 1H, *min*, *J* = 7.6 Hz), 6.21 (d, 2H, BT, *J* = 8.8 Hz), 6.00 (d, 1H, *Maj*, *J* = 7.6 Hz), 4.47-4.45 (m, 1H, *Maj* + 1H, *min*), 4.15 (d, 1H, *Maj*, *J* = 14.1 Hz), 4.10-3.67 (m, 4H, *Maj* + 5H, *min*), 3.57 (d, 1H, *min*, *J* = 12.6 Hz),

3.17-3.11 (m, 1H, *min*), 2.88-2.81 (m, 1H, *Maj*), 2.70-2.65 (m, 1H, *Maj*); **³¹P-NMR** (203 MHz, CD₂Cl₂, 233 K) δ – 83.5; **MS-ES (+)** *m/z* (rel intensity) 339.5 (15%), 338.3 (46%), 335.4 (12%), 334.5 (43%), 333.6 (30%), 332.5 (100%[M]⁺), 122.1 (26%), **MS-ES (-)** *m/z* (rel intensity) 807.5 (100%[M+5]⁻, BINPHAT); **HRMS**: Calculated for C₂₂H₁₉NCl 332.1200, found 332.1207 and calculated for C₃₂H₁₂O₆PCl₈ 802.7885, found 802.7883.

Typical procedure for the Stevens rearrangement:

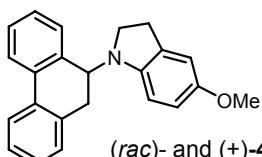
To a solution of the required ammonium salt (1.0 equiv.) in dry CH₂Cl₂ (0.5 mL per 0.01 mmol of substrate) at -80 °C was added the P₄-*t*-Bu base (1M in Hexane, 1.5 equiv.). After stirring 4h at -80 °C, under a nitrogen atmosphere, the reaction was quenched by addition of MeOH (0.5 mL per 0.01 mmol of substrate), by cannulation at -80 °C. The mixture was concentrated under reduced pressure. The residue was dissolved in a minimum amount of CH₂Cl₂ and the precipitate upon addition of Et₂O filtered. The mother liquors were concentrated in vacuo and the resulting compound was purified by column chromatography or preparative plate chromatography over basic alumina.



1-(9,10-dihydrophenanthren-10-yl)indoline 4a. Starting from 15 mg (0.040 mmol) of [3a][Br] or 45 mg (0.041 mmol) of [3a][Δ-5] or 45 mg (0.041 mmol) of [3a][Δ-5] ammonium salts, the desired compound **4a** was obtained after purification by column chromatography (basic alumina, Et₂O) as (*rac*)-**4a** (92%), (+)-**4a** (90%) and (-)-**4a** (88%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiraldak IB, 95/05/0.1%: *n*-Hexane/*i*-PrOH/ethanolamine, 0.5 mL/min, 23°C). **M.p.** 131 °C; **IR** (neat): 3067, 2925, 2847, 1606, 1490, 1474, 1450, 1260, 769, 743, 728, 712 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 293 K) δ 7.85 (dd, 1H, *J* = 7.5 Hz, *J* = 0.8 Hz), 7.80 (d, 1H, *J* = 7.5 Hz), 7.43-7.31 (m, 3H), 7.29-7.23 (m, 3H), 7.06 (m, 1H), 7.01-6.98 (m, 1H), 6.59 (td, 1H, *J* = 7.2 Hz, *J* = 0.9 Hz), 6.45 (d, 1H, *J* = 7.8 Hz), 4.92 (dd, 1H, *J* = 10.4 Hz, *J* = 5.3 Hz), 3.35-3.22 (m, 3H), 2.99-2.89 (m, 3H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 293 K) δ 151.5 (C^{IV}), 136.2 (C^{IV}), 136.1 (C^{IV}), 135.2 (C^{IV}), 134.1 (C^{IV}), 130.3 (C^{IV}), 129.0 (CH), 128.1 (2CH), 128.0 (CH), 127.6 (CH), 127.5 (2CH), 124.9 (CH), 124.3 (CH), 124.0 (CH), 117.3 (CH), 107.3 (CH), 54.0 (CH), 48.5 (CH₂), 31.6 (CH₂), 28.8 (CH₂); **MS-LR** (EI) *m/z* (rel intensity) 297 (27%[M]⁺), 179 (50%[MC₁₄H₁₁]), 119 (100%[MC₈H₈N+1]), **MS-ES (+)** *m/z* (rel intensity) 298.5 (27%[M+1]), 179.4 (100%[MC₁₄H₁₁]); **HRMS**: Calculated for C₂₂H₂₀N 298.1590, found 298.1590.

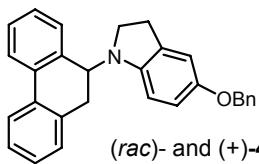
(+)-**4a**: [α]_D²⁰ +23.8 (*c* 0.1, CH₂Cl₂).

(-)-**4a**: [α]_D²⁰ -23.6 (*c* 0.1, CH₂Cl₂).



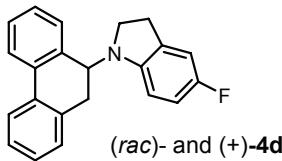
1-(9,10-dihydrophenanthren-10-yl)-5-methoxyindoline 4b. Starting from 30 mg (0.074 mmol) of [3b][Br] or 45 mg (0.041 mmol) of [3b][Δ-5] ammonium salts, the desired compound **4b** was obtained after purification by column chromatography (basic alumina, cyclohexane /Et₂O from 10 to 20%) as (*rac*)-**4b** (53%) and (+)-**4b** (52%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiraldak IB, 99.5/0.5/0.1%: *n*-Hexane/*i*-PrOH/ethanolamine, 0.5 mL/min, 23 °C). **M.p.** 168 °C; **IR** (neat): 3064, 2925, 2850, 1592, 1490, 1449, 1433, 1249, 1235, 1138, 1034, 806, 749 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 293 K) δ 7.84 (dd, 1H, *J* = 7.9 Hz, *J* = 0.8 Hz), 7.80 (d, 1H, *J* = 7.9 Hz), 7.46 (m, 1H), 7.39-7.22 (m, 5H), 6.73 (m, 1H), 6.56 (dd, 1H, *J* = 8.3 Hz, *J* = 2.7 Hz), 6.36 (d, 1H, *J* = 8.3 Hz), 4.82 (dd, 1H, *J* = 10.4 Hz, *J* = 5.3 Hz), 3.71 (s, 3H), 3.31-3.19 (m, 3H), 2.96-2.88 (m, 3H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 293 K) δ 152.8 (C^{IV}), 145.5 (C^{IV}), 136.4 (C^{IV}), 136.2 (C^{IV}), 135.1 (C^{IV}), 134.1 (C^{IV}), 132.0 (C^{IV}), 129.0 (CH), 128.1 (2CH), 128.0 (CH), 127.6 (CH), 127.5 (CH), 124.1 (CH), 124.0 (CH), 112.6 (CH), 111.7 (CH), 107.8 (CH), 56.2 (CH₃), 54.7 (CH), 49.2 (CH₂), 31.0 (CH₂), 29.1 (CH₂); **MS-LR** (EI) *m/z* (rel intensity) 327 (36%[M]⁺), 179 (44%[MC₁₄H₁₁]), 149 (100%[MC₉H₁₀NO+1]), 134 (59%), **MS-ES (+)** *m/z* (rel intensity) 328.4 (36%[M+1]), 179.4 (100%[MC₁₄H₁₁]); **HRMS**: Calculated for C₂₃H₂₂NO 328.1695, found 328.1702.

(+)-**4b**: [α]_D²⁰ +17.6 (*c* 0.1, CH₂Cl₂).



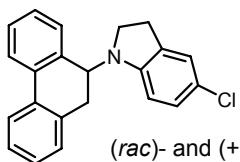
5-(benzyloxy)-1-(9,10-dihydrophenanthren-10-yl)indoline 4c. Starting from 25mg (0.052 mmol) of [3c][Br] or 45 mg (0.037 mmol) of [3c][Δ -5] ammonium salts, the desired compound **4c** was obtained after purification by column chromatography (basic alumina, cyclohexane /Et₂O from 10 to 20%) as (*rac*)-**4c** (48%) and (+)-**4c** (50%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiralpak IB, 98/02/0.1%: *n*-Hexane/*i*-PrOH/ethanolamine, 1.0 mL/min, 23 °C). **M.p.** 171 °C; **IR** (neat): 3063, 3030, 2924, 2850, 1593, 1488, 1452, 1232, 1139, 1024, 750, 736, 695 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 293 K) δ 7.83 (dd, 1H, *J* = 7.9 Hz, *J* = 0.9 Hz), 7.80 (d, 1H, *J* = 7.9 Hz), 7.47-7.21 (m, 11H), 6.81 (m, 1H), 6.64 (dd, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz), 6.35 (d, 1H, *J* = 8.5 Hz), 4.97 (s, 2H), 4.82 (dd, 1H, *J* = 10.4 Hz, *J* = 5.3 Hz), 3.34-3.19 (m, 3H), 2.96-2.85 (m, 3H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 293 K) δ 151.8 (C^{IV}), 145.8, (C^{IV}), 138.3 (C^{IV}), 136.4 (C^{IV}), 136.2 (C^{IV}), 135.1 (C^{IV}), 134.1 (C^{IV}), 132.0 (C^{IV}), 129.0 (CH), 128.8 (CH), 128.0 (5 CH), 127.9 (CH), 127.6 (CH), 127.5 (CH), 124.1 (CH), 124.0 (CH), 113.7 (CH), 113.1 (CH), 107.7 (CH), 54.6 (CH), 71.3 (CH₂), 49.1 (CH₂), 31.0 (CH₂), 29.1 (CH₂); **MS-LR** (EI) *m/z* (rel intensity) 403 (15%[M]⁺), 179 (53%[MC₁₄H₁₁]), 134 (100%), **MS-ES** (+) *m/z* (rel intensity) 404.5 (15%([M+1])), 226.5 (52%[C₁₅H₁₄NO⁺²]), 179.3 (100%[MC₁₄H₁₁])); **HRMS**: Calculated for C₂₉H₂₆NO 404.2008, found 404.2004.

(+)-**4c**: $[\alpha]_D^{20}$ +18.2 (*c* 0.1, CH₂Cl₂).



5-fluoro-1-(9,10-dihydrophenanthren-10-yl)indoline 4d. Starting from 35 mg (0.088 mmol) of [3d][Br] or 50 mg (0.044 mmol) of [3d][Δ -5] ammonium salts, the desired compound **4d** was obtained after purification by column chromatography (basic alumina, cyclohexane /Et₂O 99:01) as (*rac*)-**4d** (48%) and (+)-**4d** (50%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiralpak IB, 95/05/0.1%: *n*-Hexane/*i*-PrOH/ethanolamine, 0.5 mL/min, 23 °C). **M.p.** 110 °C; **IR** (neat): 3066, 2923, 2865, 1601, 1494, 1480, 1441, 1247, 1131, 863, 792, 766, 751, 742, 727 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 293 K) δ 7.84 (dd, 1H, *J* = 7.9 Hz, *J* = 0.9 Hz), 7.80 (d, 1H, *J* = 7.6 Hz), 7.43-7.23 (m, 6H), 6.82 (dt, 1H, *J_{H-H}* = 2.8 Hz, *J_{H-F}* = 8.5 Hz), 6.70 (td, 1H, *J_{H-H}* = 2.8 Hz, *J_{H-F}* = 8.5 Hz), 6.33 (dd, 1H, *J_{H-F}* = 4.4 Hz, *J_{H-H}* = 8.5 Hz), 4.83 (dd, 1H, *J* = 10.4 Hz, *J* = 5.3 Hz), 3.35-3.19 (m, 3H), 2.97-2.89 (m, 3H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 293 K) δ 157.2-155.4 (d, C^{IV}, *J_{C-F}* = 233.0 Hz), 147.7 (C^{IV}), 136.0 (2C^{IV}), 135.1 (C^{IV}), 134.0 (C^{IV}), 132.1 (d, C^{IV}, *J_{C-F}* = 8.0 Hz), 129.0 (CH), 128.1 (2CH), 128.0 (CH), 127.6 (CH), 127.5 (CH), 124.2 (CH), 124.0 (CH), 113.0-112.8 (d, CH, *J_{C-F}* = 23.0 Hz), 112.6-112.4 (d, CH, *J_{C-F}* = 23.0 Hz), 107.2-107.1 (d, CH, *J_{C-F}* = 8.0 Hz), 54.5 (CH), 49.1 (CH₂), 31.2 (CH₂), 28.8 (CH₂); **¹⁹F-NMR** (212 MHz, CD₂Cl₂, 293 K) δ -128.8; **MS-LR** (EI) *m/z* (rel intensity) 315 (20%[M]⁺), 179 (61%[MC₁₄H₁₁]), 137 (100%[MC₈H₇FN+1]), **MS-ES** (+) *m/z* (rel intensity) 316.4 (20%([M+1])), 179.1 (100%[MC₁₄H₁₁])); **HRMS**: Calculated for C₂₂H₁₉NF 316.1496, found 316.1498.

(+)-**4d**: $[\alpha]_D^{20}$ +27.9 (*c* 0.1, CH₂Cl₂).

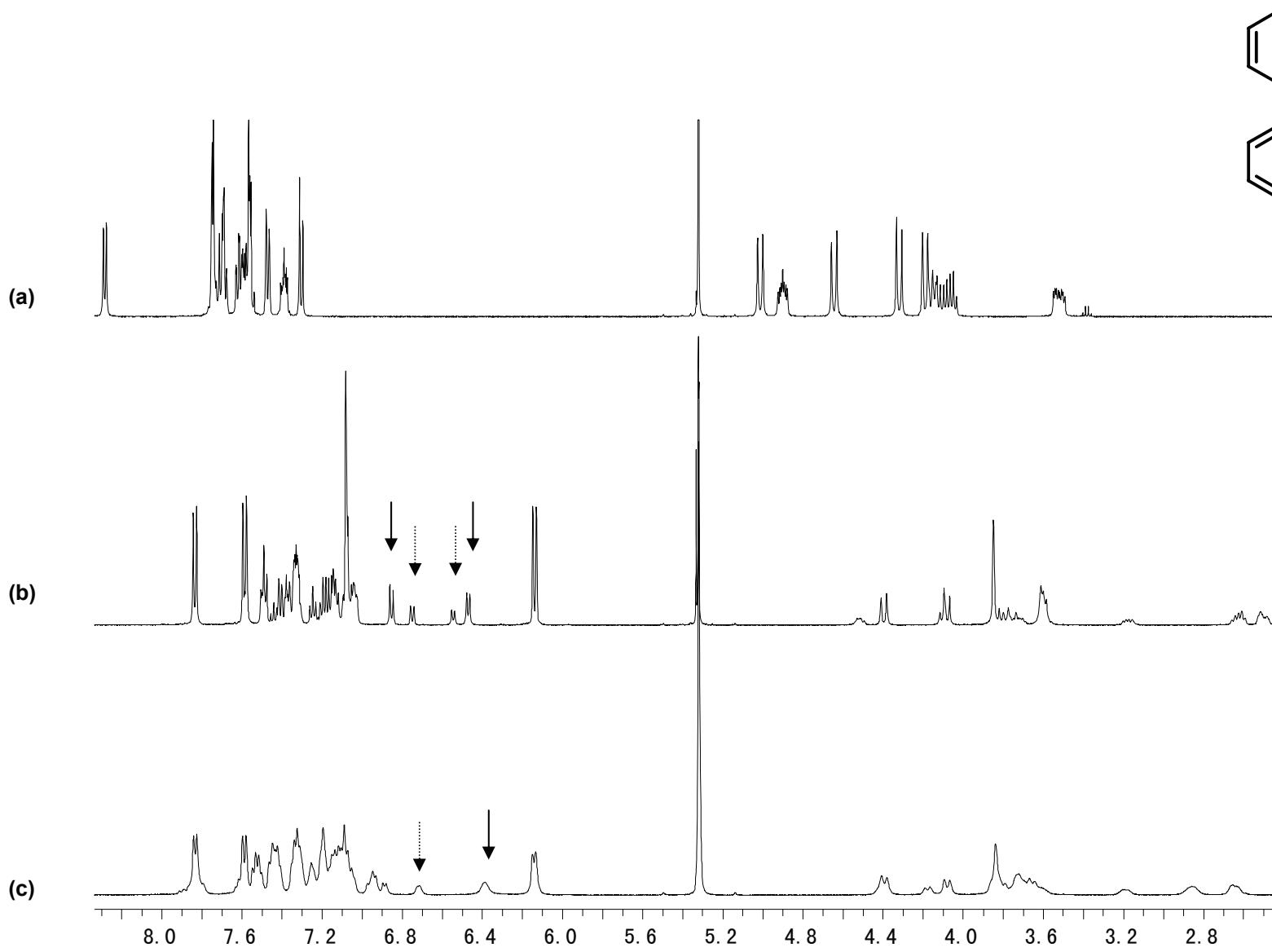
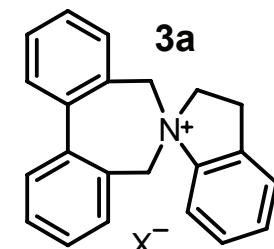


5-chloro-1-(9,10-dihydrophenanthren-10-yl)indoline 4e. Starting from 35 mg (0.085 mmol) of [3e][Br] or 50 mg (0.044 mmol) of [3e][Δ -5] ammonium salts, the desired compound **4e** was obtained after purification by column chromatography (basic alumina, cyclohexane /Et₂O 99:01) as (*rac*)-**4e** (46%) and (+)-**4e** (48%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiralpak IB, 95/05/0.1%: *n*-Hexane/*i*-PrOH/ethanolamine, 0.5 mL/min, 23 °C). **M.p.** 161 °C; **IR** (neat): 3056, 2954, 2918, 2849, 1599, 1494, 1474, 1450, 1436, 1406, 1263, 1161, 806, 769, 753, 728 cm⁻¹; **¹H-NMR** (500 MHz, CD₂Cl₂, 293 K) δ 7.85 (d, 1H, *J* = 7.9 Hz), 7.80 (d, 1H, *J* = 7.6 Hz), 7.40-7.24 (m, 6H), 7.0 (m, 1H), 6.95 (dd, 1H, *J* = 8.3 Hz, *J* = 2.3 Hz), 6.35 (d, 1H, *J* = 8.3 Hz), 4.86 (dd, 1H, *J* = 10.4 Hz, *J* = 5.3 Hz), 3.37-3.19 (m, 3H), 2.99-2.91 (m, 3H); **¹³C-NMR** (126 MHz, CD₂Cl₂, 293 K) δ 150.4 (C^{IV}), 135.9 (C^{IV}), 135.8 (C^{IV}), 135.3 (C^{IV}), 134.2 (C^{IV}), 132.5 (C^{IV}), 129.1 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.5 (CH), 127.2 (CH), 125.2 (CH), 124.5 (CH), 124.2 (CH), 107.9 (CH), 54.3 (CH), 48.9 (CH₂), 31.8 (CH₂), 28.7 (CH₂); **MS-LR** (EI) *m/z* (rel intensity) 331 (21%[M]⁺), 179 (83%[MC₁₄H₁₁]), 153 (100%[MC₈H₇ClN+1]), **MS-ES** (+) *m/z* (rel intensity) 332.5 (21%[M+1]), 179.4 (100%[MC₁₄H₁₁]), 154.3 (46%[MC₈H₇ClN+1]); **HRMS**: Calculated for C₂₂H₁₉NCl 332.1200, found 332.1216.

(+)-**4e**: $[\alpha]_D^{20}$ +20.5 (*c* 0.1, CH₂Cl₂).

Salts of Cation **3a** ^1H NMR (500 MHz, CD_2Cl_2)

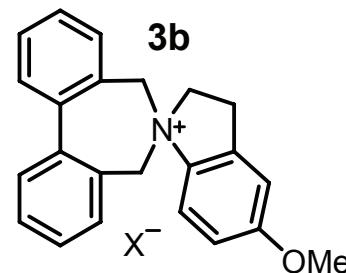
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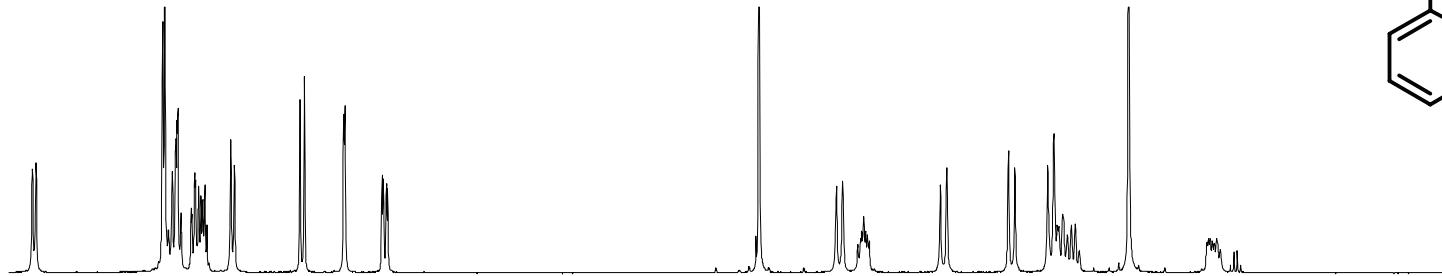
(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

Salts of Cation **3b** ^1H NMR (500 MHz, CD_2Cl_2)

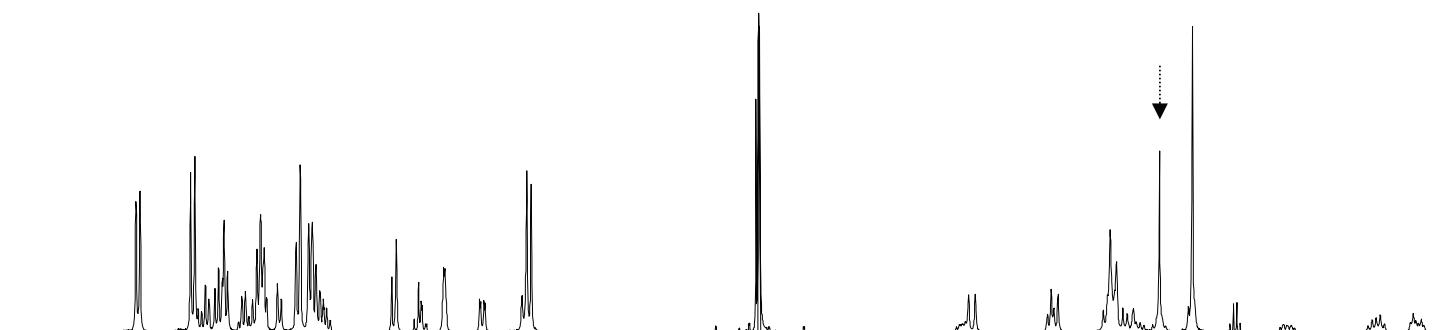
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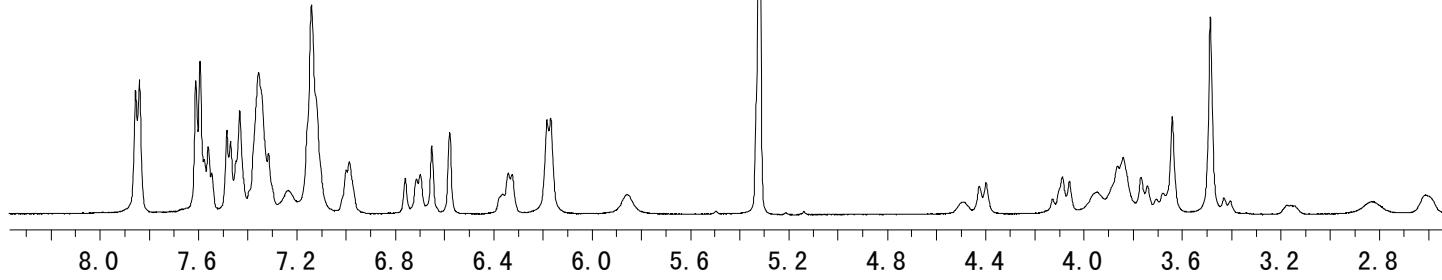
(a)



(b)



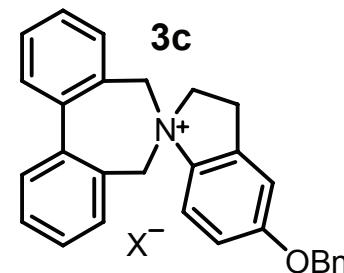
(c)



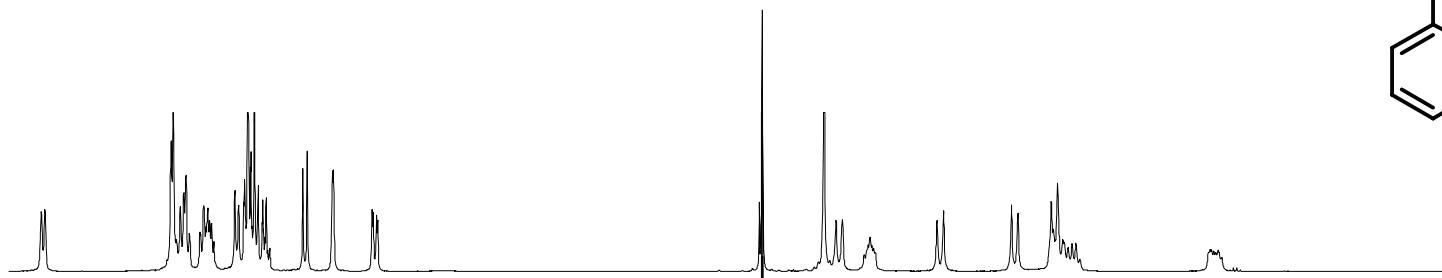
(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

Salts of Cation **3c** ^1H NMR (500 MHz, CD_2Cl_2)

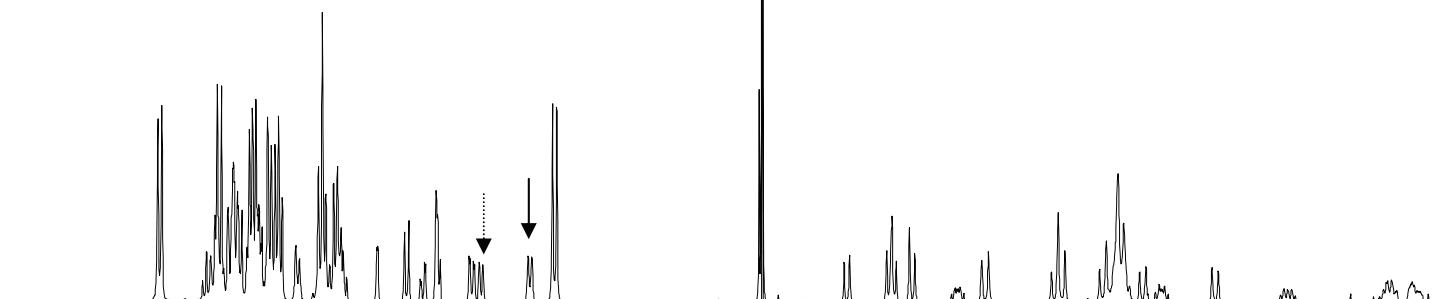
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(a)

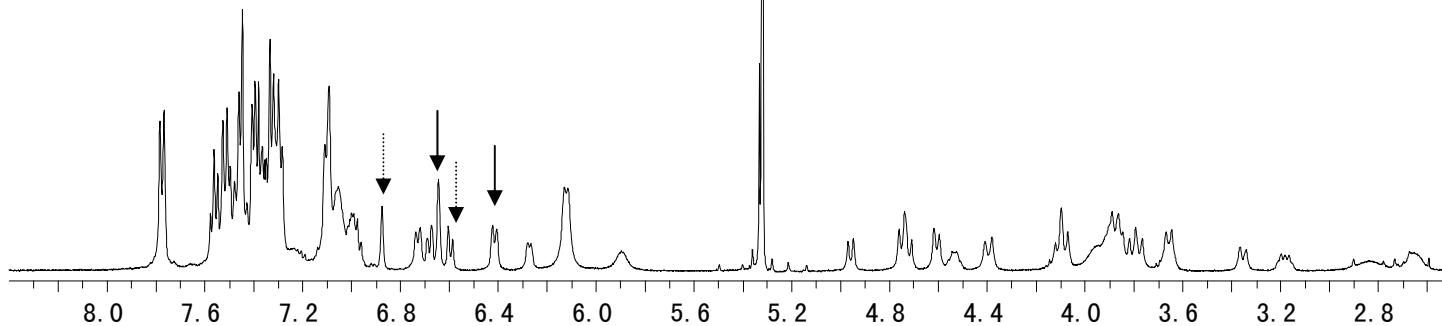


(b)



de 20%

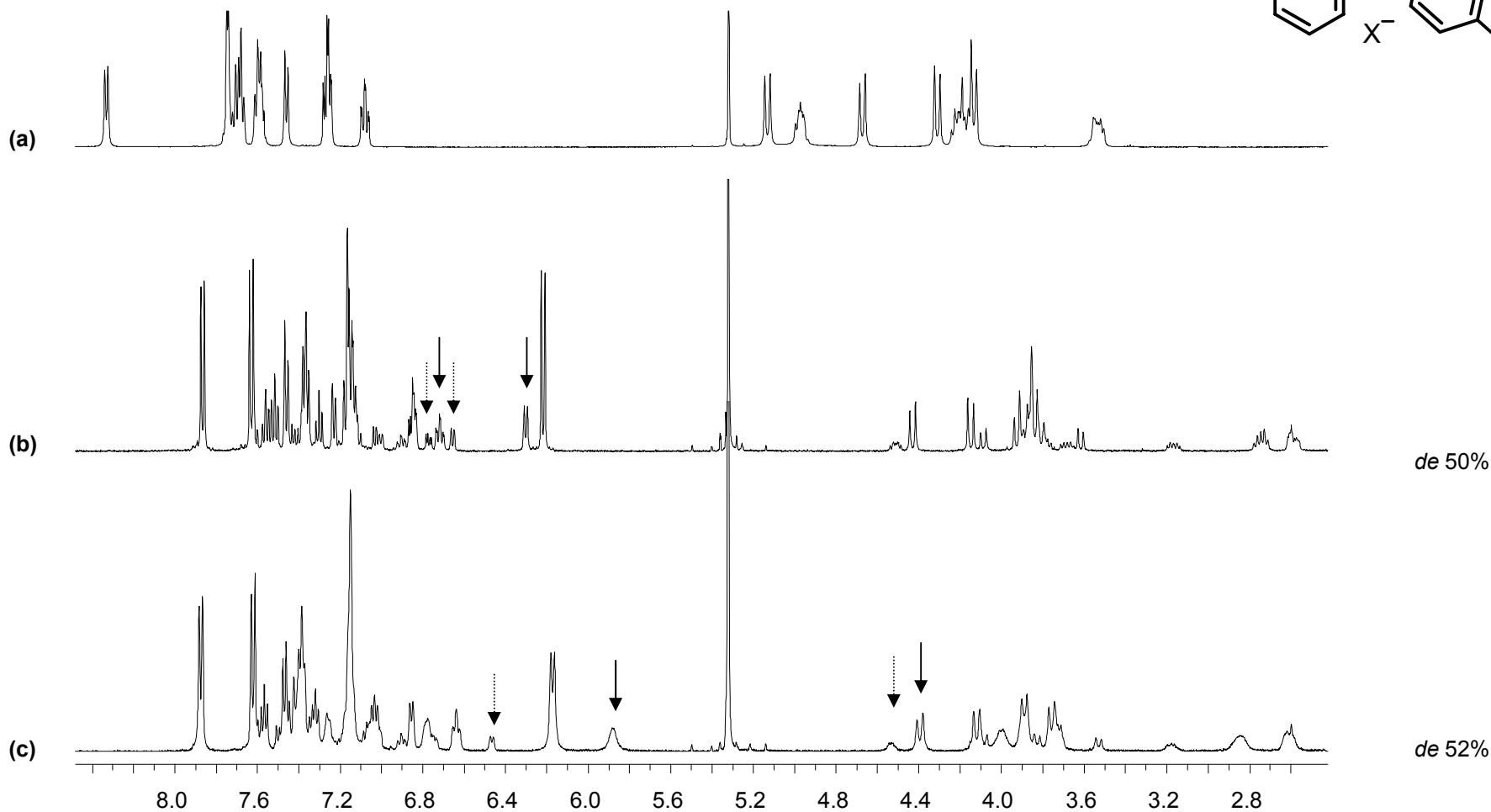
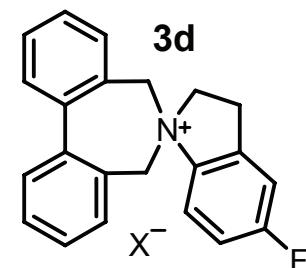
(c)



de 22%

(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

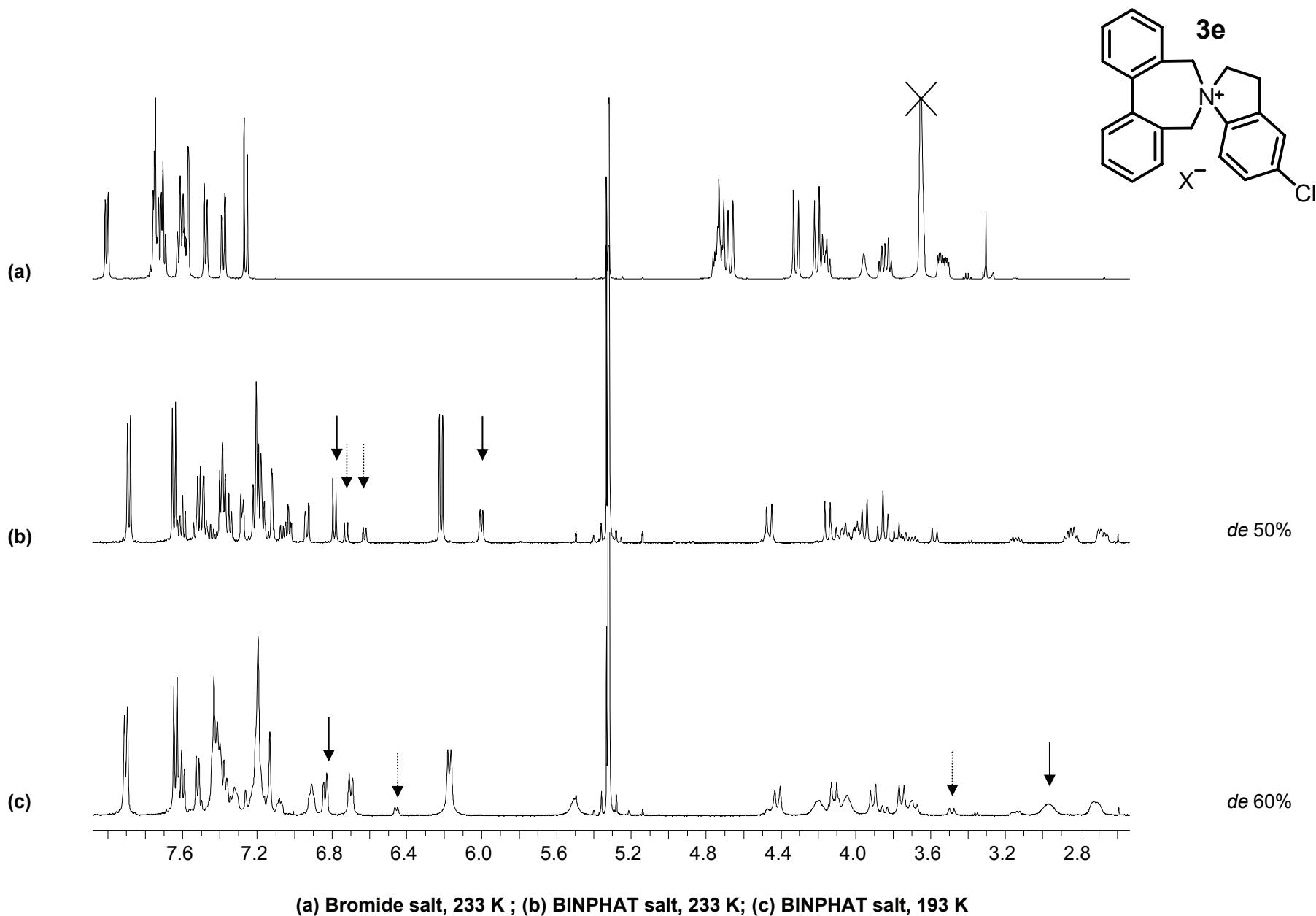
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(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

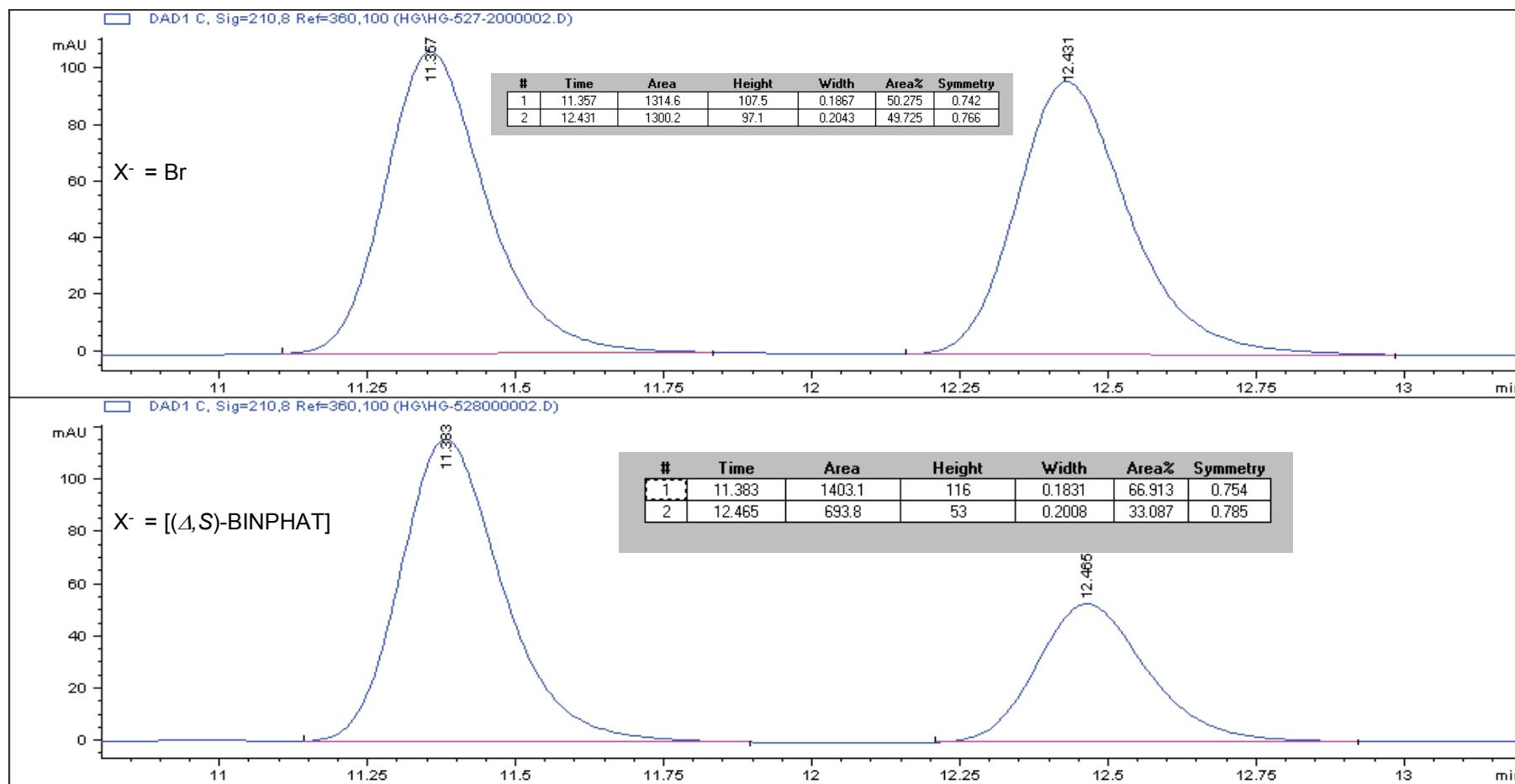
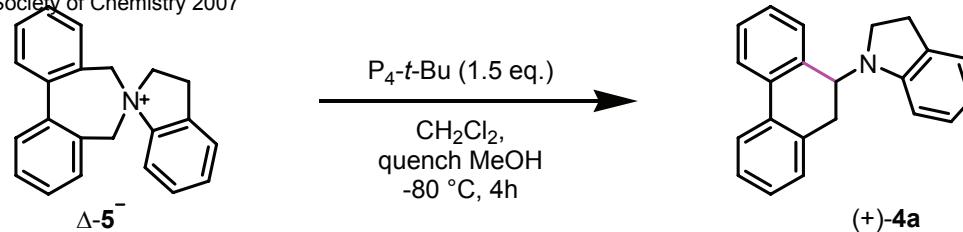
Salts of Cation **3e** ^1H NMR (500 MHz, CD_2Cl_2)

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Determination of the enantiomeric excess of (+)-4a

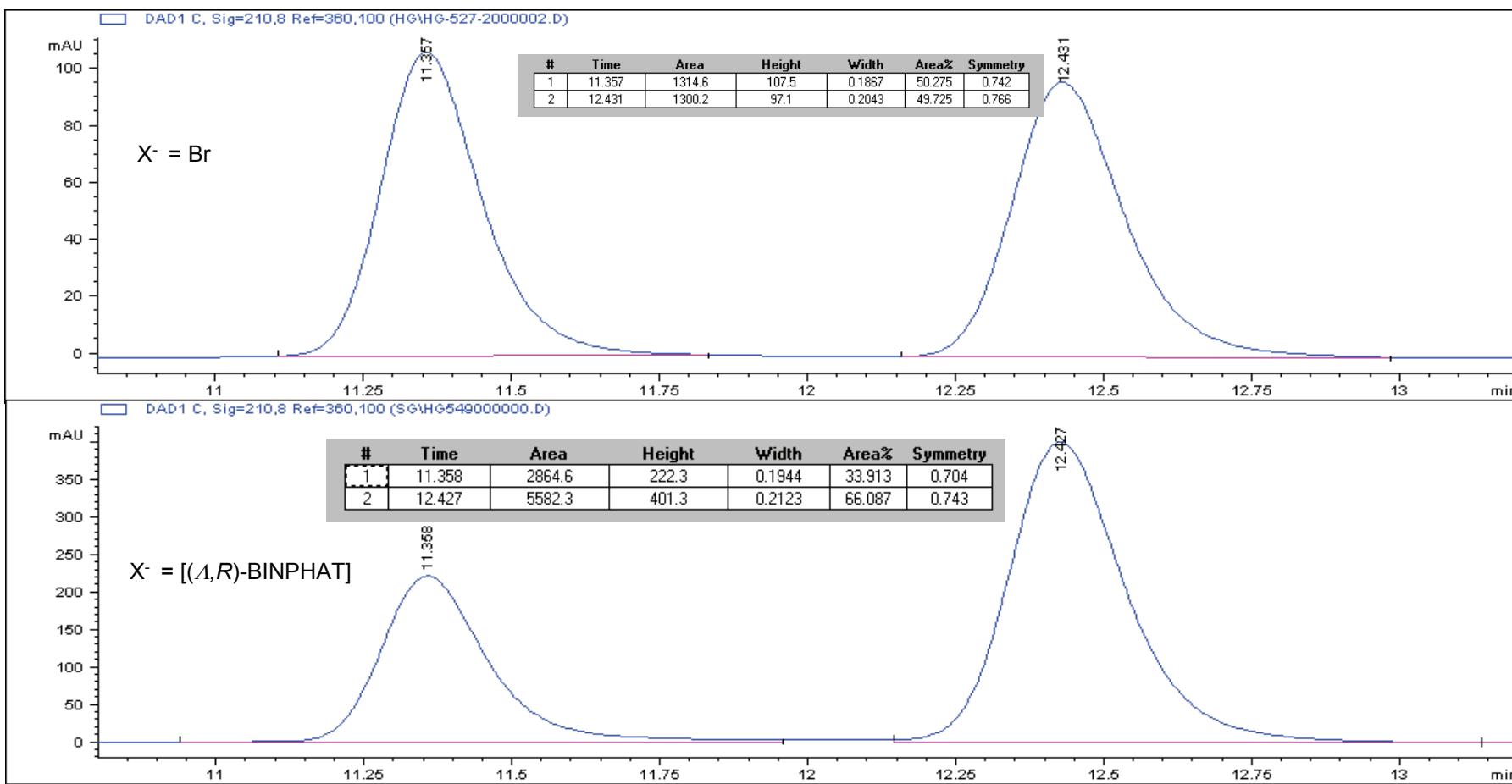
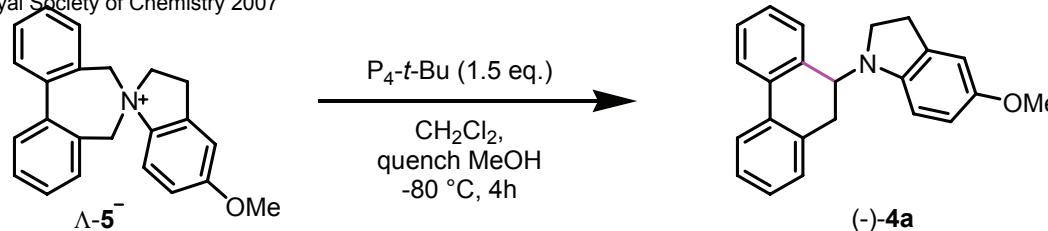
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Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanolamine 95 : 05 : 0.1%; 0.5 mL·min⁻¹; 23 °C).

Determination of the enantiomeric excess of (-)-4a

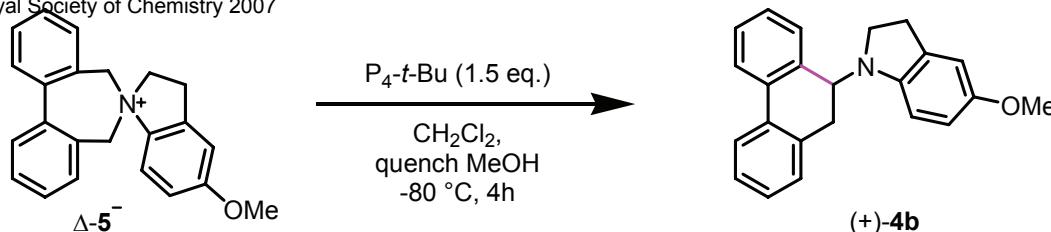
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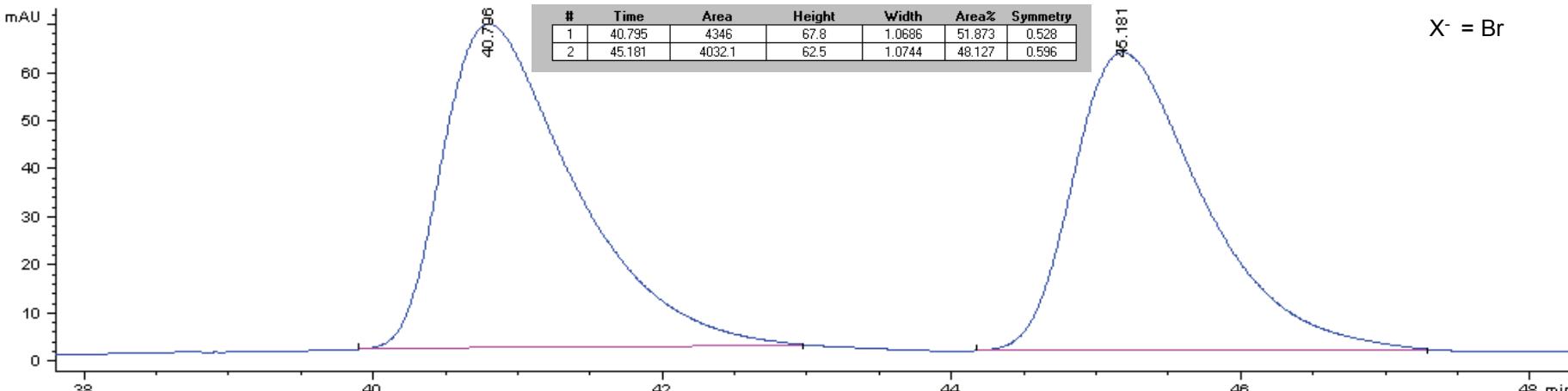
Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanolamine 95 : 05 : 0.1%; 0.5 mL.min⁻¹; 23 °C).

Determination of the enantiomeric excess of (+)-4b

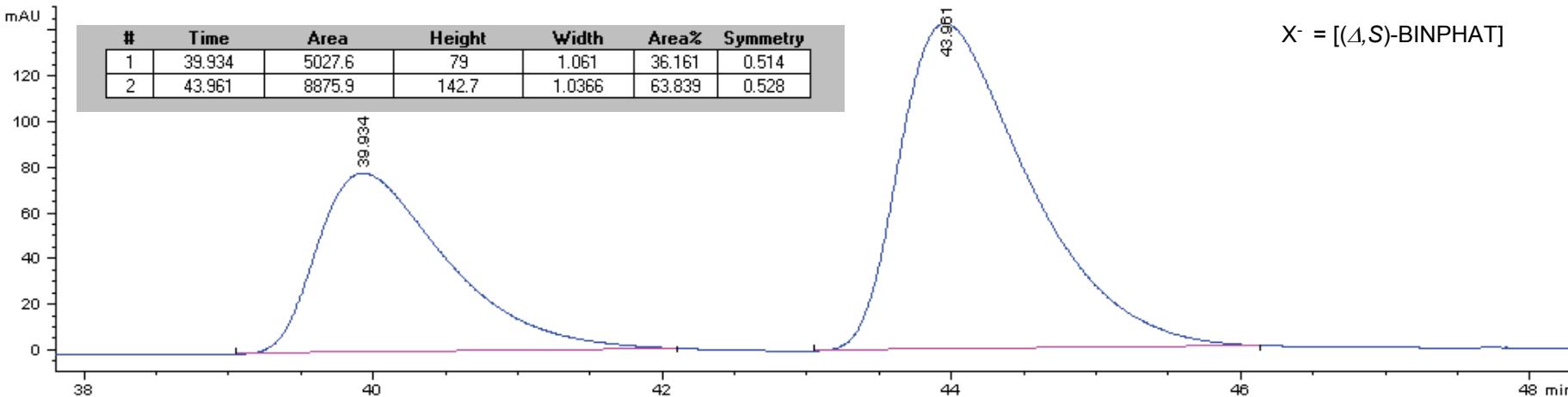
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DAD1 C, Sig=210,8 Ref=360,100 (HG\HG-512-2000001.D)



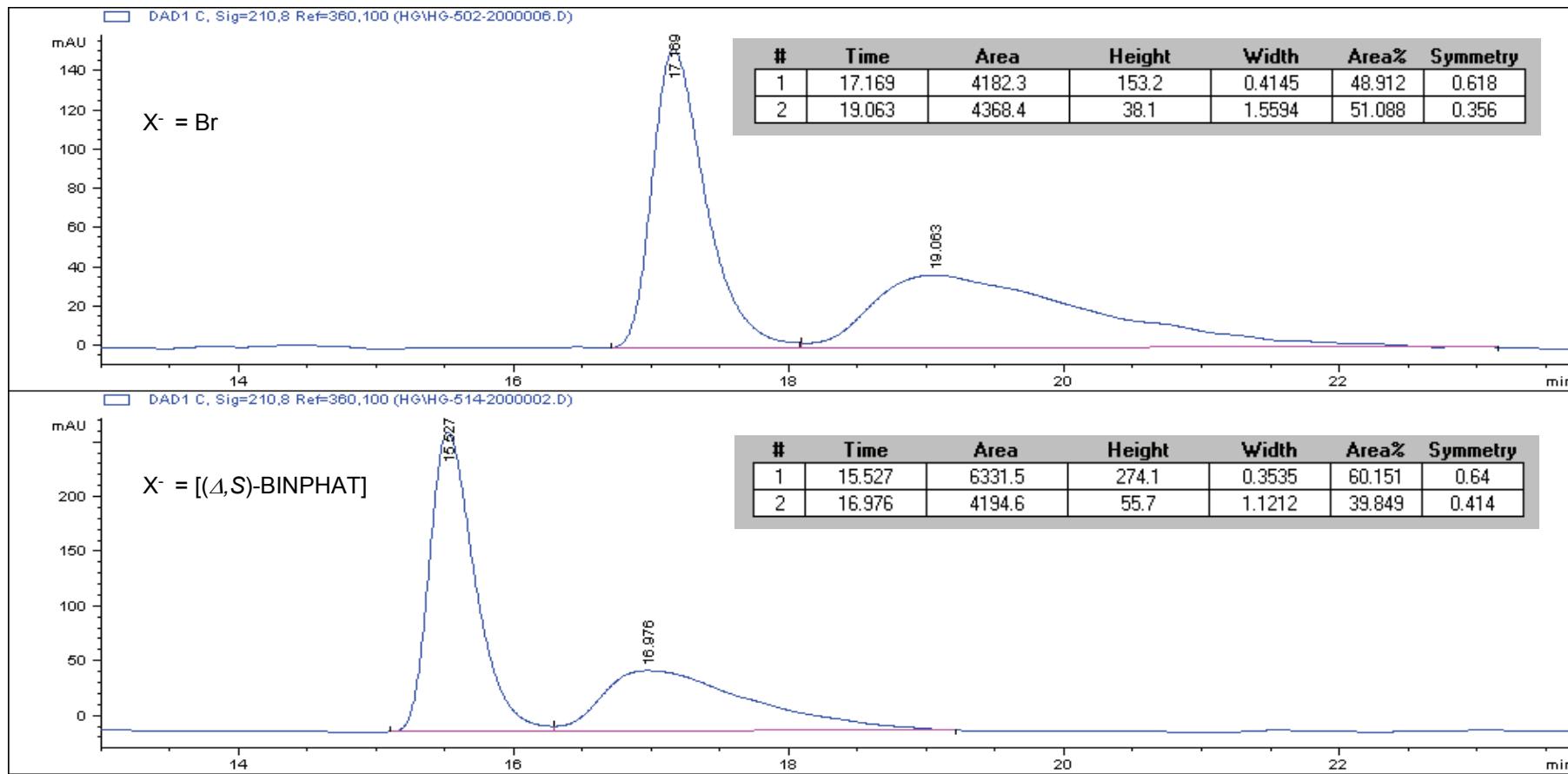
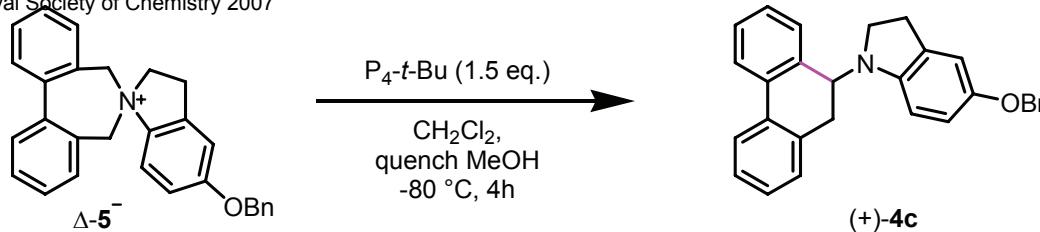
DAD1 C, Sig=210,8 Ref=360,100 (HG\HG-530-2000002.D)



Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanalamine 99.5 : 0.5 : 0.1%; 0.5 mL·min⁻¹; 23 °C).

Determination of the enantiomeric excess of (+)-4c

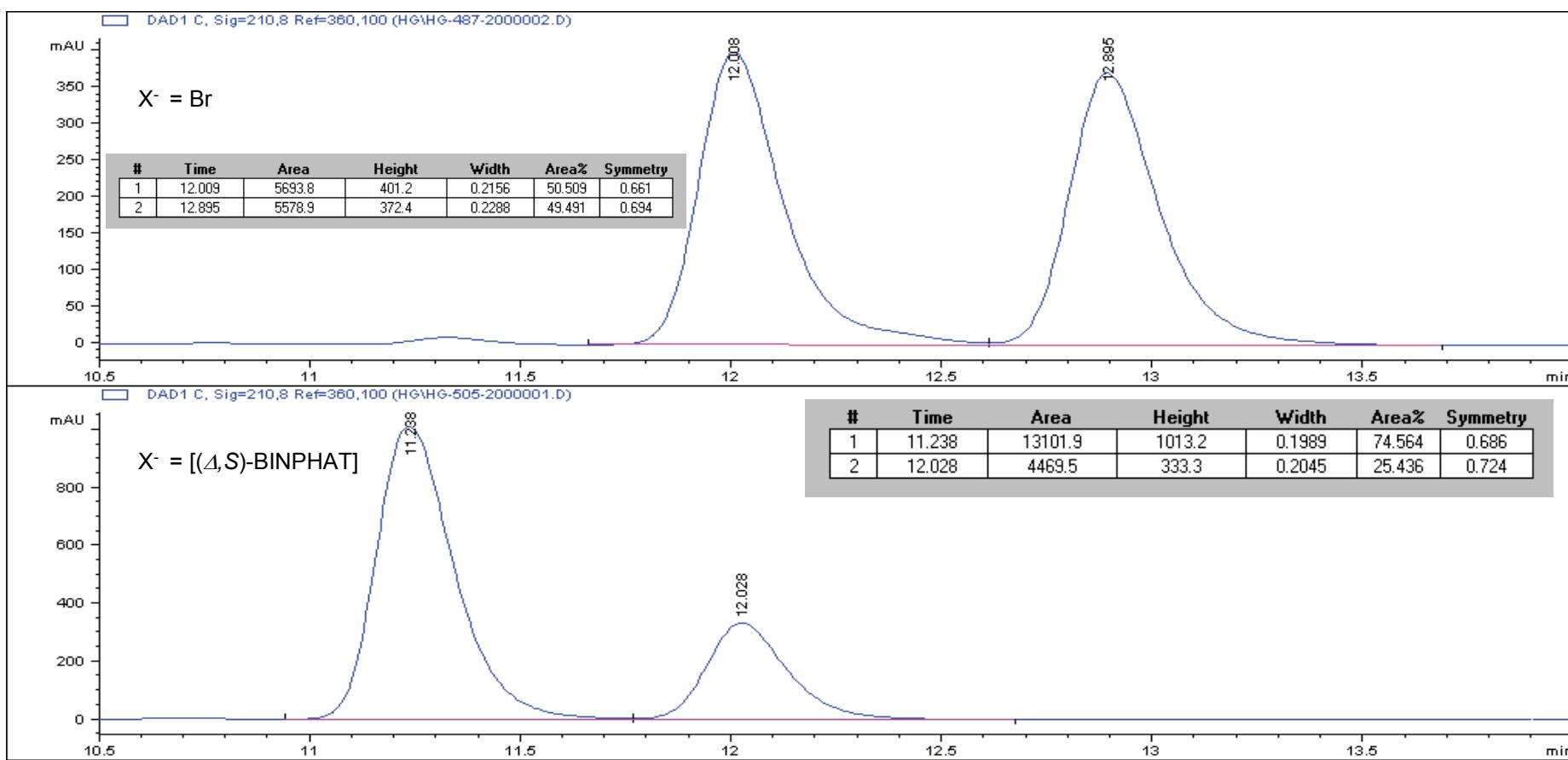
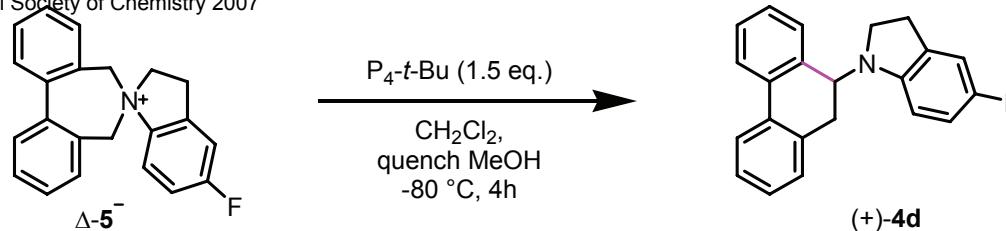
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Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanolamine 98 : 02 : 0.1%; 1.0 mL·min⁻¹; 23 °C).

Determination of the enantiomeric excess of (+)-4d

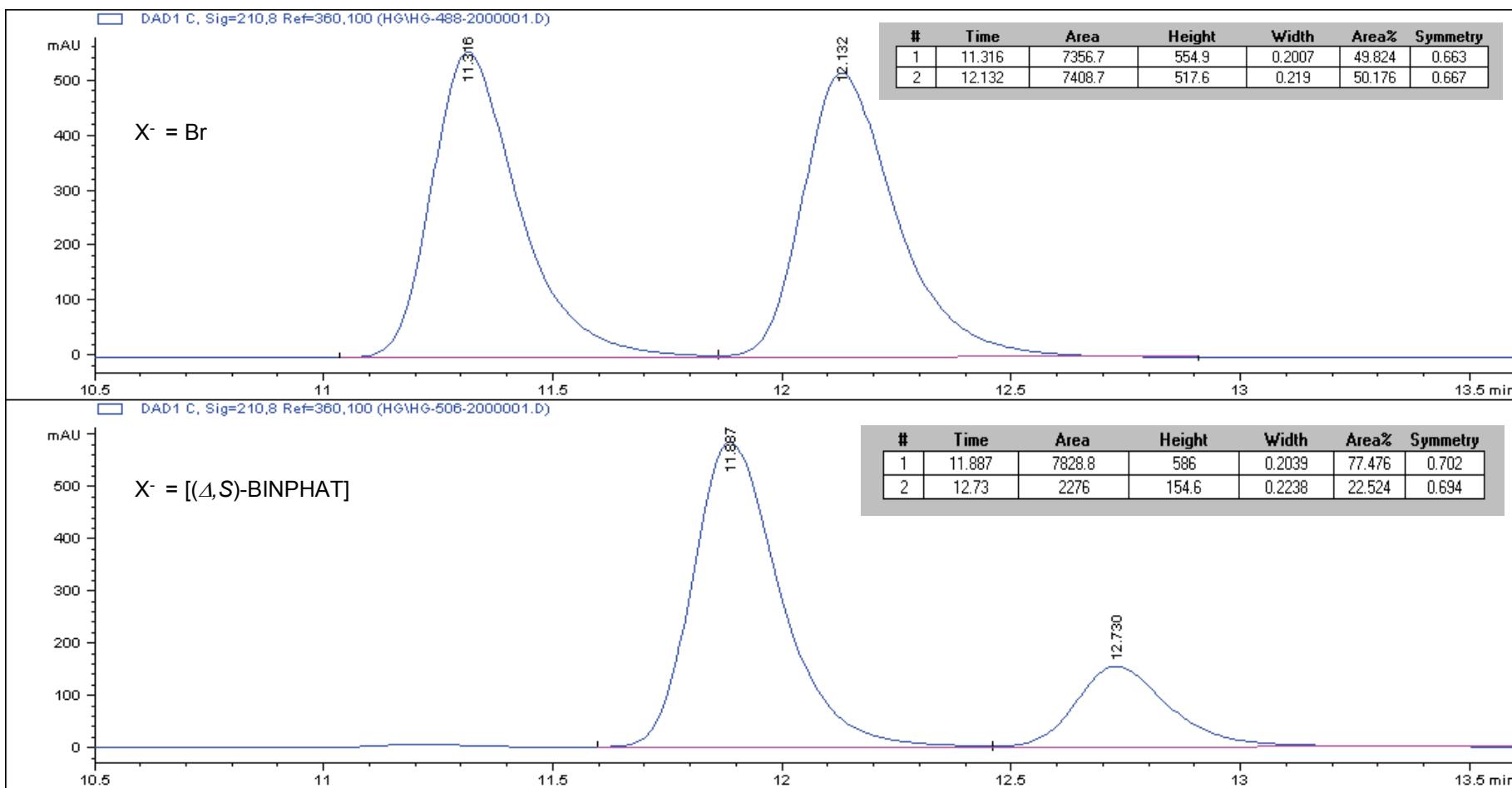
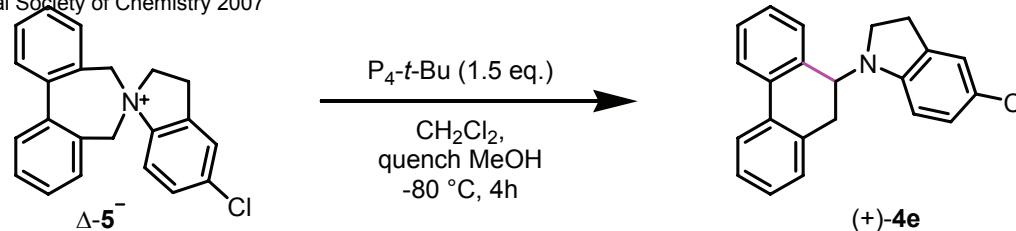
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Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanalamine 95 : 05 : 0.1%; 0.5 mL·min⁻¹; 23 °C).

Determination of the enantiomeric excess of (+)-4e

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Determined by CSP-HPLC (Chiraldak IB); *n*-Hexane / *i*-PrOH / ethanolamine 95 : 05 : 0.1%; 0.5 mL·min⁻¹; 23 °C).