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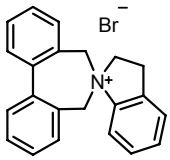
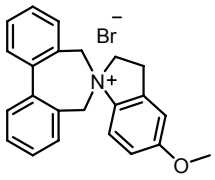
Enantioselective [1,2]-Stevens Rearrangement of Quaternary Ammonium Salts. A Mechanistic Evaluation

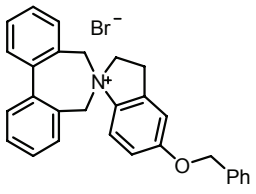
Supporting Information



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 CH_3CN (21 mL) was added K_2CO_3 (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 CH_2Cl_2 and the inorganic salts filtered. 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 CH_2Cl_2:MeOH from 99:01 to 95:05. After evaporation of the solvent, the product was dissolved in a minimum amount of CH_2Cl_2, and dropwise addition of Et_2O provided a white precipitate, which was collected by filtration and washed with Et_2O 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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_2), 64.5 (CH_2), 64.2 (CH_2), 27.2 (CH_2); **MS-ES** (+) *m/z* (rel intensity) 338.3 (23%) 323.3 (36%), 299.5 (30%), 298.5 (100%$[M]^+$); **HRMS**: Calculated for $C_{22}H_{20}N$ 298.1590, found 298.1597.

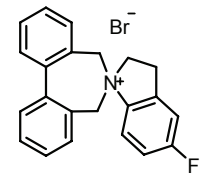


5'-methoxy-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [**3b**][Br].
To a suspension of 5-methoxyindolinium chloride salt (250 mg, 1.351 mmol, 1.0 equiv.) in CH_3CN (22 mL) was added K_2CO_3 (840 mg, 6.079 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (551 mg, 1.621 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in CH_2Cl_2: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 CH_2Cl_2:MeOH from 99:01 to 95:05. After evaporation of the solvent, the product was dissolved in a minimum amount of CH_2Cl_2:MeOH 1:1, and dropwise addition of Et_2O provided a white precipitate, which was collected by filtration and washed with Et_2O 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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_2), 64.9 (CH_2), 64.6 (CH_2), 55.9 (CH_3), 27.4 (CH_2); **MS-ES** (+) *m/z* (rel intensity) 391.5 (25%), 329.5 (29%), 328.5 (100%$[M]^+$), 323.3 (21%); **HRMS**: Calculated for $C_{23}H_{22}NO$ 328.1695, found 328.1685.

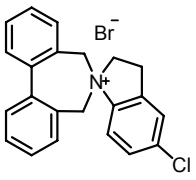


5'-(benzyloxy)-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium bromide [**3c**][Br]. To a suspension of 5-benzyloxyindolinium chloride salt (125 mg, 0.479 mmol, 1.0 equiv.) in CH_3CN (8 mL) was added K_2CO_3 (298 mg, 2.154 mmol, 4.5 equiv.) and 2,2'-bis(bromomethyl)biphenyl (195 mg, 0.574 mmol, 1.2 equiv.). The mixture was heated at 80 °C for 6h and then concentrated under reduced pressure. The residue was triturated in CH_2Cl_2: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 CH_2Cl_2:MeOH from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of CH_2Cl_2:MeOH 1:1, and dropwise addition of Et_2O provided a white precipitate, which was collected by filtration and washed with Et_2O 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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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}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 (CH_2), 67.6 (CH_2), 64.9 (CH_2), 64.6 (CH_2), 27.4 (CH_2); **MS-ES** (+) *m/z* (rel intensity) 405.5 (38%), 404.6 (100%[M]$^+$), 323.5 (28%); **HRMS**: Calculated for $C_{29}H_{26}NO$ 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 CH_2Cl_2:MeOH from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of CH_2Cl_2:MeOH 1:1, and dropwise addition of Et_2O provided a pale grey precipitate, which was collected by filtration and washed with Et_2O 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}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}C-NMR** (126 MHz, CD_2Cl_2, 233 K) δ 164.7-162.7 (d, C^{IV}, $J_{C\text{-}F}$ = 251.8 Hz), 141.4 (C^{IV}), 140.9 (C^{IV}), 140.4 (C^{IV}), 137.6 (d, C^{IV}, $J_{C\text{-}F}$ = 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, $J_{C\text{-}F}$ = 9.7 Hz), 116.2 (d, CH, $J_{C\text{-}F}$ = 24.3 Hz), 114.3 (d, CH, $J_{C\text{-}F}$ = 24.3 Hz), 67.7 (CH_2), 65.1 (CH_2), 64.7 (CH_2), 27.5 (CH_2); **^{19}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 $C_{22}H_{19}NF$ 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 CH_2Cl_2: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 CH_2Cl_2:MeOH from 99:01 to 90:10. After evaporation of the solvent, the product was dissolved in a minimum amount of CH_2Cl_2:MeOH 1:1, and dropwise addition of Et_2O provided a pale grey precipitate, which was collected by filtration and washed with Et_2O 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}H-NMR** (500 MHz, CD_2Cl_2+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}C-NMR** (126 MHz, CD_2Cl_2+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 (CH_2), 64.8 (CH_2), 64.7 (CH_2), 27.0 (CH_2); **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 $C_{22}H_{19}NCl$ 332.1200, found 332.1207.

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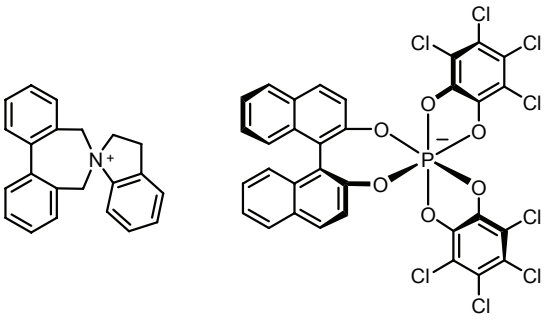
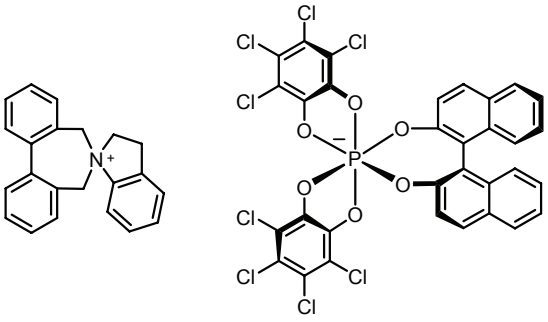
General Procedure for the synthesis of the diphenylazepinium BINPHAT salts [**3a**][*Δ*-**5**] to [**3e**][*Δ*-**5**] and [**3a**][*Λ*-**5**]

To a solution of diphenylazepinium (1.0 equiv.) in CH_2Cl_2 or in CH_2Cl_2:MeOH 1:1 (3.4 mL per 0.1 mmol of substrate) was added a solution of salt [Me_2NH_2][(*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 CH_2Cl_2 as eluent.



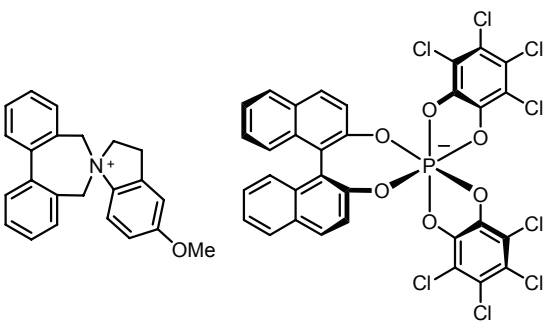
5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium [*Δ*-bis(tetrachloro-benzenediolato)mono((*S*)-1,1'-dinaphthyl-2,2'-diolato)phosphate] - [**3a**][*Δ*-**5**]

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, CH_2Cl_2); **IR** (neat): 1593, 1453, 1389, 1236, 993, 953, 820, 783, 752, 730, 698, 671 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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*); **^{31}P-NMR** (203 MHz, CD_2Cl_2, 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 $C_{22}H_{20}N$ 298.1590, found 298.1589 and calculated for $C_{32}H_{12}O_6PCl_8$ 802.7885, found 802.7901.



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

Starting from 40 mg (0.0.106 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, CH_2Cl_2).



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, CH_2Cl_2); **IR** (neat): 2926, 1723, 1594, 1488, 1451, 1388, 1269, 1230, 992, 953, 817, 781, 752, 731 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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*); **^{31}P-NMR** (203 MHz, CD_2Cl_2, 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 $C_{23}H_{22}NO$ 328.1695, found 328.1680 and calculated for $C_{32}H_{12}O_6PCl_8$ 802.7885, found 802.7918.

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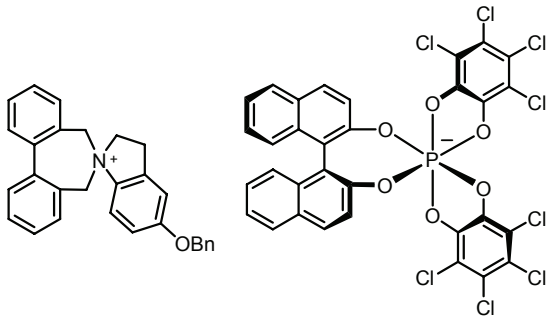
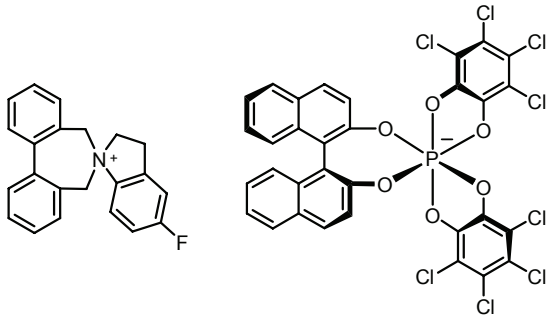


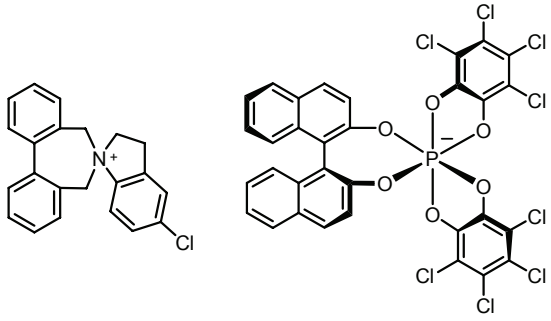
5'-(benzyloxy)-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium][*Δ*-bis(tetrachlorobenzenediolato)mono((*S*)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [**3c**][*Δ*-**5**]

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); **$[\alpha]_D^{20}$** –105.9 (*c* 0.1, CH_2Cl_2); **IR** (neat): 2925, 1739, 1594, 1485, 1451, 1388, 1236, 992, 953, 819, 782, 752, 732 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 233 K, Major *(Maj)* or minor *(min)* enantiomers of the cation) δ 7.78 (d, 2H, BT, *J* = 8.2 Hz), 7.61-7.28 (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*); **^{31}P-NMR** (203 MHz, CD_2Cl_2, 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 $C_{29}H_{26}NO$ 404.2008, found 404.2010 and calculated for $C_{32}H_{12}O_6PCl_8$ 802.7885, found 802.7884.



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); **$[\alpha]_D^{20}$** –122.7 (*c* 0.1, CH_2Cl_2); **IR** (neat): 2925, 1738, 1593, 1483, 1452, 1389, 1236, 992, 953, 818, 782, 751, 731 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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*), 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*); **^{31}P-NMR** (203 MHz, CD_2Cl_2, 233 K) δ–83.8; **^{19}F-NMR** (352 MHz, CD_2Cl_2, 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 $C_{22}H_{19}NF$ 316.1496, found 316.1500 and calculated for $C_{32}H_{12}O_6PCl_8$ 802.7885, found 802.7909.



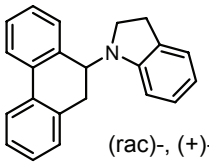
5'-chloro-5,7-dihydrospiro[dibenzo[c,e]azepine-6,1'-indolin]-1'-ium][*Δ*-bis(tetrachlorobenzenediolato)mono((*S*)-1,1'-dinaphthyl-2,2'-diolato)phosphate] or [**3e**][*Δ*-**5**]

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); **$[\alpha]_D^{20}$** –144.0 (*c* 0.1, CH_2Cl_2); **IR** (neat): 3052, 1591, 1450, 1388, 1236, 992, 952, 817, 781, 751, 726 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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*); **^{31}P-NMR** (203 MHz, CD_2Cl_2, 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 $C_{22}H_{19}NCl$ 332.1200, found 332.1207 and calculated for $C_{32}H_{12}O_6PCl_8$ 802.7885, found 802.7883.

Typical procedure for the Stevens rearrangement:

To a solution of the required ammonium salt (1.0 equiv.) in dry CH_2Cl_2 (0.5 mL per 0.01 mmol of substrate) at -80 °C was added the P_4-*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 CH_2Cl_2 and the precipitate upon addition of Et_2O filtered. The mother liquors were concentrated in vaccuo and the resulting compound was purified by column chromatography or preparative plate chromatography over basic alumina.

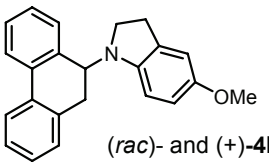


(rac)-, (+)- and (-)-**4a**

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**][*Λ*-**5**] ammonium salts, the desired compound **4a** was obtained after purification by column chromatography (basic alumina, Et_2O) as (*rac*)-**4a** (92%), (+)-**4a** (90%) and (–)-**4a** (88%) 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.** 131 °C; **IR** (neat): 3067, 2925, 2847, 1606, 1490, 1474, 1450, 1260, 769, 743, 728, 712 cm^{-1}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_2), 31.6 (CH_2), 28.8 (CH_2); **MS-LR** (EI) *m/z* (rel intensity) 297 (27%[M]$^+$), 179 (50%[$MC_{14}H_{11}$]), 119 (100%[MC_8H_8N+1]), **MS-ES** (+) *m/z* (rel intensity) 298.5 (27%[M+1]), 179.4 (100%[$MC_{14}H_{11}$]); **HRMS**: Calculated for $C_{22}H_{20}N$ 298.1590, found 298.1590.

(+)-**4a: $[\alpha]_D^{20}$** +23.8 (*c* 0.1, CH_2Cl_2).

(–)-**4a: $[\alpha]_D^{20}$** –23.6 (*c* 0.1, CH_2Cl_2).

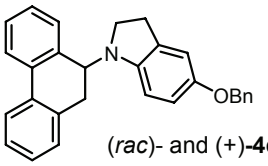


(*rac*)- and (+)-**4b**

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 /Et_2O from 10 to 20%) as (*rac*)-**4b** (53%) and (+)-**4b** (52%) respectively. The enantiomeric excess was measured using a CSP-HPLC (Chiralpak 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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_3), 54.7 (CH), 49.2 (CH_2), 31.0 (CH_2), 29.1 (CH_2); **MS-LR** (EI) *m/z* (rel intensity) 327 (36%[M]$^+$), 179 (44%[$MC_{14}H_{11}$]), 149 (100%[$MC_9H_{10}NO$+1]), 134 (59%), **MS-ES** (+) *m/z* (rel intensity) 328.4 (36%[M+1]), 179.4 (100%[$MC_{14}H_{11}$]); **HRMS**: Calculated for $C_{23}H_{22}NO$ 328.1695, found 328.1702.

(+)-**4b: $[\alpha]_D^{20}$** +17.6 (*c* 0.1, CH_2Cl_2).

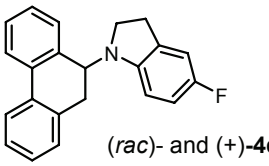
M.-H. Gonçalves-Farbos,
L.Vial and J. Lacour*



(*rac*)- and (+)-**4c**

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 /Et_2O 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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_2), 49.1 (CH_2), 31.0 (CH_2), 29.1 (CH_2); **MS-LR** (EI) *m/z* (rel intensity) 403 (15%[$M]^+$), 179 (53%[$MC_{14}H_{11}$]), 134 (100%), **MS-ES** (+) *m/z* (rel intensity) 404.5 (15%([M+1]), 226.5 (52%[$C_{15}H_{14}NO$+2), 179.3 (100%[$MC_{14}H_{11}$]); **HRMS**: Calculated for $C_{29}H_{26}NO$ 404.2008, found 404.2004.

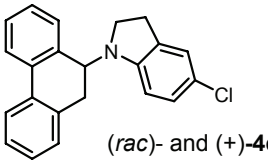
(+)-**4c: $[\alpha]_D^{20}$** +18.2 (*c* 0.1, CH_2Cl_2).



(*rac*)- and (+)-**4d**

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 /Et_2O 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, 1229, 1131, 863, 792, 766, 751, 742, 727 cm^{-1}; **H-NMR** (500 MHz, CD_2Cl_2, 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, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}F}$ = 8.5 Hz), 6.70 (td, 1H, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}F}$ = 8.5 Hz), 6.33 (dd, 1H, $J_{H\text{-}F}$ = 4.4 Hz, $J_{H\text{-}H}$ = 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 293 K) δ 157.2-155.4 (d, C^{IV}, $J_{C\text{-}F}$ = 233.0 Hz), 147.7 (C^{IV}), 136.0 (2C^{IV}), 135.1 (C^{IV}), 134.0 (C^{IV}), 132.1 (d, C^{IV}, $J_{C\text{-}F}$ = 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, $J_{C\text{-}F}$ = 23.0 Hz), 112.6-112.4 (d, CH, $J_{C\text{-}F}$ = 23.0 Hz), 107.2-107.1 (d, CH, $J_{C\text{-}F}$ = 8.0 Hz), 54.5 (CH), 49.1 (CH_2), 31.2 (CH_2), 28.8 (CH_2); **^{19}F-NMR** (212 MHz, CD_2Cl_2, 293 K) δ –128.8; **MS-LR** (EI) *m/z* (rel intensity) 315 (20%[$M]^+$), 179 (61%[$MC_{14}H_{11}$]), 137 (100%[MC_8H_7FN+1]), **MS-ES** (+) *m/z* (rel intensity) 316.4 (20%([M+1]), 179.1 (100%[$MC_{14}H_{11}$]); **HRMS**: Calculated for $C_{22}H_{19}NF$ 316.1496, found 316.1498.

(+)-**4d: $[\alpha]_D^{20}$** +27.9 (*c* 0.1, CH_2Cl_2).



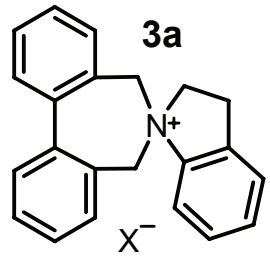
(*rac*)- and (+)-**4e**

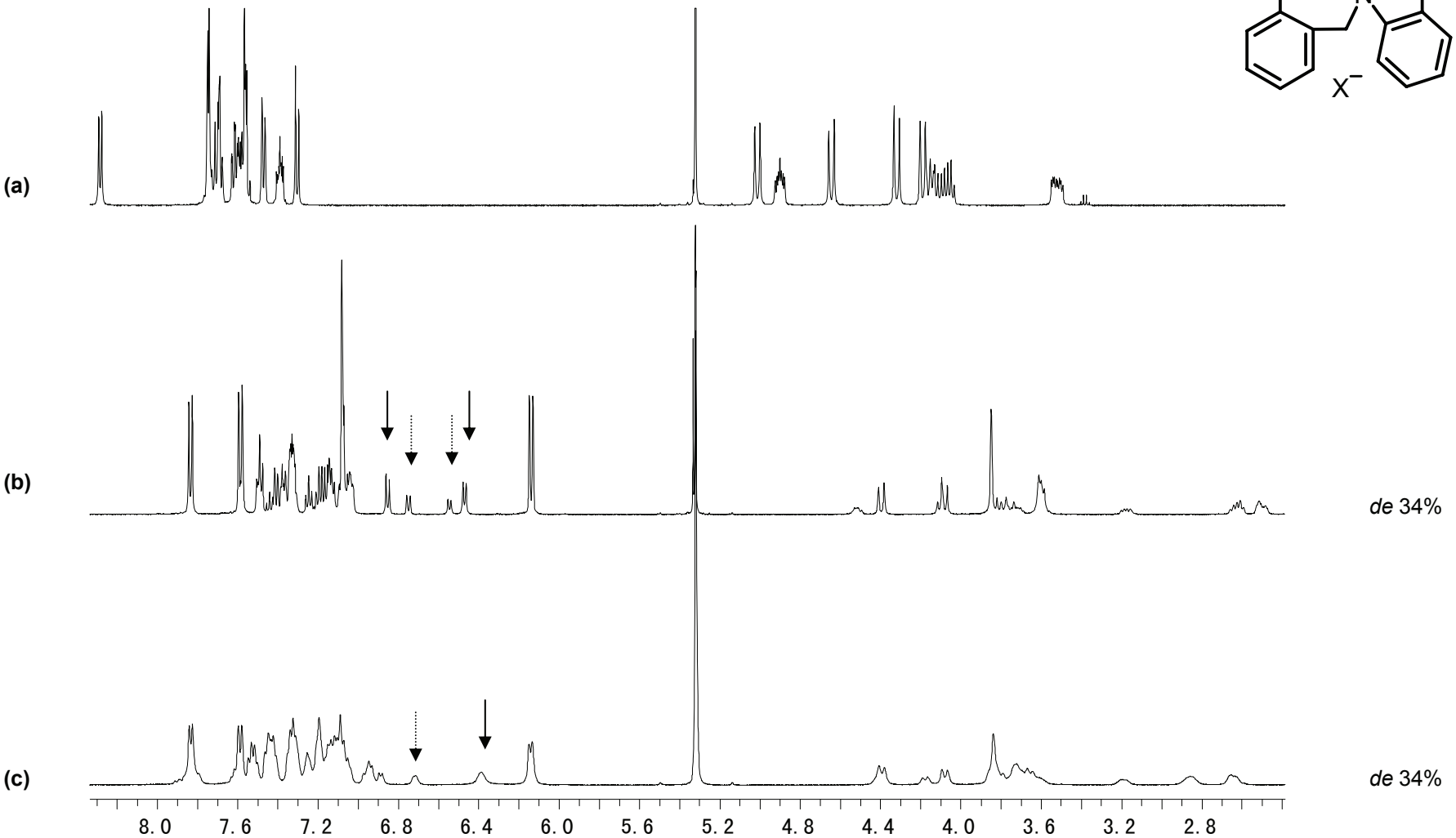
5-chloro-1-(9,10-dihydrophenanthren-10-yl)indoline 4e. Starting from 35 mg (0.085 mmol) of [**3e**][Br] or 50 mg (0.044 mmol) of [**3e**][(*Δ*)-**5**] ammonium salts, the desired compound **4e** was obtained after purification by column chromatography (basic alumina, cyclohexane /Et_2O 99:01) as (*rac*)-**4e** (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}; **^{1}H-NMR** (500 MHz, CD_2Cl_2, 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); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 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 (CH_2), 31.8 (CH_2), 28.7 (CH_2); **MS-LR** (EI) *m/z* (rel intensity) 331 (21%[$M]^+$), 179 (83%[$MC_{14}H_{11}$]), 153 (100%[MC_8H_7ClN+1]), **MS-ES** (+) *m/z* (rel intensity) 332.5 (21%[M+1]), 179.4 (100%[$MC_{14}H_{11}$]), 154.3 (46%[MC_8H_7ClN+1]); **HRMS**: Calculated for $C_{22}H_{19}NCl$ 332.1200, found 332.1216.

(+)-**4e: $[\alpha]_D^{20}$** +20.5 (*c* 0.1, CH_2Cl_2).

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

Supplementary Material (ESI) for Chemical Communications

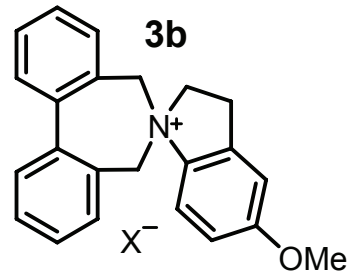


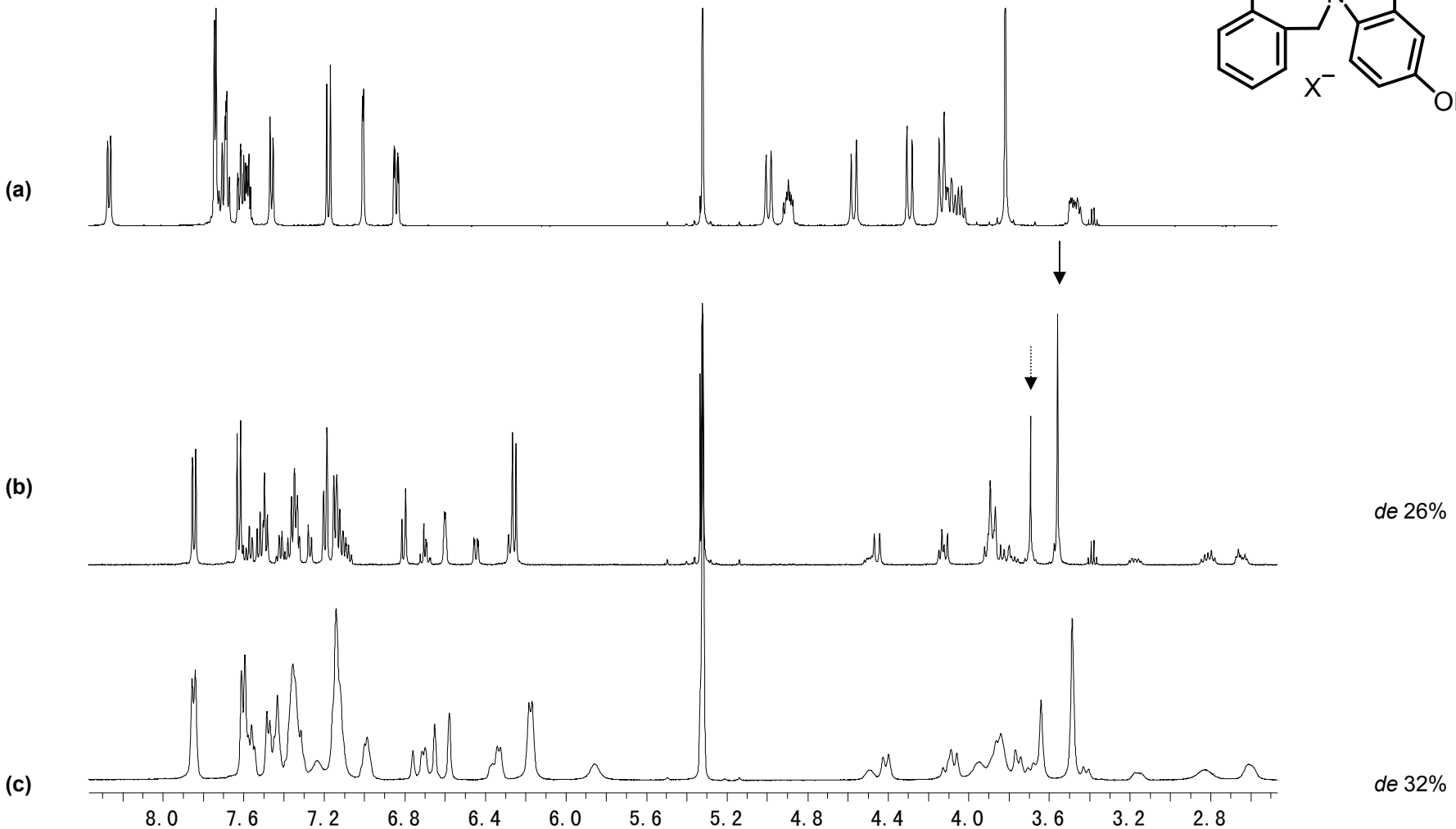


(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

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

Supplementary Material (ESI) for Chemical Communications

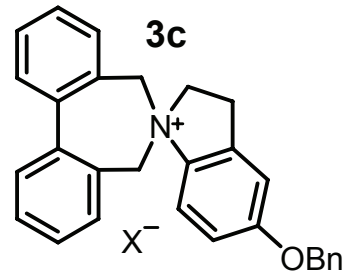


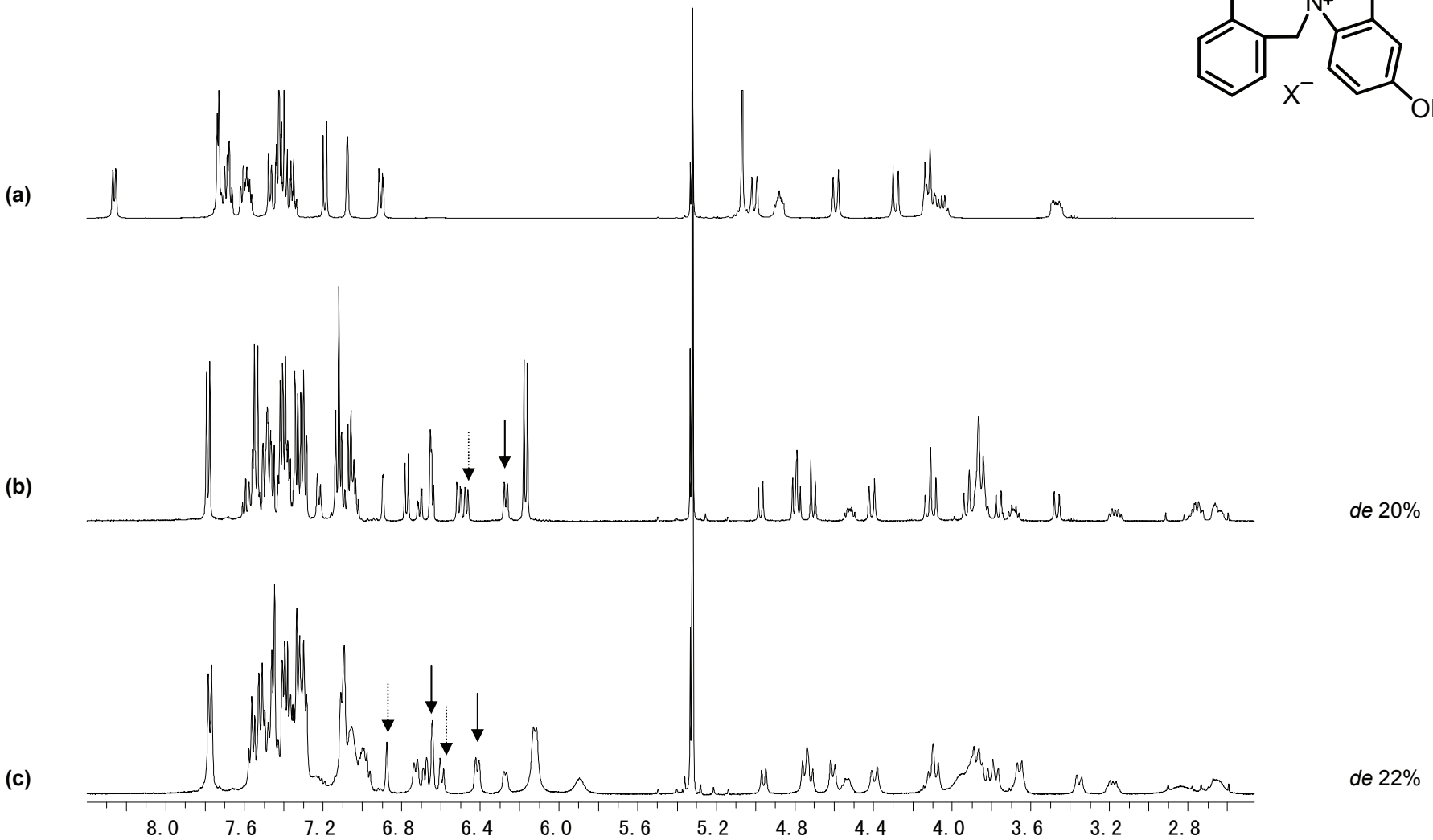


(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

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

Supplementary Material (ESI) for Chemical Communications

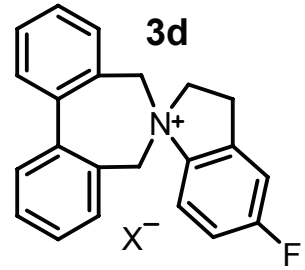


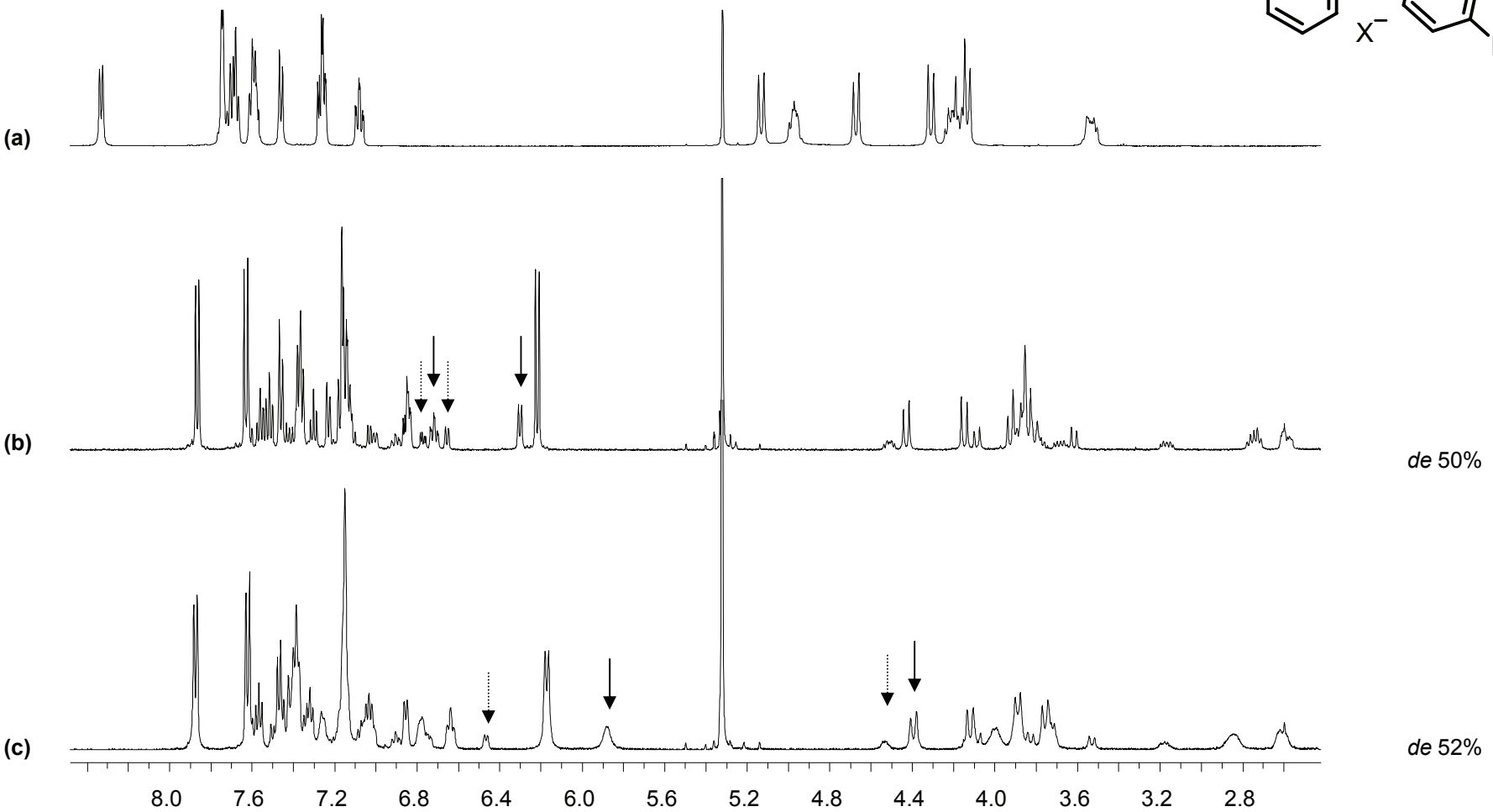


(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

Salts of Cation **3d** ^{1}H NMR (500 MHz, CD_2Cl_2)

Supplementary Material (ESI) for Chemical Communications

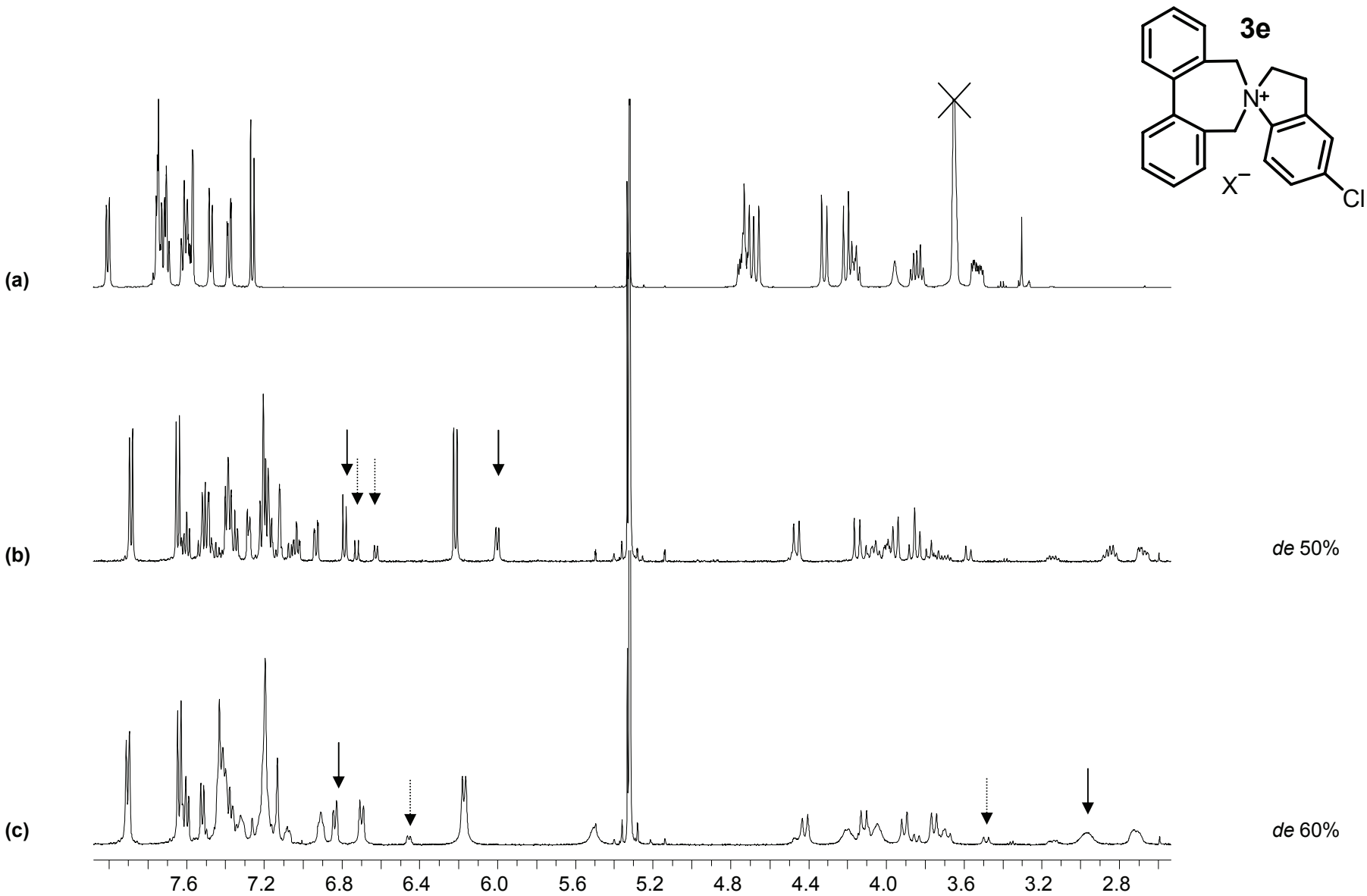




(a) Bromide salt, 233 K ; (b) BINPHAT salt, 233 K; (c) BINPHAT salt, 193 K

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

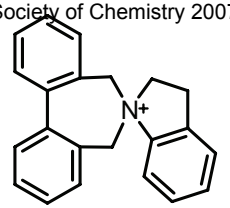
Supplementary Material (ESI) for Chemical Communications



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

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

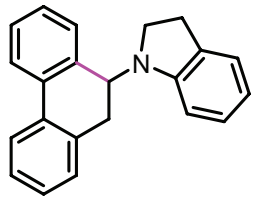
Supplementary Material (ESI) for Chemical Communications



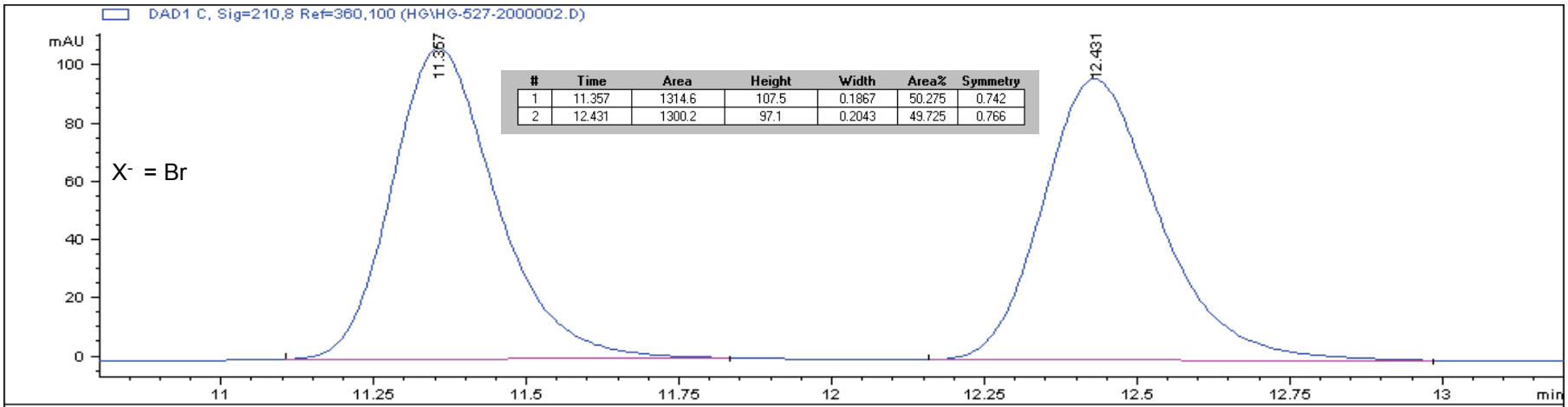
Δ-**5**$^-$

P_4-*t*-Bu (1.5 eq.)

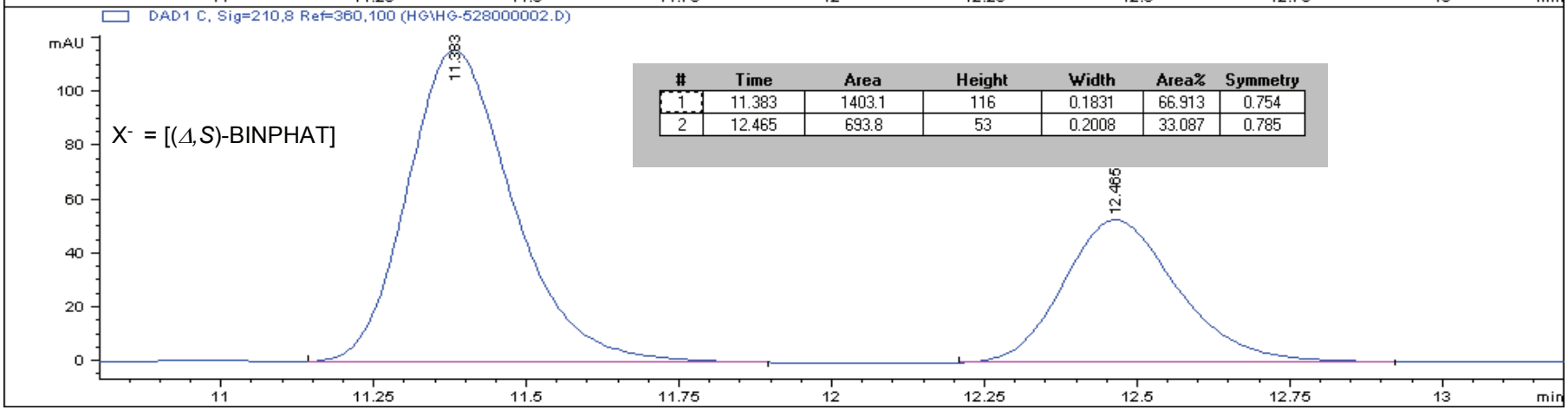
CH_2Cl_2,
quench MeOH
-80 °C, 4h



(+)-**4a**



#	Time	Area	Height	Width	Area%	Symmetry
1	11.357	1314.6	107.5	0.1867	50.275	0.742
2	12.431	1300.2	97.1	0.2043	49.725	0.766

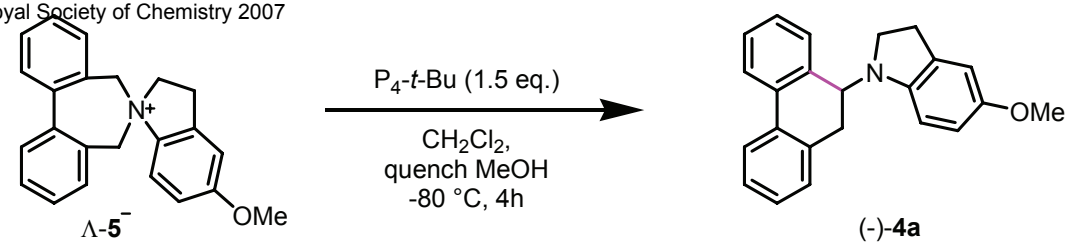


#	Time	Area	Height	Width	Area%	Symmetry
1	11.383	1403.1	116	0.1831	66.913	0.754
2	12.465	693.8	53	0.2008	33.087	0.785

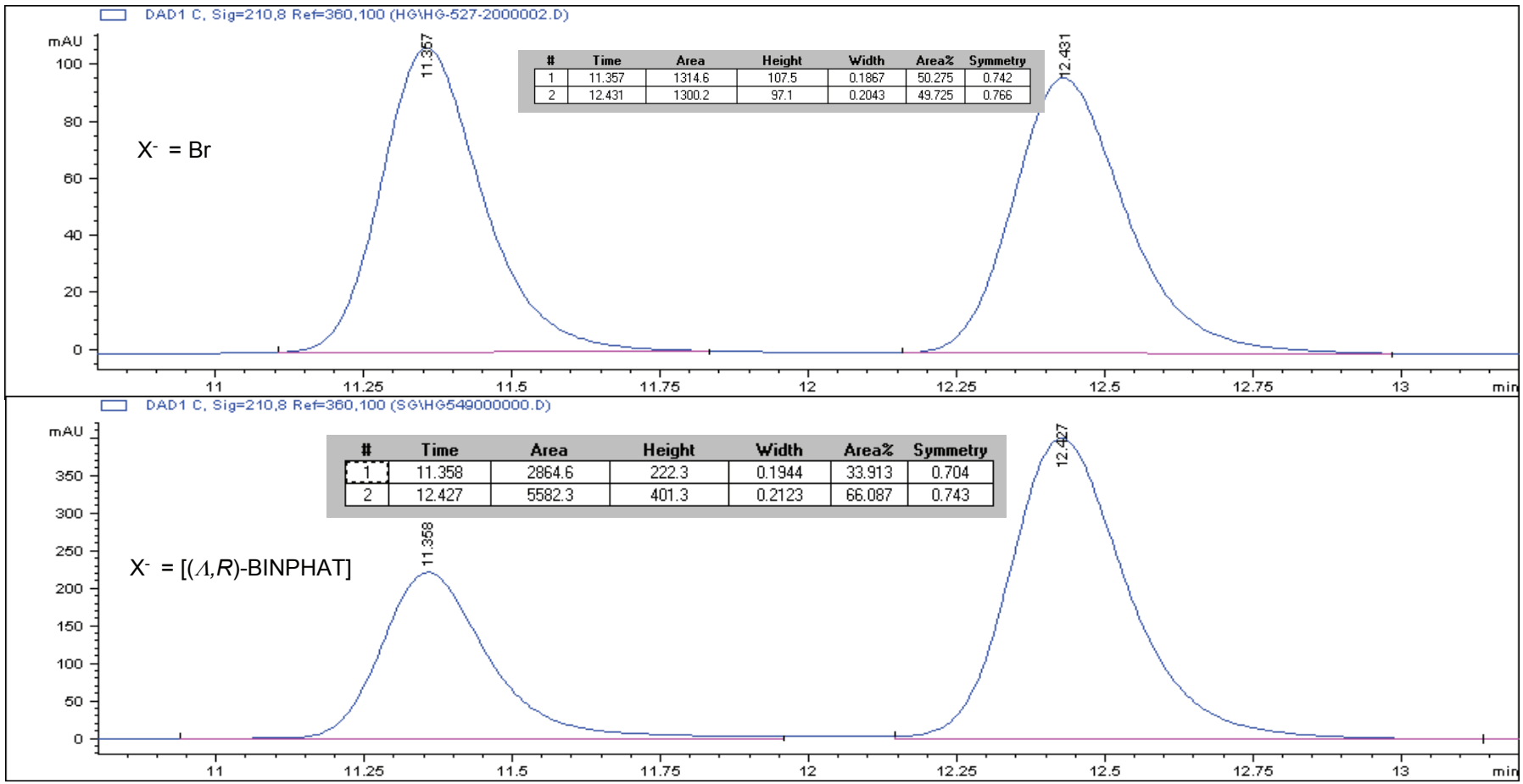
Determined by CSP-HPLC (Chiralpak IB); *n*-Hexane / *i*-PrOH / ethanolamine 95 : 05 : 0.1%; 0.5 mL.min^{-1}; 23 °C).

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

Supplementary Material (ESI) for Chemical Communications



Λ-**5**$^-$ (-)-**4a**



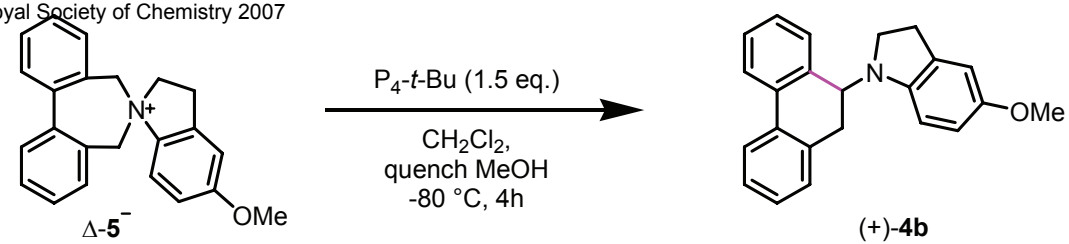
#	Time	Area	Height	Width	Area%	Symmetry
1	11.357	1314.6	107.5	0.1867	50.275	0.742
2	12.431	1300.2	97.1	0.2043	49.725	0.766

#	Time	Area	Height	Width	Area%	Symmetry
1	11.358	2864.6	222.3	0.1944	33.913	0.704
2	12.427	5582.3	401.3	0.2123	66.087	0.743

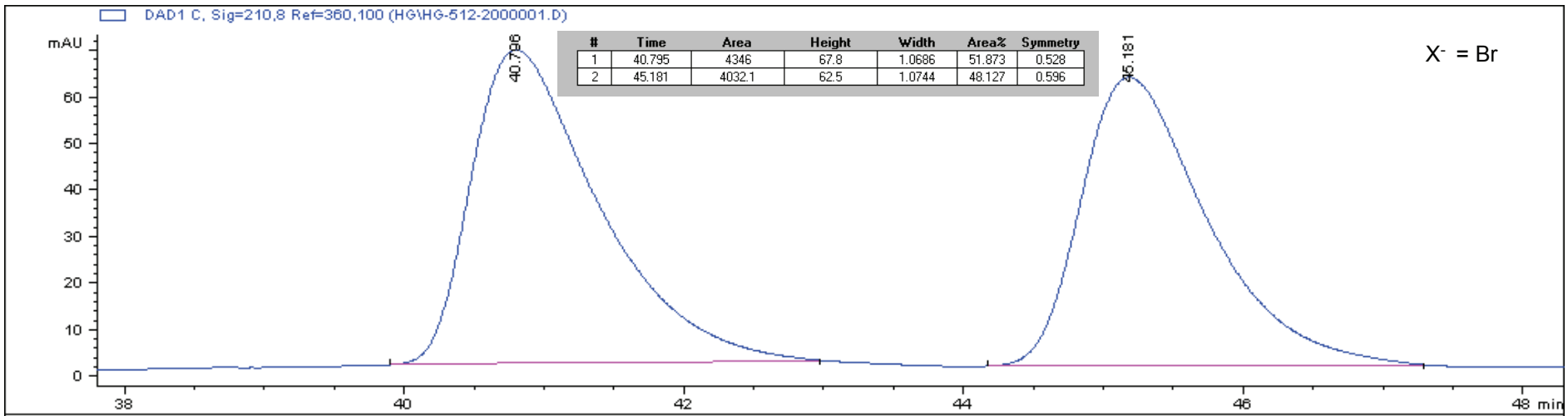
Determined by CSP-HPLC (Chiralpak IB); *n*-Hexane / *i*-PrOH / ethanolamine 95 : 05 : 0.1%; 0.5 mL.min^{-1}; 23 °C).

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

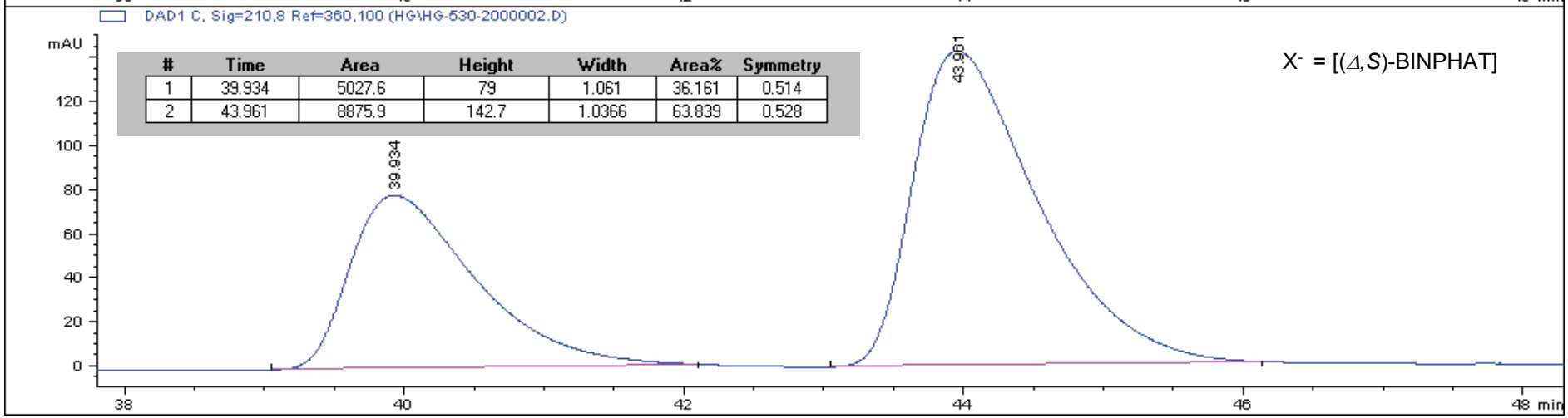
Supplementary Material (ESI) for Chemical Communications



Δ-**5**$^-$ (+)-**4b**



#	Time	Area	Height	Width	Area%	Symmetry
1	40.795	4346	67.8	1.0686	51.873	0.528
2	45.181	4032.1	62.5	1.0744	48.127	0.596

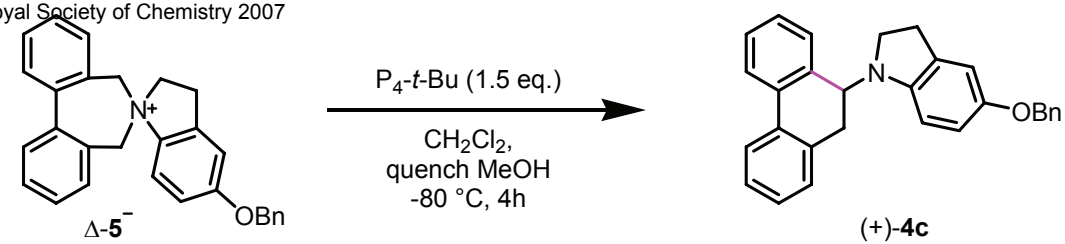


#	Time	Area	Height	Width	Area%	Symmetry
1	39.934	5027.6	79	1.061	36.161	0.514
2	43.961	8875.9	142.7	1.0366	63.839	0.528

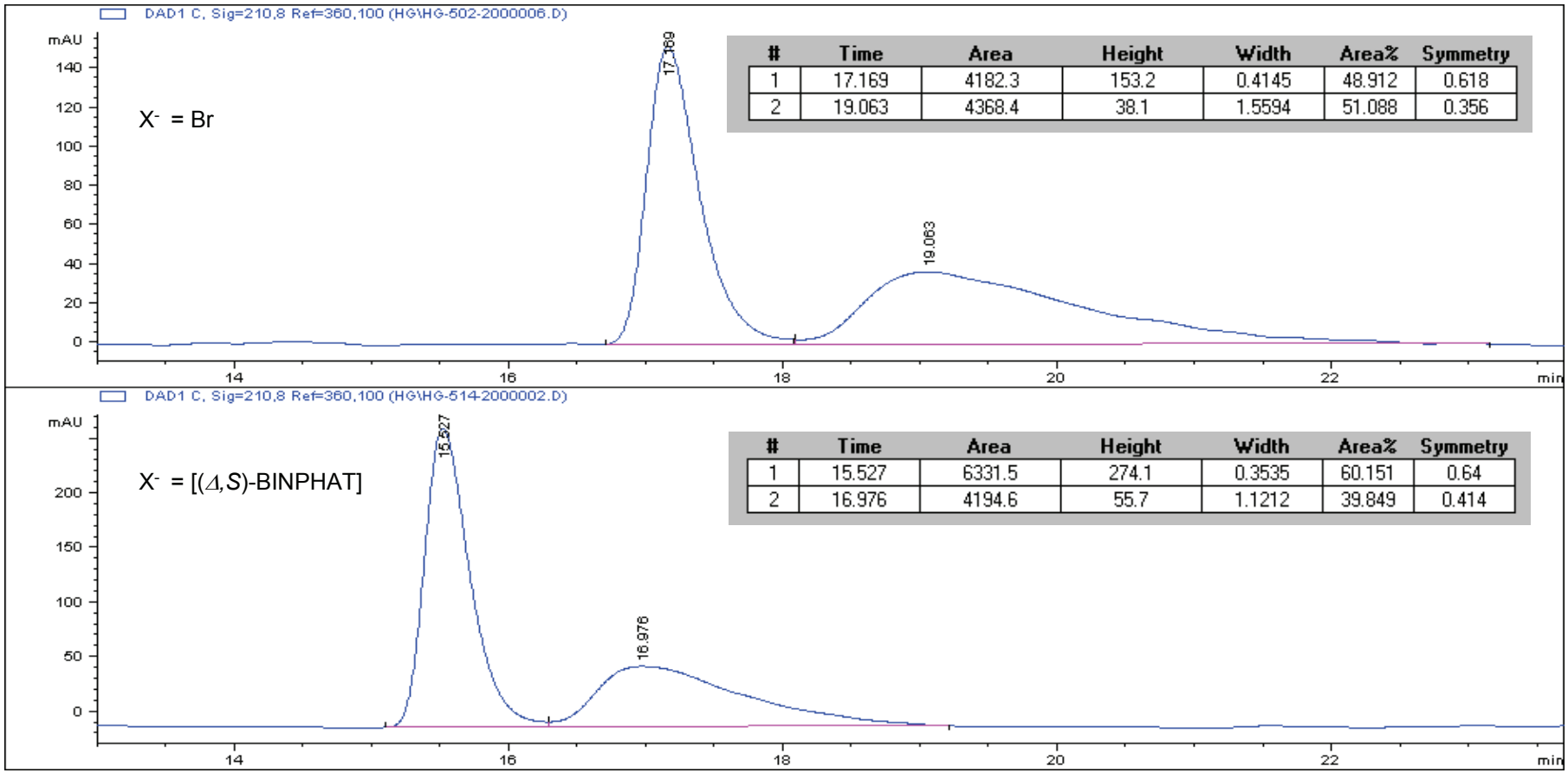
Determined by CSP-HPLC (Chiralpak IB); *n*-Hexane / *i*-PrOH / ethanolamine 99.5 : 0.5 : 0.1%; 0.5 mL.min^{-1}; 23 °C).

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

Supplementary Material (ESI) for Chemical Communications



Δ-**5**$^-$ (+)-**4c**



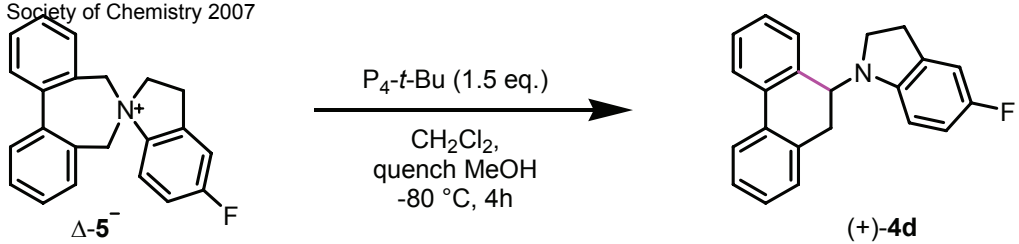
#	Time	Area	Height	Width	Area%	Symmetry
1	17.169	4182.3	153.2	0.4145	48.912	0.618
2	19.063	4368.4	38.1	1.5594	51.088	0.356

#	Time	Area	Height	Width	Area%	Symmetry
1	15.527	6331.5	274.1	0.3535	60.151	0.64
2	16.976	4194.6	55.7	1.1212	39.849	0.414

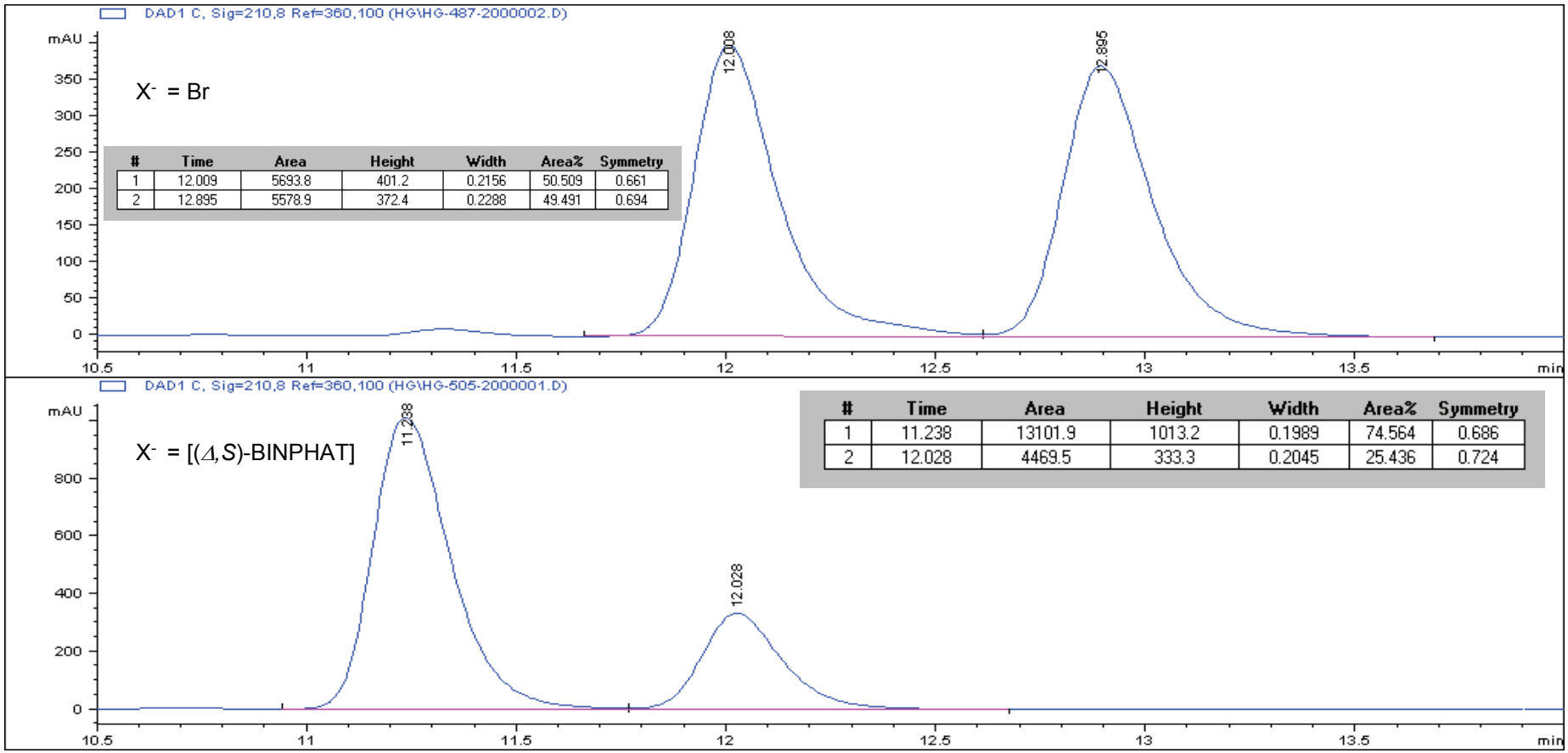
Determined by CSP-HPLC (Chiralpak IB); *n*-Hexane / *i*-PrOH / ethanolamine 98 : 02 : 0.1%; 1.0 mL.min^{-1}; 23 °C).

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

Supplementary Material (ESI) for Chemical Communications



Δ-**5**$^-$ (+)-**4d**



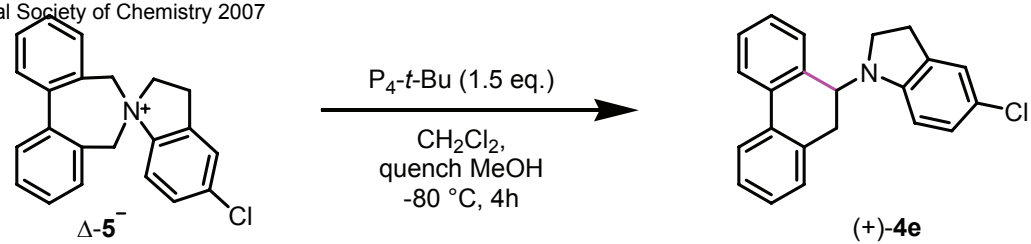
#	Time	Area	Height	Width	Area%	Symmetry
1	12.009	5693.8	401.2	0.2156	50.509	0.661
2	12.895	5578.9	372.4	0.2288	49.491	0.694

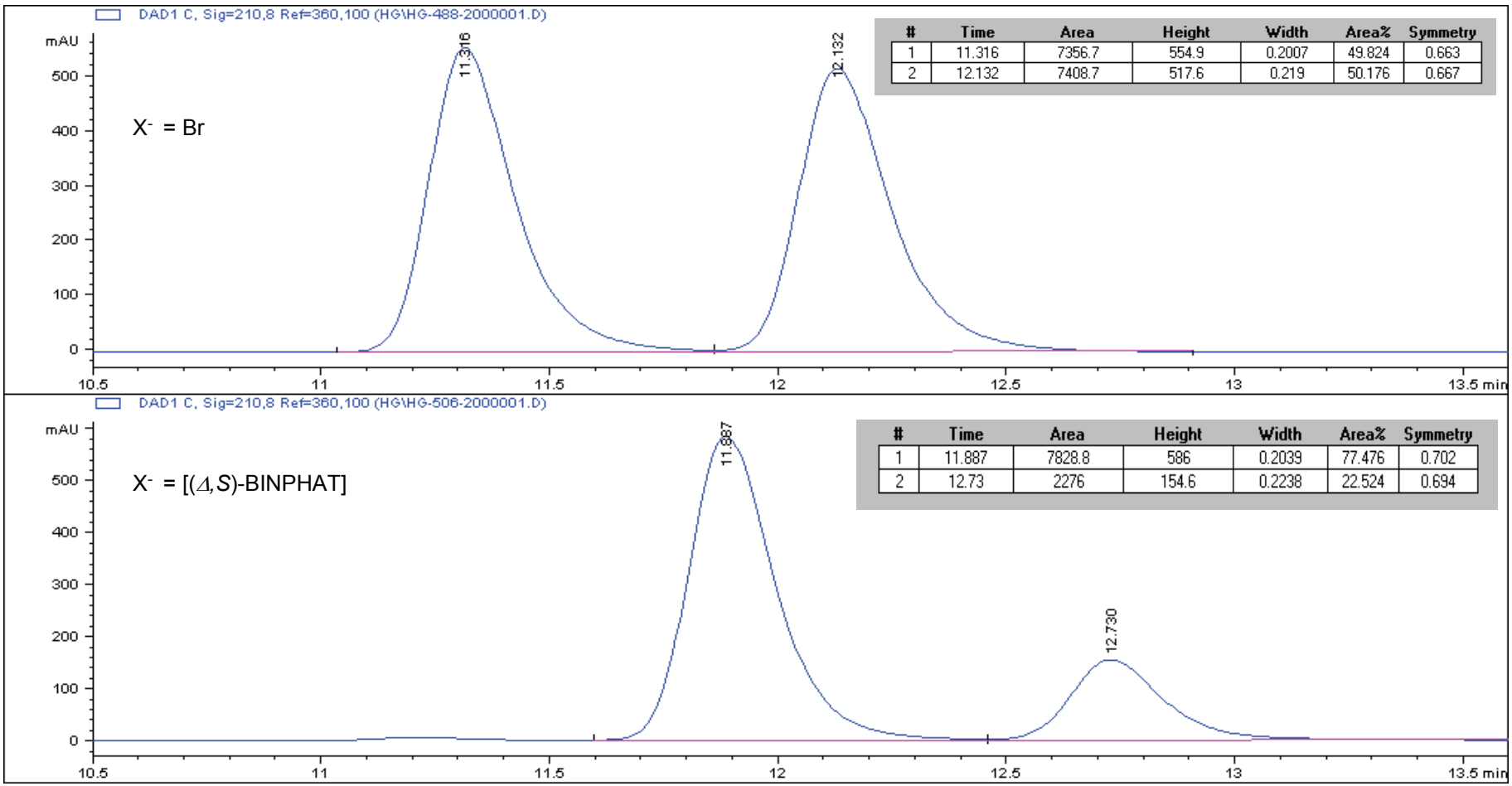
#	Time	Area	Height	Width	Area%	Symmetry
1	11.238	13101.9	1013.2	0.1989	74.564	0.686
2	12.028	4469.5	333.3	0.2045	25.436	0.724

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

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

Supplementary Material (ESI) for Chemical Communications





#	Time	Area	Height	Width	Area%	Symmetry
1	11.316	7356.7	554.9	0.2007	49.824	0.663
2	12.132	7408.7	517.6	0.219	50.176	0.667

#	Time	Area	Height	Width	Area%	Symmetry
1	11.887	7828.8	586	0.2039	77.476	0.702
2	12.73	2276	154.6	0.2238	22.524	0.694

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